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Removal of Mercury from Clayey Soils Using Electrokinetics

Krishna R. Reddy,* Carlos Chaparro, and Richard E. Saichek

Department of Civil and Materials Engineering, University of
Illinois at Chicago, Chicago, Illinois, USA

ABSTRACT

Numerous sites have been polluted with mercury as a result of accidental spills and improper disposal practices, and these mercury-contaminated sites may have adverse effects on human health and the environment. Innovative and cost-effective remediation techniques are urgently needed, and this study was performed to investigate the use of electrokinetics for mercury-contaminated soils. Initially, batch tests were performed on two soils, kaolin and glacial till, spiked with mercury(II) to investigate mercury desorption and complexation under different pH environments (pH range 2–12). The complexing agents included disodium ethylenediaminetetraacetate (Na-EDTA), potassium iodide (KI), and sodium chloride (NaCl), and these solutions were used at a concentration of 0.1 M. In addition, deionized water was used for comparison purposes. Based on the batch tests, Na-EDTA and KI were identified as the complexing agents with the greatest potential. The removal efficiency of these complexing agents was then examined by conducting electrokinetic experiments that employed the same solution concentration (0.1 M) and voltage gradient

*Correspondence: Krishna R. Reddy, Department of Civil and Materials Engineering, University of Illinois at Chicago, 842 West Taylor St., Chicago, Illinois 60607, USA; E-mail: kreddy@uic.edu.



(1.0 VDC/cm) conditions. These tests indicated that for both soils, KI was a more effective complexing agent than Na-EDTA under electrokinetics. For the kaolin soil, the electrokinetic treatment using KI removed approximately 97% of the initial contaminant present (500 mg/kg of Hg(II)), leaving a residual concentration of 16 mg/kg of Hg in the soil, whereas on the glacial till soil, KI removed only 56% of the initial contaminant present (500 mg/kg of Hg(II)), leaving a residual concentration of 220 mg/kg of Hg in the soil. The lower Hg removal from glacial till is attributed to the presence of organic matter, which increased mercury adsorption or the formation of insoluble mercury surface complexes.

Key Words: Electrokinetic remediation; Electrokinetics; Soils; Remediation; Metals; Mercury.

INTRODUCTION

Mercury contamination from improper disposal practices and/or accidental spills potentially threatens human health and the environment; however, there are many factors that may affect mercury behavior. The nature of the release, such as the form of the Hg species and its concentration, as well as the soil properties and aqueous chemistry into which it was discharged are important considerations. Davis et al.^[1] note that the moisture, organic, and sulfur contents of the soil as well as the microorganisms that are present are of particular concern when assessing mercury transport, fate, and bioaccessibility. The toxicity of mercury depends on a number of variables, including the species of mercury, the path of exposure, and the concentration. Deleterious human health effects have been well documented, and mercury has been proven to cause severe damage to the central nervous system, dementia, and kidney failure.^[1,2]

In the past, mercury-contaminated soils were excavated and then transported to a regulated landfill that could accept mercury waste. Excavation, however, is inefficient and has disadvantages such as high transportation costs and the possible exposure of the contaminants to the employees or the public. Therefore, more emphasis has been placed on conducting the remediation process at the site using an in-situ or ex-situ technology. According to the United States Environmental Protection Agency (USEPA), the best demonstrated available technology (BDAT) for the remediation of mercury-contaminated soils is ex-situ thermal treatment (such as thermal desorption and/or incineration).^[2] A drawback of thermal treatment is that it is typically associated with high costs, so there exists a need for a new, efficient and cost-effective remediation technology for the rapid rehabilitation of mercury-contaminated sites.

Electrokinetic remediation is one of the most promising in-situ or ex-situ soil decontamination processes, and it is capable of concurrently removing a variety of heavy metals from soils. Many investigations have shown that it is effective at the removal of heavy metals such as lead, chromium, copper, nickel and cadmium from different types of soils.^[3-11]



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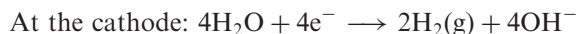
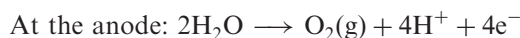
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The primary objective of this study was to investigate using the electrokinetic process as a cost-effective extraction method for the treatment of mercury(II)-contaminated soils. Mercury(II) was selected because it is stable in well-oxygenated soils, which are often present under terrestrial conditions.^[12] For this investigation, two types of soils, kaolin and glacial till, were artificially contaminated with Hg(II) in the laboratory. After the soils were contaminated, they were used along with three different complexing agents in a series of batch tests at different pH conditions to evaluate Hg(II) desorption and complexation. Then, the same soils were used along with the two best complexing agents in bench-scale laboratory experiments to assess Hg(II) removal by the electrokinetic process.

BACKGROUND

The demand for innovative and cost-effective remediation technologies for contaminated soils has stimulated an intense effort to employ electrochemical technologies, particularly electrokinetic remediation. This remediation technique can be implemented under in-situ or ex-situ conditions, and it employs conduction phenomena in soils under an electric field to transport chemical species (ionic and nonionic) from the soils to the electrode locations. These species are subsequently removed from the electrode locations via a collection system that is engineered for each specific application.

An in-situ electrokinetic system consisting of electrodes and a power supply is used to surround the contaminated soil as shown in Fig. 1. The cathode is the negative electrode and the anode is the positive electrode. Basically, the power supply acts as an electron pump that inserts electrons at the cathode and removes them at the anode. To maintain electrical neutrality, oxidation–reduction (redox) reactions occur. At the cathode, neutral atoms, ions, or molecules gain electrons and are reduced, while at the anode, neutral atoms, ions, or molecules lose electrons and they are oxidized. An important electrokinetic redox reaction to consider is the electrolysis of water at the electrodes, which occurs according to the following reactions:



Electrokinetic remediation basically involves three electrokinetic transport processes: electromigration, electroosmosis, and electrophoresis.^[10] Electromigration describes the transport of ionic species that are present in the pore fluid, and this process includes the migration of H^+ and OH^- towards the oppositely charged electrode. The electromigration process conducts electrical current through a soil–water system; moreover, as the ions electromigrate towards the electrodes, they transfer momentum to water molecules, thereby generating an electroosmotic flow. Electroosmosis depends on the net amount of ionic migration towards an electrode location, and, in low permeability, clayey soils, the net ion migration may be high and it could significantly affect the decontamination process. The

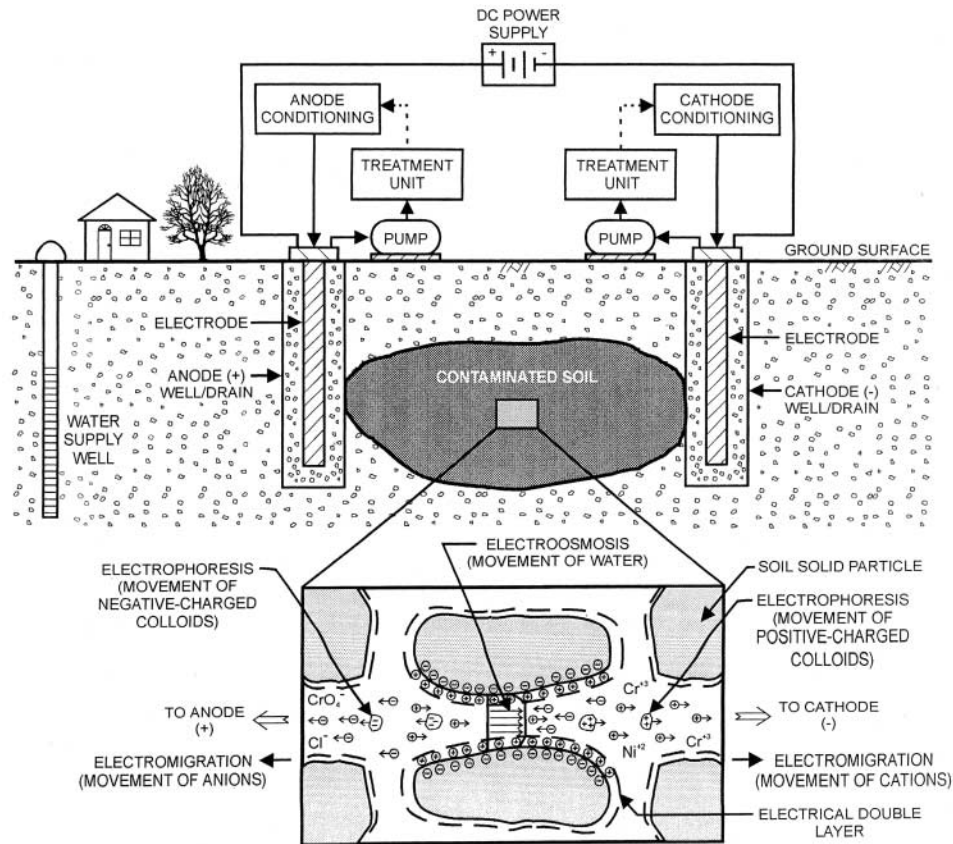


Figure 1. Schematic of electrokinetic remediation of soils.

following Helmholtz–Smoluchowski (H–S) equation is often used to estimate the average electroosmotic flow velocity (v_{eo}).^[11]

$$v_{eo} = -\frac{D\epsilon_0\zeta}{\eta} E_x$$

In the H–S equation, the flow velocity is proportional to the electrical gradient (E_x), zeta potential (ζ), and dielectric constant (D), and it is inversely proportional to the viscosity (η). The (ϵ_0) term represents the permittivity of a vacuum ($8.854 \times 10^{-12} \text{ C/V m}$), and the dielectric constant and viscosity are properties of the fluid. Generally, when the pH is below its Zero Point Charge (ZPC), a soil has a positive zeta potential and the electroosmotic flow occurs towards the anode. Conversely, when the pH is above the ZPC, the soil has a negative zeta potential and the electroosmotic flow occurs towards the cathode. Alternatively, the electroosmotic flow velocity is given by:

$$v_{eo} = K_e E_x$$



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where K_e is referred to as the electroosmotic conductivity. Electrophoresis is the migration of charged colloids, but, in a compact soil system, electrophoresis is less important since colloid-sized particles are generally restrained from movement.

As mentioned earlier, one of the most important redox reactions in electrokinetics concerns the electrolysis of water. This is because the ionic products of the electrolysis reactions may electromigrate towards the oppositely charged electrode location. Thus, as a consequence of electromigration, an acidic (H^+) front of solution may move from the anode towards the cathode, and/or an alkaline (OH^-) front of solution may move from the cathode towards the anode. The rate of electromigration may also be affected by ionic mobility, and, since hydrogen ions are smaller and have a greater mobility than hydroxyl ions, the acidic front generally moves faster through the soil.^[10] It should be noted that the changes in the surface charge of the soil particles (zeta potential) and the pore fluid properties (such as dielectric constant and viscosity) could affect the electroosmotic flow. In addition, the electrical gradient may not be uniform through the soil, so the electroosmotic flow is generally not uniform spatially or temporally.^[11] As a result, the electroosmotic coefficient K_e commonly varies with time, and such changes may cause the electroosmotic flow to cease or to reverse in direction.

Mercury primarily exists in the natural environment as either a metal (Hg^0) or a cation (Hg^{2+}), and the adsorption of mercury to soils depends on the ligands that are present, particularly OH^- , Cl^- , and organic anions.^[12] In this present study, emphasis was placed on more soluble mercury compounds, such as mercury(II) hydroxide ($Hg(OH)_2$) and mercury(II) chloride ($HgCl_2$), because soluble mercury compounds may be more easily transported and may have greater bioavailability.^[1] The chemical speciation of mercury with a single ligand (OH^-) is shown in Fig. 2(a) as a function of pH, and the stability of selected Hg^{2+} complexes (for a 1:1 complex) are shown in Fig. 2(b), which indicates that Hg^{2+} forms strong complexes with the ligands I^- , Br^- , Cl^- , and OH^- .

Studies on electrokinetic remediation of Hg-contaminated soils are scarce. Cox et al.^[13] investigated using an iodine/iodide (I_2/I^-) lixiviant solution located at the cathode for the electrokinetic remediation of HgS-contaminated soils. The objective of their study was to use the lixiviant solution to oxidize the HgS compounds in the soil and cause the mercury to be released as a soluble (HgI_4^{2-}) complex. This anion complex would then electromigrate towards the anode reservoir where it could be removed. Cox et al.^[13] explain that the electrokinetic remediation of Hg-contaminated soils was difficult due to the low solubility of mercury compounds in most natural soils. Mercury pollution, however, may be released in a variety of different forms besides HgS, such as an elemental form (Hg^0), and it may then convert to other species such as $HgCl_2$, $Hg(OH)_2$, or toxic organic forms like dimethylmercury $[CH_3]_2Hg$.^[2] Gilmour and Henry^[14] determined that Cl^- and OH^- inorganic ligands would dominate in normal water systems because they are present at high concentrations and possess large stability constants. Henke et al.^[2] reported that the aqueous solubilities of $HgCl_2$, Hg_2Cl_2 , and HgO are 70,000, 2.0, and 53 mg/L, respectively, whereas the solubility of HgS is only 10 μ g/L.

In the present study, the soils used possessed a low amount of sulfide, and the experiments were aimed at simulating an accidental spill or industrial release of

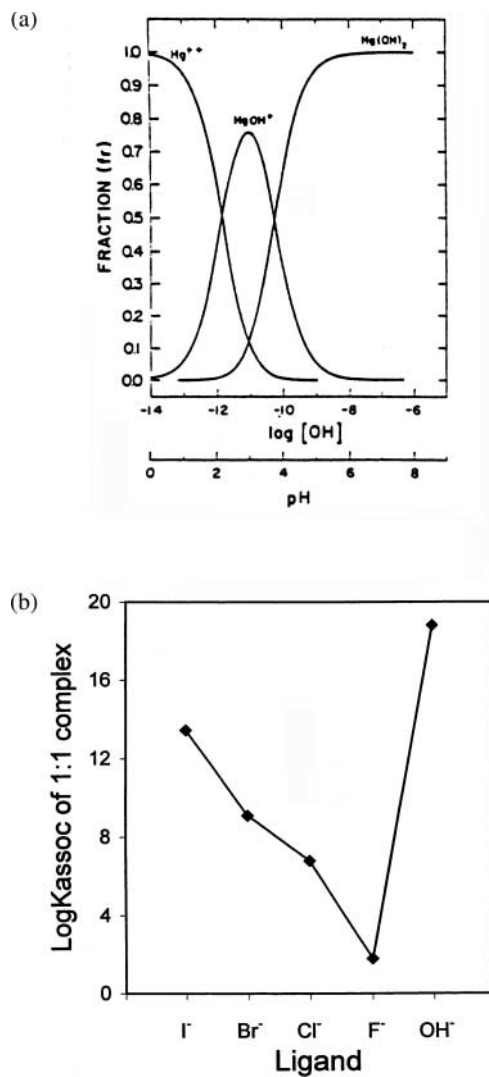


Figure 2. Mercury: (a) speciation and (b) complexation.

mercury into a common soil environment, where there would be a greater tendency for Hg to associate with Cl⁻ and/or OH⁻. Like the investigation by Cox et al.,^[13] in a few experiments this study used an iodide solution (KI) at the cathode to form HgI₄²⁻ complexes that would electromigrate towards the anode for removal. In the present study, however, strong oxidizing conditions were not crucial since the initial state of the Hg contaminant was HgCl₂ and not a relatively insoluble species like HgS.



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The effects of pH, chloride, and organic substances on the behavior and adsorption of mercury has been the topic of several research studies.^[17,18] Barrow and Cox^[15] and Yin et al.^[16] both determined that the maximum mercury adsorption occurred at around pH 3 to 5, and at higher pH values the adsorption decreased considerably. Yin et al.^[16] explain that the adsorption was dependent on the mineral surface charge. At pH values below 3, the soil surface is positively charged and repels soluble cations such as Hg^{2+} and HgCl^+ , whereas at slightly higher pH values (between 3 and 5), the charge reduces and new species form that are attracted to the mineral surface. It seems that a high amount of hydroxo-Hg species (HgOH^+ , HgOHCl , and $\text{Hg}(\text{OH})_2$) form over the small (3 to 5) range in pH, and they may be readily adsorbed.^[16] The amount of mercury adsorption decreases at higher pH values, and the reduced adsorption has been attributed to different factors. Barrow and Cox^[15] suggest that at a higher pH, the surface potential becomes more negative and there is a decrease in the amount of HgOH^+ with a corresponding increase of $\text{Hg}(\text{OH})_2$. Yin et al.^[16] found that the dissolution of organic matter occurred at higher pH values, and this reduced organic adsorption sites in the soil and enhanced Hg complexation with soluble organic ligands. Generally though, many other authors, such as Semu et al.,^[17] Trost and Bisque,^[18] and Anderson,^[19] state that Hg has an affinity for organic matter, and, therefore, it is more difficult to remove mercury from soils rich in organic matter. Lumsdon et al.^[20] and Yin et al.^[16] both determined that the presence of chloride (Cl^-) may lower Hg adsorption in soils, but the effect appears to be somewhat dependent on the organic content.

The purpose of this study is to systematically investigate the effects of different ligands such as OH^- , Cl^- , and I^- as well as the chelating agent EDTA on the electrokinetic remediation of Hg(II)-contaminated soils. In addition, this study was performed to investigate the effects of soil composition on the electrokinetic removal of Hg(II). The results of this study form a basis for understanding the transient chemical and physical processes that occur during the application of an electric potential under different soil compositional environments, and the data from these experiments may be incorporated into predictive electrokinetic mathematical models.

EXPERIMENTAL METHODOLOGY

A laboratory testing program was developed to characterize Hg(II) desorption from soils in the presence of different ligands (complexing agents), and to investigate the electrokinetic remediation technique for Hg(II) removal from soils when using the complexing agents with the highest desorption capabilities.

Soils Tested

Two types of soils, kaolin and glacial till, were used for this investigation. The kaolin was a commercially available soil that was obtained from the Thiele Kaolin Company in Georgia. The glacial till was a field-derived soil that was obtained from a project site within the Chicago metropolitan area. Physical and chemical tests were

**Table 1.** Properties of soils used for this study.

Property	Kaolin	Glacial till
Mineralogy	Kaolinite: 100% Muscovite: trace Illite: trace	Quartz: 31% Feldspar: 13% Carbonate: 35% Illite: 15% Chlorite: 4–6% Vermiculite: 0.5% Smectite: trace
Particle size distribution (ASTM D 422)		
Gravel	0%	0%
Sand	4%	20%
Silt	18%	44%
Clay	78%	36%
Atterberg limits (ASTM D 2487)		
Liquid limit	50.0%	21.7%
Plastic limit	27.4%	11.7%
Plasticity index	22.6%	10.0%
Specific gravity (ASTM D 854)	2.60	2.71
Moisture-unit weight relationships (Harvard miniature compaction test)		
Maximum dry unit weight	14.4 kN/m ³	18.5 kN/m ³
Optimum moisture content	27%	14.50%
Hydraulic conductivity/ coefficient of permeability	1.3×10^{-7} cm/s	4.1×10^{-8} cm/s
Porosity	46%	30%
Activity	0.29	0.28
Cation exchange capacity (ASTM D 9081)	1.0–1.6 meq/100 g	13–18 meq/100 g
pH (ASTM D 4972)	4.9	8.2
Organic content (ASTM D 2974)	Near 0%	2.8%
USCS classification (ASTM D 2487)	CL	CL

conducted to characterize these soils, and a summary of the test results is provided in Table 1. As seen from the results, the two soils are significantly different in their properties and these properties may be comparable or correlated to various clay soils encountered under field conditions.

Batch Tests

Batch tests were performed on soils spiked with mercury(II). The objective was to determine the complexing agent that would effectively desorb mercury from the soils under different pH conditions. The complexing agents selected for this study were disodium ethylenediaminetetraacetate (Na-EDTA), potassium iodide (KI), and



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sodium chloride (NaCl). These solutions contain ligands that form strong, stable complexes with mercury.^[21-23]

All three complexing agents were used at concentration of 0.1 M, and deionized water was used for comparison purposes. The pH of the soil-solution mixtures was adjusted to preselected values (specifically, pH = 2, 4, 6, 8, 10, and 12). The two types of soil selected in this study also permitted an assessment of the effects of soil chemistry on mercury desorption.

Sample Preparation

The two clean soils were air dried and pulverized to allow the soil to pass through #20 sieve (0.85 mm). After calculating the total amount of soil needed, the soil was weighed and placed in a large glass pan. The amount of mercury chloride necessary to contaminate the soil to 500 mg Hg(II) per kg of dry soil of mercury was weighed and dissolved in deionized water. The mercury chloride solution was then added to the soil and mixed with a stainless steel spoon until the mixture had a homogeneous appearance. The soil was allowed to equilibrate for 24 h, it was mixed again, and then it was dried in an oven at 60°C for 24 h. Finally, the dry soil was pulverized and thoroughly mixed and the initial concentration of Hg was measured.

Testing Procedure

Each sample contained a gram of dry Hg-spiked soil. The soil for each sample was weighed and placed into a 40-mL glass vial. Then, 20 mL of the prescribed complexing agent was added to each sample in the vial. Each vial was shaken, and the pH was adjusted to the preselected values by adding dilute HNO₃ and/or NaOH. After achieving the preselected pH values, all the vials were shaken continuously for 24 h to reach sample equilibrium. Next, the pH and redox potential were measured again and compared with the initial adjusted pH values. Following this step, the soil was filtered and centrifuged to separate the aqueous and solid phases. From each sample 10 mL of the supernatant was collected into a new 50 mL vial. The supernatant was then analyzed for mercury concentration. Duplicate soil samples were tested to ensure the accuracy and reproducibility of the test results.

Electrokinetic Testing

From the batch desorption tests, Na-EDTA and KI were determined to be the complexing agents with the highest desorption capabilities, so these complexing agents were selected for electrokinetic testing.



Sample Preparation

The contaminated samples of kaolin and glacial till were prepared by mixing these soils with mercury chloride solution in a manner similar to that used for the spiked samples prepared for the batch tests. The amount of water used was based on producing an initial target water content of 35% for the kaolin and 18% for the glacial till, and the target Hg(II) concentration for both soils was 500 mg/kg. These water contents were selected to yield wet of optimum conditions for better soil workability and to represent typical field moisture conditions. The target Hg(II) concentration was based on a mercury release from a natural gas industry site, but it was recognized that contaminant concentrations vary widely and are site specific. The moist, contaminated sample was allowed to equilibrate for a period of one hour. The equilibrated soil sample was then packed into a cylindrical electrokinetic cell (6.2 cm internal diameter and 19.1 cm long) in uniform layers and compacted with a stainless steel handheld pestle. A portion of the soil sample was retained for the measurement of initial Hg concentration, moisture content, and pH. The soil in the cell was then allowed to equilibrate for another 24 h.

Electrokinetic Test Setup and Testing Procedure

The electrokinetic cell was connected to the anode assembly at one end and to the cathode assembly at the other end. The main components of each anode and cathode assembly are filter papers, a porous stone, and a graphite electrode as shown in Fig. 3. The electrodes reside in the watertight chambers, which are connected to measuring reservoirs at one end, and to the soil specimen cylinder at the other end. The soil specimen is separated from these water-filled chambers by two porous stones, one each side of the soil specimen. To set up the test, the electrokinetic cells were placed in a horizontal configuration as shown in Fig. 3. The anode and cathode reservoirs were filled with deionized water, or the selected complexing agent (Table 2), a power supply was connected to the electrodes, and a constant voltage gradient was applied to the soil across the electrodes.

Experimental progress was monitored every day by measuring the voltage across the soil and the current generated (by means of a digital multimeter), and the time dependent liquid movement through the soil was measured by means of the graduated levels on the anode and cathode reservoirs. In addition, the pH of the solution in each reservoir was measured. The anode and cathode reservoirs were emptied and refilled with the appropriate solution on weekly basis. The solutions that were removed from the electrode reservoirs were then analyzed for mercury.

After a selected period of voltage application, the reservoirs and the electrode assemblies were disconnected, the specimen was extruded from the electrokinetic cell, and the soil was sliced into five uniform sections. Each section was analyzed for water content, pH, and mercury concentration. This allowed for a characterization of the changes in soil chemistry and the variation of Hg concentration across the soil specimen.



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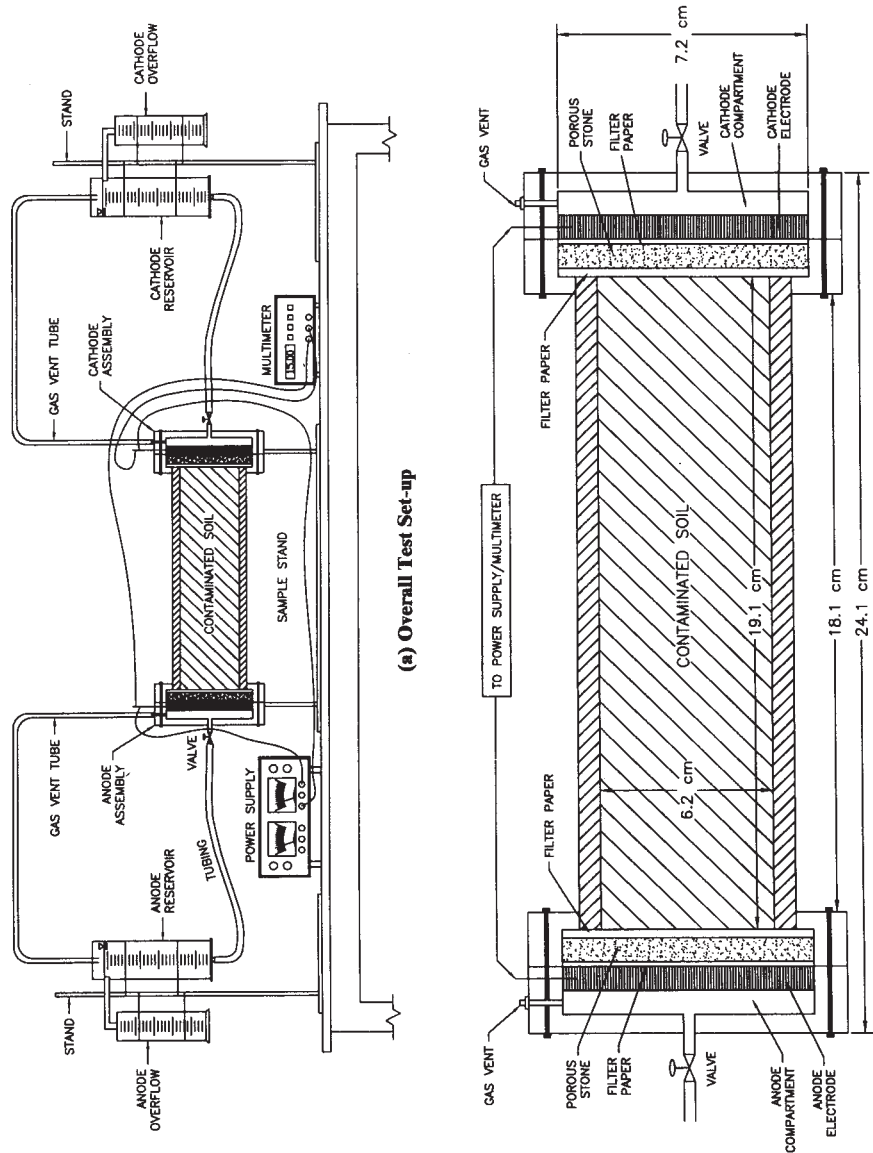


Figure 3. Schematic of electrokinetic test setup.

**Table 2.** Electrokinetic testing program.

Test no.	Test designation	Soil	Initial Hg(II) concentration (mg/kg)	Purging solution		Voltage gradient (V/cm)	Purpose
				Anode	Cathode		
1	K-Hg-water	Kaolin	500	Deionized water	Deionized water	1.0	Baseline testing
2	Gt-Hg-water	Glacial till	500	Deionized water	Deionized water	1.0	
3 ^a	K-Hg-NaEDTA1	Kaolin	500	Deionized water	D-WATER/ 0.1 M Na-EDTA	1.0	
4 ^a	Gt-Hg-NaEDTA1	Glacial till	500	Deionized water	D-WATER/ 0.1 M Na-EDTA	1.0	Enhancement using EDTA and KI
5	K-Hg-NaEDTA2	Kaolin	500	Deionized water	0.1 M Na-EDTA	1.0	
6	K-Hg-KI1	Kaolin	500	Deionized water	0.1 M KI	1.0	
7	Gt-Hg-KI1	Glacial till	500	Deionized water	0.1 M KI	1.0	

^aTests 3 and 4 were initially conducted with deionized water in both anode and cathode reservoirs. After 2 weeks, the deionized water in the cathode was replaced with 0.1 M Na-EDTA.



Electrokinetic Testing Program

A total of seven electrokinetic tests were performed as summarized in Table 2. The only parameters that varied in these tests were the soil type and the type of complexing agent. The initial mercury concentration (500 mg/kg), the voltage gradient (1 VDC/cm), and the complexing agent concentration (0.1 M) were the same for all seven tests. In addition, for all seven tests, the complexing agent was always supplied from the cathode reservoir and deionized water was supplied from the anode reservoir.

Tests 1 and 2 were conducted on the kaolin and glacial till soils, respectively, and plain deionized water was supplied from both the cathode and the anode reservoirs as a baseline for comparison purposes. Tests 3 and 4 were also conducted on the kaolin and glacial till soils, respectively. In these tests, however, deionized water was only used initially to remove as much Hg as possible without a complexing agent, and then, after 2 weeks, the deionized water at the cathode was replaced with 0.1 M Na-EDTA. Test 5 was conducted on the kaolin soil and used 0.1 M Na-EDTA at the cathode from the beginning. Tests 6 and 7 were conducted on the kaolin and glacial till soils, respectively, and used the 0.1 M KI complexing agent solution from the beginning.

Chemical Analysis of Mercury in Soils and in Aqueous Samples

The cold vapor atomic absorption spectrometry (CVAAS) technique was used for mercury detection.^[24,25] Prior to analysis, all aqueous and soil samples were pretreated, by means of acid digestion, to release mercury from the matrix constituents. This left the mercury in a free ionic state that could be rendered into the volatile elemental mercury Hg⁰ form by a reducing agent (SnCl₂). This mercury vapor is then released into the carrier gas and swept into a detection cell where the 2537-X resonant emission energy from a mercury vapor lamp is passed through it. The absorption of 2537-X energy is then monitored through a narrow band-pass filter using an ultraviolet-sensitive photomultiplier.

Soil Sample Digestion

Acid digestion of the soil was performed in accordance with USEPA Method 245.5 (1991).^[25] For this method, the soil was first dried for 24 h at 60°C. Approximately 0.1 g samples of the representative dried soil were weighed, and each sample was placed in a 50 mL bottle. Then, 2.5 mL of deionized water and 2.5 mL of aqua regia were added to each bottle. Immediately, the bottles were capped, mixed thoroughly, and placed in a water bath for two minutes at 95°C. The bottles were allowed to cool to room temperature, and then 25 mL of deionized water and 7.5 mL of potassium permanganate solution were added. The bottles were capped and mixed thoroughly and then placed in a water bath for 30 min at 95°C. After the hot water bath, the bottles were allowed to cool to room temperature,



and then 3 mL of sodium chloride–hydroxylammonium ($\text{NaCl-NH}_2\text{OH-HCl}$) were added to reduce the excess permanganate. The supernatant of the sample was then analyzed using CVAAS. Duplicate samples were analyzed to ensure the accuracy and reproducibility of the soil digestion procedure.

Aqueous Sample Digestion

Acid digestion of aqueous samples was performed in accordance with USEPA Method 245.1 (1994).^[24] This method first involved transferring 10 mL of each aqueous sample into a 50 mL bottle. Then, 0.5 mL of concentrated sulfuric acid (H_2SO_4) and 0.25 mL of concentrated nitric acid (HNO_3) were added and the solutions were mixed. After mixing, 1.5 mL of potassium permanganate solution (KMnO_4) was added to each container. The samples were then shaken and additional portions of KMnO_4 solution were added, if necessary, until the purple color persisted for at least 15 min. Then, 0.8 mL of potassium persulfate solution ($\text{K}_2\text{S}_2\text{O}_8$) was added, the bottles were capped and mixed thoroughly, and then they were placed in a water bath for 2 h at 95°C. After heating, the bottles were allowed to cool to room temperature, and 0.6 mL of sodium chloride–hydroxylammonium ($\text{NaCl-NH}_2\text{OH-HCl}$) was added to reduce the excess permanganate. The aqueous sample was then analyzed using CVAAS. Duplicate samples were analyzed to ensure the accuracy and reproducibility of the aqueous sample digestion procedure.

Quality Control

As mentioned previously, the chemical analysis of the soil and aqueous samples included the testing of duplicate samples to ensure reproducibility and accuracy. In addition, during CVAAS, each sample was analyzed twice to ensure accuracy. If a significant difference between samples or outlying values occurred, retesting was performed, however, for the majority of the tests, the concentrations that were measured in the duplicate samples were within a small range ($\pm 10\%$) of each other, especially when the mercury was present at a high concentration.^[26] In comparison to the initial contaminant concentration in the soil, the variation in chemical analysis was deemed to be acceptable. The average percent recovery of mercury for the spiked soil samples was about $114 \pm 7\%$ for the four tests performed on kaolin soil (two tests with Na-EDTA, one test with KI and one baseline test using deionized water).^[26] Similarly, the average percent recovery for the spiked soil samples was about $105 \pm 22\%$ for the three tests conducted with the glacial till soil (one test with Na-EDTA, one test with KI, and one baseline test using deionized water). The slightly greater recovery measured by chemical analysis as compared to the initial mass of mercury spiked into the soil was likely caused by a non-uniform mercury distribution within the soil. The good recovery of mercury from the spiked soils validates the accuracy of the acid digestion and CVAAS analysis.

Table 3 shows the mass balance analysis for all the electrokinetic tests performed on glacial till and kaolin soils. The mass balance compares the initial mass of



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Table 3. Mass balance analysis.

Purging solution (test number)	Initial mercury mass in soil (mg)	Residual Hg mass in the soil after the electrokinetic treatment (mg)	Mercury removed at anode reservoir (mg)	Mercury removed at cathode reservoir (mg)	Percentage of mercury removed from the soil cell ^a
Tests conducted on kaolin					
Deionized water (test 1)	456	399	15.8	0.0	12.5%
Na-EDTA (test 3)	403	252	12.6	0.4	37.5%
Na-EDTA (test 5)	406	410	12.1	0.21	0.0%
KI (test 6)	408	13.7	81.6	0.0	96.6%
Tests conducted on glacial till					
Deionized water (test 2)	429	421	0.0	0.0	1.0%
Na-EDTA (test 4)	538	379	0.5	0.0	29.5%
KI (test 7)	545	240.4	178.9	0.1	56.0%

^aThe percentage of Hg removed from the soil cells was calculated based on the initial Hg mass in the soil and the residual Hg mass in the soil after the electrokinetic treatment.



mercury present in the soil prior to electrokinetic treatment to the sum of the final mass of mercury remaining in the soil upon test completion added to the mass that accumulated in the anode and cathode reservoirs.

The electrokinetic experiment using the KI complexing agent on the kaolin soil had the lowest mass balance of about 23%, while the KI test on the glacial till soil had a mass balance of 77%. The first and second tests using the Na-EDTA solution on the kaolin soil had mass balances of 66 and 104%, respectively, and the Na-EDTA test on the glacial till soil had a mass balance of 71%. The low mass balance that was calculated for tests such as the KI test on kaolin may be attributed to the amount of Hg that was either volatilized or attached to the walls of the anode compartment and/or the anode electrode (evidence of this was observed visually). To some extent, Hg could also have been trapped in the porous stones; however, no special analysis was performed to extract this adsorbed or trapped Hg. The baseline deionized water test conducted on the kaolin soil only produced a little (12%) Hg removal, and Hg was not removed from the baseline deionized water experiment on the glacial till soil. These baseline tests, however, had mass balances of 91% for kaolin and 98% for glacial till. Therefore, the mass balance discrepancies in the tests using the KI solution are mainly attributed to adsorption and volatilization of mercury at the anode.

RESULTS AND ANALYSIS

Batch Test Results

The batch tests were conducted on the mercury-contaminated soils, kaolin and glacial till, using the three complexing agents, KI, Na-EDTA and NaCl, at a concentration of 0.1 M. Deionized water was also used for comparison, and different initial pH conditions were established by using HNO₃ and/or NaOH to adjust the pH values to 2, 4, 6, 8, 10, and 12. Figures 4(a) and (b) present the percentage of mercury desorption that occurred from the kaolin and glacial till soils, respectively. This percentage was calculated from the amount of mercury desorbed from the soils, which was equal to the amount of Hg measured in the supernatant at the end of the batch tests. As indicated by these results, deionized water and NaCl were ineffective for desorbing Hg in both soils. Moreover, KI and Na-EDTA had the highest desorption capabilities, with KI generally being the most effective, especially in glacial till. These results suggest that soil properties and composition, specifically surface area and/or organic content, affected mercury desorption, and the stronger adsorption to glacial till is attributed to its more varied mineralogy and greater organic content. The glacial till was found to possess clay minerals such as illite and chlorite (Table 1) that commonly have larger surface areas than kaolinite. Mitchell^[28] notes that the specific surface area of illite is about 65 to 100 m²/g, whereas kaolinite has a specific surface area of only around 10 to 20 m²/g. Furthermore, the glacial till possessed a 2.8% organic content, whereas kaolin had an organic content near 0%. Lumsdon et al.^[20] suggests that organic surfaces are the largest sinks for metals, even when there is a low organic content, and Yin et al.^[16] mention that organic matter



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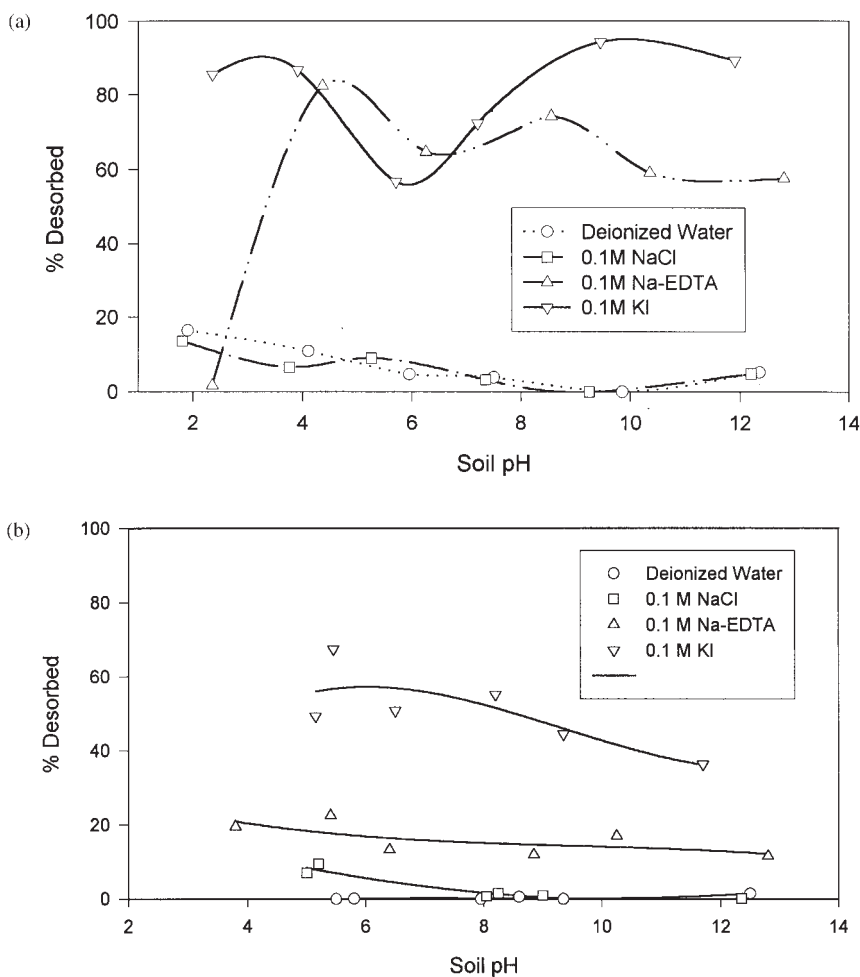


Figure 4. Desorption of mercury using different extractants: (a) kaolin and (b) glacial till.

has a stronger affinity for Hg(II) and, compared to inorganic components, organic matter has a greater surface area.

Although variations were observed in Hg desorption with changes in pH, the effects with deionized water were less pronounced than in other studies, such as the ones by Barrow and Cox^[15] or Yin et al.^[16] In these other studies, however, the soils were substantially different and the initial concentration of Hg was much lower. By observing Figs. 4(a) and (b), there does not appear to be a significant trend for Hg desorption with changes in pH in either soil, kaolin or glacial till. Since the deionized water and NaCl complexing agent had low Hg desorption in both soils, emphasis is placed on the KI and Na-EDTA solutions. In kaolin, KI accomplished the highest desorption at low pH values (2 to 4) and at high pH values (10 to 12), and the lowest

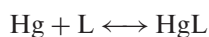


desorption occurred at a pH value near 6. The Hg desorption from kaolin by Na-EDTA showed a different behavior as the pH varied. At the lowest pH value (near 2), the Na-EDTA had a very low removal, which indicated that it was thermodynamically favorable for EDTA to complex other cations such as H^+ instead of Hg at this pH. At higher pH values, of about 4 to 12, the amount of Hg desorption significantly increased and remained above 50%, with a maximum Hg desorption of 82% at around a pH of 4.

For the kaolin samples, the initially adjusted pH value remained nearly constant and did not change after the 24-h period of shaking and equilibration. Conversely, for the glacial till samples, if the initially adjusted pH value was 2, 4, or 6, it often increased considerably after the 24-h period of shaking and equilibration. The increase in pH for these glacial till samples was attributed to the high acid buffering capacity of this soil due to the presence of carbonates. As seen in Table 1, the glacial till soil was found to possess a carbonate content of approximately 35%. Therefore, it was difficult to maintain a pH lower than about 5 within the glacial till.

The Hg desorption in the glacial till with KI decreased as the pH increased, and Hg desorption was 68% at a pH of around 5 and it gradually reduced to 37% at a pH of about 12. The Hg desorption in glacial till by Na-EDTA only slightly decreased as the pH increased, and the Hg desorption averaged approximately 15 to 20% over the range of pH values tested. It is of interest to note that Yin et al.^[16] observed an increase of Hg desorption with increasing pH, and they attributed the increase to the greater dissolution of organic matter at high pH. Yin et al.^[16] used distilled deionized water, however, in the present study, Hg desorption was accomplished by adding different complexing agents. Therefore, in this study, it is possible that the greater dissolution of organic matter at high pH resulted in organic complexes with the ligands from the complexing agents, and, consequently, there were not as many ligands available to form Hg complexes, so lower Hg desorption occurred.

Clearly, Hg removal efficiency depends on the type of soluble complexes that Hg forms with the free ligands. For instance, KI is a complexing agent that allows the formation of soluble complexes with Hg(II), and HgI_4^{2-} has a stability constant of 29.8.^[26] The next most effective complexing (chelating) agent was Na-EDTA, which also forms a soluble complex with mercury. Chelates, however, such as EDTA, are different from single bond, metal cation-ligand complexes, because chelates are anions that have two or more organic functional groups that may share pairs of electrons with a central metal cation.^[26] In order to adequately assess the stability constant of a chelating agent, competing metal cations need to be considered. Due to the complexity of chelating agents in soils, Lindsey^[26] uses a mixed equilibrium concentration constant ($K_{0.01}^m$) for an ionic concentration of 0.01 M. The mixed equilibrium constant means that the reactions and products are given as concentrations except for H^+ , OH^- , and e^- , which are expressed as activity. For the EDTA ligand, Lindsey^[26] reported $K_{0.01}^m$ values of 22.5 and 25.9 at 25°C for the following two reactions, respectively:





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Ringbom^[27] found that the stability constant of the Hg-EDTA complex changes with pH and, for a pH of 12, the stability constant was 23.3, while for a pH of 2, it was 8.1. This corresponds to the low removal of Hg in the kaolin at this pH. Finally, the Cl^- ligands form soluble complexes with mercury, and HgCl_4^{2-} has a stability constant of 14.5 ($\log K^\circ$ at 25°C where terms are expressed as activity),^[26] but, as seen in the batch test results, the NaCl complexing agent was relatively ineffective.

Electrokinetic Test Results

Electric Current

Figures 5(a) and (b) show the electrical current values for the electrokinetic tests performed on kaolin and glacial till, respectively. All the tests were conducted under the same applied constant-voltage gradient of 1.0 VDC/cm.

For the electrokinetic tests conducted with the kaolin soil, the initial current value for all four tests was about 2.5 mA, and the variations in current seem to correlate to the complexing agent that was used. For the baseline test using deionized water, the current decreased gradually until it reached a value of 0.35 mA at day 30. The current then remained at approximately this same value until the end of the experiment. For the first Na-EDTA test, which used deionized water for two weeks and then used Na-EDTA, initially, the current gradually decreased until it reached a value of 0.6–1.0 mA at around day 10, which was similar to the behavior in the deionized water test. Then, however, the current gradually increased to 3.0–3.5 mA at day 50, and the current remained near this value until the end of the experiment. By comparing this test to the deionized water test, it is evident that the increase in current was caused by the Na-EDTA solution and the presence of metal cation-EDTA complexes. In the experiment that was started with Na-EDTA at the cathode, the current initially reduced, like the tests previously described, but over time, the current gradually increased and behaved similarly to the first EDTA test. It should be remembered that the original moisture content of the soil was established by using deionized water, and the migration (by electromigration and electroosmosis) of the complexing agent into the soil is generally not uniform, spatially or temporally. For the kaolin test that used KI, the current increased and oscillated back and forth from around 2 mA to over 5 mA until day 33. Then, the current oscillation increased substantially and reached a maximum value of 13.7 mA at day 63. Thereafter, the current decreased rather erratically with time until it reached approximately 1.5 mA at the end of the test (i.e., at day 103). The elevated current levels in the KI test were associated with the replenishment of the KI solution, which was performed weekly basis. Compared to the tests described earlier, the high current in the KI experiment may have been an indication of the increased ionic activity and complex formation, such as HgI_4^{2-} .

For the electrokinetic tests with glacial till, the initial current value for all the tests was about 17.1–21.9 mA. The baseline test using deionized water had an initial current value of 17.4 mA. Then, the current decreased sharply until it reached a value of around 5 mA at day 12, and the current remained close to this value until the end

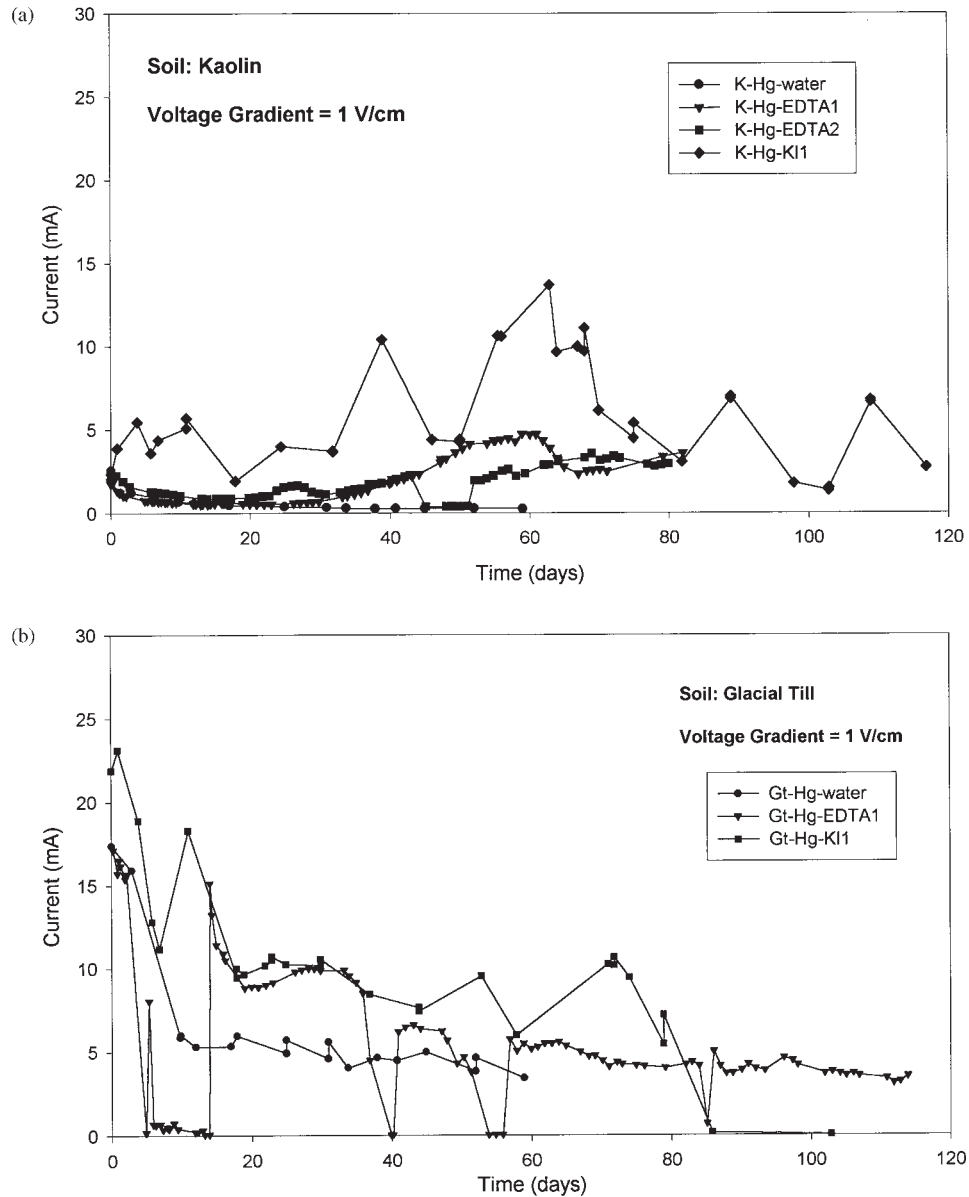


Figure 5. Current variation across the cell vs. time for the electrokinetic tests on: (a) kaolin and (b) glacial till.

of the test (i.e., at day 58). Compared to the kaolin test using deionized water, the glacial till exhibited a significantly higher current, and this was attributed to the higher carbonate content and more varied composition and mineralogy. For the test using Na-EDTA, the average current decreased with time from its initial



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value of 17.1 mA until it reached a value of around 6 mA at day 40. Later, the current continued decreasing, but at a slower rate, until it attained a value of approximately 3.5 mA at the end of the test. The test using KI had a much higher initial current value of 21.9 mA. Then, apparently as a result of electromigration, less and less ions remained in the soil-solution, so the ionic activity diminished, and the average current value gradually decreased until the end of the test. As in the KI test with kaolin, elevated current levels were commonly associated with the weekly replenishment of the KI solution, which thereby increases the available ions. Furthermore, the higher current observed in the tests using the EDTA and KI complexing agents suggests that there was increased ionic activity associated with these solutions due to the formation of complex species such as Hg-EDTA and HgI_4^{2-} .

Finally, it should be mentioned that the electrolysis reactions, which occur at the electrodes, and the subsequent electromigration of electrolysis products (H^+ and OH^-) toward the oppositely charged electrode, could have significantly affected the current. These ions may neutralize other ions in solution or react with each other to produce H_2O , which, over time, reduces the ionic concentration and the current.

Electroosmotic Flow

Figures 6(a) and (b) present the cumulative electroosmotic flow through the soil specimens during the electrokinetic tests performed on kaolin and glacial till, respectively. Using this data, the coefficient of electroosmotic conductivity (K_e) was calculated as follows.

$$K_e = \left(\frac{Q}{t}\right)\left(\frac{l}{A}\right)\left(\frac{L}{\Delta E}\right)$$

where Q is the volume of flow, t is the time period, A is the cross-sectional area of the sample, L is the length of the sample, and ΔE is the average electric potential difference across length of the soil specimen.

In the electrokinetic tests conducted on kaolin soil, the flow varied in rate as well as direction, depending on the complexing agent that was used. The baseline test with deionized water had a flow rate that was nearly zero, flowing just 17 mL towards the cathode during the entire test duration. In the first Na-EDTA test (which employed deionized water for the first two weeks), the flow occurred towards the cathode, and the coefficient of electroosmotic conductivity (K_e) was calculated to be around 1.1×10^{-6} – 2.04×10^{-6} cm²/s volt during the first 60 days. After the first 60 days, the flow rate in this test reduced to a slightly lower K_e value of 7.3×10^{-7} cm²/s volt. In the second Na-EDTA test (which started with Na-EDTA), the flow was similar to the first test and occurred towards the cathode. For the test conducted with KI, the flow occurred towards the anode during the first 70 days, and the K_e was calculated to be 4.0×10^{-6} cm²/s volt. After the initial 70 days, the flow rate slightly decreased and the K_e was calculated to be 1.5×10^{-6} cm²/s volt.



As mentioned earlier in the background discussion, the surface charge of the soil particles (zeta potential), the pore fluid properties (such as dielectric constant and viscosity), and the electrical gradient may vary through the soil, so the electroosmotic flow is generally not uniform. Moreover, these physical/chemical changes in the soil may cause the electroosmotic flow to even cease or to reverse in direction. It is also important to recall that the electromigration process generates electroosmotic flow. As the ions electromigrate towards the electrodes, they transfer momentum to the solution molecules, and the flow is related to the net amount of ionic migration towards an electrode location. Therefore, compared to the other electrokinetic tests performed in the kaolin soil, the high current observed earlier in the KI test,

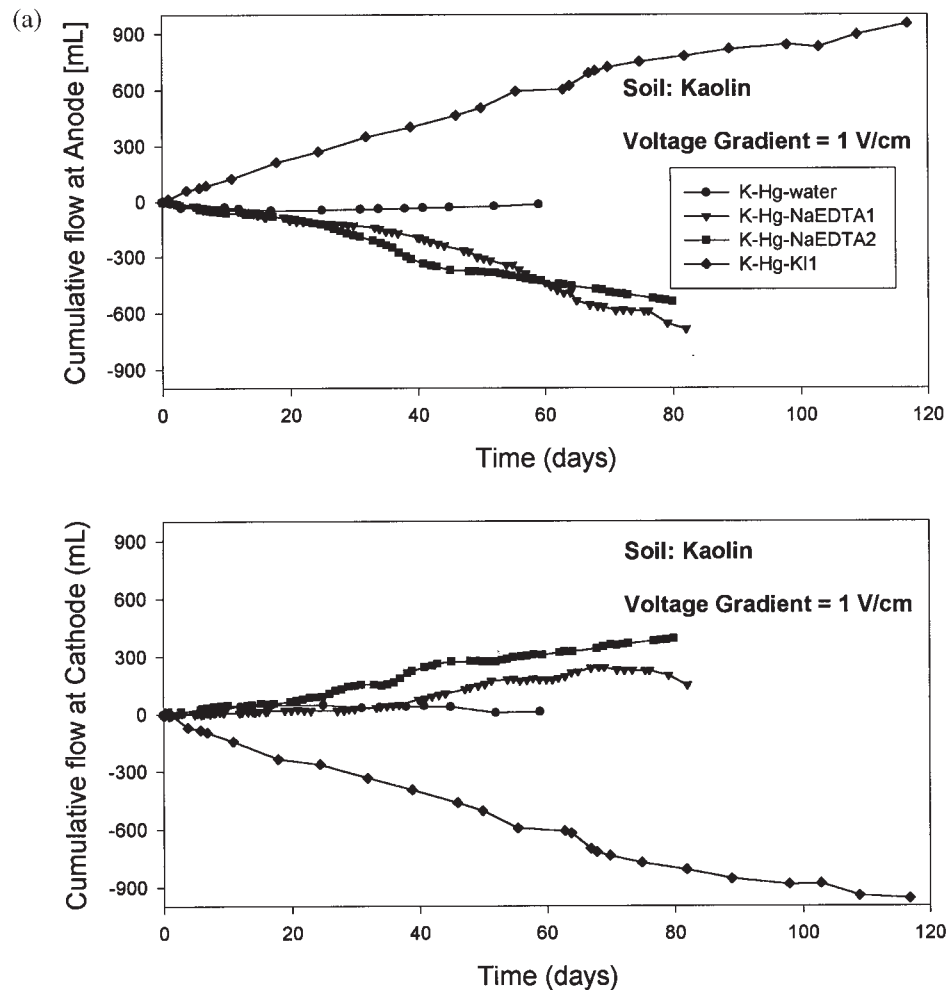
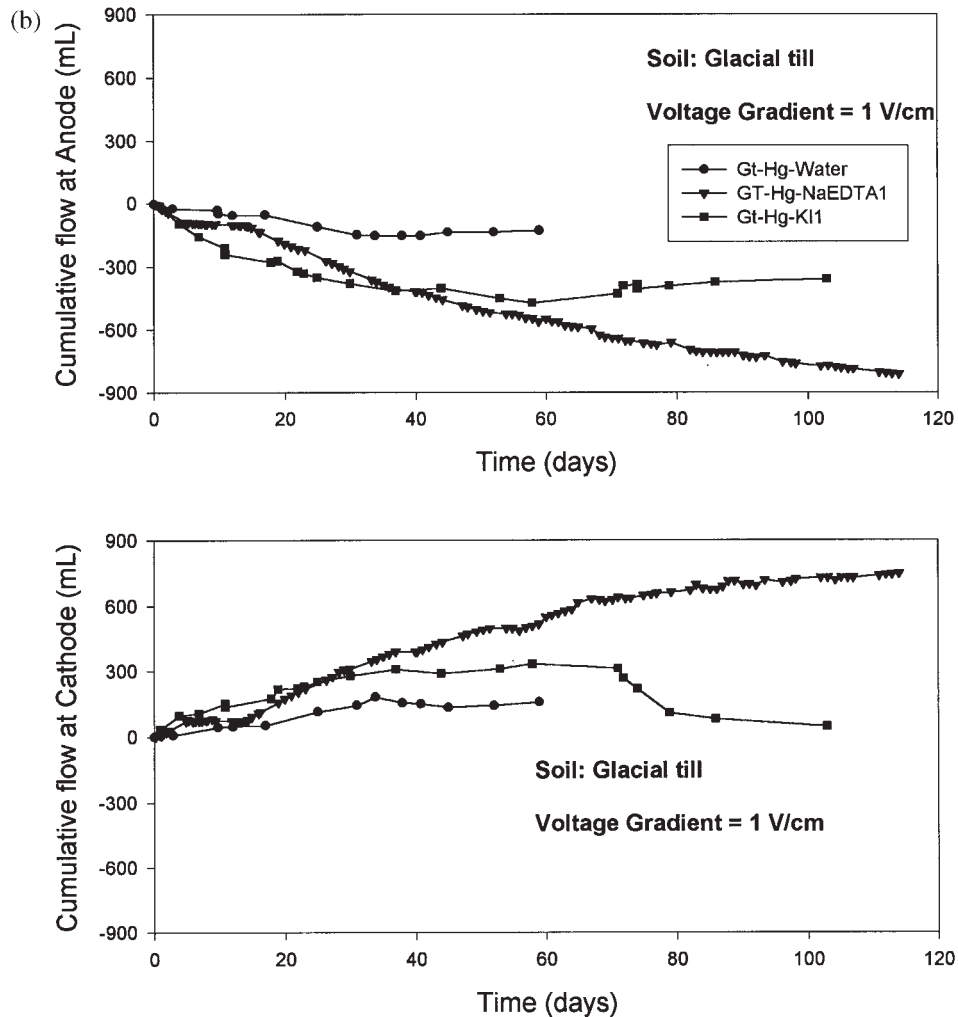


Figure 6. Cumulative electroosmotic flow vs. time for the electrokinetic tests on: (a) kaolin and (b) glacial till.



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*Figure 6.* Continued.

correlates to the elevated electroosmotic flow. Furthermore, since the flow in this test was directed towards the anode, it indicates that the net amount of electromigration was towards the anode, and this suggests that ions were in the form of anions or anionic complexes such as HgI_4^{2-} .

Similarly to the tests conducted on kaolin, the tests performed on glacial till also had an electroosmotic flow that varied in rate as well as direction, depending on the complexing agent that was used. In the baseline test, the flow occurred towards the cathode during the first 30 days, and K_e was calculated to be $1.9 \times 10^{-6} \text{ cm}^2/\text{s volt}$. After the first 30 days, the flow was insignificant. Compared to the deionized water test conducted on kaolin, it is likely that the greater K_e value in glacial till was due to



the more varied soil composition. For the glacial till test using Na-EDTA, the flow occurred towards the cathode during the first 65 days, and the K_e was calculated to be $3.6 \times 10^{-6} \text{ cm}^2/\text{s volt}$. Then, the flow rate decreased to around $9.5 \times 10^{-7} \text{ cm}^2/\text{s volt}$. For the test using KI, flow occurred towards the cathode during the first 10 days, and K_e was calculated to be $6.4 \times 10^{-6} \text{ cm}^2/\text{s volt}$. Then, from day 10 until day 58, the flow was reduced and the K_e was calculated to be $1.7 \times 10^{-6} \text{ cm}^2/\text{s volt}$. Next, the flow changed its direction and started to flow slowly toward the anode. For the KI test, the flow measurements indicate that, initially, cation electromigration towards the cathode dominated, possibly due to the smaller size and greater mobility of cations such as H^+ . With time, however, the number of electromigrating cations decreases due to processes such as cations exchanging other cations in the soil, cations reaching the cathode, or cations being neutralized by anions. As a result, after about 58 days, the electromigration of anions began to dominate in the KI test performed on glacial till. Evidently, as discussed with the deionized water tests, the difference between the glacial till and kaolin tests was due to the glacial till's more varied soil composition.

Soil pH

Figures 7(a) and (b) present the pH distributions across the kaolin and glacial till specimens, respectively, upon completion of the electrokinetic tests. Before conducting the electrokinetic treatment, the pH of the initial Hg(II)-contaminated kaolin was 4.5 and the pH of the initial Hg(II)-contaminated glacial till was 7.5.

The pH distribution within the kaolin for the electrokinetic test using deionized water was uniform with a value of approximately 5.5, which was slightly higher than the initial soil pH. The pH distributions within the kaolin for the two tests using Na-EDTA were also approximately uniform along the length of the cells, and both tests had a pH of approximately 3.5 (lower than the initial soil pH). The pH profile in the kaolin test conducted using the KI complexing agent varied from approximately 2 near the anode to approximately 13 near the cathode, showing that even though the electroosmotic flow was primarily towards the cathode, electromigration and electroosmosis of the alkaline solution (OH^- ions) generated by electrolysis at the cathode was occurring towards the anode. Moreover, it is likely that the anionic complexes generated in the KI test, such as HgI_4^{2-} , also contributed to the migration of alkaline solution into the soil.

The pH distribution within the glacial till for the electrokinetic test using deionized water varied from about 6 near the anode to 10.5 near the cathode, and, since the initial pH was 7.5, it appears that the electromigration of products from the electrolysis reactions (H^+ and OH^-) were the primary cause of the pH changes. The pH profile for the Na-EDTA test was similar to the deionized water experiment, although the higher electroosmotic flow in this test may have contributed to the slightly lower pH values of the sections closest to the anode. The glacial till test using the KI complexing agent had a pH that varied from approximately 10.5 near the anode to approximately 13 near the cathode. The higher than initial pH across the soil profile in the KI test is evidence that the alkaline (OH^-) solution generated



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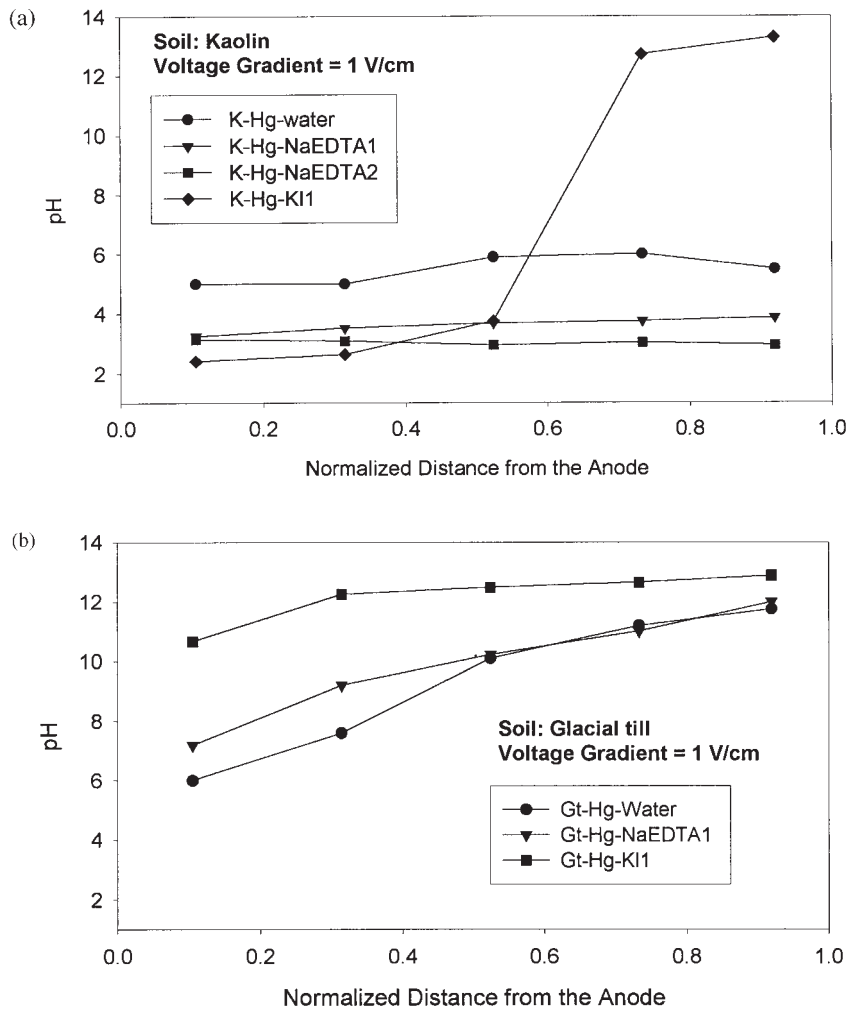


Figure 7. pH distribution across the specimen upon completing the electrokinetic tests on: (a) kaolin and (b) glacial till.

by the electrolysis reaction at the cathode was electromigrating towards the anode. This was suggested earlier during the analysis of the electroosmotic flow in this test. Generally, the higher pH in the glacial till is attributed to the high acidic buffering capacity caused by the 35% carbonate content (Table 1).

Mercury Removal

For the all the electrokinetic tests performed in this research, Hg was primarily detected in the solution at the anode reservoir, and only a few tests detected a minor



amount of Hg at the cathode. This indicates that the migration of the Hg mainly occurred toward the anode electrode as an anion complex. Figures 8(a) and (b) present the cumulative amount of Hg that was measured in the anode reservoirs for the tests conducted on the kaolin and glacial till soils, respectively. From these results, it is obvious that in both soils the KI complexing agent was much more effective at Hg removal than the Na-EDTA solution. It was also evident from the results of both soils that the highest amount of Hg removal occurred within the first 20 days, and then rate of the Hg removal diminished substantially.

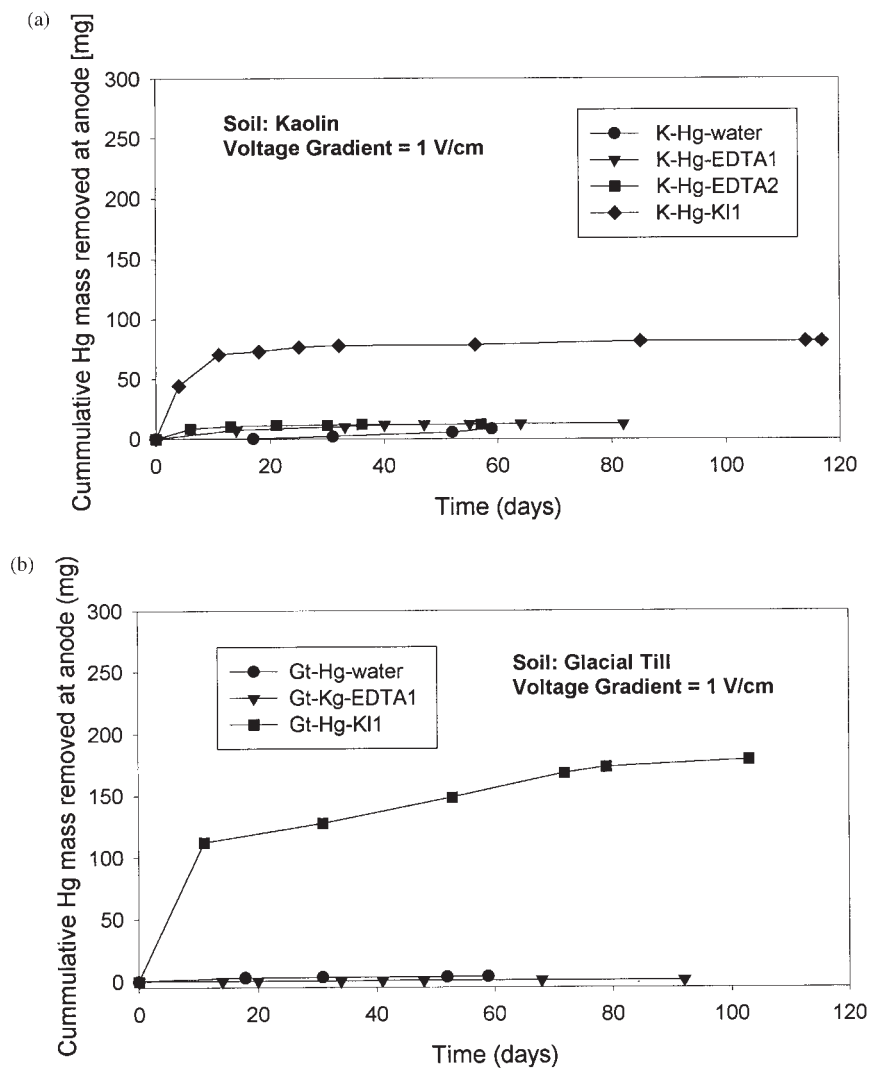


Figure 8. Cumulative mercury removal at the anode reservoir vs. time for the electrokinetic tests on: (a) kaolin and (b) glacial till.



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Once the Hg is solubilized in the soil-solution in the form of an anionic complex, such as Hg-EDTA or HgI_4^{2-} , it electromigrates towards the anode. In the kaolin tests conducted using EDTA, the flow was consistently directed towards the cathode, but Hg was detected in the anode, which indicates that electromigration was mainly responsible for Hg removal. In the KI test conducted on kaolin, it is likely that the Hg complexes principally electromigrated towards the anode, and electroosmosis may have also contributed to Hg removal since it was directed towards the anode in the KI test. In the tests conducted on glacial till soil, Hg removal at the anode was attributed to electromigration and not to electroosmosis. This is because in the glacial till experiments, the flow occurred towards the cathode, except for a minor amount of flow reversal towards the anode near the end of the KI experiment. Apparently, based on the tests conducted with KI on the kaolin soil, the highest contaminant removal efficiency occurs when the electromigration of the contaminant and electroosmotic flow are in the same direction.

Figures 9(a) and (b) show the residual mercury distribution across the kaolin and glacial till specimens, respectively, upon completion of the electrokinetic tests. As seen in Fig. 9(a), for the kaolin experiments, the deionized water test, which had the lowest cumulative Hg removal, showed residual concentrations in the soil that were similar to the initial concentration (500 mg/kg), as expected. In addition, the KI test on kaolin, which had the highest cumulative Hg removal, showed the lowest (only 13.7 mg) of residual Hg along the soil profile. The first Na-EDTA test conducted on kaolin had residual Hg concentrations that were evenly distributed across the soil profile and the values were close to the initial concentration, but the second Na-EDTA experiment exhibited a highly concentrated region in the interior sections of the soil and low concentrations near the electrodes. This somewhat peculiar Hg concentration profile for the last Na-EDTA test may have been a result of changes in electroosmotic flow. Since the electroosmotic flow was mainly towards the cathode, the Hg nearest the anode may have been transported with the deionized water towards the interior soil sections. The low Hg concentration near the cathode in this same test may be explained by the electromigration of Hg-EDTA complexes towards the anode; however, later, due competition for EDTA by other, more thermodynamically favorable cations, such as H^+ , the Hg was deposited in the middle soil sections.

As seen in Fig. 9(b), the experiments conducted with glacial till had residual mercury concentrations that were generally distributed uniformly across the soil profile, especially for the baseline deionized water test and the test using the KI complexing agent. As observed earlier in the kaolin soil, the deionized water test had Hg concentrations that were similar to the initial target (500 mg/kg) value. To the contrary, the KI test on glacial till had the highest cumulative removal and the lowest residual concentrations in soil, probably due to the formation of HgI_4^{2-} complexes. Lastly, the Na-EDTA test on glacial till showed relatively low Hg concentrations along most of the soil profile, but mercury accumulated near the anode electrode. As discussed previously for the second Na-EDTA test on kaolin, it is possible that the electromigration of Hg-EDTA complexes towards the anode occurred; but, as these complexes approached the anode, there were competing

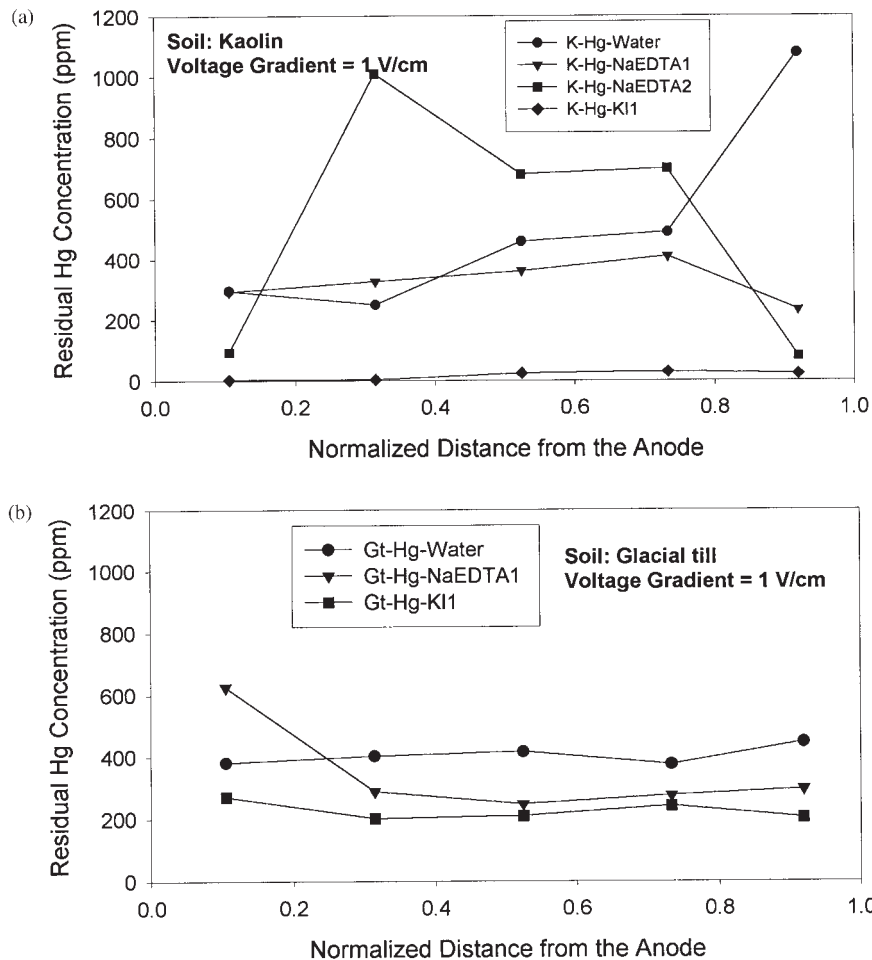


Figure 9. Residual mercury distribution across the specimen upon completing the electrokinetic tests on: (a) kaolin and (b) glacial till.

cations for EDTA, such as H^+ , so the Hg was deposited when the EDTA complex exchanged cations near the anode section.

Table 3 presents the percentage of mercury that was removed from the tests upon completion of the electrokinetic treatments. From these results, it can be concluded that the electrokinetic tests run with KI complexing agent were the most effective tests for removing Hg from the two soils used in this investigation. The lower Hg removal observed in electrokinetic tests conducted with Na-EDTA contrasts with the results obtained in the batch tests, which indicated that a significant amount of Hg could be desorbed from the soils. Apparently, the complexes that were formed by Na-EDTA and Hg were pH dependent, and these complexes did not migrate to the anode as expected.



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Overall, this study showed that electrokinetics could reduce the initial Hg concentration of 500 mg/kg substantially, and the residual concentrations were 16 mg/kg and 220 mg/kg in the kaolin and glacial till soils, respectively. From the regulatory point of view, individual states can impose corrective action levels that must be achieved after remediation. For example, states such as Pennsylvania, Louisiana, and South Carolina require a clean up level of 20 mg/kg total Hg. This means that the clean up level can be achieved by electrokinetic treatment with potassium iodide (KI) solution for soils such as kaolin. However, the residual mercury concentration in the glacial till soil exceeded the clean up level. Other states, such as Oklahoma, require a clean up level of 4 mg/kg total mercury, and Kansas requires 2 mg/kg in residential areas. Thus, further optimization and enhancement of electrokinetic treatment is needed to meet these very low Hg remediation levels. In addition, more comprehensive electrokinetic laboratory testing of actual field contaminated soils is necessary to assess the effects of aged contamination and multiple contaminants on remedial efficiency.

SUMMARY AND CONCLUSIONS

This research assessed using electrokinetics to remediate mercury-contaminated soils. Two types of soil, kaolin and glacial till, were used in this research to study the remediation process with soils of possessing different physical/chemical properties. Batch tests were performed to study desorption from Hg-contaminated soils using three complexing agents (KI, Na-EDTA, and NaCl) as well as deionized water for comparison. Electrokinetic tests on the same Hg-contaminated soils were then conducted using the two best complexing solutions, KI and Na-EDTA, and deionized water for comparison. Based on the test results, the following conclusions were drawn:

For both the kaolin and glacial till soils, the batch tests detailed the behavior of Hg desorption with pH, and they verified the correlation between Hg removal and the stability constant of the Hg-complexes that formed. For example, the potassium iodide (KI) solution resulted in the formation of a soluble (HgI_4^{2-}) complex with a high stability constant of 29.8. The other complexing agents, Na-EDTA and NaCl, formed Hg complexes that had lower stability constants, so, as expected, they were less effective at Hg desorption. The batch test results also verified that the Na-EDTA stability constant changes with pH. As shown in the kaolin soil, Hg-EDTA complexes did not form at low pH values, and this indicates that at low pH it may have been thermodynamically favorable for this chelating agent to complex other cations such as with H^+ .

Based on the batch test results, KI was a better complexing agent than Na-EDTA, but electrokinetic testing was conducted because the complex physical and chemical processes that occur during electrokinetics are quite different than those that occur during batch experiments. Nevertheless, the results of the electrokinetic tests agreed with the preliminary results given by the batch tests, so it appears



that batch testing can be an adequate screening technique to assess complexing agents for use under electrokinetics.

The results from both the batch tests and electrokinetic tests demonstrated the high acid buffering capacity of the glacial till soil, which was a result of its 35% carbonate content. In the batch tests, the samples of glacial till soil that were initially adjusted to a low pH value, had a considerably higher pH value after the 24 h shaking and equilibration period. In the electrokinetic tests conducted on glacial till, the pH measurements showed that predominantly alkaline conditions existed throughout the soil profile after the electrokinetic treatment was completed. For the kaolin soil, however, which does not have much of an acid buffering capacity, predominantly acidic conditions existed throughout the soil after electrokinetic treatment.

In batch tests as well as in the electrokinetic tests, Hg desorption was higher in the kaolin soils than in the glacial till soils. This indicates that the soil composition and its physical/chemical properties significantly affect Hg desorption. The glacial till soil possessed a more complicated mineralogy, a higher organic content, and possibly a greater surface area, and these properties were attributed to lowering Hg removal. In addition, the high (35%) carbonate content also affected Hg removal. In the glacial till tests using KI, the soil had a pH that was over 10 throughout most of the soil specimen, and, based on the batch tests, KI showed less Hg desorption at high pH. It appears that in the glacial till, the dissolved organic species at high pH values may have reduced the amount of ligands available for the forming Hg complexes.

Once the mercury is desorbed from the soil, it is solubilized as an anionic complex species, such as HgI_4^{2-} , which then electromigrates towards the anode electrode. In most of the electrokinetic tests, however, the electroosmotic flow predominantly occurred in the opposite direction, towards the cathode electrode. Since very little or no Hg was detected at the cathode reservoir, it is obvious that electromigration was the responsible mechanism for contaminant transport. It should be noted though, that the best Hg removal results (97%) occurred in the KI test on the kaolin soil, when electromigration and electroosmotic flow were both directed towards the anode.

The initial mercury concentration of 500 mg/kg was reduced to 16 mg/kg in kaolin and 220 mg/kg in glacial till under the effect of a voltage gradient of 1.0 VDC/cm and a KI complexing agent concentration of 0.1 M. These results indicate that electrokinetics has great potential for the remediation of Hg-contaminated soils, but future testing is needed to quantify the effects of multiple contaminants and/or aged contamination, oxidizing/reducing soil conditions, Hg speciation, and Hg retention by organic matter.

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