Chapter 2

Literature Review

2.1 General

A review of literature pertaining to the electrokinetic remediation technology and various factors affecting its efficacy are presented in this chapter. A brief description on the historical background and the mechanism of electrokinetic remediation are also presented for the sake of completeness.

2.2 Historical Background

Reuss (1808) noted the transport of water towards cathode under the influence of the electric current when applied through porous media. The uses of direct electric currents for electroosmotic consolidation and stabilization of fine grained deposits have been investigated by geotechnical engineers since the late 1930’s. Effective applications of processes have been demonstrated for slope stabilization, chemical alteration of dry soils, concentration, separation, and stabilization of polluted dredging, soil consolidation and dewatering, reduction of negative skin friction of piles and increasing the capacity of friction piles (Casagrande 1952, 1983; Casagrande et al., 1961; Gladwell, 1965; Mise, 1961; Esrig, 1968; Wan and Mitchell, 1976; Gray and Somogyi, 1977; Johnston and Butterfield, 1977; Banerjee and Mitchell, 1980a, 1980b).

Most of this research has shown feasibility in geotechnical engineering applications; however the effects of the application of electric gradients and electroosmosis on electrochemical changes of the soil medium have entertained limited attention. The potential for the electrokinetic remediation for contaminated soil was realized in the 1980s, when scientists noted high levels of heavy metals along with pore water transported by electroosmosis (Azzam and Oey, 2000). Systematic early theoretical work was done by Smoluchowski (Lyklema, 2003). Since then a number of different applications of the electrokinetic remediation technology have emerged in which study of removal of heavy metals and radionuclide from the low permeability soils utilizing electrokinetic phenomena is conducted (Lageman, 1993; Ho et al., 1999; Kim et al., 2002; Yang, 2001; Azzam and Oey, 2000). Though electrokinetic technology appears relatively easy to implement in field, the fundamental reactions are complex (Saichek and Reddy, 2005) and a thorough understanding
of physical, chemical and electrochemical processes involved in process is essential for effective implementation.

2.3 Studies on Electrokinetic Remediation

The first attempt of removal of heavy metals by electrokinetic was in the early 1980s (Hamnett, 1980; Segall et al., 1980; Agard 1981). In several studies, successful transport of a large number of heavy metals through soils under influence of electric fields and thereby their subsequent removal onto an electrode or into the solution surrounding the electrode (catholyte or anolyte) has since been demonstrated. Feasibility and cost effectiveness of electrokinetics for the extraction of heavy metals such as copper, zinc and cadmium from soils have been demonstrated through bench scale laboratory studies (Runnels and Larsen 1986; Hamed 1990; Pamukeu et al. 1990; Acar et al. 1992 and 1993). A large number of works on electrokinetic remediation has been carried out in the laboratory.

Majority of the works are on spiked synthetic soils. Artificial soil, mostly kaolinite is commonly used, however experiments have been performed even on other clay minerals, sand, peat, mixtures of Clay minerals and clay, and natural soils. Yeung et al., 1997, presented the review of the apparatus for the bench scale testing in laboratory. Either a constant voltage DC power supply with a potential gradient in the range 0.2 to 2 VDC/cm (Probstein and Hicks, 1993) is supplied or as an alternate, current density may be maintained at a constant value, commonly in the range of 0.025–5 A/m² (Acar et al., 1991; Hamed et al., 1991). Experimentation is carried out for the durations spanning from a few hours to several months. A low current is necessary to avoid heating effects which can adversely affect the contaminant removal, osmotic flow etc. During experimentation, moisture content of the soil, conductivity, pH of the pore solution and contaminant distribution throughout the soil samples are often measured by analyzing materials at different normalised distances from either anode or cathode. Current, voltage, fluid flow, and chemical composition of effluent may be monitored continuously during experiment.

Gray and Schlockers, 1969, investigated the effect of pH in controlling changes in soil composition and the feasibility of pH buffering during electrochemical treatment. Their results demonstrated that composition and physical properties of clayey soils are altered when aluminum is introduced in the anolyte. Lockhart (1983) concluded that reasonable concentrations of electrolytes are not necessarily detrimental to electroosmotic dewatering. Putnam (1988) and Acar et al.(1989) discussed the effect of electrolysis reactions at the electrodes on soil pH. Acar et al. (1989) showed that the acid generated at the anode sweeps across the soil specimen ultimately decreasing the soil pH. Puri and Anand, 1936; Gibbs,
1966; Vadyunina, 1968, studied removal of salt or alkalis from soils by electrokinetic remediation.

As such metals are usually present as cations. They, therefore, are transported mainly by electrokinetic migration toward the cathode. However, it is not necessarily that all metals move towards cathode. Certain elements, like Cr, may be present as oxy-anions and their transport would be to the anode (Banerjee, 1987; Lindgren et al., 1994; Pamukcu and Wittle, 1994). Experiments on Cr, Cu, and other heavy metals were carried out by Lageman et al., 1989 with average removal up to 76%. The metals were removed from clay, peat, and even from argillaceous sand. Transport of Cr and other metals in kaolinite, bentonite, and sand-bentonite mixture was investigated, where in, average removal of 85–95% for Cd, Co, Ni, and Sr was observed (Pamukcu and Wittle, 1992, 1994).

Lageman et al., 1990 studied the feasibility of removal of a range of aromatic organic compounds using electrokinetic remediation. Effective removal was demonstrated for acetic acid and phenol (Shapiro et al., 1989; Shapiro and Probstin, 1993), hydrocarbons and trichloroethene (Bruell et al., 1992), phenol (Acar et al., 1992), and hexachlorobenzene (Pamukcu and Wittle, 1994). For modeling transport by means of electroosmosis, p-nitrophenol has been used (Pamukcu and Wittle, 1994; Ho et al., 1995). Transport of immiscible, nonpolar organic compounds is less effective although they may be moved by electroosmosis (Mitchell, 1991). A brief summary of such studies conducted on Cu and Cr is described in following table 2.1.(a & b) (Page and Page, 2002).

**Table 2.1 (a). Studies conducted in electrokinetic remediation for Cu contaminants**

<table>
<thead>
<tr>
<th>Heavy Metal Specie</th>
<th>Soil Class</th>
<th>Sample Type</th>
<th>Source of Contaminant</th>
<th>Removal Enhancement by</th>
<th>Enhancement done at</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Kaolinite</td>
<td>Synthetic</td>
<td>Spiked</td>
<td>Na Citrate ± HNO₃</td>
<td>Anode+Cathode, HNO₃ in Cathode</td>
<td>Eykholt and Diniel 1994</td>
</tr>
<tr>
<td>Cu</td>
<td>Silty Sand</td>
<td>Synthetic</td>
<td>Spiked</td>
<td>None</td>
<td>-</td>
<td>Rummells and Larson 1986</td>
</tr>
<tr>
<td>Cu</td>
<td>Sand</td>
<td>Synthetic</td>
<td>Spiked</td>
<td>None</td>
<td>-</td>
<td>Rummells and Wahl 1993</td>
</tr>
<tr>
<td>Cu</td>
<td>Sand</td>
<td>Synthetic</td>
<td>Spiked</td>
<td>Conductive Solution</td>
<td>Cathode</td>
<td>Li et al 1996</td>
</tr>
<tr>
<td>Cu</td>
<td>Sand</td>
<td>Synthetic</td>
<td>Spiked</td>
<td>Conductive Solution</td>
<td>Cathode</td>
<td>Li et al 1998</td>
</tr>
<tr>
<td>Cu</td>
<td>Silica Flour</td>
<td>Synthetic</td>
<td>Spiked</td>
<td>NaNO₃</td>
<td>Anode</td>
<td>McKinley and Peat 2000</td>
</tr>
<tr>
<td>Cu</td>
<td>Soil</td>
<td>Natural</td>
<td>Polluted</td>
<td>Ion Exchange Membranes</td>
<td>Anode+Cathode</td>
<td>Jensen et al 1994</td>
</tr>
<tr>
<td>Cu</td>
<td>Loamy Sand</td>
<td>Natural</td>
<td>Polluted</td>
<td>Ion Exchange Membranes</td>
<td>Anode+Cathode</td>
<td>Hansen et al 1997</td>
</tr>
<tr>
<td>Cu</td>
<td>Loam</td>
<td>Natural</td>
<td>Polluted</td>
<td>Conductive Solution</td>
<td>Cathode</td>
<td>Li et al 1997</td>
</tr>
<tr>
<td>Cu</td>
<td>Soil</td>
<td>Natural</td>
<td>Polluted</td>
<td>Ion Exchange Membranes</td>
<td>Anode+Cathode</td>
<td>Ribeiro and Mexia 1997</td>
</tr>
<tr>
<td>Heavy Metal Specie</td>
<td>Soil Class</td>
<td>Sample Type</td>
<td>Source of Contaminant</td>
<td>Removal Enhancement by</td>
<td>Enhancement done at</td>
<td>Reference</td>
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<td>------------------------</td>
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<td>---------------------</td>
</tr>
<tr>
<td>Cr</td>
<td>Sand</td>
<td>Synthetic</td>
<td>Spiked</td>
<td>Fe Anode</td>
<td>-</td>
<td>Haran et al 1996</td>
</tr>
<tr>
<td>Cr</td>
<td>Sand</td>
<td>Synthetic</td>
<td>Spiked</td>
<td>Conductive Solution</td>
<td>Cathode</td>
<td>Li et al 1997</td>
</tr>
<tr>
<td>Cr</td>
<td>Kaolinite &amp; Glacial Till</td>
<td>Synthetic mixing in Natural Till</td>
<td>Spiked</td>
<td>None</td>
<td>-</td>
<td>Reddy and Parupadi 1997</td>
</tr>
<tr>
<td>Cr</td>
<td>kaolinite, Na - Montmorillonite &amp; Glacial Till</td>
<td>Synthetic mixing in Natural Till</td>
<td>Spiked</td>
<td>None</td>
<td>-</td>
<td>Reddy et al 1997</td>
</tr>
<tr>
<td>Cr</td>
<td>Kaolinite &amp; Soil</td>
<td>Synthetic mixing in Natural Soil</td>
<td>Spiked</td>
<td>Alkali + NaOCl</td>
<td>Anode+Cathode</td>
<td>Le Hecho et al 1998</td>
</tr>
<tr>
<td>Cr</td>
<td>Soil</td>
<td>Natural</td>
<td>Spiked</td>
<td>None</td>
<td>Anode+Cathode</td>
<td>Lindgren et al 1994</td>
</tr>
<tr>
<td>Cr</td>
<td>Soil</td>
<td>Natural</td>
<td>Spiked</td>
<td>Lysimeter Electrodes + pH Control</td>
<td>Anode+Cathode</td>
<td>Mattson and Lindgren 1995</td>
</tr>
<tr>
<td>Cr</td>
<td>Alkaline Soil</td>
<td>Natural</td>
<td>Polluted</td>
<td>Simulated Rain Water + pH Control</td>
<td>Anode+Cathode</td>
<td>Weng et al 1994</td>
</tr>
<tr>
<td>Cr</td>
<td>Loamy Sand</td>
<td>Natural</td>
<td>Polluted</td>
<td>Ion Exchange Membranes</td>
<td>Anode+Cathode</td>
<td>Hansen et al 1997</td>
</tr>
<tr>
<td>Cr</td>
<td>Loamy Sand</td>
<td>Natural</td>
<td>Polluted</td>
<td>Conductive Solution</td>
<td>Cathode</td>
<td>Li et al 1997</td>
</tr>
</tbody>
</table>

### 2.4 Factors affecting Electrokinetic Remediation

The major factors affecting the efficiency of the electrokinetic remediation have been studied by many scientists.

#### 2.4.1 Effect of pH

Electrolyte composition changes when dissolved substances get removed from the soil sample either by entering the catholyte/anolyte or by depositing on the cathode. This is pronounced in the case for many metal ions, such as Cu (Runnells and Larson, 1986; Hamed et al., 1991; Acar et al., 1994). Even changes occur by evolution of chlorine gas for example in saline soil (Hamnett, 1980) at the anode. The electrolysis of pore water is the predominant process in moist soils, which results in formation of $\text{H}^+$ ions and oxygen at the anode and $\text{OH}^-$ ions and hydrogen at the cathode. Hindered migration would result into the local change in pH of the pore solution and therefore acidity increases with time at the anode and alkalinity increases at the cathode (Fernandez-Gonzalez, 1966; Gray and Schlocke, 1969). An increase in the concentrations of ions like Mg, Al, and Fe is often seen because of increased acidity and other ions like Si and Al because of increased alkalinity (Grim, 1968).
Al ions are commonly detected in pore solutions of soils which have undergone electrokinetic remediation (Dzenitis, 1997; West et al., 1997).

An acid front moves across the soil sample from the anode toward the cathode and a base front moves from the cathode to the anode (Acar et al., 1991). The movement of acid front is faster than the base front because the mobility of $H^+$ exceeds that of $OH^-$ resulting into electroosmotic flow toward the cathode. With passing time the entire soil sample usually becomes acidic except near cathode. However, the movement of acid front is slower when the soil itself is highly buffered or alkaline (Reddy et al., 1997) or when reactive anodes such as Fe are used for the favored reaction of formation of Fe$^{++}$ (Haran et al., 1996, 1997). Water forms where the acid and base fronts meet. That results into a sharp change in pH, which affects the solubility of contaminants and their adsorption to the soil.

Different ions may be stable at different pH values, for example, metal cations are stable under acidic conditions while oxy anions are stable under alkaline conditions. The solubility of metal ions is at minimum where the pH changes sharply, and they precipitate as metal hydroxides, very similar to isoelectric focusing (Gray and Schlocker, 1969). This has been observed experimentally for many heavy metal ions (Hamed et al., 1991; Hicks and Tondorf, 1994; Acar et al., 1994 and Eykholt and Daniel, 1994). This can be illustrated as shown in Fig. 2.1.

Fig 2.1. Precipitation of metal hydroxides in response to sharp change in pH (Palmer, 1997)

The position of precipitation is also affected by nature of the contaminants, other species present in the pore solution, the type of soil and the conditions of processing. To achieve a successful decontamination, metal ion solubility is required to be maintained by a low or a high pH throughout the soil and by avoiding the conditions resulting in precipitation. So the control of pH is a very important factor.
2.4.2 Effect of Field Strength and Electrical Conductivity (EC)

Changes in pH and change in ionic strength arising during electrokinetic remediation, results in to nonuniform electrical conductivity and voltage profiles (Miller, 1955; Cambefort and Caron, 1961; Hamed et al., 1991; Segall and Bruell, 1992). The most noticeable drop in conductivity and subsequent rapid change in field strength are generally near the cathode. This is in response to the sharp pH jump (Cambefort and Caron, 1961) and also in response to the precipitation of heavy metal ion contaminants as solid hydroxides (Hamed et al., 1991). This can be illustrated by Fig 2.2, shown below,

![Fig 2.2. Change in potential difference in response to change in pH and concentration (Eykholt and Daniel, 1994)](image)

The resultant steep potential gradient near the cathode causes a higher rate of electroosmotic flow in this region (Hamed et al., 1991; Alshawabkeh and Acar, 1996), and the same is reinforced by the high negative value of the zeta potential near the cathode (Eykholt and Daniel, 1994). However, flow through other parts of the soil may not be sustained at this level and negative pore pressures, which can result in consolidation, develop even with open electrodes (Casagrande, 1949; Miller, 1955; Mise, 1961; Esrig, 1968). Overall flow reduces as the acid front is produced at the anode. This acid front passes through the soil and lastly, the very high resistance by precipitated metal hydroxides and bubbles of gases generated causes fluid flow to become minimal.

Though, by electromigration significant removal continues even when electroosmosis has declined or ceased, provided concentration of ions are sufficient in pore solution (Probstein and Hicks, 1993; Acar et al., 1994; West and Stewart, 1995). Conductivity falls in the region of the pH jump as ions are removed, by means of water formation, precipitation, adsorption, and/or complexation. The rate of removal of contaminant ions becomes slow (because removal is only by electromigration). The conductivity of the soil actually increases with time in some tests, probably because of ionic species dissolving as a result of pH changes (Acar and Alshawabkeh, 1996) or because of temperature rises (Lageman et al., 1989; Ho et al., 1997).
2.4.3 Effect of Zeta Potential

Both pH and ionic strength of the pore fluid, which change continuously during electrokinetic remediation, affect the value of the zeta potential (Miller, 1955; Hunter, 1981). Increased acidity causes the zeta potential to become less negative and even to attain positive values at low pH (Lorenz, 1969). This is illustrated in the Fig 2.3, shown below,

![Fig 2.3. Effect of pH on zeta potential (Andrew P Shapiro, 1996)](image)

Flow rates have been observed to decrease if the pH of the electrolyte is depressed below neutral and to increase at alkaline pH values (Shapiro and Probstein, 1993; Hamed and Bhadra, 1997). The observed increase in fluid flow rate near the start of treatment has been explained in terms of the high negative value of the zeta potential near the cathode because of increased OH\(^-\) ion concentration (Eykholt and Daniel, 1994). Correspondingly, small or even positive values of zeta potential have been used to explain the observations that fluid flow eventually decreases with time and, in some instances, reverses direction toward the anode (Shapiro and Probstein, 1993; Eykholt and Daniel, 1994; West and Stewart, 1995; Yang and Lin, 1998). Sometimes initial flow in the direction of the anode has been observed and is probably a consequence of the low pH of the starting conditions (Dzenitis, 1997). The changes in flow rates as a consequence of changes in pH can be explained by chemical osmosis.

The zeta potential also tends to become more positive as ionic strength of the pore solution increases (Hunter, 1981). For kaolinite, a decrease in rate of electroosmotic flow with increase in ionic concentration has been observed (Gray and Mitchell, 1967). The nature of the ions present makes the situation even more complex, for example, increasing concentrations of hydrolysable metal cations, such as Cu\(^{2+}\), cause the zeta potential to become more positive, the effect of which is the greatest at intermediate pH values (Hunter and James, 1992). Sufficiently high concentrations of ions causes reversal of flow (Casagrande, 1952; Ray and Ramsey, 1987). The reversal of polarity in the zeta potential has been demonstrated by West and Stewart 1995.
2.4.4 Effect of Soil Chemistry

Attempts have been made to study the effects of soil chemistry on electrokinetic remediation. Some of the studies show the effects of the organic matter (Cox et al., 1996), iron oxides (Reddy et al., 1997) or both (Ribeiro and Mexia, 1997). Soil characteristics like adsorption, ion exchange, and buffering capacity influence kinetics of contaminant removal (Grim, 1968; Sposito, 1984). Sorption occurs in soil irrespective of the concentrations of heavy metal. Clay minerals, organic matter, silica/aluminium/iron/manganese oxides, carbonates and phosphates are the predominant physical soil components that have the ability to sorb heavy metals (Kjeldsen and Christensen, 1996). Soil contaminant interaction is especially high in fine-grained soils. Adsorption isotherms and ion exchange capacities have been determined directly in electrokinetic remediation experiments (Hamed et al., 1991; Yeung et al., 1996; Puppala et al., 1997; Reddy et al., 1997; Sah and Chen, 1998; Chen et al., 1999).

Ionic contaminants are required to be desorbed before they can be removed. Decontamination is most rapid at concentrations above the ion exchange capacity of the soil. Soils which adsorb strongly having high cation exchange capacities, (e.g. illitic and bentonitic clays) are difficult to decontaminate compared to clays like kaolin having low cation exchange capacities. This can be correlated with electroosmotic flow rates, being higher in kaolin and lower in illitic and bentonitic clays (Gray and Mitchell 1967).

Changes in pH affect the adsorption characteristics of the soil. H\(^+\) ions, generated by electrolysis of water, are effective at desorbing metal cations as the acid front passes through the soil. Similarly, OH\(^-\) ions produced at the cathode aid desorption of anions, such as CrO\(_4\)^{2-} (Weng et al. 1994) and there is evidence that they may also help certain organic molecules to desorb (Se-gall et al. 1980). As per Kjeldsen and Christensen (1996), sorption in soil is reversible and desorption can happen to the same extent as sorption, because, sorption is primarily associated with the particle surfaces and the metal bonds are readily exposed to changes in the aqueous phase. The availability of H\(^+\) and OH\(^-\) ions in the pore solution is determined by the buffering capacity of soils. Buffering capacity is measured in clays used in laboratory experiments (Acar and Alshawabkeh, 1993; Jacobs and Probstein, 1996; Yeung et al., 1996; Dzenitis, 1997). The interaction between different clays and metal ions is investigated (Reddy et al., 1997; Reddy and Parupudi, 1997). Much of the laboratory work on electrokinetic remediation has been carried out using relatively pure kaolinite having low buffering capacity compared to natural soils containing metal oxides or carbonates (Acar and Alshawabkeh 1993). Problems caused at an actual remediation site due to the high buffering capacity of the soil have been described by Lageman et al. 1989.
Many heavy metals form insoluble precipitates. They can influence or control their solubility in the aqueous phase. Many heavy metals form nonsoluble hydroxycomplexes like malachite (Ottosen et al., 2000a) at neutral and higher/alkaline pH, (Kjeldsen and Christensen, 1996). Heavy metals can also co-precipitate with secondary soil minerals (Kjeldsen and Christensen, 1996).

Dissolved complexes formed with heavy metals increase the solubility and the mobility of the metal. The possible complexes formed by a heavy metal ion depend on the heavy metal ions coordination number, i.e. the number of ligands that can be attached to the metal ion. A ligand that forms one bond to a metal ion is called a unidentate ligand and other ligands that form more than one bond are called chelates. Chelates can form two bonds to a heavy metal ion (bidentate) or more than two bonds (polydentate). The most known polydentate ligand is EDTA, which effectively surrounds the heavy metal ion, making this a very stable complex. Other ligands for heavy metal complexation can be both organic and inorganic substances (Zumdahl, 1992).

### 2.4.5 Effect of Water Content

The extent of saturation of the soil is the factor that alters the electroosmotic flow rate and thereby decontamination of the soil (Gray and Mitchell, 1967; Mitchell and Yeung, 1991; Lindgren et al., 1994; Laursen, 1997). Some of the consequences of drying out of soil having lower moisture or higher temperature due to the application of current are shrinkage and cracking of the soil resulting into development of uneven flow paths and eventual cessation of fluid flow. Uneven moisture distributions and regions of consolidation may arise during electrokinetic remediation are associated with the development of negative pore pressures (Hamed et al., 1991; Acar and Alshawabkeh, 1996; Eykholt, 1997).

The negative pore pressures results from uneven flow rates caused either by variations in pH or electric field strength or zeta potential (Miller, 1955; Mise, 1961; Esrig, 1968; Eykholt, 1997). The cause of drying of soils is the heating effect of the electric current (Fernandez-Gonzalez, 1966; Shapiro and Probstein, 1993). Although increasing temperature might be advantageous under carefully controlled conditions as it increases the rate of any chemical reaction (Krause and Tarman, 1995; Penn and Savvidou, 1997). Desiccation can cause problems, particularly in large samples and in field trials (Lageman et al., 1989; Ho et al., 1997; Lindgren et al., 1998). The effect is likely to be more severe in unsaturated soils but may not be denied even in initially saturated soils.
2.4.6 Effect of Soil Structure

Alterations may occur to soil structure and its properties during electrokinetic remediation (Mitchell, 1991; Yeung, 1994). Certain clay minerals, such as montmorillonite, show dramatic changes, both physical and chemical, resulting in water loss and shrinkage (Grundl and Reese, 1997).

Deposition in the soil by compounds such as metal hydroxides can clog pores and cause the flow to cease. These compounds may form by reaction between hydroxyl ions near the cathode and heavy metal contaminants. Such compounds may also be formed by the reaction of hydroxyl ions with Al\(^{3+}\) introduced into the soil from Al anodes (Endell and Hoffmann, 1936; Gray and Schlocker, 1969), or Al\(^{3+}\) from soil minerals dissolved because of the acid conditions, (West et al., 1997) or Fe\(^{2+}\) ions from Fe anodes (Harton et al., 1967; Bjerrum et al., 1967). Therefore, for remediation of metal contaminated soils, it is necessary to prevent precipitation of insoluble metal compounds. In some field trials increased fluid flow has been observed as a consequence of increased hydraulic permeability in contrast to the previous effects (Puri and Anand, 1936; Lageman et al., 1989). This may be explained by the flocculation of clay particles by interaction with polyvalent cations (Coletta et al., 1997).

2.4.7 Effect of Nature of Electrodes and their Arrangement

Any conductive material that does not corrode in a basic environment can be used as cathode. Important considerations for the choice of the electrical material are (Alshawabkeh; Yeung; Bricka, 1999),

- Electrical conduction properties of material
- Availability of material
- Ease of the fabrication to the form required for the process
- Ease of installation in the field
- Material fabrication and installation cost

Generally, inert electrodes are preferred as they avoid introducing contamination from dissolution of the anode material though, in some cases, reactive anodes, such as iron, have been employed (Haran et al., 1996, 1997; Ho et al., 1997, 1999). They need to have porous casings and open access to the electrode compartments so that solutions and gases can flow through them. A common choice of material for both electrodes in laboratory studies is graphite, while, in field activated titanium with an electrocatalytic coating of mixed oxides or conductive ceramics are sometimes used. The rate of decontamination depends on size, shape, and arrangement of electrodes and their spacing. Very little research has been carried out into optimum values for these parameters (Renaud and probstein, 1987; Jin and Sharma,
Factors affecting the selection of electrode configuration include location and size of any inactive field spot that can be developed, number and cost of electrodes per unit area to be treated and time requirements of the designed remediation process (Alshawabkeh; Yeung; Bricka, 1999).

### 2.4.8 Enhancement Techniques

In order to control and improve contaminant removal, various methods have been proposed. Simple periodic reversal of electrode polarity results in more uniform conditions between the electrodes (Wan and Mitchell, 1976). It avoids excessive buildup of chemicals within the soil and other complications, such as cracking of the soil. Electrode polarity reversal is put into practice in hybrid techniques like the Lasagna Process (Ho et al., 1995, 1997). Enhanced removal of contaminants involves maintaining them in a soluble form. The addition of chemical conditioning agents at the electrodes and the use of nontoxic purge liquids, such as water and sodium chloride solution, transported into the soil from the anode compartment have been patented (European Patent No. 0312174A1, 1989; and U.S. Patent No. 5,074,986, 1991). Alternatively, the electrodes can be flushed to eliminate harmful products (Probstein and Hicks 1993); thus, washing the cathode with tap water has resulted in removal of OH$^-$ ions and therefore almost completes elimination of Zn (Hicks and Tondorf, 1994). Control over development of a pH gradient may be exerted by buffering the soil (Gray and Schlocker, 1969; Baraud et al., 1997, 1998).

The choice of enhancing agent depends on the type of contaminant and soil conditions. Addition of water at the anode is essential in unsaturated soils to replace water lost at the cathode (Shmakin, 1985; Mattson and Lindgren, 1995). Flushing the soil with acid aids desorption and transport of metal cations to the cathode (Acar and Alshawabkeh, 1993; Reed et al., 1995; Sah and Chen, 1998). Care must be taken not to increase contamination levels. Naturally occurring weak acids are less harmful, for example, hydrochloric acid which may destroy soil fabric and possibly result in chlorine being formed at the anode. Flushing the soil with solutions containing nontoxic cations has been shown to reduce remediation times while restoring some of the natural soil constituents lost during the process (Coletta et al., 1997).

The use of acetic acid to depolarize the cathodic reaction has been tested successfully on soil contaminated by U salts (Acar and Alshawabkeh, 1993) and Pb compounds (Acar and Alshawabkeh, 1993; Rodsand et al., 1995; Puppala et al., 1997) and a significant reduction in energy expenditure shown for soils containing a mixture of ions of Ca, Cr, Cu, Fe, Pb, and Zn (Alshawabkeh et al., 1997). Nitric acid, added to the cathode compartment, has been shown to achieve virtually complete removal of Pb from kaolinite (Denisov et al., 1996). A novel method for avoiding precipitation of heavy metals in the soil involves their transport...
into a conductive solution inserted between the cathode and the soil (Li et al., 1996, 1997). When the soil contains deposits of sparingly soluble metal compounds, e.g. carbonates, phosphates, hydroxides, and sulfides, remediation becomes difficult. Longer remediation time is required in addition the use of greater quantities of enhancing agents (Lageman, 1993; Acar et al., 1993; Hicks and Tondorf, 1994). Under these conditions, other reagents, such as oxidizing/reducing agents or ligands, may be tried. An iodine/iodide mixture has been used to aid the removal of mercury (Cox et al., 1996). Successful removal of Cr has been obtained under alkaline conditions in the presence of sodium hypochlorite (LeHecho et al., 1998). Several workers have used ethylene diamine tetra acetic acid (EDTA) to the cathode compartment in order to increase removal of metals (Reed et al., 1995; Yeung et al., 1996; Yeung et al., 1997; Wong et al., 1997). The EDTA–metal complexes can be separated to recover both the metal and the EDTA (Allen and Chen, 1993). Enhancing agent can alter the sorption characteristics of metal contaminants and even make remediation more difficult (Yeung et al., 1996).

2.5 Copper and Chromium Chemistry

A review of chromium and copper chemistry was also carried out. It provides a better insight of the mechanisms like adsorption, desorption, precipitation and migration of these chemicals in the presence of an electric field.

2.5.1 Copper in soil

Copper is an essential nutrient for both plants and animals. The natural concentration of copper in terrestrial soil is about 30 mg/kg and is only toxic in high concentrations. Contaminated soil has typically a copper concentration between 50 – 22000 mg/kg (Kjeldsen, Christensen, 1996). Copper contamination of soil originates mainly from wood preservation, metal foundry and manufacturing industries. Table 2.2 shows classification of copper contaminated soil at different pollution levels (Frederiksberg kommune et al., 2001).

<table>
<thead>
<tr>
<th>Level 1 (clean soil)</th>
<th>Level 2 (slightly Polluted)</th>
<th>Level 3 (polluted soil)</th>
<th>Level 4 (very polluted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;500 mg/kg</td>
<td>500&lt; &amp; &lt;750 mg/kg</td>
<td>750 mg/kg</td>
<td>&gt; 750 mg/kg</td>
</tr>
</tbody>
</table>

Copper in the terrestrial environment is mainly found as Cu (I) or Cu (II). Cu (I) is very unstable in water, so Cu (II) is the dominant ion species, as Cu^{2+} (Kjeldsen Christensen, 1996).
2.5.1.1 Sorption of copper

Sorption is a significant process for distribution and retardation of Cu(II) in soil. Sorption of copper is pH dependent and copper is mainly bound to organic matter, oxides and clay (Baker and Senft, 1995): Organic matter > iron/manganese – oxides >> clay particles

In soils with pH higher than 5.5, copper and copper complexes will be specific-sorbed (Baker and Senft, 1995). Thus, the specific-sorbed copper will not contribute to cation exchange processes or be released to the pore water by this process. According to Kjeldsen and Christensen (1996) and Atanassova and Okazaki (1997), the Freundlich or the Langmuir sorption isotherm can describe copper sorption.

2.5.1.2 Desorption

Sorption and desorption of copper in acidic soils has been studied on artificial copper contaminated soils (spiked soils) (Atanassova, 1994, Atanassova and Okazaki, 1997) with an aim of determination of how the copper was distributed between specific and non specific sorption. The desorbed amount of copper corresponds to the nonspecific bound copper. The total desorbed amount of copper varied from soil to soil, but was in the range of 39 – 88% indicating a significant amount of copper to be specific-sorbed to the soil and thus difficult to mobilize. The same experiments on the clay fraction of the soil gave a higher desorption rate, 50 – 95%. The highest desorption rate was observed in clay with low organic matter content indicating strong sorption of copper to organic matter in the soil (Baker and Senft, 1995). The desorption increases with decreasing pH values.

2.5.1.3 Precipitation

Cu (II) will precipitate with oxides, hydroxides and carbonates under aerobic conditions. The most important precipitation reactions are (Kjeldsen and Christensen, 1996):

\[
\begin{align*}
\text{Cu(OH)}_2 & \leftrightarrow \text{Cu}^{2+} + 2\text{OH}^- \\
\text{CuCO}_3 & \leftrightarrow \text{Cu}^{2+} + \text{CO}_3^{2-}
\end{align*}
\]

Clearly, at high pH values, precipitation of Cu (II) will be important.

2.5.1.4 Complexation

Copper forms organic and inorganic complexes with different ligands, especially sulfate, chloride, hydroxide and carbonate. The dominating complexes in natural soil are, (Kjeldsen and Christensen, 1996):

\[
\begin{align*}
\text{Cu}^{2+} + \text{SO}_4^{2-} & \leftrightarrow \text{CuSO}_4 \\
\text{Cu}^{2+} + \text{Cl}^- & \leftrightarrow \text{CuCl}^- \\
\text{Cu}^{2+} + 2\text{OH}^- & \leftrightarrow \text{Cu(OH)}_2
\end{align*}
\]
Cu\(^{2+}\) + 3OH\(^{-}\) ↔ Cu(OH)\(_{3}^{-}\)  \(\text{(2.6)}\)
Cu\(^{2+}\) + 2CO\(_{3}^{-}\) ↔ Cu(CO\(_{3}\))\(_{2}^{-}\)  \(\text{(2.7)}\)
Cu\(^{2+}\) + 3NH\(_{3}\) ↔ Cu(NH\(_{3}\))\(_{2}^{+}\)  \(\text{(2.8)}\)
Cu\(^{2+}\) + 4NH\(_{3}\) ↔ [Cu(NH\(_{3}\))\(_{4}\)]\(^{2+}\)  \(\text{(2.9)}\)

Furthermore, Cu (II) will form complexes with organic matter, and these complexes are characterised by inner-sphere bindings and thus, make this kind of copper immobile. At high pH, complexation of copper will be important for the distribution in the soil (Kjeldsen and Christensen, 1996).

2.5.1.5 Copper in soil solution

The occurrence of copper in natural soil solution is typically between 0.5 – 100 g/l, whereas contaminated soil solutions contain copper concentrations up to 10000 g/l. The distribution of copper in soil solution may typically be 30 - 35% as dissolved Cu\(^{2+}\) ions, 50 – 55% as carbonate complexes and a small fraction of other complexes for a calcareous soil. In contaminated soil solution copper forms complexes and hardly any dissolved Cu\(^{2+}\) ions is present (Kjeldsen and Christensen, 1996).

2.5.2 Chromium in Soil

Chromium, like copper, is an essential nutrient for plants and animals, but when in high concentration, can result in allergic reactions. Hexavalent chromium is classified as carcinogenic. The natural concentration of chromium in terrestrial soils is 1–100 mg/kg and 25–3400 mg/kg in polluted soil. Chromium contaminations of soils originate from combustion of fossil fuels, different metal industries and wood preservation (Kjeldsen and Christensen, 1996). Table 2.3 shows how chromium contaminated soil is classified at different pollution levels (Frederiksberg kommune et al., 2001).

**Table 2.3. Classification of soils polluted with chromium (modified from Frederiksberg kommune et al., 2001).**

<table>
<thead>
<tr>
<th>Level 1</th>
<th>Level 2</th>
<th>Level 3</th>
<th>Level 4</th>
</tr>
</thead>
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<tr>
<td>(clean soil)</td>
<td>(slightly polluted)</td>
<td>(polluted soil)</td>
<td>(very polluted soil)</td>
</tr>
<tr>
<td>&lt; 500 mg/kg</td>
<td>&gt; 750 mg/kg &amp; &gt; 500 mg/kg</td>
<td>750 mg/kg</td>
<td>&gt; 750 mg/kg</td>
</tr>
</tbody>
</table>

Chromium is found in different oxidation states, but the most stable in natural environment are trivalent chromium Cr (III) and hexavalent chromium Cr (VI). Cr (III) forms hydroxide complexes at pH > 4 and occurs as Cr\(^{3+}\) at lower pH. Cr (VI) occurs as HCrO\(_{4}\) at pH 4-6 and as CrO\(_{4}^{2-}\) (chromate) at higher pH values. This makes Cr (VI) more mobile of the two chromium oxidation states. Reduction of Cr (VI) to Cr (III) makes Cr (III) more stable of the two species (Kjeldsen and Christensen, 1996).
2.5.2.1 Sorption

Sorption for Cr (VI) as chromate (CrO$_4^{2-}$) depends on pH, type of clay minerals in the soil and the concentration of the competing anions. Chromate sorbs to hydroxy groups on iron and aluminium oxides in the soil. Since chromate is a negatively charged species, the amount of chromate removed by sorption is low due to the very low number of positively charged sites on the soil particles (Kjeldsen and Christensen, 1996). Tzou et al. (1998) found that chromate sorption was greater in acidic soils than in alkaline soils. Sorption of trivalent chromium can take place, although its behavior is predominantly controlled by precipitation.

2.5.2.2 Desorption

Tzou et al. (1998) investigated chromate desorption in both acidic and alkaline soils. Desorption of chromate is higher in the acidic soils than that in alkaline soils. Desorption increases with longer equilibrium times, however desorption is not in the same order as the sorption. This indicates that most of the chromate will bind more strongly to the soil.

2.5.2.3 Precipitation

Cr(III) will precipitate with hydroxide in natural environment (Kjeldsen and Christensen, 1996): Cr(OH): Cr$^{3+} + 3$OH$^-$, Cr(VI) can also precipitate with cations, but precipitation of Cr(III) is most significant.

2.5.2.4 Complexation

Cr(VI) does not form complexes when it is present as chromate. Cr (III) readily forms complexes with both organic and inorganic ligands. In the environment, complexation with hydroxide is the most significant (Kjeldsen and Christensen, 1996).

\[
\begin{align*}
\text{Cr}^{3+} + \text{OH}^- & \leftrightarrow \text{CrOH}^{2+}, \\
\text{Cr}^{3+} + 2\text{OH}^- & \leftrightarrow \text{Cr(OH)}^+
\end{align*}
\]  

2.5.2.5 Chromium in soil solution

The occurrence of chromium in soil solution is typically between 0.1–10 g/l and the same in contaminated solution is up to 1500 g/l. In soil solution, chromium occurs as chromium–hydroxy complexes (Kjeldsen and Christensen, 1996).

2.6 Modeling the Electrokinetics

Different models are prepared on the decontamination by the electrokinetic remediation. Sheu, et al. developed a finite element model for predicting the ground water contaminant concentration governed by advection and dispersion, taking into accounts the
first order degradation of the contaminant to model the transport phenomenon in ground water. A similar model was developed by Mohamad, et al. to simulate advection, dispersion, and biological reactions of contaminants. Brouyere modeled the migration of contaminants through variably saturated dual porosity, dual permeability chalk.

Javadi and Al-Najjar developed a coupled transient finite element model for simulation of the flow of water and air and contaminant transport in unsaturated soils considering the effects of temperature, air flow, chemical reactions and mobile and immobile water in the soil. Chau developed a prototype expert system for the incorporation of model manipulation for flow and water quality in an expert system shell, to enable integration of numerical modeling techniques for improved decision-making. Hafiz Ahmad et al. developed a mathematical model including the combined effects of electromigration of a copper species, convection due to electroosmosis, diffusion and buoyancy force. Chemical equilibrium expression, sorption of chemical species and hydrolysis reactions are also considered in the model. Analytical and numerical hybrid methods like analytical element method and boundary element method have also been used for modeling of contaminant transport.

Li et al. used a hybrid approach to simulate contaminant transport in the 3D subsurface. Liao, et al. developed a semi-analytical solution for two dimensional equations governing transport of Light Non-Aqueous Phase Liquids (LNAPL) in unconfined aquifers. Mc Dermott et.al, modeled the efficiency of the removal of organic contaminants from water using a micro porous polypropylene hollow fiber membrane module using hybrid numerical and analytical approach. Wang et.al developed another numerical-analytical hybrid model for solving equations describing the transport of contaminants in two dimensional homogeneous porous media. Andrew P. Shapiro developed a 1D model of transport of chemical species in the Lasagna™ process.

2.7 Cost Estimates of Decontamination by Electrokinetic

Schultz(1997) presented a methodology for estimating costs of electrokinetic remediation, which is described here in brief. In general, the total costs for full scale in situ implementation of the technology may have five major components:

(1) Costs for fabrication and installation of electrodes;

\[
N = \frac{F}{L^2}
\]  \hspace{1cm} (2.12)

Where, \(N\) = Number of electrodes per unit area of soil to be treated; \(F\) = Factor depending on electrode configuration = 3 for the given 1D electrode configuration. \(L\) = Spacing between line of anodes and line of cathodes
\[ C_{\text{electrode}} = C_1 \frac{F}{L^2} \]  

(2.13)

Where, \( C_{\text{electrode}} \) = electrode costs per unit volume of soil to be treated; \( C_1 \) = unit costs for material, fabrication, drilling, preparation of borehole and placement of the electrode

(2) **Cost of electric energy;**

\[ C_{\text{energy}} = \frac{C_2 \phi}{3,600,000 \times \beta} \]

(2.14)

Where, \( C_{\text{energy}} \) = electric energy cost per unit volume of soil treated (\$/m\(^3\)); \( C_2 \phi \) = electric energy cost (\$/kWh) and \( \beta \) can be read from the figure below (electrical field strength of 50 V/m),

![Fig 2.4. Relationship between Energy Expenditure and Electrode Spacing (Electric Field Strength=50V/m) (Alshawabkeh; Yeung; Bricka, 1999)](image)

(3) **Cost of enhancement agent if necessary;**

\[ C_{\text{Chemical}} = \frac{C_3}{\zeta} \]

(2.15)

Where, \( C_{\text{Chemical}} \) = Cost of chemical per unit volume of soil to be treated; \( C_3 \) = cost of the chemical per unit volume (\$/m\(^3\)); \( \zeta \) = remediation efficiency of the chemical

(4) **Costs of Any Post Treatment if Necessary;**

If the effluent from the process required post treatment or a small portion of the treated soil needs to be removed due to accumulation of a high concentration of contaminant that can-not be extracted, there will be post treatment costs. These costs are highly site and contaminant specific. They are also dependent on the enhancement agent used in the process. Therefore, they have to be quantified on a case-by-case basis.

(5) **Fixed costs.**

Fixed costs include mobilization and demobilization costs of various equipment, site preparation, security, progress monitoring, insurance, labor, contingency, and miscellaneous
expenses. The total costs per unit volume of soil to be treated are thus given by

\[ C_{\text{total}} = C_{\text{electrode}} + C_{\text{energy}} + C_{\text{chemical}} + C_{\text{post treatment}} + C_{\text{fixed}} \]  \hspace{1cm} (2.16)

The total cost per unit volume of soil as reported by Alshawabkeh; Yeung; Bricka, 1999; is $39.52. The U.S.Army reported the following costs for remediation project of a 1,000 cube yard metal contaminated soil (US Army, 2000). Total capital cost $890.988, Total operation and Maintenance cost $3,02,062. This reveals that the remediation project had total cost of $1,193,050, with a calculated unit cost of $1,193 per cubic yard which is approximately $1,560 per m$^3$. Other authors (Virkutyte et al, 2002) reported $85 per m$^3$ for Lasagna process. The information presented leads to the conclusion that a technology such as Lasagna is the cost efficient. Unfortunately, the process being very much site specific there cannot be a fixed estimated cost.