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PHOSPHORIC ACID EXTRACTION AND RARE EARTH RECOVERY FROM APATITES OF THE BRAZILIAN PHOSPHATIC ORES

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Abstract Various experiments led in laboratory on the concentrate of Angico dos Dias phosphate allowed us to define the following steps in the process of hydrochloric treatment: 1 – Acidification of the concentrate by HCl at 20% during two hours at ambient temperature (solid/liquid ratio of 40%, agitation speed of 200 rpm). In these conditions, the solubilisation rates of CaO and P_2O_5 are commonly superior to 95% (around 80% for $(REE)_2O_3$) ; 2 – Precipitation, at ambient temperature, of Na_2SiF_6 after the addition of a sodium salt to the chlorophosphate solution. The precipitate gotten reveal that more than 80% of the fluorides, initially present in the phosphate rock, can be recovered as sodium fluorosilicates ; 3 – Liquid-liquid extraction of the phosphoric acid by the tributylphosphate. The aqueous phase obtained is treated by ammonia so as to precipitate the rare earth elements as a phosphate concentrate. The application of the process practically does not allow the formation of residues or liquids. The (REE) recovery rate of 80% constitutes a valorization source of the proposed process.

Keywords: phosphoric acid production, fertilizer industry, rare earth elements recovery, phosphate rock, hydrochloric acid route.

1. Introduction

The sulphuric acid route for phosphate rock (intended to the fertilizers industry) presents many inconveniences: impossibility to recover high commercial value by-products such as the rare earth elements, existence of severe restrictions imposed by the legislation on environmental protection, 250 millions of tons of impure and radioactive phosphogypsum annually produced, environmental problems bound to the phosphogypsum storage (pollution of the ground and surface waters etc). This technology of phosphate rock treatment of is by far the most widespread (essentially, because of the economic imperatives). Nowadays, it is the only one used in Brazil. For this country, which does not have any economic deposits of sulfur, the choice of another process imposes itself, on the one hand to reduce sulfur imports and, on the other hand, to reduce the environmental nuisances generated at the time of the phosphogypsum formation. On this purpose, it is necessary to study alternative routes and methodologies so as to make a choice for the one that offers the most ecological, economic and technical advantages.

The hydrochloric acid route can be presented as an interesting alternative to the traditional sulfuric acid route thanks mainly to the recovery of commercially valuable by-products, as for example, the rare earth elements. This article refers to the rare earths recovery in the context of the phosphoric acid production (fertilizer industry) from the phosphatic ore Angico dos Dias (Brazil) using the hydrochloric acid as leaching agent. There are several methods for purifying the phosphoric acid. The most widely used involves the liquid-liquid extraction. The main components of the leachate, which include the crude phosphoric acid, have the following qualitative behavior in relation to the organic extractant:

- easily extracted : H_3PO_4, H_3AsO_3 ;
- extracted with more or less difficulty (considering the nature of the solvent used): H_2SO_4, HF, H_2SiF_6;
- extracted very poorly : Al^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, UO_2^{2+}, …
- in the industrial process of purification by extraction, there are two classes of molecular solvents depending on their solubility in water:
- the solvents relatively soluble in water: light alcohols such as butanol, isobutanol and isopropanol ;
- the solvents, whose solubility in water is very low, for example the tributylphosphate TBP $(C_4H_9O)_3PO$, which was used in the process.

For this study, the first optimized were the parameters related with the chlorine leaching (hydrochloric acid concentration of 20%, solid/liquid ratio of 40%, stirring speed of 200 rpm and reaction time of 2h). The chemical composition of the leachate obtained (as major constituents Ca, P and F) is shown in Table 1.

2. Removal of fluorine

In order to avoid any contamination problems of the fertilizers, due to the fluorinated acids (in particular, H_2SiF_6), it is necessary to eliminate such acids before extraction. On this purpose, the

precipitation in the form of H_2SiF_6 after addition to the leachate of a sodium salt NaCl was chosen. Ten series of tests were carried out from on liter of leachate: 100 ml of leachate were added to various amounts of NaCl at ambient temperature with stirring during 30 minutes. The reactive mixtures were filtered and the precipitates dried and milled before being analyzed by X-ray diffraction. The solutions were analyzed by ion chromatography, especially for the fluoride ions.

The hydrochloric acid route for the production of phosphoric acid can be shown by reaction (1):

$$Ca_{10}(PO_4)_6F_2 + 20\ HCl \rightarrow 6H_3PO_4 + 10CaCl_2 + 2HF \qquad (1)$$

The addition of NaCl reveals to be efficient in the precipitation of Na_2SiF_6 according to reaction (2):

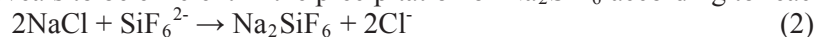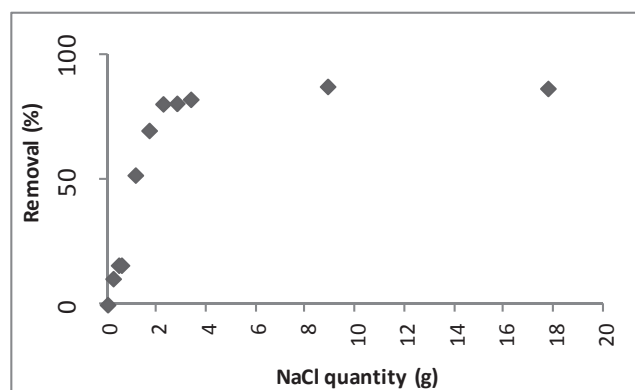$$2NaCl + SiF_6^{2-} \rightarrow Na_2SiF_6 + 2Cl^- \qquad (2)$$

Fig. 1 shows the evolution of the percentage of removal of fluorine from the leachate as a function of the amount of sodium salt added.

Table 1. Chemical composition of the leachate resulting from the hydrochloric attack of the concentrate from Angico dos Dias (Brazil).

Components (g/l)	Composition (g/l)
P_2O_5	116
CaO	151,5
$(REE)_2O_3$	2,95
F	8,8

Fig. 1. Removal of fluorine in the leachate obtained by Na_2SiF_6 precipitation after the addition of a sodium salt (analyses by ion chromatography).

The precipitation of Na_2SiF_6 is more effective at room temperature using twice the stoichiometric amount of NaCl required (according to reaction (2)). In a typical test, 3.36g of NaCl (twice the stoichiometric amount necessary) were added to 100 ml of leachate (fluoride content = 8.74g/l) and subjected to stirring for half an hour. The precipitate obtained, analyzed by X-ray diffraction, showed that more than 80% of the fluorides initially present in the rock can be recovered after hydrochloric acid leaching as Na_2SiF_6.

3. Separation CaCl$_2$ – H$_3$PO$_4$

As it is impossible to crystallize the calcium chloride from the leachate, *e.g.*, as in the case of the nitric acid route where $Ca(NO_3)_2 \cdot 4H_2O$ can be precipitated by simple cooling, we used the tributylphosphate to separate the calcium chloride from the phosphoric acid. The extraction tests were carried out in continuous mode using a laboratory mixer/settler of 4 stages (organic phase/ aqueous phase ratio = 1).

A single-stage mixer/settler successively performed the following operations: (i) bringing into contact in the mixer the multi-components A phase to be purified and the B phase of extraction (insoluble in the previous) which selectively extract one or several elements (solutes) from A phase ; (ii) separation into two phases, by gravity, of the emulsion formed in a settler associated with each mixer. The two phases are then in countercurrent to the contiguous stages. The successive mixing/separation operations allow the transfer of the solute from A to B thereby creating an A' phase, impoverished (or refined), and an enriched B solvent (or extract). At each stage, a motor unit, interchangeable and adjustable in height, drags one mixture and pumping turbine station. This aspires the phases from the settlers of the adjacent stages, puts them in contact and takes in the settler the emulsion thus created in the mixer, the transfers from one stage to another are made through distributors above the overflow.

It has been demonstrated (Pereira, 2003) that three successive extractions with an organic phase/aqueous phase ratio of 1 are sufficient to extract the entire amount of phosphate initially present in the leachate. This ratio was selected on mainly economical, since the use of solvent is reduced. The results are shown in Table 2.

The liquid-liquid extraction carried out on three of the four-stages mixer/settler allowed the recovery of almost 96% of phosphate initially present in the leachate without any fluoride. Calcium ions, account also for 9% in the organic extract. The latter may subsequently be eliminated during the treatment

of the organic phase. The rare earth elements largely remain in the aqueous phase. The chloride ions are more than 60% concentrated in the refined. Significant amounts of iron are retained in the organic extract.

Table 2. Liquid-liquid extraction of the hydrochloric leachate by the tributylphosphate (extraction on three stages with an O/A of 1).

	Leachate (V = 500ml)		Refined (V = 324.67ml)		Extract
	Concentration (g/l)	Weight (g)	Concentration (g/l)	Distribution (%)	Distribution (%)
P_2O_5	116	58	8.45	4.73	95.27
CaO	151.5	75.75	212.38	91.03	8.97
Cl^-	275.2	137.6	266.45	62.87	37.13
$(REE)_2O_3$	2.95	1.475	4.5	98.97	1.03
Fe	2.7	1.35	0.18	4.3	95.7
Al	1.9	0.95	2.85	97.3	2.7

4. Rare earth elements recovery

Not too much attention has been given to the economically viable recovery of the rare earth elements as by-products of the phosphoric acid production, when the phosphate rock/concentrate is done following the nitric or hydrochloric acid route. The rare earths have good commercial value, numerous applications and, according to Chinese researchers, are excellent micronutrients in agriculture, improving from 8 to 10% the productivity of various cultivars (CRE, 2005; Zhou, 1993). In carbonatites without specific mineral occurrences of rare earths-bearing fluorine and strontium ore, the bastnasite and monazite are the minerals from the apatite group that usually contain most of these elements, together with its most common variety, the fluorapatite, whose unitary cell is composed of $Ca_{10}P_6O_{24}F_2$.

The rare earths are present in apatites as accessory elements, ranging from some tenths percent to about 20% (Dutra and Formoso, 1995). Dutra and Formoso (1995) studied 22 samples of apatites and phosphate rocks and concluded that:
- all the carbonatite apatites have REE (Rare Earth Elements) contents exceeding 1000 ppm ;
- in Brazil, the highest values were found in rocks of the carbonatitic complex of Angico dos Dias-Bahia (7483ppm), Araxa-Minas Gerais (6347ppm) and Catalao-Goias (5585ppm).

It was observed that most part of the rare earth elements (over 90%) remained in the aqueous phase after the liquid-liquid extraction by the tributylphosphate. Considering the study by Abashi and Awadalla (1986), we opted for a precipitation of the REE. After extraction by the tributylphosphate on three stages, 20 ml of refined were then added to various amounts of ammonia and of oxalic acid in different conditions but always under stirring for 30 minutes. The precipitates were dried, crushed and calcined (1000° C) before being analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP/AES). To do this, we proceeded to stripping in its excess hydrochloric acid. The pH of the aqueous-ammonia mixture remained constant throughout the reaction. In Fig. 2, we represent the variation of the pH of the reactive mixture as a function of the volume of ammonia added.

The Fig. 3 and 4 show the recovery of the solid phase CaO, P_2O_5 and $(REE)_2O_3$ by ammonia only or by ammonia and oxalic acid.

The rare earth elements recovery is excellent regardless of the treatment which has been subjected to the aqueous refined. After treatment with ammonia only, its recovery was very close to 100% using an additional volume of 5ml. In parallel, the rare earth concentrate present some phosphate impurities. Somewhat, less than 90% of phosphates from the aqueous refined (low phosphate content, since the great majority is present in the organic phase after extraction by the tributylphosphate) is in the residue obtained. The content of this residue remains very low. After treatment with oxalic acid and ammonia, the (REE) recovery is total whatever the amount of ammonia added.

The main drawback of this aqueous refined treatment lies in the presence in the residue of large amounts of CaO (more than 90% of the CaO from the aqueous refined very rich in this oxide). Furthermore, for reasons of cost (removal of one process step), it is preferred the processing of the aqueous refined by ammonia only to recover the rare earth elements.

With this method, a recovery rate of approximately 80% of the REE initially present in the phosphate rock (in the form of a rare earth phosphate concentrate) is achieved.
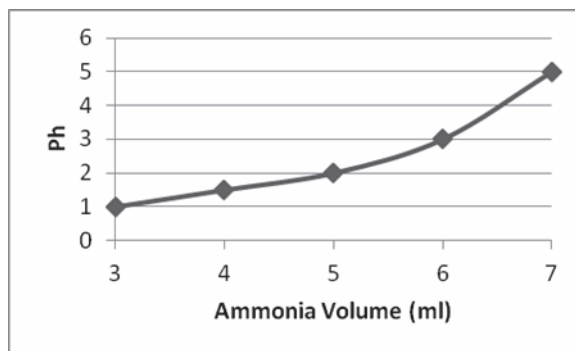

Fig. 2. Variation of the pH of the reactive mixture in function of the volume of ammonia added.
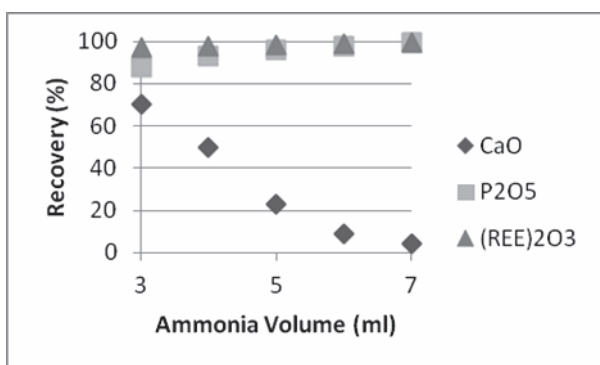

Fig. 3. CaO, P_2O_5 and $(REE)_2O_3$ recovery in solid phase (calcined residue) versus the volume of ammonia added – aqueous refined treated by ammonia (ICP/AES analyses).
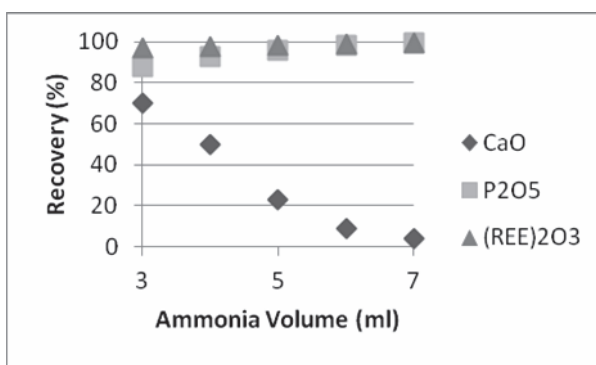

Fig. 4. CaO, P_2O_5 e $(REE)_2O_3$ recovery in solid phase (calcined residue) versus the volume of ammonia added – aqueous refined treated by ammonia and oxalic acid (ICP/AES analyses).

5. Conclusions

Various laboratory experiments carried out on the concentrate of Angico dos Dias allowed us to define the following process of hydrochloric treatment:

1 – Acidification of the concentrate by HCl at 20% during two hours at ambient temperature (solid/liquid ratio of 40%, agitation speed of 200rpm). In these conditions, the solubilisation rates of CaO and P_2O_5 are superior to 95% (around 80% for $(REE)_2O_3$);

2 – Precipitation, at ambient temperature, of Na_2SiF_6 after addition to the chlorophosphate solution of a sodium salt. The precipitate obtained reveals that more than 80% of the fluorides, initially present in the phosphate rock, can be recovered as sodium fluorosilicates;

3 – Liquid-liquid extraction of the phosphoric acid by the tributylphosphate. The aqueous phase obtained is treated by ammonia to precipitate the rare earth elements as a phosphate concentrate.

The process used does not allow the formation of residues or liquids. The REE recovery at the rate of 80% constitutes a valorization source of the proposed process.

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