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The Hydrochloric Acid Route for Phosphate Rock

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ABSTRACT

When phosphate rock is leached with hydrochloric acid, radium can be removed by co-precipitation with $Ba_{0.4}Ca_{0.6}SO_4$ and uranium by extraction with a 5% solution of tributyl phosphate in hexane or Varsol. Phosphoric acid is then separated from calcium chloride solution and other impurities by extraction with undiluted tributyl phosphate. The lanthanides can be precipitated from the raffinate by NH_3 , and $CaSO_4 \cdot 2H_2O$ by H_2SO_4 to regenerate HCl for recycle. The organic phase containing H_3PO_4 can be stripped by NH_3 to yield ammonium phosphate and to regenerate the tributyl phosphate for recycle. Fluorine can be precipitated from the initial leach solution as Na_2SiF_6 .

Key words: Phosphate rock, hydrochloric acid, uranium, lanthanides, radium, fluorine.

1 INTRODUCTION

The present technology of phosphate rock treatment suffers from the fact that a large tonnage of impure radioactive gypsum is produced.^{1–5} For each ton phosphate rock treated about 1.5 tons of gypsum are produced containing about 40 pCi g⁻¹.⁶ Since the phosphate rock treated worldwide by this process is about 150 million tons annually, the amount of phosphogypsum produced is enormous. The problem with this gypsum is that it emits the radioactive gas radon which has a short half life and which disintegrates to a radioactive solid, hence its danger to the respiratory system for those who come in contact. Utilization of phosphogypsum is therefore restricted and its disposal raises problems. Removal of radium from

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phosphogypsum is difficult and prohibitively expensive. In addition, in the present technology all the lanthanides present in the rock, which may be as high as 1%, are lost in the gypsum.⁷ These problems can only be solved by modifying the present technology such that sulfuric acid is not used for attacking the phosphate rock.

The use of nitric acid for treating phosphate rock has been studied and found to be an acceptable route that can yield a high grade fertilizer with the minimum of pollution.⁸⁻¹⁰ The use of hydrochloric acid, on the other hand, did not receive the attention it deserved.¹¹⁻¹⁵ Like nitric acid, hydrochloric acid will solubilize all the phosphate rock except the siliceous gangue minerals. It would be, therefore, possible to precipitate the radium by conventional methods and dispose of it in a controlled way before processing the solution further to separate calcium and produce ammonium phosphate fertilizer. Should calcium be precipitated by sulfuric acid, then the gypsum produced will be free from radioactivity and at the same time hydrochloric acid will be regenerated for recycle.

A property unique to hydrochloric acid is that if leaching is conducted in a reducing atmosphere then nearly all the uranium present in the rock will remain in the insoluble residue (which is usually about 10% of the weight of the rock), thus, there will be a ten fold enrichment of uranium in a single step. The purpose of the present work was to examine this modified technology, and follow the behavior of fluorine and the lanthanides as well.

2 EXPERIMENTAL

2.1 Materials

1. Phosphate rock from Florida analyzed as shown in Table 1 and ground to -200 mesh was obtained from a fertilizer producer in New Brunswick.
2. Two types of iron powder were used: Baker Analyzed Reagent 98.9% Fe. and Atomet 99.5% Fe.
3. Tributyl phosphate, $(C_4H_9O)_3PO$, b.p. 180-183°C (Aldrich) was used for extractive studies either alone or diluted with hexane or Varsol (Gulf. Canada).
4. Reagent grade hydrochloric acid, oxalic acid, sodium chloride, barium chloride, and sodium sulfate.

TABLE 1
Analysis of Florida phosphate (dry basis)^a

	%		%
P ₂ O ₅ (total)	31.22	K ₂ O	0.15
CaO	47.26	MgO	0.58
SiO ₂	7.91	MnO	0.027
F	3.94	Al ₂ O ₃	1.10
CO ₂	3.52	Fe ₂ O ₃	1.18
Na ₂ O	0.65	Organic matter	0.24
Ln ₂ O ₃	0.5	U	0.012

^a Moisture 1.9%.

2.2 Procedure

The stoichiometric amount of hydrochloric acid calculated according to the analysis of the rock was a 2.5 ml of 28% HCl per gram of rock. Tests were conducted using the stoichiometric and 20% excess. Two leaching tests were conducted; one in ambient air and the other under reducing conditions. A weighed amount of phosphate rock was added portion wise to a known volume of acid while stirring. The temperature rises until 40°C because of the exothermic nature of the reaction and foaming takes place due to the decomposition of carbonates. When the total amount was added, agitation was continued until no more gases evolved. A batch of 1 kg rock usually took about 60 min for dissolution. When dissolution was conducted under reducing atmosphere, the same procedure was used except a certain amount of iron powder was mixed with the powdered rock before leaching. The slurry was then filtered to remove the insoluble gangue minerals which were then examined by an optical microscope and by X-ray diffraction. The clear solution was then analyzed for uranium, iron, calcium, magnesium, manganese, aluminium, lanthanides, chloride ion, and P_2O_5 .

Tributyl phosphate was used to study the transfer of uranium and other ions in the organic phase. Extraction and stripping experiments were conducted by agitating the organic and aqueous phases in open vessels with magnetic stirrers for 10 min; then transferring to a separating funnel to effect the separation of phases. Extraction was always conducted in three stages at organic:aqueous ratio 1:1 unless otherwise stated.

2.3 Analysis and equipment

1. Uranium was determined spectrophotometrically using arsenazo 1;²⁶ nitric acid was added before extraction with tributyl phosphate to form the uranium nitrato complex. When iron was added during leaching, the analytical determination was slightly modified to remove the excess iron in the strip solution. This necessitated an additional extraction stage.
2. Lanthanides were determined after oxalate precipitation by titration with ethylene diamine tetraacetic acid (di-sodium salt), EDTA, using arsenazo 1 as indicator.²⁷
3. Radium was determined by the emanation method using RD/RDU-200 Radon detector for alpha counting of solutions.²⁶
4. Atomic absorption spectroscopy was used for determination of calcium, magnesium, iron, manganese, and aluminium while P_2O_5 was analyzed gravimetrically.
5. Chlorides were determined gravimetrically by precipitation with silver nitrate.
6. X-ray diffraction analysis and scanning electron microscope were used for examination of precipitates.

3 RESULTS AND DISCUSSION

In all leaching tests the insoluble residue was about 10% of the weight of the rock

and was mainly quartz. However, the behavior of uranium was different; in tests conducted in ambient air all the uranium was found in solution while in tests conducted under reducing atmosphere the uranium was mainly in the residue, in agreement with previous workers. The effect of iron powder to regenerate the reducing atmosphere on the dissolution of uranium is shown in Fig. 1. It can be seen that about 0.8 g iron powder per 100 g rock was enough to keep about 85% of the uranium in the residue. However, all attempts to recover uranium from this residue were unsuccessful. Therefore, this route was abandoned until the behavior of uranium in the residue is clarified.† All leaching tests were, therefore, conducted in ambient air.

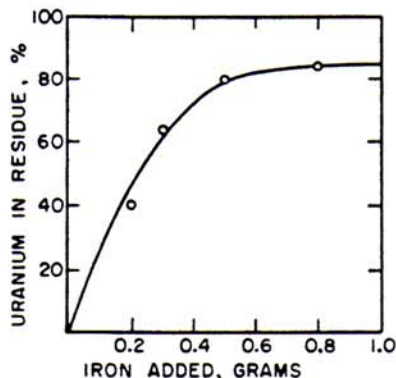


Fig. 1. Behavior of uranium during the leaching of 100 g phosphate rock in presence of iron powder.

3.1 Removal of radium

Removal of radium was achieved by adding to the leach solution a saturated solution of BaCl_2 followed by a solution Na_2SO_4 to precipitate BaSO_4 which acted as a carrier for radium. Figure 2 shows the effect of adding BaCl_2 to a leach solution obtained from 100 g rock to which 0.1 g Na_2SO_4 was added. It can be seen that a small amount of BaCl_2 was enough to precipitate most of the radium. In a

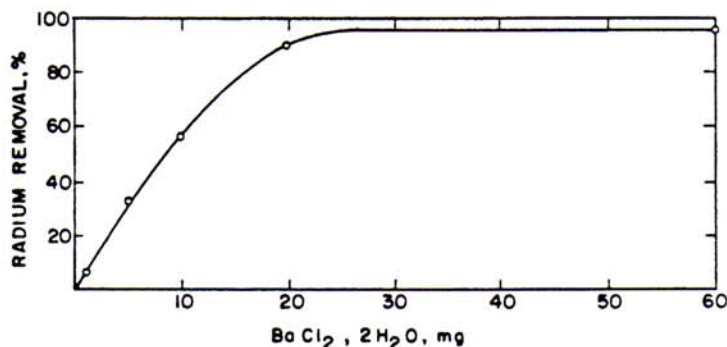


Fig. 2. Removal of radium by co-precipitation with BaSO_4 . Solution derived from 100 g phosphate rock. 0.1 g Na_2SO_4 added and variable amounts of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.

† This will be the subject of a future report.

typical experiment 0.02 g $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and 0.1 of Na_2SO_4 were added to 312 ml leach solution (100 g phosphate rock) and the precipitate obtained was 0.1 g and contained all the radium. X-ray diffraction analysis indicated that the precipitate was $\text{Ba}_{0.4}\text{Ca}_{0.6}\text{SO}_4$ (ASTM card No. 24-93).

The behavior of radium in this case is different from leaching phosphate rock in nitric acid medium reported earlier where appreciable amounts of Ba^{2+} and SO_4^{2-} ions were needed and the precipitate obtained was also larger.⁸ It seems that in nitric acid medium the crystallization of barium nitrate, which is not an efficient carrier for radium, was inevitable and this demanded the addition of a large amount of Ba^{2+} ion for an effective removal of radium. Any $\text{Ba}(\text{NO}_3)_2$ that co-precipitated with the sulfate was removed during washing and therefore could not be detected in the X-ray diffraction pattern of the precipitate.

3.2 Extraction of uranium from solution

It was found that uranium could be completely extracted from leach solution by tributyl phosphate. However, it was also found that all the phosphoric acid and iron, an appreciable amount of chloride and calcium ions, and small amounts of manganese, aluminium, and magnesium were also co-extracted; the lanthanides, on the other hand, all remained in the aqueous phase as shown in Table 2. Figure 3 shows the extraction of uranium and phosphoric acid by tributyl phosphate at various organic:aqueous phase ratios, while Figs 4 and 5 show the distribution isotherms for the same systems.

Extraction could be made more selective towards uranium if the concentration of tributyl phosphate is reduced to about 5% in the organic phase as shown in Fig. 6; phosphoric acid co-extracted was negligible.

3.3 Separation of calcium

It was not possible to crystallize calcium chloride from solution in analogy with the

TABLE 2
Extraction of Defluorinated Leach Solution with Tributyl Phosphate. Three Stage Extraction at Organic: Aqueous Ratio 1:1

	<i>Feed solutions^a</i> (volume=162 ml) concentration (g liter ⁻¹)	<i>Raffinate</i> (volume=105 ml)		<i>Organic phase^b</i> (volume=542 ml)	
		Concentration (g liter ⁻¹)	Distribution (%)	Weight (g)	Distribution (%)
P_2O_5	94.77	1.5	1.0	15.15	99
Ca	97.2	127.33	83.72	2.6	16.28
Cl^-	275.1	263.62	62.51	16.71	37.49
U	0.038	0	0	0.006	100.0
Ln_2O_3	1.63	2.51	100	0	0
Fe	2.6	0.16	4.1	0.4	95.9
Al	1.85	2.7	96.5	0.01	3.5
Mn	0.06	0.06	68.1	0.003	31.9
Mg	1.0	1.42	93.5	0.01	6.5

^a Obtained by leaching 50 g rock.

^b Obtained by difference.

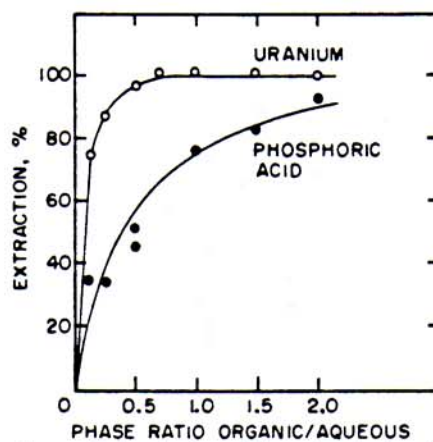


Fig. 3. Extraction of uranium and phosphoric acid by tributyl phosphate (100%), one stage at different organic aqueous ratio.

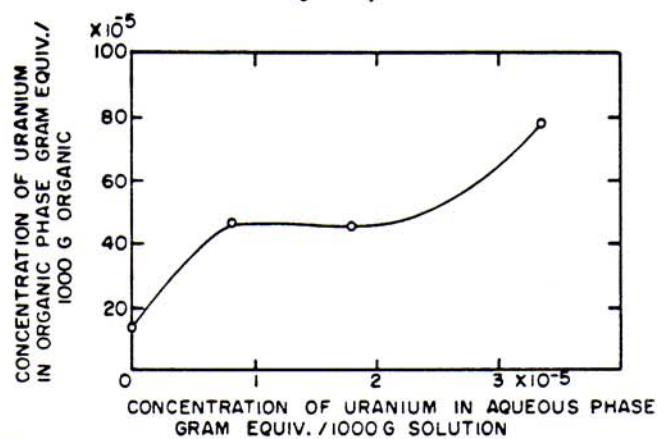


Fig. 4. Distribution isotherm of uranium between HCl solution and tributyl phosphate.

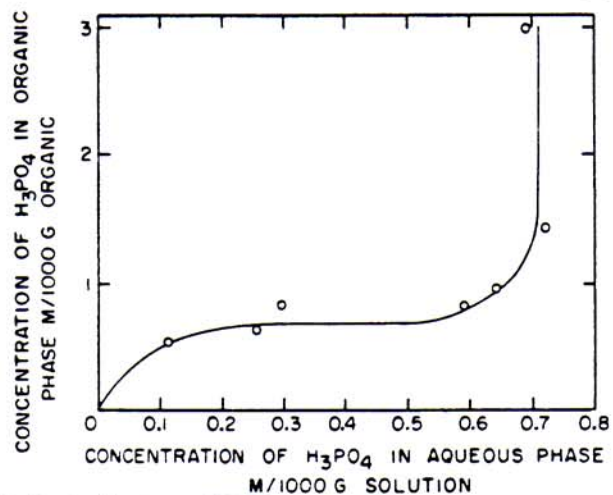


Fig. 5. Distribution isotherm of H₃PO₄ between HCl solution and tributyl phosphate.

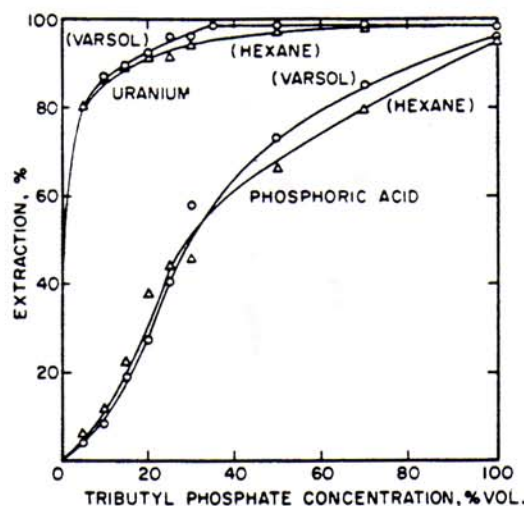


Fig. 6. Extraction of phosphoric acid and uranium by tributyl phosphate in hexane and Varsol. three stage at organic:aqueous ratio 1:1.

nitric acid route where $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was deposited on cooling. Therefore, tributyl phosphate was used to separate calcium chloride from phosphoric acid as indicated in Table 2. All calcium chloride co-extracted could be removed selectively from the organic phase by scrubbing with the minimum amount of water, provided that the stoichiometric amount of hydrochloric acid was used for leaching the rock as shown in Fig. 7(A). If excess HCl was used in leaching, then appreciable amounts of HCl would be retained in the organic phase as shown in Fig. 7(B).

3.4 Recovery of the lanthanides

As indicated earlier the lanthanides were not extracted from the leach solution by tributyl phosphate. Under such conditions it was possible to precipitate them by ammonia at pH 2.0. In a typical test, 4.2 g were obtained per 100 g rock, which when dissolved and precipitated as oxalate gave 3 g, and when ignited to oxide

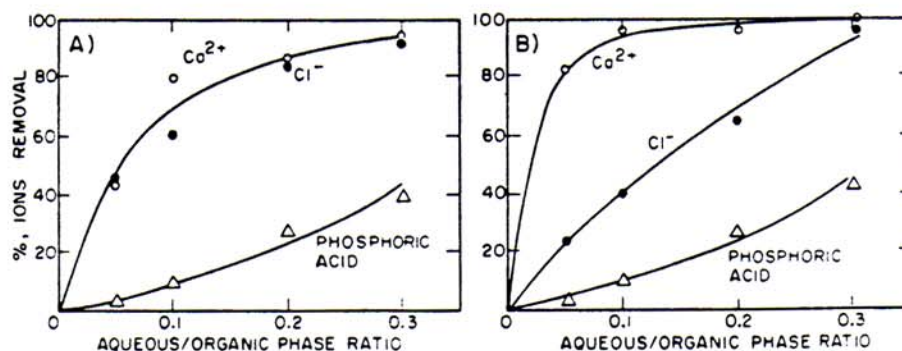


Fig. 7. Scrubbing of loaded tributyl phosphate with cold water in one stage. (A) Leaching phosphate rock with stoichiometric amount of hydrochloric acid. (B) Leaching with 20% excess HCl.

gave 1.11 g, analyzing 30% Ln_2O_3 and 70% CaO . This represents about 60% recovery.

3.5 Defluorination

Phosphate rock contains about 4% fluorine, and during leaching a minor part of it volatilizes as HF and SiF_4 and is usually recovered in industrial installations. However, there is a major amount that remains in solution and not only contaminates the fertilizer produced but also lowers its grade. It was, therefore, thought that removal of this fluorine would be beneficial to the quality of fertilizer and also a way of conserving the natural resource if this could be recovered in a useful form. The addition of NaCl was effective in precipitating sodium fluorosilicate according to: $2\text{NaCl} + \text{SiF}_6^{2-} \rightarrow \text{Na}_2\text{SiF}_6 + 2\text{Cl}^-$. Precipitation of sodium fluorosilicate is best conducted at ambient temperature using twice the stoichiometric amount of NaCl . In a typical experiment 40 g NaCl were added to 1.5 liter leach solution (500 g phosphate rock) while stirring for 30 min. The precipitate collected weighed 32 g which shows that 96% of the fluorine present in the rock remains in solution and can be recovered as Na_2SiF_6 .

3.6 Regeneration of hydrochloric acid

When fluorosilicate ion, radium, uranium, phosphoric acid, and the lanthanides were removed from the leach solution, it was possible to precipitate pure gypsum by adding the stoichiometric amount of sulfuric acid. $\text{CaCl}_2 + \text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{HCl}$, thus regenerating hydrochloric acid for recycle. In a typical test when 50 g rock were treated as above, 60 g white crystalline platelets of gypsum were obtained (Fig. 8).



Fig. 8. Crystals of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ precipitated from calcium chloride solution by H_2SO_4 (800 \times).

3.7 Recovery of phosphoric acid

As indicated earlier, tributyl phosphate was effective in separating phosphoric acid from calcium chloride. Stripping the loaded organic phase with hot water to

recover H_3PO_4 was possible, but the acid obtained was dilute. It was found that adding NH_3 gas directly to the organic phase was effective in precipitating ammonium phosphates. The product obtained when washed with a small amount of hexane and dried was examined by X-ray diffraction; the compounds identified (in decreasing importance) are shown in Table 3.

TABLE 3
Compounds Identified in the Ammonium
Phosphate Product by X-Ray Diffraction
Analysis

<i>Product</i>	<i>ASTM card No.</i>
$\text{NH}_4\text{H}_2\text{PO}_4$	6-0125
$(\text{NH}_4)_2\text{HPO}_4$	29-111
$\text{NH}_4\text{H}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4$	28-62
$\text{Ca}_2\text{Fe}(\text{PO}_4)_2(\text{OH}) \cdot 1\frac{1}{2} \text{H}_2\text{O}$	5-0571

4 PROPOSED PROCESS

Based on the experimental work outlined above, the following process is proposed (Fig. 9):

- 1 Phosphate rock is leached with the stoichiometric amount of HCl at 40°C . When reaction is complete, the mixture is filtered to remove the insoluble residue.
- 2 Sodium chloride is added to the solution to precipitate sodium fluorosilicate which is removed by filtration.
- 3 Barium chloride and sodium sulfate are added consecutively to remove radium by co-precipitation with barium sulfate.
- 4 Uranium is extracted from solution by 5% tributyl phosphate in hexane or Varsol. The organic phase is stripped with ammonia to precipitate uranium and regenerate the tributyl phosphate for recycle.
5. Phosphoric acid is then extracted by tributyl phosphate. The organic phase is scrubbed with a small amount of water to remove any chloride ion co-extracted. The organic phase contains all the phosphate values present in the rock. This can be recovered by precipitation with gaseous NH_3 and filtration to regenerate of tributyl phosphate for recycle.
6. The aqueous phase can be treated by NH_3 to precipitate the lanthanides. After filtration, H_2SO_4 may be added to precipitate pure gypsum and regenerate hydrochloric acid for recycle.

5 CONCLUSIONS

The present technology of phosphate rock treatment can be slightly modified to eliminate the pollution problem due to radioactive gypsum by introducing hydro-

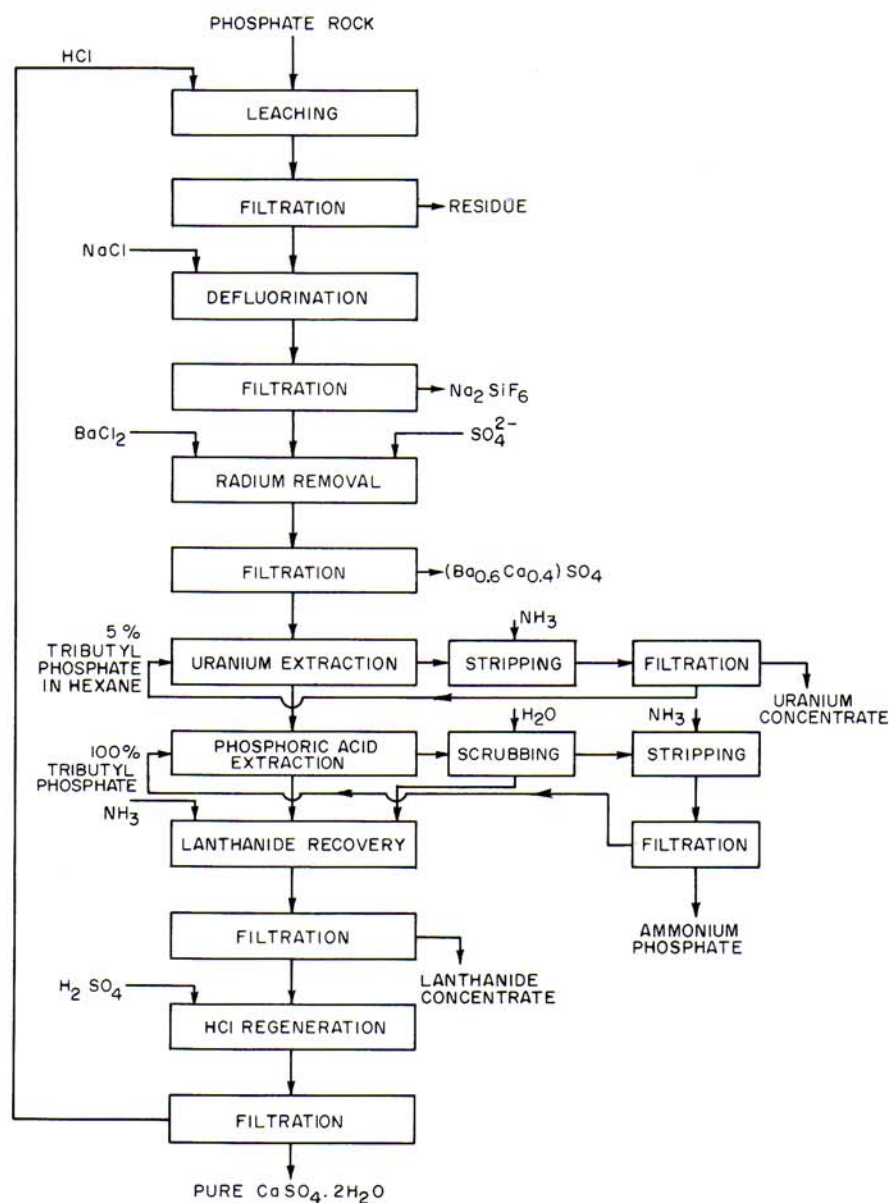


Fig. 9. Proposed flowsheet for the treatment of phosphate rock with hydrochloric acid.

chloric acid in a closed circuit. When the rock is leached with HCl, the insoluble residue will be only the siliceous gangue. Radium in solution can be eliminated by conventional methods. Calcium chloride is then separated from phosphoric acid by extracting the latter with tributyl phosphate. Ammonium phosphate fertilizer can be stripped from the organic phase by ammonia and the tributyl phosphate is recycled. Hydrochloric acid can be regenerated for recycle by adding H₂SO₄ to

precipitate pure non-radioactive gypsum. The process can be further improved by inserting the following steps;

1. Defluorination of the leach solution to recover fluorine as sodium fluorosilicate.
2. Recovery of uranium from the leach solution before the separation of calcium chloride, by extraction with a 5% tributyl phosphate solution in a hydrocarbon diluent such as hexane or Varsol.
3. Recovery of the lanthanides from calcium solution before the precipitation of gypsum, by precipitation with ammonia.

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