

Review

Electro kinetic remediation of contaminated habitats

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Electrokinetics (EK) is a process that separates and extracts heavy metals, radionuclides and organic contaminants from saturated or unsaturated soils, sludge, and sediments. A low intensity direct current is applied across electrode pairs that have been implanted in the ground on each side of the contaminated soil mass. The electrical current causes electroosmosis and ion migration (electromigration) and electrophoresis, which move the aqueous phase contaminants in the subsurface from one electrode to the other. Contaminants in the aqueous phase or contaminants desorbed from the soil surface are transported towards respective electrodes depending on their charge. The results of several laboratory studies have demonstrated excellent contaminant removal efficiencies by the use of the electrokinetic process (Pamukcu and Wittle, 1992; Probst and Hicks, 1993). However, recent field applications of the electrokinetic technology have also shown anomalous results (Guzman et al., 2000; Lageman, 1993), which have been attributed mainly to the interaction of the contaminants with naturally occurring electrolytes, humic substances and mixed wastes which are present in the subsurface (Lageman, 1993; Acer et al., 1994). In order to use electrokinetic remediation in the field successfully, the different geochemical interactions that occur in the field soils under induced electricity must first be accurately determined. In addition, mechanisms and their effects can be altered in order to enhance the removal efficiency of lock in non-critical contaminants in the soil by immobilization. Numerous field studies have proven the commercial viability and technical effectiveness of the electrokinetic remediation. However, there is still a lot of scope and avenues to cover in this newly developed technology which are subject to further research.

Key words: Electorkinetics, electromigration, electrolysis, electroosmosis.

INTRODUCTION

In recent years, the contamination of subsurface soils and groundwater from landfills, industrial activities and other sources has generated enormous public concern and has created an urgent need to find feasible solutions to the problem. Soil and groundwater contamination has been one of the most expensive and time-consuming issues faced by environmental professionals (Reddy et al., 2006). Although many different *in situ* soil remediation technologies are available, electrokinetics offers many advantages. Being easy to operate, it is economically viable and applicable for a variety of contaminants. This

review presents an overview of the electrokinetic phenomena, as well as previously performed research activities.

ELECTROKINETICS

The term "electrokinetics" (EK) refers to the introduction of an electrical gradient (as opposed to a hydraulic or pressure gradient) in the soil to mobilize or promote the migration of water and/or various chemical species towards the preferred electrode. Electrokinetics as a soil remediation technology is relatively young, having become an alternative procedure for the removal of toxic chemical species in ionic form in the soil (Lageman et al., 1989) in the late 1980's.

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Abbreviations: EK, Electrokinetics; DC, direct current; CEC, cation exchange capacity; TCE, halogenated hydrocarbon; BTEX, non halogenated organic pollutants; PAH, polynuclear aromatic hydrocarbons.

electrode pairs that have been implanted in the ground on each side of the contaminated soil mass. The electrical current causes electro osmosis and ion migration (electromigration) and electrophoresis, which move the aqueous phase contaminants in the subsurface from one electrode to the other. Contaminants in the aqueous phase or contaminants desorbed from the soil surface are transported towards respective electrodes depending on their charge. The contaminants may then be extracted to a recovery system or deposited at the electrode. Surfactants and complexing agents can be used to increase solubility and assist in the movement of the contaminant.

ELECTROKINETIC REMEDIATION

Genesis /development of electrokinetic remediation

Reuss (1808) observed the electrokinetic phenomena when a DC current was applied to a clay-water mixture. Water moved through the capillary towards the cathode under the electric field. When the electric potential was removed, the flow of water immediately stopped. Napier (1846) distinguished electroosmosis from electrolysis and found the electric potential difference through a membrane resulting from streaming potential. Helmholtz first treated electroosmotic phenomena analytically in 1879. A mathematical basis was provided. Pellat (1904) and Smoluchowski (1921) later modified it to apply to electrophoretic velocity.

Cassagrande's studies in stabilizing clays by Electro-osmosis started in the early 1930's. The introduction of an electrical gradient into the soil to stabilize it mainly by removal of the water has its beginnings 70 years ago. Most of the studies during this early period were directed towards removal of water for soil stabilization and were generally concentrated on the dewatering of fine gravel soils by electroosmosis.

Several Russian researchers used electromigration in prospecting for metals in the 1960's. The early 1980's showed marked interest in the exploration of EK Technologies for the removal of toxic chemical species in ionic form in the soil in Europe and the US (Lageman et al., 1989). This successful application encouraged further researches and field studies resulting in breakthroughs in the understanding of the various processes in EK for *in situ* remediation of contaminated soils (Table 1).

Process and mechanisms

When an electric field is created across a soil volume, it provides a driving force that may induce mass movement of particles, similar to the effect of other driving forces, such as pressure gradient, concentration gradient and thermal gradient. In particular, the application of an electric field causes the following main transport

phenomena in soils: Electroosmosis, electromigration, electrophoresis. All these electrokinetic phenomena are highly influenced by the surface charge densities of the soil particles, and therefore by the soil mineralogical composition.

Electroosmosis

Electroosmosis is a bulk transport of water, which flows through the soil as a result of the applied electrical field (Lynch et al., 2007). The fluid migration occurs mostly from the anode to the cathode, due to the predominance of a negative charge on the soil particle surfaces. In fact, the electroosmotic flow is caused by the fact that when an electric field is applied to a soil, the excess of cations close to soil particles surface (double layer) tend to move towards the cathode. The movement of these ions and of the water molecules associated with these species (hydration shells), imparts a net strain on the pore fluid surrounding the hydrations shell.

This strain is transformed into a shear force because of the viscosity of the pore fluid. In sum, as there is usually an excess of cations close to soil particles, the electric fields leads to a net force towards the cathode which results in a pore fluid flux in this direction (Acar et al., 1995). Hence, the electric field causes the pore fluid to flow from the anode compartment to the cathode, producing a flux and forcing the water table to arise in the cathode compartment.

Electromigration

The second transport mechanism generated by the voltage gradient is electromigration, which is the movement of ions in the pore solution under the influence of an electric field. Positive ions (cations) migrate towards the cathode while negative ions (anions) are transported towards the anode. Because of electromigration, ions tend to concentrate near the opposite charged electrode (Reddy et al., 2006).

The electromigration of cations and anions towards the electrode opposite in charge is proportional to the ion concentration in the pore water solution and to the electric field strength (Kim et al., 2005). The ionic mobility is a term used to describe the rate of migration of a specific ion species under a unit electric field. In soils, the rate of ionic migration can be better defined by the effective ionic mobility, which also accounts for soil porosity and tortuosity, which can significantly affect ion migration (Alshawabkeh, 2001).

Electrophoresis

Electrophoresis consists of the movement of charged particles and colloids under the influence of an electrical

Table 1. Summary of electrokinetic investigation.

Contaminant	Investigator	Soil type	Chemical constituent	Initial (ppm)	Current (mA/cm ²)	Duration (h)	Removal (%)	
Inorganics	Lageman et al. (1989)	Fine sand, river slush	Cd, Cr, Ni, Pb, Hg, Cu, Zn	0.5 – 901	3.94	16	50 – 99	
	Hammed et al. (1991)	Kaolinite	Pb(II)	118 – 145	0.012 – 0.037		75 – 95	
	Pamukcu and Wittle (1992)	Kaolinite, montmorillonite, sand-clay mix	Cd, Co, Ni, Sr	40 – 8603	3.94	24 – 48	16.5 – 95	
	Lindgren et al. (1991)	Fine to medium sand	Cr, dye mix	420	0.23 – 0.85	1.5 – 20.5	85	
	Probstein and Hicks (1993)	Kaolinite	Zn	500	1.0 -2	16	98	
	Eykholt and Daniel (1994)	Kaolinite	Cu		0.25 – 0.275	16	95	
	Acar et al. (1994)	Kaolinite	Cd(II)	99 – 114	0.037	716 – 1027	90 – 95	
	Shapiro et al. (1989); Hicks and Tondorf (1994)	Kaolinite	Phenol	125	3.94	960 – 2400	95	
	Organics	Acar et al. (1992)	Kaolinite	Phenol	500	0.037	78 – 144	85 – 95
		Bruell et al. (1992)	Kaolinite	Benzene, TCE, toluene, <i>m</i> -xylene, hexane, isooctane	0.4 – 150	0.4	48 – 600	7 – 27
Radionuclide	Acar et al. (1992); Ugaz et al. (1994)	Kaolinite	Uranium, thorium, radium	50 – 1000 Ci/g	0.01	520	95	

field. When a direct current (DC) electric field is applied across a colloidal suspension, charged particles and colloids that are suspended in the pore fluid are electrostatically attracted to one of the electrodes and repelled from the other. Similarly to the electromigration process, positively charged particles tend to move towards the cathode and negatively charged particles tend to move towards the anode. For example, negatively charged clay particles tend to move towards anode (Ahmad, 2004). Usually, for environmental applications, electrophoresis is less important than electroosmosis and electromigration in terms of mass flux although in some cases

electrophoresis may play a role in decontamination, e.g. if the migrating colloids have the contaminants adsorbed on them.

Factors affecting electrokinetic technology

Electromigration rates in the subsurface depend upon grain size, ionic mobility, contamination concentration, total ionic concentration, and significantly upon the soil pore water current density and pH. The direction and quantity of the contaminant movement is influenced by the contaminant concentration (anions versus cations), soil

type and structure, pH, interfacial chemistry, and current density of the soil pore water. The efficiency of extraction relies upon several factors such as the type of species, their solubility in the specific soil, their electrical charge, their concentration relative to other species, their location and form in the soil, and availability of organic matter in the soil. Electrokinetics is applicable in zones of low hydraulic conductivity, particularly with high clay content. The technology is most efficient when the cation exchange capacity (CEC) and the salinity are low. During electrokinetic treatment, electrolysis results in the formation of H⁺ and OH⁻. These migrate toward one another by

electrokinetic processes. As these two fronts meet, a rapid transition from low to high pH occurs, creating a region of minimum solubility of metals. These sharp discontinuities in *pH* induced within the soil mass by electrokinetics could result in a deposition front where minerals are precipitated in soil pores, markedly reducing permeability and inhibiting recovery. This can be prevented by flushing the cathode with water or a dilute acid to arrest the migration of the OH⁻ front into the soil (Cox et al., 1996).

The mass flux transported during the electrokinetic process depends on the transient geochemistry that takes place under the influence of an induced electrical field. Specifically, the sorption–desorption, precipitation–dissolution, and oxidation–reduction behaviour of the contaminants during the electrokinetic process significantly affect the remediation efficiencies.

Sorption refers to the partitioning of the contaminants from the solution or pore fluid to the solid phase or soil surface. Sorption includes adsorption and ion exchange and it is dependent on (1) The type of contaminant (2) the type of soil (3) the pore fluid characteristics. Desorption is the reverse process and is responsible for the release of contaminants from the soil surface. Both sorption and desorption are affected by soil pH changes caused by the migration of H and OH ions, which are produced by the electrolysis reactions (Acar and Alshawabkeh, 1993). The pH dependent sorption–desorption behaviour is generally determined by performing batch experiments using the soil and contaminant of particular interest.

The precipitation and dissolution of the contaminant species during the electrokinetic process can significantly influence the removal efficiency of the process (Acar and Alshawabkeh, 1993). The soil decontamination process is affected by the hydrogen ions generated at the anode migrating across the contaminated soil and neutralizing the hydroxyl ions at the cathode. However, in some types of soils, the migration of the hydrogen ions will be hindered due to the relatively high buffering capacity of the soil. The presence of the hydroxyl ions at the cathode will increase the pH value (pH 10 – 12).

In a high pH environment, heavy metals will precipitate, and the movement of the contaminants will be impeded. The high pH and the low heavy metals concentration condition at the cathode may also lead to the formation of a negatively charged complex species at the cathode compartment. The movement of these negatively charged complex species towards the anode and of the heavy metals towards the cathode relies upon the relative mobility of the hydrogen and hydroxyl ions. In other words, species migration ceases at a region closer to the cathode where the pH varies substantially because this is most likely to be where heavy metals accumulate and eventually precipitate, clogging soil pores and hindering the remediation process. For efficient contaminant removal, it is essential to prevent precipitation and to have the contaminants in dissolved form during the

electrokinetic process.

Oxidation and reduction reactions are important when dealing with metallic contaminants such as chromium. Chromium exists most commonly in two valence states; Trivalent chromium Cr(III) and hexavalent chromium Cr(VI). Cr (III) exists in the form of cationic hydroxides such as Cr(OH)₂ and it will migrate towards the cathode during electrokinetic remediation. However, Cr(VI) exists in the form of oxyanions such as CrO₄ which migrate towards the anode. The valence state depends on the soil composition, especially the presence of reducing agents such as organic matter and Fe(II) and/ or oxidizing agents such as Mn(IV), so it is important to know the valence state of metals and their possible redox chemistry. Electrode conditioning procedures are sometimes necessary to induce favourable geochemistry and, as a result promote greater remediation efficiency.

Advantages

Compared to conventional remediation technologies, electrokinetics has several advantages, such as the following:

Simplicity

It is easy to operate and requires simple equipment.

Safety

There is minimal exposure to the operating personnel and the surrounding environment.

Flexibility

It can be used as an *in-situ* or *ex-situ* remediation system, as a delivery system, as a containment system, or as a combination of these systems. It is applicable for a wide range of media: It may be used for soils, sludges, sediments, and/or groundwater. Electrokinetics is ideal for subsurface conditions that possess low permeability soils or soil deposits with stratified layers or lenses of variable permeability. Here the conventional remedial methods are commonly deficient. It is also applicable for a variety of contaminants: It may be used for metals, volatile or semi-volatile organic compounds, and radionuclides.

Disadvantages

Based on the results of laboratory tests and field applications, electrokinetics has been shown to be a

promising method of covering ionic and water-soluble contaminants. However, the process has the following limitations, such as: The electrokinetic process is limited by the solubility of the contaminant and the desorption of contaminants from the soil matrix. Heavy metals in their metallic state have not been successfully dissolved and separated from soil samples. The process is also not efficient when the target ion concentration is low and non-target ion concentration is high. Acidic conditions and electrolytic decay can corrode some anode materials. Conventional electrokinetic remediation requires contaminants to migrate from their initial location to an electrode. In some cases, the migration path could be long or there could be stagnant zones between wells where the rate of migration is particularly slow, both of which result in incomplete remediation of the contaminated zone. Moreover, sharply convergent electrical fields can result in heating and potential losses in the vicinities of electrodes. A pH-related deposition can cause contaminants to be removed from solution prior to arrival at the ground surface of point of removal (Murdoch, 1995). Electrolysis reactions in the vicinity of the electrodes may cause changes in ambient pH that may change the solubility and speciation of the contaminants. Heterogeneities or subsurface anomalies at sites, such as building foundations, rubble, large quantities of iron or iron oxides, large rocks or gravel, or submerged cover materials such as seashells, can reduce removal efficiencies. The presence of buried metallic conductors or insulators in the soil and reduction/oxidation and pH changes induced by the process electrode reactions can reduce the effectiveness of the process. Precipitation of species close to the cathode has been an impediment to the process. Heavy metals can prematurely precipitate close to the cathode at their hydroxide solubility value if the chemistry of the electrolyte at the electrodes is not altered or controlled (unenhanced electrokinetic remediation).

Solution to limitation

Desorption may be enhanced by using surfactants. Precipitation of the contaminants may be prevented by different methods, such as depolarizing the anode reaction by fluid conditioning such as calcium hydroxide and/or depolarizing the cathode reaction by an acid solution such as acetic acid. Oxidation may be enhanced by introducing oxidants such as hydrogen peroxide. In addition to the economic considerations, any of the selected procedures for conditioning the electrokinetic process must satisfy the following criteria: (1) Prevent the precipitation and adsorption of contaminants; (2) prevent the production of hydrogen ions in a relatively short period of time that will lead to the reduction of electro-osmosis flow and cationic contaminants removal; (3) prevent any reaction with contaminants that causes

precipitation; (4) prevent toxic effects on the soil.

Application

In situ electrokinetic treatment has been developed largely to address contaminants present in low permeability soils. Although this application is relatively new, the oil industry employs electrokinetics for enhanced recovery over the past several decades. The first successful demonstration of the use of electrokinetics for soil remediation was performed in the Netherlands in 1986. Contaminants affected by electrokinetic processes include: Heavy metals (Pb, Hg, Cd, Ni, Cu, Zn, Cr), radioactive species (Cs¹³⁷, Sr⁹⁰, Co⁶⁰, Ur), toxic anions (nitrates, sulphates), cyanides, petroleum hydrocarbons (diesel fuel, gasoline, kerosene and lubricating oils), explosives, mixed organic / inorganic contaminants, halogenated hydrocarbon (TCE), non halogenated organic pollutants (BTEX), polynuclear aromatic hydrocarbons (PAH).

RESEARCH GAPS AND FUTURE NEEDS

Electrokinetics is fast emerging as a cost effective *in-situ* and *ex-situ* soil remediation technology for the removal of organic and inorganic contaminants. Numerous field scale tests have proven the commercial viability and technical effectiveness of the process when compared to other commercially available methods. The ability of EK to enhance the removal process by various mechanisms has been shown to demonstrate its effectiveness in ground remediation technology. In addition, these mechanisms and their effects can be tailored or altered in order to: (1) Speed up removal with the use of reagents, chemical surfactants etc; (2) lock in non-critical contaminants in the soil by immobilization; (3) enhance removal of target contaminants while retarding some; (4) most field technologies use expensive nonreactive metals as electrodes such as titanium or titanium coated metals. The consideration for the use of carbon forms (graphite, activated carbon or carbon fibers) needs to be further exploited, as these are relatively inexpensive and easier to produce. In addition, carbon in its various forms is available and indigenous to almost all countries. Particularly in the third world, where environmental controls in the past have been absent or sadly lacking, use of locally available and cheap electrodes could render the technology available to the poorest of nations; (4) study of various electrode geometries to enhance electroconductivity or allow increased surface area exposure. Use of hollowed out electrodes to allow pumping in and out of absorption media and chemicals to enhance the EK Process; (5) Electricity usage of the process although still reasonable can be further reduced to increase the cost effectiveness of the process. This

can be addressed with the use of more electroconductive electrodes, enhancing the soil's electroconductivity by addition of chemicals, etc; (6) research into other reagents and chemical processes that can decompose the soluble organic contaminants or absorb contaminants for immobilization.

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