

Mechanisms of lead, copper, and zinc retention by phosphate rock

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“Capsule”: *Phosphate-induced formation of fluoropyromorphite is primarily responsible for Pb immobilization by phosphate rock, whereas Cu and Zn retention is mainly attributable to the surface adsorption or complexation.*

Abstract

The solid–liquid interface reaction between phosphate rock (PR) and metals (Pb, Cu, and Zn) was studied. Phosphate rock has the highest affinity for Pb, followed by Cu and Zn, with sorption capacities of 138, 114, and 83.2 mmol/kg PR, respectively. In the Pb–Cu–Zn ternary system, competitive metal sorption occurred with sorption capacity reduction of 15.2%, 48.3%, and 75.6% for Pb, Cu, and Zn, respectively compared to the mono-metal systems. A fractional factorial design showed the interfering effect in the order of Pb > Cu > Zn. Desorption of Cu and Zn was sensitive to pH change, increasing with pH decline, whereas Pb desorption was decreased with a strongly acidic TCLP extracting solution (pH = 2.93). The greatest stability of Pb retention by PR can be attributed to the formation of insoluble fluoropyromorphite [Pb₁₀(PO₄)₆F₂], which was primarily responsible for Pb immobilization (up to 78.3%), with less contribution from the surface adsorption or complexation (21.7%), compared to 74.5% for Cu and 95.7% for Zn. Solution pH reduction during metal retention and flow calorimetry analysis both supported the hypothesis of retention of Pb, Cu, and Zn by surface adsorption or complexation. Flow calorimetry indicated that Pb and Cu adsorption onto PR was exothermic, while Zn sorption was endothermic. Our research demonstrated that PR can effectively remove Pb from solutions, even in the presence of other heavy metals (e.g. Cu, Zn).

1. Introduction

Significant effort has been made to evaluate the effectiveness of phosphate on in situ remediation of contaminated waters and soils (Basta et al., 2001; Cotter-Howells and Caporn, 1996; Hettiarachchi et al., 2000; Ma et al., 1995; Yang et al., 2001). Phosphate minerals, i.e.

phosphate rock (PR) and hydroxyapatite, have been shown to effectively immobilize Pb from various contaminated waters and soils (Cao et al., 2002; Ma et al., 1995; Ryan et al., 2001). Takeuchi and Arai (1990) suggested that Pb immobilization resulted from the formation of a more stable lead phosphate, such as Ca_(10-x)Pb_x(PO₄)₆(OH)₂ via an ion exchange mechanism where aqueous Pb replaces Ca on the hydroxyapatite lattice. Ma et al. (1995), on the other hand, proposed dissolution of phosphate rock and subsequent precipitation of a pyromorphite-like mineral (Pb₁₀(PO₄)₆X₂, X = OH, Cl, F) as the primary mechanism. In addition to Pb, phosphate rock can also remove Zn and Cd from aqueous solutions. The possible mechanisms for metal retention

by phosphate minerals included: (1) ion exchange processes at the surface of PR (Middelburg and Comans, 1991; Xu et al., 1994); (2) surface complexation (Xu et al., 1994); (3) precipitation of some amorphous to poorly crystalline, mixed metal phosphates (Ma et al., 1995); and (4) substitution of Ca in PR by other metals during recrystallization (coprecipitation) (Chen et al., 1997; Jeanjean et al., 1994; Xu et al., 1994). However, it is difficult to quantify the relative contribution from each mechanism that is responsible for metal removal and it appears that all four mechanisms may work together. As such, estimating the extent of each mechanism contributing to metal retention by PR has not been reported. In addition, contaminated soils commonly encountered multi-metals including Pb, Cu, Zn, Cr, Cd and Ni (Ma et al., 1995). Competitive retention of these metals onto phosphate minerals has not been well studied, and individual metal immobilization mechanisms are still not fully understood.

Metal sorption is a competitive process between metals in solution and those sorbed onto the solid surface (Echeverria et al., 1998; Harter, 1992). Consequently, solution metal composition strongly affects metal retention onto solid surfaces. Many multi-metal sorption studies focused on the effects of Ca, Mg, and K on heavy metal retention by soil (Elrashidi and O'Connor, 1982). Harter (1992) evaluated the sorption of Ni, Co, and Cu in binary and ternary systems. Nickel did not affect copper sorption, but Co retention decreased in proportion to Ni sorption due to their chemical similarity. Many studies, looking at the sorption of heavy metals (i.e. Pb, Cu, Zn, Cd, and Ni) using pure minerals (i.e. goethite, alumina, kaolinite, and zeolite), have demonstrated greater Pb selectivity relative to other heavy metals (Ahmed et al., 1998; Gomes et al., 2001).

Fractional factorial designs are a powerful tool commonly used to identify factors or variables that have an effect on a certain response (Echeverria et al., 1998). In a system characterized by several potentially influential factors, fractional factorial designs are most useful because it is possible to determine which variables are most important. Among those important variables, the magnitude and the direction of their influence can also be determined. Because of the complexity of the retention process, it is useful to combine sorption isotherms with fractional factorial designs to provide information about competition of heavy metals for solid-surface sites (Echeverria et al., 1998). Flow calorimetry, which directly and quantitatively measures the heat of a sorption reaction on an interface, is ideally suited for measuring interactions at the liquid–solid interface (Steinberg, 1981). This helps to better understand the binding strength of a particular reactive species onto the solid surface. Flow calorimetry has been used to study the surface chemistry of solids

(Appel et al., 2002; Rhue et al., 2002), but no study has been conducted on the surface reaction of metals with phosphate minerals.

The objective of this research was to characterize the mono-metal and multi-metal interactions of Pb, Cu, and Zn on the surface of PR. The specific aims were: (1) to compare metal sorption and desorption onto PR in mono-metal and multi-metal systems; (2) to examine the individual effect of a metal on the retention of other metals based on a fractional factorial design; (3) to determine the enthalpies of Pb, Cu, and Zn interfacial reactions onto PR using flow calorimetry; and (4) to quantify the contributions from different mechanisms responsible for metal retention by PR.

2. Materials and methods

The mineral phosphate rock (PR) used in this study was from PCS Phosphate Mining Company (White Springs, Florida). The PR sample was classified as ground concentrated. Its preparation included air-drying, passing through a 0.425-mm sieve, and rinsing with deionized water. Fluoroapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$) was identified as a major component of this PR, contributing its great potential to retain heavy metals in aqueous environments (Singh et al., 2001). The characteristics of the PR were presented in Singh et al. (2001). All reagents were of analytical grade, and deionized water was used throughout the experiment. Individual aqueous solutions of Pb, Cu, and Zn were prepared at concentrations of 15 mM from their nitrate salts. Solution ionic strength was controlled at 0.05 M using a KNO_3 background electrolyte solution. The experiments were run in triplicate.

2.1. Sorption of mono-metal and multi-metal

Two sets of experiments were designed including pH-control sorption system and pH-free control sorption system. For the pH-control sorption, a series of 30 mL of 0.05 M KNO_3 containing different concentrations (0–0.6 mM) of either one or an equal-molar mixture of Pb, Cu, and Zn were added to 0.100 g of PR. The suspensions were shaken at 30 ± 1 rpm on a reciprocating shaker for 24-h at 25 ± 2 °C, which was required to reach equilibrium based on our preliminary kinetic experiments (data not shown). Solution pH was controlled at 5.5 ± 0.2 with diluted HCl and NaOH. The supernatants were separated by centrifugation at $13,200 \times g$ for 25 min, and filtered through a 0.45- μm polypropylene membrane filter. The filtrate was retained for analysis of pH, P, Ca, Pb, Cu, and Zn. Treatment blanks carrying 30 mL of 0.05 M KNO_3 with 0.100 g of PR were included. The amount of adsorbed metal was taken as the difference between the amount added initially and that remaining in

solutions after equilibration. In addition to the solution analysis, the solid residue of mono-metal reaction was collected at the end of reaction and dried at 35 °C. The dried solid residue was prepared on the tiles for X-ray powder diffraction analysis.

In comparison to the pH-control system, an acidity free control system was set up to elucidate what happened to the proton during metal uptake. To 0.100 g of PR, a set of 30 mL of 0.05 M KNO₃ containing different concentrations (0–0.6 mM) of individual Pb, Cu, and Zn were added. The suspensions were shaken at 30 ± 1 rpm on a reciprocating shaker. After 24-h equilibration, solution pH was recorded.

2.2. Desorption of multi-metal

To determine the stability of the heavy metal adsorbed by PR, desorption experiments were conducted. Four extracting solutions of varying pH were prepared to evaluate the stability of PR after interaction with aqueous metal solutions. Two of the extracting solutions were prepared from acetic acid at pH 2.93 and 4.93 following the extraction fluids used in the EPA Toxicity Characteristic Leaching Procedure (USEPA, 1992). The other two extracting solutions used in this study were slightly acidic at pH 7 and neutral at pH 9 prepared by diluting concentrated HNO₃ and NaOH solution.

After multi-metal sorption experiments as described in Section 2.1, the remaining solid residues from PR reaction with 0.4 mM metals were chosen and washed twice with deionized water and supernatants were discarded immediately after 25-min of centrifugation. The washed residues were then treated with 30 mL of the extracting solutions of pH 3–9 and the slurries were shaken on a reciprocating shaker for 24 h. The slurries were centrifuged and their supernatants were filtered and analyzed for pH, Cu, Pb, and Zn.

2.3. Competitive effects of multi-metal

To ascertain the individual effects of a metal on the retention of other metals, a fractional factorial design, for three variables at two levels and four runs, was applied (Echeverria et al., 1998). The two levels included an initial metal concentration corresponding to the capacity, which is determined as the Point *B* from a mono-metal sorption isotherm (Echeverria et al., 1998), and an initial concentration of zero. According to Gregg and Sing (1982), Point *B* is the amount of metal retained at the plateau or at the beginning of the linear portion above the isotherm's knee, which is obtained from the intersection of tangents to the origin and plateau of isotherms. Each experiment was carried out by equilibrating 0.100 g of PR with 30 mL of 0.05 M KNO₃ solution containing the concentrations of metals corresponding to the experimental design (Table 3).

Solution pH was adjusted at 5.5 ± 0.2 with diluted HCl and NaOH. The amount of each metal retained by the PR in each experiment was determined as previously described for sorption isotherms in Section 2.1. The interfering effect of one metal on the other metals was assessed on a relative basis by comparing the retained amount with Point *B* of mono-metal isotherms.

2.4. Calorimetric measurements

Heats (ΔH) of Pb, Cu, and Zn sorption onto PR were determined using flow calorimetry (Appel et al., 2002; Rhue et al., 2002). Amounts of 120 ± 0.5 mg of PR (0.25–0.50 mm) were placed in the column of the flow calorimeter. The mobile phase of 30 mM KNO₃ flowed through the column using a total pressure drop of about 100 cm of water. Flow rates were controlled with a precision needle valve at the outlet side of the calorimeter and were generally in the range of 0.27–0.35 mL/min. After a satisfactory baseline was obtained with 30 mM KNO₃ equilibration, solution of 15 mM Ca(NO₃)₂ was then reacted with the K-saturated PR and heats of exchange were determined. The K and Ca solutions were cycled through the PR sample several times. This was done to check for heterogeneity between PR samples and thus, enabled determination of a correction factor for differences in PR samples, based on exchange thermodynamics and not PR weight. Furthermore, this ensured the system to behave normally when the K and Ca peak areas were of equal and opposite magnitude (indicative of an exchange process).

Once the K/Ca cycles were complete, 15 mM Pb(NO₃)₂, Cu(NO₃)₂ or Zn(NO₃)₂ solutions were, respectively, reacted with the Ca-saturated PR and the heat was determined. This process was repeated three to five times for each solution composition in order to determine if the exchange reactions were reversible. The heat data were averaged and standard deviations calculated.

Each of the PR samples reacted with Pb, Cu, and Zn then underwent several cycles of K/Ca solution. This was done to enable a comparison between the original (i.e. prior to metal introduction to the PR) energetics of K/Ca exchange and post-metal energetics of K/Ca exchange in order to ascertain changes in the energetics of cation exchange as a function of metal introduction. These solid residues were then extracted from the flow calorimeter column, washed with deionized H₂O and dried in the air. The dried solid was digested in HNO₃/H₂O₂ with USEPA Method 3050. The Pb, Cu, and Zn found were assumed to be chemisorbed (Appel et al., 2002).

2.5. Analysis methods

Metal (Ca, Pb, Cu, Zn, etc.) concentrations were analyzed using either a flame atomic absorption

spectrometer (Varian 220FS) or a graphite furnace atomic absorption spectrophotometer (Perkin–Elmer model SIMMA 6000), depending on metal concentrations. Multi-level standards (Fisher Scientific) were prepared in 2% nitric acid. Elemental analysis followed a USEPA approved QA/QC plan with a blank, a duplicate, and a spike every 20 samples. Total phosphate (PO_4) concentrations were determined using visible spectroscopy via the ascorbic acid/molybdate method (Olsen and Sommers, 1982). Solution pH was determined using a Fisher Scientific Accumet model 20 pH/conductivity meter.

Selected solid residues were examined with an X-ray diffractometer. X-ray diffraction analyses were performed on a computer-controlled X-ray diffractometer equipped with a stepping motor and graphite crystal monochromator. Scans were conducted from 2 to 60° at a rate of $2^\circ\theta$ per minute. Selected solid residues were also observed under a scanning electron microscope (SEM, JSM-6400/TN500, JEOL, USA) equipped with X-ray energy dispersive spectroscopy (EDS).

3. Results and discussion

3.1. Sorption of Pb, Cu, and Zn under mono-metal and multi-metal reaction conditions

As expected, PR was effective in retaining all three metals; however, sorption isotherms for Pb, Cu, and Zn at $25 \pm 2^\circ\text{C}$ and $\text{pH } 5.5 \pm 0.2$ exhibited differences in shape and in the amount of metal retained (Fig. 1). Sorption behaviors of Cu and Zn were similar in both mono-metal (Fig. 1a) and multi-metal (Fig. 1b) systems, and significantly different from that of Pb. In the case of Pb sorption, it was very efficient. For initial Pb concentrations of up to 0.4 mM , the equilibrium Pb concentrations were nearly at the detection limit of the analytical method employed. The obtained sorption patterns were similar to those observed elsewhere (Mavropoulos et al., 2002; Singh et al., 2001). According to Echeverria et al. (1998), isotherms that have similar equilibrium concentrations for different amounts of metal added reflect a precipitation mechanism. It appeared to be consistent with the hypothesis of Ma et al. (1995), who proposed that Pb retention by hydroxyapatite is controlled by hydroxyapatite dissolution, followed by hydroxypyromorphite precipitation. Similarly, PR induced reactions in the presence of Pb could be simplified as follows

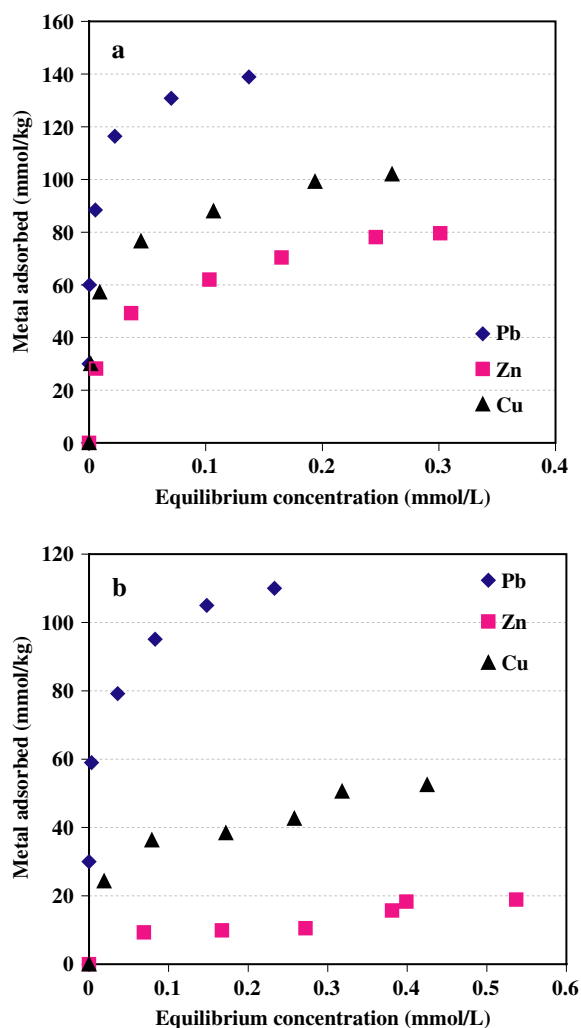
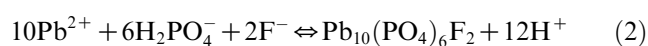


Fig. 1. Adsorption isotherms of (a) mono-metal and (b) multi-metal on phosphate rock at pH 5.5 and 25°C .

In the current investigation using PR, fluoropyromorphite ($\text{Pb}_{10}(\text{PO}_4)_6\text{F}_2$) formation was confirmed by XRD and SEM element map from the residual solid after 0.4 mM Pb was equilibrated with PR (Fig. 2). The XRD patterns showed fluoropyromorphite peaks (2.95 \AA and 2.98 \AA) after Pb reaction with PR, but not in the control (Fig. 2a). SEM element map showed the association of Pb with P instead of Ca as expected from PR (Fig. 2b).

Copper and Zn retention gradually increased with increasing initial concentration and then leveled off (Fig. 1). The shape of this isotherm reflects surface adsorption or complexation mechanism (Echeverria et al., 1998). XRD analysis did not show any mineral formation in the solid of Cu or Zn reaction with phosphate (Fig. 2a), as reported in other studies (Ma et al., 1994; Xu et al., 1994). Xu et al. (1994) suggested that the dominant sorption mechanism involved Zn interaction with hydroxyapatite surface functional

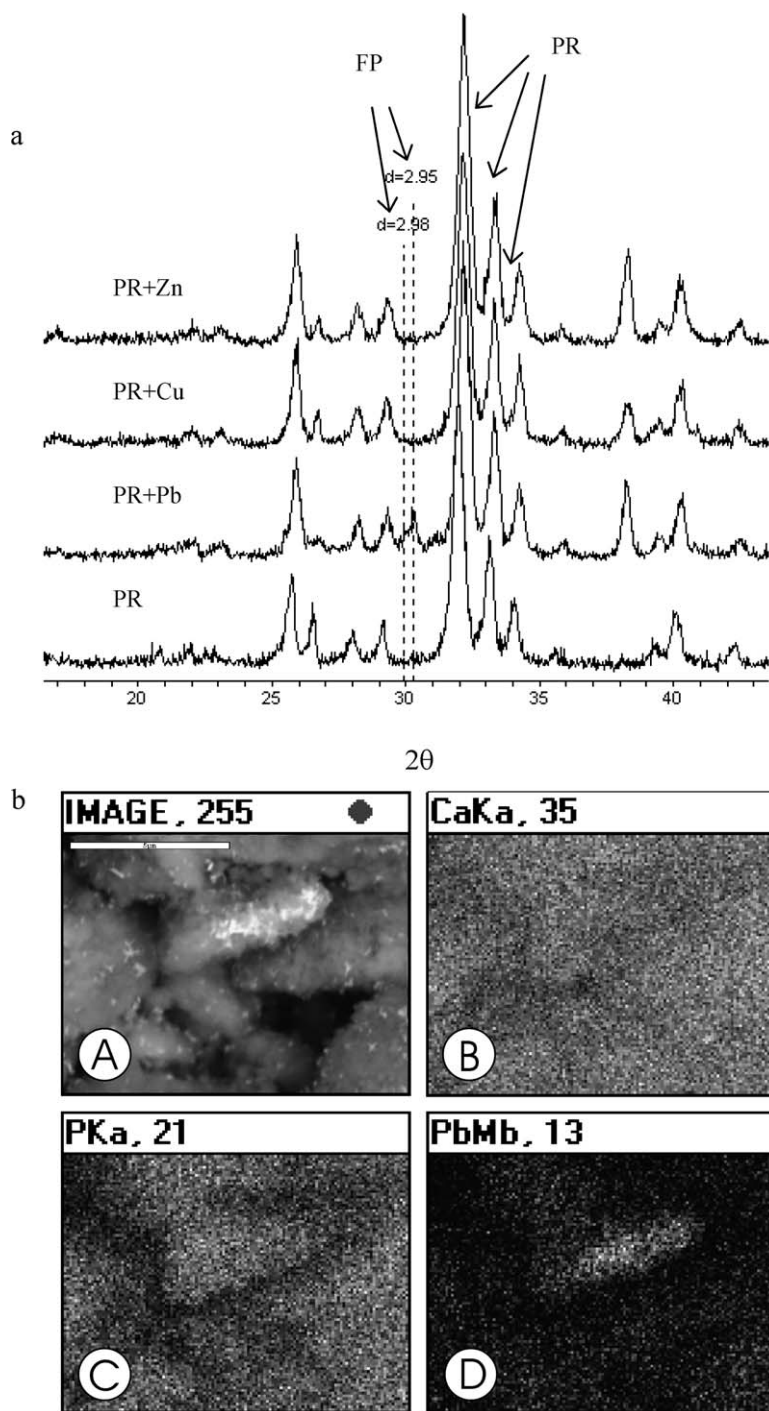


Fig. 2. X-ray diffraction patterns of (a) the residual solids from phosphate rock reaction with 0.4 mM Pb, Cu, and Zn; and (b) SEM element dot map of the residual solids from phosphate rock reaction with 0.4 mM Pb. FP, fluoropyromorphite; PR, phosphate rock. (A), fluoropyromorphite crystal; (B), Ca; (C), P; and (D), Pb. Scale bar = 5 μm .

groups such as $\equiv\text{POH}$ and coprecipitation of Zn with Ca into the apatite structure.

In the Pb–Cu–Zn ternary system, competition among metals affected sorption of all metals. The initial linear part of the isotherms was shorter and the knee was sharper (Fig. 1b) when compared with mono-metal sorption (Fig. 1a). Competitive metal retention by PR suggested

that complexation mechanisms may have contributed partially to metal sorption by PR. Nevertheless, fluoropyromorphite precipitation was still the main mechanism for Pb retention but not for Cu or Zn, as demonstrated by XRD analysis (data not shown). This was apparent at Pb concentrations of <0.3 mM. Reduction of fluoropyromorphite precipitation at greater Pb concentration

Table 1
Langmuir parameters for the sorption of mono-metal and multi-metal onto phosphate rock

| | Mono-metal | | | Multi-metal | | |
|----|-------------------------|--------------------------------|------------------|---------------------|-------------------|----------------|
| | Point B^a (mmol/kg) | C_s^m (mmol/kg) ^b | B_L^c (L/mmol) | Point B (mmol/kg) | C_s^m (mmol/kg) | B_L (L/mmol) |
| Pb | 132 ± 22.3 ^d | 138 ± 26.1 | 351 ± 45.7 | 110 ± 21.1 | 117 ± 23.5 | 56.3 ± 6.45 |
| Cu | 101 ± 18.2 | 114 ± 12.4 | 32.2 ± 5.61 | 51.2 ± 6.78 | 58.9 ± 7.11 | 20.5 ± 3.91 |
| Zn | 79.6 ± 10.3 | 83.2 ± 13.6 | 12.7 ± 3.22 | 18.3 ± 1.25 | 20.3 ± 2.33 | 2.62 ± 0.55 |

^a Point B is the amount of metal retained at the plateau or at the beginning of the linear portion above the isotherm's knee, which is obtained from the intersection of tangents to the origin and plateau of isotherms.

^b C_s^m , Langmuir adsorption capacity.

^c B_L , Langmuir bounding related to interaction energies.

^d Mean ± standard deviation ($n = 3$).

may result from the competition of Cu and Zn for phosphate ions (Chen et al., 1997; Mavropoulos et al., 2002).

The characteristics of heavy metal sorption onto PR could be well described by the Langmuir model

$$C_e/C_s = C_e/C_s^m + 1/C_s^m \cdot B_L \quad (3)$$

where C_s^m denotes the Langmuir maximum capacity (mmol/kg); C_e is the concentration (mmol/L) in the equilibrium solution; C_s is the measured sorption per unit weight of PR (mmol/kg); and B_L represents the Langmuir bonding term related to interaction energies (L/mmol). Table 1 summarized Point B , C_s^m , and B_L values based on the application of the Langmuir model to mono-metal and multi-metal competitive sorption. As expected, values of Point B , C_s^m , and B_L were greater in mono-metal sorption than in the competitive sorption for all three metals. However, the amount of sorption varied with metals, following a descending order of $Pb > Cu > Zn$ (Table 1). In the ternary Pb–Cu–Zn system, competitive sorption resulted in maximum sorption reduction by 15% for Pb, 48% for Cu, and 75% for Zn, relative to the mono-system. The values of Point B , C_s^m , and B_L for Pb clearly indicated that PR has the highest affinity for Pb.

During metal retention by PR, solution Ca increased with increasing metal disappearance (Fig. 3a). The greatest increase was found with Pb sorption. Unlike Ca, P decreased with increasing metal reduction. The largest P reduction was also found with Pb sorption (Fig. 3b). The fact that Pb sorption by PR induced the greatest increase in solution Ca concentration as well as the largest decrease in P concentration is consistent with the hypothesis that Pb retention by PR was through the dissolution of PR (release Ca and P into solution) and formation of fluoropyromorphite (consumption of P). Though, to a lesser extent, Ca levels increased and P levels decreased upon reaction of Cu and Zn with PR. Thus, we cannot exclude the possibility of Cu- and Zn-phosphate precipitation or coprecipitation of Cu and Zn with PR. In the studies of hydroxyapatite with aqueous Zn, Ma et al. (1994) speculated precipitation of amorphous to poorly crystalline Zn phosphate. Xu et al. (1994) suggested possible coprecipitation of Zn with Ca

to form solid when aqueous Zn reacted with apatite. However, according to LeGeroes and LeGeroes (1984), cations with ionic radii smaller than Ca^{2+} (0.099 nm) have a lower probability of being incorporated into an apatite structure compared with larger ionic radii of Pb

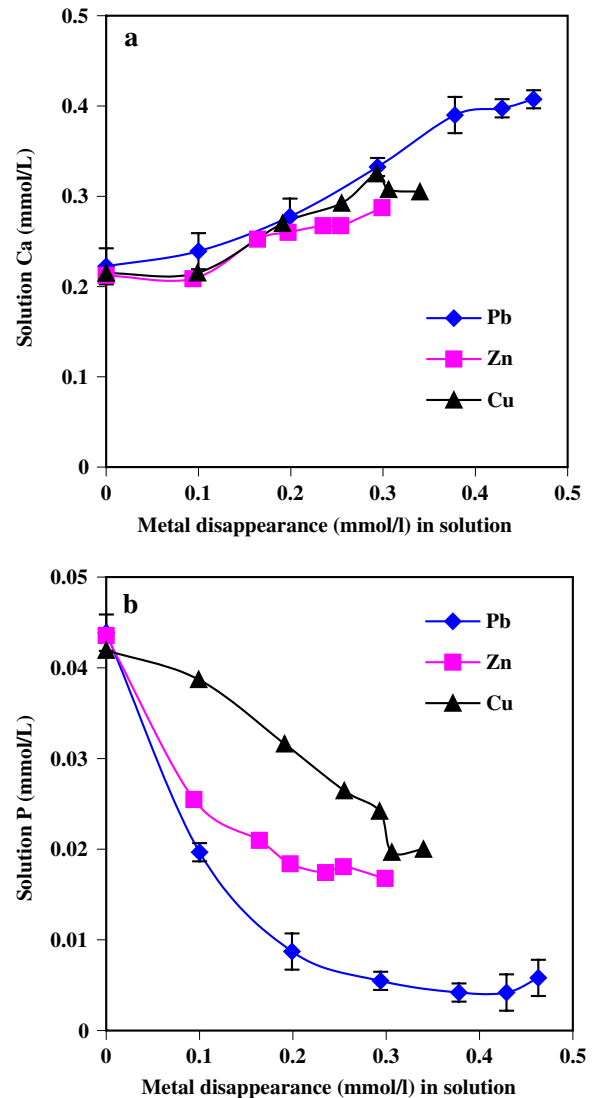


Fig. 3. Calcium (a) and P (b) in equilibrium solution as a function of metal disappearance.

(0.118 nm). Therefore, coprecipitation of Zn (0.088 nm) and Cu (0.087 nm) with Ca in the presence of PR would be less likely to occur compared to Pb.

Calcium was the main cation in PR, constituting 34.3% on a mass basis (Singh et al., 2001). Calcium release appeared to be related to the amount of Pb, Cu, and Zn sorbed (Fig. 3a). The amount of Ca released in mono-metal isotherms upon addition of Pb, Cu, and Zn showed a linear function with the amount of each metal sorbed (Fig. 4a). A linear relationship with a slope = 0.92 ($r^2 = 0.96$) was obtained when Ca released was plotted as a function of Pb sorbed. The nearly 1:1 ratio of $\text{Ca}_{\text{released}}/\text{Pb}_{\text{sorbed}}$ may indicate equal displacement of Ca by Pb during dissolution of PR and formation of fluoropyromorphite (Singh et al., 2001). Substitution of Pb for Ca during fluoropyromorphite formation may also have contributed to Pb retention. Slopes for Cu and Zn were 0.65 ($r^2 = 0.92$) and 0.41 ($r^2 = 0.93$), respectively, indicating other retention mechanisms

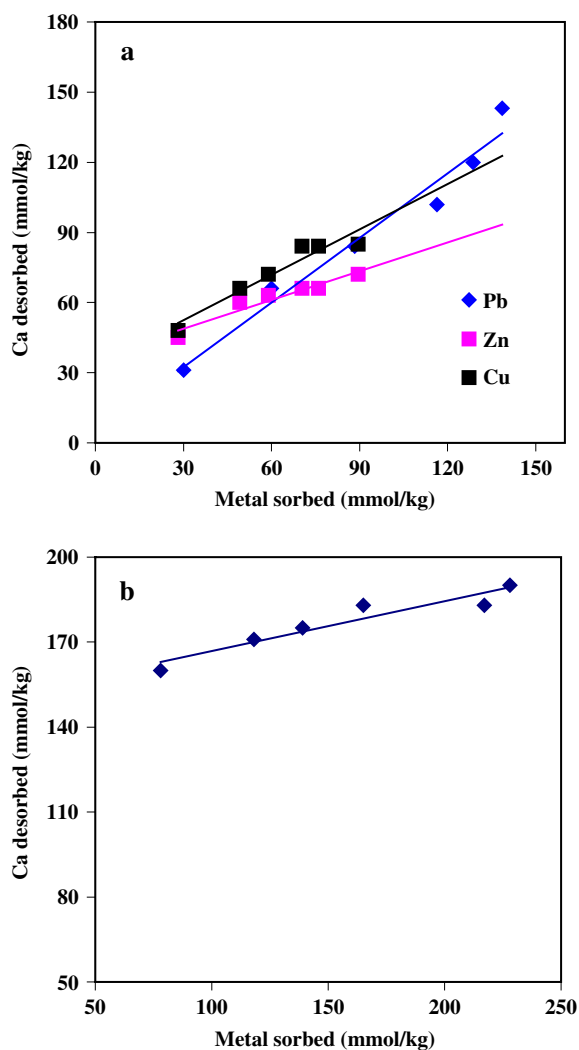
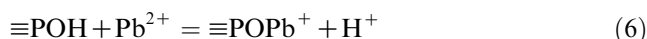
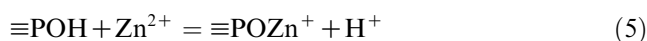
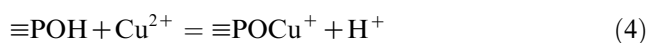


Fig. 4. Correlation between metal sorbed and Ca released at (a) mono-metal system and (b) multi-metal system.

than cationic exchange, probably surface complexation. For the multi-metal sorption, although a positive linear correlation was still observed between the amount of Ca released and the amount of total metal sorbed (Fig. 4b), the molar ratios of $\text{Ca}_{\text{released}}/\text{M}_{\text{sorbed}}$ were reduced to 0.17 ($r^2 = 0.96$) due to the competitive complexation (Chen et al., 1997).

In order to know what happened about the proton change during the metal uptake, the reaction system was free of acidity control and the final pH was monitored at different initial metal concentrations. Obviously, metal uptake caused a significant decrease of solution pH by up to 1.5 unit change (Fig. 5). Similar results were observed in previous studies (Mavropoulos et al., 2002; Singh et al., 2001; Xu et al., 1994). In this study, metal retention induced pH reduction from 6.83 to 5.38–5.56, which was less than the PZC of PR, i.e. 6.87. In a pH range of <6.87 , $\equiv\text{POH}$ is a dominant functional group for PR (Wu et al., 1991). Visual MINTEQ modeling (Gustafsson, 2001) indicated that $>85\%$ Cu and Zn were present in Cu^{2+} and Zn^{2+} . Thus, when Cu and Zn were mixed with phosphate rock, complexation occurred on the PR surface, partially displacing the H^+ ions and resulting in pH decline as described in Eqs. (4) and (5):



In the case of Pb, although PR dissolution consumed H^+ (Eq. (1)), fluoropyromorphite precipitation liberated an equal amount of H^+ (Eq. (2)). In other words, in theory uptake of Pb via fluoropyromorphite precipitation should not cause a net pH change (Mavropoulos

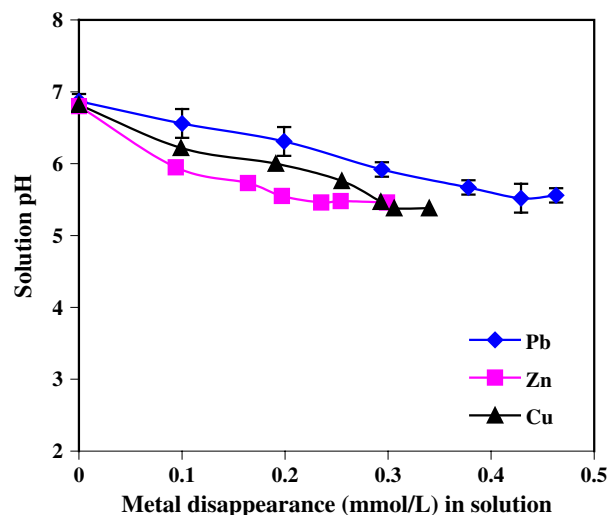


Fig. 5. Final solution pH as a function of solution metal disappearance.

et al., 2002). If this is the case, then other surface mechanisms besides PR dissolution and fluoropyromorphite precipitation may have contributed to pH decrease. One possibility was Pb complexation at the PR surface as shown in Eq. (6). So the solution pH decrease could be linked to the proton liberated by Pb complexation at $\equiv\text{POH}$ sites.

Visual MINTEQ modeling (Gustafsson, 2001) indicated that the solutions were undersaturated with respect to $\text{Pb}(\text{OH})_2$ or $\text{Cu}(\text{OH})_2$. Thus, the reduction in solution pH cannot be contributed to hydrolysis of Pb^{2+} or Cu^{2+} . Clearly, more metal disappearance (adsorbed by PR) would release more H^+ , resulting in a greater pH reduction (Fig. 5).

3.2. Competition-induced inhibition

The effects of the other two metals on the retention of the third metal, determined by the fractional factorial design, are shown in Fig. 6. Because metals were not added in the same initial concentrations (Table 2), and to avoid possible distortions, results are expressed as percentage of the retained metals with respect to Point B of mono-metal isotherms. In the ternary system, Pb, Cu, and Zn sorption reflected a remarkably competitive effect as shown in Fig. 1. The presence of other metals significantly reduced the sorption of the third metal. The percentage of metals sorbed onto the PR was in the order of Pb (60–68%) > Cu (42–56%) \gg Zn (<10%), compared to the mono-metal sorption. Therefore, Pb is the metal that experienced the least reduction in the competitive sorption process, consistent with the results of Ma et al. (1994), i.e. Cu and Zn had little influence on the Pb immobilization in the presence of phosphate. Conversely, Pb significantly inhibited the retention of Cu and Zn (Ma et al., 1994). According to Fig. 6, Zn had less influence than Cu on Pb retention, whereas Zn was most affected in the competitive sorption. The results showed that PR was most effective in Pb immobilization even in the ternary competitive system.

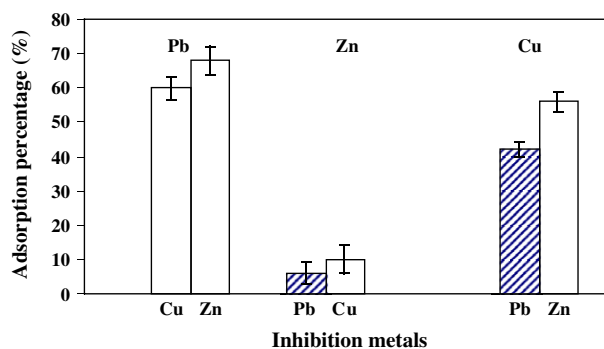


Fig. 6. Percentage of sorption of Pb, Cu, and Zn by phosphate rock in the fractional factorial experiment (in relation to the Point B of individual metals).

Table 2

Initial concentrations of Pb, Cu, and Zn (mmol/L) in the fractional factorial experiments

| Run | Factors | | |
|-----|---------|------|------|
| | Pb | Cu | Zn |
| 1 | 0.51 | 0.44 | 0 |
| 2 | 0 | 0.44 | 0.49 |
| 3 | 0.51 | 0 | 0.49 |
| 4 | 0 | 0 | 0 |

3.3. Desorption of sorbed metals

Heavy metal desorption from PR depended on the pH of the extracting solutions (Fig. 7). Copper and Zn desorption significantly increased with pH decrease. In the pH range of 3–9, Cu and Zn were desorbed by up to 35% and 55% of total adsorbed, respectively (Fig. 7). As described above, a substantial fraction of sorbed Cu and Zn was weakly bound by complexation, thus, pH reduction induced greater Cu and Zn solubility. However, Pb desorption was different from those of Cu and Zn. First, much less Pb was desorbed, i.e. <12% in the pH range of 3–9 (Fig. 7). Also, the Pb desorption decreased as pH decreased from 4.93 to 2.93, though Pb desorption increased as pH decreased from 9.0 to 4.93, like Cu and Zn. Inconsistent Pb desorption responding to solution pH may indicate that not all the Pb was chemisorbed by precipitating as fluoropyromorphite, and a fraction of Pb was weakly adsorbed or complexed on the surface of PR. Comparing the total amount of the immobilized Pb with the Pb incorporated into the hydroxypyromorphite phase, Mavropoulos et al. (2002) concluded that up to 30% of Pb was immobilized by other surface mechanisms such as adsorption or complexation besides apatite dissolution and

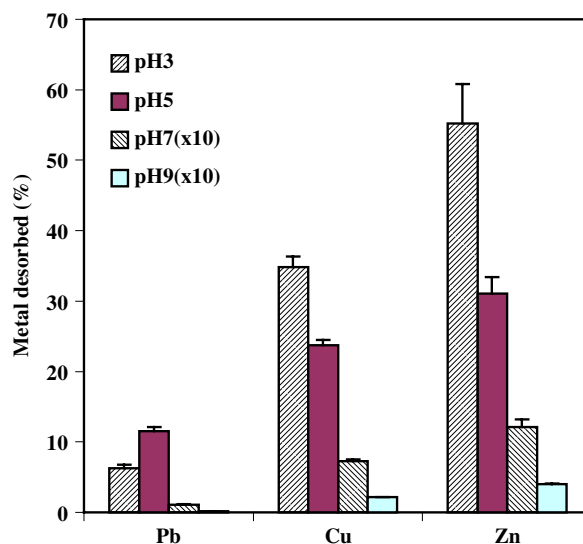


Fig. 7. Effects of pH on Pb, Cu, and Zn desorption after 0.4 mM metal reaction with phosphate rock.

hydroxypyromorphite crystallization. So the high acidity of pH = 2.93 is likely to induce dissolution of both weakly-bound Pb and PR, facilitating formation of fluoropyromorphite and leading to reduction of Pb desorption (Basta et al., 2001). It should be pointed out that TCLP solution of pH 2.93 contains a high acetate concentration (0.15 M), thus, acetate may complex with Pb to form $\text{Pb}(\text{CH}_3\text{COO})_2$, increasing Pb solubility. However, $\text{Pb}(\text{CH}_3\text{COO})_2$ would be ultimately transformed into insoluble fluoropyromorphite. Comparing desorption of the three metals, it appears that Zn and Cu sorption to PR is sensitive to pH, whereas Pb-phosphate precipitation stayed intact under a wide range of pH from 3 to 9. It suggested a greater stability of Pb immobilization, compared to Cu and Zn. This again demonstrates that PR could be used effectively to remove Pb from wastewater or remediate Pb-contaminated soil and sediments through formation of fluoropyromorphite even at low pH and in the presence of other contaminants.

3.4. Flow calorimetric analysis of Pb, Cu, and Zn sorption

Flow calorimetry enables the direct measurement of the heat associated with a reaction (Rhue et al., 2002; Steinberg, 1981). This is related to the enthalpy change (ΔH), which, in the case of surface reactions, provides information about the binding strength of a particular ionic species to the solid (Appel et al., 2002). In the present study, the sorption of Pb and Cu by PR was exothermic with heats of 19.1 and 14.3 kJ/mol, respectively, whereas sorption of Zn was endothermic, 7.25 kJ/mol (Table 3).

Heats for K/Ca exchange before and after Cu and Zn sorption were not significantly different (data not shown), which is consistent with the weaker binding of these metals to the PR surface. This was evidenced by the small amount of non-exchangeable Cu and Zn (retarded in the column after K/Ca exchange following Pb sorption), i.e. 25.5 and 4.33% of the maximum sorbed, respectively (Tables 1 and 3). By comparison, the heat for K/Ca exchange following Pb sorption was less than half of what it was before Pb sorption,

consistent with an irreversible sorption of Pb to the PR surface. Phosphate rock irreversibly sorbed 108 mmol Pb/kg of PR (non-exchangeable) (Table 3), accounting for 78.3% of the maximum sorption capacity (Table 1). The sorption of Pb was mainly attributed to the precipitation via fluoropyromorphite. XRD analysis of the solid samples taken from the calorimeter following Pb treatment indicated the presence of fluoropyromorphite (data not shown). The reversibly sorbed Pb, 21.7%, could have been held by surface sorption/complexation reactions, more like those binding Cu and Zn to the PR surface.

4. Conclusions

Phosphate rock has the highest affinity for Pb, followed by Cu, and then Zn. The sorption of Pb, Cu, and Zn onto PR was well characterized by the Langmuir model. Multi-metal addition induced competitive sorption among the three metals, with the interfering effect of $\text{Pb} > \text{Cu} > \text{Zn}$.

Lead immobilization was primarily attributed to phosphate-induced fluoropyromorphite formation, and to a lesser extent, to the surface adsorption or complexation. Up to 78.3% of sorbed Pb was irreversibly chemisorbed onto the PR via formation of fluoropyromorphite precipitation. In comparison, Cu and Zn were less chemisorbed (i.e. 25.5 and 4.33%) with the rest via surface adsorption or complexation. Reduction in solution pH during metal retention supports the hypothesis of Pb, Cu, and Zn surface adsorption or complexation. Sorption of Pb and Cu by PR was exothermic and that for Zn was endothermic.

Acknowledgements

This research was supported in part by the Florida Institute of Phosphate Research (Contract No. 01-01-172). The authors would like to thank Dr. Willie G. Harris for his assistance in mineral analysis and Mr. Thomas Luongo for his assistance in chemical analysis and in pre-reading the manuscript.

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Table 3

Heats of sorption, solution pH, and non-exchangeable metal measured based on flow calorimetric analysis

| Metals | Heats (ΔH , kJ/mol) | Input pH/output pH | Non-exchangeable metal (mmol/kg PR ^a) | % of total metal retained |
|--------|------------------------------|--------------------|---|---------------------------|
| Pb | -19.1 ± 3.52^b | 5.18/5.11 | 108 ± 12.1 | 78.3 |
| Cu | -14.3 ± 2.76 | 5.33/5.36 | 29.1 ± 2.17 | 25.5 |
| Zn | 7.25 ± 0.92 | 5.41/5.44 | 3.60 ± 0.43 | 4.33 |

^a Phosphate rock.

^b Mean \pm standard deviation ($n = 3$).

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