Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Separation of Lead Ions on Francolite Surfaces

M. Prasad[a]; S. S. Amritphale[a]; S. Saxena[a]; Navin Chandra[a]
[a] REGIONAL RESEARCH LABORATORY (C.S.I.R.), BHOPAL, INDIA

To cite this Article Prasad, M. , Amritphale, S. S. , Saxena, S. and Chandra, Navin(2000) 'Separation of Lead Ions on Francolite Surfaces', Separation Science and Technology, 35: 15, 2431 — 2442

To link to this Article: DOI: 10.1081/SS-100102347

URL: http://dx.doi.org/10.1081/SS-100102347

SEPARATION SCIENCE AND TECHNOLOGY, **35**(15), pp. 2431–2442, 2000

Separation of Lead Ions on Francolite Surfaces

M. PRASAD,* S. S. AMRITPHALE, S. SAXENA,
and NAVIN CHANDRA
REGIONAL RESEARCH LABORATORY (C.S.I.R.)
HOSHANGABAD ROAD HABIBGANJ NAKA
BHOPAL 462 006, INDIA

ABSTRACT

The separation of aqueous Pb^{2+} onto a low-grade ($<15\%$ P_2O_5) carbonate-substituted rock phosphate (Francolite) mineral from Madhya Pradesh (India) was investigated. The effects of different parameters such as initial concentration of Pb^{2+}, particle size of Francolite, and amount of substrate on lead-ion separation were studied under natural conditions by equilibrating different amounts of Francolite with aqueous lead solutions of different concentrations. Francolite was found capable of lead-ion separation at par with hydroxyapatite or high-grade ($>25\%$ P_2O_5) rock phosphate. Francolite was found very effective in removing Pb^{2+} with a minimum lead removal of 82–99.9% and a maximum LRC (lead removal capacity) of 0.082 g of lead/g of Francolite.

Key Words. Francolite; Separation; Heavy metal; Fluoropyromorphite

INTRODUCTION

Lead is potentially very toxic to mammals and aquatic animals. Its presence in the environment as a result of extensive industrial applications, such as hot-dip galvanizing, lead acid batteries, paint industries, mining and extraction activities (1) ceramic glazing industries, etc. and widespread disposal of heavy-metal ions, whether in soils, water bodies, or any other matrices, poses serious health hazards to living organisms. The permissible limits of lead in industrial effluents and drinking waters are 0.10 and 0.05 mg/L, respectively (2).

---

* To whom correspondence should be addressed.

Some in-place treatment technologies, such as immobilization, which includes sorption (adsorption, ion exchange, and precipitation/co-precipitation), chemical degradation, and biodegradation have been reported (1, 3, 4, 5) to be effective for the removal of heavy-metal ions.

Sorption at solid substrate materials is considered the most suitable process for heavy-metal separation from solutions at low concentrations. The only sorbent typically used for low concentration of heavy-metal ions is active carbon, which separates by adsorbing relatively low amounts of metal ions and is not selective as to the type of metal under consideration. The severe limitation of this process, however, lies in the high cost of the substrate material and difficulty in regeneration and recyclability. Clays and related minerals have also been explored as sorbents for combatting pollution not only for organic species (5–8) but also for heavy-metal ions (9–12). However, their industrial and environmental applications as sorbents are extremely limited.

Hydroxyapatite, which rarely occurs in nature, has been used in wastewater treatment (13) and has a very high capacity for removing divalent heavy-metal ions from water (14). Different amounts of different grades of hydroxyapatite have been utilized (15, 16) for the separation of various heavy-metal ions such as lead, zinc, copper, cadmium, etc. as single and multiple species from aqueous solutions using sorption techniques under different pH conditions. However, hydroxyapatite is not found suitable for commercial applications because of its high cost.

High-grade (30% P_2O_5) rock phosphate has also been utilized (1) for the removal of different heavy-metal ions from aqueous solutions, and it was reported to be effective in Pb separation ranging from 38.8 to 100%. The high-grade rock phosphates already find major applications in phosphoric acid and fertilizer manufacture. However, the low-grade (<15% P_2O_5) rock phosphate, which is generally considered as waste for fertilizer manufacturing, may also be explored to find an application for heavy-metal separation.

Madhya Pradesh, the second largest state in India in terms of reserves of rock phosphate, has a majority of the low-grade (<15% P_2O_5) reserves at Hirapur and Jhabua. These reserves are considered as waste by manufacturers of phosphatic fertilizer. The present investigation has been undertaken to examine the utility of this very-low-cost and environmentally friendly francolite mineral for the separation of Pb^{+2} ions from aqueous solutions.

MATERIAL AND EXPERIMENTAL/ANALYTICAL METHODS

Representative samples of low-grade carbonatic rock phosphate (francolite) from Jhabua (Madhya Pradesh) were collected for the present study with the help of M.P. State Mining Corporation, Bhopal. To ensure that the rock phos-

TABLE 1
Chemical Analysis of Francolite Samples

Constituents	Weight percent
P_2O_5	12.50
SiO_2	26.50
CaO	32.60
Fe_2O_3	1.59
Al_2O_3	6.08
MgO	0.06
TiO_2	0.49
* L.O.I.	19.12
F	1.06

* L.O.I. = Loss on ignition.

phate samples do not contain soluble lead, 0.5 g francolite sample of -150 $+105$ micron size was equilibrated with 100 mL warm deionized water (~60°C) for 30 minutes and filtered. The filtrate was analyzed for lead content and observed to contain <0.01 mg/L lead ions.

Dionex 500 Ion Chromotography and GBC-902 Atomic Absorption Spectrophotometer were used for the analysis of Ca^{2+} and Pb^{2+}. The results of chemical analyses of rock phosphate samples are shown in Table 1. X-ray diffraction analysis of francolite samples before and after lead adsorption was conducted with the help of a Philips X-ray machine using filtered Cu–K_α radiation at 40 kV and 20 mA.

Test solutions were prepared from 1000 mg/L stock solution of lead ions by serial dilution. Different amounts (0.05 g to 1.5 g) of francolite samples were equilibrated with 100 mL of 5.0, 10.0, 50.0, 100.0, and 500 mg/L of Pb^{2+} ion solutions prepared in deionized water. The suspensions were shaken continuously on a mechanical shaker for 10 min and allowed to stand for 30 min followed by filtration through No. 42 Whatman filter paper. The filtrates were analyzed for pH, Ca^{2+}, and Pb^{2+} ions and the residues, after drying, were examined through x-ray powder diffraction.

RESULTS AND DISCUSSION

Effects of particle size of francolite, initial lead concentration, and amount of substrate (francolite) on sorption of Pb^{2+} ions were studied separately for evaluating the importance of influencing parameters. Experimental works were further carried out with different amounts of rock phosphate samples. They were equilibrated with aqueous solutions of different size fractions and lead concentrations.

Effects of Particle Size of Francolite Samples on Pb Separation

Francolite samples of particle sizes ranging from as coarse as −420 +200 micron to as fine as −53 micron were equilibrated with 100 mL solutions of 100 mg/L at 25°C. The results of % lead-ion separation versus size fraction of sample are given in Fig. 1. It is observed that with a decrease in the particle size down to −150 +105 micron, the % lead separation increases. However, with a further decrease in the particle size down to −53 micron, the % separation of lead ions becomes independent of the particle size of the francolite sample. The main function of apatites (phosphate rock), for separation of any cation, is to supply P (in the form of $H_2PO_4^-$ after dissolution) to precipitate Pb^{2+} in aqueous solutions (1) on sorbent (apatites) surfaces. Hence the initial increase in % lead separation with decrease in particle size may be ascribed to a better liberation of phosphate from rock phosphate in the fine size ranges, but after certain fineness (−150 +105 micron) the availability of P remains constant; thus % lead separation also becomes constant.

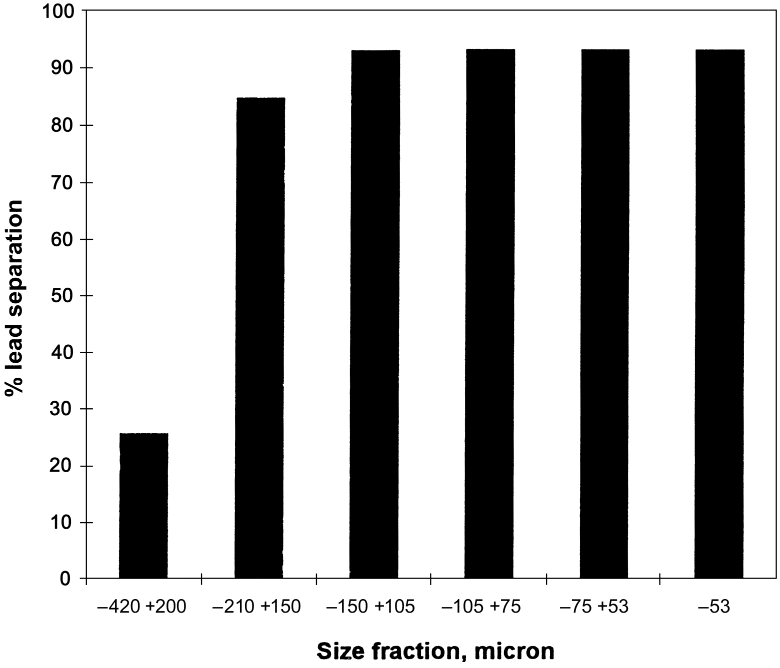

FIG. 1 Plot of size fraction of francolite vs % lead separation (initial Pb concentration 100 mg/L).

Effect of Quantity of Substrate on Separation of Pb^{2+} Ions

To study the effect of quantity of substrate material on % lead separation, 0.05 to 1.5 g of francolite samples were equilibrated with solutions containing 100 mL of 5, 10, 50, and 100 mg/L Pb^{2+} ions. The results are shown in Fig. 2. In solutions containing lower concentrations of Pb^{2+} ions (viz., 5, 10, and 50 mg/L), a sharp rise in % separation is observed as the quantity of francolite is increased gradually from 0.01 g, and at higher quantities of sorbent ($\geq$0.5 g), the % separation becomes constant. However, in the case of 100 mg/L lead ions in solution, the % lead separation increases slowly and reaches

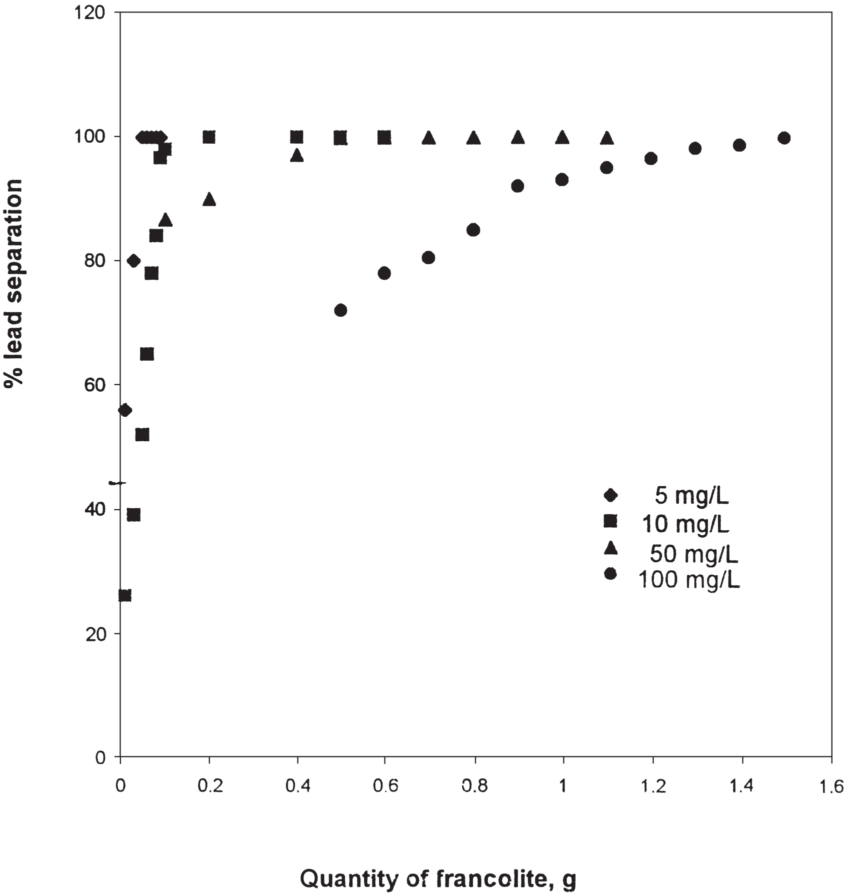

FIG. 2 Plot of quantity of francolite vs percentage of lead separation.

99% only when 1.5 g substrate is used. This fact is brought out more clearly from the plot of % lead separation versus minimum quantity of francolite sample required to bring down the concentration of lead ions in solution to within the permissible limit (cf. Fig. 3) from test solutions containing 5, 10, 50, and 100 mg/L Pb^{2+}. It is observed that with increasing Pb^{2+} concentration in solution, the quantity of francolite samples required also increases.

Effect of Initial Pb^{2+} Concentration on Pb Separation Process

The effect of variation of Pb^{2+} ion concentration in solution from 5.0 to 500.0 mg/L on % lead separation and loading capacity, using 0.5 g francolite sample of −150 +105 micron fraction size as substrate material is shown in Table 2. The % lead separation is observed to be better than 99% from solutions containing up to 50 mg/L lead ions. However, with a further increase in

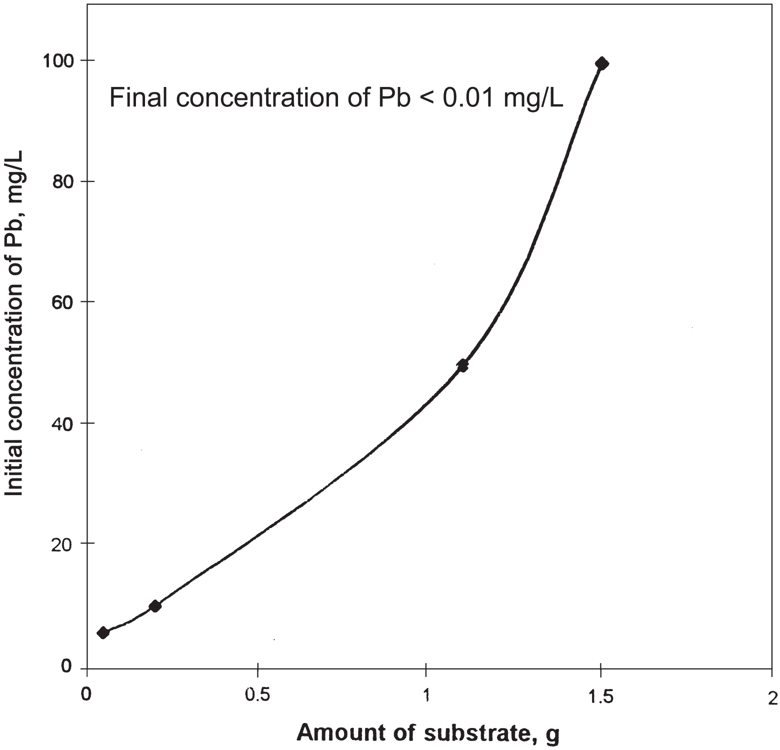

FIG. 3 Plot of minimium amount of substrate (francolite) required to bring the concentration of lead ions to within permissible limits.

TABLE 2
Effect of Initial Concentration on Separation of Pb^{2+}

Pb^{2+} concentration, mg/L		Effectiveness, mg/g	% Separation of Pb^{2+}
Initial	Final		
5.0	0.003	0.994	99.94
10.0	0.008	1.998	99.92
50.0	0.120	9.976	99.76
100.0	7.000	18.600	93.00
500.0	90.000	82.000	82.00

lead-ion concentration in test solutions beyond 50 mg/L, the % lead separation is found to decrease significantly. It is thus observed that francolite samples were very effective in reducing Pb^{2+} concentration to below 0.05 mg/L (the current EPA action level for lead) when the initial concentrations were up to 10.0 mg/L.

The effectiveness of lead separation (mg/g loading of lead on francolite) is observed to increase with increase in the initial lead-ion concentration in solution indicating increased leaching of Ca^{2+} and in turn, enhanced availability of $[(PO_4)_3(CO_3)_3F\ OH]$ negatively charged species to react with lead ions to form fluoropyromorphite. The increased leaching of calcium ions is attributed to a decrease in the pH of solutions with increasing lead-ion concentrations in solutions (cf. Table 2).

Mechanism of Lead Separation by Francolite:

It is difficult to ascertain the exact reaction mechanisms responsible for the retention of lead ion by francolite or hydroxyapatite. But the sorption process, which generally involves species attachement from a solution to its coexisting solid surface by three types, namely *surface adsorption, absorption* or diffusion into the solid, and *precipitation* or coprecepitation, appears to be the governing mechanism for retention of lead by rock phosphate (16, 17). It has been shown (14) that the primary mechanism of lead separation by fluorapatite is governed by its *dissolution,* Eq. (1) in acidic environments followed by subsequent *precipitation,* Eq. 2, of a fluoropyromorphite $[Pb_{10}(PO_4)_6F_2]$-like mineral. This proposed hypothesis of a dissolution–precipitation process for lead separation may be reduced to a generalized sorption process.

$$Ca_{10}(PO_4)_6F_2 + 12H^+ \xrightarrow[\text{dissolution}]{} 10Ca^{2+} + 6H_2PO_4^- + 2F^- \quad (1)$$

$$10\,Pb^{2+} + 6H_2PO_4^- + 2F^- \xrightarrow[\text{precipitation}]{} Pb_{10}\,(PO_4)_6F_2 + 12H^+ \quad (2)$$

In addition to the above hypothesis, where P in the form of $H_2PO_4^-$ helps in precipitating Pb in aqueous solution, the possibility of exchange of Ca by Pb ions also cannot be ruled out (15). It may be interpreted that the dissolution of apatites also provides Ca (Eqs. 1, 3), which exchanges with aqueous Pb, leading to precipitation of a fluoropyromorphite-like mineral.

For sedimentary phosphorite, the principal phosphate mineral is substituted by carbonate apatite, i.e., francolite. For the present investigation, the rock phosphate is of sedimentary origin, and it has been verified by both x-ray and IR spectroscopy (18, 19) that the francolite is the principal phosphate mineral. In such a case the above stoichiometric Eq. (1) and (2) may be written as Eqs (3) and (4), assuming equal presence of PO_4^{3-} and CO_3^{2-}, F^- and OH^-) as

$$Ca_{10}\,(PO_4)_3\,(CO_3)_3\,F\,OH + 6H^+ \xrightarrow[\text{dissolution}]{} 10Ca^{2+} + 3H_2PO_4^- + 3CO_3^{2-} + F^- + OH^- \quad (3)$$

$$10Pb^{2+} + 3H_2PO_4^- + 3CO_3 + F^- + OH^- \xrightarrow[\text{precipitation}]{} Pb_{10} \times (PO_4)_3\,(CO_3)_3\,F\,OH + 6H^+ \quad (4)$$

It is evident from the above Eqs. (3) and (4) that lead separation chiefly depends on the solubility of the rock phosphate (apatites). The higher the solubility of apatites, the more effective they are in separating Pb^{2+} from solutions, because the main function of apatites in this case is to supply P (in the form of $H_2PO_4^-$) to precipitate Pb^{2+} from aqueous solutions. Solubility of rock phosphate is measured by the release of Ca^{2+} in the solution, which increases with the initial concentration of Pb^{2+} in the solution, along with pH, while the amount of phosphate rock added was kept constant at 0.5 g. Higher pH of filtrate is caused by more dissolution of rock phosphate and the resulting release of more Ca^{2+} into the solution. More dissolution of rock phosphate at a higher initial concentration is caused by the increasingly acidic nature of Pb solution and thus provides more H^+.

Effectiveness of Francolite

The effectiveness or lead-removal capacity (LRC) of francolite has been calculated based on the quantity of lead removed per unit of weight of francolite for different initial Pb^{2+} concentrations and compared with the results of other workers (1). All the results are shown in Table 3. For an initial concentration of 500 mg/L, the effectiveness (0.082) of FA (francolite) is nearly 1.52 times less when compared to the effectiveness (0.125) of HA (hydroxyapatite). The lower Pb removal capacity of FA can be attributed to FA having a lower solubility than HA. Furthermore, the phosphate-bearing minerals, i.e., FA and HA, are of different qualities (grades) in both cases. At the same time, HA has been reported to be about six times more effective (14) in reducing Pb concentrations than phosphate rocks on a unit of solid weight basis.

TABLE 3
Comparison of Effectiveness of Different Phosphate Rocks

Initial Pb conc., mg/L	Final Pb. conc., mg/L	% Pb separation	Effectiveness (g of Pb/g of RP)	Type of rock phosphate	Grade (% P_2O_5)
500*	90.0	82.00	0.082	FA^{rrlb}	12.5
100*	7.0	93.00	0.0186	FA^{rrlb}	12.5
50*	0.12	99.70	0.0099	FA^{rrlb}	12.5
10*	<0.01 <Acceptable limit	99.93	0.0028	FA^{rrlb}	12.5
500**	<Acceptable limit	100.00	0.1250	HA^{Ma}	30.0
10^+	<Acceptable limit	99.50	0.0200	PR^{Ma}	30.0
10^+	<0.01	99.8	0.0100	FA^{rrlb}	12.5

* Refers to 0.5g, ** refers to 0.2 g, and + refers to 0.1 g of substrate.

FA: Francoite; HA: Hydroxyapatite; PR: Phosphate rock; rrlb: rrl, Bhopal, and Ma: Ma et al. (1).

A comparison of the performance of high-grade fluorapatite (30.0% P_2O_5) with that of the low grade used in the present study (12.5% P_2O_5), shows that from a solution containing 10 mg/L lead ions in solution, both % lead separation and effectiveness (LRC) are only marginally lower for a low-grade sample (cf. Table 3). A similar observation has been made by Richert and Binner (16), who reported that the lower the purity of hydroxyapatite, the higher its capacity to remove lead from solutions. Thus the abundantly available low-grade francolite sample can be effectively used for lead separation from solutions in place of more costly, high-grade rock phosphate.

X-ray Diffraction Studies of Francolite Samples Before and After Treatment with Aqueous Lead Solutions

The x-ray diffractograms of francolite samples before and after treatment with Pb^{2+} solutions of different concentrations are shown in Figs. 4A to E. The x-ray diffraction pattern of the untreated francolite sample (cf. Fig. 4A) shows the presence of fluorapatitie as the major mineral phase along with other mineral phases of calcite quartz, magnatite, and dolomite. The treatment of the francolite sample with increasing concentrations of lead ions in solution leads to a gradual decrease in the intensities of peaks corresponding to calcite and fluroapatite (cf. Fig. 4B–E). The treatment also leads to the appearance of peaks corresponding to the formation of fluoropyromorphite, whose intensity increases with increasing lead-ion concentration in solution. The gradual disappearance of calcite peaks can be ascribed to francolite dissolution and of fluorapaptite peaks to the conversion of fluorapatite and calcite to fluoropyromorphite phase.

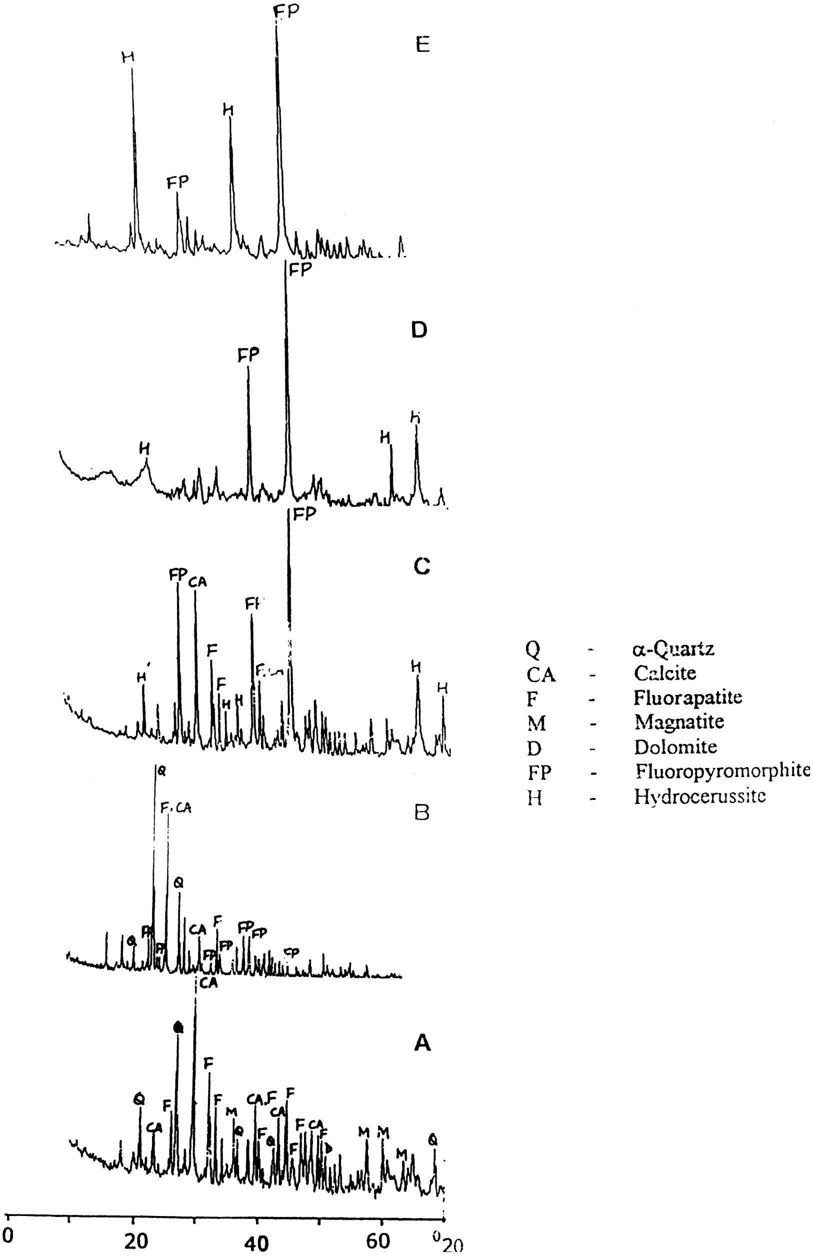

FIG. 4 X-ray diffraction patterns of francolite samples before (A) and after treatment with 100 mL of 10 mg/L (B), 50 mg/L (C), 100mg/L (D), and 500 mg/L (E) lead solution.

TABLE 4
Unit Cell Dimensions of Francolite Samples

	Cell constant	
Types of francolite	a, A°	c, A°
1. Original francolite	9.3378	6.8506
2. Francolite treated with 10 mg/L Pb solution	9.3723	6.8924
3. Francolite treated with 50 mg/L Pb solution	9.3853	6.9006
4. Francolite treated with 100 mg/L Pb solution	9.4125	6.9345
5. Francolite treated with 500 mg/L Pb solution	9.5292	7.0534

It is believed that the increased impurity levels (in the form of substitutions) resulted in increased numbers of lattice defects, which are reported to be ideal adsorption–exchange sites (15, 20). The unit cell dimensions of apatite lattices are expected to change because of the differences in sizes of cations, namely Ca^{+2} and Pb^{+2}. The crystal dimensions of hydroxyapatite before and after treatment with heavy-metal solutions were determined by Suzuki et al. (20) and a change in lattice parameters was observed. In the present investigation, crystal dimensions of untreated and treated rock phosphate samples were also determined. The values of cell constants ("a" and "c") are observed to increase (Table 4) indicating an expansion of the lattice due to incorporation of Pb^{2+} having a larger ionic radius as compared to Ca^{2+}. As the Pb-ion concentration increased, a corresponding increase in the values of cell constants was also noticed.

From the above investigation on Pb separation from aqueous solutions using low-grade rock phosphate, it has emerged that rock phosphate containing carbonate in the apatite lattice as a substitution for phosphate may provide better results in comparison to phosphate rock of higher grade containing no or less carbonate in apatite lattice.

CONCLUSIONS

1. Low-grade (12.5% P_2O_5) carbonate-substituted rock phosphate, i.e., francolite of Jhabua, Madhya Pradesh (India), which presently remains unutilized, can be effectively utilized for the separation of lead from aqueous Pb solutions in the concentration range 5.0 to 500 mg/L.
2. The performance of low-grade (12.5% P_2O_5) francolite samples for both % lead separation and lead-removal capacity is comparable to high-grade fluorapatite

3. Unit cell dimensions exhibited changes, i.e., values of cell constants gradually increased after treating francolite with Pb solutions of various higher concentrations.
4. Dissolution–precipitation and Ca exchange for Pb ions appear as the dominant processes of separation acting together, and both are considered as possible governing mechanisms in the present experiment.

ACKNOWLEDGMENTS

The authors are thankful to Director, R. R. L. Bhopal for his keen interest in the present investigation and to M. P. State Mining Corporation, Bhopal for supplying low-grade rock phosphate samples. Thanks are also due to Shri B. Kujur and Shri J. Konar for their help in chemical analysis.

REFERENCES

1. Q. Y. Ma, S. J Traina, S. J. Logan, and J. A. Ryan, *Environ. Sci. Technol., 29,* 1118, (1995).
2. U. S. Environmental Protection Agency, *Environmental Lead and Public Health,* Washington, DC, 1971.
3. M. C. Fuerstenau, D. A. Elgillani, and D. Miller, *Trans. AIME, 247,* 11, (1970).
4. S. W. Claek, and S. R. B. Cooke, *Ibid., 241,* 334 (1968).
5. R. Sims, D. Sorensen, J. Sims, J. Mc Lean, R. Mahmood, R. Dupont, J. Jurinak, and K. Wagner, *Contaminated surface soils: in place treatment techniques,* Noyes Publications, Park Ridge, NJ 1986.
6. T. A. Wolfe, T. Demirel, and E. R. Bauman, *Clays Clay Miner., 33,* 301–311, (1985).
7. R. C. Zeike and T. J. Pinnavala, *Ibid., 36,* 403–408, (1988).
8. S. A. Boyd, S. Shaobai, J. F. Lee, and M. Mortland, *Ibid., 36,* 125–130, (1988).
9. M. Harper and C. J. Purnell *Environ. Sci. Technol. 24,* 55–62, (1990).
10. C. P. Huang and O. J. Hao, *Environ. Technol. Lett., 10,* 863–874, (1989).
11. L. Daza, S. Mendioroz, and J. A. Pajares, *Clays Clay Miner. 19,* 14–21, (1991).
12. J. M. Zamzow, B. R. Eichbaum, K. R. Sandgren, and D. E. Shanks, *Sep. Sci. Technol., 25,* 1555–1569, (1990).
13. Q. Y. Ma, S. J. Traina, S. J. Logan, and J. A. Ryan, *Environ. Sci. Technol. 28,* 1219, (1994).
14. Q. Y. Ma, S. J. Traina, S. J. Logan, and J. A. Ryan, *Ibid., 28,* 408–418, (1994).
15. J. Reichert and J. G. P. Binner, *J. Mater. Sci., 31,* 1231–1241, (1996).
16. X. Yuping and S. W. Franklin, *Environ. Sci. Technol., 28,* 1472–1480, (1994).
17. C. Xiaobing, V. Judith, J. Wright, L. Conca, and M. P. Loni, *Environ. Sci. Technol., 31,* 624–630, (1997).
18. M. Prasad, A. K. Majumder, G. M. Rao, and T. C. Rao, *Minerals Metall. Proc., 12*(2), May, 92–96, (1995).
19. M. Prasad and T. C. Rao, *Indian Mining Eng. J., 38*(3), March 19–26, (1999).
20. T. Suzuki, T. Ishigaki, K. Hayakawa, and M. Miyake, *J. Chem. Soc., Faraday Trans., 80* 3157, (1984).

Received by editor August 30, 1999
Revision received December 1999