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PHENANTHRENE DEGRADATION IN LOW PLASTICITY CLAY USING AN ALTERNATING CURRENT

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Disha C. Shah

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PHENANTHRENE DEGRADATION IN LOW PLASTICITY CLAY USING AN ALTERNATING CURRENT

By

Disha C. Shah

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ABSTRACT

PHENANTHRENE DEGRADATION IN LOW PLASTICITY CLAY USING AN ALTERNATING CURRENT

By

Disha C. Shah

Polycyclic aromatic hydrocarbons (PAHs) are relatively common and persistent contaminants present in soils at contaminated sites. In this study, the effect of sinusoidal alternating current (AC) on the concentration of phenanthrene in spiked low plasticity clay was evaluated in a lab-scale setup. The key hypothesis evaluated was that an AC signal can generate oxidation reactions in clay soil due to the capacitive properties of charged clay mineral surfaces saturated with dielectric water to cause degradation of benzene rings in PAHs. The effect of an AC application in phenanthrene spiked clay was evaluated based on these two key parameters: (1) initial concentration; and (2) magnitude of applied AC. Four cells were subjected to an AC having frequency equal to 60 Hz for time periods ranging from 60 to 160 days. The clay was spiked for initial phenanthrene concentration of 500 and 50,000 mg/kg and the peak to peak voltage applied ranged from 20 to 70 V (root mean square average ~ 14.1 to 49.4 V). The key finding of this study was that in the lab-scale setup, sinusoidal AC did not decrease the concentration of phenanthrene in the spiked low plasticity clay over the test period when compared to control samples subjected to similar temperature conditions but not subjected to an AC.

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LIST OF ABBREVIATIONS

AC = Alternating Current

DC = Direct Current

GC = Gas Chromatography

ASE = Accelerated Solvent Extractor

GF = Granular Filter

DI WATER = Distilled water

DRE = Destruction and Removal Efficiency

ECRT = Electrochemical Remediation Technology

EO = Electro osmosis

H-S = Helmholtz - Smoluchowski

LTTD = Low Temperature Thermal Desorption

PAH = Polyaromatic hydrocarbons

PCB = Polychlorinated Biphenyls.

PL = Plastic Limit

LL = Liquid Limit

PI = Plasticity Index

USCS = Unified Soil Classification System

CL = Clay

FID = Flame Ionisation Detector

VOC = Volatile organic compounds

SVOC = Semi-volatile organic compounds

LIST OF SYMBOLS

I = Current

V= Voltage

Z = Impedance

Ψ = surface potential

pH_{zpc} = pH at zero point of charge

σ_o = permanent charge

σ_H = variable charge

σ_{is} = inner sphere charge

σ_{os} = outer sphere charge

σ_p = total particle charge

qA = Electro osmotic flow rate

k_e = coefficient of electro osmotic permeability

E = Electric field strength

A = cross-sectional area normal to flow direction

V_A = Electro osmotic flow velocity

D = Dielectric constant

ζ = Zeta Potential

η = viscosity of fluid

n = porosity of medium

V_o = voltage amplitude

ω = angular frequency

f = frequency

I_o = maximum current

$Vrms$ = Root mean square voltage

Xc = Capacitive Reactance

C = Capacitance

C_{energy} = Energy costs

C_2 = cost in $/kWh

β = lumped property of contaminant

Φ = electrode spacing or phase difference

u = ionic mobility of species

τ = tortuosity factor

R_d = delay factor

σ = electrical conductivity of soil

C_0 = Target initial concentration of phenanthrene

Cp = Capacitance in parallel

Cs = Capacitance in series

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Contaminated soil or sediment consists of hazardous substances in solid, liquid and/or gaseous form mixed within the soil. Usually, contaminants in the soil are physically or chemically attached to soil particles, or, if they are not attached, are trapped in the void space of soil matrix or are in aqueous phase of the pore water. Leaching of contaminants from soil into infiltrated water poses major groundwater and surface water contamination concerns. Because of food and drinking water contamination concerns, it is necessary to remediate contaminated soil.

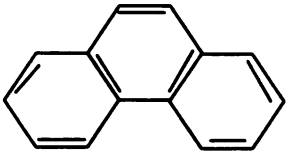
Key contaminants in soils or sediments can be grouped into: (1) inorganic; or (2) organic. Among inorganic contaminants, arsenic and lead are common contaminants (ATSDR 1990). Among organic contaminants, volatile organic compounds (VOCs) such as benzene and semi-volatile organic compounds (SVOCs) such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons (PAHs) and pesticides are the common contaminants (ATSDR 1990). Among many PAHs that exist in the environment, phenanthrene, naphthalene, benzo(a)pyrene and fluoranthene are most common in soils or sediments. Phenanthrene is the contaminant that was used in this study as the model PAH. Due to widespread occurrence of PAHs, novel treatment technologies for contaminated soils is necessary.

1.2 PAH CONTAMINATION IN SOILS

1.2.1 Physical and Chemical Properties of PAH'S

PAHs represent a large class of organic compounds containing two or more fused aromatic rings made up of carbon and hydrogen atoms. At ambient temperature, PAHs are in solid state. The general characteristics common to the class are: relatively high melting and boiling points, low vapor pressure, and very low water solubility which tends to decrease with increasing molecular weight. PAHs are soluble in many organic solvents and are highly lipophilic. They are chemically rather inert. Reactions that are of interest with respect to their environmental fate and possible sources of loss during atmospheric sampling are photodecomposition and reactions with nitrogen oxides, nitric acid, sulfur oxides, sulfuric acid, ozone, and hydroxyl radicals. As PAHs are hydrophobic and have low solubility in water, their affinity for the aquatic phase is relatively low. However, in spite of the fact that most PAHs are released into the environment via the atmosphere, considerable concentrations are also found in the hydrosphere because of their low Henry's law constant. As the affinity of PAHs for organic phases is greater than that for water, their partitioning coefficients between organic solvents, such as octanol, and water are relatively high. Their affinity for organic fractions in sediment, soil, and biota is also high. Hence, PAHs accumulate in organisms in water and sediments and in the food chain. Table 1-1 presents a summary of physical and chemical properties of phenanthrene.

Table 1-1: Physical and Chemical Properties of Phenanthrene

Description	Phenanthrene
CAS No.	85-01-8
Chemical Structure	
Chemical formula	$C_{14}H_{10}$
Molecular Weight (g/mol)	178.22
Appearance	colorless crystalline solid [a,c]
Melting point (°C)	100 [b]
Boiling point (°C)	340 [b]
Vapor Pressure	6.8×10^{-4} mm Hg at 25°c [b]
Density	0.980 g/cm^3 at 4°C [b]
Solubility	Insoluble in Water (1.2 mg/L) [b] Soluble in glacial acetic acid, and other organic solvents like ethanol, benzene, carbon disulfide, carbon tetrachloride, diethyl ether and toluene [a]
Octanol / water Partition coefficient	4.15 – 4.45 [d]

Note : [a] Budavari et al., 1989; [b] ATSDR ,1990; [c] U.S. EPA, 1987; [d] Mabey et al., 1982.

1.2.2 History and Sources of PAH Contamination

PAHs occur abundantly in nature and are made by natural processes as well as man-made processes. Pure PAHs usually exist as colorless, white, or pale yellow-green solids in nature. PAHs can be derived in nature by burning gas, coal or oil, forest fires and volcanic eruptions. PAHs can also be formed by cigarette smoke, burning jet engine, oils, from internal combustion engines, heating of any type of carbon-based material like coal, tar, rubber, wood, oil, etc. Other sources where PAHs are produced include refining of petroleum oil, coal ash used as fill, and incomplete combustion of crude oil. Commercial processing of coal leads first to coal-tars, which are further processed to yield pitch, asphalt, impregnating oils (creosotes for the preservation of wood), and residue oils such as anthracene oil (IARC 1985). The concentration of PAH in coal-tars is generally 0.75 to 1 %. Naphthalene and phenanthrene are the most abundant compounds, occurring at concentrations of 5-10%. Long term health effects of exposure of PAHs include kidney and liver damage, jaundice and short-term health effects include eye irritation, nausea, vomiting, diarrhea and confusion (Illinois Department of Public Health).

Phenanthrene is a PAH derived from fractional distillation of high-boiling coal tar oil. It is ubiquitous in air, land and water following incomplete combustion of fossil fuels and woods. Based on inadequate data from animal bioassays and no human data available, U.S. EPA (1993a, 1987) has placed phenanthrene in weight-of-evidence group D, not classifiable as to human carcinogenicity.

Currently there is no commercial production of phenanthrene in United States (U.S. EPA 1987) Phenanthrene can be used in the manufacture of dyestuffs, explosives, drugs,

in the synthesis of phenanthrenequinone, and in biochemical research (Sax and Lewis 1987). A derivative, cyclopentenophenanthrene, has been used as a starting material for synthesizing bile acids, cholesterol, and other steroids (IARC 1983). Some of the known sources of phenanthrene in the atmosphere are vehicular emissions, coal and oil burning, wood combustion, coke plants, aluminum plants, iron and steel works, foundries, municipal incinerators, synfuel plants, and oil shale plants (U.S. EPA 1987), manufacturing natural gas plants (MGP), mining, herbicides, pesticides and oil spills. It is widely distributed in the aquatic environment and has been identified in surface water, tap water, wastewater, and dried lake sediments. It has also been identified in seafood collected from contaminated waters and in smoked and charcoal-broiled foods (IARC 1983). Phenanthrene is one of the many PAHs on EPA's priority pollutant list (ATSDR 1990).

1.2.3 Conventional PAH Cleanup Technologies

Generally PAHs are neutral and non-polar organic compounds comprising of two or more benzene rings, which are fused together through two or more carbon atoms (National Research Council 1997). Various conventional remediation technologies have been used for PAH contaminated soils or sediments. Presented below is a brief description of each of the conventional technologies used.

1.2.3.1 Thermal Desorption

For thermal desorption, contaminated soils are heated such that organic contaminants and water volatilize. Thermal Desorption can be categorized into two processes based on the temperature ranges: (1) low temperature thermal desorption (90 to 320 °C) and high temperature thermal desorption (320 to 560 °C). Low temperature thermal desorption (LTTD) is an ex-situ means of physically separating volatile and

semi-volatile organic contaminants from soils. Contaminated soil is placed in a chamber, and heated to volatilize the associated hydrocarbons. The exhaust gases, containing the hydrocarbons are consumed in an oxidizing unit, and are subsequently cooled and passed through a bag house to remove particulate matter. The treated soil can then be returned to the original excavation site as clean backfill. LTTD technology can be utilized as a mobile soil remediation solution to satisfy on-site clean up. The cost of operating the system can range from $50/tonne to $80/tonne, depending upon the soil type, moisture content and the level of contamination (USEPA 1990). Clay soil is difficult to treat using this method because of the tendency to stick to process equipment and to aggregate into large clumps which inhibits heat transfer in the thermal desorption process (USEPA 1998).

1.2.3.2 Soil Washing

Soil washing is a water-based or co-solvent based process for scrubbing soils ex-situ or in-situ to remove contaminants. The process removes contaminants from soils in one of the following two ways:

- by dissolving or suspending them in the wash solution
- by concentrating them into a smaller volume of soil through particle size separation, gravity separation, and attrition scrubbing (similar to those techniques used in sand and gravel operations).

Contaminants sorbed onto fine soil particles are separated from bulk soil in a water-based system on the basis of particle size. The wash water is augmented with a basic leaching agent, surfactant, or chelating agent or by adjustment of pH to help remove organics and heavy metals. Soils and wash water are mixed ex-situ in a tank or other

treatment unit. The wash water and various soil fractions are usually separated using gravity settling or by using hydrocyclones. Semi volatiles, pesticides, heavy metals and a wide range of organic and inorganic contaminants can be cleaned from coarse grained soils. By using this method, however it is difficult and expensive to remove organics adsorbed onto clay-size particles.

1.2.3.3 Soil Flushing

In-situ soil flushing is the extraction of contaminants from the soil with water or other suitable aqueous solutions. Soil flushing is accomplished by passing the extraction fluid through in-place soils using an injection or infiltration process. Extraction fluids with the desorbed contaminants or reaction by-products can be of disposal concern. They must be recovered from the underlying aquifer and possibly recycled or reused in the process. Low permeability clay soils or heterogeneous types of soils are difficult and expensive to treat using this treatment method (USEPA 1997).

1.2.3.4 Incineration

High temperatures ranging from 870 to 1,200 °C are used to volatilize and combust (in the presence of oxygen) organics in hazardous wastes. Often auxiliary fuels are employed to initiate and sustain combustion. The destruction and removal efficiency (DRE) for properly operated incinerators exceeds the 99.99% requirement for hazardous waste and can be operated to meet the 99.99% requirement for PCBs and dioxins. Heavy metals can produce a bottom ash that requires stabilization before disposal.

Volatile heavy metals, including lead, cadmium, mercury, and arsenic, leave the combustion unit with the flue gases and require the installation of gas scrubbing systems

for removal. Thus, this treatment technology may not be effective for soil containing metals and soil having a low organic content may be costly to incinerate. This technology is not applicable to soil requiring in-situ treatment (US EPA 1997).

1.2.3.5 Chemical Extraction

Chemical extraction does not destroy wastes but is a means of separating hazardous contaminants from soils, sludges, and sediments. Thus, reducing the volume of the hazardous waste that must be treated. The technology uses an extracting chemical. Waste contaminated soil and extractant are mixed in an extractor, thereby dissolving the contaminants. The extracted solution is then placed in a separator, where the contaminants and extractant are separated for treatment and further use. Hydrochloric acid and organic solvent can be used as extractant and are respectively called Acid Extraction and Solvent Extraction. Solvent extraction is generally least effective on very high molecular weight, organic, and very hydrophilic substances. Higher clay content also reduces extraction efficiency and requires longer contact times.

1.2.3.6 Solidification/Stabilization

Solidification or stabilization reduces the mobility of hazardous substances and contaminants in the environment through both physical and chemical means. Contaminants are physically bound or enclosed within a stabilized mass (solidification), or chemical reactions are induced between the stabilizing agent and contaminants to reduce their mobility (stabilization). Generally inorganics including radionuclides can be "locked" using Solidification/Stabilization. It is not common and less effective for using this technology for organics such as PAHs.

1.2.3.7 Composting

Contaminated soil is excavated and mixed with bulking agents and organic amendments such as wood chips, hay, manure, and vegetative (e.g., potato) wastes. Proper amendment selection ensures adequate porosity and provides a balance of carbon and nitrogen to promote thermophilic, microbial activity. Composting is a controlled biological process by which organic contaminants (e.g., PAHs) are converted by microorganisms under aerobic and anaerobic conditions to innocuous and stabilized byproducts. Typically, thermophilic conditions (54 to 65 °C) must be maintained to properly compost soil contaminated with hazardous organic contaminants. The increased temperatures result from heat produced by microorganisms during the degradation of the organic material in the waste. In most cases, this is achieved by the use of indigenous microorganisms. The composting process can be applied to soils and lagoon sediments contaminated with biodegradable organic compounds.

1.2.3.8 Enhanced Bioremediation

Enhanced bioremediation is a process in which indigenous or inoculated micro-organisms (e.g., fungi, bacteria, and other microbes) degrade or metabolize organic contaminants found in soil and/or ground water, converting them to innocuous end-products. Nutrients, oxygen, or other amendments may be used to enhance bioremediation and contaminant desorption from subsurface materials. Enhanced bioremediation techniques have been successfully used to remediate soils and groundwater contaminated with fuel, volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs including PAHs), and pesticides. Pilot-scale studies have demonstrated microbial degradation of soils contaminated with munitions waste. While

bioremediation cannot degrade inorganic contaminants such as metals, it can be used to immobilize these contaminants. Bioremediation is not well suited for soils with low permeability (e.g., fine clays). Higher permeability is required to allow the nutrients to reach the indigenous microorganisms. The bioremediation of soil contaminated with polycyclic aromatic hydrocarbons (PAH) often is limited by a low bioavailability of the contaminants. Tiehm et al. (1997) showed that a surfactant-enhanced PAH mobilization resulted in an increased PAH degradation as compared to the treatment without surfactant.

1.2.3.9 Phytoremediation

It is a typical in-situ treatment system. Phytoremediation is a process that uses plants to remove, transfer, stabilize, and destroy contaminants in soil and sediment. Contaminants can be organic or inorganic. Phytoremediation is applicable for the remediation of select metals, pesticides, solvents, explosives, crude oil and PAHs. It is not effective for strongly sorbed (e.g., PCBs) and weakly sorbed contaminants (FRTR). Phytoremediation of organic pollutants depends on plant-microbe interactions in the rhizosphere, but the extent and intensity of such rhizosphere effects are likely to decrease with increasing distance from the root surface. Also results from natural and engineered phytoremediation systems provide strong evidence that vegetated soils mitigate polycyclic aromatic hydrocarbon (PAH) contamination. However, the mechanisms by which PAH mitigation occurs and the impact of plant organic matter on PAH attenuation remains unclear. (Gregory et al. 2005)

1.2.3.10 Photodegradation

Photodegradation, also known as photolysis, is a method used where sunlight or some other source of ultraviolet rays, in the presence of hydrogen peroxide (H_2O_2), are used to lyse the ring structure of the PAHs. This leaves the PAHs more susceptible to microbial attack. Normally, the ring structure is broken down by wavelengths of 295 to 300 nm, (website, university of waterloo, CA). It has been found that the heavier the molecule is, the more susceptible it is to photodegradation. Also, as light penetration decreases with increased depth, photodegradation also decreases (CRC press online, 1999).

1.2.3.11 Electrokinetic Remediation Technology

Electrokinetics is a process that separates and extracts heavy metals, radionuclides, and organic contaminants from saturated or unsaturated soils, sludges, and sediments. Electrokinetic remediation is a process in which a low-voltage direct-current electric field is applied across a section of contaminated soil to move and remove contaminants. The electrical current causes electro osmosis and ion migration, which move the aqueous phase contaminants in the subsurface from one electrode to the other. Contaminants in the aqueous phase or contaminants desorbed from the soil surface are transported towards respective electrodes depending on their charge. The contaminants may then be extracted to a recovery system or deposited at the electrode. Surfactants and complexing agents can be used to increase solubility and assist in the movement of the contaminant. In addition, reagents may be introduced at the electrodes to enhance contaminant removal rates (EPA 1995). Saichek and Reddy (2005) surfactants were added to increase solubility of phenanthrene.

1.2.4 Key Challenges

The conventional technologies discussed above have specific disadvantages as listed below:

1. The conventional treatment technologies are ineffective in low permeability soil like natural clays. Most of the problem of PAH contamination persists in clayey soils since they have a high tendency to sorb PAHs. Clay soils adsorb strongly and have high a cation exchange capacity. They are also good conductor of electricity when saturated. It is comparatively easier to remediate sandy soils because of high hydraulic conductivity (or 10^{-5} cm/s). It is easier to pump treatment liquids and extract effluents into a sandy soil and treat it because of large pore spaces. Whereas, the same technology for clayey soil having hydraulic conductivity less than 10^{-6} cm/s would require tremendous amount of pressure to treat the same area of land because of comparatively tighter arrangement of clay particles.
2. When ex-situ treatment is carried out, the treatment is too expensive due to the cost of soil excavation.
3. Certain conventional treatment technologies do not allow reuse of the treated soil.
4. Not all the treatments are efficient and cost effective.
5. Naphthalene and phenanthrene are by far the most abundant PAH compounds, occurring at concentrations of 5-10%, Hence remediation of soil contaminated with Phenanthrene is considered herewith in this research. In addition Reddy et al. (1997) have studied the effect of direct current applied in phenanthrene

contaminated soil. In this research project, an alternating current is used to evaluate the degradation of phenanthrene in spiked low plasticity clay.

CHAPTER 2

ELECTROCHEMICAL REMEDIATION

Most conventional technologies are not well suited for low permeability soils or soils having high organic matter content. Electrochemical remediation has been a topic of research for the remediation of contaminated clayey soil. (Acar et al. 1995; Saichek and Reddy 2005). Acar et al. (1995) have shown that Electrokinetic remediation is appropriate for organics, inorganics and radionuclides.

Electrochemical remediation involves passage of direct or alternating current through soil. The technique can be performed in-situ or ex situ. Its advantages include close control over the direction of movement of water and dissolved contaminants, even through heterogeneous soils, possible retention of contaminants within a confined zone (Page & Page 2002). The ECRT is very different from the classical Electrokinetic remediation technology. A typical electrochemical setup is shown in Figure 2-1. Typically electrodes are inserted initially into the area surrounding the contaminated soil. A relatively low voltage alternating current is applied across the electrodes. Since the process requires a conducting pore fluid, it is generally applicable for clayey soils that are saturated (Acar et al. 1995).

A power generation system, which includes a power supply, a transformer kit was used to generate the required alternating current and apply it to the test cells. The transformer is used to adjust the voltage. A sinusoidal voltage was generated and current I, was calculated using Ohm's law as shown in Eq. 2-1:

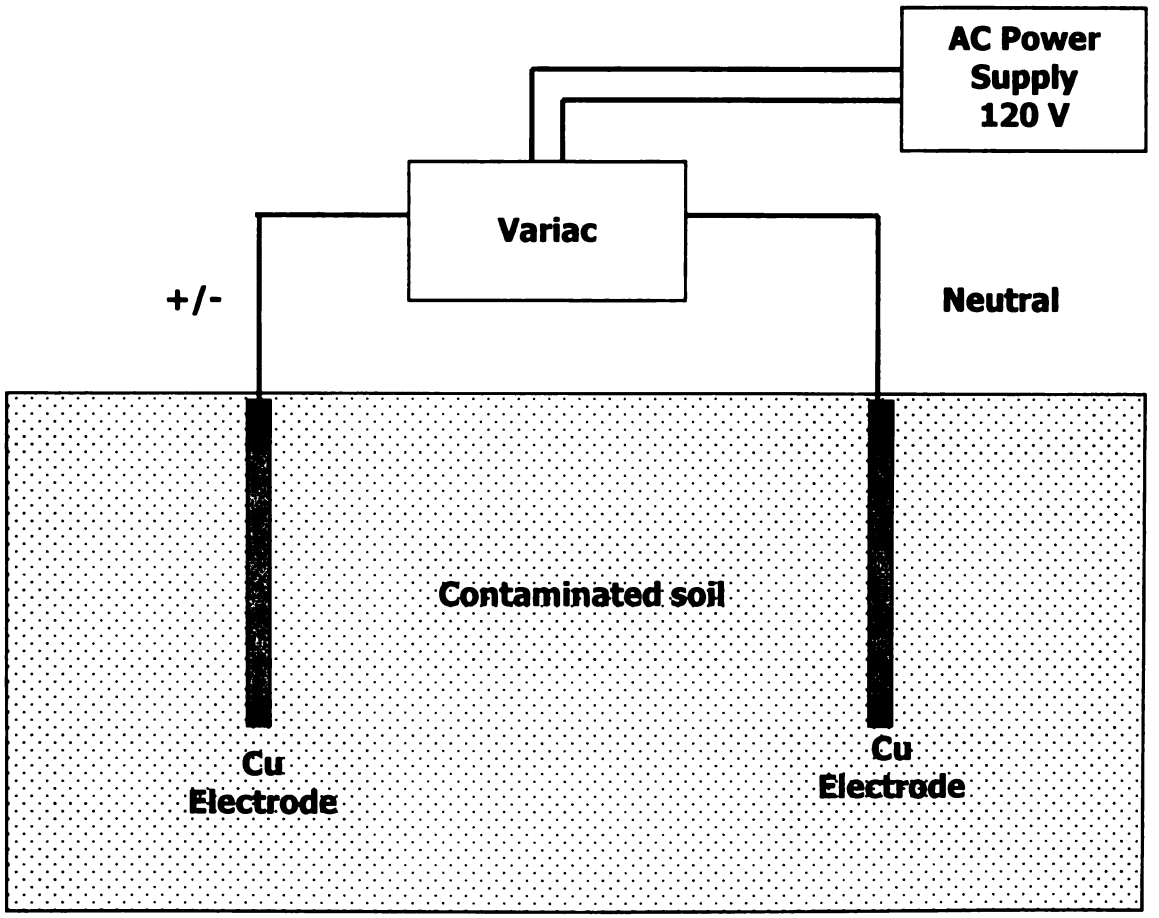


Figure 2-1: Typical Electrochemical Cell Setup

$$I = V/Z \quad (2\text{-}1)$$

where V= voltage applied across the cell and Z = impedance of the system

2.1 ECRT PRINCIPLES

2.1.1 Point of zero charge

Schwarzenbach et al. (1993) calculated that most of the counter ions are located within 1 to 30 nm of the clay mineral surface. Clay mineral surfaces can be covered with hydroxyl ions, electron rich atoms or ligands, and a diffuse double layer consisting of counter ions at 1 to 30 nm of the surface after reaching equilibrium. Moreover, the surface hydroxyls may undergo proton exchange reactions with the aqueous solution. These reactions mainly depend on the solution composition and the pH. Apart from H+ and OH- , other species can also bind with the surface and contribute to the surface charge, which as a group, they are called potential determining species (Stumm and Morgan 1996).

Consider an oxide molecule at the surface where the metal (M) atom is bound to the surface and the hydroxyls exhibit the following reactions Eq. 2-2 and 2-3 with H^+ (Schwarzenbach et al. 1993).

$$M\text{–}OH^{+2} \rightarrow M\text{–}OH + H^+ \quad (2\text{-}2)$$

$$M\text{–}OH \rightarrow M\text{–}O^- + H^+ \quad (2\text{-}3)$$

As pH increases, both the reactions move in forward direction and the surface potential decreases as it becomes more difficult to move H^+ away from the oxide surfaces (Schwarzenbach et al. 1993) . Here $M\text{–}OH^{+2}$ is called protonated surface sites and MO^- is

called deprotonated surface sites. When only H^+ and OH^- species are considered, the abundance of protonated and deprotonated sites determines the surface charge. In case of equal concentration of these species, the surface attains a zero net charge, and the pH at which the surface potential (ψ) exhibits a zero net charge is called the zero point of charge (pHzpc).

Thus, at low pH, the protonated ($M–OH^{+2}$) specie has greater concentration and determines the surface charge. The surface potential is positive in this case. Whereas at higher pH, MO^- is higher in concentration and surface potential is negative and deprotonated specie determines the surface charge.

The charges on clay minerals are basically divided into two main categories: permanent or variable charge. Sposito (1989) describes permanent charge (σ_o) of the mineral surface as the negative charge due to the isomorphic substitution, while the variable charge due to protonation of the surface. The variable charge (σ_H) is a function of pH and is equal to the number of moles of H^+ minus the number of moles of OH^- that forms complexes with the surface functional groups. In addition to the permanent and variable surface charge densities, other permanent species besides H+ and OH- may bind to the mineral surface. Sposito (1989) describes these species as inner sphere or outer sphere charges. Hence total particle charge (σ_p) is presented in Eq. 2-4

$$\sigma_p = \sigma_o + \sigma_H + \sigma_{is} + \sigma_{os} \qquad (2\text{-}4)$$

Where σ_o is always negative whereas other charges depends on the composition of the solution. The pH at which net particle charge $\sigma_p = 0$ is pH_{zpc} since the ionic species in solution do not contribute to the charge of mineral surface.

2.1.2 Contaminant Transport Mechanisms

The electrochemical remediation is accomplished through various contaminant transport mechanisms such as electromigration, electro osmosis, electrophoresis and diffusion (Probstein and Hicks 1993).

2.1.2.1 Electromigration

Electromigration refers to migration of ionic species in an applied electric field. In case of clay soil, electromigration is one of the dominant modes of contaminant transport. The ionic mobility is related to electrical conductivity of the solution and is therefore affected by concentration, ionic charge, and temperature. The major influences on electromigration during electrochemical remediation are field strength (as for electro osmosis), ionic concentration, and charge of ionic species present. Typical ionic mobilities in soil are 3×10^{-8} $m^2/V.s$, except for H^+ and OH^-, which have mobilities one order of magnitude greater (Page & Page 2002).

2.1.2.2 Electrophoresis

Electrophoresis is the movement of electrically charged particles suspended in a liquid by the action of an electric field (Glenn et al. 1996). Mainly, electrophoresis is due to migration of colloidal or larger sized particles. Electrophoresis of clay colloids may play an important role in decontamination if the colloids migrate with adsorbed chemicals. Electrophoresis movement can contribute to the transport of contaminants in the form of colloidal electrolytes or ionic species.

2.1.2.3 Electro osmosis

Electro osmosis (EO) is the transport of pore fluid under an electrical gradient (USEPA 1997). Electro osmotic flow may provide the key for increasing soil–solution–contaminant interaction though low permeability regions because it is capable of producing a substantial flow through these regions that is far superior to the flow achieved by an ordinary hydraulic gradient. In addition, once the contaminants are desorbed from the soil and are solubilized into solution, electro osmosis facilitates advective transport of the contaminant-laden solution towards the electrode compartment for removal.

Electro osmosis provides increase in soil solution and contaminant interaction through low permeability regions because it is capable of producing a substantial flow through these regions that is far superior to the flow achieved by an ordinary hydraulic gradient. Moreover, advective transport is facilitated due to electro osmosis for transporting the contaminated solution towards the electrodes.

Clay surfaces are negatively charged, hence when they are surrounded by aqueous solution, counter ions concentrate adjacent to the particle surface of the clay. This region is known as diffuse double layer. Under an electrical potential, electro osmotic flow is produced because the locally excess ions migrate in a plane parallel to the surface of the particle towards the oppositely charged electrode. After application of electric gradient, the counter ions in the double layer may be tightly held in place due to electrostatic forces, but the excess counter ions that are far away from the double layer are mobile (Eykholt 1992). Therefore, a shear layer exists that divides the fixed and mobile region. This shear plane is located at a specific distance from the charged particle clay surface.

The electric potential at this distance is called zeta potential (ζ). Zeta potential can be a function of many parameters including type of clay mineral, ionic species that are present, pH, temperature and ionic strength (Vane and Zang 1977). The zeta potential of the soil varies during the process and can affect the rate and direction of electro osmotic flow. (Miller 1955; Shapiro and Probstein 1993; Eykholt and Daniel 1994; West and Stewart 1995).

Electro osmotic flow rate can be represented by Eq. 2-5 which is analogous to Darcy's law (Page & Page 2002).

$$qA = - k_e EA \tag{2-5}$$

where qA = Electro osmotic flow rate; k_e = coefficient of electro osmotic permeability; E = electric field strength or negative potential gradient; and A = cross sectional area normal to flow direction.

The Helmholtz – Smoluchowski (H-S) theory is a widely accepted theory for electro osmotic flow. It applies to the system with larger pore size relative to electric diffuse double layer. The H-S equation is represented in Eq. 2-6:

$$V_A = - D \zeta E / \eta \tag{2-6}$$

where V_A= electro osmotic flow velocity; D = Dielectric constant; ζ = zeta potential; E = applied voltage gradient; and η = viscosity of fluid.

According to Eykholt (1992), for negatively charged mineral surfaces, the zeta potential ζ is negative, the counter ions are cations and the electrical gradient E is positive in the direction of the cathode. So by H-S equation (Eq. 2-3), the velocity and flow should be directed towards the cathode. Conversely, for positively charged particle

surfaces, the zeta potential is positive and hence counter ions are anions, but the electrical gradient remains positive in the direction of the cathode. Which means, due to positive zeta potential, the velocity and direction of electro osmotic flow is negative and towards anode.

Further, the electro osmotic flow can be given by Eq. 2-7 as follows.

$$qA = D\,\zeta\,E\,n\,A/\,\eta \tag{2-7}$$

where n = porosity of the medium.

Combining Eq. 2-2 and 2-4, coefficient of electro osmotic permeability can be found out.

$$k_e = D\,\zeta\,n\,/\,\eta \tag{2-8}$$

2.1.2.4 Diffusion

Diffusion of ions becomes significant near the electrodes as concentration gradients develop (Probstein and Hicks 1993). However, diffusion is a slow process and Electromigration and Electro osmosis are two dominant processes occurring in clayey soils.

2.1.3 Physics of ECRT

Direct current (DC) involves current flowing in one direction only, whereas for alternating current (AC), the voltage oscillates in a sine wave (Eq. 2-9) or any other shaped wave pattern varying with time. Equation 2-9 shows the AC voltage function.

$$V = V_o \sin\omega t \tag{2-9}$$

where V = alternating voltage; V_o = voltage amplitude; ω = frequency; and t = variable time. Resistance in an AC circuit is represented in the Figure 2-2. Because Ohm's law (Eq. 2-1) is applicable to an AC circuit, combining Eq. 2-1 and Eq. 2-9, we get the following relation.

$$I = (V_o/Z) \sin\omega t = I_o \sin\omega t \qquad (2\text{-}10)$$

where I_o = maximum current.

In a household circuit in North America, the AC frequency is 60 Hz. The angular frequency is related to the frequency, f, by Eq. 2-11.

$$\omega = 2\pi f \qquad (2\text{-}11)$$

V_o represents the maximum voltage, which in a household circuit in North America is about 170 volts. The average value of the voltage in the household is 120 volts. The averaging method used to obtain such value is called root mean square (rms). Voltages and currents for AC circuits are generally expressed as rms values. For a sine wave, the relationship between the peak and the rms average is as shown in Eq. 2-12.

$$V_{rms} = 0.707 \times V_o \qquad (2\text{-}12)$$

A capacitor consists of two parallel plates separated by dielectric fluid or material. An ideal capacitor, once fully charged, blocks the flow of current across the dielectric material between the plates. Whereas, a "leaky" capacitor allows a current to flow once charged. Clay can be considered as a leaky capacitor as shown in Figure 2-3 where the charged flaky particles act as the parallel plates and the aqueous solution in the pores (e.g., water) acts as a dielectric fluid. In an ideal capacitive unit, current shall lead the

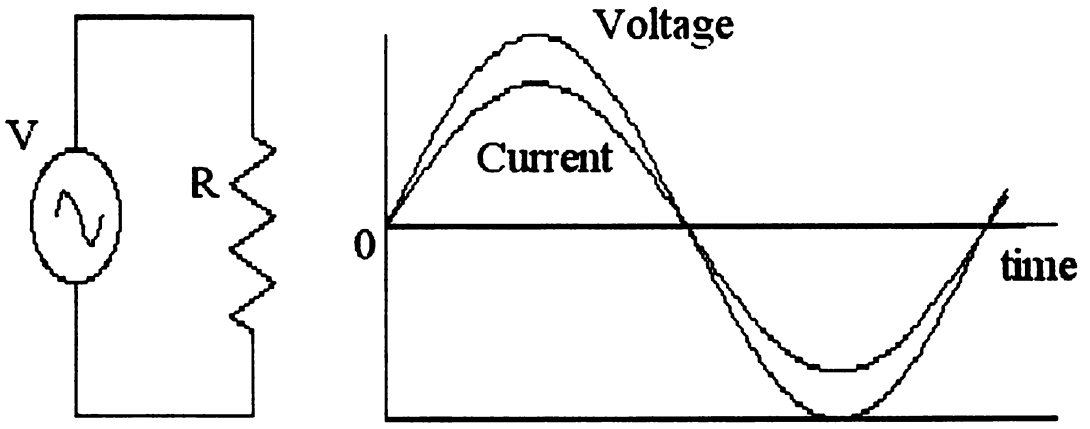


Figure 2-2: Resistance in an AC Circuit

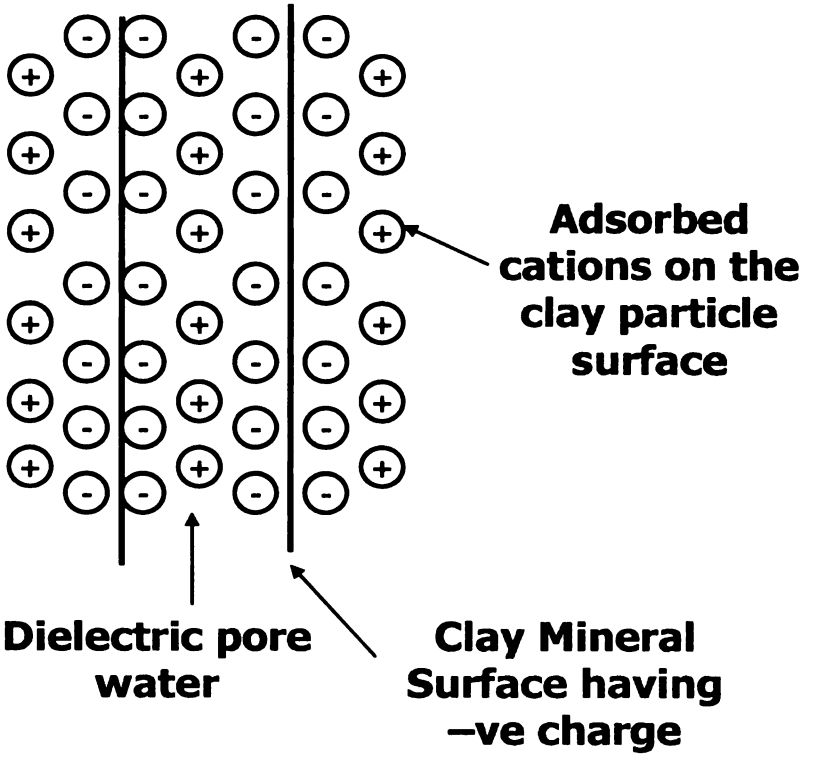


Figure 2-3: Clay a "Leaky" Capacitor

voltage by 90^{o} which also means the same as the phase difference between current and voltage is 90^{o} or that current reaches the peak before voltage. The AC power supply produces an oscillating voltage. The description of full one cycle of voltage (Elementary Physics, 2000, Boston University) is as follows

Step 1: At point a (see Figure 2-4) the voltage is zero and the capacitor is uncharged. Initially, the voltage increases quickly. The voltage across the capacitor matches the power supply voltage, so the current is large to build up charge on the capacitor plates. The closer the voltage gets to its peak, the slower it changes, meaning less current has to flow. When the voltage reaches a peak at point b, the capacitor is fully charged and the current is momentarily zero.

Step 2 - After reaching a peak, the voltage starts dropping. The capacitor must discharge now, so the current reverses direction. When the voltage passes through zero at point c, it's changing quite rapidly. To match this voltage the current must be large and negative.

Step 3 - Between point's c and d, the voltage is negative. Charge builds up again on the capacitor plates, but the polarity is opposite to what it was in step one. Again the current is negative, and as the voltage reaches its negative peak at point d the current drops to zero.

Step 4 - After point d, the voltage heads toward zero and the capacitor must discharge. When the voltage reaches zero it's gone through a full cycle so it's back to point 'a' again to repeat the cycle.

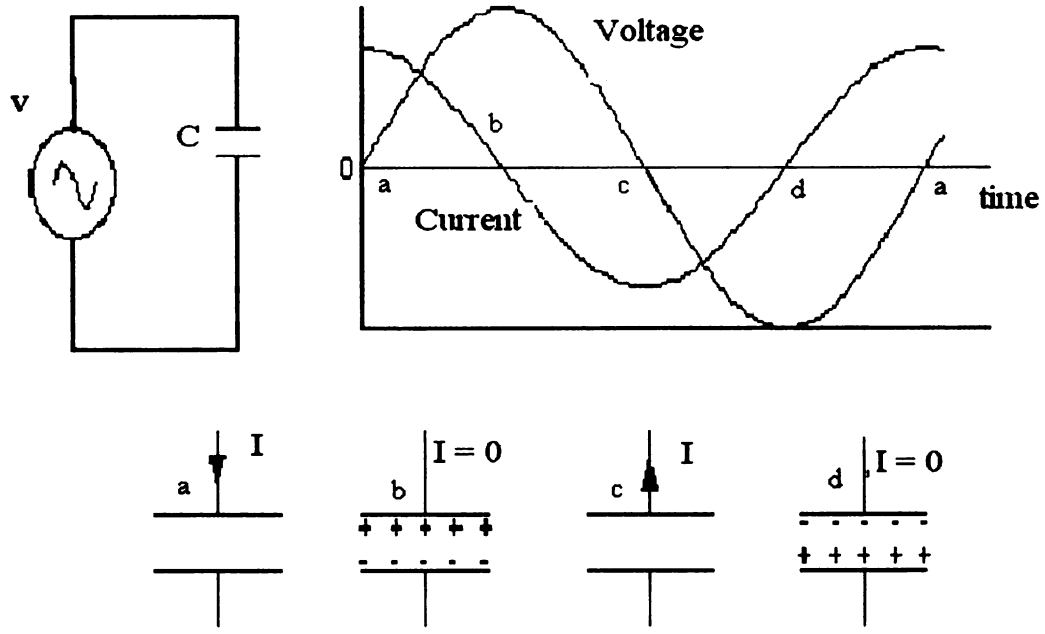


Figure 2-4: Capacitance in an AC Circuit

The larger the capacitance of the capacitor, the more charge has to flow to build up a particular voltage on the plates, and the higher the current will be. The higher the frequency of the voltage, shorter the time available to change the voltage, so the larger the current has to be. The current, then, increases as the capacitance increases and as the frequency increases. This is known as capacitive reactance and is measured in ohms. There is an inverse relationship between current and resistance, so the capacitive reactance is inversely proportional to the capacitance and the frequency: Hence a capacitor in an AC circuit exhibits a kind of resistance called capacitive reactance (X_c), measured in ohms. This depends on the frequency of the AC voltage, and is given by Eq. 2-13:

$$X_c = 1/\omega C = 1/2\pi fC \qquad (2\text{-}13)$$

where X_c = capacitive reactance; ω = angular frequency; f = frequency and C = capacitance.

In an ideal capacitor, no energy is lost because the capacitor stores charge and releases it. In this case, energy is stored in the electric field between the capacitor plates. The amount of energy stored in a capacitor is given by Eq. 2-14:

$$\text{Energy in a capacitor: } E = \tfrac{1}{2} CV^2 \qquad (2\text{-}14)$$

Electrons have negative (-) electrical charges. Because opposite charges attract, they will move toward an area consisting of positive (+) charges. This movement is made easier in an electrical conductor, such as a metal wire. The electricity in the wire with AC supply moves in one direction for a while and then reverses its direction. The charge at the ends of the wire alternates between negative (-) and positive (+). If the charge is

negative (-), that pushes the negatively charged electrons away from that terminal. If the charge is positive (+), the electrons are attracted in that direction.

2.1.4 ECRT Chemistry

The predominant process occurring in the electrochemical cell is the electrolysis of water in the moist soil, which results in formation of H^+ ions and oxygen at the anode and OH^- and Hydrogen at the cathode as represented in Eq. 2-15 and 2-16.

$$H_2O \rightarrow 1/2\ O_2(g) + 2H^+(aq) + 2e^-$$ Water is oxidized at the anode (2-15)

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$ Water is reduced at cathode (2-16)

Due to the electrolysis reactions, there is a decrease in pH near the anode and increase in pH at the cathode as the generated protons and hydroxyl ions migrate towards oppositely charged electrode. An acid front moves across the soil sample from the anode toward the cathode and a base front moves from the cathode to the anode (Acar et al. 1991). The acid front moves faster than the base front because the mobility of H^+ exceeds that of OH^- and the direction of electro-osmotic flow is generally toward the cathode. The soil usually becomes acidic throughout most of its volume, except close to the cathode. There are exceptions to this, e.g., when the soil itself is highly buffered or alkaline (Reddy et al. 1997).

2.2 FACTORS AFFECTING ELECTROKINETIC REMEDIATION

2.2.1 Electrolyte Composition and pH

Changes to the electrolyte composition occur when dissolved substances are removed from the soil sample, by entering the electrolyte, by depositing on cathode as is the case for the metal ions like copper (Page & Page 2002). The dominant process is

electrolysis of water in moist soils which results in an immediate local change in pH due to the formation of H^+ and oxygen at anode and OH^- ions and hydrogen at cathode. The acidity at the anode and alkalinity at the cathode increase with time

Due to the change in pH, some soil minerals dissolve because of the changing composition of the solution. Due to increase in acidity, concentration of certain ions like Mg, Fe and Al increases and increase in alkalinity increases the concentration of Si and Al ions in the solution (Grim 1968).

For metals, various ions may be stable at different pH values. Metal cation like Zn^{+2} is stable under acidic conditions, and oxyanion like ZnO_2^- under alkaline conditions. At the point where pH changes suddenly, the solubility of these metal ions is at a minimum and they precipitate as metal hydroxides (Gray and Schlocker 1969). Successful removal of the contaminants depends on maintaining metal ion solubility at either a low pH or a high pH throughout the soil and avoiding the conditions resulting in precipitation. Thus, control of pH is of major importance.

2.2.2 Zeta Potential

The clay particle surfaces usually carry negative charge, and hence the zeta potential of clay soils is usually negative resulting into net electro osmotic flow towards cathode. Values of Zeta potential varies due to change in pH and ionic strength of solution. Increased acidity causes zeta potential to become less negative and even to attain positive values of zeta potential at low pH (Lorenz 1969). Flow rate decreases if the pH is depressed below neutral and increases at alkaline pH values (Shapiro and Probstein 1993). Zeta potential becomes more positive with increase in ionic strength of

the solution. Increasing concentration of metals like Cu, Co and Cd causes the zeta potential to become more positive (Hunter and James 1992).

2.2.3 Voltage and Current Levels.

The electric current intensities used in most Electrokinetic studies (Alshawabkeh et al. 1999) are in the order of a few tens of milliamperes per square centimeter. Although a high current intensity can generate more acid and increase the rate of transport to facilitate the contaminant removal process, it increases power consumption tremendously as power consumption is proportional to the square of electric current. An electric current density in the range of 1 to 10 A/m^2 has been demonstrated to be the most efficient for the process (Alshawabkeh et al. 1999). However, appropriate selection of electric current density and electric field strength depends on the electrochemical properties of the soil to be treated, in particular the electrical conductivity. The higher the electric conductivity of the soil is, the higher the required electric current density will need to be to maintain the electric field strength required. An optimum electrical current density or electric field strength should be selected based on the soil properties, electrode spacing, and time requirements of the process.

2.2.4 Soil Structure

Clogging of pores and eventual cessation of flow can result from deposition of metal hydroxide compounds in the metal contaminated soil. These metal hydroxides are formed due to reaction between hydroxyl ions near the cathode and heavy metals present in the soil. Some clay types like montmorillonite show dramatic changes in the soil structure resulting in water loss and shrinkage (Grundl and Reese 1997). Therefore, it is

necessary to prevent precipitation in the soil while remediating heavy metal contaminated soil.

2.2.5 Water Content

The extent of saturation of the soil is another factor that alters the electro-osmotic flow rate (Gray and Mitchell 1967; Mitchell and Yeung 1991; Lindgren et al. 1994; Laursen 1997) and hence decontamination of the soil. Uneven moisture distributions and regions of consolidation may arise during electroremediation associated with the development of negative pore pressures (Hamed et al. 1991; Acar and Alshawabkeh 1996; Eykholt 1997). The negative pore pressures result from uneven flow rates caused by variations in pH and hence electric field strength and zeta potential (Miller 1955; Mise 1961; Esrig 1968; Eykholt 1997).

Another cause of drying of soils during electroremediation is the heating effect of the electric current (Fernandez-Gonzalez 1966; Shapiro and Probstein 1993). Although increasing temperature increases the rate of any chemical reaction and therefore might be advantageous under carefully controlled conditions (Krause and Tarman 1995; Penn and Savvidou 1997), desiccation can cause problems, particularly on large-scale samples and in field trials (Lageman et al. 1989; Ho et al. 1997; Lindgren et al. 1998). The effect is likely to be more severe in unsaturated soils but occurs even in soils which are initially saturated. Some of the consequences of drying out are shrinkage and cracking of the soil, development of uneven flow paths, and eventual cessation of fluid flow.

2.2.6 Soil Chemistry

Characteristics of the soil, which influence kinetics of contaminant removal, include adsorption, ion exchange, and buffering capacity (Grim 1968; Sposito 1984). Soil contaminant interaction is especially high in fine-grained soils. Adsorption isotherms and ion exchange capacities have been determined directly in electroremediation experiments (Hamed et al. 1991; Yeung et al. 1996; Puppala et al. 1997; Reddy et al.1997; Sah and Chen 1998; Chen et al. 1999). Ionic contaminants must be desorbed before they can be removed and decontamination is most rapid at concentrations above the ion exchange capacity of the soil. Soils which adsorb strongly and have high cation exchange capacities, e.g., illitic and bentonitic clays, are thus more difficult to decontaminate than clays, like kaolinite, with low cation exchange capacities. This correlates with electro osmotic flow rates, which are high in kaolin and low in illitic and bentonitic clays (Gray and Mitchell 1967).

Changes in pH affect the adsorption characteristics of the soil. H^+ ions, generated by electrolysis of water, are effective at desorbing metal cations as the acid front passes through the soil. Similarly, OH^- ions produced at the cathode aid desorption of anions, such as CrO_4^{-2} (Weng et al. 1994) and there is evidence that they may also help certain organic molecules to desorb (Segall et al. 1980). The availability of H^+ and OH^- ions in the pore solution is determined by the buffering capacity of soils.

2.2.7 Electrode Material, Configuration, and Spacing

Chemically inert and electrically conducting materials such as graphite, coated titanium, or platinum are used as anode to prevent dissolution of the electrode and generation of undesirable corrosion products in an acidic environment. If necessary,

sacrificial electrodes can also be used as anode. Any conductive materials that do not corrode in a basic environment can be used as cathode (Alshawabkeh et al. 1999). Important considerations for the choice of electrode material are: (1) electrical conduction properties of the material; (2) availability of the material; (3) ease of fabrication to the form required for the process; (4) ease of installation in the field; and (5) material, fabrication, and installation costs. Regardless of the material selected for the electrode, the electrode has to be installed properly in the field so that it can make good electrical contact with the subsurface. Moreover, the design must make provisions to facilitate exchange of solution with the subsurface through the electrode. The size, shape, and arrangement of electrodes and the distance between them will also affect rates of decontamination. Most bench-scale and large-scale laboratory and pilot-scale field studies on electrokinetic remediation performed to date have been one-dimensional (1-D). Effective and efficient full-scale field application will require an optimal electrode configuration. 1-D, two-dimensional (2-D), or axisymmetrical electrode configurations may be adopted.

For a 1-D electrode configuration, sheet electrodes can be installed in the field by a procedure similar to the installation of wick drains. The electrodes are practically driven into the soil. Using electrode trenches is another 1-D application. However, an approximately 1-D electric field can also be obtained by lines of rod electrodes placed in boreholes. It is probably the easiest method to install and the most cost-effective approach for in-situ remediation. However, this configuration may develop spots of inactive (dead) electric field between electrodes of the same polarity. Hexagonal, square, or triangular electrode configurations can be used for 2-D field implementation.

In a hexagonal electrode configuration, electrodes form honeycomb cells containing a cathode surrounded by six anodes as shown in Fig. 2-5(a). In a square configuration, electrodes form square cells containing a cathode surrounded by four, eight, or may be even more anodes as shown in Fig. 2-5(b). Similarly, in a triangular configuration, electrodes form triangles containing one cathode surrounded by three anodes as shown in Fig. 2-5(c). In these configurations, the cathode is placed at the center and the anodes are placed on the perimeter to maximize the spread of the acidic environment generated by the anodes and to minimize the extent of the basic environment generated by the cathode. These configurations of electrodes generate 2D nonlinear electric fields. Spots of inactive electric field can still develop in these configurations during electrokinetic processing of contaminated soils. However, the areas of these inactive spots are smaller than those developed in the approximate 1-D configuration containing parallel lines of anodes and cathodes. In a 1-D configuration, the electric current density, i.e., current per unit area, is independent of location. In 2-D configurations, however, the electric current density increases linearly with distance toward the cathode. Therefore, the electric field strength also increases linearly with distance toward the cathode (Alshawabkeh et al. 1999).

2.3 EFFICIENCY AND APPLICABILITY OF THE TREATMENT

New unproven technologies may offer greater effectiveness at a lower cost but with greater risks. Traditional clean up technologies as discussed before can be expensive and time consuming and sometimes not effective. Nevertheless, given the substantial

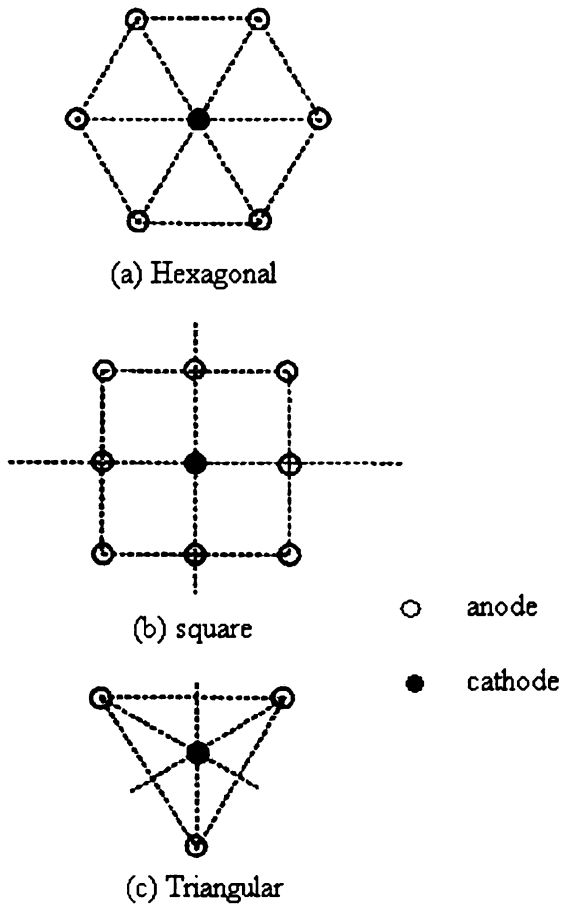


Figure 2-5: Different Configuration of Electrodes

limitations and high costs of conventional treatment technologies, the need to find cheaper and more effective technologies will continue to increase.

2.4 COST OF THE TREATMENT

In general, the total costs for full-scale in-situ implementation of the technology may have five major components: (1) Costs for fabrication and installation of electrodes; (2) cost of electric energy; (3) cost of enhancement agent if necessary; (4) cost of any post-treatment if necessary; and (5) fixed costs (Alshwabekh et al. 1999). These costs are discussed in detail as follows.

2.4.1 Cost of Fabrication and Installation of Electrodes

Cost of electrodes depends on the material type, installation type and dimensions of the electrodes. The number of electrodes per unit volume of soil to be treated depends on electrode configuration and spacing. The installation costs depend on the method of installation, depth of the electrodes to be installed, and number of electrodes to be installed. The total costs of electrodes per unit volume of soil to be treated include the material and fabrication costs of the electrodes and their installation costs in the field.

2.4.2 Electric Energy Costs

The total energy costs for the remediation depends mainly on the cost per KWh of electricity. Alshwabekh et al. (1999) gives the formula for energy expenditure for remediation cost per unit volume of the soil. The formula is presented in Eq. 2-17.

$$C_{energy} = C_2 \times \Phi / 3{,}600{,}000 \times \beta \qquad (2\text{-}17)$$

where C_{energy} = Energy cost; C_2 = cost in \$/kwh and β is a lumped property of the contaminant and the soil as presented in Eq. 2-18. It represents the rate of transport of specific specie per unit electric current density; Φ is electrode spacing or phase difference;

$$\beta = nu\tau + K_e / R_d \sigma \quad \text{in } (m^3/C \text{ or } (m/s)/ (A/m^2)) \tag{2-18}$$

where σ = electric conductivity of soil (S/m); n = porosity; u = ionic mobility of species; τ = tortuosity factor; K_e= coefficient of electro osmotic conductivity of soil and R_d is the delay factor similar to the retardation factor of the advection dispersion contaminant transport and can be introduced to account for the extra time required for the acid transport, metal desorption, dissolution, etc.

2.4.3 Cost of Enhancement Agent

If the use of enhancement agent is necessary, the cost of chemical should be considered. Cost of the enhancement agent can be based on the desired remedial efficiency.

2.4.4 Cost of Post Treatment

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

2.4.5 Fixed Costs

Fixed costs include mobilization and demobilization costs of various equipment, site preparation, security, progress monitoring, insurance, labor, contingency, and miscellaneous expenses. The equipment will not be consumed in a particular project. However, there is capital, depreciation, or rental cost involved.

Thus the total costs per unit volume of the soil to be treated can be given by summation of all the types of costs discussed above.

CHAPTER 3

EXPERIMENTAL METHODOLOGY

3.1 EXPERIMENTAL PROCEDURE

The overall experimental procedure followed is outlined below in Figure 3-1. Each step is discussed in detail in the following sections. Four sets of experiments were designed as presented in Table 3-1 to gain a better understanding of the degradation phenomena of phenanthrene in the soil. Also controls were designed for each test to study the effect of natural biodegradation and heat. Figure 3-2 displays some of the pictures of the experimental setup in the lab. Images in this thesis are presented in color.

3.1.1 Soil Properties

The clay used in the study was obtained from Michigan State University campus in East Lansing. Here the clay has been referred to as "MSU blue clay" because of its grayish-blue appearance. The index properties of the MSU blue clay are presented in Table 3-2. According to Unified Soil Classification System (USCS), MSU blue clay is classified as low plasticity clay (CL).

3.1.2 Sample Preparation

3.1.2.1 Grinding the Sample

MSU blue clay consisted of chunks. Hence, first step was to process the soil sample to make it finer and uniform. It was crushed using a mallet. The crushed soil was passed through Sieve # 20 (mesh size = 0.85 mm).The soil passing through the sieve was oven dried and spiked.

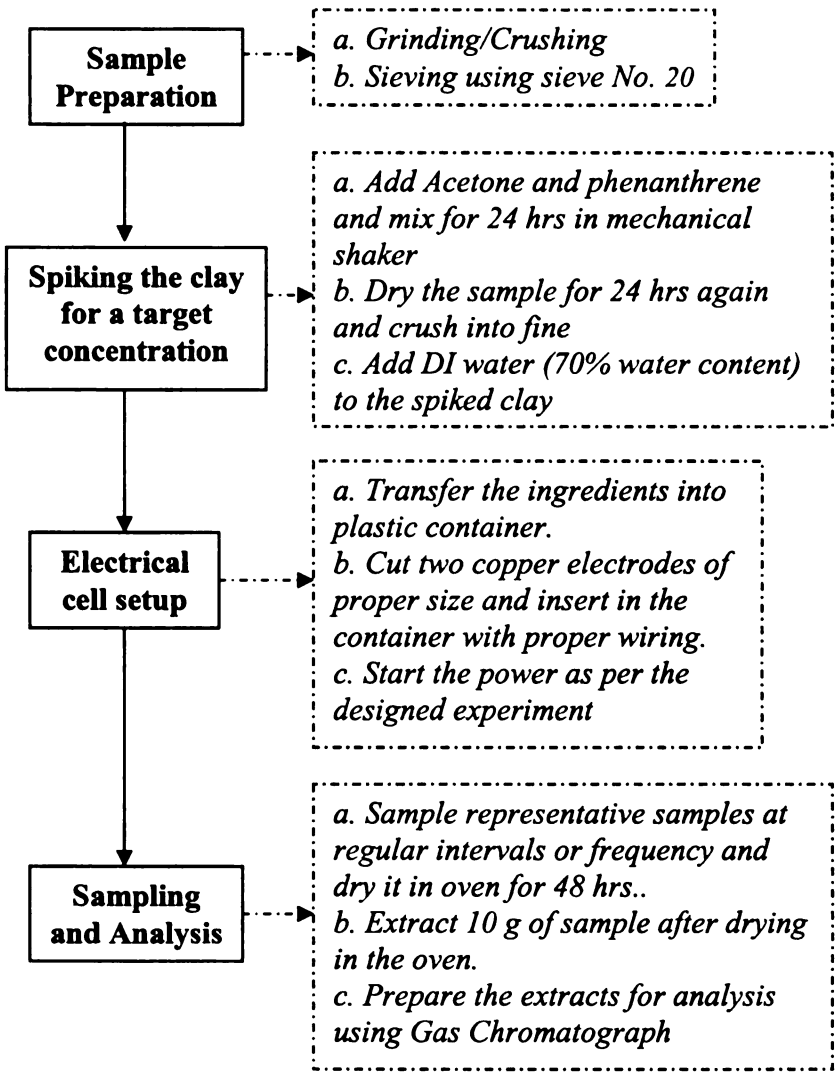


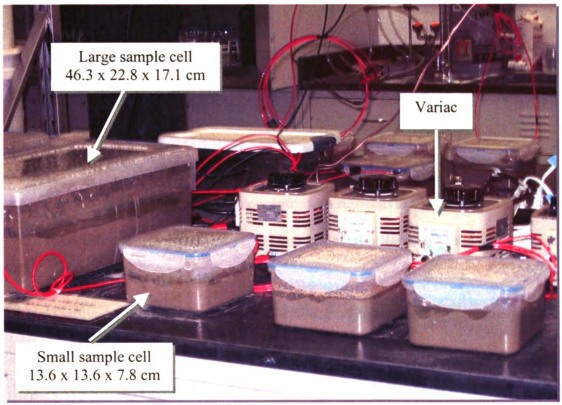
Figure 3-1: Overall Experimental Procedure

Table 3-1: Testing Program.

Name	Test ID	Target Phenanthrene Concentration (mg/kg)	AC Voltage applied (Vpeak)	Cell size (m x m x m)	Container type
Test 1	T-1	500	20	0.136 x 0.136 x 0.078	Plastic
Control 1	C-1	500	Ambient conditions	1000L	Glass Bottle
Test 2	T-2	50,000	20	0.136 x 0.136 x 0.078	Plastic
Control 2	C-2	50,000	Ambient conditions	0.136 x 0.136 x 0.078	Plastic
Test 3	T-3	500	70	4.63 x 2.28 x 1.71	Plastic
Control 3	C-3	500	At 70 °C in temperature chamber	2000 L	Glass Bottle
Test 4	T-4	50,000	35	0.136 x 0.136 x 0.078	Plastic
Control 4	C-4	50,000	At 70 °C in temperature chamber	0.136 x 0.136 x 0.078	Plastic

Notes: 1) The frequency of the input AC voltage was 60 Hz.

2) Two cell sizes were selected as per the second last column.



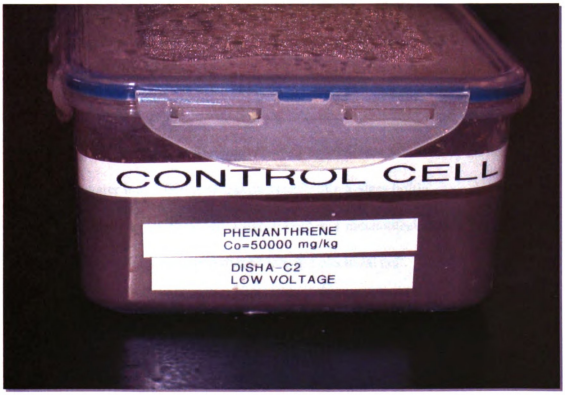


Figure 3-2: Pictures of Experimental Test cells

3.1.2.2 Spiking the sample

The sample was spiked for two different concentrations: 500 mg/kg and 50,000 mg/kg of Phenanthrene in dry clay. Following procedure was followed to spike the sample.

1) Weighed 0.5 g and 50 g of Phenanthrene in a glass vial to achieve 500 and 50,000 mg/kg of spiked target concentrations respectively.
2) Phenanthrene was dissolved in just enough amount (approximately 100 ml) of acetone and mixed thoroughly.
3) Dissolved solution was added into 1,000 g of oven-dried processed soil in a glass bottle.
4) Acetone was added into the soil until the whole sample was in a slurry form and then mixed properly using a mechanical shaker for 24 hrs.
5) The mixture was left to air dry in an aluminum foil tray under an exhaust hood for approximately 24 hrs until acetone volatilized.
6) After drying, the sample was crushed into finer and uniform soil using a mallet.
7) A target gravimetric water content equal to 70% was achieved by adding 700 ml of DI water into 1,000 g of spiked sample into a glass bottle.
8) The spiked clay with added water is kept in a mechanical shaker for 24 hrs and then the contents were transferred into the electrical cell.

Table 3-2: Index Properties of MSU Blue Clay

Plastic Limit (PL)	24 %
Liquid Limit (LL)	49.5 %
Plasticity Index (P.I.)	25.5 %

3.1.3 Electrolytic Cell Setup

After transferring the contents into the plastic container, the cell was connected to the power source using the following procedure.

1) Copper electrodes of appropriate size (depending on the size of the electrolytic cell) were cut. 190 mm x 120 mm was the size of electrodes for the larger cell and 110 mm x 65 mm size electrodes were cut for the smaller cell. The initial thickness of the electrodes was 2 mm. The electrodes were inserted at both ends of the container with a space of about 2 cm from the walls and the cell. The spacing between the electrodes was 37 cm in the larger cell and 10.5 cm in the smaller cell.
2) The electrodes were connected to two cables (red & black) and were connected to a variac.
3) The variac was set to a desired voltage output as per Table 3-1.
4) Plugged in the variac into the wall power outlet (120 VAC) to get the experiment started.
5) Initial samples were collected at time t=0. Details for analysis and sampling are discussed in the next section. As the experiment progressed, samples were collected at a predetermined frequency to evaluate potential changes in the phenanthrene concentration.

3.2 SAMPLING AND ANALYTICAL METHODS

Presented below is a list of materials and equipment used during the sampling and analysis.

Instruments/Equipments: Balance, Hot Air oven @ 40 °C, Transformers, couple of wires, clamps, switches, and Accelerated Solvent Extractor and Gas Chromatograph for extraction and analysis

Chemicals and Materials: Phenanthrene (98% pure), Acetone, Dichloromethane, crucibles, steel extraction cell kit, a pestle, filter paper, Diatomaceous earth, Ottawa Sand, beaker, 2 syringes, small GC vials, large glass extraction vials, etc. Figure 3-3 to 3-8 displays pictures of some of the instruments and equipments used during the experiment.

3.2.1 Sampling Frequency

Sampling frequency varied for each experiment. However, typically test cells were sampled at a frequency of 0, 2, 4, 8, and 15 and 30 and then after every 2 weeks for experiment for Test T-3, T-4, C-3. The second and fourth day sampling period was skipped because previous experiments indicated no appreciable change in concentration during this period. The sampling was done at t = 0 before starting the experiment to establish the average initial concentration.

3.2.2 Sampling Method

Crucibles were cleaned with Alconox detergent and DI water before any sampling event. Also, before any type of monitoring or sampling event, the power was turned off. Samples were collected from anode, cathode and middle of the test cell. This was followed by thoroughly mixing the sample in the test cell. All the samples were kept in the oven for drying purpose for 48 hrs at 40 °C and collecting three more samples at random locations. Phenanthrene extraction was followed after oven drying.

Figure 3-3: Hot Air Oven

Figure 3-4: Samples kept for Drying in Hot Air Oven

Figure 3-5: Steel Extraction Cells

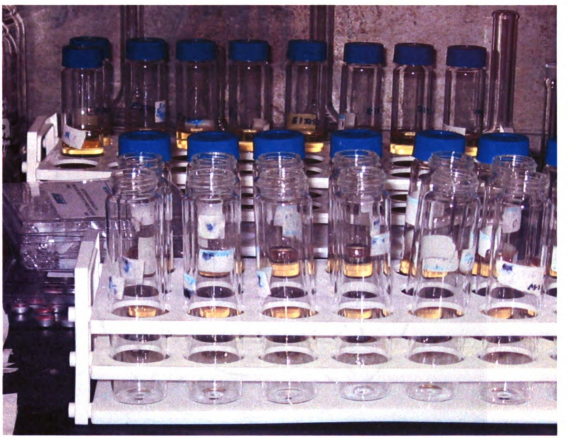


Figure 3-6: Glass Vials Used for Extraction

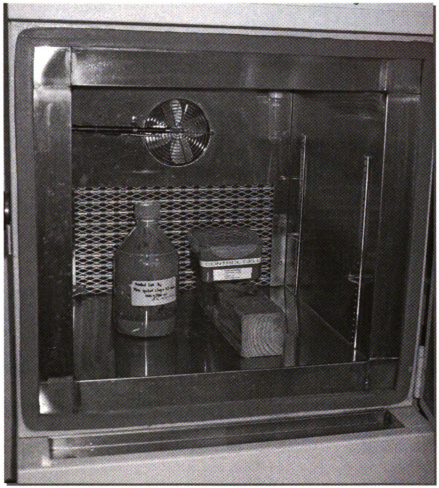


Figure 3-7: Interior of the Temperature Chamber

Figure 3-8: Variacs Used for the Test Cells

3.2.3 Extracting the Sample

In order to analyze the concentration of phenanthrene using gas chromatography, phenanthrene had to be extracted in a solution phase. Extraction of phenanthrene from the clay was achieved using the Dionex Accelerated solvent extractor (ASE) Model No. 200 as shown in the Figure 3-9.

The oven-dried sample was crushed lightly with a pestle. Ten grams of the sample was weighed in a crucible. After that, 2.5 g of diatomaceous earth was added to the sample to remove any moisture, if present. The sample was mixed properly using a spatula. The mixture was poured into the steel extraction cell of the ASE. A filter paper (GF/B filter size 19.8 mm, Whatman Glass fiber fiter) was kept at the bottom of the cell before adding the sample. The extraction cell was filled with Ottawa sand until the cell was full. The lid of the cell was tightly closed. When the extraction cells got ready, glass vials (same in number as the extraction cells) were pre-weighed and kept in the lower compartment of ASE. The extraction cells that were prepared were kept in the upper compartment of ASE. Acetone and Dichloromethane was used as solvents to extract phenanthrene from the clay in an aqueous phase. Once the extraction was done, the glass vials that are filled with sample extract are weighed. These samples were stored in a refrigerator if they were not analyzed right away.

3.2.4 Preparing the Stock Solution

The stock solution was prepared before analyzing the sample extract. The stock solution was used as standard for the GC. The method to prepare stock solution for both 500 and 50,000 mg/kg of phenanthrene concentration is described below.

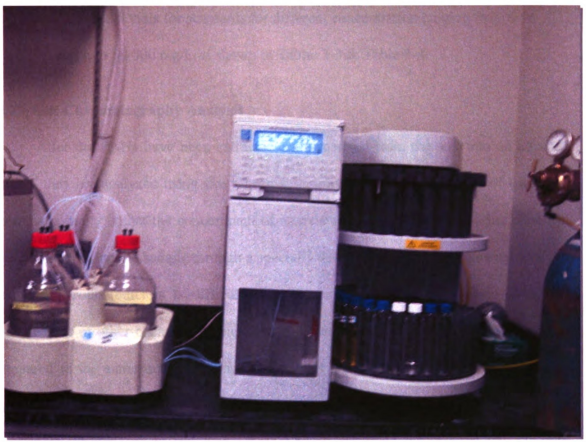


Figure 3-9: Dionex Accelerated Solvent Extractor Model No. 200

- Added 0.125 g of Phenanthrene to 25 ml solvent (acetone + dichloromethane at 1:1 ratio by volume) to produce 5,000 ppm phenanthrene solution.
- Added 1.25 g of Phenanthrene to 25 ml solvent (acetone + dichloromethane at 1:1 ratio by volume) to produce 50,000 ppm phenanthrene solution.
- Prepared 5 vials for standards for different concentration ranging from 9.98 mg/L to 50,000 mg/L as shown in Table: 3-3 & Table 3-4.

3.2.5 Gas Chromatography Analysis

After the PAHs have been extracted and separated from the soil into an aqueous phase, they are analyzed using Gas Chromatography. The main advantage of using gas chromatography is that the contaminant of interest is separated from the other chemical species by passing the sample through a specially designed column. Instrumental analysis using spectrophotometers is difficult since extreme care must be used to avoid the interference of other chemical species, and the standards and calibration curves must be prepared in the same manner as the regular tests are to be run (Sawyer and McCarty 1978).

Gas chromatography involves a sample being vaporized and injected onto the head of the chromatographic column. The sample is transported through the column by the flow of inert, gaseous mobile phase. The column itself contains a liquid stationary phase which is adsorbed onto the surface of an inert solid. Nitrogen is used as the carrier gas which is chemically inert. The carrier gas system also includes a molecular sieve to remove water and other impurities.

Table 3-3: Preparation of Standard Solutions for 5,000 ppm Phenanthrene Solution

Concentration (mg/L)	**Volume of phenanthrene solution (stock in μL)**	**Volume of acetone (ml)**
9.98	6	3
19.92	12	3
49.5	30	3
99.8	60	3
192.31	80	2

Table 3-4: Preparation of Standard Solution of 50,000 ppm Phenanthrene Solution

Concentration (mg/L)	**Volume of phenanthrene solution (stock in mL)**	**Volume of acetone (ml)**
1,000	0.5 (5,000 mg/L stock)	2
5,000	Stock	5,000 ppm Stock
10,000	0.5 (50,000 mg/L stock)	2
16,666.67	1 (50,000 mg/L stock)	2
21,428.57	1.5 (50,000 mg/L stock)	2
50,000	Stock	50,000 ppm Stock

The injector contains a heated chamber containing a glass liner into which the sample is injected through the septum. The carrier gas enters the chamber and can leave by three routes (when the injector is in split mode). The sample vaporizes to form a mixture of carrier gas, vaporized solvent and vaporized solutes. A proportion of this mixture passes onto the column, but most exits through the split outlet. The septum purge outlet prevents septum bleed components from entering the column.

The effluent from the column is mixed with hydrogen and air, and ignited. Organic compounds burning in the flame produce ions and electrons which can conduct electricity through the flame. A large electrical potential is applied at the burner tip, a collector electrode is located above the flame. The current resulting from the pyrolysis of any organic compounds is measured. Flame Ionization Detectors (FIDs) are mass sensitive rather than concentration sensitive; this gives the advantage that any changes in mobile phase flow rate do not affect the detector's response. The FID is a useful general detector for the analysis of organic compounds. It has high sensitivity, a large linear response range, and low noise. It is also robust and easy to use, however, it destroys the sample. Figure 3-10 shows the Gas Chromatograph used during the experiments for this project. The make and model no. of Gas Chromatograph used during the project was Perkin Elmer and Autosystem 610N0081901 respectively. The oven temperature of Gas Chromatograph was maintained to 150 degree Celsius at 0 min and increase of 40 degrees per minute to 250 degree Celsius. The maximum temperature of oven was maintained at 350 °C. The carrier gas, i.e. nitrogen gas flow rate was maintained to 10 ml/min during the analysis of the phenanthrene.

Figure 3-10: Gas Chromatograph Instrument

3.3 QUALITY CONTROL OF THE EXPERIMENT

During the course of the experiments, appropriate quality control procedure including replicate samples and instrument calibration were followed. The calibration standards for the phenanthrene analyses by GC were prepared for two different concentration ranges, and each analysis was calibrated with at least 5 standards ranging from 9 mg/L to 192 mg/L for 5,000 ppm phenanthrene solution and at least 6 standards ranging from 1,000 to 50,000 mg/L for 50,000 ppm phenanthrene solution. The linearity of the calibration graph was always checked to make sure that the regression coefficient was close to one.

CHAPTER 4

RESULTS AND DISCUSSION

The key objective was to evaluate if phenanthrene, a PAH, can be broken down (decomposed) using an application of alternation current. This objective was accomplished by carrying out experiments listed in Table 4-1.

The key hypothesis tested in this project was alternating current when passed through a clay soil generates oxidation reactions due to capacitance of clay-water double layer system. Such reactions are caused by electrons supplied and released due to the charging and discharging of the clay-water double layer system during the positive and negative cycles of an AC. These reactions can breakdown PAHs. Table 4-1 below presents a summary of the tests conducted.

4.1 AVERAGE PHENANTHRENE CONCENTRATION

Extraction efficiency was measured by spiking 20 g of clay with 0.001 g of phenanthrene to achieve a target concentration of 500 mg/kg. Acetone was used to dissolve phenanthrene and then mixed with the soil thoroughly in a crucible. The sample was analyzed following the same method as described in Section 3.2.3 to 3.2.5 for extraction and analysis of phenanthrene. The extraction efficiency ranged from 83 % to 99 %.

The concentration of phenanthrene measured in the clay for the tests presented in Table 4-1 is presented in this section. Average phenanthrene concentration of the test samples and their controls was measured is shown in Table 4-2. Average Phenanthrene concentration was represented by analysis of 6 samples collected from each test cells and 3 samples from the control cells. The error bars shown in the plots represent the

Table 4-1: Summary of Tests

Test	Initial Concentration (C_0, mg/kg)	Test duration	V_{peak}	V_{rms}	Z_{avg} (Ω)	$I_{rms} = V_{rms}/Z_{avg}$ (mA)	Sample size m x m x m
T-1	500	60	20	14.1	140	100	0.136 x 0.136 x 0.078
T-2	50,000	60	20	14.1	215	65	0.136 x 0.136 x 0.078
T-3	500	160	70	49.4	245	200	4.63 x 2.28 x 1.71
T-4	50,000	60	35	24.7	4,120	6	0.136 x 0.136 x 0.078

Table 4-2: Average Phenanthrene Concentration in Test and Control Cells

Test ID	Test / Sample description	Target Concentration (C_0, mg/kg)	Test duration	Average Phenanthrene Concentration (mg/kg)					
				t = 0 day	t = 5 day	t = 10 day	t = 15 day	t = 30 day	t = 60 day
T-1	Low voltage	500	60	322	263	345	334	327	312
C-1	Control for T-1	500	100	413	418	386	--	351	329
T-2	Low Voltage	50,000	60	47,972	41,644	51,687	51,936	41,879	47,512
C-2	Control for T-2	50,000	60	49,671	49,601	58,358	55,381	57,274	54,142
T-3	High Voltage	500	160	412	400	408	372	374	345
C-3	Control for T-3	500	120	427	381	447	393	364	323
T-4	High Voltage	50,000	60	38,748	40,440	53,045	41,745	47,931	47,141
C-4	Control for T-4	50,000	60	36,572	49,496	46,604	54,781	51,586	50,461

Note: Frequency f equal to 60 Hz used for all tests listed above

maximum and minimum range of the phenanthrene concentration in the experimental cells.

4.1.1 V_{peak} = 20 V

4.1.1.1 Target concentration equal to 500 mg/kg

Test T-1 was carried out for a total duration of 60 days. Figure 4-1 shows the graph of average phenanthrene concentration versus Time for Test T-1. Control C-1 for the test was kept in the ambient environment without applying any electricity in a 1,000 L glass bottle. There is no significant difference between the control and the test cell in the concentration of phenanthrene.

4.1.1.2 Target concentration equal to 50,000 mg/kg

Test T-2 was carried out for a total duration of 60 days. Figure 4-2 shows the graph of average phenanthrene concentration versus Time for Test T-2. A control C-2 for test was kept in the ambient environment without applying any electricity in a similar type of plastic container. There is no significant difference between the control and the test cell in the concentration of phenanthrene.

4.1.2 V_{peak} = 70 V and 35V

4.1.2.1 Target concentration equal to 500 mg/kg

Test T-3 was carried out at a peak to peak voltage of 70 V for duration of 160 days. Figure 4-3 shows the graph of average phenanthrene concentration versus time for Test T-3. Control C-3 for the test was kept in the temperature chamber at 70 ^{o}C to simulate the elevated temperature conditions without applying any electricity in a 2,000 L glass bottle. There is some decrease in the phenanthrene concentration due to the

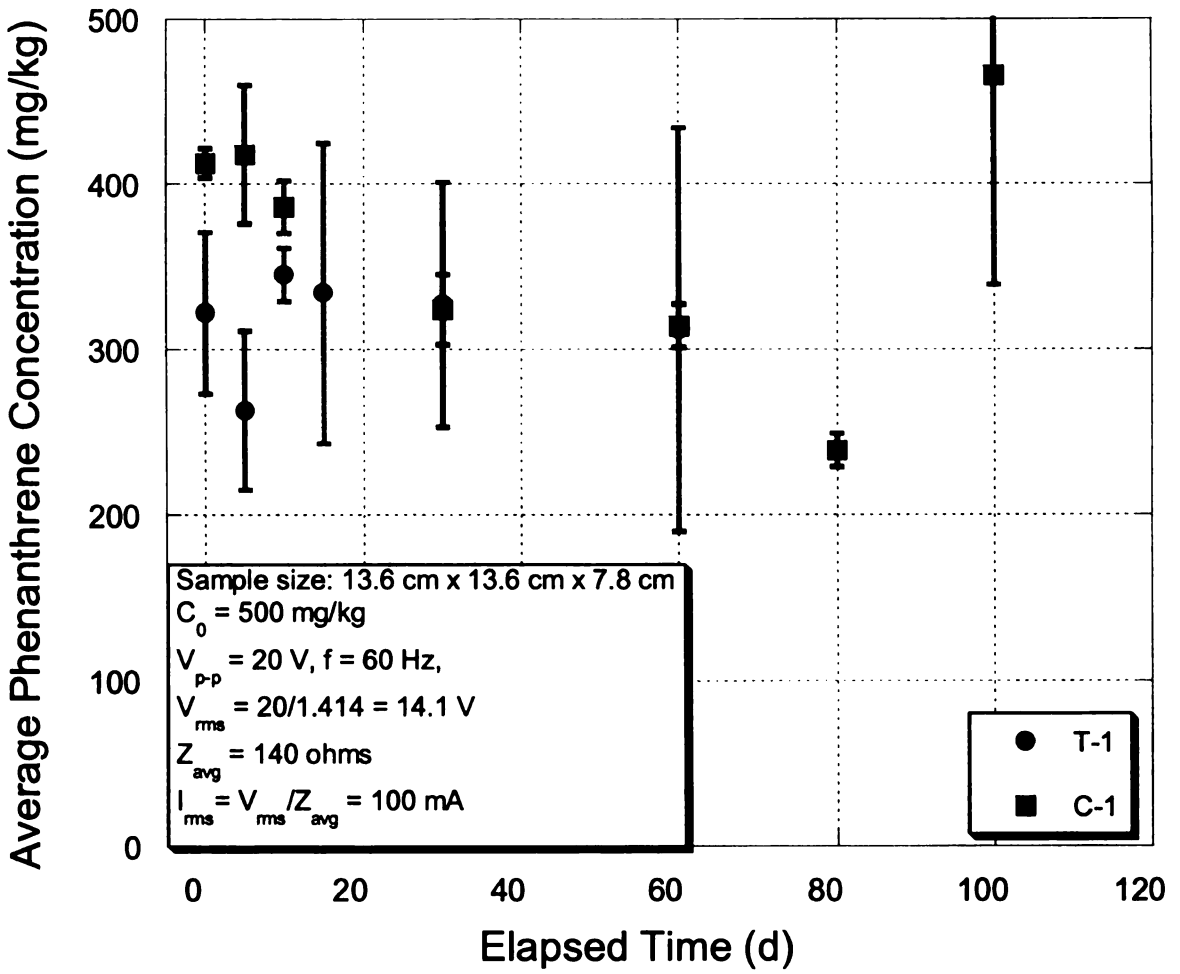


Figure 4-1: Average Phenanthrene Concentration vs. Time for T-1 and C-1

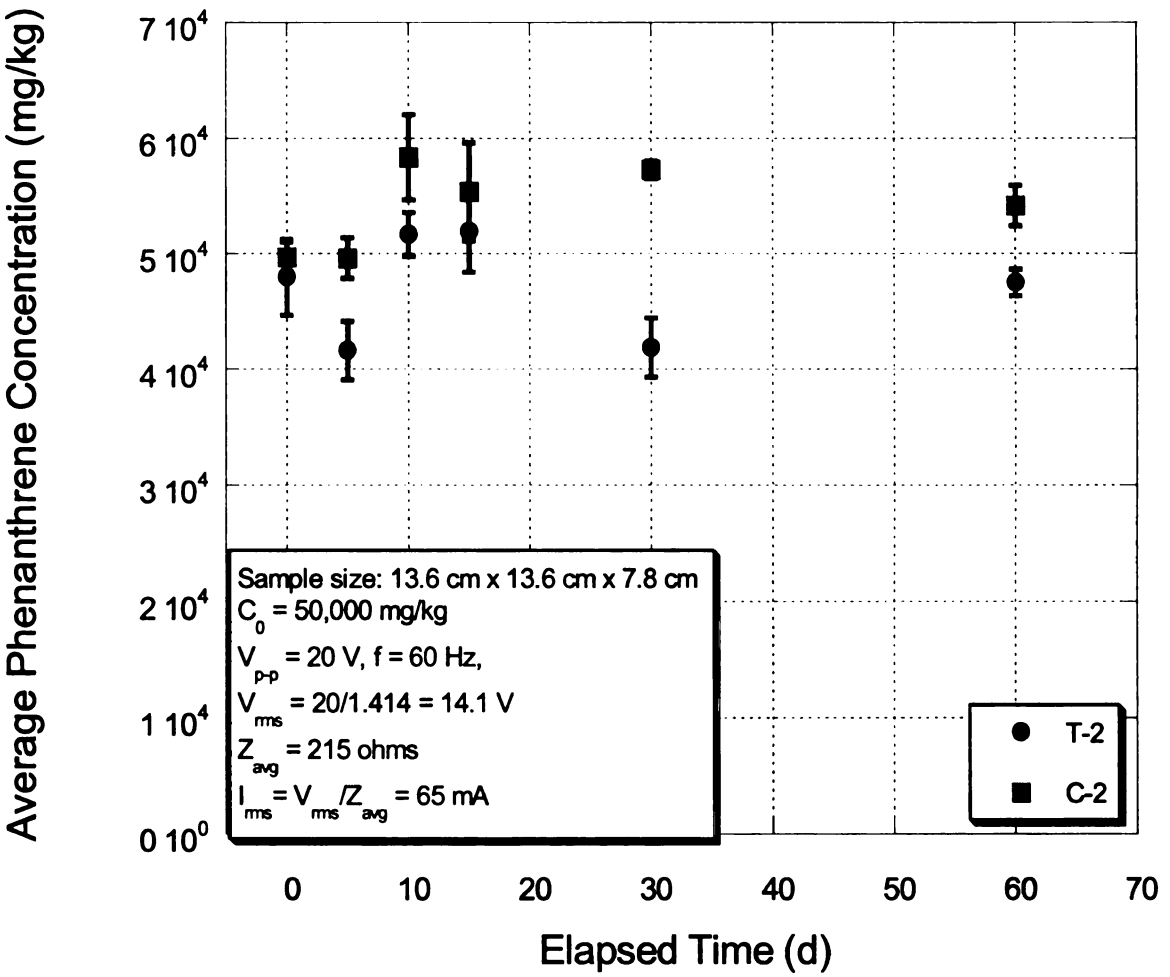


Figure 4-2: Average Phenanthrene Concentration vs. Time for T-2 and C-2

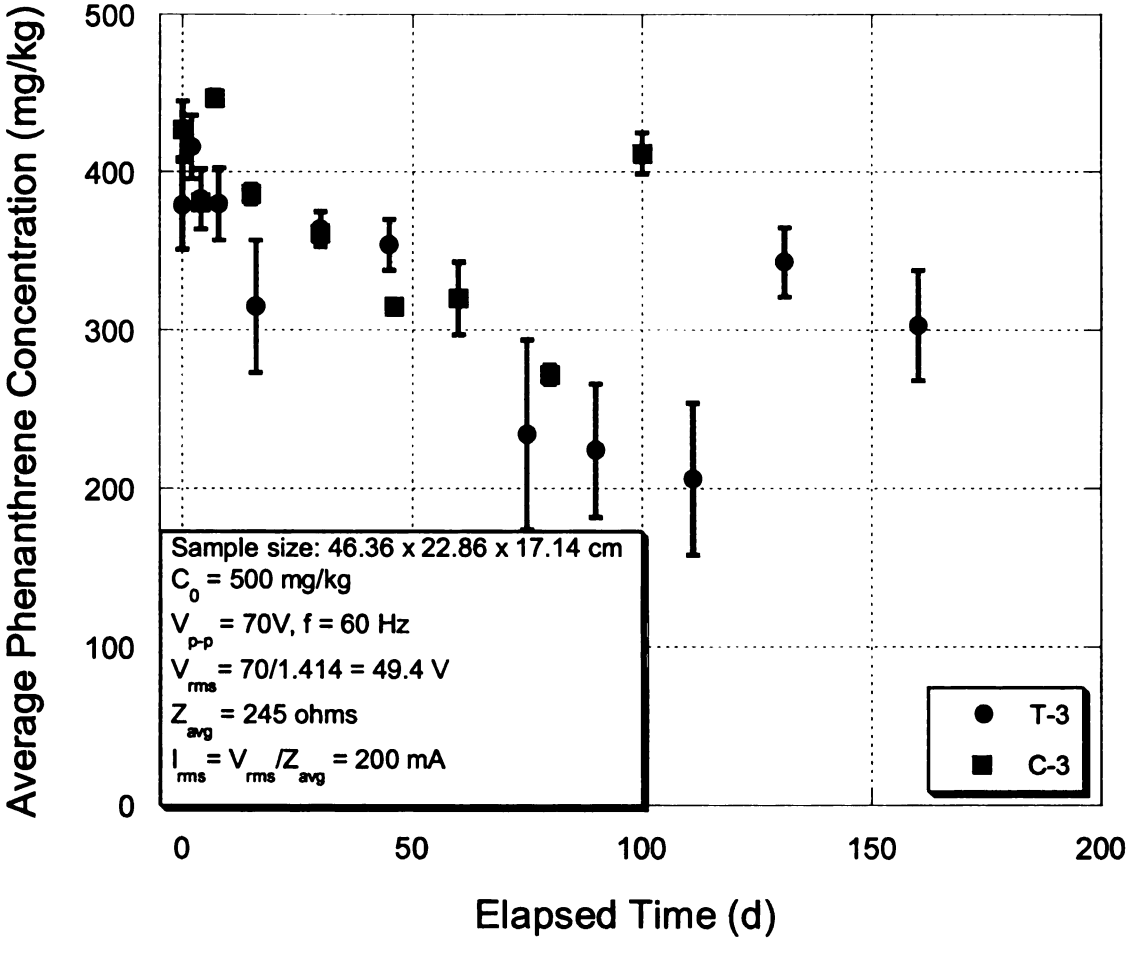


Figure 4-3: Average Phenanthrene Concentration vs. Time for T-3 and C-3

application of an alternating current in the test cell. However, the control also shows a similar decrease. The decrease in phenanthrene concentration in both the test and control cells may be due to biological activity resulting in biodegradation.

4.1.2.2 Target concentration equal to 50,000 mg/kg

Test T-4 was carried out for a peak to peak voltage of 35 V for duration of 60 days. Figure 4-4 shows the graph of average phenanthrene concentration versus time for Test T-4. Control C-4 for the test was kept in a temperature chamber at 70 °C to simulate the high temperature conditions without applying any electricity in a similar plastic container. There is no significant difference between the control and the test cell in the concentration of phenanthrene.

4.2 EFFECT on pH

To minimize extreme pH changes, which occur when a DC is applied, an AC is used in these tests. Copper electrode plates were used in the experiments. Figure 4-5 presents a plot of pH versus normalized distance from Anode presented by Reddy and Saichek (2004) to show the effect on pH due to continuous application of DC electrical signal on the sample. The pH in the soil was measured along the length of the soil sample in this study. The pH was observed in the range of 2.5 to 5.5 at the end of the test. According to Reddy and Saichek (2004) low pH values caused a minor increase in electro osmotic flow due to higher dissolution rate. In this study, the average pH values ranged from 7.5 to 6.0 which show a relatively small variation in pH when an AC is applied.

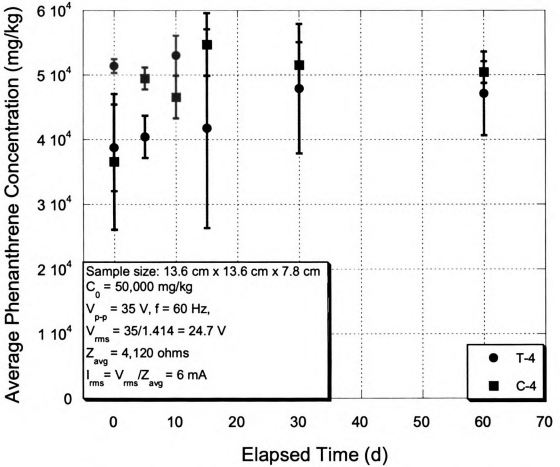


Figure 4-4: Average Phenanthrene Concentration vs. Time for T-4 and C-4

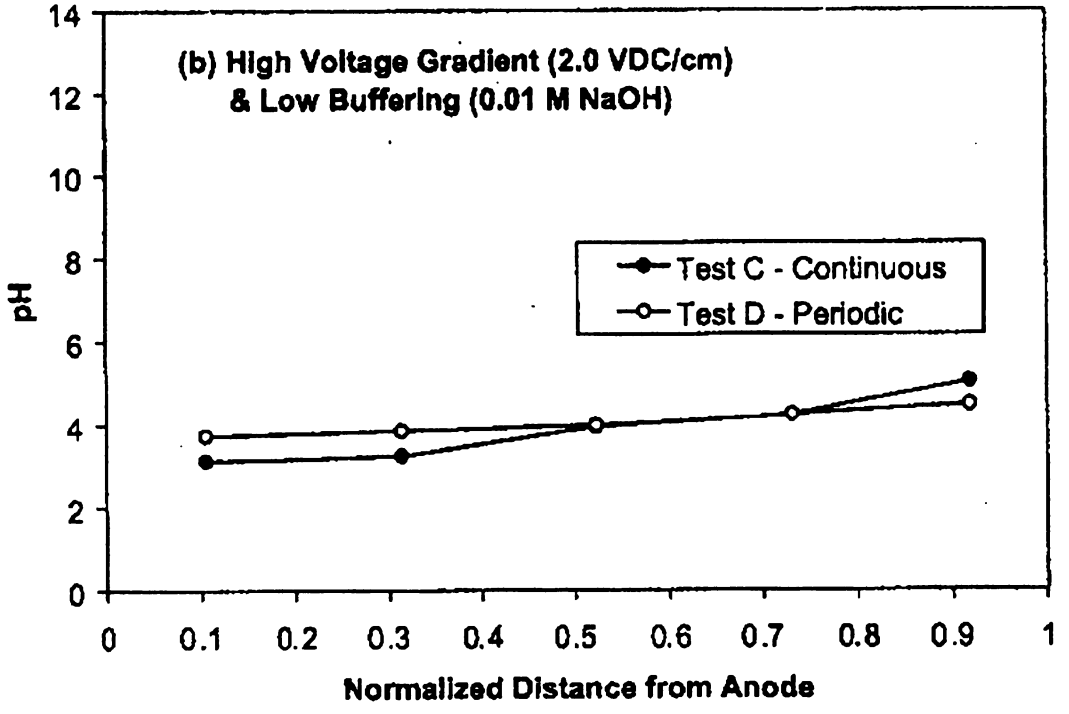


Figure 4-5: Effect on pH when DC is applied. (Adapted from Reddy and Saichek 2004)

Table 4-3 shows a summary of the pH values at anode, center and cathode region for the tests conducted. Due to the electrolysis reactions occurring at anode and cathode, H^+ ion is formed at anode which should result in a decrease in the pH at anode and increase in pH at cathode due to formation of OH^- ions. The results show that pH at anode decreases faster with time, indicating formation of H^+ ion at anode and faster movement of acid front because of high mobility of H^+ as compared to OH^- ions (Acar et al. 1991). However, the pH does not increase near the cathode significantly due to less mobility of OH^- ion and because the direction of electro-osmotic flow is generally towards the cathode. The pH values in the middle of the cell show that soil is gradually becoming acidic throughout most of its volumes, except near to the cathode. (Reddy et al. 1997).

Figures 4-6, 4-7, 4-8 and 4-10 show pH versus time for Test cell T-1, T-2, T-3 and T-4 respectively. The pulsating AC is connected to anode and neutral is connected to cathode. Figure 4-6 shows that pH at cathode decreased initially but then gradually started increasing and the pH at anode started decreasing gradually. However, it was observed that pH at cathode was always higher at all the measurement points as compared to pH at anode.

Figure 4-7 shows pH versus time for Test cell T-2. Similar high values of pH at cathode can be observed at the end of the test with a decrease in pH from 10.6 to 7.1 at anode. pH values in middle of the soil shows decrease in pH gradually after many fluctuations indicating acidic characteristics throughout the volume of soil.

Table 4-3: pH and Temperature in Test Cells

Test	pH/Temp	Location	t = 0 day	t = 5 day	t = 10 day	t = 15 day	t = 30 day	t = 60 day
T – 1	pH	Anode	7.0	7.4	7.2	6.3	6.1	6.6
		Mid	7.6	7.7	7.1	7.0	5.8	6.1
		Cathode	7.4	7.1	6.4	5.9	6.3	6.3
	Temp (°C)	Anode	22.3	26.5	28.4	27.1	26.8	26.6
		Mid	22.4	27.2	28.3	27.6	26.8	25
		Cathode	22.2	26.9	28.1	27.4	26.6	24
T – 2	pH	Anode	7.4	6.7	8.4	6.4	6.0	5.5
		Mid	7.8	7.5	7.8	6.3	6.2	5.4
		Cathode	7.7	7.3	7.7	5.6	5.9	5.6
	Temp (°C)	Anode	23.1	27.4	26.4	25.5	25.5	23.7
		Mid	23.2	27.9	26	26	25.4	24.4
		Cathode	22.5	27.5	25.7	25.8	25.3	23.4
T – 3	pH	Anode	10.6	9.1	8.5	9.6	8.4	7.8
		Mid	8.7	9.3	9.2	8.8	8.3	8.3
		Cathode	7.8	9.4	9.2	9.4	8.6	8.2
	Temp (°C)	Anode	22.9	57.8	52.6	47.9	53.1	47.4
		Mid	23.0	59.2	61.1	58.6	54.7	59
		Cathode	22.7	57.7	52.4	52.2	49.2	48
T – 4	pH	Anode	8.9	6.8	7.5	7. 0	6.0	6.4
		Mid	9.0	8.0	8.0	7.8	7.0	6.9
		Cathode	9	6.6	7.0	7.2	6.9	6.5
	Temp (°C)	Anode	24.5	42.5	38.6	37.0	37.9	30.4
		Mid	24.4	43	41.6	40.0	38.2	33.4
		Cathode	24.1	41.5	38.1	37.6	36.0	31.2

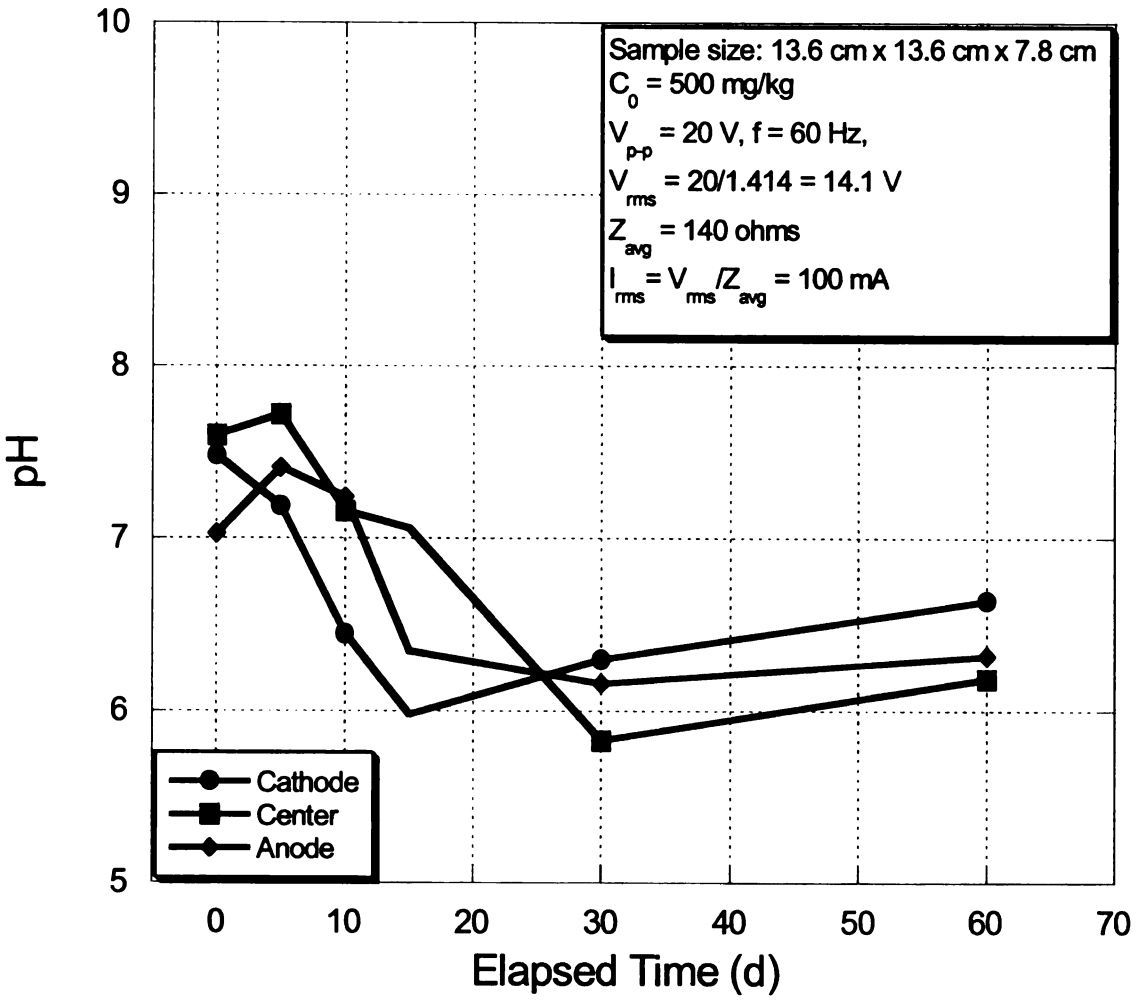


Figure 4-6: pH vs. Time for Test Cell T-1

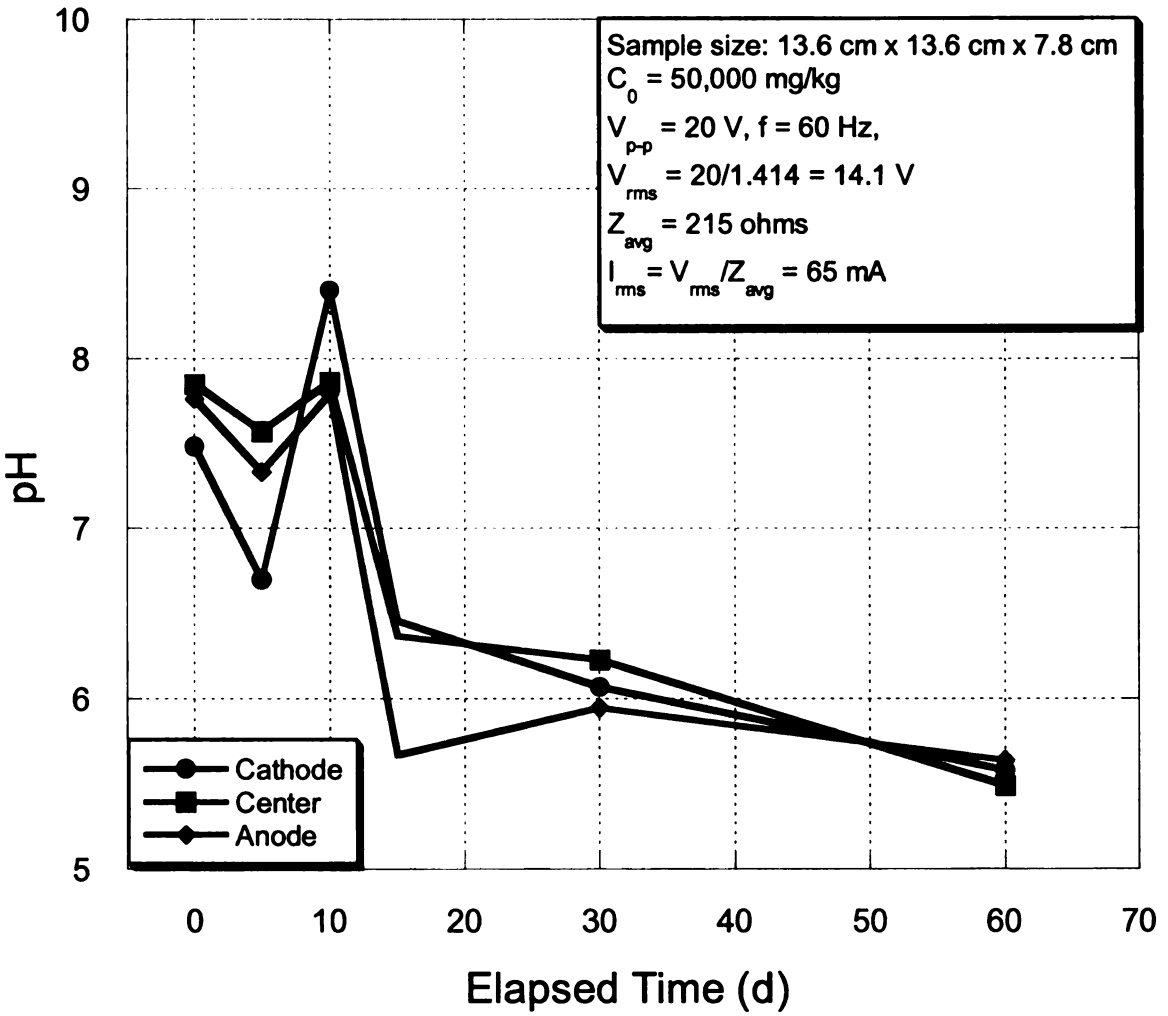


Figure 4-7: pH vs. Time for Test Cell T-2

Figure 4-8 shows pH versus time for test cell T-4. The pH values at anode show a sudden decrease in 10-day sampling event with a higher pH at cathode. Figure 4-10 shows pH versus time for test cell T-3. However, it does not conform to the expected trend. This may be due to calibration error during pH measurement. The 30-day reading shows a decrease in pH at cathode which may be due to slower base front as compared to movement of acid front towards anode.

Figure 4-9 and 4-11 show the variation of pH in the control cells C-3 and C-4 kept for higher concentration (50,000 mg/kg) in ambient environment conditions and in temperature chamber @ 70 ^{0}C, respectively. As shown in Figure 4-10, under ambient conditions the pH was observed to decrease gradually after a sudden increase in pH from 7.8 to 5.8.

4.3 EFFECT ON TEMPERATURE

Temperature can be important factor affecting the effectiveness of the remediation process. Temperature was monitored throughout the experiments. Figures 4-12, 4-13, 4-14, and 4-16 show the temperatures at anode, center and cathode of the test cells T-1, T-2, T-3 and T-4 during the term of the experiment. Figure 4-15 and 4-17 show the temperatures in control cells C-3 and C-4. All tests where an AC was applied show heating and temperature rise of the soil sample due to the Joule heating phenomenon.

The graph for cell T-1 and T-3 shows constant temperatures ranging from 22 to 28 ^{o}C at most times which is because of ambient conditions. For test cell T-2 the plot of temperature versus time displays a higher temperature range from 50 to 60 ^{o}C due to higher amount of electric current passing through the cell. The plot for test cell T-4 displays that the temperature increases up to 42 ^{o}C at a point.

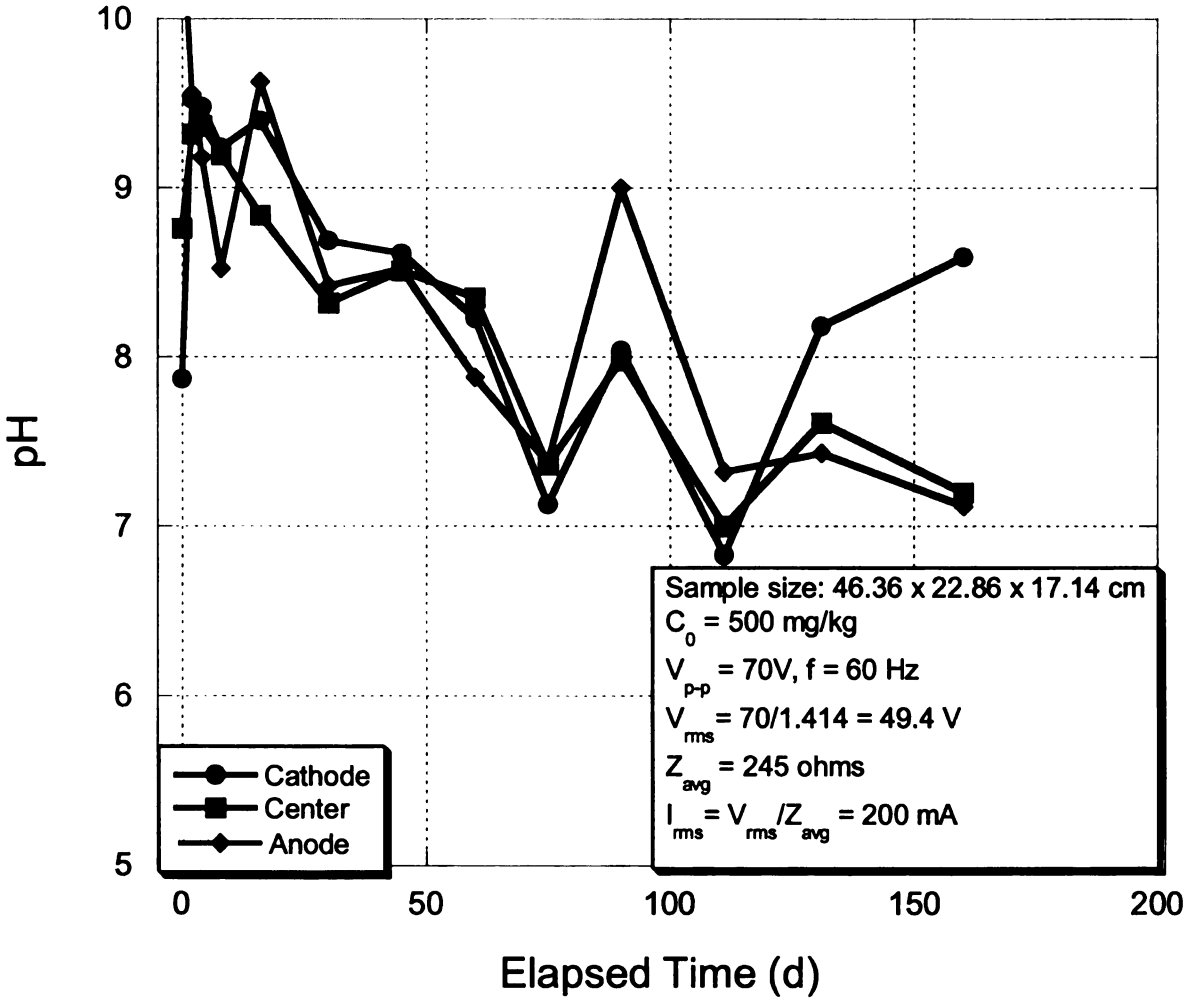


Figure 4-8: pH vs. Time for Test Cell T-3

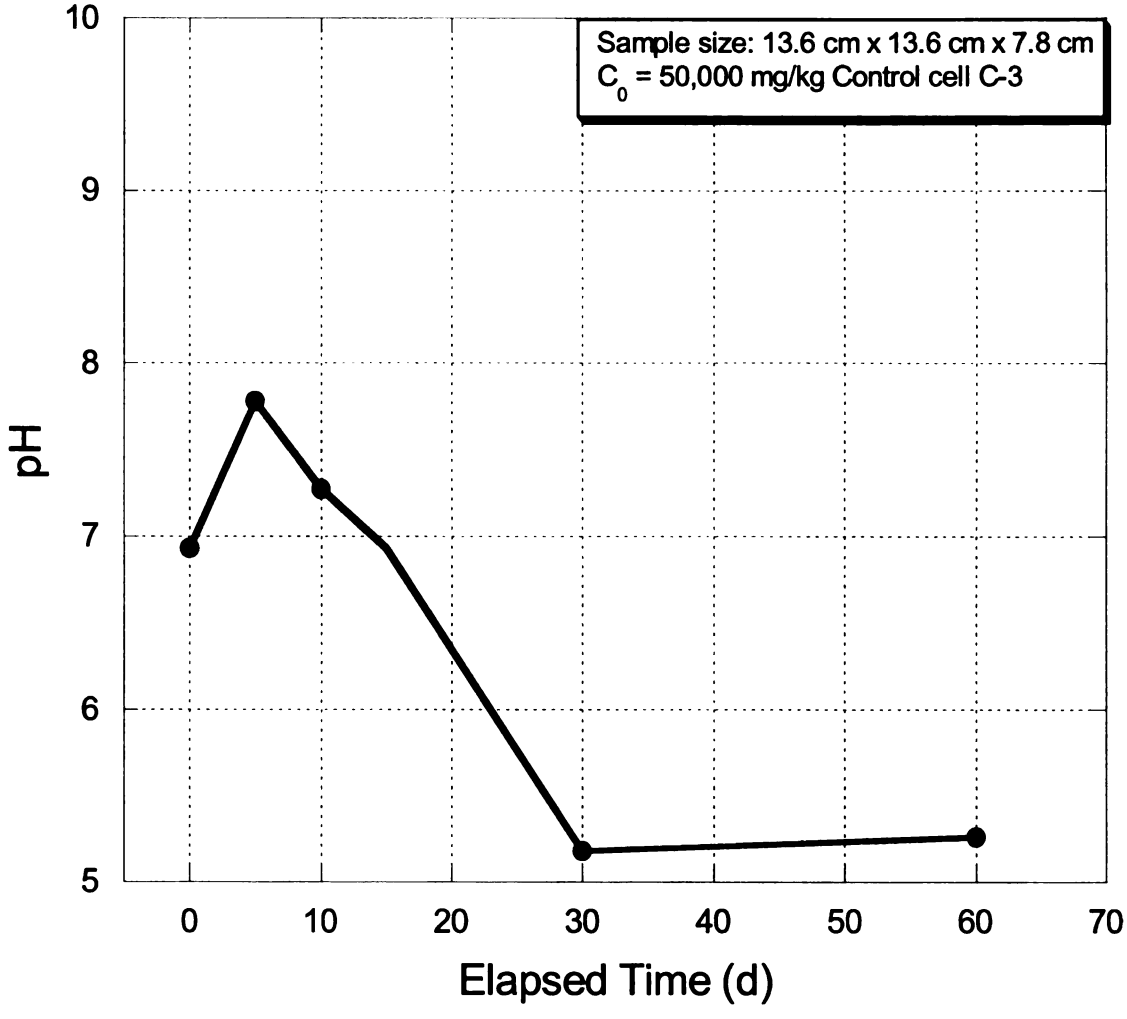


Figure 4-9: pH vs. Time for Control Cell C-3

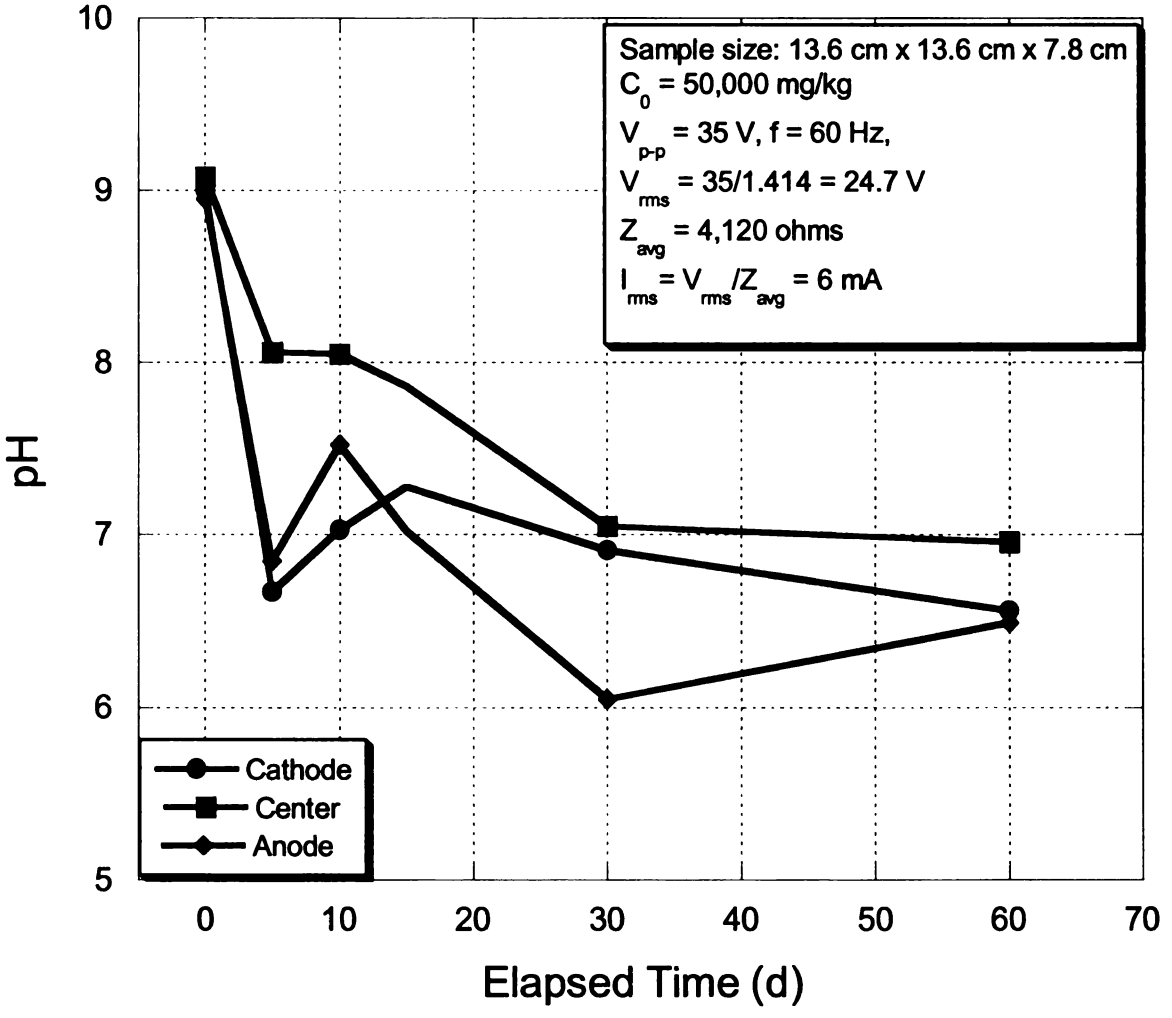


Figure 4-10: pH vs. Time for Test Cell T-4

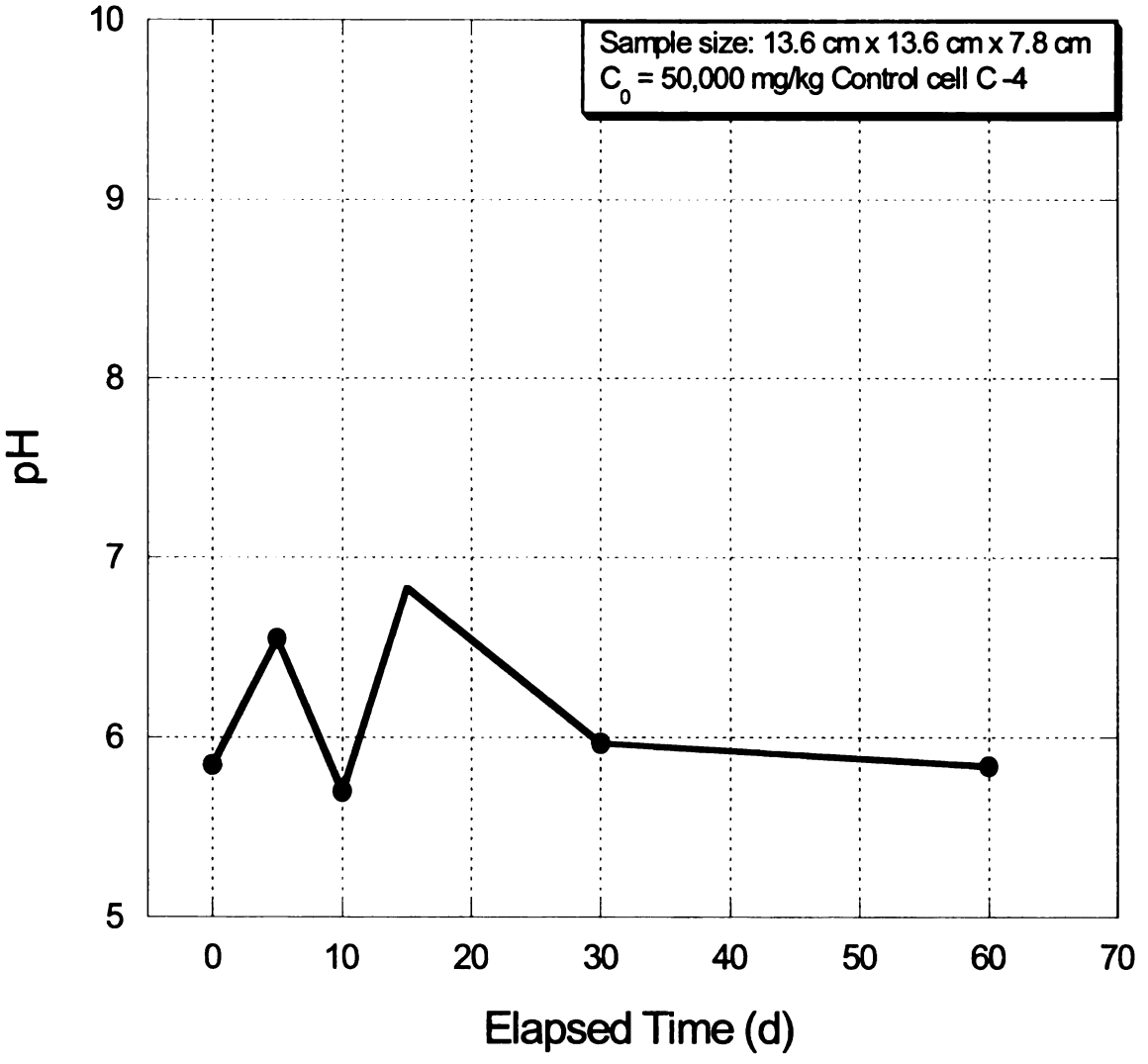


Figure 4-11: pH vs. Time for Control Cell C-4

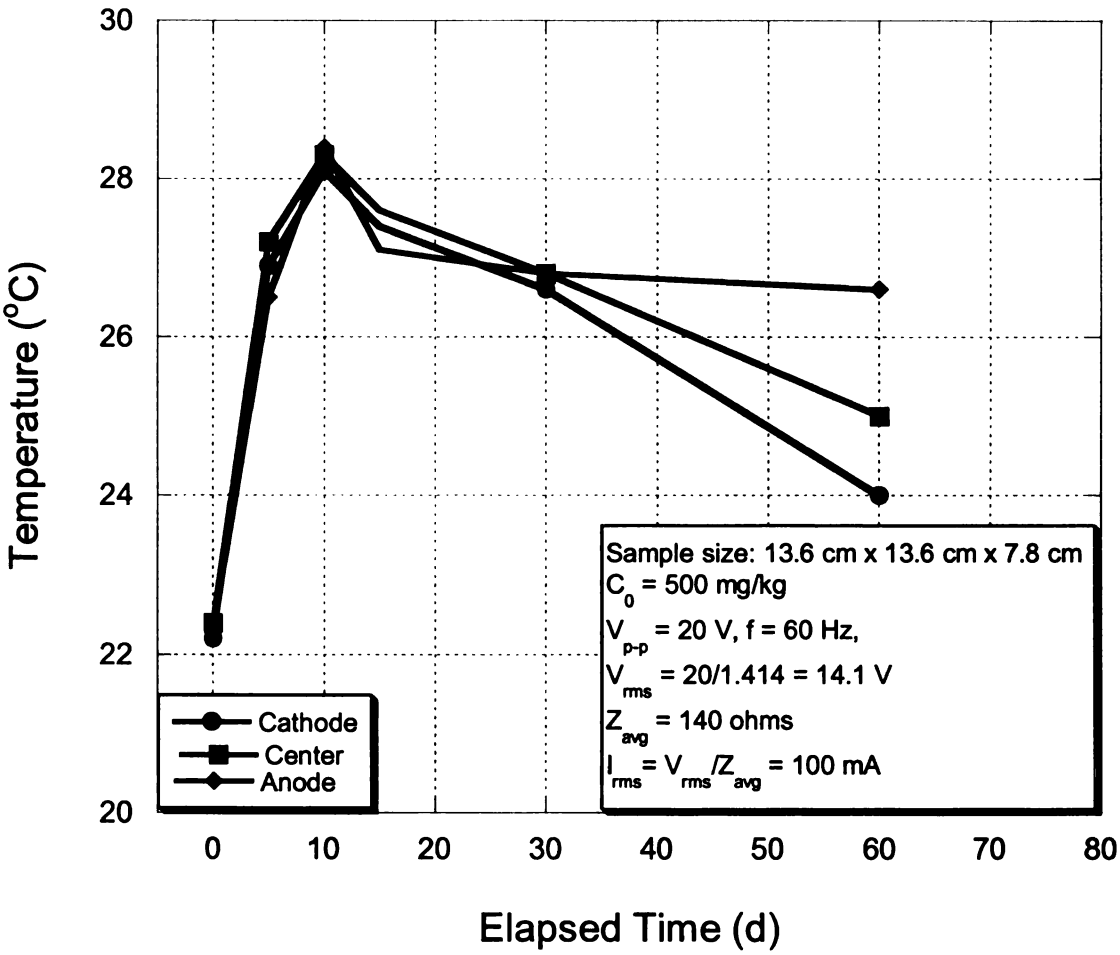


Figure 4-12: Temperature vs. Time for Test Cell T – 1

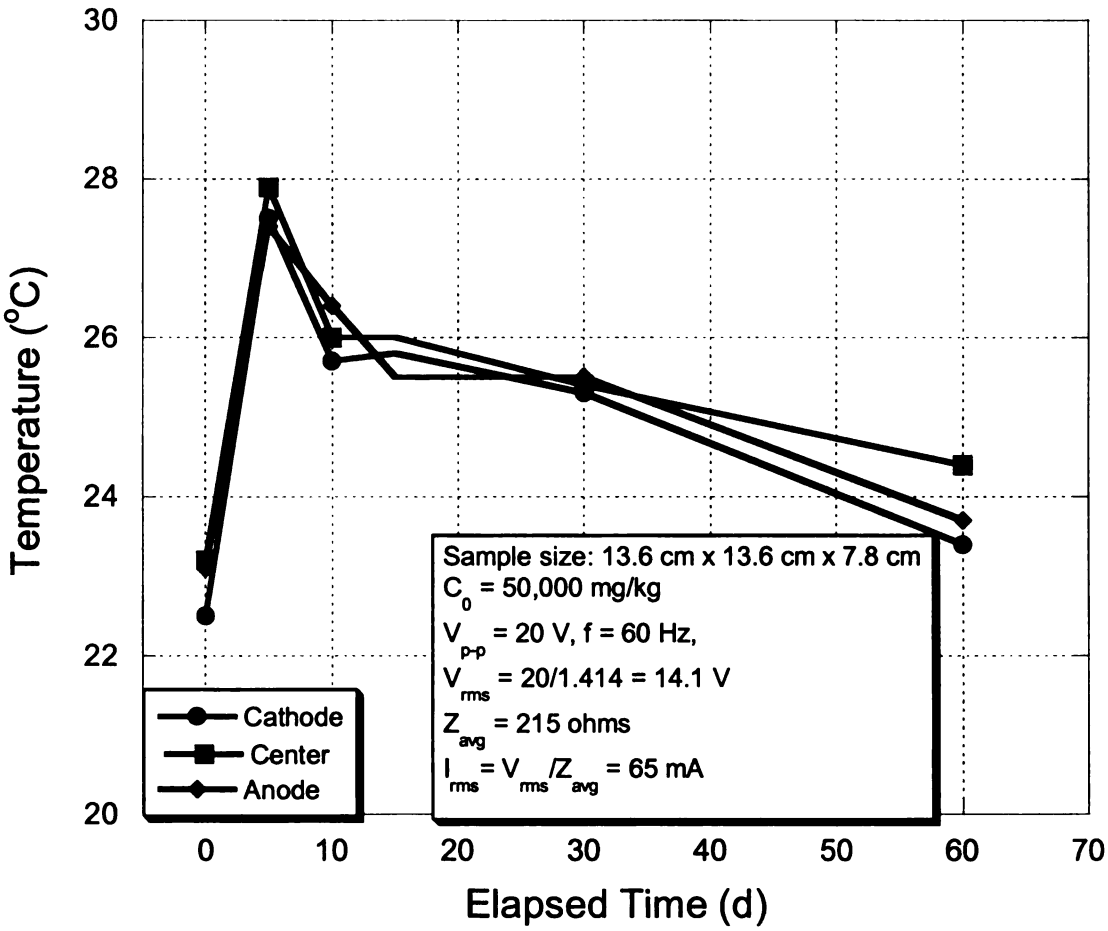


Figure 4-13: Temperature vs. Time for Test Cell T – 2

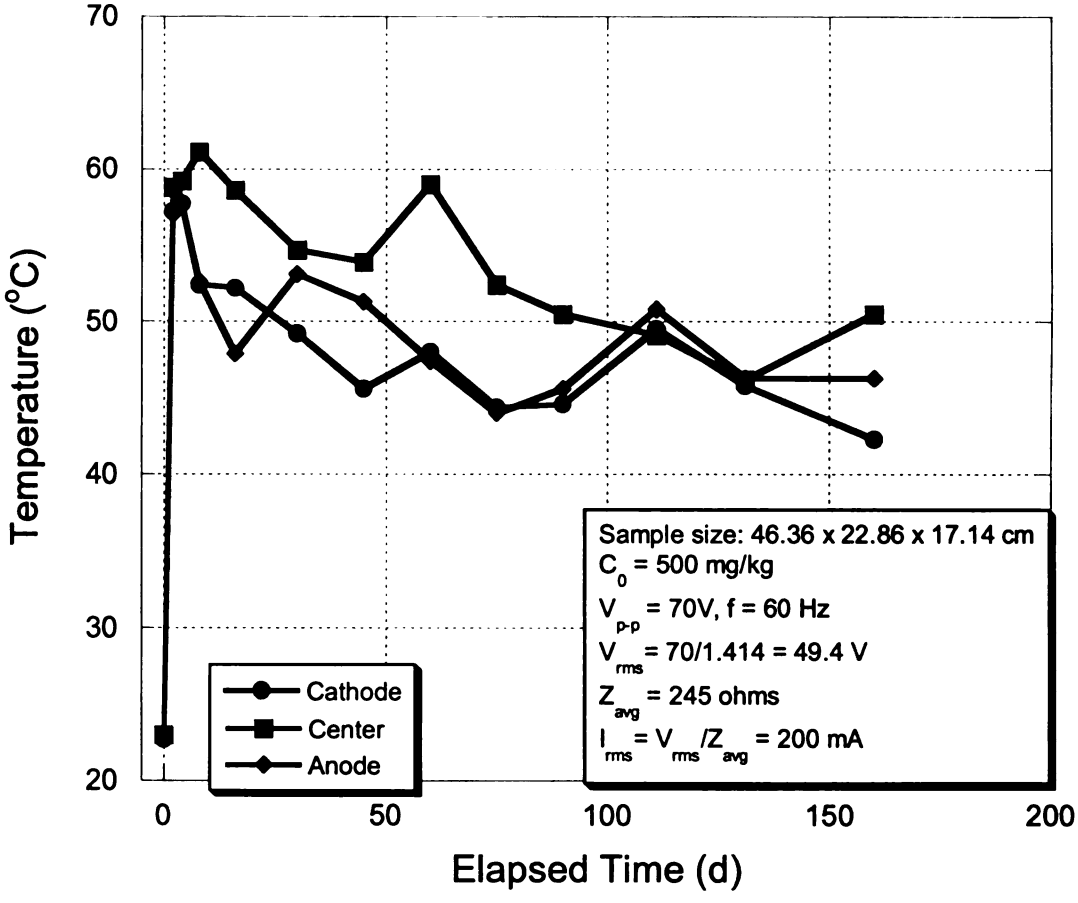


Figure 4-14: Temperature vs. Time for Test cell T – 3

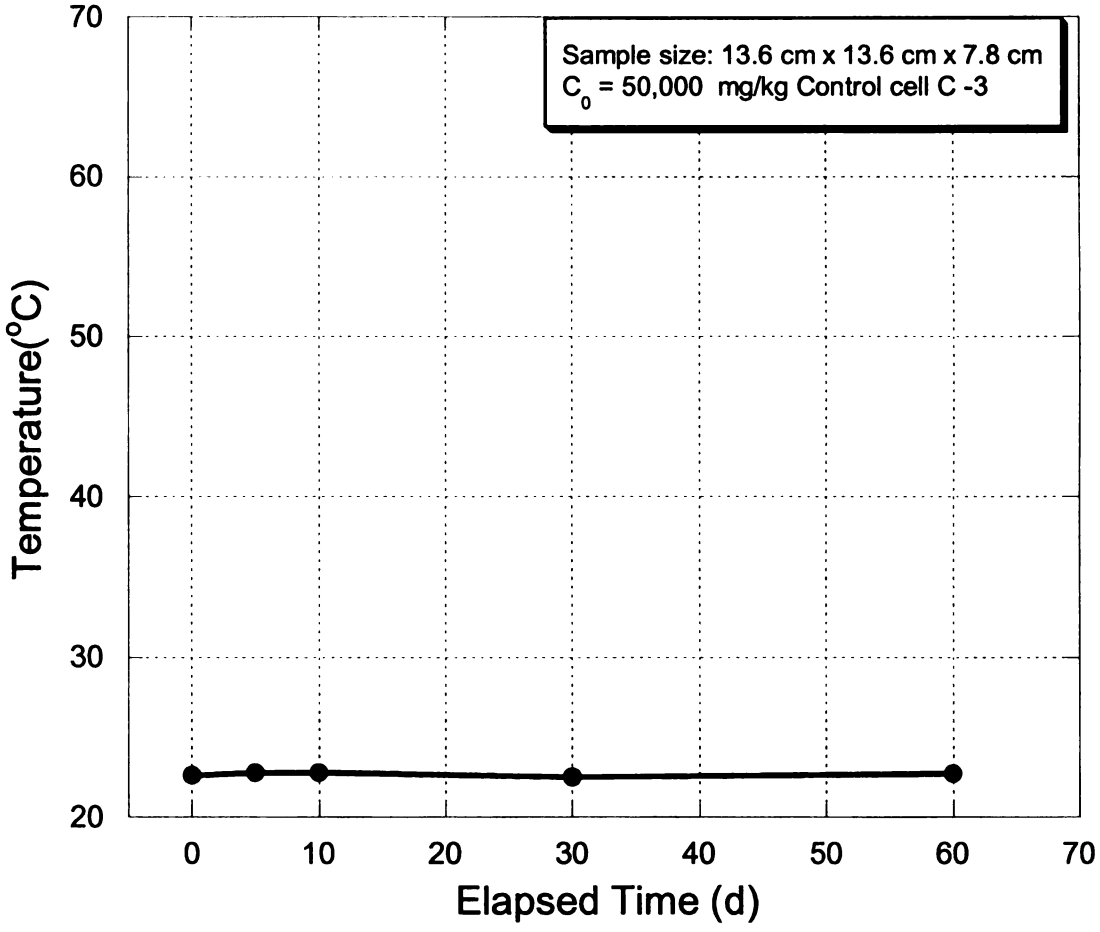


Figure 4-15: Temperature vs. Time for Control Cell C – 3

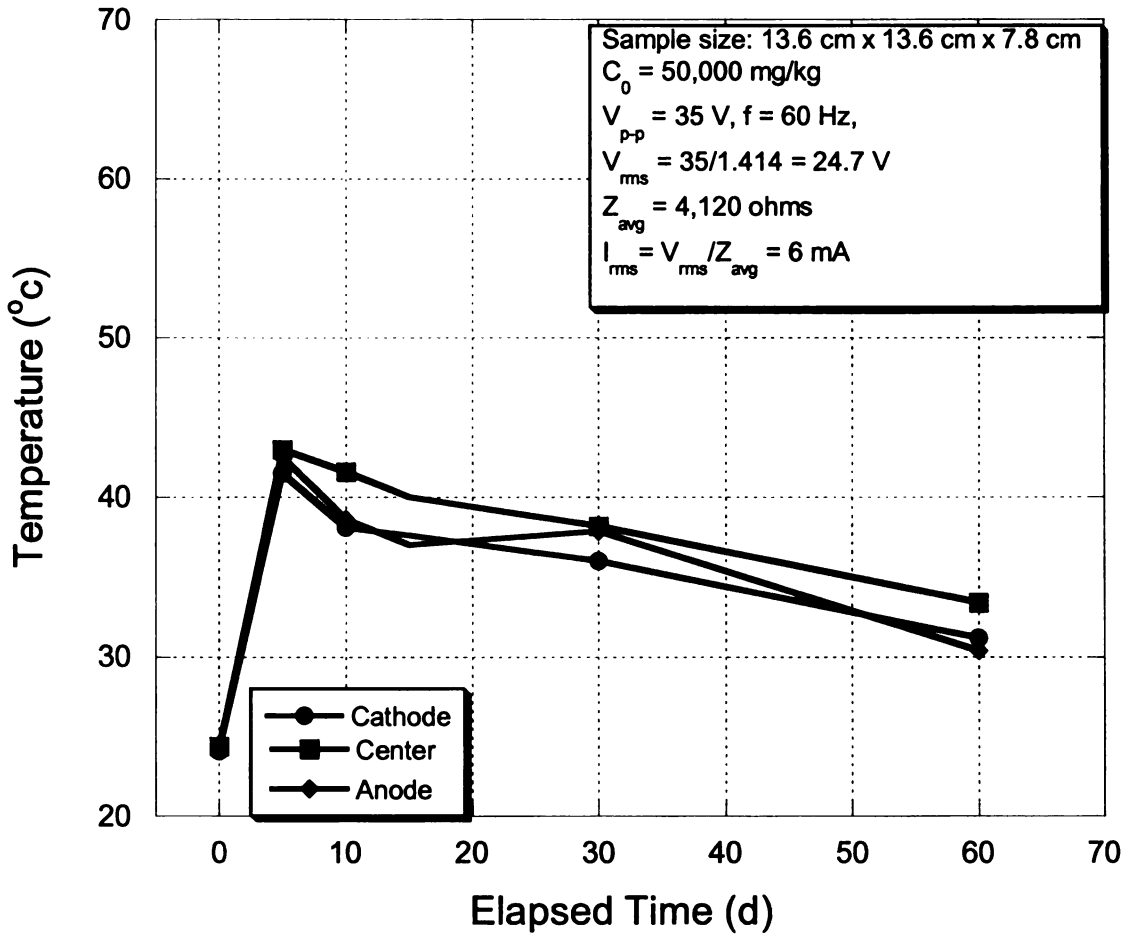


Figure 4-16: Temperature vs. Time for Test Cell T – 4

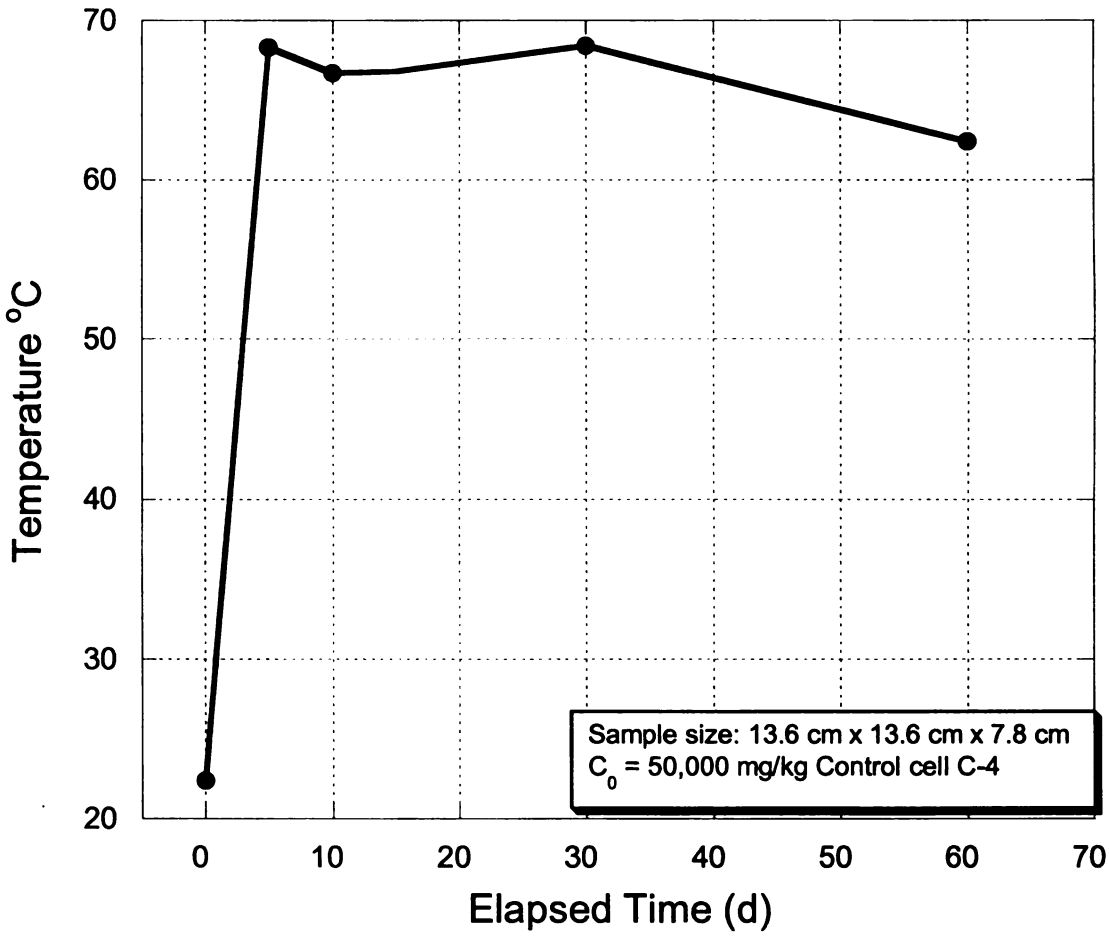


Figure 4-17: Temperature vs. Time for Control Cell C – 4

This is due to reinitialization of the cell T-4 when it was started. Initially the cell was set up at 70 V in parallel which was too high for the sample size of the test cell, which made it heat fast enough and the sample started boiling at a point. The test was re-started again but the temperatures of soil did not reach ambient values as compared to the T-1 cell. It always had higher temperature ranging form 28 to 40 °C. The control cells C-1, C-2 and C-3 displayed a constant temperature of approximately 22 °C. While C-4 is control cell kept in Temperature chamber at 70 °C.

4.4 ELECTRICAL PARAMETERS

Electrical parameters including capacitance in series and parallel and Impedance of the cell were measured periodically during the tests. All measurements were done at a 100 Hz frequency using an LCR meter. The meter is designed to measure the parameters at different range of frequency from 100 Hz to 10000 Hz. The LCR meter did not have an option to measure these parameters at 60 Hz which was the frequency of the applied AC. Other electrical parameters like capacitance can be measured in series and parallel both and denoted as Cs and Cp with units in Farads. The Cp and Cs were observed to decrease as time passed for all the tests. Figure 4-18 and 4-19 show plots of Cp and Cs versus time for test cell T-1 respectively.

Soil impedance or resistance is sensitive to moisture content of the soil and thus can be used to calculate the volumetric water content of the soil. Change in temperature can result in change in impedance of soil. Figure 4-20 displays variation of resistance with time for test cell T-1. With time, the total resistance of the cell increased from 102 to 196 ohms in 60 days with an average Z value of 140 ohms. As time passed, pH of the soil decreased and resistance of the soil increased. Figure 4-21 show fluctuations in

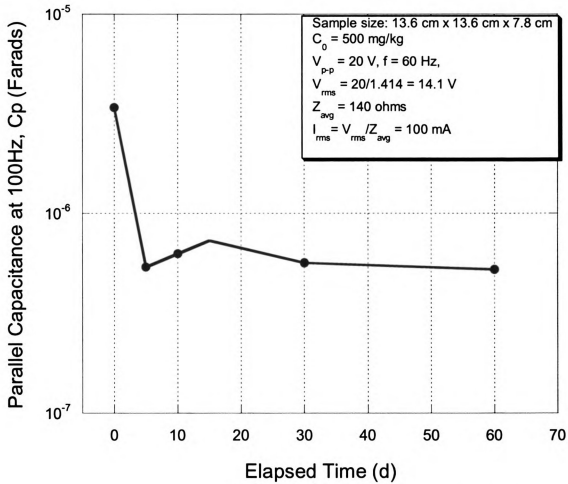


Figure 4-18: Cp (Parallel Capacitance) vs. Time for Test Cell T-1

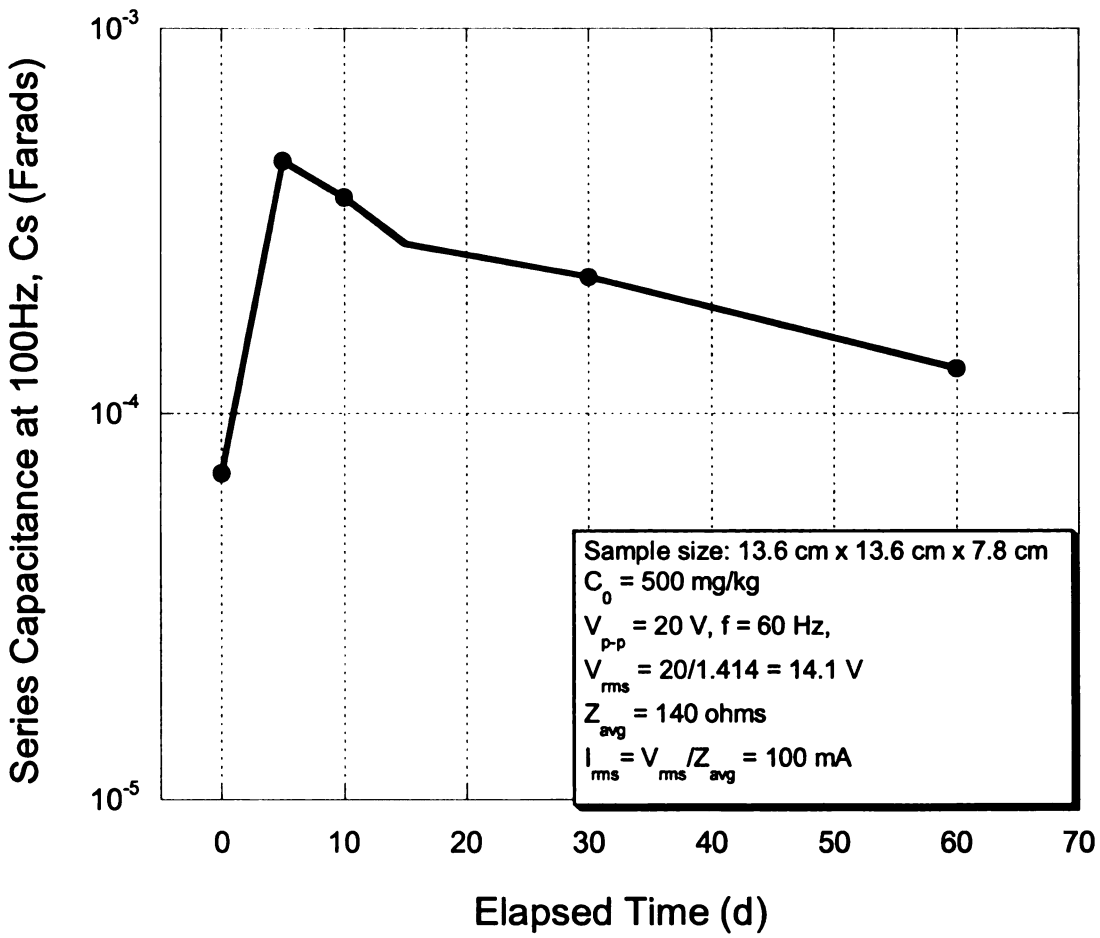


Figure 4-19: Cs (Series Capacitance) vs. Time for Test Cell T-1

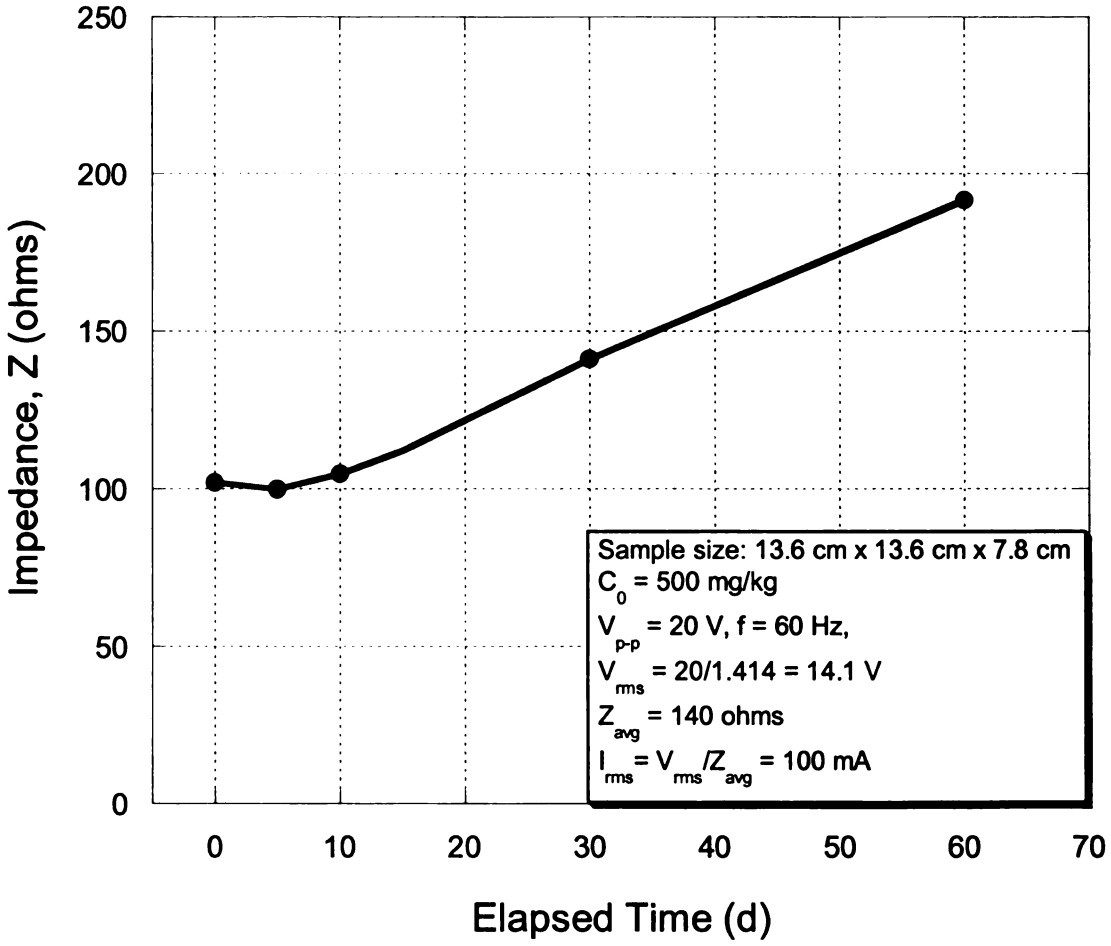


Figure 4-20: Z (Impedance) vs. Time for Test Cell T-1

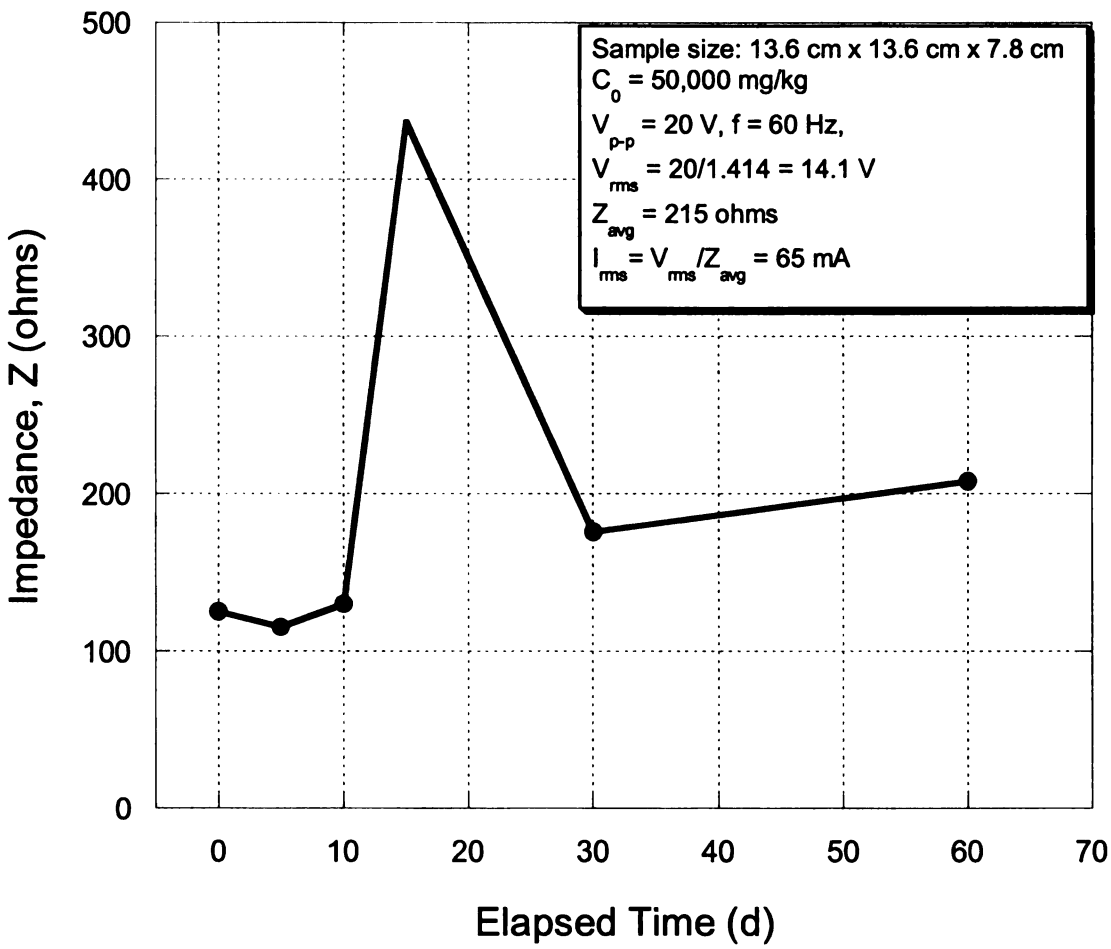


Figure 4-21: Z (Impedance) vs. Time for Test Cell T-2

impedance with an average value of 250 ohms in test cell T-2. Figure 4-22 shows a plot of impedance of Test cell T-3 versus time displaying sudden changes in impedance with an average value of 245 ohms.

4.5 CORROSION OF ELECTRODES

It is known that DC stray currents can accelerate the corrosion process in buried metallic structures. This is also evident from Figure 4-5 in which relatively low pH values were observed with higher dissolution rate for a DC application. At the positions where the AC current leaves the metal to enter the surrounding soil, electrochemical corrosion may appear. The amount of corrosion (weight of metal lost) is related to the electrical charge that has passed the metal-soil interface. In terms of net electrical charge AC stray currents would not cause corrosion as the current-direction is reversed during each half cycle, Hence the net direction of the current is zero. However, the actual AC current flowing due to an AC voltage present may not be symmetrical for the positive and the negative half-cycle, due to the non-linear electrical behavior of the interface between metal and soil. Low frequency alternating current induces less corrosion as compared to high frequency of alternating current (Chin 1984). Table 4-4 shows thickness of electrodes at the end of the test period.

Test cell T-2 shows some corrosion of the electrode but the other three test cells do not show significant corrosion. Electrodes of test cell T-4 has corroded more compared to Test cell T-3 due to higher intensity of current passing through it.

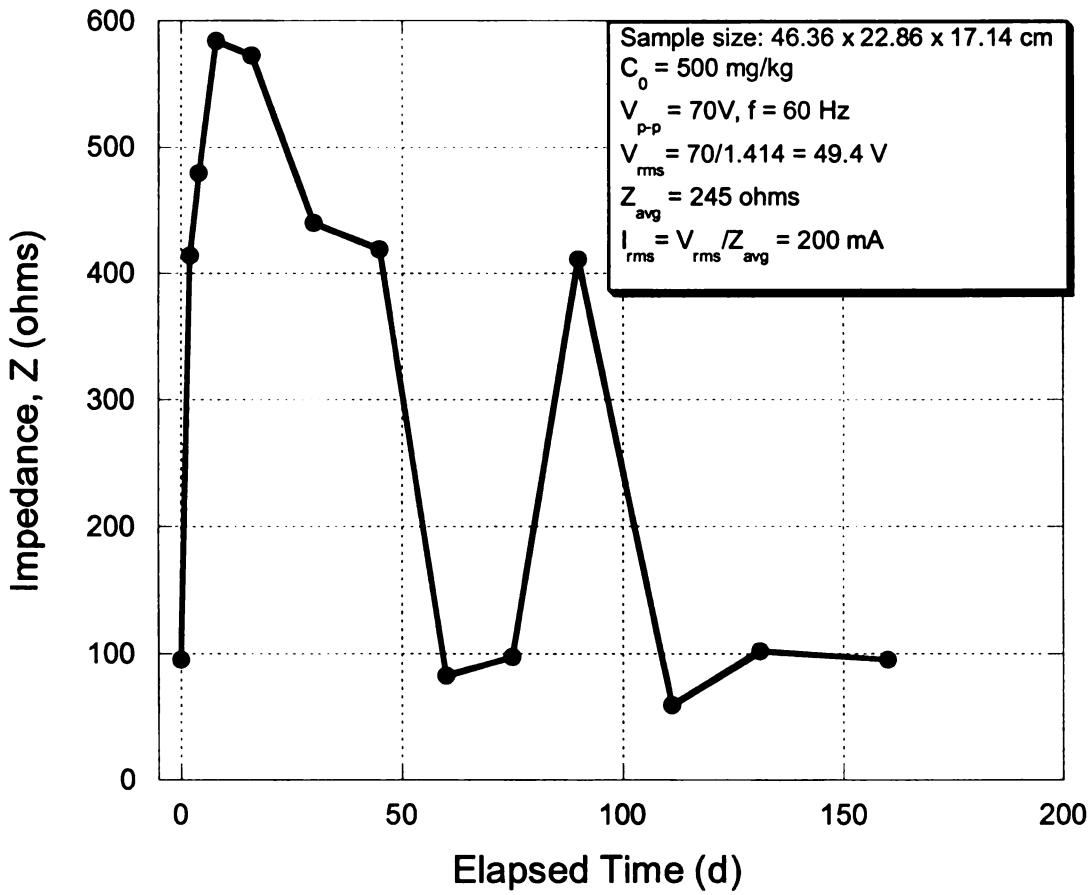


Figure 4-22: Z (Impedance) vs. Time for Test Cell T-3

Table 4-4: Thickness of Electrodes at the End of Test

Test	Thickness of electrode (mm)	
	Anode	Cathode
T-1	1.94 (3%)	1.96 (2%)
T-2	1.93 (3.5%)	1.72 (14%)
T-3	1.74 (13%)	1.79 (10.5%)
T-4	1.89 (5.5%)	1.62 (19%)

Notes: 1) The initial thickness of electrodes was 2 mm.
2) The values in the parenthesis show the percent decrease in the thickness.

CHAPTER 5

SUMMARY AND CONCLUSIONS

Polycyclic aromatic hydrocarbons (PAHs) are contaminants that are present in soils at contaminated sites ubiquitously. While conventional technologies such as "soil washing" exist to cleanup PAHs in coarse-grained soils, these technologies are ineffective in clayey soils due to the strong affinity of PAHs to clay mineral surfaces and low hydraulic conductivity of clay soils. In this project, the effect of sinusoidal alternating current (AC) on the concentration of phenanthrene in spiked low plasticity clay was evaluated in a lab-scale setup. The key hypothesis evaluated was, an AC electrical signal can generate oxidation reactions in clay soils due to the capacitive properties of charged clay mineral surfaces saturated with dielectric water to cause degradation of benzene rings in PAHs. No enhancement agents were added to the spiked clay during the application of the AC.

The effect of application of an AC on the concentration of phenanthrene in spiked clay was evaluated on the basis of these two key parameters: (1) initial concentration of phenanthrene; and (2) the magnitude of applied AC. Total four sample cells were subjected to an AC for a time period ranging from 60 to 160 days. The initial phenanthrene concentration in the spiked clay was 500 and 50,000 mg/kg and the peak to peak voltage applied ranged from 20 to 70 volts (root mean square average = 14.1 to 49.4 volts). This resulted in a root mean square current that ranged from 0.006 to 0.2 amperes. Copper plate electrodes having an initial thickness equal to 2 mm were used to apply the AC. The key parameters monitored throughout the testing period included: (1)

phenanthrene concentration in the clay; (2) pH of the clay; (3) temperature of the clay; (4) electrode thickness change; and (5) capacitance and impedance of the clay.

The phenanthrene concentration in the cells monitored over the duration of the tests when compared with control samples (samples not subjected to an AC) indicated insignificant decrease or change in the phenanthrene concentration in the clay. Adsorption of phenanthrene on the plastic cell walls was not measured in this study. However, results from glass and plastic control cells indicated that the adsorption is relatively small compared to the initial spiked concentrations used in this study.

Over the duration of the tests, the average pH of the spiked clay dropped from about 7.5 to 6.0. It was also observed that the thickness of the copper electrodes decreased from 2 mm to about 1.7 mm during the 60-day duration of the tests. Formation of an acid front is primarily responsible for the dissolution of the electrodes. However, compared to a DC application, the electrode decay rate is relatively slow when an equivalent AC is used. Due to Joule heating, the temperature of the cells subjected to AC increased to up to 60° C within 160 days after an AC was applied. Control sample subjected to a similar temperature increase (without an AC application) indicated no appreciable decrease in phenanthrene concentration. The impedance of the clay increased during the testing period primarily due to the increase in the temperature of the clay.

Based on the results, the key conclusion of this study is that in a lab-scale setup, sinusoidal AC at a frequency equal to 60 Hz does not cause appreciable decrease in the concentration of phenanthrene in spiked low plasticity clay. Further studies including degradation of phenanthrene in other media and chemicals subjected to an AC needs to be carried out.

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