
REMEDIATION OF LEAD-CONTAMINATED SOIL WITH EDTA: BATCH AND COLUMN STUDIES

D.M. Heil¹, Z. Samani², A.T. Hanson², S. Hu², and B. Rudd², ¹Department of Agronomy and Horticulture, New Mexico State University, and ²Civil, Agricultural, and Geological Engineering Department, New Mexico State University, Las Cruces, NM, 88003, Phone: 505-646-2219, FAX: 505-646-6041

ABSTRACT Chelate extraction using ethylenediaminetetraacetic acid (EDTA) and other chelates has been demonstrated to be an effective method of removal of Pb from many contaminated soils. However, column leaching of Pb from alkaline soils with EDTA has been problematic due to extremely low soil permeability. The purpose of this study was to determine the effect of the addition of KOH and Ca(Cl)₂ to K₂H₂EDTA extraction solution on Pb removal and hydraulic conductivity. A Pb-contaminated soil was sampled from an abandoned lead-acid battery recycling facility. Both batch shaker extractions and column leaching experiments were completed using five different EDTA extract solutions. Addition of Ca(Cl)₂ only to K₂H₂EDTA did not change the amount of Pb removed by batch extraction, and Pb solubility was only slightly decreased by the addition of both Ca(Cl)₂ and KOH. Lead solubility was observed to decrease as pH was increased by the addition of KOH. The amount of time required to leach 6.0 l of extraction solution through the soil columns varied from 2 to 33 days. The addition of Ca(Cl)₂ and/or KOH resulted in increased soil hydraulic conductivity. However, Pb removal was diminished with the addition of Ca(Cl)₂ and KOH because of decreased Pb solubility and also a shorter residence time of the extract solution in the column. The hydraulic conductivity was related to residual calcium carbonate content, suggesting that dissolution of CaCO₃ and subsequent production of CO₂ gas in soil pores was partially responsible for the observed reductions in soil permeability.

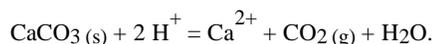
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INTRODUCTION

Lead contamination of soils is a common problem throughout the world. The principal sources of soil contamination are automotive and salvage yards and secondary lead smelters. Currently, the United States Environmental Protection Agency favors permanent treatment of contaminated soils over other alternatives such as disposal or containment. Metal extraction with the aid of a chelating agent is a widely used technique. Ethylenediaminetetraacetic acid (EDTA) is one of the most popular and powerful chelating agents and has been widely used for lead extraction from contaminated soils.

Laboratory tests have shown that batch extraction with EDTA is effective in removing lead from some of the contaminated soils tested [1-6]. Although these same soil washing methods used in the laboratory could be scaled up to treat larger amounts of soil, it may be more practical and economical to leach the soil by either column or heap leaching. A major problem in remediation of lead-contaminated soils with EDTA is the dramatic reduction of soil permeability. Hanson, *et al.* [7] found that the permeability of a calcareous soil contaminated by lead-acid battery recycling operations (the Cal-West Superfund site) was decreased to an extremely low rate when leached with di-potassium, di-hydrogen EDTA. During the leaching of soil columns in their experiments, bubbles were

observed to form in soil macropores, beginning near the top of the column. This may be the result of dissolution of calcium carbonate minerals (present in the soil at 5% content by mass) as indicated by the following reaction:



Since the pH of the 0.10 M EDTA extract solution used was acidic (pH < 4.0), this solution can be expected to dissolve CaCO_3 and produce carbon dioxide gas as shown in the reaction above. It has also been determined from batch extraction experiments that a high proportion of $\text{K}_2\text{H}_2\text{EDTA}$ added to the Cal-West soil formed complexes with calcium [6], which would further contribute to the dissolution of calcium carbonate and $\text{CO}_2(\text{g})$ production by driving the above reaction to the right-hand side.

Increasing the pH of the EDTA extract solution by the addition of a base such as KOH should minimize the solubility of CaCO_3 . The addition of equi-molar amounts of Ca and EDTA should eliminate the removal of Ca from exchange sites and the soil solution, and also inhibit the dissolution of calcite. However, either of these adjustments may decrease the solubility of lead in the soil. It has previously been determined that Pb removal from the Cal-West soil was enhanced at acid pH [6]. The addition of Ca to the extract solution may also be expected to decrease Pb extraction due to higher levels of Ca^{2+} in solution, which could result in competition between Pb and Ca for complexation to EDTA. Therefore, the purpose of the current research was to determine the effects of adjustment of the chemical composition of EDTA extract solution on both hydraulic conductivity and Pb removal from the Cal-West soil.

EXPERIMENTAL METHODS

Batch extractions

Batch extractions of the < 2 mm size fraction of the Cal-West soil were completed by adding 150 ml of EDTA solution to 10 grams of soil in 250 ml centrifuge bottles. The concentration of $\text{K}_2\text{H}_2\text{EDTA}$ was adjusted to give a molar ratio of total EDTA in the extracting solution to total Pb in the soil varying from 0.30 to 30.0. For the Cal-West soil, this corresponded to a concentration of EDTA from $.001 \text{ mol l}^{-1}$ to 0.10 mol l^{-1} . The extraction at the highest molar ratio of EDTA was repeated to provide Pb solubility data at low soil Pb levels. The effect of pH adjustment and addition of $\text{Ca}(\text{Cl})_2$ on Pb extraction was evaluated by preparing five series of extract solutions. The first series contained equivalent concentrations of $\text{K}_2\text{H}_2\text{EDTA}$ and $\text{Ca}(\text{Cl})_2$. The second series contained $\text{K}_2\text{H}_2\text{EDTA}$ only. The third series contained $\text{K}_2\text{H}_2\text{EDTA}$ adjusted to a pH of 7.0 with KOH. The fourth series contained equivalent concentrations of $\text{K}_2\text{H}_2\text{EDTA}$ and $\text{Ca}(\text{Cl})_2$, with the final pH adjusted to 7.0. The fifth series contained equivalent concentrations of $\text{K}_2\text{H}_2\text{EDTA}$ and $\text{Ca}(\text{Cl})_2$, with the same amount of KOH added to adjust the pH of the $\text{K}_2\text{H}_2\text{EDTA}$ solution in the absence of $\text{Ca}(\text{Cl})_2$ to 7.0. Seven concentrations of EDTA were prepared for each series, except that only the lowest (molar ratio = 0.30) and highest (molar ratio = 15.0) EDTA concentrations were used for the fourth series. Each treatment was done in triplicate. After 72 hours of shaking, the bottles were centrifuged for 15 minutes and then the extract solution was filtered through $.45 \mu\text{m}$ pore size filters. Total Pb concentration in the extract solutions was determined by atomic absorption spectroscopy. The pH and Ca^{2+} ion activity were also measured by ion selective electrodes.

Extraction kinetics

Batch shaker extractions were conducted using series 2, 3, and 5 extract solutions from above at a total EDTA concentration of 0.05 M in order to evaluate the effects of pH adjustment and Ca(Cl)₂ addition on extraction kinetics. The procedure was identical to that described previously except that samples of extract solution were collected at 3, 6, 15, and 30 minutes and also at 1, 2, 6, 24, 48, and 72 hours. The concentration of Pb reached a maximum value after 24 hours of shaking for each of the extract solutions, and did not increase with longer periods of shaking. Although the final total dissolved Pb concentration was different for the three EDTA solutions, the fraction of the equilibrium Pb concentration which was reached at each of the sampling times was very similar for each of the solutions. Subsequently, the values of Pb dissolution rate constants calculated for the three extract solutions were very similar.

Extraction kinetics experiments were done at saturation moisture content without mixing to more accurately simulate Pb dissolution in soil columns. This was done by adding 10.0 ml of 0.05 M K₂H₂EDTA solution to 2.5 grams of soil in 20 ml plastic syringes. Extract solution was sampled after 3, 6, 15, 30 minutes and 1, 2, 6, 24, and 72

hours of contact by connecting syringes to filter holders containing 0.22 µm pore size filters and then placing on a vacuum filtration chamber. Approximately 1 ml of extract solution was collected at each sampling; 20 ml water was added to provide enough solution for analysis, and the dilution factor was recorded. Total Pb concentration was measured by atomic absorption spectroscopy.

Column experiments

Extraction solutions containing 0.05 M K₂H₂EDTA and KOH and/or Ca(Cl)₂ at the same composition as the 5 series of batch extract solutions were prepared as listed in Table 1. Leaching experiments were conducted by placing 800 grams of soil in each of five 30 cm x 5 cm glass columns. The height of soil in each column was 27 cm. A total of 6.0 l of extract solution was leached through each column. Columns were initially wetted to saturation from the bottom to avoid entrapment of air in the soil pore space. A constant hydraulic gradient was maintained throughout leaching of all columns by using a fixed-level solution reservoir [8]. Solution was ponded above the soil layer in each column to a depth of 2.0 cm. Leachate solutions were collected in increments of approximately 100 ml initially

TABLE 1. CHEMICAL COMPOSITION OF EDTA EXTRACT SOLUTIONS USED IN COLUMN EXPERIMENTS.

Extract Solution	[K ₂ H ₂ EDTA]	[Ca(Cl) ₂]	[KOH]	pH
	mol l ⁻¹			
A	0.05	0.05	0	3.23
B	0.05	0	0	3.70
C	0.05	0	0.049	7.00
D	0.05	0.05	0.111	7.00
E	0.05	0.05	0.049	3.85

and increasing to approximately 500 ml at the end of leaching. The volume of effluent and time of collection was recorded for the determination of hydraulic conductivity. The pH and calcium ion activity of each effluent sample was measured immediately after collection. The concentration of Pb in each extract solution was also measured by atomic absorption spectroscopy. After leaching, the soil was removed from each column with a plunger and divided into five sections, each of 5.4 cm length. The final soil pH was measured as a saturated paste. Total residual Pb concentration in the leached soil was measured following digestion in aqua regia and hydrofluoric acid [9]. The residual content of calcium carbonate was determined by a gravimetric method [10].

ANALYSIS OF DATA

Batch extractions

Measurements of EDTA concentration in Cal-West soil extract solutions using anion chromatography showed that at least 98% of added EDTA remained soluble after reaction with the soil. Consequently, the mole fraction of Pb-EDTA complex was calculated by dividing the measured Pb concentration by the total added EDTA concentration. The corresponding remaining soil Pb concentration was obtained by subtracting the amount of dissolved Pb from the initial total soil Pb concentration. This analysis provided Pb dissolution isotherms for each of the five EDTA extract solutions.

Kinetic extraction experiments

Lead dissolution kinetics can be described by the following first-order rate equation [11]:

$$\frac{dC}{dt} = K(C_{eq} - C), \quad (1)$$

where C = concentration of lead in the bulk solution; C_{eq} = equilibrium Pb concentration; and K = first-order rate constant.

The integrated form of this equation may be used to determine the value of the coefficient K from experimental data:

$$\ln(C_{eq} - C_t) = \ln C_{eq} - Kt, \quad (2)$$

where C_t is the concentration of Pb at time t . The concentration of Pb dissolved at any time is then expressed as

$$C_t = C_{eq} - \exp(\ln C_{eq} - Kt). \quad (3)$$

RESULTS AND DISCUSSION

Batch extractions

The solubility of Pb as a function of residual soil Pb concentration was the highest for extract solution series 1 and 2 (Figure 1). The addition of KOH to increase the pH of the extracting solutions to 7.0 decreased Pb solubility (series 3 in Figure 1). Extract solution series 5, which consisted of addition of $\text{Ca}(\text{Cl})_2$ plus the same amount of base used in series 3, exhibited lower Pb solubilities than series 3 at residual soil Pb concentrations of greater than 2,500 ppm (Figure 1), probably resulting from interference by Ca^{2+} complexing to EDTA. However, Pb solubility was greater for series 5 than for series 3 at soil Pb concentrations below 2,500 ppm. This was due to the acidification of the soil by series 5 extraction solution at high concentrations of added EDTA (Table 2). The amount of Pb extracted by series 4 was 93.4% and 84.6% of the amounts extracted by series 5 at EDTA concentrations of 2.5 and 50 mM, respectively (data not shown). This was the result of a much higher pH with series 4 than with series 5 after reaction with the soil (Table 2). The pH of the soil after reaction with series 4 extract solution was higher than

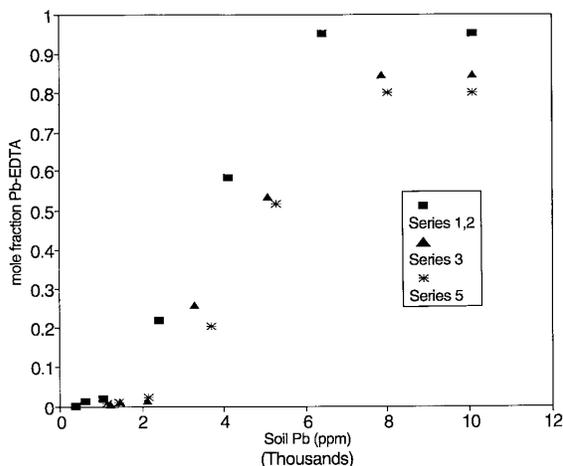


FIGURE 1. LEAD SOLUBILITY ISOTHERMS FOR THE CAL-WEST SOIL IN EDTA EXTRACT SOLUTION.

the pH of either the untreated soil (approximately 8.10) or the pH of the extracting solution (7.00). The buffering capacity of the soil was exceeded at high concentrations of acidic EDTA solutions (series 1, 2, and 5), resulting in a drastic reduction of soil pH (Table 2).

Kinetic extraction experiments

The first-order dissolution rate equation did not adequately model dissolution of Pb from the Cal-West soil in the presence of EDTA due to a substantial decrease in the experimentally-measured lead release rate between three and six minutes reaction time

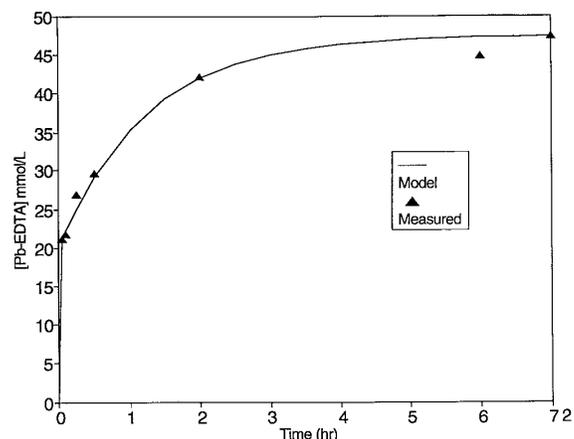


FIGURE 2. TIME-DEPENDENT DISSOLUTION OF Pb BY EDTA EXTRACT SOLUTION AND FIT OF DATA TO THE TWO-REGION KINETIC MODEL.

(Figure 2). Since no other data points were measured at a reaction time of less than three minutes, it was not possible to determine a rate constant for reaction times shorter than this. The experimental data was modeled by applying a two-region model. A rapidly dissolving phase was considered to release the amount of Pb measured after three minutes. A second, more slowly dissolving phase was modeled by the first-order rate equation (Equation 2). A deconvolution of the amounts of Pb released after three minutes by the two separate phases was accomplished by calculating the concentration of Pb released by the slow phase after three minutes (0.97 mmol l^{-1}),

TABLE 2. SOIL pH AFTER BATCH EXTRACTION WITH EDTA.

[EDTA] mol l ⁻¹	Series 1	Series 2	Series 3	Series 4	Series 5
	pH				
0.0025	8.06	8.44	8.87	8.97	8.52
0.025	5.91	5.85	7.20		6.40
0.05	3.87	4.99	7.14	9.34	5.70
0.10	3.74	4.78	7.08		4.01

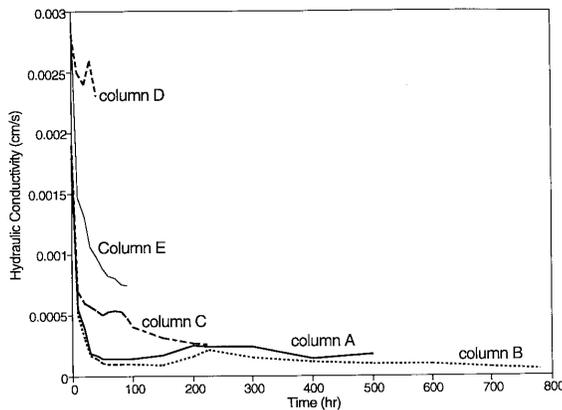


FIGURE 3. CHANGE IN HYDRAULIC CONDUCTIVITY OF SOIL COLUMNS WITH TIME.

and subtracting this amount from the total Pb concentration dissolved at that time. The value of the overall rate constant, K , was 0.80 hr^{-1} . Soluble Pb concentrations calculated by this two-region model accurately fit the experimental data (Figure 2).

Column experiments

The five EDTA extract solutions which were tested resulted in very different hydraulic conductivities when leached through the Cal-West soil (Figure 3). Initial hydraulic conductivities were comparable for all five extraction solutions (Figure 3). The Cal-West soil is coarse-textured (75% sand, 20% silt, and 5% clay) and was highly permeable in the early stages of leaching. The total amount of time required to leach 6.0 l of extract solution through columns A, B, C, D, and E was 23, 33, 9, 2, and 4 days, respectively. Soil macropores were observed to fill with gas bubbles, beginning at the top of the columns, especially in columns A and B. The gas bubbles are presumably CO_2 caused by the dissolution of calcium carbonate. The presence of gas in the macropores caused a change from saturated to unsaturated flow and a significant

reduction in hydraulic conductivity as shown in Figure 3. The magnitude of the observed reduction in the hydraulic conductivities in the five soil columns follows the same trend as residual calcium carbonate content (Table 3), suggesting that a CO_2 production mechanism was responsible for the observed decreases in hydraulic conductivity.

Lead removal was greatest from columns A and B (Table 4), which is consistent with Pb solubility isotherms determined from batch extractions (Figure 1). The soil in the upper sections of columns leached with acid EDTA solutions were acidified to a greater extent compared to lower column sections (Table 5). The EDTA extract solution used in column A was observed to precipitate after preparation, both in the solution reservoir and also at the edges of the top of the column. This resulted in a lower EDTA concentration actually leaching through column A, which is likely responsible for the slightly higher residual soil Pb in column A vs. column B. Analysis of the hydraulic conductivities of the five columns and the pore volume of the soil column (200 ml) suggests that extraction of Pb from columns A and B should not be limited by kinetics of Pb dissolution, given that equilibrium Pb dissolution was essentially reached after six hours of reaction in batch experiments (Figure 2). However, the hydraulic conductivities observed in columns C, D, and E indicate that equilibrium between the extract solution and the soil will not be reached in these columns. Residual Pb concentration was less for column C than for column E, possibly the result of greater Pb solubility (at soil-Pb concentrations greater than 2,500 ppm) and also a longer contact time between soil and extract solution in column C due to a lower flow rate. The amount of Pb removed from column D was much less than from column E, although only a slight difference in Pb solubility was

indicated from batch extractions. The ineffectiveness of extraction of Pb from column D is, therefore, attributable to the short contact time resulting from the relatively high hydraulic conductivity compared to column E.

CONCLUSIONS

Dissolution of calcium carbonate minerals inherent to the calcareous soil and subsequent CO₂ gas production appears to be responsible for the extreme reduction in hydraulic conductivity observed when leaching the Cal-West soil with acidic K₂H₂EDTA. A similar problem can be expected when leaching other calcareous soils with acidic EDTA. The hydraulic

conductivity of soil columns was greatly increased by increasing the pH and/or adding Ca(Cl)₂ to the EDTA extract solution. However, Pb removal was diminished, apparently the result of a combination of decreased equilibrium Pb solubility and a kinetically limited Pb dissolution in columns with higher flow rates. Extract solution C may be considered to be the optimal selection for remediation of this particular soil, given the desirable combination of Pb removal and length of extraction time required. Furthermore, the use of extract solution C minimized the breakdown of soil structure and maintained soil pH near the native value. These results also clearly illustrate that both Pb removal

TABLE 3. CALCIUM CARBONATE CONTENT IN SECTIONED SOIL COLUMNS LEACHED WITH EDTA EXTRACT SOLUTIONS.

Depth cm	Column				
	A	B	C	D	E
	% CaCO ₃				
0-5.4	0.59	0.12	0.72	4.62	0.82
5.4-10.8	0.62	0.12	0.87	5.12	0.87
10.8-16.2	1.32	0.12	1.62	4.37	3.62
16.2-21.6	3.12	0.00	2.67	4.62	3.37
21.6-27	3.90	1.12	3.12	5.47	4.37
Average	1.91	0.30	1.88	4.84	2.61

TABLE 4. RESIDUAL Pb CONTENT IN SECTIONED SOIL COLUMNS LEACHED WITH EDTA.

Depth cm	Column				
	A	B	C	D	E
	Pb (ppm)				
0-5.4	219	199	252	3,130	236
5.4-10.8	219	193	312	4,120	490
10.8-16.2	368	272	692	5,340	1,200
16.2-21.6	722	333	1,315	4,670	1,405
21.6-27	750	460	1,425	4,790	1,475
Average	456	291	800	4,410	961

and soil permeability are sensitive to the chemical composition of the extract solution, and “over-adjustment” of the extract solution may cause undesirable results.

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REFERENCES

1. H.A. Elliott and G.A. Brown, Comparative evaluation of NTA and EDTA for extractive decontamination of Pb-polluted soils, *Water, Air, and Soil Pollut.*, 45 (1989) 361-369.
2. B. Tuin and M. Tels, Removing heavy metals from contaminated soils by extraction with hydrochloric acid, EDTA, or hypochlorite solutions, *Environ. Tech.*, 11 (1990) 1039-1052.
3. G.A. Brown and H. Elliott, Influence of electrolytes on EDTA extraction of Pb from polluted soil, *Water, Air, and Soil Pollut.*, 62 (1992) 157-165.
4. W.F. Kemner and E.R. Krishnan, Electromembrane process for recovery of lead from contaminated soils, In: *Innovative Hazardous Waste Treatment Technology Series, Vol. 2: Physical/Chemical Processes*, Technomic Publishing Co., Inc., Lancaster, PA., 1990, pp. 87-96.
5. A.T. Hanson, B. Dwyer, R. Jacquez, and Z. Samani, Colloidal and interfacial aspects of groundwater and soil clean-up, American Chemical Society, (1992).
6. D. Heil, A.T. Hanson, and Z. Samani, The competitive binding of lead by EDTA in soil and implications for heap leaching remediation, *Radioactive Waste Management and Environmental Restoration Journal*, 20 (1996) 111-127.
7. A.T. Hanson, Z. Samani, B. Dwyer, and R. Jacquez, Heap leaching as a solvent-extraction technique for the remediation of metals-contaminated soils, In: *Transport and Remediation of Subsurface Contaminants*, A.C.S. Symposium Series 491, 1992, pp. 9-21.
8. A. Klute and C. Dirksen, Hydraulic conductivity and diffusivity: Laboratory methods, In: A. Klute (Ed.), *Methods of*

TABLE 5. THE FINAL pH OF SECTIONED SOIL COLUMNS LEACHED WITH EDTA EXTRACT SOLUTIONS.

Depth cm	Column				
	A	B	C	D	E
0-5.4	3.44	4.89	7.04	9.40	4.05
5.4-10.8	3.62	5.08	7.20	9.85	5.79
10.8-16.2	4.16	5.31	7.34	10.00	6.28
16.2-21.6	6.31	6.73	7.47	10.00	6.33
21.6-27	6.42	7.45	7.63	9.99	6.72

Soil Analysis Part I, Physical and Mineralogical Methods, American Society of Agronomy, Madison, WI, 1986, pp. 687-734.

9. C.H. Lim and M.L. Jackson, Dissolution for total elemental analysis, In: A.L. Page (Ed.), Methods of Soil Analysis Part II, Chemical and Microbiological Properties, American Society of Agronomy, Madison, WI, 1982, pp. 1-12.
10. S.J. Gale and P.G. Hoare, Quaternary Sediments, Petrographic Methods for Study of Unlithified Rocks, Belhaven Press, 1991.
11. M.V. Ruby, A. Davis, J.H. Kempton, J.W. Drexler, and P.D. Bergstrom, Lead bioavailability: Dissolution kinetics under simulated gastric conditions, Environ. Sci. Tech., 26 (1992) 1242.