



Project Summary

Bench-Scale Recovery of Lead Using an Electromembrane/Chelation Process

This report presents the results of a bench-scale treatability test to investigate key process parameters influencing an innovative chelation-electrodeposition process for recovery of metals from contaminated soils. A series of electromembrane tests were conducted at the U.S. Environmental Protection Agency (EPA), Test and Evaluation Facility in Cincinnati, OH, to examine the effects of membranes, chelating agents, electrodes, current density, iron, and lead concentration on lead recovery. The tests were conducted with a synthetic lead solution composed of chelating agent and various lead species. In this study, disodium ethylenediaminetetraacetic acid (EDTA), tetrasodium EDTA, and pentasodium diethylenetriamine pentaacetic acid (DTPA) were used as chelating agents because of the stable lead-chelate compounds that are formed with these agents and because of the prevalence with which these chelating agents are used in soil washing. Lead species used in this study included lead sulfate and basic lead carbonate.

Results of this study showed that the tests using disodium and tetrasodium EDTA under the same conditions resulted in similar lead recoveries. Reuse of the disodium EDTA, tetrasodium EDTA, and DTPA solutions proved feasible because similar lead removals were observed in tests conducted with fresh and regenerated solutions. A comparison of the data obtained in the tests employing initial target lead concentrations of 0.8% and 4% showed that a higher percentage of lead was recovered in the 0.8% lead solution test but that the total amount of lead recovered was greater in the 4% lead solution test. Based on data from tests using DuPont Nafion®* and Ionics membranes, it appeared that the

Nafion® membrane tests resulted in higher lead removal efficiencies. Tests conducted with DTPA and tetrasodium EDTA solutions and lead and cadmium electrodes showed that the cadmium electrodes were definitely superior in the tetrasodium EDTA tests, but no significant increase in lead recovery using the cadmium electrodes was observed in the tests with DTPA solutions.

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

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. 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, Resource Conservation and Recovery Act-approved landfill, in accordance with hazardous waste regulations. This approach 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

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



associated with the landfilling approach. Thus, there is great incentive to develop alternative methods that will clean up contaminated sites.

Soil characterizations done on several metal-contaminated soils at battery reclamation sites have shown that the predominate lead species are lead sulfate, lead carbonate, lead dioxide, and elemental lead. The average lead concentration in these soils is approximately 4%. Calcium and iron are also found in appreciable quantities in these soils. Soil screening tests done on several metal-contaminated soils by soil washing showed that a majority of the metals are adsorbed on the fine soil fraction (less than 250 μm).

In 1986, PEI Associates in a study for the National Science Foundation, used an electromembrane reactor (EMR) process to recover lead from an EDTA-lead chelate solution. The bench-scale tests were performed with actual chelate generated from lead-contaminated soils at a battery reclamation site. The PEI study examined

the effect of system variables such as current density, pH, current efficiency, and chelate concentration. The purpose of the present bench-scale study was to examine the effects of membranes, chelating agents, types of electrodes, current density, iron levels, and lead concentration on lead recovery. In this study, however, a synthetic lead-chelate solution was tested rather than a lead-contaminated soil because soil chelation has been previously studied. The composition of the synthetic lead-chelate solution was similar to one that would be obtained after chelation of soils from typical battery reclamation sites.

A goal of this bench-scale study was to recover the lead on the cathode while regenerating the chelating agent in its sodium salt form in the cathode chamber. The sodium form of the chelating agent was also used for preparing the synthetic lead-chelate solution.

Experimental Conditions

The reactor was constructed from a commercial 10-gal aquarium of 1/4 in.-

thick thermoplastic. It was divided into two chambers by a thermoplastic frame that acted as a support for the cation-exchange membrane. A 7-by-7-in. membrane was mounted inside a frame with gasketing materials and nylon screws and wing nuts. (Figure 1).

Two types of membranes were used in this study: an Ionics 61AZL386 membrane and a DuPont Nafion® membrane. The Ionics membrane is a modacrylic, fiber-backed, cross-linked, sulfonated copolymer, cation-exchange membrane with a specific weight of 14 mg/cm², a thickness of 0.6 mm, a burst strength of 8 kg/cm², and a 2.7 meq/dry gram resin capacity. The Nafion® membrane is a perfluorosulfonic acid cation-exchange membrane that is reinforced with Teflon, has a weight of 6.3 g/dm², and is 0.43 mm thick. Both membranes have low electrical resistance, high permselectivity, high burst strength, and long-term resistance to aqueous acid, alkaline, and mild oxidizing solutions; both are able to withstand harsh chemical and physical treatment.

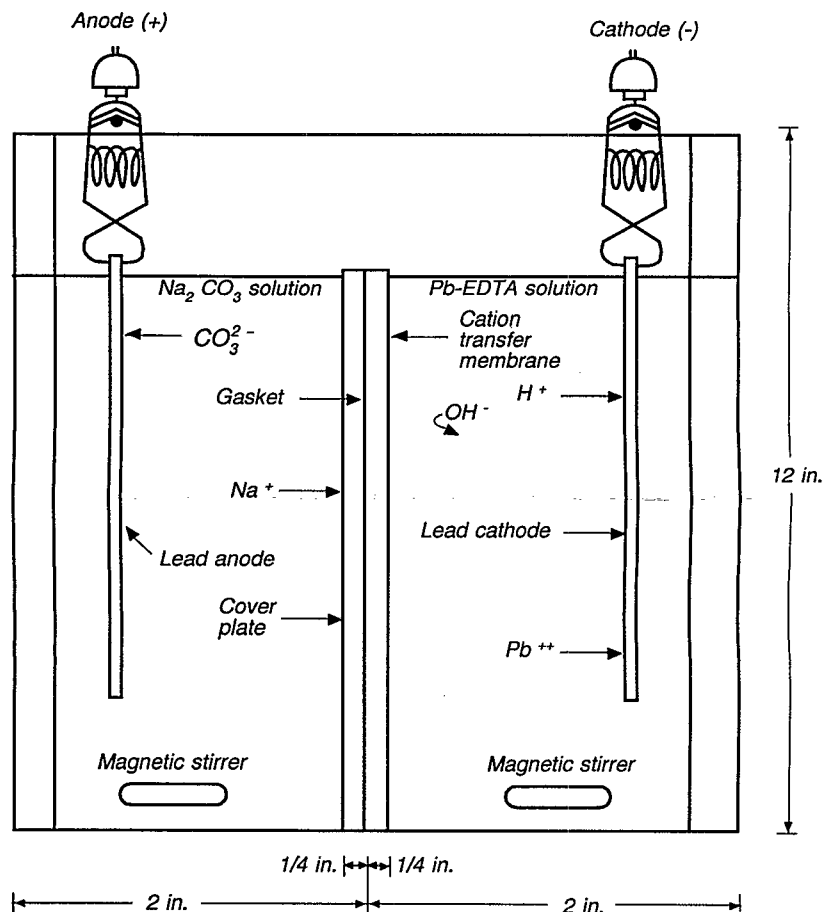


Figure 1. Schematic of electromembrane reactor.

The cathode chamber was filled with 4 L of lead-chelate solution adjusted to the experimental pH with sodium hydroxide or sulfuric acid. A 5% sodium carbonate solution (Na_2CO_3) was placed in the anode chamber to provide sodium to replenish the sodium-chelate. A pH meter was used to measure the solution pH in both the anode and cathode chambers. The highest lead-chelate stability constant for both tetrasodium EDTA and DTPA occurs at a pH of approximately 9. The optimum lead-chelate stability constant occurs at a pH of approximately 5 for disodium EDTA. A stoichiometric solution of 2 moles of sodium per mole of lead that is plated (onto the cathode) is required to regenerate the sodium salt form of the chelating agent. In the bench-scale experiments, twice the stoichiometric quantity of sodium carbonate required was placed in the anode chamber to prevent depletion of sodium ions. The 5% by weight sodium carbonate solution in the anode chamber provided enough sodium ions to carry the current across the membrane.

The electrodes were placed in the anode and cathode chambers approximately 1 in. from the membrane. Current densi-

ties were adjusted to 15 or 25 ma/cm^2 on the power supply unit, which corresponds to approximately 4.7 or 8.9 amps, respectively. Experiments using the EMR were conducted for a total period of 3 to 5 hr. Samples of the solutions in the cathode and anode chambers were taken at 30-min intervals to determine the quantity of the lead plated onto the cathode and the depletion of sodium ions in the anode chamber. After the third hour of the reaction, however, the samples were taken at 1-hr intervals. This sampling schedule provided an indication of the optimal time needed for plating out the lead.

One set of electrodes used in the electromembrane tests was made from lead sheet with approximate dimensions of 7 by 10 in. In a second set of tests, cadmium electrodes were used with the same dimensions as the lead electrodes. Each electrode was supported across the top of the aquarium approximately 1 in. from the membrane surfaces. The electrodes were wired and connected to a DC power supply with the capabilities for controlling amperage and measuring both current and voltage. The solutions in both the anode and cathode chambers were mixed using

magnetic stirrers to create turbulence for enhanced mass transfer. The type of chelating agent, type of membrane, current density, lead concentration, and reaction time were varied to examine the effects of these parameters on lead recovery. Table 1 presents the experimental matrix for the bench-scale electromembrane reactor study.

Results and Conclusions

Preliminary jar tests performed in this study determined that lead dioxide and elemental lead could not be chelated by any of the chelating agents studied (disodium EDTA, tetrasodium EDTA, and pentasodium DTPA), but that lead sulfate and lead carbonate could be completely chelated by all three chelating agents. The optimal chelating-agent-to-lead molar ratios were determined to be 1:1 for disodium EDTA, 1:1.5 for tetrasodium EDTA, and 1:2 for DTPA.

A comparison of the tests using disodium EDTA and tetrasodium EDTA under the same conditions showed that both forms of EDTA produced about the same lead recovery. Based on the treatability study data, there appears to be no advan-

Table 1. Electromembrane/Chelation Study Experimental Matrix

Chelating agent	Run No.	Current Density, ma/cm^2	Lead Conc., %	Membrane	Reaction Time, hr	pH
Tetra-sodium EDTA	1	25	0.8	DuPont Nafion	3	9
Tetra-sodium EDTA	2	25	0.8	DuPont Nafion	3	9
Tetra-sodium EDTA regenerated solution*	3	25	0.8	DuPont Nafion	5	9
DTPA (diethylenetriamine pentaacetic acid)	4	15	0.8	DuPont Nafion	3	9
DTPA	5	25	0.8	DuPont Nafion	3	9
DTPA regenerated solution†	6	15	0.8	DuPont Nafion	3	9
DTPA	7	25	0.8	DuPont Nafion	5	9
DTPA	8	25	4	DuPont Nafion	3	9
DTPA	9	25	4	DuPont Nafion	5	9
DTPA regenerated solution†	10	25	4	DuPont Nafion	4	9
DTPA	11	15	4	DuPont Nafion	5	9
Tetra-sodium EDTA	12	25	4	DuPont Nafion	3	9
Tetra-sodium EDTA*	13	25	4	DuPont Nafion	3	9
Di-sodium EDTA	14	25	0.8	DuPont Nafion	3	5
Di-sodium EDTA regenerated solution‡	15	25	0.8	DuPont Nafion	3	5
DTPA (Cadmium electrodes)	16	25	4	DuPont Nafion	3	9
DTPA (Cadmium electrodes)	17	15	0.8	DuPont Nafion	3	9
DTPA (Cadmium electrodes)	18	25	4	DuPont Nafion	3	9
Tetra-sodium EDTA (1.5% iron)	19	25	4	DuPont Nafion	3	7
Tetra-sodium EDTA (1.5% iron)	20	25	4	DuPont Nafion	3	9
Tetra-sodium EDTA (1.5% iron)	21	25	4	DuPont Nafion	3	11.5
DTPA (Ionics membrane)	22	25	4	Ionics	3	9
DTPA (Ionics membrane)	23	15	0.8	Ionics	3	9
DTPA (Ionics membrane)	24	15	0.8	Ionics	3	9

* Experiment was performed using the tetra-sodium EDTA solution from runs 2 and 12.

† Experiment was performed using the DTPA solution regenerated from runs 4 and 9, respectively.

‡ Experiment was performed using the di-sodium EDTA solution regenerated from run 14.

tage in using one sodium form of EDTA over the other. The use of DTPA as the chelating agent resulted in lower lead recoveries (based on data using a solution containing 0.8% initial lead concentration).

The data from the regenerated chelating agent solution tests showed that the lead removals were comparable to those from the original solutions.

A comparison of the data obtained in the tests performed using initial target lead concentrations of 0.8% and 4% showed that a higher percentage of lead was recovered in the 0.8% lead solution test, but that the total amount of lead recovered was greater in the 4% lead solution test. One possible reason the lead removal rates were not higher in the electromembrane tests conducted with 4% lead-chelate was the limited surface area of the cathode. The cathode appeared to be "saturated" with lead, and therefore the lead may have been inhibited from plating onto the cathode and thus remained in the solution. These data also indicate that the use of a higher percentage lead solu-

tion results in more lead recovery and higher current efficiencies.

A comparison of the tests conducted with 15 and 25 ma/cm² current densities showed that the lead recovery rates and current efficiencies were higher at a 25 ma/cm² current density.

Lead recovery efficiencies of the Nafion® and Ionics membranes were compared to determine if the type of membrane used had any effect on lead recovery. Based on the data from the tests in the 0.8% lead solution, it appears that the Nafion® membrane is slightly superior to the Ionics membrane. A cost analysis was not performed to determine the economic benefits of using either membrane.

The tests with lead and cadmium electrodes were compared using DTPA solutions and tetrasodium EDTA solutions. In tests conducted with tetrasodium EDTA, the cadmium electrodes were definitely superior to the lead electrodes with respect to lead recovery rates. The tests with DTPA solutions, however, did not reveal a significant increase in lead recovery when using the cadmium electrodes.

In this study, the chelating agent solutions were regenerated once; however, it is unknown whether there is a limit to regeneration that will produce an unusable chelating agent solution. Multiple generations of the chelating agent should be investigated, especially with soil, to determine the extent of regeneration of the chelating agent.

The bench-scale treatability program was designed as a screening study and was not intended to enable development of rigorous conclusions regarding the various experimental parameters. No quantitative criteria were established to determine significant differences between or among runs. The conclusions that have been made in the report are intuitively apparent from different sets of data. Certain conclusions are not fully supported by all the data collected for the report.

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

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

The complete report, entitled "Bench-Scale Recovery of Lead Using an Electromembrane/Chelation Process," (Order No. PB95-176996; Cost: \$27.00, subject to change) will be available only from

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