

**EMERGING TECHNOLOGIES FOR  
THE REMEDIATION OF  
METALS IN SOILS  
ELECTROKINETICS**

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**-FINAL-**

**December 1997**

**Prepared by  
Interstate Technology and Regulatory Cooperation  
Work Group  
Metals in Soils Work Team  
Emerging Technologies Project**

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Established in 1995, the Interstate Technology & Regulatory Council (ITRC) is a state-led, national coalition of personnel from the environmental regulatory agencies of some 40 states and the District of Columbia; three federal agencies; tribes; and public and industry stakeholders. The organization is devoted to reducing barriers to, and speeding interstate deployment of, better, more cost-effective, innovative environmental techniques. ITRC operates as a committee of the Environmental Research Institute of the States (ERIS), a Section 501(c)(3) public charity that supports the Environmental Council of the States (ECOS) through its educational and research activities aimed at improving the environment in the United States and providing a forum for state environmental policy makers. More information about ITRC and its available products and services can be found on the Internet at [www.itrcweb.org](http://www.itrcweb.org).

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## **EXECUTIVE SUMMARY**

Electrokinetic remediation is a developing technology for in-situ removal of heavy metals and radionuclides from contaminated soil. This document provides general information on the technology, including background, applicability and potential advantages and limitations of electrokinetic remediation techniques. In addition, this technology overview discusses current approaches to electrokinetic remediation and identifies future research and development needs. Data from several case studies are presented, as are regulatory and stakeholder concerns related to electrokinetic technology implementation at contaminated sites. While the technology can be applied to treat a variety of contaminants, this document focuses mainly on the remediation of metals in soils.

Membership on this work team was open to all ITRC members. Participants with expertise or interest in metals treatment technologies in their states elected to join the team and contributed consistently to the development of this work product. Members of the RTDF (Remediation Technologies Development Forum) IINERT technology team (In-Place Inactivation and Natural Ecological Restoration Technologies) also participated on this team and helped to provide an industry perspective. A representative from the U.S. Army Corps of Engineers and the Department of Energy actively participated on the team. Support was also provided by the United States Environmental Protection Agency and the Department of Defense. Input regarding public and community concerns for these technologies was provided by ITRC public stakeholder representatives.

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# EMERGING TECHNOLOGIES FOR THE REMEDIATION OF METALS IN SOILS ELECTROKINETIC REMEDIATION

## 1.0 INTRODUCTION

Electrokinetic remediation is a developing technology for in-situ removal of heavy metals and radionuclides from contaminated soil. The application of direct current and a subsequent voltage gradient in a porous medium leads to two transport phenomena; ionic species in the soil-water solution will migrate to the oppositely charged electrode (electromigration), and a bulk flow of soil-water is induced toward the cathode (electroosmosis). The combination of these two transport phenomena leads to a movement of contaminant ions towards one of the electrodes. The direction and rate of movement of an ionic metal species will depend on its charge, both in magnitude and polarity, as well as the magnitude of the electroosmosis-induced flow velocity. Non-ionic species will be transported along with the electroosmosis-induced water flow.

## 1.1 Background

The demand to develop innovative and cost-effective in-situ remediation technologies in waste management stimulated the effort to employ conduction phenomena using electric fields to remove chemical species from soils (Acar et al., 1993). This technique is variably known as electrokinetic remediation, electro-reclamation, electrokinetic soil processing, electro-chemical decontamination, electrorestoration or electrochemical soil processing. Attempts to leach metals from soils by electro-osmosis date back to the 1930s. In the past, research focused on removing unwanted salts from agricultural soils. Electrokinetics has also been used for dewatering of soils and sludges since the first recorded use in the field in 1939 (USEPA, 1994). Electrokinetic extraction has been used in the former Soviet Union since the early 1970s to concentrate metals and explore for minerals in deep soils. By 1979, research had shown that the content of soluble ions increased substantially in electro-osmotic consolidation of polluted dredgings, while heavy metals were not found in the effluent (USEPA, 1994). By the mid-1980s, numerous researchers had realized independently that electrokinetic separation of heavy metals from soils could be a potential remedial option.

Electrokinetics utilizes either low-level DC current between the electrodes, or an electric voltage potential difference across electrodes placed in the ground in an open flow arrangement. Existing groundwater or externally supplied processing fluid is used as the conductive medium. Open flow arrangement at the electrodes allows ingress and egress of the processing or pore fluid into and out of the porous medium. The low-level DC utilized in electrokinetic remediation results in physico-chemical and hydrological changes in the soil mass, leading to species transport phenomena in the porous media. The species input into the system at the electrodes (either by the electrolysis reactions, or through the cycling processing fluid) and the species in the pore fluid will be transported across the porous media by conduction phenomena in soils under electric voltage gradient fields. This transport, coupled with sorption, precipitation and dissolution reactions, comprises the fundamental mechanisms affecting the electrokinetic process. Extraction and

removal are accomplished by electrodeposition, precipitation or ion exchange either at the electrodes or in an external extraction system placed in a unit cycling the processing fluid (Acar et al., 1993).

## 1.2 Applicability

Electrokinetic remediation technology is usually deployed in one of the following ways (Geokinetics, 1997):

- **In-situ remediation.** Electrodes are placed directly in the ground and contamination is recovered with minimal disturbance to the site.
- **Batch operation.** Contaminated media is transported to a batch facility and treated ex-situ.
- **Electrokinetic Ring Fence.** A chain of electrode pairs are deployed in-situ to recover ionic contamination from groundwater as it flows past the electrodes.

In-situ remediation in any of several configurations is often the most desirable option at a site. The applicability of each method is dependent upon site-specific conditions and contaminants. Electrokinetic technology is applicable to water soluble contaminants, but not to non-polar organics, due to lack of charge. The technology is most applicable at sites with homogeneous soils that are fine-grained and exhibit both high permeabilities and high moisture contents. The technology is most efficient when salinity and cation exchange capacity (CEC) are low.

## 1.3 Potential Advantages and Limitations of Electrokinetics

### Advantages

- May be able to treat soils not accessible for excavation;
- Potentially effective in both the saturated and unsaturated zone;
- Applicable in soils of low hydraulic conductivity, particularly with high clay content;
- Can treat both organic and inorganic contaminants.

### Limitations

- The solubility of the contaminant and the desorption of contaminants from the soil matrix may limit the success of the technology;
- The process may not be efficient when the target ion concentration is low and the non-target ion concentration (background) is high;

- The technology requires the presence of a conducting pore fluid to mobilize contaminants;
- Heterogeneities or anomalies found at sites, such as submerged foundations, rubble, large quantities of iron or iron oxides, and large rocks or gravels may reduce removal efficiencies.

**Table 1-1** presents an overview of specific data needs for electrokinetic remediation.

**Table 1-1  
Data Needs and Site Applicability for Electrokinetic Remediation**

<b>Data Needs</b>	<b>Basis / Applicability</b>
Hydraulic Conductivity	Technology applicable in zones of low hydraulic conductivity, particularly with high clay content
Depth to water table	Technology may be applied differently in saturated and unsaturated soils
Areal extent of contamination	To assess electrode and recovery well placement
Electroosmotic permeability	To estimate the rate of contaminant and water flow that can be induced
Cation exchange capacity (CEC)	Technology most efficient when CEC is low
Metals Analysis	Technology applicable to water soluble contaminants, but not to non-polar organics
Salinity	Technology most efficient when salinity is low. Chlorine gas can be produced by reduction of chlorine ions at the anode
Identification of half cell potentials	Characterizes possible reactions
Contaminant transference number	Characterizes total current required to remediate the site

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Data Needs	Basis / Applicability
Porewater pH	Affects contaminant valence state and its tendency to precipitate out of solution

## 2.0 APPROACHES TO ELECTROKINETICS TECHNOLOGY

### 2.1 General

The electrokinetic transport phenomena pertinent to in-situ remediation include electroosmosis (movement of water in response to an electric field), electrophoresis (movement of a charged particle or colloid in an electric field), and electromigration (movement of solute ions in the electric field). Electrokinetic remediation is accomplished by implanting electrodes in the soil with application of a relatively small direct electrical current across the electrodes. Ions in solution will migrate toward the electrode of opposite charge by electromigration. Experimental results indicate that the electromigration rates depend significantly on the soil pore water current density. The process efficiency is not as dependent on the fluid permeability of soil as it is on the pore water electrical conductivity and the path length through the soil. Both of these characteristics are functions of the soil moisture content.

Removal of contaminants at the electrode may be accomplished by several means, including electroplating, precipitation or co-precipitation at the electrode, pumping of water near the electrode, or complexing with ion exchange resins (PRC, 1996). An alternate method suggested is adsorption into the electrode. This may be feasible because some ionic species will change valence near the electrode (depending on the soil pH) making them more likely to adsorb.

The direction and quantity of contaminant movement is influenced by contaminant concentration, charge or ionic character (anions versus cations), soil type and structure, interfacial chemistry, and current density in the soil pore water. For the process to work, the soil moisture content must be above a minimum value. This minimum moisture content can be estimated from the residual moisture content of a soil, also called "immobile water." Preliminary results indicate that the optimum soil moisture content for electromigration is less than saturation, due to competing effects of tortuosity and pore water content. This value may be between 10 and 20%.

### 2.2 Site Screening

Before electrokinetic remediation is undertaken at a site, a number of field and laboratory

screening tests must be conducted to determine if the site is amenable to the technology:

- **Field conductivity surveys:** The natural spatial conductivity variability should be delineated because buried metallic or insulating material can induce variability in the electrical conductivity of the soil and, therefore, the voltage gradient. In addition, it is important to assess if there are deposits that exhibit very high electrical conductivity, where the process may be inefficient.
- **Chemical analysis of water:** The pore water in the vadose zone should be analyzed for dissolved major anions and cations, as well as for the concentration of the contaminant(s). Electrical conductivity and pH of the pore water should be measured, and an estimate of the contaminant transference number should be made.
- **Chemical analysis of soil:** The buffering capacity and geochemistry of the soil should be determined.

### 2.3 Current Applications

Electrokinetic remediation technology has recently taken significant strides. Electrokinetics Inc. of Baton Rouge, LA has completed large-scale pilot studies using spiked and naturally contaminated soil deposits under the USEPA SITE program. In collaboration with the US Army Waterways Experiment Station, Electrokinetics Inc. is currently carrying out a field study of extracting lead from soils at a Firing Range that belongs to the US Army. Other vendors have begun utilizing electrokinetics in the field, but data on completed projects is not yet available.

### 3.0 RESEARCH AND DEVELOPMENT—FUTURE NEEDS

Electrokinetic extraction of metals from soils has undergone bench-scale and pilot-scale testing. As noted above, premature precipitation of metal species close to the cathode compartment has been a bottleneck for the process. Acetic acid depolarization techniques and other depolarization schemes have been developed (EK, 1993) to circumvent this problem. Extraction of heavy metals by bench and pilot-scale tests from 'real world' soils retrieved from numerous sites demonstrates that the technology may be applied efficiently and cost-effectively. Currently, field demonstration studies are ongoing in the US.

Electrokinetic remediation is a developing technology. Projected performance will be determined after a predictive model for migration rates is developed. In such a predictive model, migration rate is a function of moisture content, sand grain size, ionic mobility, pore water, current density,

contaminant concentration, and total ionic concentration. More field work is needed to validate the results of any models that are developed.

## **4.0 CASE STUDIES AND RESULTS**

### **4.1 USEPA Site Program**

Three pilot-scale studies were conducted by Electrokinetic Inc. under the USEPA SITE program; two tests using kaolinite spiked with lead at initial concentrations of 850 mg/kg and 1,500 mg/kg, and another using fine sand and kaolinite mixture spiked with lead at 5,322 mg/kg. The kaolinite used had lead adsorption capacity of about 1,100 mg/kg. Lead nitrate salt was used as the source of lead. Tap water was used both as the catholyte and the anolyte. Other details of testing are presented by Alshawabkeh and Acar (3) and EK (5). More than 90% of the lead in the soil is transported across to the cathode compartment. Lead prematurely precipitates close to the cathode compartment at its hydroxide solubility value if the chemistry of the electrolyte at the electrodes is not altered or controlled (unenhanced electrokinetic remediation). One objective of these pilot-scale tests was to formalize and validate the principles of multi-species transport under electric fields. An appreciation of the relation between the mechanics and chemistry is only possible when precipitation close to the cathode compartment is allowed. Therefore, pilot-scale tests did not employ enhancement techniques.

The development of the theoretical formalisms pertaining to multi-species transport under electric fields and the preparation of the associated numerical model and design/analysis packages are supported by the USEPA under the Gulf Coast Hazardous Substance Research Center program at Lamar University. The total lead profile predictions of the model pertinent to the specific initial and boundary conditions in the pilot-scale test are given on the following page in Figure 4-1. The lead and the acid generated by the electrolysis reactions at the anode were released into the pore fluid either by dissolution or by the aqueous phase reactions. They then travel towards the cathode compartment under the multi-species transport phenomena in soils under electric fields. Lead precipitates close to the cathode compartment at its hydroxide solubility value with the increase in the hydroxide concentration due to the prevailing cathodic reaction. The 50 day predictions shown in Figure 4-1 are compared with the pilot-scale test results in Figure 4-2. The agreement between the theoretical model and the pilot-scale test results demonstrate that the principles of the process are well rationalized and understood. The design analysis package which will include the generalized model is being developed through a joint effort between Electrokinetics Inc. and US Army Waterways Experiment Station.

The need to overcome the problem of precipitation close to the cathode compartment prompted Electrokinetics Inc. and the US Army Waterways Experiment Station to evaluate the feasibility of employing different techniques to enhance the process. The objective of the study was to promote transport of the positively charged species into the catholyte where they could be removed either by

**Figure 4-1.** Prediction of total lead concentration across the electrodes using the Finite Element Model for Multi-Species Transport in Soils under Electrical Fields (FEM-MTSE) [Boundary and Initial Conditions pertinent to the Pilot-Scale Study are employed; 100 elements are used] (3,5).

**Figure 4-1.** Prediction of total lead concentration across the electrodes using the Finite Element Model for Multi-Species Transport in Soils under Electrical Fields (FEM-MTSE) [Boundary and Initial Conditions pertinent to the Pilot-Scale Study are employed; 100 elements are used] (3,5).

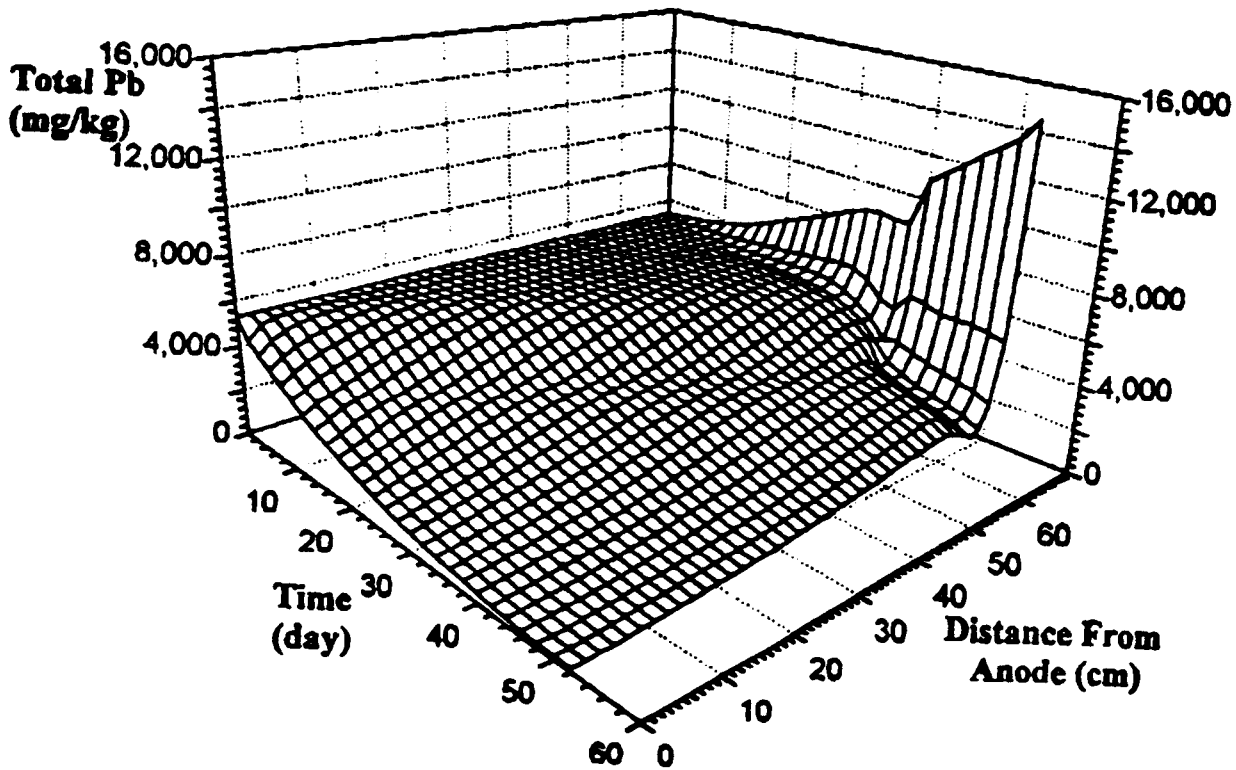
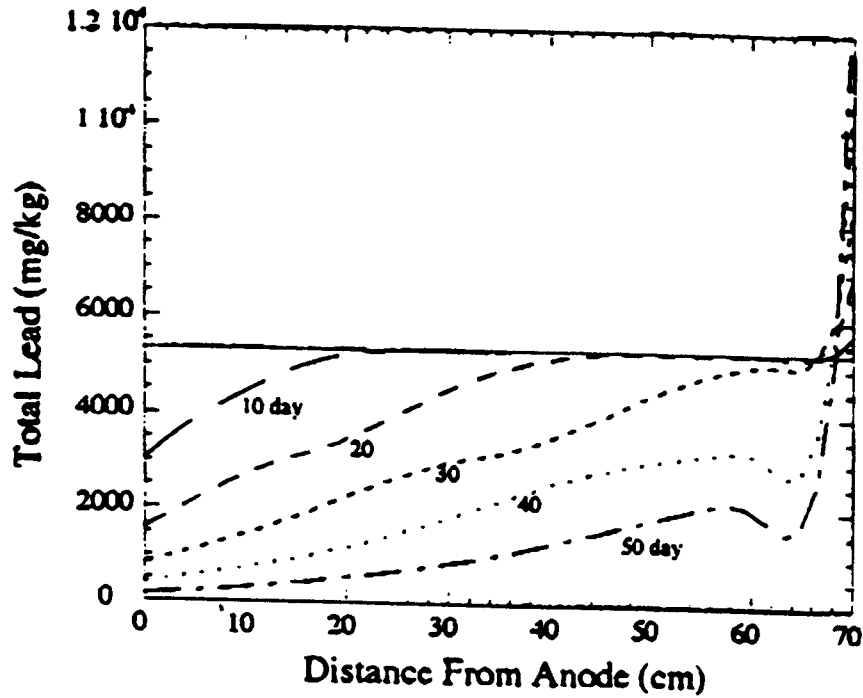
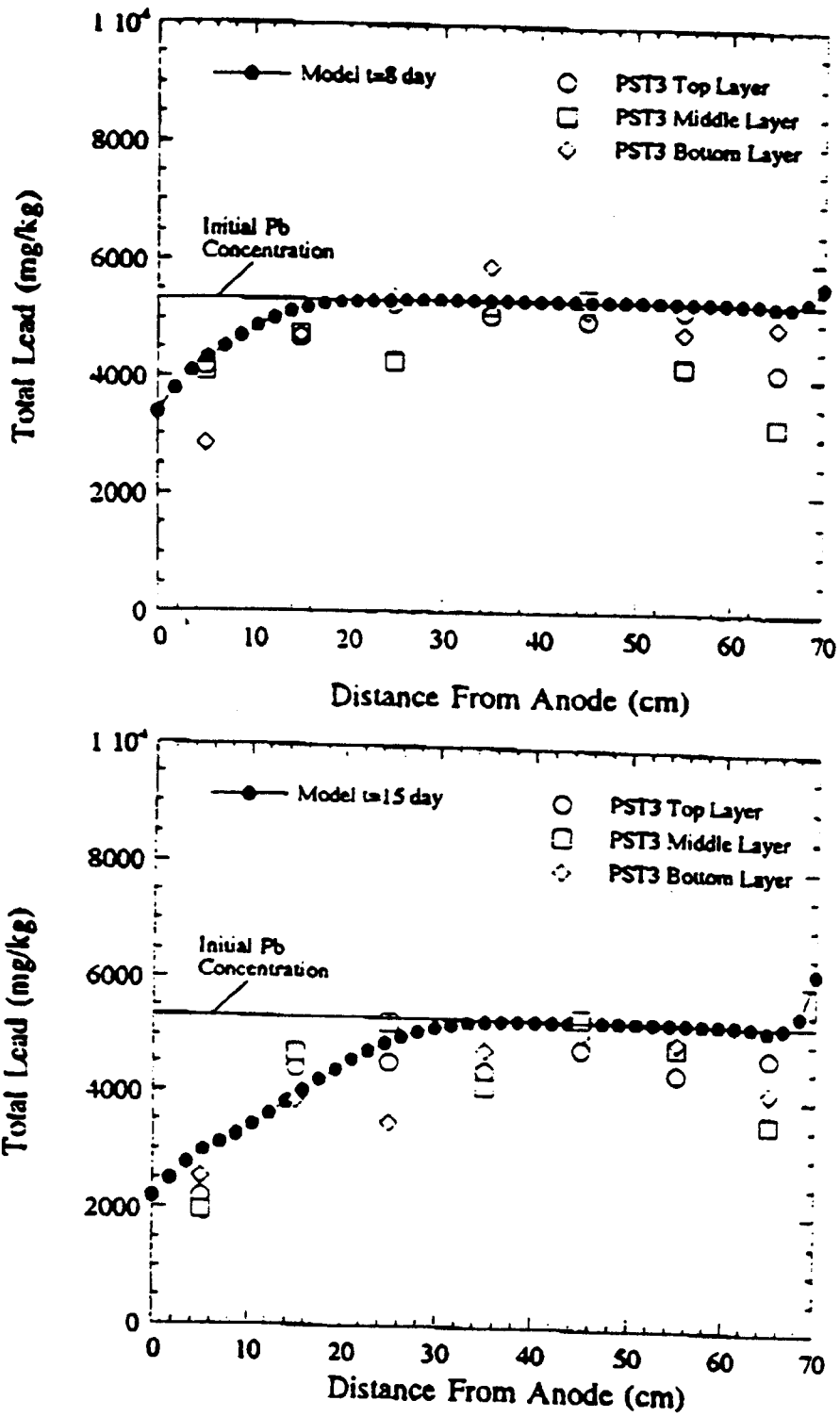


Figure 4-2. Comparison of lead profile predicted by the FEM-MSTEF with those measured in the pilot-scale study (3,5).



electro deposition, membrane separation, or ion exchange. Acar and Alshawabkeh (1) discuss the need for enhancement and propose different enhancement techniques to prevent the encountered precipitation. The solubility of the species by the anodic acid and the migration under electrical fields are important considerations in electrokinetic remediation. The most soluble species will come out in solution first and be transported towards the respective electrode.

Although the acetic acid depolarization technique is successfully being used in the remediation of lead, chromium, zinc and other heavy metals from soils in the US and Europe, the technique generates significant amounts of liquid requiring secondary processing. Electrokinetics Inc. has developed an electrode system (CADEX(TM)) that promotes electrodeposition of the species and minimizes the need for secondary processing.

In collaboration with the US Army Waterways Experiment Station, Electrokinetics Inc. is currently conducting a field-scale demonstration study at Fort Polk, Louisiana. The site is located in a creek bed. The surface deposits within the first two feet are contaminated with lead at concentrations of 3,500 mg/ kg (+/- 500 mg/kg). The lead in the deposits leached from the bullets in a firing range from years of exposure to the environment. Preliminary chemical speciation and corrosion studies indicate that minute quantities of lead leach from the individual particulates and the contamination is mainly due to the quantity of the bullets left at the site. An area of about 2,000 ft<sup>2</sup> is being processed. CADEX(TM) electrode system is being used for the project. Onsite remediation is expected to continue for about six months to a year, with a goal of attaining levels of 100 mg/kg or less across the site. USEPA will conduct an independent evaluation of the demonstration study through the SITE program.

#### **4.2 Electrokinetic Remediation of Chromium at Sandia Laboratories- Field Study**

The Chemical Waste Landfill (CWL) was a chemical disposal site for Sandia National Laboratories in Albuquerque, New Mexico from 1962 to 1985. During this time, chemicals were separated by type and disposed in unlined trenches. It is estimated that over 4290 gallons of chromic sulfuric acid solution was disposed into unlined chromic acid pits. The chromium was disposed in hexavalent form. The very low organic fraction present in the native soil suggests that the chromium should remain in the hexavalent form. This anionic hexavalent chromium adsorbs weakly to the soil beneath the landfill, resulting in a mobile contaminant that has apparently migrated to a depth of at least 23 meters below the ground surface (15).

An electrokinetic process was demonstrated in one of these unlined chromic acid pits during the summer and fall of 1996. The purpose of the demonstration was to show that an electrokinetic process could be used to extract chromate contamination from in situ unsaturated soils without significantly altering the soil moisture content. The treatment zone was located in a 3.7 meter

square over the area exhibiting the greatest degree of contamination (see Figure 3 on the following page).

The electrode layout and spacing were chosen to produce as uniform (or planar) an electric field as possible while minimizing the effects of soil heating. The active treatment horizon was 1.8 meters thick, placed at 2.4 to 4.3 meters below the surface. A total of fifteen electrodes were installed for the demonstration. During the installation of the electrodes, numerous soil samples were collected to characterize the site. One row of five anodes were placed in the center of the pit, and two rows of five cathodes were placed six feet to the north and south of the row of anodes near the edge of the chromate plume.

The electrode assemblies used are a unique, patented design using porous ceramic casings filled with electrolyte solution in which a drive electrode is deployed. The electrolyte solution is held under tension inside the porous ceramic housing by an applied vacuum which prevents saturation of the adjacent soil. Application of an electric potential to the electrodes causes chromate anions in the soil porewater to migrate toward the anode electrode assemblies. The chromate migrates through the porous ceramic into the electrolyte solution. During operation, a small amount of the electrolyte solution is periodically pumped out of the anode assembly and into waste barrels. This effluent stream is sampled and analyzed to determine the concentration and removal rate of chromate.

The soil samples collected during electrode casing installation were extracted with deionized water. The water mass to soil mass ratio was 2:1. The soil water mixture was shaken for one hour and allowed to settle. Supernate was recovered and passed through a 0.45  $\mu\text{m}$  filter. The pH and electrical conductivity of the extract was measured and the chromate concentration was determined spectrophotometrically by the highly sensitive and selective diphenylcarbazide method. Samples from the effluent of each electrode assembly were collected daily and the amount of effluent removed from each electrode was monitored. The pH and electrical conductivity of the aqueous samples was measured and the chromate concentration was determined spectrophotometrically by the same diphenylcarbazide method. The electrical current passed through each electrode was measured and datalogged.

In Figure 4-4, the transference number of chromate in the effluent of each of the five anodes is plotted against time for the first 100 hours of the demonstration. In Figure 4-5, the cumulative charge of chromate removed (in coulombs) from each anode is plotted against the cumulative electrical charge (in amp-hours) passed through each anode. The transference number for chromate is the slope of these curves. Both figures are found on the following pages.

Figure 4-3. Plan view and cross-sectional view of field demonstration layout.

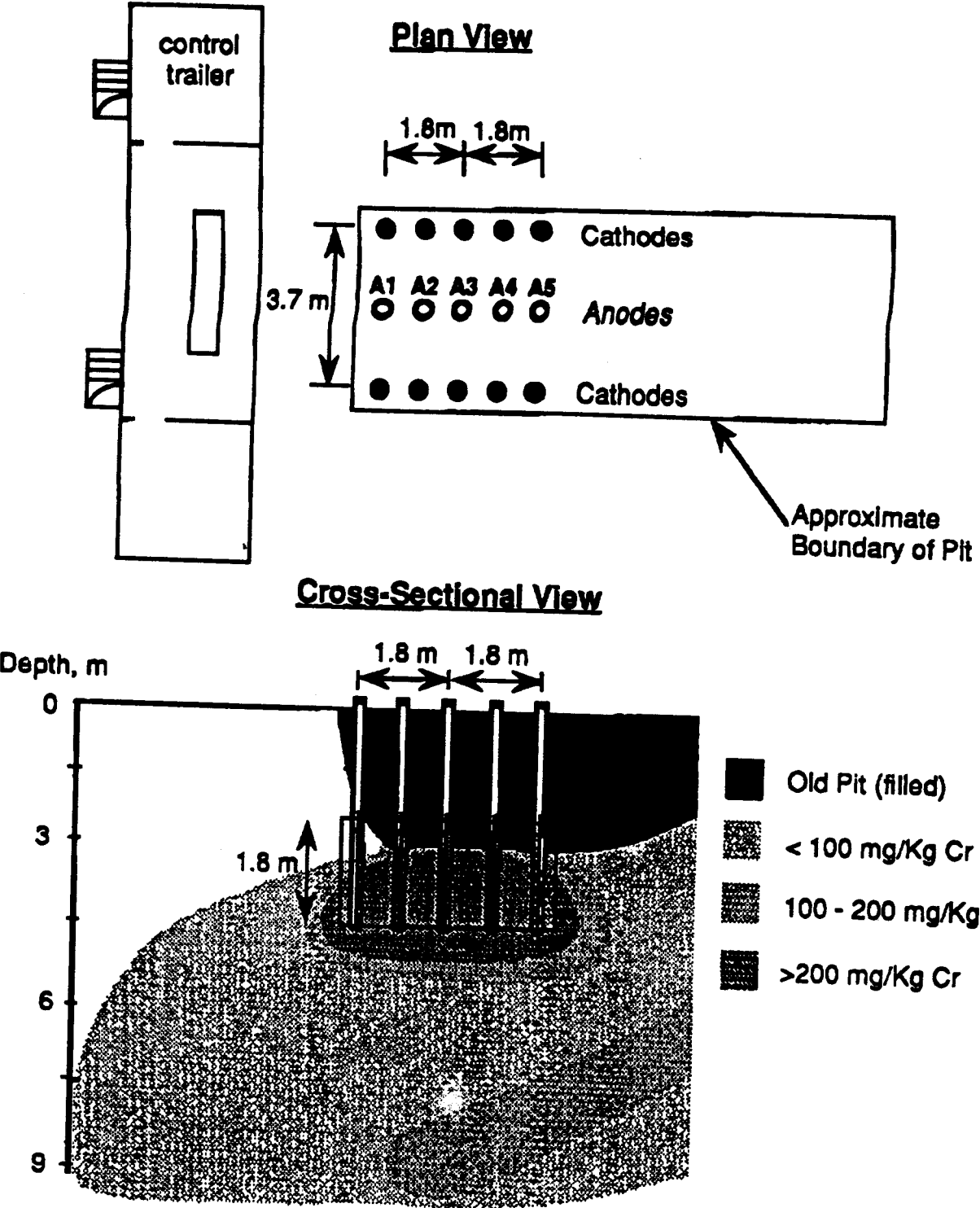


Figure 4-4. Percent transference of chromate in each anode for first 100 hours of operation

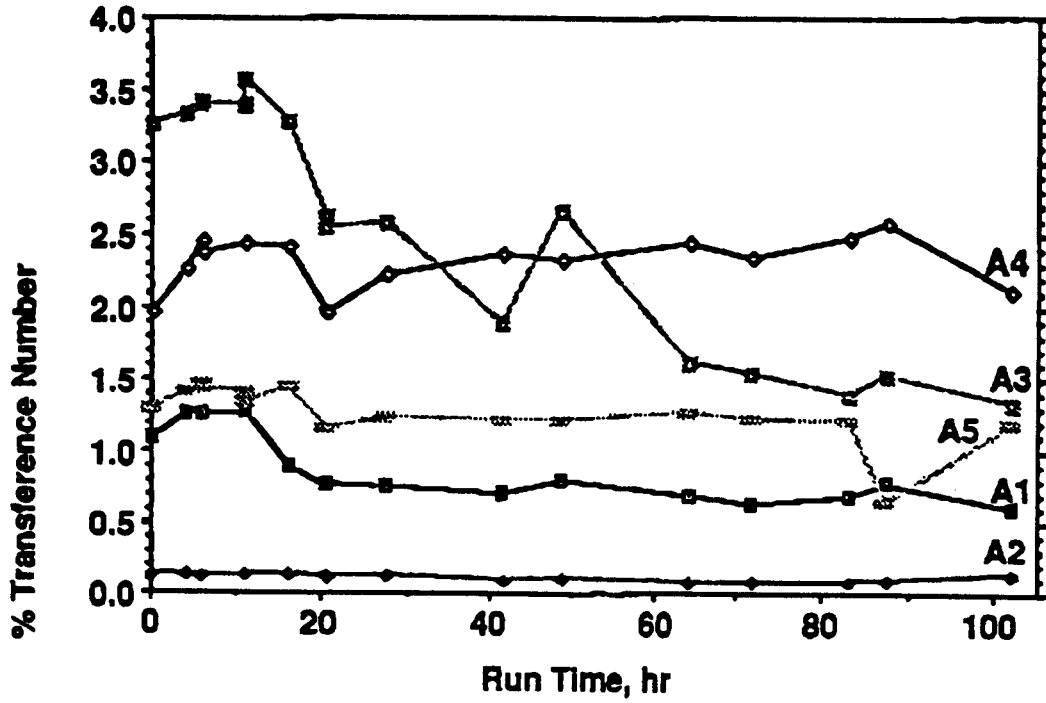
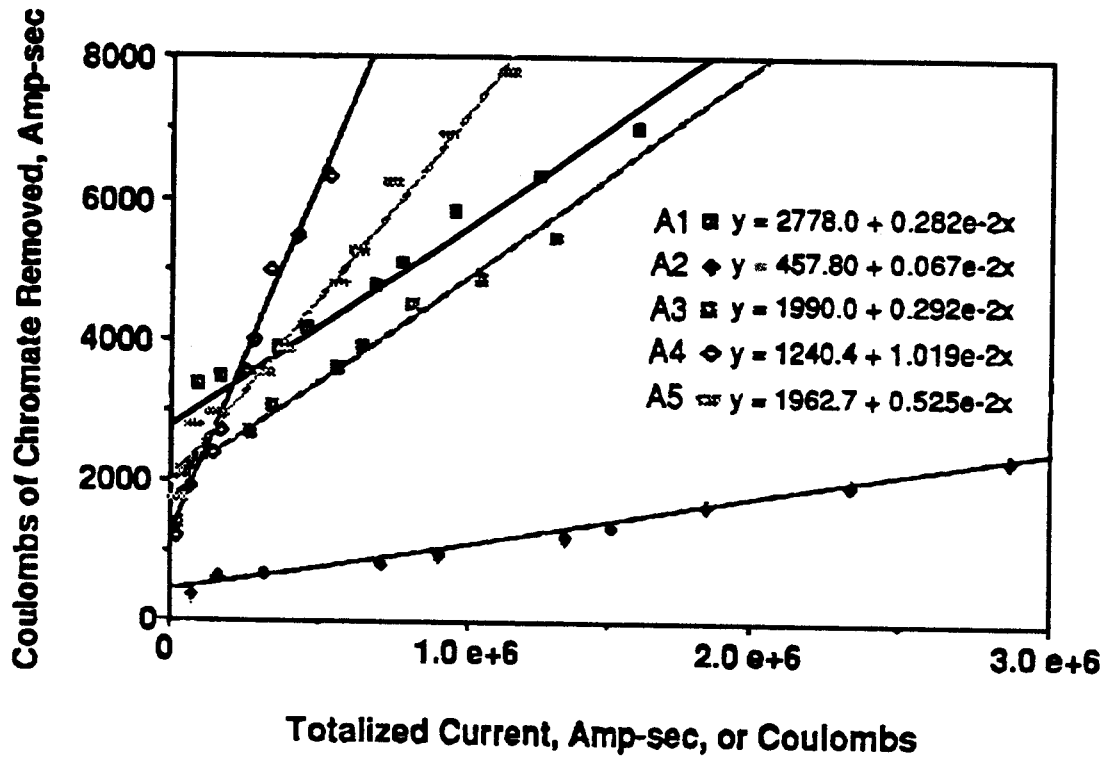


Figure 4-5. Coulombs of charge associated with the chromate removed from each anode versus the total coulombs of charge applied to the anode for first 100 hours of operation



measured in deionized water extracts of soil samples collected from between 2.4 and 4.3 meter depths in the boreholes drilled for each of the five anodes. Also presented in Table 4-1 are the steady-state, conductivity-based, chromate transference numbers for each anode from Figure 4-4, and the current-based chromate transference numbers for each anode from Figure 4-5.

**Table 4-1**  
**Chromate Transference Numbers (%) in Soil and Anode Effluent Samples From the First 100 Hours of Operation**

Anode	Pre-test Soil Extract conductivity-based	Anode Effluent conductivity-based	Anode Effluent current-based
A1	1.04%	0.70%	0.28%
A2	0.13	0.15	0.07
A3	2.40	1.50	0.30
A4	2.50	2.50	1.02
A5	4.00	1.25	0.53

The conductivity-based chromate transference numbers from the pre-test soil extracts ranged from 0.13% to 4.0%. This would indicate that anode 5 should extract chromate most efficiently, followed by anodes 4 and 3. Anode 2 should extract chromate least efficiently. The conductivity-based chromate transference numbers in the effluent from each anode quantitatively compare with the soil extract transference numbers (with the exception of anode 5). In initial operation, anode 4 extracted chromate most efficiently and at the level predicted by the pre-test analysis, while anode 2 extracted chromate least efficiently at the level predicted. Deviation of the transference numbers of the anode effluent from the soil extract can be expected due to the heterogeneity of the chromate contamination. The two should only agree well to the extent that the soil samples represent the soil through which the electrical current is flowing. This appears to be the case for anodes 2 and 4 but not for anode 5. The good overall agreement is encouraging because it suggests a strong tie between a simple characterization method and the performance of the electrokinetic extraction process.

While there is quantitative agreement between the conductivity-based chromate transference numbers in the soil extract and anode effluent, both are expected to significantly overestimate the true chromate transference. The current-based chromate transference should provide a lower, more accurate assessment. As demonstrated in the last column of Table 4-1, the values are generally 55 to 60% lower than the conductivity-based values.

## 5.0 REGULATORY ISSUES RELATED TO ELECTROKINETICS

From a regulatory viewpoint, the following concerns need to be addressed:

- **What is an acceptable time frame for clean-up?**

Electrokinetic technologies may take longer than conventional technologies due to the fact that as target levels become low (<100 mg/kg), the operational efficiency of the technology decreases. The technology may be most applicable at sites where long term remediation is being considered.

- **How will confirmatory sampling be conducted due to the nature of the technology?**

Application of electrokinetics may result in residual pockets of contamination in close proximity to soils that have been completely remediated. Contaminant concentrations may fluctuate widely across extremely small distances (centimeters). As such, sample locations and frequencies must be chosen carefully and conservatively.

- **What long and short term impacts may be imposed on the site and surrounding environment?**

There is some concern about the condition of site soils once remediation is complete. Regulators are concerned that soil may not be able to sustain growth due to the chemical, physiological and biological impacts on soil media due to the application of electrical currents. The technology may be more applicable at industrial sites where the concerns noted above may not be an issue.

- **To what extent do site heterogeneities affect efficiency rates? How can these anomalies be assessed by regulators?**

Electrokinetic technologies work best at sites with homogeneous soils and contamination. Hot spots may pose a problem, as with nearly any remedial technology. Areas with no contamination may also be of concern, due to the creation of “dead zones” where transference does not occur. A large degree of small-scale site characterization may be needed to address system design and compliance sampling issues.

- **Prolonged application of direct current can significantly modify soil properties. Will acidic fronts at the anodes or strong basic conditions at the cathodes be created?**

If soils are left in place after remediation, either of the situations mentioned above may occur. If

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the metals are removed below the threshold limit but the pH of the residual soils is either very low or very high, RCRA waste restrictions may still apply. The application and design of the system must take this into account.

- **Most of the time, soils near cathodes will be excavated (or groundwater will need to be disposed of). Will soils near anodes have to be excavated as well (and/or groundwater re-circulated)?**

While this is largely an engineering concern, regulators and problem holders must be aware of the need for removal of the contaminants through either groundwater recirculation or excavation. The final waste stream will need to be disposed in accordance with applicable regulations.

The ITRC plans to monitor the development of this technology and address these and other regulatory issues in a "Technical and Regulatory Guidance" document, for deployment of electrokinetics technologies.

## 6.0 COST

The cost of electrokinetic remediation is dependent on specific chemical and hydraulic properties of soils present at the site. Ongoing pilot-scale field studies indicate that the energy consumption in extracting heavy metals from soils may be approximately 500 kW-hr / m<sup>3</sup> or more at an electrode spacing of 1.0-1.5 m. The direct cost would be approximately \$25 / m<sup>3</sup>, or about \$0.05 / kW-hr, at this level of energy consumption. The energy consumption rate can be lowered significantly if cathodic depolarization techniques are used since no low conductivity zone would be formed around the cathode compartment (Acar et al., 1993). The total power consumed is directly proportional to the time required for migration to achieve the cleanup level desired. A typical migration rate would be approximately 2.5 cm per day. For an electrode spacing of 2 to 3 m, the corresponding time frame for remediation would be approximately 100 days. An estimated price range per unit of soil treated is given as follows:

Electro-Petroleum, Inc.	\$60-\$110 per yd <sup>3</sup> (faxed information)
Dupont R&D	\$65 per yd <sup>3</sup>
Electrokinetics, Inc.	\$20-\$100 per yd <sup>3</sup>
Geokinetics International	\$75-\$225 per yd <sup>3</sup>

Price estimates do not always include indirect costs associated with remediation, such as excavation, permits, and treatment of residues. Price comparisons should be based on comparable sites and scopes of remediation activities for each vendor. Factors which have a significant effect

on unit price are:

- Initial and target contaminant concentrations
- Concentration of non-target ions, or conductivity of pore water
- Soil characteristics and moisture content
- Quantity of waste
- Depth of contamination
- Residual waste handling and processing
- Site preparation requirements
- Electricity and labor rates

## **7.0 PUBLIC AND STAKEHOLDER CONCERNS**

Electrokinetics shows promise as a potentially effective technology for the remediation of metal contaminated soils. Because electrokinetics is an in-situ technology which requires relatively little site disturbance and limited use of heavy equipment for excavation and off-site disposal of soil, it is expected to meet with positive response from responsible parties and community stakeholders associated with specific sites. Electrokinetic methods have a relatively long research history (since the 1930s), and have been investigated for contaminant application since the early to mid 1980s. It is important to note, however, that there are still many questions on the technology being addressed by researchers and regulatory agencies

Electrokinetics' applicability can often be site-specific and may pose concerns pertaining to the mobility of compounds, metals and contaminants present. For public or community stakeholders, the addition of water in unsaturated soils might be a concern due to the potential of hydraulically washing contaminants out of the capture zone. An unsaturated soil extraction electrode system may need to be designed to minimize this problem.

Secondary impacts of treatments or mechanical processes used in support of electrokinetic methods must be disclosed during all stages of project development and mitigated to the greatest degree. For example:

- What are the potential impacts of materials used in electroplating or ion exchange?
- What energy sources are being used, and what impact will they have on the environment?

Technology developers must address these and other concerns, to maximize the range of sites where electrokinetics technologies may be used.

## 8.0 CONCLUSIONS

Electrokinetic extraction of metals from soils has undergone bench-scale testing and pilot-scale testing. A theoretical model has been developed and its numerical implementation has been completed. The predictions of this model compared with the results of the pilot-scale studies demonstrate that the principles of the technique have been well rationalized. Currently, the model is being generalized and additional information is being incorporated. Construction guidelines will be written upon completion of the field studies. When cost-effectiveness and technical feasibility of other remedial options prohibit their use, electrokinetic remediation may offer an alternative at sites contaminated with inorganic species. The technique also is in the process of being scrutinized and developed for injection, specifically to enhance the in-situ bioremediation of organic species through injection of process additives, nutrients and microorganisms.

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# **APPENDIX A**

## **Acronyms**

## ACRONYMS

CEC	Cation Exchange Capacity
CWL	Chemical Waste Landfill
DC	Direct Current
FEM-MTSE	Finite Element Model for Multi-Species Transport in Soils under Electrical Fields
IINERT	In-Place Inactivation and Natural Ecological Restoration Technologies
ITRC	Interstate Technology and Regulatory Cooperation Working Group
LA	State of Louisiana
mg/kg	milligrams per kilogram
RCRA	Resource Conservation and Recovery Act
RMIES	RMI Environmental Services, Inc.
RTDF	Remediation Technologies Development Forum
USEPA	United States Environmental Protection Agency

## **APPENDIX B**

**ITRC Work Team Contacts**  
**ITRC Fact Sheet**  
**Product Information**  
**User Survey**

## **ITRC METALS IN SOILS TEAM PROJECT CONTACTS**

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# **APPENDIX C**

## **Case Study**

**ELECTROKINETIC DEMONSTRATION AT  
SANDIA NATIONAL LABORATORIES:  
USE OF TRANSFERENCE NUMBERS FOR SITE  
CHARACTERIZATION AND PROCESS EVALUATION**

This work was performed at Sandia National Laboratories, which is operated for the U.S. Department of Energy  
under Contract No. DE-AC04-94AL85000

**Presented at:**

**The Waste Management Conference**

**Tucson, Arizona**

**March, 1997**

# Electrokinetic Demonstration at Sandia National Laboratories: Use of Transference Numbers for Site Characterization and Process Evaluation\*

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## ABSTRACT

Electrokinetic remediation is generally an *in situ* method using direct current electric potentials to move ionic contaminants and/or water to collection electrodes. The method has been extensively studied for application in saturated clayey soils. Over the past few years, an electrokinetic extraction method specific for sandy, unsaturated soils has been developed and patented by Sandia National Laboratories. A RCRA RD&D permitted demonstration of this technology for the *in situ* removal of chromate contamination from unsaturated soils in a former chromic acid disposal pit was operated during the summer and fall of 1996. This large scale field test represents the first use of electrokinetics for the removal of heavy metal contamination from unsaturated soils in the United States and is part of the US EPA Superfund Innovative Technology Evaluation (SITE) Program.

Guidelines for characterizing a site for electrokinetic remediation are lacking, especially for applications in unsaturated soil. The transference number of an ion is the fraction of the current carried by that ion in an electric field and represents the best measure of contaminant removal efficiency in most electrokinetic remediation processes. In this paper we compare the transference number of chromate initially present in the contaminated unsaturated soil, with the transference number in the electrokinetic process effluent to demonstrate the utility of evaluating this parameter.

## INTRODUCTION

Heavy metal contamination of soils and ground water is a widespread problem at EPA Superfund sites, DOE-operated sites, and privately-owned facilities throughout the nation. Currently, the only available method for remediating heavy-metal contaminated soil is by excavation followed by soil washing or relocation. One possible technique for *in-situ* removal of such contaminants is through the use of electrokinetics. To conduct electrokinetic remediation, electrodes are implanted into the ground and a direct current is imposed between the electrodes. Metal ions migrate toward an electrode where they can be removed.

Methodologies for evaluating a site for electrokinetic remediation and designing an approach with associated predictions of cleanup level, remediation time, and cost are not well established. The design problem should be considered in two parts. First, an estimate of the total amount of electrical current required must be made. This will require knowing not only the mass of contaminant to be removed, but also the efficiency of current usage or transference number which depends primarily on the chemical nature of the contamination problem. Secondly, a determination must be made of how the current will be applied over what time period. This requires additional physical knowledge of the site such as contaminant plume geometry, soil resistivity and expected temperature changes which when coupled with the electrode layout determines the voltage and electrical power requirements.

\* This work was performed at Sandia National Laboratories which is operated for the U.S. Department of Energy under Contract No. DE-AC04-94AL85000 and funded by DOE/OST through the Subsurface Contaminant Focus Area.

The scope of this paper is to discuss methods for estimating the transference number of chromate in unsaturated soil and make comparisons with the chromate transference number realized in a large scale electrokinetic extraction process. The methodology should be useful for characterizing electrokinetic remediation of any water soluble ionic contaminant from saturated or unsaturated soil. Water soluble heavy metal contaminants are typically oxyanions such as chromate. Other heavy metals which can exist as water soluble oxyanions include arsenic, molybdenum, selenium, technetium and uranium. Some heavy metal contaminants, such as lead, mercury or plutonium, typically exist in soil as a precipitated solid phase. Such contaminants must first be dissolved into the porewater before removal by an electric field is possible. The current efficiency for this case depends additionally on the dissolution process and is therefore more complicated to determine.

## BACKGROUND

### Field Demonstration

The Chemical Waste Landfill was the chemical disposal site for Sandia National Laboratories in Albuquerque New Mexico from 1962 to 1985. During this time, chemicals were separated by type and disposed in unlined trenches. It is estimated that over 4290 gallons of chromic sulfuric acid solution were disposed into unlined chromic acid pits. The chromium was disposed in the form of hexavalent chromium and the very low organic fraction present in the native soil suggests the chromium should stay in the hexavalent form. Such anionic hexavalent chromium adsorbs weakly to soil beneath the CWL (1). Thus, in its present form, the chromium is mobile in the environment and has apparently migrated to a depth of at least 23 meters below the ground surface.

An electrokinetic process was demonstrated in one of these unlined chromic acid pits during the summer and fall of 1996. The purpose of the demonstration was to show that an electrokinetic process could be used to extract chromate contamination from *in situ* unsaturated soils without significantly altering the soil moisture content. The treatment zone of the electrokinetic field demonstration was located in a 3.7 meter by 3.7 meter area over the most highly contaminated known area (see Figure 1). The electrode layout and spacing were chosen to produce as uniform (or planar) an electric field as practical while minimizing soil heating effects. The active treatment horizon was 1.8 meters thick and placed at 2.4 to 4.3 meters below the surface where the greatest amount of contamination was located. A total of fifteen electrodes were installed for the demonstration. During the installation of the electrodes numerous soil samples were collected to characterize the site. One row of five anodes were placed in the center of the pit. Two rows of five cathodes were placed six feet north and six feet south of the row of anodes near the edge of the chromate plume.

The electrode assemblies used are a unique, patented design (2,3) which uses porous ceramic casings filled with electrolyte solution in which a drive electrode is deployed. The electrolyte solution is held under tension inside the porous ceramic housing by an applied vacuum which prevents saturation of the adjacent soil. Application of an electric potential to the electrodes cause chromate anions in the soil porewater to migrate toward the anode electrode assemblies. The chromate migrates through the porous ceramic into the electrolyte solution. A small amount of the electrolyte solution is periodically pumped out of the anode assembly and into waste barrels. This effluent stream was sampled and analyzed daily to determine the concentration and removal rate of chromate.

### Transference Numbers

The fraction of current carried by a particular ionic species in response to an electric field is defined as the transference number (sometimes called the transport number) (4,5):

$$T_i = I_i / I_{\text{total}} = i_i / i_{\text{total}} \quad (1)$$

where:  $T_i$  is the transference number for species  $i$ , unitless  
 $I_i$  is the current carried by species  $i$ , amps or C/s  
 $I_{tot}$  is the total current, amps or C/s  
 $i_i$  is the current density carried by species  $i$ , amps/m<sup>2</sup>  
 $i_{tot}$  is the total current density, amps/m<sup>2</sup>

From dimensional analysis it is evident that the transference number is also the fraction of the charge of species  $i$  transfers in a given time period:

$$T_i = \text{Charge}_i / \text{Charge}_{tot} \quad (2)$$

where:  $\text{Charge}_i$  is the charge carried by species  $i$  over a given time period, C  
 $\text{Charge}_{tot}$  is the total charge for the same time period, C

Considering the electrokinetic extraction system where current is passed through the electrode at a constant rate and effluent is extracted at a constant rate, Eqn. (2) may be evaluated:

$$T_i = c_i V z_i F / I_{tot} t \quad (3)$$

where:  $c_i$  is the concentration of species  $i$ , mol/m<sup>3</sup>  
 $z_i$  is the charge of ionic species  $i$ , unitless  
 $F$  is Faraday's Constant, 96500 C/mol  
 $V$  is the volume extracted in time  $t$ , m<sup>3</sup>  
 $t$  is the given time period, s

The differential form of Ohm's Law can be expressed as:

$$i = \sigma d\phi/dx \quad (4)$$

where:  $d\phi/dx$  is the voltage gradient, volts/m  
 $\sigma$  is the electrical conductivity, S/m  
 $i$  is the current density, amps/m<sup>2</sup>

From Eqns. (1) and (4) it is evident that the transference number is also equal to the ratio of the electrical conductivity of the particular ion and the conductivity of the bulk solution:

$$T_i = \sigma_i / \sigma_{tot} \quad (5)$$

where:  $\sigma_i$  is the electrical conductivity of species  $i$ , S/m  
 $\sigma_{tot}$  is the electrical conductivity of the bulk solution, S/m

The electrical conductivity of the bulk solution can be easily measured directly with a conductivity meter. The electrical conductivity of species  $i$  can be estimated from the measured concentration of species  $i$  and the equivalent ionic conductivity extrapolated to infinite dilution which is tabulated in many reference books (6):

$$\sigma_i \approx c_i \Lambda_{0i} \quad (6)$$

where:  $c_i$  is the concentration of species  $i$ , mol/m<sup>3</sup>  
 $\Lambda_{0i}$  is the equivalent ionic conductivity of species  $i$  extrapolated to infinite dilution, m<sup>2</sup> S/mol

Eqn (5) then becomes:

$$T_1 = c_1 \Lambda_0 / \sigma_{\text{sol}} \quad (7)$$

Using the estimate of  $\sigma_1$  provides an upper limit estimate of  $t_1$  because the equivalent ionic conductivity is greatest at infinite dilution and decreases as the concentration increases. For solutions with ionic strengths of 0.1M or higher, decreases of 20 to 50% can be expected.

## EXPERIMENTAL

The soil samples collected during electrode casing installation were extracted with deionized water. The water mass to soil mass ratio used was 2:1. The soil water mixture was shaken for one hour and allowed to settle. Supernate was recovered and passed through a 0.45  $\mu\text{m}$  filter. The pH and electrical conductivity of the extract was measured and the chromate concentration was determined spectrophotometrically by the highly sensitive and selective diphenylcarbazide method. (7)

Samples from the effluent of each electrode assembly were collected daily and the amount of effluent removed from each electrode was monitored. The pH and electrical conductivity of these aqueous samples was measured and the chromate concentration was determined spectrophotometrically by the same diphenylcarbazide method. The electrical current passed through each electrode was measured and datalogged.

## RESULTS

In Figure 2, the transference number of chromate in the effluent of each of the five anodes is plotted against time for the first 100 hours of the demonstration. The transference numbers were evaluated using Eqn. (7).

In Figure 3, the cumulative charge of chromate removed (in coulombs) from each anode is plotted against the cumulative electrical charge (in amp-hours) passed through each anode. From Eqn (3), the transference number for chromate is the slope of these curves.

The average chromate transference number measured in the deionized water extracts of soil samples collected from 2.4 to 4.3 meter depths in the boreholes drilled for each of the five anodes are presented in Table I. The transference numbers were calculated using Eqn. (7). Also presented in Table I are the steady-state, conductivity based, chromate transference numbers for each anode from Figure 2 and the current based chromate transference numbers for each anode from Figure 3.

Table I Chromate transference numbers (as percent) in soil and anode effluent samples from the first 100 hours.

Anode	Pre-test Soil Extract conductivity based	Anode Effluent conductivity based	Anode Effluent current based
A1	1.04%	0.70%	0.28%
A2	0.13	0.15	0.07
A3	2.40	1.50	0.30
A4	2.50	2.50	1.02
A5	4.00	1.25	0.53

## DISCUSSION

As presented in Table I, the conductivity based chromate transference numbers from the pre-test soil extracts ranged from 0.13% to 4.0%. This characterization would indicate that anode 5 should extract chromate most efficiently, followed by anodes 4 and 3. Anode 2 should extract chromate least efficiently. The conductivity based chromate transference numbers in the effluent from each anode quantitatively compare with the soil extract transference numbers (with the exception of anode 5). In initial operation, anode 4 extracted chromate most efficiently and at the level predicted by the pre-test analysis while anode 2 extracted chromate least efficiently at the level predicted by the pre-test analysis. Deviation of the transference numbers of the anode effluent from the soil extract can be expected due to the heterogeneity of the chromate contamination. The two should only agree well to the extent the soil samples represent the soil through which the electrical current is flowing. This appears to be the case for anodes 2 and 4 but not anode 5. However, the overall good agreement is encouraging because there seems to be a strong tie between this simple characterization method and the performance of the electrokinetic extraction process.

While there is quantitative agreement between the conductivity based chromate transference numbers in the soil extract and anode effluent, both are expected to significantly overestimate the true chromate transference. The current based chromate transference should provide a lower, more accurate assessment and as presented in the last column of Table I, the values are generally 55 to 60% lower than the conductivity based chromate transference numbers. This is just a bit lower than expected from the concentration dependence of the equivalent ionic conductivity used in Eqn. (7).

## CONCLUSIONS

The conductivity based chromate transference numbers from the pre-test soil extracts are in good agreement with the conductivity based chromate transference numbers in the effluent from each anode suggesting that the simple characterization method used provides valuable performance predictions. As expected, the theoretically more accurate current based chromate transference numbers were 55 to 60% lower than the conductivity based values. Methods for accounting for the concentration dependence of the equivalent ionic conductivity in complex ionic mixtures required to more accurately predict the actual electrokinetic extraction performance are presently under development.

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