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FINAL REPORT

**The Remediation of Lead Contaminated Soils
using Solvent Extraction
Chelation Techniques**

MASTER *1/8*

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I. Introduction

The work reported here is preliminary work leading to the development of an innovative technology for treating a mixed waste problem at Los Alamos National Laboratory (LANL). The specific problem being addressed by this research is the result of research activity at the Meson Physics Facility (LAMPF). The LAMPF facility conducts high energy neutron research. Lead BB's (diameter <1 mm) were placed in containers and used as shielding during experiments. This lead was stored in piles on the ground when it was not in use, and it sometimes sat for extended periods of time, perhaps as long as 20 years. The lead was mobilized overtime, and contaminated the underlying soil. Because of the neutron bombardment, a portion of the lead ^{207}Pb became radioactive ^{210}Pb , and the lead became both a "listed waste" and radioactive, which classified it as a mixed waste. The contaminated soil has been removed from the site and placed in drums for storage until a suitable treatment technology can be identified. The contents of the barrels consists of a mixture of lead contaminated soil and lead BB's.

It is believed that this research project has provided information which makes development of a suitable technology possible, not only not only to address this problem but for a number of other similar problems at this and other facilities. LANL has a number of other types of contaminated soil which have been placed in barrels for storage, and which may lend themselves to treatment using a small scale solvent extraction technology suitable for treating barrel quantities of soil. In the summer of 1993, 160+ barrels of Hg and Pu contaminated soils were placed in storage. The Hg is a soft lewis acid and the Pu is a hard lewis acid. Thus, if the appropriate extraction solutions are identified, it should be possible to use this treatment technology to separate the Hg and Pu from the soil and from each other.

Treatment hardware based on the results of this years work, is described in the last section of this report. The proposed hardware, to be developed in the next fiscal year, will use a combination of density classification and solvent extraction to treat the contaminated soil. Density classification will be used to separate the lead BB's from the soil. Solvent extraction will then be used to remove the remaining lead from the soil and to remove the ^{210}Pb from the BB's. The material removed from the outside of the BB's and the material removed from the soil will be concentrated on a weak base anion exchange resin, and then precipitated. Based on previous experience with small scale pad work, it is anticipated that this technology should produce lead concentrations in the soil below background values (10-15 mg Pb/Kg of soil) and the soil should easily pass the TCLP test.

Background

Lead, which is classified as a heavy metal, has long been recognized as a toxin and threat to human health. Lead is a poison by ingestion, a carcinogen of the lungs and kidneys and an experimental teratogen. (Sax *et al.* 1987) Lead has been shown to be a neurotoxin, and has greater toxicity in children than in adults. (Lansdown *et al.* 1986) Lead, like many other heavy metals, often accumulates in soils. Typical background levels of lead resulting from parent materials averages 10 ppm. (Brown *et al.* 1992) In New Mexico background levels in the range of 20 to 40 mg/Kg are common. Excessive levels of lead in soils are most often from anthropogenic sources. The three main sources of lead contamination are: (1) lead alkyls used as gasoline additives for antiknock properties since 1923; (2) various lead refining processes (i.e. battery

smelting); and (3) mining operations, especially those involving galena ore (PbS weathered to PbSO_4 and PbCO_3). A fourth and less common source, but certainly significant at specific DOE sites, lead used as a shielding agent to block α and β radiation. Roughly one-third of the more than 1200 Superfund sites on the NPL (National Priority List) are lead contaminated. (Krishnamurthy, 1992) The state of New Mexico contains lead contaminated sites in Los Alamos, in Socorro County (44 acres at Cal-West Metals), and other sites related to mining activity (e.g. Cleveland Mill site, Grant County, 12,000 yd^3 of leaching tailings.) The annual flux of anthropogenic lead to the atmosphere is estimated to be 4.5×10^6 t. (Grondin *et al.* 1986) Although the soil is often the first depositional media to be contaminated, organic and dissolved species of anthropogenic lead have shown to be quite mobile in the subsurface. The US EPA has set the Primary Drinking Water Standard for lead at 0.05 milligrams per liter, and the MCL at 5mg/l. (40 CFR 141.60 - .63, 1991) On Superfund sites (according to CERCLA) the action level for lead in soils is 500 mg Pb/Kg soil. (US EPA, 1990) Treated soils must be tested according to the Toxicity Characteristic Leaching Procedure (TCLP) using acetic acid. The effluent from this test must contain lead lower than the MCL in order to be considered non-hazardous.

Because such a large number of lead contaminated sites exist and require remediation, the development of a economical process capable of both *large and small scale* treatment is needed. Currently, many individuals are investigating both physical and chemical treatment processes for the treatment of soils at these sites. One of the more promising technologies is solvent extraction. In essence, the lead in the soil (found as various species) is brought into solution using a chelating agent. This solubilized lead is then removed from the soil fraction. Once an acceptable level of lead removal has been achieved, the soil is considered "clean" of lead.

There are two commonly considered soil solvent extraction technologies; soil washing and heap leaching. The "soil washing" treatment technologies use solvent extraction and high liquid to solid ratios to attain their goals. Typically, short treatment times are achievable, but the high energy (for agitation) and liquid inputs required, often make "soil washing" uneconomical.

Heap leaching is a process adapted from the mining industry where leftover tailings are "washed" of their precious metals using specific agents. The gold and silver mining industries use sodium cyanide (NaCN) at high pH (10.5 to avoid CN^- offgassing), while the copper industry uses sulfuric acid (H_2SO_4). These processes are equilibrium driven and have shown to have extremely high removal efficiencies (90%-100%), but do require some time to complete. In general the process is as follows: (1) the matrix (be it soil or crushed ore) is piled upon an impermeable leach pad with specified drainage characteristics; (2) the extractant (solvent) is introduced at the top of the heap and allowed to percolate down through the heap under the force of gravity; (3) The solubilized metal solution is then separated so that the metal can be concentrated (for resale or disposal) and the solvent can be reused. Although the term 'heap' may impose negative connotations for the technology, it is possible to design it as a closed system.

Heap leaching technology for the remediation of contaminated soils is little similar to the mining process, except for two factors. First, in remediation, minimum remaining metal concentrations (*minimum contaminant levels*) are governmentally regulated, not profit driven. Second, mining operations are often dissolving solid fractions from crushed ore whereas remediation operations attempt to remove a

contaminant from a soil surface where colloid interactions are dominant. The required technologies already exist (soil handling equipment, leach pad design standards, soil agglomerators, solvent application mechanisms) and technology transfer should be promising.

Main Research Objectives

The goals of this research is to demonstrate solvent extraction technology of lead contaminated soils, and propose a technology which is a hybrid of the two technologies discussed above. Initial activities addressed the lead extraction from the soil. The first step was teoretical modelling studies to develope an array of ligands for teesting. The modelling was followed by small batch scale extractions to identify potential extraction solutions and identify reaction characteristics. The last step was scale up to column scale studies. In the column scale studies extraction solution:soil matrix interactions were investigated, such as changes in hydraulic conductivity induced by the ligand, and interactions between the ligands and other metals in the soil matrix. The column, as used in this study, mimics the inside of a soil heap. The chelation reaction is greater than zero order (i.e. concentration dependent), thus reaction efficiency is optimized in a "flow through" column reactor.

Secondary Research Objectives

Additional studies have investigated volume reduction of the ligand:metal waste stream using ion exchange, separation of the ligand metal complex using precipitation methods, development of process control hardware, extraction solution distribution hardware, and treatment uniformity in a heap or a closed box reactor. This work is also discussed in this report.

II. Experimental Procedures

A. Speciation Modeling (computer aided)

Anthropogenic lead in the soil environment will interact with both the carbonate system and the hydroxide system as well as organic matter (humic and fulvic acids). Other common minerals such as aluminum, iron and manganese also form oxide and hydroxide species in soils, and carbonates are commonly found with calcium, magnesium, and sodium. These are all *solid phases*, which may interfere with ligand mediated dissolution. There are also *liquid phases* or *solution chemistry* to consider. The solution interactions without a ligand present are shown in the following mole fraction diagrams.

In terms of Hard:Soft:Acid:Base (HSAB) theory, divalent lead can be classified as a borderline acid. This means that depending upon the conditions, lead can act as a hard Lewis acid, or a soft Lewis acid. Hard and soft Lewis acids tend to react with hard and soft Lewis bases respectively. The borderline classification leaves many options open for possible ligands capable of chelating lead in soil. To make initial selections of ligands to be modelled, complexing compounds having a critical stability constant greater than 10 for Pb^{2+} were considered to have potential as lead extractants. Modelling studies were initiated to select the appropriate operating conditions for a particular extractant in removing lead from soil. The computer program SPEPLOT, which calculates mole fraction of certain species under varying pH conditions using stability constants (Log K), was used in modelling the solution chemistry. Generally, the total concentrations of the dissolved constituents in a soil solution represent the sum total of the free and complexed forms of the constituents that are considered stable compounds. Speciation indicates the relative distribution of a constituent among its possible chemical forms at certain conditions. Stability constants are a ratio of the concentration of the complex to the concentrations of the constituents. For example, with the Pb:EDTA complex in solution, a simple classification of the various species present is given by:

$$Pb_{tot} = [Pb^{2+}] + [Pb:EDTA] + [Pb(OH)] + [Pb(OH)_2] + [Pb(OH)_3] + [Pb_2(OH)] + [Pb_3(OH)_4] + [Pb_4(OH)_4] + [Pb_6(OH)_8] + [Pb(CO_3)_2]$$

where at 25° C:

$$K_1 = \frac{[Pb:EDTA]^{2-}}{[Pb^{2+}][EDTA^{4-}]} = 10^{17.88}$$

$$K_2 = \frac{[Pb(OH)]^+}{[Pb^{2+}][OH^-]} = 10^6$$

$$K_3 = \frac{[Pb(OH)_2]}{[Pb^{2+}][2(OH)^-]} = 10^{10.3}$$

$$K_4 = \frac{[Pb(OH)_3]}{[Pb^{2+}][3(OH)^-]} = 10^{13.3}$$

$$K_5 = \frac{[Pb_2(OH)]^+}{[2Pb^{2+}][OH^-]} = 10^{7.9}$$

$$K_6 = \frac{[Pb_3(OH)_4]^{2+}}{[3Pb^{2+}][4(OH)^-]} = 10^{31.7}$$

$$K_7 = \frac{[Pb_4(OH)_4]^{4+}}{[4Pb^{2+}][4(OH)^-]} = 10^{35.1}$$

$$K_8 = \frac{[Pb_6(OH)_8]^{10+}}{[6Pb^{2+}][2(OH)^-]} = 10^{67.4}$$

$$K_9 = \frac{[\text{Pb}(\text{CO}_3)_2]^{2-}}{[\text{Pb}^{2+}][2(\text{CO}_3)^{2-}]} = 10^{8.2}$$

and

$$\text{EDTA}_{\text{tot}} = [\text{EDTA:H}_1] + [\text{EDTA:H}_2] + [\text{EDTA:H}_3] + [\text{EDTA:H}_4] + [\text{EDTA:H}_5] + [\text{EDTA:Pb}^{2+}] + [\text{EDTA:Ca}^{2+}] + [\text{EDTA:Mg}^{2+}] + [\text{EDTA:Na}^{2+}] + [\text{EDTA:Fe}^{2+}]$$

where at 25° C:

$$K_1 = \frac{[\text{EDTA:H}_1]^3}{[\text{H}^+][\text{EDTA}^{4-}]} = 10^{10.17}$$

$$K_2 = \frac{[\text{EDTA:H}_2]^2}{[2\text{H}^+][\text{EDTA}^{4-}]} = 10^{6.11}$$

$$K_3 = \frac{[\text{EDTA:H}_3]}{[3\text{H}^+][\text{EDTA}^{4-}]} = 10^{2.68}$$

$$K_4 = \frac{[\text{EDTA:H}_4]}{[4\text{H}^+][\text{EDTA}^{4-}]} = 10^{2.0}$$

$$K_5 = \frac{[\text{EDTA:H}_5]^+}{[5\text{H}^+][\text{EDTA}^{4-}]} = 10^{1.5}$$

$$K_6 = \frac{[\text{Pb:EDTA}]^{2-}}{[\text{Pb}^{2+}][\text{EDTA}^{4-}]} = 10^{17.88}$$

$$K_7 = \frac{[\text{Ca:EDTA}]^{2-}}{[\text{Ca}^{2+}][\text{EDTA}^{4-}]} = 10^{10.61}$$

$$K_8 = \frac{[\text{Mg:EDTA}]^{2-}}{[\text{Mg}^{2+}][\text{EDTA}^{4-}]} = 10^{8.83}$$

$$K_9 = \frac{[\text{Na:EDTA}]^{3-}}{[\text{Na}^+][\text{EDTA}^{4-}]} = 10^{1.64}$$

$$K_{10} = \frac{[\text{Fe:EDTA}]^{2-}}{[\text{Fe}^{2+}][\text{EDTA}^{4-}]} = 10^{14.27}$$

This system may be fine tuned further by considering the carbonate and hydroxide species with the calcium, magnesium, sodium, and iron. The difficulty of modeling greatly increases as more and more soil constituents are considered and the equilibrium speciation must be computed. Thus, computer calculation of the mole fractions becomes an attractive approach. In order for the SPEPLOT program to predict the speciation in a soil solution, the following information must be input: (1) the total measured concentrations of the metals and the ligands, (2) pH values, (3) conditional stability constants for all possible metal complexes and protonated forms of the ligand, and (4) mass balance expressions for each constituent (both free and complexed forms). Using this input, mass balances are calculated around the total concentrations for the metal and the ligand, complexes, and free ion species and concentrations are found.

There are three viable strategies for developing extraction solutions: acid/base solubilization, oxidation/reduction (redox) solubilization and ligand/metal complex formation. In this study, the latter strategy was addressed. Based upon binding or formation constants (Log K_f) for various lead:ligand systems, three chelators showed promise for the solubilization of lead: EDTA (Ethylene diamine tetra acetic acid), TIRON (1,2-Dihydroxybenzene-3,5-disulfonic acid), and d-gluconic acid (D-2,3,4,5,6-Pentahydroxyhexanoic acid). It is important (if not essential) that the ligand:metal complex formed remains anionic so that interaction with the soil matrix is minimized. Speciation plots were generated for simple systems of lead with the various ligands to predict an optimal operating pH. Chemical structures for the three ligands follow.

EDTA

Ethylenediaminetetraacetic acid

TIRON

1,2-Dihydroxybenzene-3,5-disulfonic acid

D-gluconic acid

D-2,3,4,5,6-Pentahydroxyhexanoic acid

The Lead:EDTA complex at 25° will form with a $\text{Log } K_f = 17.88$. If we examine a speciation plot of the simple system where lead and EDTA are present in equal (1:1) molar concentrations, we see at low pH, the complexation sites on the ligand are dominated by protons, and the lead is free in solution. However, an increase in pH results in an increase in binding potential for the lead. At a pH of 3, half on the lead present in solution is complexed by the EDTA, and at a pH of 4, all of the lead has been chelated. Although hydroxide is present in this system, it is not capable of competing with this EDTA concentration, and thus the seven possible lead hydroxide species are suppressed, and do not form. Keep in mind that this is a simple system *in solution*. The next step in solution speciation modeling is to add other elements that can interfere with the reactions. This would include the hydroxide and carbonate system that interact with the lead, and other common minerals expected to be present and interact with the EDTA, such as calcium, magnesium, iron and aluminum.

To the same model, let's add free calcium and magnesium in equal concentration to the lead and EDTA. Calcium will complex with the EDTA with a $K_f = 10.61$, and magnesium with a $K_f = 8.83$. From this model, it is evident that the calcium is capable of competing with the lead for EDTA at high pH. At a pH of about 11.25, about 50% of the EDTA is complexed to lead, and the other 50% is complexed to calcium. The lead that is freed starts forming hydroxide species, and predominantly forms $\text{Pb}(\text{OH})_3$ above pH 12. Note that at these concentrations, magnesium has a minor effect on the EDTA activity, and mostly interacts with hydroxide ions.

We see in the next system, where the calcium and magnesium concentrations have been reduced to half that of the lead, the calcium still is capable of competing for EDTA complexation.. Lead and calcium are equally complexed at pH 12, and the calcium and magnesium remain as free ions in solution until about a pH of 10, where they begin to speciate with hydroxides. When the model contains the carbonate system, these ions still remain free, although calcium begins to react with $(\text{CO}_3)^{2-}$ right after pH 7, and magnesium right after pH 9. The $(\text{CO}_3)^{2-}$ anion mainly reacts with protons up to pH 9, peak interaction with calcium occurs at pH 11, and with magnesium at pH 10.5. Note also in this model, that at pH 13, 10% of the EDTA is complexed by magnesium, while the other 90% is complexed to calcium and lead. Some 'free' EDTA may also exist at this pH.

Dominating the system with ten times as much calcium as lead, magnesium, and EDTA, shifts the point of equal complexation between Pb and Ca back to pH 10. This is certainly excessive, and large quantities of calcium are present in the system, some tied to hydroxide species, and the rest as free ions. Again, with dominating calcium and lead, magnesium does not compete for EDTA complexation. This model predicts that the EDTA will release the Pb (to form hydroxides) and by pH 11, 95% of the calcium is complexed. This presents a possible method for separation of the Pb:EDTA complex, and recycle of the EDTA back for Pb removal in the soil, making chemical chelation by EDTA an economically viable option. Further modeling can predict the minimum calcium concentration needed for the maximum effect on the EDTA complex.

The TIRON ligand will form a LM complex with a $\text{Log } K_f = 11.95$ and a LM_2 complex with a $\text{Log } K_f = 18.28$ at 25°C . Looking at a speciation plot for the lead and TIRON system, we see that below a pH of about 4, there is no complexation of the lead. Above a pH of 4, the speciation predicts a 50% complexation of the lead present in solution. The other 50% of the lead forms hydroxy species, especially at alkaline pH. However, by increasing the ligand metal ratio to 2:1, the lead hydroxy species are removed from the system.

For lead and D-Gluconic Acid system, a speciation model was prepared for Pb^{2+} , free ligand, protons (H^+) and hydroxides (OH^-). Based upon solution speciation, this model predicted essentially low formation (20% of total species) for the single metal:ligand complex between pH 4 and 7. This complex only has a stability constant

of 2.6 at 25°C. However, this model also predicted the formation of an $ML(OH)_2$ complex with a $K_f=15.71$ for 85% of the total species at a pH around 10.5. Formation of this complex would be ideal for lead removal at alkaline pH (a condition where EDTA has proved ineffective.)

The next variable to consider as contributed from the soil matrix will be the oxidation-reduction potential (Eh), measured in volts. This is related to the thermodynamic properties for the lead species. The following Eh-pH diagram is for a system containing lead, sulfur, carbon, oxygen, and hydrogen. This model assumes activities of the dissolved species to be: $Pb=10^{-6}$, $S=10^{-3}$, $C=10^{-3}$. Under reducing conditions, galena (PbS) occupies the Eh-pH space. In the absence of sulfur (or where sulfur activity is negligible), native lead remains stable. In conditions which would be present at the LAMPH site (high Eh, moderate pH), the dominant species would be $PbCO_3$.

B. Soils and Batch Scale Studies

In order to experimentally test the predictions from the computer models, a simple procedure was used to achieve complete contact between a contaminated soil and a specific ligand. For the batch scale studies, a 6:1 liquid to solid ratio was employed using 5g of soil with 30 ml of extractant in a 50 ml centrifuge tube. Some quick investigations indicated that an 8 hour contact time rotated at 10 rpm was adequate for the ligand/soil system to equilibrate.

Recall that solvent extraction is being investigated so that it can be applied to the remediation of a soil from the Messon Physics Facility (LAMPF) at LANL. At the site, piles of old shielding lead had been sitting for more than 30 years, and some of the lead had mobilized, contaminating the soil below. This soil was then removed from the site and stored in drums to be treated at a later date. Due to the DOE internal regulations mandating a *MIXED WASTE GENERATION MORATORIUM*, it was not possible to work directly with the soil, and a substitute was necessary.

For the batch tests, a 'surrogate' contaminated soil was generated using lead nitrate ($\text{Pb}(\text{NO}_3)_2$) at a loading of 2000 ppm (mg/kg). A highly developed 'clean' (i.e. no background lead) soil was obtained 40 feet above a road cut on N.M. State Road 4 (East Jemez bench) and labeled **Longmire1**. This soil was found to have 15% sand, 22% clay, and 63% silt. Using USDA agriculture classifications, this would be termed a *silty clay loam*. Of the clay fraction, 30% was found to be Illite & Smectite, and another 30% Kaolinite, 20% Illite, and 20% Calcium Smectite. The quartz in the clay size was found to be minimal. This soil was also found to have 4.1% organics and a background lead concentration of 35ppm. It is noted that, the clay fraction

percentages reported here are approximate, since an error of $\pm 20\%$ is not unrealistic for this type of analysis.

The soil was prepared by passing it through a 0.25" sieve and agglomerated material was crushed as needed. Then 400 grams of soil were placed in two 2 liter containers. One batch of soil was to be loaded with lead, and the other was to remain unleaded (for blanks). 800 mg of lead ($1279 \text{ mg Pb(NO}_3)_2$) was necessary to contaminate 0.4 kg of soil to a 2000 ppm level. Using a 1:1 liquid/solid ratio, 400 ml of H_2O was used per container. These were rotated at 30 rpm for 65 hours. The leaded soil/liquid system equilibrated at a pH of 7.45, while the unleaded system equilibrated at a pH of 8.45. The mixture was then centrifuged and the supernatant checked for lead using a Varian™ Inductively Coupled Plasma (ICP) AES. A 100% transfer of lead from the aqueous matrix to the soil matrix was achieved. The soil was removed and air dried on trays for 18 hours. The soil was then ground using a mortar and pestle for use in the batch experiments.

As a second "clean" surrogate soil, some soil was obtained from the LAMPH site near where the lead shielding was stored on the ground. Attempts were made to determine a background lead level for this soil. However, there was a large variability due to the random presence of lead shot ($<1\text{mm}$ in diameter). The soil contained no organics or clays, and was not highly developed. Essentially it resembled crushed tuff bedrock found at the site. This LAMPH "soil" contained particle sizes ranging from silts to sands. Whether or not the soil/lead shot ratio is at all similar to the actual contaminated soil removed from the site remains to be determined.

Batch tests were performed to *screen* the selected ligands and test their capability for lead removal. Each of the three ligands: EDTA, Tiron, d-gluconic acid was scrutinized under 9 conditions; three ligand:metal molar ratios (5:1, 10:1, 20:1) and three pH levels (4,7,10). Although the pH of the extractant ligand was set initially, due to the high buffering capacity of the Longmire 1 soil, the pH always equilibrated to approximately 7 for those batch tests. However, for the LAMPH batch tests, the samples were buffered a bit more basic than the initial solution pH (e.g. $4 \rightarrow 6$, $7 \rightarrow 9$, and $10 \rightarrow 11$.) No attempts were made to further adjust the system pH during the 8 hour rotation period. The following results were obtained.

EDTA proved to be the most effective removal agent for lead from both Longmire 1 soil and the LAMPH soil. With EDTA, successful removals (around 85% for Longmire soil and 94% for LAMPH soil) were achieved with the low ligand metal ratio of 5 to 1. The initial pH of the EDTA appeared to have little effect on the removal using EDTA.

The pH appeared to have little effect on the Pb removal using Tiron with the Longmire1 soil except at the lowest ligand metal ratio of 5:1 where increasing the pH from 4 to 10 decreased the removal efficiency from 33% to 2%. However, once the L:M ratio was increased to 10:1, the same change in pH *increased* the removal from 70% to 79%. Further increase of the L:M ratio resulted in no significant increase in Pb removal. It appears that in the Longmire1 soil at a low L:M ratio, there is another metal which is out competing the lead for the ligand as the pH is increased. This causes a reduction in lead solubilization. With a higher L:M ratio there is enough ligand to satisfy the demand exerted by the competing metal and solubilize the lead present in the soil. With the LAMPH soil, pH appears to have little effect on the removal efficiency of Pb, except again at the low 5:1 L:M ratio, where about 10% increase occurred in the removal (83% to 92%) when the initial ligand pH was raised from 4 to 10. Once the

L:M ratio was increased to 10:1, 94% removal was achievable at all pH conditions, and further increase of the L:M to 20:1 had no increasing effect on the Pb removal.

The d-gluconic acid was expected to form $ML(OH)_2$ complexes at high pH, however very poor Pb removals occurred at all conditions, possibly due the buffering capacity of the soil. With the LAMPH soil, water was capable of removing 40%-50% of the Pb in the sample. This indicates that many of the lead species present (quite likely carbonates and hydroxides) are not bound tightly to the soil. This is to be expected as the soil is not highly developed and contains no significant quantities of clays, with which the strongest bonding interaction occurs.

From the batch studies one must conclude that all three of the extraction systems still hold promise, but EDTA and Tiron hold more promise.

C. Column Scale Extraction Studies

The next order of scale up for the Pb removal was the column study. At this size scale, the variables effecting hydraulic conductivity and soil matrix interferences can be identified. Also addressed is the number of bed volumes required to clean the soil to an acceptable limit.

Column #1

For the first column, Longmire1 soil was 'spiked' to 2000 ppm lead using $Pb(NO_3)_2$, resulting in 6720 mg of Pb in 3.36 kg of the soil. This was done using a spray nozzle under a fume hood. The soil was spread evenly 0.5 inches deep in trays and sprayed from a distance of 2 to 3 inches. The soil was allowed to dry for 48 hours, and then loaded into the column, resulting in a total bed volume of 3.12 liters. Dipotassium EDTA at a concentration of 0.01M was selected as the extracting ligand instead of tetrasodium EDTA because once the sodium is replaced by lead on the EDTA molecule, it can interact with the cation exchange sites on the clay fraction of the soil. This can result in a "swelling" of the clay which greatly reduces the hydraulic conductivity of the column, sometimes reducing the flow to zero. At 2000 ppm Pb, 0.01 M EDTA gives a ligand:metal ratio of 1:3 for the entire soil column mass. However, the interaction between the ligand and the metal in the column is taking place across a thin layer of soil, which represents the active volume, and not across the entire column. Thus, the L:M ratio is not the same as the L:M ratio for the batch tests were contact and

interaction were based on the entire soil mass. The effective L:M ratio will be much higher than the 1:3 would indicate.

Initially 0.01M di-K EDTA was applied at a rate of approximately 250 ml/hour. Once the column was completely wetted, hydraulic loading rates as high as 400 ml/hr were used. The flow rate averaged around 325 ml/hour. Because the removal of the lead from the soil is concentration dependent, the highest quantities are removed in the first one-third of the run. For this column, 50% lead removal was achieved within 1.25 bed volumes and 80% at 2.1 bed volumes. The last 20% of removal is characteristically asymptotic. As the lead concentration in the soil drops, so does the driving force for chelation. This column was shut off at 92.26% removal achieved in 9.18 bed volumes, resulting in 0.5 grams of Pb left in the soil column.

Column #2

A second column was set up using the "clean" soil characteristics of the LAMPH site. A soil mass of 3.828 kg was 'spiked' to 2000 ppm of Pb, again using $\text{Pb}(\text{NO}_3)_2$, resulting in 7656 mg of Pb in the soil. This represents a total soil volume of 2.5 liters. However, unknown to the investigators at the beginning of the tests, the soil was contaminated with lead BB's. The background level of lead in this soil sample was estimated to be around 12,000 ppm due to the presence of the lead shot particles >100 mm in diameter. This averaged 66 mg of lead in a 5 gram sample for 17 replicates. For this column, background Pb was taken to be 12,000 ppm and with a 2,000 ppm spike, the total 14,000 ppm Pb resulted in 53.6 grams of Pb in the soil column.

The risk of compromising hydraulic conductivity was not a limiting factor in this column due to the negligible clay fraction of the LAMPH soil. A solution of 0.01M Dipotassium EDTA was applied as the removal ligand. Based on the assumptions of the lead concentration, this would be a ligand: metal ratio somewhere in the neighborhood of 1:25.

The column was run for 7.90 bed volumes (19.9 liters of 0.01M EDTA) during which 46% of the lead was extracted. Due to time constraints, and the unknowns associated with quantifying the background lead in the soil, this column run was ended before all of the lead was extracted from the soil in the column. However, due to the consistent high levels of lead seen in the last 10 liters of extraction solution, it is

believed that the remaining BB's will be completely dissolved. The concentration of lead in the last extractant sample was 450.7 ppm Pb. It appears that the system may have become dissolution kinetics limited, and reducing the hydraulic loading rate may increase Pb concentration in the extraction solution.

Column #3

In the third column run, 3.17 kg of Longmire1 soil were spiked to 2000 ppm Pb and loaded into a 2.61 liter bed volume to be treated using TIRON. The column contained a total of 6,346 mg of Pb. The ligand was applied first at a strength of 0.01M and then at a strength of 0.1M.

Throughout the entire column run, hydraulic conductivity was poor (<0.25 liters/hour), and the lead removal was also poor. The solute out of the column was a deep red color (like Italian wine), which rarely exceeded 50 ppm Pb. After 3 days, and 3.4 bed volumes, a total of 6.18% of the lead had been removed. This test was considered a failure, and the column run was terminated. It is believed that the Tiron was selecting another metal from the soil matrix in preference to the lead.

D. Soil Agglomeration with the Column Studies

In cases where the soil is unable to provide a flow rate which is acceptable for timely removal of the contaminant, agglomeration may be employed. Agglomeration has been used effectively in the mining industry for the leaching of Au(Gold), Ag(Silver), and Cu(Copper). (McClelland, *et al.* 1983) In these cases, mine tailings were agglomerated, and leached for their precious metals. Agglomeration is the forming of soil aggregates which are 3/8-3/4 inches in diameter. The agglomeration process encourages clay and fine materials to adhere to the coarser particles to create a coating of fines around the coarse particles. Agglomeration can be accomplished in a rotating drum (cylinder) in which the feed enters at one end and exits at the other. Detention time for an agglomerate ranges from 10 to 20 seconds. The rate and method of water application, angle of the cylinder, and rotation speed are all variables that can be optimized for the particular soil and binder quantities in the reactor. Agglomeration will prevent preferential flow paths caused by the swelling and shrinking of clays, migration of fines, and erosion in the soil heap. The process also allows the control of the buffering capacity of the soil. In these studies, low ratios of Portland Concrete were used to add a cohesive factor to the soil.

Previous studies (McClelland, *et al.* 1985) indicated that Portland cement was necessary in the ratio of 50 lb per ton of tailings in order for adequate binding to occur. However, lower binder ratios were acceptable if Portland cement was mixed with lime in equal proportions prior to addition to the tailings. Also concluded from these studies was that there is an optimal moisture content (22% in their study) at which percolation rate is maximized, and that curing periods greater than 24 hours aid in maintaining an acceptable percolation rate. It was also shown in this study that coarse water droplet application was capable of achieving agglomeration, while atomized water droplets did not. The dominant mechanism effecting contact between the ligand and the soil agglomerate is capillary action, through which the ligand is drawn into the agglomerate. Once agglomerate saturation has been achieved, excess ligand will be forced out of the agglomerate and will move down toward the bottom of the soil in the reactor.

Column #4

For the fourth column run. Longmire1 soil was used. However, it was agglomerated to improve hydraulic conductivity, as well as to maintain buffering capacity to a pH between 10 and 11. A mass of 3.949 kg of soil was 'spiked' to 2000 ppm Pb using $\text{Pb}(\text{NO}_3)_2$ resulting in 7898 mg of Pb in the soil. For the agglomeration procedure, the 2.5 liters of soil were mixed with 150 ml of Type I Portland Cement to act as an aggregate stimulus. The dry mixture was rotated in a cement mixer while water was added at the "break point" using a spray device. The idea is that each drop of water will act as a point around which an aggregate can grow. Making this happen is more of an art than a science, and the way the water is applied greatly effects the quality and size of the aggregates. For this trial, aggregates were formed that ranged in diameter from 5 mm to 5 cm. These were dispensed and collected from the mixer and allowed to cure for 48 hours in a tray and contained in plastic. After this, they were loaded into a column and resulted in a bed volume of 4.25 liters.

The choice of ligand for this column run was d-gluconic acid. Although this ligand showed poor binding capability in the batch test study, it was felt that this may have been due to the buffering of the soil, which tended towards neutral pH. If the buffering range of the soil could be shifted between pH 10 and 11, there may be the proper environment for the formation of the $\text{ML}(\text{OH})_2$ complex that the speciation plots

predicted. Unfortunately, any metals solubilized in the column, didn't make it out of the soil column. The results of this trial were dismal to say the least, with less than 0.2% lead removal in 6 bed volumes. Either the $\text{ML}(\text{OH})_2$ complex was not forming, or else it was forming, but it had such a high affinity for the soil, that it stayed on the soil matrix. Either way, the lead stayed on or with the soil.

Column #5

In the fifth column run, a soil from the Cal-West Superfund site near Lemitar, New Mexico was used. This 44 acre site was used as a lead-acid battery recycling facility from 1979 to 1981. Further research and development relating to lead recovery was conducted at the site from 1982 to 1984. Previous work (Kirby, J., 1992) showed 50% lead removal in 1 bed volume using 0.05M di-potassium EDTA. However, the hydraulic loading rate was as low as .016 liters per hour. For our experiment, 5.019 kg of this soil was agglomerated with 400 ml of Type I Portland Cement and 500 ml of deionized water. Agglomeration was performed as in preparation for column #4. However, this soil is a silty loam, containing 90% fines of which only 6% are clays (koalinite, illite / smectite, and chlorite). This high fines content resulted in extremely slow hydraulic conductivity through the column (starting around 300 ml/hr, and finishing around 15 ml/hr) Also due to the high fines content, a much high ratio of cement to soil was needed in order for the soil to agglomerate. This soil is highly contaminated, and unlike the surrogate soils, it has undergone field weathering, increasing the bonding between the lead and the soil. The Cal-West Superfund site contains hot spots with lead levels as high as 100 grams / kg (i.e. 1%). For this representative sample, an average contamination of level of 10,640 mg/kg (ppm) was assumed. (Kirby, J., 1992) Thus this soil column contained around 53.4 grams of lead. Final bed volume for this column was 4.5 liters.

This agglomerated soil now possessed a buffering capacity in the alkaline range. The lead extraction was performed using 0.01 M EDTA which bonds Pb^{2+} very poorly above a pH of 10. In an attempt to buffer the Pb:EDTA reaction zone to an acceptable pH, 1M sodium bicarbonate (Na_2CO_3) was fed simultaneously with the EDTA. This produced a column effluent pH of between 9 and 10, and lead was removed as high as 250 ppm in the peak removal sample. This is still low however, compared to peaks of over 1000 ppm with the surrogate Longmire 1 soil. In 6.5 bed volumes, a total of less than 7% of the lead (3.47 grams) was removed. It is believed

that the large amount of Portland Cement used in the aggregation process may have formed impermeable aggregates.

The following conclusions were drawn from the column studies:

- EDTA is the extraction solution of choice.
- It appears that all of the Pb can be extracted from the LAMPH soil.
- A great deal of work is needed to understand agglomeration.

III. Separation of the Pb/EDTA complex

If one is to recycle the extraction solution (EDTA), it will be necessary to separate the Pb from the EDTA, and then put the EDTA back into service. There are a number of important issues to resolve before this can be accomplished at a production scale, including; concentrating dilute Pb:EDTA solutions, separating the Pb:EDTA complex, and removing the lead from the solution after the complex is separated. The work addressing these issues will be discussed in the following sections.

A. Column Studies with Cation Exchangers

Immobilized Peat as a Biosorptant

As an initial exploration into the separation of the lead:EDTA complex, the idea emerged that a solution of the complex could be passed over (or through) a column containing an agent capable of binding lead. This agent, if it was a strong enough cation exchanger, may be capable of competing with the EDTA for binding of the lead.

The application of a bio-media for ion exchange was appealing, especially from a cost perspective. Synthetic resins average \$100+ per pound, while immobilized (chemically modified) peat averages \$10 per pound. Raw peat is abundant in many areas throughout the world and generally is older than 1000 years. Peat is often described as an organic soil consisting of organic residues resulting from the partial degradation of plants, animals, microorganisms, and their wastes. Peat formation is common in wet areas where oxygen is limited. The anaerobic conditions result in the incomplete degradation of organic matter to recalcitrants (such as lignin and cellulose) which are the main constituents of peat. Carboxyl and phenolic hydroxyl functional groups are common on most humic substances including peat. These functional

groups have high cation exchange capacities and have been shown to be effective at removing metals from solution through ion exchange and complexiometric mechanisms. Peat has been used effectively to treat many industrial wastewaters in removing: heavy metal compounds, organic compounds, proteins, and pollutants in dye-house effluents. (Ansted, *et al.* 1984).

The use of raw peat has some disadvantages. Due to its low porosity, it is highly impermeable to water, which limits its application in column reactors. It also leachs humic materials, which can greatly increase the TOC of the effluent. Raw peat can, however, be "immobilized" by treatment with sulfuric acid (H_2SO_4). This results in a material that is both granular in nature, making it acceptable for column use, and it is resistant to leaching. The immobilization process entails trapping the biomass in a porous polysilicate framework, resulting in a matrix well suited to continuous saturated flow in fixed bed systems.

The general procedure for immobilization of the peat involves drying the raw peat to a constant weight at 100°C for 24 hours. The peat is then mixed with H_2SO_4 in a full contact (batch) type reactor at the ratio of 4 ml to 1.2 grams dried peat. This solution is then slowly heated to 150°C in a fume hood and maintained there for 2 hours with stirring. Following this, the solution is cooled and thoroughly washed with distilled water until no pH change is noted in the water. The peat material is again dried in an oven for 24 hours at 110°C followed by grinding with a mortar and pestle and sieving for the desired size range (40/60 mesh in this instance.) Before the peat is loaded into a column reactor, the quantity needed is further size classified in solution using a settling time cut-off based on Stoke's Law to eliminate extremely small particles. Size uniformity has been shown to be an important factor when considering binding capacities.

In this initial trial, lead and EDTA were prepared (reagent grade) in a 3:1 ratio, with 3000 ppm Pb^{2+} (0.014 M) and 0.043 M EDTA and the pH adjusted to 5.0. A 15 ml bed volume was loaded with 5.059 grams of 40/60 mesh immobilized peat. The flow rate was set at 0.833 ml/min (or 1/18 Bed Vol/Min) and fractions collected for each bed volume. The column effluent was then analyzed for lead using a Perkin Elmer Flame Atomic Adsorption with acetylene gas. This setup was linear upto 20 ppm and so dilutions as high as 1:100 were required. At 1 bed volume 214 ppm had exited the column, and 2740 ppm by bed volume 2. AA analysis showed the influent at 2900 ppm, and 95% breakthrough in 2 bed volumes can be considered unsuccessful. The column was then stripped using 150 ml of 1M Thiourea / 0.1M HCl and <10 ppm of Pb^{2+} were found. Thiourea has the following structure.

Thiourea
(Thiocarbamide)

Using the same peat column, a 3:1 solution was prepared as before and the pH adjusted to 7.0. Under the same conditions (flow and collection) as before the solution was eluted through the peat column in order to remove the Pb:EDTA complex. However, as before, 80% breakthrough occurred in the second bed volume collected,

and 100% breakthrough within 5 bed volumes. Effluent pH ranged from 3.1 initially to 6.6 after 59 bed volumes. Stripping again showed low lead removal.

Using the same conditions as before, with only 1:1 molar ratio at an influent pH 3.0. 37% breakthrough occurred in bed volume 1 and 100% breakthrough by bed volume 4. The effluent pH stayed around 2.5.

The influent pH was reduced to 1.5 for a 1:1 molar ratio solution at 3000 ppm, however, again no significant binding occurred. Other experiments were run with influent concentration around 100 ppm and 1:1 molar ratios, still no binding occurred. Based upon these experiments, it is evident that the peat material is not capable of competing with the EDTA for the lead.

Synthetic Cation Exchange Resins

After testing the immobilized peat, it seemed possible that although this material was a cation exchanger, it did not possess a strong enough capacity to compete with the EDTA for the lead. Two synthetic resins were selected to see if they were capable of this. Amberlite™ IRC-718, a strongly acidic cation exchange resin, and Bio-Rad Chelex® 100, a weakly acidic cation exchange/chelating resin were investigated.

Rohm & Haas Amberlite™ IRC-718

This polymer was selected because it is a strongly acidic cation exchange polymer with carboxylic acid groups on acrylic (styrene-divinyl benzene) resin. This resin has a cation exchange capacity of 1.1 meq/ml of wet resin and is highly selective for Pb^{2+} over more common ions such as Mg^{2+} and Ca^{2+} .

This resin was tested in conjunction to the immobilized peat material at the similar conditions as previously and also proved ineffective at separating the Pb:EDTA complex by competing for the lead. Complex breakthrough occurred at 1 bed volume.

Bio-Rad Chelex® 100

Although this material is a weakly acidic cation exchange resin, it has a selectivity for divalent ions to monovalent ions of 5000:1. This resin is also a styrene-divinylbenzene copolymer. In addition to carboxylic acid groups, this polymer contains paired iminodiacetate ions which act as chelating groups for multivalent metal cations.

This resin was tested following the IRC-718 under the same conditions and was also ineffective at separating the Pb:EDTA complex by competing for the lead. Complex breakthrough occurred immediately.

B Removal of the Lead through Chemical Precipitation

The fact that the Pb:EDTA complex forms with such a high stability constant indicates that equilibrium will tend to shift in the direction of maintaining this complex. Precipitation is based upon altering the chemical equilibria of the system by exceeding the solubility product for the species. Treatment by precipitation must address both equilibrium and kinetic relationships. Based upon equilibrium, theoretical calculations can be made concerning the concentration of the complex in solution at equilibrium, the required quantity of precipitant, and the resulting mass of sludge formed. For a free metal in solution, the solubility product can be expressed as: $K_{sp} = (A^{b+})^a (B^{a-})^b$

where () indicates the activity of the species in solution. Generally, an increase in the ionic strength causes an increase in the metal solubility. Concentration can be substituted for activity in dilute solutions. Although equilibrium calculations are useful in predicting effects when the precipitation reaction goes to completion, these reactions are typically kinetically limited. In other words, insufficient time is available to achieve equilibrium. The following table shows K_{sp} values for various lead compounds.

Compound	Formula	K_{sp}
Lead Carbonate	$PbCO_3$	1.6×10^{-13}
Lead Chloride	$PbCl_2$	1×10^{-4}
Lead Chromate	$PbCrO_4$	1.8×10^{-14}
Lead Hydroxide	$Pb(OH)_2$	2.5×10^{-16}
Lead Oxalate	PbC_2O_4	3.0×10^{-11}
Lead Sulfate	$PbSO_4$	1.9×10^{-6}
Lead Sulfide	PbS	7×10^{-26}

The three steps in a standard precipitation reaction are: nucleation, crystal growth, and agglomeration and ripening of the solids. Factors effecting the precipitation reaction include: ionic strength, pH, complexation, and temperature. Ionic strength lowers the metal activity and metal solubility is increased. Except in the case of carbonate precipitants, metal solubility increases as a function of temperature. Complexation of the metal by an organic ligand can greatly interfere with removal efficiency by keeping the complexed metal in solution. Typically due to kinetic constraints, three times more precipitating agent is needed than predicted using equilibrium equations.

Work In Progress

In approaching the precipitation of lead from the EDTA complex, jar tests will be performed in order to optimize pH, mixing requirements, settling characteristics, and sludge production. Centrifugation will be used to separate the sludge from the supernatant and 2 analytical approaches utilized. Sludge can be resolubilized in acid and analyzed for lead using Flame Atomic Adsorption, while the supernatant will be analyzed for remaining Pb:EDTA complex and free (or lightly complexed) EDTA using a Dionex Ion Chromatograph. Calibration and standardization for these complexes has already been performed in the 10^{-4} mM and 10^{-2} mM range.

Two economic chemicals that can be used for precipitation are soda ash (Na_2CO_3) and Lime ($CaOH$). In solution, soda ash will provide a reactive carbonate ion according to the following:

Also, lime will react in solution according to the following reactions:

C. Identifying a characteristic peak for EDTA and lead complexes

Using an ultraviolet/visible range spectrophotometer, some simple tests were run as a qualitative alternative to using a Dionex HPLC for analysis of free and/or complexed EDTA.

Initially, three solutions were prepared; (1) a 500 ml stock solution of Pb:EDTA in a 1:1 molar ratio. Lead was present at 100 ppm. The resulting molarity for both the lead and EDTA was 0.2413 mM; (2) a 500 ml stock solution of Pb:EDTA in a 1:2 molar ratio. Lead was still present at 100 ppm, but the resulting EDTA molarity was 0.4826 mM; (3) a 500 ml stock solution of solitary dipotassium EDTA at 0.2413 mM. Dilutions were made from each solution to a concentration of 50 ppm and 10 ppm (relative to lead). The following results were obtained.

The UV/VIS range was scanned from $\lambda=190$ nm to 350 nm at a rate of 60 nm/min. The chart speed was set at 5 cm/min. The upper limit for the instrument was set at 2 absorbance units. For the solitary dipotassium EDTA @ 100 ppm (relative to Pb), a characteristic peak was observed at $\lambda=193$ nm. When EDTA and lead were in a 1:1 ratio at 10 ppm (relative to Pb), two characteristic peaks were observed at $\lambda=240.2$ nm and $\lambda=200$ nm. Lastly, with the 2:1 EDTA:Pb complex, two characteristic peaks were observed at $\lambda=241.7$ nm and $\lambda=200$ nm respectively. Both solutions containing lead at the two higher concentrations (50 ppm & 100 ppm) exceeded the set confidence scale at 2 AU.

It appears that the peak occurring around 240 nm to 241 nm in the ultraviolet range is for the Pb:EDTA complex, while the peak around 200 nm is for the dipotassium 'free form' of the EDTA. Application of this method for quantitative analysis of lead and EDTA complexes would be beneficial in the sense that the concentration could be monitored in "real time" at those wavelengths in field applications to determine various concentrations of the complexed and recycled EDTA effluent streams. However the need for dilution makes this technology inappropriate. Also it is known that humic materials may leach from the soil matrix during treatment operations, and numerous humic materials also have characteristic peaks in the $\lambda=240$ nm range. Unless the humics were removed prior to analysis, they would certainly contribute an element of interference.

IV. Volume reduction in the soil treatment waste stream

A. Employment of Cation Exchangers in scavenging for free lead.

In employing EDTA as the solvent extraction ligand for lead removal from soil, the complexed metals leave the soil in an anionic form. However, it is also possible that trace amounts of lead may leave the soil in already solubilized forms, some of which will be cationic. In order to scavenge these from the effluent stream, a cation exchanger would be necessary. Three types of resins have been considered for this application, synthetic strong cation exchange resin, synthetic chelating resin, and immobilized peat was considered for its capabilities of binding lead at low concentrations.

Binding of free Pb on a biosorptant material

Knowing that the Pb:EDTA complex is inherently anionic, and that immobilized peat material possess a significant *cation* exchange capacity, it appeared to be valuable to establish a baseline for the binding of free lead on the material. The binding of metals onto immobilized peat is not straightforward and interaction between particular metals and functional groups is known to vary depending upon such solution conditions as: pH, ionic strength and temperature. Studies in the chemistry department at New Mexico State University have shown that with an influent concentration of 10 ppm metal, the immobilized peat biosorptant has the following binding capacities: 85.2 mg Pb²⁺/g peat, 109.7 mg Hg²⁺/g peat, 50.1 mg Cu²⁺/g peat. The order of selectivity exhibited by the immobilized peat follows.

First, a 15 ml bed volume was loaded with 5 grams of peat. A feed solution containing 3000 ppm Pb²⁺ as Pb(NO₃)₂ was prepared at an equilibrium pH of 5.1. Again running at a flow rate of 0.833 ml/min (1/18 BVM), fractions were collected for every fourth bed volume. However, 42% breakthrough occurred within 4 bed volumes, 74% breakthrough within 8 bed volumes and complete breakthrough shortly thereafter. Stripping with 1 M Thiourea/0.1M HCl indicated that lead binding had occurred, however, such a high concentration of lead for such a small bed volume clearly was out of balance.

Next, a 5ml bed volume was filled with 1.6 grams of 40/60 mesh immobilized organic peat, and a 65 ppm influent solution was prepared of free lead using lead nitrate. Flow rate was still 0.833 ml/min (1/6 BVM). The breakthrough curve is shown below.

This application of peat appears more promising than the previous applications considered. It is not competitive with commercial synthetic resin at high metal concentrations. However, the peat appears suitable for scavenging low levels of metals. The levels of lead that are removed from the soil without chelation (thus remaining cationic) should hover at low levels, where the peat biosorptant can successfully bind them.

Synthetic Cation Exchange Resins

Although these resins had been examined for use in separation of the Pb:EDTA complex previously, they were also examined for their ability to exchange and strip free species of lead. The peat material has been shown to be effective at removing low levels of lead, but is not as effective when the lead levels exceed a few hundred parts per million. From before, the Rohm & Haas Amberlite™ IRC-718 and the BioRad Chelex® 100 were column tested. Both resins proved extremely effective at binding and releasing lead. However, because Chelex® 100 is priced much more expensive for use in small quantities for in molecular biology applications and the Amberlite™ is priced competitively for industrial applications, if it is necessary to use a synthetic cationic resin, the Amberlite™ would be the resin of choice.

B. Employment of Synthetic Weak Base Anion Exchange Resins for removal of chelated lead.

Solvent extraction of soil in a column or heap produces a consistent pattern, if concentration of metal in elutriant is plotted against volume of elutriant. The result is a high (peak) concentration in the first elutriant samples, followed by declining concentrations as the concentration gradient decreases. Thus, the farther through the treatment (i.e. the closer to the MCL), the lower the levels of lead are in the effluent. Because low liquid to solid ratios are an important element to this design, it will be necessary to remove and concentrate the Pb:EDTA complex from both peak and dilute solutions. This will allow internal process water to be routed elsewhere for re-use in the system, while regenerate solutions from the anion exchange solution will be highly concentrated. This high concentration of Pb:EDTA in the regenerant solution improves the efficiency of removing the lead from the complex using a precipitation method.

Based upon previous anion exchange studies of Pb:EDTA complexes (Dudzinska, M.R. *et al.* 1991), the use of a weak-base anion exchange resin is preferred over a strong-base resin in order to maximize regeneration (stripping) efficiency. Also, previous leaching studies have shown that when large quantities of soil are leached using EDTA, humic materials also leach from the soil matrix. Some of the humic materials are capable of exchanging with anionic resins, and with strong base resins these humics are almost impossible to remove. This results in rapid resin fouling. With weak base resins, the humic material is readily strippable, although it still competes with the Pb:EDTA complex for binding sites. As a solution to this interference problem, it may be possible to selectively remove the humic material on a granular activated carbon (GAC) column through an absorption mechanism while the Pb:EDTA complex passes on to the anion-exchange column.

Initial studies into the exchangeability of the Pb:EDTA complex employed a synthetic resin manufactured by Rohm and Haas company: AMBERLITE IRA-68 Anion Exchange Resin. This resin is an acrylic, gel, weakly basic resin. It contains tertiary-amine functionality in a cross linked acrylic matrix. A sample breakthrough curve follows, with an influent concentration of 400 ppm Pb, 10 ml bed volume and flow rate of 2.5 ml/min.

Work In Progress

To perform reliable system design calculations it is necessary to perform a significant number of column runs using the resin of interest and the solution matrix of interest. Variables of interest are empty bed contact time, regenerate strength and regenerate contact time. Optimization of empty bed contact time (through flow rate) for maximum removal efficiency is critical. Further, operating conditions must achieve a balance between the mass of the resin, regeneration efficiency and chemical requirements, in order to minimize the overall cost of this treatment process.

V. Proposed Field scale schematic for heap leach solvent extraction:

The treatment hardware discussed here will use a combination of density classification and solvent extraction to treat the contaminated soil. Density classification will be used to separate the lead BB's from the soil. Solvent extraction will then be used to remove the remaining lead from the soil and to remove the ^{210}Pb from the BB's. The material removed from the outside of the BB's and the material removed from the soil will be concentrated on a weak base anion exchange resin, and then precipitated. Based on the experience with the small scale pad work, it is anticipated that this technology should produce lead concentrations in the soil below background values (10-15 mg Pb/Kg of soil) and the soil should easily pass the TCLP test.

The objective of this technology is to treat 55 gallon drum quantities of contaminated soils using ligand based solvent extraction. The system constraints for the technology being developed are given below:

- **The system must be suitable for handling barrel quantities of contaminated soils.** Contaminated soil is frequently excavated and placed in barrels for storage. One barrel can be treated at a time, yielding excellent process control, and excellent QA/QC opportunity. Once the hardware is

proven, it will be a small matter to modify the system for other contaminated soils. The user will simply need to identify alternative extraction solutions.

- **The system must operate in an unsaturated mode.** Most soil washing systems commercially available today operate in the saturated mode, with volumetric water to soil ratios of 10:1 to 100:1. This produces an extremely large volume of very dilute waste. A system operating in the unsaturated mode provides two benefits. First, the volume of the secondary waste stream is minimized, since the water:soil ratio is <1.0 . Second, the contaminant is kept concentrated, which makes recovery of the contaminant more efficient.

- **The reactor must be designed to provided good process control and good QA/QC.** When treating radio-active waste it is imperative that one demonstrate there are no untreated portions of the soil.

- **The system must provide adequate control of fugitive dust.** Again, when handling radio-active materials, it is important that dust emissions be controlled.

An overview schematic of the proposed system is shown in the figure on the following page. The various components of this system have undergone at least bench scale testing with the exception of the lead particulate removal system.

The next few paragraphs will track a barrel of contaminated soil through the entire treatment process shown in the accompanying figure. A barrel will be removed from storage and will have a flexible transfer tube attached to the open end of the barrel. The flexible tube will be fastened airtight, and will control fugitive dust. The contents of the barrel will be dumped into a coarse screen to remove all large materials. The flexible tube will form the connection between the barrel and the screen. As the soil and lead BB's pass through the coarse screen it will flow through an air classifier. The air classifier will separate the lead BB's from the soil. The lead BB's will drop down a shaft to a pan below the soil washing reactor. The soil will drop into the soil washing reactor. The various components of the system will be discussed in the following sections.

A. Reaction Vessel

Large Scale Lead Reactor Studies (By Dave Pickens)

According to the soil-mass balances all of the tests which have been performed on lead contaminated soils removed more than 95% of the lead, while the leachate-mass balances show better than 89% removal for all tests. The process removal efficiency for all of the tests conducted with both hexavalent chromium and lead contaminated soils are shown in the table below. This data is all for 1/2 cubic meter soil volumes(760 Kg soil/test) treated in the conical heap and enclosed box configurations.

Summary of data for the field-scale tests.

Test: (All tests contaminated to 500 mg/kg)	Percent Removed by Soil Mass Balance	Percent Removed by Leachate Mass Balance	Overall Bed Volumes Used	Final TCLP (mg/l) (Pass if value <5 mg/l)
Pajarito Soil, Cr VI, Box	99.0	106.0	2.36	0.1
Pajarito Soil, Cr VI, Pile	99.1	93.6	2.61	0.02
Harkey Soil, Cr VI, Box	71.2	86.1	1.51	0.28
Pajarito Soil, Pb II, Pile	95.8	89.1	6.05	0.07
Pajarito Soil, Pb II, Box, Rep. 1	97.8	93.0	2.88	0.18
Pajarito Soil, Pb II, Box, Rep. 2	98.1	90.1	4.03	1.14

Based on this data it is anticipated that acceptable soil cleanup levels can be reached. There is also data available from these tests which indicate the uniformity of treatment is extremely good. The box reactor was cored at a number of points and soil samples taken from top middle and bottom of each core. This soils data showed very good uniformity, with residual concentrations of lead in the soil ranging from 13-17 mg/Kg. These values are below general background levels for soils from this region.

Reactor Characteristics

The system capable of remediating lead contaminated soils through chelation with EDTA should minimize side-stream volume while maximizing Pb removal efficiency. If the soil contained any large quantities of particulate lead, it would be beneficial to remove these initially by two methods: (1) Coarse screening to remove any particles greater than 1 inch in diameter, and (2) air classification to separate small particulate lead (quite likely lead shot bbs). The second would be a density separation, and would follow *Stokes law* as follows:

$$v_t = \frac{g(\rho_p - \rho_a)d^2}{18\mu}$$

where:

v_t = the terminal settling velocity of particle (m/s)

g = gravitational force (9.81 m/sec²)

ρ_p = particle density (kg / m³)

ρ_a = air density (kg / m³)

d = particle diameter (m)

μ = dynamic viscosity of air (N s/m²)

Within the reaction vessel, the contaminated soil would be deposited in the treatment area, while the particulate lead would be channeled to a contact chamber located beneath the soil treatment area. Here, the particulates would essentially be washed using ligand exiting the soil treatment area. This would aid in minimizing interference from other chelated soil constituents (e.g. Ca²⁺, Mg²⁺, Fe²⁺, Al³⁺) because the particulates represent a large enough mass to ensure lead chelation through an equilibrium driving force. The main purpose of the reaction vessel is to clean the contaminated soil. EDTA is applied at an appropriate concentration (variable through

the treatment) using an application system to spray the ligand and ensure uniform distribution. Pregnant leachate (Pb:EDTA complex) is removed from the bottom of the reactor and pumped through the next unit process, granular activated carbon. The end of the treatment vessel is a sampling point, at which standard Eh and pH conditions as well as free Pb^{2+} will be monitored in real time using probe/electrode. Also measured (in appropriate intervals) will be lead concentration by flame AA and complex concentration by HPLC.

B. Extraction Solution Distribution (By Kevin Krause)

A uniform flow of the extraction solution through the soil is critical. In the mining industry drip irrigation has replaced the more traditional sprinklers or 'Bagdad wigglers' in larger scale solvent extraction operations. In many cases the solution application rate has been reduced by as much as 30% to 50% without a loss in metal recovery or a reduction in rate of recovery (Keane, 1991). An even distribution of the drip irrigation emitters and a consistent flow from those drip emitters is the goal of the delivery system. The set of drip emitters to be used are Rain Bird Model Rain Bug non-pressure compensating drip irrigation emitters rated at a maximum flow rate of 7.57 liters per hour (2 gph). A pressure regulating valve ahead of the system will maintain pressure.

A number of delivery systems were tested. The delivery system functioned properly with the exception of the actual drip emitters. The emitters were a source of tremendous flow variability. The emitters specified above were selected on the basis of being able to deliver a constant, fixed flow rate once the system was set.

Summary of Drip Irrigation Emitters tested

Emitter	Flow Rating lph (GPH)	Accepted Y/N	Comments
Rain Bird Model Rain Bug	7.75 (2.0)	Y	Non-pressure compensating, single emitter. Fairly even flows between emitters.
Agrifilm Poly-flo	1.9 (0.5)	N	Pressure compensating, multiple (4) emitter. Extremely variable flows at low operating pressures.
Raindrip Model R144C	3.78 (1.0)	N	Pressure compensating, multiple (6) emitter. Extremely variable flows at low operating pressures.

C. Humics Removal

Besides lead being removed from the soil, humic materials leach out as well. These materials do not effect the treatment, although they do cause some interference with the following ion exchange treatment. Granular activated carbon (GAC) is employed to remove the humic materials from the Pb:EDTA waste stream from, while

allowing the complex to pass. This treatment column also acts like a rapid sand filter to some degree, trapping solid particles in the pore spaces. Allowances will be made so that the GAC can be backwashed (bed fluidization 20-50%) prior to steam treatment for carbon reactivation.

D. Ion Exchange

Because the efficiency of lead removal varies over time, and this system seeks to minimize the volume of waste created, ion exchange will be employed to concentrate various constituents of the waste stream. Synthetic anion exchange (weak-base) resin will be used to concentrate the Pb:EDTA complex. Proper design of the ion exchange system will allow full binding of the soil effluent constituents, resulting in a treated effluent that can be used as process water throughout the system. One ideal use of this water is for maintaining appropriate EDTA concentrations. It is expected that the cationic lead species will be present to a limited degree in the soil, and thus these cation exchange columns will require much less frequent regeneration, as is desired. The anionic resin, however, will be the workhorse of the system, going through numerous loading and regeneration cycles. A dilute base solution (5-10%) will be used to strip the Pb:EDTA complex from the anionic resin, this regenerate will be fed directly into a combination rapid mix/flocculation reactor for treatment. Breakthrough for both ion exchangers will be predictable based upon capacity isotherms, however, real time monitoring of pH will be used as a primary indicator.

E. pH Control (*By Brad Rudd*)

Successful solvent extraction of lead contaminated soils requires accurate pH control throughout the multiple stage process. The stages include: EDTA solvent extraction, GAC filtration of the effluent, Amberlite ion exchange of filtration effluent, separation of the Pb:EDTA complex, and precipitation of lead with possible recycle of EDTA for further use. Each of these stages requires a varied pH range for optimal performance.

Formation of the Pb:EDTA complex in solvent extraction can be hampered by high pH. This can be a problem when treating agglomerated soils. The addition of concrete during agglomeration can raise the pH to a point where extraction will be inefficient. In this situation the pH of the EDTA influent must be lowered to offset the alkalinity of the soil. In most cases of non-agglomerated soils the buffering capacity of the soil should be sufficient to maintaining an acceptable pH range for successful extraction.

Heap effluent must be filtered through GAC to remove humics. If not removed, these humics can cause plugging in the ion exchange columns. For successful removal of humics on the GAC column it is desirable that the humic acids not be hydrolyzed. This is best accomplished at a pH above seven. Again, this pH range should not be difficult to achieve in most non-agglomerated soils.

Following humic removal, the Pb:EDTA complex is captured and concentrated in an Amberlite ion exchange column. Since this is a weak base anion exchange resin, the process is most efficient at low pH. Process monitoring and control of pH at this stage is critical. Effluent from the GAC filter must be monitored and corrected continuously to maintain the acceptable pH range. Upon column exhaustion, the Amberlite column must be fluidized and then stripped with NaOH. Monitoring pH will determine when the column is exhausted and resin regeneration is required. As the

lead-EDTA complex binds with the resin, hydroxides are released from the binding sites. Therefore, the effluent pH will be significantly higher than the influent pH. However, the effluent pH will drop over time as the number of binding sites is reduced. When effluent pH approximates influent pH, the column is exhausted. Any subsequent raise in the pH of the effluent of this stage is beneficial to the following stage.

The final stage in this process is the separation of the lead-EDTA complex and the possible re-use of EDTA. The complex can be separated and the lead precipitated at a high pH. At this stage pH will be monitored and brought to the acceptable range by mixing a base with the wash effluent of the ion exchange stage. The fluid will then pass through a plate settler to remove the precipitated lead and recover the EDTA.

This is a fairly complex control problem, which can be solved inexpensively using a micro-computer based A/D card with commercial control software. All process monitoring and control will be accomplished using a Strawberry Tree Inc. Analog Connection ACPC. The ACPC uses an A/D converter to digitize information from its analog inputs. It can measure temperature, pressure, flow, and other analog inputs from sensors or instruments. It turns heaters, fans, pumps, etc. on and off to control the inputs at preset levels. Ten input ranges span 25 millivolts to 10 volts and 1 milliamp to 50 milliamps full scale. These ranges enable acceptance of almost any sensor, including pH probes. The system, without the computer but including the software, costs approximately \$2,000.

Initial tests have shown pH to be a very linear function of voltage and current. The Orion model 720A pH/ISE meter's recorder output is a 1:1 ratio of the probe's electrical output. This electrical output varies linearly from positive potentials at low pH, through zero potential at neutral pH, to negative potentials at high pH. As can be seen in the graph, the potential ranges from +0.4 volts to -0.4 volts in most operational pH ranges.

Using the software provided with the A/D board, various probes at various process stages can be programmed to monitor the correct pH range for each process. If pH falls outside of the acceptable range, the computer will turn on or off the appropriate pump(s) via relays to correct the problem. All pH data will be automatically logged to disk for process records and later analysis.

F. Separation of Lead and EDTA Complex

Rapid Mix/Flocculation Tank

Specific volumes of the anionic column regenerate will be fed into the rapid mix tank. A pH controlled pump will feed the appropriate quantity of liquid base (possibly $\text{Ca}(\text{OH})_2$) so that the Pb:EDTA complex will be separated, precipitation of the lead will occur, and lightly complexed EDTA will be left in solution. Energy will be input to the mixture in the tank using propeller and/or paddle type mechanisms in order to maximize floc formation.

Parallel Plate Settler

The solution from the tank will be fed into a parallel plate settler. The object of this treatment unit is to effectively separate the lead precipitate from the solubilized EDTA. The concept behind this type of settling unit is the counter current principle (or upflow principle). Plates angled at 55° to the horizontal divide the settling basin into n number of settling cells. Each plate extends beyond the water level to insure complete cell separation. Because this settler will be used for light hydroxide flocs, hydraulic control of inlet and outlet flows will be critical. The flow will enter through the inlet flume located in the bottom of the settler, and through a series of orifices and baffles, will be distributed into each settling cell. As each n^{th} fraction passes along the plate, kinetic energy is reduced and the heavy precipitate floc drops into the sludge hopper (in the reactor bottom), while the recycled EDTA solution easily passes up and over the plate into the outlet channel. The concentrated lead sludge can then be collected from the settler, while the EDTA solution is fed back to the system head for reuse in further lead extraction.

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Solution System

13 SPECIES

1 METAL : Pb @ 0.001M

1 LIGAND : TIRON @ 0.002M

- 1: .00 1 0 0 M
- 2: .00 0 1 0 L
- 3: -7.78 1 0 -1 M(OH)
- 4: -17.26 1 0 -2 M(OH)₂
- 5: -28.04 1 0 -3 M(OH)₃
- 6: -5.88 2 0 -1 M₂(OH)
- 7: -23.42 3 0 -4 M₃(OH)₄
- 8: -20.02 4 0 -4 M₄(OH)₄
- 9: -42.84 6 0 -8 M₆(OH)₈
- 10: 11.80 0 1 1 LH
- 11: 19.00 0 1 2 LH₂
- 12: 11.95 1 1 0 ML
- 13: 30.23 1 2 0 ML₂

pK_{sp} = 15.60 M(K_{sp})