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ALKALINE SOLUBILIZATION OF BRAZILIAN ALUMINUM PHOSPHATE ORE

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ABSTRACT

The North/Northeast region of Brazil contains several deposits of aluminum phosphate ore. The most important deposits are located at "Serra de Pirocáua" (mountain ridge region) and Trauíra Island in the State of Maranhao, and at Itacupim Island, in Pará. The deposits are estimated at about 25 million tons of ore, having crandallite-goyazite (calcium-strontium-aluminum phosphate) as the main mineralogical component.

The objective of this paper is to present an alternative route which allows the recovering of phosphorus and aluminum compounds from these rocks.

An experimental study was carried out on laboratory scale with the aim of solubilization of aluminum phosphate by an alkaline wet-process. By processing an aluminum phosphate rock sample from Trauíra Island containing 27% P_2O_5 and 29% Al_2O_3, extraction efficiencies of about 70% for P_2O_5 and 94% for Al_2O_3 could be achieved.

Sodium phosphate was the main product obtained. Two other by-products, calcium phosphate and sodium aluminate solution (which may have economical value if used as raw material in other processes) were also produced.

INTRODUCTION

Fourteen aluminum phosphate deposits are known in the states of Pará (PA) and Maranhao (MA), North/Northeast region of Brazil (Figure 1).

The deposits which present possible commercial exploitation are located at Itacupim Island (PA), Trauíra Island and "Serra de Pirocáua" (mountain ridge region) (MA). In these deposits the known sources are about 25 million tons of ore with a P_2O_5 content ranging from 16 to 29% at Trauíra, 10 to 28% at Pirocáua and 8 to 20% at Itacupim.

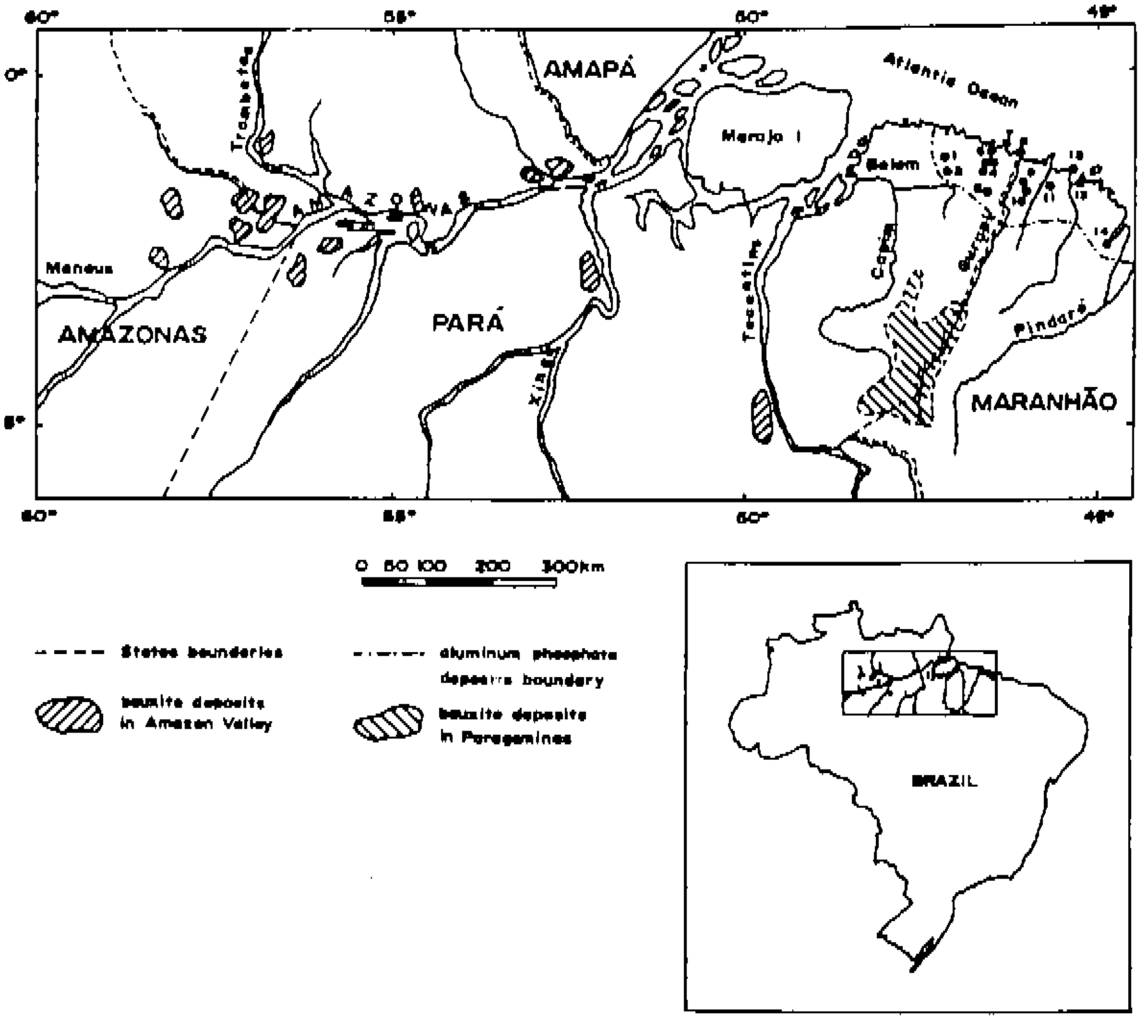


Figure 1 - Aluminum phosphate ore deposits in North/Northeast region of Brazil.

The main mineralogical composition of these deposits, crandallite-goyazite (calcium-strontium-aluminum phosphate) is found incorporated to other aluminum phosphate minerals in smaller amounts such as wardite (at Trauira), gibbsite (at Itacupim) and wavellite, variscite and augelite (at Pirocáua). More information about the geology of the aluminum phosphate deposits in Brazil may be found in previously published papers [1,2].

The P_2O_5-containing aluminum phosphate ore contains low available P_2O_5 levels and is not acceptable for direct application. A chemical treatment is necessary to increase the available phosphorus content.

A number of papers had been published, dealing with the potential of aluminum phosphate containing-rock as phosphatic fertilizer and in the aluminum compound production.

Laboratory scale tests for the thermal treatment process were carried out and presented good results in citrate solubility tests [3,4]. A slow-release action in water was also reported.

In another study, laboratory scale tests for the wet-process of solubilization were carried out with 50% H_2SO_4 and 65% HNO_3 [5]. The low solubility values found in these tests indicate that the thermal treatment seems to be the best route for the solubilization of phosphorus contained in these kinds of rocks. In thermal process, aluminum is not recovered and it remains in immobilized form in the final product [3].

In a very recent paper on the subject in Brazil, a sample of aluminum phosphate rock previously calcined was reacted with HCl solution. $AlCl_3$ was obtained by a crystallization process [6]. In other experiments a study for the recovery of the strontium contained in aluminum phosphate rock as well as other elements present in the acid solution was conducted.

The objective of this paper is to study some conditions for the alkaline wet-process as an alternative solubilization route for Brazilian aluminum phosphate rock . A number of studies about this process have been presented using other kinds of aluminum phosphate rocks with mineralogical composition similar to the observed in Brazilian deposits.

The process involves simultaneous extraction of phosphorus and aluminum with the production of high-grade sodium phosphate by a crystallization process, while leaving a sodium aluminate solution as a by-product [7,8,9,10]. Within this study an alternative route may be applied to produce calcium phosphate by treatment of aluminum phosphate rock with sodium hydroxide solution and calcium oxide. Aluminum is recovered as sodium aluminate solution.

PROCEDURE

A rock sample from Trauira Island with 100% passing in 200 Tyler Mesh (0,074 mm) was employed in this study. The chemical composition is presented in Table 1.

NaOH solution was prepared by dissolution of high analysis reagent grade in water.

TABLE 1 - Chemical composition of the Trauira Island aluminum phosphate rock sample, in per cent

P_2O_5	Al_2O_3	Fe_2O_3	CaO	MgO	SiO_2	Na_2O	F
27.2	29.3	4.31	6.91	0.10	2.84	1.28	0.50

Concentration of 200 g/l NaOH solution and temperature of 90°C were chosen as the levels suitable for the first laboratory scale tests. Other parameters include :

* retention times of 15, 30, 45 and 60 minutes

* mol ratio $NaOH/P_2O_5$ and $NaOH/Al_2O_3$

  A - 10% below the stoichiometric values

  B - stoichiometric values $NaOH/P_2O_5 = 6$ and $NaOH/Al_2O_3 = 2$

  C - 10% above stoichiometric values

* CaO influence in the selective extraction of aluminum to product a calcium phosphate-containing insoluble phase.

Other tests were also conducted in order to evaluate the effect of the concentration of NaOH solution and temperature.

50 g of ground rock were added to the NaOH solution, under mechanical stirring and heating. After reaction the slurry was immediately filtered under vacuum. The insoluble phases were washed with hot water and dried for 3 hours in an oven at 100°C. Total P_2O_5 and 2% citric acid P_2O_5 solubility tests were determined by colorimetric method as vanado-molybdate complex. Mineralogical compositions were examined by X-ray diffraction. The filtrates were employed for sodium phosphate crystallization exploratory tests.

RESULTS AND DISCUSSION

Table 2 presents the retention time effect in the extraction in 200 g/l NaOH solutions.

The yield of the extracted fractions of P_2O_5 and Al_2O_3 range from 55.9% to 69.9% and from 80.5% to 93.6% respectively.

TABLE 2 - Retention time effect in the extracted fractions of P_2O_5 and Al_2O_3 in 200 g/l NaOH solution, 90°C

Mol Ratio	Time (min)	% of P_2O_5 extracted	% of Al_2O_3 extracted
A		55.9	80.5
B	15	59.6	85.7
C		63.4	91.7
A		56.0	81.7
B	30	62.5	88.4
C		65.4	94.4
A		62.5	83.3
B	45	65.4	91.0
C		69.1	93.7
A		63.6	86.3
B	60	69.1	92.5
C		69.9	93.6

EFFECT OF TEMPERATURE AND CONCENTRATION OF THE NAOH SOLUTIONS

The Tables 3 and 4 present the effect of the concentration of NaOH solution and temperature.

Concentrations of 150 and 250 g NaOH/l solutions were tested.

Experimental tests were carried out with mol ratio C, within a temperature range from 80 to 100°C and retention time of 30 and 60 minutes. A condition was also carried out for mol ratio B.

In all the tests, it was observed there was a small influence of the temperature and concentration on the extracted fraction of Al_2O_3.

TABLE 3 - Effect of the 150 g/l NaOH solution and temperature on extracted fractions of P_2O_5 and Al_2O_3

Mol Ratio Time (minutes) Temperature (°C)	B 60 90	C* 30 80	C 60 80	C 60 90	C 30 100	C 60 100
% P_2O_5 extracted	65.4	65.4	66.2	66.9	66.9	67.6
% Al_2O_3 extracted	94.5	95.2	89.7	96.7	96.9	97.0

TABLE 4 - Effect of the 250 g/l NaOH solution and temperature on extracted fractions of P_2O_5 and Al_2O_3

Mol Ratio Time (minutes) Temperature (°C)	B* 60 90	C 30 80	C* 60 80	C* 60 90	C 30 100	C* 60 100
% P_2O_5 extracted	64.0	66.2	63.2	57.4	66.2	61.8
% Al_2O_3 extracted	67.5	95.3	69.6	84.6	96.7	81.8

* difficult filtration

CALCIUM PHOSPHATE AND INSOLUBLE PHASES IN NAOH SOLUTIONS

The Table 5 presents the results of the Al_2O_3 extracted in NaOH solution containing CaO.

CaO was added to reaction in stoichiometric amount to product a calcium phosphate-containing insoluble phases.

50 g of ground aluminum phosphate rock and 200 g/l NaOH solution containing CaO, were mixed under mechanical stirring during 60 minutes at 90°C.

About 90% of the Al_2O_3 were extracted as sodium aluminate solution.

TABLE 5 - Extraction of P_2O_5 and Al_2O_3 in 200 g/l NaOH containing CaO

Mol Ratio	% P_2O_5 extracted	% Al_2O_3 extracted
A	6.76	88.5
B	4.19	89.6
C	1.47	88.7

Tables 6, 7, 8 and 9 present the analysis of P_2O_5 in the insoluble phases in NaOH solutions.

TABLE 6 - Analysis of P_2O_5 - insoluble phases in 200 g/l NaOH solution

Mol Ratio Time (minutes) Temperature (°C)	B* 60 90	C 30 80	C* 60 80	C* 60 90	C 30 100	C* 60 100
% P_2O_5 Total (A)	24.3	24.5	21.9	24.3	24.2	23.9
2% CAS P_2O_5 sol.(B)	22.0	21.6	19.3	23.1	23.1	22.7
(B/A) x 100	90.5	88.2	88.1	95.1	95.4	95.0

TABLE 7 - Analysis of P_2O_5 - insoluble phases in 150 g/l NaOH solution

Mol Ratio Time (minutes) Temperature (°C)	B* 60 90	C 30 80	C* 60 80	C* 60 90	C 30 100	C* 60 100
% P_2O_5 Total (A)	24.3	24.5	21.9	24.3	24.2	23.9
2% CAS P_2O_5 sol.(B)	22.0	21.6	19.3	23.1	23.1	22.7
(B/A) x 100	90.5	88.2	88.1	95.1	95.4	95.0

TABLE 8 - Analysis of P_2O_5 - insoluble phases in 250 g/l NaOH solution

Mol Ratio Time (minutes) Temperature (°C)	B* 60 90	C 30 80	C* 60 80	C* 60 90	C 30 100	C* 60 100
% P_2O_5 Total (A)	15.9	24.2	16.7	21.8	24.4	19.9
2% CAS P_2O_5 sol.(B)	14.4	21.6	16.3	21.1	22.3	19.2
(B/A) x 100	90.6	89.3	97.6	96.8	91.4	96.5

TABLE 9 - Analysis of P_2O_5 - insoluble phases in 200 g/l NaOH solution containing CaO

Mol Ratio	A	B	C
% P_2O_5 Total (A)	25.2	25.5	23.2
2% CAS P_2O_5 sol.(B)	18.8	18.8	17.7
(B/A) x 100	74.6	73.7	76.3

Figures 2 and 3 show the X-ray diffraction patterns of the insoluble phases obtained from solubilization tests. (Refer to following pages).

Unreacted crandallite-goyazite (CG), wardite (W) and calcium phosphate as fluorapatite (FA) and hydroxiapatite (HA) were identified. This suggests that calcium phosphate was precipitated when the reaction was taking place, and explains for the citric acid soluble form. High levels of 2% citric acid P_2O_5 soluble are observed making them suitable for direct application in the agriculture.

SODIUM PHOSPHATE CRYSTALS

In these tests the conditions for crystallization of the products were not determined.

Crystals were obtained by slow cooling of the filtrate under room conditions and they were in varied shapes. From some filtrate crystals of needle shape was observed. In the tests which allowed high values of solubilization of P_2O_5 and Al_2O_3 (mol ratio C, 200 g/l NaOH) a recovery of about 81% sodium phosphate was observed.

The crystals were examined by X-Ray diffraction which presented products crystallized as trissodium dodecahydrate form ($Na_3PO_4.12H_2O$). The X-ray diffraction of the crystals is presented in Figure 4.

This product is suitable for the preparation of detergents, clarifying sugar, and in textile and pharmaceutical industries. The use as phosphatic fertilizer it is not advisible in the Brazilian arid regions [10].

SODIUM ALUMINATE SOLUTIONS BY-PRODUCT

Sodium aluminate solution has important industrial applications. It is a product highly consumed in water treatment systems as flocculant, softening water and pH controller, usually as 15 and 35% solutions.

A procedure for recovering the aluminum contained in sodium aluminate solution may be conducted through precipitation as hydrated alumina [11].

After removal of the solid the filtrate containing NaOH solution should be concentrated to the initials levels and then recycled to reactor for the solubilization of aluminum phosphate ore.

CONCLUSIONS

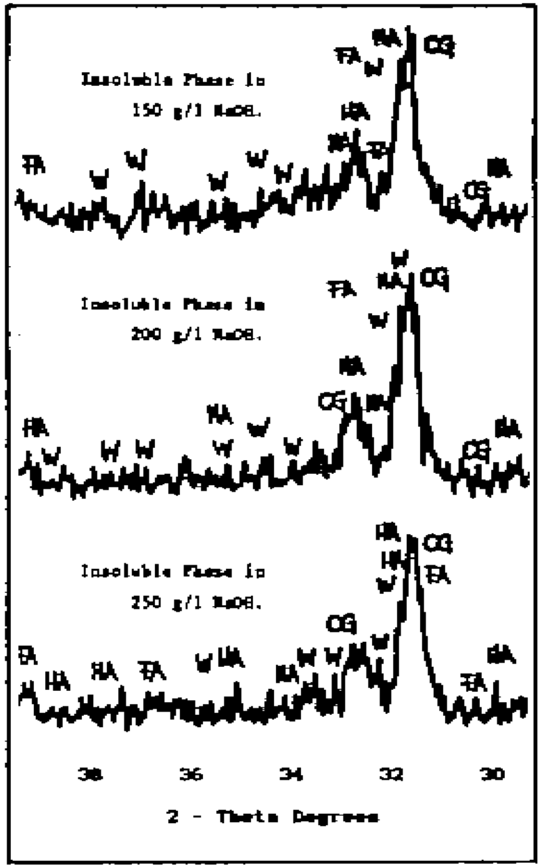
From the results it is possible to conclude:

- High levels of Al_2O_3 and P_2O_5 can be recovered through the production of high-grade sodium phosphate and sodium aluminate solution as by-product.

- Calcium phosphate-containing insoluble phases with a high 2% citric acid soluble P_2O_5 suitable for fertilizer use can be obtained when calcium oxide was added in the solubilization step.

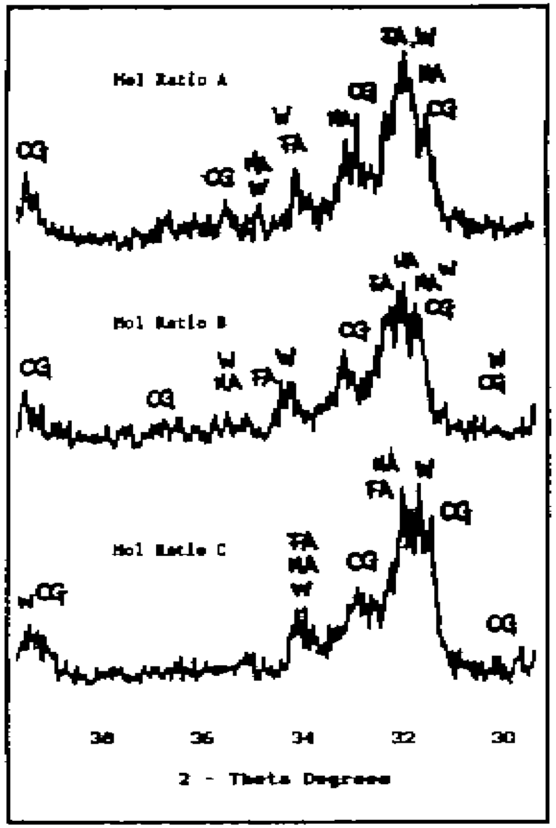
- The use of insoluble phases as fertilizer may be considered because of its high 2% citric acid P_2O_5 solubility.

Figure 2



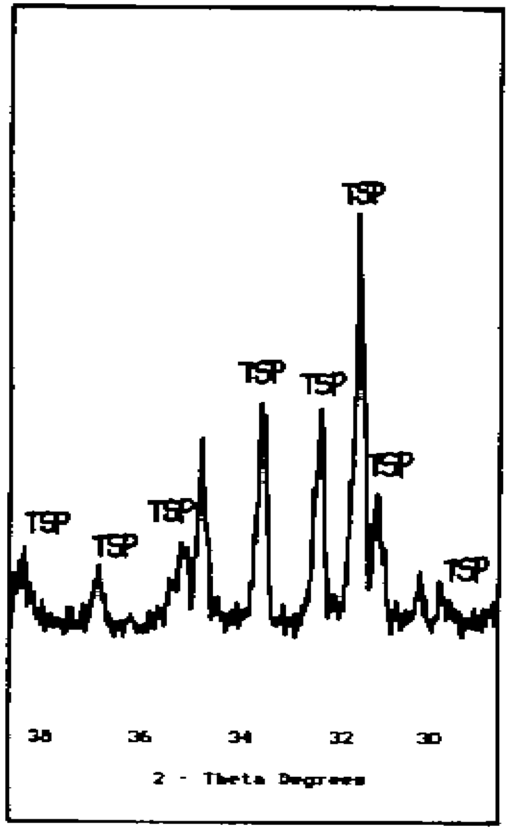
X-ray diffraction patterns of the insoluble phases in 150, 200 and 250 g/l NaOH solutions.
CG: Crandalite-goyazite; W: Wardite
FA: Fluorapatite; HA: Hidroxiapatite

Figure 3



X-ray diffraction patterns of the insoluble phases in 200 g/l NaOH solution containing CaO.
CG: Crandalite-goyazite; W: Wardite
FA: Fluorapatite; HA: Hidroxiapatite

Figure 4



X-ray diffraction patterns of the crystals obtained.
TSP - Trisodium Phosphate

In future, we intend to carry some studies on:

- determination of the conditions for trisodium phosphate crystallization and,
- obtaining alumina from sodium aluminate solution.

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