

AQUEOUS Pb REDUCTION IN Pb-CONTAMINATED SOILS BY FLORIDA PHOSPHATE ROCKS

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(Received 17 March, 1997; accepted in revised form 22 June, 1998)

Abstract. Lead contamination is of great environmental concern due to its effect on human health. This study investigated the feasibility of using Florida phosphate rocks (PR) to immobilize aqueous Pb from Pb-contaminated soils. Occidental Chemical PR effectively immobilized Pb from 13 Pb-contaminated soils, but its effectiveness was affected by soil pH and extent of Pb contamination, with aqueous Pb reduction ranging from 21.8 to 100%. Longer reaction times improved aqueous Pb reduction. Six out of 7 Florida PR effectively immobilized aqueous Pb from the Burch Loam soil. Phosphate rock from Cargil Fertilizer was ineffective, with aqueous Pb reduction of 4.73%. The relative effectiveness of 6 Florida PR to immobilize aqueous Pb, excluding Cargil Fertilizer PR, was: Occidental Chemical > CF Chemical > Nu Gulf Industries > Agri-Chemical > IMC > Agrico Chemical. Phosphate rock solubility (as estimated by acid extraction and X-ray diffraction) failed to predicate the effectiveness of PR to immobilize aqueous Pb from Pb-contaminated soils, partially due to the complexity and kinetics of reactions between PR and soils. Our results demonstrate that PR has a potential to cost-effectively treat Pb-contaminated soils.

Keywords: contamination, heavy metal, immobilization, lead, remediation

1. Introduction

Lead contamination in soils is increasingly recognized as a public health hazard due to its toxicity to humans and animals, especially to children. Lead concentrations in uncontaminated soils range from 2 to 200 mg kg⁻¹ (Lindsay, 1979). However, elevated Pb concentrations have been reported in many soils resulting from anthropogenic activities. A soil is generally considered contaminated with Pb when its total Pb concentration exceeds 300 mg kg⁻¹ (EPA, 1993), and remediation is required when total Pb concentration is above 400 mg kg⁻¹ (OSWER, 1994). A national survey in the U.K. indicates that total Pb concentrations in garden soils ranges from 13 to 14 100 mg kg⁻¹ (Cotter-Howells and Thornton, 1991). A soil sample, obtained from a former battery-cracking site in Florida, had Pb concentrations up to 135 000 mg kg⁻¹ (Trnovsky *et al.*, 1987). Soils obtained from long-term polluted sites via industrial and urban sources from Britain, France, Norway and Japan contained Pb concentrations of 187 to 47 187 mg kg⁻¹ (Alloway and Morgan, 1985). As a result of such widespread Pb contamination in soils, considerable attention and resources are being focused on remediating Pb-contaminated soils.

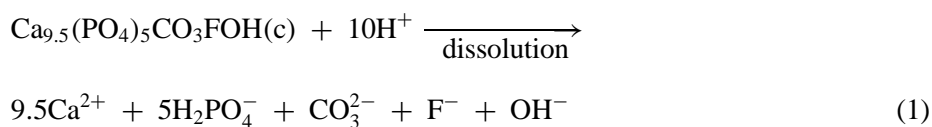
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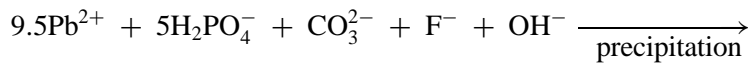


Technologies to remediate Pb-contaminated soils include chemical, physical and biological treatments. However, most current treatment technologies are either very costly or only partially effective. For example, excavation and off-site disposal of contaminated soil removes contaminants from human exposure, but is costly (\$282–480 Mg⁻¹ soil) (EPA, 1993). *In situ* stabilization of Pb-contaminated soil is a cost-effective remediation method. Remediating a lead battery-cracking site *in situ* using a phosphate additive costs as little as \$55 Mg⁻¹ soil (Showdhury *et al.*, 1994).

The primary objective in remediating Pb-contaminated soil is to reduce Pb bioavailability to acceptable levels. Bioavailability can be approximated by Pb solubility in soil, because dissolved Pb is the most bioavailable fraction of total Pb (Chaney *et al.*, 1988). Phosphate and phosphate-containing minerals have been shown to reduce bioavailable Pb in soils, e.g. phosphate basic slag from wastes of steel metallurgy reduces water-soluble Pb in one soil from 0.25 to 0.07 mg kg⁻¹. As a result, Pb uptake by ryegrass (bioavailable Pb) was reduced from 4.9 to 1.4 mg kg⁻¹ (Mench, 1994). Aqueous P reduces citric-acid extractable Pb (bioavailable Pb) from 1337 to 764 mg kg⁻¹ in a Pb-contaminated soil; it was projected that such a reduction in soil Pb concentrations would result in human blood Pb reduction from 8.5 to 5.4 μg dL⁻¹ using the Lead5 Biokinetic Uptake Model (Rabinowitz, 1993). Phosphate addition (0.5% on a soil weight basis) reduced Pb concentrations (Toxicity Characteristic Leaching Procedure) in a Pb contaminated soil from 2692–22388 to 21.0–189 mg kg⁻¹, i.e. below the target value for corrective action (Chowdhury *et al.*, 1994). Additionally, we have shown that hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) effectively immobilized aqueous Pb in the presence of elevated concentrations of anions (NO₃⁻, Cl⁻, F⁻, SO₄²⁻) or cations (Al³⁺, Cd²⁺, Cu²⁺, Fe²⁺, Ni²⁺, or Zn²⁺), which may be present in Pb-contaminated soils (Ma *et al.*, 1993, 1994a, b). Phosphate rock (PR) also effectively immobilized Pb from both aqueous Pb solutions and a Pb-contaminated soil (Ma *et al.*, 1995). The primary mechanism of Pb immobilization in these systems is through dissolution of hydroxyapatite or PR, and subsequent precipitation of a pyromorphite-like mineral (Ma *et al.*, 1993, 1995). Our hypothesis was supported by the results of Ruby *et al.* (1994), who demonstrated that Pb was converted from galena to insoluble lead phosphate in a soil contaminated containing both P and Pb. They further demonstrated that formation of pyromorphite-like mineral significantly reduced Pb bioavailability.

Dissolution of PR and subsequent precipitation of a carbonated fluoropyromorphite-like mineral can be described by the following simplified equations (assuming equal molar concentrations of F⁻, OH⁻, and CO₃²⁻ as an example):





Dissolution of PR increases aqueous Ca, P and OH⁻ concentrations, whereas flu-ropypromorphite precipitation reduces P and OH⁻ concentration. Theoretically speaking, the higher the solubility of PR, the more effective the material should be in reducing aqueous Pb concentrations. We have shown that the more soluble the hydroxyapatite, the more effective it is in reducing aqueous Pb (Ma *et al.*, 1993). The effectiveness of PR in immobilizing Pb from contaminated soils thus primarily depends on its ability to provide soluble P in soil solution. Other factors are also important such as reaction time and properties of PR and soil, because they directly affect the solubility of PR in soils and how PR reacts with Pb in soils.

Because of its ready availability and low cost, PR has been widely used as a fertilizer, and its solubility has been studied extensively (Chien, 1977a, 1982; Chien *et al.*, 1980; Chien and Friesen, 1992; McClellan, 1979). However, the feasibility of using PR to immobilize aqueous Pb from Pb-contaminated soils has been rarely researched. PR, a complex assemblage of phosphate minerals, is mainly composed of microcrystalline carbonate fluorapatite (McClellan, 1979). Its solubility in soils increases as the degree of carbonate substitution increases (McClellan, 1979) and can be estimated by measuring P concentrations in weak acids (2% formic acid or citric acid) or variation in peak positions of X-ray diffraction (XRD) (the angular difference between the 004 and 410 peaks) (Chien, 1979; Jahnke, 1984). Since the primary function of PR in immobilizing Pb from Pb-contaminated soils is to supply soluble P to react with Pb, solubility of PR can theoretically be used to predict the effectiveness of PRs in treating Pb-contaminated soils.

Although 14 PRs effectively reduce aqueous Pb concentrations, and two PRs (Occidental and CF Chemical) effectively immobilize aqueous Pb from a contaminated soil (Ma *et al.*, 1995), further research is needed to test additional PRs with various Pb-contaminated soils. Because properties of PRs and soils vary greatly, investigation of additional PRs and soils will help to understand factors controlling Pb immobilization by PR. In the current study, Pb immobilization tests were expanded to 7 Florida PRs and to 13 Pb-contaminated soils via batch experiments. The primary objectives of this research were two fold: (1) to investigate the effectiveness of different Florida PRs in immobilizing aqueous Pb from a variety of Pb-contaminated soils; and (2) to test the feasibility of using PR solubility to predict the effectiveness of Pb immobilization by PRs in Pb-contaminated soils.

TABLE I
Locations and sources of Pb contamination for soils used in this research

Soil name	Abbreviation	Location	Contamination source
Antilan	AN	Apple orchard, WA	PbHAsO ₄
Twin	TW	Apple orchard, WA	PbHAsO ₄
Burch	BU	Apple orchard, WA	PbHAsO ₄
Burch Loam	BL	Apple orchard, WA	PbHAsO ₄
Pogue	PG	Apple orchard, WA	PbHAsO ₄
Pogue Loam	PL	Apple orchard, WA	PbHAsO ₄
East Field 1	EF1	Residential area, MT	Smelter
East Field 2	EF2	Residential area, MT	Smelter
BPS	BP	Berks County, PA	Battery acid
RRS	RR	Tacoma, WA	Shooting range
AEC 1-1	DA	Bridgeport, CT	Burning ground
Area 40	DU	Tacoma, WA	Sheet Pb
PTC	PT	Bartlesville, Oklahoma	Smelter

2. Materials and Methods

2.1. CHARACTERIZATIONS OF Pb-CONTAMINATED SOILS

Sample locations and contamination sources of the 13 Pb-contaminated soils used in this study are presented in Table I. Total elemental concentrations, suspension pH values and soil organic matter contents of these soils are shown in Table II.

2.2. CHARACTERIZATION OF FLORIDA PHOSPHATE ROCKS

Seven Florida PR samples were used in this experiment. The mining company where samples were obtained and their abbreviations are as follows: Occidental Chemical Corp. (OC), C.F. Chemical Inc. (CF), Agri-Chemical Corp. (AC), Agrico Chemical Company (ACC), Nu-Gulf Industries Inc. (NG), IMC Corp. (IMC) and Cargil Fertilizer Inc. (CFI). Except CFI, total elemental compositions and specific surface areas of these materials can be found in Ma *et al.*, 1995. The specific surface area of CFI, as measured by N₂-BET adsorption with a Micromeritics, Flowsorb 2300 surface area analyzer, is 11.0 m² g⁻¹; total Ca and P concentrations are 31.4 and 13.3%, and total Cd, Cu, Ni, Pb, and Zn concentrations are 18, 19, 18, 55, and 102 mg kg⁻¹.

TABLE II
Total elemental concentrations and suspension pH of the 13 Pb-contaminated soils

	pH ^b	SOM ^a	Si	Al	Fe	Ca	K	Mg	P	Pb	Mn	Ba	Zn	Cu	Ni	Cd
	————— (%) —————									————— mg kg ⁻¹ —————						
AN	8.59	2.4	26.7	36.9	10.5	10.0	6.21	1.00	0.08	198	613	608	89	0	12	4.0
TW	7.28	2.3	28.1	9.09	2.64	2.46	1.30	0.77	0.08	705	551	763	115	20.5	9.3	4.1
BU	5.85	2.5	26.5	8.71	3.85	2.11	1.46	0.88	0.10	2680	762	594	154	48.4	29	14
BL	5.83	2.5	26.3	8.54	3.82	2.20	1.65	1.00	0.16	2749	760	633	166	58.0	19	20
PG	6.70	3.2	28.1	7.85	3.08	1.84	1.83	0.84	0.07	399	692	860	76	0	21	2.4
PL	6.56	2.9	28.2	7.81	2.91	2.07	1.97	0.91	0.16	930	646	861	88	88	39	20
EF1	6.78	2.1	25.8	6.88	3.50	1.55	2.60	0.85	0.14	5970	673	751	2430	1260	19	158
EF2	6.80	2.2	28.1	7.34	3.51	1.52	3.01	0.87	0.13	4480	664	748	1310	639	19	93
BP	6.14	1.5	19.9	5.71	3.34	3.18	0.62	0.52	0.05	40100	642	384	86	120	20	62
RR	7.03	3.8	30.1	7.26	3.05	1.37	2.01	0.75	0.09	6682	876	1210	633	102	30	41
DA	7.51	1.9	29.0	4.85	1.85	0.39	1.30	0.29	0.03	12500	1520	518	782	1010	29	41
DU	5.53	12	20.7	5.41	12.0	1.76	0.78	0.96	0.09	7640	1060	2630	5680	2620	21	6.4
PT	7.51	6.1	28.2	3.05	3.54	1.53	1.05	0.21	0.10	1300	544	486	574	241	98	41

^a Soil organic matter content.

^b Measured in 1:2 soil: water suspensions after 24 hr.

2.3. EXPERIMENTAL PROCEDURES

2.3.1. *Lead Immobilization from Pb-Contaminated Soils by OC Phosphate Rock*

Due to its known effectiveness in immobilizing aqueous Pb (Ma *et al.*, 1995), OC PR was selected to test the feasibility of using Florida PR to immobilize Pb from 13 Pb-contaminated soils. In this study, 4 g of each soil was reacted with 0, 0.5, or 1 g of PR in 40-mL polycarbonate centrifuge tubes containing 25 mL of deionized water. The suspensions were shaken from 2 to 96 hr.

2.3.2. *Lead Immobilization from Burch Loam Soil by Florida Phosphate Rocks*

Due to its relatively high Pb concentration, Burch Loam soil was used to study the feasibility of using Florida PRs to immobilize aqueous Pb from a Pb-contaminated soil. In this study, 4 g of Burch Loam soil was reacted with 0, 0.5, or 1 g of each PR in 40-mL polycarbonate centrifuge tubes containing 25 mL of deionized water. The suspensions were agitated on a shaker for 2 hr.

2.3.3. *Solubility and Dissolution of Phosphate Rocks*

Phosphate rock solubility should theoretically correlate with the effectiveness of PR in immobilizing aqueous Pb from Pb-contaminated soils. To test if this is the case with 7 Florida PRs, acid-soluble P was determined shaking 0.3 g of each PR with 30 mL 2% citric acid for 30 min (Axelord, 1979). Phosphate rock solubility was also estimated by comparing the variation in the position of XRD peaks (represented by the angular difference between the 004 and 410 peaks) (Jahnke, 1984).

Dissolution kinetics of two PRs in water, representing the most (OC) and least (CFI) effective PRs in immobilizing Pb, were examined by shaking 0.3 g of each PR with 15 mL of deionized water for up to 384 hr in 40-mL polycarbonate centrifuge tubes at room temperature of 25 ± 1 °C.

2.4. ANALYTICAL METHODS

All experimental treatments in this study were prepared in triplicate and were conducted in acid-washed (10% HNO₃) polycarbonate labware. All soil and PR samples were digested using a HF-HCl/HNO₃ dissolution procedure in a Parr Bomb (Bernas, 1968). The digested solutions were analyzed for total elemental concentrations by an inductively coupled plasma spectrophotometer. Suspensions of soil and PR were centrifuged at 14K RPM ($15\,400 \times g$) for 20 min using a Beckman model J2-21 centrifuge. After centrifugation, the supernatants were filtered through 0.2 μm Nucleopore polycarbonate membrane filters. The filtrates were analyzed for total P, Ca, Pb, and solution pH.

Total metal concentrations were determined using a Perkin-Elmer 2380 atomic adsorption spectrophotometer equipped with a graphite furnace atomizer. Total dissolved P was measured colorimetrically with a Shimadzu UV160U Spectrophotometer (Olsen, 1982). Solution pH was determined using a Fisher Scientific

Accumet model 20 pH/conductivity meter. Phosphate rock samples were examined by a XRD system with stepping motor and graphite crystal monochromator 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 sec per $0.05^\circ 2\theta$. All XRD analyses were performed using backfilled, randomly oriented mounts.

3. Results and Discussion

Sources of Pb contamination in soils can be generally classified into three broad categories: agricultural activities, such as application of the insecticide PbHAsO₄; industrial activities, such as mining and smelting; and urban activities, such as use of Pb-gasoline and Pb-paint. Our soil samples reflected the first two categories of Pb contamination (Table I). In addition to high Pb concentrations, some of these soils contained high levels of other trace metals (Table II). For example, soil EF1, EF2 and PT had high levels of Zn, Cu, and Cd, whereas soils RR and DU contained high concentrations of Zn and Cu. Soil pH ranged from 5.5 to 8.6 (Table II).

Among the 15 PR materials tested to date (Ma *et al.*, 1995), CFI PR contains the greatest Pb concentration (55 mg kg^{-1}). Total Pb concentrations of the other six Florida PRs used in this study (OC, CF, AC, ACC, NG, and IMC) are 0.0, 7.6, 0.0, 0.0, 0.0, and 27 mg kg^{-1} . XRD analysis of the PR samples indicates that they were mainly carbonated fluorapatite ($\text{Ca}_{10}(\text{PO}_4, \text{CO}_3)_6\text{F}_2$); the second most abundant mineral was quartz (SiO_2) (Figure 1). Trace amounts of dolomite ($\text{CaMg}(\text{CO}_3)_2$) and calcite (CaCO_3) were also present in some samples.

3.1. LEAD IMMOBILIZATION FROM Pb-CONTAMINATED SOILS BY OC PHOSPHATE ROCK

In a previous study, CF and OC PRs significantly reduced aqueous Pb concentrations from Burch soil; aqueous Pb reduction ranged from 56.8 to 100% in various column experiments (Ma *et al.*, 1995). In this study, batch experiments were conducted to investigate the effectiveness of OC PR to immobilize dissolved Pb from 13 contaminated soils.

OC PR effectively immobilized aqueous Pb from all 13 Pb-contaminated soils, but its effectiveness varied considerably with soils; a minimum of 22% of aqueous Pb was immobilized after 2 hr (Table III). The effectiveness of Pb immobilization greatly increased with increasing PR addition, indicating that more dissolved P was available to react with Pb in soils at greater PR loading (Table III). Lead immobilization ranged from 22 to 94% at addition of 0.5 g of PR, but increased to 33 to 100% at addition of 1 g of PR (Table III). The efficiency of Pb immobilization on a unit weight basis (aqueous Pb reduction/g PR) decreased at greater PR loading rates; e.g. Pb% immobilized from BU soil increased from 59 to only 67% as PR loading doubled from 0.5 to 1 g (Table III).

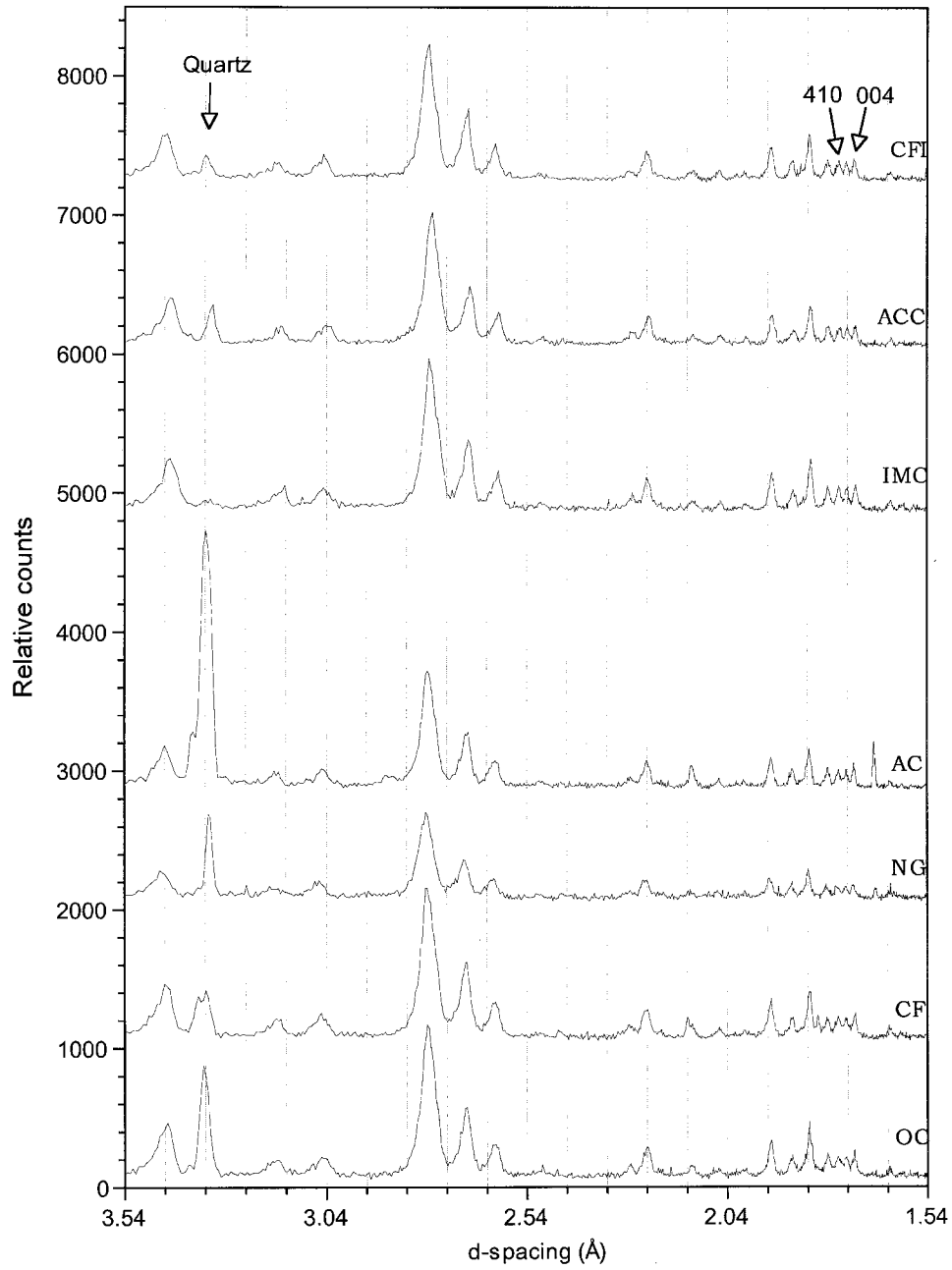


Figure 1. X-ray diffraction patterns of seven Florida phosphate rocks used in this study. Unmarked peaks represent carbonated fluorapatite.

TABLE III
 Aqueous Pb, P, and Ca concentrations and filtrate pH of the 13 soils after reaction with different amounts of OC phosphate rock (PR) for 2 hr

g of PR	AN	TW	BU	BL	PG	PL	EF1	EF2	BP	RR	DA	DU	PT
Aqueous Pb concentrations (n mole L ⁻¹)													
0	59±1.0	248±1.1	2290±31	1070±26	194±3.1	150±12	127±3.6	294±14	1800±31	1020±23	418±27	138±15	64±5.5
0.5	46±0.1	99±3.1	947±40	ND ^a	69±9.8	ND	25±1.7	58±13	107±7.0	749±23	171±4.6	40±2.3	23±1.5
1	31±1.1	70±1.1	762±19	218±16	55±3.1	36±3.9	17±0.8	29±1.5	49±2.7	682±17	41±3.8	25±0.3	0
Aqueous P concentrations (μ mole L ⁻¹)													
0	13±0.5	1.0±0.1	9.7±0.3	11±0.7	1.6±0.4	4.6±0.2	0.7±0.0	0.8±0.1	0	0.1±0.0	0	0.1±0.0	0.24±0.1
0.5	40±3.5	6.8±0.6	40±3.8	ND	11±0.5	ND	0.6±0.1	1.5±0.1	0.3±0.0	1.8±0.0	1.2±0.0	1.7±0.1	0.28±0.1
1	42±1.8	7.3±0.0	36±2.6	36±1.1	11±0.4	13±0.9	0.8±0.0	1.8±0.0	0.6±0.1	2.4±0.1	1.3±0.0	2.5±0.2	0.15±0.0
Aqueous Ca concentrations (μ mole L ⁻¹)													
0	38±7.5	95±18	70±3.3	100±7.9	206±12	116±2.2	713±10	576±21	2380±6.1	185±1.7	159±2.9	319±7.6	629±10
0.5	94±6.1	137±6.3	150±1.7	ND ^a	227±6.1	ND	1040±29	580±20	2430±47	243±7.9	225±5.2	355±9.6	874±12
1	128±5.6	183±2.3	175±5.0	250±36	244±7.5	208±9.7	1090±17	753±31	2660±54	287±7.6	260±14	414±14	996±16
Filtrate pH													
0	9.2±0.2	7.0±0.0	6.6±0.0	6.4±0.0	7.0±0.0	6.6±0.0	7.1±0.0	7.2±0.1	6.2±0.1	7.3±0.0	7.4±0.0	6.0±0.0	7.0±0.5
0.5	8.2±0.1	6.9±0.0	6.8±0.0	ND	7.0±0.1	ND	7.3±0.0	7.3±0.1	6.6±0.3	7.3±0.0	7.4±0.0	6.2±0.0	7.9±0.0
1	7.9±0.0	6.9±0.1	6.8±0.0	6.7±0.0	7.0±0.0	6.7±0.1	7.5±0.1	7.3±0.0	6.5±0.0	7.3±0.0	7.3±0.0	6.0±0.0	7.9±0.0

^a Not determined.

Dissolved Pb concentrations in the blanks (soil plus deionized water), ranged from 59 to 2290 nmol⁻¹ after 2 hr of reaction. Thus, most soils were above the current EPA Pb action level of 72.4 n mole L⁻¹ excluding AN and PT soils (Table III). Dissolved Pb concentrations, after reaction with 0.5 g of PR, were reduced to below 72.4 n mole L⁻¹ in 55% of the soils tested. As the PR level was increased to 1 g, aqueous Pb concentrations were reduced to below 72.4 n mole L⁻¹ in all but three soils. The final Pb concentrations in the three soils were 762 (BU), 218 (BL) and 682 (RR) nmol L⁻¹ (Table III). These soils had the highest (BU), third (BL) and fourth (RR) highest water soluble Pb (2290, 1070, and 1020 nmol L⁻¹) among the 13 soils tested. The initially high aqueous Pb concentrations in these soils likely contributed to the final high Pb concentrations after reaction with PR, as indicated by the correlation coefficient ($r = 0.72$) of the two factors.

The impact of soil properties on the effectiveness of PR in immobilizing Pb was analyzed by correlating the net aqueous Pb concentration reduction (aqueous Pb concentration difference at addition of 0 and 1 g PR after 2 hr reaction) (Table III) with soil pH, soil organic matter content, and total Pb concentration in soils (Table II). Their correlation coefficients were -0.52, 0.32 and 0.65, respectively. It was expected that higher pH reduced the effectiveness of Pb immobilization by PR due to lower PR solubility. This result is consistent with our hypothesis that Pb immobilization was probably through dissolution of PR and precipitation of pyromorphite-like mineral. If Pb reduction in soils were through Pb adsorption by either soils or PR, then higher pH would result in higher Pb adsorption due to increased cation exchange capacity. Poor correlation (0.32) between the net aqueous Pb reduction and soil organic matter content also supports our hypothesis. Correlation between the net Pb reduction and total Pb concentrations (0.65) in soils suggests that more aqueous Pb was immobilized in soils containing greater amount of total Pb.

Theoretically, dissolution of PR increases Ca, P, and OH⁻ concentrations in solution (Equation (1)). In general, increasing PR addition increased total Ca and P concentrations due to more PR dissolution. Filtrate pH was either unaffected or increased with increasing rate of PR addition. The only exception to this trend was AN soil, which with a filtrate pH of 9.2 for the unamended soil, was obviously sodic. Addition of Ca source (PR) lowered filtrate pH of AN soil possibly due to equilibration of solution HCO₃⁻ with newly formed CaCO₃.

Reaction time significantly affected Pb immobilization by PR, as well as dissolved Pb in the control treatments. Dissolved Pb concentrations in the control treatments increased up to 24 hr, but then decreased up to 96 hr (Figure 2). In a previous column experiments (Ma *et al.*, 1995), Pb concentrations of the control treatments decreased from 1958 to 356 nmol L⁻¹ as incubation time increased from 24 to 168 hr. The mechanism for aqueous Pb reduction after 24 hr of reaction was unclear, possibly due to both chemical and biological reactions. Dissolved Pb concentrations after reaction with 1 g of PR were much lower than those in the control treatments, but followed a trend similar to those in the control treatments

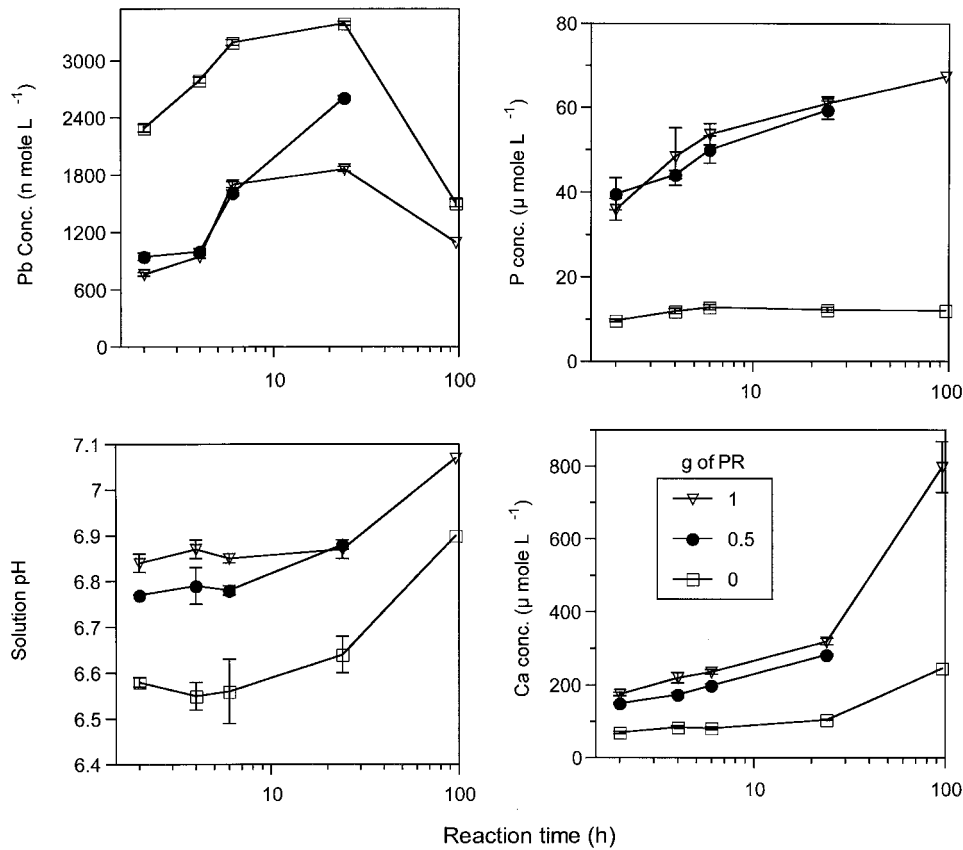


Figure 2. Effect of reaction time and quantity of phosphate rock on aqueous Pb immobilization in BL soil by OC phosphate rock. Error bars stand for standard deviations of three replicates.

(Figure 2). Filtrate pH, and total P and Ca concentrations generally increased with reaction time, but total Ca concentration increases were much greater than total P. As reaction time increased from 24 to 96 hr, P concentration in Burch Loam soil (after reaction with 1 g of OC), increased by 10%, whereas Ca concentration increased by 150% (Figure 2). No carbonate or other impurities were detected by XRD other than quartz and carbonated fluorapatite in OC PR. Thus, assuming congruent dissolution of OC PR, increases in P and Ca concentrations should be similar. Part of the P dissolved from PR likely reacted with Pb, possibly reducing P concentrations relative to Ca concentrations. Such a mechanism supports our hypothesis of PR dissolution and subsequent precipitation of carbonated fluoropytomorphite-like mineral. However, it was also possible that microbial activities and P reactions with other soil components, e.g. iron and aluminum oxide and clay minerals, resulted in partial decrease in P concentrations.

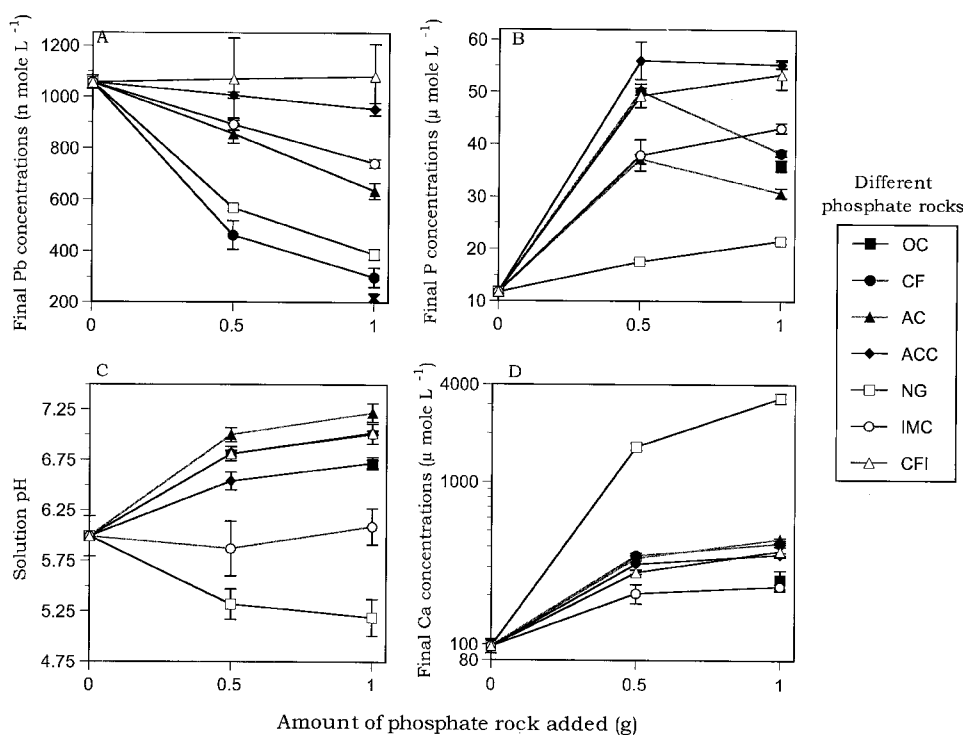


Figure 3. Final concentrations of Pb, Ca, and P, and filtrate pH of Burch Loam soil after reaction with Florida phosphat rocks for 2 hr. Errors bars stand for standard deviations of three replicates.

3.2. LEAD IMMOBILIZATION FROM BURCH LOAM SOIL BY FLORIDA PHOSPHATE ROCKS

All Florida PRs, except CFI, effectively immobilized aqueous Pb from BL soil (Figure 3). Lead immobilized ranged from 0% (CFI) to 79% (OC). The relative effectiveness of various PRs in immobilizing aqueous Pb in BL soil was OC > CF > NG > AC > IMC > ACC > CFI (LSD at $\alpha = 0.05$). The effectiveness of these PRs in immobilizing Pb from aqueous Pb solutions was different. Ma *et al.* (1995) observed the effectiveness to be CF > OC > ACC > AC > IMC > NG (LSD at $\alpha = 0.05$), when 0.1 g of PR was reacted with 200 mL of 48.2 $\mu\text{mol L}^{-1}$ Pb. NG was the least effective in immobilizing aqueous Pb from solutions, but was third most effective in immobilizing Pb from Pb-contaminated soils; whereas ACC, which was the least effective in immobilizing Pb from Pb-contaminated soils, but was the third most effective in immobilizing Pb from aqueous solutions. Apparently, the effectiveness of PR in immobilizing Pb depends on both the properties of PR and soil, as well as reaction time.

The dissolved Pb concentration in the BL soil (control treatment) was 1056 nmol L⁻¹, much greater than the EPA action level of 72.4 n mole L⁻¹ (Figure 3). All PRs effectively reduced aqueous Pb concentrations and their effectiveness increased

with increasing PR addition. However, none of the PRs used in this study reduced dissolved Pb concentrations in BL soil below $72.4 \text{ n mole L}^{-1}$ after 2 hr reaction, even at a PR addition of 1 g. The quantity of PR used in this study to react with Pb-contaminated soils is extremely high (0.125 to 0.25 g PR g^{-1} soil). The fact that no PR even at 0.25 g g^{-1} soil could reduce aqueous Pb in BL soil below $72.4 \text{ n mole L}^{-1}$ implies a remediation limitation associated with the relative low solubility of PR. More soluble P sources would have to be mixed with PR to increase Pb immobilization efficiency in such a contaminated soil. More soluble P sources could quickly reduce aqueous Pb to below acceptable level, while PR would supply a constant P source in soil to react with Pb for long term Pb immobilization, especially in an environment where P may be removed by plants or microbes.

Final Ca concentrations in solution, for all the PRs tested, increased with increasing PR addition. Final P concentrations increased with increasing PR addition, except with CF and AC. As more aqueous Pb was immobilized by PR (at higher addition rates), the rate of P consumption due to precipitation by Pb was probably faster than that of P dissolution from PR, thus decreasing P concentrations (Figure 3). The final filtrate pH generally increased with increasing amount of PR, except NG. Decreases in solution pH with increasing additions of NG contradict the expected result of increased OH^- release (increased pH) accompanying dissolution of PR. Solution pH in B2 soil started around 6, but dropped to 5 after addition of 1 g of NG. However, no other impurities were detected in the NG PR other than quartz and acarbonated fluorapatite by XRD (Figure 1). The effect of PR on soil pH varies from no effect to a slight increase of 0.2 to 0.4 pH units, depending on the rate of PR addition and the solubility of PR (Equation (1)). (Hammond, 1979). It was unclear why reaction between BL soil and NG PR resulted in a pH reduction, which was accompanied by significant increase in Ca concentrations (Figure 3).

3.2.1. Solubility and dissolution of phosphate rocks

The effectiveness of PR as a P fertilizer or Pb immobilization material in soils depends on the material's ability to supply P to soil solutions. The only difference is that P is taken up by plants in the former case, whereas P is bound in P-Pb minerals in the later case. Of course, P can also be sorbed by or react with other soil components such as iron and aluminum oxides and clays. The solubility of PR as a fertilizer can be estimated by several chemical extractions (Chien, 1982). An attempt was made to assess if such estimation can be used to predict the effectiveness of PR in immobilizing Pb from Pb-contaminated soils. Measured citric-acid soluble P of NG, IMC, ACC, CF, CFI, OC and AC PRs were, 331 ± 18 , 371 ± 70 , 393 ± 25 , 406 ± 26 , 406 ± 20 , 407 ± 85 and $432 \pm 50 \text{ mg L}^{-1}$. Analysis of variance indicated that there was no significant difference among these P levels at $\alpha = 0.01$. Clearly, the citric soluble P content of PRs fails to predict the effectiveness of PR in immobilizing Pb after 2 hr. However, it may suggest that these PRs are equally effective in immobilizing Pb from Pb-contaminated soils given adequate reaction time, i.e. equilibrium conditions.

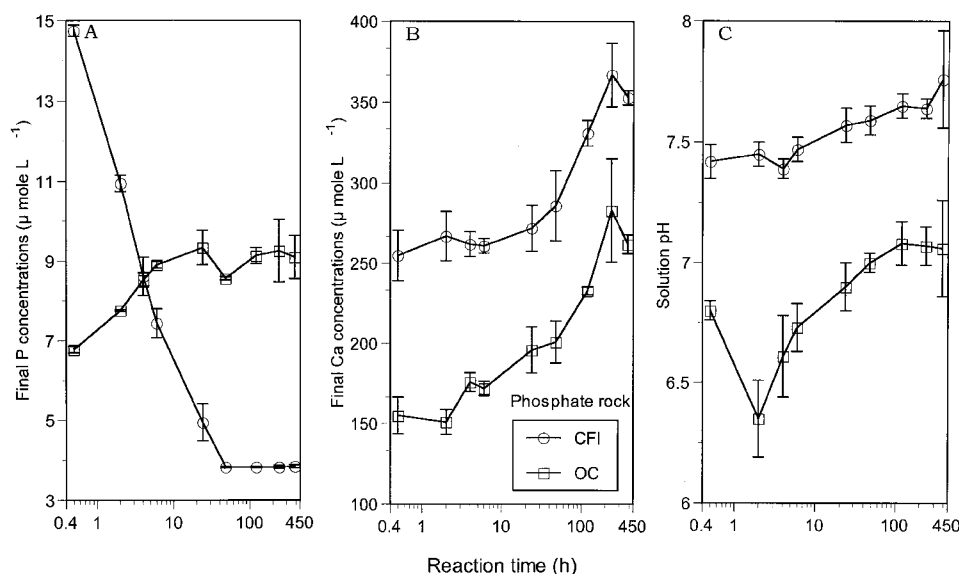


Figure 4. Final Ca and P concentration, and filtrate pH after CFI and OC phosphate rocks reaction with water for up to 384 hr. Error bars stand for standard deviations of three replicates.

Another estimate used to predict the solubility of PR is the extent of carbonate substitution for phosphate. In general, PR solubility increases as carbonate substitution for phosphate in the apatite structure increases (Chien, 1977b). There is a good correlation between the angular distance between peaks 004 and 410, and the carbonate content of PRs (Jahnke, 1984). However, measured angular distances between these two peaks of the 7 Florida PRs studied were not correlated with their effectiveness in immobilizing Pb (Figure 1). There were minor changes, if any, in angular distances between peaks 004 and 410 of the 7 Florida PRs studied, although their effectiveness in immobilizing Pb, after 2 hr, varied greatly from sample to sample. Again, PR solubility fails to predict the effectiveness of PR in immobilizing Pb after 2 hr. However, Pb immobilization by PR was tested only for 2 hr, thus the lack of any correlation against studied measures of PR solubilities may be due to the non-equilibrium conditions chosen for this study.

A dissolution study examined why OC was the most effective and CFI was the least effective in immobilizing Pb from Pb contaminated soil. With increasing reaction time, final P concentrations increased in OC PR solutions up to 48 hr (Figure 4). From 48 hr to 16 d, P concentrations remained nearly constant, indicating that there is little dissolution beyond 48 hr and that the system reached an equilibrium with respect to P. On the other hand, P concentrations in CFI PR solutions decreased up to 48 hr (Figure 4). Decreased P concentrations in CFI system may reflect precipitation of trace amount of soluble P, initially present in PR, to less soluble P mineral. However, no difference in XRD patterns of CFI PR at different reactions times was observed (data not shown). Both filtrate pH and Ca concentra-

tions in CFI systems increased with reaction time and were greater than those of OC system. These data are consistent with the reduced effectiveness of CFI compared to OC PR since higher pH reduces PR solubility, and higher Ca concentrations suppress PR dissolution (Equation (1)). Further, this explanation is consistent with our hypothesis that Pb immobilization is mainly a dissolution/precipitation process.

Our results demonstrate that Florida PRs effectively immobilized Pb from various Pb-contaminated soils (except CFI). Material effectiveness is affected by the properties of PR and soil, as well as reaction time. *In situ* Pb immobilization using PR can be a cost-effective alternative to treat Pb-contaminated soils, but the quantity of PR needed can be uneconomic high for some highly contaminated soils. More soluble P sources would have to be mixed with PR for field application to increase the effectiveness of Pb immobilization in such soils.

Acknowledgements

This research was sponsored in part by the Florida Institute of Phosphate Research (Contract No. 93-01-111). The authors thank Dr. G. A. O'Connor for reviewing the manuscript.

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