Electrokinetic soil remediation — critical overview

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Abstract

In recent years, there has been increasing interest in finding new and innovative solutions for the efficient removal of contaminants from soils to solve groundwater, as well as soil, pollution. The objective of this review is to examine several alternative soil-remediating technologies, with respect to heavy metal remediation, pointing out their strengths and drawbacks and placing an emphasis on electrokinetic soil remediation technology. In addition, the review presents detailed theoretical aspects, design and operational considerations of electrokinetic soil-remediation variables, which are most important in efficient process application, as well as the advantages over other technologies and obstacles to overcome. The review discusses possibilities of removing selected heavy metal contaminants from clay and sandy soils, both saturated and unsaturated. It also gives selected efficiency rates for heavy metal removal, the dependence of these rates on soil variables, and operational conditions, as well as a cost–benefit analysis. Finally, several emerging in situ electrokinetic soil remediation technologies, such as Lasagna™, Elektro-Klean™, electrobioremediation, etc., are reviewed, and their advantages, disadvantages and possibilities in full-scale commercial applications are examined. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Every year, millions of tonnes of hazardous waste are generated in the world. Due to inefficient waste handling techniques and hazardous waste leakage in the past, thousands of sites were contaminated by heavy metals, organic com-

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niques yet. Because of uncertainty, lack of appropriate methodology and proven results, many in situ projects are currently under way. It is likely that there will not be a single universal in situ soil-treatment technology. Instead, quite a large variety of technologies and their combinations suitable for different soil remediation situations will be developed and implemented.

Although the successful and environmentally friendly soil treatment technologies have not been completely investigated and implemented, there are several techniques which have attracted increased interest among scientists and industry officials. These are:

- Bioremediation — despite a demonstrated ability to remove halogenated and non-halogenated volatiles and semi-volatiles, as well as pesticides, this technique has failed to show efficient results in removing heavy metals from contaminated soils.
- Thermal desorption — this treats halogenated and non-halogenated volatiles and semi-volatiles, as well as fuel hydrocarbons and pesticides. It has failed to demonstrate an ability to remove heavy metals from contaminated soils.
- Soil vapour extraction — there are several promising results in reducing the volume of treated heavy metals. Nevertheless, this technique cannot reduce their toxicity.
- Soil washing — this technique has demonstrated potential effectiveness in treating heavy metals in the soil matrix.
- Soil flushing — according to laboratory-scale experiments, this is efficient in removing heavy metals from soils, despite the fact that it cannot reduce their toxicity.
- Electrokinetic soil remediation.

As none of the other in situ soil remediation techniques has demonstrated the efficient removal of heavy metals, there was a necessity to develop other methods to remediate soil contaminated by heavy metals.

Electrokinetic soil remediation is an emerging technology that has attracted increased interest among scientists and governmental officials in the last decade, due to several promising laboratory and pilot-scale studies and experiments. This method aims to remove heavy metal contaminants from low permeability contaminated soils under the influence of an applied direct current. However, regardless of promising results, this method has its own drawbacks. First of all, the whole electrokinetic remediation process is highly dependant on acidic conditions during the application, which favours the release of the heavy metal contaminants into the solution phase. However, achieving these acidic conditions might be difficult when the soil buffering capacity is high. In addition, acidification of soils may not be an environmentally acceptable method. Second, the remediation process is a very time-consuming application; the overall application time may vary from several days to even a few years. There are some other limitations of the proposed technique that need to be overcome: i.e. the solubility of the contaminant and its desorption from the soil matrix; low target ion concentration and high non-target ion concentration; requirement of a conducting pore fluid to mobilise contaminants; and heterogeneity or anomalies found at sites, such as large quantities of iron or iron oxides, large rocks or gravel, etc. (Sogorka et al., 1998).

According to the experiments and pilot-scale studies conducted, metals such as lead, chromium, cadmium, copper, uranium, mercury and zinc, as well as polychlorinated biphenyls, phenols, chlorophenols, toluene, trichlorethane and acetic acid, are suitable for electrokinetic remediation and recovery.

2. Theoretical, design and operational considerations

2.1. Theoretical aspects

The first electrokinetic phenomenon was observed at the beginning of the 19th Century, when Reuss applied a direct current to a clay–water mixture (Acar and Alshawabkeh, 1993). However, Helmholtz and Smoluchowski were the first scientists to propose a theory dealing with the electroosmotic velocity of a fluid and
the zeta potential under an imposed electric gradient ($\zeta$) (Acar and Alshawabkeh, 1993). Sibel Pamukcu and her research group have derived the following Helmholtz–Smoluchowski equation:

$$u_{EO} = \frac{\varepsilon \zeta}{\mu} \frac{\partial \phi}{\partial x}$$  \hspace{1cm} (1)

where $u_{EO}$ is the electroosmotic velocity, $\varepsilon$ is the dielectric constant of the pore fluid, $\mu$ is the viscosity of the fluid and $\partial \phi/\partial x$ is the electric gradient (Pamukcu and Wittle, 1992).

When DC electric fields are applied to contaminated soil via electrodes placed into the ground, migration of charged ions occurs. Positive ions are attracted to the negatively charged cathode, and negative ions move to the positively charged anode. It has been experimentally proved that non-ionic species are transported along with the electroosmosis-induced water flow. The direction and quantity of contaminant movement is influenced by the contaminant concentration, soil type and structure, and the mobility of contaminant ions, as well as the interfacial chemistry and the conductivity of the soil pore water. Electrokinetic remediation is possible in both saturated and unsaturated soils.

Electrokinetic soil treatment relies on several interacting mechanisms, including advection, which is generated by electroosmotic flow and externally applied hydraulic gradients, diffusion of the acid front to the cathode, and the migration of cations and anions towards the respective electrode (Zelina and Rusling, 1999). The dominant and most important electron transfer reactions that occur at electrodes during the electrokinetic process is the electrolysis of water:

$$\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 1/2 \text{O}_2(\text{g}) + 2\text{e}^-$$

$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2(\text{g})$$  \hspace{1cm} (2)

The acid front is carried towards the cathode by electrical migration, diffusion and advection. The hydrogen ions produced decrease the pH near the anode. At the same time, an increase in the hydroxide ion concentration causes an increase in the pH near the cathode. In order to solubilise the metal hydroxides and carbonates formed, or different species adsorbed onto soils particles, as well as protonate organic functional groups, there is a necessity to introduce acid into the soil. However, this acid addition has some major drawbacks, which greatly influence the efficiency of the treatment process. The addition of acid leads to heavy acidification of the contaminated soil, and there is no well-established method for determining the time required for the system to regain equilibrium.

The main goal of electrokinetic remediation is to effect the migration of subsurface contaminants in an imposed electric field via electroosmosis, electromigration and electrophoresis. These three phenomena can be summarised as follows:

- Electroosmosis is the movement of soil moisture or groundwater from the anode to the cathode of an electrolytic cell.
- Electromigration is the transport of ions and ion complexes to the electrode of opposite charge.
- Electrophoresis is the transport of charged particles or colloids under the influence of an electric field; contaminants bound to mobile particulate matter can be transported in this manner.

The phenomena occur when the soil is charged with low-voltage direct current. The process might be enhanced through the use of surfactants or reagents to increase the contaminant removal rates at the electrodes. Upon their migration to the electrodes, the contaminants may be removed by electroplating, precipitation/co-precipitation, pumping near the electrode, or complexing with ion exchange resins.

Electromigration takes place when highly soluble ionised inorganic species, including metal cations, chlorides, nitrates and phosphates, are present in moist soil environments. Electrokinetic remediation of soils is a unique method, because it can remediate even low-permeability soils.

Other mechanisms that greatly affect the electrochemical remediation process are electroosmosis, coupled with sorption, precipitation and disso-
olution reactions (van Cauwenberghe, 1997). This is the reason why all the appropriate processes should be taken into consideration and investigated before implementation of the technique can take place.

Once the remediation process is over, extraction and removal of heavy metal contaminants are accomplished by electroplating at the electrode, precipitation or co-precipitation at the electrode, pumping water near the electrode, or complexing with ion exchange resins. Adsorption onto the electrode may also be feasible, as some ionic species will change their valency near the electrode (depending on the soil pH), making them more likely to adsorb (van Cauwenberghe, 1997).

Prediction of THE decontamination time is of great importance in order to estimate possible power consumption and to avoid the occurrence of reverse electroosmotic flow, i.e. from the cathode to the anode, during the process (Baraud et al., 1997, 1998). The phenomenon of reverse electroosmotic flow is not well understood and should be further investigated.

Decontamination velocity depends on two parameters (Baraud et al., 1997, 1998):

- Contaminant concentration in the soil solution, which is related to the various possible solid/liquid interactions (adsorption/desorption, complexation, precipitation, dissolution, etc.) and to the speciation of the target species.
- Velocity in the pore solution when species are in the soil solution and not engaged in any reactions or interactions. The velocity depends on different driving forces (electric potential gradient, hydraulic head differences and concentration gradient) and is not closely related to soil properties, except for the electroosmosis phenomenon.

The success of electrochemical remediation depends on the specific conditions encountered in the field, including the types and amount of contaminant present, soil type, pH and organic content (Acar and Alshawabkeh, 1993).

For in situ conditions, the contaminated site itself and the immersed electrodes form a type of electrolytic cell. Usually, the electrokinetic cell design in laboratory experiments consists of an open-flow arrangement at the electrodes, which permits injection of the processing fluid into the porous medium, with later removal of the contaminated fluid (Sogorka et al., 1998; Reddy and Chinthamreddy, 1999; Reddy et al., 1997, 1999; Zelina and Rusling, 1999).

It seems that there is a controversy as to where electrodes should be placed to obtain the most reliable and efficient results. It is obvious that imposition of an electrical gradient by having inert electrodes results in electroosmotic flow to the cathode. Many authors propose that positioning of the electrodes directly into the wet soil mass produces the most desirable effect (Sims, 1990; Acar and Alshawabkeh, 1993; Reddy et al., 1999; Sogorka et al., 1998). Through seeking improvements in experiments, some researchers tend to place the electrodes not directly into the wet soil mass, but into an electrolyte solution, attached to the contaminated soil, or else to use different membranes and other materials (van Cauwenberghe, 1997; Baraud et al., 1998; Benazon, 1999). In order to maintain appropriate process conditions, a cleaning agent or clean water may be injected continuously at the anode. Thus, contaminated water can be removed at the cathode. Contaminants at the cathode may be removed by electrodeposition, precipitation or ion exchange.

Electrodes that are inert to anodic dissolution should be used during the remediation process. The most suitable electrodes used for research purposes include graphite, platinum, gold and silver. However, for pilot studies, it is more appropriate to use much cheaper, although reliable, titanium, stainless steel, or even plastic electrodes. Using inert electrodes, the electrode reactions will produce H\textsuperscript{+} ions and oxygen gas at the anode and OH\textsuperscript{-} ions and hydrogen gas at the cathode, which means that if pH is not controlled, an acid front will be propagated into the soil pores from the anode and a base front will move out from the cathode.

It has been proved by experiments that when heavy metals enter into basic conditions, they adsorb to soil particles or precipitate as hydrox-
ides, oxyhydroxides, etc., and in acidic conditions, those ions desorb, solubilise and migrate.

Another important parameter in the electrokinetic soil-remediation technique is the conductivity, since this, together with soil and pore fluid, affects the electroosmotic flow rate.

The conductivity of soil depends on the concentration and the mobility of the ions present, i.e. contaminant removal efficiencies decrease with a reduction in contaminant concentration (Reddy et al., 1997, 1999; Reddy and Chinthamreddy, 1999; Zelina and Rusling, 1999). This is due to hydrogen ion exchange with cationic contaminants on the soil surface, with release of the contaminants. As the contaminant is removed, the hydrogen ion concentration in the pore fluid increases, resulting in an increasing fraction of the current being carried by the hydrogen ions rather than by the cationic contaminants.

It is possible to conclude that the variables which have impact on the efficiency of removing contaminants from soils are:

- Chemical processes at the electrodes;
- Water content of the soil;
- Soil type and structure;
- Saturation of the soil;
- pH and pH gradients;
- Type and concentration of chemicals in the soil;
- Applied current density; and
- Sample conditioning.

In addition, insoluble organics, such as heavy hydrocarbons, are essentially not ionised, and the soils in contact with them are not charged. The removal of insoluble organics by electric field is limited to their movement out of the soil by electroosmotic purging of the liquid, either with water and surfactant to solubilise the compounds, or by pushing the compounds ahead of a water front (Probstein and Hicks, 1993).

Ionic migration is the movement of ions subjected to an applied DC electric field. Electromigration rates in the subsurface depend upon (van Cauwenberghe, 1997):

- Soil porewater current density;
- Grain size;
- Ionic mobility;
- Contaminant concentration; and
- Total ionic concentration.

The process efficiency is not as dependent on the fluid permeability of soil as it is on the porewater electrical conductivity and path length.

Fig. 1. Electroosmosis and electromigration of ions (adapted from Acar et al., 1994, 1996; Acar and Alshawabkeh, 1996).
through the soil, both of which are a function of the soil moisture content. As electromigration does not depend on the pore size, it is equally applicable to coarse and fine-grained soils (van Cauwenbergh, 1997).

Electroosmosis in water-saturated soil is the movement of water relative to the soil under the influence of an imposed electric gradient. When there is direct current applied across the porous media filled with liquid, the liquid moves relative to the stationary charged solid surface. When the surface is negatively charged, liquid flows to the cathode. Acar et al. (1994, 1996) have conducted numerous experiments and found that this process works well in wet (i.e. water-saturated) fine-grained soils and can be used to remove soluble pollutants, even if they are not ionic. The dissolved neutral molecules simply go with the flow. Fig. 1 shows a schematic representation of this process.

An excess negative surface charge exists in all kinds of soil. For example, many clays are anionic, colloidal poly-electrolytes. The surface charge density increases in the following order: sand < silt < kaolinite < illite < montmorillonite. Injection of clean fluid, or simply clean water, at the anode can improve the efficiency of pollutant removal. For example, such a flushing technique using electroosmosis has been developed for the removal of benzene, toluene, trichlorethane and m-xylene from saturated clay.

According to that stated above, the main factors affecting the electroosmotic transport of contaminants in the soil system are as follows:

- Mobility and hydration of the ions and charged particles within the soil moisture;
- Ion concentration;
- Dielectric constant, depending on the amount of organic and inorganic particles in the pore solution; and
- Temperature.

Most soil particle surfaces are negatively charged as a result of isomorphous substitution and the presence of broken bonds (Yeung et al., 1997).

Experiments have determined the dependence of the zeta potential of most charged particles on solution pH, ionic strength, types of ionic species, temperature and type of clay minerals (Vane and Zang, 1997). For water-saturated silts and clays, the zeta potential is typically negative, with values measured in the 10–100-mV range.

However, if ions produced in the electrolysis of water are not removed or neutralised, they lower the pH at the anode and increase it at the cathode, accompanied by the propagation of an acid front into the soil pores from the anode and a base front from the cathode. This process can significantly effect the soil zeta potential (drop in zeta potential), as well as the solubility, ionic state and charge, level of adsorption of the contaminant, etc. (Yeung et al., 1997).

In addition, different initial metal concentrations and sorption capacity of the soil may produce soil surfaces that are less negative, which at the same time may become positive at a pH of approximately the original zero-point charge (Yeung et al., 1997). Similarly, chemisorption of anions makes the surface more negative. Electroosmotic flow from the anode to the cathode promotes the development of a low-pH environment in the soil. This low-pH environment inhibits most metallic contaminants from being sorbed onto soil particle surfaces and favours the formation of soluble compounds. Thus, electroosmotic flow from the anode to cathode, resulting from the existence of a negative zeta potential, enables the removal of heavy metal contaminants by the electrokinetic remediation process.

The pH of the soil should be maintained low enough to keep all contaminants in the dissolved phase. Nevertheless, when the pH becomes too low, the polarity of the zeta potential changes and reversed electroosmotic flow (i.e. from the cathode to the anode) may occur. In order to achieve efficient results in removing contaminants from soils, it is necessary to maintain a pH low enough pH to keep metal contaminants in the dissolved phase and high enough to maintain a negative zeta potential (Yeung et al., 1997). Despite this apparently easily implemented theory, simultaneous maintenance of a negative zeta potential and
dissolved metal contaminants remains the greatest obstacle in the successful implementation of the electrokinetic soil remediation process.

2.2. Design considerations

In order to obtain efficient and reliable results, electrokinetic remediation of soil should be implemented under steady-state conditions. It is obvious that during the remediation process, other reactions, such as transport and sorption, and precipitation and dissolution reactions, occur and affect the remediation process.

There have been numerous indications of the importance of heat and gas generation at electrodes, the sorption of contaminants onto soil particle surfaces and the precipitation of contaminants in the electrokinetic remediation process (Acar and Alshawabkeh, 1993; Lageman, 1993; Zelina and Rusling, 1999). These processes should be further investigated, because it is believed that they may weaken the removal efficiency for heavy metal contaminants. It is reported that different physicochemical properties of the soil may influence the removal rates of heavy metal contaminants, due to changed pH values, hydrolysis, and oxidation and reduction reaction patterns.

In order to enhance the electrokinetic remediation process, several authors recommend the use of a multiple anode system, which is shown in Fig. 2.

2.3. Operational considerations

As there are several experimental techniques to remediate coarse-grained soils, in situ electrokinetic treatment has been developed for contaminants in low-permeability soils. Electrokinetics is applicable in zones of low hydraulic conductivity, particularly with a high clay content.

Contaminants affected by electrokinetic processes include:

- Heavy metals;
- Radioactive species (Cs\textsubscript{137}, Sr\textsubscript{90}, Co\textsubscript{60}, uranium);
- Toxic anions (nitrates and sulfates);
- Dense, non-aqueous-phase liquids (DNAPLs);
- Cyanides;
- Petroleum hydrocarbons (diesel fuel, gasoline, kerosene and lubricating oils);
- Explosives;
- Mixed organic/ionic contaminants;
- Halogenated hydrocarbons;
- Non-halogenated pollutants; and
- Polynuclear aromatic hydrocarbons.

Heavy metal interactions in the soil solution are governed by several processes, such as (Sims, 1990):

- Inorganic/organic complexation;
- Acid–base reactions;
- Redox reactions;
- Precipitation/dissolution reactions; and
- Interfacial reactions.

The choice of appropriate soil for electrokinetic remediation process should be made with extreme caution and possible soil pre-treatment experiments should be carried out.

Soils that may be used for the electrokinetic remediation process should have (Sims, 1990):

- Low hydraulic conductivity;
- Water-soluble contaminants (if there are any poorly soluble contaminants, it may be essential to add solubility-enhancing reagents); and
• Relatively low concentrations of ionic materials in the water.

It is reported that with applied electric fields, the most suitable soils for heavy metal remediation are kaolinite, clay and sand (Sims, 1990). As recommended, clay has low hydraulic conductivity, reducing redox potential, slightly alkaline pH (which is suitable for the remediation of several heavy metal contaminants), high cation exchange capacity and high plasticity. Under normal conditions, migration of ions is very slow, but is enhanced by electrical fields or hydraulic pressure.

The highest degree of removal of heavy metals (over 90% of the initial contaminant) has been achieved for clayey, low-permeability soils, whereas for porous, high-permeability soils, such as peat, the degree of removal was only 65% (Chilingar et al., 1997). Laboratory results showed that electrokinetic purging of acetate and phenol from saturated kaolinite clay resulted in greater than 94% removal of the initial contaminants. However, this methodology needs to be further investigated, because phenol has been reported to be toxic to humans and the environment.

3. Removal of metals

If heavy metal contaminants in the soil are in ionic forms, they are attracted by the static electrical force of negatively charged soil colloids. The attraction of metal ions to the soil colloids primarily depends on the soil electronegativity and the dissociation energy of ions (Sah and Chen, 1998). If there are appropriate pH conditions, heavy metals are likely to be adsorbed onto the negatively charged soil particles. The main sorption mechanisms include adsorption and/or ion exchange. Desorption of cationic species from clay surfaces is essential in extraction of species from fine-grained deposits with high cation-exchange capacity.

As Acar and his research group have indicated (Acar and Alshawabkeh, 1993, 1996; Acar et al., 1994, 1996; Sah and Chen, 1998), the sorption mechanisms depend on the surface charge density of the clay mineral, the characteristics and concentration of the cationic species, and the presence of organic matter and carbonates in the soil. The mechanism is also significantly dependent on the pore fluid pH. The higher the content of carbonates and organic material in soils, the lower the heavy metal removal efficiency, which is why the former should be further investigated and taken into the consideration.

During numerous experiments, a decrease in current density was observed (Acar and Alshawabkeh, 1993, 1996; Acar et al., 1994, 1996; Sah and Chen, 1998). The possible reasons might be as follows:

Activation polarisation: during the electrokinetic remediation process, gaseous bubbles (O2 and H2) cover the electrodes. These bubbles are good insulators and reduce the electrical conductivity, subsequently reducing the current.

Resistance polarisation: after the electrokinetic remediation process, a white layer was observed on the cathode surface. This layer may be the insoluble salt and other impurities that were not only attracted to the cathode, but also inhibited the conductivity, with a subsequent decrease in current.

Concentration polarisation: the H+ ions generated at the anode are attracted to the cathode and the OH− ions generated at the cathode are attracted to the anode. If acid and alkaline conditions are not neutralised, the current also drops.

It is possible to conclude that soil containing heavy metal contaminants influences the conductivity.

Interaction of the pollutants with the soil also affects the remediation process. In order to increase the solubility of complexes formed, or to improve electromigration characteristics of specific heavy metal contaminants, an enhancement solution may be added to the soil matrix.

Sometimes electroosmotic flow rates are too low, and it may be necessary to flush the electrodes with a cleaning agent, or simply clean tap water (Probstein and Hicks, 1993). In addition, the electrode may be surrounded by ion-exchange
material to trap the contaminant and prevent its precipitation. It is essential to know the buffering capacity of the soil in order to alter the pH with suitable solutions or clean water. Many groundwaters contain high concentrations of bicarbonates, which consume added hydrogen ions to form carbonic acid, or hydroxyl ions to form carbonate ions. It is vital to draw attention to the limited solubility of metal carbonates, as well as the need for evaluation of sulfide, sulfate, chloride and ammonia effects, which may occur when these compounds are introduced into the soil system during the remediation process (Probstein and Hicks, 1993).

New alternatives have been suggested for the remediation of heavy metals from soils without having low pH conditions (Probstein and Hicks, 1993). When the metal enters the region of high pH near the cathode, it may adsorb onto the soil, precipitate, or form hydroxo complexes. At higher pH values, the solubility increases because of the increasing stability of soluble hydroxo complexes. Despite favourable soluble complexes, the dissolution process may be time-consuming and too slow to be successfully implemented.

Concerning the process of transport of contaminants and their derivatives, two major phenomena were indicated (Chilingar et al., 1997):

1. The flow of contaminant solution through a solid matrix due to Darcy’s law and electrokinetics; and
2. Spatial redistribution of dissolved substances with respect to the moving liquid due to the diffusion and migration of charged particles.

The total movement of the matter of the contaminant solution in the DC electric field can be expressed as the sum of four components (Chilingar et al., 1997):

- The hydrodynamic flow of liquids driven by the pressure gradient;
- The electrokinetic flow of fluids due to interaction of the double layer with the DC field;
- The diffusion of components dissolved in the flowing solution; and
- The migration of ions inside moving fluids due to the attraction of charged particles to the electrodes.

The very questionable concept that removal of heavy metals in the direct current field is effective was also expressed, because electromigration of ions is rapid and does not depend on the zeta potential. In order to prove or disapprove this, further investigations of this concept should be carried out. Despite some disagreements, it was agreed that in order to obtain efficient and reliable results and control the remediation process, there is a need to provide continuous control of the pH in the vicinity of the electrodes (Acar and Alshawabkeh, 1993, 1996; Acar et al., 1994, 1996; Chilingar et al., 1997). One possible way to achieve this is periodic rinsing of the cathode with fresh water.

Experiments have proved that electrical field application in situ leads to an increase in temperature, which in turn reduces the viscosity of hydrocarbon-containing fluids (Chilingar et al., 1997). The reduction in fluid viscosity leads to an increase in the total flow rate.

It is reported (Chilingar et al., 1997) that in order to accelerate the fluid transport in situ, electrical properties of soils, such as electrical resistivity and the ionisation rate of the flowing fluids that can affect the total rate flow, should consider. In an applied DC field, some soil types showed an increase in their hydraulic permeability, which allows us to conclude that direct current may accelerate fluid transport. However, this method is not applicable to some clays, because under the DC field, those clays become amorphous. It is possible to avoid such a transformation if interlayer clay water is trapped and is not able to leave the system.

From the numerous laboratory and field experiments and studies conducted, it is possible to conclude that migration rates of heavy metal ions (i.e. removal efficiencies) are highly dependent on soil moisture content, soil grain size, ionic mobility, pore water amount, current density and contaminant concentration (Acar and Alshawabkeh, 1993, 1996; Acar et al., 1994, 1996; Chilingar et al., 1997; Sah and Chen, 1998). Also, in order to assure the efficient and successful heavy metal
removal from soils, one of the main drawbacks of this process must be solved, which is premature precipitation of metal species close to the cathode compartment.

3.1. Limitations of the technique

The removal of heavy metals from soils using electrokinetic remediation has some limitations, which have been widely discussed among many scientists and researchers. For example, the surface of the electrode attracts the gas generated from the electrolytic dissociation process and increases the resistance, which significantly slows down the remediation process (Sah and Chen, 1998). It is obvious that soil resistance is lower in the earlier stages of the electrokinetic process, and therefore a lower input voltage is required. When the electrokinetic process continues, gas bubbles from electrolytic dissociation cover the whole cathode surface and the resistance increases. To continue the soil remediation process, the input voltage must be increased to maintain the same current, which also increases the voltage gradient. \( \text{OH}^- \) ion that are formed react with cations and form a sediment, which plugs the spacing between soil particles, subsequently hindering the electrical current and decreasing the diffusive flow over time when the voltage is applied (Sah and Chen, 1998).

3.2. Enhancement and conditioning

To overcome the premature precipitation of ionic species, Acar and his research group have recommended using different enhancement techniques to remove or to avoid these precipitates in the cathode compartment. Efficient techniques should have the following characteristics:

- The precipitate should be solubilised and/or precipitation should be avoided.
- Ionic conductivity across the specimen should not increase excessively in a short period of time to avoid a premature decrease in the electroosmotic transport.

- The cathode reaction should possibly be depolarised to avoid the generation of hydroxide and its transport into the specimen.
- Depolarisation will decrease the electrical potential difference across the electrodes, which would result in lower energy consumption.
- If any chemical is used, the precipitate of the metal with the new chemical should be perfectly soluble within the pH range attained.
- Any special chemicals introduced should not result in any increase in toxic residue in the soil mass.
- The cost efficiency of the process should be maintained when the cost of enhancement is included.

It is obvious that an enhancement fluid increases the efficiency of contaminated soil treatment; however, there is a lack of data which would clarify further soil and contaminant interactions in the presence of this fluid.

As a depolariser (i.e. enhancement fluid) in the cathode compartment, it is possible to use a low concentration of hydrochloric or acetic acid (Acar and Alshawabkeh, 1993, 1996; Acar et al., 1994, 1996). The main concern with hydrochloric acid as the depolariser is that due to electrolysis, the chlorine gas formed may reach the anode, as well as groundwater, and increase its contamination. Acetic acid is environmentally safe and it does not fully dissociate. In addition, most acetate salts are soluble, and therefore acetic acid is preferred in the process.

The anode reaction should also be depolarised, because of the dissolution and release of silica, alumina and heavy metals associated with the clay mineral sheets over long exposure to protons (Acar and Alshawabkeh, 1993, 1996; Acar et al., 1994, 1996).

In order to accomplish both tasks successfully, it is better to use calcium hydroxide as the enhancement fluid to depolarise the anode reaction, and hydrochloric acid as the enhancement fluid to depolarise the cathode reaction. The use of an enhancement fluid should be
examined with extreme care to prevent (Yeung et al., 1997):

- The introduction of a secondary contaminant into the subsurface;
- The generation of waste products or by-products as a result of electrochemical reactions; and
- The injection of an inappropriate enhancement fluid that will aggravate the existing contamination problem.

4. Electrokinetic soil remediation processes

4.1. Removal of heavy metals using cation-selective membrane

In alkaline medium, heavy metals are likely to be adsorbed onto the soil particles and form insoluble precipitates. The high pH region in closest proximity to the cathode is the main obstacle to heavy metal removal (Acar and Alshawabkeh, 1993, 1996; Acar et al., 1994, 1996; Li et al., 1997; Li and Neretnieks, 1998; Li and Li, 2000; Yeung et al., 1997). However, the latest experimental studies show that it is possible to deal with the pH impact (Li et al., 1997; Li and Neretnieks, 1998; Li and Li, 2000). A conductive solution, which simulates the groundwater conditions, was placed between the cathode and the soil to be treated. However, the length of conductive solution must be at least twice the length of the treated soil, which may be impossible to implement at a site. In addition, the solution has to be placed in a special container, which would significantly increase the costs of the overall remediation process. The pH buffer capacity, cation exchange capacity of the medium, and interactions of the solution with the soil may affect the speed of the advancement of the acidic and the basic fronts and the location of the pH jump (Li and Li, 2000). In order to overcome these obstacles, a new method was proposed which should significantly improve the overall remediation process. To reduce the relative length or volume of the water in the system, a cation-selective

![Diagram of electrokinetic cell with cation-selective membrane](image-url)
membrane is placed in front of the cathode (Li et al., 1997; Li and Neretnieks, 1998; Li and Li, 2000) (Fig. 3).

Due to an applied electric current, ions move to the electrodes, according to their charges. The cation-selective membrane, placed between the soil and cathode, allows cations and very few anions to pass through it. This is why almost all the hydroxyl ions produced at the cathode remain on the cathodic side of the membrane. The hydrogen ions generated at the anode move through the soil and into the membrane. The basic front cannot pass through the membrane, where it meets the acidic front. The main pH changes occur near the membrane (Li et al., 1997; Li and Neretnieks, 1998; Li and Li, 2000). It is possible that the membrane determines the pH jump and may control the cathode solution volume. A cation-selective membrane maintains the low soil pH during the remediation process and significantly reduces the length of the conductive solution required. Hence, the proposed electrokinetic cell consist of the treated soil, a conductive solution, which is placed between the soil and the membrane, and the cathode compartment with electrolyte solution, which is between the membrane and cathode. After numerous experiments, it has been observed that the smaller the volume of conductive solution, the higher the pH will be and the larger will be the leakage of the anions through it (Li et al., 1997; Li and Neretnieks, 1998; Li and Li, 2000).

However, a small amount of anions passing through the membrane may be favourable for the remediation process. Precipitation decreases the remediation time, because this reduces the concentration of heavy metals in the liquid phase (Li and Li, 2000). At the same time, back-diffusion of heavy metals is greatly reduced, since the concentration of heavy metals near the membrane does not exceed the solubility of the metals. It has been proved by experiments that precipitation decreases the electrical energy consumption, because the potential drop between the electrodes and the remediation time are proportional to the distance between the electrodes (Li et al., 1997; Li and Neretnieks, 1998; Li and Li, 2000).

4.2. Removal of heavy metals using surfactant-coated ceramic casings

For many years, the main emphasis of electrokinetic soil remediation was on saturated, fine-grained soils and clays, which led to the misconception that electrokinetics was not suitable for unsaturated, sandy soils. Laboratory experiments proved that with appropriate technology and well-designed methods, it is possible to remediate heavy metals from unsaturated and sandy soils (Mattson and Lindgren, 1995). The treatment of unsaturated soils has several limitations. The electrical conductivity of soil depends on the moisture content (Mattson and Lindgren, 1995). During electroosmotic migration through the soil, the water content near the anode is reduced. As the moisture content decreases, the soil conductivity becomes too low for the electrokinetic remediation application. In order to control the hydraulic flux of water in the treated soil, the use of porous ceramic casings has been proposed. During the application, it should be remembered that the direction of electroosmotic flow in porous ceramic media has a strong influence on the amount of water being added to the soil from the ceramic casings. Anode ceramic casting would be suitable for long-term electrokinetic remediation processes if it was ensured that electroosmotic flow occurred from the surrounding soil towards the interior of the anode casting (Mattson and Lindgren, 1995). As efficient electrokinetic remediation in unsaturated soils depends on the water amount at the anode, there is a necessity to continuously inject water during the whole remediation process. Despite the addition of water, it is important to maintain unsaturated conditions in the soil, because excess water may cause saturated conditions and contaminants will be able to migrate into the deeper layers of the soil.

A number of experiments with an anode ceramic casting were conducted and it was proved that it is possible to remove heavy metal contaminants from unsaturated, sandy soils using the electrokinetic remediation technique (Mattson and Lindgren, 1995).

First of all a laboratory cell was designed and constructed, which consisted of a plastic con-
tainer filled with buffering solution. The polyvinyl chloride plate glued to the bottom of the container, the porous ceramic castings, woven wire cathode and graphite anode are shown in Fig. 4. The most suitable buffering solution for this experiment is a phosphate solution with a pH of 6 (Mattson and Lindgren, 1995). To overcome the hydraulic counterflow, the experiment should only be conducted until the fluid level difference between the inner and outer reservoirs becomes \(\pi / 4 \text{ cm} \) (Mattson and Lindgren, 1995).

After laboratory experiments, a number of field studies were conducted and the initial results obtained are very promising. It is possible to state that the use of anode ceramic casting may significantly improve the application of electrokinetic remediation in unsaturated soil media.

### 4.3. Lasagna™ process

In 1995, a novel integrated method for in situ electrokinetic remediation of soils, called Lasagna™, was developed and implemented at the Paducah site, in Kentucky, USA. This technology is useful for removing heavy metal contaminants from heterogeneous, low-permeability soils (Ho et al., 1997, 1999).

In brief, the Lasagna™ process contains the following concepts:

- The creation of several permeable ‘treatment’ zones in close proximity through the whole soil matrix by adding sorbents, catalytic reagents, buffering solutions, oxidising agents, etc.
- Application of an electric current in order to transport contaminants into the ‘treatment’ zones created.

The Lasagna™ process has several advantages in comparison to other techniques. First, it is possible to recycle the cathode effluent by aiming it back to the anode compartment, which would favour neutralising of the pH and simplify water management. In addition, the fluid flow may be reversed by simply switching the polarity (Ho et al., 1999). The switching of polarity promotes multiple contaminant passes through the ‘treatment’ zones and helps to diminish the possibility of non-uniform potential and pH jumps in the soil system.

Two schematic Lasagna™ model configurations were suggested: horizontal (Fig. 5) and vertical (Ho et al., 1999).

The process was called ‘Lasagna’ due to the layering of treatment zones between the electrodes. The formation of horizontal fractures in over-consolidating clays due to the horizontal electrodes and vertical pressuring system make this method especially effective in removing contaminants from deeper layers of the soil (Ho et al., 1997).
In addition, for shallow contamination which does not exceed 15 m and in not over-consolidated soils, the vertical treatment configuration is more appropriate (Ho et al., 1997) (Fig. 6).

According to laboratory experiments and promising pilot-scale studies at the Paducah site in Kentucky, Lasagna™ technology may become one of the most widely used electrokinetic remediation technologies for removing heavy metal contaminants from various soils. Nevertheless, there are several technological and other limitations, which should be improved for future studies. It is obvious that Lasagna™ technology is potentially capable of treating multiple contaminants in clay and laden soils, but additional experiments and studies should be conducted in order to assure that the treatment process is compatible for individual contaminants. In addition, one of the biggest technology drawbacks is the entrapment of gases formed by electrolysis and the assurance of good electrical contact to the electrodes. To increase the Lasagna™ process efficiency, there were attempts to implement bioremediation in ‘treatment’ zones. It is believed that bioremediation together with electrokinetic remediation may significantly increase the overall removal of heavy metals, as well as other contaminants, from clays and other soils.

4.4. Electro-Klean™ electrical separation

Electro-Klean™ technology is applied in situ, as well as ex situ, in Louisiana, USA. This is a new methodology, which is used to remove heavy metals, radionuclides and specific volatile organic contaminants from saturated and unsaturated sands, silts, fine-grained clays and sediments. This technology uses two electrodes to apply DC directly into the contaminated soil mass (van Cauwenberghe, 1997). In order to improve the remediation efficiency, enhancement fluids, mostly acids, are added into the soil. The main limitation of this technique is the high buffering
capacity of the soils and different coexisting chemicals and their concentrations.

4.5. Electrokinetic bioremediation

Electrokinetic bioremediation technology is designed to activate microbes and other microorganisms present in soils by the use of selected nutrients to promote the growth, reproduction and metabolism of micro-organisms capable of transforming organic contaminants in soil (van Cauwenberge, 1997). Nutrients reach the organic contaminants by specially applied bioelectric technology. It is believed that this technology may be very successful in the future, because it does not require an external microbial population to be added into the soil system. In addition, nutrients may be uniformly dispersed over the contaminated soil or directed to a specific location (van Cauwenberge, 1997) and the method avoids the problems associated with transport of micro-organisms through fine-grained soils (Fig. 7).

Despite promising results, this technology has some major limitations. Sometimes the concentration of organic pollutant exceeds the toxic limit for the microbial population and micro-organisms die. Simultaneous bioremediation of various organic contaminants may produce by-products, which are highly toxic to micro-organisms. Those by-products may significantly inhibit the bioremediation rates.

4.6. Electrochemical geooxidation

Electrochemical geooxidation is used in Germany to remediate soil and water contaminated with organic and inorganic compounds (van Cauwenberge, 1997). The in situ process involves the application of an electrical current to probes driven into the ground. The applied current creates favourable conditions for oxidation-reduction reactions, which lead to the immobilisation of inorganic contaminants in the soil or groundwater matrix between the electrode locations. The main advantage of this technology is that there is no need to use catalysts for the oxidation-reduction reactions, because in almost all soils, natural catalysts, such as iron, magnesium, titanium and elemental carbon, are present. The limitations of this technology are the very long remediation time and the lack of proven results.

4.7. Electrochemical ion exchange

This technology employs a series of electrodes, placed in porous castings, which are supplied with circulating electrolytes. During the remediation process, ion contaminants are captured in these
electrolytes and pumped to the surface, where they are passed through an electrochemical ion exchanger (van Cauwenberghe, 1997). This method is used to remove heavy metals, halides and specific organic species from different types of soils. The most important limitation of this technology is that it is a very expensive procedure for cleaning effluents containing low levels of contaminants.

4.8. Electrosorb™

Electrosorb™ technology is mostly used in Louisiana, USA, and uses cylindrical electrodes coated with a specially designed polymer material. This polymer is impregnated with pH-regulating chemicals in order to prevent pH jumps (Reddy and Chinthamreddy, 1999). During the remediation process, electrodes are placed in boreholes in the soil and direct current is applied. Ions move through the pore water to the electrode, where they are trapped in the electrode polymer matrix. Although there are no indications of the limitations of the technique proposed, it is believed that in order to be commercially available, it should be further investigated.

5. Remediation of specific heavy metal contamination

As the heavy metal contaminants in a soil and solution primarily exist in the form of salts and ions, the potential of an electrokinetic remediation technique depends on the quantity of those compounds.

5.1. Removal of cadmium and lead

Under alkaline conditions, cadmium and lead in the soil may become sediments of hydroxides \([\text{Cd(OH)}_2, \text{Pb(OH)}_2]\) and carbonates \((\text{CdO}_3, \text{PbCO}_3)\). Soil pH determines the concentrations of hydroxide and carbonate in the soil solution, which play a crucial role in the formation of heavy metal complexes in soil (Sah and Chen, 1998).

In order to understand the migration of Pb and Cd between electrified vs. non-electrified soil samples under different times, locations and solution types, it is important to use heavy metal formal analysis (Sah and Chen, 1998). Also, due to varying stability of different heavy metals in the soil, there is a necessity to determine appropriate application times for electrokinetic remediation and the pH of the soil.

Experiments conducted show that Pb-contaminated soil is usually quite difficult to remediate. However, high removal rates for Pb, as well as Cd, were obtained in experiments where HCl solution was used (Acar and Alshawabkeh, 1993; Sah and Chen, 1998).

If the environment near the cathode is basic, it may favour the formation of the insoluble hydroxide \(\text{Cd(OH)}_2\). However, this Cd species may not be mobile under advective flow (Acar and Alshawabkeh, 1993, 1996; Acar et al., 1994, 1996).

In order to improve the removal rates of cadmium and lead from soils, the following proposals should be considered (Sah and Chen, 1998):

- Experiments showed that soil could absorb more Pb than Cd, which should be taken into consideration in further laboratory experiments, as well as pilot-scale studies.
- Cd-spiked samples have revealed a higher current density than Pb-spiked samples during the remediation process. A thin, white oxidant film was found on the cathode, which reduced the conductivity and removal efficiency of metals. Thus, an enhancement fluid should be added at the electrodes, or the electrodes must be cleaned regularly during the application.
- The use of HCl acid increased the removal rates of lead and cadmium. In order to achieve optimal removal results, acid solution has to be added to the soil solution.

5.1.1. Lead migration in soils

Cationic heavy metals, such as Pb, are most soluble at a low pH. As the \(\text{H}^+\) produced at the anode moves across the soil sample, cationic metals which were sorbed or precipitated onto the soil particles are, in many cases, solubilised and
may be able to undergo transport by diffusion, as well as via electrokinetic remediation processes, such as advection by electroosmotic flow and electrolytic migration. Diffusion and electrolytic migration of OH$^-$ ions produced at the cathode increase the pH of the system near the cathode and may precipitate desorbed ions (Viadero et al., 1998). This is shown schematically in Fig. 8.

Experiments showed that at a pH above 4–4.5, lead was either adsorbed onto the soil and/or precipitated as Pb(OH)$_2$ (s), which reduced the conductivity of the soil by removing cations from the liquid (Viadero et al., 1998). At high pH, most of the lead is retained in hydroxide and carbonate phases.

5.1.2. Cadmium migration in soils

When the initial pH is low, the conductivity of the medium is high, and very low electrical potential gradients are initially generated across the specimen (Acar and Alshawabkeh, 1993, 1996; Acar et al., 1994, 1996; Probstein and Hicks, 1993; Mattson and Lindgren, 1995; Sah and Chen, 1998; Viadero et al., 1998).

Numerous experiments have been conducted to remove cadmium from kaolin. In kaolin, without the addition of a reducing agent and in the presence of humic acid and ferrous iron, low pH conditions exist throughout most of the soil, except near the cathode. As low pH conditions favours the dissolution of Cd species, cadmium is transported to the cathode compartment (Pamukcu, 1997). Low-concentration Cd specimens exhibit a larger influx of water than high Cd concentration specimens for the same level of electricity (Pamukcu, 1997).

\[ H^+ + e^- \rightarrow (1/2)H_2 \]

\[ Cd^{2+} + 2e^- \rightarrow Cd^0 \]

\[ Cd(OH)_2(s) + 2e^- \rightarrow Cd^0 + 2OH^- \] (3)

When the current density is greater than 5 mA/cm$^2$, secondary temperature effects are reported to decrease the efficiency of electroosmotic flow (Hansen et al., 1997).

5.2. Removal of arsenic and chromium

The main substance used for desorbing cationic species is hydronium ions H$_3$O$^+$ produced at the anode during the electrolysis process. However, there are several major drawbacks of this process: it induces a dissolution of major soil components, such as carbonates, as well as oxides (Fe, Mg) when strongly acidified (Hecho et al., 1998).

Anionic species are removed by the hydroxide ions generated at the cathode. It is necessary to add an anionic oxidising agent, which would migrate to the anode through the soil matrix (Hecho et al., 1998). Chromium(III) can be oxidised into Cr(VI) as anionic species, which can be desorbed in alkaline medium. This method is useless with arsenic, because all soluble arsenic species are anionic above pH 9 and arsenic(V) is more strongly sorbed that arsenic(III).

In order to remove chromium from soils, it is necessary to oxidise Cr(III) first to chromium(VI), Fig. 8. Lead removal from soils (according to 29).
which is anionic. The removal of arsenic is not as complicated as that of chromium. The literature indicates that arsenic(III) is more soluble than arsenic(V), so the use of an oxidising agent does not seem useful.

Two alkaline reagents, i.e. sodium carbonate and sodium hydroxide, are used to enhance the remediation process (Reddy and Chinthamreddy, 1999). Earlier, two alternatives, i.e. hydrogen peroxide and sodium hypochlorite, were used as oxidising agents. However, experiments proved that hydrogen peroxide tends to reduce very rapidly in the soil, and only hypochlorite was used for further laboratory and pilot studies (Hansen et al., 1997; Hecho et al., 1998).

5.2.1. Chromium migration

Chromium can exist in valence states ranging from −2 to +6; however, +3 and +6 are the only two valence states that prevail under subsurface conditions (Reddy et al., 1997, 1999; Reddy and Chinthamreddy, 1999). Hexavalent chromium(VI) is highly mobile and toxic in comparison to Cr(III). Cr(VI) exists as anions, specifically hydrochromate (HCrO$_4^-$), dichromate (Cr$_2$O$_7^{2-}$) and chromate (CrO$_4^{2-}$), and will migrate towards the anode during the electrokinetic remediation process. On the other hand, Cr(III) exists as a cation Cr$_3^{3+}$ and may form cationic, neutral and anionic hydroxy complexes, specifically Cr(OH)$_2^{2+}$, Cr(OH)$_3^{+}$, Cr(OH)$_4^{3-}$, Cr(OH)$_5^{2-}$ and Cr(OH)$_6^{3-}$. Cr(III) may also exist as other cationic, neutral and anionic inorganic and organic complexes, depending on the ligands present (Reddy and Chinthamreddy, 1999).

In acidic regions and at relatively low redox potentials, Cr(III) exists as Cr$_3^{3+}$ and forms cationic complexes Cr(OH)$_2^{2+}$. Being positively charged, Cr(OH)$_2^{+}$ will migrate towards the cathode during the electrokinetic remediation process. Cr(III) precipitates as its hydroxide [Cr(OH)$_3$] between pH 6.8 and 11.3, while at higher pH values, Cr(III) may form anionic hydroxy complexes [Cr(OH)$_2^{2-}$ and Cr(OH)$_3^{3-}$] (Reddy et al., 1997, 1999; Reddy and Chinthamreddy, 1999).

The removal of chromium from soils by electrokinetic remediation is highly efficient if the chromium exists as Cr(VI) (Acar and Al-shawabkeh, 1993, 1996; Acar et al., 1994, 1996; Reddy et al., 1997, 1999; Reddy and Chinthamreddy, 1999; Sah and Chen, 1998). If reducing agents, such as organic matter, sulfides or ferrous iron, are present in natural soils, Cr(VI) is likely to be reduced to Cr(III), which may significantly affect the electrokinetic migration of chromium, as well as the migration of co-existing metals such as Ni(II) and Cd(II) (Reddy et al., 1997, 1999; Reddy and Chinthamreddy, 1999).

As chromium species favour alkaline conditions in soils, an alkaline reagent must be injected into the soil system in order to neutralise H$_3$O$^+$ ions.

In order to enhance the electrokinetic remediation application, an oxidising agent — sodium hypochlorite — needs to be injected at the cathode compartment (Reddy et al., 1999). Hypochlorite ions can migrate towards the anode and oxidise trivalent chromium to hexavalent chromium, which in turn migrates towards the anode.

After close investigation of the effects of reducing agents on chromium species migration, it was observed that when the chromate front meets the anodic reaction product Fe$^{2+}$ in a region adjacent to the anode, it reacts to form Cr$^{3+}$ and Fe$^{3+}$ species:

$$\text{Fe}^{2+} + \text{Cr}^{6+} \rightleftharpoons \text{Fe}^{3+} + \text{Cr}^{3+} \quad (4)$$

Thus, further migration of chromate is inhibited due to redox reactions with ferrous ions (Haran et al., 1996). Cr(III) is immobilised in sand due to the formation of complex sulfates and hydroxides. When the pH is increased, Cr(III) is likely to be precipitated as chromic hydroxide:

$$\text{Cr}^{3+} + 3\text{OH}^- \rightarrow \text{Cr(OH)}_3 \quad (5)$$

The reduction reaction is controlled by two important factors, the amount of Fe(II) in the sand and the soil pH (Haran et al., 1996):

$$\text{Fe} \leftrightarrow \text{Fe}^{2+} + 2\text{e}^- \quad (6)$$

Cr(VI) exists predominantly as HCrO$_4^-$ at low pH and as CrO$_4^{2-}$ at high pH in solution (Reddy et al., 1997):

$$\text{S} \rightarrow \text{OH} = \text{S} \rightarrow \text{O}^- + \text{H}^+ \quad (7.1)$$
where \( S\text{--OH} \) represents a typical surface functional group, and \( M^+ \) and \( L^- \) represent a cation and anion, respectively.

These complexation reactions are highly pH-dependent, because the extent of surface deprotonation (Sogorka et al., 1998) and protonation reactions (Acar and Alshawabkeh, 1993) is controlled by the solution pH (Reddy et al., 1999).

5.2.2. Chromium removal from different soils

Different experiments were conducted to obtain results for chromium removal efficiency from several types of naturally occurring soils, such as kaolin and glacial till (Acar and Alshawabkeh, 1993; Mattson and Lindgren, 1995; Reddy et al., 1997, 1999; Reddy and Chinthamreddy, 1999; Sah and Chen, 1998).

The presence of reducing agent in soils, such as humic acid, did not retard the chromium migration, either in kaolin or in glacial till; actually, it enhanced chromium migration towards the anode (Reddy and Chinthamreddy, 1999). On the other hand, ferrous iron, another reducing agent naturally present in soils, showed moderate retardation of chromium migration. Finally, the presence of sulfides showed the highest rate of retardation of chromium species migration towards the anode. It is possible to conclude that when a reducing agent was present, higher Cr(III) concentrations were observed near the anode. On the other hand, the reduced Cr(III) tends to migrate towards the cathode, resulting in high Cr(III) concentrations in the section near the anode. Cr(VI) adsorption onto soil decreases with an increase in soil pH (Reddy et al., 1997).

5.2.2.1. Glacial till. Glacial till has high buffering capacity because of the presence of carbonates in this soil. It is reported that there are no traces of acid front formation in glacial till (Reddy and Chinthamreddy, 1999). Carbonates have the ability to neutralise \( H^+ \) ions generated, and block development of an acidic pH environment near the anode. The adsorption of \( HCrO_4^- \) onto the soils is significant, but the adsorption of \( CrO_4^{2-} \) is negligible (Reddy et al., 1999). It is obvious that high pH in glacial till causes all Cr(VI) to exist as CrO_4^{2-}, which therefore results in low adsorption of species onto the soil. Soluble \( CrO_4^{2-} \) ions are transported to the anode by electromigration.

The possibility of Cr(VI) conversion to Cr(III) was evaluated (Reddy et al., 1997, 1999). It was proved that without reducing agents in the soil, significant Cr(VI) reduction to Cr(III) would not occur.

Iron deposits of hematite, pyrite and goethite occur in abundance in natural soils. When there are slightly alkaline conditions in glacial till, Cr(VI) exists predominantly in the form of CrO_4^{2-}, and it is reported in the literature that CrO_4^{2-} adsorption onto Fe_2O_3 is significant. In addition, hematite may react with constituents of glacial till, which may favour further removal of Cr(VI) in the pore water (Reddy et al., 1997).

5.2.2.2. Kaolin. A distinct pH gradient developed in kaolin causes Cr(VI) to exist as both \( CrO_4^{2-} \) and \( HCrO_4^- \) species (Reddy and Chinthamreddy, 1999). In addition, alkaline conditions near the cathode favour the existence of Cr(VI) in the form of \( CrO_4^{2-} \), which does not adsorb to the soil, and therefore most Cr(VI) exists in solution and migrates toward the anode. On the other hand, \( CrO_4^{2-} \) ions enter an acidic region near the anode, which favours the formation of \( HCrO_4^- \) ions. As mentioned earlier, \( HCrO_4^- \) adsorbs significantly to the soil, which retards Cr(VI) migration.

5.2.3. Arsenic migration and removal

In alkaline conditions, arsenic species do not demonstrate well-expressed adsorption, although As(V) is usually more strongly adsorbed than As(III). It is indicated that alkaline conditions favour arsenic electromigration, although it is very slow and time-consuming (Acar and Alshawabkeh, 1993; Acar et al., 1996; Mattson and Lindgren, 1995; Haran et al., 1996; Sah and Chen, 1998; Viadero et al., 1998). In order to enhance the electromigration process, sodium hypochlorite...
is introduced into the process. To achieve the process efficiency desired and improve the system performance, it is necessary to inject an enhancement solution directly into the cathodic compartment (Reddy et al., 1997, 1999; Reddy and Chinthamreddy, 1999).

5.3. Removal of mercury

Electrokinetic remediation of Hg-contaminated soils is very difficult because of the low solubility of Hg in most natural soils. The predominant species of insoluble Hg in the soils are HgS, Hg(I) and Hg2Cl2 (Cox et al., 1996). Several years ago, a new method for Hg removal from soils was introduced. It uses an I2/I− lixiviant solution to solubilise Hg from contaminated solids. Oxidation of reduced insoluble Hg by I2 releases Hg(II), which is complexed as soluble HgI42− and Hg ions are ready to migrate through the soil towards the anode and be removed (Cox et al., 1996):

\[
\text{HgS + I}_2 + 2\text{I}^- \leftrightarrow \text{HgI}_4^{2-} + \text{S}_{(\text{oxidised})}
\]

\[
\text{Hg(I) + I}_2 + 2\text{I}^- \leftrightarrow \text{HgI}_4^{2-}
\]

\[
\text{HgO + 4I}^- \leftrightarrow \text{HgI}_4^{2-} + \text{O}^{2-}
\]  

Once solubilised, Hg is able to migrate through the soil and be removed.

It should be mentioned that iodide solution and I2 crystals introduced near the cathode react to form I3− complex. Reduced forms of insoluble Hg can be oxidised by either I2 or I3−; however, transport of oxidant through the soil is dependent on the electromigration of the I3− anion. The HgI42− complex formed via reactions with lixiviant solution is removed from the soil by electromigration towards the anode.

A pH jump was observed during the electrokinetic remediation process. It is believed that this pH increase may be caused by the following reaction, if an excess of Cl− is present under aerobic conditions (Cox et al., 1996):

\[
\text{O}_2 + 2\text{Hg} + 8\text{Cl}^- + 2\text{H}_2\text{O} \rightarrow 2\text{HgCl}_4^{2-} + 4\text{OH}^-
\]  

(9)

Mercury removal may be more efficient if chloride or another suitable component is added to the soil system (Hansen et al., 1997). Additional chloride ions are able to mobilise the mercury, forming complex ions which are easily transported out from the soil by electromigration. For instance, hypochlorite may be a suitable compound, which oxidises metallic mercury, forming HgCl42−:

\[
\text{HOCl + Hg + 3Cl}^- \rightarrow \text{HgCl}_4^{2-} + \text{OH}^-
\]  

(10)

Although some promising results have been demonstrated, this method has several major drawbacks. First, in the presence of any organic matter, hypochlorite may form toxic, halogenated organic compounds, which are dangerous for humans and may severely harm the environment. In addition, if not removed before the electrokinetic remediation process begins, metallic mercury would inhibit the overall remediation process due to its electric conductivity.

5.4. Removal of zinc and copper

All calcium and magnesium should be removed before removal of zinc is initiated. The use of enhancing solutions, such as sodium acetate, increases the removal efficiency for metal ions, as well as reduces the process time. It is obvious that the cations with lower interaction energy will be removed first and will be followed by cations with higher interaction energy.

After the number of experiments, the sequence of heavy metal removal from soils using sodium acetate as enhancement fluid was proposed (Cox et al., 1996): Ni2+ ≈ Cd2+ > Ca2+ > Cr > Zn2+ > K+ ≈ Mg2+ > Cu2+ > Pb2+.

Also, several experiments were conducted with distilled water as the enhancement fluid and the following results were observed (Cox et al., 1996). Ca2+, Mg2+, Zn2+, K+ and Pb2+ percentage removal efficiencies were low and sometimes close
to zero. Only Ni$^{2+}$ and Cr had removal efficiencies quantified as medium–high.

A schematic electrolytic cell for the removal of copper from contaminated soil was proposed by Cox et al. (1996) (Fig. 9).

The electrolytic cell is divided into three parts and the contaminated soil and electrodes are separated by anionic and cationic exchange membranes. The anode and cathode compartments contain electrolyte solution at constant pH 3.

A low pH value was maintained to keep copper dissolved in the soil, thus making migration towards the cathode and subsequent removal from the soil feasible. Despite the fact that almost all of the copper was found in the cathode compartment, a certain amount was found in the anion membrane. It was also suggested that copper found in the anionic membrane may be due to its capability of forming complexes with different ligands present in soils (Ribeiro et al., 1997).

5.5. Other metals

Strontium remains as a divalent ion over a large pH range. The cathode should not affect strontium, since it will remain a divalent ion, even at high pH (Pamukcu, 1997).

In alkaline solution, the predominant species of Co$^{2+}$ are either positively charged ions or hydroxide Co(OH)$_2$ salts. It is apparent that at high pH, cobalt tends not to precipitate onto soil particles, and may therefore be removed.

According to the experiments, if Ca$^{2+}$ ions are removed first, then Zn$^{2+}$ follow, and finally Cu$^{2+}$ and Pb$^{2+}$ ions are removed (Hansen et al., 1997; Hecho et al., 1998). In order to mobilise contaminants, energy may be wasted in dissolving lime and carrying harmless Ca$^{2+}$ ions out of the soil. It is obvious that further research concerning other suitable soil pre-treatment methods to mobilise contaminants need to be investigated and carried out (Hansen et al., 1997; Hecho et al., 1998; Viadero et al., 1998).

6. Heavy metal removal efficiency from contaminated soils

Electrokinetic remediation techniques have demonstrated 85–95% efficiency in removing ar-

<table>
<thead>
<tr>
<th>Soil</th>
<th>Cd(%)</th>
<th>Cr(%)</th>
<th>Ni(%)</th>
<th>Pb(%)</th>
<th>Hg(%)</th>
<th>Cu(%)</th>
<th>Zn(%)</th>
<th>As(%)</th>
<th>Co(%)</th>
<th>Sr(%)</th>
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<tr>
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<td>64</td>
<td>91</td>
<td>54</td>
<td>60</td>
<td>71</td>
<td>94</td>
<td>66</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>River mud</td>
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<td>93.1</td>
<td>88.4</td>
<td>69</td>
<td>26.5</td>
<td>-</td>
<td>54.6</td>
<td>54.7</td>
<td>92.2</td>
<td>97.8</td>
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<td>93.9</td>
<td>66.9</td>
<td>42.5</td>
<td>-</td>
<td>36.3</td>
<td>27.2</td>
<td>95.9</td>
<td>96</td>
</tr>
<tr>
<td>Kaolinite and humic substances</td>
<td>86.6</td>
<td>93.5</td>
<td>93.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>64.4</td>
<td>64.3</td>
<td>89.4</td>
<td>92.3</td>
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<td>98</td>
<td>96.8</td>
<td>95.9</td>
<td>83</td>
<td>78.3</td>
<td>-</td>
<td>54.5</td>
<td>54.7</td>
<td>97.5</td>
<td>99</td>
</tr>
<tr>
<td>Clayey sand</td>
<td>86.6</td>
<td>93.5</td>
<td>93.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>64.4</td>
<td>64.3</td>
<td>89.4</td>
<td>92.3</td>
</tr>
</tbody>
</table>
copic, cadmium, chromium, cobalt, mercury, nickel, manganese, molybdenum, zinc, antimony and lead from low-permeability soils, i.e. clay, peat, kaolinite, high-purity fine quartz, Na and sand–montmorillonite mixtures, as well as from agrillaceous sand (Yeung et al., 1997). In addition, highest removal efficiencies, i.e. more than 90% of heavy metals, were obtained in kaolinite (Pamukcu and Wittle, 1992). However, for porous, high-permeability soils, such as peat and river sediment, the removal efficiency was approximately 65% (Chilingar et al., 1997).

A low pH profile in fine-grained soils may contribute to higher efficiency for metallic contaminant removal. In addition, the low acid/base buffering capacity of kaolinite also contributes to the higher heavy-metal removal efficiency for this type of soil (Hamed et al., 1991; Hicks and Tondorf, 1994). Soils with a high content of humic substances have higher cation exchange and buffering capacity, which is why electrokinetic remediation efficiencies may decrease (Table 1).

It is very important to improve the removal efficiency of heavy metals from high sorption-capacity clays, such as illitic mixture, i.e. synclays. Despite all the earlier accomplishments, electrokinetic remediation of such soils still requires higher current density, remediation time, energy expenditure and costs in comparison to kaolinite (Puppala et al., 1997).

7. Cost–benefit analysis

There are several factors that influence the cost of the electrokinetic remediation process. These are as follows (van Cauwenberghe, 1997):

- Soil characteristics and moisture content;
- Contaminant concentrations;
- Concentrations of non-target ions and conductivity of the pore water;
- Depth of the remediated soil;
- Site preparation requirements; and
- Electricity and labour costs.

During numerous laboratory experiments, it was determined that if the distance between electrodes was 1–1.5 m, the total removal of heavy metals from contaminated soil would require approximately 500 kW h/m³ of energy. Energy expenditure is directly proportional to the complete removal of contaminants from soil, i.e. remediation time (van Cauwenberghe, 1997). The total energy consumption can be lowered if appropriate cathodic polarisation techniques are used (Acar and Alshawabkeh, 1997; Li and Li, 2000). The migration rate of contaminants through the soil matrix is approximately 2–3 cm/day. If the distance between the electrodes is 2–3 m, the time frame for successful remediation would be more than 100 days (van Cauwenberghe, 1997). However, the use of a cation-selective membrane reduces the remediation period to 10–20 days.

The situation with in situ experiments is slightly different. The main parameters that influence the overall process cost are as follows:

- Soil properties;
- Depth of contamination;
- Cost of accommodating electrodes and placing treatment zones;
- Clean-up time; and
- Cost of labour and electrical power.

In order to avoid soil overheating and shorten the required time frame, the cost-optimised distance between electrodes needs to be maintained at 3–6 m for most soils (Lageman, 1993; Ho et al., 1997, 1999). Electrode construction costs account for up to 40% of the overall remediation costs. Other expenses are (Ho et al., 1997):

- 10–15% for electricity;
- 17% for labour;
- 17% for materials; and
- Up to 16% for licenses and other fixed costs.

The first in situ electrokinetic remediation technique implemented, the Lasagna™ process, has reduced the clean-up time and power input required, as well as the total costs, by inserting treatment zones between the electrodes. Treatment zones diminish the need for above-ground waste handling and are cheaper to implement.
Table 2
Cost–benefit analysis of selected techniques

<table>
<thead>
<tr>
<th>Technique</th>
<th>Costs</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lasagna™</td>
<td>50–120 $USD/m³ approximately</td>
<td>Mandrel/tremie-tube method of Emplacement will be used instead of earlier proposed steel plate Electrodes with wick drains and carbon-filled treatment zone</td>
</tr>
<tr>
<td>Soil heating/vapour extraction technology</td>
<td>65–123 US$/yd³</td>
<td></td>
</tr>
<tr>
<td>Chemical oxidation (with potassium permanganate or hydrogen peroxide)</td>
<td>130–200 US$/m³</td>
<td>Technique was mostly used to remove DNAPLs in situ</td>
</tr>
</tbody>
</table>

than electrodes (Ho et al., 1997). Ho et al. (1997) have presented a comparison of the cost–benefit analysis for selected techniques, which is shown in Table 2.

8. Conclusions

Electrokinetic soil remediation is an emerging in situ technology with demonstrated efficiency to remediate fine-grained soils, and especially to remove heavy metals from the soil matrix (Table 3). According to that stated in the articles reviewed, it is possible to draw the following conclusions on the main advantages of this technique:

- Electrokinetics is very targetable to any specific location, because treatment of the soil occurs only between two electrodes.
- Electrokinetics is able to treat contaminated soil without excavation being necessary.
- Electrokinetics is most effective in clay, because it has a negative surface charge, and in soils with low hydraulic conductivity.
- Electrokinetics is potentially effective in both saturated and unsaturated soils.
- Electrokinetics is able to treat both organic and inorganic contaminants, such as heavy metals, nitrates, etc.
- Electrokinetics demonstrated the ability to remove contaminants from heterogeneous natural deposits.
- Good cost effectiveness.

Despite all the advantages, this technique has some limitations, which are:

- The solubility of the contaminant is highly dependent on the soil pH conditions.
- The necessity to apply enhancing solution.
- When higher voltage is applied to the soil, the

Table 3
Conclusions on heavy metal removal from contaminated soils

<table>
<thead>
<tr>
<th>Metal</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead and Cadmium</td>
<td>Successful removal is obtained only under acidic conditions</td>
</tr>
<tr>
<td>Chromium</td>
<td>High removal rates were achieved with the use of HCl solution</td>
</tr>
<tr>
<td>Chromium</td>
<td>Significant part of Cr(VI) is reduced to Cr(III) if there are sulfides or other reducing agents present in the soil</td>
</tr>
<tr>
<td>Chromium</td>
<td>Low chromium migration was observed in the soil in the presence of sulfides and no retardation in the soil with humic acid</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Sufficient arsenic removal is achieved only in alkaline conditions</td>
</tr>
<tr>
<td>Mercury</td>
<td>Migration of arsenic is accelerated by an oxidising agent</td>
</tr>
<tr>
<td>Mercury</td>
<td>Efficient mercury removal is achieved using I₂/I⁻ lixiviant solution</td>
</tr>
<tr>
<td>Mercury</td>
<td>Higher removal efficiency is obtained using chloride or other suitable component added to the soil</td>
</tr>
</tbody>
</table>
efficiency of the process decreases due to the increased temperature.
- Removal efficiency is significantly reduced if soil contains carbonates and hematite, as well as large rocks or gravel.

In order to guarantee efficient electrokinetic remediation of soil, among other variables, it is important to investigate physicochemical contaminant–soil interactions and the impact of enhancing agents on these interactions, the occurrence of reverse electroosmotic flow and the influence of organic substances present in the remediated soil.

References

Benazon N. Soil remediation. Hazard Mater Manage 1999;October/November.


