

LEAD CONTAMINATION REMOVAL BY SOIL WASHING

by

ROBERT A. EVANGELISTA
Roy F. Weston, Inc.
Response Engineering and Analytical Contract
Edison, NJ 08837

and

ANDRE P. ZOWNIR
U.S. Environmental Protection Agency
Environmental Response Team
Edison, NJ 08837

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ANDRE P. ZOWNIR
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ABSTRACT

The U.S. EPA's Environmental Response Team and their Response Engineering and Analytical Contractor (REAC) performed bench-scale studies to determine the feasibility of soil washing with ethylenediaminetetraacetic acid (EDTA) as a means of removing lead contamination from soils at two abandoned battery reclamation sites, Lee Farm and Sapp Battery. Soil characterization of these sites found increasing lead concentration in decreasing soil particle size. Prior to washing, soils were classified into 3 fractions: oversized, coarse, and fine. Soil washing consisted of EDTA chelation followed by water rinse. The cleanup criteria for the Lee Farm and Sapp Battery were EP Tox lead (5 mg/l and total lead (79 mg/g), respectively. For the Lee Farm coarse fraction soil, a total lead reduction of 91.0 to 97.1 percent was achieved while meeting the EP Tox lead criterion. For the Sapp Battery coarse soil fraction, a total lead reduction of 85.4 to 89.3 percent was achieved but the total lead clean-up criterion was exceeded (221 - 407 ug/g lead). Also, for the Sapp Battery fine soil fraction total lead reduction was 86 percent but total residual lead was 7135 ug/g. Soil washing with EDTA was found to be effective for reducing lead contamination in certain soil fractions.

INTRODUCTION

The Environmental Response Team (ERT) of the U.S. Environmental Protection Agency (U.S. EPA), established in 1978 under the National Contingency Plan, provides expertise in, and resources for, engineering studies to test alternative and innovative remediation technologies for Federal, State, and local agencies. The U.S. EPA Regions IV and V requested engineering support from the ERT to explore the applicability of soil washing, an alternative and innovative technology, to remediate two similar sites; Lee Farm in Woodville, Wisconsin, and Sapp Battery in Jackson County, Florida. At these two rural sites, the soil was contaminated with lead and lead compounds as a result of the processing and disposal of spent lead storage batteries. Preliminary remedial investigations at these sites indicated the contaminated material consisted of mostly soil and broken battery casings. This paper details the results of the bench-scale soil washing studies performed by the ERT and their Response Engineering and Analytical Contractor (REAC). The purpose of these studies was to explore the feasibility of soil washing with ethylenediaminetetraacetic acid (EDTA), a chelating agent, to treat lead contaminated materials. Chelating agents, such as EDTA, have the ability to bind with metal cations that would result from solubilizing metal salts, such as existed at the two sites.

Early efforts to chelate heavy metals focused on metal availability for plant uptake from soil and metal extraction from sewage sludge [1,2]. Early soil washing experiments used chelating agents on heavy metal spiked soils. Connick, et al. preadsorbed metal salts onto soil contained in columns and rinsed the soils with 0.14M ethylenediaminetetraacetic acid (EDTA) resulting in a 63, 93, 94, 100, and 86 percent removal of lead, zinc, nickel, cadmium, and copper, respectively [3,4]. Farrah and Pickering extracted preadsorbed clays to demonstrate the effectiveness of the metal-binding clay fraction. The binding energies of heavy metals to

soil changes with time until an equilibrium is established; therefore, the mobilization of heavy metals contaminants from preadsorbed soils, used in the previous studies, may not be representative of aged contaminated soils at hazardous waste sites [2,4]. Aged soils are more difficult to remediate by extraction due to the more tenacious contaminant binding. Other experimenters have explored chelation of soils from hazardous waste sites. At the Western Processing site, Ellis and Fogg used an EDTA sequential extraction to reduce lead, nickel, cadmium, copper, and chromium by 96, 22, 100, 75, and 52 percent, respectively [6]. In a pilot-scale study, the U.S. EPA Office of Research and Development, Releases Control Branch used EDTA in their soil washing system at Leeds, AL [7]. Additional chelating agents have also been explored. At Georgia Tech, use of ammonium pyrrolidinedithiocarbamate extracted 95 percent of the lead from the soil, while nitrilotriacetic acid was found to be less effective than EDTA for lead removal [8,9]. The Lee Farm and Sapp Battery studies used EDTA as the chelating agent of choice based on these previous efforts in lead removal from soils.

METHODS

Grain size distribution of the whole (unclassified) soils was determined by sequential screening with sieve sizes ranging from 0.25-in (6.35 mm) to # 325 (0.044 mm). Soil was placed on top of the largest screen and sprayed with water. All screening was performed with deionized water (DI) until water leaving the screen appeared clear. Soil remaining on the sieve was dried and weighed, then analyzed for total lead content. Soil passing through the screen was placed on top of the next smaller screen and the process repeated.

For lead analyses, each dried and weighed soil sample was placed in a Teflon-lined digestion bomb with concentrated nitric acid, then heated in an oven for one hour at 60°C and 12 hours at 120°C. After cooling, the soil extract was analyzed with a Spectra-Scan multi-channel DC Plasma Emission Spectrometer. U.S. EPA Method 1310 was used for Extraction Procedure Toxicity (EP Tox) analysis [10].

To facilitate soil handling and soil-liquid separation, the soil from both the Lee Farm and the Sapp Battery sites was classified into three fractions prior to soil washing. These fractions were designated: oversized, greater than 0.25-in; coarse, # 140 mesh (0.100 mm) to 0.25-in; and fine, less than # 140 mesh. The choice of particle size for the fractions was based on the anticipated performance of off-the-shelf soil-liquid separation equipment. Whole soil was classified by wet screening prior to EDTA-chelation experiments. For classification, soil was placed into a 5-gallon vessel containing a 0.25-in mesh and sprayed with DI water. The minus 0.25-in soil slurry was wet screened on a # 140 sieve until the water appeared clean. The less than # 140 soil fraction was allowed to settle overnight and the supernatant decanted. The following tests treated the coarse and oversized fractions of Lee Farm site soil, and the coarse and fine fractions of Sapp Battery site soil.

The soil washing tests used a four step process: extraction, a polish rinse, and two water rinses. For chelation, a 20 percent (w/w) aqueous solution of tetrasodium EDTA adjusted to pH 7.0 was mixed with a soil

fraction in a two liter reactor for 45-minutes at 100 rpm. In the Sapp Battery study, the effects of 10 percent EDTA and shorter chelation duration were also explored. The soil loading (the percent, w/w, of soil in the chelation solution) was 25-percent; however, a 45-percent loading was explored during the Lee Farm tests. Soil-liquid separation between steps was achieved by vacuum filtration in a Buchner funnel for Lee Farm, and by centrifugation for Sapp Battery. The polish rinse consisted of a 0, 2, or 5 percent EDTA solution mixed for 20-minutes with the chelated soil. This step was eliminated during the Sapp Battery trials, and an additional DI water rinse was substituted.

For the sequential chelations of Lee Farm soil, a 20 percent EDTA solution was repeatedly exposed to a new batch of contaminated soil at a 25% loading. The coarse soil fraction was chelated for 15-minutes followed by a 5-minute 2-percent EDTA polish and two water rinses. After extraction, the chelation was saved to extract the next sample of contaminated soil.

The Lee Farm oversized (plus 0.25 in) soil fraction was treated with an EDTA-free water wash rather than an EDTA extraction. The wash consisted of low pressure spraying the oversized material with a measured amount of deionized (DI) water based on a soil/water weight ratio.

RESULTS

Soil Characterization

Whole soil was characterized for particle size distribution, total lead, and EP Tox lead. Wet screening for particle size distribution revealed differences between soil samples from within the same site. The percent of soil comprising each fraction varied between samples from the Lee Farm site and the Sapp Battery site. From Lee Farm, the fine fraction varied from 10.2 to 25.5 percent of the whole soil, whereas for Sapp Battery, the variation was 15.3 to 22.4 percent. For the oversized fraction, samples from Lee Farm ranged from 19.0 to 28.7 percent. These results show the difficulties in obtaining homogeneous samples. For the oversized fraction, a large object or two can significantly affect the proportion of material retained by the largest screen. This variability between samples from the same site was observed with the oversized fraction because this fraction contained mostly stones, wooden debris, and broken polypropylene and bakelite battery casings.

Total lead analysis on the various soil particle distributions after wet screening showed that lead concentration increased with decreased soil particle size. At Lee Farm, the observed difference in lead concentration between the largest and smallest particles was greater than 2.5 orders of magnitude, and a Sapp Battery soil sample contained nearly 2.4 orders of magnitude greater lead concentration in the smallest particles (Figure 1). Thus, the fine fraction contained the majority of the soil's lead contaminant.

For the Lee Farm site, the investigation used the criteria of less than 5 mg/l EP Tox lead to designate the soil as non-hazardous. Therefore, EP Tox analyses was performed only for this site. EP Tox on the unclassified Lee Farm soil ranged from 43.0 to 68.7 with a mean of 60.2 mg/l lead. The



Figure 1. Lead distribution in soil by particle size

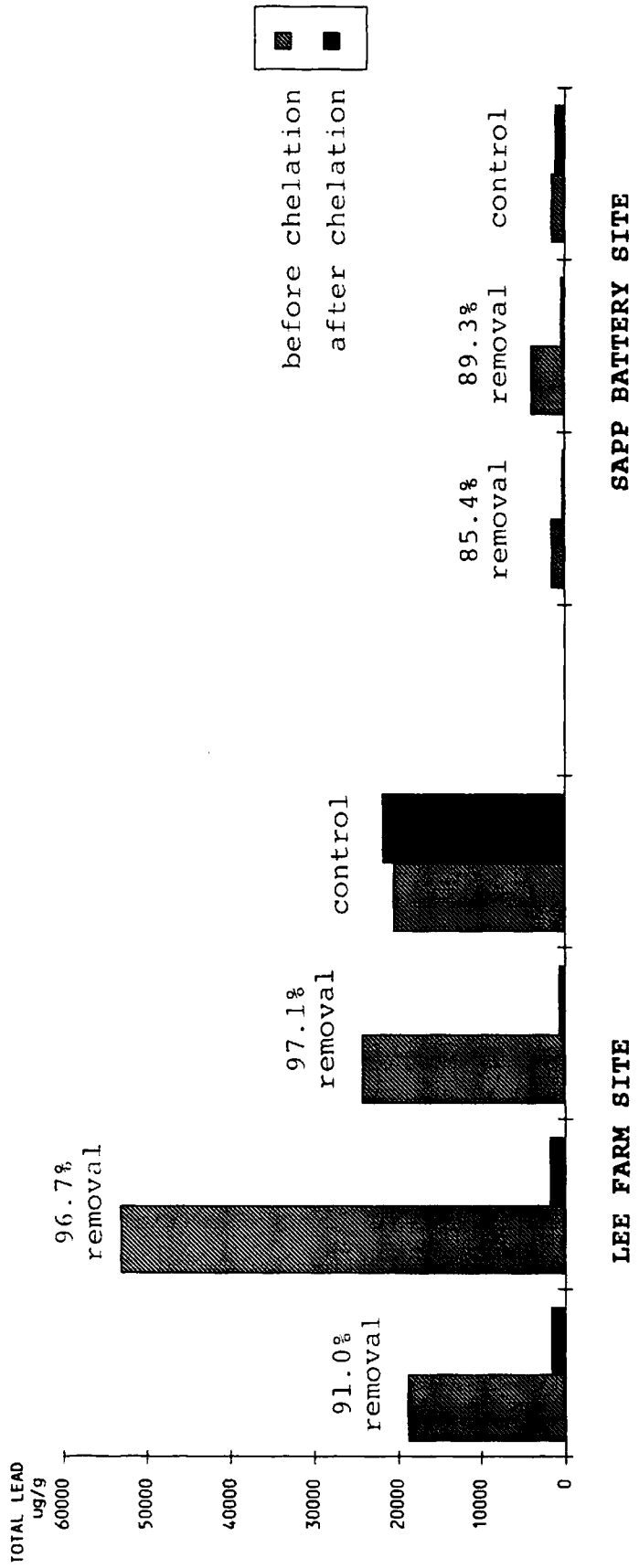


Figure 2. Lead removal from coarse soil fraction by EDTA chelation

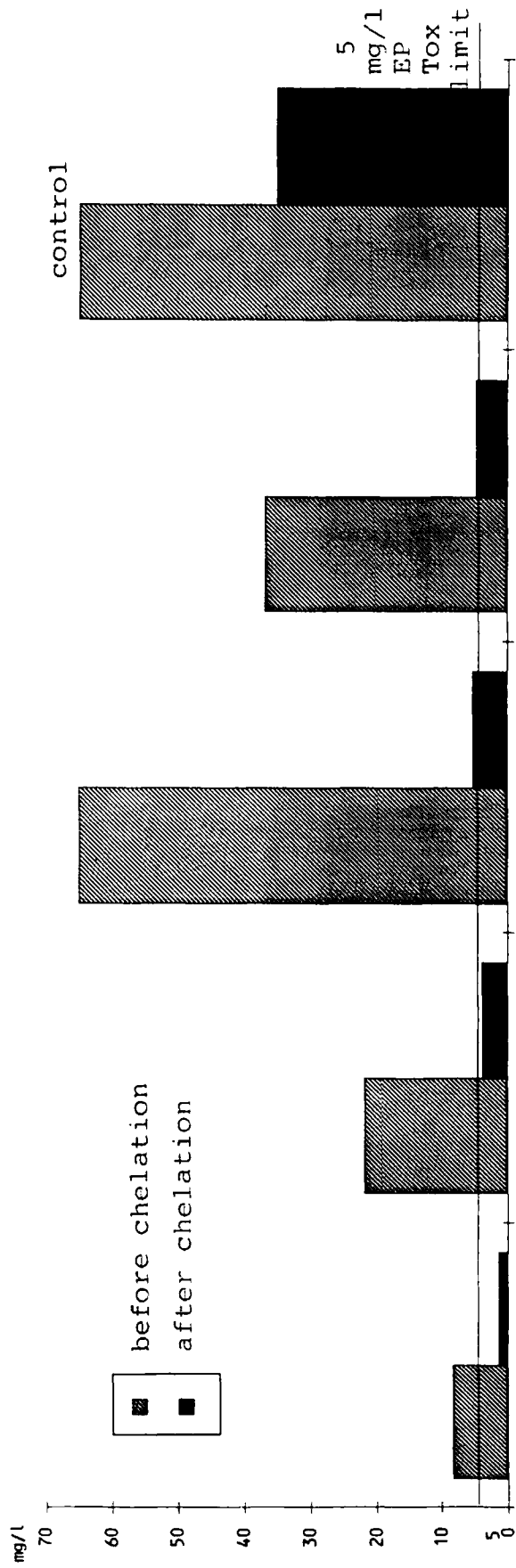


Figure 3. EP Tox lead reduction in the coarse fraction by EDTA chelation for the Lee Farm site

loading during chelation, EDTA concentration in the polish rinse, reaction time of the soil with the chelant, and EDTA concentration in the extraction.

The increase in chelation soil loadings from 25 to 45-percent did not significantly change the percentage of lead removed from the Lee Farm soil. In the 25-percent soil mixture, 97.1-percent of the lead was removed, while 91.0 to 96.7 percent was extracted from the 45-percent slurry. Therefore, the chelating ability of fresh extractant did not diminish with greater amounts of contaminant loading. This may be due to the excess in chelant.

The EDTA polish rinse was not only ineffective, but also detrimental to soil washing. The objective of the EDTA polish rinse was to remove residual lead from the soil after chelation. However, exposing soil to an EDTA polish rinse after chelation did not lower total lead in the treated soil; moreover, soil treated with the polish rinse had a high EP Tox lead content (Figure 4). The polish rinse caused more residual EDTA to remain in the washed soil, even after the two subsequent water rinses. This residual EDTA contained chelated, and therefore mobile, lead which was easily extracted during the EP Tox analysis.

Reductions in the soil-chelant reaction time can be made without sacrificing the effectiveness of the treatment. A 45-minute reaction, or contact time, was used to extract both soils. To explore the feasibility of a shorter reaction time, liquid chelant samples were drawn from the slurry at different intervals during Lee Farm soil extraction. A rapid uptake in lead by the chelant was observed. To correlate the rapid uptake by the chelant with the reduction of total lead in soil, another experiment explored the affect of shorter reaction duration on the residual total lead in extracted soil. The optimum soil-chelant contact time was 15-minutes. The 5-minute chelation shows promise, but more experiments are needed to verify that this reaction time can produce soil with low residual total lead.

An extraction solution containing reduced EDTA concentration produced results similar to the standard EDTA solution. A 10-percent EDTA solution was used to chelate both coarse and fine Sapp Battery soil fractions at the same extraction conditions used for the standard 20-percent EDTA solution (see Methods section). All other tests used the standard solution. No apparent differences in the washed soils' residual total lead resulted from the less concentrated solution. A 10-percent solution appeared to adequately reduce lead contamination. An additional set of sequential experiments tested the point at which the chelation solution would be considered ineffective.

The sequential chelations were performed to replicate a full-scale soil washing process in which soil is added to an extraction vessel in a batch-wise or continuous manner. This experiment was designed to explore the amount, or rate of, spent chelant removal from the extraction vessel and its subsequent replacement with fresh stock. After 11 chelations with the same EDTA solution, lead contamination was still being removed from the Lee Farm coarse fraction soil (Figure 5), and the average EP Tox lead concentration in treated soil remained under the 5 ppm criteria (Figure 6).

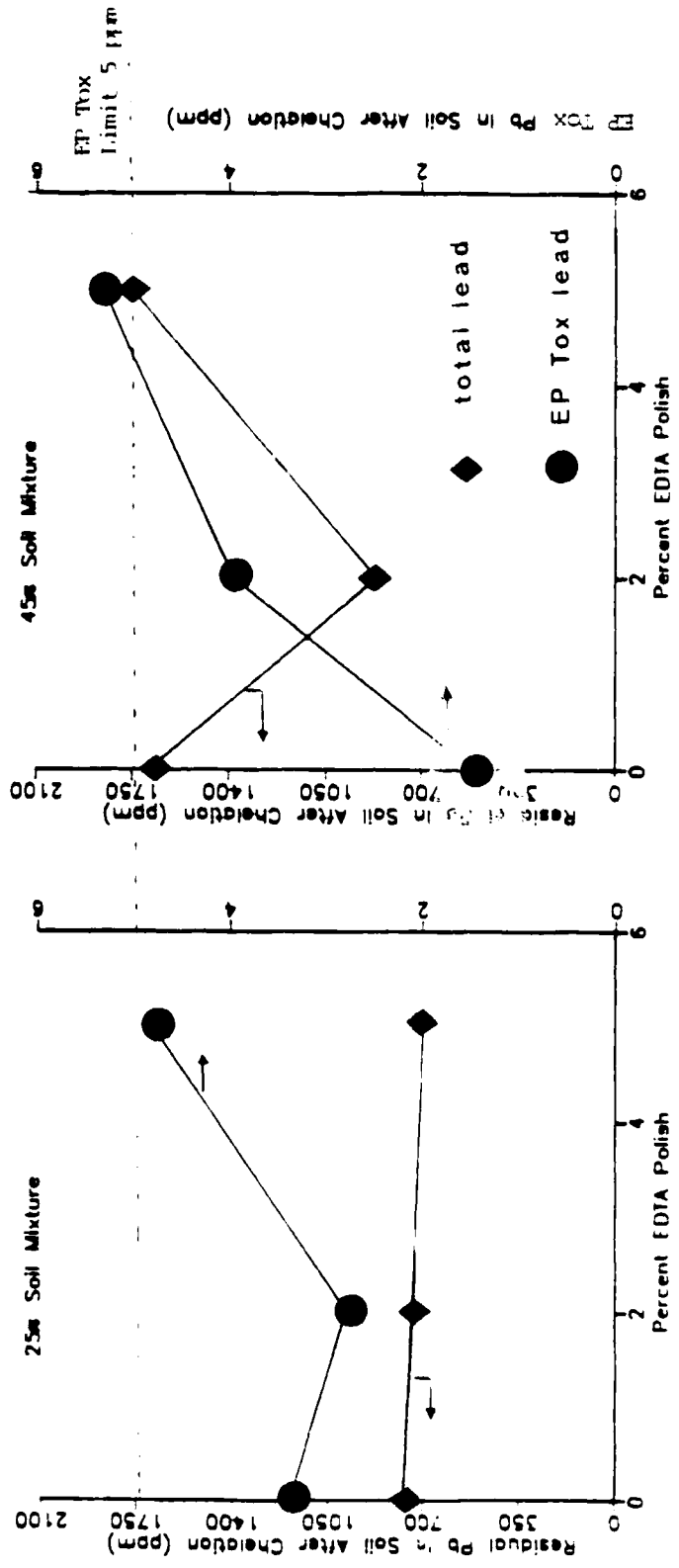


Figure 4. The effect of the polish rinse on residual total lead and EP Tox lead

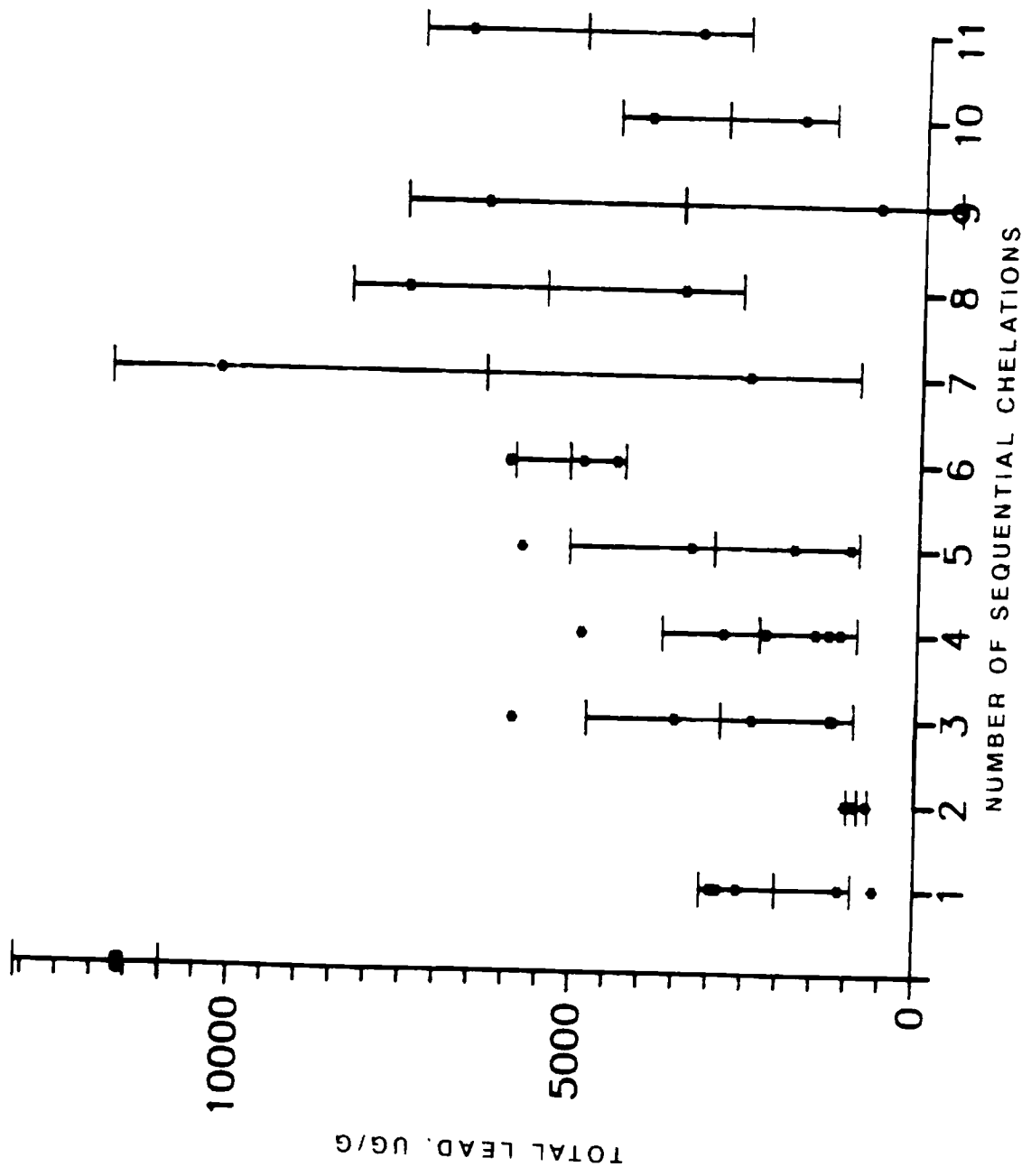


Figure 5 Residual total lead in soil after sequential chelations

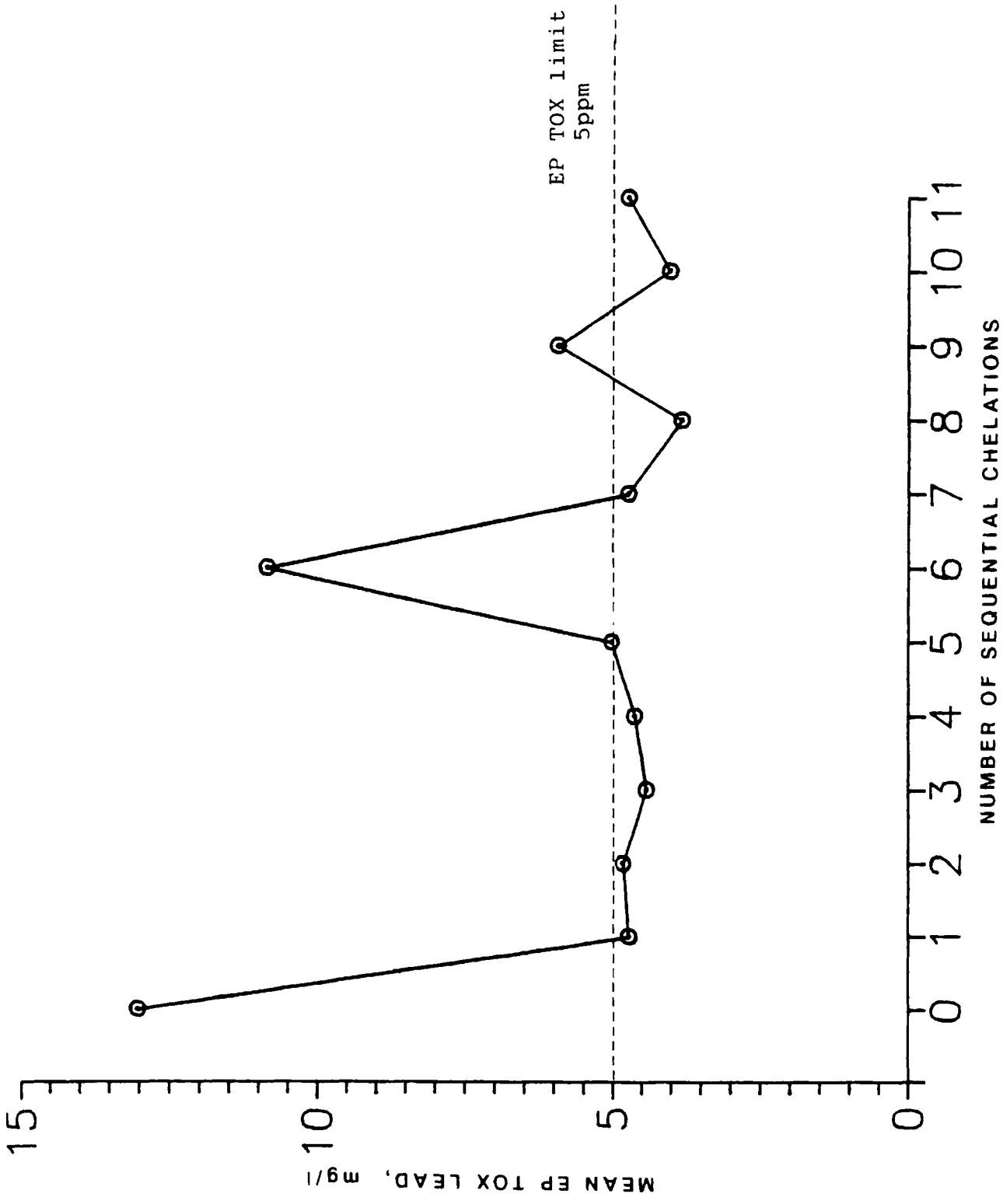


Figure 6. Residual EP Tox lead in soil after sequential chelations

The non-chelation, water-spray technique used to decontaminate the oversized soil reduced EP Tox lead concentrations. Since most of the lead contamination was in the small soil particles, the objective of this technique was to remove lead contaminated soil attached to the oversized fraction. To achieve the objective of physically removing the attached soil from the oversized fraction, the use of EDTA was unnecessary. As the volume of water used to spray increased, the EP Tox lead concentration decreased (Figure 7). After washing, however, the irregular surface of the rocks and battery casings still retained enough contaminated soil to yield excessive levels of EP Tox lead. The EP Tox values were the criteria of cleanliness. To achieve EP Tox levels below the 5 ppm limit, the rocks and casings must be sufficiently washed to remove all adhering soil.

DISCUSSION

Several factors characteristic of Superfund type soils combine to make these matrixes particularly difficult to remediate. One factor observed during soil characterization was the non-homogeneity between soil samples from different sites as well as among samples from the same site. This non-homogeneity was manifested as differences in contamination levels and soil characteristics. Other factors, such as contamination concentration fluctuations and soil fraction volumetric variations, add to the complexity of remediation. In addition, a matrix with such a wide particle size distribution (from boulders to 0.6 micron clay particles) has overwhelmed past attempts at soil washing. Further, these studies found the greatest concentration of lead in the smallest particle size fraction, and this fraction is the most difficult to dewater, a critical operation in soil washing. Therefore, the most important task for the engineer is to design a process with the flexibility to handle contaminant concentration and material volume variations. The best first step in accomplishing flexibility of design is to classify the soil according to particle size. This study classified the soils prior to extraction into 3 fractions according to particle size: oversized (greater than 0.25 in.), coarse, and fines (less than 0.100 mm). Such classification allows the process to be custom designed for each fraction. For example, remediation of the oversized fraction did not involve a chemical extractant. Also, floatables can be removed they enter the main flow of the soil washing system. Further, classification produces a soil matrix with a narrow particle size range; therefore, soil/liquid separation of the coarse and fine fractions can be tailored to each fraction.

EDTA proved to be an effective lead extractant. It achieved similar lead removals from soils of both sites. These removals agree well with the 95 percent lead removals achieved by other studies on aged Superfund type soils [6,8]. In addition, the extraction of lead from the Lee Farm coarse fraction met the clean-up criteria of 5-mg/l EP Tox lead in most washings. This makes soil washing a technically feasible option for the coarse fraction from this site. However, soil washing could not attain the 79 ug/g total lead criteria for Sapp Battery soil. Quite possibly, a multiple wash using additional extraction agents, such as those used by Ellis and Fogg, could mobilize additional soil-bound lead into the extractant [6].

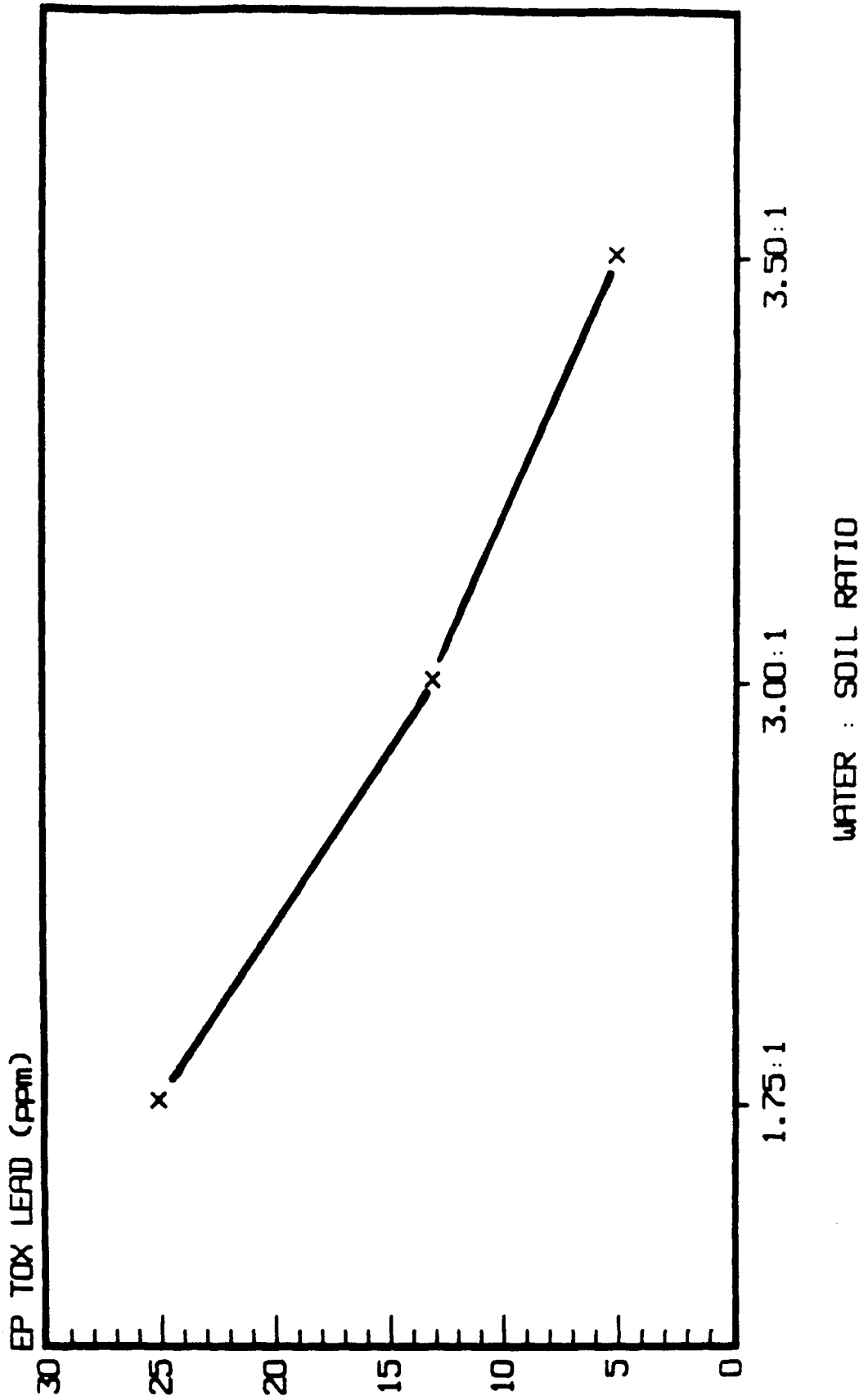


Figure 7 The effect of water spray volume on the residual EP Tox lead in the oversize fraction

The investigation into the effects of certain process factors yielded results that could produce an economical treatment process. No loss in treatment effectiveness occurred with the 45-percent soil loading during extraction. Furthermore, the results of lead uptake by the chelation solutions, and the residual total lead concentration of the treated soils sampled during the chelation reaction, indicated that a 15-minute reaction time is optimum. Both these results lead to the design system with a high soil throughput that would be effective in lowering treatment costs.

This study yielded additional information to aid in the design of an economical process. The study found that the incorporation of an EDTA polish rinse following the extraction step reduced the acceptability of the treated soil with no beneficial reduction in total lead as expected. Also, the polish rinse exhibited increasing EP Tox lead values with increasing polish EDTA concentrations. The EP Tox procedure is sensitive to the amount of mobile lead. During the extraction steps, all efforts are focused on mobilizing the lead contaminant with, in this case, a chelation solution. After extraction, the primary concern is removal of the mobile contaminant (Pb-EDTA complex) through sequential soil-liquid separation and rinsing. The introduction of a polish rinse leaves residual EDTA lead complex in the soil. This highly mobile species is readily picked up in the EP Tox analysis, and is a cause of treated soil exceeding the EP Tox limitation. Therefore, the elimination of the EDTA polish rinse would produce a simplified process and reduce treatment costs.

For the batch or continuous operation of a soil washing process it is necessary to know when, or at what rate, to add fresh extractant. The addition of fresh chelant is determined by the acceptability of the final product (i.e., clean soil). The sequential extraction experiments attempted to determine when fresh chelant should be added. However, physical limitations in the experimental procedure precluded sufficient chelations from being performed to make this determination. The test did find that acceptably clean soil (based on the residual EP Tox lead) was produced after eleven sequential chelations with the free-EDTA concentration was reduced to approximately 5 percent. Thus, the experiments indicate that soil could be remediated even at low free-EDTA concentrations.

CONCLUSION

In conclusion, these studies showed:

- o Soil classification, prior to extraction, was an essential step in soil washing;
- o EDTA was an effective extraction agent for lead contaminated soil;
- o After soil washing, Lee Farm site soil met the 5 mg/l EP Tox lead clean-up criteria; the Sapp Battery site soil did not meet the 79 ug/g total lead clean-up criteria;
- o Incorporating high soil loading and shorter reaction time will improve process efficiency;

- o The EDTA polish rinse is detrimental to soil washing and should be eliminated;
- o Sequential chelation with the same chelant solution did not adversely affect lead removal;
- o Finally, soil washing is an emerging technology that may have an application treating lead and other heavy metal contaminants in soil.

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