Journal of Soil Contamination, 8(2):197–216 (1999)

Oxidation and Mobility of Trivalent Chromium in Manganese-Enriched Clays during Electrokinetic Remediation

Supraja Chinthamreddy and
*Krishna R. Reddy**

[1]Department of Civil and Materials Engineering, University of Illinois at Chicago, 2095 Engineering Research Facility, 842 West Taylor Street, Chicago, Illinois 60607

This article presents the results of an investigation that assessed the extent and effect of oxidation of Cr(III) in manganese-enriched clays on the electrokinetic remedial efficiency. Because chromium commonly exists along with nickel and cadmium at contaminated sites, the effects of changes in chromium redox chemistry on the migration of the coexisting nickel and cadmium was also studied. Bench-scale electrokinetic experiments were conducted using two different clays: kaolin, a typical low buffering soil, and glacial till, a high buffering soil. Tests were performed with 1000 mg/kg of Cr(III), 500 mg/kg of Ni(II), and 250 mg/kg of Cd(II), both with and without the presence of 1000 mg/kg of manganese. All of these experiments were conducted under a constant voltage gradient of 1.0 VDC/cm. The experimental results showed that in the presence of manganese, percentages of oxidation of Cr(III) into Cr(VI) ranged from 67% in kaolin to 28% in glacial till even before the application of induced electric potential. The low extent of oxidation of Cr(III) in glacial till may be attributed to the initial precipitation of Cr(III) as $Cr(OH)_3$ resulting from high soil pH, reducing aqueous Cr(III) concentrations present within the soil. In kaolin, Cr(III), Ni(II), and Cd(II) under electric potential migrated toward cathode and precipitated near the cathode due to high soil pH. When manganese was present in kaolin, Cr(VI) that was formed due to the oxidation of Cr(III) migrated toward anode and adsorbed to the soil surfaces near the anode region due to low soil pH. However, remaining Cr(III) as well as Ni(II), and Cd(II) migrated towards and precipitated near the cathode due to high soil pH. In kaolin, the migration of Ni(II) and Cd(II) was retarded in the presence of manganese due to a larger soil zone of elevated pH near the cathode. In glacial till, the migration of Cr(III), Ni(II) and Cd(II) was insignificant due to precipitation resulting from high soil pH caused by the high buffering capacity of the soil. Cr(VI) that resulted from the partial oxidation of Cr(III) in the presence of manganese, however, migrated toward the anode. Overall, this study demonstrated that the effects of manganese on Cr(III) oxidation in low buffering soils can be significant, which can in turn affect the extent and direction of chromium migration under induced electric potential.

KEY WORDS: *electrokinetics, electrokinetic remediation, clays, heavy metals, chromium, nickel, cadmium, remediation, oxidizing agents, manganese, laboratory testing.*

---

* Corresponding author.

INTRODUCTION

The remediation of chromium contaminated soils traditionally has been a difficult task because of the transitional nature, longevity, and toxicity of chromium. Chromium can exist in valence states, which vary from –2 to +6; however, the trivalent (Cr(III)) and hexavalent (Cr(VI)) states are the most stable forms that exist in the surface and subsurface environments. Cr(III) exists as cation, Cr^{+3}, and hydroxo complexes such as $CrOH^{2+}$, $Cd(OH)_3^0$, and $Cr(OH)_4^-$. Out of these complexes, the cationic Cr(III) species, Cr^{+3} and $CrOH^{2+}$, are mostly prevalent over a wide pH range. These cationic Cr(III) species are less mobile due to their limited solubility and sorption by negatively charged clay surfaces. Cr(VI) most commonly exists as oxyacids or anions such as hydrochromate ($HCrO_4^-$), dichromate ($Cr_2O_7^{2-}$), and chromate (CrO_4^{2-}). All of these anionic Cr(VI) species are quite soluble and thus are quite mobile in the subsurface environment.

Although Cr(III) compounds have no established mammalian toxicity data, these compounds are considered to pose a low-level health risk. The Cr(VI) compounds, however, have been characterized as more toxic because of their carcinogenic, irritative, and corrosive properties. Therefore, the most common strategy for remediating chromium-contaminated soils has been to reduce the Cr(VI) to Cr(III) by using Fe(II)-containing salts or organic acids. Although this approach is efficient, the possibility of Cr(III) oxidizing into Cr(VI) exists under certain soil compositional environments, particularly when manganese content in the soils is high (Bartlett and James, 1979). The manganese content in the soils may also be increased due to changes in groundwater chemistry and surface infiltration conditions. If Cr(III) is oxidized into Cr(VI), there is a greater health hazard due to higher mobility and toxicity of Cr(VI). Therefore, it is critical to investigate the extent of Cr(III) oxidation into Cr(VI) in the presence of manganese and assess the consequent implications on the selected remedial approach.

Recently, electrokinetics or electrokinetic remediation has been shown to have great potential for remediating chromium contaminated soils that contain both Cr(VI) and Cr(III) (Acar *et al.,* 1995; Reddy *et al.,* 1997; Reddy and Parupudi, 1997). The electrokinetic remediation essentially involves installing electrodes into the ground to completely surround the contaminated soil, and then applying a low DC current or voltage gradient across the electrodes. Each electrode is strategically designated as either a cathode or an anode before the application of the electric potential. As a result of electroosmotic transport and ionic migration, the contaminants are collected at the electrode where they are extracted and then recovered. In remediating chromium-contaminated soils, Cr(VI) species migrate toward the anode, while Cr(III) species migrate toward the cathode. Reddy and Chinthamreddy (1999a) have systematically investigated the electrokinetic migration of chromium existing singly as Cr(VI) and Cr(III) and existing as a combination of these two chromium states in two different clays. Following this study, Reddy and Chinthamreddy (1999b) also investigated the effects of naturally occurring reducing agents such as organic matter, ferrous iron, and sulfides in the two different clays on the reduction of Cr(VI) into Cr(III) and the consequent effects on the electrokinetic remedial efficiency. The electrokinetic remedial efficiency of chromium contaminated soils may also depend on the presence of naturally occurring oxidizing agents; however, it has not been investigated in previous studies.

The oxidation of Cr(III) in the presence of naturally occurring oxidizing agents in soils, particularly manganese, can increase the amount of soluble Cr(VI) in the soil. The extent of Cr(III) oxidation is mostly dependent on the initial concentrations of Cr(III), the amount of high valence state manganese, and the soil pH (Bartlett and James, 1979). The objective of this article is to investigate the extent of oxidation of Cr(III) in clays in presence of manganese and to assess the consequent effects on the electrokinetic remedial efficiency for these clays. Because chromium commonly exists along with nickel and cadmium at contaminated sites such as electroplating waste sites, the effects of the changes in chromium redox chemistry on the migration of coexisting nickel and cadmium were also studied. In this study, bench-scale electrokinetic experiments were conducted on two different clays that contained Cr(III), Ni(II), and Cd(II). These experiments were conducted for two different scenarios, both with and without the presence of Mn in the clays. Based on these test results, the extent of Cr(III) oxidation and the overall migration behaviors of chromium, Ni(II), and Cd(II) were assessed.

EXPERIMENTAL PROCEDURE

Experimental Conditions

Two different soil types were selected for this study, kaolin and glacial till. The mineralogical composition and properties of these soils have been reported previously by Reddy et al. (1997) and Reddy and Parupudi (1997). Kaolin is a commercially prepared soil that primarily consists of kaolinite mineral, whereas glacial till is a field soil consisting of many different clay minerals. The kaolin possesses low acid buffering capacity, while the glacial till possesses high acid buffering capacity due to high carbonate content. Together, these two soils encompass a wide range of different soil types with various buffering capacities. For this study, the first set of two experiments was conducted by spiking both soils with Cr(III), Ni(II), and Cd(II) in concentrations of 1000 mg/kg, 500 mg/kg, and 250 mg/kg, respectively. These concentrations were selected to represent typical electroplating waste site field conditions. Another set of two electrokinetic experiments was conducted with these soils using the same Cr(III), Ni(II), and Cd(II) concentrations, but also adding Mn in a concentration of 1000 mg/kg. Manganese was selected to represent the naturally occurring oxidizing agent (Bartlett and James, 1979; Eary and Rai, 1987; Saleh *et al.,* 1989). All four experiments were conducted under a constant voltage gradient of 1.0 VDC/cm.

Electrokinetic Testing

For each test, approximately 1100 g of dry soil was first contaminated with Cr(III), Ni(II), and Cd(II). Chromic chloride, nickel chloride, and cadmium chloride were used as sources of Cr(III), Ni(II), and Cd(II), respectively. Potassium permanganate was used as the source of manganese. The amounts of these chemicals required to yield the desired initial concentrations were weighed and dissolved individually in deionized water. These contaminant solutions were then added to the soil and the soil was mixed thoroughly with a spatula in an HDPE container. A total of 375 ml of deionized water was used to yield a 35% moisture content in kaolin, and 285 ml of deionized water was used to yield a 25% moisture content in glacial till. These moisture contents resulted in a liquidity index of 50% for both soils, which are indicative of typical field moisture conditions.

The contaminated soil was then placed in an electrokinetic reactor in small layers and each layer was uniformly compacted. The soil was then allowed to equilibrate for 24 h. A schematic of the electrokinetic reactor is shown in Figure 1. Essentially, the reactor consists of a cell, two electrode compartments and two reservoirs, and a power source (Reddy *et al.,* 1997; Reddy and Chinthamreddy, 1999a). The pH, redox potential, and electrical conductivity (EC) of the soil was measured both before and after equilibration. After equilibrating the soil, the electrode reservoirs were filled with potable water. Potable water was used for this study rather than deionized water because potable water will most likely be the primary water source at actual field sites. A constant voltage gradient of 1.0 VDC/cm was then applied across the soil sample. The current, electroosmotic flow, pH, redox potential, and EC variations in both the anode and cathode reservoirs were monitored at various time intervals. Each test was continued until the current was stabilized and the electoosmotic flow was negligible.

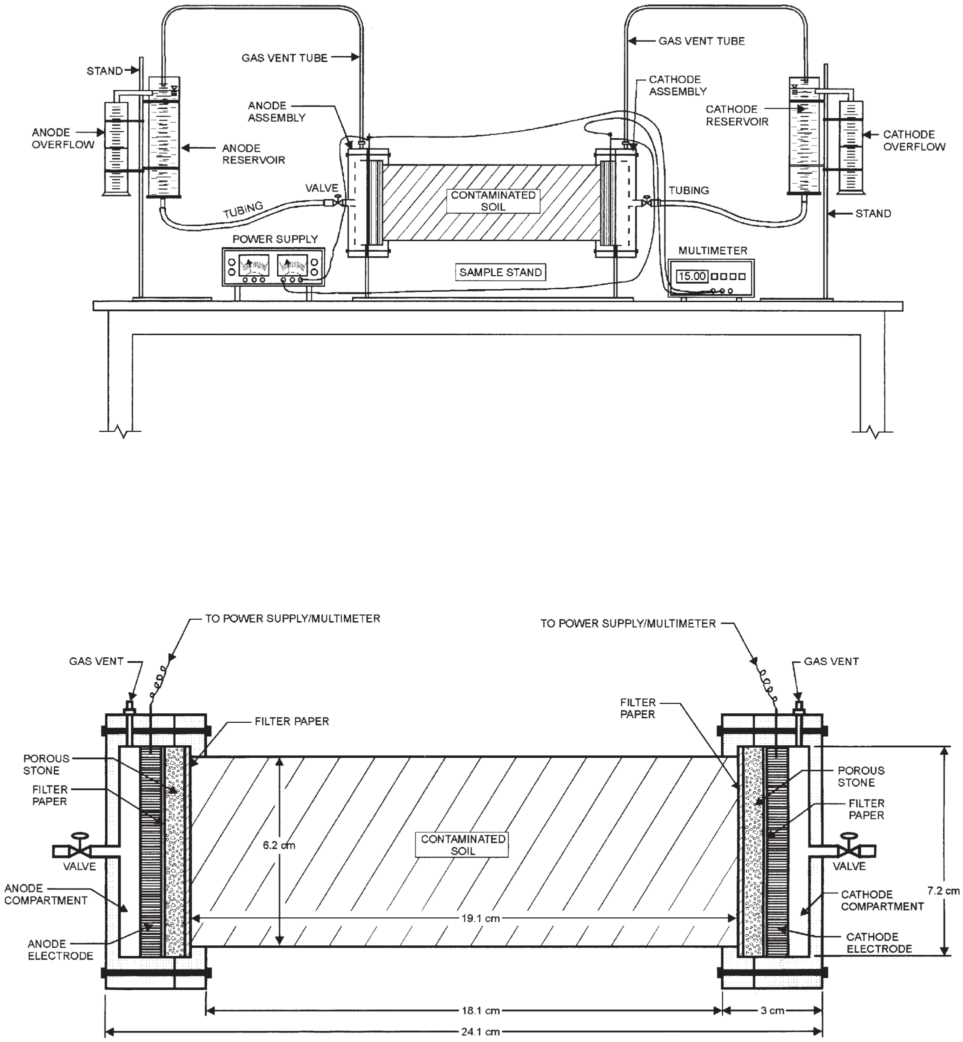

FIGURE 1

Schematic of electrokinetic test set-up.

At the end of testing, aqueous solutions from both the anode and the cathode compartments and the anode and cathode reservoirs were collected. Volumes, pH, redox potential, and EC of these solutions were measured and recorded. The soil sample was extruded from the electrokinetic cell and sectioned into five parts and each part was weighed. Then, the moisture content, pH, redox potential, and EC of each soil section was measured. Representative specimens from each soil section were acid digested in accordance with the USEPA procedure 3050 to extract the total chromium, nickel, and cadmium. Representative specimens from each soil section were alkaline digested in accordance with the USEPA procedure 3060A to extract the hexavalent chromium. Atomic absorption spectrophotometry was then used to determine the concentrations of total and hexavalent chromium, nickel, and cadmium. The detailed description of these analytical test procedures is given by Reddy and Chinthamreddy (1999a).

RESULTS AND DISCUSSION

Soil Conditions Prior to Electrokinetic Treatment

Table 1 summarizes the pH, redox potential, electrical conductivity, and contaminant concentrations of both the kaolin and glacial till, both with and without manganese prior to electrokinetic treatment. The pH values were decreased slightly in the presence of manganese, dropping from 3.83 to 3.23 in kaolin and 6.74 to 6.69 in glacial till. Nevertheless, the pH values show that kaolin is an acidic soil, whereas glacial till was shown to be a slightly acidic to neutral soil. The redox potentials ranged from 378 to 414 mV in kaolin and 212 to 218 mV in glacial till. The lower redox potentials in glacial till may be due to the presence of naturally occurring reducing agents contained in this soil. The electrical conductivity (EC) values ranged from 2820 to 4270 μS/cm in both kaolin and glacial till. These values indicate approximately the same amounts of dissolved species present in both soils. The dissolved species in the glacial till also include the naturally occurring electrolytes present in this soil.

The measured initial total chromium concentrations for all of the tests ranged from 1002 to 1048 mg/kg. These concentrations were very close to the initial target concentration of 1000 mg/kg. The measured Ni(II) and Cd(II) concentrations ranged from 341 to 460 mg/kg, and 161 to 240 mg/kg, respectively, for both soils. These concentrations were lower than the initial target concentrations of 500 mg/kg for Ni(II) and 250 mg/kg for Cd(II). Such differences in the measured and targeted concentrations were also found in other related studies (Reddy and Chinthamreddy, 1999a) and can be attributed to the nonuniform distribution of the contaminants in the specimens selected for the chemical analysis.

As mentioned earlier, all of the chromium that was initially introduced into the soils was in the form of Cr(III). In order to determine the extent of Cr(III) oxidation, the Cr(VI) concentrations in the soils were measured and are summarized in Table 1. In the absence of manganese, the measured Cr(VI) concentrations were 58 mg/kg in kaolin and 46 mg/kg in glacial till. These low

TABLE 1
Soil Conditions Prior to Electrokinetic Treatment

Soil	Oxidizing agent	pH	Redox potential (mV)	EC (μS/cm)	Cr(total) (mg/kg)	Cr(VI) (mg/kg)	Ni(II) (mg/kg)	Cd(II) (mg/kg)
Kaolin	None	3.83	378	2820	1016	58	401	161
	Manganese	3.23	414	3720	1002	667	367	211
Glacial till	None	6.74	212	4270	1048	46	460	240
	Manganese	6.69	218	3770	1033	293	341	215

Cr(VI) concentrations show that the initially introduced Cr(III) remained mostly as Cr(III). However, in the presence of manganese, the measured Cr(VI) concentrations were 667 mg/kg in kaolin and 293 mg/kg in glacial till. These Cr(VI) concentrations show that approximately 67% of Cr(III) was oxidized into Cr(VI) in kaolin, and 30% of Cr(III) was oxidized into Cr(VI) in glacial till. When Cr(III) oxidizes to Cr(VI), the manganese acts as the electron acceptor and reduces from Mn(VII) or Mn(IV) to Mn(II). The reduction of manganese and the oxidation of Cr(III) can be expressed by the following oxidation-reduction reactions:

$$2Cr^{3+} + 2MnO_4^- + 3H_2O \rightarrow Cr_2O_7^{2-} + 2MnO_2 + 6H^+$$

$$Cr^{3+} + MnO_4^- + 2H_2O \rightarrow HCrO_4^- + MnO_2 + 3H^+$$

$$2Cr^{3+} + H_2O + 3MnO_2 \rightarrow Cr_2O_7^{2-} + 3Mn^{2+} + 2H^+$$

Based on stoichiometry, only partial oxidation of Cr(III) occurred in both soils. In kaolin, a significant amount of Cr(III) was oxidized into Cr(VI) because most of the Cr(III) existed in the aqueous phase because the soil pH was less than 4 and therefore was able to react with manganese. In glacial till, however, the Cr(III) oxidation was limited because Cr(III) precipitated as $Cr(OH)_3$ because the soil pH was greater than 6, which caused the low aqueous Cr(III) present in the soil to react with manganese.

Overall, the experimental results showed that the oxidation of Cr(III) into Cr(VI) decreases with an increase in the soil pH, which is primarily due to a decrease in the solubility of Cr(III) with an increase in soil pH. The stoichiometry between manganese and Cr(III) to produce Mn(II) and Cr(VI) may not agree in certain soils because of Cr(III) adsorption or precipitation in soils that limit the aqueous Cr(III) available for the reaction with manganese. In addition, stoichiometry may not be satisfied due to simultaneous dissolution and formation of intermediate manganese oxide reaction products (Eary and Rai, 1987).

Observations during Electrokinetic Processing

The measured current variations with time for all of the experiments are shown in Figure 2. From this figure, it can be seen that, for the most part, the current increased initially, then decreased, and finally stabilized. In kaolin, the current increased to 55 mA within 20 h of testing, and then decreased and stabilized

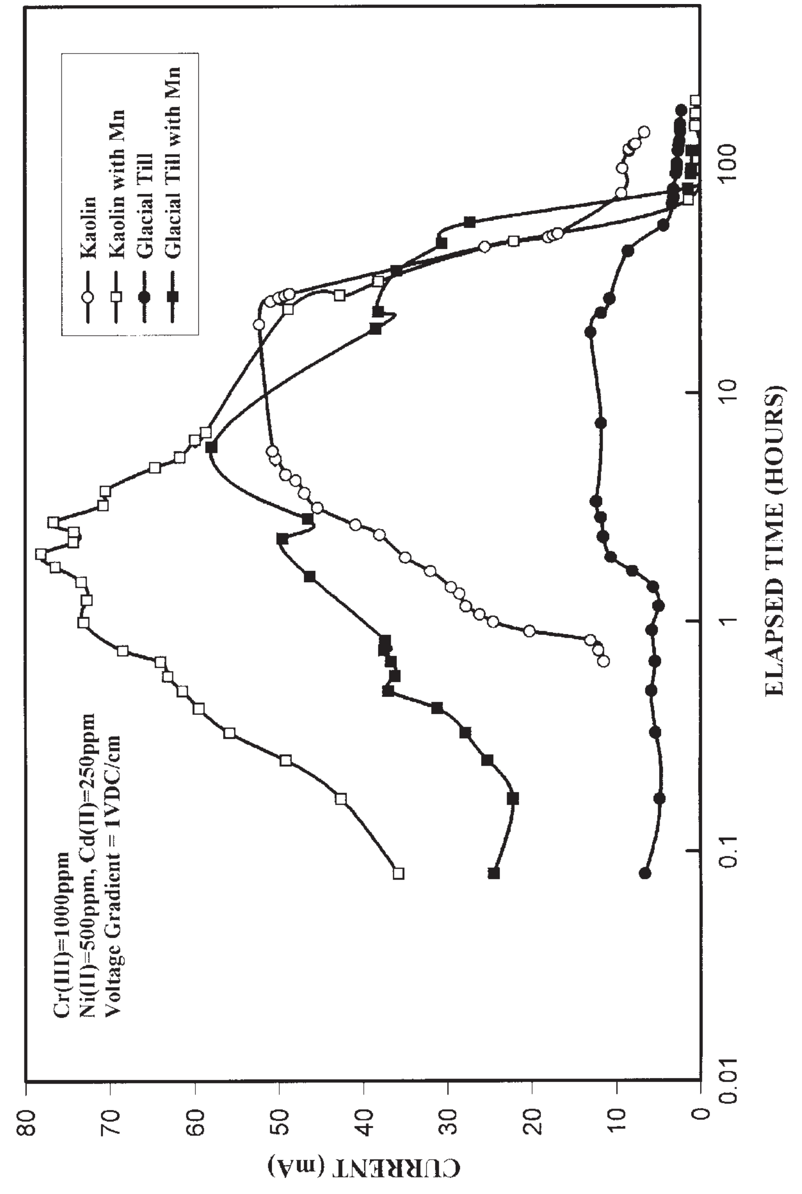

FIGURE 2

Current measurements.

at 8 mA. However, when manganese was present in kaolin, the current increased to approximately 78 mA within 2 h of testing and then decreased and stabilized at 0.2 mA. The high current in the beginning of this experiment may be due to the presence of Cr(III), Ni(II), and Cd(II) initially in aqueous form because the soil pH was less than 4. In addition, the presence of manganese ions as well as the presence of Cr(VI) species resulting from the oxidation of Cr(III) further increased the current flow. However, at later stages of electrokinetic processing, Cr(III), Ni(II), and Cd(II) were precipitated due to increased soil pH near the cathode. The Cr(VI), if present, was adsorbed to the soil surfaces due to the decreased soil pH near the anode. As a result of the removal of these contaminants from solution, the amounts of ionic species in the pore water decreased significantly, which in turn caused low current flow through the sample.

When manganese was not present in glacial till, the current increased to only about 15 mA within 20 h of testing and then decreased and stabilized at 2 mA. This low current flow may be attributed to the immediate precipitation of Cr(III), Ni(II), and Cd(II), which is due to the initial soil pH greater than 6. However, when manganese was present in glacial till, the current increased to 58 mA within 9 minutes, then decreased and stabilized at 0.2 mA. The high current flow initially may be attributed to the presence of manganese ions as well as the presence of Cr(VI) that resulted from the partial oxidation of Cr(III). Both of these ions existed in the aqueous phase under high pH conditions. Overall, the results show that the current flow is proportional to the amount of ionic species present in the pore water. The presence of manganese ions, and the Cr(VI) species that resulted from the oxidation of Cr(III), increased the current flow through both soils. These results also show that the initial EC of soils shown in Table 1 are significantly effected by the application of electric potential due to the production of H^+ and OH^- as well as the transient changes in the amount of dissolved species.

Initially, both the anode and cathode reservoirs were filled with potable water to the same elevation. During the electrokinetic process, electroosmotic flow was determined by measuring the outflow volume and water levels in both the anode and cathode reservoirs. The average electroosomotic flow rate in kaolin was found to be 0.61 ml/h when manganese was not present, and the flow was decreased to 0.38 ml/h when manganese was present. In glacial till, the electroosmotic flow rate ranged from 0.26 to 0.31 ml/h, both with and without the presence of manganese in the soil. These differences in electroosmotic flow may be attributed to the changes in zeta potential due to the transient and spatial changes in the soil pH and the amounts of dissolved chemical species present in the soils.

The potable water used in the reservoirs had an initial pH of 7.8, redox potential of 158 mV, and electrical conductivity of 280 μS/cm. During the electrokinetic process, the pH, redox potential, and electrical conductivity of the aqueous solutions in both the anode and the cathode reservoirs were measured. The results for both soils showed that with increasing time: (1) the pH decreased at the anode, whereas it increased at the cathode, (2) the redox potential increased at the anode, whereas it decreased at the cathode, and (3) the electrical conductivitities increased in both the anode and cathode reservoirs. Table 2 summarizes the final pH, redox potential, and electrical conductivity values of combined aqueous solutions collected from the anode compartment and reservoir and the cathode compartment and reservoir at the termination of the application of electric potential. From Table 2, it can be seen that the pH at the anode was decreased to a value ranging from 1.84 to 3.62, while the pH at the cathode was increased to a value ranging from 11.65 to 12.38 in both soils. On the other hand, the redox potential at the anode was increased to a value ranging from 395 to 487 mV and the redox potential at the cathode was decreased to a value ranging from –125 to –67 mV for the two soils.

The pH and redox potential values measured at the electrodes demonstrate that electrolysis of water occurred at the electrodes which results in acidic and oxidizing conditions at the anode, and alkaline and reducing conditions at the cathode (Acar and Alshwabekh, 1993). The electrical conductivity values are reflective of the amount of dissolved ionic species present in the aqueous solutions. In the kaolin tests, high EC values were observed at the cathode when compared with those measured at the anode. However, in the glacial till tests, the EC values measured at the anode were significantly higher than those measured at the cathode. The higher EC in the anode in glacial till tests may be attributed to the transport of natural anionic electrolytes such as Cl^- into the anode reservoir.

Soil Conditions After Electrokinetic Treatment

pH, Redox Potential, and Electrical Conductivity. The pH, redox potential, and electrical conductivity profiles for both soils after electrokinetic processing are shown in Figures 3(a), 3(b), and 3(c), respectively. The pH profiles show that in kaolin, the pH was decreased to approximately 2 throughout the soil except in the last section near the cathode where the pH was increased to 11.5. When manganese was present in kaolin, the pH profile was similar to that observed in the test without manganese, except that the pH in the last two sections near the cathode were increased to 9.8 and 12.8, respectively. These pH changes show that hydroxyl ions generated at the cathode migrated faster into the soil in the

TABLE 2
Conditions at Electrodes After Electrokinetic Treatment

		Anode compartment and reservoir[a]			Cathode compartment and reservoir[a]		
Soil	**Oxidizing agent in soil**	**pH**	**Redox potential (mV)**	**Electrical conductivity (μS/cm)**	**pH**	**Redox potential (mV)**	**Electrical conductivity (μS/cm)**
Kaolin	None	1.84	487	10330	12.38	–123	22400
	Manganese	2.16	478	8620	12.26	–125	15830
Glacial till	None	2.15	479	7240	11.65	–67	1099
	Manganese	3.62	395	14640	12.00	–86	2680

[a] Initially filled with potable water (pH = 7.8, Redox = 158 mV, and EC = 280 μS/cm).

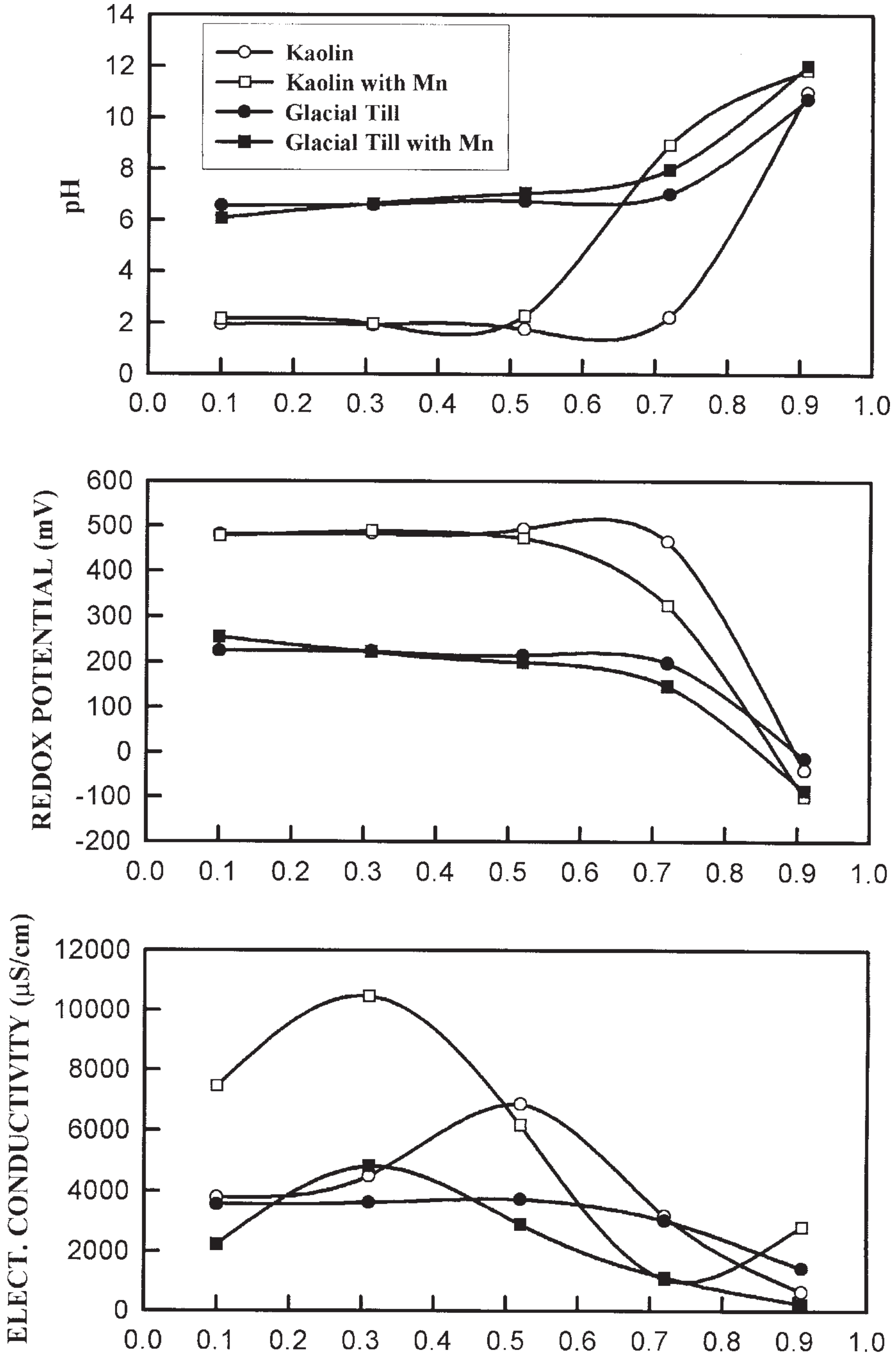

FIGURE 3

pH, redox, and electrical conductivity profiles.

presence of manganese. In glacial till, the pH ranged from 6 near the anode to over 12 near the cathode in both tests, both with and without manganese. The high pH conditions in the glacial till were attributed to higher acid buffering capacity of the soil due to the presence of significant amounts of carbonates in this soil (Reddy *et al.*, 1997). The pH changes induced in the soils due to induced electric potential can significantly influence the chemistry of heavy metals, which are discussed in later sections of this article.

The redox potentials in Figure 3(b) show that oxidizing conditions existed throughout the soil except near the cathode regions for both the kaolin and glacial till tests. The redox potentials values were lower in glacial till than those values measured in kaolin. The low redox potentials in glacial till may be attributed to the presence of naturally occurring reducing agents such as organic matter that are present in the soil.

The electrical conductivity profiles in Figure 3(c) show that EC values are low near the cathode and high near the anode for both the kaolin and glacial till tests. Particularly, the EC values near the anode were high because of the presence of higher amounts of hydrogen ions and dissolved chemical species in these regions, as discussed in the following sections.

Chromium Migration. The distribution of chromium in both soils after electrokinetic processing is shown in Figure 4. Figure 4(a) shows the measured total chromium concentrations, and Figure 4(b) shows the measured Cr(VI) concentrations. The Cr(III) concentrations were calculated by subtracting the Cr(VI) concentrations from the total chromium concentrations and are shown in Figure 4(c). From Figure 4(a), it can be seen that, in the case of kaolin without manganese, Cr(total) concentrations decreased near the anode and increased near the cathode, and a significant migration of chromium toward the cathode took place. In this test, negligible amounts of Cr(VI) were observed throughout the soil, and as shown in Figure 4(b), most of the chromium existed as Cr(III), as shown in Figure 4(c). Cr(III) exists as cationic species at low soil pH; therefore, the Cr(III) migrated toward the cathode. When Cr(III) species approach the cathode, they are precipitated as chromium hydroxide due to the high soil pH in this region. Table 3 shows that most of the chromium remained in the kaolin, and only trace amounts of chromium migrated into the anode and cathode reservoirs.

As seen in Figure 4(a), a significantly different Cr(total) profile was observed when manganese was present in the kaolin. The Cr(total) concentrations were negligible near the cathode; however, these concentrations increased moving toward the anode. The highest Cr(total) concentrations were found in the middle of the soil specimen. As stated earlier, even though the

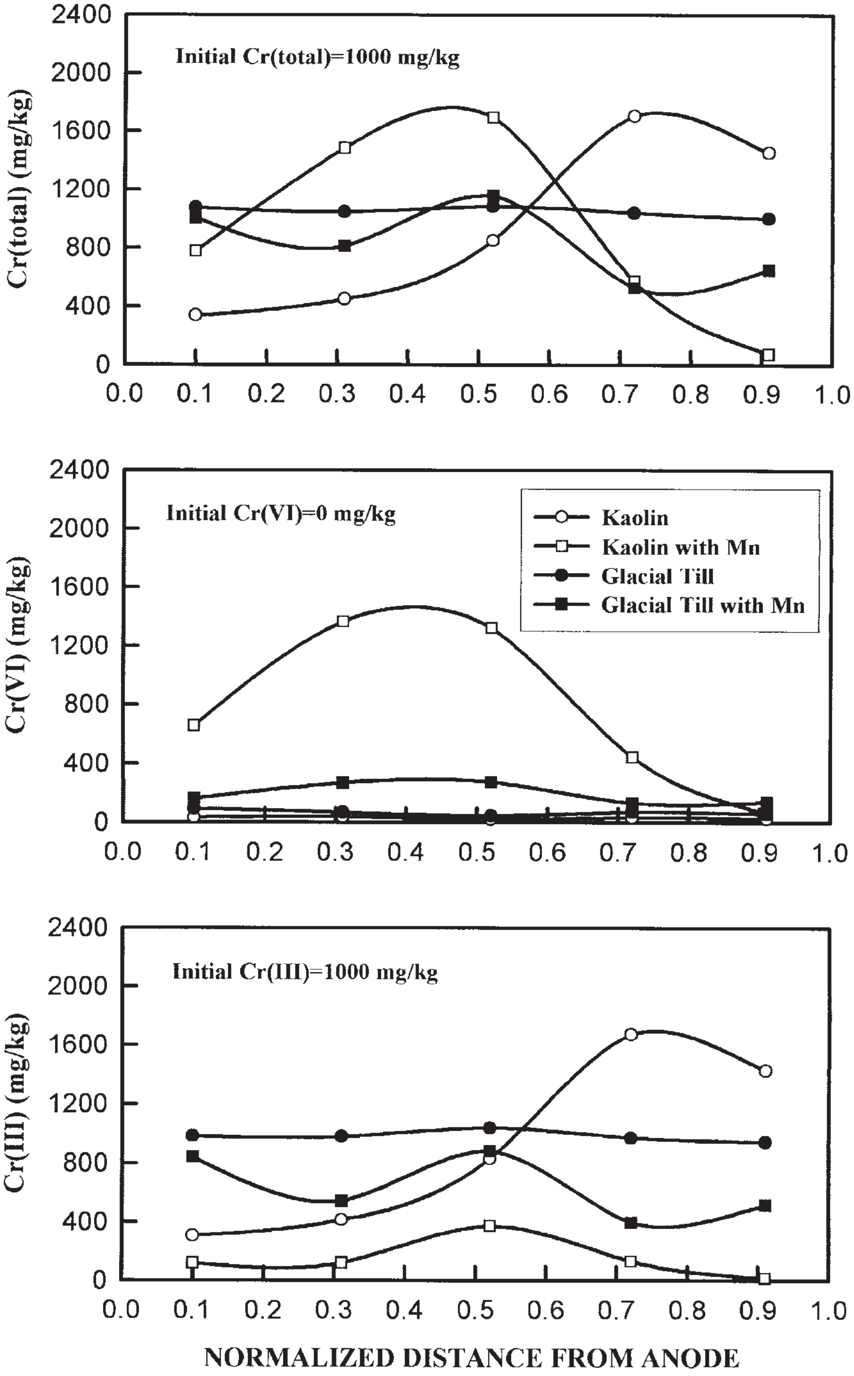

FIGURE 4

Chromium concentration profiles: (a) total chromium, (b) hexavalent chromium, and (c) trivalent chromium.

Cr(total) was introduced in the form of Cr(III), Cr(III) was partially oxidized into Cr(VI) due to the presence of manganese. The Cr(VI) and Cr(III) concentration profiles in Figures 4(b) and 4(c) show the extent of Cr(III) oxidation into Cr(VI). Because Cr(VI) exists as oxyanions, it will migrate toward the anode. A significant amount of Cr(VI) migrated from the cathode region because of low adsorption of Cr(VI), which was due to high soil pH. Because the Cr(VI) adsorption increases with a decrease in the soil pH, Cr(VI) migration was retarded in the regions of low soil pH. Because the soil pH was less than 3 in the three sections near the anode, most of the Cr(VI) in these sections was adsorbed to the soil and, as a result, high Cr(VI) concentrations were found in these sections. Table 3 shows that most of the chromium remained in the soil and a negligible amount of chromium was detected in the reservoirs.

When manganese was not present in the glacial till, chromium was distributed uniformly throughout the soil, as seen in Figure 4(a), with concentrations approximately equal to the initial chromium concentration. This result shows that the migration of chromium did not occur. From the Cr(VI) and Cr(III) concentration profiles shown in Figures 4(b) and 4(c), respectively, it can be seen that the chromium that was initially introduced as Cr(III) remained as Cr(III) throughout the soil sample. Because of high pH conditions throughout the soil, the Cr(III) precipitated as $Cr(OH)_3$, which resulted in no chromium migration. However, when manganese was present in the glacial till, partial oxidation of Cr(III) into Cr(VI) occurred. Figures 4(b) and 4(c) show that the extent of Cr(III) oxidation into Cr(VI) was severely limited. As stated earlier, the limited oxidation of Cr(III) into Cr(VI) is attributed to the initial precipitation of Cr(III) because of high soil pH, which made less aqueous Cr(III) available for a reaction with manganese. The small amount of Cr(VI) that resulted from Cr(III) oxidation may have existed as an oxyanion and migrated toward the anode as evident from the Cr(VI) concentration profiles shown in Figure 4(b). The remaining Cr(III) exists as $Cr(OH)_3$ and its migration is negligible.

Overall, the experimental results show that Cr(III) oxidation in the presence of manganese depends on the soil pH that, in turn, depends on the buffering capacity of the soil. In low-buffering soils, significant oxidation of Cr(III) into Cr(VI) can occur, which can drastically alter the extent and direction of chromium migration during the electrokinetic processing. Therefore, one must carefully assess the potential effects of manganese on the speciation of chromium during the design of electrokinetic remediation systems.

Nickel and Cadmium Migration. The distribution of coexisting contaminants, specifically Ni(II) and Cd(II), is shown in Figures 5(a) and (b) and Table 3. These results show that in kaolin when manganese was not present, both Ni(II)

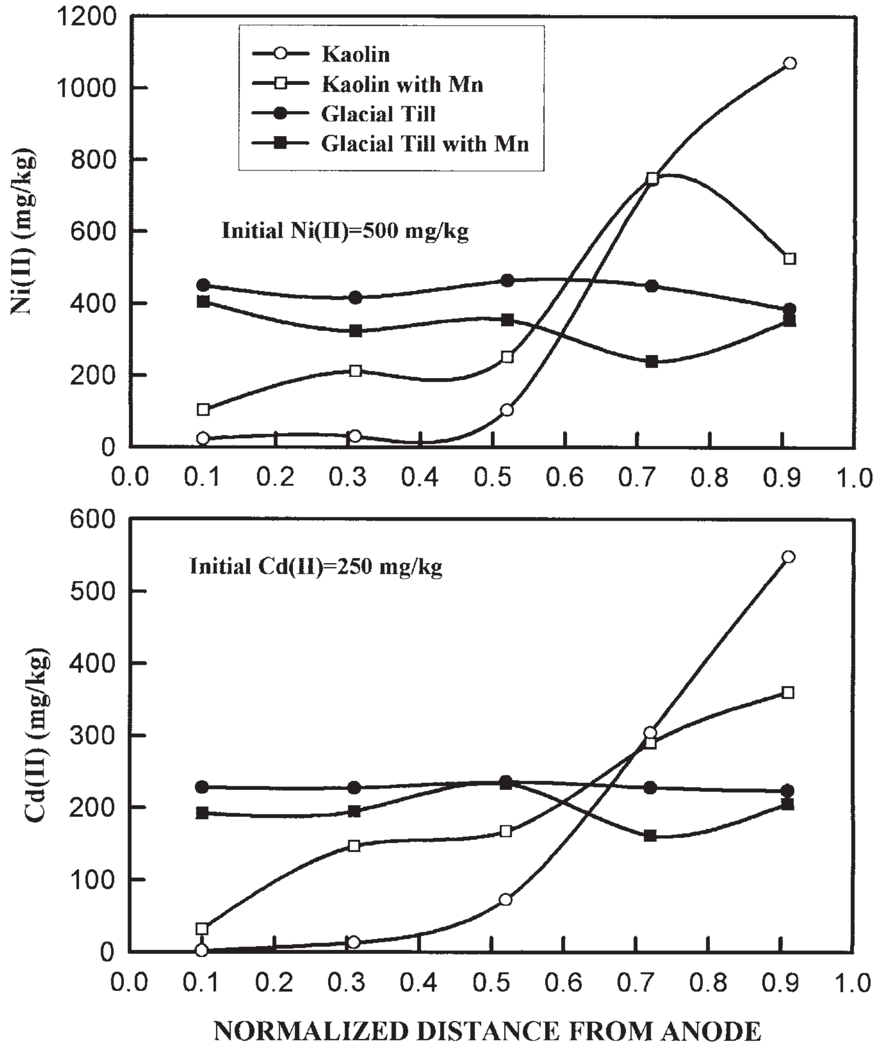

FIGURE 5

Ni(II) and Cd(II) concentration profiles.

and Cd(II) migrated toward the cathode and then precipitated near the cathode similar to that of Cr(III). However, when manganese was present in kaolin, high pH conditions existed in the two soil sections near the cathode. As a result, Ni(II) and Cd(II) precipitated in these sections and also restricted the migration of Ni(II) and Cd(II) from the anode regions. This situation resulted in high Ni(II) and Cd(II) concentrations throughout the soil when compared with the test conducted without manganese, as shown in Figures 5(a) and 5(b). Therefore, the

TABLE 3
Mass Balance Analysis

Soil	Oxidizing 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)	843.12	764.70	1.40	ND[b]	91
		Ni(II)	332.84	310.44	0.68	0.01	93
		Cd(II)	133.94	141.79	0.01	0.01	106
	Manganese	Cr(total)	795.00	757.91	1.74	0.08	96
		Ni(II)	291.56	280.40	10.56	0.03	100
		Cd(II)	167.47	150.57	0.02	0.01	90
Glacial till							
	None	Cr(total)	1002.86	981.55	12.38	0.07	99
		Ni(II)	440.31	405.72	4.21	0.02	93
		Cd(II)	229.57	213.57	ND	0.21	93
	Manganese	Cr(total)	971.20	801.10	11.93	0.16	84
		Ni(II)	321.19	318.02	0.02	0.02	99
		Cd(II)	202.07	186.66	0.69	ND	93

[a] Based on the measured initial concentrations.
[b] ND = not detected.

results suggest that the pH conditions influenced by the presence of manganese may restrict the migration of Ni(II) and Cd(II) toward the cathode. In glacial till, as seen in Figures 5(a) and 5(b), because of high pH conditions, both Ni(II) and Cd(II) were precipitated throughout the soil without any migration; therefore, the presence of manganese in this soil was inconsequential on the migration of the coexisting contaminants.

CONCLUSIONS

Based on the results of the experiments, the following conclusions can be drawn:

1. In both kaolin and glacial till, Cr(III) was partially oxidized into Cr(VI) in the presence of manganese. For the test conditions used in this study, 67% of Cr(III) was oxidized into Cr(VI) in kaolin and 28% of Cr(III) was oxidized into Cr(VI) in glacial till. The Cr(III) oxidation in kaolin was significant because of the low soil pH that caused significant aqueous Cr(III) to become available to react with manganese. In glacial till, high pH conditions caused precipitation of Cr(III), thereby severely limiting the amount of aqueous Cr(III) to react with manganese.
2. Under induced electric potential in kaolin, Cr(III) migrated significantly toward the cathode and precipitated near the cathode due to high soil pH. However, in the presence of manganese, significant Cr(III) was oxidized into Cr(VI). Because Cr(VI) exists as oxyanions, it migrated toward the anode and, because of the low soil pH near the anode regions, Cr(VI) was adsorbed onto the soil surfaces.
3. Under induced electric potential in glacial till, the pH remained above 6 throughout the soil for conditions both with and without the presence of manganese. This high pH is attributed to the high acid buffering capacity of the soil. As a result, Cr(III) precipitated throughout the soil. A limited amount of Cr(III) was oxidized into Cr(VI) in the presence of manganese and this Cr(VI) migrated toward the anode.
4. The coexisting contaminants, Ni(II) and Cd(II), migrated significantly towards the cathode in kaolin. In the presence of manganese in kaolin, the migration of Ni(II) and Cd(II) was retarded due to a larger soil region with high pH conditions existing near the cathode. In glacial till, Ni(II) and Cd(II) precipitated due to high soil pH for both with and without the presence of manganese.

5. The presence of manganese is shown to have significant influence on the oxidation and mobility of Cr(III) in low buffering soils, and it should be properly accounted in the design of electrokinetic remediation systems. The effects of manganese on Cr(III) oxidation in high buffering soils are insignificant because of the precipitation of Cr(III) due to high soil pH.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the Institute of Gas Technology and the Campus Research Board for providing funding for this project. The authors wish to thank Art Anderson of UIC Research Resource Center for his assistance in analytical testing.

REFERENCES

Acar, Y. B. and Alshawabkeh, A. N. 1993. Principles of electrokinetic remediation. *Environ. Sci. Technol.* **27(13),** 2638–2650.

Acar, Y. B., Gale, R. J., Alshawabkeh, A. N., Marks, R. E., Puppala, S., Bricka, M., and Parker, R. 1995. Electrokinetic remediation: basics and technology status. *J. Hazard. Mater.* **40(2),** 117–137.

Bartlett, R. and James, B. 1979. Behavior of chromium in soils: III. oxidation. *J. Environ. Qual.* **8(1),** 31–35.

Eary, L. E. and Rai, D. 1987. Kinetics of chromium(III) oxidation to chromium(VI) by reaction with manganese dioxide, *Environ. Sci. Technol.* **21(12),** 1187–1193.

Fendorf, S. E. and Zasoski, R. J. 1992. Chromium(III) oxidation by δ-MnO_2. 1. Characterization. *Environ. Sci. Technol.* **26(1),** 79–85.

Hicks, R. E. and Tondorf, S. 1994. Electrorestoration of Metal Contaminated Soils. *Environ. Sci. Technol.* ACS, **28(12),** 2203–2210.

Probstein, R. F. and Hicks, R. E. 1993. Removal of contaminants from soils by electric fields. *Science,* **260,** 498–503.

Rai, D., Eary, L. E., and Zachara, J. M. 1989. Environmental chemistry of chromium. *Sci. Total Environ.* **86,** 15–23.

Reddy, K. R. and Parupudi, U. S. 1997. Removal of chromium, nickel and cadmium from clays by in-situ electrokinetic remediation. *J. Soil Contamin.* **6(4),** 391–407.

Reddy, K. R., Parupudi, U. S., Devulapalli, S. N., and Xu, C. Y. 1997. Effects of soil composition on removal of chromium by electrokinetics. *J. Hazard. Mater.* **55(1–3),** 135–158.

Reddy, K. R. and Chinthamreddy, S. 1999a. Effects of initial form of chromium on electrokinetic remediation in clays. in review.

Reddy, K. R. and Chinthamreddy, S. 1999b. Electrokinetic remediation of heavy metal contaminated soils under reducing environments. in review.

Saleh, F. Y., Parkerton, T. F., Lewis, R. V., Huang, J. H., and Dickson, K. L. 1989. Kinetics of chromium transformations in the environment. *Sci. Total Environ.* **86,** 25–41.