

Electrokinetic remediation of soils at complex contaminated sites: Technology status, challenges, and opportunities

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ABSTRACT: Subsurface contamination has become a widespread and pervasive global problem. Heavy metals and organic compounds often coexist, and such mixed contaminant distribution within the subsurface is highly dependent on particle and macro-scale heterogeneities. Vast amounts of resources have been invested to develop efficient remediation technologies, yet few have been successful. In-situ remediation is often preferred due to lower site disturbance, safety, simplicity, and cost-effectiveness. However, the effectiveness of in-situ technologies depends largely on contaminant chemistry and subsurface heterogeneities (including particle-scale heterogeneities, e.g. fine-grained soils, soils with reactive minerals and/or organic matter, and macro-scale heterogeneities, e.g. irregular soil layers and/or lenses). Under complex site and contaminant conditions, electrokinetic remediation has great potential. This paper presents the status of this technology based on numerous laboratory investigations and limited field demonstrations, the challenges in applying this technology at actual field sites and opportunities for electrokinetics as an efficient and economical remedy for complex contaminated sites.

Keywords: Electrokinetic Remediation; Soils; Pollution; Heavy Metals; Organic Compounds

1 INTRODUCTION

Polluted sites pose a serious hazard to public health and the environment. The United States Environmental Protection Agency (USEPA) estimated that over 217,000 sites require urgent cleanup at an estimated cost of over \$187 billion (USEPA, 1997). Soil and groundwater contamination has been a major problem at these sites. The types of contaminants encountered at these sites include heavy metals such as lead (Pb), chromium (Cr), nickel (Ni), cadmium (Cd) and mercury (Hg), and organic compounds such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Heavy metals and organic contaminants are often found to coexist at many sites.

Recently, environmental professionals have focused on risk-based approaches to remediating polluted sites. Risk assessment includes detailed site characterization, human and ecological risk quantification and selection of remedial goals (Sharma and Reddy, 2004). The end-use of the site is also taken into consideration in the risk assessment process. If the risk posed by the contamination is unacceptable, remedial action must be selected and implemented to achieve the remedial goals in an efficient and cost-effective manner. Remediation of polluted sites can also help preserve the green lands (pristine land) from pollution due to industrial development as well as provide opportunities for economic growth.

Several technologies have been developed to remediate contaminated sites (Sharma and Reddy, 2004). These technologies can be grouped under *ex situ* or *in situ* technologies. *Ex situ* remediation technologies involve removing the contaminated soils and/or groundwater from the subsurface and then treating them on-site or off-site. On the other hand, *in situ* remediation technologies involve treating the contaminated soils and/or groundwater in-place without removal from the subsurface. Often, *in situ* remediation technologies are preferred because they minimize site disturbance and reduce exposure of the contaminants to personnel and the surrounding public. In addition, *in situ* technologies are often simple and less costly. Common *in situ* soil remediation technologies include soil vapor extraction, soil flushing, solidification and stabilization, thermal desorption, vitrification, bioremediation, and phytoremediation. Common *in-situ* groundwater remediation technologies include pump and treat, air/ozone sparging, flushing, permeable reactive barriers, immobilization, chemical oxidation, and bioremediation. All of these remediation technologies are based on physicochemical, thermal or biological processes that aim to remove the contaminants from the soils and groundwater or immobilize and/or detoxify the contaminants within the soils and groundwater.

The USEPA has documented inadequate performance of various remediation technologies implemented at numerous polluted sites (USEPA, 2000,

2006). The inadequate performance of the remediation technologies may be attributed to complex site conditions, such as: (1) clayey soils are difficult to remediate because of their low permeability and complex composition (mineralogy and organic content); (2) many common technologies fail under heterogeneous subsurface conditions (e.g., clay lenses within sand formation); (3) hydrophobic organic contaminants such as PAHs and PCBs are difficult to treat; (4) very few technologies are available to cleanup sites contaminated with heavy metals; and (5) very few technologies exist that can remediate sites contaminated by mixed contaminants (e.g., organic compounds combined with heavy metals and/or radionuclides). There is an urgent need to develop new technologies that can overcome these challenges as well as be cost-effective (Reddy, 2010). *In situ* electrokinetic remediation has great potential to fill this need.

A comprehensive electrokinetic remediation research program has been on-going at the University of Illinois at Chicago since 1993. The main objectives of this research program are to: (1) investigate geochemistry/biogeochemistry during electrokinetic remediation in different soil and contaminant environments, and (2) investigate methods to engineer geochemistry/biogeochemistry to favor enhanced contaminant remediation. The results of this research have provided the most comprehensive fundamental knowledge to develop electrokinetic remediation as a practical soil and groundwater remediation technology. The research approach includes bench-scale experiments to investigate process fundamentals and optimal operational parameters and mathematical modeling to serve as a screening and optimization tool.

This paper provides an overview of fundamental aspects of electrokinetic remediation and describes different studies conducted to assess the effectiveness of electrokinetic remediation to cleanup soils polluted by various types of contaminants in clayey soils and/or heterogeneous soils. The challenges and opportunities of applying electrokinetic remediation in the field are highlighted. Attempts to integrate electrokinetic remediation with other technologies such as chemical oxidation, bioremediation and phytoremediation, to make the technology practical, efficient and economical are summarized.

2 ELECTROKINETIC REMEDIATION TECHNOLOGY

An electrokinetic remediation technology for the *in-situ* treatment of contaminated sites consists of drilling wells (drains or trenches) in which electrodes are installed and then applying a very low direct current electric potential. Pumping and conditioning systems may be needed at the electrodes depending on the site conditions. A schematic of an *in situ* electrokinetic remediation system is shown in Figure 1. Similarly, electrokinetic treatment may

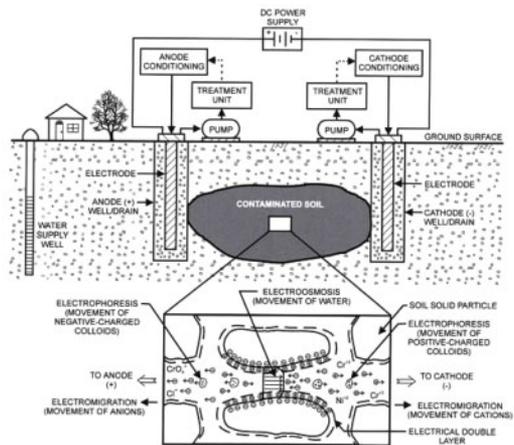


Figure 1. Schematic of *in-situ* electrokinetic remediation system.

be accomplished *ex-situ* by using specially designed above-ground reactors. Generally, the contaminants accumulated at the electrodes are removed by either adsorption onto the electrodes or withdrawal followed by treatment. Electrokinetic remediation offers the following advantages as compared to conventional remediation methods: (1) simplicity – requires simple equipment; (2) safety – the personnel in the vicinity are not exposed to contaminants; (3) wide range of contaminated media – can be used for soils, sludges, sediments, and groundwater (particularly well-suited for low-permeability clays and heterogeneous soil deposits within the vadose zone where conventional remedial methods have proven to be ineffective or expensive); (4) wide range of contaminants – can be used for metals, organic compounds, radionuclides, or a combination of these contaminants; (5) flexibility – can be used as an *in-situ* or *ex-situ* remediation system, and it can be easily integrated with other remediation technologies such as bioremediation; and (6) cost-effectiveness- requires low electrical energy (relative to other thermal technologies) leading to lower overall cost, with costs ranging from \$20 to \$225 per cubic yard depending on the site-specific conditions.

The successful implementation of electrokinetic remediation requires a thorough understanding of the transport mechanisms and physico-chemical processes that affect the transport and fate of contaminants under an induced electric potential. The major contaminant transport mechanisms under an induced electric potential are: (1) *electroosmosis* – bulk movement of pore fluid through the electrical double layer in clayey soils, generally occurring from anode to cathode; (2) *electromigration* – transport of ions and ion complexes within the pore fluid towards oppositely charged electrodes; (3) *electrophoresis* – transport of charged colloids, micelles, bacterial cells, etc. within the pore fluid towards oppositely charged electrodes; and (4) *diffusion* – transport of chemicals due

to concentration gradients (Acar and Alshawabkeh 1993). Electroosmosis is the major transport process for non-polar organic compounds, while electromigration is the dominant transport process for ionic compounds. These two processes govern the overall contaminant migration in compact soil systems; and the roles of the other two processes, electrophoresis and diffusion, are often negligible. However, electrophoresis may be a significant contaminant transport process in contaminated sludge and sediments.

Research conducted to date shows that the electrochemical processes are quite complex and are influenced by local geochemistry. As a result of the induced electric potential, electrolysis of water occurs at the electrodes. The electrolysis reactions generate H^+ ions and O_2 gas at the anode and OH^- ions and H_2 gas at the cathode. The gases may be allowed to escape into the atmosphere, while the H^+ ions migrate towards the cathode and OH^- ions migrate towards the anode. Depending on the extent of migration of H^+ and OH^- ions, pH changes occur across the soil. Generally, low pH (acidic) conditions exist near anode and high pH (basic) conditions exist near cathode. The pH changes in the soil will affect the geochemical processes, namely adsorption and desorption, precipitation and dissolution and oxidation and reduction.

The lower soil pH near the anode causes desorption and solubilization of cationic (negatively charged) metals, such as Pb, Ni and Cd, enhancing their electromigration towards the cathode. However, the higher pH near the cathode causes these metals to adsorb and/or precipitate, hindering electromigration and removal at the cathode. The change in pH also affects the surface charge of soil particles. If the pH is less than the point of zero charge (PZC), the soil surfaces are positively charged. However, if the pH is greater than the PZC, the soil surfaces will be negatively charged. PZC is the pH at which the net charge on the particle surfaces is zero. The changes in surface charge will affect the diffuse double layer, consequently affecting the electroosmotic flow and adsorption of contaminants. Thus, changes in surface charge will affect the migration and removal of both organic and metal contaminants. Therefore, the effects of pH and other geochemical (redox potential, electrolyte concentration, etc.) changes under applied electric potential on the site-specific soil and contaminant conditions and remediation should be assessed.

For electrokinetic remediation to be feasible, contaminants must be desorbed and/or solubilized in the soil. H^+ transport causes desorption or solubilization of cationic metals, while OH^- transport causes desorption of anionic metals. Electromigration of cations and anions occurs towards the cathode and anode, respectively. Electroosmotic advection also causes ions and non-polar organics to transport towards the electrodes. The contaminants are then captured in the electrolyte at electrodes and treated above-ground using common wastewater treatment technologies.

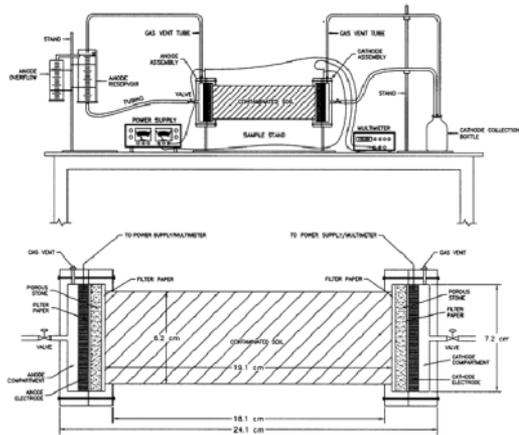


Figure 2. Schematic of typical bench-scale electrokinetic test setup.

3 ELECTROKINETIC REMOVAL OF HEAVY METALS

3.1 Systems effects

Several series of bench-scale experiments have provided valuable information on the geochemistry and transport of heavy metals under applied electric potential. Figure 2 shows the typical bench-scale electrokinetic test setup used. Experiments have been conducted using kaolin and glacial till, spiked with typical heavy metals such as Cr, Ni, Cd, and Hg, individually and in combinations. Kaolin is a clayey soil with homogeneous mineralogy, while glacial till represents a field soil with complex mineralogy. Typical properties of these two soils are summarized in Table 1. The simultaneous testing on these two soils under identical contaminant and treatment conditions allowed the investigation of soil compositional effects on the extent of heavy metal removal. Cr, Ni and Cd were chosen as typical heavy metals as they are commonly prevalent, toxic and need to be remediated (e.g., electroplating sites). In addition to the spiked soils, experiments were also conducted on highly variable actual field soils obtained from sites contaminated with multiple heavy metals. Most of the experiments were conducted under an electric potential of 1 VDC/cm, as this voltage gradient was found to be optimal and practical (Reddy and Shirani 1997).

The removal of heavy metals when they exist individually and in combination in soils was investigated using the soils that were contaminated with Cr(VI) only, with Ni(II) only, and with Cr(VI), Ni(II), and Cd(II) combined (Reddy et al. 2001; Reddy and Parupudi 1997; Reddy et al. 1997). Typical results shown in Figure 3(a) demonstrate that cationic metals migrate towards the cathode, but their migration is retarded by high pH near cathode. In contrast, as shown in Figure 3(b), anionic metals migrate towards anode, but their migration is slowed by low pH near anode.

Table 1. Properties of kaolin and glacial till soils.

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 D422)	0%	0%
Gravel	4%	20%
Sand	18%	44%
Silt	78%	36%
Clay		
Atterberg limits (ASTM D2487)	50% 27.4%	21.7% 11.7%
Liquid limit	22.6%	10.0%
Plastic limit		
Plasticity index		
Specific gravity (ASTM D854)	2.6	2.71
Hydraulic conductivity (cm/s) (ASTM D5084)	1.0×10^{-8}	4.1×10^{-8}
pH (ASTM D4972)	4.9	8.2
Cation exchange capacity (meq/100 g) (ASTM D9081)	1–1.6	13–18
Organic content (ASTM D2974)	~ 0	2.8%
USCS classification (ASTM D2487)	CL	CL

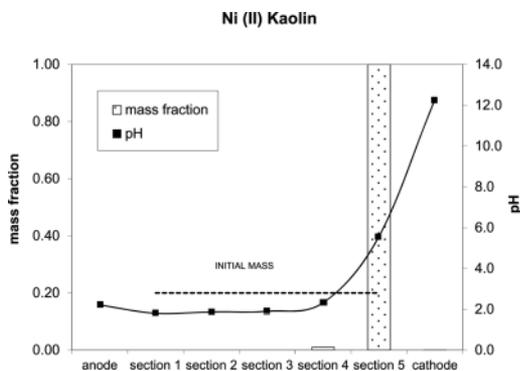


Figure 3a. Migration and removal of Ni(II) in kaolin due to electrokinetic treatment.

Electromigration is the most dominant transport process for heavy metals. The different compositions of soils lead to different contaminant migration behavior. For example, glacial till soil possesses high acid buffering capacity due to its high carbonate content and the soil remains alkaline even after the application of electric potential. The high soil pH hinders the migration of cationic metals and enhances the migration of anionic metals (Figures 3(c) and 3(d)).

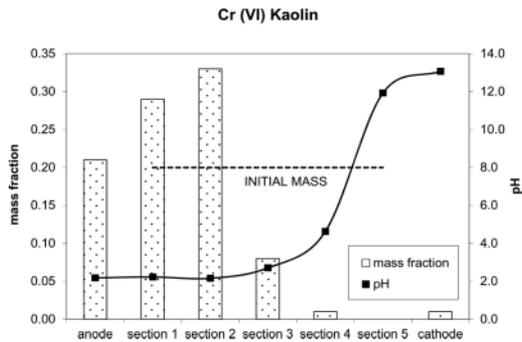


Figure 3b. Migration and removal of Cr(VI) in kaolin due to electrokinetic treatment.

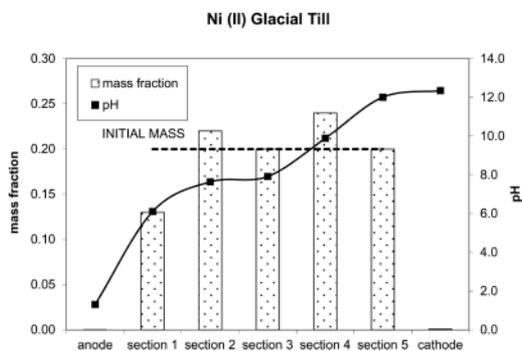


Figure 3c. Migration and removal of Ni(II) in glacial till due to electrokinetic treatment.

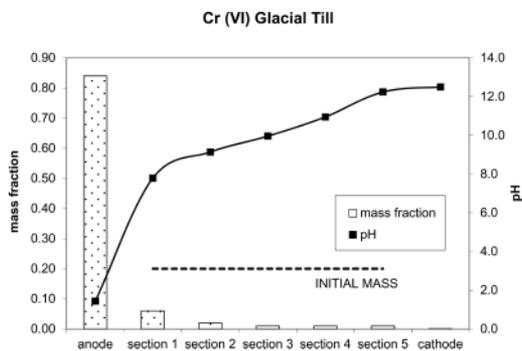


Figure 3d. Migration and removal of Cr(VI) in glacial till due to electrokinetic treatment.

It was found that in kaolin, a significant pH variation occurred due to electric potential application, affecting the adsorption-desorption and dissolution-precipitation, as well as the extent of migration of the contaminants. In glacial till, however, pH changes were not affected significantly. In both kaolin and glacial till, the migration of Cr(VI) and Ni(II) was higher when they were present individually compared to when they existed together with Cd(II). Cr(VI) migration as single or combined contaminant was lower in kaolin as compared to that in glacial till. This result was due to

the low pH conditions created near the anode in kaolin that led to high Cr(VI) adsorption to the clay surfaces. In glacial till, however, Ni precipitated with or without the presence of co-contaminants due to high pH conditions in the soil. Overall, this study demonstrated that adsorption, precipitation and reduction are the significant hindering mechanisms for the removal of heavy metals using electrokinetic remediation. The direction of the contaminant migration and overall removal efficiency depend on the polarity of the contaminant, the presence of co-contaminants and the geochemistry and composition of the soil.

The transient behavior of Cr, Ni and Cd during electrokinetic remediation was assessed by performing electrokinetic experiments with 1, 2, 4, and 10 d of treatment time (Reddy and Al-Hamdan 2008). In all tests, the contaminants were Cr(VI), Ni(II) and Cd(II) combined in the soil. Results showed that in kaolin, the extent of Ni(II) and Cd(II) migration towards the cathode increased as the treatment time increased. Unlike kaolin, in glacial till the treatment time had no effect on Ni and Cd migration because of its high buffering capacity. In both kaolin and glacial till, the extent of Cr(VI) migration towards the anode increased as the treatment time increased. However, Cr(VI) migration was higher in glacial till as compared to kaolin due to the higher pH. In all tests, some Cr(VI) was reduced to Cr(III), and the Cr(VI) reduction rate to Cr(III) as well as the Cr(III) migration were significantly affected by the treatment time.

The initial moisture content of the soils as well as initial contaminant concentrations can also influence the electrokinetic remediation (Reddy et al. 2002). These aspects were investigated by conducting experiments with soils at different moisture contents (30, 50 and 70%) with same heavy metal contaminants, Cr(III), Ni(II) and Cd(II), at concentrations of 1000, 500 and 250 mg/kg, respectively. Then, two additional experiments were conducted at lower Cr(III), Ni(II) and Cd(II) concentrations of 500, 250 and 125 mg/kg and 250, 125 and 62.5 mg/kg, respectively. These tests all used the same moisture content of 30%. The results revealed that the electrical current and electroosmotic flow increased considerably when the soil contained higher moisture content (70%), but the moisture content effect on heavy metal contaminant migration and removal appeared to be minimal. Furthermore, these experiments indicated that the moisture content remains nearly the same during the electrokinetic process. The results showed that soils possessing higher contaminant concentrations could have a lower percentage of contaminant migration and removal. Although similar amounts of removal occurred for the Cr(III) contaminant, Ni(II) and Cd(II) migration was evidently inhibited when the three co-contaminants were present in the test using the highest concentrations of 1000, 500 and 250 mg/kg, respectively.

Some heavy metals can have several valence states and the electrokinetic removal can depend on the contaminant valence state (Reddy and Chinthamreddy

2003). For example, Cr can exist as Cr(III) or Cr(VI). In order to investigate this aspect, electrokinetic experiments were conducted with soils containing Cr(III) alone, Cr(VI) alone or a combination of Cr(III) and Cr(VI), all with the same total Cr concentration of 1000 mg/kg. Ni(II) and Cd(II) in concentrations of 500 mg/kg and 250 mg/kg, respectively, were also introduced into the soils as co-contaminants to simulate typical electroplating waste constituents. The test results showed that Cr migration was highest when it was present in kaolin in the Cr(III) form and in glacial till in the Cr(VI) form. When Cr was present in Cr(III) form, migration occurred towards the cathode due to the existence of Cr(III) as cation and cationic hydroxide complexes. Cr(III) migration was not observed in glacial till because of precipitation that resulted from the high pH conditions that existed throughout the glacial till. However, when Cr was present in Cr(VI) form, the migration occurred towards the anode, due to the existence of Cr(VI) as soluble oxyanions. The migration of Cr(VI) was higher in glacial till as compared to kaolin due to alkaline conditions that existed in the glacial till, resulting in negligible Cr(VI) adsorption to soil solids. When Cr was present as a combination of Cr(VI) and Cr(III), Cr(VI) migrated towards the anode, while Cr(III) migrated towards the cathode. For these cases, the total Cr migration was lower than the migration observed when only Cr(III) was present in kaolin or when only Cr(VI) was present in glacial till. No migration was observed for the co-contaminants Ni(II) and Cd(II) in glacial till due to precipitation as a result of alkaline conditions. In kaolin, however, Ni(II) and Cd(II) migrated towards the cathode. The test results showed that significant removal of contaminants from the soils was not achieved for the processing periods utilized.

The presence of natural oxidizing or reducing agents in the soil can influence speciation of the contaminants and affect their electrokinetic removal (Reddy and Chinthamreddy 1999; Chinthamreddy and Reddy 1999). To investigate this, bench-scale electrokinetic experiments were conducted using the soils with and without a reducing agent. The reducing agent used was either humic acid, ferrous iron or sulfide, at a concentration of 1000 mg/kg. The soils were then spiked with Cr(VI), Ni(II) and Cd(II) at concentrations of 1000, 500 and 250 mg/kg, respectively, and tested under an induced electric potential of 1 VDC/cm for a duration of over 200 h. The reduction of Cr from Cr(VI) to Cr(III) occurred prior to electrokinetic treatment. The extent of this Cr(VI) reduction was found to be dependent on the type and amount of reducing agents present in the soil. The maximum reduction occurred in the presence of sulfides, while the minimum reduction occurred in the presence of humic acid. The concentration profiles in both soils following electrokinetic treatment showed that Cr(VI) migration was retarded significantly in the presence of sulfides due to the reduction of Cr(VI) to Cr(III) as well as an increase in soil pH. This low migration of Cr is attributed to: (1) migration of Cr(VI) and the reduced

Cr(III) fraction in opposite directions, (2) low Cr(III) migration due to adsorption and precipitation in high pH regions near the cathode in kaolin and throughout the glacial till, and (3) low Cr(VI) migration due to adsorption in low pH regions near the anode in both soils. Ni(II) and Cd(II) migrated towards the cathode in kaolin; however, the migration was significantly lessened in the presence of sulfides due to increased pH through most of the soil. Initial high pH conditions within the glacial till resulted in Ni(II) and Cd(II) precipitation, so the effects of reducing agents were inconsequential. Therefore, one must characterize the soils for the presence of the reducing agents, particularly sulfides, in soils that may affect redox chemistry and soil pH, ultimately affecting the electrokinetic remediation process. Similarly, the effects of naturally occurring oxidizing agents should also be carefully assessed.

3.2 Geochemical assessment

In order to better understand speciation and distribution of heavy metals before and after electrokinetic remediation, various geochemical analyses including transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX) and X-ray diffraction (XRD) and sequential chemical extractions as well as geochemical modeling were performed.

TEM, EDX and XRD: A detailed investigation of physical distribution of heavy metals in kaolin soil and the chemical and structural changes in kaolinite minerals that result from electrokinetic remediation was performed by TEM, EDX and XRD analyses on the soil samples before and after electrokinetic remediation (Roach et al. 2009). Results showed that the heavy metal contaminant distribution in the soil samples was not observable using TEM and EDX. X-ray diffraction patterns showed a decrease in peak height with decreasing soil pH value, which indicates the possible dissolution of kaolinite minerals during electrokinetic remediation. The changes in particle morphology were found to be insignificant, but a relationship was found between the crystallinity of kaolin and the pH changes induced by the applied electric potential.

Sequential Extractions: Sequential extractions were performed on the contaminated soils before and after electrokinetic treatment to provide an understanding of the distribution of the contaminants in the soils (Reddy et al. 2001). The speciation of contaminants after electrokinetic treatment showed that a significant change in exchangeable and soluble fractions occurred. In kaolin, exchangeable and soluble Cr(III), Ni(II) and Cd(II) decreased near the anode and increased near the cathode, whereas exchangeable and soluble Cr(VI) decreased near the cathode and increased near the anode. In glacial till, exchangeable and soluble Cr(III), Ni(II) and Cd(II) were low even before electrokinetic treatment and no significant changes were observed after the electrokinetic treatment. However, significant exchangeable and soluble Cr(VI) that was present in glacial till prior to

electrokinetic treatment decreased to non-detectable levels near the cathode and increased significantly near the anode. In both kaolin and glacial till, low migration rates occurred as a result of contaminants existing as immobile complexes and precipitates.

Geochemical Modeling: The speciation of the metals was predicted using the chemical speciation program MINEQL+. The results showed that the speciation and distribution of cationic metals [Ni, Cd and Cr(III)] in glacial till soil remain unaffected or slightly affected during electrokinetics (Al-Hamdan and Reddy 2008). This is attributed to the high pH and buffering capacity of the glacial till, leading the metals to precipitate in the soil prior to and after electrokinetics. This study showed that during electrokinetics, Cr(VI) exists as anionic complex and migrates towards the anode and the migration is greatest in case of a single-contaminant system. The study also showed that near the anode in the absence of any reducing and oxidizing agent, Cr(VI) mostly adsorbed, and some of Cr(VI) reduced to Cr(III) and migrated towards the cathode and finally precipitated due to high pH conditions. Ni and Cd remain adsorbed or precipitated due to the high pH conditions throughout the soil.

A geochemical assessment of how the contaminants are held within the kaolin soil under induced electric potential was also made by using the equilibrium model MINEQL+ (Al-Hamdan and Reddy 2006). As the soil pH changes due to applied electric potential, the adsorption of the Cr(VI), Ni(II) and Cd(II) by kaolin was implemented as an electrostatic behavior. The FITEQL 4.0 model was used to determine the equilibrium constants of the electrostatic adsorption model of kaolin for the metals by optimizing the experimental titration and adsorption data of kaolin. The adsorbed and precipitated forms of Cr(III), Ni(II) and Cd(II) increased near the cathode and decreased near the anode, whereas the adsorbed form of Cr(VI) increased near the anode as well as in the middle region. However, the precipitated form of Cr(III), Ni(II) and Cd(II) as Cr_2O_3 or $\text{Cr}(\text{OH})_3$, $\text{Ni}(\text{OH})_2$ and $\text{Cd}(\text{OH})_2$, respectively, dominated over their adsorbed form as they got closer to the cathode.

A one-dimensional transport model was developed to predict the transient transport and speciation of heavy metals in soil during electrokinetic remediation as a function of time and space (Al-Hamdan and Reddy 2008). The model assumes: (1) pH-dependent adsorption of contaminants to the soil surface; (2) sensitivity of soil surface potential and electroosmotic flow to the pore water properties; and (3) synergistic effects of multiple chemical species on electrokinetic remediation. The model considers that: (1) electrical potential in the soil is constant with time; (2) surface complexation reactions are applicable in the highly concentrated clay suspensions; (3) the effect of temperature is negligible; and (4) dissolution of soil constituents is negligible. The predicted pH profiles, electroosmotic flow and transport of Cr, Ni, and Cd in kaolin soil during electrokinetic remediation were found to reasonably agree with the bench-scale electrokinetic

experimental results. The predicted contaminant speciation and distribution (aqueous, adsorbed and precipitated) allowed for an understanding of the transport processes and chemical reactions that control electrokinetic remediation.

3.3 Enhancement strategies

Several investigations have demonstrated that using water as an electrolyte does not advance the removal of heavy metals from the soils. Therefore, different strategies are needed to enhance removal efficiency. These strategies include: (1) increasing treatment duration, (2) increasing electric potential gradient, (3) applying electric potential in different modes (e.g., continuous, periodic, AC/DC combinations, etc.), (4) using cation/anion exchange membranes in the electrodes, (5) circulating electrolytes, and (6) using enhancement (electrode conditioning) solutions such as organic acids (e.g. acetic acid, citric acid) and chelating agents (e.g. EDTA, DTPA). The use of enhancement solutions has been found to be the most promising strategy to achieve high removal efficiency.

Batch and electrokinetic experiments were conducted to investigate the removal of different heavy metals from kaolin soil by using ethylenediamine tetraacetic acid (EDTA) as a complexing agent (Reddy et al. 2004). Experiments were conducted on kaolin spiked with Cr(VI), Ni(II) and Cd(II) at concentrations of 1000, 500 and 250 mg/kg, respectively, which simulate typical electroplating waste contamination. The batch experiments revealed that highly successful removal of these heavy metals (62–100%) was possible by using either a 0.1 M or 0.2 M EDTA solution over a wide range of pH conditions (2–10). However, the results of the electrokinetic experiments using EDTA at the cathode showed low heavy metal removal efficiency. Using EDTA at the cathode along with the pH control (NaOH) at the anode increased the pH throughout the soil and achieved high (95%) Cr(VI) removal, but the removal of Ni(II) and Cd(II) was limited due to the precipitation of these metals near the cathode. Apparently, the low mobility of EDTA and its migration direction, which opposed electroosmotic flow, prevented EDTA complexation from occurring.

Subsequently, several other purging solutions were evaluated to enhance the removal of the heavy metals from kaolin (Reddy and Chinthamreddy 2003). The removal of heavy metals from the soil using tap water as the purging solution was very low. When 1 M acetic acid was used as the purging solution in the cathode, the removal of Cr, Ni and Cd was increased to 20, 19 and 13%, respectively. Using 0.1 M EDTA as the purging solution in the cathode, 83% of the initial Cr was removed; however, the Ni and Cd removal was very low. A sequentially enhanced electrokinetic remediation approach involving the use of water as a purging solution at both the anode and cathode initially, followed by the use of acetic acid as the cathode purging solution and a NaOH alkaline solution as the anode purging solution, was tested. This sequential approach

resulted in a maximum removal of Cr(VI), Ni(II) and Cd(II) of 68–71, 71–73 and 87–94%, respectively. This study shows that the sequential use of appropriate electrode purging solutions, rather than a single electrode purging solution, is necessary to remediate multiple heavy metals in soils using electrokinetics.

A similar investigation was performed on glacial till soil (Reddy and Chinthamreddy 2004). The electrolyte solutions tested were 0.1 M EDTA, 1.0 M acetic acid, 1.0 M citric acid, 0.1 M NaCl/0.1 M EDTA, and 0.05 M sulfuric acid/0.5 M sulfuric acid. The results showed that 46–82% of the Cr(VI) was removed from the soil, depending on the purging solution used. The highest removal of Ni(II) and Cd(II) was 48 and 26%, respectively, achieved by using 1.0 M acetic acid. Although cationic contaminant removal was low, the use of 0.1 M NaCl as an anode purging solution and 0.1 M EDTA as a cathode purging solution resulted in significant contaminant migration towards the soil regions adjacent to the electrodes. Compared to low buffering capacity soils, such as kaolin, the removal of heavy metals from the glacial till soil was low, likely due to the complex composition of glacial till.

Besides Cr(VI), Ni(II) and Cd(II), another toxic metal of great concern is mercury (Hg) and its removal from soils using electrokinetics was investigated (Reddy et al. 2003). Initially, batch tests were performed with soils spiked with Hg(II) to investigate Hg desorption and complexation under different pH environments (pH 2–12). The complexing agents included 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 (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 Hg adsorption or the formation of insoluble Hg complexes.

Further studies investigated optimizing the iodide-enhanced electrokinetic treatment for the removal of Hg from soils (Reddy et al. 2003). Experiments were conducted at two voltage gradients (1.0 or 1.5 VDC/cm) to evaluate the effect of the voltage gradient when employing a 0.1 M KI solution. Additional experiments were performed to assess the effect of using a higher iodide concentration (0.5 M KI) when

using a 1.5 VDC/cm voltage gradient. The tests conducted on the kaolin soil showed that when the 0.1 M KI concentration was employed with the 1.0 VDC/cm voltage gradient, approximately 97% of the Hg was removed, leaving a residual concentration of 16 mg/kg in the soil. The tests conducted on glacial till indicated that it was beneficial to use the higher (0.5 M KI) iodide concentration and the higher (1.5 VDC/cm) voltage gradient to enhance Hg removal, because, under these conditions, a maximum of 77% of the Hg was removed from the glacial till, leaving a residual concentration of 116 mg/kg in soil after treatment. Compared to kaolin, the lower Hg removal from the glacial till soil is attributed to its more complex soil composition, such as the presence of carbonates and organic matter, which caused Hg(II) to adsorb to the soil and/or exist as an immobile chemical species.

The above studies were conducted on soils spiked uniformly with heavy metals; however, soils at contaminated sites often possess variable compositions and multiple metals (Reddy and Ala 2005). In order to investigate the effects of field conditions, a clayey soil contaminated with multiple heavy metals was obtained from an actual contaminated site. In addition to the contaminants present on-site, additional Pb and Hg were added to soils in order to simulate the source zone contamination. Bench-scale electrokinetic experiments were conducted under a voltage gradient of 2 VDC/cm and a hydraulic gradient of 1.4 using four different extracting solutions (0.2 M EDTA, 0.2 M DTPA, 0.2 M KI and 10% HPCD). EDTA and KI were found to be efficient in the removal of Pb and Hg, respectively. On a 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 Hg from the field soil.

4 ELECTROKINETIC REMOVAL OF ORGANIC CONTAMINANTS

4.1 System effects

Many sites around the globe are contaminated with polycyclic aromatic hydrocarbons (PAHs) such as phenanthrene and chlorinated aromatic and nitroaromatic compounds such as pentachlorophenol (PCP), 2,4-dinitrotoluene (2,4-DNT), and lindane. There are several Superfund sites (surface and subsurface soils) contaminated with these toxins, which are considered priority pollutants by the USEPA. Remediation of these contaminants is more complicated in low permeability and/or heterogeneous soils. These contaminants are difficult to remove from soils due to their low solubility and strong adsorption to soil surfaces and organic matter. Electrokinetically enhanced *in situ* flushing using solubilizing agents, (i.e. surfactants, cosolvents and cyclodextrins) has the potential to remove these contaminants from low permeability clay soils. A solubilizing agent is used to increase contaminant desorption and solubilization, and an

applied electric potential facilitates contaminant transport primarily by electroosmosis and/or electrophoresis (Saichek and Reddy 2005; Cameselle and Reddy 2012). Electroosmotic flow generally improves soil-solution-contaminant interaction, especially in zones of high organic content and/or low hydraulic conductivity. The electrokinetically enhanced remediation process is fairly simple to implement and operate, but the fundamental reactions that govern the remediation method are complex. An adequate knowledge of the contaminant transport mechanisms and the physical, chemical and electrochemical processes is essential in order to optimize system performance.

4.2 Remediation of PAHs

An investigation was conducted to evaluate electrokinetically enhanced flushing for the removal of PAHs from kaolin and glacial till using different flushing solutions: deionized water, a surfactant, or a cosolvent (Reddy and Saichek 2003). The results indicated that the contaminant was more strongly bound to the glacial till than the kaolin, and this was attributed to its higher-organic content. The glacial till also generated a greater electrical current and electro-osmotic flow, and this was probably a result of its higher-carbonate content and more diverse mineralogy. Based on the contaminant mass remaining in the soil, it was apparent that the surfactant or cosolvent solution caused contaminant desorption, solubilization, and/or migration in both soils, but PAH removal efficiency was low. Additional evaluation of surfactants to remove PAHs during electrokinetics was performed by Saichek and Reddy (2003).

Different cosolvents (*n*-butylamine, tetrahydrofuran or acetone) were further investigated on glacial till with phenanthrene (Li et al. 2000). Desorption equilibrium was investigated by batch tests. Water or 20% (v/v) cosolvent solution was constantly supplied at the anode. The concentration of phenanthrene in the effluent collected at the cathode was monitored for 100 to 145 days. Results showed that the presence of *n*-butylamine significantly enhanced the desorption and electrokinetic transport of phenanthrene; about 43% of the phenanthrene was removed after 127 days or 9 pore volumes. The effect of acetone was not as significant as butylamine. The effluent flow in the tetrahydrofuran experiments was minimal, and phenanthrene was not detected in the effluent. The use of water as the conducting solution did not cause observable phenanthrene migration.

It is proposed that in soils with low buffering capacity (e.g., kaolin), controlling the pH at the anode to counteract the electrolysis reaction and prevent low pH conditions, which are responsible for low electroosmotic flow, will improve contaminant removal (Saichek and Reddy 2003). Three different flushing solutions [deionized water, a surfactant or a cosolvent with and without a 0.01 M NaOH solution] at the anode to control the pH were tested. The test using deionized water with pH control generated a higher electroosmotic flow than the equivalent test performed

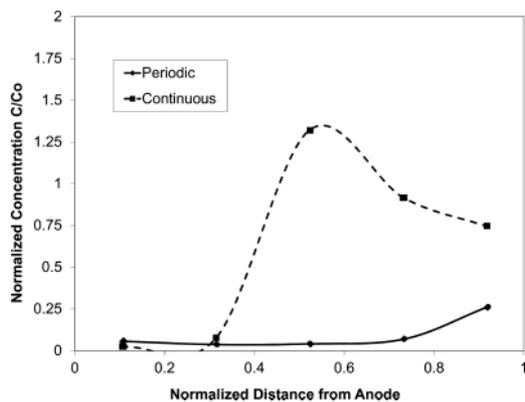


Figure 4a. Migration and removal of phenanthrene in kaolin during pulsed (periodic) electrokinetic treatment.

without pH control, but the electroosmotic flow difference between the surfactant and cosolvent tests with and without pH control was minor compared to that observed with the deionized water tests. Controlling the pH was beneficial for increasing contaminant solubilization and migration from the soil region adjacent to the anode, but the high contaminant concentrations that resulted in the middle or cathode soil regions indicated that subsequent changes in the soil and/or solution chemistry caused contaminant deposition and low overall contaminant removal efficiency.

To improve removal efficiency, pulsed electrokinetics was investigated. It consists of a periodic voltage application on a 7-day cycle of 5 days of continuous application and 2 days of “down time,” when the voltage was not applied (Reddy and Saichek 2004). The periodic voltage effects were evaluated by performing four different bench-scale electrokinetic tests with the voltage gradient applied continuously or periodically, under relatively low voltage (1.0 VDC/cm) and high anode buffering (0.1 M NaOH) as well as high voltage (2.0 VDC/cm) and low anode buffering (0.01 M NaOH) conditions. For all the tests, kaolin clay soil was spiked with 500 mg/kg phenanthrene. A nonionic polyoxyethylene surfactant, Igepal CA 720, was used as the flushing solution in all tests. The results of these experiments show that considerable contaminant removal can be achieved by employing a high, 2.0 VDC/cm, voltage gradient along with a periodic mode of voltage application (Figure 4a). The increased removal was attributed to increased phenanthrene solubilization and mass transfer due to the reduced flow of the bulk solution during the down time as well as to the pulsed electroosmotic flow that improved flushing action (Figure 4(b)). Overall, such studies have shown that electrokinetic remediation is a viable technique to remove hydrophobic organic compounds from soils.

4.3 Remediation of chlorinated aromatic and nitroaromatic contaminants

An investigation was undertaken to determine if low permeability soils contaminated with PCP can be

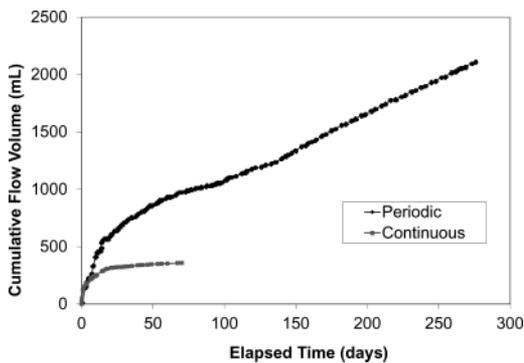


Figure 4b. Electroosmotic flow in kaolin during pulsed (periodic) electrokinetic treatment.

remediated using the electrokinetic technique (Reddy et al. 2011). A total of six tests were performed using kaolin soil spiked with 100 mg/kg of PCP. The first three tests were performed with an applied voltage gradient of 1 VDC/cm, where each test employed one of the three different flushing solutions: deionized water, electrolyte or buffered electrolyte. The other three tests were performed using the same electrolyte solution, but each employed a voltage gradient of 2 VDC/cm under constant and periodic application modes and constant voltage gradient with electrolyte liquid recirculation. The results showed that PCP can be degraded in an electrokinetic system via direct electrochemical reduction at the electrodes. The degradation of PCP ranged from 52% to about 78% depending on the conditions present. As the applied voltage gradient across the PCP-contaminated soil increased, the electroosmotic flow and PCP migration toward the cathode increased, resulting in higher PCP degradation. In the tests with electrolyte flushing solution, PCP degradation was about 58% and 65% under the applied voltage gradients of 1 and 2 VDC/cm, respectively. The mode of application of voltage potential across the PCP-contaminated soil showed a noticeable effect on the system pH and electroosmotic flow and hence the PCP degradation. The highest PCP degradation (i.e., 78%) was in the test with constant 2 VDC/cm voltage gradient and recirculation application. Overall, this study demonstrated that electrokinetic technology has the potential to remediate PCP-contaminated clay soils by the direct reductive process. The electroosmotic flow and the degree of PCP degradation during electrokinetics were dependent on the applied potential gradient and properties of the aqueous phase such as pH, ionic strength and presence of carbonates.

Nitroaromatic compounds have also been successfully degraded via electrokinetics. Khodadoust et al. 2006 assessed the removal of 2,4-dinitrotoluene (2,4-DNT), a munitions waste constituent and an industrial intermediate, from contaminated soils using enhanced electrokinetic remediation. Kaolin and glacial till soils were spiked with 480 mg of 2,4-DNT/kg of dry soil and deionized (DI) water and cyclodextrin solutions were used as purging solutions. Cyclodextrin was

selected as a nonhazardous solubility enhancer for enhancing the desorption and removal of 2,4-DNT from soils in EK remediation. Two aqueous solutions of hydroxypropyl-cyclodextrin (HPCD) at concentrations of 1 and 2% were selected for kaolin and glacial till, respectively, based on results for batch extraction of 2,4-DNT from the same soils. Less 2,4-DNT remained in the kaolin soil (up to 94% transformed) than in the glacial till soil (20% transformed) due to strong retention of 2,4-DNT by the soil organic matter in glacial till. For kaolin, less 2,4-DNT remained in the soil using HPCD solutions than using DI water. For glacial till, comparable levels of 2,4-DNT remained in the soil for both EK solutions. Since no 2,4-DNT was detected in the effluents from the EK cells, the decrease in 2,4-DNT concentration in the kaolin and glacial till soils was attributed to electrochemical transformation of 2,4-DNT to other species.

A comparative assessment on the removal of PCP, lindane and DNT using electrokinetic technique was performed (Reddy et al. 2011). Three bench-scale electrokinetic experiments were conducted on kaolin soil. In each test, the soil was spiked with one of the following contaminants: PCP, lindane and DNT at target concentrations of 100, 500 and 1000 mg/kg, respectively. The applied voltage gradient across the soil in each test was 1 volt direct current (VDC)/cm for about 500 h. The study demonstrated that degradation of PCP, lindane and DNT occurred during electrokinetics without using any solubilizing or reducing agents in the flushing solution. Results showed that PCP, lindane and DNT were degraded by a direct electrochemical reduction at the electrodes. Contaminant degradation across the soil ranged from 40% to 95%, 28% to 80%, and 26% to 60% for PCP, lindane and DNT, respectively. The effectiveness of the electrochemical reduction of the contaminant during electrokinetics depended on the contaminant solubility and soil pH. Overall, this study demonstrated that electrokinetic technology has the potential to remediate chlorinated aromatic and nitroaromatic contaminants in low permeability soils via direct reduction.

5 ELECTROKINETIC REMOVAL OF MIXED CONTAMINANTS

Previous studies have shown that electrokinetic remediation has potential to remove heavy metals and organic compounds when they exist individually in low permeability soils. Mixed contaminants, a combination of heavy metals and organic contaminants, are often encountered at contaminated sites (e.g., manufactured gas plant sites). Electrokinetic remediation can induce substantial and uniform electroosmotic flow through low permeability and heterogeneous soils, and remove both metals and organic contaminants by electromigration, electroosmosis and electrophoresis (Reddy et al. 1999).

The feasibility of using surfactants in electrokinetic remediation was evaluated to remove PAHs in the

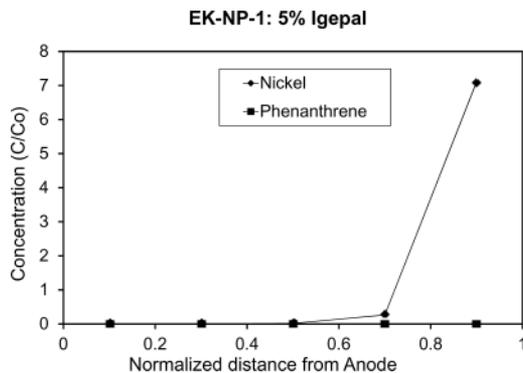


Figure 5. Simultaneous removal of phenanthrene and nickel during electrokinetic remediation using surfactant (Igepal).

presence of heavy metals from clayey soils (Maturi et al. 2009). Kaolin was selected as a model clayey soil and it was spiked with phenanthrene and Ni at a concentration of 500 mg/kg-dry wt. each to simulate typical mixed contamination. Bench-scale electrokinetic tests were performed using deionized water and two different surfactants, Igepal CA-720 and Tween 80, at 3% and 5% (w/w) each at the anode. These solutions at the anode were circulated and were buffered with 0.01 M NaOH to maintain neutral pH conditions. A periodic voltage gradient of 2 V/cm (with 5 days on and 2 days off cycles) was applied for all the tests. There was a significant migration of phenanthrene towards cathode in all the tests. Among all the extractant solutions used, complete removal of phenanthrene was observed using 5% Igepal CA-720 (Figure 5). In case of Tween 80, the low electroosmotic flow limited the delivery of Tween 80 into the soil and therefore, limited phenanthrene solubilization and transport. Nickel electromigrated as a cation towards the cathode and precipitated in the soil near the cathode due to the high pH in all tests. Overall, Ni migration pattern was not affected by the presence of phenanthrene and the extracting solutions used in this study.

Instead of surfactants, the feasibility of using cyclodextrins was evaluated for the same soil and contaminant conditions (Maturi and Reddy 2006). Bench-scale electrokinetic experiments were conducted using hydroxypropyl b-cyclodextrin (HPCD) at low (1%) and high (10%) concentrations and using deionized water in control test. A periodic voltage gradient of 2 VDC/cm (with 5 days on and 2 days off) was applied to all the tests, and 0.01 M NaOH was added during the experiments to maintain neutral pH conditions at anode. In all tests, Ni migrated as Ni^{2+} ions towards the cathode and most of it was precipitated as $\text{Ni}(\text{OH})_2$ within the soil close to the cathode due to high pH condition generated by electrolysis reaction. Even though high flow was generated in tests using deionized water and 1% HPCD, migration and removal of phenanthrene was low due to low solubility of phenanthrene in these solutions. The test with 10%

HPCD solution showed higher solubility of phenanthrene, which caused it to migrate towards the cathode, but further migration and removal was retarded due to reduced electric current and electroosmotic flow. Approximately one pore volume of flushing resulted in about 50% removal of phenanthrene from the soil near the anode.

Subsequently, the feasibility of using cosolvents to enhance the electrokinetic removal of PAHs was investigated (Maturi and Reddy 2008). Experiments were performed using *n*-butylamine (cosolvent) at concentrations of 10 and 20% and deionized water, each mixed with 0.01 M NaOH solution and circulated at the anode to maintain alkaline conditions. A periodic voltage gradient of 2 VDC/cm in cycles of 5 days on and 2 days off was applied in all the tests. During the initial stages when the soil pH was low, Ni existed as a cation and electromigrated towards the cathode. However, as the soil pH increased due to hydroxyl ions generated at the cathode and also flushing of high pH *n*-butylamine solution from the anode, Ni precipitated with no further migration. Phenanthrene was found to migrate towards the cathode in proportion to the concentration of *n*-butylamine. The extent of phenanthrene removal was found to depend on both the electroosmotic flow and the concentration of *n*-butylamine, but the presence of Ni did not influence the transport and removal of phenanthrene.

In the above cases, heavy metals were not effectively removed from the soil. Therefore, the feasibility of using surfactants and organic acids sequentially and vice versa during electrokinetic remediation was evaluated for the removal of both PAHs and heavy metals from the soils (Reddy et al. 2009). Bench-scale electrokinetic experiments were performed with the sequential anode conditioning using (1) 1 M citric acid followed by 5% Igepal CA-720; (2) 1 M citric acid followed by 5% Tween 80; and (3) 5% Igepal CA-720 followed by 1 M citric acid. A periodic voltage gradient of 2 V/cm with 5 days on and 2 days off cycles was applied in all the tests. A removal of about 96% of phenanthrene was observed in the test with 5% Igepal CA-720 followed by 1 M citric acid sequence. Most of the Ni (90%) migrated from anode to cathode in this test; however, it precipitated in the section very close to the cathode due to the high pH conditions. Conversely, the removal efficiency of Ni was about 96 and 88% in the tests with 1 M citric acid followed by 5% Igepal CA-720 sequence and 1 M citric acid followed by 5% Tween 80 sequence, respectively. However, the migration and removal efficiency of phenanthrene in both of these tests were very low. Overall, it can be concluded that the sequential use of 5% Igepal CA-720 followed by 1 M citric acid may be an effective remedial strategy to remove coexisting heavy metals and PAHs from clayey soils.

The above investigations were conducted using kaolin or glacial till spiked with phenanthrene and Ni. At actual contaminated sites, the soil composition can be varied and multiple metals and PAHs could be present. To investigate the effectiveness of

electrokinetics on field soils, a manufactured gas plant (MGP) soil contaminated with PAHs and heavy metals was used in laboratory tests (Reddy et al. 2006). Four flushing agents, which included two surfactants (3% Tween 80, and 5% Igepal CA-720), one cosolvent (20% *n*-Butylamine) and one cyclodextrin (10% hydroxypropyl- β -cyclodextrin or HPCD) were examined to enhance the solubilization of PAHs in the soil. Four electrokinetic experiments were conducted at 2.0 VDC/cm voltage gradient and 1.4 hydraulic gradient. It was found that the cosolvent increased the soil pH, while the surfactants and HPCD did not induce substantial change. Electroosmotic flow was the highest with the cosolvent, while the lowest flow was observed with Tween 80 surfactant. Igepal CA-720 surfactant yielded the highest removal efficiency due to the partial solubilization of PAHs, causing some PAHs to migrate towards the cathode. Heavy metals were found to be strongly adsorbed/precipitated and showed negligible migration behavior in all the tests. Based on the contaminant mass remaining in the soil, it is apparent that further optimization of the electrokinetic system is required to improve PAH removal efficiency for the MGP soil.

A similar study was conducted on contaminated sediment obtained from Indiana Harbor (Reddy and Ala 2005). The sediment is a fine-grained material with high moisture (78%) and organic (19%) contents and is contaminated with a wide range of PAHs and heavy metals (Reddy et al. 2010). Four bench-scale electrokinetic experiments were conducted at 2.0 VDC/cm of constant voltage gradient using two surfactants: 5% Igepal CA-720 and 3% Tween 80, a cosolvent: 20% *n*-butylamine and a cyclodextrin: 10% HPCD as flushing solutions for the solubilization/desorption of PAHs. The mobility and removal of heavy metals was also investigated while flushing these solutions. The experimental results show that 20% *n*-butylamine and 5% Igepal 720 systems are effective for the partial solubilization of the PAHs in the sediments; however, both 3% Tween 80 and 10% HPCD systems are ineffective for desorption/solubilization of PAHs in the sediment. None of the selected flushing agents is effective for the removal of heavy metals from the contaminated sediment. The low removal of PAHs and heavy metals is attributed to the high organic content and high acid buffering capacity of the sediment.

Electrokinetic remediation is generally applied to low permeability soils, but it can also be applied to sandy soils to solubilize and enhance removal of the contaminants. An integrated use of hydraulic flushing and electrokinetic treatment was investigated for the remediation of silty sand contaminated by both PAHs and heavy metals. The soil was collected from another polluted former manufactured gas plant (MGP). Four bench-scale experiments were conducted to analyze the ability of the combined hydraulic flushing and the electrokinetic treatment for the simultaneous removal of PAHs and heavy metals. Sequential flushing with EDTA or Igepal CA-720 was tested with or without the

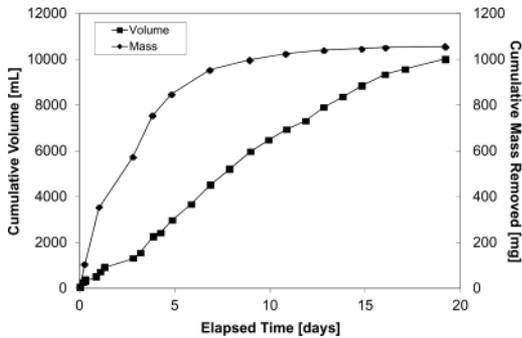


Figure 6a. Flow and mass of phenanthrene removal from sand during surfactant flushing.

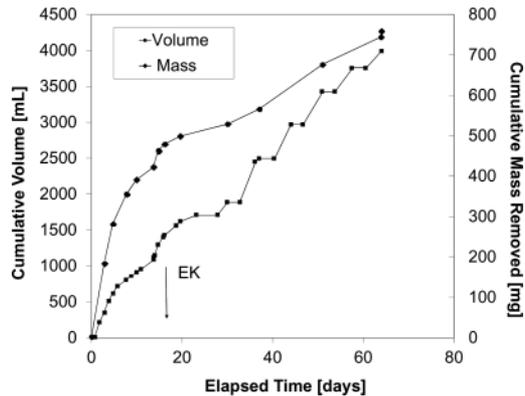


Figure 6c. Flow and mass of phenanthrene removal from soil profile with top clay layer and bottom sand layer during electrokinetically enhanced surfactant flushing.

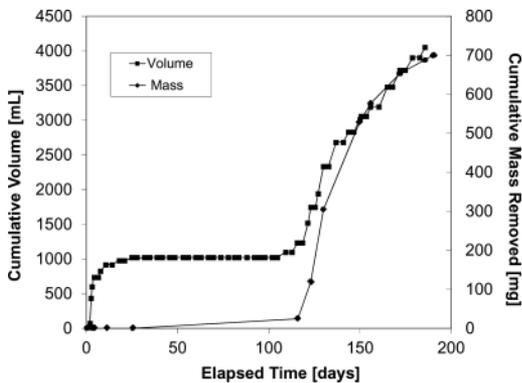


Figure 6b. Flow and mass of phenanthrene removal from kaolin during electrokinetically enhanced surfactant flushing.

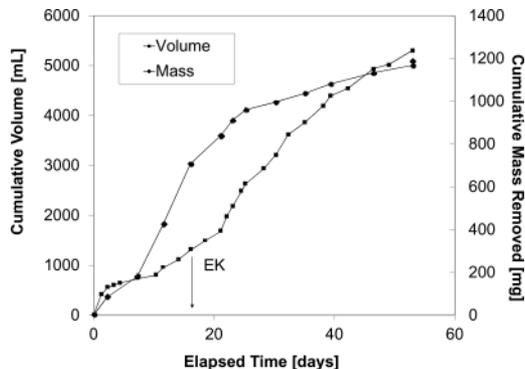


Figure 6d. Flow and mass of phenanthrene removal from sand layer with interbedded clay lenses during electrokinetically enhanced surfactant flushing.

simultaneous application of a low intensity direct electric field (1 VDC/cm). The best results were obtained with 0.2 M EDTA flushing in two stages (without and with voltage gradient, 1 VDC/cm), followed by 5% Igepal flushing in two stages (without and with 1 VDC/cm). Heavy metals were removed mainly during the EDTA flushing, with removal efficiencies of about 60% for Zn, 80% for Pb and 30% for Cu. During Igepal flushing, no heavy metals were removed, but PAHs were removed, including 40% phenanthrene, 30% pyrene and 20% benzo[a]pyrene. Combining electrokinetics with hydraulic flushing did not improve contaminant removal from the soil.

6 ELECTROKINETIC REMEDIATION IN HETEROGENEOUS SUBSURFACE

Generally, subsurface conditions are heterogeneous in nature consisting of clay layers and sand layers and/or clay layers interbedded in sand formations. Common remediation techniques based on hydraulic flushing can only remediate sand formations and the contamination associated with clay layers and lenses cannot be remediated. An investigation was undertaken to determine the applicability of electrokinetic remediation technology to treat contaminated soils

under soil heterogeneities such as layers, lenses, and mixtures of different soils (Saichek and Reddy 2005). Specifically, this study evaluated surfactant-enhanced electrokinetic remediation of PAHs under heterogeneous soil conditions. A series of bench-scale experiments was conducted using two soils (sand and kaolin) spiked with a representative PAH compound (phenanthrene) in a two-dimensional electrokinetic test apparatus under various layered, lens, or mixed soil configurations (Figure 6). In addition, the homogeneous sand and kaolin soils were each tested alone for comparison purposes. All the experiments employed the same nonionic surfactant (5% Igepal CA-720) flushing solution and a low (0.05) hydraulic gradient. The results showed that the surfactant flushing under the low hydraulic gradient alone was sufficient for complete removal of the contaminant from the homogeneous sand profile (Figure 6(a)), whereas the electroosmotic flow generated by the application of a DC 2.0 V/cm electric potential in a periodic mode considerably enhanced the removal efficiency for the homogeneous and heterogeneous soil profiles containing kaolin (Figures 6(b), 6(c)

and 6(d)). The voltage gradient varied spatially and temporally through the soil profiles and affected the electroosmotic flow and contaminant removal.

7 CHALLENGES AND OPPORTUNITIES

7.1 Challenges

Electrokinetic remediation is uniquely applicable to remediate complex sites containing low permeability and heterogeneous soils contaminated by heavy metals, organic contaminants or both. However, many practical challenges need to be overcome to make this technology feasible for field application. Some of these challenges include:

- The effectiveness of the technology is sensitive to variable *in situ* geochemistry. Hence, laboratory test results may not be reflective of expected variable geochemical conditions in the field.
- The complex field soil and aged multiple contaminants lead to low remedial efficiency as compared to laboratory demonstrations using spiked, homogeneous soils.
- The remediation time can be longer and difficult to predict, making the technology unattractive if the site needs to be closed quickly for future development.
- Except for the *in situ* electrochemical reduction of some organic contaminants, the contaminants are transported into the electrode wells/trenches; effluent needs to be pumped out and treated above ground either on-site or off-site. The treatment of such effluent requires regulatory permits and incurs additional treatment costs.
- The technology cost is high due to high cost of materials such as electrodes and electrode conditioning solutions and electrical power.
- It may be difficult to get regulatory approval to inject electrode conditioning solutions (e.g., EDTA, surfactants, etc.) into the ground as the fate and risk of their residual presence in the subsurface is unknown.
- Many investigations are based on spiked soils and very limited information is available on field contaminated sites. The well documented field pilot studies are extremely scarce.
- Full-scale applications are very limited in the US. Some field applications such as Lasagna@process are well documented.
- Technology developers' information on pilot or full-scale field applications is often incomplete. For example, Lageman (2005) reported several successful full-scale field applications dealing with inorganic contaminants in the Netherlands, but information available on design, implementation and monitoring is limited. US-based Electro-Petroleum, Inc. claims completion of several projects, but it has not published detailed technical information.
- As the technology is material- and energy-intensive, it may not be as sustainable as other technologies.

7.2 Opportunities

Implementation of electrokinetic remediation as a stand-alone technology to remove contaminants from soils may be inefficient, uneconomical and unsustainable. Nevertheless, electrokinetic remediation is uniquely applicable for complex sites with low permeability/heterogeneous soils and mixed contaminants. For such sites, the common remediation technologies (e.g. pump and treat, soil flushing, permeable reactive barriers, chemical stabilization/oxidation, *in situ* bioremediation, and soil heating) may not be effective or efficient. Integrating electrokinetic remediation judiciously with common technologies to overcome the limitations of the common technologies may provide an effective and efficient remedial strategy for complex sites. For example, electrokinetic remediation may be integrated with common technologies such as chemical oxidation/reduction, bioremediation and phytoremediation to remediate sites with the following advantages: (1) organic contaminants can be detoxified within the soil, hence no effluent treatment is required; (2) removes metals from soils, providing a long-term, effective solution; (3) remediates mixed contaminants (both metals and organic contaminants); (4) cost-effective; (5) practical; and (6) green and sustainable with a renewable energy source (e.g., solar power). Some examples of integrated technologies are presented below.

7.3 Coupled electrokinetic-chemical oxidation technology

Fenton Oxidation of PAHs: An integrated electrochemical oxidation process that utilizes electrokinetics (EK) to deliver the oxidant (5–10% hydrogen peroxide, H₂O₂) and chelant (40 mM EDTA or DTPA) or iron chelate (1.4 mM Fe-EDTA or Fe-DTPA) to oxidize PAHs in soils was investigated (Reddy and Chandhuri 2009). Batch and bench-scale EK experiments were conducted using: (a) kaolin spiked with phenanthrene at 500 mg/kg and (b) former manufactured gas plant (MGP) soil, a high buffering silty soil, contaminated by a variety of PAHs (1493 mg/kg). Batch experiments showed that chelant solutions dissolve native iron minerals to form soluble Fe-chelates that remain available even at higher pH conditions of soil for the Fenton-like oxidation of the PAHs. In EK experiments, a 5–10% H₂O₂ solution was delivered from the anode and a chelant solution or iron-chelate was delivered from the cathode. Preflushing of soil with 5% ethanol and ferrous sulfate (1.4 mM) prior to oxidant delivery was also investigated. An electric potential of 2 VDC/cm was applied in all tests to induce electroosmotic flow for 5–8 days for kaolin and 25 days for the MGP field soil. In the absence of any chelating agent, phenanthrene oxidation was catalyzed by native iron present in kaolin soil, and 49.8–82.3% of phenanthrene was oxidized by increasing H₂O₂ concentration from 5–10%. At 5% H₂O₂ concentration, phenanthrene oxidation was not increased by using 40 mM EDTA, 40 mM DTPA or 1.4 mM Fe-DTPA,

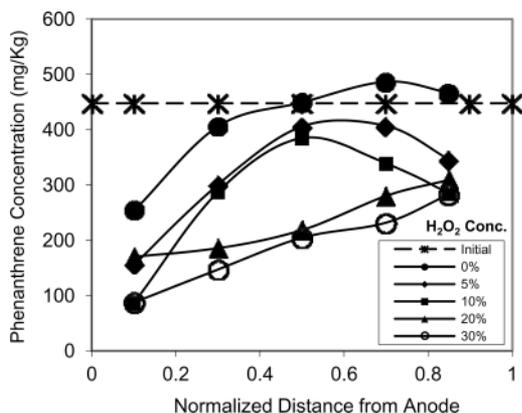


Figure 7a. Residual phenanthrene distribution after integrated electrokinetic Fenton-like oxidation treatment.

but it increased to 70% using 1.4 mM Fe-EDTA. Maximum phenanthrene oxidation (90.5%) was observed by 5% ethanol preflushing and then treating with 5% H₂O₂ at the anode and 1.4 mM Fe-EDTA at the cathode. However, preflushing with 1.4 mM ferrous sulfate did not improve phenanthrene oxidation. The findings of the MGP field soil test indicated that delivery of 5% H₂O₂ alone resulted in oxidation of 39.8% of total PAHs (especially 2- and 3-ring PAHs). The use of EDTA and Fe-EDTA did not increase PAHs oxidation in this soil. Overall, an optimized *in situ* combined technology of EK and Fenton-like process has the potential to oxidize PAHs in low permeability and/or high buffering soils.

Fenton-Oxidation of PAHs and Simultaneous

Removal of Heavy Metals: The coupled Fenton-like oxidation and electrokinetic remediation was also investigated for mixed contaminants (combination of heavy metals and PAHs). This remediation process aims at oxidation of organic contaminants and simultaneous removal of heavy metals. Fenton's reagent, consisting of H₂O₂ and native iron catalyst, is utilized for chemical oxidation. Laboratory batch and electrokinetic experiments were performed on kaolin spiked with Ni and phenanthrene each at a concentration of 500 mg/kg of dry soil to represent typical heavy metal and PAH contaminants found at contaminated sites. Experiments were conducted using H₂O₂ solution in 5%, 10%, 20% and 30% concentrations and also using deionized (DI) water as control (Reddy and Karri 2008). For electrokinetic experiments, a voltage gradient of 1 VDC/cm was applied and H₂O₂ solution was introduced at the anode for a total duration of four weeks. Batch tests showed that phenanthrene oxidation increases from 76% to 87% when the H₂O₂ concentration increases from 5% to 30%. The electrokinetic experiments showed substantial electroosmotic flow in all the tests. Oxidation of phenanthrene increased with increasing concentration of H₂O₂; a maximum of 56% oxidation was observed with 30% H₂O₂ (Figure 7a). Nickel migrated from anode to cathode. This migration was more pronounced in the H₂O₂ tests as compared

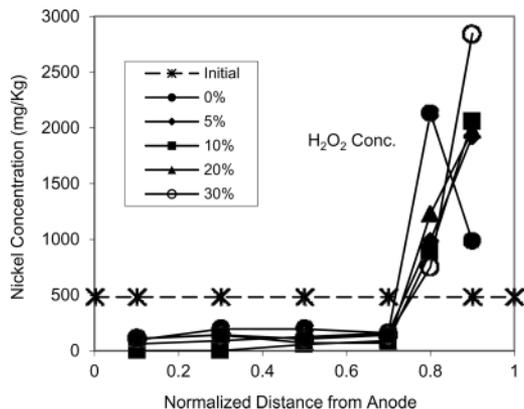


Figure 7b. Residual nickel distribution after integrated electrokinetic Fenton-like oxidation treatment.

to the DI baseline test. Nickel precipitated in all the tests near the cathode due to high pH conditions (Figure 7b). These results emphasize that the optimization of H₂O₂/catalyst concentration and voltage gradient as well as the control of soil pH are required to increase the removal of Ni and the oxidation of phenanthrene.

In a supplemental study, the effect of voltage gradient on the remedial efficiency was investigated by testing two voltage gradients, 1 and 2 VDC/cm (Reddy and Karri 2006). The H₂O₂ solution in two different concentrations at 5% and 10% was introduced at the anode, and each experiment was conducted for a total duration of four weeks. The results showed that increasing the voltage gradient from 1 VDC/cm to 2 VDC/cm did not increase the electroosmotic delivery of H₂O₂ significantly. About 28% and 34% of the phenanthrene were oxidized within the soil in the 5% and 10% H₂O₂ experiments, respectively, under 1 VDC/cm. The phenanthrene oxidation increased to about 32% and 42% using the 5% and 10% H₂O₂ concentrations, respectively, under 2 VDC/cm. Ni migrated towards the cathode and then precipitated close to the cathode, due to high pH conditions in all the experiments. The Ni migration was slightly higher in the case of 2 VDC/cm than in the case of 1 VDC/cm, due to greater migration of the acidic pH front towards the cathode under 2 VDC/cm. Overall, the results showed that an increase in the voltage gradient from 1 VDC/cm to 2 VDC/cm improved overall remedial performance slightly.

Persulfate Oxidation of PCBs: Persulfate is another oxidant used for remediation purposes. Integrating electrokinetic remediation with persulfate has the potential to facilitate the delivery of persulfate in low permeability soils as well as activate oxidizing radicals and simultaneously induce oxidative/reductive reactions directly in the soil. In order to investigate this, a series of laboratory batch and bench-scale electrokinetic experiments were conducted using kaolin spiked with 50 mg/kg of 2,20,3,50 tetrachlorobiphenyl (PCB 44), a representative PCB (Yükselen-Aksoy and Reddy 2013). Persulfate oxidation activators [elevated

temperature (45°C) and high pH (at the cathode)] were investigated to maximize the PCB degradation. In addition, the effect of oxidant dosage on PCB degradation was investigated. The electrokinetically enhanced temperature-only activated persulfate oxidation test resulted in better PCB 44 remediation (77.9%) than the temperature and high-pH activated persulfate oxidation (76.2%) over a 7-day period. The optimal dosage for effective remediation was 30% Na-persulfate (76.2%) because a 20% concentration of the oxidant yielded a lower rate of degradation (55.2%) of PCB 44. These results are encouraging for the use of electrokinetically enhanced persulfate oxidation for the effective remediation of PCBs in soils.

In a supplemental study, the glacial till soil was investigated to determine the effects of soil type on electrokinetic-persulfate treatment (Yukselen-Aksoy and Reddy 2012). The activation of persulfate improved the oxidation of PCB in kaolin, but the effect in the glacial till was insignificant. The final pH values of the kaolin were around 1, while they were around 7 for glacial till because of the high buffering capacity of glacial till. Low pH conditions are also shown to activate persulfate, leading to higher PCB oxidation. The degradation of PCB 44 was significantly higher for the kaolin than the glacial till. In kaolin, the highest level of PCB oxidation, 77.9%, was achieved with temperature activated persulfate in 7 days. However, in the glacial till the highest PCB oxidation was 14.4% with 30% Na-persulfate concentration without any activation. The high buffering capacity, nonhomogeneous mineral content and high organic content of glacial till may have contributed to the low persulfate oxidation of PCB.

Permanganate Oxidant Delivery: Potassium permanganate (KMnO_4) is another common oxidant used for remediation purposes. A bench-scale study was conducted to investigate the feasibility of using electrokinetics as a method of delivering KMnO_4 into kaolin. KMnO_4 was introduced at the anode, the cathode and both electrodes to investigate (1) the extent of oxidant transport via electroosmosis and electromigration and (2) to investigate the stability of the oxidant at each electrode location. Separate tests were performed under different voltage gradients to explore the effect of electric potential on oxidant transport and stability. Results indicate that (1) electromigration is not as effective as electroosmotic advection for the transport of permanganate into the soil and (2) permanganate may not be stable under the pH-redox conditions that are imposed by the application of electric potential. Additional research is being conducted to explore the stability of permanganate under electrokinetic environments and to determine whether a substantial amount of permanganate can be injected into low-permeability soils.

7.4 *Coupled electrokinetic-chemical reduction technology*

Zero-valent iron (ZVI) has been demonstrated to effectively dehalogenate organic contaminants in the

subsurface. ZVI is also used commonly in permeable reactive barriers for treating groundwater. Recent synthesis of nanoscale iron particles (NIP) allow them to be injected into contaminated soil zones for reduction of the organic contaminants. However, bare NIP were found to be unstable, while lactate modified NIP (LMNIP) was found to be stable and ideal for transporting through the subsurface soils. The challenge is delivery of the LMNIP in low permeability soils; hence electrokinetics was proposed to be used to inject LMNIP into the contaminated soils. This approach was evaluated in bench-scale electrokinetic experiments performed at constant voltage gradient with DNT spiked kaolinite at a concentration of 920 mg/kg (Reddy et al. 2011). Bare NIP or LMNIP (4 g/L) was injected at some distance away from the anode. Aluminum lactate 10% (w/w) was used as modifier for LMNIP. The results showed 41–65% of DNT degradation in the soil near the anode, while it was lower at 30–34% near the cathode. The highest DNT degradation was achieved using LMNIP. The total degradation of DNT was attributed to both NIP and electrochemical process. Overall, it was found that electrokinetic system can enhance the delivery of LMNIP in low permeability soils for the degradation of energetic organic contaminants such as DNT.

7.5 *Coupled electrokinetics-bioremediation technology*

Electrokinetics can serve as an effective nutrient delivery system for bioremediation of contaminants in low permeability soils. Bioremediation can include degradation of organic contaminants or immobilization of heavy metals. A preliminary laboratory investigation was performed wherein electrokinetics was used for the delivery of nutrients to metal-reducing microorganisms in a low permeability clayey soil (Reddy et al. 2003). In particular, the microorganisms were used to reduce a toxic and mobile Cr(VI) to a less toxic and immobile form Cr(III). Three bench-scale electrokinetic experiments were conducted using kaolin artificially contaminated with Cr(VI) at an initial concentration of 1000 mg/kg. All the experiments included a control test without micro-organisms or nutrients, a test with microorganisms but without nutrients and a test with microorganisms and supplemental nutrients, specifically acetate, phosphate and ammonium. The results showed that acetate and phosphate amendment by electrokinetics was effective because both nutrients electromigrated into the soil. Moreover, the results indicate that employing the microorganism cultures improved Cr(VI) reduction. These results suggest that nutrient amendment by electrokinetics for the bioremediation of heavy metals has great potential; however, the microbial strains responsible for Cr(VI) reduction must be identified so the electrokinetic system can be engineered to provide the optimal nutrient, pH and environmental conditions for these strains. Several other studies have reported enhanced bioremediation of organic contaminants using electrokinetics (Reddy and Cameselle 2009).

7.6 Coupled electrokinetics-phytoremediation technology

Phytoremediation involves the removal, stabilization or degradation of contaminants in soils and groundwater by plants. Both organic and inorganic contaminants can be accumulated in plant tissues or degraded via enzymatic activity. Alternatively, contaminants can be transformed to other chemical species less bioavailable in the soil. The different mechanisms involved in phytoremediation include: rhizofiltration, phytodegradation, phytoaccumulation (or phytoextraction), phytostabilization, and rhizodegradation (also called phytostimulation). The combination of phytoremediation and electrokinetic remediation has been proposed in an attempt to avoid the limitations of phytoremediation. The electric field may enhance the removal of the contaminants by increasing the bioavailability of the contaminants by desorption and improved mobility of polar species. Some significant variables that affect the coupled technology are: the use of AC or DC current, the voltage level, the mode of voltage application (continuous or periodic), the change in soil pH caused by the electrolysis of water at the electrodes, and the possible addition of facilitating agents to enhance the mobility and bioavailability of the contaminants. Limited laboratory studies are reported on combined electrokinetics and phytoremediation (Reddy and Cameselle 2009), but the most critical issue is on how it can be readily implemented in the field.

8 CONCLUSION

Although many technologies have been developed to remediate polluted sites, a substantial number of them are ineffective or inefficient for complex sites containing low permeability soils, heterogeneous soils or mixed contaminants. Electrokinetic remediation technology has great potential for *in-situ* remediation of low permeability and/or heterogeneous soils that have been contaminated by organics, heavy metals or a combination of these contaminants. However, electrokinetic remediation is highly dependent on site-specific geochemical conditions such as the soil composition, native electrolytes, contaminant aging, and contaminant mixtures. Several research studies have been undertaken to develop fundamental geochemical characterization and enhance geochemistry for effective electrokinetic remediation. Electrokinetic remediation can be easily integrated with conventional remedial systems to enhance remedial efficiency and decrease overall remedial cost. Field pilot tests and full-scale studies are limited, and many practical issues on implementing the technology at actual sites are yet to be resolved.

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