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In Situ and Dump Leaching of Phosphate Rock

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Phosphate deposits with low carbonate content can be leached in situ or in dumps by dilute HCl or HNO₃ to get a solution of monocalcium phosphate (eq 1). The acid concentration is critical: values higher than 10% HCl and 20% HNO₃ cause blocking of the bed because of the formation of insoluble dicalcium phosphate and values lower than these cause the recovery to be low. P₂O₅ values can be recovered from the leach solution by crystallization of the double salt CaXH₂PO₄·H₂O, where X = Cl or NO₃; this can be decomposed at 200–250 °C to form dicalcium phosphate (eq 4 and 5). In this step, about 40% of the acid required for the leaching step can be recovered for recycle; the remainder can be regenerated by reacting the mother liquor with H₂SO₄ (eq 6 and 7). Radium can be separated from solution before the crystallization step so that nonradioactive gypsum can be obtained.

Phosphate rock can be divided into two types: sedimentary and igneous deposits. Each of these in turn can be divided into two types: those containing significant amounts of carbonates and those containing minor amounts of carbonates (Lawver et al., 1978). Deposits of the latter type are widespread, for example, in Central Florida, Tennessee, Western USA, North Africa, and Kola Peninsula. Central Florida is one of the largest phosphate producers in the world; a typical deposit is shown in Figure 1 (anonymous, 1983). The mineralogical analysis of these deposits is approximately 28% calcium phosphate (Ca₃(PO₄)₂, bone phosphate of lime), 36% silica sand (SiO₂), and 34% clay minerals. To get 1 ton of a commercial product, 4.2 tons of overburden must be removed to expose 3.36 tons of ore, which is processed by physical and mechanical means to get the concentrate (1 ton), 1.4 tons of tailings, and 0.95 tons of slime waste (clays) as summarized in Figure 2 (Lawver et al., 1978, 1984). The problems facing this technology are as follows (anonymous, 1975; Balazik, 1983; Scheiner et al., 1982; White et al., 1975; Raulerson and Williams, 1983): (1) enormous material handling (6.55 tons of waste/ton of product) over long distances which is done by pumping the material as water slurry; (2) enormous long time for the slime waste to settle (years) in ponds prepared for this purpose (hence large areas and huge quantities of water are tied in this circuit), and (3) revegetation of the overburden and tailings piles, mandatory for protection of the environment and land reclamation.

A large part of the product obtained is exported and the remainder is treated in Florida with H₂SO₄ to produce H₃PO₄ for making ammonium phosphate fertilizer. Another problem of this processing is the production of large amounts of gypsum-containing radium, the decay product of uranium, originally present in the rock. Each ton of phosphate rock treated by H₂SO₄ produces 1.5 tons of gypsum, which represents an additional disposal and land problem.

The purpose of the present work was to introduce to the phosphate industry a technology widely used in the hydrometallurgy of nonferrous metals, namely, in situ and dump leaching (Habashi, 1969; Schlitt and Hiskey, 1981; Schlitt, 1979, 1985; anonymous, 1981; Hiskey, 1984; Dahl, 1985). Applying in situ leaching technology, also known as solution mining, to extract phosphate values from the deposit without transportation of the rock and to find ways to recover these values from solution as a concentrate suitable for shipping to processing plants or for export is new to the phosphate industry. In situ leaching, however, is used extensively for recovering copper, uranium, potash, and other salts. In one system of this technology, the

leaching agent is injected into the deposit, and the solution containing the solubilized minerals is pumped to the surface through special collecting holes drilled for the purpose of recovering the values and recycling the solution after adjusting its composition. Figure 3 shows a typical in situ leaching operation actually used in the uranium industry. A similar technology is used for extracting sulfur from underground by the Frasch process since the beginning of this century, and extensive testing has been carried out recently for the recovery of coal by underground gasification.

When treating phosphate rock in situ, it will not be possible to use the common and the cheapest acid, H₂SO₄, because gypsum formed during leaching will block its passage. Therefore, the more expensive acids HCl and HNO₃ must be used. These acids, although expensive, have the advantage of solubilizing rapidly not only P₂O₅ content of the rock but also the uranium, the lanthanides, and the radium present; hence, their recovery or disposal (in the case of radium) can be conducted. In case of H₂SO₄ leaching in conventional plants, only uranium can be recovered because the lanthanides and radium are retained in the gypsum (Hignett, 1985). Uranium in the rock is about 0.015% and the lanthanides about 0.5%. Considering the large tonnage of rock treated and the ease with which these metals can be recovered without interfering with the production of the fertilizers, it becomes evident that the rock treated in this way represents an important source for these metals.

Beside the expensive acids HCl and HNO₃, it may also be possible to use sulfuric acid for in situ leaching of phosphate rock. This acid is obtained by dissolving SO₂ in water—a gas that may be a waste product of the nonferrous metal industry.

There are also circumstances when it is desired to leach mined phosphate ore or a phosphate impurity from certain metallic ores, for example, pyrochlore, ilmenite, etc. In this case, the dump leaching technology may be used; i.e., a terrain is prepared on which the crushed ore is piled and the leaching acid is introduced at the top of the pile and collected at the bottom—a system that is also extensively used for gold, copper, and uranium ores (Habashi, 1969).

In the present work, experiments were conducted to explore this possibility and to find methods for recovering the phosphate values as a high-grade concentrate suitable for shipment to the processing plant or for export.

Experimental Section

Materials. Phosphate rock sample was obtained from central Florida analyzing 18.22% P₂O₅, which corresponds to 40% calcium phosphate and 60% insoluble gangue

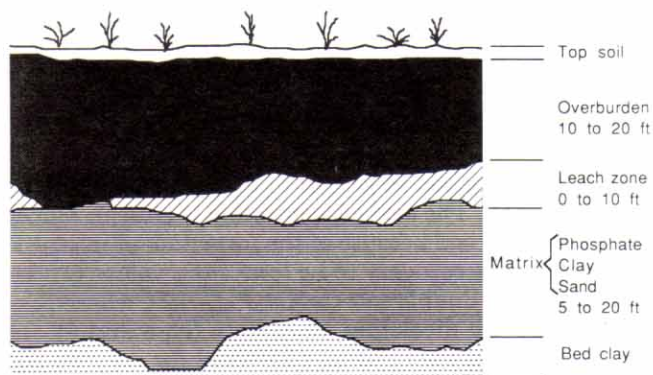


Figure 1. Typical cross section of the central Florida phosphate deposits (anonymous, 1983).

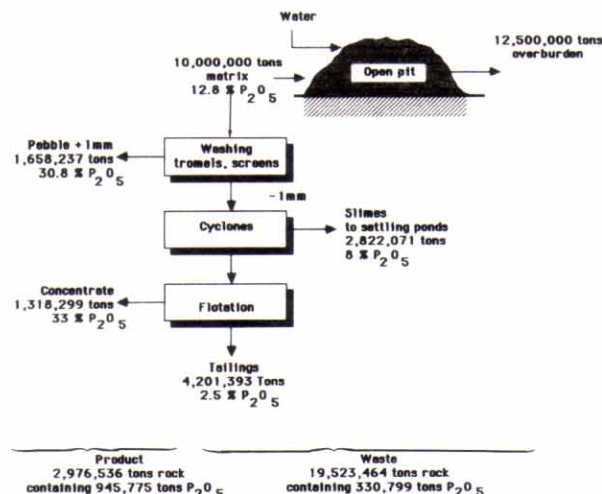


Figure 2. Typical material balance for central Florida phosphate processing (Lawver et al., 1978).

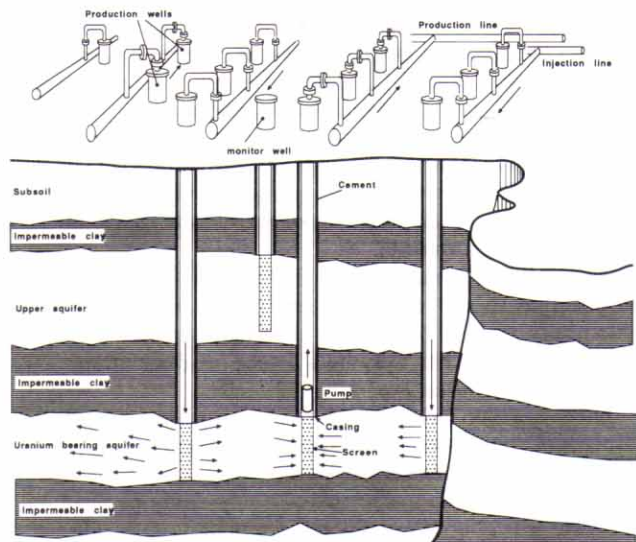


Figure 3. Typical in situ leaching operation for uranium ores.

minerals (clays and silica sand). Since mining the rock is conducted by high-pressure water jets, the sample was wet and represents the actual granulometry of the mined rock. No attempt was done to crush or grind the material; only it was dried at 80 °C overnight to represent the original rock as much as possible. The sample was composed mainly of lumps of about 0.5 cm in size with about 20% fines.

Methods and Equipment. Dried phosphate rock samples were packed in 100-g batches in vertical glass

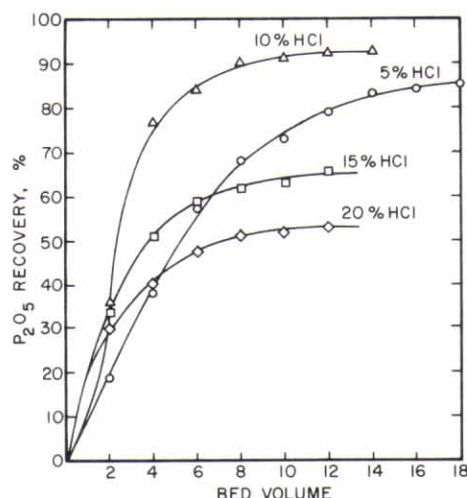


Figure 4. Cumulative recovery of P_2O_5 from phosphate rock in a static bed by HCl.

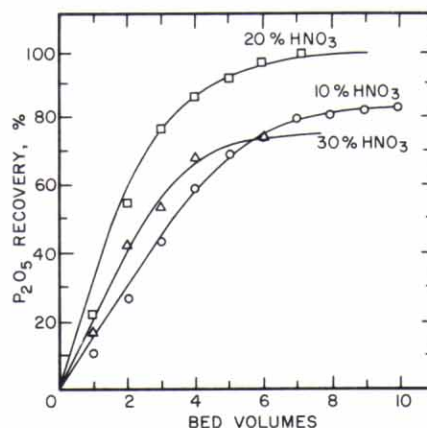


Figure 5. Cumulative recovery of P_2O_5 from phosphate rock in a static bed by HNO_3 .

tubes 3.6 cm diameter and 90 cm long closed with rubber stopper at the bottom, having an opening with a stop cock. The height of the bed was 7 cm, and its volume was 71 cm³. Acid solutions of different concentrations were added portionwise in amounts equal to one or two bed volumes at a time. The solution collected was analyzed for P_2O_5 , and the time needed for an acid bed volume to percolate through the bed was noted.

Acids used were reagent-grade HCl and HNO_3 diluted with distilled water to the desired concentration. Sulfurous acid was prepared by bubbling SO_2 in water; by noting the change in weight and in volume, the acid concentration was calculated. P_2O_5 was determined by titration (Wilson, 1954). Fluoride ion was determined by precipitation as Na_2SiF_6 and weighing; metal ions were determined by atomic absorption. X-ray diffraction analysis was used to identify the products obtained.

Results and Discussion

Leaching with HCl and HNO_3 . While HCl and HNO_3 of different concentrations were allowed to percolate through a static bed of phosphate rock, the following observations were made: (1) There was an optimal acid concentration for which the recovery of P_2O_5 was maximum. In the case of HCl, this maximum was at 10%, and for HNO_3 it was at 20% as shown in Figures 4 and 5, respectively. The existence of this optimal concentration can be explained by the formation of monocalcium phosphate at low acid concentration according to



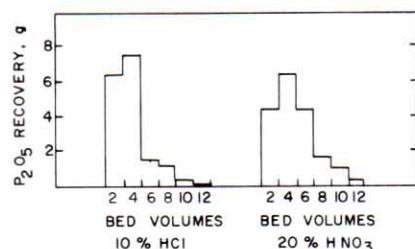


Figure 6. Dissolution of phosphate rock in static bed by 10% HCl and 20% HNO₃.

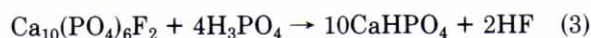
Table I. Analysis of Phosphate Rock Leach Solutions

	10% HCl route	20% HNO ₃ route
P ₂ O ₅ , g/L	57.37	125.7
Ca, g/L	56.5	133.5
Mg, g/L	0.57	0.92
Fe, g/L	0.71	1.47
Al, g/L	2.88	7.21
F, g/L	1.32	0.61
P ₂ O ₅ /Ca	1.02	0.94

and phosphoric acid at high acid concentration according to



Phosphoric acid formed at the top of the bed reacts further with apatite on its descent in the bed to form dicalcium phosphate which is insoluble in water and therefore is retained in the bed:



(2) When monocalcium phosphate is the principal product in solution, the first portions of the acid dissolve the great part of P₂O₅ in the rock and this takes a relatively long time, 8–12 h. After that, leaching is quite rapid (2–5 h) as shown in Figure 6, because the bed becomes porous. On the other hand, at high acid concentrations when the conditions are favorable for the formation of dicalcium phosphate as mentioned above, the bed becomes blocked and the percolation of the solution takes a few days.

(3) When conditions are favorable for the formation of monocalcium phosphate, recoveries of P₂O₅ were more than 90%. Recovery is reduced to 50% if dicalcium phosphate forms, since a large portion of the phosphate value is retained in the bed.

(4) A typical analysis of leach solutions of 10% HCl and 20% HNO₃ is shown in Table I, from which the remarkable low concentration of fluorine in solution can be noted (wet process phosphoric acid contains 10–20 g/L of F). This seems to be due to the nature of the leaching process (no agitation, ambient temperature, and percolating solution) which favors the formation of insoluble fluorine compounds, e.g., CaF₂, which are retained in the bed.

(5) Table II shows also that the HNO₃ leach solution is more concentrated than the HCl solution, which is expected because of the increased lixiviant concentration. However, the ratio P₂O₅/Ca is practically the same in both cases (1.02 and 0.94).

Effect of Recycle. Since the acid concentration played a decisive role in leaching, all tests were conducted with 10% HCl and 20% HNO₃ where the formation of monocalcium phosphate was favorable and percolation of the acid through the bed was smooth and relatively rapid. However, at these concentrations, the amount of acid present was about 3 times the stoichiometric amount with respect to the apatite present in the bed. The leach solutions can, therefore, be recycled until all the free acid is consumed. This was confirmed experimentally as shown

Table II. Leaching 100-g Portions of Phosphate Rock in Static Beds with 10% HCl: Effect of Recycling the Leach Solution

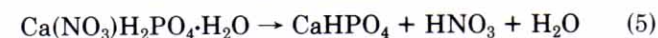
	bed, g	soln, mL		P ₂ O ₅ recovered	
		in	out	wt, g	%
original bed	100	994	860	16.64	91.1
first recycle	100	860	670	13.56	74.4
second recycle	100	670	605	11.95	65.6
third recycle	100	605	552	0.08	0.4

in Table II: the solution obtained by leaching 100 g of rock by 10% HCl could be recycled twice to leach two fresh batches of rock, each 100 g. Recoveries were 74.4% and 65.5%, respectively. If the solution is used to leach a third batch, no rock can be dissolved (0.4% recovery) because no free acid is available. If the third recycle is neglected, then the cumulative leach solution will contain 42.15 g of P₂O₅ in 605 mL, i.e., 69.7 g/L at an overall recovery of 77.1%. In these tests, the beds were not washed with water to displace the entrained solution. Should this be done, recovery should increase but, of course, the concentration of P₂O₅ in the solution will decrease. However, washing is essential to recover both P₂O₅ and the Cl⁻ or NO₃⁻ values.

It can be concluded that leaching of phosphate rock in static beds is effective provided that conditions are favorable for the formation of monocalcium phosphate in solution and the beds are washed with a minimum amount of water to minimize losses. All leach solutions studied for phosphate values recovery were recycled solutions containing mainly monocalcium phosphate and about 70 g/L of P₂O₅ in the case of HCl and 79 g/L of P₂O₅ in the case of HNO₃.

Treatment of Leach Solution. Since P₂O₅ values in the leach solution are mainly in the form of monocalcium phosphate, crystallization was considered as a suitable route for recovery because of the great difference in solubilities of monocalcium phosphate and both CaCl₂ and Ca(NO₃)₂; the solubility of monocalcium phosphate is 3 g/100 g of H₂O at 30 °C, while that of CaCl₂ is 93 g/100 g of H₂O and that of Ca(NO₃)₂ is 121 g/100 g of H₂O. From an engineering point of view, this can be done by solar evaporation in ponds. However, on evaporating the leach solutions, it was not monocalcium phosphate that crystallized out but a double salt. Thus, from HCl leach solution, the double salt calcium chloride phosphate, CaCl₂·Ca(H₂PO₄)₂·2H₂O (or CaClH₂PO₄·H₂O), as identified by X-ray diffraction (ASTM Card 1-704) was obtained (Erlenmeyer, 1857; Fox and Clark, 1938, 1943; *Gmelin's Handbuch der Anorganischen Chemie*, 1961; Taperova and Shul'gina, 1946; Vol'fkovich and Loginova, 1944; Walter-Levy et al., 1955). From HNO₃ leach solution, the double salt Ca(NO₃)₂·Ca(H₂PO₄)₂·2H₂O (or CaNO₃H₂PO₄·H₂O) known as nitrate phosphate (ASTM Card 21-144) was obtained (Frazier and Lehr, 1968). The double salts are soluble in water but are always contaminated by a small fraction (about 10%) of insoluble dicalcium phosphate, CaHPO₄ and CaHPO₄·2H₂O. After the crystals were separated, the mother solution contained mainly CaCl₂ or Ca(NO₃)₂ depending on the acid used.

Decomposition of the Double Salts. The double salts were found to decompose at low temperature (200–250 °C) to form dicalcium phosphate and acid vapors as follows:



In this operation, the acid vapors can be condensed or washed with water for recovery, while the residue which is typically analyzed as 40% P₂O₅ can be marketed as a high-grade phosphate product. A typical analysis of

Table III. Analysis of Dicalcium Phosphate Product

	10% HCl route	20% HNO ₃ route
P ₂ O ₅ , %	38.8	42.9
Ca, %	35.0	35.1
Mg, %	0.22	0.51
Fe, %	0.30	0.71
Al, %	1.25	3.26
P ₂ O ₅ /Ca	1.14	1.22

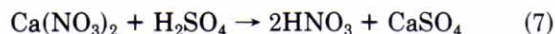
Table IV. Comparison between HCl and HNO₃ Routes

	HCl route		HNO ₃ route	
	leach soln	product	leach soln	product
P ₂ O ₅ /Mg	100.6	176.4	136.6	81.1
P ₂ O ₅ /Fe	80.8	129.3	85.5	60.4
P ₂ O ₅ /Al	19.9	31.0	17.4	13.2

products from HCl and HNO₃ routes is shown in Table III from which it can be seen that the product from the HNO₃ route is richer in P₂O₅ but at the same time contains more impurities than the HCl route.

In Table IV, the impurities in the two routes are again compared. It can be seen that, in the HCl route, the ratios P₂O₅/Mg, P₂O₅/Fe, and P₂O₅/Al always increased when the leach solution is compared with the dicalcium phosphate product. The increase is nearly the same in all cases. On the other hand, in HNO₃ these ratios decreased and the decrease is also nearly the same. This suggests that, in the HCl route, a larger part of the impurities Mg, Fe, and Al will leave the circuit with the product, while this will not take place in the HNO₃ route. To keep the level of impurities in the recycle solution at a tolerable level, a bleed solution may be necessary in the HNO₃ route.

Regeneration of Acid. It was shown above that a part of the acids is recovered during the decomposition of the double salts. Another part can be recovered by adding H₂SO₄ to the mother liquor at ambient conditions and filtering off the gypsum formed:

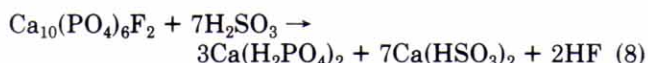


The solutions are relatively dilute (and they should be kept for optimal leaching conditions), and therefore it is not expected that acid vapors or nitric gases that complicate recovery would form. There was also no filtration problems with gypsum when this was attempted.

To get a radioactivity-free gypsum, radium must be separated in an earlier step. This can be readily achieved by adding SO₄²⁻ ion followed by a calculated amount of BaCl₂ solution and filtering off the precipitate formed (Awadalla and Habashi, 1985; Habashi et al., 1987).

Leaching with H₂SO₃. Little work has been done on the leaching of phosphate rock with H₂SO₃ (Hughes and Cameron, 1931). The present work showed that leaching of phosphate rock with sulfurous acid was not successful for the following reasons:

(1) Recovery was always low, and when the solution was recycled to the same bed, only a slight increase in recovery was observed. For example, on leaching with 10.6% H₂SO₃ solution, the recovery of P₂O₅ was 30%, which increased to 31% after recycle. The leaching process can be represented by



(2) On evaporating the leach solution, a mixture of tricalcium phosphate and calcium sulfite formed instead of a double salt, as identified by X-ray diffraction analysis.

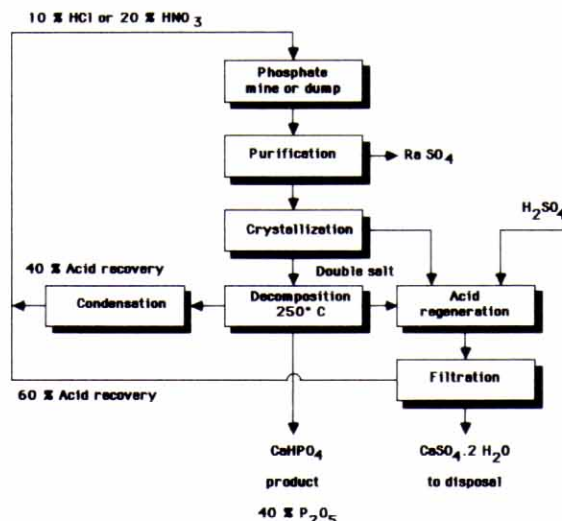
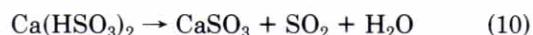
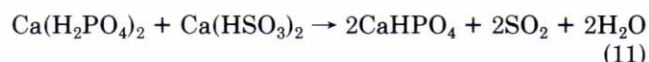


Figure 7. Proposed process for in situ or dump leaching of phosphate rock.

This can be explained by the fact that the products of the above reaction decompose according to



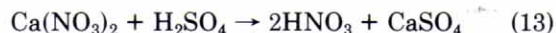
and not according to the desired reaction



As a result, this route is not recommended because it will not be possible to separate Ca₃(PO₄)₂ and CaSO₃ since both are insoluble in water.

Conclusions

Based on this study, the following process is proposed (Figure 7). Phosphate rock is leached with 10% HCl or 20% HNO₃ in situ to get a solution of monocalcium phosphate. The solution is then crystallized to get the double salts CaClH₂PO₄·H₂O or Ca(NO₃)H₂PO₄·H₂O depending on the acid used. The crystals are then separated and decomposed at 200–250 °C to get dicalcium phosphate product. In this operation, about 40% of the acid required for the leaching step is recovered for recycle. The remaining 60% can be regenerated by reaction of the mother liquor with H₂SO₄:



To get a radioactivity-free gypsum, radium must be separated in an earlier step. This can be readily achieved by adding SO₄²⁻ ion followed by a calculated amount of BaCl₂ solution and filtering off the precipitate formed.

In this process, the cost of removing the overburden, mining, beneficiation, disposal of tailings, and slimes is eliminated. On the other hand, the technology of in situ leaching must be mastered. Since this technology can be readily transferred from the metal industry, it is believed that the overall economics will be favorable.

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Registry No. HCl, 7647-01-0; HNO₃, 7697-37-2; CaCl₂, 108373-68-8; Ca(NO₃)₂·Ca(H₂PO₄)₂, 97102-02-8; CaH₃PO₄, 7757-93-9.

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