18 Electroremediation of Heavy Metal-Contaminated Soils —Processes and Applications

Alexandra B. Ribeiro and Jose M. Rodríguez–Maroto

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18.1 GENERAL PRINCIPLE

Electrokinetic remediation uses an electric current density of the order of milliamps per square centimeter applied to the cross-sectional area of a soil mass between the electrodes, producing electric potential drops of the order of volts per centimeter. The main interest in electrokinetic soil remediation in environmental cleanup operations lies in an attempt to concentrate and confine contaminants close to an electrode and remove them if possible. Several authors [1–6] have critically reviewed the state of knowledge of this cleanup technology.

The general principle of the electrokinetic process is shown in Figure 18.1. Due to the electric field present when a low-level direct current (DC) is passed between a pair of electrodes placed in a system containing charged particles (e.g., moist contaminated soil), the pollutant species are driven towards one of the electrodes, from where they may be removed. Three main mechanisms are responsible for this movement: electromigration, electroosmosis, and electrophoresis. On inert electrodes, the electrode reactions can be controlled to produce H^+ ions at the anode and OH^- ions at the cathode. If pH in the soil is not controlled, an acid front will propagate into the soil pores from the anode, and an alkaline front will move out from the cathode. In Figure 18.1, the contaminated soil volume is separated from the electrolyte solutions by passive membranes to prevent the soil mixing with the electrolytes.

18.2 DEFINITIONS AND SOME ASPECTS RELATED TO THE TRANSPORT OF SPECIES

Electrokinetic extraction of contaminants from soil involves the simultaneous flows of fluid, electricity, and chemicals under the combined influences of hydraulic, electrical, and chemical gradients. Thus, coupled flows that occur as flows of one type are induced by driving forces or gradients of another type [7]. The net transport of contaminants depends on several complex interactions. Electrokinetic soil remediation invokes three main mass-transport phenomena: electromigration (migration of ionic and/or polar species); electroosmosis; and electrophoresis. Other types of mass transport, such as diffusion and hydraulic convection, are usually present in some extension.

18.2.1 ELECTROMIGRATION

Electromigration is the movement of ions under an applied electric field. It is the predominant transport mechanism in soils under an electric potential gradient [8], particularly when dealing with soluble charged species like the heavy metal cations Pb^{2+}, Cd^{2+}, Cu^{2+}, or Zn^{2+}. Here, the soil zeta

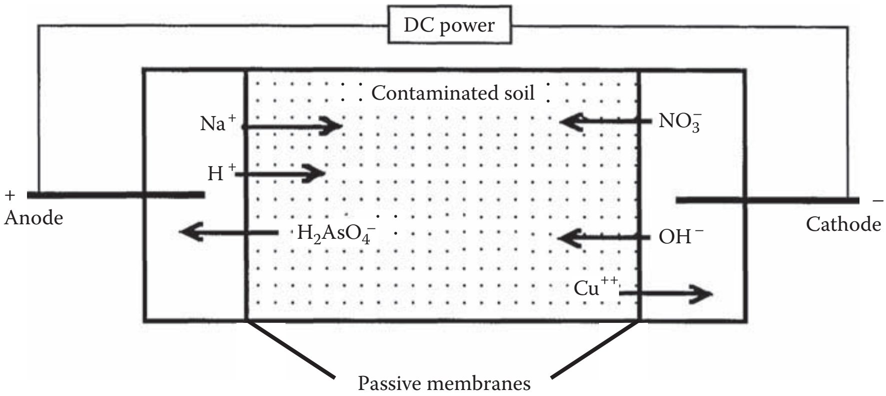


FIGURE 18.1 Schematic principle of the electrokinetic process.

potential may be absent or small [9]. Positive ions are driven towards the cathode and negative ions towards the anode. The electromigration transport is given by:

$$J_m = -\, u^* \, c \, \Phi_e \tag{18.1}$$

where J_m is the migrational flux; u^* and c the ionic mobility and concentration of species; and Φ_e the gradient of electric potential.

The current efficiency of electromigration of a specific ionic species is expressed as the proportion of electrical charge carried by the species of interest, relative to the amount of charge carried by all charged species in solution [10].

18.2.2 ELECTROOSMOSIS

Electroosmosis describes the mass flux of pore fluid relative to soil particles under the influence of an imposed electric potential gradient. When an electrical field applies across a wet soil mass, cations are driven towards the cathode and anions towards the anode. As the ions migrate, they carry their water of hydration and they exert a viscous drag on the pore fluid around them [7].

Electromigration of the species within the diffuse double layer will induce an electroosmotic pore fluid transport towards the electrode polarized with a charge opposite that in the double layer. This transport is generally from the anode to the cathode because the species in the diffuse double layer are often positively charged [8]. However, it may reverse under certain circumstances; when the electrolyte concentration is high and the pH of the pore fluid is low, it is possible to reverse the polarity of the surface charge and initiate a reversed electroosmotic flow, from cathode to anode [4,11–13].

Electroosmosis is the major mechanism of removal of uncharged and/or weakly dissociated organic contaminants (phenols, for instance), where the soil has a finite zeta potential [14,15]. The electroosmotic flux, J_{eo}, is usually obtained from expressions such as:

$$J_{eo} = -\, k_e \, c \, \Phi_e \tag{18.2}$$

where k_e is the electroosmotic permeability of soil.

The electroosmotic component of transport will almost disappear in coarse sands and high-plasticity clays at low water contents (electromigration will dominate). In fine sands, silts, and low-activity clays at high water contents and low conductivities, electroosmotic transport would be as significant a transport mechanism as electromigration [8].

18.2.3 ELECTROPHORESIS

Electrophoresis is the movement of a charged colloid under an applied electric field. The charged particles are attracted to one of the electrodes and repelled from the other [7]. Negatively charged clay particles move towards the anode. Electrophoresis involves discrete particle transporting through a liquid, which, as a whole is at rest. This movement can be neglected — usually in systems where the solid phase is stationary, like soil systems [16]. However, in unconsolidated soils, the electrophoresis may play a role in the cementation of the soil; if the electric current is applied to slurry, the role of electrophoresis is significant [2].

18.2.4 DIFFUSION

Diffusion is the movement of species under a chemical concentration gradient. In free solutions, it is usually expressed by Fick's law and in porous media as well. However, in the latter case, the effective diffusion coefficient must be obtained correcting the diffusive coefficient, to take into account the porosity and the tortuosity effects, which can decrease this transport more than one order of magnitude. The diffusive flux in soils, J_d, can be calculated by:

$$J_d = - D^* \nabla c \tag{18.3}$$

where D^* is the effective diffusion coefficient and ∇c is the concentration gradient.

In general, in the usual conditions for the electrokinetic treatments, this is a secondary transport and can be important only in some areas of soil where gradients are especially high. The areas where acid and basic fronts, or metal cations and hydroxyl ions, are to meet can be an example.

18.2.5 ADVECTION BY HYDRAULIC GRADIENTS

In general, the transport under fluid advection generated by hydraulic gradients is not an important contribution to global transport. However, one of the applications of electrokinetic treatment is to act as a reactive barrier to avoid the advance of contamination into groundwater. Particularly in this case, the hydraulic gradients convert in an important driving force to the movement of water and, therefore, of the solved contaminants across the electrical barriers.

In any case, the mass flux from hydraulic gradients, J_h, can be calculated by:

$$J_h = - k_h \, c \nabla h \tag{18.4}$$

where k_h is the hydraulic conductivity of the soil and ∇h is the hydraulic gradient. Yeung [17] has analyzed the importance of coupling effects between hydraulic and electrical gradients of fluid flow quantity in fine-grained soils.

18.3 REACTIONS IN THE ELECTRODE COMPARTMENTS

The applied electric current normally leads to electrolysis of water at the electrodes, generating an acidic medium at the anode and an alkaline medium at the cathode. The water electrolysis reactions can be described by:

$$\text{Anode: } 2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^- \tag{18.5}$$

$$\text{Cathode: } 4H_2O + 4e^- \rightarrow 2H_2\uparrow + 4OH^- \tag{18.6}$$

However, when the concentration of ions in the electrolytes is increased, other electrode processes may take place at the surface of inert electrodes. Equation 18.7 and Equation 18.8 are examples in which the Me^{n+} is a metal ion with n positive charges.

$$\text{Cathode: } Me^{n+} + ne^- \rightarrow Me \tag{18.7}$$

$$\text{Cathode: } Me(OH)_n + ne^- \rightarrow Me + nOH^- \tag{18.8}$$

Equation 18.7 represents the deposition of the metal at the cathode surface. Metals can also precipitate as oxides, hydroxides, carbonates, and phosphates, depending on pH, the chemical constituents of the pore water, and current flow [18].

If chlorides occur in the solution, chlorine gas can be produced:

$$\text{Anode: } 2Cl^- \longrightarrow Cl_2\uparrow + 2e^- \tag{18.9}$$

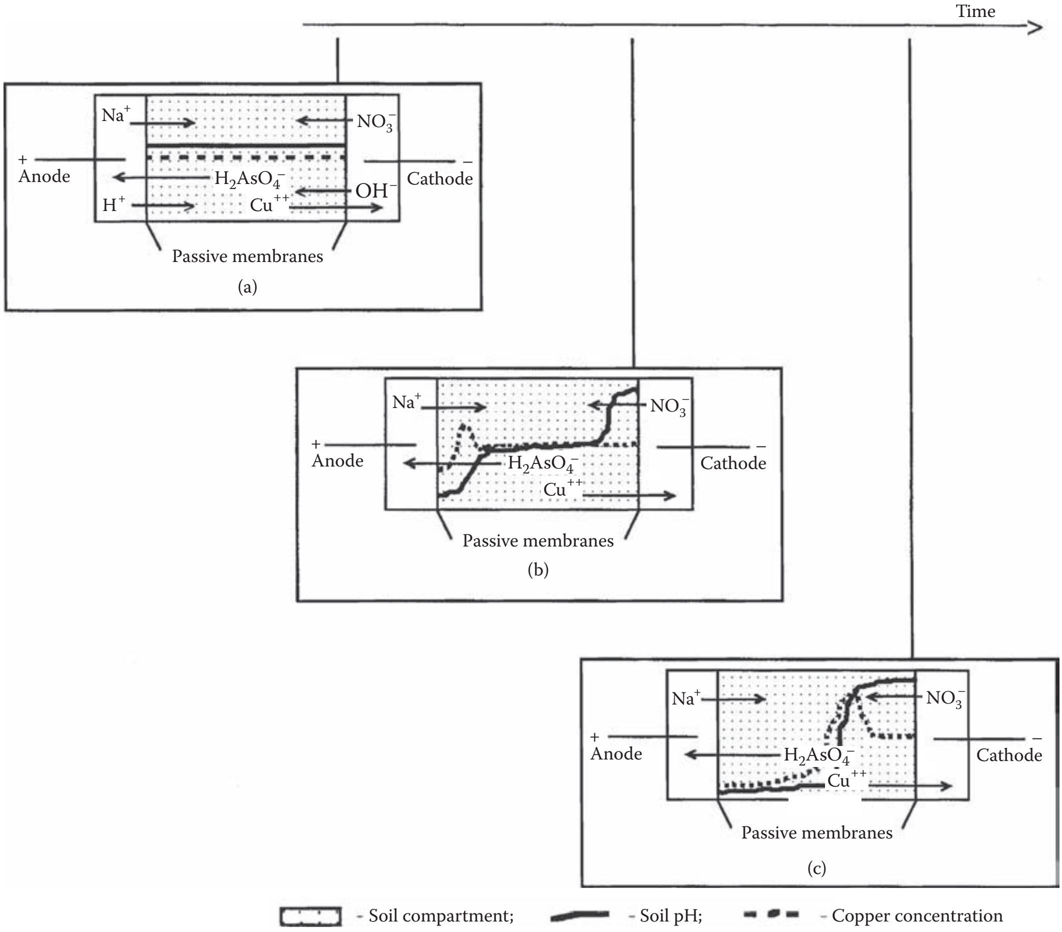


FIGURE 18.2 Soil pH and Cu^{2+} concentration profiles during electrokinetic remediation.

The reactions in Equation 18.5 and Equation 18.6 are the primary causes of the pH changes in the soil system chemistry during electrokinetics, when the technique is applied without conditioning the process fluid at the electrodes (unenhanced electrokinetic remediation). The development of the acid and the alkaline fronts can have a significant effect on the magnitude of electroosmosis, as well as on solubility, ionic state and charge, and level of adsorption of the contaminants [19].

Figure 18.2 shows schematically the soil pH and the Cu^{2+} concentration ($[Cu^{2+}]$) profiles that tend to be created during the electrokinetic soil remediation process [10]. In this figure:

- Before applying the current, the soil pH and the $[Cu^{2+}]$ are constant through the whole soil compartment. Then, when a dc current starts to pass, the soluble positive ions start to be driven towards the cathode and the negative ions towards the anode. At the electrodes, H^+ ions or OH^- ions will be created and will also move towards the opposite electrode. If $NaNO_3$ is used as electrolyte solution, Na^+ and NO_3^- will be present and will cross the barriers (passive membranes), starting their movement in the direction of one of the two electrode compartments.
- As time passes, the H^+ ions produced at the anode induce the propagation of an acid front in the soil, and the OH^- ions at the cathode induce an alkaline front. Due to the decrease in the soil pH near the anode compartment, a solubilization of Cu ions is promoted. These ions will move towards the cathode. A decrease in $[Cu^{2+}]$ takes place

near the passive membrane, which separates the soil from the anode compartment, with a concomitant increase of [Cu^{2+}] a bit further into the soil. Due to the high soil pH near the cathode compartment, a precipitation of Cu will also happen in the soil, and Cu^{2+} does not move into this electrode compartment.

- Soil pH and [Cu^{2+}] profiles reflect the propagation of the H^+ ions from anode compartment into the soil and of the OH^- ions from the cathode compartment. Because the ionic mobility of H^+ is 1.8 times higher than the mobility of OH^-, the pH fronts meet in the soil at approximately two-thirds of the distance from the anode compartment. Until this distance, the [Cu^{2+}] is low, reflecting the solubilization/desorption and movement to which the Cu ions were submitted. A peak of [Cu^{2+}] develops in the soil, due to the soil pH change, which may induce precipitation of the Cu ions when their hydroxide solubility is exceeded.

18.4 OTHER TYPES OF PHENOMENA RELATED TO MOBILITY OF SPECIES

Contaminants can undergo several types of phenomena, which can be divided into two classes [16]: those that would occur in the absence of the applied electric field, such as

- Ion exchange
- Adsorption–desorption of the contaminant from soil surfaces
- Precipitation–dissolution reactions
- Interactions between soluble chemical constituents in the pore water

The second class comprises those that occur because of the electric field, such as (1) plating of a metal on the electrode(s); and (2) electrolysis of water in the electrode compartments.

In the case of the second class, plating of a metal can be minimized by proper selection of the electrode. The nature of electrode reactions during electrokinetic treatment of soil depends on the material of the electrodes and the type and concentration of chemical species in the fluid around the electrodes [3]. For electrokinetic remediation purposes, inert electrodes (i.e., electrode material such as carbon, platinum, or titanium, which do not take part in the reaction) are mostly used (see Section 18.12).

18.4.1 Ion Exchange and Sorption

The soil particles and specialty clays have an active surface, which can interact with contaminants to their sorption or ion exchange. The large surface of some types of clays such as montmorillonite or illite increases this capacity of retention and the negative charges present usually in their structures attract cations, making their movement difficult. In this sense, the presence of other nontoxic ions (H^+, Na^+, etc.) competing for the same fixation sites, promoting their desorption, can help to increase the mobility of the contaminants.

On the other hand, when sorption/desorption is evaluated in soils, equilibrium isotherms are commonly used, assuming that the contaminants sorbed reach instantaneous equilibrium at all times. However, this assumption is only valid if movement of species is slow enough, but usually, in electrokinetic remediation, the migration velocity of species is high and therefore the kinetics of the sorption process is relevant to evaluate its effects on remediation.

18.4.2 Precipitation and Dissolution

A great variety of natural species is in a solid phase or in pore aqueous solution (e.g., CO_3^{2-}, SO_4^{2-}, S^{2-}) in the natural soils and, if the contaminants react with them, precipitation can occur. Moreover, the acid or basic fronts or other ions generated or introduced in the electrode compartments can also produce precipitation or dissolution of the contaminants. Thus, the natural buffer capacity of the soils to remediate, as well as the ions proceeding of their own electrokinetic process, must be considered in order to know the effect on dissolution/precipitation and therefore on the contaminants' mobility and soil electric conductivity.

18.4.3. MOVEMENT OF AN ACID FRONT AND AN ALKALINE FRONT IN THE SOIL COMPARTMENT

The acid (H^+ ions) generated at the anode advances through the soil towards the cathode by [11,20]:

- Ion migration due to electrical gradient
- Pore fluid advection due to electroosmotic flow
- Pore fluid flow due to any externally applied or internally generated hydraulic potential difference
- Diffusion due to the chemical gradients developed

The alkaline medium developed at the cathode first advances towards the anode by ionic migration and diffusion. However, the transport of OH^- in the soil is overshadowed by any electroosmotic advection and neutralization by the H^+ ions transported to this zone (generation of water takes place within this zone) [4,11].

According to Acar and Alshawabkeh [20], the extent of the "meeting zone" is controlled by the dissolution/precipitation chemistry of the species available in the soil; their interaction with the soil and with the hydrogen/hydroxide ions; and the electrochemistry of the species produced and/or injected in the electrode compartments. In fact, the acid–alkaline fronts that meet close to the cathode compartment within the soil, coupled with precipitation of hydroxide species in the high pH zone, result in the development of a low conductivity region close to the cathode.

18.4.4 MOVEMENT OF CONTAMINANTS

As a consequence of different phenomena previously explained, acidification of the soil facilitates desorption of the contaminants. The driving mechanisms for the transport of the species in the soil are the same as those for the acid/base transport. As a result, cations tend to accumulate at the cathode and anions at the anode, and transfer of H^+ and OH^- ions across the medium is continuous. Extraction and removal are accomplished by electrodeposition, precipitation, or ion exchange at the electrodes or in an external extraction system placed in a unit cycling the processing fluid [11,21,22].

Extraction of contaminants by electrokinetic methods is based on the assumption that the contaminant is in the liquid phase in the soil pores [23] or in exchangeable positions in the solid phase, in contact with the previous one. Electroosmotic advection should be able to transport nonionic as well as ionic species through the soil towards the cathode. This is, perhaps, best achieved when the state of the material (dissolved, suspended, emulsified, etc.) is suitable for the flowing water to carry it through the tight pores of soil without causing a plug of concentrated material to accumulate at some point in the soil [23].

Polar organic molecules, ionic micelles, and colloidal electrolytes should migrate under the influence of an electric field, as well as being transported by the water. The size of these molecules or micelles and their tendency to agglomerate or be adsorbed onto soil surfaces are probably the main factors that control their removal from soil pores by electrokinetics [23]. Removal of cationic species, on the other hand, should be enhanced by the electroosmotic flow of water as they migrate towards the cathode electrode compartment by the applied potential [23]. In noncompact soils, concurrent colloidal transport may be significant in altering the microstructure of the porous medium and in facilitating the transport of adsorbed metal ions and organics [24].

The concentration of the metal on the soil strongly influences the retention energy and the operative removal mechanism. At low concentrations of metals, removal is most likely due to desorption. Numerous sorption sites on soils have a wide range of binding energies. At low metal concentrations, the high energy-binding sites are occupied first. At higher metal concentrations, the high energy-binding sites are completely occupied and the lower energy-binding sites begin to fill, resulting in a decrease in the average metal–soil binding energy. As a result, it is easier to remove a given percentage of the metal from the more highly contaminated soil. However, even for the highly contaminated soil, it becomes progressively harder to remove the remaining metals (i.e., metals associated with the high energy-binding sites). On the other hand, the formation of insoluble compounds on the soil surface or in the pore liquid can occur if the concentration of the metal is high; if the soil pH is alkaline; or if anions such as Cl^- and SO_4^{2-} are present in sufficient quantity [16].

The relative magnitude of contribution of either process (electroosmosis and electromigration) to decontaminate under a given set of initial and boundary conditions is determined by the soil and contaminant type, as well as their interaction, is yet unclear. At low concentrations of cations, electroosmotic water flow may contribute a significant percentage to, if not be totally responsible for, the overall decontamination process. At high concentrations of ionic species, electrolytic migration and intensity of electrochemical reactions may play more important roles than electroosmosis in the decontamination process [23].

Detailed descriptions of the coupled transport processes of fluid, electricity, and contaminants during electrokinetics, and associated complicated features generated by various electrochemical reactions, have been given by several authors [3,7,9,12,25,26].

18.5 RELEVANCE OF THE TECHNIQUE

An electrical gradient is a much more effective driving force than a hydraulic gradient for moving a fluid, particularly through fine-grained soils of low hydraulic conductivity [3]. In fact, the values of hydraulic conductivity of different soils can differ by orders of magnitude (from 1×10^{-9} to 1×10^{-4} cm/s because it varies with the square of some effective pore size). However, the values of the coefficients of electroosmotic conductivity range generally from 1×10^{-5} to 10×10^{-5} $cm^2/V.s$ and are relatively independent of the soil type [7,25].

Electrokinetic remediation appears to be one of the most effective techniques for restoration of polluted sites. The obtained results, at different scales, show that electrokinetic remediation of soils can be an effective technology in heterogeneous and fine textured soils (clayey to fine sandy soils) because, in gross texture soils, other technologies can present good enough cleanup rates and better economic results. According to Yeung et al. [13], the technology is particularly effective and economical in fine-grained soils where pump-and-treat technology is impractical, if not impossible. The complementary nature of the electromigrational component of mass flux to electroosmotic mass flux is the reason why electrokinetic remediation can be a technically feasible and cost-effective means of extracting soluble and predominant species from all types of soils. Electromigrational flux will transport the species even when electroosmotic flux ceases or does not develop [4].

Soils of high water content (preferably saturated) and low physical and chemical fixation capacity are the most favorable to electrokinetic application. However, Sandia National Laboratories [27] in a demonstration into the program SITE, removed hexavalent chromium with acceptable efficiencies from an unsaturated soil. An optimal moisture content was determined to be in the range 10 to 12% w/w, corresponding to approximately 25% saturation.

The soils with a high buffer capacity are difficult to be electroremediated and it is close to obligatory to enhance the process by means of chemical reagents [28,29]. Thus, in soils with high content in illite, montmorillonite, carbonates, hematite, or other metallic oxides, the electrokinetics may need special operative conditions to be effective.

Electrokinetic technology has been applied to multiple types of contaminants. In general terms, it is possible to affirm that electrokinetics is not a selective technology transporting species because the electric potential is the driven force for electromigration of all (natural and contaminants) ions. Furthermore, the electroosmotic flow transports all the solutes in pore aqueous phase without distinction. Therefore, there is no reason to limit the type of contaminant to be removed, although naturally, its speciation in soil is a determining factor to the efficiency. A chemical element can be presented inside the soil as many different contaminant species; a precipitated solid (carbonate, sulphide, hydroxide, etc.); sorbed phase on mineral or organic matter; solved in the aqueous phase; and others with very different mobility, depending on environmental conditions.

18.5.1 *IN SITU* VS. *EX SITU* PROCESSES

A trend favors developing natural *in situ* rather than *ex situ* processes. The *in situ* processes are expected to have minimal construction and mobilization costs compared with alternatives for excavating or mixing contaminated soils for use in other *in situ* or *ex situ* technologies. The costs of remediation may be increased further when using disturbed soil in *ex situ* technologies by inadvertent contamination of uncontaminated soils [30]. In some cases, excavation of soil for *ex situ* treatment is not feasible (e.g., under buildings that must not be demolished) and electromigration provides a means to recover these contaminants *in situ* in a cost-effective manner [31].

Applied as the cleaning agent to a contaminated soil, the electric current promotes a redistribution of contaminants within the soil from fractions more tightly bound into the soluble and the exchangeable fractions, and those most weakly bound to soil particles or nonspecifically adsorbed. During the electrokinetic process, electromigration is one of the most important mechanisms by which the pollutant species are driven towards one of the electrodes, where they may be removed. Because electromigration requires the ions to be in solution and in exchangeable forms, the referred redistribution of contaminants shows that electrokinetics is very promising for the remediation of soils. However, care must be taken in order not to interrupt the decontamination process (by interrupting the electric current) at a stage at which the removal is still happening because increased mobility of heavy elements would endanger other ecosystem sections — groundwater, for example [32–34].

The fact that the technique requires a conducting pore fluid in a soil mass may be a shortcoming if concerns about introducing an external fluid in the soil [4] are present. *Ex situ* use of the technology minimizes or excludes this problem. Due to the previously presented, *ex situ* (on-site or off-site) treatment may be most desirable because it allows the joined actions [10]:

- Possibility to judge easily whether the soil is in a condition assuring a successful project; whether its contamination occurs in concretions or in solid forms (as paint residues); or whether the soil contains metal or isolating objects, which make a pretreatment compulsory/necessary
- Pretreatment such as sieving and/or incubation with an acid or with a complexing agent
- Making soil sorting and pollution uniform by their types, possibly to submit to different treatment processes (e.g., a certain coarser or finer soil fraction, considered more or less polluted, by a contaminant, sorted out and submitted to other soil cleaning processes in a nearby available plant)
- Soil homogenization (e.g., wood, stones, and metal pieces can easily be taken out when the soil is excavated and clay lumps can be reduced to pieces) contributing to increasing the efficiency of the process
- Confining the soil volume, thus allowing a much easier monitoring of the process without exposing the environment to possible risks

- Consideration of the possibility of a downstream, controlled phytoremediation scheme (e.g., using heavy metal plant accumulators) to profit from the soluble contaminants, taking advantage of the plant uptake and without endangering groundwater
- Climatic considerations (cover or not cover the processing units)

A lot of contaminated areas currently submitted to remediation correspond to places that became dear due to urban expansion. A common target consists of building at the place and the necessity to remove the soil, in any case. Excavation and transport are, then, already considered a part of the plan, without taking into consideration the best remediation practices. Advantages to an *ex situ* remediation approach can be taken from this procedure.

18.5.2 Disadvantages that Interfere with Efficiency of the Process

The electrokinetic soil remediation previously described serves to concentrate and confine contaminants close to an electrode. However, when the media that separate the electrode compartments from the soil are passive membranes, some disadvantages can be depicted. The ions from the electrolytes are able to move across the passive membranes into the soil and out on the other side of the soil compartment because of their electric charge. Due to the soil cation exchange capacity, some of the heavy metal ions may be exchanged with other cations, which are not soil contaminants. In this case, it is preferable to have a transport of cations into the soil. However, if the transport of these cations is more rapid than the cation exchange process, it results in a transport of harmless cations from the anode to the cathode. This raises the costs of the method and results in inefficient remediation if the electrolytes are more mobile than the heavy metals in the soil in the electric field.

Care must be taken when considering the electrolyte solutions to be used in the process because they may create additional problems to the soil. For example, in the case of using $NaNO_3$ as electrolyte solution, Na^+ ions will pass from the anode compartment into the soil, where they may promote deflocculation of the clay soil fraction during their transport through the soil into the cathode compartment.

When the technique is applied without conditioning (unenhanced electrokinetic remediation), water electrolysis reactions at the electrode compartments (Equation 18.5 and Equation 18.6) promote the development of an acid and an alkaline front in the soil. The rate at which the hydrogen and hydroxide ions are produced is fixed by the current and occasionally also by competition of other types of electrode processes. The mobility of H^+ is higher than the mobility of OH^-, so an accumulation of contaminants (e.g., heavy metals) appears close to the cathode compartment. Excavation of the soil volume in the accumulation zone may be a way of attaining the soil-cleaning target concentrations. However, the excavated soil volume must be submitted to proper treatment and/or disposal, so a transfer of the contaminants always occurs at least point-wise.

These limitations may be overcome by the use of ion exchange membranes instead of passive membranes or using enhancing chemical reagents.

18.6 PROCESS ENHANCEMENT WITH CHEMICAL REAGENTS

The physicochemical soil-contaminant interactions occurring during the electrorestoration have a high impact on the efficiency of cleanup. Along with the electrokinetic processes, many kinds of independent or related reactions are simultaneously or alternatively occurring; this is a very good chance for electrokinetic remediation of soils to improve its results by means of stimulating the favorable and diminishing the unfavorable reactions. Thus, in a natural way, the Faradic reactions in the electrodes generate acid and basic fronts that can be accelerated or restrained to promote high or low necessary pH in the soil pore water. This is why different enhancement methods have been basically proposed to control the high pH.

These methods include adding chemical enhancing reagents to improve metal solubility in the soil [35–38], using the CEHIXM process [39], and conditioning cathode and anode pH [40–44]. In some studies, water with added caustic or lime was circulated through the anode compartment in order to control the pH, favoring the electroosmotic flow (permeability 0.5 to 2.5 10^{-5} $cm^2/V.s$) and increasing the efficiency of the process. However, it is important that extremely high pH does not occur in the anode because an increased degree of undesirable soil swelling can be produced in this case.

The enhancing agents will further complicate the chemistry of the soil-contaminant reactions and must be carefully considered. In this sense, the enhancement by pH conditioning of electrodes has been modeled [45–47], allowing calculation of the pH and contaminant profiles in the soil and select operative conditions to get an optimized enhancement.

When no external ions are added in the electrolytes, the electrical current is expected to be at a low level [42] because metal hydroxides and others are precipitated near the cathode. The precipitation of species decreases concentration of ionic species in the soil pore fluid, decreases electrolyte strength, and renders a zone of low conductivity. The formation of this high-resistance zone causes a significant increase in the voltage drop across the soil if a constant current is operated, increasing the energy expenditure. Thus, the use of pH conditioning solutions to control the catholyte pH can stop or diminish the generation of the basic front and limit the precipitation of metals, resulting in an increase in conductivity and decreasing the voltage drop.

The use of solutions to a partial or total neutralization of OH^- in the catholyte renders acid soils that usually can generate electroosmotic flow towards the anode, producing positive or negative effects on the removal efficacy [38,44,48]. In addition, when agents to complex metals are used, it is necessary to take into account the opposite movement of the metal positive ion and the negative charged complex metal agent. This last phenomenon, with metal simultaneously moving towards anode and cathode, probably will produce a high accumulation of metal in the middle part of the soil. A list of very important characteristics of the enhancing reagents for a good performance has been reported (literally from Alshawabkeh et al. [49]):

- They should not form insoluble salts with the contaminant within the range of pH values expected to develop during the process.
- They should form soluble complexes with the contaminant that can electromigrate efficiently under DC electric field.
- They should be chemically stable over a wide range of pH values.
- They should have higher affinity for the contaminant than the soil particle surface.
- They and the resulting complexes should not have a strong affinity for the soil particle surface.
- They should not generate toxic residue in the treated soil.
- They should not generate an excessive quantity of wastewater or the end products of the treatment process should be amenable to concentration and precipitation after use.
- They should be cost effective, including reagent cost and treatment costs for the waste collected and/or wastewater generated.
- They should not induce excessive solubilization of soils or minerals or increase the concentrations of any species in the soil pore fluid.
- If possible, they should complex with the target species selectively.

Also, the electrokinetic process permits the supply to the soil of other external reagents by electromigration and/or electroosmotic flow. Moreover, when the soil receives electrical energy under certain conditions, it can become a network of microelectrolytic cells generating *in situ* the necessary environment to bring out reduction or oxidation reactions permitting the enhancement of the electroremediation. The latter, as electroosmotic flow, is a result of the double diffuse layer that, under electrical current, acts as a condenser, due to the low conductivity of soil solid particles

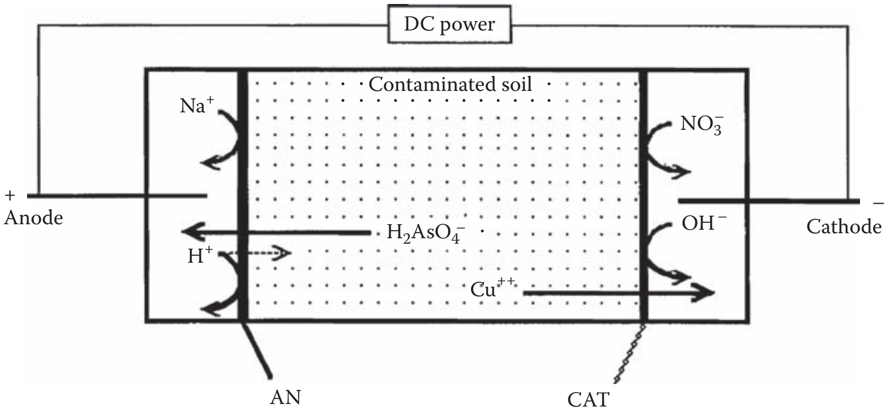


FIGURE 18.3 Schematic principle of the electrodialytic process. AN = anion exchange membrane; CAT = cation exchange membrane.

and the high conductivity of the surrounding pore aqueous phase. In this sense, a successful reduction of Cr(VI) inside the soil by means of supply of ferrous iron and electrical energy has been recently reported [50].

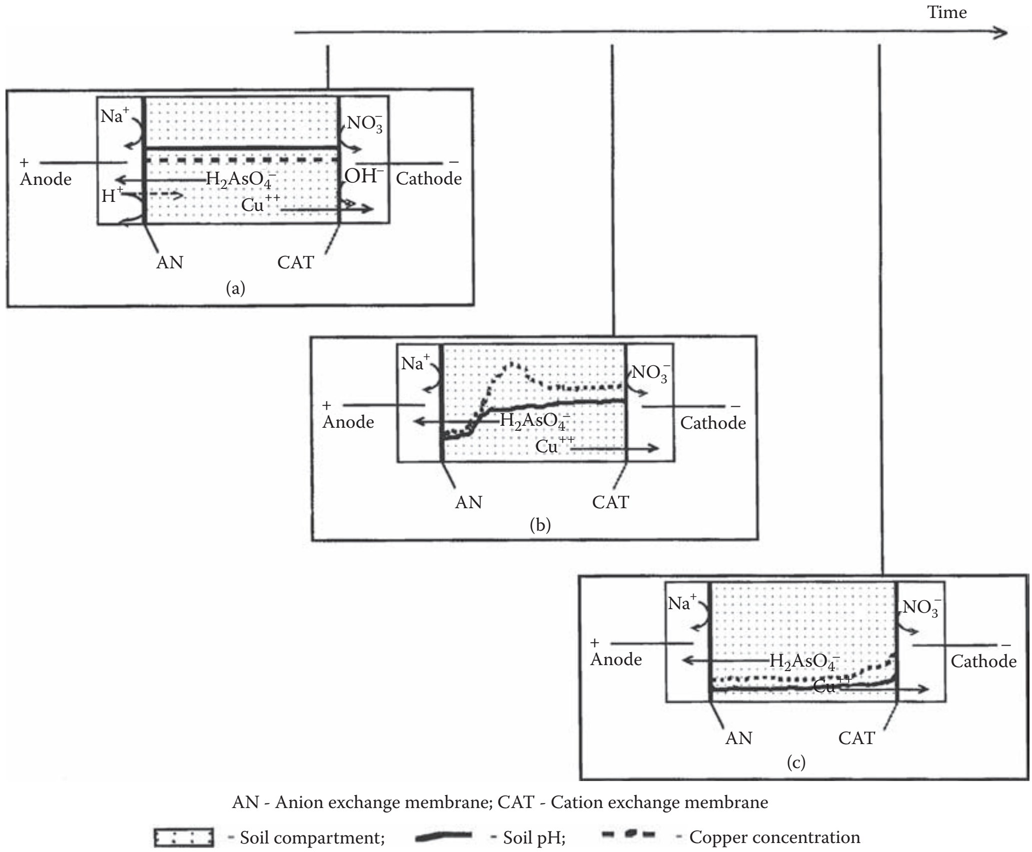
18.7 ELECTRODIALYTIC SOIL REMEDIATION

Electrodialytic remediation is a technique for removal of contaminants from polluted substrates. The method is based on a combination of the electrokinetic movement of ions (e.g., in a contaminated soil) with the principle of electrodialysis [10]. The general principle of the electrodialytic process is presented in Figure 18.3. It is similar to the electrokinetic remediation process (depicted in Figure 18.1), apart from the ion exchange membranes (instead of passive membranes), which are used to separate the contaminated soil volume (central cell compartment) from the two electrode compartments at the extremes.

An anion exchange membrane, AN, interposed between the anode compartment and the soil, will prevent cations from passing from this electrode compartment into the soil (apart from H$^+$, which can be an exception) and will allow anions to pass from the soil into this compartment. Similarly, a cation exchange membrane, CAT, interposed between the soil and the cathode compartment, will prevent the passage of negatively charged ions into the soil and will permit the cations (e.g., heavy metals and natural cations present in the soil) to pass from the soil into the cathode compartment (Figure 18.3).

The method has mostly been applied on a bench scale to heavy metal-contaminated soils [2,31–33,52–59]. The electrodialytic concept [51] has been the research topic of the Environmental Electrochemistry Group at the Technical University of Denmark (EEG/DTU). Laboratory electrodialytic cells are under continuous development to improve the transport processes; in addition, the concept has been scaled up into a pilot plant scale remediation cell, in collaboration with a commercial company (Soilrem Holding A/S, previously the Danish company A·S Bioteknisk Jordrens). The Technical University of Denmark is also running a pilot plant called "MegaLab" at the DTU Campus.

Due to the electric field present when a DC is passed between a pair of electrodes and placed in a system having charged particles (e.g., contaminated, moist soil), the pollutant species (and natural ions in the soil) are driven towards one of the electrodes, from where they may be removed. The three main mass-transport phenomena invoked during electrokinetic soil remediation (electromigration, electroosmosis, and electrophoresis) continue to act during the electrodialytic process. Electrodialysis provides some improvements over the electrokinetic concept [10]:



AN - Anion exchange membrane; CAT - Cation exchange membrane

▨ - Soil compartment; ▬ - Soil pH; ■ ● ■ - Copper concentration

FIGURE 18.4 Soil pH and Cu^{2+} concentration profiles during electrodialytic remediation.

- CAT acts as a "rectifier," only allowing cations to pass, which should lead to higher efficiencies for the heavy metal transport to cathode. AN is not a complete rectifier because it may let H^+ pass. Although this is known to happen [60], it has not been fully explained and its extension is unknown.
- There will be no flow of electrolytes between the two electrode compartments (assuming that the membranes are ideally permselective).
- The soil is continuously emptied of anions and cations until no more metal ions are available to be transported (indicated by a substantial rise in the resistance over the soil volume).
- The resistance will presumably increase until a certain level and become constant.

Figure 18.4 shows schematically the soil pH and the copper concentration ($[Cu^{2+}]$) profiles that will be developed during the electrodialytic remediation process [10]. A comprehensive overview on the study of practical and theoretical aspects concerning the use of ion exchange membranes in electrodialytic soil remediation can be found in Hansen [56]. In Figure 18.4 [10]:

- First, before applying the current, the soil pH and the $[Cu^{2+}]$ are constant through the whole soil compartment. Then, when a dc current starts to pass, in the soil compartment the soluble positive ions start to be driven towards the cathode and the negative ions towards the anode. At the inert electrodes, H^+ ions and OH^- ions will be formed. However, due to the CAT, the OH^- ions will not be able to pass from the cathode compartment into the soil. The AN will retard but not prevent the passage of H^+ ions from the anode compartment into the soil; this means that an acid front will start to propagate from this electrode compartment into the soil. If $NaNO_3$ is used as electrolyte solutions, Na^+ and NO_3^- will be present in the electrode compartments. However, due to AN and CAT, respectively, these ions will stay in the corresponding electrode compartments.

- As time passes, soluble cations and anions present in the soil compartment continue to move towards the electrode of opposite charge. Due to the usual cation exchange capacity of the soil, there are more "free" cations to move than anions. If the current density used in the process is high compared with the ion velocity in the soil solution, the result is that not enough mobile anions will be available in the soil compartment to cross the AN into the anode compartment. At the interface of AN/soil, the water present will dissociate into H^+ ions and OH^- ions and the OH^- ions will cross the membrane towards the anode; the H^+ ions will add to the electromigration, moving towards the cathode compartment. An acid front will be formed and propagate into the soil from the vicinity of the AN in the direction of the cathode. These H^+ ions join with the H^+ ions, which could pass from the anode compartment, through the membrane, into the soil. The promoted acid front and the concomitant decrease in the soil pH will facilitate the desorption/dissolution of copper in the soil. A decrease in $[Cu^{2+}]$ happens near AN, with an increase in $[Cu^{2+}]$ a bit further into the soil.
- If enough time is given for the process, the acid front will sweep through the whole soil volume. The decrease in the pH will facilitate the redistribution of Cu from forms more tightly bound to soil particles into forms that can electromigrate. The $[Cu^{2+}]$ will decrease in the soil because Cu^{2+} ions will pass into the cathode compartment. Eventually, the whole soil volume will attain copper levels that can be considered acceptable from a remediation point of view.

18.7.1 CHARACTERISTICS OF ION EXCHANGE MEMBRANES FOR ELECTRODYALITIC REMEDIATION

Since 1948, ion exchange membranes have been applied to a variety of processes:

- To concentrate or dilute ions, as in demineralization of potable water, desalination of brackish water to drinking water, and concentration of seawater for salt production [61]
- To LiCl battery chemistry [62] and waste water treatment [63]
- To exclude OH^- ions generated in the cathode to migrate from the cathode compartment towards soil [64,65]
- For the electrodialytic remediation previously discussed

In the electrodialytic remediation, the use of the selective membranes increases the efficiency of the removal process. In an electrodialytic cell for soil remediation purposes, the ion exchange membranes should be characterized by [10,56]:

- Good conducting properties (high conductivity and thereby low electric resistance) in order to have a low power consumption
- Good chemical stability over a wide pH range and in the presence of oxidizing agents
- Low degree of swelling so that, during the remediation process, no problems will develop due to changes in shape and size
- Good mechanical stability and the possibility that, after regeneration the membranes can be reused in the cell in reproducible conditions

- A lower electroosmotic transport of water than the soil volume to maintain a wet interface between the soil and the membrane, in order to ensure contact between the soil and the membrane
- A high exchange capacity in order to maximize the fluxes of counter-ions and minimize electrical resistance
- High selectivity for opposite charged ions and a high permeability (high permselectivity), in order not to waste electricity in the transport of co-ions through the membranes and into the soil volume

The selective membrane bounding the cathode compartment must be resistant to strong bases; meanwhile, the anion exchange membrane near the anode must resist strong oxidant and acidic conditions.

18.7.2 ELECTRODIALYTIC VS. ELECTROKINETIC TECHNIQUES: EXPECTED IMPROVEMENTS

In addition to the previous advantages, the presence of the ion exchange membranes does not allow the ions of the electrolyte solutions (in Figure 18.4, Na^+ and NO_3^- ions from the exemplified $NaNO_3$ electrolytes) to pass into the soil compartment. Therefore, the presence of the membranes allows the use of any kinds of electrodes, inert or reacting ones. Without the membranes, the use of reacting electrodes would be out of the question because their electrode processes could possibly create new polluting ions, which could be transported into the soil. Even in the case of the formation of harmless ions (due to the electrode processes), current would be wasted in moving them, contributing to make the whole process more expensive [10].

The ion exchange membranes also prevent the removed species from the soil compartment from passing again into the soil. These species will stay in the electrode compartment to which they were transported, although some may change polarity in certain medium conditions. The Cu^{2+} transported to the cathode compartment is an example because it might form $HCuO_2^-$ at very high pH [66]; however, due to the presence of the cation exchange membrane, these ions will stay inside the cathode compartment.

Although the soil acidification favors remediation, when the increase in the hydrogen ion concentration is considered in conjunction with electromigration of a species of interest, a substantial increase in the hydrogen ion transference number may hinder transport of other species. This means that the acidification should be controlled to a limit at which the desorption will occur but, at the same time, the acidification should be kept at a minimum so that the transference number of H^+ ions is not higher than needed. Otherwise, energy would be wasted in carrying the H^+ ions from the anode to the cathode, and the soil would end with a low pH, incompatible with any further use after treatment [2]. The desired control of the pH is possible in the electrokinetic (EK) and in the electrodialytic (ED) soil remediation cells; however, the latter case is easier to control, due to the use of the ion exchange membranes.

18.8 GEOMETRY OF ELECTROKINETIC SYSTEMS

In order to analyze the effect of the geometry of the system in soil electroremediation, it is convenient to conduct a separated study dependent on the scale application: laboratory and larger scales, pilot plant and field tests. However, common in both cases is a clear lack of experimental and theoretical studies on two-dimensional systems and electrodes that can be installed horizontally or vertically.

18.8.1 LABORATORY EXPERIMENTS

Most of the laboratory experiments have been carried out in one-dimensional arrangements, although with some differences among them. One kind of laboratory experiment employs different planar electrodes for cathode and anode; others employ cylindrical electrodes.

Thus, for example, in electroosmotic remediation, Schultz [67] used a panel consisting of galvanized steel screen and a piece of corrugated plastic wrapped in a geotextile as a cathode. The cathode compartment was a cavity filled with coke particle or a panel consisting of iridium-oxide coated expanded titanium mesh sandwiches between two pieces of perforated corrugated plastic, then wrapped in a geotextile. In this way, the soil and the electrode were separated and the corrugated plastic easily extracted the electrode fluids. Recently, a one-dimensional cell, 10 cm in length and diameter with planar electrodes, was used in bench tests [68] for electrokinetic removal of chromium and cadmium.

Other authors use two cylinders of graphite [44] or platinum wires [50] as electrodes; the electrokinetic removal of copper from Chinese red soil 600 g inside a PVC column with a length of 10 cm and 6.5 cm in diameter [44] has been recently studied. A two-dimensional modeling and laboratory arrangement for experimental validation has also been recently reported using cylindrical graphite electrodes [69].

18.8.2 FIELD APPLICATIONS

In field applications and pilot plants one-dimensional and two-dimensional systems have been used. In the simplest configuration, a group of sheet electrodes, electrode trenches, or lines of rod electrodes placed in boreholes produce a one-dimensional approach (Figure 18.5). In some cases, the field system is designed in a similar way to the laboratory installation but with larger electrode panels. Thus, Schultz [67] inserted electrode panels about 50 cm wide into the soil to an average depth of 4.5 m for a system 3 m × 10 m. The 10-m row of anode panels consisted of 16 panels with an average gap of 12 cm between them. The 10-m row of cathode panels consisted of 15 panels separated by 15 cm each. The final arrangement of the electrodes was similar to pile sheets (Figure 18.5a). DC power was supplied by a rectifier capable of delivering 65 A at 120 V.

Sandia National Laboratories [27] also essayed a one-dimensional configuration at a chromium-contaminated site of the U.S. Department of Energy in Albuquerque, New Mexico. The electrode system consisted of an anode row and four rows of cathodes parallel to the anode row, two at each side; all were 6 m depth and separated 1 m each one of the immediate (Figure 18.5b). In this way, overall hexavalent chromium efficiency rates varied from 36 mg/kW-h up to 136 mg/kW-h, operating with a limited maximum current of 15 A per electrode.

Another, more recent field scale demo study [68] was conducted on (9.14 m × 4.57 m × 3 m) soil at the Naval Air Weapon Station (NASW), Point Mogu, California. The electrokinetic system included a matrix of electrodes. Three cathodes were centered between six anodes (Figure 18.5c). The anode–cathode distance was about 4.5 m and the depth of the electrode wells was 3 m. The spacing between same polarities' electrodes was 1.5 m. The anode consisted of 0.9 m long, 2.54 cm diameter titanium hollow tubes (Eltech) with an iridium oxide coating. The cathode electrodes were constructed of 3.2 mm × 5.2 cm × 3 m long (shortened to 1.2 m after 118 days) stainless steel mesh. The anode and cathode wells were capped with PVC couplings for easy removal. Electrical power was applied to the electrode array via three 10-kW power supplies.

Also, commercial applications have used one-dimensional configurations. Thus, in 1987, the first electrokinetic commercial remediation project was conducted in a former paint factory contaminated with lead and copper in Groningen, the Netherlands [70]. The system consisted of a vertical array of alternating anodes and cathodes spaced on 3-m intervals (Figure 18.5d). After 430 hours of operation, lead content was reduced 70% and copper 80%.

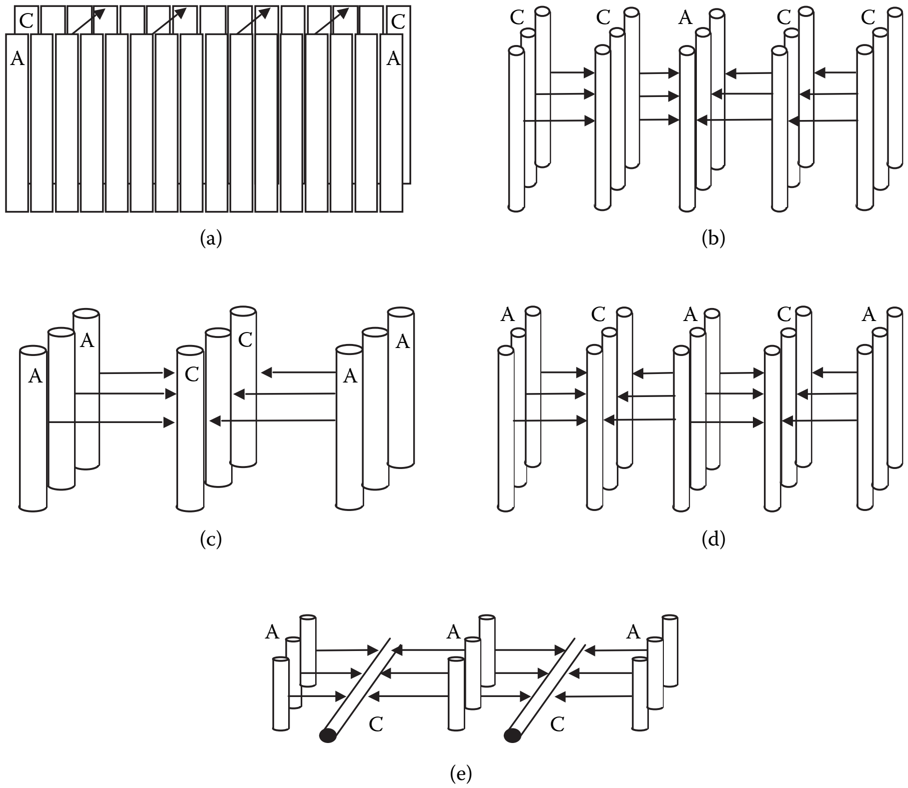


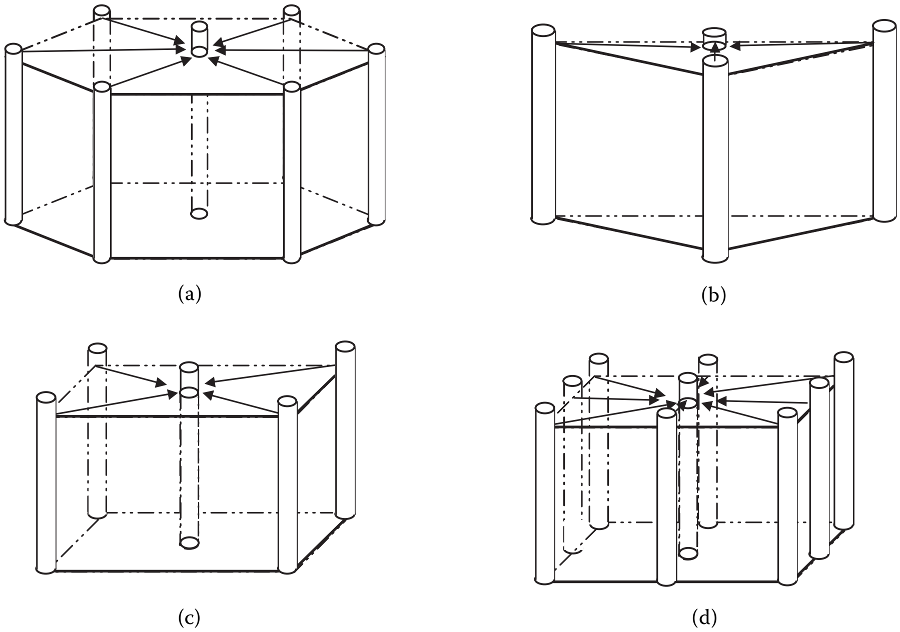
FIGURE 18.5 One-dimensional configurations for electrokinetic remediation at field scale.

One of the larger commercial electrokinetic remediations was carried out in a Dutch Royal Air Force base in 1992 with 2600 m^3 of soil contaminated with cadmium and other heavy metals [70]. This operated a hybrid vertical–horizontal system consisting of large tubular cathodes and short vertical anodes (Figure 18.5e). The tubular anodes were separated at 1.5-m intervals between the cathodes. The electrokinetics reduced the cadmium from 7300 to 47 ppm in 580 days.

These one-dimensional arrangements usually have the advantage of being the simplest and most cost-effective configuration. The frequent existence of areas of inactivity of electric fields or dead zones between electrodes of the same polarity are disadvantages. For this reason, the efficiency of the operations carried out with one-dimensional systems depends especially on spacing between electrodes of the same polarity (anode–anode or cathode–cathode) determining the number of electrodes required. If spacing between same-polarity electrodes is decreased, dead area inside the interest dominiom is minimized, improving the efficiency. Naturally, this also results in an increase of the cost of the equipment.

If two-dimensional systems are employed, the performance is very similar, although when two-dimensional configurations are employed, usually the principal objective is the generation of a radial or axial-symmetrical flow from the peripheral electrodes to the central electrode. If the selected contaminants to be removed are positive ions of heavy metals, the peripheral electrodes will be anodes and the center will be occupied by the cathode favoring the apparition of high concentrations of cations around the central zone and their easier and faster removal. If anions are to be removed, the polarity of electrodes reverses this position.

The peripheral electrodes can be ordered according to different geometrical distributions: hexagonal, square, and triangular, or, ideally, in any way close to a circle (Figure 18.6). The number


(a) (b)

(c) (d)

FIGURE 18.6 Two-dimensional configurations for electrokinetic remediation at field scale.

of outer electrodes corresponding to an inner electrode depends not only on the geometrical configuration but also on additional technical decisions.

Thus, the central electrode is surrounded by six peripheral electrodes in the hexagonal distribution (Figure 18.6a) and in the triangular by three (Figure 18.6b). However, if a square distribution is used, the center can be surrounded by four (Figure 18.6c), eight (Figure 18.6d), or even more electrodes with opposite charge to the central electrode. Also, these two-dimensional configurations generate the corresponding dead zones, without electrical activity. Obviously, the extension and situation of these areas strongly depend on the selected geometrical configuration and the number of electrodes in the system; however, in general terms, these dead zones in two-dimensional systems are smaller than in one-dimensional arrangements.

Electrical field spatial distribution indicates [71] that dead area in all the cells has a shape of a curvilinear triangle whose base is the distance between same-polarity electrodes (Figure 18.7). The height of this triangular area depends on processing time, electrode spacing, and alignment. The height of this triangle is expected to be larger in the case of one-dimensional compared to two-dimensional configurations due to the electrode alignment. An approximate practical method for comparing the efficiency between configurations assumed that this height is half the length of the triangle base for one-dimensional and a quarter of the length of the base for two-dimensional applications [71]. Figure 18.7 shows approximate distributions of the resulting inactive spots for selected configurations.

Another important difference between one- and two-dimensional configurations is that the current density is constant between the different polarity electrodes in the former and increases from external to center electrodes in the latter. Also, as another geometrical consequence, the soil volume extension swept for the desired acid or basic front proceeding from the outer electrodes is favored with respect to this in the one-dimensional installations.

In both types of configurations, the highest is the total number of electrodes in the installation, the highest is the cost, the more cost of immobilized capital and less time to do the cleanup. This produces two partial costs going in opposite directions and, therefore, an optimization of them is recommended to reach a minimum total final cost.

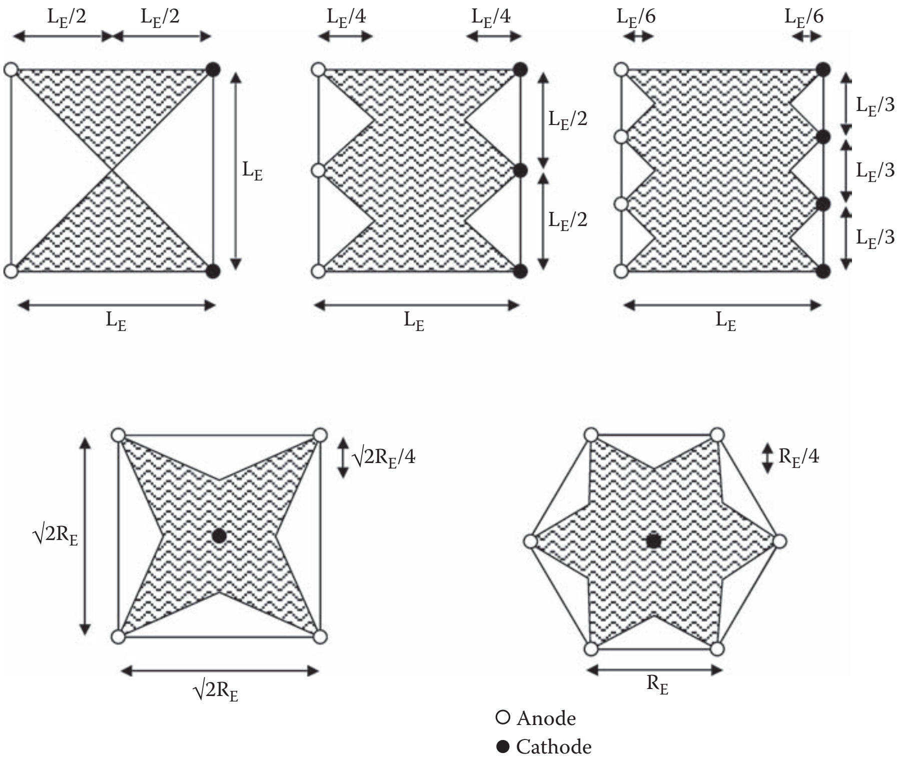


FIGURE 18.7 Approximate evaluation of ineffective areas for one and two-dimensional electrode configurations. (Modified from Alshawabkeh, A.K. et al., *J. Soil Contamination*, 8, 617, 1999. With permission.)

18.8.3 NUMBER OF ELECTRODES

A comparison of the number of electrodes required per unit surface area for one-dimensional, two-dimensional, hexagonal, and square configurations has been published [71]. In the one-dimensional configuration, three cases were provided in which the spacing among same-polarity electrodes equals: (1) spacing among opposite-polarity electrodes; (2) one-half of opposite-polarity spacing; and (3) only one-third of opposite-polarity spacing. Then, the number of electrodes is calculated based on unit of surface area. Considering a unit cell, the number of electrodes per unit area is

$$N = \left[\frac{F_1}{L_E^2}\right]_{1D\,flow} = \left[\frac{F_1}{\pi R_E^2}\right]_{2D\,flow} \qquad (18.10)$$

where

N (L^{-2}) is the number of electrodes per unit surface area of site to be treated
L_E (L) and R_E (L) are one- and two-dimensional opposite-polarity electrode spacing, respectively
F_1 (dimensionless) is a shape factor depending on geometrical configuration of the system [71]

F_1 is calculated by addition of the fractions of outer electrodes corresponding to one central electrode because, usually, the outer electrodes are serving to several unit cells.

Table 18.1 shows the values of the F_1 for selected configurations [71]. Approximate calculations of the percentage of ineffective area for each configuration are also summarized. For one-

TABLE 18.1
Impact of Electrode Configuration on Electrode Requirements and Size of Ineffective Areas

	Electrode spacing				No. electrodes per unit area		Ineffective area	
Configuration	Opposite charge	Same charge	No. electrodes per cell	Area of cell	N	Percent increase	$A_{ineff.}$	Percent area
1-D	L_E	L_E	1	L_E^2	$1/ L_E^2$	0	$L_E^2/2$	50
1-D	L_E	$L_E/2$	2	L_E^2	$2/ L_E^2$	100	$L_E^2/4$	25
1-D	L_E	$L_E/3$	3	L_E^2	$3/ L_E^2$	200	$L_E^2/6$	17
Square	R_E	$R_E\ \sqrt{2}$	2	$2\ R_E^2$	$1/ R_E^2$	0	R_E^2	50
Hexagonal	R_E	R_E	3	$1.5R_E^2\sqrt{3}$	$2/R_E^2\sqrt{3}$	15.5	$3R_E^2/4$	29

Source: Alshawabkeh, A.K. et al., *J. Soil Contamination*, 8, 617, 1999. With permission.

dimensional configurations, the ineffective area is half of total area, when the spacing of the electrodes of the same polarity is equal to the opposite-charge electrode spacing. Thus, it is not practical to use such a scheme unless remediation is implemented in two stages in which the electrode polarity can be changed.

This is also the case for the two-dimensional square arrangement. The results show that one-dimensional configurations with the same-polarity electrode spacing of one-half and one-third of opposite-polarity require an increase of 100 and 200% in number of electrodes when compared with the same of equal electrode spacing. With respect to two-dimensional configurations, the hexagonal configuration needs only 15% more electrodes than square configuration.

18.9 ELECTRIC OPERATIVE CONDITIONS

The most usual operation procedure drives a constant current through the soil during the cleanup with usual values about a few amperes per square meter (0.1 to 10 A/m^{-2}) of current density [67] and potential gradients depending on soil resistance (0.02 S/m^{-1}) from 100 to 400 V/m^{-1}. Obviously, if a higher current intensity is used, the process is faster, but consumes a much more important quantity of energy because the power consumption is proportional to the square of current intensity. If the soil has a high conductivity, it is necessary to operate with higher values of electric intensity than if it has a high resistance because the current must be distributed to move not only contaminants ions but also the natural ions present in the soil.

Other authors [44,72,73] prefer to operate in a laboratory, applying constant DC potential gradients in the range 30 to 400 V/m^{-1}. In this operative mode, when the resistance of the soil increases, the electrical current naturally goes down. Obviously, in this case, the conductivity control of soil is determining for cleaning time because the capacity of the electromigration to move ions basically depends on intensity through the soil. If the process operates to constant voltage and is not controlled [72,73], at the beginning of operation, a sharp increase in the protons and hydroxyl concentrations is produced in the anode and cathode compartments, respectively, and is responsible for the corresponding increment of electric current and cleanup rate. Afterwards, the depletion of free ions due to extraction and neutralization results in a high resistance in a specific zone of the soil and a high useless drop potential. This effect produces a reduction of the most important electrokinetic processes (electromigration or electroosmotic flow). It has been calculated [45,46] that, operating with a higher applied voltage, the meeting time between acid and basic fronts and the subsequent neutralization becomes shorter, usually resulting into lower energy efficiency.

In some cases, the authors [68] prefer to operate using a constant current density (5 A/m^{-2}) at laboratory scale, but use constant voltage (45 to 60 V 10 to 13 V/m^{-1}) at field scale, with a resultant electric current from soil resistance (10 to 17 A/m^{-2}). Electrokinetics, Inc. [70] reported that the addition of Cadex™ as an enhancement agent at the cathode removed 98% of the total cadmium, 40% of total lead, and 35% of total chromium at the same site (Point Mugu), with an energy expenditure of 3500 kw/h/m^3 of soil for 1200 h of treatment. A conclusion of this comparison is that if no extremely longer periods of cleanup are desired, a higher current density in the field (10 A/m^{-2}) is to be recommended to achieve better removal rates.

A secondary effect of current application to soil during electrokinetics is an increase in temperature because some electrical energy is transformed into thermal energy. This affects the cleanup in a different way, depending on whether the system is operated under constant current or constant voltage conditions. If under constant current, an increase in the pore water temperature will not affect the electromigration, but the electroosmotic flow will decrease. On the other hand, if the system operates at constant voltage, temperature increase will produce an increment of the electromigration [74]. In any case, the optimal electrical conditions of operation are directly related with the design of the system (geometry and electrode spacing) and all of the variables of the system must be jointly analyzed.

18.9.1 CURRENT EFFICIENCY: CRITICAL CURRENT DENSITY THROUGH MEMBRANES

The current efficiency is important when an electric field is applied over an ion exchange membrane. The counter-ion transport number normally decreases with increasing electrolyte concentration. In the electrodialytic process, the progressing electrolyte accumulation in one compartment and depletion in the other cause electrolyte diffusion; this counteracts the selective transference and reduces the current efficiency. The effects of transference and diffusion are not additive, so the description of the transport processes becomes complex.

The critical current density is another important aspect to consider when an electric field is applied over an ion exchange membrane. If the current density over the membrane is increased continuously, at a certain value, the current efficiency will drop sharply and the potential drop across the membrane will rise sharply. This is because, in the membrane, the current is carried almost exclusively by the counter-ions, whereas in the solution it is carried by the counter-ions and co-ions. Therefore, the transference of counter-ions away through the membrane is higher than the transference in the solution up to the membrane surface. The difference must be compensated by convection and diffusion. The resistance in the membrane will increase until water dissociation at the surface becomes a further source of ions [75]. In the case of a cation exchange membrane, the H^+ ions will assist in transporting the electrolyte cations through the membrane; however, the OH^- ions are transferred back to the solution [76] and the opposite in an anion exchange membrane.

18.10 REMEDIATION TIME REQUIREMENTS

In different configurations, the time required for remediation is a function of contaminant transport rates and electrode spacing. Some authors [67,71] have provided practical methods to estimate it in one-dimensional systems. Thus, neglecting the hydrodynamic dispersion and assuming, as usual, homogeneous soil and linear electric field, the linear velocity of cations through the soil with typical electroosmotic flow is:

$$\mathrm{v} = \frac{\left(u^* + k_e\right)}{R_t}\Phi_e \tag{18.11}$$

where

u^* ($L^2V^{-1}T^{-1}$) is the effective ionic mobility of the species in soil
k_e ($L^2V^{-1}T^{-1}$) is the coefficient of electroosmotic permeability

Φ_e (VL^{-1}) is the voltage gradient

R_t (dimensionless) is a time-delay factor to account for the time required for contaminant desorption and dissolution

The value of R_t depends on soil type, pH, and type of contaminant. Sorption retardation factor (R_d) can be used to estimate R_t (R_t =1 for nonreactive contaminants). However, the values of R_t might be different from R_d because R_t should account for time delay due to all chemical reactions (solubilization, complexation, and desorption), but R_d values account only for sorption.

Time required to remediation T_R (T) is calculated using this velocity and opposite-polarity electrode spacing, L_E, as:

$$T_R = \frac{1}{\beta}\frac{L_E}{\sigma^*\Phi_e} \tag{18.12}$$

where σ^* (siemens L^{-1}) is the effective conductivity in the soil medium and β ($L^3\ C^{-1}$) is a lumped property of the contaminant and the soil that measures the rate of reactive transport of a species relative to the electric conductivity of a medium, given by:

$$\beta = \frac{\left(u^* + k_e\right)/R_t}{\sigma^*} \tag{18.13}$$

Typical values of β for contaminated fine-grained soils are estimated to be in the range of 10^{-8} to 10^{-6} $m^3\ C^{-1}$ [48]. If time is to be calculated using current density, Equation 18.12 becomes

$$T_R = \frac{1}{\beta}\frac{L_E}{I_d} \tag{18.14}$$

where I_d (amps L^{-2}) is electric current density.

In treatments employing two-dimensional systems, it is assumed that radial electrical distribution, R_w, is the radius of central well (usually cathode), R_E, is the distance between central and peripheral electrodes, and Z is the depth of the site. The difference between this case and the one-dimensional case is that the current density in radial flow is a function of the radial distance (r); however, in both cases, it assumes operating with a constant total current. The electric current per unit depth for the radial transport is given by:

$$I_z = \left(2\pi r\right)\sigma^*\Phi_r \tag{18.15}$$

where I_z (amps L^{-1}) is the current per unit depth and Φ_r (VL^{-1}) is the radial voltage gradient.

Contaminant transport rate depends on the voltage gradient, which is a nonlinear function of the radial distance. Ignoring dispersion and accounting for ion migration and electroosmosis, the radial velocity of ions transport is given by

$$v(r) = \frac{\left(u^* + k_e\right)}{R_t}\Phi_r \tag{18.16}$$

where $v(r)$ (LT^{-1}) is the radial velocity of reactive species transport. Substituting Φ_r from Equation 18.15 into Equation 18.16 yields:

$$\mathrm{v}(r) = \beta \frac{I_Z}{2\pi r} \tag{18.17}$$

The velocity of contaminant transport is a nonlinear function of the radial distance even if the soil is homogeneous and isotropic. The time required for the contaminants to be transported from the outside electrodes (anodes) to the center electrode (cathode) is calculated integrating along the radius $dt = dr / v(r)$ from R_w to R_E, leading to:

$$T_R = \frac{\pi}{\beta} \frac{\left(R_E^2 - R_W^2\right)}{I_Z} \tag{18.18}$$

In order to provide time evaluation as a function of the voltage, a transformed voltage expression, Φ_R (V), which is constant along the radius, is given by:

$$\Phi_R = \frac{I_Z}{\pi \sigma^*} \tag{18.19}$$

Substituting the value of I_z from Equation 18.19 and simplifying because $(R_W)^2 << (R_E)^2$, Equation 18.18 yields:

$$T_R = \frac{1}{\beta} \frac{R_E^2}{\sigma^* \Phi_R} \tag{18.20}$$

The form of Equation 18.20 for radial transport is similar to the form of Equation 18.12 for one-dimensional transport. In both, β and σ* are soil properties and Φ_e and Φ_R are constants if the first ones are. However, the comparison of the two equations shows that, although T_R is a function of the linear distance between the electrodes for the one-dimensional case, it is a function of square of the radial distance for two-dimensional configurations. This is important for selection of electrode spacing. Selection for radial spacing in radial systems is much more critical than for one-dimensional systems because time and cost remediation will significantly increase when radial spacing increases.

18.11 ENERGY CONSUMPTION

If a large area is to be electrokinetically remediated, alternating rows of anodes and cathodes, the power input per unit volume of uniform soil, assuming steady state operation, can be calculated for an anode–cathode pair of rows such as:

$$\frac{Power}{Soil\ volume} = \frac{\mathrm{I}\Delta \mathrm{V}}{\mathrm{v_s}} = \frac{(\Delta V)^2 / R}{d Y L_E} = \frac{\sigma^* (\Delta V)^2}{L_E^2} \tag{18.21}$$

where

I is the current applied
ΔV is the applied electrical potential
v_s is the soil volume
R is the electrical resistance between the anode row and the cathode row

σ^* is the soil electrical conductivity
d is the treated depth
Y is the length of the electrode row
L_E is the anode–cathode separation distance

The electrical field energy per soil volume (E) is the product of the preceding expression and the duration, T_R, of the remediation project:

$$E = \frac{Power.\ Time}{Soil\ volume} = \frac{I(\Delta V)T_R}{\mathrm{v_s}} = \frac{\sigma^* T_R (\Delta V)^2}{L_E^2} \tag{18.22}$$

However, as explained previously, time depends on applied potential and anode–cathode distance and can be substituted in the expression by a function of these ones.

As an example, if only electroosmotic remediation is operating on soil, the necessary time to the clean up equals the ratio between necessary water to purge from the soil ($N\omega\mathbf{v}_s$) and electroosmotic flow rate $Q_{EO} = k_e\ d\ Y\ (\Delta V)/L_E$, where N is the number of pore volumes of soil to be clean (directly related to retention factor, R_t); ω is the soil porosity; and k_e is the electroosmotic permeability.

Combining both, the necessary time to remediation is:

$$T_R = \frac{N\omega L_E^2}{k_e(\Delta V)} \tag{18.23}$$

This may be rearranged to express the required applied potential to complete the remediation project within the desired time, T_R:

$$(\Delta V) = \frac{N\omega L_E^2}{k_e T_R} \tag{18.24}$$

The substitution of this potential applied in the equation for energy consumption renders an equation for energy consumption as a function of the cleanup time and characteristics of the system, but not of the electrical operation conditions:

$$E = \frac{Power.\ Time}{Soil\ volume} = \frac{\sigma^* N^2 \omega^2}{k_e^2}\left(\frac{L_E^2}{T_R}\right) \tag{18.25}$$

This indicates that a soil maintaining its physical and chemical characteristics from laboratory to field, only maintains its energetic consumption per volume unit if also it maintains the ratio (L_E^2/T_R) in both scales.

In conclusion, several factors affect energy requirements for electrokinetic remediation at a specific site, including the properties of soil and contaminants, electrode configuration, and time of operation. As previously explained, the current or potential is changing along the process because soil resistance is doing it; the energy consumption does it as well. However, these kinds of approximate procedures using average values permit an estimative calculation of the energy expenditure per unit volume of treated soil for electrokinetic remediation with one- and two-dimensional configurations of electrodes:

$$\frac{Energy}{Soil\ volume}=\frac{\mathrm{I}(\Delta\mathrm{V})T_R}{\mathrm{v_s}}=\left(\frac{\mathrm{I}_d\left(\Delta\mathrm{V}\right)T_R}{L_E}\right)_{1-D}=\left(\frac{\mathrm{I}_Z\left(\Delta\mathrm{V}\right)T_R}{\pi\left(R_E^2-R_W^2\right)}\right)_{2-D} \tag{18.26}$$

18.12 ELECTRODE REQUIREMENTS

The electrode should be electrically conductive, chemically inert, porous, and hollow. The anode operates under highly corrosive conditions and needs to be very resistant. Chemically inert and electrically conducting materials such as graphite, coated titanium, or platinum have been used as anodes, to prevent dissolution of electrodes and generation of undesirable corrosion products in an acidic–oxidant environment.

The requirements for the cathode are much smaller; thus, any conductive material that does not corrode in the basic environment can be used. The hollow in the electrode is to act as outlet of solutions from the subsurface or as inlet for enhancing reagents. Special electrodes have also been used combining the electrokinetic and lysimeter technologies, to allow the operation under unsaturated conditions without significantly altering the soil moisture content [27]. In these, the ceramic of anodes was treated with hydrochloric acid and a surfactant to alter its negative zeta potential and to prevent electroosmotic flow out of the anodes.

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