Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Krishna R. Reddy Associate Professor[a]; Prasanth R. Ala[a]
[a] Department of Civil and Materials Engineering, University of Illinois at Chicago, Chicago, Illinois, USA

To cite this Article Reddy Associate Professor, Krishna R. and Ala, Prasanth R.(2005) 'Electrokinetic Remediation of Metal-Contaminated Field Soil', Separation Science and Technology, 40: 8, 1701 — 1720
To link to this Article: DOI: 10.1081/SS-200059606
URL: http://dx.doi.org/10.1081/SS-200059606

Separation Science and Technology, 40: 1701–1720, 2005

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1081/SS-200059606

Electrokinetic Remediation of Metal-Contaminated Field Soil

Krishna R. Reddy and Prasanth R. Ala
Department of Civil and Materials Engineering, University of Illinois at Chicago, Illinois, USA

Abstract: This study evaluates the electrokinetic remediation of a low permeability field soil contaminated with heavy metals. The soil was contaminated with a wide range of heavy metals; but, in order to simulate the actual source zone contamination, the soil was also spiked with lead and mercury at 1000 mg/Kg each. Four bench-scale electrokinetic experiments were conducted at a voltage gradient of 2.0 VDC/cm and a hydraulic gradient of 1.4 using four different extracting solutions, namely 0.2 M ethylenediamine tetra acetic acid (EDTA), 0.2 M diethylene triamine penta acetic acid (DTPA), 0.2 M potassium iodide (KI), and 10% hydroxypropyl-β-cyclodextrin (HPCD). EDTA and KI were found to be efficient in the removal of lead and mercury, respectively. On the mass-efficiency basis, the EDTA-enhanced system is found to be more effective for the simultaneous removal of a variety of metals, while KI was found to be effective for the selective removal of mercury from the field soil.

Keywords: Electrokinetics, heavy metals, lead, mercury, remediation, soils, clays

INTRODUCTION

Numerous Superfund sites throughout the United States are contaminated with toxic metals (1). Contamination of soils with heavy metals resulted from several activities, including mining, smelting, and metal treatment operations, vehicle emissions, and deposition or leakage of industrial wastes (2). Metals, unlike many hazardous organic constituents, cannot be degraded or readily detoxified and pose a long-term threat to the environment. Once reaching

Received 7 March, 2005, Accepted 15 April, 2005

Address correspondence to Krishna R. Reddy, Associate Professor, Department of Civil and Materials Engineering, University of Illinois at Chicago, 842 West Taylor Street, Chicago, Illinois 60607, USA. E-mail: kreddy@uic.edu

the soil matrix, they can be strongly retained; ensuring prolonged adverse impacts on environmental quality and human health. The most common remedial practice for the restoration of sites contaminated with heavy metals has been the excavation and disposal in a hazardous waste landfill (3). The stringent environmental regulations have encouraged the development of new treatment technologies for the soil decontamination. The conventional technologies to decontaminate heavy metal-polluted soils include soil washing/flushing and stabilization/solidification; however, these technologies are ineffective or expensive to remediate low permeability soils (4). The electrokinetic remediation method is regarded as an effective technique particularly for soils having low hydraulic conductivity (5–12). Electrokinetic remediation involves application of a low electric potential to remove the contaminants. The dominant removal mechanisms are electroosmosis, in which the electric field induces movement of pore fluid, and electromigration, in which the electric field induces movements of ions (5–13). Other physicochemical interactions also occur, such as acid-base reactions, aqueous complexation, and precipitation (5, 13, 14). Generally, electromigration is more important for the removal of ionic contaminants (5, 8–12,14).

Evans (15) has classified the mechanism of metal retention in soils into two major categories: (a) adsorption of ions to the surface of soil components, e.g., clay and organic matter, and (b) precipitation of discrete metal compounds, e.g., oxides, carbonates, and sulfides. For successful decontamination of heavy metal ions, it is important to convert the precipitated and sorbed metal ions into dissolved forms. Thus, it is expected that the feasibility of the electrokinetic remediation method depends strongly on mineralogical composition as well as on soil organic matter content. The use of solubilizing/complexing agents, such as chelating agents and other extractants, is one of the possible approaches to enhance the efficiency of removing these metals from the soils.

The aim of this study is to evaluate the performance of various extracting agents (EDTA, DTPA, KI, and HPCD) to enhance the effectiveness of electrokinetic remediation system for the removal of toxic metals from a low permeability field soil. The contaminated field soil was characterized in detail for its physical and chemical properties. A series of bench-scale electrokinetic experiments was conducted using various extracting solutions to assess the extent of contaminant migration and removal under enhanced electrokinetic remediation systems.

EXPERIMENTAL METHODOLOGY

Soil Characterization

The soil used in this study was obtained from a contaminated industrial site (near Chicago, Illinois) containing heavy metals such as lead, cadmium, mercury, and arsenic. The soil samples collected were thoroughly homogenized. The homogenized sample was analyzed for different physical properties and chemical constituents. All the physical properties were determined according to the corresponding ASTM standard methods (16) and are presented in Table 1. Figure 1(a) shows the grain size distribution of the contaminated soil. The homogenized soil sample was also analyzed by the standard EPA method SW 6020 for heavy metals (17). Table 2 shows these results and indicates the presence of low concentrations of metals in the soil. The soil obtained was not from the highly contaminated locations, and previous site characterization studies indicated that the soils in the source zones contain high concentrations of lead (Pb) and mercury (Hg). Therefore, to simulate this heavy contamination conditions, the field soil was spiked with 1000 mg/kg of Pb and Hg each.

The presence of calcium carbonate or other compounds such as magnesium carbonate or sodium carbonate causes high buffering capacity of the soil. Buffering capacity of soil refers to the capability of soil to neutralize acid. Buffering capacity of the contaminated soil was determined by titration analysis using 0.5 M nitric acid as titrant solution. A soil slurry sample was prepared by mixing 20 g of soil in 200 mL of deionized water. The acid was added incrementally to the slurry while it was being mixed with a magnetic stirrer. A deionized water sample was used as a control sample. The equilibrium pH of the slurry was measured with a pH meter (Thermo Orion model 720 A). The results, as shown in Fig. 1(b), show that buffering capacity of the aqueous soil slurry with a solids concentration of 8.5% is found to be

Table 1. Properties of field contaminated soil

Property	Test method	Value
Specific gravity	ASTM D 854	2.52
Grain size distribution	ASTM D 422	%gravel = 0 % sand = 5.2 % fines = 94.8
Atterberg limits	ASTM D 4318	LL = 50.0 PL = 24.0 PI = 26.0
Max. dry density	ASTM D 1557	1.64 g/cm^3
Optimum moisture content	ASTM D 1557	23.5%
Hydraulic conductivity	ASTM D 5084	8.64×10^{-9} cm/s
pH	ASTM D 2974	7.22
Redox potential	ASTM D 2974	178.7 mV
Electrical conductivity	ASTM D 2974	2.45 μS/cm
Organic content	ASTM D 2974	2.63%
USCS classification	ASTM D 2488	CH — fat clay (high plasticity clay)

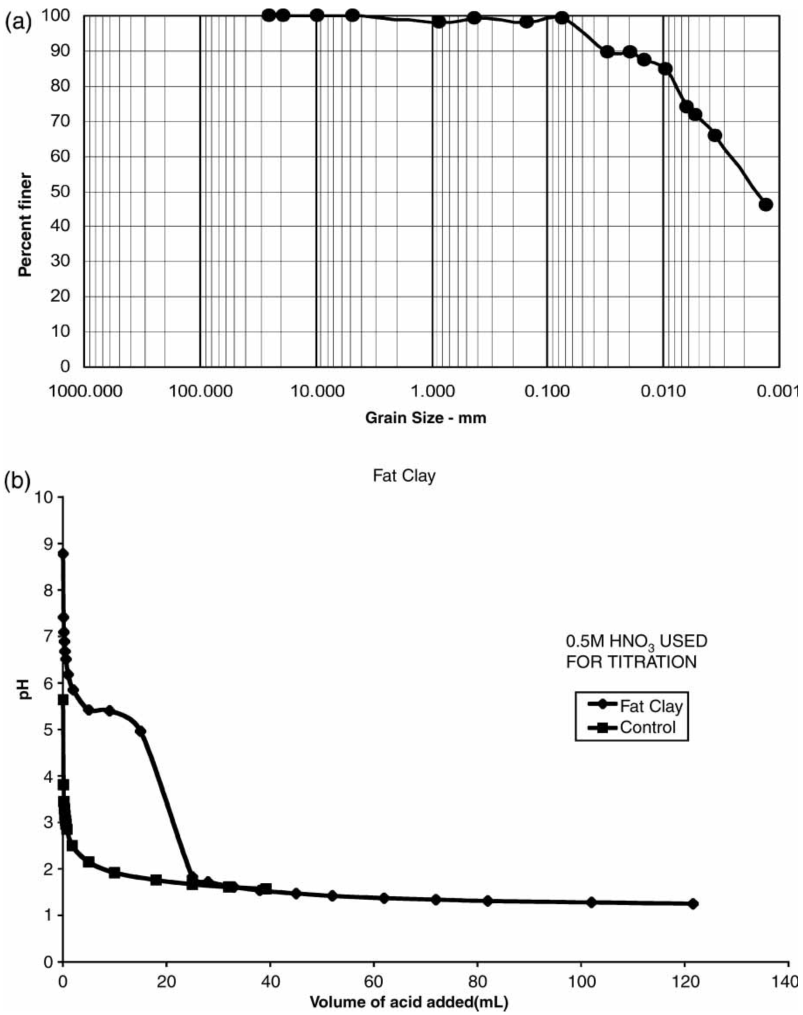

Figure 1. (a) Grain size distribution of field contaminated soil. (b) Acid buffering capacity of field contaminated soil.

3.7 eq/kg (dry soil) at the inflection point of the titration curve (pH 6.2). This indicates that the soil possesses high acid buffering capacity.

Electrokinetic Test Setup

Figure 2 shows the schematic of the electrokinetic test setup used for this study and has been described in detail by Reddy and Parupudi (18). The test setup consists of an electrokinetic cell, two electrode compartments, two

Table 2. Initial contaminants found in field soil based on USEPA SW6020 and SW7471A methods (17)

Chemical	Concentration (mg/kg-dry)
Aluminum	11900
Arsenic	8.58
Barium	66.5
Beryllium	0.697
Calcium	20000
Chromium	20.1
Cobalt	16.2
Copper	20.4
Iron	21300
Lead	11.7
Magnesium	13300
Manganese	718
Nickel	35.1
Potassium	2860
Silver	<0.5
Sodium	341
Vanadium	20
Zinc	40.6
Mercury	0.042

electrode reservoirs, a power source, and a multimeter. Plexiglas cells having outside diameter of 3.9 cm, inside diameter of 3.2 cm, and a total length of 12.9 cm were employed in this study. Each electrode compartment was also made of Plexiglas and consists of a valve to control the flow into the cell, Whatman filter paper, a slotted graphite electrode, and a porous stone. The electrode compartments were connected to either end of the cell using screws. The electrode reservoirs were made of 1.0 cm inner diameter. Plexiglas reservoirs were connected to the electrode compartments using Tygon tubing. Exit ports were created in the electrode compartments, and the tubing was attached to these ports to allow the gases generated due to the electrolysis of water to escape. The other end of these gas tubes was connected to the reservoirs to collect any liquid that was removed along with the gases. A power source was used to apply a constant voltage to the electrodes, and a multimeter was used to monitor the voltage and measure the current flow through the soil sample during the test.

Test Variables

Table 3 shows the details of the four experiments conducted for this study. All of the experiments were conducted under a constant voltage gradient of

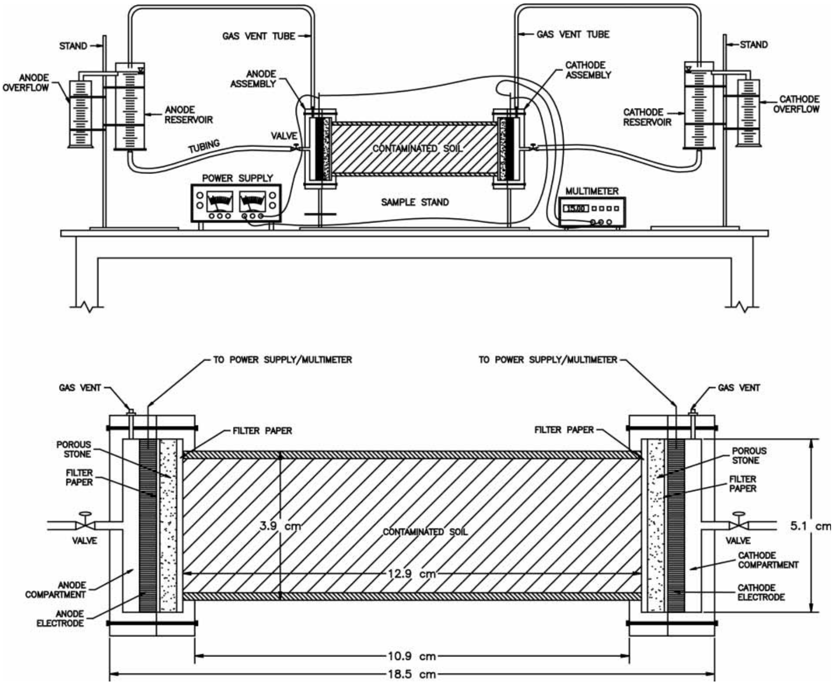

Figure 2. Electrokinetic test setup.

2.0 VDC/cm. The hydraulic gradient that existed under these experimental conditions was found to be approximately 1.4, and was not sufficient to generate substantial hydraulic flow because of the low permeability of the soil. Purging solutions evaluated to enhance solubilization of metals for this study included: three different chelants (0.2 M EDTA, 0.2 M DTPA, and 0.2 M KI), and a modified cyclodextrin (10% HPCD). These purging solutions and their concentrations were selected based on a series of batch experiments (19). Deionized water was found to be ineffective for the removal of metals from the soil (19).

Table 3. Electrokinetic testing program

Test number	Voltage gradient (VDC/cm)	Anode solution	Cathode solution	Pore volumes
1	2.0	Deionized Water	0.2 M EDTA	1.9
2	2.0	Deionized Water	0.2 M DTPA	1.5
3	2.0	Deionized Water	0.2 M KI	0.28
4	2.0	10% HP-β-CD	Deionized Water	0.8

Testing Procedure

The soil was placed in the electrokinetic cell in layers and compacted uniformly using a hand compactor. The compacted soil samples had dry densities of 1.9–2.0 g/cm^3 and moisture contents of 23.1–23.2%. The electrode compartments were then connected to the electrokinetic cell. In each electrode compartment, filter papers were inserted between the electrode and the porous stone as well as between the porous stone and the soil. The electrode compartments were connected to the anode and cathode reservoirs using Tygon tubing. The cathode reservoir was filled with a selected chelant solution or KI and the anode reservoir was filled with deionized water. While in the test with 10% HPCD, the anode reservoir was filled with the purging solution i.e., 10% HPCD, and the cathode reservoir was filled with deionized water. The water level in both reservoirs was monitored and adjusted carefully throughout the tests in order to maintain a constant hydraulic gradient across the specimen. The electrokinetic cell was then connected to the power supply (Hewlett Packard DC model 6205B) and a constant voltage gradient of 2.0 VDC/cm was applied to the soil sample. The fluid levels in both anode and cathode reservoirs were measured to determine the direction and extent of flow at different time periods. Each test was terminated when the current, flow rate, or contaminant concentration in reservoirs was significantly reduced or unchanged.

At the completion of each test, aqueous solutions from the anode and cathode reservoirs and the electrode assemblies were collected and the volumes were measured. Then, the reservoirs and the electrode assemblies were disconnected, and the soil specimen was extruded from the cell using a mechanical extruder. The soil specimen was sectioned into three parts at distances of 0 to 4.3 cm (Section1), 4.3 to 8.6 cm (Section 2), and 8.6 to 12.9 cm (Section 3) from the anode, respectively. Each part was weighed and preserved in a glass bottle. From each soil section, 10 g of soil was taken and mixed with 10 mL of a 0.01 M $CaCl_2$ solution in a glass vial. The slurry was shaken thoroughly by hand for several minutes and the solids were allowed to settle for an hour. This slurry was then used for measuring the soil pH, redox potential, and electrical conductivity. The pH, redox potential, and electrical conductivity of the aqueous solutions from the electrodes were also measured. The pH was measured using Digi-Sense digital pH meter that was calibrated using standardized pH solutions. The moisture content of each soil section was also determined in accordance with ASTM D2216 (16).

Chemical Analyses

Representative samples of reservoir solutions, soil sections, and the initial soil for each test were analyzed for total metals. The total metals were analyzed using ICP-MS in accordance with the USEPA Method SW6020/SW7471A (17). To ensure accuracy of the test results, new electrodes, porous stones, and tubing were used for each experiment, and the electrokinetic cell and compartments were washed thoroughly and then rinsed first with tap water and finally with deionized water to avoid cross-contamination between the experiments.

RESULTS AND ANALYSIS

The results of the electrokinetic experiments were analyzed to assess the electric current, electroosmotic flow, and contaminant removal during the electric potential application as well as the moisture content, pH, redox potential, electrical conductivity, and residual contaminant distribution in the soil after the experiments were terminated.

Electric Current Density

The measured electric current densities with elapsed time for all the tests are shown in Fig. 3. The current densities for each test were obtained by dividing current values measured during the testing by the cross-sectional area of the electrokinetic cell. In general, the current density values increased rapidly in the first 24-hour period followed by gradual decrease with slight fluctuation in the subsequent 150 h for all tests conducted. However, the current density was found to be maximum for the EDTA system and lowest for the KI system for the entire test duration. The higher initial values of current densities support the contention that the initial contents of soluble metals

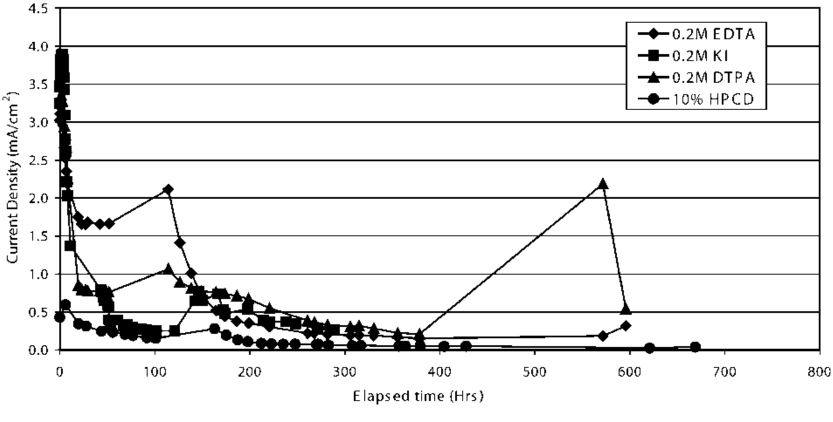

Figure 3. Measured electric current density.

increase because of the availability of a greater number of free ions and due to electrolysis. This behavior can be explained by considering that when the purging fluids pass through the soil, the solubilization of the metals occurs and the ionic strength of pore fluid is increased. The initial current reaches its peak value due to the strong ionic concentration of the pore fluid and also due to the electromigration of contaminants towards their respective electrode. Then, current value gradually decreases because of decrease in the electromigration of the cations and anions in the pore fluid. In addition, the products of the electrolysis reactions or other chemical species may reduce the current by neutralizing the migrating ions. For instance, H^+ ions migrating towards the cathode could be neutralized by OH^- ions migrating towards the anode, thereby forming water and diluting the number of ions in solution. Time-dependent pH changes due to electrolysis reactions could also affect the current by causing changes such as mineral dissolution or chemical precipitation/dissolution. Unless purging solutions, which introduce additional nonreactive ions as charge carriers, are used, the current commonly diminishes over time (5–14). Introducing electrolyte solutions can also have a negative effect on the current because it could reduce the zeta potential and the thickness of the diffuse double layer (20, 21).

Electroosmotic Flow

Figure 4 represents the electroosmotic flow data for all tests. It can be seen that flow behavior was dependent on the purging solutions used. The electroosmotic flow decreases with elapsed time in all tests. Maximum electroosmotic flow was observed within the EDTA system, while the lowest flow was

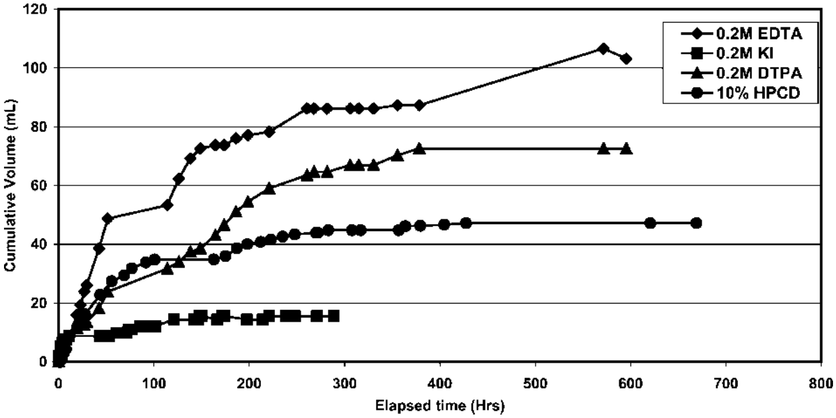

Figure 4. Measured electroosmotic flow.

observed with KI system. The electroosmotic flow variation is found to be consistent with their respective trend as observed for the variation in current densities in all the tested systems and decreases as follows: EDTA system > DTPA system > 10% HPCD system > KI system.

These analyses showed that the current varies significantly with elapsed time, and this was attributed to the physicochemical processes, such as the electromigration of ionic species and the electrolysis reactions. These processes affect the surface charge of the soil particles (zeta potential) and the pore fluid properties, such as dielectric constant and viscosity, with time, and hence influence the electroosmotic flow. Initially, during the beginning of the test, when the current is high (electromigration is high), the transfer of momentum to the surrounding fluid molecules may be substantial. This often corresponds to a significant volume of electroosmotic flow. A high ionic strength, however, can also be detrimental for electroosmotic flow, because it reduces the thickness of the diffuse double layer and, thereby constricts the electroosmotic flow. The charge on the soil surface must also be considered, because when the pH is below its ZPC, the soil particle surfaces possess a positive zeta potential and the electroosmotic flow occurs towards the anode, and when the pH is above the ZPC, the soil particles have a negative zeta potential and the electroosmotic flow occurs towards the cathode (5, 11, 21). For all tests, soil pH was high and the electroosmotic flow was observed from anode to cathode.

Moisture Content, pH, Redox Potential, and Electrical Conductivity

The variation of moisture content with normalized distance from the anode after the electrokinetic treatment is shown in Fig. 5(a). The normalized distance is defined as the distance to the specific location from the anode divided by the total distance from the anode to the cathode. In general, moisture content of the soil near the anode increased slightly, while the moisture content near the cathode decreased slightly. However, for all the tests, moisture content increases throughout the sample. Changes in moisture contents are evident, which can be attributed to the variations in the electroosmotic flow that occurred as a result of the changes in parameters such as the ionic strength, conductivity, and/or electrical gradient. These results suggest that the electroosmotic flow might not be uniform and there might be changes in pore pressures (21). As implied earlier, it is possible that regions where the electroosmotic flow was high created a pressure gradient so that the solution was pulled from regions where the electroosmotic flow was lower. Since the solution was continuously transported through the soil, the moisture content did not substantially deviate from the initial moisture content. These results suggest that the initial moisture content stays approximately constant throughout testing, and this is important because, as seen previously with the current and electroosmotic

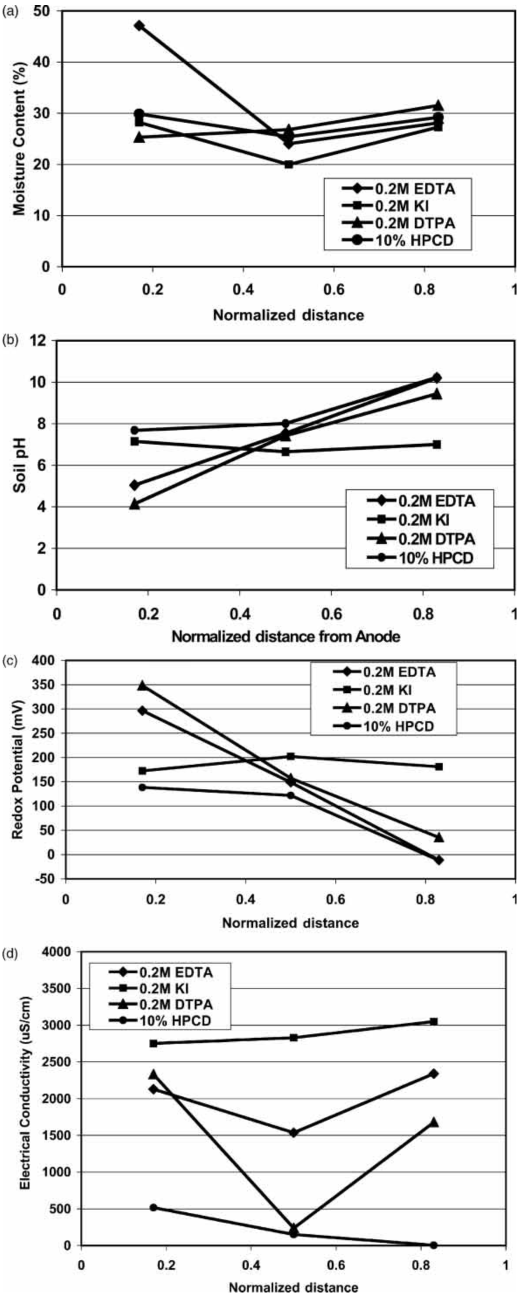

Figure 5. (a) Measured moisture content of the soil after electrokinetic testing. (b) Measured soil pH after electrokinetic testing. (c) Measured redox potential of soil after electrokinetic testing. (d) Measured electrical conductivity of soil after electrokinetic testing.

flow, the initial moisture content can significantly affect the electrokinetic remediation processes.

The electrolysis of water results in the formation of H^+ ions (low pH solution) at the anode and OH^- ions (high pH solution) at the cathode, and, primarily due to electromigration, these ions tend to migrate towards the oppositely charged electrode(s). However, because of high acid buffering capacity of the soil, the H^+ ions are neutralized and the H^+ ions are not allowed to migrate through the soil. However, OH^- migrate through the soil towards the anode. Figure 5(b) shows the normalized distance from the anode vs. the soil pH for all the tests. The initial pH of the soil was 7.22. Figure 5(b) illustrates that an acidic front of solution, which was generated by the electrolysis reaction at the anode decreased the pH slightly in the first section near the anode in the EDTA and DTPA enhanced systems, while it remains close to the initial pH in KI and 10% HPCD enhanced systems. The pH gradually increased from the anode to cathode in almost all the tests. The electroosmotic flow in all the tests decreased considerably and remained constant towards the end of the test. When electroosmotic flow reduces, electromigration causes the OH^- at the cathode to migrate into the soil, thereby increasing the pH near the cathode region.

The redox potentials as shown in Fig. 5(c) show that the redox potentials follow the opposite trend to that observed for pH. Redox potentials were low for the HPCD test while it was found to be comparably higher for the EDTA and DTPA systems. Electrical conductivity values [Fig. 5(d)] show that the KI system had higher electrical conductivity and it increased slightly from the anode to the cathode. On the other hand, the tests conducted with chelants (i.e., in EDTA and DTPA systems) had higher electrical conductivity values near the anode that reduces in the middle section and then further increases in the cathode section. While in the HPCD system the electrical conductivity values decrease slightly from the anode to the cathode.

Residual Contaminant Distribution

After the electrokinetic treatment, the soil samples were mechanically extruded and sectioned into three equal parts: S-1 (near anode), S-2 (middle), and S-3 (near cathode). The contaminant concentrations determined for each of these sections helped to understand the residual contaminant distribution and the migration behavior of the contaminants. Analyses of these results show some interesting trends of metal removal in all the systems that depend upon the purging solution affinity and selectivity towards the metal.

For the EDTA test, Fig. 6(a) shows that in general, the concentration of metals increased from Section S-3 to Section S-1. This shows that metals migrated towards the anode. This may be due to the fact that EDTA solution was introduced at the cathode that led to electromigration of

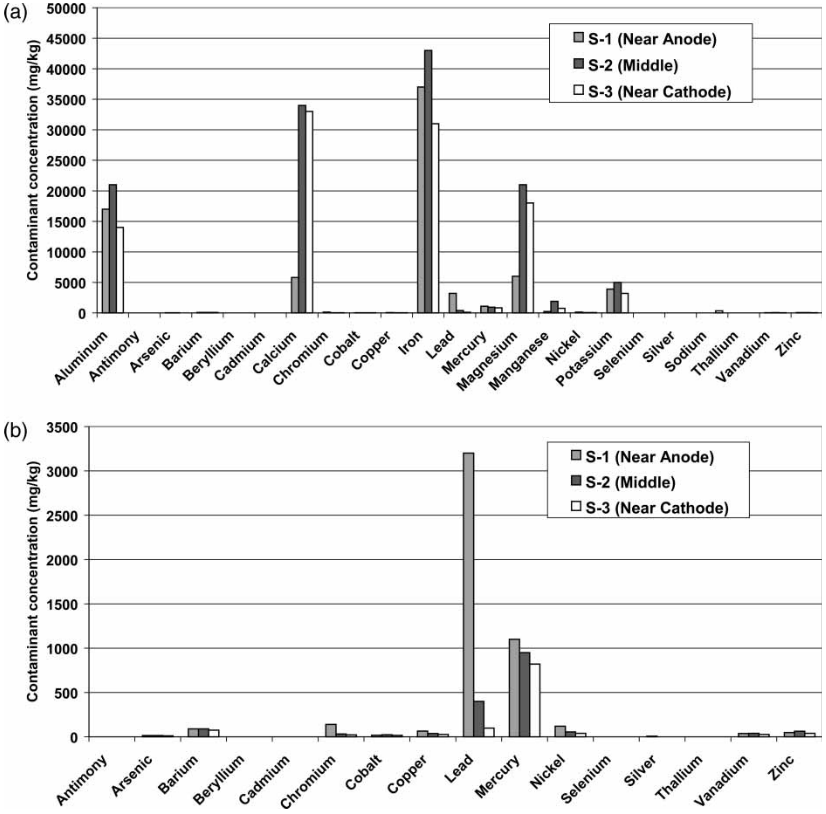

Figure 6. (a) Distribution of metals after electrokinetic treatment with EDTA. (b) Distribution of toxic metals after electrokinetic treatment with EDTA.

$EDTA^{-4}$ into the soil. Subsequently, the EDTA complexed with the metals present in the soil, and these EDTA-metal complexes, being anionic, electromigrated towards the anode in the early stages of the experiments. This results into the appreciably lower concentration of metals in the soil section close to cathode. As shown in Fig. 6(b), the migration of lead from cathode to anode was more significant as compared to mercury, indicating the process to be efficient for the treatment of lead-contaminated soil in the presence of other metals. It should be noted that approximately 2 pore volumes of electroosmotic flow occurred from anode to cathode, which hindered the migration of contaminants in the opposing direction, i.e., from cathode to anode.

In the DTPA system [Fig. 7(a)], the metal concentrations in sections S-1, S-2, and S-3 do not show any particular trend. The variation in the concentrations appears to be due to heterogeneous distribution of the metals in the soil. Figure 7(b) shows that the migration of lead from the cathode towards

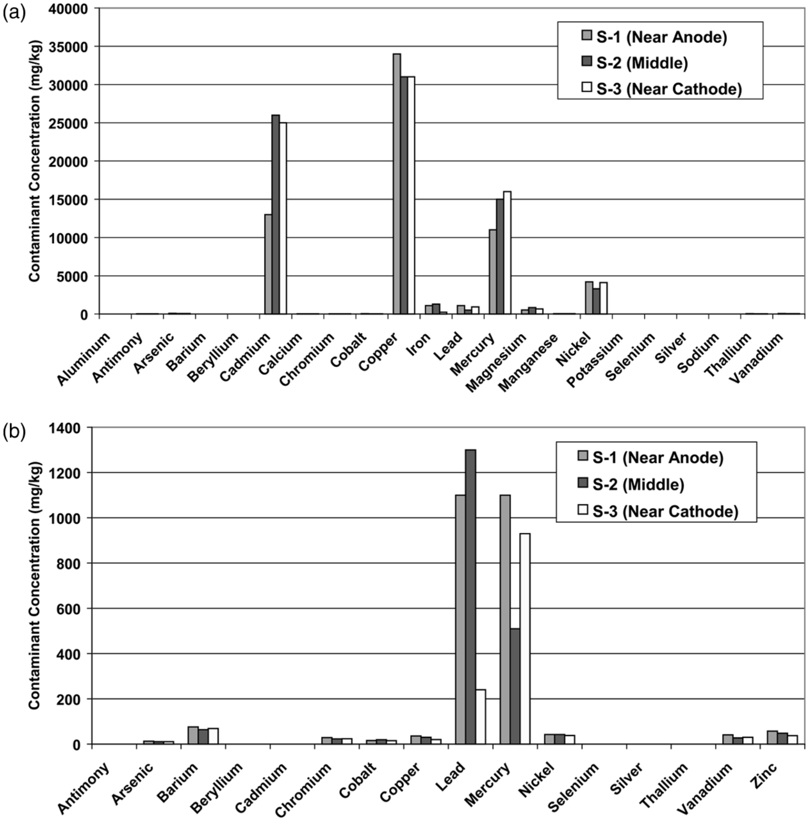

Figure 7. (a) Distribution of metals after electrokinetic treatment with DTPA. (b) Distribution of toxic metals after electrokinetic treatment with DTPA.

the middle section was more significant than mercury. Similar to EDTA, DTPA formed anionic complexes with lead and caused it to migrate towards the anode. These results show that DTPA is not effective for solubilization of the metals from the soil in comparison to the EDTA system. Similar to the EDTA test, high electroosmotic flow (approximately 1.5 pore volumes) occurred from anode to cathode in the direction opposite to the migration of metals by electromigration.

Figure 8(a) reflects that the KI enhanced system shows there is no significant changes in the metal concentrations of different sections. However, Fig. 8(b) shows appreciable migration of mercury occurred towards the anode, and a substantial removal of mercury from the soil is observed. However, KI did not have much effect on complexation and migration of lead, and the concentration of lead in all sections remained the same as initial concentration. KI was introduced at the cathode and anionic iodide ions electromigrated into the soil. The iodide formed anionic complexes

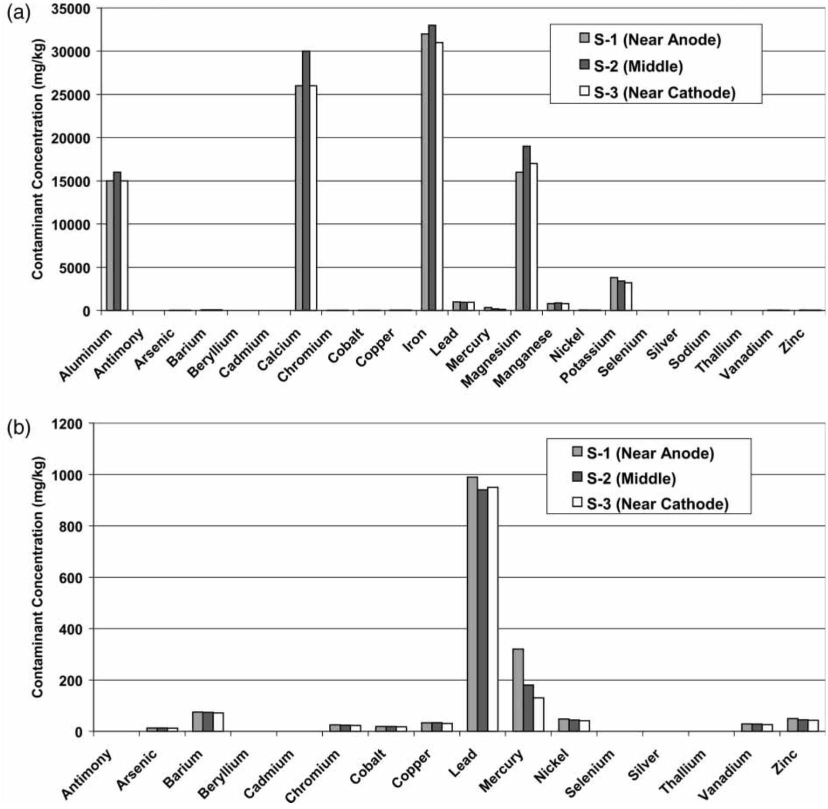

Figure 8. (a) Distribution of metals after electrokinetic treatment with KI. (b) Distribution of toxic metals after electrokinetic treatment with KI.

with mercury and lead to transport towards the anode. In this test, electroosmotic flow occurred from anode to cathode, but it was very low (approximately 0.3 pore volumes). This indicates that KI enhanced systems are highly efficient for the selective treatment of mercury-contaminated soils.

Test with HPCD [Figs. 9(a) and 9(b)] show no significant removal of metals from the soil matrix. This implies that the migration of metals towards the electrodes was insignificant in the HPCD enhanced system. In this test, HPCD was introduced at the anode and the aim was to transport it into the soil by electroosomosis. However, the measured electroosmotic flow was less than 1 pore volume, which led to low delivery of HPCD into the soil. The soil contains significant amount of organic matter and the metals are strongly adsorbed on this organic matter. In addition, the high pH of the soil may have caused some metals to precipitate. Because of the adsorption and precipitation, metals did not exist in pore water and did not migrate. Batch tests also showed that the HPCD was not effective for the desorption and/or dissolution of metals in the soil (19).

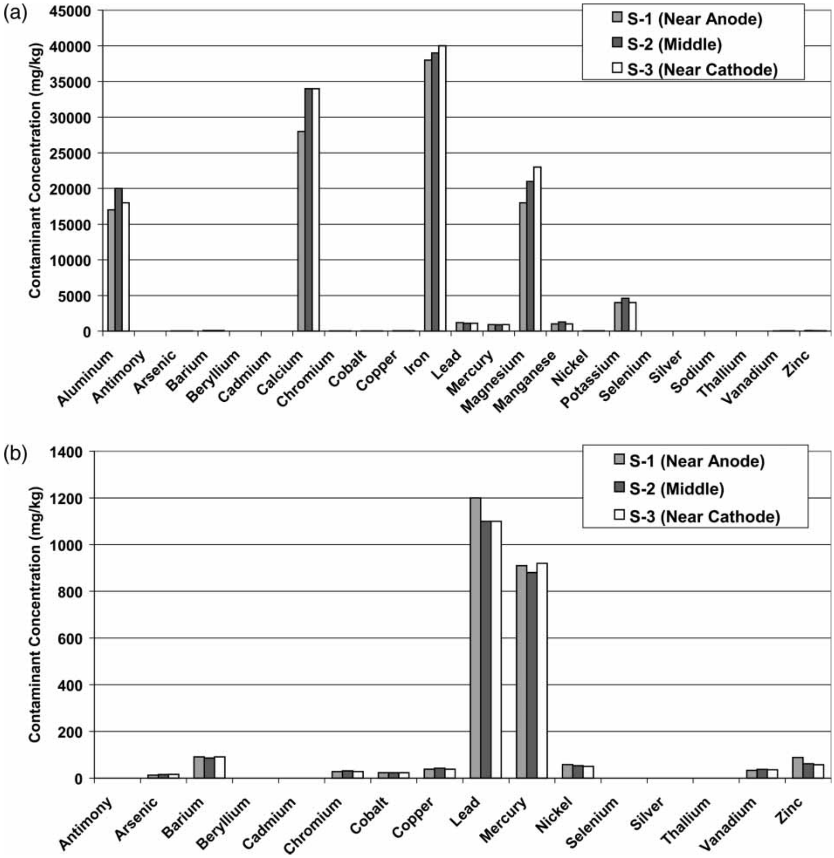

Figure 9. (a) Distribution of metals after electrokinetic treatment with HPCD. (b) Distribution of toxic metals after electrokinetic treatment with HPCD.

Figure 10 compares the distribution of lead in all the studied systems i.e., EDTA, DTPA, KI, and HPCD enhanced system. It is found that significant migration and subsequent removal of lead was observed in the EDTA system in comparison to the other systems. This may be due to the fact that the complexation of Pb by EDTA in a soil depends upon the stability of the solid forms of Pb, including Pb-minerals and adsorbed Pb, and also the levels of competing cations. The competition between Pb, Fe, and Ca for binding to EDTA may be evaluated with the following reactions

$$\mathrm{Pb}^{2+} + \mathrm{EDTA}^{4-} \longleftrightarrow \mathrm{PbEDTA}^{2-} \tag{1}$$

$$\mathrm{Fe}^{3+} + \mathrm{EDTA}^{4-} \longleftrightarrow \mathrm{FeEDTA}^{-} \tag{2}$$

$$\mathrm{Ca}^{2+} + \mathrm{EDTA}^{4-} \longleftrightarrow \mathrm{CaEDTA}^{2-} \tag{3}$$

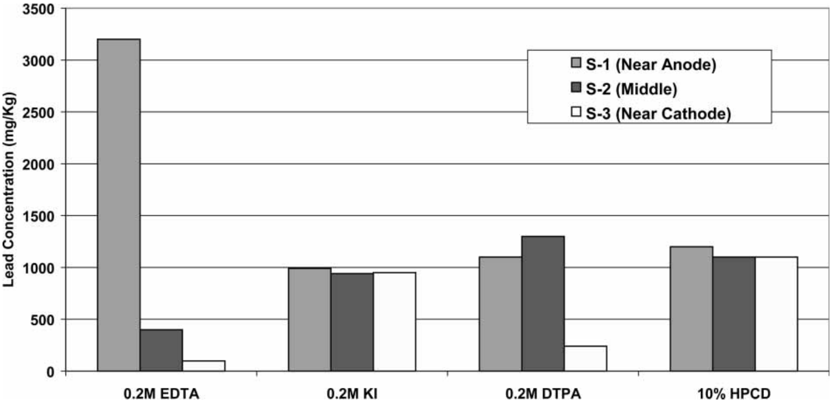

Figure 10. Distribution of lead after electrokinetic treatment.

The mole fraction of the PbEDTA complex is the fraction of added EDTA, which binds with Pb, and is defined by the equation

$$\alpha\text{Pb-EDTA} = [\text{PbEDTA}^{2-}]/[\text{EDTA}]_T \tag{4}$$

where $[\text{EDTA}]_T$ is the total soluble concentration of EDTA. Since the concentration of the uncomplexed EDTA^{4-} species is very low in the presence of strongly complexed cations, the total EDTA concentration may be expressed by the following mass balance equation

$$[\text{EDTA}]_T = [\text{PbEDTA}^{2-}] + [\text{FeEDTA}^{-}] + [\text{CaEDTA}^{2-}] \tag{5}$$

Since only certain target metals in contaminated soils would be extracted out of the soil environment, other metals (i.e., Fe, Ca, Mg, and Al) will stay in soils. The selectivity of chelating agents to the target metals depends upon the strength/stability of the complexes. This also explains the difference of extraction affinity of EDTA and DTPA system for the target metal lead. The pKeq value ranges from 18.0–23.2 for lead-EDTA complex and 18.66–26.40 for lead-DTPA complex in their respective systems. Further, it is found that the selectivity ratio of $\text{pK-Pb}^{2+}/\text{pK-Fe}^{3+}$ was found to be 1.26 value in comparison to $\text{pK-Pb}^{2+}/\text{pK-Fe}^{3+}$ of DTPA, which is 1.14. This indicates the higher stability of lead EDTA complex under the influence of competing ion i.e., Fe in comparison with DTPA systems. Thus the removal of lead was found to be more efficient in the EDTA system because of the high stability of PbEDTA complex.

As seen in Fig. 11, the removal of mercury was found to be effective in the studied KI system. Mercury remains in immobilized form as solid Hg(OH)_2 in the pH range of 5–12, which cannot be removed by washing with water and also with chelants and HPCD. Formation of ionic species Hg(OH)_3^- accounts for dissolution of mercury at high pH. Iodide ions play an important role in

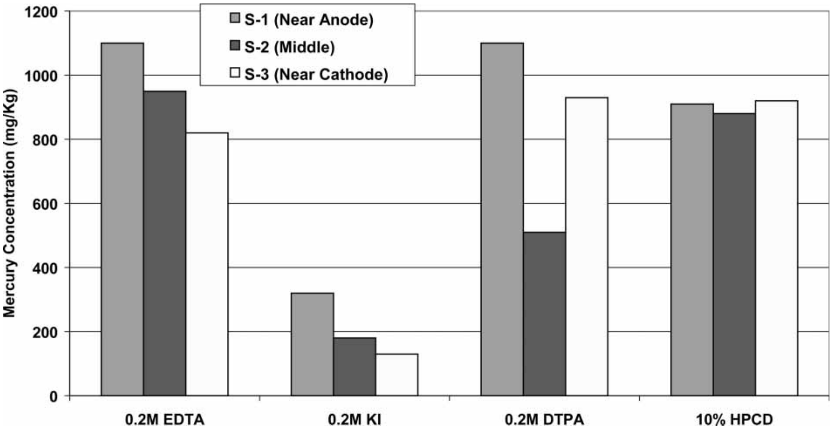

Figure 11. Distribution of mercury after electrokinetic treatment.

extracting mercury from the soil because it forms a soluble complex with mercury, HgI_4^{2-} as shown below

$$\text{Soil-Hg(OH)}_x + 4\text{I}^- \rightarrow \text{HgI}_4^{2-}(\text{aq}\cdot) + x\text{OH}^- + \text{Soil} \qquad (6)$$

The higher mercury removal by KI than by other extractants is due to the fact that the stability constant of HgI_4^{2-}, 29.8, is much higher than the complex formed in the EDTA and DTPA systems.

Overall, in all of the experiments, the migration of lead was found to be more effective in EDTA systems, while the migration of mercury was efficient in the KI enhanced system. However, the actual removal of the contaminants from the soil was very low for all the tests, with maximum removal efficiencies less than 20%.

CONCLUSIONS

Extraction of heavy metals from contaminated soil depends on the extracting solution. This study demonstrated the use of three chelating agents (EDTA, DTPA, and KI) and a modified cyclodextrin (10% HPCD) to enhance the electrokinetic remediation of heavy metals from the contaminated soil. The experimental results show that the selection of an appropriate extractant/chelants is essential, which enhances the metal removal efficiency and renders the possibility for a complete metal decontamination of soil. Based on the experimental results, the following conclusions may be drawn:

1. The dominant transport mechanisms were electroosmosis and electromigration. It is observed that a substantial electroosmotic flow was induced in the soil treated with the 0.2 M EDTA followed by DTPA and HPCD.

However, the electroosmotic flow was less in the KI system. The extent of metal migration and removal in all of the tests was controlled by the extent of solubilization/complexation of the metals with the extracting solution and electromigration process.

2. Soil pH changes in all of the studied systems. It is found that the soil pH decreases in the soil section close to the anode in the EDTA and DTPA enhanced systems, while it is found to be high at the cathode end. In the case of the HPCD enhanced system, soil pH remains close to initial soil pH in the section near the cathode and is found to be high near the cathode that might had hindered the migration of metal-HPCD complexes, resulting in the poor removal efficiency of this system. No appreciable change in the soil pH was observed in the KI enhanced system, indicating that the removal of metals in the KI enhanced system does not alter the geochemical properties of the soil. The high acid buffering capacity of the soil neutralized H^+ generated at the anode and prevented significant decrease in soil pH.
3. It is observed that the EDTA enhanced system was found to be effective for the removal of lead due to the formation of more stable Pb-EDTA complex in the presence of other competing ions. Mercury was efficiently removed in the KI system as HgI_4^{2-}. The HPCD system was found to be ineffective for the solubilization of the metals due to its inability to accommodate the metals into its cavity. Thus, the choice of which type of extractant to be used to enhance the metal removal will depend on a suite of site-specific factors, including the contaminant types and soil geochemical properties.
4. A significant migration of the metals occurred towards the electrodes within the soil; however, migration into the electrode reservoirs depends upon the stability of the metal-extractant complexes that was hindered due to the adsorption, precipitation, and reduction of the contaminants in the soil. Additional research is warranted to determine appropriate enhancement strategy that will remove the contaminants from the soil.

ACKNOWLEDGMENTS

The financial support for this project was received from the State of Illinois (Technology Challenge Grant) and STAT Analysis Corporation, and this support is gratefully acknowledged. The authors are thankful to Kranti Maturi, Saurabh Sharma, Surendra Kumar, and Craig Chawla for their assistance in this project.

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