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Treatment of phosphate rocks with hydrochloric acid

Habib Shlewit

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Abstract Phosphate rocks were leached with hydrochloric acid; and radium was removed by co-precipitation with BaSO_4 . Uranium and lanthanides were extracted by di(2-ethyl hexyl) phosphoric acid and tributyl phosphate. Phosphoric acid was then separated from calcium chloride solution and other impurities by extraction using undiluted iso-amyl alcohol. Gypsum was precipitated by sulfuric acid to regenerate hydrochloric acid for recycling. Fluorine was precipitated from the initial leach solution as Na_2SiF_6 .

Keywords Phosphate rock · Hydrochloric acid · Lanthanides · Radium and fluorine

Introduction

The present technology of phosphate rock treatment suffers from the production of large amounts of impure radioactive gypsum [1–3]. For each ton phosphate rocks treated, about 1.5 tons of gypsum is produced containing about 1.48 Bq g^{-1} [4]. Since the phosphate rock treated worldwide by this process, enormous amounts of phosphogypsum are produced (about 150 million tons annually). The problem with this gypsum is the emission of the radioactive gas radon. Hence, it is danger to the respiratory system for those who come in contact. In addition, in this technology all the lanthanides present in the rock, which may be as high as 1% are lost in the gypsum [5]. This problem can be overcome only by modifying the present technology such that sulfuric acid is not used for attacking the phosphate rock. Using

nitric acid for treating phosphate has been studied and found to be acceptable route that can yield a high-grade fertilizer with the minimum pollution [6, 7]. The use of hydrochloric acid, did not receive much attention [8–11]. Solutions containing mono-calcium phosphate obtained by leaching phosphate rock using diluted hydrochloric acid were treated for uranium and lanthanides recovery prior to P_2O_5 recovery. The separation of lanthanides with similar chemical properties is a challenging task. It is achieved by using the process of solvent extraction [12].

The purpose of the present work was to examine this modified technology where, hydrochloric acid was used instead of sulfuric acid, remove impurities (fluorine, radium, and uranium) remain in the produced leach solution, and propose a closed cycle process including recovery of lanthanides.

Experimental

Materials

- Syrian phosphate rocks from different deposits (P_x) as shown in Table 1, ground to-220 meshes.
- Tri butyl phosphate (TBP) and iso-amyl alcohol from Merck, and di(2-ethyl hexyl) phosphoric acid (DEHPA) from Sigma were used for extraction.
- Reagent grade hydrochloric acid, oxalic acid, sodium chloride, barium chloride and sodium sulfate from Merck were employed.

Procedure

Hydrochloric acid was used as leach solution. The stoichiometric amount of acid calculated according to the

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Table 1 Characteristics of the Syrian phosphate deposits (P_x) (dry basis)

Element/deposits	P1	P2	P3	P4	P5	P6	P7	P8	P9
SiO ₂ %	9.50	6.23	10.41	9.32	9.44	9.53	8.67	8.21	8.97
Al ₂ O ₃ %	0.31	0.28	0.26	0.25	0.27	0.24	0.23	0.24	0.25
MgO%	0.75	0.66	0.24	0.25	0.26	0.23	0.24	0.23	0.24
CaO%	48.62	42.55	47.45	46.33	47.21	46.63	45.87	45.56	46.32
Fe ₂ O ₃ %	0.21	0.18	0.16	0.15	0.16	0.16	0.15	0.15	0.15
P ₂ O ₅ %	25.36	33.00	28.43	29.45	29.55	28.93	30.21	30.78	30.58
F%	0.002	1.75	3.21	3.02	3.15	3.22	2.98	2.78	3.18
Sr ppm	1458.02	—	—	—	—	—	—	—	—
Ba ppm	268.56	—	—	—	—	—	—	—	—
V ppm	72.50	70.00	125.32	128.12	127.33	127.54	128.21	127.33	125.67
Cr ppm	114.34	—	—	—	—	—	—	—	—
Cu ppm	8.54	—	—	—	—	—	—	—	—
Zn ppm	145.22	140.00	1132.2	129.15	131.54	130.56	131.43	130.15	128.54
Cd ppm	8.33	—	9.21	8.76	9.05	8.95	—	—	—
U ppm	58.76	53.55	110.55	115.45	120.00	113.33	114.54	114.00	114.65
La ppm	23.44	21.44	48.00	52.33	68.00	64.00	55.50	60.45	70.65
Ce ppm	45.33	42.33	47.33	48.00	61.33	61.00	58.00	59.00	62.00
Sm ppm	15.32	13.67	15.70	16.20	19.40	19.20	18.60	19.20	20.50
Nd ppm	27.21	25.64	32.00	35.00	40.50	39.00	37.00	41.00	51.00
Gd ppm	3.26	3.12	—	—	—	—	—	—	—

analysis of the rock was added. Tests were carried out using the stoichiometric plus 20% excess of HCl. Leaching tests were conducted using dry and ground phosphate (P₉) in different concentration of HCl. A weighed amount of phosphate rock was added portion wise to a known volume of HCl while stirring. The temperature rises because of the exothermic nature of the reaction and foaming takes place due to the decomposition of carbonates. The slurry was then filtered to remove the insoluble gangue minerals, which were then examined by XRD. The clear solution was then analyzed for P₂O₅, Ca²⁺, Mg²⁺, Fe³⁺, Al³⁺, lanthanides (Las) and uranium.

Tri-butyl phosphate (TBP) and DEHPA in hexane were used to extract uranium selectively. Diluted DEHPA in toluene was used then to extract Lanthanides. Iso-amyl alcohol used to extract phosphoric acid. Extraction and stripping experiments were conducted by agitating the organic and aqueous phases in open vessels with magnetic stirrers, and phases were separated using laboratory centrifugal equipment.

Analysis and equipment

Uranium was determined in aqueous phase by fluorometric technique and in organic phase was calculated by mass balance.

Total lanthanides concentrations were determined spectrophotometrically using Arsenazo III [13], ICP-MS and NAA.

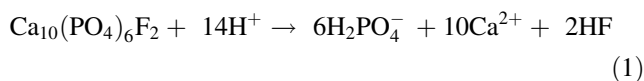
Radium was determined by gamma spectrometry using HPGe detector.

Other elements were determined by atomic absorption spectroscopy, while P₂O₅ was analyzed gravimetrically.

Results and discussion

Effect of the leach acid concentration

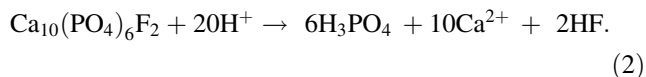
Leaching of the dried phosphate sample with different concentration of HCl was carried out by mixing stoichiometric amount of HCl plus 20% extra. Tests showed that using 10% v/v was the optimal acid concentration for which the recovery of P₂O₅ and the dissolution of the phosphate sample were maximum as shown in Table 2. The existence of this optimal concentration of HCl can be explained by the formation of mono-calcium phosphate at low acid concentration according to:



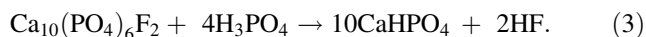
and phosphoric acid will form if high acid concentration is used, according to

Table 2 Percentage of the sample dissolution and the P₂O₅% recovery as a function of HCl concentration

v/v %HCl	3	5	7	9	10	11	13	15	20
Wt% sample dissolution	35	60	72	80.5	86	79.5	69	34	34
Wt% P ₂ O ₅ recovered	35	65	70	79	85	72	55	43	40



Phosphoric acid formed reacts farther with phosphate rock to form di-calcium phosphate, which is insoluble in water:



Experiments carried out, showed that, when mono-calcium phosphate is the principal product in solution (Eq. 1) dissolution takes a relatively long time 2 h. A typical analysis of leach solutions of 10% HCl is shown in Table 3.

It is clear from the above table, that concentration of fluorine is relatively high which, may be attributed to leaching process. A farther advantage of using diluted acid for leaching phosphate rock is the formation of fluorosilicic acid instead of HF, i.e., fluorine present in the rock will not be volatilized during leaching and cause pollution problems but, remain in solution, from which it can be recovered as Na₂SiF₆.

Treatment of leach solution

Since most of the P₂O₅ in the leach solution is mainly in the form of mono calcium phosphate. Analysis showed that more than 85% of uranium, lanthanides, radium and fluorine transferred into the leach solution.

Removal of radium

Removal of radium from the leach solution was achieved by adding a saturated solution of BaCl₂ followed by a

Table 3 Composition of the phosphate rock leach solution 10% HCl

P ₂ O ₅ % (w/v)	27
CaO% (w/v)	25
MgO% (w/v)	0.21
Fe ₂ O ₃ % (w/v)	0.14
Al ₂ O ₃ % (w/v)	0.23
F%	1.9
La (mg/l)	63
Ce (mg/l)	58
Nd (mg/l)	50
Sm (mg/l)	17
U (mg/l)	54

Table 4 Percentage of radium removed as a function of BaCl₂·2H₂O (mg)

Radium removal%	23	42	61	73	86	87
BaCl ₂ ·2H ₂ O (mg)	5	14	20	30	40	60

solution of Na₂SO₄ to precipitate BaSO₄. Table 4 shows effect of BaCl₂ added to a leach solution obtained from 200 g rock phosphate to which 0.25 g Na₂SO₄ was added on the radium recovery percentage. It can be seen that a small amount of BaCl₂ was sufficient to precipitate most of radium. XRD analysis indicated that the precipitate was Ba_{0.4}·Ca_{0.6}·SO₄. Analysis also showed that a negligible amount of lanthanides content have been co-precipitated with the above precipitant.

Uranium extraction

Tests showed that uranium can be co-extracted from the leach solution completely using 100% of TBP in four extraction stages, and phase ratio org/aq = 1/1, but also showed that phosphoric acid and iron were extracted completely, an appreciable amount of Cl⁻, Ca²⁺, Mg, Al and Mn were also co-extracted. Lanthanides on the other hand remain in the aqueous phase as shown in Table 5, where, E% is defined as the ratio of the element concentration in organic to that in aqueous multiplied by 100.

Extraction of uranium carried out by different concentrations of TBP in hexane, in four extraction stages, and phase ratio org/aq = 1/1. Results in Table 6 show that at

Table 5 (E %) of the co-extracted elements by 100% v/v of TBP

Elements	P ₂ O ₅	Ca	Cl	U	Ln ₂ O ₃	Fe	Al	Mn	Mg
E%	99	16.3	38.1	99.5	0	96	3.4	3.2	7

Table 6 (E %) of uranium and H₃PO₄ as a function of TBP v/v% in hexane

v/v% TBP	5	10	20	40	80	100
E% of U	80	86	90	95	95	95
E% of H ₃ PO ₄	2	4	25	52	75	99

Table 7 Lanthanides extraction E % as a function of DEHPA concentrations in toluene

[DEHPA] mole/l	0.05	0.1	0.2	0.3
E %	42	61	85	87

Table 8 Characteristics of H_3PO_4 produced

Element	P_2O_5	Fe	Cr	V	Ca	Cl^-	F^-	U	Zn	As	Cu
Concent.	19.2%	2 mg/l	–	1 mg/l	12 mg/l	–	–	< 1	2 mg/l	–	< 2 mg/l

high TBP concentration, uranium extraction was not selective, but at low TBP concentration it was rather selective for uranium compared with H_3PO_4 extraction.

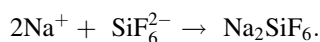
Uranium extracted selectively using synergistic solvents of TBP and DEHPA in hexane. Results showed that using the molar ratio of $\text{DEHPA/TBP} = 4/3$ in hexane will lead to more than 95% of uranium extraction in three extraction stages and phase ratio of 1/1.

Recovery of fluorine

Syrian phosphate rock contains up to 3% fluorine. When using conventional technology, a small fraction of this element is volatilized as HF or SiF_4 gases, which are captured in the gas scrubbing system. When diluted HCl is used, all the fluorine remains in solution as fluorosilicate ion SiF_6^{2-} due to the interaction with silica in the raw material [14]:



This ion is precipitated as sodium fluorosilicate by adding a sodium salt:



The precipitate is a potential source for fluorine used in the aluminum industry.

Lanthanides extraction

The solution remains (raffinate) after uranium extraction contains lanthanides and P_2O_5 . It is possible to precipitate lanthanides by ammonia, and dissolve the precipitant by nitric acid and precipitate again by oxalic acid at certain

conditions. In this process a large amount of Ca according to the lanthanides amount will co-precipitate.

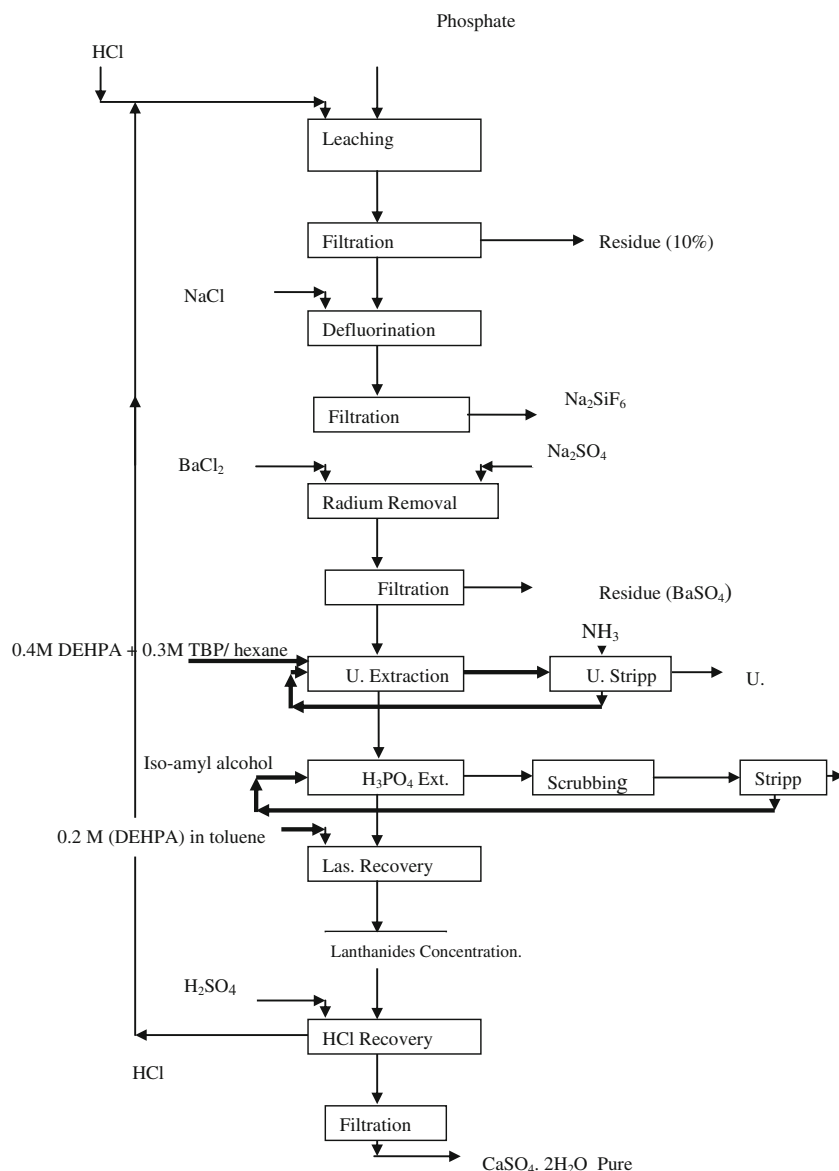
In this work, lanthanides were extracted using a selective solvent DEHPA in toluene. Tests showed that using 0.2 M DEHPA/toluene (as shown in Table 7) applying the following conditions: phase ratio $\text{org/aq} = 1/1$, three extraction stages and at the laboratory temperature, more than 85% of the total lanthanides were extracted.

Phosphoric acid extraction

As indicated earlier, TBP was effective to recover phosphoric acid, and was discussed in details in our previous works [15, 16]. In this present work, undiluted iso-amyl alcohol is used, but phosphoric acid obtained was diluted. More than 80% of H_3PO_4 has been extracted in three extraction stages, the phase ratio was $\text{org/aq} = 1/1$ at the laboratory temperature. Two scrubbing stages with pure and diluted H_3PO_4 were carried out to eliminate entrainment impurities, and two stripping stages with distilled water were carried out to produce relatively diluted and pure phosphoric acid. Table 8 shows characteristics of this produced acid.

Regeneration of hydrochloric acid

The raffinate leach solution is free of uranium, lanthanides, fluorine and phosphoric acid. It was possible then to precipitate pure gypsum by adding stoichiometric amount of sulfuric acid, thus generating HCl for recycling. More than 55% of HCl was regenerated in this process. The diagram below shows the flow sheet of the proposed process for the treatment of phosphate rocks with HCl .



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