ELECTROKINETICS FOR REMOVAL OF LOW-LEVEL RADIOACTIVITY FROM SOIL

by

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ABSTRACT

The electrokinetic process is an emerging technology for in situ soil decontamination, in which chemical species, both ionic and nonionic are transported to an electrode site in soil. These products are subsequently removed from the ground via collection systems engineered for each specific application. Electrokinetics refer to movement of water, ions and charged particles relative to one another under the action of an applied direct current electric field. In a porous compact matrix of surface charged particles such as soil, the ion containing pore fluid may be made to flow to collection sites under the applied field. The process was demonstrated in the laboratory to show the viability of the electrokinetic treatment to move "contamination" through soil types of hydraulic conductivity as low as $10^{-6}$ cm/s to a directed location.

The work presented here describes part of the effort undertaken to investigate electrokinetically enhanced transport of soil contaminants in synthetic systems. These systems consisted of clay or clay-sand mixtures containing known concentration of a selected heavy metal salt solution. These metals included surrogate radionuclides such as Sr, Cs and U, and an anionic species of Cr. Degree of removal of these metals from soil by the electrokinetic treatment process was assessed through the metal concentration profiles generated across the soil between the electrodes. Removals of some metal species up to 99% were achieved at the anode or cathode end of the soil upon 24 to 48 hours of treatment or a maximum of 1 pore volume of water displacement toward the cathode compartment. Transient pH change through the soil had an effect on the metal movement as evidenced by accumulation of the metals at the discharge ends of the soil specimens. This accumulation was attributed to the precipitation of the metal and increased cation retention capacity of the clay in high pH environment at the cathode end. In general, the reduced mobility and dissociation of the ionic species as they encounter areas of higher ionic concentration in their path of migration resulted in the accumulation of the metals at the discharge ends of the soil specimens.

The results of the laboratory study presented here indicate that electrokinetic enhancement of contaminant transport in soils is a viable technology of soil decontamination. The development of this technology for wide range of applications hinges upon better understanding of the transient chemical and physical processes during application of current through soil/contaminant systems. The testing has clarified the need for site specific design and control of the treatment operation so that once the contaminant is mobilized, it is kept in motion until transported out of the soil to a collection system in the most efficient manner. Chemical (pH control, complexing agents, etc.) and physical enhancement methods may be necessary in some situations to accomplish this goal.
INTRODUCTION

Electrokinetically enhanced transport of contaminants is perhaps one of the most promising \textit{in situ} decontamination processes capable of removing heavy metals and organic contaminants from soils, sludges and lagoons feasibly. The significance of the technology appears to be in its projected low operation cost and its potential applicability to a wide range of contamination situations. It is also viewed by researchers and industry as potential "problem solver" when all else appear non-workable or fail to remediate a site. Present day urgency to develop feasible technologies to cleanup soils and groundwater makes it germane to spend the time and effort necessary to look at the fundamental mechanisms associated with the technology and to develop it into a well-engineered and reasonably predictable process for field applications.

In this work, successful application of the technique was demonstrated on pure soil-contaminant-mixtures in the laboratory. The results of the work presented here also indicated that, further development of the technology for a wide range of applications in the field hinges upon the better understanding of the transient processes during application of a DC current through soil. Some of these processes, such as net electroosmotic water flux and transient acid-base distributions, have been studied in the past and were confirmed in this study. The simultaneous interactions between different transient and physical processes that may take place in a complex system of soil, water and contaminant are discussed. These processes have been identified as the physical and chemical interactions between soil components and the contaminants; soil surface physico-chemistry and its variation with pore fluid chemistry; speciation and distribution of the contaminants.

A study of 5 soil types with 11 heavy metal elements and 6 organic compounds, confirmed that electrokinetic treatment of soils is a promising decontamination process that is capable of removing contaminants from clayey soils. The degree of success of decontamination appeared to be parameter specific, more dependent on the type of the contaminant to be removed than the type of the medium contaminated. Those contaminants whose chemistry were least affected by the transient chemical and physical processes during electrokinetics exhibited a significantly higher degree of removal than those that were affected. This trend was consistent despite the variations in soil type and properties. The contaminant levels selected in this program were typical of levels to be found at various DOE sites. The results of the full laboratory investigation can be found in other publications (Pamukcu and Wittie, 1992 and Wittie and Pamukcu, 1993). This paper deals with the radioactive cationic species of general interest: uranium, strontium and cesium. In addition, experimental results for chromium are presented as an example of migratory trend of an anionic species for comparison.
BACKGROUND

Historical Development of Electroosmosis Theory in Soils

Electroosmotic phenomenon was first discovered by Reuses in 1808. The phenomenon was first treated analytically by Helmholtz in 1879, which later was modified by Pellat in 1904 and Smoluchowski in 1921. This theory is widely known as Helmholtz-Smoluchowski (H-S) theory which relates electroosmotic velocity of a fluid of certain viscosity and di-electric constant, through a surface charged porous medium of electrokinetic potential, \( \zeta \) (zeta potential), under an electric gradient. The theoretical computation of electroosmotic water transport, by this theory does not always agree well with experimental observations. The electrokinetic potential term in the H-S theory varies with pH and ionic concentration of the pore fluid, which is not a constant during electrokinetic treatment. Similarly, electric gradient is not constant in time and space due to the changing resistivity and oxidation/reduction state of the soil and also the aqueous solution near the electrodes.

A notable approach to electrokinetic process in porous medium was made by Spiegler (1958). He considered the interactions of the mobile components of soil (water and ions) on each other and the frictional interactions of these components with the pore walls. The true electroosmotic flow was expressed as the difference between the measured water transport and the ion hydration in moles per Faraday. This quantity was suggested to be directly proportional to concentration of free water in the soil pores and indirectly proportional to the concentration of mobile counterions in moles per volume. This suggested the phenomenon of water transport in the opposite direction of electroosmotic flow by the electromigration of the anions. Therefore, at any time during electrokinetic treatment, if the concentration of anionic species in the free water exceeds the cationic species, the opposite flow may retard the net water flow toward the cathode.

Gray and Mitchell (1967) showed experimentally that the electroosmotic flow increases with increasing water content of most soils, however decreases with increasing electrolyte concentration of the pore fluid. This electrolyte concentration effect is more evident in clays with high anion retention capacity, such as kaolinite, as opposed to montmorillonite (Bohn, 1985). Therefore high electroosmotic flows are observed in kaolinite than montmorillonite type of clays at the same concentration of dilute solutions of electrolytes. This is consistent with the prediction of electroosmotic water transport according to Donnan concept.
Khan (1991) proposed a modified theory of electroosmotic flow through soil. In this theory the true electroosmotic flow is directly proportional to the current carried by the surface of the charged solid constituents of soil. The slipping plane potential (electrokinetic potential) used in H-S theory of electroosmotic flow is replaced by a constant surface potential which is invariable with electrolyte concentration. Hence, true electroosmotic flow becomes independent of electrolyte concentration in the pore fluid. The measured values agree well with the predicted flow using this modified theory. It also agrees with Speigler's formulation and much earlier observations of Napier in 1848 who stated that "...the measurable endosmose (electroosmosis) seems to be greatest when the current has greatest difficulty to pass through, and when the decomposition (of water) was least". This follows that the true electroosmotic flow is large when ratio of the surface current to the electrolytic current (carried by the ions in the pore fluid) is large due to reduced concentration of ions in the pore fluid.

Definitions and Some Theoretical Aspects of Electrokinetics

Electrokinetic treatment of soils invokes three electrokinetic processes: electroosmosis, electrolytic migration of ionic and polar species, electrophoresis and electrophoretic migration of colloidal electrolytes or ionic micelles.

Electroosmosis produces a rapid flow of water in low permeability soils and probably contributes significantly to the decontamination process in clay soils by advection transport. The current efficiency or the time rate of volume of water flow per current in electroosmosis is given by the following equation, where the surface conductivity, \( \lambda_s \), of capillary surfaces in soil medium is considered (Hunter, 1984):

\[
V/I = -\varepsilon_0 \varepsilon \eta (\lambda_0 + 2\lambda_s/r)
\]

where,

- \( V \) = volume of water flow per time;
- \( I \) = current;
- \( r \) = radius of the capillary;
- \( \lambda_0 \) = specific conductance of the bulk liquid;
- \( \lambda_s \) = surface conductance of the capillary;
- \( \varepsilon_0 \) = permittivity in free space,
- \( \varepsilon \) = dielectric constant of the medium,
- \( \eta \) = viscosity of the medium,
- \( \zeta \) = electrokinetic potential.

Surface current is due to the ionic motion in a region close to the solid surface called the diffuse layer. In narrow capillaries with low ionic concentrations and thick diffuse layers, a
disproportionate fraction of the current flows in this layer due to the low conductivity of the bulk fluid and high conductivity of the diffuse layer. Experimental evidence show that current efficiency decreases with increasing ionic concentration in the bulk fluid. This can be explained readily from Equation 1, since $\lambda_0$ is expected to increase with increasing fraction of ions in the solution. There is also evidence that $\zeta$ and $\theta/\eta$ decrease with increasing ionic concentration. The surface conductance also changes with ionic concentration. As the fraction of ions in the bulk liquid increase, the diffuse double layer shrinks toward the particle. The shear plane where the electrokinetic potential is measured, shifts away from the particle surface so that majority of the charge is now compensated by an immobile layer of ions in the diffuse double layer called the Helmholtz layer. Therefore the charge density in the mobile portion of the diffuse double layer decrease, giving rise to a lower surface conductivity, $\lambda_S$. As a result of this lowered conductivity a smaller portion of the current flows on the capillary surface. In contrast, in presence of low ionic concentration the diffuse double layer is swollen and much of the charge is compensated by the ions in the mobile portion of the diffuse double layer. Therefore, the capillary surface conductivity is high and so is the fraction of the current that is transmitted on the surface. A detailed study of the significance of surface conductance on the prediction of electroosmotic flow as it relates to contaminant transport in soils is presented by Khan and Pamukcu (Khan (1991) and Khan et al. (1993)).

**Electrolytic migration** of ions is perhaps the major cause of conduction of current through a porous medium containing moderately concentrated aqueous solution of electrolytes. The ions migrate toward the electrode opposite to their charge. Their net velocity of migration, $v_i$, can be determined by superpositioning of three velocity components, $v_i^{\infty}$, $v_i^{\text{relaxation}}$, and $v_i^{\text{electrophoresis}}$, as given by the following equation (Kortum and Bockris, 1951):

$$v_i = v_i^{\infty} + v_i^{\text{relaxation}} + v_i^{\text{electrophoresis}}$$  \hspace{1cm} (2)

where, $v_i^{\infty}$ is the velocity of ion type $i$ in infinite dilution, $v_i^{\text{relaxation}}$ and $v_i^{\text{electrophoresis}}$ are the retardation effects due to non uniform distribution of charge density around the moving ion and viscous drag of the counter ions moving in the opposite direction, respectively. These effects arise from the ionic atmosphere structure that develops in ionic solutions. Owing to electrostatic interaction and thermal motion, in a time average, there will be more negative ions than positive ions in the region of a positive ion, and vice versa. This region of ions (regarded spherical in shape) carrying a charge density of sign opposite to that of the central ion is called the ionic atmosphere of the central ion. The potential of an ion then depends on the interaction between the ion and its surrounding atmosphere.
Debye-Huckel (1923) calculated the potential, \( \psi \), of the central ion with respect to its surrounding ionic atmosphere at a distance of closest approach to the ion. Accordingly:

\[
\psi = (z_1 \varepsilon_0 / \theta a) - (z_1 \varepsilon_0 / \theta)(\kappa/(1+\kappa a))
\]

where, \( z_1 \) = valence of central ion, \( \varepsilon_0 \) = electronic charge, \( \kappa \) = Debye-Huckel parameter; \( \theta \) = dielectric constant of the medium inside the ionic atmosphere sphere, and \( a \) = distance of closest approach to the central ion or sum of the radii of the oppositely charged ions in contact. The first term on the right hand side is the potential at the surface of the ion and it is solely due to the charge of the ion itself. The second term is dependent on the ionic concentration and it is due to the ionic atmosphere surrounding the central ion. The inverse of \( \kappa \), or \( 1/\kappa \), is taken as the thickness of the spherical ionic atmosphere.

If an external potential gradient is applied on a solution of a selected ion, it will tend to migrate with a velocity, \( v_i \), determined by its characteristic ionic mobility and independent of the presence of other ions. The ionic atmosphere, however, being oppositely charged to the central ion, will tend to migrate in the opposite direction taking with them their solvent sheaths. The central ion therefore travels against a medium moving in the opposite direction which results in an additional viscous drag on the ion. This phenomenon is called the electrophoretic effect. Another effect which retards the ionic velocity is the relaxation effect (Onsager, 1928). This phenomena comes about as the central ion is suddenly moved in its atmosphere, the atmosphere will tend to attain an asymmetrical shape about the central ion due to time lapse between the responses of the central ion and the ionic atmosphere. If the central ion moves steadily in the applied electric field, the effect of a permanent distortion of the ionic atmosphere will tend to retard the ionic velocity. The average charge density will tend to decrease in front of the moving ion and it will decrease behind it. The excess charge behind the ion exercises an electrostatic retardation on the moving ion. The magnitude of retardation of the electrophoretic and the relaxation effects are directly proportional to the ionic concentration. As the ionic concentration increases the charge density of the ionic atmosphere increases, therefore the forces associated with the electrophoretic and electrostatic retardation increase.

Electrophoresis is the migration of charged colloids in soil-liquid mixture. In a compact system of porous plug, electrophoresis of should be of less importance since the solid phase is restrained from movement. In some cases, however, electrophoresis of clay colloids may play a role in decontamination if the migrating colloids have the chemical species of interest adsorbed.
on them. An important contribution of electrophoretic movement to contaminant transport may be when the contaminants are in the form of colloidal electrolytes or ionic micelles. Colloids that are made up of ionizable groups attached to large organic molecules, macro molecules, aggregate of ions belong to a class of substances known as colloidal electrolytes or ionic micelles. Ionic micelles form by aggregation of particles of like sign when the attractive dispersive forces are greater than the coulombic repulsive forces between the groups (Kortum and Bockris, 1951). Micelle formation is promoted as the concentration of the aggregating groups increase. Ionic micelles often carry a high charge owing to the many ions they contain. Although they are large in size and exhibit higher frictional drag in motion, the high charge will tend to increase their mobility at a greater rate than the frictional drag would tend to reduce. Therefore ionic micelles often exhibit high conductance in dilution.

The conductance of ionic micelle solutions increases with increasing concentration owing to build up of charge with further aggregation. However, with many systems there is a sudden and sharp decrease of conductance at a critical concentration which is attributed to: (1) increasing association of the ionic colloids which results in increased fraction of neutral colloids; (2) retarding interionic forces (electrophoretic and relaxation effects) which could be especially powerful with the large charges that these ionic micelles carry. At high electrolyte concentrations of the bulk liquid, the double layer around the micelle shrinks causing the ratio of the particle radius to its diffuse layer thickness, (κa), to increase. This reduction signifies an appreciable compensation of the charge on the micelle so that at small distances the electrostatic repulsion is reduced. As a result the micelles tend to coagulate, thus their mobilities are retarded. A numerical solution provided by O'Brien and White (1978) shows the variation of electrophoretic mobilities with electrokinetic potential (Q) and κa. They show that, for large κa values (κa>3) increasing electrokinetic potential beyond a threshold value actually results in reduced mobility for ionic micelles and colloidal electrolytes.

Other Electrokinetic Processes in Soils

One of the Important aspects of electrokinetics in soil-water systems is the transient migration of an acid front from the anode site to the cathode site during treatment (Acar, et. al, 1990; Shapiro et. al, 1989). When water decomposes, it is reduced to hydrogen gas at the cathode and oxidized to oxygen gas at the anode. This results in progressive reduction of pH at the anode site, and increase of pH at the cathode site. Subsequently the hydronium ions produced at the anode migrate toward the cathode whereas the hydroxide ions produced at the cathode migrate toward the anode. The ionic mobility of the hydronium ion is nearly twice as
high as that of the hydroxide ion and its migration is further enhanced by the electroosmotic flow of water toward the cathode. The benefits of increased hydrogen ion concentration would be most evident in extraction of metals since, hydrogen ion will tend to exchange with metal ions held on clay surfaces and low pH condition is favorable for the dissolution of most metal precipitates making them available to migrate or be transported. In natural soils, however, the buffering capacity is often high which would tend to neutralize the acid front and maintain a higher pH environment.

The transient and spatial variation of pH affect soil surface properties such as cation exchange capacity, ion (cation and anion) adsorption capacity, and magnitude of electrokinetic potential, $\zeta$, and its sign. Furthermore, speciation and solubility of the contaminants are often pH dependent. The distribution of these contaminants would be transient and spatially varied with pH and redox potential during electrokinetic treatment. The pH-redox conditions at a point at any time during the treatment would determine the solubility and speciation of most heavy metal constituents. These conditions may limit or enhance the movement of the metals to an electrode site.

Extraction of contaminants by electrokinetic method is based on the assumption that the contaminant is in liquid phase in the soil pores. Electroosmotic advection should be able to transport non-ionic as well as ionic species through soil toward the cathode. This is perhaps best achieved when the state of the material (dissolved, suspended, emulsified, etc.) is suitable for the flowing water to carry it through the tight pores of soil without causing an immovable plug of concentrated material to accumulate at some distance from the anode. Polar organic molecules, ionic micelles and colloidal electrolytes should migrate under the influence of field as well as being transported by the water. The size of these molecules or micelles, their tendency to agglomerate or be adsorbed on to soil surfaces are probably the main factors that control their removal from soil pores by electrokinetics. Removal of cationic species on the other hand, should be enhanced with the electroosmotic flow of water as they migrate toward the cathode electrode by the applied potential. It is yet unclear the relative magnitude of contribution of either process (electroosmosis and electrolytic migration) to decontamination under a given set of initial and boundary conditions determined by the soil and contaminant type and also their interaction. However, recent findings indicate that at low concentrations of cations, electroosmotic water flow may contribute a significant percentage, if not all, to the overall decontamination process (Khan, 1991). At high concentrations of the ionic species, electrolytic migration, intensity of electrochemical reactions, auxiliary water movement by frictional dragging of water by ions (cations and anions) may play more important roles than electroosmosis in the decontamination process.
One of the indicators often used to characterize electroosmotic process is the current efficiency or, the time rate of volume of water flow per current. Experimental as well as analytical treatment (Equation 1) of the matter show that the current efficiency decreases with the ionic concentration of the soil pore water (Renaud and Probstein, 1987; Gray and Mitchell, 1967; and Pamukcu and Wittle, 1992). Current efficiency increase with decreasing ionic concentration as the conductivity of the soil surface increase and the water flow is primarily controlled by the mobile layer of ions in the diffuse double layer of the clay capillary, rather than the frictional dragging of the migrating ions in the bulk fluid. This type of flow is probably closer to true electroosmotic flow in which the contribution of ionic motion in the bulk fluid to the overall flow is minimum. Additional evidence to support this finding was presented by Pamukcu and Wittle (1992, 1993) where the ionic concentration effect on the measured current efficiency appeared to be most pronounced in clays with high anion retention capacity. At the same concentrations of dilute solutions of electrolytes, kaolinite clay with higher anion retention capacity showed consistently higher electroosmotic flow than montmorillonite clay with lower anion retention capacity. This observation suggested that the anionic dragging of water toward anode diminished the net flow toward the cathode compartment in the montmorillonite clay. This also provided an explanation to the lower current efficiency observed in these clays in contrast to that observed in kaolinite clays.

Application of Electrokinetics to Soil Decontamination

Electrokinetics have been used for dewatering of soils and sludges since the first recorded use in the field by Casagrande in (1939). Work and subsequent research in electrokinetic decontamination of soils have been accelerated in recent years, probably after the report of the detection of high concentrations of metals and organics in electroosmotically drained water of a dredged sludge in the field by Segall and co-workers in 1980. Other field work (Lageman, 1989; Banerjee, et al, 1988) has been conducted since then with reasonable success of heavy metal transport.

Hamnett (1980) performed laboratory studies on electrically induced movement of ions in sand. In evaluating the electrolytic migration of ions of different salts, he found that smaller ions (i.e. Na) were more mobile than larger ions (i.e. K, Ca, Ni). Acar et al. (1991) and Hamed et al. (1991) showed that the migration of an acid front from the anode toward the cathode is significant in the removal of heavy metals from clay soils. Shapiro and co-workers (1989) developed a model for electroosmosis to predict transient behavior of concentration profiles for
chemical species in solution. The model agreed well with experimental results of acetic acid removal from soil via electrokinetics.

A simple prediction method was suggested by Khan (1991). The theoretical approach developed for electroosmotic flow was used to predict the contaminant removal from soil when the contaminants were either present at low concentrations in the soil pores or they were not adsorbed onto the charged surfaces, so that the true electroosmotic flow was the dominant mechanism for their migration. Tracer experiments in kaolinite clay utilizing O-Nitrophenol and zinc as representative contaminants were conducted. O-Nitrophenol represents a poorly adsorbed organic compound, the adsorption of which was measured on the order of 0.01 mg/g of soil. The zinc concentration used was 325 mg/kg of dry soil which was slightly over than the typical maximum concentration of naturally occurring zinc (10 - 300 mg/kg) in soils. There was good agreement between the measured removal of the contaminant and the predicted removal using electroosmotic flux of water based on clay surface current. Experiments with higher concentrations of zinc showed clearly the effect of speciation and precipitation on the efficiency of the electrokinetic transport of metals (Pamukcu et al, 1991).

INVESTIGATION

Experimental Procedures

An laboratory program was undertaken to investigate the feasibility of electrokinetic treatment of clay mixtures containing heavy metals. The test matrices were prepared in the laboratory by compressing slurries of clay to compact saturated soil samples. Each clay slurry was mixed with solution of one heavy metal salt of a predetermined concentration. The mixing water of the slurries were also changed as distilled water, a solution of a humus product representing humic acids in natural soils, and water with dissolved salts representing the ionic constituents of a selected groundwater type. Each specimen type (clay, pore solution and metal type) was prepared in triplicate and tested under the same conditions, but with variable duration of treatment for some of the triplicate sets. A matrix of metals and soil types constituted the materials for producing artificial contaminated soil systems in the laboratory. Metals evaluated in the program were representative of those found at a majority of DOE sites. They included the classes of metals (Cd, Hg, Pb, Ni, Zn), surrogate radionuclides (Co, Cs, Sr, U), anions (HAsO₄, Cr₂O₇). Five soil types were studied: kaolinite clay, Na-montmorillonite clay, sand with 10% Na-montmorillonite, kaolinite clay with simulated groundwater, and kaolinite clay with humic
substances solution. The minimum test duration was 24 hours in general. A number of the replicate tests were extended into longer periods (up to 48 hours) to investigate the transient behavior of the transport. During each test, the systems were monitored for voltage, current, inflow and outflow of liquid through the soil. After the test, the soil samples were analyzed to construct metal and organic contaminant concentration and also pH profiles along the length of the sample to assess the success of decontamination.

In this paper, only the results pertaining to the surrogate radionuclides (Cs, Sr, U) and an anionic species, CrO}_7 are presented and discussed.

**Materials**

The clays used in preparing the soil matrices were kaolinite (Georgia kaolinite) and Na-montmorillonite (bentonite), both obtained commercially. The sand specimens were prepared with washed beach sand passing No. 40 sieve and retained on No. 100 sieve. This variation in soil mineral matrix was intended to investigate the process in so assumed difficult situations of remediation when the ionic species are strongly held on the clay surface (Na-montmorillonite case), or when the electroosmotic flow efficiency might be reduced due to reduced surface charge density (sand case). The sand matrix was prepared with the clean beach sand mixed homogeneously with 10% Na-montmorillonite by dry weight.

The pore solutions were distilled water, humic solution and simulated groundwater. The humic solution was prepared by dissolving a commercially obtained humus product in distilled water at a concentration of 900 ppm. The organic carbon content of this stock solution was 257 as measured in mg C/l. This corresponded to DOC values typically measured in groundwaters associated with very high organic carbon fields, such as oil fields. The pH of this solution was 9.4. The simulated groundwater was prepared following an approximate formula of the groundwater salt constituents typically found in the Jefferson County of Idaho State. The pH of groundwater sampled in that region was measured at 8.2, and contained a substantial amount of (212 ppm) bicarbonate. The simulated groundwater did not contain this component and it's pH was measured as 7.9.

The salts used in preparing solutions of the 4 metals and the metal concentration of each resulting solution as well as the resulting concentration of the metal in soil and the soil slurry pH prior to electrokinetic treatment are given in given in Table 1. In general the pHs of the mixtures were moderately acidic or near neutral.
Table 1. Some Chemical Properties of the Contaminated Soil Specimens Used In E-K

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Metal</th>
<th>Salt Formula</th>
<th>Initial Solution Concentration mg/l</th>
<th>Initial Soil Concentration mg/kg&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Initial pH of Soil Slurry</th>
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<td>693</td>
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<tr>
<td>KS</td>
<td>Cr</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;CrO&lt;sub&gt;7&lt;/sub&gt;</td>
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<td>1850</td>
<td>4.91</td>
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<td>KS</td>
<td>Sr</td>
<td>SrCl&lt;sub&gt;2&lt;/sub&gt;.6H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>1000</td>
<td>4432</td>
<td>7.83</td>
</tr>
<tr>
<td>KS</td>
<td>U</td>
<td>in 2% HNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>100</td>
<td>1108</td>
<td>8.42</td>
</tr>
<tr>
<td>KS</td>
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<td></td>
<td>..........................</td>
<td>..........................</td>
<td>7.34</td>
</tr>
<tr>
<td>KS</td>
<td>Cs</td>
<td>CsNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1000</td>
<td>853</td>
<td></td>
</tr>
<tr>
<td>KS</td>
<td>Cr</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;CrO&lt;sub&gt;7&lt;/sub&gt;</td>
<td>3000</td>
<td>972</td>
<td>8.79</td>
</tr>
<tr>
<td>KS</td>
<td>Sr</td>
<td>SrCl&lt;sub&gt;2&lt;/sub&gt;.6H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>1000</td>
<td>483</td>
<td>8.2</td>
</tr>
<tr>
<td>KS</td>
<td>U</td>
<td>in 2% HNO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>100</td>
<td>98</td>
<td>7.58</td>
</tr>
</tbody>
</table>

<sup>1</sup> KS: Kaolinite/distilled water; KH: Kaolinite/humic solution; KG: Kaolinite/ground water
MS: Na-montmorillonite/distilled water; SS: Sand/10% Na-montmorillonite/dist. water

<sup>2</sup> Average of three replicate samples
Procedures

The slurries would be mixed at 100% water content of the kaolinite clay, 50% water content of the sand mixture, and 200 - 300% water content of Na- montmorillonite clay, all by dry weight of the solid components. The mixing would be done in large batches (2-3 gallons) with a tall hand held mixer. Then the slurry would be poured into individual compression units referred to as 'consolidometers' as shown in Figure 1. The operation of these units are presented elsewhere (Khan, 1991). The main features of the consolidometers are that they are capable of applying small increments of sustained stress (pneumatically) while allowing for the excess fluid to drain out slowly. This procedure creates, homogeneous, near saturated soil matrices compacted to a constant density and pressure. The most beneficial aspect of these custom manufactured units is that at the end of the consolidation process, the densified soil sample is packed into a cylindrical soil chamber (3.556 cm ID and 7.62 cm long) which can be detached from the unit and installed into the electrokinetic cell used in this investigation (Figure 2). As a result, the soil specimen is not disturbed by handling such as trimming and placement.

All the specimens were consolidated to 200 kPa pressure. Although there is evidence, from this work and also others that, electroosmotic flow increases with consolidation pressure in clay soils, it is not well known to what extent the increased flow contributes to decontamination when the contaminant migration is not governed by electroosmosis. The average initial and final dry densities and water contents of the five artificial soil types are given in Table 2. The average water contents increased from the initial state to after electrokinetic treatment state by about 3 to 20 %, whereas the bulk densities showed reduction by about 0.5 to 9%. These changes indicated that during the treatment, the electroosmotic water flow did not cause any volume contraction of the soil, on the contrary, the degree of saturation increased and some particulate material was lost to the water chambers due to electrophoretic migration.

At the completion of each consolidation period, the tube containing the packed soil would be removed, the top extruding portion trimmed and stored for quantitative chemical and water content analysis. Samples of the waters extracted during consolidation were also taken for chemical analysis to assess the degree of metal retention by clays. The approximate period of consolidation to 200 kPa pressure was around 24 hours for the kaolinite slurries and it was around 7 days for the Na- montmorillonite clays slurries. This period was much less for the bentonite mixed sand specimens, but the pressure increment periods for these were kept similar to that of the kaolinite specimens for consistency. When the soil cylinder was removed from the
consolidometer, weighted and sampled, it would be ready for mounting on the electrokinetic apparatus, the schematic diagram of which is given in Figure 2.

Table 2. Average Water Content and Dry Density of Specimens Before and After Electrokinetic Treatment

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Before E-K</th>
<th>After E-K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water Content</td>
<td>Bulk Density</td>
</tr>
<tr>
<td>KS</td>
<td>47.3%</td>
<td>1.64 g/cm³</td>
</tr>
<tr>
<td>KH</td>
<td>51.4%</td>
<td>1.66 g/cm³</td>
</tr>
<tr>
<td>KG</td>
<td>32.8%</td>
<td>1.83 g/cm³</td>
</tr>
<tr>
<td>MS</td>
<td>271.3%</td>
<td>1.14 g/cm³</td>
</tr>
<tr>
<td>SS</td>
<td>51.3%</td>
<td>1.87 g/cm³</td>
</tr>
</tbody>
</table>

The details of the electrokinetic apparatus used in this study are also provided elsewhere (Khan, 1991). It should be noted that there is no standard apparatus for measuring electrokinetic water flow in soils. The ones that are used in similar work elsewhere have been shown to produce consistent results. The equipment used in this particular program was developed with attention given to a few concerns. These were addressed by providing larger electrode surfaces than soil surface to achieve low current density, by isolating the electrodes from soil surfaces to minimize electrode reactions at these boundaries, and by providing convenient ports for gas expulsion from the electrode sites and also for extracting inflow (anode site) and outflow (cathode site) water samples for analysis. The main features of these units are: the electrodes reside in water tight chambers which are connected to measuring burettes at one end, and to the soil specimen cylinder at the other end. The soil specimen is separated from these water filled chambers by carborandum porous stones. This allows the contaminants to come out into the liquid phase and not be deposited on the electrodes. These units can be operated under constant potential or constant current. The time dependent water movement through the soil can be measured on the inflow (anode side) and outflow (cathode side) tubes on individual control panels. These panels are each equipped with a pressure regulator and gauge for hydraulic potential application capability. The control panels also carry small pumps to drain the electrode chamber periodically as necessary in order to remove the extracted material and alleviate concentration polarization.
The tests, results of which are reported here were conducted under a constant potential of 30 VDC across electrodes. The voltage in soil and the current generated were measured simultaneously with the flow measurements. The tests were continued for at least 24 hours. For a number of randomly selected combinations of soil, pore fluid and metal, the termination times were varied between the triplicate samples from 24 hours to up to 48 hours. For a number of extended hours of treatment, the electrode chambers (both anode and cathode) were drained at around 24 hours and refilled with the appropriate pore water used in the soil specimen. This was done to alleviate concentration polarization and the high pH gradients created between the chambers which was thought to reduce water flow rate originally. However, this practice did not prove to be effective for increased contaminant removal or water flow rate, since the pH in the electrode compartment waters build up to their previous levels in a matter of minutes.

At the termination of each experiment, the electrode chamber waters would be collected. These water samples were analyzed for the particular metal extracted and their pHs were measured. The cathode water pHs ranged from around 10 to 12, whereas the anode water pHs ranged from 2 to 3 in general. The cathode chamber water was acidified to solubilize the metal precipitates created at the high pH environment in that chamber. The soil specimen would then be extracted, pH measurements taken at the anode end, center and the cathode end. Specimens from each one of these locations were collected for chemical analysis of the particular metal extracted.

Results

The analysis of the data showed metal migration in all soil specimens. Considering the lowest concentration of a particular metal achieved at one of the three locations (anode end, center, cathode end) of the soil cylinder, the metal removal success was up to 99% for the durations of treatment which did not exceed 50 Hs. This removal is computed as 1 minus the ratio of the remaining concentration to the original concentration of the metal. Table 3 summarizes the average of percentage of metal concentration reduction for three replicate specimens at the location of lowest concentration measurement after 24 to 48 hours of electrokinetic (E-K) treatment. Also shown in Table 3 are the average cumulative fraction of pore volume of water transported through the specimens toward the cathode compartment during the treatments. The variations in these concentration reduction percentages appeared to depend on soil matrix, the metal and pore fluid type. They appeared to have little or no correlation with the volume of flow achieved during treatment.
Table 3. Average Percent Reduction of Metal Concentration (at the lowest concentration location) and Pore Volume Fraction of Water Transported Toward Cathode Chamber

<table>
<thead>
<tr>
<th>Metal</th>
<th>K3</th>
<th>CI</th>
<th>K5</th>
<th>MS</th>
<th>S3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Cr</td>
<td>93</td>
<td>0.18</td>
<td>97</td>
<td>0.15</td>
<td>95</td>
</tr>
<tr>
<td>Cs</td>
<td>72</td>
<td>0.85</td>
<td>74</td>
<td>0.30</td>
<td>77</td>
</tr>
<tr>
<td>Sr</td>
<td>98</td>
<td>0.41</td>
<td>98</td>
<td>0.88</td>
<td>99</td>
</tr>
<tr>
<td>U</td>
<td>79</td>
<td>0.35</td>
<td>70</td>
<td>0.69</td>
<td>85</td>
</tr>
</tbody>
</table>

PV: Pore volume of water transported to the cathode chamber during treatment

As observed from Table 3, for the cationic species, the volume of water represented as the fraction of pore volume for each soil specimen ranged between 0.25 and near 1.00. The flow for the anionic form of Cr was consistently lower than that of the cationic species. This demonstrated the effect of water dragging action of migrating ions on the net flow toward cathode. In the case of Cr₂O₇⁻, as the anion migrates toward the anode, it drags along with it sufficient amount of water to measurably reduce the net flow toward the cathode, which is the electroosmotic flow.

Figures 3 through 6 show the fraction of metal with respect to its original quantity in soil, found at different locations in the cylindrical soil specimen as well as in the anode and cathode compartment waters. These graphs represent the average data for three replicate specimens for each soil type. It should be noted here that, the metal concentration analysis across the soil specimens were made by sampling only three points along each specimen. The actual concentration profile at the time of sampling may not be well represented by the linear or best fit distributions assumed between the consecutive points. Therefore, it is not possible to predict degree of removal of the contaminant from the areas under the concentration curves, neither it is possible to arrive at an accurate mass-balance prediction. Nevertheless, the data presented are consistent and show a clear trend of metal migration toward an electrode site in each case.

As observed from the first three figures (Sr, Cs, U), the cations are transported to the cathode end of the soil where they tend to accumulate. The transport mechanism is probably all governed by electromigration since there appears to be very little or no correlation between the
measured fraction of the metals in the cathode chamber or the fraction gradient in the soil and the quantity of water transported (see Table 3). In Figure 6, chromate is removed into the anode chamber and a majority of it has accumulated on the anode end of the soil. This migration took place in the opposite direction of water flow, since a net water flow was measured toward the cathode for all the chromate contaminated specimens.

All the metals, both anionic and cationic, accumulated at their discharge locations creating zones of high concentrations of metal (sometimes over that of the original). These zones are perhaps very narrow residing at the interface between the soil and the electrode chamber, which is analogous of depositing the metal on an electrode if it was in contact with soil. In the case of cations, the production of hydroxide in the cathode chamber is one of the major causes of the phenomena. As the hydroxide ions migrate into the soil, they create a high pH zone in the soil before they encounter the oncoming hydronium ions and be neutralized. This zone may lessen in thickness as the acidic front penetrate more toward the cathode end of the soil, however, as long as there is a high pH gradient at this discharge end, the metals would tend to form hydroxide complexes and start to precipitate from solution in a thin zone of soil at the interface of electrode chamber water. Another effect of high pH is on the adsorption capacity of the clay soils. Hydroxide ions are potential makers, which subsequently cause the cation adsorption capacity of the soil to increase. Therefore, at high pH, the surface potential will increase, leading to thicker diffuse layers and increased surface conductivity. Since, the bulk liquid conductivity would be reduced with precipitation, the combined effect should actually signal increased electroosmotic water transport and current efficiency. This suggests that with extended duration of treatment, the accumulated metal may be transported into the electrode chamber by the steady but slower action of electroosmotic advection.

A similar accumulation is observed with the chromate ion which migrates toward a low pH area (Figure 6). This occurrence demonstrates the effect of another important phenomena that delays the metal discharge from soil by electrokinetics. If a triggering mechanism, such as increased adsorption, precipitation, starts delaying the removal at the discharge location, the metal concentration will quickly build up there as more of the ions migrate into the area. When the ions encounter the high concentrations their velocities decrease due to the electrophoretic and relaxation effects discussed above. In the case of chromate, increased potential for anion adsorption of the clay at low pH may have triggered the accumulation of the metal at the anode end. Nevertheless, it is remarkable to observe the relatively high removal of Cr into the anode chamber in the presence of opposing water flow.
Strontium

Strontium remains a divalent ion for a large range of pH values. Figure 7 shows the average pH distribution from anode to cathode end of three replicate specimens of five soil types. The pH ranges from about 2 to 10, through which Sr is expected to remain a divalent ion. Figure 8 shows typically, the normalized concentration profiles of Sr for the three specimens of kaolinite and distilled water soil. Specimen labeled as KGSrHM1 showed a slight accumulation of the metal at the cathode end by the end of 24 hours of treatment. The pore volume fraction of water transported for this specimen was measured to be approximately 0.4. When the duration of treatment was increased beyond 2 days, the cathode end concentration diminished resulting with a more or less uniform distribution of the metal throughout soil. The pore volume fraction of water for this specimen which is labeled as KGSrHM3 was 0.6. Long term tests on Sr contaminated kaolinite soil with distilled water showed nearly complete removal of the metal after about 4 pore volumes of water transport (Wilkowe, 1992). This suggests that the removal rate is not constant and decreases with duration of treatment depending upon the interactions between the soil and the metal. The accumulation of the metal at the cathode end (Figure 3) is attributed initially to the increased ion retention capacity of the soil which subsequently triggers the concentration increase and deceleration of the migrating ions at this end. However, with extended treatment, the electroosmotic flow enhances the removal at a steady but slower rate. Figure 9 shows the steady state flow achieved for up to 18 pore volume of water flow through Sr contaminated kaolinite soil. As observed, after about 4 pore volumes of flow, (by which nearly all Sr was removed from soil) the measured current dropped to a constant value of 0.5 mA and stayed constant throughout the treatment. This shows depletion of the bulk current carriers and mobilization of the surface conductance of the clay which is now constant at constant ionic concentration.

Cesium

Cesium is a monovalent cation which is a strong exchanger in most clays. Similar results were observed with Cs as those of Sr. In the Cs case, however, the rate of removal appeared to be slower than the Sr case. This is perhaps due to the lower ionic mobility and larger ionic atmosphere of Cs which resulted in lowered electromigration velocity. The affinity of the clay to Cs may have also contributed to the delayed response. It is interesting to note the reduced initial Cs concentration with the humic solution in the pore fluid. In making the slurry specimens, the humic solution was first mixed with the cesium salt before adding the clay to make the slurry. It appears that most of the cesium was retained on the organic component of the humic solution.
which was drained out during the consolidation of the slurry. The affinity of the humic solution to Cs is also evident in Figure 4, in which there is a significant fraction of Cs removed into the cathode chamber in kaolinite clay with humic solution as the pore fluid and also as the permeant. During the period of tests (24 to 48 hours), more than 40% of the metal was transported into the cathode chamber of the kaolinite soils, as can be seen in Figure 4.

Figures 10 through 13 show the post E-K concentration profiles of Cs achieved in replicate specimens of 4 soil types. In general, the concentration profiles shifted down in a uniform manner with increasing duration of treatment. The repeatability of data for similar durations of treatment and similar initial concentrations of Cs was good.

Uranium

Uranium removal was not as efficient as that of Sr and Cs, however, there was definite migration of the metal toward the cathode end where it accumulated at concentrations higher than the original (Figure 5). Uranium was introduced into the soil as the uranyl salt from a series of hydroxide complexes. Below the pH of 6 they are cationic in nature. At approximately pH 6, the $\text{UO}_2(\text{OH})_2\cdot\text{H}_2\text{O}$ precipitate. At higher pHs, the anion hydroxide species such as, $\text{UO}_2(\text{OH})_3^-$ and $\text{UO}_2(\text{OH})_4^{2-}$ occur which would than migrate in the opposite direction of electroosmotic water flow. These species may not be able to travel to the anode chamber since they would encounter a low pH environment on the way and tend to change form and sign. However, as long as a high pH gradient prevail at the interface of the soil and water at the cathode end, the uranium would be difficult to transport into the water phase by electromigration. Therefore very little fraction of the metal is encountered in the cathode chamber which probably was transported prior to the high pH build up, and by electroosmotic advection and diffusion. The effect of diffusion is also evident in the anode chamber, in which there is nearly as much Uranium as there is in the cathode chamber. Migration of anionic species might have contributed to removal into the anionic chamber also.

Chromium

Figures 14 and 15 show typical migration of chromate toward the anode. Chromate (chromium in the hexavalent oxidation state) is an anion which carries a negative two charge. As observed, the concentration profiles shift downward with increased duration of treatment with slight accumulation at the anode end of the soil. Figure 6 shows that, approximately 30% of the Cr is extracted into the anode chamber by the end of 24 to 48 Hs of treatment. As discussed
before, the remarkable aspect is that the electromigration of the ion takes place regardless of the water flow in the opposite direction. Also owing to the water dragging action of the migrating anion, the flow measured at the cathode end was consistently less than that of cationic transport cases. The concentration gradients across the soils for the Cr cases were less than the others, signaling the retarding effect of the electroosmotic flow in the opposite direction. Once again, there was accumulation of the metal at the discharge end due to anion retention and deceleration of the ionic motion due to electrophoretic and relaxation effects.

CONCLUSIONS

The main conclusion of this research has been that electrokinetics promises to be a viable technology to remove contaminants from soils. The interaction of various processes that take place simultaneously is yet to be understood to better predict the efficiency of the process in a variety of soil-contaminant situations. The results presented in this paper shed light on the influence of electrochemistry and physico-chemistry of the soil-contaminant system on the process. The transient acid front movement in soil from anode site to cathode, is beneficial for metal desorption and dissolution, which in turn contributes to the removal process. However, the transient pH condition cause formation of complex species of some metals which may hinder the process, or in some cases enhance it. pH also affects the surface charge characteristics of clay soils, either enhancing desorption or adsorption. Therefore pH control at both ends (anode and cathode) should create suitable environments for the metal ions to remain in solution and in the bulk pore liquid, so that they can be extracted in a feasible manner. If these factors that trigger ion concentration build up at the discharge ends of a soil-electrode system can be controlled or alleviated, then electromigration alone should be sufficient to remove metal contaminants from soil with minimum water flow.

This study demonstrated that substantial migration of the surrogate radioactive metals such as Sr, Cs, and U is achieved by electrokinetics in short durations of treatment in which the water flow through the soil was on the order of half the total volume of pores in the soil matrices. For Sr and Cs, total removals of the metals up to 80% into the cathode water chamber was achieved for the short durations of treatment. Substantial migration and cathode end accumulation of Uranium occurred in all soil types tested. Little removal of U (less than 20%) into the electrode chamber waters was achieved due to precipitation and speciation of the metal in the soil. However substantial reduction of the metal was achieved at the anode side half of the soil. Cr, as an anionic species, moved toward anode against the electroosmotic water flow. In
this case, up to 30% total removal of Cr was achieved for net water flows of less than 0.2 fraction of pore volume of the soil specimens.

ACKNOWLEDGMENTS

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Figure 1. Consolidation Apparatus to Compress Soil Slurry

Figure 2. Schematic Diagram of the Electrokinetic Apparatus and Control Panel
Figure 3. Average Distribution of Fraction of Strontium in Soil and Electrode Chamber Waters After E-K

Figure 4. Average Distribution of Fraction of Cesium in Soil and Electrode Chamber Waters After E-K
Figure 5. Average Distribution of Fraction of Uranium in Soil and Electrode Chamber Waters After E-K

Figure 6. Average Distribution of Fraction of Chromium (anionic form) in Soil and Electrode Chamber Waters After E-K
Figure 7. Average pH Distribution in Strontium Contaminated Soils

Figure 8. Concentration Profiles of Sr in Kaolinite/Groundwater Soil Samples After E-K
Figure 9. Electroosmotic Flow and Current Versus Time for Extended E-K Testing of Strontium Contaminated Kaolinite/Distilled Water Soil Sample
Figure 10. Concentration Profiles of Cs in Kaolinite/Distilled Water Soil Samples After E-K

Figure 11. Concentration Profiles of Cs in Kaolinite/Humic Sol. Soil Samples After E-K
Figure 12. Concentration Profiles of Cs in Kaolinite/Groundwater Soil Samples After E-K

Figure 13. Concentration Profiles of Cs in Sand/Na-Montmorillonite/Distilled Water Soil Samples After E-K
Figure 14. Concentration Profiles of Cr in Kaolinite/Groundwater Soil Samples After E-K

Figure 15. Concentration Profiles of Cr in Kaolinite/Distilled Water Soil Samples After E-K
DATE: February 11, 1993

SUBJECT: Review of Feasibility of Electrokinetic Extraction at the Aladdin Plating NPL Site in Pennsylvania

FROM: Randy A. Parker
Environmental Engineer, Risk Reduction Engineering Laboratory

TO: Gregory Ham, RPM
Eastern Pennsylvania Remedial Section

I have reviewed the Remedial Investigations Summary for the Aladdin Plating Superfund site with respect to the feasibility of using electrokinetics for remediation of hexavalent chromium in the shallow water-bearing zone. With electrokinetics, contaminants present in the groundwater and/or desorbed from the soil will be transported towards the electrodes depending on their charge. The valence of the chromium at this site is such that the movement of chromium would be from cathode to anode. Electro-osmotic flow, water transport due to electrical gradients, is in the direction from anode to cathode. Therefore, with electrokinetic extraction, the flow of chromium at this site is opposite the induced hydraulic flow. For maximum efficiency of the electrokinetic process, the induced hydraulic and electric flows should have the same direction.

Possible options for more effective electrokinetic removal of the chromium are to use lead electrodes in the electrokinetic process and remove the chromium as a lead chromate precipitate, or to add iron(II) to the groundwater to reduce the chromium from a 6 state to a 3 state. Chromium (III) would flow from anode to cathode, the same direction as the electro-osmotic flow.

Information on the cost of a treatability study of electrokinetics at this site are unavailable at this time because this technology is still in the bench and pilot scale stages with work performed mostly on soils. No data has been published for field-scale efforts or treatability studies.