EDTA-Enhanced Metal Contaminant Removal from Soils by Electric Fields

by

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Submitted to the Department of Mechanical Engineering
in partial fulfillment of the requirements for the degree of

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Abstract

The study here concerns the use of chelating agents in electrokinetic soil remediations. In particular, emphasis is placed on the removal of metal contaminants. Amid the electrokinetic soil remediation processes are electroosmosis and electromigration. Electroosmosis is generally possible only when low permeability soils are involved, in contrast to electromigration, a process that is applicable to both high and low permeability soils. Electroosmosis is suitable for the purging of uncharged contaminants whereas electromigration is useful for the mobilization and removal of charged contaminants only. Electromigration is generally faster than electroosmosis and well suited to the removal of metal contaminants as these contaminants are usually charged. Problems arise when applying the electromigration process if the metal waste is not in the aqueous phase (metal precipitates) or if the metal waste takes the form of an uncharged complex. Many anions have the ability to precipitate dissolved metals, and thus pose a certain problem for electromigration metal waste removal processes. Chelating agents are useful as these agents have the ability to solubilize metal precipitates in the presence of the fore mentioned precipitating anions. The study focused upon the use of the EDTA chelate to solubilize and remove precipitated lead and zinc precipitates (in sand pore solution) under the influence of electric fields. The results demonstrated that the EDTA chelate is highly capable of solubilizing and mobilizing lead and zinc carbonate precipitates, as in all trials, a sizable portion of the precipitated waste was solubilized and removed.

Thesis Supervisor: Ronald F. Probstein
Title: Ford Professor of Engineering

Acknowledgments

First and foremost, I would like to thank Prof. Probstein for the opportunity to participate in this research project. I am also greatly appreciative of the help I received from Dr. Hicks throughout the project. I am particular thankful to the help John Dzenitis has provided throughout my research, as well as the guidance I received from Richard Jacobs concerning the analytical model. Finally, I would like to extend my gratitude towards Ms. Virginia Brambilla, who was always helpful.

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Chapter 1

Introduction

Electrokinetic soil remediation is among the more promising techniques by which contaminants can be removed from low permeability soils and other porous media where the standard pump-and-treat approach cannot be readily applied. Amid the electrokinetic soil remediation processes are elecroosmosis and electromigration. Electroosmosis may be useful in mobilizing and removing uncharged contaminants while electromigration can be highly effective in the clean up of charged contaminants. Electromigration is the movements of charged ions in a fluid medium when these ions are subjected to electric fields (see figure 1.1). The migration velocity of the charged ions is directly proportional to the direction and strength of the electric field applied to the ions. The ability to influence the speed and direction of the charged contaminants during its removal renders the electromigration soil remediation process highly desirable. Sites containing metal wastes such as lead and other hazardous metals are promising candidates for this type of remediation. Extensive research in to this area of soil clean up have been conducted by Probstein et.al.. The research presented here is a continuation of the efforts under taken earlier by the Probstein research team. The work here centers upon the use of chelating agents to enhance the abilities of the electromigration waste removal process.

As the electromigration process moves charged ions in a fluid medium with electric fields, it is of the utmost importance that the waste to be removed is in the aqueous phase

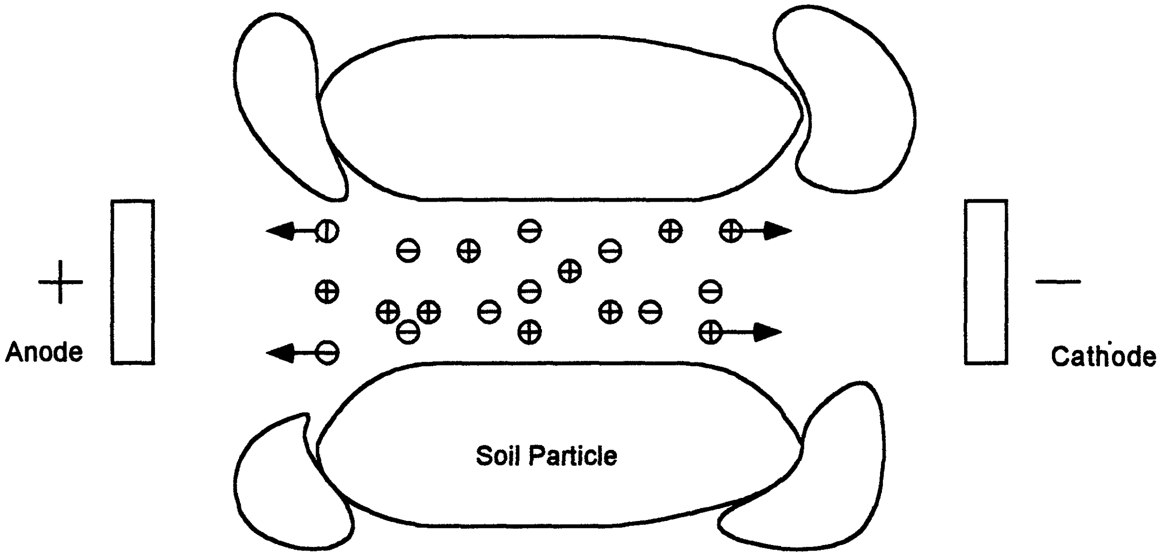


Figure 1.1: The electromigration schematic

and is charged. In some metal waste sites, the soil contains hazardous metal ions in its pore solution along with other compounds (in addition to the metal ions's counter ion). Depending upon what other compounds are present in the soil's pore solution, the purging of the metal waste by electromigration may or may not be possible. The presence of carbonate ions, for instance, can dramatically reduce the solubility of lead and therefore take the metal to be purged out of the aqueous phase and beyond the reach of electric fields; rendering the electromigration transport process useless. The role of the chelating agent is to solubilize the precipitated metal in the above scenario by complexing the metal. The metal must therefore have a greater affinity for the chelating agent than it does for precipitating chemicals and the metal-chelate complex must yield a net charge for electromigration to be feasible.

The research focuses on the use of the EDTA chelate to solubilize precipitated lead and zinc. A series of experiments were setup in which the metals in question are placed in saturated sand in a fully precipitated state. The chelate was then introduced into the pore solution by electromigration in an attempt to solubilize and excavate the precipitated metals.

Chapter 2

Theoretical Model

This chapter presents the theoretical model employed to describe the fore mentioned electromigration waste purging process. This model was first developed by Richard Jacobs [2] of M.I.T. for electrokinetic soil remediation. The model is of importance here as the basic principles of the electromigration waste removal process is identical to the concepts behind those processes that the model to be presented here was originally developed for. The more general form of this model represents well the state of the system of interest here.

The model reflects upon the various interactions of ion migration, mass diffusion coupled with chemical and electrochemical chemical reactions. The mass transport aspects of the system is described here by systems of convection-diffusion equations while the electric fields and current flow are represented by the Nernst-Planck equation.

2.1 System Modeling

For the purpose of this model, the soil/contaminant system will be defined by the set of species and elements in the system. To follow the evolution of the system in time, the concentration of each species must be accounted for by the time dependent mass transport equations; taking the following form:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot j_i + R_i$$

where

j_i : is the total flux of species i, and

R_i : is the rate of production of specie i by chemical reactions

In the numerical simulation employing this model thus far, the characteristic time of the chemical reactions was taken to be much smaller than the characteristic time of transport as the systems simulated exhibited this trait. The rate of kinetics far exceeds the rate of transport, implying that chemical equilibrium can be assumed at each time step. In the system discussed here, the above assertion does not hold as the dissolution of precipitated metals is a process requiring a considerable amount of time in relation to transport time scales. Depending upon the size of the metal precipitate, the metal in question and the chemical composition of the metal precipitate the dissolution time scale of the metal precipitate may or may not be negligible next to the transport time scale.

The system discussed here is made up of the following species:

$$\{Na^{+}, K^{+}, Pb^{2+}, Zn^{2+}, H^{+}, Cl^{-}, OH^{-}, NO_3^{-}, SO_4^{2-}, CO_3^{2-}, EDTA^{m}\}$$

$m = 0 \rightarrow -4$

and the following possible complexes :

$$\{(EDTA)Pb^{2-}, (EDTA)Zn^{2-}, (EDTA)Na^{3-}, PbCO_3 \cdot S, PbSO_4 \cdot S,$$
$$ZnCO_3 \cdot S\}$$

S - metal complex in precipitate form

The pH of the system is controlled in a manner so as to avoid metal-hydroxyl ion complexes.

2.2 Transport Equations

In this section the transport equations used to describe the electrokinetic contaminant removal process are presented. The general derivation procedure follows the scheme introduced by Jacobs [2], with sections concerning fluid convection and soil tortuosity omitted. As the soil in the system presented here is sand and no pressure forces are applied to generate bulk fluid motion, fluid convection is taken to be zero and tortuosity is taken to be unity. The effects of species adsorption on to the soil will also be discussed briefly, even though the model is still incomplete in this area.

The phenomenological relationships for each of the major transport mechanisms (electromigration and diffusion) are examined and assembled into the equation modeling the total species flux, with the law of the conservation of mass applied to derive the transport equations. The transport equations are based on the capillary model of porous media. In this model, the interstitial space between particles in the medium is represented by sets of parallel cylindrical capillaries. The medium is also assumed to be isotropic, so the set of parallel capillaries can be oriented in any direction. Since the soil medium of interest here is sand, the interstitial passages is taken to be straight and thus resulting in a tortuosity of one.

2.2.1 Mass Transport Mechanisms

Electromigration

When a gradient in the electrostatic potential is applied to a fluid medium, an electrical force will be exerted on the ionic species in the fluid medium; a force that is proportional to the electric field. The migration velocity that results from this force is shown by Probstein [1] as

$$u_i^m = -\upsilon_i z_i F \nabla \cdot \phi \tag{2.1}$$

where

υ_i : is the mobility of species i,

z_i : is the charge number of species i, and

F : is Faraday's constant

The contribution of electromigration to the total species flux $\dot{j}_i^m$ is given by

$$\dot{j}_i^m = u_i^m c_i \tag{2.2}$$

Combining equations 2.1 and 2.2 yields the electromigration flux to be

$$\dot{j}_i^m = -\upsilon_i z_i F c_i \nabla \cdot \phi \tag{2.3}$$

Diffusion

A gradient in chemical potentials give rise to a phenomenon known as diffusion. Diffusion is the process by which mass in regions of stronger chemical potential move into regions of weaker chemical potential. Diffusion is a consequence of random molecular motion and is analogous in many ways to the transport of heat and momentum in a fluid [1]. In dilute solutions, the mass flux that results from diffusion is given by Fick's law,

$$\dot{j}_i^d = -D_i \nabla c_i \tag{2.4}$$

where

D_i : is the diffusion coefficient of species i

Total Species Flux

The effects of the two transport mechanisms will now be superimposed to yield the total species flux:

$$j_i = j_i^m + j_i^d \tag{2.5}$$

Combining equations considered earlier into equation 2.5 yields

$$j_i = u_i^m c_i - D_i \nabla c_i \tag{2.6}$$

$$j_i = -\upsilon_i z_i F \nabla c_i - D_i c_i \tag{2.7}$$

Mass Conservation and Transport Equations

The transport equations can be derived by applying the law of conservation of mass for each species in an infinitesimal control volume, yielding

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot j_i + R_i \tag{2.8}$$

where

R_i : is the rate of production of species I by chemical reactions

Combining equations 2.7 and 2.8 and using the fact that for incompressible fluid flows $\nabla \cdot u = 0$, results in

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot (u_i^m c_i) + D_i \nabla^2 c_i + R_i \tag{2.9}$$

2.2.2 Adsorption

The effect of adsorption of various species in the soil pore solution by the soil is modeled with linear adsorption isotherm. The model is expressed by equation 2.10 and simply translates into the assumption that the amount of a given specie adsorbed is proportional to the concentration of that specie in the pore solution.

$$c_i^{ads} = k_i^{ads} c_i \tag{2.10}$$

where

k_i^{ads} : is the effective adsorption equilibrium constant of species i, and

c_i^{ads} : is the amount of adsorbed species expressed in volume concentration

The model in this area is still incomplete and various experiments are currently conducted (by John Dzenitis) to gain greater physical understanding of the adsorption phenomenon.

2.3 Chemical Equilibrium

As mentioned earlier in the chapter, not all of the reactions in the system considered here can be taken to be in equilibrium with respect to transport time scales. In particular, the metal precipitate dissolution process has a time scale comparable to that of species transport by electromigration. Despite the fore mentioned fact, the equilibrium properties of the various species in the system are still extremely important. In the following section, the implications of the equilibrium properties concerning the various chemical reactions in the system are examined.

2.3.1 Equilibrium Concentrations

Key Reactions:

$$\frac{[PbCO_3]_s}{[Pb^{2+}][CO_3^{2-}]} = k_{sb1}\,(1.259x10^{13}) \qquad (2.11)$$

$$\frac{[PbSO_4]_s}{[Pb^{2+}][SO_4^{2-}]} = k_{sb2}\,(6.310x10^{7}) \qquad (2.12)$$

$$\frac{\left[Pb(EDTA)^{2-}\right]}{\left[Pb^{2-}\right]\left[EDTA^{m-}\right]} = k_{sb3}\,(6.310x10^{19}) \qquad (2.13)$$

$$\frac{[ZnCO_3]_s}{[Zn^{2+}][CO_3^{2-}]} = k_{sb4}\,(1.0x10^{10}) \qquad (2.14)$$

$$\frac{\left[Zn(EDTA)^{2-}\right]}{\left[Zn^{2+}\right]\left[EDTA^{m-}\right]} = k_{sb5}\,(1.995x10^{18}) \qquad (2.15)$$

In the series of metal complexing reactions shown, $k_{sb1} \rightarrow k_{sbn}$ are the corresponding stability constants of the chemical reactions. The stability constants determine the concentrations of the various forms of metals at equilibrium. These constants are of great interest as the high stability constant in all five equations indicate relatively high levels of metal complex concentration and very low levels of free metal concentration. Indeed, the free metal concentration in solution would be very low if comparable amounts of complexing agents (carbonate ion, EDTA chelate) are also present. The metal complexes formed in the reaction depicted by equations 2.11, 2.12, and 2.14 are metal precipitates and thus not soluble. Herein lies the great utility of the EDTA chelate; its complexes with lead and zinc (2.13,2.15) are soluble and exhibit a net charge of -2, fulfilling the requirements of electromigration. The high

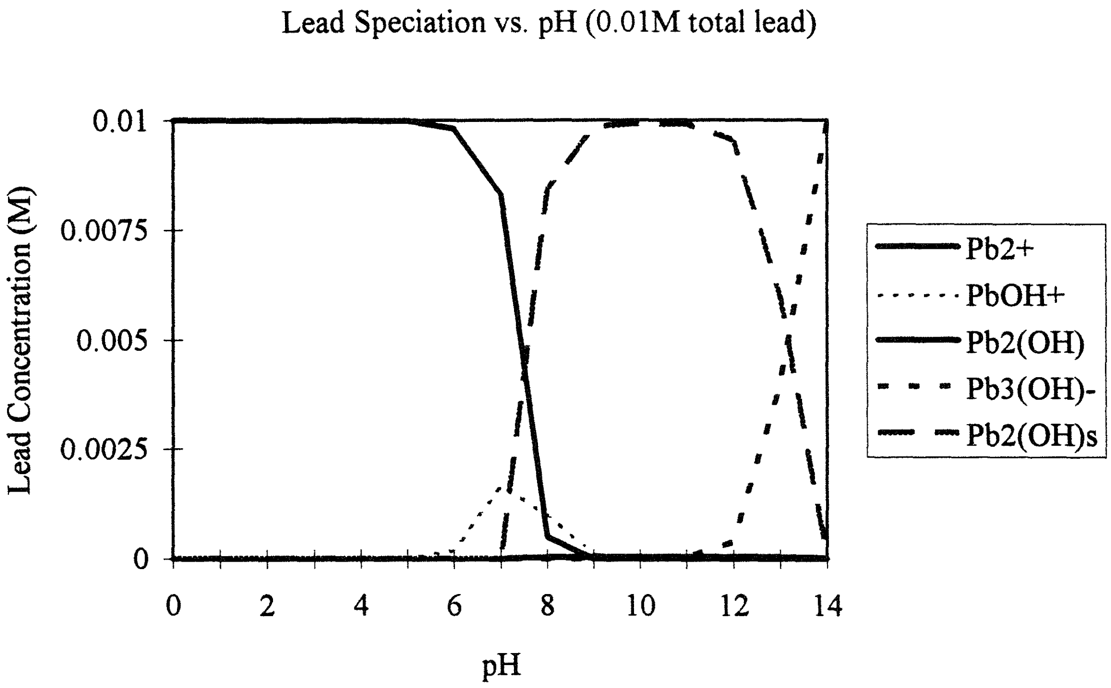

Lead Speciation vs. pH (0.01M total lead)

Figure 2.1a

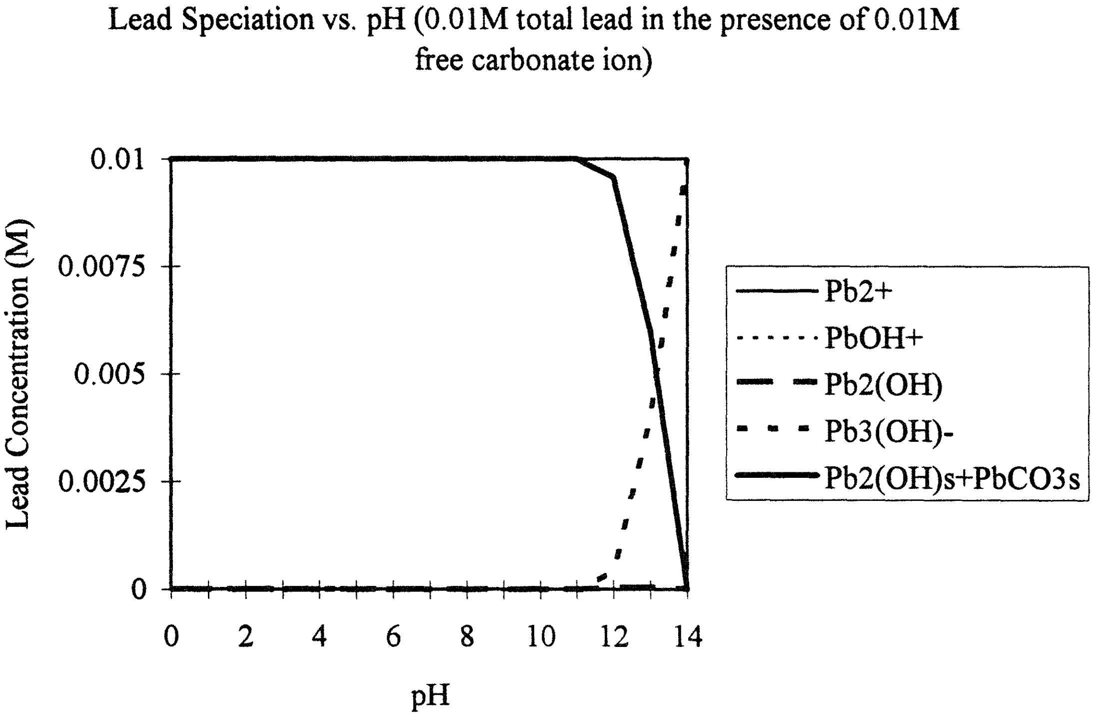

Lead Speciation vs. pH (0.01M total lead in the presence of 0.01M free carbonate ion)

Figure 2.1b

Lead Speciation vs. pH (0.01M total lead in the presence of 0.01M free sulfate ion)

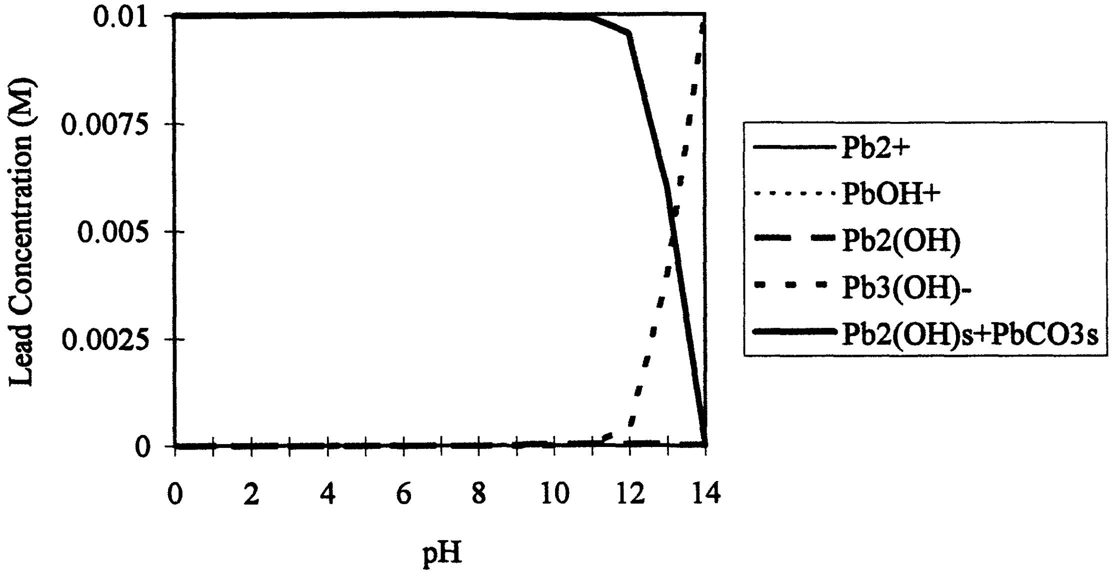


Figure 2.1c

Zinc Speciation vs. pH (0.01M total zinc)

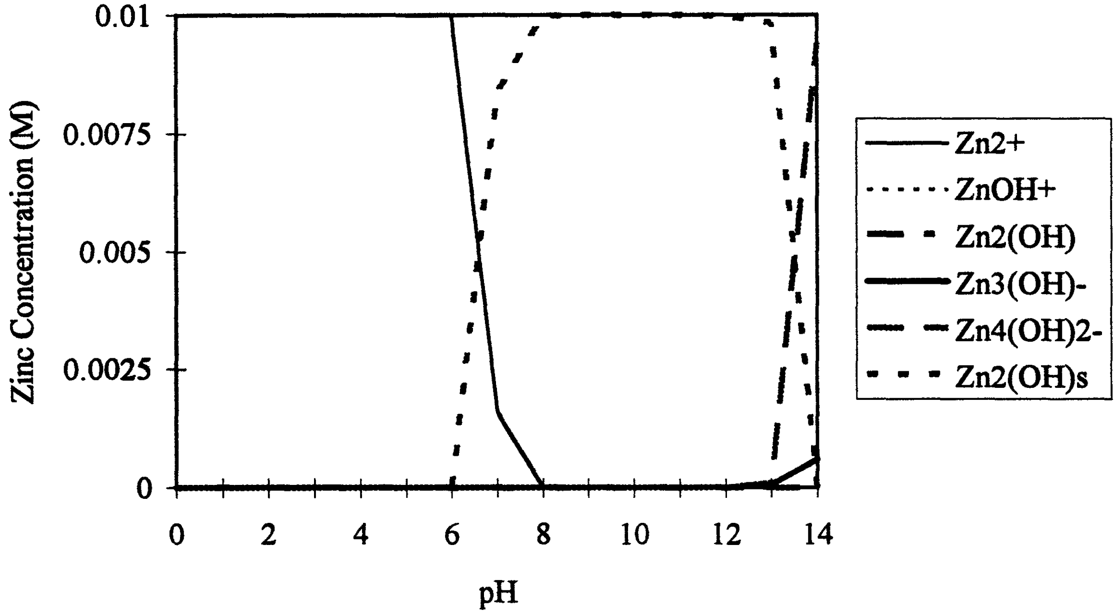
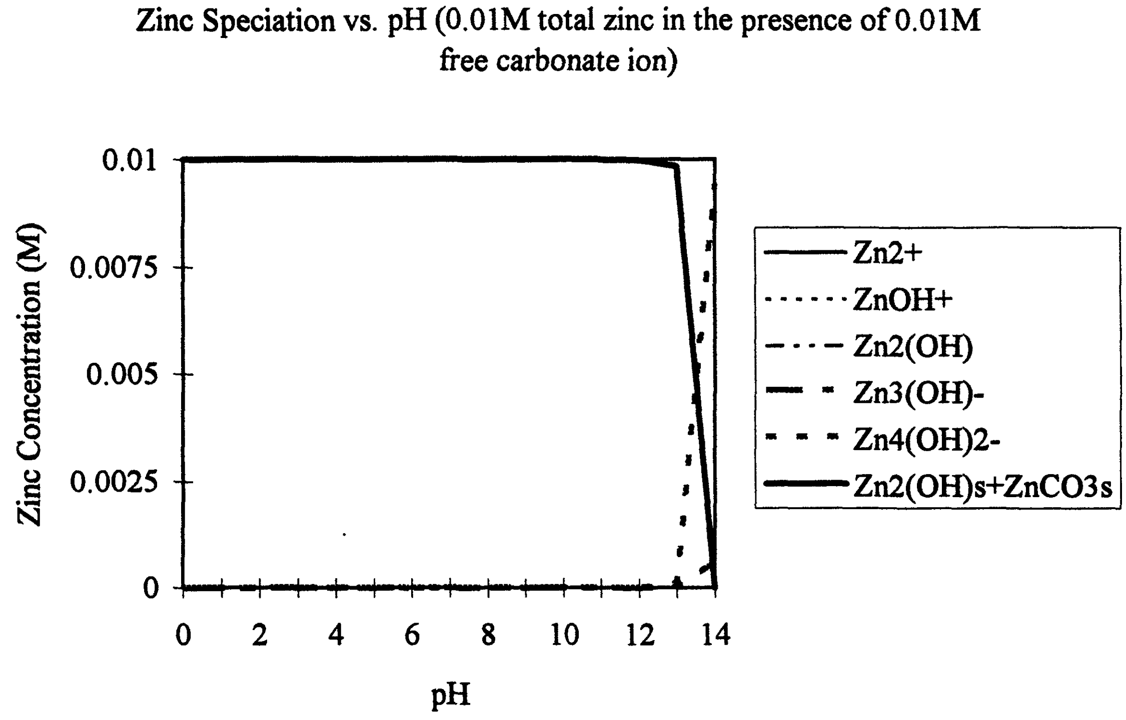


Figure 2.2a



Zinc Speciation vs. pH (0.01M total zinc in the presence of 0.01M free carbonate ion)

Figure 2.2b

stability constants enjoyed by the EDTA-metal complexes reflect upon the fact that the EDTA chelate can be used to solubilize large concentrations of metal even in the presence of strong precipitating agents such as the carbonate ion. Figure 2.1-2.2 depicts the speciation of lead and zinc versus pH in the presence of various precipitating anions. It is evident that the solubility of the metals of interest here is severely reduced by the presence of these precipitating anions.

2.3.2 Electrochemical Reactions

The electrochemical reactions that take place at both the anode and cathode impact greatly upon the system of interest here (see figure 2.3). The graphite electrode is inert and thus does not participate in the electrochemical reactions, leaving only the electrolysis of water at both anode and cathode and the oxidation of EDTA at anode the sole electrochemical reactions transpiring.

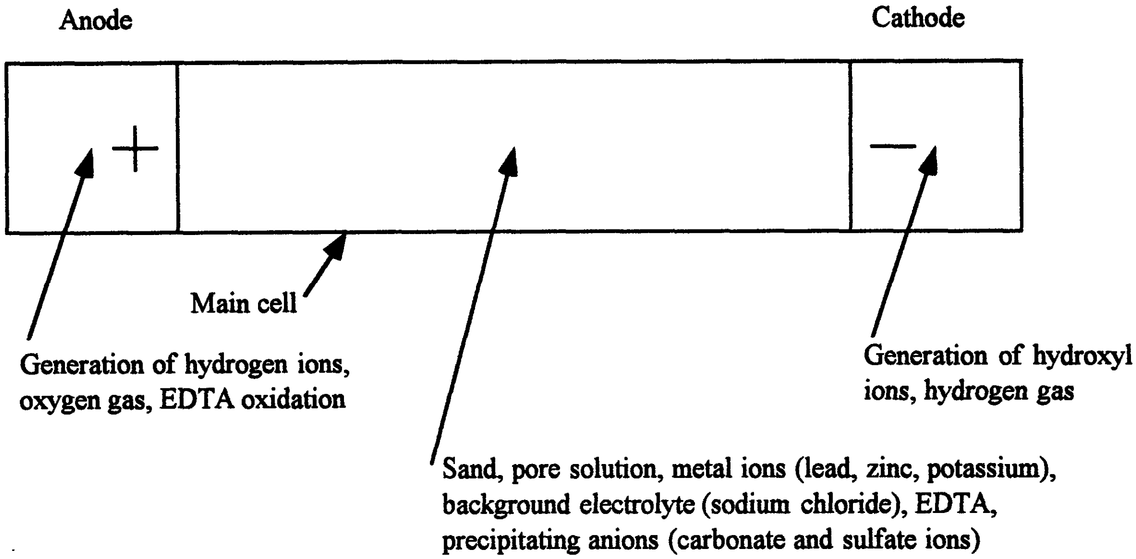


Figure 2.3: The electrochemical system

The electrolysis of water can be described by the following pair of equations:

at the cathode,

$$4H_2O + 4e^- \rightarrow 2H_2(g) + 4OH^- \tag{2.16}$$

at the anode,

$$2H_2O \rightarrow O_2(g) + 4H^+ + 4e^- \tag{2.17}$$

The rate of species generation caused by electrochemical reactions can be obtained by the use of Faraday's law of electrolysis, which simply states the the rate of oxidation at anode and reduction at cathode of water is directly proportional to the quantity of charge that passes through the electrodes. If the current through the cell is **i**, the rates of species production at each electrode in mol/s are:

at the cathode,

$$\dot{R}_{OH^-} = \frac{i}{F} \tag{2.18}$$

$$\dot{R}_{H_2} = \frac{i}{2F} \tag{2.19}$$

at the anode,

$$\dot{R}_{H^+} = \frac{i}{F} \tag{2.20}$$

$$\dot{R}_{O_2} = \frac{i}{4F} \tag{2.21}$$

where F is the Faraday number.

The oxidation of EDTA at anode is considerably more complex, involving the ligand degenerating into simpler molecules. The process is of interest here to the extent that when the EDTA chelate is complexed with divalent metal ions (especially lead and zinc), it is highly resistant to the electrochemical oxidation that it would otherwise be vulnerable to [3].

The electrolysis of water at each electrode produces hydroxyl ions at cathode and hydrogen ions at the anode. By electromigration, the hydroxyl ions move toward the anode and the hydrogen ions move toward cathode. The two fronts meet at a point between the two electrodes in the cell, creating a region of low conductivity as the two ions neutralize eah other to form water. This process help give rise to a phenomenon known as isoelectric focusing [4] and can potentially halt the transport of various ions by electromigration. The experiments to be presented were all setup to avoid this unpleasant phenomenon.

Chapter 3

Experiments

This chapter presents the experimental setup and procedure of the EDTA enhanced contaminant removal process.

3.1 Experimental Setup

All experiments involving electromigration were conducted in a plexiglass cell 0.2 m long and 0.032 m in diameter (see figure 3). At the ends of the plexiglass cell are two piece end caps that house the electrode wells (see figure 3). The wells are each linked to a larger reservoir and fluid is circulated between the electrode wells and their respective reservoirs by peristaltic pumps. The outer end caps house the carbon electrodes that are connected to a power supply. Passive electrodes are placed between the main cell and the inner end caps (see figure 3). The gas generated by electrolysis of water is vented from the tubes atop the inner end cap. The purge solution pumped from the peristaltic pumps entered the electrode wells from the side and exited through the same opening as the gas generated from electrolysis; flowing back to the reservoirs (see figure 3). All the electromigration experiments were executed with sand as the soil from which contaminants are to be purged. Membrane filters of 0.45 μm and 0.05 μm in pore diameter were placed next to the passive electrodes to prevent any pressure fluctuations from pumping solution through the porous sand (see figure 3). The EDTA transport experiments were carried out with 400 ml reservoirs at both the anode and cathode while the metal precipitate removal experiments were conducted with 1000 ml reservoir at the

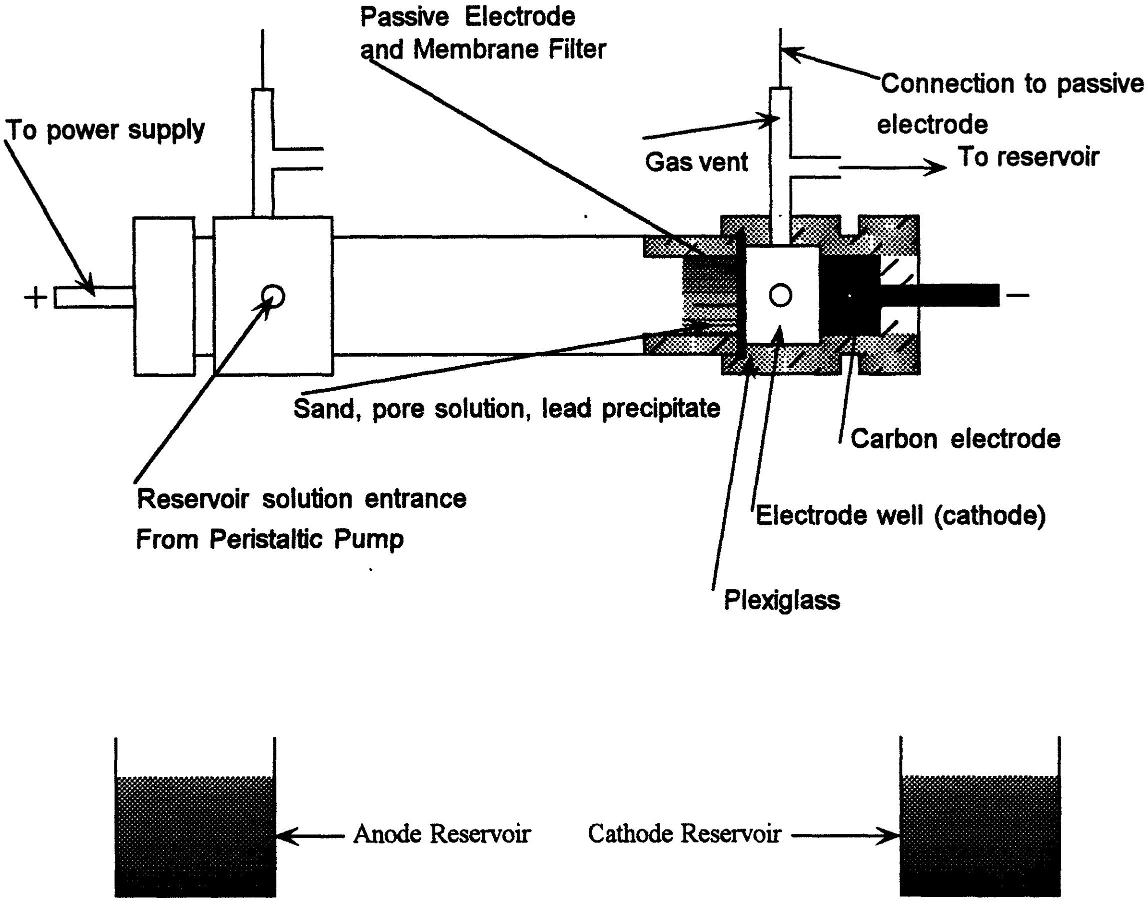


Figure 3.1: Experimental Setup

anode.

3.2 Experimental Procedure

The experiments conducted to investigate the EDTA chelate's ability to solubilize and remove precipitated metals from sand by electromigration can be grouped into three sections; EDTA transport experiments, metal precipitate removal experiments and EDTA oxidation experiments. The objective of the EDTA transport experiments is the verification of the ligand's ability to be transported by electromigration through the pore solution of sand. The objective of the metal precipitate removal experiments is also the primary objective of the project presented here; to purge precipitated metal from the pore solution of sand through the use of a complexing agent. The purpose of the EDTA oxidation experiments is simply the verification of the observation that the EDTA chelate can undergo electrochemical oxidation [6].

3.2.1 EDTA Transport Experiment

1. 400 ml of 0.3 M sodium hydroxide solution was made by dissolving the appropriate amount of sodium hydroxide pellets in distilled water. This solution served as the anode reservoir solution.

2. 400 ml of 0.2 M EDTA solution was made by dissolving the appropriate amount of EDTA powder and sodium hydroxide pellets in distilled water. This solution served as the cathode reservoir solution.

3. 100 ml of 0.2 M sodium chloride solution was made by dissolving the appropriate amount of sodium chloride in distilled water. This solution served as the sand pore solution.

4. The plexiglass cell to be used in the experiment was attached to the inner end cap at one end, with the aluminum passive electrode and membrane filters placed between the cell and the inner end cap (see figure 3.1a).

5. Approximately 55 ml of the sand pore solution was pored into the cell (see figure 3.1a). The sand pore solution is pored into the plexiglass cell prior to the addition of sand to avoid trapping air in the cell.

6. Sufficient amount of sand was pored into the cell to fill the cell completely (see figure 3.1b).

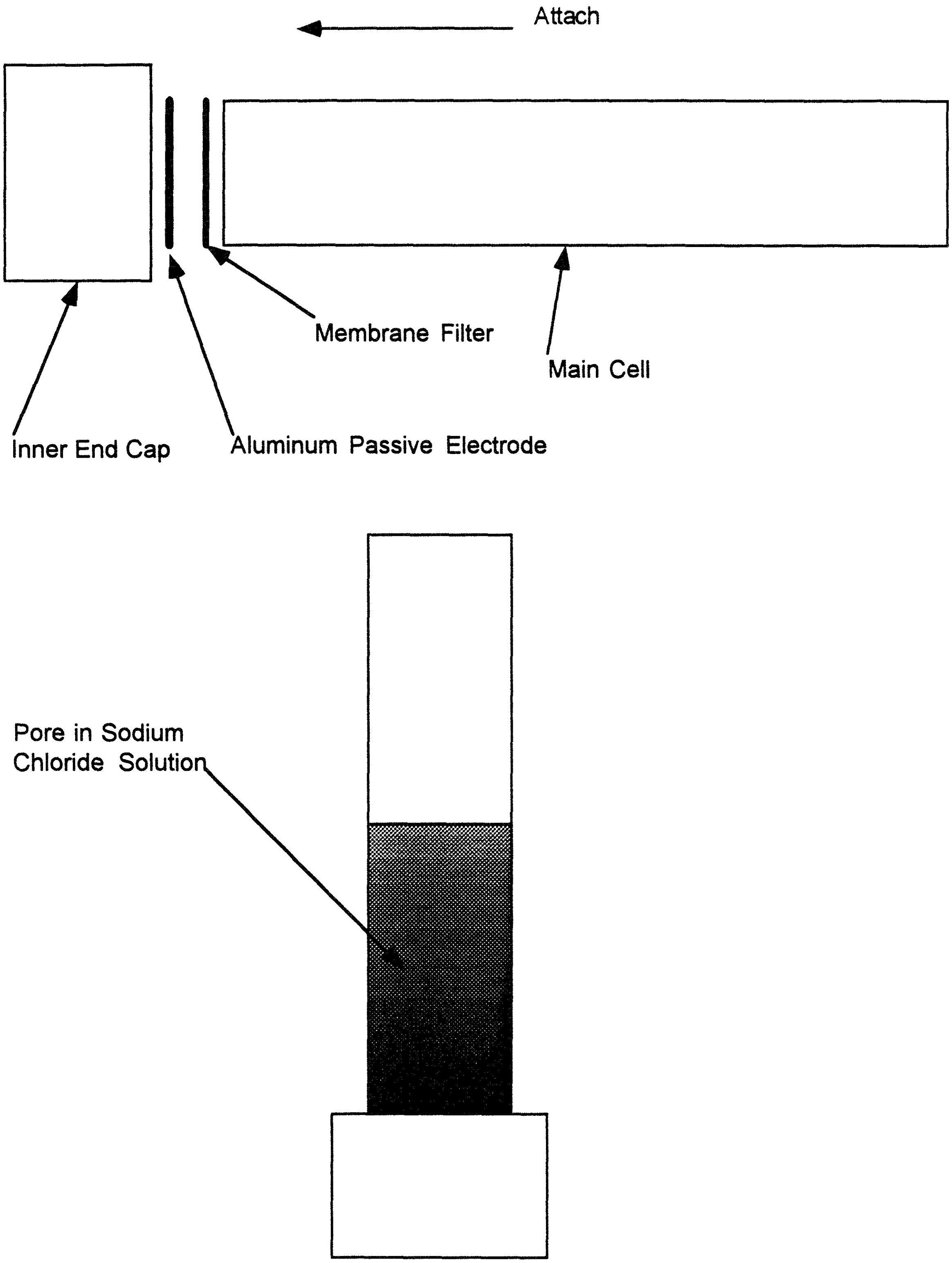

Attach
Membrane Filter
Main Cell
Inner End Cap
Aluminum Passive Electrode
Pore in Sodium Chloride Solution

Figure 3.2a

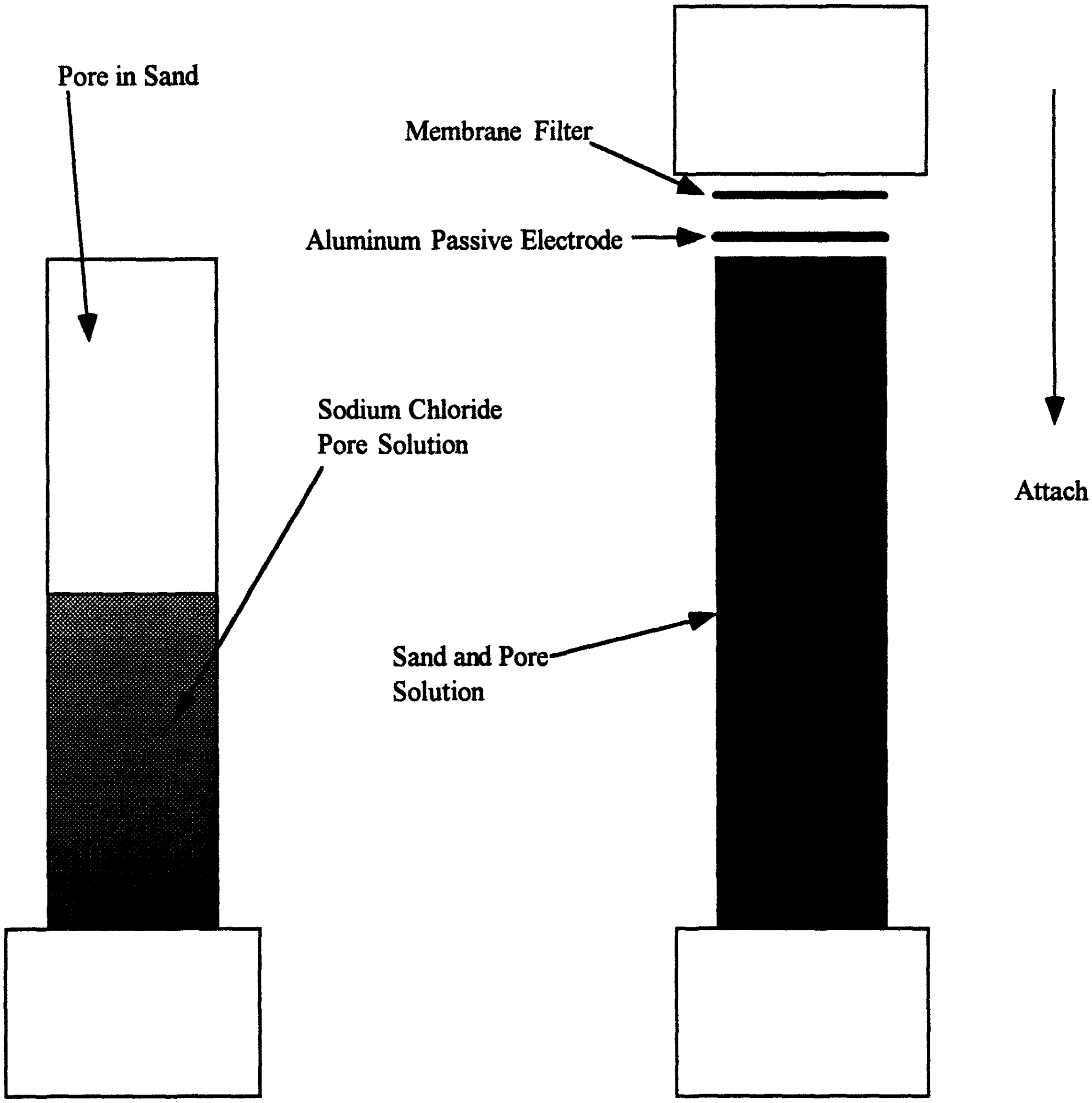


Figure 3.2b

7. The plexiglass cell was closed by attaching the second inner end cap to the cell (see figure 3.2b).

8. The outer end caps were attached to the inner end carps at both ends (see figure 3.2c).

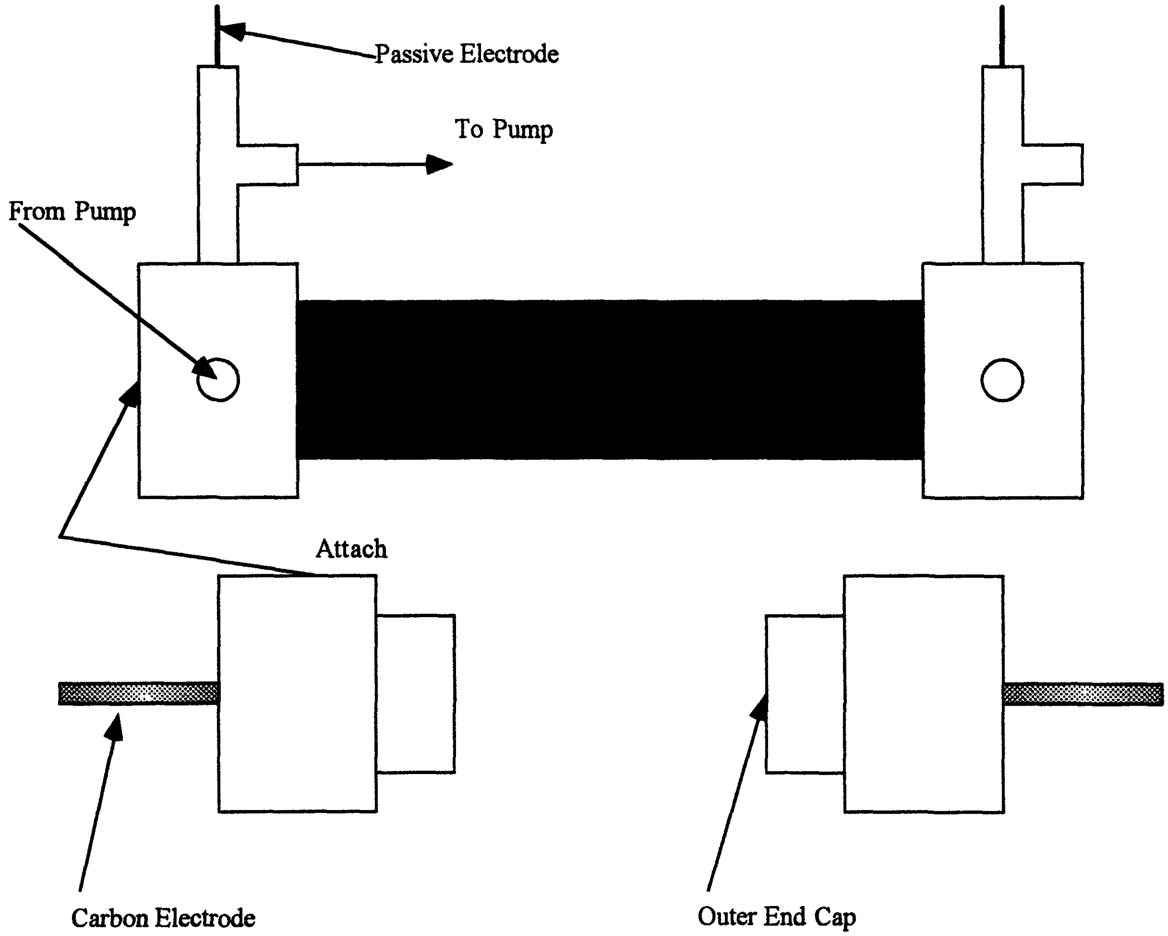


Figure 3.2c

9. The anode purge solution was pumped in a re-circulating manner between the anode electrode well and the anode reservoir. The cathode purge solution was pumped in a re-circulating fashion between the cathode electrode well and the cathode reservoir (see figure 3.1).

10. The power supply was connected to the experiment by the carbon electrodes. The voltage applied was adjusted until the voltage drop measured across the passive electrodes reached the desired (30 V) value.

11. The concentration of the EDTA chelate was measured periodically at both the anode and cathode. The current that passed through the cell was also registered periodically.

3.2.2 Metal Precipitate Removal Experiments*

1. 1000 ml of 0.2 M sodium hydroxide solution was made by dissolving the appropriate amount of sodium hydroxide pellets in distilled water. This solution served as the anode reservoir solution.

2. 400 ml of 0.2 M EDTA solution was made by dissolving the appropriate amount of sodium hydroxide pellets and EDTA powder in distilled water. This solution served as the cathode reservoir solution.

3. 100 ml of 0.2 M sodium chloride solution was made by dissolving the appropriate amount of sodium chloride in distilled water. This solution served as the sand pore solution.

4. The plexiglass cell to be used in the experiment was attached to the inner end cap at one end, with the aluminum passive electrode and membrane filters placed between the cell and the inner end cap (see figure 3.1a).

5. 10 ml of 0.1 M lead nitrate solution was pored into the cell. 1 ml of 1.0 M potassium carbonate solution was added to the lead solution to precipitate the lead (see figure 3.2d).

6. Sufficient amount of sand was added to the solution in the cell to achieve saturation (see figure 3.2d).

7. Approximately 45 ml of sodium chloride pore solution was pored into the cell (see

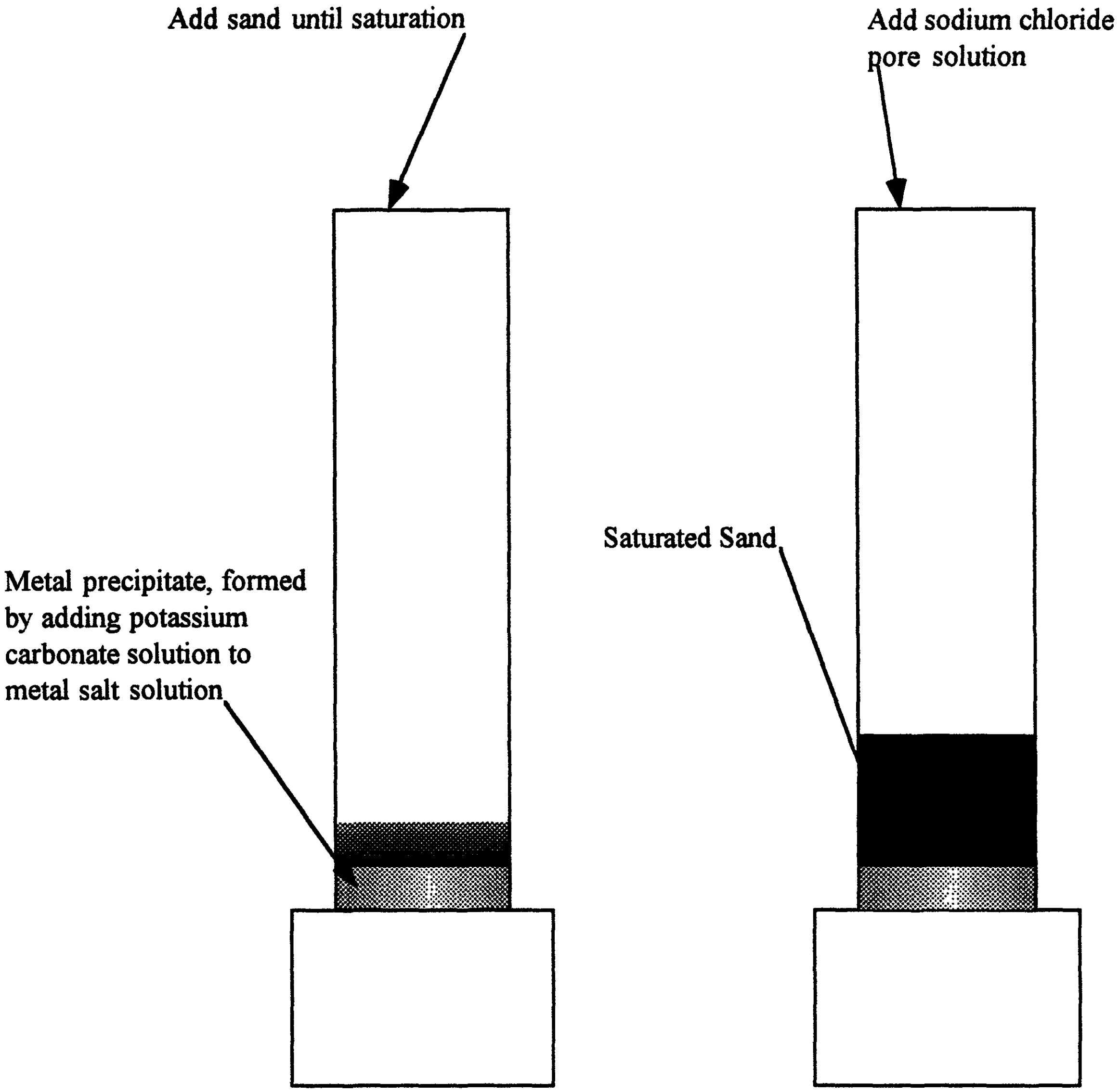


Figure 3.2d

figure 3.2d).

8. Sufficient amount of sand was pored into the cell to fill the cell completely (see figure 3.1b).

9. The plexiglass cell was closed by attaching the second inner end cap to the cell (see figure 3.2b).

10. The outer end caps were attached to the inner end carps at both ends (see figure 3.2c).

11. The anode purge solution was pumped in a re-circulating manner between the anode electrode well and the anode reservoir. The cathode purge solution was pumped in a re-circulating fashion between the cathode electrode well and the cathode reservoir (see figure 3.1).

12. The power supply was connected to the experiment by the carbon electrodes. The voltage applied was adjusted until the voltage drop measured across the passive electrodes reached the desired (30 V) value. The end of the cell with the metal precipitate served as the cathode end.

13. Samples were taken periodically from the anode reservoir (EDTA-lead complex destination) for lead concentration analysis (all lead concentration analysis were done with Plasma 40 Emission Spectrometer of Perkin-Elmer Corporation).

14. The pH of both the anode and cathode were measured at fixed intervals and the current passing through the cell was also recorded. The concentration of the EDTA chelate in the cathode was registered as well.

15. For the mixed metal experiments, 5ml of 0.1 M lead nitrate and 5 ml of 0.1 M zinc sulfate were used as the contaminant in place of 10 ml 0.1 M lead nitrate. Since lead sulfate is not soluble under most conditions, the precipitating agent for lead in this scenario is the sulfate anion while zinc is precipitated by the carbonate anion.

* Experiments were also carried out with different initial electrolyte concentrations in the pore solution as well as different EDTA concentrations in the cathode reservoir.

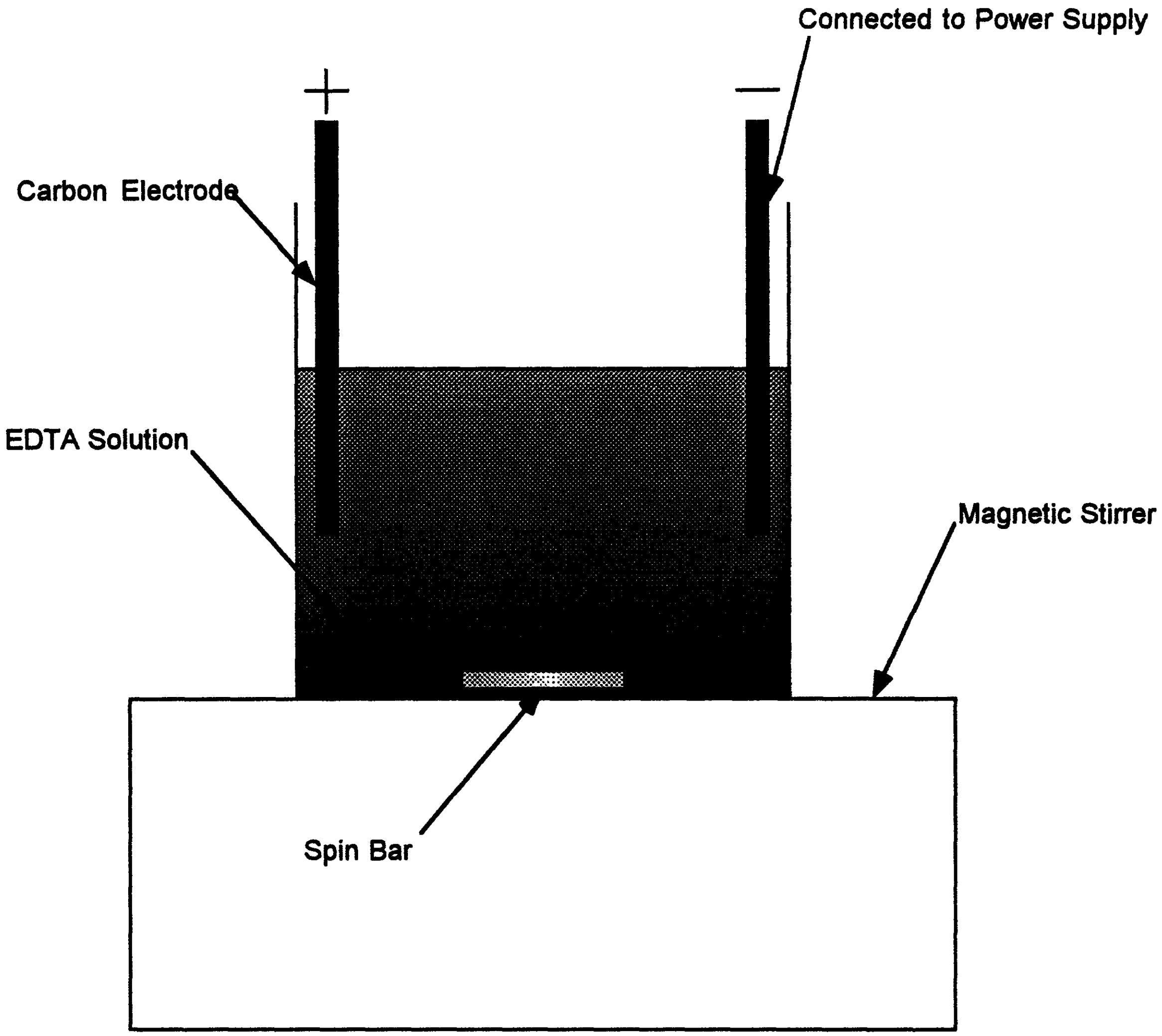


Figure 3.2e

3.2.3 EDTA Oxidation Experiments

1. The desired concentration of EDTA solution (400 ml) was prepared and placed in a 600 ml beaker (see figure 3.2e).

2. Carbon electrodes wre connected to the power supply and placed into the breaker. The beaker was placed atop a magnetic stirrer and a spin bar was placed in the beaker (see figure 3.2e).

3. The power supply was adjusted to deliver the desired current.

4. The concentration of EDTA was measured periodically.

Chapter 4

Experimental Results

This chapter presents the data obtained from the various experiments conducted to test the EDTA chelate's ability to solubilize and remove precipitated metals in saturated sand. A voltage drop of 30 volts was applied across the cell used in all contaminant removal experiments, as described in the previous chapter. In experiment I, the initial sand pore solution had an electrolyte concentration of 0.2 M and the cathode reservoir consisted of a 0.2 M EDTA solution. The metal contaminant in experiment I was lead (10 ml 0.1 M lead nitrate solution), precipitated by 1 ml 1.0 M potassium carbonate solution. Experiment II was identical to experiment I except for the electrolyte concentration of the initial sand pore solution and the cathode reservoir EDTA solution, which were 0.1 M sodium chloride and 0.1 M EDTA respectively. Experiment III had the same setup as experiment II with the exception that the 10 ml 0.1 M lead nitrate contaminant was replaced by 5 ml of 0.1 M lead nitrate and 5 ml of 0.1 M zinc sulfate. Experiment IV was identical to experiment III but with different electrolyte concentrations in the sand pore solution sand cathode reservoir, which were 0.05 M sodium chloride and 0.05 M EDTA respectively. Experiment V had the same chemical setup as experiment I, but efforts were made to spread the precipitate as opposed to the standard setup (see chapter 3). Experiment VI was identical to experiment I in every way besides the fact that this experiment had an initial sand pore solution of 0.1 M sodium chloride against the 0.2 M sodium chloride in experiment I. The first experiment conducted to examine the EDTA chelate's ability to purge precipitated metal contaminant is here labeled the exploratory experiment. This experiment is different from all others presented here in that the lead was precipitated by 2.0 M sodium chloride as opposed to 1.0 M potassium carbonate. In addition, the results from the EDTA oxidation test are also presented in this chapter; of which a detailed description of the setup is given in chapter 3.

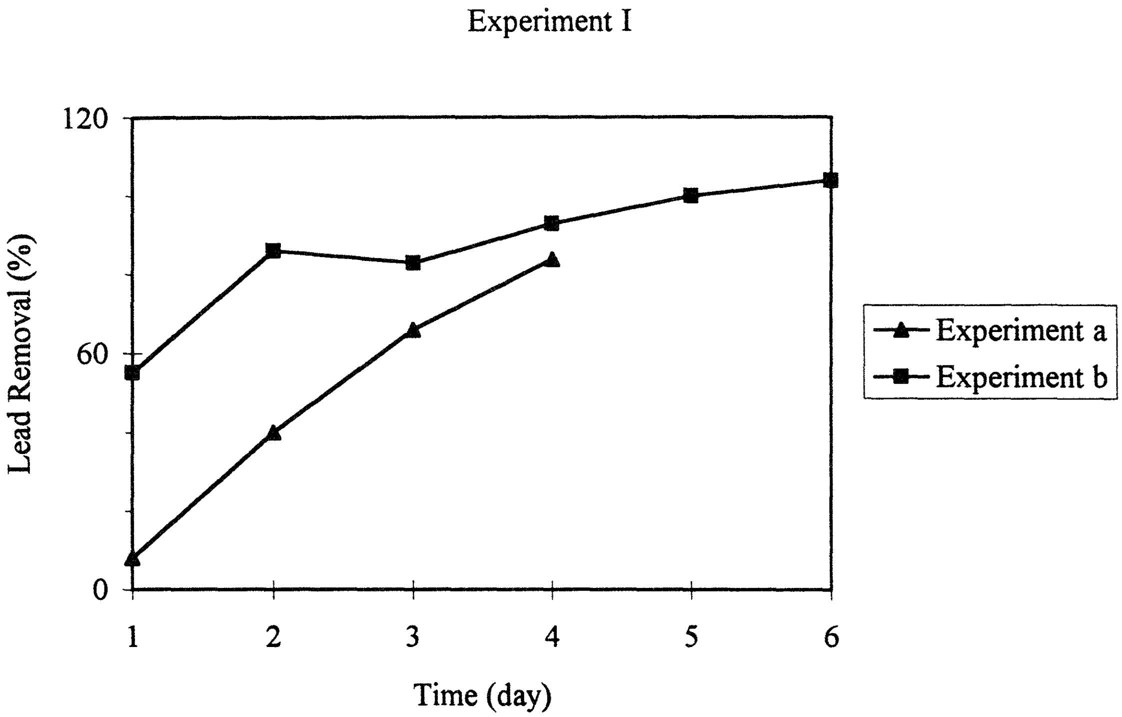


Figure 4.1a

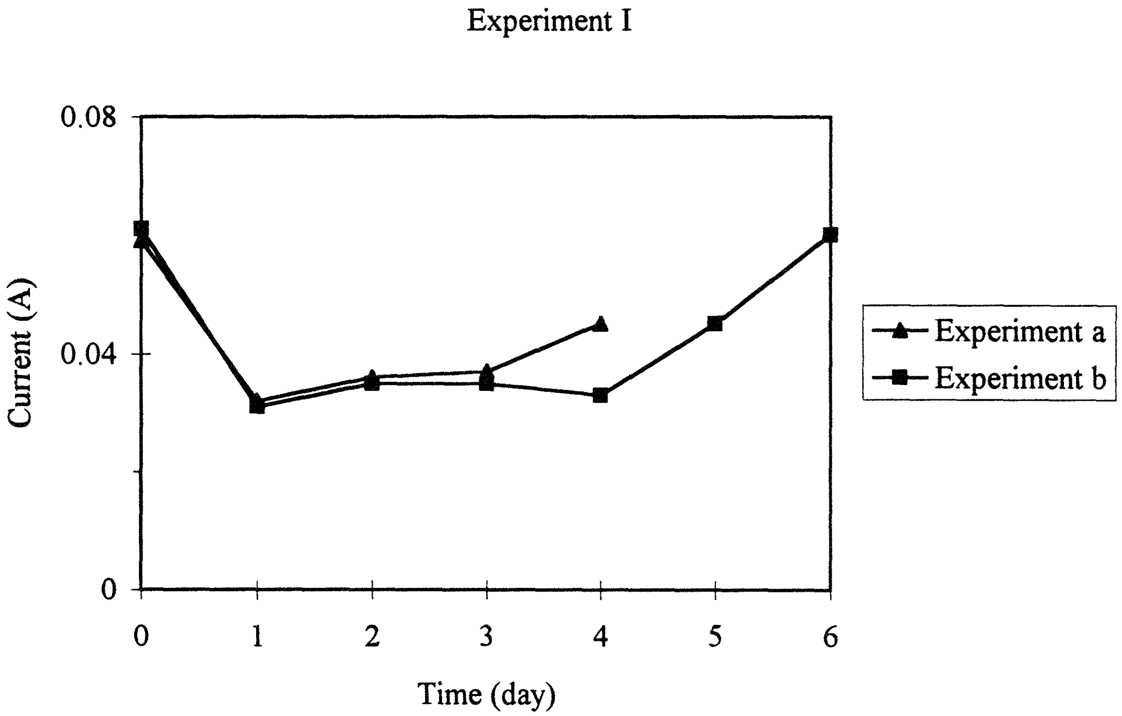


Figure 4.1b

Experiment I

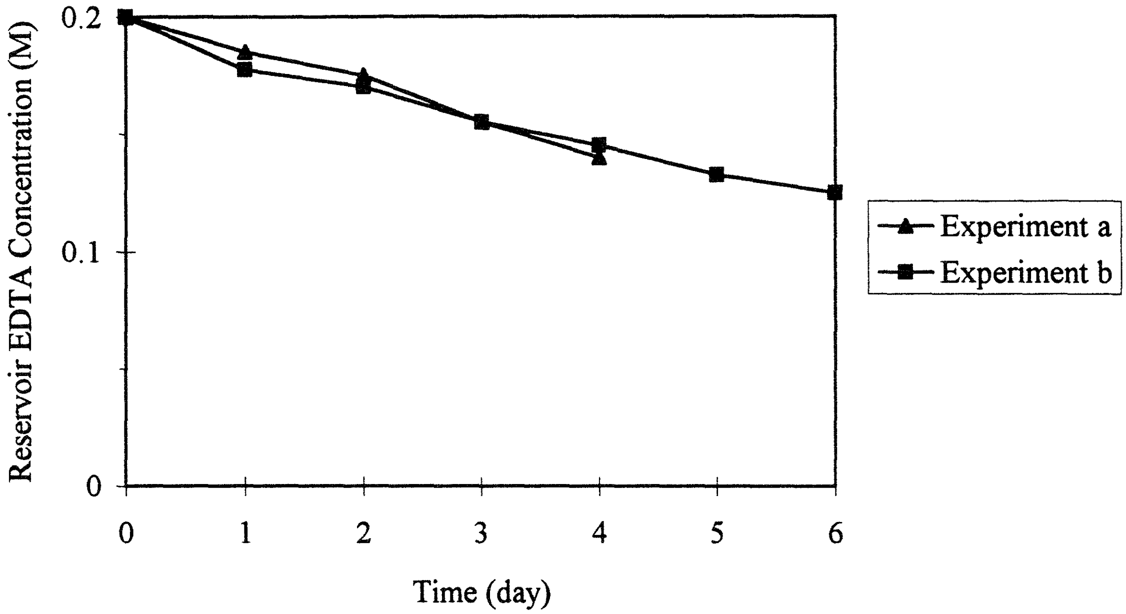


Figure 4.1c

Experiment I

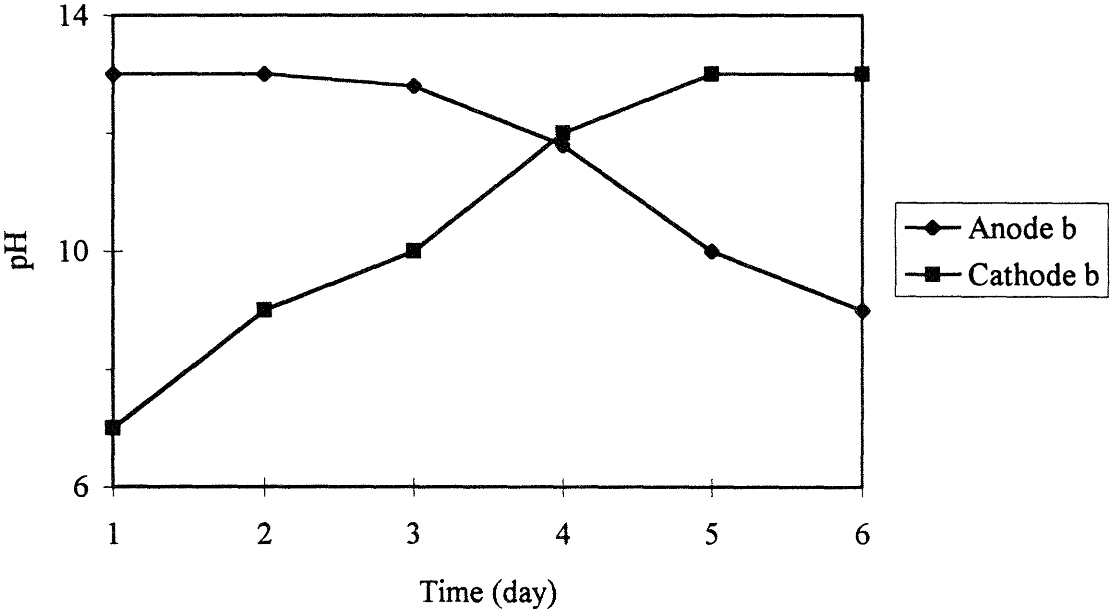


Figure 4.1d

Experiment II

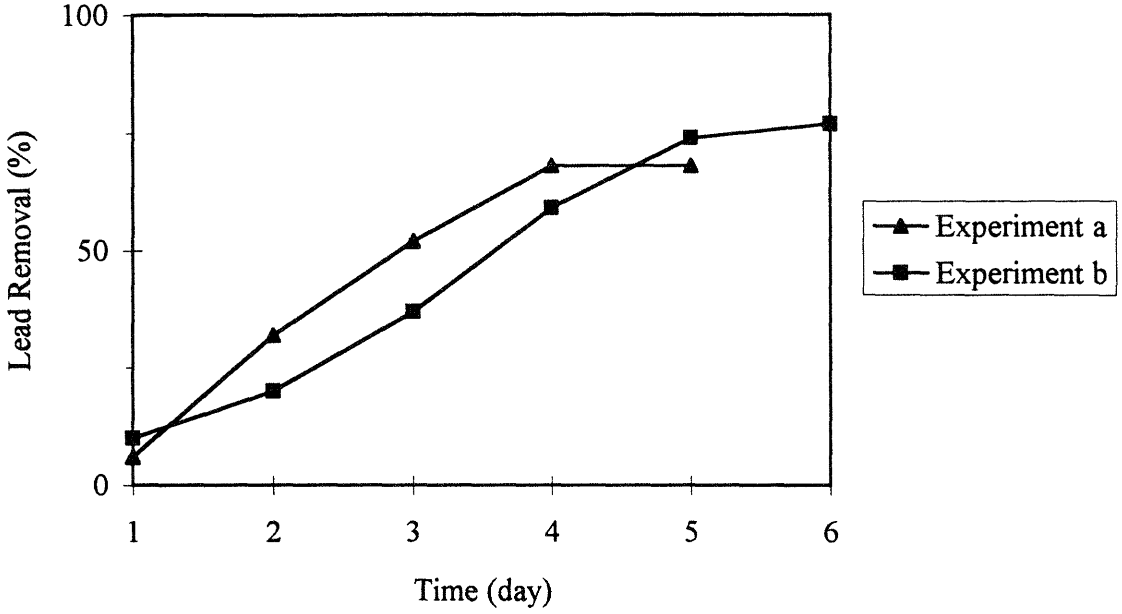


Figure 4.2a

Experiment II

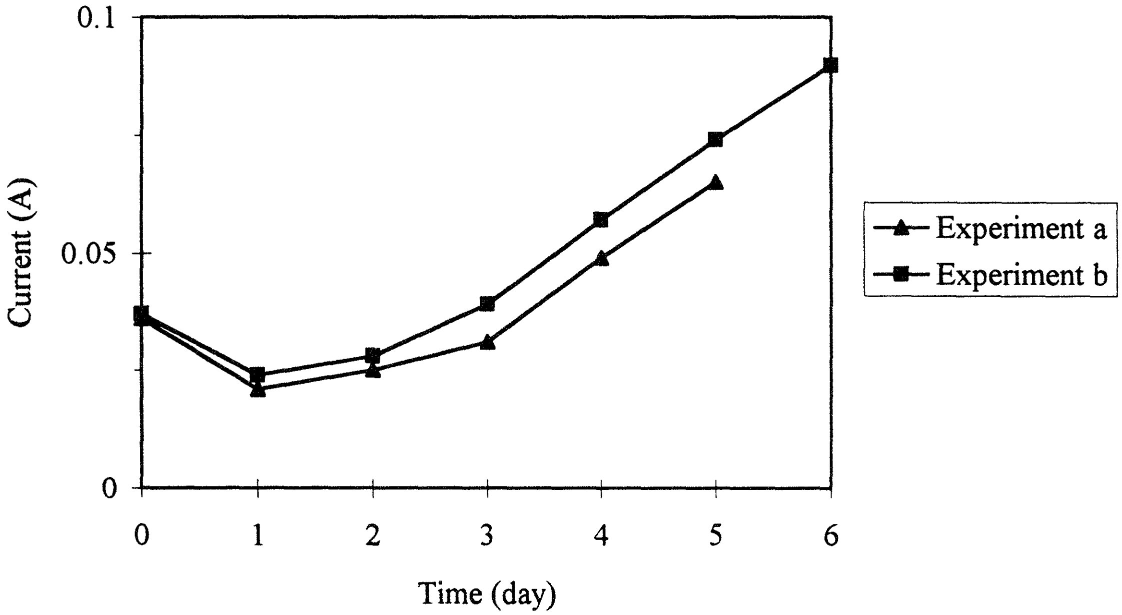


Figure 4.2b

Experiment II

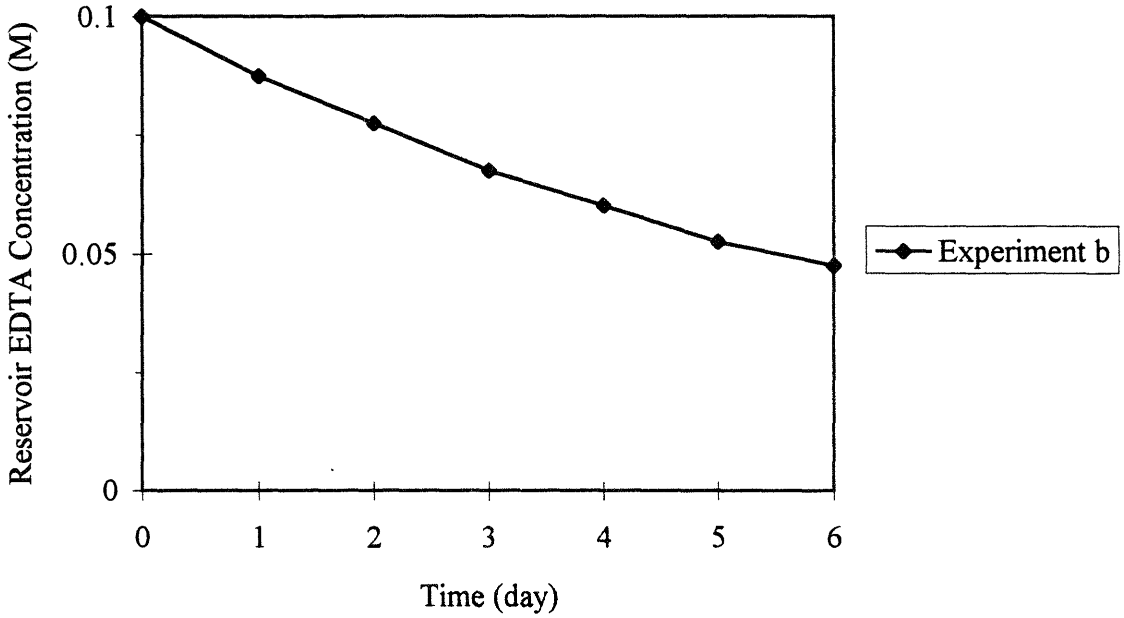


Figure 4.2c

Experiment II

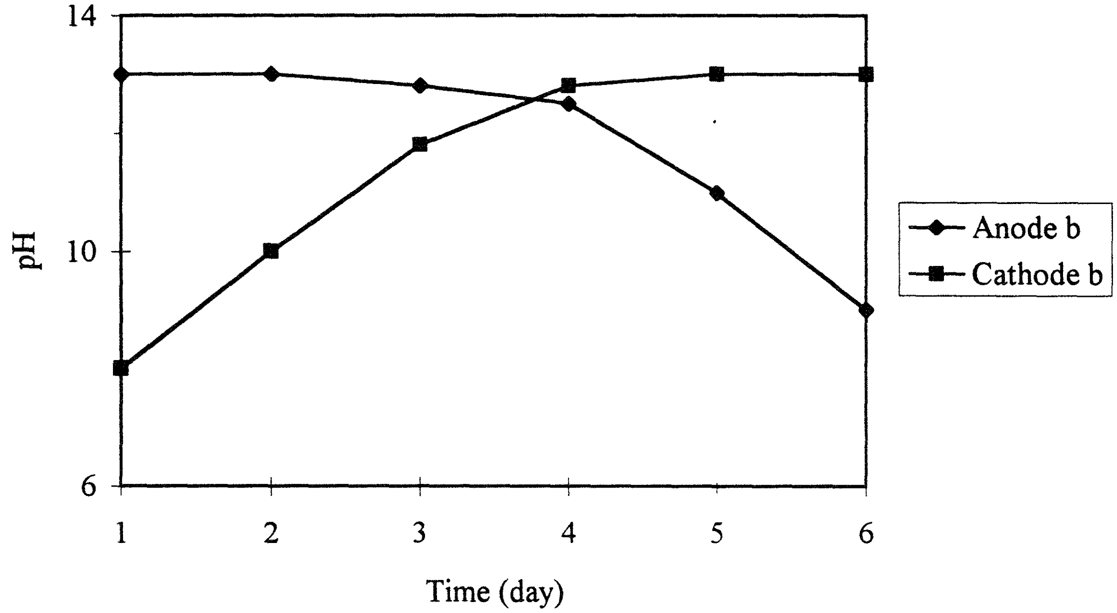


Figure 4.2d

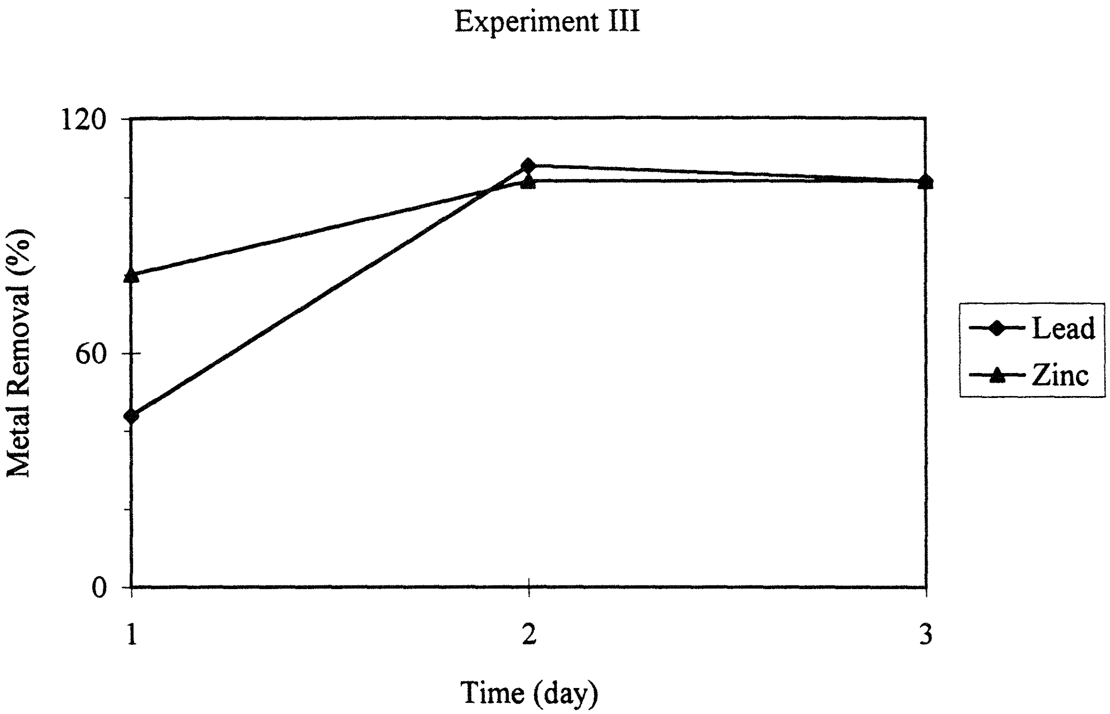


Figure 4.3a

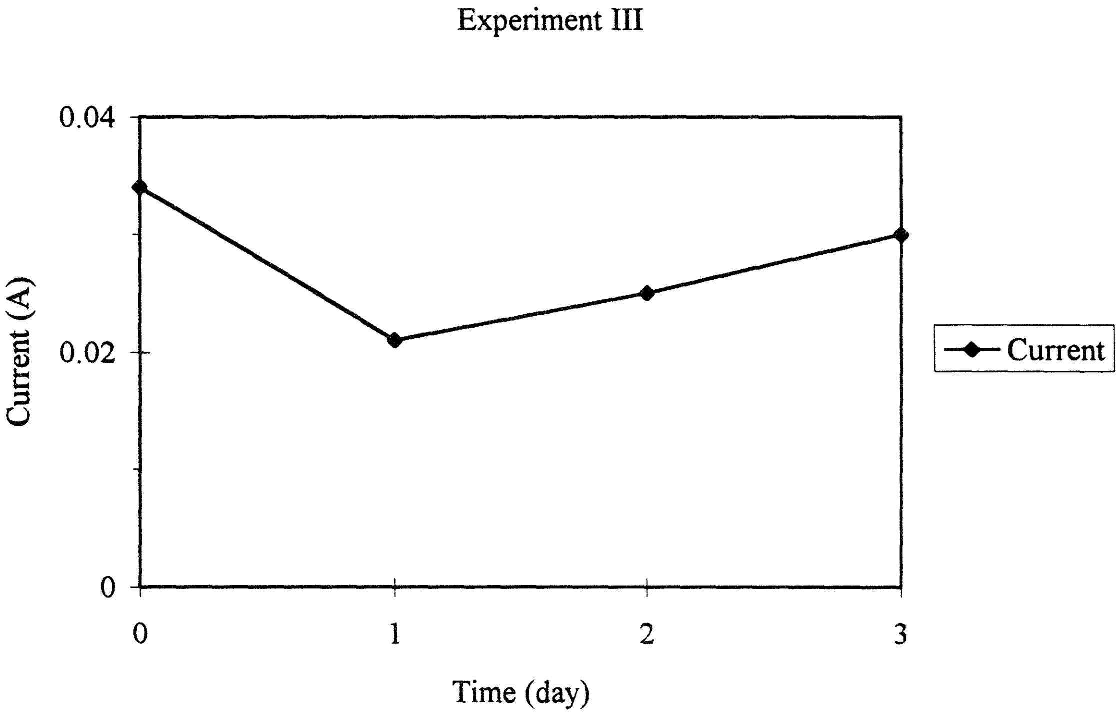


Figure 4.3b

Experiment III

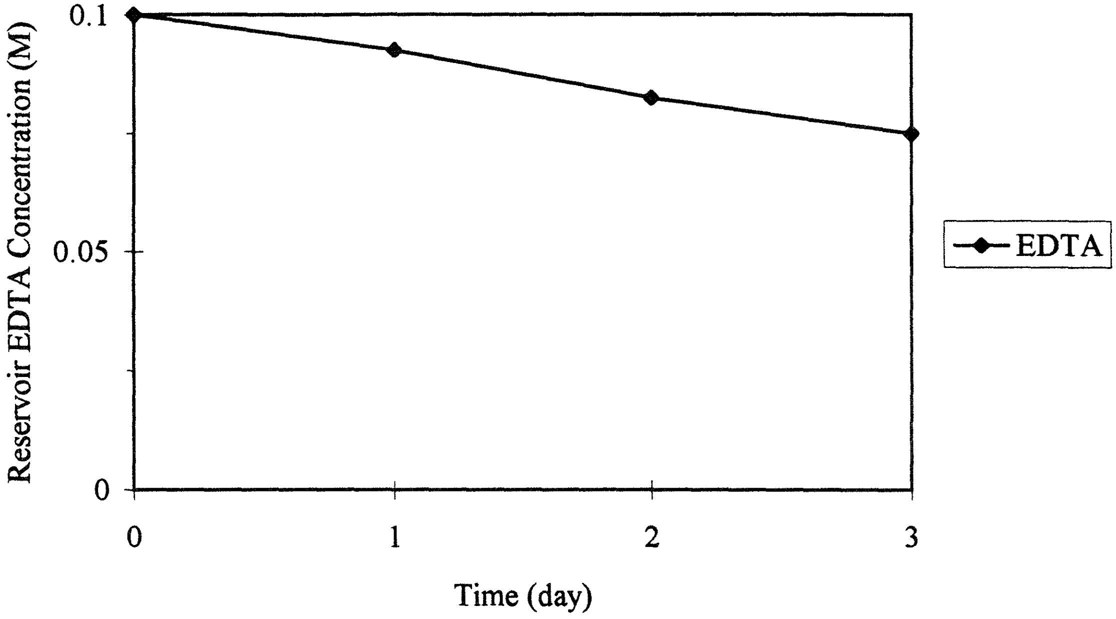


Figure 4.3c

Experiment III

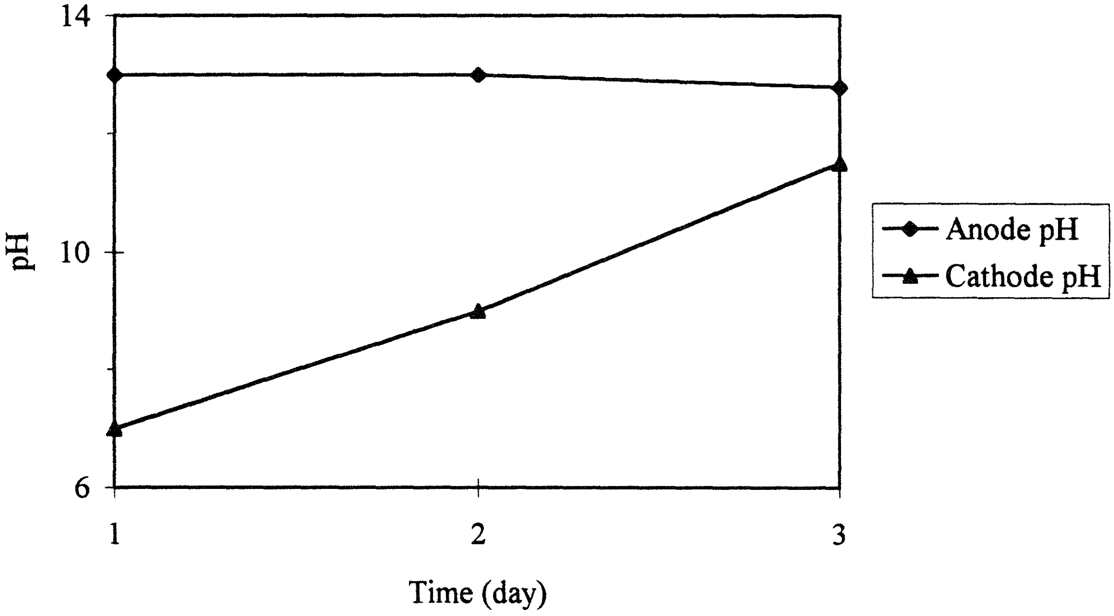


Figure 4.3d

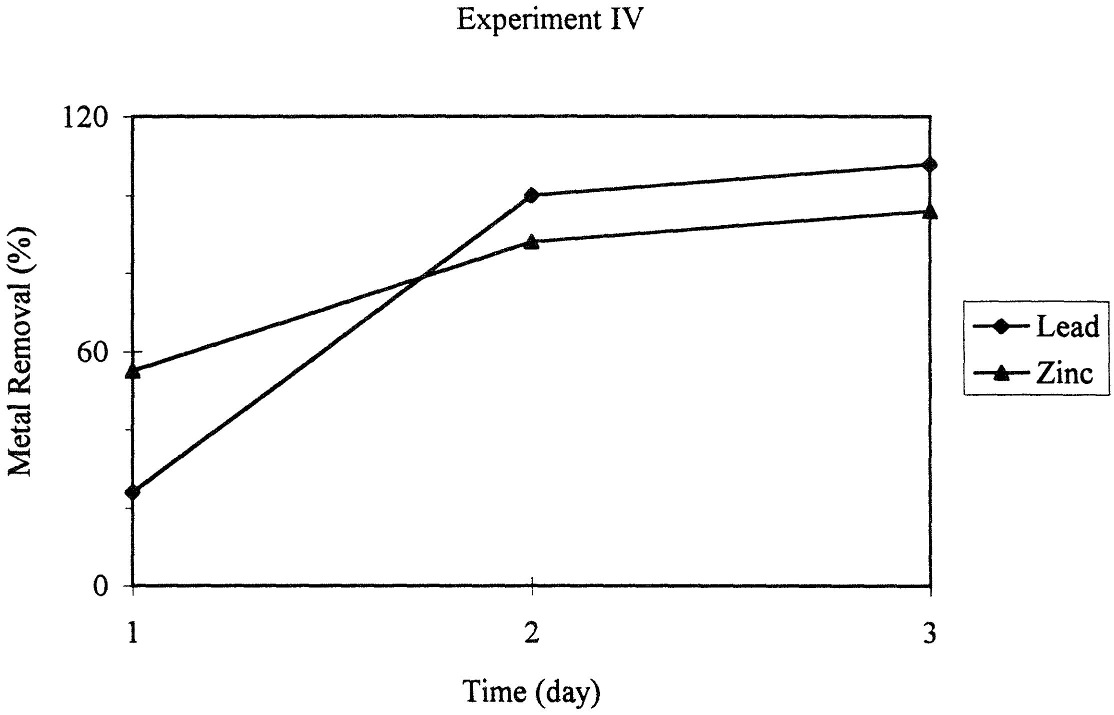

Experiment IV

Figure 4.4a

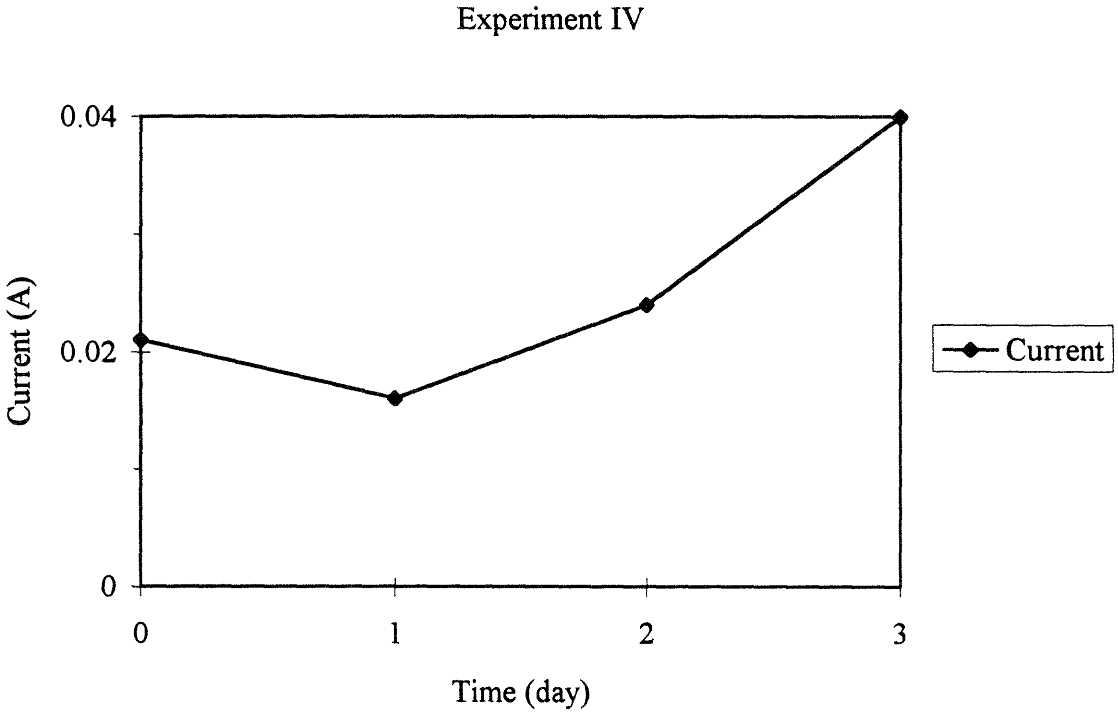

Experiment IV

Figure 4.4b

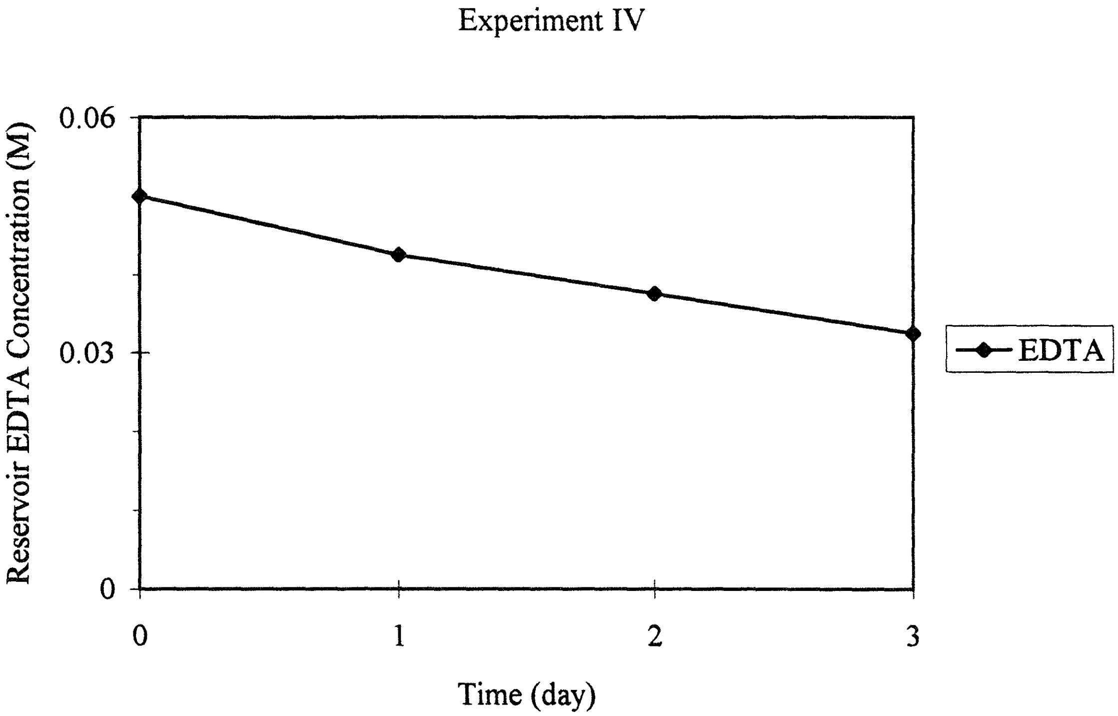

Experiment IV
Reservoir EDTA Concentration (M)
0.06
0.03
0
0
1
2
3
Time (day)
EDTA

Figure 4.4c

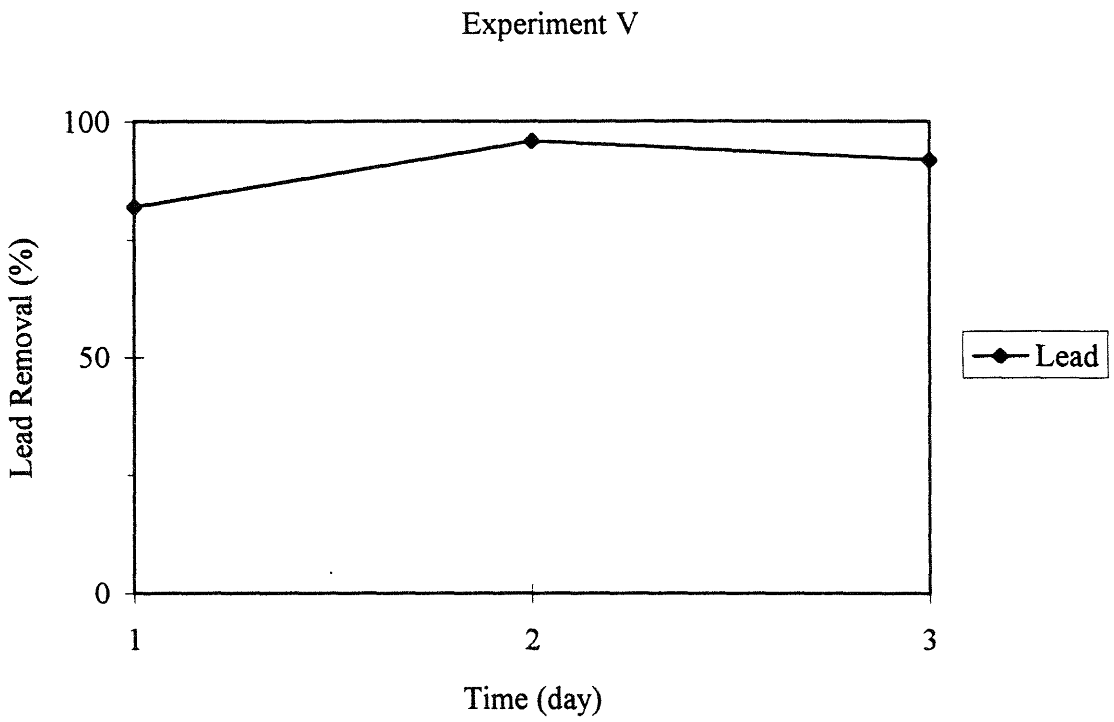


Figure 4.5a

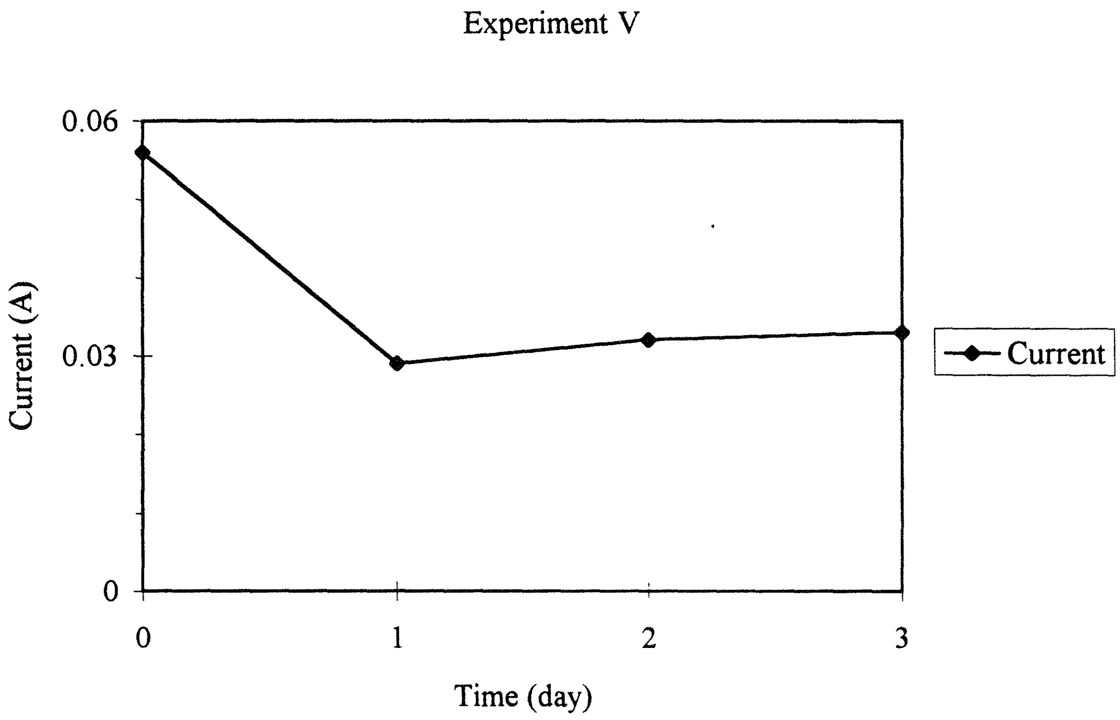


Figure 4.5b

Experiment V

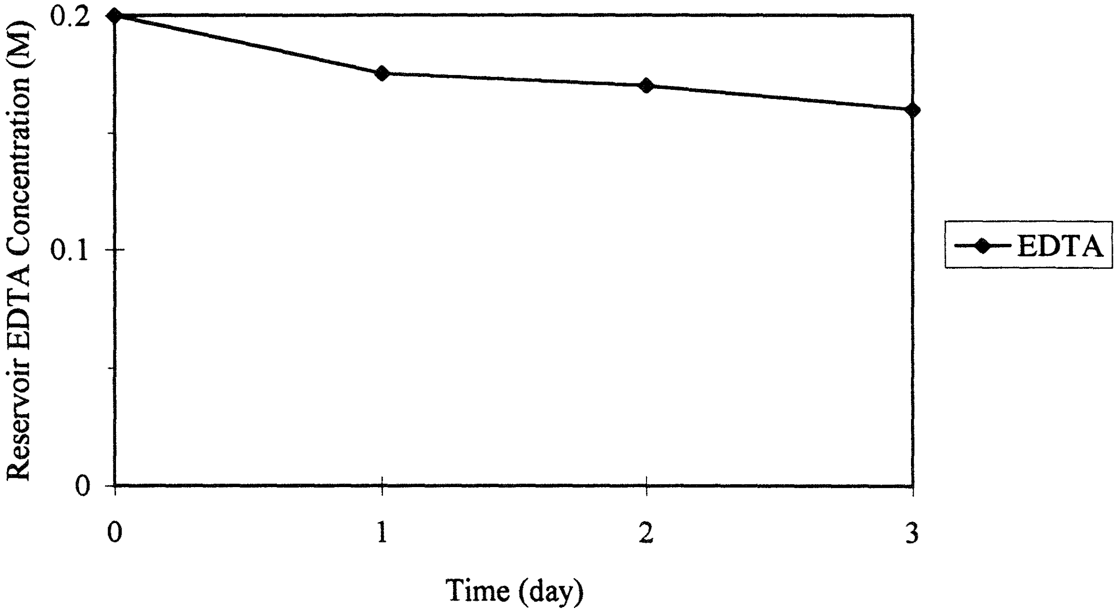


Figure 4.5c

Experiment V

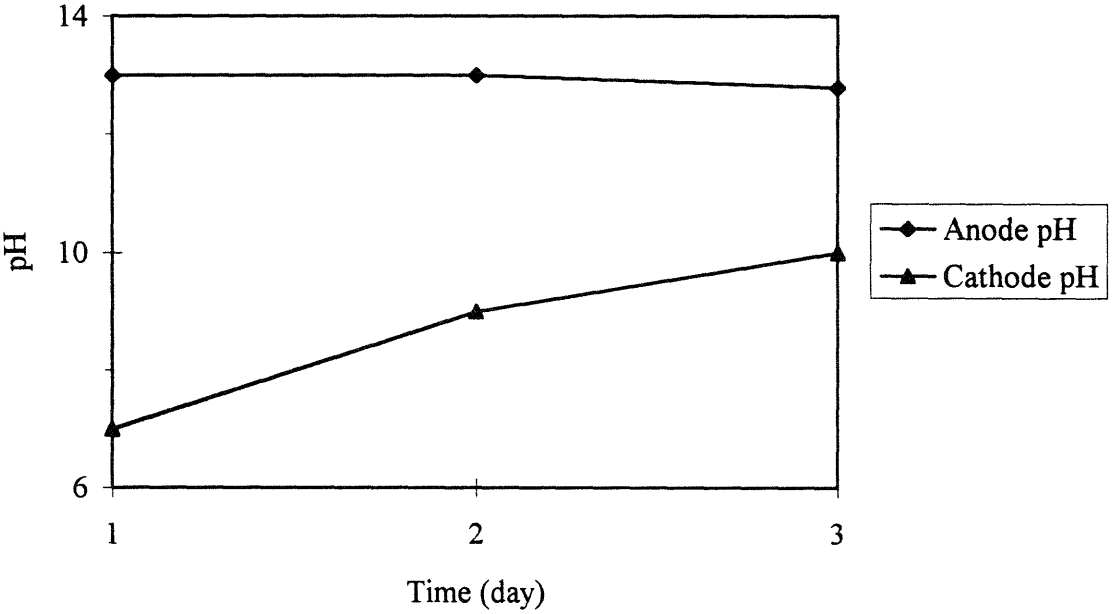


Figure 4.5d

Experiment VI

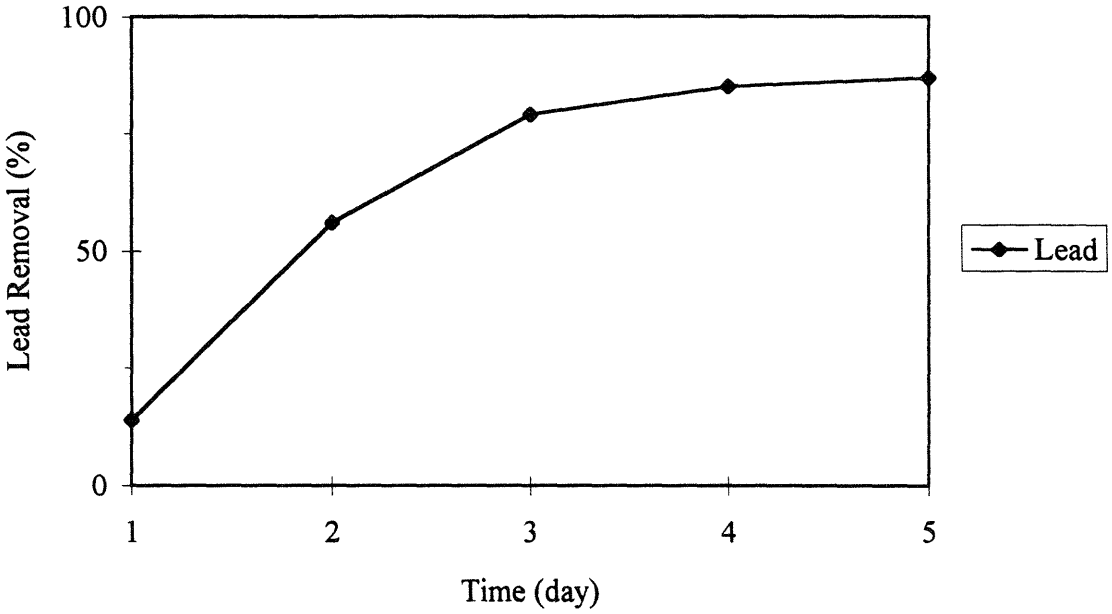


Figure 4.6a

Experiment VI

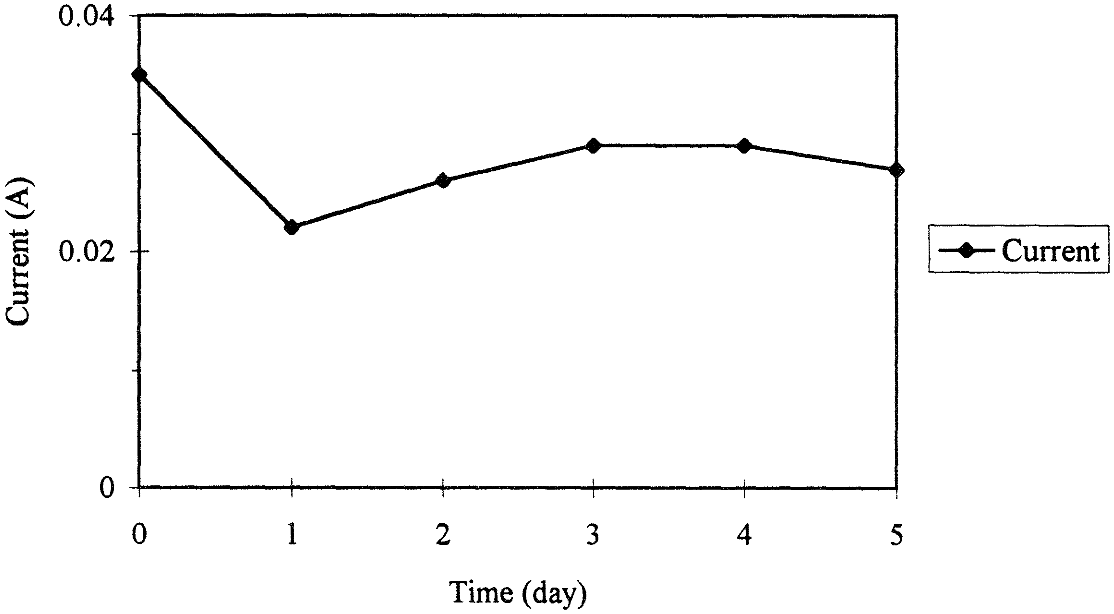


Figure 4.6b

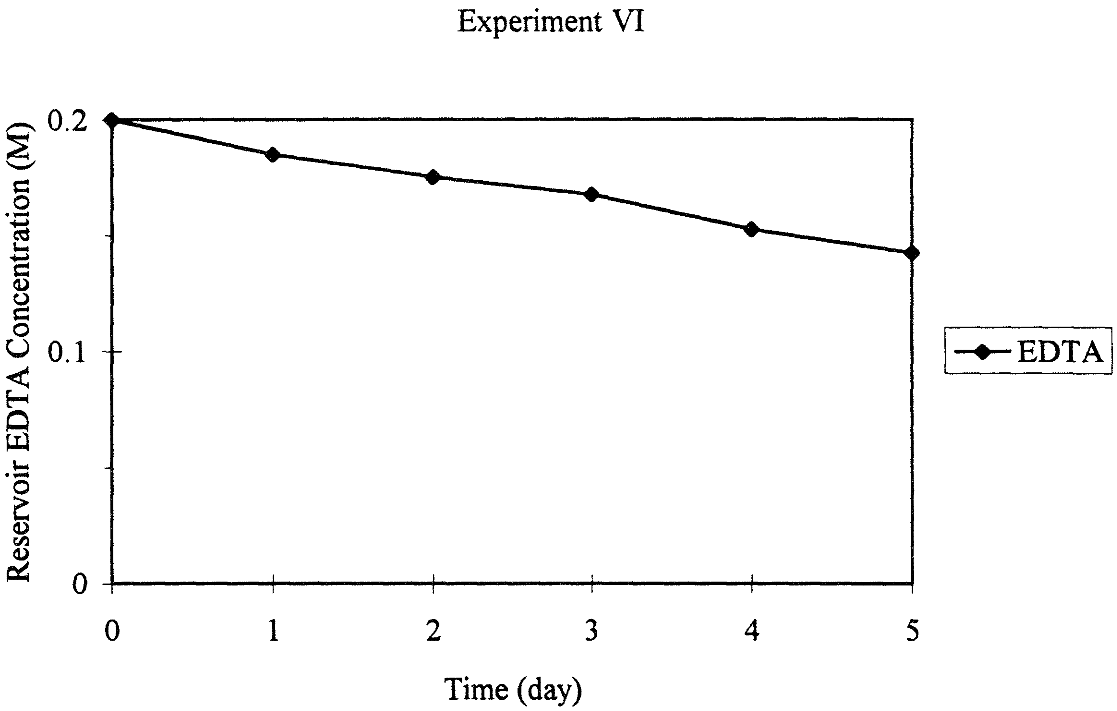


Figure 4.6c

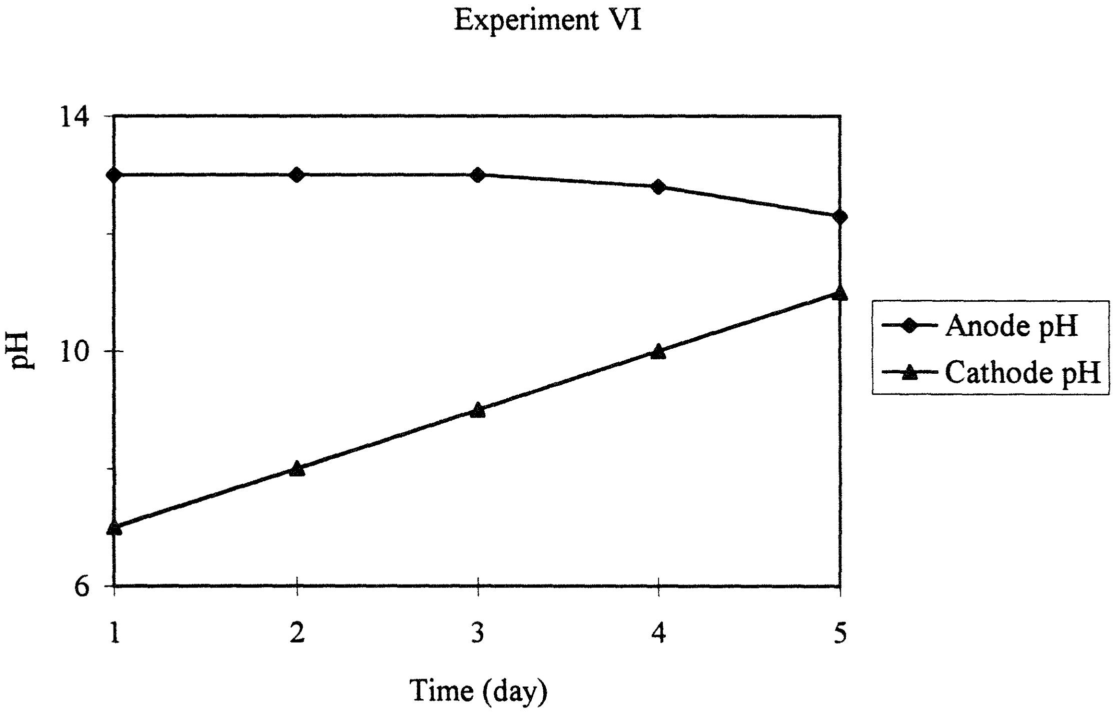


Figure 4.6d

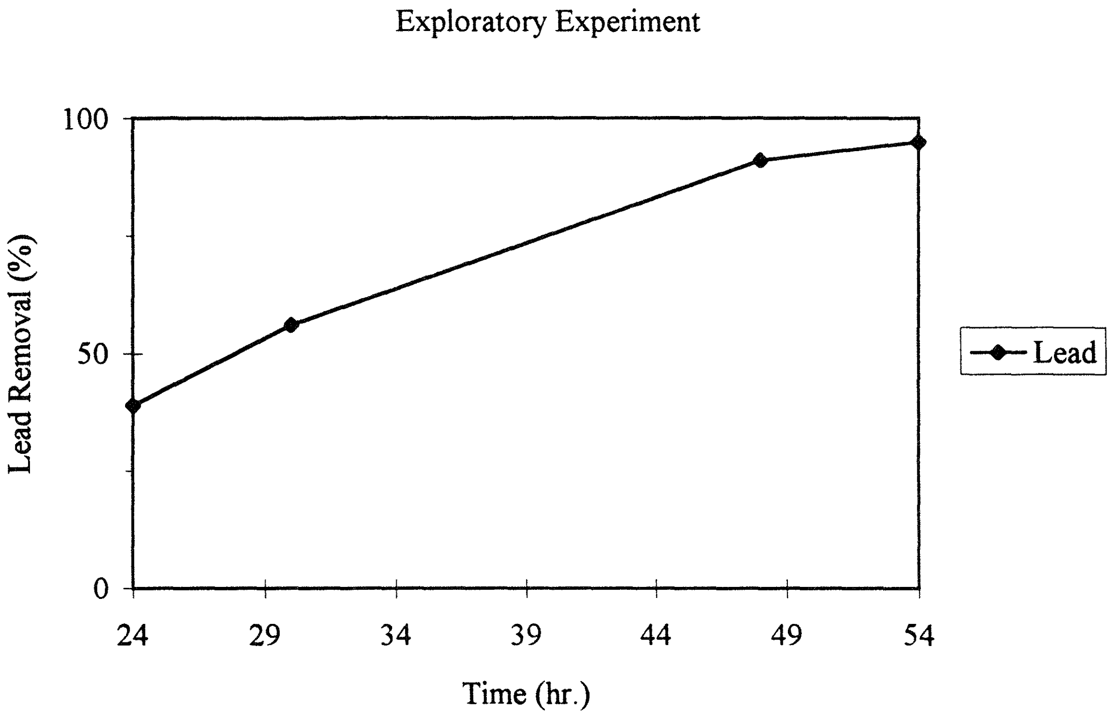


Figure 4.7

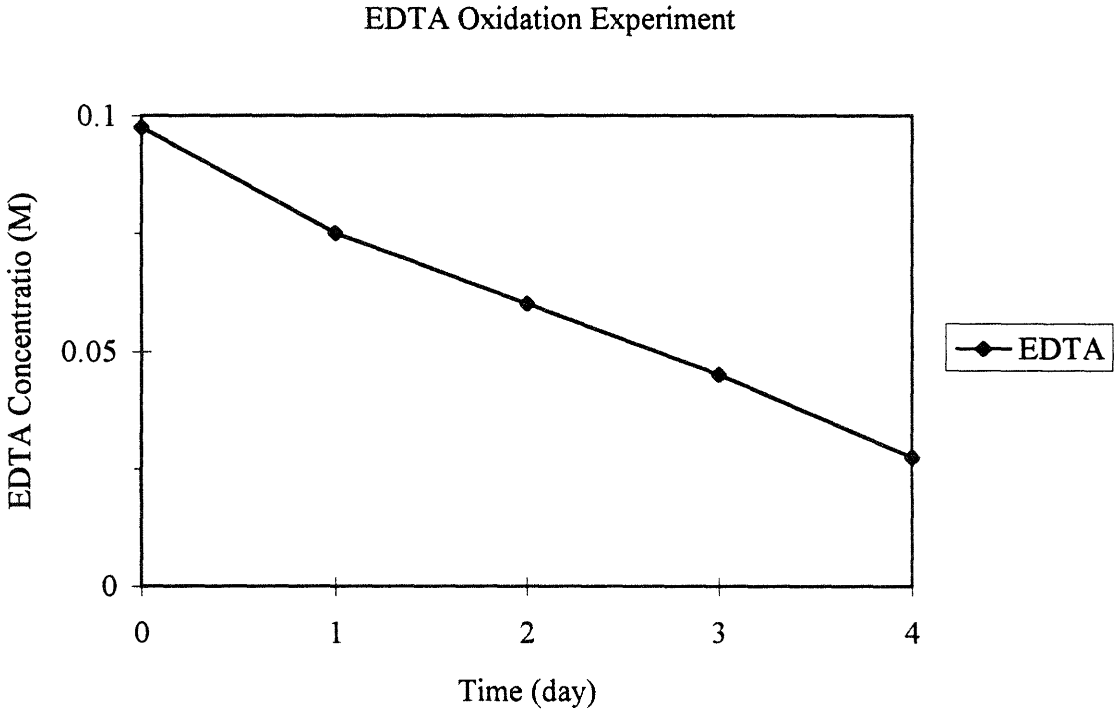


Figure 4.8

Experimet	Removal Efficiency	Length of Experimet	EDTA Efficiency at 80 % Removal (mole metal/mole EDTA)
Ia	84 %	4 day	3.5 %
Ib	104 %	6 day	7.3 %
IIa	68 %	5 day	3.2 % *
IIb	77 %	6 day	3.7 % *
III) Lead) Zinc	104 % 104 %	3 day	15.4 0% 26.7 %
IV) Lead) Zinc	108 % 96 %	3.day	20.0 % 17.6 %
V	96 %	3 day	8.2 %
VI	87 %	5 day	4.5 %

* Never reached 80 % efficiency, the efficiency at the conclusion of the experiment is reported instead. All experiments were terminated either after all metal contaminants have been removed or after the removal process has stopped.

Chapter 5

Conclusions and Future Work

The experimental data presented in the previous chapter demonstrated that the EDTA chelate is highly capable of purging precipitated metal contaminants from the pore solution of sand subjected to electric fields. In all of the experiments conducted, a sizable percentage, if not all, of the metal contaminant was removed by the end of the experiment. The efficiency with which the EDTA chelate accomplishes its task seemed to be dependent upon the type of metal complex (precipitate) in question. The higher the stability constant between the metal and its precipitating anion, the longer it took the EDTA chelate to solubilize the precipitate and remove the metal waste. Experiments in which the lead was precipitated by sulfate anions exhibited relatively high EDTA efficiencies, contrasting with the markedly lower EDTA efficiencies turned in by those experiments in which the lead was precipitated by carbonate anions. The distribution of the precipitate also impacted upon the ease with which the EDTA chelate can solubilize and remove the metal precipitate. In experiments where the metal precipitate was more uniformly distributed, the metals were removed much faster. Both of the observations fore mentioned are in agreement with chemical kinetics and are therefore unsurprising.

The experimental results and the conclusions drawn from those results represents a first step in the realization of the use of EDTA as an effective tool in soil remediation by means of electric fields. More work needs to be done in the modeling of the system in question. In particular, the role of kinetics and parameters such as back ground electrolyte concentrations, pore solution pH and soil chemistry should be explored and accounted for in a comprehensive mathematical model.

Bibiography

[1] R.F. Probstein, *Physiochemical Hydrodynamics. An Introduction*. Butterworth. Boston. 1989.

[2] R.A. Jacobs, M.S. Thesis, M.I.T., 1993

[3] H.E. Allen and P.H. Chen, "Remediation of Metal Contaminated Soil by EDTA Incorporating Electrochemical Recovery of Metal and EDTA," *Enviromental Progress*, Vol. 12, no. 4 pp. 284-292

[4] R.A. Jacobs. Personal communication.