

Effects of soil composition on the removal of chromium by electrokinetics

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Abstract

Electrokinetic experiments were conducted on three different types of soil: glacial till, kaolin and Na-montmorillonite, in order to investigate the effect of soil mineralogy and naturally occurring hematite (Fe_2O_3) on the removal of chromium from these soils. Batch tests were also performed to characterize Cr(VI) adsorption onto these soils. This study has shown that soils which contain high carbonate buffers, such as the glacial till, hinder the development of an acid front, which results in alkaline conditions throughout the soil during electrokinetic remediation. However, soils possessing low buffering capacity, such as kaolin and Na-montmorillonite, favor the development of an acid front which results in a distinct pH gradient with pH values varying from 2 near the anode to over 11 near the cathode. The results from the adsorption tests showed that Cr(VI) adsorption onto soils depends on the soil type and soil pH. The adsorption of Cr(VI) was found to be governed by soil surface complexation reactions and was significant in Na-montmorillonite, moderate in kaolin and low in glacial till. The Cr(VI) adsorption was found to be pH dependent, with low adsorption occurring at high pH values and high adsorption occurring at low pH values. The low adsorption of Cr(VI) under alkaline conditions in the glacial till resulted in high Cr(VI) removal during electrokinetics. Moderate Cr(VI) adsorption in the acidic regions in kaolin resulted in lower Cr(VI) removal than in the glacial till. High Cr(VI) adsorption in acidic regions of Na-montmorillonite resulted in low Cr(VI) migration. The presence of hematite or iron oxide in soils on the removal of Cr(VI) by electrokinetics depends on the soil

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mineralogical composition. In soils such as glacial till, the presence of iron oxide creates complex geochemistry and retards Cr(VI) removal. However, in homogeneous clays such as kaolin and Na-montmorillonite, the presence of iron oxide does not significantly affect Cr(VI) removal by electrokinetics. © 1997 Elsevier Science B.V.

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1. Introduction

Chromium is a major soil contaminant at numerous industrial sites and at many of the Superfund sites throughout the United States [1]. The extensive use of chromium in metallurgy, leather tanning, electroplating, lumber, power generation and other industries has led to its release into the subsurface environment. Chromium concentrations as high as $15\,000\text{ mg l}^{-1}$ in the groundwater have been detected at some Superfund sites [2,3]. Chromium occurs in two stable oxidation states in the soil, Cr(III) and Cr(VI). Cr(VI) occurs as oxyanions, HCrO_4^- (bichromate ion), CrO_4^{2-} (chromate ion), and $\text{Cr}_2\text{O}_7^{2-}$ (dichromate ion). Due to the toxic and carcinogenic properties of Cr(VI) and its greater mobility in soils compared to the relatively immobile and non-toxic Cr(III), Cr(VI) oxyanions are of great concern [4]. As a result, the remediation of chromium-contaminated sites is a top priority in order to protect public health and the environment.

The current practice for remediating chromium-contaminated sites usually involves excavation of the contaminated soil, followed by soil washing. Recent laboratory studies on Cr(VI) removal by soil washing have shown promising results, but these studies have also acknowledged that the soil type greatly affects the removal effort [5,6]. Further, this remediation method involves the excavation of soil, which is a time-consuming and costly process. Recently, attention has been focused on developing cost-effective, in-situ treatment technologies for remediating chromium-contaminated sites. Electrokinetic remediation is one such in-situ technology that has significant potential for effectively and economically removing chromium from soils.

Since 1990, several studies have been reported on the potential use of electrokinetic technology for soil remediation (e.g., [7–13]). These studies have demonstrated that electrokinetic technology is a cost-effective and efficient in-situ method for remediating contaminated soils. Most of these previous studies were performed using commercial minerals (e.g. kaolinite) and individual chemicals (e.g. lead, zinc, cadmium), and only a few of them have actually dealt with chromium. Recent field applications of electrokinetic technology have shown that soil composition plays an important role in the removal of the contaminants from soils (e.g., [14,15]). These results showed that the presence of naturally occurring buffering agents in soils such as bicarbonates and hydroxides hindered the migration of cationic contaminants and resulted in low contaminant removal.

Research began in 1993 at the University of Illinois at Chicago (UIC) to evaluate the applicability of electrokinetic technology for the remediation of chromium-contaminated glacial soil deposits. Such deposits are prevalent in the Midwestern United States (e.g., [16]). These soils possess a complex composition and it is essential to understand the

geochemistry of the chromium in these soils in order to develop good control factors for field application of electrokinetic remediation. Soil mineralogy and naturally occurring substances such as iron, organic matter and sulfides will affect the various geochemical processes, such as adsorption and redox chemistry, which take place during electrokinetic remediation. A thorough understanding of these geochemical processes is vital because they dictate the oxidation state and migration of chromium (Cr(III)/Cr(VI)). Ideally, in order to remove all of the chromium from soils by electrokinetics, chromium should exist in the Cr(VI) form. The three Cr(VI) species, HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} , are soluble over a wide pH range and, in general, are weakly adsorbed to soil solids [17]. Conversely, Cr(III) tends to form cationic hydroxides such as $\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}_2(\text{OH})_4^{2+}$, $\text{Cr}_6(\text{OH})_{12}^{6+}$ and $\text{Cr}_6(\text{OH})_{15}^{3+}$ in solution. These species are insoluble over a wide pH range and are known to adsorb highly to soil solids. Further, precipitation of Cr(III) as amorphous $\text{Cr}(\text{OH})_3$ severely restricts the mobility of Cr(III) [17]. For these reasons, electrokinetic removal of chromium in the form of Cr(VI) will be more efficient than the removal of chromium in the form of Cr(III).

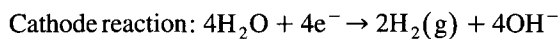
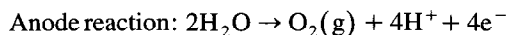
The purpose of this paper is to present the results of laboratory experiments which were performed to investigate the effects of soil composition, in particular, soil mineralogy and the presence of hematite, on Cr(VI) removal efficiency by the electrokinetic process. In this study, three soils: glacial till, kaolin, and Na-montmorillonite, were tested. The first series of experiments was conducted in order to evaluate the effect of soil mineralogy on the remedial efficiency of Cr(VI), and the second series of experiments was conducted in order to study the effect of naturally occurring hematite in soils on the remedial efficiency of Cr(VI). Additional experiments are currently being performed at UIC to evaluate the effects of organic matter, sulfides, and mixed contaminants on the electrokinetic removal efficiency of Cr(VI) from these soils. These test results will help to understand the geochemical interactions and, based on this understanding, rational methods for enhancing contaminant removal will, if necessary, be investigated.

This paper first provides background information on electrokinetic remediation and then presents the factors which affect contaminant migration during electrokinetic remediation. The paper also reviews previous laboratory and field investigations which have assessed the suitability of using electrokinetic remediation to remove chromium from contaminated soils. The paper then presents the laboratory experiments performed on chromium-contaminated glacial till, kaolin and Na-montmorillonite. These experiments were first performed on soils which did not contain iron oxide, and then repeated for soils which contained iron oxide. These results are then used to describe the effects of soil mineralogy and iron oxide on the migration of Cr(VI) during the electrokinetic process.

2. Background

Electrokinetic remediation consists of applying a low level DC current or a low voltage gradient across electrodes which are inserted in the contaminated soil. As a

result of this induced electric potential, electrolysis of water occurs at the electrodes which can be described by the following redox reactions [9,12]:



The oxygen gas generated at the anode and the hydrogen gas generated at the cathode are allowed to escape out of the soil. The H^+ ions generated at the anode and the OH^- ions generated at the cathode will migrate towards the opposite electrode. The extent of migration of H^+ ions and OH^- ions depends upon the buffering capacity of the soil. In soils with a low buffering capacity, a distinct pH gradient ranging from 2 near the anode to 12 near the cathode is generally developed [12]. Under an induced electric potential, the soil contaminants will migrate towards either the cathode or the anode, depending on the charge, cationic or anionic. The Cr(VI) species, being anionic in form, will migrate towards the anode while the Cr(III) species, being cationic in form, will migrate towards the cathode.

Previous research has shown that the principal contaminant migration mechanisms that occur during the electrokinetic remediation process are electroosmosis, electromigration, diffusion and electrophoresis [7,9,12]. Electroosmosis is the movement of pore water under an electrical potential difference from the anode to the cathode, and is mainly affected by the soil porosity and the zeta potential of the soil medium [8,11]. Electroosmosis is more effective for the removal of cationic contaminants than for anionic contaminants. Electromigration is the movement of ions in the pore fluid of the soil under the influence of an electric current. This mechanism is of great significance for both anionic and cationic contaminants. Acar and Alshawabkeh [12] evaluated the relative contribution of electroosmosis and electromigration on cationic contaminant migration and concluded that the effects of electromigration can be greater than those of electroosmosis in this respect. However, Gray and Mitchell [18] reported that electroosmosis contributed a significant percentage to the overall migration of cations, at least when the cation concentrations were low. The effect of electroosmosis and the significance of electromigration on anionic contaminants such as Cr(VI) are not reported in literature. Diffusion plays a relatively constant and often insignificant role in both cationic and anionic contaminant transport [12,19]. Electrophoresis, which refers to the transport of charged particles under the influence of an electric current, may be an important mechanism for sludges, but it is not significant for contaminant transport in soils [8].

The feasibility and efficiency of electrokinetic remediation depends on the geologic, hydraulic, chemical and electrical conditions. In order to design effective electrokinetic remediation systems, one must thoroughly evaluate all of these conditions including their coupling effects. The results from field tests [14] indicated that a thorough understanding of geochemical processes is necessary to obtain good remedial results. The geochemical environments involved in electrokinetic remediation, especially at chromium-contaminated sites, can be assessed in terms of pH and Eh variations, as detailed below.

2.1.1. Effect of pH variation

pH is one of the major factors which determines the mobility of contaminants in soils. The transient nature of pH variation between the two opposite electrodes renders heterogeneous and transient conditions for several major reaction types. The reactions directly regulated by pH include adsorption and desorption, dissolution and precipitation, complexation and speciation [20]. The low pH near the anode promotes the desorption of most heavy metals and cations. Conversely, the high pH near the cathode results in the desorption of anionic contaminants. The high pH near the cathode could also result in the precipitation of metals at their respective hydroxide solubility values [21,7,22,23,20]. McLean and Bledsoe [22] suggested that these conclusions on pH effects may not hold true when significant complexation of metal with organic matter occurs.

2.1.2. Effect of Eh variation

The oxygen and hydrogen generated in the electrolysis reactions can alter the redox state of the contaminants if they enter the soil [20]. The redox system can also be extremely complex if other redox species such as Fe(II)/Fe(III), sulfide/sulfate, and organic matter are present in the soil [24–26]. Similar to pH variation, redox reactions can lead to a transient Eh variation in the soil. Secondary redox reactions can also contribute to the Eh variation during electrokinetic remediation [12].

Eh–pH or Pourbaix diagrams are commonly used in assessing redox conditions in soil environments. Fig. 1 shows an Eh–pH diagram for chromium oxidation/reduction between two opposite electrodes. The two oxidation states of chromium, Cr(III) and Cr(VI), complicate the geochemical conditions which control chromium mobility. Fig. 1 shows that, in the presence of chloride, the evolution of Cr takes on two different paths for oxidizing and reducing environments [20]. It should be emphasized that Eh–pH diagrams can only provide a rough guide based on redox equilibrium in the system [27]. The understanding of an actual system, as in electrokinetic remediation, requires careful measurement of each redox species in the system.

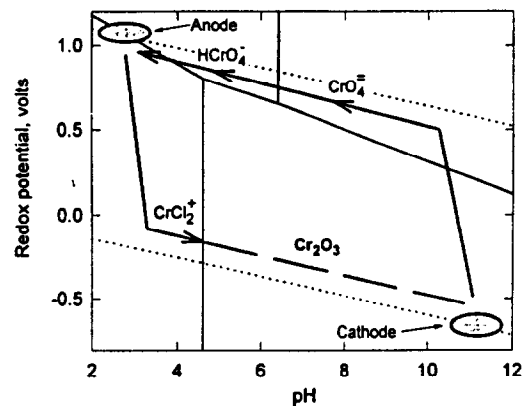


Fig. 1. Effect of pH and redox potential on chromium removal [20].

2.2. Previous studies on chromium removal

2.2.1. Previous laboratory investigations

Most of the previous studies on electrokinetic remediation of soils have focused on cationic contaminants. Few studies have been reported on the removal of anionic contaminants by electrokinetic remediation. In fact, only two investigations to date have been reported to evaluate the electrokinetic removal efficiency of chromium from contaminated soils [28,29]. Out of these, only one study by Lindgren et al. [29] dealt with Cr(VI). A brief description of these chromium studies is provided below.

Hamed [28] conducted experiments on saturated kaolin specimens loaded with Cr(III) to investigate the feasibility and efficiency of the electrokinetic process. These tests were conducted with an initial Cr(III) concentration of 120 ppm. The test results indicated that 60 to 70% of the Cr(III) was removed from the anode zone while a large amount of Cr(III) was precipitated at the cathode zone. A significant amount of chromium was also found to be electroplated at the cathode.

Lindgren et al. [30] studied the feasibility of using electrokinetics to remove anionic contaminants, similar to chromate ion, from saturated and unsaturated sands. They conducted experiments which consisted of transport visualization of dye in sand, under both saturated and unsaturated conditions, with a constant current of 10 mA being applied. Sand obtained from a chemical waste landfill was used in this study. The rate of electromigration of the dye in an imposed electric field was monitored photographically. The characteristics of the electromigration rate were reported to be similar in both the saturated and unsaturated sand. The electromigration rate was also observed to be concentration dependent. The more diluted dye migrated at a faster rate than the concentrated dye, which resulted in a diffuse leading edge and a sharp, concentrated trailing edge.

In another series of experiments, Lindgren et al. [29] studied the effect of moisture content on the electromigration rate of anionic contaminants and compared the migration behavior of chromate ions with that of surrogate dye ions. Both sodium dichromate and pure FD&C Red No. 40 were used as contaminants. The molar concentration of the contaminant, either dye or chromate, in the pore water was kept constant at 0.02 M for all of the experiments. A constant current of 10 mA was applied to the soil for up to 24 h. For the experiments conducted with the dye, photographs of the dye locations were taken at one hour intervals. These experiments revealed that maximum electromigration occurred at an optimum moisture content of 14 to 18% for the soil tested. The experiment conducted with chromate showed that Cr(VI) migrated towards the anode. A mass balance analysis performed after this test could only account for 56% of the initially introduced chromate. To determine whether the chromate was adsorbed on the graphite electrode, additional special analyses were performed on the electrodes. These analyses showed that a significant amount of Cr(VI) had adsorbed to the anode graphite electrode. This study also reported that part of the Cr(VI) may have been reduced to Cr(III).

2.2.2. Previous field investigations

Field-scale demonstrations of the electrokinetic technique are very important in order to identify and evaluate operational parameters, predict efficiency for different types of

contaminants, and understand the effect of contaminant interaction with co-disposed wastes. To date, only two studies have been reported on field testing of electrokinetics at chromium-contaminated sites. Banerjee et al. [2] conducted bench-scale tests to assess the suitability of electrokinetics for remediation at the United Chrome Products Superfund site in Corvallis, Oregon, where approximately 1000 gallons of chromium plating were discharged. The chromium contamination levels at the site varied from $15\,000\text{ mg l}^{-1}$ in the groundwater at the source to 10 mg l^{-1} in the groundwater several feet away from the site. The bench-scale tests were performed using both electrokinetics and pumping and hydraulic leaching. A high chromium removal rate was observed in tests where electrokinetics was combined with periodic pumping.

Electrokinetic remediation has been used by the Geokinetics Company (The Netherlands) in performing several field tests in clay, peat and fine argillaceous sand [14]. The contaminants removed in these field experiments included lead, zinc, arsenic, cadmium, nickel and chromium. The initial concentrations of these contaminants in the soil ranged from 11 to 7300 mg kg^{-1} . The results of the tests involving chromium, however, were not published.

2.2.3. Limitations of previous laboratory and field investigations

As mentioned earlier, the laboratory investigations aimed at removing Cr(VI) from soils were limited to the determination of an optimum moisture content for the maximum electromigration rate of the chromate ion, and a comparison between the electromigration rates of the analogous dye and the chromate ion. The only field investigation reported [2] was partially successful in removing chromium, but this success was limited by inadequate site characterization. This review of literature on chromium removal by electrokinetics demonstrates that the research done to date on this subject is inadequate. As of now, no investigation has been performed on chromium removal from soils of varying composition. At this point, it is necessary to note that real field conditions are extremely complex due to the presence of various naturally occurring substances and substances that are co-disposed of along with the waste. It is essential to understand and characterize these conditions by laboratory simulation in order to apply the electrokinetic remediation technique to actual field conditions.

3. Experimental methodology

A laboratory testing program was developed at UIC to characterize the adsorption behavior of chromium and to investigate the electrokinetic removal of chromium from soils of different mineralogical composition and which contained iron oxide (Fe_2O_3). The following sections present the details of adsorption testing and the electrokinetic test procedures.

3.1. Soils tested

Three different soils, namely glacial till, kaolin, and Na-montmorillonite, were investigated in this study. The glacial till was obtained from an actual project site in

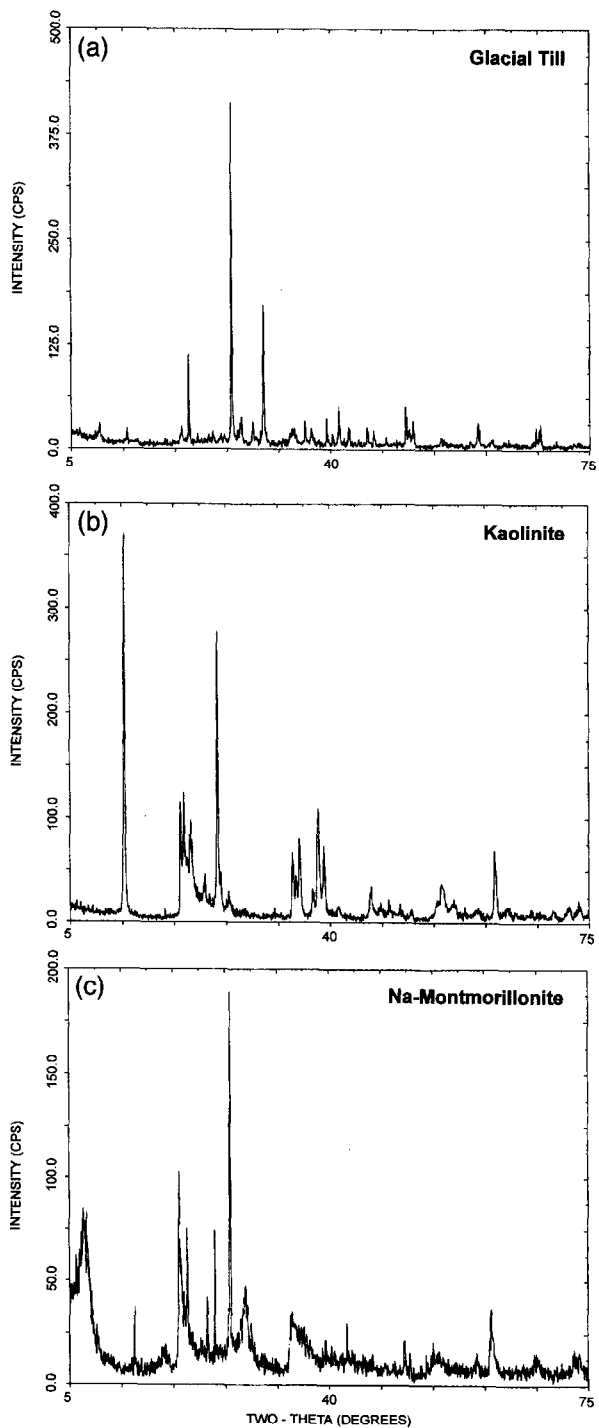


Table 1
Composition and properties of soils tested

	Glacial till	Kaolin	Na-montmorillonite
Source	DuPage County, Illinois, Obtained by the authors	KGa-1a: Washington County, Georgia Obtained from Clay Minerals Society, MO	SWy-2: Crook County, Wyoming, Obtained from Clay Minerals Society, MO
Mineralogy	quartz: ~ 31% feldspar: ~ 13% carbonate: ~ 35% illite: ~ 15% chlorite: ~ 4–6% vermiculite: ~ 0.5% smectite: trace	kaolinite: ~ 100%	montmorillonite: ~ 99% quartz: ~ 1% carbonate: trace
Cation exchange capacity, meq/100 g (ASTM D9081)	13.0–18.0	1.6	70.2
Initial pH (ASTM D4972)	7.7–8.3	5.0	9.7
% finer than 0.075 mm (ASTM D422)	84	100	100
Atterberg limits:			
LL (%)	29–31	44	595
PL (%) (ASTM D2487)	16–17	29	62

DuPage County, Illinois. Kaolin and Na-montmorillonite are commercial clay minerals and were obtained from the American Clay Minerals Society. The mineralogies of these soils have been determined on the basis of the X-ray diffraction testing procedure and published literature [31]. Fig. 2 shows the X-ray diffraction records for the three soils. The approximate mineralogical composition of each soil is summarized in Table 1. The cation exchange capacity (CEC), pH, fines content and Atterberg limits for these soils have been determined on the basis of standard testing procedures, and the results are summarized in Table 1. Each of the three soils possesses a distinct mineralogy and chemical properties; therefore, the soil mineralogical effects on electrokinetic remediation can be adequately investigated.

3.2. Adsorption testing

Adsorption testing on the three soils was performed in order to understand the behavior of Cr(VI) under different concentrations and pH environments. Potassium dichromate (99.9% reagent grade) dissolved in deionized water was used to obtain the desired Cr(VI) concentrations in the soil specimens. All adsorption or batch experiments were performed at room temperature on the three soils in general accordance with ASTM Standard D3987 [32]. 50 ml of deionized water which contained Cr(VI) concentrations of 1, 5, 10, 15, 20, 30, 40, 50, 100, 250, 500 and 1000 mg l⁻¹ were added to 5 g

Fig. 2. (a) X-ray diffraction record for glacial till. (b) X-ray diffraction record for kaolin. (c) X-ray diffraction record for Na-montmorillonite.

of glacial till and kaolin samples. 40 ml deionized water containing Cr(VI) concentrations of 0.5, 2.5, 5, 7.5, 10, 15, 20, 25, 50, 125, 250 and 500 mg l⁻¹ were added to 2 g of the Na-montmorillonite samples. The pH of the samples was not adjusted. The pH of glacial till, kaolin and Na-montmorillonite samples ranged from 6.7 to 8.7, 3.9 to 4.9, and 8.3 to 9.1, respectively.

Adsorption tests were also performed to determine the effect of pH on Cr(VI) adsorption in kaolin. For these tests, three sets of kaolin samples were prepared. The first set consisted of five samples each containing 5 g kaolin mixed with 50 ml deionized water containing 10 mg l⁻¹ Cr(VI) concentration. The pH of these samples was adjusted to a preselected constant value ranging from 2 to 10 using dilute HNO₃ and dilute NaOH. The other two sets also consisted of five samples each prepared and pH adjusted following the same procedure as the first set of samples, except that the second set of samples had constant initial Cr(VI) concentrations of 50 mg l⁻¹. The third set of samples had constant initial Cr(VI) concentrations of 100 mg l⁻¹.

It was not possible to evaluate the pH dependence of Cr(VI) adsorption in glacial till. Glacial till possesses a high buffering capacity which made it impractical to adjust the pH. Nor were pH-controlled adsorption tests performed in Na-montmorillonite samples in this study; however, Cr(VI) adsorption behavior onto Na-montmorillonite at different pH values is reported to be similar to that on kaolin [17].

All adsorption test samples were equilibrated for a period of 24 h by gently shaking at 100 rpm using an ORBIT shaker. The samples were then centrifuged at 7500–15 000 rpm. The Na-montmorillonite samples were centrifuged for longer periods of time in order to separate the solid phase from the liquid phase. The sample supernatant was analyzed for chromium concentrations, using an atomic absorption spectrophotometer in accordance with the USEPA Method 7197A [33].

3.3. Electrokinetic testing

A total of six experiments were conducted on the three soils to investigate the influence of soil mineralogy and the effect of hematite or iron oxide (Fe₂O₃) in these soils on the removal of Cr(VI).

3.3.1. Electrokinetic test apparatus

A schematic of the electrokinetic test apparatus used for this study is shown in Fig. 3. The cylindrical test cell, which accommodates the soil sample, is made of plexiglass and has an inside diameter of 6.2 cm and a length of 19.1 cm. This cell is connected to the anode assembly at one end and to the cathode assembly at the other end. Provisions are made in these anode and cathode assemblies for attaching filter papers, a porous stone and a graphite electrode from the soil sample end face. These assemblies also provide gas vents to remove gases generated at the electrodes due to electrolysis. A small electrode compartment is provided at each electrode. The electrode assemblies are connected to reservoirs by suitable tubing. Valves are provided at each electrode assembly which control the flow of water from the reservoirs into the assembly. A power supply is connected to the electrodes to provide the desired voltage gradient across the sample.

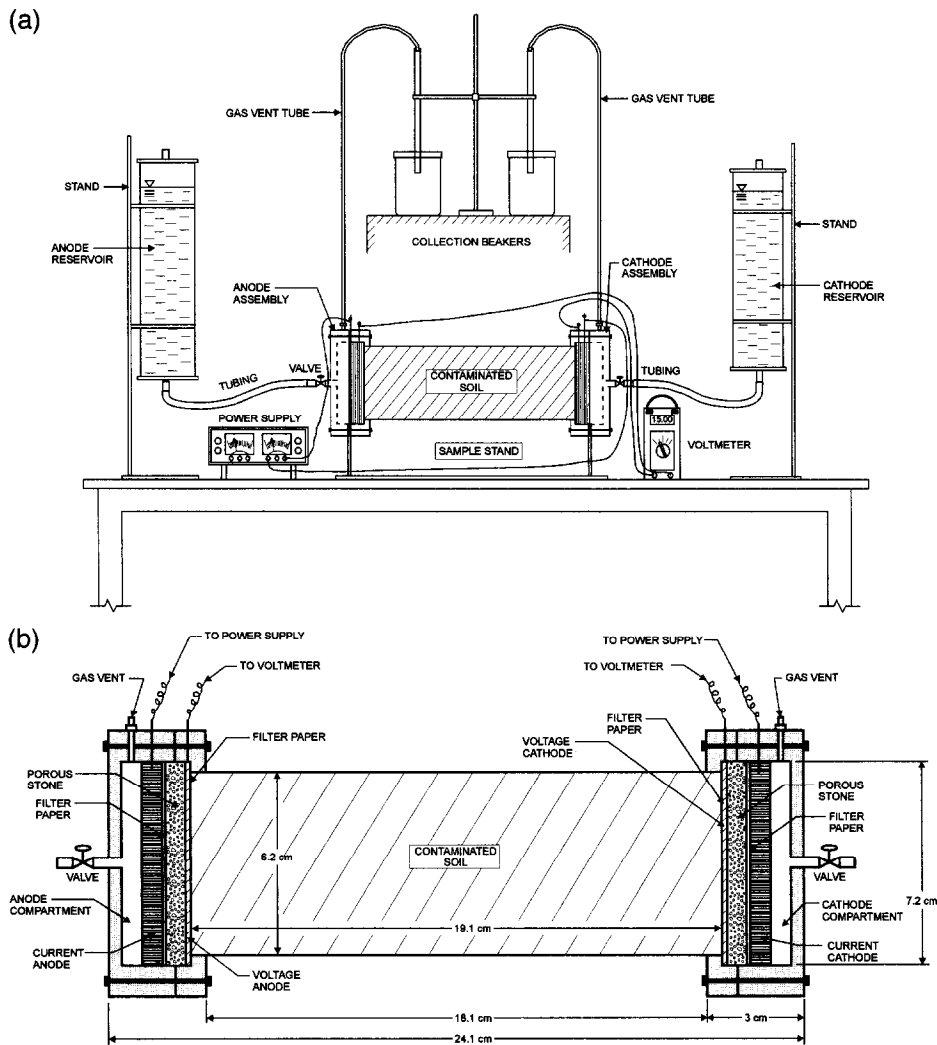


Fig. 3. (a) Schematic diagram of electrokinetic test set-up. (b) Details of the electrokinetic test cell.

3.3.2. Sample preparation

Potassium dichromate (99.9% reagent grade) dissolved in deionized water was used to contaminate the soil specimens. All of the experiments in this study were conducted with a 500 mg kg^{-1} Cr(VI) soil concentration. The tests involving iron oxide were conducted by contaminating soil specimens with 300 mg kg^{-1} of iron using Fe_2O_3 (99.9% reagent grade). Deionized water was used as the pore solution.

For each sample preparation, 1100 g of soil was mixed with deionized water containing 0.55 g Cr(VI) as $\text{K}_2\text{Cr}_2\text{O}_7$. In experiments involving glacial till and kaolin samples, Cr(VI) was dissolved in 330 ml of deionized water and the solution was then

mixed with the soil sample, using a wide stainless steel spatula. This procedure resulted in an initial moisture content of 30% for these soils. In experiments involving Na-montmorillonite samples, Cr(VI) was dissolved in 1100 ml deionized water and then mixed homogeneously with the soil. This method resulted in an initial water content of 100% for Na-montmorillonite. Contaminated soil samples were then allowed to equilibrate for a period of 1 h. The equilibrated soil sample was then placed in the electrokinetic cell in uniform layers and compacted with a stainless steel handheld pestle. A portion of the soil sample was retained to measure the initial Cr(VI) concentration, pH and water content.

3.3.3. Testing procedure

A constant voltage of 25 V DC or a constant voltage gradient of 1.3 V cm^{-1} DC was applied across the experimental cell for all of the tests. Identical hydraulic heads were maintained at each end of the cell so that the hydraulic gradient across the soil sample would be negligible. Each electrokinetic experiment was conducted for a duration of four days. At the end of the test duration, the soil from the test cell was carefully extruded. The soil specimen was sectioned into 0–4 cm, 4–8 cm, 8–12 cm, 12–15.5 cm and 15.5–19.1 cm slices starting from the cathode. Each section was then weighed.

A portion of each soil section was used to measure the pH and water content. 300–400 ml of deionized water was added to the remaining soil from each section. The soil–water suspensions were shaken vigorously for approximately 1 h. Soil particles were allowed to settle, and the supernatant was filtered through a $0.45 \mu\text{m}$ PTFE filter paper. Two portions of clear supernatant were sampled and analyzed for chromium using USEPA Method 7197A (flame atomic absorption) [33]. A Video 22 AA/AE spectrophotometer was used for the analysis. The detection limit for the technique used was approximately 0.05 ppm_w in solution. All of the analyses were performed in duplicate. Since this leaching procedure does not leach out chromium in trivalent form, the measured chromium concentrations represent Cr(VI) concentrations [34].

The water leaching procedure was followed for only the glacial till and kaolin, not for the Na-montmorillonite. Because of the swelling behavior of Na-montmorillonite, large volumes of deionized water would have been required to achieve soil suspension and then leach Cr(VI). Hence, the Na-montmorillonite soil sections were acid digested in accordance with USEPA Method 3050 [33]. For this method, 1–2 g of representative soil is used and 10 ml of 1:1 nitric acid is added to the soil. The mixture is heated to 95°C and refluxed for 10–15 min. 5 ml conc. nitric acid is then added and the mixture is refluxed for 30 min, and then this step is repeated to ensure complete oxidation. Using a ribbed watch glass, the sample is allowed to evaporate to 5 ml without boiling. Then 2 ml water and 3 ml 30% hydrogen peroxide are added and the sample is heated until the effervescence subsides. The sample is then cooled. Hydrogen peroxide is added in 1 ml aliquots and alternate warming and cooling of the sample is repeated until the effervescence disappears. Then 5 ml conc. HCl and 10 ml deionized water are added to the sample, which is refluxed for an additional 15 min without boiling. After the sample is cooled, it is made up to a volume of 100 ml and centrifuged until a clear supernatant is obtained. The supernatant was analyzed in duplicate for chromium, using an atomic absorption spectrophotometer. The measured chromium represents the total chromium

present in the soil sample. Aqueous samples, collected in the anode and cathode compartments and the anode and cathode reservoirs, were also analyzed for pH and chromium concentration.

4. Results and discussion

4.1. Adsorption test results

Fig. 4 shows the adsorption test results for the three soils. Maximum adsorption was observed to occur in Na-montmorillonite, followed successively by kaolin and glacial till. The adsorption data were found to follow the Langmuir type isotherm [35]. This result indicates that Cr(VI) removal from solution appears to be limited to the external surfaces of these soils. The Cr(VI) adsorption on Na-montmorillonite is significantly higher than the Cr(VI) adsorption on kaolin and glacial till. This result is mainly due to the larger surface area of Na-montmorillonite which provides significantly more surface functional groups with which Cr(VI) can complex. The surface areas of kaolin and glacial till are smaller and, as a result, the adsorption is less significant. In addition, the pH of the adsorption isotherm samples for glacial till was approximately 7.5–8.0; within this pH range, Cr(VI) exists primarily as CrO_4^{2-} . Low adsorption of Cr(VI) has been associated with CrO_4^{2-} and high pH [17].

The pH-controlled adsorption tests allowed the evaluation of the pH dependence of Cr(VI) adsorption on kaolin. These test results, shown in Fig. 5, clearly illustrate the significant pH dependence of adsorption in kaolin for the three different Cr(VI) concentrations of 10, 50 and 100 mg l^{-1} . In general, adsorption of Cr(VI) decreased with increasing pH. For kaolin, Cr(VI) adsorption was higher in the low pH range of 2–6 and

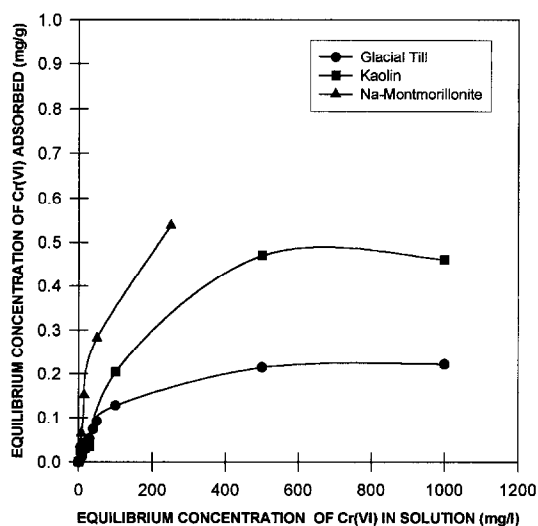


Fig. 4. Adsorption isotherms of Cr(VI) for glacial till, kaolin and Na-montmorillonite.

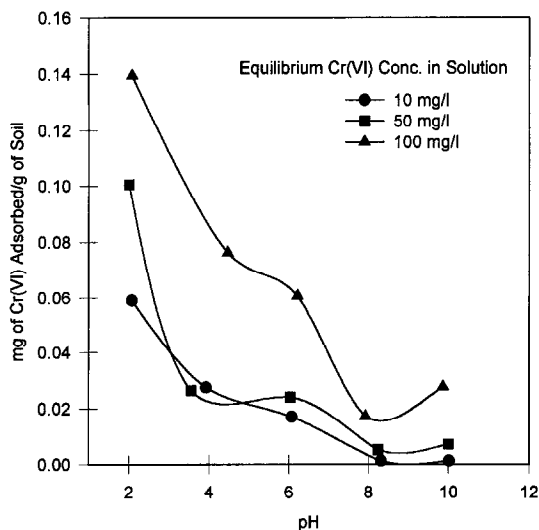
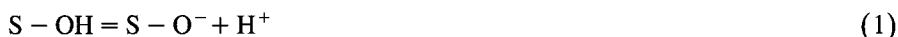


Fig. 5. Effect of pH on Cr(VI) adsorption for kaolin.

significantly lower in the pH range of 8–10. In the latter pH range, adsorption of Cr(VI) was negligible for low Cr(VI) concentrations of 10 and 50 mg l⁻¹ while adsorption was low for higher Cr(VI) concentrations of 100 mg l⁻¹.

Previous studies have shown that Cr(VI) exists predominantly as HCrO₄⁻ at low pH values and as CrO₄²⁻ at high pH values in solution [21]. The adsorption of cations and anions to soil surfaces can be described by the following complexation reactions according to the surface complexation model [36]:



where S-OH represents a typical surface functional group, M⁺ and L⁻ represent a cation and an anion, respectively. These complexation reactions are highly pH dependent because the extent of surface deprotonation, reaction (1), and protonation, reaction (2), is controlled by the solution pH. The solution pH at which the surface of a soil particle carries no charge is called the point of zero charge (PZC). If the solution pH is greater than PZC, the surface is negatively charged, which would allow more cation adsorption. When the pH is less than PZC, the surface is positively charged, which allows more anion adsorption [36]. Kaolin and montmorillonite are reported to have PZC values of approximately pH 3.5 and 2.0, respectively [27]. At pH values above these PZC values, the clays carry overall negative charges in suspension. Adsorption of Cr(VI) anions is expected to decrease with further increase of pH. The adsorption test results obtained in this study are consistent with the surface complexation model.

4.2. Electrokinetic test results

Electrokinetic experiments were conducted on the three soils, using an initial Cr(VI) concentration of 500 mg kg^{-1} , in order to determine the influence of the soil composition on the chromium removal efficiency. These tests are designated as EK-GT-1 for glacial till, EK-K-1 for kaolin and EK-NaM-1 for Na-montmorillonite. Electrokinetic experiments were also conducted with a Cr(VI) concentration of 500 mg kg^{-1} and an iron concentration of 300 mg kg^{-1} as Fe_2O_3 , in order to evaluate the effect of hematite on the chromium removal efficiency. These tests are designated as EK-GT-1F for glacial till, EK-K-1F for kaolin and EK-NaM-1F for Na-montmorillonite. Figs. 6–8 show the chromium concentrations and pH values with respect to normalized distance from the cathode for glacial till, kaolin and Na-montmorillonite, respectively. A discussion of these test results is presented below.

4.2.1. Effect of soil type

The concentration profiles in Figs. 6–8 show an increase in chromium concentration with increasing distance from the cathode. These results indicate that the initially introduced Cr(VI) is migrating toward the anode. The pH distribution across the soil sample for all three soils is also shown in Figs. 6–8. From these results, it can be seen

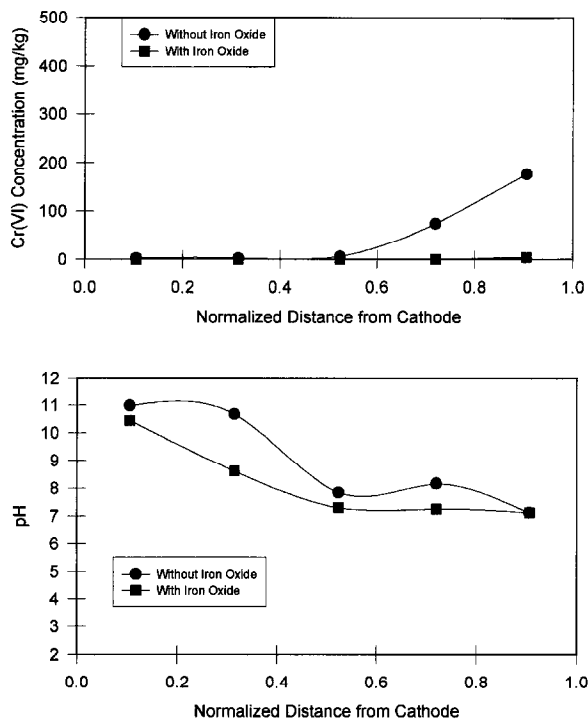


Fig. 6. Electrokinetic experimental results for glacial till.

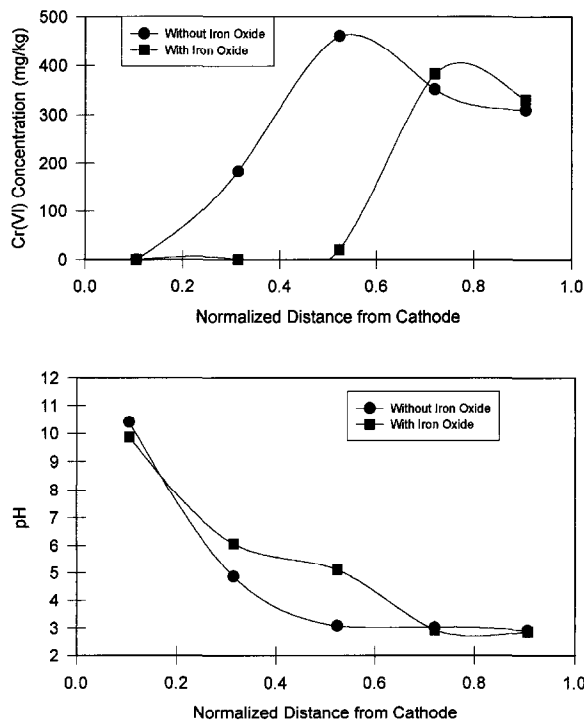


Fig. 7. Electrokinetic experimental results for kaolin.

that a distinct pH gradient was developed in the kaolin and Na-montmorillonite. The pH ranged from approximately 11 near the cathode to approximately 2 near the anode. However, a distinct pH gradient such as this was not observed in the glacial till. The pH across the glacial till specimen varied from 7.5 near the anode to 10.5 near the cathode. The presence of a high pH environment across the glacial till sample is due to a high carbonate content which increases the buffering capacity of this soil. The carbonates neutralize the H^+ ions generated electrochemically and suppress the development of an acidic pH environment near the anode.

These pH variations in different soils have profound effects on the mobility of Cr(VI) and, consequently, on the electrokinetic removal efficiency. At lower pH values or acidic environments, Cr(VI) exists as the $HCrO_4^-$ ion, while at higher pH values or neutral to alkaline conditions, Cr(VI) exists as the CrO_4^{2-} ion. Griffin et al. [17] reported the distribution of these two Cr(VI) species for different pH and Cr(VI) concentrations. They also studied the adsorption behavior of these Cr(VI) species onto soils and reported that the adsorption of $HCrO_4^-$ onto soils is significant but the adsorption of CrO_4^{2-} onto soils is negligible. This pH dependence on chromium speciation and the differences in adsorption characteristics of different chromium species explain the different chromium removal rates obtained from the electrokinetic experiments in this study.

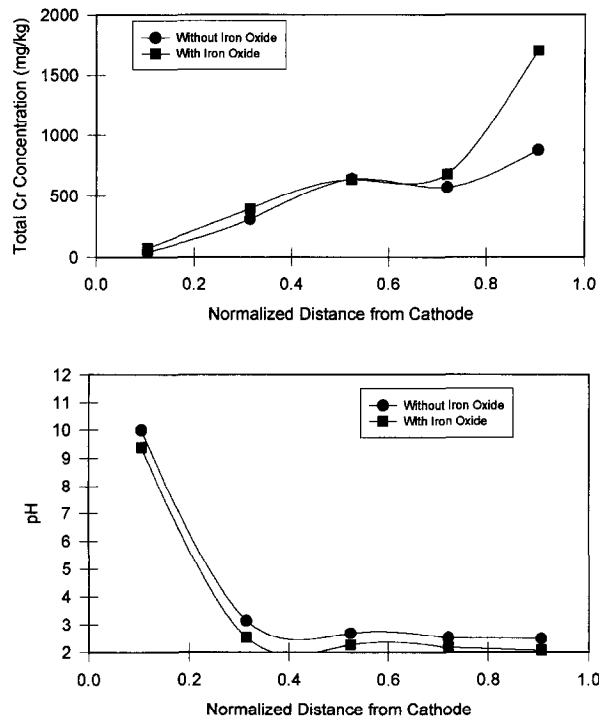


Fig. 8. Electrokinetic experimental results for Na-montmorillonite.

The presence of a high pH throughout the glacial till (Fig. 6) caused all of the Cr(VI) to exist as CrO_4^{2-} , which resulted in low adsorption to the soil. These CrO_4^{2-} ions in the pore water were then transported to the anode by electromigration. It should be mentioned here that, on the basis of the water level changes in the reservoirs, electroosmosis was observed to occur in the glacial till. However, the effect of electroosmosis was not strong enough to hinder CrO_4^{2-} migration to the anode. Most of the CrO_4^{2-} from the soil was flushed into the anode compartment and into the anode reservoir. In Fig. 6, the concentration profile for glacial till shows low Cr(VI) concentrations across the soil specimen. An analysis of aqueous samples from both the anode compartment and the anode reservoir revealed very high Cr(VI) concentrations, which suggests that most of the Cr(VI) was removed by electrokinetics.

Table 2 shows the mass balance analysis for this test, based on the measured Cr(VI) values in all of the soil sections, the anode and cathode compartments, and the anode and cathode reservoirs. As seen from Table 2, 56% of the Cr(VI) was accounted for at the end of this test. A careful assessment of this low mass balance was performed. The possibility of Cr(VI) reduction to Cr(III) was evaluated and it was determined that significant Cr(VI) reduction to Cr(III) would not occur because of the absence of reducing agents such as organic matter. Visual observation of the porous stones and electrodes indicated that a significant amount of chromium was either adsorbed or

Table 2
Cr(VI) mass balance analysis for glacial till and kaolin

Soil Type	Test	Initial Contaminant mass in soil (mg)	Contaminant mass after electrokinetic treatment					Mass balance (%)
			Remaining in soil (mg)	Anode compartment (mg)	Cathode compartment (mg)	Anode reservoir (mg)	Cathode reservoir (mg)	
Glacial till	EK-GT-1	441.15	48.67	52.16	0.20	142.68	1.44	56
	EK-GT-1F	435.18	1.05	18.16	0.09	10.59	ND	7
Kaolin	EK-K-1	422.34	209.19	36.92	0.22	3.45	ND	59
	EK-K-1F	425.00	126.74	94.94	0.03	16.10	ND	56

ND, Not detected.

trapped; however, no special analysis was used to extract this adsorbed or trapped Cr(VI). One test performed by Lindgren et al. [29] on sandy soil with chromate also yielded similar low mass balance. Further evaluation made by Lindgren et al. suggested that the Cr(VI) is adsorbed significantly to the anode graphite electrode. This evaluation also indicated the possible reduction of Cr(VI) to Cr(III) and subsequent adsorption of Cr(III) to the soil where it cannot be extracted by water. Additional electrokinetic tests reported by Reddy and Parupudi [37], which involved measuring both Cr(VI) and total Cr in glacial till contaminated with electroplating wastes, also support this conclusion.

A distinct pH gradient developed in kaolin causes Cr(VI) to exist in both CrO_4^{2-} and HCrO_4^- species (Fig. 7). The concentration profile, also shown in Fig. 7, indicates that moderate migration of Cr(VI) occurred in this soil as compared to the high migration in glacial till. Alkaline conditions near the cathode favor Cr(VI) to exist in the form of CrO_4^{2-} , which does not adsorb to the soil; therefore, most Cr(VI) exists in solution and migrates towards the anode. This migration is evident from the pH-dependent adsorption data shown in Fig. 5 and the negligible Cr(VI) concentrations detected in the soil near the cathode, as shown in Fig. 7. As the CrO_4^{2-} ions migrate towards the anode, they may form HCrO_4^- because of the acidic environment at the anode. HCrO_4^- adsorbs significantly to the soil, which retards the Cr(VI) migration. Low Cr(VI) concentrations were therefore detected in the anode compartment and reservoir.

A detailed mass balance for this test is presented in Table 2. The overall mass balance of Cr(VI) in this experiment was 59%, which suggests that some of the Cr(VI) was adsorbed to the graphite electrode at the anode. Some of the Cr(VI) may also have been partially reduced to Cr(III) at the anode and adsorbed to the soil near the anode.

The migration of Cr(VI) in Na-montmorillonite appears to be similar to the Cr(VI) migration in kaolin (Fig. 8). A low pH environment near the anode favors adsorption of Cr(VI), while alkaline pH conditions near the cathode result in negligible Cr(VI) adsorption. Because of the acid digestion procedure which was followed for analytical testing, the chromium concentrations that were measured represent the total chromium. Cr(VI) concentrations were measured in the anode compartment and reservoir. A total chromium mass balance of 82% was obtained in this experiment. Most of the chromium remained in the soil, which suggests that Cr(VI) is relatively immobile in this soil due to high adsorption.

4.2.2. Effect of iron oxide

Iron deposits of hematite, pyrite and goethite occur in abundance in natural soils. In this study, experiments were conducted on three soils to investigate the influence of hematite on the electrokinetic remediation of Cr(VI). For these experiments, soils were contaminated with potassium dichromate and iron oxide (Fe_2O_3) to yield target concentrations of 500 mg kg^{-1} for Cr(VI) and 300 mg kg^{-1} for iron (Fe). The soils were equilibrated for approximately 1 h. After equilibration, the Cr(VI) concentrations were measured in the glacial till and the kaolin and the total chromium concentration was measured in Na-montmorillonite. The measured Cr(VI) concentrations in glacial till and kaolin were found to be significantly lower than the targeted concentration of 500 mg kg^{-1} . The Cr(VI) concentrations were reduced from 500 to 56 mg kg^{-1} in glacial till and from 500 to 150 mg kg^{-1} in kaolin. Only the total chromium could be measured in Na-montmorillonite and this was found to be equal to the initial Cr(VI) concentration. The observed lower Cr(VI) concentrations in both glacial till and kaolin are attributed to the presence of iron oxide in these soils. The initial pH of the glacial till was 7.7, indicating that Cr(VI) exists predominantly in the form of CrO_4^{2-} , and it is reported in the literature that CrO_4^{2-} adsorption onto iron oxide (Fe_2O_3) is significant [25]. In addition, hematite may have reacted with the constituents of glacial till, which may have favored further removal of Cr(VI) from the pore water. The initial pH of the kaolin was about 5, suggesting that Cr(VI) exists in both HCrO_4^- and CrO_4^{2-} forms. The partial adsorption of Cr(VI) onto iron oxide may have contributed to the lower Cr(VI) concentration detected in this soil. Published literature shows that Fe_2O_3 is stable over a wide range of Eh and pH conditions and also that amorphous $\text{Fe}(\text{OH})_3$ can precipitate under slightly acidic to alkaline conditions [27]. These factors, combined with the water extraction method used for Cr(VI) analysis, explain the observed Cr(VI) concentrations in these soils prior to electrokinetic remediation.

The results of electrokinetic experiments on glacial till, kaolin and Na-montmorillonite with iron oxide are plotted in Figs. 6, 7 and 8, respectively, along with the results from the tests which were conducted without iron oxide. Fig. 6 shows that alkaline conditions existed in the glacial till in the presence of iron oxide during electrokinetics because of the high buffering capacity of the soil due to its high carbonate content; therefore, the acid front was not developed in this soil. Alkaline pH conditions of 7 to 7.4 were detected in the soil near the anode, while the pH ranged from 8.6 to 10.4 in the soil near the cathode. These pH values were slightly lower than the values that were measured in the experiment conducted in the absence of Fe_2O_3 . In the presence of Fe_2O_3 , negligible Cr(VI) concentrations were detected in the soil, anode and cathode compartments and reservoirs (see Table 2). The overall mass balance of Cr(VI) in this experiment was 7%, compared with a 56% mass balance in the experiment conducted in the absence of Fe_2O_3 . It should be noted that the low Cr(VI) concentration profile shown in Fig. 6 is illusive because it indicates a higher removal of Cr(VI) when iron oxide was present; however, the mass balance analysis shows that most of the Cr(VI) actually remained in the soil.

The initial pH of the glacial till in this experiment, as mentioned earlier, was 7.7. At this pH value, Cr(VI) exists as CrO_4^{2-} . On the basis of the results of the adsorption tests, the adsorption of CrO_4^{2-} onto glacial till is insignificant at this pH (Fig. 4). However,

adsorption of CrO_4^{2-} onto Fe_2O_3 and $\text{Fe}(\text{OH})_3$ has been reported to be significant [25,38]. Rai et al. [25] reported adsorption of Cr(VI) onto pure iron oxide to vary from 90% to 30% at pH values of 7 to 8, respectively. This significant adsorption behavior of CrO_4^{2-} onto iron oxide caused the removal of Cr(VI) from the pore water. In addition to the adsorption, Cr(VI) may have undergone other reactions with the glacial till in the presence of the iron oxide. Baron et al. [39] reported the finding of two iron-chromate precipitates, namely $\text{KFe}_3(\text{CrO}_4)_2(\text{OH})_6$ and $\text{KFe}(\text{CrO}_4)_2 \cdot 2\text{H}_2\text{O}$, in a silty soil contaminated with chrome plating solutions. These precipitates significantly immobilized Cr(VI) in the solution. Similar geochemical conditions were present in our experimental system where chromate solution was added to a mixture of iron oxide and glacial till. The basic nature ($\text{pH} > 7$) of the glacial till would favor the formation of $\text{KFe}_3(\text{CrO}_4)_2(\text{OH})_6$, which can significantly reduce the Cr(VI) concentration in solution.

Although the pH in the glacial till ranged from 7 to 10.4 after the electrokinetic treatment, the migration of Cr(VI) during electrokinetics was insignificant because of the low Cr(VI) concentration in the pore water prior to treatment. The water extraction procedure used in this study did not leach out the adsorbed Cr(VI) onto the iron oxide which was present in the soil. Furthermore, as with the tests conducted without iron oxide, the reduction of Cr(VI) to Cr(III) and the adsorption of the latter to the soil near the anode and the graphite electrode may also have contributed to the extremely low mass balance for Cr(VI). These test results demonstrate that the presence of Fe_2O_3 in soils such as glacial tills creates complex geochemistry and inhibits Cr(VI) removal by electrokinetics.

The results of the electrokinetic experiment on kaolin in the presence of iron oxide are shown in Fig. 7. The absence of strong buffering species such as carbonates in this type of soil allowed the development of an acid front in the soil. The pH was approximately 3 in the soil near the anode and increased to a pH of about 10 near the cathode. The addition of Fe_2O_3 to the soil resulted in an increase in pH in the soil located a distance away from the cathode and the anode. The Cr(VI) concentrations detected in the soil near the cathode were significantly lower than those detected near the cathode in the experiment conducted without Fe_2O_3 . The Cr(VI) concentrations in the soil near the anode were similar to those detected near the anode in the experiment conducted without Fe_2O_3 , as illustrated in Fig. 7. Higher Cr(VI) concentrations were detected in the anode compartment and reservoir than were detected in the same locations in the experiment without Fe_2O_3 (see Table 2). The overall Cr(VI) mass balance for this experiment was 56%, compared with a 59% mass balance for the experiment without Fe_2O_3 .

In kaolin, the pH was about 3 near the anode, suggesting that HCrO_4^- was the predominant Cr(VI) species; however, near the cathode, the pH was about 10, which suggests that CrO_4^{2-} was the only Cr(VI) species [17]. The pH of the soil away from either electrode ranged from 5 to 6, indicating that both HCrO_4^- and CrO_4^{2-} were present in the soil. These pH variations influence Cr(VI) adsorption onto kaolin and Fe_2O_3 . At high pH values, adsorption of Cr(VI) onto kaolin and Fe_2O_3 is insignificant; hence, in the high pH regions near the cathode, Cr(VI) migration was higher than in the experiment conducted without Fe_2O_3 . In the low pH regions of the soil near the anode, Cr(VI) migration was similar to that in the experiment conducted without Fe_2O_3 .

Table 3
Total chromium mass balance analysis for Na-montmorillonite

Test	Initial Contaminant mass in soil (mg)	Contaminant mass					Mass balance (%)
		Remaining in soil (mg)	Anode compartment (mg)	Cathode compartment (mg)	Anode reservoir (mg)	Cathode reservoir (mg)	
EK-NaM-1	202.63	163.99	1.85	0.13	0.50	0.19	82
EK-NaM-1F	199.34	178.59	0.31	0.06	2.80	ND	91

ND, Not detected.

Overall, this resulted in higher Cr(VI) migration in the presence of Fe_2O_3 . The low mass balance of 56% was attributed to adsorption of the Cr(VI) to the anode graphite and reduction to Cr(III) and subsequent adsorption to the soil near the anode, as explained for the tests without iron oxide.

The electrokinetic test results for investigating the influence of Fe_2O_3 on Na-montmorillonite, under similar test conditions as those for glacial till and kaolin, are presented in Fig. 8. Because of the high plasticity of Na-montmorillonite, a large quantity of water would have been required to produce a suspension for Cr(VI) measurement. The use of this method was not feasible and, hence, the samples were acid digested. The acid digestion procedure oxidizes Cr(III) to Cr(VI); therefore, the measured concentrations represent the total chromium in the soil. Test results showed that a strong acidic front was developed. Very little chromium was detected in the anode compartment and reservoir. Most of the chromium was present in the soil, as in the results obtained for the kaolin test (Fig. 7). The presence of most of the chromium in the soil was due to the high adsorption of chromium, as shown in Fig. 4. A high mass balance of 91% was obtained for the total chromium and most of the chromium was detected in soil, as shown in Table 3. Since the results obtained were for the total chromium, it is not possible to explain these results with respect to the individual chromium species.

5. Summary and conclusions

Laboratory experiments were conducted on three different soils: glacial till, kaolin and Na-montmorillonite, in order to evaluate the effect of soil mineralogy on the removal of Cr(VI) by the electrokinetic remediation technique. Additional electrokinetic experiments were also conducted on these soils to investigate the effect of naturally occurring hematite on the removal of Cr(VI). The experiments were conducted with an initial Cr(VI) concentration of 500 mg kg^{-1} and an iron concentration of 300 mg kg^{-1} in the form of iron oxide, under an induced DC voltage gradient of 1.3 V cm^{-1} for four days. In addition to these electrokinetic experiments, adsorption experiments on the three soils were conducted at varying Cr(VI) concentrations and different pH values in

order to understand the adsorption behavior of Cr(VI). Based on the results of these experiments, the following conclusions can be drawn:

1. The adsorption of Cr(VI) in soils depends significantly on the soil mineralogy. For glacial till and kaolin, the Cr(VI) adsorption was low, while the Cr(VI) adsorption onto Na-montmorillonite was high. The pH of the soil plays an important role in the adsorption of Cr(VI). A low soil pH favors substantial Cr(VI) adsorption, while a high soil pH will cause the adsorption of Cr(VI) to be negligible.
2. The presence of buffering species such as carbonates prevents the development of an acid front and causes alkaline conditions to exist in the soil during electrokinetics. This observation was evident from the glacial till that was tested, which had about 35% carbonates. In low buffering soils, such as kaolin and Na-montmorillonite, an acid front develops and, consequently, acidic conditions exist near the anode while alkaline conditions exist near the cathode. These differences in pH which exist during the electrokinetic remediation process will affect Cr(VI) speciation and adsorption and, consequently, will affect the remedial efficiency. Cr(VI) removal from the glacial till was higher than Cr(VI) removal from both the kaolin and Na-montmorillonite because of low adsorption of Cr(VI) under alkaline conditions.
3. The effect of hematite or iron oxide in soils on the removal of Cr(VI) by electrokinetics depends on the soil mineralogical composition. In soils such as glacial till, the presence of iron oxide creates complex geochemistry and retards Cr(VI) removal. However, in homogeneous clays such as kaolinite and Na-montmorillonite, the presence of iron oxide does not significantly affect Cr(VI) removal by electrokinetics.

This study clearly demonstrates that a thorough understanding of the effects of the mineralogical composition of the soil and the effects of other naturally occurring soil substances such as hematite is vital in order to successfully use the electrokinetic remediation technique in actual field applications.

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