Electrokinetic remediation: Basics and technology status

Yalcin B. Acar[a,*], Robert J. Gale[b], Akram N. Alshawabkeh[c],
Robert E. Marks[c], Susheel Puppala[c], Mark Bricka[d], Randy Parker[e]

[a] Civil Engineering Department, Louisiana State University, Baton Rouge, LA 70803, USA
[b] Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA
[c] Electrokinetics Inc., The Louisiana Business and Technology Center, South Stadium Drive, LSU,
Baton Rouge, LA 70803, USA
[d] US Army Corps of Engineers, Waterways Experiment Station, Vicksburg, MS 39180, USA
[e] Risk Reduction Engineering Laboratory, USEPA, Cincinnati, OH 45268, USA

Abstract

Electrokinetic remediation, variably named as electrochemical soil processing, electromigration, electrokinetic decontamination or electroreclamation uses electric currents to extract radionuclides, heavy metals, certain organic compounds, or mixed inorganic species and some organic wastes from soils and slurries. An overview of the principals of the electrokinetic remediation technique in soils is presented. The types of waste and media in which the technology could potentially be applicable are outlined and some envisioned environmental uses of conduction phenomena in soils under electric fields are presented. The current status of the electrokinetic remediation technique and its limitations are discussed through a review of the bench-scale and pilot-scale tests. The recent findings of research on different techniques that may improve the technology's effectiveness are mentioned and the status of ongoing efforts in wide-scale implementation and commercialization of the technique in the USA are described.

1. Introduction

Electrokinetic remediation, variably named as electrokinetic soil processing, electromigration, electrochemical decontamination or electroreclamation, uses electric currents to extract radionuclides, heavy metals, certain organic compounds, or mixed inorganic species and organic wastes from soils and slurries [1–19]. The application of electric current has several effects: (1) it produces an acid in the anode compartment that is transported across the soil and desorbs contaminants from the surface of soil particles [20–25], (2) it initiates electromigration of species available in the pore fluid
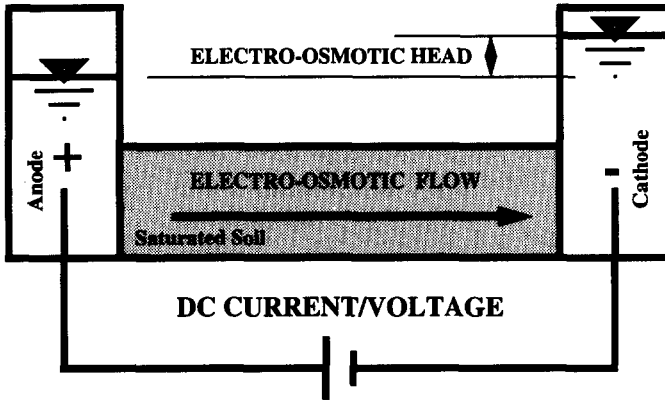
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* Corresponding author.

Fig. 1. A schematic diagram of electroosmotic transport of fluid across a soil specimen.

and those introduced at the electrodes [2, 6, 15, 20, 22, 25] and (3) it establishes an electric potential difference which may lead to electroosmosis generated flushing of different species [2, 4, 6, 14, 16, 19, 20, 25]. This paper provides an overview of electrokinetic remediation process in soils, outlines the types of waste and media in which the technology could potentially be applicable, examines some envisioned environmental uses of electrokinetic transport phenomena, discusses the current status of the technique through a review of the bench- and pilot-scale tests, looks at current research on different techniques that may improve the technology's effectiveness, and reports the status of evolving engineering design/analysis packages.

2. Background

Electrokinetic remediation is a controlled application of electrical migration and electroosmosis together with the electrolysis reactions at the electrodes. Electroosmosis is one of the different transport processes generated in soils under an electric current [26–29]. Electroosmosis and electrophoresis are defined as the mass flux of pore fluid and charged particles, respectively, under an electric field. Fig. 1 conceptualizes electroosmosis. The fluid in the anode compartment would flow across the soil mass to the cathode compartment under an electric field. The flow will cease when the counteracting flux under the hydraulic gradient equals the electroosmotic fluid flux or, if the soil surface potential approaches zero charge as a result of changes in pore fluid composition [2]. Fig. 2 conceptualizes electrophoresis through transport of negatively charged particles towards an anode under an electric field.

Most clay minerals have a net negative charge largely caused by imperfections developed in the mineral lattice during their formation. Elements of similar size and charge replace the ones in a perfect clay mineral lattice during formation (isomorphous substitution) leading to an overall charge deficiency in the mineral. Other reasons for charge deficiency are broken edges or the existence of natural organic
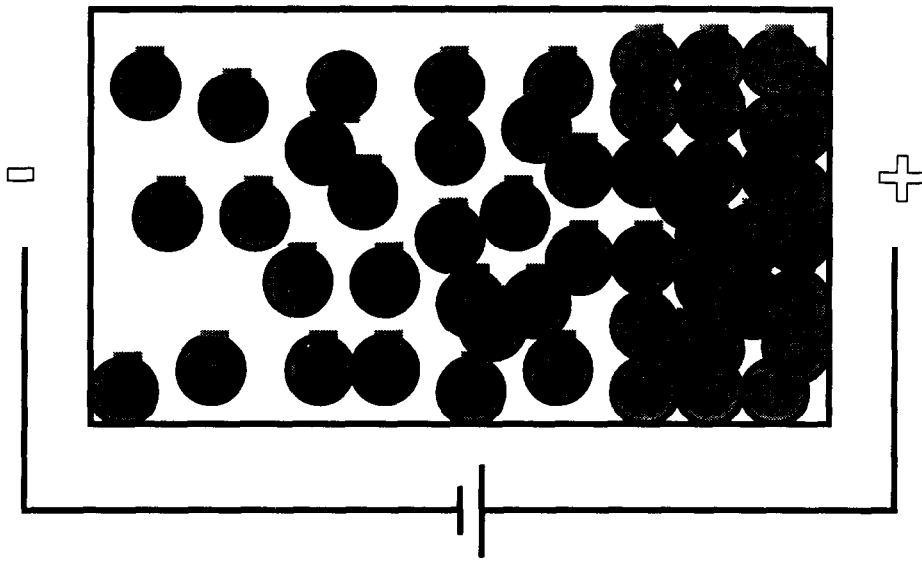
Fig. 2. A schematic diagram of electrophoresis of charged particles under electric field.

species (such as humic acids) in the soil mass. An excess negative charge exists in all types of soils, while the total electrical charge per unit surface area (surface charge density) increases as the specific surface (surface area per unit weight) of the soil mineral increases. For example, the surface charge density increases in the following order: sand < silt < kaolinite < illite < montmorillonite.

The interaction of the species in the pore fluid with a negatively charged surface results in alignment of the ionic species as conceptualized in Fig. 3. The excess negative charge in the soil results in attraction and cluster of excess cations close to the surface, while the neutrality of charge in the pore fluid is maintained by the equivalent concentration of anionic and cationic species elsewhere. When an electric field is established along the capillary, the excess cations close to the surface move towards the cathode. The movement of these species and any water molecules closely associated with these species imparts a net strain on the pore fluid surrounding their hydration shells. This strain translates into a shear force through the viscosity of the pore fluid. Since there is usually an excess amount of cations close to the surface, the net force and momentum towards the cathode results in a pore fluid flux in the same direction. This pore fluid flux, as a result of the electrical potential gradient along the capillary, is named 'electroosmosis' . Generally, the wider the zone with excess cations (diffuse double layer), the farther is the extent of the strain field to the center of the capillary, the more uniform will be the strain field and the more the electroosmotic flow. The thickness of the diffuse double layer; however, depends upon the magnitude of the charge density on the soil surface, the concentration of the ions in the pore fluid, the valence of the cations, and the dielectric properties of the pore fluid. When the ionic concentration increases, the thickness of the diffuse double layer and the extent
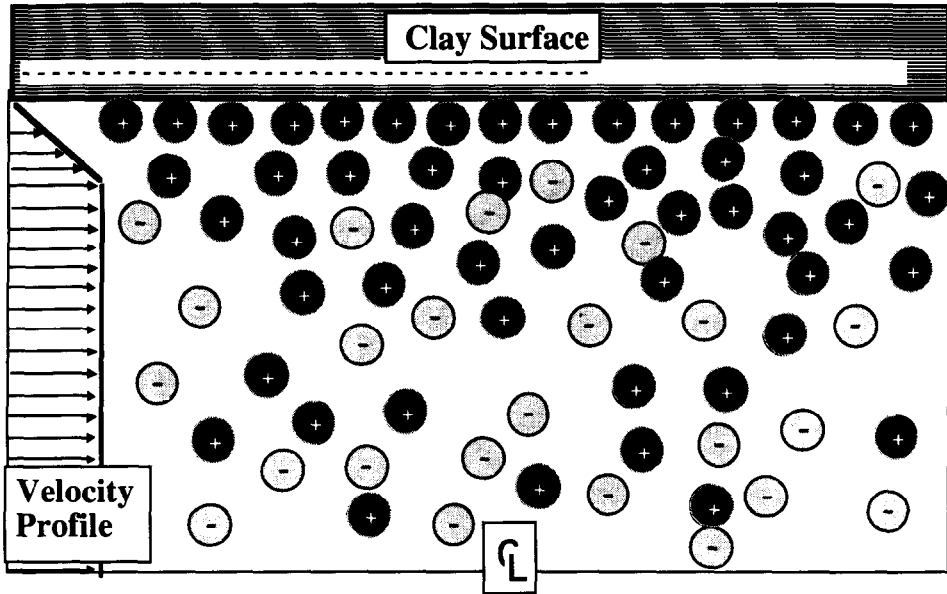
Fig. 3. A schematic diagram of the alignment of ionic species within the electric field developed by the soil surface and the pore fluid velocity profile generated when an electric field is applied along the capillary normal to the direction of the electric field of the surface.

of the strain field resulting in pore fluid flow will be reduced and the electroosmotic pore fluid flux will be confined more to the periphery of the capillary. As a result, electroosmotic flux will substantially decrease to become unmeasurable by conventional techniques. We also note that when the electrolyte concentration is high and the pH of the pore fluid is low, it is possible to reverse the polarity of the surface charge and initiate an electroosmotic flux towards the anode [2,30,31]. In general, electroosmotic flux will be maximum (approximately 10^{-4} $(cm^3/s)/(cm^2)$) under an electric gradient of 1 V/cm) in low activity clays (activity is defined as the plasticity index divided by the percent clay particles less than 2 μm size), at high water contents and low electrolyte concentrations, since the thickness of the diffuse double layer will be maximum while the pore fluid conductivity will be minimized (on the order of 100 μS/cm or less) under these conditions.

Ionic species in the pore fluid are transported across the soil mass both by electromigration and also by electroosmotic transport [2,14,20,25]. Fig. 4 presents a schematic representation of this migration process under an electric field. Acar and Alshawabkeh [2] introduce λ_e (the ratio of ionic mobility of a species to electroosmotic coefficient of permeability of a soil) as a transport number which provides a sense of the mass flux of species by ionic migration under electric fields with respect to electroosmosis. Fig. 5 presents the change in λ_e for hydrogen, hydroxyl, lead and carbonate ions versus the range of electroosmotic coefficient of permeability, k_e, reported in experiments. When k_e is maximum, the mass flux by electroosmosis will almost be equal to the mass flux by migration for most ionic species. Hydrogen and
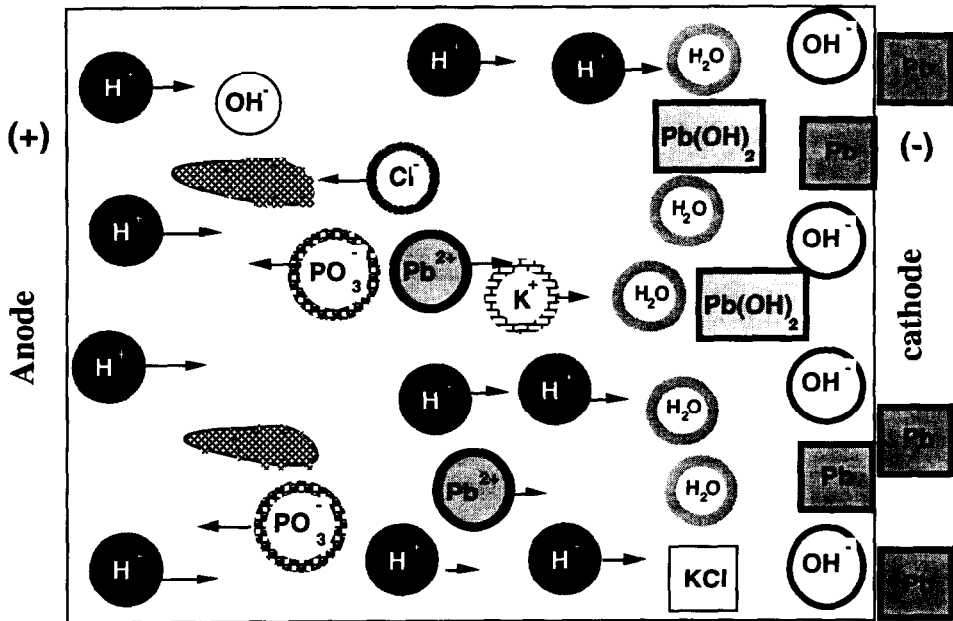
Fig. 4. Migration across the soil under an electrical field also depicting generation and transport of water electrolysis products (H^+/OH^- ions) and the water auto-ionization reaction close to the cathode.
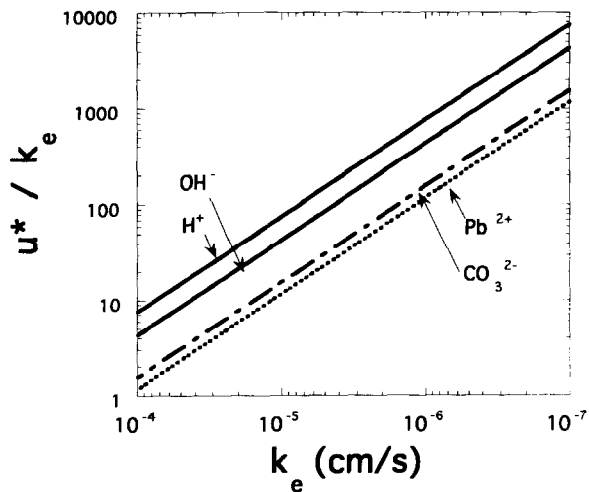

Fig. 5. The ratio of the effective ionic mobility, u*, of H^+, OH^-, Pb^{2+} and CO_3^{2-} to the coefficient of electroosmotic permeability, k_e, versus the electroosmotic coefficient permeability.
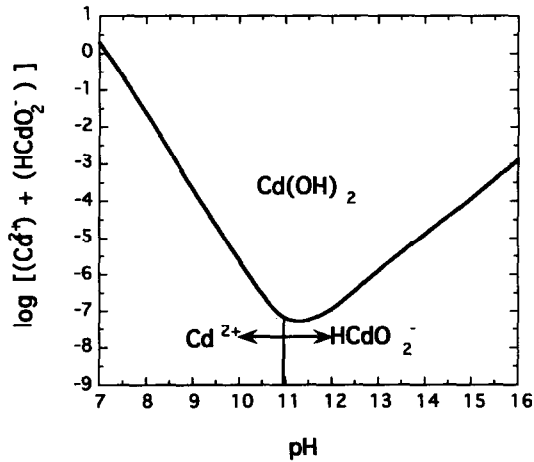
Fig. 6. The Pourbaix diagram for cadmium [32].

hydroxyl ion, however, will have an order of magnitude higher transport number mainly due to the relative ease with which these ions can associate/dissociate with water molecules as they migrate under electrical gradients. The complementary nature of migrational component of mass flux to electroosmotic mass flux is the reason why electrokinetic remediation can be a technically feasible and cost-effective means of extracting soluble and predominant species from all types of soils. Migrational flux will transport the species even when electroosmotic flux ceases or would not develop.

Electrolysis reactions at the electrodes need to be considered together with the mass flux of species that ensues in the electric field. Transport of the hydrogen (protons) and hydroxyl ions generated at the electrodes by the electrolysis reactions are also depicted in Fig. 4. The fact that the mobility of the proton under electrical field is about two times the hydroxyl ion mobility is a factor that can make it dominate a system that contains both [2]. In unenhanced electrokinetic remediation, the protons that transport across the soil mass meet the hydroxyl ion close to the cathode compartment resulting in generation of water within that zone [2, 4, 6]. The sweep of the acid front across the soil mass also assists in desorption of the cationic species concentrated on the soil surface. If desired, this hydrogen ion generation and transport can be used as an acid washing process in electrokinetic remediation. Transport of metal contaminant species in a soil capillary and their electrodeposition on the cathode and/or precipitation at their hydroxide solubility value within the zone close to the cathode also are shown in Fig. 4. As a result of the water autoionization reaction and species precipitation within this zone of pH change (from about 2 to over 7), the ionic conductivity decreases significantly within this zone (to less than 1 μS/cm).

For a proper assessment of the transport of a particular species, it is necessary to consider its behavior in an environment with widely varying pH values. Fig. 6 presents

the Pourbaix diagram for cadmium [32]. We note that cadmium, like most other heavy metals, could complex into a negatively charged species at high pH. This negatively charged species then could be transported towards the anode under the electric field. In unenhanced electrokinetic remediation, the rise in the pH in the cathode compartment may result in negative complexation of heavy metals and their transport towards the zone of pH change, ultimately precipitating as insoluble hydroxides within this zone [2, 12]. The formation of the low conductivity zone, transport of species to this zone, and precipitation within this zone can be avoided by using enhancement and conditioning schemes; e.g. depolarization of the cathode reaction by acetic acid [2, 31].

The authors note that the electrokinetic remediation technique requires the presence of a pore fluid in the soil pores both to conduct the electrical field and also to transport the species injected into, or extracted from, the soil mass. It may be possible to saturate certain partially saturated soils by electroosmotic advection of the anolyte [33], however, it is essential to engineer the process under such circumstances.

3. Treatable wastes and media

Electrokinetic remediation can be used to treat soils contaminated with inorganic species, organic compounds, and radionuclides. Inorganic species tested and reported include lead, cadmium, chromium, mercury, zinc, iron and magnesium [3, 6, 7, 9–11, 13, 18, 19, 31, 35]. Radionuclides tested include uranyl, thorium and radium [33]. Experimental data on the transport and removal of polar organic species such as phenol [5] and acetic acid [14] are reported, while transport of nonpolar ones such as BTEX compounds (benzene, toluene, ethylene and xylene) below their solubility values also have been disseminated [8]. Acar et al. [20] report that it was not possible to remove hexachlorobutadiene from kaolinite at concentrations varying from 10 mg/kg to 1000 mg/kg. Hexachlorobutadiene transport in kaolinite was only possible when sodium dodecylsulfate is used as a surfactant in the anode compartment. Applicability of the electrokinetic remediation technique to nonpolar organic species by enhancing the technique through the use of different micelles (surfactants) is under investigation [34].

The technique is envisioned also to be used for the injection of nutrients, electron acceptors and other process additives to affect and enhance in situ bioremediation of organic species [35]. Studies are ongoing at LSU and Electrokinetics Inc. to evaluate the feasibility of this scheme.

4. Operation and maintenance

A typical processing diagram is shown in Fig. 7. A series of anodes and cathodes are placed in the ground and a current is established across the electrodes. Processing
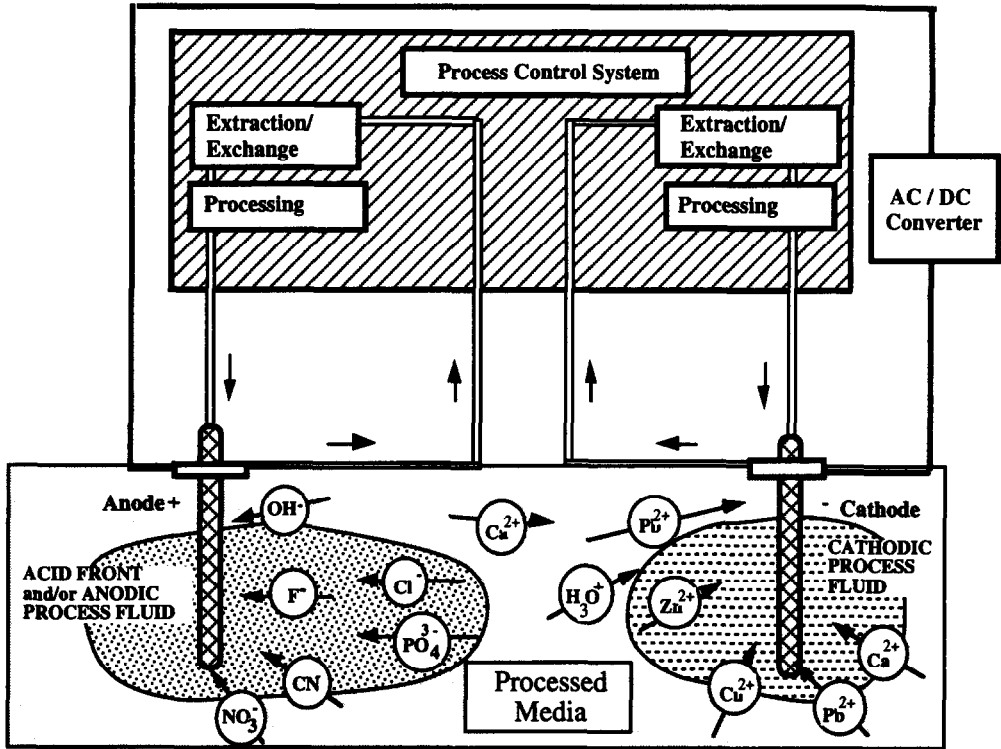
Fig. 7. A schematic diagram of one electrode configuration and geometry used in field implementation of the electrokinetic remediation technique [2].

fluids may be circulated at the electrodes. These fluids can serve both as a conducting media and as a means to extract/exchange the species and introduce others. Another use of processing fluids is for control and/or depolarization or modification of any or both electrode reactions. The electrode reactions are depolarized either to prevent premature precipitation of the incoming species at their hydroxide solubility values, or in establishing an enhanced transport of species. The process fluid chemistry can be conditioned to supply an influx of chemical species in the soil at the electrode receptacles. The advance of the process fluid (acid and/or the conditioning fluid) across the electrodes assists in desorption of species and dissolution of carbonates and hydroxides. Electroosmotic advection and ionic migration lead to their transport and subsequent removal. Some species electrodeposit on the electrodes, or they are extracted through the use of chemical processes or ion exchange systems within the process control container. We note that in partially saturated soils, the electrode configuration presented in Fig. 7 can be employed only when the permeability of the processed deposit is relatively low, or a low permeability deposit underlies this zone.
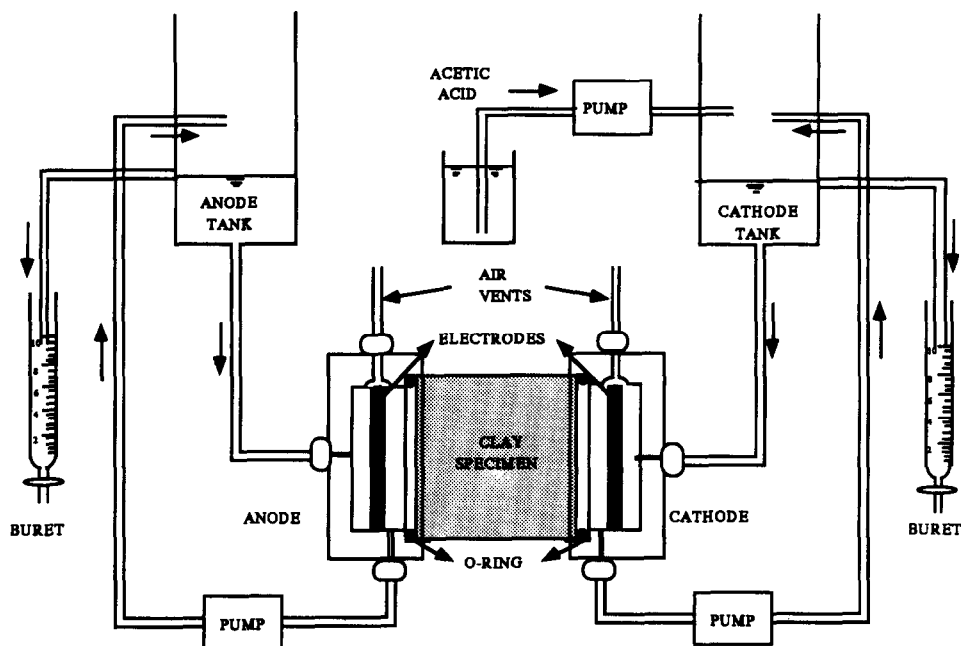
Fig. 8. A schematic diagram of the set-up used at Louisiana State University and Electrokinetic Inc. for the bench-scale testing of electrokinetic extraction of species from soils [31].

5. Bench- and pilot-scale applications

5.1. Bench-scale studies – inorganic species

Fig. 8 presents a one-dimensional test set-up used at Louisiana State University (LSU) and Electrokinetics Inc. for bench-scale testing of species extraction from soils. The set-up is designed to establish the rate and efficiency of removal in electrokinetic soil processing. Enhanced remediation experiments are conducted by circulating process fluids at both ends. Acar and Alshawabkeh [2] discuss different enhancement techniques for the extraction of heavy metals. Removal in this set-up is evaluated under a constant electrical current. Inert carbon electrodes are used to avoid the introduction of new species to the system through electrode oxidation and/or reduction. In bench-scale experiments, due to its low-cost, carbon is preferred over noble metals. In field implementation of the technique, the use of higher grade carbon anodes may be preferred, while low grade metal electrodes may be used as cathodes.

When a specimen of 10 cm diameter and 10 cm length is used and a current of about 5 mA is applied across a Georgia kaolinite specimen placed in the acrylic cylinder, an electroosmotic flow of over 80 ml a day may be encountered after an initial induction period of several hours. This flow gradually decreases to zero [3,6,36]. In the case that the ionic concentration of the species is high, it is possible to encounter no

electroosmotic flow. Acar et al. [3] have demonstrated the efficient removal of cadmium even when there is no electroosmotic flow, validating the hypothesis that electrical migration is as significant a species transport mechanism in electrokinetic remediation as electroosmosis. Thus the technique can be used efficiently both in sands and clays.

In a typical experiment with spiked specimens, testing is continued for a fixed period of time. The estimate of the test duration requires an estimate of the amount of acid needed to bring the pH of the soil down to a value which will release the species of concern. Once the species are solubilized, transport by ionic migration is on the order of 1–80 cm/day under an electric field of 1 V/cm. Buffer capacity tests are often necessary to determine the necessary H^+ ion production and/or addition. The time it will take for the acid front to reach a specific point across the electrodes can be estimated from the ionic mobilities of the species of concern and acknowledge of the relative transport efficiencies. Hydrogen ion mobility in the pore fluid is about 80 cm/day under an electric gradient of 1 V/cm. This rate decreases to about 1–8 cm/day in kaolinite due to sorption reactions coupled with other aqueous phase reactions (e.g. water autoionization reaction) and it will further decrease if dissolution reactions exist, i.e. if the ionic strength increases and the rate of the reactions are slow [36, 37]. In most cases, mass flux by migration will be at least one order of magnitude greater than that by diffusion [2, 37]. The voltage gradient may be increased above 1 V/cm; however, other considerations such as heating of the soil and the practical considerations for electrode spacing also need to be evaluated. Consequently, the test duration will vary from one soil to another. At this state of the art it is difficult to preestimate the duration of the experiments specifically due to the difficulty to speciate the salts in the soils and the need to conduct separate experiments to establish the dissolution kinetics of such salts with the incoming acid generated and/or introduced at the anode. For example, for a 10 cm diameter and a 10 cm long spiked kaolinite specimen processed at 100 μA/cm², at least one week of process time may be necessary. If species are present as precipitates, the duration of the tests will be longer.

In order to evaluate the effectiveness of contaminant desorption and transport, after a certain period of electrolysis, the specimen is removed and sliced into a number of segments (10 segments for a 10 cm specimen). Each is analyzed for pH, conductivity and concentration of the species. The electrodes and electrolytes are separately analyzed and the mass balance is calculated. Several bench-scale studies have been reported to establish the fundamentals of electrokinetic remediation of soils or slurries. Most of these studies are discussed by Alshwabkeh [37], Acar [1], Acar and Hamed [38] and Hamed [39]. Following is a brief summary of the results of some of the work disseminated by the researchers at LSU.

5.1.1. Lead

At LSU, the work to formalize the acid/base distributions under electric fields preceded tests to assess the feasibility of removing species by electrokinetics [21, 39]. Early experiments employed spiked Georgia kaolinite specimens. Fig. 9 presents the final lead profiles in lead spiked kaolinite specimens. Lead was first loaded at concentrations below the cation exchange capacity of this mineral (1.06 meq/100 g). In
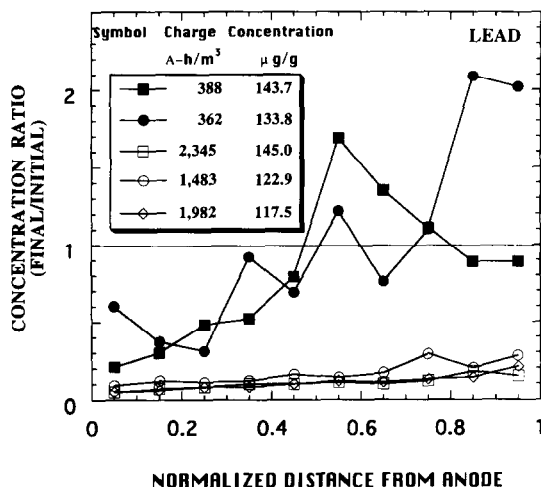
Fig. 9. Lead profiles across the electrodes in kaolinite spiked with 123 to 145 mg/kg of lead and processed under a current density of 127 μA/cm² (closed symbols are for shorter duration tests and less charge input in the system) [6, 39].

experiments with a shorter duration (or total charge passed), the lead was found redistributed across the specimen because of desorption from the mineral surface in the zone close to the anode compartment and precipitation close to the cathode at its hydroxide solubility limit [6]. In longer duration tests, however, the lead was found removed from the specimen due to the transport of the acid across the kaolinite specimen coupled with the prevailing electromigration of lead. The energy expended in these tests, which displayed complete removal of lead, varied between 30 to 60 kilowatt hours per cubic meter. In tests at higher concentrations of lead (up to 1500 mg/kg) removal was achieved across the cell, while a zone of precipitation was encountered close to the cathode compartment (Fig. 10). It is interesting to note that although the total charge input and the current density varied in these tests, most of the lead was found precipitated on/or close to the cathode. At the cathode compartment, the high concentration of the hydroxyl ions leads to precipitation of the incoming lead from the anode section. As previously discussed, a negatively charged lead complex can be formed at the cathode compartment. These species will be transported to the zone of pH change and they will precipitate at a lower pH, focusing all the lead in this zone.

5.1.2. Cadmium

Fig. 11 contains the results of experiments conducted to investigate cadmium removal from spiked kaolinite specimens at a concentration of about 99–114 mg/kg. Cadmium metal was found electrodeposited on the cathode and/or precipitated on the cathode as cadmium hydroxide [4]. These experiments with cadmium demonstrate that the transport efficiency and extraction can be as efficient in specimens that
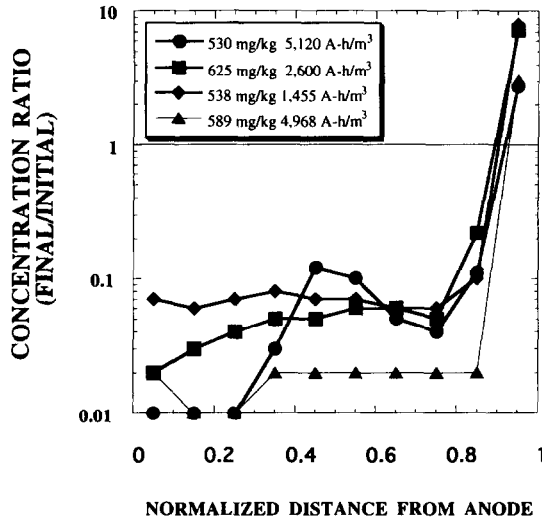
Fig. 10. Lead profiles across the electrodes in kaolinite spiked with 530 to 625 mg/kg of lead and processed under a current density of 127–370 µA/cm^2 (total charge input varies between 1500 and 5000 A h/m^3) [39].
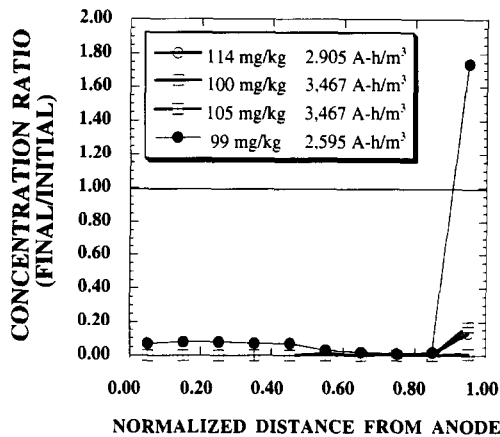

Fig. 11. Cadmium profiles across the electrodes in kaolinite processed at a current density of 370 µA/cm^2 (voltage gradients varied between 2 and 4 V/cm in a 10 cm length and 10 cm diameter specimen) [4].

did not display any electroosmotic transport as the specimens that did. This illustrates the significance of electrical migration for the transport of ionic species under electric fields. We also note that formation of the precipitate close to the cathode compartment has fluctuated the voltage across the specimen increasing the energy expenditure [4].
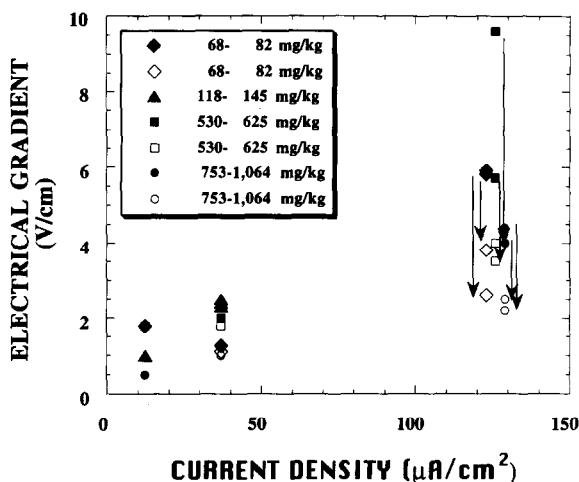
Fig. 12. The change of electrical gradient with respect to current density in kaolinite specimens spiked with lead (open symbols show the lower bound and closed symbols display the upper bound) [39].

5.1.3. Chromium

Studies have been conducted using kaolinite spiked with Cr^{3+}. The extraction of chromium in this oxidation state from kaolinite at initial concentrations of about 100 mg/kg by unenhanced electrokinetic processing is complicated by the ease of hydrolysis of this heavy metal [39]. The relatively low concentration of this heavy metal with respect to the cation exchange capacity of this clay (1.06 meq/100 g), stronger sorption of chromium on the clay surface and its precipitation due to lower hydroxide solubility value are among the reasons why a low efficiency of removal (50% or less across the specimen) is obtained in these tests.

5.1.4. Concentration and current density effects

Experiments by Hamed [39] have studied the effect of the level of concentration and current density on removal rates. It was interesting to find out that increasing the current density did not assist removal efficiency but increased the energy expenditure. Fig. 12 shows that electrical gradients increased with an increase in current density. It is noted that the current density multiplied by the average electric gradient across the cell gives the power expenditure [4]. Erratic fluctuations in the electrical gradient increased the energy expenditure in tests at higher current densities. Random precipitation of species in the high pH zone close to the cathode compartment is expected to form the high resistivity zones, which in turn cause fluctuations of the electrical potential difference across the electrodes. Such precipitation is a consequence not only of the higher pH but also of the metal concentration (Fig. 5).

5.1.5. Radionuclides

Acar et al. [33] have studied removal of uranyl, thorium and radium salts from spiked Georgia kaolinite using unenhanced electrokinetic remediation. Uranyl nitrate
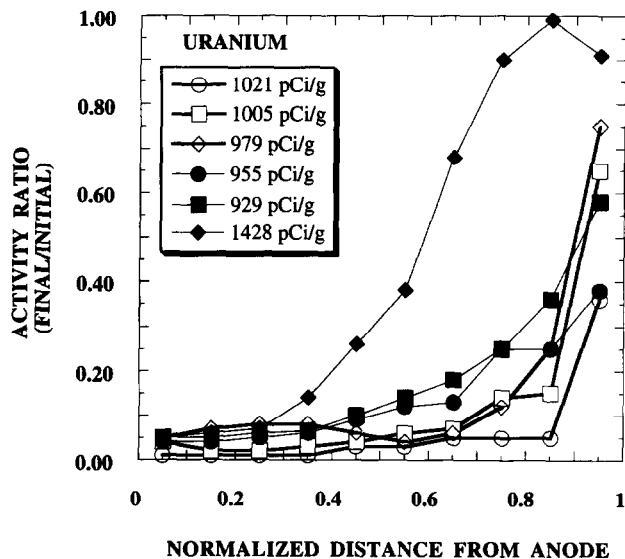
Fig. 13. Uranyl profiles across the electrodes in kaolinite spiked with uranyl nitrate and processed for 85 to 550 h under a current density of 127 μA/cm² (closed symbols are for shorter duration tests; energy expenditure varied between 84 and 205 kWh/m³) [33].

was used to spike the kaolinite. The results are presented in Fig. 13. The precipitate close to the cathode compartment is uranium hydroxide. This premature precipitation of the migrating ions, when confronted with the hydroxide ions generated at the cathode, is the fundamental reason why conditioning techniques are necessary. Although uranyl ion displayed ease in transport, extraction of thorium and radium was not successful using unenhanced electrokinetic remediation. It is hypothesized that radium may form insoluble salts with the kaolinite hindering the mobilization and transport process. Electrokinetic remediation technique will not be successful if the species of concern are salts that cannot be dissolved by the acid generated by the electrolysis reaction or one that may be introduced at the anode and transported across the soil.

5.1.6. Enhancement/conditioning

The effects of injecting chemical conditioners at the anode and the cathode are currently being investigated by Electrokinetics Inc. in collaboration with the US Army Waterways Experiment Station at Vicksburg, Mississippi [31]. These conditioners can modify the chemical reactions that take place at the electrodes and enhance the effectiveness of the system. For example, acetic acid depolarizes the reaction at the cathode. When acetic acid is added at the cathode, the main reaction becomes the reduction of proton and evolution of hydrogen. The migration of acetate anions into the system, create soluble complexes since most acetate salts are soluble. In one test, acetic acid successfully solubilized uranium at 1000 mg/kg (Fig. 14). In this
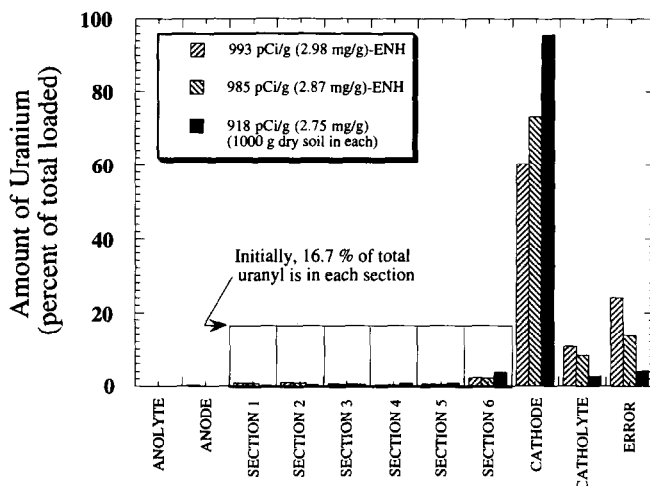
Fig. 14. Uranyl mass balance across the specimen in tests where the cathode reaction is depolarized by conditioning the cathode using acetic acid [2].

test, uranium was solubilized and removed in the effluent as well as precipitating at the cathode as hydroxide.

Similar studies were conducted on clays contaminated with thorium at concentrations of 1500 to 2000 mg/kg. Thorium ion has four charges and adsorbs very strongly onto clay. LSU researchers have proposed that conditioning the cathode with acetic acid will prevent the formation of the upstream base which causes the insoluble metal hydroxide precipitation that blocks the pores of the clay. Wieberen [40] has proposed the use of hydrochloric acid to condition the cathode reaction. There are concerns with the use of this acid in electrokinetic remediation: (1) chloride ion may be oxidized at the anode releasing chlorine gas, (2) some chloride salts are insoluble (e.g. lead chloride), and (3) its introduction in the groundwater may pose problems.

The use of chelating agents is another option for complexing and transporting heavy metals or radionuclides. The use of EDTA in extracting zinc is reported [41]. Currently, the LSU group also is trying to identify a chelating agent to solubilize radium, which ordinarily forms a highly insoluble sulfate that is hypothesized to intercalate or bind strongly with the clay structure. As a result, radium resists electrokinetic removal in bench-scale studies. Extraction was not possible without enhancement in tests at 1 ng/g and as many as 3 pore volumes of flow. A chelating agent could be used to process the media with mixed radionuclides, such as radium, strontium and thorium. Alternatively, radium-contaminated media could be flushed with ammonium ions introduced at the cathode in the form of ammonium hydroxide and the soil could be maintained basic instead of acidic. There also exists the possibility of flushing the soil with the base generated at the cathode compartment, if the acid produced at the anode is depolarized and neutralized.
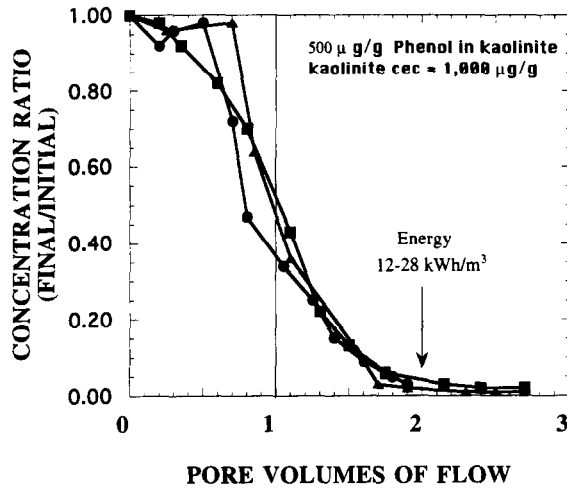
Fig. 15. Phenol breakthrough in the effluent in electrokinetic processing of phenol spiked kaolinite [5].

The effectiveness of micelles for the removal of polar organic compounds, such as hexachlorobutadiene, is being studied. A micelle is an aggregate of charged particles that is nonpolar on the inside. Polar organic contaminants can be solubilized into the mobile micelles allowing them to be flushed from the soil [33]. Preliminary results show that negatively charged micelles at the anode permit transport of hexachlorobutadiene from kaolinite [20]. However, the interactions between the surfactant and the clay surface are quite complex so studies in this avenue are as yet premature. We find that some cationic surfactants may even reverse the electroosmotic flow in a capillary.

5.2. Bench-scale studies – organic species

5.2.1. Phenol

Phenol removal has been investigated by spiking kaolinite specimens with 500 mg/kg of phenol. The results are presented in Fig. 15. The effluent concentration is presented as a function of pore volumes of flow [5]. It is quite interesting to note that most of the phenol originally in the kaolinite specimens is removed in two pore volumes of flow. Phenol is one of the easier organic species to remove by electrokinetic soil processing because it is water miscible and it protonates in an acid to produce positively charged species. It would function just as any other cationic species in removal by electroosmotic advection, electromigration and the protonation generated by the acid front. It is noted that only 10 to 30 kWh/m^3 of energy expenditure and two pore volumes of flow was sufficient to remove 95% of the phenol in the specimen.
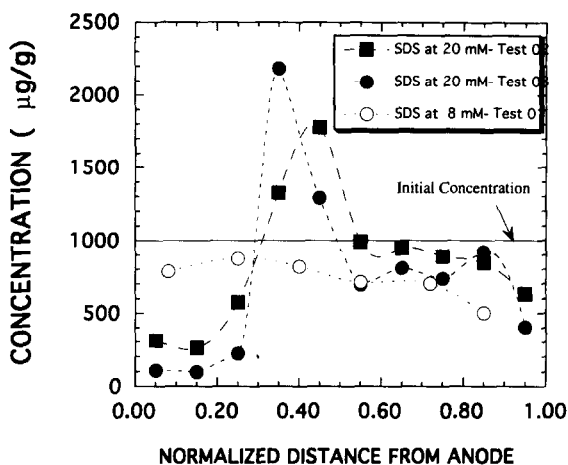
Fig. 16. Hexachlorobutadiene transport in kaolinite when sodium dodecylsulfate is introduced in the anode compartment at concentrations above and below the critical micelle concentration [5].

5.2.2. Hexachlorobutadiene

It was not possible to remove hexachlorobutadiene from kaolinite at concentrations ranging from 10 mg/kg to 1000 mg/kg, although there was an electroosmotic flow in the experiments. Hexachlorobutadiene was transported only when sodium-dodecylsulfate (SDS), a negatively charged surfactant, was placed in the anode compartment at a concentration above its critical micelle concentration (CMC) and the process was reinitiated (Fig. 16). As this negatively charged species will migrate towards the anode, net transport displayed in Fig. 16 can be attributed either to electroosmotic advection or possibly a more complex interaction among the species.

5.2.3. TNT

Surfactant enhanced removal of TNT and other explosive residues by electrokinetics is currently under investigation at LSU [42].

5.2.4. Pilot-scale studies

In collaboration with the Environmental Protection Agency's Risk Reduction Engineering Laboratory (EPA-RREL), the LSU–Electrokinetics Inc. group has completed ex situ pilot-scale studies of electrokinetic soil processing in the laboratory. Laboratory studies indicate that lead is removed from 2 ton specimens of kaolinite at an energy cost of about \$15 to \$30/m^3 within a period of 3 months [36, 37].

At a site in Baton Rouge, lead concentrations at one location were found to be as much as 100 000 mg/kg. These high concentrations, together with presence of basic shells rendering calcium concentrations of up to 90 000 mg/kg, have been major

obstacles to the efficiency of electrokinetic processing of the soil in this region. Migration and precipitation of calcium as bicarbonates and hydroxides are observed to clog the pores preventing transport of lead [2]. It was found that it would be necessary to supply as much as 10 times the amount of acid necessary without the basic shells in order to remove the lead [2]. However, at locations where the concentrations are lower (10 000 mg/kg) and such high concentrations of shells are not encountered, bench-scale studies demonstrate that lead can be successfully removed by unenhanced and enhanced remediation.

Specimens retrieved from real-world sites have been successfully remediated in bench-scale experiments at Electrokinetics Inc. US Army Waterways Experiment Station partnering with Electrokinetics Inc. is in the process of carrying out a site specific pilot-scale study of electrokinetic remediation in Louisiana. Pilot-scale field studies have also been reported in the Netherlands on soils contaminated with lead, arsenic, nickel, mercury, copper and zinc [10, 43]. In one study, the process has removed 75% of the lead from fine sand with an initial concentration of 9000 mg/kg. Another study achieved a 90% removal of arsenic from clay with an initial concentration of 300 mg/kg. Both of these studies used energy levels of 60 to 200 kWh/m^3 and involved chemical conditioning of the anolyte and the catholyte [40].

6. Design/analysis methods

There is a need to develop design/analysis packages for the field implementation of the technology. Empirical, semi-empirical correlations, and comprehensive theoretical modeling are possible avenues to follow. Theoretical modeling efforts enhance the state of the art and understanding as long as the prediction obtained with these models are compared with carefully conducted, well-instrumented pilot-scale and field-scale studies.

A comprehensive theoretical treatise of electrokinetic phenomena, including the mechanics and the chemistry associated with the process, has been presented by Alshawabkeh and Acar [25] and Alshawabkeh [37]. Alshawabkeh and Acar [36, 44] demonstrate that the predictions of this model provide very good agreement with the results of the pilot-scale studies conducted.

7. Advantages and limitations

The advantage of the technology is its potential for cost-effective in situ and/or ex situ use. The fact that the technique requires a conducting pore fluid in a soil mass may be considered as one shortcoming if there are concerns in introduction of an external fluid in the soil. We also note that the technique requires that the species be solubilized either by the advancing acid front or by chemicals introduced in the process fluid. If this solubilization cannot be achieved, it is not possible to extract the species of interest.

8. Summary and conclusions

The increasing demand to solve the challenging problems in environmental restoration has stimulated the desire to use electrical fields for subsurface species transport. Multi-component species transport under electric fields has become an area that has gained increasing attention and interest in the last decade. Species transport mechanisms under electric fields are now proposed to be employed for the in situ remediation of soils from inorganic and organic species, for the injection of nutrients, electron acceptors and other process additives in in situ bioremediation of subsurface deposits, for the injection of surfactants that enhance solubilization and transport, for the injection of grouts in soil stabilization and waste containment, for precipitation of species in migrating plumes, for soil and pore fluid characterization and species extraction using penetrating probes, for diversion systems for contaminant plumes, and for leak detection systems in containment barriers and repair of failing containment barriers. Support by the Environmental Protection Agency, the Department of Defence (US Army Waterways Experiment Station), the Department of Energy, the National Science Foundation, and private industry (e.g. Dow Chemical, E.I. DuPont and deNemours Company, Monsanto Corporation and the General Electric Company) coupled with the efforts of researchers from academic and public institutions have demonstrated the feasibility of moving electrokinetic remediation to pilot-scale testing and demonstration stages. This technique is quite tempting since it would offer a solution to remediate sites which would otherwise be cost-prohibitive. There exists the need to conduct well-planned and well-instrumented pilot-scale and field studies to evaluate the technology in the field. Timely dissemination of the successes/failures, controversial aspects, the difficulties encountered in these efforts and establishment of a feedback mechanism between the field practitioners and the engineering/scientific research community will pave the path to potential commercialization and wide-scale implementation of the electrokinetic remediation technology.

References

[1] Y.B. Acar, Electrokinetic soil processing; a review of the state of the art, in: R. Borden and I. Juran (Eds.), Grouting, Soil Improvement and Geosynthetics, Proc. of ASCE Grouting Conference, New Orleans, 1992, ASCE Geotechnical Special Publication No. 30, Vol. 2, pp. 1420–1432.

[2] Y.B. Acar and A.N. Alshawabkeh, Principles of electrokinetic remediation, Environ. Science and Technology 27 (1993) 2638–2647.

[3] Y.B. Acar and R.J. Gale, Electrochemical Decontamination of Soils and Slurries, US Patent No. 5, 137, 608, Commissioner of Patents and Trademarks, Washington, DC, August 11, 1992.

[4] Y.B. Acar, J.T. Hamed, A.N. Alshawabkeh and R.J. Gale, Cadmium Removal from Soils by Electrokinetics, Géotechnique, Thomas Telford House, Institution of Civil Engineers, London, United Kingdom, 44 (1994) 239–254.

[5] Y.B. Acar, H. Li and R.J. Gale, Phenol removal from kaolinite by electrokinetics, J. Geotechnical Eng., 118 (1992) 1837–1852.

[6] J.T. Hamed, Y.B. Acar and R.J. Gale, Pb(II) removal from kaolinite using electrokinetics, J. Geotechnical Eng., ASCE, 112 (1991) 241–271.

[7] S. Banerjee, J. Horng, J.F. Ferguson and P.O. Nelson, Field scale feasibility of electrokinetic remediation, Unpublished Report Presented to USEPA, Land Pollution Control Division, RREL, CR 811762-01 (1990) p. 122.

[8] C.J. Bruel, B.A. Segall and H.T. Walsh, Electro-osmotic removal of gasoline hydrocarbons and TCE from clay, J. Environ. Eng., ASCE, 118 (1992) 84–100.

[9] D. Kelsh (Ed.), Proceedings of the Electrokinetics Workshop, Atlanta, GA, Jan. 22–23, 1992, Atlanta, Ga; Office of Research and Development, US DOE, Washington, DC, 1992.

[10] R. Lageman, P. Wieberen and G. Seffinga, Electro-reclamation: theory and practice, Chemistry and Industry, Society of Chemical Industry, London, 9 (1989) 585–590.

[11] S. Pamukcu and J.K. Wittle, Electrokinetic removal of selected heavy metals from soil, Environ. Prog., 11 (1992) 241–250.

[12] R.F. Probstein and R.E. Hicks, Removal of contaminants from soils by electric fields, Science, 260 (1993) 498–504.

[13] D.D. Runnels and C. Wahli, In situ electromigration as a method for removing sulfate, metals and other contaminants from ground water, Ground Water Monitoring Review, 11 (1993) 121.

[14] P.O. Renauld and R.F Probstein, Electro-osmotic control of hazardous waste, Physicochemical Hydrodynamics, 9 (1987) 345–360.

[15] D.D. Runnels and J.L. larson, A laboratory study of electromigration as a possible field technique for the removal of contaminants from ground water, Ground Water Monitoring Review, Summer 1986, 81–91.

[16] A.P. Shapiro and R.F. Probstein, Removal of contaminants from saturated clay by electroosmosis, Environ. Sci. Technol., 27 (1993) 283–291.

[17] A.P. Shapiro, P. Renauld and R.F. Probstein, Preliminary studies on the removal of chemical species from saturated porous media by electro-osmosis, Physicochemical Hydrodynamics 11 (1989) 785–802.

[18] B.M. Shmakin, The method of partial extraction of metals in a constant current electrical field for geochemical exploration, J. Geochem. Explor., 23 (1985) 35–60.

[19] J.K. Wittle and S. Pamukcu, Electrokinetic Treatment of Contaminated Soils, Sludges and Lagoons, Final Report to Argonne National Laboratory, Contract No: 02112406, Electro-Petroleum Inc., Wayne, PA (1993) p. 49.

[20] Y.B. Acar, A.N. Alshawabkeh and R.J. Gale, Fundamentals Aspects of Extracting Species from Soils by Electrokinetics, Waste Management, Vol. 12, Pergamon, New York, 1993, 1410–1421.

[21] Y.B. Acar, R.J. Gale, G. Putnam and J.T. Hamed, Electrochemical processing of soils: its potential use in environmental geotechnology and significance of pH gradients, in: Proc. of the Sec. Int. Symp. on Environmental Geotechnology, Shanghai, China, May 14–17, 1989, Envo Publishing, Bethlehem, PA, 1, 25–38.

[22] Y.B. Acar and A.N. Alshawabkeh, Modeling conduction phenomena in soils under an electrical current, in: Proc. of the 15th Int. Conf. on Soil Mechanics and Foundation Engineering, New Delhi, India, Oxford and IBH Publishing Co., New Delhi, India, (2) 1994, pp. 669–672.

[23] Y.B. Acar, R.J. Gale and G. Putnam, Electrochemical processing of soils: theory of pH gradient development by diffusion and linear convection, J. Environ. Sci. and Health, Part (a); Environ. Sci. Eng., 25 (1990) 687–714.

[24] Y.B. Acar, J.T. Hamed, R.J. Gale and G. Putnam, Acid/base distribution in electro-osmosis, Bulletin of the Transportation Research, Record No. 1288, Soils Geology and Foundations, Geotechnical Eng. (1990) 23–34.

[25] A.N. Alshawabkeh and Y.B. Acar, Removal of contaminants from soils by electrokinetics: a theoretical treatise, J. Environ. Sci. Health, 27 (1992) 1835–1861.

[26] L. Bjerrum, J. Moum and O. Eide, Application of electro-osmosis on a foundation problem in a Norwegian quick clay, Geotechnique, London, England, 17 (1967) 214–235.

[27] L. Casagrande, Stabilization of soils by means of electro-osmosis – state of the art, J. Boston Society of Civil Engineers, ASCE, 69 (1983) 255–302.

[28] M.I. Esrig, Pore pressures, consolidation, and electrokinetics, J. of Soil Mechanics and Foundation Division, ASCE, 94 (1968) 899–921.

[29] D.H. Gray and J.K. Mitchell, Fundamental aspects of electro-osmosis in soils, J. Soil Mechanics and Foundation Division, ASCE, 93 (1967) 209–236.

[30] J. Eykholt and D.E. Daniel, Impact of system chemistry on electroosmosis in contaminated soil, J. Geotechnical Eng., ASCE, 120 (1994) 797–815.

[31] Y.B. Acar, S. Puppala, R. Marks, R.J. Gale, A.N. Alshawabkeh and M. Bricka, An investigation of selected enhancement techniques in electrokinetic remediation, Report presented to US Army Corps of Engineers Waterways Experiment Station, Electrokinetics Inc., Baton Rouge, Louisiana, 1994.

[32] M. Pourbaix, Atlas of Electrochemical Equilibra, Translated from French by J.A. Franklin, Brussels, CEBELCOR.

[33] Y.B. Acar, R.J. Gale, A. Ugaz, S. Puppala and C. Leonard, Feasibility of removing uranium, thorium and radium from kaolinite by electrochemical soil processing, Phase I Project Report, USEPA-RREL Cooperative Agreement No. CR816828-01-0, Electrokinetics Inc., Baton Rouge, July 1992, p. 243.

[34] M.R. Taha, Y.B. Acar, R.J. Gale and M. Zappi, Surfactant Enhanced Electrokinetic Remediation of NAPLs in Soils, First International Congress on Environmental Geotechnics, Edmonton, Alberta, Canada, July 10–15, 1994 (in press).

[35] R.E. Marks, Y.B. Acar and R.J. Gale, In situ remediation of contaminated soils containing hazardous mixed wastes by bio-electrokinetic remediation and other competitive technologies, in: D.L. Wise and D.J. Trantolo (Eds.), Remediation of Hazardous Waste Contaminated Soils, Vol. 18, Marcel Dekker, New York, 1994, pp. 405–436.

[36] A.N. Alshawabkeh and Y.B. Acar, Electrokinetic remediation: I. pilot-scale study, J. Geotechnical Eng., ASCE (submitted: June 1994, in review).

[37] A.N. Alshawabkeh, Theoretical and experimental modeling of removing contaminants from soils under electric field, Ph.D. Dissertation, Louisiana State University, 1994.

[38] Y.B. Acar and J.T. Hamed, Electrokinetic soil processing in remediation/treatment; synthesis of available data, Bulletin of the Transportation Research, Record No. 1312 (1992) 152–161.

[39] J.T. Hamed, Decontamination of soil using electroosmosis, Ph.D. Dissertation, Louisiana State University, 1990.

[40] P. Wieberen, A process for electroreclamation of soil material, an electric current system for application of the process, and an electrode housing for use in the electric current system, European Patent Specification, Publication Number 0312174 B1 (1992).

[41] R.F. Probstein, Remediation of Metal contaminated soil by Electric fields, in: Proc. of the Twentieth Annual USEPA-RREL Research Symposium, EPA/600/R-94/011 (1994) 210–215.

[42] Y.B. Acar and R.J. Gale, TNT removal from soils by electrokinetics, Proposal submitted to USArmy-WES, Office of Research Coordination, Louisiana State University, 1992.

[43] R. Lageman, Electroreclamation, Environ. Sci. Technol., 27 (1994) 2648–2650.

[44] A.N. Alshawabkeh and Y.B. Acar, Electrokinetic remediation: II. theory, J. Geotechnical Eng., ASCE (submitted: June 1994, in review).