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Feasibility of Using Solvent Extraction to Remediate Soils Contaminated with High Concentrations of Lead

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FEASIBILITY OF USING SOLVENT EXTRACTION TO REMEDIATE SOILS CONTAMINATED WITH HIGH CONCENTRATIONS OF LEAD

By

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ABSTRACT

FEASIBILITY OF USING SOLVENT EXTRACT TO REMEDIATE SOILS CONTAMINATED WITH HIGH CONCENTRATIONS OF LEAD

By

Brent LaSalle Wilson

Coincident high concentrations of organic compounds and metals in contaminated soils reduce the effectiveness of conventional treatment trains. Solvent extraction may be an alternative that can remove both the organic compounds and the metals. Solvent extraction enhances the amount of lead an acidic solution removes from sandy soil. Soil, water and organic extractant are mixed to an emulsion while controlling pH to 3.0 with hydrochloric acid. The extraction reaches equilibrium within 30 minutes. Four sequential 60-minute extractions were performed on a batch of soil. The organic extractant is di-(2-ethylhexyl) phosphate (DEHPA). The calcium form, Ca-DEHPA, reduces pH drop during extraction. Extractions were successful using DEHPA concentrations from 0.1 to 1.0 moles per liter in hexane. The organic extractant reduced the lead concentration in the sandy soil from 79,893 to 2,494 ppm. Extraction with only an aqueous solution reduced the lead concentration to 17,883 ppm. Lead is stripped from the extractant by contact with strong acid. Thus, the organic extractant enhances lead removal from highly contaminated soils with the potential for recycle.

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I. INTRODUCTION

The Comprehensive Environmental Response, Compensation and Liability Act of 1980, known as Superfund, and the Superfund Amendments and Reauthorization Act of 1986 mandated that the Environmental Protection Agency (EPA) remediate uncontrolled hazardous waste sites. As a result of these two acts, the EPA currently has 1,275 uncontrolled hazardous waste sites on the National Priority List (NPL). Of the sites on the NPL, 1,073 list lead as a contaminant of concern.[1] When metals and organics are both present in high concentrations, complications occur in the selection of remediation treatments.

When treatment is deemed appropriate, soils contaminated with organic waste have commonly been incinerated, while soils contaminated with metals have been stabilized and solidified with pozzolanic materials. When both constituents are present, the EPA will recommend a "treatment train" consisting of incineration followed by solidification/stabilization. Usually this "treatment train" approach is appropriate since the incinerator destroys the organics and the metals pass through the incinerator leaving in the ash. The "treatment train" approach, however, is not feasible in cases when the volatility of metals would cause unacceptable emissions from the incinerator stack.

An example of such a problem, is a request by Pacific Power and Light Company for a variance from treatment rules for a site contaminated with "hot spots" containing 1,100 mg/kg of PCBs and 87,700 mg/kg of lead.[2] The "treatment train" approach of incineration followed by solidification/stabilization is inhibited by the high concentrations of lead which will volatilize in the incinerator and exit the incinerator stack. Because permits for incinerators limit the feed rate of lead to minimize the lead emissions, incineration of this soil would result in violations of air pollution permits for the incinerators at practical feed rates. This problem will become greater when Clean Air Act regulations significantly lower the acceptable emission limits of metals.[3]

The other treatment, solidification/stabilization of wastes containing high concentrations of organics and metals is not feasible.[4] The high concentrations of organics hinder particle dispersion, hydration and matrix hardening reactions that cause the material to set-up. High concentrations of certain lead compounds may also retard cement hydration and matrix growth in the material being stabilized. If the materials do not set-up, then the "stabilized" material will leach both organics and metals.[5] The Universal Treatment Standards (UTS) place rigorous requirements on stabilization/solidification techniques.[6] The UTS are lowering the acceptable amounts of leachable materials from waste prior to disposal. As a result, these lower levels require a greater degree of immobilization during treatment prior to disposal. For lead, the previous limit from a Toxicity Characteristic Leaching Procedure (TCLP) analysis was 5.0 ppm.[7] The new UTS limit for lead is 0.7 ppm.

While the above "treatment train" may be an appropriate remediation for some of the uncontrolled hazardous waste sites containing both metal and organic compounds, it is apparent with the high incidence of lead that alternative methods of remediation need to be developed. One such alternative method may be the use of solvent extraction to remove both the organic and metal compounds from the soil.

The use of solvent extraction to remove organic contaminants from soil and sludge has been successfully demonstrated by the B.E.S.T. Solvent Extraction Technology process, CF Systems Corporation Solvent Extraction, and other pilot-scale solvent extraction systems.[8, 9, 10] This type of physical extraction is classic "solvent extraction" where separation occurs purely by differences in physical properties such as polarity. During physical extraction the solute is of identical chemical form in both phases. A type of solvent extraction that removes metals involves a chemical reaction between the metal species present in the aqueous phase and one or more components of the organic or solvent phase. When the metal ion is extracted from the aqueous phase it's charge is neutralized by the organic component. This type of extraction is also referred to as liquid ion exchange. This type of extraction requires the metal contaminant to be solubilized in the aqueous phase prior to extraction in the organic phase.

The use of chemical extraction has been used in copper mining since 1968 and in the nuclear industry since 1950.[11] However, very little information is available on the use of solvent extraction to remove lead from soils. For this reason, it appeared that research into the use of a liquid ion extractant to further the use of solvent extraction would be of interest. If a good physical extractant for organic contaminants can be demonstrated as an acceptable solute for the liquid ion extractant, then the resulting combination may be useful for the simultaneous removal of organic compounds and metals from contaminated soils. The purpose of this research is to determine the feasibility of using a chemical extraction process to remediate lead contaminated soils.

II. THEORETICAL CONSIDERATIONS

A. Solvent Extraction

Solvent extraction is based on the principle that a solute can distribute itself between two solvents which are immiscible due to differences in polarity.[12] This distribution can then be utilized to separate solutes, by leaving an undesirable, co-solubilized solute behind. In a solvent extraction circuit, a metal-bearing aqueous solution is contacted with an organic solvent by turbulent mixing. During this extraction phase, some of the metal is transferred to the organic phase. The phases separate during settling and the metal-loaded solvent (organic phase) is sent to a stripper where the metal is transferred into another aqueous phase. After stripping, the solvent is recycled back to the extraction stage. A simplified flow diagram of the extraction circuit is shown in Figure 1.

The flow diagram in Figure 1 represents the liquid phases of an extraction circuit used to remove lead from soil. Prior to the liquid phase extraction, lead is released into the aqueous phase by an acid. An organic extractant is then used to remove the lead ion from the aqueous phase. By removing the lead ion from the aqueous phase, the organic extractant will reduce the lead concentration in the aqueous phase which should enhance the rate of lead solubilization into the aqueous phase. A schematic of the reactions between the soil phase, aqueous phase and the organic extractant are represented in Figure 2. Based on this principle, different types of extraction systems were analyzed to identify a system

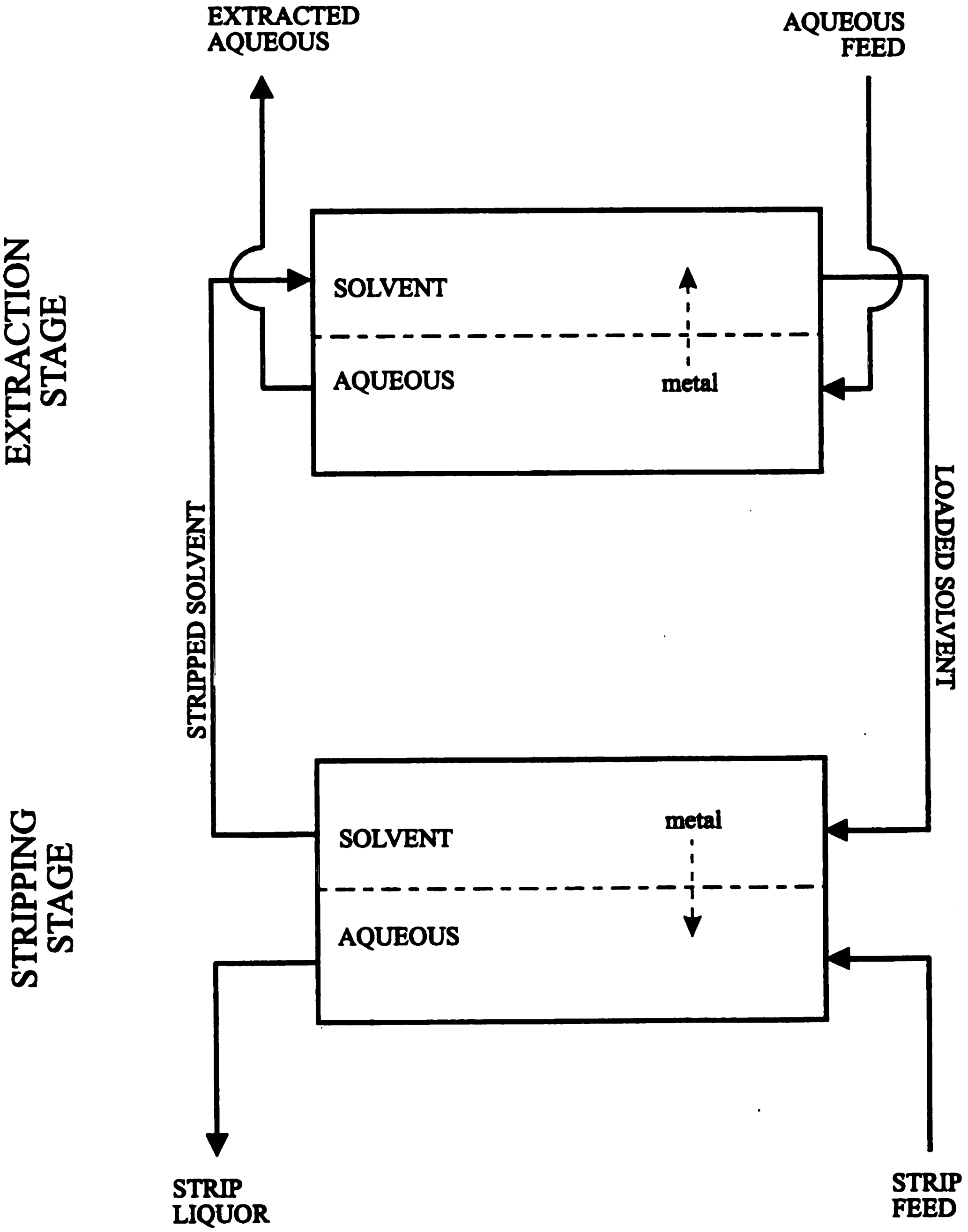


Figure 1. Extraction Cycle

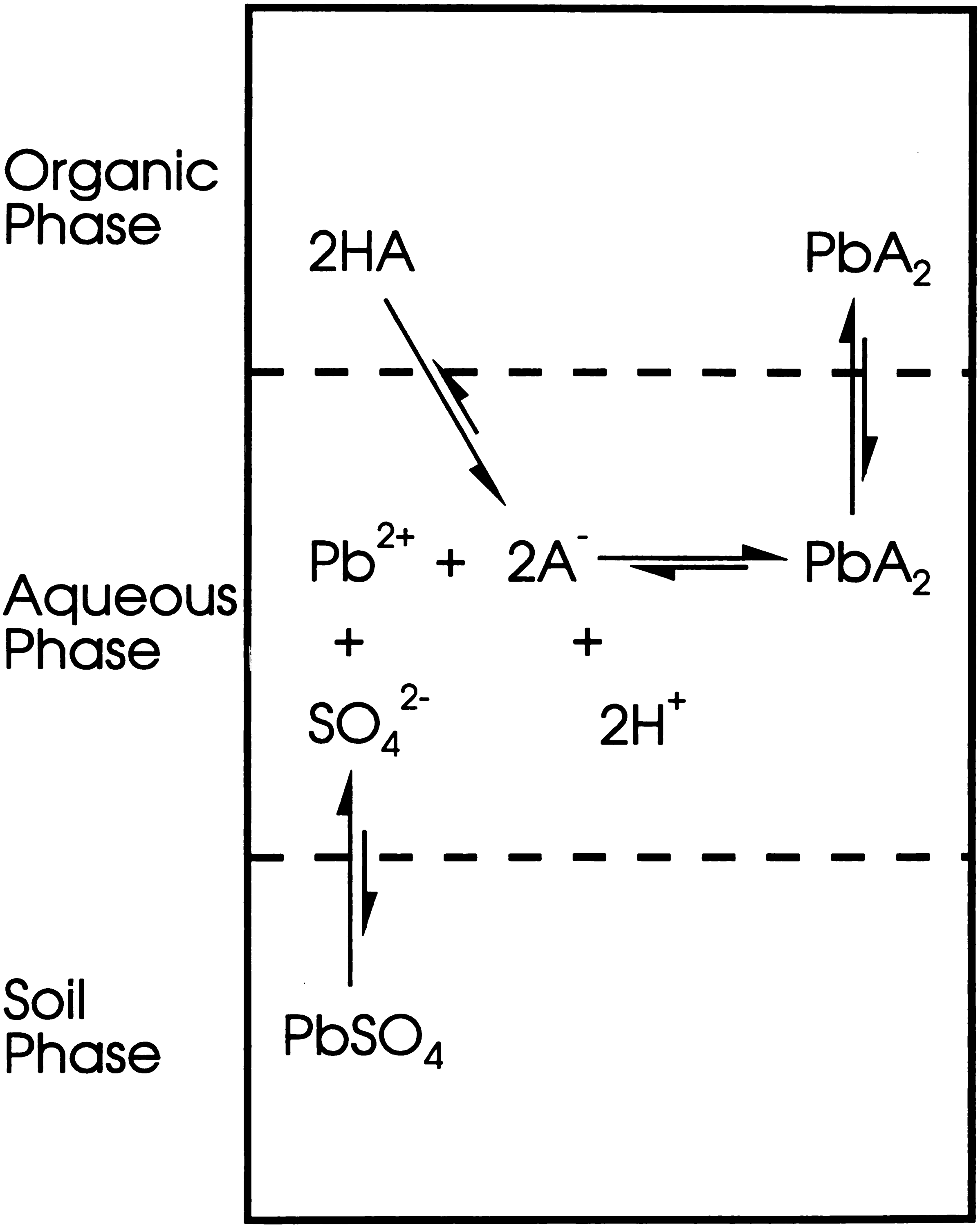


Figure 2. Reactions between Soil, Aqueous and Organic Phases

which could extract lead and which might be compatible in a soil extraction system.

In solvent extraction systems, water is usually used for the polar phase and an organic solvent is used for the nonpolar phase. The driving force during an extraction is based on the fact that it takes less energy to produce a hole in a non-polar solvent than in a polar solvent because the forces binding the molecules in the non-polar solvent are much smaller. As a result, an uncharged species will be more soluble in non-polar solvents than polar solvents. However, due to other thermodynamic considerations, there will remain a minimum concentration of the solute in the polar solvent.

The driving force for the extraction of an ionic species is similarly explained when solvation by an organic solvent causes a favorable change in free-energy. The process by which polar and nonpolar solutes are extracted can be divided into two categories; physical extraction and chemical extraction. The division is based on the process used to enable a favorable free-energy change.

1. Physical Extraction

a. Theory of Physical Extraction

Physical extraction is the more classic "solvent extraction" where separation occurs purely by differences in physical properties such as polarity. A non-polar solute requires a solvating agent, such as the waters of hydration, to maintain solubility in the polar solvent. As a result, a non-polar solute will have a higher solubility in a non-polar solvent. The favorable free-energy change for the extraction process comes from the removal of the waters of hydration as the non-polar solute transfers into the non-polar solvent. During this type of transfer, the solute does not change it's chemical form. A simple equilibrium equation for a physical extraction needs to only represent the concentration of the solute, X, in each of the phases as follows:

$$X_{org} \Leftrightarrow X_{aq} \tag{1}$$

In this type of extraction, the Nernst distribution law is usually valid and the extraction coefficient, E, is represented by:[13]

$$E = \frac{X_{org}}{X_{aq}} \tag{2}$$

b. Physical Extraction in Soil Remediation

The use of physical extraction processes to remove organic contaminants from soil and sludge have been successfully demonstrated by the B.E.S.T. process, CF Systems organics extraction system, and other Pilot-Scale Solvent Extractions.[8, 9, 10] However, neither the B.E.S.T. process nor the CF Systems have shown the ability to remove both organics and metal contaminants. Physical extraction processes are limited to those metals which have significant solubilities as uncharged species. Metals are normally solubilized in aqueous solutions as hydrated metal ions which have little or no tendency to transfer into an organic phase. In order for the hydrated metal ion to transfer to the organic phase, chemical extraction is required.

2. Chemical Extraction

a. Theory of Chemical Extraction

A chemical extraction processes involves the transfer of an ion from the polar, aqueous phase, to the non-polar, organic phase. To make the process of extracting an ion into a non-polar phase have a favorable free-energy change, two major requirements must be met: the ion's charge has to be neutralized and some or all of the water of hydration has to be replaced by some other molecule or ion.[14] Thus, the solute changes chemical form during phase transfer. This process is referred to as "liquid-liquid ion exchange" or "liquid-ion exchange". The chemical extraction processes which meet the major requirements of charge neutralization and waters of hydration replacement can be divided into three major categories: those which involve compound formation, those which involve ion association, and those which involve solvation.

b. Chemical Extraction by Compound Formation

The first category, compound formation, is the most widely understood due to its extensive use in analytical chemistry. An extraction which involves compound formation complexes the metal ion with an ion having an opposite charge in the aqueous phase thus forming a neutral species. The resulting neutral species is readily extractable in organic solvents having relatively low dielectric constants. In addition to charge neutralization, this complex also replaces some or all of the waters of hydration. There are two types of extraction which use compound formation: chelating extractants and acidic extractants.

Chelating extractants replace the coordinated water to form covalent compounds that are soluble in nonpolar solvents. A chelating compound acts as a polyfunctional base capable of occupying two or more positions of the coordination sphere on the metal ion during compound formation.[15] The distribution coefficients between aqueous and organic solvents for chelating compounds may be as high as several thousand. Chelating compounds are used extensively in the analytical chemistry of metals,[16] however, the large expense of the chelates prohibits use on large-scale industrial applications.[14] Another factor limiting the use of chelating compounds in industrial applications is the limited solubility of the chelate complexes in organic solvents.[16, 17] The equation for a chelating reaction is:

$$M_{aq}^{n+} + nHL_{org} \Leftrightarrow ML_{norg} + nH_{aq}^{+} \qquad (3)$$

where an aqueous solution contains metal ions M^+ and hydrogen ions H^+ in contact with an organic solvent containing ligand anions L. The distribution ratio or extraction coefficient, E is calculated as the total concentration of metal in the organic phase, $[ML_n]_{org}$, divided by the total concentration of metal in the aqueous phase, $[M^{n+}]_{aq}$:

$$E = \frac{[ML_n]_{org}}{[M^{n+}]_{aq}} \tag{4}$$

The equilibrium constant, K_E, for the chelating reaction described by equation 3 is calculated as:

$$K_E = \frac{[ML_n]_{org}[H^+]^n_{aq}}{[M^{n+}]_{aq}[HA]^n_{org}} \tag{5}$$

The other types of extractant that involve compound formation are acidic extractants. Two common types of acidic extractants are carboxylic and sulphonic acids. These acidic extractants involve a cation exchange reaction similar to chelation where the hydrogen ion associated with the extractant is exchanged for the metal cation. Acidic extractants differ from chelating extractants as a result of the composition of the extracted species and solvent phase properties. The coordination requirements of the metal are usually unsatisfied and the hydration shell of the metal ion is not destroyed. To achieve a high distribution ratio, it is usually necessary to use a polar diluent which replaces the remaining water of hydration.[16] The acidic extracts, carboxylic and sulphonic acids, and their metal salts have relatively high solubilities in the aqueous phase resulting in relatively low extractive powers.[16] As a result, the acidic extractants have very low popularity. Little information is available about the use of carboxylic and sulphonic acidic extractants for lead extraction.

Another group of compounds which may be classified as an acidic extractant due to the similar ion exchange process are the organophosphorus compounds.

The organophosphorus compounds differ from the carboxylic and sulphonic acids because they meet the coordination requirements of the metal. This and other properties allow the organophosphorus compounds to also be classified as solvating extractants. The organophosphorus compound, di-(2-ethyl-hexyl) phosphate, has been able to reduce lead concentrations from millpond wastewater solids.[18] The solvating extractants and their capabilities are discussed as the third category of chemical extractants.

c. Chemical Extraction by Ion Association

The second category of chemical extractants involves ion association as the mechanism to allow a charged metal ion to solubilize in the organic phase. Commercial processes using ion-association systems generally use long chain aliphatic amine or ammonium salts as the extractant.[13] Ion association, also known as outer-sphere complexation, results from the physical attractive forces between oppositely charged species. For example a positively charge metal ion, M^+, will associate with a negatively charged anion, Y^-, in the aqueous phase to form a metal ion-anion complex, MY^-:

$$M^{n+} + mA^- \Leftrightarrow MA_m^{(m-n)-} \tag{6}$$

The anion, A^- in this complex is then exchanged for a different anion from the extractant during the extraction reaction. This requires the extractant to be present as a salt containing the anion for exchange. The amine is converted to the salt form by contacting the amine, R_3N, in the solvent phase with an aqueous acid, HX, to form an amine salt in the organic phase:

$$R_3N_{org} + HX_{aq} \Leftrightarrow R_3NH^+ \cdot X^-_{org} \tag{7}$$

Contacting the organic phase containing the amine salt and the aqueous phase containing the metal ion-anion complex results in extraction by the following reaction

$$MA_{m}^{(m-n)-}{}_{aq} + (m-n)(R_3NH^{+} \cdot X^{-})_{org} \Leftrightarrow (R_3NH)^{+}_{m-n}\, MA^{-}_{m\,org} + (m-n)X^{-}{}_{aq} \qquad (8)$$

There are a few ion-association extractions, however, where the metal ion-anion complex is solubilized into the organic phase by forming uncharged pairs or clusters with the extractant. An example of this type of reaction is:

$$(R_3NH)^{+}_{2} \cdot A^{2-}{}_{org} + M^{2+} \cdot A^{2-}{}_{aq} \Leftrightarrow (R_3NH)^{+}_{2} \cdot M^{2+} \cdot A^{4-}{}_{org} \qquad (9)$$

A problem with understanding ion exchange processes is related to the activities of the compounds which differ from the concentrations represented by the previous examples. This change in activities is due to the high ionic strengths of the solutions. The neutral species that is formed during the ion association of a positive metal ion may also involve anions from the aqueous phase along with some of the waters of hydration. An equation for ion association has been developed by Bjerrum which is empirically expressed as:[13, 15]

$$M^{+} + B^{-} \Leftrightarrow (M^{+}, B^{-}) \qquad (10)$$

with the counter ion and waters of hydration represented as B^{-}. The equilibrium equation is

$$K = \frac{[(A^{+}, B^{-})]}{[A^{+}][B^{-}]} \qquad (11)$$

where concentrations do not always correlate with activities. Without the use of activities in the equation for the extraction coefficient, making predictions of extraction results for ion association reactions are difficult. For most extractions involving ion association, the mechanisms of the extraction are represented by empirical correlations. Bjerrum has developed a theory which relates the formation of such complexes to several various parameters in an extraction such as the dielectric constant of the solvent, temperature, and size of the ions involved.[13, 15] The presence of salts and the dissolved organic solvent in the aqueous phase can decrease the dielectric constant of the aqueous phase to the point where extensive ion association occurs in the aqueous phase which decreases the extractability of the metal.[15]

In addition to the sensitivity of ionic strengths in an ion association extraction system, the type of anion present is very important. For example, hydrochloric acid may be desirable for dissolution of lead from the soil phase, but it is generally observed that metal extractions are greater from alkali chloride solutions than from hydrochloric acid solutions at the same chloride concentration.[13]

d. Chemical Extraction by Solvation

Solvation is the third category of chemical extractants where the extraction is based on the power of oxygen containing organic extractants to solvate inorganic molecules or complexes.[13] The two main oxygen-containing groups of extractants are oxygen bonded to carbon such as ethers, esters, alcohols and ketones and oxygen bonded to phosphorus such as alkyl-phosphate esters. The main difference between the two groups involves the use of water during complexation.[16, 19] For extraction systems involving ethers and ketones, water is a necessary part of the complexation as shown in the following reaction:[12, 13, 16]

$$M^{n+} + lNO_3^- + (w-sx)H_2O + sL(H_2O)_x \Leftrightarrow M(NO_3)_l(H_2O)_w L_s \qquad (12)$$

where the equilibrium constant, K_E, is calculated as:

$$K_E = \frac{[M(NO_3)_l(H_2O)_w L_s]_{org}}{[M]_{aq}[NO_3]_{aq}^{l}[L(H_2O)_x]_{aq}^{s}[H_2O]_{aq}^{(w-sx)}} \qquad (13)$$

The commercial applications for alcohols have been mainly for the extraction of acids and not for the extraction of metals. The only ketone used in commercial applications has been methyl isobutyl ketone (MIBK). It has been limited to the separation of two groups of rare earth metals.[13] Metal sulfates are generally not extractable by these reagents.[19]

As a contrast to the oxygen bonded to carbon extractants, the alkyl-phosphate esters compete favorably with water in the first hydration sphere of the metal ion. As a result, water is frequently eliminated from the organic phase metal complex in extraction systems using alkyl-phosphate esters.[12, 13] A reaction where the metal ion, X, is extracted by the alkyl-phosphate DEHPA is;

$$M^{n+}_{aq} + n(HX)_{2org} \Leftrightarrow M(HX_2)_{norg} + nH^{+}_{aq} \tag{14}$$

where the equilibrium constant, K_E, is calculated as:

$$K_E = \frac{[M(HX_2)]_{org}[H^{+}]^{n}_{aq}}{[M^{n+}]_{aq}[(HX)_2]^{n}_{org}} \tag{15}$$

This extraction coefficient shows a power dependence on the reagent concentration and an inverse power dependence on the hydrogen-ion concentration.

The phosphoric acid esters are not monomeric in most organic diluents and tend to self-associate. This self-association of the phosphates has been shown to affect the distribution coefficients of metal extractions.[16, 20] A comparison of the monomerized and dimerized forms of DEHPA showed the latter to have an extraction coefficient approximately 40 times greater.[21] Equation 14 shows DEHPA self-associating as a dimer. When inert diluents are used, the monoalkyl phosphates are polymeric while the dialkyl phosphates are dimeric. As less inert diluents with increasing polarity are used, self-association of the extractant is replaced by association with the diluent.[22] Self-association is greatest with the inert solvent hexane and decreases with more strongly hydrogen-bonding solvents. Association with the diluent decreases in the order: hexanol < tributyl phosphate < di-isopropyl ether < chloroform <carbon tetrachloride < hexane.[12]

When the metal loading of phosphoric acid esters becomes greater, dimerization of the extractant has been shown to decrease. This decrease in dimerization changes equation 14 to:[16]

$$M^{n+}_{aq} + nHX_{org} \Leftrightarrow MX_{n\,org} + nH^{+}_{aq} \qquad (16)$$

and the equilibrium constant, K_E, is calculated as:

$$K_E = \frac{[MX_n]_{org}[H^+]^n_{aq}}{[M^{n+}]_{aq}[HX]^n_{org}} \qquad (17)$$

Changes in the extractant dimerization with different solvents and with different metal loading rates make predictions of the extraction coefficient difficult.

For organophosphorous compounds, the extractability increases in the order: phosphine oxide > phosphinate > phosphonate > phosphate. While the solubility in aqueous solutions decreases for the same order. Extraction data for lead from aqueous solutions was only available for the phosphate di-(2-ethylhexyl) phosphate, DEHPA. A collection of extraction data by De, et al.,[12] indicates that lead is 90% extractable from a 0.01 M HCl solution using 1.5 M di-(2-ethylhexyl) phosphoric acid (DEHPA) in toluene. Extraction data collected by Shah, et al., shows that DEHPA is an effective solvent in removing lead from millpond wastewater solids. [18] The process by Shah, et al., uses only two phases: the solid phase and the extractant phase which consisted of DEHPA and toluene. The two phase process reduced the millpond sludge concentration from 2430 mg/kg to 1240 mg/kg with an optimal solvent to sample ratio of 20 mL/g. Using a hazardous substance for the extractant diluent will likely require subsequent treatments. The high ratio of solvent usage to sample may also be an economic concern. Information on the two phase extraction process by Shah, et al. was published after the experiments in Chapter III were performed.

B. Parameters Affecting Extraction Equilibrium and Kinetics

In the process of removing lead from soil, there are two representative equations. The first represents the dissolution of lead from soil into the aqueous phase as a lead ion:

$$PbSO_{4_s} \Leftrightarrow Pb^{2+}_{aq} + SO_4^{2-}{}_{aq} \tag{18}$$

The second represents the extraction of the lead ion from the aqueous phase to the organic phase:

$$Pb^{2+}_{aq} + 2HDEHPA_{org} \Leftrightarrow Pb(DEHPA)_{2_{org}} + 2H^+_{aq} \tag{19}$$

There are several variables which affect the equilibrium and/or kinetics for these reactions. These variables include: (1) pH effects on dissolution, (2) pH effects on extractant, (3) pretreatment, (4) temperature, (5) extractant concentration, (6) acids, (7) mass transfer and diffusion, and (8) viscosity. Each of these are discussed in the following paragraphs.

1. pH effects on dissolution

The solubility of lead ions favorable for extraction, significantly increases as pH decreases.[23] The rate of dissolution also tends to be rapidly accelerated by a lower pH.[23] The Pourbaix diagram in Figure 3 shows how the thermodynamically stable form of lead under typical water conditions is strongly dependent on pH. At a pH lower than approximately 6, the most stable form of lead is the dissolved ion, Pb^{2+}, which is favorable for extraction. From a pH of approximately 6 to 8 the

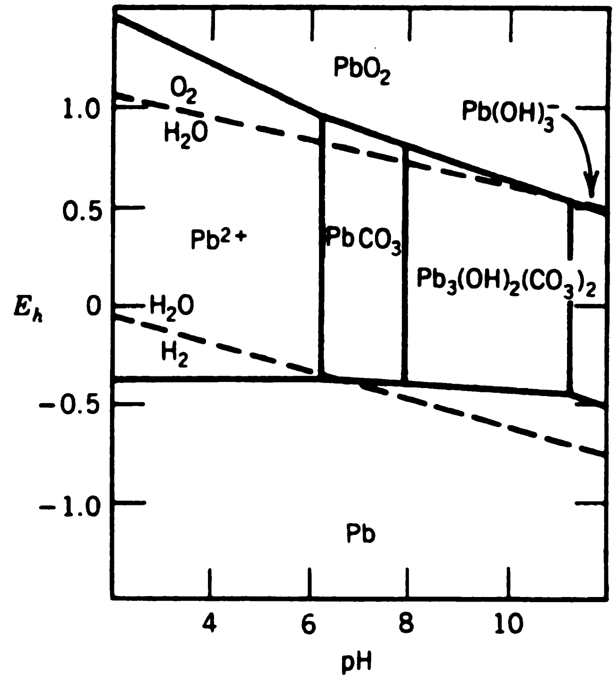


Figure 3. Pourbaix Diagram showing Thermodynamically Stable forms of Lead.[23]

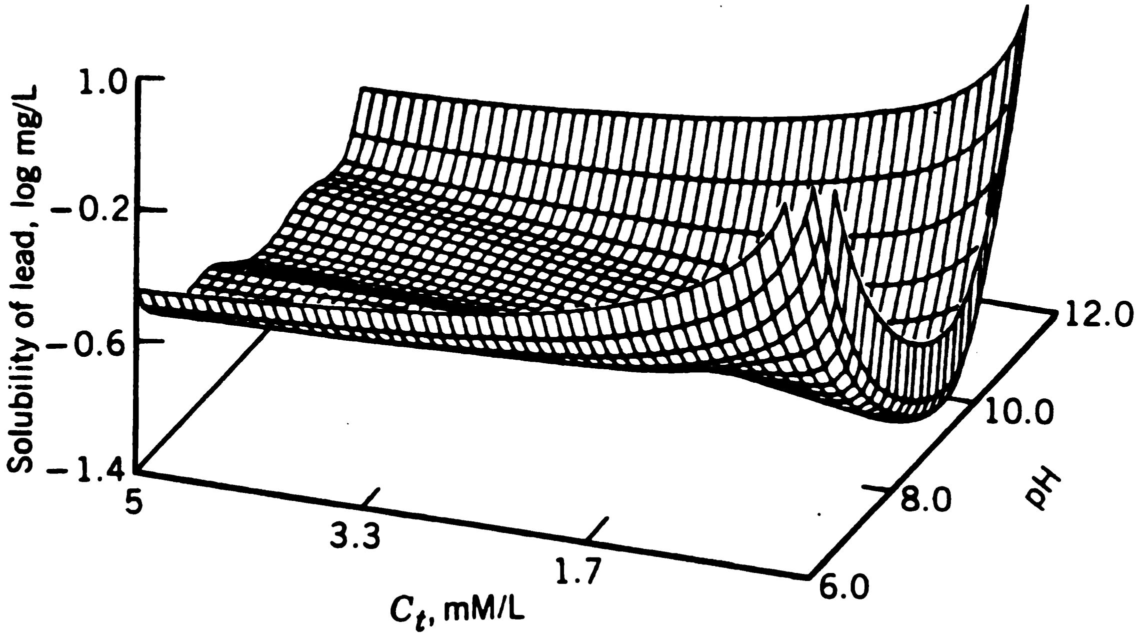


Figure 4. Three Dimensional Plot of Lead Solubility as a Function of pH and Total Inorganic Carbonate.[24]

most stable form is PbCO3, which is nearly insoluble and unfavorable for extraction. Above pH 8 the stable forms are $Pb_3(OH)_2(CO_3)_2$ or the elemental form Pb; neither of which is favorable for extraction. The increased solubility of lead as pH decreases is also shown by Figure 4.[24]

2. pH effects on Extractant

An acidic extractant releases protons during the extraction process which subsequently increase acidity and lowers pH. A lowered pH can significantly reduce the extraction coefficient for the metal ion. This release of protons is shown by the extraction of lead ions using the acid form of DEHPA during high metal loading;

$$Pb^{2+}_{aq} + 2HDEHPA_{org} \Leftrightarrow Pb(DEHPA)_{2_{org}} + 2H^{+}_{aq} \tag{20}$$

As the extraction proceeds to the right, the pH decreases and inhibits further extraction of the lead ion. Decreasing the pH of the aqueous phase will also cause the reaction to shift to the left. The concentration of the hydrogen ion has a 2nd order effect on the equilibrium constant, K_E:

$$K_E = \frac{\left[Pb(DEHPA)_2\right]_{org}\left[H^+\right]^2_{aq}}{\left[Pb^{2+}\right]_{aq}\left[HDEHPA\right]^2_{org}} \tag{21}$$

The reverse reaction occurs during stripping where excess acid is added; shifting the equilibrium to the left.

The pH of the aqueous solution can also have a significant impact on the extraction kinetics of an acidic extractant.[13] Acidic extractants are weak organic acids which dissociate at a certain pH known as the pKa value.[25] Dissociation of an organic acid, A, is shown by the following reaction;

$$HA \Leftrightarrow H^+ + A^- \tag{22}$$

For the acidic extractant, DEHPA, the pKa value is 1.40. This means that for a pH greater than the pKa (i.e. pH > 1.40) the active binding site of the extractant becomes available through dissociation as shown by the following reaction;

$$POOH \Leftrightarrow POO^- + H^+ \tag{23}$$

When the pH is less than the pKa, pH < 1.4, the active binding site does not become available and the extraction will not occur.

The pH of the extraction system also impacts the rate of lead solvation into the aqueous phase and the maximum lead concentration. As pH decreases, the rate of dissolution and solubility of lead increase. Conversely, as pH increases the rate of dissolution and solubility of lead decreases.

As a result, a compromise is needed between a higher pH which will enhance the extent of extraction and a lower pH which enhances the dissolution of lead sulfate.

3. Pretreatment

To minimize the drop in pH caused by protons released during the extraction, the acidic extractant may be converted to a salt form in a prior conditioning reaction by the following reaction:[13, 26]

$$2HDEHPA_{org} + Ca^{2+}(OH^-)_{2_{aq}} \Leftrightarrow Ca(DEHPA)_{2_{org}} + 2H_2O_{aq} \tag{24}$$

Converting the acidic extractant to the calcium salt as a conditioning step prior to extraction results in the release of a calcium ion, which is neutral except for buffering effect, in place of hydrogen protons. Calcium is a divalent salt and combines with two molecules of DEHPA. Thus, the calcium ion (Ca^{2+}) and the lead ion (Pb^{2+}) are exchanged on a one to one ratio. Release of the neutral salt is shown in the extraction of lead ions using the calcium form of DEHPA (Ca-DEHPA):

$$Pb^{2+}_{aq} + Ca(DEHPA)_{2_{org}} \Leftrightarrow Pb(DEHPA)_{2_{org}} + Ca^{2+}_{aq} \tag{25}$$

As the extraction proceeds to the right, pH effects are minimized. Where increasing the hydrogen ion concentration has a 2nd order impact on the extraction coefficient, increasing the calcium ion concentration will only have a 1st order impact where the extraction coefficient, K_E, is calculated as;

$$K_E = \frac{[Pb(DEHPA)_2]_{org}[Ca^{2+}]_{aq}}{[Pb^{2+}]_{aq}[Ca(DEHPA)_2]_{org}} \tag{26}$$

Having a lower specificity than lead, calcium does not significantly compete for the extractant. Calcium also helps to maintain the ionic strength of the aqueous phase and thus lower variations in activity coefficients.

4. Temperature

As the temperature of an extraction process increases, a decrease in the distribution ratio has been generally observed for most extractants.[16] Measured heats of reaction for DEHPA extractions show the process to be exothermic.[27] For an exothermic reaction, the equilibrium will be shifted towards the reactants as energy is added to the system. The extraction of uranium from an HCl solution using DEHPA, showed a decrease in the extraction coefficient from 9 to 5 as the temperature increased from 10°C to 50°C.[27] Temperature variations can also have a significant impact on the extraction kinetics.[13, 26] Organic solvents often have an appreciable temperature coefficient of expansion, which must be taken into account when performing analytical determinations. Solvent losses can also become significant as temperatures increase due to increased vapor pressures.

Temperature also impacts the rate of dissolution into the aqueous phase and the solubility. As temperature increases, the rate of dissolution and solubility increases.

As a result, a compromise is needed between a higher temperature which increases dissolution rates and solubility in the aqueous phase and a lower temperature which minimizes solvent or diluent losses and enhances the extent of extraction.

5. Extractant Concentration

The concentration of the extractant in the organic phase affects the extraction coefficient and the metal loading capacity. For a given metal ion concentration in the aqueous phase, the extraction coefficient will increase with an increase in the extractant concentration in the organic phase. This increase in the extraction coefficient generally occurs as a linear relationship for a system having a fixed metal ion concentration, pH, and phase ratios as long as the metal concentration doesn't exceed the limits of the extractant.[13] Increasing the concentration of the extractant also increases the metal loading capacity. As the metal capacity increases, the flow rate of the extractant phase decreases; this results in smaller equipment sizes and lower stripping costs.

6. Acids

An acid used to lower the pH and increase the rate of lead dissolution from the soil phase may affect the rate of dissolution, the maximum lead solubility in the aqueous phase, and the extractability of the dissolved metal. Lead sulfate has a much lower solubility than other lead salts and is commonly found at CERCLA sites. Dissolution into the aqueous phase is represented by the following equation:

$$PbSO_{4_s} \Leftrightarrow Pb^{2+}_{aq} + SO^{2-}_{4\ aq} \qquad (27)$$

where solubility is a function of pH. Using sulfuric acid to lower the pH of the aqueous solution increases the concentration of the sulfate ion which inhibits the dissolution of lead by causing the equilibrium to shift to the left. This is commonly known as the common ion effect.[28]

The acid used to dissolve lead will create anionic species which are known to affect the extractability of metals.[13] The effect may be great enough to completely inhibit the extraction as shown by carboxylic acid extractants and metal sulfates. The acid may also cause a non-coalescing third phase to form.

7. Mass Transfer and Diffusion

The kinetics of metal extractions are generally limited more by the rate of mass transfer and diffusion than by the rate of the chemical reaction.[13] To minimize the limitations caused by diffusion, the amount of surface area between the two phases is increased by mixing. Increasing the mixing power increases the amount of dispersion of one phase into the continuous phase which increases the amount of surface area available for mass transfer and reaction. Increasing the mixing power, or turbulence, also increases the coefficient for mass transfer which is proportional to the Reynolds number.[20] However, excessive mixing power can result in coalescing problems when stable or semi-stable emulsions are created.

The mass transfer coefficient for a dissolved lead ion from the solid interface to the bulk liquid is also increased with increasing mixing.

8. Viscosity

Viscosity of the phases in the extraction system affects the kinetics of extraction and the mixing power requirements. Increasing viscosity decreases the rate of mass transfer which decreases the extraction kinetics and increases the required mixing times. The viscosity of the extractant phase is affected by the diluent and generally increases with increasing concentration of the extractant. The mixing power requirements for the extraction system are impacted by the settling velocity which is inversely proportional to the viscosity. As the viscosity decreases the settling velocity increases, and the required mixing power to maintain the soil in suspension increases.[29] The viscosity of the aqueous and organic phase are also affected by temperature. As the temperature increases, the viscosity decrease.

C. Desirable Properties of Extractants and Diluents

When considering a solvent mixture, extractant and diluent, for use in a large scale operation, it is important to consider other properties in addition to the ability of the extractant to remove lead. A system that is excellent for microanalysis may be useless for large-scale operations.[12] Following is a list of characteristics that a solvent should have:[13]

1. Low Cost

When considering a large scale system, it is important for the solvent to have a low purchase cost and to be commercially available in large quantities. Solvents which are not commercially available tend to have significantly higher purchase costs.

2. Nonhazardous

It is important that components of the solvent not be on the EPA list as a hazardous substance. Using a hazardous substance will likely make the soil hazardous for that substance. DEHPA is not currently on the EPA list of hazardous substances.

3. Chemical Stability

It is important that an extractant to be stable enough to withstand many months of recycling in a solvent extraction circuit without degrading chemically. Extractants which are not chemically stable increase operating expenses due to replacement costs and disposal costs. When compared to other organophosphorous extractants, DEHPA has greater stability to hydrolysis and greater chemical stability.[12, 13, 16]

4. Extraction Kinetics

To minimize mixing times, it is important for the solvent to have good extraction kinetics. A solvent which has poor extraction kinetics will require extended mixing times which will increase the size of the equipment used in an extraction system. Specific information was not available on the extraction kinetics of lead by DEHPA, however, DEHPA is known to have generally good kinetics of extraction. Wide industrial uses and the determination that DEHPA extracts the heavier rare earths better than the lighter rare earths suggests that DEHPA should have good extraction kinetics for lead.

5. Metal Loading Capacity

In commercial solvent extraction processes, the loading capacity of the extractant is very important.[13] A solvent with a higher loading capacity will operate at a lower flowrate, which is of considerable economic importance. The metal loading capacity of DEHPA appears to be high based on the extractability of lead and large extraction coefficients for other metal extraction systems.[12, 13]

6. Good Stripping Characteristics

In order to re-use an extractant for subsequent extractions, it is important for the extractant to have good stripping characteristics. A solvent with poor stripping characteristics will require increased flowrates in the stripping operation. Poor stripping characteristics may be an indication that frequent extractant replacement will be required.

7. Low Solubility in the Aqueous Phase

To minimize solvent losses and thus minimize solvent replacement costs, it is important for the extractant to have a very low solubility in the aqueous phase.[30] DEHPA is superior to other metal extractants because of its lower solubility in water.[12]

8. High Solubility in Aliphatic Diluents

Extractants are seldom used in the concentrated form. The extractant is usually diluted with an organic liquid that is considered to be inert in relation to the extraction mechanism. For example, kerosene is an inert organic liquid commonly used as a diluent in commercial operations. DEHPA has been found to be exceedingly soluble in organic solvents.[12]

9. Viscosity

When considering a diluent, it is important to consider the relative impacts on viscosity. A diluent which has a higher viscosity will either require more power for agitation and/or will decrease extraction kinetics.

10. Non-volatile and Non-flammable

These two parameters usually go together when considering non-halogenated organic substances. A solvent which is volatile will be difficult to contain in an extraction process and could produce flammable situations. A volatile solvent will also have significant replacement costs. Vapor pressure information was not available for DEHPA however, having a large molecular weight of 322.4, DEHPA should have a very low vapor pressure.

11. Good Coalescing Properties

It is important for a solvent to have good coalescing properties, when the agitation has ceased, and to not form a stable emulsion. A solvent with good coalescing properties will minimize the settling times required prior to phase separation. Density and interfacial surface tension have a large impact on coalescing rates.[30] An increasing difference in density between the solvent phase and the aqueous phase will increase the coalescence rate. The greater the interfacial surface tension between the phases, the greater the coalescing rate and the greater the requirement for mechanical agitation.

12. Versatility

When evaluating an extractant, it is important to consider the ability to extract other metals. For example, if a soil is contaminated with other toxic metals, the extractant might be able to simultaneously remove these other metals in addition to lead. However, versatility may hamper the overall extraction process if the soil contains large quantities of metals that are nontoxic such a iron (III). The extractability of metals generally follows the order: quadri- > ter- > bi- > univalent metals. For metals having the same charge, extraction increases for decreasing ionic radius. The versatility of DEHPA has been proven by it's commercial use for the extraction of many metals including uranium, cobalt, nickel, rare earths, and vanadium.[12, 13]

D. Combination of Extractants

1. Organic Phase

Physical extraction methods have not proven to be effective at removing metals from soils, therefore a chemical extractant will be utilized in the non-polar, organic phase. The solvating extractant DEHPA was chosen because it meets the criteria of desirable properties discussed above. The selection of DEHPA was also influenced by information indicating that lead is about 90% extractable from a 0.01M HCl solution using 1.5 M DEHPA in toluene.[12] The use of toluene as a diluent does not meet the criteria of a desirable diluent because it is on EPA's hazardous substance list.

To replace toluene as the diluent for the organic phase, another aliphatic diluent, hexane, was chosen because of its inert properties which increase the dimerization of DEHPA and enhances the extractability of metals.[13, 21, 27] Kerosene could have chosen as a diluent, but was avoided due to the unknown components; some of which may not be inert. Hexane meets the criteria of desirable properties discussed above with the exceptions of volatility, which increase losses due to evaporation, and flammability, which introduces process hazards. The relatively low purchase price of hexane makes evaporative losses a minor concern.

Although hexane is characteristically hazardous because of its flammability, it is not listed as hazardous because of toxicity. The high volatility of hexane implies that it can be removed from soil by moderate thermal treatment.

2. Aqueous Phase

The constituents of concern in the aqueous phase are pH and the type of acid used. Extraction data indicates that lead is about 90% extractable from a 0.01M HCl solution using 1.5 M DEHPA in toluene.[12] The extraction data also indicates that DEHPA has a pKa of 1.40, a log E of 3.42 and a dimerization constant of 4.47. For an aqueous solution containing 0.01 M of HCl, the pH would be approximately 2.0 when the extraction began with decreasing pH as the extraction continues. As a result, the pH would begin to approach the pKa for DEHPA. If the extractant is unable to ionize due to a pH lower than the pKa, the extractant will not be able to form a complex with a metal ion and the extraction will not occur.[13] Therefore, a higher pH might increase the extraction coefficient. The tradeoff to increasing the pH is a decreased solubility of lead in the aqueous solution which would also have a reversal effect on the net amount of lead extracted. After considering the ability to dissolve lead in the aqueous solution, the reversal effects of acidic solutions on the extraction equilibrium and the pKa for DEHPA, it was assumed that a pH of 3.0 would be a good starting point to determine if the use of DEHPA increases the extraction of lead from soils.

For the other constituent of concern in the aqueous phase, the type of acid, there are two important considerations: the impacts of the acid on the extractability of the solvated metal and the rate at which the metal is solvated. When comparing the extraction of metals from various acid solutions it has generally been observed that a greater number of metal chlorides than metal nitrates are extractable by phosphorous esters and the extraction from sulfate solutions is generally poor.[12] The impacts of these acids on the rate of solvation of the metal was unknown requiring further testing to determine compatibilities.

III. EXPERIMENTAL APPARATUS AND PROCEDURES

To determine if the use of a liquid ion extractant would enhance the removal of lead from contaminated soils, four groups of experiments were performed. The results from the each experiment were used to determine the design for subsequent experiments. In the first group of experiments, the liquid ion extractant, diluent and soil were emulsified with various acids to check for compatibility. In the second group of experiments, the acid which was determined to be most compatible from the first experiment was used to dissolve lead sulfate into an aqueous solution. The aqueous solution containing the lead sulfate was then emulsified with the liquid-ion extractant to determine if a favorable extraction would occur. The liquid ion extractant was also pretreated with calcium hydroxide to determine if the pH drop would be minimized during the extraction and thus increase the extraction coefficient. In the third group of experiments, soil was loaded with lead sulfate. The lead was then removed from the soil using the acid selected from the first group of experiments and the liquid-ion extractant selected from the second group of experiments. Extraction kinetics and the amount of lead removed from the soil were also evaluated in the third group of experiments. In the fourth group of experiments, the liquid-ion extractant loaded with lead from the third group of experiments was mixed with the selected acid to determine if the extractant could be stripped for possible re-use in subsequent extractions.

A. Solvent and Soil Compatibility with different Acids

To determine which acid would be compatible with the extractant, diluent, water and sandy soil and to ensure that the emulsified combination would not exhibit undesirable characteristics such as crud formation, the following were combined in 150 mL beakers:

20 grams	Ludington sand with organic content of 0.2%,
20 mL	Hexane,
20 mL	DEHPA,
20 mL	0.01 N Acid.

The four acids added to the 150 mL beakers were:

Hydrochloric acid,
Acetic acid,
Sulfuric acid,
Nitric acid.

A magnetic stir bar was added to each beaker and mixed at a high enough speed to emulsify the solution for 1 minute. The mixing was stopped and the phases were observed for coalescing properties.

B. Lead Extraction from an Aqueous Solution

In the second group of experiments, the acid which was determined to be most compatible from the first experiment, that is hydrochloric acid, was used to dissolve lead sulfate into an aqueous solution. The aqueous solution containing the lead sulfate was then emulsified with DEHPA in hexane to determine if a favorable extraction would occur. The aqueous solution containing the lead sulfate was also emulsified with DEHPA which had been pretreated with calcium to determine if the pH drop would be minimized during the extraction and thus increase the extraction coefficient. The procedures used in these experiments are discussed in the following paragraphs.

1. Lead Extraction with DEHPA

Lead sulfate was dissolved with an HCl solution, pH adjusted and extracted with a 0.2 M DEHPA in hexane solution. The concentration of lead in the aqueous solution was measured before and after the extraction to determine the amount of lead extracted into the DEHPA/hexane solution. A flow chart of the experimental process showing solution preparations, extraction, and the points when samples were taken is shown in Figures 5 and 6.

a. Dissolved Lead Aqueous Solution

To prepare an aqueous solution having a target concentration of 10,000 mg/L of lead from lead sulfate, 1.474 g of lead sulfate was dissolved in 0.1 liter of 50:50 volume percent solution of HCl and deionized water at 100°C. Reagent grade HCl, produced by Mallinckrodt, was used for this and subsequent procedures having an indicated concentration of 37 weight percent. A titration of the HCl against a known concentration of sodium hydroxide determined the actual concentration of the HCl to be 42 weight percent. Because the solution precipitated upon cooling to room temperature, it was reheated to 35 °C and additional 50:50 HCl and deionized water was added. The dissolved lead sulfate is Solution A in Figure 5. To determine the resulting concentration of Solution A, Sample 1 was taken and diluted by a ratio of 1000:1 with 2% nitric acid in de-ionized water.

b. Aqueous Solution Preparation for Extraction

To prevent the reversal effect that a low pH can have on an extraction, the pH of the dissolved lead sulfate solution was adjusted prior to extraction with the DEHPA solution. To prepare the pH adjusted solution, 50 mL of Solution A was

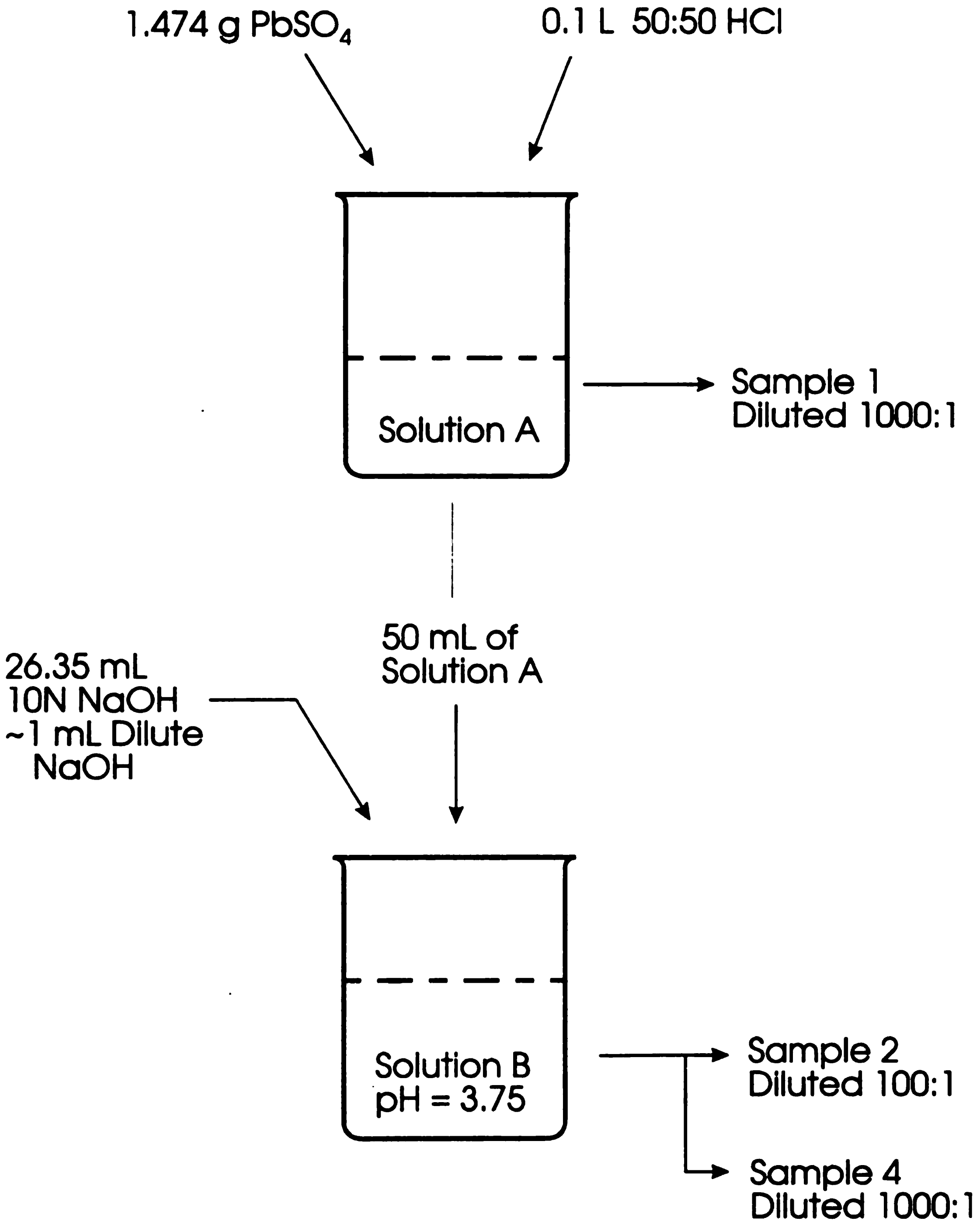


Figure 5. Flow Chart of Lead Sulfate Solution Preparation and Samples Taken

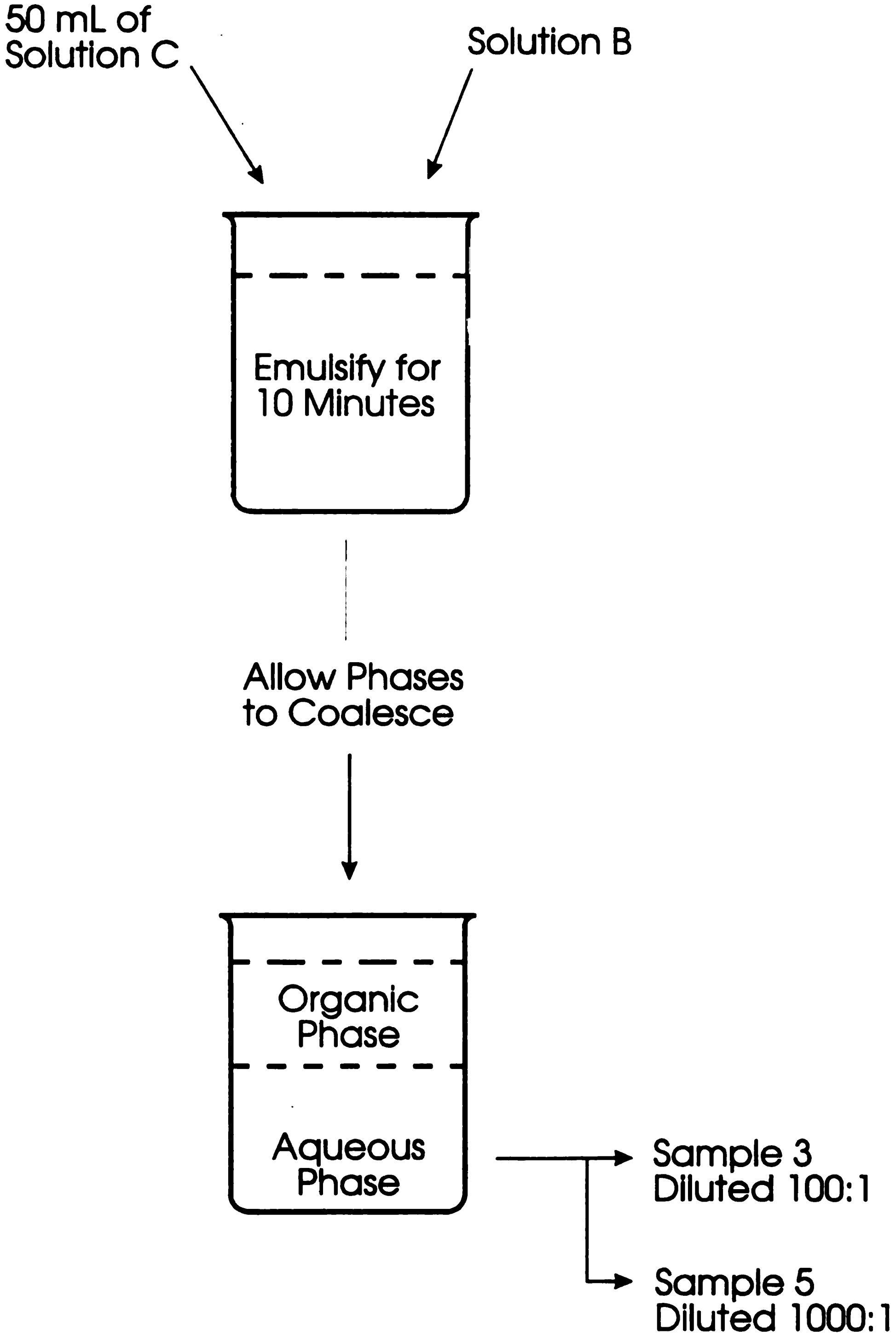


Figure 6. Flow Chart of Lead Extraction with DEHPA and Samples Taken

placed into a 100 °F water bath and adjusted to a pH of 3.75 by adding 26.35 mL of 10N sodium hydroxide and approximately 1 mL of dilute sodium hydroxide. The pH adjusted solution with dissolved lead sulfate was labeled Solution B (see Figure 5). Sample 2 was taken and diluted by a ratio of 100:1 (see Figure 5). Further dilution of Sample 2 by a ratio of 10:1 was required because the absorbance values were not within the calibrated range. The sample having a dilution ratio of 1000:1 was labeled Sample 4.

c. DEHPA Extractant Preparation

A 0.2 Molar DEHPA solution was prepared by placing 6.45 g of DEHPA, having a molecular weight of 322.4 grams/mole, into a 100 mL volumetric flask and diluting to volume with hexane. The DEHPA/hexane mixture was labeled Solution C. Reagent grade DEHPA, purchased from Sigma Chemical Company, was used for all extractions.

d. Extraction Procedure

To minimize variations in the extraction coefficient caused by temperature variations, Solution B and 50 mL of Solution C were placed in a 100°F water bath (see Figure 6). After both solutions had been heated to 100°F, the DEHPA solution was added to the beaker containing the aqueous solution and the solution was stirred with a magnetic stir bar at a rate sufficient to cause phase mixing for 10 minutes. Mixing was then stopped and the phases were allowed to coalesce.

To determine the amount of lead extracted from the aqueous phase, Sample 3 was taken and diluted by a ratio of 100:1 (see Figure 6). Further dilution of Sample 3 by a ratio of 10:1 was required because the absorbance values were not within the calibrated range. The sample having a dilution ration of 1000:1 was labeled Sample 5.

To determine if a significant change in pH occurred which could affect the equilibrium or inhibit the extraction, the pH of the aqueous phase was sampled after mixing stopped and the phases coalesced.

e. Aqueous Phase Sample Preparations

Aqueous samples were diluted using a 2% solution of HNO_3 in de-ionized water. A known amount of the sample was added using a Gilson Pipetman® to a partially filled volumetric flask. After addition of the sample, the volumetric flask was filled to the indication mark with 2% HNO_3 solution. Suspended particles were not evident in the aqueous samples and centrifugation was not used.

f. Sample Analysis by Atomic Absorption Spectrophotometry

The lead ion concentration in samples was determined using atomic absorption spectrophotometry on a Perkin-Elmer 1100 unit. Samples were aspirated into an air-acetylene flame following Method 7420, Lead (Atomic Absorption, Direct Aspiration)[31] and operating instructions from Perkin-Elmer. Readings were made at 283.3 nm.

Samples were measurement in the linear range of 0 to 10 mg/L. When the samples were greater than 10 mg/L, they were diluted and re-analyzed. When the concentration exceeds 20 mg/L the absorption curve becomes non-linear due to absorption interference. A calibration curve was constructed using a blank and three standards for each series of samples analyzed. The method of standard additions was initially used, but discontinued because matrix interference did not appear to be significant.

Before calibration, the Perkin-Elmer manual suggested waiting 15 minutes for the lamp to warm-up and stabilize. However, the baseline did not stabilize until the lamp was operated for two hours. Five replicates were taken for each sample with an integration time of 3 seconds. A blank solution was aspirated between samples. The surface of each sample was kept at a constant elevation relative to the nebulizer. As the elevation of the sample decreases, the absorbance for that sample correspondingly decreases.

The operating conditions in Table 1 were used to produce a lean-blue, oxidizing flame. The operating conditions for the aqueous samples are standard settings for the Perkin-Elmer unit. The organic conditions were varied until a lean-blue, oxidizing flame was produced similar to that of the aqueous conditions.

Table 1 - Atomic Adsorption Flow Rates for Calibration and Sample Analysis.

	Air (liters/min.)	Acetylene (liters/min.)	Nebulizer Uptake (mL/min)
Aqueous Samples	9.0	2.5	8.0
Organic Samples	10.3	0.9	5.0

g. Calibration Standards for Aqueous Sample Analysis

A lead reference solution from Fischer Scientific, which had a concentration of 1,000 ppm ±1%, was used to prepare standards for calibration. A volumetric flask was partially filled with a 2% HNO_3 solution. The amount of reference solution needed to make a standard was added using a Gilson Pipetman®. The volumetric flask was then filled to the indication mark with a 2% HNO_3 solution. The 2% HNO_3 solution without lead was used for a blank solution during calibration and between aspirations.

h. pH Determinations

pH values were measured using an Orion Research Incorporated, Model 720 pH meter with an Orion Research Incorporated, Model 91-55, 91-56 Combination pH Electrode. The pH meter was calibrated daily using reference solutions of pH 2.00 and pH 7.00.

i. Analysis

The concentration of lead in a solution, $[Pb]_x$, is calculated as the product of the corresponding sample concentration, $[S]_x$, and the dilution ratio of the sample, DR_x:

$$[Pb]_x = [S]_x \times DR_x \tag{28}$$

The mass of lead extracted, Pb_{ext}, from the aqueous phase was calculated as the product of the aqueous phase volume, Vol_{aq} and the difference between the initial concentration of lead in the aqueous phase, $[Pb]_{aq,\ initial}$, and the final concentration of lead in the aqueous phase, $[Pb]_{aq,\ final}$:

$$Pb_{ext} = Vol_{aq} \times \left([Pb]_{aq,\,initial} - [Pb]_{aq,\,final} \right) \tag{29}$$

To determine the concentration of the lead in the organic phase, $[Pb]_{org}$ the mass of lead extracted from the aqueous phase, Pb_{ext}, was divided by the volume of the organic phase, Vol_{org}:

$$[Pb]_{org} = \frac{Pb_{ext}}{Vol_{org}} \tag{30}$$

The extraction coefficient for dissolved lead, E_{diss}, was calculated using Equation 4 where the concentration of dissolved lead in the organic phase, $[Pb]_{org\text{-}diss}$, was divided by the concentration of dissolved lead in the extracted aqueous phase, $[Pb]_{aq\text{-}diss}$:

$$E_{diss} = \frac{[Pb]_{org-diss}}{[Pb]_{aq-diss}} \tag{31}$$

2. Lead Extraction with Ca-DEHPA

The lead sulfate solution (see III.B.1.a) was pH adjusted and extracted with the calcium form of a 0.2 M DEHPA/hexane solution. The concentration of lead in the aqueous solution was measured before and after the extraction to determine the amount of lead extracted into the Ca-DEHPA/hexane solution. A flow chart of the experimental process showing solution preparations, extraction, and the points when samples were taken is shown in Figures 7 and 8.

Samples were prepared as indicated in III.B.1.e, the samples were analyzed as indicated in III.B.1.f, calibration standards were prepared as indicated in III.B.1.g, pH values were determined as indicated in III.B.1.h, and an analysis of the extraction results was determined as indicated in III.B.1.i.

a. Aqueous Solution Preparation for Extraction

To prevent the reversal effect that a low pH can have on an extraction, the pH of the dissolved lead sulfate solution from III.B.1.a was adjusted prior to extraction with the DEHPA solution. To prepare the pH adjusted solution, 50 mL of Solution A (see III.B.1.a) was placed into a 100°F water bath and adjusted to a pH of 3.80 by adding 26.45 mL of 10N sodium hydroxide and 2.35 mL of dilute sodium hydroxide. To determine the initial concentration of Solution A, Sample 1 was taken and diluted by a ratio of 1000:1 as indicated in Figure 5. The pH adjusted solution with dissolved lead sulfate was labeled Solution B (see Figure 7). The final volume of Solution B was 78.8 mL. Sample 2 was taken and diluted by a ratio of 500:1 (see Figure 7).

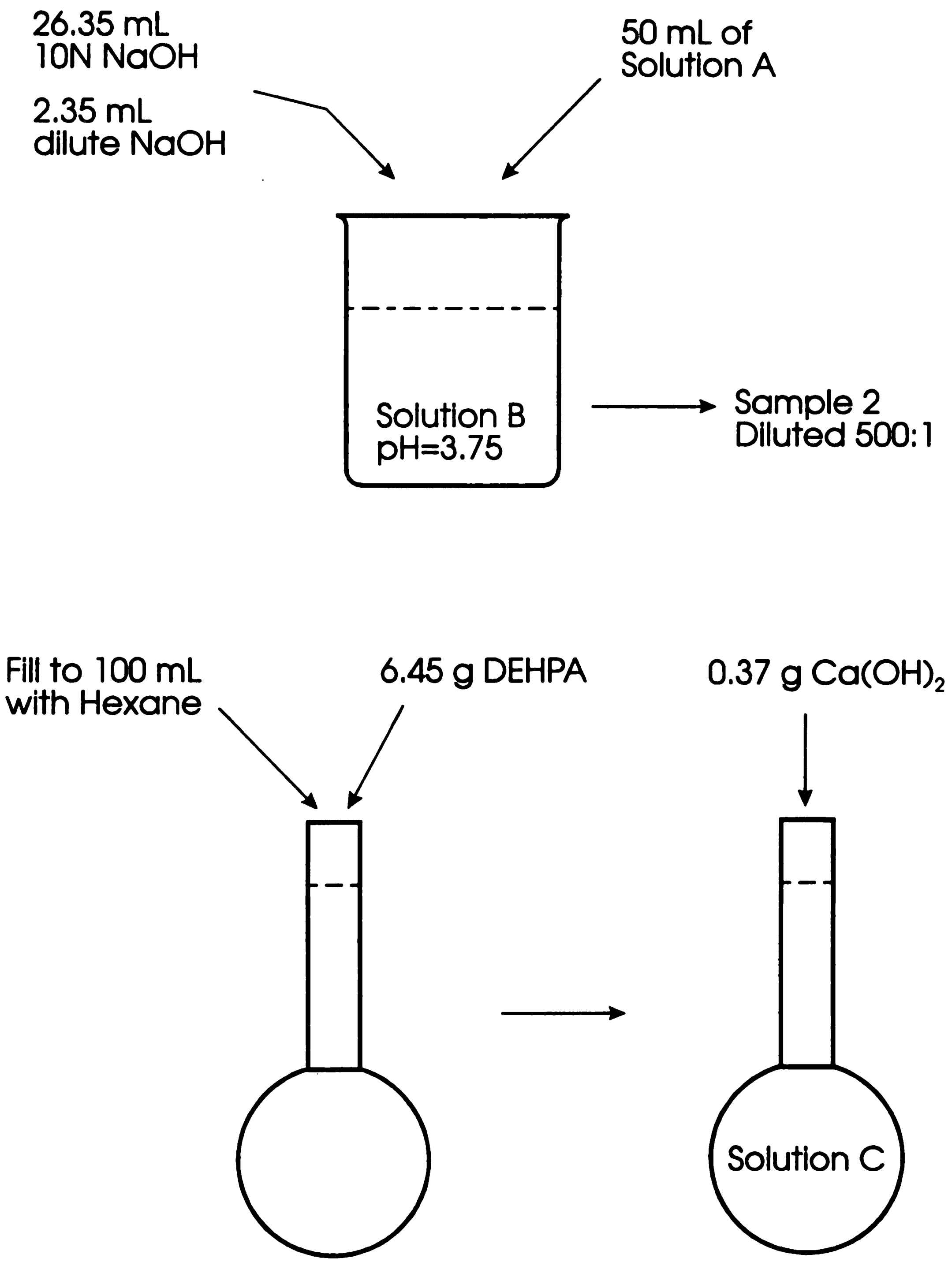


Figure 7. Preparation of Solutions for Ca-DEHPA Extraction and Samples Taken

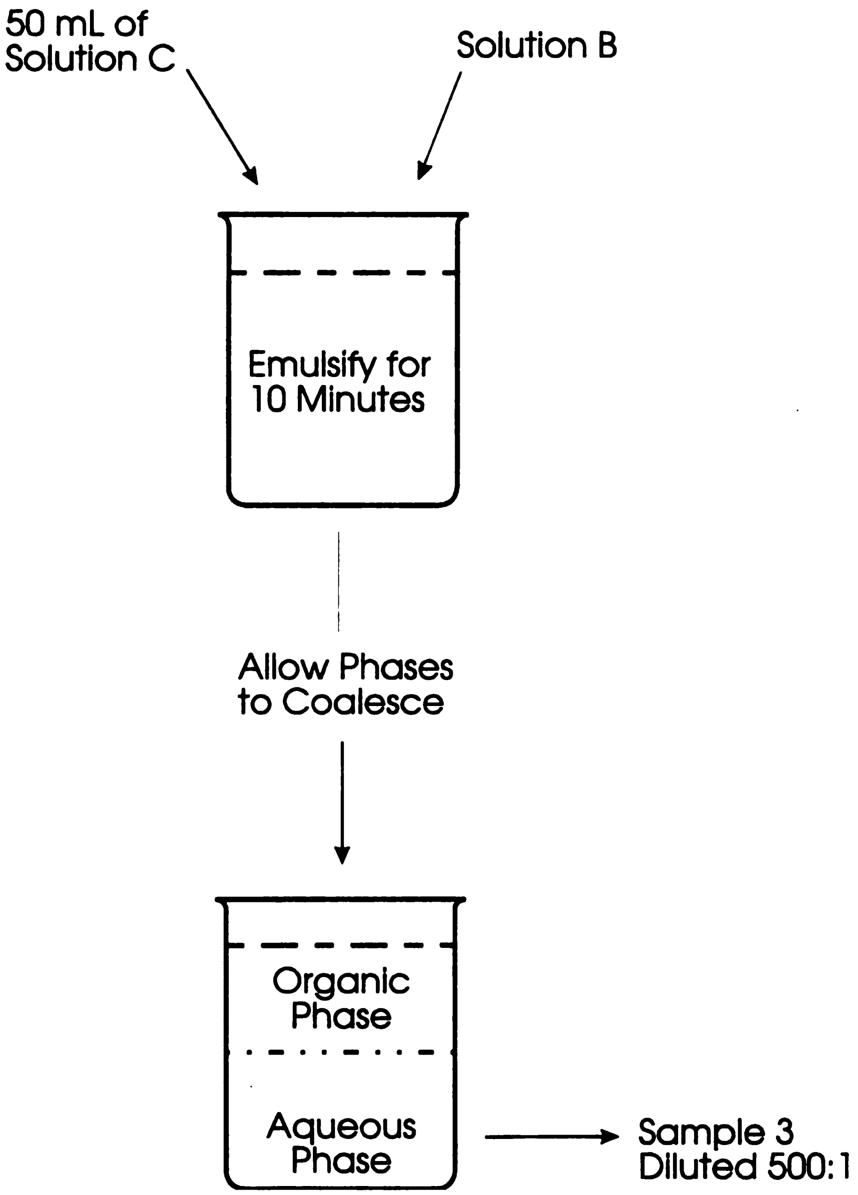


Figure 8. Flow Chart of Lead Extraction with Ca-DEHPA and Samples Taken

b. Ca-DEHPA Extractant Preparation

The 0.2 molar Ca-DEHPA solution was prepared in two steps: a 0.2 molar DEHPA solution was prepared, then calcium hydroxide, $Ca(OH)_2$, was added. The 0.2 molar DEHPA solution was prepared by placing 6.45 g of DEHPA, having a molecular weight of 322.4 grams/mole, into a 100 mL volumetric flask and adding hexane. Calcium hydroxide was added at a ratio of 0.25 moles calcium hydroxide to 0.1 moles of DEHPA. The amount of calcium hydroxide added was 0.37 grams. The solution was stirred for two hours using a magnetic stir bar. The DEHPA/hexane mixture was labeled Solution C (see Figure 7).

c. Extraction Procedure

To minimize variations in the extraction coefficient caused by temperature variations, Solution B (lead sulfate/HCl) and 50 mL of Solution C (Ca-DEHPA/hexane) were placed in a 100°F water bath (see Figure 6). After both solutions had been heated to 100°F, the DEHPA solution was added to the beaker containing the aqueous solution and the solution was stirred with a magnetic stir bar at a rate sufficient to cause phase mixing for 10 minutes. Mixing was then stopped and the phases were allowed to coalesce.

To determine the amount of lead extracted from the aqueous phase, Sample 3 was taken and diluted by a ratio of 500:1 (see Figure 8).

To determine if a significant change in pH occurred which could affect the equilibrium or inhibit the extraction, the pH of the aqueous phase was sampled after mixing stopped and the phases coalesced.

C. Extraction of Lead from Soil

In the third group of experiments, a series of extractions were performed on soil which had been loaded with lead sulfate to determine if a liquid-ion extractant would enhance the lead removal rate. The series of extractions use the acid from the first group of experiments, which is hydrochloric acid, and the liquid-ion extractant from the second group of experiments, which is Ca-DEHPA. During the first series of extractions samples were taken from the aqueous and organic phases at timed intervals to evaluate extraction kinetics and the time required to reach equilibrium. Sequential extractions were performed on a contaminated soil sample to evaluate the effect of subsequent extractions on the time required to reach equilibrium. The second series of extractions used twice the extraction time, which was determined in the first series of extractions, along with enhanced sample analysis to determine the amount of lead removed by chemical extraction and physical entrainment of particulates. Four sequential extractions were performed in the second series of extractions to determine the total amount of lead that could be removed from the soil. The third series of extractions involved four sequential extractions without use of the liquid-ion extractant, to establish a baseline for comparison of extraction enhancements associated with the liquid-ion extractant.

1. Preparation of Ludington Sand Spiked with Lead Sulfate

To evaluate lead extraction capabilities, Ludington sand was spiked with lead sulfate. Lead was dissolved into hydrochloric acid, mixed with the Ludington sand, and precipitating onto the soil as lead sulfate by adding sodium sulfate while cooling and stirring. A flow chart of the soil spiking process showing solution preparations, mixing, precipitation, and where samples were taken is shown in Figures 9, 10 and 11.

Aqueous phase samples were prepared as indicated in III.B.1.e and analyzed as indicated in III.B.1.f with an increased integration time of 10 seconds.

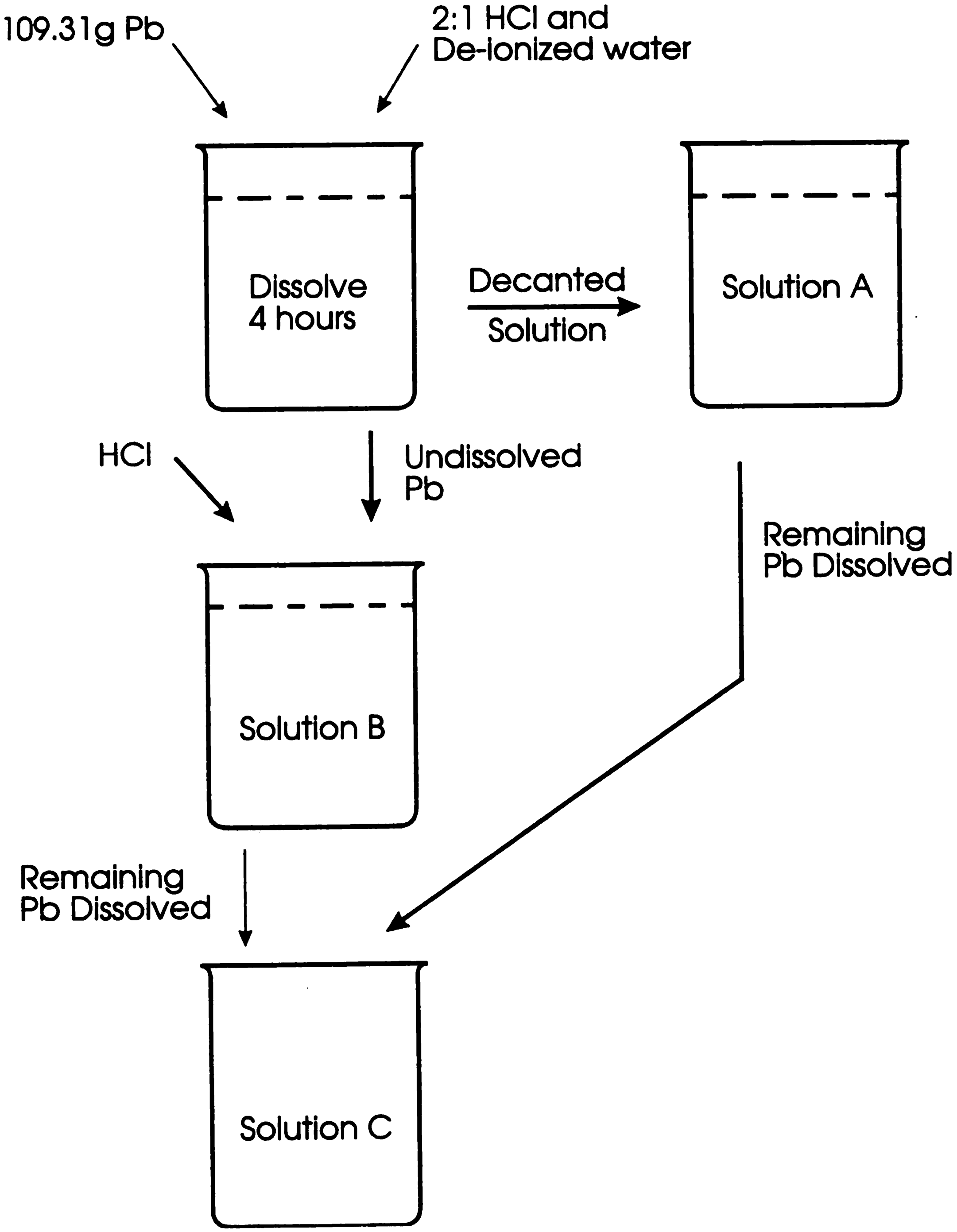


Figure 9. Flow Chart of Lead Dissolved for Soil Spiking

a. Dissolved Lead Solution

To prepare 1 kg of lead spiked soil, 109.31 g of elemental lead in granular form was placed in a 1 L beakers. 37% hydrochloric acid mixed with deionized water, at a ratio of 2:1 consecutively, was added to the beaker and the solution was heated at 190°F while stirring for four hours. The dissolved lead solution was then decanted from the undissolved lead. The decanted solution of dissolved lead is Solution A in Figure 9. Additional 2:1 hydrochloric acid was added to the undissolved lead and heated while stirring for an additional 3 hours. The lead that dissolved in the additional hydrochloric acid is Solution B in Figure 9. Solutions A and B were then consolidated as Solution C in Figure 9.

b. Sodium Sulfate Solution

The amount of sodium sulfate necessary to provide a 1:1 molar ratio with the dissolved lead, and thus cause precipitation as lead sulfate, was determined. The amount of lead dissolved was 109.31 g, with a molecular weight of 207.2 g per mole, which equals 0.5276 moles of lead. The molecular weight of sodium sulfate, which is 142.04 g per mole, times the number of moles at a 1:1 ratio, which is 0.582 moles, equals 74.93 g of sodium sulfate.

A solution of sodium sulfate was prepared by dissolving 74.87 g of sodium sulfate into 500 mL of deionized water. The dissolved sodium sulfate is Solution D in Figure 10.

c. Precipitation of Lead Sulfate on Ludington Sand

One kg of Ludington sand, having an organic content of 0.2 weight percent, was placed in a beaker and heated to 105°F to prevent precipitation due to cool temperatures. The dissolved lead, Solution C, was added to the heated soil and briefly stirred. The dissolved sodium sulfate, Solution D, was then added to precipitate the dissolved lead as lead sulfate onto the soil. The Ludington sand with precipitating lead sulfate is Solution E in Figure 10. Solution E was stirred for one and a half hours and then evenly divided between five 1 L beakers and continuously stirred while cooling over night. A Phipps & Bird Inc. stirrer was used for the five 1 L beakers. The stirring blade was placed close to the bottom of the beaker to ensure that all of the soil was stirred during precipitation and cooling.

After cooling and precipitating over night, the aqueous phase was decanted from each 1 L beaker and collected in a 1-gallon glass container. The decanted liquid from the 1 L beakers is Solution F in Figure 11. To determine the concentration of lead in Solution F, Sample 1 was taken and diluted by a ratio of 1000:1. The soil in the 1 L beakers was dried with low heat and collect in a single 1 L beaker.

d. Analysis of Soil Concentration by Aqueous Phase Mass Balance

The concentration of lead in the soil phase was determined by mass balance. The difference between the initial mass of lead and the mass of lead in Solution F, which is the product of the lead concentration in Sample 1 and the volume of Solution F, is the mass of lead in the soil phase. The mass of lead divided by the mass of soil is the resulting concentration of lead in the soil phase.

The concentration of lead in Solution F, $[Pb]_F$, is calculated as the product of the concentration of Sample 1, $[S]_1$, and the dilution ratio of Sample 1, DR_1:

$$[Pb]_F = [S]_1 \times DR_1 \tag{32}$$

The mass of lead in Solution F is, Pb_F, is calculated as the product of lead concentration in Solution F, $[Pb]_F$, and the volume of Solution F, Vol_F:

$$Pb_F = Vol_F \times [Pb]_F \tag{33}$$

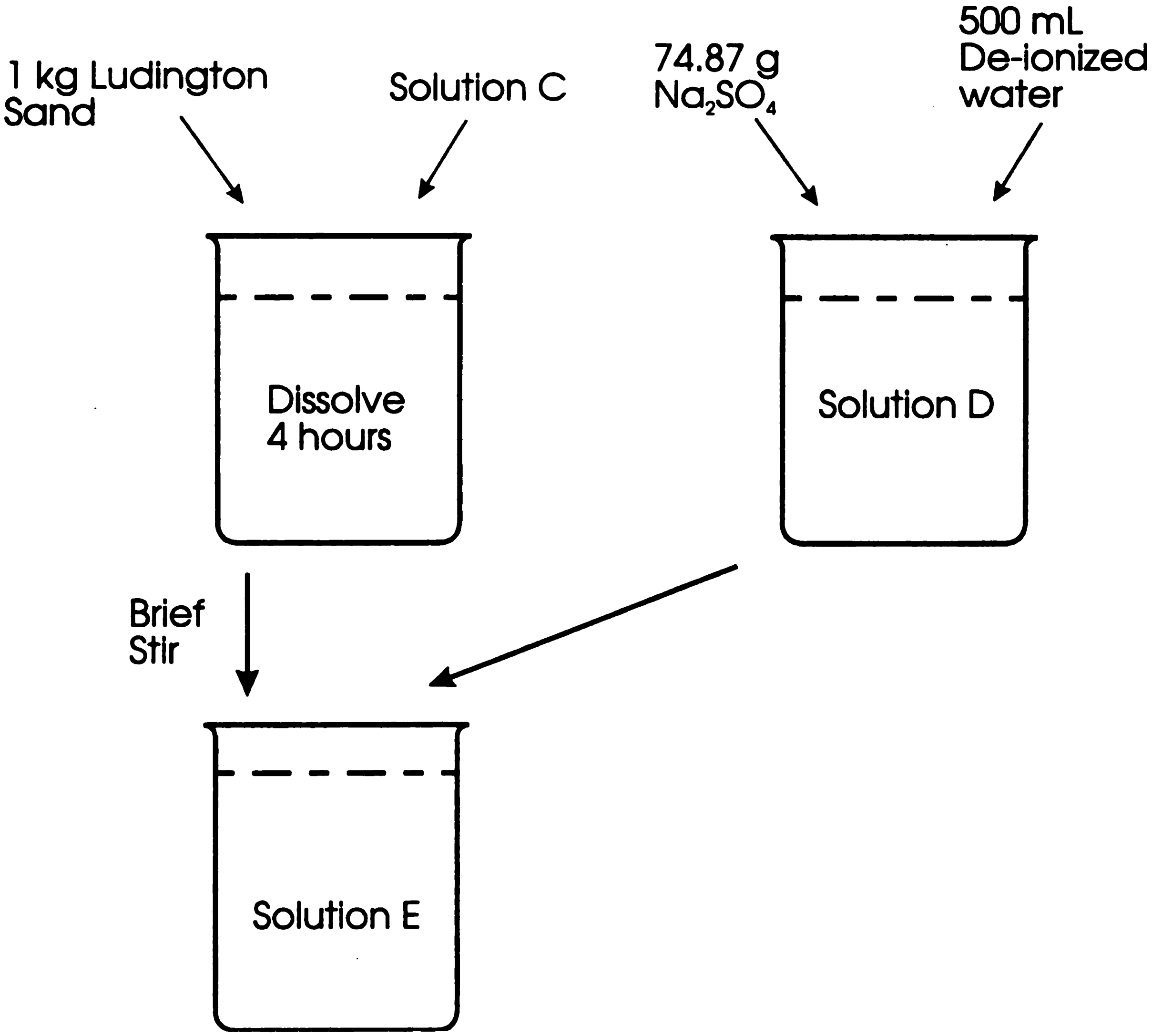


Figure 10. Flow Chart of Lead Sulfate Precipitation on Ludington Sand

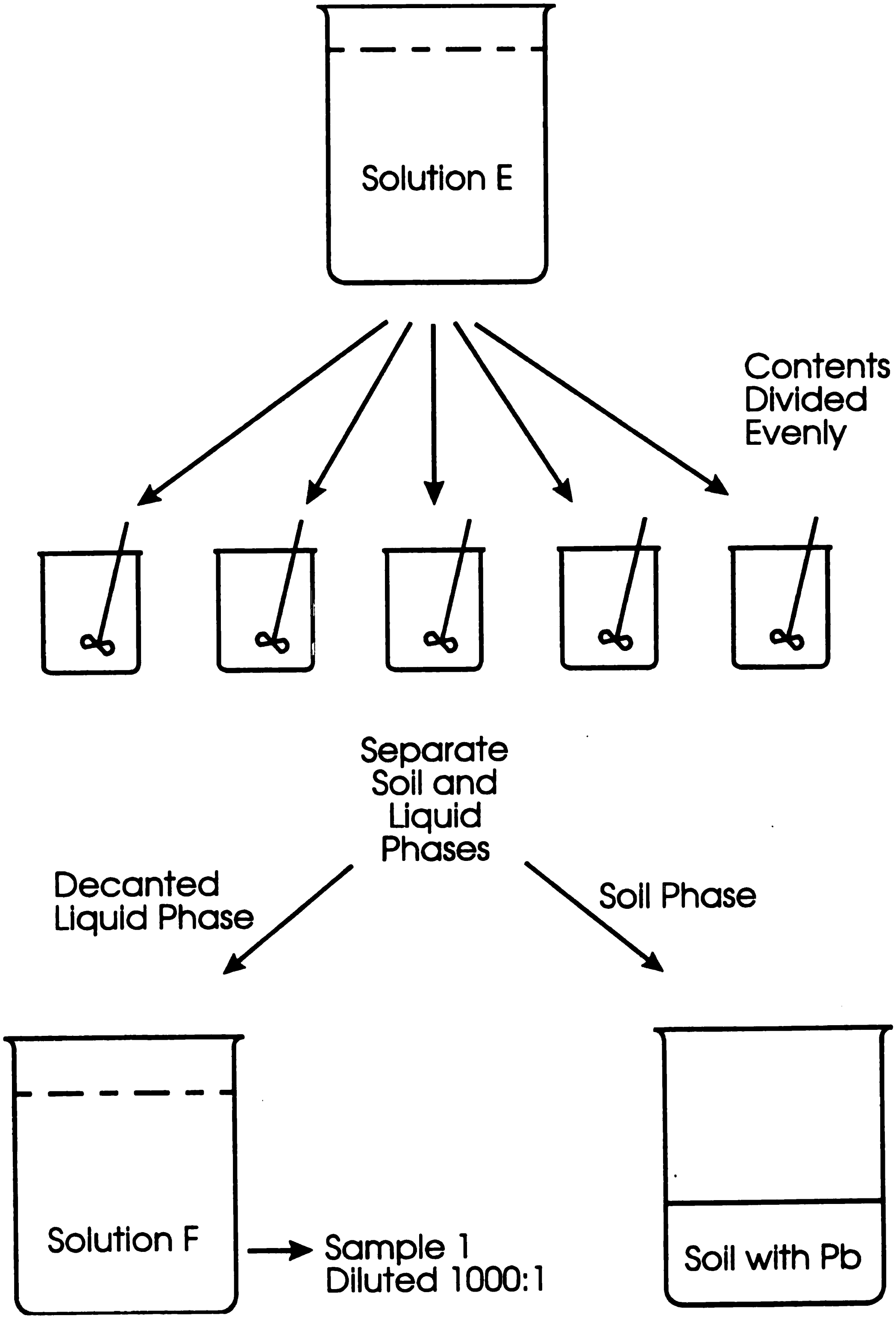


Figure 11. Flow Chart of Spiked Soil Consolidation and Sampling

The difference between the initial mass of lead dissolved into Solution C, Pb_{init}, and the mass of lead in Solution F, Pb_F, is the mass of lead in the soil phase, Pb_{soil}:

$$Pb_{soil} = Pb_{init} - Pb_F \tag{34}$$

The concentration of lead in the soil phase, $[Pb]_{soil}$, is the mass of lead in the soil phase, Pb_{soil}, divided by the sum of the soil mass, 1 kg, and the mass of lead in the soil phase, Pb_{soil}:

$$[Pb]_{soil} = \frac{Pb_{soil}}{1kg + Pb_{soil}} \tag{35}$$

e. Analysis of Soil Concentration by Acid Digestion

The concentration of lead in the soil phase was also determined using Method 3050, Acid Digestion of Sediments, Sludges, and Soils.[32] The spiked soil was mixed thoroughly to ensure homogeneity. Ten samples were taken, weighed to the nearest 0.01g and placed in ceramic crucibles. 10 mL of 1:1 nitric acid was added to each sample, mixed and covered with a watch glass. The samples were then heated to 95°C and refluxed for 10 to 15 minutes without boiling. The samples were allowed to cool, and 5 mL of concentrated nitric acid added. The watch glass was replaced and the samples were refluxed for 30 minutes. To ensure complete oxidation, the samples were allowed to cool, 5 mL of concentrated nitric acid was added, the watch glass was replaced and the samples were refluxed for another 30 minutes.

The solution was then evaporated to 5 mL without boiling and allowed to cool. After cooling, 2 mL of de-ionized water was added and 3 mL of 30% hydrogen peroxide was added. The sample was covered with a watch glass and warmed on the hot plate to start the peroxide reaction. Excess effervescence caused losses of samples 1 and 4. After the effervescence subsided the samples were cooled. The process of adding 1 mL aliquots of 30% hydrogen peroxide and heating unit the effervescence subsided was repeated until a total of 10 mL of 30% hydrogen peroxide had been added.

After the last addition of hydrogen peroxide and the samples were allowed to cool, 5 mL of concentrated hydrochloric acid was added and 10 mL of de-ionized water was added. The samples were covered with a watch glass and refluxed for an additional 15 minutes without boiling. The samples were cooled and the liquid phase was decanted into 100 mL volumetric flasks. Samples 2, 3 and 5 were filtered using a Wattman filter paper.

After addition of the sample, the volumetric flask was filled to the indication mark with de-ionized water as directed by Method 3050. The addition of de-ionized water caused a precipitate to form in the volumetric flasks. To eliminate the possibility of lead precipitate in the samples, 2 mL of nitric acid was added to the volumetric flasks with a pipette and the solutions were heated until all crystals dissolved. The total volume of each sample was 102 mL. The heated solution was then diluted by a ratio of 50:1 as described in III.B.1.e.

To determine the lead concentration in a spiked soil sample, $[Pb]_{soil,x}$, the mass of lead in the digested sample solution, $Pb_{dgst,x}$, was divided by the corresponding initial sample mass, S_x:

$$[Pb]_{soil,x} = \frac{Pb_{dgst,x}}{S_x} \tag{36}$$

The mass of lead in the digested sample, $Pb_{dgst,x}$, was calculated as the product of the sample concentration, $[S]_x$, the dilution ration, DR_x, and the volume of the digested sample, Vol_x, divided by the ratio of water densities, $\rho_{95,20}$:

$$Pb_{dgst,x} = \frac{[S]_x \times DR_x \times Vol_x}{\rho_{95,20}} \tag{37}$$

The ratio of water densities, $\rho_{95,20}$,is used to account for the decreased mass of digested sample taken at 95°C, which was used to make the 50:1 sample dilutions. The ratio of water densities was calculated as the density of water at 95°C, $\rho_{95°C}$, divided by the density of water at 20°C, $\rho_{20°C}$:

$$\rho_{95,20} = \frac{\rho_{95}}{\rho_{20}} \tag{38}$$

2. Kinetic Extraction study

In the first series of extractions, samples were taken from the aqueous and organic phases at timed intervals to evaluate extraction kinetics and the time required to reach equilibrium. Sequential extractions were performed on a contaminated soil sample to evaluate the effect of subsequent extractions on the time required to reach equilibrium. The acid from the first group of experiments, that is hydrochloric acid, and the organic extractant from the second group of experiments, that is Ca-DEHPA were used to extract lead from soil prepared in III.C.1.

Subsequent extractions on a contaminated soil sample were performed by removing the lead loaded organic phase at the end of the first extraction and replacing it with fresh extractant. The extraction was repeated and after the second extraction, the organic phase was replaced with fresh extractant and the extraction was repeated. Thus, the soil was sequentially extracted three times with fresh extractant.

A flow chart of the experimental process showing solution preparations, sequential extractions, and sample points is shown in Figures 12, 13 and 14.

Samples were analyzed as indicated in III.B.1.f using a calibration curve from

0 to 20 ppm lead. Calibration standards were prepared as indicated in III.B.1.g, and pH values were determined as indicated in III.B.1.h. The concentration of lead in the aqueous and organic phases was determined as indicated in III.B.1.i, Equation 28. The extraction coefficient, E, for each extraction was calculated as indicated in III.B.1.i, Equation 31.

a. Organic Extractant Preparation

A 1.0 molar Ca-DEHPA was prepared in two steps: a 1.0 molar DEHPA solution was prepared, then calcium hydroxide, Ca(OH)2 was added. The 1.0 molar DEHPA solution was prepared by placing 161.23 g of DEHPA, having a molecular weight of 322.4 grams/mole, into a 500 mL volumetric flask and adding hexane to the indication mark. Calcium hydroxide was added at a ratio of 0.25 moles calcium hydroxide to 1.0 moles of DEHPA. The amount of calcium hydroxide added was 9.27 grams. The solution was stirred with a magnetic stir bar for a minimum of two hours prior to use. Preparation of the 1.0 molar Ca-DEHPA solution is shown in Figure 12.

b. Kinetic Extraction Procedure

The extraction vessel used for the kinetic extraction was a 500 mL graduated cylinder, which had been cut-off at the 250 mL mark, in combination with a mixer assembly. The mixer assembly was a Barnant Mixer, Series 10, Model 700-5400 drive motor along with a 3 bladed, 1.5 inch diameter propeller. The extraction vessel was placed in a 100°F water bath to control the extraction temperature as shown in Figure 13.

The order of ingredients added to the extraction vessel was; soil, de-ionized water then organic extractant. Adding the water prior to the extractant wetted the soil and minimized entrainment of extractant in the soil phase. The amount of lead

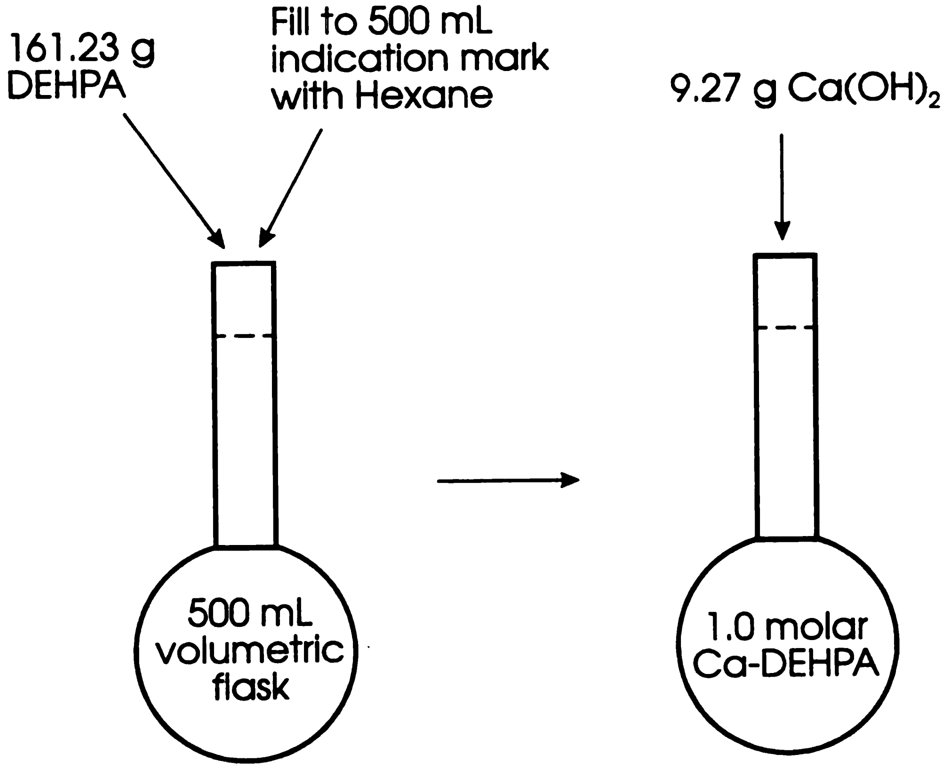


Figure 12. Preparation of 1.0 molar Ca-DEHPA

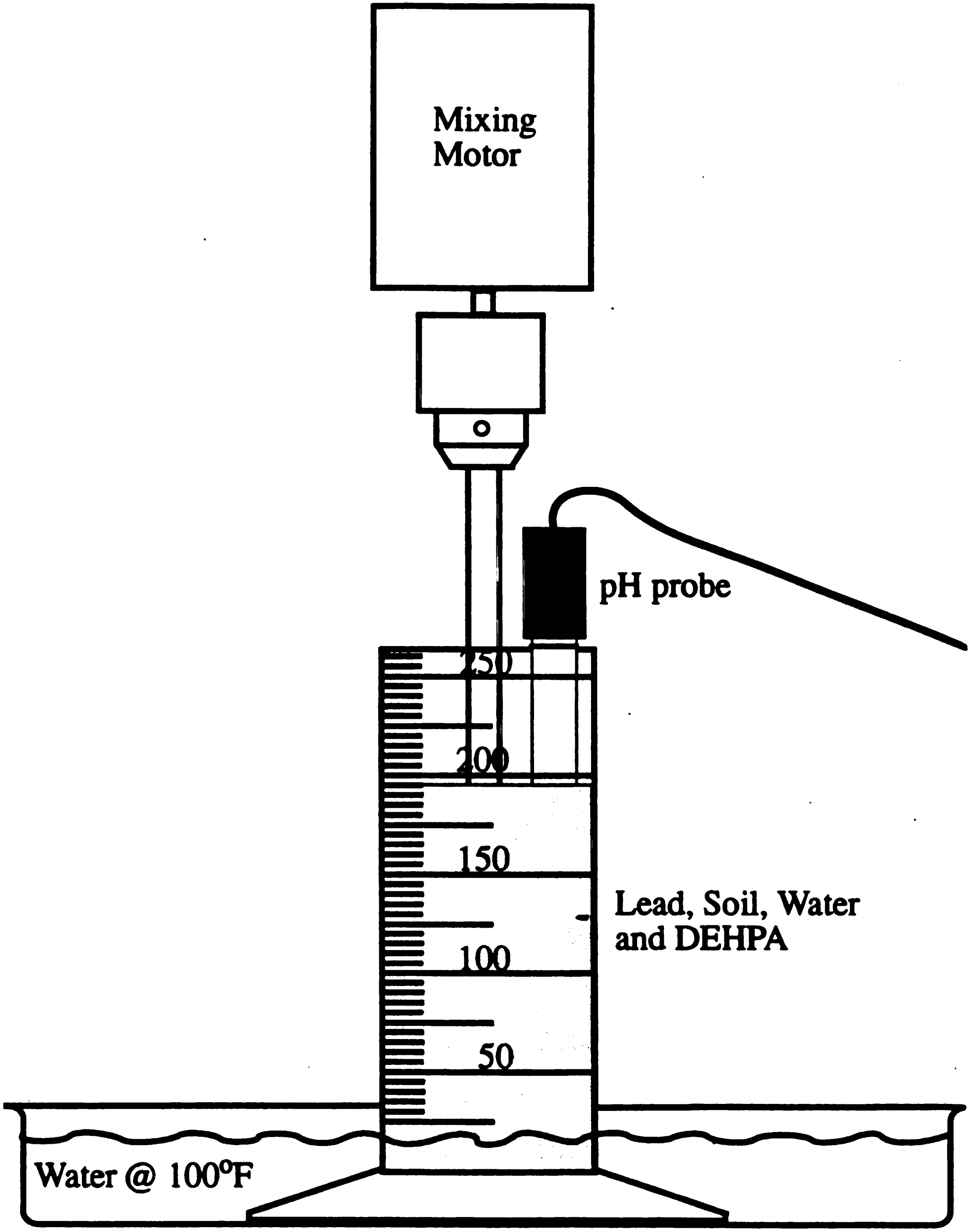


Figure 13. Extraction Apparatus

contaminated soil was 50.005 grams from III.C.1, the volumes of de-ionized water and 1.0 molar Ca-DEHPA were both 50 mL. The total volume of contents in the extraction vessel was 130 mL.

The impeller from the mixer was then placed into the extraction solution at an angle of 10 to 15° from the vertical with the impeller located off center. Mixer angle and off center location of the impeller improve mixing and minimize batch swirl.[29] The mixer was then operated at a speed sufficient to emulsify the contents without excessive rpms. Excessive mixer speed caused sample losses and the creation of a crud layer that would not separate.

When mixing was first initiated, the pH was adjusted to 3.0 using hydrochloric acid. After the initial start of mixing, slight decreases in pH were controlled by adding sodium hydroxide. The top of the extraction vessel was partially covered with wax paper to minimize evaporative losses of hexane.

When mixing had progressed for 4 minutes, mixing was stopped and the cover and mixer propeller were removed from the solution. The total volume of contents in the extraction vessel was compared to the initial volume, which was 130 mL, and hexane was added to compensate for evaporative losses. Mixing was then resumed for one minute to ensure that a sample of the organic phase would be representative. The phases were allowed to coalesce and a 5 mL sample, representing 5 minutes of extraction, was taken from the organic and aqueous phases. The 5 minute samples were labeled 1-O-5 and 1-A-5 for the organic and aqueous phases consecutively. The first character for a sample represents the extraction sequence number, the second character represents the phase sampled, and the last character represents the extraction time. Samples were taken from the organic and aqueous phases using a Gilson Pipetman®. The process of mixing, correcting total volume with hexane, mixing to homogenize the organic phase and

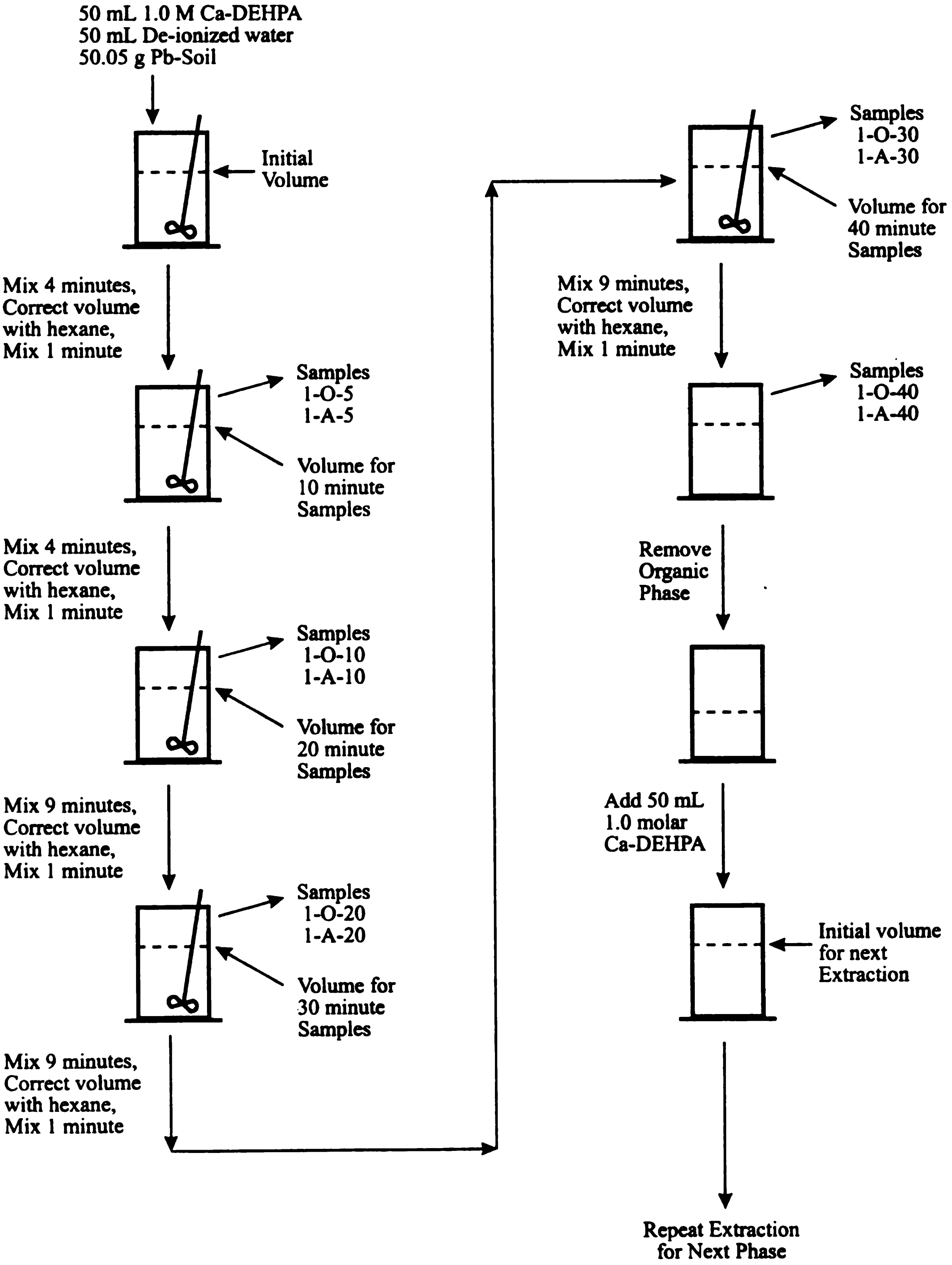


Figure 14. Flow Diagram of Kinetic Extraction Process

taking samples to represent the total time extracted is illustrated in Figure 14.

After the 5-minute samples were taken, extraction was continued for another 4 minutes. The total volume of contents was compared to the initial volume, which was 130 mL, minus sample volumes, which is 10 mL, and the total volume was corrected with hexane to 120 mL. Mixing was resumed for 1 minute, the phases were allowed to coalesce, and 5 mL samples were taken from the organic and aqueous phases to represent 10 minutes of extraction. The 10 minute samples were labeled 1-O-10 and 1-A-10 for the organic and aqueous phases consecutively.

After the 10-minute samples were taken, extraction was continued for another 9 minutes. The total volume of contents was compared to the initial volume minus total sample volume, which is 20 mL, and the total volume was corrected with hexane to 110 mL. Mixing was resumed for 1 minute, the phases were allowed to coalesce, and 5 mL samples were taken from the organic and aqueous phases to represent 20 minutes of extraction. The 20 minute samples were labeled 1-O-20 and 1-A-20 for the organic and aqueous phases consecutively. The process of mixing for 9 minutes, correcting total volume with hexane, mixing an additional minute, and taking samples was repeated to represent extraction times of 30 and 40 minutes.

After the 40 minute samples were taken, the remainder of the organic phase was carefully removed with a Gilson Pipetman® and replaced with 50 mL of fresh 1.0 molar Ca-DEHPA solution. De-ionized water was added to return the aqueous volume to 50 mL. The second extraction on the soil sample was performed as previously described with extraction sample times of 10, 20, 30 and 40 minutes.

After the 40 minute samples were taken from the second extraction, the remainder of the organic phase was carefully removed with a Gilson Pipetman® and replaced with 50 mL of fresh 1.0 molar Ca-DEHPA solution. De-ionized water was added to return the aqueous volume to 50 mL. A third subsequent extraction was performed on the soil sample as previously described with extraction sample times of 10 and 20 minutes. The third extraction was stopped at 20 minutes due to a change in color of the organic phase and the formation of crud.

To verify that evaporative losses were not due to DEHPA, 8.387 g of DEHPA was placed on a watch glass and left uncovered for 14 hours.

c. Aqueous Phase Sample Preparations

The 5 mL samples from III.C.2.b were centrifuged for ten minutes to remove suspended solids from the aqueous phase. A Chermle – Compact Centrifuge, Model Z230, was used at a speed of 5,500 rpm, which generates an RCF of 3,310 g. A known amount of the centrifuged sample was added to a volumetric flask, partially filled with a 2% HNO_3 solution, using a Gilson Pipetman®. After addition of the centrifuged sample, the volumetric flask was filled to the indication mark with 2% HNO_3 solution.

d. Organic Phase Sample Preparations

The 5 mL samples from III.C.2.b were centrifuged for ten minutes to remove suspended solids from the organic phase. A Chermle – Compact Centrifuge, Model Z230, was used at a speed of 5,500 rpm, which generates an RCF of 3,310 g. A volumetric flask was partially filled with a solution containing 20% isopropyl alcohol (IPA) and 80% methyl isobutyl ketone (MIBK). A known amount of the centrifuged sample was added to the volumetric flask with a Gilson Pipetman®. After addition of the centrifuged sample, the volumetric flask was filled to the indication mark with the 20% IPA /80% MIBK solution.

e. Calibration Standards for Analysis of Organic Samples

A lead reference solution from Fischer Scientific, which had a concentration of 1,000 ppm ±1%, was used to prepare standards for calibration. A volumetric flask was partially filled with a the 20% IPA /80% MIBK solution. The amount of reference solution needed to make a standard was added using a Gilson Pipetman®. The volumetric flask was then filled to the indication mark with the 20% IPA /80% MIBK solution. The 20% IPA /80% MIBK solution, which did not contain lead, was used for a blank solution during calibration and between aspirations.

f. Analysis of Extraction Kinetics

The concentrations of lead in the organic and aqueous phases were plotted for all three sequential extractions as a function of time to determine when there is no longer a change in the lead concentration. When the lead concentration no longer changes, the phases are at equilibrium and the extraction has effectively reached completion. The time required for an extraction can then be determined.

3. Sequential Extraction with Modified Sample Analysis

In the second series of extractions the time required to reach equilibrium, which was determined in III.C.2 to be 30 minutes, was increased to 60 minutes per extraction to ensure equilibrium conditions. The acid from the first group of experiments, which is hydrochloric acid, and the organic extractant from the second group of experiments, which is Ca-DEHPA were used to extract lead from soil prepared in III.C.1. Four 60 minute sequential extractions were performed in the second series of extractions. After completion of the an extraction, the organic phase was removed and replaced with fresh extractant and the extraction was repeated. This was repeated until the soil was sequentially extracted four times with fresh extractant. After the last extraction, the concentration of lead in the extracted soil was determined using Method 3050, Acid Digestion of Sediments, Sludges, and Soils.[32]

Samples of the organic phase were only taken at the end of an extraction to eliminate significant volume changes that occur when samples are taken during an extraction. A sample of the aqueous phase was only taken after the last extraction. Sample preparation for the organic and aqueous phases was modified to determine the amount of lead removed by chemical extraction and the amount of lead removed by physical entrainment of fine particulates.

A flow chart of the experimental process showing the extractions procedure, and sample points and sample preparation is shown in Figures 15 and 16.

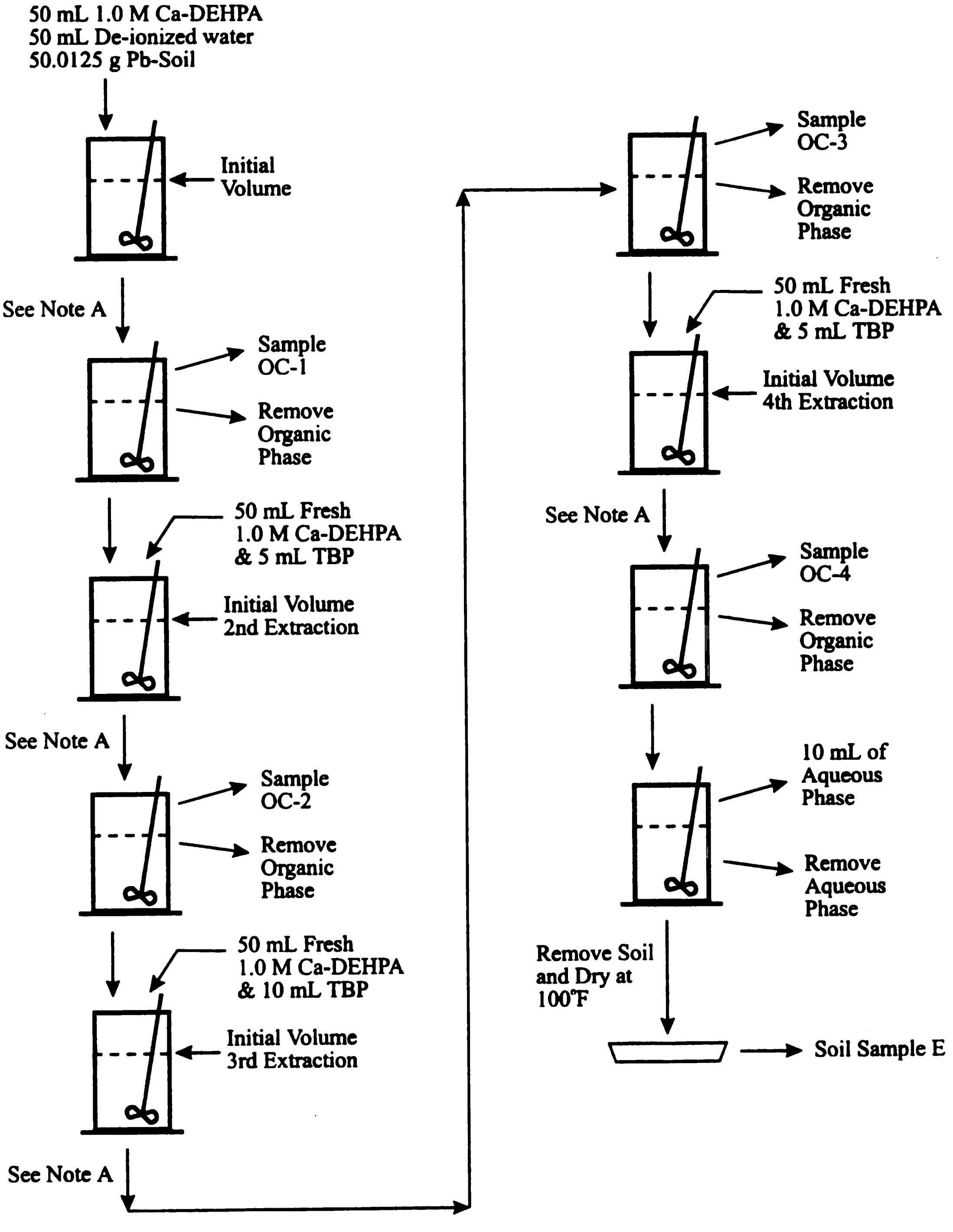
Samples were analyzed as indicated in III.B.1.f using a calibration curve from 0 to 20 ppm lead. Aqueous phase calibration standards were prepared as indicated in III.B.1.g, and organic phase calibration standards were prepared as indicated in III.C.2.e. pH values were determined as indicated in III.B.1.h.

a. Organic Extractant Preparation

The organic extractant was prepared as described in III.C.2.a using 162 g of DEHPA and 9.26 g of $Ca(OH)_2$.

b. Sequential Extraction Procedure

The extraction vessel described in III.C.2.b and shown in Figure 13 was used for the four, 60-minute sequential extractions. The order of ingredients added to the extraction vessel was; soil, de-ionized water then organic extractant. Adding the water prior to the extractant wetted the soil and minimized entrainment of extractant in the soil phase. The amount of lead contaminated soil was 50.0125 grams from III.C.1, the volumes of de-ionized water and 1.0 molar Ca-DEHPA were both 50 mL. The total volume of contents in the extraction vessel was 130 mL.



Note A - Mix 60 minutes, correcting the volume with hexane every 15 minutes. Mix 1 minute after last correction.

Figure 15. Flow Diagram of Extraction Process

The impeller from the mixer was then placed into the extraction solution as described in III.C.2.b. When mixing was first initiated, the pH was adjusted to 3.0 using hydrochloric acid. After the initial start of mixing, slight decreases in pH were controlled by adding sodium hydroxide. The top of the extraction vessel was partially covered with wax paper to minimize evaporative losses of hexane.

When mixing had progressed for 15 minutes, mixing was stopped, the cover was removed from the extraction vessel and the mixer propeller was removed from the solution. The total volume of contents in the extraction vessel was compared to the initial volume, which was 130 mL, and hexane was added to compensate for evaporative losses. Mixing was then resumed. The process of mixing for 15 minutes and correcting for evaporative losses with hexane was repeated until 60 minutes of extraction had taken place.

After 60 minutes of extraction, the total volume was corrected and the extraction was mixed for one minute to ensure mixing of the organic phase prior to taking a sample. The phases were allowed to coalesce for 15 minutes and a 10 mL sample, representing the first 60 minute extraction, was taken from the organic phase using a Gilson Pipetman®. The organic phase sample from the first 60 minute extraction was labeled OC-1 which is an abbreviation for organic concentration, extraction number 1. The process of mixing, correcting total volume with hexane, mixing to homogenize the organic phase and taking a sample to represent the first extraction is illustrated in Figure 15.

After the first 60 minute organic sample was taken, the remainder of the organic phase was carefully removed with a Gilson Pipetman®. The total volume of organic phase removed, including the 10 mL sample, was 50 mL. Fifty milliliters of fresh 1.0 molar Ca-DEHPA solution was then added to the extraction vessel. To minimize third phase formation, 5 mL of tri-n-butyl phosphate, TBP, was added to the extraction solution.[13] This increased the volume of the organic phase to 55 mL and the total volume of the extraction to 135 mL. The 60-minute extraction was repeated as previously described with four volume corrections at 15 minute intervals and one additional minute of mixing after the last volume correction.

After the second 60 minute extraction, a 10 mL organic sample was taken and labeled OC-2. The remainder of the organic phase was carefully removed with a Gilson Pipetman®. The total volume of organic phase removed, including the 10 mL sample, was 55 mL. Fifty milliliters of fresh 1.0 molar Ca-DEHPA solution was then added to the extraction vessel. To minimize third phase formation, 10 mL of tri-n-butyl phosphate, TBP, was added to the third extraction solution.[13] This increased the volume of the organic phase to 60 mL and the total volume of the extraction to 140 mL. The 60-minute extraction was repeated as previously described with four volume corrections at 15 minute intervals and one additional minute of mixing after the last volume correction.

After the third 60 minute extraction, a 10 mL organic sample was taken and labeled OC-3. The remainder of the organic phase was carefully removed with a Gilson Pipetman®. The total volume of organic phase removed, including the 10 mL sample, was 60 mL. Fifty milliliters of fresh 1.0 molar Ca-DEHPA solution was then added to the extraction vessel. To minimize third phase formation, 5 mL of tri-n-butyl phosphate, TBP, was added to the fourth extraction solution.[13] This increased the volume of the organic phase to 55 mL and the total volume of the extraction to 135 mL. The 60-minute extraction was repeated as previously described with four volume corrections at 15 minute intervals and one additional minute of mixing after the last volume correction.

After the fourth 60 minute extraction, a 10 mL organic sample was taken and labeled OC-4. The remainder of the organic phase was carefully removed with a Gilson Pipetman®. The total volume of organic phase removed, including the 10 mL sample, was 55 mL. A 10 mL sample of the aqueous phase was taken and labeled AC, which represents the final aqueous phase lead concentration. The remainder of the aqueous phase was then removed with a Gilson Pipetman®.

The extracted soil sample was dried at 100°C for two hours, weighed and dried for another 20 minutes at 550°C and weighed again. A soil sample was taken and labeled E as indicated in Figure 15.

c. Aqueous Phase Sample Preparation with Suspended Solids Digestion

The 10 mL aqueous sample from III.C.3.b, which was AC, was centrifuged for 20 minutes to remove suspended solids from the liquid phase. A Chermle – Compact Centrifuge, Model Z230, was used at a speed of 5,500 rpm, which generates an RCF of 3,310 g. A sample of the solubilized lead concentration in the aqueous phase was prepared by taking a sample from the clear centrifuged liquid with a Gilson Pipetman® and diluting by a ratio of 100:1 as described in III.B.1.e. The diluted solution is Sample AC-100 in Figure 16.

A sample of the lead concentration in the aqueous phase due to suspended solids was prepared by removing the remaining aqueous phase from the centrifuged sample and performing acid digestion on the remaining solids. 10 mL of 1:1 nitric acid was added to the sample, mixed and covered with a watch glass. The sample was then heated to 95°C and refluxed for 10 to 15 minutes without boiling. The sample was allowed to cool, and 5 mL of concentrated nitric acid added. The watch glass was replaced and the sample was refluxed for 30 minutes. To ensure complete oxidation, the sample was allowed to cool, 5 mL of concentrated nitric acid was added, the watch glass was replaced and the sample was refluxed for another 30 minutes.

The solution was then evaporated to 5 mL without boiling and allowed to cool. After cooling, 2 mL of de-ionized water was added and 3 mL of 30% hydrogen peroxide was added. The sample was covered with a watch glass and warmed on the hot plate to start the peroxide reaction.. After the effervescence subsided the sample was cooled. The process of adding 1 mL aliquots of 30% hydrogen peroxide and heating unit the effervescence subsided was repeated until a total of 10 mL of 30% hydrogen peroxide had been added.

After the last addition of hydrogen peroxide and the sample was allowed to cool, 5 mL of concentrated hydrochloric acid was added and 10 mL of de-ionized water was added. The sample was covered with a watch glass and refluxed for an additional 15 minutes without boiling. The sample was cooled and transferred to a 100 mL volumetric flasks. The culture tube was rinsed with 5 mL of HCl and 10 mL of de-ionized water. The solution in the volumetric flask was heated for 15 minutes, allowed to cool and filled to the indication mark with de-ionized water. The diluted solution of acid digested solids is Sample AP in Figure 16. Sample AP was further diluted by a ratio of 50:1 and labeled AP-50.

d. Organic Phase Sample Preparation with Suspended Solids Digestion

The 10 mL samples from III.C.3.b were centrifuged for 20 minutes to remove suspended solids from the organic phase liquid. A Chermle – Compact Centrifuge, Model Z230, was used at a speed of 5,500 rpm, which generates an RCF of 3,310 g. A sample of the lead concentration in the organic phase as a result of extraction was prepared by taking a sample from the clear centrifuged liquid with a Gilson Pipetman® and diluting in a volumetric flask partially filled with a solution containing 20% isopropyl alcohol (IPA) and 80% methyl isobutyl ketone (MIBK). The volumetric flask was then filled to the indication mark with the 20%

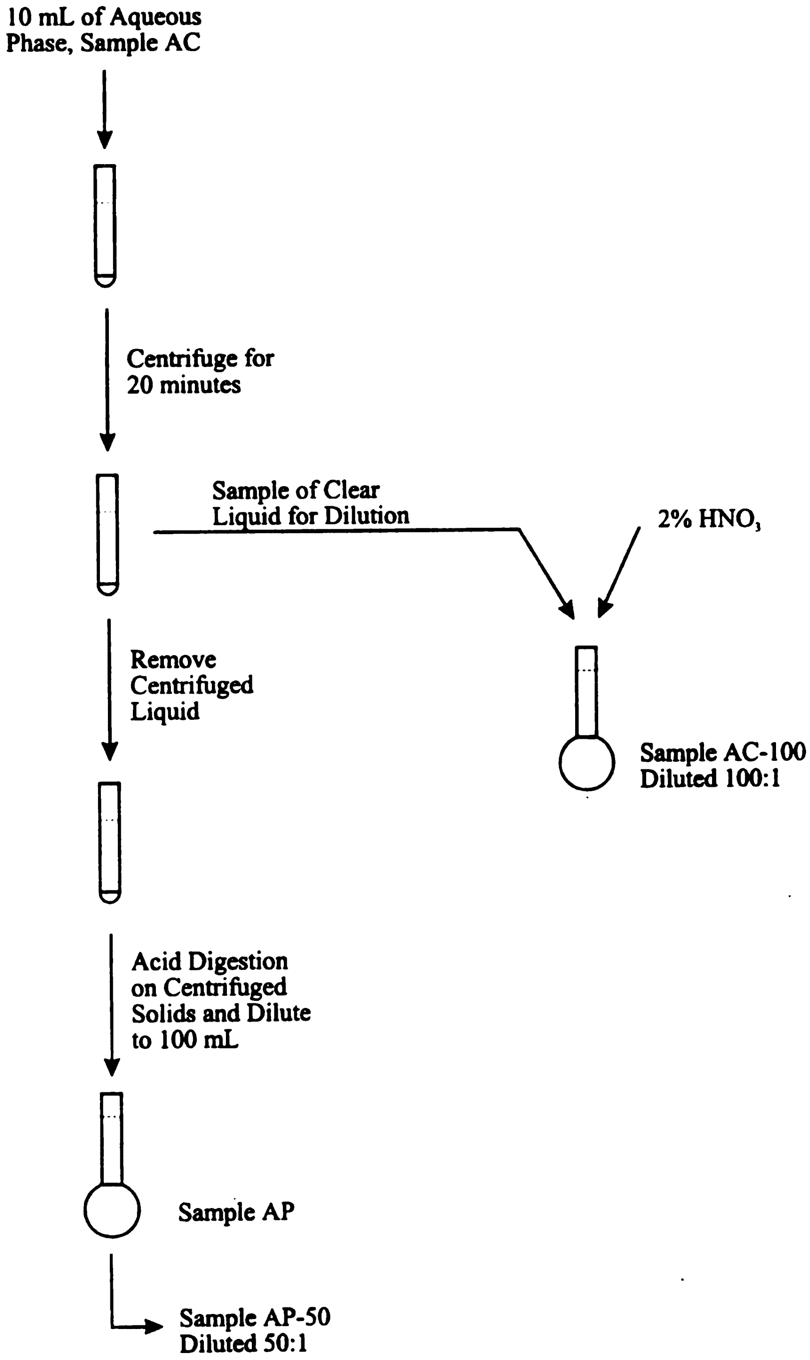


Figure 16. Flow Diagram of Aqueous Phase Sample Preparation with Suspended Solids Digestion

IPA /80% MIBK solution. Samples OC-1, OC-2 and OC-3 were diluted at a ration of 2,000:1 and labeled OCD1, OCD2 and OCD3 consecutively. The sample OC-4 was diluted at a ratio of 1,000:1 and labeled OCD4. The process of centrifuging and diluting the clarified sample is similar to the process used for the aqueous sample illustrated in Figure 16.

A sample of the lead concentration in the organic phase due to suspended solids was prepared by removing the remaining liquid phase from the centrifuged samples and performing acid digestion on the remaining solids as described in III.C.3.c. The diluted solution of acid digested solids from centrifuged samples OC-1, OC-2, OC-3 and OC-4 were labeled OP1, OP2, OP3 and OP4 consecutively. The sample OP1, OP2, OP3 and OP4 were diluted by an addition ration of 100:1 and labeled OP1-100, OP2-100, OP3-100 and OP4-100.

e. Analysis of Remaining Lead in Soil by Acid Digestion

To determine the concentration of lead in the soil after 4 sequential extractions, the sample from III.C.3.b, which was labeled E, was weighed to the nearest 0.01 grams and prepared similar to the Acid Digestion process described in III.C.1.e. Instead of filtering the acid digested sample prior to final dilution, the acid digested sample was centrifuged for 10 minutes to remove suspended solids. The liquid from the centrifuged sample was then diluted to 100 mL using a volumetric flask and labeled E1. The sample E1 was then diluted by a ratio of 10:1 and labeled E1-10.

f. Analysis of Sequential Extractions

The mass of lead the sequential process removed by chemical extraction was calculated as, $\sum Pb_{ext,x}$. The mass of lead removed during the sequential extraction as suspended solids in the organic phase was, $\sum Pb_{susp,x}$. The mass of lead remaining in the aqueous phase, Pb_{aq}, and the extracted soil, $Pb_{soil\text{-}ext}$, was also determined. To perform a mass balance, the initial mass of lead in the soil, $Pb_{soil\text{-}init}$, was calculated and compared to the total mass of lead in the extracted soil, $Pb_{soil\text{-}ext}$, the aqueous phase, Pb_{aq}, the mass of lead chemically extracted, $\sum Pb_{ext,x}$, and the mass of lead removed in the organic phase as suspended solids, $\sum Pb_{susp,x}$. The removal efficiency of the extraction process, R_{eff}, was calculated based on lead concentrations in the soil. Extraction coefficients were calculated for dissolved lead, E_{diss}, suspended lead, E_{susp}, and total lead, E_{tot}, in the organic and aqueous phases.

The mass of lead removed by a chemical extraction, $Pb_{ext,x}$, was calculated as the product of lead concentration in the centrifuged sample, $[Pb]_{OC\text{-}X}$, and the corresponding volume of organic phase removed from the extraction vessel, $Vol_{ext,x}$,:

$$Pb_{ext,x} = Vol_{ext,x} \times [Pb]_{OC-X} \tag{39}$$

Lead concentration in the centrifuged sample, $[Pb]_{OC\text{-}X}$, was calculated as the product of lead concentration in the diluted sample, $[Pb]_{OCDx}$, and the dilution ratio, DR_x.

$$[Pb]_{OC-X} = [Pb]_{OCDx} \times DR_x \tag{40}$$

The mass of lead removed by the organic phase as suspended solids for an extraction, $Pb_{susp,x}$, was calculated as the product of lead mass in a digested sample of suspended solids, $Pb_{dgst,x}$, and the ratio of the volume of organic phase removed, $Vol_{ext,x}$, to the volume of organic phase centrifuged, $Vol_{cent,x}$:

$$Pb_{susp,x} = Pb_{dgst,x} \frac{Vol_{ext,x}}{Vol_{cent,x}} \tag{41}$$

The lead mass in a digested sample of suspended solids, $Pb_{dgst,x}$, was calculated as the product of digested sample concentration, $[Pb]_{OP1\text{-}100}$, the dilution ration, DR_x, and the volume of the digested sample, Vol_{dgst}:

$$Pb_{dgst,x} = [Pb]_{OP1-100} \times DR_x \times Vol_{dgst} \tag{42}$$

The mass of lead remaining in the aqueous phase, Pb_{aq}, was the sum of lead mass dissolved in the aqueous phase, $Pb_{aq\text{-}diss}$, and lead mass in the aqueous phase as suspended solids, $Pb_{aq\text{-}susp}$:

$$Pb_{aq} = Pb_{aq-diss} + Pb_{aq-susp} \tag{43}$$

The mass of dissolved lead in the aqueous phase, $Pb_{aq\text{-}diss}$, was calculated as the product of the dissolved lead sample concentration, $[Pb]_{aq\text{-}diss}$, the sample dilution ratio, DR_x, and the volume of aqueous phase removed from the extraction vessel, Vol_{aq}:

$$Pb_{aq-diss} = [Pb]_{aq-diss} \times DR_x \times Vol_{aq} \tag{44}$$

The lead mass in the aqueous phase as suspended solids, $Pb_{aq\text{-}susp}$, was calculated as the product of lead mass in a digested sample of suspended solids, $Pb_{aq\text{-}dgst}$, and the ratio of the volume of aqueous phase removed, $Vol_{aq\text{-}tot}$, to the volume of aqueous phase centrifuged, $Vol_{aq\text{-}cent}$:

$$Pb_{aq-susp} = Pb_{aq-dgst} \frac{Vol_{aq-tot}}{Vol_{aq-cent}} \tag{45}$$

The lead mass in the digested sample of suspended solids, $Pb_{aq\text{-}dgst}$, was calculated as the product of digested sample concentration, $[Pb]_{AP\text{-}50}$, the dilution ration, DR_{AP}, and the volume of digested sample, Vol_{dgst}:

$$Pb_{aq-dgst} = [Pb]_{AP-50} \times DR_{AP} \times Vol_{dgst} \tag{46}$$

The mass of lead remaining in the extracted soil, $Pb_{soil\text{-}ext}$, was calculated as the product of the extracted soil concentration, $[Pb]_{soil\text{-}ext}$, and the final mass of soil, S_{final}:

$$Pb_{soil-ext} = [Pb]_{soil-ext} \times S_{final} \tag{47}$$

The extracted soil concentration, $[Pb]_{soil\text{-}ext}$, was calculated as the lead mass in the digested sample, which is the product of the digested soil concentration, $[Pb]_{dgst\text{-}soil}$, the dilution ratio, DR, and the digested sample volume, Vol_{dgst}, divided by the mass of soil sample digested, S_{dgst}:

$$[Pb]_{soil-ext} = \frac{[Pb]_{dgst-soil} \times DR \times Vol_{dgst}}{S_{dgst}} \tag{48}$$

The removal efficiency of the extraction process, R_{eff}, was calculated as the difference between initial soil concentration, $[Pb]_{soil\text{-}init}$, and extracted soil concentration, $[Pb]_{soil\text{-}ext}$, divided by the initial soil concentration, $[Pb]_{soil\text{-}init}$:

$$R_{eff} = \frac{\left([Pb]_{soil-init} - [Pb]_{soil-ext}\right)}{Pb_{soil-init}} \tag{49}$$

The initial lead mass in soil, $Pb_{soil\text{-}init}$, was calculated as the product of initial lead concentration in soil, $[Pb]_{soil\text{-}init}$, and the initial mass of soil extracted, S_{init}:

$$Pb_{soil-init} = [Pb]_{soil-init} \times S_{init} \tag{50}$$

4. Extraction of Contaminated Soil without Liquid-Ion Extractant

The third series of extractions involved four sequential extractions without use of the liquid-ion extractant, DEHPA, to determine the amount of lead that would be removed. The amount of lead removed without the liquid-ion extractant allows a comparison to the amount of lead removed with the liquid-ion extractant.

The extraction in III.C.3 was performed using de-ionized water which was pH adjusted to 3.00 with hydrochloric acid. The organic phase, which contained the liquid-ion extractant, was not included. A flow chart of the experimental process showing, extraction steps and points when samples were taken is shown in Figure 17.

After completion of a 60 minute extraction, the aqueous phase was removed and replaced with fresh de-ionized water and the extraction was repeated. This was repeated until the soil was sequentially extracted four times with fresh de-ionized water. After the last extraction, the concentration of lead in the extracted soil was determined using Method 3050, Acid Digestion of Sediments, Sludges, and Soils.[32]

Samples were analyzed as indicated in III.B.1.f using a calibration curve from 0 to 20 ppm lead. Aqueous phase calibration standards were prepared as indicated in III.B.1.g, and organic phase calibration standards were prepared as indicated in III.C.2.e. pH values were determined as indicated in III.B.1.h.

a. Sequential Extraction Procedure

The extraction vessel described in III.C.2.b, and shown in Figure 13, was used for the four, 60-minute sequential extractions. The order of ingredients added to the extraction vessel was; soil, then de-ionized water. The amount of lead contaminated soil was 50.0032 grams from III.C.1, the volume of de-ionized water was 50 mL.

The impeller from the mixer was then placed into the extraction solution as described in III.C.2.b. When mixing was first initiated, the pH was adjusted to 3.0 using a dilute solution of sodium hydroxide. The top of the extraction vessel was partially covered with wax paper to minimize evaporative losses.

After 60 minutes of extraction, the phases were allowed to coalesce for 20 minutes and the aqueous phase was carefully removed with a Gilson Pipetman®.

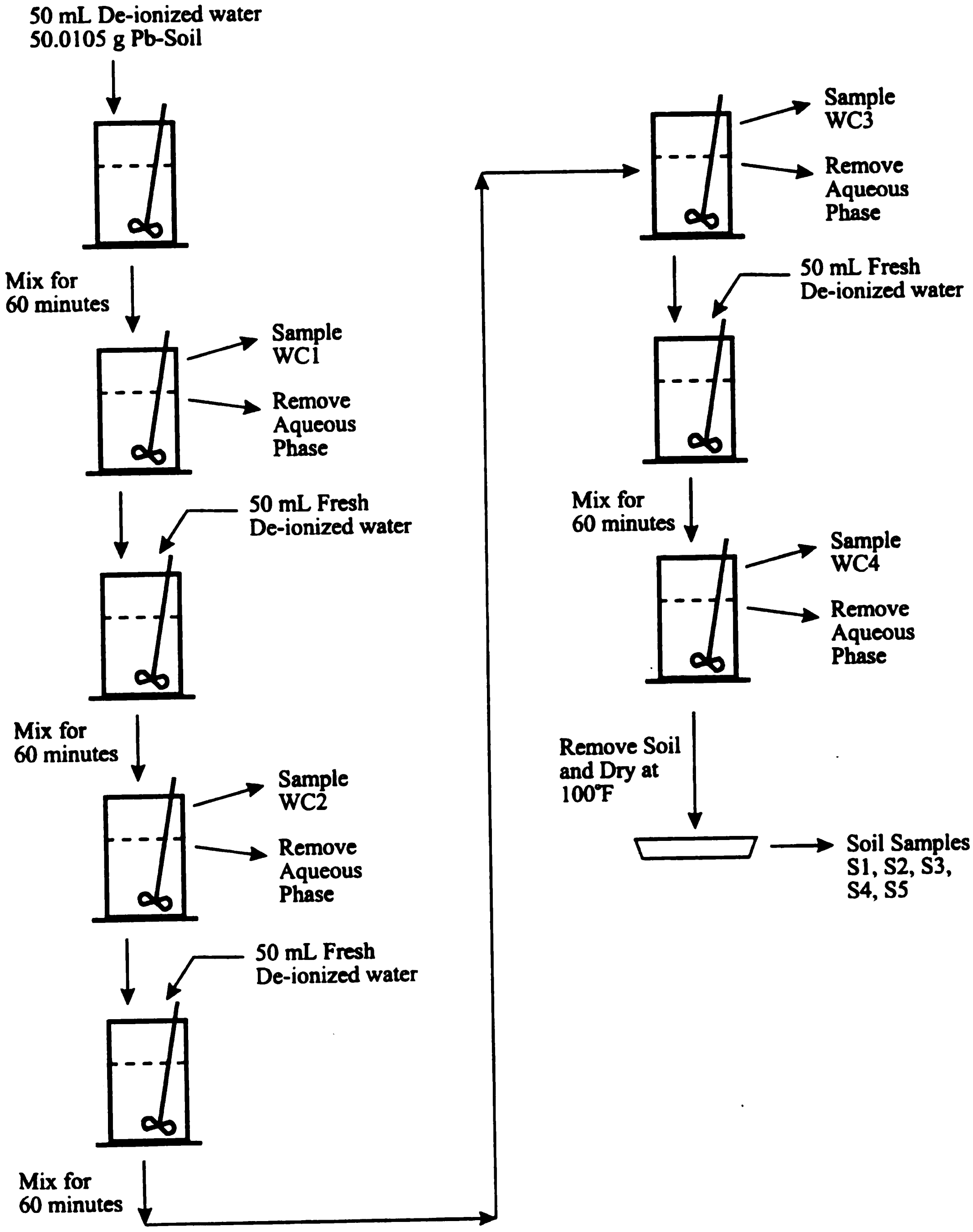


Figure 17. Flow Diagram of Sequential Extractions without DEHPA

The mass of aqueous phase removed was 54.3163 g. A 10 mL sample, representing the first 60 minute extraction, was taken from the aqueous phase using a Gilson Pipetman®. The aqueous phase sample from the first 60 minute extraction was labeled WC1 as shown in Figure 17. Fifty milliliters of fresh de-ionized water was then added to the extraction vessel and the 60-minute extraction was repeated.

After the second 60 minute extraction, the aqueous phase was carefully removed with a Gilson Pipetman®. The mass of aqueous phase removed was 51.1472 g. A 10 mL sample, representing the first 60 minute extraction, was taken from the aqueous phase using a Gilson Pipetman®. The aqueous phase sample from the first 60 minute extraction was labeled WC2 as shown in Figure 17. Fifty milliliters of fresh de-ionized water was then added to the extraction vessel and the 60-minute extraction was repeated.

After the third 60 minute extraction, the aqueous phase was carefully removed with a Gilson Pipetman®. The mass of aqueous phase removed was 48.3478 g. A 10 mL sample, representing the first 60 minute extraction, was taken from the aqueous phase using a Gilson Pipetman®. The aqueous phase sample from the first 60 minute extraction was labeled WC3 as shown in Figure 17. Fifty milliliters of fresh de-ionized water was then added to the extraction vessel and the 60-minute extraction was repeated.

After the fourth 60 minute extraction, the aqueous phase was carefully removed with a Gilson Pipetman®. The mass of aqueous phase removed was 45.3409 g. A 10 mL sample, representing the first 60 minute extraction, was taken from the aqueous phase using a Gilson Pipetman®. The aqueous phase sample from the first 60 minute extraction was labeled WC3 as shown in Figure 17.

The extracted soil sample was dried at 100°C for four hours and weighed. The final mass of soil after extraction was 45.3409 g. Soil samples were taken and labeled S1, S2, S3, S4 and S5 as indicated in Figure 17.

b. Aqueous Phase Sample Preparation with Suspended Solids Digestion

Aqueous phase samples, which includes preparation of samples to analyze suspended solids, were prepared as indicated in III.C.3.c. The clear centrifuged liquid from Sample WC1, which represent the dissolved lead concentration, was diluted by a ratio of 100:1 and labeled WC1-100. The clear centrifuged liquid from Samples WC2, WC3 and WC4 were diluted by a ratio of 1000:1, as described in III.B.1.e, and labeled WC2-1000, WC3-1000, and WC4-1000 consecutively. The diluted solution of acid digested solids from centrifuged Samples WC1, WC2, WC3 and WC4 were further diluted by a ratio of 50:1 and labeled WP1-50, WP2-50, WP3-50, and WP4-50 consecutively.

c. Analysis of Remaining Lead in Soil by Acid Digestion

To determine the concentration of lead in the soil after 4 sequential extractions, the Sample S1, S2, S3, S4 and S5, from III.C.4.a, were weighed to the nearest 0.01 grams and prepared as described in III.C.3.e. During the digestion process, some contents for Samples S1 and S3 were lost and the samples were discarded from analysis. The digested Samples S2, S4 and S5 were then diluted by a ratio of 50:1 and labeled S2-50, S4-50 and S5-50 consecutively.

d. Analysis of Sequential Extraction without DEHPA

The mass of lead the sequential process removed by dissolution in the aqueous phase was calculated as, $\sum Pb_{aq\text{-}diss}$. The mass of lead removed during the sequential extraction as suspended solids in the aqueous phase was, $\sum Pb_{aq\text{-}susp}$. The mass of lead remaining in the extracted soil, $Pb_{soil\text{-}ext}$, was also determined. To perform a mass balance, the initial mass of lead in the soil, $Pb_{soil\text{-}init}$, was calculated and compared to the total mass of lead in the extracted soil, $Pb_{soil\text{-}ext}$, the mass of lead removed by dissolution in the aqueous phase, $\sum Pb_{aq\text{-}diss}$, and the mass of lead removed in the aqueous phase as suspended solids, $\sum Pb_{aq\text{-}susp}$. The removal efficiency of the extraction process, R_{eff}, was also calculated.

The mass of lead removed by an extraction as dissolved lead in the aqueous phase was calculated using Equation 43. The mass of lead removed by an extraction as suspended solids in the aqueous phase was calculated using Equations 44 and 45. The mass of aqueous phase removed from each extraction in was equivalently used as volume in units of mL for equations 43 and 44. The extracted soil concentration was calculated using equation 47 and the mass of lead remaining in the extracted soil was calculated using Equation 46. The removal efficiency of the extraction process was calculated as indicated in Equation 48.

D. Stripping Lead from the Loaded Extractant

The DEHPA/hexane extractant loaded with lead was mixed with the selected acid from the first group of experiments, that is hydrochloric acid, to determine if the extractant could be stripped for possible re-use in subsequent extractions.

Samples of the organic phase were prepared as indicated in III.C.2.c. The samples were analyzed as indicated in III.B.1.f using a calibration range of 0 to 20 mg/L.

1. Stripping Procedure

A solution of extractant loaded with lead was prepared by combining the undiluted organic samples from the 60 minute extractions in III.C.3.b. The solution of combined samples did not contain any suspended solids because the samples had been previously centrifuged as described in paragraph III.C.3.d. A sample of the combined samples was diluted at 500:1 and labeled SD1. For each stripping solution, 5 mL of the loaded extractant and the corresponding quantity of

12.5 N hydrochloric acid was placed in a centrifuge tube. The stripping solutions were prepared as indicated in Table 2.

The mixture of extractant and acid were mixed for 10 minutes using a Fischer Scientific® Touch Mixer and then centrifuged for 10 minutes. A sample of the centrifuged solution was taken and diluted at a ratio of 100:1 with a solution of 20% isopropyl alcohol and 80% methyl isobutyl ketone. The samples were labeled SD2, SD3, and SD4 for the solutions S2, S3 and S4 consecutively.

Table 2 - Ratios and Volumes used for Stripping Solutions

Stripping Solution	Phase Ratio Organic:Acid	Organic Volume (mL)	Acid Volume (mL)
S2	5:1	5.0	1.0
S3	10:1	5.0	0.5
S4	15:1	5.0	0.33

2. Analysis

The concentration of lead in a solution, $[Pb]_x$, is calculated as the product of the corresponding sample concentration, $[S]_x$, and the dilution ratio of the sample, DR_x (see Equation 28).

The stripping efficiency, SE, is calculated as the difference between the initial concentration in the organic phase, $[Pb]_{org,\ initial}$, and the final concentration of the organic phase after stripping, $[Pb]_{org,\ final}$, divided by the initial concentration in the organic phase, $[Pb]_{org,\ initial}$;

$$SE = \frac{[Pb]_{org,\,initial} - [Pb]_{org,\,final}}{[Pb]_{org,\,initial}} \times 100 \qquad (51)$$

The concentration factor, CF, is calculated as the product of the stripping efficiency, SE, and the volume ratio, VR, between the organic phase and the stripping phase;

$$CF = SE \times VR \qquad (52)$$

IV. RESULTS

To determine if the use of a liquid ion extractant would enhance the removal of lead from contaminated soils, four groups of experiments were performed. The results from the each experiment were used to determine the path forward for subsequent experiments.

A. Results of Solvent and Soil Compatibility with different Acids

When mixing was stopped for the mixture containing hydrochloric acid, the three phases quickly separated. The organic phase was the top layer and the aqueous phase was below it. The soil was on the bottom. Crud formation did not occur for the mixture containing HCl.

When mixing was stopped for the mixtures with the other acids, the phases did not separate completely. There were either droplets of the organic phase entrapped in the soil phase or there were droplets containing soil at the aqueous-organic interface. The size of the droplets were from 1 to 2 millimeters in diameter.

Based on good coalescing properties for the extraction mixture, the general preference of phosphorous acids to extract metal chlorides, and the absence of a common ion effect which would inhibit the dissolution of lead sulfate, hydrochloric acid was chosen for subsequent extractions.

B. Results of Lead Extraction from an Aqueous Solution

1. Results of Lead Extraction with DEHPA

The pH of the aqueous solution before extraction was 3.75 and after extraction, the pH was 1.75.

Adding sodium hydroxide to adjust the pH of the lead aqueous solution increased the volume from 50 mL to 77.35 mL and decreased the lead concentration from 5,530 mg/L to 3,520 mg/L. The pH of the aqueous solution before extraction was 3.75 and after extraction, the pH was 1.75. The extraction decreased the concentration of lead in the aqueous phase from 3,520 mg/L to 2,500 mg/L. The amount of lead extracted from the aqueous phase was 78.90 mg. The concentration of lead in the DEHPA/hexane extractant increased from 0 mg/L to 1,580 mg/L. The extraction coefficient for the extraction with DEHPA was 0.63.

The DEHPA/hexane successfully extracted lead from the aqueous phase. The decrease in the final pH of the aqueous phase may have inhibited the extraction as shown in Equation 20.

The measured concentrations of the solutions and the calculations used are shown in Appendix I.

2. Results of Lead Extraction with Ca-DEHPA

Adding sodium hydroxide to adjust the pH of the lead aqueous solution increased the volume from 50 mL to 78.8 mL and decreased the lead concentration from 4,590 mg/L to 3,030 mg/L. The pH of the aqueous solution before extraction was 3.80 and after extraction, the pH was 4.08. The extraction decreased the concentration of lead in the aqueous phase from 3,030 mg/L to 1,790 mg/L. The amount of lead extracted from the aqueous phase was 97.71 mg. The concentration of lead in the Ca-DEHPA/hexane extractant increased from 0 mg/L to 1,954 mg/L. The extraction coefficient with Ca-DEHPA was 1.09.

Using the calcium form of DEHPA prevented the pH of the aqueous phase from significantly decreasing and resulted in a higher extraction coefficient. A higher final pH in the aqueous phase prevented extraction reversal caused by a decreasing pH as shown in equation 20. Using the calcium form of DEHPA did not cause a noticeable change in the coalescing properties.

The measured concentrations of the solutions and the calculations used are shown in Appendix II.

C. Results of Extraction of Lead from Soil

1. Results of Soil Concentration by Aqueous Phase Mass Balance

The concentration of lead in Solution F, was 8,870 ppm and the volume of Solution F was 2,523 mL. The calculated mass of lead in Solution F was 22.379 g. The difference between the initial mass of lead, which was 109.31 g, and the mass of lead in Solution F was 86.936 g. The resulting concentration of lead in the soil phase was determined to by 79,983 ppm.

The measured concentrations of the solutions and the calculations used are shown in Appendix III.

2. Results of Soil Concentration by Acid Digestion

The average soil concentration was determined to be 68,196 mg/kg with a standard deviation of 13,385 mg/kg. The digested samples 1 and 4 were not analyzed because of sample losses. The concentrations of the remaining soil samples as shown in Table 3.

The measured concentrations of solutions and the calculations used are shown in Appendix IV.

Table 3 – Lead Concentrations in Soil Samples.

Soil Sample	Concentration (mg/kg)
2	96,519
3	64,275
5	67,416
6	62,286
7	72,798
8	69,031
9	49,918
10	48,618

3. Results of Kinetic Extraction Study

The concentrations of lead in the aqueous phase during the kinetic extraction are indicated in Table 4. The concentrations of lead in the organic phase during the kinetic extraction are indicated in Table 5. A plot of lead concentration in the aqueous and organic phases as a function of time for the first sequential extraction, which is Extraction 1, is shown in Figure 18. The results of Figure 18 indicate that the lead concentration had stopped changing and the extraction was complete after 30 minutes for the first extraction. A plot of lead concentration as a function of time for the second sequential extraction, which is Extraction 2, is shown in Figure 19. The results of Figure 19 indicate that the lead concentration had stopped changing and the extraction was complete after 20 minutes for the second extraction. A plot of lead concentration as a function of time for the third sequential extraction, which is Extraction 3, is shown in Figure 20. The results of Figure 20 indicate that the lead concentration was still changing at 20 minutes of

Table 4 - Lead Concentrations in Aqueous Phase during Kinetic Extraction

Extraction Number	Extraction Time (min.)	Lead Concentration (mg/kg)
1	5	197
1	10	211
1	20	1,310
1	30	1,569
1	40	1,610
2	10	719
2	20	726
2	30	791
2	40	816
3	10	111
3	20	118

Table 5 - Lead Concentrations in Organic Phase during Kinetic Extraction

Extraction Number	Extraction Time (min.)	Lead Concentration (mg/kg)
1	5	1,761
1	10	5,480
1	20	16,340
1	30	18,900
1	40	18,960
2	10	10,690
2	20	14,680
2	30	14,720
2	40	14,280
3	10	1,230
3	20	5,360

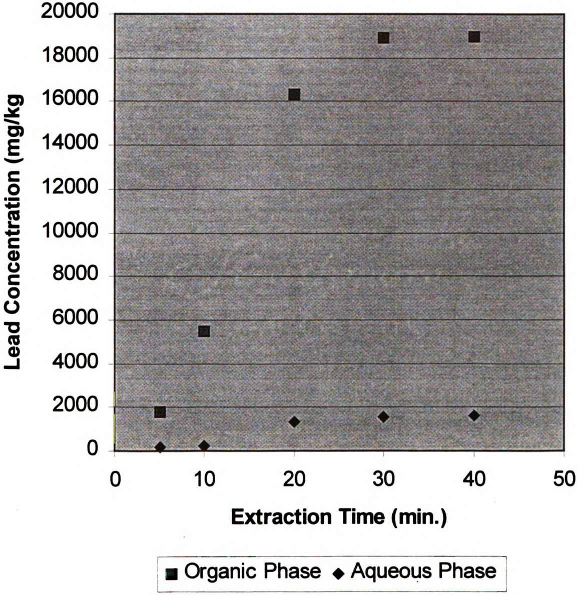


Figure 18. Lead Concentration as a function of Time for Extraction 1.

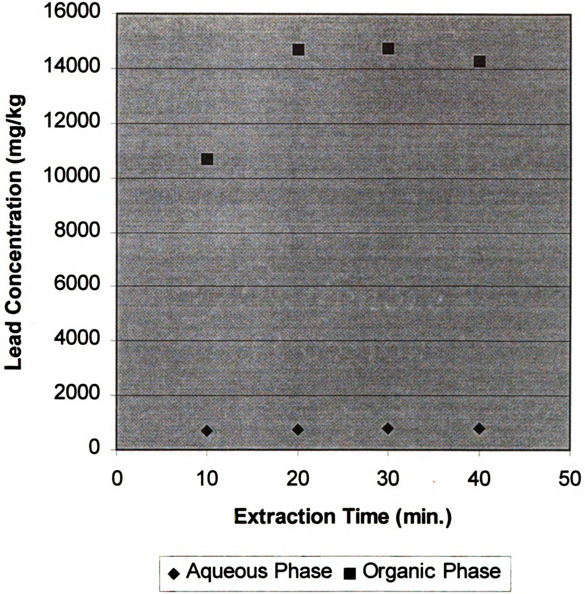


Figure 19. Lead Concentration as a function of Time for Extraction 2.

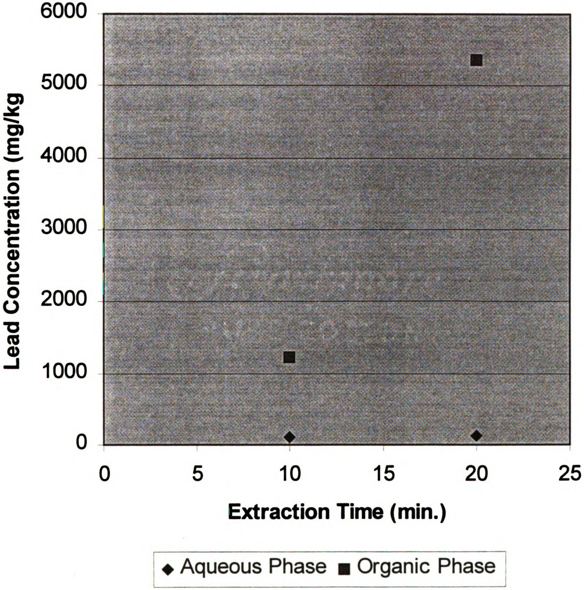


Figure 20. Lead Concentration as a function of Time for Extraction 3.

extraction. There were not enough data points for the third extraction to determine the time required to reach equilibrium. The third extraction was stopped at 20 minutes due to a change in color of the organic phase and the formation of crud. This may have been due to a higher mixer speed between 10 and 20 minutes of extraction.

The longest time indicated to reach equilibrium for an extraction was 30 minutes from the first extraction. To ensure adequate extraction time for subsequent experiments, an extraction time of 60 minutes was used.

Extraction coefficients, which were based on solubilized lead concentrations, were 11.78, 17.50 and 45.42 for the first, second and third extractions consecutively. The extraction coefficient increased during subsequent extractions as the metal loading decreased. Lead concentrations in the organic and aqueous phases along with the corresponding extraction coefficient are summarized in Table 6.

The measured concentrations of solutions and the calculations used are shown in Appendix V.

Table 6 – Extraction Coefficients during Kinetic Extraction Study

Extraction Number	Organic Concentration (ppm)	Aqueous Concentration (ppm)	Extraction Coefficient
1	18,960	1,610	11.78
2	14,280	816	17.50
3	5,360	118	45.42

4. Results of Sequential Extractions

The use of four 60 minute sequential extractions reduced the lead concentration in soil from 79,983ppm to 2,494ppm. Thus, the lead concentration in soil was reduced by 96.88%.

The mass of lead removed by each phase of the extraction and the mass of lead remaining in the aqueous phase and extracted soil is summarized in Table 7. The mass of lead initially in the soil was 4,000 mg. In the organic phase, the mass of lead removed through chemical extraction was 1,698 mg and the mass of lead removed as suspended solids was 1,455 mg. For chemical extraction, there was a decreasing trend in the mass of lead removed during subsequent extractions. However, the mass of lead removed as suspended solids in the organic phase did not show a decreasing or increasing trend. For the aqueous phase, the amount of remaining dissolved lead was 47.1 mg and the amount of lead as suspended solids was 68.1 mg. Acid digestion determined that there was 105.6 mg of lead remaining in the extracted soil. A mass balance, which was able to account for 84.3 percent of the lead is shown in Figure 21.

The measured concentrations of solutions and the calculations used are shown in Appendix VI.

Table 7 – Lead Mass Summary for Extraction with DEHPA

Extraction Phase	Lead Mass (mg)
$Pb_{ext,1}$	828.3
$Pb_{ext,2}$	700.7
$Pb_{ext,3}$	81.6
$Pb_{ext,4}$	86.9
$Pb_{susp,1}$	372.0
$Pb_{susp,2}$	533.5
$Pb_{susp,3}$	183.0
$Pb_{susp,4}$	366.9
$Pb_{aq\text{-}diss}$	47.1
$Pb_{aq\text{-}susp}$	68.1
$Pb_{soil\text{-}ext}$	105.6
Total	3,373.7
$Pb_{soil\text{-}init}$	4,000.2
Percent Accounted	84.3%

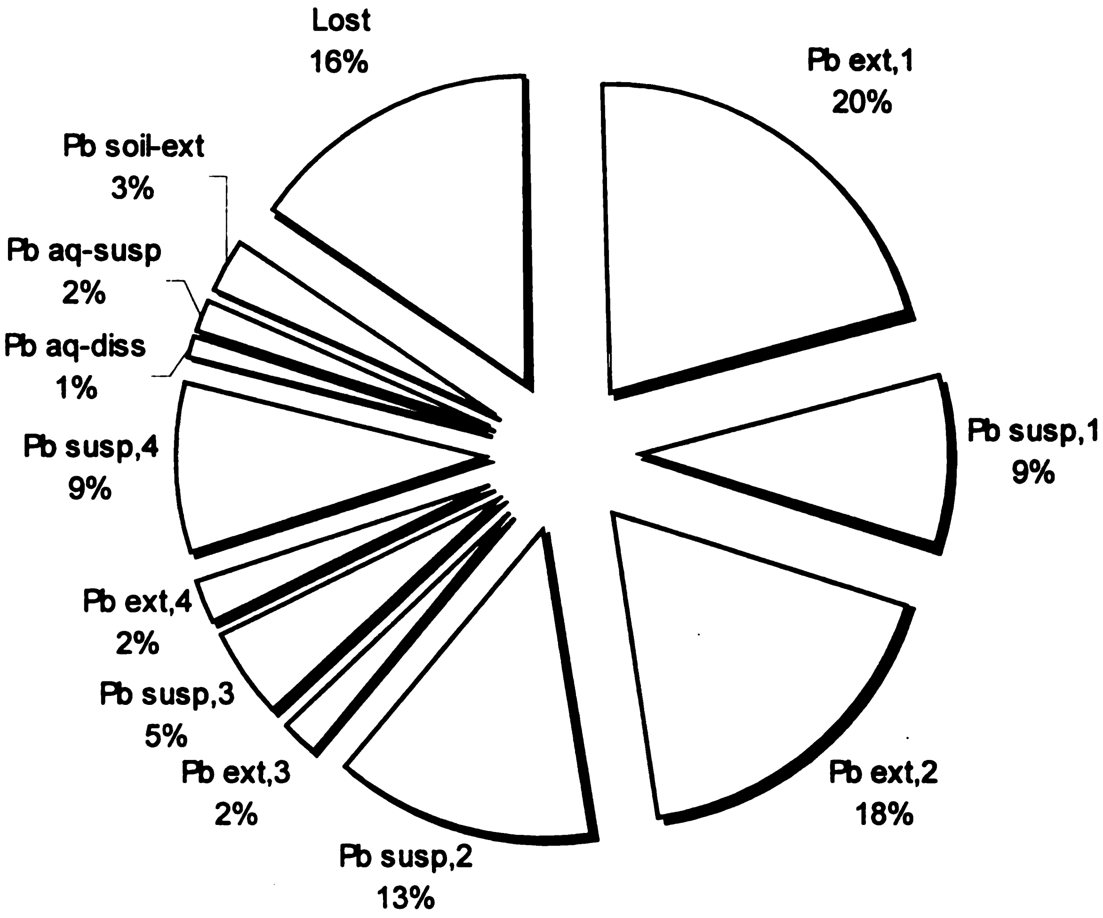


Figure 21. Mass Balance for Lead Extraction with DEHPA Extraction

5. Results of Extraction without Liquid-Ion Extractant

The use of four 60-minute sequential extractions reduced the lead concentration in soil from 79,983ppm to 17,883ppm. Thus, the lead concentration in soil was reduced by 77.64%.

The mass of lead removed by each phase of the extraction and the mass of lead remaining in the aqueous phase and extracted soil is summarized in Table 8. The mass of lead initially in the soil was 3,999.4 mg. In the aqueous phase, the mass of dissolved lead removed by extraction was 1,049.0 mg and the mass of lead removed as suspended solids was 795.5 mg. For dissolved lead, there was an increasing trend in the mass of lead removed during subsequent extractions. However, for lead removed as suspended solids, there was a decreasing trend in the mass of lead removed during subsequent extractions. Acid digestion determined that there was 810.8 mg of lead remaining in the extracted soil. A mass balance, which was able to account for 66.4 percent of the lead is shown in Figure 22.

The measured concentrations of solutions and the calculations used are shown in Appendix VII.

Table 8 – Lead Mass Summary for Extraction without DEHPA

Lead Source	Lead Mass (mg)
$Pb_{diss,1}$	92.3
$Pb_{diss,2}$	200.5
$Pb_{diss,3}$	360.2
$Pb_{diss,4}$	396.0
$Pb_{susp,1}$	345.9
$Pb_{susp,2}$	368.3
$Pb_{susp,3}$	51.3
$Pb_{susp,4}$	30.0
$Pb_{soil\text{-}ext}$	810.8
Total	2,655.3
$Pb_{soil\text{-}init}$	3,999.4
Percent Accounted	66.4%

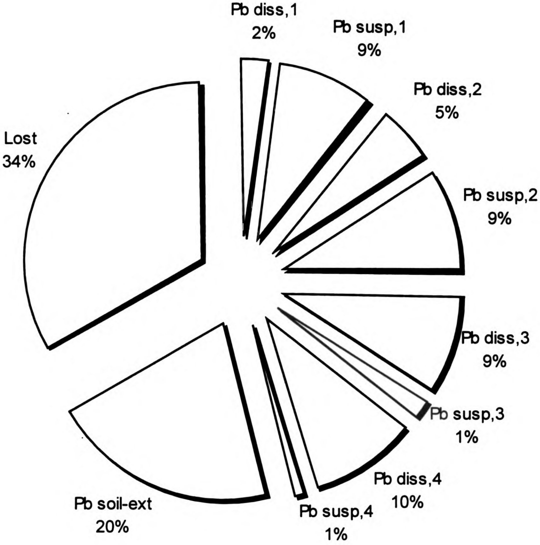


Figure 22. Mass Balance for Lead Extraction without DEHPA Extraction

D. Results of Stripping Lead from the Loaded Extractant

Mixing the loaded extractant and the hydrochloric acid solution created a white precipitate. Some of the white precipitate was in the aqueous phase and some of the white precipitate was entrained in the extractant. The precipitate was removed from the extractant phase when centrifuged.

The lead was effectively stripped from the DEHPA/hexane extractant at greater than 99 percent for all three phase ratios. The concentration of lead in the loaded extractant mixture was 16,080 mg/L. At a phase ratio of 5 mL extractant to 1 mL hydrochloric acid, the initial extractant concentration of 16,080 mg/L was reduced to 63 mg/L; which is a 99.61 percent stripping efficiency. For the phase ratio of 10:1, the final extractant concentration was 57 mg/L; which is a 99.65 percent stripping efficiency. For the phase ratio of 15:1, the final extractant concentration was 49 mg/L; which is a 99.70 percent stripping efficiency.

The concentration factors for lead from the extractant phase to the acidic phase were 4.98, 9.96, and 14.95 for the stripping ratios of 5:1, 10:1 and 15:1 consecutively.

The measured concentrations of the solutions and the calculations used are shown in Appendix VII.

V. CONCLUSIONS

Four groups of experiments were performed to determine if the use of a liquid ion extractant would enhance the removal of lead from contaminated soils. In the first group of experiments it was determined that hydrochloric acid was compatible with the liquid ion extractant, diluent and soil when emulsified.

In the second group of experiments, lead sulfate was dissolved by hydrochloric acid and the pH was adjusted to 3.75. An organic solution was prepared having a concentration of 0.2 Moles per liter DEHPA in hexane. The aqueous and organic phases were emulsified and the dissolved lead was extracted into the organic phase. The resulting extraction coefficient was 0.63. Using the calcium form of the extractant, Ca-DEHPA, it was determined that a drop in pH could be minimized, which increased the amount of lead extracted and the extraction coefficient. Using the calcium form of the extractant increased the extraction coefficient to 1.09.

In the third group of experiments, kinetics of the extraction process and the total amount of lead removed from the contaminated soil were evaluated. Contaminated soil was prepared by precipitating lead sulfate onto sandy soil. The contaminated soil was determined by mass balance to have a lead concentration of 79,983 ppm. The calcium form of the extractant, Ca-DEHPA, was used at a 1.0 molar concentration. The pH of the aqueous phase was controlled to 3.0. When a mixing speed was used in excess of the speed which ensured suspension of the soil phase in the emulsion, soil became entrapped in the organic phase.

By taking samples at timed intervals during three sequential extractions on a batch of soil, it was determined that the extraction had reached equilibrium within 30 minutes. The organic extractant was replaced with fresh extractant every 40 minutes. During subsequent extraction experiments, a duration of 60 minutes was used to ensure that equilibrium had been reached. Increasing the molar concentration of the extractant and lowering the pH increased the extraction coefficients. Extraction coefficients of 11.78, 17.50 and 45.42 were obtained during the evaluation of extraction kinetics.

Another series of four, 60-minute sequential extractions were performed to determine the total amount of lead that could be removed from the contaminated soil. Mixing was continuous during each of the 60-minute sequential extractions. The calcium form of the extractant, Ca-DEHPA, was used at a 1.0 Molar concentration. The pH of the aqueous phase was controlled to 3.0.

Based on the initial mass of lead in the contaminated soil, 42.44 percent was removed by chemical extraction, 36.38 percent was removed as suspended solids, 2.88 percent remained in the aqueous phase, 2.64 percent remained in the soil, and 15.66 percent was unaccounted. An analysis of the extracted soil determined that the final lead concentration was 2,494 ppm. The initial lead concentration in soil was 79,983 ppm. The extraction process with DEHPA reduced the lead concentration by 96.88%.

To determine the efficiency of the extraction process without the organic extractant, four sequential extractions were performed on a batch of soil using only an aqueous phase. Mixing was continuous during each of the 60-minute sequential extractions. The pH of the aqueous phase was controlled to 3.0.

Based on the initial mass of lead in the contaminated soil, 26.23 percent was removed as dissolved lead, 19.89 percent was removed as suspended solids, 20.28

percent remained in the soil, and 33.61 percent was unaccounted for. An analysis of the extracted soil determined that the final lead concentration was 17,883 ppm. The initial lead concentration in soil was 79,983 ppm. The extraction process without DEHPA reduced the lead concentration by 77.64%.

The sequential extraction process that used the organic extractant DEHPA to remove lead from the aqueous phase was seven times more effective at removing lead from the contaminated soil than the extraction that only used an aqueous solution pH adjusted to 3.0.

In the fourth group of experiments, the liquid-ion extractant was contacted with hydrochloric acid to determine if the extractant could be stripped for possible re-use in subsequent extractions. The initial concentration of lead in the extractant was 16,080 ppm and did not contain any suspended solids. Phase ratios of organic extractant to acid were 5:1, 10:1 and 15:1. The concentrations of the extractant after contact with hydrochloric acid and centrifuging were 63, 57 and 49 mg/L consecutively. Consequently, 99.7 % of the lead was stripped from the organic extractant DEHPA.

VI. ENGINEERING APPLICATIONS

An engineering application for the evaluated solvent extraction process, is the remediation of sandy soils contaminated with lead. The solvent extraction may prove to be useful on other types of soil with clay and/or organic content. A process flow diagram which shows the use of solvent extraction for removing lead from contaminated soil, solvent recycle and waste water treatment is shown in Figure 23.

In the process flow diagram of Figure 23, lead contaminated soil enters an extractor where acid, water and recycled solvent are added. The soil is mixed to provide increased surface area between the phases, which improves mass transfer. After the required time for extraction, the contents of the extractor are placed in a sepaerator where the phases are allowed to coalesce. After coalescing, each of the three phases are removed and processed. The cleaned soil is sent to a thermal desorption unit to removed residual hexane. After desorption the soil is available for re-use or disposal if the lead concentration meets the treatment criteria. If the cleaned soil has not met the treatment criteria, then the soil will need to be stabilized.

The water which leaves the separator is passed through counter current extractor to remove dissolved lead prior to re-use or discharge after passing through a waste water treatment process. Waste water treatment is anticipated due dissolved organics, from hexane and DEHPA, and suspended solids from the soil phase.

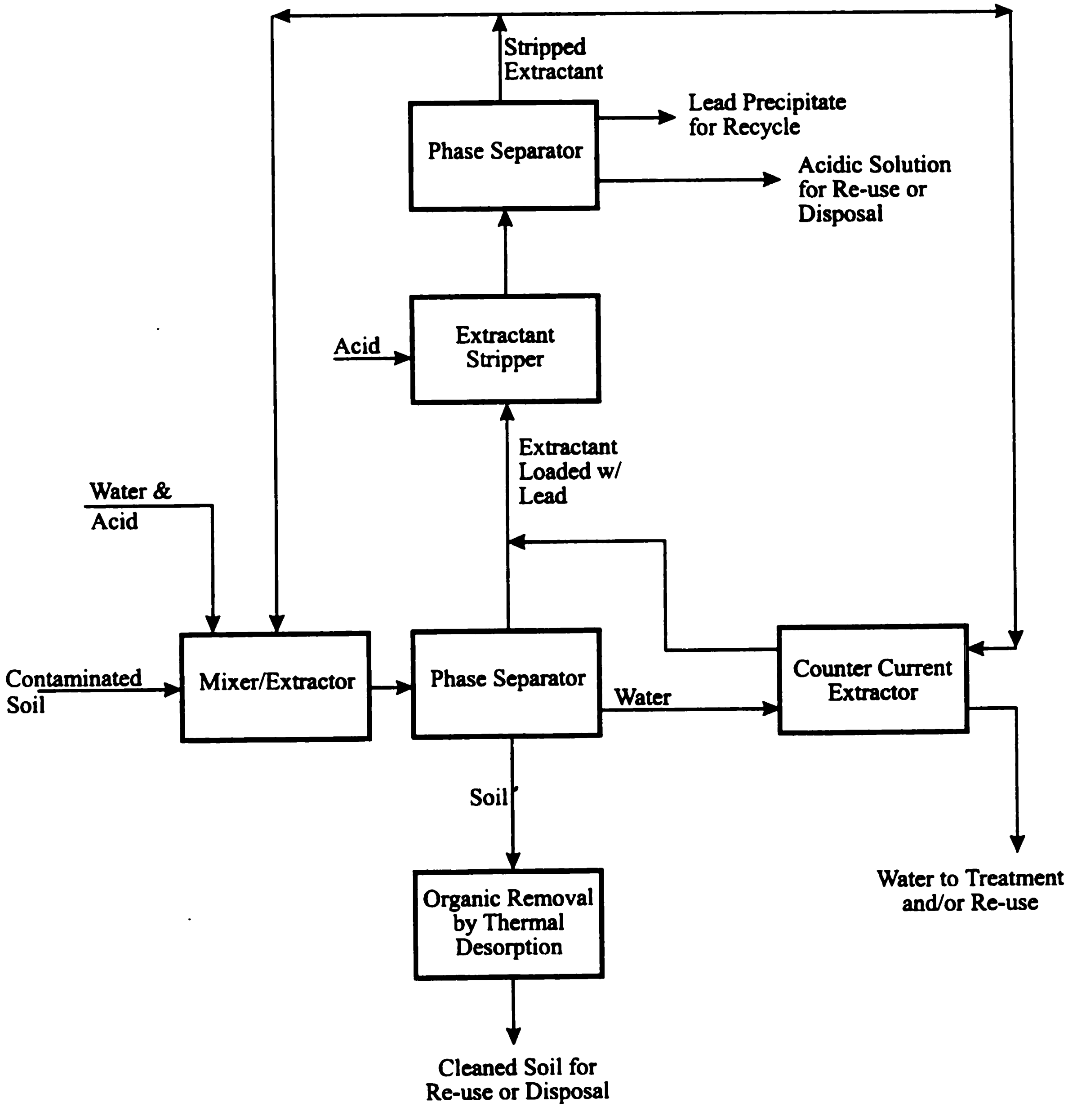


Figure 23. Process Flow Diagram for Lead Extraction from Soil

The extractant leaving the separator and counter current extractor, which is loaded with lead, is sent for stripping. During the stripping process, acid is added and the lead passes from the organic extractant phase into the aqueous acid phase. The stripped extractant and acid aqueous phases are then separated. Due to the presence of lead precipitate suspended in the organic phase, a centrifuge may be required. The clean solvent leaving the separator can then be re-used in the extractor vessel or as a pretreatment in the counter current extractor.

The lead precipitate and acidic solution leaving the separator can then be recycled by a smelter. There is a possibility that the acidic solution leaving the separator could be reintroduced into the stripper.

VII. RECOMMENDATIONS

Areas of research that could improve the extraction of lead from contaminated soils include; optimization of process conditions for the current extraction process, an evaluation of other organophosphorous extractants, possible separations of the organophosphate extractant from the organic phase, the use of acetone to increase lead solubility in the aqueous phase, the use of different salts to buffer pH, an evaluation of the mechanism responsible for lead particulate extraction, an evaluation of solvent extraction on different types of soils, and an evaluation of the extractant after recycle.

For the current extraction process, the pH of the aqueous phase can be varied to determine the value that removes the greatest amount of lead. The molar concentration of DEHPA can also be varied to determine the optimal concentration. Using a sealed mixer will minimize hexane losses that cause fluctuations in the molar concentration of DEHPA. Different buffer salts can also be evaluated to determine the effects on lead extraction. Mixing speed can also be varied to evaluate the effects of power input on the rate of extraction.

The use of organophosphorous compounds, which have lower dissociation constants, can be evaluated for use in the extraction process. An extractant with a lower dissociation constant may tolerate lower pH values that increase the solubility of lead.

Lead contaminated soils frequently contain other hazardous organics which would be simultaneously extracted into the organic phase. Once the organic extractant is loaded with these undesirable organics, the organic extractant can no longer be used. If a method of separating the extractant DEHPA from the organic phase could be developed, then the extraction process could be used to treat lead contaminated soils which also contain heavy organics such as PCB.

Lead has been shown to be sparingly soluble in 0.5 molar HCl, but increases considerably in the presence of acetone.[19] The use of acetone could be evaluated to determine if the extraction of lead will be increased without decreasing the chemical stability of DEHPA or decreasing the extraction coefficient due to a decrease in dimerization.

For each sequential extraction performed during the extraction kinetics experiment, there was a greater concentration of suspended lead solids in the organic extractant phase than in the aqueous phase. One cause for the increased lead particulate concentrations could be a chemical attraction between the lead and the extractant. The greater concentration in the organic phase could be due to a greater viscosity that would decrease the settling velocity of the lead particulate. Further studies could evaluate the amount of particulate removed due to decreased settling velocity in the organic phase, by performing the extraction procedure with a mixture of hexane and another inert compound which would have the same viscosity as the hexane and DEHPA mixture.

Experiments could be performed to determine the effectiveness of solvent extraction on different soil types. Soils with high organic content and/or high clay content may interact with the organic extractant which could cause entrapment and extractant losses.

Effectiveness of the extractant after several cycles of loading and stripping could be evaluated to determine the impacts on life-cycle costs for a large-scale operation.

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Appendix I

Analysis of Lead Extraction with DEHPA

Table 9 – Lead Extraction with DEHPA Calibration and Sample Analysis Absorbance Readings

Solution	Dilution Ratio	Concentration (ppm)	SD	RSD (%)
Blank		0.037	0.000	0.4
1 ppm		0.003	0.000	8.6
3 ppm		3.85	0.038	1.0
5 ppm		4.27	0.054	1.3
10 ppm		7.79	0.039	0.5
Sample 1	1000:1	5.53	0.072	1.3
Sample 2	100:1	>10		
Sample 3	100:1	>10		
Sample 4	1000:1	3.52	0.103	2.9
Sample 5	1000:1	2.50	0.040	1.6

Table 10 – Calculated Solution Concentrations for Lead Extraction with DEHPA

Sampled Media	Concentration (ppm)
Solution A	5,530
Solution B	3,520
Solution B - Extracted	2,500

Volume of Solution B 77.35 mL

Volume of Organic Phase 50.0 mL

Amount of lead extracted from the aqueous phase, Pb_{ext}:

$$Pb_{ext} = Vol_{aq} \times \left([Pb]_{aq,\,initial} - [Pb]_{aq,\,final}\right)$$

$$Pb_{ext} = 77.35\ mL \times \left(3{,}520\ mg/L - 2{,}500\ mg/L\right)$$

$$Pb_{ext} = 78.90\ mg$$

Concentration of lead in the organic phase, $[Pb]_{org}$:

$$[Pb]_{org} = \frac{Pb_{ext}}{Vol_{org}}$$

$$[Pb]_{org} = \frac{78.90\ mg}{0.050\ L}$$

$$[Pb]_{org} = 1{,}580\ mg/L$$

Extraction Coefficient, E:

$$E = \frac{[Pb]_{org}}{[Pb]_{aq}}$$

$$E = \frac{1{,}580\ mg/L}{2{,}500\ mg/L}$$

$$E = 0.63$$

Appendix II

Analysis of Lead Extraction with Ca-DEHPA

Table 11 – Lead Extraction with Ca-DEHPA Calibration and Sample Analysis Absorbance Readings

Solution	Dilution Ratio	Concentration (ppm)	SD	RSD (%)
Blank		0.000	0.001	99.9
1 ppm		0.004	0.000	3.5
3 ppm		3.01	0.083	2.7
5 ppm		4.99	0.052	1.0
10 ppm		9.81	0.106	1.1
Sample 1	1000:1	4.59	0.080	1.7
Sample 2	500:1	6.06	0.052	0.9
Sample 3	500:1	3.58	0.121	3.4

Table 12 – Calculated Solution Concentrations for Lead Extraction with Ca-DEHPA

Sampled Media	Concentration (ppm)
Solution A	4,590
Solution B	3,030
Solution B - Extracted	1,790

Volume of Solution B	78.8 mL
Volume of Organic Phase	50.0 mL

Amount of lead extracted from the aqueous phase, Pb_{ext}:

$$Pb_{ext} = Vol_{aq} \times \left([Pb]_{aq,\,initial} - [Pb]_{aq,\,final}\right)$$

$$Pb_{ext} = 78.80\ mL \times \left(3{,}030\ mg/L - 1{,}790\ mg/L\right)$$

$$Pb_{ext} = 97.71\ mg$$

Concentration of lead in the organic phase, $[Pb]_{org}$:

$$[Pb]_{org} = \frac{Pb_{ext}}{Vol_{org}}$$

$$[Pb]_{org} = \frac{97.71\ mg}{0.050\ L}$$

$$[Pb]_{org} = 1{,}954\ mg/L$$

Extraction Coefficient, E:

$$E = \frac{[Pb]_{org}}{[Pb]_{aq}}$$

$$E = \frac{1{,}954\ mg/L}{1{,}790\ mg/L}$$

$$E = 1.09$$

Appendix III

Analysis of Lead Concentration in Soil by Aqueous Phase Mass Balance

Table 13 – Calibration and Sample Analysis Absorbance Readings for Aqueous Phase Analysis to Determine Lead Soil Concentration

Solution	Dilution Ratio	Concentration (ppm)	SD	RSD (%)
Blank		-0.04	0.032	80.5
1 ppm		1.02	0.026	2.5
3 ppm		3.37	0.036	1.1
5 ppm		4.57	0.023	0.5
10 ppm		8.76	0.033	0.4
Sample 1	1000:1	8.87	0.059	0.7

Calculated Concentration of Solution F	8,870 ppm
Volume of Solution F	2,523 mL

Mass of lead in Solution F is, Pb_F:

$$Pb_F = Vol_F \times [Pb]_F$$

$$Pb_F = 2{,}523 mL \times 8{,}870 mg/L$$

$$Pb_F = 22.379 g$$

The mass of lead in the soil phase, Pb_{soil}:

$$Pb_{soil} = Pb_{init} - Pb_F$$

$$Pb_{soil} = 109.316 - 22.379 g$$

$$Pb_{soil} = 86.936 g$$

The concentration of lead in the soil phase, $[Pb]_{soil}$:

$$[Pb]_{soil} = \frac{Pb_{soil}}{1kg + Pb_{soil}}$$

$$[Pb]_{soil} = \frac{86.936 g}{1kg + 86.936 g}$$

$$[Pb]_{soil} = 79{,}983 ppm$$

Appendix IV

Analysis of Soil Concentration by Acid Digestion

Table 14 – Analysis of Soil Concentration by Acid Digestion Calibration and Sample Analysis Absorbance Readings

Solution	Dilution Ratio	Mean Absorbance	Concentration (ppm)	SD	RSD (%)
Blank		0.000	0.0	-	-
3 ppm		0.022	3.05	0.009	0.3
5 ppm		0.037	5.15	0.013	0.3
10 ppm		0.071	9.98	0.006	0.1
20 ppm		0.138	20.07	0.087	0.4
Sample 2	50:1	0.160	23.48	0.041	0.2
Sample 3	50:1	0.108	15.41	0.057	0.4
Sample 5	50:1	0.118	16.83	0.073	0.4
Sample 6	50:1	0.115	16.42	0.019	0.1
Sample 7	50:1	0.132	19.09	0.073	0.4
Sample 8	50:1	0.122	17.44	0.033	0.2
Sample 9	50:1	0.085	11.89	0.022	0.2
Sample 10	50:1	0.084	11.72	0.029	0.2

Table 15 - Calculated Soil Concentrations using Acid Digestion

Soil Sample	Digested Sample Concentration (ppm)	Dilution Ratio	Sample Volume (mL)	Mass of Initial Soil Sample (g)	Calculated Soil Concentration (ppm)
2	23.48	50:1	102	1.2795	96,519
3	15.41	50:1	102	1.2610	64,275
5	16.83	50:1	102	1.3131	67,416
6	16.42	50:1	102	1.3866	62,286
7	19.09	50:1	102	1.3793	72,798
8	17.44	50:1	102	1.3288	69,031
9	11.89	50:1	102	1.2528	49,918
10	11.72	50:1	102	1.2679	48,618

Example Calculation

The ratio of water densities is:

$$\rho_{95,20} = \frac{\rho_{95}}{\rho_{20}}$$

$$\rho_{95,20} = \frac{961.902\text{ kg/m3}}{998.204\text{ kg/m3}}$$

$$\rho_{95,20} = 0.9696$$

The mass of lead in digested Sample 2 is:

$$Pb_{dgst,2} = \frac{[S]_2 \times DR_2 \times Vol_2}{\rho_{95,20}}$$

$$Pb_{dgst,2} = \frac{23.48ppm \times 50:1 \times 102mL}{0.9696}$$

$$Pb_{dgst,2} = 123.50mg$$

The lead concentration in soil Sample 2 is:

$$[Pb]_{soil,2} = \frac{Pb_{dgst,2}}{S_2}$$

$$[Pb]_{soil,2} = \frac{123.50mgPb}{1.2795gSoil}$$

$$[Pb]_{soil,2} = 96{,}519ppm$$

Appendix V

Analysis of Kinetic Extraction Study

Table 16 – Kinetic Extraction Study Aqueous Phase Calibration and Sample Analysis Absorbance Readings

Solution	Mean Absorbance	Concentration (ppm)	SD	RSD (%)
Blank	-0.061	0.00	0.000	0.3
3 ppm	0.018	3.00	0.000	1.6
5 ppm	0.032	5.21	0.028	0.5
10 ppm	0.062	8.86	0.022	0.2
20 ppm	0.121	19.64	0.054	0.3
1-A-5	0.012	1.97	0.008	0.4
1-A-10	0.013	2.11	0.010	0.5
1-A-20	0.080	13.10	0.026	0.2
1-A-30	0.096	15.69	0.039	0.2
1-A-40	0.098	16.10	0.010	0.1
2-A-10	0.045	7.19	0.017	0.2
2-A-20	0.045	7.26	0.012	0.2
2-A-30	0.049	7.91	0.021	0.3
2-A-40	0.051	8.16	0.026	0.3
3-A-10	0.007	1.11	0.032	2.8
3-A-20	0.007	1.18	0.011	0.9

Table 17 - Calculated Concentrations of Aqueous Phase during Kinetic Extraction Study

Sample	Dilution Ratio	Concentration (ppm)
1-A-5	100:1	197
1-A-10	100:1	211
1-A-20	100:1	1,310
1-A-30	100:1	1,569
1-A-40	100:1	1,610
2-A-10	100:1	719
2-A-20	100:1	726
2-A-30	100:1	791
2-A-40	100:1	816
3-A-10	100:1	111
3-A-20	100:1	118

Table 18 – Kinetic Extraction Study Organic Phase Calibration and Sample Analysis Absorbance Readings

Solution	Mean Absorbance	Concentration (ppm)	SD	RSD (%)
Blank	0.025	0.03	0.000	1.5
4 ppm	0.059	4.00	0.000	0.4
8 ppm	0.114	7.35	0.030	0.4
12 ppm	0.164	11.95	0.048	0.4
20 ppm	0.239	18.86	0.045	0.2
1-O-5	0.052	3.52	0.032	0.9
1-O-10	0.080	5.48	0.023	0.4
1-O-20	0.116	8.17	0.025	0.3
1-O-30	0.113	9.45	0.019	0.2
1-O-40	0.113	9.48	0.009	0.1
2-O-10	0.149	10.69	0.018	0.2
2-O-20	0.106	7.34	0.023	0.3
2-O-30	0.106	7.39	0.013	0.2
2-O-40	0.103	7.14	0.018	0.3
3-O-10	0.019	1.23	0.011	0.9
3-O-20	0.041	2.68	0.009	0.3

Table 19 - Calculated Concentrations of Organic Phase during Kinetic Extraction Study

Sample	Dilution Ratio	Concentration (ppm)
1-O-5	500:1	1,760
1-O-10	1,000:1	5,480
1-O-20	2,000:1	16,340
1-O-30	2,000:1	18,900
1-O-40	2,000:1	18,960
2-O-10	1,000:1	10,690
2-O-20	2,000:1	14,680
2-O-30	2,000:1	14,720
2-O-40	2,000:1	14,280
3-O-10	1,000:1	1,230
3-O-20	2,000:1	5,360

Table 20 - Calculated Extraction Coefficients for Kinetic Extraction Study

Extraction Number	Organic Concentration (ppm)	Aqueous Concentration (ppm)	Extraction Coefficient
1	18,960	1,610	11.78
2	14,280	816	17.50
3	5,360	118	45.42

Appendix VI

Analysis of Sequential Extractions

Table 21 – Sequential Extraction Study Aqueous Phase Calibration and Sample Analysis Absorbance Readings

Solution	Mean Absorbance	Concentration (ppm)	SD	RSD (%)
Blank	-0.001	-0.001	0.000	28.8
3 ppm	0.019	3.00	0.000	1.0
5 ppm	0.031	4.87	0.015	0.3
10 ppm	0.065	10.06	0.068	0.6
20 ppm	0.130	19.85	0.047	0.3
AC-100	0.083	12.93	0.061	0.5
AP-50	0.023	3.74	0.033	0.9
OP1-100	0.045	7.44	0.062	0.8
OP2-100	0.058	9.70	0.029	0.3
OP3-100	0.019	3.05	0.020	0.7
OP4-100	0.040	6.67	0.031	0.5
E1-10	0.016	2.56	0.010	0.4

Table 22 – Sequential Extraction Study Organic Phase Calibration and Sample Analysis Absorbance Readings

Solution	Mean Absorbance	Concentration (ppm)	SD	RSD (%)
Blank	0.000	0.00	0.000	0.0
4 ppm	0.055	4.00	0.000	0.5
8 ppm	0.107	7.68	0.024	0.3
12 ppm	0.153	11.98	0.050	0.4
20 ppm	0.224	19.99	0.098	0.5
OCD1	0.100	7.53	0.028	0.4
OCD2	0.161	12.74	0.078	0.6
OCD3	0.010	0.68	0.006	0.9
OCD4	0.011	0.79	0.005	0.6

Table 23 – Calculated Mass of Lead Removed in Organic Phase by Chemical Extraction

Extraction	Sample	Dilution Ratio	Concentration (ppm)	Extraction Vol (mL)	Lead Mass (mg)
1	OC-1	2,000:1	15,060	50	828.3
2	OC-2	1,000:1	12,740	55	700.7
3	OC-3	2,000:1	1,360	60	81.6
4	OC-4	2,000:1	1,580	55	86.9
Total					1,697.5

Example Calculation - Lead concentration in Sample OC-1was calculated:

$$[Pb]_{OC-1} = [Pb]_{OCD1} \times DR_1$$

$$[Pb]_{OC-1} = 7.53 ppm \times 2{,}000$$

$$[Pb]_{OC-1} = 15{,}060 ppm$$

The mass of lead chemically extracted into the organic phase was:

$$Pb_{ext,1} = Vol_{ext,1} \times [Pb]_{OC-1}$$

$$Pb_{ext,1} = 50 mL \times 15{,}060 ppm$$

$$Pb_{ext,1} = 828.3 mg$$

Table 24 - Calculated Mass of Lead Removed in Organic Phase as Suspended Solids

Extraction	Sample	Digested (ppm)	Dilution Ratio	Digested Vol (L)	Extraction Vol (mL)	Centrifuge Vol (mL)	Lead (mg)
1	OP1	7.44	100:1	0.10	50	10	372.0
2	OP2	9.70	100:1	0.10	55	10	533.5
3	OP3	3.05	100:1	0.10	60	10	183.0
4	OP4	6.67	100:1	0.10	55	10	366.9
Total							1,455.4

Example Calculation - The lead mass in digested Sample OP1 was:

$$Pb_{dgst,OP1} = [Pb]_{OP1-100} \times DR_{OP1} \times Vol_{dgst,OP1}$$

$$Pb_{dgst,OP1} = 7.44ppm \times 100 \times 0.10L$$

$$Pb_{dgst,OP1} = 74.4mg$$

The mass of lead removed as suspended solids in extraction 1 was:

$$Pb_{susp,1} = Pb_{dgst,OP1} \frac{Vol_{ext,1}}{Vol_{cent,1}}$$

$$Pb_{susp,1} = 74.4mg \frac{50mL}{10mL}$$

$$Pb_{susp,1} = 372mg$$

Calculation – Dissolved lead mass remaining in aqueous phase

$$Pb_{aq-diss} = [Pb]_{AC-100} \times DR_x \times Vol_{aq}$$

$$Pb_{aq-diss} = 12.93 ppm \times 100 \times 0.0364 L$$

$$Pb_{aq-diss} = 47.1 mg$$

Calculation - Lead mass in digested sample of aqueous phase suspended solids

$$Pb_{aq-dgst} = [Pb]_{AP-50} \times DR_{AP} \times Vol_{dgst}$$

$$Pb_{aq-dgst} = 3.74 ppm \times 50 \times 0.10 L$$

$$Pb_{aq-dgst} = 18.7 mg$$

Calculation - Lead mass in aqueous phase as suspended solids

$$Pb_{aq-susp} = Pb_{aq-dgst} \frac{Vol_{aq-tot}}{Vol_{aq-cent}}$$

$$Pb_{aq-susp} = 18.7 mg \frac{36.4 mL}{10 mL}$$

$$Pb_{aq-susp} = 68.1 mg$$

Calculation – Lead concentration in extracted soil

$$[Pb]_{soil-ext} = \frac{[Pb]_{dgst-soil} \times DR \times Vol_{dgst}}{S_{dgst}}$$

$$[Pb]_{soil-ext} = \frac{2.56 ppm \times 10 \times 0.10 L}{1.0264 g}$$

$$[Pb]_{soil-ext} = 2{,}494 ppm$$

Calculation – Lead mass remaining in extracted soil

$$Pb_{soil-ext} = [Pb]_{soil-ext} \times S_{final}$$

$$Pb_{soil-ext} = 2{,}494 ppm \times 42.358 g$$

$$Pb_{soil-ext} = 105.64 mg$$

Calculation – Extraction process removal efficiency

$$R_{eff} = \frac{([Pb]_{soil-init} - [Pb]_{soil-ext})}{Pb_{soil-init}}$$

$$R_{eff} = \frac{79{,}983 ppm - 2{,}494 ppm}{79{,}983 ppm}$$

$$R_{eff} = 96.88\%$$

Calculation – Initial lead mass in soil

$$Pb_{soil-init} = [Pb]_{soil-init} \times S_{init}$$

$$Pb_{soil-init} = 79{,}983 ppm \times 50.0125 g$$

$$Pb_{soil-init} = 4{,}000.15 mg$$

Table 25 – Calculated Mass balance on Lead for Sequential Extraction

Lead Source	Lead Mass (mg)	Total Percent (%)
$Pb_{ext,1}$	828.3	20.71
$Pb_{ext,2}$	700.7	17.52
$Pb_{ext,3}$	81.6	2.04
$Pb_{ext,4}$	86.9	2.17
$Pb_{susp,1}$	372.0	9.30
$Pb_{susp,2}$	533.5	13.34
$Pb_{susp,3}$	183.0	4.57
$Pb_{susp,4}$	366.9	9.17
$Pb_{aq-diss}$	47.1	1.18
$Pb_{aq-susp}$	68.1	1.70
$Pb_{soil-ext}$	105.6	2.64
Total	3,373.7	84.34
$Pb_{soil-init}$	4,000.2	

Appendix VII

Analysis of Extraction without Liquid-Ion Extractant

Table 26 – Extraction without Liquid Ion Extractant Calibration and Sample Analysis Absorbance Readings

Solution	Mean Absorbance	Concentration (ppm)	SD	RSD (%)
Blank	0.001	0.001	0.000	26.5
3 ppm	0.021	3.02	0.000	1.0
5 ppm	0.034	4.90	0.029	0.6
10 ppm	0.068	10.44	0.015	0.1
20 ppm	0.133	20.67	0.078	0.4
WC1-100	0.113	16.99	0.067	0.4
WC2-1000	0.027	3.92	0.014	0.4
WC3-1000	0.050	7.45	0.015	0.2
WC4-1000	0.055	8.25	0.017	0.2
WP1-50	0.085	12.72	0.043	0.3
WP2-50	0.096	14.40	0.038	0.3
WP3-50	0.015	2.12	0.019	0.9
WP4-50	0.042	6.14	0.013	0.2
S2-50	0.029	4.27	0.012	0.3
S4-50	0.027	3.98	0.017	0.4
S5-50	0.030	4.45	0.015	0.3

Table 27 – Calculated Mass of Dissolved Lead Removed in Aqueous Phase

Extraction	Sample	Dilution Ratio	Concentration (ppm)	Extraction Mass (g)	Lead Mass (mg)
1	WC1-100	100:1	1,700	54.32	92.3
2	WC1-1000	1,000:1	3,920	51.15	200.5
3	WC1-1000	1,000:1	7,450	48.35	360.2
4	WC1-1000	1,000:1	8,250	48.80	396.0
Total					1,049.0

Table 28 - Calculated Mass of Lead Removed as Suspended Solids

Extraction	Sample	Digested (ppm)	Dilution Ratio	Digested Vol (L)	Extraction Mass (mL)	Centrifuge Vol (mL)	Lead (mg)
1	WP1-50	12.72	50:1	0.10	54.32	10	345.9
2	WP2-50	14.40	50:1	0.10	51.15	10	368.3
3	WP3-50	2.12	50:1	0.10	48.35	10	51.3
4	WP4-10	6.14	10:1	0.10	48.80	10	30.0
Total							795.5

Table 29 - Calculated Concentration of Lead in Extracted Soil

Soil Sample	Digested Sample Concentration (ppm)	Dilution Ratio	Sample Volume (mL)	Mass of Initial Soil Sample (g)	Calculated Soil Concentration (ppm)
S2	4.27	50:1	100	1.1886	17,962
S4	3.98	50:1	100	1.1204	17,762
S5	4.45	50:1	100	1.2412	17,926

Average = 17,883 ppm s = 106.6

Example Calculation – Lead concentration in extracted soil Sample S2

$$[Pb]_{soil-ext} = \frac{[Pb]_{dgst-soil} \times DR \times Vol_{dgst}}{S_{dgst}}$$

$$[Pb]_{soil-ext} = \frac{4.27 ppm \times 50 \times 0.10 L}{1.1886 g}$$

$$[Pb]_{soil-ext} = 17{,}962 ppm$$

Calculation – Lead mass remaining in extracted soil

$$Pb_{soil-ext} = [Pb]_{soil-ext} \times S_{final}$$

$$Pb_{soil-ext} = 17{,}883 ppm \times 45.3409 g$$

$$Pb_{soil-ext} = 810.83mg$$

Calculation – Extraction process removal efficiency

$$R_{eff} = \frac{([Pb]_{soil-init} - [Pb]_{soil-ext})}{Pb_{soil-init}}$$

$$R_{eff} = \frac{79{,}983ppm - 17{,}883ppm}{79{,}983ppm}$$

$$R_{eff} = 77.64\%$$

Calculation – Initial lead mass in soil

$$Pb_{soil-init} = [Pb]_{soil-init} \times S_{init}$$

$$Pb_{soil-init} = 79{,}983ppm \times 50.0032g$$

$$Pb_{soil-init} = 3{,}999.4mg$$

Table 30 - Calculated Mass balance on Lead for Sequential Extraction without Liquid Ion Extractant

Lead Source	Lead Mass (mg)	Total Percent (%)
$Pb_{diss,1}$	92.3	2.31
$Pb_{diss,2}$	200.5	5.01
$Pb_{diss,3}$	360.2	9.01
$Pb_{diss,4}$	396.0	9.90
$Pb_{susp,1}$	345.9	8.65
$Pb_{susp,2}$	368.3	9.21
$Pb_{susp,3}$	51.3	1.28
$Pb_{susp,4}$	30.0	0.75
$Pb_{soil\text{-}ext}$	810.8	20.27
Total	2,655.3	66.39
$Pb_{soil\text{-}init}$	3,999.4	

Appendix VIII

Analysis of Stripping Lead from Extractant

Table 31 – Stripping Lead from Extractant Calibration and Sample Analysis Absorbance Readings

Solution	Mean Absorbance	Concentration (ppm)	SD	RSD (%)
Blank	0.000	0.00	0.000	0.0
4 ppm	0.055	4.00	0.000	0.5
8 ppm	0.107	7.68	0.024	0.3
12 ppm	0.153	11.98	0.050	0.4
20 ppm	0.224	19.99	0.098	0.5
SD1	0.279	32.16	0.356	1.1
SD2	0.009	0.63	0.010	1.6
SD3	0.008	0.57	0.005	0.8
SD4	0.007	0.49	0.006	1.2

Table 32 - Calculated Concentrations and Percent of Lead Stripped from the Organic Extractant

Extractant Solution	Dilution Ratio	Concentration (ppm)	Percent Stripped	Concentration Factor
S1	500:1	16,080		
S2	100:1	63	99.61	4.98
S3	100:1	57	99.65	9.96
S4	100:1	49	99.70	14.95