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Extraction of lead using EDTA: factors affecting extraction, effects of amorphous iron and recycling of used EDTA

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Extraction of lead using EDTA:
Factors affecting extraction, effects of amorphous iron and recycling of used EDTA

by

Chulsung Kim

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirement for the degree of

DOCTOR OF PHILOSOPHY

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This is to certify that the doctoral dissertation of

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has met the dissertation requirements of Iowa State University

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ABSTRACT

The effects of major cations present in soils, soil:extractant ratio, and EDTA:lead stoichiometric ratio on the extraction efficiency of lead using EDTA were studied for three different Superfund soils, one rifle range soil, and one artificially lead-contaminated soil. Extraction of lead from the lead-contaminated soils was not affected by a soil:extractant ratio as low as 1:3 but instead was dependent on the quantity of EDTA present. Results of the experiments showed that the extraction efficiency for each soil was different, but if sufficiently large amount of EDTA was applied (EDTA:lead stoichiometric ratio greater than 10), all the lead may be extracted except for a Superfund soil from a lead mining area. The differences in extraction efficiencies may be due to the major cations present in soils which may compete with lead for active sites on EDTA. Among the cations present, ferric ions probably competed most strongly with lead for EDTA ligand sites for pH values less than 6. In addition, Cu and Zn may have a potential to compete with Pb for EDTA ligand sites. At high pH values, Ca may have an effect on lead extraction. Experimental results showed that addition of EDTA to soil solution resulted in a very large increase in metals solubility. The total molar amount of major cations extracted was as much as 20 times more than the added molar amount of EDTA. For some of the soils tested, the extraction efficiency of lead may be affected by being occluded in the Fe and Mn oxides present in the soil. While major cations present in the soil may be one of the factors affecting lead extraction efficiency, the type of lead species present may also play a role.

Bench-scale experiments were conducted with three different artificially prepared lead-contaminated soils with and without addition of amorphous iron to investigate the amorphous iron effects on the lead extraction. The lead species in each of the artificially prepared soil were lead sulfate, lead carbonate and lead phosphate. The experimental results indicated that amorphous iron effects on lead extraction was dependent on the equilibrium pH and lead species present. Amorphous iron was found to compete with lead for EDTA at pH values below 6.0. For different lead species present, amorphous iron was found to affect lead sulfate-contaminated soil the most while lead carbonate-contaminated soil was the least affected. At high pH values (higher than neutral pH), amorphous iron effect was not significant.

A method to recycle used Pb-EDTA was proposed. The proposed method consists of substituting the Pb ions with Fe ions. This was then followed by precipitation of the uncomplexed Pb ions with phosphate or sulfate ions. Fe ions were then precipitated out at high pH using sodium hydroxide. According to the experimental results, lead ions can be separated from EDTA by substitution with added Fe (III) ions and precipitated with phosphate or sulfate ions. Fe-precipitated recycled EDTA solution was found to have higher lead extraction efficiencies than that of untreated Fe-EDTA solution. In addition, experimental results showed that recycled used EDTA with phosphate precipitation was slightly more superior than recycled used EDTA with sulfate precipitation. Both recycled EDTA solutions (phosphate and sulfate precipitation) showed similar or slightly lower extractive abilities when compared to fresh EDTA solution. Experimental results indicated the recycled used EDTA solution can be recycled several times without losing its extractive power.

GENERAL INTRODUCTION

Soil is a complex heterogeneous medium comprising of mineral and organic solids, aqueous and gaseous components. The minerals present are usually weathered rock fragments and secondary minerals precipitated or recrystallized as solids from soluble substances such as clay, hydrous oxides of iron, aluminum and manganese and sometimes carbonates (usually $CaCO_3$). The organic matter comprises of microorganisms, dead plant materials and colloidal humus formed by the action of microorganisms on plant litter. These solid components are usually clustered together in the form of aggregates, thus creating pores of various sizes filled with either water or air.

Some of the solid components have the ability to adsorb metal ions. However, the adsorption phenomenon differs between materials and is strongly influenced by the pH, redox conditions and the concentration of the ions present in the aqueous soil solution. Besides adsorption, precipitation, co-precipitation, organic and inorganic complex bonding may also retain the heavy metals in solid phase. However, it is difficult to be precise about which particular process is responsible for the retention of metals in any particular soil. Heavy metals may be retained in soil for a long time through the mechanisms mentioned above and may continue to threaten human health and the environment.

Lead is one of the heavy metals which has been used by humans for over several thousand years. With this long history of utilization of lead, our valuable resources such as land and ground water have been contaminated with lead as a result of human activities such as mining, smelting, automobile battery production and vehicle emission.

Once soil has been contaminated with lead, lead is retained for a long time due to its low solubility and high affinity to be sorbed in soil matrix unless the external aqueous environment is changed. As long as lead stays in soil or water, it could be harmful to human beings and living resources through several exposure pathways.

Several treatment methods have been developed to remediate lead-contaminated soil. One of the treatment methods is the extraction technology in which chelating agents are used to solubilize lead by forming soluble lead coordination compounds. EDTA is one of the major polydentate ligands used in soil extraction technology and has been shown to be effective in cleaning up lead-contaminated soils. However, up to date, most research have emphasized the extractive power of EDTA from lead-contaminated soils rather than the effects of soil and solution properties. In addition, most research to date used high concentrations of EDTA for extraction purposes and not much work has been done to optimize EDTA usage. Another issue which has not been fully investigated is that soil extraction generates a large volume of wastewater and there is no feasible method available to reduce and recycle the wastewater generated.

Research on the effects of major cations and lead species present in the soil on lead extraction efficiency will be investigated. A recycling method for used EDTA solution is proposed. The extractive ability of recycled used EDTA solution over several cycles on various lead-contaminated soils will be investigated.

In order to address the deficiency in the study of lead extraction from lead-contaminated soils, this research has the following objectives:

I. to investigate the effects of major cations present in soils such as Fe, Al, Ca, Zn, Cu, Mg, Mn, soil:extractant ratio, and EDTA:lead stoichiometric ratio on the extraction efficiency of lead using EDTA.

II. to study the effects of amorphous ferric oxides on the extraction of lead from lead-contaminated soils with EDTA.

III. to develop a feasible method for recycling used EDTA wastewater for further treatment of the lead-contaminated soils.

To achieve the objectives, the research will be composed of three parts. The first part addresses the effects of major cations and optional EDTA usage for lead extraction from lead-contaminated soils with EDTA. The second part addresses the effects of amorphous iron oxides on lead extraction from lead-contaminated soils with EDTA. Finally, the last part addresses a method for the recycling of used EDTA wastewater. The presentation of the dissertation will also include a brief introduction on sources of lead pollution and the fate of lead in soil.

LITERATURE REVIEW

Lead Sources and Species in Soil

Since 1700, global yearly production of lead has grown from 9.25×10^7 kg to more than 3.048×10^9 kg (Rhue et al., 1992). In 1978, more than 4 million tonnes of refined lead, mined ores and recycled lead were produced of which recycled lead accounted for 14 % of the total required lead (Harrison and Laxen, 1981). United States (US) accounted for 18 % of the total global annual production of refined lead. The production of lead-acid batteries accounted for almost 60 % of the total lead consumption in 1981. The other major usage of lead is for the production of organic lead compounds for the automobile industry. About 10 % of the total annual refined lead are used for the production of organic lead compounds such as tetraalkyl lead (TAL) compounds (Harrison and Laxen, 1981). These TALs have been used as antiknock agents and have provided a convenient and inexpensive means to maintain the octane rating of gasoline. Due to legislative restriction, the consumption of leaded gasoline is declining in industrialized countries. Although only lead-free gasoline is used in the US, leaded gasoline is still being used in many other countries. Extensive use of lead antiknock additives in gasoline has made lead the most widely distributed toxic heavy metal in the urban environment. Approximately 70 to 80 % of the TALs in the gasoline may be discharged into the atmosphere (Davis and Cornwell, 1991).

Airborne lead from automobiles and lead smelting refiners may precipitate out through gravitational settling and scavenging by raindrops. These mechanisms have been found to increase the lead concentration of surface soil. The concentrations of lead in uncontaminated soil range from 10 to 200 ppm (Davies, 1988). Tetramethyl lead and tetraethyl lead in discharged antiknock additives or partially combusted leaded gasoline may be adsorbed from aqueous solution onto soil. Because trialkyl lead (R_3Pb^+) is relatively more stable than dialkyl lead (R_2Pb^{2+}) in the environment, the adsorbed species are rapidly degraded to trialkyl lead (R_3Pb^+) and the decomposition is faster in the presence of light than in darkness (Jarvie et al., 1981). The Me_2Pb^{2+} and Et_2Pb^{2+} forms, however, are preferably adsorbed onto amorphous Fe (III) hydrous oxide (Rhue et al, 1992). Because TALs are generally used as additives for automobile gasoline, it is generally true that soils adjacent to roads with heavy traffic would have relatively higher lead contents.

An important source of lead contamination in soil is through industrial activities such as mining, smelting, reclamation of lead from batteries, automobile applications and sewage sludge disposal. Many of the contaminated sites and Superfund sites are a result of indiscriminate disposal of wastes from these industrial activities.

As mentioned earlier, lead-acid battery manufacturing is a major consumption of lead. Reclamation of lead from used batteries involved the breaking of the used batteries to recover the lead. The recovered lead is usually melted on site. Breaking of the batteries usually results in lead of various physical forms such as dust, pastes, chips and chunks and chemical forms such as elemental, oxides, carbonates, hydroxide, sulfate of lead to be dispersed resulting in gross contamination of the lead-acid reclamation site. For example, a typical automobile battery contains about 9 kg of lead and approximately 2 liters of 15 - 20% sulfuric acid. Because of the sulfuric acid in the battery, the predominant species of lead at battery reclamation sites are lead sulfate ($PbSO_4$), lead oxide (PbO), lead dioxide (PbO_2) and lead element (Pb). In carbonates soils, however, lead carbonate ($PbCO_3$), hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) or lead hillite ($Pb_4SO_4(CO_3)_2(OH)_2$) may be present as the major lead species in lead-contaminated soil (Royer et al., 1992).

Lead mining is another major source of lead contamination. Galena (PbS) and its oxidation products anglesite ($PbSO_4$) and lead jarosite ($PbFe_6(SO_4)_4(OH)_{12}$) are the dominant minerals in sulfide/sulfate assemblage while manganese lead oxides, lead phosphate and lead oxides are the major compounds in oxide/phosphate assemblage (Davis et al., 1993). Due to the high solubility of lead oxides, lead oxides are not stable under the general environment. For this reason, lead oxides may be changed to less soluble lead phosphate. Of the minerals found at lead mines, PbS and $PbSO_4$ are the dominant products in mining areas (Davis et al., 1993). Lead minerals found at lead smelting area are similar to that of lead mining area. Lead sulfate ($PbSO_4$) and lead sulfide (PbS) are the major products found at these sites while lead oxide is present at a lower concentration (Clevenger et al., 1991).

A human activity which has contributed towards lead contamination of the environment is the use of lead in shotgun pellets and in bullets. For example, for the year 1984, 800 tons of lead was used for shotgun lead pellets in Denmark while 250 tons of lead was used for gasoline additives (Jorgensen and Willems, 1987). In Finland itself, 1,600 tons of ammunition were disposed of annually in the environment in areas such as hunting forests and rifle range areas (Manninen and Tanskanen, 1993). Jorgensen and Willems (1987) found that 5 - 17 % of the crust material (metallic lead) of lead pellets in shooting-range soil were transformed within 6 - 13 years into different forms of lead compounds depending on the environmental conditions. Some of the transformed products on the crust material of pellets include hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), cerussite ($PbCO_3$), and the less common anglesite ($PbSO_4$). Most of the contamination at the shooting range were found in the top soil layer. The lead-contaminated soils have the potential to contaminate ground water through the leaching of lead although the mobility of lead is relatively low compared to other major heavy metals in soils. In a study done by Manninen and Tanskanen (1993), it was found that lead pellets can be dissolved in water to a concentration of 15 ppm within one month and the dissolved lead may be strongly fixed by the humus layer. They also indicated that soil fauna may be the primary transmitter of lead into food chain other than plants.

Another source of lead contamination is the land application of sewage sludge. According to a study conducted by Tien and Huang (1991), lead can be adsorbed very strongly onto sludge solid surface. Their results showed that the order of adsorption of metals onto sludge surface is as follows: Hg > Pb > Cu > Co > Cd > Zn > Ni. Sludge has an average lead concentration of 800 ppm and long term land application of sludge containing lead may result in the lead contamination of the land (Harrison and Laxen, 1981).

Toxicity of Lead to Human Being

Widespread use of lead in our environment has exposed humans to varying concentrations of lead via a number of sources. In soils and sediments, lead and its compounds are very stable due to their low solubility. Because of its persistency, lead and its compounds may continue to threaten humans by becoming accessible to the food chain.

Lead can be taken up by human beings through inhalation and ingestion. Because small lead particles or dust contaminated with lead may be present in the atmosphere, these may be readily inhaled by humans. $PbSO_4$ and $PbO \cdot PbSO_4$ are the major lead compounds in atmosphere in the vicinity of lead smelters (Harrison and Laxen, 1981) with PbBrCl and α-$2PbBrCl \cdot NH_4Cl$ being the major compounds in traffic areas where leaded-gasoline are used. A single cigarette contains about 4 to 12 μg of lead and may result in an increase of lead intake into human body (Harrison and Laxen, 1981). Food and drinking water are also major sources of lead intake to human body. Sources of lead from drinking water are old lead pipes and lead solder used in water distribution system. Consumption of vegetables and fruits contaminated with lead is one of the pathways of lead exposure, although, it has been known that only small amounts of lead in soil can be taken up by plants (Davies, 1990). Lead from the consumption of meat is an unlikely source since lead in animals is generally stored in their bones. Exposure of ingested lead results in rapid absorption into the red blood cells followed by final storage in bones. Some of the lead stored in the bones may reenter the bloodstream.

Infant and young children absorb ingested lead more readily than older children and young adults. The concentration of lead in the blood stream (PbB) is an important parameter because PbB is associated with hemoglobin (oxygen carrier). It has been shown that the amount of lead in the bloodstream may be correlated to the concentration of lead in soil (Marcus and Cohen, 1988). Generally, PbB is related to anemia, kidney damage and impaired reproductive function. PbB also interferes with vitamin D metabolism and may result in impaired cognitive performance, delayed neurological and physical development and elevations in blood pressure. US EPA has classified lead as a probable human carcinogen. Among these damages to human, the most fatal effect of PbB is associated with the central nervous system. High levels of exposure to lead may result in stupor, coma and may progress to death. The low threshold levels of lead in the blood which are unlikely to cause a neurotic effect are 1.2 ppm for adults and 1.0 ppm for children (Harrison and Laxen, 1981).

Heavy Metals Retention in Soil

Heavy metals retention in soil is generally controlled by soil clay and humus. Soil clays and humus have high surface area with charged sites. These charged sites play an important role in immobilizing metals through adsorption. Adsorption is one of the solute transfer mechanisms for ions from a solution phase to a solid phase. Other mechanisms of immobilizing metal ions include complexation and precipitation. Broadly speaking, these solute transfer mechanisms occur simultaneously and therefore, it may be difficult to distinguish one individual process from the others. One of the solute transfer mechanisms may be more dominant than others depending on the local chemical and physical environments which will govern the solute transfer from aqueous phase to solid phase. Through adsorption, precipitation, and complexation, heavy metal ions may be retained strongly by soils for a long time.

Adsorption

There are two kinds of adsorption mechanisms according to the strength of the adsorbate-adsorbent interaction (McBride, 1994). The first type of ion adsorption is chemical adsorption or chemisorption, or specific adsorption. For chemisorption, a covalent or short-range electrostatic bond is formed between the molecule and the surface. The cations usually penetrate the coordination shell of the structural atom and are bound via covalent bonds or electrostatically with O or OH groups of the structural cations (Yong et al., 1992). Chemisorption is usually limited to monolayer adsorption. In chemisorption, reactions including complexation with organic functional groups and bonding on variable-charge minerals (e.g., oxides, allophane) are more selective and less reversible than physical adsorption. In certain circumstances, chemisorption may even immobilize metal cations.

The other type of adsorption is physical adsorption or non-specific adsorption. This type of adsorption is the result of weak electrostatic attraction forces. The bonding interaction of physical adsorption is weaker than that of chemisorption and may result in multilayer adsorption. In the case of physical adsorption, higher valenced ions with their smaller hydrated size, are more easily adsorbed onto clay particles due to low steric hindrance and high electrostatic force. Cation exchange can be regarded as physical adsorption.

Generally, layer silicate clay has physical adsorption sites and oxides and hydroxides of Fe, Al, and Mn, and noncrystalline aluminosilicates (allophanes) provide surface sites for chemisorption (McBride, 1994). The ion exchange equilibrium between metal ion Me^{a+} in solution and ion M^{b+} in clay may be expressed as

$$bMe^{a+} + aM^{b+}{}_{clay} = bMe^{a+}{}_{clay} + aM^{b+}$$

The equilibrium constant may be expressed as

$$K = \frac{[Me^{a+}]^{b}{}_{clay}[M^{b+}]^{a}}{[Me^{a+}]^{b}\,[M^{b+}]^{a}{}_{clay}} = K_d \frac{[M^{b+}]^{a}}{[Me^{a+}]^{b}} \quad \text{where } K_d = \frac{[Me^{a+}]^{b}{}_{clay}}{[M^{b+}]^{a}{}_{clay}}$$

where [M] and [Me] are the concentrations of metal ions in solution, $[M]_{clay}$ and $[Me]_{clay}$ are the concentrations of metal ions adsorbed onto the clay. K_d is defined as the distribution coefficient. The K_d values may be used to measure the affinity of the adsorbate onto the adsorbent. A large K_d value would mean that more metal ions would be adsorbed onto clay (Garcia et al., 1986).

The pH_{50} value is another simple way of expressing the adsorption selectivity of the adsorbent for metal ions. The pH_{50} is the pH at which K_d is equal to 1, i.e., where 50 % of the introduced metal ions are adsorbed onto clay while the other half are present in solution. Small pH_{50} values mean that the adsorbent has a greater selectivity for a particular metal ion (Pul et al., 1988). Kinniburgh et al. (1976) measured the relative affinity of heavy metals on freshly precipitated Fe and Al gels. They found that the pH_{50} values of lead were 3.1 for Fe gels and 5.2 for Al gels. These values are relatively lower than for Ni (5.6 for Fe gels and 6.3 for Al gels), Zn (5.4 for Fe gels and 5.6 for Al gels) and Co (6.0 for Fe gels and 6.5 for Al gels). Based on their results, lead may be more strongly adsorbed onto soil oxides than other common heavy metals.

The very strong attraction between lead and soil clays usually result in chemisorption. The adsorption of lead onto soil clays is pH dependent. As pH increases, adsorption of lead increases. However, an increase in pH also results in an increase in lead precipitation. For this reason, at high pH, it is difficult to quantify how much of the introduced lead from contaminated sources is adsorbed or precipitated.

Precipitation

When metal ions are introduced at concentrations higher than the solubility of the metal and the adsorption capacity of the adsorbent, the excess metal ions are expected to be formed as mineral precipitates. Precipitation occurs in two stages: nucleation and particle growth. Nucleation is a condensation of ions to very small particles. The very fine precipitate with a disordered lattice, is generally formed from oversaturated (supersaturated) solutions. These small particles may grow to bigger particles as a result of diffusion of ions and further precipitation from the solution onto the small particles. In soil solution, different kinds of ions are present resulting in heterogeneous nucleation. Heterogeneous nucleation are thermodynamically more favorable as mineral and organic surfaces present in soil can catalyze the nucleation step of crystallization (McBride, 1994). These amorphous precipitates and newly precipitated active forms may change to either inactive forms or more stable forms over time.

Hydroxides, carbonates, sulfides and sulfates of most heavy metals have relatively low solubility. Solubility diagrams which show the solubility of the metals as a function of pH, may be used for rough prediction of the quantity of metal ions in solution in the presence of precipitated metals.

Chemisorption is a two dimensional surface process while precipitation is a three dimensional nucleation process (Anderson et al., 1981). Since the chemical bonds formed in both mechanisms are alike, it is not easy to distinguish between adsorption (especially chemisorption) and precipitation. The pH of both soil and the solution and concentration of the solutes are the most important factors controlling precipitation. Lead concentration in lead-contaminated soil is usually high enough such that the solubility of lead in soil solution may be exceeded and that the adsorption capacity of lead in soil may be met resulting in precipitation of lead on the surface of the soils.

Complexation

The majority of the solutes in soil solution, are composed of free hydrated ions and various coordinated compounds complexed with organic or inorganic ligands (Sparks, 1995). Complexation is the bonding of metal ions to organic or inorganic ligands. The majority of ligands are anions or neutral molecules. These ligands contain one or more pairs of unbounded electrons. When ligands donate one electron-pair to one metal atom, the ligands are called monodentate ligands. Ligands with two or more electron-pairs and form two or more electron donor bonds with the same metal are called polydentate ligands or chelate ligands. The formed compounds are called coordination compounds, complex compounds or chelates. These coordination compounds are bonded through Lewis acids and bases interaction.

In soil matrix, there are many different kinds of functional groups in the liquid phase or on solid phase which may act as ligands controlling the reactivity of metal ions in soil matrix. These are two types of complexes : inner- and outer-sphere complexes. An inner-sphere complex is formed when there are no water molecules between the metal ion and ligand. An outer-sphere complex is formed when at least one water molecule is positioned between the metal ions and ligands. Outer-sphere complexes are less stable than inner-sphere complexes. Uncharged complexes such as an ion pair are one of the outer-sphere complexes found in the aqueous phase. When surface functional groups react with a dissolved metal atom or ion, a stable compound is formed which is called surface complexation (Sposito, 1984).

The major functional groups may be categorized into inorganic and organic functional groups. The inorganic functional groups are OH^-, Cl^-, SO_4^{2-}, CO_3^{2-}, PO_3^{3-}, CN^-. The complex compounds formed between the metal ions and inorganic ligands are much weaker than those formed with organic ligands such as amines and phenols (Yong et al., 1992). Because soil organic matter has ligands such as carboxyl, phenolic, alcoholic and carbonyl groups, soil organic components have an affinity for heavy metal cations. In this case, strong ionic and covalent bonds are formed. For this reason, metal adsorption on soil organic matter may be viewed as a chemisorption mechanism. However, organic matter with negatively charged surfaces also function as sites for physical adsorption. Therefore, adsorption of metals on organic matter is via either chemisorption or physical adsorption mechanism. Observed order of affinity of divalent metal ions for soil organic matter is as follows: Cu > Ni > Pb > Co > Ca > Zn > Mn > Mg (McBride, 1994). There are no consistent rules of metal selectivity for organic matter but generally cations with higher electronegativity have higher selectivity. Metals complexed with soil organic matter can be retained onto solid phase or dissolved with the soil organic matter depending on the type of soil organic matter, i.e., dissolved, suspended or bottom sediment organic matter (Thurman, 1985). These soil organic matters can also extract metals from minerals by complexation. At pH values higher than 6.5, humic and fulvic acids can extract Pb, Mn, Ca, and Cu from galena (PbS), pyrolusite (MnO_2), calcite ($CaCO_3$) and malachite ($Cu_2(OH)_2CO_3$), respectively (Sparks, 1995).

The interaction between metal ions and organic and inorganic ligands in soil can be predicted by the hard soft acid base (HSAB) rule. Based on the rule, hard acid including Ca and Mg prefer to react with hard bases such as O^{2-}, OH^-, SO_4^{2-} and PO_4^{3-} and hard sites of soil organic matter such as phenolic and carboxyl sites. On the other hand, soft acids such as Pb and Cu, like to complex with soft bases such as CN^-, CO and soft sites of soil organic matter containing N- and S- sites (Rodgers, 1994, Sparks, 1995). The order of stability between fulvic acid and several metal ions is as follow: Fe(III) > Cu(II) > Pb(II) > Ca(II) > Zn(II) > Mn(II) > Mg(II) (Sparks, 1995).

When polydentate ligands react with metal ions or atoms, the value of the thermodynamic stability constant is usually much higher than the stability constant of complexation with monodentate ligands. The higher stability constant may be due to enthalpy and entropy effects. Generally, entropy effects is greater than enthalpy effects. For example, for the reaction of hydrated metal ion which has six coordination number with monodentate ligands, 6 M of ligands will be used for the complexation of 1 M of metal releasing 6 M of water from the metal ion. For this reason, the total number of moles in solution does not change. However, when metal ion forms a coordination compound with a hexadentate ligand, 1 M of hexadentate ligand can be used for the complexation of 1 M of metal ion with a release of 6 M of water. In this case, there is a net increase of 5 M in solution resulting in an increase of disorder. Therefore, entropy is more positive indicating a thermodynamically favorable reaction. This entropy effect is called the chelate effect (Cotton et al., 1987).

Lead Solubility in Aqueous System

In the soil matrix, the reactions between the constituents in the soil solution and soil particles would affect the physical-chemical properties of the soil. Metals release as a result of a spill or leakage from a hazardous waste source will undergo various chemical reactions in the soil depending on the chemical conditions of the soil such as pH, Eh, etc. In nature, these interactions include complexation, precipitation, adsorption and ion exchange on clay, organic matter and oxides. Complex formation may tend to keep metals in the solution phase while adsorption, ion exchange and precipitation reactions remove them from soil solution into the solid phase.

Because different lead compounds have different solubility, use of the solubility diagrams will provide an indication of the solubility of the metals as a function of the solution pH. The solubility products of major lead compounds and equilibrium constants of lead hydrolysis are shown in Table 1. Figure 1 shows the solubility of lead hydroxide and lead oxide compounds. According to this figure, lead hydroxide has lower solubility than other lead oxides over all pH values and will control lead solubility. However, for lead-contaminated soils, besides lead hydroxide, other species of lead compounds such as lead sulfate and lead carbonate may be present.

Table 1. Solubility products and equilibrium constants of common lead compounds

Equilibrium Reaction	Constant	Eq. #
PbO (yellow) $+ 2H^+ = Pb^{2+} + H_2O$	log K = 12.89	(1)
PbO (red) $+ 2H^+ = Pb^{2+} + H_2O$	log K = 12.72	(2)
$Pb(OH)_2(c)^* + 2H^+ = Pb^{2+} + 2H_2O$	log K = 8.16	(3)
$PbCO_3$ (cerussite) $+ 2H^+ = Pb^{2+} + CO_2(g) + H_2O$	log K = 4.65	(4)
$PbCO_3 \cdot PbO(c) + 4H^+ = 2Pb^{2+} + CO_2(g) + 2H_2O$	log K = 17.39	(5)
$Pb_3(CO_3)_2(OH)_2(c) + 6H^+ = 3Pb^{2+} + 2CO_2(g) + 4H_2O$	log K = 17.51	(6)
PbS (galena) $= Pb^{2+} + S^{2-}$	log K = -27.51	(7)
$PbSO_4$ (anglesite) $= Pb^{2+} + SO_4^{2-}$	log K = -7.79	(8)
$PbSO_4 \cdot PbO(c) + 2H^+ = 2Pb^{2+} + SO_4^{2-} + H_2O$	log K = -0.19	(9)
$PbSO_4 \cdot 2PbO(c) + 4H^+ = 3Pb^{2+} + SO_4^{2-} + 2H_2O$	log K = 11.01	(10)
$PbSO_4 \cdot 3PbO(c) + 6H^+ = 4Pb^{2+} + SO_4^{2-} + 3H_2O$	log K = 22.30	(11)
$PbSiO_3(c) + 2H^+ + H_2O = Pb^{2+} + H_2SiO_4^{o}$	log K = 5.94	(12)
$Pb_2SiO_4(c) + 4H^+ = 2Pb^{2+} + H_2SiO_4^{o}$	log K = 18.45	(13)
$Pb(H_2PO_4)_2(c) = Pb^{2+} + 2H_2PO_4^-$	log K = -9.85	(14)
$PbHPO_4(c) + H^+ = Pb^{2+} + H_2PO_4^-$	log K = -4.25	(15)
$Pb_3(PO_4)_2(c) + 4H^+ = 3Pb^{2+} + 2H_2PO_4^-$	log K = -5.26	(16)
$Pb_4O(PO_4)_2(c) + 6H^+ = 4Pb^{2+} + 2H_2PO_4^- + H_2O$	log K = 2.24	(17)
$Pb_5(PO_4)_3OH + 7H^+ = 5Pb^{2+} + 3H_2PO_4^- + H_2O$	log K = -4.14	(18)
$Pb^{2+} + H_2O = PbOH^+ + H^+$	log K = -7.70	(19)
$Pb^{2+} + 2H_2O = Pb(OH)_2^{o} + 2H^+$	log K = -17.75	(20)
$Pb^{2+} + 3H_2O = Pb(OH)_3^- + 3H^+$	log K = -28.09	(21)
$Pb^{2+} + 4H_2O = Pb(OH)_4^{2-} + 4H^+$	log K = -39.49	(22)
$2Pb^{2+} + H_2O = Pb_2OH^{3+} + H^+$	log K = -6.40	(23)
$3Pb^{2+} + 4H_2O = Pb_3(OH)_4^{2+} + 4H^+$	log K = -23.89	(24)
$4Pb^{2+} + 4H_2O = Pb_4(OH)_4^{4+} + 4H^+$	log K =-20.89	(25)
$6Pb^{2+} + 8H_2O = Pb_6(OH)_8^{4+} + 8H^+$	log K = -43.58	(26)

* (c) crystalline forms

^{o} aqueous solution species

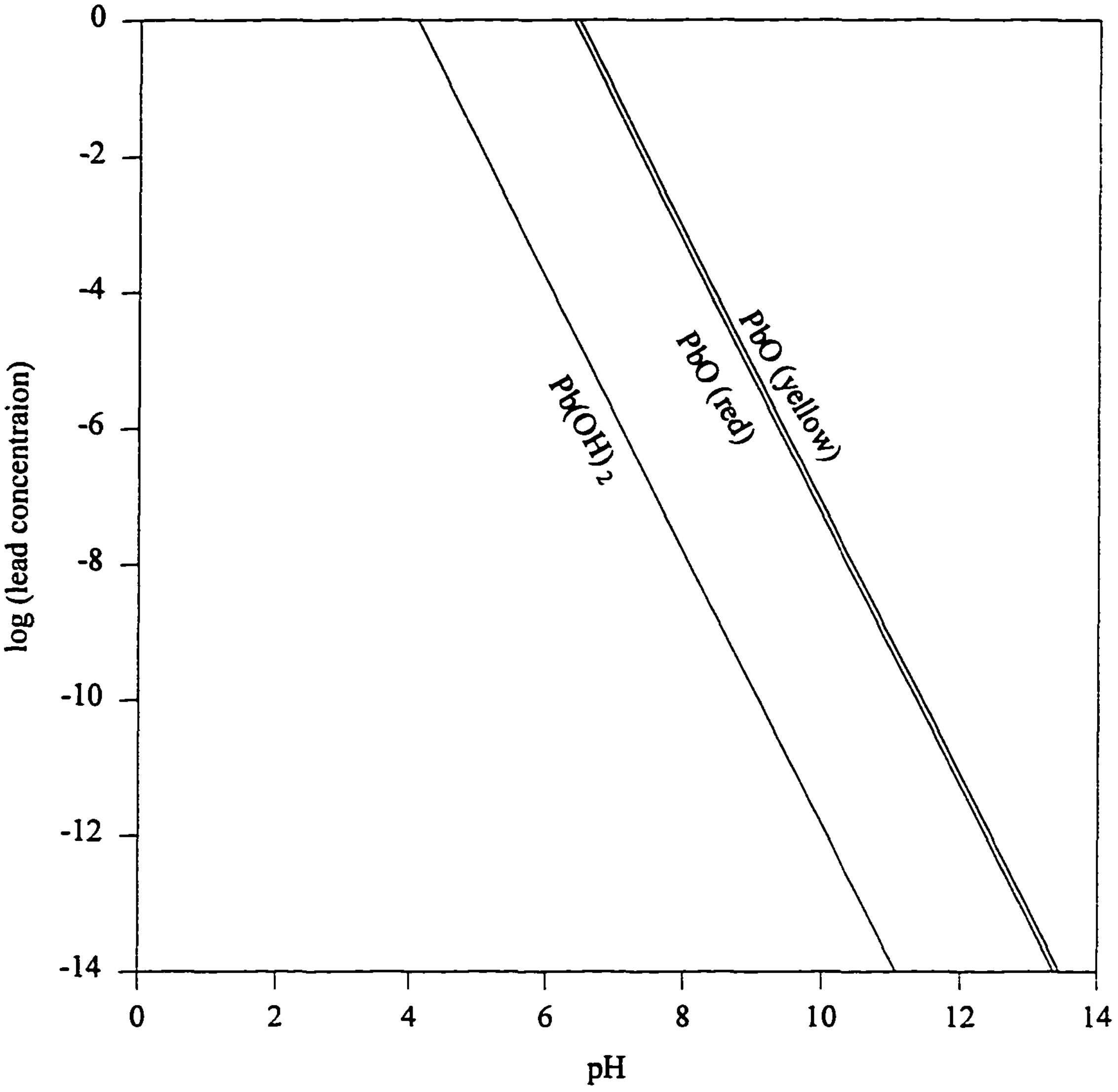


Figure 1. Solubility diagram of lead hydroxide and lead oxides

Figure 2 shows the solubilities of various lead carbonate for two different partial pressures of CO_2. For a typical CO_2 partial pressure of 0.0003 atm, $PbCO_3$ has identical solubility as the $Pb_3(CO_3)_2(OH)_2$. Since the partial pressure of CO_2 in soil is generally higher than that of the atmosphere due to respiration of plant root and organic matter oxidation by microorganisms (Lindsay, 1979), computing the solubilities of various carbonate species for a CO_2 partial pressure of 0.003 atm indicate that the $PbCO_3$ (cerussite) is more stable than the $Pb_3(CO_3)_2(OH)_2$. Therefore, cerussite is the main lead carbonate species which governs the solubility of lead from lead carbonate compounds.

The solubility diagram (without hydrolysis) of the lead sulfate family with the equilibrium sulfate concentration of 0.1M is shown in Figure 3. Based on this diagram, Pb solubility is controlled by $PbSO_4$ under acidic condition. But for higher pH conditions, lead solubility mainly depends on $PbSO_4 \cdot 2PbO$. Besides lead sulfate compounds, Galena, (PbS) is one of the major lead minerals found at lead mining and smelting sites (Davis et al., 1993; Clevenger et al., 1991). Because galena has a very low solubility product, it remains in soil as solid phase (Figure 3).

According to equations 14 through 18 in Table 1, solubilities of lead phosphate compounds depend on the concentration of $H_2PO_4^-$ ion present in solution. Figure 4 is drawn with an assumption that the equilibrium phosphate concentration is 0.1 M. According to this figure, we can roughly expect that under strong acidic conditions, $Pb(H_2PO_4)_2$ is the major lead phosphate species controlling the solubility of lead in solution while under weak acidic and weak alkaline conditions, $PbHPO_4$ and $Pb_3(PO_4)_2$ are the major lead phosphate compounds controlling lead solubility.

The solubilities of phosphate compounds with 0.1 M of the equilibrium phosphate ion concentration at pH 7 are about $10^{-10.4}$. The solubility is much smaller than the lead sulfate solubility (about $10^{-6.8}$ M) with 0.1 M of the equilibrium sulfate ion concentration or lead oxide compounds solubilities (about $10^{-5.8}$ M) or lead carbonate compounds (about $10^{-5.8}$ M) with 0.0003 atm of equilibrium CO_2 partial pressure. Based on the results, compounds of lead phosphate family are considered to be the least soluble lead compounds in the normal soil environmental pH. At strong alkaline conditions, lead carbonate family may be the least

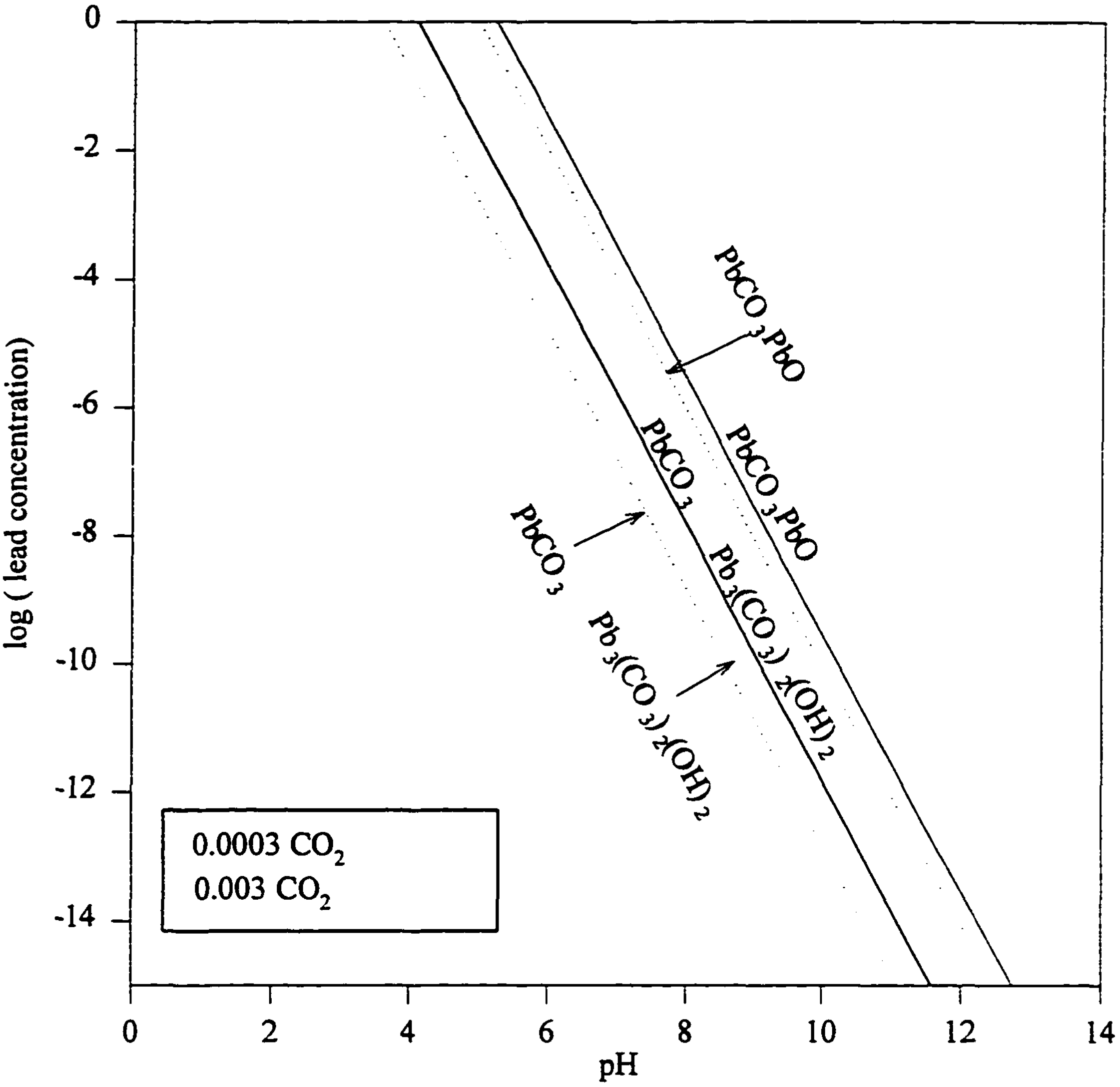


Figure 2. Solubility diagram of various lead carbonate compounds

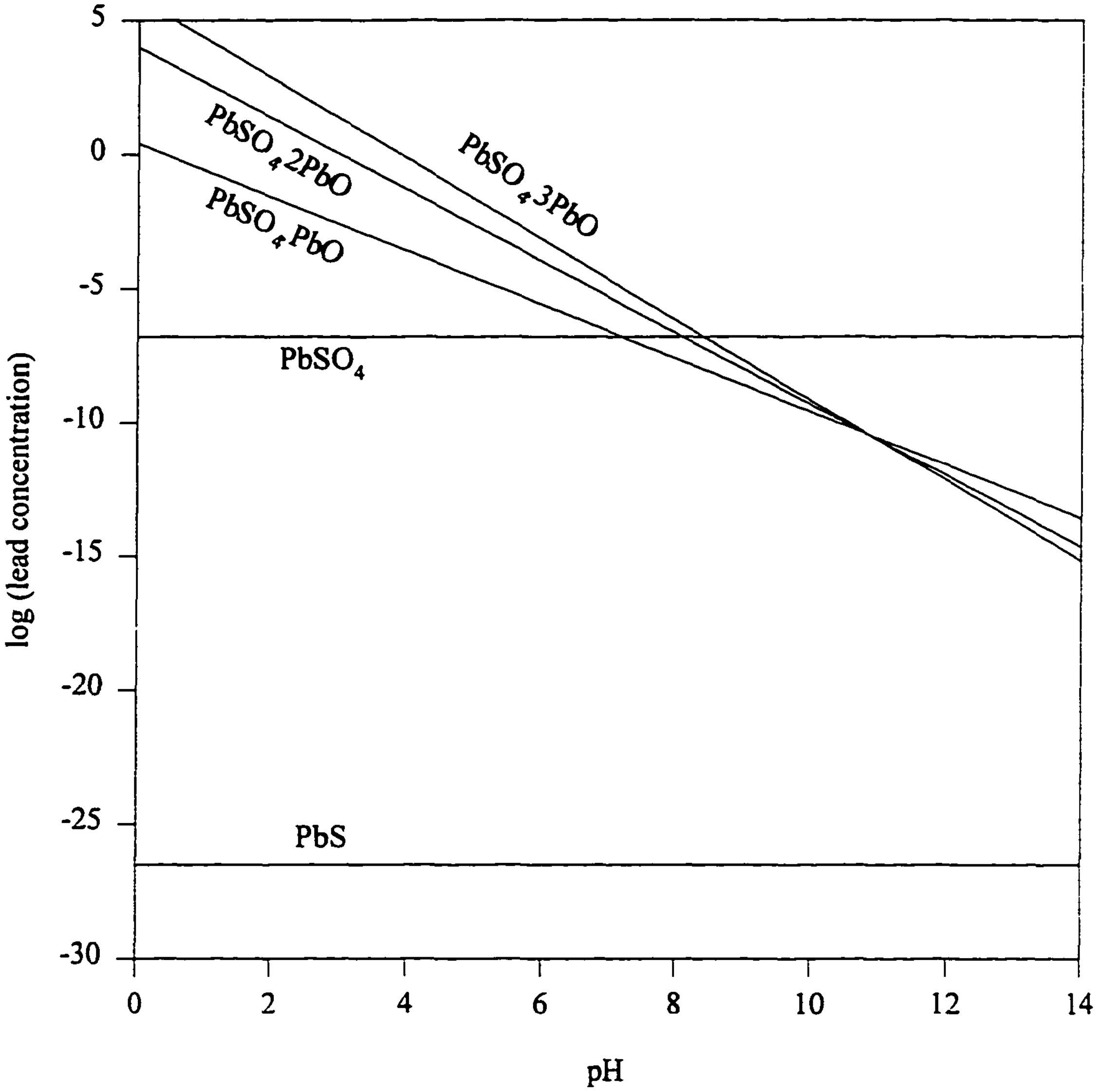


Figure 3. Solubility diagram of lead sulfide and lead sulfate compounds with 0.1 M of equilibrium [SO_4^{2-}] and [S^{2-}] concentrations

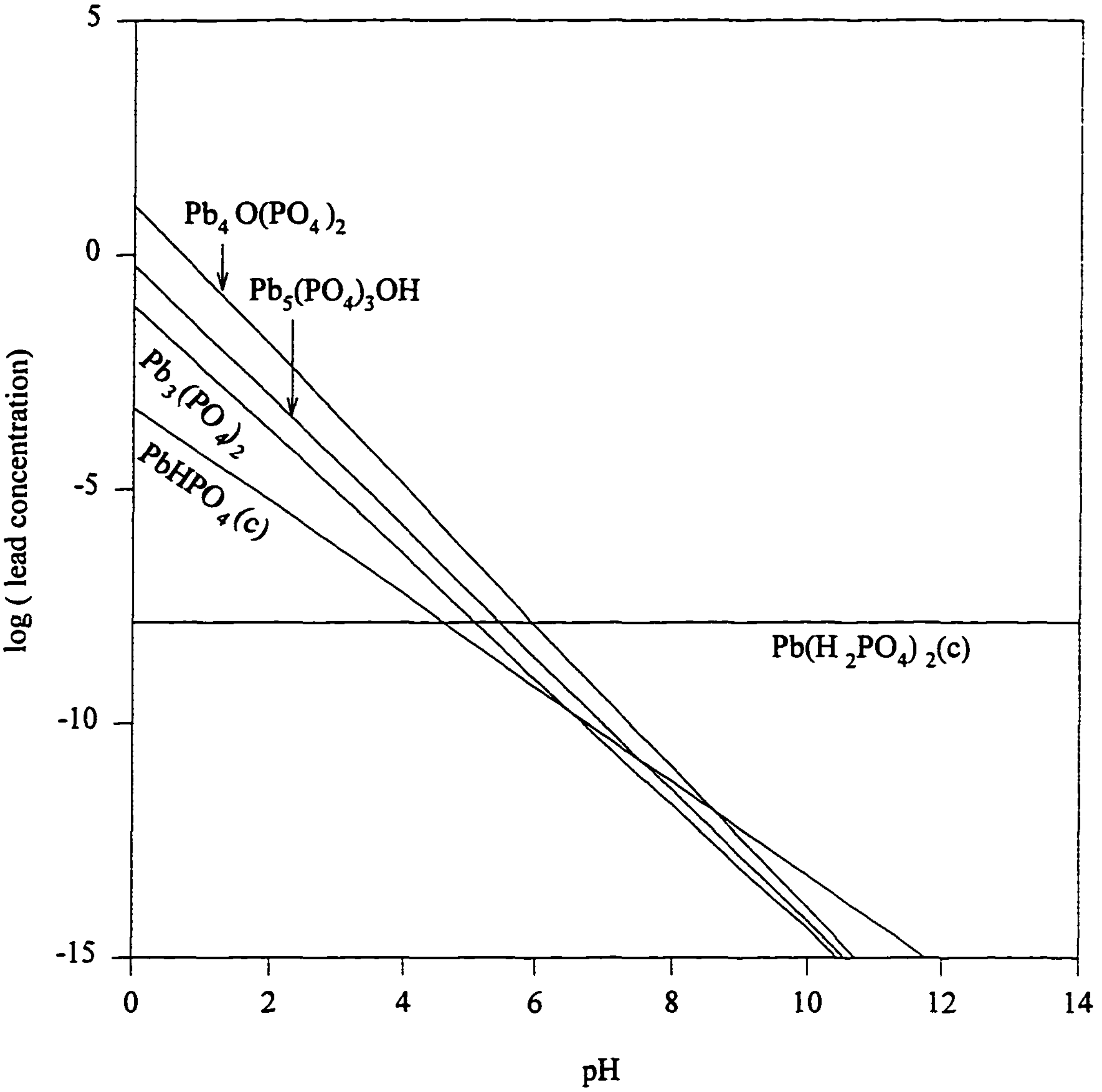


Figure 4. Solubility diagram of lead phosphate compounds with 0.1 M of of equilibrium $[H_2PO_4^-]$ concentration

soluble lead compounds. Santillan-Medrano and Jurinak (1975) noted that in noncalcareous soils, the solubility of lead may be regulated by phosphate concentration while $PbCO_3$ could be important in calcareous soil.

Remediation Technologies for Heavy Metal-Contaminated Soil

Various technologies have been introduced to remediate heavy metal-contaminated soil. The remediation of contaminated soil is based on two common approaches. The first approach is immobilization of metals by increasing the retention of the metals in the soil or decreasing the mass transfer rate of the metals. The other approach is the removal of metals from the soil matrix by extraction or leaching.

The immobilization options for lead-contaminated soils are solidification/stabilization and vitrification. Cement is generally used for immobilizing metals such as lead. Because the pH of the cement mixture is high (approximately 12), most multivalent cations are converted into insoluble hydroxides or carbonates which are resistant to leaching. Vitrification converts contaminated soil through thermal treatment process into a chemically inert, glassy and stable form with very low leachability (Royer et al., 1992). One negative aspect of these methods is that they all result in a product that still contains the metal. In addition, the soil is not returned to its original state or to a material suitable for reuse.

The other approach is extraction technology. Heavy metals may be extracted from contaminated soils through in-situ or ex-situ (following excavation) method. In the case of in-situ soil flushing, the aqueous extractive agent is introduced into the contaminated soil through surface flooding or sprinklers. The percolating extractant promotes mobilization of contaminants from the contaminated soil. At the base of the contaminated soil zone, the flushing fluid is recovered using subsurface drainage pipes, trenches or wells. In-situ cleanups are harder to implement than ex-situ cleanups because it is difficult to completely control the critical soil remediation process parameters such as temperature, pH, and the spatial flow of fluids (Chawla et al., 1991). In addition, the extractive agent may adhere or react with soil reducing the effectiveness of the extractive agent. If the contaminants are relatively insoluble or tightly bound to the soil and if there is a lack of an adequate supply of process water, soil flushing may not be cost effective.

In the case of ex-situ extraction of lead-contaminated soils, the operation can be performed on a batch basis or continuously. This method employs chemical and physical extraction and separation processes to remove contaminants from the contaminated soil. The process entails excavation of the contaminated soil, mechanical screening to remove various oversize materials, separation of coarse- and fine-grained fractions and treatment of the fractions followed by disposal of the generated residuals. Ex-situ treatment method may be expensive depending on the volume of contaminated soil to be treated and the hauling distance between the contaminated site and the treatment facility.

The amounts of heavy metals extracted from the contaminated soil depend on the soil type and the extraction agent. Two types of extraction agents have been used for the removal of heavy metals from soil: acids and chelating agents. Strong acid solutions (pH 0.5 to 4.0) may cause crystalline structural damage of soil during extraction. In addition, handling and storage of corrosive liquids such as acid require special care (Randall et al., 1985). However, due to the low cost of acids, acid treatments have been used for remediation purposes. Soil washing with chelating agents depends on the ability to form stable soluble metal complexes with the insoluble metals. Removal of lead with chelating agents is quite efficient and may overcome some of the problems caused by the use of acid solution. However, the high cost of chelating agents has restricted the wide use of chelating agents for the remediation of metal-contaminated soils, even though chelating agents are still the market standard choice of treatment. There are five major considerations in the selection of complexing agents for soil remediation (Rulkens et al., 1984).

1) Reagents should be able to form highly stable complexes over a wide pH range at 1:1 ligand-to-metal molar ratio
2) Biodegradability of the complexing agents and metal complexes should be low (especially if the complexing agent is to be recycled for reuse in the process)
3) Metal complexes formed should be non-adsorbable on soil surfaces

4) The chelating agent should have low toxicity and low potential for environmental harm
5) The reagents should be cost effective
6) The reagents should be easy to use.

Although no compounds ideally satisfy all these criteria, there are several aminocarboxylic acids which form remarkable stable complexes with numerous metal ions. Currently, several kinds of chelating agents are being used to extract heavy metals from contaminated soil. These chelating agents are N-2-acetaminodiacetic acid (ADA), trans-1,2-diaminocyclohexanetetraacetic acid (CDTA), ethylenediaminetetraacetic acid (EDTA), ethylene-N,N'-bis(o-hydroxyphenylglycine) (EHPG), nitrilotriacetic acid (NTA). s-carboxymethylcysteine (SCMC), and diethylenetriaminepentaacetic acid (DTPA) etc.. Among these chelating agents, EDTA has been shown to be the most effective chelating agent for the remediation of lead-contaminated soils (Elliott and Brown, 1989, Peter and Shem, 1992, Slavek and Pickering, 1986 and Tedaldi, 1993).

Lead Solubility with EDTA

EDTA is a hexadentate ligand compound. As mentioned earlier, the formation of soluble Pb-EDTA complex is thermodynamically favorable due to the chelate effect. For this reason, the addition of EDTA to a solution containing lead compounds will increase the dissolved lead concentration. Since the concentration of EDTA species would change with pH and that each EDTA species has different stability constant, the reactivity of lead with EDTA would also change depending on the pH of the solution. Table II shows the stability constants of EDTA and several major metal EDTA reactions.

Figure 5 and Figure 6 show the Pb-EDTA solubility of $PbSO_4$ and $Pb(H_2PO_4)_2$ as computed using the stability constants in Table 1 and Table 2. To draw these figures, it was assumed that the equilibrium concentrations of SO_4^{2-}, $H_2PO_4^-$ as 0.1 M and $EDTA^{4-}$ as 0.001 M. These figures show that the solubility of Pb-EDTA in the presence of SO_4^{2-} or $H_2PO_4^-$ is controlled by PbH_2EDTA and PbH_3EDTA^+ for pH values less than 4. For pH values above

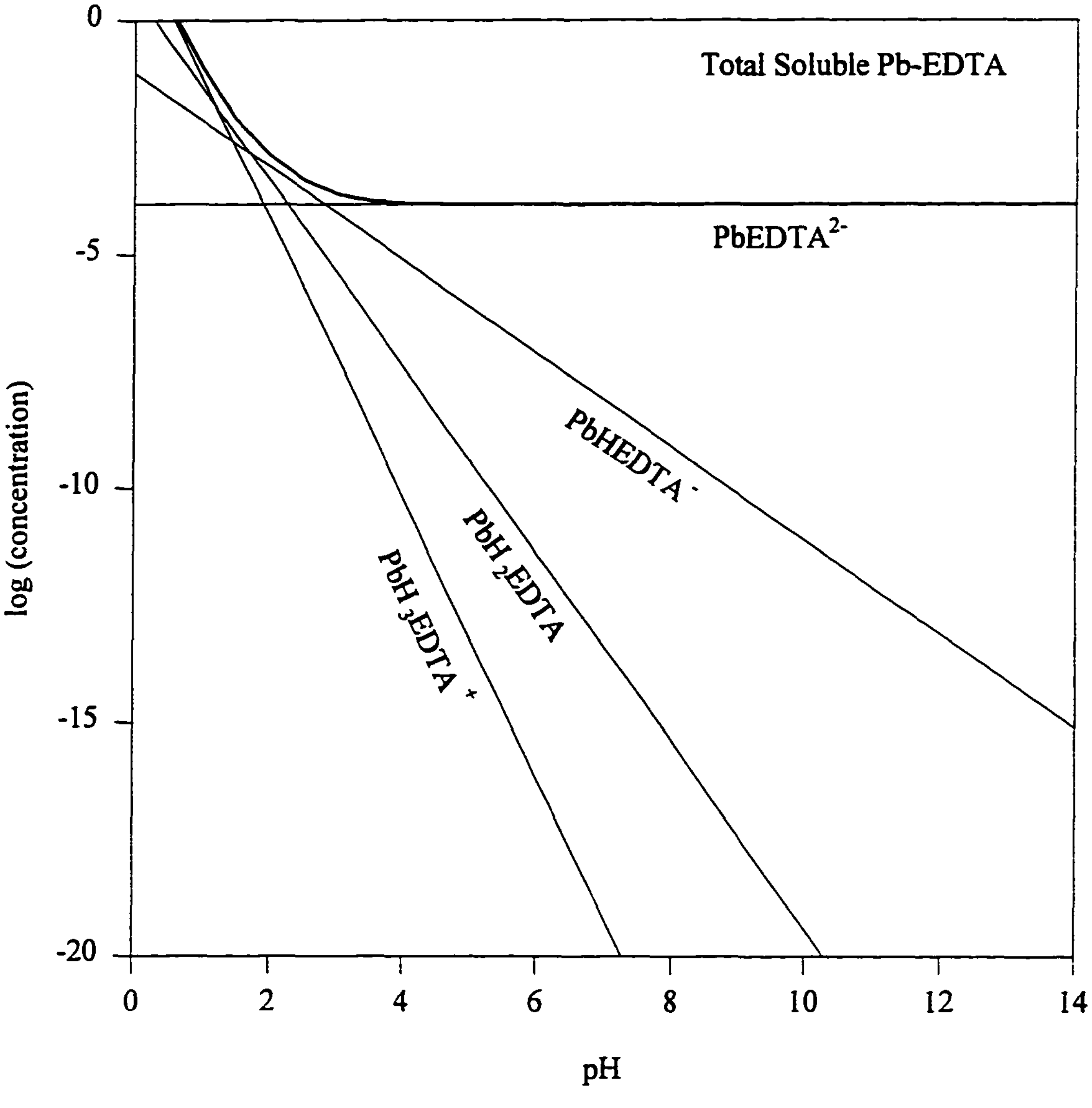


Figure 5. The solubility of Pb-EDTA from $PbSO_4$ with equilibrium concentration of [SO_4^{2-}] of 0.1 M and [$EDTA^{4-}$] of 10^{-15} M

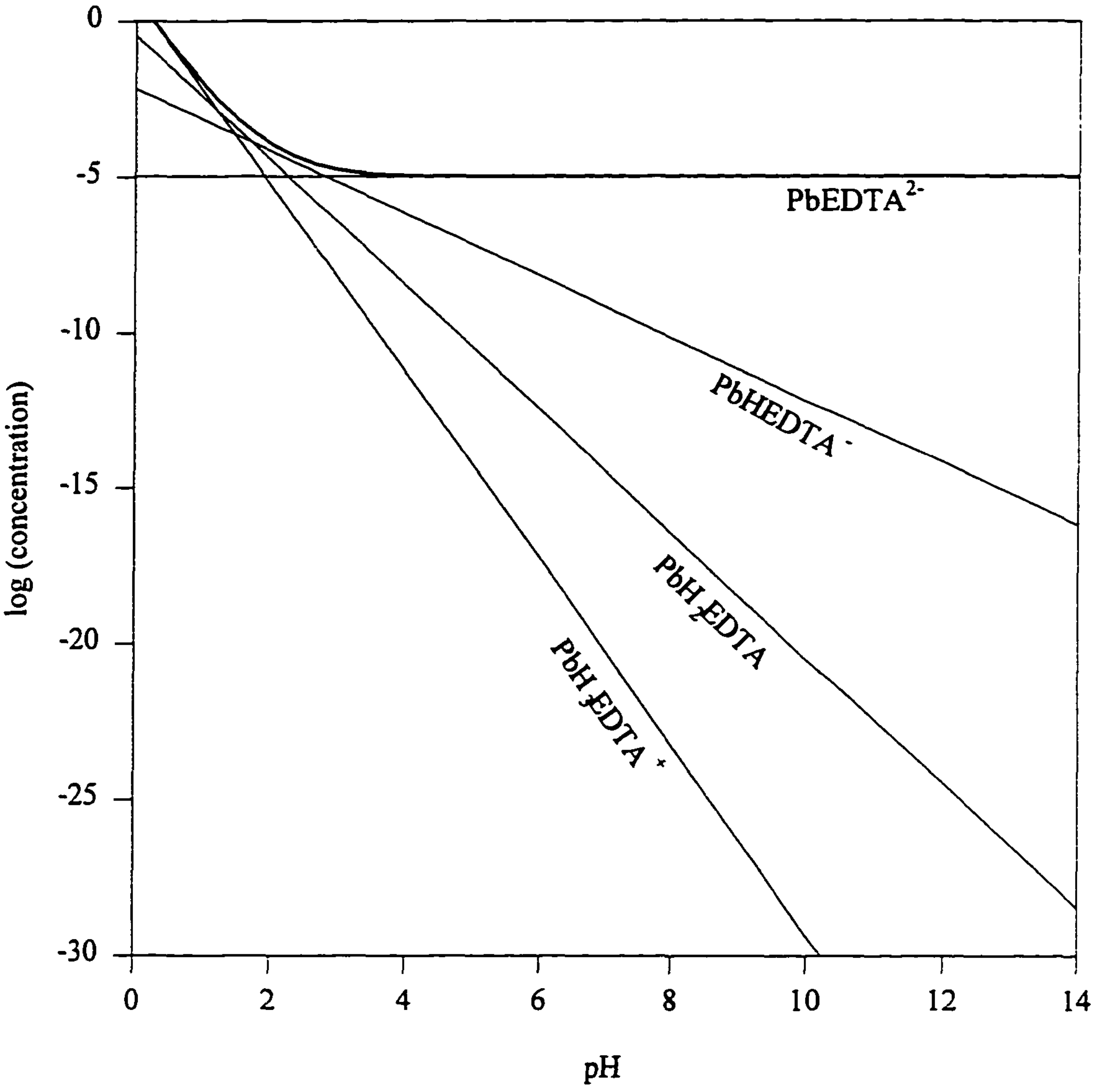


Figure 6. The solubility of Pb-EDTA based on $Pb(H_2PO_4)_2$ with equilibrium concentration of $[H_2PO_4^-]$ of 0.1 M and $[EDTA^{4-}]$ of 10^{-15} M

Table 2. Stability constants of EDTA and metal-EDTA reactions (Lindsay, 1979)

Reaction	Log K ($\mu = 0.1$)	eq. #
$H_4EDTA = H^+ + H_3EDTA^-$	-2	(1)
$H_3EDTA = H^+ + H_2EDTA^{2-}$	-2.67	(2)
$H_2EDTA = H^+ + HEDTA^{3-}$	-6.16	(3)
$HEDTA = H^+ + EDTA^{4-}$	-10.26	(4)
$Ca^{2+} + EDTA^{4-} = CaEDTA^{2-}$	10.61	(5)
$Ca^{2+} + H^+ + EDTA^{4-} = CaHEDTA^-$	13.79	(6)
$Mg^{2+} + EDTA^{4-} = MgEDTA^{2-}$	8.83	(7)
$Mg^{2+} + H^+ + EDTA^{4-} = MgHEDTA^-$	12.68	(8)
$Fe^{3+} + EDTA^{4-} = FeEDTA^{-1}$	25.10	(9)
$Fe^{3+} + HEDTA^{3-} = FeHEDTA$	16.20	(10)
$Fe^{3+} + H_2EDTA^{2-} = FeH_2EDTA^+$	8.70	(11)
$FeEDTA^{-1} + OH^- = Fe(OH)EDTA^{2-}$	6.31	(12)
$Fe(OH)EDTA^{2-} + OH^- = Fe(OH)_2EDTA^{3-}$	4.39	(13)
$Fe(OH)_2EDTA^{3-} + OH^- = Fe(OH)_3EDTA^{4-}$	1.50	(14)
$Zn^{2+} + EDTA^{4-} = ZnEDTA^{2-}$	16.44	(15)
$Zn^{2+} + H^+ + EDTA^{4-} = ZnHEDTA^-$	19.44	(16)
$Cu^{2+} + EDTA^{4-} = CuEDTA^{2-}$	18.70	(17)
$Cu^{2+} + H^+ + EDTA^{4-} = CuHEDTA^-$	21.70	(18)
$Mn^{2+} + EDTA^{4-} = MnEDTA^{2-}$	13.81	(19)
$Mn^{2+} + H^+ + EDTA^{4-} = MnHEDTA^-$	16.91	(20)
$Pb^{2+} + EDTA^{4-} = PbEDTA^{2-}$	17.88	(21)
$PbEDTA^{2-} + H^+ = PbHEDTA^-$	2.8	(22)
$PbHEDTA^- + H^+ = PbH_2EDTA$	1.7 ($\mu = 1.0$)	(23)
$PbH_2EDTA + H^+ = PbH_3EDTA^+$	1.2 ($\mu = 1.0$)	(24)

4, the solubility is governed by $PbEDTA^{2-}$ where the solubility is a constant value of $10^{-4.97}$ for lead phosphate and $10^{-3.9}$ for lead sulfate compounds. As shown in Table 1 and Table 2, the solubility equations of $PbSO_4$ and $Pb(H_2PO_4)_2$ and the complexation stability equation between $EDTA^{4-}$ and Pb^{2+} are independent of pH. For this reason, the solubility of Pb-EDTA is constant in the presence of $PbSO_4$ and $Pb(H_2PO_4)_2$ for pH values higher than 4. For pH values less than 4, the complexation reactions between lead and H_2EDTA^{2-} and H_3EDTA^{-} are dependent on pH values resulting in an increase of Pb-EDTA solubility.

The solubilities of $PbCO_3$ and $Pb(OH)_2$ with EDTA have a different trend than lead sulfate and lead phosphate compounds. Figure 7 and 8 show the Pb-EDTA solubility in the presence of the lead carbonate for two different CO_2 partial pressures and lead hydroxide, respectively. The solubilities of lead carbonate-EDTA and lead hydroxide EDTA complexes decreased as pH increased. This may be due to the solubilities of lead carbonate and lead hydroxide since the solubilities of lead carbonate and lead hydroxide decreased for an increase in pH (Figure 1 and 2).

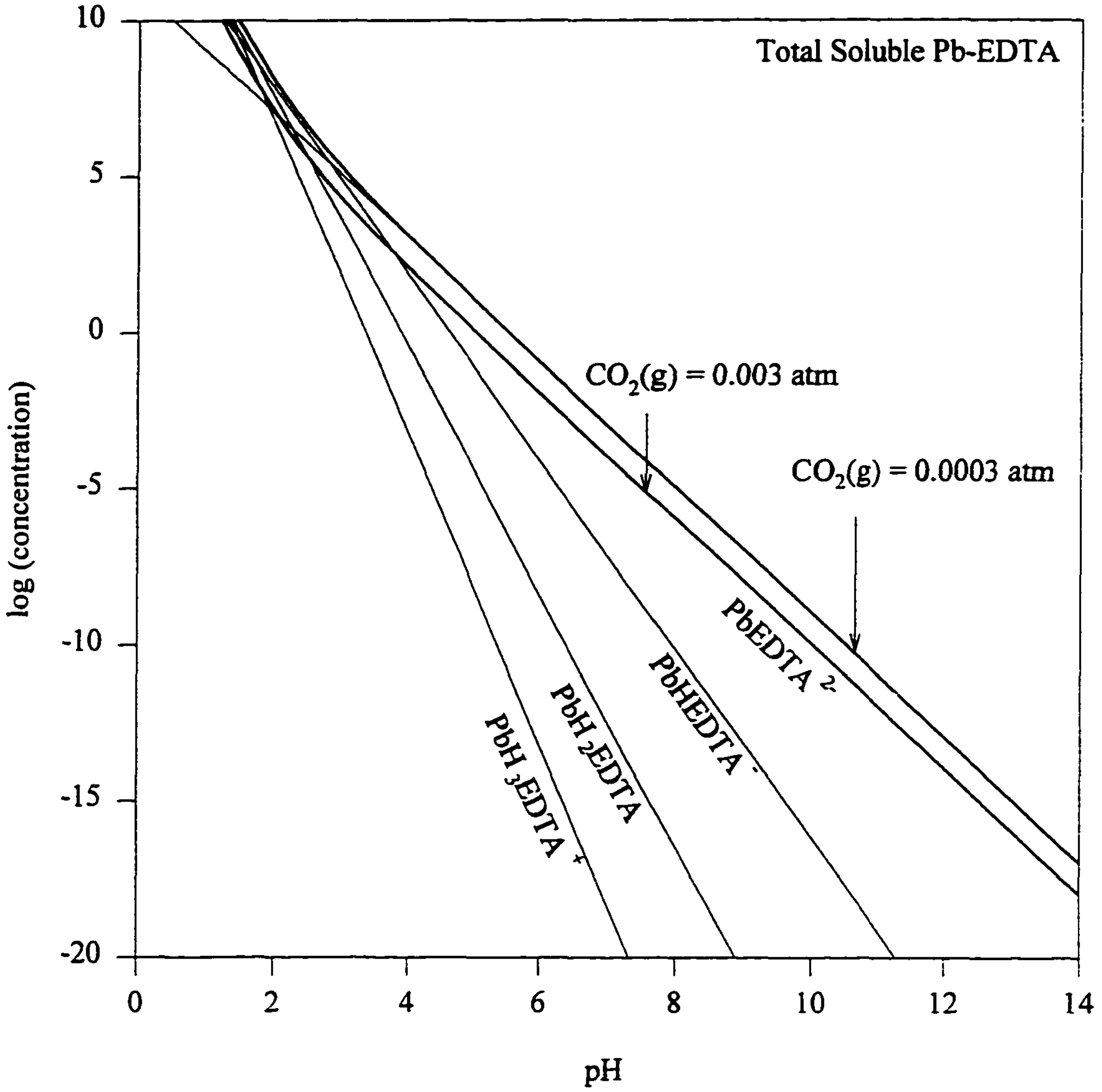


Figure 7. The solubility of Pb-EDTA based on $PbCO_3$ with P_{CO_2} of 0.003 and 0.0003 atm and equilibrium concentration of $[EDTA^{4-}]$ of 10^{-15}

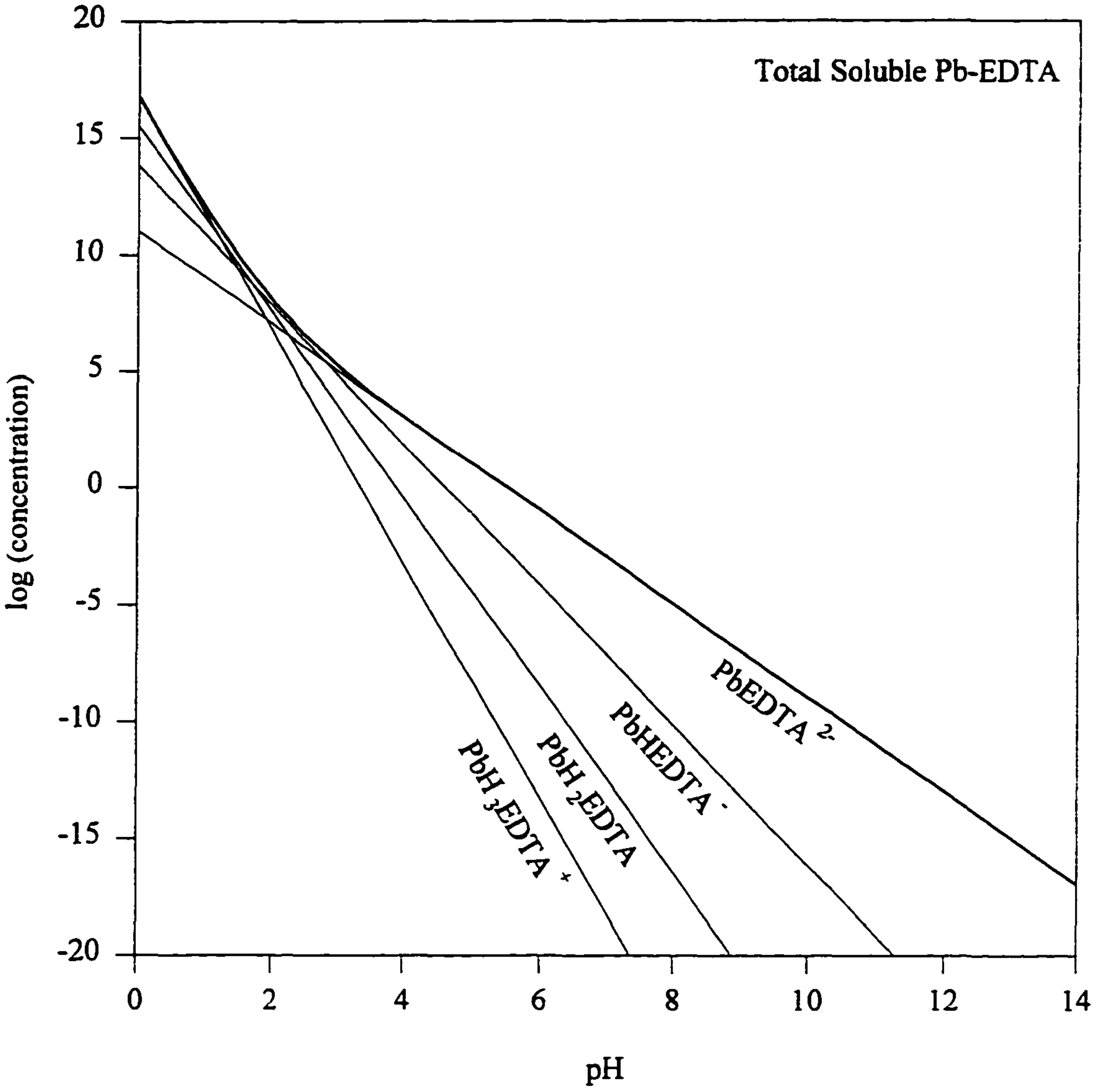


Figure 8. The solubility of Pb-EDTA based on $Pb(OH)_2$ with equilibrium $[EDTA^{4-}]$ of 10^{-15} M

PART I. FACTORS AFFECTING LEAD EXTRACTION WITH EDTA FROM ACTUAL LEAD-CONTAMINATED SOILS

INTRODUCTION

The uncontrolled discharge and disposal of products and wastes with heavy metals have resulted in the contamination of valuable land resources and aquifers. Because heavy metals do not degrade to harmless end products and may be toxic to biological systems, heavy metal-contaminated soils will be of an environmental concern for a long time. Lead is one of the concerned heavy metals.

The major source of lead contamination of soil is a result of human activities such as lead mining and smelting, disposal of lead-based paint, automobile industry including battery reclamation, etc. Pellets from shotguns and bullets from rifles are also one of the many sources of lead contamination in the environment. The concentration of lead in uncontaminated soil is between 20 and 200 ppm with an average value of 10 ppm (Lindsay, 1979). Urban soils show higher lead concentration than rural area mainly due to motor vehicles using leaded gasoline (Davies, 1988). Other human activities such as lead mining, smelting, battery reclamation sites may cause extremely high lead contamination of the environment. Elliott and Brown (1989) found that the lead concentration of an automobile battery recycling facility area may be as high as 21 % (w/w). Austin et al. (1993) reported that the lead concentration in the soil at an old smelter site may be as high as 30,000 ppm. Lead commonly exist in the environment as Pb(II) and Pb(IV) with Pb(II) being more dominant in soils than Pb(IV). The major lead compounds in soils are lead sulfate, lead carbonate, lead phosphate, and lead oxides and hydroxides. The common lead minerals in each group are presented in Table 3.

Various techniques have been introduced to remediate metal-contaminated soils. One of these techniques is to separate the metals from soil by using chelating agents to form soluble metal-chelate complexes. Chelating agents such as ethylenediamine tetraacetic acid (EDTA) have been shown to have good extraction properties of heavy metals from soils. Because the coordination number of lead ion is six, six-coordinate complex of lead ions such as Pb-EDTA is one of the more stable lead complexes. Ideally, the minimum EDTA molar concentration needed to extract lead from contaminated soil should be the same as the molar

Table 3. Major lead minerals in soil

Lead oxide family	Lead sulfate family	Lead silicate family	Lead phosphate family	Lead carbonate family	Other minerals
PbO,	$PbSO_4$,	$PbSiO_3$,	$Pb_3(PO_4)_2$,	$PbCO_3$,	PbS (galena)
PbO_2,	$PbSO_4 \cdot PbO$,	Pb_2SiO_4	$Pb_4O(PO_4)_2$,	$PbCO_3 \cdot PbO$,	
$Pb(OH)_2$,	$PbSO_4 \cdot 2PbO$,		$Pb(H_2PO_4)_2$,	$PbCO_3 \cdot Cl_2$,	
Pb_3O_4	$PbSO_4 \cdot 3PbO$		$PbHPO_4$,	$Pb_3(CO_3)_2(OH)_2$	
			$Pb_5(PO_4)_3Cl$		

concentration of lead in the soil. However, EDTA is a non-specific chelating agent and it reacts with other metals present in soil. Therefore, solutions with an EDTA molar concentration higher than the molar concentration of lead in soil may be required to achieve maximum lead extraction from Pb-contaminated soils.

Even though treatment of heavy metal-contaminated soils with EDTA is regarded by US EPA as an innovative site remediation technology, not much work has been done to systematically study EDTA-heavy metal extraction efficiencies as influenced by the soil and soil solution conditions. The objectives of this study are to investigate the effects of major cations present in soils such as Fe, Al, Ca, Zn, Cu, Mg, Mn on the extraction efficiency of lead using EDTA. Several lead-contaminated soils will be used and variables such as soil : extractant ratio and EDTA : lead stoichiometric ratio will be investigated.

Fate of Lead in Soil

Lead ions, from a spill or leakage of hazardous materials wastes, are absorbed by soil, displacing metal ions already weakly bound to the soil (Campanella et al., 1989). If the Pb ion solubility is exceeded, the released lead ions would precipitate out onto the soil by forming various lead minerals depending on the soil and solution conditions.

The mobility of lead in soils depends on the cation adsorption capacity of the soil. The cation adsorption capacity is a function of organic matter content, iron and manganese oxides and hydroxides, pH and redox properties of the soil. Organic matter has been shown to be the principal reason for lead immobilization (Filipek et al., 1990) and it may be more important than minerals as an adsorbent (Tada et al., 1982). Soils with high organic matter tend to exhibit high lead concentration (Salim, 1983, Miller et al., 1986). The reactive groups such as hydroxyl, phenolic and carboxylic easily form strong complexes with lead. Austin et al. (1993) found that at a relatively undisturbed area, downward movement of lead was only 3 inches over a 100 year period. On the other hand, Stevenson et al. (1979) showed that for soils in semihumid region with high organic content, lead was found to move downward further than expected. Stevenson et al. (1979) speculated that the movement of lead may be due to the movement of soluble lead complexes with organic matter.

Surface area of the soil particles has been shown to provide a measure of the adsorption capacity of the soil. Higher lead concentration is found in the fine fraction of soil because as particle size decreases the surface area per unit weight increases (Tada et al., 1982). Salim (1983) confirmed the surface area effect on the adsorption of lead and he reported that the amount of lead adsorbed is not proportional to the particle weight but the surface area. Elkhatib et al. (1991) also demonstrated that the clay (silt clay) has a higher capacity of adsorption than the sandy soil. As surface area increases, more lead ions can easily access to the active sites on clay particles resulting in cation exchange or specific adsorption and co-precipitation (Austin et al., 1993; Peter et al., 1992). Precipitation seems to be associated with Pb immobilization by forming lead minerals such as lead carbonate and lead sulfate (Zimdahl and Skogerboe, 1977). In lead-contaminated soil, the concentration of Pb is generally high such that precipitation is considered to be the major mechanism of Pb retention in soil.

The soil-water redox potential is also one of the major factors influencing adsorption of lead onto soil matrix. Oxidizing conditions can result in not only the oxidation of lead but also the oxidation of other elements (such as ferrous iron to ferric iron). The formation of other oxidized species (such as iron and manganese oxides) which have high adsorption capacity for lead can influence the solubility or retention of lead in soil. Thus oxidation conditions are not favorable for the solubility and removal of lead from soil. Under reducing conditions, a reverse effect may occur resulting in an increase in lead concentration in the solution. Since most introduced lead may be retained in the top soils where oxidizing conditions are more likely than reducing conditions, lead mobilization is less likely to occur under oxidizing conditions of the soil solution.

Ionic potential is also an important factor controlling adsorption and release of Pb in soil. When the ionic potential is high, more cations compete with lead ions for adsorption sites on the surface of the soil matrix resulting in a decrease in the capacity of the soil to adsorb lead. Elliott and Brown (1989) showed that using 0.5 M of $NaClO_4$ with EDTA increased the Pb extraction from lead-contaminated soil. In contrast, Swallow et al. (1980) reported that the presence of 0.5 mole of $NaClO_4$ did not affect the sorption of lead onto ferric hydroxide. They also showed that the sorption of lead dramatically decreased at any given pH in the presence of 0.5 M of Cl^-. The decrease in adsorption may be due to the complexation of Pb with Cl^- ions.

Temperature may be an important factor controlling the adsorption of lead. Elkhatib et al. (1991) showed that as the temperature increased from 298 to 318K (25-45°C) the adsorption of lead increased. Similarly, Salim (1980) observed a small increase of lead adsorption as temperature increased from 25 to 60 °C .

The quantity of oxides in soil systems has an important effect on the adsorption capacity of the soil. Oxides compounds have high surface area per unit weight and have the capacity to co-precipitate or adsorb large amounts of any metal ions present in the associated aqueous phase. Gadde and Laitinen (1973) showed that lead is specifically adsorbed onto the hydrous ferric oxides and the extent of adsorption varies significantly with the pH and lead concentration. Also lead sorption steadily increased with pH up to pH 8.1. Swallow et al. (1980) found that ionic strength changes did not affect lead sorption onto ferric oxides unless the indifferent anion is chloride. Manganese oxides have also a high adsorption capacity for lead. The adsorption capacity of manganese is about 40 times greater than that of ferric hydrous oxides (Mckenzie, 1980). Ferric oxide effects on the lead adsorption will be discussed in PART II of the dissertation.

The pH of an aqueous solution is an important factor for adsorption of lead. Under acidic conditions, adsorption of lead is reduced considerably because of the competition between hydrogen ions and the lead ions for adsorption sites. Hydrogen ions are smaller than lead ions and are therefore more easily attracted to the active adsorption sites (Salim, 1983).

The amount of lead present in the aqueous phase is one of the driving forces that determine the adsorption and fate of lead in soil. Once the limited numbers of active sites are occupied, the rest of lead ions would either remain dissolved in solution or precipitate out depending on the aqueous phase conditions. Because lead ions may be retained in soil for a long time, treatment technologies will be needed for the decontamination of lead-contaminated soil.

EDTA Complexation with Metals in Soil

The six-coordinated complex compounds are by far the most prevalent forms of complexation compounds (Huheey, 1983). When hexadentate EDTA is introduced into soil, it may react with most metals present in soil. Based on the stability constants of metal-EDTA reactions (Table 2), ferric ion has the highest reactivity for EDTA ligand. Although the stability constants provide a good guide with regards to the metal reactivity with EDTA, the actual reactivities of the metal-EDTA reactions in soil are also influenced by the solubility of each metal.

Although much research has been conducted to investigate the fate of metals in soil, there is still much uncertainty with regards to the major metal species which control the solubility of the metal ions in solution. This is due in part to the many different forms of metal species which may be present in the soil system. Moreover, each soil will contain different amounts of metals. In addition, metal compounds in soil matrix may be distributed throughout the various fractions in soils such as exchangeable, organically bound, oxides bound and precipitated form. Approximate amounts of metal ions which partitioned into each faction of soil may be measured using sequential extraction methods (Miller et al., 1986, Tessier et al., 1979, Schuman, 1985). However, sequential extraction methods are not accurate and current surface analysis equipment are unable to determine the metal species present in soil. For these reasons, it is impracticable to estimate the solubility of metals from each fraction and the metal species present in soil. Many studies have been conducted to compare theoretical and experimental solubility relationships of metals in soils. As a result of that, it has been known that amorphous iron is the major ferric compounds controlling the solubility of ferric ions in soil (Norvell and Lindsay, 1982). Also, it has been shown that $CaCO_3$ (calcite) controls the solubility of Ca in alkaline soil (Lindsay, 1979). In calcareous soils, Mn solubility is controlled by $MnCO_3$ (rhodocrosite) for pe + pH values below 16 (Schwab and Lindsay, 1983) while in oxidized conditions, MnO_2 (pyrolusite) is the major Mn compound which controls Mn solubility (Lindsay, 1979). For other metals, the major metal compounds controlling the solubility in soil solution were obtained only by using theoretical thermodynamic data due to the limitations mentioned above. To overcome the restrictions, experimental approaches with actual soils have been undertaken to investigate the actual solubilties of metals in soil as a function of pH using competitive chelation method with EDTA or DTPA (diethylenentriaminepentaacetic acid). Since for these experiments, the metal species were not identified, new nomenclatures expressing the solubility of metals in soils such as soil-Mg and soil-Zn solubilities were used. Even though these solubility values were obtained experimentally with many different soil samples, their values could vary depending on the source of soil, metal sources, and soil solution properties. Unfortunately, these values are the only available data for metal solubility in soil unless the solid samples were prepared artificially. The solubilities of several different metals in soils are shown in Table 4.

Table 4. Metal solubilities in soils

reaction	log K ($\mu = 0.1$)	references
Soil-Fe + $3H^+ = Fe^{3+} + 3H_2O$	2.7	(Norvell and Lindsay, 1982)
Soil-Cu + $2H^+ = Cu^{2+}$	2.8	(Norvell and Lindsay, 1972, Lindsay, 1979)
Soil-Zn + $2H^+ = Zn^{2+}$	5.7	(Ma and Lindsay, 1990, 1993)
Soil-Mg = Mg^{2+}	-3.0	(Lindsay, 1979)

Several experiments and theoretical calculations have been done to investigate the heavy metal-EDTA equilibria in soils. Norvell and Lindsay (1969, 1972) reported that Mn solubility in soil is too low to form stable complexes with any common chelating agents such as EDTA. They also showed that when pure Zn-EDTA or Cu-EDTA solutions were introduced to several acid and calcareous soils at a pH less than 5.7, most Zn and Cu were precipitated out by substitution with Fe(III) ions present in the soil. Also, in calcareous soil for an equilibrium pH higher than 7.85, the Zn and Cu ions which were complexed with EDTA were partially substituted by Ca ions present in the soil. Norvell (1972) computed the mole fraction of applied EDTA associated with Ca(II), Mg(II), Al(III) and Fe(III) in soil for a pH range of 4 to 9. For the development of his stability diagrams, he assumed that $CaCO_3$ (calcite), soil-Mg and Al(III) hydrous oxides and amorphous Fe(III) hydrous oxides in soil, represented the activities of Ca(II), Mg(II), Al(III) and Fe(III), respectively. He showed that the applied EDTA was exclusively complexed with ferric ions for pH values less than 6.3 while for pH values above 6.8, Ca-EDTA was predominant. At pH range between 6.3 and 6.8, some competition for EDTA occurred between ferric and calcium ions. According to his computation, the maximum mole fraction of Al-EDTA was 0.0004 at a pH value of 6.5 and for Mg-EDTA, the mole fraction was constant at 0.1 for pH values higher than 8.2. Sommers and Lindsay (1979) extended the work of Norvell and developed metal-EDTA stability diagrams as a function of pH and redox potential for Ca(II), Mg(II), Zn(II), Cu(II), Mn(II), Pb(II), Al(III) and Fe(III). They used the same assumptions as Norvell (1972) and assumed that soil-Zn, soil-Cu, MnO_2 (pyrolusite), and $Pb_3(PO_4)_2$ represented the activities of Zn, Cu, Mn and Pb, respectively and that the sum of pe+pH value was 17 which represented slightly oxidized soil. Based on their computation, at a low pH value of 5, ferric ions complexed with about 80 % of the applied EDTA while slightly more than 10 % of the applied EDTA was complexed with Pb. The rest of the EDTA was complexed with other metals in the following order, Cu > Mn > Zn > Al > Ca > Mg. However, at neutral pH, the reactivity of metals to EDTA was changed. More than 90 % of the applied EDTA was computed to be complexed with Pb and about 5 % of the EDTA was complexed with Zn. Other residual EDTA were estimated to be complexed with the remaining metals in the following order, Ca > Cu > Mn > Fe. Based on these calculations, the mole fraction of Mg-EDTA and Al-EDTA were less than 10^{-4} which could be regarded as negligible. At a high pH value of 9, Pb may exclusively complexed with EDTA. The order for other metals complexed to EDTA is Ca > Zn > Mg > Cu > Mn > Fe. However, an earlier work by Ringbom (1963), also showed that at pH values less than 6, Fe ions were the most reactive metal ions in solution but for pH value higher than 7, calcium ions were found to complex with EDTA, reducing the amount of other metal complexes. Experimental work conducted by Brown and Elliott (1992) showed that for pH values higher than 6, lead extraction was decreased by the addition of calcium ions until pH 8 where the extraction efficiency of lead remained constant at about 30 % of the lead extraction efficiency at pH 6.

In summary, the computations of Sommers and Lindsay showed that at low pH values, Fe-EDTA complex is the predominant species while at high pH values, Pb-EDTA is the major complexed species in soil solution, even in calcareous soil, when the soil contains lead compounds. However, calculations done by Ringbom and the work done by Brown and Elliott, showed that calcium ions may compete with lead ions for EDTA resulting in a reduction of lead extraction efficiency.

Lead Extraction with EDTA

The solubility of free EDTA in water is approximately 0.2 % at 22°C. The solubility is very low compared to other salts of EDTA such as anhydrous disodium salt and tetrasodium salt which have a solubility of 10.8 % and 60 %, respectively. Free EDTA is not very soluble but will remain in solution in the presence of certain metals as a result of complexes formation. Most metal-EDTA complexes retain their ionic characters and cannot be extracted with water-immisible organic solvents (Deshpande et al., 1968). The stability constant (log k) for Pb-EDTA is 18.3 (Table 2), making EDTA an effective complexing agent with lead. EDTA has been shown to be highly effective in remediating lead-contaminated soils (Cline et al., 1993, Norvell, 1984). The factors affecting adsorption and precipitation as described earlier also affect the extraction of lead from lead-contaminated soils. Therefore, low pH, reducing conditions and high ionic strength may enhance extraction of lead from lead-contaminated soils. EDTA is a hexadentate chelate which forms a very stable coordination compound with lead which has a coordination number of six. One lead ion needs one EDTA molecule to form a Pb-EDTA coordinate compound.

pH of the extracting solution is an important factor as it affects the extraction efficiency of contaminated soil. Lead is generally more soluble under acidic conditions but decreases moderately as the pH becomes more alkaline. However, Elliott and Brown (1989) reported that the removal of lead using EDTA is not strongly pH-sensitive. They showed that when 0.04M EDTA solution was applied, the extracted amount of lead did not change much for pH values between 5 and 10. Even in the absence of EDTA, a substantial increase in lead recovery can be observed below pH 5. Lead is believed to be very mobile in acidic soil solution (Sheppard and Thibault, 1992). Filipek and Pawlowski (1990) showed that at low pH values, extractability increased considerably as a result of a decrease in organic and mineral colloid binding forces which in turn promoted metal leaching through the soil without the addition of EDTA. As the pH becomes more alkaline, the ability of chelants to enhance lead solubility decreased. A probable reason is that hydrolysis of metals with hydroxide ions may be favored over complexation by EDTA (Elliott et al., 1989). Elliott and Brown (1989) showed that for pH values less than 5 and with an EDTA:lead molar ratio of two, more than 90 % of lead was extracted from a lead-contaminated soil. Cline et al. (1993) showed that more than 80 % of lead may be extracted with EDTA from an artificially lead carbonate-contaminated soil. They showed that lead sulfate was slightly more resistant to EDTA extraction with an extraction efficiency of less than 70 %.

High ionic strength may reduce the adsorption of lead on soil matrix, therefore, increasing the ionic potential may enhance the remediation of lead-contaminated soils. Elliott et al. (1989) observed that high ionic strength of the solution may enhance lead extraction. Brown and Elliott (1992) noted that total lead recovery over the pH range of 5 to 9 increased in the presence of 0.5 M of monovalent cations. Temperature also affected the extraction efficiency of lead from lead-contaminated soil. Adams et al. (1988) showed that as temperature increased, more lead ions were separated from the solid phase. However, they concluded that EDTA is a very reactive chelating agent so that extraction under room temperature is effective enough to extract lead from lead-contaminated soils. According to Adams et al.'s results, high temperature is a favorable condition for both sorption and desorption with EDTA.

Most studies have used different reaction times for their extraction experiments: 24 hours (Cline et al., 1995) and 5 hours (Elliott and Brown, 1989). Kinetic studies conducted by Peters and Shem (1992) showed that the extraction of lead with EDTA was fast with steady-state conditions being achieved within one hour. However, it is noteworthy to point out that the soil used in their experiments were artificially contaminated. Therefore, reaction time may be different for different soils and solution conditions since lead may be adsorbed, co-precipitated out with iron and manganese on the soil surface or may be present in the soil pores. As presented above, most of the studies conducted thus far were focused on the extraction efficiencies of lead from soil and the studies were conducted using artificially contaminated soil except for the work done by Elliott and Brown (1989). The research presented here will attempt to address some of the current research deficiencies by conducting lead extraction experiments using actual lead-contaminated soils. Also, work will be done at unit Pb:EDTA stoichiometric ratios, to understand the effects of soil cations on lead extraction over a large pH range.

MATERIALS AND METHODS

Sample Characterization and Preparation

Soil samples from actual lead-contaminated sites were used for this research. Three samples were collected from Superfund sites in New Mexico and one sample was taken from a rifle range in Florida. One soil sample, oxidized glacial till, was artificially contaminated with lead. The three Superfund sites will be identified as Cuba, Cleveland and Cal-west. Cuba soil came from a lead smelter area while Cal-west soil was taken from a former battery recycling and smelter facility area. Cleveland soil came from an abandoned lead mining area. The rifle range soil sample was collected from a small arms firing range at Mayport, Florida. The oxidized glacial till was obtained from the geotechnical laboratory at Iowa State University, Ames, Iowa. All the soil samples were air dried, screened through sieve number 25 (0.707 mm) to remove large particles including lead pellet particles and organic debris before it was placed in non-metallic containers with screw caps.

The oxidized glacial till was contaminated with lead by mixing 200 grams of the soil sample with adequate amount of lead nitrate solution for 48 hours. The Pb-contaminated soil was air dried, ground and sieved with a number 25 sieve. The target lead concentration of the artificially contaminated soil was 2,500 ppm.

Each soil sample was characterized by measuring the soil pH, specific surface area, cation exchange capacity (CEC) and soil organic carbon (SOC). Soil pH was measured using an Accumet model 25 pH/Ion meter with a glass pH-indicating electrode and a calomel reference electrode. Soil-water ratio used for pH measurement was 1:2. Cations present in the soil such as Pb, Fe, Al, Mg, Mn, Ca, Cu and Zn were determined using Smith Hieftje 12 atomic absorption spectrophotometer after the soil samples have been acid digested. The total mass of cations present was assumed to be equal to the sum of the acid extracted cations (Pb, Fe, Al, Mg, Mn, Ca, Cu and Zn) which were assumed to be the dominant cations in soil. For Fe ions, oxalate extractable iron concentration was also measured and it will be referred to as amorphous iron for brevity in presentation.

The CEC of each soil was determined using the Polemio and Rhoades (1977) method. Five grams of air-dried soil were placed in a 50 ml polypropylene centrifuge tube and 30 ml of saturating solution (0.4N NaOAc-0.1N NaCl, 60% ethanol, pH 8.2) were added. The slurry was shaken for 5 minutes. The slurry was then centrifuged at 1000 rpm until the supernatant liquid was clear (about 5 minutes). The supernatant liquid was decanted and discarded. Fresh saturating solution was added and the slurry was again shaken for 5 minutes. After four successive equilibration and decantation of the supernatant, 30 ml of extracting solution (0.5 N of $Mg(NO_3)_2$) was added and was shaken again for 5 minutes. The slurry was centrifuged and the supernatant decanted into a 100 ml volumetric flask. The extraction step was repeated two more times with fresh extracting solution. The supernatants were then made up to a total volume of 100 ml with nano pure water. Sodium in the extracting solution was determined using the atomic absorption spectrophotometer and the Cl^- concentration was measured using the Argentometric method (Greenberg et al., 1992). CEC was calculated using the following equation:

$$\text{CEC in meq/100 g} = 2 \times \{(\text{Na in meq/liter}) - (\text{Cl}^- \text{ in meq/liter}) \times (\text{Na/Cl})_{\text{sat.sol}}\}$$

where $(\text{Na/Cl})_{\text{sat.sol}}$ is the Na/Cl ratio of the saturating solution as a unit of equivalent.

The basic assumption of this method is that the exchangeable sites were saturated with sodium and then substituted with magnesium ions releasing the sodium ions. Measurement of the released sodium ions per unit weight of used soil sample is the CEC. However, small amount of sodium may be carried over from the saturation solution into the extracting solution. The final term in the equation was adopted to correct the amount of sodium released from the soil.

The SOC of each soil was measured using the Walkley-Black method (Nelson et al., 1982). Five grams of each soil sample were placed in a 500 ml erlenmeyer flask. Ten ml of 1 N $K_2Cr_2O_7$ solution were added and stirred gently to disperse potassium dichromate solution in the soil followed by adding 20 ml of concentrated H_2SO_4. The slurry was shaken vigorously for 1 minute followed by 30 minutes of reaction time. After that, 200 ml of nano pure water was added to the flask and few drops of o-phenanthroline indicator were added. The solution was then titrated with 0.5 N $FeSO_4$ solution. To standardize the $Cr_2O_7^{2-}$ solution, a blank solution (without soil) was prepared and titrated. The organic carbon content was calculated according to the following equation, using a correction factor f = 1.30.

$$\text{Organic C (\%)} = \frac{(\text{meq } K_2Cr_2O_7 - \text{meq } FeSO_4)(0.003)(100)(1.3)}{\text{weight of soil (g)}}$$

where 0.003 is a unit transfer factor from meq to g.

The specific surface area of the each soil sample was measured using a method suggested by Carter et al. (1966). The soil samples were treated with H_2O_2 to remove organic matter using a method suggested by Kunze and Dixon (1986). Two grams of the prepared soil samples were placed on a previously weighed aluminum container. The container was placed in an oven and dried for 24 hours at 110°C. The dried container with soil was weighed and approximately 3 ml of reagent-grade ethylene glycol monoethyl ether (EGME) was added to form a soil-adsorbate slurry. The aluminum container was transferred into a desiccator and the desiccator was evacuated for 45 minutes using a vacuum pump. The dessicator was allowed to stand at room temperature for 6 hours and the vacuum was released. The weight of the aluminum can was determined immediately and the sample was placed back into the desiccator. This procedure was repeated until the container attained a constant weight. The specific surface area was calculated using the following equation:

$$\text{Specific surface area } (m^2/g) = \frac{\text{Weight of EGME}}{\text{weight of pretreated soil sample x } 0.000286}$$

where 0.000286 is the weight of EGME needed to cover monolayer on $1m^2$ of surface.

Extraction procedure

Three sets of extraction experiments were conducted to assess (i) the solution:soil mass ratio on lead extraction efficiency, (ii) the effects of EDTA:Pb stoichiometric ratio, and (iii) the effects of major cations on lead extraction efficiencies. A typical extraction procedure consists of placing 1 gram of soil in a 50 ml polypropylene centrifuge tube and after adding a measured volume of EDTA solution and diluted HNO_3 or NaOH solution into the centrifuge tube for pH adjustment purposes, the slurry was shaken with a Burrell wrist-action shaker for up to 7 days. The sample was then centrifuged for 30 minutes at 3,000 rpm followed by filtration using 0.45 μm membrane filter paper to separate the solution from the soil. The pH of the filtrate was measured and adequate amount of the filtrate was extracted and preserved in a 100 ml volumetric flask with 5 % (v/v) nitric acid. Major cation concentrations mentioned earlier were then analyzed using an atomic absorption spectrophotometer. Separate experiments using nano pure water at different pH values, adjusted with diluted HNO_3 or NaOH solution, were conducted to check the solubility of metals in water.

To assess the solution:soil mass ratio on lead extraction efficiencies, the volumes of EDTA solution used were 3, 5 and 10 ml giving solution:soil mass ratios of 3, 5 and 10, respectively while the mass of soil used was 1 gram. Two types of soils, rifle range soil and artificially contaminated oxidized till were used for these experiments.

For the experiments to study the effects of EDTA:Pb stoichiometric ratio, applied EDTA concentration varied from 0.0001 to 0.2 M giving an EDTA:Pb stoichiometric ratio of 0.1 to 100. All five soils were used to study the impact of EDTA:Pb stoichiometric ratio on lead extraction efficiency.

To study, the effects of major cations on lead extraction efficiency, the concentration of EDTA used was up to 0.005 M giving an EDTA to lead stoichiometric ratio close to one. The EDTA solution was selected so as to prevent an underestimation of the metals with low concentrations in soil and to control the extracted amount of major cations. In addition, optimization of EDTA usage would require the minimum amount of EDTA needed to maximize lead extraction and yet be not affected by competing cations. Measurement of the major cations extracted will provide information on the influence of various cations and lead species on the optimum EDTA concentration needed for lead extraction.

RESULTS AND DISCUSSIONS

Selective properties and the major cations concentrations of lead-contaminated soils used in this research are shown in Table 5. All the soil samples except for Cleveland soil has a soil pH approximately 8. Cleveland soil is acidic with a pH of 2.68. In addition, Cleveland soil has a high amorphous iron content (31,720 mg/kg) and calcium content (103,900 mg/kg) while the other soils have low amorphous iron content (between 300 - 500 mg/kg) and calcium content of 7,000 to 20,000 mg/kg. The lead content in Cal soil was 13,260 mg/kg which is expected of a battery recycling facility. The rifle range soil has a lead content of approximately 6,600 mg/kg of which some of the lead may be fine lead fragments from bullets.

Lead extraction efficiencies for different soil:solution ratios and EDTA:Pb stoichiometric ratios are presented in Figure 9 and 10 for the oxidized till soil and the rifle range soil, respectively (Bold lines are drawn in Figure 9 and Figure 10 and subsequent Figures to assist reading of the graphes unless stated). Extraction time for these experiments was 24 hours. These figures demonstrate that the ratio of soil to EDTA solution (on a mass basis) used in the experiments has no effect on the extraction of lead from both contaminated soils but instead was dependent on the quantity of EDTA present even for a soil:EDTA solution ratio as low as 1:3. It is interesting to note that the extraction efficiency for the rifle range soil was gradual for higher EDTA:Pb stoichiometric ratio while for the artificially contaminated oxidized till soil, the change in extraction efficiencies seem to be quite steep for a small change in the EDTA:Pb stoichiometric ratio. Since wastewater generated from the extraction process should be treated before disposal, reducing the volume of wastewater would reduce the treatment costs and may make soil washing a more economical technology.

Figure 11 shows that the results of the lead extraction from actual lead-contaminated soils and the artificially contaminated oxidized till for Pb:EDTA stoichiometric ratios of between 0.1 and 100 and over a 24-hour extraction period. The extraction time of 24 hours was used for this set of experiments because most research in the literature reported an extraction time of 24 hours or less. In addition, all extraction experiments were conducted without pH

Table 5. Soil properties and major cations concentrations of lead-contaminated soil samples

Sample	% Organic Carbon	CEC (meq/100g)	Specific Surface Area (m^2/g)	pH	Pb	Fe*	Mn	Al	Ca	Mg	Cu	Zn
					(ppm)							
Cal	2.52	17.51	15.39	8.13	13,260	316	2,820	14,330	12,410	5,270	30	86
Cuba	2.26	17.84	37.33	8.55	4,180	544	384	25,940	19,580	6,780	129	1,860
Rifle	0.18	5.75	0.66	8.47	6,238	328	21	2,440	7,450	436	279	70
Cleveland	0.10	4.32	4.41	2.68	1,247	31,720	91	707	103,900	115	557	1,078
Oxidized**	0.75	11.61	9.68	8.16	2,413	-	-	-	-	-	-	-

* amorphous iron concentration

** major metal cations were not measured

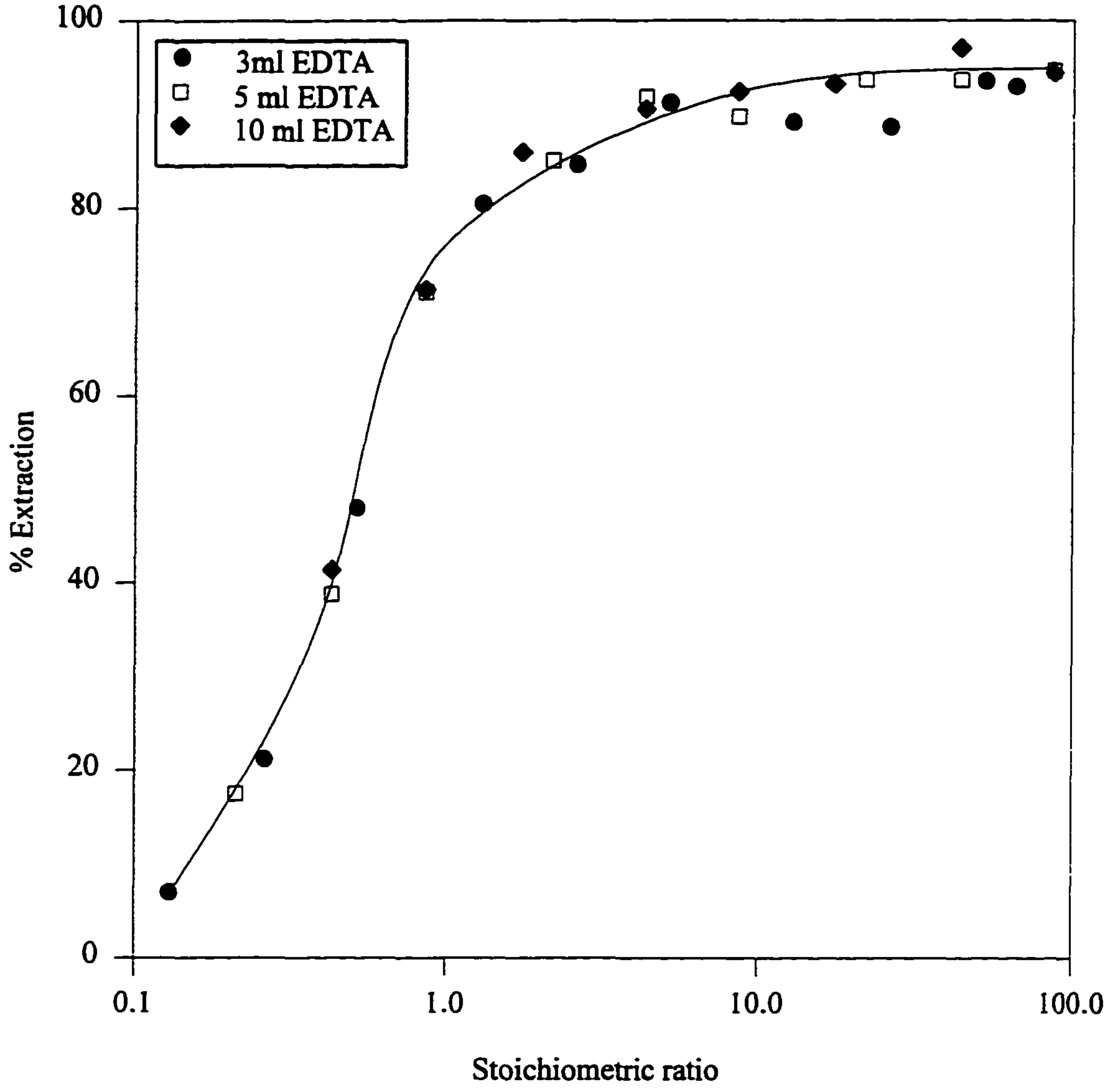


Figure 9. Stoichiometric and volume ratio effects on lead extraction with artificially contaminated oxidized glacial till

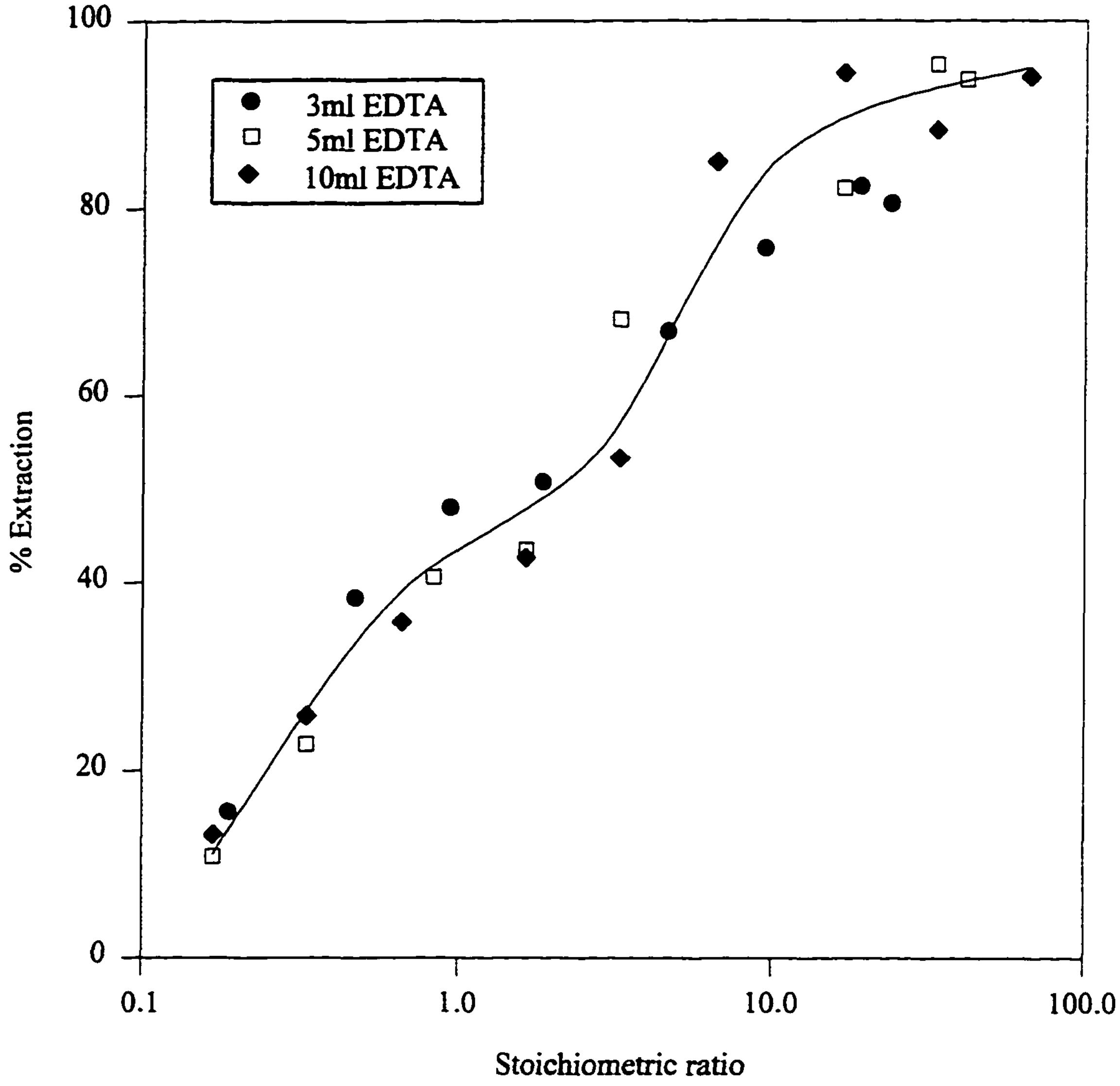


Figure 10. Stoichiometric and volume ratio effects on lead extraction with rifle range soil

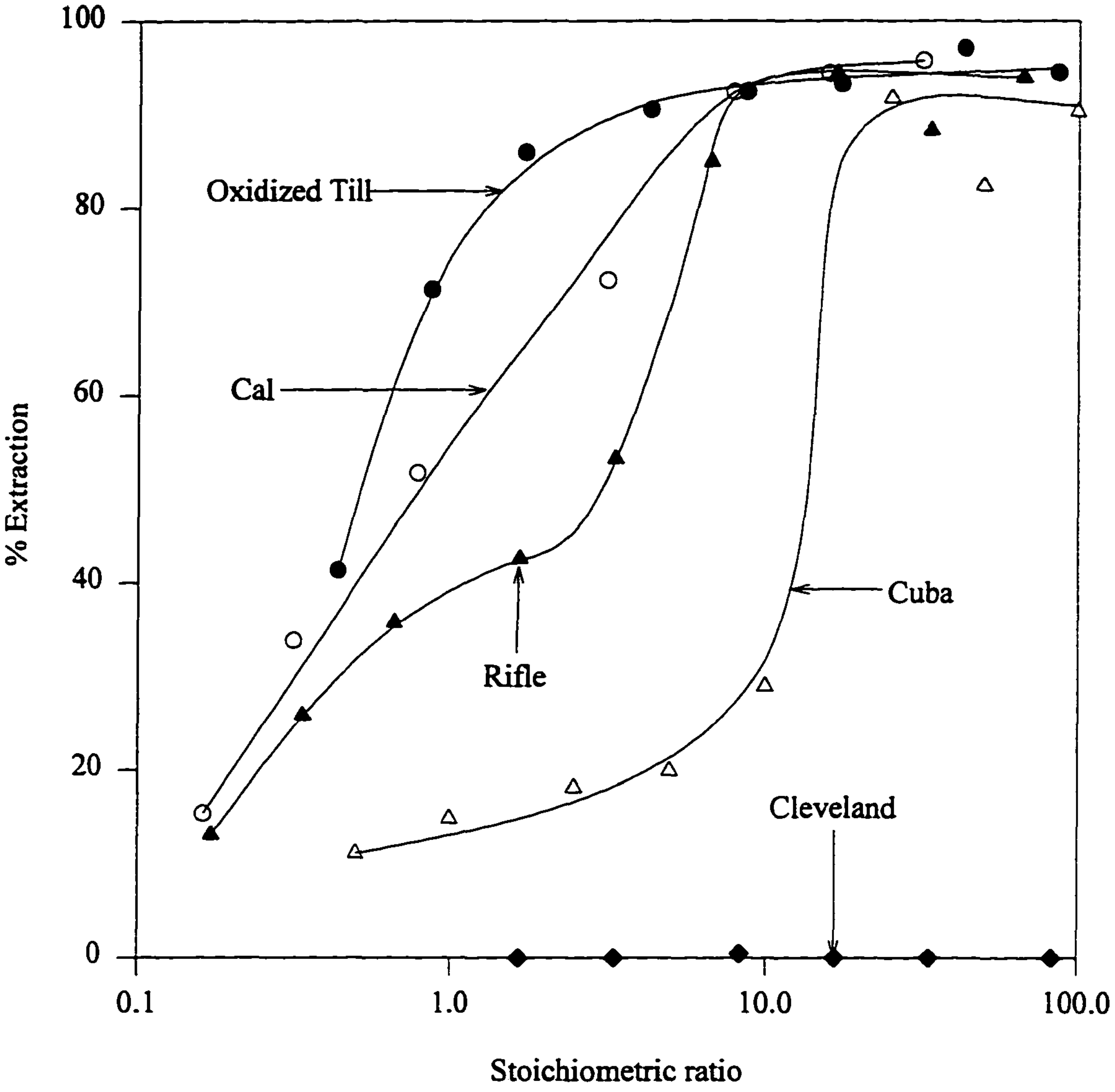


Figure 11. Lead extraction from different lead-contaminated soil using 1 gram of soil with 10 ml of different EDTA solution

adjustment. This figure demonstrates that lead extraction efficiency for each soil was different and that lead extraction was a function of the stoichiometric ratio of the applied EDTA concentration to total lead concentration in the soil sample. However, if sufficiently large amount of EDTA was applied, all the lead may be extracted for certain soils. Figure 11 shows that for a unit stoichiometric ratio of EDTA to total lead concentration, about 80 % of lead from artificially contaminated oxidized glacial till soil were extracted. Approximately 55 % of lead from Cal West soil, about 40 % from a Rifle range soil, about 10 % from Cuba mill soil were extracted while none of the lead was extracted from Cleveland soil.

The different lead extraction efficiency for different soils at unit stoichiometric ratio of the applied EDTA to the Pb may be due to the different soil and solution properties such as cations present in soil and dissolved in the solution, and lead species present in the soil sample. EDTA is a nonspecific chelating agent and therefore will react with metal ions other than lead. Because each metal ion has different reactivity with EDTA, the competition between lead ion and other metal ions is dependent on the dissolved concentration of the specific metal ion and the stability constant between the specific metal ion and EDTA.

As shown in Figure 11, EDTA concentrations above unit stoichiometric requirement would be needed for most soils to maximize lead extraction. For example, an EDTA:Pb stoichiometric ratio of at least 7 is needed to achieve over 90 % lead extraction efficiency for the oxidized till soil while a stoichiometric ratio of at least 25 was needed for the Cuba soil. Among the actual lead-contaminated soils, lead extraction from Cal soil seemed to be easier than the other three lead-contaminated soils. Lead was extracted more efficiently from the rifle range soil than the Cuba soil. The results shows that although EDTA may easily extract lead from lead-contaminated soils, for certain types of soils extraction may be inhibited. It should be noted that although artificially contaminated soil may facilitate consistency in the soil samples needed for experimental purposes, extraction of artificially contaminated soil tends to be much easier than actual lead-contaminated soils.

In the case of Cleveland soil, lead was not extracted at all with very high stoichiometric ratio of EDTA to Pb (up to 300 EDTA:Pb stoichiometric ratio) within 24 hours extraction time. The possible reasons are that the applied EDTA may completely precipitated out due to the low pH value of the soil or may react with the dissolved iron ions as seen by the high amorphous iron of the Cleveland soil (Table 5) or that the lead was occluded within the different oxides in the soil matrix. Another possible reason is the type of lead species present such as lead sulfide which has very low solubility. Figure 12 shows the molar amount of extracted metals from Cleveland soils with water and 0.005 M EDTA (EDTA:Pb ratio = 8.3) without pH adjustment. The pH of the solutions were 3.15 for 0.005 M EDTA solution and 2.70 for water. This figure shows that significant amount of iron was extracted with 0.005 M EDTA solution - the amount of iron extracted was approximately equal to 90 % of the applied molar amount of EDTA. For calcium, the extracted molar amount with water and EDTA was about 3 molar times higher than the applied EDTA. The extracted Zn, Cu, and Mg with water were slightly more than the 0.005 M EDTA solution. This may be due to the low pH of water. Lead was not extracted at all with both water and 0.005 M EDTA solution. It is probable that the overwhelming presence of amorphous iron and calcium may play an important role in suppressing lead extraction at low pH values.

When 0.2 M EDTA solution (EDTA:Pb ratio = 330) was applied to Cleveland soil for up to 15 days, approximately 10 % of the lead was extracted. The pH of the solution was 4.3. Figure 13 presents the lead and iron extraction efficiency over time. Lead was not extracted at all over a 24-hour period with 0.2 M EDTA solution. Lead and iron extraction seemed to reach a steady state value after 13 days. As more iron was extracted, more lead was extracted. A possible reason for this observation is that lead ions may be strongly adsorbed or occluded in the iron preventing lead ions from complexing with the applied EDTA. Therefore, only after iron was dissolved, lead was available for complexation with the available EDTA. The fact that the lead extraction reached a constant concentration when iron extraction also reached a constant value may provide evidence testifying to this reason.

A separate experiment was conducted with Cleveland soil using 0.2 M EDTA in which the solution pH was controlled at a pH value of 8.7. For this experiment, lead was not extracted at all after 24 hours. At this pH, the effects of iron with EDTA will be minimized (Part II will discuss the amorphous Fe effect on Pb extraction) but yet no lead was extracted. It is also probable that the lead species in Cleveland soil has very low solubility such as PbS

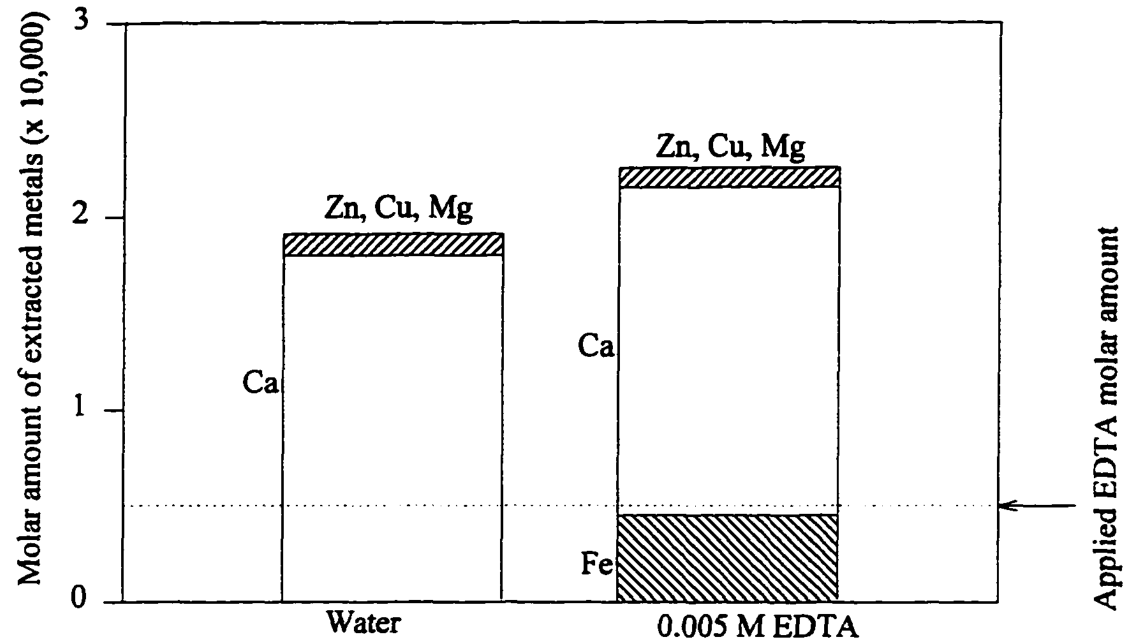


Figure 12. The molar amount of extracted metals with water and 0.005 M EDTA solution at pH value of 3.15 for EDTA and 2.7 for water

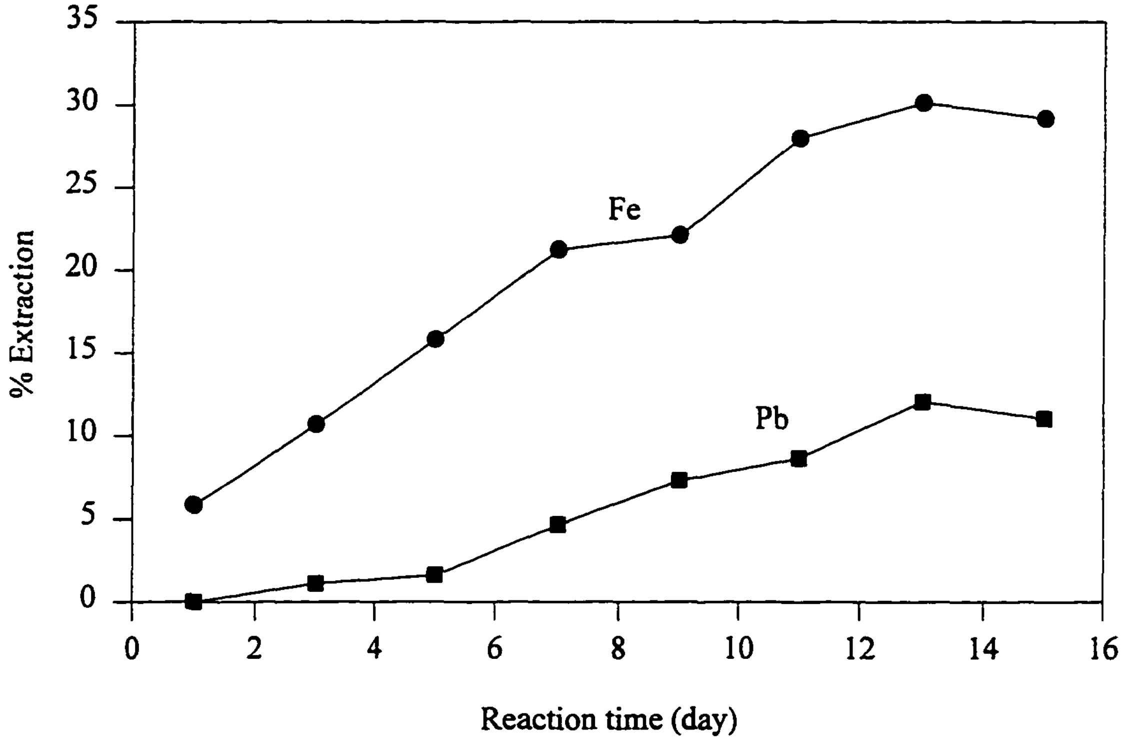


Figure 13. Lead and amorphous iron extraction from Cleveland soil with 0.2 M EDTA solution over time

which requires a long time to complex with EDTA. Work done by Clevenger et al. (1991) showed that EDTA solubilized pure lead species in a reaction period of 1.5 hours except for lead sulfide where only 4 % of the lead sulfide was complexed with EDTA. The extraction results of Cleveland soil appeared to suggest that lead species in the lead-contaminated soil may affect lead extraction along with the presence of certain types of cations such as ferric ions in soil.

Figure 14 shows the lead extraction efficiencies of Cal soil, Cuba soil and the rifle range soil with water and different EDTA concentrations (0.005 M, 0.002 M, 0.003 M, respectively), and different reaction times. The EDTA:Pb stoichiometric ratio were 0.78 for Cal soil, 1.0 for Cuba soil and 1.0 for a rifle range soil. This figure shows that the Pb could be dissolved in water for a pH value less than 6 depending on the soil type. Lead species which dissolved in water at pH value of 4 are believed to be the relatively soluble water species such as lead carbonate and lead oxides compounds. The solubility diagrams shown in Figure 1 and 2 may explain the solubility of lead in water from lead-contaminated soils.

For Cal soil, the percent lead extraction at pH 6 was 78 % which was similar to the EDTA:Pb stoichiometric ratio applied. This may imply that for Cal soil, most of the applied EDTA appeared to be complexed with lead at pH 6. But for pH value less than 6, the extraction efficiency of lead was slightly lower. This may be due to the effects of other major cations such as Fe ions competing with lead ions for EDTA ligand sites. For Cuba soil, with a unit stoichiometric ratio of EDTA solution, only 50 % of lead in soil was extracted in 24-hour for pH values less than 6. For the rifle range soil, at pH value less than 6, the amount of lead extracted was from 60 % to 80 % but steady state conditions were not achieved within the 24-hour reaction time.

For a 7-day reaction time and for pH values less than 6, there was no difference in lead extraction efficiency from Cal and Cuba soil compared to the extraction efficiency for 24 hours. However, for the rifle range soil, lead extraction increased up to approximately 90 % in 7 days. For pH values above 6, 24 hours of reaction time was not enough to reach steady state for all three soil tested. For a 7-day reaction, lead extraction efficiency of Cal soil increased significantly over a pH range of 6 to 9 to approximately 78 %. For pH values

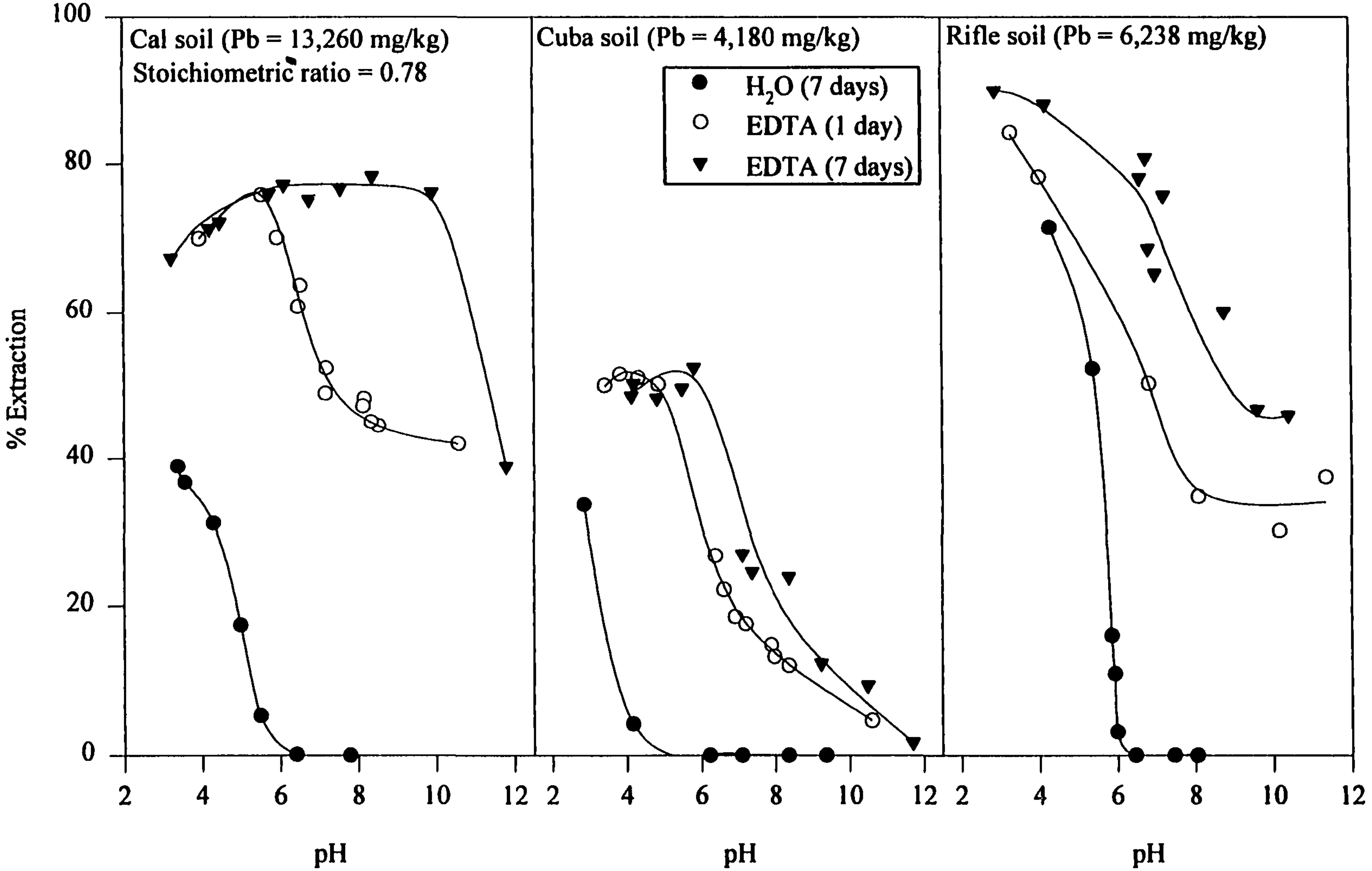


Figure 14. Lead extraction efficiencies of three different soil samples with water and EDTA solutions and different reaction times-EDTA:Pb stoichiometric ratio = 0.78 for Cal soil and 1 for Cuba and Rifle soils

higher than 9, lead extraction efficiency was reduced sharply. A probable reason for the lower extraction efficiency was that the higher hydroxide concentration at high pH values may result in the formation of lead hydroxide compounds of low solubility. In the case of Cuba soil, the lead extraction efficiency increased by approximately 10 % while lead extraction efficiency for the rifle range soil increased by about 20 % for pH values between 6 and 10. Based on the lead extraction efficiencies shown in Figure 14, lead in Cal soil was more easily extracted than the rifle range soil and Cuba soil. The probable reasons were that lead compounds in Cal soil may be easily dissolved as compared to the lead compounds in the rifle range soil and Cuba soil or may be located where the lead was easily exposed to the applied EDTA. Among the fractions present in soil, EDTA can complex with lead partitioned to exchangeable, organically bound and oxide absorbable fraction of the soil. However, metals located inside oxide compounds may not complexed with EDTA unless the coated materials were dissolved first (Elliott, 1989). These oxides may exist as connectors between metal particles or act as adsorbent for metal ions. These oxides may coat the metal ions reducing the possibility of reaction between the metals ions and solutes present in solution (Jenne, 1968). For example, Elliott et al. (1989) and Borggaard (1979) showed that the complexation of Fe and Mn oxides with EDTA was kinetically limited at high pH values due to low solubility. In addition, estimations made by Sommers and Lindsay showed that Fe and Mn oxides were compounds with very low reactivity with EDTA at pH values above 7. Therefore, if lead were occluded by these oxides compounds, it can be expected that lead extraction would be restricted unless the oxides dissolved first. Although measurement of the Fe and Mn oxides were not made due to the detection limitation of analytical equipment, this possible reason should not be excluded for the lower lead extraction efficiency at high pH values.

Figure 15 shows the Fe extraction efficiencies for the three different lead-contaminated soils while Mn extraction efficiencies for Cal and Cuba soils are shown in Figure 16. For the rifle range soil, the Mn concentration in soil was too low to provide any appreciable change in the final extraction solution. Based on these figures, percent extraction of iron and manganese was higher for low pH values. Consequently, as Fe and Mn were dissolved, at

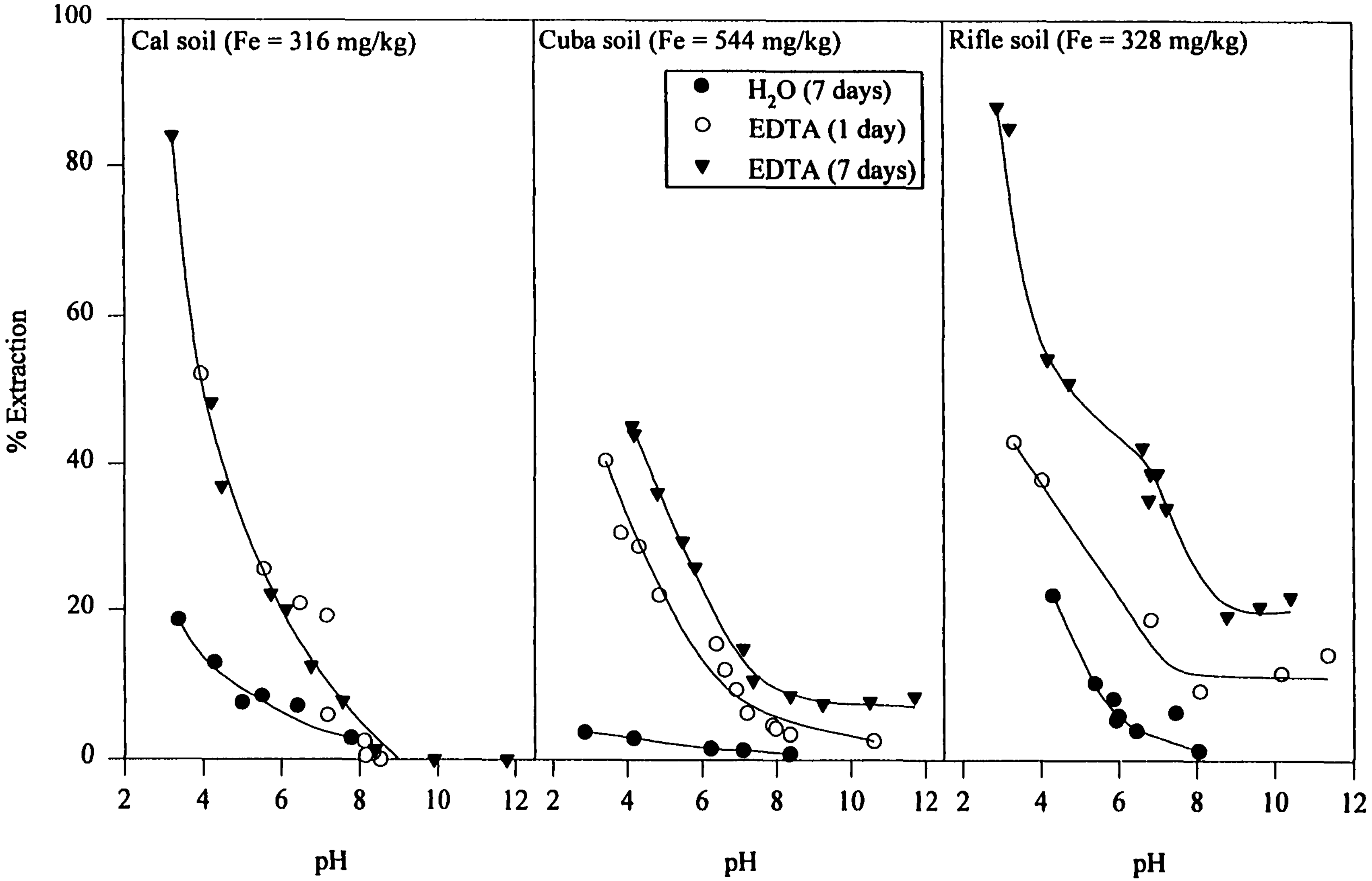


Figure 15. Amorphous iron extraction efficiencies of three different soil samples with water and different reaction times EDTA concentrations were 0.005M, 0.002M and 0.003M for Cal, Cuba and Rifle soils, respectively

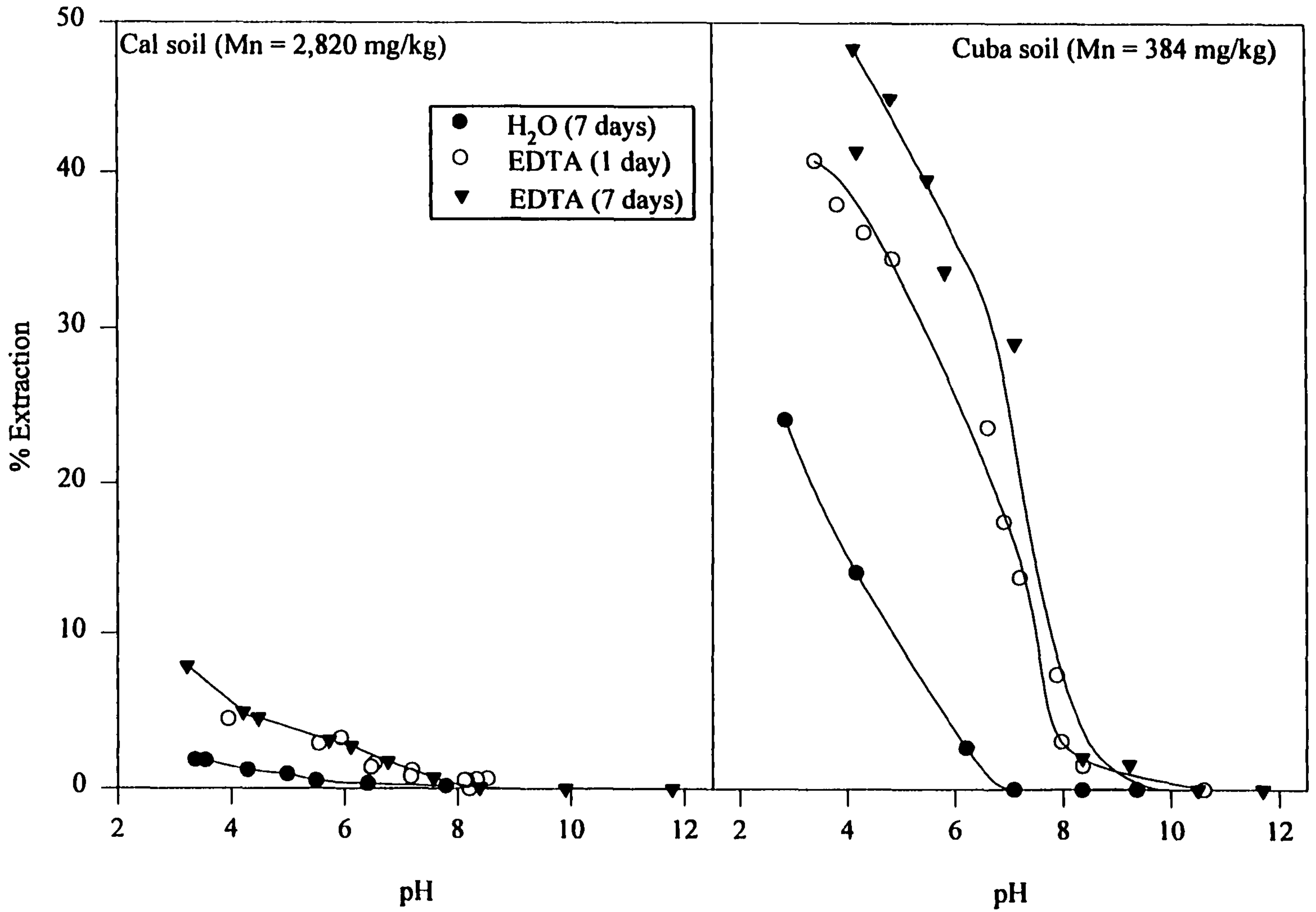


Figure 16. Manganese extraction efficiencies of three different soil samples with water and different reaction times EDTA concentrations were 0.005M and 0.002M for Cal and Cuba soils, respectively

low pH values, lead ions occluded by ferric and manganese oxides could be complexed with EDTA. As pH increases, the extracted amount of these oxides decreased rapidly due to low solubility. For Cal soil, the extraction of Fe and Mn with EDTA reached a steady-state value after 24 hours. In contrast, the molar amount of lead extracted in Cal soil continued to increase over the 7-day reaction time. Based on this observation, it may be speculated that in Cal soil, negligible amounts of lead might be associated with ferric and manganese oxides. Therefore, ferric and manganese oxides might not have affected lead extraction for pH values higher than 7 resulting in lead extraction efficiency similar to the EDTA stoichiometric ratio even for pH value up to 9.

Unlike Cal soil, the molar amount of extracted lead from Cuba soil over a 7-day reaction period did not increase much when compared to the 1-day extraction time. Similar observations were made with the molar amount of extracted Fe and Mn from Cuba soil over 1-day and 7-day reaction time. Based on the experimental results, lead extraction from Cuba soil might be partly affected by ferric and manganese oxides especially at high pH values. As for the rifle range soil, the lead extraction efficiencies were between the extraction efficiencies of Cuba and Cal soils. The difference in iron extracted from one day to seven days was much more than the difference in iron extracted over six days for both Cal and Cuba soil. This larger difference was reflected in the difference in the amount of lead extracted from one day to seven days. Since the Mn concentration in the rifle range soil was low, it is probable that ferric oxides affected lead extraction in rifle range soil. Based on the experimental results, it appeared that dissolved iron ions may compete with lead for pH values less than 6 and that Mn and Fe oxides may play role in lead extraction from lead-contaminated soil for pH >7.

Calcium and magnesium extraction from the lead-contaminated soils are shown in Figure 17 and 18. For pH values less than 5, most of the calcium in the three contaminated soils was extracted with water. For pH > 8, no calcium was extracted with water. For magnesium, relatively small amount was extracted with water as compared to calcium ions for all three soils. Like calcium, magnesium was not extracted with water for pH values greater than 8.

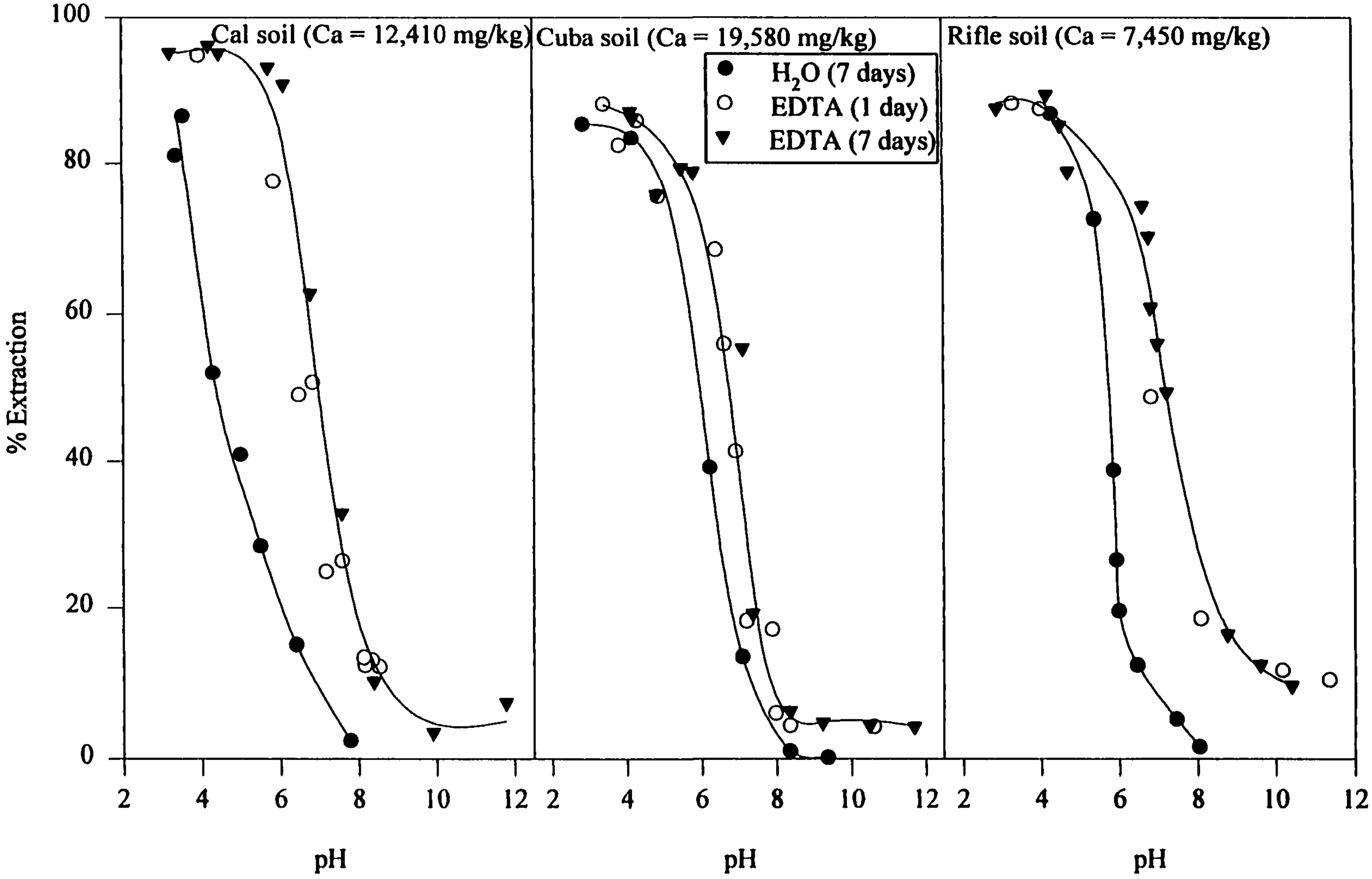


Figure 17. Calcium extraction efficiencies of three different soil samples with water and different reaction times EDTA concentrations were 0.005M, 0.002M and 0.003M for Cal, Cuba and Rifle soils, respectively

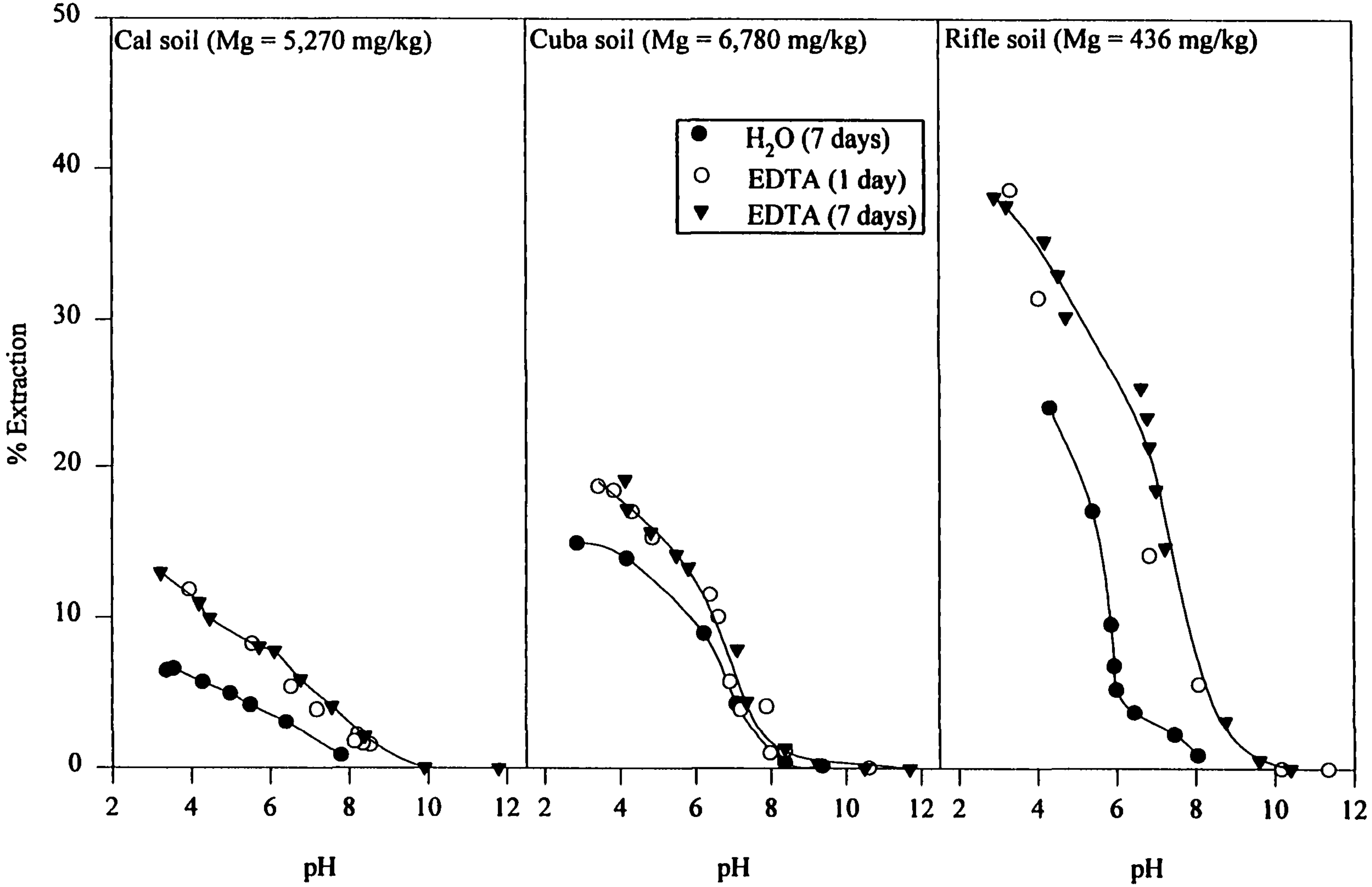


Figure 18. Magnesium extraction efficiencies of three different soil samples with water and different reaction times EDTA concentrations were 0.005M, 0.002M and 0.003M for Cal, Cuba and Rifle soils, respectively

When EDTA solution was applied, the extracted amount of both Ca and Mg were higher than the applied EDTA. The difference between the molar amount of extracted calcium with EDTA and water from the three soils were as much as 20 times higher than the molar amount of the applied EDTA for pH values between 6 and 10. Although the dissolved amount of Mg was relatively much lower than Ca, significant amounts of Mg was dissolved with the addition of EDTA for pH values up to 10. The estimation done by Sommers and Lindsay (1979) and Ringbom (1963) showed that Mg was the less reactive metal ion with EDTA when compared with Pb, Fe, Mn, Cu and Ca for pH values between 4 and 9. The experimental results obtained appeared to suggest that the addition of EDTA has changed the solution properties considerably resulting in an increase in the dissolution of major metals. The specific mechanism for the dissolution is probably unknown. The dissolution of metals would result in a corresponding increase in anion concentrations. It is probable that the released anions may form soluble ion pair complexes with the dissolved metals. For example, Ca and Mg easily form ion pairs with phosphate anions, carbonate anion and SO_4^{2-} ion while Mn also forms ion pairs with HPO_4^{2-}, CO_3^{2-} and SO_4^{2-} ions in solution (Bohn et al., 1985). Another possible reason for high Ca and Mg extraction by adding EDTA is that the Fe and Mn oxides and hydroxides compounds which were dissolved by EDTA have very high adsorption capacity of other metals. Therefore, solubilizing the Fe and Mn oxides increase the solubility of adsorbed metals.

Both magnesium and calcium extractions were not depend on the reaction time. These dissolved Ca and Mg ions may have an effect on lead extraction for high pH values due to competition with lead ions for ligand sites on EDTA. Ringbom (1963) computed the reactivity between several metals ions and EDTA which showed that calcium ions may compete with lead ions for high pH values with the maximum effects for pH values higher than 12. In contrast, Sommers and Lindsay (1979) estimated that lead in soil has higher reactivity with EDTA than calcium carbonate at high pH values. Experimental work conducted by Brown and Elliott (1992) showed that the extraction of lead from battery recycling site soil was reduced when calcium salt was added to the EDTA solution for pH values higher than 6. This reduction effect appeared to increase for higher pH values. They also showed addition of magnesium could reduce lead extraction for pH values higher than 6 but the effect was not as strong as that of calcium ions. It is therefore, probable that for high pH values, calcium released by EDTA may compete with lead ions for EDTA ligand sites.

Figure 19 and Figure 20 show the extraction of copper and zinc from Cuba and rifle range soils. Cuba soil has a significant amount of zinc and both Cuba and the rifle range soils have small amount of copper (Table 5). In the case of copper, the molar amount of extracted copper from both soils were not dependent on the reaction time, i.e., steady state values were obtained after 24 hours of reaction time. It is probable that copper was not occluded by ferric and manganese oxides. However, for Zn in Cuba soil, the extracted molar amount was dependent on the reaction period making it likely that part of the zinc in soil matrix was occluded with ferric and manganese oxides. Estimation made by Sommers and Lindsay (1979) showed that lead in soil was more reactive with EDTA than copper and zinc over most pH range. The aqueous computation done by Ringbom (1963), however showed that copper has a slightly higher reactivity with EDTA than lead while zinc is less reactive with EDTA than lead for pH range between 4 and 10. Based on the calculations done by others and since it is impractical to determine the major species of zinc and copper present in the soils, it is probable that Cu and Zn ions may compete with lead ions for EDTA ligand sites depending on the specie of metals in soil.

To illustrate the probable competitive effects of metal ions with Pb ions, the results presented in Figure 21 to 23 will be summarized by adding the molar amount of metals extracted for both pH 4.5 and pH 7.0. At the pH value of 4.5, the reactivity order for EDTA is as follows: Fe > Pb > Cu > Zn >Mn > Ca > Mg while at neutral pH the reactivity decreases as follow: Pb > Zn > Cu > Ca > Mn > Fe > Mg (Sommers and Lindsay, 1979 and Norvell and Lindsay, 1969). The plots in Figure 21 and 23 will follow the above orders with the most reactive metal ions at the bottom of the stack followed by the second most reactive and so forth.

Figure 21 shows that the molar ratio extraction of metals to EDTA for Cal soil at pH value of 4.5 and 7. The extracted amount of lead at pH 7 was slightly higher than the amount of lead extracted at pH 4.5. It is interesting to note that the sum of molar amount of lead and

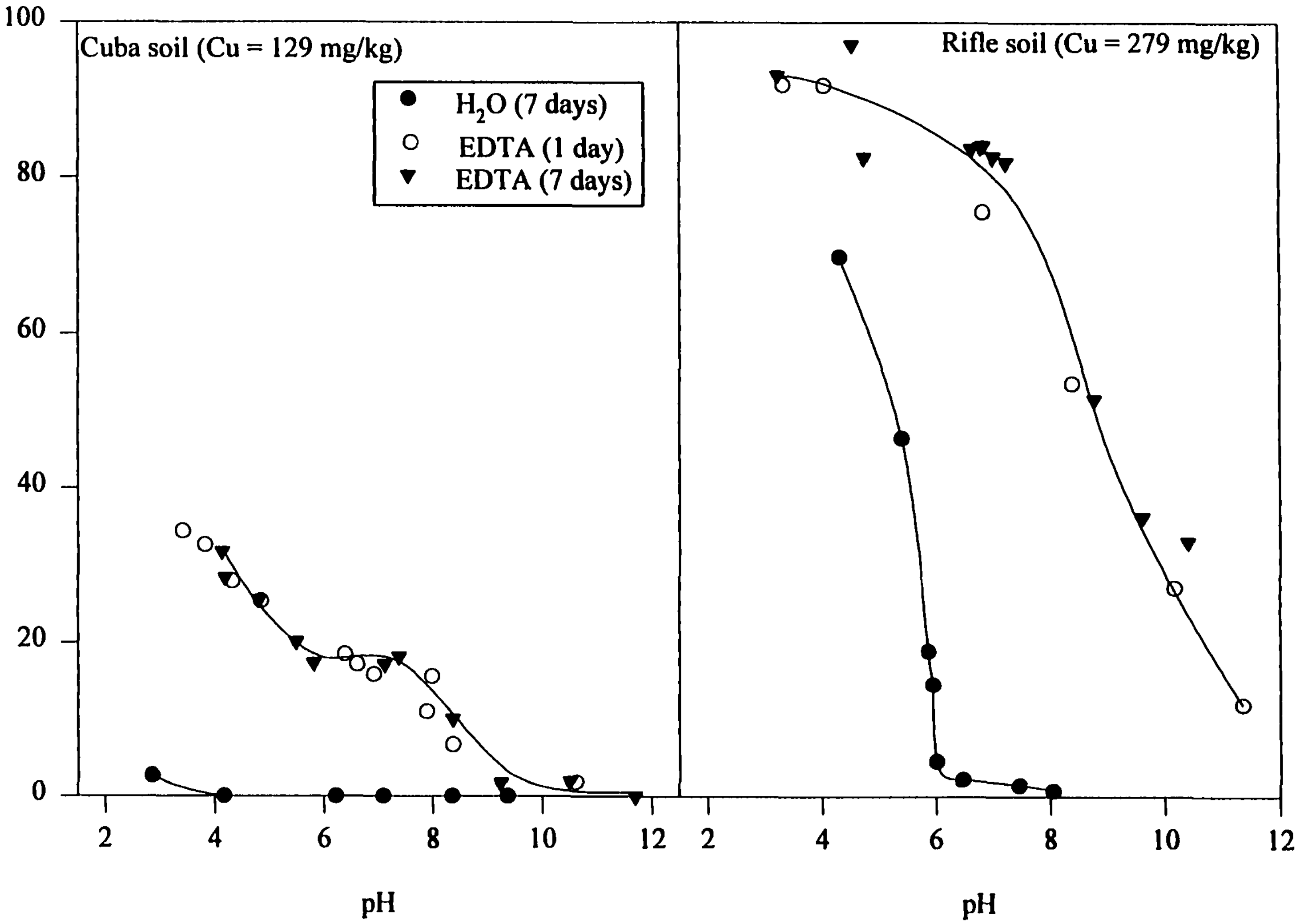


Figure 19. Copper extraction efficiencies of three different soil samples with water and different reaction times EDTA concentrations were 0.002M, and 0.003M for Cuba and Rifle soils, respectively

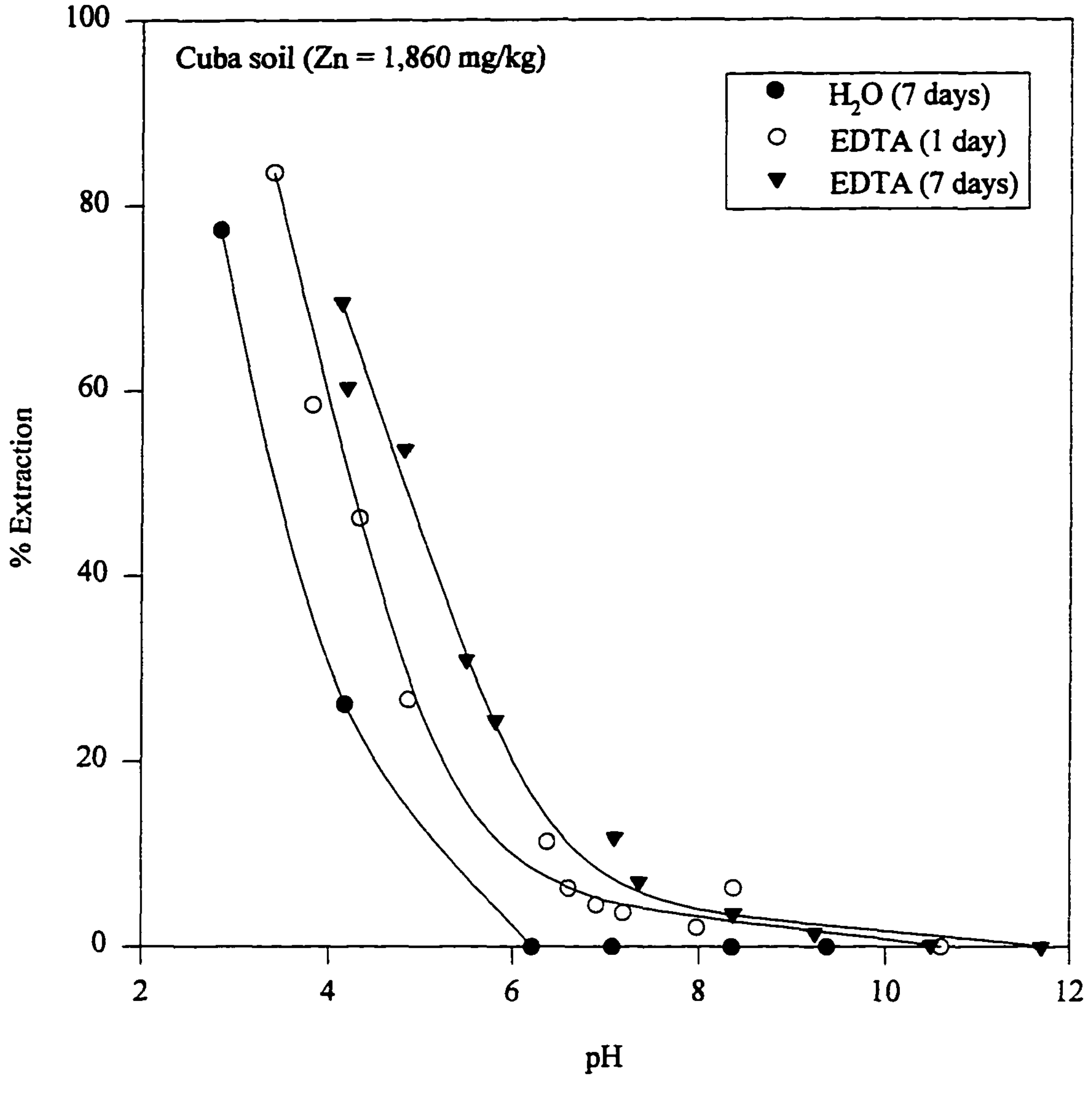


Figure 20. Zinc extraction efficiencies of Cuba soil with water and 0.002M EDTA solution with different reaction times

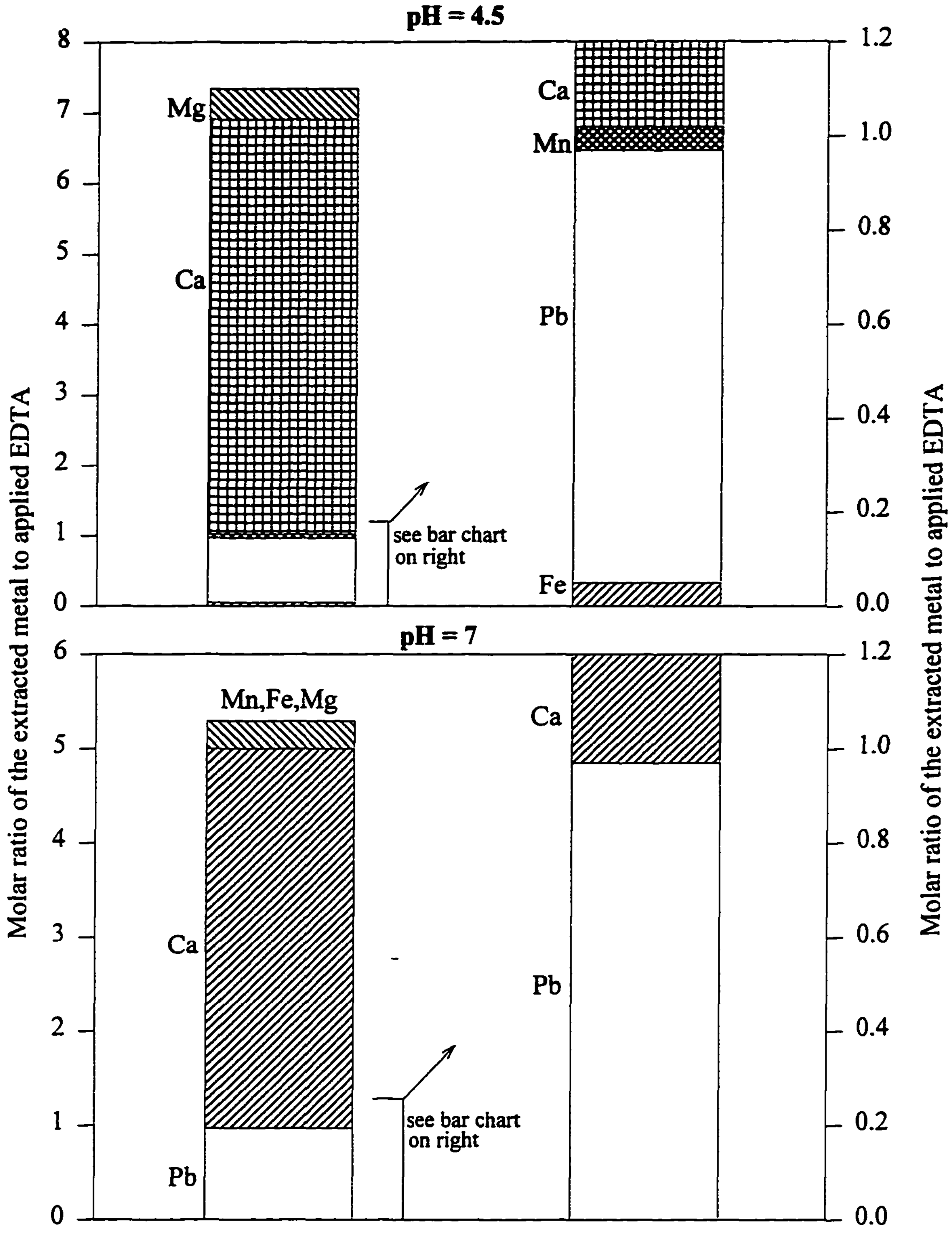


Figure 21. The molar ratio of the extracted metals to EDTA at pH values of 4.5 and 7 from Cal soil

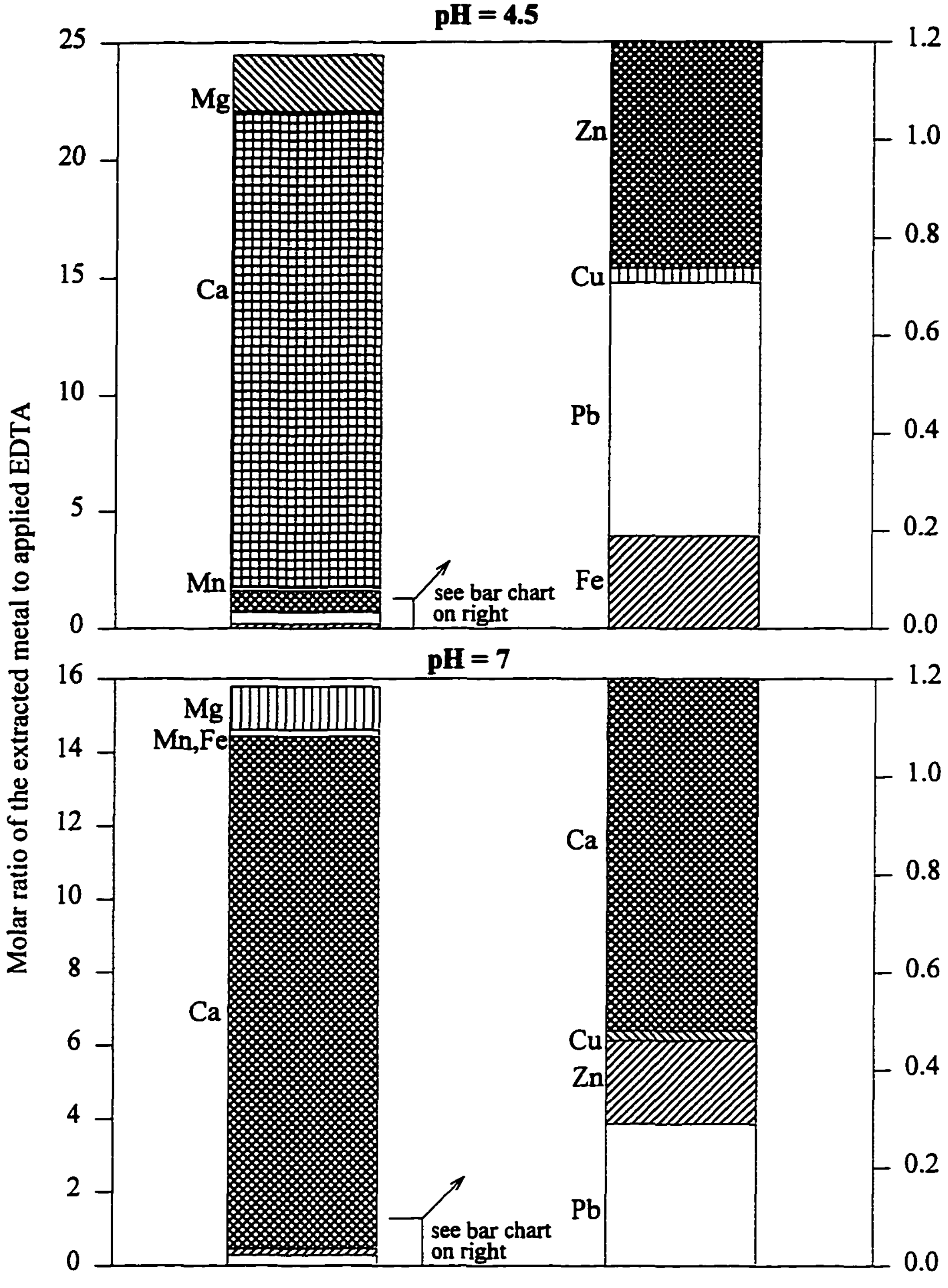


Figure 22. The molar ratio of the extracted metals to EDTA at pH values of 4.5 and 7 from Cuba soil

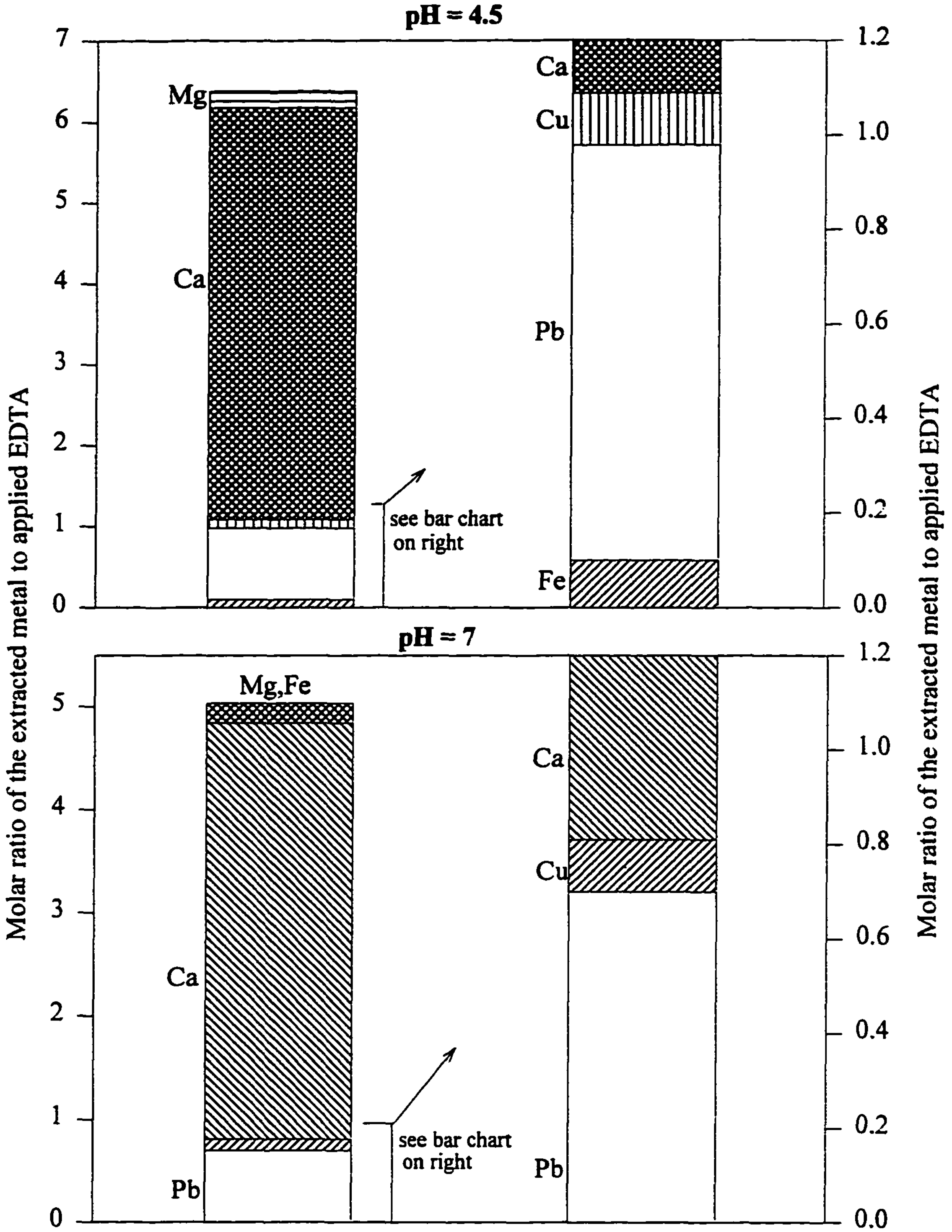


Figure 23. The molar ratio of the extracted metals to EDTA at pH values of 4.5 and 7 from Rifle soil

iron extracted at pH 4.5 was same as the molar amount of lead at pH of 7 which is equal to the amount of EDTA applied. This could mean that at pH 4.5, the dissolved iron competed with lead ions for EDTA ligand sites. At pH 7, lead has the highest reactivity and therefore, the molar amount of lead extracted could be equal to the molar amount of EDTA applied. As expected, the extracted amount of Fe and Mn would be lower at high pH values.

Figure 22 shows the molar ratio of the extracted metals to the applied EDTA for Cuba soil at pH values of 4.5 and 7. At pH 4.5, only half of the applied EDTA seemed to be complexed with lead. Based on the order of reactivity of metals with EDTA, competition between lead and dissolved metal ions such as Fe, Cu, and Zn for EDTA ligand sites may be a reason. Fe molar amount was about 20 % of the applied EDTA while the extracted molar amount of Zn was the same as the applied EDTA molar amount. Small amounts of copper was extracted at pH of 4.5. At pH 7, the extracted amount of Mn and Fe was lower than that at pH 4.5 along with a similar decrease in the lead and zinc extraction. A probable reason is that part of lead and zinc present in soil might be occluded by Fe and Mn oxides resulting in lower lead and zinc extraction efficiency at neutral pH value. Small amounts of copper was extracted from Cuba soil and the extracted amount was not changed at pH value of 4.5 and 7 while the extracted lead and zinc amount decreased to approximately 30 % and 10 % of the applied EDTA molar amount, respectively. The extraction efficiency of copper for both pH values imply that copper was not inhibited by Mn and Fe oxides and therefore, it is probable that at pH 7, copper may continue to compete with lead for EDTA ligand sites while calcium ions may also be in competition with lead ions.

Figure 23 shows the molar ratio of the extracted metals to EDTA from Rifle range soil. At pH 4.5, the sum of the extracted molar amount of lead and iron was similar to the applied EDTA molar amount. Lead forms 90 % of applied EDTA while iron forms the other 10 %. Like Cuba soil, at neutral pH, very small amount of Fe was extracted with a corresponding decrease in lead extraction. Copper extraction from the rifle range soil was not changed for both pH values. The decrease in lead extraction at neutral pH may be due to a partial amount of lead occluded by Fe oxides in soil. Copper and calcium probably played a role in competing for EDTA ligand sites. Dissolved calcium ions may reduce the lead extraction for pH value higher than 7. As mentioned earlier, the dissolved molar amount of calcium was at least five times higher than the molar amount of the applied EDTA.

In summary, for the three actual lead-contaminated soils, lead extraction tends to be higher at lower pH values. This might be due to the substitution of adsorbed lead ions with high concentration of hydrogen ion. For pH values less than 6, dissolved Fe ions may decrease lead extraction efficiency by competing with lead for EDTA ligand sites. Experimental results also show that several other factors may affect lead extraction efficiency from lead-contaminated soil. The major factors which control lead complexation with EDTA were solution pH, lead species present in soil matrix, and where the lead is located. Other heavy metals such as Fe, Zn, Ca and Cu, may compete with lead for active sites on the EDTA resulting in reduction of lead extraction over all pH ranges. Since the information about the heavy metal species in soil cannot be directly confirmed or determined, the degree of competition for each heavy metal could not be determined. Based on the above results, addition of EDTA for soil washing may change the solution properties resulting in an increase in the dissolution of metals.

CONCLUSIONS

Based on the experimental results, it was shown that the ratio of soil to EDTA solution (on a mass basis) as low as 1:3 had no effect on the extraction of lead from the contaminated soil but instead was dependent on the quantity of EDTA present. Using different actual lead-contaminated soils, results of the experiments showed that the extraction efficiency for each soil was different but if sufficiently large amount of EDTA was applied, all the lead may be extracted for certain types of soils. The EDTA:Pb stoichiometric ratio needed varied from as low as 7 for artificially contaminated soil to as much as 25 for Cuba soil. For one of the soils tested, even with an EDTA:Pb stoichiometric ratio of 300, very low amounts of lead (< 10 %) were extracted.

The molar amount of all the extracted metals due to the addition of EDTA was more than the molar amount of applied EDTA. Steady-state conditions appeared to be reached more easily for pH values less than 6. Without the addition of EDTA, lead was only extracted for pH values less than 6. For pH less than 6, dissolved ferric ions may compete with EDTA, therefore, reducing the lead extraction efficiency. Although the nature of the metal species is not known, the experimental results appeared to indicate that besides competition amongst metal cations for EDTA ligand sites, other mechanisms such as occlusion of lead in Fe and Mn oxides may play a role in controlling the extraction of lead. In addition, for pH value less than 6, some metal ions like Fe, Cu, Zn may compete with lead and for pH value higher than 6, dissolved Ca and Cu ions may possibly compete with lead for EDTA in reducing the amount of lead extracted.

PART II. EFFECTS OF AMORPHOUS IRON OXIDES ON EXTRACTION OF LEAD FROM LEAD-CONTAMINATED SOIL WITH EDTA

INTRODUCTION

Iron is the fourth most abundant element of the earth's crust (5.1 % by mass), and the average content of iron in soil is approximately 3.8 % (Lindsay, 1979) and in clay is approximately 10 % (Follett, 1965). In primary minerals, most of the iron is located in Fe(II) silicates such as pyroxines, biotites and olivines. Fe(III) also can be found in sulfides such as pyrite, FeS_2 (Schwertmann and Cornell, 1991).

Oxyhydroxides and oxides of iron are among the first products of weathering and soil formation (Aldridge and Churchmann, 1991). During weathering, these iron-containing minerals are dissolved as a result of hydrolysis and oxidation/reduction reactions. The released iron is precipitated as ferric oxides and hydroxides. Ferric ions are initially precipitated out as amorphous hydrous ferric oxides which includes oxides and hydroxides. These hydrous ferric oxides with their large surface area have high capacity to co-precipitate or adsorb metal ions in the aqueous phase. Over time, the amorphous hydrous ferric oxides will change to more stable crystal products (Schwertmann and Fisher, 1973). At room temperature and atmospheric pressure, amorphous hydrous ferric oxides may be stable for months (Swallow et al., 1980).

There are thirteen iron oxide, oxyhydroxides and hydroxides known to date (Schwertmann and Cornell, 1991). Among these, goethite (α-FeOOH) and hematite (α-Fe_2O_3) are the representative crystal forms of iron oxides because these two crystalline iron oxides are thermodynamically the most stable iron oxides under aerobic surface conditions (Schwertmann and Cornell, 1991). Other crystalline oxides are thermodynamically less stable, but under certain conditions, their formation may be kinetically favored (Atkinson et al., 1968; Schwertmann and Cornell, 1991). Goethite crystals are formed from dissolved Fe(III) ions which are produced by the dissociation of ferrihydrite, a major amorphous ferric oxide. On the other hand, hematite is formed through an internal dehydration and rearrangement within the ferrihydrite aggregates (Schwertmann and Murad, 1983). However, when crystallization inhibitors are present, ferrihydrite can remain stable for a long time (Schwertmann and Cornell, 1991). Such inhibitors include organic materials, phosphate and silicate species - all of which are widespread in natural environments. Inhibitors stabilize ferrihydrite and retard its transformation to more stable minerals.

The solubility of amorphous hydrous ferric oxides may be a few thousand times more than the solubility of the crystalline oxides. Table 6 shows the equilibrium constants for the most common ferric oxides found in soils. Norvell and Lindsay (1982) found that the activity of Fe^{3+} ions in soil solution is usually slightly less than that of pure amorphous hydrous ferric oxide. They proposed that $Fe(OH)_3$ (soil) should be the reference solid phase controlling the solubility for Fe^{3+} in soils. Fe-soil phase is considered as an amorphous phase having a structural order that is more orderly than freshly precipitated amorphous $Fe(OH)_3$.

Table 6. Equilibrium constants of common ferric oxides in soils.

Equilibrium Reaction	
$Fe(OH)_3$ (amorp.) + $3H^+ = Fe^{3+} + 3H_2O$	log K = 3.54
$Fe(OH)_3$ (soil) + $3H^+ = Fe^{3+} + 3H_2O$	log K = 2.70
(1/2) γ-Fe_2O_3 (maghemite) + $3H^+ = Fe^{3+}$ + (3/2) H_2O	log K = 1.59
γ-FeOOH (lepidocrocite) + $3H^+ = Fe^{3+} + 2\ H_2O$	log K = 1.39
(1/2) α-Fe_2O_3 (hematite) + $3H^+ = Fe^{3+}$ + (3/2) H_2O	log K = 0.09
α-FeOOH (goethite) + $3H^+ = Fe^{3+} + 2\ H_2O$	log K = -0.02

The solubility diagram of various oxides is presented in Figure 24. As shown in Figure 24, solubility of ferric ions in soil solution is controlled by the solubility of amorphous iron oxide. Since the activity of ferric ions in soil matrix is slightly lower than the activity of pure amorphous hydrous ferric oxides, solubility of the ferric ions in soil may not be governed by amorphous hydrous ferric oxides {$Fe(OH)_3$ (amorp.)} but by hydrous ferric oxides in soil {$Fe(OH)_3$ (soil)}.

Iron combined with silicate in a lattice structure called residual and silicate iron are inactive and may not be extracted with reducing agents, chelating agents or weak acid because it may not be in contact with the applied agents. However, the free iron oxides

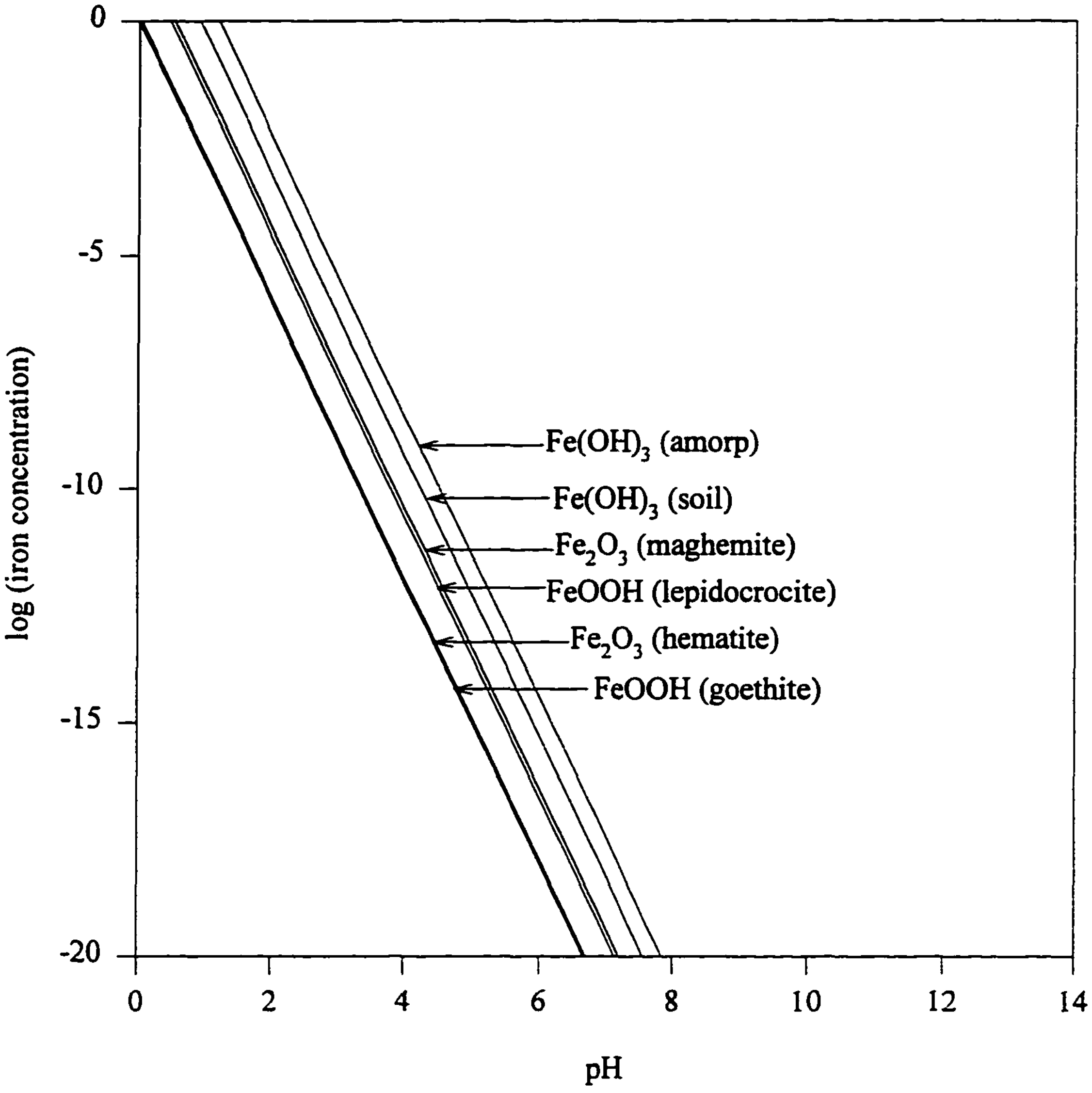


Figure 24. Activities of Fe^{3+} for Fe(III) oxides and soil-Fe

which include amorphous and crystalline iron oxides may be attacked by the chemical reagents resulting in leaching. Because amorphous hydrous ferric oxides may control the solubility of ferric ions in soils, leaching of metals by chemical reagents may be affected by amorphous iron oxides present in soil.

A few methods have been introduced to determine the amorphous hydrous ferric oxides content in soils. The basic approach in the mentioned methods is to reduce ferric ions to more soluble ferrous ions. Many scientists have used acidified ammonium oxalate not only for its reducing power but also for its complexing ability with amorphous iron. Acidified ammonium oxalate has been used as far back as 1992 for the removal of free iron from soil (Tamm, 1922). Schwertmann (1964) showed that acidified ammonium oxalate extracted most of the amorphous hydrous ferric oxides in the darkness. Sunlight has been shown earlier by Deb (1950) to promote the extraction of both amorphous and crystal iron oxide with acidified ammonium oxalate solution. Two years later, McKeague and Day (1966) confirmed that most of the amorphous iron oxides may be extracted using acidified ammonium oxalate over an optimum pH range of 2 to 3. McKeague and Day (1966) recommended pH 3 as the extraction pH to abate the destruction of mineral components and they suggested an extraction time of 4 hours to prevent the extraction of crystal ferric oxides. This acidified ammonium oxalate solution has been used for a long time for measuring amorphous iron content in soil even though there are uncertainties with regards to the use of the acidified ammonium oxalate solution. Borggaard (1976) used EDTA to extract the amorphous iron oxide from soil and found that EDTA can extract only a limited amount of iron. The amount of EDTA extractable iron was shown to be nearly equal to the amount of iron extracted after 4-5 hours with acid-ammonium oxalate solution at pH 3.0. On the other hand, Slavek and Pickering (1986) showed that 70 - 75% of freshly precipitated amorphous hydrous ferric oxides dissolved in EDTA solution (0.005 - 0.05 M) while only 45 - 55 % of 4 weeks aged hydrous ferric oxides would dissolve. They also showed that goethite did not dissolve in the extracting solution.

The amount of amorphous iron in soil is dependent on the soil type and its weathering history. For example, Adhikari et al. (1985) found that the percent of amorphous iron in alluvial soils was 0.57 to 1.08 % making up to approximately 65 to 87 % of the free iron in five different surface soils. In paddy soils, free iron was approximately 30 - 40 % of the total iron present while amorphous iron accounted for about 52 - 95 % of the free iron (Nikolayeva et al., 1987). In clays, the total irons were in a range of 11 to 27 % with amorphous iron concentrations between 1,900 and 7,300 ppm (Deb, 1950). McKeague and Day (1966) also reported that the ratio of amorphous iron to free iron may vary from zero to 0.8.

Amorphous and crystalline hydrous ferric oxides with their high specific surface area and a capacity to co-precipitate play a significant role in the retention of heavy metals in soils. Each different mineral form exhibits different adsorption behavior. The affinity order of metals for freshly precipitated hydrous ferric oxides is as follows: Pb > Cu > Zn > Ni > Cd > Co (Kinniburgh et al., 1976) while hematite has a similar order (McKenzie, 1980). In the case of goethite, the affinity sequence is Cu > Pb > Zn > Ni > Co > Ca (Forbes et al., 1976). According to the results above, both amorphous and crystalline hydrous ferric oxides have a strong affinity for lead. Adsorption of lead on the surface of hydrous ferric oxides depends on the system pH and lead concentration. The pH at which half of the added lead ion (pH_{50}) was adsorbed by aged hydrous ferric oxides and goethite was 6.0. But for freshly precipitated hydrous ferric oxides, the pH_{50} value was approximately one pH unit lower (Slavek and Pickering 1986). Ainsworth et al. (1994) also showed that the pH_{50} value for lead on freshly precipitated hydrous ferric oxides was 4.7. As mentioned earlier in the literature review section, metal ions with smaller pH_{50} value have the greater selectivity for a particular metals. For this reason, amorphous hydrous ferric oxides have a higher affinity for lead ions than the crystalline hydrous ferric oxides. Variations in ionic strength from 0.005 to 0.5 and changes in the nature of the background electrolyte from $NaClO_4$ to a complex artificial sea water mix did not affect the sorption of lead onto amorphous ferric oxides (Swallow et al., 1980). But the presence of Cl^- decreased dramatically the percentage of Pb^{2+} sorbed at any given pH since chloride forms di- and trichloro complexes with lead ions.

Ainsworth et al. (1994) observed that for hydrous ferric oxides aged for 21 weeks, the adsorption of lead was completely reversible with time. On the other hand, Schultz et al. (1987) observed that a measurable fraction of the bound lead on ferrihydrite was not easily desorbed. This fraction increased with increasing pH and with the desorption duration at high pH. Slavek and Pickering (1986) showed that with 0.05 mole of EDTA, more than 90 % of sorbed lead was extracted from one month-aged hydrous ferric oxides and goethite and more than 80 % sorbed lead was extracted from two kinds of Fe ores - goethite and hematite ore and pure hematite ore. However, for freshly precipitated hydrous ferric oxides, the same EDTA solution extracted slightly more than 70 % of lead.

For the reasons mentioned above, i.e., higher capacity for adsorption of lead, low extraction efficiency of lead with EDTA, and higher solubility than crystalline hydrous ferric oxides, it is expected that amorphous hydrous ferric oxides may be more important than crystalline hydrous ferric oxides in affecting lead extraction using EDTA. However, the high lead concentration of lead-contaminated soils tends to exceed the number of available active adsorption sites on the soil. Most of the lead found in lead-contaminated soil are in precipitated form. Under such circumstances, the solubility and reactivity of the ferric ions with EDTA would be one of the important factors affecting lead extraction with EDTA.

The log value of the stability constant for EDTA-Fe(III) (log K=25.1) is about seven orders of magnitude larger than that for EDTA-Pb (log K=18.3). Table 2 presents the equilibrium constants for complexes of EDTA-lead ions and EDTA-ferric ions. If the complexing ability of EDTA with lead and iron were compared based on the stability constants, soluble Fe(III) ions appeared to inhibit or compete with Pb for ligand sites on EDTA. Because amorphous ferric hydroxides have higher solubility product values, high concentrations of amorphous ferric hydroxides in soil may result in more soluble Fe(III) which may compete with lead for EDTA resulting in a reduction in the extraction efficiency of lead. Figure 25 presents the reactions of ferric ions and EDTA as a function of pH with the equilibrium concentration of EDTA of 10^{-25} M. As shown in Figure 25, Fe-EDTA solubility would decrease as the pH increased. This may be due to the low solubility of amorphous iron oxides at high pH values.

Cottingham and Jones (1957) showed that the Fe-EDTA behavior in soil was influenced by the amounts of clay and calcium carbonates. They postulated that the chelate was rapidly sorbed by clay, the extant of which was not greatly affected by time and there was a loss of

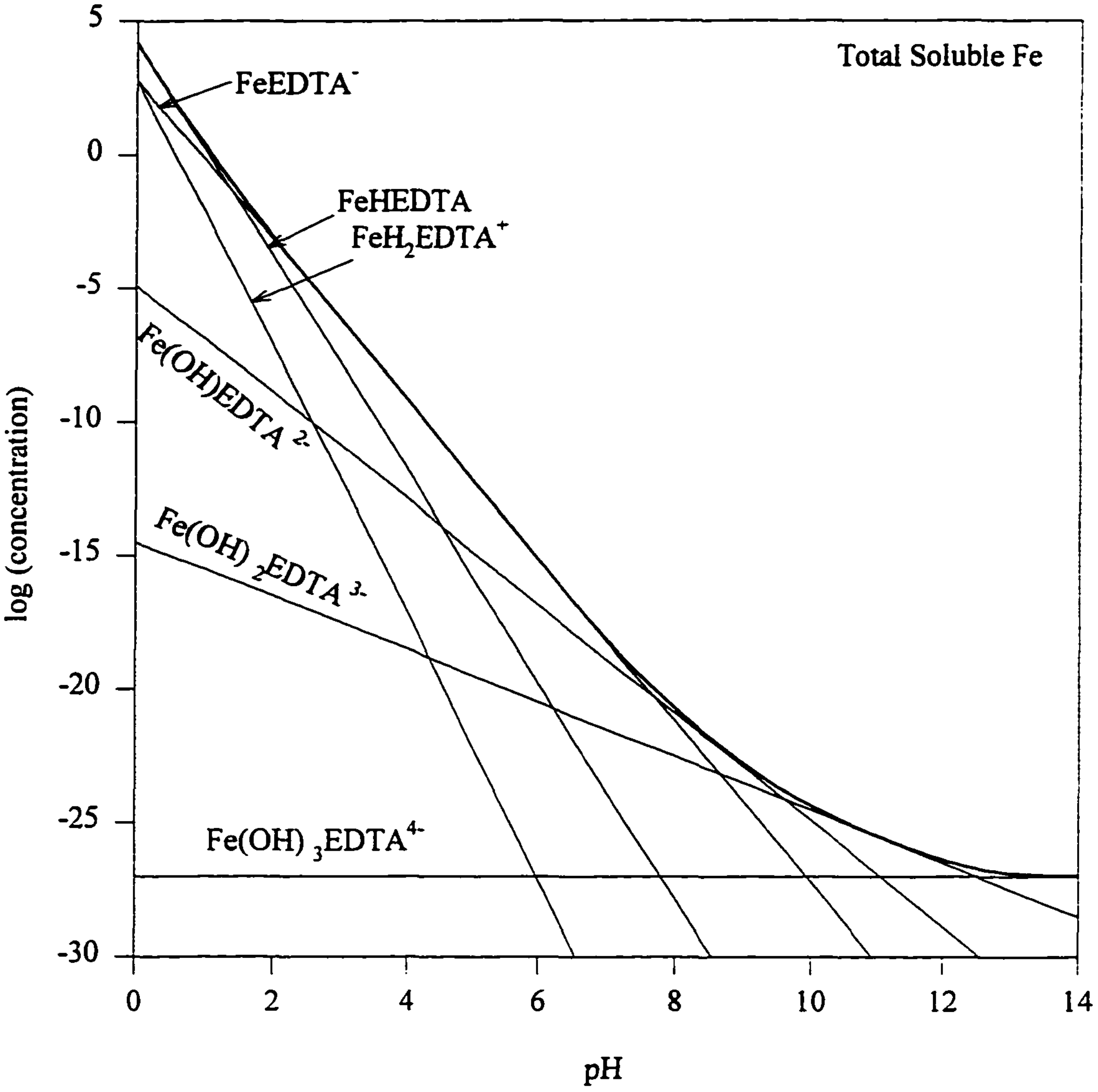


Figure 25. The solubility of Fe based on the amorphous $Fe(OH)_3$ in soil with 10^{-25} of equilibrium $[EDTA^{4-}]$ concentration

iron from the chelate due to the substitution of calcium in the chelate molecule with subsequent precipitation of the iron. Lindsay and Norvell. (1969) extended their research further and observed that the substitution was possible only for high pH values because at high pH (generally higher than pH 7), Ca-EDTA was more stable than the Fe-EDTA complex. They also showed several equilibrium relationships between calcium, iron (III), zinc ions and EDTA. They proved that at low pH (<6), most EDTA would react with iron(III) ions, and at high pH (>7), EDTA prefers calcium ions. Between pH 6 and 7, zinc ions were predominantly combined with EDTA. They used the equilibrium constants to predict the results and showed the EDTA-metal preference at different pH values. At the same time, Norvell and Lindsay (1969) showed that manganese was less reactive with EDTA than zinc and copper at any pH as evident from their relatively low stability constants.

To date, there are various studies on the adsorption/desorption of lead on ferric oxide compounds. However, there is only one study assessing the effect of iron on lead extraction with EDTA. Elliott et al. (1989) reported that a small amount of iron was dissolved and that iron did not affect lead extraction for an EDTA extraction study. However, the study was conducted using a single contaminated soil from a battery recycling site. They concluded that iron was not extractable and might be part of the soil structure. However, considering the study conducted in Part I, the results showed that iron appeared to compete with lead ions for the applied EDTA at pH values less than 6.

As explained earlier, different forms of iron oxides have different impact on EDTA extraction. Since amorphous ferric ions are more easily dissolved, it is possible that amorphous iron may affect lead extraction. Experimental studies in this area will further contribute towards an understanding of the effects of iron on the application of chelating agents on lead extraction.

The objective of this research is to investigate both theoretically and experimentally the effects of amorphous ferric oxides and different lead species on the extraction of lead from lead-contaminated soil with EDTA. The approach taken to investigate the effects of amorphous ferric oxides was two-fold. Firstly, the pH ranges over which the extraction efficiency of lead for different lead species was affected by amorphous ferric oxides will be investigated using chemical speciation modeling. Secondly, lead extraction studies for different lead species over a range of pH values, and EDTA concentrations will be conducted to investigate the effects of these variables on lead extraction efficiency. The experimental results will be compared to the theoretical modeling results.

MATERIALS AND METHODS

Sample Preparation

Quartz sand for the experiments were obtained from a construction area located about two miles north of Ames, Iowa. The sand was air dried and screened between sieve number 100 (0.15 mm) and sieve number 35 (0.5 mm). To prepare the sand for the experiments, iron oxides were precipitated first on the samples followed by precipitation of different lead species. The procedures to prepare artificially contaminated soil are as follows. Two hundred grams of sieved sand was added to 200 ml of 0.25 M $Fe(NO_3)_3.9H_2O$ solution. The slurry was shaken with a wrist action shaker for 24 hours. The soil samples were then air dried and ground to pass through sieve number 35 but retained by sieve number 100. The target amorphous iron content was 1,500 mg/kg.

Different lead species were then precipitated separately on different soil samples. The target lead concentration in soil was 5,000 mg/kg. To precipitate $PbSO_4$ on the soil samples, 200 ml of a solution containing adequate amount of $Pb(NO_3)_2$ and K_2SO_4 was shaken with 200 grams of iron-coated soil. To provide enough anion concentration to react with lead ions in solution, the initial concentration of the anions was adjusted to 0.1 M which was approximately 4 times larger than lead ions concentration. After shaking for 24 hours, the soil samples were air dried. The dried soils were then ground and sieved using a number 100 and a number 35 sieves. To precipitate lead carbonate compounds, $NaCO_3$ was added instead of K_2SO_4. Similarly, to precipitate lead phosphate compounds, $NaH_2PO_4.H_2O$ was added.

In addition to the soil with approximately 1,500 ppm of iron and $PbSO_4$ contamination, two other soils with different iron content were prepared. One soil sample was prepared without the addition of iron in the soil sample and the other soil sample had an amorphous iron content of 3,000 mg/kg which was approximately 2 times higher than the soil prepared using the procedure above. The two different soils were contaminated with $PbSO_4$ using the method mentioned above. The target lead concentration was approximately equal to 5,000 mg/kg.

Experimental Methods

Extraction studies were conducted as described in Part I. For these experiments, 10 ml of nanopure water or EDTA solution were added to a 50 ml of polypropylene centrifuge tube containing 1 gram of contaminated soil. Reaction time was 24 hours. To adjust the pH, dilute nitric acid and sodium hydroxide solution were used. After shaking, the slurry was filtered using a 0.45 μm membrane filter paper and the pH of the solution was measured. Adequate amount of filtrate was collected and analyzed for metals concentrations with an atomic absorption spectrophotometer. The removal efficiencies were calculated using the following equation.

Removal Efficiency of metal (%) = metal extracted * 100 / Initial weight of metal in soil

Extraction efficiency of lead and iron were investigated over pH values between 3 and 11. It was assumed that all the iron ions complexed with EDTA came from the amorphous iron. To confirm the effects of amorphous iron on lead extraction, experiments were conducted for the high amorphous iron soil samples and the soil without amorphous iron.

Amorphous Iron Measurement

The amorphous iron content in soil samples were measured using the method proposed by McKeague et al (1966). In this method, 0.2 M of ammonium oxalate solution with a pH of 3.4 - 3.5 adjusted by adding 0.2 M of oxalic acid solution was used. One gram of a soil sample was placed in a 50 ml polypropylene centrifuge tube and 40 ml of the extraction solution was added. The centrifuge tubes were covered with aluminum foil to shield the samples from light and the samples were shaken for 4 hours. The reacted solution was then filtered with 0.45 μm membrane filter paper. Adequate amount of filtrate was diluted with nano pure water and acidified with 5 % (v/v) nitric acid in 100 ml volumetric flask. Iron in the solution was measured with an atomic absorption spectrophotometer and was assumed as the total amorphous iron concentration of the soil samples. It should be noted that the amorphous iron concentration measured here was one of operational convenience. Obviously, the actual amorphous iron concentration may or may not be the same as the oxalate extractable iron although some researches have found that the concentrations were similar (McKeague and Day, 1966). In this research, the oxalate extractable iron will be referred to as amorphous iron for brevity in presentation.

Prediction of EDTA Complexation with Lead

The extraction of lead and amorphous ferric iron from lead-contaminated soil may be computed using thermodynamic data such as equilibrium constants, solubility products, and complexation stability constants. The basic approach in these calculations is that the ferric ions which will react with EDTA are derived from only amorphous hydrous ferric oxides in soil. This assumption is reasonable because amorphous ferric compounds have the highest solubility products when compared to other ferric compounds as shown in Table 6 and Figure 24.

To assess the effect of amorphous iron on the extraction of lead from various lead species, the total sum of the possible $Fe(III)\text{-}HnEDTA^{(n-1)}$ concentrations will be compared to the total sum of $Pb(II)\text{-}HnEDTA^{(n-2)}$ concentrations of any lead species. To calculate Pb-EDTA solubility in the presence of $PbSO_4$ and $Pb(H_2PO_4)_2$, the equilibrium concentrations of SO_4^{2-}, $H_2PO_4^-$ ions and $EDTA^{4-}$ ions were assumed as a fixed constant over the pH range. For $PbCO_3$, the CO_2 partial pressure was assumed as 0.0003 atm. Using the equilibrium equations shown in Table 1 and Table 2, a new equilibrium equation was developed which contains specific lead species, H^+, and one of $Pb(II)\text{-}HnEDTA^{(n-2)}$ complexed forms. With the fixed equilibrium concentrations of SO_4^{2-}, $H_2PO_4^-$ ions and $EDTA^{4-}$ ions, the possible concentration of each $Pb(II)\text{-}HnEDTA^{(n-2)}$ complex was calculated. The sum of each concentration of $Pb(II)\text{-}HnEDTA^{(n-2)}$ complex was assumed to be the total possible Pb-EDTA concentration at specific pH value. For the calculation of $Pb(OH)_2$-EDTA and $Fe(OH)_3^-$ EDTA complexes the equilibrium concentration of EDTA was assumed as 0.001 M. By comparing the total metal-EDTA concentrations, the mole fractions of Pb-EDTA and Fe-EDTA were calculated.

To apply this calculation for the prediction of lead and iron extraction, the following assumptions were used: (i) for all pH range, the applied EDTA will be complexed 100 % with metals, (ii) for low pH values, when the calculated dissolved molar amount of lead or ferric compounds using solubility product constants is higher than the molar amount of metal-EDTA complex, the extracted amounts of metals will be controlled by solubility, and (iii) for high pH values, when $Pb(OH)_2$ solubility is less than the $PbSO_4$ and $Pb(H_2PO_4)_2$, the total solubility of Pb-EDTA will be controlled by $Pb(OH)_2$ solubility. Appendix I shows a detailed calculation of metal-EDTA solubility and mole fractions.

The experimental results will be compared to the predictions using thermodynamic data mentioned above and MINTEQA2 program.

RESULTS AND DISCUSSIONS

Solubility Prediction of EDTA Complexation with Lead

The total soluble Fe(III)-EDTA and Pb(II)-EDTA based on amorphous ferric hydroxides in soil and lead species such as $PbCO_3$, $Pb(OH)_2$, $PbSO_4$ and $Pb(H_2PO_4)_2$ with fixed equilibrium concentrations of SO_4^{2-} and H_2PO^{4-} as 0.1 M and $EDTA^{4-}$ as 10^{-25} M, are presented in Figure 26. As shown in Figure 26, the Pb-EDTA complex concentrations from lead $PbCO_3$ and $Pb(OH)_2$ were identical when the partial pressure of CO_2 was 0.0003 atm and $PbCO_3$ or $Pb(OH)_2$ were more reactive with EDTA than amorphous ferric hydrous oxides in soil over all pH range. Therefore, it is probable that for lead species such as lead carbonates and lead hydroxide, amorphous ferric hydrous oxides may not have an effect on lead extraction with EDTA. However, for both $PbSO_4$ and $Pb(H_2PO_4)_2$, it appeared that for pH values less than about 6, amorphous ferric hydrous oxides may be more reactive with EDTA than $PbSO_4$ and $Pb(H_2PO_4)_2$. Therefore, a lower lead extraction efficiency may be expected at pH less than 6.0, if insufficient EDTA was introduced. At high pH values, it appeared that the Pb-EDTA complex concentration in the presence of $PbSO_4$ and $Pb(H_2PO_4)_2$, may be decreased due to the low solubility of $Pb(OH)_2$. However this solubility decrease may not affect much the Pb-EDTA complexation because $Pb(OH)_2$ has higher reactivity with EDTA than the reactivity of amorphous ferric hydrous oxides.

The solubility of possible lead sulfate family of compounds is presented in Figure 27. Similarly, the solubility of lead phosphate and lead carbonate family of compounds with same M of equilibrium EDTA concentration are presented in Figure 28 and Figure 29. The data presented in the figures show the relative reactivities of lead species with EDTA to the reactivity of amorphous hydrous ferric oxides with EDTA in soils. For lead sulfate family of compounds, amorphous hydrous ferric oxides appeared to be less reactive with EDTA than lead sulfate family of compounds in soil for pH values higher than 6. However, as pH decreases, amorphous ferric hydrous oxides have higher reactivity than lead sulfate family of compounds except for $PbSO_4{\cdot}3PbO$. $PbSO_4$ is the least reactive lead species among the lead

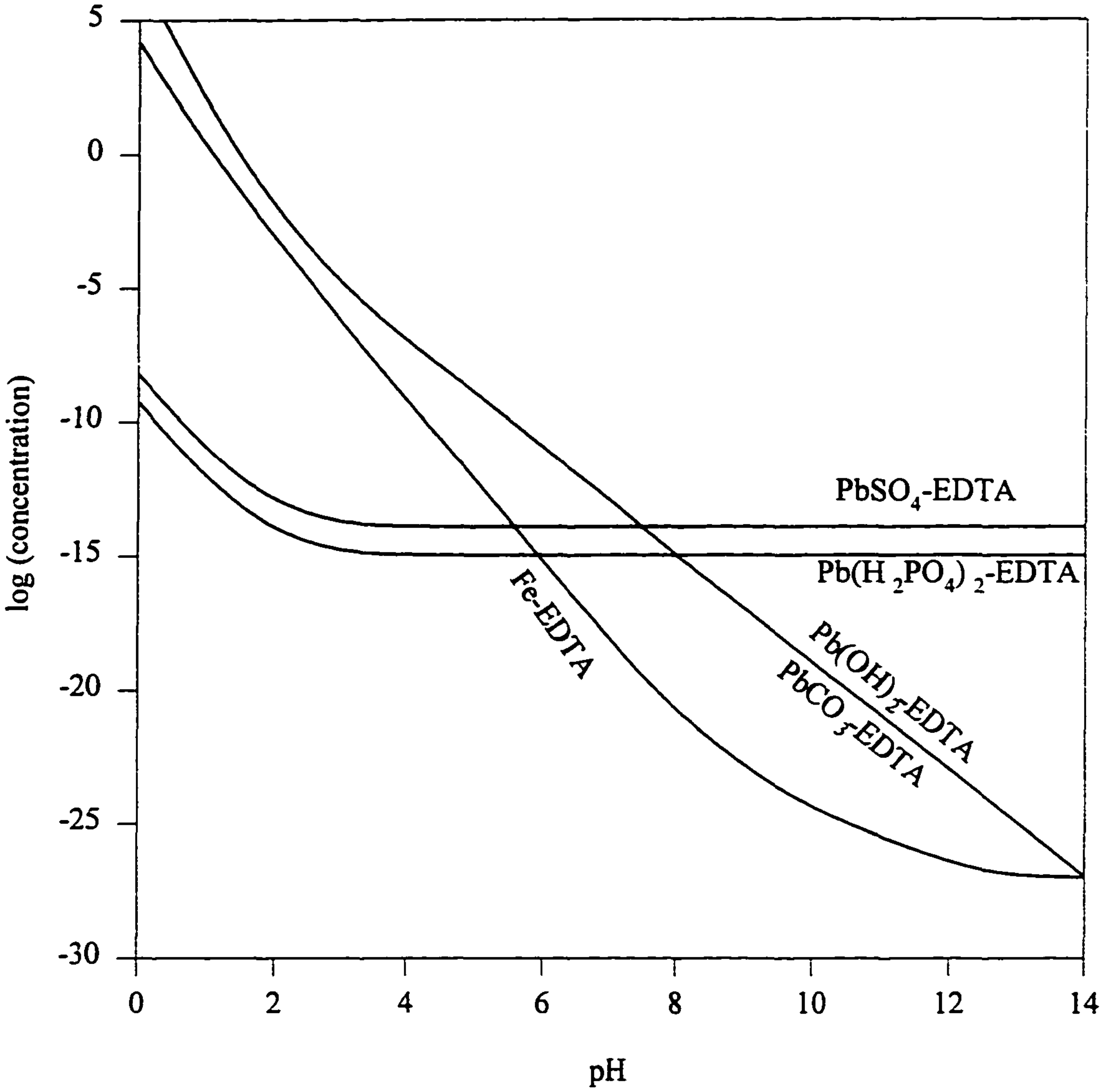


Figure 26. The solubilty of Fe-EDTA and different species Pb-EDTA with amorphous soil $Fe(OH)_3$, and equilibrium concentratration of $[SO_4^{2-}]$ and $[H_2PO_4^-]$= 0.1, $[EDTA^{4-}] = 10^{-25}$ M and $P_{CO_2} = 0.0003$ atm

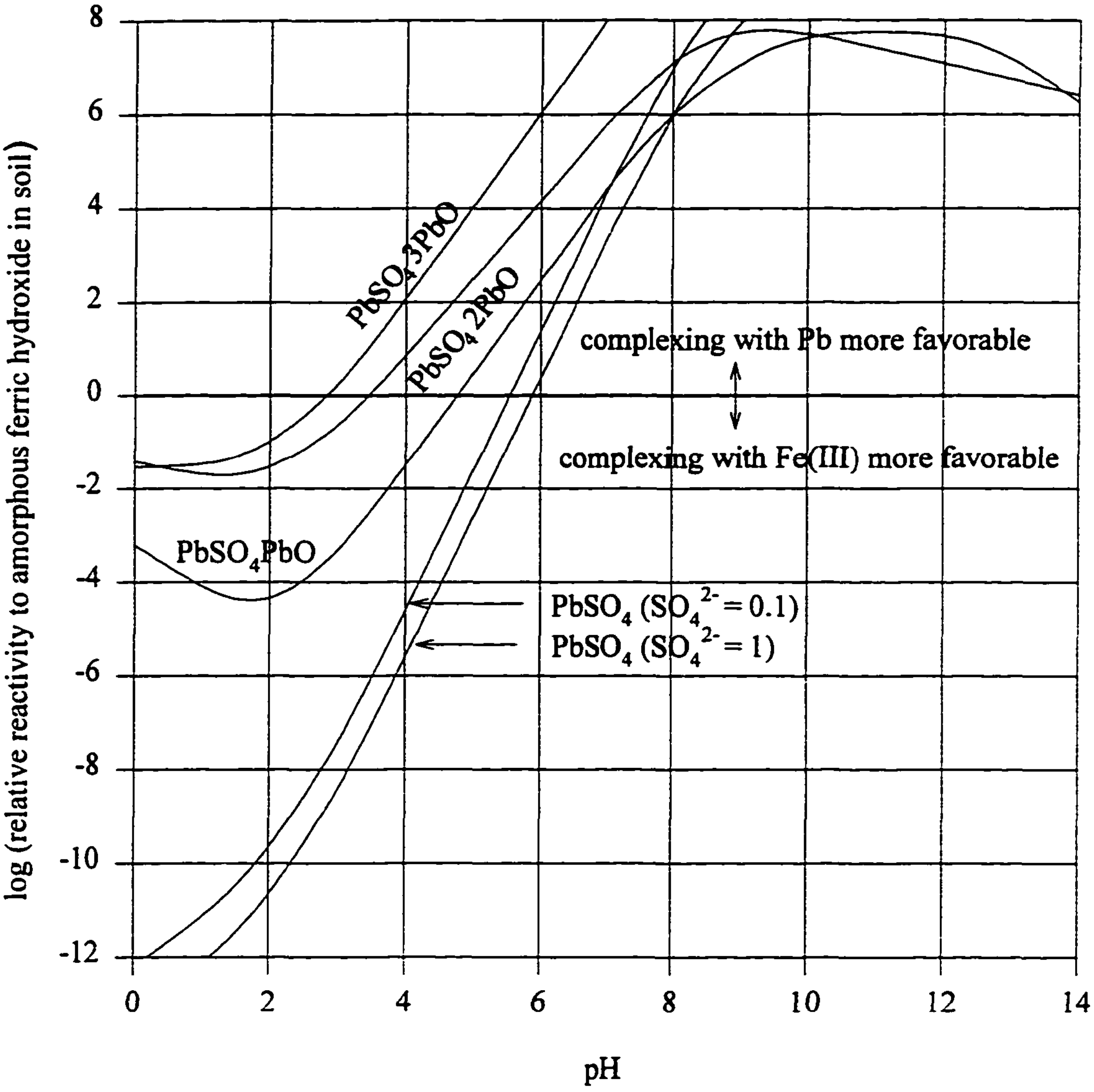


Figure 27. Relative reactivity of lead sulfate family with EDTA compared to amorphous hydrous ferric oxide in soil with eqilibrium concentration of $[SO_4^{2-}]$ of 0.1 M

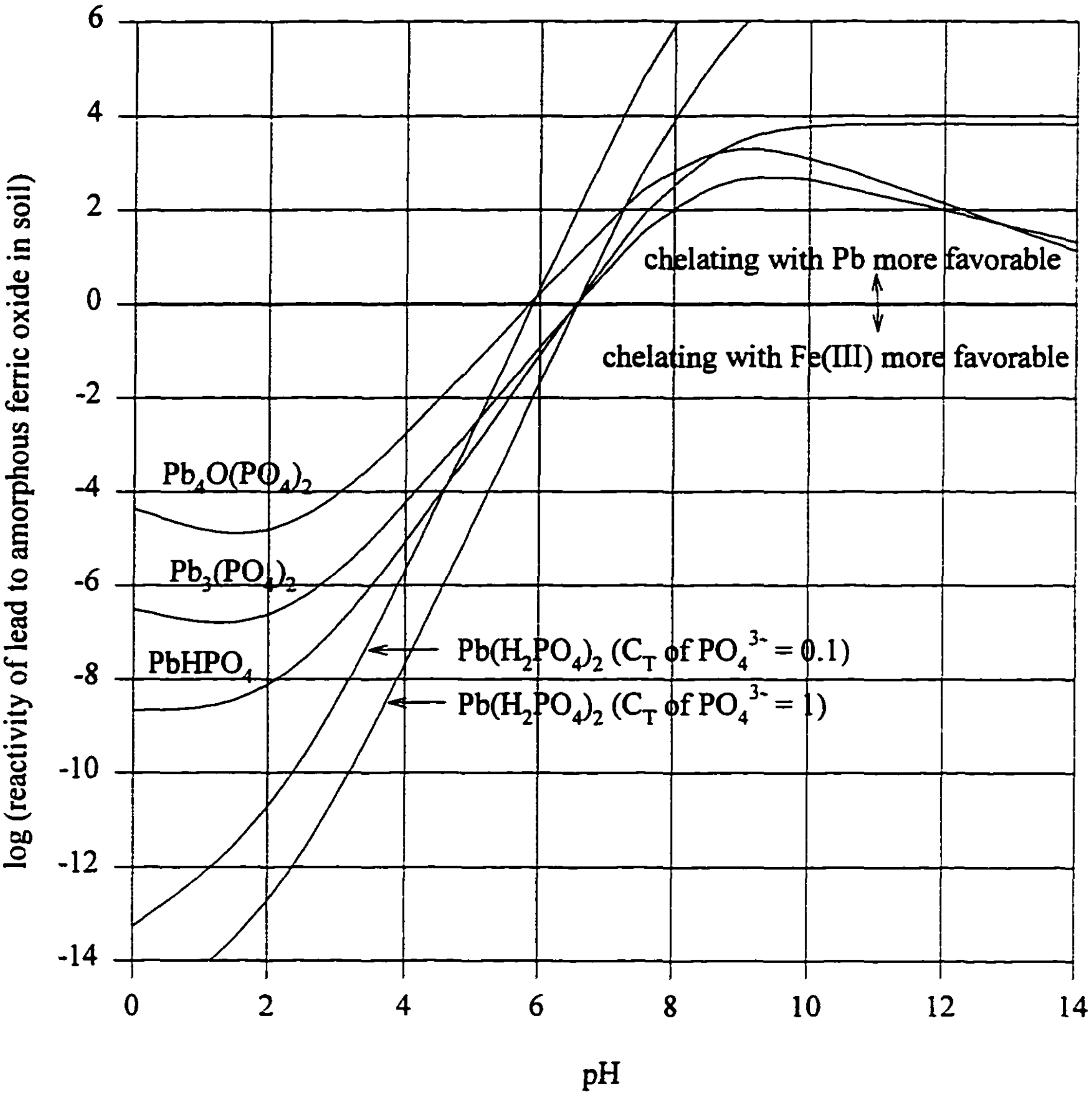


Figure 28. Relative reactivity of lead phosphate family with EDTA compared to amorphous hydrous ferric oxide in soil with equilibrium concentration of $[H_2PO_4^-]$ of 0.1 M

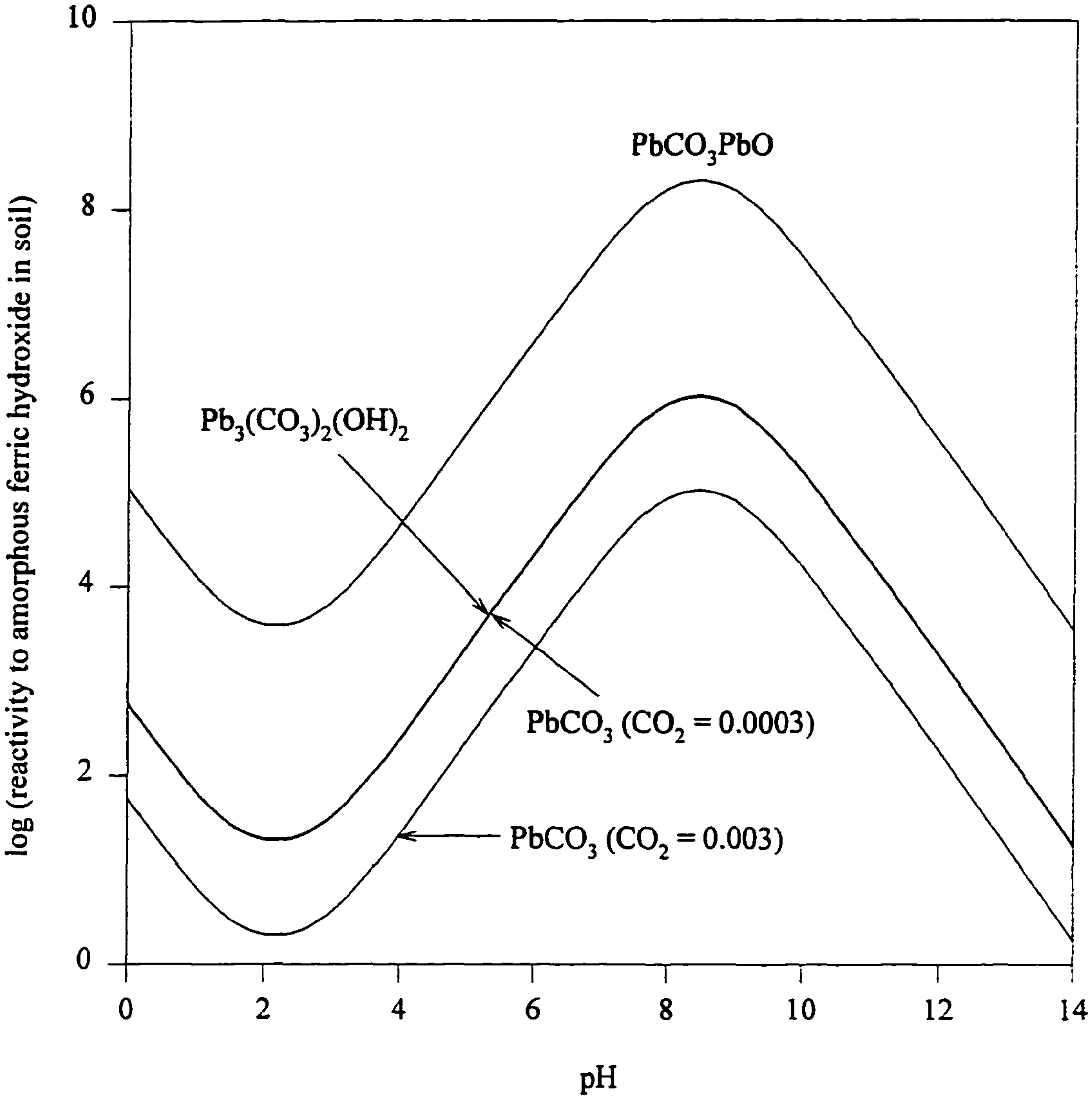


Figure 29. Relative reactivity of lead carbobate family with EDTA compared to amorphous hydrous ferric oxides in soil with equilibrium $P_{CO_2} = 0.0003$

sulfate family of compounds for pH values below 6. As shown in Figure 27, high sulfate ion concentration in soil moisture can decrease the reactivity of lead compounds to EDTA due to the lower solubility of lead sulfate compounds.

For pH values less than 6, the extraction of lead phosphate family of compounds seems to be affected by the presence of amorphous hydrous ferric oxides in soil (Figure 28). It appears that amorphous ferric hydrous oxides will inhibit lead extraction at pH values less than 6, if the lead species present is a lead phosphate compound. If unit stoichiometric molar concentration of EDTA to lead in soil is added, it is probable that the added EDTA would react with iron ions from amorphous hydrous ferric oxides and then the remaining EDTA would form chelates with lead ions from the lead phosphate or lead sulfate compounds for pH values below 6.

The relative reactivity of lead carbonate family of compounds with EDTA is higher than the reactivity of Fe(III) with EDTA as shown in Figure 29. This shows that lead carbonate family of compounds is not affected by the amorphous ferric hydrous oxides. Therefore, lead carbonate compounds may be extracted more easily than lead phosphate and lead sulfate compounds. Since Pb-EDTA complex concentration of $Pb(OH)_2$ is identical to $PbCO_3$ complex concentration, lead hydroxide compound may have higher reactivity with EDTA than that of amorphous ferric hydrous oxides resulting in a low effect on lead extraction from $Pb(OH)_2$-contaminated soil.

Using the relative reactivity, mole fraction diagram was drawn with the same molar amount of lead, iron and EDTA in the presence of $PbSO_4$, $PbCO_3$, $Pb(H_2PO_4)_2$ and amorphous ferric hydrous oxides. This mole fraction diagram is shown in Figure 30. The mole fraction diagram shows that at low pH values, most applied EDTA was complexed with Fe ions in the presence of $PbSO_4$ and $Pb(H_2PO_4)_2$ while lead carbonate is more reactive with EDTA than amorphous ferric hydrous oxides. However, for all lead species, at high pH values, the lead ions were more favorable in forming complexes with EDTA than the iron ions.

In summary, relative reactivity diagrams calculated using stability constants showed that extraction of lead from lead-contaminated soil would be inhibited by the amorphous ferric

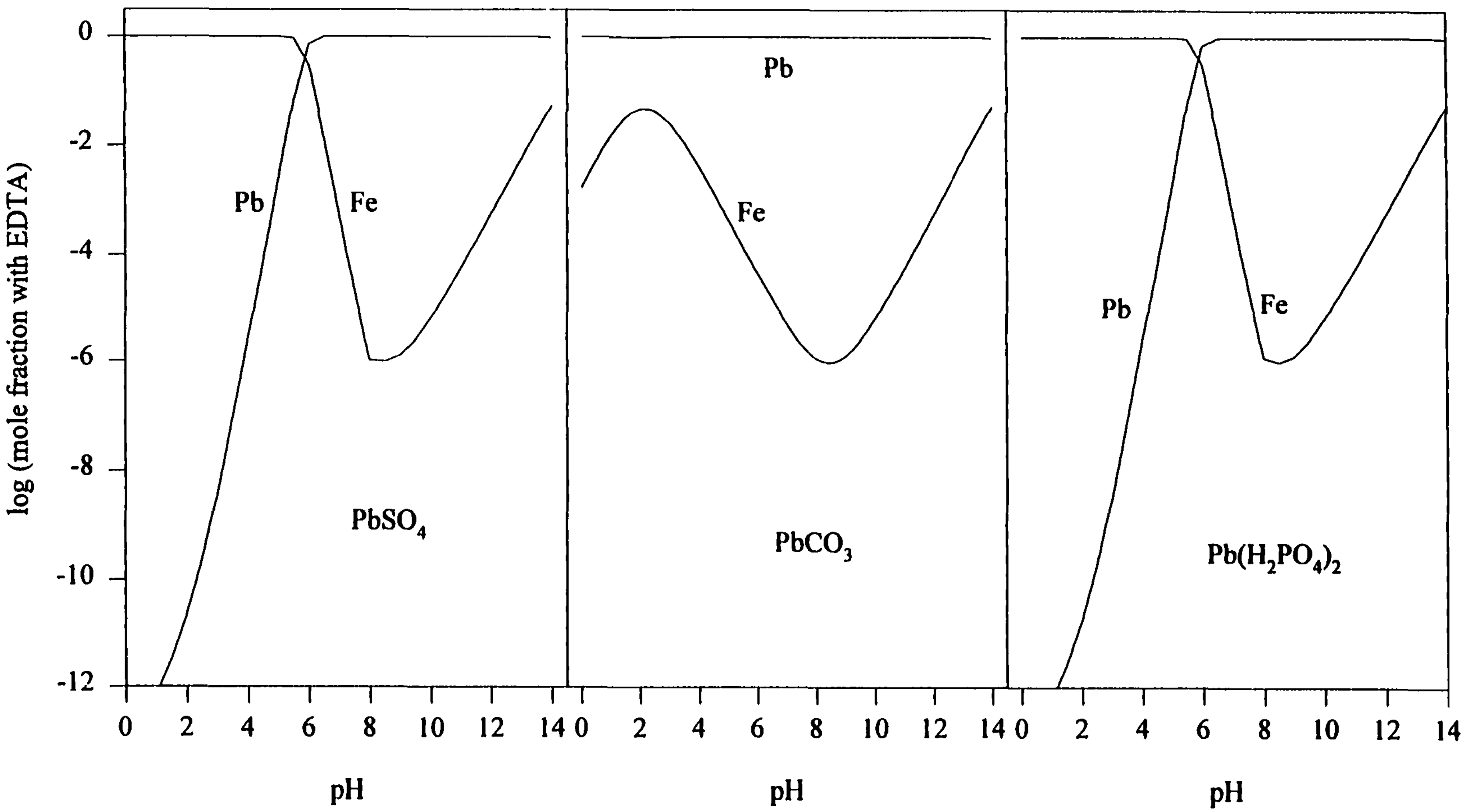


Figure 30. Mole fraction diagram with same molar amount of Pb, Fe and EDTA in the presence of PbSO$_4$, PbCO$_3$, Pb(H$_2$PO$_4$)$_2$, Pb(OH)$_2$ and amorphous hydrous ferric oxides in soil

iron if the lead species in soils were lead sulfate and lead phosphate compounds for pH values below 6. For lead carbonate family of compounds and lead hydroxide, ferric ions have minimum impact on lead extraction. According to above analysis, amorphous hydrous ferric oxides may play an important role for the extraction of lead from lead compounds depending on the lead species present in contaminated soil, pH and EDTA concentration.

Results of Lead Extraction Experiments

The sand used for the extraction experiments has a CEC of 2.66 meq/100g, specific surface area of 47 cm^2/g, organic matter of 0.01 % and soil pH of 8.04. Table 7 presents the lead and amorphous iron concentrations of the artificially prepared lead-contaminated soil. The sand used has an iron content of 261 mg/kg while the high amorphous iron sand has an iron content of 3,360 mg/kg. Lead concentrations in the contaminated soil varied from 3,300 mg/kg to 5,158 mg/kg. In the text, we will refer to the sand samples with no iron added as no-Fe sample, the sand samples with 3,360 mg/kg iron as high amorphous iron sample, and the sand samples with 1,344 to 1,816 mg/kg iron as medium amorphous iron sample.

Table 7. Lead and amorphous iron concentrations of artificially-contaminated soil samples

Sample	Pb concentration ppm (mole/kg)	amorphous Fe Conc. ppm (mole/kg)
$PbSO_4$ - amorphous Fe	5,158 (2.49E-2)	1,404 (2.51E-2)
$PbCO_3$ - amorphous Fe	3,300 (1.59E-2)	1,816 (3.24E-2)
$Pb(H_2PO_4)_2$ - amorphous Fe	4,843 (2.34E-2)	1,344 (2.40E-2)
$PbSO_4$ - high amorphous Fe	4,502 (2.17E-2)	3,360 (6.0E-2)
$PbSO_4$ - non-Fe addition	3,948 (1.91E-2)	261 (4.66E-3)

Lead extraction efficiencies of lead sulfate-contaminated soil prepared with no-Fe sand sample are presented in Figure 31. The EDTA:Pb stoichiometric ratio used for extraction

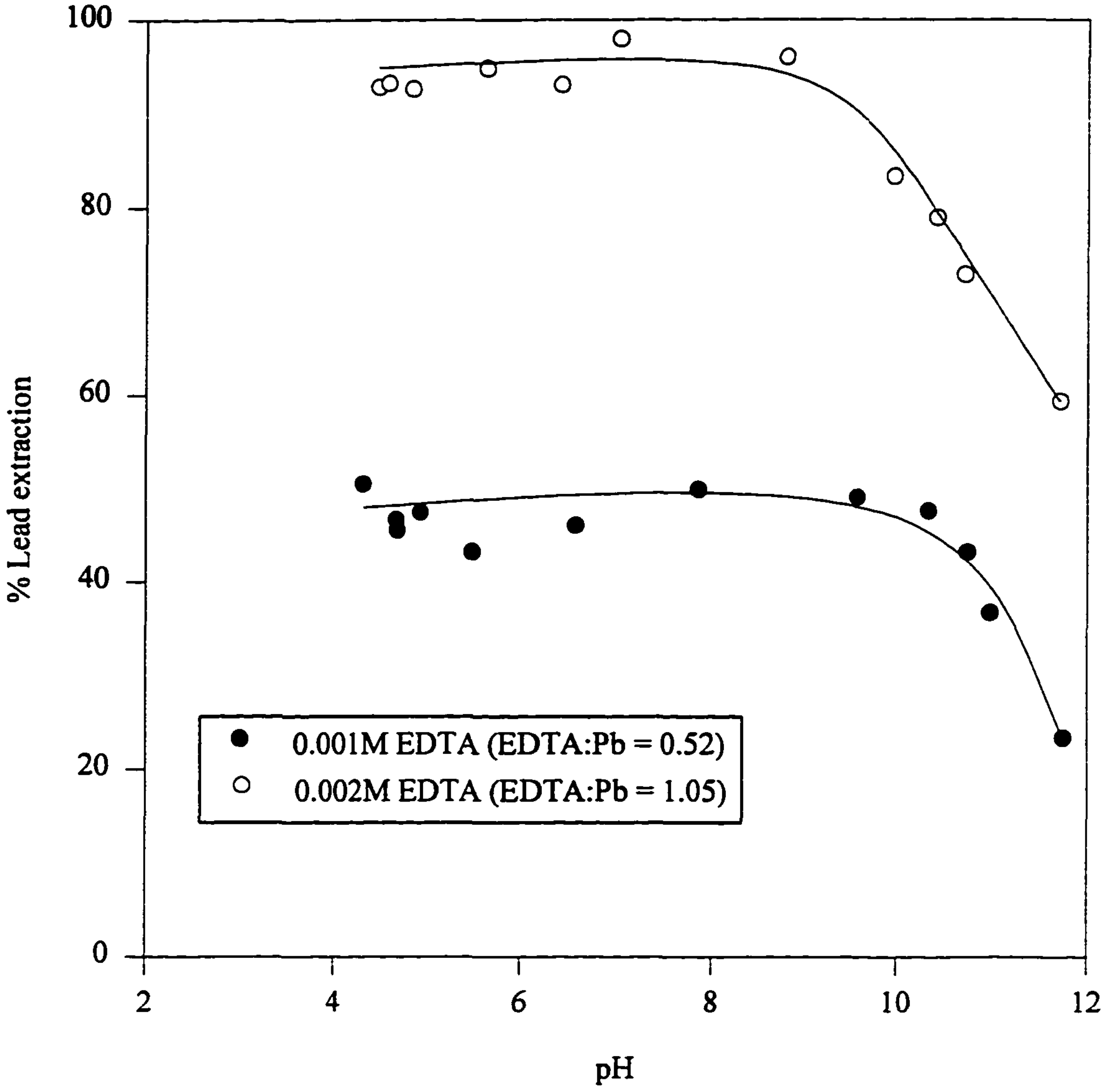


Figure 31. Lead extraction efficiencies of $PbSO_4$-contaminated soil prepared with no Fe sample for various pH with 0.001 and 0.002 M EDTA solutions

purposes were 0.52 and 1.05. The lead extraction efficiency did not change much over the pH range from 4 to 9. In addition, the molar amount of extracted lead was approximately the same as the molar amount of EDTA applied indicating that extraction of lead by EDTA was not inhibited.

Figure 32 shows the extraction of lead and iron from $PbSO_4$-contaminated soil prepared with medium amorphous iron sand using water, 0.001 M and 0.002 M EDTA solutions. For extraction with water, iron dissolution increased sharply below pH 4. Because of the higher solubility of ferric ions in water for pH less than 4, delineating the effects of amorphous iron on lead extraction may be difficult and, therefore, the discussion on the experimental results will be for solution with pH values greater than 4. Above pH 7, the extracted amounts of lead and iron were very low due to the low solubility of lead and amorphous ferric compounds.

For the extraction experiments with 0.001 and 0.002 M EDTA, the results showed that at low pH values (between pH 4 and 6), more iron ions were complexed with EDTA than lead ions. pH 6 appeared to be the demarcation pH in which Pb-EDTA complexes began to be more dominant than Fe-EDTA complexes, probably due to the low solubility of amorphous ferric oxides. However, for $pH > 10$, lead extraction decreased again. At high pH values, a longer time was needed to reach steady state conditions and hydrolysis of dissolved lead may be more favorable than the EDTA complexation.

Figure 33 shows the lead and ferric extraction from a $PbSO_4$-contaminated soil prepared with high amorphous iron sand sample. The extraction results were similar to the medium amorphous iron soil sample, i.e., at low pH values, lead extraction efficiency was very low due to the effect of ferric ions and at pH values above 7, lead was extracted more than ferric ions. The amorphous iron effect on lead extraction may be shown more clearly in Figure 34. When a high EDTA concentration was applied (Pb:EDTA stoichiometric ratio of 1: 2.01) to $PbSO_4$-contaminated soil using medium amorphous iron soil sample, most of the lead and amorphous iron were extracted at low pH values. However, applying a similar molar concentration (Pb: EDTA stoichiometric ratio of 1:2.30) to $PbSO_4$-contaminated soil using high amorphous iron sand sample, lead extraction was still reduced over much of the pH

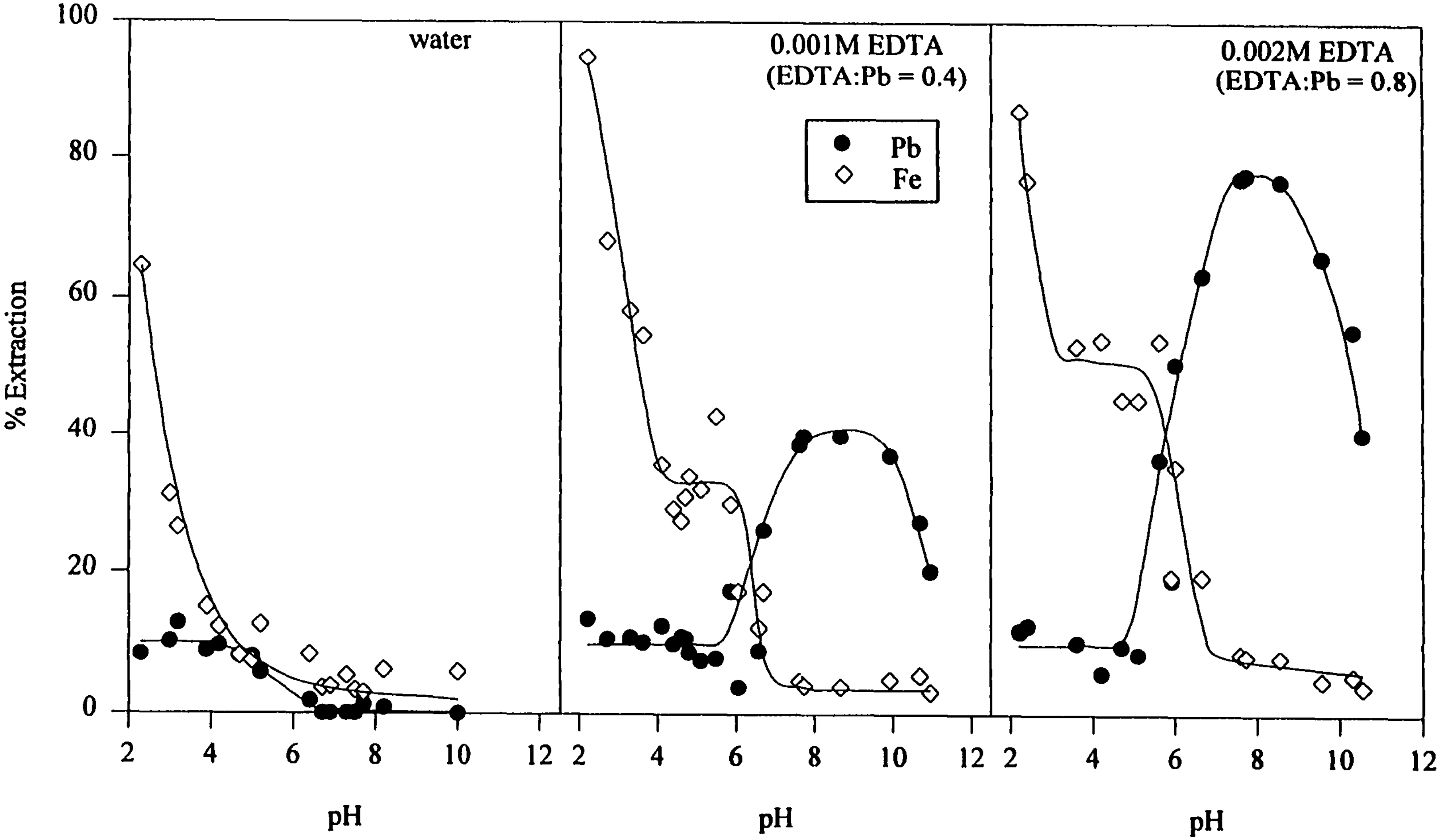


Figure 32. Lead and iron extraction efficiencies of $PbSO_4$-contaminated soil prepared with medium amorphous iron sand for various pH values with water and different concentration of EDTA solutions

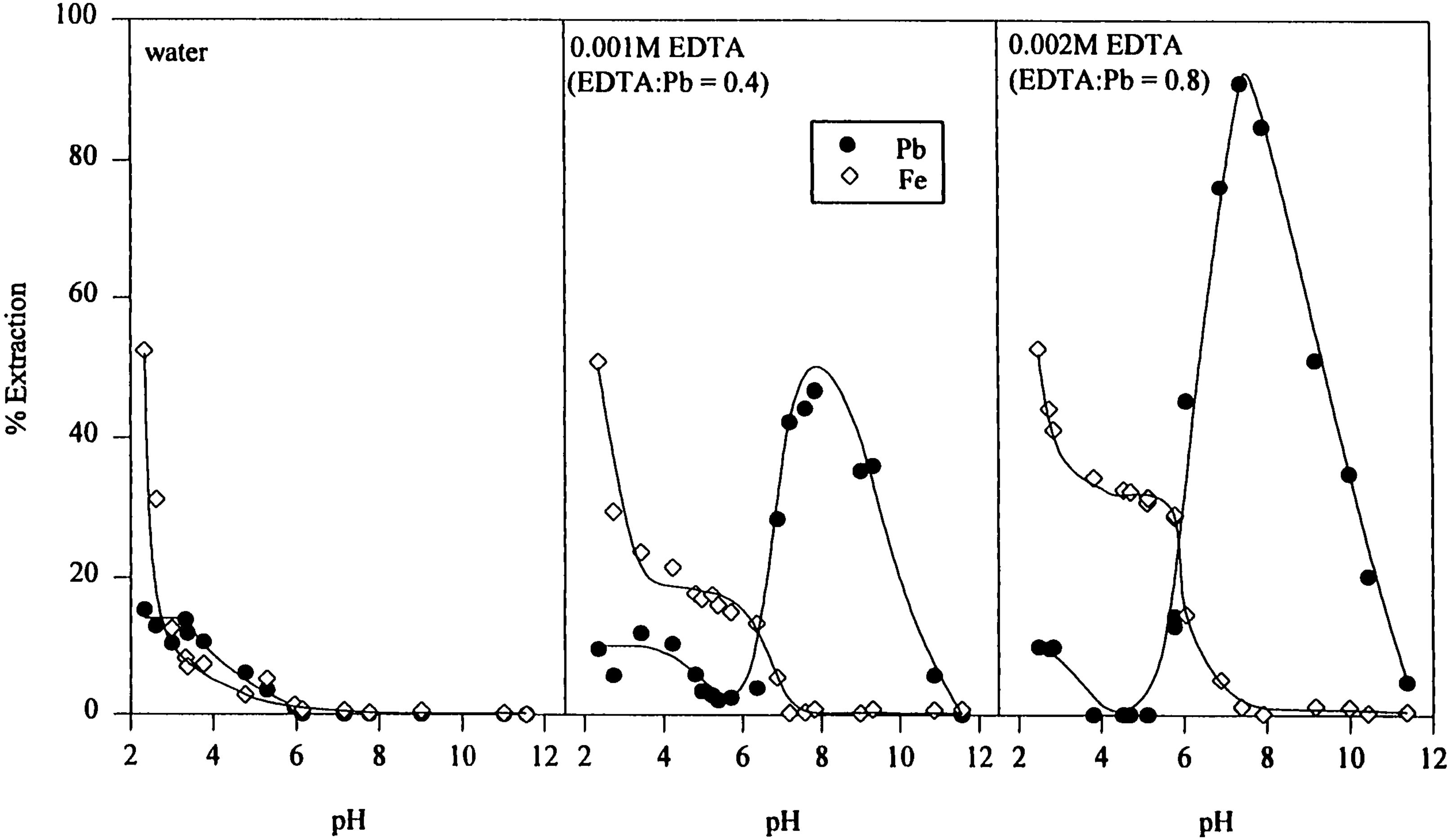


Figure 33. Lead and iron extraction efficiencies of $PbSO_4$-contaminated soil prepared with high amorphous iron sand for various pH values with water and different concentration of EDTA solutions

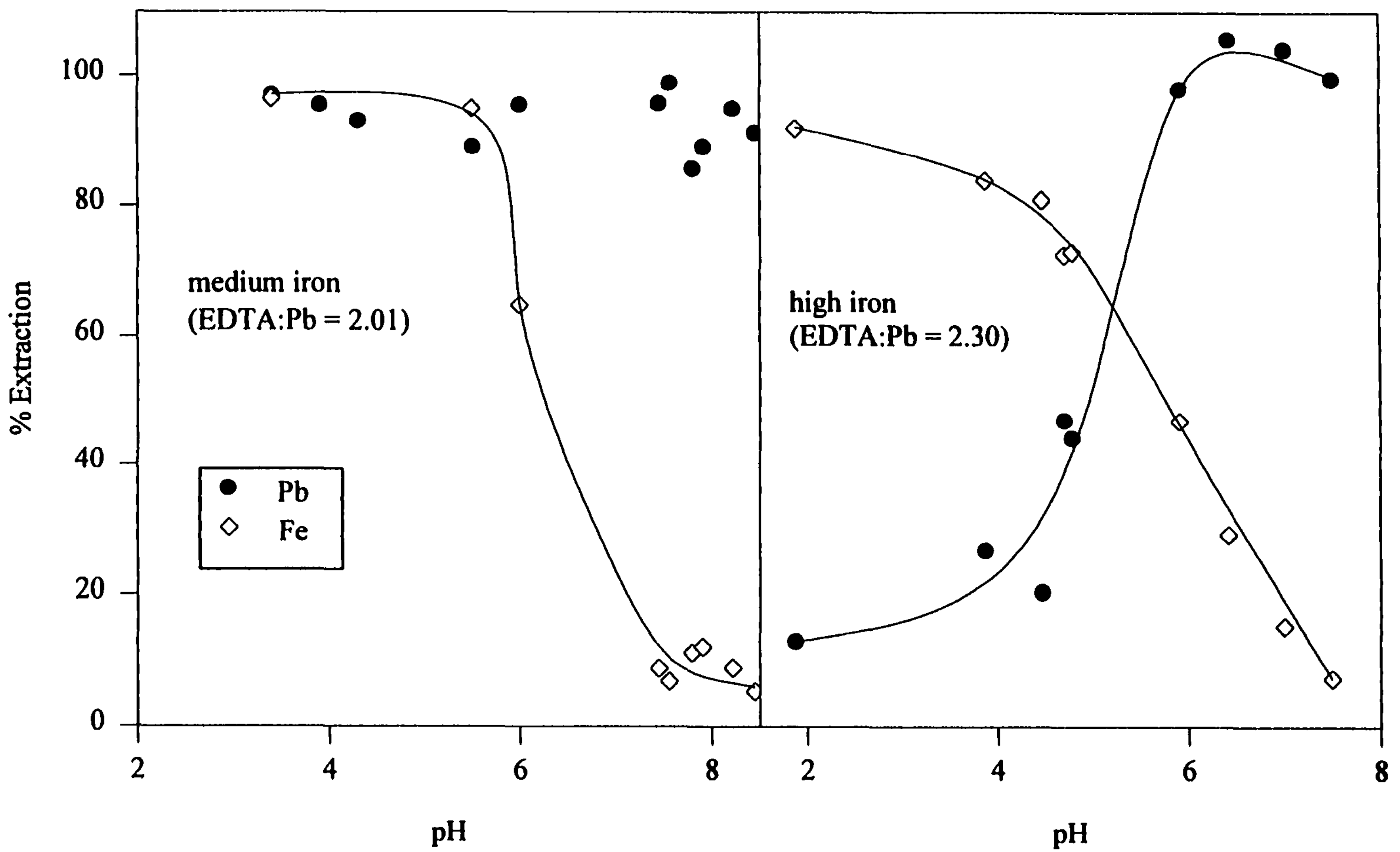


Figure 34. Lead and iron extraction efficiencies of $PbSO_4$-contaminated soil prepared with medium and high amorphous iron sand for various pH values with 0.005M EDTA solution

range as seen in Figure 34. For the $PbSO_4$-contaminated soil with high amorphous iron content, most of the applied EDTA may be complexed with Fe ions resulting in the reduction of lead extraction at low pH values. However, around neutral pH, almost all of the lead was extracted while low amounts of ferric ions were extracted. According to the above results, the amount of EDTA needed to get maximum extraction of lead from lead sulfate-contaminated soil, at low pH values, was approximately equal to the sum of the amounts of lead and amorphous iron in the soil. However, at high pH values, the amount of required EDTA to get maximum extraction results should be approximately equal to the amount of lead in soil. To minimize usage of EDTA but without sacrificing extraction efficiency, the pH of the extraction conditions should be approximately equal to neutral pH when the lead species is lead sulfate compounds.

Figure 35 presents the results of lead and amorphous iron extraction from lead carbonate-contaminated soil using water, 0.001 M and 0.002 M EDTA solution at various pH values. As presented in the figure, lead carbonate compounds in soils can be easily extracted with water under weak acidic conditions. With 0.001 M EDTA solution, lead extraction was higher than amorphous iron extraction indicating that over all pH ranges, lead carbonate compounds in soil were more reactive than amorphous iron. At high pH values, lead extraction efficiencies were lower probably due to the low solubility of lead. Similarly, with 0.002 M EDTA (Pb:EDTA stoichiometric ratio of 1:1.26), almost 100 % of lead was extracted while 10 - 70 % of iron was extracted depending on the pH. According to the experimental results, approximately the same amount of EDTA as lead in soil was required to extract the maximum amount of lead from lead carbonate-contaminated soil. As predicted by the stability constants, the amorphous iron effects on the lead extraction of lead carbonate-contaminated soil may be neglected.

Figure 36 presents the results of lead and amorphous iron extraction from lead phosphate-contaminated soil with water, 0.001 M, and 0.002 M EDTA solutions. For water only, lead extraction efficiencies were higher for pH values less than 4. Extraction of lead from lead phosphate with water was much less than lead carbonate. With 0.001 M EDTA solution, iron extraction was preferred over lead for pH between 3 and 6. Above pH 6, iron extraction was

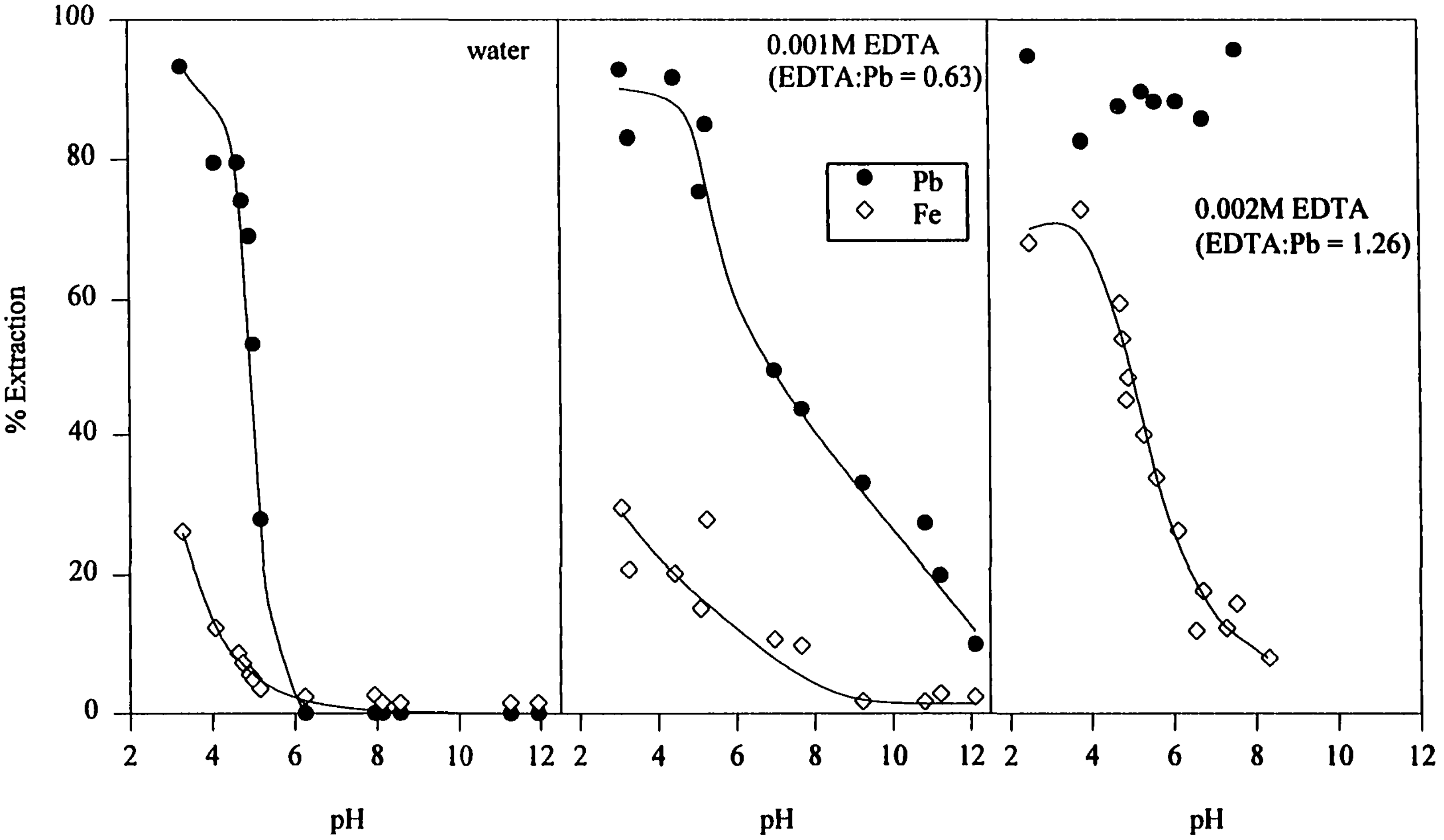


Figure 35. Lead and iron extraction efficiencies of $PbCO_3$-contaminated soil prepared with medium amorphous iron sand for various pH values with water and different concentration of EDTA solutions

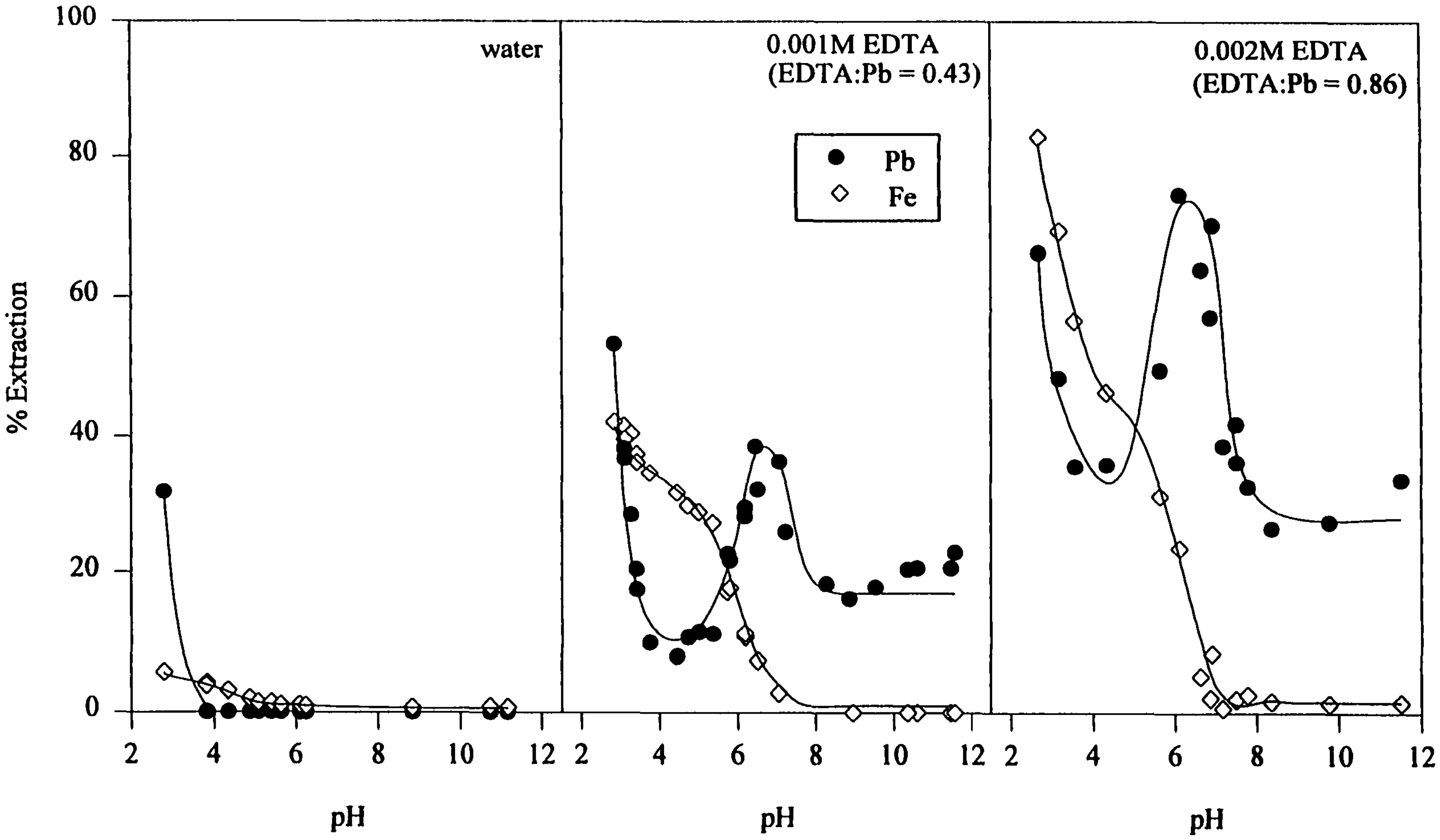


Figure 36. Lead and iron extraction efficiencies of lead phosphate-contaminated soil prepared with medium amorphous iron sand for various pH with water and different concentration of EDTA solutions

reduced with Pb extraction reaching a maximum between pH 6.5 and 7 before decreasing to a constant value above pH 8. The same Pb and Fe extraction pattern was observed for a 0.002 M EDTA solution. This indicates that iron competes with lead for EDTA sites for pH values less than 6. When sufficient EDTA was added, i.e., 0.005 M EDTA (Pb:EDTA stoichiometric ratio of 1:2.14), about 90 % of lead was extracted for pH less than 7 while the % of iron extracted was greater than 95 % (Figure 37). For pH greater than 8, the percent of lead extracted was about 60 % while iron extraction was less than 10 %.

Extraction of lead from lead phosphate-contaminated soil should be harder than lead sulfate-contaminated soil as predicted by the stability constants. However, for 0.001 M and 0.002 M EDTA solution, lead extraction for lead phosphate appeared to be higher than lead sulfate-contaminated soil. The reason might be due to the type of lead phosphate species formed during sample preparation. In the case of lead sulfate contaminated soil, $PbSO_4$ might be the dominant lead species in the contaminated soil. However, when lead ions react with phosphate ions ($H_2PO_4^{-1}$), the soil might be contaminated with a mixture of different kinds of lead phosphate compounds such as $Pb(H_2PO_4)_2$, $PbHPO_4$, $Pb_3(PO_4)_2$, $Pb_4O(PO_4)_2$, $Pb_5(PO_4)_3OH$. Because each lead phosphate species has a different solubility, the presence of different lead phosphate species might have an effect on the solubility of lead from lead phosphate-contaminated soil. Some of lead phosphate compounds have high solubility, therefore, lead phosphate compounds which have high solubility might compete with the amorphous iron for complexation with EDTA.

It is interesting to note that the amount of lead extracted with water only from lead phosphate contaminated soil was also higher than the lead extracted from lead sulfate-contaminated soil for a pH range of 2 and 4. If solubility predictions were made using $Pb(H_2PO_4)_2$ and $PbSO_4$ as the lead species in the soil, then the concentration of lead in water should be low since $Pb(H_2PO_4)_2$ has a lower solubility than the solubility of $PbSO_4$ for these pH ranges (Figure 3 and Figure 4). It is therefore probable as concluded earlier that more soluble lead phosphate compounds than $Pb(H_2PO_4)_2$ were obtained during the sample preparation. Considering the results, prediction using stability constants between $Pb(H_2PO_4)_2$

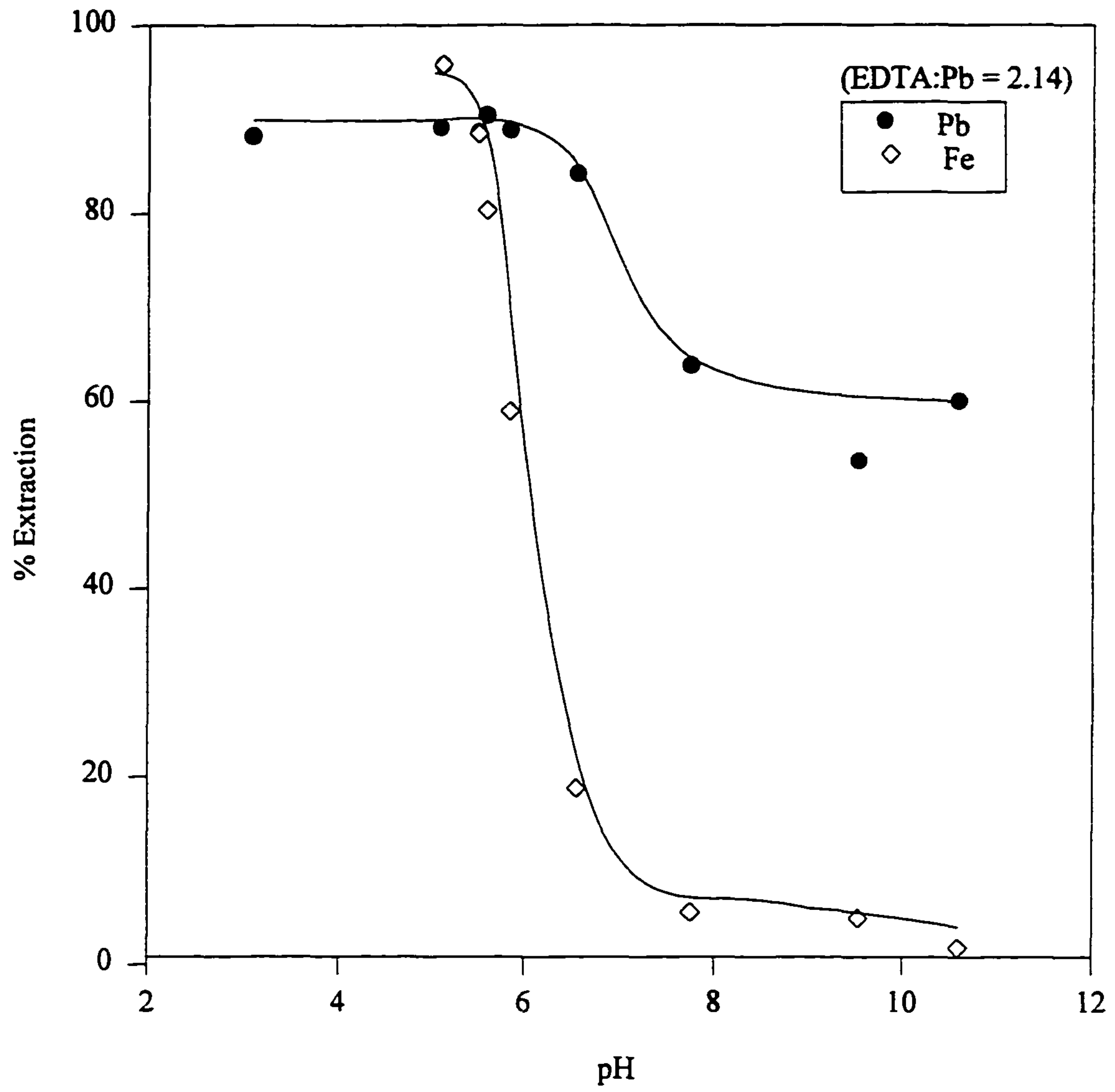


Figure 37. Lead iron extraction efficiencies of lead phosphate-contaminated soil prepared with medium iron sand with 0.005M EDTA solution

and EDTA might overestimate the amorphous iron effects on lead extraction from lead phosphate-contaminated soil.

Another interesting point to note in the extraction of lead from lead sulfate and phosphate-contaminated soil with EDTA:Pb stoichiometric ratio less than 2 was that there was a narrow optimum pH range of 6.5 and 7 whereby maximum lead extraction was achieved.

Figure 38 shows the lead and iron extraction from $PbSO_4$-contaminated soil prepared with medium iron samples with 0.001 M EDTA solution compared to the predictions by using thermodynamic data and MINTEQA2 program. Similarly, lead and iron extraction from $PbCO_3$ and lead phosphate-contaminated soils were compared to the predictions by using thermodynamic data and MINTEQA2 program are shown in Figure 39 and 40. For $PbSO_4$-contaminated soil, the lead and iron extraction efficiencies have similar trend as the prediction line using thermodynamic data such as solubility product and stability constant (Figure 38). For high pH values, there was some deviation between actual lead extraction efficiency and predicted lines implying that the steady state was not reached within in the 24 hours reaction. For $PbCO_3$-contaminated soil, thermodynamic calculation may underestimate the solubility of ferric ions at low pH value. For pH values higher than 9, the solubility of lead carbonate predicted by MINTEQA2 program increased due to the formation of soluble $Pb(CO_2)_2^{2-}$ ions.

It is worthy to note that for lead phosphate-contaminated soil, the prediction of Pb-EDTA solubility in the presence of $Pb(H_2PO_4)_2$ using the thermodynamic calculation was not matched at all. Instead of $Pb(H_2PO_4)_2$, Pb-EDTA solubility from $Pb_3(PO_4)_2$ was used. As shown in Figure 40, the prediction line and actual lead extraction efficiency showed similar trend. For this reason, $Pb_3(PO_4)_2$ might be precipitated instead of $Pb(H_2PO_4)_2$ during the lead-phosphate-contaminated soil sample preparation.

Based on the experimental and theoretical results, amorphous ferric ion played an important role for lead extraction from lead-contaminated soil. However, the effect of iron was dependent on lead species and pH of the solution. To obtain maximum lead extraction efficiency with stoichiometric ratio of EDTA to lead of less than 2, the equilibrium pH is the

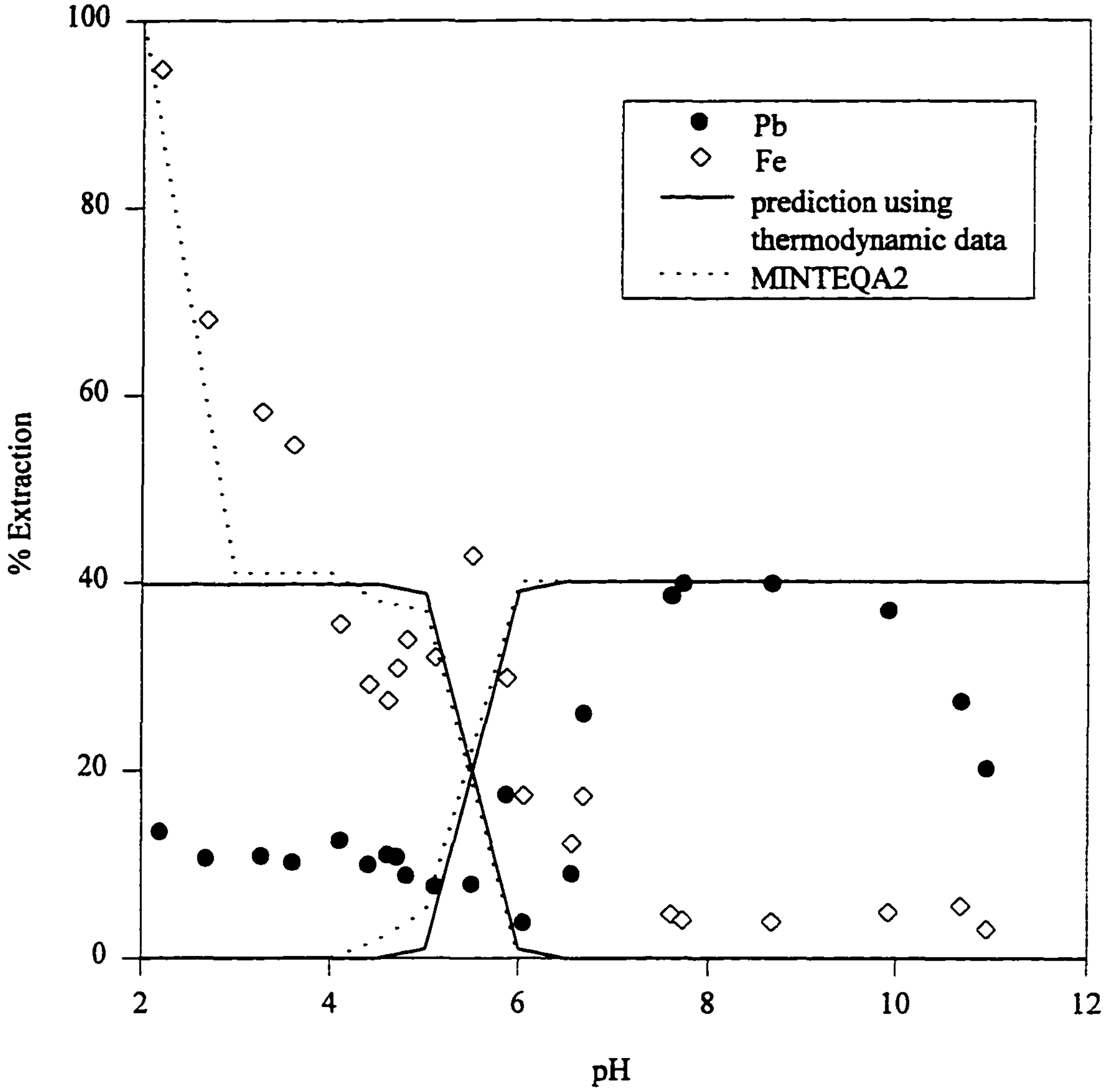


Figure 38. Lead and iron extraction from $PbSO_4$-contaminated soil prepared with medium amorphous iron sample with 0.001 M EDTA solution compared to thermodynamic calculation and MINTEQA2 program

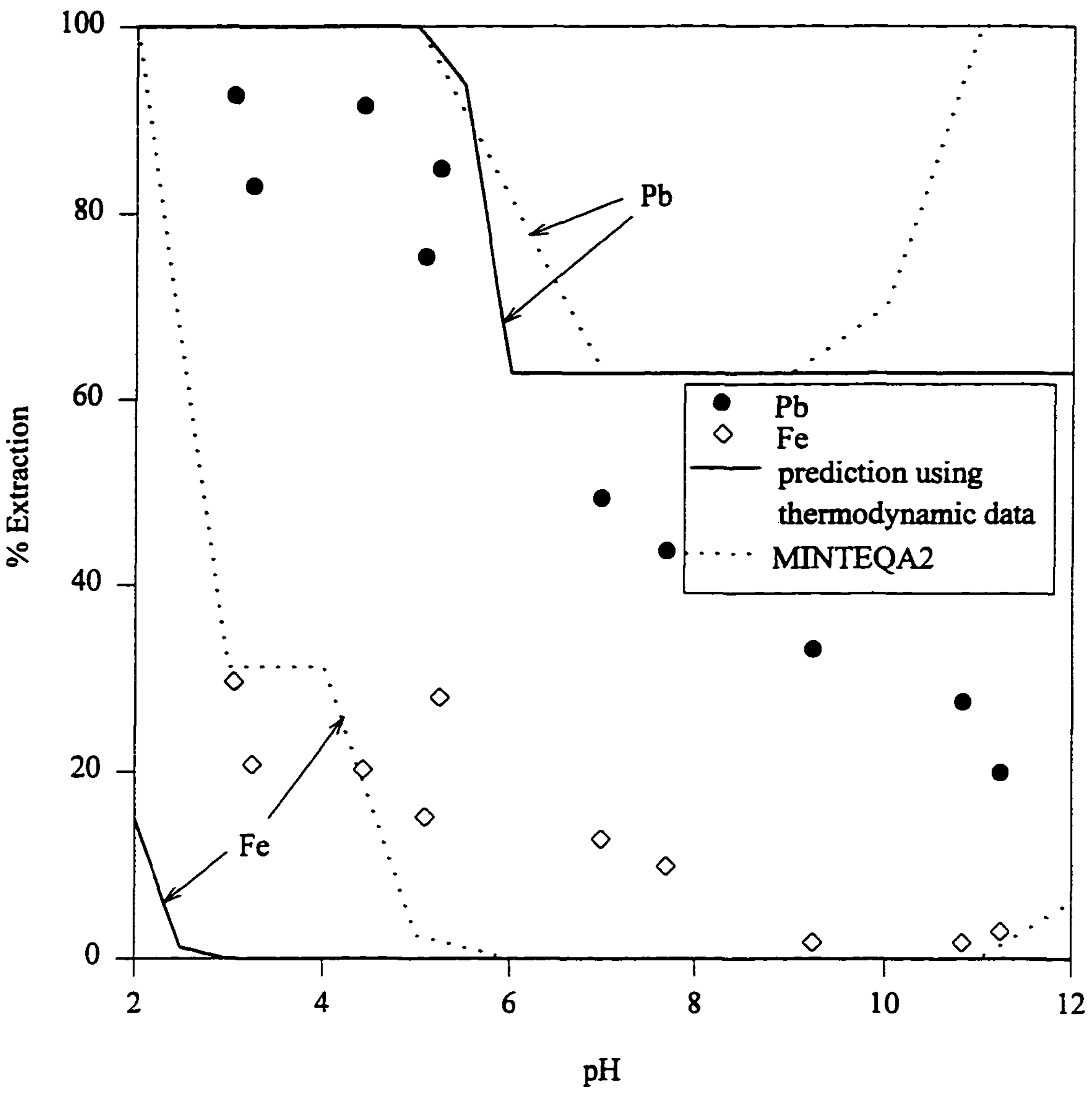


Figure 39. Lead and iron extraction from $PbCO_3$-contaminated soil prepared with medium amorphous iron sample with 0.001 M EDTA solution compared to thermodynamic calculation and MINTEQA2 program

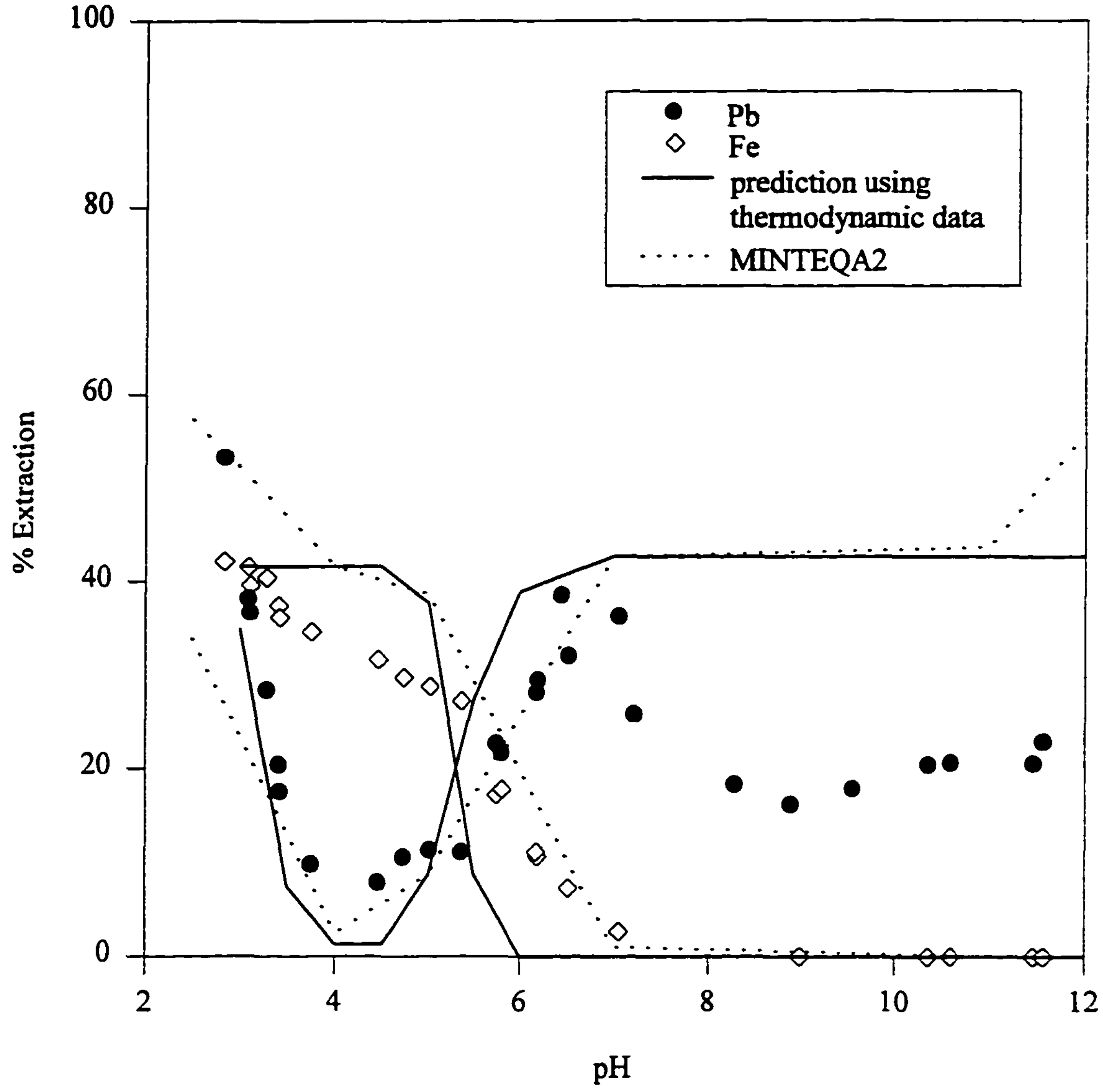


Figure 40. Lead and iron extraction from lead phosphate-contaminated soil with medium amorphous iron sample with 0.001 M EDTA solution compared to thermodynamic calculation and MINTEQA2 program

most important factor controlling the lead extraction. According to the experimental results, neutral pH was the optimum pH for lead extraction from lead sulfate or lead phosphate-contaminated soil with high content of amorphous iron. However, for lead carbonate-contaminated soil, amorphous iron did not affect lead extraction over a wide pH range.

CONCLUSIONS

Amorphous iron in soil may compete with lead for EDTA in the extraction of Pb from lead-contaminated soil. Computation using stability constants, solubility products and equilibrium constants, showed that amorphous iron may reduce lead extraction depending on the pH and lead species present in soil. Similarly, experiments conducted with varying amount of amorphous iron content indicated that the extraction efficiency of Pb was affected especially for pH values less than 6.0. The percent of extracted lead depended on the EDTA:Pb stoichiometric ratio, pH, lead species and amorphous iron concentration. The experimental results showed that the effect of amorphous iron on lead extraction appeared to be dominant at pH less than 6 for EDTA:Pb stoichiometric ratio equal to 2:1 with a soil having an amorphous iron content of 3,360 mg/kg. Besides the effect of amorphous iron on lead extraction, the lead extracted in the presence of amorphous iron was also dependent on the lead species.

Lead extraction from lead carbonate-contaminated soil was not affected much by amorphous iron. However, lead extraction from lead sulfate-contaminated soil in the presence of amorphous iron was severely affected for pH values less than 6 and the pH range of 7 to 9 should be retained to obtain optimum lead extraction efficiencies with EDTA:Pb stoichiometric ratio less than 2:1. For lead phosphate-contaminated soil, similar amorphous iron effect was observed for pH less than 6 but the extent of amorphous iron effect was less than the effect on lead sulfate-contaminated soil. In the case of lead phosphate-contaminated soil, the optimum pH range for lead extraction was narrow between pH 6.5 and 7. If low amounts of EDTA is used for soil washing, i.e., for EDTA:Pb stoichiometric ratio less than 2:1, pH control is very important.

In summary, the degree of difficulty of extraction of various lead species using EDTA:Pb stoichiometric ratios of less than or equal to 2:1 were:

Lead sulfate > Lead phosphate > Lead carbonate.

PART III. RECYCLING OF USED EDTA WASTEWATER

INTRODUCTION

Soil washing with chelating agents depends on the ability of the chelating agents to form stable metal complexes which are soluble in an aqueous system. EDTA is considered to be one of few effective chelating agents for the extraction of metals from soil. Because of its effectiveness, much research have been conducted with EDTA for the remediation of metal-contaminated soil. Although EDTA is the standard choice for extractive treatment technologies, the high cost of the EDTA has restricted the wide use of EDTA for the remediation of metal-contaminated soils. Soil remediation using EDTA solution will generate a large volume of wastewater containing metal-EDTA complexes which must be treated before disposal. Besides reducing the volume of wastewater, recycling of used EDTA will help to reduce chemical costs for the treatment of metal-contaminated soils. Unfortunately, there is currently no practical way of recycling used EDTA although several researchers have proposed various methods of recycling EDTA wastewater.

Some of the earlier recycling studies found in the literature were concerned with the recovery of metals from metal-EDTA complexes. Cartwright (1961) showed that metal ions may be precipitated from the metal-EDTA solution. For an iron-EDTA solution, Cartwright precipitated iron as hydrated iron hydroxide by oxidizing the EDTA with hydrogen peroxide at approximately 100°C. In addition, he precipitated lead ions as lead phosphate using the same approach except that phosphoric acid was added prior to oxidation by hydrogen peroxide. Daignault et al. (1982) proposed an approach to separate the lead from the used lead-EDTA by oxidizing the EDTA with hydrogen peroxide followed by the precipitation of lead as a lead sulfide by adding sodium sulfide. Although metals may be recovered, EDTA was oxidized to smaller organic compounds such as formaldehyde, ethylenediamine and carbon dioxide, making it useless for recovery of EDTA and reuse for further treatment.

Two USSR scientists, Gordievskii and Gurinov (1961) proposed regenerating EDTA from copper-EDTA solution by electrolysis using a cation-exchange membrane. They suggested that when no cation exchange membrane was installed, EDTA was oxidized on the surface of the anode. According to their results, EDTA regeneration depends on the kind of anolyte (solution in anode compartment). Basic anolyte such as sodium carbonate yielded more EDTA than an acidic anolyte such as hydrochloric and sulfuric acid. One N sodium carbonate solution yielded 94 % of EDTA while recovery rates for hydrochloric acid and sulfuric acid were 91.1 % and 87.9 %, respectively. However, their paper was short and did not present experimental results making it difficult to fully evaluate their method. Work done by Johnson et al. (1972) on the same method confirmed that EDTA was oxidized on the Pt anode in an acidic sulfate solution when a cation-exchange membrane was not installed. Allen et al. (1993) showed that more than 90 % of lead might be precipitated and more than 90 % of EDTA might be recovered through electrolysis. Research done by Turner et al. (1994) on the electromembrane process showed that 99.3 % of lead might be recovered with 91 % of EDTA recovered. All these electrochemical experiments were bench-scale experiments using pure lead-EDTA solution. Although EDTA was recovered, the recovered EDTA was not used to further demonstrate that it may still be used to remediate metal-contaminated soils. The electromembrane process is not without any problems. According to Allen et al. (1993) only metal ions and protonated EDTA complexes could be reduced and nonprotonated EDTA complexes such as Pb-EDTA^{2-} were not reduced. In addition, the pH of the cathode compartment was found to increase as a result of the production of hydroxyl ions which led to the formation of more nonprotonated metal-EDTA complexes and a reduction in efficiency. Also, high pH values (>10) in the cathode compartment resulted in membrane degradation. In the anode compartment, the pH of the solution decreased as a result of the production of protons at anode. For these reasons, several operating problems must be addressed before the electromembrane system can be a practical and feasible system for recycling EDTA.

Kennedy (1986) showed that ferric ions may be precipitated from Fe-EDTA solution with calcium ions by increasing the pH of the solution to more than 12.5. To form iron floc, calcium hydroxide was added in amounts between 0.25 and 5 % (w/w). With this suggested method, he precipitated out more than 99 % of the ferric ions from the 1,040 ppm Fe-EDTA solution. This method may be a feasible way of recycling Pb-EDTA solution. Rudd et al. (1995) tried to recover EDTA from a solution of Pb-EDTA complexes by precipitating the lead ions as lead hydroxide-precipitation or addition of sulfide for lead sulfide precipitation at high pH. The work reported by Rudd et al. (1995), however, did not show the effectiveness of the recycled EDTA solution in treating lead-contaminated soil. According to their results, the hydroxide-precipitated effluent did not reach the minimum acceptable lead concentration for direct discharge as a secondary waste stream. The hydrogen sulfide system, however, precipitated out the lead to a satisfactory lead concentration at high pH. A disadvantage with using sulfide is that hydrogen sulfide gas may be released during the reaction, therefore, making it difficult to safely operate this system at an actual treatment system.

There are currently no practical means of recycling used Pb-EDTA wastewater from soil washing system. The objectives of this section are to develop a method for recycling lead-EDTA wastewater and to assess the effectiveness of the recycling method for repeated use in the treatment of lead-contaminated soils.

Hypothesis

When lead-contaminated soil is washed with EDTA solution, the extracted solution consists of Pb-EDTA complexes, other metal-EDTA complexes (generally Ca-, Fe-, Mg-, and Mn-) depending on the soil characteristics and some residual EDTA. Among these metal-EDTA complexes, lead-EDTA is the main complex because lead ion has a relatively higher stability constant with EDTA than the stabilities of other metal ions except for ferric ions at low pH values. The recycling approach proposed will exploit the higher stability of Fe(III)-EDTA complexes over Pb-EDTA complexes at low pH. For example, Norvell and Lindsay (1969), showed that at low pH values, ferric ions can substitute for the zinc and manganese ions complexed with EDTA. In addition, Sommers and Lindsay (1979) showed that for a solution with the same molar concentration of lead, iron and EDTA, Fe(III)-EDTA was found to be more dominant than the Pb-EDTA at a pH value less than 5.2. Based on the above studies, ferric ions will be added to the Pb-EDTA solution at low pH values to compete for the active sites of EDTA by substituting for lead complexed with EDTA. Ferric chloride or ferric nitrate will be used to provide the ferric ions. Both ferric chloride and ferric nitrate compounds are very soluble and pH adjustment will not necessary as the hydrolysis of the added ferric ions will be sufficient to decrease the solution pH where the substitution for lead will be favorable.

Figure 41 shows the complexation results of lead ion and ferric ions with EDTA for the same molar concentration of lead ions, ferric ions and EDTA ions over a range of solution pH. To plot Figure 41, the concentrations of anions, chloride or nitrate were assumed to be three times more than the total molar concentration of lead, iron and EDTA ions. The calculations were computed using MINTEQA2 program. It shows that for pH value less than 7, EDTA was more reactive with ferric ions than lead ions. Based on these results, lead ions already complexed with EDTA may be substituted with ferric ions if the pH was less than 7. It is interesting to note that use of ferric chloride and ferric nitrate compounds have similar reactivity with EDTA in solution.

After Pb-EDTA complexes have been converted to Fe-EDTA complexes, lead ions may be precipitated out at low pH values. The precipitation of lead metals will be conducted using sulfate and phosphate ions. For the same molar concentration of each anion present in solution, lead phosphate has a lower solubility than lead sulfate for pH values less than neutral pH. In the presence of chloride ions, the solubility of lead ions in a phosphate solution may be further reduced through the precipitation of chloropyromorphite $Pb_5(PO_4)_3Cl$ ($\log K = -25.05$). The precipitated lead will then be separated from the solution and the treated Fe-EDTA solution may then be used again as an extraction solution. By raising the pH of the solution to greater than 7, ferric ions complexed with EDTA will most likely be substituted with lead ions present in the soil.

The proposed method can be extended further by precipitating the Fe in the recycled Fe-EDTA solution before applying the Fe-EDTA solution to the lead-contaminated soil. Because ferric ions have very low solubility at high pH values, precipitation of ferric hydroxide at high pH would be favorable even though Fe may be complexed with EDTA. The Fe-precipitated EDTA solution may be a better recycling product as it may be used even at low pH values for the remediation of lead-contaminated soils. Figure 42 shows the flow diagram of the recycling procedures. In this research, the lead extraction efficiency with Fe-

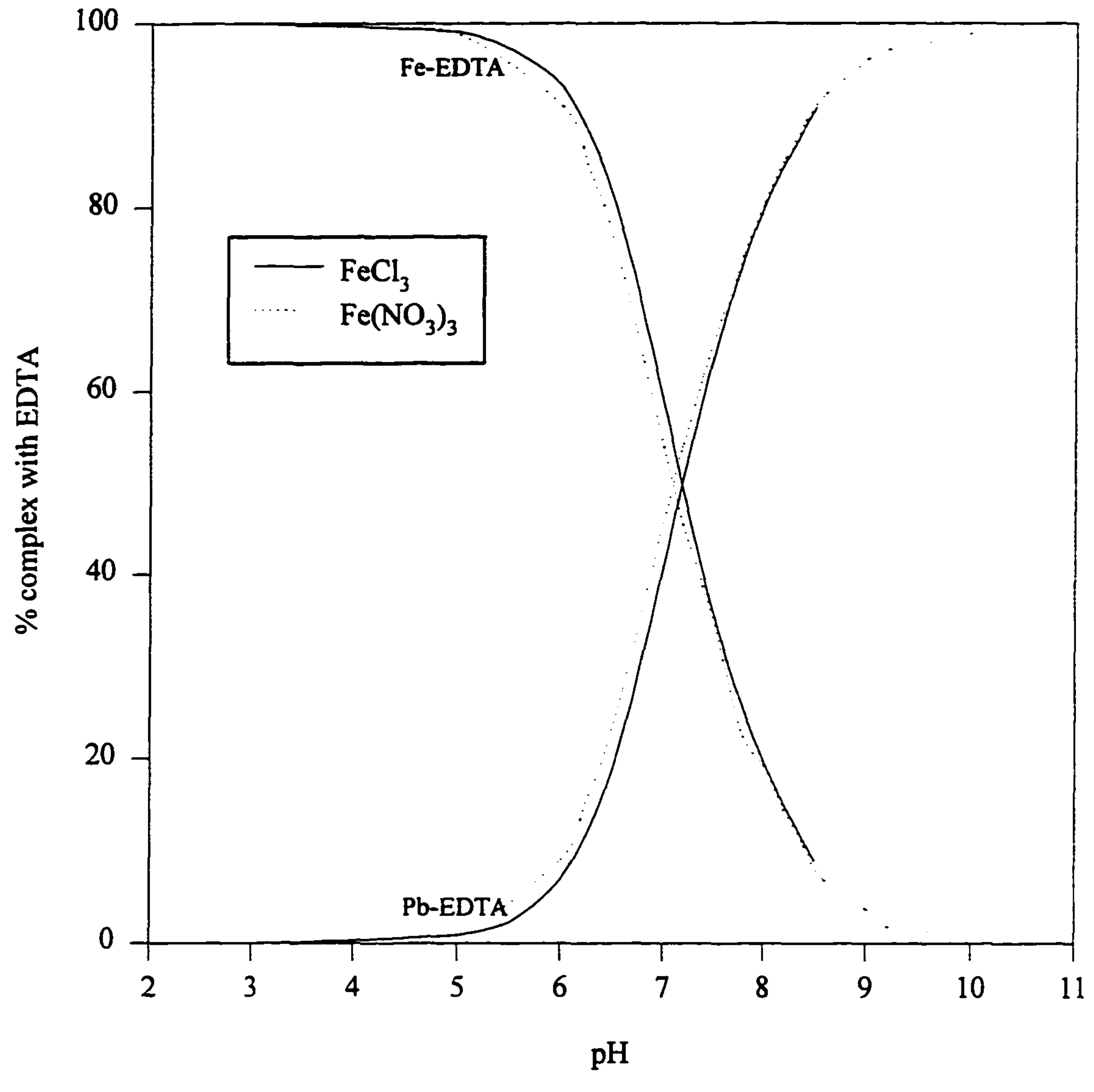


Figure 41. Lead and iron complexation with EDTA for various pH using the same molar concentration of Pb-EDTA solution and $FeCl_3$, and $Fe(NO_3)_3$

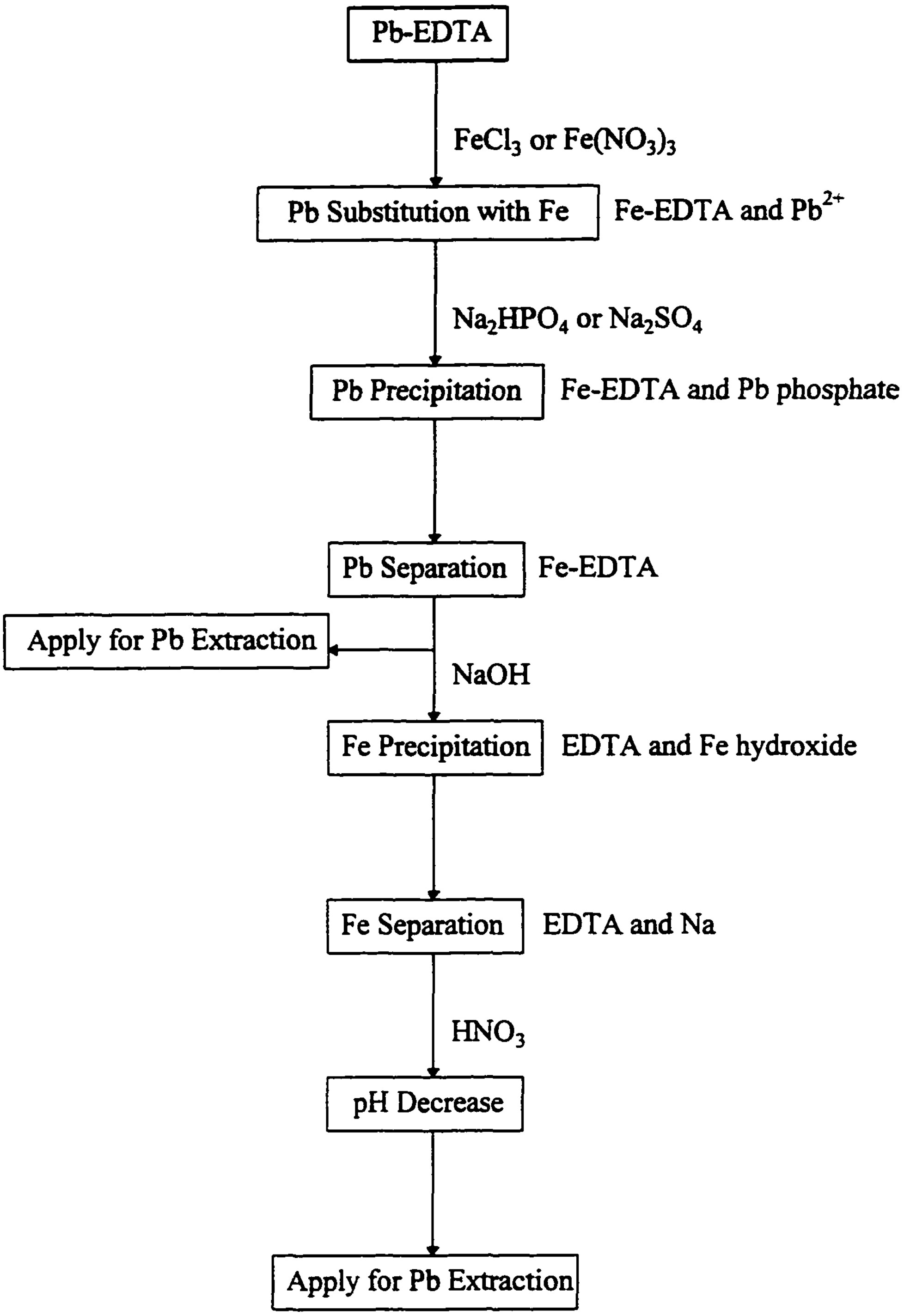


Figure 42. Flow diagram of the recycling system

EDTA and Fe-precipitated EDTA will be compared to obtain the better recycling procedure for further application of the recycled EDTA. In addition, the effectiveness of recycled EDTA solution using phosphate and sulfate to precipitate the lead ions will also be compared.

MATERIALS AND METHODS

The experiments conducted to test the hypotheses are as follows:

I. precipitation of Pb from Pb-EDTA using prepared Pb-EDTA stock solution to determine the use of ferric and phosphate compounds

II. use of recycled Pb-EDTA stock solution to determine its extraction efficiency

III. application of the recycling process over several cycles to assess the extraction efficiencies of recycled Pb-EDTA.

Experimental Procedures using Stock Solution

Stock solution preparation

Experiments were conducted using prepared stock solution of Pb-EDTA. The stock solution was prepared by adding adequate amount of lead sulfate to 2,000 ml nano pure water. The mixture was mixed for 24 hours. A small aliquot of the lead sulfate solution was filtered with a 0.45 μm filter paper and analyzed for dissolved lead ions concentration. Na_2EDTA of slightly lower molar concentration than the added lead was added to the lead sulfate solution and stirred for 24 hours. Similarly a small aliquot of the stock solution was filtered and analyzed for lead concentration. The target lead and EDTA concentration was 0.005 M.

The stock solution was then filtered with a 0.45 μm filter paper to separate the residual solid lead sulfate from the stock solution. It was assumed that all the dissolved lead was complexed with EDTA. To indirectly show that all the EDTA was complexed by lead, 10 ml of the prepared stock solution was reacted with 1 gram of lead-contaminated soil for 24 hours. The lead concentration of the stock solution before and after reacting with lead-contaminated soil for 24 hours was found to be the same. The experimental results indicated indirectly that there was no available EDTA left in the stock solution to complex with lead in the contaminated soil.

Lead precipitation from Pb-EDTA stock solution

The optimum amount of ferric compounds needed to substitute for lead ions complexed with EDTA was conducted using different amounts of ferric chloride with 10 ml of the Pb-EDTA stock solution in a 50 ml of polypropylene centrifuge tube. The pH of the solution was not adjusted. Addition of ferric chloride, however, resulted in a solution pH of between 2 and 4. The solution was shaken for 24 hours followed by the addition of sodium phosphate solids to achieve an initial phosphate concentration of 0.15 M. The solution was shaken for 10 hours and centrifuged for 10 minutes at 3,000 rpm followed by filtration with a 0.45 μm filter paper. Preliminary experiments showed that the reaction time of 24 hours for ferric substitution process and 10 hours for lead precipitation process were sufficient to reach steady state conditions. Lead and iron concentrations in the filtrate were then measured with atomic absorption spectrophotometer.

A kinetic study was conducted using the investigated optimum amounts of ferric compounds to determine the minimum required reaction time to reach steady state conditions with 0.15 M of initial phosphate concentration. To find the optimum concentration of phosphate needed to precipitate lead ions, the optimum amounts of ferric compounds was added to Pb-EDTA solution and allowed to react for 6 hours. Different amounts of phosphate was then added to Fe-EDTA stock solution and mixed for 10 hours. The slurry was filtered with a 0.45 μm membrane filter paper and the lead concentration of the filtrate measured. The difference in the lead concentration of the initial Pb-EDTA stock solution and the final filtrate solution was assumed to be the removal efficiency of lead from the Pb-EDTA solution.

Extraction Efficiency Procedures for Recycled Pb-EDTA Stock Solution

To investigate the lead extraction efficiency of recycled Pb-EDTA solution, extraction studies were conducted using Fe-EDTA solution prepared from Pb-EDTA solution. The Fe-EDTA stock solution was prepared by adding Fe ions to Pb-EDTA stock solution with a Fe/Pb ratio of 1.5, allowing a reaction time of 6 hours followed by adding phosphate with initial phosphate concentration of 0.15 M. The slurry was then filtered. Because Fe ions have the highest reactivity with EDTA at low pH values, the application of Fe-EDTA solution for the extraction of lead from lead-contaminated soil may be limited to only high pH values. However, when Fe ions are separated from the Fe-EDTA solution by precipitation, the Fe-precipitated EDTA solution may be applied for a wider pH range for remediation of Pb-contaminated soils. To prepare Fe-precipitated EDTA solution, the pH of the Fe-EDTA stock solution was increased to higher than 13 by addition of NaOH pellets. The solution was filtered with a 0.45μm filter paper to separate the precipitated ferric ions. To compare the lead extraction efficiency of Fe-EDTA and Fe-precipitated EDTA solution at different pH values, 1 gram of Cal soil was shaken with 10 ml of each prepared EDTA solution in a 50 ml polypropylene centrifuge tube for 24 hours. The pH was controlled with sodium hydroxide solution and diluted HNO_3 solution. The slurry was then filtered with a 0.45 μm filter paper. The pH of the filtrate was measured. The difference in lead concentration before and after the application of the Fe-EDTA or Fe-precipitated EDTA solution was assumed to be the amount of lead extracted from lead-contaminated soil. The lead extraction efficiencies using recycled EDTA solutions were then compared to the lead extraction efficiencies with fresh EDTA solution.

Extraction Efficiency Study using Recycled used Pb-EDTA Solution from Extraction of Lead-Contaminated Soil

To investigate the lead extraction strength of once recycled Pb-EDTA solution compared to fresh EDTA solution, one set of batch experiments was conducted with Cal soil. Six grams of Cal soil were reacted with 60 ml of 0.1 M EDTA solution for 12 hours. The slurry was filtered with a 0.45 μm filter paper. The lead concentration in the filtrate was measured. The filtrate was divided into two batches. For the first batch, twenty ml of the filtrate was used to react with 2 grams of fresh Cal soil for 12 hours. This procedure was repeated again three more times. For each reaction, the mass ratio of EDTA solution to soil was held constant at 10:1. For the second batch of filtrate, Fe(III) with a molar amount of about 1.5

times higher than the molar amount of EDTA was added in the form of $Fe(NO_3)_3 \cdot H_2O$. The solution was shaken for 6 hours after which adequate amount of disodium phosphate was added to make a initial phosphate concentration of 0.2 M. Right after the phosphate had dissolved, the slurry was filtered with a 0.45 µm filter paper. Adequate amount of NaOH pellets was then added to the filtrate to increase the pH to higher than 13 to precipitate out the iron. The final solution was filtered with a 0.45 µm filter paper and the lead concentration in this final solution was measured. Nitric acid was added to adjust the pH of the filtrate to the initial pH (pH = 4.6) of fresh 0.1 M EDTA solution. The pH adjusted filtrate was then applied to fresh Cal soil. Extraction experiments were conducted with a reaction time of 12 hours. The slurry was filtered again and the filtrate was applied to another fresh Cal soil without further treatment for three more times. The lead extraction efficiencies of fresh EDTA solution and recycled EDTA solution over several extraction cycles were compared with each other.

Another set of experiments was conducted to determine the extraction efficiency of recycled used EDTA over several extraction cycles. Soil samples used were Cal soil and rifle range soils. Twenty grams of Cal and Rifle range soil were reacted for 12 hours with 200 ml of 0.05 M and 0.03 M of EDTA solution, respectively. The EDTA:Pb stoichiometric ratios were 7.8 and 9.96, respectively. The slurries were filtered with 0.45 µm filter paper and lead concentration in the filtrate was analyzed. A portion of the filtrate was applied to a new soil sample and reacted 12 hours. This procedure was repeated three more times. The remaining portion of filtrate was recycled using the procedure described above with Fe substitution, Pb precipitation and Fe precipitation steps. Before applying the recycled EDTA solution, the pH of the recycled solution was adjusted to approximately the soil pH of 8.2. After the first extraction, the solution was filtered and recycled over three or four more times. In these recycling tests, sulfate ions were used besides phosphate ions for the precipitation of lead from Fe-EDTA solution to investigate the lead precipitation efficiency from Fe-EDTA solution and the lead extraction efficiency from Pb-contaminated soils for sulfate ions and phosphate ions.

RESULTS AND DISCUSSIONS

Lead Precipitation from Pb-EDTA Stock Solution

As presented in the Materials and Methods Section, the proposed scheme for recycling EDTA would include adding Fe(III) ions to exchange for the Pb complexed with EDTA followed by the addition of sulfate or phosphate ions to precipitate the uncomplexed lead ions at low pH values. The test results of the precipitation of lead with Fe(III) ions added to a 0.005 M of Pb-EDTA stock solution are presented in Table 8. This Table presents the results of the effect of phosphate and sulfate ions in precipitating the dissolved uncomplexed lead ions in the form of lead phosphate or lead sulfate compounds. For a Fe/Pb ratio of 1.44 and 1.41, the percent of lead precipitation with phosphate and sulfate were 99 % and 100 %, respectively. Without the use of these ions, 91 % of lead was precipitated. The results showed that a Fe(III) molar amount of 1.5 times more than the applied EDTA molar amount was enough to remove most of the lead ions from the Pb-EDTA solution. A molar concentration of Fe(III) which is 1.5 times higher than the concentration of EDTA solution will be chosen for Fe(III) kinetic study and for the used EDTA recycling experiments.

Addition of a same molar amount of disodium phosphate as monosodium phosphate had the same lead precipitation efficiency but with a significant increase in the final pH of the solution (Table 8). Use of disodium phosphate may be more appropriate for Fe-EDTA application because the high pH of the final solution was more favorable for the treatment of Pb-contaminated soil. Furthermore, the high pH would mean that the required amount of NaOH needed to increase the pH to precipitate Fe(III) ions may be reduced. For this reason, the disodium phosphate was chosen to precipitate lead from used EDTA solution in the recycling experiments using actual lead-contaminated soils. Similar lead precipitation results were obtained when potassium sulfate was introduced instead of phosphate ions (Table 8).

Figure 43 shows the kinetics of substitution of Fe(III) ions for Pb ions in Pb-EDTA stock solution. The Fe/Pb ratio used was 1.5 with an initial 0.15 M phosphate ion concentration. The results showed that a reaction time of 1 hour was sufficient to substitute Fe(III) ions for

Table 8. Percent lead removal from the 0.005 M Pb-EDTA (Pb = 1,040 ppm) stock solution depending on the added amounts of iron compounds with 6 hour reaction for Fe substitution step and 10 hour reaction for Pb precipitation step

Sample #	ratio of Fe/Pb	added phosphate $NaH_2PO_4 \cdot H_2O$	Final Pb concentration (ppm)	lead precipitation (%)	pH
1	0.72	0.15 (M)	301.4	72	3.5
2	0.72	0.15 (M)	291.6	73	3.5
3	1.44	0.15 (M)	15.6	99	3.3
4	1.44	0 (M)	93.8	91	2.5
5	2.16	0.15 (M)	0	100	3.0
6	2.16	0 (M)	140.8	87	2.2
7	1.5	0.15 *	1.9	99.9	7.6
8	1.41	0.15 (M) **	10	99.9	3.1

* with $Na_2HPO_4 \cdot 7H_2O$ and right after phosphate was dissolved, the slurry was filtered.

** with K_2SO_4

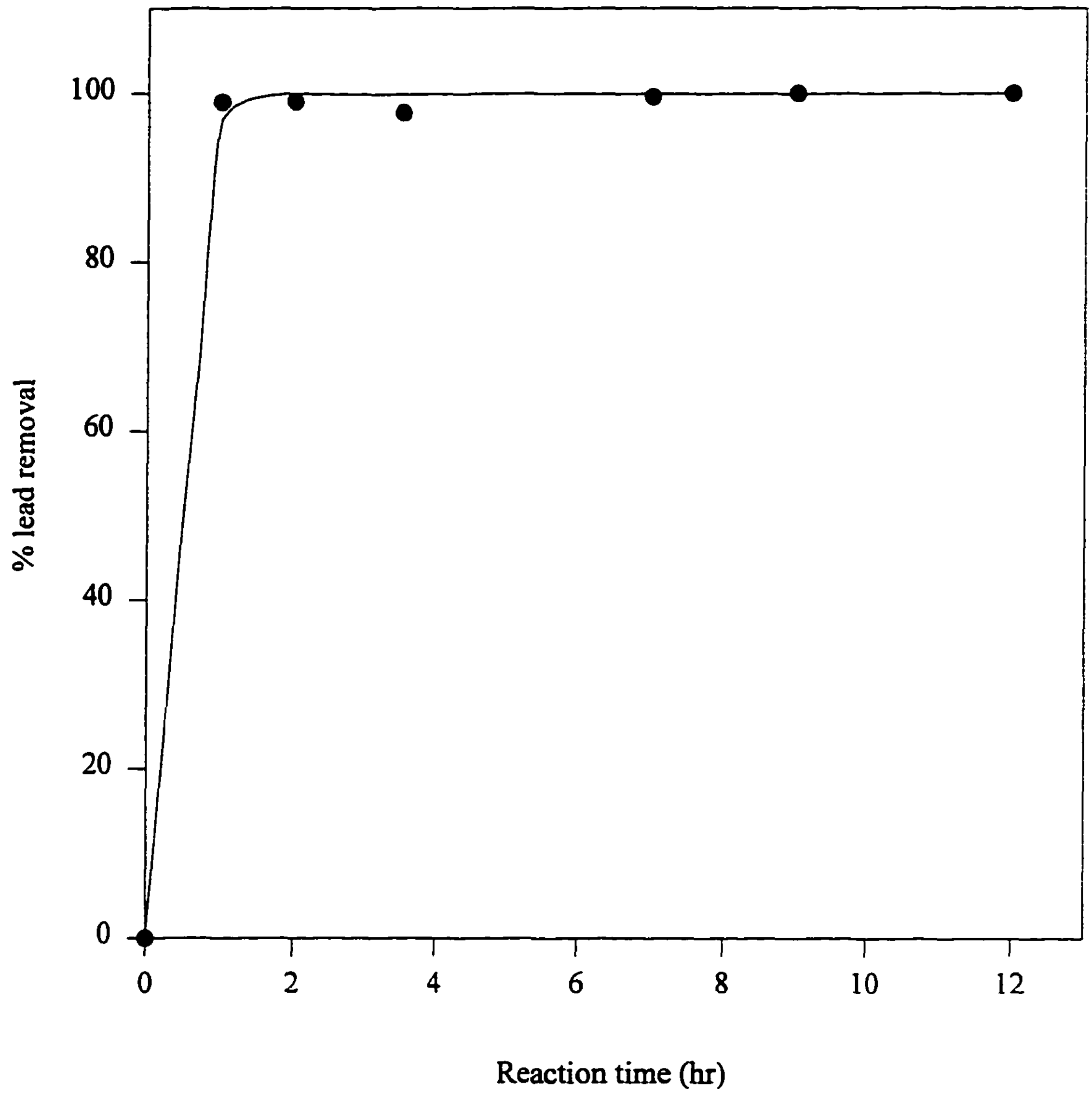


Figure 43. Pb ion removal efficiency from Fe-EDTA solution over time (Fe/Pb ratio = 1.5, initial phosphate concentration = 0.15 M)

Pb ions in a 0.005 m Pb-EDTA stock solution. A 6 hours reaction time for Fe and Pb-EDTA was chosen for the recycling reactions.

Experimental results to determine the initial phosphate concentration needed to precipitate uncomplexed lead ions from 0.005 M Pb-EDTA stock solution are presented in Figure 44. The figure shows that about 0.04 M of initial phosphate concentration was enough to achieve 100 % lead removal. For the recycling experiments with actual lead-contaminated soils, an initial phosphate concentration of 0.2 M was chosen.

Figure 45 shows that Fe(III) ions may be precipitated out from Fe-EDTA solution depending on the pH of the solution. Most of Fe ions which might be complexed with EDTA could be precipitated out at pH 13 as shown in Figure 45. It seems that hydrolysis of ferric ions at high pH values was a more thermodynamically favorable process than its complexation with EDTA.

Extraction Efficiency of Recycled Pb-EDTA Stock Solution

To further test the recycling hypothesis, Fe-EDTA solution and Fe-precipitated EDTA solution prepared from 0.005 M Pb-EDTA stock solution were applied to Cal soil at different pH values. Figure 46 shows that the pH of the solution played an important factor in determining the lead extraction efficiency of the recycled Fe-EDTA solution.

Compared to fresh and Fe-precipitated EDTA solutions, Fe-EDTA solution has the least lead extractive power for pH less than 7 (Figure 46). For pH above 7, extraction efficiency of Fe-EDTA solution was about half of the extraction efficiency of fresh EDTA solution. A reason for the higher extraction efficiencies at pH above 7 was that the hydrolysis of ferric ions might provide some ligand sites on the EDTA for Pb. In addition, for high pH, lead could substitute for Fe ions complexed with EDTA because lead has a higher reactivity with EDTA than iron. At low pH values, the extraction efficiency of lead using Fe-EDTA solution was low at about 5-7 %. The reason was that for pH less than 6, the reactivity of iron was stronger than that of lead ions resulting in low lead extraction efficiency.

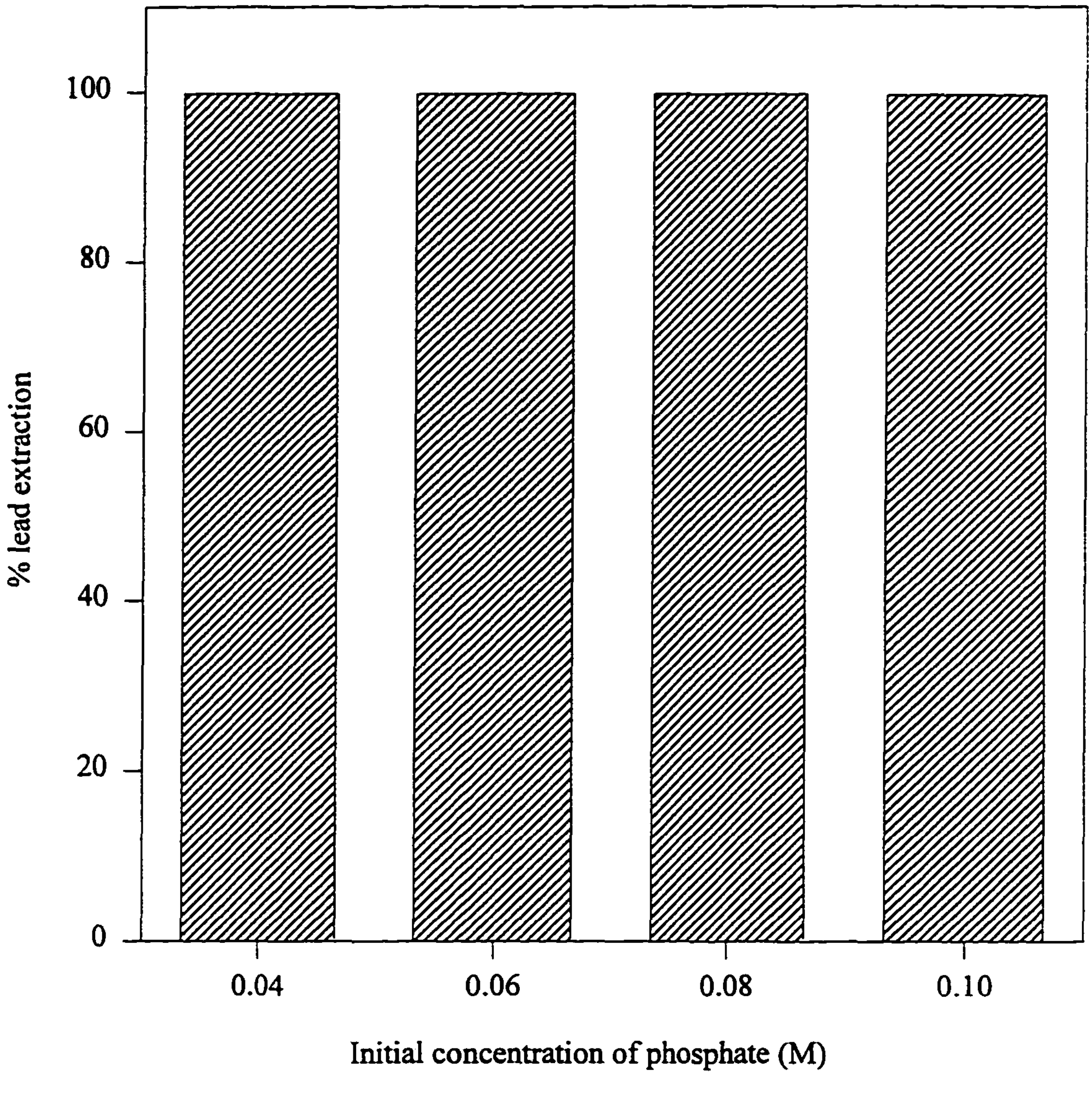


Figure 44. Lead removal efficiency from Pb-EDTA solution for various initial phosphate concentrations with Fe/Pb ratio of 1.5 and 6 hours reaction time for Fe substitution step

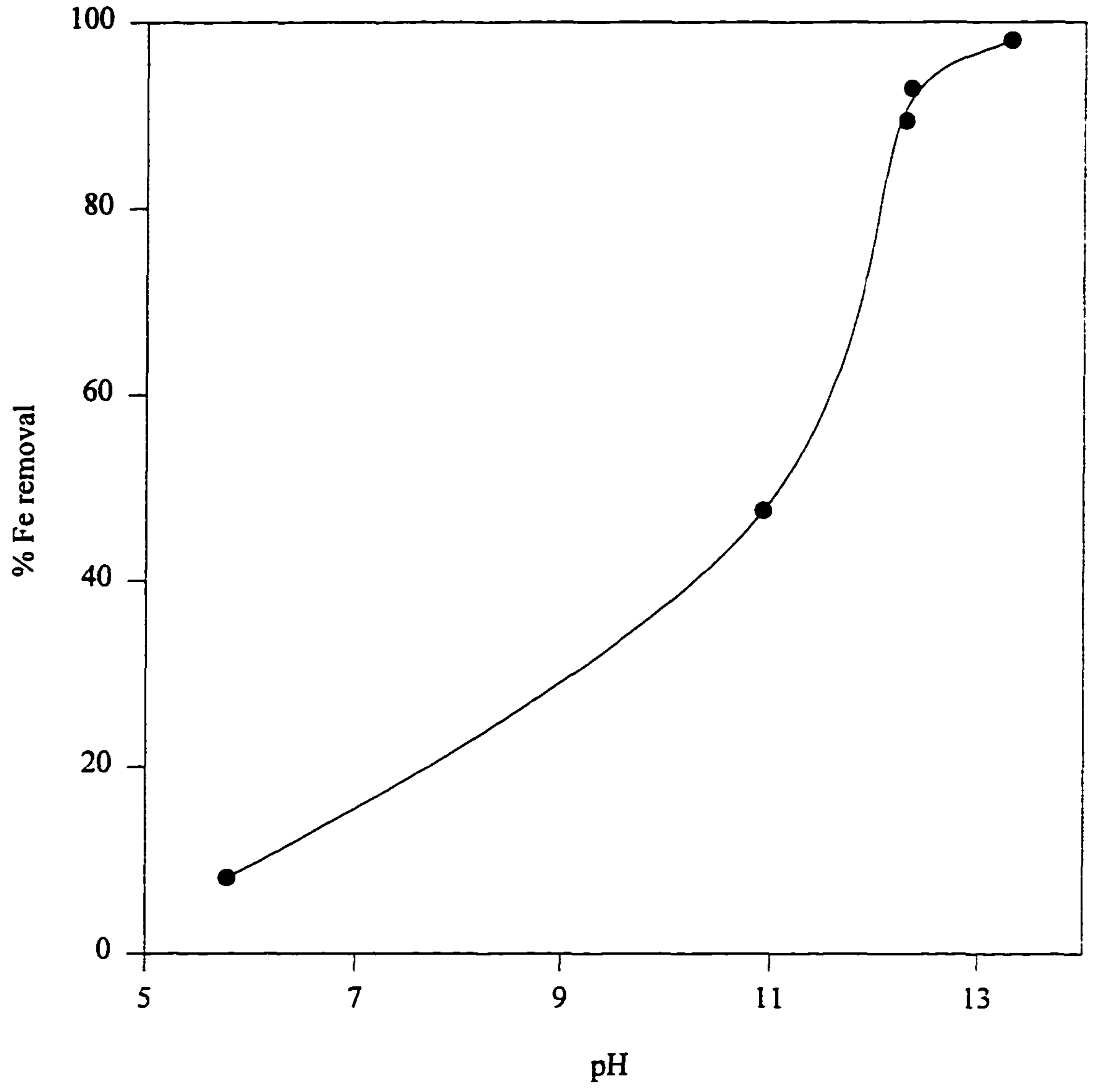


Figure 45. Percent Fe(III) removal from Fe-EDTA solution at different pH

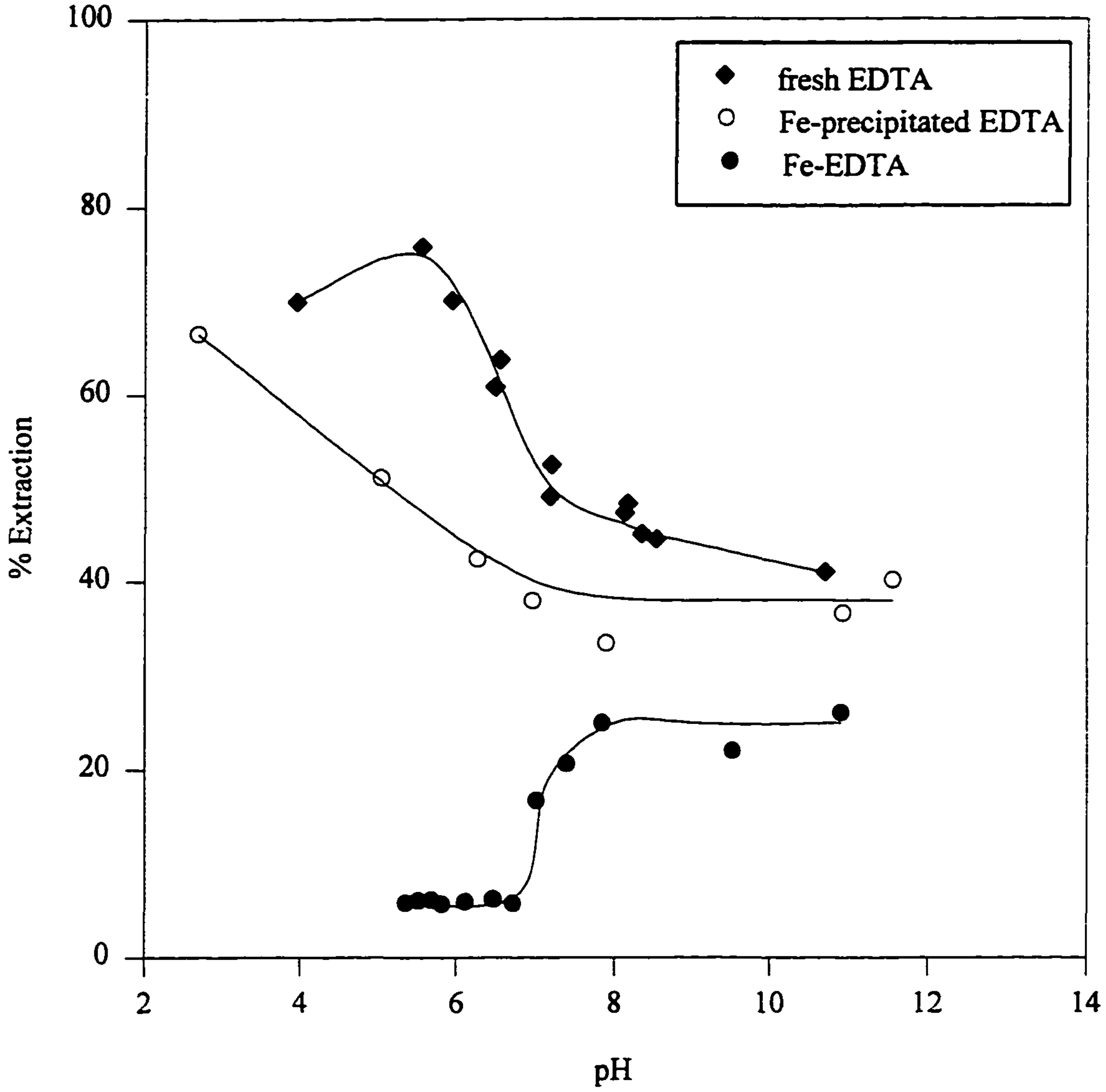


Figure 46. Pb extraction efficiency of two different recycled 0.005 M EDTA solutions for various pH values as compared to fresh 0.005 M of EDTA

The efficiency of lead extraction of the recycled EDTA solution was increased by precipitation of the Fe ions from the Fe-EDTA solution before applying to the lead-contaminated soil. According to the results shown in Figure 46, Fe-precipitated EDTA solution had much higher lead extraction efficiency than Fe-EDTA solution over the pH range tested. The extraction efficiency of the Fe precipitated recycled EDTA solution was about 65 to 95 % of the extraction efficiency of the fresh EDTA solution from pH 4 to 11. Precipitating the Fe out from the recycled waste EDTA extraction solution before further application would increase the extraction efficiency of the recycled EDTA solution. For this reason, the Fe precipitation step was included for used EDTA recycling test to increase the lead extraction efficiency from Pb-contaminated soil.

Extraction Efficiency using Recycled Used Pb-EDTA Solution from Extraction of Lead-Contaminated Soil

Figure 47 shows the lead extraction efficiencies of Cal soil with fresh 0.1 M and 0.05 M EDTA solutions and once recycled used 0.1 M EDTA solution. This figure shows that there was not much difference in the lead extraction efficiency between fresh 0.1 M EDTA solution and once recycled 0.1 M EDTA solution. The used EDTA solutions for all three (0.1 M EDTA, 0.05 M EDTA and recycled 0.1 M EDTA solution) were then used again to assess the remaining extractive abilities. The second extraction experiments showed that recycled EDTA solution had higher lead extraction efficiency than the 0.05 M EDTA solution. For the third, and fourth extraction experiments, the extraction efficiencies of the recycled EDTA were similar to that of the 0.1 M EDTA solution. It may be assumed that the amount of EDTA before and after the recycling procedure was similar to that of 0.1 M EDTA solution.

Figure 48 shows the lead extraction efficiencies of Cal soil with 0.05 M EDTA solution over several cycles. For each cycle, the used EDTA solution was treated using phosphate and sulfate ions to precipitate the uncomplexed lead ions. This figure shows that recycled EDTA had much higher lead extraction efficiency than the extraction efficiency of consecutive

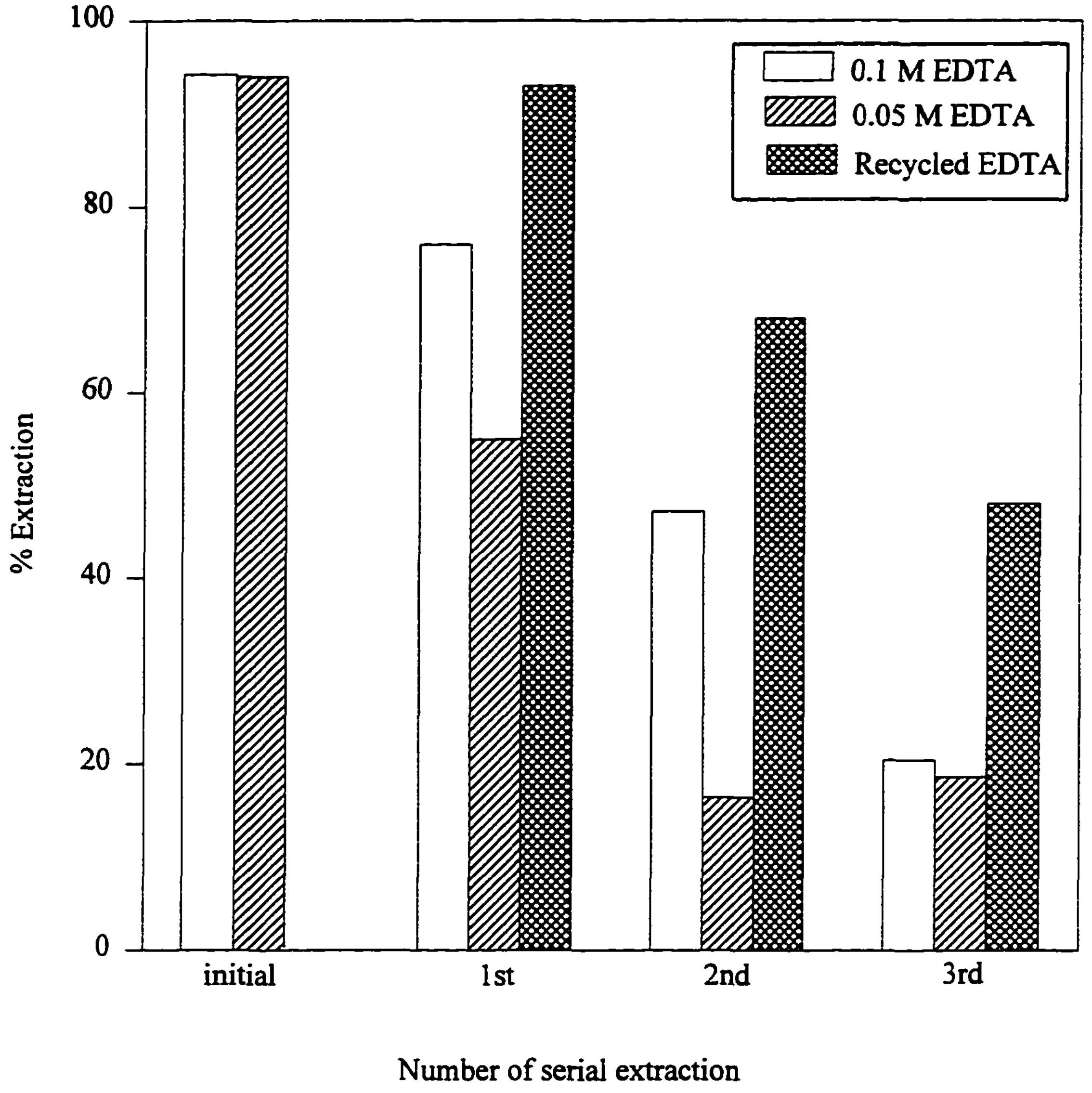


Figure 47. Serial lead extraction from Cal soil with 0.1M and 0.05 M of fresh EDTA solutions and 0.1 M of once recycled EDTA solution

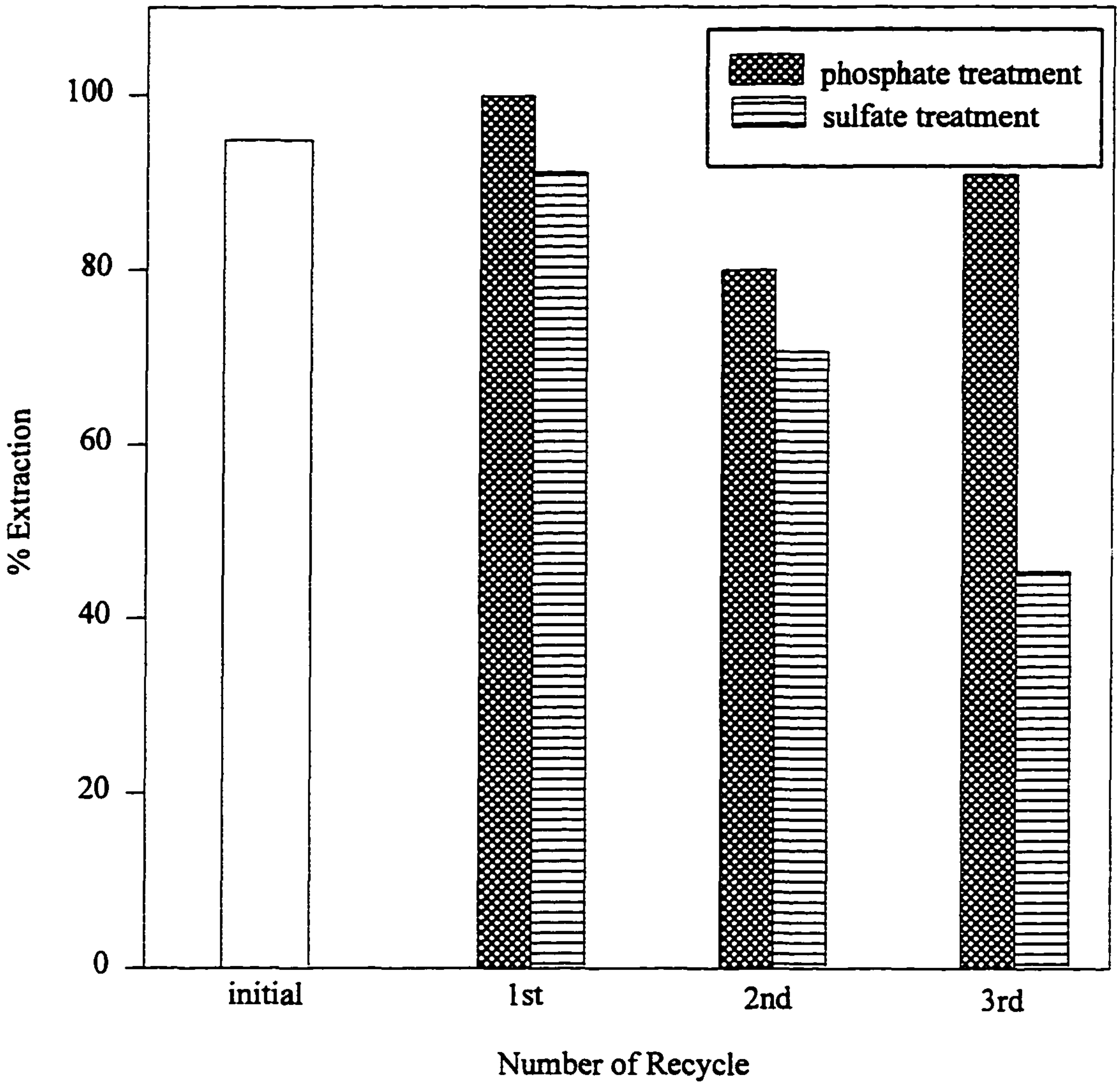


Figure 48. Lead extraction from Cal soil with and without recycling treatment with 0.05 M EDTA solution

application of the EDTA solution over the cycles. The extraction efficiencies for the recycled EDTA were between 80 % to 100 %. Phosphate treated recycled solution was better than the sulfate treated recycled solution for lead extraction from Cal soil.

Based on the equilibrium constants for ferric phosphate and ferric sulfate (Table 9), ferric phosphate compounds has a lower stability constant than the ferric sulfate compounds and when equimolar amount of phosphate and sulfate ions are present in solution, the equilibrium ferric ion concentration is much lower with phosphate ions than the concentration with sulfate ions. As a result, phosphate ions would be a better precipitating agent than sulfate ions while sulfate ions may be present in the solution without precipitating with the available ferric ions until either ion concentration is high enough for precipitation as a form of $Fe_2(SO_4)_3$.

Table 9. Equilibrium reactions for ferric phosphate and ferric sulfate

Equilibrium reaction	Constant
$FePO_4 + 2H^+ = Fe^{3+} + H_2PO^{4-}$	log K =-5.37
$Fe_2(SO_4)_3 = 2Fe^{3+} + 3SO_4^{2-}$	log K =2.89

Figure 49 shows the lead extraction efficiency of rifle range soil with fresh 0.03 M of EDTA and recycled 0.03 M EDTA solution. The extraction efficiencies of the recycled Fe-precipitated EDTA using phosphate were about 75 % to 100 % of the extraction efficiency of fresh EDTA solution. Similar results were obtained using sulfate as the precipitating anions, although the extraction efficiencies were slightly lower. These experiments confirmed that the recycled EDTA solution may be as efficient as fresh EDTA solution for removing lead from rifle range soil even after it was recycled the third time. The merits of recycling used EDTA solution can not be underestimated since for every gram of soil at least 5 to 10 grams of extractive wastewater will be produced (assuming a solution:soil ratio of 5 to 10). If the wastewater can be recycled at least 3 times, the volume of generated will be reduced by at least three times. Although we have done our experiments for only three cycles, we believe

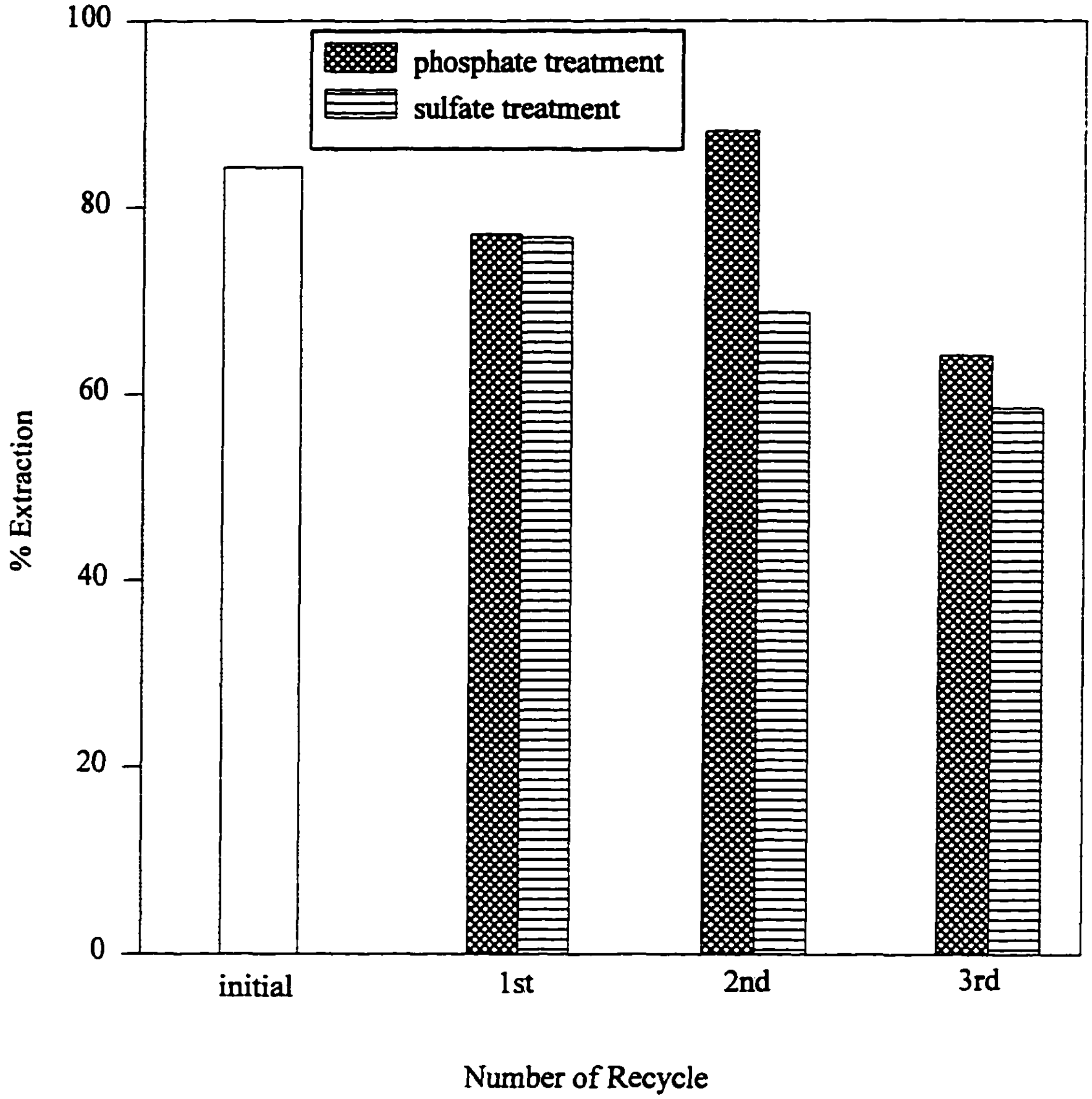
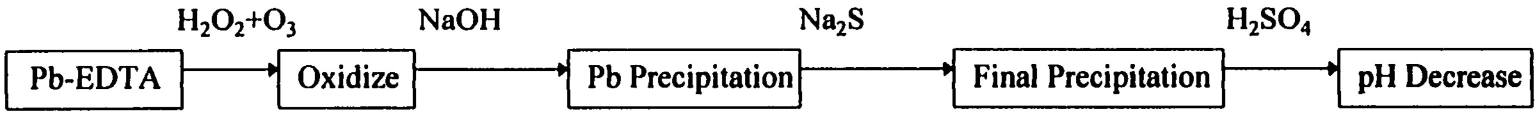
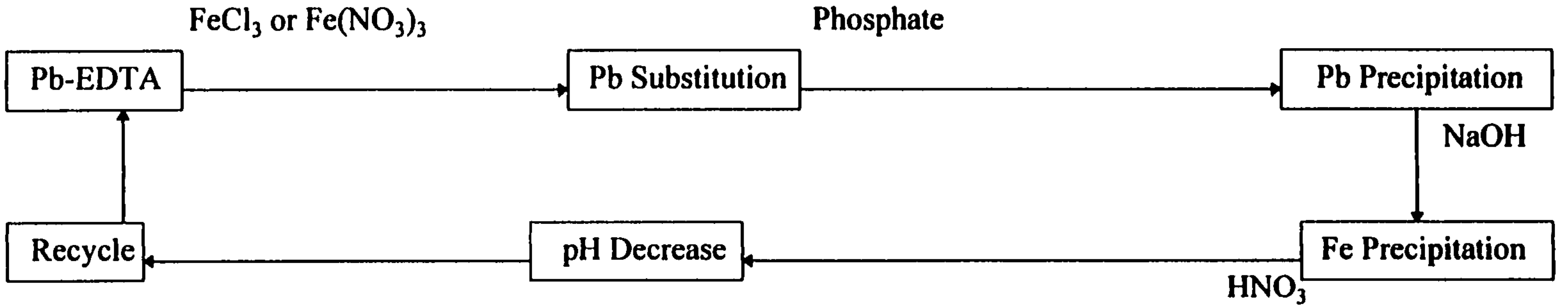


Figure 49. Lead extraction from a rifle range soil with and without recycling treatment with 0.03 M EDTA solution

that the recycled EDTA can continue to be recycled for several more cycles. In addition to a reduction of wastewater, there will be savings in the amount of EDTA used. The extra costs in chemicals needed such as ferric chloride, phosphate and sodium hydroxide may be marginal since the wasted EDTA must be treated with some chemicals probably hydrogen peroxide, sulfide and sodium hydroxide to oxidize EDTA and precipitate out the lead before it can be disposal of. Figure 50 shows a comparison of the EDTA wastewater treatment process with the EDTA recycling treatment process. Table 10 shows the cost for each process based on the approximate chemical prices. According to the Table 10, when the EDTA wastewater is recycled for two times, the chemical cost for EDTA recycling treatment can be reduced to about half of the EDTA wastewater treatment process. In summary, the EDTA recycling process can reduce not only the volume of EDTA wastewater effluent but also the chemical cost of the treatment process.



EDTA Treatment Process



EDTA Recycling Method

Figure 50. The comparison of the conventional EDTA wastewater treatment process with the EDTA recycling treatment process

Table 10. The required chemical cost comparison of EDTA wastewater treatment with the EDTA wastewater recycling treatment including fresh EDTA solution for 100 kg of lead-contaminated soil with 1,000 liter of 0.05 M EDTA solution with an assumption of 20 % loss of the EDTA solution during recycling process

	Conventional EDTA treatment		EDTA recycling treatment	1st recycle treatment	2nd recycle treatment
EDTA	$ 1,000	EDTA	$ 1,000	$ 200	$ 200
H_2O_2	$ 1,700	$FeCl_3$	$ 110	$ 110	$ 110
NaOH	$ 65	Na_2HPO_4	$ 880	$ 880	$ 880
NaS_2	$ 30	NaOH	$ 65	$ 65	$ 65
H_2SO_4	$ 40	HNO_3	$ 40	$ 40	$ 40
Total	$ 2,835	Total	$ 2,095	$ 1,295	$ 1,295

	Total cost for conventional EDTA wastewater treatment		Total cost for recycling of EDTA wastewater treatment
initial	$ 2,835	initial	$ 2,095
2 nd	$ 5,670	1 st recycle	$ 3,390
3 rd	$ 8,505	2 nd recycle	$ 4,685

CONCLUSIONS

A method to recycle waste Pb-EDTA solution has been presented. Based on the experimental results, the waste Pb-EDTA solution can be recycled several times without loosing its extractive abilities. The recycled method include substituting the Pb complexed with EDTA with Fe(III) ions at low pH values and the uncomplexed lead ions precipitated out with either phosphate or sulfate ions. Fe(III) in the Fe-EDTA solution was then precipitated out at high pH. The Fe-precipitated EDTA solution was found to be just as effective as fresh EDTA and may be recycled several times without losing its extractive power. The Fe-EDTA solution was also found to be effective but only for high pH values.

Precipitation of lead using phosphate ions was found to give a slightly better recycled EDTA solution than precipitation with sulfate ions. The recycled method proposed will provide considerable reduction in the wastewater generated for the soil washing technology and also will reduce the cost of EDTA usage.

GENERAL CONCLUSIONS AND FUTURE STUDIES

Extraction of lead from lead-contaminated soils was not affected by a soil:extractant ratio as low as 1:3 but instead was dependent on the quantity of EDTA present. Results of the experiments showed that the extraction efficiency for each soil was different but if sufficiently large amount of EDTA was applied (EDTA:lead stoichiometric ratio greater than 10), all the lead may be extracted except for a Superfund soil from a former mining area.

The sum of the molar amounts of the extracted metals from soil with the addition of EDTA was found to be more than the molar amount of applied EDTA. Since information on metal species controlling the solubility in each soil sample cannot be determined with current analytical methods, it was not practical to draw accurate conclusion with regards to the factors controlling the solubility and complexation competition in soil. However, experimental results implied that Fe ions may compete with lead ions at pH values less than 6. Similarly, Zn and Cu ions may compete with lead ions but to a lesser extent. For high pH (>7), calcium may compete with lead ions for EDTA ligand sites. Experimental results also indicated that for some soils, the lead may be occluded in Fe and Mn oxides present in the soil. Dissolution of Fe and Mn oxides resulted in a corresponding increase in lead extraction.

Amorphous irons in soil may compete with lead for EDTA ligand sites in the extraction of Pb from lead-contaminated soil. Experiments conducted with varying amounts of amorphous iron content indicated that the extraction efficiency of Pb was effected especially for pH values less than 6.0. The percent extracted depends on the lead:EDTA stoichiometric ratio, pH, lead species and amorphous iron concentration. The effect of amorphous iron on lead extraction appeared to be dominant at pH less than 6 for lead:EDTA stoichiometric ratio of less than 1:2. Besides the effect of amorphous iron on lead extraction, the lead extracted in the presence of amorphous iron also depended on the lead species present in the soil. The order of difficulty of extraction for lead:EDTA stoichiometric ratios less than 1:2 were:

Lead sulfate > Lead phosphate > Lead carbonate.

Lead extraction from lead carbonate-contaminated soil was not affected much by amorphous iron. However, lead extraction from lead sulfate-contaminated soil was severely affected by amorphous iron for pH values less than 6. For lead-phosphate-contaminated soil, similar amorphous iron effect was observed for pH less than 6 but the extent of amorphous iron effect was less than the effect on lead sulfate-contaminated soil. In the case of lead phosphate-contaminated soil, the optimum pH range for lead extraction was narrow between pH 6.5 and 7. For Pb:EDTA stoichiometric ratio less than 1:2, the pH range which must be maintained to ensure optimum extraction efficiency was between 6.5 and 8.

Based on the experimental results, used EDTA could be recycled several times without loosing its power of extracting lead from lead-contaminated soil. The lead in used EDTA solution may be separated by adding Fe(III) ions at low pH and the uncomplexed lead ions may be precipitated out with phosphate and sulfate ions. The lead removed Fe-EDTA solution was found to have extractive capabilities only at high pH values. However, when the Fe(III) ions were removed at high pH with sodium hydroxide, the solution was found to have much higher extraction power than the extraction power of the Fe-EDTA solution over a wider pH range. The Fe-precipitated recycled EDTA solution may be recycled several times without loosing its extractive powers. Use of phosphate to precipitate lead resulted in a recycled EDTA solution with slightly better extraction capacities than with using sulfate to precipitate lead.

Some future studies are as follows:

I. The investigation of the effects of major anions such as sulfate and phosphate present in soils on the lead extraction using EDTA
II. The investigation of the phosphate and sulfate ions removal from the recycled EDTA wastewater to improve the EDTA recycling efficiencies
III. Development of a feasible EDTA recycling method for soil washing wastewater other than lead-contaminated wastewater.

APPENDIX I

SAMPLE CALCULATIONS

The followings are the steps needed to compute the mole fraction of Pb-EDTA and Fe-EDTA in the aqueous phase. It is assumed that the equilibrium concentration of $[SO_4^{2-}]$ = 0.1M and [EDTA] = 1 M, and the equilibrium pH = 7. Calculations will be conducted using equilibrium constants, solubility product and stability constants. Given data are follows:

Stability constants of EDTA and metal-EDTA reactions (Lindsay, 1979)

Reaction	Log K ($\mu = 0.1$)	eq. #
$H_4EDTA = H^+ + H_3EDTA^-$	-2	(1)
$H_3EDTA = H^+ + H_2EDTA^{2-}$	-2.67	(2)
$H_2EDTA = H^+ + HEDTA^{3-}$	-6.16	(3)
$HEDTA = H^+ + EDTA^{4-}$	-10.26	(4)
$PbSO_4$ (aglesite) $= Pb^{2+} + SO_4^{2-}$	-7.79	(5)
$Pb^{2+} + EDTA^{4-} = PbEDTA^{2-}$	17.88	(6)
$PbEDTA^{2-} + H^+ = PbHEDTA^-$	2.8	(7)
$PbHEDTA^- + H^+ = PbH_2EDTA$	1.7 ($\mu = 1.0$)	(8)
$PbH_2EDTA + H^+ = PbH_3EDTA^+$	1.2 ($\mu = 1.0$)	(9)
$Fe(OH)_{3\,soil} + 3H^+ = Fe^{3+} + 3H_2O$	2.70	(10)
$Fe^{3+} + EDTA^{4-} = FeEDTA^{-1}$	25.10	(11)
$Fe^{3+} + HEDTA^{3-} = FeHEDTA$	16.20	(12)
$Fe^{3+} + H_2EDTA^{2-} = FeH_2EDTA^+$	8.70	(13)
$FeEDTA^{-1} + OH^- = Fe(OH)EDTA^{2-}$	6.31	(14)
$Fe(OH)EDTA^{2-} + OH^- = Fe(OH)_2EDTA^{3-}$	4.39	(15)
$Fe(OH)_2EDTA^{3-} + OH^- = Fe(OH)_3EDTA^{4-}$	1.50	(16)

From equations, 5 and 6,

$PbSO_4 + EDTA^{4-} = PbEDTA^{2-} + SO_4^{2-}$ log K = 10.09 (17)

from this equation, $[PbEDTA^{2-}] = 10^{10.09}\,[EDTA^{4-}] / [SO_4^{2-}] = 10^{11.09}$

Addition of equations of 17 and 7 gives

$PbSO_4 + H^+ + EDTA^{4-} = PbHEDTA^- + SO_4^{2-}$ log K = 12.89 (18)

from this equation, $[PbHEDTA^-] = 10^{12.89}\,[EDTA^{4-}]\,[H^+] / [SO_4^{2-}] = 10^{6.89}$

Addition of equations of 18 and 8 gives

$PbSO_4 + 2H^+ + EDTA^{4-} = PbH_2EDTA + SO_4^{2-}$ log K = 14.59 (19)

from this equation, $[PbH_2EDTA] = 10^{14.59}\,[EDTA^{4-}]\,[H^+]^2 / [SO_4^{2-}] = 10^{1.59}$

Addition of equations of 19 and 9 gives

$PbSO_4 + 3H^+ + EDTA^{4-} = PbH_3EDTA^+ + SO_4^{2-}$ log K = 15.79 (20)

from this equation, $[PbH_3EDTA^+] = 10^{15.79}\,[EDTA^{4-}]\,[H^+]^3 / [SO_4^{2-}] = 10^{-4.41}$

The possible Pb-EDTA species in the presence of $PbSO_4$ are

$[Pb\text{-}EDTA] = [PbEDTA^{2-}] + [PbHEDTA^-] + [PbH_2EDTA] + [PbH_3EDTA^+]$

$= 10^{11.09} + 10^{6.89} + 10^{1.59} + 10^{-4.41} = 1.23$ E11

log [Pb-EDTA] = 11.09

The solubility of $PbSO_4$ with an equilibrium concentration of 0.1 M of SO_4^{2-} and 1 M of $EDTA^{4-}$ is 1.23 E11.

For $Pb(OH)_2$,

$[Pb\text{-}EDTA] = [PbEDTA^{2-}] + [PbHEDTA^-] + [PbH_2EDTA] + [PbH_3EDTA^+]$

$= 10^{12.04} + 10^{7.84} + 10^{2.54} + 10^{-3.26} = 1.1$ E12

[Pb-EDTA] is controlled by $PbSO_4$ because $PbSO_4$-EDTA < $Pb(OH)_2$-EDTA

For $Fe(OH)_3$, with same method shown above:

$[Fe\text{-}EDTA] = [FeEDTA^-] + [FeHEDTA] + [FeH_2EDTA^+] + [Fe(OH)EDTA^{2-}] +$
$[Fe(OH)_2EDTA^{3-}] + [Fe(OH)_3EDTA^{4-}]$

$= 10^{6.7} + 10 + 10^{-7.18} + 10^{5.85} + 10^{3.8} + 10^{-2} = 5.73$ E6

$\log[Fe\text{-}EDTA] = 6.76$

The mole fraction of [Pb-EDTA] = 1.23 E11 / (1.23 E11 + 5.73 E6) = 0.9999

The mole fraction of [Fe-EDTA] = 5.73 E6 / (1.23 E11 + 5.73 E6) = 4.65 E-5

APPENDIX II

RAW DATA

Figure 9

3ml Stoi.	% Extrac.	5ml Stoi	% extrac.	10ml Stoi.	% Extrac.
0.1300	7.0000	0.2100	17.5000	0.4300	41.4000
0.2600	21.2000	0.4300	38.8000	0.8600	71.4000
0.5200	48.0000	0.8600	71.1000	1.7200	86.0000
1.2900	80.5000	2.1500	85.1000	4.2900	90.6000
2.5800	84.7000	4.2900	91.9000	8.5900	92.5000
5.1600	91.3000	8.5900	89.8000	17.1700	93.3000
12.8800	89.2000	21.4700	93.7000	42.9300	97.1000
25.7600	88.7000	42.9300	93.7000	85.8700	94.5000
51.5200	93.6000	85.8700	94.7000	171.7300	95.5000
64.4000	93.0000	107.3300	93.2000	214.7800	97.2000

Figure 10

3ml Stoi.	% Extrac.	5ml Stoi	% extrac.	10ml Stoi.	% Extrac.
0.0900	7.0000	0.1700	10.8000	0.1700	13.1500
0.1900	15.6000	0.3300	22.8300	0.3300	25.8700
0.4700	38.4000	0.8300	40.6200	0.6600	35.8100
0.9400	48.0000	1.6600	43.4800	1.6600	42.6700
1.8800	50.7000	3.3200	68.1700	3.3200	53.3200
4.7100	66.9000	16.6100	82.2100	6.6400	85.0300
9.4100	75.8000	33.2200	95.3200	16.6100	94.4200
18.8300	82.4000	41.5200	93.7200	33.2200	88.3900
23.5400	80.6000			66.4300	94.0000

Figure 11

Cal. Stoi.	% Extrac.	Cuba. Stoi.	% Extrac.	Cleve. Stoi.	% Extrac.
0.1700	13.1500	0.4952	11.1817	1.6600	0.0000
0.3300	25.8700	0.9904	14.8920	3.3200	0.0000
0.6600	35.8100	2.4761	18.1449	8.2999	0.4800
1.6600	42.6700	4.9522	19.9746	16.5998	0.0000
3.3200	53.3200	9.9043	29.0216	33.1997	0.0000
6.6400	85.0300	24.7608	91.8424	82.9992	0.0000
16.6100	94.4200	49.5215	82.4905		
33.2200	88.3900	99.0431	90.4193		
66.4300	94.0000				

Figure 14

Cal soil	water	0.005 M EDTA (1 day)		0.005 M EDTA (7 days)	
pH	% extrac.	pH	% extrac.	pH	% extrac.
7.7900	0.0000	10.5700	42.0827	11.7900	38.8889
6.4100	0.0995	8.5300	44.5701	9.9100	76.1921
5.5000	5.3032	8.3400	45.1282	8.3900	78.3623
4.9900	17.4118	8.1600	48.3786	7.5700	76.7438
4.2900	31.1463	8.1200	47.3605	6.7700	75.2311
3.5500	36.6742	7.1900	52.5528	6.1200	77.2311
3.3700	38.9072	7.1700	49.1101	5.7300	75.9916
		6.5300	63.7745	4.4800	72.1795
		6.4700	60.8824	4.2100	71.2896
		5.9400	70.1358	3.2300	67.3982
		5.5500	75.8484		
		3.9500	69.9661		

Cuba soil	water	0.002 M EDTA (1 day)		0.002 M EDTA (7 days)	
pH	% extrac.	pH	% extrac.	pH	% extrac.
2.8500	33.6842	3.4100	50.1643	4.1300	48.6890
4.1700	4.1627	3.8200	51.6667	4.1900	50.3828
6.2200	0.0000	4.3200	51.2105	4.8100	48.4105
7.0900	0.0000	4.8500	50.3110	5.4900	49.7455
8.3600	0.0000	6.3800	26.6603	5.8100	52.6077
9.3700	0.0000	6.6100	22.1435	7.1100	26.8708
		6.9100	18.5455	7.3700	24.5263
		7.2000	17.5789	8.3700	23.8278
		7.8900	14.7730	9.2400	12.3086
		7.9800	13.1579	10.5000	9.3158
		8.3700	11.9807	11.7000	1.7225
		10.6100	4.6316		

Rifle soil	water	0.003 M EDTA (1 day)		0.003 M EDTA (7 days)	
pH	% extrac.	pH	% extrac.	pH	% extrac.
8.0500	0.0000	11.3500	37.4200	10.4000	46.0500
7.4600	0.0000	10.1700	30.1000	9.6100	46.8500
6.4600	0.0000	8.0800	34.8200	8.7700	60.1500
6.0000	3.1000	6.8300	50.4000	7.2300	75.7600
5.9400	10.9100	4.0300	78.2600	7.0000	65.3200
5.8600	15.9800	3.3100	84.2500	6.8300	68.6400
5.3900	52.4400			6.7800	80.8200
4.3000	71.5000			6.6200	78.1200
				4.1800	88.0600
				2.9100	89.8900

Figure 15

Cal soil	water	0.005 M EDTA (1 day)		0.005 M EDTA (7 days)	
pH	% extrac.	pH	% extrac.	pH	% extrac.
7.7900	2.7800	8.5300	0.0000	11.7900	0.0000
6.4100	6.9600	8.3400	0.7859	9.9100	0.0000
5.5000	8.3500	8.1600	0.5125	8.3900	1.2658
4.9900	7.4100	8.1200	2.3529	7.5700	7.6582
4.2900	12.8500	7.1900	5.7416	6.7700	12.3418
3.3700	18.6100	7.1700	19.1456	6.1200	19.9367
		6.4700	20.8544	5.7300	22.1266
		5.5500	25.5886	4.4800	37.0380
		3.9500	52.2152	4.2100	48.3798
				3.2300	84.0506

Cuba soil	water	0.002 M EDTA (1 day)		0.002 M EDTA (7 days)	
pH	% extrac.	pH	% extrac.	pH	% extrac.
2.8500	3.5294	3.4100	40.5882	4.1300	45.2941
4.1700	2.7574	3.8200	30.7721	4.1900	44.1618
6.2200	1.4338	4.3200	28.8750	4.8100	36.2353
7.0900	1.2132	4.8500	22.0588	5.4900	29.6177
8.3600	0.7353	6.3800	15.4412	5.8100	25.9191
		6.6100	11.9485	7.1100	14.8162
		6.9100	9.2647	7.3700	10.5147
		7.2000	6.0662	8.3700	8.4559
		7.8900	4.4485	9.2400	7.3346
		7.9800	4.0441	10.5000	7.6838
		8.3700	3.3088	11.7000	8.3824
		10.6100	2.4265		

Rifle soil	water	0.003 M EDTA (1 day)		0.003 M EDTA (7 days)	
pH	% extrac.	pH	% extrac.	pH	% extrac.
8.0500	1.2200	11.3500	14.0900	10.4000	21.9300
7.4600	6.1600	10.1700	11.5200	9.6100	20.6000
6.4600	3.7700	8.0800	9.1500	8.7700	19.3200
6.0000	5.7600	6.8300	18.7800	7.2300	34.2100
5.9400	5.2200	4.0300	38.0500	7.0000	38.9300
5.8600	8.0500	3.3100	43.1500	6.8300	38.9300
5.3900	10.2400			6.7800	35.3700
4.3000	22.1000			6.6200	42.4500
				4.7300	51.2200
				4.1800	54.4400
				3.2200	85.2800
				2.9100	88.2000

Figure 16

Cal soil	water	0.005 M EDTA (1 day)		0.005 M EDTA (7 days)	
pH	% extrac.	pH	% extrac.	pH	% extrac.
7.7900	0.1560	8.5300	0.6383	11.7900	0.0000
6.4100	0.3121	8.3400	0.5851	9.9100	0.0000
5.5000	0.5106	8.2100	0.0000	8.3900	0.0709
4.9900	0.9220	8.1600	0.5319	7.5700	0.7021
4.2900	1.1915	8.1200	0.5319	6.7700	1.7518
3.5500	1.8085	7.1900	1.1702	6.1200	2.7660
3.3700	1.8511	7.1700	0.7801	5.7300	3.1262
		6.5300	1.6135	4.4800	4.5872
		6.4700	1.3830	4.2100	4.9787
		5.9400	3.2979	3.2300	7.9433
		5.5500	2.9255		
		3.9500	4.5213		

Cuba soil	water	0.002 M EDTA (1 day)		0.002 M EDTA (7 days)	
pH	% extrac.	pH	% extrac.	pH	% extrac.
2.8500	24.1667	3.4100	40.8333	4.1300	48.3333
4.1700	14.0625	3.8200	37.9427	4.1900	41.4375
6.2200	2.7083	4.3200	36.0900	4.8100	44.9167
7.0900	0.0000	4.8500	34.3800	5.4900	39.5833
8.3600	0.0000	6.6100	23.7000	5.8100	33.5938
9.3700	0.0000	6.9100	17.5000	7.1100	29.1146
		7.2000	13.7500	8.3700	2.0833
		7.8900	7.4479	9.2400	1.6406
		7.9800	3.1300	10.5000	0.0000
		8.3700	1.5625	11.7000	0.0000
		10.6100	0.0000		

Figure 17

Cal soil	water	0.005 M EDTA (1 day)		0.005 M EDTA (7 days)	
pH	% extrac.	pH	% extrac.	pH	% extrac.
7.7900	2.4034	8.5300	12.2375	11.7900	7.4788
6.4100	15.0709	8.3400	13.0920	9.9100	3.5059
5.5000	28.3358	8.2100	12.6585	8.3900	10.2230
4.9900	40.9121	8.1600	12.3779	7.5700	32.8429
4.2900	52.1554	8.1200	13.4553	6.7700	62.7362
3.5500	86.4595	7.5900	26.3493	6.1200	90.7893
3.3700	81.0925	7.1700	24.8885	5.7300	93.0967
		6.8300	50.8469	4.4800	95.0162
		6.4700	49.1857	4.2100	96.1095
		5.8500	77.6121	3.2300	95.1100
		3.9500	94.7114		

Cuba soil	water	0.002 M EDTA (1 day)		0.002 M EDTA (7 days)	
pH	% extrac.	pH	% extrac.	pH	% extrac.
2.8500	85.3115	3.4100	88.1062	4.1300	87.0766
4.1700	83.4270	3.8200	82.4980	4.1900	86.1710
6.2200	39.1461	4.3200	85.8292	4.8100	75.8382
7.0900	13.5281	4.8500	75.5669	5.4900	79.3692
8.3600	1.0419	6.3800	68.5986	5.8100	78.8764
9.3700	0.1798	6.6100	56.0501	7.1100	55.4525
		6.9100	41.3687	7.3700	19.1685
		7.2000	18.2022	8.3700	6.3432
		7.8900	17.1124	9.2400	4.8478
		7.9800	6.0776	10.5000	4.4494
		8.3700	4.4617	11.7000	4.2778
		10.6100	4.2921		

Rifle soil	water	0.003 M EDTA (1 day)		0.003 M EDTA (7 days)	
pH	% extrac.	pH	% extrac.	pH	% extrac.
8.0500	1.5800	11.3500	10.5100	10.4000	9.7200
7.4600	5.3100	10.1700	11.7800	9.6100	12.4900
6.4600	12.4400	8.0800	18.5500	8.7700	16.4800
6.0000	19.5600	6.8300	48.9000	7.2300	49.5500
5.9400	26.4300	4.0300	87.4100	7.0000	56.0800
5.8600	38.7400	3.3100	88.1800	6.8300	60.8700
5.3900	72.5500			6.7800	70.2900
4.3000	86.7800			6.6200	74.2500
				4.7300	78.8900
				4.5300	85.1900
				4.1800	89.3800
				2.9100	87.5100

Figure 18

Cal soil	water	0.005 M EDTA (1 day)		0.005 M EDTA (7 days)	
pH	% extrac.	pH	% extrac.	pH	% extrac.
7.7900	0.8767	8.5300	1.5939	11.7900	0.0000
6.4100	3.0892	8.3400	1.6698	9.9100	0.0417
5.5000	4.2353	8.2100	2.2391	8.3900	2.1632
4.9900	4.9829	8.1600	1.8027	7.5700	4.1328
4.2900	5.7381	8.1200	1.8027	6.7700	5.9203
3.5500	6.6034	7.1900	3.9222	6.1200	7.7989
3.3700	6.4934	6.5300	5.4402	5.7300	8.0759
		5.5500	8.2619	4.4800	9.9355
		3.9500	11.8311	4.2100	10.9526
				3.2300	12.9336

Cuba soil	water	0.002 M EDTA (1 day)		0.002 M EDTA (7 days)	
pH	% extrac.	pH	% extrac.	pH	% extrac.
2.8500	14.8673	3.4100	18.7168	4.1300	19.1622
4.1700	13.8938	3.8200	18.4263	4.1900	17.1646
6.2200	8.9735	4.3200	16.9917	4.8100	15.6271
7.0900	4.3481	4.8500	15.2566	5.4900	14.1239
8.3600	0.4130	6.3800	11.5487	5.8100	13.3186
9.3700	0.1416	6.6100	10.0944	7.1100	7.9381
		6.9100	5.8053	7.3700	4.4779
		7.2000	3.9587	8.3700	1.3864
		7.8900	4.1858	9.2400	0.3407
		7.9800	1.0619	10.5000	0.0324
		8.3700	1.1799	11.7000	0.0000
		10.6100	0.0324		

Rifle soil	water	0.003 M EDTA (1 day)		0.003 M EDTA (7 days)	
pH	% extrac.	pH	% extrac.	pH	% extrac.
8.0500	0.9200	11.3500	0.0000	10.4000	0.0000
7.4600	2.3200	10.1700	0.0000	9.6100	0.6000
6.4600	3.7800	8.0800	5.6700	8.7700	3.2100
6.0000	5.3000	6.8300	14.1300	7.2300	14.6300
5.9400	6.8700	4.0300	31.5200	7.0000	18.5000
5.8600	9.5900	3.3100	38.6600	6.8300	21.4400
5.3900	17.0600			6.7800	23.4100
4.3000	24.0800			6.6200	25.4400
				4.7300	30.2800
				4.5300	33.0200
				4.1800	35.2700
				3.2200	37.5700
				2.9100	38.1700

Figure 19

Cuba soil	water	0.002 M EDTA (1 day)		0.002 M EDTA (7 days)	
pH	% extrac.	pH	% extrac.	pH	% extrac.
2.8500	2.6446	3.4200	34.3802	4.1300	31.7355
4.1700	0.0000	3.8200	32.6198	4.1900	28.3636
6.2200	0.0000	4.3200	27.9091	4.8100	25.4546
7.0900	0.0000	4.8500	25.3554	5.4900	20.0992
8.3600	0.0000	6.3800	18.5124	5.8100	17.3554
9.3700	0.0000	6.6100	17.1901	7.1100	17.1901
		6.9100	15.8678	7.3700	18.1818
		7.8900	10.9091	8.3700	9.9174
		7.9800	15.6159	9.2400	1.7355
		8.3700	6.6116	10.5000	1.9504
		10.6100	1.8116	11.7000	0.0000
Rifle soil	water	0.003 M EDTA (1 day)		0.003 M EDTA (7 days)	
pH	% extrac.	pH	% extrac.	pH	% extrac.
8.0500	0.7200	11.3500	11.8300	10.4000	33.1200
7.4600	1.4500	10.1700	27.1000	9.6100	36.3400
6.4600	2.2200	8.3800	53.7300	8.7700	51.6100
6.0000	4.5200	6.8300	75.7000	7.2300	82.0100
5.9400	14.5700	4.0300	91.7200	7.0000	82.7000
5.8600	18.9200	3.3100	91.8300	6.8300	84.1700
5.3900	46.4500			6.7800	83.9900
4.3000	69.8900			6.6200	83.7400
				4.7300	82.5800
				4.5300	97.0800
				4.1800	108.4400
				3.2200	93.0300

Figure 20

Cuba soil	water	0.002 M EDTA (1 day)		0.002 M EDTA (7 days)	
pH	% extrac.	pH	% extrac.	pH	% extrac.
2.8500	77.4194	3.4100	83.6129	4.1300	69.5484
4.1700	26.1290	3.8200	58.5000	4.1900	60.3871
6.2200	0.0000	4.3200	46.2000	4.8100	53.6516
7.0900	0.0000	4.8500	26.6129	5.4900	30.8903
8.3600	0.0000	6.3800	11.2903	5.8100	24.3548
9.3700	0.0000	6.6100	6.2903	7.1100	11.7419
		6.9100	4.5161	7.3700	6.9785
		7.2000	3.6667	8.3700	3.5484
		7.9800	2.0430	9.2400	1.4677
		8.3700	6.3432	10.5000	0.1183
		10.6100	0.0000	11.7000	0.0000

Figure 31

pH (0.001)	% Extrac. (0.001)	pH (0.002)	% Extrac. (0.002)
4.3200	50.5100	4.4800	92.9100
4.6800	46.6900	4.5900	93.3500
4.6900	45.5600	4.8500	92.7400
4.9400	47.5200	5.6400	94.9100
5.4900	43.2400	6.4100	93.1900
6.5700	46.1000	7.0200	98.0200
7.8600	49.9500	8.8000	96.0800
9.5800	49.1300	9.9700	83.4300
10.3400	47.6400	10.4200	78.9700
10.7400	43.2300	10.7100	72.9400
10.9700	36.7800	11.7100	59.4000
11.7500	23.4000		

Figure 32

Water		0.001M EDTA		0.002M EDTA	
pH	% Extrac. (Pb)	pH	% Extrac. (Pb)	pH	% Extrac. (Pb)
2.3000	8.4500	2.2000	13.4900	2.2000	11.8700
3.0000	10.2400	2.7000	10.6800	2.4000	12.7200
3.2000	12.8900	3.2900	10.9200	3.6000	10.2400
3.9000	8.8900	3.6200	10.1900	4.2000	5.9500
4.2000	9.7700	4.1000	12.5600	4.7000	9.7700
4.7000	8.2400	4.4000	10.0200	5.1000	8.6400
5.0000	8.1400	4.6000	11.0000	5.6200	36.4700
5.2000	5.8000	4.7000	10.7500	5.9100	19.0300
6.4000	1.8000	4.8000	8.7900	6.0100	50.6600
6.7000	0.0000	5.1000	7.6500	6.6600	63.4700
6.9000	0.0000	5.4900	7.9100	7.6000	77.2400
7.3000	0.0000	5.8600	17.3900	7.7300	77.7100
7.5000	0.0000	6.0500	3.8200	8.5600	76.8700
7.7000	1.2400	6.5700	9.0000	9.5600	65.9600
8.2000	0.8100	6.6900	26.1000	10.3200	55.5000
10.0000	0.0000	7.6100	38.6200	10.5600	40.2600
		7.7300	39.9200		
		8.6600	39.8700		
		9.9200	37.0500		
		10.6800	27.3600		
		10.9500	20.2200		

Figure 32 (continued)

Water		0.001M EDTA		0.002M EDTA	
pH	% Extrac. (Fe)	pH	% Extrac. (Fe)	pH	% Extrac. (Fe)
2.3000	64.5500	2.2000	94.8600	2.2000	86.8600
3.0000	31.2100	2.7000	68.1300	2.4000	76.9200
3.2000	26.4300	3.2900	58.3200	3.6000	53.2000
3.9000	15.0600	3.6200	54.7100	4.2000	54.1800
4.2000	12.3500	4.1000	35.6600	4.7000	45.5100
4.7000	8.2300	4.4000	29.2300	5.1000	45.4100
5.0000	7.5000	4.6000	27.4500	5.6200	54.0000
5.2000	12.6300	4.7000	30.9000	5.9100	19.4900
6.4000	8.4600	4.8000	33.9400	6.0100	35.4700
6.7000	3.6100	5.1000	32.0600	6.6600	19.4900
6.9000	3.8600	5.4900	42.8600	7.6000	8.7100
7.3000	5.3900	5.8600	29.9000	7.7300	8.3300
7.5000	3.2600	6.0500	17.3100	8.5600	8.1700
7.7000	2.9900	6.5700	12.2600	9.5600	4.9300
8.2000	6.2900	6.6900	17.2900	10.3200	5.5900
10.0000	6.0000	7.6100	4.7100	10.5600	3.9300
		7.7300	4.0900		
		8.6600	3.9000		
		9.9200	4.9300		
		10.6800	5.5900		
		10.9500	3.1400		

Figure 33

Water		0.001M EDTA		0.002M EDTA	
pH	% Extrac. (Pb)	pH	% Extrac. (Pb)	pH	% Extrac. (Pb)
2.3400	15.2000	2.3500	9.5400	2.4800	9.9200
2.6200	12.7900	2.7300	5.6800	2.7400	9.6200
3.0000	10.2400	3.4200	11.8600	2.8400	9.9200
3.3300	13.7300	4.2200	10.3400	3.8100	0.0000
3.3800	11.7700	4.8000	5.8800	4.5300	0.0000
3.7700	10.5100	4.9700	3.4000	4.7000	0.0000
4.7700	6.0000	5.2300	2.7900	5.1100	0.0000
5.3000	3.4700	5.3800	2.0600	5.1200	0.0000
5.9600	0.9300	5.7100	2.4700	5.1300	0.0000
6.1500	0.0000	6.3600	3.8700	5.7700	12.8700
7.1600	0.0000	6.8800	28.4900	5.7800	14.3600
7.7700	0.0000	7.1900	42.3700	6.0500	45.3900
9.0200	0.0000	7.5900	44.3100	6.8900	76.2300
11.0300	0.0000	7.8300	46.8200	7.3900	91.0400
11.5700	0.0000	9.0000	35.3900	7.9100	84.8400
		9.3100	36.1500	9.1700	51.0400
		10.8700	5.7700	9.9800	35.0200
		11.5700	0.0000	10.4400	20.2800
				11.3800	4.8000

Figure 33 (continued)

Water		0.001M EDTA		0.002M EDTA	
pH	% Extrac. (Fe)	pH	% Extrac. (Fe)	pH	% Extrac. (Fe)
2.3400	52.3600	2.3500	50.7800	2.4800	52.7200
2.6200	31.2100	2.7300	29.5700	2.7400	44.2700
3.0000	12.4300	3.4200	23.7300	2.8400	41.2500
3.3300	8.1500	4.2200	21.5600	3.8100	34.4800
3.3800	6.9000	4.8000	17.7100	4.5300	32.7200
3.7700	7.2600	4.9700	16.8800	4.7000	32.4600
4.7700	2.7900	5.2300	17.5100	5.1100	30.9400
5.3000	5.1600	5.3800	16.0000	5.1200	31.6700
5.9600	1.3400	5.7100	15.0000	5.1300	31.6100
6.1500	0.6200	6.3600	13.3100	5.7700	28.8300
7.1600	0.5400	6.8800	5.4300	5.7800	29.1700
7.7700	0.2100	7.1900	0.2600	6.0500	14.6300
9.0200	0.5100	7.5900	0.3700	6.8900	5.1100
11.0300	0.1900	7.8300	0.8300	7.3900	1.1800
11.5700	0.0000	9.0000	0.2500	7.9100	0.1500
		9.3100	0.8100	9.1700	1.2400
		10.8700	0.7200	9.9800	1.0700
		11.5700	0.7900	10.4400	0.2600
				11.3800	0.5000

Figure 34

pH (medium)	% Extrac. (medium) Pb	pH (high)	% Extrac. (high) Pb
3.4000	96.9800	1.8800	13.0000
3.9000	95.3700	3.8700	26.7100
4.3000	92.9400	4.4700	20.4100
5.5000	88.9200	4.7000	46.9600
6.0000	95.4400	4.7800	44.1800
7.4500	95.6600	5.9100	97.9600
7.5600	98.9100	6.4200	105.8000
7.8000	85.5800	7.0000	104.1800
7.9100	88.9900	7.5000	99.5600
8.2200	94.9200		
8.4500	91.1500		

pH (medium)	% Extrac. (medium) Fe	pH (high)	% Extrac. (high) Fe
3.4000	96.4100	1.8800	91.8300
3.9000	112.1200	3.8700	83.7900
4.3000	110.2300	4.4700	80.8800
5.5000	94.8600	4.7000	72.5000
6.0000	64.8000	4.7800	72.9600
7.4500	8.8700	5.9100	46.7900
7.5600	6.9000	6.4200	29.2500
7.8000	11.2700	7.0000	15.3900
7.9100	12.2100	7.5000	7.4100
8.2200	8.9900		
8.4500	5.3400		

Figure 35

Water		0.001M EDTA		0.002M EDTA	
pH	% Extrac. (Pb)	pH	% Extrac. (Pb)	pH	% Extrac. (Pb)
3.2700	93.0900	3.0600	92.6500	2.4900	94.6700
4.0800	79.5400	3.2600	82.9400	3.7800	82.4900
4.6400	79.5700	4.4300	91.5300	4.7200	87.3400
4.7400	74.0700	5.0900	75.3600	5.2800	89.4700
4.9100	69.0300	9.2400	33.1500	5.5900	88.0000
5.0000	53.3000	10.8200	27.4900	6.1100	88.0700
5.1700	27.9900	11.2300	19.9300	6.7300	85.5800
6.2600	0.0000	12.1200	10.0800	7.5500	95.5700
7.9500	0.0000	6.9800	49.3800		
8.1300	0.0000	7.6800	43.7100		
8.5700	0.0000	5.2400	84.8000		
11.2700	0.0000				
11.9500	0.0000				

Figure 35 (continued)

Water		0.001M EDTA		0.002M EDTA	
pH	% Extrac. (Pb)	pH	% Extrac. (Pb)	pH	% Extrac. (Pb)
3.2700	26.2100	3.0600	29.6400	2.4900	68.0600
4.0800	12.4600	3.2600	20.7800	3.7800	72.8000
4.6400	8.7900	4.4300	20.2200	4.7200	59.4900
4.7400	7.3300	5.0900	15.2000	4.7800	54.1200
4.9100	5.6200	9.2400	1.7600	4.8600	45.0300
5.0000	4.9100	10.8200	1.7300	4.9100	48.3000
5.1700	3.5800	11.2300	2.9100	5.2800	40.0000
6.2600	2.4300	12.1200	2.4300	5.5900	33.8700
7.9500	2.6400	6.9800	10.8000	6.1100	26.3700
8.1300	1.5700	7.6800	9.9100	6.5500	12.0300
8.5700	1.5400	5.2400	27.9800	6.7300	17.6900
11.2700	1.5900			7.2900	12.4100
11.9500	1.5900			7.5500	15.8900
				8.3300	8.1200

Figure 36

Water		0.001M EDTA		0.002M EDTA	
pH	% Extrac. (Pb)	pH	% Extrac. (Pb)	pH	% Extrac. (Pb)
2.8100	31.7000	3.0900	41.5600	2.6800	66.3000
3.8400	0.0000	3.2800	40.4500	3.1800	48.4400
3.8300	0.0000	3.4100	37.4400	3.5600	35.6100
4.3500	0.0000	3.7500	34.6200	4.3300	35.8700
4.8800	0.0000	4.4600	31.6700	5.6500	49.6100
5.0900	0.0000	4.7300	29.7500	6.1200	74.5000
5.4100	0.0000	5.0100	28.7900	6.6400	63.9300
5.6400	0.0000	5.7400	17.2200	6.8800	57.1800
6.1000	0.0000	6.1900	10.6400	6.9200	70.1600
6.2500	0.0000	8.9700	0.0000	7.1800	38.6800
8.8300	0.0000	10.6000	0.0000	7.5000	41.8900
10.7500	0.0000	11.4700	0.0000	7.5100	36.2800
11.1800	0.0000	2.8400	42.1300	7.7900	32.5700
		3.1100	39.6400	8.3600	26.4600
		3.4200	36.1800	9.7700	27.3900
		5.3600	27.2300	11.5200	33.6500
		5.8000	17.8000		
		6.1800	11.1300		
		6.5200	7.2900		
		7.0600	2.6800		
		10.3600	0.0000		
		11.5700	0.0000		

Figure 36 (continued)

Water		0.001M EDTA		0.002M EDTA	
pH	% Extrac. (Pb)	pH	% Extrac. (Pb)	pH	% Extrac. (Pb)
2.8100	5.6500	2.8400	53.2800	2.6800	82.8400
3.8400	4.1300	3.1100	36.7200	3.1800	69.3200
3.8300	3.7500	3.4200	17.5500	3.5600	56.6700
4.3500	3.0400	5.3600	11.0900	4.3300	46.4300
4.8800	1.9000	5.8000	21.6900	5.6500	31.1500
5.0900	1.3400	6.1800	28.1600	6.1200	23.5700
5.4100	1.3500	6.4400	38.5700	6.6400	5.1800
5.6400	0.9800	6.5200	32.1000	6.8800	2.0800
6.1000	1.0500	7.0600	36.3000	6.9200	8.3300
6.2500	0.8900	7.2200	25.8800	7.1800	0.6300
8.8300	0.6300	8.2800	18.3700	7.5000	1.8800
10.7500	0.8200	8.8700	16.2200	7.5100	1.9000
11.1800	0.7100	9.5400	17.9100	7.7900	2.5300
		10.3600	20.4400	8.3600	1.6100
		11.5700	22.9400	9.7700	1.3100
		3.0900	38.2100	11.5200	1.4300
		3.2800	28.4000		
		3.4100	20.4300		
		3.7500	9.8100		
		4.4600	7.8600		
		4.7300	10.5600		
		5.0100	11.3400		
		5.7400	22.7100		
		6.1900	29.4400		
		10.6000	20.6700		
		11.4700	20.6200		

Figure 37

pH (Pb)	% Extrac. (Pb)	pH (Fe)	% Extrac. (Fe)
3.0800	88.2700	5.1000	95.8900
5.0800	89.2300	5.5000	88.5400
5.1000	95.8200	5.5900	80.3600
5.5000	88.6700	5.8400	59.0000
5.5900	90.5000	6.5600	18.7500
5.8400	88.9000	7.7500	5.5700
6.5600	84.2900	9.5100	4.9600
7.7500	63.8700	10.6000	1.7900
9.5100	53.6700		
10.6000	60.0600		

Figure 43

Reaction time (hr)	% lead removal
0.0000	0.0000
1.0000	98.9400
2.0000	99.0300
3.5000	97.6800
7.0000	99.6100
9.0000	100.0000
12.0000	100.0000
24.0000	100.0000

Figure 45

pH	% iron removal
5.7900	8.1200
10.9300	47.5800
12.3000	89.4300
12.3500	92.9300
13.3000	98.1000

Figure 46

pH (Fe-EDTA)	% extrac. (Pb)	pH (Fe-treated EDTA)	% extrac. (Pb)	fresh EDTA	% extrac. (Pb)
5.3500	5.8122	2.6800	66.5158	10.7100	41.0800
5.5100	6.0558	5.0300	51.1086	8.5300	44.5701
5.6800	6.1229	6.2600	42.4510	8.3400	45.1282
5.8100	5.7195	6.9500	38.0373	8.1600	48.3786
6.1100	5.9608	7.8900	33.5294	8.1200	47.3605
6.4500	6.2217	10.9300	36.6855	7.1900	52.5528
6.7000	5.7436	11.5600	40.2338	7.1700	49.1101
7.0000	16.7406			6.5300	63.7745
7.3900	20.6431			6.4700	60.8824
7.8400	25.0009			5.9400	70.1358
9.5200	22.0278			5.5500	75.8484
10.9100	26.0453			3.9500	69.9661

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