



Project Summary

A Literature Review Summary of Metals Extraction Processes Used to Remove Lead from Soils

Numerous Superfund sites throughout the United States are contaminated with toxic metals. Battery reclamation, lead smelting, and lead-based paint manufacturing are examples of processes that can result in lead-contaminated soils.

The objective of the report summarized here is to review and evaluate literature relating to metals extraction technologies, soil characterization, chelating agents, and membranes. The literature assessment provides insight regarding potential operating problems that can be identified and avoided when extraction processes are used to recover lead from soils.

This Project Summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Metals, unlike many hazardous organic constituents, cannot be degraded or readily detoxified. Toxic metals represent a long-term threat in the soil environment. The cleanup of metal-contaminated sites has traditionally involved excavation of the wastes and contaminated soils with subsequent disposal at an off-site, RCRA-approved landfill, in accordance with hazardous waste regulations. This process is expensive because of the special precautions (e.g., double liners) required to prevent leaching of toxic metals from the landfills. In addition to increasing costs

and dangers to public safety from large-scale transportation of wastes, long-term environmental liability is also a concern associated with the landfilling approach. Thus, there is great incentive for the development of alternative methods for cleanup of contaminated sites.

Chemical or physical fixation of the contaminated soils, which immobilizes the lead (or other heavy metals), is required before landfilling. The drawbacks of this approach, however, include (1) the need for future monitoring of heavy metals on site, (2) questionable longevity of fixation chemicals, (3) unknown biosystem (plant/animal uptake) effects, and (4) the potential need of a soil cap to prevent wind erosion problems.

The use of extraction processes to recover heavy metals (e.g., lead) from contaminated soils is a more attractive alternative. The goal of this approach is to treat the contaminated soil to an acceptable level, protecting groundwater and surface water resources, and then to return the "clean" soil to the site from where it originated.

Metals Extraction Technologies and Soil Characterization

Several technologies have been or are currently being developed to remove metals from contaminated soils.

The Bureau of Mines (BOM) has developed a process that employs acid leaching to convert lead sulfate and lead dioxide to lead carbonate, which is soluble in nitric acid. Lead is recovered by precipitation with sulfuric acid to produce a lead sulfate product. The BOM has also devel-

oped a process to convert the lead compounds to lead carbonate with ammonium carbonate and ammonium bisulfite, followed by leaching with fluosilicic acid. Lead is then recovered using an electrowinning process.

The TerraMet™ soil remediation system developed by COGNIS, Inc., leaches and recovers lead from contaminated soils, sludges, or sediments by using a proprietary aqueous leachant. Various forms of lead, including metallic lead, soluble ions, and insoluble lead oxides and salts, are amenable for leaching via this process.

A soil recycling process developed by the Toronto Harbor Commission employs a treatment train using three technologies. The first stage involves soil washing to reduce the volume and concentrate the contaminants into a fine slurry. The second stage employs acidification and selective chelation to dissolve heavy metals. The third stage involves chemical hydrolysis followed by biodegradation to destroy organic contaminants in the slurry. All metals may be recovered in their pure form by using this process.

The U.S. Environmental Protection Agency (EPA) has conducted research on a lead extraction process involving the following steps: (1) conversion of lead sulfate to lead carbonate with ammonium carbonate, (2) conversion of lead carbonate to lead acetate and oxidation of lead to lead acetate with acetic acid and oxygen, (3) conversion of lead dioxide into lead acetate, and (4) conversion of lead acetate to lead sulfate with sodium sulfate. Table 1 presents the results of the lead extraction process used to treat a synthetic lead-contaminated soil. The amount of lead recovered was approximately 80% for the experiments performed with 1,000 and 5,000 mg/kg lead-contaminated soils.

A lead recovery process developed by Kaur and Vohra uses a surfactant liquid membrane to recover lead (II) from wastewaters. The lead first diffuses through a stagnant film and reacts with di(2-ethylhexyl) phosphoric acid to form a lead complex. The lead complex then diffuses through a membrane and is transported to an organic interface. Lead is then stripped by an internal phase reagent and recovered.

In 1986, PEI Associates, in a study for the National Science Foundation, used an electromembrane reactor (EMR) process to recover lead from an ethylenediamine tetraacetic acid (EDTA)-lead chelate solu-

tion (Table 2). Bench-scale tests were performed with actual chelate generated with the use of lead-contaminated soil from a battery reclamation site.

EPA Region V and PEI Associates have developed an on-site soil washing process for recovery of lead from contaminated soils. Contaminated soil from a battery reclamation site was washed with a chelating agent followed by addition of sodium sulfide to precipitate the chelating agent from the wash solution. Two chelating agents were evaluated for the soil wash: EDTA and NTA (nitrilotriacetic acid). The ratio of soil to chelating solution depends on how contaminated the soil is. EDTA was determined to be the more efficient chelating agent for lead removal.

Soil characterization performed before soil washing was used to treat the metal-contaminated soils showed that a majority of the metals are adsorbed on the fine soil fraction (less than 250 μm). The predominant species of lead found at many of the examined battery breaking and reclamation sites were lead sulfate, lead carbonate, and lead dioxide. Because the chelating agent may chelate both the metal and soil particles, techniques to eliminate the formation of colloids will need to be employed to effectively separate the chelate solution and solid fractions. Because of the slow dissolution of iron oxides in soil, the presence of iron in soil does not appreciably affect the chelation of lead with EDTA. A pH of 2 appears to represent a critical value for lead solubilization.

Chelating Agents

Many metals extraction processes for soils involve the use of chelating agents, and selecting appropriate chelating agents is important when extracting lead from contaminated soils. The quantity and type of chelating agent used, pH, and contact time are all important factors because they influence both the process economics and lead extraction efficiencies.

The selective complexation of one metal in the presence of other metals depends on there being a large difference between the stability constants of the two metals. Carboxylic acids such as EDTA and NTA are hydrolytically stable at high temperatures and pH levels. EDTA forms stable 1-to-1 complexes with most metals, especially those of the transition metal group. Table 3 presents the stability constants for chelating agents that are commonly used in soil washing. Enough chelating is needed to combine with the target metal ions as well as with any competing metal ions that could displace the target metal. Factors affecting the stability of metal che-

late include the size and number of rings, substituents on the rings, and the nature of the metal and donor atoms. The pH at which the soil is washed with a chelating agent is important if one or several metals are to be selectively chelated. In many soils, particularly those with high concentrations of clay, calcite (CaCO_3) may be present in concentrations of up to 30% to 60%. High quantities of calcium carbonate may affect the equilibrium constants of the metal chelates.

Metals may be removed from the chelate through acidification or by precipitation with a hydroxide, sulfide, or oxalate. Where EDTA is used as the chelating agent, mineral acids may cause dissociation of the metal-EDTA complex as a result of the strong competition for the formation of a protonated EDTA specie from H^+ . Precipitation of EDTA can only occur on acidification if the concentration of the protonated EDTA species is greater than its solubility. Under alkaline conditions ($\text{pH} > 9$), the complex ion can be dissociated by precipitation of the metal as a hydroxide. Based on the stability constant for EDTA and the solubility of the hydroxide product, the cation would be completely dissociated from the metal-EDTA complex by direct hydroxide precipitation in only a few cases [e.g., Fe(III)].

Membranes

Membrane technologies are often used to recover metals from waste streams. For the successful separation of cation and anions, the selection of an appropriate membrane is critical. A membrane must be durable, able to withstand harsh chemical and physical treatment, stable at high temperatures, and possess low electrical resistance. Membranes are manufactured from a variety of materials ranging from polymers to sulfonic acids. Polymeric membranes are characterized by the following polymer properties: the large, average size of their macromolecules, their size distribution, their architecture, the specific nature of their chemical groups in the chain, and the aggregate state of the macromolecules. Although the integrity of the membrane tends to increase with molecular weight, the higher molecular weight polymer membranes may decrease the ion selectivity.

Not only are the properties of a membrane important, but the operating conditions are also important. Process parameters such as pH and fluid turbulence affect the rate in which the ions are transported across the membrane. In electromembrane processes, which utilize a membrane to separate the cathode and

* Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Table 1. Lead Removal Efficiency for Three-Step Extraction Process*

Step No.	Reagent	Lead (ppm) in Filtrate	Filtrate Vol. (mL)	% Pb Removed
Total Pb = 10,000 mg/kg:				
I	Ammonium carbonate	0.776	1980	0.0165
II	Oxygen + acetic acid	62.598	1820	4.5557
	Washing	32.774	545	0.714
III	Manganese acetate	12.225	1910	0.934
	Washing	5.202	495	0.103
TOTAL				6.370
Total Pb = 5,000 mg/kg:				
I	Ammonium carbonate	5.545	1850	0.6883
II	Oxygen + acetic acid	428.55	1860	63.77
	Washing	94.373	465	3.51
III	Manganese acetate	96.623	1840	14.21
TOTAL				82.18
Total Pb = 1,000 mg/kg				
I	Ammonium carbonate	2.583	1800	1.860
II	Oxygen + acetic acid	75.347	1910	57.56
	Washing	24.116	450	4.36
III	Manganese acetate	21.316	1865	15.90
TOTAL				79.68

* 250-g soil; ratio of soil to solution, 1:8.

Table 2. Summary of Lead Recoveries for Bench-Scale Experiments Done by Using an Electromembrane Reactor

Experiment Number	Starting Lead, %	pH	Current Density, ma/cm ²	Time, hr	% Lead Removed
1	1.0	11	15	2.0	88
2	3.0	4	15	6.0	93
3	0.2	8	15	0.5	25
4	0.2	4	15	0.5	31
5	0.2	11	5	1.25	42
6	0.2	11	15	0.5	30
7	0.2	11	25	0.3	26
8	1.0	11	25	1.25	88
9	3.0	11	25	3	87

Table 3. Stability Constants of Metal Chelates

Metal	Log K			
	STPP*	Citric Acid	NTA†	EDTA‡
V(III)				25.9
Fe(III)		10.9	15.9	25.1
In(III)			15.0	25.0
Th(IV)			12.4	23.2
Hg(II)			12.7	21.8
Cu(II)	8.7	6.1	12.7	18.8
VO(II)				18.8
Ni(II)	6.7	4.8	11.3	18.6
Y(III)			11.4	18.1
Pb(II)		5.7	11.8	18.0
Zn(II)	7.6	4.5	10.5	16.5
Cd(II)		4.2	10.1	16.5
Co(II)	6.9	4.4	10.6	16.3
Fe(II)	2.5	3.2	8.8	14.3
Mn(II)	7.2	3.4	7.4	14.0
V(II)				12.7
Ca(II)	5.2	3.5	6.4	10.7
Mg(II)	5.7	2.8	5.4	8.7
Sr(II)	4.4		5.0	8.6
Ba(II)	3.0		4.8	7.8
Rare earths			10.4-12.5	15.1-20.0

* STPP = sodium tripolyphosphate.

† NTA = nitrilotriacetic acid.

‡ EDTA = ethylenediaminetetraacetic acid.

anode chambers in an electrolytic cell, the speed and direction of the ionic flow depend on the current potential and density as well as the resistance of both the anode and cathode chamber solution characteristics. The solute transport rate of a liquid adjacent to the membrane can be controlled by diffusion through the membrane. Film diffusion tends to occur when membrane diffusion coefficients are high, or where the membrane is very thin, and when there is little difference between the concentration of the species in solution and in the membrane. The energy requirement for ionic transport in the electromembrane is a function of the electrical resistance of the solutions and membrane and the back electromotive forces caused by concentration gradients. The resistance of the membrane depends on the transport processes occurring around the membrane; the electrical resistance of a solution depends on the solute concentration and solution conductivity. Examination of the literature showed that there are currently no commercial or full-scale membrane technologies for the recovery of lead from soils.

Summary

Several lead recovery methods have been or are currently being developed to extract lead from contaminated soils. Many of these technologies involve washing the soil with a reagent to initially extract the lead into solution, followed by a lead recovery step that may include precipitation of lead as lead sulfate or recovery of lead by electrowinning. Although most of these processes are in the developmental stage, they have potential to progress into pilot- or full-scale applications.

Soil characterizations performed on metal-contaminated soils show that a majority of the metals are adsorbed on the fine soil fraction (less than 250 μm). Soil washing with EDTA produces colloids consisting of fine soil particles, which create difficulties in solid-liquid separation. Adding a filter aid before filtration appears to allow better separation of the fine particles from the liquid fraction.

The predominant species of lead found at many battery breaking and reclamation sites are lead sulfate, lead carbonate, and lead dioxide. Because of the slow dissolution of iron oxides in soil, the presence of iron in soil does not appreciably affect the chelation of lead with EDTA. A pH of 2 seems to represent a critical value for lead solubilization.

The tendency for a metal to chelate with a chelating agent is determined by the stability constant, which is highly de-

pendent on pH of the solution. In several studies, EDTA and NTA have been used to recover metals from waste streams. Both chelating agents are relatively stable at high temperatures and pH levels.

Many metal recovery technologies employ membranes for metals separation. Important characteristics that need to be considered in the selection of a mem-

brane include low electrical resistance; high permselectivity (exclusion of anions); and durability to withstand high temperatures, low and high pH solutions, and chemical and physical treatment for removal of deposits. The amount of current, concentration of ions in the anode chamber, and stirring rate of solutions in both the anode and cathode chambers must be controlled

to maintain steady-state conditions in the boundary layers of the membrane.

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The Project Summary was prepared by the staff of IT Corporation, Cincinnati, OH, 45246.

Ronald J. Turner is the EPA Project Officer (see below).

The complete report, entitled "A Literature Review Summary of Metals Extraction Processes Used to Remove Lead from Soils," (Order No. PB94-140613; Cost: \$19.50, subject to change) will be available only from:

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