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DESIGN OF THE SURFACTANT ENHANCED ELECTROKINETIC SYSTEM FOR HYDROCARBONS REMOVAL FROM CLAYEY SOILS IN PILOT SCALE CONDITIONS

By George Hatem

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ABSTRACT

DESIGN OF THE SURFACTANT ENHANCED ELECTROKINETIC SYSTEM FOR HYDROCARBON-REMOVAL FROM CLAYEY SOILS IN PILOT SCALE CONDITIONS

George Hatem

In soils rich with humus, natural organic matter, and clayey fractions, the partition of hydrophobic organic compounds (HOCs) to the solid phase is much higher than to the aqueous phase. This fact can be related to their sorption on organic fraction of soil, and their higher affinity to the clayey material. Cleanup of such contaminated sites using conventional methods such as pump-and-treat or excavation and further thermal destruction can be lengthy, expensive and in some cases ineffective. Generally, a successful remediation process depends on the degree of contaminant desorption from solid to the aqueous phase. HOCs, which due to their properties will not be easily removed and transported within clayey matrix, make several remediation technologies ineffective. Therefore the use of surfactants as agents for apparent solubility enhancement and mobility promotion of HOCs, has been a subject of intensive research (Nash 1986; McDermott 1988; Rajput 1989). Unfortunately, the classical surfactant introduction is limited to highly permeable soils (sandy soils), which leaves clayey soil remediation a matter of concern. The exploration of a technology, which can solve this problem, has been a matter of great interest for the past few years.

Electrokinetics (EK), which is an emerging technology due to its applicability in low permeable soils (clays), seems to be a promising methodology for solving the above mentioned problems. EK is associated with applying a DC current between electrodes

inserted into contaminated soil to promote a movement of species into both perforated electrodes, and further extraction of contaminants through these electrodes. However several works have shown some limitations in its use. Among these limitations, the formation of a basic zone near the cathode, which creates a precipitation area preventing contaminants from reaching the cathode. In addition to this, contaminants attracted by clay particles are less susceptible for electroosmotic transport. Natural clay containing carbonates, amorphous material or organic matter creates a supplementary problem for EK application in full-scale field conditions.

The presented work is a combined effort of developing an improved EK system being able to apply surfactants to HOC-contaminated clayey soils. This work was concentrated on the design, which could be applied in natural conditions and would eliminate the development of a high pH zone in the cathode area, avoid precipitation and decrease the electrolysis of electrodes. The developed electrokinetic system combined with surfactant supply permitted to remove 80 % of phenanthrene in pilot scale conditions through the use of a combination of new designed multifunctional electrodes which can be directly applied in the field to perform electrokinetic remediation of HOCs from clayey soils.

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1. INTRODUCTION

Contamination by hydrophobic organic compounds (HOC) is a major and prevalent source of soil contamination (Mueller et al. 1989). Creosotes, spillage of crude oil substances, diesel fuel, and wood treating processes are among the common sources of soil contamination. For example, in the U. S. over 60% of hazardous materials spilled are oily in nature (Rittman and Johnson 1989), and in Quebec, 69% of the contamination is of organic form. In addition, petroleum products comprise the major portion, followed by polycyclic aromatic hydrocarbons, chlorinated, phenolic, and monocyclic aromatic hydrocarbons (Environment Quebec 1994). Diesel fuel consisting of 60% polyaromatic hydrocarbon (PAHs) is the major component of hydrocarbon-contaminated sites and aquifers, (Block et al. 1991).

1.1. Petroleum Hydrocarbon Compounds

Petroleum Hydrocarbon products are obtained from naturally-occurring reservoirs of crude petroleum. Petroleum products have a vast array of uses; fuel for vehicles and industry, heating oils, lubricants, raw materials in manufacturing petrochemicals, pharmaceuticals and solvents. Almost 65% of petroleum products are used as a fuel, which is stored underground, prior to its use. These underground storage tanks create the major source of contamination. Hydrocarbons (HC) are composed of two elements, hydrogen and carbon, in a vast array of combinations.

I- non-aromatic hydrocarbons (*aliphatic* HC):

The most simple forms are the straight chain HC (alkanes C_nH_{2n+2}) followed by isomeric hydrocarbons which are HCs sharing the same chemical formula but different structural arrangements. The straight chain isomer is called anormal isomer and prefixed with an *n*-, while a branched isomer is called iso (when they have equal branches on each carbon) and prefixed with an *i*-. Branched isomers are an important component of gasoline products because they burn more slowly that straight chain isomers which give them a higher octane rating.

The entire families of straight and/or branched hydrocarbons that are saturated (having no carbon – carbon double bonds) are called *Alkane* or *Paraffins*. This family comprises about 40 to 70% of gasoline products and at least 90 to 100% of all heavier petroleum products.

When carbon forms multiple bonds with other carbon atoms, the resulting compounds are called unsaturated HC or *Alkenes*. These compounds are more toxic than Alkanes and they comprise up to 3% by weight of gasoline products. When a triple bond between carbons exist, the compounds are called *Alkynes*. These compounds are very active and do not occure in nature. Their main use is in petrochemical industry. If both ends of the chain is closed on itself as a circle, the resulting products are called *Cycloalkanes* and *Cycloalkenes*.

II- Aromatic hydrocarbons;

The name of this group derives from the fact that many members have distinctive odors. Compounds belong to this family of HCs bear high toxicity. Benzene is the prototypical compound of this family. If the hydrogen is replaced with other groups of atoms (*alkyles*), the resulting product is called an alkylbenzene. If chlorine was the substitution compound, the resulting products are called chlorinated HCs, recognized as hazardous and persistent compounds (e.g. PCBs). Toluene, ethylbenzene, xylene, are other aromatic compounds, which together with benzene are called BTEX compounds.

III- Polycyclic Aromatic HCs (PAHs):

PAHs are compounds with multiple benzene rings. These compounds can be found in diesel fuel and in the exhaust of gasoline and diesel engines. Some PAHs are known to be carcinogenic to humans and can be very difficult to remediate because of their ability to sorb to soil particles and their resistance to biodegradation.

Typical sites contaminated by hydrocarbons are manufacturing plants, petroleum refineries, fuel and chemical storage facilities, gasoline service stations, and vehicle depots (Long 1993). These compounds are characterized by high molecular weight, low aqueous solubility and hydrophobicity, which, attribute to their strong sorption to soil matrices and slow migration through hydrogeological system, these properties render them as a source of soil and aquifer contamination.

1.2. Scope of the Problem

Hydrocarbon compounds are low soluble compounds with a high molecular weight; persistent in soil and acting as a source of ground water contamination. Table 1 shows the major hydrocarbon compounds, their solubility and octanol-water partition coefficient.

Subsurface hydrocarbon contamination is a multi-phase phenomenon, reflects the nature of the soil as a complex multi-phase medium (Appendix 1). Hydrocarbons behaviour depends on several parameters such as their solubility, octanol-water partition coefficient (K_{ow}), vapour pressure, Henry's constant, molecular weight, and chemical structure. All these factors complicate remediation efforts.

Table 1 Some Hydrocarbon Compounds and their Characteristics

Chemical	Solubility mg/l	Molecular Weight g/mol	Vapour pressure [mm Hg]	Log K_{ow}
Benzo (a) anthracene	2.5×10^{-4}	228.3	2.20E-08	5.91
Benzo (a) pyrene	4.9×10^{-5}	252.32	5.60E-09	6.5
Carbon tetrachloride	800	153.81	9.00E+01	2.83
Chlorobenzene	472	112.56	1.17E+1	2.92
Chloroform	8×10^{-3}	119.37	1.60E+02	1.97
M – Cresol	2780	108.15	1.00E+00 @53°	1.96
Cyclohexane	60	84-18	C	3.44
1, 1 – Dichloroethane	4.962	98.96	-	1.79
1, 2 – Dichloroethane	8426	98.96	1.80E+02	1.47
Ethane	2.4×10^{-3}		6.10E+01	2.06
Ethanol	∞	46.08		- 0.31
Ethyl benzene	152	106.18	7.50E+01	
Methane	6.7×10^{-3}		7.00E+00	
Methylene chloride	1.3×10^{4}	84.93		1.15
Naphthalene	33		3.49E+02	3.36
Phenanthrene	6.2	178.24		4.57
Styrene	515	104.16	9.60E-4 @ 25° C	2.95
Toluene	515	92.15	5.12E+00	2.69
			2.20E+01	

Source: Hemond and Fechner 1994; Lagrega 1994.

On the contrary, the physical nature of the geological formation of the contaminated sites and the limited accessibility, increase the complexicity of the remediation effort. The optimal approach and solution selected for a given contamination problem should be site and problem specific which will define the most cost effective method based on a site and contaminant specific characterization, followed by a feasibility study that answers the following questions:

1- extent of contaminant movement and transformation;

2- effectiveness of various treatment methods;

3- validity of combining more than one technology (hybrid method);

4- *in-situ* or *ex-situ* treatment duration and cost;

5- the impact on the neighbouring environment.

The standard treatment technologies for hydrophobic organic compounds (HOC) contaminated sites have proven to be effective in specific conditions. However, the same methods can be found to be ineffective due to high costs and limited applications in particular site conditions (e.g. clayey soils).

In soils rich with humus, natural organic matter, and clay soils (Appendix 1), the presence of HOC in the solid phase is much higher than in the aqueous phase. This fact can be related to their sorption on humus and organic fractions of the soil, and their higher affinity to the clay. Remediation of such contaminated sites using conventional methods like pump and treat or excavation and incineration can be lengthy, expensive and in some cases ineffective. The remediation process often depends on desorption of the contaminant from the soil surface and its subsequent incorporation into the bulk aqueous phase. Therefore, aqueous phase remediation should be accomplished through engineered technologies.

Due to their above-mentioned properties, HOCs are not easily transported form the solid phase to the aqueous phase, thereby rendering them unaffected by conventional treatment methods.

The use of conditioning liquids (e.g. surfactants) as agents for apparent solubility and mobility enhancement of (HOC) has been a subject of intensive research (Nash 1986; McDermott 1988; Rajput 1989). As stated previously, if the contaminated site consists of a high fraction of clay materials, the uniform introduction of conditioning liquids presents a challenge. Due to the physio-chemical properties of clay (Appendix 1) commonly used methods for surfactant applications cannot be applied. Therefore, electrokinetics (EK) methods could only be tested with an anticipation of success.

Electrokinetics is an emerging technology, which due to its applicability in low permeable soils seems to be promising. EK is associated with applying a direct and/or alternative current between electrodes inserted into a contaminated area to promote a movement of species into electrodes. However several works (Acar et al. 1996; Elektorowicz et al. 1996) revealed some limitations in its use. Among these limitations are the formation of a basic zone near the cathode, which creates a precipitation area. In addition, the contaminants that are attracted to clay particles are less susceptible to electroosmotic transport. These facts provide the need for improvement to EK technology.

Considering the above-mentioned facts, it is necessary to develop a new sustainable remediation method for PAH removal from clayey soil. Consequently, research on an EK system has to be performed in order to recognize the dependence of the electrokinetic process on particulate elements of the system. Methods of sustainable development have to be used in order to permit the newly developed EK system to be applied successfully in situ. Particular attention has to be paid to the design, which will alleviate the extreme pH zones without using chemical products. On the other hand, extensive research has to be carried out for electrokinetic transport of conditioning liquids, especially surfactants. In addition, the efficiency of the method in comparison to other available technologies must be performend. Consequently, the literature review has to include several issues such as clayey soil behavior, PAH-soil interactions, surfactant characteristics and applications and principles of electrokinetics.

2. SOIL CONTAMINANT INTERACTION

2.1. Impact of Soil Phases on Contaminant Processes in Soil

Soil is a complex medium with regards to its structure, properties, and behaviour. Soil constituents and their properties have a significant influence on the fate of contaminants and on remediation processes. Secondary minerals and organic materials present in soil have the largest influence on contaminant fate, which is the major issue in any remediation action, due to their ability to exchange cationic contaminants (i.e. heavy metals) and the adsorption of organic pollutants. Therefore, for a better understanding of contaminant fate, a review of subsurface constituents is presented in Appendix 1.

In Quebec, illite can be found in abundant amounts within the clayey portion of the natural soil. Therefore, research should be connected to sites containing an important fraction of illite. This clay material is described below in order to emphasis its role in the fate of contaminants. Other clay materials are described in Appendix 1.

2.1.1. Illite

Due to the differences between clay minerals such as cation exchange capacity (CEC), specific surface area (SSA) and structure, they bear different relevance to the sorption of contaminants. For example, expanding clays such as montmorillonite would be a perfect liner for contaminated sites, because of its high CEC, which increase its ability to attract organic and inorganic compounds. This attraction is the result of cumulated Van der Wall forces, which attract organic compounds (Rao and Yong 1991). Meanwhile its decontamination would be a challenge. Kaolinite clays, because of their tight structure can adsorb organic molecules only on the surface of their structure. Therefore, decontamination of such minerals is easier than the former group. The properties of illite minerals are situated between kaolinite and montmorillionite.

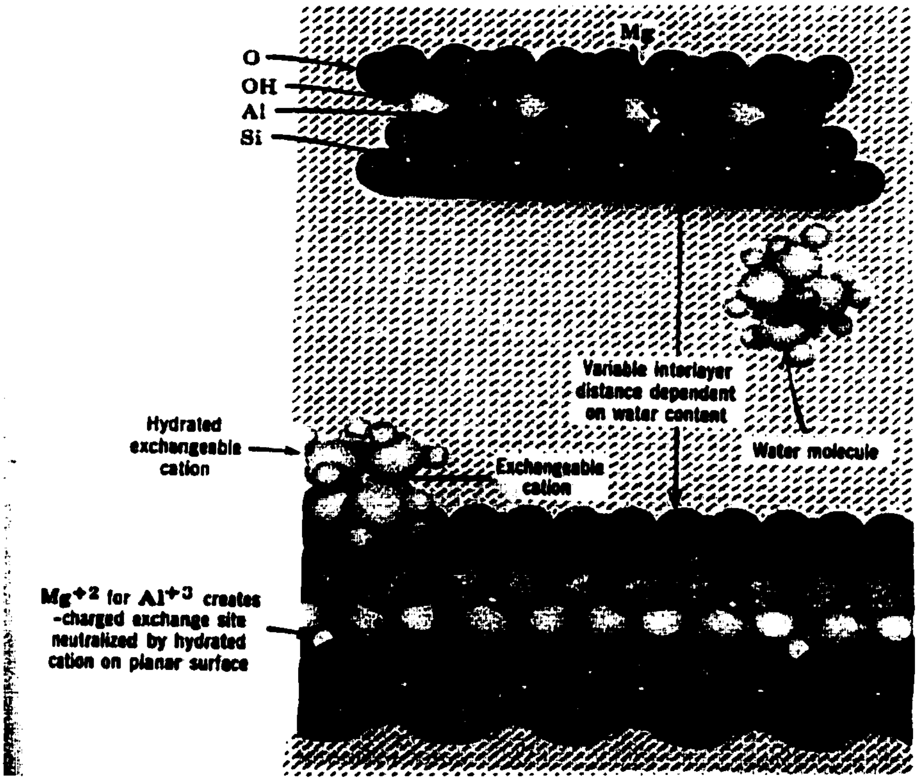
This group of illite minerals is identified as colloid-sized particles. They have repeated layers of alumina sheets between two silica sheets (2:1, silica to alumina) with sufficient interlayer K^+ to limit expansion on wetting. Illite belongs to the mica group of secondary minerals, however the K^+ content of illite is less than that of micas (Foth 1984). It is believed that illite formation takes place in potassium rich sediments subjected to low-temperature metamorphism. In addition to K^+, these sediments also contain expanding clays such as vermiculite or montmorillonite (Appendix 1). The process of illite formation is initiated as K^+ replaces some of the interlayer cations in the vermiculitic and montmorillonitic clays, and is completed when heat and pressure causes the dehydration and collapse of these clays into a less-expanded forms (Foth 1984).

The general formula for micas is $K_2(Si_6Al_2)Al_4O_{20}(OH)_4$, which indicates that two aluminum atoms have replaced two silicon atoms in the tetrahedral sheet. This replacement is known as isomorphous substitution, and it leaves two residual negative charges, which are balanced by K^+ ions that fit between two adjacent layers. The potassium acts as a bridge, which holds the adjacent layers together firmly.

The loss of the interlayer potassium results in a partial loss of bonding between layers, however these layers do not expand or separate and the vertical spacing between them remain the same. A loss of interlayer potassium will create negatively charged structures, which are satisfied by the adsorption of hydrated cations such as calcium, magnesium or hydrogen. This altered mineral is called hydrous mica. Figure 1 illustrates 2:1 clay mineral hydrous mica (illite). This figure shows: (1) some tetrahedral Al^{+3} substituted for Si^{+4}, which create a negatively charged lattice, (2) potassium bridges that neutralize most of the lattice charge and hold the layers together to form non-expanding lattice, and (3) adsorption of hydrated cations on an exchange site created by aluminum substitution.

Continued leaching and complete removal of interlayer potassium allows the layers to separate or expand. The complete loss of potassium results in an expansion of the structure and a high CEC. The SSA for illite is 80 m^2/g and its CEC is 25 cmol/kg.

In addition to illite, natural clayey soils can have a certain fraction of oxides, hydrous oxides, carbonates and sulphates (see Appendix 1).



(Source:Fouth 1984, Fundamentals of Soil Science)

Figure 1 Model of Mineral Hydrous Mica

2.2. The Effects of Organic Soil Constituents on the Fate and the Transport of Contaminants

Soil organic matter plays a significant role in the fate of organic and inorganic soil contaminants because their pH dependent charge, which can affect the state and existence of contaminants in the subsoil.

Soil organic matter is a mixture of nonhumic and humic substances (Appendix 1). The ability of humic substances to interact with hydrophobic organic compounds (HOC) is due primarily to their high content of O-containing functional groups, including -COOH; phenolic-; aliphatic-; and enolic-OH; and C=O structures of varying types. The interaction affects the mobility and leaching of organic contaminants (hydrocarbons) not only negatively by adsorption, but also positively by creating a higher aggregate stability. Furthermore organic matter has a positive effect on hydrocarbon mobility and leaching by the formation of water-soluble adducts between poorly water-soluble hydrocarbons and readily water-soluble humic substances (Takimoto et al. 1998).

Under natural conditions, soil humic substances (see Appendix 1) interact strongly with the mineral fractions such as aluminosilicate clays, and hydrous Fe and Al oxides. Since organic matter interacts with and coats clay surfaces, essentially blocking potential adsorption sites, the competition between clay surfaces and organic coatings for hydrophobic organic compound (HOC) adsorption in the neutral system becomes an important consideration (Browman and Chesters 1977).

Contribution of clay content to adsorption was evidenced mainly at soil organic carbon contents below 5 %. In soils with an organic carbon content exceeding 5 to 8 % only organic surfaces appear to be available in bonding (Browman and Chesters 1977). The results obtained by Li and Bowman (1998) confirmed the notion that the structures of natural organic matter as well as its quantity, controls the sorption of nonpolar organics to soils and sediments. Their results showed that the sorption of perchloroethylene (PCE) by surfactant modified zeolite was proportional to the fraction of organic carbon content.

2.2.1. The Effects on Organic Pollutants

The fate of organic pollutants in the soil and subsoil are affected by the presence of soil constituents, where processes such as adsorption, partitioning, solubilization, hydrolytic degradation, and photo-decomposition will affect to a greater or lesser degree, their fate (Senesi and Miano 1995). These reactions can lead to intermediate products having different properties than the parent compounds with respect to their migration in soil.

The adsorption process between organic pollutants and soil organic matter has been a focal point of several researchers. Petruzzelli and Helfferich (1993) showed that the adsorption of organic compounds to the soil was via specific mechanisms with different strengths. These mechanisms include: 1) ionic bonding, 2) hydrogen and covalent bonding, 3) electron donor or acceptor mechanism, 4) cation bridge, 5) Van der Waals forces, and 6) water bridging.

The adsorption processes may vary from completely reversible to totally irreversible processes and can occur on insoluble immobile organic fractions such as humic acids (HA), or on dissolved or suspended mobile fractions such as fulvic acids (FA) (Appendix A). Therefore soil organic matter in the form of HA or FA, can facilitate or attenuate the transport of organic pollutants being adsorbed to a dissolved fraction of organic matter or to an immobile organic matter fraction (Senesi 1995). Kakimoto et al., (1998) showed that the organic coating on alumina and kaolin soil, in the form of HA, will facilitate the absorption of TCP (three tricrestyle phosphate) onto soil. They showed that the amount of adsorbed TCP was constant between pH 4 and 9. Carter and Suffet (1982) showed that the concentration of dissolved humic substances, soil solution, temperature and pH will effect the magnitude of pollutant solubility enhancement. Humic substances (HS)such as a soluble part are regarded as a "microscopic organic phase" similar to a micelle, therefore their surface activity is an important property that promotes interactions especially with hydrophobic organic pollutants. They act as a surfactant in enhancing their solubility (Chiou et al., 1986). Wershaw et al., (1969) reported that at a given concentration of a dissolved HS, relatively insoluble nonionic pollutants are most easily solubilized. Kile and Chiou (1989) related the solubility increase to the pollutant adsorption or partitioning, or an overall increase in solvency. Comparing the solubility enhancement of compounds with different water solubility, Boehm and Quinn (1973) observed that the solubility enhancement decreased with increasing intrinsic water solubility of the pollutant.

In a laboratory study Lesage et al. (1994) showed that the dissolution enhancement of PAHs could be achieved using humic acid as a surfactant. Their studies concluded that by increasing the concentration of humic acid in soil by 20 fold, a 3-fold increase in apparent solubility of phenanthrene could be achieved. This solubility enhancement decreases by increasing the pH and ionic strength of the soil. The tests conducted on BTEX compounds showed that the more soluble the compounds, the less solubility enhancement occurs.

Although humic and fulvic acids are different in size and conformation, their behaviour can be attributed to their flexible and sponge-like structure which may trap and even fix organic pollutants (Shnitzer, 1978). This is related to the presence of carboxylic (COOH) and phenolic (OH) groups in humic and fulvic fractions of humus. These groups are regarded as a source of pH dependent negative charge HS. The negative charge is formed by the dissociation of a carboxylic group (COOH) which can yield $-COO^- + H^+$, and a phenolic group. The dissociation of the former group takes place in a pH range of 4.5 to 7, while the dissociation of the (OH) group takes place at higher pH. Carboxyl groups account for 50% of the CEC of soil organic matter at pH 7. Another 30% of the organic matter CEC at pH 7 can be divided between quinonic hydroxyls, phenolic hydroxyls, and enolic hydroxyls. Heterocyclic nitrogen structures may contribute up to 10% of the organic matter CEC at pH 7 (Sparks 1986).

2.2.2. The Effects on Inorganic Contaminants

Humus and in particular humic acid can also interact with metal ions, metal oxides, and metal hydroxides present in soil forming complexes of different solubility and chemical and biological stabilities related strongly to pH. Kendorff and Schnitzer (1980) examined the interaction of humic acid with a solution containing equimolar concentration of 11 different ions. Their results showed that with rising pH and HA concentrations there is an increase in sorption efficiency on HA. However this efficiency decrease with increasing metal concentration.

At pH 2.4, the order of sorption is

$$Hg > Fe > Pb > Cu = Al > Ni > Cr = Zn = Cd = Co = Mn$$

At pH 3.7, the order is

$$Hg > Fe > Al > Pb > Cu > Cr > Cd = Zn = Ni = Co = Mn$$

At pH 4.7 the order is

$$Hg = Fe = Pb = Cu = Al = Cr > Cd > Ni = Zn > Co > Mn$$

At pH 5.8, the order is

$$Hg = Fe = Pb = Al = Cr = Cu > Cd > Zn > Ni > Co > Mn$$

2.3. The Effects of Contaminants Characteristics on their Fate

The effects of soil constituent on the fate of contaminants have been clarified in previous sections. However, an important role in the fate of these contaminants is governed by physical and chemical characteristics of the contaminants. Among these characteristics are:

I- Ionic character - Non-ionized substances are highly mobile in soils since they are not adsorbed to soil particles. This includes most chlorinated hydrocarbons, however, a reasonable solubility in water is the only condition for their mobility. Because soil colloids are negatively charged, substances of cationic character are immobilized if their concentration is below the cation exchange capacity of the soil. Acid substances are slightly adsorbed due to their negative charge. Their adsorption is mainly by the organic components of the soil and to a lesser extent, by hydrous oxides of iron and aluminium (Browman and Chesters 1977).

II- Solubility in water - Substances with a solubility in the order of 1 mg/L are considered to be of low solubility and therefore slightly mobile, although they could have a non-ionic character. From the standpoint of their mobility, substances whose concentration in aqueous solution exceeds 500 mg/L can be considered soluble and mobile. However, it should be noted that comparison should be restricted to chemicals with the same properties, e.g., substances with the same ionic character (Yong et al. 1992; Hemond and Fechner 1994).

III- Polarity - In general, polar substances are more strongly bound to soil than non-polar substances.

IV- Volatility - Volatility could be correlated with the substance's mobility in the medium. Volatile substances are mobile in the soil medium in their gaseous form. Substances with vapour tension below 0.9678×10^{-5} N/cm^2 at 25°C are considered non-volatile, between 0.9678×10^{-2} and 0.9678×10^{-4} N/cm^2 intermediate and above 0.9678×10^{-2} strongly volatile (Cole 1994).

2.4. The Source and the Character of Electrical Charges on Soil

2.4.1. Origin and Type of Surface Charge in Soils

I- Isomorphic Substitution: structural imperfections due to ion substitution or site vacancies, frequently result in a permanent charge on soil particles. In theory, this charge can be positive or negative (Fripiat 1964). The substitution is restricted to a lower valance element with one with a higher valency (e.g. Al^{3+} for Si^{4+} and Mg^{2+} or Fe^{2+} for Al^{3+}). This situation leads to a deficiency of positive charge on the crystal lattice (Zelanzy 1982; Johanson and Dunning 1959) and the resulting charge is generally negative on the clay structure (Tan 1982).

II- Ionic Dissolution - dissociation of surface sites or the adsorption of hydrogen or hydroxyl ions can result in a negative or positive charge on the surface (Kalb and Curry 1969). This is viewed as chemi-sorption of H_2O to form a hydroxylated surface. The sign and the magnitude of the surface charge is related to the adsorbed ions onto the hydroxylated surface. Many minerals in soil bear this type of charge, e.g., oxides and/or hydroxides of Al, Fe, Mn, Si, Ti. kaolinite and because of it broken edges,reflects similar source of charge.

III- Ionization - this source of charge is related mainly to the organic fraction of soil. It is the process by which a colloid acquires its charge either by dissociation of H^+ from or onto the active functional group. The generated charge is dependent on the dissociation constant of the functional group and the pH, it could be positive or negative.

$$R-COOH \Leftrightarrow R \bullet COO^- + H^+$$

$$R-NH_2 + H_2O \Leftrightarrow R \bullet NH_3^+ + OH^-$$

Charged sites in soils can bear two types of charge, permanent charge and variable pH dependent charge. The permanent charge is the historically recognized charge type, which arises from the cationic substitution in the inorganic fraction of soil. This type of charge is dependent on the absolute concentration of the mineral. On the other hand, variable charge arises from surface reactions and is dependent on factors such as pH and solvent character. The organic fraction of soil is the most important source of variable charges (Sparks 1986). Clay minerals with a 2:1 structure (illite, smectite, vermiculite) have permanent charge.

Other clay minerals and hydrous oxides of iron and aluminum and humic acid, have a pH dependent charge which increases as pH increases. Table 2 presents the charge type for various soil components and Table 3 summarises the sources of electrical charge on clay soils and humus.

Table 2 Surface Charge Type of Various Soil Components

Kaolinite	Illite	Smectites	Vermiculite	Fe & Al oxides	Allophane	Humic acid
pH Dependent	Permanent	Permanent	Permanent	pH Dependent	pH Dependent	pH Dependent

Source: Wild 1993,

Negative charges are balanced by the adsorption of cations. These cations can be either adsorbed and held in interlayer spaces, which make them practically non-exchangeable, or can be held on the edges of the particles surface, where their access to the outer solution is easier (exchangeable cations).

Anions can be adsorbed by two mechanisms:

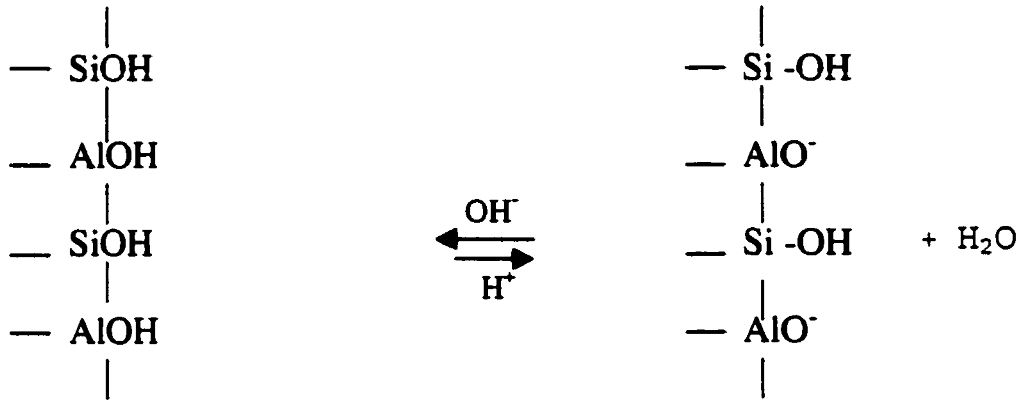
1- At low pH, positive charges can be developed on the surface of hydrated oxides of iron and aluminium and 1:1 clay minerals (Table 2), therefore, Cl^-, and NO_3^- are adsorbed. Adsorption is, however, blocked by competition from organic anions originated from organic matter.

Table 3 Sources of Electrical Charge on Soil Clays and Humus

1- Permanent negative charge on 2:1 and 2:2 clay minerals due to isomorphous substitution.

2- pH dependent charges:

(a) negative charges at broken surfaces and edges of clay minerals



(b) negative charges on humus due to dissociation of carboxyl and phenolic hydroxyl groups

$$-COOH \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} -COO^- + H_2O$$

$$>COH \underset{H_+}{\overset{OH^-}{\rightleftharpoons}} >CO^- + H_2O$$

(c) negative and positive charges on hydrous oxides of iron and aluminium

$$>FeOH \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} >FeO^- + H_2O$$

$$>FeOH_2^+ \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} >FeOH + H_2O$$

Source: Wild. A, Soils and the Environment, 1993.

2- Another mechanism is called "ligand exchange" where anions and metals (Fe, Al) in hydrated oxides or clay minerals form a surface complex.

$$- Fe - OH_2^+ + H_2PO_4^- \rightarrow - Fe - O - PO_3H_2^0 + H_2O;$$

$$- Fe - OH_2^+ + HPO_4^{2-} \rightarrow - Fe - O - PO_3H^- + H_2O;$$

The negative charge on the soil surface is increased as a consequence of these reactions (Wild 1993).

2.5. Contaminant Fate in the Subsurface

When a contaminant is introduced into the subsurface (i.e. chemical spill, hydrocarbons from gasoline stations), it is transported to other locations in the soil, by pore water (liquid phase) through advection, dispersion, diffusion, and suction in the vadose zone. Depending on the permeability of the soil some transport mechanisms can prevail. Clayey soils have low permeability and therefore molecular diffusion is the typical transport mechanism.

Organic and inorganic chemicals being transported through the subsurface are influenced by this complex medium, particularly by the constituents of the phase(s) in which they are present. As a result they undergo two main processes: 1) Transformation and 2) Transport. Consequently there are sub-processes, which organic chemicals can undergo:

- Adsorption, accumulation, decomposition of organic chemicals by plants, animals and microorganisms and its participation in the food chain;
- Adsorption to soil particles;

- Volatilization;
- Infiltration
- Gravity transport within the soil medium;
- Suction phenomena.

Therefore the total fate of chemical pollutants is a combined process where complex physico-chemical and biological reactions - eg. physico-sorption, chemico-sorption, precipitation and or complexation processes, degradation, and hydrolysis- are take place within the distinct phase(s) and the phases interface. This results in the accumulation of parent contaminants by the soil and generation of by-products which can be more toxic than the parent compound. These processes are governed by the properties of the soil constituents and chemical characteristics of the contaminants.

Precipitation can affect mostly inorganic contaminants and it takes place when the ionic activity of the solute exceeds the solubility product. The presence of anions such as carbonate, phosphate, silicate, hydroxide, or sulphide (soils can have a certain fraction of those anions) may lead to precipitation especially of multivalent cations as insoluble compounds. Dilution or a change in redox potential may return precipitated compounds to solution. Precipitation can occur on the surface of the solids, or in the case of high solute concentration, can occur in pore water.

Complexation occurs when a central metallic cation is coordinated to two or more inorganic or organic groups by coordinate covalent bonds. Sorption is the change in concentration of chemical in solid phase as a result of mass transfer between the liquid phase and the solid phase. It is the process in which the solutes (ions, molecules, and compounds) are partitioned between the liquid and the solid interface. Sorption processes can be recognized as adsorption, which is the adherence of the chemical to the solid surface, and as an absorption, which is when the chemical is taken up into the solid. Hydrophobic Organic compounds (HOC) may be adsorbed by soil organic matter as well as by inorganic soil fractions. The relation between the adsorption at both sites depends on soil properties as well as structure of the HOCs (Browman and Chesters 1977).

Secondary minerals, amorphous materials and organic matter (Appendix 1) have the largest influence on contaminant fate, which is the major issue in any remediation action, due to their ability to exchange ionic inorganic contaminants and the adsorption of organic pollutants. Therefore, particular attention should be focused on soil processes in order to design a cost-effective and reliable method of treatment.

3. CONVENTIONAL SOIL REMEDIATION METHODS

Treatment technologies can be generally classified into two major groups, 1- *in situ*, where remediation application are carried out without soil disturbance, when site characteristics or existing regulations prevent any excavation. 2- *ex-situ*, where contaminated soil is excavated and treated on site, off site or disposed in landfills (without treatment). This method is often used when immediate action is needed to remove the contaminants from the site. Both methods have advantages and disadvantages and site-specific costs, and regulations will dictate their applicability. Another classification of remediation methods is based on the procedure used in treatment whether it is physical, biological, thermal, or chemical treatment.

3.1. *Ex-situ* processes

As stated above, this method is a common approach when there is immediate and urgent need for decontamination. This technique can release of contaminant vapours, and addition excavation does not eliminate the problem, therefore, there is an additional need for remediation or disposal of contaminants.

3.1.1. Physical/Chemical Processes

1- Thermal Treatment: thermal desorption is an innovative, non-incineration technology for treating soils contaminated with organic compounds (Fox et al., 1991). It is proven for treating non-hazardous wastes and can be used for treating petroleum-contaminated soils. This process involves the use of inert gas heated to a temperature lower than the temperature used in incineration (450 – 600^0C), in orser to increase the vapour pressure of organic contaminants and transfer them from the solid or liquid phase to the gaseous phase. It can be used for volatile organic compounds, semivolatiles, PCBs, and arsenic contaminated soils.

2- Incineration: is one of the most effective treatments available for high molecular weight chlorinated hydrocarbons and PCBs. It is a controlled combustion using high temperature (>1800 °C), for complete contaminant mineralization (99.9999%). Due to its high cost, it should not be considered for treating petroleum hydrocarbon-contaminated soils.

3- Soil Washing: although this method is used *in-situ* as well as *ex-situ*, it has proven to be more effective as an *ex-situ* method. It overcomes problems associated with the in-situ process (low hydraulic conductivity, channelling, and contamination of underlying aquifers). It removes water-soluble contaminants from soil by dissolving them in solvents. However, tightly bound contaminants are difficult to remove by washing (Roberts 1998). Soil washing is a very complex process. Figure 2 illustrates a flow sheet of a soil washing system. The excavated soil is screened and treated with solvents to dissolve the contaminants. Clean soil is separated from solvent via combination of decanters, driers, filters, etc., Solvents can be recycled after contaminant removal. To help mobilize contaminants, organic and aqueous agents can be used (Roberts 1998). Surfactants can also be used to treat the soil (Acar et al. 1993; Abdul and Gibson 1991; Elektorowicz et al. 1995).

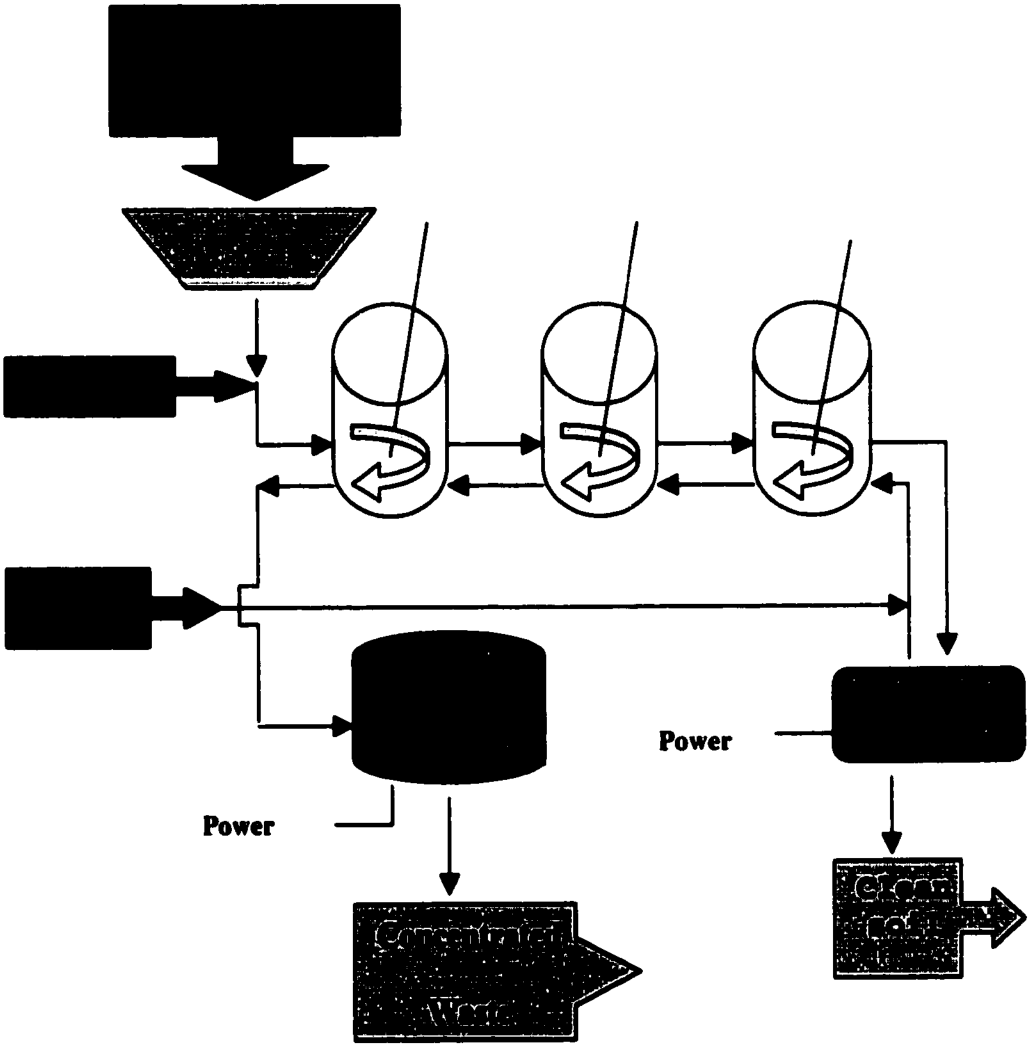


Figure 2 Flow sheet of a soil washing system

4- Chemical Treatment: in this method soil is treated with peroxide (Ram et al., 1993), or alkaline solutions of pH: 10.5 (Hupka and Wawrzacz 1996), to release the contaminants. After their release, contaminant destruction can be achieved by indirect electro-oxidation (Leffrange et al. 1995).

5- Chemical Extraction: solvent extraction has been used to treat PAHs (Weisman et al. 1994). Excavated soil is treated through heap leaching and liquid/solid contractors (Ram et al. 1993).

6- Supercritical Fluid Oxidation: Supercritical water oxidation is fast and can lead to total oxidation of the organic compounds (Roberts 1998). Supercritical water is an excellent solvent for extraction of mineral oil fractions from soil, and the resulting effluents are biologically degradable. Treated soils can have residual HC contamination of less than 200 ppm and the gas stream is rich in CO_2 and water.

7- Supercritical Fluid Extraction: it is a relatively new technique which uses fluid CO_2 to remediate contaminated soil (Elektorowicz and Ju 1997). The extraction is limited by adsorption, therefore addition of water will facilitate the process (Zytner et all. 1995).

8- Volatilization: this process includes mechanical volatilization (excavation), enclosed mechanical aeration (rotary drums), pneumatic conveyer systems temperature and high velocity air flow), and low temperature thermal stripping (Ram et al. 1993; Layman et al. 1990).

9- Steam Extraction: this method is still in a laboratory scale test phase. However it proved to be efficient in PAHs, solvents and diesel fuel removal (Hudel et al. 1995).

10- Solidification/ Stabilization: this approach incorporates chemical or biological stabilization processes to treat excavated contaminated soil (Ram et al. 1993). The binding agent used in this method is carbon-grade fly ash. However new agents are in development such as activated carbon, organo-clay, and proprietary rubber particulates.

11- Encapsulation: micro-encapsulation of HC involves the use of two water-based products, an emulsifier, which is specifically selected for different HCs and soil type, and a reactive silicate. The first stage dissolves and emulsifies the hydrocarbons, while the second applies the reactive silicate, which reacts with the emulsifier to form non-soluble solid silica cell (Roberts 1998).

3.1.2. Biological processes

1- Landtreatment/Land farming: it involves the controlled application of wastes to soil for degradation or transformation by the resident microorganisms. This process is viewed as a double function process, which involves disposal and treatment of contaminated soils. However, the process maintenance is intensive, since one has to avoid the accumulation of contaminants to toxic levels, a production of undesirable degradation products, and uncontrolled runoff or leach through the soil. (Arora et al. 1982). This method has been practiced worldwide for over 100 years and by the petroleum industry for more than 25 years. A detailed review of this technology is provided by Roberts (1998).

2- Composting: this process allows for biological decomposition of organic material under controlled conditions. The process involves the activity of a succession of mesophilic and thermophilic microorganisms (Wilson and Jones 1993). The soil is piled and mixed with an organic bulking agent, such as straw or wood chips.

The success rate is predicated on aeration, pH, moisture, and nutrient level control.

3- Bioreactors: bioreactors are used to contain the treated soil. Soil containment can permit control of sensitive and important factors such as temperature, pH, nutrients, oxygen, and microorganisms. There are several types of bioreactors among them- Bioslurry Reactors; Dual Injected Turbulent Suspension Reactor; Gravel Slurry Reactors; Tubular Reactors; Blade-Mixing Reactors; Prepared Bed Reactors; Enclosed Reactors; Fermenters; Fungal Compost Bioreactors; Combination Reactors; Pressure Reactors; and Wafer Reactors. A detailed review can be found in Roberts (1998).

4- Biopiles: the treated soil is placed in mounds resembling large compost heaps and covered to prevent the uncontrolled emission of vapours. For aeration purposes, periodical soil turning is necessary.

5- Vacuum Heap Biostimulation System: this system employs natural decontamination processes utilizing bio-stimulation of natural, contaminant adapted microorganisms (Eiermann and Bolliger 1995).

6- Vegetation: Vegetation can enhance the rate and extent of degradation of PAHs in contaminated soil (Santharam et al., 1994). It has been established that the population of microorganisms in the rhizosphere is significantly greater than that in the non-vegetated soil.

7- Photolysis: Wilson and Jones (1993) reported that the use of photolysis can render PAHs more susceptible to microbial attack.

3.2. *In-Situ* Processes

Some of the methods applied ex-situ can also be adapted for use in-situ. The following is a short review of these methods according to their classification.

3.2.1. Physical/Chemical Processes

1- Shallow soil mixing: it involves mixing cement or bentonite, or other reagentsin order to modify properties and thereby remediate contaminated soils (Roberts 1998). This method can be combined with soil vapour extraction (SVE) for extracting volatile organic compounds (VOC) from soils (Johns and Nyer 1996).

2- Oxidation/Reduction: when hydrocarbons exist in high concentration thereby creating that create a toxic environment for bacteria, in situ chemical oxidation can be used to oxidize hydrocarbons using air, hypochlorites, ozone, and peroxide (Roberts 1998). The soil must have a sufficient permeability to allow the air or peroxide solution to reach the contaminants and reaction products to move out.

3- Hydrolysis: is a chemical reaction involving cleavage of a molecular bond by reaction with water (Amdurer et al. 1985). The rate of hydrolysis can be accelerated by raising the pH of the solutions (base-catalysed hydrolysis). For shallow contamination, surface application of lime, sodium carbonate, or sodium hydroxide followed by surface application of water may be appropriate. For deeper deposits, subsurface delivery or injection of alkaline solutions may be required (Roberts 1998).

4- Neutralization: Is a pre-treatment process that involves injecting dilute acids or bases into the ground water to adjust the pH.

5- Stabilization/Solidification: same as in *Ex-Situ* treatment.

6- Mobilization: It includes the addition of surfactants for contaminant mobilization (for a wider review, see chapter 5).

7- Soil flushing/ Washing/ Pump and treat/ Extraction: soil flushing is an extraction process to remove contaminants from soil. An aqueous solution is injected to the contaminated area and the flushing solution is later pumped to the surface for further treatment. Soil flushing methods remove contaminants by dissolving and/or by mobilizing them. Extraction methods use extraction agent mixed with the contaminated soil to dissolve or disperse the contaminants from the soil into the extracting agent, which is further pumped, cleaned and reused.

8- CROW Process: The Contained Recovery of Oily Wastes process is used to recover Dense, Non-Aqueous-Phase Liquids (DNAPLs) (Johnson and Leuschner 1992). It uses hot water displacement to isolate the contaminants. The oily material floating with the water is displaced to production wells by sweeping the subsurface with hot water.

9- Injection-extraction process: it is an improved soil washing process where contaminated zone is isolated, and nontoxic biodegradable surfactants are injected from the injection network and pumped out through specially designed wells (Ross et al., 1995).

10- Air Stripping: this process involves the transfer of volatile hydrocarbon compounds from water into the air within specially designed structures called "packed towers". The air stream leaving the tower is treated further to comply with air emission regulations. Further gas treatment can use such technologies as carbon adsorption, or catalytic incineration. The problems related to this method are that its frequent scaling due to the build up of insoluble metal salts, suspended solids, or biological growth on the packing media (Long 1993).

11- Soil Vapour Extraction: it employs a blower or vacuum pump connected to small diameter vertical wells or lateral trenches to reduce the vapour pressure in the soil and increase the volatilization of contaminants (Burke and Rhodes 1995).

12- Air Sparging: this process is used in conjunction with a vapour extraction system. It employs injection of air below the water table so the volatile components are transferred to the unsaturated zone where they can be removed by a vapour recovery system (Roberts 1998).

13- Detoxifier™: it is an innovative process involving the adaptation of drilling technology for delivery of treatment agents in dry, liquid, slurry, or gaseous form to the soil. The treated agents can be ambient or heated air or aqueous solutions containing surfactants and oxidizing agents (Roberts 1998).

14- Soil Heating: this process uses heat to increase the vapour pressure of contaminants. Heat may be applied by: a- hot air injection; b- steam injection; c- radio frequency heating (Ram et al., 1993).

15- Vitrification: it is a soil-melting technology. It uses electric current passed between electrodes, to heat the soil to high temperatures (1500 – 2000^{0}C). The soil and contained material are converted to a stable glass. Organic contaminants and natural organic compounds are volatilized and removed through vapour extraction (Johns and Nyer 1996).

16- Tensiometric Barriers: it is called a dry barrier, and it is produced by injecting dry air into an unsaturated formation to reduce the soil moisture content (Tomson et al., 1996). Reducing soil moisture can reduce hydraulic conditions of the unsaturated media to a point where liquid-phase transport becomes negligible.

17- Hydraulic/Pneumatic Fracturing: this method is not a remediation method by itself, however it is adapted in combination with other methods when the soil has a low coefficient of permeability, to provide fractures to the soil in order to improve the flow of fluids or gases (Kidd 1996). Hydraulic fracturing is accomplished by injecting high pressure water into the soil followed by injection of fracturing fluid which breaks down to leave the fractures permeable. Pneumatic fracturing is accomplished by applying high-pressure air, which produce pneumatic fracturing.

18- Active Barriers: these kind of barriers use ultramicrobacteria which can penetrate the pores of a soil, initially developing a weak adhesion to the particle surfaces. Subsequent nutrient stimulation then results in a formation of a bio-film, which is generated by further cell growth and production of exopolymers. The bio-film develop a strong surface adhesion and result in clogging of the soil pores spaces (Turner)

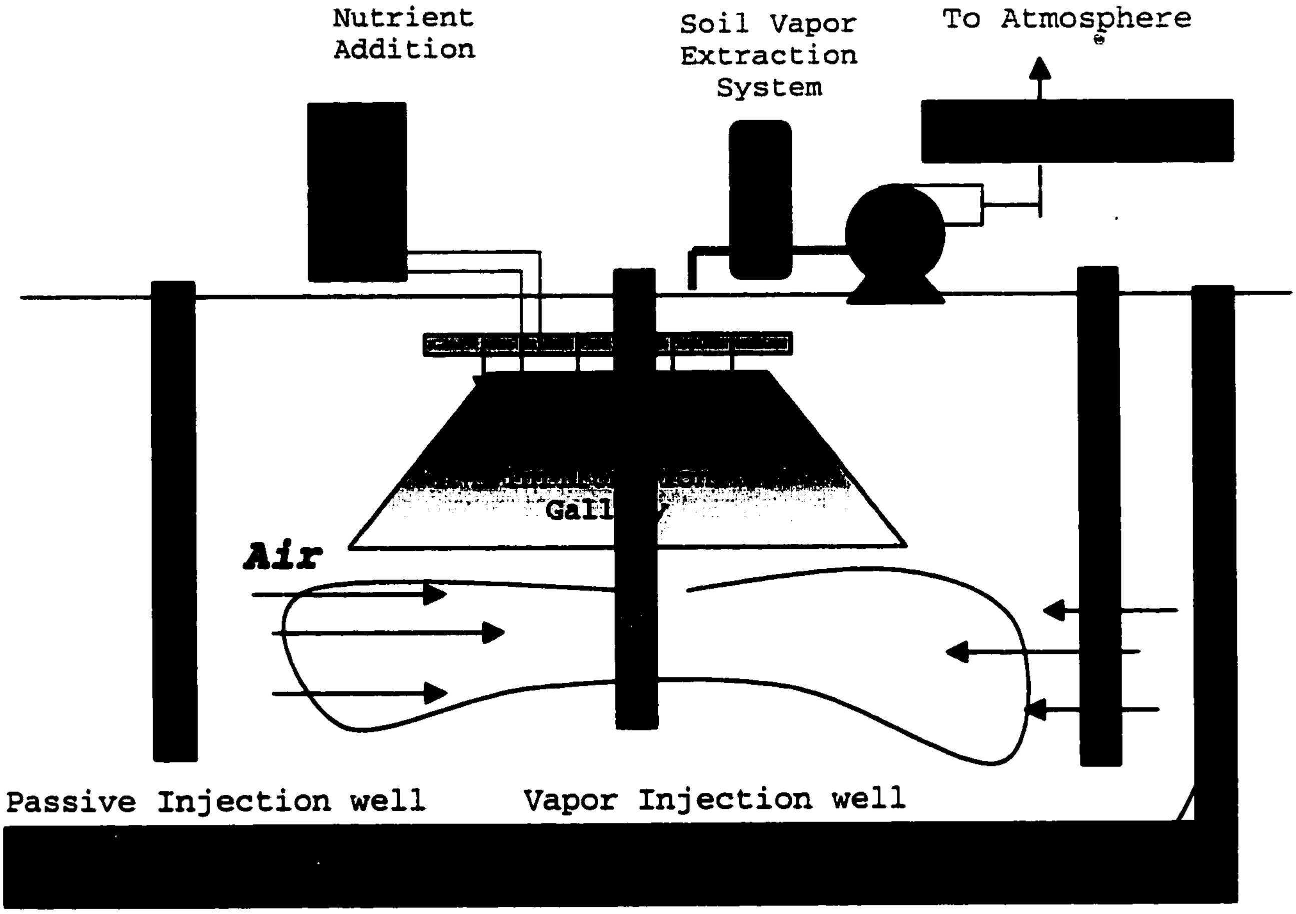
19- Lazagne Electrokinetic ™: it allows the movement of PAH into treatment zones and dechlorination in place. Titanium mesh placed upon ground surface acted as one of the electrodes (anode). Horizontal graphite filled soil fractures created at depth of 4 m acted as the other electrode (cathode) (Davis-Hoover et al. 1999).

3.2.2. Biological Soil Treatment Processes

1- Bioremediation/Bioreclamation: : this process can be used *in-situ* as well as *ex-situ*. It carries different microbial processes such as mineralization, detoxication, and co-metabolism (Alexandre 1980) to breakdown organic compounds present in soil. Microorganisms, such as bacteria and fungi, which are present naturally in most soils, initiate these processes. The native capability of the microorganisms can be stimulated and specially developed microbes can be added to the site. A detailed review of this technology is provided in Roberts (1998). Figure 3 illustrates unsaturated zone bioremediation system.

2- Bioventing: this method combines the beneficial effects of both, bioremediation and SVE. Hot vapour will remove the volatile portion of HC and by the same time will stimulate the biodegradation of the heavier HC such as diesel fuel, jet fuel, and fuel oils (Brown et al., 1993).

3- Bioslurping: this method employs the application of subatmospheric pressure to remove free floating products (NAPL) from the water table, and to free the nondrainable LNAPL retained in the vadose zone, saturated zone and capillary fringe as well as to remove the part of the NAPL which exists in a gaseous form (Baker and Bierschnek 1996).



Source: Long (1993)

Figure 3 Unsaturated Zone Bioremediation System

4- Biopurge/Biosparge: it uses low-volume airflow to regulate soil moisture, oxygen, nutrients, and microorganisms. When the vapour is injected above the ground water table, it is called biopurging, and when the vapour is injected below the ground water, it called biosparge (Burke and Rhodes 1995).

5- Deep Soil Fracture Bioinjection™: it involves injecting a slurry, oxygen, nutrient, and cultures into the subsurface, in an overlapping grid pattern that covers the entire contaminated area (Burke and Rhodes 1995).
6- Combined Air-Water Flushing: it employs the use of air injection and suction wells with the use of sprinkled water, and nutrients (Roberts 1998).
7- Biopolymer Shields: it is used to reduce soil permeability and create a contaminant barrier. It employs the use of slim-forming bacteria to the soil matrix to produce a biopolymer barrier (Yang et al. 1994).
8- Bioscreens: this technology employs the creation of a local zone that exhibits a high pollutant retention capacity, increased biodegradation of hazardous wastes, and immobilization of dissolved heavy metals (Rijnaarts et al. 1995).
9- Phytoremediation: it uses the root system of plants to accumulate contaminants or to enhance biodegradation (Johns and Nyer 1996).

3.3. Conclusions

The above-mentioned review of conventional treatment technologies revealed certain disadvantages and deficiencies, which can be summarized as follows:

1- Ex-Situ Methods: Despite the fact that these methods proved to be effective for all soils type and contaminants, they are very costly and complex. In addition undesirable toxic vapours can be released during the excavation process (Ram et al., 1993).
2- In-Situ Methods: Although these methods proved to be less expensive than Ex-Situ methods however, their adaptability is conditioned with specific site and contaminants characterization. For example, the majority of these methods are applicable in highly

permeable soils, which leaves the treatment of silty and clayey soils a questionable matter.

Therefore there is a need to explore and develop a new technology which can overcome the deficiencies and the disadvantages of the conventional methods and in particular can be adopted to clayey soils and silty clay soil where conventional methods have failed. The following chapter deals with electrokinetics as an emerging technology, which can be combined with other technologies for contaminant transport, mobilization and removal.

4. ELECTROKINETIC TECHNOLOGY

Electrokinetics is an emerging technology for site remediation, which offers the possibility of introducing a greater flow through fine-grained soils, thus inducing contaminant movement that could not otherwise be achieved. As an *in situ* treatment method, it offers the removal of organic as well as non-organic contaminants at relatively low cost compared with other technologies (Ex-Situ incineration, soil washing, etc.,)

The applicability of this method in clayey soils is considered a breakthrough in the process of soil decontamination. As it was stated in Chapter 3, non of the conventional treatment technologies offered adaptability to this kind of soil (heterogeneous fine-grained soils), because of the low coefficient of permeability (less than 10^{-8} m/s). Fine-grained soils pose a significant problem to any potential remediation technology. Among these problems are: I- low hydraulic conductivity that restricts the fluid volumetric flow rate; II- large specific surface area that provides numerous active sites for surface reactions; III- the fact that these reactions are dynamic and reversible which is a result of its dependency on pH (Alshawabkeh et al. 1999). Thus, there is a growing need for an *in-situ* technology for the remediation of contaminated fine-grained soils.

4.1 Principles and Definition

Electrokinetics is a complex phenomenon induced by an applied electric field across a soil-water system (Swartzbaugh et al. 1990). Commonly used names are electrokinetic remediation, electroremediation, electroreclamation, electrorestoration, electrochemical soil processing, or electrochemical decontamination (Acar and Alshawabkeh 1993). It uses a low-level direct current in the order of mA/cm^2 of cross sectional area between the electrodes or an electric potential gradient up to a few volts per cm across an electrodes (Shapiro and Probstien 1993; Acar and Gale 1992).

The application of a DC-electric field in a soil water system causes very complex phenomena to occur which can be collectively referred to as electrokinetic (Swartzbaugh et al. 1990). There are three principal mechanisms which take place under the action of an electric field: 1- electromigration, 2- electroosmosis, and 3- electrophoresis (Yeung and Datla 1995; Hicks and Tondorf 1994; Probstein and Hicks 1993; Banerjee et al. 1988). Electromigration is defined as the transport of charged ions in solution. Electroosmosis is the mechanism when a liquid containing ions moves relatively to a stationary charged surface (effected by electrical current). The movement of these charged ions will create a drag force which pulls the pore fluid along resulting in electroosmosis. Electrophoresis is a process where colloidal particles move relative to a stationary liquid (Mitchell 1993). A detailed review of these flow processes is described by Yeung (1994).

Each of the above mentioned processes will generate a flux. The contribution of each flux to the total mass flux is a function of several compositional and environmental variables (soil mineralogy, pore fluid composition, electrochemical properties of the species in pore fluid, porosity and tortuosity of the porous medium) (Acar and Alshawabkeh 1993). Table 4 presents the constitutive relations for each flux and defines the associated parameters affecting transport. Any use of an electrical field in restoration of waste sites will require the identification of a dominant mechanism for moving the contaminant (Kelsh 1992).

4.1.1. Electroosmotic Flow Modelling and Description

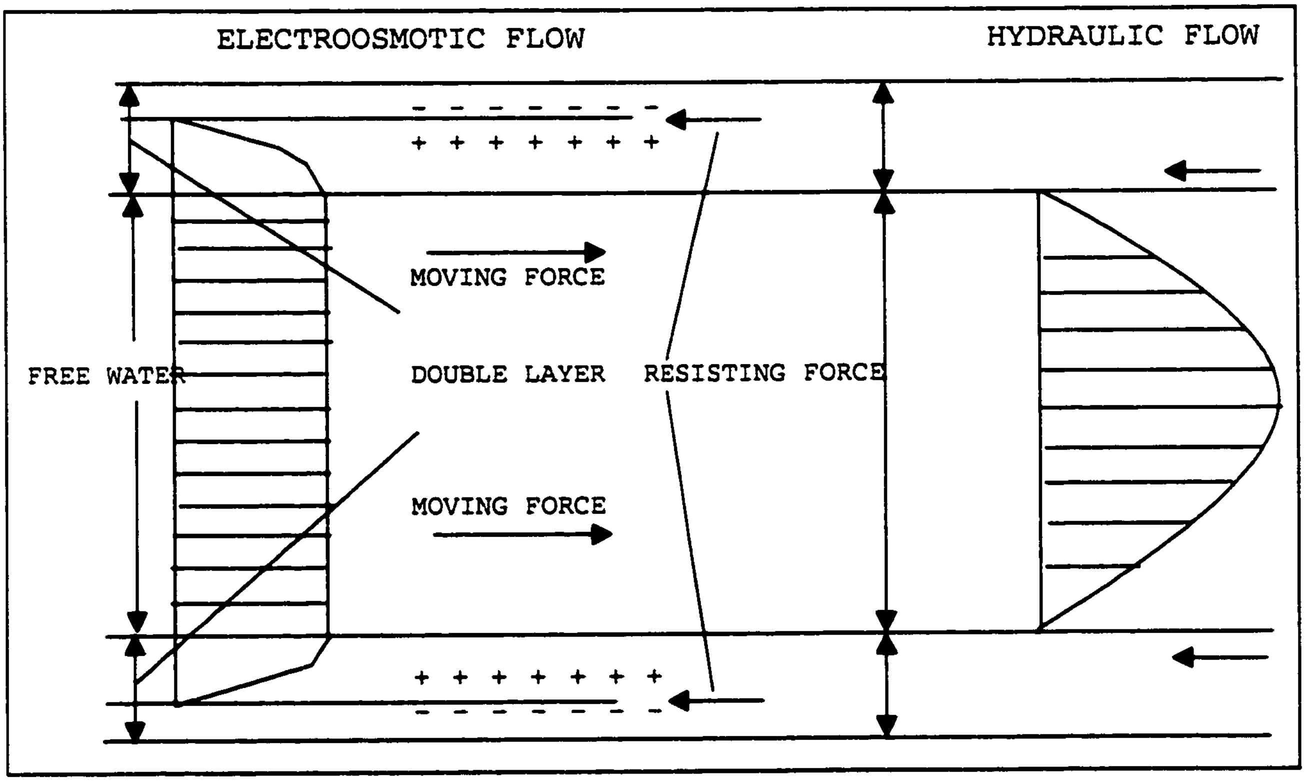
The electroosmotic phenomenon was first observed by Reuss in 1809, (Swartzbaugh et al. 1990). He observed that when a direct electrical potential is applied across a porous medium, water moves through the capillary toward the cathode. When the electric potential is removed, the flow of water immediately stops.

Table 4 The constitutive relationships between the significant fluxes and potential gradients associated with species transport in soils under an electrical field

Flux and associated parameters	*Constitutive relationships and associated formalisms proposed for the constants*
Diffusive mass flux, J_j^d Effective diffusion coefficient, D_j^* Molar concentration, C_j Tortuousity factor, τ; porosity, n Diffusion coefficient, D_j	$J_j^d = D_j^* \nabla(-C_j)$ $D_j^* = D_j \tau n$
Migrational flux, J_j^m Effective ionic mobility, U_j^* Electrical potential, E Valance, Z_j; Faraday's constant F Universal gas constant R Absolute temperature, T	$J_j^m = U_j^* C_j \nabla(-E)$ $U_j^* = U_j \tau n = [1/RT] D_j^* Z_j F$
Electroosmotic mass flux, J_j^c Electroosmotic pore fluid flux, q_e Molar concentration of water, C_w Electroosmotic permeability, K_e Coefficient of electroosmotic water transport efficiency, K_j Effective bulk electrical conductivity, σ^* Permitivity of the medium, ε Zeta potential, ζ viscosity, η A, B constants Total concentation of the electrolyte, C_t	$J_j^c = (C_j/C_w)\, q_e$ $q_e = K_e \nabla(-E) = K_I$ $K_i = K_e/\sigma^*$ $K_e = = (\zeta\, \varepsilon / \eta)\, n$ $\zeta = A - B \log C_t$

Source: Acar and Alshawabkeh (1993).

In 1879, Helmholtz provided a mathematical basis to this theory that is still accepted up to this moment with slight changes (Cassagrande 1952). In a cylindrical capillary, Helmholtz distinguished between the free water and the boundary film of water immediately adjacent to the wall of the capillary (Figure 4). Under hydraulic pressure, only the free water is susceptible to the movement, thus under an applied field, both free water and the adjacent layer are mobilized toward the cathode because of the dominate positive charge on the adjacent layer.



Source: Electroosmotic stabilization of soils, Journal of the Boston Society of Civil Engineers (1952)

Figure 4 Comparison of EO Flow with Hydraulic Flow in a Single Capillary

The movement is related to the drag between the bulk of the liquid in the pore water phase and the thin adjacent layer (Probstein and Hicks 1993). The drag force arises from the movement of the ions under the influence of the electrical field. As they move, they drag the liquid with them, giving rise to a macroscopic flow. The magnitude of this flow will clearly depend on the amount of charge in the pores. Since this charge is equal and opposite to the charge on the particles, measurements of electroosmotic flow can in principle be used to determine the zeta-potential ξ or vice versa. Therefore, the resulting flow is proportional to the zeta-potential and the applied electrical field (Probstein, 1989). However, it is insensitive to pore size (Michell, 1993) and soil type (Michell, 1993; Yeung, 1994 b). This movement forms the basis of electrokinetic soil de-watering and decontamination.

The flow rate of the fluid through the soil depends on the magnitude of the applied electrical gradient, the flow resistance of soil, and the fractional drag exerted by the migrating ions on the water molecule (Gray and Mitchell 1967).

According to Eykholt and Daniel (1994), electroosmotic (EO) flow can be modeled using similar approach to Darcy's Law (Casagrande 1952):

$$\boxed{q_e = K_e\, i_e\, A = K_i I = (K_e / \sigma)\, I} \tag{1}$$

Where:

q_e = EO flow rate [cm^3/s]

A = cross sectional area [cm^2]

i_e = potential gradient [V/cm]

K_e = coefficient of electroosmotic permeability [$cm^2/V.s$]

I = current [A]

K_i = EO water transport efficiency coefficient [$cm^3/A.s$]

σ = conductivity [mS/m]

The coefficient of electroosmotic permeability, K_e is a soil property parameter, which indicates the hydraulic flow velocity under a unit electrical gradient. According to the Helmholtz-Smoluchowski theory (Mitchell, 1993) K_e can be given as:

$$\boxed{K_e = -(\zeta \varepsilon / \eta)\, n} \tag{2}$$

Where:

ζ = Zeta potential [V];

ε = electrical field permitivity [$8.854 \bullet 10^{-12}$ C/V.m] or [N/V^2];

η = Viscosity of the pore fluid [pa sec];

n = porosity.

The values of the K_e are generally between $1 \bullet 10^{-9}$ and $10 \bullet 10^{-9}$ ($m^2/V.s$) and as it is clear from its equation, its value is porosity dependent and pore size independent.

4.1.2. Electrophoresis

Electrophoresis is the mirror image of electroosmosis, where charged particles are transported under the influence of an electrical field relative to a stationary liquid phase (Probstein 1989, Mitchell 1993). In clayey soils the movement is toward the anode. This process is important in electrokinetic soil remediation when surfactants are introduced as an enhancing agent to solubilize hydrophobic compounds rendering them susceptible for transport toward one of the electrodes depending on the charge of the micelle (particle like). The surfactant type will determine this charge.

4.1.3. Electromigration Description and Model

The applied electrical field will induce the transport of ionic species in solution. The direction of ionic migration is dictated by the charges of the ions (Probstein and Hicks, 1993). The ionic mobilities of ions (U) in free dilute solutions under the influence of a unit electrical field, are in the range of 1×10^{-8} to 1×10^{-7} M^2/Vs (Dean 1992). However, the velocity of ions in soil pores in a unit electrical field (1V/m), which is given by effective ion mobility U*, is considerably lower that the ionic mobility, U. The relationship between both mobilities is presented through the use of the Nernst-Einstein equation (Taha 1996).

$$\boxed{U^* = U\,\tau\,n = (D^*\,|Z|\,F)/RT} \qquad (3)$$

Where:

D^* = effective diffusion coefficient of the contaminants [cm^2/s];

Z = the charge of the species;

F = Faraday's constant [96.485 C/mol];

R = universal gas constant [8.3144 J/K.mol];

T = absolute temperature [K].

Practical ranges of U* in saturated fine-grained soils are given by Mitchell (1991). He estimated that U* values for different ions can range from 1×10^{-8} to 3×10^{-9} ($m^2/V.s$) (Mitchell, 1991). Reported results showed that the mass transport by the ionic migration, will be at least 10 times higher than mass transport by the electroosmotic advection, and it may reach values as high as 300 in late stages of the process (Acar and Alshawabkeh, 1993).

In cases where the ionic strength is high due to the presence of inorganic contaminants or dissolved salts, the ζ is small and transport occurs mainly by electromigration (Hicks and Tondorf, 1994). As the concentration of specific species will decrease relative to total electrolyte concentration, its efficiency under the electrical field will decrease subsequently.

4.1.4. Mathematical Model for Contaminant Transport under Electrical Gradient

When a direct current is applied to a soil system it creates in addition to hydraulic and concentration gradients, an electrical gradient and the mass balance conservation can be formalized as:

$$\boxed{n(\partial C/\partial t) = -(\nabla \cdot J) + nR} \qquad (4)$$

Where:

n = soil porosity

C = contaminant concentration in the pore fluid [g/L]

t= time

R = reaction term for contaminants (includes all chemical and physical reactions)

J = total flux [g/Lm^2].

The total flux can be described as (Alshawabekeh and Acar 1996)

$$\boxed{J = -D^*(\partial C/\partial x) - C(U^* + K_e)(\partial E/\partial x) - CK_h(\partial h/\partial x)} \qquad (5)$$

Where:

D^* = effective diffusion coefficient of the contaminants [cm^2/s];
x = longitudinal distance [cm];
U^* = effective ionic mobility [cm^2/Vs];
K_e = electroosmotic permeability coefficient [cm^2/Vs];
E = electric field;
K_h = hydraulic conductivity of the soil [cm/s];
H = hydraulic gradient [cm].

D^* can be related to the diffusion coefficient in free solution D by:

$$\boxed{D^* = D\,\tau\, n} \tag{6}$$

Where:

τ : is the tortuosity of the soil medium

Using equations [1] and [2], the one dimensional flux equation can be written as (Alshawabekeh and Acar 1996).

$$\boxed{\begin{aligned} n(\partial C/\partial t) &= D^*(\partial^2 c/\partial x^2) + c[(U^* + K_e)(\partial^2 E/\partial x^2) + \\ &K_h(\partial^2 h/\partial x^2)] + (\partial C/\partial x)\,[(U^* + K_e)(\partial E/\partial x) + K_h(\partial h/\partial x)] + nR \end{aligned}} \tag{7}$$

If the sorption was the only reaction between the contaminants and the soil medium, the term R will be represented mathematically as:

$$\boxed{R = -(\rho/n)(\partial s/\partial t) = -(\rho/n)(\partial s/\partial c)(\partial C/\partial t)} \tag{8}$$

Where:

ρ = bulk dry density of the soil [kg/m^3]

S = sorbed concentration [mol/g]

Upon assumption of a linear adsorption isotherm, the distribution coefficient of the species (K_d), which determines the amount of the species adsorbed to the soil, can be given as:

$$\boxed{\partial s/\partial C = K_d} \qquad (9)$$

By combining equations [8] and [9] and substituting them in equation [7], the mass transport in one dimentional equation with adsorption being the only process between the soil and contaminants can be presented as (Taha 1996):

$$\boxed{\begin{array}{l}(\partial C/\partial t)\,(1+(\rho/n)K_d) = (D^*/n)(\partial^2 c/\partial x^2) + c/n[(U^* + K_e)\,(\partial^2 E/\partial x^2) + \\ K_h(\partial^2 h/\partial x^2)] + (1/n)(\partial C/\partial x)\,[(U^* + K_e)\,(\partial E/\partial x) + K_h(\partial h/\partial x)]\end{array}} \qquad (10)$$

Where the term on the left side of the equation is called the retardation factor (R_d).

$$\boxed{R_d = 1 + (\rho/n)K_d} \qquad (11)$$

This equation is valid only for adsorption processes.

4.2. Zeta Potential and its Effect on Electrokinetic (EK) Flow

The value of the zeta potential depends on soil properties as well as ionic strength and pH of the saturating liquid (Sposito 1984; Hunter and Alexander 1963; Williams and Williams 1978). A typical ζ is approximatly 10-100 mV. For water saturated silts and clays, ζ is typically negative (Probstein and Hicks 1993), and in a 100 V/m electrical field, water will flow toward the cathode at a velocity of around 10 cm/d (Hicks and Tondorf, 1994; Shapiro and Probstein 1993).

As long as ζ is negative the flow toward the cathode will persist. However, dropping in the value of pH at the anode will reduce the magnitude of zeta potential and therefore reducing the flow by the time Eq. [1] and [2]. Therefore it is expected that the EO flow will cease at certain stage of the process (isoelectric point) PZC where zeta potential is zero. Parks (1967) measured the point of zero charge for kaolinite, their results indicated that PZC can vary from 3.3 to 4.6 depending on the clay source. Lorentz (1969) obtained a value for the ZPC near 4 for kaolinite. When pH is below the isoelectric point, ζ is positive and a flow reversal can be monitored (Ekholt and Daniel 1994).

In order to sustain a flow from the anode to the cathode, the generated acid at the anode must be neutralized. The neutralization can be achieved through treating both electrodes with water (Elektorowicz 1995). Taha (1996) demonstrated that by using this treatment the amount of EO flow can be doubled.

The effect of soil saturating liquid pH on the ζ was evaluated by Shapiro and Probstein (1993). Their results showed that the flow rate obtained from 0.1 M acetic acid treated kaolin soil was 4 times higher than the flow rate obtained from 0.5 M treated kaolin soil. The higher concentration of acetic acid caused the clay to have a ζ of smaller magnitude than the clay treated with a lower acetic acid concentration. They also stated that another electrochemical processes (anode corrosion) could have a direct effect on the clay's ζ. A nearly 10 fold increase in the magnitude of the zeta potential of a kaolinite clay as the pH varied from 3.5 to 5 was observed by Street and Buchanan (1956). Mise (1961) has shown that K_e for kaolinite at pH 10 is nearly five times greater than for the same soil at pH=2. Hunter (1982) and Kruyt (1952) reported the effect of pH and ion concentration of pore fluid on zeta potential. Zeta potential was reported to decrease linearly with the logarithm of the pH of the soil medium.

Most of the available models for electrokinetic transport are based on assumptions that electrical gradient and zeta potential are constant (Hamed 1990; Segall and Bruell 1992). These assumptions are not true for the reasons that electroosmotic flow is time dependent and this dependency can be attributed to the change in zeta potential and electrical field distribution in the specimen with time (Probstein, 1993). Changes in the electrical gradient with time were also reported by Esrig (1968) and Hamed (1990). They observed voltage losses near the cathode which were attributed to an increase in pH and precipitation in the cathode area. Shapiro *et al.* (1989) presented an electrokinetic model based on non uniform values of zeta potential and electrical gradient.

4.3. Electrodes Reactions and its Effect on EK

In systems where its chemistry is uncontrolled externally, electrolysis chemistry will dominate at the boundaries (Acar and Alshawabkeh, 1993). When electrical energy is supplied to an electrolytic cell, an oxidation-reduction reaction takes place immediately. The power supply acts as an electron pump pushing electrons into the cell at the cathode and removing them at the anode. To maintain the neutrality of the system, oxidation-reduction reactions take place within the cell.

Electrolysis of water produces H^+ ions at the anode and OH^- ions at the cathode according to:

$$\boxed{\begin{array}{l} 2H_2O - 4e^- \rightarrow O_2 + 4H^+ \quad \text{(anode)} \\ 4\,H_2O + 4e^- \rightarrow 2H_2 + 4\,OH^- \quad \text{(cathode)} \end{array}} \qquad (12)$$

One Faraday (96,500 coulombs/g-equiv.) of charge will generate one mole of H^+ and OH^- at the anode and the cathode respectively. A current of 10 mA will produce $3.73 \bullet 10^{-4}$ moles of OH^- and H^+ every hour. Knowing the liquid volume, the rate of increase in H and OH concentrations per hour can be calculated and consequently the pH.

The oxidation and dissolution of the iron anode can occur according to the following equation:

$$\boxed{Fe \rightarrow Fe^{++} + 2e^-} \qquad [13]$$

Metals can precipitate as oxides, hydroxides, carbonates, and phosphate complexes, depending upon the chemical constituents of the pore water, pH and electrical current flow (Segall et al. 1992). If chlorides are present at elevated levels, the production of chlorine gas can occur at the anode.

$$\boxed{2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-} \quad (14)$$

If the ions produced due to the electrode reactions are not removed or neutralized, it will lower the pH at the anode and raise it at the cathode. This situation will generate two fronts; an acidic front moving toward the cathode from the anode and a basic front moving toward the anode from the cathode (Probstein and Hicks 1993).

The advancing acid front causes a decrease in K_e associated with an increase in conductivity in the anode compartment and a corresponding drop in zeta potential (Hamed et al., 1991). The decrease in both K_e and the electrical potential gradient will lead to a decrease in EO flow, making the mass flux by electromigration 1-2 orders of magnitude greater than the EO mass flux (Hamed et al., 1991).

As the strong base from the cathode diffuses into the soil, ξ becomes increasingly negative in that region. The field intensity also increases and this can contribute to the flow in the cathode region toward the anode.

The generated acid at the anode advances toward the cathode by ion migration due to electrical gradient, pore fluid advection due to electroosmotic flow, pore fluid flow due to externally or internally generated hydraulic potential difference, and diffusion due to the developing chemical gradient. The alkaline medium developed at the cathode advances toward the anode by ionic migration and diffusion (Acar and Alshawabkeh, 1996; Shapiro and Probstein, 1993). However, hydrogen ions mobility is dominant because it is 1.8 times more mobile than the hydroxyl ion. Therefore, the migration of the base front is halted by the electroosmotic advection and neutralization caused by the hydronium ions being transported to this zone (Acar and Alshawabkeh, 1993). The precipitation of metal ions is accomplished where those fronts meet, this point called the isoelectric point where the concentrations of negative ions and positive ions are equal.

Within this context it should be noted that the soil-buffering capacity can play an important role in retarding these generated fronts. The higher the buffering capacity of the soil, the higher is its efficiency to retard acidic and basic fronts. High soil content of salts and organic species, which can react with the acid, will increase the buffering capacity of the soil. Kaolinite soils have a low buffering capacity and acidic conditions generated from the migration of the acid front toward the cathode can be developed easily (Acar 1993). Illite soils tend to be resistant to pH decrease because of their higher buffering capacity (Acar, 1993).

The electrochemical reactions in the electrodes are responsible for large changes in local pH. Whether the EO flow is toward the cathode or the anode, the impact of reactions on electrodes will decrease the flow. If the EO flow was initially toward the cathode, reflecting a negative ξ, it would bring the low pH solution from the anode into contact with the clay. This would cause the ξ to decrease in magnitude and even become positive in regions near the anode (flow reversal). On the other hand, if the EO flow was initially toward the anode, reflecting a positive ξ, then the high pH liquid from the cathode would enter the sample and change the ξ to negative values in the cathode region.

The effectiveness of electrokinetic techniques for contaminant removal depends on the prevention of acid and base front generation and maintaining a certain pH level within the soil so that the contaminants remain mobile (in the case of metals), and no precipitation of naturally existing compounds can occur (like carbonates, sulphates). In order to avoid precipitation and accomplish a high percentage of removal, a flushing system at the cathode had to be introduced to permit the removal of hydroxyl groups. The use of a conditioning solution in the anode area increases the solubility, to provoke complexation, or chelation in order to enhance the electromigration characteristics of specific contaminants (Eykholt and Daniel 1994).

Geokinetics conducted a field experiment at a galvanizing plant with sandy clay soil contaminated with zinc. They obtained a 20% zinc removal after 8 weeks of treatment (Legeman, 1993). The low removal efficiency was related to the presence of ammonium and ammonia known for their high buffering capacity, which minimized the development of the acidic front in the soil (Lageman, 1993).

Acar et al. (1993) proposed the use of an acid that forms a soluble salt with transported species for cathode depolarization. Acetic acid was proposed as depolarisation agent because of its environmentally safe nature and because it does not fully dissociate. Weiberen Pool (1989) suggested the use of calcium hydroxide for depolarization of the anode.

Calcium hydroxide has been applied since the 1950s for electrokinetic purposes.

4.4. Past Research Efforts

Geotechnical engineers have used electrokinetic processes for many years to consolidate fine-grained soils (Gray and Mitchell 1967; Esrig 1968; Gray 1970; Mitchell 1993; Wan and Mitchel 1976). Cassagrande (1949) in mid 30s was one the first engineers who used EO for soil dewatering and stabilizing. He used the technique to increase the effective stresses in the soil for a construction project in Germany. In Norway, EO was used during the construction of a submarine pen. The technology has also been utilized to dewater mine tailings and mineral sediments (Sprute and Kelsh 1982; Lokhart, 1983), to stabilize soil under building foundations, to stabilize earth filled dams, and to dewater soil under airport runways (Cassagrande 1952). Since the 1980s this methodology has been used to fence off hazardous waste and industrial sites (Lageman 1993). Electrokinetic fencing combines both remediation and pollution prevention. Mitchell (1986), Probstein and Renaud (1986) presented densification and/or in situ soil cementation using EK for the purpose of creating barriers around contaminated zones. The possibility of using an electrokinetic barrier and electrokinetic fencing to control the subsurface migration of contaminants has been suggested and discussed by Lageman et al. (1989), Mitchell and Yeung (1991), and Yeung (1993 b, 1993 c).

Recent laboratory experiments show that this technique can be used in combination with other remediation techniques such as pumping, biodegradation, and vacuum extraction. When combined with electrical heating, can remove polar and nonpolar organic chemicals from soil and ground water (Lageman, 1993).

It should be noted that soil type does not impose any significant limitation on the technology. However, the rate and the efficiency of contaminant transport depend heavily on soil type and variability of environmental conditions. Soil with a high degree of saturation, high water content and low activity provides the most favourable conditions for the transport of the contaminants by electroosmotic advection and ionic migration. However, soils with high activity, such as illite, montmorillonite, and impure kaolinite, exhibit high acid/base buffer capacity and require excessive acid and/or enhancement agents to desorb and solubilize contaminants before transportation and removal (Yeung et al. 1996, 1997; Puppala et al. 1997).

4.4.1. Organic Pollutants Removal

Soils contaminated by organics can be classified by whether the organic compounds are soluble or insoluble in water. Insoluble organics, such as heavy hydrocarbons, are essentially not ionized (hydrophobic). The removal of hydrophobic compounds can be achieved by electroosmotic purging using surfactants to solubilize the compounds and mobilize them by an advanced surfactant front (Elektorowicz and Hatem 1999). The removal of chlorinated solvents and phenolic compounds using electro-osmosis was the subject of several studies (Elektorowich et al. 1996).

The ability to remove soluble organics from clays by an applied electrical field has been demonstrated in some laboratory experiments. Shapiro et al. (1989) used DC to remove phenol and acetic acid from saturated and compacted kaoline. They concluded that the primary mechanism of contaminant removal was electroosmosis, and 95% of the contaminants were removed by passage of only 1.5 pore volumes of purge solution. Tap-water was used as a purge solution for phenol (450 mg/l), and 0.1 M NaCl as a purge solution for 0.5 M acetic acid. The authors demonstrated that the flow generated by electrical field application was time dependent and they related it to the changes of the pH profile with time. As it was discussed before, the zeta potential is pH dependent, and in the case of acetic acid, which has a lower pH than phenol, electro-osmotic flow was also lower. The lower pH, the lower the zeta potential because of the increase in absorbance of hydrogen ions, which neutralizes the negative charge on the soil, and led to a lower electro-osmotic velocity (Probstein 1993). Bruell et al. (1992) achieved a removal rate between 15% and 25% for benzene, trichloroethylene, toluene, and m-xylene for a treatment period of 2 to 5 days. Shapiro and Probstein (1993) concluded that the ability of an acid to buffer the electrode reactions plays a key role in the removal process. Probstein et al. (1991) suggested the use of nontoxic solutions as an enhancing agent for contaminant removal. Such reagents might include buffering compounds to control pH or enhance the zeta potential, desorption, and solubility. Products of the electrodes reactions such as hydroxyl ions at the cathode can be removed using such reagents. Shapiro and Probstein (1993) showed that the use of an alkaline purge solution led to a removal that was twice as high than the one with an acid purge.

Recently, electrokinetic techniques are used for *in-situ* contaminant removal from soil (Runnels and Larson 1986; Lageman et al. 1989; Banerjee et al. 1988; Probstein and Hicks 1993; Acar and Hamed 1991; Hamed et al. 1991; Acar 1992 a, b; Acar et al. 1992; Bruell et al. 1992; Pamukcu and whittle 1992; Shapiro and Probstein 1993; Elektorowicz and Choudhury 1997, 1998). The transport of organic species was also reported in several works (Segal and Bruell 1992; Acar et al., 1993; Wittle and Pamucku 1993). Fleurea and Dupeyrat (1988) showed that oil and brine could be recovered from sandstone by the application of an electrical field. The removal of acetic acid, phenol, gasoline hydrocarbons, and TCE was demonstrated by several researchers (Elektorowicz and Hatem 1996, Shapiro et al., 1989 a, 1989 b; Acar et al. 1992, 1993; Bruell et al., 1992; Segal and Bruell 1992; Shapiro and Probstein 1993).

Many industrial sites especially gas manufacturing plants contain mixed organic and inorganic compounds, each of which may interact differently with the soil. Therefore, the remediation of such sites has to proceed in stages: the first of which is metal removal due to electromigration, the second, organic contaminant removal by other electrokinetic phenomena (Elektorowicz et al. 1995).

4.4.2. Inorganic Contaminants Removal

Metals to be transported by electromigration, have to be in soluble form, carrying a charge. Furthermore, the polarity of the charge should not be changing as the metal migrates toward an electrode. However, changes in solubility and polarity occur as a result of electrolysis reactions at the electrodes (Chapter 4.3) and reactions with naturally present substances in the pore fluid (Lageman et al. 1989).

The fact that the metal ions are positively charged and most of the clays are negatively charged, the electromigration of these cations can be enhanced by electroosmosis or electromigration. Acar et al. (1989 b) suggested that the migration of acidic front generated from the production of hydrogen ions at the anode, would aid metal solubilization from the soil. Although the promotion of these acidic conditions will suppress the electroosmotic flow (Chapter 4.3), metals removal will not be affected because of their presence as charged ions and their mobility is accomplished by electromigration and diffusion (Probstein 1993). In this study less than 5% of zinc was collected through the cathode well, the remaining zinc was accumulated in the cathode area were an isoelectric point was reached. Therefore, Probstein (1993) suggested flushing the cathode with tap water. Eykholt (1994) observed the same precipitation region in an experiment with copper removal. Attempts to flush the copper from the precipitation zone by cathode or anode acid treatment, or addition of complexation agents have failed. In Corvallis, United Chrome Products Superfund Site, the electrokinetic treatment proved the removal of 95% of the chromium. Using two separate systems with two different chemicals to control the environment around the electrodes, Geokinetics, in a field experiment on contaminated site with copper and lead, obtained 74% removal during 430 hours of treatment. In a commercial remediation project, Geokinetics had a goal to clean up an arsenic contaminated site. After 50 days of action, an average removal of 30% was achieved. The low removal efficiency was believed to be related to the presence of metal objects at the site. Efficient transportation and removal of inorganic species has been reported in several works (Runnels and Larson 1986; Hamed 1990; Pamukcu et al. 1991; Banerjee et al. 1988; Hamed et al. 1991; Eykholt 1992; Runnels and Wahli 1993; Wittle and Pamukcu 1993; Pamukcu and wittle 1993; Probstein 1994; Rodstand et al. 1995; Choudhury and Elektorowicz 1997; Elektorowicz et al. 1996).

A field study reported by Banerjee et al. (1988) investigated the feasibility of using electrokinetics in conjunction with pumping in order to decontaminate a site from chromium. The migration of inorganic contaminants in ground water under the influence of an electrical field was described in detail by Ferguson and Nelson (1986). Hamnett (1980) studied the factors, which can effect the removal of contaminants from soil. The technique has been used successfully to remove chromium from a Super-Fund site at Corvallis, Oregon (Banerjee

1987). Lageman et al. (1989) used the technique to remove heavy metals from clay, peat, and argillaceous sand. Hamed et al. (1991) employed electrokinetics to remove lead from kaolinite, and Acar et al. (1994) to remove cadmium from saturated kaolinite. Pamukcu and Wittle (1993) used the technology to remove 85-95% of the original concentration of cadmium, cobalt, nickel, and strontium from laboratory samples prepared with Georgia kaolinite, Na-montmorillonite and sand -montmorillonite mixture.

Li, et al. (1998) proposed a method which can deal with the pH increase near the cathode and the prevention of heavy metal precipitation. They suggested the placement of a length of tube filled with solution between the soil and the cathode. The precipitation of heavy metals occurred in the solution and not in the soil. Another method developed by the authors suggested the placement of a cation selective membrane in the front of the cathode to stop the advancement of the hydroxyl front toward the anode. This will ensure a low pH in the soil. The authors' achieved 90% removal of copper from sand using this technique.

Because contaminants can exist in different chemical forms but the only form available for elektrokinetic transport is the dissolved one, therefore, the use of enhancement techniques has been considered. Most contaminants can be transformed to their dissolved forms using solubilization agents. These agents should fulfill the following important characteristics (Alshawabkeh et al. 1999): 1) they should not form insoluble salts with the contaminant in the range of pH values expected to be developed during the process; 2) they should form soluble complexes with the contaminant that can electromigrate efficiently under a direct current electric field; 3) they should be chemically stable over a wide range of pH values; 4) they should have a higher affinity to a contaminant than to soil particles; 5) they should not generate toxic residues; 6) the generated product of the treatment process should not pose a volume problem; 7) they should be cost effective; 8) they should not produce an excessive solubilization of soil minerals or increase the concentration of any regular species in the soil pore fluid; 9) if possible, they should make complexes with the target species in a selective manner.

Several of the above-mentioned characteristics are also applied to the agent involved in the solubilization of organic contaminants. In this case, surface active agents are the most suitable for solubilization of PAHs.

5. SURFACTANTS

5.1. Introduction

The affinity of Hydrophobic Organic Compounds (HOC) into the solid phase of soil rich in humus, organic matter and clayey particles (refer to Chapter 2.2) is much higher than its affinity for the aqueous phase (Karickhoff, 1984). Cleanup of such contaminated soil using conventional methods like the pump-and-treat or excavation/ incineration appear to be lengthy, expensive and in some cases, ineffective (Chapter 3.3). The remediation process often depends on desorption of contaminants from the soil surface, and incorporaton of pollutants into the bulk aqueous phase. Due to their properties, PAHs are not easily transported form the solid to the aqueous phase, especially in soil containing fine fractions. Subsequently, they are unaffected by conventional treatment methods. Therefore, the use of surfactants as agents for the apparent solubility enhancement and mobility promotion has been a subject of intensive research (Nash, J. H. 1986; McDermott, J. B. 1988; Rajput, V. S. 1989).

Worldwide industrial production of surfactants rose from 35 000 tons in 1950 to 4.3 million tons in 1990 (Cain 1994). However, the use of surfactants in soil remedation is a new concept, particularly when it is combined with electrokinetic technology. The combination of both technologies (surfactant & EK) has been thought to take advantage of electrophoretic flow in addition to EO flow (discussed in Chapter 4). This chapter will provide an overview on surfactants, their types, characteristics, and behaviour.

5.2. Definition and Classification

Properties of surfactants are derived from their nature as amphiphilic chemicals which have dual characteristics: hydrophilic and hydrophobic. These characteristics are derived from polar and non-polar regions, which allow the molecules to concentrate at interfacial surfaces: air-water, oil-water, and solid liquid interfaces (Cain 1994). Surfactants can be classified according to their nature, which can be synthetic or biological.

5.2.1. Biological Surfactants or Natural Surface Active Chemicals

Naturally existing surface-active compounds fulfil the amphiphilic requirements by hydrophillic, oxygen containing functional groups (carbohydrate, a hydrophillic amino acid such as glutamate, aspartate, lysine, or arginin, or a hydrophillic peptide). The hydrophilic part is joined to a hydrophobic aliphatic or aromatic moieties which can have different structures: lipid structure, isoprenoid (cholesterol), hydrophilic part with amino peptides including the aminoacids, phenylalanine, leucine, isoleucine, valine, or alanine (Thangamani et al. 1994). Humic substances may exist in association with solid matrices or as dissolved aggregates that have micelle-like structures (Wershaw 1986).

Bacteria, yeasts, and fungi that have the capability to synthesize surfactants, during their growth on insoluble substratesare commonly referred to as biosurfactants (Georgiou et al., 1992). The primary classes of microbial surface-active compounds are: 1) glycolipids, 2) amino acid containing lipids, 3) phospholipids, 4) fatty acids, 5) peptides, and 6) polymeric biosurfactants. These bio-surfactants can be associated with the cell wall or excreted as extracelluar material. Excreted surfactants cause emulsification of hydrocarbons in solution, whereas cell-associated surfactants facilitate hydrocarbon uptake. As a result, such extracellular and cell wall associated molecules have the potential to:

1- promote cellular attachment to hydrophobic surfaces;
2- affect the distribution of cells between oil and water phases;
3- emulsify substances that are insoluble in water;
4- mediate transport of hydrophobic substrates into the cell (Thangamani et al., 1994).

5.2.2. Industrial or Synthetic Surfactants

Synthetic surfactants can be classified according to the nature of the hydrophillic portion of the molecule (Figure 5).

Anionic surfactants - when the head group carries a negative charge. This is the largest group of surfactants. The major subgroups of this class are the alkali carboxylates (soaps), sulphates, and phosphates. Branched hydrophobic moities of these surfactants markedly slow their biodegradation.

Cationic surfactants - when the head group carries a positive charge. This group of surfactants can be divided into two categories: 1) heterocyclic materials; 2) Alkyl nitrogen compounds.

Zwitterionic or amphoteric surfactants - when the head group can carry both negative and positive charges. They are used potentially in cases where there is biological contact, therefore, their production is in small quantities.

Nonionic surfactants - when the head group carries no charge. It derives its solubility from highly polar groups.

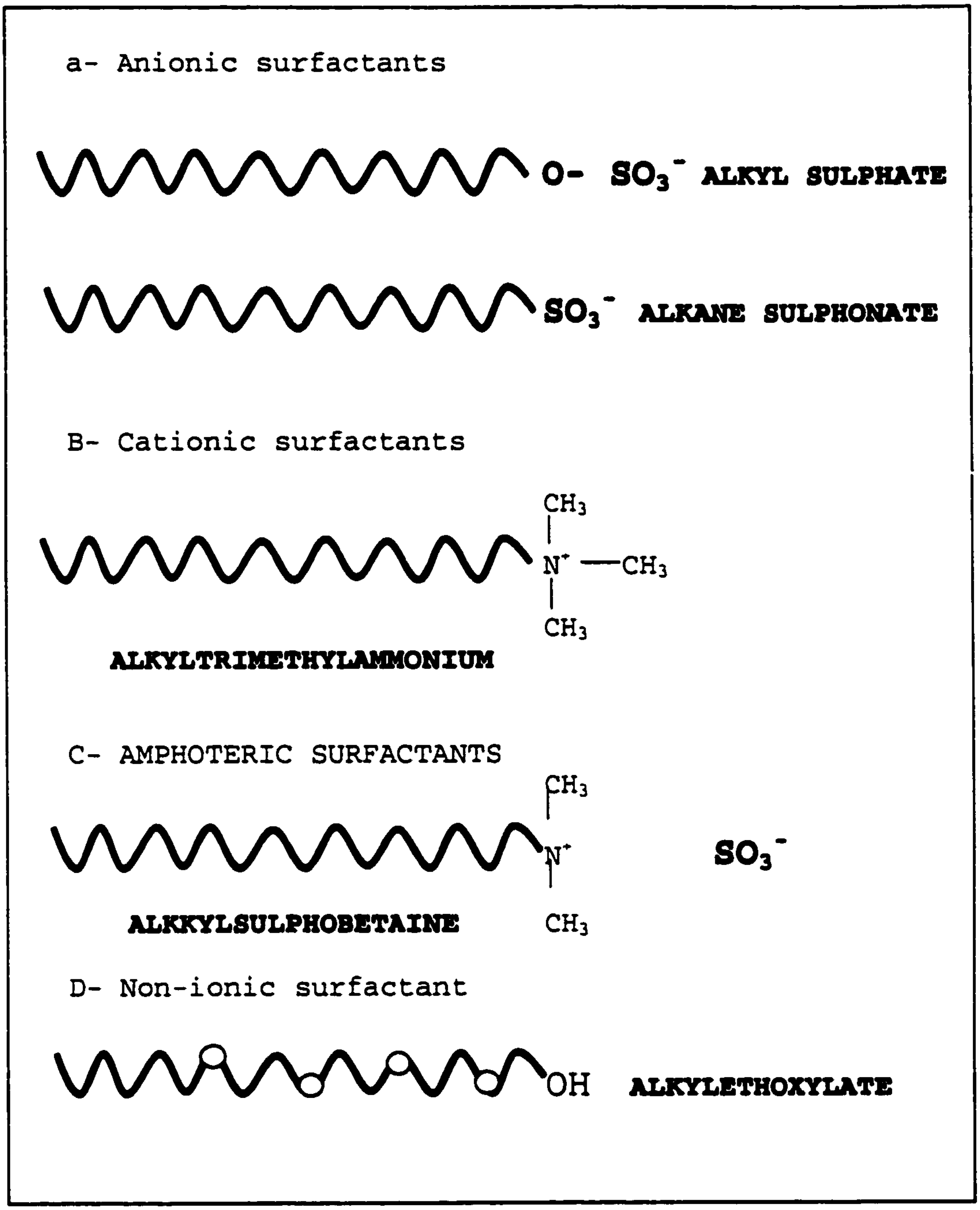
There are two common classes of these surfactants: I) alkyl ethoxylates; and II) alkylphenol ethoxylates. The alkyl or alkylphenol moieties are nonpolar and hydrophobic; the ethylene oxides moieties are polar and hydrophillic.

5.3. Theory of surfactants

Micelle formation is a phenomenon unique to surfactants. A dynamic cluster is formed when the bulk solution concentration of a given surfactant is greater than a specific threshold value defined as the critical micelle concentration (CMC) (Figure 6). Systems with a such surfactant concentration are called Supra CMC System. The CMC is a function of surfactant structure, the temperature of surfactant solution, the concentration of added electrolytes and other amphiphili (Harwell 1992).

Clusters could have spherical, spheroidal, or rodlike structures with hydrophobic interiors. The micelles are 3-4 nm diameter droplets with a polar coating (Tanford 1980). Hydrophillic chains and polar solvents surround the hydrophobic core of the micelle, which is formed from hydrophobic portions of each molecule. Micelle presence is results in the formation of a hydrophobic pseudophase ("micellar pseudophase") (Halle 1987). The region exterior to the micelles is called the aqueous pseudophase, which is a mixture of water, and non-aggregated surfactant monomers at the CMC (Hunter ,1987). The average number of surfactant molecules in each micelle is called the "aggregation number" (Edwards, 1991), which is between 50 to 200 (Harwell 1992). The CMC is different for every surfactant (Rosen, 1989), and is typically between 0.1 and 10 mM/L.

Surfactants have the capability to enhance the removal of HOC by means of two mechanisms.



Source: Cain *(1994)*.

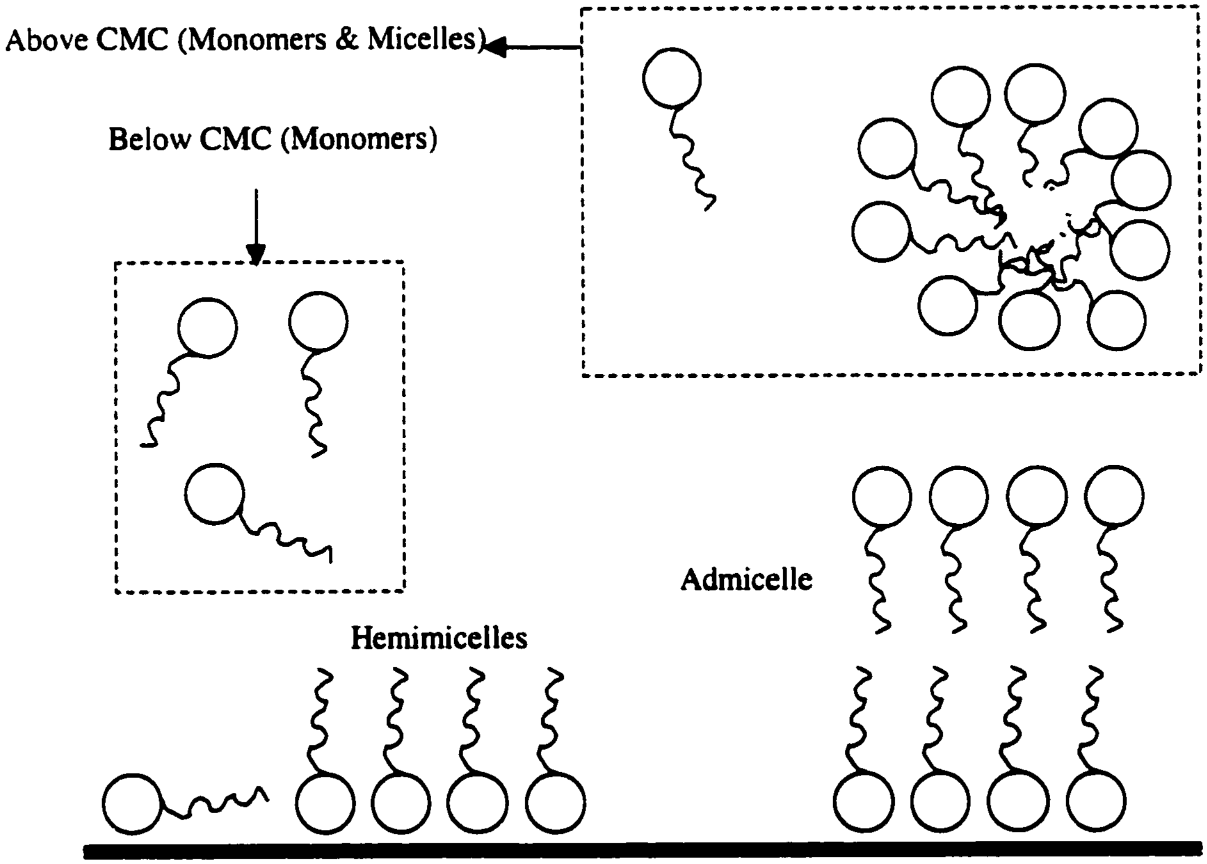
Figure 5 Classification and Structure of some typical Surfactants

The first is the solubilization, which is a result of micelle formation. The second is the mobilization of HOC, where the interfacial tension between the HOC and the soil phase is lowered by the surfactant.

5.3.1. Removal Mechanisms

5.3.1.1.Solubilization

The organic interior of micelles acts as an organic pseudophase into which organic contaminants can be partitioned. This phenomenon is called solubilization (Mittal 1977).



Source: Harwell J. H. Environmental Science and Technology, Vol. 26 No. 12 1992

Figure 6. Examples of Surfactant Micellization

Depending on the contaminants charge, solubilization can occur at three locations within a micelle: the hydrophobic core of the micelle, the polar surface of the micelle, and the transition region between the core and the surface of the micelle (Harwell 1992).

Non-polar contaminants such as octane are solubilized in the hydrophobic core of the aggregate, therefore the greater the size of the hydrophobic moity is, the larger the room for contaminant partitioning in. Amphiphilic contaminants such as hexanol, are solubilized in the transition region, therefore the use of surfactants with bulky head-groups may increase the sites for contaminant solubilization. The partition coefficient of the contaminants decreases with increasing concentration due to competition for available sites in the transition layer (Harwell 1992).

In an aqueous system, the extent to which a solute will concentrate in a micelle can be related to the octanol-water partition coefficient K_{ow}. In general, the larger the K_{ow} of a solute the greater will be its tendency to concentrate inside the micelle. Other factors which define the amount of organic compounds that is solubilized in micelles are surfactant structure, aggregation number, micelle geometry, ionic strength and chemistry of the solution, and temperature (Attwood 1983).

In supra-CMC systems, surfactant solubilization potential can be characterized by the molar solubilization ratio (MSR). The MSR represent the number of moles of HOC solubilized per mol of micellar surfactant (Attwood 1983). The MSR for a system of micellar surfactant and water can be calculated experimentally by calculating the slope of a plot of apparent HOC solubility versus micellar surfactant concentration. For hydrophobic compounds, it may be calculated as (Edwards 1991):

$$\boxed{MSR = (S_{HOC,mic} - S_{HOC,cmc})/(C_{surf} - CMC)} \qquad (15)$$

Where:

$S_{HOC,mic}$ = total apparent solubility of HOC in moles per litter in micellar solution at a particular surfactant concentration grater than the CMC;

$S_{HOC,cmc}$ = apparent solubility of a HOC compound in moles per litter at the CMC;

C_{surf} = surfactant concentration at which $S_{HOC,mic}$ is evaluated.

Surfactant solubilization potential (the amount of HOC, which partitions into surfactant micelles) can also be characterized in terms of the partitioning of the micelle-water partition coefficient. HOC are distributed between two pseudophases, a micellar hydrophobic pseudophase, which contain a solubilized HOC, and an aqueous pseudophase external to the micelles that consist of aqueous solution saturated with surfactant monomers, which contain a dissolved HOC. The equilibrium distribution of HOC between the micellar pseudophase and the aqueous pseudophase can be characterized by a partition coefficient K_m which represents the ratio of the mole fraction of HOC in the micellar pseudophase X_m,, to the mole fraction of HOC in the aqueous pseudophase X_a (Edwards et al. 1991).

$$\boxed{K_m = X_m/X_a} \qquad (16)$$

Values of K_m for several HOCs are provided by Edwards et al., (1991) and for by Valsaraj et al., (1977). These values change with surfactant dose as a result of changes in the aqueous-pseudophase concentration.

Although it is been found that below CMC limits there is no increase in solubilization of organic compounds (Edwards et al. 1991, Rouse et al. 1993, Edwards et al. 1994), Kile and Chiou (1989); Kile et al., (1990) found that significant solubilization enhancement can be achieved below the CMC. This fact is of significant importance because it minimizes the use of surfactants.

5. 3. 1.2. Mobilization

Mobilization has a greater potential than solubilization to increase the rate of remediation, however, uncontrolled movement of the free phase liquid can create a risk to the environment. In the saturated zone, the presence of HOC can be as a trapped phase NAPL. The interface between the water-wet soil surface and NAPL is characterized by NAPL-water interfacial tension (IFT). The forces that trap organic liquids are dominated by capillarity (adhesive-cohesive forces), which is proportional to the IFT at the HOC-water interface (Wilson et al. 1990).

The design of a surfactant system for mobilization of a trapped phase (NAPL) begins with designing a system with ultra-low IFT $<< 3\text{-}10\times10^{-5}$ N/cm (Rosen 1989). Typical values of IFT for NAPLs and water are $30\text{-}50\times10^{-5}$ N/cm) (Wilson et al. 1990).

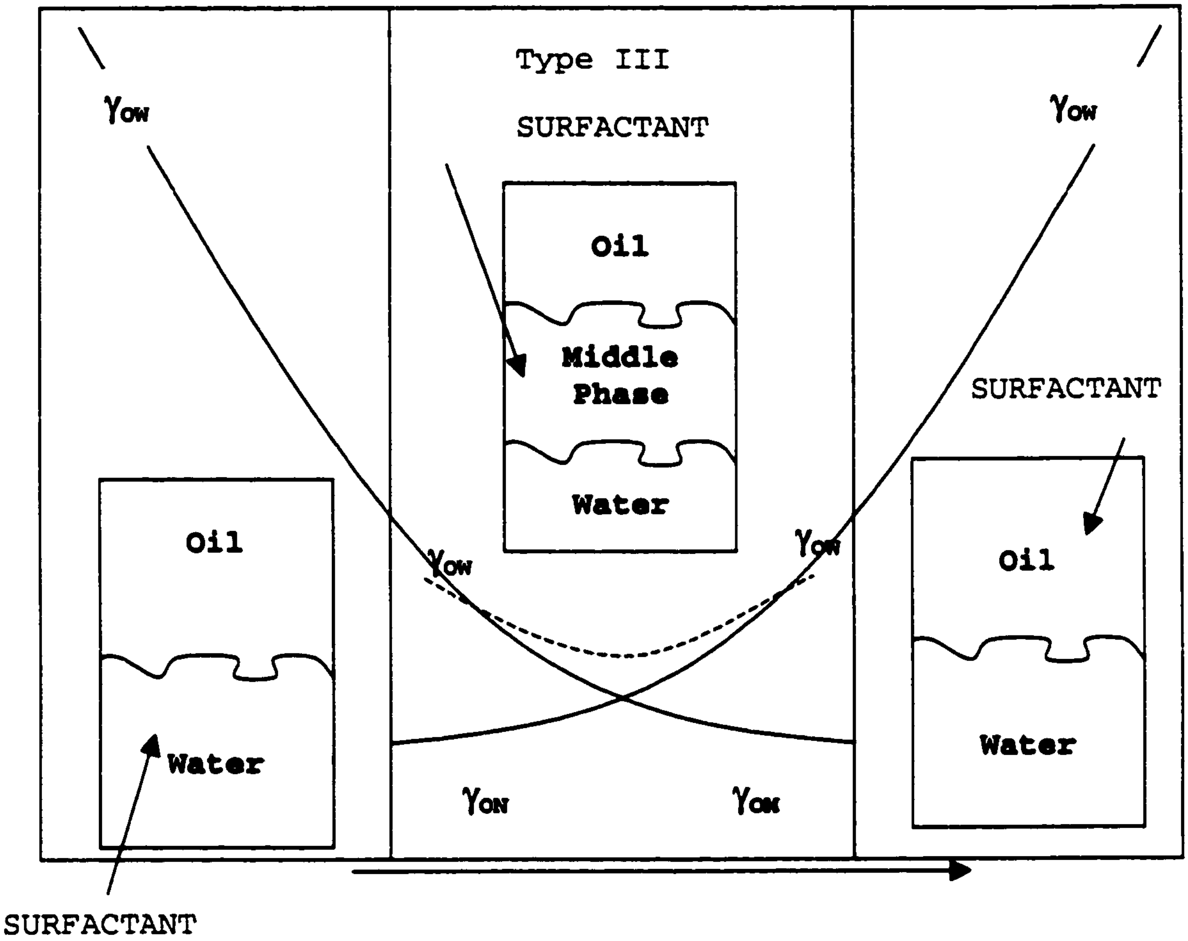
In order to attain an ultra-low IFT, the surfactant (or surfactant mixture) must be matched to the nature of the trapped phase (Rosen 1989). Often a surfactant system is developed to optimize the efficiency and stability of the system. Two method can be used to examine the appropriateness of a surfactant for specific contaminant: 1) the hydrophilic/lipophilic balance method (HLB), and 2) Winsor method.

HLB method - It is a scale, which can match surfactant structure to certain organic chemicals for optimum emulsification in water. The higher the HLB number, the more water- soluble the surfactant. However, the HLB method is not adequate for selecting surfactants because the impact of temperature and electrolytes on surfactant performance have not been quantitatively incorporated into the HLB method.

Winsor systems and parameter diagram - A relationship between IFT and a phase behaviour can define a stage where a middle phase micro-emulsion is formed (Winsor Type III micro-emulsion). Three types of Winsor Systems are illustrated in Figure 7. In the Type I system, the surfactant is too water-soluble and is in the form of oil-swollen micelles in the aqueous phase. In the Winsor Type II system, the surfactant is too oil soluble and virtually all the surfactant is found in the form of water-swollen reverse micelles in the oil phase. The Winsor Type III system is said to be balanced, the surfactant having nearly equal affinity for both phases. This form a new phase (a middle phase micro-emulsion) that contains all of the surfactant and large quantities of the organic chemical and water. A detailed review of these methods is provided by West and Harwell (1992).

5. 4. Surfactant Effects on Soils and Contaminants

The distribution of HOCs in the liquid/soil phase system is different in the presence or absence of surfactants. In the absence of surfactants, the dissolved concentration of HOC molecules is up to its water solubility limit. When equilibrium is reached between the dissolved HOCs and the sorbed HOCs onto soil, the distribution coefficient can be defined as the ratio of the number of moles of sorbed HOC per gram of soil to the number of moles of HOC in the aqueous phase per litre of solution (Figure 8).



Increasing Temperature (for polyoxyethylated nonionics)

Increasing Salinity for ionics

Decreasing Water Solubility (any series of surfactants)

Source: West and Harwell 1992.

Figure 7. Relationship of phase behaviour and IFT values

Where:

γ_{OW} – octanol-water IFT
γ_{OM} – octanol-middle phase IFT

γ_{ON} – octanol-NAPL IFT

$$\boxed{K_d = (n_{sorbed}/w_{soil})(v_{aq}/n_{aq})} \tag{17}$$

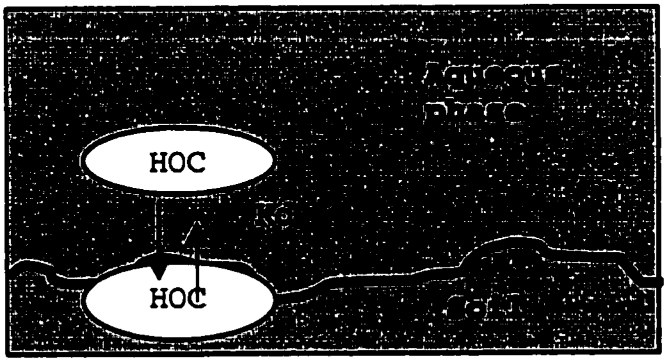
where

$n_{aq=}$ = equilibrium number of moles of HOC in solution ;

n_{sorbed} = equilibrium number of moles of HOC sorbed onto soil;

w_{soil} = weight of the soil in grams;

v_{aq} = volume of the aqueous solution in liters.



Source: Edwards et al., 1994. Surfactant Solubilization of Organic Compounds in Soil /Aqueous Systems

Figure 8 Two phase Soil/Aqueous Systems in the absence of Surfactant

In the presence of surfactant, the soil/water partition coefficient for HOC may differ from that of K_d, because of the increasing amount of organic carbon. The sorption of HOC is in relation with the organic carbon content of the soil (Karickhoff et al. 1979). Sorbed surfactants into the soil can effect the organic carbon content and thereby effect the HOC sorption. The change in the HOC sorption capacity can lead to a modified partition coefficient $K_{d,cmc}$ which is the ratio of the number of moles of HOC sorbed per gram of soil to the number of moles of HOC dissolved per liter of solution at the CMC.

$$\boxed{K_{d,cmc} = (n_{sorb,cmc}/w_{soil})(v_{aq}/n_{aq,cmc})} \qquad (18)$$

where

$n_{aq,cmc}$ = equilibrium number of moles of HOC in surfactant solution at the CMC;

$n_{sorb,cmc}$ = equilibrium number of moles of HOC sorbed onto soil at the surfactant CMC.

or

$$\boxed{K_{d,cmc} = Kd(S_w/S_{cmc})(f_{oc}^*/f_{oc})} \qquad (19)$$

where

f_{oc}^* = is the effective fractional organic carbon content of a solid after surfactant sorption;

S_w = is the HOC solubility limit in water (mol/L);

S_{cmc} = is the HOC solubility limit in monomeric surfactant solution at the CMC (mol/L).

The sorption of nonionic organic compounds from water to the surfactant phase has been well documented (Boyd et al., 1988; Valsaraj 1989; Smith et al., 1990; Holsen et al., 1991; Park and Jafe 1993). It has been found that the HOC sorption capacity for soils with initially low organic carbon content will be affected more by surfactants sorption than soils with high organic carbon content (Lee et al., 1989; Holsen et al., 1991). In a study of the adsorption of tricresyle phosphate (TCP) onto alumina and kaolin soils, Takimoto et al., (1998) found that the adsorption was enhanced with increase in dodecylbenzenesulfonate (DBS) adsorbed to the soil. They found that the adsorptive capacity of TCP on minerals coated with HA was less than if it was coated with DBS.

Edwards et al. (1994) obtained a linear relationship between sorbed HOC (phenanthrene) and its concentration in the bulk solution. This linearity could suggest that surfactant effects on HOC distribution can be characterized independently of HOC concentration.

The fractional mass of HOC in the bulk solution can either decrease or increase depending on surfactant dose. As surfactant dose increase from zero, there is an initial decrease in the fractional mass of HOC in the bulk solution (at low doses the sorbed surfactant enhance HOC sorption). For small supra-CMC and sub-CMC values of C_{surf}, the effect of sorbed surfactant on enhancing HOC sorption at low surfactant doses dominate the effect of the bulk solution surfactant in enhancing the solubilization of HOCs.

Seko, et al. (1998) studied the partitioning of HOC to sorbed surfactants. They evaluated the partitioning of two HOC, phenanthrene and naphthalene, to surfactant micelles from kaolinite. Their study showed that at low sorbed surfactant levels, K_{ss} (sorbed surfactant partition coefficient) was at their highest value and then decreased with increasing surfactant sorption densities. K_{ss} values for sodium dodecylsulfate (SDS) were always larger than the corresponding micellar partition coefficient (K_{mic}) values. For Tween 80, however, K_{ss} values were higher than K_{mic} values only at the lower sorbed surfactant densities. The overall results demonstrated that surfactant sorption to the solid phase can lead to an increase in HOC retardation where equilibrium conditions are applicable. It should be noted here, that this effect is desirable when the treatment objectives are to immobilize the HOCs by removing them from the liquid phase. However, the effects can be undesirable when the objectives are HOC mobilization.

Enhanced sorption of HOC at sub-CMC or low supra-CMC bulk solution surfactant concentrations may have important environmental implications for the injection of micellar nonionic surfactant solution into a sandy aquifer polluted by a hydrophobic organic contaminant. A low bulk solution surfactant concentration at the boundaries of an injected surfactant plum my strongly retard HOC movement at those boundaries. At the same time, the contaminant at the interior of the surfactant plume may be highly solubilized and mobile within surfactant micelles. Such a system would create an inherent barrier system around the focus of remediation, helping to prevent mobilized contaminants from migrating beyond the micellar margins of the surfactant plume.

Apart from effecting the physical properties of contaminants and soil organic carbon content, surfactants may affect the mechanical properties of the soil (Cabral et al. 1995). Fleureau et al. (1988) observed that two cationic surfactants significantly affected the swelling characteristics of a kaolinite soil. They also observed that the reduction in strength of the samples treated with anionic surfactants were more significant than in the case of cationic surfactants. The saturation of soil mass could also alter the soil properties. Compression occurs as a result of reduction in the suction forces or capillary forces acting within the soil pores (Holtz and Hilf 1961; Morgenstern, and De Matos 1975), a reduction of inter-granule friction forces (Jennings and Knight 1957), and destruction of cementation bonds (Booth 1975; Lamb and Whitman 1979; Lodbell 1981). Cabral et al. (1995) performed a test to evaluate the submergence and the effect of surfactant introduction on the compression of till samples. The test suggested that, considerable compression occurred as a result of submergence. Additional compression occurred as a result of anionic surfactant introduction. They did not observe a significant compression in the case of nonionic surfactant introduction.

5. 5. Surfactants Loss to the Soil

Apart from modifying the soil/water partition coefficient, the sorption of surfactants to the solid phase can reduce the effectiveness of the surfactant by reducing its active concentration. At very low concentrations, adsorbed surfactant monomers begin to aggregate and form micelle-like structures called admicelles or hemimicelles (Figure 5). Once these structures form on the solid surface, sorption of additional surfactant may rapidly increase until a complete bilayer of surfactant covers the solid surface. The tendency of surfactants to form admicelles or hemimicelles is dependent on the interaction between the hydrophillic moiety of the surfactant and the solid surface. When there is an attractive interaction between the head group and the solid surface, such as with cationic surfactants and clays, a complete bilayer of surfactant may cover the surface. However when there is a repulsive interaction, as with anionic surfactants and clays, sorption may be very low. Sorption may be either high or low depending on surfactant solubility. The higher the water solubility of the surfactant, the lower is its tendency for adsorption. For technological purposes, it was demonstrated that a portion of surfactant was lost to the soil (Taha 1996).

The strength by which surfactants adsorb to the solid surface are controlled by several factors:

1- the chemical nature of the surfactant (anionic, cationic, nonionic);
2- the size of the chain and the level of branching;
3- the nature of the solid surface, its charge density and sign, surface area, CEC, type of functional groups, octanol-water partition coefficient;
4- the type and strength of the interactions between the solid surfaces and the contaminants;
5- the characteristics of the pore fluid, such as pH, electrolyte and surfactant concentration, temperature, etc.

Surfactant adsorption to solid surfaces is mainly due to three mechanisms:

1- attractive-repulsive interactions between the hydrophillic group and the surface's functional groups (electrostatic, complexation, and hydrogen bonding);
2- attraction of the hydrophobic group by the surface;
3- lateral interactions between adsorbed surfactants (Harwell 1992).

The sorption of surfactants onto soils has been investigated by several researchers (Hand and Williams 1987; Di Toro et al., 1990; Harwell 1992; Rouse et al., 1993; Sun and Boid 1993). Sorption of non-ionic surfactants onto soil inorganic surfaces can be found in several publications (Rosen 1989; Clunie 1983; Bohmer et al., 1990; Somasundaran et al., 1990). The sorption of nonionic surfactants onto the liquid organic phase can be found in the publications of Crook. et al., (1965). A greater sorption capacity of HOC on cationic surfactants was related to their affinity to soil humic matter (charged surfaces) (Lee et al., 1989), and for anionic surfactants to the positively charged surfaces (Holsen et al., 1991). The lower sorption to humic matter is attributed to its high polar functional group content (Lee et al. 1989) or it being a mixture of both polar and non-polar functional groups. The major difference between non-ionic surfactant and humic matter molecules is that the polar and nonpolar portions of the individual surfactant molecules are segregated in space, whereas humic matter contains many polar chemical groups reported to be interpressed with and/or attached to otherwise non-polar humic regions (Stevenson1982; Wershaw 1986).

Sun and Boid (1993) found that the solute partition coefficient of non-ionic organic compounds between water and petroleum sulfonate-oil surfactant emulsions in the solution were slightly higher than the partition coefficient between water and soil sorbed surfactant, they concluded that the surfactant phase sorbed onto soil is nearly as effective as the organic phase of the emulsion. Edwards et al. (1992) showed that 97% of non-ionic surfactant, (alkylphenol ethoxylate surfactant C8PE9.5) of sub-CMC aqueous phase concentration, was sorbed onto soils. Park (1995) conducted an experiment on two different soils, sandy soil with low organic carbon content and topsoil with higher organic carbon content, using phenanthrene as a nonionic organic contaminant. The results showed that soils having a higher organic content exhibit a stronger uptake of the anionic surfactant. The results also showed that the transfer of phenanthrene from soil to the treated oxide is faster for soil with low organic matter content. The recovery rate for soil specimen 1 and soil specimen 2 was 99% and 98% respectively. Evaluating the sorption of non-ionic surfactant on hydrophillic surfaces such as spherosil silica sol, Somasundaran et al. (1991) found that by increasing C_{surf} one order of magnitude higher than the CMC concentration, the amount of surfactant sorbed to the soil was 35 times the amount sorbed at the CMC concentration. Doren et al. (1975) listed that in concentrations 2 times less than the CMC, the sorption of Triton X-100 on HCl washed sand was 4 times higher than at the normal CMC concentration. Contradictory results were obtained by Edwards et al. (1994), who observed that an increase in Triton X-100 concentration, two orders of magnitude above the CMC led to a 15-fold increase in sorption of non-ionic surfactant on Lincoln fine sand. For Morton soil with 0.96% organic carbon content the results were substantially different. Triton X-100 attained a maximum sorption value at the CMC (Liu et al., 1992). Based on numerous observations by Clunie et al. (1983), results obtained by Edwards et al. (1994) and Somasundaran et al. (1991), it was concluded that sorption of non-ionic surfactant molecules on silica sand initially occurs as the hydrophillic moieties of the surfactant molecules undergo relatively strong interaction with the silica surface through hydrogen bonding. At higher concentrations the hydrophobic moieties of the sorbed surfactant molecules project out into bulk solution. A mutual attraction between adjacent hydrophobic moieties is predominant process at high concentrations. This concept was supported also by Doren et al. (1975) and others (Bohmer et al. 1990).

5. 6. Surfactant Selection

A careful selection of surfactants and their concentrations is required to prevent soil colloid dispersion and to control the size of the micelles. These phenomena can lead to clogging of the soil pores and movement of the contaminated solution from the contaminated zone (API, 1985; Nash and Traver 1986). In addition to particles dispersion and soil clogging, the toxicity character of the surfactant, its ease of removal from the subsurface, adsorption on the soil surface, and dispersion of soil colloids, are among the factors, which must be accounted for. Therefore, the use of appropriate surfactants in soil remediation is an issue of greate concern.

Choosing a surfactant usually follows certain criteria, among them are the cost of the surfactant, their toxicity, physical and chemical properties, the relationship between the surfactants and the interfacial phenomena in the medium of concern, and finally the relationship between surfactant properties and its behavior in the medium.

Although surfactant manufacture's provide characteristic data for their products such as chemical formula, boiling point, freezing point, specific gravity and CMC, these data are not sufficient for surfactant evaluation. Taha (1996) suggested the use of the following criteria:

I- Toxicity - Most surfactants are toxic, but at the concentration in which they are usually found in the lakes and rivers they are not toxic (Swisher 1987). Toxicity data supplied by the manufacture's in the MSDS (as very harmful, harmful, or less harmful) are not sufficient for detailed evaluation of the surfactant in question. Although some surfactants have been approved by U. S. FDA (Food and Drug Administration) and the EPA, the vast majority of them have not been evaluated form the point of view of their hazardous nature.

II- Cost - Because the cost of any remedial action is a crucial element in the treatment process, the cost of surfactants is a principle criterion. According to the surfactant consumption in the US, anionic surfactants consist of 73% of the US consumption followed by 21% for nonionics and 6% with cationics (Taha 1996).

III - Aqueous solubility - Because surfactants are prepared in water solutions, their solubility in water is one of the fundamental aspects in any remedial action.

IV - Organic solubility - Surfactants are introduced to provide a preferable hydrophobic environment for absorbed organics to the soil (solubilization) and at the same time mobilizing these organics, which facilitate their transport by EO flow and ionic migration.

V - Surfactant losses - The existence of hydrogen bonding groups on the soil surface and the fact that the soil surface is negatively charged render cationic surfactants less efficient because of their loss to soil surface. Nonionic surfactants also showed high affinity to soil particles due to hydrophobic sorption (Edwards et al. 1994). Another pathway of surfactant loss is their decomposition as a result of electrode reactions, precipitation and crystallization. Temperature may also play an important role in surfactant looses (precipitation and crystallisation). The temperature at which the solubility of ionic surfactant is equal to the CMC of the surfactant is known as the Kraft point. In remediation actions, the temperature should be kept above the Kraft point. In ground water systems the temperature can drop below the Kraft point and that can cause the surfactant to lose some of its concentration due to precipitation and crystallization. Therefore a technique of lowering the Kraft point of a surfactant structure to make it more amenable to ground water conditions is usually adopted. This technique is done by branching the hydrophobic moiety, increasing the bulkiness of the hydrophillic moiety, or by using a co-surfactant.

VI - Potential for EK transport/ migration transport – Under an electrical gradient cationic micelles will be moving in the same direction as the EO flow. Anionic micelles will migrate in an opposite direction to the EO flow. Nonionic micelles will only flow by EO (Taha

1996).

VII – CMC - It indicates the amount of the surfactant to be used. The lower the CMC, the less surfactant is needed. Nonionic surfactants have a lower CMC, followed by anionics, and cationics (James et all. 1987). Groves (1987) showed that the CMC is inversely proportional to the chain length of the hydrophobic group.

VIII – Biodegradability - Surfactants have to be biodegradable in the environment in order to eliminate their possible adverse effects. However, they also have to resist biodegradation for a certain time to maintain their effectiveness and possible recycling. Straight chain surfactants are more biodegradable than branched chain. Nonionic surfactants are more resistant to biodegradation.

IX - Co-surfactants - The use of surfactants can be coupled by the use of co-surfactants. These products are introduced to the soil to improve the remediation process by reducing the surfactant adsorption to the soil or to improve the overall performance of the process. Inorganic salts and/or bases, and polymers are used as co-surfactants.

5. 7. Past Research Efforts

5. 7. 1. Solubility Enhancement

The effects of surfactants on enhancing the apparent solubility of PAHs has been a topic of investigation by various researchers since 1934 (Edwards 1991; Ellis et al., 1987, Vigon and Rubin 1989; Kile and Chiou 1989; Liu et al., 1991). The effect of several nonionic and anionic surfactants on the solubilization of anthracene, phenanthrene, and pyrene to soil has been investigated (Liu et al., 1991; Rittman and Johnson 1989). Klevence (1950) studied the solubilization of benzene and 12 different PAH compounds in potassium laureate solution. Edwards et al., (1992) evaluated the effect of 8 different nonionic surfactants on the solubilization of pyrene. The reported results showed that the best performing surfactants were nonionic ethoxylate surfactants. Sodium dodecyl benzene sulfonate surfactant has been ineffective in dissolving pyrene. The author reported that in a soil aqueous system, the apparent solubility of HOCs in bulk solution in the presence of non-ionic surfactant is a linear function of surfactant dose. The author suggested that, as the number of micelles in the bulk solution increases, there is a linear partitioning of HOC between the soil and aqueous pseudophase and between the aqueous pseudophase and the micellar pseudophase (Edwards et al., 1992a). Edwards and Luthy (1992) noted that in a monomeric solution the increase in apparent solubility is almost 2 to 3 orders of magnitude for PAHs. On the other hand Kile and Chiou (1989) noted that the solubility of DDT in a solution of non-ionic surfactant C8PE9.5 at a surfactant concentration equal to the CMC is about 1 order of magnitude greater than that of DDT in pure water.

Roy et al. (1997) used natural surfactants derived from the plant "Sapindaceae" to solubilize hexachlorobenzene and phenanthrene. Their results showed that, a 10% natural surfactant solution could increase the solubilization of HOC several hundred times. Their results also confirmed the general trend of linear proportionality for the solubilization of hydrophobic compounds by a surfactant above CMC. The authors performed a comparison between commercial (synthetic) surfactants and natural (biological) surfactants for their efficiency in HOC solubilization on the basis of grams of surfactants required in 1 L of water to solubilize 1 mg of organics. Soil flushing experiments using natural (biological) surfactants proved to be 20 to 100 times more efficient than using water as a flushing agent. However, the amount of HOC recovered as a percent of initial contamination was 0.4% and 4% using 0.5% and 1% surfactant solution (Roy et al. 1997).

Thangamani et al. (1994) performed a comparison between the solubility enhancement, of synthetic surfactant "alkyl benzene sulfonate" and biological surfactant (rhamnolipid) for hexadecane. It was found that in two-phase systems (organic and aqueous phase or soil and aqueous phase), the biological surfactant was capable of solubilizing about 20 times more hexadecane than the synthetic surfactant. In a three-phase system, (soil/organic/aqueous) the biological surfactant showed 23 times higher solubilization capability of hexadecane than synthetic surfactants. Wittle and Pamukcu (1993) used sodium dodecylebenzene sulfonate to enhance the transport of chlorobenzene, hexachlorobenzene and phenol.

5. 7. 2. Mobility Enhancement

The use of surfactants to wash contaminants such as petroleum products and other organic contaminants was a subject of numerous laboratory studies. In studies by the EPA (EPA/600/2-85/129,1985) Murban crude oil, polychlorinated biphenyl (PCB), pentachlorophenol (PCP), were washed using two surfactants in batch and column experiments. Studies by the American Petroleum Institute, publication No.4390, 1979 and 1985, reported that gasoline was washed in a mixture of 2% each of nonionic and anionic surfactant in water. Nash and Traver (1986) used a 2% aqueous solution of each surfactant (Hyonic PE90/Richonate YLA) to remove aromatic and chlorinated hydrocarbons and petroleum products from soil in batch, column and field experiments. A group of alcohol ethoxylate surfactants was found to be the most effective among 10 commercial surfactants for washing an oil from sandy soil (Abdul et al. 1990a). Several factors were evaluated in this study including the minimum surface tension of the aqueous surfactant solution, the extent of soil and oil dispersion and the extent of washing oil from the soil.

Abdul et al. (1992) conducted a pilot test on a fill soil in sites contaminated with PCBs and oil. During 70 days of washing with non-ionic ethoxylated alcohol surfactant (Witconol SN70) with 0.75% aqueous solution, a removal efficiency of 10.7% for PCBs and 10.5% of oil was achieved after 5.8-pore volume.

Abdul et al. (1990) used 0.5% ethoxylated alcohol surfactant to wash automatic transmission fluid. Their results indicated that 80% removal could be achieved in comparison to 23% removal by washing.

Aronstein et al. (1991) conducted a study on the effect of low concentration surfactants on the release of contaminants from soil. The results showed that the use of anionic surfactants did not enhance the desorption of phenanthrene and biphenyl in Lima silt loam soil with 7.6% organic matter. Phenanthrene and biphenyl desorption was affected by using nonionic surfactants. For Edwards muck soil with 32.9% organic matter content, neither non-ionic nor anionic surfactants resulted in contaminant desorption. The study concluded that, nonionic surfactants were able to stimulate the degradation of phenanthrene.

Tran and Gale (1992) used sodium dodecylsulfonates (SDS) to remove hexachlorobutadiene (HCBD). They used SDS concentration of 8 mM to 20 mM. At 8 mM which is the CMC of SDs, little removal or migration for the HCBD was observed.

Increasing the concentration to 20 mM resulted in an improvement in migration improvement. At a bench scale test, the authors used a cationic surfactant (cetyltrimethylammonium chloride CTAC). They showed an ineffectiveness of the treatment at the CMC concentration and 20 times above.

Randi, et al., (1998) used an anioinic surfactant (steol CS – 330) to mobilize TCE – DNAPL form sand in column tests. The authors showed that mobilization was maximized when surfactant foam was injected in a pulsed operation.

5. 7. 3. Mineralization Enhancement

In addition to the solubilization and mobilization effect of surfactants on HOCs present in soil, it has been discovered that their presence can enhance the microbial activities in the soil which can lead to the mineralization of HOC. Several researchers reported the effect of surfactants in enhancing microbial activity in soils. Rittman (1989) observed a stimulation of microbial degradation of lubricating oil in soil in the presence of a surfactant. Aronstein et al. (1991) have reported that low concentration of surfactants may promote the mineralization of sorbed aromatic compounds. Laha and Luthy (1991) have observed complete inhibition of phenanthrene mineralization by selected nonionic surfactants at supra-CMC concentrations in soil-water systems. Jahan (1993) examined the effect of four different nonionic surfactants (Triton X-114, Corexite 0600, Tween 40 and Brij 35) of a low concentration (25 mg/l), on the biodegradation of phenanthrene coated sand. His results showed that Twin 40 and Corexite 0600 enhanced phenanthrene degradation which was also observed by Jahan (1993). The observed enhancement rate decreased with time following the decrease in soluble substrate availability. The enhanced mineralization is attributed to the enhanced solubilization of phenanthrene in the presence of surfactants, which make it more bioavailable

Edwards (1992) studied the mineralization of phenanthrene in a soil aqueous system as a function of time with varying concentrations of nonionic surfactant Triton X-100 (C8PE9.5). The study found that at sub-CMC doses, the nonionic surfactant did not enhance the bioavailability and subsequent mineralization of phenanthrene. However, at surfactant concentrations above 0.05% (v/v) the microbial mineralization of phenanthrene was completely inhibited. The inhibition was related to the toxic effects above certain concentration, preferential use of surfactant as a substrate, lowering of aqueous phase PAH concentration due to solubilization, or an interference of surfactant with microbial metabolic processes. However, the toxicity effect was shown to be reversible when supra-CMC surfactant doses were diluted to aqueous concentrations less than the CMC. Schmidt et al. (1989), and Martin et al. (1991) reported a relationship between the microbial degradation of certain hydrocarbon contaminants and simultaneous production of bio-surfactants. They reported that the enhanced production of microorganisms was due to their growth on certain insoluble carbon substrates including alkane hydrocarbons and vegetable oils (Cooper 1984). The application of surfactants in contaminant remediation is not limited to its use in soil. Contaminated water also could be treated using surfactants. The treatment of water contaminated with nonionic organic compounds using surfactant treated oxides has been documented in several papers (Park and Jaffe' 1993; Scamehorn and Harwell 1988; Valsaraj 1989 and 1992). Studies showed that at pH values of most natural waters, oxide particles have a positively charged surface, this positive charge will attract anionic surfactant from solution into their surface creating a hydrophobic layer (non-polar phase), which acts as a partition medium for non-ionic organic contaminants (Smith et al. 1990; Smith and Jaffe 1991).

The use of surfactants in hydraulic recovery of groundwater has been studied by Abdul et al. (1990), Edwards et al. (1991), West and Harwel (1992), Panel et al. (1993). The Texas Research Institute (between 1979 and 1985) achieved 60% removal of petroleum from a 3-D model and 70% removal from a 2-D model and 80% removal from a 1-D model using 2% mixture of anionic and nonionic surfactant. Ellis et al. (1985) achieved 90% removal of PCBs, chlorinated phenols, and petroleum hydrocarbons by using a 1.5% surfactant solution.

The review of electrokinetic and surfactants as treatment technologies point to certain facts shared almost by all experiments. The vast majority of conducted tests were lab scale tests conducted on artificial soil, mostly kaolinite. In addition, most studies have been performed on one-dimensional models and no experimental data are available to evaluate the performance of two-dimentional or three-dimensional systems (Alshawabkeh et al. 1999). Another fact is that reports concerning the combination of both technologies (EK & surfactants) for soil decontamination are limited.

6. RESEARCH OBJECTIVES

Based on the literature review and previous research performed in the Environmental Engineering Laboratory at Concordia University, the research objectives were formulated as follows:

General objectives:

The development of a new sustainable electrokinetic system in pilot scale applications, for the removal of HOC from clayey soils with the incorporation of surfactants as an enhancement agent for solubilization and mobilization of hydrocarbons

Particular objectives:

Particular objectives were as follows:

- regulate the pH of the soil in the cathode area;
- prevent carbonate precipitation near the cathode;
- prevent anode oxidation;
- avoid electrochemical decomposition of the surfactant in the anode;
- provide up-scaling processes for the system;
- design of new sustainable electrodes based on the up-scaling process;
- verify the HOC remediation system design performance in a pilot scale.

Four tests were carried out in order to achieve the above mentioned objectives;

1) small scale test, 2) intermediate scale test, 3) preliminary tests (PT) and 4) pilot scale test.

6.1. Phase I (Small scale tests):

Objectives of the tests performed at this phase were:

1) to evaluate the influence of electrodes influence on the remediation process;

2) to define the problems associated with EK phenomena;
3) to determine the best arrangements of barriers in order to optimize the area of surfactant introduction;
4) to evaluate the soil response to surfactant introduction from the point of view of:
    a) pH distribution; b) water content distribution; c) voltage distribution.
5) to determine the best arrangements of barriers in order to optimize the area of surfactant introduction.

6.2. Phase II (intermediate scale test)

The derived conclusions from phase I where applied to phase II. In this phase two major issues were addressed: a) the up-scaling of a new electrical system, and b) system performance regarding different washing liquids. In this context, the objectives of this phase were as follows:

1) to evaluate the system response upon increasing the distance between the electrodes;
2) to design a washing system close to the cathode;
3) to define the influence of electrode washing on the system chemistry;
4) to define the impact of washing liquids: a) water; b) surfactant (above CMC).

6.3. Preliminary Tests (PT):

This phase was designed to address the following issues:

1) to determine the most appropriate method to measure phenanthrene concentration in the soil;
2) to determine the methodology required for proper contaminant introduction into the soil;

3) to define the surfactant type, concentration, and its pH for use in phase III;
4) determine the effects of different pH solutions on soil pH.

6.4. Phase III (Pilot scale test):

Results from phase II served as a foundation to design a full scale of multi-functional electrodes for the pilot scale test. This design was carried out with the following considerations:

1) effective supply of surfactant upon appropriate attachment to washing systems;
2) maximization of phenanthrene removal;
3) design simplicity and feasibility of formulation in the field;
4) resistance to soil clogging by fine particles;
5) chemically resistance and the use of an inexpensive material;
6) verification of the sustainable electrokinetic system for PAH removal.

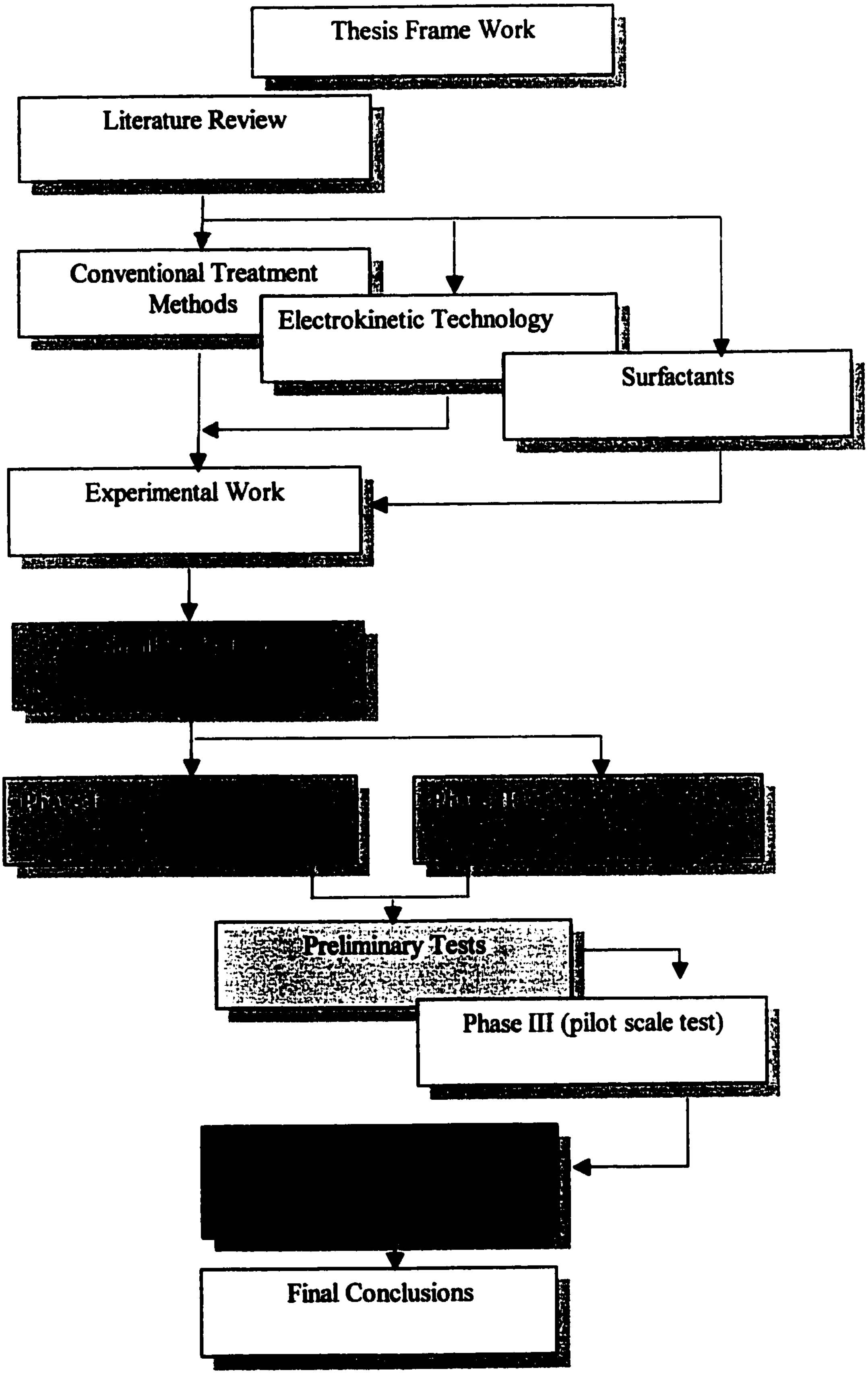
An adequate and proper surfactant supply system with an efficient washing system were thought to be primary elements for a new development in contaminant removal, which is the aim of any remediation effort.

NEW CONTRIBUTIONS

1. The electrokinetic removal of non polar compounds (phenanthrene) was successfully demonstrated (50 to 90%) on the pilot scale;
2. The amphoteric surfactant, applied upon electric field, showed successful removal of PAH (diesel fuel and phenanthrene) from soil;
3. A new method for soil pH control during *in-situ* electrokinetic contaminant removal, respecting all aspects of the sustainable development, was created;

4. The up-scaling method for electrokinetic systems for soil remediation from non polar PAHs was investigated, optimized and successfully described;
5. The transport of amphoteric surfactant micelles in soil was monitored by the continuous measurement of electrical parameters;
6. The original multi-functional removable electrodes for electrical potential supply and modifier injection were designed and optimized on a pilot scale;
7. The original multi-functional removable electrodes for electrical potential supply and contaminant extraction were designed and optimized on a pilot scale;
8. The surfactants were transported under electrokinetic phenomena within natural, randomly collected clayey soil.

Figure 9 Thesis Frame Work Scheme



7. METHODOLOGY

Figure 9 describes the framework scheme used to achieve the above-mentioned objectives. The chart shows that the experimental work consisted of four major components designated as, phase I, phase II, batch tests phase, and phase III.

Phase I – tests were conducted on small-scale cells with an 8-cm distance between its electrodes. The tests were designated as Test-I-6, Test-I-7, Test-I-9 and Test-I-11.

Phase II – was conducted using larger cells, where the distance between the electrodes was 16 cm. The experiments were designated as Test-II-8, Test-II-10, and Test-II-12.

Batch tests phase - this phase was carried out to provide introductory information needed for future development of phase III. The information obtained helped to determine the type of the surfactant for use and its molar concentration. In addition, it helped to develop a methodology for measurements of phenanthrene concentration in the soil.

Phase III – this phase represented an optimization phase for the laboratory scale tests. It was conducted on a pilot scale cell with 50-cm distance between newly designed electrodes.

The following protocols were prepared for the above mentioned phases in which field conditions were simulated regarding three major elements:

- Soil, where natural soil was used as a test soil
- Cells, where an open top system design was used in all tests
- Electrodes, where a new design was directly applicable in the field

Phase I - this phase was designed to evaluate the introduction of permeable zones in different locations and the effect of a given location on the pH profile in the soil.

Phase II – in this phase the following issues were addressed:

1- process scaling-up and its effect on

- electrical parameters
- pH profile
- Permeable Zone locations

2- Evaluation of the system performance regarding different surfactant systems;

3- final set-up design performance

Phase III – in this phase the following issues were addressed:

1- pilot system set-up e.g. (contaminant introduction)

2- evaluation of two different electrode/barrier designs

3- system performance upon up-scaling to the field dimensions

7.1. Soil description and preparation:

As it was stated above, natural soil has been chosen as a fundamental base for all testing. Phase I and II were conducted using soil designated as 6-4 with general characteristics described in Table 5. Phase III was conducted on a soil designated as 6-5 (Table 6). The chosen soils underwent a series of preparation steps aimed for their use in electrokinetic experiments. The following is a brief description of the soil preparation:

1. Wet core soil samples obtained from a geotechnical company (Inspec-sol) were shredded on a large screen mesh to reduce its size for later drying and crushing;
2. Shredded soil samples were then air dried for 100 hours and crushed in a cylindrical rotor equipped with graphite bars. The crushed soil was then sieved through a No. 200 mesh;

3. The portion remaining on the sieve underwent a repeated crushing until fine-grained material was obtained.
4. The crushed soil was then extensively mixed to ensure its homogeneity and representative samples from the mixed soil were taken for soil analysis.

Table 5 Soil 6-4 Characteristics

Metal content atomic adsorption	**Ca**	**Cr**	**Cu**	**Fe**	**K**
mg/kg	9315.70	100.5	77.38	61269.91	14897.72
Metal	Mg	Na	Ni	Pb	Zn
mg/kg	27887.62	218.95	44.20	31.11	142.8

CEC	**Conductivity** **Ms/cm for 1:10 Soil/water (g/ml)** Hesse, P. A. methode 2510	**Total oil & grease mg/kg** infrared analysis	**Mineral oil & grease mg/kg** infrared analysis	**TOC** Weight loss	
				Organic carbon %	**Organic matter** %
21	**0.28**	**28.55**	**24.53**	**1.4**	**2.41**

Phosphorous **%** Hesse, P. R. method 4300 p	**Ammonium** **mg/L** Potentiometric method	**HCO_3** **mg/L** volumetric acid titration	**Cl** **mg/L** Hesse, P. R. 4500 Cl-B method	**SO_4** **mg/L** Total sulphur
0.011	1.9	61	141.80	2

Quartz x-ray diffraction	**Feldspar** x-ray diffraction	**Calcite** x-ray diffraction	**Dolomite** x-ray diffraction	**Illite** x-ray diffraction	**Chlorite** x-ray diffraction	**Kaolinite** x-ray diffraction
%	28	4	3	15	5	4

Table 6 Soil 6-5 Characteristics

Soil Mineralogy	**Metals Content**	**Others**
• Quartz 4.6 %	**• Fe : 273 mg/kg**	**• Carbonate Content 4.5 %**
• Feldspar 21 %	**• K : 176 mg/kg**	**• Organic Matter 1.3 %**
• Dolomite 3.2 %	**• Ca : 250 mg/kg**	**• CEC 21 meq/100 g**
• Amphibole 6 %	**• Ni : 31 mg/kg**	**• Specific gravity 2.75**
• Illite 49.8 %	**• Pb : 9 mg/kg**	**• SO_4 : 0.6 ppm**
• Chlorite 14.1 %		**• pH : 7.60**
• Kaolinite 1.3 %		

Note: Soil characterization methods were based on Hesse, P. R. "Text book of soil chemical analysis.

7.2. Description of installation:

7.2.1. Electrokinetic cells:

Several parameters were involved in choosing the appropriate electrokinetic cells, which were: 1) reflecting field conditions, 2) cost. Unlike the conventional Plexiglass cylindrical cells, which were used in the majority of electrokinetic research, the cells, which were used in these tests, were chosen to have a top open structure. Therefore, they allowed for direct access to the soil, easy sampling and permitted direct measurements of electrical parameters. It was required that the cells were also easy to handle (light and small) and chemically resistant, (tolerating different chemicals like the hydrocarbons and surfactants). Considering these aspects, polyethylene cells were chosen for all tests. Three different cells were used in each phase and each cell's dimensions were as follows:

Phase I: length = 12.25 cm, width = 5.3 cm, and depth = 5.3 cm.

Phase II: length = 23.5 cm, width = 5.3 cm, and depth = 5.3 cm.

Phase III: length = 65 cm, width = 38 cm, and depth = 16 cm.

7.2.2. Electrodes

7.2.2.1 Electrode filters

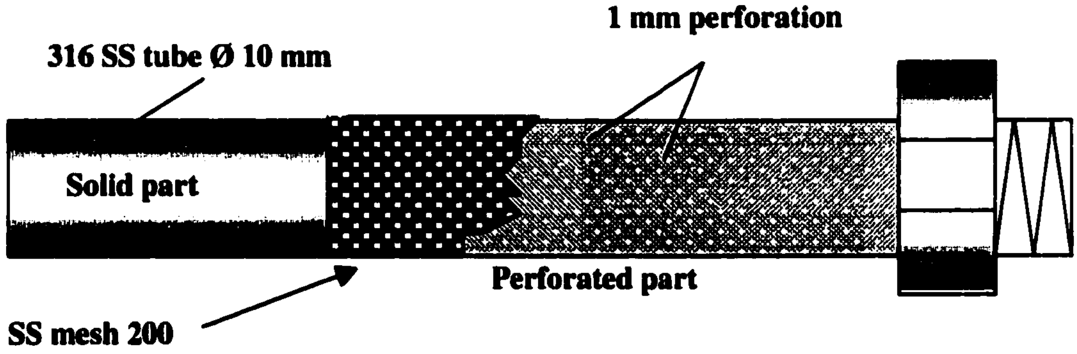
Electrode filter design was carried out with a consideration that it could be upgraded for field conditions. Therefore the following requirements were considered:

1. Maximizing of treatable (extracted) liquid removal by maximizing the surface area in contact with the soil;
2. Minimization the contact resistivity by increasing the contact surface with the soil;
3. Avoid clogging by soil particles;

4. Design simplicity and effectiveness;
5. Chemical resistance;
6. Possibility to introduce conditioning liquids and collection of electrokinetically transported liquids

Based on the above-mentioned requirements, stainless steel seamless perforated tubes (type 316) were chosen as electrodes. To prevent soil particle removal and electrode clogging, stainless steel mesh (size 200) was used as a filter surrounding the electrodes. Open-end electrodes were chosen as an optimal design, which helped for the injection of the conditioning liquid in the anode and the extraction of treatable cathode liquid. Figure 10 illustrates electrode filter designs used in the three phases.

Electrode design in phase I and II



Electrode design used in phase III

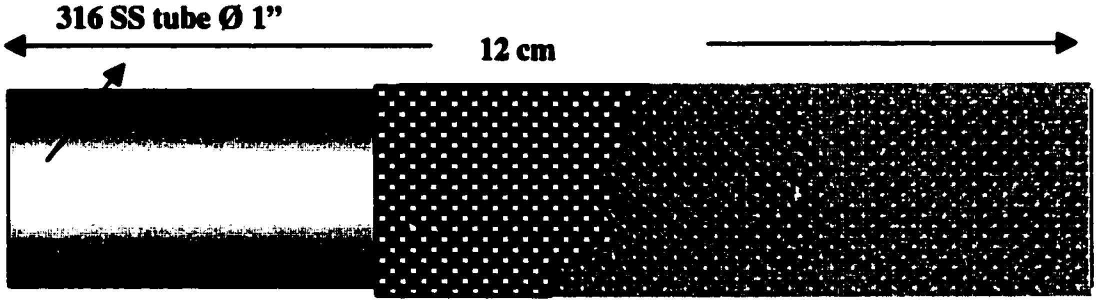


Figure 10 Electrode Design used in Phase I, II, and III

7.2.2.2. Probe electrodes

Electrical parameters along the distance between the anode and the cathode, were monitored during the tests using special probe-electrodes. These electrodes were inserted into the soil to a certain depth (3 cm). However a portion was maintained 1.5 cm above the soil surface. Voltage distribution between the electrodes was monitored by direct measurements of the potential value between electrode filters and each probe-electrode. The distance between each probe was 1cm.

The choice of the probe material was based on certain requirements:

1. Small contact resistivity;
2. Low oxidation;
3. Small internal resistance;

Platinum probe-electrodes proved to be the best in fulfilling the above-mentioned requirements, however, due to their high cost and the difficulties associated with their handling due to their softness, silver probes were used as an adequate alternative. Figure 11 illustrates probe-electrodes set on a Plexiglass base.

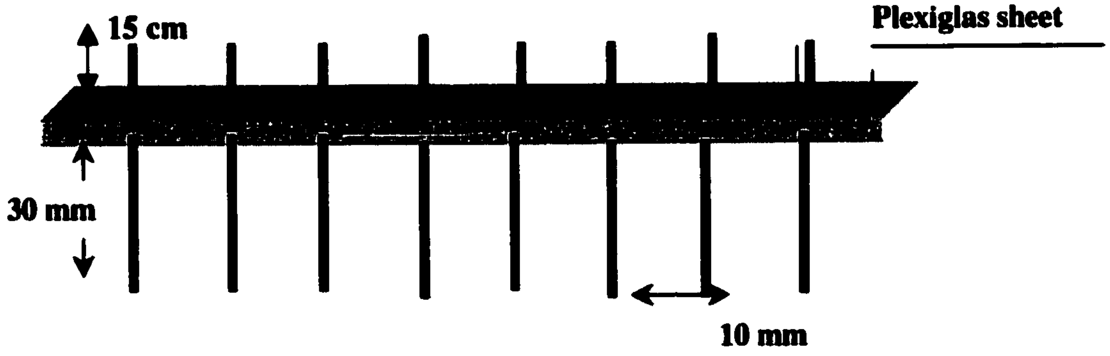


Figure 11 Probe Electrodes placed on a Plexiglass Holder

7.2.3. Electrical Equipment

A TES-6230 power supply, which can supply a voltage up to 10 V and amperage up to 1A, was used to supply a direct current to the cells. For electrical measurements, a multimeter (TES-2712) was chosen to provide an accurate reading up to 1 mV and 0.0001 amperes.

7.2.4. Conditioning Liquid Supply System (CLSS)

In the design of the Conditioning Liquid Supply System (CLSS) the following requirements were considered:

1. No head pressure;
2. Continuous liquid supply;
3. Controlled liquid level;

Therefore, a conditioning liquid reservoir was connected to the cell through a hydraulic valve. This solution proved to be simple and at the same time fulfilled the above-mentioned requirements. Flexible and chemical resistant tubing (Nalgene) were used in the system. The hydraulic valve permitted to control the liquid level in the soil so that no overflow would occur during the test. The same valve system was used to supply the surfactant to the soil. Figure 12 describes the system schematically.

7.2.5. Surfactant Supply System

Supplying surfactant to the electrokinetic cell was done using the system described in section 7.2.4 with slight modifications. The presented system used a perforated teflon tube instead of the SS tube to avoid its interference with the electrical field and prevent a chemical reaction between the surfactant and the supplying tube. Delivered surfactant entered the porous area (fine sand) called the "Barrier" prior to its transport through the cell. The perforated area ensured a homogeneous distribution of surfactant on the entire soil section. For practical reasons and to support the sand, a rigid PVC net was used as a confinement compartment for the sand. Figure 13 illustrates this part of the electrokinetic cell.

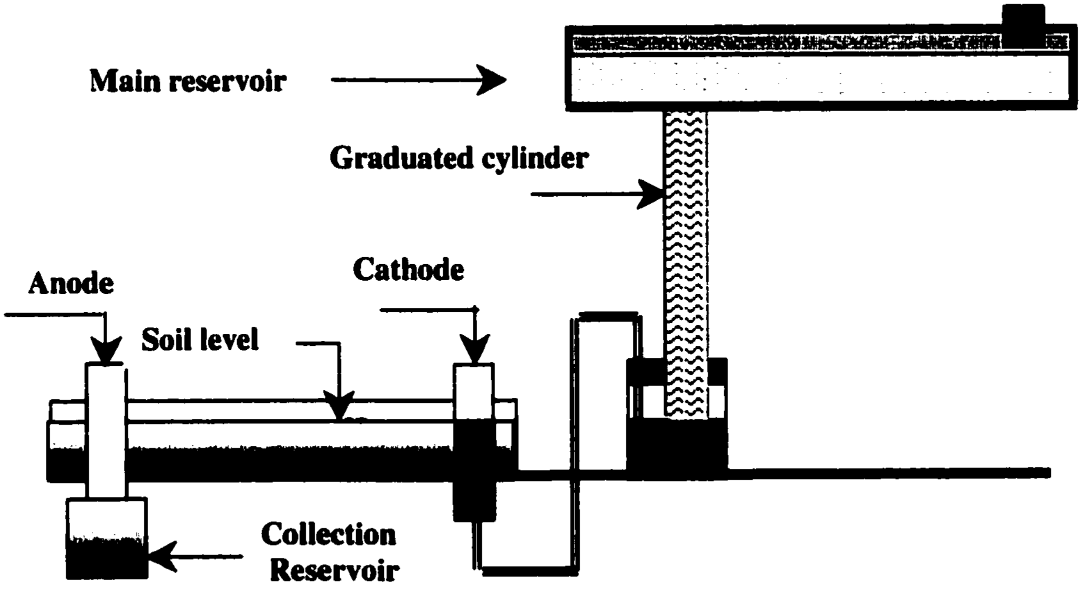


Figure 12 Conditioning Liquid Supply System

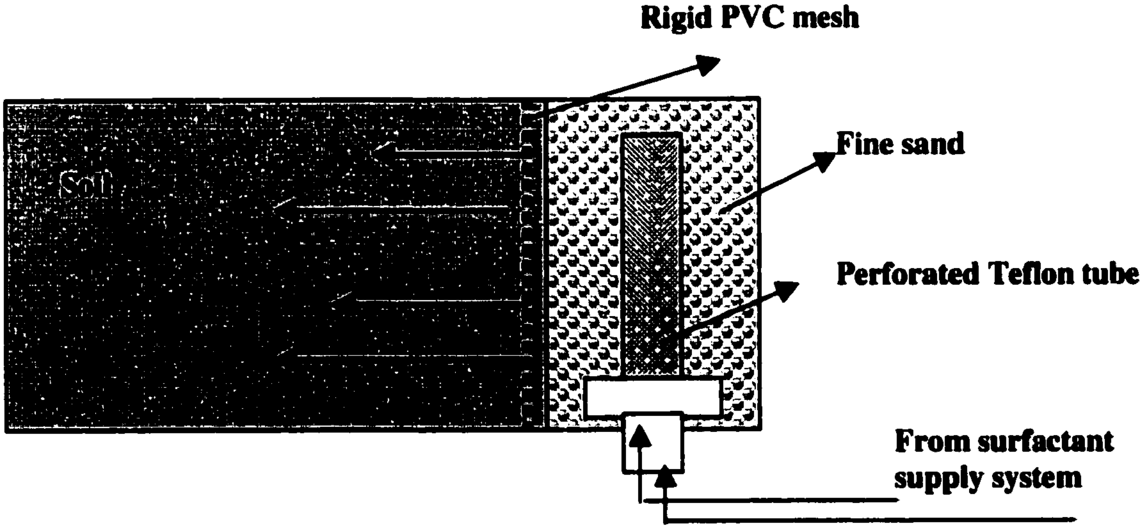


Figure 13 Permeable Zone Configuration within the Soil

7.2.6. Washing System:

The washing system was designed with respect to certain requirements:

1. Simple in operation;
2. Adaptable to a field scale;
3. Automated;
4. Permit the monitoring of physical and chemical parameters of effluents;
5. Rechargeable;

The washed area was fitted with discharge and recharge tubes made from nonmetallic and chemically resistant material to avoid its interference with the electrical field and the chemical reactions between the effluent and the tube material. Teflon tubes were thought to be adequate for this purpose. The tubes were perforated and placed in fine sand, which served in the case of a discharge tube as an effective filter to prevent soil particles from entering into the system, and in the case of a recharge tube, as a buffering phase, which absorbed the pulsation caused by the pump.

A Multi-channel cartridge pump equipped with a flow regulator was used to circulate the liquid through the main reservoir. The Tygon type tubing was used in all connections to avoid chemical reactions between the washed liquid and the tubing.

The main reservoir had a 1-L capacity and the effluent circulating through it was constantly monitored and sampled for pH and chemical analysis. The content of the main reservoir was replaced with fresh washing liquid when its pH reached certain limits. Schematic illustration of the washing system is illustrated in Figure 14.

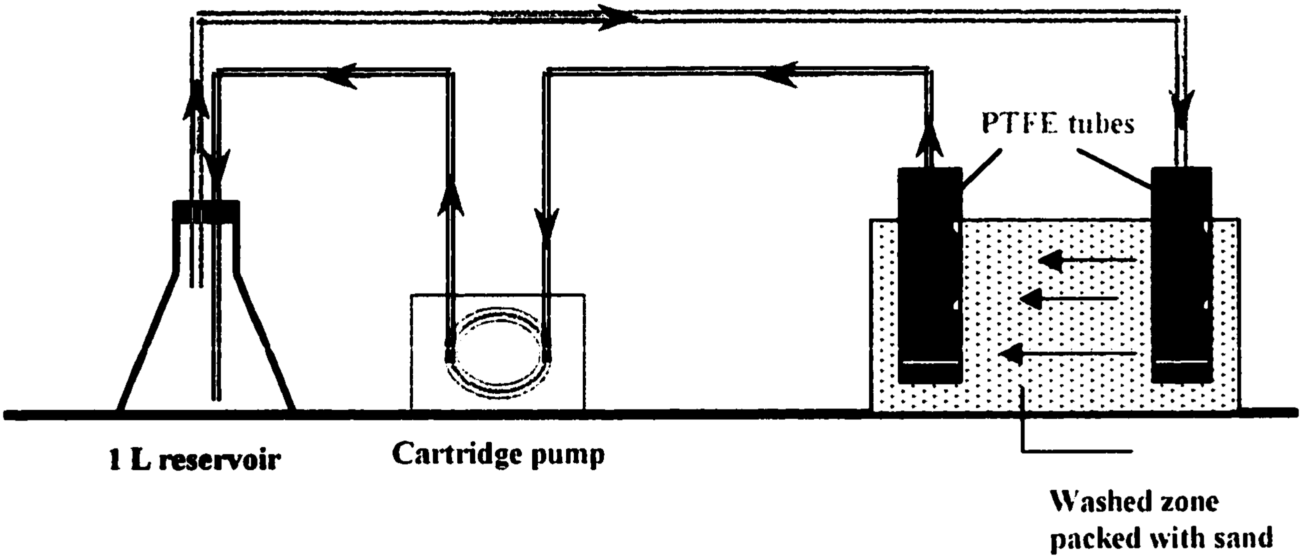


Figure 14 Washing System Design

7.3. Analysis and measurements

7.3.1. During the experiments

I- Measurements of electrical parameters

Potential distribution along the distance between the cathode and the anode was monitored during the test. Readings were carried out using TES 2712 type Multimeter. Each reading represented a potential gradient between the cathode and the subsequent probe electrode. Total current between the electrodes was also monitored. This allowed for continuous monitoring of electrokinetic phenomena.

II- pH measurements

- Cathode liquid

The pH values of the catholyte collected daily were measured during each test using the Fisher Accumet Model 800 pH-meter and the Gel-filled combination semi-microelectrode Orion model 91-15.

- Washing liquid

The pH value of the washing liquid was monitored where it was necessary. Liquid samples were taken from the main reservoir and measured (using the same apparatus used in cathode liquid measurements). The pH value was a critical indicator for the replacement of the washing liquid.

III - Metals content

- metal content in the cathode liquid.
- metal content in the washing liquid

Daily samples from both liquids were filtered and analyzed for its content of Ca, K, Fe, Zn and Pb using the Atomic Absorption Spectroscopy type 902 double beams GBC.

IV - Organic Compounds content (where it was applicable)

The measurements of organic compound content and their identification in both cathode liquid and washing liquid was accomplished through the use of the UV-VIS spectrophotometer (Perkin Elmer 552 and Lambda 2S).

V - The volume of injected and extracted liquids

Daily volume measurements were taken for all supplied liquids (conditioners and surfactants) and the extracted liquid.

7.3.1. After the experiment

After the tests, the soil was subjected to sampling along the distance between the anode and the cathode. The sampling scheme for the cells with an 8-cm electrode distance is shown in Figure 15. Each sample had a 1-cm thickness. Soil samples were then subjected to the following tests:

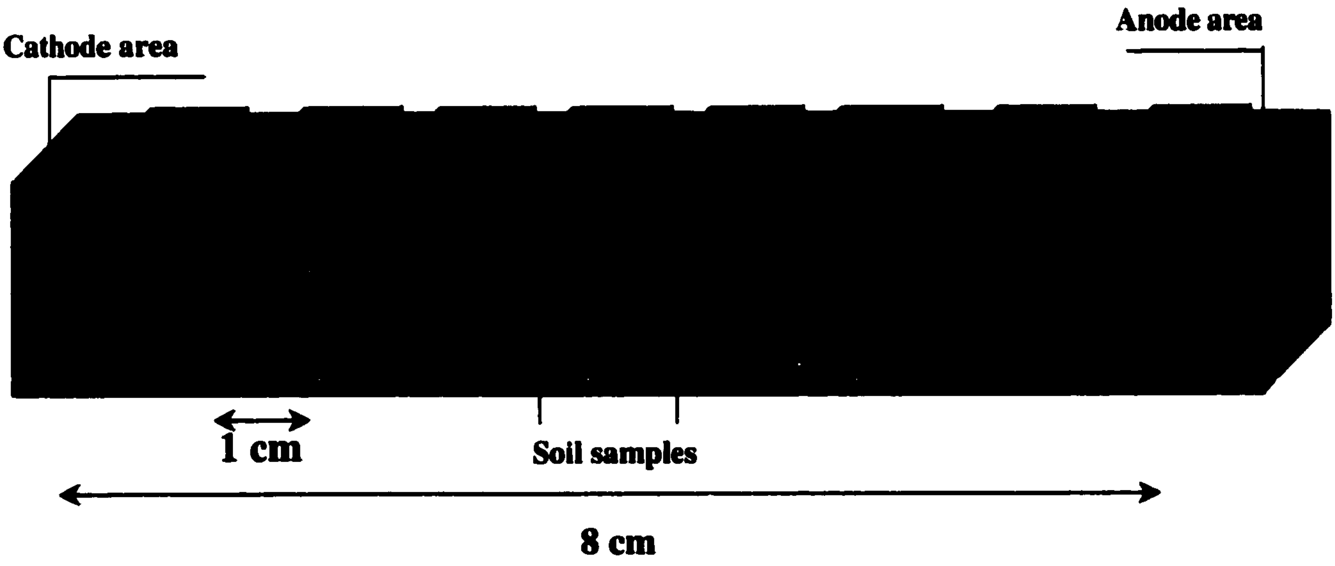


Figure 15 Soil Dividing Scheme

I - Moisture content

The ASTM standard method (No ASTM 2216-90 vol. 4.08) was used to determine the moisture content of the soil samples. Soil samples were oven dried for 24 hours at a temperature of 105 C°. After drying, soil samples were placed into a desiccator for 15 minutes to allow the sample to cool without absorbing air-moisture. The samples were then weighed and water content was calculated according to the equation:

$$\boxed{W = (M_w/M_s) * 100\ \%}$$

Where: M_w: mass of water,

M_s: mass of dry soil.

II – pH measurements

The pH measurements of soil samples were conducted according to the following procedure: 7.5 ml of distilled water was added to 3 g of soil sample in scintillation vials. Vials were then placed on a shaker for 1 hour; then the suspension left to be settled for 30 min. Then the pH of this suspension was measured using the same pH meter and pH electrode described in chapter 7.3.1.II.

III - Metals content

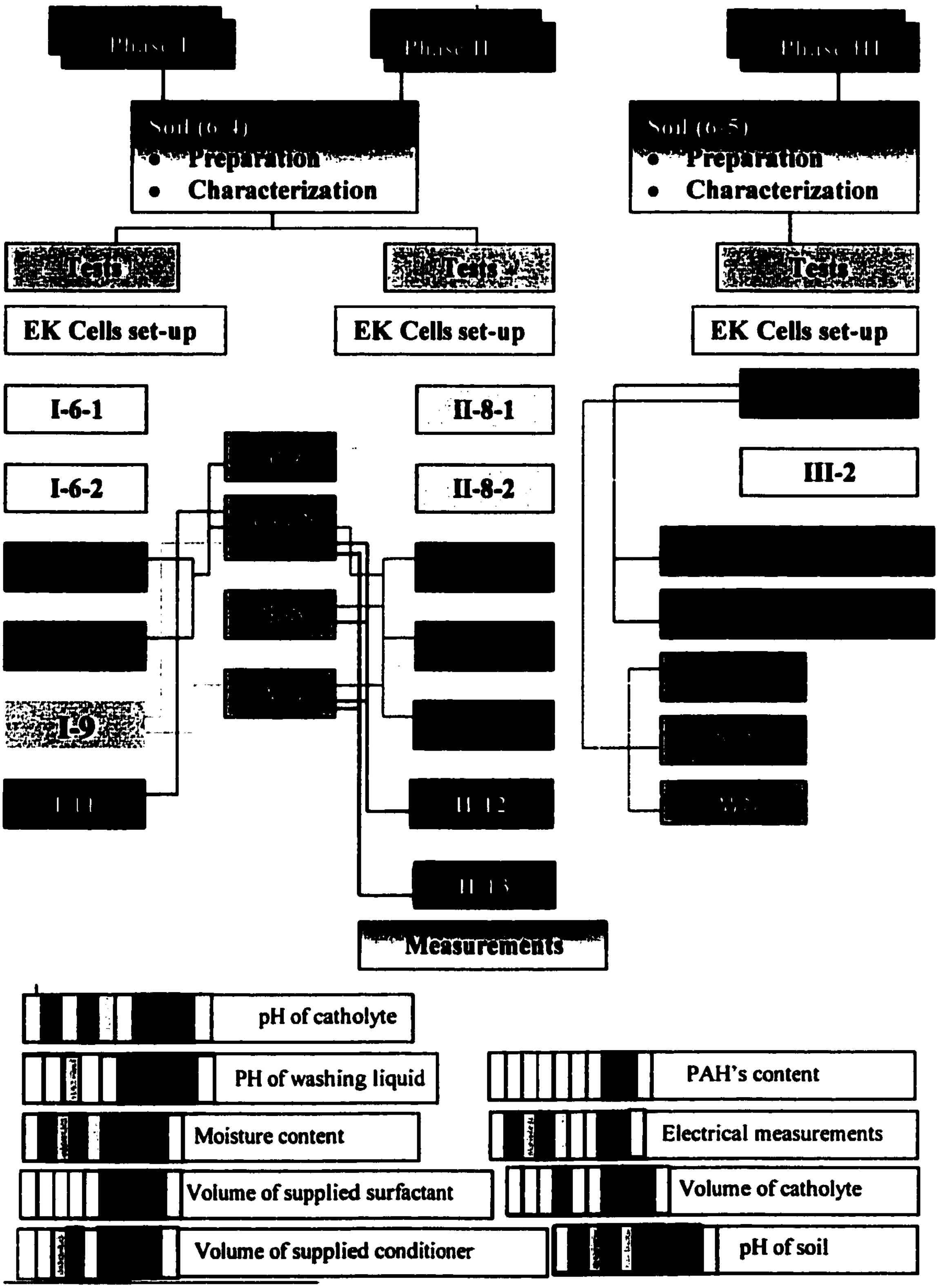
The effect of electrokinetics on the redistribution of metals in the cell along the distance between the cathode and the anode was evaluated by measuring the content of metals in soil samples. The new distribution of metal, particularly Ca and K, will reveal if any mobility or re-concentration of metals happened and would define the areas of significant concentration. The measurements were conducted as the follows:

Preserved soil samples let to be air-dried, then they were well grinned. Then 1 g of each sample was subjected to a metals digestion procedure according to EPA method 3050. After filtration samples were analyzed with the AA spectrophotometer.

IV - Organic compound content:

Soil samples, designated to be analyzed for their content of organic compounds, were subjected to solvent extraction and the extracts were analyzed for their organic content with the UV/Vis spectrophotometer after determining a calibration curve in separate batch tests. The type of solvent extraction depended on the organic compound being studied. For each compound, UV spectra and a calibration curve was obtained. Certain bands from the spectra were identified and the measurements were conducted based on these bands.

The distribution of the above mentioned measurements are included in the chart in Figure 16. This chart shows a methodical approach to the up-scaling process of EK removal of HOCs from clayey soil. This chart is helps in the visualization of the systematic improvements/optimization performed for particular cells in phase I, II, and III.



[1] Legend: SPZ : saturated permeable zone, CLSS : conditioning liquid supply system, SSS : surfactant supply system, WS : washing system, I-6-1 : phase No. – Test No. – Cell No.

Figure 16 Methodology for up-scaling process

8. EXPERIMENTAL WORK

8.1. Phase-I

As it was stated previously, this phase consisted of four experiments I-6, I-7, I-9, and I-11. The investigation of an area for optimal surfactant introduction and the effects of different locations as well as the thickness of sand supply zones on the pH profile in soil were tested in experiments I-6 and I-7. Finally, the development of a washing system was studied in experiment I-9. During this phase an evaluation of electrical field distribution within the electrokinetic cell was conducted in experiment I-11. Tests were conducted using natural non-contaminated soil (type 6-4) described in section 7.1. An initial water content of 40 % was provided and the soil was left to swell for 24 hours before packing to the cell. The soil was placed in the cell through multiple layers (1 cm each). Maximum precautions were taken to avoid the buildup of air cavities in the cell during filling. To minimize moisture loses during the test duration, polyethylene film was used to cover the cell's top surface. Gases produced during the tests were emitted through the unsealed open-end electrodes.

A description of the electrokinetic cells used in this phase will be provided in detail for each test separately. Cell parameters and arrangements are described in Table 7.

Table 7 Parameters and technical arrangements of cells in phase I

Test	Distance mm A-C	Barrier Thickness mm B1	Barrier Thickness mm B2	Distance C-B Mm	Distance C-B mm
I-6-1	80	10	20	35	20
I-6-2	80	10 Near C	20 A	35	20
I-7-1	80	20 Near C	40 C	10	30
I-7-2	80	10 Near A	40 C	40	20
I-9-1 & 2	80	-	40 C	-	-
I-11	80	N/A	N/A	N/A	N/A

A = anode, C = cathode

8.1.1. Experiment I-6

Experiment objectives:

With respect to the permeable zones (PZ), different locations were investigated in this test. The system response was evaluated based on electrical parameters and the pH distribution within the soil. Identification of a suitable area for surfactant introduction was also one of the objectives of this test.

Set-up:

This test was performed on two three-dimensional cells with 8-cm distance between the cathode and the anode. The supplied voltage was 2.4 V and the total initial current was 1.5 mA. Both cells shared the same location for the permeable zones (in the anode area), however, they differed in the location of the second permeable zone. In cell I-6-1 the second PZ has been placed 2-cm apart from the first zone situated at the anode. In cell I-6-2 this barrier was situated 2-cm from the cathode. A schematic drawing of these cells are presented in Figures 17 and 18. A supply system was not connected to the anode in this test, however their saturation was maintained during the test by adding tap water directly to their open ends. The test lasted 5 days during which electrical parameters and pH of cathode liquids were monitored. Monitoring of electrical parameters was conducted by direct measurements at the probe electrodes, distributed through the distance between electrodes. These distances were measured for cell I-6-1 as: 3-10-20-30-60-70 mm, and for cell I-6-2 3-30-40-50-60 mm.

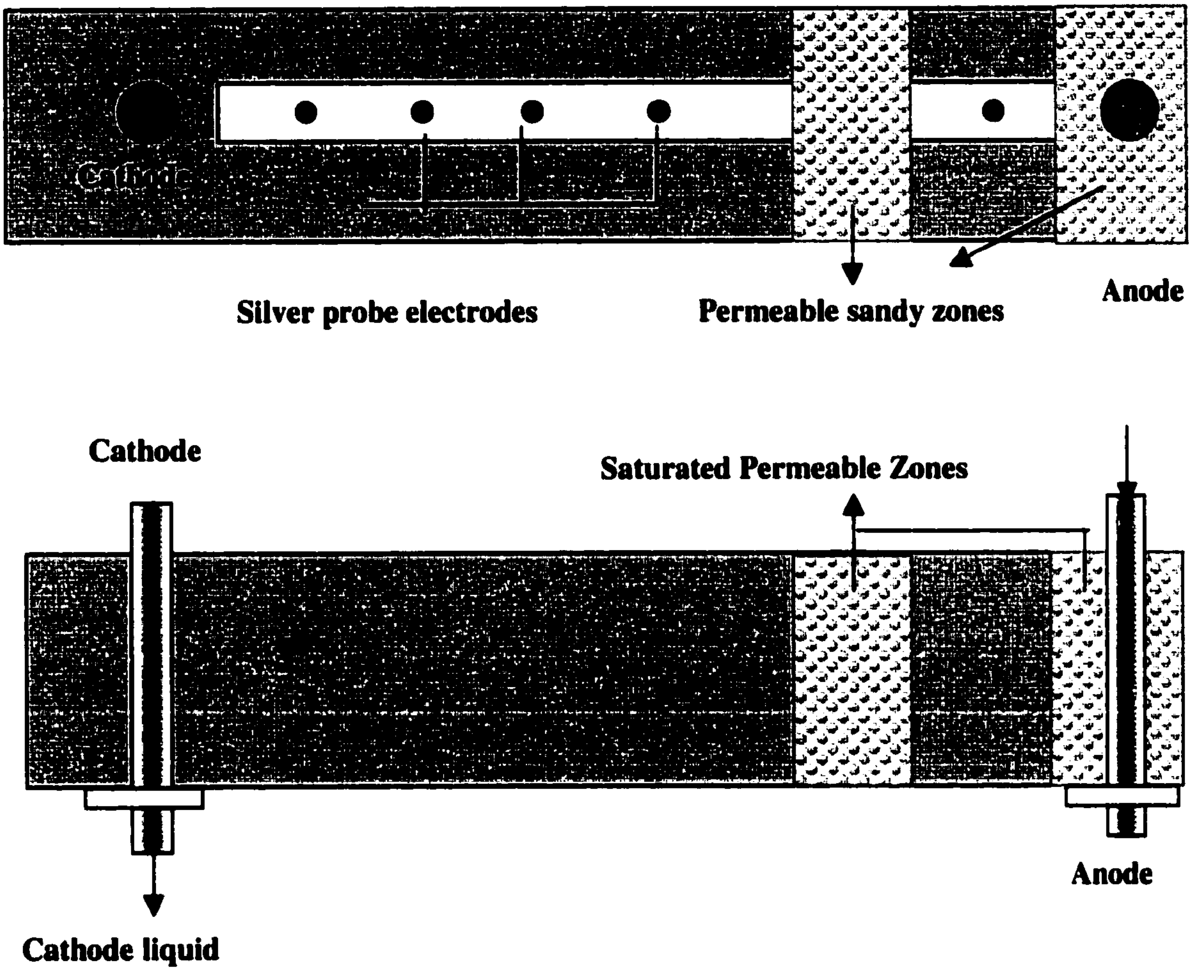


Figure 17 Schematic configuration of cell I-6-1

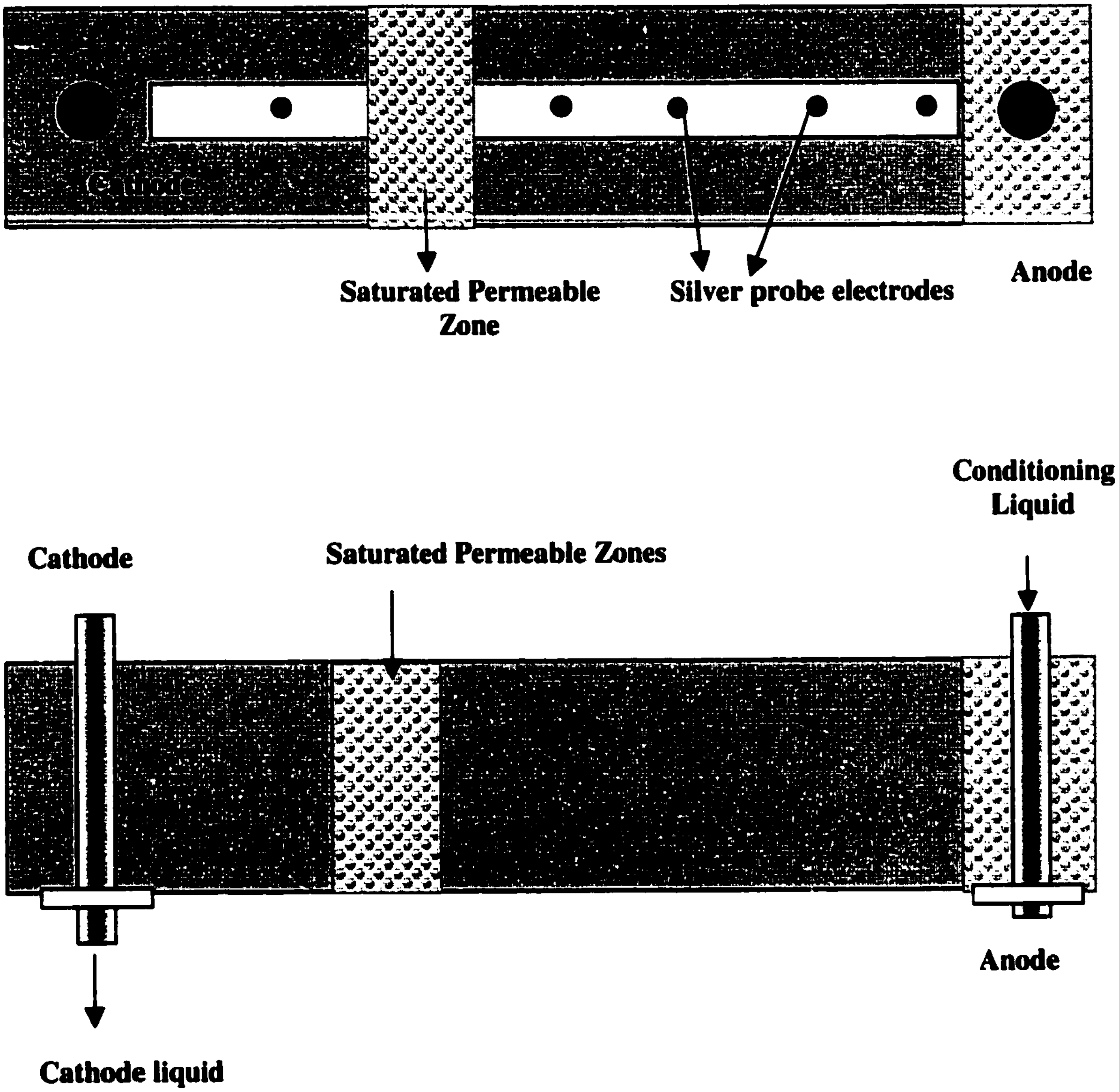


Figure 18 Schematic configuration of cell I-6-2

Results and discussion:

Table 8 present pH values of catholyte collected from cell I-6-1 and cell I-6-2. The results are presented graphically in Figure 19. Values from cell I-6-1 were not plotted because liquid was not collected at the cathode in the first 4 days of the test. The lack of catholyte liquid in cell I-6-1 suggested that the placement of the two permeable zones near each other would interfere with the electrokinetic flow causing a significant delay.

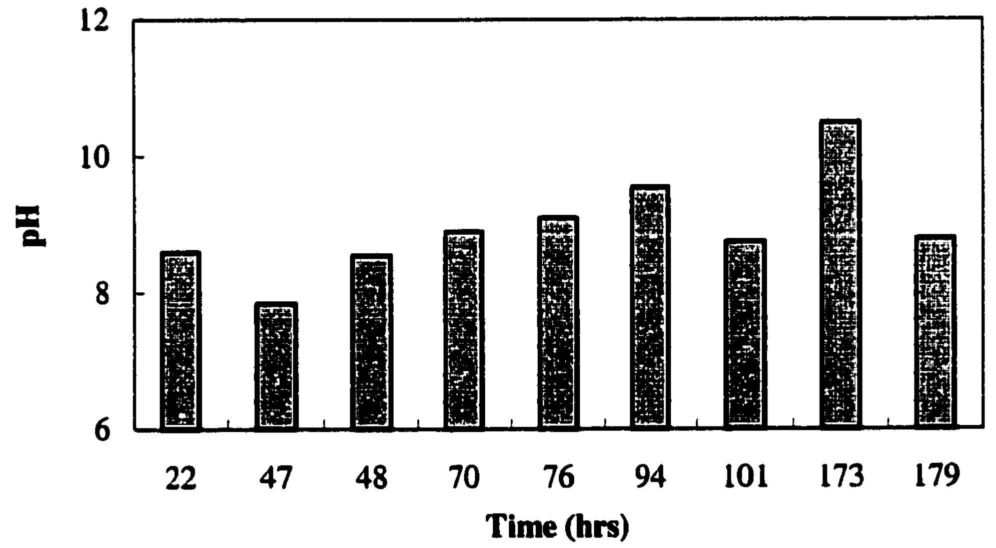


Figure 19 pH of Catholyte Liquid (I-6-2)

In cell I-6-2, the pH of the catholyte liquid kept moderate values (below 10) with the exception of a maximum of 10.5 (173 hours). After this time, the pH returned to 8.8. This suggests that placing a permeable zone near the cathode achieved its purpose in diluting the concentration of hydroxyl ions generated at the cathode.

When the test was terminated, soil sampling was conducted so that the distance between the electrodes was divided into five samples. Samples were tested for its pH and water content values (Table 9).

Table 8 The pH of extracted liquid

Date	Hours	Test1-6-1	Test1-6-2
Day 1	22	No extraction	8.6
Day 2	47	No extraction	7.85
Day 2	48	No extraction	8.55
Day 3	70	No extraction	8.9
Day 3	76	No extraction	9.1
Day 4	94	No extraction	9.55
Day 4	101	No extraction	8.75
Day 5	173	11.7	10.5
Day 5	179	11.7	8.8

Table 9 Distribution of Water Content and pH of Soil Samples

Sample No. From the cathode to the anode						
I-6-1	***1***	***2***	***5***	***6***	***7***	***8***
W. C [%]	39. 48	39. 90	39.52	37.65	44.00	45.36
pH	8.55	8.20	8.05	8.15	7.70	8.00
Sample No. From the cathode to the anode						
I-6-2	***1***	***3***	***4***	***5***	***6***	***8***
W. C [%]	42.20	43.39	36.08	40.05	43.20	45.33
pH	7.9	8.00	8.05	8.15	8	7.95

The relation between the pH of soil samples and the distance from the cathode is shown graphically on Figures 20 and 21. A uniform distribution of pH in both cells was observed. However, a lower pH near the cathode in I-6-2 was observed due to the location of Permeable Zone-2 (PZ-2). Moisture content showed an increase from the cathode to the anode area. This distribution was expected due to the placement of the permeable zone in the anode area.

It should be noted, that the water delivery system was the same for both cells and the total input of water was 105 ml (average of 15 ml per day).

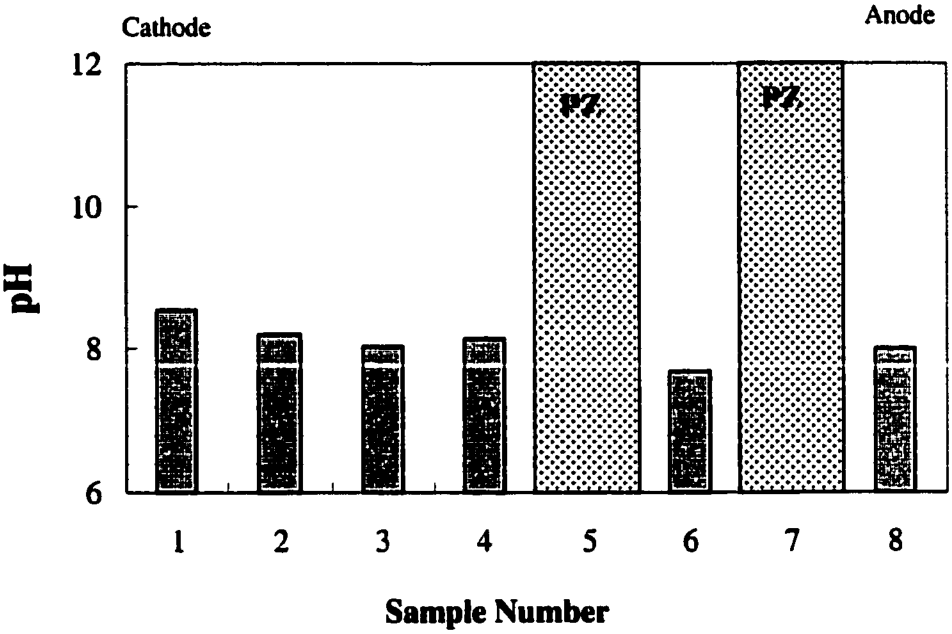


Figure 20 pH of Soil Samples (I-6-1)

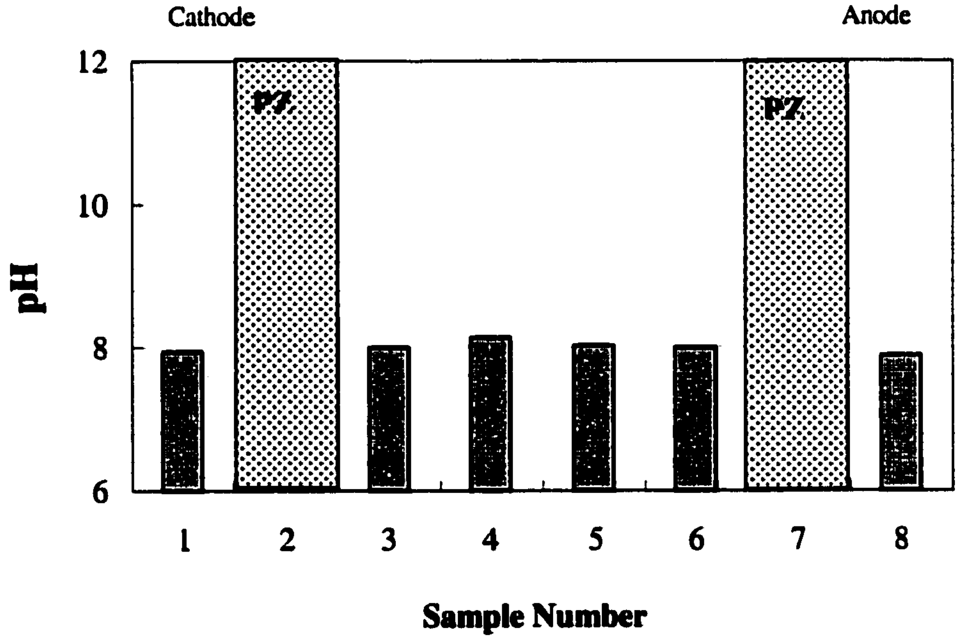


Figure 21 pH of Soil Samples (I-6-2)

The presence of soil particles in the permeable zones after the 5th day, was evaluated as a percentage of the total weight of sand (Table 10).

Table 10 Percentage weight of soil particles penetrated into the permeable zone

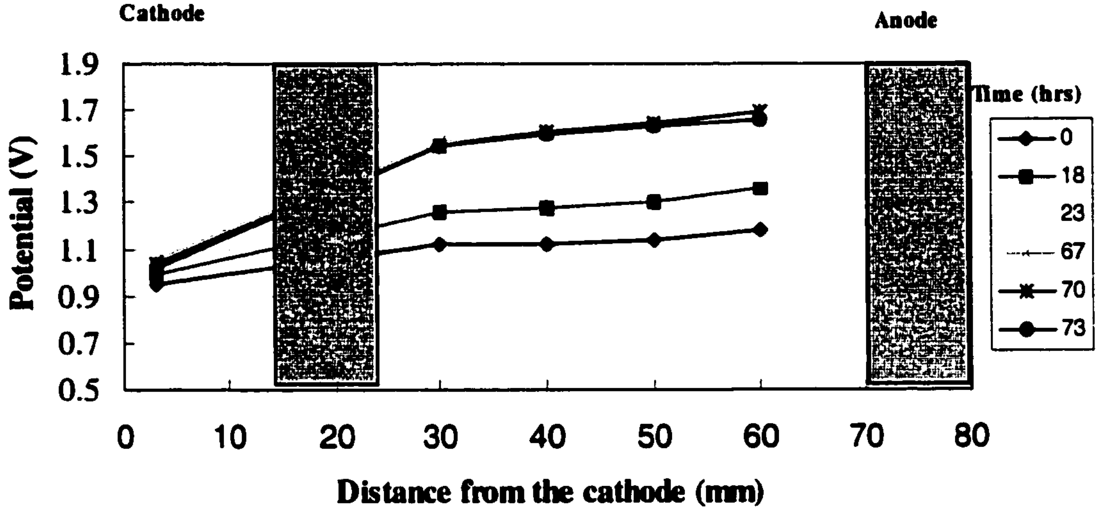
	PZ1	*PZ-2*
I-6-1	6	1
I-6-2	1	0.6

Table 10 shows that the penetration of clay particles was 6 times higher in the PZ situated in central part of the cell. The carbonate content in the permeable zones (PZ-1 & PZ-2) and in the soil adjacent to them is presented in Table 11. The upper number represents the carbonate content of the soil particles that penetrated into the zone, and the number beneath represents the carbonate content for the soil particles in a area next to the sand layer. The table shows that the carbonate content in I-6-1 is 10 % higher than in I-6-2 in PZ-1 and PZ-2. Also, the carbonate content in PZ-1 was observed to be two times higher than its content in the adjacent soil in I-6-1. This value was raised to three times in the case of I-6-2.

As stated previously, potential measurements at each probe were conducted. Results of measurements were presented to show the potential at each probe, varied as a function of time and distance. The relationship between the potential and the distance from the cathode is presented in Figures 22 and 23. Figures 24 and 25 present the relationship between the potential (at each probe) and time. In I-6-1, a uniform potential gradient was observed between 10 and 40 mm, however a higher gradient was observed near the cathode (between probes 1 and 2 located at 10 and 20 mm consequently), which can be related to the precipitation near the cathode area. The presence of the permeable zone also caused a higher gradient between probes 4 and 5 (40 and 50 mm), this gradient decreased when moving toward the anode. No significant changes in the voltage values within the time have been recorded (with exception to cathode area). This fact can explain the lack of the extraction in cell I-6-1.

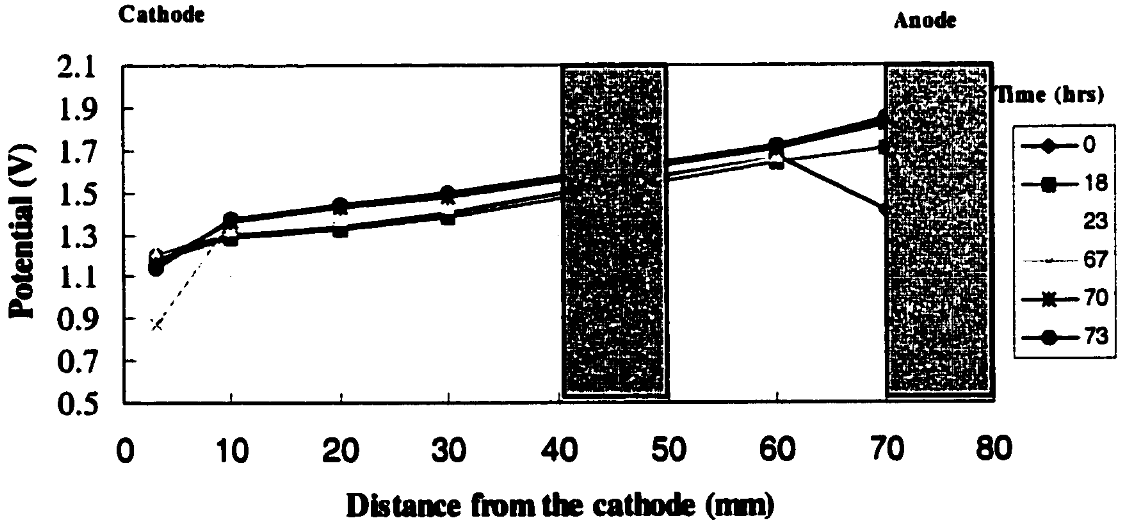
Table 11 Carbonate Content

Test	*Samples*	*PZ-1*	*PZ-22*
I-6-1	Particles in PZ	0.89	0.91
	Adjacent soil	0.45	0.37
I-6-2	Particles in PZ	0.72	0.82
	Adjacent soil	0.24	0.66



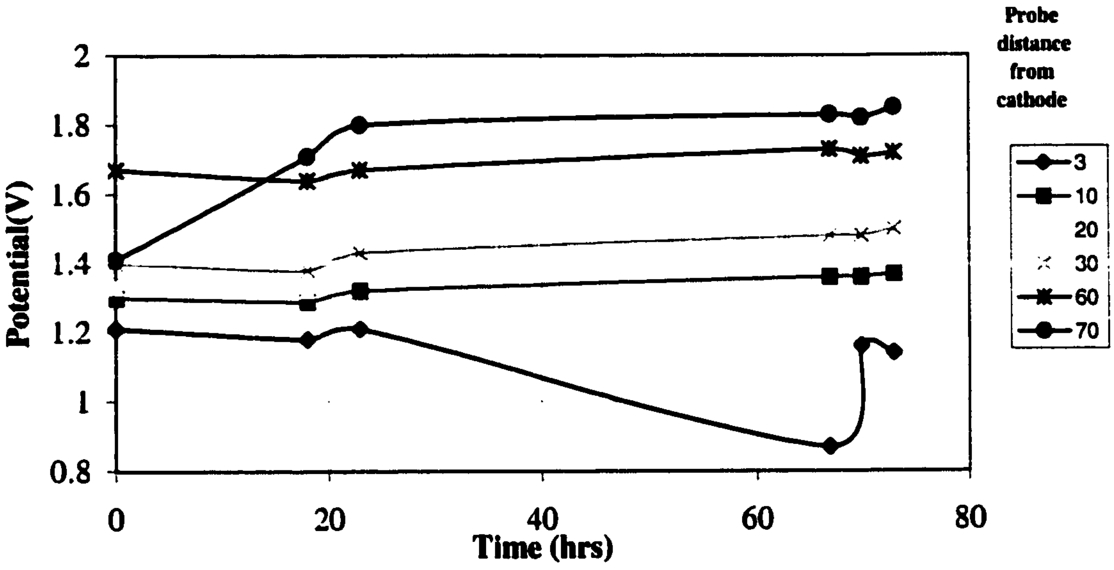
I-6-1

Figure 22 Distribution of Potential vs. Distance Measured in Probes at Different Time



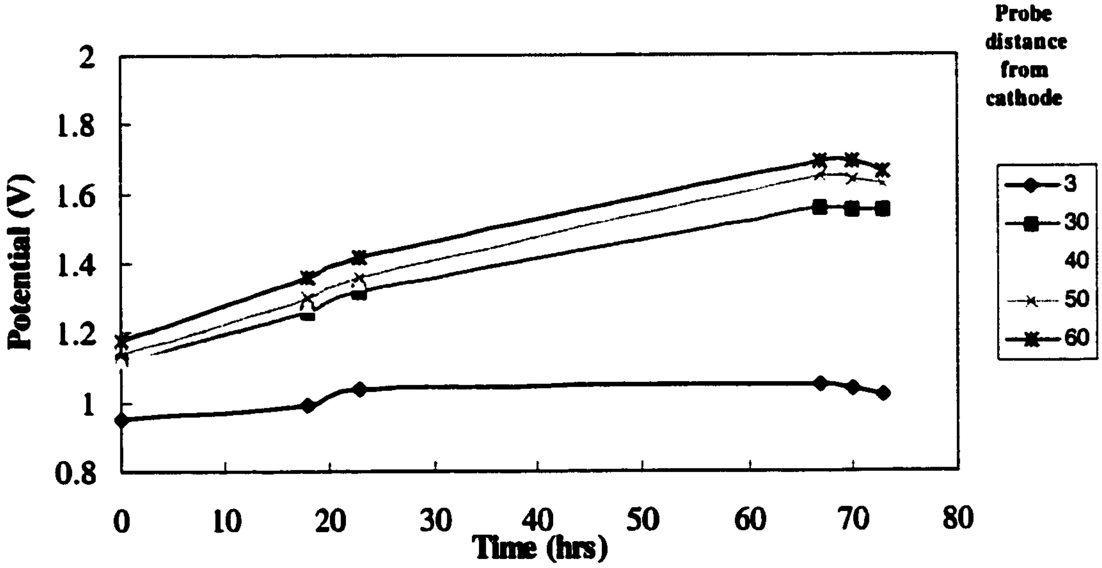
I-6-2

Figure 23 Distribution of Potential vs. Distance Measured in Probes at Different Time



(I-6-1)

Figure 24 Distribution of Potential vs. Time Measured in Probes at Different Locations



(I-6-2)

Figure 25 Distribution of Potential vs. Time Measured in Probes at Different Locations

The final potential gradient was similar in both cells. However the gradients and the variance with time were different. In the beginning cell I-6-2 had a very small gradient, which was followed by a relatively constant one between zones. I-6-1 seems to have a constant gradient from the beginning to the end. The PZ evidently influenced the voltage distribution with time.

8.1.2. Experiment I-7

Experiment objectives:

This experiment was similar to previous experiments (I-6) with objectives related to the location of permeable zones in order to optimise electrokinetic removal of HOC.

Set-up:

Cells I-7-1 and I-7-2 used in this experiment were similar to those used in experiment I-6. The cells shared the same dimensions and distance between electrodes; however, they differed in the placement of the permeable zones. In cell I-7-1, a permeable zone was placed in the cathode area and the second zone was placed 4 cm from the anode. For cell I-7-2, the first permeable zone was located in the same location as cell I-7-1, however, the second zone was placed 2 cm apart from the anode. Figures 26 and 27 illustrate a schematic drawing of the cells used in this test.

Anodes in both cells were connected to a Conditioning Liquid Supply System (CLSS) and the Permeable Zones (PZ) were saturated during the test by adding tap water directly. The total liquid supplied to both cells was determined each day and totalled 200 ml. It should be noted that at this stage no distinction has been made between the consumption rates of conditioning liquid in each cell, later tests would take this distinction under consideration. The initial voltage supplied was 2.4 volts and the current was 0.9 mA. Soil type 6-4 had an initial moisture content of 46%. During the test electrical parameters were monitored by direct measurements at the probe electrodes, which were distributed along the distance between the electrodes. The test lasted 10 days and upon its termination, destructive soil sampling was conducted.

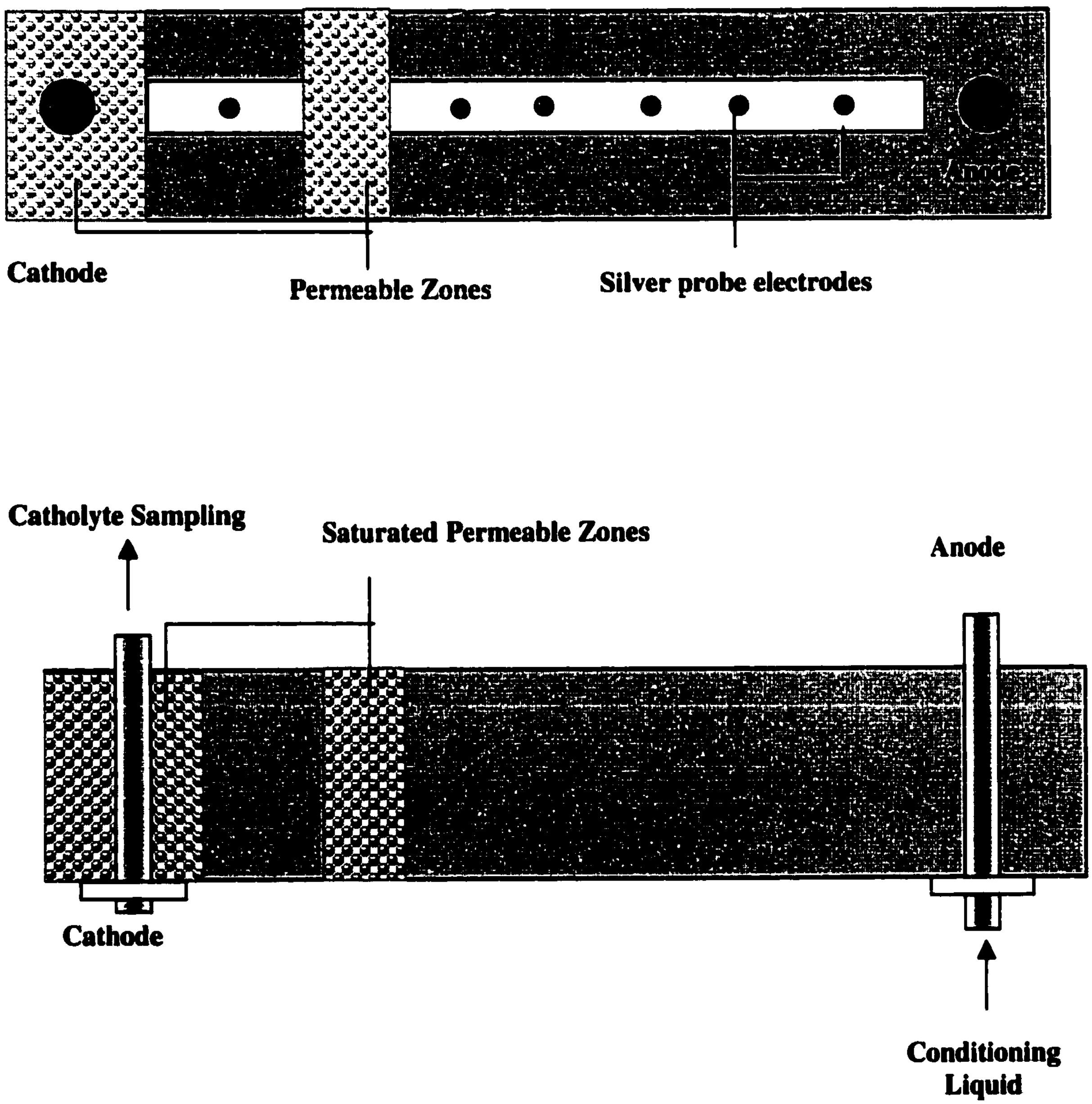


Figure 26 Schematic configuration of cell I-7-1

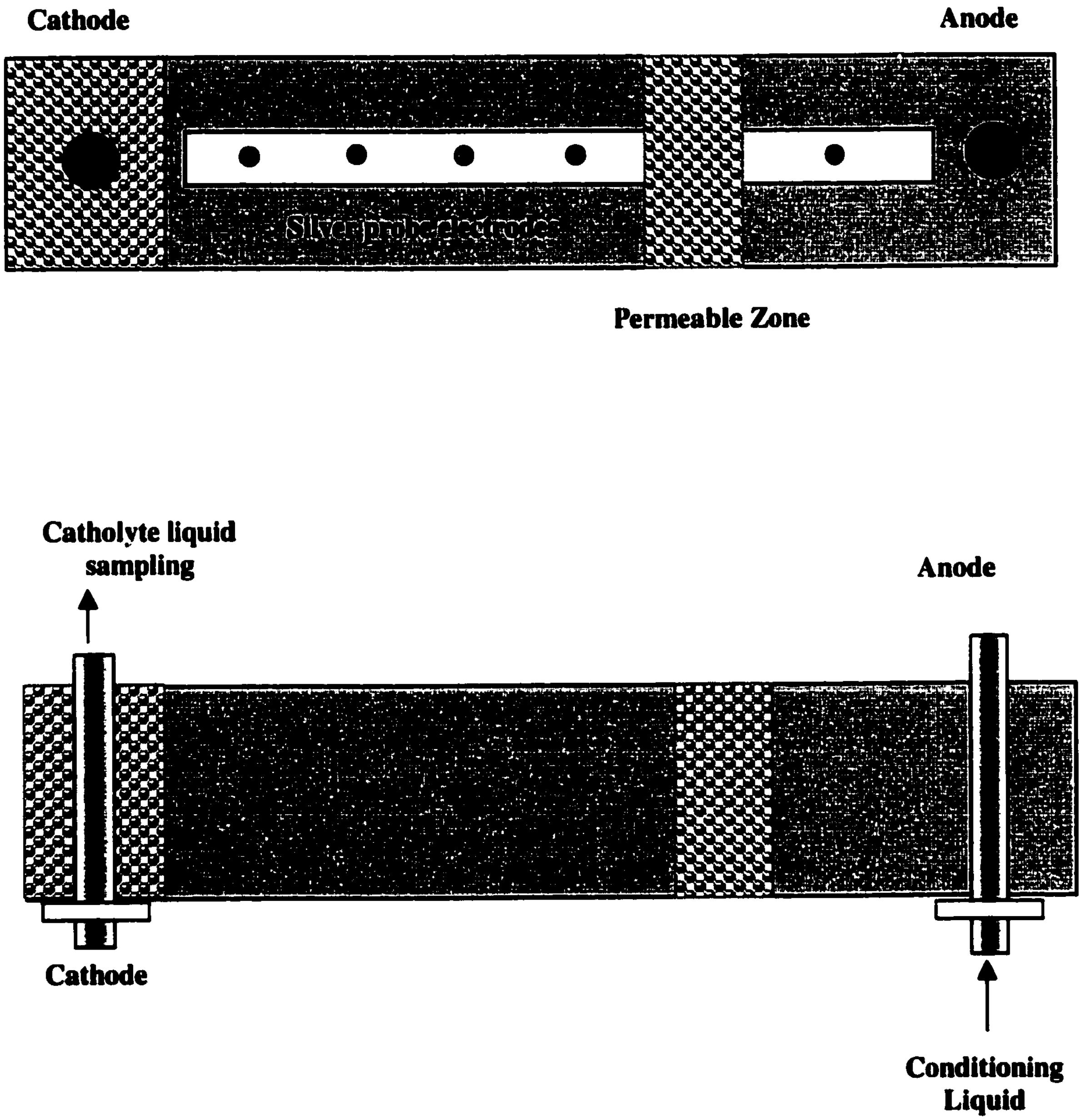


Figure 27 Schematic configuration of cell I-7-2

Results and discussion:

Samples of catholyte liquid from both cells were tested for its pH values (Table 12). The data show that the pH of the catholyte liquid reached a high value (11.5) in both cells during the first day of the experiment. This high pH value was maintained during the test. The results are presented in Table 12 and Figures 28 & 29.

Table 12 Catholyte pH Values

Time	*I-7-1*	*I-7-2*
5	9.2	9.5
17	11.5	11.4
23	11.7	11.4
42	11.8	11.5
48	12.0	11.3
133	12.25	11.9
141	12.2	11.7
159	12.2	11.9
166	12.3	11.7
183	12.2	11.9
191	12.4	11.9
208	12.3	11.9
215	12.3	11.7
233	12.5	12.0

The presence of a saturated PZ in the cathode area facilitated the generation of hydroxyl ions, which caused an increase in the pH within this region.

When the test was terminated, 4 samples were taken from each cell (with numbering starting from the cathode) and subjected to pH and moisture content analysis. The results of these analyses are presented in Table 13 and plotted in Figures 28 & 29. It was evident that the placement of the permeable zone directly in the cathode led to higher pH values in the soil (when compared to experiment I-6). Combination of zones in cell I-7-2 performed better than the one in I-7-1 where its maximum pH value reached 8.88 compared to 9.18 in I-7-1 close to the cathode. The better performance of I-7-2 and I-6-2 led to the conclusion that placing two PZs near each other will have a negative effect on the process.

Table 13 pH and Water Content (WC) of Soil Samples

Sample No. *I-7-1*	*1*	2	*3*	*4*
pH	9.2	8.4	8.35	8.25
W. C [%]	47	44.75	44.75	44.25
Sample No. ***I-7-2***	***1***	**2**	***3***	***4***
W. C [%]	49.75	48.8	48.1	44.3
pH	8.9	8.6	8.6	8.4

Results of electrical measurements are plotted in Figures 32 to 35. Figures 32 and 33 present the potential change as a function of time and Figures 34 and 35 present the potential distribution as a function of the distance between the cathode and the anode.

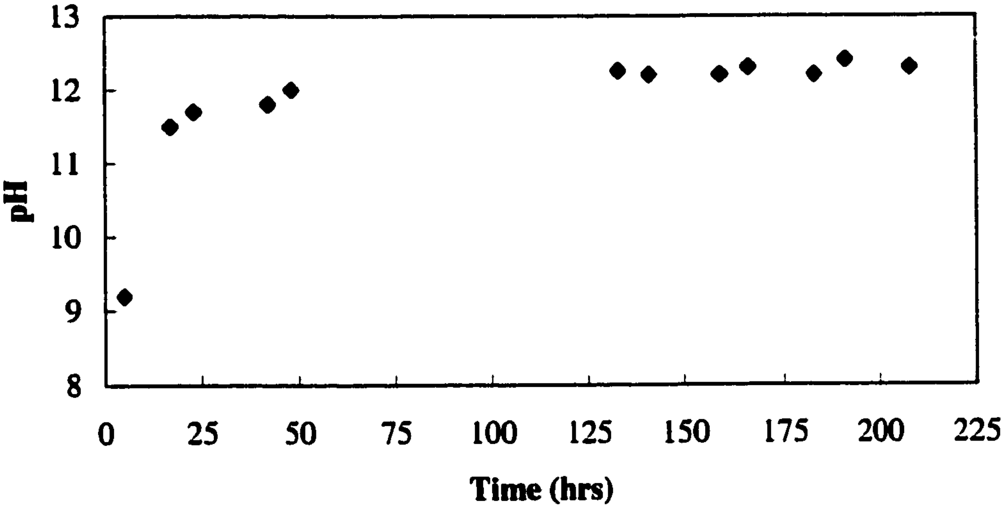


Figure 28 pH of cathode liquid in cell I-7-1

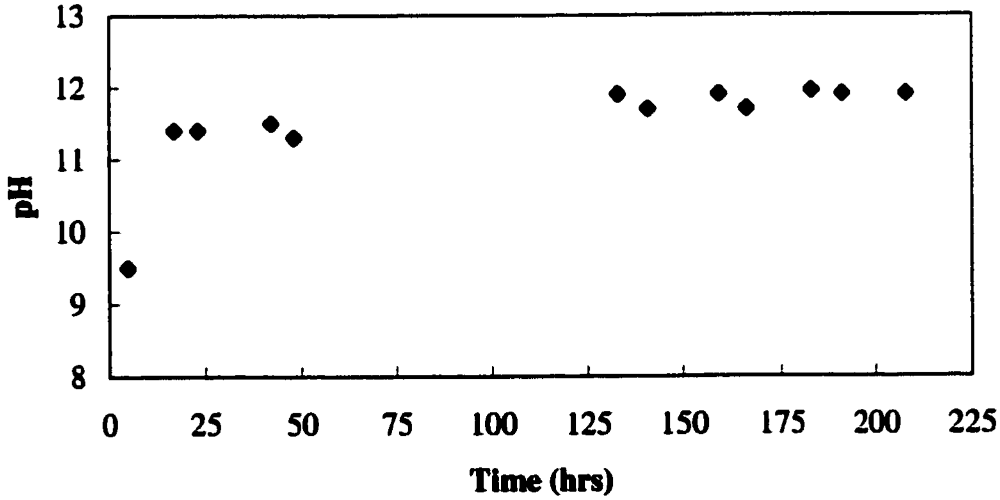


Figure 29 pH of cathode liquid in cell I-7-2

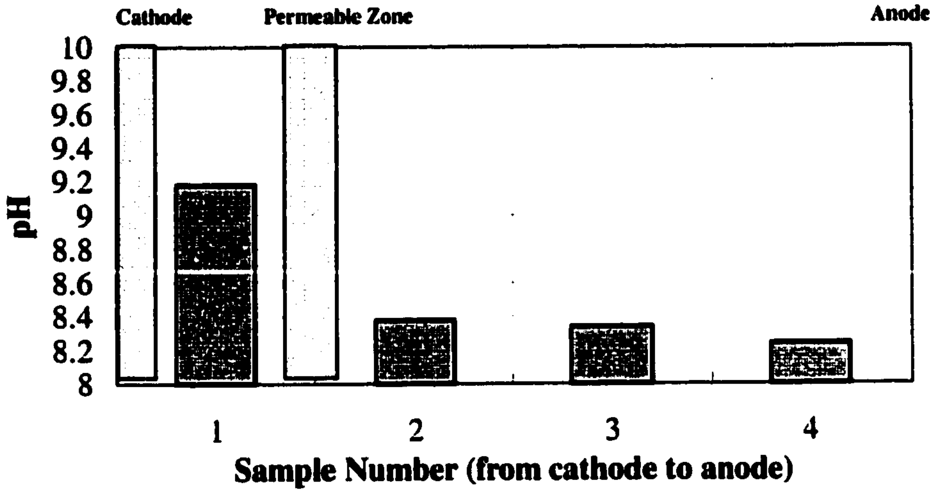


Figure 30 Distribution of pH of soil samplesin cell I-7-1

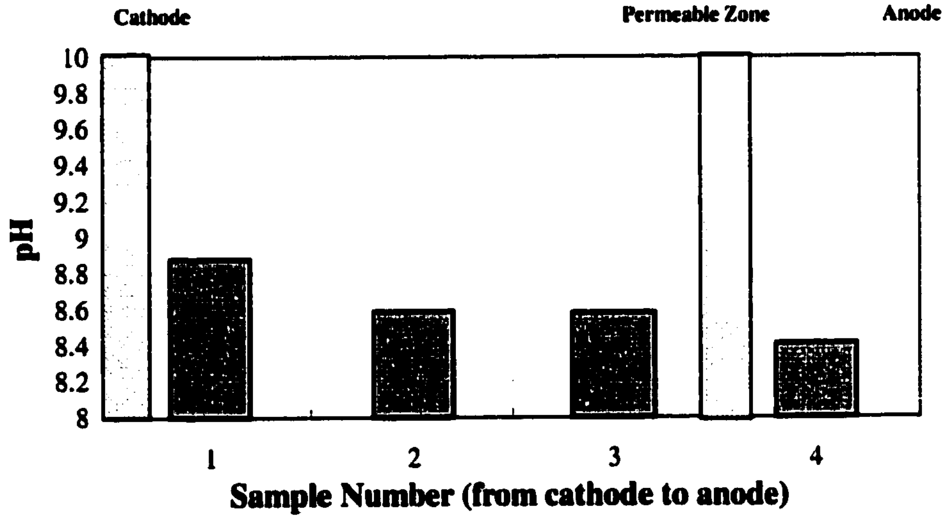


Figure 31 Distribution of pH of soil samples in cell I-7-2

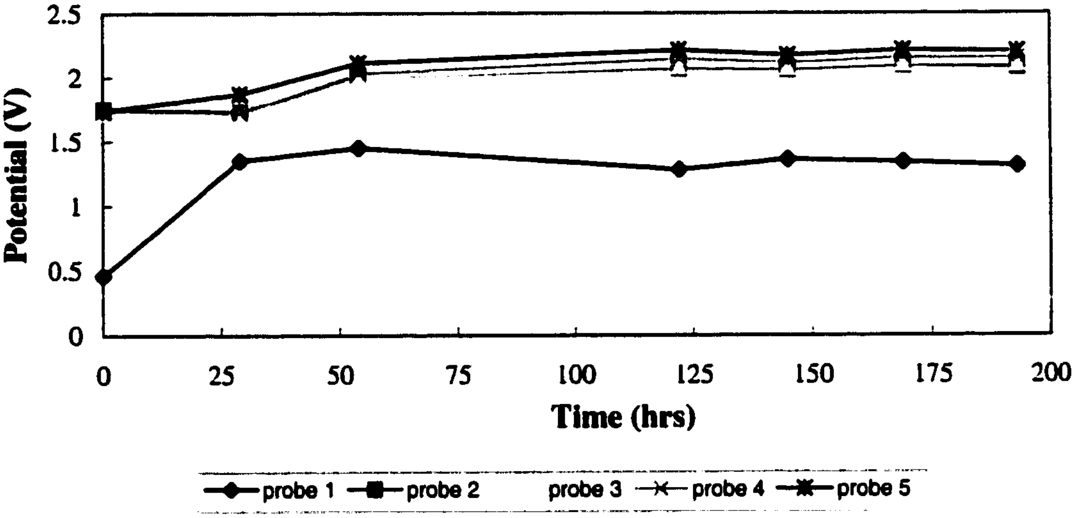


Figure 32 Potential Distribution vs. Time at Each Probe Electrode (I-7-1)

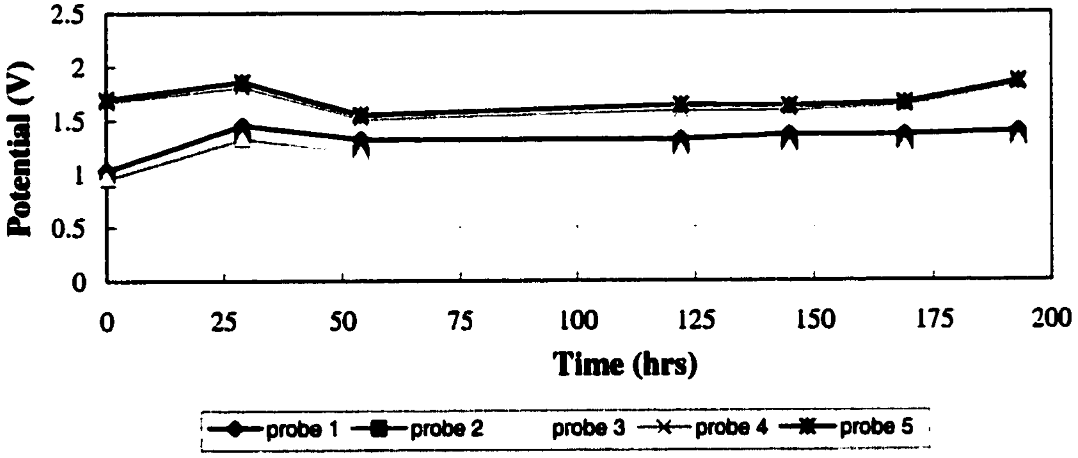


Figure 33 Potential Distribution vs. Time at Each Probe Electrode (I-7-2)

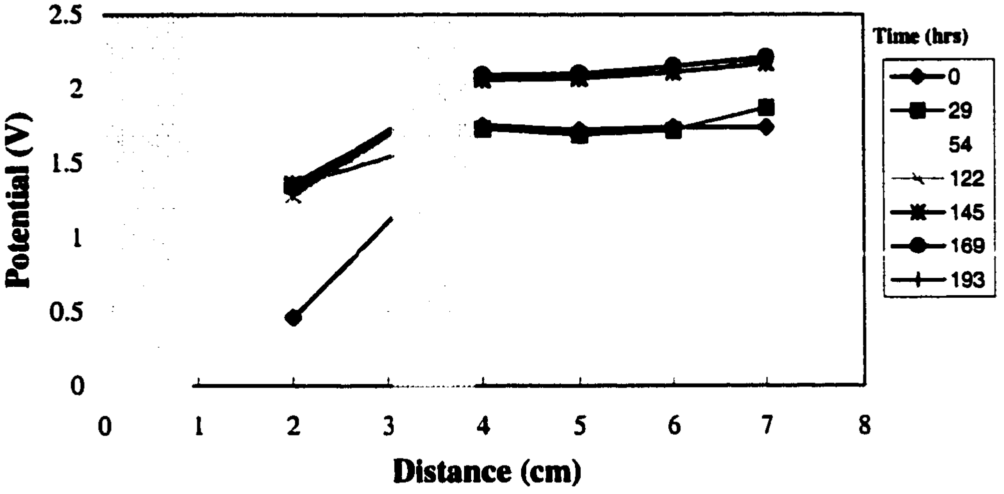


Figure 34 Potential Distribution vs. Distance from the Cathode Measured at Different Time for cell I-7-1

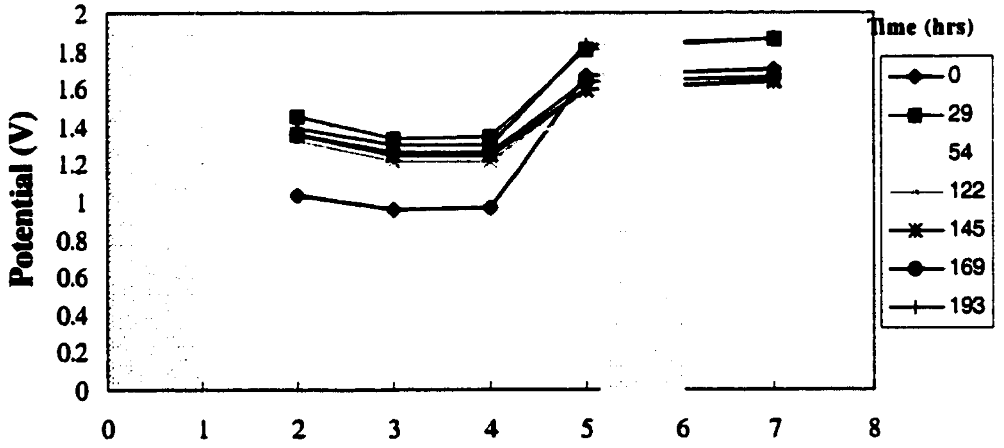


Figure 35 Potential Distribution vs. Distance from the Cathode Measured at Different Time for cell I-7-2

The graphics indicated that in cell I-7-1, the potential value in each probe remained almost the same during the test with the exception of probe 1, where a jump in the potential value from 0.46 V to 1.35 V within the first 30 hours of the test was observed. In cell I-7- 2, all probes showed noticeable jump in the potential within the first 30 hours of the test. The maximum gradient was recorded in probe 1 (0.42 V) and a minimum was recorded in probe 5 (0.16 V). Within the next 20 hours, a slight drop in the potential values was recorded for all probes. This drop was maintained throughout the test in probes 1, 2 and 3. Probes 4 and 5 showed a second jump in its potential value at 175 hours. This gradient made their potential values similar to the values posted after 30 hours.

8.1.3. Experiment I-9

Experiment objectives:

This experiment was conducted to test the performance of the electrokinetic cell after the introduction of a washing system in the cathode area.

Set-up:

Short cells with an 8-cm distance between its electrodes supplied with a total current of 2.4 volts was chosen for this test. A 3.5-cm permeable zone connected to a closed circle washing system was placed in the cathode area. The anode was connected to a Conditioning Liquid Supply System (CLSS). The cell was packed with type 6-4 soil with an initial moisture content of 40%. Eight probe electrodes were used along the distance between the electrodes to monitor electrical parameters. The pH of the washing liquid was monitored during the test and the liquid was refreshed when its pH value reached a maximum of 9. Tap water was used as a washing liquid. The cell set-up is presented schematically in Figure 36. The test lasted 8 days and upon its termination, soil sampling was conducted.

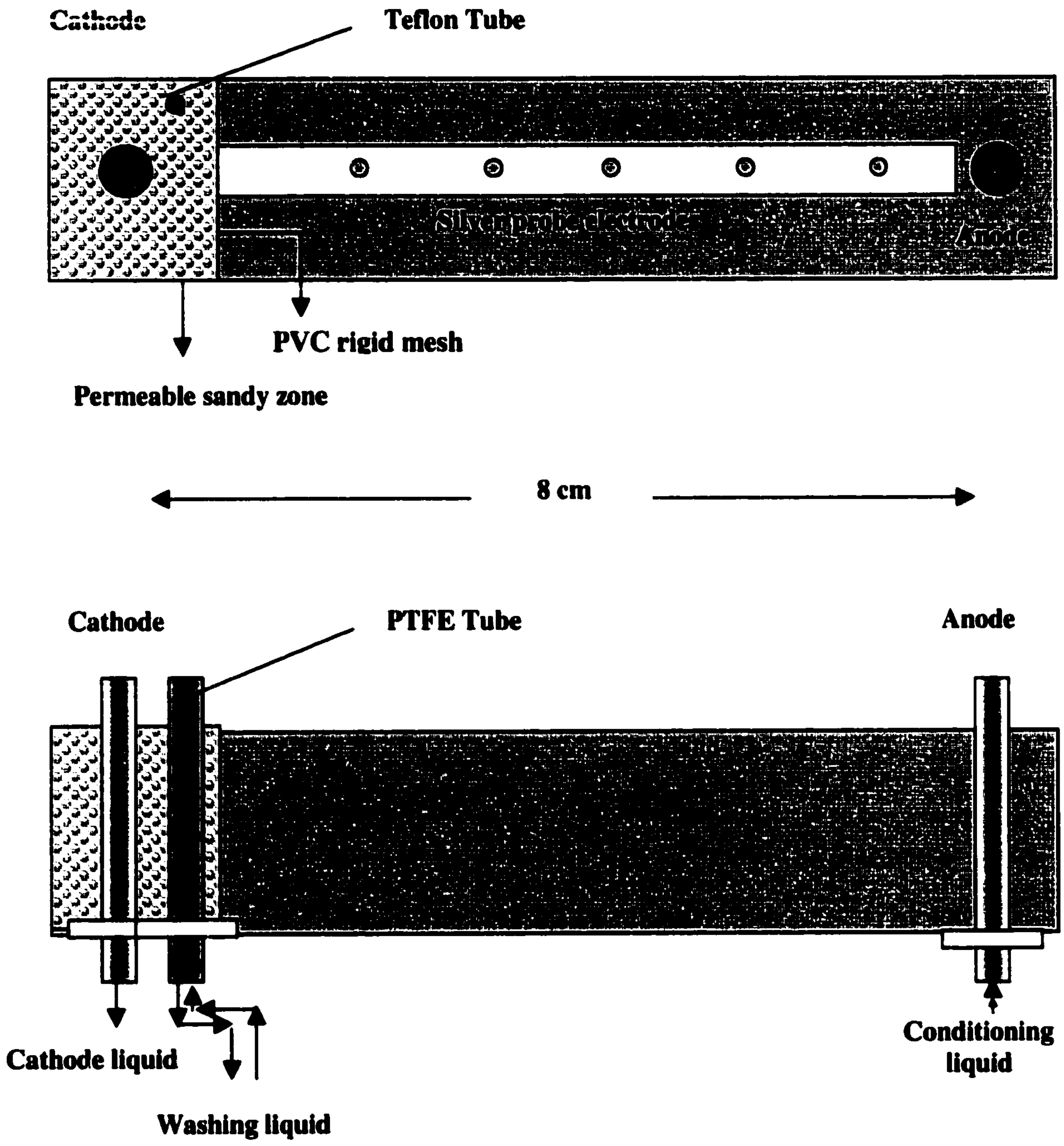


Figure 36 Schematic Configuration I-9

Observations:

Although the test lasted 8-days, it was found that the volume of the injected liquid (conditioning liquid) was very small (50 ml).

Results and discussion:

The pH of the washing liquid was measured during the test and the results are shown in Table 14.

Table 14 pH of Cathode Liquid

Time (hrs)	*pH*
0.0	8.07
2.0	8.21
19.0	8.38
27.0	8.43
94.0	9.48
99.0	9.82
115.0	10.11
117.0	Change the water
123.0	7.72
139.0	8.3
146.0	8.66
163.0	8.9

The result shows that with the introduction of a washing system, the generation of high pH was considerably delayed. A value of 9.5 was reached in I-9 after 95 hours compared with 5 hours needed in I-7 to produce the same value. It should be noted that an optimum pH value in the catholyte liquid could be maintained by a continuously monitoring the pH of the washing system.

When the test was terminated, soil sampling was conducted according to the scheme presented in Figure 37:

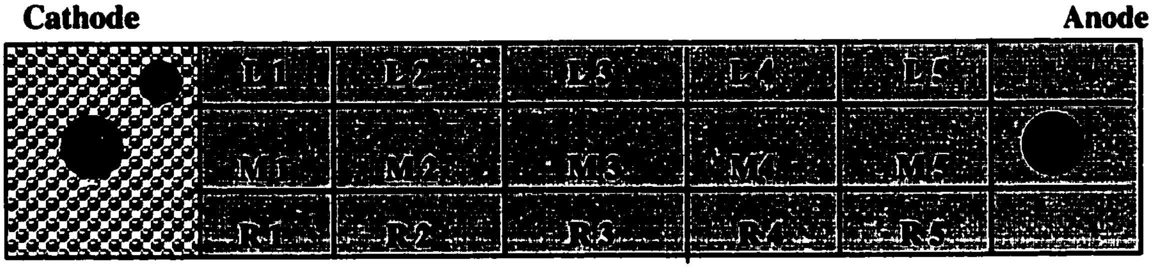


Figure 37 Cell Dividing Scheme for Experiment I-9

Samples were subjected to pH and moisture content measurements. The results are presented in Table 15. There was no discrepancy in pH values for L5, M5, and R5. The pH values ranged between 8.42 and 8.47. Samples near the cathode area L1, M1, and R1 had very similar pH values (between 7.6 and 7.9). This similarity in pH for sections L, M and R indicate that the effect of the electrical field was not confined to a narrow area along the distance between the electrodes. Therefore, the effect of electrical field can form an objective for further investigation.

Figures 38 and 39 show the changes in pH profile and water content within the soil in the left (L), middle (M), and right sections.

Table 15 pH and water content of soil samples in cell I-9

Right Section	*pH*	*W.C [%]*	*Middle Section*	*pH*	*W.C [%]*	*Left Section*	*pH*	*W.C [%]*
1	8.32	42.42	1	8.42	42.40	1	8.47	42.07
2	8.14	40.48	2	7.90	40.54	2	8.10	41.00
3	7.86	39.28	3	8.08	40.55	3	8.12	36.60
4	7.83	40.00	4	8.04	40.95	4	8.16	40.00
5	7.60	40.75	5	7.90	39.6	5	7.72	40.56

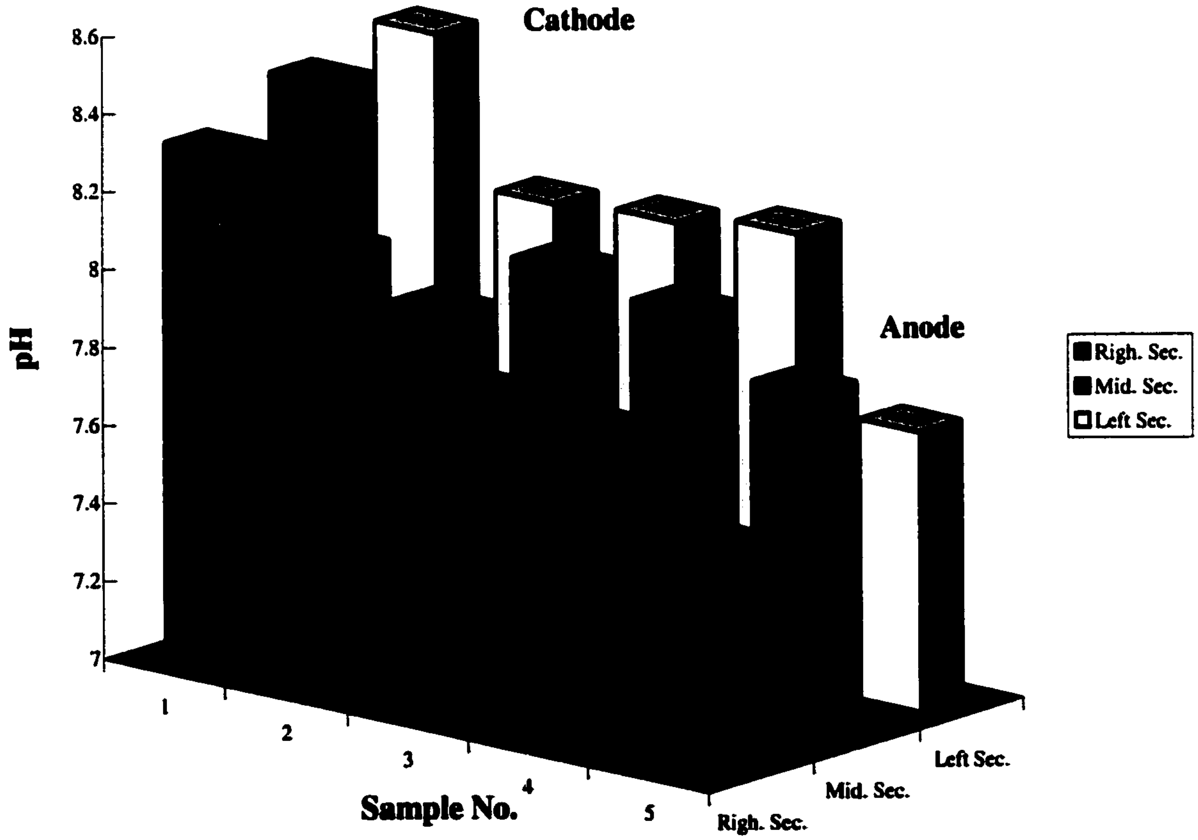


Figure 38 pH of Soil Samples in cell (I-9)

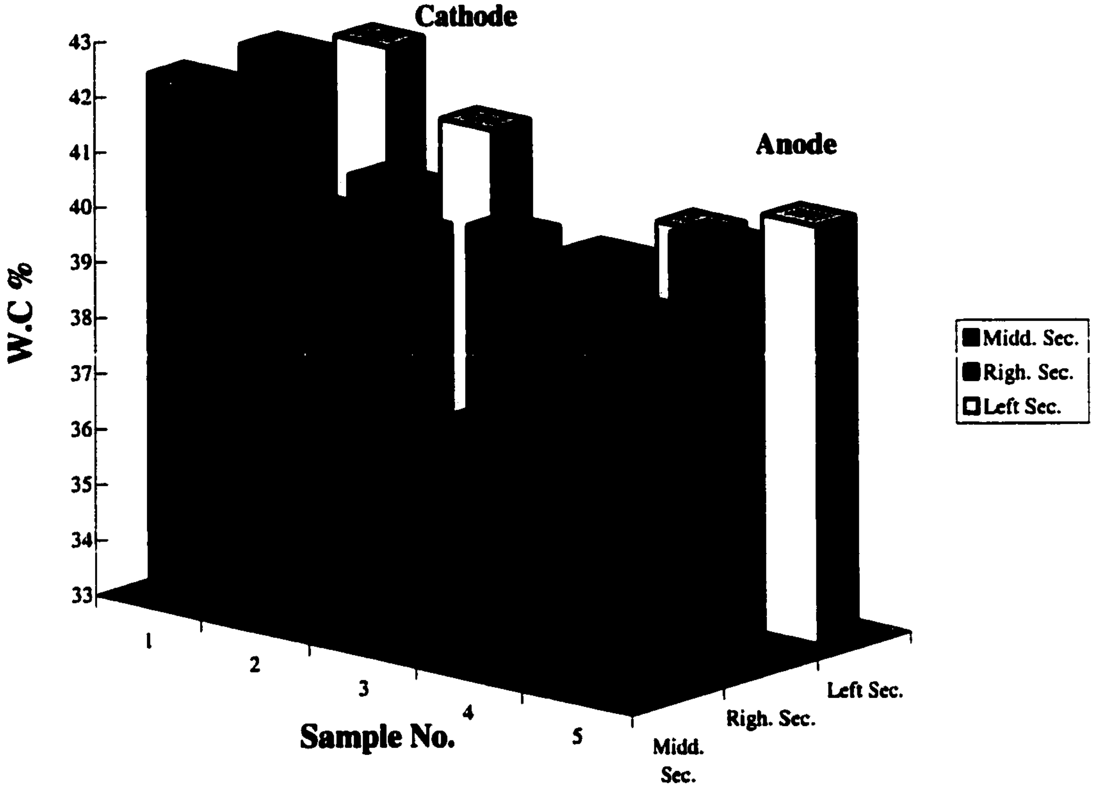


Figure39 Water Content of Soil Samples in cell (I-9)

Monitoring of the potential distribution between the electrodes was conducted through direct measurements of potential at 8 probe electrodes distributed evenly along the distance between the anode and the cathode. Figure 40 presents the relationship between the potential value and the distance from the cathode. The figure shows that a maximum potential value of 2.28 V was measured at 118 and 163 hours. The potential gradient between probe 1 and 8 at the beginning of the test was 0.42 V. This gradient increased to 0.63 V after 163 hours. This slight increase could be attributed to the effect of the washing system, which prevented the generation of a high pH zone near the cathode called in electrokinetic (precipitation zone). Also supplying the anode continuously with a conditioning liquid prevented the soil from drying and crack formation. Figure 40 also shows that all probes display a logarithmic increase in potential. This pattern persisted through half the distance between electrodes. After that distance, the potential values were steady up to the last probe (near anode). The relationship between the potential in each probe with time also has been plotted in Figure 41. The graph shows that within the first 26 hours there was an almost linear increase in potential value at all probes. This value persisted untill 118 hours and the reported gradient ranged from 0.77 V for probe 1 and 1.23 V for probe 8. A slight drop in potential was noticed at 150 hours, and subsequently maintained until the end of the test. A direct relationship between the pH of the washing system and an increase in potential at the probes can be established based on the fact that a decrease in potential was reported after changing the water in the washing system (at 117 hours).

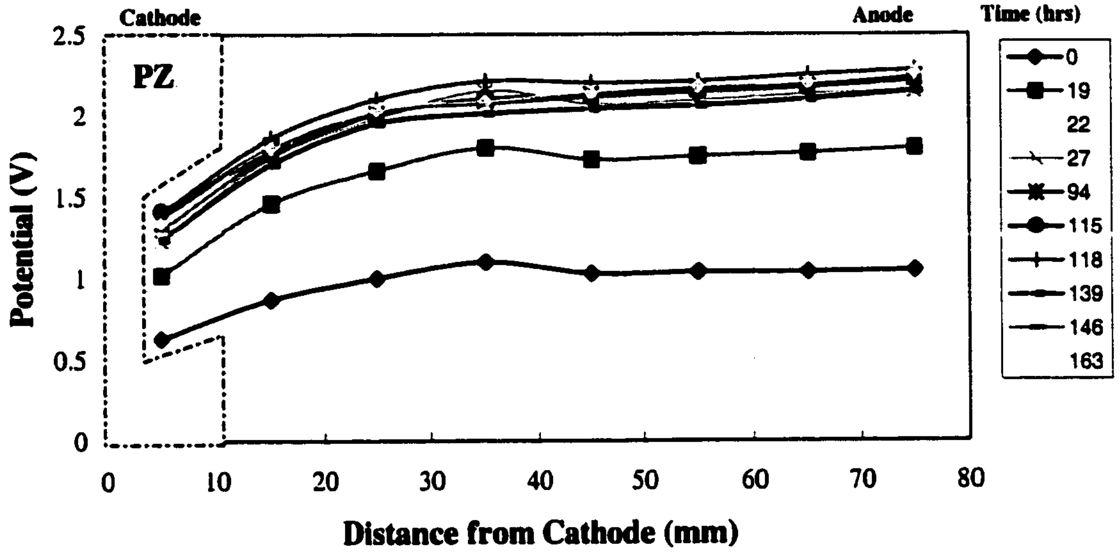


Figure 40 Potential Distribution vs. Distance Measured in subsequently situated Probes at Different Time

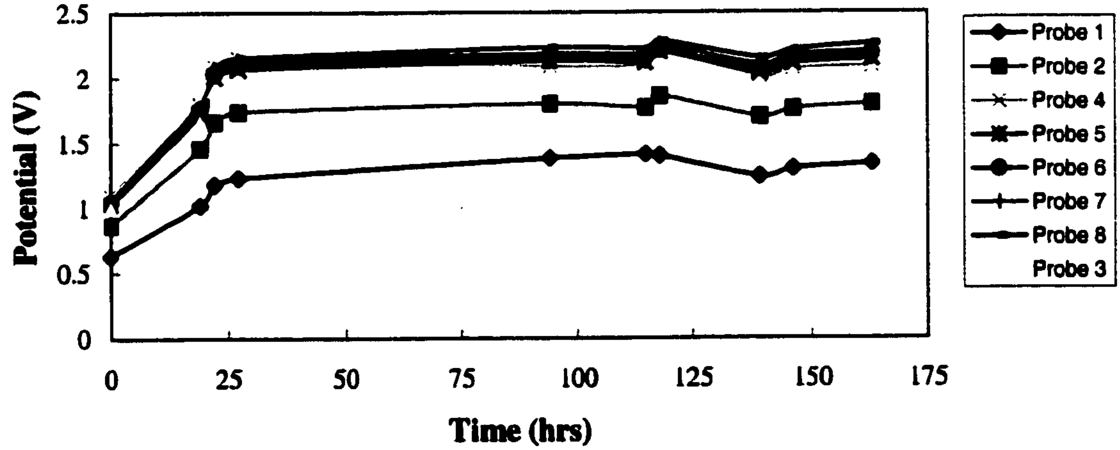


Figure 41 Potential Distribution vs. Time Measured in subsequently situated Probes Starting form the Cathode Area

8.1.4. Experiment I-11

Experiment objectives:

This experiment was conducted to test the distribution of the electrical field in two-dimensions. The outcome of this test will determine the extent of the electrical field in a direction perpendicular to the distance between the electrodes and permit conclusions to be made with respect to the effectiveness of this method.

Set-up:

A square cell (I-11) was chosen to conduct this test. Two electrodes were situated along the line dividing the cell in half. Between these electrodes, 8 probe electrodes were inserted in the soil. Apart from the main probe electrode set, an additional two sets at each side of the main set were inserted in the soil. Therefore, a total of 40 probes distributed evenly within the cell were used to track the development of the electrical field through the test (Fig. 42). The distance between cathode and anode was 8-cm and the total current between them was 2.4 volts. Soil type 6-4 was used with an initial water content of 40%. The anode was connected to a Conditioning Liquid Supply System, however no permeable zones or washing system were used. Apart from monitoring electrical parameters, the pH of the catholyte was monitored. The test lasted 32 days and upon its termination, destructive soil sampling was conducted.

Observations:

- Formation of white powder around the cathode was observed after 2-days of the test;
- Formation of a dark brown area around the anode;
- At the last stages of the test the electrical gradient declined;

- The total volume of injected conditioning liquid in the anode was 265 ml and the extracted catholyte totalled 195 ml.
- There was no interruption in catholyte flow, however the catholyte pH during the test was high (12.3 – 12.5).

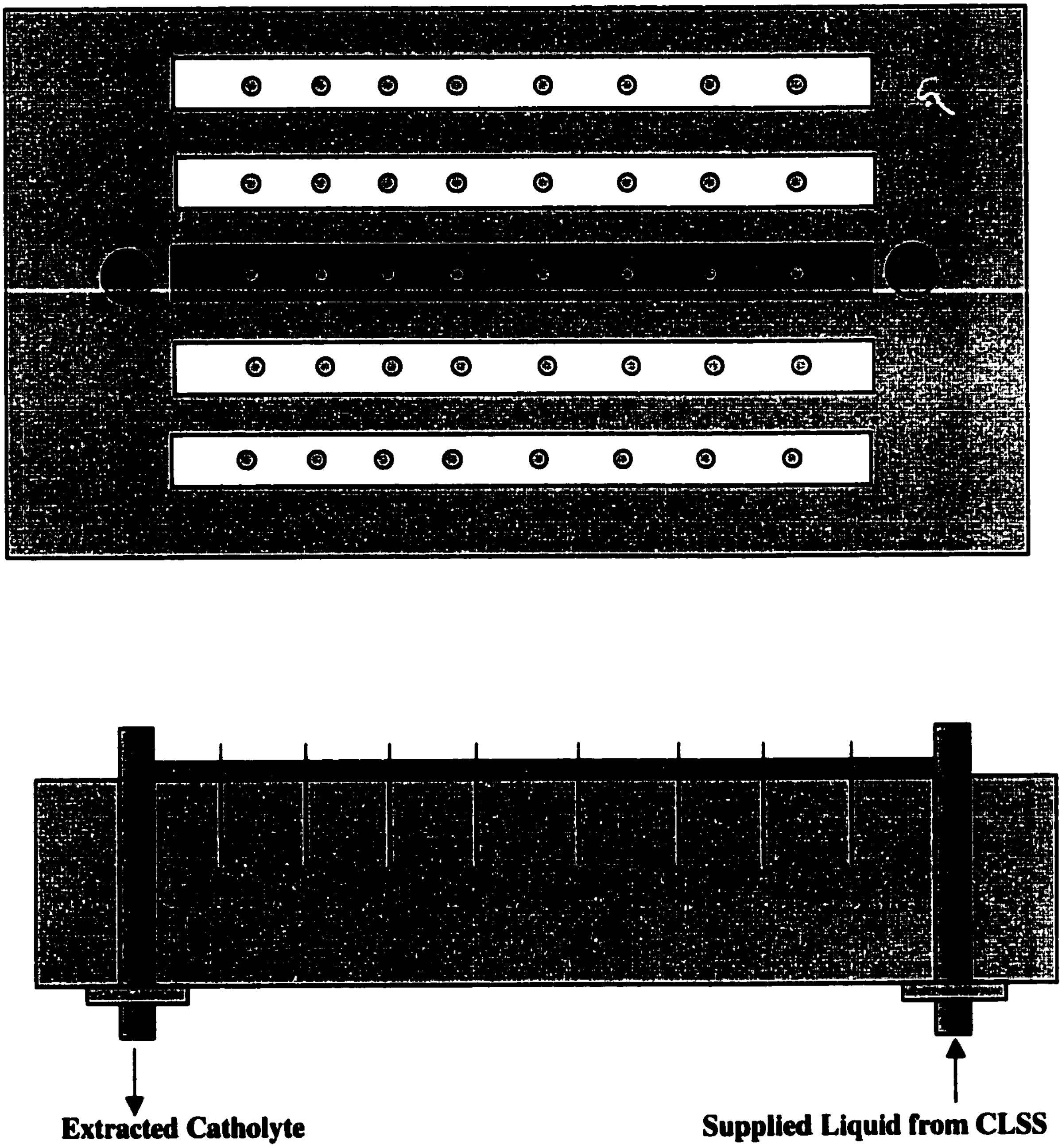


Figure 42 Schematic Drawing of cell I-11

Results and discussion:

Soil sampling

Figure 43 presents a schematic diagram for the soil-sampling regime. The width of the cell was divided into five sections, a subdivision of these sections followed in a way that section-1 had 10 divisions, section-2 had 5 divisions, section-3 and section-4 had 7 divisions and section-5 had 5 divisions. The discrepancy in the number of the subdivisions in each section was related to practical restraints. The results of pH and water content related to these samples are listed in Table 16.

The results show that section "3" (the section along the electrodes) has been subjected to the most changes in the moisture content where the maximum difference in the soil samples was 7%. On the other hand, the difference in WC profiles in sections 1, 2, 4, & 5 were 3%.

The absence of a cathode washing system influenced the pH values of the soil samples near the cathode and also section 3 was influenced the most followed by sections 2 and 4. The influence of the basic zone generated at the cathode did not reach sections 1 & 5 where the pH value of the soil samples was in the range of 8. Supplying the anode continuously with conditioning liquid also had a direct effect on eliminating soil dehydration in the anode area and consequently preventing soil cracking and process interruption. It is important to point out that the value of pH in the soil samples near the anode was kept at a level of pH 7.

Table 16 pH and water content of soil samples

Section 1	1	2	3	4	5	6	7	8	9	10
pH	8.03	8			7.8	7.68			7.58	7.54
W/C %	40.56	40.86	41.1	39.68	41.79	40.76	40.23	40.44	41.46	41.33
Section 2	1	2	3	4	5					
pH	10.65		7.69		7.48					
W/C %	41.82	38.99	40.98	42.01	41.3					
Section 3	1	2	3	4	5	6	7			
pH	10.9			7.85			7.73			
W/C %	37.9	33.78	39.37	38.6	38.29	35.08	41.08			
Section 4	1	2	3	4	5	6	7			
pH	10.74			8.08			7.22			
W/C %	36.63	45.45	36.56	39.34	39.43	36.76	38.42			
Section 5	1	2	3	4	5					
pH	8.1		7.85		7.66					
W/C %	38.44	38.21	38.88	36.41	38.2					

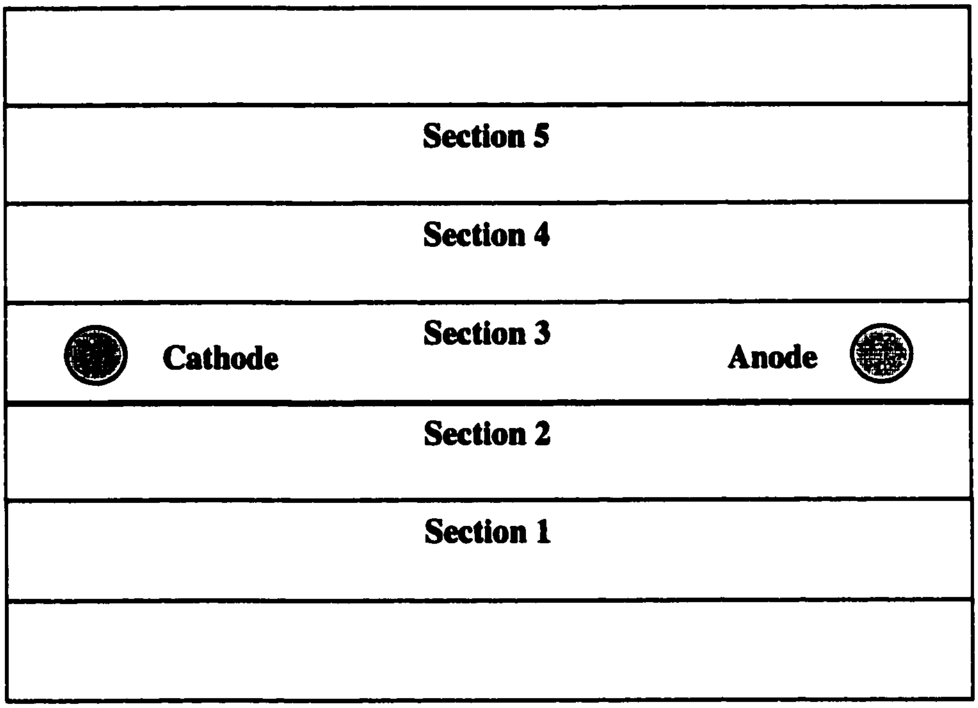


Figure 43 Dividing Scheme of cell I-11

Monitoring of the 2-D potential distribution in the cell was conducted through direct measurements at the 40 probes distributed evenly in the cell. The relationship between the potential and the distance from the cathode in the main section (section 3) is presented in Figure 44. A maximum potential of 2.56 V was recorded at probe 8 at 210 hours. A minimum potential of 1.34 V was recorded at probe 1 at 258 and 306 hours. The graphs also show that the potential had a linear trend along the distance between the electrodes with a gradient changing from 0.76 V at the beginning of the test to 1.07 V at the end. Figure 45 presents the relationship between the potential in each probe and the time. The graph indicates that probe 1 did not show any significant potential change during the test. Changes started to show in probe 2 and became more significant in probes

3 to 8. The main changes occurred between 128 and 258 hours where the potential showed a significant increase and then a sharp drop (Fig. 45). The relationship between potential and distance from the cathode and between potential and time for sections 1,2,4, and 5 are presented in Figure 46 to 53. The graphs show that for section 1, the gradient between probe 1 and probe 8 dropped from 0.34 V at time = 0 to 0.21 V at time = 380 hours. The potential in probe 1 increased by 0.17 V after 380 hours. The same change was reported for probe 8 (Fig. 47, 48). In section 2, the potential gradient between probe 1 and 8 was 0.58 V/cm at the beginning of the test. This gradient dropped to 0.44 V/cm by the end of the test. The potential in probe 1 changed from 1.5 V (at the beginning) to 1.62 V (by the end). Probe 8 showed a decrease of 0.02 V during the test. In section 4, the gradient between probe 1 and 8 was 0.06 V/cm at he beginning of the test, and this value changed to 0.33 V/cm by the end of the test. Probe 1 had a 0.51 V increase in potential during the test compared with 0.78 V for probe 8. In section 5, a gradient of 0.15 V was recorded between probe 1 and 8, and this value persisted throughout the test. The same change in potential occured during the test for probe 1 and 8 (0.45 V).

All sections witnessed a rapid increase followed by a sharp decrease in potential within 138 and 283 hours. However the highest value was recorded in section 4 between 210 and 234 hours. The results show a uniform distribution of the electrical field.

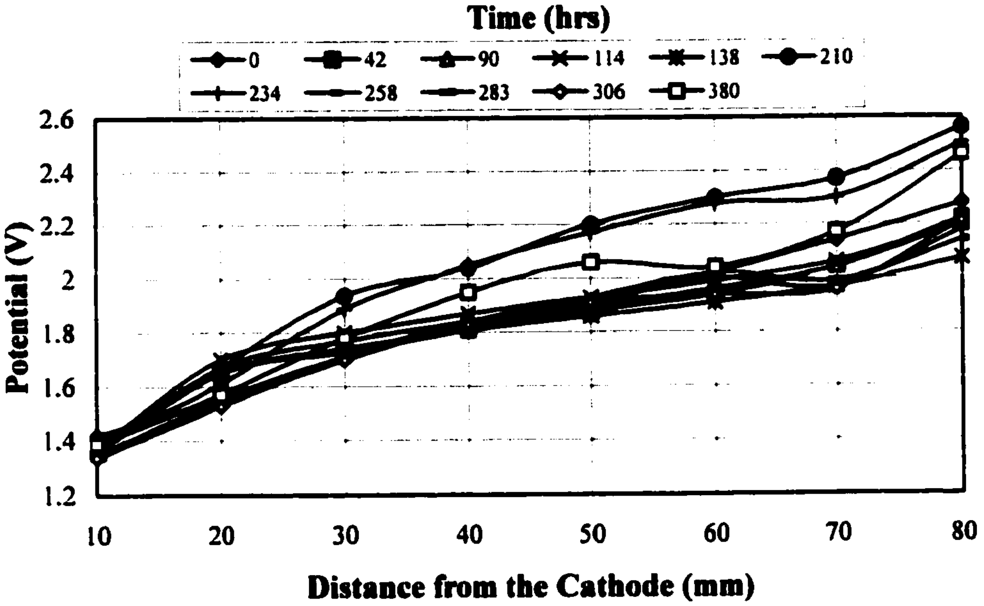


Figure 44 Potential Distribution vs. Distance from the Cathode Measured at Different Times for Section 3

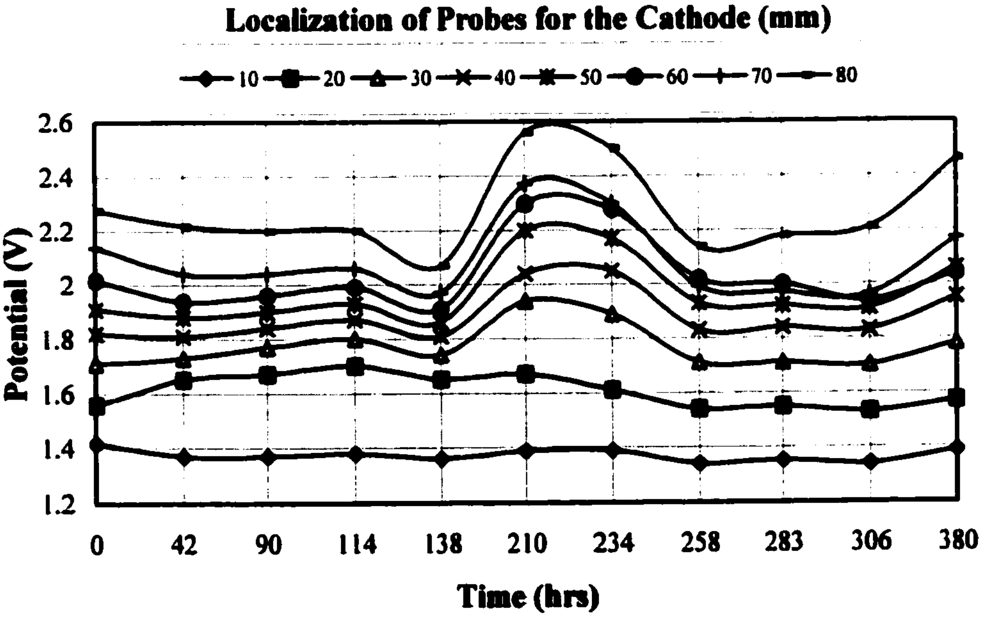


Figure 45 Potential Distribution vs. Time Measured at Different Probes for Section 3

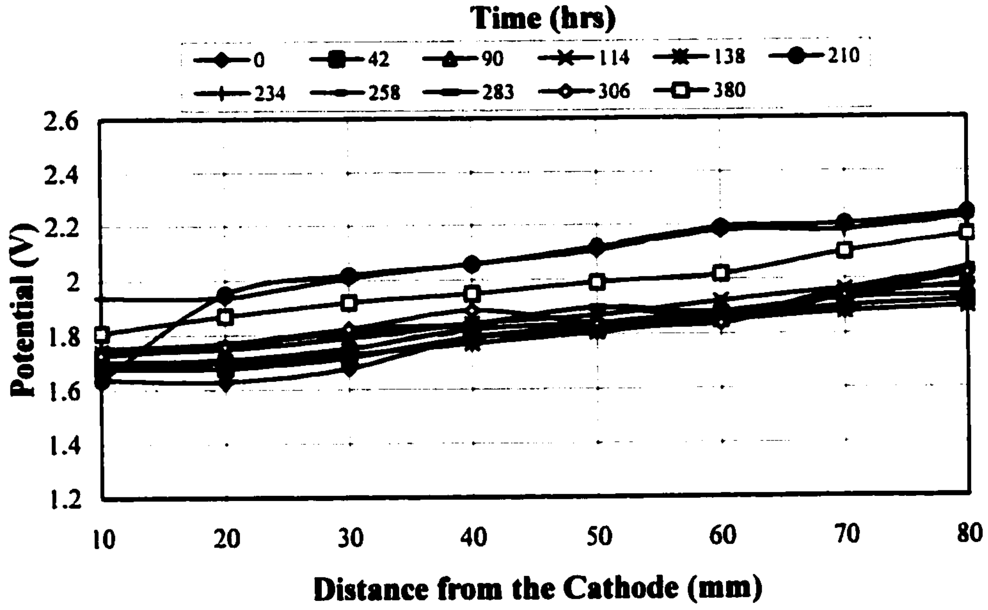


Figure 46 Potential Distribution vs. Distance from the Cathode Measured at Different times for Section 1

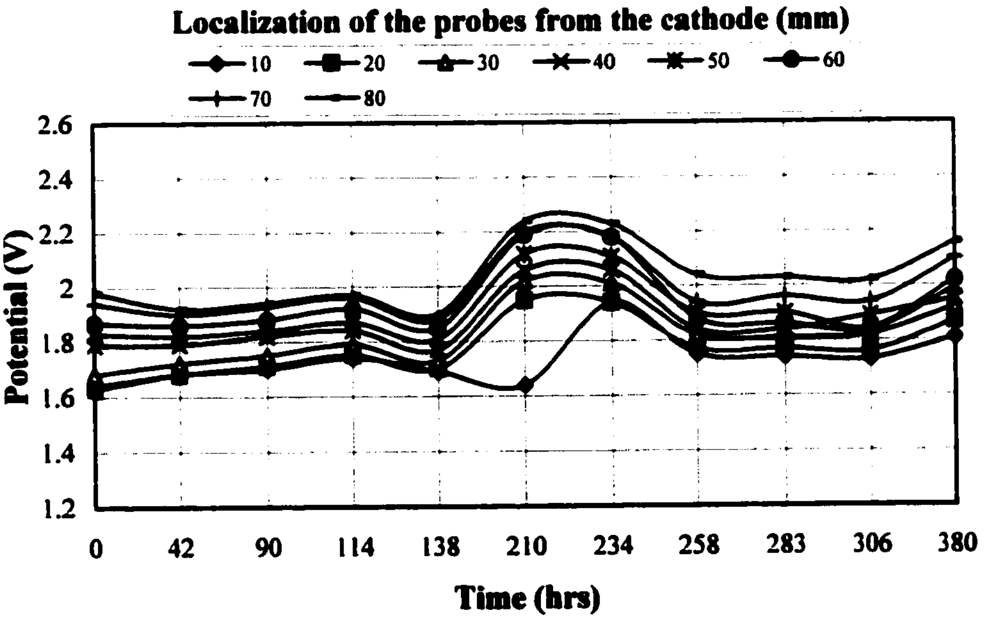


Figure 47 Potential Distribution vs. Time Measured at Different Probes for Section 1

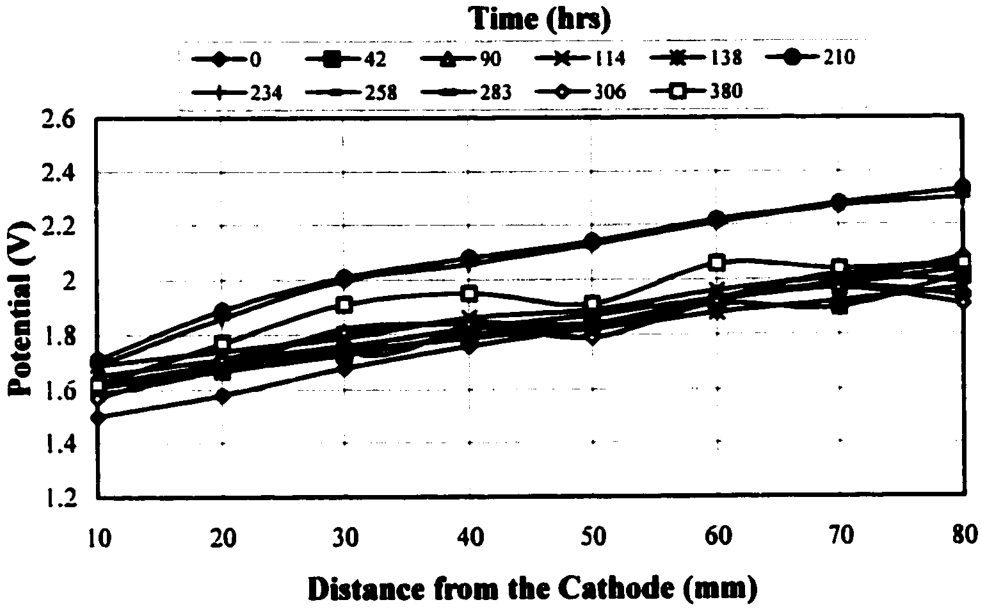


Figure 48 Potential Distribution vs. Distance from the Cathode Measured at Different Times for Section 2

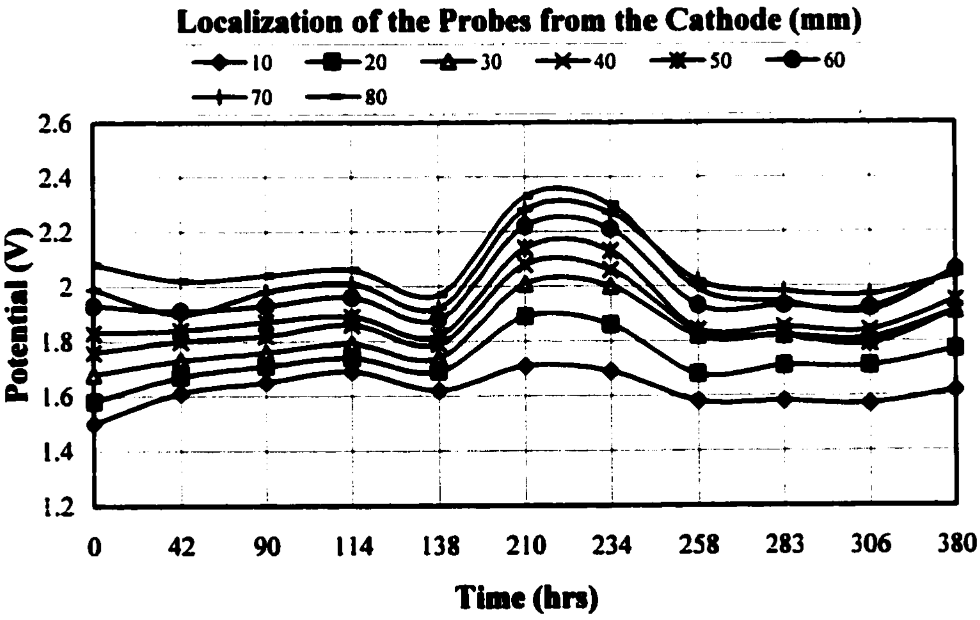


Figure 49 Potential Distribution vs. Time Measured at Different Probes for Section 2

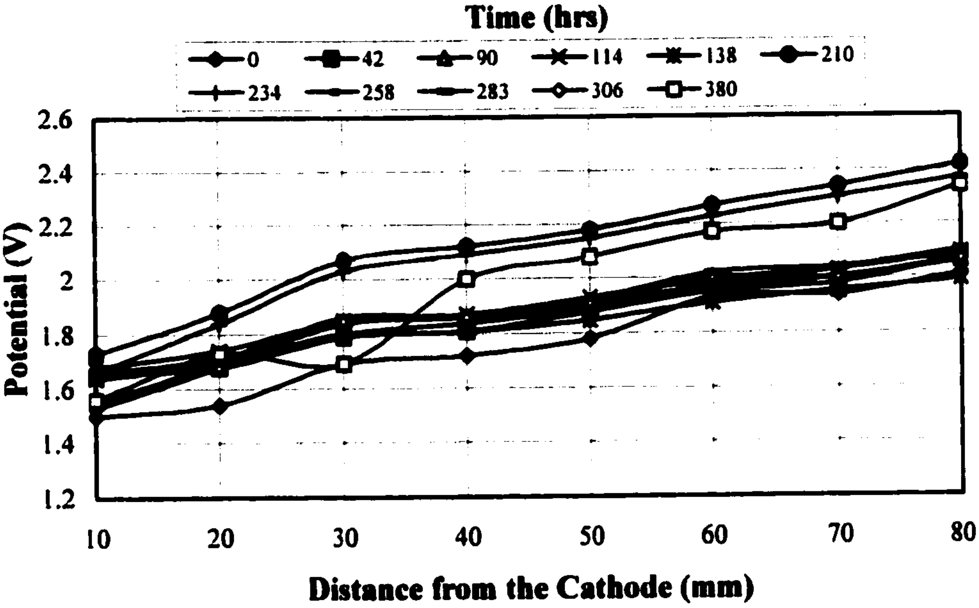


Figure 50 Potential distribution vs. Distance from the Cathode Measured at Different Times for Section 4

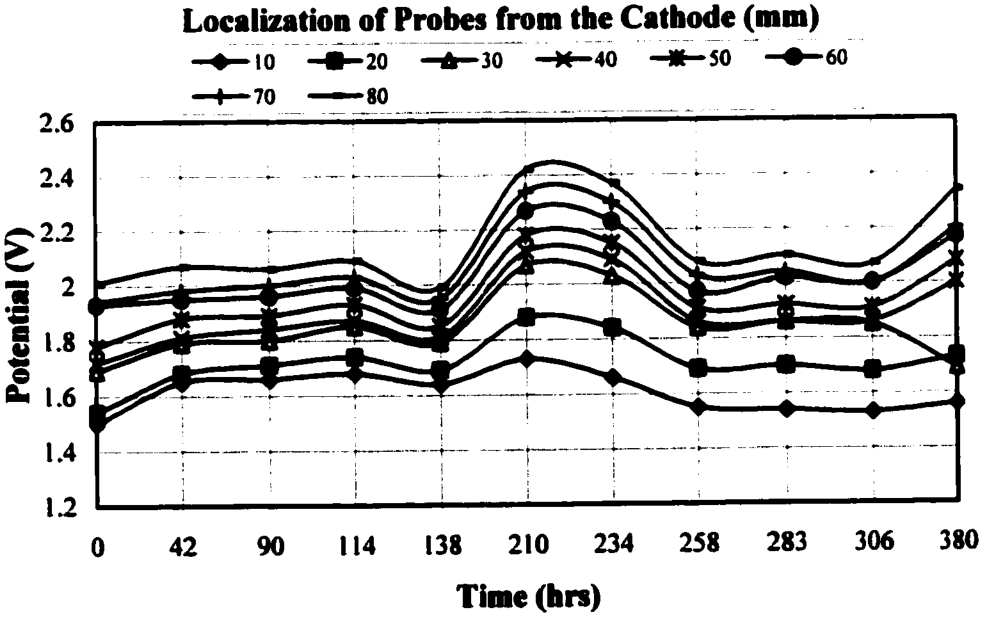


Figure 51 Potential Distribution vs. Time Measured at Different Probes for Section 4

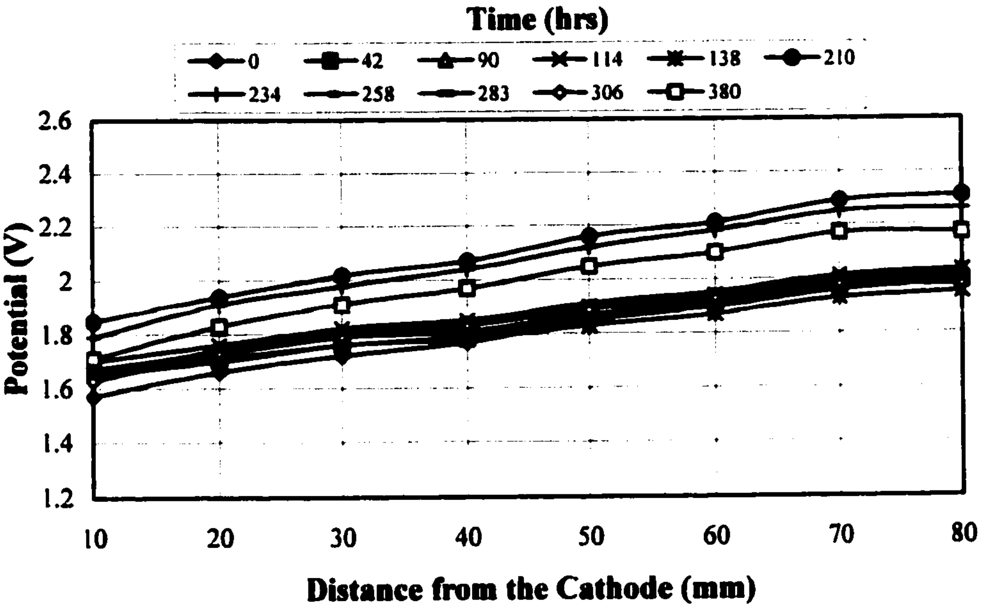


Figure 52 Potential Distribution vs. Distance from the Cathode Measured at Different Times for Section 5

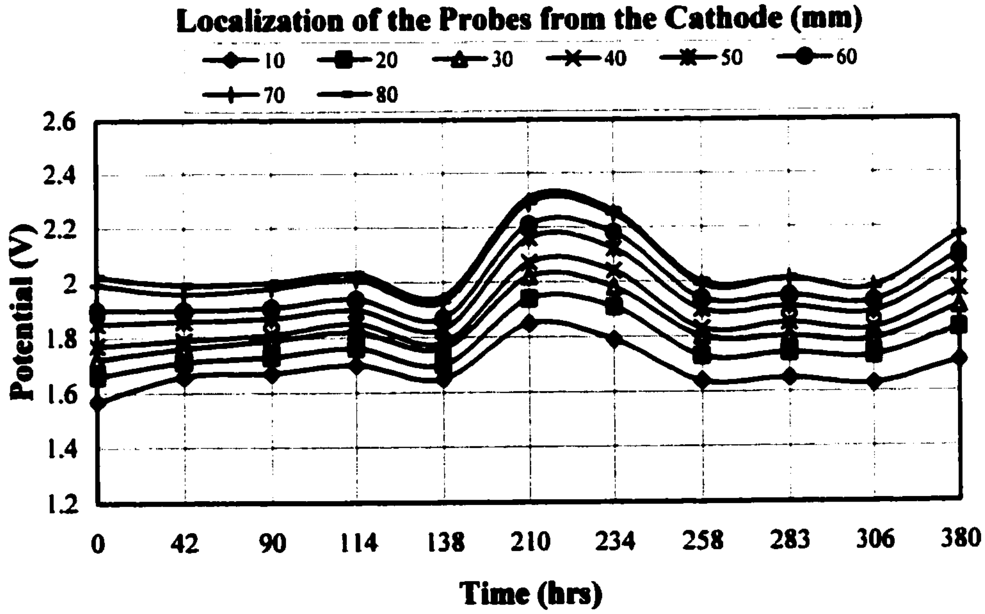


Figure 53 Potential Distribution vs. Time Measured at Different Probes for Section 5

8.2. Phase II

This phase consisted of four experiments II-8, II-10, II-12, and II-13. Tests were conducted on upgraded (larger) scale cells, using the same type of soil (6-4) that was used in phase-I. The installations of phase II were described in sections 7.1. and 7.2. Cell installation soil preparation and packing followed the same procedure as described in phase-I.

During phase II an evaluation of the electrokinetic system for HOC removal was performed using an electrode distance of 16 cm. The performance of washing system and system behaviour due to the introduction of two different surfactants was also tested. Finally, an entire set-up, equipped with a Conditioning Liquid Supply System (CLSS), Surfactant Supply System (SSS) and washing System (WS) was tested and evaluated on a cell contaminated with diesel fuel. Cells parameters and arrangements are described in Table 17.

8.2.1. Experiment II-8

Objectives:

This test was conducted to evaluate the system performance upon increasing the distance between the anode and cathode. The effect of permeable zone placement on the pH distribution was also monitored.

Set-up:

The test was conducted on two cells sharing the same set up, They differed in the distance between electrodes; a that 16 cm distance between the electrodes was chosen for cell II-8-1, and 8 cm was chosen for cell II-8-2. Two Permeable Zones (PZ) (1 cm each) were placed in each cell. Each zone was placed 2 cm from the electrode. Anodes and the closest Permeable Zones in both cells, were connected to a Conditioning Liquid Supply System (CLSS). A schematical drawing of these cells is presented in Figure 54 & 55.

Table 17 Cells Parameters and Technical Arrangements

Tests	Distance [mm] A-C	PZ Thickness [mm] B1	Barrier Thickness [mm] B2
Cells			
II-8-1	160	10	10
II-8-2	80	10	10
II-10-1, 2 & 3	160	10 Near A	40 C
II-12	160	10	10
II-13	160	10	10

Initial moisture content of 40% was used for cell packing. To estimate moisture losses during the packing procedure, soil samples were taken from each packed cell and its moisture content was determined. The test showed that 5% of the moisture has been lost during packing and preparation procedures. The supplied voltage for each cell was proportional to the distance between its electrodes, to obtain a gradient of 0.4 V/cm, so cell II-8-1 was provided with 4.8 volts and cell II-8-2 with 2.4 Volts.

Electrical parameters were monitored during the test by conducting measurements through 16 probe electrodes placed in cell II-8-1 and 8 probes in cell II-8-22. Apart from electrical measurements, pH of the catholyte was monitored and the volume of liquid injected daily into both cells was recorded reaching a total volume of 325 ml.

Test II-8 lasted for 9 days and upon its termination, a destructive soil sampling was conducted.

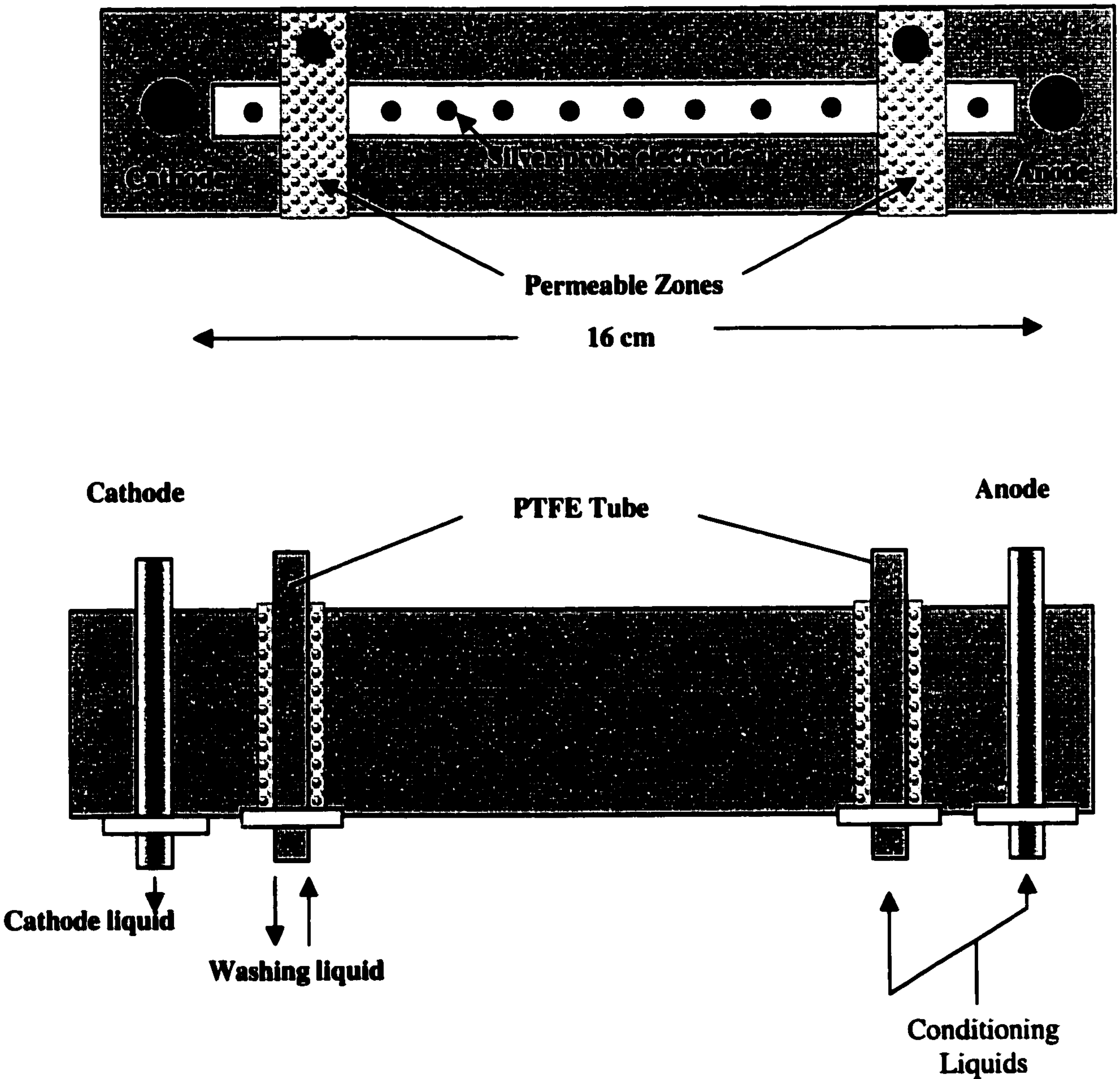


Figure 54 Schematic configuration of cell II-8-1

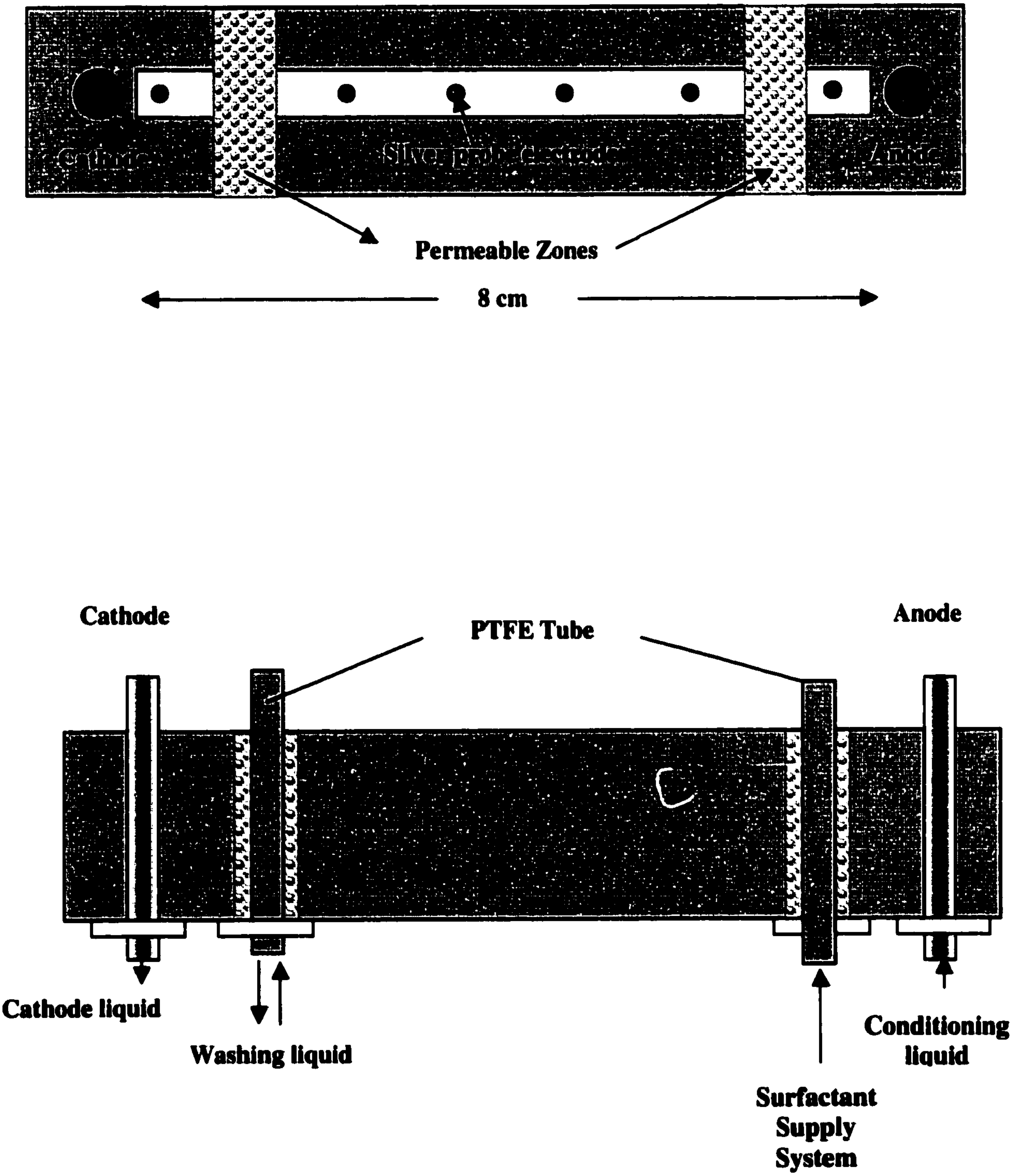


Figure 55 Schematic configuration of cell II-8-2

Results and discussion:

The results of pH analysis for the catholyte liquids indicated that the pH value increased quickly and was in the range of 12-13 in both cells (Tab. 18). The pH values increased rapidly, which can be attributed to the lack of a washing system in the PZ near the cathode. Analysing moisture content and pH profiles in the soil was achieved by obtaining nine samples taken from II-8-1 and six samples from II-8-2. The results are shown in Table 19. Figures 56 & 57 show the pH profile in the soil for both cells. The graphs indicate that the pH profile in both cells was similar and showed no changes along the distance between the PZs. The only exception was the part of the soil adjacent to the cathode where the pH value reached 10.3 and 9.4 for cell II-8-1 and II-8-2 respectively. This difference can be largely attributed to the higher potential supplied to cell II-8-1. The graphs also show that the PZ prevented the basic front from advancing to the anode side and in the matter the acid front from advancing to the cathode side.

Table 18 pH of Catholyte Liquid

Day	Time (hr)	Cell II-8-1	Cell II-8-2
1	18	10.6	12.7
2	42	12.5	12.7
3	67	12.9	12.6
7	187	12.9	12.6
8	211	11.3	12.1
9	235	12.3	12.1

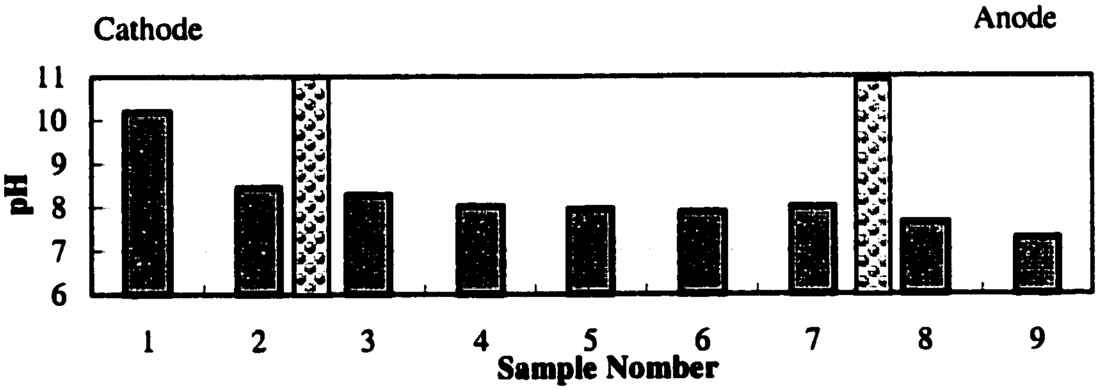


Figure 56 pH of Soil Samples in cell II-8-1

Table 19 pH and Moisture Content in Cell II- 8-1 and Cell I-8-2

II-8-1 Sample No.	1	2	3	4	5	6	7	8	9
pH	7.29	7.64	8	7.9	7.95	8.02	8.1	8.27	10.3
WC %	40.43	43.67	41.6	38.67	38.08	38.46	40.59	41.06	36.7

II-8-2 Sample No.	1	2	3	4	5	6
pH	7.62	7.93	7.86	7.9	8.5	9.39
WC %	39.24	39.9	38.19	39.45	37.28	41.71

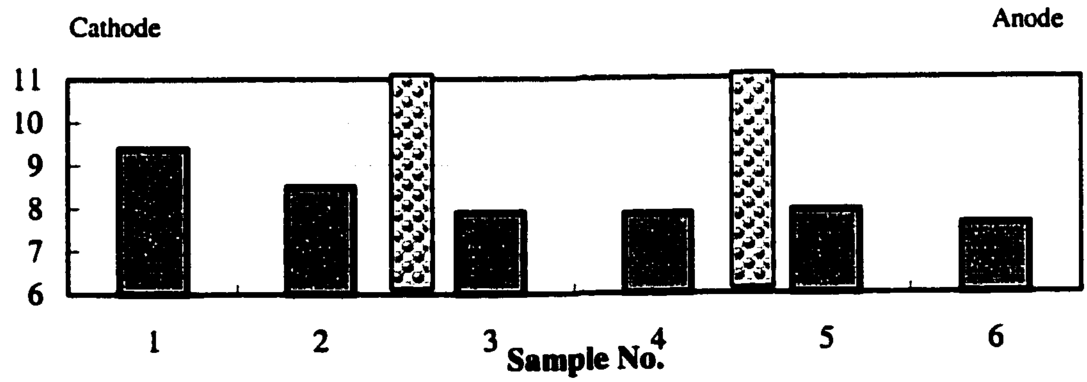


Figure 57 pH of Soil Samples in Cell II-8-2

The results of electrical parameter measurements are plotted in Figure 59 to 62. The relationship between potential distribution and the distance from the cathode is shown in Figure 58 & 59 for cell II-8-1 &II-8-2 respectively. In cell II-8-1 three distinct areas were recognized (before and between the PZs). The area between the PZs showed a gradual and stable increase in the potential as a function of the distance from the cathode. The instabilities were developed between the probes separated by the PZ's. The major increase happened in the cathode side between probes 2 and 3, which are separated by the PZ, where the potential gradient increased from 0.78 V at the beginning of the test to 2 V by the end. On the other hand, the developed gradient between probes 12 and 13 (anode side) decreased from 0.44 V to 0.27 V by the end of the test. In cell II-8-2 the same pattern was recognized, however, a lower gradient was observed between the three areas. The potential increase near the cathode can largely be attributed to the presence of the PZ which showed a higher resistance. This zone showed an increase in carbonate content with time, as shown in the results for I-6. This caused the potential to rise in this section and highlighted the need to wash this area. The presence of the PZ near the anode did not influence the process as much as the PZ near the cathode, however the decrease in the gradient suggested that the delivery system (SSS) did not have a negative impact on the process. The relationship between the potential distribution and time are presented in Figures 60 and 61. The graphs show that the potential values did not show large changes with time, it displayed a linear pattern with no recognizable instabilities. It led to the conclusions that a scaled-up electrokinetic system did not change its behaviour as the distance between electrodes increased.

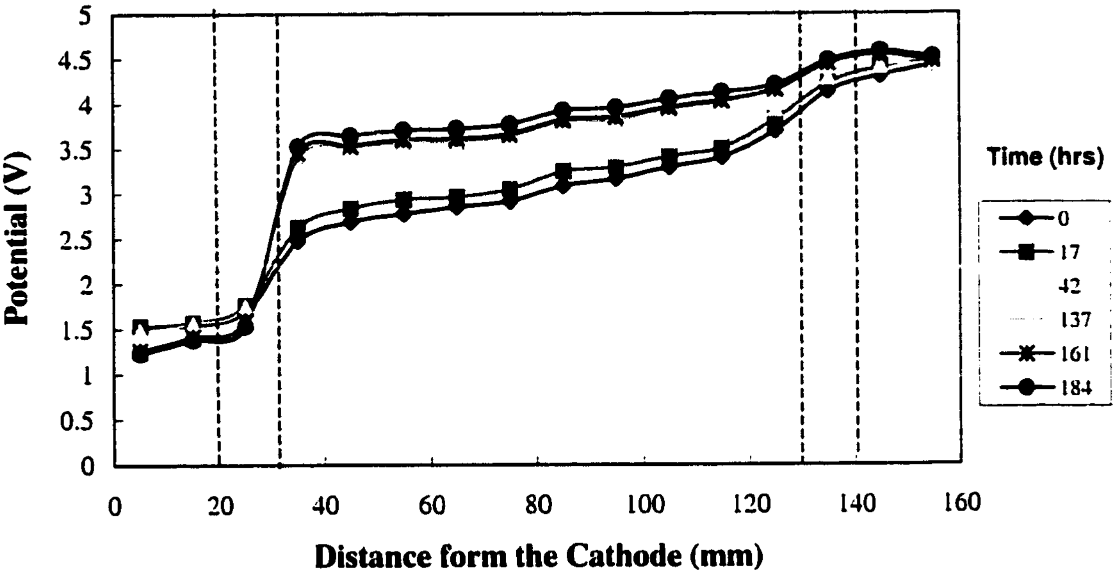


Figure58 Voltage Distribution vs. Distance from Cathode in Cell II-8-1

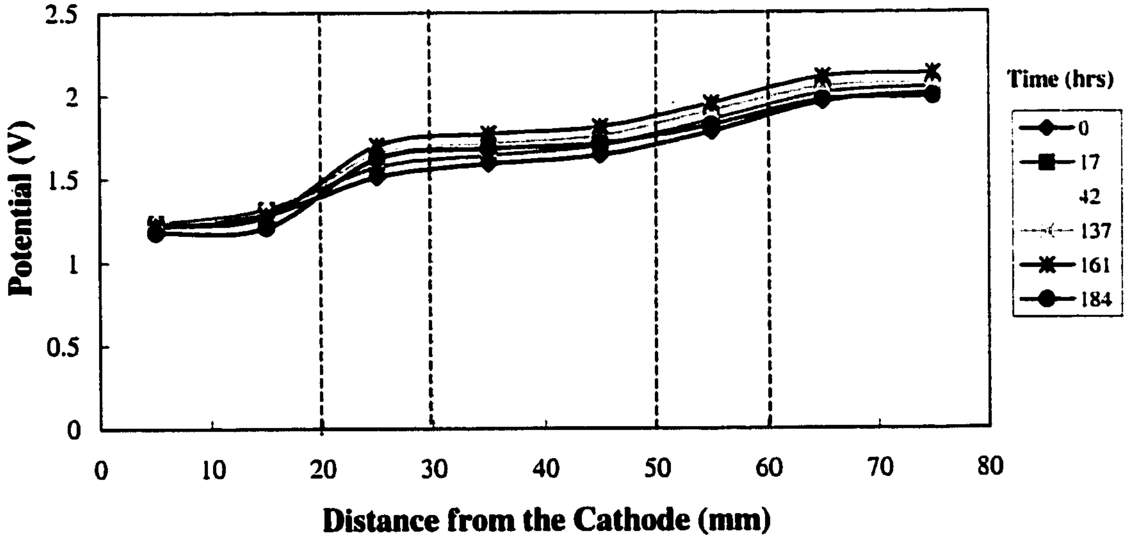


Figure 59 Voltage Distribution vs. Distance from Cathode in Cell II-8-2

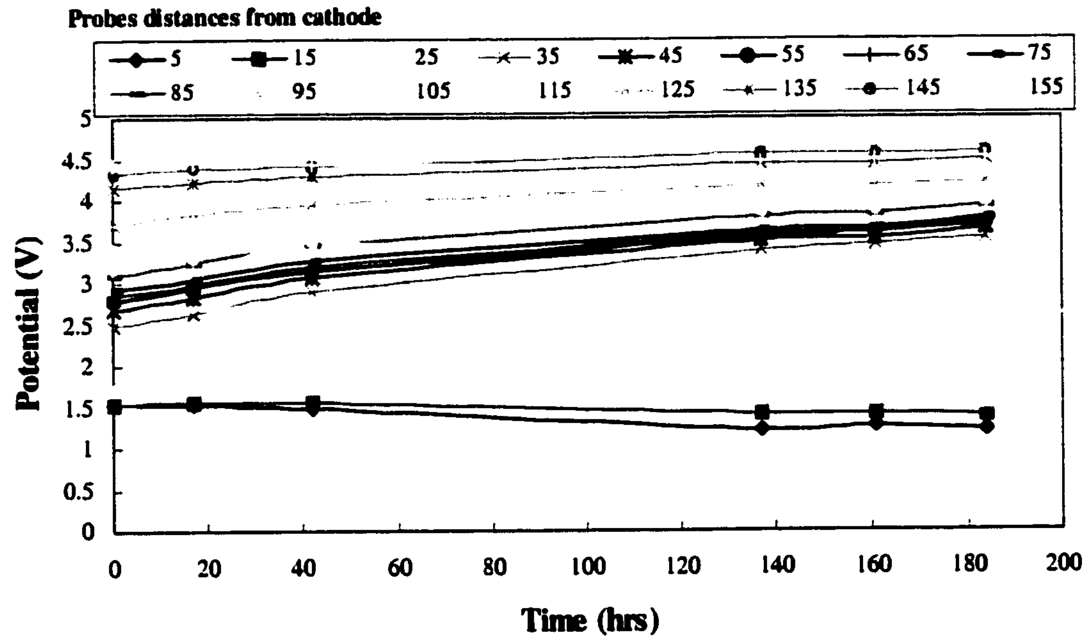


Figure 60 Voltage Distribution vs. Time Measured for Each Probe in Cell II-8-1

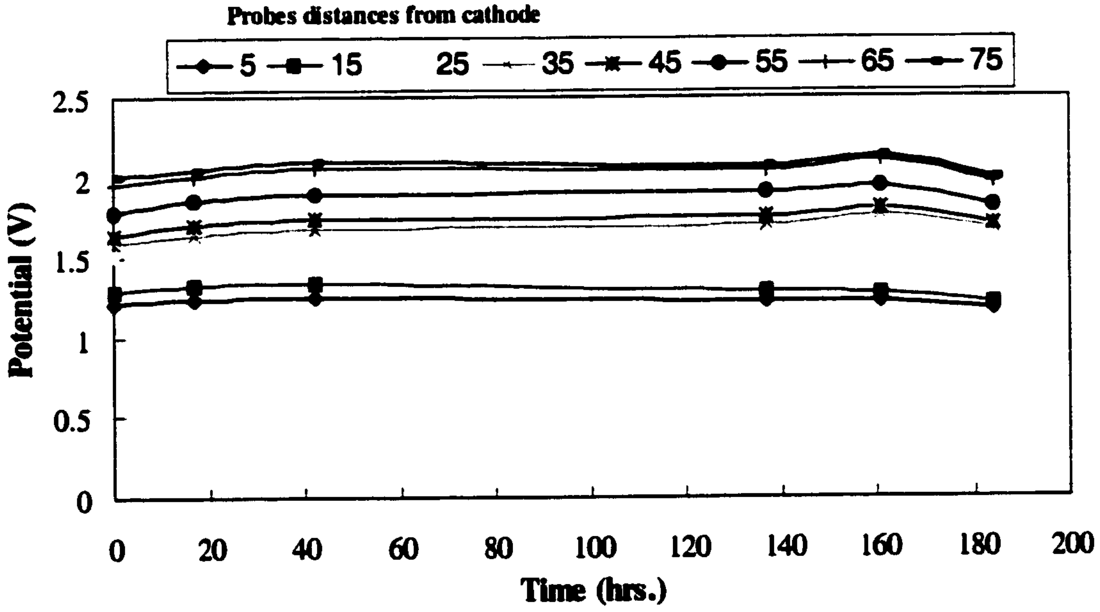


Figure 61 Voltage Distribution vs. Time Measured for Each Probe in Cell II-8-2

8.2.2. Experiment II-10

Objectives:

This test was carried out to verify the viability of the permeable zones as an area for surfactant introduction, and to evaluate system performance (pH, electrical parameters) upon the introduction of different washing solutions. Also, the performance of the washing system was evaluated in this stage.

Set-up:

Three identical polyethylene cells (type II) were used in this experiment. The cathode and the anode in each cell were placed 16-cm apart. These electrodes were perforated and covered with a stainless steel mesh to prevent clogging (Fig.10). Soil (type 6-4), with an initial water content of 40% was used. The cells were connected in parallel to a DC power supply, which supplied each cell with 4.8 volts.

Figure 62 shows schematically, the set–up used in this test. Each cell consisted of two permeable zones. One permeable zone was placed within 2-cm distance from the anode and connected to a Surfactant Supply System (SSS) described previously in section 7.2.5 (Fig. 12). The cathode was placed directly in the second permeable zone, which was connected to a Washing System (WS) illustrated in Figure 14. Anodes were connected to a Conditioning Liquid Supply Systems (CLSS) similar to the one illustrated in Figure 12.

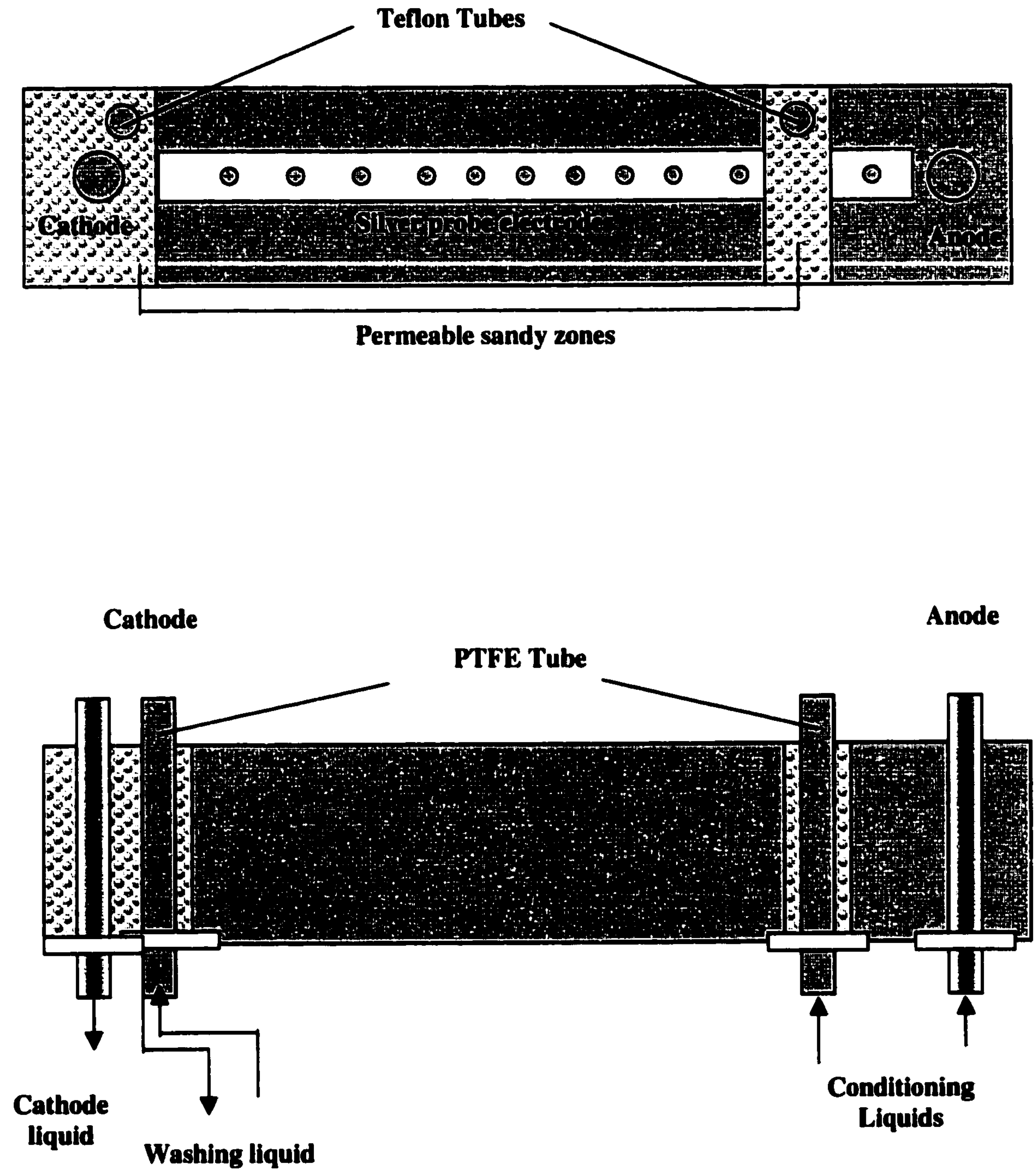


Figure 62 Schematic Configuration of Cells II-10-1, II-10-2, & II-10-3

The test lasted 25 days and within the first 6 days of the test, all three cells were washed with water which was supplied through the SSS. At day 7, surfactant type 101 (Triethylamine hydrochloride) was introduced in cell II-10-2 and surfactant type 401(Alkyldimethylbetaine) was introduced in cell II-10-3. In cell II-10-1, water was used as a conditioning liquid. During the test, samples from washing liquids were tested for pH and liquids were changed periodically when the pH was excessively high (e.g. pH = 11). Upon termination, a destructive soil sampling was conducted and the soil samples were tested for pH and moisture content values.

Results and discussion:

Soil along the distance between the electrodes was devided into 10 samples. Table 20 presents the results of soil samples analysis (pH and WC).

The pH profiles of the soil samples (Fig. 63 to 65) showed a similar distribution as a function of distance from the cathode. Similarities to the previous distribution (in small cells where an 8 cm distance between electrodes was kept) were also observed. A moderate pH was monitored along the cell, which proved that the washing system had a positive effect in regulating the pH of the soil. In cell II-10-1 (control), the pH was slightly higher especially in the cathode area. The introduction of surfactant evidently influenced the pH distribution. In the case of the water supply, it was suggested to change the washing liquid more often in order to prevent it from high pH values. It should be noted that use of cationic or amphoteric surfactant had no significant effects on the pH profile in the soil.

Table 20 Water Content and the pH of Soil Samples

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
PH	10.97	10.15	8.25	8.15	8.13	8.1	7.8	7.63	7.63	7.42
WC %	40.93	40.49	40.12	39.37	40.43	41.08	40.16	43.37	42.52	42.60
II-10-2	1	2	3	4	5	6	7	8	9	10
PH	9.85	8.32	8.18	8.15	8.15	8.14	8.09	8.09	7.8	7.55
WC %	40.44	40.39	39.77	39.87	39.59	39.93	40.21	40.49	41.46	40.53
II-10-3	1	2	3	4	5	6	7	8	9	10
PH	10.76	8.47	8.62	8.28	8.23	8.24	8.15	8.04	7.94	7.88
WC %	38.37	38.84	42.91	39.96	38.98	37.37	39.34	39.49	38.68	40.09

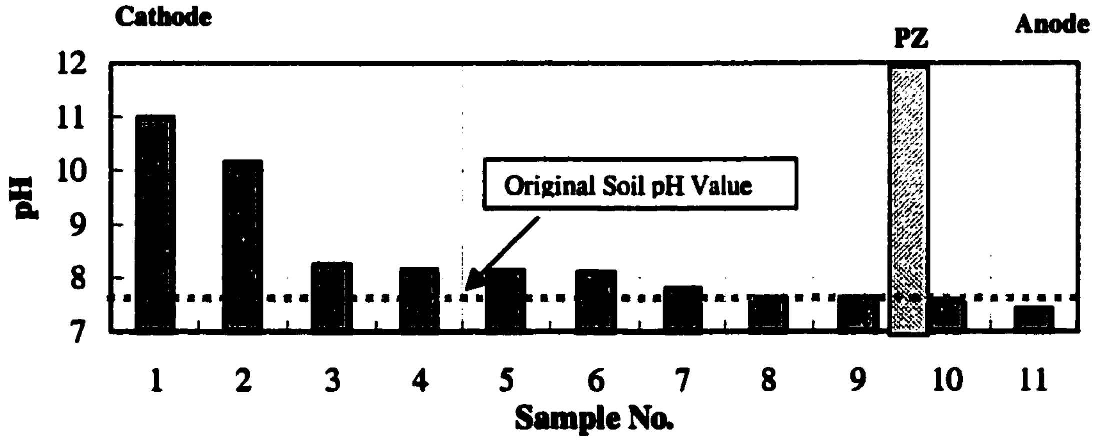


Figure 63 Distribution of pHfrom cathode in Cell (II-10-1)

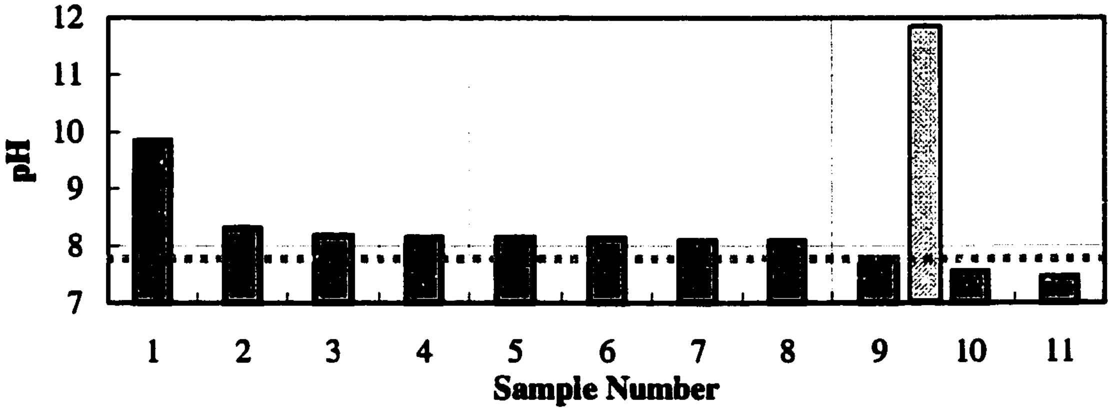


Figure 64 Distribution of pH from Cathode in Cell II-10-2

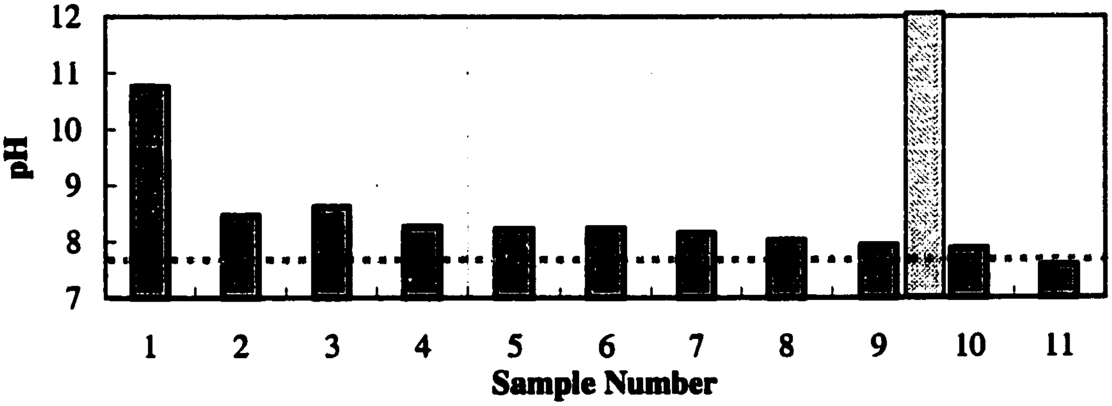


Figure 65 Distribution of pH from Cathode in Cell II-10-3

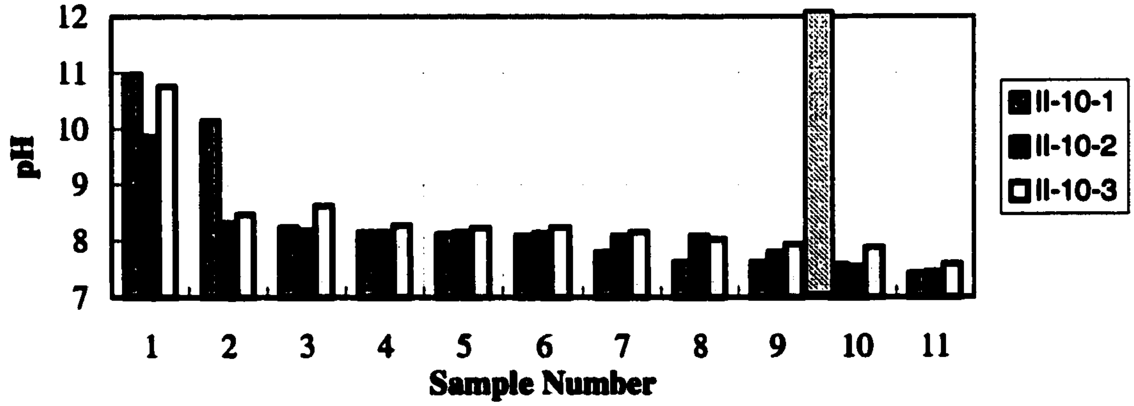


Figure 66Comparision of soil samples pH for Cells II-10-1, 2, & 3

8.2.3. Experiment II-12

Objectives:

The objectives of this test were to evaluate the overall performance of the electrokinetic cell being equipped with a Conditioning Liquid Supply System, Surfactant Supply System and Washing System.

Set-up:

The experiment was carried out on a long cell (type II) with a 16-cm distance between anode and cathode. Similarly to tests conducted previously, 6-4 type soil was used with an initial moisture content of 40%. Cell packing and soil preparation followed the same procedures as in previous tests (II-8, II-10). Electrodes were connected to a DC power supply and the total voltage supplied was 4.8 volts.

The anode was connected to a Conditioning Liquid Supply System (CLSS) already described in Figure 12 and amphoteric surfactant (401) was introduced to the cell through a 1-cm Permeable Zone situated 2-cm apart from the anode, using the SSS described in section 7.2.5. The cathode was not directly washed, however a 1-cm permeable zone placed 2-cm from the cathode was washed using the Washing System already described in Figure 14. A schematic drawing of this test is shown in Figure 67.

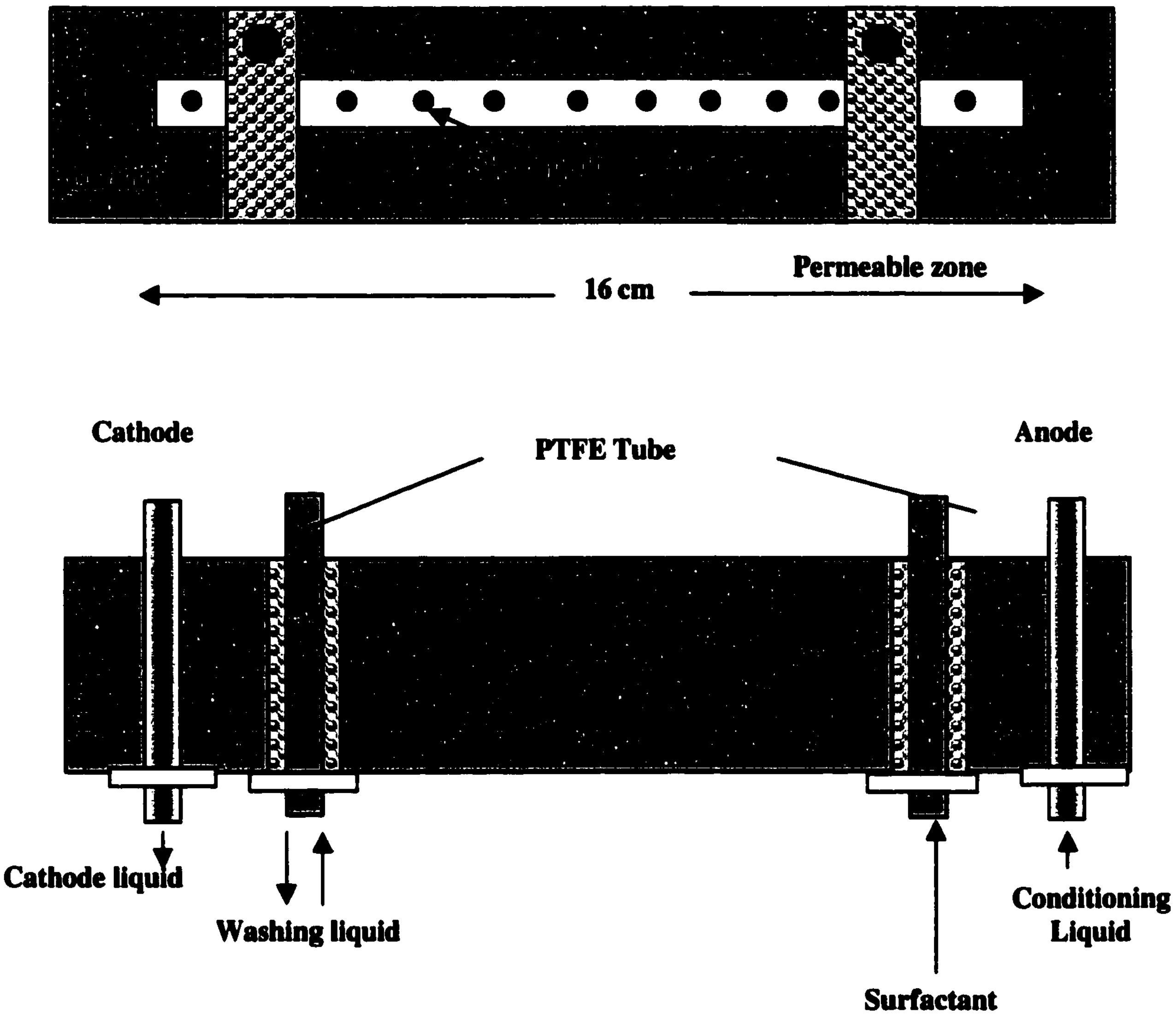


Figure 67 Schematic Configuration of the Cell II-12

During the test, samples from washing liquid and catholyte liquid were tested for its pH periodically. The test lasted 10 days and upon its termination a destructive soil sampling has been conducted. Soil samples were tested for pH and moisture content.

Results and discussion:

The results of the pH analysis for the washing liquid and catholyte liquid (Tab.21) show that controlling the pH value in the washing system (e.g. pH = 8 to 9) resulted in a relatively low pH in the catholyte liquid, in comparision to previous tests. A graphical plot of these results (Figure 68) shows a slightly higher value of catholyte pH than that of the washing liquid

Table 16 pH of catholyte and washing liquid

Day	*Time (hrs)*	*Permeable Zone*	*Cathode*
1	0.25	8.10	-
2	24.00	8.56	8.64
3	47.00	8.2	9.1
4	71.00	8.67	9.56
5	100.00	8.52	8.99
6	126.00	8.53	9.21
7	150.00	8.5	8.82
8	174.00	8.42	9.21

The volume of water introduced to the anode and surfactant to the PZ was determined on a daily basis and presented in Table 17. A plot of cumulative values (Figure 69) shows a rate that was twice as high than the surfactant.

Table 17 Volume of Daily Introduced Surfactant and Conditioning Liquids to

Cell II-12

[illegible]	[illegible]	[illegible]	[illegible]
8.03	10	0.0	18
9.03	34	13	18
10.03	58	0.0	7
11.03	82	13	14
12.03	109	0.0	8
13.03	132	0.0	10
16.03	202	25	20
17.03	226	0.0	7
Total		51	102

Analysis of the moisture content for soil samples was done according to the procedures described in section 7.3.1. The results are plotted in Figure 70. A slight increase (6%) in moisture content in the soil samples was observed (except for the soil surrounding the cathode). This can be related to the interference of systems such as the CLSS, SSS, and WS. The soil pH profile is presented in Figure 71. The graph shows that the pH value within the cell was maintained in the range between 8 and 8.5 with the exception of the part of the soil, which was in contact with the cathode where its pH reached 9. This relatively low pH (compared to II-10) could be attributed to the fact that the pH of the washing liquid was kept below 9.

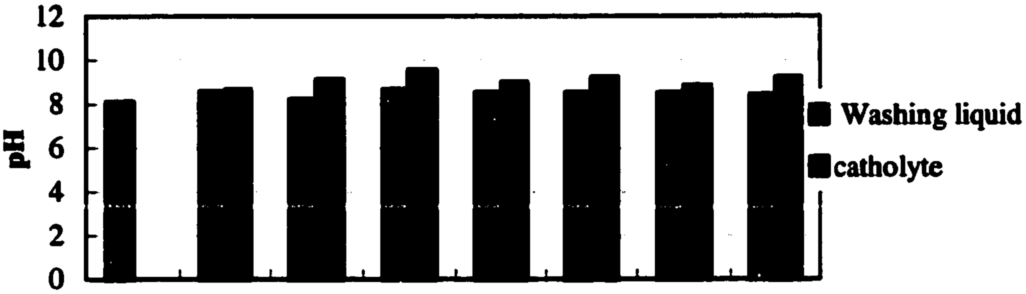


Figure 68 Comparision between pH of Washing and Catholyte liquids (cell II-12)

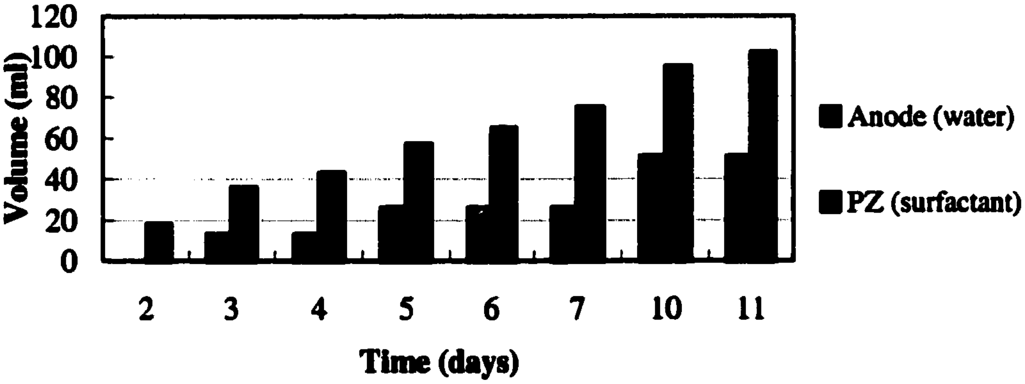


Figure 70 Cumulated Volumes of Injected Water in Anode and Surfactant in Permeable Zones

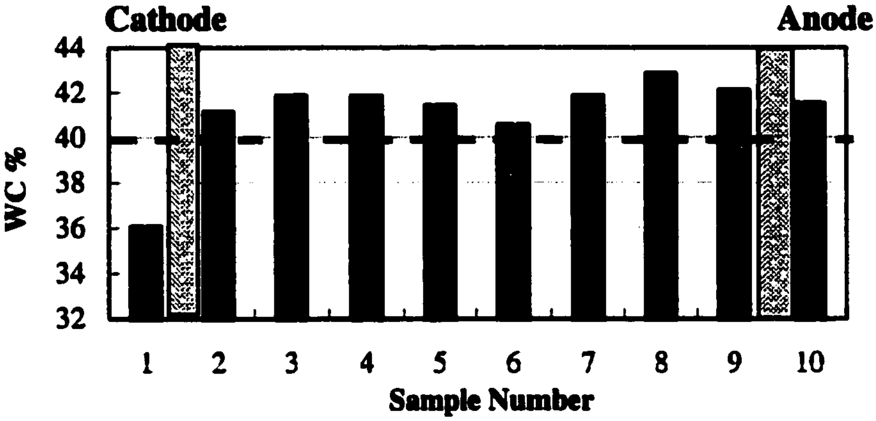


Figure 70 Water Content of Soil Samples (Cell II-12)

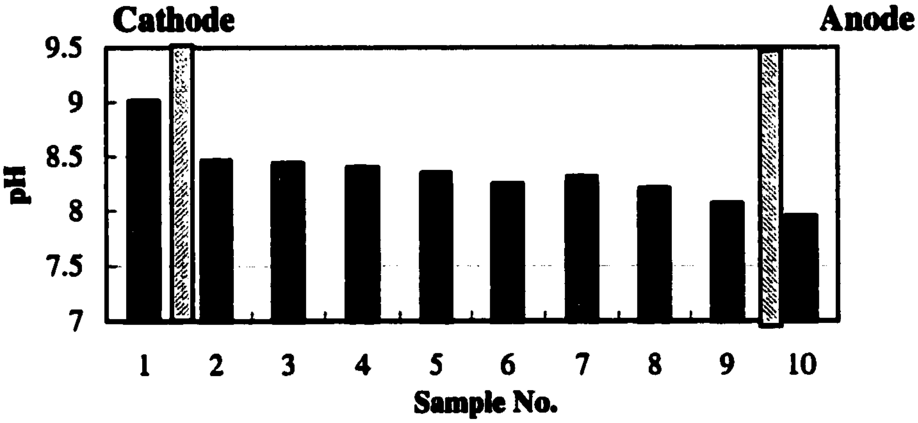


Figure 71 pH of Soil in Cell II-12

8.2.4. Experiment II-13

Objectives:

This test was intended to be concluding stage of phase II. It was conducted to demonstrate the effectiveness of the Surfactant Enhanced EK System (SEES), developed in all previous tests, as an optimal method for the remediation of hydrophobic organic compounds (HOC).

Set-up:

The test was conducted on two cells with dimensions analogous to the cells used in phase II (16-cm between the electrodes). The cells were built following the same procedures; therefore each electrode was fitted 2-cm from the permeable zone. The permeable Zone close to the anode was connected to the Surfactant Supply System but the cathode oriented permeable was attached to the Washing System. Anodes in both cells were also connected to a Conditioning Liquid Supply System. Soil type (6-4) artificially contaminated with a 49 g/kg of diesel fuel was used. Cell packing and soil preparation followed the same procedures as in previous tests. Electrodes were connected to DC power supply and the total voltage supplied was 4.8 volts. A schematic diagram of the cells is shown in Figure 72.

The test lasted 35 days during which II-13-1 was washed with water throughout the test duration. Cell II-13-2 was washed with water for the first 10 days. A surfactant type 101 (cationic) was subsequently introduced to the cell through (SSS). Electrical measurements were conducted daily (voltage and current changes). The volume of injected conditioning liquid and/or surfactants was measured on daily basis, pH of the washing system was monitored and catholyte liquid was collected for volume and pH was measurements. Upon test termination, destructive soil sampling was conducted. Samples were tested for pH, water content, and diesel fuel content.

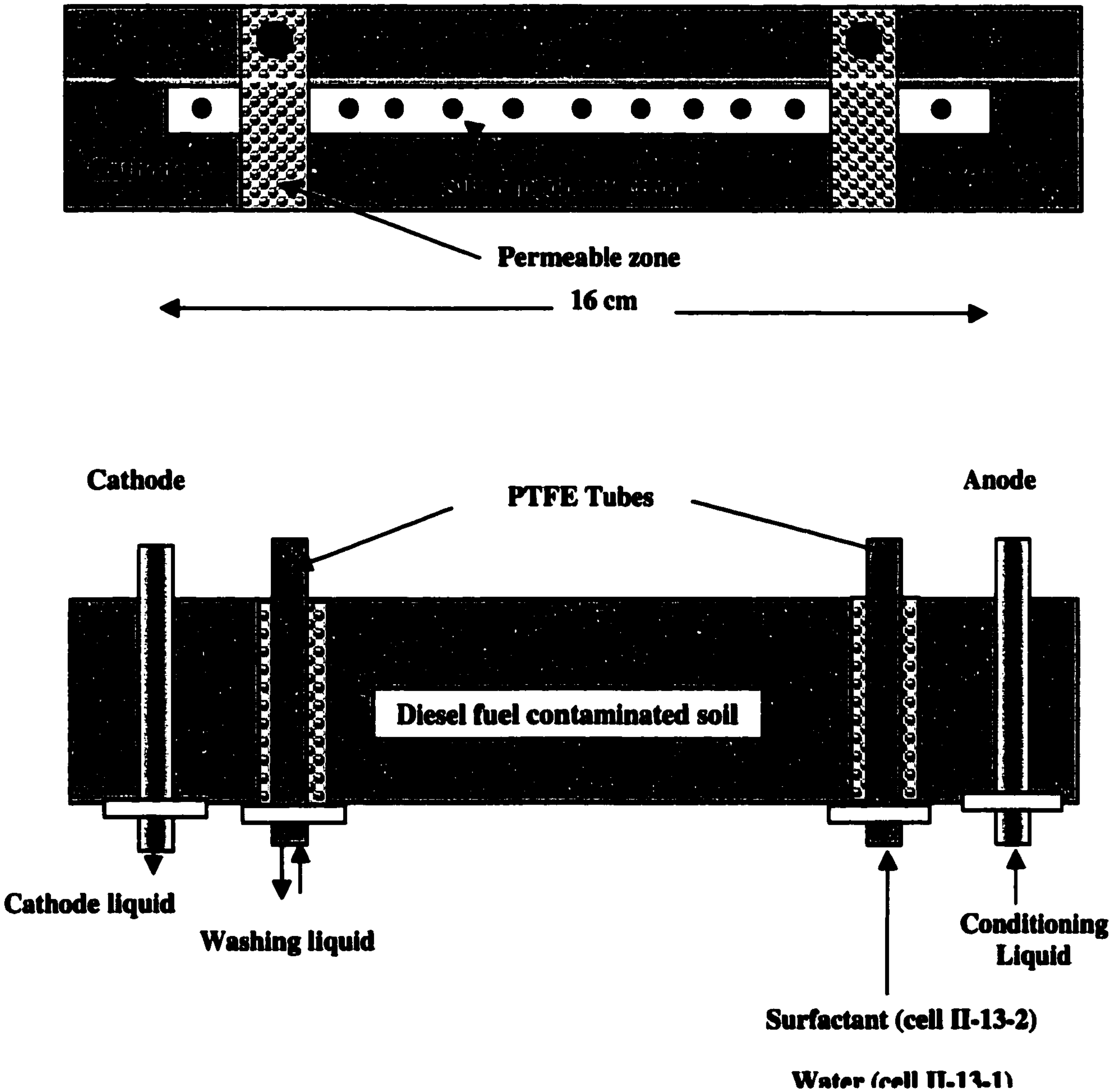


Figure 72 Schematic configuration of cell II-13-1 and II-13-2

Results and discussion:

Figure 73 shows the accumulated volume of cathode liquids from II-13-1 and II-13-2. The results showed that test II-13-2 (surfactant enchanced) generated three times higher volume of catholyte (750-ml) than II-13-1, which generated 240-ml. The cumulative catholyte volume in cell II-12-2 followed a logarithmic curve. The cumulated catholyte volume in cell II-13-1 showed an exponential increase. Volumes of conditioning liquids introduced in the anode oriented PZ,s were also monitored and measured on a daily basis (Fig. 74). The graph shows that a higher volume of anode conditioning liquid was introduced in II-13-2 (1325-ml) compared with 210-ml introduced in II-13-1. This fact suggests that the EK process was much slower in cell II-13-1 than in cell II-13-2. The high volume of surfactant introduced in the PZ of cell II-13-2 reduced the amount of anode conditioning liquid (water) required for this cell. This fact was evident when comparing the amount of the liquid introduced to cell II-13-1 and cell II-13-2 (Fig. 75). Almost twice the amount of anode conditioning liquid (130 ml) was introduced to cell II-13-1 compared with 70 ml introduced in cell II-13-2.

Figure 76 presents the pH changes of catholyte liquid as a function of time. The graphs show a similar pattern of pH distribution with the time in both cells. This pattern stayed at high values (pH = 12) for almost 600 hours and then went to a pH = 9 value for almost another 200 hours after which the high pH value returned. The distribution of the pH profile within the soil is presented in Figure 77. Fourteen samples were taken from each cell and analyzed for pH. A uniform pH distribution within the soil matrix can be recognized throughout the cells (Fig. 77) where a moderate pH was uniform along the distance between the electrodes (pH = 8). This fact was a direct result of keeping the pH of the washing liquid within 8 – 9 (Fig. 78). This points to the importance of washing and conditioning systems in generating a low and uniform pH distribution within the soil.

Considering the above-mentioned results, once can conclude that surfactant introduction into an electrokinetically enhanced system will have a positive impact on system performance (see Figures 73 and 74). However, it should be noted that the presence of surfactant did not influence the soil pH values in both cells.

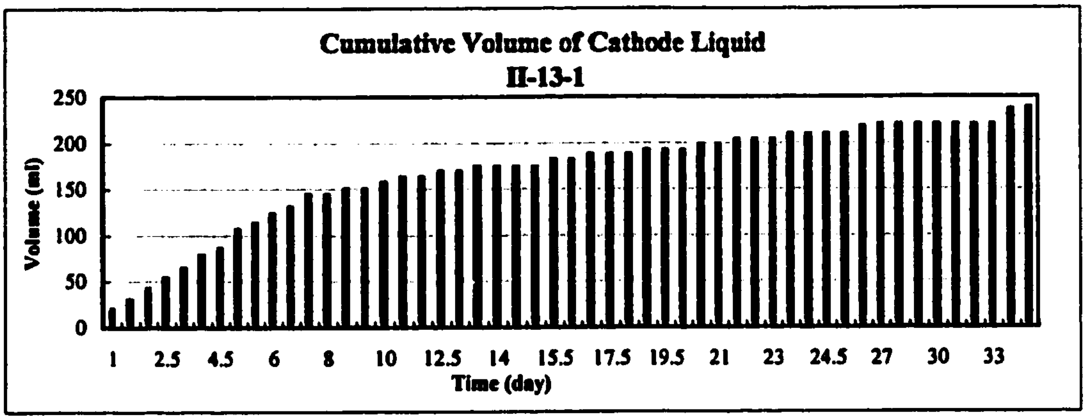
Monitoring of electrical parameters within the soil was achieved through direct measurements of potential at 16 probe electrodes distributed evenly along the distance between the electrodes. The change in current was also monitored during the test. The relationship between the voltage value at each probe and its distance from the cathode at different times is presented in Figure 79. The graph shows that the presence of the Permeable Zone divided the cell into three hypothetical zones, i.e. zone 1 which is confined between probe 1 and probe 3, zone 2 which is confined between probes 3 and 14, and zone 3 between probe 14 and 16.

The voltage gradient between zone 1 and zone 2 disappeared after 140 hours, but the gradient persisted between zones 2 and 3. A linear uniform potential distribution was monitored in zone 1 and 2 (Fig. 79), however, a relatively small gradient was developed between probe 1 and 14. The total voltage between probe 1 and 16 started with 2.43 volts at 0 hours and increased to 3.6 volts at 21 hours. The maximum measured voltage of 3.69 volts was measured at 143 hours and a minimum of 2.89 volts was measured at 487 hours. The total voltage ended with 3.34 volts at 838 hours. It is important to indicate that the major portion of the potential developed between probe 1 and 16 was confined between probes 14 and 16 (Fig. 79) with a relatively small gradient left between probes 1 and 14 (0.1 V/cm).

Figure 80 shows the relationship between the voltage measured in each probe and its distance from the cathode for II-13-2. The graph also shows that the presence of the permeable areas resulted in the creation of 3 distinct zones. However, the voltage distribution between them was completely different from what was observed in cell II-13-1. The gradient between these areas persisted throughout the test. Although the area between the permeable zones showed a similar uniform linear voltage distribution as in cell II-13-1, the voltage values measured in the probes were considerably higher than those measured in cell II-13-1. The total voltage between probe 1 and 16 started with 1.96 Volts at 0 hours and increased to 3.44 Volts at 21 hours (peak value). A minimum voltage of 2.64 Volts was monitored at 264 hours. The total gradient ended with 2.98 Volts at 838 hours. Measuring the gradient in cell II-13-2 between probe 1 and 14 throughout the time showed that a relatively higher value developed when compared with cell II-13-1 (0.15 V/cm). The higher voltage gradient in cell II-13-2 was attributed to a higher EO flow. The volume of liquids injected and extracted from cell II-13-2 indicated a high EO flow.

The changes in potential values at each probe as time progressed are presented in Figure 81 and 82 for cell II-13-1 and II-13-2 respectively. The graph shows that all probes behaved in the same way, with a sharp decrease during the first 150 hours. The exception was observed at probes 15 and 16. After that time, a pulsative pattern developed.

The development of such a pattern can be largely attributed to the washing system in the cathode area where the washing liquid was changed periodically. Cell II-13-2 also showed a similar distribution versus time, however, the pulsative pattern was less visible and the voltage values did not drop throughout the test. Figure 84 presents diesel fuel analysis in soil samples for cell II-13-1 and II-13-2. An average of 25% removal was achieved, however, there was no drastic differences between the removal rates in both cells.



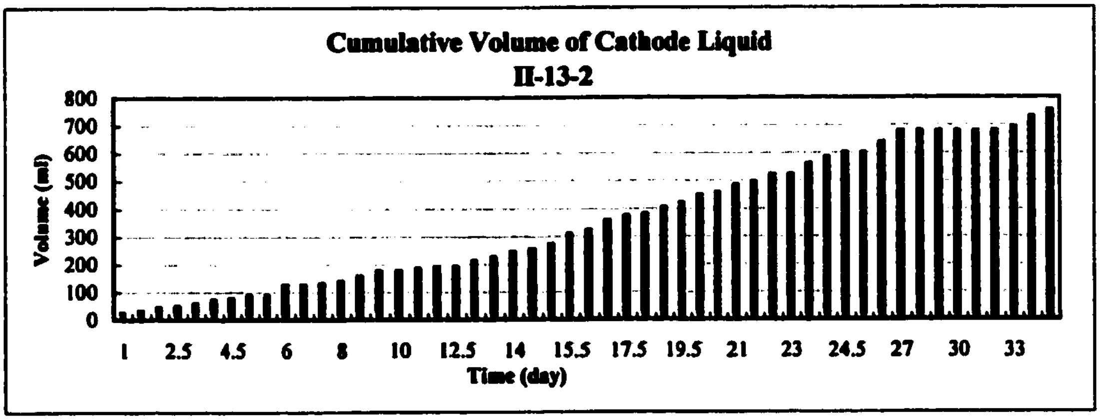


Figure 73 Cumulative Volume of Cathode Liquids for cell II-13- 1 and II-13-2

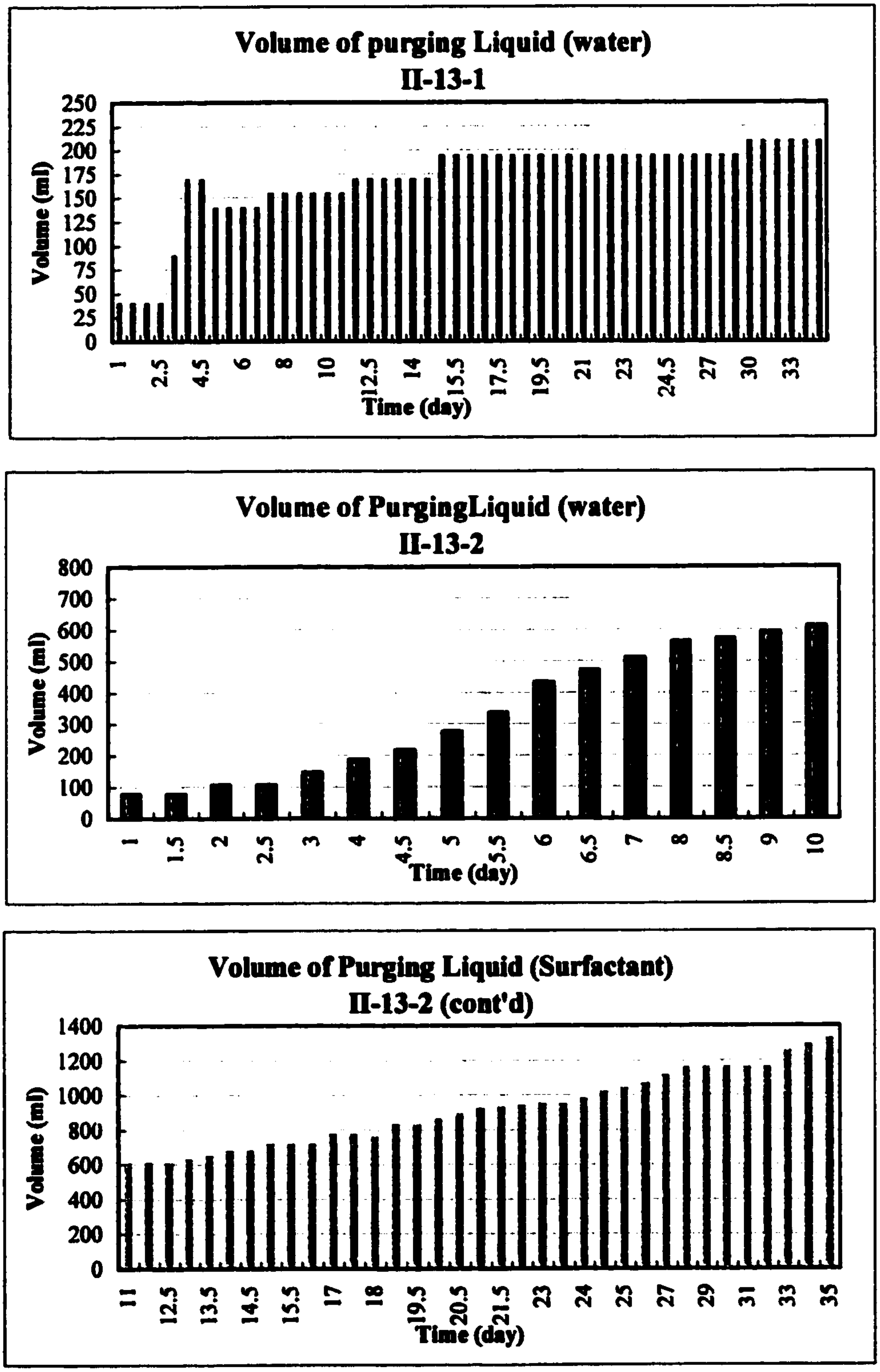
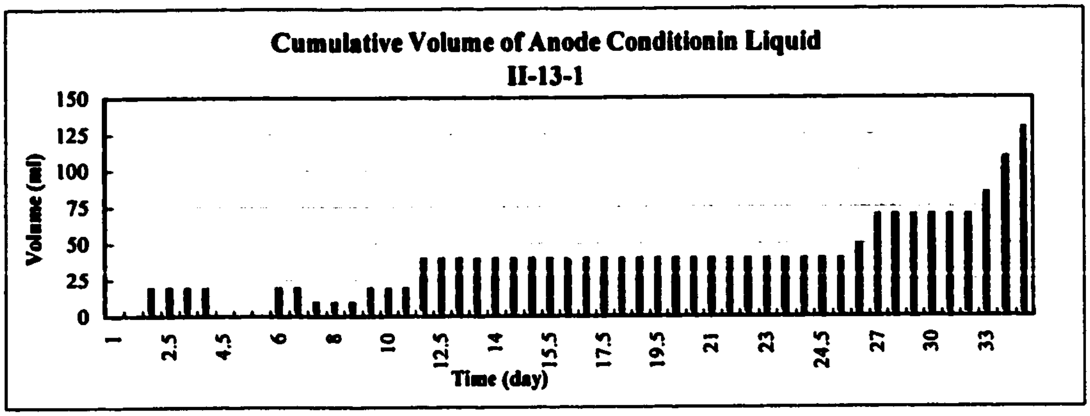


Figure 74 Cumulative Volume of Surfactant and/or Water Injected through the PZs near the Anode (II-13-1 and II-13-2)



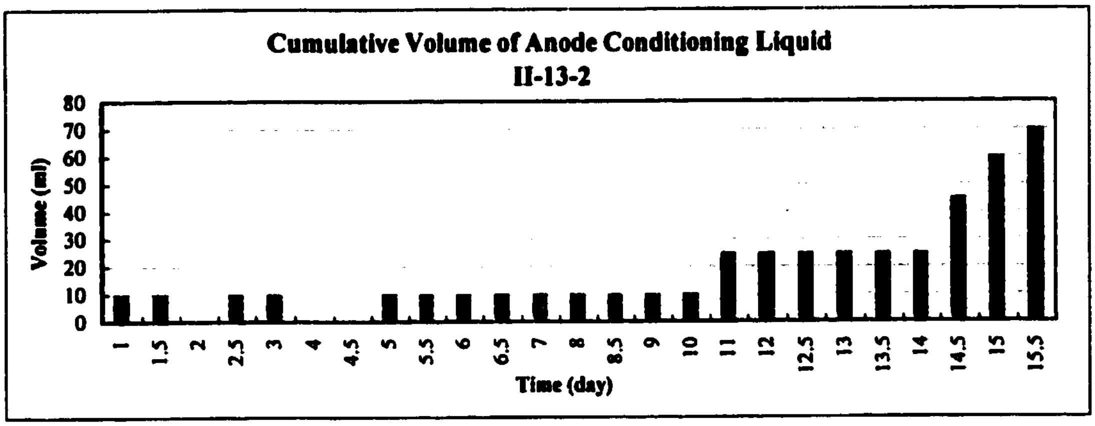
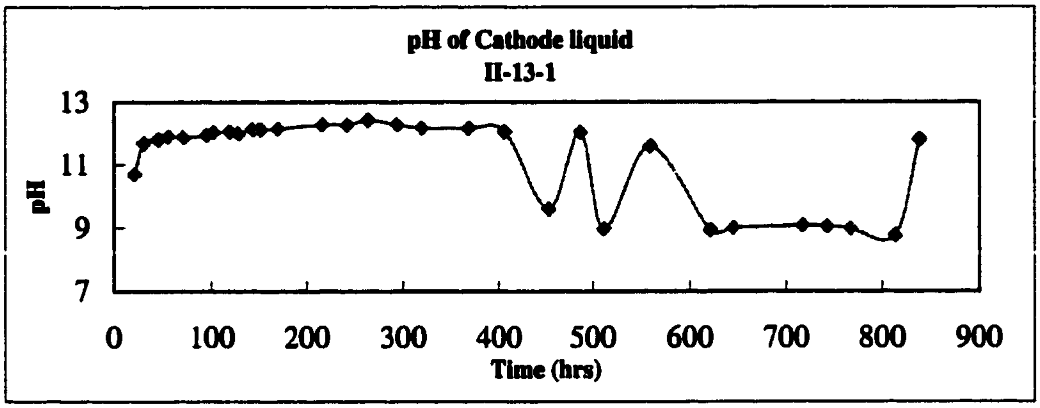


Figure 75 Cumulative Volume of Anodes Conditioning Liquids (II-13-1 and II-13-2)



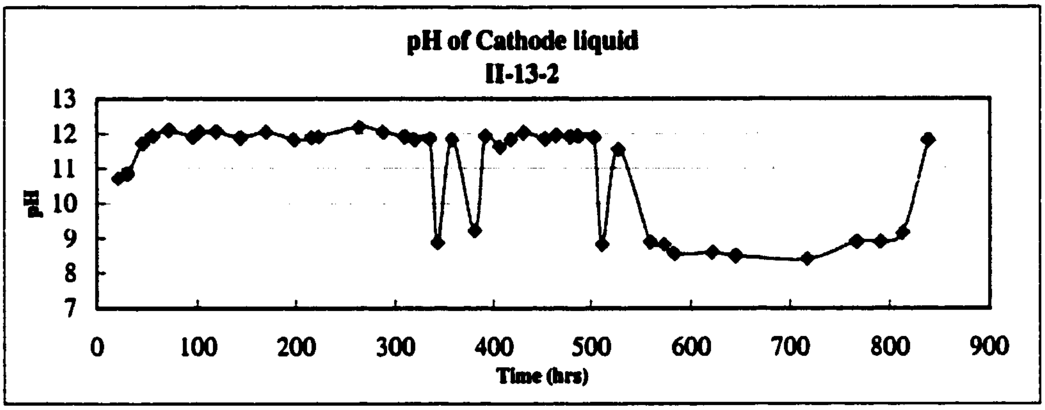
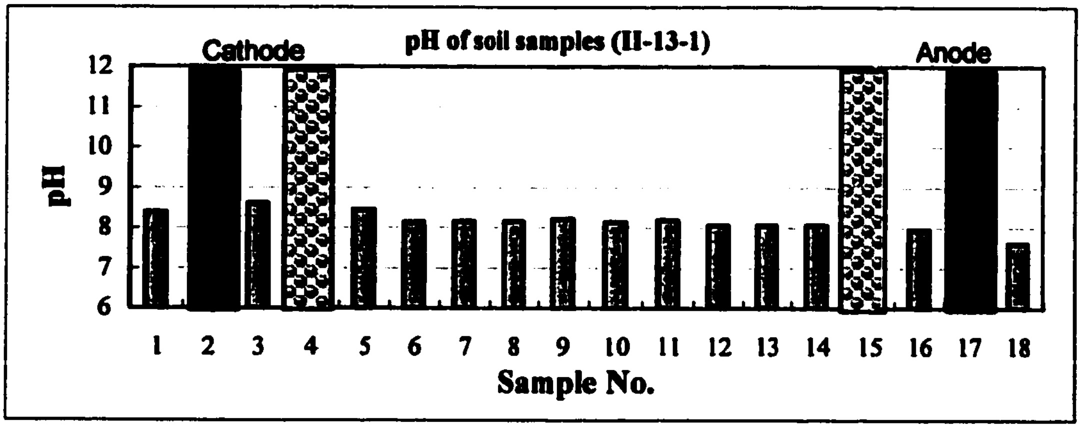


Figure 76 pH Values Cathode Liquid during the Test II-13



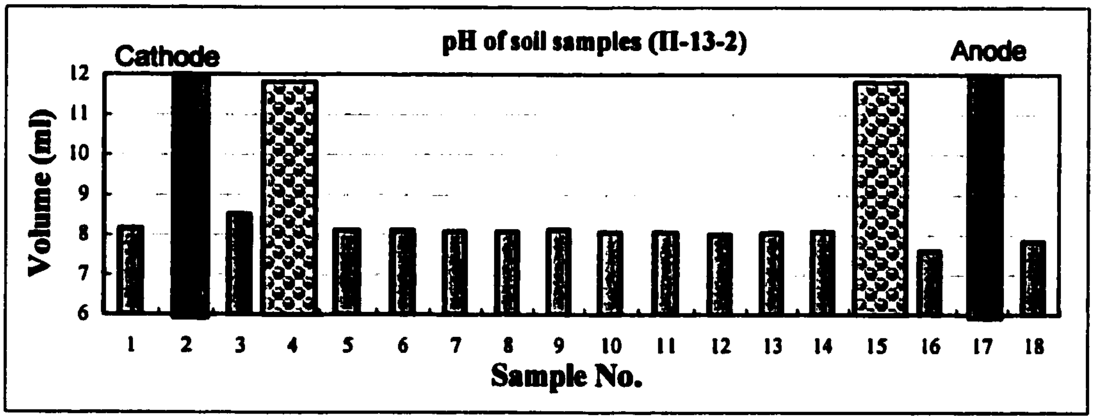
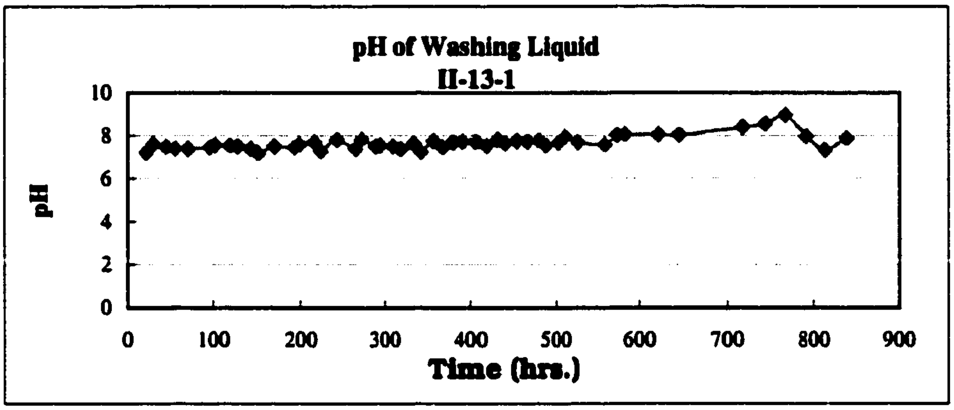


Figure 77 pH of Soil Samples (II-13-1 and II-13-2)



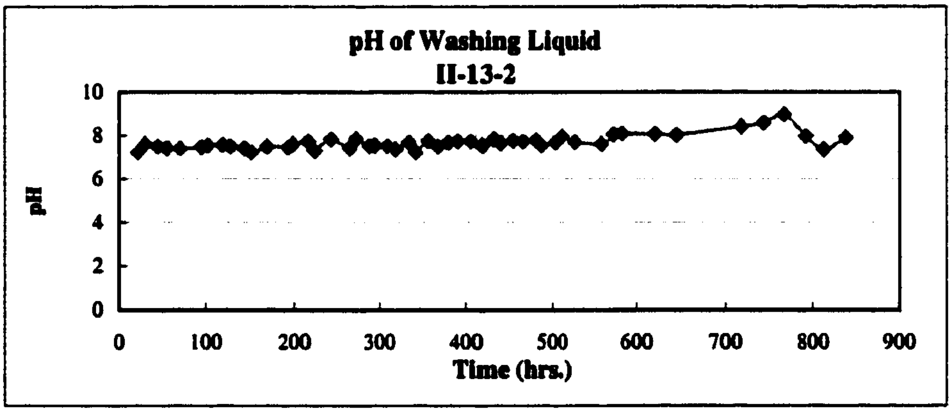


Figure 78 pH of Washing Liquid in cells II-13-1 II-13-2

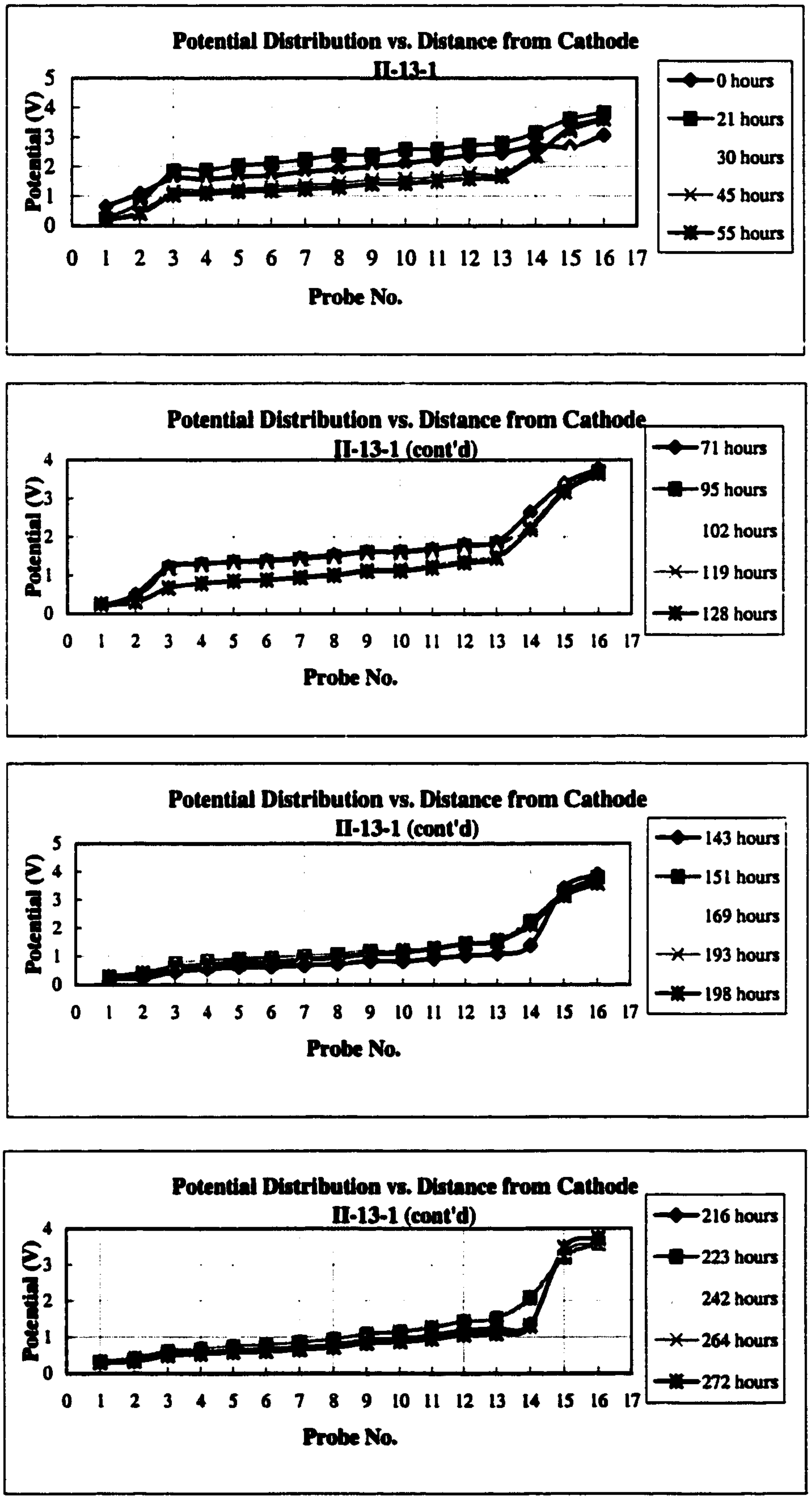
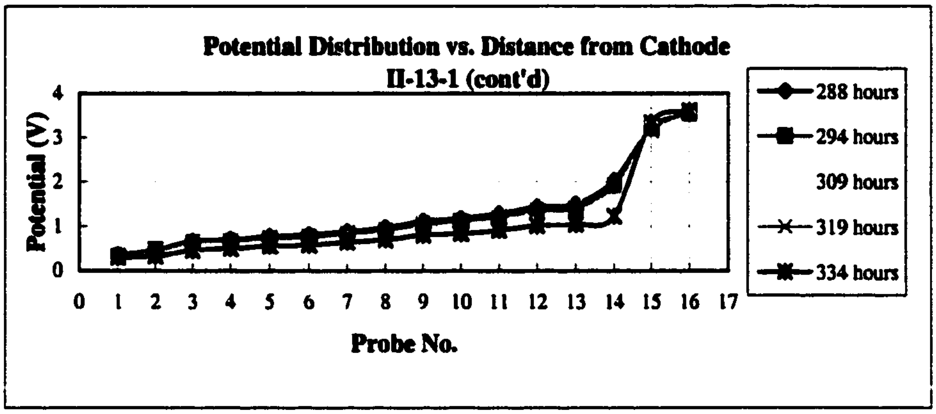
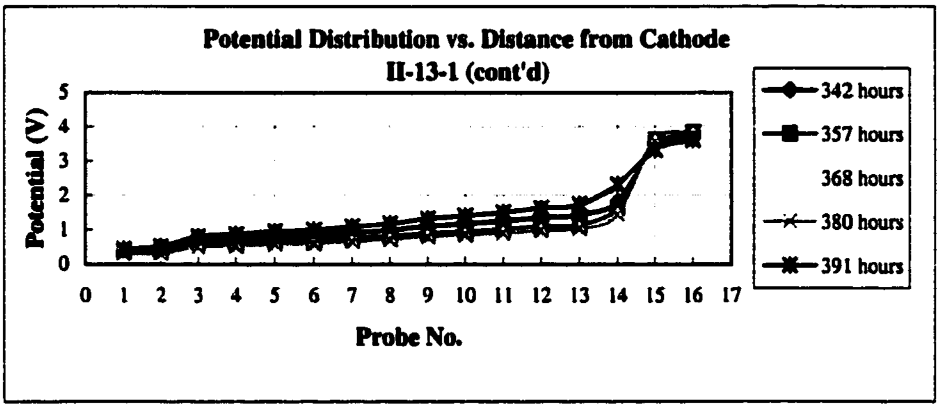


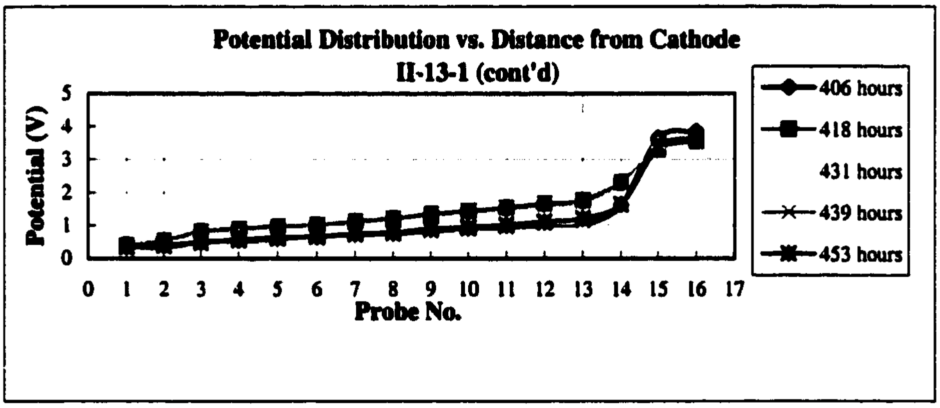
Figure 79 Potential Distribution vs. Distance from Cathode



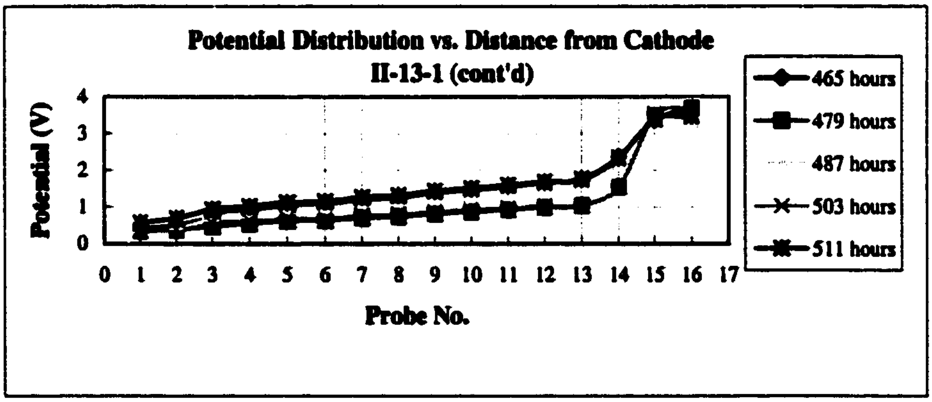
Potential Distribution vs. Distance from Cathode II-13-1 (cont'd)



Potential Distribution vs. Distance from Cathode II-13-1 (cont'd)



Potential Distribution vs. Distance from Cathode II-13-1 (cont'd)



Potential Distribution vs. Distance from Cathode II-13-1 (cont'd)

Figure 79 Potential Distribution vs. Distance from Cathode

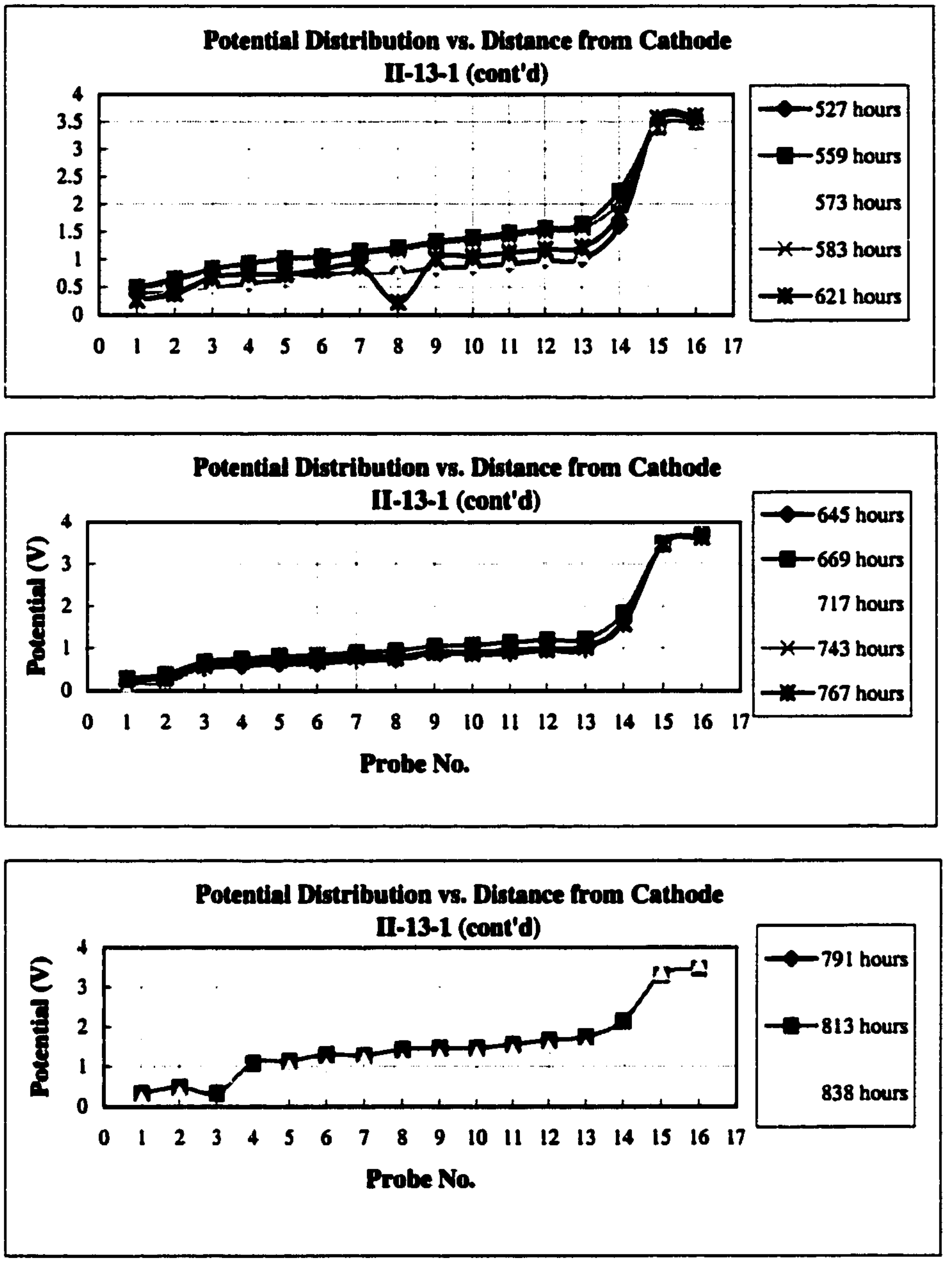


Figure 79 Potential Distribution vs. Distance from Cathode

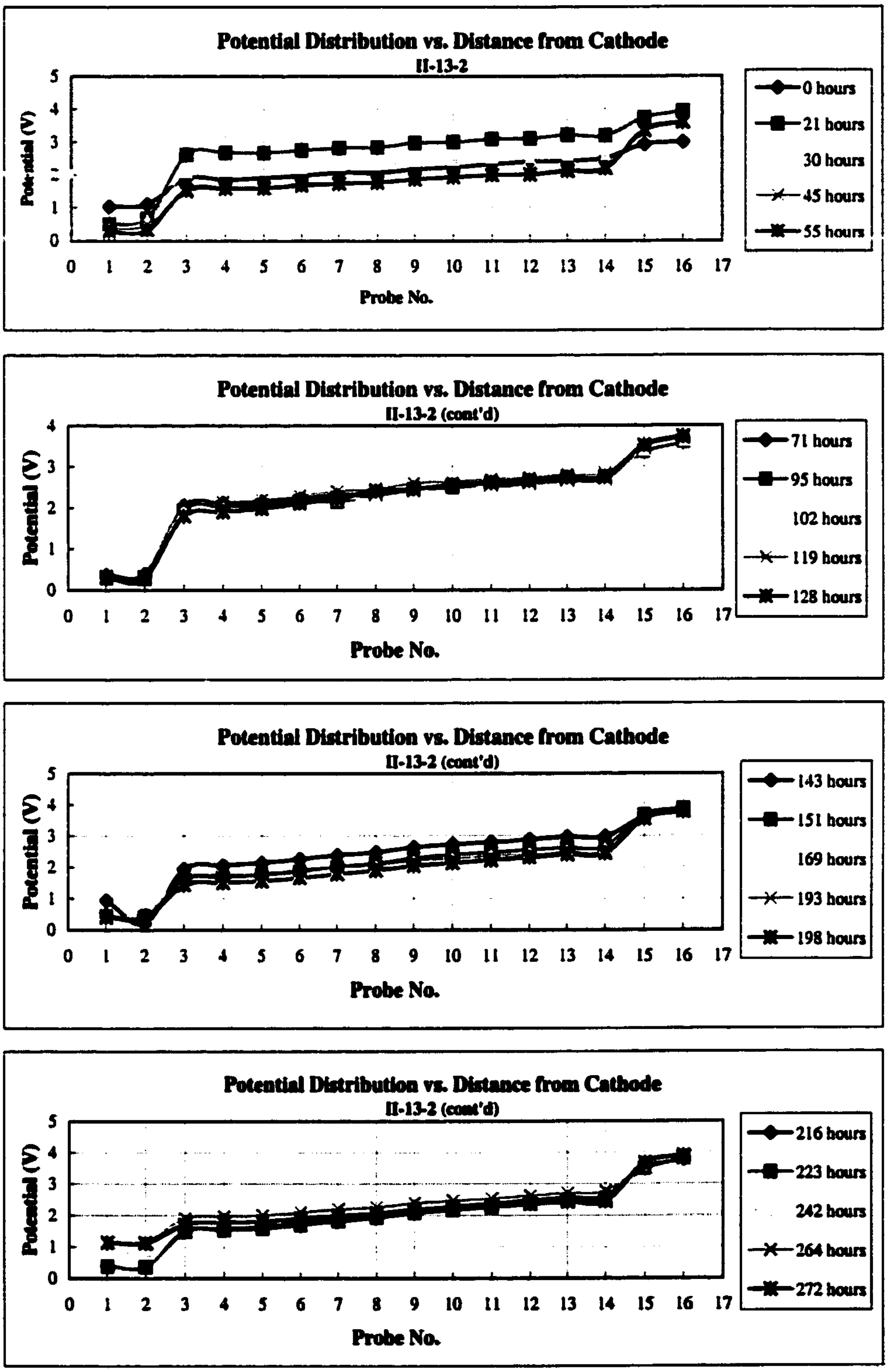
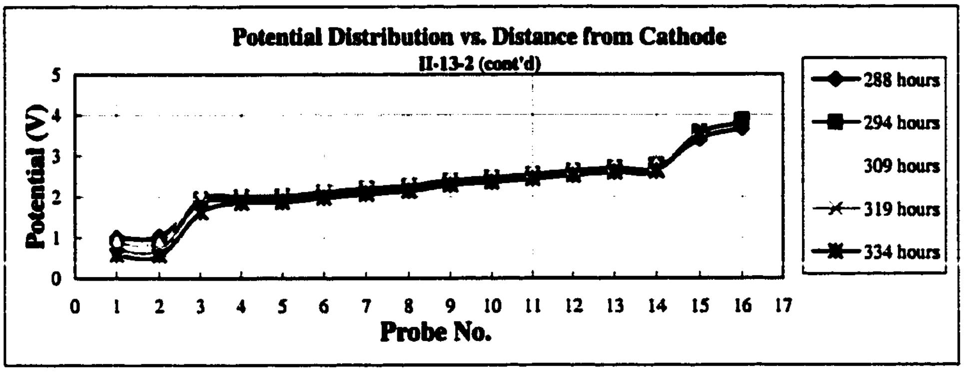
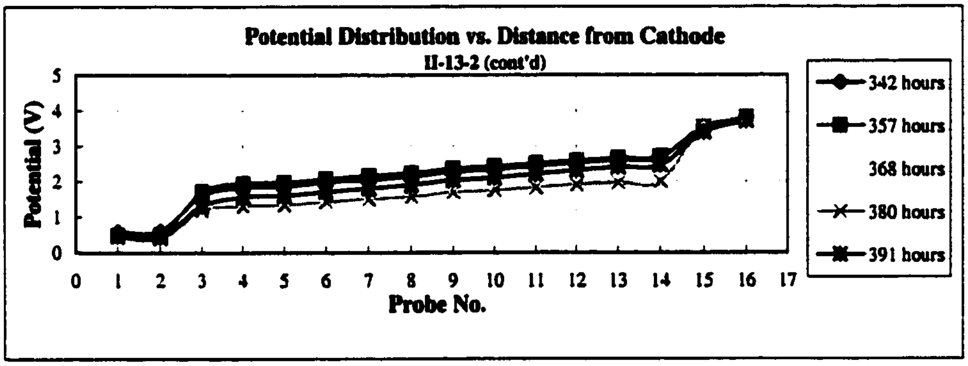
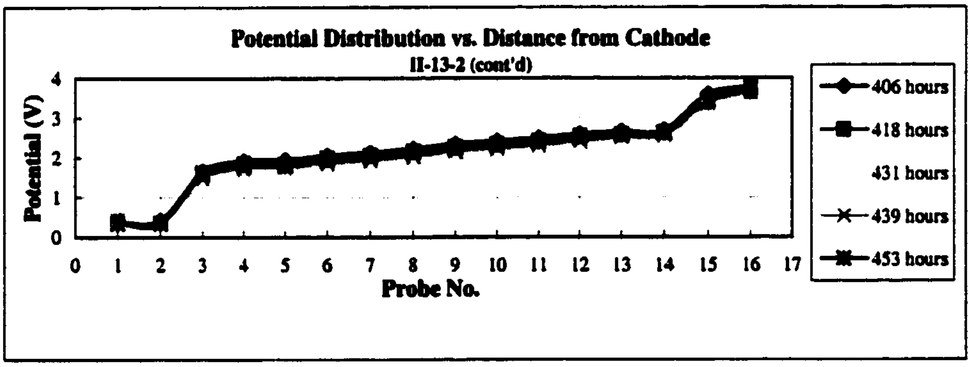


Figure 80 Potential Distribution vs. Distance from Cathode







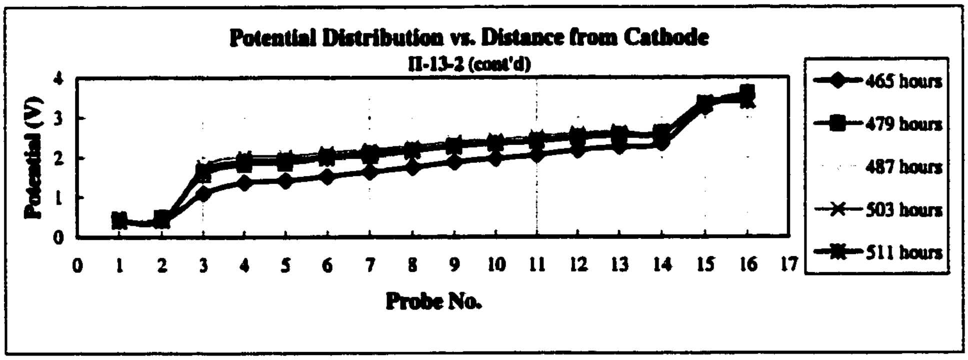


Figure 80 Potential Distribution vs. Distance from Cathode

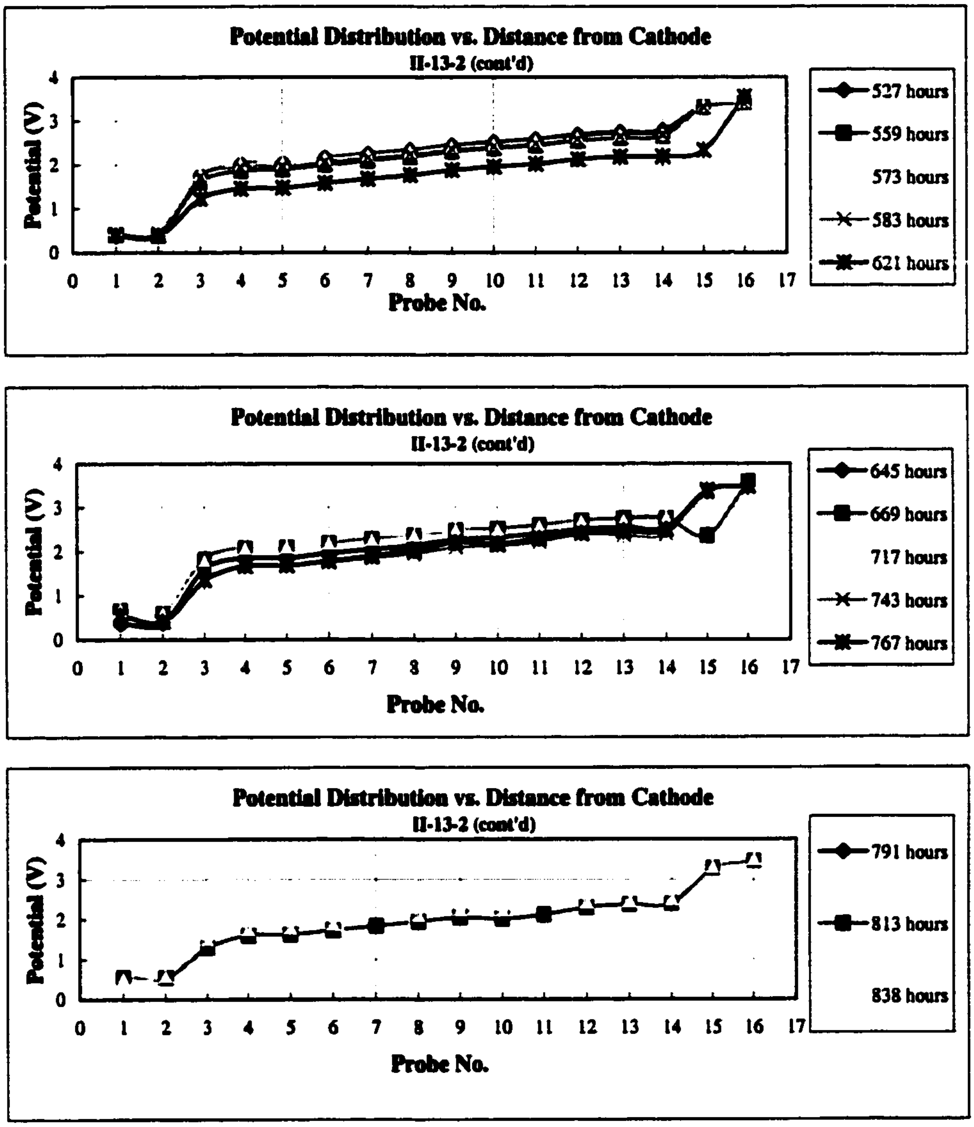


Figure 80 Potential Distribution vs. Distance from Cathode

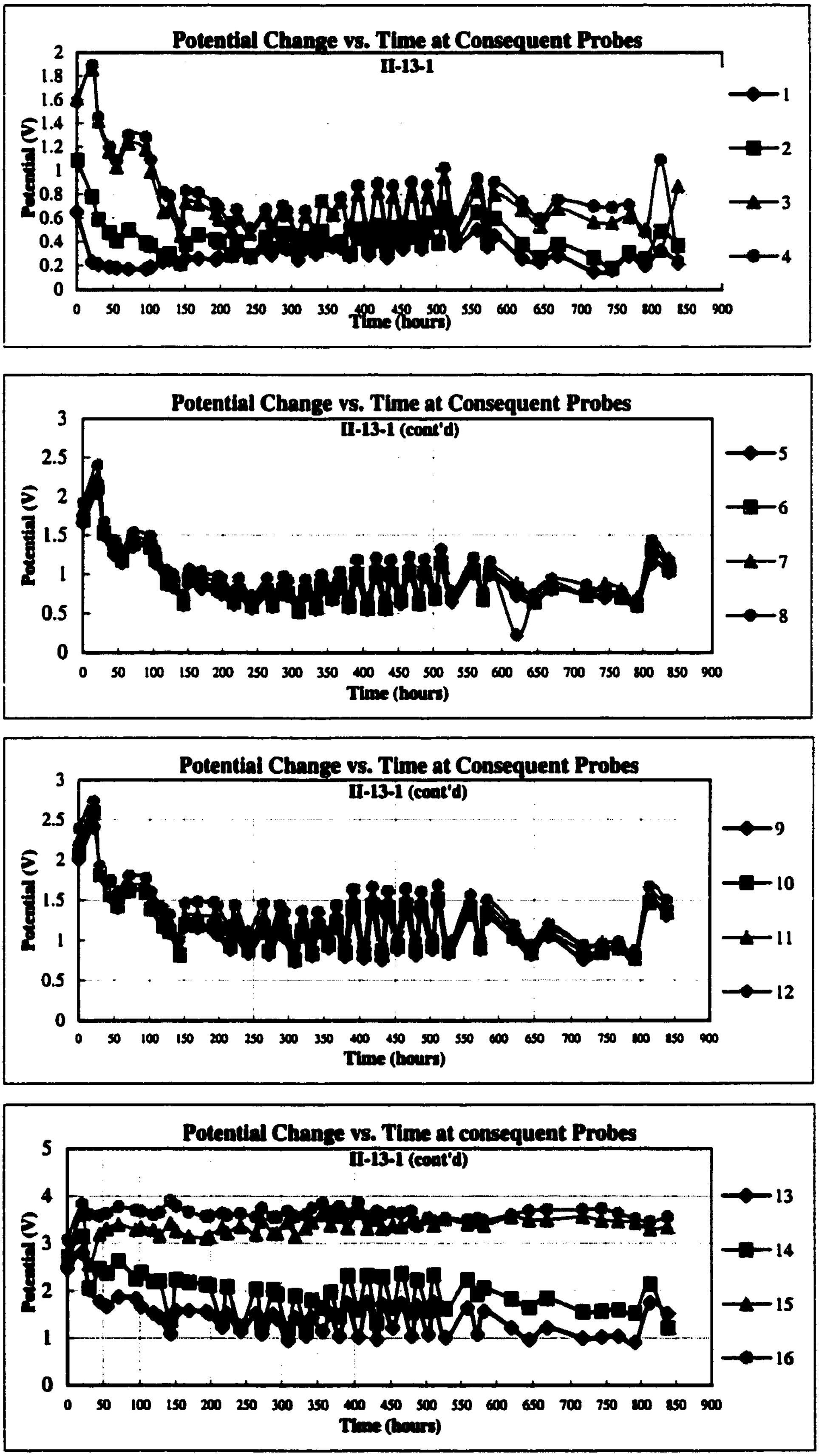


Figure 81 Voltage Distribution vs. Time Measured in subsecquent Probes; cell II-13-1

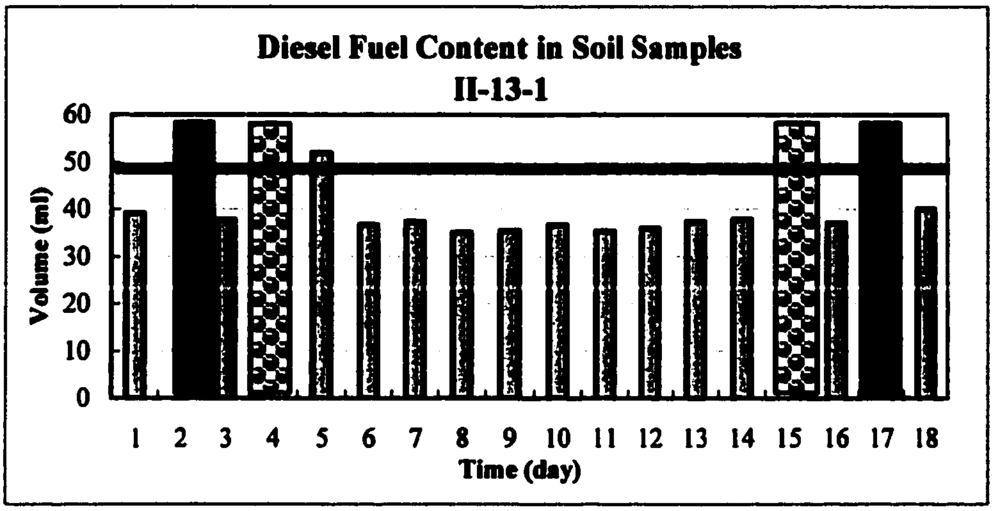
Table 40 Concentration of Commonly Found Ions in Soil Solutions

Ion	*Concentration mg/l*	*Ion*	*Concentration mg/l*
Ca	10-200	NO_3-N	5-200
Mg	5-100	SO_4-S	10-100
K	1-40	H_2PO_4-P	0.01-0.6

Source: From Alan Wild, Soils and the Environment, Cambridge University Press, 1993.

I- Adhesive soil moisture - Soils, which appear quiet dry nevertheless, contain an amount of water as a very thin film of moisture, which surrounds the surfaces of the individual particles. The soil obtains this moisture from the water surrounding or from the atmosphere by attraction and is held by adhesion, or from the aqueous vapor present around them, by condensation. It is the adhesion, which result in a spreading of water over the surface of the soil particles as a film when liquid water comes in contact with dry soil particles. The force in which adhesion water is bound to the particle could reach 10,330 atm (kN/cm^2).

This moisture dose not take part in ground water table fluctuation, it dose not transmit hydrostatic pressure, its not affected by gravity, it will not move in the liquid form under the influence of capillary forces, and it cannot be evaporated under ordinary conditions. The difference between the weight of air dried sample and its weight after oven-drying at



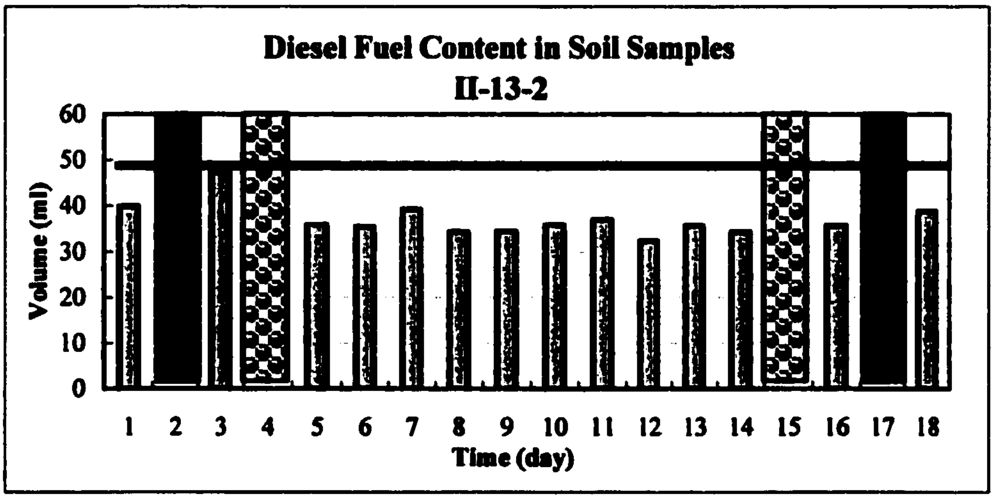
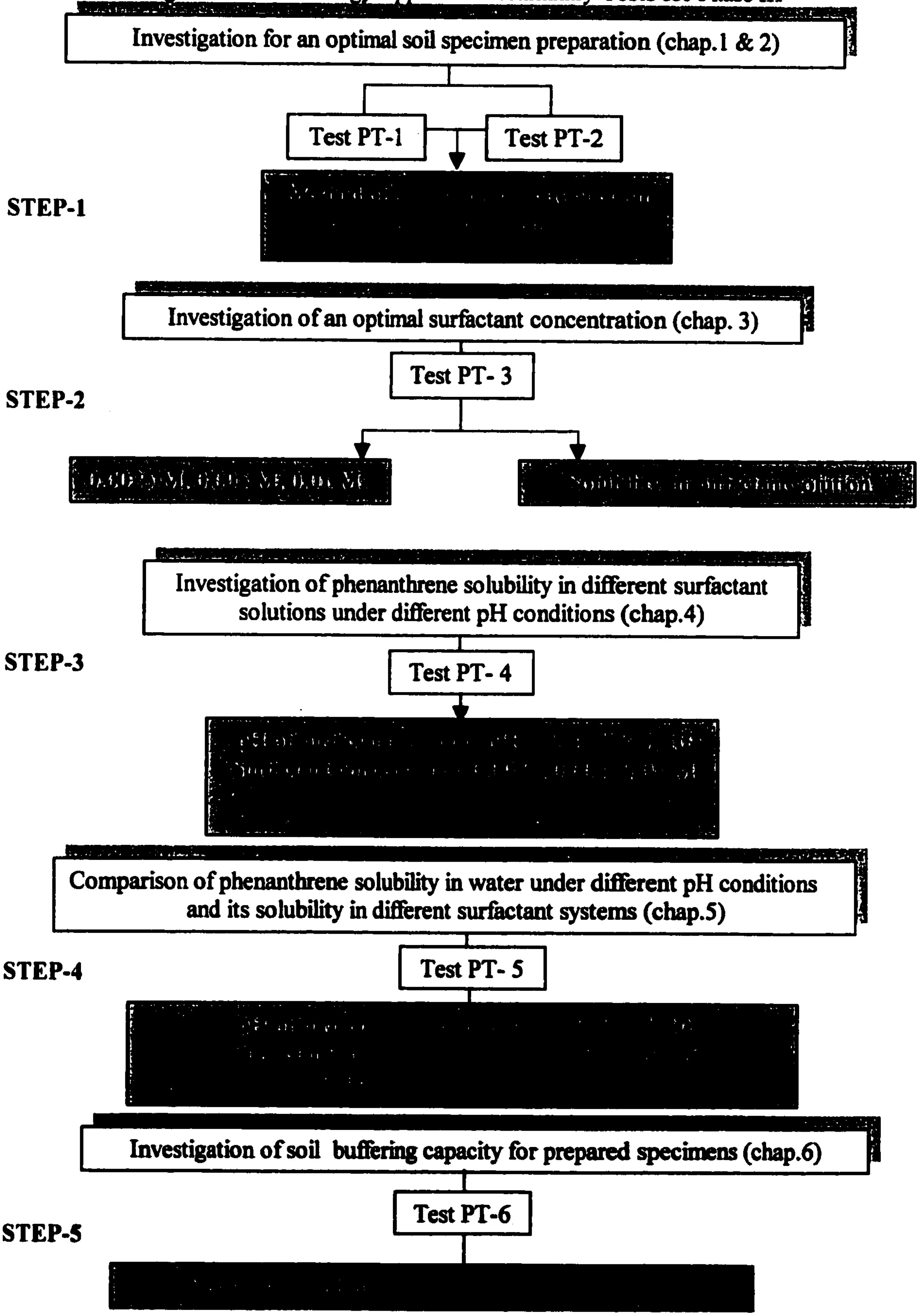


Figure 83 Diesel Fuel Content in Soil Samples Measured from the Cathode to the Anode (II-13-1 2)

Figure 84 Methodology Applied to Preliminary Tests for Phase III



8.3. Preliminary Tests for Phase III

The quality of results depends on specimen preparation. This relation is particularly important where tests have to reflect field conditions. Preliminary Tests (PT-1 to PT-6) investigated the most adequate specimen preparation.

Phenanthrene was chosen as a representative compound of HOC's because of its low aqueous solubility and high partition properties to soil. Since phenanthrene has low water solubility, its presence in the soil usually is achieved by introducing it throughout a carrier. In nature, phenanthrene can enter the soil as being part of a compound such as diesel fuel or being dissolved in a solvent as a carrier. In this experiment, solvents are thought to assume the carrier role and to provide a dispersion of phenanthrene in excess of its water solubility. Methanol, due to the fact that it has no effect on surfactant solubilization, methanol was used as an agent in increasing phenanthrene solubility.

A series of batch tests were performed to determine the optimal method of providing phenanthrene to the soil and to evaluate the solubility of phenanthrene in different surfactant concentrations and under different pH values. In addition, the buffering capacity of the soil was tested in a separate test. The test sequence and objectives are shown in Figure 84.

8.3.1. Preliminary Test PT-1

The objective of this test was to evaluate the adsorption rate of the phenanthrene onto the soil as a function of phenanthrene concentration in the carrier. Four stock solutions of phenanthrene in methanol were prepared with concentrations of 125, 250, 500 and 1000 mg/l. A 30-ml sample of each solution was mixed with 6 g of dry soil in duplicate samples and shaken for 42 hours at room temperature. Samples were then centrifuged at 37 000 rpm for 30 min. The aliquot from each sample was then tested for phenanthrene content.

Duplicate samples of pure methanol, methanol-phenanthrene solutions, and soil in pure methanol were also analyzed and used as a background correction.

Results:

The portion of phenanthrene adsorbed to the soil was calculated by determining the phenanthrene concentration in the aliquot based on the standard curve described in Appendix (2). Table 23 shows the results of phenanthrene concentration in the aliquot presented in mg/l. The results indicated that no adsorption was observed except for the lowest concentration (125 mg/l) where 35.5 mg/l was adsorbed to the soil. These poor adsorption results could be related to the short period of time for which the soil and the phenanthrene solutions were in contact with each other, and to the fact that phenanthrene has a greater affinity to methanol than to the soil.

8.3.2. Preliminary Test 2

This test was performed to evaluate the adsorption of phenanthrene onto the soil after introduction, using methanol as a carrier. The contact time between the solvent solution and the soil was longer than the time set for PT-1.

To meet this objective, a slurry of soil-methanol-phenanthrene was formed by mixing 500 g of dry soil with phenanthrene-methanol solution containing 300-mg phenanthrene. To ensure proper dispersion of the phenanthrene in the soil, the soil was divided into five equal portion of 100 g. A volume of 60 mg of phenenthrene-methanol solution was added to each portion to reach a concentration of 600 mg/kg. The mixture was kept in suspension on a rotor for 24 hours and then left to sit for 228 hours in glass containers. After that period, the containers were uncovered and the methanol was allowed to evaporate for 120 hours. Soil portions from the five containers were mixed together on a rotor for 2 hours. After mixing, three samples (6-g each) were taken randomly from the contaminated mixed mass of soil and were subjected to a desorption test.

A volume of 30 ml of methanol was added to each soil sample and shaken for 67 hours at room temperature. The long shaking time was chosen to ensure a complete desorption because test related to this kind of desorption kinetics were non-existent in literature. The mixture was then centrifuged and the supernatant was analyzed for phenanthrene content.

Results:

The results of desorption test are presented in Table 23. Approximatly 28% of the phenanthrene was desorbed to the liquid phase after performing PT-2. The table shows that an average of 440 mg/kg of phenanthrene had been retained on the soil phase. This method was adapted for soil preparation in phase III.

Table 23 Concentration of Phenanthrene in aliquot after performing adsorption test PT-1

	MeOH	Sol.1 125 mg/l	Sol.2 250 mg/l	Sol.3 500 mg/l	Sol.4 1000 mg/l	Soil + Sol.1 mg/l	Soil + Sol.2 mg/l	Soil + Sol.3 mg/l	Soil + Sol.4 mg/l	Soil + MeOH mg/l
Sample 1	0.091	117.6	155.2	310.3	625.1	94.3	216	424.9	765.5	20.3
Sample 2	0.0	105.5	179.5	317.4	644	106.5	198.9	380.3	646	28.4
Average	0.0455	111.55	167.35	313.85	648.05	100.4	207.45	402.6	705.75	24.35

Table 24 Concentration of Phenanthrene after performing Adsorption Test PT-2

Sample No.	Concentration of phenanthrene in aliquot [mg/l]	Concentration of phenanthrene in soil [mg/kg]
1	92.29	418.35
2	83.67	461.45
3	87.52	437.6
Average		439.13

8.3.3. Preliminary Test PT- 3

Due to the fact that in phase III it would necessitate the introduction of an amount of surfactant for phenanthrene solubilization and transport, test PT-3 was performed to evaluate the solubility of phenanthrene at different molar concentrations of surfactant. Three stock solutions of Alkyl Dimethylbetaine surfactant were prepared with concentrations above its CMC such as 0.0025 M, 0.005 M and 0.1 M. A volume of 30-ml at each surfactant concentration was mixed with 5-grams of phenanthrene contaminated soil samples (440 mg/kg). All samples were prepared in duplicate, and for background corrections, non-contaminated soil samples were also tested. Samples were placed on a shaker for 67 hours. After shaking, samples were centrifuged at 35 000 rpm for 30 min. The concentration of the phenanthrene in the aliquot was determined according to the following steps:

I- *Define a wavelength where dissolved phenanthrene in surfactant solution can be identified.* The following analytical procedure was used:

An excess amount of phenanthrene was stirred in 0.005 M surfactant solution for 24 hrs. An undissolved portion was then filtered and the aliquot was measured by UV spectrophotometer to determine its absorbency range. The results along with the chosen wavelength for phenanthrene identification within the range of 1 ABS are presented in Table 25 and Figure 85.

Table 25 Results of UV Spectrometer for Phenanthrene-Surfactant (0.005 M) System

Wavelength nm	DATA
346.8	0.013
343.2	0.001
330.8	0.015
320	0.004
295.2	0.901
289.6	0.401
283.2	0.727
281.2	0.694
276	0.963
272	0.86
253.2	3.667
226.8	0.313
221.2	1.262
219.6	1.195
212.8	1.962
199.2	-1.792
192	0.469
190.8	0.204

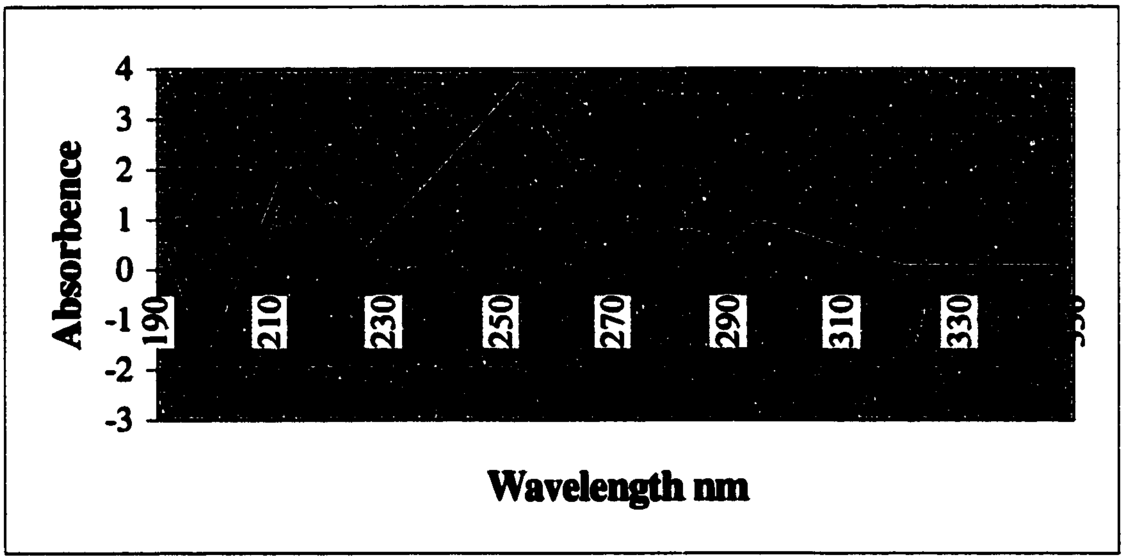


Figure 85 Phenanthrene-Surfactant System UV spectra

II- Prepare standard curves for surfactant solutions:

50 ml of each surfactant solution (0.0025, 0.005, 0.01 M) was stirred with an excess amount of phenanthrene (0.1g) for 67 hours to achieve saturation. The un-dissolved portion of phenanthrene was then filtered and the aliquot was then analyzed at 295.2 nm using the UV/vis spectrophotometer. To give these absorbency values a meaning in terms of concentration, 0.005 M solution of surfactant with a known phenanthrene concentration (125 mg/l) was analyzed and its absorbency value (0.901 ABS) was related to the above mentioned ABS, as shown in Table 26.

Table 26 Standard Curve for Wave Length

Wave length: 295.2 nm		
Surfactant Concentration	**Phenanthrene Concentration**	**Absorbence**
0.0025 M	50 mg/l	0.444 ABS
0.005 M	100 mg/l	1.204 ABS
0.01 M	300 mg/l	2.944 ABS

These values served as an approximate maxima for phenanthrene concentration in a given surfactant concentration for the preparation of the standard curve.

III- *Prepare standard curve Based on results from step 2.*Results for all tested concentration of surfactant are presented in Table 27.

Table 27 Standard curve Data for Different Surfactant-phenanthrene Systems

[illegible]	ABS	Conc. mg/l	[illegible]	ABS	Con. Mg/l	[illegible]	ABS	Con. mg/l
[illegible]	0.048	2.4	[illegible]	0.091	3.58	[illegible]	0.154	3.64
	0.097	4.8		0.184	7.16		0.263	7.28
	0.202	9.6		0.486	14.33		0.508	14.57
	0.417	19.2		0.859	28.66		1.034	29.14

IV- ***determine phenanthrene concentration in the aliquots***, **based on the standard curves defined in PT- 3. The results are presented in Table 28.**

Table 28 Concentration of Phenanthrene in Aliquot after Tests PT-3

	0.0025 M	0.005	0.01
Non-contaminated soil (mg/l of surfactant)	5.721	3.743	3.411
Contaminated soil (sample 1)	7.953	5.089	4.313
Contaminated soil (sample 2)	8.233	5.548	4.341
Average	8.093	5.3185	4.327
Net desorbed (mg/l of surfactant)	2.372	1.5755	0.916
Net desorbed (mg/kg of soil)	11.86	7.877	4.58
% of the initial concentration	2.7	1.79	1.043

The results indicate that a 0.0025 M solution had the highest dissolution capacity of phenanthrene to the surfactant phase.

8.3.4. Preliminary Test (PT-4)

This test was performed to evaluate the solubility of phenanthrene in a surfactant solution under different pH conditions. A standard soil pH test was performed on soil samples mixed with surfactants at three different molar concentrations. Each surfactant solution was treated with an acidic or a basic solution in a way that it would have four different pH values simulating acidic and basic conditions. Soil samples (5 g) were stirred with 30 ml of each solution for 67 hours and then centrifuged for 30 min at 35 000 rpm. The aliquot was then tested for its phenanthrene content. Samples were prepared according to the following protocol:

	Concentration of Surfactant	pH of Solution
	0.0025 M	7
Non Contaminated Soil	0.005 M	7
	0.01 M	7
	0.0025 M	2
	0.0025 M	4
Contaminated Soil	0.0025 M	7
	0.0025 M	8.5
	0.0025 M	10
	0.005 M	2
	0.005 M	4
Contaminated Soil	0.005 M	7
	0.005 M	8.5
	0.005 M	10
	0.01 M	2
	0.01 M	4
Contaminated Soil	0.01 M	7
	0.01 M	10
	0.01 M	2

Test results of these investigations are presented in Table 29.

Table 29 Phenanthrene Removal Rate Reported with Soil Weight and Surfactant Concentration

	UV Absorbence				Removal Rate	
	N.C.S	C.S.1	C.S.2	Average	Surfactant (mg/l)	Soil (mg/kg)
	0.0025 M	0.0025 M	0.0025 M	0.0025 M	0.0025 M	0.0025 M
pH = 2		11.442	6.558	9	3.279	16.395
pH = 4		9.023	9.349	9.186	3.465	17.325
pH = 7	5.721	7.953	8.233	8.093	2.372	11.86
pH = 8.5		10.791	10.605	10.698	4.977	24.885
pH = 10		9.256	7.535	8.3955	2.6745	13.3725
0.005 M	**0.005 M**	**0.005 M**	**0.005 M**	**0.005 M**	**0.005 M**	**0.005 M**
pH = 2		4.662	4.662	4.662	0.919	4.595
pH = 4		6.533	8.109	7.321	3.578	17.89
pH = 7	3.743	5.098	5.548	5.323	1.58	7.9
pH = 8.5		7.058	6.139	6.5985	2.8555	14.2775
pH = 10		6.533	7.617	7.075	3.332	16.66
0.01 M	**0.01 M**	**0.01 M**	**0.01 M**	**0.01 M**	**0.01 M**	**0.01 M**
pH = 2		5.609	5.976	5.7925	2.3815	11.9075
pH = 4		5.609	5.525	5.567	2.156	10.78
pH = 7	3.411	4.313	4.341	4.327	0.916	4.58
pH = 8.5		5.497	5.497	5.497	2.086	10.43
pH = 10		6.511	6.596	6.5535	3.1425	15.713

N.C.S – Non contaminated soil, C.S.1 – Contaminated soil batch 1, C.S.2. – Contaminated soil batch 2

The results show that among the three different concentrations, the 0.0025 M surfactant concentration showed better removal for all pH values, except for pH = 10, where a 0.01 M solution showed a slightly higher solubilization efficiency. However, an overall evaluation confirms the conclusion form test PT-3 regarding the highest efficiency of the 0.0025 M surfactant.

8.3.5. Preliminary Test (PT-5)

This test was performed to evaluate the following issues:

- The effects of changing water pH on the solubility of phenanthrene
- The effects of a longer desorption time (120 hrs).

Preparation for this test followed the methodology described in PT-4. Soil samples were treated with different solutions in various conditions as described below.

	Concentration of Surfactant	pH of Surfactant Solution	pH of Water Solution
			2
			4
Non Contaminated Soil			7
			8.5
			10
	0.0025 M	2	
	0.0025 M	4	
Non Contaminated Soil	0.0025 M	7	
	0.0025 M	8.5	
	0.0025 M	10	
	0.005 M	2	
	0.005 M	4	
Non Contaminated Soil	0.005 M	7	
	0.005 M	8.5	
	0.005 M	10	
	0.01 M	2	
	0.01 M	4	
Non Contaminated Soil	0.01 M	7	
	0.01 M	8.5	
	0.01 M	10	
			2
			4
Contaminated Soil			7
			8.5
			10
	0.0025 M	2	
	0.0025 M	4	
Contaminated Soil	0.0025 M	7	
	0.0025 M	8.5	
	0.0025 M	10	
	0.005 M	2	
	0.005 M	4	
Contaminated Soil	0.005 M	7	
	0.005 M	8.5	
	0.005 M	10	
	0.01 M	2	
	0.01 M	4	
Contaminated Soil	0.01 M	7	
	0.01 M	8.5	
	0.01 M	10	

After 120 hours, samples specimens were subjected to UV analysis. Results of these investigations are presented in Table 30.

Table 30 Phenanthrene Removal Rate Reported with Soil Weight and Surfactant Used

Solution	**UV Absorbence**		**Removal Rate**	
water	**N.C.S**	**C.S**	**Surfactant (mg/l)**	**Soil (mg/kg)**
2	6.558	11.674	5.116	25.58
4	6.326	10.14	3.814	19.07
7	6.465	13.814	7.349	36.745
8.5	6.465	10.372	3.907	19.535
10	6.465	10.698	4.233	21.165
0.0025 M				
2	4.372	8.977	4.605	23.025
4	7.814	9.953	2.139	10.695
7	7.628	10.651	3.023	15.115
8.5	5.767	12.14	6.373	31.865
10	6.326	10.279	3.953	19.765
0.005 M				
2	2.298	4.793	2.495	12.475
4	4.071	8.339	4.268	21.34
7	4.399	10.372	5.973	29.865
8.5	5.483	7.026	1.543	7.715
10	4.629	7.157	2.528	12.64
0.01 M				
2	2.396	3.58	1.184	5.92
4	3.298	5.327	2.029	10.145
7	4.399	6.342	1.943	9.715
8.5	4.51	5.355	0.845	4.225
10	3.833	5.525	1.692	8.46

N.C.S – Non contaminated soil, C.S. – Contaminated soil batch 1

8.3.6. Preliminary Test (PT-6)

This test was performed to evaluate the effects of introducing acidic or basic conditions on the pH of the soil in order to measure the impact of the buffering capacity of the natural soil used in research. The results of these investigations (Table 31) showed that the soil has a good tolerance for acidic and basic condition.

Table 31 Surfactant–Soil System Response upon Different pH Conditions

	pH of Surfactant Solution			
	2	**4**	**8.5**	**10**
0.0025 M				
Sample 1	7.119	8.09	8.048	8.134
Sample 2	7.121	8.11	8.173	8.131
0.005 M				
Sample 1	7.038	8.088	8.105	8.133
Sample 2	7.030	8.088	8.016	8.077
0.01 M				
Sample 1	7.039	8.125	8.247	8.193
Sample 2	7.010	8.16	8.193	8.252

8.4. Pilot scale test (phase III)

Conclusions from preliminary, phase I and phase 2 testing fumed the foundation for the design and testing of the electrokinetic system for enhanced phenanthrene removal with synthetic surfactant on multi-functional electrodes for the pilot scale test. The main requirements considered in the design of the pilot test system were: 1) to operate with a natural soil, 2) to simulate natural dimensions of the system in the field. Therefore, authentic electrodes, had to be designed under the following considerations:

1) Provide an effective supply of surfactant upon appropriate attachment to washing systems;
2) maximize catholyte removal,
3) simple and feasible design in field conditions,
4) design a system resistant to soil clogging by fine particles,
5) design a system that is chemically resistant,
6) use inexpensive material.

Objectives:

The main objective of this test was the design of an effective EK system for pilot scale application of surfactant for removal of HOC (phenanthrene) from clayey soils. Particular objectives are:

1- the verification of the conclusions which were made from small scale testing and incorporate them into a pilot scale test;
2- the investigation of the effect of introducing permeable zones on electrical parameters and their distribution in the soil;
3- the adaptation of electrode design (developed on a small scale) to a pilot scale;

4- the verification of EK remediation system performance on a pilot scale and the applicability of this system in-situ.

8.4.1. Experimental set-up

The methodology used in the set-up of this experiment followed the methodology used in experiments conducted in the previous phases in order to ensure the continuity of the up-scaling process.

8.4.1.1. Electrokinetic Cell

A polyethylene box with dimensions 65 × 38 × 16 cm was used to conduct the pilot scale test. A rigid molding was prepared for the cell to prevent deformation during the soil compaction process. A plywood box reinforced with a metallic mesh served as a case for the molding made from a water-plaster of paris mixture. Cell III was fixed to the box and the mixture filled the gap between the box and the cell through openings on the upper sides of the box. The procedure was accompanied by continuos shaking to eliminate air cavities. A schematic description of the cell with the molding is shown in Figure 87 and an illustration of the cell in its ready state is shown in Figure 90.

8.4.1.2. Soil preparation

Natural clayey soil (type 6-5) was used to perform tests in phase III. Preparation of the soil for pilot scale testing was accomplished in four stages:

<u>Stage 1: Soil characterization</u>. This stage involved a precise soil characterization followed by soil preparation, done in accordance to the protocol used for soil type 6-4 (refer to Chapter 7.1). The use of this protocol ensured and maintained consistency between tests in phase II and III.

A sieve analysis test showed that 99 % of the soil passed through the No. 200 sieve, which indicates the clayey nature of the soil material. Figure 86 shows soil mineralogy obtained from X-ray defraction analysis. Other physio-chemical characteristics are presented in Table 32.

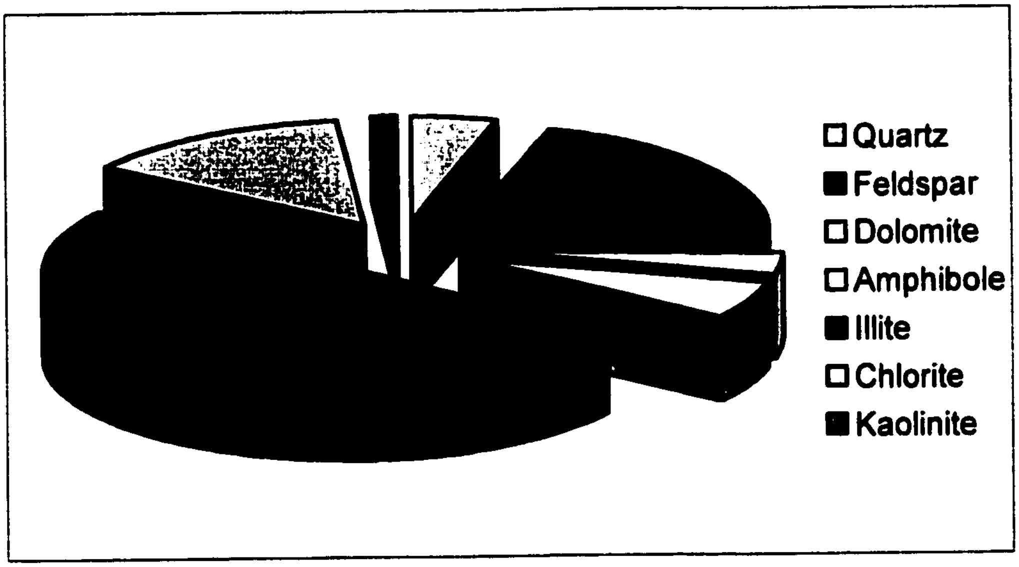


Figure 86 Soil Mineralogy as obtained from X-ray Defraction

Table 32 Initial Soil Characteristic used in Phase III

Cation Exchange Capacity 21 meq/100g
[illegible]
Organic Matter Content 10.3%
[illegible]
Total Kjeldahl Nitrogen 0.042 %
[illegible]
Sulfate content 0.6 ppm as SO_4^{2-}
[illegible]

Stage 2: Soil Contamination Process. This stage involved spiking the dry soil with a desired concentration of phenanthrene. The results obtained from PT-1 and PT-2 defined to define the most efficient method of providing a homogeneous distribution of phenanthrene within the soil.

According to the procedures followed in PT-2, dry non-contaminated soil was divided into 100 portions of 0.5 kg each. Each portion was placed in a glass container and a methanol-phenanthrene solution consisting of with 300 mg of phenanthrene added to each 0.5 kg portion to form slurry. Containers were sealed and placed on a rotor for 24 hrs. The slurry was then allowed to sit for 7 days, during which the samples were rotated every 4 hrs. After this period, methanol was allowed to evaporate and all soil portions were combined together and mixed thoroughly. Five samples were then taken from different locations and subjected to a desorption test to verify the homogeneity and actual initial phenantrene concentration.

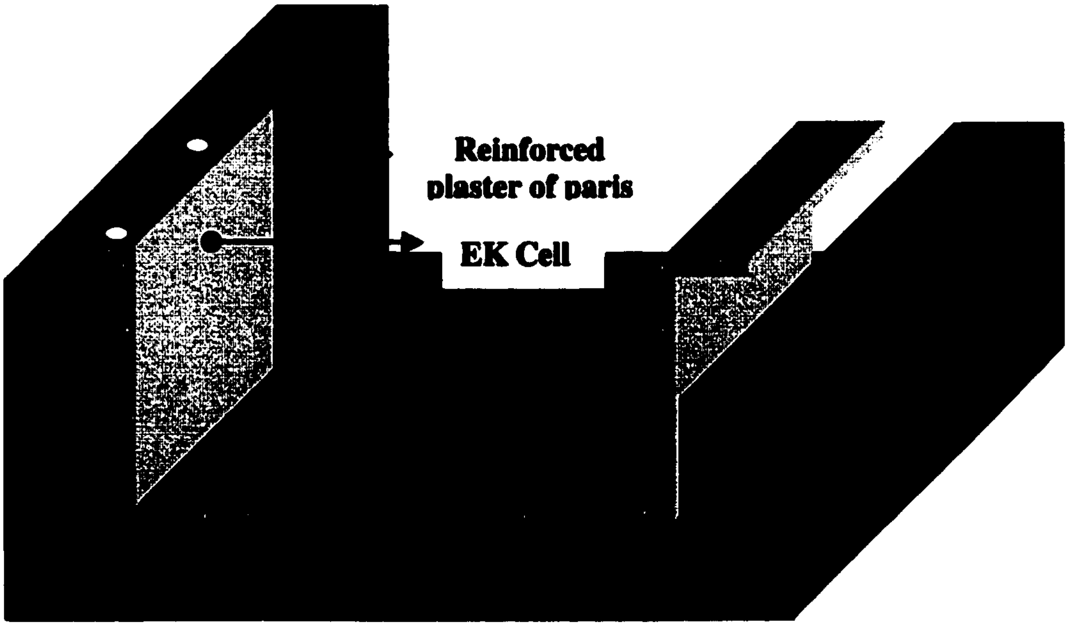


Figure 87 Schematic Drawing of the EK Cell with the Molding

Stage 3: Providing Moisture Content. Because of the large soil quantity used in this test, a special method was used to provide homogeneously distributed moisture. Therefore, the soil was divided into 50 portions. Each portion was provided with the desired moisture through several steps including the use of an electrical sprayer, which provided the soil with a known volume of water. This procedure was done in a container in order to minimize the moisture loss. The applied methodology involved raising the moisture content of the soil portions gradually and reducing the number of portions in each step.

Stage 4: Cell Filling Procedures. Moist soil with spiked phenanthrene was left to sit for 48-hrs before it was transferred to the cell. To avoid any moisture loss during cell filling, the soil was cooled to 8 ^{0}C and later placed in the cell in 10 uniform layers. Each layer was carefully tamped to avoid the creation of air cavities.

8.4.1.3. Electrode Filter Design and Placement:

As it was mentioned in the study's objectives, a new design of electrodes was required. An open electrodes design was chosen to facilitate the emission of gases created through electrode reactions (Chapter 7.2.2.1) and to simulate field conditions. The electrodes design was based on the conclusions derived from phase I and II, and on extended research on electrode materials (Elektorowicz et al. 1995). Subsequently the optimization process led to the design of two types of electrodes:

Type I electrode: A stainless steel (SS 316) perforated 2.5-cm tube was covered with a SS mesh (size 200). The anode was surrounded with a sandy zone of 1in. (2.5-cm) thickness separated from the contaminated soil by a fiberglass mesh. The fiberglass served as a mechanical support structure during the compaction of the clayey soil.

Type II electrode: 1 inch (2.5-cm) stainless steel (SS 316) perforated tube was covered with a SS mesh (size 200) and 1 inch thick clayey material surrounded the electrode followed by another 1 inch thick sandy zone. A fiberglass mesh also was also used as a casing for each layer protecting the electrodes when the soil was subjected to the filling and compaction process in the cell.

To test the behavior of both electrodes in the EK system, the cell was divided into two parts, named Set 1 and Set 2. Type I electrode acted as a cathode and type II electrode acted as an anode in Set 1. In Set 2, the type II electrode was used for both anode and cathode. A schematic drawing of both electrode types and their layout in the cell is shown in Figure 88 and Figure 89. The Packed cell with electrodes before applying an electric field is shown in Figure 90.

8.4.1.4. Surfactant supply system (SSS): The design of the system was based on the conclusions made from phases I & II. However, a new system design was developed considering several new factors; among them: 1- continuous monitoring and control of the surfactant supply for each electrode; 2- refilling the system without interrupting the process; 3- unlike the previous system, the new system would supply the surfactant upward and not downward. A schematic drawing of the surfactant supply system is shown in Figure 91 and an illustration of the system connected to both anodes is presented in Figure 92. The system consisted of multiple feeding chambers (the number was dictated by the number of anodes) with a volumetric cylinder connected to a main supply reservoir. Each chamber was equipped with two regulators. The first was from the upper end of the cylinder, which was used to cut the supply to the cylinder at the time when the main chamber was refilled, and the other was from the lower side of the cylinder end and was used to refill the cylinder.

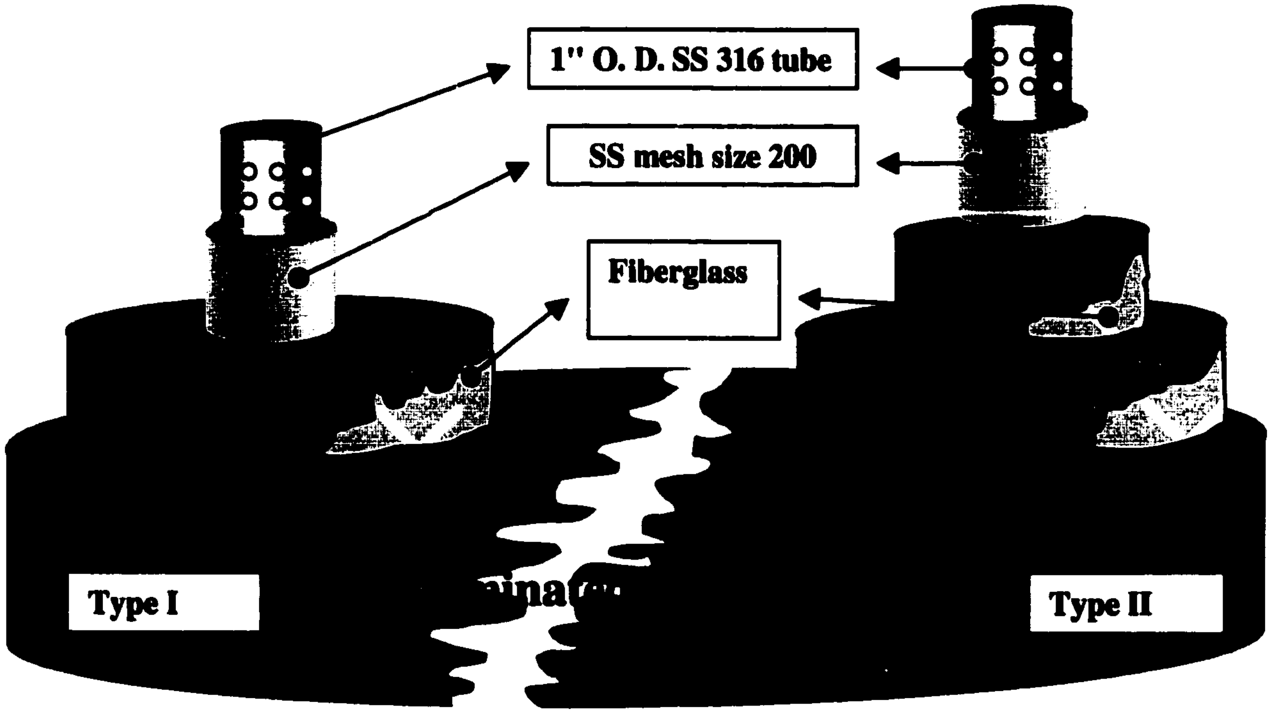


Figure 88 Design of electrodes for Pilot Scale Test

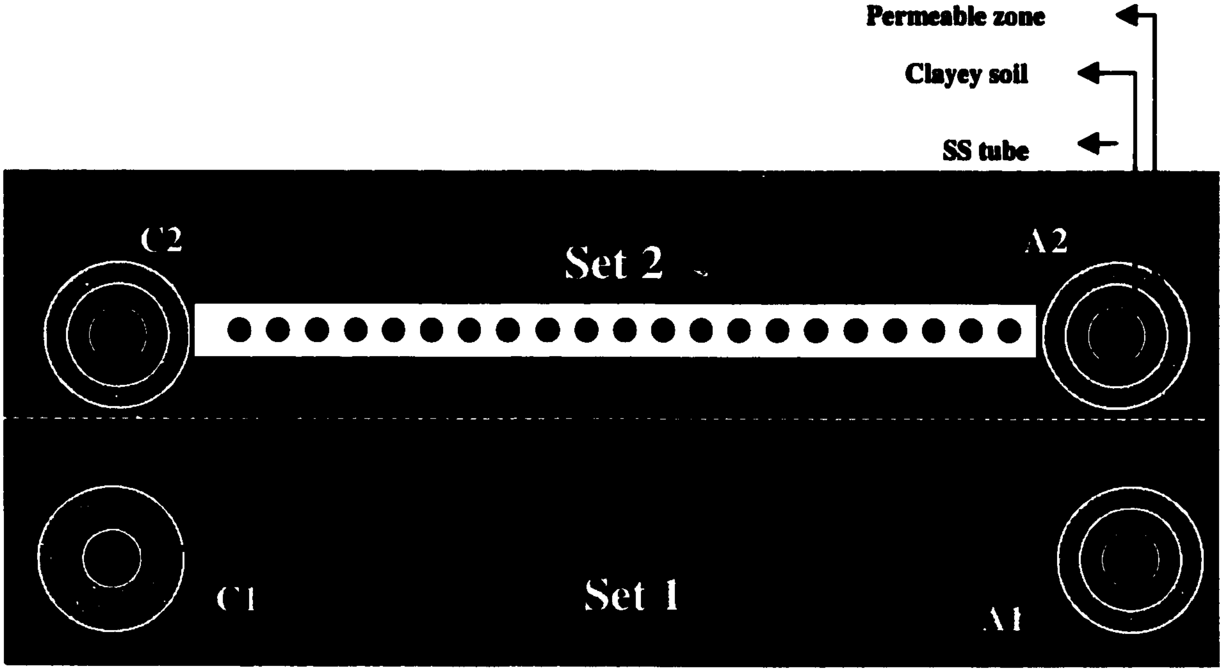


Figure 89 Electrokinetic Cell Configuration in Phase III

Surfactant selection:

Based on the conclusions derived from the batch tests, *"Alkyl Dimethylbetaine"* surfactant at 0.0025 M concentration was chosen for this test. The chemical formula of the surfactant is C_{12} - C_{14} - $N^{+}(CH_3)_2\ CH_2COO^{-}$ and the molecular weight is 327. The critical micelle concentration of this surfactant as supplied by the manufacturer is 0.00099 M.

Figure 90 Vertical View of Cell III Filled with Contaminated Soil

8.4.1.5. Washing System

This washing system was tested in previous phases and used to wash the permeable zones near the cathodes. At this stage, the system was connected to the cathode permeable zone, hence, was an integral part of the electrode design. The system consisting of a multi-channel cartridge pump, flexible tygon type tubing, and a dilution reservoir. Figure 93 shows the set-up of a washing system with two dilution reservoirs. The liquid in the dilution reservoir was refreshed occasionally to prevent its pH value from rising.

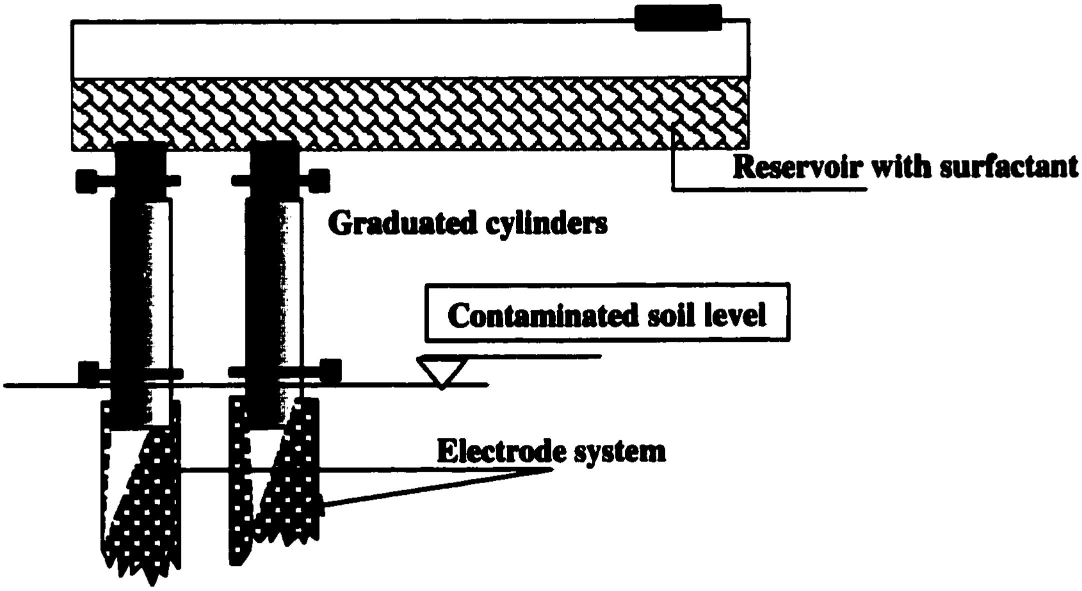


Figure 91 Schematic drawing of Surfactant Supply System (SSS)

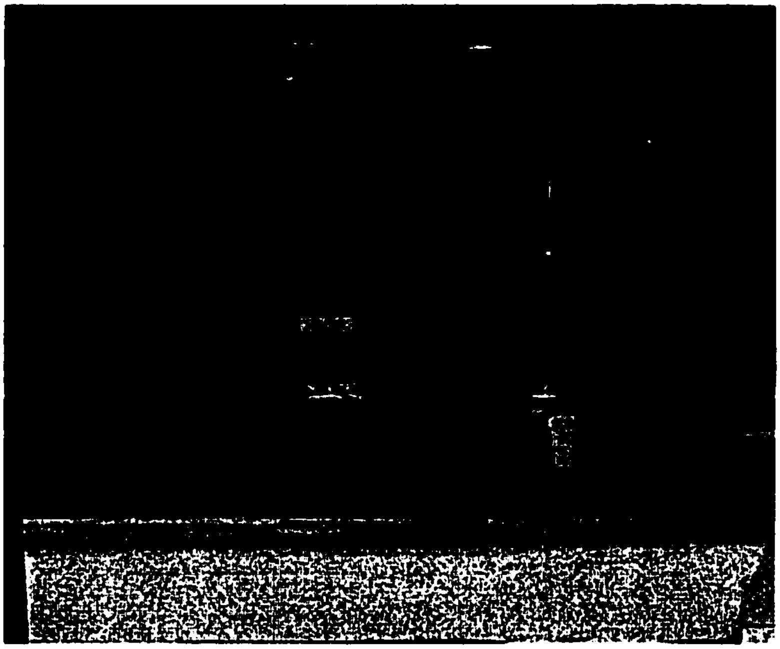


Figure 92 Surfactant Supply System Connected to the Cell III

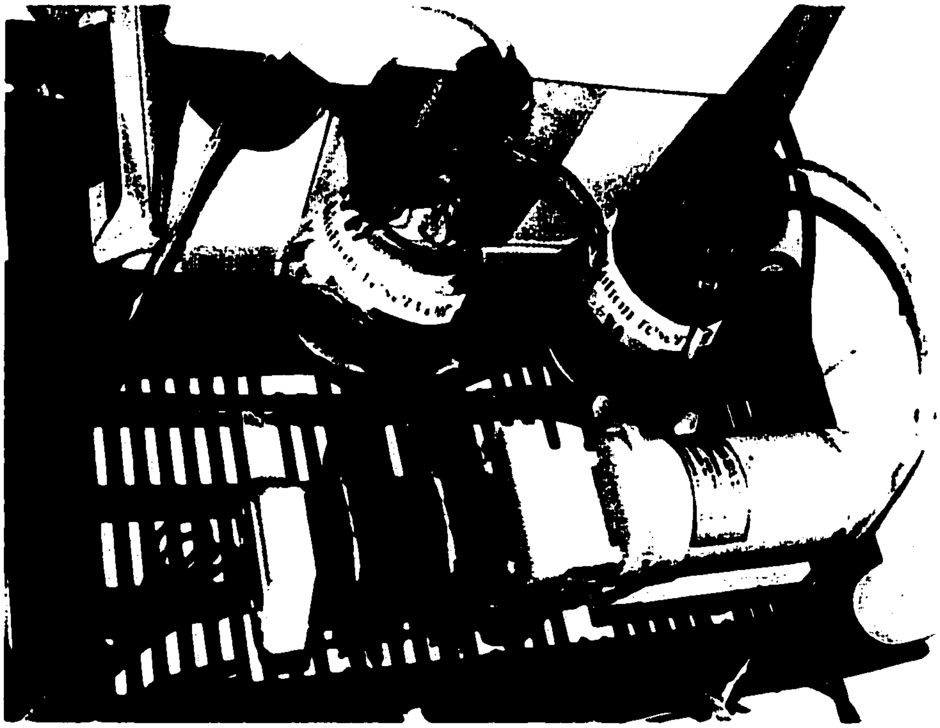


Figure 93 Washing System for Cell III

8.4.2. Measurements:

The evaluation of the overall system performance was possible through numerous measurements, which were conducted before, during, and after the test. These measurements were a vital tool to better understand and interpret the results of soil remediation process. Table 33 lists these measurements.

Table 33 Measurements Conducted Before, During and After the test

Prior the Tests	**Cation Exchange Capacity** **pH** **Organic Matter Content** **Carbonate Content** **Total Kjeldahl Nitrogen** **Specific gravity** **Sulfate test** **Metals content** **Moisture content**
During the Tests	Electrical parameters pH of washing liquid pH of cathode liquid Volume of conditioning liquid Volume of supplied surfactant
After the Tests	Moisture content pH of soil samples Phenanthrene content

The methodology and equipment used for these measurements were described in Chapter 7.3.

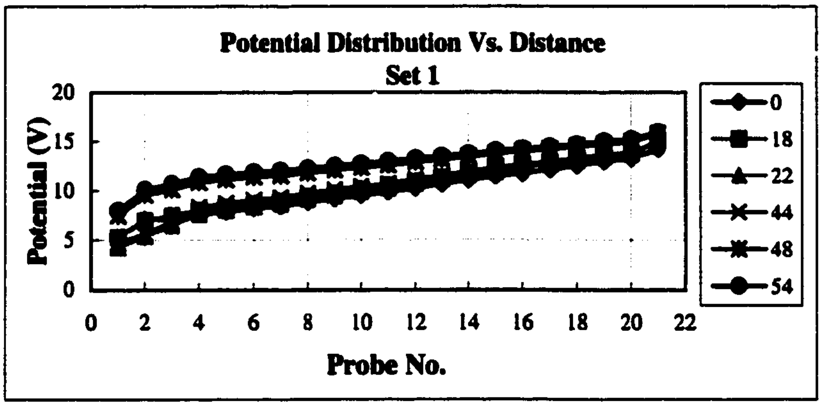
8.4.3. RESULTS AND DISCUSSION

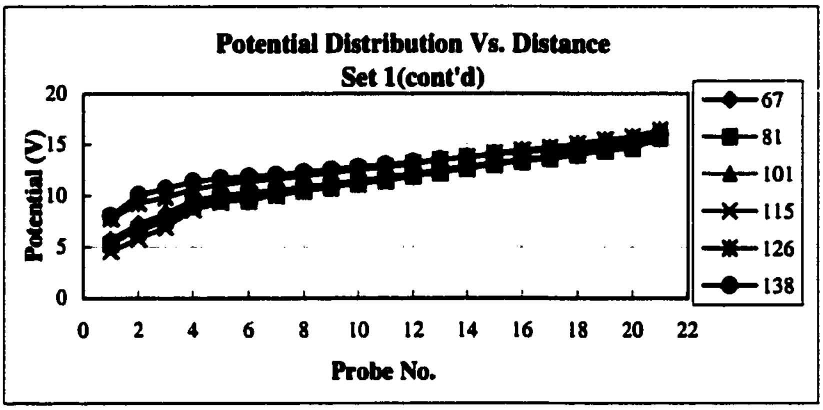
8.4.3.1. Electrical parameters

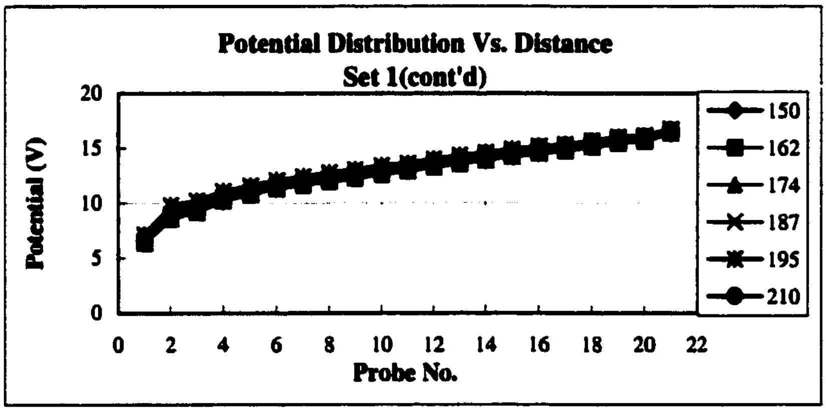
8.4.3.1.1. Potential distribution:

The relationship between the potential at each probe and its distance from the cathode measured at different time is presented in Figure 94. The graphics show that the potential distribution pattern can be divided into two distinct zones. The distinction between these zones was clearer after 150 hours. The first zone is confined between probe 1 and 2 and the second zone is the one confined between probe 2 and 21. In zone-I the gradient started with 1.8 V/cm at 0 hours and ended with 3.23 V/cm at 1060 hours, with a minimum value of 0.67 V/cm measured at 101 hours and a maximum value of 4.52V/cm measured at 48 hours. The potential distribution pattern in zone-2 had a series of linear distributions with varying gradients throughout the experiment. This gradient started at 0.375 V/cm and finished with 0.43 v/cm with a minimum gradient of 0.3 V/cm measured at 54 hours and a maximum gradient of 0.63 V/cm measured at 749 hours. Figure 95 and Figure 96 shows a comparison between total gradient change throughout the test between probes 1 and 21, 2 and 21, and 1 and 2 for Set 1 and 2 respectively. The graphs show that the gradient change between probe 1 and 2 express less flocculation than the gradient between probe 2 and 21.

Figure 97 presents potential distribution between the cathode and the anode measured in consecutive probe electrodes at different times for set 2. The graphs show that unlike set 1, any distinction between different zones disappeared. The potential distribution differed from the one measured in set 1. This gradient started with 0.45 V/cm at 0 hours and ended with 0.57 V/cm with a minimum of 0.147 V/cm at 48 hours and a maximum of 0.77 V/cm at 773 hours.







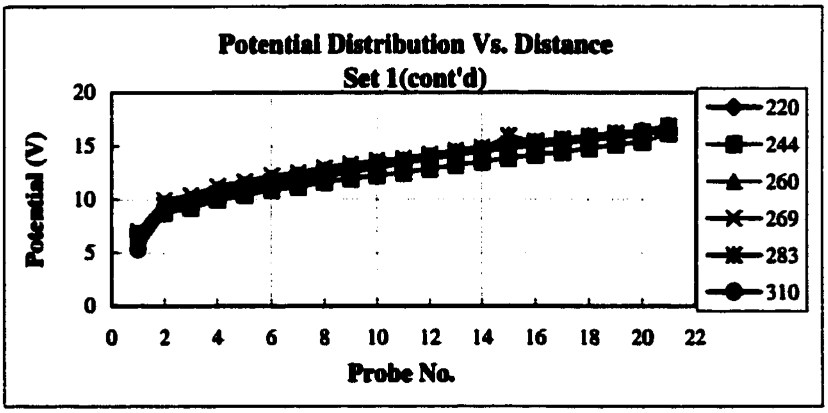
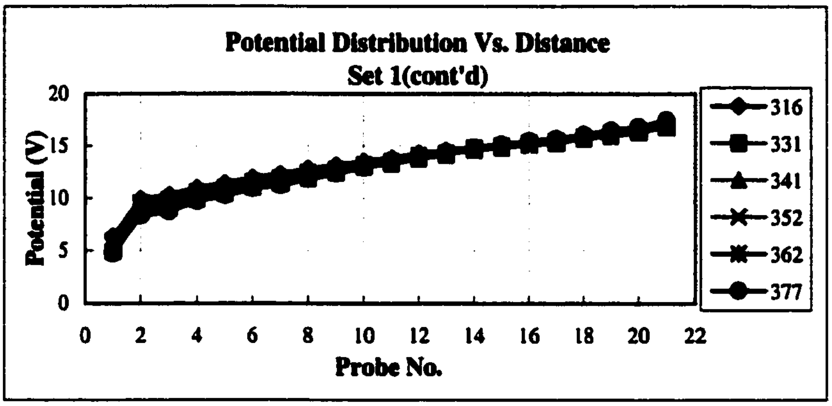
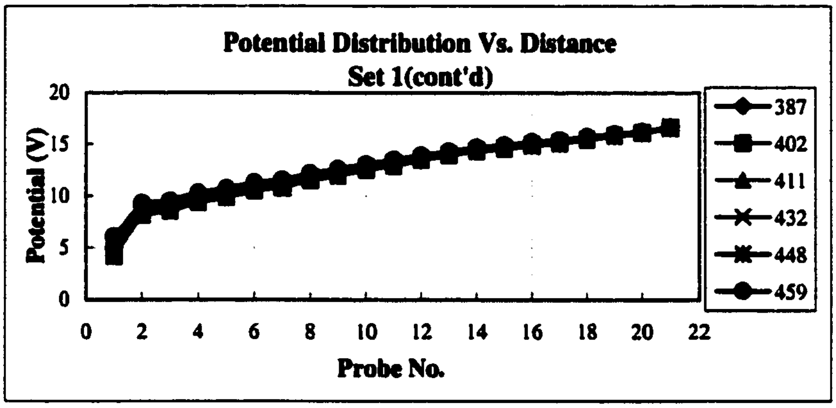
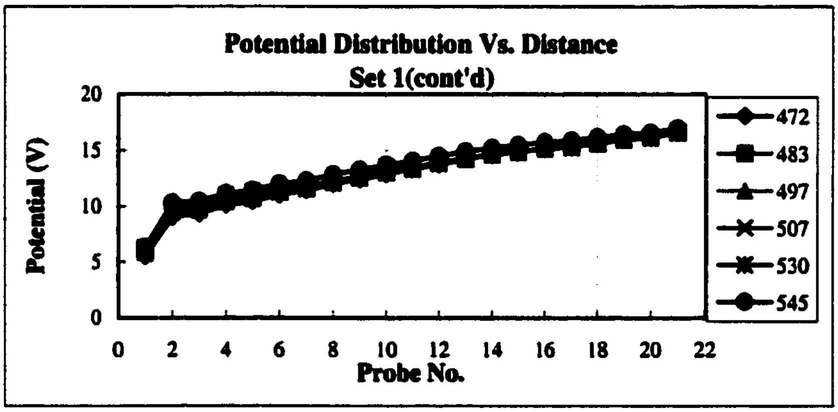


Figure 94 Potential Distribution vs. Distance Measured at Subsequent probes for Set 1







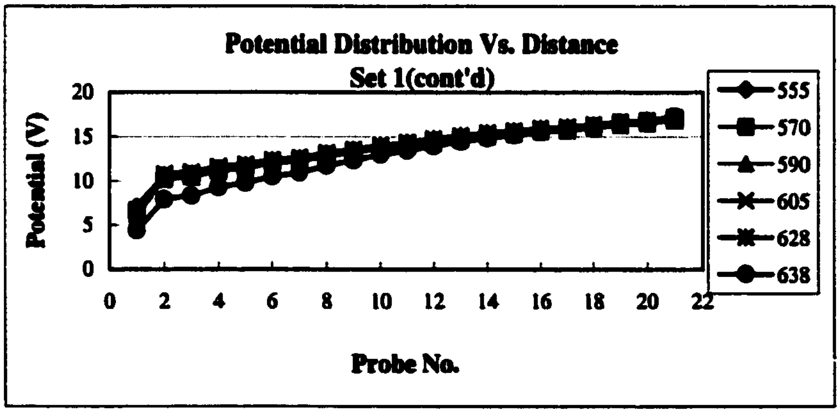
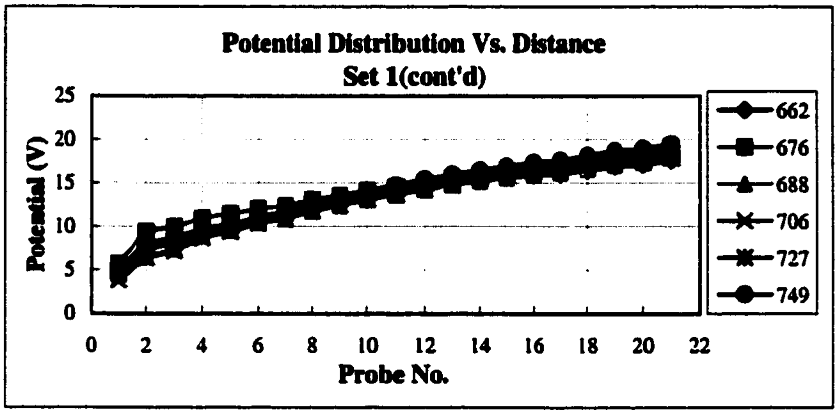
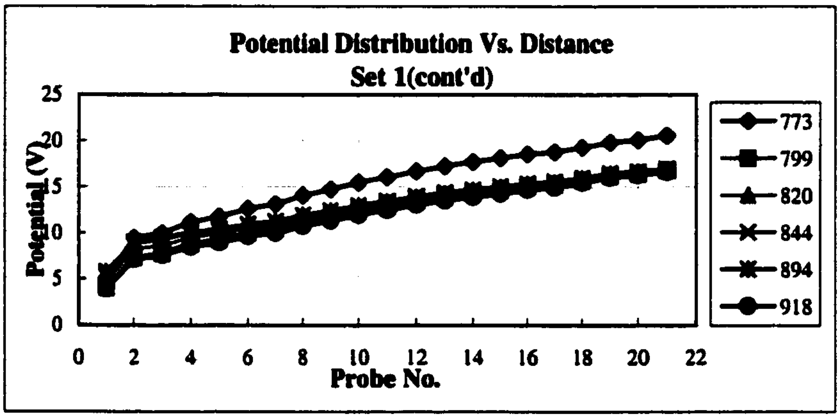


Figure 94 Potential Distribution vs. Distance Measured at Subsequent probes for Set 1





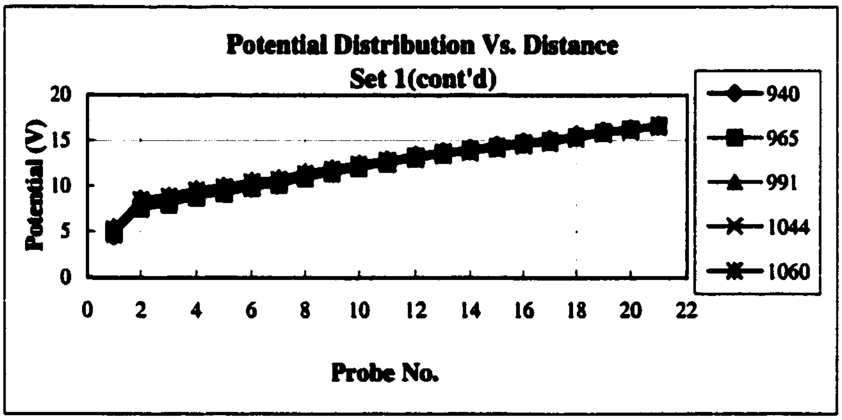


Figure 94 Potential Distribution vs. Distance Measured at Subsequent probes for Set 1

The distinction in the potential distribution and the gradient measured between both sets suggested that the design of the electrode (cathode) in set 1, which was the only difference between both sets, was the cause of the sharp drop in the gradient for set 1 and reducing the overall gradient along the distance between the cathode and the anode.

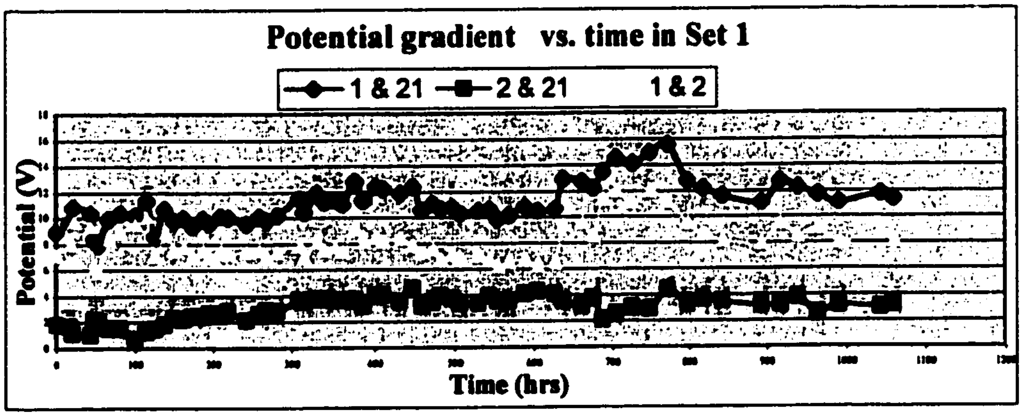


Figure 95 The Change in Potential Gradient in Set 1

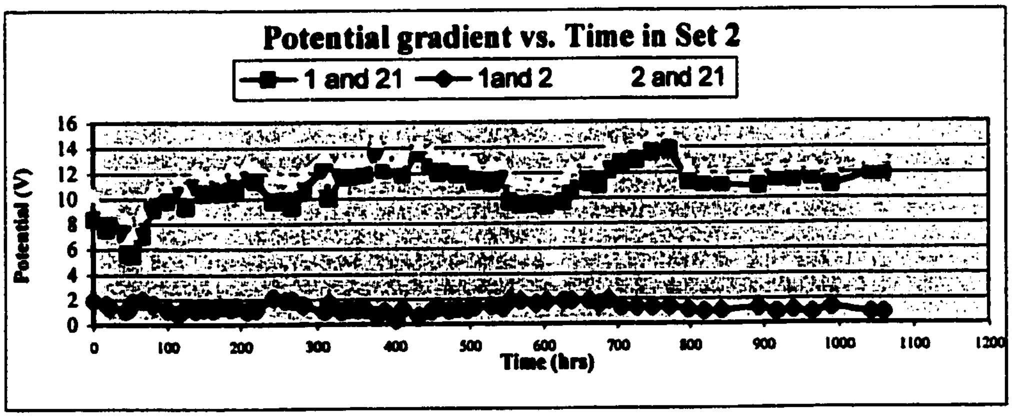
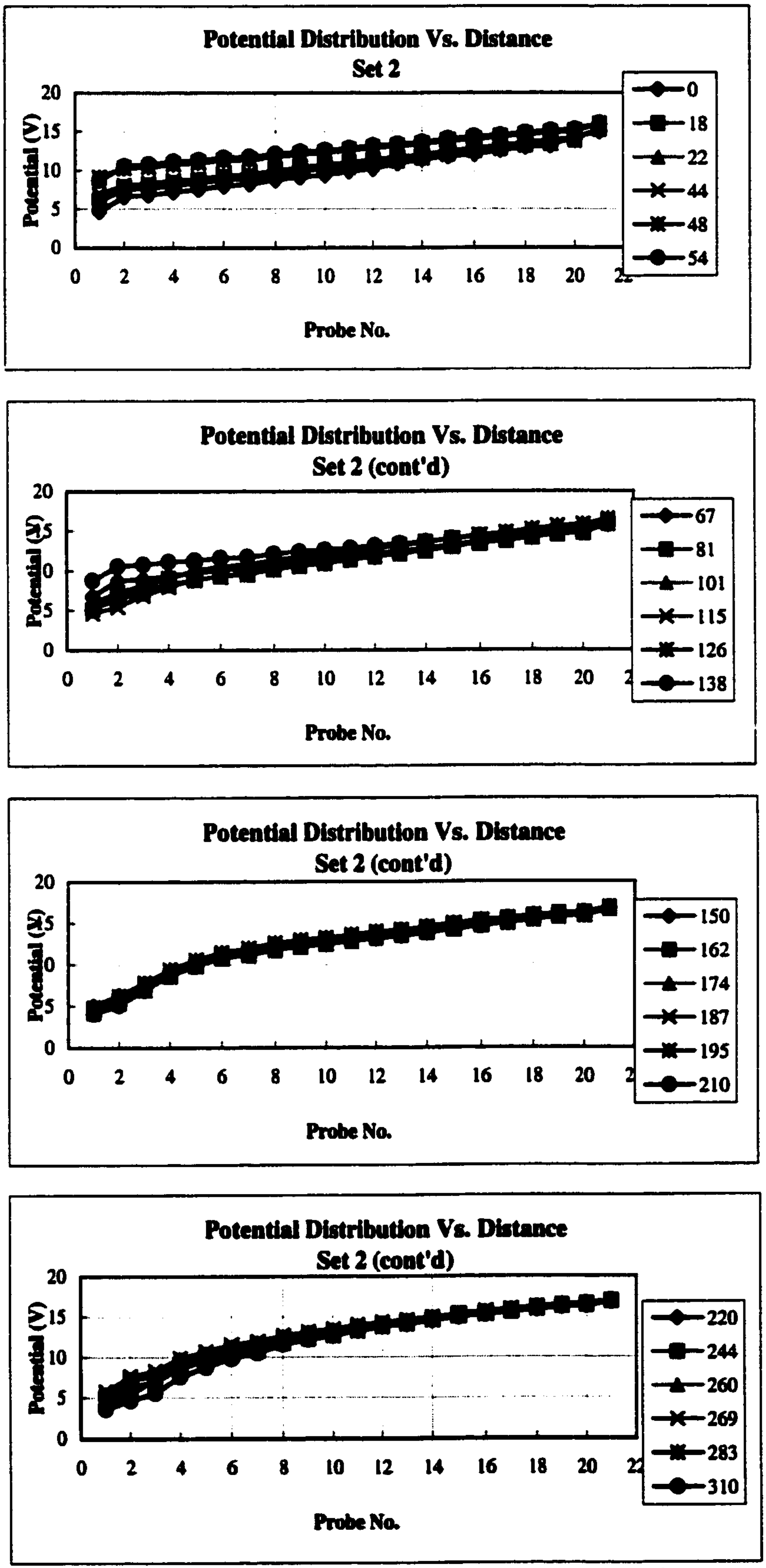


Figure 96 The Change in Potential Gradient in Set 2.



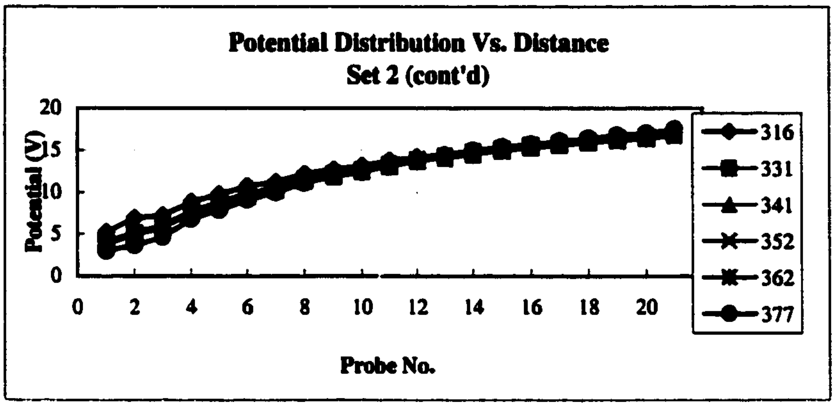
Potential Distribution Vs. Distance Set 2

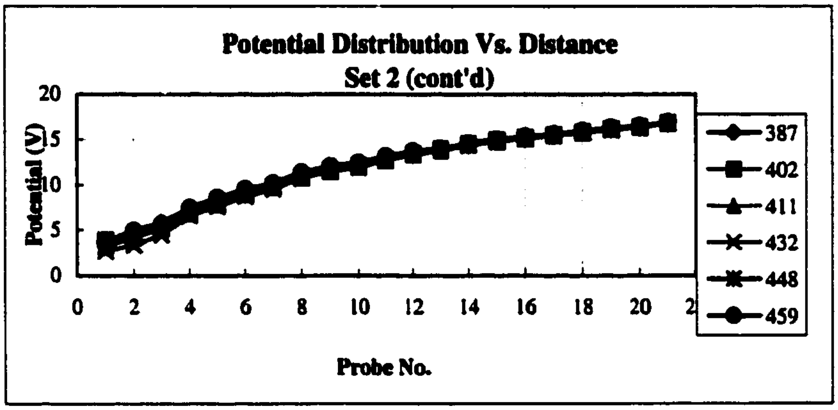
Potential Distribution Vs. Distance Set 2 (cont'd)

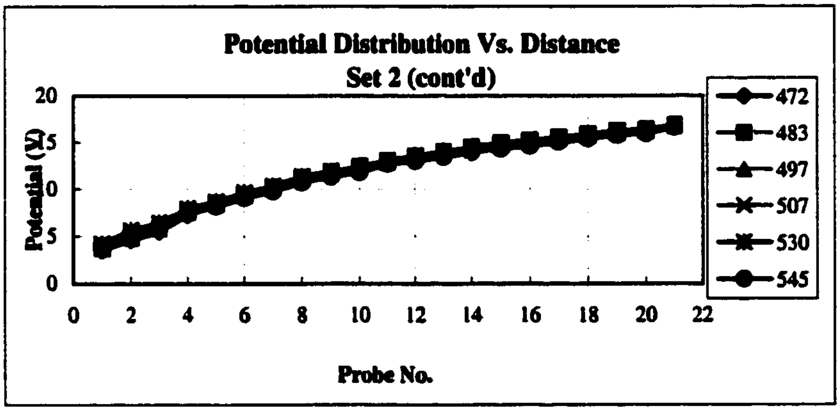
Potential Distribution Vs. Distance Set 2 (cont'd)

Potential Distribution Vs. Distance Set 2 (cont'd)

Figure 97 Potential Distribution vs. Distance Measured at Subsequent probes for Set 2







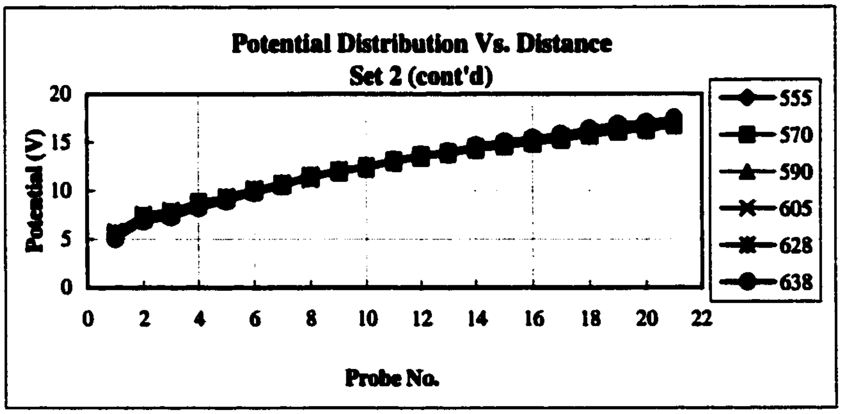


Figure 97 Potential Distribution vs. Distance Measured at Subsequent probes for Set 2

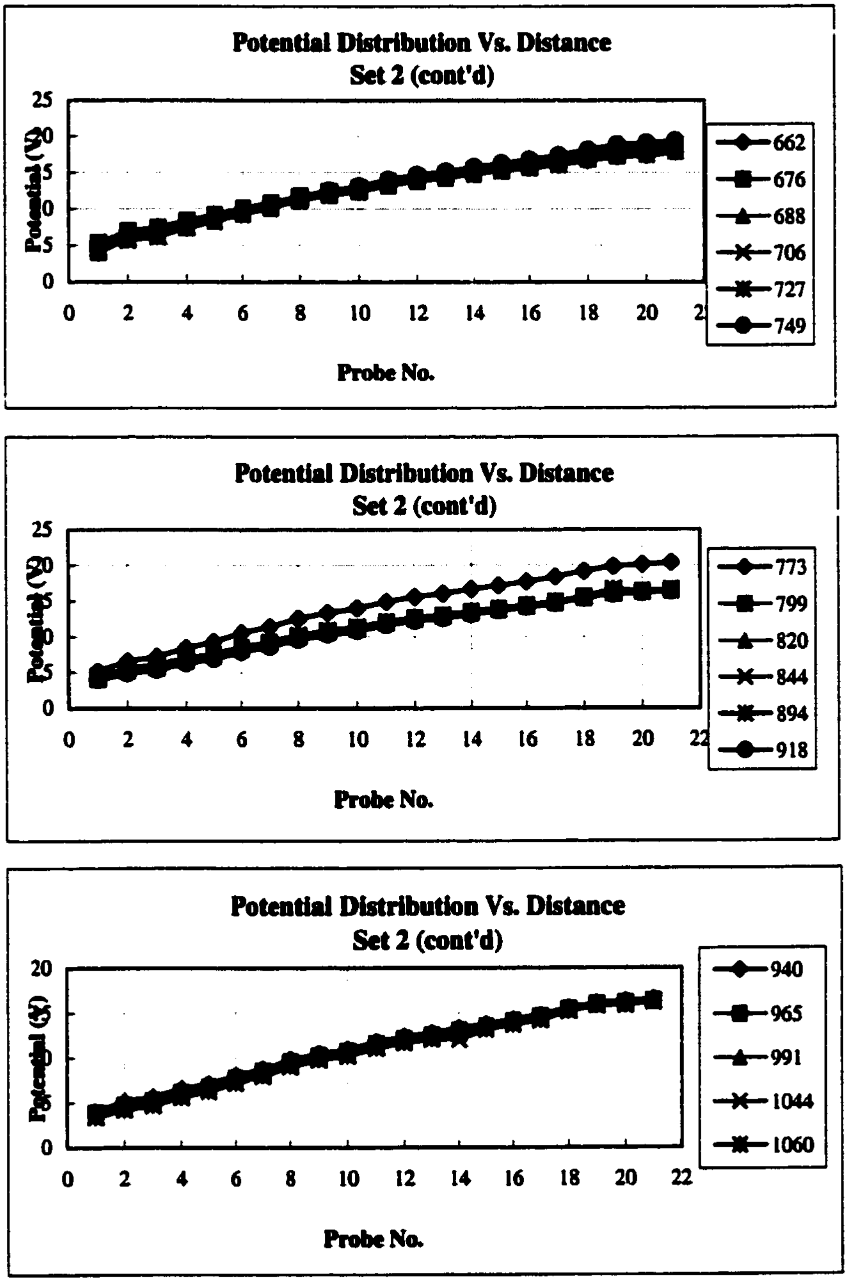


Figure 97 Potential Distribution vs. Distance Measured at Subsequent probes for Set 2

The relationship between potential changes in each probe with time is presented in Figure 98 for set 1 and Figure 99 for set 2. The graph shows that all probes in each cell had a similar distribution pattern with excessive instabilities.

Comparison of potential change versus time in corresponding probes from both cells, pointed to a fact that the differences in the distribution pattern in both cells started to diminish while gradually moving away from the cathode. Both patterns had almost the same values starting from probe 10. This fact suggests that the effect of the cathode design for cell 1 on the electrical parameters extended to almost half the cell.

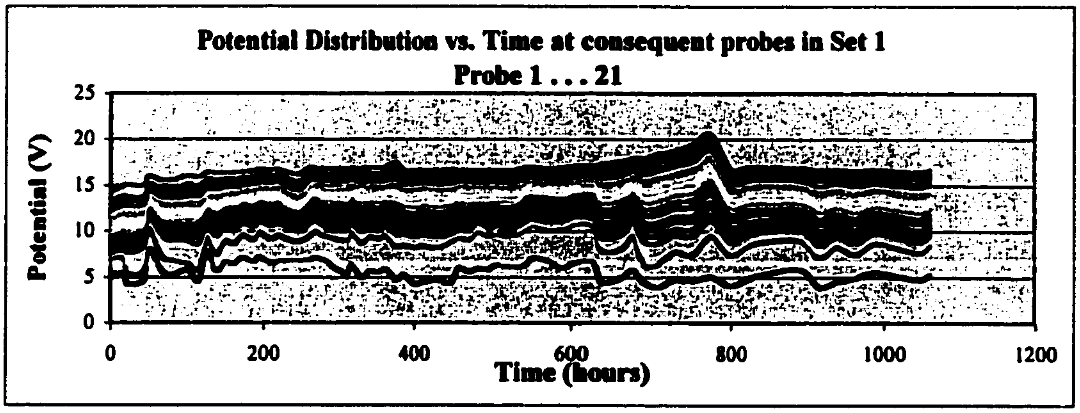


Figure 98 Potential Distribution vs. Time at consequent probes in Set 2

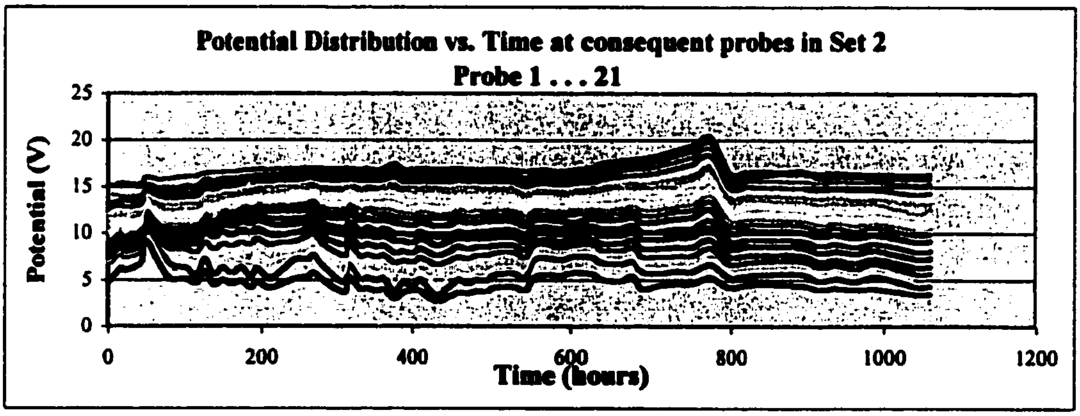


Figure 99 Potential Distribution vs. Time at consequent probes in Set 2

8.4.3.1.2. Resistance distribution:

The Resistance distribution versus distance was calculated based on potential values at each probe and the supplied current at different times.

The relationship between resistance and the distance are presented in Figure 100 and Figure 101 for set 1 and set 2 consequently.

In set 1, although resistance changes with time were observed; the overall distribution pattern within the soil was similar. A logarithmic distribution along the distance was observed. In the area near the cathode, the resistance increased sharply between probe 1 and 2. The initial gradient between these probes was 30 Ohms at the beginning of the test and then increased to 452 Ohms after 1060 hours of tests. On the other hand, the gradient between probe 2 and 21 was 119 Ohms at the beginning of the test (6.26 Ohms/cm) and increased to 1142 Ohms (60.10 Ohm's/cm) after 1060 hours.

Figure 102 illustrates the resistance distribution vs. distance at the beginning and at the end of the test. The graph shows that a dramatic increase in the resistance occurred, especially near the anode area where the resistance value increased from 237 Ohms to 23330 Ohms. On the other hand, the resistance in cathode area (probe 1) increased from 88 Ohms to 735 Ohms.

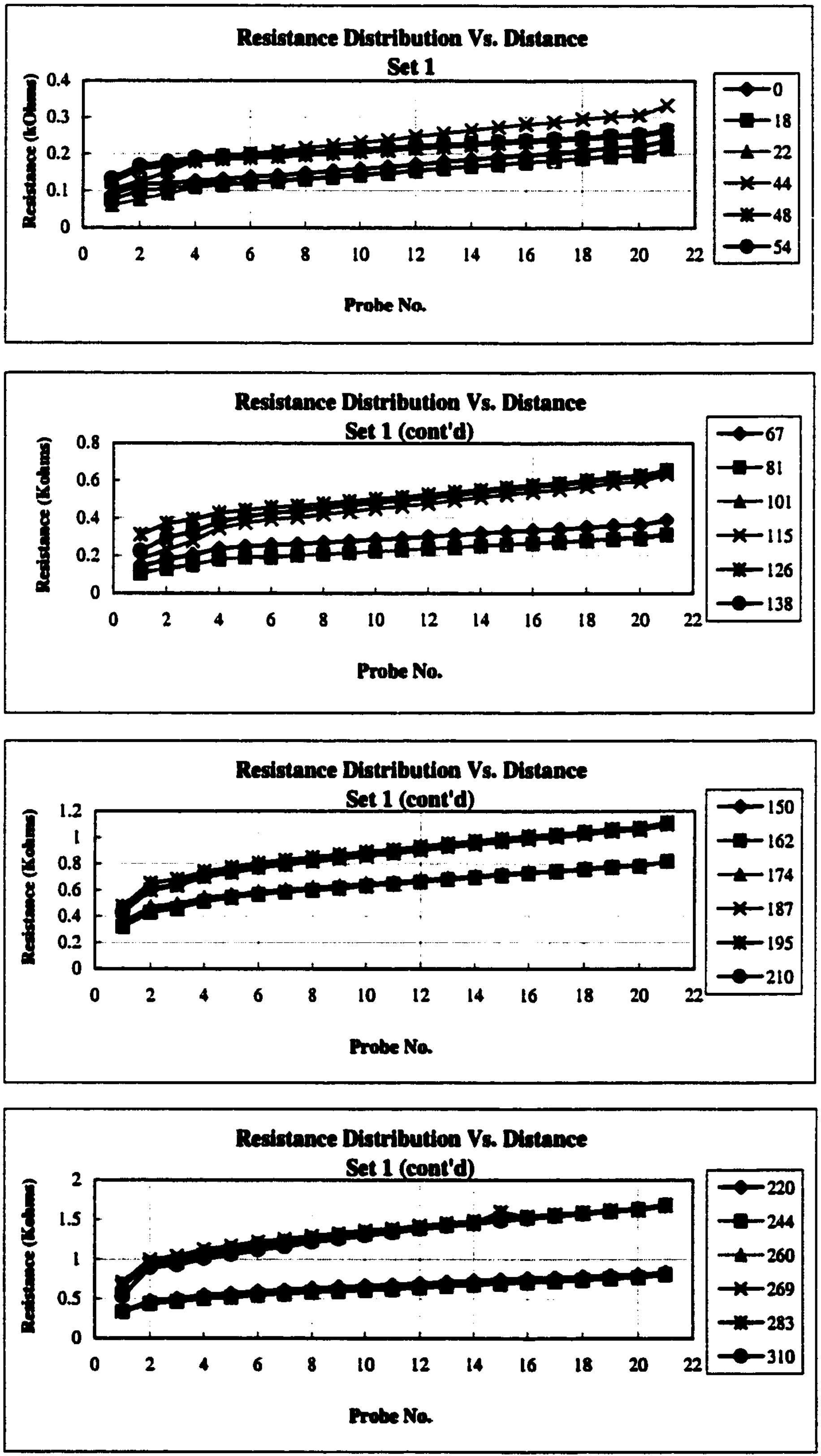
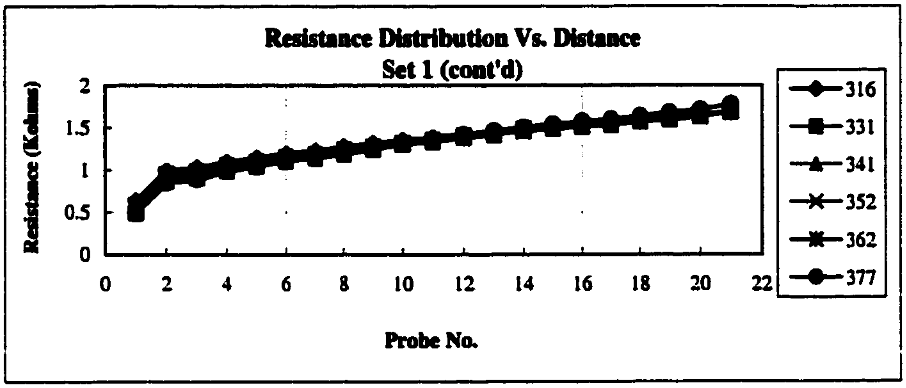
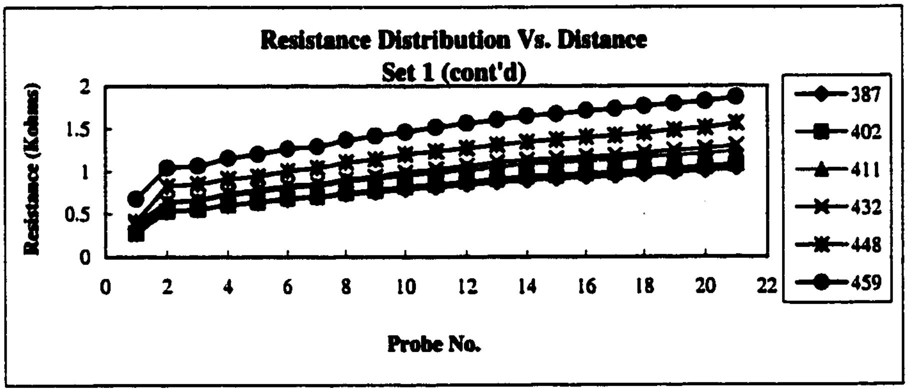
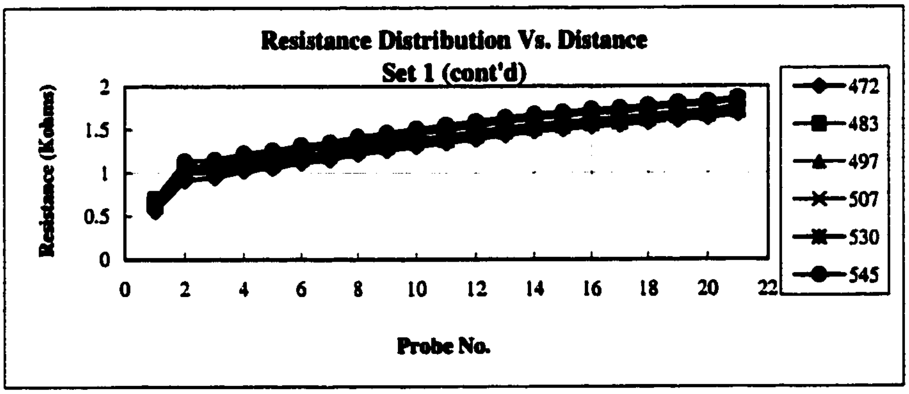


Figure 100 Resistance Distribution vs. Distance for Set 1







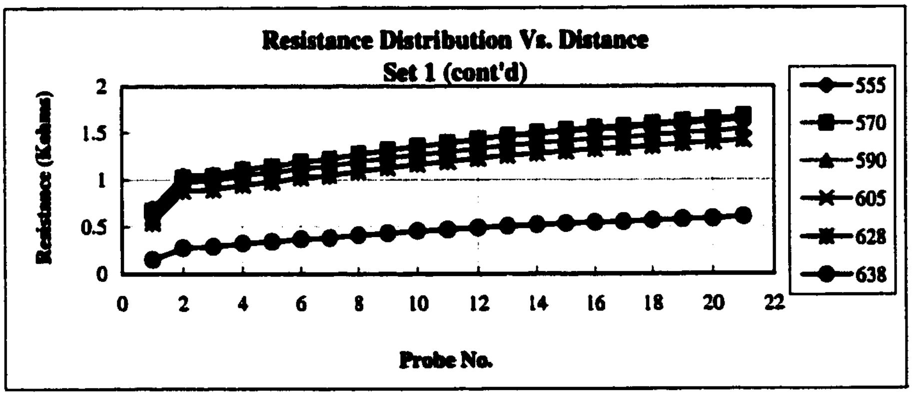
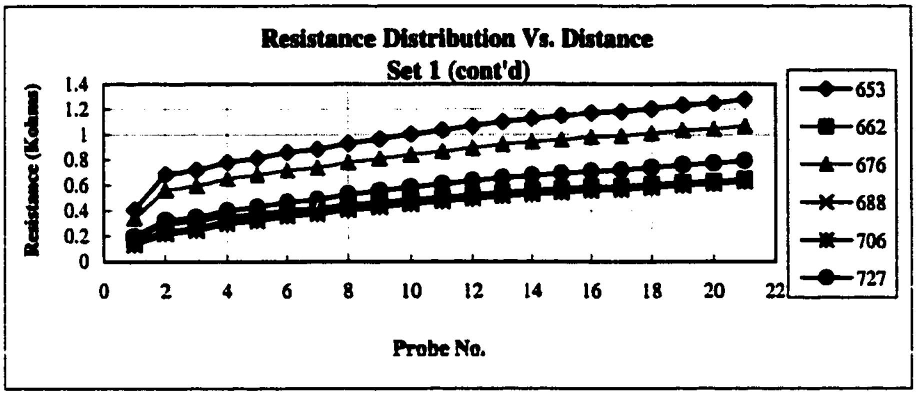
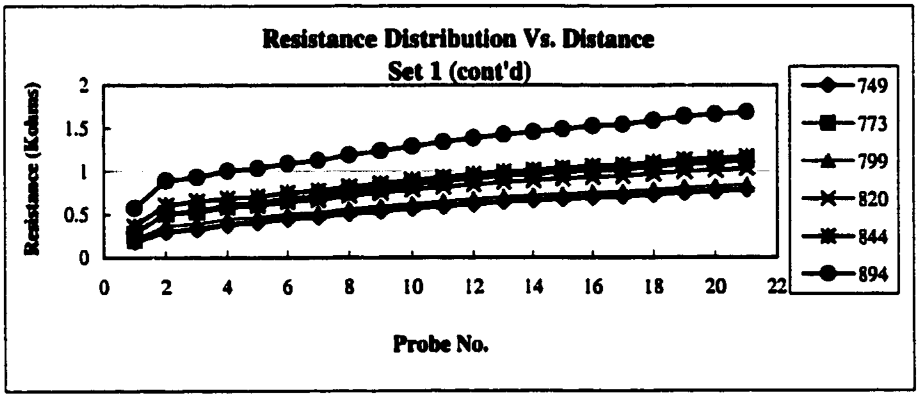


Figure 100 Resistance Distribution vs. Distance for Set 1





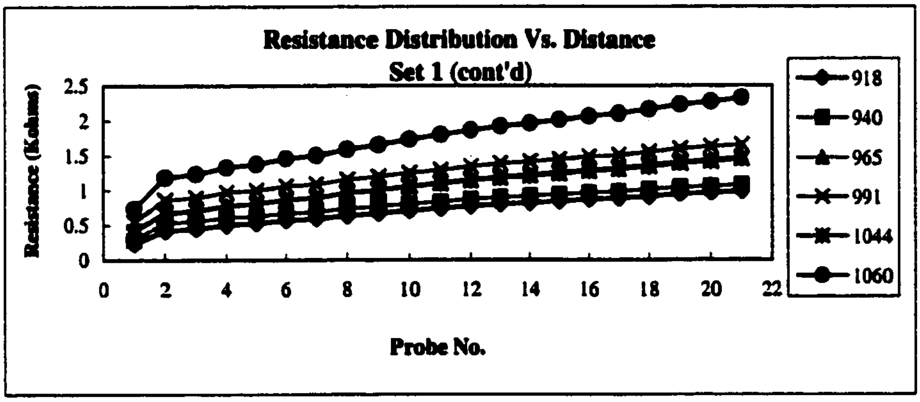


Figure 100 Resistance Distribution vs. Distance for Set 1

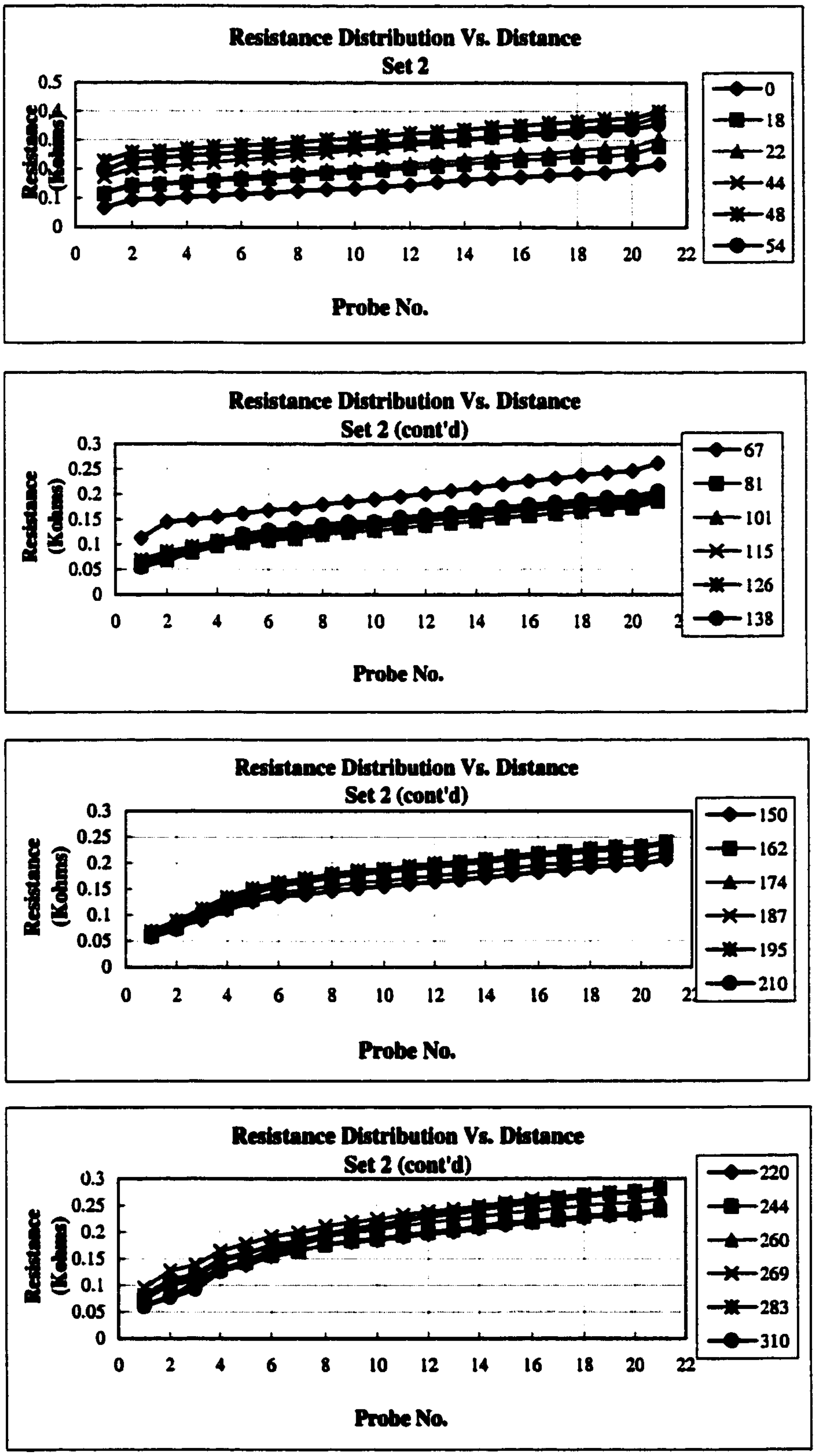
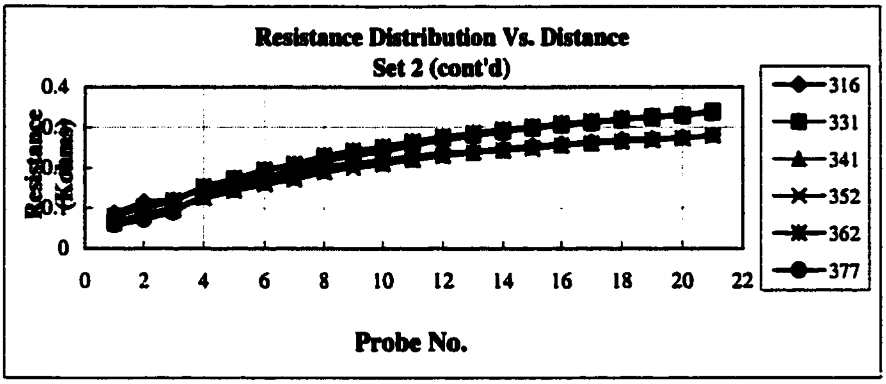
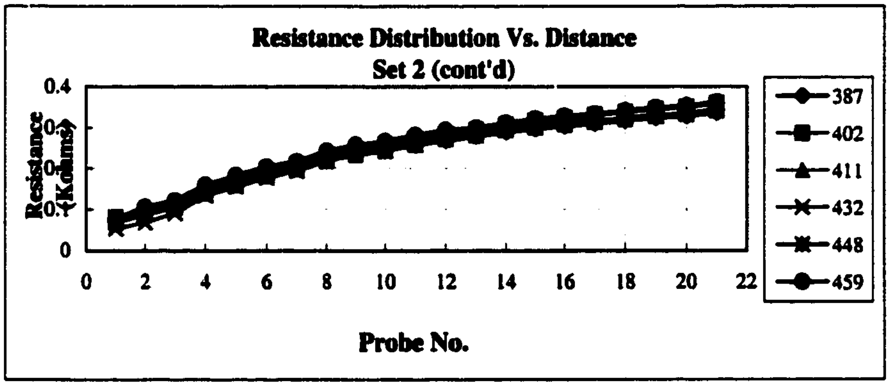
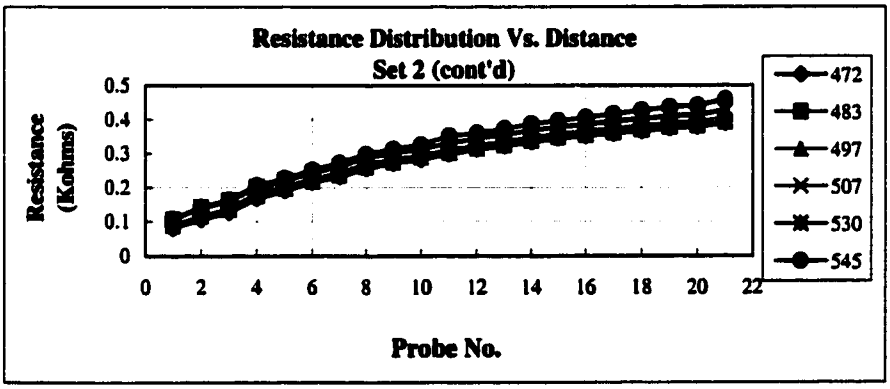


Figure 101 Resistance Distribution vs. Distance for Set 2







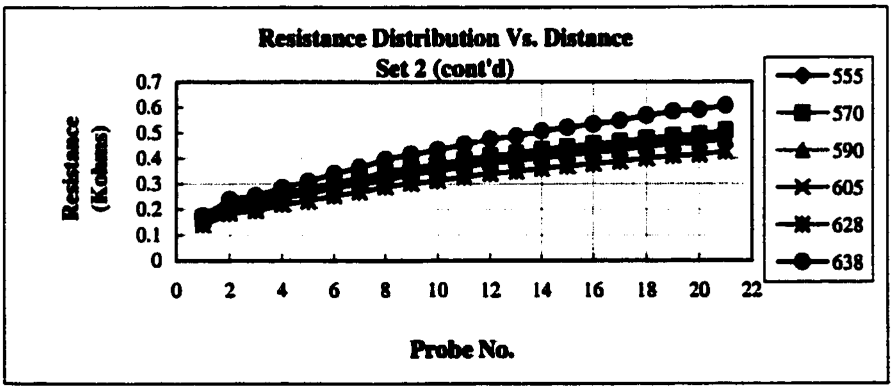


Figure 101 Resistance Distribution vs. Distance for Set 2

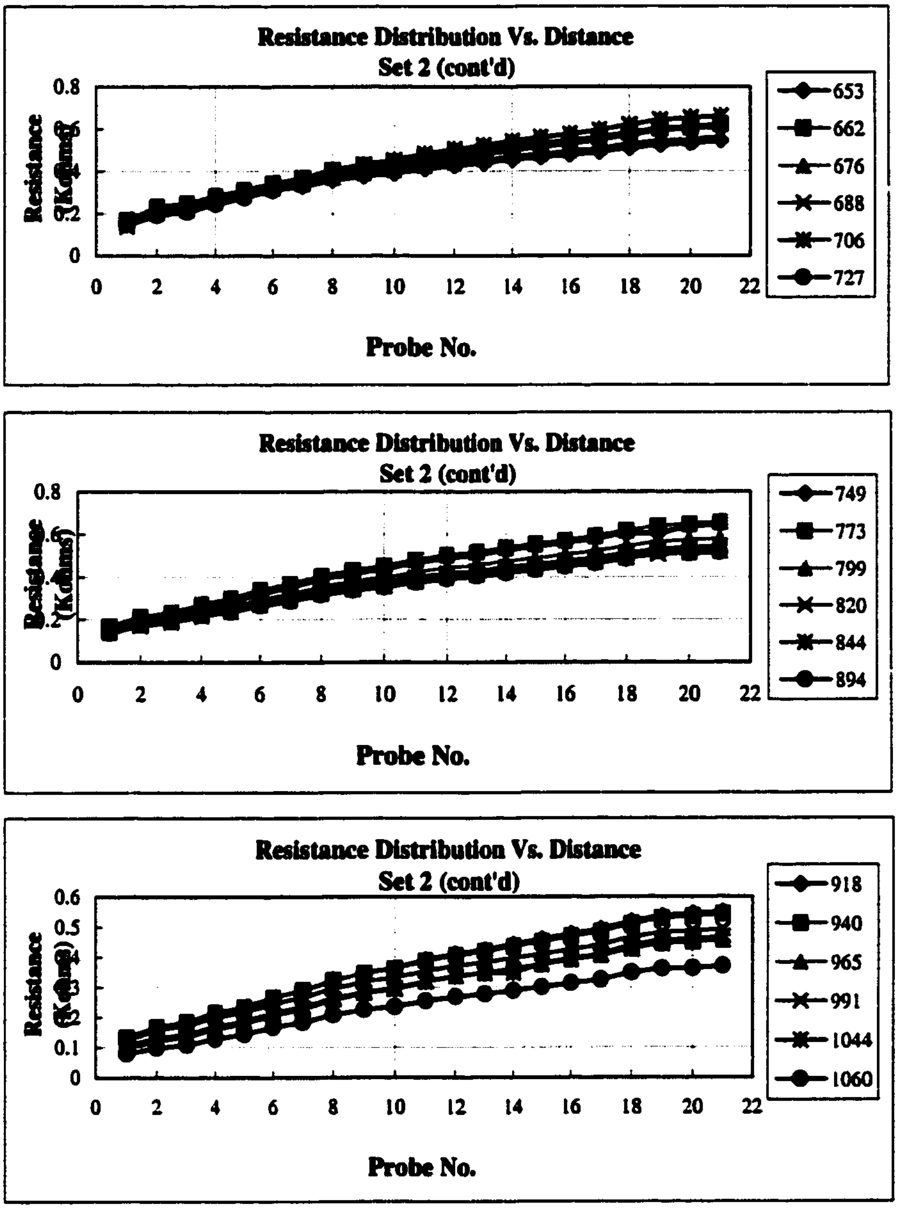


Figure 101 Resistance Distribution vs. Distance for Set 2

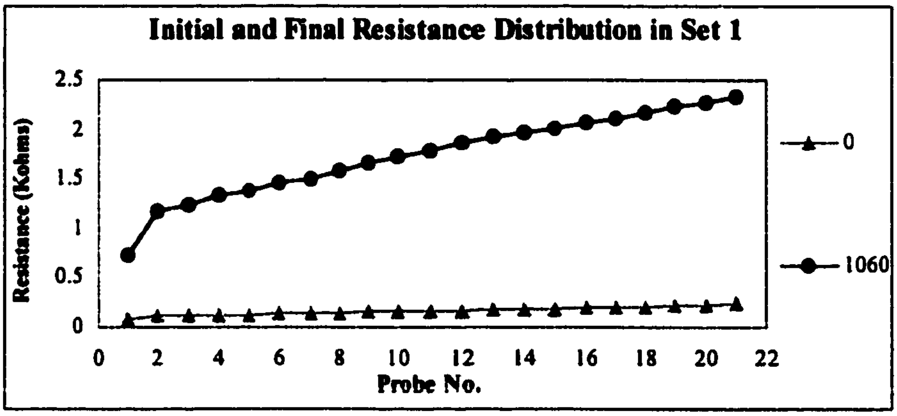


Figure 102 Initial and Final Resistance Distribution in Set 1

In set 2, resistance values were much lower (Fig.101) than the values recorded in set 1, especially in anode area and at the end of the test. Resistance distributions were also different, for instance the absence of the area where the resistance gradient witnessed a dramatic increase was noticed. In cathode region, the initial resistance difference between probe 1 and 2 was with 27 Ohms and reached a minimum of 10 Ohms after 115th hour and a maximum of 65 Ohms after 688th hour ending with 20 Ohms after 1060 hours. A quiet lower values from what was observed in set 1. The difference between probe 2 and 21 did not show great changes as in set 1. It started with 123 Ohms (6.47 Ohms/cm) and reached a minimum of 107 Ohms (5.63 Ohms/cm) after 81 hours, and a maximum of 457 Ohms (24.05 Ohms/cm) after 706 hours ending with 272 Ohms (14.3 Ohms/cm) after 1060 hours.

Figure 103 illustrates the resistance distribution versus distance at the beginning and at the end of the test. The graph shows that the change in resistance in the cathode area was negligible (67 to 77 Ohm). The increase in the anode area was also small (217 Ohms to 370 Ohms).

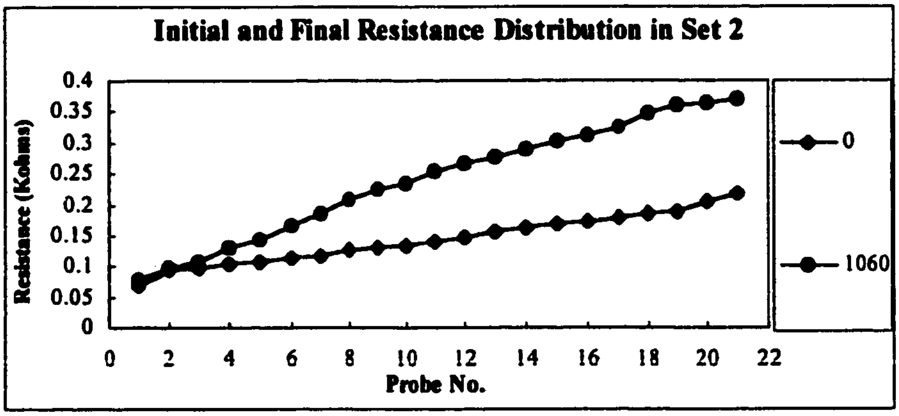


Figure 103 Initial and Final resistance Distribution in Set 2

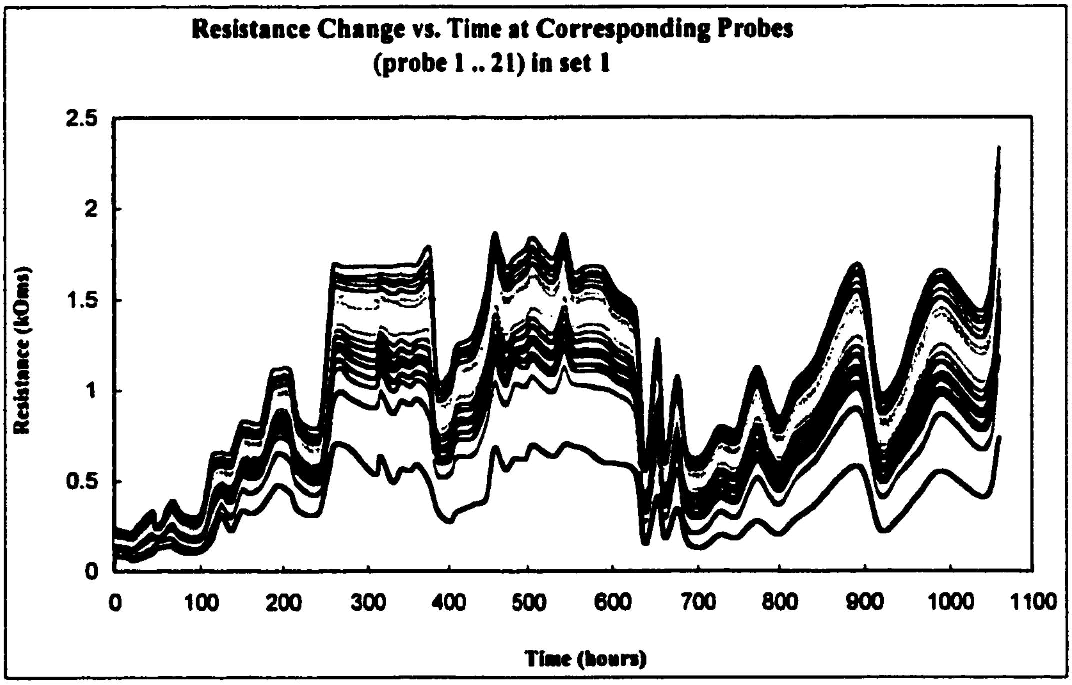


Figure 104 Resistance Distribution vs. Time Presented for each Probe in Set 1

The relationship between resistance values at each probe and the elapsed time are presented in Figures 104 and 105 for Set 1 and 2 respectively. The graphs indicate that the resistance in probes showed several high and lows which indicate the changing ionic strength in the cell. Comparing both graphs one can recognize two major differences among them, which are the distribution pattern versus time and the overall resistance developed at the end of the test.

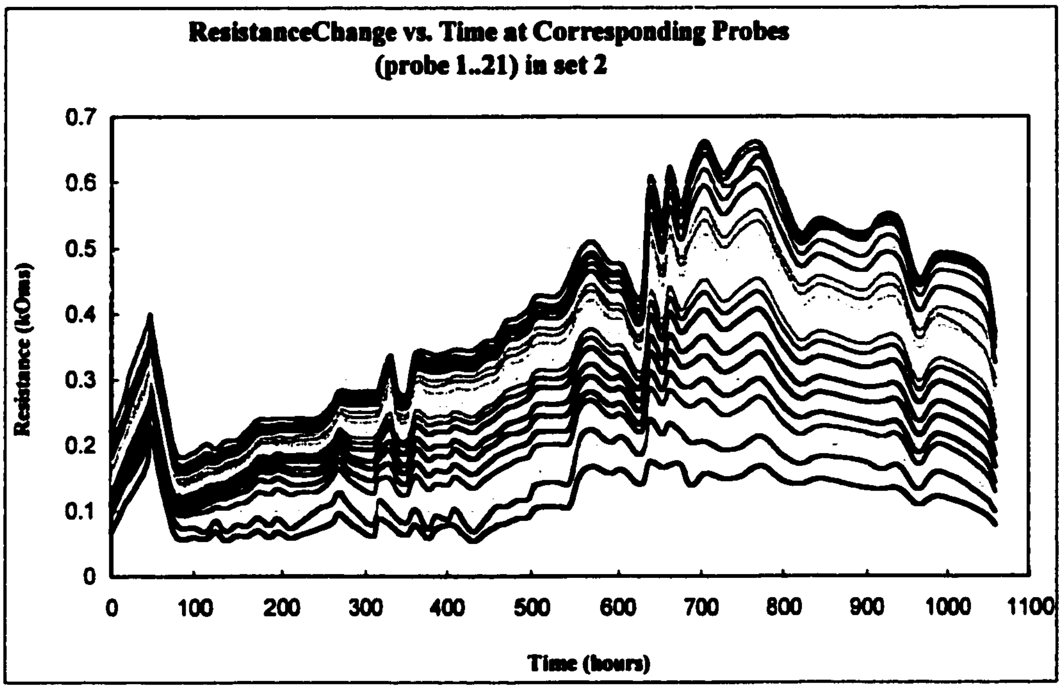


Figure 105 Resistance Distribution vs. Distance Presented for Each Probe in Set 2

8.4.3.2. Soil sampling and Analysis

After the test was terminated, an extensive destructive soil sampling was performed (Fig.106). Cell III was divided vertically into two levels designated of U.L. (Upper level), and L.L (Lower level). Each section was then divided into 91 samples in such a way that the width of the cell was divided into eight rows; the later was then subdivided into 17 samples. This method of soil sampling was necessary to ensure that the distribution pattern of the soil pH and phenanthrene content would be representative of a pilot scale test.

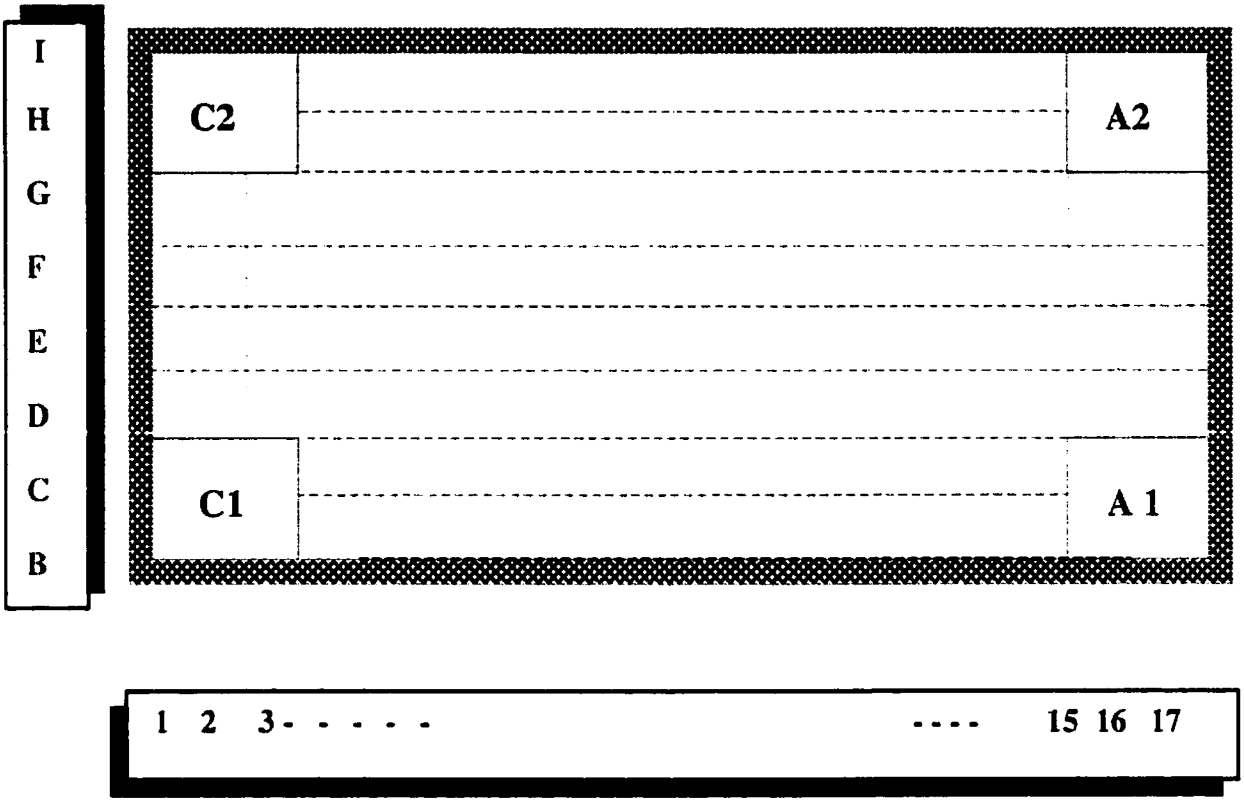


Figure 106 Soil Sampling Diagram

8.4.3.2.1. Soil pH

pH measurements of the soil samples were performed according to the protocol described in chapter 7.3.2.2. Figure 107 illustrates the pH distribution within the cell presented for corresponding rows of both sets. The results indicate lower pH values in set 2. The graphs shows that a maximum pH value of 11.03 was recorded in section B in the proximity of the cathode. The same area in section I showed a pH value of 8.44. pH values measured in the anode areas were also lower in section I (7.64) compared with 7.9 in section B. pH profiles measured for sections C and H in both sets also show that a better distribution developed in section H (set 2). Measured pH values in the proximity of the cathode for this section was 8.91 compared with 10.11 in section C (set 1) at the same location. In the anode areas, the recorded pH values for both sets showed lower values in section H (7.11) than in section C (8.12). Sections E and F, which were away from the electrodes, showed a similar pH distribution along the cell as can be seen in Figure 107. The results obtained indicated that electrode design II, which was adapted to both electrodes in set 2, succeeded in the prevention of generating a high pH zone near the cathode. This substantially reduced the production of hydroxide ions and prevented hydroxide precipitation and soil clogging.

Figure 108 presents the pH distribution for the lower section (L.L) at different sections from set 1 and set 2. Corresponding sections from both sets developed showed pH distributions for samples 6 up to the anode area. The most significant differences were recorded for samples between the cathode and sample 6. In the case of sections C and H, differences were also visible in sample No. 7. It should be noted that in all sections, the recorded values were lower in set 2 than in set 1.

The results from upper and lower levels showed that the design II electrodes showed excellent behavior. They also demonstrated the possibility of pH control in the field due to an accurate design and placement of electrodes. These results confirmed the conclusions obtained from phase I and phase II.

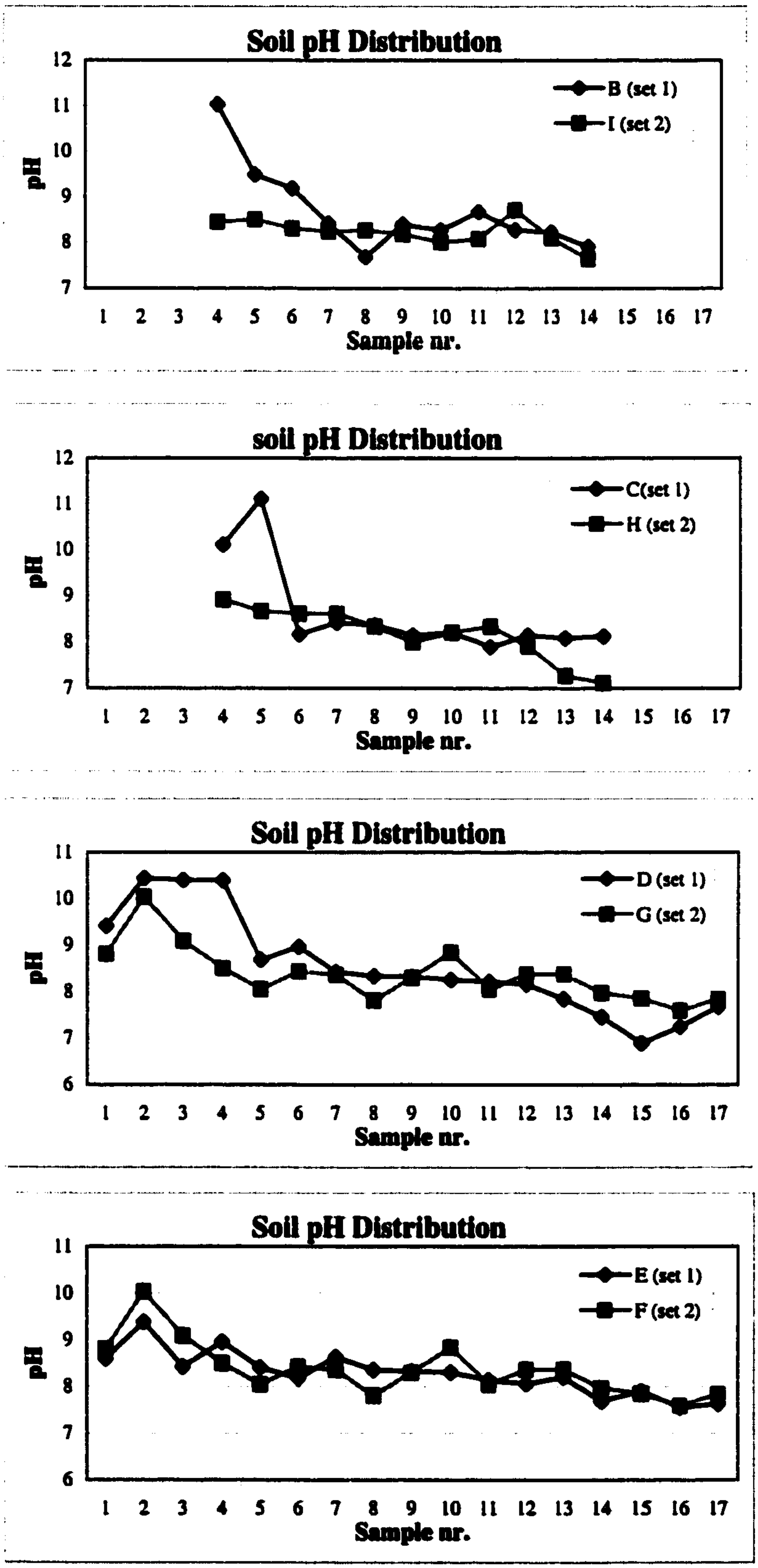


Figure 107 pH Distribution in Upper Level vs. Distance from the Cathode

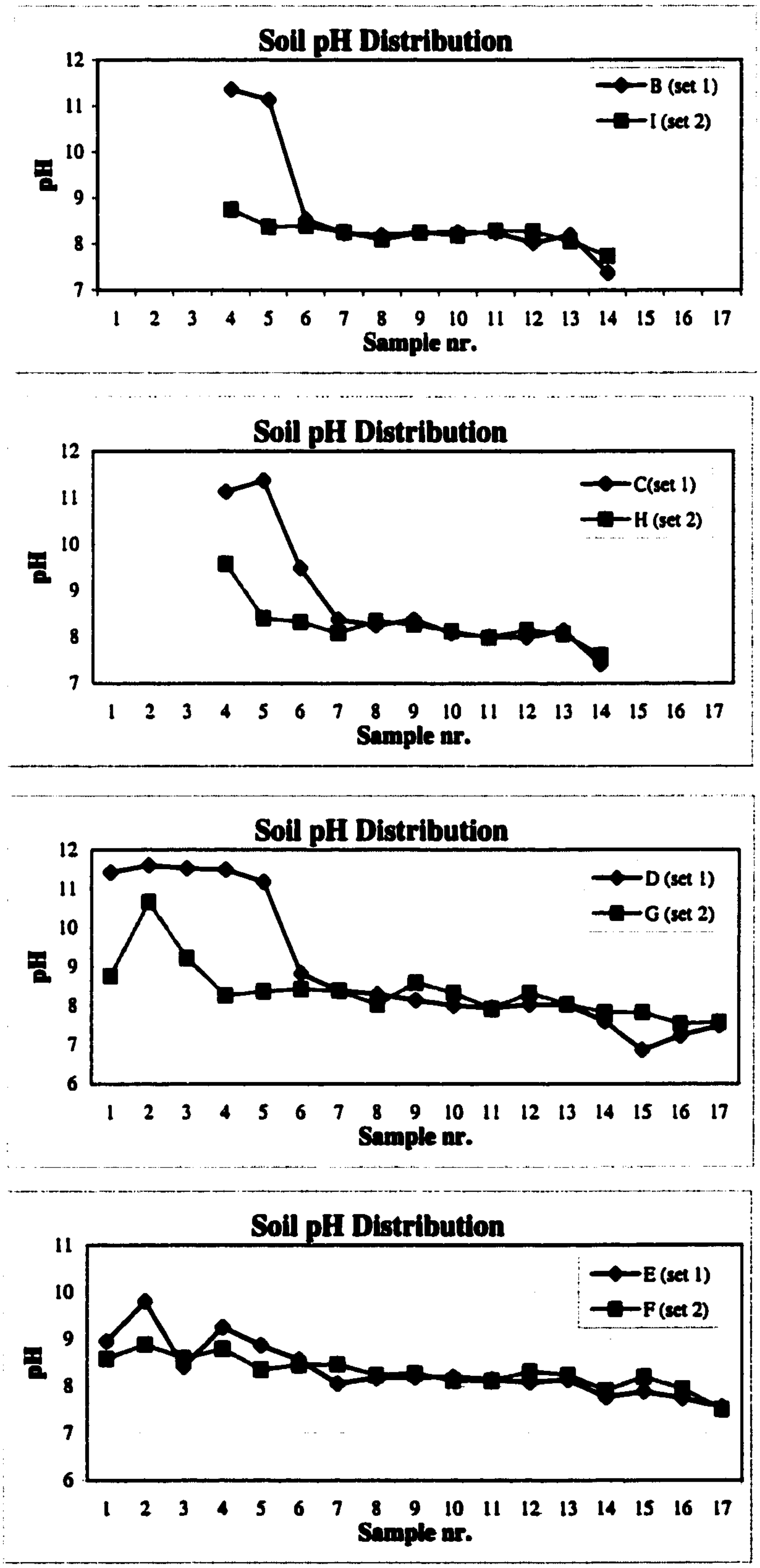


Figure 108 pH Distribution in Lower Level vs. Distance from the Anode

8.4.3.3. Volume of Liquids Supplied to Anode Area

8.4.3.3.1. Volume of Supplied Surfactant

Figure 109 presents the relationship between the volume of surfactant consumed versus time for set 1 and set 2 due to electrokinetic transport. Total volumes of surfactant were 675 ml, and 1358 ml for set 1 and set 2, respectively. It can be seen that the amount of surfactant consumed in set 2 was twice as high as that in set 1 (Fig.109 b). The average daily volume supplied was 15.35 ml for set 1 and 30 ml for set 2 (Fig.109.a). The larger amount of surfactant supplied to set 2 indicates a higher mobility coupled with less resistance within the soil matrix in set 2. These results suggest that set 2 presented better conditions for surfactant supply and consequently for the distribution of HOC.

8.4.3.3.2. Volume of Anode Conditioning Liquid

Daily volumes of conditioning liquid supplied to the anodes in both sets were recorded (Fig.110 a). Figure 110 b presents measurements of cumulative volume versus time for both sets. In addition the graphs show, that daily amounts supplied for both sets were similar and the total supplied liquid was almost the same volume as the volume of the supplied surfactant. The volume of liquid reached 1353 ml in set 1 and 1485 ml in set 2. This indicated that the amount of anode conditioning liquid required was not affected by the cathode design, as in the case of surfactant supply.

8.4.3.3.3. Phenanthrene Removal Efficiency

Soil samples were tested for the amount of residual phenanthrene content left after the test. Measurements were based on the methodology adapted after preliminary testing. Contaminated soil samples (not subjected to electrokinetics EK) were tested for phenanthrene content and the results were used as a reference for samples subjected to test III. Figure 111 presents the removal efficiency in upper layer for corresponding sections in set 1 and set 2. The results show a higher removal efficiency (from 80 – 95 %) in areas close to the cathode in all ranges, for both sets. The central area between electrodes (up to section 14) also demonstrated a removal between 80 and 93 %. In the area close to the anode, the removal was the lowest, however, over 50 % removal was reported in that area. The removal rate achieved using surfactant enhanced electrokinetic surpasses any other remediation method adapted for *in-situ* conditions on clayey soil. Both sets showed a slightly different removal efficiency of phenanthrene. Samples situated within B and I ranges (situated between electrodes) showed very small differences. The removal within areas situated farther from the electrodes (e.g. D, G), show a better performance for set 2.

Figure 112 presents the removal of phenanthrene in the lower layer for set 1 and set 2. A comparison between corresponding sections of set 1 and set 2 shows higher removal (85-99 %) in set 2. This efficiency is achieved in the distance between the cathode and sample No. 12. In the same area, set 1 had a removal efficiency between 40 % (range D) and 99 % (range C). A lower removal (48 to 70 %) in both sets was observed between sample No. 12 and the anode.

It is concluded that coupling the supply of surfactant 401 (tested in preliminary study) with electrokinetic enhanced the mobility of phenanthrene. The enhancement was observed in the entire cross section of the tested area (upper and lower layers). The transport of micelles formed from the amphoteric surfactant (*Alkyl Dimethylbetaine*) occurred during the test (1060 hours).

Time is a limiting factor in the described conditions; a longer period of testing could probably increase the removal rate through the anode area. The systematic analysis of 91 samples showed that the configuration of anodes and cathodes does not create dead zones, and removal differences in horizontal levels, vary slightly.

The comparison between upper and lower levels showed that electrokinetic phenomena decrease within depth. This decrease depends on the type of electrodes (design I is slower than design II) used.

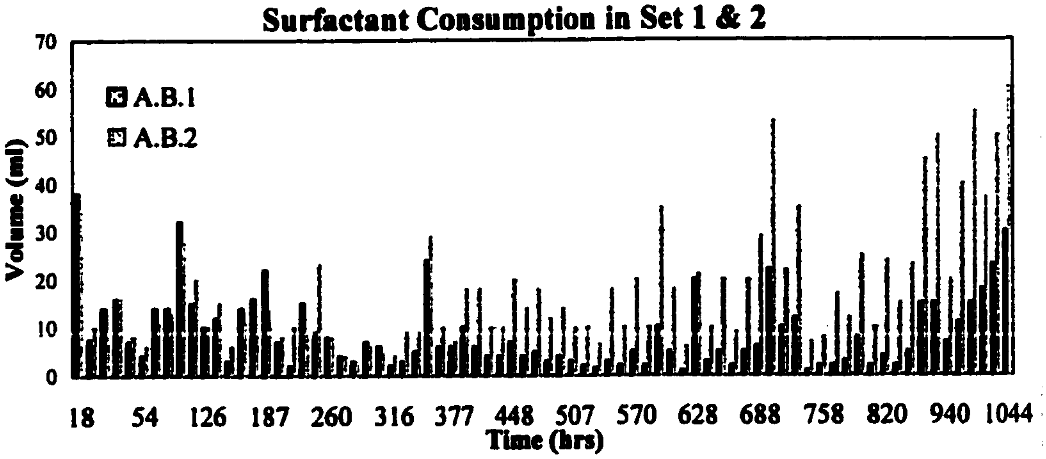


Figure 109(a) Daily Consumption of Surfactant vs. Time in Set 1 and 2

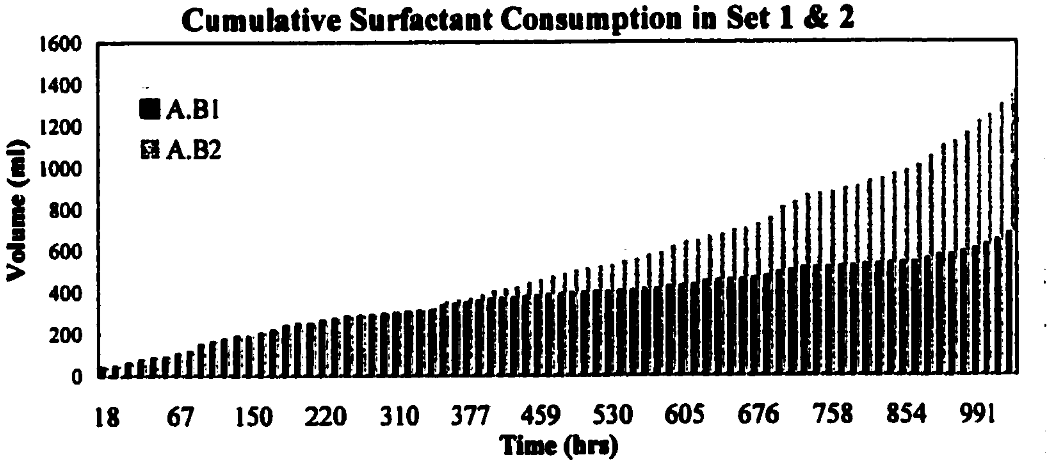


Figure 109 (b) Cumulative volume of Surfactant Supplied to Set 1 and 2

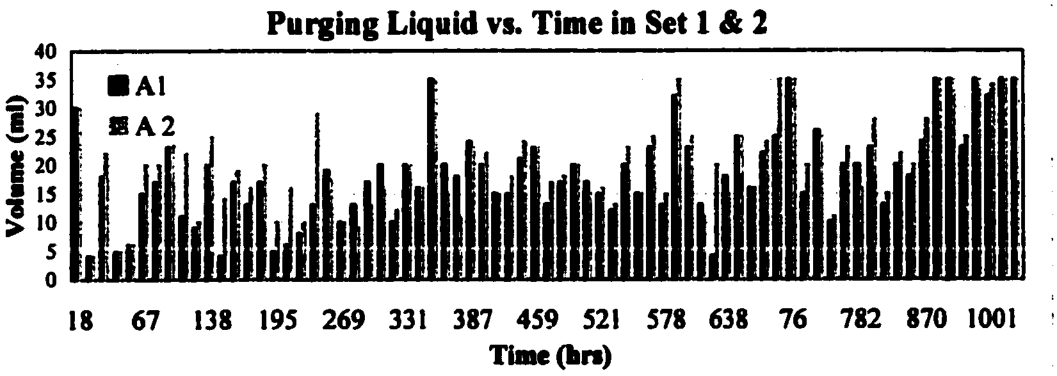


Figure 110(a) Daily Consumption of Anode Conditioning Liquid vs. Time in Set 1 and 2

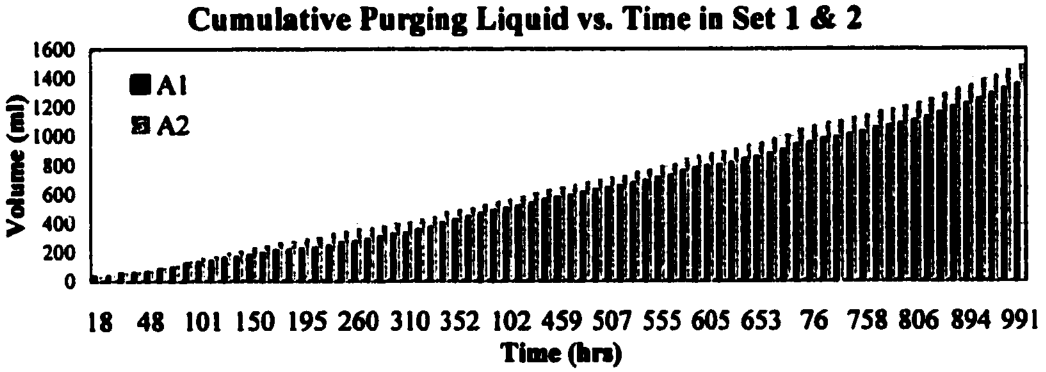


Figure 110(b) Cumulative Consumption of Anode Conditioning Liquid vs. Time in Set 1 and 2

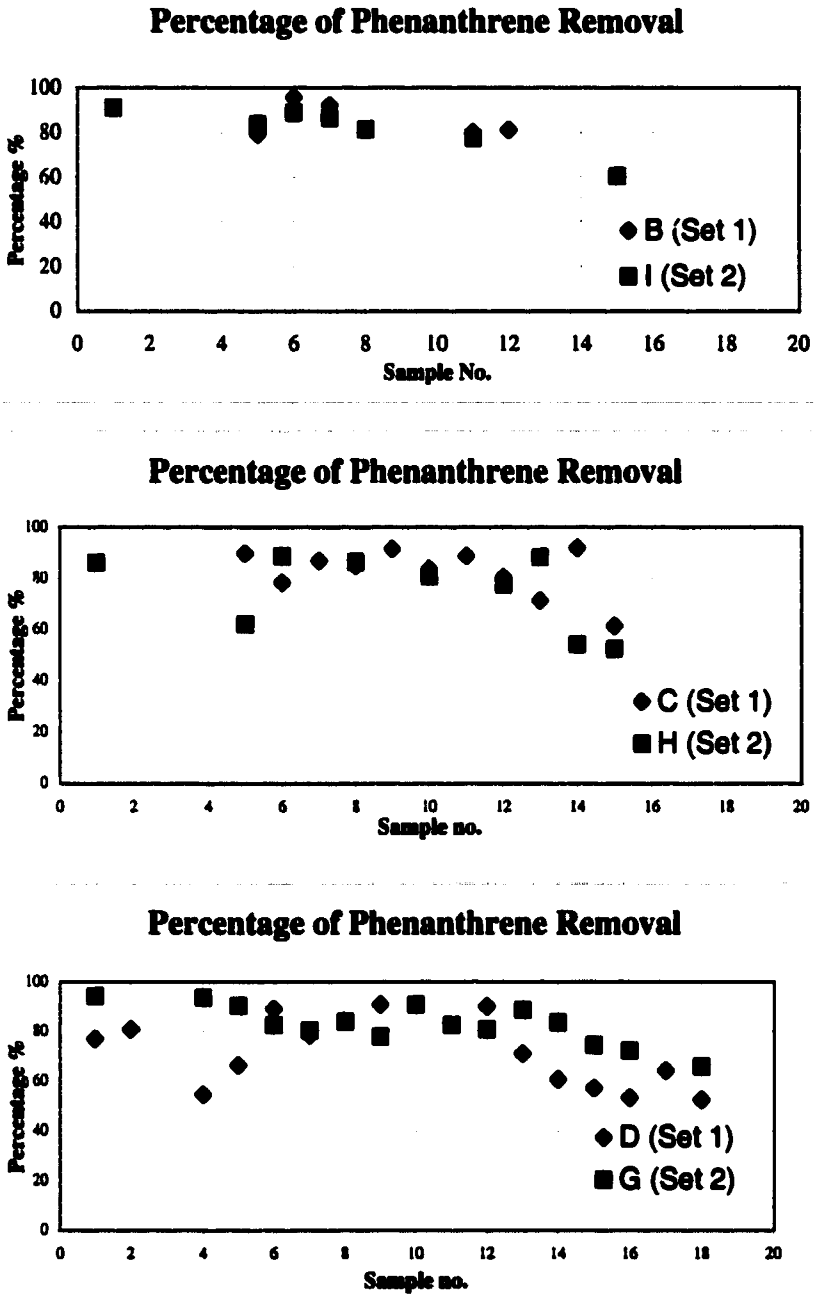
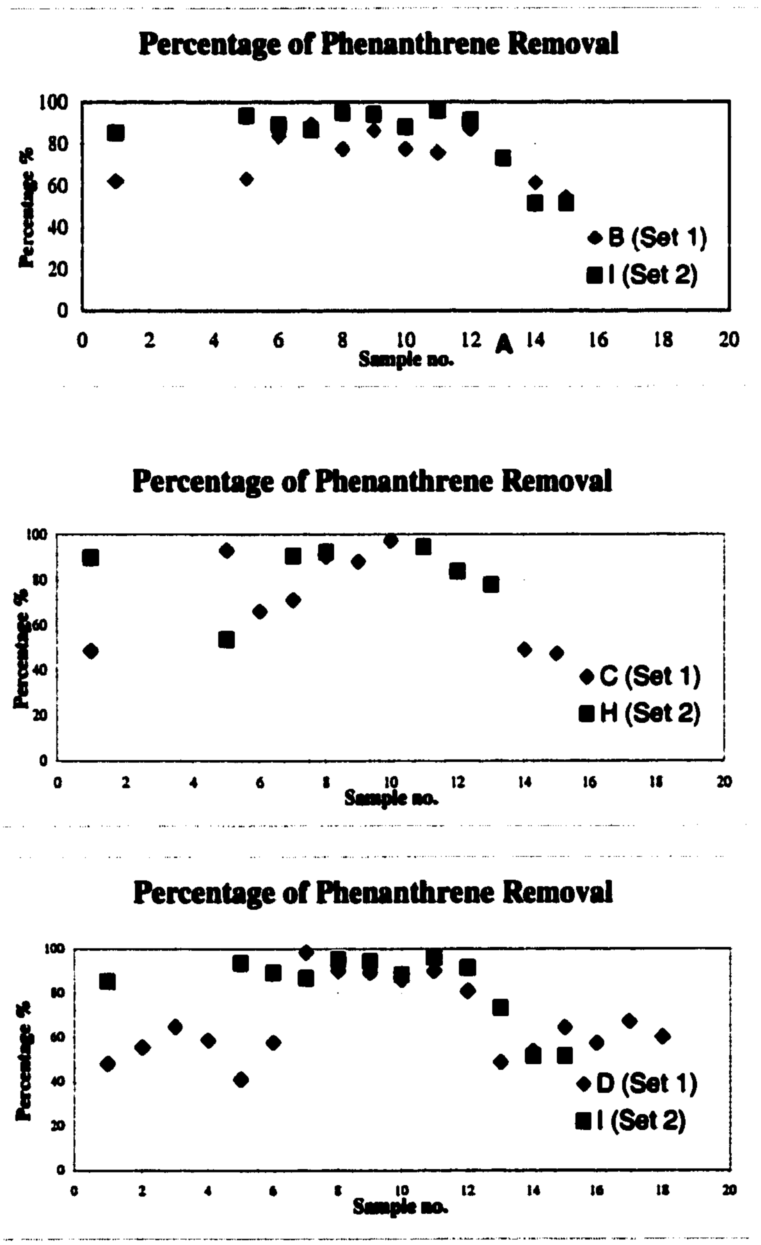


Figure111 Percentage of Phenanthrene Removal In Soil Samples
Upper Level (UL)



Percentage of Phenanthrene Removal

Percentage of Phenanthrene Removal

Percentage of Phenanthrene Removal

Figure 112 Percentage of Phenanthrene Removal In Soil Samples
Lower Level (UL)

9. CONCLUSION AND RECOMMENDATION

1. The performed experimental tests (in the three phases) achieved the following:

1.1. Design a new electrokinetic system capable of regulating the pH in the soil between the electrodes; subsequently, it

- prevented anode extensive oxidation
- eliminated the causes for surfactants precipitation at the anode
- avoided the eventual precipitation of metals (contained in the soil and/or released due to electrode electrolysis)
- confirmed the use of a non expensive material for electrodes construction

1.2. Design a system capable of introducing and transporting of synthetic surfactants through the soil by means of electrokinetics

1.3. Design a system capable of solubilization and desorption of hydrophobic organic compounds from the solid phase to the liquid phase in soil

2. Results from two research phases confirmed the possibility of diesel fuel removal using enhanced electrokinetic method
3. Results showed an excellent response of natural soil components to the application of the electrokinetic method
4. Pilot tests from the phase three showed an excellent confirmation of the conclusions raised from lab scale tests
5. Design of new multi functional electrodes (used in pilot scale) which permitted the removal of phenanthrene from clayey soil by 80%

6. Phase three test showed that the application of the same multi-component construction of anode and cathode is the best configuration in system performance
7. The design of multi-functional electrodes prevented the clogging of perforated electrodes with fine particles
8. Preliminary tests permitted:

8.1. To define in an accurate way the introduction of an amophoteric surfactant, which was applied for the first time in electrokinetic method

8.2. To determine the most appropriate concentration of surfactant applied by electrokinetic method to illite soil

8.3. To determine the method of phenanthrene measurements in soil samples using UV/VIS spectrometry

9. Results showed the feasibility of the application of a sustainable method such as electrokinetics enhanced with amphoteric surfactant to non polar organic contaminants from clayey soil

RECOMMENDATIONS FOR FUTURE WORK:

It is recommended to perform a mathematical prediction model for system application in various soil conditions, evaluation of the scale-up-process on other PAHs for their removal by means of electrokinetics. The comparative studies for various phenanthrene concentrations in soil could be performed. The variation of phenanthrene removal efficiency due to various types of clayey soils may be done and finally the use of natural energy as a power source for cost minimization can be evaluated too.

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APPENDIX 1

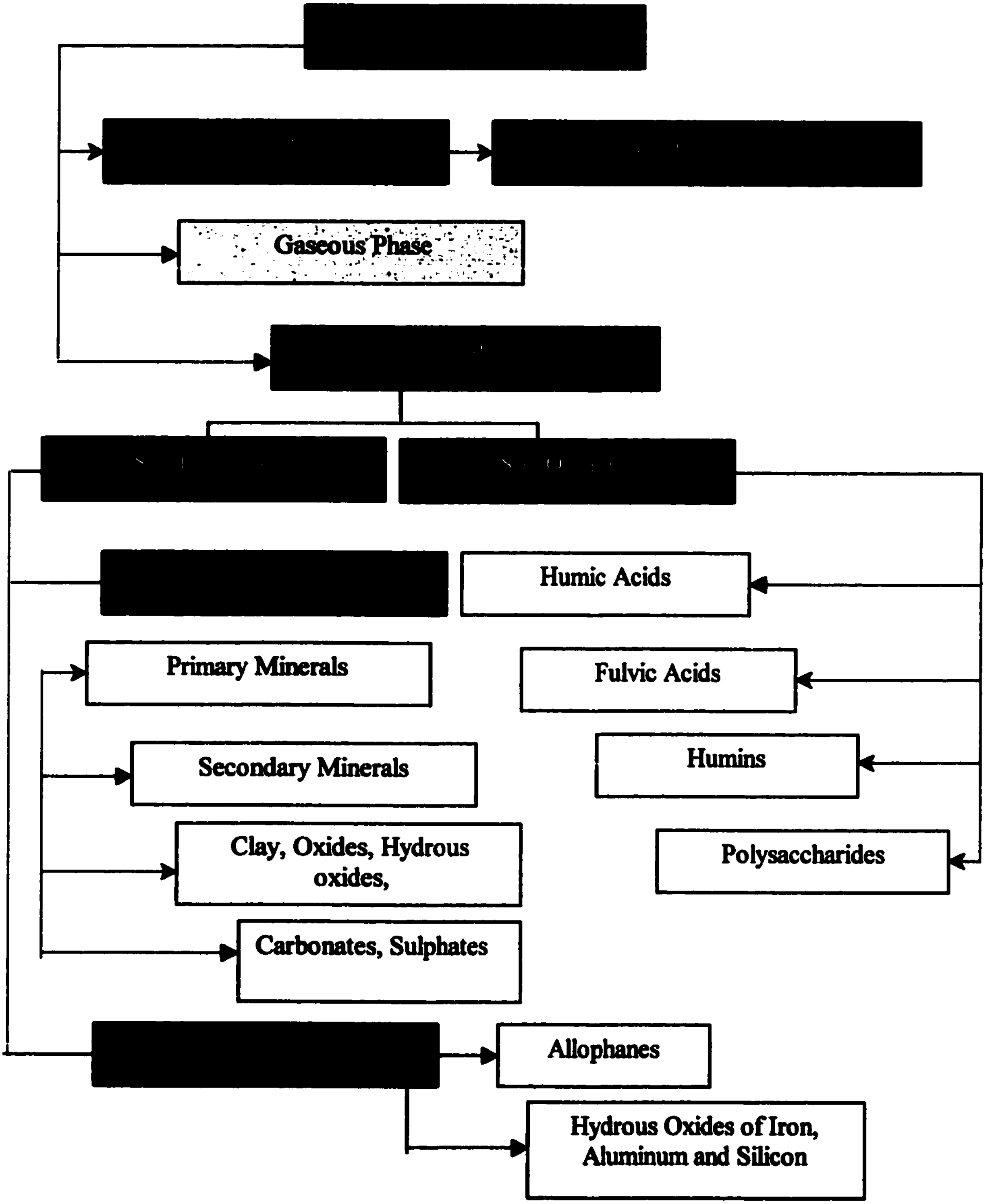


Figure 113 Principle Soil Components

PRINCIPLE SOIL COMPONENTS

Soil subsurface can be divided into tow major zones; 1- saturated 2- unsaturated. These zones can share the same constituents but they differ with the percentages of water. The major constituents are:

a- Mineral matter originated from rock;

b- Organic matter of both living and dead organisms that has usually accumulated over a period of time through a biological activities;

c- Soil moisture containing mineral and organic matter in a colloidal state or in solution;

d- Soil air with a contaminants in gaseous state often present in.

Figure 113 presents a scheme of major soil components with a focus on the solid phase. The solid phase represents the core component among soil constituents; it provides the framework of the soil. Within this framework liquid phase and gaseous phase share the enclosed pore system. There is a continuous flux shared between the last two phases, which is the result of water air interchange (evaporation, dissolution), whereas the solid-phase is in relatively stable state (Hausenbuiller 1978).

1.1. Mineral Matter

Inorganic matter typically constitutes the major portion of the soil's composition (Marshall 1965). The inorganic portion of soil consists largely of crystalline minerals and amorphous compounds. Crystalline minerals are typically subdivided into primary, secondary minerals and others, like oxides and hydrous oxides of aluminum, silica, and iron, carbonates and sulphates. Amorphous compounds are called allophanes. They have the same chemical composition of crystalline minerals however they differ from them by having disordered structure. The major elements, which make the bulk of the earth's soil inorganics are presented in Table 34.

Table 34 Content of the most Abundant Ions in the Earth's Crust

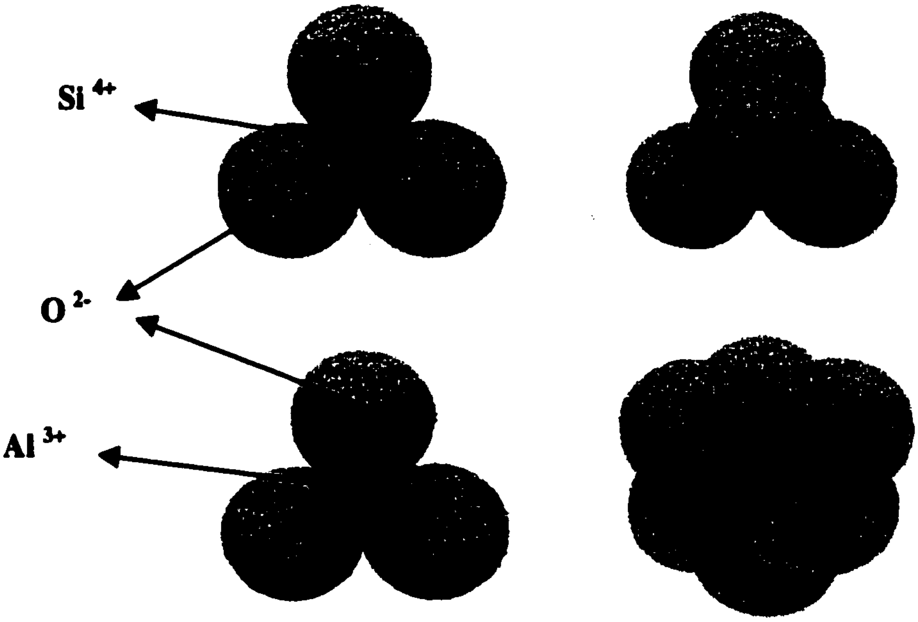
Ion	*Percent by weight*	*Percent by volume*
O^{2-}	46.6	93.9
Si^{4+}	27.7	0.8
Al^{3+}	8.1	0.5
Fe^{2+}	5.0	0.4
Mg^{2+}	2.1	0.3
Ca^{2+}	3.6	1.0
Na^{+}	2.8	1.3
K^{+}	2.6	1.8

Source: Hausenbuiller R. I., Soil Science principles and practices 1978.

Silicate minerals (i.e. contain most Si and O) are the most common minerals in the soil. A number of silicates also have substantial quantities of Al (i. e. aluminosilicates). Feromagnesian minerals, which contain both Mg and Fe, are important constituents too.

There are two fundamental structural units for silicate minerals. One contains four O^{2-} ions packed together in four-sided tetrahedron, in the other, six oxygen's are arranged in eight-sided octahedron. Each of these structures is held firmly by the presence of cations, which, fit into the internal space formed between the oxygen ions. Si^{4+} and because of its small size will fits into the terahedral structure. Some times aluminum ions can occur in tetrahedral unit but by being larger, they provide less stability to the unit. Al^{3+} will fill the space in the octahedral unit, however sometimes this space is filled by larger divalent ions Mg^{2+}, Fe^{2+}, and Ca^{2+}, Al^{3+} provide more stable unit than divalent ions.

Tetrahedron unit forms the bulk of the silicate minerals. Minerals consist of combination of both tetrahedra and octahedra units, which form different silica minerals. Figure 114 shows both units in a 3-D concept.



Source: Hausenbuiller R. I., Soil Science principles and practices 1978.

Figure 114 Arrangements of Ions in Tetrahedra units (A), and Octahedra Units (B)

1.1.1. Crystalline minerals

I- <u>Primary Minerals</u> - are defined as those derived in unaltered form a parent rock through physical weathering processes (Foth 1984). Typical examples are quartz, feldspar, micas, amphiboles, and pyroxenes, their approximate content in the earth's crust is given in Table 35.

Table 35 Approximate Content of Major Primary Minerals in the Earth's Crust

Mineral	*Content %*
Feldspars	59
Amphibole and pyroxene	17
Quartz	12
Biotite	4
Others	8

source: R. I. Hausenbuiller, Soil science 1978

The main characteristics of primary minerals are their low cation exchange capacity, low specific surface area and high particle size, which make them passive components regarding the fate and the transport of pollutants in the subsoil.

II- Secondary Minerals - are the results of the weathering processes on the primary minerals (Yong 1992). They comprise the major portion of the clay-sized fraction in soil.

There are three types of crystalline alumino-silicates in the clay fraction, each with layers stacked one above the other, with each layer consist of the following:

1 tetrahedral: 1 octahedral sheet, as in kaolinite and halloysite;

2 tetrahedral: 1 octahedral sheet, as in illite, vermiculite, and smectites (montmorillonite);

2 tetrahedral: 1 octahedral sheet plus an octahedral interlayer of magnesium hydroxide or aluminum hydroxide as in chlorite.

Table 36 summarizes the basic secondary minerals and their physical and chemical properties.

Natural soil contains a combination of different clay materials. The character and properties of certain soil is related to the ratio of clay minerals in it.

Kaolinites

Kaolinites are clays with 1:1 structure. The structural formula is $Al_2(Si_2O_5)(OH_4)$. It is formed from the direct weathering of orthoclase feldspar:

$$2KAl\,Si_3O_8 + 11H_2O + 2KOH + 4Si(OH)_4 + Al_2Si_2O_5(OH)_4$$

Figure 116 illustrates 1:1 kaolinite structure with 3 layers held by hydrogen bonding between oxygen and hydroxyl.

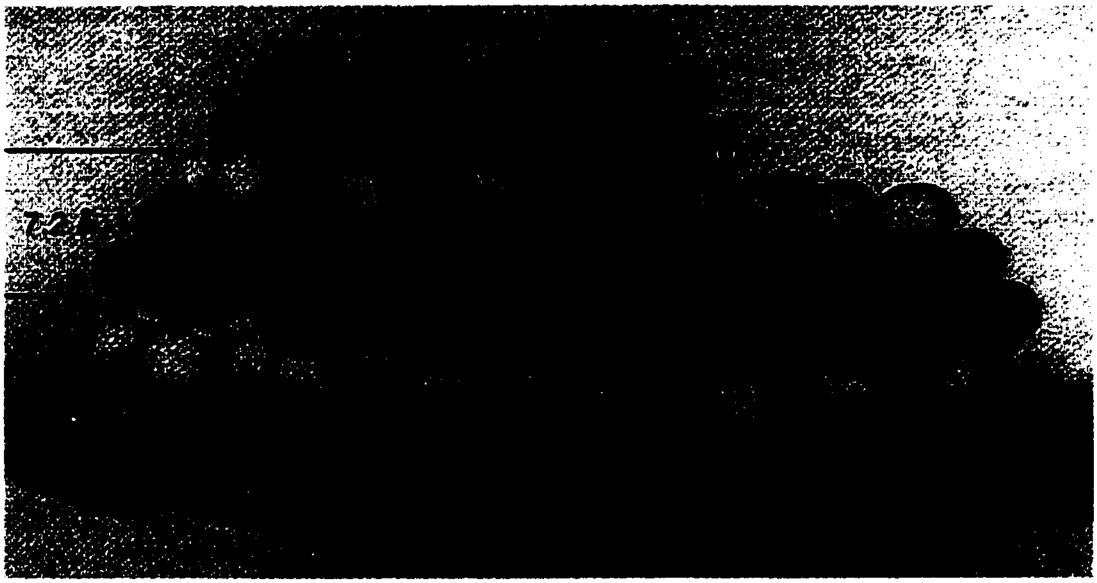


Figure 115 Kaolinite as 1:1 Clay Mineral

Source: Foth 1984, Fundamentals of soil science

The crystal is composed of aluminum octahedra sheets stacked above silica tetrahedron sheets. Kaolinite has stable and strong structure due to the strong hydrogen bonds between the alternating sheets.

This tight structure (with exception to halloysite, which can occur in hydrated form with a layer of water between each layer of kaolinite crystal) result in a little isomorphous substitution in kaolinite structure (source of charge) and very little if not zero permanent charge (Tan 1982). However, its cation exchange capacity (CEC), which is in the range of 3 – 15 cmol/kg, is attributable to the presence of negative electrical charge, which is a result of broken bonds between the oxygen and silicon and between oxygen and aluminum (act as a second source of charge). The negative charge is a pH dependent ie., increase as the pH increase. The broken bonds attract hydrogen and hydroxyl from pore water. These ions can be readily exchanged with other cations. The specific surface area (SSA) of the kaolinite is 10 – 20 m^2/g.

<u>Chlorites</u>

The composition of chlorite is variable but its general formula is reported as: $(Mg, Fe, Al)_6 (Si, Al)_4 O_{10} (OH)_8$. Chlorites are hydrated magnesium and aluminum silicates clays with a mica 2:1 structure and a gibbsite or brucite sheet $Mg(OH)_2$ sandwiched between the two silica tetrahedra sheets in the interlayer. Resulting in final structure of 2:1:1 clays. The brucite or gibbsite layer of chlorite can be dissolved out in warm acid. The cation exchange capacity of the chlorite is a result of the substitution of aluminum for silicon resulting in a negative charge, and magnesium for iron and /or aluminum, resulting in a positive charge (Tan 1982). Those charges neutralize each other with a balance of negative charge, therefore chlorites has very small charge and its CEC is 10 – 40 cmol/kg and a SSA of 70 – 150 m^2/g (Yong et al., 1992).

Illites This particular type of clays has been discussed in chapter 2.

Montmorillonite

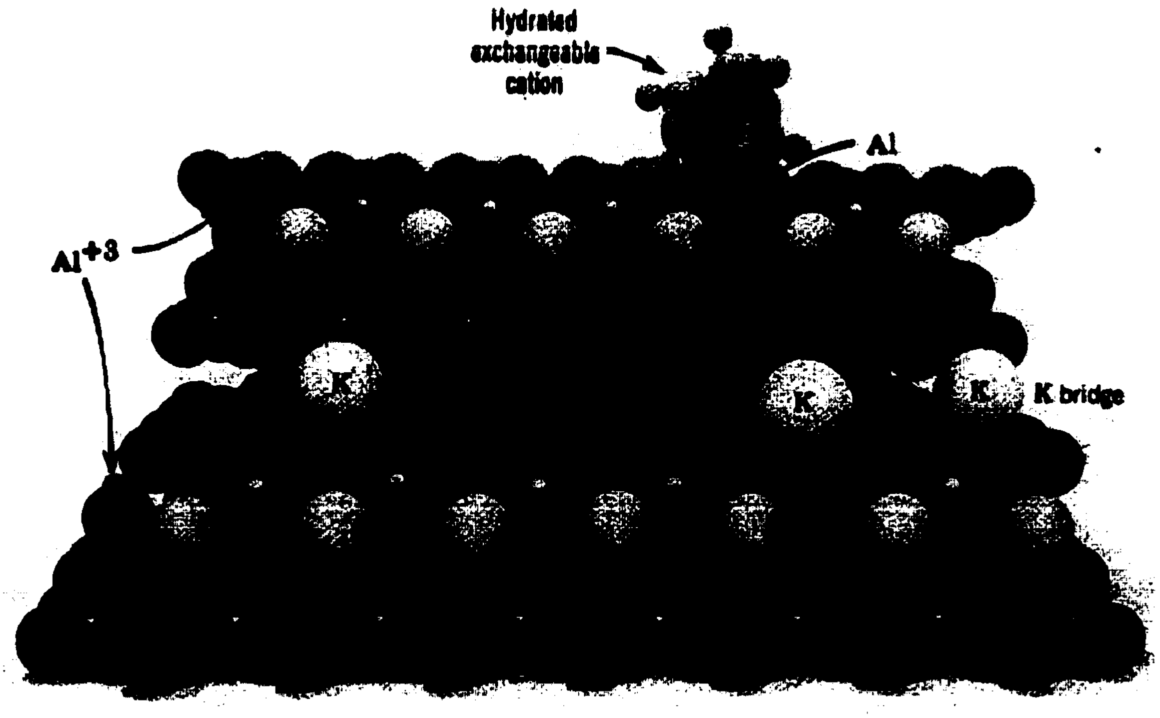
General formula of montmorillonite is $Si_8(AlMg)_4O_{20}(OH)_4$. Montmorillonite sometimes is called smectites, and the name montmorillonite is reserved for the hydrated aluminosilicate species. Its structure consists of one aluminum octahedral sheet sandwiched between two silica tetrahedra sheets. Figure 116 illustrates monmorillonite mineral.

Table 36 Properties of Typical Secondary Minerals

Mineral	***Type***	***CEC cmol/kg***	***SSA m2/g***	***Interlayer condition***	***Layer thickness nm***	***Isomorphous Substitution***
Kaolinites	1:1 Non-expanding	3-15	10-20	Strong H bonding	0.7	--
Chlorites	2:1:1 Partially or Non-expanding	10-40	70-150	Brucite or gibbsite sheets	1.4	Al for Si Al for Mg
Vermicullite	2:1 Expanding	100-150		Moderate bonding Complete loss of K	>0.94	
Illite	2:1 Non-expanding	25	80	Partial K loss Strong bonding	>94	Al for Si
Montmorillonites	2:1 Expanding	80-120	600-800	very high	>0.96	Al for Si Mg for Al Fe for Al

Source: Foth, 1984, Fundamentals of soil science

The component layers are not bonded strongly, as a result, in contact with water the mineral exhibits interlayer swelling, causing the volume of the clay to double. These minerals have the same structure as mica clays, however, the size of particles are much smaller.



Source: (Foth 1984)

Figure 116 2:1 clay mineral model

The SSA is large (600 – 800 m^2/g) and CEC is high (80 – 120 cmol/kg). Because of large SSA which is exposed on dispersion in water, these minerals exhibit strong plasticity and stikiness when wet (Tan 1982). The CEC is the result of isomorphous substitution which occurs mainly in the alumina sheet, with magnesium or iron substituting for aluminum. As a result of its high CEC, specific surface area and swelling-shrinking potential, montmorillonite is highly effective for the retardation of the transported inorganic chemicals i.e., heavy metals and organic compounds. The adsorption of organic compounds leads to formation of organo-mineral complexes. Organic ions can form mono or double layers in the interlayer position when it replaces inorganic cations (Tan 1982).

Due to the high differences between clay minerals such as in CEC, SSA values and structure they bear different relevance to adsorption, for example in expanding clays such as montmorillonite, the adsorption of organic and inorganic ions takes place within the interlayers. Such clays would be a perfect liner for contaminated sites. Meanwhile its decontamination will be a real challenge. Kaolinite clays, and because of its tight structure can adsorb organic molecules only on the surface of their structure where hydroxyl groups are located. Therefore, decontamination of such minerals will be easier than the former group. Properties of illite minerals are situated between kaolinite and montmorillionite.

Oxides and Hydrous Oxides

Although, iron and aluminium oxides and hydrous oxides are rarely above 5% by weight in soils, they are an important source of pH dependent charge in soils. Their high surface area combined with their frequent occurrence as grain coatings result in high activity.

Typical examples of oxides and hydrous oxides that are commonly found in the subsurface are as follows:

1. Haematite, Fe_2O_3; 2. Goethite, $FeO(OH)$; 3. Gibbsite, $Al(OH)_3$ (Foth 1984).

Typically, the surfaces of those oxides and hydrous oxides consist of broken bonds. In hydrous oxides, the hydroxyl groups of one layer are almost directly opposite to the hydroxyl groups of the adjacent layer. The layers are held together by hydrogen bonds between opposite OH groups. It should be noted that the surface charge of these soil materials is pH dependent, therefore, in acidic condition they may have a weak electronegative charge, and in alkaline soil condition they may develop an electropositive charge and typically have a point of zero charge in the range of 4.0-5.0. Isomorphous substitution of aluminum and/or Mn for some of the iron in iron oxides frequently occurs (Tan 1982).

The most common hydrous oxides in soil are aluminium and ferric hydrous oxide, which have an amphoteric character. The adsorption capacity (CEC) of iron minerals ranges from 30-300 cmol/kg. This adsorption can take a form of an electrostatic adsorption, which occurs for example between phosphate ions and heavy metal cations, or type of covalent bonding (Tan 1982). The iron oxide minerals can change soil properties influencing (sorption/desorption effect) and provoke cementation.

Carbonates and Sulphates

Carbonates and sulphates are characterized by high water solubility's (relative to the secondary minerals and amorphous oxides) (Yong et al., 1992), low CECs and low specific surface areas. They include compounds containing carbonate, sulphate and bicarbonate in combination with one or more metallic ions (typically Ca, Mg, and Na). Calcite ($CaCO_3$), magnesite ($MgCO_3$), dolomite ($CaMg(CO_3)$), and nahcolite ($NaHCO_3$) are common examples of carbonate minerals (Yong et al., 1992). Gypsum ($CaSO_4 \cdot 2H_2O$) is the most abundant of the sulphate minerals found in soil.

The presence of carbonates can influence remediation processes because of several factors like, their high water solubility's, their low CEC, their low SSA, and their role in pH alteration (eg. Calcite which is the only form of calcium carbonate widespread in soils, has a major influence on the pH of soils for its presence or absence) (Greenland and Hayes 1978). Hydrolysis of carbonates produces an excess of OH^- which is sufficient to account for a pH as high as 8.3. When Na_2CO_3 is present, the production of hydroxyl is grater and pH may go as high as 10 (Fouth 1984). Beside that, carbonates of transitional group of metals (Ca, K, Na, Mg, etc.,) that can occur in soils tend to precipitate in soil pores reducing its permeability (Greenland and Hayes 1981).

1.1.2. Amorphous Inorganics

Noncrystalline materials can occur as major soil constituents in certain cases. This material is simply disordered but has the same chemical makeup as crystalline materials. An important difference is the relative surface areas, which can exceed many times the surface area of crystalline materials (900-1100 m^2/g) (Sparks 1986). Higher surface area will render these compounds an important source of pH dependent charge, more reactive and may result in changes in variable surface charge by affecting mineral solubility. The most important of those compounds in soils are allophanes (Sparks 1986). Allophane is a name given to those compounds consisting of silica, alumina and water, with a minor proportion of iron, magnesium, calcium, etc. The composition of allophane is AL_2O_3 : SiO_2 (Marshall 199) with a ratio of 1.05 : 1.15 (Sparks 1986). It is uncertain whether allophane is regarded as highly dispersed and intimate mixture of silica gel and hydrous aluminum oxide or whether it represent a hydrous aluminum silicate. (Grim 199) suggests that the allophanes are random arrangements of silicon and aluminum ions. Soils with large quantities of allophane characterize low bulk density values, high plasticity, although they are non sticky when wet (Tan 1982). The CEC is 150 cmol/kg and the amount increases with increase in pH. The adsorption of anions can be divided into nonspecific "electrostatic adsorption" which increase with decreasing pH, and specific adsorption "covalent bonding" which fix the anions with a strong bond (Tan 1982).

1.2. Organic matter

Organic matter is an important component of soil due to the fact that it is a source of pH dependent charge. In some cases like in sandy soil, organic matter is the predominant source of charge. Soil organic matter refers to all organic carbon-containing substances in soils. They could comprise as little as 0.1% of the soil bulk mass as in desert soils to close to 100% as in peat. Soil may contain between 1: 5% organic matter in the top layer (Schnitzer 1995).

The organic components of soils comprise both living and non-living components. The term organic matter in this study will refer to the non-living components, which originates from the decay of animals and plants. Classification of organic matter in soil can be done either by state of degradation or into humic and nonhumic material, which is based on extraction procedure.

Humic substances can be divided into fractions that differ in solubility in acids and alkalis. Following this category: I - Humic acids are soluble in base but precipitate in acid; II - Fulvic acids are soluble in both base and acid; III – Humins are insoluble in base and alkali (Figure 117).

Humic substances (HS) consist of physically and chemically heterogeneous mixtures of relatively high-molecular-weight, yellow-to black-colored organic compounds of mixed aliphatic and aromatic nature (Stevenson 1982). Approximately 60 to 70% of total soil-organic carbon occurs in HS, and the estimated levels of soil organic carbon on the earth surface occurring as HS are $30 \bullet 10^{14}$ kg (Stevenson 1982).

The nonhumified substances are carbohydrates, amino acids, proteins, lipids, nucleic acids, lignin. These compounds consist of recent non-decomposed organic compounds, which are in process of being decomposed to humic substances unless they are adsorbed by clay or when they occur in anaerobic conditions.

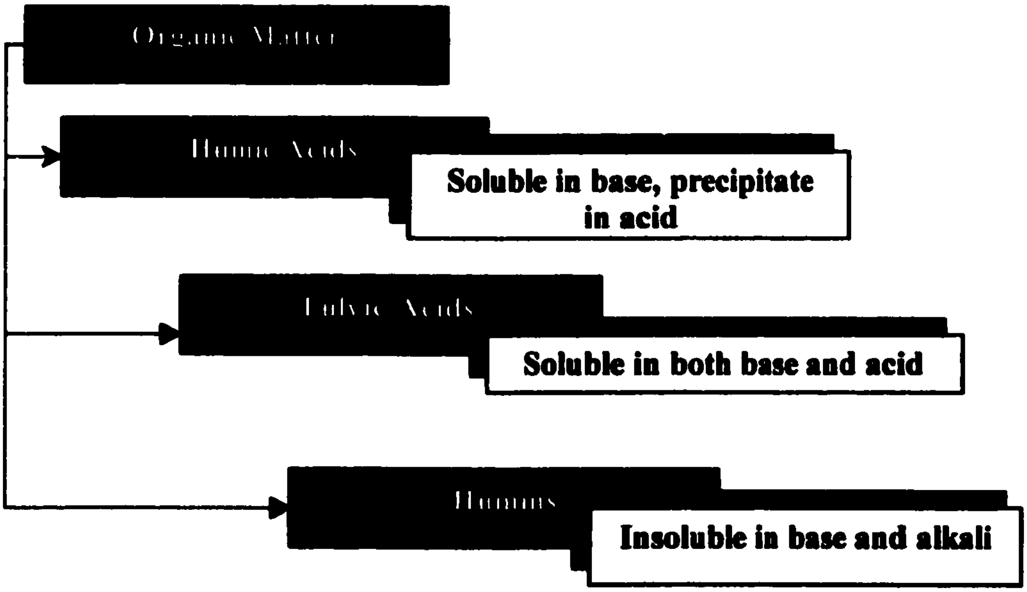


Figure 117 Classification of Organic Matter regarding its Acid Solubility

Fulvic acids are distinguished from humic acids based on their solubility in both acidic and basic solutions. They generally have molecular weights in the range of 1000-2000. They contain appreciably more sulphur and oxygen than humic acids, but less carbon, hydrogen, and nitrogen. Table 37 shows average chemical composition of soil humic substances. The major functional groups significant for these compounds are carboxylic, phenolic OH, alcoholic OH, carbonyl (Schnitzer, 1991). The structure and composition of humic acids are more complex than those of fulvic acids, which generally feature more oxygen-containing functional groups, and lower molecular weight (Table 38) (Langford et al., 1983).

Humins are generally composed predominantly of carbon with small amounts of nitrogen and polysaccharides.

The average composition of organic matter in Canadian soils according to the Research Center of Agriculture Canada (Schnitzer, 1991) is: carbohydrates - 10%; nitrogen compounds (including proteins, peptides, amino acids, ammonia, purines, pyrimidines, and unidentified nitrogen substances) - 10%; alkanes, fatty acids, fats, waxes, resins - 10%; and humic substances (humic acid, fulvic acid, and humin) - 70% .

Table 37 Average Chemical Composition of Soil Humic Substances

Component	*Humic acid (g/Kg)*	*Fulvic acid (g/Kg)*
C	564	509
O	329	448
H	55	33
N	41	7
S	3	11

Source: Schnitzer, M. and Khan, S.U. 1978, Soil organic matter, Elsevier, Amesterdam.

Polysaccarides are part of soil organic matter. They contribute to 10 - 15% of humus carbon and they can reach 50% of organic carbon when they are in liquid phase (Greenland. and Hayes 1981). However, their occurrence and specific function remains subject of speculation and debate (Chenu 1995). Reported literature defines them as naturally occurring soil bio-polymers which play an important role in promoting and maintaining soil structure (Martin and Haider 1971; Lynch and Bragg 1985).

Table 38 Comparison of Functional Groups in Humic and Fulvic Acids

	Humic acids *cmol/Kg*	*Fulvic acids* *Cmol/Kg*
Total acidity	660	1240
COOH	450	910
Phenolic OH	210	330
Alcoholic OH	280	360
Quinonoid C=O	250	60
Ketonic C=O	190	250
OCH_3	30	10

Source: Schnitzer, M. and Khan, S.U. 1978, Soil organic matter, Elsevier, Amesterdam.

They consist of sugar units, some are residual from plants, but the identity of sugar components indicates that most are synthesized by the soil microorganisms (i.e., bacteria, fungi and algae). The sugar units contain sugar acids known as "uronic acids" which act as glue in cementing soil particles together as aggregates. Among the simple saccharides: glucose, saccharose, and lactose. Their decomposition is associated with the formation of aliphatic organic acid.

Polysaccharides form an interface between the microorganisms cell and the surrounding soil constituents in form of capsule or as a slim (Chenu 1995). This form of existence can enhance the resistance of bacteria to desiccation (Pena-Gabiales and Alexander 1979). The use of polysaccharides as an inoculant carriers for microbes was reported by Foster (1988). Another role of polysaccharides is their ability to enhance water retention capability of clay, sand materials, and microbes in small changes in water potential (Roberson and Firestone 1992), (Chenu 1998, 1993). The buffering role of polysaccharides against water fluctuation may operate during rehydration of soils also (Kieftet al., 1987). Their role in increasing the tolerance of bacteria to toxic concentrations of metals was reported in (Green et al., 1992). Another important role polysaccharides is their ability to enhance the microbes cell adhesion to soil particles (Sutherland 1984).

The above stated review, reveal the complexity of the medium in which the organic and inorganic contaminants are preset. The different soil constituents have a direct effect on the fate of these contaminants. Therefore, before any remediation action, an extensive study has to be performed on the soil for better understanding of ongoing processes and its behavior during the remediation process.

1.3. Liquid Phase of Soil

In vadose zone, the part of subsurface water, which occupies partially voids in the soil above the ground water table, contains solutes and dissolved gases. The importance of liquid phase in environmental engineering arises from the fact that contaminants are immobilized and transported within this phase. Soil remediation technologies, in most cases, are based on contaminant transportation. The remediation process can get more difficult within the fact that dissolved solutes and gases in soil pores can enter in reactions with the contaminants and create less soluble products with a higher molecular weight compound.

The most often found gases dissolved in porous water are CO_2, CH_4, NH_3, O_2, H_2S, and also NO, SO_2, N_2O. Their concentration in soil solution is dependent on its equilibrium constant which is described by Henry's Law as:

$$\boxed{K_H = [G_s]/P_G}$$

Where

G_s is the concentration of gas in solution,

P_G is the partial pressure of the gas in soil air,

K_H is the equilibrium constant.

Table 39 gives values of K_H for gases, which are transferred between soils and the atmosphere. It can be noticed that, ammonia and sulphur dioxide are very soluble, hydrogen sulphide, carbon dioxide, and nitrous oxide are moderately soluble, and nitric oxide, methane and oxygen have low solubility.

The composition of solutes in soil varies over a wide range due to the differences in the parent material, conditions of soil formation, land use, and deposition of salts and gases from the atmosphere. As shown in (Table 40) soil solution contains Ca, Mg, K, SO_4-S, NO_3-N, Cl_2, H_2PO_4-P. It also contain Si $(OH)_4$ and some times NH_4^+, and in acid soils often ions like Al^{3+}, $AlOH^{2+}$ and Mn^{2+} may be present in addition to organic acids and dissolved organic matter.

Table 39 Values at 25°C of K_H for Solubility of Gases in Water

Gas	*K_H ($mol\, m^{-3}\, atm^{-1}$)*	*Gas*	*K_H ($mol\, m^{-3}\, atm^{-1}$)*
CO_2	34.1	NO	1.88
CH_4	1.50	O_2	1.26
NH_3	$5.76 \bullet 10^4$	SO_2	$1.24 \bullet 10^3$
N_2O	25.6	H_2S	$1.02 \bullet 10^2$

Source: From Stumm, W. and Morgan, J.J 1981, Aquatic Chemistry. Wiley, New York.

Water in soil can occur in the form of adhesion water, cohesion water and gravitational water (Foth 1984).

105^{0}C determine the amount of adhesive moisture in a soil which can reach 17% in clays and 7% in silts and 1% in sands.

II- Cohesion water - is attached to the to the surfaces of the soil particles as a film upon the layer of the adhesion moisture film. This film moisture is held by molecular forces of considerable intensity but not as large as in the case of adhesion water film.

Cohesion water film is connected to the ground water level but not affected by gravity because it is retained in soil by forces that exceed gravity (Foth 1984). This moisture can migrate in the soil from point of higher potential to point of lower potential. The greater is the specific area the more cohesive water the soil particles can contain.

III- Gravitational water By definition this water poses the excess of the amount of moisture the soil can retains. It translocate as a liquid and it can be drained away by the forces of gravity and transmits hydraulic pressure.

If saturated soil allowed to drain it will loose water. If any pressure or suction is applied to the soil, more water will be lost. The existence of the small pores in the soil will determine the suction required for removing the water. The more soil pores are small the higher suction is required to remove water from the soil.

Water in soil is held by certain forces, These forces affect its energy, the difference in energy between free water, and soil water is called a soil water potential. There are three forces that act on soil water and contribute to its total potential. These are: capillary forces (matric forces), which gives matric potential, gravity forces, which gives gravity potential, and osmosis forces, which gives osmotic potential (Wild 1993). These various potentials are additive to give total water potential. The gravitational potential is due to the position of the water in a gravitational field. This potential poses a positive sign and is responsible for the movement of water through saturated soils and from high to low elevations. The matric potential poses a negative sign and is responsible for the movement of water from the soil into plant roots, seeds, and microorganisms. Matric potential in many conditions is the main component of the total water potential. In fine soils the amount of work required to extract a unit volume of water is much higher than in large size particles soils. The osmotic potential also poses a negative sign and is created mainly by the adsorption of water molecules by the ions of soluble salts. In natural soils the salt content is low, the reason why osmotic potential has a little significance, on the other hand saline soils the osmotic potential could be the controlling potential (Foth 1984).

The knowledge and understanding of soil water potential is important for cost effective assessment remediation technology particularly were soil water had to be extracted and treated. Important characteristics of porous solution:

I- The osmotic pressure- dependent on the concentration of water-soluble substances and the degree of their dissociation.

II- pH- the pH of soil can affect directly the course of chemical, physio-chemical, and biological processes in the soil.

III- The buffering capacity- it is the ability to restrict the changes in pH value. It depends on the presence of weak acids and bases and their salts. The most effective buffer system in soil solution is the mixture $H_2CO_3 + Ca(HCO_3)_2$ or a mixture of phosphoric acid and phosphates.

IV- Oxidation reduction potential (Eh)- it is the measure of redox activity in soil solution. Low values of Eh -200-200 mV are characteristic of reduction conditions; high values (above 550 mV) indicate strong oxidizing conditions.

V- Soil colloids- they can originate from organic or/and inorganic sources. Their importance related to their electrically charged surfaces. Negative charge is dominant in the case of clay and humic substances because of the dissociation of carboxy and phenolic group. The positive charge may be obtained from the hydroxides of aluminum and iron. Certain colloids can be amphoteric, in acid medium they can release OH^- and become positively charged; in basic medium they release H^+ ions and become negatively charged.

Another important characteristic for colloidal dispersed particles in soil solution is their high surface area where they could reach 10^7 m^2/cm^3. Therefore, due their charges and high surface areas, their ability to bind ions, water, and gases is an important in soil remediation.

1.4. Gaseous phase

Water and gases occupy approximately one half of the total volume of representative mineral surface soil. Soil air differs from that of the atmosphere in several respects. First, the soil air is not continuous, being located in the maze of soil pores separated by soil solids. This fact accounts for its variation in composition from place to place in the soil. In local pockets, reactions involving the gases can greatly modify the composition of the soil air. Soil air generally has higher moisture content than the atmosphere, the relative humidity approaching 100% when soil moisture is optimum.

Third, the content of carbon dioxide is generally higher and that of oxygen lower than that found in the atmosphere. Carbon dioxide is often several hundred times more concentrated than the 0.03% commonly found in the atmosphere. Oxygen decreases accordingly, and in extreme cases may be no more than 10 to 12% as compared to about 20% for normal atmosphere.

APPENDIX 2

Standard curve preparation

Before proceeding in any tests, a way for phenanthrene detection in different solutions had to be defined for qualitative measurements. Due to the aromatic structure of phenanthrene (Chap 1.) the UV/VIS spectrophotometer was chosen as an adequate way to analyze contaminated soil samples.

To find the range of phenanthrene absorbency and its wavelength, a 200 mg/l methanol-phenanthrene solution was scanned in the UV spectrophotometer. The results showed a high absorbency value (6 ABS) corresponding to this concentration. To keep the absorbency value in the range of 1 ABS, a dilution to 10 mg/l was performed. The solution was scanned again and the results allowed for defining the absorbency range and the wavelength associated with it. The obtained data are presented in Figure 118 and Table 23 along with the chosen absorbency and the wavelength.

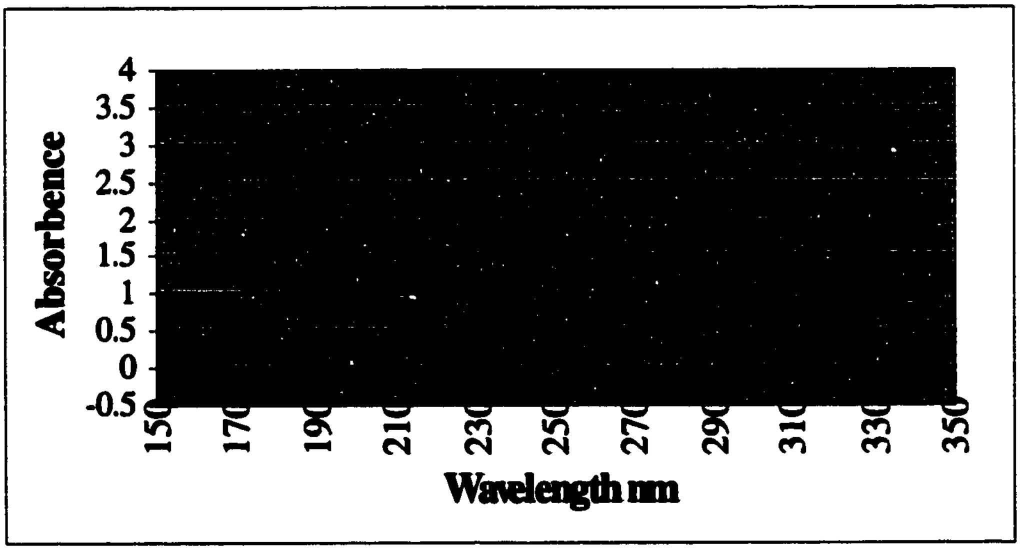


Figure 118 Spectra of the Water-Phenanthrene System

The defined wavelength under which the phenanthrene could be identified was used as a base to prepare a standard curve. Four solutions of phenanthrene in methanol (1.25, 2.5, 5.0, 10.0 mg/l) defined the curve. The data shown in Table 41 were used to form a standard curve.

Table 41 Data from UV/VIS Spectrophotometer

345.6	-0.033
342.4	-0.044
329.6	-0.032
306.4	-0.044
292.4	0.783
286.8	0.265
280.8	0.595
278	0.52
273.6	0.774
269.6	0.671
250.4	3.769
225.6	0.445
219.6	1.229
218.4	1.198
211.2	2.029
196.4	0.52
194.8	0.945
194	0.697
192	1.12
190.8	0.433

Table 42 UV Results for Various Phenanthrene Concentration

Wavelength: 292.4 nm RESID. ERR.: 0.03153		
STD. No.	Absorbency	Conc. mg/l
1	0.11300	1.25
2	0.22400	2.5
3	0.53900	5
4	0.97000	10.0

STD. No. – Standard Number.