

Heavy Metal Interactions with Phosphatic Clay: Sorption and Desorption Behavior

S. P. Singh, L. Q. Ma,* and W. G. Harris

ABSTRACT

Heavy metals produced and released during agricultural and industrial activities may pose a serious threat to the environment. This study investigated the effectiveness of phosphatic clay, a by-product of the phosphate mining industry, for immobilizing heavy metals (Pb^{+2} , Cd^{+2} , and Zn^{+2}) from aqueous solutions. A batch equilibrium technique was adopted to evaluate metal sorption in the presence of 0.05 M KNO_3 background electrolyte solution. The amounts of metals sorbed onto phosphatic clay decreased in the order $Pb^{+2} > Cd^{+2} > Zn^{+2}$. Desorption data suggest that a large fraction of metals sorbed onto phosphatic clay stayed intact under a wide variation in extracting solution pH (ranging from 3 to 10). Desorption rates were slowest for Pb followed by Cd and Zn. Only 8.1 to 23.1% of Pb, 8.4 to 45% of Cd, and 21.9 to 73.9% of Zn sorbed on phosphatic clay was mobilized by USEPA toxicity characteristic leaching procedure (TCLP) solutions at pH 2.93 ± 0.05 and 4.93 ± 0.05 , respectively. Formation of fluoropyromorphite [$Pb_{10}(PO_4)_6(F_2)$], confirmed by scanning electron microscopy (SEM) and X-ray diffraction (XRD), after reaction of aqueous Pb with phosphatic clay suggested that precipitation remained the dominant mechanism for Pb removal from aqueous solution. In the case of aqueous Cd and Zn interaction with phosphatic clay, we are not able to confirm the formation of a new amorphous and/or crystalline phase on the basis of available information. Other possible sorption mechanisms for Cd and Zn may include sorption and coprecipitation. Thus, phosphatic clay may be an effective amendment for in situ immobilization of heavy metals in contaminated soils and sediments.

PHOSPHATE mining in Florida produces large quantities of waste phosphatic clay. At current mining rates approximately 100 000 Mg d^{-1} of waste phosphatic clay is produced, creating a major disposal problem for the phosphate mining industry. Phosphatic clay characteristically has a high content of apatite [$Ca_{10}(PO_4)_6(OH,F,Cl)_2$], up to 24 to 32% of total dry weight, which is too fine to recover during processing. In addition, phyllosilicate minerals (mainly smectite, polygorskite, and kaolinite) constitute a major fraction of phosphatic clay (Hawkins, 1973; Blue and Mislevy, 1980). This clay has a high cation exchange capacity (CEC) and neutral to slightly acidic pH. These properties suggest that addition of phosphatic clay as a binding agent to immobilize heavy metals could be a cost-effective approach for the remediation of soils, sediments, and water contaminated with heavy metals.

Land disposal of municipal and industrial wastes and applications of fertilizers and pesticides in agriculture has contributed to a continuous accumulation of heavy metals in soils (Adriano, 1986; Alloway and Jackson, 1991), and there is increased concern regarding the environmental impacts of agricultural practices on the bioavailability of heavy metals. The bioavailability and mo-

bility of these metals in soil strongly depends on the extent of their sorption with solid phases. Partitioning of heavy metals between solid and aqueous phases is controlled by properties such as surface area, surface charge (induced by the formation of organic coatings on the surface), pH, ionic strength, and concentration of complexing ligands (Petrovic et al., 1999). Metal immobilization through precipitation and adsorption is also considered a common mechanism to decrease the hazards of heavy metal in contaminated soils (Malakul et al., 1998; Ma et al., 1993).

In situ immobilization is a promising approach that has the potential to remove metals from solutions and/or stabilize metals in soils (Ma et al., 1993). When using this approach, two important factors need to be considered: (i) the system must be effective under a variety of existing geochemical conditions and (ii) immobilized metals should be stable and remain nonleachable under varying environmental conditions. Generally, in situ immobilization of metals involves minimization of contaminant mobility by transferring the metals from labile to nonlabile phases via physically, chemically, or biologically induced transformations. Behavior of heavy metals in a soil is governed largely by their sorption and desorption reactions with different soil constituents. Although desorption is an important process controlling the availability and mobility of heavy metals in contaminated soils, it has received much less attention than the sorption process. It is important to understand various processes and factors controlling the desorption behavior of sorbed metals.

Metal bioavailability is related to solubility rather than total concentration, which must be taken into account when developing remediation strategies (Traina and Laperche, 1999). For example, a major limitation for in situ Pb immobilization in contaminated soils is the limited solubility of Pb minerals present in the existing soil environment. Lead carbonate (cerussite) has been identified as a major Pb mineral in many contaminated soils, particularly from battery recycling sites (Royer et al., 1992; Nedwed and Clifford, 1997). Effective Pb immobilization using phosphorus amendments requires enhanced solubility of the existing Pb minerals by inducing acidic conditions to promote pyromorphite [$Pb_{10}(PO_4)_6(OH,F,Cl)_2$] formation, with the Pb in the pyromorphite being much less bioavailable than Pb associated with cerussite. These resulting acidic conditions will also enhance the mobility of other heavy metals, increasing the risk of their leaching to ground water. Phosphatic clay possesses a high potential to adsorb these metals. Phosphatic clay could also have the secondary benefits of improving fertility, structure, and soil moisture-holding capacity when added to sandy soils (Gonzalez et al., 1991).

Abbreviations: SEM, scanning electron microscopy; TCLP, toxicity characteristic leaching procedure; XRD, X-ray diffraction.

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Most studies on heavy metal sorption and related mechanisms have been focused on individual synthetic mineral sorbents. For example, hydroxyapatite has been investigated as a potential agent to treat heavy metal-contaminated soils, sediments, wastes, and wastewater, especially in the cases of Pb, Cd, Zn, and U (Ma et al., 1993; Xu and Schwartz, 1994; Chen et al., 1997; Arey et al., 1999). However, minerals such as smectite, illite, kaolinite, and Fe–Mn oxides have potential to act as binding agents for heavy metals. Adsorption behaviors of these individual minerals have been studied extensively (Griffin and Au, 1977; Yong et al., 1990; Siantar and Fripiat, 1995; Spark et al., 1995; Lothenbach et al., 1998; Kraepiel et al., 1999). To our knowledge, no efforts have been made to evaluate the sorption and desorption behavior of phosphatic clay with respect to heavy metals. Phosphatic clay is a heterogeneous mixture of several minerals, which interact with heavy metals in a variety of ways for which the reaction and mechanisms are still not well understood. Identifying the sorption mechanisms of heavy metals by phosphatic clay is important to predict its efficiency for heavy metal immobilization in the contaminated soil and sediment environments.

The main objective of this study was to evaluate the heavy metal immobilization potential of phosphatic clay. The specific goals were to (i) examine the sorption of heavy metals onto phosphatic clay; (ii) estimate the leachability of reaction products using both acidic and basic extracting solutions; (iii) characterize the reaction products of phosphatic clay after interaction with aqueous Cd, Pb, and Zn solutions; and (iv) elucidate the mechanisms of heavy metal sorption and desorption in the presence of phosphatic clay. These results would be useful when evaluating the heavy metal immobilization potential of phosphatic clay in contaminated sites.

MATERIALS AND METHODS

Characterization of Phosphatic Clay

The phosphatic clay used in this study was obtained from the PCS Phosphate Mining Company, White Springs, FL. Clay sample preparation included air-drying, crushing by mortar and pestle, passing through a 60-mesh sieve, and rinsing with deionized water. Characterization of the clay included surface area measurement, mineralogical analysis, particle morphology assessment, and total elemental analysis. The measured surface area of the phosphatic clay sample was $33.65 \pm 1.19 \text{ m}^2 \text{ g}^{-1}$, determined by the single point BET (N_2) adsorption procedure. The elemental composition of phosphatic clay expressed in mass percentage (% w/w) was Si 17.52%, Ca 12.79%, Al 6.51%, Fe 1.75%, Mg 0.96%, and P 5.24%. Relatively high contents of Al, Si, Ca, and P reflect the presence of apatite and phyllosilicates as its major constituents. Phosphatic clay mineralogy was determined both prior to and after various aqueous metal treatments using XRD in conjunction with standard cation-saturation procedures for identification of expandable phyllosilicates (Whittig and Allardice, 1986). X-ray diffraction analyses were conducted on a computer-controlled X-ray diffractometer equipped with stepping motor and graphite crystal monochromator. Scans were conducted from 2 to 60° at a rate of 2° per min. Particle morphology of phosphatic clay was assessed by SEM and elemental spectra for individual

particles were obtained using energy-dispersive X-ray spectroscopy (EDS) during SEM observations. The apatite and phyllosilicates (i.e., especially smectite) were identified as major phosphatic clay components possessing great potential to reduce the mobility and bioavailability of heavy metals in the contaminated aqueous environment.

Sorption Experiment

Deionized water from a Barnstad (Dubuque, IA) Nano-Pure system was used in rinsing and preparation of samples. Labware used for each experiment was cleaned in detergent first, and then washed in 10% HNO_3 , and finally rinsed with deionized water. Individual aqueous solutions of Cd, Pb, and Zn were prepared at concentrations of 5180 mg L^{-1} (25 mM), 5058 mg L^{-1} (45 mM), and 4904 mg L^{-1} (75 mM), respectively, from their nitrate salts. The pH values of these initial stock solutions were 4.06, 4.36, and 5.72, respectively. All chemicals used in these experiments were analytical reagent grade.

All metal sorption studies were performed using batch experiments. A 30-mL aliquot of 0.05 M KNO_3 background electrolyte solution containing variable metal concentrations ranging from 0 to 200 mg L^{-1} was equilibrated with 0.1 g phosphatic clay powder in 40-mL polycarbonate centrifuge tubes. The slurries were shaken on a reciprocating shaker operated at $30 \pm 1 \text{ rpm}$ at a room temperature of $25 \pm 3^\circ\text{C}$ for 24 h. For kinetic studies, sorption experiments were performed up to approximately 144 h. The supernatant was separated by centrifugation (Beckman [Fullerton, CA] J-2-21) at 10 000 rpm for 20 min. Samples without phosphatic clay were prepared by identical procedures as the sorption samples to determine the exact initial concentration. Metal concentrations in the filtrates after passing through 0.45- μm membrane pore size filters were analyzed using flame atomic absorption spectrophotometers (PerkinElmer [Norwalk, CT] Models 3030 or SIMMA 6000, depending on metal concentrations). Multilevel standards (Fisher Scientific, Pittsburgh, PA) were prepared in 2% HNO_3 acid. Total P was measured colorimetrically with a Shimadzu (Kyoto, Japan) 160 U spectrophotometer as ascorbic-reduced phosphomolybdate (Olsen and Sommers, 1982). Solution pH was determined using a Fisher Scientific Accumet Model 20 pH/conductivity meter. The amount of adsorbed metals was taken as the difference between the amount added initially and that remaining in solution after equilibration. All measurements were run in duplicate.

Desorption Experiment

In order to evaluate the reversibility of heavy metals sorbed onto phosphatic clay, their desorption characteristics were also determined. Three extracting solutions of varying pH values were prepared to estimate metal leachability from phosphatic clay after interaction with aqueous metal solutions. Two acidic solutions were prepared from acetic acid at $\text{pH } 2.93 \pm 0.05$ and 4.93 ± 0.05 following the technique for preparation of extraction fluids as discussed in the USEPA toxicity characteristic leaching procedure (USEPA, 1995). The other extracting solution used in this study was an alkaline solution, $1 \times 10^{-4} \text{ M}$ NaOH (e.g., pH 10 solution), prepared by diluting concentrated NaOH solution with deionized water.

Solid residues remaining in the centrifuge tubes after sorption experiments were thoroughly washed three times with deionized water and the supernatants discarded immediately after 15 min of centrifugation. Washed residues from each group were treated with 30 mL of each leaching solution and the slurries were shaken on a reciprocating shaker for 24 h. Slurries were centrifuged and their supernatants were filtered with 0.45- μm

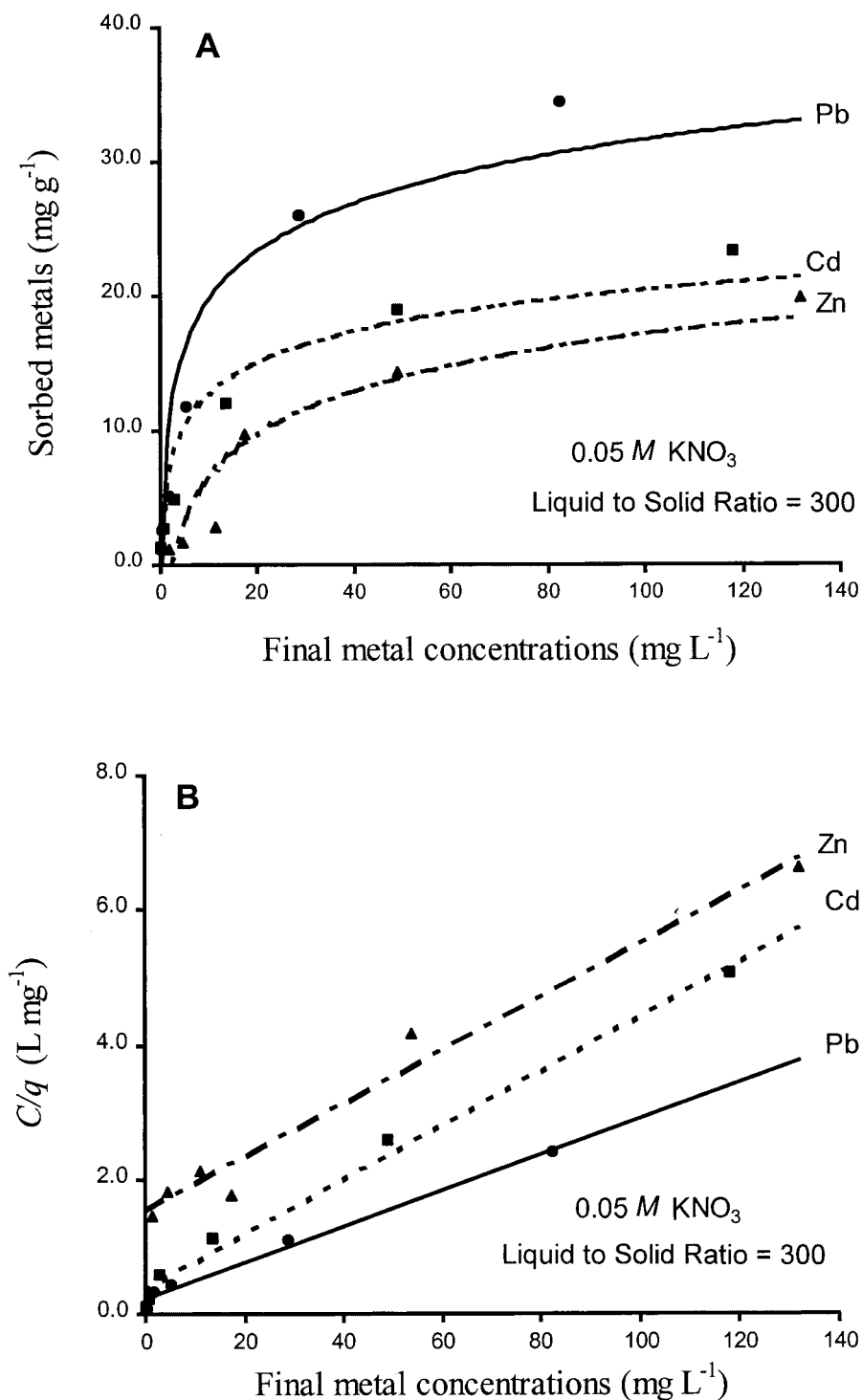


Fig. 1. Langmuir sorption isotherms of Pb⁺², Cd⁺², and Zn⁺² on phosphatic clay (A) and their linear fittings (B) after the transformation using the Langmuir equation.

membrane pore size membrane filters and analyzed for metal concentrations as described above for the sorption experiment.

RESULTS AND DISCUSSION

Sorption Isotherms

The experimental data of the single metal sorption isotherms of Cd(II), Pb(II), and Zn(II) are shown in Fig. 1A.

These isotherms represent the sorption behavior of metals on phosphatic clay as a function of increasing aqueous metal ion concentrations after an equilibration of 24 h. Overall, the sorption behaviors of Cd and Zn were similar to each other, with differences in the amounts sorbed. They both are different from Pb sorption behavior. Phosphatic clay was effective in sorbing all three metals. Metal sorbed onto phosphatic clay varied in the

Table 1. Langmuir parameters for the sorption of heavy metals onto phosphatic clay.

Metal	M^\dagger	b^\ddagger	R^2
	mg g ⁻¹	L mg ⁻¹	
Pb	37.2	0.125	0.99
Cd	24.5	0.111	0.98
Zn	25.1	0.026	0.97

[†] Maximum sorption capacity.

[‡] Sorption constant.

following descending order: Pb⁺² > Cd⁺² > Zn⁺². For initial concentrations ≤ 10 mg L⁻¹, final concentrations approached levels greater than limits of detection. According to Brümmer et al. (1983), isotherms with similar equilibrium concentrations obtained from different initial metal concentrations indicate a precipitation mechanism. Our sorption data appear consistent with a precipitation mechanism below a threshold value dependent on the ligand, presumably PO₄³⁻. Most sorption isotherms in this study were characterized by decreasing slopes as aqueous metal concentration increased beyond the threshold, indicating a high affinity of the adsorbent for high concentrations of the adsorbate.

Heavy metal sorption onto phosphatic clay above threshold concentrations has been analyzed using the Langmuir model to evaluate parameters associated with their sorption behaviors. The linear form of Langmuir equation is represented by:

$$\frac{C}{m} = \frac{C}{M} + \frac{1}{bM} \quad [1]$$

where C is the equilibrium concentration (mg L⁻¹), m is the amount of heavy metals sorbed onto phosphatic clay (mg g⁻¹), M is the maximum sorption capacity (mg g⁻¹), and b is the sorption constant (L mg⁻¹). The sorption data were fit to a linear form of the Langmuir equation and are plotted in Fig. 1B. Langmuir sorption parameters of phosphatic clay for each of the three metals were calculated by using least squares fitting, and their values are shown in Table 1. In all cases, correlation coefficients (R^2) for the linear regression fit were ≥ 0.97. Sorption parameters for phosphatic clay showed variability among the three metals, as reflected by their sorption maxima and Langmuir affinity constants (Table 1). Results showed that M for phosphatic clay remained highest for Pb, followed by Zn and Cd.

It is possible that the presence of apatite [Ca₁₀(PO₄)₆(F,Cl,OH)₂] and other minerals in phosphatic clay significantly enhanced its sorption capacity for heavy metals through a dissolution and precipitation mechanism, particularly in the case of Pb. Higher m values for phosphatic clays suggested its higher affinity for Pb and Cd compared with Zn (Table 1 and Fig. 1B). In the case of Pb, slight deviations were observed at higher concentrations (i.e., above an equilibrium concentration of approximately 75 mg L⁻¹). At high initial concentration of Pb_{aq} ≥ 100 mg L⁻¹, our data support the hypothesis of Ma et al. (1993) that dissolution of apatite and subsequent precipitation of pyromorphite contributed largely to aqueous Pb removal. Hydrolysis of Pb is expected for

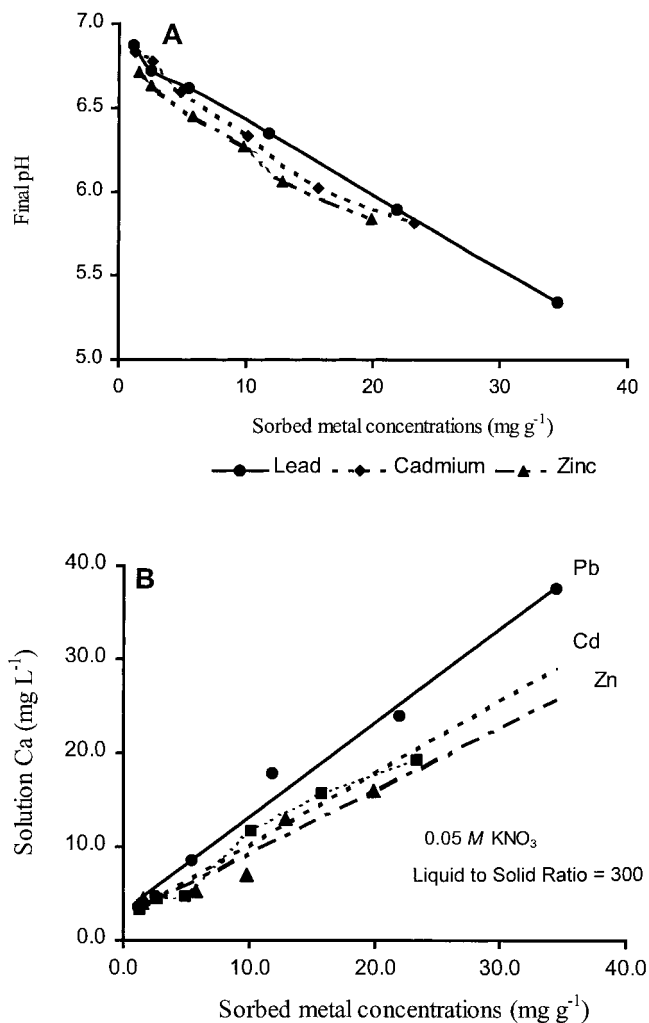


Fig. 2. Relationships between sorbed metals and final pH (A), and between sorbed metals and total Ca concentrations in the final solution (B) after 24 h of metal interaction with phosphatic clay.

Pb within these systems given the pH (approximately 6), which may enhance adsorption and (surface) precipitation (Sparks, 1995).

During the sorption experiments, pH and concentrations of Ca and P in the equilibrium solutions were also measured. After interactions of phosphatic clay with heavy metals, P concentrations in the solutions were reduced to below our detection limit, equivalent to the P concentration in the reagents blank (data not shown). In the absence of metal addition, equilibrium pH tends to remain close to neutral. Interaction of phosphatic clay with metal solution caused a decrease in solution pH by approximately 1.5 units as the amount of sorbed metals increased. Solution pH decreased as the initial metal concentration increased since these metals act as weak Bronsted acids. However, the pH during interaction of aqueous metal solution with phosphatic clay remained highest for Pb, followed by Cd and Zn (Fig. 2A). In addition to the precipitation reaction, Pb retention onto phosphatic clay might be supplemented by the sorption of Pb hydroxy complexes (Yong et al., 1990).

In order to examine whether precipitation was ther-

Table 2. MINTEQ-A2 input parameters and calculated saturation indices for selected metal phosphate mineral phases, based on the average equilibrium data during their interactions with phosphatic clay.

Metal	Input parameters [†]				Saturation index (log Ω)		
	pH	Ca	PO ₄	Metal conc.	[Pb ₁₀ (PO ₄) ₆ (F ₂)]	Cd ₃ (PO ₄) ₂	Zn ₃ (PO ₄) ₂ ·4H ₂ O
			mg L ⁻¹				
Pb ⁺²	7.25	40	<0.1	82.5	8.41	–	–
Cd ⁺²	6.35	40	<0.1	118.2	–	–4.58	–
Zn ⁺²	6.35	40	<0.1	131.9	–	–	–8.85

[†] Equilibrium pH and anion concentrations.

modynamically feasible, the speciation program MINTEQ-A2 was used to calculate saturation indices. The saturation index is defined as the log of the ion activity product divided by the solubility product. Thermodynamic calculations used the measured pH, PO₄, total Ca, Cd, Pb, and Zn concentrations in each final solution with the ionic strength of 0.05 *M*. Calculated saturation indices for the aqueous metal solution equilibrated with phosphatic clay are presented in Table 2. Thermodynamic calculations show that final solutions are supersaturated with respect to pyromorphite. On the other hand, final solutions remained undersaturated with respect to either Cd₃(PO₄)₂ or Zn₃(PO₄)₂·4H₂O (hopeite) for Cd and Zn, respectively (Table 2). This suggests that alternate sorption reactions and solid phases control Cd and Zn solubility during their interactions with phosphatic clay.

Correlation between the amounts of Ca mobilized into solution and the amounts of aqueous metals removed by phosphatic clay were approximately linear (Fig. 2B). The slope for the Pb sorption isotherm vs. Ca concentration was 0.999 with $R^2 = 0.95$. The observed loss of Pb from solution coupled with gain of Ca and formation of fluoropyromorphite points toward two potential mechanisms: apatite dissolution and precipitation of fluoropyromorphite or exchange of Pb with Ca within the apatite. On the other hand, slopes for Cd and Zn were 0.77 ($R^2 = 0.97$) and 0.67 ($R^2 = 0.92$), suggesting other retention mechanisms in addition to cationic exchange, such as surface complexation (Echeverria et al., 1998). We assumed that most Ca in solution was obtained from the dissolution of phosphatic clay components (e.g., fluoroapatite and carbonate minerals) after interactions of phosphatic clays with aqueous metal solutions.

Simultaneous changes in solution pH and Ca concentration make it difficult to determine whether the increase in Ca concentration was the consequence of ion exchange with heavy metals, further phosphatic clay dissolution due to a decrease in pH, or other mechanisms. According to LeGeroes and LeGeroes (1984), cations with ionic radii smaller than Ca⁺² (0.099 nm) have less of a chance to be incorporated into an apatite structure compared with cations with larger ionic radii. Therefore, precipitation of Zn²⁺ (0.069 nm) with Ca⁺² would be less likely compared with the larger cations Pb⁺² (0.118 nm) and Cd⁺² (0.097 nm). This explanation is consistent with our data and those of Ma et al. (1994). In the case of phosphatic clay, it appears that several mechanisms are involved in the removal of metals from aqueous solution.

Solid Phase Examination

X-ray diffraction analysis of phosphatic clay after its interaction with aqueous Pb solutions at the highest concentration (approximately 500 mg L⁻¹) confirmed the formation of fluoropyromorphite as evidenced by its large diffraction peaks at 0.292 nm (Fig. 3). In the case of Cd and Zn sorption onto phosphatic clay, XRD patterns were identical with those of the original phosphatic clay, with no significant morphological differences (data not shown) even at their highest concentrations. Based on the available information, we were unable to confirm whether amorphous and/or short-range crystalline solid phases (e.g., Cd and Zn phosphates) were formed during their interactions with phosphatic clay. In the studies of the interactions of hydroxyapatite with aqueous Cd and Zn, Ma et al. (1994) speculated precipitation of amorphous to poorly crystalline Cd and Zn phosphates.

Lead-bearing crystals were located using SEM back scattered electron image (BSI) signal strength. Figure 4 represents a BSI micrograph reflecting the presence of a cluster of lath-like pyromorphite crystals as a major solid-phase Pb mineral in phosphatic clay after its interaction with aqueous Pb solution at the highest concentration. The distribution of pyromorphite components was evaluated by a dot-mapping experiment. These crystals were confirmed to be rich in Pb and P, but not Ca (Fig. 5). X-ray diffraction analysis also confirmed pyromorphite formation in aqueous Pb-treated clay. Xu and Schwartz (1994) suggested possible coprecipitation of Cd and Zn with Ca to form solid solutions when aqueous metal solutions interacted with apatite. However, we were unable to confirm the clustering of these metals with Ca, or in any other form, using SEM and energy-dispersive techniques. Coprecipitation of Cd and Zn into phosphatic clay components (e.g., apatite) cannot be excluded on the basis of our measurements. Coprecipitation has been advanced as an explanation for the slow uptake often observed in metal sorption experiments (McBride, 1980).

Desorption of Sorbed Metals

Heavy metal desorption from phosphatic clay depend on the use of extracting solutions (Table 3). The amounts of Cd and Zn desorbed by acidic solutions remained high compared with Pb. Depending upon the amount of metals initially sorbed, the percentage of desorption using a TCLP extracting solution at pH 2.93 varied from 9.8 to 23.1 for Pb, 8.4 to 45.0 for Cd, and 29.8 to 73.9 for Zn. Under alkaline extracting conditions, sorbed

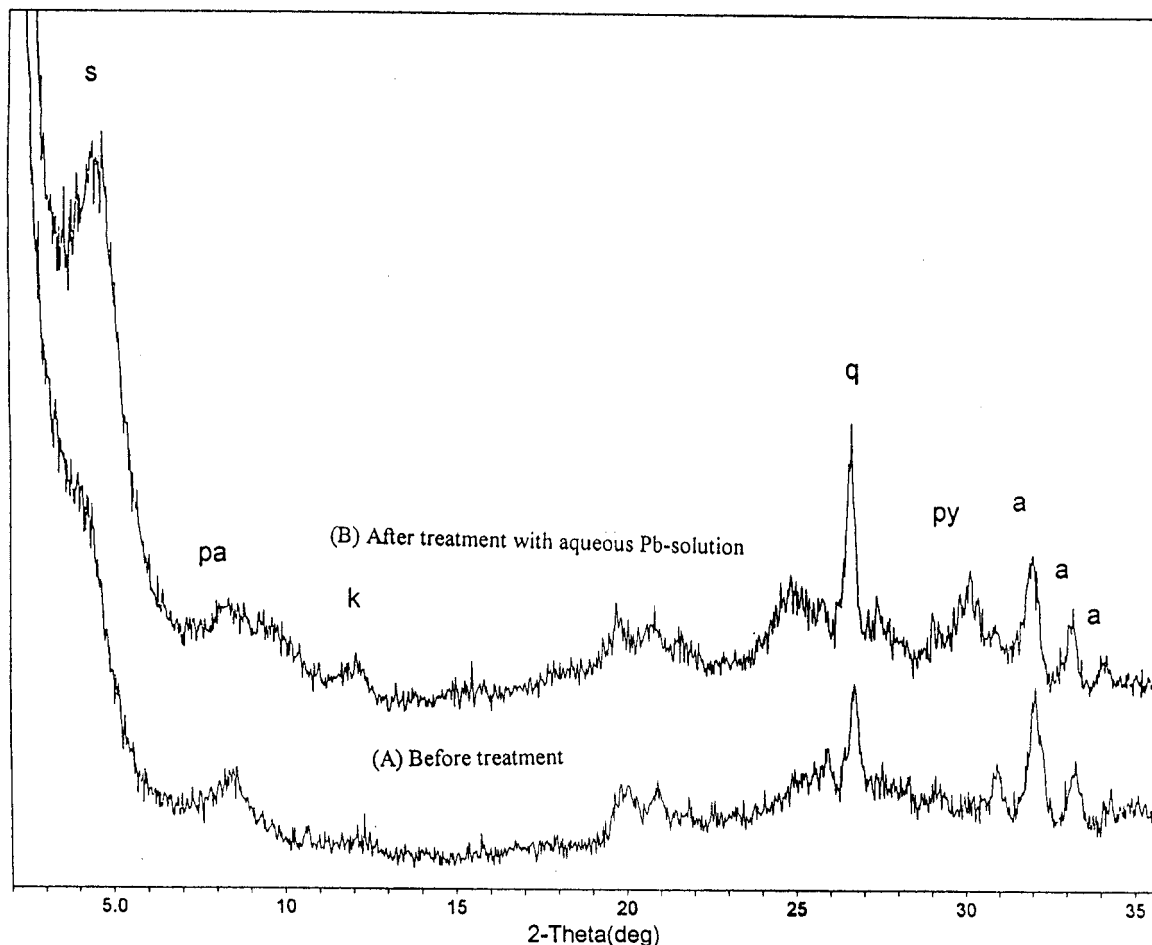


Fig. 3. X-ray diffraction patterns of phosphatic clay before Pb sorption (A) and after Pb sorption (B). Mineral abbreviations: s (smectite), pa (polygorskite), k (kaolinite), q (quartz), py (pyromorphite), and a (apatite).

metals remained more stable compared with acidic conditions. Thus, it appears that the fluoropyromorphite formed during the Pb sorption process remained more stable than surface complexes of Zn and Cd.

Although absolute amounts of metals desorbed into the extracting solutions increased with increasing sorption onto phosphatic clay, their relative amounts (e.g., percent of total sorbed metal contents) decreased with increasing sorption. Decreases in metal desorption with increasing sorbate amount may be accounted for by in-

creased proportion of less readily desorbed solid phases (e.g., precipitates) formed during the sorption process. It might be possible that several retention processes such as precipitation, coprecipitation, diffusion, and surface sorption contribute simultaneously toward metal removal from aqueous solutions because phosphatic clay is a heterogeneous mixture of several minerals. For the metals studied, the desorbed amount decreased continuously with increasing pH, with only trace amounts being desorbed above pH 7.

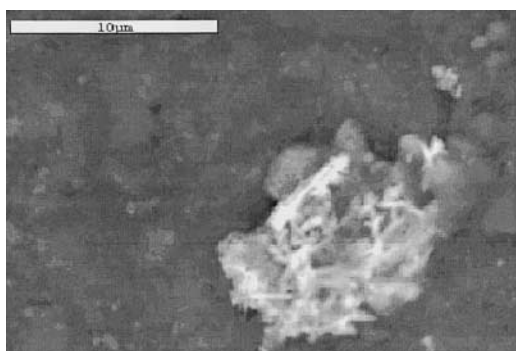


Fig. 4. Scanning electron microscopy (SEM) back scattered electron image (BSI) micrograph of pyromorphite in aqueous Pb-treated phosphatic clay showing cluster of lath-like pyromorphite crystals.

Table 3. Desorption percentage of heavy metals previously sorbed onto phosphatic clay during sorption experiment.

Metals	Sorbed [†] mg g ⁻¹	Desorption		
		TCLP pH 2.9 [‡]	TCLP pH 4.9 [‡]	H ₂ O pH 10
		%		
Pb	11.7	23.1	17.9	1.5
Pb	21.0	20.0	13.8	0.5
Pb	93.0	9.8	8.1	2.4
Cd	10.1	23.2	17.4	1.2
Cd	19.9	45.0	33.0	0.3
Cd	35.9	8.4	14.5	2.4
Zn	7.3	73.9	28.7	0.4
Zn	22.5	46.6	33.3	1.7
Zn	40.8	29.8	21.9	6.0

[†] Metals sorbed on phosphatic clay.

[‡] Toxicity characteristic leaching procedure extracting solutions at pH 2.93 ± 0.05 and 4.93 ± 0.05.

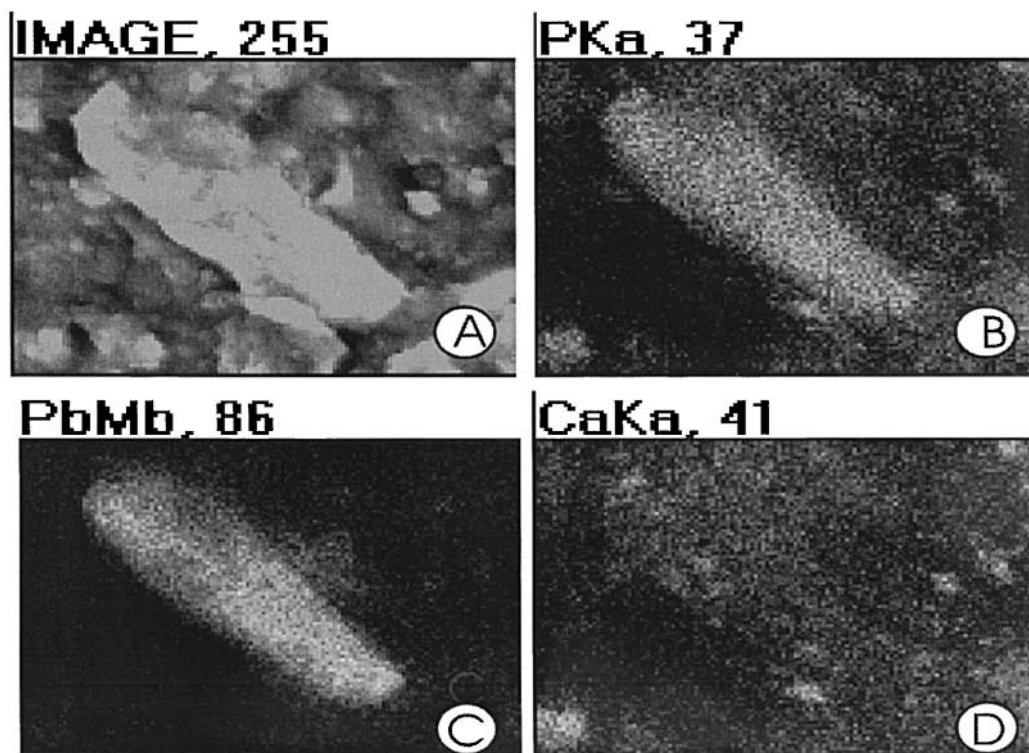


Fig. 5. Energy dispersive X-ray spectroscopy (EDS) dot-mapping of pyromorphite particle in aqueous Pb-treated phosphatic clay. (A) Selected pyromorphite crystal. (B) Presence of Pb in pyromorphite. (C) Presence of P in pyromorphite. (D) Absence of Ca in pyromorphite.

Desorption of sorbed metals from phosphatic clay revealed clear differences in their sorption behavior. Among the studied metals, Pb showed the greatest resistance to desorption followed by Cd and Zn (Table 3). Xu and Schwartz (1994) and Chen et al. (1997) observed similar desorption behavior for metals sorbed onto hydroxyapatite. Exceptionally low desorption of Pb from phosphatic clay confirmed the importance of apatite in retaining Pb, since only a small percentage of sorbed Pb was released even by TCLP solution at pH 2.93. Lead was tenaciously held to phosphatic clay due to substantial amounts of fluoroapatite, only small percentages of which could be removed. Pyromorphite remained the most stable lead mineral under a wide range of geochemical conditions. This suggests that phosphatic clay could be used effectively to remediate Pb-contaminated soils and sediments.

The sorption of metals from solution is not necessarily a simple process involving a single species. In most cases, more than one species is being sorbed onto more than one type of surface site during the sorption process (Spark et al., 1995). From comparison of sorption and desorption data, it is apparent that, in addition to metal-phosphate formation, several other possible mechanisms may have contributed simultaneously to heavy metals removed by phosphatic clay, including surface complexation, ion exchange, diffusion, and precipitation of metal carbonates. The significant differences between the amounts of metals desorbed from the phosphatic clay suggests differences in their sorption mechanisms. In contrast to Pb and Cd, substantial amounts of Zn were released into the TCLP extracting solutions. This preferential release

suggests that Zn is sorbed to available surface sites of phosphatic clay with little diffusion into apatite structure. Lothenbach et al. (1998) also observed similar behavior for desorption of sorbed Cd and Zn from montmorillonite. Such results clearly demonstrate that waste phosphatic clay could potentially be a cost-effective stabilization agent for treating Pb-contaminated soils, thereby meeting essential requirements of environmentally sustainable technology. However, caution should be given to Cd and Zn remediation with this method.

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Fractionation of Copper, Nickel, and Zinc in Metal-Spiked Sewage Sludge

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ABSTRACT

The enrichment or *spiking* of sewage sludge with heavy metals for experimental purposes is a fairly widely used, although sometimes controversial, technique. A study was undertaken, using a sequential fractionation scheme, to assess the degree of incorporation of Cu, Ni, and Zn into sewage sludge samples spiked with these metals and incubated for 6 mo. For all three metals, substantial proportions of the metals were incorporated into the sludge matrix, particularly as evidenced by their occurrence in the *oxide-bound*, *organic-bound*, and *residual* fractions. In particular, for Cu very little of the added copper remained in the sludge supernatant solution after 6 mo of incubation and, apart from at the highest level of Cu addition, there was very little difference in the fractional distribution of Cu between the Cu-spiked and non-Cu-spiked sludges. For Ni and Zn, however, although there was substantial incorporation of these metals into the sludge, the higher levels of Ni and Zn addition resulted in greater proportions of the metals in the most soluble fractions (*soluble*, *exchangeable*, *specifically sorbed*) compared with nonspiked sludges. The fractionation data for Ni also showed that large additions of Cu and Zn can affect the fractional distribution of Ni in the sludge. The drying of sewage sludge prior to analysis was shown to increase metal solubility in the sludge samples, and the potential implications of this finding for the prediction of sludge metal bioavailability are discussed.

THE enrichment or *spiking* of sewage sludge with heavy metals for experimental purposes is a fairly widely used technique (for example, Davis and Carlton-Smith, 1981; Street et al., 1977; Coppola et al., 1988; Forge et al., 1993; Obbard et al., 1993). Spiking may be undertaken to (i) increase the rate of buildup of metals in soils treated with sludge without having to apply excessive amounts of sludge to the soil, or (ii) distinguish the effects of increasing amounts of a single metal from the effects of other metals or other types of contaminants present in the sludge. Unfortunately, in the absence of small-scale treatment plants, metal-spiking of sludge is often carried out using the final digested sludge materials produced at local municipal treatment plants. This of course means that the metals added as a spike do not undergo the same processes as those metals already present in the sewage entering the treatment plant. For this reason, the spiking of sewage sludge with simple metal salts is controversial, since there is no certainty that the added metals will be present in the same forms as those metals already present in the sludge. This is important because there is evidence that the bioavailability of metals added to soil as metal salts may differ from the bioavailability of metals added in nonspiked sewage sludge (Bell et al., 1991). In an attempt to overcome this problem, before they are used, sludges spiked with additional metals are commonly incubated for a

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