A LITERATURE REVIEW SUMMARY OF METALS EXTRACTION PROCESSES USED TO REMOVE LEAD FROM SOILS

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The EPA is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report presents the major findings of a literature review to investigate metals extraction processes for recovering lead from soils. Key issues such as soil characterization and use of chelating agents are addressed, and descriptions of various metals extraction technologies are discussed in this report. The information provided in this report will assist in identifying lead extraction process options for treating lead-contaminated soils.

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ABSTRACT

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 could result in lead-contaminated soils. Metals, unlike many hazardous organic constituents, cannot be degraded or readily detoxified. This report presents information on metals extraction technologies that are currently in various stages of development, soil characteristics that affect metals extraction, chelating agents used in the soil washing of lead-contaminated soils, and membranes used to separate metal cations. The information presented in this report was obtained from a literature search conducted to investigate metals extraction processses for recovering lead from soils.

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EXECUTIVE SUMMARY

The objective of this report is to review and evaluate literature relating to metals extraction technologies, soil characterization, chelating agents, and membranes. Based on the literature assessment, potential operating problems could be identified and avoided regarding the extraction of lead from soils.

The information presented in the following report is derived from journal articles, books, research documents, and phone conversations with experts in the field of lead recovery, chelating agents, and membranes.

The findings from a treatability study performed by IT for the National Science Foundation are also presented. The remainder of the report discusses metals extraction technologies, soil characterization, chelating agents, and membranes. All of these factors will play a key role in the success of lead extraction from soils and the recovery of lead through the use of various metals recovery processes.

SECTION 1

INTRODUCTION

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. 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. Furthermore, periodic monitoring may be necessary. 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 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.[1]

The on-site treatment of wastes and contaminated soils to recover heavy metals (e.g., lead) is a more attractive alternative. The goal of the on-site approach is to treat the contaminated soil to an acceptable level, protecting groundwater and surface

water resources, without physically removing or isolating the contaminated soil from the contiguous environment.

A literature review was conducted in order to provide the latest available information on lead removal/recovery processes including use of chelating agents and/or membranes and to define important parameters for treatability testing. The literature search was conducted through a review of the DIALOG database. Relevant journal articles, conference papers, research reports, and books that describe soil washing, chelating agents, and electromembrane and metals recovery processes were reviewed.

The report is divided into sections that describe each major parameter to be studied. Section 2 presents a summary of the literature containing information on metals extraction technologies and soil characteristics for use in soil washing studies. The section describes the findings from full-scale soil treatment processes and the soil characteristics that affect lead removal from soil. Section 3 presents a summary of information on chelating agents and their properties. This section also presents the physical properties that influence chelation of lead, including formation constants, solubility, and stability constants. Results of treatability studies using various chelating agents to remove metals are also provided in this section. Section 4 presents a summary of the literature on membranes. Physical properties such as permeability, capacity, and burst strength are discussed. This section also discusses important operating parameters such as membrane potentials and current density. Section 5 presents a summary of the key findings of the literature survey.

SECTION 2

METALS EXTRACTION TECHNOLOGIES AND SOIL CHARACTERIZATION

At the onset of the literature survey effort, articles on soil characterization and soil washing of lead-contaminated soils were reviewed to determine the conditions that are conducive to extraction and recovery of lead from soil. The following soil properties must be taken into consideration when soil washing is performed: soil pH, clay content, contamination levels, and moisture content. The following subsections present a summary of the important considerations regarding the recovery of lead by various metals extraction processes.

2.1 METALS EXTRACTION TECHNOLOGIES

A paper by William Schmidt (1990) of the Bureau of Mines (BOM) summarizes the results of EPA's investigation into alternatives for treating contaminated soils found at many battery reclamation sites. The BOM process 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. Figure 1 presents a flow diagram of the acid leaching process. The BOM has also developed a process to convert the lead compounds to lead carbonates with ammonium carbonate and ammonium bisulfite, followed by leaching with fluosilicic acid. Figure 2 shows the process flow diagram of the fluosilicic acid leaching process. Lead is recovered from the acid solution by electrowinning. Any remaining lead in the soil would be leached with 0.5 percent nitric acid solution.[2]

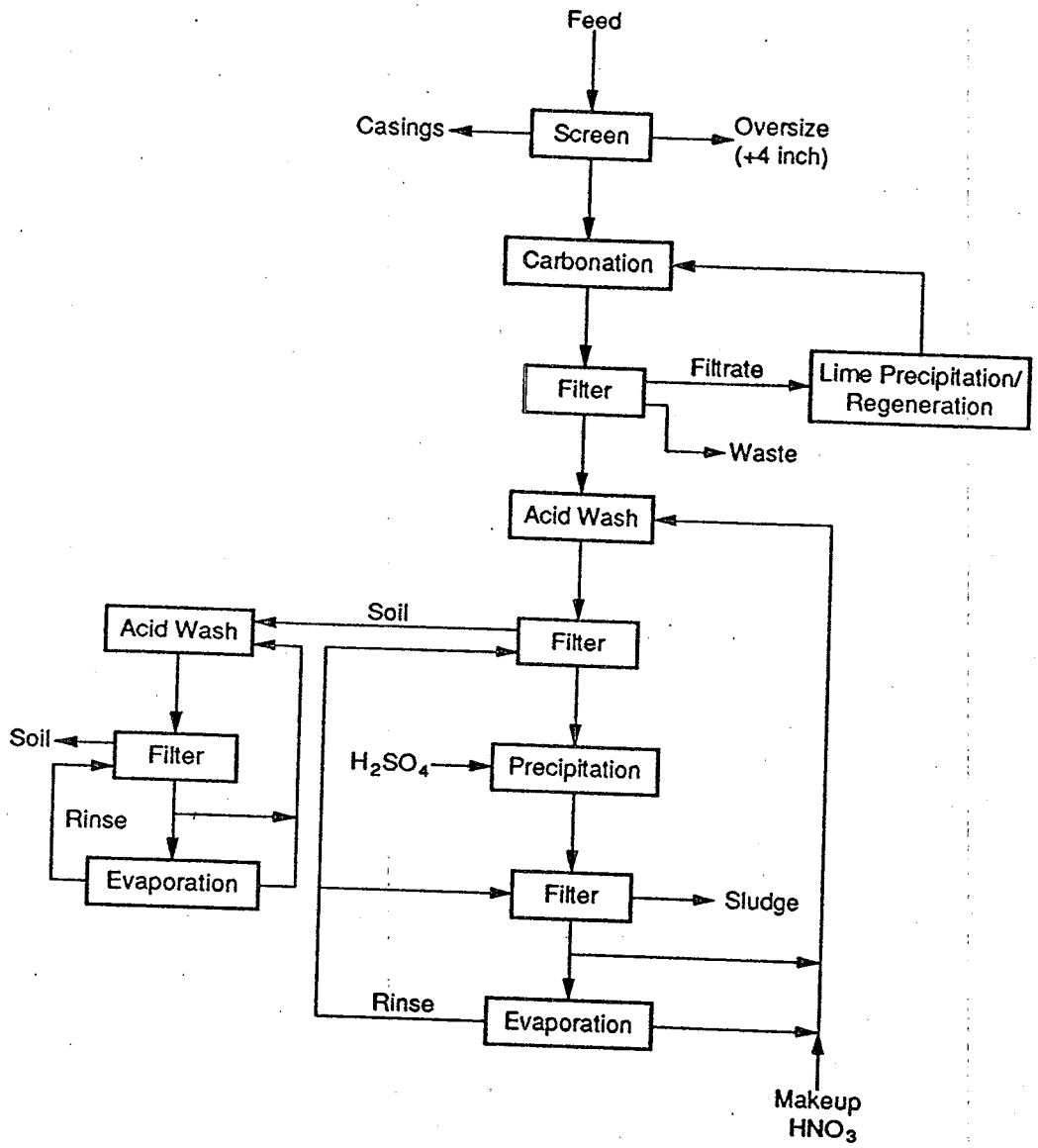


Figure 1. Bureau of Mines Acid Leaching Process.[2]

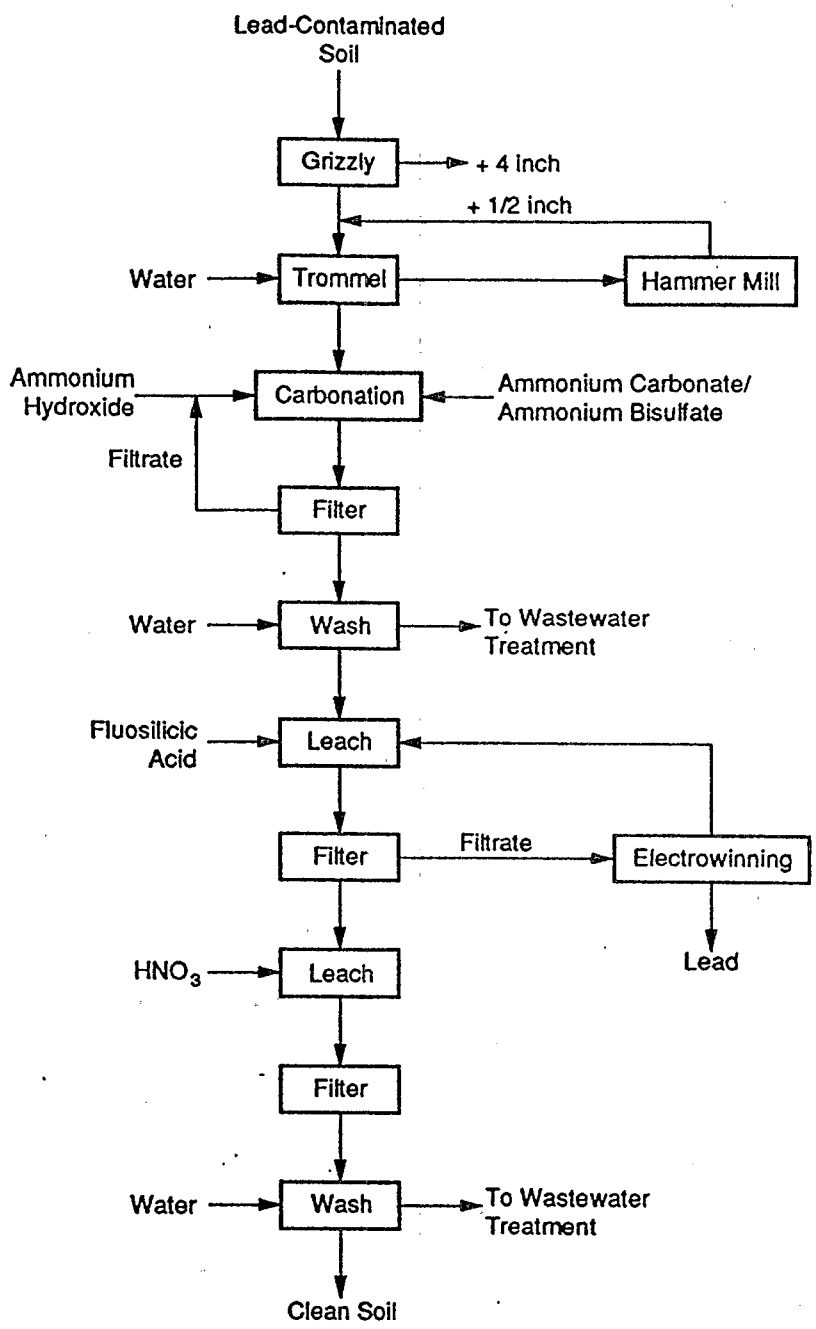


Figure 2. Bureau of Mines Fluosilicic Acid Leaching/Electrowinning Process for Treatment of Lead-Contaminated Soils.[2]

The TerraMet™* soil remediation system developed by COGNIS, Inc., leaches and recovers lead from contaminated soil, sludge, or sediment. Lead in the form of metallic lead, soluble ions, and insoluble lead oxides and salts may be leached with a proprietary aqueous leachant. The first step of the process involves dry screening of the soil to remove any oversized material. In the second step, the lead contaminants are dissolved and recovered from the aqueous leachate by a metals recovery process such as ion exchange or reduction. The aqueous leaching solution is recovered and the lead can be regenerated and recycled. Any residual leachate in the treated soil is nontoxic and biodegradable. Figure 3 presents a flow diagram of the TerraMet™ metals leaching process. Contaminated soils that may be treated by this process include battery recycling sites, scrap yards, and metal plating shops. A bench-scale test was conducted using 17,000 ppm lead-contaminated soil, which was treated to less than 300 ppm residual lead. A pilot-scale system is currently being assembled for additional testing.[3]

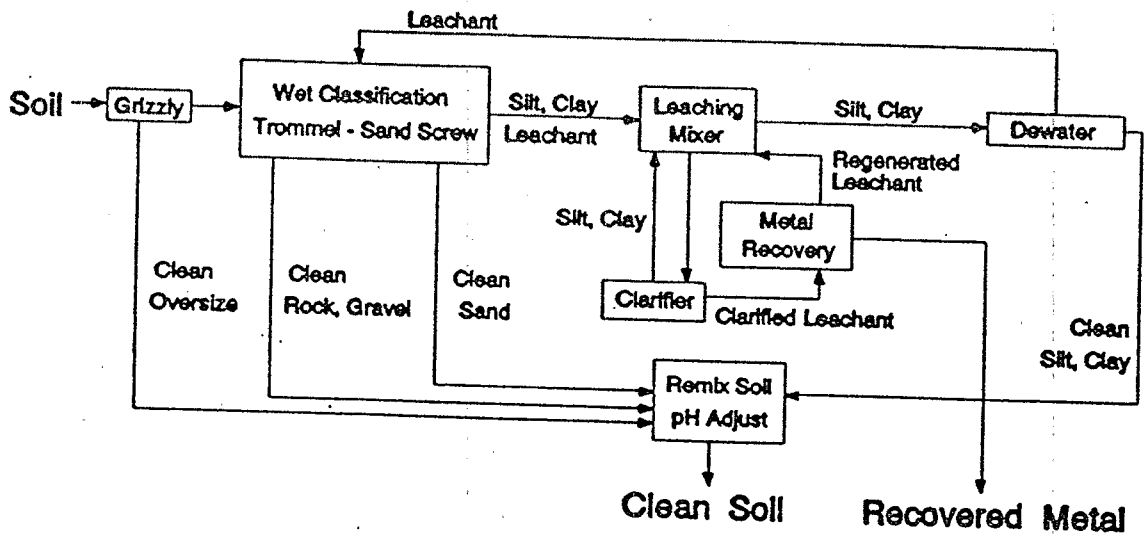


Figure 3. TerraMet™ Lead Removal Process[3]

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

A soil recycling process developed by the Toronto Harbor Commission employs three technologies operating in series. The first stage involves soil washing for reducing the material volume and concentrating the contaminants in a fine slurry. The second stage employs acidification and selective chelation for dissolution of heavy metals. All metals may be recovered in their pure form. The third stage involves chemical hydrolysis followed by biodegradation to destroy organic contaminants in the slurry. The soil recycling process was demonstrated at a Toronto Port Industrial District site used for metals finishing and refinery and petroleum storage.[3]

A lead recovery process developed by Kaur and Vohra (1992) uses a surfactant liquid membrane to recover lead (II) from wastewaters. The process consists of four steps: 1) emulsification of the stripping phase into the carrier containing the membrane, 2) continuous contact of the effluents with the emulsion, 3) separation of the emulsion, and 4) splitting of the emulsion. The surfactant liquid membrane (SLM) system consists of a membrane phase [di(2-ethyl hexyl) phosphoric acid (D2EHPA), n-hexane, and span-80], an aqueous internal phase (sulfuric acid), and an external phase [Pb(II) in water]. Figure 4 presents a schematic of the three phases. The SLM system involves the following steps: 1) Pb(II) ions in the external phase diffuse through the aqueous stagnant film and react with the D2EHPA at interface 1, 2) a Pb(II) complex is formed at interface 1, which diffuses through the membrane phase, and the lead transports to the organic interface 2, and 3) the lead is then stripped by the internal phase reagent at interface 2. Bench-scale studies showed that with a 2 percent D2EHPA concentration, approximately 87 percent of the Pb(II) was extracted. These tests also determined that up to 100 percent Pb(II) extraction could be achieved with a 10 percent D2EPHA concentration. Acidification of the aqueous medium was observed to substantially decrease the amount of metal ion extracted. The decrease in metal ion extraction with increased acidification is caused by the increase in common ion concentration.[4]

Krishnamurthy (1992) of the U.S. Environmental Protection Agency (EPA) has conducted research on a lead extraction process involving the conversion of lead

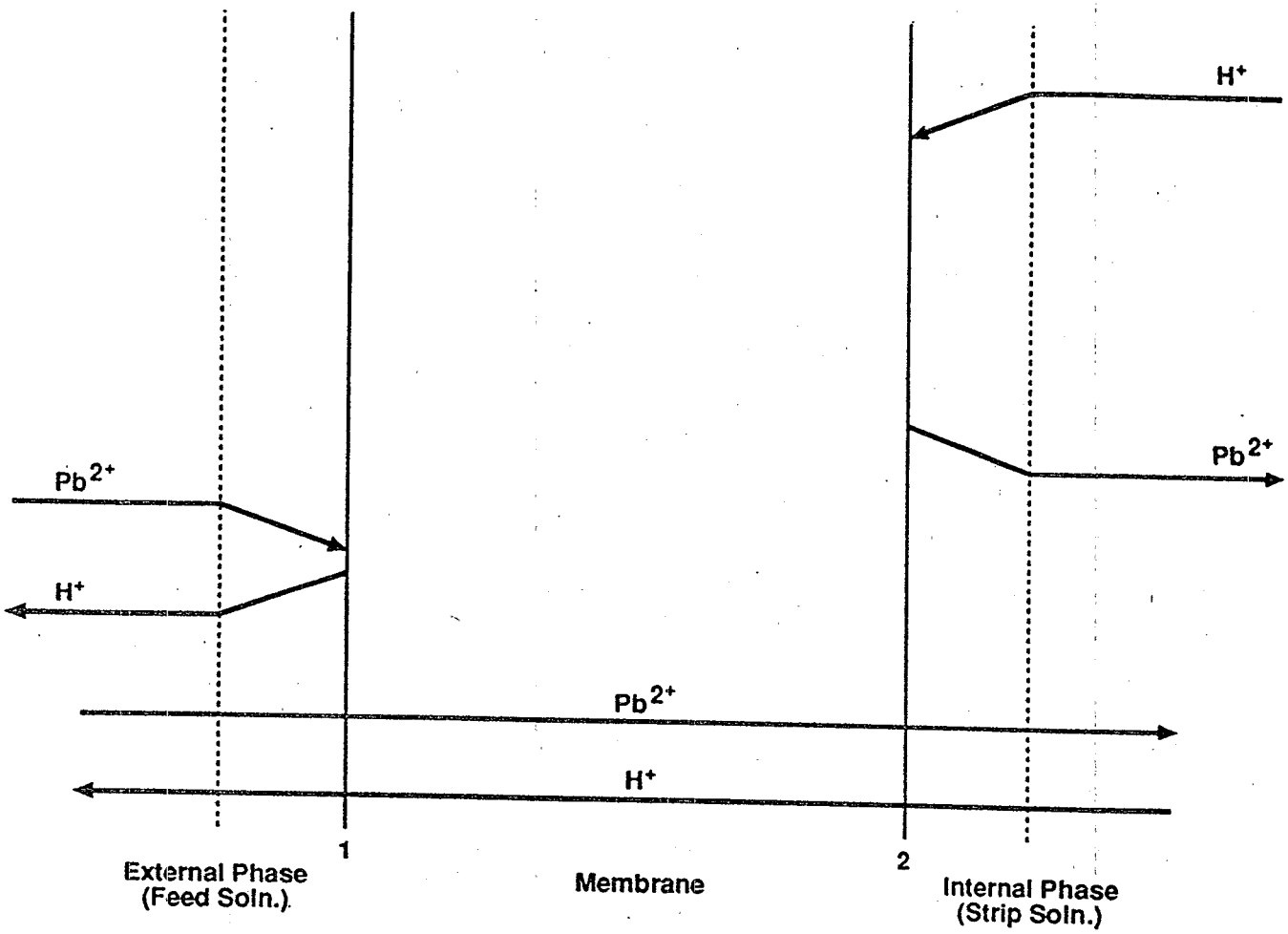


Figure 4. Surfactant Liquid Membrane System.[3]

sulfate to lead carbonate with ammonium carbonate, lead carbonate to lead acetate and oxidation of lead to lead acetate with acetic acid and oxygen, conversion of lead dioxide into lead acetate, and the final conversion of lead acetate to lead sulfate with sodium sulfate.[5]

Two separate bench-scale studies were performed to determine the recovery of lead sulfate. The first set of tests examined each form of lead individually to determine the reaction completion after the addition of the various reagents. Up to 94 percent of the lead was solubilized in acetic acid solution. The solubility of lead in oxygenated acetic acid was determined to range from 72 to 96 percent. The final test of the first series of experiments showed that approximately 33 to 60 percent of lead dioxide is converted to lead acetate with manganese acetate.[5]

The second series of bench-scale tests involved treatment of a synthetic lead-contaminated soil. A clean soil was spiked with 10,000 mg/kg total lead in the following percentages: lead sulfate - 60 percent, basic lead carbonate ($PbCO_2.Pb(OH)_2$) - 20 percent, elemental lead - 10 percent, and lead dioxide - 10 percent. The soil was first treated with ammonium carbonate for 30 minutes and filtered. Acetic acid and oxygen are then added followed by water washing of the filtrate. The final step involves the addition of manganese acetate and acetic acid followed by filtration. Table 1 presents the results of this first treatability study. Approximately 80 to 89 percent of the lead was recovered in the three-step process. The experiments were repeated using soil spiked with 1,000 and 5,000 mg/kg total lead. The amount of lead recovered in these experiments was approximately 80 percent. Table 2 presents the results of all three lead concentration tests.[5]

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 solution. Figure 5 presents a diagram of the EMR. The bench-scale test was performed with actual chelate generated by use of lead-contaminated soil from a battery reclamation site. The study examined the effect

TABLE 1. LEAD REMOVAL EFFICIENCY FROM CONTAMINATED SOIL (250 g; Total Pb = 10,000 mg/kg; Soil/Soln. Ratio 1:8)[a]

Step No.	Reagent	Lead (ppm) in filtrate	Filtrate Vol. (mL)	% Pb removed
I	Ammonium carbonate	5.401	1860	0.375
II	Oxygen + acetic acid	847.262	1866	65.07
	Washing	207.268	440	3.65
III	Manganese acetate	183.215	1880	13.78
	SUBTOTAL			82.88

[a] Reference 5.

of system variables such as electrode potential, current density, pH, current efficiency, and chelate concentration. The EDTA chelate solution was adjusted to pH levels of 4, 8, and 11 with sulfuric acid or sodium hydroxide. The amount of lead in solution was varied from 0.2, 1, and 3 percent by weight to determine the effect of lead concentration on plating efficiency. From the PEI study, the following conclusions were made: 1) the higher lead concentrations (1, 2, and 3 percent by weight) yielded nearly 90 percent lead recovery, whereas the 0.2 percent concentration recovered 40 percent of the lead during the same experimental time period; 2) the optimum EDTA/Pb molar ratio for the chelation reaction is 1.5 to 2, and the reaction is essentially complete within one hour; 3) a pH of 12 effectively prevented the chelation of other metals, particularly iron; 4) the initial pH of the chelate solution had no apparent effect on lead removal; 5) the current density of the electromembrane reactor showed a slight inverse relationship with respect to the current efficiency; and 6) higher current densities resulted in faster plating rates, but yielded a spongy lead deposit on the cathode. Table 3 presents lead recoveries for the electromembrane bench-scale experiments.

The economics of the electromembrane process is driven by the recovery of lead metal and regeneration of the chelating agent, which makes the process cost competitive with other treatment/disposal methods (e.g., landfilling). Comparative

TABLE 2. LEAD REMOVAL EFFICIENCY FOR THREE-STEP EXTRACTION PROCESS (250-g soil/solution ratio 1:8)[a]

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	1965	15.90
	TOTAL			79.68

[a] Reference 5.

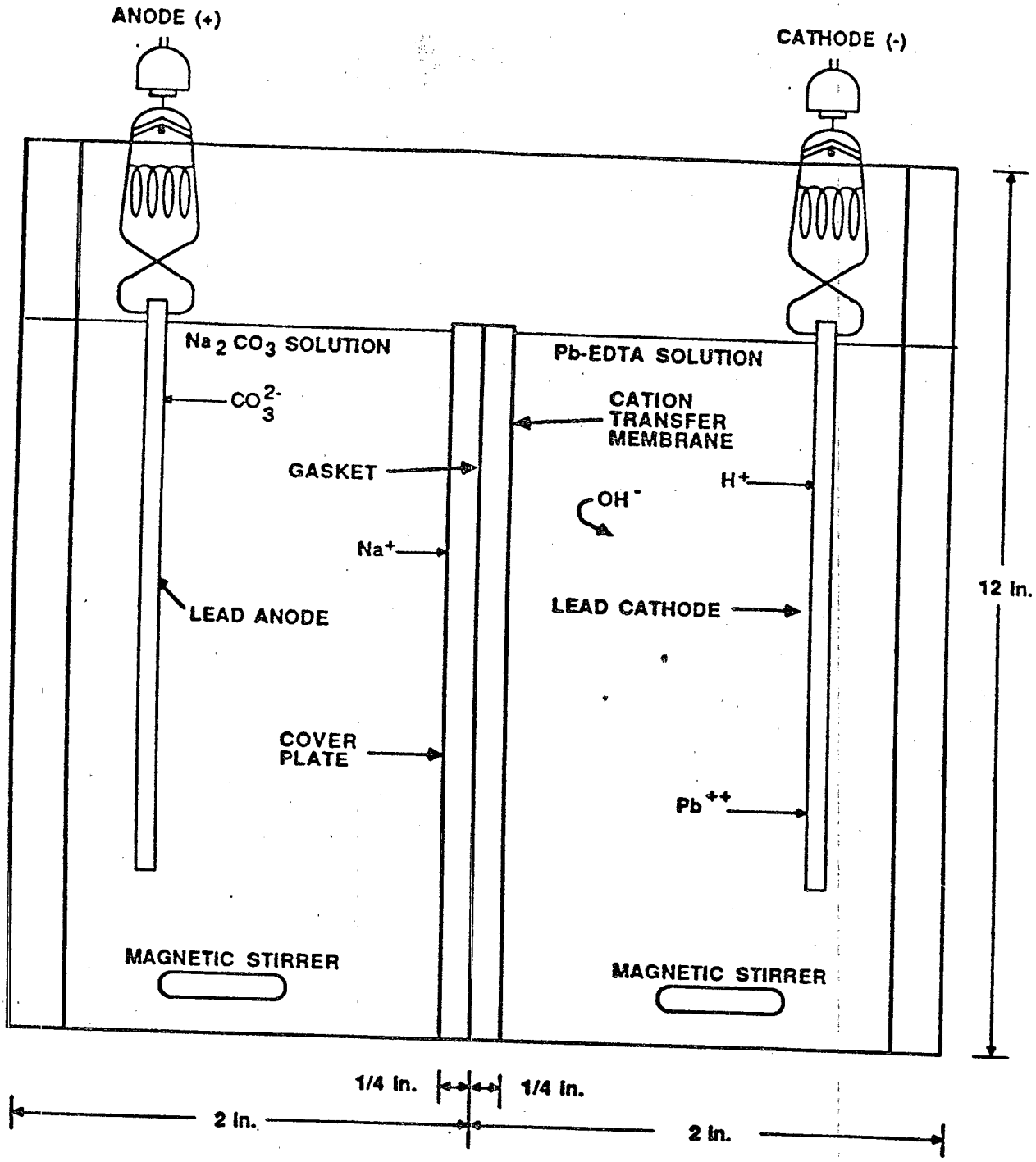


Figure 5. Electromembrane reactor for PEI lead recovery study.[1]

TABLE 3. SUMMARY OF LEAD RECOVERIES FOR EMR EXPERIMENTS[a]

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

[a] Reference 1.

and nature of the material. The higher the lead content, the higher is the potential credit for lead recovery. Although the processing time and the amount of raw materials will be proportionally higher than for disposal methods, the lead credit makes the electromembrane process cost competitive with land disposal methods.[1]

Soil washing is an established technology for removing metals from contaminated soils. Table 4 presents the soil washing results for several battery breaking wastes. The following extraction agents were investigated in the soil washing experiments: water, a surfactant, and tetra-sodium EDTA. Soil washing did not remove significant amounts of lead in any of the soil particle size categories. EDTA was found to be effective in leaching lead from the soil; lead removal, however, was shown to be highly dependent on the form of lead present. Different forms of EDTA appear to be effective for various lead species. While testing the process, the Bureau of Mines determined that the predominant species found at lead-contaminated battery

TABLE 4. RESULTS OF SOIL WASHING ON BATTERY BREAKER WASTES[a]

Site name	Untreated: Predominant lead species	Untreated: Average total lead (mg/kg)	Untreated: EP toxicity (mg/L)	Wash solution	Percent lead reduction in treated material by soil particle size category: No. 10 screen	No. 60 screen	Fines
Old Man's Township	$PbCO_3$	48,000	300	Water	-219	53.5	4.38
				Surfactant	-104	33.3	24.1
				EDTA[b]	-148	48.9	14.1
C&R Bat.	$Pb_3(CO_3)_2(OH)_2$	68,400	418	Water	26.7	23.7	27.6
				Surfactant	2.78	27.4	23.8
				EDTA[b]	-140	16.2	64.7
Schuylkill	$PbCO_3$	4,700	55.5	Water	81.0	54.0	37.3
				Surfactant	66.4	62.7	43.7
				EDTA[b]	98.1	50.2	15.0
Gould Soil	$PbSO_4$ PbO_2	27,600	148	Water	-13.6	-13.6	-50.0
				Surfactant	7.21	60.3	-189
				EDTA[c]	67.5	68.7	44.7
Gould Casings	$PbSO_4$ PbO_2	209,000	1,830	Water	82.9	-	34.1
				Surfactant	78.8	-	49.0
				EDTA[b]	79.7	-	44.3
J&R Frabicating	$Pb_4SO_4(CO_3)_2(OH)_2$	4,194	N/A[d]	Water	-54.7	51.8	-227
				EDTA[c]	-80.7	67.3	-47.7
				EDTA[e]	-216	35.2	-59.0
				EDTA[f]	74.2	63.9	-11.9
				EDTA[g]	-17.0	69.5	-17.8
Pesses Chemical Co.	N/A	271	0.171	Water	84.6	-15.1	59.0
				EDTA[c]	92.5	10.7	59.4
				EDTA[e]	92.6	-38.0	70.7
				EDTA[f]	89.1	-50.6	73.1
				EDTA[g]	90.5	-10.7	67.0

[a] Reference 2.

[b] 3:1 molar ratio for EDTA to total chelatable metals, pH = 7-8.

[c] 0.0160M, pH = 7-8.

[d] Not available.

[e] 0.0148M, pH = 7-8.

[f] 0.0210M, pH = 7-8.

[g] 0.0210M, pH = 11-12.

breaking sites were lead metal, lead sulfate, lead carbonate, and lead dioxide.[2] Table 5 presents the results of the laboratory-scale tests that were performed by the Bureau of Mines (BOM) in order to select the use of disodium or tetrasodium EDTA.[2]

TABLE 5. SELECTIVITY OF VARIOUS SODIUM EDTA FORMS IN LEACHING VARIOUS LEAD SPECIES[a]

EDTA form (5% solution)	pH	Percent removed		
		PbO_2[b]	$PbSO_4$[b]	Pb metal[c]
Di-sodium	5	100	0	2.7
Tetra-sodium	10	0	100	23.6

[a] Reference 2.

[b] After 3 hours at 20°C.

[c] After 2 hours at 60°C and 72 hours at 20°C.

Another drawback encountered in the soil washing studies involved the extreme difficulties in filtering or otherwise effecting a solid-liquid separation. Because most of the lead is found on the greater than 200-mm-size particles, the EDTA tends to chelate with both the lead and the soil particle creating a colloid that is difficult to separate.[2]

Soil washing experiments were performed with tap water, an anionic surfactant (0.5 percent), and tetrasodium EDTA (3-to-1 molar ratio) for 30-minute contact times at a 10-to-1 solution-to-soil ratio. The experimental results indicated that total lead content was not appreciably reduced by the soil washing process. Table 6 presents the results of the soil washing study. The results of the tests with synthetic soils determined that soil washing efficiency depends upon the length of time a metal is in contact with soil particles.[6]

A paper by EPA discusses the techniques of soil washing using EDTA at two pH levels. Table 7 presents the results of the soil washing study. The results show that 1) contaminant removal capabilities are highly dependent on particle size (most contamination was found on the fines), 2) fine particles have a high adsorption

TABLE 6. RESULTS OF BENCH-SCALE SOIL WASHING OF VARIOUS LEAD-CONTAMINATED SOILS[a]

Site/Waste	Untreated Soil			Percent Lead Reduction in Treated Soil			
	Predominant lead species	Average total lead (mg/kg)	EP toxicity (mg/L)	Wash solutions tested	>2 mm	250 μm to 2 mm	<250 μm (fines)
Old Man's Township	$PbCO_3$	48,000	300	Water	NR	53.5	4.38
				EDTA[b]	NR	48.9	14.1
C&R Battery	$Pb_3(CO_3)_2(OH)_2$	68,400	418	Water	26.7	23.7	27.6
				EDTA[b]	NR	16.2	64.7
Schuykill	$PbCO_3$	4,700	55.5	Water	81.0	54.0	37.3
				EDTA[b]	98.1	50.2	15.0
Gould Soil	$PbSO_4$	27,600	148	Water	NR	53.6	NR
	PbO_2			EDTA[b]	67.5	68.6	44.7
Gould Casings	$PbSO_4$	209,000	1,830	Water	82.9	-	34.1
	PbO_2			EDTA[b]	79.7	-	44.3
J&L Fabricating	$Pb_4SO_4(CO_3)_2(OH)_2$	4,194	N/A	Water	NR	51.8	NR
				EDTA[c]	NR	67.3	NR
				EDTA[d]	NR	35.2	NR
				EDTA[e]	74.2	63.9	NR
				EDTA[f]	NR	69.5	NR
SARM III	$PbSO_4$	12,776	N/A	Water	99.4	97.9	N/A
	PbO_2			EDTA[b]	99.5	98.9	N/A

NR = no reduction
N/A = not available

[a] Reference 6
[b] 3:1 molar ratio for EDTA to total chelatable metals, pH = 7-8
[c] 0.0160M, pH = 7-8
[d] 0.0148M, pH = 7-8
[e] 0.0210M, pH = 7-8
[f] 0.0210M, pH = 11-12

TABLE 7. SUMMARY OF REMOVAL EFFICIENCIES OBTAINED FOR BENCH- AND PILOT-SCALE EVALUATIONS OF SOIL WASHING

Study	Contaminant	Wash solutions tested	Removal efficiencies obtained
PEI[a,b]	Arsenic	Tap water	> 2 mm soil = 96%
	Cadmium		< 2 mm soil = 44%
	Chromium	5.4% EDTA	> 2 mm soil = 97%
	Copper		< 2 mm soil = 77%
	Lead		
	Nickel		
	Zinc		
Leeds, Alabama[c]	Lead	13% EDTA	> 2 mm soil = 94%
			< 2 mm soil = 97%

[a] Reference 7.

[b] Removal efficiencies presented for this study are an average of organic and metals contaminant reduction efficiencies obtained under the washing conditions specified.

[c] Reference 8.

capacity for contaminants and can be difficult to separate from washing fluid, 3) materials handling is a critical issue for effective treatment, and 4) the wash solution must be tailored to the site. The predominant lead species found in the six soils studied were lead carbonates, lead sulfates, and lead oxides.[9]

An article by U.S. EPA Region V and PEI Associates discusses the results of an on-site soil washing process for recovery of lead from contaminated soils. The soil was washed with a chelating agent followed by use 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). EDTA was mixed with water to form a 10 percent by weight solution. The contaminated soil was treated by a 30-to-70 soil-to-solution ratio. 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. In order to determine the optimum reaction time, samples were removed at 10, 20, 30, and 60 minutes and every hour thereafter for up to a 4-hour reaction time. Table 8 presents the rate of lead removal. Approximately 95 percent removal was achieved within 2 hours.[10]

TABLE 8. EFFECT OF REACTION TIME ON TREATMENT OF CONTAMINATED SOIL[a]

Sample treatment time (min.)	Lead concentration (mg/L)
10	3290
20	4330
30	4120
60	3720
120	4710
180	5120
240	4820

[a] Reference 10.

In a study performed by PEI Associates, Inc., and Bruck, Hartman, & Esposito, Inc., four different concentrations of EDTA solutions were used to wash soil samples from the Pesses Chemical site in Fort Worth, Texas. The test solutions consisted of water, 0.01 M EDTA solution (pH 7 to 8), 0.015 M EDTA solution (pH 7 to 8), 0.02 M EDTA solution (pH 7 to 8), and 0.02 M EDTA solution (pH 11 to 12). The soil was contaminated mainly with cadmium, copper, lead, and nickel. Results of the soil washing tests indicated that none of the chelate wash solutions substantially reduced the total metals in any of the soil fractions examined. Table 9 presents the results of Toxicity Characteristics Leaching Procedure (TCLP) tests for lead. The soil fractions were divided into greater than 2 mm, 0.25 mm to 2 mm, and less than 0.25 mm. The highest concentrations of metals were associated with the 0.25- to 2-mm particle size fraction. In the study, the leachable lead content of the coarse fraction (greater than 2 mm) was reduced to below the detection limit (0.062 mg/L).[11]

The Bureau of Mines contaminated soil treatment method investigation determined that the soil fines form colloidal suspensions when mixed with EDTA solutions, which blind the filters. It was recommended that a filter aid be added to the soil/solution mixture in order to improve its dewatering characteristics.[11]

TABLE 9. ANALYTICAL RESULTS FOR TCLP LEAD IN SOIL SAMPLES[a]

Test	>2mm (mg/L)			0.25 mm to 2 mm (mg/L)			<0.25 mm (mg/L)		
	A	B	Average	A	B	Average	A	B	Average
Water	1.18	0.548	0.864	0.144	<0.062	<0.103	0.673	0.668	0.670
EDTA 0.105 mol, pH 7-8	<0.062	<0.062	<0.062	0.310	0.300	0.305	0.286	0.309	0.297
EDTA 0.105 mol, pH 11-12	<0.062	<0.062	<0.062	1.13	0.330	0.730	0.548	0.382	0.465
Untreated soil: 0.213/0.382 (average 0.297) mg/liter									

[a] Reference 11.

A treatability study conducted by EPA and PEI Associates (1988) examined the recovery of lead-contaminated soils from the Lee's Farm site in Woodville, Wisconsin. Information on the physical difficulties of soil washing with EDTA was provided. Lead concentrations in this soil ranged from 1.5 to 6 percent. Excessive material handling problems were encountered when EDTA was used to treat the soil. According to field personnel, the agitation combined with EDTA solution caused excessive soil particle breakdown. These ultra-fine particles clogged the filter and were unsettleable in the process configuration. This condition also resulted in fines carryover into the EDTA/lead recovery system, which eventually failed because of excessive suspended solids loading.[12]

A study performed at the University of Saskatchewan (1976) used 11 different types of extraction solutions to remove lead from four different soil samples. The methods of lead extraction are presented in Table 10. The soils were treated with 10 ppm $PbCl_2$ labelled with lead-210 and incubated for 7 weeks. The five extractants that provided the best lead removal from the soil were 6N HNO_3, 3N HNO_3, 1N HNO_3, 0.5N EDTA, and diethylenetriamine pentaacetic acid (DTPA). Table 11 presents the results of the lead extraction study. Approximately 93 to 98 percent of the lead was recovered by use of 6N HNO_3, and approximately 80 percent of the lead could be recovered by DTPA and EDTA.[13]

In 1987, PEI Associates conducted a bench-scale soil washing study using Standard Analytical Reference Matrix (SARM) prepared soils. The experiments were conducted with two wash solutions: Dow Chemical Versene 100 (containing EDTA) and Institutional Formula Tide (produced by Procter and Gamble). Temperature variations from 78° to 120°F had little effect on contaminant reduction efficiencies. The variation of pH from 12 to 8 produced no additional metal removal. A 15-minute reaction time was selected for the chelant washes based on the results presented in Figure 6. Two EDTA molar ratios were used to wash the higher metal-contaminated SARM soil: a 1-to-1 and 3-to-1 ratio of moles of EDTA to total moles of metals present. The 3-to-1 EDTA molar ratio solution removed a higher amount of metals in the middle soil fraction (250 μm to 2 mm). Table 12 presents the results of the soil

TABLE 10. METHODS OF LEAD EXTRACTION[a]

	Weight of Air-Dry Soil Used (g)	Soil Extract	Outline of Procedure
Total Pb	2	-	Digestion with hot concentrated HNO_3 with lead taken up in HCl
1 N NH_4OAc (pH 7)	10	1:5	24-h equilibration and filtration
0.05 M $CaCl_2$	10	1:5	24-h equilibration and filtration
0.05 M EDTA – 1 N $HH_4(CO_3)_2$	10	1:2	
DPTA - TEA	10	1:2	Shaking for 2 h and filtration
0.5 $NaHCO_3$ (pH 8.5)	5	1:20	Shaking for 1/2 h and filtration
2.5% (v/v) AcOH	5	1:20	Shaking for 45 min. and filtration
0.5 M $BaCl_2$	5	1:10	Shaking for 2 h and filtration
6 N HNO_3	5	1:3	
3 N HNO_3	5	1:3	Overnight equilibration and filtration
1 N HNO_3	5	1:3	
0.1 N HNO_3	5	1:3	

[a] Reference 13.

TABLE II. RECOVERY OF ADDED LEAD IN VARIOUS EXTRACTS[a]

	Percent lead recovered															
	Total		0.05 M $CaCl_2$		0.5 M $BaCl_2$		1N NH_4OAc		2.5% AcOH		0.5 M $NaHCO_3$		0.05 M EDTA		DPTA-TEA	
Soil sample	Percent	SD[b]	Percent	SD	Percent	SD	Percent	SD	Percent	SD	Percent	SD	Percent	SD	Percent	SD
Asquith	100.2	3.7	0.4	0.06	4.0	0.04	11.0	1.1	13.9	1.4	29.1	0.7	71.9	2.3	80.4	3.9
Oxbow (I)	97.8	5.4	Trace	-	0.1	0.01	1.0	0.2	2.8	0.07	5.3	0.05	83.9	2.6	82.7	8.3
Oxbow (II)	98.0	6.1	Trace	-	0.2	0.01	1.1	0.05	3.0	0.09	5.4	0.08	86.5	2.1	89.2	5.0
Waitville	100.0	3.2	Trace	-	0.3	0.02	0.9	0.09	2.2	0.06	5.4	0.10	66.6	1.6	67.0	1.8

[a] Reference 13.

[b] SD = standard deviation from eight observations.

TABLE 12. SOIL WASHING RESULTS: SARM III (HIGH ORGANICS, LOW METALS)[a] (ppm)

Contaminant	Initial concentration	Water Wash			3:1 Molar Chelant Wash		
		>2 mm	250 µm to 2 mm	<250 µm	>2 mm	250 µm to 2 mm	<250 µm
Volatile organics							
Acetone	358	0.74	1.7	16	0.96	2.6	3.3
Chlorobenzene	11	0.008	0.16	1.6	0.011	0.23	1.2
1,2-Dichloroethane	5	<0.004	0.024	0.084	0.002	0.034	<0.050
Ethyl benzene	144	0.040	1.3	34	0.054	2.0	20
Styrene	32	0.026	<0.30	6.4	ND[b]	0.55	3.0
Tetrachloroethylene	20	0.002	0.16	3.0	0.006	0.23	2.2
Xylene	325	0.10	2.6	58	0.091	3.6	31
Total volatile organic reduction		>99.9%	99.3%	86.7%	99.9%	99.0%	>92.2%
Semivolatile organics							
Anthracene	181	<5.6	480	1,800	1.7	540	1,800
Bis(2-ethylhexyl) phthalate	114	2.2	7.4	1,100	3.4	9.4	790
Pentachlorophenol	30	9.2	40	59	<6.6	13	<96
Total semivolatile organic reduction		>94.8%	NR[c]	NR	96.4%	NR	NR
Inorganics							
Arsenic	652	54.6	102	1,160	36.6	51.0	243
Cadmium	2,260	372	276	290	116	110	110
Chromium	1,207	3.8	14.8	2,590	3.2	9.2	1,940
Copper	9,082	68.4	264	20,800	38.6	104	2,250
Lead	14,318	122	491	30,600	98.1	171	1,470

(continued)

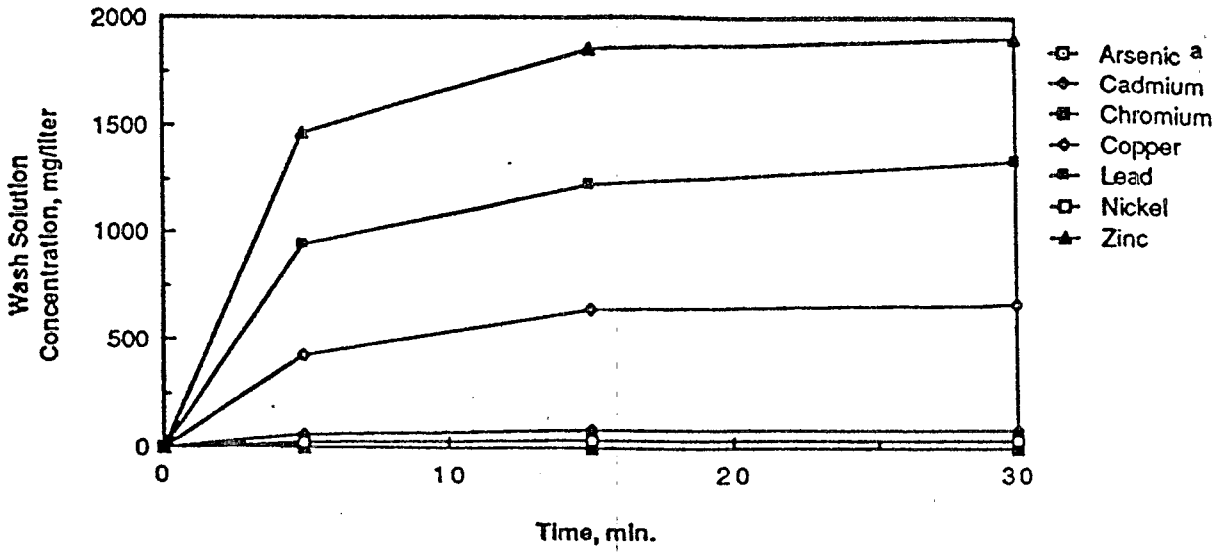
TABLE 12 (continued)

Contaminant	Initial concentration	Water Wash			3:1 Molar Chelant Wash		
		>2 mm	250 µm to 2 mm	<250 µm	>2 mm	250 µm to 2 mm	<250 µm
Inorganics (cont'd.)							
Nickel	1,489	18.6	42.2	1,570	17.5	28.2	472
Zinc	31,871	558	1,010	48,200	500	519	6,760
Total metal reduction		98.0%	96.4%	NR	98.4%	98.4%	78.2%

[a] Reference 14.

[b] ND = not detected.

[c] NR = no reduction in overall contamination.



[a] Arsenic and nickel overlap in this figure.

Figure 6. Reaction time for a 1:1 molar chelant wash using EDTA.[14]

washing study. The reduction of metal contaminants appears to be affected more by the use of the various wash solutions in the fine soil fraction (less than 250 μm) than in the other soil fractions. It was determined that a significant fraction of the contaminants are attached to the fines (silt, humus, and clay). The coarse material may be cleaned by simply separating out the fines. The data indicate that water alone can efficiently remove a significant portion of the contamination from the >2-mm soil particle fraction.[14]

2.2 SOIL CHARACTERIZATION

Soil characterization is necessary to determine optimum conditions for the metals extraction processes. Soil properties that influence the process employed for lead recovery include soil particle size, clay content, moisture content, quantity and species of metals, soil pH, and total water-soluble solids. These characteristics will govern both the physical and chemical operations of the process employed to recover

metals from contaminated soils. The following subsection describes soil conditions commonly found at lead-contaminated soil sites.

As described in Subsection 2.1, a significant amount of metals is adsorbed onto small particle-size fractions (less than 250 μm) than is adsorbed onto larger soil particle fractions (250 μm to 2 mm, and greater than 2 mm). Because the chelating agent may chelate both the metal and soil particle, techniques to eliminate this phenomenon will need to be employed in order to effectively separate the chelate solution and solid fractions. One method suggested called for the addition of a filter aid prior to soil dewatering.

Barth and Traver (1989) report on experiments performed by EPA to evaluate a treatment process consisting of soil washing followed by solidification/stabilization. Soils from battery cracking sites and synthetic soils were characterized for the following physical and chemical properties: 1) grain size distribution, 2) predominant clay species, 3) moisture content, 4) pH, 5) cation exchange capacity, 6) humic acid content, 7) total organic carbon, 8) total lead, 9) leachable lead, and 10) predominant lead species. Table 13 presents the results of the waste characterization.[6]

Wozniak and Huang (1982) discuss the results of a process developed to remove cadmium, copper, lead, nickel, and zinc from sludges. The process consists of solubilization of heavy metals by acidification followed by the separation of solids from the liquid fraction. The amount of metal removed from the sludge was found to be dependent upon pH, solids concentrations, specific types of metals, and length of acidification times. Removal of lead at pH 3 was much lower than at pH 1.5 and pH 2. A pH of 2 seemed to represent a critical value for lead solubilization similar to cadmium and copper. Table 14 presents the results of the acidification study. Maximum lead removal rates were 100, 81, and 30 percent at a 0.5 percent solids concentration for pH 1.5, 2, and 3, respectively.[15]

A document by PEI Associates, Inc., discusses the feasibility of using soil washing and stabilization/solidification to reduce lead contamination at several metals

TABLE 13. TOTAL LEAD CONTENT OF TREATED SOIL RECOVERED ON NUMBER 10 AND NUMBER 60 SCREENS[a]

Site	Whole soil untreated	Water wash	Surfactant wash	Chelate wash
Total lead recovered on No. 10 screen (>2 mm, mg/kg)				
A	57,150	153,100	98,100	119,050
B	75,850	50,150	66,500	164,200
C	3,230	893	1,580	886
D	27,150	31,350	25,610	8,965
E	5,194	6,487	Not analyzed	1,081
F	210	42	Not analyzed	30
SSM[b]	14,318	122	Not analyzed	98
Total lead recovered on No. 60 screen (0.25 - 2 mm, mg/kg)				
A		22,300	32,000	24,550
B		52,200	46,670	57,350
C		2,160	1,755	2,340
D		12,800	10,960	8,670
E		2,020	Not analyzed	1,516
F		312	Not analyzed	408
SSM[b]		401	Not analyzed	171
Total lead content of treated soil passing through both No. 10 and No. 60 screens (<0.25 mm, mg/kg)				
A		14,650	36,450	41,250
B		49,500	52,100	24,170
C		2,949	2,645	3,995
D		41,400	42,700	15,250
E		13,698	Not analyzed	4,693
F		111	Not analyzed	73
SSM[b]		30,600	Not analyzed	1,470

[a] Reference 15.

[b] Synthetic Soil Matrix.

TABLE 14. MAXIMUM METAL REMOVALS FROM SLUDGE SOLIDS FOR AN ACID EXTRACTION STUDY[a]

		Cadmium		Chromium		Copper		Lead		Nickel		Zinc	
pH	Solids concentration (%)	Max metal removal (%)	Time (h)	Max metal removal (%)	Time (h)	Max metal removal (%)	Time (h)	Max metal removal (%)	Time (h)	Max metal removal (%)	Time (h)	Max metal removal (%)	Time (h)
1.5	0.5	100	3	57	6	100	12	100	6	100	3	100	3
	1.0	90	3	42	6	90	24	88	12	90	12	100	3
	2.5	80	3	30	6	80	12	40	6	80	24	100	6
2.0	0.5	100	6	30	6	93	24	90	24	100	3	100	6
	1.0	90	6	25	6	80	24	80	12	90	12	100	6
	2.5	87	6	18	6	45	24	25	6	75	12	100	12
3.0	0.5	100	24	10	6	0	-	30	24	100	24	100	24
	1.0	70	12	10	6	0	-	20	24	80	24	85	24
	2.5	10	12	5	6	0	-	5	12	65	24	65	24

[a] Reference 15.

recycling Superfund sites. Soil characteristics were studied to determine their relationship to metals removal. The presence of calcite signifies the presence of a carbonatedform of lead such as $Pb(CO_3)_2(OH)_2$ or $Pb_4SO_4(CO_3)_2(OH)_2$. Lead in the soil was distributed among the soil fractions rather than being concentrated in the smaller particles. The use of agitation during soil washing and the use of filter aids are recommended to improve dewatering characteristics and filtering rate.[16]

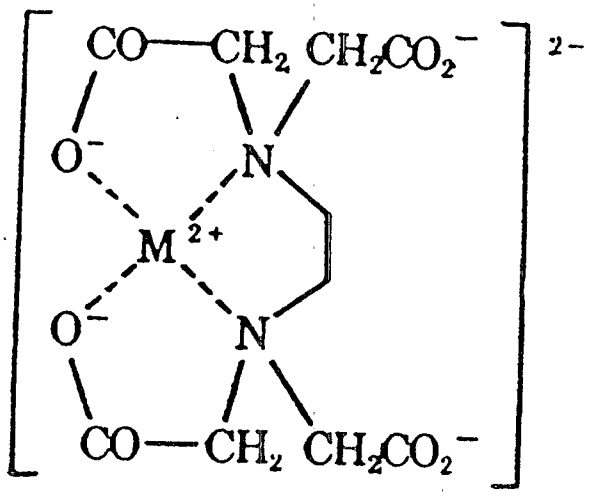
SECTION 3

CHELATING AGENTS

Selecting the appropriate chelating agents is also 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 following subsections describe the physical properties and results of previous studies in which various chelating agents were used in metals extraction.

3.1 PHYSICAL PROPERTIES

Kirk-Othmer's Encyclopedia of Chemical Technology describes what a chelating agent is and how it forms bonds with metals. The molecular structure of metal-EDTA chelate is presented in Figure 7. For the selective complexation of one metal in the presence of other metals, there must be a large difference between the stability constants of the two metals. Table 15 presents the stability constants for a number of chelating agents and metals. Enough chelating agent is needed to combine with the target metal ion as well as any competing metal ions that could displace the target metal. Some factors affecting the stability of metal chelate include the size and number of rings, substituents on the rings, and the nature of the metal and donor atoms. Five- and six-membered rings are more stable than other ring formations because the coordination angles prohibit the formation of three-membered rings, and closure is unlikely for more than seven-membered rings because of competing reactions to form linear chains. Substituents on the ring may produce steric hindrance effects or alter the availability of donor atom electrons for coordination.[17]



(11)

Figure 7. Structure of Metal-EDTA Chelate.[17]

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TABLE 15. STABILITY CONSTANTS OF METAL CHELATES[a]

Metal	Log K			
	STPP[b]	Citric acid	NTA[c]	EDTA[d]
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

[a] Reference 17.

[b] STPP = sodium tripolyphosphate;

[c] NTA = nitrilotriacetic acid;

[d] EDTA = ethylenediaminetetraacetic acid.

A book entitled "Chemistry of the Metal Chelate Compounds" provides stability constants for several metal chelates. An increase in oxidation potential is a possible indication of a metal complex formation. The coordination with a donor group increases the oxidation potential and therefore increases the relative stability of the higher valence state.[18]

A representative of Hampshire Chemical was contacted regarding the chelating agents the company manufactures: EDTA, DTPA, and NTA. For EDTA solutions at a pH level above 12, insoluble metal salts are formed, and at a pH above 7, the chelation of iron decreases. For DTPA, the chelation of lead decreases at approximately pH 9. Figure 8 presents metal chelating results at various pH levels for the three chelating agents. The pH level in 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 percent. Soils typically have a pH range of 5 to 8. High quantities of calcium carbonate may affect the equilibrium constants of the metal chelates.[19,20] Chelation value is defined as milligrams of calcite per gram of chelating agent used. The manufacturer recommended that 1.4 parts EDTA per part lead be used, and 1.9 parts DTPA per part lead be used for the chelation study. NTA requires approximately 4.2 parts NTA per part lead because it forms weaker bonds and is a less-effective chelating agent than DTPA and EDTA for chelating lead. The cost per pound of chelating agents was quoted at approximately $1.20/lb for EDTA acid, $1.40/lb for DTPA acid, and $0.45/lb for NTA.[20]

Martell and Calvin (1952) suggested that water-soluble chelating agents be used for regeneration so that the metal chelate may be rapidly formed and dissociated.[18] Carboxylic acids such as EDTA and NTA are hydrolytically stable at high temperatures and pH levels. The solubility levels of the sodium salts of EDTA are presented in Table 16. The trisodium salt of NTA has a solubility of 50 grams per 100 ml of water at 25°C. Figures 9 and 10 show how EDTA and NTA chelating abilities are affected at various pH levels.[21,25]

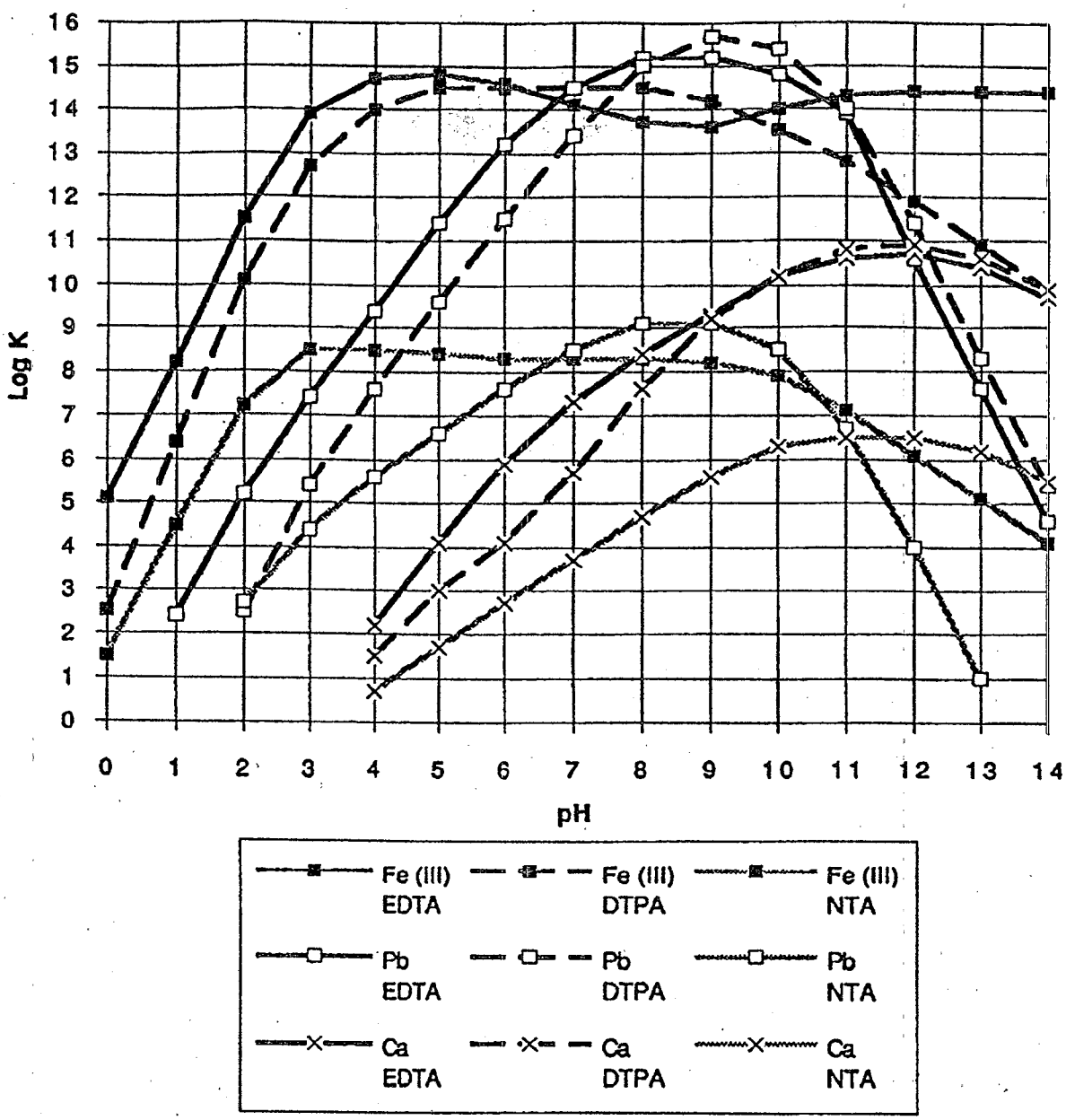

Figure 8. Stability constants for EDTA, DTPA, and NTA.[20]

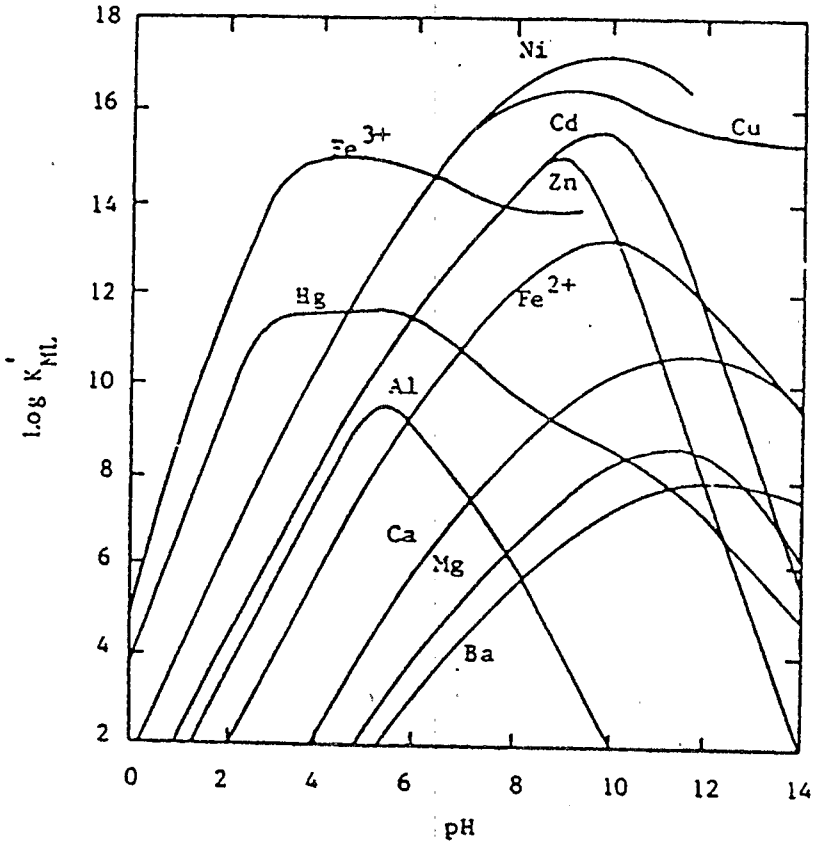

Figure 9. Stability constants for metal-EDTA complexes as a function of pH.[26]

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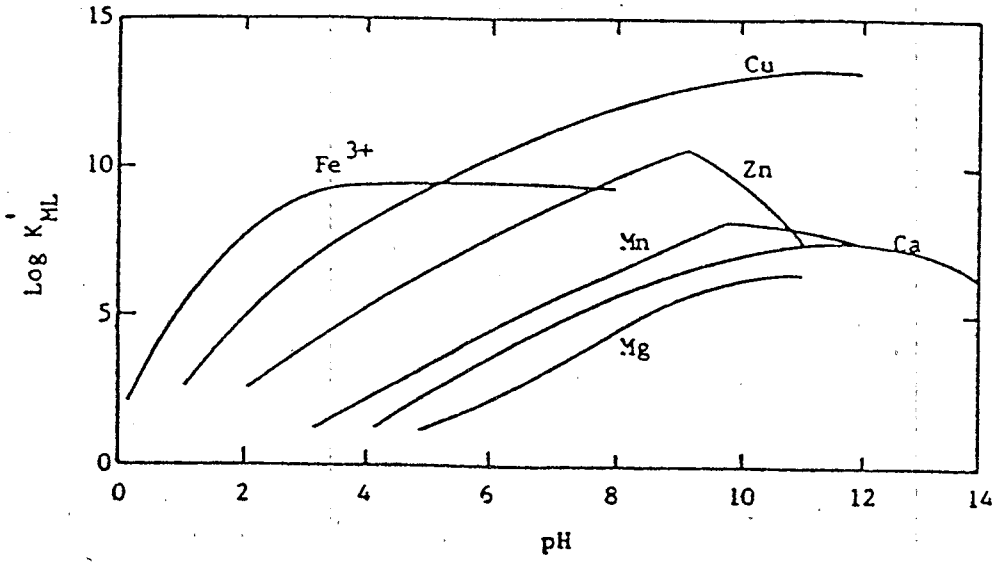

Figure 10. Stability constants for metal-NTA complexes as a function of pH.[27]

TABLE 16. SOLUBILITY OF EDTA AND ITS SODIUM SALTS IN WATER AT DIFFERENT TEMPERATURES (g/100 mL of Solution)[a]

Substance	pH	22°C	40°C	80°C
H_4L	2.2	0.2	0.2	0.5
NaH_3L	3.5	1.4	1.4	2.1
Na_2H_2L	4.7	10.8	13.7	23.6
Na_3HL	8.4	46.5	46.5	46.5
Na_4L	10.6	60.0	59.0	61.0

[a] References 23 and 24.

Ku and Yen (1991) discuss their experimental results involving the precipitation of metals from wastewater in the presence of chelating agents.[22] Precipitation of copper and lead by hydroxide precipitation was greatly inhibited by the presence of NTA at pH levels of less than 9 because of the formation of metal-NTA complexes. In the presence of strong chelating agents such as EDTA and NTA, the formation of lead chelates is more favorable than the formation of lead sulfide. Decreasing the pH intensifies this effect because the formation of hydrogen sulfide competes with the formation of metal sulfide compounds. Chelating agents such as citrate and tartrate form weaker bonds with metals than do EDTA and NTA and show little influence on residual lead concentration. At low pH levels, hydrogen sulfide tends to form and thus decreases the level of lead sulfide. In the neutral pH ranges, lead forms stable chelates with EDTA and NTA. For pH levels above 10, the formation of lead hydroxide complexes becomes a competing reaction for some weak chelating agents and increases the soluble lead concentration. For strong chelating agents, however, no significant decrease in chelating ability occurs above pH 10. The predominant specie between lead and EDTA above pH level 4 is PbEDTA-2, whereas for pH levels of less than 3, the predominant form is PbEDTA-1. For NTA, a similar phenomenon occurs: PbNTA-1 is the predominant lead chelate form for pH levels between 3 and 11. Figures 11 and 12 present the lead distribution of lead chelates at various pH levels for EDTA and NTA, respectively.[22]

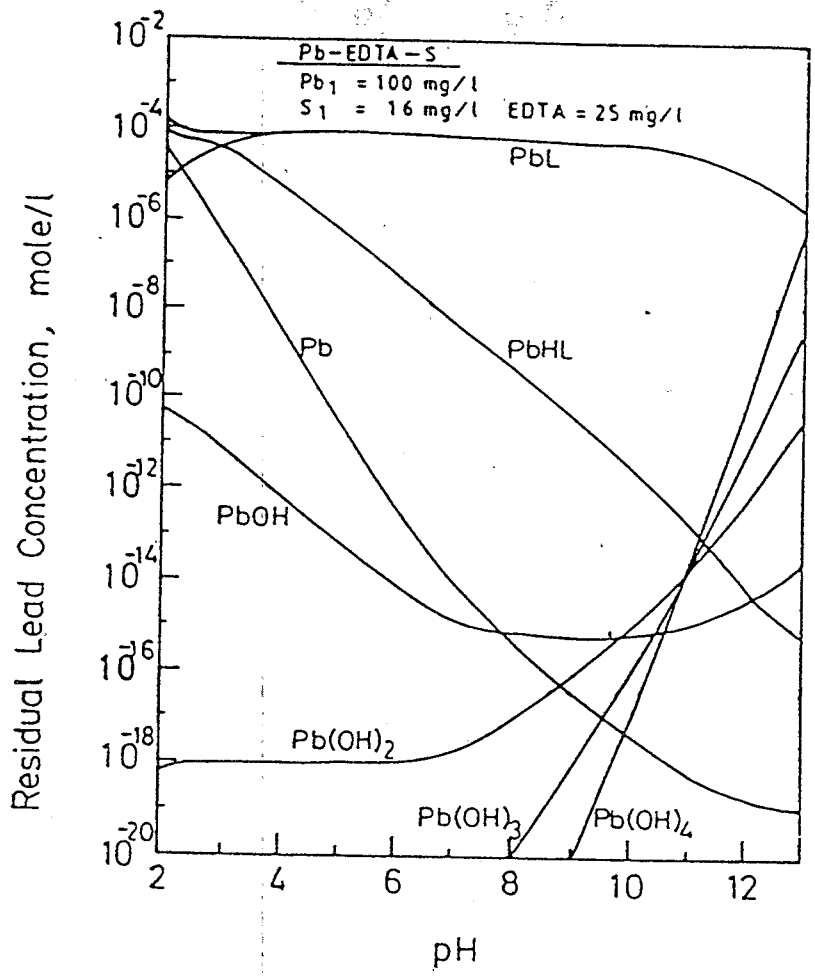

Figure 11. Lead-EDTA distribution as a function of pH.[22]

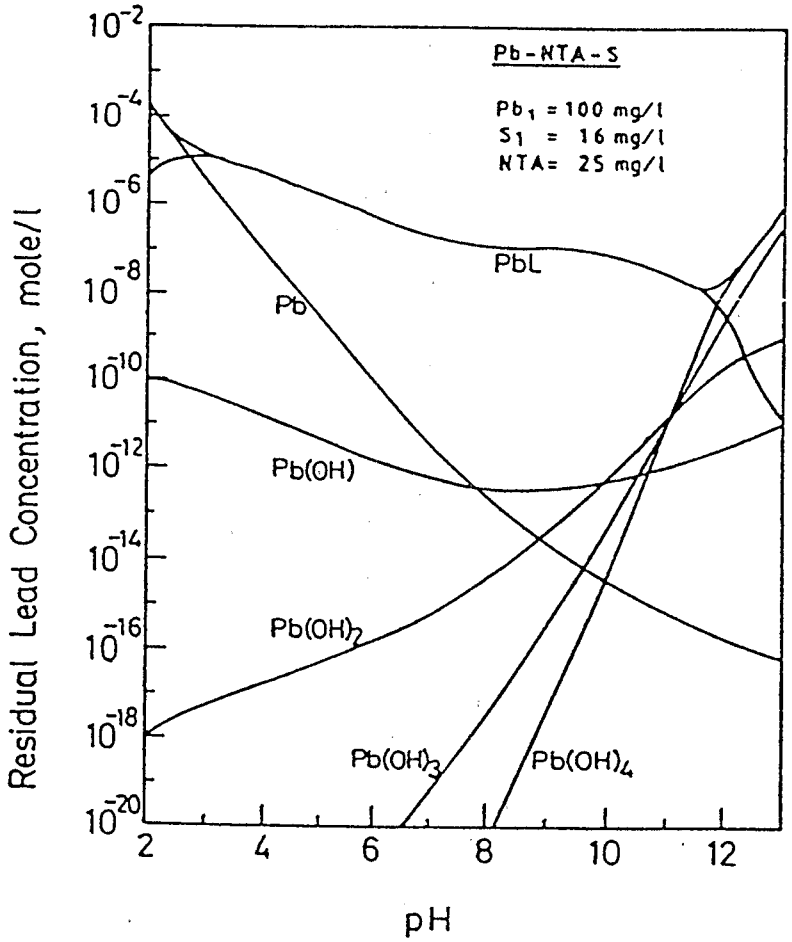

Figure 12. Lead-NTA distribution as a function of pH.[22]

3.2 TREATABILITY TESTS

Bhat and Gokhale (1964) discuss the results of experiments conducted to recover EDTA from metal-EDTA complex solutions. EDTA forms stable 1-to-1 complexes with most metals, especially those of the transition metal group. Because EDTA has a low solubility, it may be easily recovered even in dilute solutions. Metal may be removed from the chelate through acidification or by precipitation with a hydroxide, sulfide, or oxalate. Mineral acids may cause dissociation of the metal-EDTA complex (MY^{-4+m}) as a result of the strong competition for the formation of a protonated EDTA specie from H^+. The following equilibrium reaction shows this complex dissociation:

$$MY^{-4+m} + nH^+ \rightleftharpoons M^{+m} + YH_n^{-4+n}$$

Precipitation of EDTA can only occur on acidification if the concentration of the protonated EDTA species is greater than its solubility.[28]

Under alkaline conditions (pH > 9), the complex ion can be dissociated by precipitation of the metal as a hydroxide. EDTA becomes completely dissociated and a hydroxy-metal-EDTA complex may be formed. Based on the stability constant for EDTA and the hydroxide product's solubility, the cation would be completely dissociated from the metal-EDTA complex by direct hydroxide precipitation in only a few cases such as Fe(III).[28]

The sulfide precipitation method was effective in recovering both EDTA and metal. In all of the experiments, over 98 percent of the metal and 80 percent of the EDTA were removed. The metal-chelate had to be separated at 90°C because at lower temperatures, EDTA precipitated with the metal sulfides as a result of low solubility. The experiment was performed by first heating sulfuric acid to 90°C to acidify the solution at a pH of 2; then hydrogen sulfide was added to the heated solution. The metals were then precipitated and the hot solution decanted. Copper,

bismuth, cadmium, and lead also may be precipitated as sulfides from the EDTA solutions by this method.[28]

Although oxalate precipitation effectively recovered the metal, its low solubility limited its ability to recover EDTA. The oxalate precipitation method cannot be applied to very dilute (<0.002 M) solutions.[28]

A patent was developed by Lindstrom and Winget for the recovery of EDTA from ion exchange effluent solutions containing copper-EDTA complexes. In this process, rare earth elements are first adsorbed on a cation exchange resin bed. The bed is physically connected to a second cation exchange bed containing adsorbed copper. EDTA solution is then passed in sequence through the first bed to adsorb the rare earth elements, and then through the second bed containing the resin in the cupric cycle. High-calcium hydrate lime was used to separate the copper from the complex. Calcium replaces copper and forms an EDTA-calcium complex and $Cu(OH)_2$ precipitate. The filtrate containing the calcium-EDTA complex is recovered by filtration and is treated with sulfuric acid down to a pH below 3 to precipitate EDTA.[29]

A study performed by Pennsylvania State University examined the use of electrolytes as a means to modify EDTA extraction of lead from highly contaminated soil. In a 5-hour extraction using 0.04 M EDTA (1-to-1 ratio of lead to EDTA) at a pH range of 5 to 9, approximately 65 percent of the lead was released from the soil. Electrolytes consisting of Na^+, Li^+, and NH_4ClO_4 salts in a 0.5 M solution were used to increase the lead desorption to approximately 80 percent. This increase in lead desorption was attributed to the exchange displacement of soil-bound lead and increased the solubility of lead-containing species at higher ionic strength. Figure 13 shows the relative lead recovery rates for the various electrolytes studied. With the divalent electrolytes [$(Ca(ClO_4)_2$ and $Mg(ClO_4)_2$] at a 0.167 M solution, a similar recovery was observed. At higher pH levels, however, calcium and magnesium suppressed the lead dissociation because of competing chelation with EDTA. Figure 14 presents the results obtained with divalent electrolytes.[30]

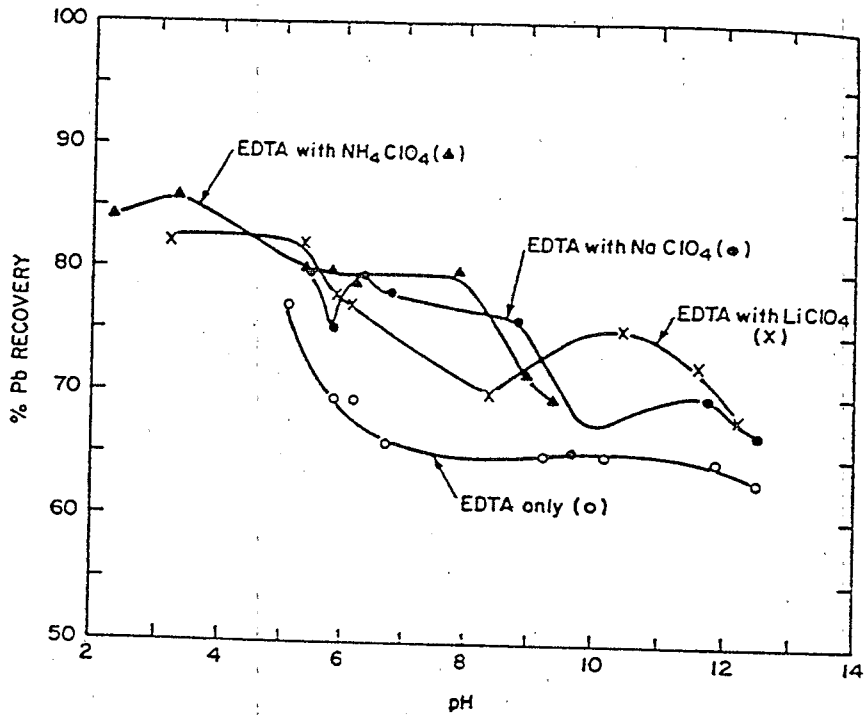

Figure 13. Effect of electrolytes on pH-dependent recovery of lead.[30]

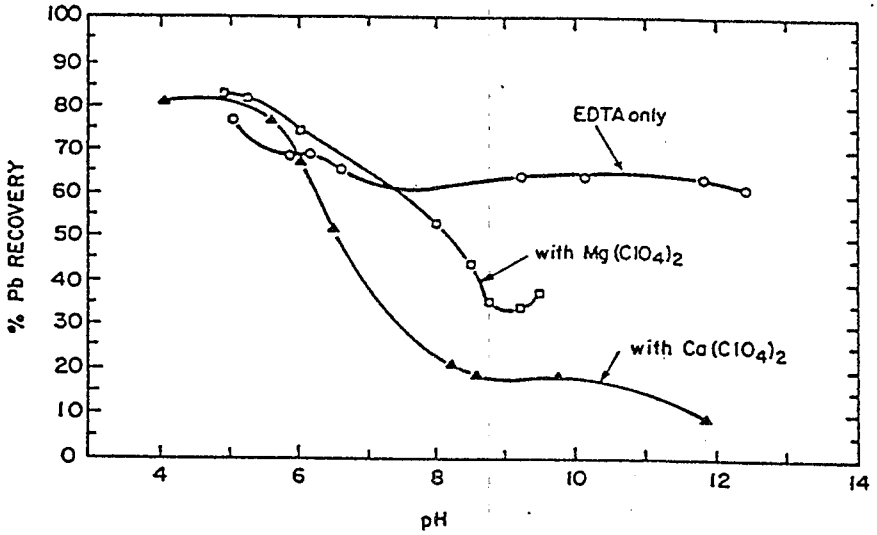

Figure 14. The effect of 0.167 M $Ca(ClO_4)_2$ and $Mg(ClO_4)_2$ on the pH-dependent release of Pb by EDTA from the soil.[30]

The U.S. EPA performed a treatability study to evaluate in situ methods for treating releases of hazardous materials from uncontrolled waste disposal sites. The study was conducted by using a three-agent sequential extraction technique to recover lead and other metals from contaminated soil. The soil contained five toxic heavy metals: cadmium, chromium, copper, lead, and nickel. Preliminary shaker table studies using EDTA, hydroxylamine hydrochloride, acidic buffer, and DTPA showed that EDTA was the best extractant for all metals. Table 17 presents the results of the shaker table study. The three-agent sequential extraction study was conducted with soil washing solutions of EDTA followed by hydroxylamine hydrochloride and then citrate buffer. Table 18 presents the results of the three-agent study. Lead appeared to be easily removed by the EDTA; further removal occurred with citrate. This study demonstrated that weaker agents do not remove the metals as efficiently as EDTA alone.[31]

A study was conducted to investigate how the solubility of lead is affected by the presence of iron in soil during soil washing with EDTA. The results indicate that an abundance of iron in the soil does not interfere with the solubility of lead. When iron solubility was inhibited by increases in pH, the solubility of lead was unaffected. The kinetically slow dissolution of iron oxides in the soil in the presence of EDTA is thought to be the limiting factor for the interference by iron in lead displacement.[32]

In an experiment conducted by Norvell (1984), five chelating agents [DTPA, EDTA, ethyleneglycol-bis(2-aminoethylether) tetraacetic acid (EGTA), hydroxyethylene-diaminetriacetic acid (HEDTA), and NTA] were compared as extractants for aluminum, iron, manganese, zinc, copper, cadmium, and nickel in 25 soils. The experiments were conducted with 0.005 M chelating agent, 0.01 M $CaCl_2$, and 0.1 M acetic acid-ammonium acetate buffer at a solution pH of 5.3 and a 5-to-1 extractant-to-soil ratio. DTPA, EDTA, and HEDTA were the most effective agents for extracting all seven of the metals used in testing. The extracting solutions were formulated to maintain a relatively constant pH and concentration of Ca^{+2} in all soils. These conditions were intended to retard dissolution of $CaCO_3$ in soils and to yield clear filtrates by promoting effective flocculation.[33]

TABLE 17. SINGLE-AGENT SHAKER TABLE EXTRACTION EFFICIENCIES[a]

Soil metals (ppm)	Cd 47	Cr 349	Cu 219	Ni 214	Pb 2,480
EDTA (0.1 M at pH 6), % extracted	114	24	62	14	106
Hydroxylamine hydrochloride (0.1 M in acetic acid), % extracted	86	32	43	20	80
Citrate buffer (0.1 M at pH 3), % extracted	77	24	48	14.5	65
Pyrophosphate (0.1 M), % extracted	5.4	9.6	29	2.9	9.7
DPTA (0.005 M in 0.1 M Triethanolamine), % extracted	59	2	48	2	67

[a] Reference 31.

TABLE 18. THREE-AGENT SEQUENTIAL EXTRACTION EFFICIENCIES: SOIL COLUMN TESTS[a]

Soil metals (ppm)	Cd 47	Cr 349	Cu 219	Ni 214	Pb 2,480
Water, % extracted by water	0.2	0	0	0	0.1
EDTA (0.1 M at pH 6), % extracted by agent	60.5	12.2	47.1	6.8	60.1
Hydroxylamine hydrochloride (0.1 M in acetic acid) % extracted by agent	23.8	8.9	0.7	8.7	2.3
Citrate buffer (0.1 M at pH 3), % extracted by agent	3.6	12.2	0.2	4.8	8.8
Water wash, % extracted by water	0.4	1.1	0.1	0.5	0.5
Total % extracted	88.5	34.4	48.1	20.8	71.8

[a] Reference 31.

SECTION 4

MEMBRANES

In an electromembrane process, the selection of a membrane is critical for the successful separation of cations and anions. A membrane must be durable, able to withstand harsh chemical and physical treatment, stable at high temperatures, and possess low electrical resistance. Several articles were reviewed to provide information on the selection of membranes. The following subsections provide an overview of the pertinent information contained in these articles.

4.1 PROPERTIES OF MEMBRANES

Membranes are manufactured from a variety of materials ranging from polymers to sulfonic acids. Polymeric membranes are characterized by the following polymer properties: large average size of the macromolecules, their size distribution, their architecture, the specific nature of their chemical groups, the arrangements of these groups in the chain, and the aggregate state of the macromolecules. The highest molecular weight (MW) polymer should be evaluated before a particular polymeric membrane is selected. Although the integrity of the membrane tends to increase with MW, the higher MW polymer membranes may show a decrease in ion selectivity. Membranes produced by a dry phase-inversion process generally need a higher MW polymer than those produced by a wet process. Also, membranes made of polymers with narrow MW distributions are preferable to those with broad distributions, and single-viscosity grades are preferable to blends of two viscosity grades.[21]

In a journal article by Houng Loh, et al. (1990), two microporous membranes, polypropylene Celgarde® and Teflon Plastolon®, were selected to evaluate the morphology of polymeric membranes. The membranes were examined for conductivity, stability, surface morphology (determined by scanning electron microscope), and

tensile strength. This study determined that Teflon membranes exhibit higher conductivity than polypropylene membranes. The tests also determined that the ionic permeability of an electromembrane can be regulated with the electrically controllable oxidation state of the polymer.[34]

DuPont manufactures a Nafion® perfluorosulfonic acid cation-exchange membrane that is reinforced with Teflon, is 0.43 mm thick, and has a weight of 6.3 g/dm. The membrane has excellent stability properties to withstand the most harsh conditions. The Nafion 324 membrane is a reinforced membrane composed of 1500 and 1100 equivalent weight copolymer layers. This membrane is primarily used to produce 10 to 20 percent NaOH and to recover metal ions. The Nafion 417 reinforced membrane is a 1100 equivalent weight polymer used in the electroplating industry to regenerate chromic acid solutions and to recover metals.[35]

The Ionics CR 67 membrane is an acrylic fiber-backed cation-transfer membrane with a specific weight of 13.7 mg/cm^2, a thickness of 0.6 mm, a burst strength of 7 kg/cm^2, and a minimum capacity of 2.10 meq/dry gram resin. The membrane is primarily used in electrodialysis reversal units and was used in the electromembrane reactor for the 1986 PEI bench-scale study. These membranes must be kept wetted at all times to prevent the membrane from cracking.[1,36,37]

4.2 OPERATING PARAMETERS

Both the properties of a membrane and the conditions under which the membrane is operated are important. Process parameters such as pH and fluid turbulence affect the rate in which the ions are transported across the membrane. The following articles were reviewed to determine the operating conditions that should be considered for the design of an electromembrane reactor.

A book entitled "Synthetic Polymeric Membranes" provides an overview of the various membranes and the mechanism in which they operate. In electromembrane processes, 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, such as charge classification and valence state. The solute transport

rate of a liquid adjacent to the membrane can be controlled through the membrane. Film diffusion tends to occur when film 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.[21]

The membrane potential is the difference in electric potential between two electrolyte solutions separated by a permeable or semipermeable membrane. The membrane potential is dependent upon the properties of the mobile and fixed ions and is usually independent of membrane thickness or cross-sectional area. The membrane potential is the sum of the diffusion potential within the membrane, the Donnan (phase boundary) potential, and the diffusion potential of the films with partial or total film control. Ideal membrane potentials (Ei) can be calculated by the following equation:[21]

$$Ei = \frac{2RT}{F} \ln (a1/a2)$$

where

Ei = membrane potential

R = ideal gas law constant

T = temperature

F = electricity, Faradays

a1, a2 = mean activities of the solutions in the anode and cathode chambers

Diffusion of a substance across a concentration gradient is defined by Fick's first law of diffusion that the flux (J) is proportional to the concentration gradient:[21]

$$J = -D\, \partial c/\partial x$$

where D = diffusion coefficient

$\partial c/\partial x$ = change in concentration

The current density [calculated as milliamps (ma)/cm^2] that can be applied across a membrane is limited by concentration polarization. Figure 15 presents an

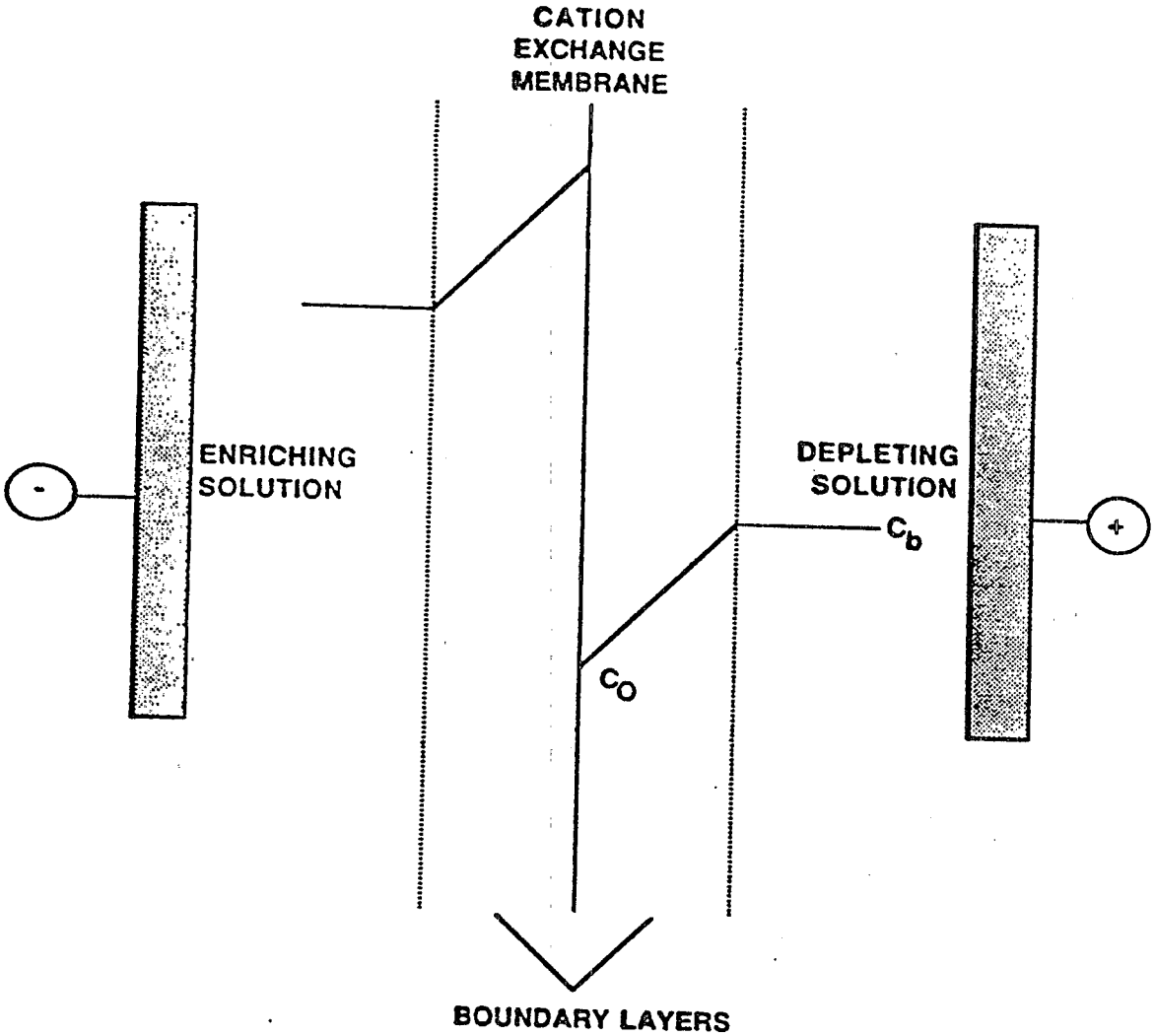

Figure 15. Concentration gradients in the electromembrane reactor.[38]

Extracted from: "Physiochemical Aspects of Electromembrane Processes," Chapter 2, in Industrial Processing With Membranes. Davis, T. A. and Brockman, G. F. Lacey, P.E., and Loeb, S. (editors). Copyright ©, 1972. Wiley-Interscience. Reprinted by permission of John Wiley & Sons, Inc.

illustration of concentration gradient. The cation exchange membrane in the center is highly permeable to cations and almost impermeable to anions. Cations are transferred through the membrane faster than they can arrive from the solution on the right or leave the solution on the left by electrical transfer. Thus, the concentration at the left interface increases until concentration gradients are established. At this point, additional fluxes are needed to maintain steady-state conditions in the boundary layers.

If the current is raised high enough, the concentration at the right interface will approach zero. During the operation of the electromembrane reactor, the ion concentration in the anode chamber is depleted as ions are transported across the membrane. If the concentration decreases too much in the anode chamber, the ion concentration will approach zero; therefore, excessive energy will be required to transfer any additional ions. In order to avoid the anion depletion, the bulk concentration in the anode chamber must be maintained.[1]

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 taking place around the membrane. The electrical resistance of a solution depends on the solute concentration and solution conductivity.[1]

The velocity in which an ionic species is transferred by an electrochemical driving force or potential gradient (ui) in the x direction is defined by the following equation:

$$ui = - k \, dE/dx$$

where k = the proportionality constant

E = potential

The electrochemical potential is the sum of the chemical and electrical potential. The velocity is proportional to the ionic mobility, mi, expressed in units of $cm^2/V\text{-}sec$; therefore, the velocity may be expressed as:

$$ui = -mi\ Zi\ dE/dx$$

where Zi = the ionic charge

If the potential is to be expressed in chemical terms, the proportionality factor of velocity is D cm^2/sec:[39]

$$ui = -D\ d\ln Ci/dx \qquad \text{(Fick's first law)}$$

where D = diffusion coefficient

Ci = concentration of ionic species

SECTION 5

SUMMARY

A literature review of metals extraction technologies, soil characterization, chelating agents, and membranes was conducted to define important parameters regarding lead recovery from soils. The following is a summary of the important findings that may impact lead recovery.

5.1 METALS EXTRACTION TECHNOLOGIES AND SOIL CHARACTERIZATION

Several technologies have been or are currently being developed for removal of metals from contaminated soils and wastewaters. The goals of the metal extraction processes are to recover enough lead from the soil so that the soil will pass the Toxicity Characteristic Leaching Procedure (TCLP) test for metals, and to recover a lead product that is marketable.

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 precipitating with sulfuric acid to produce a lead sulfate product. The BOM has also developed 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. Lead remaining in the soil after leaching will be leached with a 0.5 percent nitric acid solution.

The TerraMet™ soil remediation system developed by COGNIS, Inc. leaches and recovers lead from contaminated soils, sludges, or sediments. Lead in the form of metallic lead, soluble ions, and insoluble lead oxides and salts may be leached with a proprietary aqueous leachant.

A soil recycling process developed by the Toronto Harbor Commission employs three technologies operating in series. 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 for dissolution of heavy metals. All metals may be recovered in their pure form using this process. The third stage involves chemical hydrolysis followed by biodegradation to destroy organic contaminants in the slurry.

EPA has conducted research on a lead extraction process involving the conversion of lead sulfate to lead carbonate with ammonium carbonate, lead carbonate to lead acetate and oxidation of lead to lead acetate with acetic acid and oxygen, conversion of lead dioxide into lead acetate, and the final conversion of lead acetate to lead sulfate with sodium sulfate.

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(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 conducted a study for the National Science Foundation using an electromembrane reactor (EMR) process to recover lead from an ethylenediamine tetraacetic acid (EDTA)-lead chelate solution. The bench-scale test was performed with actual chelate generated using lead-contaminated soil from a battery reclamation site.

U.S. EPA Region V and PEI Associates have developed an on-site soil washing process for recovery of lead from contaminated soils. The soil was washed with a chelating agent followed by use 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 is highly dependent on the site because of varying levels of contamination. EDTA was determined to be the more efficient chelating agent for lead removal.

The soil characterizations performed prior to the soil washing 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 coarse material (greater than 2 mm) was found to have fewer contaminants than the other soil fractions, and could be cleaned by separating the soil fractions and treating the smaller soil fractions. Soil washing with EDTA formed colloids consisting of fine soil particles that created difficulties in solid-liquid separation. It was suggested that the addition of a filter aid prior to filtration would enable better separation of the fine particles from the liquid fraction. EDTA was used extensively as a soil washing solution at various concentrations and pH levels. In most cases, EDTA was able to remove approximately 80 percent of the lead from the metals-contaminated soils.

The predominant species of lead found at many of the battery breaking and reclamation sites examined were lead sulfate, lead carbonate, and lead dioxide. Calcite signifies a presence of carbonated forms of lead. 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.

5.2 CHELATING AGENTS

The tendency for a metal to chelate is determined by the stability constant, which is highly dependent on the pH of the solution. EDTA and DTPA have approximately the same lead-chelation abilities and are relatively similar in cost ($1.20/lb and $1.40/lb, respectively). Approximately three times as much NTA is required to chelate lead than is required for EDTA and DPTA, but the cost of NTA is substantially lower ($0.45/lb). All three chelating agents are relatively stable at high temperatures and pH levels. In several studies, EDTA, NTA, and DTPA have been used to recover metals from waste streams.

5.3 MEMBRANES

Important characteristics that need to be considered in the selection of a membrane include low electrical resistance, high permselectivity (exclusion of anions), 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 in order to maintain steady-state conditions in the boundary layers of the membrane. Both the Ionics CR 67 and the DuPont Nafion® membranes are stable at extreme pH levels, exhibit high burst strength, and are permeable to cations and highly impermeable to anions. Examination of the literature has shown that there is no commercial or full-scale membrane technologies for the recovery of lead from soils.

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