CHEMICAL AND ENGINEERING ASPECTS OF HEAVY METAL-CONTAMINATED SOILS

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ABSTRACT

Important factors controlling the fate of heavy metals in soils systems include the soil solution pH, the presence of complexing ligands, and a number of soil properties, such as texture and organic matter content. The adsorption of metals is an important process that controls low metal concentrations in soils. It can be described as a surface complexation reaction with soil particle surfaces. Adsorption of cationic metals is favored at higher pH; oxyanionic metals and metalloids are adsorbed at low pH. At high metal concentrations, specific metal-containing geochemical phases may be important. Limited technologies have been developed for the remediation of metal-contaminated soils; these include excavation and removal, stabilization and solidification, and soil washing. The form of the metal contamination determines the bioavailability of the metal in the soil matrix and affects the success of metal washing from the soil.

RESUMEN

El destino de los metales pesados en el suelo está controlado por factores importantes, incluyendo el pH de la solución del suelo, la presencia de ligantes complejos y una serie de propiedades del suelo, tales como textura y contenido de materia orgánica. La adsorción de metales es un proceso importante que controla sus bajas concentraciones en el suelo. Este proceso puede ser descrito como una reacción compleja de superficie sobre las partículas del suelo. La adsorción de metales catiónicos es favorecida a pH altos; en tanto que los metales oxianiónicos y los metaloides son adsorbidos a pH bajos. A concentraciones altas de metales pueden ser importantes las fases geoquímicas que contienen metales específicos. Se han desarrollado tecnologías limitadas para la remediación de suelos contaminados con metales; éstas incluyen excavación, remoción, estabilización, solidificación y lavados del suelo. La forma de contaminación del metal determina la biodisponibilidad del mismo en la matriz del suelo y afecta la eficiencia del lavado del metal del suelo.

INTRODUCTION

Although all soils contain trace levels of heavy metals, anthropogenic and natural activities have resulted in increased metal levels in many soils. In some cases, metal concentrations have been elevated to the extent that they pose risks to humans and the environment. Common metals found in contaminated environments include lead, cadmium, copper, nickel, zinc, and chromium. Arsenic, although correctly characterized as a metalloid, is usually included in this group.

Metal contamination problems have resulted from metallurgical, mining, and plating activities. Lead is the most common metal contaminant in soils; additional sources of lead have included disposal of automobile batteries and firearm materials in shooting ranges. Arsenic contamination has resulted from its historical use as a pesticide and a wood preservative, although some areas are naturally rich in available arsenic.

This review briefly summarizes some of the reactions and processes important when elevated levels of heavy metals are present in soils. Important variables controlling metal mobility (which is related to bioavailability and risk) are discussed. Methods to characterize metal-contaminated soils are presented. Finally, a brief discussion is presented on technologies employed for cleanup and remediation of these soils.

Soils and metals

Both the physics and chemistry of soils are important to understanding metal reactions and cleanup. Soil particulates are classified according to size, as presented in **table I**. Combinations of the different soil classes result in the various classifications of soil texture. Metal contamination is generally more of a problem in soils with higher amounts of clay. Clays are more chemically active than the other soil components and this fraction tends to accumulate the largest fraction of metals.

Both organic and inorganic soil components contribute to metal interactions. Inorganic materials within the clay fraction include aluminosilicates and oxides of iron, aluminum, manganese and titanium. Surface functional groups that are chemically active toward ions in the soil solution are formed on these minerals.

In a similar manner, organic matter that is ubiquitous in soil systems contains organic functional groups, generally carboxyl or phenolic based, that can complex with heavy metals. Strong metal affiliations with the soil result when organic matter exists as coatings on soil particulates. Soils with high organic contents tend to have elevated capacities for metal adsorption.

In the natural environment, concentrations of dissolved free metals, such as Pb^{2+}, are very low. This is especially true in soil solutions. The chemical matrices of soil solutions are complicated and metal ions bind to form aqueous complexes with both inorganic and organic ligands. Inorganic complexes can form with hydroxide, carbonate, and chloride ions (i.e., $PbOH^+$, $PbCO_3^0$, and $PbCl^+$), among others. Dissolved organic matter can complex heavy metals as well.

Metal affiliation with soils
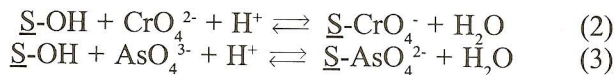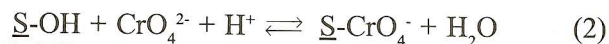#### Low metal concentrations

Because of the vast amount of chemically active surface sites within a soil, most heavy metals sorb strongly to the soil particulates, limiting the metal mobility. Metal sorption to soil components is generally described using the concept of *surface complexation*. Surface complexation is analogous to homogeneous complexation in solution. The active functional groups on the soil surface, either inorganic or organic, can bind with the metal through covalent interactions.

$$\underline{S}\text{-OH} + Pb^{2+} \rightleftharpoons \underline{S}\text{-OPb}^+ + H^+ \qquad (1)$$

The $\underline{S}$ represents the soil surface, either inorganic or organic, with an affiliated hydroxyl functional group. This surface group reacts with the metal, binding it to the soil particle/organic molecule.

As Equation 1 demonstrates, the reaction of metals with soil components is strongly dependent on solution pH; cationic metal adsorption is favored at high pH. At low pH, less metal adsorption onto the soil occurs and the metals are more mobile. **Figure 1** demonstrates the adsorption characteristics of several metals onto titanium dioxide. The effect of pH is clear as strong adsorption is noted above pH 7. Also note that each metal adsorbs to a different degree.

In aqueous solution, hexavalent chromium and arsenic(III) and (V) exist, not as cations, but as anions. As a result, their affiliations with the soil functional groups are different. Example reactions include:

$$\underline{S}\text{-OH} + CrO_4^{2-} + H^+ \rightleftharpoons \underline{S}\text{-CrO}_4^- + H_2O \qquad (2)$$
$$\underline{S}\text{-OH} + AsO_4^{3-} + H^+ \rightleftharpoons \underline{S}\text{-AsO}_4^{2-} + H_2O \qquad (3)$$

As reactions 2 and 3 indicate, the adsorption of anions is also pH dependent. However, in these cases, the adsorption occurs at low pH and the metal oxyanion is mobile at higher pH.

TABLE I. USDA SOIL CLASSIFICATIONS

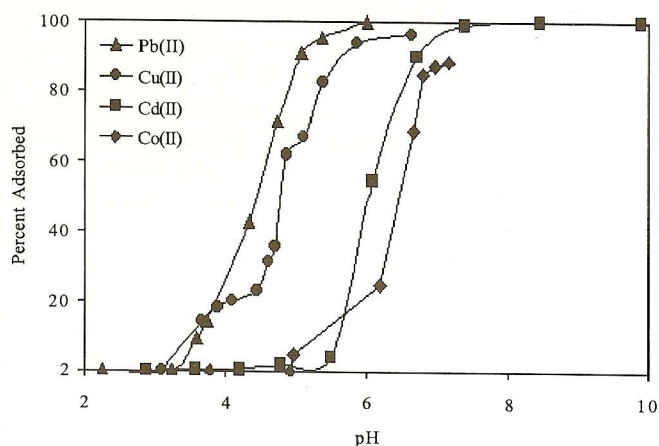| Class	Particle Size
Gravel	2-15 mm
Sand	0.075-2 mm
Silt	0.002-0.075 mm
Clay	<0.002 mm

Fig. 1. Adsorption of 10^{-4} M Pb(II), Cu(II), Co(II), and Cd(II) onto 2 g/L titanium dioxide

High metal concentrations

When metal concentrations in the soil matrix become higher, surface adsorption sites become saturated, limiting further sorption. As this occurs, the possibility exists for the formation of metal (hydr)oxide polymers on the surface of the soil particulates. This surface polymerization occurs as a transition from the specific adsorption of individual metal ions to the formation of an individual phase of heavy metal precipitate on the surface. Usually the surface polymerization/precipitation results in clusters of metal precipitate.

Heavily contaminated soils may also have originated from the input of a metal already present as a solid geochemical phase. Examples include the disposal of a metal-containing solid or sludge, and the exposure and weathering of a metal mineral, such as in the case of mine spoils.

At high concentrations, metals may be present in the soil in several phases, depending on the initial geochemical form, the chemical makeup of the soil solution, and other aspects important to the weathering process. With lead, possible forms include metallic lead; lead paint; various carbonate, phosphate, and oxide minerals; and lead sulfide. Lead strongly affiliates with soil components and adsorbed lead is also likely.

Characterization of contaminated soils

Characterization of metals-contaminated soil is critical to fundamental understanding of the health risks posed to humans near a contaminated site and in the evaluation of technologies under consideration to remediate the soil. It is clear that a total-metals analysis, based on a digestion process, is insufficient in quantifying soil health risks. The metals in the soil may be bound tightly within the soil matrix, be in a form that is very insoluble and immobile, or may be physically covered or coated with another precipitate that prevents the exposure of the metal compound. In such cases, high total-metal levels may pose minimal health and environmental risks.

Chemical sequential extraction processes have been developed as a tool to assist in determining specific geochemical phases that metals affiliate with. In a sequential extraction, the soil is exposed to increasingly harsh chemical treatments and the amounts of metals released are determined. Each treatment is designed to liberate metals from a specific soil phase; the metals released are assigned to the respective phase. The most popular sequential extraction process has been that of Tessier *et al.* (1979). The steps involved in their sequential extraction are presented in **table II**.

TABLE II. SEQUENTIAL METAL EXTRACTION PROCEDURE OF Tessier *et al.* (1979)

Extraction	Attributed Geochemical Phase
1 M MgCl$_2$	Extractable
1 M NaOAc	Carbonate
1 M NH$_2$OH, -HCl	Fe-Mn Oxide
25 % HOAc, 96 °C	
0.02 M HNO$_3$,	Organic
30 % H$_2$O$_2$, 85 °C	
Digestion	Residual

Problems with sequential extractions are well known and have been documented. These problems include re-adsorption phenomena and reactions that are not specific to each "phase" designation. Sequential extractions were developed to speciate metals in relatively uncontaminated soils and sediments and their extension to characterize extensively contaminated soils provides even more room for errors in designating metals to specific soil phases. Nonetheless, sequential extractions do provide information on the relative strength of the metal affiliation with the soil components. As discussed in the next section, this information can be used to gauge cleanup efficiency and metal bioavailability and risk.

Yarlagadda *et al.* (1995) evaluated three industrial soils contaminated with lead and copper using the sequential extraction process listed in **table II**. In one soil, most of the lead (>60 %) was affiliated with the "carbonate" phase. In the other two, however, the "Fe-Mn oxide" phase dominated lead affiliation; this extraction released 50 to 75 % of the total lead. Lead association in different size fractions were also evaluated. Interestingly, the lead distribution was essentially independent of the soil size fraction.

The lead micromineralogy of Montana mine spoils was evaluated by Davis *et al.* (1993). Thirteen different lead phases were identified in the soil samples. Dominant lead phases were MnPb oxides, Pb phosphates, and Pb oxides.

Due to low solubility and isolation by mineral coatings, >80 % of the lead was considered to be "stable" and thus was not bioavailable (Davis *et al.* 1992, 1993). Differences in lead availability were invoked to explain the absence of a relationship between blood-lead levels found in children and total lead levels in the local soil. Recent studies of lead and arsenic bioavailability have been published (Davis *et al.* 1997, Ruby *et al.* 1996, 1999).

Remediation of contaminated soils

Few technologies exist for the cost-effective cleanup of soils contaminated with heavy metals. In many cases, still the most common method of cleanup is to excavate the contaminated soil and haul it to a secured landfill for burial. While addressing the immediate problem and site, this operation does not decontaminate the soil and some risks are transferred to the landfill site. Additional hazards and concerns are encountered with dusts and emissions from the soil during the excavation and transportation operations.

A second method employed to reduce the risks from metals in soil is stabilization and solidification (S/S). The use of Portland cement represents the most common S/S process. Portland cement is added to the soil, possibly employing an in-situ process. The cement is mixed with the soil using a large drill or set of mixing blades. The cement forms a solid matrix with the soil, physically isolating the metals from the surrounding soil solution. Also, chemical binding mechanisms hold metals to the soil and cement material at the high pH of the mixture.

While effective in reducing metal leachability and mobility, the S/S process leaves the metals in place within the soil/cement matrix, and can render the soil infertile. Recently, chemical methods to reduce the bioavailability of metals in soils have been examined (Laperche *et al.* 1996, 1997).

Soil washing can be employed to remove metals from contaminated soils, although the process can be expensive due to the materials handling issues involved. If the metals are concentrated in the fine fraction of the soil, a simple washing process with size separation can be implemented to remove the fines from the soil. The fines are disposed of in an appropriate landfill and the less-contaminated coarse material is replaced to the site. In the chemical soil washing process, either a strong acid or a strong metal chelating agent (such as EDTA) can be used. The chemical wash solution is mixed with excavated soil. The acid or chelate desorbs metals from the soil surface (in the case of acid, this is the reverse of Equation 1) and dissolves metals from metal solid phases. The washed soil is returned to the site, although its biological productivity may have been adversely altered by the harsh chemical wash. The wash water is treated as a metal-containing waste water and may be recycled back to the washing process. A number of studies on soil washing effectiveness and modeling have been recently published (Hanson *et al.* 1993, Van Benschoten *et al.* 1994, Cline and Reed 1995, Davis and Singh 1995, Yarlagadda *et al.* 1995, Reed *et al.* 1996, Van Benschoten *et al.* 1997, Davis and Hotha 1998, Davis *et al.* 1998, Ganguly *et al.* 1998a, b, Rampley and Ogden 1998, Pagilla and Canter 1999).

TABLE III. LEAD RELEASE FROM CONTAMINATED SOILS USING VARIOUS SEQUENTIAL EXTRACTIONS (Van Benschoten *et al.* 1997)

		Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7
Total Lead (mg/kg)		11933	2307	5913	3199	4808	1394	4249
Dominant Lead Phases*		Carb	Met	Carb & Ox	Mostly Sulf	Carb & Ox	Carb,Ox, Sulf	Ox & Fe Sulf
Extractant	**Attributed Phase**	**Percent Lead Extracted**						
DI Water	Water Soluble	1.8	7.3	2.7	0.5	2.3	1.0	0.0
0.5 M Ca(NO$_3$)$_2$	Exchangeable	31.2	8.7	4.6	2.7	5.4	4.8	5.0
0.05 M AgNO$_3$ + 0.1 M Ca(NO$_3$)$_2$	Ag-displaceable	25.6	2.8	9.0	2.0	19.4	14.7	2.2
1 M NaOAc, pH 5	Carbonate	25.5	26.0	57.9	25.7	60.7	8.6	21.8
0.1 M NH$_2$OH·HCl + 0.1 M HNO$_3$	Easily Reducible	7.5	10.9	9.6	14.7	5.1	2.9	3.8
0.1 M Na$_4$P$_2$O$_7$, pH 10	Organic	2.7	7.4	2.9	9.2	1.4	4.1	5.9
0.25 M NH$_2$OH·HCl + 0.25 M HNO$_3$	Fe oxide (amorphous)	2.4	11.6	3.8	12.2	2.0	7.6	28.2
0.4 M NH$_2$OH·HCl + 25 % v/v CH$_3$COOH, 90 ºC	Fe oxide (crystalline)	1.1	14.6	6.1	21.8	2.5	48.1	24.6
1 M HNO$_3$	Sulfide	1.1	4.1	2.7	4.1	0.3	5.3	1.9
Microwave digestion w/ HNO$_3$ & HClO$_4$	Residual	1.1	7.6	0.8	7.1	0.9	2.9	6.6

*As determined using scanning electron microscopy; Carb = Pb carbonates; Ox = Pb oxides; Sulf = Pb sulfates; Met = Pb associated w/ various metal oxides; Fe Sulf = Pb iron sulfate

The efficiency of a soil washing process depends on the affiliation of the metals within the contaminated soil matrix. Van Benschoten *et al.* (1997) performed a ten-step sequential extraction of lead from seven soils collected from several industrial sites. Removal of more than 80% of the lead required anywhere from four to eight extraction steps (**Table III**). For six of the soils examined, soil washing at pH 1 produced removals corresponding to the 5th- 7th extraction. It was indicated that detrital lead (characterized as Fe-oxide(am)-bound, Fe oxide(crystalline)-bound, sulfide, and residual) was not removed by the pH 1 wash. Nonetheless, because this lead was difficult to remove from the soil, it may be non-mobile.

Davis and Hotha (1998) evaluated the washing of ten different forms of lead, including adsorbed lead, from soils artificially contaminated at 5000 mg Pb/kg. Results indicated that the lead contamination forms could be divided into two groups. One group, including adsorbed lead, lead oxide, lead carbonate, lead sulfate, and basic lead carbonate was easily removed from the soil matrix by acid washing. However, five other compounds, lead dioxide, lead sulfide, lead paint, lead dimethyldithiocarbamate (an organolead compound) and lead metal were resistant to the acid wash (**Figure 2**). Essentially the same groupings resulted from washing with EDTA, indicating the importance of the form of the metal, rather than the total metal concentration in evaluating washing efficiency.

These studies on lead suggest that susceptibility to soil washing and bioavailability may be related issues. Soils that contain lead in forms that are bioavailable are also likely to be successfully remediated through soil washing. Soils that contain lead that is resistant to successful washing, however, may not pose significant health risks because the lead is likely to not be bioavailable. In these cases, soil washing should not be considered and other remediation technologies, or even no action, should be explored due to the resulting low risks.

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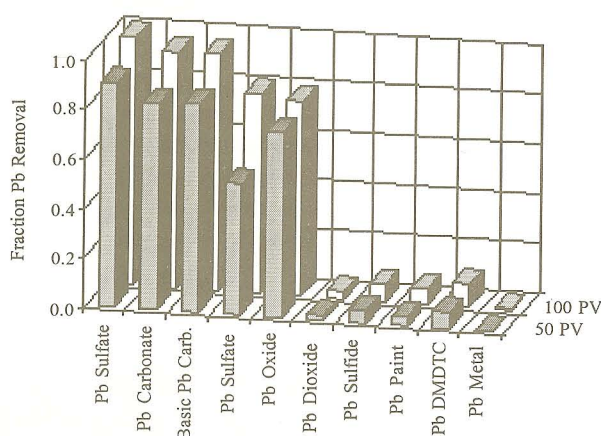Pagilla K.R. and Canter L.W. (1999). Laboratory studies on

Fig. 2. Efficiency of acid washing, after passage of 50 and 100 pore volumes (PV), of soils contaminated by different lead compounds. Columns of 12 g contaminated soil were washed with water at pH 2 (from HNO_3) containing 5×10^{-2} M $NaNO_3$ background electrolyte. Each soil was artificially contaminated at 5000 mg Pb/kg. The pore volume of each sample was approximately 4.0 cm³ and the soil contact time was approximately 1.3 min.

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