

In Situ Lead Immobilization by Apatite

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Lead contamination is of environmental concern due to its effect on human health. The purpose of this study was to develop a technology to immobilize Pb *in situ* in contaminated soils and wastes using apatite. Hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] was reacted with aqueous Pb, resin-exchangeable Pb, and Pb-contaminated soil material. The effectiveness of natural apatite to attenuate Pb was also tested. Hydroxyapatite reduced initial Pb concentrations of 5–500 mg L^{-1} to 0.18–19.7 $\mu\text{g L}^{-1}$. Aqueous Pb in Pb-contaminated soil materials was reduced from 2273 to 36 $\mu\text{g L}^{-1}$ after reaction with hydroxyapatite. We hypothesize that Pb was immobilized by dissolution of hydroxyapatite and precipitation of hydroxypyromorphite [$\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$]. The effective removal of Pb from aqueous solution, exchange resin, and Pb-contaminated soil material suggests that apatite has the potential to immobilize Pb *in situ* in Pb-contaminated soils and wastes.

Introduction

Lead is a heavy metal and is potentially toxic to mammals. Its extensive use and widespread disposal in the environment have resulted in numerous cases of Pb-contaminated soils and wastes (1). Thus, it is important to develop a method to minimize Pb solubility and bioavailability in these environments and to reduce aqueous Pb below the U.S. EPA action level of 15 $\mu\text{g L}^{-1}$ (2).

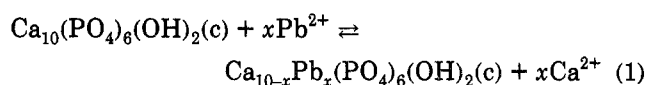
Currently, there are many technologies employed to clean up contaminated soils and wastes including thermal, biological, and physical/chemical treatments (3). Both thermal and biological treatments are ineffective in removing heavy metals from contaminated sites. Physical/chemical treatments are often costly and destructive. Sims et al. (4) reported many in-place treatment technologies such as soil flushing, immobilization (sorption, ion exchange, and precipitation), chemical degradation, biodegradation, and attenuation for contaminated surface soils. Among them, immobilization is a promising technology for cleaning up contaminated soils and wastes.

Czupryna et al. (5) tested many chemicals to immobilize heavy metals *in situ*. These included standard cation-exchange resins, Devoe-Holbein metal-scavenging molecules, natural materials (clays, molecular sieves, and greensand), hydrated lime, and ferrous sulfate. Most of these materials are either expensive or not very effective in removing heavy metals. According to Nriagu (6–9), phosphate minerals would appear to have potential to immobilize Pb in Pb-contaminated soils and wastes due to low solubility of lead orthophosphates. Of all the phosphate minerals, the apatites are by far the most abundant (10). Fluorapatite [$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$] (FA) is the major natural apatite mineral, including the partially carbonated or hydroxylated varieties. Hydroxyapatites

(HA), especially the carbonated variety, are of prime interest to biologists because they make up the mineral portion of teeth and bones in all animals.

Synthetic HA has been used to remove Pb from aqueous solution (11–17). It has been widely used as a cation exchanger in wastewater treatment and has a very high capacity for removing divalent heavy metal ions from water (13). However, previous investigators have not reported the effectiveness of Pb removal as measured by the final aqueous Pb concentrations [Pb]. These authors also provide little evidence to support the conclusion of cation substitution mechanisms for Pb removal by HA. Takeuchi and Arai (17) reported that lower pH resulted in greater Pb adsorption by HA. If cation substitution was responsible for Pb removal, then lower pH would result in less Pb adsorption because more HA would dissolve and less HA would be available for cation substitution at lower pH. However, the results of Takeuchi and Arai (17) can be explained alternatively by a precipitation mechanism. More HA dissolved at low pH, and thus there was more P reacting with Pb to form hydroxypyromorphite (HP).

The exact reaction mechanisms responsible for the retention of Pb by HA are not clear, yet such knowledge is necessary to understand the behavior of Pb in phosphate-rich environments. Furthermore, this information would aid in the development of *in situ* immobilization technologies for remediation of Pb-contaminated soils, sediments, and waters. Three types of reactions may control Pb immobilization by HA: surface adsorption, cation substitution, or precipitation. According to Takeuchi et al. (16), Pb was first adsorbed on the surface of HA, and then cation substitution (which these authors called “ion exchange”) with Ca occurred. They concluded that this process was controlled by liquid-film diffusion and took place at the surface of the HA particles. Similar conclusions were drawn by Suzuki et al. (14) as described by the following equation:



This reaction cannot explain changes in P concentrations [P] during the Pb immobilization process nor the associated changes in solution pH. The major evidence to support the cation substitution theory was that the molar ratio of Pb removed/Ca released stayed at an approximate value of 1 in their experiments. However, this phenomenon can also be explained in terms of dissolution/precipitation. In other words, 10 mol of Pb is consumed with each mol of HP precipitated, and 1 mol of HA has to dissolve to supply P, and thus 10 mol of Ca is released to solution (eqs 2 and 3).

We hypothesize that HA dissolution and HP precipitation is the main Pb immobilization process as described

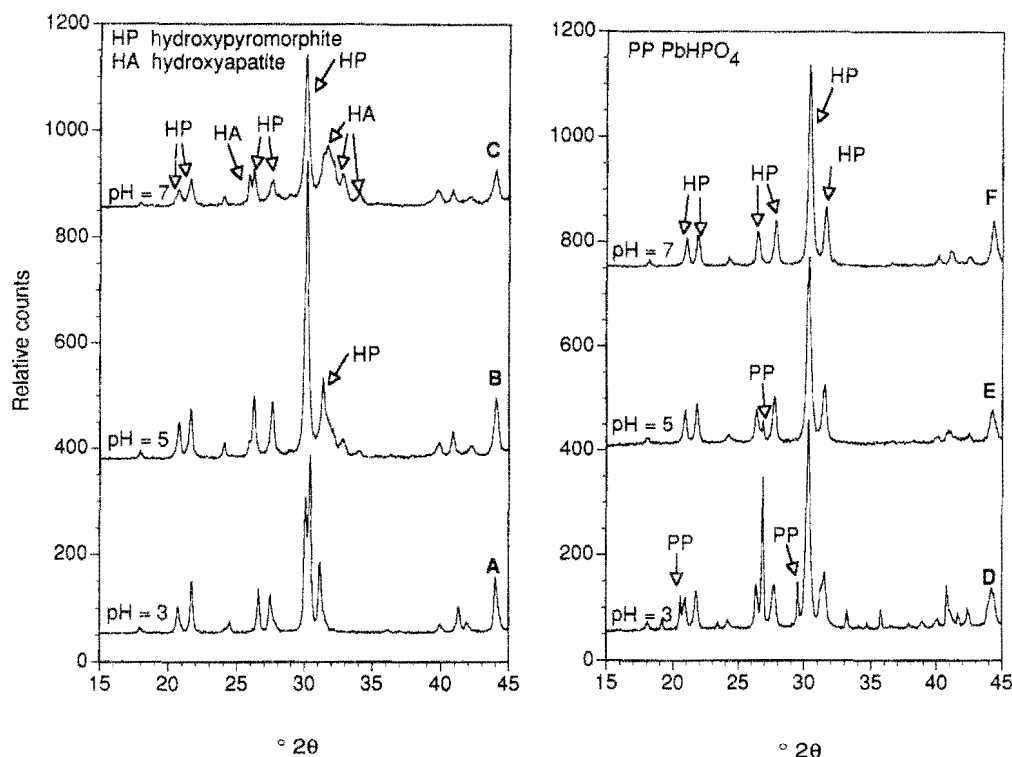


Figure 1. XRD patterns of the reaction products of hydroxyapatite and dissolved P with Pb at different pHs.

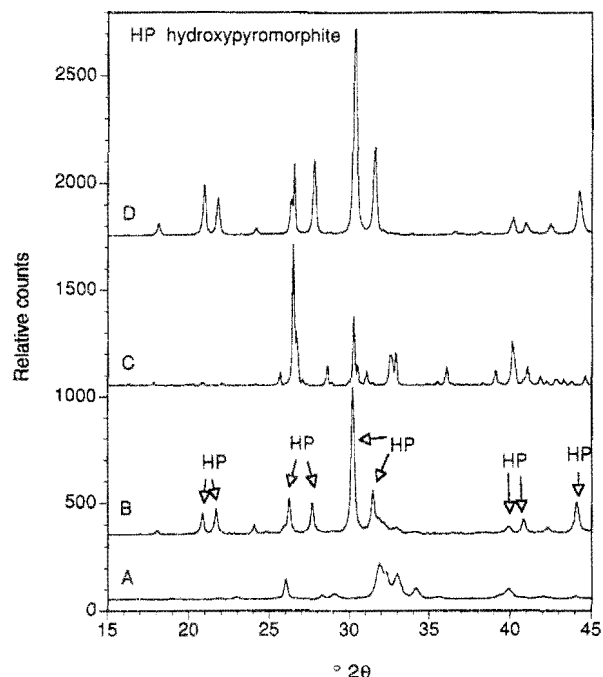
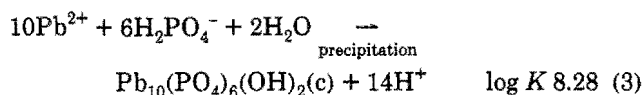
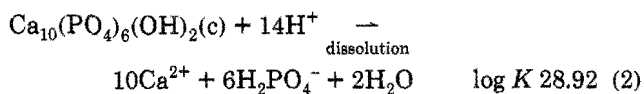


Figure 2. XRD patterns of (A) hydroxyapatite (HA); (B) HA after reaction with 500 mg of Pb L⁻¹; (C) CaHPO₄ (DCP); and (D) DCP after reaction with 500 mg of Pb L⁻¹.

below (18):



The objectives of the present study were (1) to elucidate the mechanism of Pb immobilization by apatite and (2)

to study the feasibility of using apatite to immobilize Pb from aqueous solution Pb, resin-exchangeable Pb, and Pb-contaminated soil materials.

Materials and Methods

Mechanism of Pb Immobilization by HA. (a) *Immobilization of Aqueous Pb by HA and Aqueous P at Controlled pHs.* The hypothesis of HA dissolution and HP precipitation was tested by reacting both HA and aqueous P with aqueous Pb, at pH values of 3, 4, 5, 6, and 7. Aqueous Pb of 500 mg of Pb L⁻¹ (150 mL) was reacted with 0.2 g of HA or 0.07 g of NaH₂PO₄·H₂O. The quantity of HA or NaH₂PO₄·H₂O used was sufficient to form enough solid sample for analysis. A constant pH value was maintained throughout the reaction period of 1 h with a Mettler DL 70 autotitrator. Hydroxyapatite from GFS Chemicals (Columbus, OH) and aqueous Pb as Pb(NO₃)₂ were used throughout the experiment unless otherwise specified.

(b) *Immobilization of Aqueous Pb by HA and CaHPO₄.* The mechanism of Pb immobilization by HA was further tested by reacting CaHPO₄ (DCP), HA, or a mixture of HA + DCP with aqueous Pb. Reagent-grade calcium phosphates from Fisher Scientific, GFS Chemicals, and Bio-Rad mainly consisted of CaHPO₄ (DCP), HA and a trace amount of DCP (HA + DCP), and HA, respectively, as determined by X-ray diffraction (XRD). The surface areas were determined to be 0.55, 44.54, and 60.54 m² g⁻¹ for DCP, HA + DCP, and HA samples, respectively.

Calcium phosphate (0.1 g) was reacted with 200 mL of 100 and 500 mg of Pb L⁻¹ on a reciprocating shaker for 2 h. The lead/calcium phosphate ratios ranged from 200 to 1000 mg/g. Preliminary experiments indicated that 200 mg of Pb/g of HA was the maximum ratio to effectively control aqueous [Pb] below 15 µg L⁻¹ in 2 h. High lead/calcium phosphate ratios were used to more readily observe the mineralogical changes of the reaction products. The

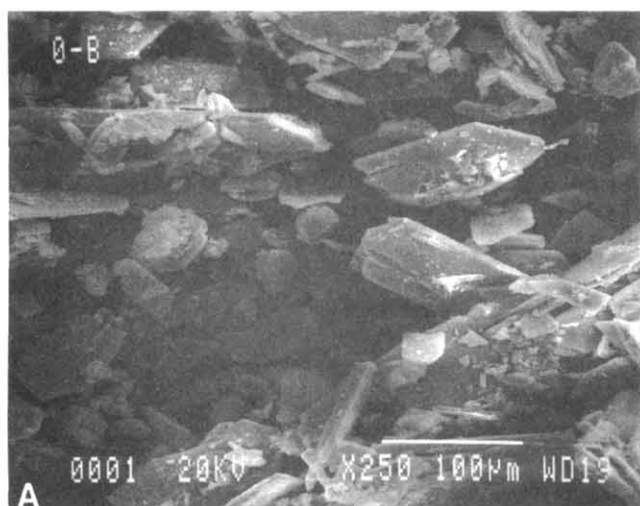


Figure 3. SEM micrographs of hydroxyapatite (A) and hydroxyapatite after reaction with 500 mg of Pb L⁻¹ (B).

initial pH values of the solutions were all adjusted to 6 with dilute NaOH.

Immobilization of Pb from Aqueous Solutions, Exchange Resin, and Pb-Contaminated Soil Material by Apatite. (a) *Immobilization of Aqueous Pb by HA.* Reagent-grade HA (0.2 g) was reacted with 50-mL solutions containing 0, 50, 100, and 500 mg of Pb L⁻¹, respectively. The Pb/HA ratio ranged from 12.5 to 125 mg/g, and the suspensions were shaken for 0.5, 1, 2, 4, 8, and 24 h.

The reaction period was further shortened to study the kinetics of Pb immobilization by HA; 0.2 g of HA was reacted with 150-mL solutions containing 500 mg of L⁻¹. The suspensions were shaken for 0.5, 1, 5, and 10 min.

Eight liters of 1 mg of Pb L⁻¹ and 2 L of 5 mg of Pb L⁻¹ solution were reacted with 0.2 g of HA on a shaker for 1 h. This provided a large Pb/HA ratio allowing us to measure the effects of comparatively dilute Pb solutions on the mineralogy of the reaction products with XRD.

(b) *Immobilization of Aqueous Pb by Natural Apatite.* The ability of natural apatite (NA) to attenuate Pb was studied by reacting 0.2 g of three NAs with 200 mL of 1 and 5 mg of Pb L⁻¹ on a shaker for 1 h. The NAs were from North Carolina, central Florida, and Idaho and had surface areas of 15.19, 8.91, and 3.66 m² g⁻¹, respectively, as measured by N₂-BET adsorption with a Micromeritics, Flowsorb 2300 surface area analyzer. Analysis of XRD indicated that these NAs were primarily fluorapatite.

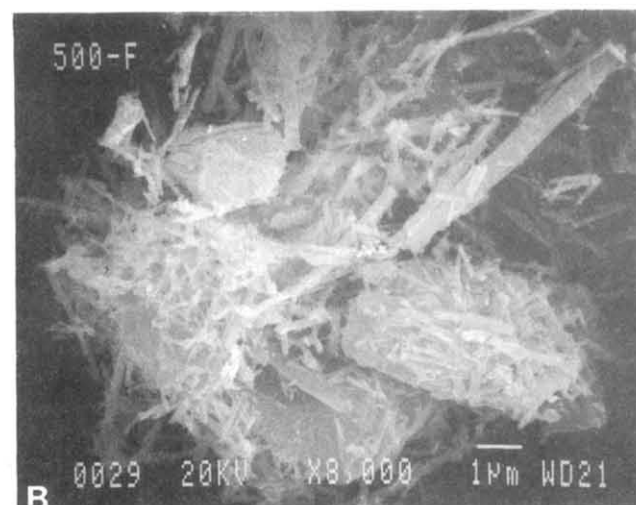
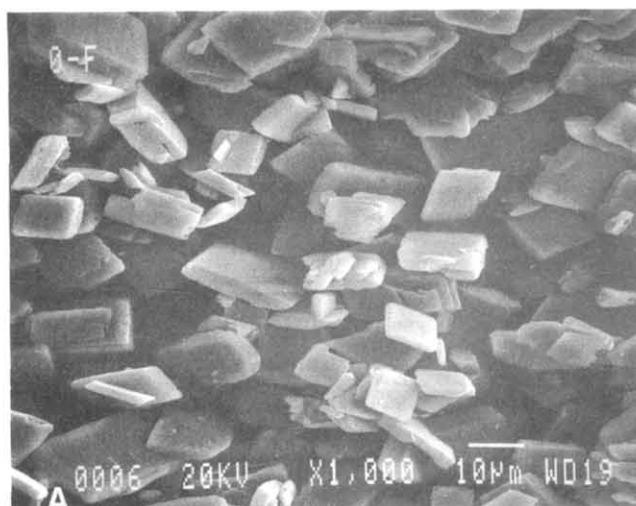


Figure 4. SEM micrographs of CaHPO₄ (A) and CaHPO₄ after reaction with 500 mg of Pb L⁻¹ (B).

(c) *Immobilization of Exchangeable Pb by HA.* The ability of HA to immobilize exchangeable Pb is important in Pb-contaminated soils, since exchangeable Pb is likely to be more dominant than aqueous Pb. A total of 3 g of Pb-saturated resin (Dowex 50W-X8) was reacted with 0.2 g of HA in 200 mL of deionized water on a shaker for 0.5, 1, and 2 h.

(d) *Immobilization of Dissolved Pb in Pb-Contaminated Soil Material by HA.* The ability of HA to attenuate Pb in Pb-contaminated soils and wastes was studied by reacting 6 g of soil material with 30 mL of distilled deionized water containing 0, 0.5, 1, and 2 g of HA on a shaker for 5, 24, and 48 h. The suspensions were then centrifuged at 15000 rpm for 20 min, and the filtrates (0.2 µm) were analyzed for Pb. The solid waste was obtained from the Brown's Battery Breaking Site, an abandoned lead acid battery processing/recycling facility in Tilden Township, Berks County, Pennsylvania. The site is located in the floodplain of the Schuylkill River. The solid waste had a pH of 4.3, and a total [Pb] of 2100 mg kg⁻¹.

Analytical Methods. All the suspensions were filtered through 0.2-µm pore diameter, Nucleopore polycarbonate membrane filters at the end of the reaction, and the filtrates were analyzed for total Ca, P, Pb, NO₃, and pH. All experimental treatments in this study were prepared in triplicate and were conducted in acid-washed (0.1 N HCl) polycarbonate labware.

Table I. Effects of P Sources and Initial Pb Concentrations on Final Aqueous P and Pb Concentrations

initial Pb (mg L ⁻¹)	P (mg L ⁻¹)			Pb (μg L ⁻¹)		
	HA	HA + DCP	DCP	HA	HA + DCP	DCP
0	2.35 ± 0.09 ^a	9.55 ± 0.24	6.26 ± 0.36	1.33 ± 0.12	1.44 ± 0.16	1.44 ± 0.16
100	2.04 ± 0.09	8.87 ± 0.17	13.8 ± 0.68	5.55 ± 0.74	6.21 ± 0.79	2.99 ± 0.48
500	0.87 ± 0.12	8.58 ± 1.34	47.9 ± 1.66	89400 ± 14	8990 ± 4.0	13.8 ± 1.1

^a Means and standard deviations of triplicate samples.

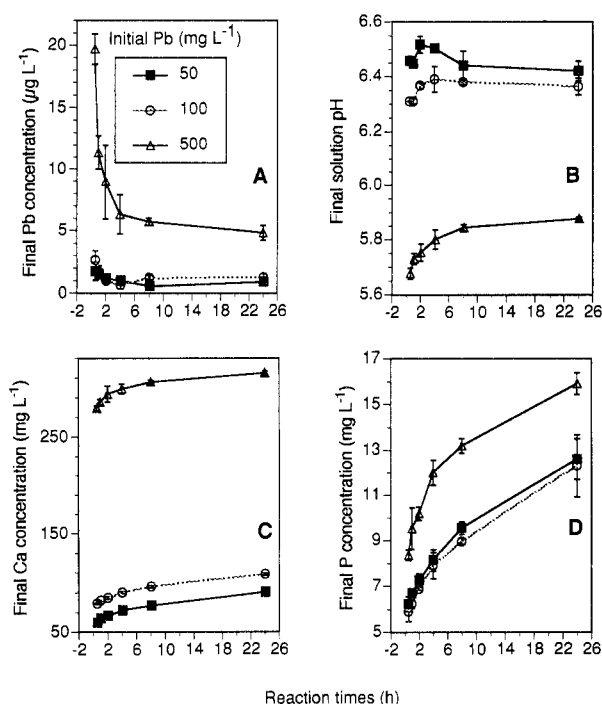


Figure 5. Effect of reaction time and initial Pb concentrations on Pb, Ca, and P concentrations, and solution pH after reaction of Pb with hydroxyapatite.

A Perkin-Elmer 3030B atomic absorption spectrophotometer was used to analyze total dissolved Ca and Pb (>1 mg L⁻¹), and a Varian SpectraAA-20 atomic absorption spectrometer equipped with a graphite furnace atomizer was used to measure total dissolved Pb (≤1 mg L⁻¹). Total NO₃ concentrations were determined using a Lachat Quickchem autoanalyzer (method 10-107-04-1-A). Total dissolved P was measured colorimetrically with a Beckman DU-6 spectrophotometer (19).

Selected samples were examined with XRD. All XRD analyses were conducted with a Philips X-ray diffractometer (Philips Electronic Instrumentation Co., Mahwah, NJ) using Cu K-α radiation at 35 kV and 20 mA. Measurements were made using a step-scanning technique with a fixed time of 4 s per 0.05° 2θ. A total of 601 data points were obtained from 15 to 45° 2θ. All XRD analyses were performed using back-filled, randomly oriented mounts.

Some samples were also analyzed with a JEOL 200CX scanning transmission electron microscope (STEM; JEOL Inc., Peabody, MA) operated with an accelerating voltage of 200 kV. This unit was equipped with a Tracor Northern (Tracor Northern, Middleton, WI) energy-dispersive (EDS) X-ray analyzer. The sample was ultrasonically dispersed in a small volume of water before being mounted on a poly(vinyl formal)-coated, Cu transmission electron microscope grid. The grids with the sample were then carbon coated. Electron micrographs, electron diffraction

patterns, and EDS X-ray spectra were collected from selected particles.

Selected samples were observed with a JEOL JSM-A20 scanning electronic microscope (SEM; JEOL, USA Inc., Peabody, MA) using a Tracor Northern (5500) analyzer equipped with 5502 upgrade. The samples were mounted on stainless steel stubs using double-stick tape and then coated with Au and Pd.

Results and Discussion

Mechanism of Pb Immobilization by HA. (a) *Immobilization of Aqueous Pb by HA and Aqueous P at Controlled pHs.* We have hypothesized that Pb immobilization by HA was mainly through HA dissolution/HP precipitation. If our hypothesis is correct, HP will form when either HA or aqueous P is reacted with aqueous Pb. The XRD patterns of the reaction products of aqueous Pb with HA and aqueous P are presented in Figure 1. Hydroxypyromorphite was formed in the presence of HA at all pH values tested (Figure 1A–C). At pH 3, little HA was detected, indicating that most of the HA had dissolved. The HA peaks became stronger with increasing pH, while HP showed the strongest peaks at pH 5. There was also a peak split at 30.1° 2θ at pH 3, which has not been clearly identified at present. Hydroxypyromorphite was also identified at all pHs in the presence of aqueous P (Figure 1D, E). At pH 3, PbHPO₄ was formed in addition to HP. Given enough time, it is likely that all of the HP would have converted to PbHPO₄ at pH 3, since PbHPO₄ has lower solubility than HP. At pH 7, HP was the only mineral detected by XRD. Aqueous P and Pb removed from solution at pH 7 had a molar ratio of 3:5, which matched that of HP. Formation of HP by reacting aqueous Pb with either aqueous P or HA strongly supports our hypothesis of HA dissolution and HP precipitation.

(b) *Immobilization of Aqueous Pb by HA and CaHPO₄.* Hydroxyapatite and DCP were reacted with aqueous Pb to further verify our hypothesis. Sharp, narrow XRD patterns for HP revealed a high degree of crystallinity subsequent to reacting HA with 500 mg of Pb L⁻¹, suggesting rapid crystallization (Figure 2B). The HP peaks became stronger and those of HA became weaker at the 500 mg of Pb L⁻¹ level compared to those at the 100 mg of Pb L⁻¹ level (data not shown). Similar XRD patterns were obtained from the DCP samples reacted with Pb (Figure 2D), indicating that the final product (HP) was not dependent upon the structure of the original calcium phosphate.

The SEM micrographs show needle-shaped HP formed from reacting DCP or HA with 500 mg of Pb L⁻¹ (Figures 3 and 4). Table I summarizes the final [P] and [Pb] after calcium phosphate reaction with aqueous Pb. In the absence of Pb, dissolved [P] from these solids followed the order HA + DCP > DCP > HA, which was affected by both the solubility of the solids and their surface areas

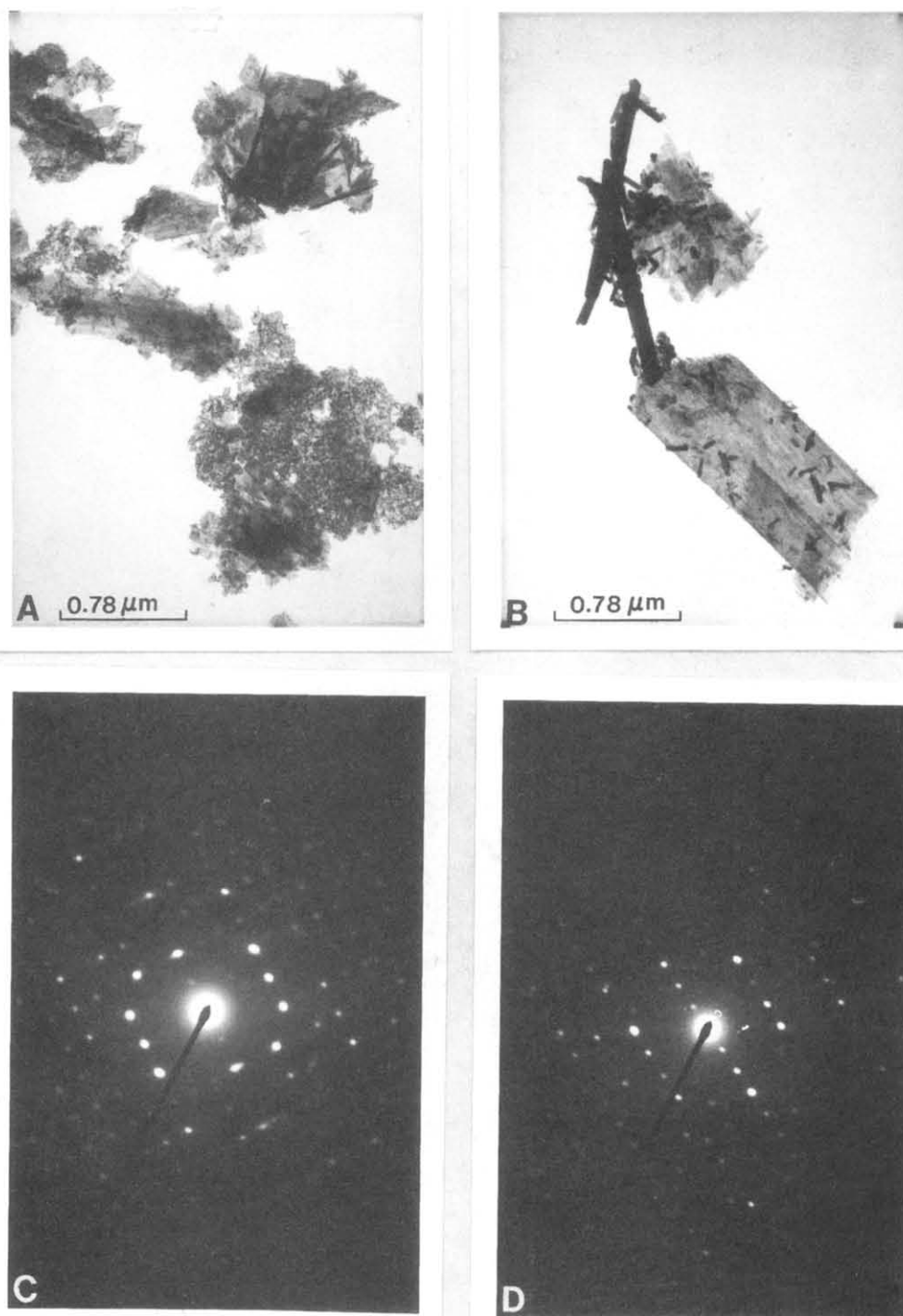


Figure 6. STEM micrographs and single-crystal XRD patterns: (A) hydroxyapatite (HA); (B) HA after reaction with 100 mg of Pb L⁻¹, pyromorphite (rod-shaped) and HA (flat sheet) were present; (C) XRD of HA; and (D) XRD of pyromorphite. The photos of XRD were enlarged from 3 × 5 to 4 × 5.

(44.5, 0.55, and 60.5 m² g⁻¹, respectively). In contrast, dissolved [P] were greatest for DCP, followed by HA + DCP, and then HA, when the solids were reacted with Pb (Table I). Calcium phosphates from all three sources were effective in maintaining [Pb] below 10 μg L⁻¹ when the initial [Pb] was 100 mg L⁻¹ (Table I). However, at an initial [Pb] of 500 mg L⁻¹, DCP was most effective, followed by HA + DCP; HA was the least effective in reducing [Pb]. The final [Pb] was inversely related to the final [P].

Clearly, these three solids show distinctly different morphologies (Figures 3 and 4). Whereas the X-ray and electron microscope (EM) data do not rule out the

possibility that some of the Pb may have been adsorbed to the surface of HA and DCP particles, it is evident that most of the Pb precipitated with phosphate to form a discrete HP phase near the surface of HA or DCP. The chemical data further support our hypothesis of HA dissolution and HP precipitation. It is evident that the removal of Pb from solution was not related to original surface area of calcium phosphate solids but rather to the total concentration of dissolved P. Thus, the effectiveness of HA or other P-containing minerals in reducing aqueous [Pb] was proportional to their solubilities.

Immobilization of Pb from Aqueous Solutions, Exchange Resin, and Pb-Contaminated Soil Material

by Apatite. (a) *Immobilization of Aqueous Pb by HA.* Initial [Pb] of 50, 100, and 500 mg L⁻¹ were reduced to 0.55–1.73, 0.64–2.62, and 4.80–19.7 µg L⁻¹, respectively, after reaction with HA (Figure 5A). Greater initial [Pb] resulted in slightly greater final [Pb] (Figure 5A). The [Pb] of the 500 mg of Pb L⁻¹ solution was reduced to 19.7 µg L⁻¹ after 0.5 h, and it was further reduced to 4.46 µg L⁻¹ after 8 h. Thus, almost all the Pb was removed within 0.5 h of reaction through precipitation of HP, and further Pb reduction may be due to adsorption by HA or HP. In all cases, aqueous [Pb] was reduced below the EPA action level of 15 µg of Pb L⁻¹ after 1 h.

Solution pH was an important parameter in this system. The pH values of the 50, 100, and 500 mg of Pb L⁻¹ solutions before reaction with HA were 5.14, 5.10, and 4.71, respectively. In all cases, the solution pH increased after 0.5 h, and the highest pH values were measured in the samples with the lowest initial [Pb] (Figure 5B). The solution pH for the 500 mg of Pb L⁻¹ treatment increased with reaction time, which was due to greater HA dissolution at initial low pH values. The pH values for the other two treatments did not change much with reaction time. Increases in solution pH were caused by HA dissolution (eq 2). This would not occur if cation substitution was the main mechanism for Pb immobilization (eq 1).

Dissolved Ca concentrations [Ca] and [P] increased with an increase in reaction time and initial [Pb] (Figure 5C, D). High initial [Pb] resulted in lower solution pH and thus increased HA solubility. On the other hand, more Pb was reacted with P, and thus more HA was dissolved to supply P. Equilibrium with respect to Ca was not reached even after 192 h (data not shown). In eq 2, HA dissolution consumes H⁺ and releases both Ca and P to solution. In eq 3, the precipitation of Pb as HP removes dissolved Pb and P and releases H⁺ to solution. At any time, the actual concentration of solutes is the result of both of these reactions. Throughout the reaction, [Ca] was much higher than [P]. At initial [Pb] of 500 mg L⁻¹ and reaction time of 24 h, [Ca] and [P] were 315 and 15.9 mg L⁻¹, respectively. Assuming HA dissolved congruently, then 146 mg of P L⁻¹ should be in solution, almost 10 times as much the measured P. The low observed [P] suggests that most of the dissolved P formed HP. There was no change in NO₃ concentrations during the reaction, indicating that NO₃ did not participate in the precipitation of HP (data not shown).

A detailed examination of STEM micrographs of HA after reaction with 100 mg of Pb L⁻¹ indicated major differences in morphology between HA and HP (Figure 6A, B). The HA had two kinds of morphology: large flat sheets and small loose particles. Hydroxypyromorphite is rod-shaped and formed near the surface of HA (Figure 6B). The single crystal XRD confirmed the presence of HA (flat sheet) and HP (rod) (Figure 6C, D). The EDS X-ray spectra show high levels of Pb and trace amounts of Ca in rod-shaped HP and vice versa in flat sheet HA (data not shown).

The surface area (SA) of the HA samples after reaction with aqueous Pb was measured. Reaction time did not affect the SA of HA samples significantly, except at the 500 mg of Pb L⁻¹ treatment, where the SA decreased slightly with increasing time. This effect was not obvious for lower initial [Pb]. The average SAs and standard deviations of 50, 100, and 500 mg of Pb L⁻¹ treated samples were 43.33 ± 0.91, 43.05 ± 0.87, and 41.74 ± 0.71 m² g⁻¹,

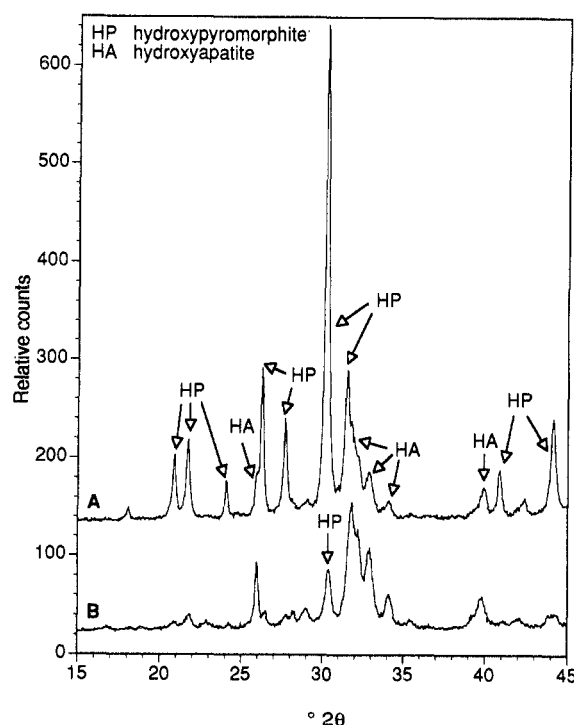


Figure 7. XRD patterns of hydroxyapatite after reaction with 1 mg of Pb L⁻¹ for 2 h (A) and after reaction with 500 mg of Pb L⁻¹ for 0.5 min.

respectively. They decreased with increasing initial [Pb], which agrees with Miyake et al. (11), who reported that the cell dimension of Pb-substituted HA was larger than that of the corresponding HA and close to that of HP. Both STEM and SA data indicate that Pb was removed by formation of discrete HP crystals.

If our hypothesis of dissolution/precipitation is correct, then Pb immobilization should have occurred as soon as HA is in contact with aqueous Pb. The XRD patterns of the reaction products demonstrate that HP was formed after 0.5 min, and there was no significant change in the XRD patterns after longer reaction (Figure 7A). Lead removal by HA was rapid, and 93% was removed within 0.5 min.

The experiments discussed to this point all utilized high concentrations of dissolved Pb (50–500 mg L⁻¹). This facilitated the identification of reactions products with XRD and EM, but it is not clear if these same reactions would occur in the presence of lower concentrations of aqueous Pb. The interactions of HA with large volumes of 1 and 5 mg of Pb L⁻¹ solutions allowed us to produce sufficient quantities of reaction product for XRD analysis. Hydroxypyromorphite was formed even at these lower initial [Pb] (Figure 7B). The HP peaks were not as strong as those measured at the higher [Pb] but they were still evident. The effective removal of low aqueous concentrations of Pb suggests that HA can effectively immobilize Pb at both high and low concentrations.

(b) *Immobilization of Aqueous Pb by NA.* Different naturally occurring apatites were reacted with aqueous Pb. These minerals are currently mined, and detailed information on their composition was discussed by McClellan and Gremillion (20) and Lehr (21). When no Pb was present, [Pb] after 1 h reaction ranged from 0.16 to 0.53 µg L⁻¹ and represented Pb in the NA itself (Table II). All three NAs effectively reduced 1 mg of Pb L⁻¹ to <8 µg L⁻¹ (Table II). At initial [Pb] of 5 mg of Pb L⁻¹, the effectiveness of the NA was in the order: Idaho > Florida

Table II. Final Pb and Ca Concentration after Reaction of Natural Apatite with Aqueous Pb

initial Pb (mg L ⁻¹)	Pb (μg L ⁻¹)			Ca (mg L ⁻¹)		
	North Carolina	Florida	Idaho	North Carolina	Florida	Idaho
0	0.50 ± 0.18 ^a	0.16 ± 0.27	0.53 ± 0.92	3.16 ± 0.31	3.76 ± 0.43	6.41 ± 0.16
1	5.98 ± 2.58	2.50 ± 0.26	7.60 ± 2.41	2.57 ± 0.16	4.04 ± 0.53	6.51 ± 0.23
5	786 ± 16.2	24.6 ± 3.11	9.40 ± 6.47	4.03 ± 0.19	4.52 ± 0.15	7.19 ± 0.42

^a Means and standard deviations of triplicate samples.

> North Carolina. The SA of the NAs increased in the opposite order, with North Carolina > Florida > Idaho; thus, the effectiveness of the NA could not be attributed to SA. Rather it was due to the solubility of NA. Table II shows that dissolved [Ca] followed the order Idaho > Florida > North Carolina, which corresponds to the order of effectiveness of Pb removal by these NAs. Lower efficiency of NAs in immobilizing Pb was expected since they mainly consist of FA, which has lower solubility than HA. This again supports our hypothesis that Pb immobilization is through dissolution/precipitation with more soluble apatites being more effective in attenuating Pb from solution.

(c) *Immobilization of Exchangeable Pb by HA.* Resin-exchangeable Pb was also reacted with HA. No HP was detected in the HA residue (data not shown), indicating that the reaction did not occur in bulk solution. The resin was coated with a visible white precipitate after reaction, with longer reaction times producing more precipitate. The precipitate on the resin was examined with SEM-EDS, and HP was shown to have formed on the resin surface (Figure 8B). These results suggest that HP precipitation occurred on the resin surface where the local solubility product exceeded its formation constant. Thus, HA is potentially a very efficient material to facilitate Pb immobilization in Pb-contaminated soil and wastes containing exchangeable Pb.

The aqueous [Pb] in the presence of resin at reaction times of 0.5, 1, and 2 h were 0.17, 0.42, and 1.96 μg L⁻¹. However, [Pb] increased in the presence of HA at corresponding reaction times (1.34, 3.56, and 17.3 μg L⁻¹). This increase in [Pb] was attributed to Ca dissolved from HA and subsequent displacement of adsorbed Pb²⁺ ions from the surface of the cation-exchange resin. Thus, HA not only immobilizes Pb but also supplies cations (Ca) to displace Pb from the exchange sites into solution.

(d) *Immobilization of Dissolved Pb in Pb-Contaminated Soil Material by HA.* Hydroxyapatite was mixed with contaminated soil materials to test its feasibility in reducing Pb in more complicated matrices. The aqueous [Pb] of the waste decreased with increasing HA addition (Figure 9). The initial [Pb] of the soil material after 5 h of reaction was 2273 μg L⁻¹; it was reduced to 220 μg L⁻¹ after reacting with 0.5 g of HA and further reduced to 36 μg L⁻¹ after reacting with 2 g of HA. Lead concentrations increased slightly with reaction time in the control, from 2273 to 3370 μg L⁻¹. Thus, the amount of HA added is important in controlling dissolved [Pb] in this material, and the reaction was essentially complete after the first sampling period (5 h). Jurinak and Santillan-Medrano (22), using equilibrium solubility calculations to describe the reaction of Pb with noncalcareous soils, reported that the main mechanism regulating Pb solubility was the precipitation of Pb(OH)₂ and HP. In the present study, it is likely that HA removed dissolved Pb from contam-

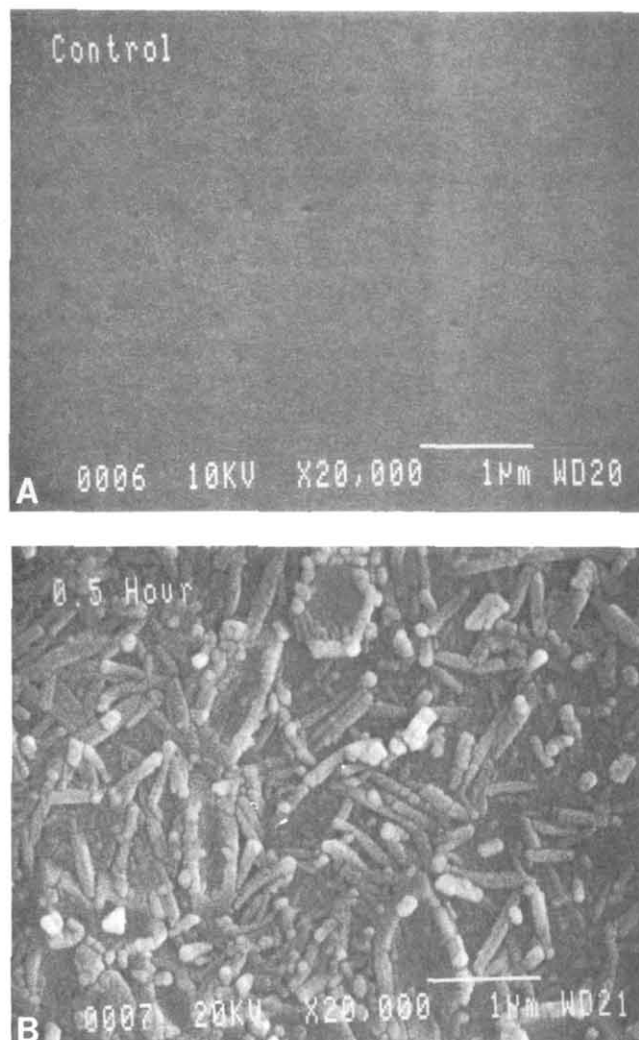


Figure 8. SEM micrographs of the resin surface before (A) and (B) after reaction with aqueous Pb.

inated soil materials through the formation of HP. However, verification of this hypothesis awaits further study.

Summary and Conclusions

Hydroxyapatite was effective in attenuating Pb in aqueous solution, from resin-exchange sites, and dissolved Pb from contaminated soil material. The immobilization process was rapid, near completion in 30 min. Natural apatite was also shown to be effective in removing Pb from aqueous solution. Results of chemical and XRD analysis and EM micrographs strongly support the mechanism of dissolution of HA/precipitation of HP. Aqueous [P] is the key factor in determining the effectiveness of Pb immobilization by apatite. Thus, pH also plays a role since it determines apatite solubility. Optimal removal of aqueous Pb is achieved when the solution pH is low

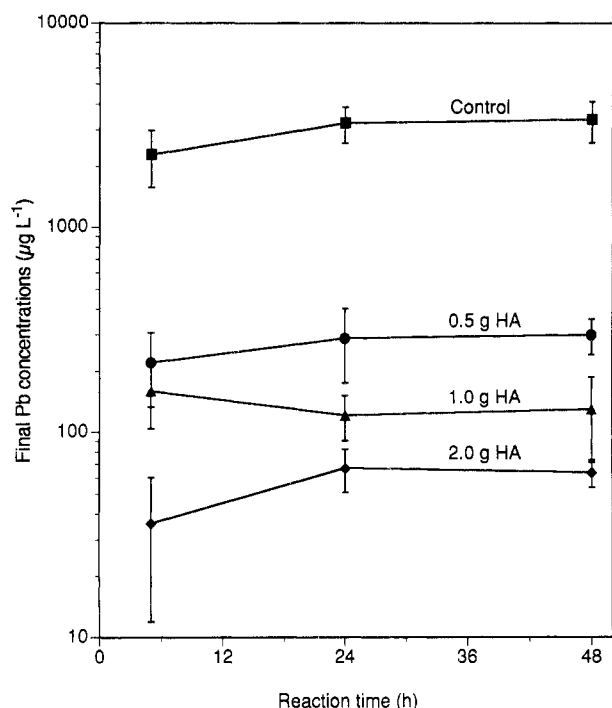


Figure 9. Effect of hydroxyapatite (HA) on Pb attenuation in Pb-contaminated soil material.

enough to dissolve apatite and supply P to react with Pb, yet high enough to keep the solubility of HP low. Apatite not only supplies P to immobilize Pb but also provides Ca to replace Pb from exchange sites. This is especially important in contaminated soils and solid wastes where much of the Pb is nonsoluble but labile. The final product of Pb immobilization is primarily HP, which supports low [Pb] even at a pH value as low as 3. We believe that apatite has great potential for attenuating soluble Pb in Pb-contaminated soils, wastes, and landfill leachates. The ready availability and rapid Pb immobilization of apatite and the apparent environmental stability of the reaction product suggest that this approach might have great merit for low-cost *in situ* immobilization of Pb-contaminated materials.

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Abbreviations used: HA, hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$]; HP, hydroxypyromorphite [$\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$];

FA, fluorapatite [$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$]; [Pb], total dissolved Pb concentrations; [Ca], total dissolved Ca concentrations; [P], total dissolved P concentrations; SA, surface area; EDS, energy dispersive; XRD, X-ray diffraction; EM, electron microscope; SEM, scanning electron microscope; STEM, scanning transmission electron microscope; DCP, CaHPO_4 ; NA, natural apatite.

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