

REMOVAL OF LEAD AND CHROMIUM FROM CONTAMINATED SOIL: COLUMN STUDIES

J. Pichtel, Angela Covey, and K. Lukscay

Department of Natural Resources and Environmental Management
Ball State University
Muncie, Indiana 47306-0495

ABSTRACT: Ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) were evaluated in column studies (each 0.1, 0.01, or 0.001 M) for their ability to extract lead (Pb) and chromium (Cr) from contaminated soil ($Pb_{tot} = 1300$ mg/kg; $Cr_{tot} = 4940$ mg/kg; pH = 10.3) collected at an abandoned industrial facility. The EDTA was eluted at pH 3.0, 5.5 (ambient), and 10.0, and the NTA at pH 3.0 and 11.1 (ambient). The efficiency of Pb and Cr solubilization was influenced by solution pH and chelant-metal chemistry; the EDTA, a hexadentate ligand, solubilized both metals more effectively than did the quadridentate NTA. Lead and Cr removal increased with higher EDTA concentrations; however, higher NTA concentrations did not remove significantly greater amounts of Pb or Cr ($P < 0.05$). The 0.1 M EDTA at pH 3.0 and 10.0 removed 86.5% and 87.1% Pb after 200 pore volumes, respectively. The 0.1 M NTA (pH 3) recovered 29.5% soil Pb. The 0.1 M EDTA, pH 5.5, recovered 40.9% soil Cr, and the 0.1 M NTA at pH 11.1 removed 28.5%. The lower Cr removal compared to that for Pb may be explained by the chemical forms of each metal in the soil: 89.8% Cr occurs in residual forms, which are not readily extractable except by exhaustive processes. In contrast, only 45.7% Pb occurs in residual form. Initial flushing with 0.1 N HCl followed by chelant flushing did not significantly improve removal of either Pb or Cr. Pb removal via soil flushing was equal or greater in effectiveness to that by *ex-situ* processes.

KEYWORDS: Chromium, EDTA, lead, NTA, soil flushing.

INTRODUCTION

Soils at numerous industrial sites are contaminated with heavy metals (Richards, *et al.*, 1993; Cairney, 1987). Metal-rich sites pose potential hazards to public health and the environment via contamination of groundwater and surface water as well as through plant uptake.

The use of technologies which eliminate or reduce the hazardous characteristics of waste is now being given greater priority over traditional contaminant removal methods, such as excavation followed by landfilling. Available treatment technologies for remediating metal-contaminated soils include solidification/immobilization processes, soil washing (*ex-situ*), and soil flushing (*in-situ*).

Metals on weathered metalliferous sites occur in complex forms (Kabata-Pendias and Pendias, 1992), and their mobility is controlled by several chemical and physical phenomena, including soil pH, soil type, cation exchange capacity,

particle size, contaminant concentration, and the presence of organic and inorganic compounds. Many of these factors are interdependent (Reed, *et al.*, 1995). Metal removal efficiencies during soil flushing depend not only on soil characteristics but also on metal characteristics, extractant chemistry, and processing conditions. Chelating agents, such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA), bond with the metal to facilitate solubilization in the extraction medium. The ability to form stable metal complexes makes EDTA and NTA effective extractants for metal-contaminated soils (Davis and Singh, 1995; Elliott and Brown, 1989; Cline, *et al.*, 1993).

Chelants vary in effectiveness for Pb or Cr removal; the result is affected by the presence of different solid forms of the metals in the soils, differences in pH during extraction, and interference from other cations which complex with the chelate (Elliott and Brown, 1989; Brown and Elliott, 1992; Tuin and Tels, 1990; Hsieh, *et al.*, 1989; Shirk and Farrel, 1985). The solid forms of Pb or Cr present in a soil depend on the source of the contamination and also the extent of redistribution of the metal in the soil following contamination. After Pb or Cr is added to soil, they may be redistributed by the formation of secondary mineral precipitates, adsorption onto soil mineral particles, or by complexation with soil organic matter (Heil, *et al.*, 1996).

In certain situations, remediation via *ex-situ* processes may be difficult if a site contains utilities or structures. Thus, an *in-situ* treatment process (i.e., forcing an extractant through an intact soil to flush out metals) would alleviate some of these problems. In general, *in-situ* technologies are able to treat large volumes of soil more economically and more safely than *ex-situ* technologies because there is no excavation (Reed, *et al.*, 1995). However, little fundamental research has been carried out on the *in-situ* flushing of metals (Davis and Singh, 1995).

Recent soil treatment studies have assessed remediation effectiveness of soils spiked with soluble metal salts (Cline and Reed, 1995; Reed, *et al.*, 1995; Davis and Singh, 1995; Chen, *et al.*, 1995; Macauley and Hong, 1995). The removal efficiencies measured may be greater than those observed when washing contaminated soils which have been weathered for long periods. In the current study, the authors investigated the use of several solutions for Pb and Cr removal from a soil contaminated for decades with metals in various insoluble forms. Specifically, the objectives were to (1) assess the relative abilities of EDTA and NTA in the *in-situ* extraction of Pb and Cr from a contaminated soil and to (2) compare the effectiveness of *in-situ* and *ex-situ* metal removal from the soil. In a previous study (Pichtel and Pichtel, 1997), EDTA and NTA solutions were assessed for their relative abilities in the *ex-situ* washing of a Pb- and Cr-contaminated soil. Based on these studies, EDTA and NTA concentrations of 0.1, 0.01, and 0.001 M were selected as soil flushing solutions for the present study.

EXPERIMENTAL METHODS

The soil material, a mixture of native soil and industrial waste, was collected from a closed chemical facility in the United Kingdom. Sample preparation

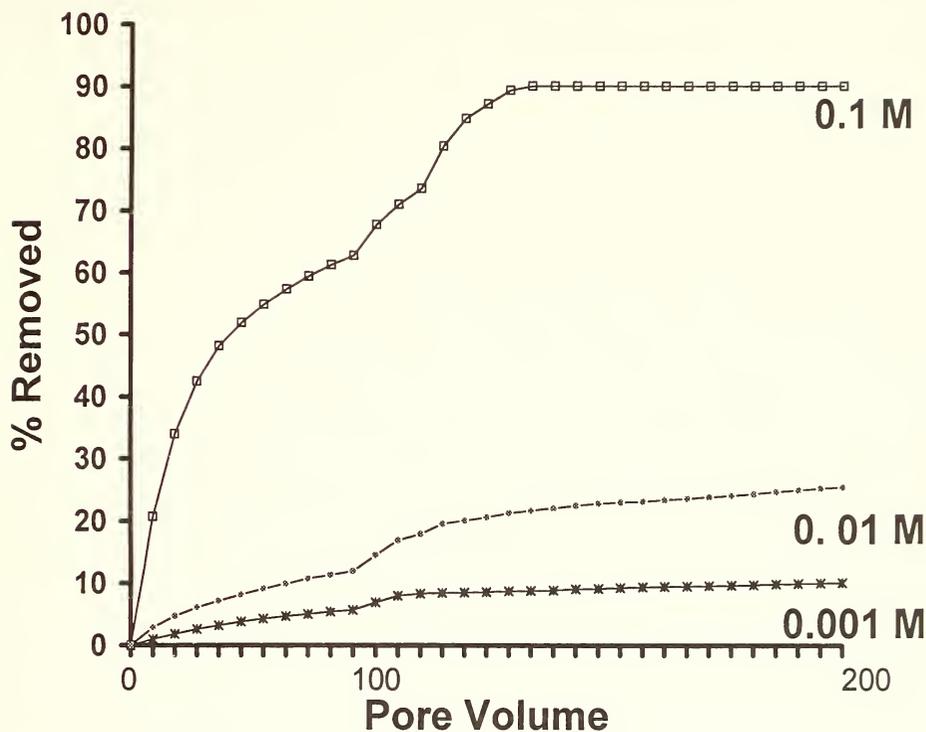


Figure 1. Pb recovery from soil using EDTA at ambient pH (5.5).

as well as the chemical and physical analyses are described elsewhere (Pichtel and Pichtel, 1997). The soil had a pH of 10.3, 1300 mg Pb/kg, and 4940 mg Cr/kg. The soil contained 82.8% sand-sized particles, making it suitable for soil flushing processes. A sand fraction of 50-80% or more typically increases the effectiveness of soil washing (U.S. Environmental Protection Agency, 1991).

Column studies were conducted using PVC columns measuring 2-cm internal diameter and 5 cm in length. Contaminated soil was packed in the column with a final bulk density of 1.1 g/cm³. The column was plugged at both ends with rubber stoppers and glass wool. Flushing solutions were introduced from the bottom of the columns to saturate the soil. A flow rate of 2.0 ml/min was established for all columns on a Masterflex Model 7568 peristaltic pump. Extraction solutions included ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) at 0.1, 0.01, and 0.001 M. Solutions were used at the ambient pH value (5.5 for EDTA and 11.1 for NTA) or at pH 3.0 using HCl, and 10.0 (EDTA only) using NaOH. In one set of experiments, a solution of 0.1 M HCl was passed through the columns for the first 100 pore volumes with subsequent flushing by either 0.1 M EDTA or 0.1 M NTA (ambient pH).

Column effluent samples were acidified with concentrated HNO₃. Concentrations of soluble Pb and Cr were measured via flame atomic absorption spectrophotometry (Perkin-Elmer model 2240, Norwalk, Connecticut; Perkin-Elmer,

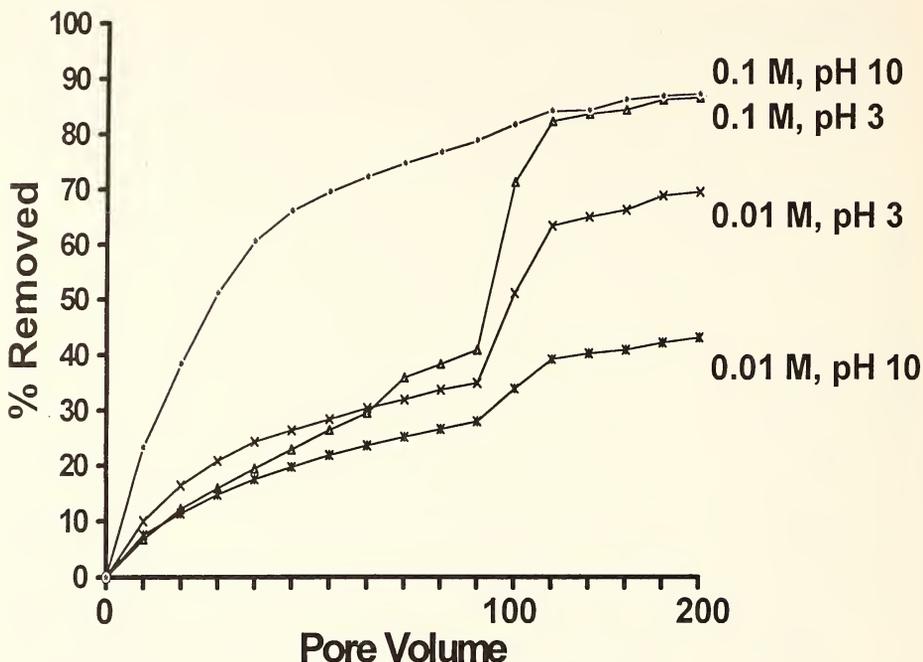


Figure 2. Pb recovery from soil using EDTA at pH 3.0 and 11.0.

1982). Detection limits of 0.19 and 0.08 mg/L were measured for Pb and Cr, respectively, using standards prepared from commercial reagents.

Comparison of metal levels removed from the soil by EDTA and NTA were performed using a one-way analysis of variance and the Student-Newman-Keuls Test, if a significant difference was detected ($P < 0.05$). SigmaStat (version 2.0 on a Windows format) was used for all calculations.

RESULTS AND DISCUSSION

Lead Removal Efficiencies. Lead removal by 0.1 M EDTA was initially rapid (Figure 1). The overall extraction process is consistent with the two-step metal desorption process described by Tuin and Tels (1990), Backes, *et al.* (1995), and Cline and Reed (1995); that is, a rapid initial desorption was followed by gradual release. The lower extraction efficiency after the first 20-25 pore volumes is presumably a result of stronger Pb binding to soil solids with decreasing metal contamination, because binding energies associated with low sorption densities are substantial (Benjamin and Leckie, 1981). Additionally, the removal of progressively more stable Pb minerals or a slow rate of release of Pb^{2+} from solid Pb phases may be responsible (Heil, *et al.*, 1996). Reed, *et al.* (1995) measured significant Pb removal from contaminated soil columns after only 1-4 pore volumes, after which little additional Pb removal occurred.

After 100 pore volumes, the 0.1 M EDTA solution at ambient pH removed 71% of the soil Pb, which was significantly greater ($P < 0.05$) than the 16.8%

and 8.0% removed by the 0.01 M and 0.001 M solutions, respectively (Figure 1). After 200 pore volumes, 89.8% of the soil Pb was extracted with 0.1 M EDTA; however, removal at 0.1 M and 0.001 M remained virtually unchanged. Common soil metals (*e.g.*, Ca^{2+} , Na^{+} , etc.) may compete with Pb for the chelating agent so that excess chelant quantities (*i.e.*, well above equimolar concentrations) are needed to ensure complete contaminant removal (Reed, *et al.*, 1995). A chelant concentration of at least 0.00025 M is required for 1:1 concentrations of Pb:extractant.

The 0.1 M EDTA solution at pH 3 removed 82.2% Pb after 100 pore volumes, and 63.3% was recovered with the 0.01 M solution (Figure 2). Heil, *et al.* (1996) measured increased Pb removal from three soils as EDTA pH decreased. The solubility of many Pb minerals, including $\text{Pb}(\text{OH})_2$, PbO , and PbCO_3 as well as other Pb-crystalline solids, will increase as pH is decreased (Lindsay, 1979). Protonation weakens the metal-lattice bonds, increasing the dissolution rate. Both proton- and ligand-enhanced dissolution mechanisms may be operating simultaneously (Stumm and Wieland, 1990).

When the EDTA pH was increased to 10, the 0.1 M solution removed 84.2% Pb after 100 pore volumes, and the 0.01 M solution removed 39.2% (Figure 2). At pH values of 11 or above, EDTA is present in the completely ionized tetranegative form and binds strongly to transition metal cations. EDTA was found effective for Pb recovery from soil at high solution pH values in studies by Elliott and Brown (1989). Lead solubilization may be partly the result of solubilization of soil organic matter or the formation of Pb hydrolysis complexes (Heil, *et al.*, 1996). Heil, *et al.* (1996) found, in alkaline solutions, that a high percentage of EDTA complexed with Ca and, to a lesser degree, with Mg and other cations. The soil in the current study contained 8.2% Ca and 6.0% Mg (Pichtel and Pichtel, 1997); both may compete with target metals for the chelant. The log stability constants for CaEDTA^{2-} and CaNTA^{-} are 10.7 and 6.4, while the K_s for MgEDTA^{2-} and MgNTA^{-} are 8.8 and 5.4, respectively. The K_s for PbEDTA^{2-} and PbNTA^{-} are 18.0 and 11.3, respectively (Martell and Smith, 1974).

The present data demonstrates equal or greater Pb extractability in columns compared to batch extractions. In batch studies, 0.1 M EDTA was successful, both at $\text{pH} < 4.5$ and $\text{pH} > 12.5$, in removing $> 90\%$ soil Pb after a single washing (Pichtel and Pichtel, 1997). Lead removal efficiencies were high in columns compared to batch studies (Reed, *et al.*, 1995). Lead release during column flushing is apparently enhanced by the higher concentration gradient.

The quantities of Pb removed from contaminated soils via chelant extraction varies. A solution of 0.08 M EDTA removed over 90% of soil Pb from a Pb battery-contaminated soil (Elliott and Brown, 1989). Brown and Elliott (1992) measured 80% Pb recovery from the same soil at pH 4.0 and 0.04 M EDTA. Tuin and Tels (1990) measured variable Pb extraction from contaminated soils using EDTA following acidification.

An increase in NTA concentration resulted in an insignificant increase in Pb solubilization (Figure 3). After 200 pore volumes, the 0.1 M NTA solution at

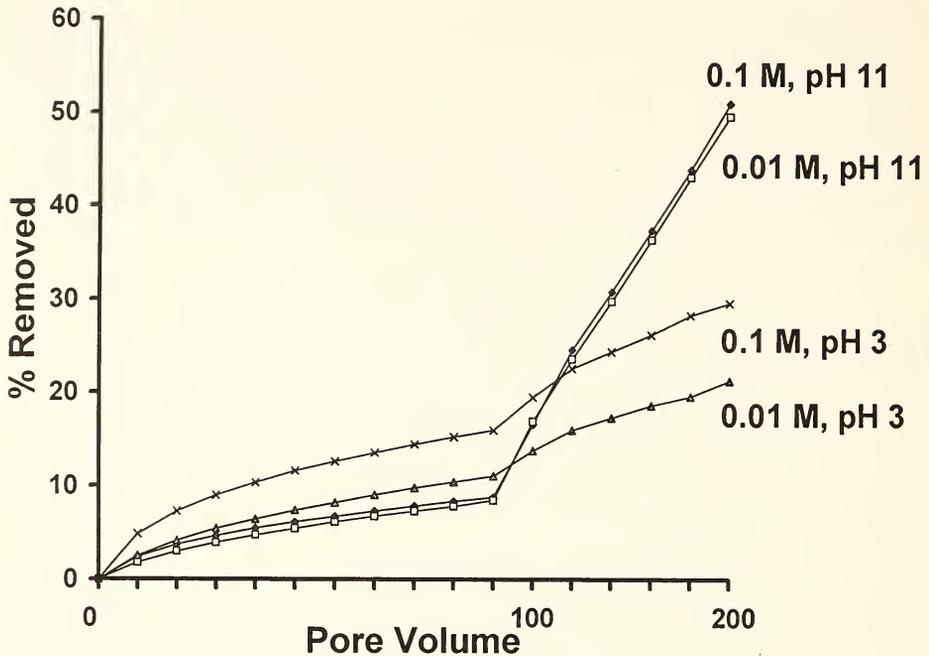


Figure 3. Pb recovery from soil using NTA at pH 3 and ambient pH (11.1).

ambient pH (11.1) removed 50.9% of the soil Pb, which was not significantly greater than the 49.5% removed by the 0.01 M solution. The 0.1 M NTA solution at pH 3 removed 22.5% after 100 pore volumes and 29.5% after 200 pore volumes. A total of 21.2% was recovered with the 0.01 M solution after 200 pore volumes (Figure 3). In batch studies, a range of 12% to 38% Pb was removed from this soil in 0.1 M NTA under acidic conditions (Pichtel and Pichtel, 1997), which was not significantly different from those measured in the current *in-situ* study.

Lead recovery in NTA was less than that accomplished by EDTA (Figures 1-3). Average Pb removed was 87.9% in 0.1 M EDTA (across all pH values) compared to 40.2% for 0.1 M NTA. The lower extraction efficiency of NTA when compared to EDTA may be due to competition among other soil cations (e.g., Ca^{2+}) for the ligands or adsorption of the Pb-NTA complex to the soil surface. Elliott and Brown (1989) suggest that NTA:Pb ratios greater than 1:1 reduced Pb recovery because of adsorption of $\text{Pb}(\text{NTA})_2^+$ onto positively charged oxide soil components. Additionally, as a result of its weaker complexing ability, NTA is less capable than EDTA in preventing Pb hydrolysis under alkaline conditions (1989). Castle, *et al.* (1985) found a 10% EDTA solution to be superior to NTA in solubilizing Pb; a 90% to 95% removal was measured. In the present study, high concentrations of either EDTA or NTA did not reduce metal recovery.

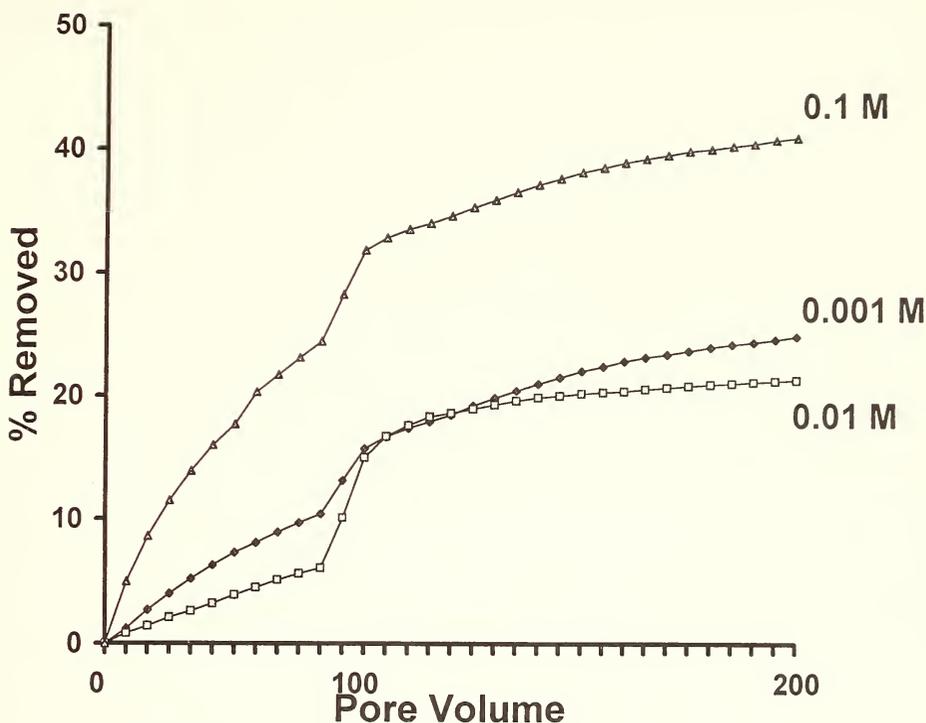


Figure 4. Cr removal from soil using EDTA at ambient pH (5.5).

Flushing the soil columns with HCl prior to chelant flushing did not significantly ($P < 0.05$) increase Pb-extraction efficiency (data not shown). Tuin and Tels (1990) measured 81% and 87% Pb removal from two soils which were first extracted by 0.1 M HCl followed by 0.1 M EDTA.

Chromium Removal Efficiencies. Overall, Cr removal from the soil was substantially lower than that of Pb (Figures 4-5). Tuin and Tels (1990) found Cr to be less readily extractable than Pb from four contaminated soils. Assink and Rulkens (1987) also measured only slight Cr removal from soil. Metal removal is based on the formation of soluble complexes. In the present study, the majority of soil Cr is not readily reactive; 89.8% occurs as the insoluble fraction (Pichtel and Pichtel, 1997). Therefore, a chelant concentration well above the stoichiometric amount is necessary for maximum removal. A minimum chelant concentration of 0.004 M is needed to form a 1:1 ratio of chelant:Cr for optimal recovery.

Increasing the EDTA concentration generally resulted in an enhanced recovery of soil Cr (Figure 4). A total of 40.9% soil Cr was removed with 0.1 M EDTA after 200 pore volumes at ambient pH, and 21.3% and 24.8% was removed at 0.01 and 0.001 M EDTA, respectively.

In batch studies, Cr recovery using EDTA at 0.1, 0.01, and 0.001 M was maximized at 34-36% up through pH 7 and, in no case, did a single EDTA wash-

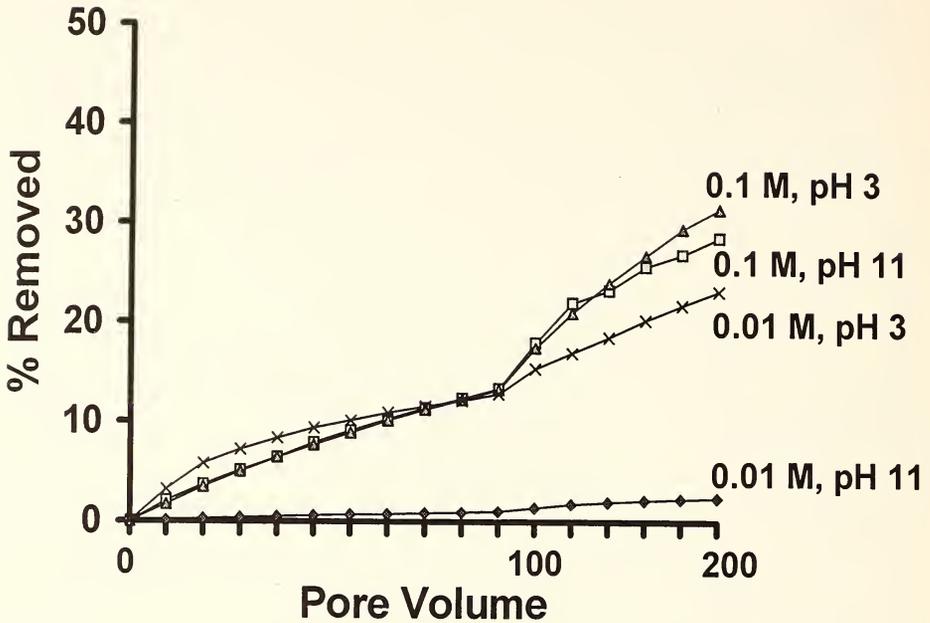


Figure 5. Cr removal from soil using NTA at pH 3.0 and ambient pH (11.1).

ing remove all the soil Cr (Pichtel and Pichtel, 1997). Hsieh, *et al.* (1989) found that Cr removal from a contaminated soil with EDTA ranged from 35–83% for 6 to 10 washing cycles, which demonstrates the difficulty of removing all adsorbed Cr. Shirk and Farrel (1985) measured only 12% Cr recovery from a contaminated soil using EDTA. The poor removal results for Cr may be a result of the presence of immobile Cr^{3+} species, occurring as oxide compounds (Tuin and Tels, 1990).

Chromium removal by 0.1 M NTA (ambient pH 11.1) after 100 pore volumes was 21.9%, while that by 0.01 M was 1.7% (Figure 5). Beyond pH 10.3 (*i.e.*, $\text{pK}_{\text{a}3}$), the chelant exists as NTA^{2-} and, to a lesser extent, as NTA^{3-} , both of which allow for partial complexation with the soil Cr. Precipitation as insoluble oxides is a strongly competing reaction in this pH regime, however. When the pH was set at 3.0, Cr removal after 100 pore volumes was essentially unchanged with 0.1 M NTA (20.9%); however, removal increased to 16.9% at 0.01 M. Banat, *et al.* (1974) found negligible Cr solubilization from two river sediments (pH 6.8 and 7.1) using NTA in batch studies, even after 200 h shaking time. In batch tests, Cr removal using 0.1 M NTA over a range of pH values did not exceed 14.0% (Pichtel and Pichtel, 1997).

The stability constant for the formation of CrEDTA^- is 17 orders of magnitude higher than that for CrNTA (Martell and Smith, 1974); hence, the EDTA should be more effective at removing Cr from the soil. The weaker complexing ability of NTA limits its ability to prevent hydrolysis. Furthermore, since all

the functional groups of the EDTA are involved in the complexation, little opportunity exists for bridging to the soil surface (Elliott and Brown, 1989). Additional recovery of Cr at high pH may be limited by the strong affinity of basic cations such as Ca and Mg for the chelant. Ca^{2+} will strongly bind with the chelant at high pH. When the columns were first acidified with HCl, elution by EDTA or NTA (ambient pH) did not remove significantly greater quantities of Cr compared to chelant flushing alone (data not shown).

CONCLUSIONS

Removal of both Pb and Cr from a contaminated, strongly buffered alkaline mixture of soil and weathered industrial waste was typically enhanced in column studies when EDTA and NTA concentrations were increased. For a non-pre-treated (*i.e.*, non-acidified) soil, washing with EDTA above equimolar concentrations was more effective than washing with NTA. NTA is less expensive than EDTA, and less NTA is required, on a weight basis, to form 1:1 complexes with metals. The slow dissolution kinetics of the Pb- and Cr-solid phases may deter total metal removal by a chelant, and long-term flushing would be needed for complete metal recovery.

The extent of Pb and Cr solubilization is partly a function of pH. However, to completely acidify the soil would prove too costly due to the soil's extensive buffering capacity. In addition, high acid strengths destroy soil structure and dissolve much of the soil solids. From a practical standpoint, a soil solution at either pH extreme will be corrosive to field washing equipment. The recommended washing treatment for the alkaline soil/waste mixture studied, based on pH adjustment and other practical considerations, was 0.1 M EDTA without acidification.

For this study soil, *in-situ* processes appear to be equally effective as *ex-situ* processes due to the high concentration gradient for soil metals during the flushing process. Additionally, the particle size distribution of the materials is conducive to flushing; over 82% of the particles are present in the sand-sized fraction, which provides for high permeability and sufficient contact of extracting solution with the contaminants.

ACKNOWLEDGMENTS

Financial support from the Ball State University Energy Center (CERES), the Indiana Academy of Science, and the University of Stirling (Scotland) is gratefully acknowledged.

LITERATURE CITED

- Assink, J.W. and W.H. Rulkens. 1987. Cleaning soils contaminated with heavy metals: Environmental technology. *In*: K.J. De Waal and W.J. Van den Brink (Eds.), *Proceedings of the European Conference Nijhoff*. pp. 502-512, Dordrech, The Netherlands, 590 pp.
- Backes, C.A., R.G. McLaren, A.W. Rate, and R.S. Swift. 1995. Kinetics of cadmium and cobalt desorption from iron and manganese oxides. *Soil Sci. Soc. Amer. J.* 59: 778-785.
- Banat, K., V. Forstner, and G. Muller. 1974. Experimental mobilization of metals from aquatic sediments by nitrilotriacetic acid. *Chem. Geol.* 14: 199-207.

- Benjamin, M.M. and J.O. Leckie. 1981. Multiple-site adsorption of Cd, Cu, Zn, and Pb on amorphous iron oxyhydroxide. *J. Colloid Interface Sci.* 79: 209-221.
- Brown, G.A. and H.A. Elliott. 1992. Influence of electrolytes on EDTA extraction of Pb from polluted soil. *Water, Air, Soil Pollut.* 62: 157-165.
- Cairney, T. 1987. Reclaiming contaminated land. Blackie Publ., Glasgow, 260 pp.
- Castle, C., J. Bruck, D. Sappington, and M. Erbaugh. 1985. Research and development of a soil washing system for use at Superfund sites. *In: Proceedings of the Sixth International Conference on the Management of Uncontrolled Hazardous Waste Sites*, pp. 452-455, Hazardous Materials Control Res. Inst., Silver Spring, Maryland, 487 pp.
- Chen, T.C., E. Macauley, and A. Hong. 1995. Selection and test of effective chelators for removal of heavy metals from contaminated soils. *Can. J. Civil Eng.* 22: 1185-1197.
- Cline, S.R. and B.E. Reed. 1995. Lead removal from soils via bench-scale soil washing techniques. *J. Environ. Eng.* 121: 700-705.
- _____, B.E. Reed, and M. Matsumoto. 1993. Efficiencies of soil washing solutions for the remediation of lead contaminated soils. *In: A. Davis (Ed.), Hazardous and Industrial Wastes*, pp. 93-101, Proc. 25th Mid-Atlantic Industrial Waste Conf., Technomic Publ., Lancaster, Pennsylvania, 590 pp.
- Davis, A. and I. Singh. 1995. Washing of zinc(II) from contaminated soil column. *J. Environ. Eng.* 121: 174-185.
- Elliott, H.A. and G.A. Brown. 1989. Comparative evaluation of NTA and EDTA for extractive decontamination of Pb-polluted soils. *Water, Air, Soil Pollut.* 45: 361-369.
- Heil, D., A. Hanson, and S. Zohrab. 1996. The competitive binding of lead by EDTA in soils and implications for heap leaching remediation. *Radioactive Waste Manage. Environ. Restoration* 20: 111-127.
- Hsieh, H., M. Barnes, and E.Z. Aldridge. 1989. A feasibility study of the removal of chromium from selected contaminated sites. *In: Physiochemical and Biological Detoxification of Hazardous Wastes*, pp. 446-459, Technomic Publ., Lancaster, Pennsylvania.
- Kabat-Pendias, A. and H. Pendias. 1992. Trace elements in soils and plants, 2nd ed. CRC Press, Boca Raton, Florida, 365 pp.
- Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley and Sons, New York, 449 pp.
- Macauley, E. and A. Hong. 1995. Chelation extraction of lead from soil using pyridine-2,6-dicarboxylic acid. *J. Hazardous Materials* 40: 257-270.
- Martell, A.E. and R.M. Smith. 1974. Critical stability constants, vol. 1: Amino acids. Plenum, New York, 469 pp.
- Perkin-Elmer. 1982. Analytical methods for atomic absorption spectrophotometry. Perkin Elmer, Norwalk, Connecticut, 230 pp.
- Pichtel, J. and T. Pichtel. 1997. Comparison of solvents for *ex-situ* removal of chromium and lead from contaminated soil. *Envir. Eng. Sci.* 14: 97-103.
- Reed, B.E., R.E. Moore, and S.R. Cline. 1995. Soil flushing of a sandy loam contaminated with Pb(II), PbSO₄, PbCO₃, or Pb-naphthalene: Column results. *J. Soil Contamination* 4: 243-267.
- Richards, I.G., J.P. Palmer, and P.A. Barratt. 1993. Reclamation of former coal mines and steelworks. Elsevier, Amsterdam, 718 pp.
- Shirk, J.E. and C.W. Farrel. 1985. Approach to *in-situ* management of metals. *In: Proceedings of the 8th Madison Waste Conference*, pp. 52-59, Madison, Wisconsin.
- Stumm, W. and E. Wieland. 1990. Dissolution of oxide and silicate minerals: Rates depend on surface speciation. *In: W. Stumm (Ed.), Aquatic Chemical Kinetics*, pp. 367-400, John Wiley and Sons, New York, 545 pp.
- Tuin, B.J.W. and M. Tels. 1990. Removing heavy metals from contaminated clay soils by extraction with hydrochloric acid, EDTA, or hypochlorite solutions. *Environ. Technol. Let.* 11: 1039-1052.
- U.S. Environmental Protection Agency. 1991. Guide for conducting treatability studies under CERCLA: Soil washing interim guidance. Washington, D.C., EPA/540/2-91/020A, 38 pp.