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Oxalate Extraction of Pb and Zn from Polluted Soils: Solubility Limitations

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Oxalate (Ox) was used to extract Pb and Zn from industrially contaminated soils. Although Ox effectively releases metals bound by hydrous oxide soil components, it forms insoluble salts with some heavy metals unlike conventional extractants (e.g., EDTA). The insolubility of PbOx(s) ($K_{sp} = 2.74 \times 10^{-11}$) precluded the use of Ox as a single-step extractant even for soils mildly contaminated with Pb. The usefulness of Ox as a Zn extractant, however, depends on the level of soil contamination. A Zn solubility model, based on published equilibrium constants, was developed to assess Ox suitability as a function of system conditions. Precipitation of ZnOx(s) hindered Zn recovery under acidic conditions where formation of soluble oxalato complexes was small. For pH < 3, the presence of 1 M Ox actually reduced Zn release compared to simple acid washing. Although Ox displaces oxide-bound metals and thus is potentially useful in soil washing, solubility limitations must be defined for effective remediation of metal-laden soils.

KEY WORDS: *soil remediation, heavy metals, metal-contaminated soils, chelation.*

INTRODUCTION

ON-SITE remediation of metal-contaminated soils is often a major obstacle to complete clean up of hazardous waste sites. In some cases, soil washing can be used to remove inorganic contaminants like heavy metals or as a pretreatment step for other remediation techniques (Anderson, 1993). Typically, soil washing is an *ex situ* process that employs extracting reagents to displace metals from the soil into aqueous solution. After separation, the cleaned soil is redeposited at the site and the metal-laden solution undergoes further treatment. Of the more than 300 government-sponsored innovative technology field demonstration projects completed in North America, roughly one-tenth involved soil washing (USEPA, 1997). There are a number of full-scale soil washing technologies (Anderson, 1993), but process details are generally considered proprietary. This has hindered a broad appreciation of operational conditions that optimize metal recovery.

A wide range of complexing ligands have been employed for extracting metals from contaminated soils (Pickering, 1986). Several aminopolycarboxylic acids (NTA, EDTA, DTPA) have been used both analytically and commercially because they form remarkably stable complexes with a wide array of metals. EDTA probably is the most commonly reported reagent in soil washing studies. It has been shown to be extremely effective in desorbing metals from soils (Peters and Shem, 1992), although slow dissolution of oxidic soil components hinders its use in desorbing metals occluded within hydrous oxides (Elliott and Shastri, 1998).

The ability of oxalic acid and other oxalate (Ox)-containing reagents to displace metal ions from soils has been employed for many years, particularly in extracting solutions used to evaluate the plant-available or biologically active metal concentrations in soils. Grigg's reagent (acidified ammonium oxalate) has been recommended as an extractant for evaluating the fraction of soil heavy metals available to wheat plants (Misra and Pandey, 1976). Farrah and Pickering (1978) found that 0.1 M oxalic acid was able to release Pb, Zn, Cu, and Cd preadsorbed on several clays. They attributed the metal-displacing ability of oxalic acid to the formation of anionic oxalato complexes and the affinity of protonated Ox species for clay surfaces. Recently, Krishnamurti et al. (1997) documented the ability of Ox to release Cd from soils through organic complexation. In contrast to EDTA and related extractants, Ox is extremely effective in releasing metals bound to soil oxide components (Elliott and Shastri, 1998). Ox is also a naturally occurring ligand and is potentially less expensive than some commonly investigated reagents.

On the negative side, Ox tends to form sparingly soluble oxalate salts with some metals. Pickering (1986) attributed low Pb recovery from sediments by Ox solutions to the sparing solubility of Pb-oxalate species. Elliott and Shastri (1998) reported that Ox was ineffective in removing Pb from a highly contaminated soil. Based on published solubility constants, precipitation of metals displaced from the soil following Ox extraction may also constrain its use for decontaminating Zn-polluted soils. Precipitation of the displaced metal with the extracting reagent is generally not observed in most soil washing systems. However, such precipitation could be influenced by the level of contamination and various operational parameters (pH, soil/solution ratio, ionic strength).

Therefore, the purpose of this investigation was to more precisely defined the conditions under which insolubility of metal-oxalate salts limits the utility of Ox as an extractant. Recovery of Pb and Zn from two industrially contaminated soils has been investigated. Metal release by EDTA extraction was chosen to compare the pH and concentration dependence of the aminocarboxylic acids with the behavior of Ox. To help interpret the data, Zn solubility in the presence of Ox was modeled using published thermodynamic equilibrium constants. This modeling illustrates the use of a fundamental solution equilibrium approach in establishing process conditions that maximize metal recovery in soil washing systems.

MATERIALS AND METHODS

Two metal-contaminated surface soils were used in this study (Table 1). One was collected from an automobile battery recycling facility near Indianapolis, Indiana, and had extremely high Pb (21%). Soils at battery sites typically have roughly 5% Pb, with levels as high as 46% reported (Sims and Wagner, 1983). The second soil had elevated Zn and was collected from the mountain immediately adjacent and downwind from the Palmerton, Pennsylvania, smelter facility. The soils are referred to as the “Indiana” and “Palmerton” soil; the names do not designate any particular soil series or classification. Soils were ground to pass a 2-mm sieve and dried at near room temperature prior to use. The total metal levels were assessed using a triple acid ($HF-HNO_3-HClO_4$) digestion method, previously shown to provide superior recovery from highly contaminated soils (Elliott and Shields, 1988).

Batch desorption experiments were performed as follows. Depending on the desired final concentration, variable amounts of Ox or EDTA stock solutions, prepared from oxalic acid and tetrasodium EDTA, were added to 125-ml polypropylene Erlenmeyer flasks and diluted to 100 ml total volume with distilled water.

TABLE 1
Selected Properties of the Soils

	Organic matter	Sand	Silt	Clay	Pb	Zn	Cd
Soil		**%**				**mg kg^{-1}**	
Indiana	2.6	59	23	18	210,000	521	197
Palmerton	6.5	51	32	17	812	2700	280
					10[a]	50[a]	0.2[a]

[a] Typical background soil values (Lindsay, 1979; Alloway, 1990).

The soil (2 to 4 g, depending on the system) was added to the flasks just prior to initial pH adjustment. The pH was adjusted with NaOH and HNO_3 so that the final pH values would cover the pH 3 to 10 range. The samples were agitated for 24 h at room temperature on a Burrell model 75 wrist-action shaker (Burrell Corp., Pittsburgh). The extracting solutions were open to light exposure, which is known to catalyze Ox dissolution of oxyhydroxides (Pickering, 1986). After shaking, the final pH of the samples was measured and these values were used to plot the metal release data. The soil was removed by filtration through 0.45-μm filters (Gelman Scientific, Ann Arbor, MI), and metal analysis of the filtrate was done by flame atomic absorption using a Perkin-Elmer model 2380 spectrophotometer (Perkin-Elmer, Norwalk, CT). Detection limits reported by the manufacturer are 0.01 mg L^{-1} (Pb) and 0.0008 mg L^{-1} (Zn).

Zinc solubility, in the absence and presence of Ox, was evaluated using 0.01 to 1.0 *M* solutions of $Zn(NO_3)_2.6H_2O$. Adjustment of pH, shaking conditions, solids separation, and Zn analysis followed the same procedures as the desorption experiments.

RESULTS AND DISCUSSION

Comparison of Oxalate with EDTA

The influence of Ox and EDTA on solubilization of Pb from the Indiana soil is shown in Figure 1. At 0.08 *M*, the EDTA concentration represents a 2:1 ligand/

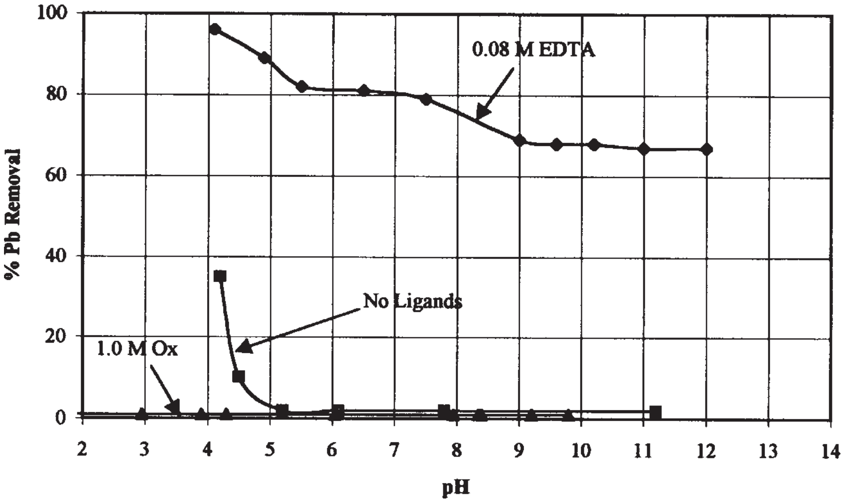

FIGURE 1

The pH-dependent release of Pb from the Indiana soil as influenced by EDTA and Ox.

metal molar ratio assuming total solubilization of the Pb. For 1 *M* Ox, the initial ligand/metal ratio was 12:1. Thus, both ligands are present in stoichiometric excess, a requirement for substantial metal recovery in washing of contaminated soils. Although present in lower concentration, EDTA dramatically enhanced Pb release relative to Ox. The ability of EDTA to complex Pb, and metals in general, is greatly superior to Ox as indicated by the relevant formation constants (Table 2). As a general rule, reagents that convert sorbed metals into anionic complexes effect high metal recoveries (Farrah and Pickering, 1977). Despite forming reasonably stable Pb-oxalato complexes (Table 2), Ox was unable to promote recovery of Pb even at 1 *M* levels. Comparing the Ox data with Pb release simply by adjusting the solution pH (designated "no ligands") reveals that processes other than complexation are involved. Even in the absence of ligands, a substantial upturn in Pb recovery occurred below pH 5. This behavior can be attributed to the acid-catalyzed dissolution of Pb-containing soil components and the displacement of Pb^{2+} from exchange sites by H^+ (see Elliott and Brown, 1989).

Figure 1 shows that Ox did not result in solubilization of Pb even under strongly acidic conditions, where it was expected. The processes that release soil-bound Pb under acidic conditions (i.e., exchange displacement by H^+, acid-catalyzed dissolution of Pb-containing phases) should operate even with Ox present. This implies that Pb is removed from solution subsequent to its displacement from the soil. The filtration technique used to separate the washed soil from the solution does not distinguish between Pb remaining on the soil and that which is displaced from the soil but subsequently precipitated from the solution phase.

This behavior is most readily explained by the insolubility of the Pb-oxalate species formed in solution. The sparing solubility of PbOx(s) is indicated by its solubility product constant (K_{sp}):

$$K_{sp} = \left[Pb^{2+}\right]\left[Ox^{2}\right] = 2.74 \times 10^{-11} \tag{1}$$

The effects soluble oxalato complex formation, Pb hydrolysis, and Ox protonation must be considered for a complete picture of Pb solubility in this system.

TABLE 2
Equilibria Relevant to the System
(Martell and Smith, 1976; CRC, 1977)

	log formation constants for 1:1 complex (I = 1 *M*, 25°C)		
Metal	**Oxalate**	***EDTA***	**Oxalate solubility product K_{sp} (I = 0, 18°C)**
Pb	4.16	17.7	2.74×10^{-11}
Zn	3.4	16.5	1.35×10^{-9}
Cd	2.73	16.5	9.0×10^{-8}

However, Eq. 1 is useful for a gross estimation of this effect. If the total oxalate concentration (Ox_T) is 1 M at high pH, Ox^{2-} will be roughly 1 M given the protonation characteristics of oxalic acid ($pK_{a1} = 1.25$, $pK_{a2} = 4.28$). Based on these conditions, the solution would be saturated with respect to PbOx(s) if Pb^{2+} exceeded 2.74×10^{-11} M. Assuming 100% Pb recovery for the conditions in Figure 1, the solution concentration of Pb would be 0.04 M. The Pb ions were then displaced into a solution containing a high enough level of Ox such that the saturation point of PbOx(s) was reached. This rough calculation explains why Pb recovery was so low in the presence of 1 M Ox.

The Indiana soil, however, is grossly contaminated with Pb so that any appreciable displacement will result in high Pb levels in the extract solution. The Palmerton soil, only modestly contaminated with Pb (812 mg/kg), was also extracted with 1 M Ox. Figure 2 shows that Ox was unable to effect any appreciable recovery of Pb even from the Palmerton soil. Assuming total Pb release from this soil, the resulting solution level should be 7.8×10^{-6} M. The PbOx(s) is so insoluble that Ox is unsuitable as a single step extractant even for soils with moderately elevated Pb. For unpolluted soils, however, the insolubility of PbOx(s) does not, apparently, hinder Pb release from soils. Misra and Pandey (1976) reported Grigg's reagent (acid ammonium oxalate) extracted more Pb from soils than 0.02 M EDTA and 0.1 N HCl, but in their case soil-extractable Pb was less than 3 mg/kg. Clearly, for soils highly enriched with Pb, the relative extraction efficiency was quite different (Figure 1).

Although the sparing solubility of PbOx(s) has been identified previously as the cause of low Pb recoveries with Ox (Pickering, 1986), we investigated the extent

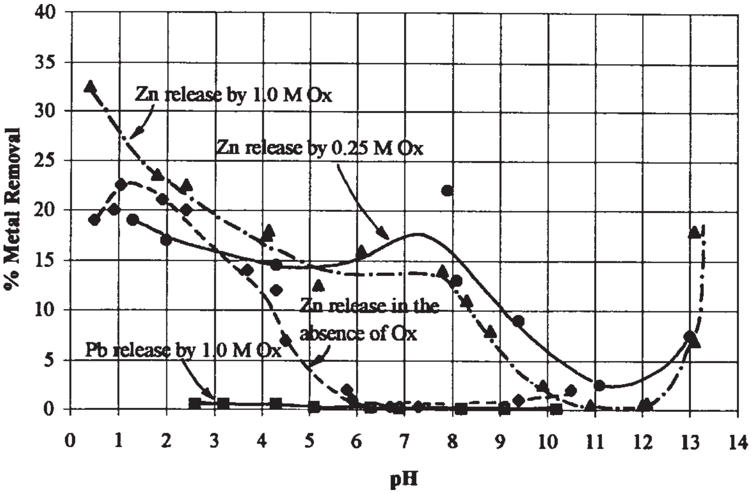

FIGURE 2

The pH-dependent removal of Zn and Pb from the Palmerton soil as influenced by Ox.

to which the same phenomena might limit extractive decontamination of Zn-polluted soils. While the K_{sp} for ZnOx(s) is roughly 100 times that of PbOx(s), Ox forms less stable soluble complexes with Zn (Table 2). Figure 2 compares Zn release with and without Ox in the extracting solvent. In the absence of Ox, Zn recovery increased under acidic conditions analogous to the behavior of Pb (Figure 1). Davis and Singh (1995) similarly found that Zn(II) removal from soil can be enhanced simply by lowering the pH of the washing solution. In our study, the ability of Ox to modify Zn removal exhibited a strong pH dependence. Under near-neutral conditions, Ox enhanced Zn removal. However, under strongly acidic or basic conditions, the presence of Ox had little impact on Zn release. Particularly noteworthy in Figure 2 was the failure of Ox to completely surppress Zn removal under acidic conditions as was observed for Pb. These data reflect the complex interplay of equilibria (precipitation, hydrolysis, Ox protonation, Zn complexation) that collectively define the amount of Zn that can exist in the solution phase. These reactions can be modeled to quantify and predict the effect of pH and Ox level on Zn recovery in this system.

Zinc Solubility in the Presence of Oxalate

A Zn solubility model was developed, based on published equilibria, to determine if the behavior of Zn in presence of Ox could explain the general Zn release patterns observed in the extraction experiments. Several solution reactions were taken into account, including the formation of mononuclear hydroxo complexes of Zn, the protonation behavior of oxalic acid, the formation of Zn-oxalato complexes (both $ZnOx^\circ$ and $Zn(Ox)_2{}^{2-}$), and the formation of Zn-containing solid phases (ZnOx(s) and ZnO(s)). One caution is warranted. A host of other reactions must be quantified to model more precisely such complex systems. For some systems, complexation with soil organic matter, precipitation of CaOx(s), and formation of carbonate-containing Zn phases and cannot be neglected and thus require chemical equilibrium models like MINTEQA2.

The Zn solubility model is based on mass balance expressions for the total zinc (Zn_T) and total oxalate (Ox_T) concentrations in the system. For Zn, the divalent aquo ion (Zn^{2+}), four hydrolysis species and two oxalato complexes were included in the mass balance expression:

$$\begin{aligned} Zn_T = P_{Zn} &+ \left[Zn^{2+}\right] + \left[ZnOH^{+}\right] + \left[Zn(OH)_2^{o}\right] + \left[Zn(OH)_3^{-}\right] + \left[Zn(OH)_4^{2-}\right] \\ &+ \left[ZnOx^{o}\right] + \left[Zn(Ox)_2^{2-}\right] \end{aligned} \tag{2}$$

where P_{Zn} represents the moles per liter of Zn removed from solution by precipitation of ZnOx(s). Similarly, the total concentration of Ox in the system includes the amount precipitated as ZnOx(s), P_{Ox}, as well as the protonated and Zn-complexed forms of soluble Ox:

$$Ox_T = P_{Ox} + \left[H_2Ox^o\right] + \left[HOx^-\right] + \left[Ox^{2-}\right] + \left[ZnOx^o\right] + 2\left[Zn(Ox)_2^{2-}\right] \qquad (3)$$

Because Zn and Ox are precipitated from solution in a 1:1 stoichiometric ratio, $P_{Zn} = P_{Ox}$. This allows Eq. 2 to be solved for P_{Zn} and substituted for P_{Ox} in Eq. 3.

Because each species in Eq. 2 can be expressed in terms of $[Zn^{2+}]$, the solubility of the oxalate salt can be brought into the combined expression through the K_{sp} expression: $[Zn^{2+}] = K_{sp} / [Ox^{2-}]$. The resulting expression can then be solved explicitly (via the quadratic equation) for the free oxalate concentration, $[Ox^{2-}]$. The individual Zn species can then be determined and summed to derive the total soluble Zn concentration, that is, the solubility of ZnOx(s) under the assumed conditions. This same procedure was repeated for zincite, ZnO(s).

Figure 3 shows the pH-dependent solubility of Zn as influenced by the Ox, with the solid lines reflecting model calculations and the data generated from batch solubility experiments. In the absence of Ox, ZnO(s) solubility is a minimum around pH 10 and progressively increases at lower and higher pH (Figure 3a). This is a common and widely recognized feature of heavy metals and explains why simply lowering the pH of an aqueous washing solution will enhance metal release, as illustrated for Pb (Figure 1) and Zn (Figure 2).

The presence of 0.25 *M* Ox had a dramatic influence on Zn solubility (Figure 3b). The data and calculations clearly show that Zn solubility is determined by the ZnOx(s) phase for pH less than about 9.7, and for more alkaline conditions, ZnO(s) becomes the stable (less soluble) phase. A comparison of Figures 3a and 3b illustrates how ligands enhance metal solubility. For example, in the absence of Ox (Figure 3a), Zn solubility is about 10^{-6} *M* at pH 9. In the presence of Ox (Figure 3b), Zn solubility was increased roughly four orders of magnitude at the same pH. This solubility increase explains why such reagents can displace metals from soils. Figure 2 shows that Ox did, in fact, enhance Zn solubility compared with the ligand-free system over the pH 5 to 10 range.

These diagrams also show precisely why Ox can potentially inhibit metal release under acidic conditions. At pH 6.0 without Ox, Zn solubility is roughly 10^{-1} *M* (Figure 3a). The presence of Ox caused Zn solubility to decrease by more than an order of magnitude (Figure 3b). Extending the ZnO(s) solubility to more acidic conditions reveals an even more dramatic oxalate-induced reduction in Zn solubility.

Solubility Limitations on Zn Displacement

This interplay of complexation and solubility reactions was reflected in the Ox extraction data. Notice that the presence of Ox caused a substantial increase in Zn

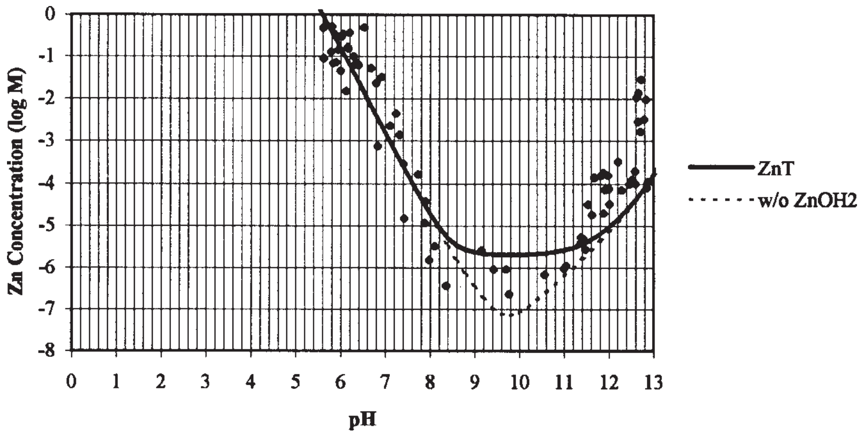

FIGURE 3A

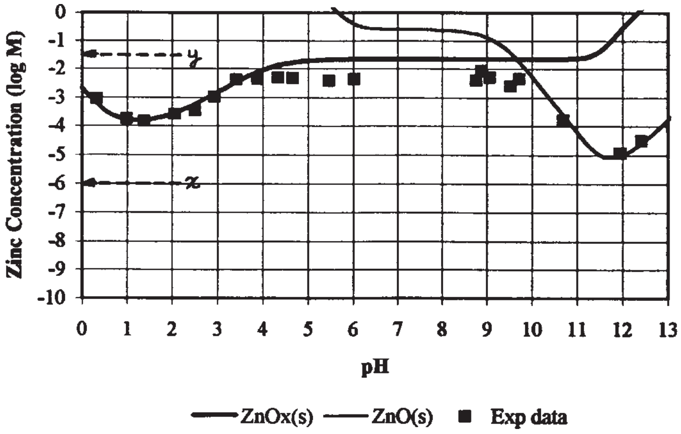

FIGURE 3B

The pH-dependent solubility of Zn: (a) Solubility of ZnO(s) and (b) solubility of ZnOx(s) and ZnO(s) in the presence of 0.25 M *Ox. Lines were generated from the solubility model, data are from batch solubility experiments. The dashed line (3a) is the calculated solubility neglecting the uncharged hydrolysis species* $(Zn(OH)_2^o$ *because its existence is questioned.*

removal over the "no ligand" data in the pH 4 to 10 range (Figure 2). For pH < 4, the presence of Ox had little clear-cut effect on Zn solubility. It might be expected that an appreciable reduction in Zn recovery would be observed under strongly acidic conditions based on calculations (Figure 3b). However, the extent to which solubility effects influence metal release depends on the amount of metal that can potentially be released into the solution.

This is illustrated in Figure 3b by two horizontal dashed arrows labeled “x” and “y”. These lines represent possible Zn_T levels that could exist in solution if 100% of the soil Zn were released into solution. If system conditions are such that the maximum Zn releasable into solution is $10^{-5.5}$ *M* (arrow “x”), oxalate-salt insolubility will not adversely impact Zn recovery from the contaminated soil. This is because the solution can never be oversaturated with respect to ZnOx(s) even if all the soil Zn is released. If maximum release would potentially result in $10^{-1.5}$ *M* Zn in solution (arrow “y”), the solubility of ZnOx(s) is exceeded before this solution level of Zn is reached. In this case, solubility of the oxalate salt is an impediment to soil decontamination by washing. For the desorption experiments shown in Figure 2, the maximum releasable Zn was roughly 10^{-3} *M*. This value just overlaps with the solubility curve for ZnOx(s), suggesting that solubility might have little or no impact on Zn recovery, depending on what fraction of the total Zn is actually capable of being desorbed under the system conditions. This was, in fact, the case (pH 1 to 4 range of Figure 2).

To further investigate this effect, the Zn concentration of the Palmerton soil was increased by adding a solution of Zn nitrate to the soil. This had the effect of increasing the maximum releasable Zn to $10^{-2.8}$ *M*. The Ox extraction of this artificially contaminated soil is shown in Figure 4. Consistent with the foregoing analysis, the presence of Ox had a more dramatic ability to hinder Zn recovery. It is noteworthy that the crossover pH at which the presence of Ox enhances Zn release in Figure 4 (about pH 3 to 4) corresponds closely to the pH at which the predicted Zn solubility exceeds the $10^{-2.8}$ *M* maximum releasable level (Figure 3b).

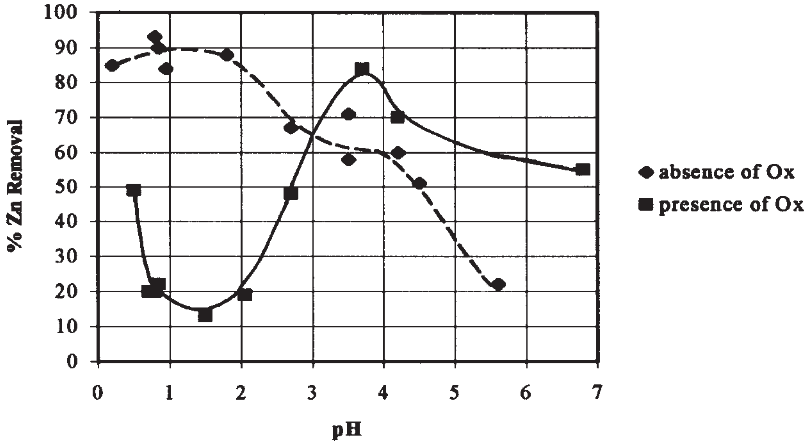

FIGURE 4

Effect of 1.0 M *Ox on Zn release from the Zn-amended Palmerton soil. Zn was added to the soil so that total Zn removal would correspond to* $Zn_T = 10^{-2.8}$ M *in the extracting solution.*

Thus, while Ox is an unsuitable extractant for Pb at almost any level of contamination, its utility for Zn depends on the degree of Zn contamination within the soil. When the contamination level was high enough so that the displaced Zn exceeded the solubility of ZnOx(s) under the process conditions, the usefulness of Ox as an extractant is compromised. Indeed, under acidic conditions, the presence of Ox can actually hinder Zn recovery (Figure 4). Simple acid leaching, in this case, will effect greater Zn recovery than ligand-enhanced extraction using Ox.

CONCLUSIONS

A host of chemical parameters influence the selection and use of chelating reagents for washing of metals from contaminated soils. These parameters can be broadly divided into those influencing the nature of the soil-bound metals or the strength of metal complexation reactions. This work indicates that the capacity of the aqueous phase to accommodate the complexed metal also dictates recovery efficiency. This has not been fully appreciated heretofore because it is not an issue with the traditional aminopolycarboxylic acids (e.g., EDTA) used as soil washing reagents. Results indicate that for Pb and Zn, precipitation of oxalate salts under acidic conditions may constrain use of Ox as a soil washing agent. Insolubility of oxalate salts may also be an issue for Cd (Krishnamurti et al., 1997) as well as Cu, Ni, and Co (Gyliene and Salkauskas, 1995). Although some systems necessitate quantifying side reactions not considered here, such as formation of CaOx(s) or carbonate-containing Zn precipitates, solubility models help define and avoid conditions where precipitation hinders metal recovery from contaminated soils.

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