PART I

INTRODUCTION AND BASIC PRINCIPLES

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OVERVIEW OF ELECTROCHEMICAL REMEDIATION TECHNOLOGIES

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1.1 INTRODUCTION

Numerous sites worldwide are found contaminated due to improper past waste disposal practices and accidental spills. Contamination of soils and groundwater is well known, but the ever-growing problem of large quantities of contaminated dredged sediments has only received attention recently. Contaminants found include a wide range of toxic pollutants such as heavy metals, radionuclides, and organic compounds. The public and the environment are being exposed to these pollutants through different exposure pathways to unacceptable dosages, leading to intolerable adverse effects on public health and the environment. The remediation of these sites has become an urgent priority to environmentalists and regulatory bodies.

Several different technologies have been developed to remediate soils, sediments, and groundwater based on physicochemical, thermal, and biological principles (Sharma and Reddy, 2004). However, they are often found to be costly, energy intensive, ineffective, and could themselves create other adverse environmental impacts when dealing with difficult subsurface and contaminant conditions. For instance, inadequate remediation has been demonstrated at numerous polluted sites due to the presence of low permeability and heterogeneities and/or contaminant mixtures (multiple contaminants or combinations of different contaminant types such as coexisting heavy metals and organic pollutants). Electrochemical remediation has been recognized as a promising technology to address such difficult contaminated site conditions, leading to several research programs worldwide for the development of this technology.

The purpose of this book is to provide the state of the art on electrochemical remediation of polluted soils, sediments, and groundwater. Specifically, an

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Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater,
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introduction to the electrophenomena in soil, various fundamental and mathematical modeling studies, laboratory investigations, and field demonstration projects have been detailed. In addition, the regulatory and economic considerations are presented. This chapter introduces the content of this book; specifically, electrochemical remediation processes, versatility in implementation, recent advancements, and future research directions are briefly summarized. The reader is referred to various chapters in the book for the detailed information.

1.2 ELECTROCHEMICAL TECHNOLOGIES FOR SITE REMEDIATION

A typical field electrochemical remediation system is shown in Figure 1.1. Initially, wells/drains are configured and drilled so they surround the contaminated

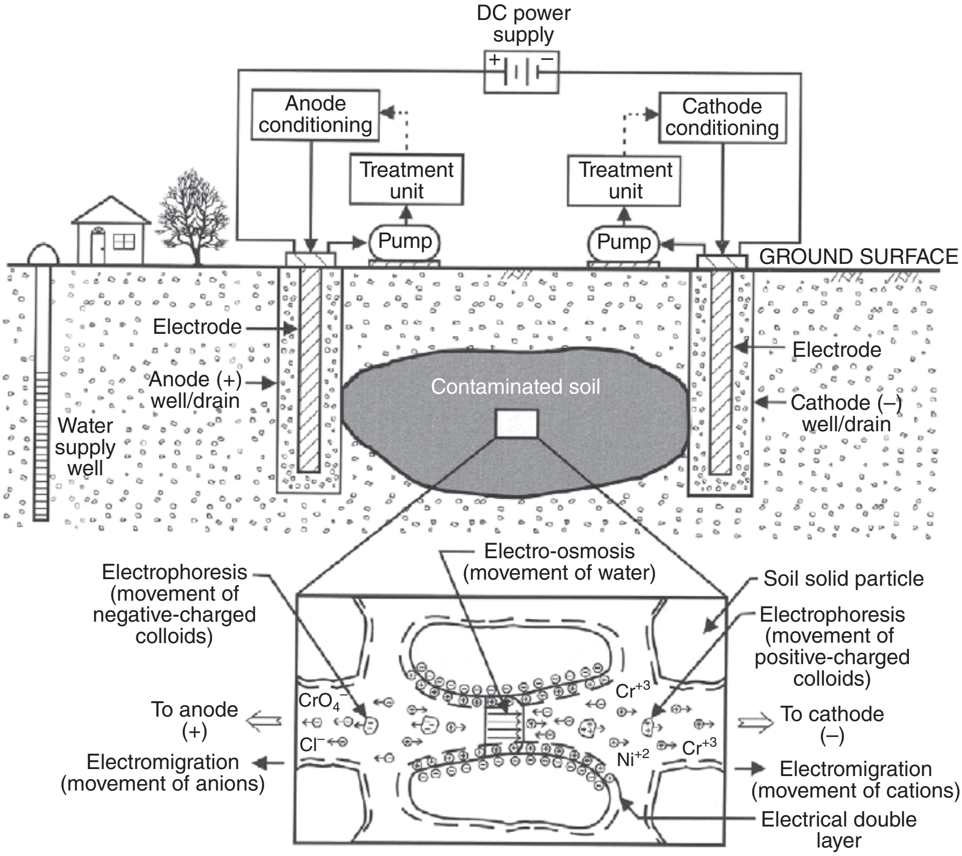

Figure 1.1. Schematic of the implementation of *in situ* electrochemical remediation systems. The electrodes are inserted into the soil and a direct electric field is applied to the contaminated site, which induces the transport of the contaminants toward the electrodes. The electrode solutions are pumped, treated, and circulated for contaminant removal. Selected electrode conditioning solutions may be used to induce favorable chemistry at the electrodes and in the soil.

region. Electrodes are then inserted into each well/drain and a low direct current (DC) or a low potential gradient to electrodes is applied. As a result of the applied electric field, several transport, transfer, and transformation processes are induced, which cause the contaminants to be transported into the electrodes where they can be removed. Alternatively, the contaminants may be stabilized/immobilized or degraded within the contaminated media. Several patents have been issued that deal with using electrochemical remediation in different creative ways.

Electrochemical remediation is also referred as *electrokinetics*, *electrokinetic remediation*, *electroremediation*, *electroreclamation*, and other such terms in the published literature. It should be noted here that when water alone is used at the electrodes, the process is known as *unenhanced electrochemical remediation*. However, when enhancement strategies (such as using conditioning solutions and ion exchange membranes at the electrodes) are used, then the process is known as *enhanced electrochemical remediation*.

Electrochemical remediation has received tremendous attention from environmental professionals because of its unique advantages over other conventional technologies. These advantages include

- flexibility to use as *ex situ* or *in situ* method;
- applicability to low-permeability and heterogeneous soils (e.g. glacial tills, lacustrine clays and silts, alluvial deposits, saprolitic formations, and loess);
- applicability to saturated and unsaturated soils;
- applicability for heavy metals, radionuclides, and organic contaminants, as well as in any of their combinations (contaminant mixtures); and
- easy integration with conventional technologies, including barrier and treatment systems.

Although implementation of the electrochemical remediation system in the field is relatively simple, its design and operation for successful remediation is cumbersome due to complex dynamic electrochemical transport, transfer, and transformation processes that occur under applied electric potential. In particular, the efficacy of electrochemical remediation depends strongly on contaminated media characteristics such as buffer capacity, mineralogy, and organic matter content, among others. If geochemistry, soil–contaminants interaction, and subsurface heterogeneity are well understood, the electrochemical remediation systems can be engineered to achieve remediation in an effective and economic manner.

Significant advances have been made toward the understanding of the fundamental processes involved in electrochemical remediation through controlled and idealized laboratory experiments. Valuable lessons have been learned from a limited number of documented field applications. Nevertheless, numerous research studies have been undertaken recently or ongoing to further understand the processes under field conditions and to develop innovative field systems so that optimized effective electrochemical remediation systems can be implemented at actual field sites.

1.3 ELECTROCHEMICAL TRANSPORT, TRANSFER, AND TRANSFORMATION PROCESSES

Upon electric field application, decomposition of water (electrolysis reactions) occurs at the electrodes. The electrolysis reactions generate oxygen gas and hydrogen ions (H^+) due to oxidation at the anode and hydrogen gas and hydroxyl (OH^-) ions due to reduction at the cathode as shown by the following reactions:

At anode (oxidation):

$$2H_2O \rightarrow O_{2(gas)} + 4H^+_{(aq)} + 4e^- \quad E^0 = -1.229\text{ V} \tag{1.1}$$

At cathode (reduction):

$$4H_2O + 4e^- \rightarrow 2H_{2(gas)} + 4OH^-_{(aq)} \quad E^0 = -0.828\text{ V} \tag{1.2}$$

Essentially, acid is produced at the anode and alkaline solution is produced at the cathode; therefore, pH in the cathode is increased, while pH at the anode is decreased. The migration of H^+ from the anode and OH^- from the cathode into the soil leads to dynamic changes in soil pH during the initial stages of electric potential application (Acar and Alshawabkeh, 1993).

The implications of these electrolysis reactions are enormous in that they impact transport, transformation, and degradation processes that control the contaminant migration, removal, and degradation during electrochemical treatment. The different transport, transfer, and transformation processes induced by the applied electric field and how these processes are impacted by the electrolysis reactions at the electrodes are fundamental to the understanding of the electrochemical remediation technologies and are briefly presented in this section.

1.3.1 Electrochemical Transport Processes

For low-permeability media, advective transport due to hydraulic flow is negligible. The application of an electric field induces the transport of contaminants and water through the contaminated media toward the electrodes due to the following transport processes (Probstein, 2003): *electromigration* (*ionic migration*), *electroosmosis*, *electrophoresis*, and *diffusion*.

1.3.1.1 Electromigration (Ionic Migration) Electromigration, also known as ionic migration, is the movement of the dissolved ionic species present in the pore fluid toward the opposite electrode. Anions move toward the anode and cations move toward the cathode. The degree of electromigration depends on the mobility of ionic species. Electromigration is the major transport process for ionic metals, polar organic molecules, ionic micelles, and colloidal electrolytes. The transport of H^+ and OH^- ions generated by electrolysis reactions is also attributed to electromigration.

The extent of electromigration of a given ion depends on the conductivity of the soil, soil porosity, pH gradient, applied electric potential, initial concentration of the specific ion, and the presence of competitive ions. The electromigrative velocity

(v_{em}) of an ion is proportional to the ion charge and the local electric gradient given by

$$v_{\mathrm{em}} = u_{\mathrm{i}}\, z_{\mathrm{i}}\, n\, \tau\, \mathrm{F}\, E, \tag{1.3}$$

where u_{i} is the ion mobility (m^2/V·s), z_{i} is the ionic valence, n is the porosity, τ is the tortuosity, F is the Faraday's constant (96,487 C/mol electrons), and E is the electric field strength (V/m). Ionic mobility (u_{i}) is defined as the velocity of the ionic species under the effect of unit electric field and is estimated using the Nernst–Einstein–Townsend relation:

$$u_{\mathrm{i}} = \frac{D_{\mathrm{i}}\, | z_{\mathrm{i}} |\, \mathrm{F}}{\mathrm{R}T} \tag{1.4}$$

where D_{i} is the molecular diffusion coefficient, R is the universal gas constant (8.314 J/K·mol), and T is the absolute temperature (K). The effective mobility u_{i}^{*} is defined by Equation 1.5 and is considered the movement of a given ion in a porous matrix with a tortuous path. The effective ionic mobility of a specific ion is a function of its molecular diffusion coefficient, soil porosity, tortuosity factor, and charge.

$$u_{\mathrm{i}}^{*} = n\, \tau\, u_{\mathrm{i}}. \tag{1.5}$$

1.3.1.2 Electroosmosis Advective flow occurs due to hydraulic gradient and electrical gradient. The hydraulic flow (q_{h}) due to hydraulic gradient (i_{h}) is defined by Darcy's law:

$$q_{\mathrm{h}} = k_{\mathrm{h}}\, i_{\mathrm{h}}, \tag{1.6}$$

where k_{h} is the hydraulic conductivity. This flow is significant for permeable soils such as sand, which possess hydraulic conductivity greater than 10^{-3} cm/s; however, this flow in clayey soils is negligible due to very low hydraulic conductivity (10^{-6}–10^{-9} cm/s).

Electroosmosis is induced under electric gradient and it is the movement of the pore fluid, which contains dissolved ionic and nonionic species, relative to the stationary soil mass, toward the electrodes. Generally, soil particle surfaces are charged (generally negatively charged) and counterions (positive ions or cations) concentrate within a diffuse double layer region adjacent to the particle surface. Under an electric potential, the locally excess ions migrate in a plane parallel to the particle surface toward the oppositely charged electrode. As they migrate, they transfer momentum to the surrounding fluid molecules via viscous forces, producing electro-osmotic flow. Electroosmosis is the dominant transport process for both organic and inorganic contaminants that are in dissolved, suspended, emulsified, or such similar forms.

In 1879, Helmholtz introduced one of the first theories concerning electroosmosis, and Smoluchowski modified it in 1914. According to the Helmholtz–Smoluchowski theory (H-S theory), the electro-osmotic flow velocity (v_{eo}) is directly proportional to the applied voltage gradient (E_z), zeta potential (ζ), and dielectric constant (D) of the fluid, and it is inversely proportional to the fluid viscosity (η):

$$v_{\mathrm{eo}} = -\frac{D\zeta}{\eta} E_z. \tag{1.7}$$

The H-S equation can also be expressed in terms of the volumetric flow rate (q_{eo}):

$$q_{\mathrm{eo}} = nA\frac{D\zeta}{\eta} E_z. \tag{1.8}$$

In this equation, n is the porosity and A is the cross-sectional area of the soil. Furthermore, it should be noted that the use of the effective porosity (n_{e}) or the porosity (n) divided by the tortuosity squared (n/τ) may be more accurate than using the porosity (n). For civil engineering applications, the electro-osmotic permeability coefficient (k_{eo}) is computed as follows:

$$k_{\mathrm{eo}} = n\frac{D\zeta}{\eta}. \tag{1.9}$$

For example, if $k_{\mathrm{eo}} = 4.1 \times 10^{-5}$ (V/s) for fine sand, and for this same soil the approximate $k_{\mathrm{h}} = 10^{-4}$ cm/s, which are reasonably close so electroosmosis will not greatly enhance the hydraulic flow through this soil. However, in lower-permeability soils such as kaolin, $k_{\mathrm{eo}} = 5.7 \times 10^{-5}$ (V/s) and the approximate $k_{\mathrm{h}} = 10^{-7}$ cm/s, so a very high hydraulic gradient of about 600 would be needed. Thus, electro-osmotic flow though low-permeability regions is significantly greater than the flow achieved by an ordinary hydraulic gradient. Electroosmosis facilitates advective transport of the solubilized contaminants toward the electrodes for removal.

As seen from Equation 1.7, the electro-osmotic flow depends on the dielectric constant and viscosity of pore fluid, as well as the surface charge of the solid matrix represented by the zeta potential (the electric potential at the junction between the fixed and mobile parts in the double layer). The zeta potential is a function of many parameters, including the types of clay minerals and ionic species that are present, as well as the pH, ionic strength, and temperature. If the cations and anions are evenly distributed, an equal and opposite flow occurs, causing the net flow to be zero. However, when the momentum transferred to the fluid in one direction exceeds the momentum of the fluid traveling in the other direction, electro-osmotic flow is produced.

The pH changes induced in the soil by the electrolysis reactions affect the zeta potential of the soil particles, and thereby affect the electro-osmotic flow. The low pH near the anode may be less than the point of zero charge (PZC) of the soil and the soil surfaces are positively charged, while high pH near the cathode may be higher than the PZC of the soil, making the soil more negative. Electro-osmotic flow may be reduced and even ceased as the soil is acidified near the anode. If the majority of the soil is acidified, the electro-osmotic flow direction may even be reversed, from typical anode to cathode to cathode to anode. This phenomenon is known as *electroendosmosis*. Understanding of such electro-osmotic flow variations is critical when remediating organic pollutants.

1.3.1.3 Electrophoresis Electrophoresis (also known as cataphoresis) is the transport of charged particles of colloidal size and bound contaminants due to the application of a low DC or voltage gradient relative to the stationary pore fluid. Compared with ionic migration and electroosmosis, mass transport by electrophoresis is negligible in low-permeability soil systems. However, mass transport by electrophoresis may become significant in soil suspension systems, and it may also be a dominant transport mechanism for biocolloids (i.e. bacteria) and micelles.

1.3.1.4 Diffusion Diffusion refers to the ionic and molecular constituent forms of the contaminants moving from areas of higher concentration to areas of lower concentration because of the concentration gradient or chemical kinetic activity. Estimates of the ionic mobilities from the diffusion coefficients using the Nernst–Einsetin–Townsend relation indicates that ionic mobility of a charged species is much higher than the diffusion coefficient (about 40 times the product of its charge and the electrical potential gradient). Therefore, diffusive transport is often neglected.

1.3.1.5 Relative Contribution of Transport Processes For soluble ionized inorganic contaminants (such as metal cations, metal anions, nitrates, and phosphates), electromigration is the dominant transport mechanism at high concentrations of ionic species, while electroosmosis is dominant at lower concentrations. For readily soluble organic compounds (such as benzene, toluene, xylene, phenolic compounds, and chlorinated solvents), electroosmosis is the dominant transport process in electrochemical remediation. Relative contribution of electroosmosis and ion migration to the total mass transport varies according to soil type, water content, ion species, and their concentration. In silts and low-activity clays, hydraulic flow is negligible in comparison with electro-osmotic flow. For ionic species, the mass transport by ionic migration is from 10 to 300 times greater than the mass transport by electroosmotic advection. Furthermore, electroosmosis decreases when the pH and zeta potential drop in the later stages of continuous electrochemical process under a constant electric potential.

When micelles (charged aggregate of molecules or particles) are formed with other species in the processing fluid, or when we deal with slurries, electrophoresis may become significant. Diffusion is an important transport mechanism, but it is a very slow process, so it is estimated to only have a minor influence on contaminant transport during electrochemical remediation.

1.3.2 Electrochemical Mass Transfer Processes

The protons (H^+) and hydroxyl (OH^-) ions generated by electrolysis reactions (Eqs. 1.1 and 1.2) migrate toward the oppositely charged electrode. Acar *et al.* (1995) determined that, generally, H^+ is about twice as mobile as OH^-, so the protons dominate the system and an acid front moves across the soil until it meets the hydroxyl front in a zone near the cathode, where the ions may recombine to generate water. Thus, the soil is divided into two zones with a sharp pH jump in between: a high-pH zone close to the cathode and a low-pH zone on the anode side. The actual soil pH values will depend on the extent of transport of H^+ and OH^- ions and the geochemical characteristics of the soil.

During the initial stages of electric potential application, the soil pH changes spatially and temporally, which leads to dynamic geochemistry, leading to mass transfer from one form (phase) to the other (solid/precipitated, sorbed, dissolved, and free phases) and changes in chemical speciation. The most important geochemical reactions that must be considered include

- sorption–desorption reactions;
- precipitation–dissolution reactions; and
- oxidation–reduction reactions.

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

The precipitation and dissolution of the contaminant species during the electrokinetic process can significantly influence the removal efficiency of the process. The solubilization of precipitates is affected by the hydrogen ions generated at the anode migrating across the contaminated soil, favoring the acidification of soil and the dissolution of metal hydroxides and carbonates, among others. However, in some types of soils, the migration of the hydrogen ions will be hindered due to the relatively high buffering capacity of the soil. The presence of the hydroxyl ions at the cathode will increase the pH value (pH = 10–12) in the electrode solution and in the soil area close to the cathode. In a high-pH environment, heavy metals will precipitate, and the movement of the contaminants will be impeded. During electrokinetic treatment, heavy metals migrates toward the cathode until reach the high-pH zone, where heavy metals accumulate and eventually precipitate, clogging soil pores and hindering the remediation process. For efficient contaminant removal, it is essential to prevent precipitation and to have the contaminants in dissolved form during the electrokinetic process.

The high pH and the low heavy metals concentration condition at the cathode may also lead to the formation of a negatively charged complex species at the cathode compartment. The movement of these negatively charged complex species toward the anode and of the heavy metals toward the cathode relies upon the relative mobility of the hydrogen and hydroxyl ions.

Oxidation and reduction reactions are important when dealing with metallic contaminants such as chromium. Chromium exists most commonly in two valence states: trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)]. Cr(III) exists in the form of cationic hydroxides such as $Cr(OH)_2^{-1}$ and it will migrate toward the cathode during electrokinetic remediation. However, Cr(VI) exists in the form of oxyanions such as CrO_4^{2-}, which migrate toward the anode. The valence state depends on the soil composition, especially the presence of reducing agents such as organic matter and Fe(II) and/or oxidizing agents such as Mn(IV), so it is important to know the valence state of metals and their possible redox chemistry to know the chemical speciation of the contaminants and their movement across the soil.

The geochemical processes are affected by the soil composition and any enhancement solutions used at the electrodes. In particular, acid buffering capacity of the soil affects the changes in soil pH. It is found that in high acid buffering soils, pH is not lowered near the anode due to buffering of the acid produced at the anode by the carbonates present in the soil, but pH increases near the cathode as OH^- ions migrate easily. Therefore, the most prominent geochemical processes during electrochemical remediation of contaminated soils include the following: (a) generation of pH gradient and buffering capacity of the soil; (b) change of zeta potential of soil particle surfaces; (c) sorption and desorption of contaminants onto/from soil particle surfaces; (d) complexation; (e) oxidation–reduction (redox) reactions; and (f) interactions of these processes. More details on these processes are presented in Chapter 3.

1.3.3 Electrochemical Transformation Processes

Chapter 2 describes the electrochemical transformation processes that occur at microscale under electric fields. Recently, it has been presented that the application of a low-intensity electric field to a soil can induce electrical transformations on clay surfaces. Those transformations can make the clay particles to act as microelectrodes that provoke redox reaction in the contaminants, especially organic pollutants. Such transformations are mainly attributed to the Faradaic current passage orthogonal to the planes in the electric double layer of clay particles, inducing redox reactions on clay surfaces. Clay particles are conceived as "microelectrodes" possessing a compact Stern layer and a diffuse layer, which mediates Faradaic reactions. As the donated (or accepted) electrons pass across the electrical double layer into and out of the bulk fluid, available species are converted into others via oxidation–reduction reactions. This effect may become significant for polarizable surfaces due to strong adsorption of the cations, anions, and molecules with electrical dipoles within the double layer, resembling the case of contaminated sediments.

Additionally, electrochemical transformations may occur when the contaminants enter into the anode or the cathode, particularly chlorinated organic compounds, which are shown to undergo reductive dechlorination at the cathode and oxidative dechlorination at the anode. Such transformations should also be considered based on the redox conditions in the electrodes and the contaminant characteristics.

1.4 ELECTROCHEMICAL REMOVAL OF INORGANIC POLLUTANTS

Inorganic pollutants include (a) cationic heavy metals such as lead, cadmium, and nickel, (b) anionic metals and inorganics such as arsenic, chromium, selenium, nitrate and fluoride, and (c) radionuclides such as strontium and uranium. The geochemistry of these pollutants can widely vary and it depends on the specific pollutant type and soil/sediment properties. The speciation and transport of these pollutants also depend on the dynamic changes in the pH and redox potential of the soil that occurs under applied electric potential. The dominant transport process is electromigration, and the soil pH changes induced by the electric field complicate the geochemistry and inorganic pollutant removal (refer to Part II).

1.4.1 Cationic Heavy Metals

Numerous studies are reported on the electrokinetic removal of heavy metals from soils (Chapter 4). Many of these studies used ideal soils, often kaolinite, as a representative low-permeability soil, which were spiked with a selected single cationic metal (such as lead and cadmium) in predetermined concentration. The spiked soil is loaded in a small-scale electrokinetic test setup and electric potential is applied. The transport and removal of the metal after specified test duration are determined. It is shown that cationic metals exist in soluble ionic form due to reduced pH near the anode regions and they are transported toward the cathode. However, when they reach near the cathode, they get sorbed or precipitated due to increased pH resulting from OH^- transport from the cathode. The actual removal from the soil is often negligible.

Several studies reported similar results based on testing of field soils. The field soils possess complex mineralogy, organic content, and buffering capacity, which results in relatively low removal of metals. One of the most important considerations is the acid buffering capacity of the soil. If the soil possesses higher acid buffering capacity, soil pH does not reduce near the anode, but it increases near the cathode. Furthermore, testing of aged field contaminated soils showed a very low metal removal due to complex soil composition and strong sorption to the soil constituents.

The major hindering factors for the removal of contaminants are sorption and precipitation of the contaminants resulting from the changes in soil pH. Therefore, in order to enhance metal removal, several enhancement strategies have been employed. These include (a) using organic/mineral acids at the cathode to reduce pH, (b) using ion exchange membranes between soil specimen and electrodes to control H^+ and OH^- ions transport into the soil so that favorable soil pH is maintained, and (c) using chelating agents that can form soluble complexes with the metals at different pH conditions. These enhancement studies have shown high removal efficiencies of cationic metals. In some cases such as elemental mercury, oxidizing agents are first introduced into the soil to oxidize mercury and transform it into ionic form and then to be able to be removed by the electromigration process.

1.4.2 Anionic Metals and Other Anionic Species

Experiments with anionic metals (such as chromium and arsenic) showed behavior opposite to that of cationic metals. The anionic metals are found to exist in soluble ionic form near the cathode and are transported toward the anode. However, when they reach near the anode, they are adsorbed due to low-pH conditions existing due to electrolysis reactions. Nevertheless, the actual removal of anionic metals was found to be greater than that of cationic metals. The use of alkaline solution to increase soil pH near the anode is found to enhance the removal of anionic metals (Chapter 4).

In addition to anionic metals, the problem of groundwater contamination with excess nitrate and fluoride is well recognized (Chapter 6). These anionic species are not as highly toxic as other anionic metals such as chromium and arsenic, but they are shown to have some adverse effects on public health and the environment. Few earlier studies investigated the removal of nitrates from the soils and groundwater using electrochemical methods, but attention on fluoride and other similar contaminants has received attention only recently. The behavior of these contaminants under electric field is similar to that of anionic metals; they electromigrate toward the anode, in opposite direction to the electro-osmotic flow. Low removal is expected near the anode due to low-pH conditions; therefore, anode conditioning with alkaline solution (e.g. NaOH) is used to increase soil pH near the anode and enhance the removal. The effects of anode conditioning on electroosmosis should be considered as it will impact contaminant removal. Alternatively, some researchers used zero-valent iron (ZVI) in the anode to increase soil pH and also to transform nitrate into nitrogen within the anode. Such strategy can also be implemented in an electrokinetic barrier system. It should also be pointed out here that nitrate is delivered into the soil purposely to enhance biostimulation in some studies, and the lessons learned from the studies dealing with the removal of nitrate can be useful for this purpose. The excess amount of nitrate should be avoided as it may be treated as contamination.

1.4.3 Radionuclides

Radioactive contamination at several sites due to improper handling of nuclear wastes and production and operation of nuclear fuel and nuclear reactors is well known (Chapter 5). The principal among radioactive materials are the following isotopes: ^{60}Co, ^{90}Sr, ^{90}Y, ^{106}Ru, ^{137}Cs, ^{144}Ce, ^{147}Pm, $^{238, 239, 240}$Pu, ^{226}Ra, and so on, and they are found to exist in near-surface soils, posing great hazard to public health and the environment. Electrochemical remediation of radionuclides is proposed to either contain within the soil or remove from soils. Electrokinetic containment is applied for preventing radioactive nuclide migration from the polluted region. Similar to heavy metals, electrochemical removal of radionuclides requires enhancement strategies. Specifically, a high-pH environment retards the removal; therefore, enhancement solutions such as acetate buffer solution ($CH_3COONa + CH_3COOH$) is injected into the anode, and acetic acid is injected periodically into the cathode to control any pH increase. Electromigration is the dominant mechanism for the removal of these contaminants. Other enhancement solutions such as NH_4NO_3 or KNO_3 are pumped into the anode and nitric acid or other acidic solution near the cathode to prevent the segregation and precipitation of metal hydroxides near or in the cathode.

1.5 ELECTROCHEMICAL REMOVAL OF ORGANIC POLLUTANTS

Earlier efforts proved that the volatile and/or soluble organic contaminants are relatively easily removed by electroremediation, as well as by other conventional remediation technologies. Recent focus has been on electroremediation of hydrophobic and persistent (hard to degrade) toxic compounds such as *polycyclic aromatic hydrocarbons (PAHs)*, *polychlorinated organic compounds [e.g. polychlorinated biphenyls (PCBs)]*, *pesticides*, *herbicides*, and *energetic compounds* in soils. Several studies investigated the electrokinetic removal of the organic pollutants as presented in Part III.

1.5.1 PAHs

Electrokinetic removal of PAHs has received greater attention (Chapter 9). In essence, the transport and removal of PAHs under electric field is found to be limited due to limited amounts these pollutants present in dissolved form in pore fluid. PAHs are hydrophobic and are sorbed to soil (especially organic matter). One fundamental requirement to enhance the removal is to solubilize the PAHs using surfactants, biosurfactants, cosolvents, and cyclodextrins. The addition of these solubilizing agents change the pore fluid properties such as dielectric constant, pH, and viscosity, as well as the surface characteristics of soil particles (e.g. use of ionic surfactants and high-pH cosolvent). These changes in fluid and soil surface properties affect the electro-osmotic flow, and thereby, removal efficiency. Electro-osmotic advection is the dominant contaminant transport and removal process; therefore, it is critical to ensure adequate electro-osmotic flow while flushing these solubilizing agents. The pH adjustment and the application of periodic electric potential are found to result in sustained electro-osmotic flow and higher removal efficiency.

1.5.2 Chlorinated Aliphatic Hydrocarbons, Chlorophenols, and Chlorobenzenes

Earlier studies focused on the removal of trichloroethylene (TCE), which is relatively more soluble than other chlorinated compounds. Maintaining adequate electro-osmotic flow was the main consideration in achieving higher removal efficiency. Anode buffering with an alkaline solution was used to maintain electro-osmotic flow. Recently, attention is focused on hydrophobic chlorinated organic compounds (Chapter 10) including chlorinated aliphatic hydrocarbons [e.g. pentachloroethylene (PCE), trichloroacetate (TCA), and TCE], chlorophenols (e.g. pentachlorophenol), and chlorobenzenes (e.g. PCBs). The removal of these pollutants is complicated by their sorption to the soil as well as their potential dissociation characteristics. Therefore, both electroosmosis and electromigration transport processes play a role in the transport and removal of these pollutants. The enhanced removal is accomplished by combinations of using solubilizing agents such as surfactants, cosolvents, and cyclodextrins and buffering anode pH to achieve higher removal by the combined electromigration and electroosmosis processes. The solubilizing agents should be carefully assessed to determine their effect on the surface charge of the soil surfaces and pH of the pore fluid and consequent impact on both electromigration and electroosmosis processes.

1.5.3 Chlorinated Pesticides and Herbicides

Sites contaminated by chlorinated pesticides (e.g. dichlorodiphenyltrichloroethane (DDT), aldrin, dieldrin, and endrin) and herbicides (e.g. atrazine, molinate and bentazone) due to agricultural activities and accidental spills have received little attention (Chapters 11 and 12). These contaminants are nonpolar in characteristics and sorb strongly to the soil. Similar to other hydrophobic organic compounds, desorption using solubilizing agents such as surfactants and cosolvents as well as buffering the anode pH are implemented to achieve high removal. One important characteristic of pesticides is that their solubility is rate limited, which causes lower aqueous-phase concentrations. Periodic electric potential application in such cases may be beneficial, but it has not been tested. Electrokinetic removal of herbicides is similar to that of pesticides and it is possible to remove these pollutants by controlling the pH both at the anode and cathode to result in favorable soil pH for desorption and electro-osmotic advection (Chapter 12).

1.5.4 Nitroaromatic and Other Energetic Compounds

The problem of soils contaminated by nitroaromatic and other energetic compounds (e.g. trinitrotoluene (TNT), dinitrotoluene (DNT), and cyclotrimethylene-trinitramine (RDX)) due to manufacturing and use of munitions has received attention only recently. These compounds are low-polarity organic molecules that exhibit low water solubility and strong affinities for complex formation with clay minerals and organic matter. Therefore, these contaminants must be desorbed, and some attempts have been made to use cosolvents, surfactants, and cyclodextrins to enhance their solubility and transport, but the removal was low. Proper consideration should be given to the charge of the specific solubilizing agents used and their complexes, if formed, as well as the potential electrochemical degradation processes that may occur within the soil or at the electrodes during the electrochemical treatment of these specific compounds (Chapter 13).

1.6 ELECTROCHEMICAL REMOVAL OF CONTAMINANT MIXTURES

Many of the fundamental and laboratory studies often deal with a selected single contaminant, either a heavy metal or an organic compound. Although these studies helped understand the fundamental processes and operational variables, the direct application of these study results to design systems for actual contaminated sites is often questioned. In addition to the soil compositional differences, contamination found at actual contaminated sites consists of multiple contaminants such as multiple heavy metals, multiple organic compounds, or a combination of heavy metals and organic compounds. Although few, there are sites contaminated in combinations of heavy metals, organic compounds, and radionuclides [e.g. Department of Energy (DOE), USA]. Synergistic effects and removal of multiple contaminants (multiple heavy metals, multiple organics, or multiple metals and organics) have been evaluated in a limited number of studies (Chapters 14 and 15).

1.6.1 Heavy Metals Mixtures

The heavy metals are affected by the various geochemical processes due to change in the soil pH as presented in Parts I, II, and IV. The sorption and desorption processes of coexisting multiple metals is quite complicated. Some of the heavy metals are tightly held than the others. If cationic and anionic metals exist, the sorption behavior of them can be quite the opposite. Therefore, the extent of transport of multiple metals depends on their aqueous concentrations and ionic mobilities. In general, the applied electric field is distributed among the multiple metals, thereby resulting in lower transport of a metal in the mixture as compared with the transport observed in the case containing only that specific metal. The dominant transport process for the removal of heavy metals is electromigration.

Several studies have been conducted on soils contaminated with multiple metals (Chapter 14). The removal of cationic metals is hindered by the sorption and precipitation near the cathode, and therefore require the lowering of soil pH near the cathode using weak organic acids, forming soluble complexes at high pH using chelating agents, or preventing high pH generation by the use of ionic exchange membranes. In case of anionic metals, pH near the anode should be increased using alkaline solutions such as NaOH to reduce sorption of these metals to the soil. When the heavy metals exist in soluble form, they are transported and removed predominantly by the electromigration process. Ion exchange membranes can also be used in the electrodes to control the soil pH to the desired level. When cationic and anionic heavy metals are found to coexist, a sequential electrochemical treatment that involves, first, the removal of cationic metals using cathode conditioning with a weak organic acid and then the removal of anionic metals using anode conditioning with an alkaline solution may be needed.

1.6.2 Heavy Metals and Organic Pollutant Mixtures

The problem of soils contaminated with mixed heavy metals and organic compounds is even complex because of the different chemistry of heavy metals and organic compounds (Chapter 15). Some studies have shown that there may be some synergistic effects that retard the contaminant transport and removal, but few other studies show the behavior of heavy metals and organic compounds similar to that observed with either heavy metals or organic compounds.

The heavy metals are removed predominantly by the electromigration process, while the organic contaminants are removed by electroosmosis. The presence of heavy metals causes the zeta potential of the soil to be less negative and even result in a positive value, affecting the electro-osmotic flow and sorption of the contaminants.

The heavy metals are affected by the various geochemical processes due to change in the soil pH as presented in Parts I, II, and IV. The removal of cationic metals is hindered by the sorption and precipitation near the cathode, and therefore require lowering of soil pH near the cathode using weak organic acids, forming soluble complexes at high pH using chelating agents, or preventing high pH generation by the use of electrode membranes. In case of anionic metals, pH near the anode should be increased using alkaline solutions such as NaOH to reduce sorption of these metals to the soil. When the heavy metals exist in soluble form, they are transported and removed predominantly by the electromigration process.

For the simultaneous removal of organic compounds, these compounds are solubilized using different solubilizing agents (surfactants, cosolvents, and cyclodextrins). They are then transported and removed mainly by the electroosmosis process. It is essential to maintain all of the contaminants in soluble form and maintain electro-osmotic flow for the removal of both heavy metals and organic compounds.

Sequential approaches are developed where (a) anionic metals are removed first and then cationic metals when mixed metal contamination is present and (b) organic compounds are removed first followed by the removal of heavy metals when coexisting heavy metal and organic contaminants are found. For example, the simultaneous electrokinetic removal of inorganic and organic pollutants (SEKRIOP) technology was developed by Elektorowicz and Hakimipour (2002), which uses ethylenediaminetetraacetic acid (EDTA) for metals mobility and zwitterionic surfactants for hydrocarbons. Cationic reactive membranes are also incorporated into this technology to capture free metallic ions generated by electrokinetic phenomena before their precipitation in the cathode area. The capture of metal–EDTA complexes was done on anionic reactive membranes.

High removal of multiple metals or coexisting metals and organic compounds (e.g. PAHs) is demonstrated in spiked soil conditions, but the performance was found inadequate in field soils from actual contaminated sites. Proper consideration should be made to reduce the treatment duration, proper handling of secondary liquid waste, and total cost in evaluating the electrochemical removal of contaminant mixtures.

1.7 SPECIAL CONSIDERATIONS IN REMEDIATING POLLUTED SEDIMENTS

Electrochemical remediation of soils, particularly clays, has been studied extensively. However, a very limited number of studies is conducted to evaluate the applicability of electrochemical remediation for the contaminated sediments. Huge amounts of contaminated sediments need to be dredged, dewatered, and treated before reuse or final disposal. Around 500 million m^3 of sediments are dredged each year for navigational purposes, and roughly 1%–4% requires dewatering and treatment prior to disposal, increasing the cost of dredging by a factor of 300–500. Sediments are characterized by a possible simultaneous presence of several types of pollutants that interact with different constituents of solid matrices. Other parameters, including moisture and salt content, may also have an influence on the suitability of different treatment options. While in soils the contaminated fine fraction typically accounts for less than 50% of total solids, in sediments this figure may be as high as 80%–95%, and due to the high surface area may contain the highest contaminant load. Electrokinetic remediation represents a promising option for contaminated sediments because it is capable of treating fine- and low-permeability materials, can also be applied *in situ*, and may represent a possible single-stage option to achieve dewatering, consolidation, and removal of organic and inorganic pollutants as well as salts.

Electrochemical removal of heavy metals in sediments often proved to be ineffective due to complex chemical composition, higher buffering capacity, and different metal speciation as compared to soils. Enhancement strategies using nitric acid, EDTA, and citric acid is found to significantly improve removal efficiency. Enhanced electrochemical removal of organic pollutants, particularly PAHs, is also studied. Generally, solubilization and removal of PAHs proved to be heavily hindered by high organic contents of sediment and the low liquid/solid ratio achievable as compared with chemical washing (Chapter 7).

1.8 ELECTROKINETIC BARRIERS FOR POLLUTION CONTAINMENT

The basic purpose of electrokinetic barriers is to prevent the migration of contaminants from its current location. These barriers are similar to traditional passive containment barriers (such as vertical slurry walls) for soil and groundwater pollution containment and active containment barriers (such as pumping systems and drainage systems) for groundwater pollution containment (Sharma and Reddy, 2004). Such barriers are often used as an interim measure prior to implementing a permanent treatment system.

Electrokinetic barriers consist of a row of electrodes bordering a high-concentration area or polluted groundwater plume. The row of electrodes is set perpendicular to the groundwater flow direction, while the depth of electrodes coincides with the lowest depth where pollutants are found. Electric current is induced into the ground by alternating anodes and cathodes. Anodes and cathodes are connected to separate closed-loop pump systems and are used to circulate electrolytes. Depending on the contaminant, pH can be controlled by conditioning the electrolytes. Periodically, contaminants from the electrolytes are also removed by different techniques such as sorption and ion exchange. More details on electrokinetic barriers can be found in Chapters 16 and 17.

1.9 COUPLED (OR INTEGRATED) ELECTROCHEMICAL REMEDIATION TECHNOLOGIES

Conventional electrochemical remediation essentially refers to the removal of contaminants from the contaminated media (soil, sediment, and groundwater), also known as *electrokinetic extraction* or *electrokinetically enhanced flushing*. As presented in Parts II, III, and IV, removal of contaminants (including contaminant mixtures) from spiked soils is possible using adaptive enhancement strategies. Despite high removal, practical implementation of such removal strategy is limited due to (a) regulatory constraints on injecting the selected enhancement solutions into the subsurface, (b) high cost, and (c) longer treatment time. Recently, electrochemical remediation is combined with other remediation technologies in order to overcome these issues as well as known deficiencies of the conventional remediation methods. Such integrated or coupled technologies investigated include

- electrokinetic biobarriers;
- electrolytic reactive barriers;
- electrokinetic–permeable reactive barriers (PRBs);
- electrokinetic–chemical oxidation/reduction;
- electrokinetic–bioremediation;
- electrokinetic–phytoremediation;
- electrokinetic–stabilization; and
- electrokinetic–thermal treatment.

A brief explanation of these integrated technologies is presented in this section.

1.9.1 Electrokinetic Biobarriers

Electrokinetic biobarriers (also known as electrokinetic biofences) are modified electrokinetic barrier used to contain and biodegrade organic pollutants in groundwater. A row of alternating anode and cathode electrodes is installed perpendicular to the groundwater flow direction. Anodes and cathodes are integrated into separate closed-loop pump systems and are used to circulate electrolytes. Electrolytes collected from anodes and cathodes are mixed above ground and circulated to maintain neutral pH. A row of infiltration filters are used to inject nutrient solutions such as nitrogen, phosphorous, and oxygen donors. These nutrients are generally electrically charged, and they can be dispersed homogeneously through the soil by electromigration. The organic pollutants transported by the groundwater are degraded by enhanced microbial activity within the downstream of the zone. Such electrokinetic biobarrier (electrokinetic biofence) has been successfully used at a site in Europe and detailed information on this field application is provided in Chapter 17.

1.9.2 Electrolytic Reactive Barriers (e^- Barriers)

Electrolytic reactive barriers (also known as e^- barriers) consist of closely spaced permeable electrodes installed in a trench perpendicular to the direction of groundwater flow intercepts a groundwater contaminant plume, similar to PRBs. Figure 1.2 shows a schematic of implementation of this remedial approach. A low electric potential applied to the electrodes induces oxidizing conditions at the anode electrodes and reducing conditions at the cathode electrodes. Using electrodes to deliver and recover electrons, thermodynamic conditions are shifted to drive transformation of target compounds to nontoxic products. A wide range of redox-sensitive contaminants such as arsenic, chlorinated ethenes (TCE, TCA), and energetic compounds (TNT and RDX), including these mixtures (difficult to treat with other technologies), may be treated using the electrolytic barriers. This remedial approach offers several advantages, including (a) effective degradation of contaminants and reaction intermediates through sequential oxidation and reduction, (b) control

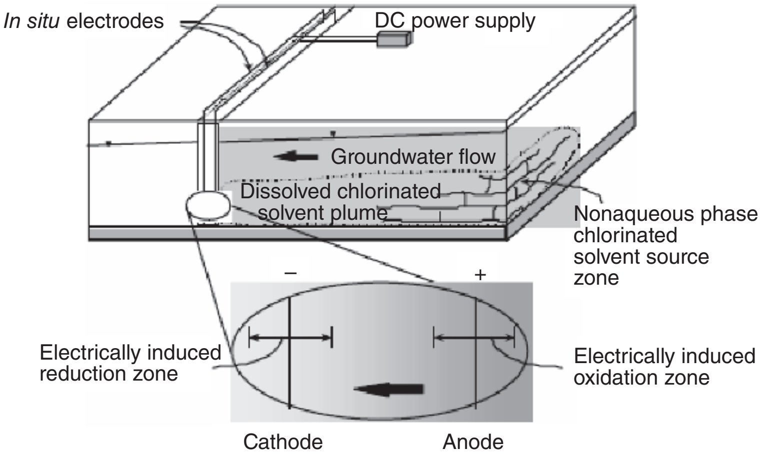

Figure 1.2. Schematic of the implementation of the electrolytic reactive barrier system (Sale, Petersen, and Gilbert, 2005). The barrier is installed perpendicular to the flow of groundwater direction and low electric current is applied to induce oxidation and reduction of contaminants at the electrodes.

accumulation of mineral precipitates via periodic reversal of electrode potentials, (c) no chemicals are introduced and no special permits required, (d) simple operation, and (e) low operation and maintenance costs. Laboratory tests and a field demonstration performed at a DOE site demonstrate that this technology is a viable option to remediate contaminated groundwater. More details on this technology can be found in Sale, Petersen, and Gilbert (2005).

1.9.3 Coupled Electrokinetic–PRBs

PRBs have been extensively used for the remediation of inorganic and organic pollutants in groundwater. Basically, PRBs consist of digging a trench in the path of flowing groundwater and then filling it with a selected permeable reactive material. As the contaminated groundwater passes through the PRB, organic contaminants may be degraded or sequestered and inorganic contaminants are sequestered, and clean groundwater exits the PRB. The reactive materials commonly considered include iron filings, limestone, hydroxyapatite, activated carbon, and zeolite. Monitoring data from several field PRB projects showed that the reactive material is clogged due to mineral precipitation resulting from flow of a high concentration of dissolved inorganic species. In addition, there may be decrease in the reactivity of the material used in the PRB. Coupling electrokinetics with PRBs is conceived to eliminate clogging of the PRB system caused by mineral precipitation and improve the long-term performance of PRBs. More research is needed toward developing a combined electrokinetic–PRB system where adaptive electrokinetic system is used to induce favorable geochemical conditions within the PRB as needed during the course of the remediation process (Chapter 23).

1.9.4 Coupled Electrokinetic–Chemical Oxidation/Reduction

It is possible to remove a wide range of organic contaminants from soils using solubilizing agents such as surfactants, biosurfactants, cosolvents, and cyclodextrins (Part III). However, there may be regulatory objections for injecting these solubilizing agents into the subsurface. In addition, posttreatment of the extracted solutions at the electrodes makes this treatment very costly. An alternative approach is to degrade the organic contaminants within the soil by injecting oxidants (e.g. hydrogen peroxide, permanganate, or persulfate) or reductants (ZVI in the form of nanoscale iron particles). The principles of chemical oxidation and reduction processes have been used for wastewater treatment for decades. However, it is challenging to introduce the oxidants/reductants into low-permeability clay soils. Combining electrokinetics with chemical oxidation/reduction facilitates delivery of the oxidants and reductants as well as increase contaminant availability in low permeability soils. Oxidants such as Fenton's reagents (H_2O_2 and Fe^{2+}) produce hydroxyl radicals, which break C-H bonds of organics into environmentally benign end products. Electrokinetics will also allow control of the soil pH and potential increase in temperature to create optimal conditions to achieve maximum oxidation (Chapters 21 and 22).

It should be noted that the electrokinetic–chemical reduction principles are the same as electrokinetic–PRB using iron filing as reactive media, but one has to wait for the contaminated water to pass through the PRB for the remediation to occur.

However, in electrokinetic–chemical reduction approach, the nanoscale iron particles are introduced into the contaminant source zone itself, thereby reducing the treatment time.

Generally, oxidants are stable only for a short period of time; therefore, electrosynthesis methods have been developed to produce oxidants on-site. Ultrasonic methods involving the application of high-intensity ultrasound are used to cause sonolysis of water to produce hydrogen peroxide and hydroxyl radicals. It should be noted that a simple combination of electrokinetics and ultrasonic waves is also investigated by some researchers, but the purpose was to enhance contaminant removal, not degradation.

Another technology known as electrochemical geo-oxidation (ECGO) is proposed, which involves application of low voltage and amperage to induce reduction–oxidation reactions at the microscale. This technology is based on the premise that soil particles act as microcapacitors that charge and discharge in a cyclic fashion. Even though low voltage and amperage are used, the energy burst on discharge at the microscale is intense, resulting in destruction of organic contaminants, theoretically to carbon dioxide and water. ECGO self-generates the agents for reduction (H as ion or radical) and oxygen (O elemental, OH and its radicals, HO_2 and its radicals) and when combing the generation of H_2O_2 with the corrosion products of steel anodes results in Fenton's reagent (refer to Chapter 32 for details). This technology is particularly attractive because no external oxidants need to be added.

1.9.5 Coupled Electrokinetic–Bioremediation

Bioremediation, which involves degradation of organic compounds using microbes, has received great attention because it is environmentally friendly, inexpensive, and requires low energy. However, it is a slow remediation processes and its effectiveness depends on the availability of nutrients, bioavailability of contaminants, and physical conditions such as temperature and moisture. Coupling electrokinetics with bioremediation (also known as electrobioremediation or electrobioreclamation) can facilitate injection of nutrients, electron acceptors, or microbes (if needed) and increase the bioavailability of contaminants, especially in low-permeability soils where hydraulic delivery techniques are ineffective. Interestingly, electrolysis reactions at the electrodes may be used to provide electron acceptors and donors. Hydrogen produced at the cathode may be used as electron donor for reductive degradation processes, while oxygen produced at the anode may be used for oxidative biodegradation. Although biodegradation is often applied to organic pollutants, few studies reported on biological immobilization heavy metals enhanced by electrokinetics. Advances are being made through additional research to optimize the electrokinetic effects on the microbial activity to achieve efficient contaminant degradation (Chapters 18 and 19).

1.9.6 Coupled Electrokinetic–Phytoremediation

Phytoremediation involves the use of living plants and their associated microorganisms to remove, degrade, or sequester inorganic and organic pollutants from soil, sediment, and groundwater. The main advantages of this method are low cost and ecological friendliness. However, this method is limited to shallow depths (limited by the root depth), slow plant growth, and also solubility and availability of the pollutant. Coupling electrokinetics with phytoremediation is aimed at increasing the availability of the contaminants and also facilitating their transport toward the root zone. The effects of electric field on soil pH, availability of nutrients, and so on may also help plant growth. Electrodes are placed strategically and a low direct current or voltage gradient is applied and the contaminants are transported by electromigration and/or electroosmosis processes toward the plant root zone. Electrode solutions of reduced toxicity toward plants can be used to enhance solubilization of the contaminants. Small-scale experiments showed that the plants are not affected by the exposed electric fields and that overall contaminant removal efficiency is controlled by different geochemical reactions. More research is needed to address organic contaminants and contaminant mixtures and possible effects on soil quality and biology (Chapter 20).

1.9.7 Coupled Electrokinetic–Stabilization

The electrochemical removal of contaminants may not be always possible or practical. For instance, a site may be too polluted to be treated to the acceptable level by any of the technologies, but it is critical to reduce the risk posed by the site contamination. The common approach used for risk reduction is stabilization and solidification (or immobilization) technology. In this approach, contaminants are transformed into a form that does not allow them to be released into the environment. Electrochemical approach may be used to stabilize the contaminated soils at a low cost and it will serve as an interim or pretreatment process to permanent treatment technologies.

Electrochemical stabilization (Chapter 8) focuses more on heavy metals than on organic pollutants, and it typically consists of converting the mobile contaminants into precipitates by injecting conditioning solutions such as alkaline solutions or reducing agents depending on the specific contaminant conditions. For example, reduction of Cr(VI) to Cr(III) by the delivery of iron (Fe^0, Fe^{2+}) is fairly well documented.

Alternatively, iron-rich sacrificial electrodes, which dissolve under acidic conditions generated at the anode by the application of electric field, may be used. The dissolved iron, in cationic form, migrates toward the cathode and then precipitates as iron-rich mineral phases (ferric iron oxyhydroxides, hematite, goethite, magnetite, and ZVI) near the cathode due to high-pH conditions. Contaminants such as Cr(VI) can react with this iron and reduce into Cr(III). Cr(VI) transport may be limited by high sorption under low-pH conditions; therefore, alkaline solution may be injected from the anode to increase the soil pH, and thereby reduce sorption and increase transport of Cr(VI) to react with iron.

1.9.8 Coupled Electrokinetic–Thermal Treatment

Thermal effects during electrochemical remediation are being studied. *In situ* thermal methods such as electrical resistance heating (ERH) have been used for site remediation, but electromotive forces that may occur during ERH are not studied. Heating resulting from electrochemical treatment involves the resistance to the passage of electrical current through soil moisture. It is this resistance to electrical flow that results in increases in temperature. Heat transport from this joule heating takes place mainly through conduction and convection. The increase in temperature decreases the viscosity of pore fluid, decreases the sorption of contaminants (increasing bioavailability), and increases the volatilization of organic contaminants. Heating results in lowering the oxidation–reduction potential in water, thereby affecting redox reactions. Elevated temperatures within the tolerable limits of microorganisms are also conducive to higher metabolic activity and enhanced biodegradation of contaminants. Proper control of increased temperature during electrochemical remediation may be exploited to enhance the overall remedial efficiency (Chapter 24).

1.10 MATHEMATICAL MODELING OF ELECTROCHEMICAL REMEDIATION

Mathematical models are useful to better understand the processes that occur under electric field and predict remedial performance in field application. Compared with laboratory studies, only few studies have been reported on the mathematical modeling of electrochemical processes and remediation. Generally, electrochemical remediation models should incorporate the contaminant transport, transfer, and transformation processes and dynamic changes in electrical conductivity, pH, and geochemical reactions. Recognizing this as a complex task, researchers have developed some simple models based on a set of simplified assumptions (Chapters 25 and 26).

First, the modeling of two dominant transport processes, electromigration (ionic migration) and electroosmosis, is critical in any electrochemical remediation modeling. Several models are reported to predict ion transport under electric field, assuming dilute solutions, rapid dissociation–association chemical reactions, and small double layer thickness. When charged ions transport under the influence of an externally applied electrical field, their concentration distributions change with time, which lead to a change in local electrical conductivity. The change in local electric conductivity directly alters the value of potential gradient at that specific point. Hence, the changing electric conductivity and electrical field describe the transport process of the species implicitly. The migration of the ions in the bulk fluid are modeled taking into consideration the changing electric field due to migration, as well as other effects such as retardation and electropheretic effects that reduce ionic mobility. These models appeared to simulate well the long-term ion distribution in the soil as the conductivity and the electric field vary in time and space.

The classical H-S equation is used to predict the electro-osmotic velocity of the fluid as a function of the electric field and the electrokinetic potential of the clay. Both of these parameters vary during electrokinetic transport, and result in a nonlinear process. New models have been developed that uncouple the electro-osmotic velocity from the applied field taking that surface conductivity and the resulting proportion of the current transferred over the solid-liquid interface are used as intrinsic properties of the clay to describe the velocity (Chapter 2). The pH changes affect the zeta potential, and thereby electro-osmotic conductivity. Thus, electro-osmotic conductivity changes as the dynamic changes in soil pH occur.

Modeling of electrolysis reactions and the corresponding changes in soil pH and geochemical reactions require knowledge of electrochemistry and geochemistry. The modeling task is exacerbated spatially and temporally due to dynamic changes in geochemical conditions. The existing chemical speciation models such as MINTEQA2 (Chapter 25) cannot be easily integrated with models developed for electrochemical remediation. Generally, modelers used the same approach followed in the general geochemical models to develop a simplified geochemical model based on the specific problem being investigated and incorporated into their transport model.

Examples of one-dimensional and two-dimensional models to predict the transport of heavy metals under constant DC current are explained in Chapter 25. This model ignores hydraulic advection, electrophoresis, diffusion, and electroosmosis processes and considers only electromigration. Electrical potential distribution is assumed to be a function of the electrical resistance of the soil and depends on the instantaneous local concentration and mobility of all the ions existing in the pore water of the soil. Local chemical equilibrium is assumed to calculate the concentration of chemical species. Validation of these and other developed models based on laboratory and field test results is critical to gain confidence in the accuracy of the model predictions.

Mathematical models are also developed to assess the performance of electrokinetic barriers (Chapter 26). In general, hydraulic advection, electro-osmotic advection, and electromigration processes are incorporated in these models. Future work needs to incorporate biochemical reactions into the modeling of the behavior of electrokinetic reactive barriers. Similarly, a suite of mathematical models is needed for predicting the performance of other integrated electrochemical remediation systems.

1.11 ECONOMIC AND REGULATORY CONSIDERATIONS

1.11.1 Economic Considerations

The general perception among environmental professionals is that electrochemical remediation is very costly. However, one must understand the site conditions where electrochemical remediation is applied and the other potential competitive technologies applicable for the same site conditions. As noted earlier, electrochemical remediation is applicable to difficult sites where low-permeability and heterogeneous soils and/or complex contaminants exist. Many conventional remediation technologies are not even applicable for such site conditions. Therefore, cost comparison is often made with the option of excavation and disposal of hazardous waste.

Unfortunately, only limited data are available on the costs associated with electrochemical remediation technologies. Laboratory studies may not provide an accurate cost estimate as compared with field pilot-scale or full-scale applications. Many field applications have been implemented in Europe, while very few have been implemented in the USA. The reported cost data are based on the specific site conditions encountered at these applications. It is determined that electrochemical remediation costs US$115–US$400 per cubic meter of soil if it is contaminated with inorganic pollutants, and US$90–US$275 per cubic meter of soil if it is contaminated with organic pollutants, and the average cost is about US$200 per cubic meter of soil (equates roughly to US$90 per ton of soil) for inorganic or organic pollutants in saturated clayey soil. These estimated costs are less than the cost of excavation and disposal as hazardous waste. As the technology matures, confidence in designing the field systems will increase, resulting in lower cost. Refer to Chapter 27 for the basis and a detailed breakdown of the costs involved in electrochemical remediation.

1.11.2 Regulatory Considerations

Similar to any other technology, the design, implementation, and monitoring of electrochemical remediation must meet all applicable environmental laws and regulations, which vary from country to country. The environmental laws and regulations may be promulgated at the national, regional, and local levels, and it is required that any field application satisfies all of these laws and regulations for any field application. In the USA, the most relevant regulations addressing the remediation of contamination are (a) the Resource Conservation and Recovery Act, (b) the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA, also known as Superfund), (c) the Clean Air Act, (d) the Clean Water Act, and (e) the Safe Drinking Water Act. These regulations provide the general cleanup process protocol, transport, and storage requirements and cleanup standards. More detailed information is presented in Chapter 28.

1.12 FIELD APPLICATIONS AND LESSONS LEARNED

Documented field applications provide invaluable information to design, assess, and further develop electrochemical remediation technologies. Over 75 field applications have been implemented in Europe, while few field applications have been implemented in the USA. The field demonstration and full-scale field implementation projects in other countries are being initiated.

1.12.1 Field Applications in the USA

The following field applications of electrochemical remediation have been reported addressing metal pollutants (Chapter 29):

- In 1989, the United States Environmental Protection Agency (USEPA) evaluated the remediation of a Superfund site heavily polluted with chromium.
- In 1994, Isotron Corporation implemented the *Electrosorb* process to evaluate the removal of uranium and organic contaminants.
- In 1996, Sandia National Laboratory addressed hexavalent chromium in an unsaturated soil at a chemical waste landfill site in Albuquerque, New Mexico.
- In 1998–2000, the US Army Environmental Center treated chromium and cadmium at NAWS Point, Mugu, California.
- In 2001–2002, Electrochemical Design Associates examined the removal of lead from soil at a Pearl Harbor naval shipyard and intermediate maintenance facility in Honolulu, Hawaii.

Overall, the field applications demonstrate that the electrokinetic treatment is an adequate tool for the remediation of polluted sites with heavy metals. However, the effectiveness of the process largely depends on the geochemical characteristics of the soil and the interaction of the pollutants with the soil. Therefore, a detailed study of each case is necessary to establish the most adequate operating conditions. It includes current intensity or voltage drop, electrode disposition, and chemical conditioning of electrode solutions. Laboratory studies can be carried out prior to the field operation in order to determine the effect of those operating conditions in the solubilization and removal of heavy metals, but it must be considered that the results at field scale can differ from those obtained in the laboratory experiments due to the change in scale.

A well-documented field application of electrochemical remediation is reported to address the problem of chlorinated solvent (TCE) in clay soil at the DOE site in Paducah, Kentucky. This process is known as Lasagna^{TM} (Terran Corporation, Beavercreek, OH) and it combines the electro-osmotic transport of TCE in pore water and degrades it in vertical curtains installed along the flow path within the soil that are filled with iron filings and kaolin clay. Pore water accumulated at the cathode is recycled by gravity back to the anode as makeup water and neutralize the acid formed at the anode. Overall, the treatment is found to be effective. The implementation and performance results are presented in detail in Chapter 30. The same Lasagna^{TM} process is implemented very recently at another site contaminated with TCE in Fonde du Lac, Wisconsin, and performance is being monitored (Chapter 30).

The electrolytic reactive barrier (electrolytic redox barrier or e^- barrier) concept is demonstrated at F.E. Warren Air Force Base in Wyoming in 2002 to remediate groundwater plume contaminated with approximately 300 μg/l of TCE. The details of barrier design and installation are provided by Sale, Petersen, and Gilbert (2005). After installation, the barrier is allowed to equilibrate with the contaminant plume for 5 months, then low-voltage DC is applied continuously for about 18 months. Under the maximum potential of 6.5 V, TCE flux is reduced by 90% with no adverse intermediates. Complementary studies are proposed at other sites to treat energetic compounds that are difficult to treat with conventional technologies.

Recently, a field demonstration of the ECGO to remediate contaminated dredged harbor sediments from Lake Superior in Duluth, Minnesota, is completed. The sediments were contaminated by PAHs, PCBs, mercury, and other miscellaneous contaminants. The dredged sediments were planned to be disposed in confined disposal facilities (CDFs). Instead of CDFs serving as perpetual containment systems, a new approach being proposed is to convert CDFs to storage, handling, and treatment facilities. ECGO demonstration was performed within this context to remediate dredged sediments within CDFs. One control cell and one demonstration cell were used. Electrodes (steel sheet pile or steel pipe) were installed at a spacing of 5–15 m in the demonstration cell, and voltages and electric currents that vary from 20 to 100 V and approximately 0.05–50 A were applied. The contaminant concentrations were monitored over a period of 4 months. Field observations showed that reactions are taking place, but concentration data were inconclusive with regard to contaminant reduction. A detailed explanation of the findings can be found in Chapter 32.

1.12.2 Field Applications in Europe

Over 75 full-scale field systems are implemented in Europe, predominantly in the Netherlands. Chapter 33 presents the generalized procedures followed for the design, implementation, and monitoring of the field systems. The major components of field systems include electrodes, electrolyte management system, and electrolyte purification. Electrochemical remediation can be implemented in batch (*ex situ*) or *in situ* modes. Predesign investigations include laboratory soil tests such as cation exchange and anion exchange tests and two special tests known as "turbo test" and "standard test" (see Chapter 33 for details). It is also recommended to conduct field geoelectrical survey to measure the electrical resistivity of the soils at the site. Moreover, remediation equipment and electrode materials are selected based on the site conditions: chemical nature and concentration of contaminants, soil type, and geochemical interactions. Performance data from large sites contaminated with inorganic and/or organic pollutants are presented in Chapter 33, and it shows that electrochemical remediation is an effective remedial method.

1.12.3 Field Application in Korea

The coupled electrokinetic–PRB concept was demonstrated at a landfill site where groundwater was contaminated by the uncontrolled release of landfill leachate (Chapter 31). Two different configuration of electrode wells were tested: The first configuration consisted of anode electrode well in the middle and the cathode wells located radially at a distance of approximately 1 m from the anode well; the second configuration consisted of one row of cathode wells in the middle of two rows of anode electrode wells at a distance of 2 m. ZVI, zeolite, slag, tires, and sand were tested for PRB materials. From the preliminary field investigations, the coupled technology of the electrokinetic–PRB system would be effective in remediating contaminated grounds, and the extraction of pollutants from the subsurface was not necessary due to the reactions between the reactive materials and the contaminants.

1.13 FUTURE DIRECTIONS

As reflected by the content of this book, many significant advances have been made toward establishing electrochemical remediation as a practical remediation technology. The field application of this technology lags far behind the laboratory and other research studies. The following issues should be addressed in order for this technology to be used in field applications and becoming an generalized commercial technology for the remediation of soils, sediments, and groundwater:

- Limit the small-scale laboratory experiments and encourage large-scale pilot tests in laboratory or in the field
- Limit the single contaminant experiments in model soils spiked in laboratory and promote the tests with actual contaminated soils with aged and multiple contaminants
- Extend the electrochemical technology to other contaminated porous matrices such as industrial wastes in order to achieve their sustainable reuse
- Promote the analysis of experimental results based on the physicochemical properties of contaminants, geochemistry of soil, reaction kinetics, equilibrium constants, and transport parameters, rather than a phenomenological analysis of contaminant removal

- Advance the fundamental research and develop predictive modeling tools; in particular, geochemical reactions in various soil and contaminant conditions should be properly characterized
- Establish quality control and quality assurance protocols for laboratory and field studies
- Assess the impacts of electrochemical remediation on soil quality and ecology
- Investigate the short-term and long-term effects on electrochemical processes
- Develop new and innovative approaches of electrochemical remediation that are less expensive and practical
- Develop electrochemical remediation systems that are ecologically safe based on sustainability considerations
- Perform and disseminate results of well-monitored field pilot-scale demonstrations
- Establish communication among the researchers and identify areas that require future research
- Develop guidance documents for the design, installation, and operation of typical electrochemical remediation systems

In summary, the importance of full-scale field demonstration projects cannot be overemphasized. The lessons from these projects are invaluable in identifying the advantages and limitations of this technology and in developing effective and economical adaptive field systems based on site-specific conditions.

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