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BENCH-SCALE STUDIES ON THE USE OF BRAZILIAN PHOSPHATE CONCENTRATES IN THE
PRODUCTION OF WET PROCESS PHOSPHORIC ACID

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ABSTRACT

Bench-scale tests were conducted to evaluate the behaviour of two Brazilian phosphate concentrates, Araxá and Catalão, in the dihydrate phosphoric acid process. Previous studies have shown that both samples are from igneous residual desposits, apatite (hydroxy-fluorapatite type) being the major constituent. Like Kola (USSR) concentrate, Araxá and Catalão concentrates are of low reactivity. Batch tests were carried out so that the following parameters could be assessed: raw materials consumption, P₂O₅ recoveries, filtration rates, quality of the acid and quality of the by-product filter cake. The results demonstrated that Araxá and Catalão concentrates are suitable for phosphoric acid manufacture. Filter cakes with well-formed gypsum crystals and good filtration properties were produced from both samples, Catalão producing a high-quality filter cake for a dihydrate process. Good performances were achieved at the following filtration rates: 5.7 tons of P₂O₅/day/m² for Araxá and 6.6 tons of P₂O₅/day/m² for Catalão, corresponding to 28% P₂O₅ filter acid. The overall yield obtained in the first case was about 96%, and 97% in the second. Raw materials data revealed a lower sulphuric acid consumption than that usually found for sedimentary phosphate concentrates.

INTRODUCTION

The "Centro de Estudos de Fertilizantes - CEFER", formed in 1976, is developing a programme for the characterisation and utilisation of Brazilian phosphates for the production of fertilizers. This programme is of particular importance to Brazil in view of the country's plans to use its own sources of recently discovered phosphate raw materials (1).

It aims, firstly, to determine the physical and chemical characteristics of the phosphates and, secondly, to assess their suitability for chemical conversion either by the thermal method or by attack with mineral acids.

CEFER is at present engaged on several studies. Characterisation, mainly consisting of determining the chemical and mineral constituents, is carried out using the specialist laboratories of the IPT. As regards production trials, laboratory-scale methods, using batch systems, are already available for some products, e.g., superphosphates, nitrophosphates, calcined phosphates and phosphoric acid.

This paper deals specifically with phosphoric acid trials conducted with two samples of Brazilian phosphates, Araxá and Catalão.

CHARACTERISTICS OF THE PHOSPHATES

These samples were, in fact, of concentrated products obtained by treatment of the phosphate rock from the Araxá and Catalão deposits in Brazil. These deposits of igneous origin (1), have apatite as the most important phosphate mineral. This apatite, which is of highly crystalline appearance (figures 1 and 2), is more in the form of hydroxyfluorapatite (3, 6) with a slight substitution of the calcium by strontium and sodium and of the phosphate (PO_4^{3-}) by carbonate (CO_3^{2-}) (4, 5).

Their origin means that the samples are of low reactivity, comparable with that of Kola phosphate, which is also of igneous origin.

The chemical analysis and the particle size distribution are given in tables 1 and 2. It can be seen that the two phosphate, Araxá and Catalão, are very rich in phosphorus with P_2O_5 contents of the order of 35% for the former and 40% for the latter. The $\text{CaO}/\text{P}_2\text{O}_5$ ratios, 1.317 for Araxá and 1.312 for Catalão, are excellent and allow us to predict low sulphuric acid consumption when producing phosphoric acid.

The main common impurities are iron, silica and titanium, which are present in proportions lower than 1% in the Catalão rock. The Araxá phosphate has also a large amount of barium, 5.6% BaO , probably in the form of barytes (3, 4). The presence of barium and titanium and of other elements detected but not measured (such as strontium, niobium) accords with the origin of the minerals covered in this study.

In both cases, the silica-fluorine ratio is low, which involves risks of corrosion from the formation of hydrofluoric acid during the attack. On the other hand, the fact that chlorine is almost non-existent eliminates any risk of corrosion from hydrochloric acid.

The Na_2O and K_2O contents are so low that there is only a slight possibility of scaling through the formation of alkaline fluorosilicates. The CO_2 and organic carbon contents are insufficient for there to be foaming problems.

The particle size distributions of the phosphates, which are of the same order of size, can be considered as very extreme for raw materials intended for phosphoric acid manufacture.

PHOSPHORIC ACID TRIALS

The trials conducted in this study aimed at determining the suitability of the samples for the preparation of wet process phosphoric acid, by the dihydrate process.

Each trial was made up of a succession of tests where phosphate and sulphuric acid were introduced simultaneously, the slurry then evolving over a defined period, before filtration. They were therefore by the batch system, with no recycling of weak acid (2).

In order to give some continuity to all these trials, each sample was obtained by preparing 1,600 g of slurry under specified conditions; half was kept for filtration and appropriate analyses; the other half was destined for the preparation of the recycle of the next test.

The attack took place at constant temperature (78°C) and homogenisation of the slurry was obtained by mechanical agitation at constant speed. The other parameters of attack investigated were as follows: liquid phase with

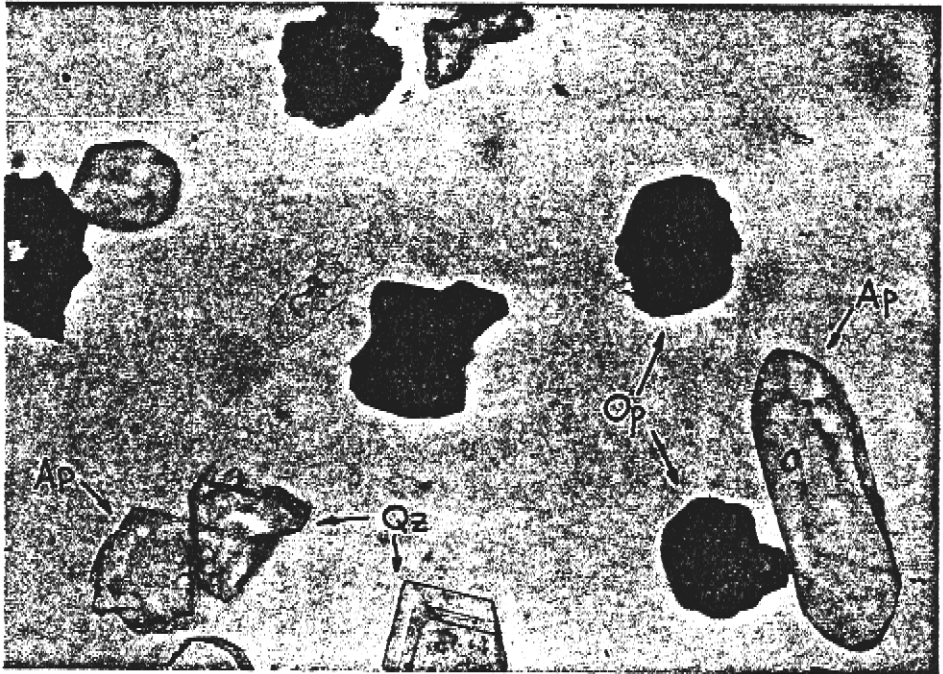


Figure 1 - Photographie (130X). Phosphate de Catalão (brut).
Fraction < 63 μ . Ap=Apatite; Qz=Quartz; Op=Opaque.

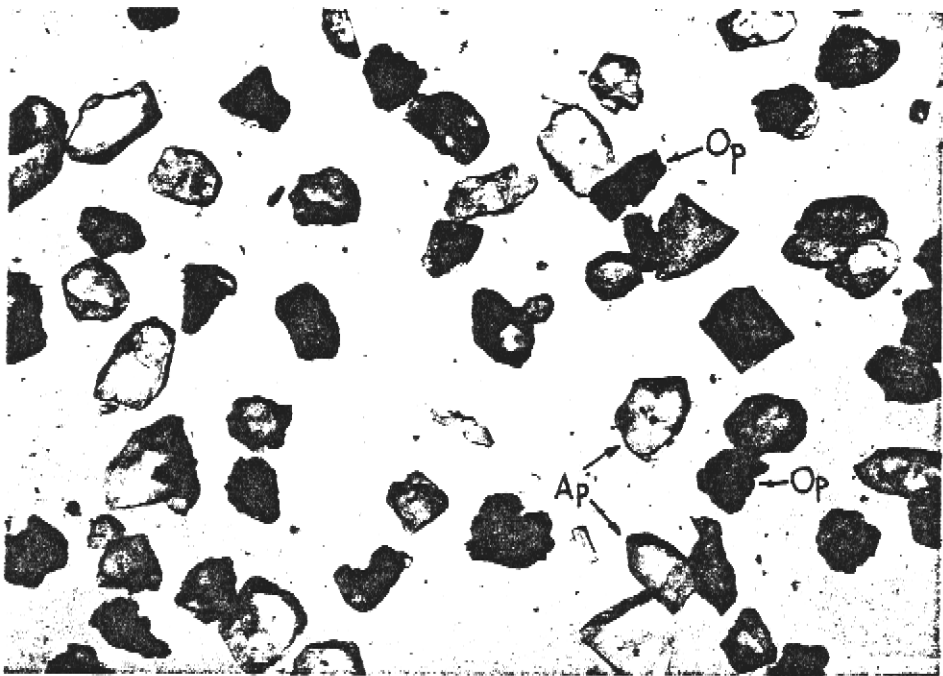


Figure 2 - Photographie (35X). Phosphate d'Araxá (concentré).
Fraction > 149 μ . Ap=Apatite; Op=Opaque.

Table 1 - Chemical analysis of the phosphates

Phosphate	Araxá	Catalão
Constituent, % (results expressed on product dried at 105°C + 5°C)		
P ₂ O ₅	35.32	40.32
CaO	46.52	52.88
SO ₃	3.08	<0.01
CO ₂	0.48	0.18
SiO ₂	1.75	0.80
F	2.28	2.64
Cl	0.006	0.005
Al ₂ O ₃	0.39	0.23
Fe ₂ O ₃	2.44	0.83
MgO	0.07	0.07
Na ₂ O	0.34	0.34
K ₂ O	0.02	0.04
TiO ₂	0.60	0.34
BaO	5.64	0.22
Organic carbon, C	0.02	0.02
Loss on calcination (CO ₂ deducted)	0.58	0.13
<hr/>		
Initial moisture content of the phosphate (loss at 105° + 5°C)	0.10	0.06

Table 2 - Particle size distribution of the phosphates

Phosphate Particle size μ	Araxá		Catalão	
	Fraction % (a)	Cumulative % (b)	Fraction % (a)	Cumulative % (b)
>500	0.03	0.03	0.05	0.05
400-500	0.03	0.06	0.30	0.35
315-400	0.20	0.26	0.63	0.98
250-315	0.96	1.22	1.39	2.37
200-250	2.73	3.95	2.89	5.26
160-200	7.27	11.22	8.05	13.31
125-160	10.22	21.44	11.50	24.81
100-125	11.45	32.89	14.17	38.98
80-100	13.09	45.98	16.01	54.99
63- 80	13.83	59.81	13.69	68.68
50- 63	10.54	70.35	10.75	79.43
40- 50	3.91	74.26	2.61	82.04
<40	25.74	100.00	17.96	100.00

(a), (b) by weight

with 28% P_2O_5 and sulphuric acid level equal to 25 g/l H_2SO_4 ; solids content, 35% (by weight). These parameters were monitored during the trials. The total duration of the attack was two and a half hours including the time for the gypsum crystallisation.

Filtration, carried out on a Büchner funnel, consisted of a series of timed operations to determine the filterability of the slurry resulting from the attack phase. The data obtained were corrected so as to correspond to the figures for an industrial filter turning at the rate of one revolution every four minutes.

DISCUSSION OF THE RESULTS

Araxá concentrate

The Araxá phosphate was found to be well suited to the manufacture of phosphoric acid and its performance can be considered as good (table 3).

A series of 12 trials was carried out without any handling problem. The results obtained are very consistent and the overall mean is fairly representative of the individual results, especially as regards the analysis of the acid, the P_2O_5 losses and the filterability.

Sulphuric acid consumption is very good compared with the results found with phosphates of sedimentary origin (7). As regards the sulphate present in the phosphate, it appears that it can be ignored for the attack. It follows that this sulphate would be linked to the barium in the form of barytes which, being insoluble, acts as diluent and is found again in the phosphogypsum.

P_2O_5 losses are acceptable and allow us to envisage a chemical yield of the order of 96%. The important contribution should be noted of the unattacked fraction, which becomes the major source of the P_2O_5 losses. Studies carried out by Robinson (9) give the co-crystallised fraction as the major one.

The average filtration time is of the order of 40 seconds, which corresponds to a filterability of around 6 tonnes of P_2O_5 per day and per square metre of filtering surface for an industrial filter turning at a rate of one revolution every four minutes. This figure, which is less than that obtained by Varsanyi et al (10) for an acid ex-Araxá with 30% P_2O_5 , is very interesting.

The acid produced reaches a P_2O_5 level (table 4) very close to the 28% desired. It is clear and slightly greyish in colour. It contains few metal ions except for iron, the content of which is high (2.73% Fe_2O_3). The figures given for SiO_2 and F correspond approximately to SiF_6^{2-} .

The phospho-gypsum (or simply gypsum) is of dark yellow colour and contains 0.4% of Fe_2O_3 and 3.7% of BaO . It has very well-formed gypsum crystals, predominantly needle-shaped (figure 3). In spite of the presence of a large amount of barium in the Araxá concentrate studies carried out previously with this phosphate (8) showed that this element has no significant effect on the process of crystallisation of gypsum from phosphoric acid manufacture.

Catalão concentrate

Like the Araxá phosphate, that of Catalão caused no difficulties in manufacture. It can be considered as easy to process.

Ten trials were conducted with good reproducibility of the results. The averages are sufficiently representative.

Sulphuric acid consumption is as good as for Araxá and phosphate consumption is lower owing to the slightly higher P_2O_5 content of the Catalão.

The chemical yield conceivable in industrial conditions is greater than 96%, the P_2O_5 losses remaining around 0.8% with respect to the gypsum produced. As regards the breakdown between the different types of losses, the proportions compared with the total observed for Araxá are more or less maintained, except for the water-soluble fraction which is higher for Catalão.

The average filtration time, of the same order of magnitude as that of Araxá, corresponds to a filtrability close to 7 tonnes of P_2O_5 per day per square metre of filtration surface area, for an industrial filter in the conditions already stated.

The acid obtained, with a P_2O_5 content (27.69%) very close to 28%, is almost colourless and contains few impurities (table 4) compared with the usual acids produced by the wet process. The figure of 1.53% SO_3 corresponds to the sulphuric acid used to maintain the sulphuric acid level at 25 g/l of H_2SO_4 . The values obtained for SiO_2 and F correspond roughly to SiF_6 .

The phosphogypsum, almost white in colour, is made up of gypsum crystals (figure 4) similar in shape to those found in the case of Araxá.

CONCLUSIONS

Considering the performances obtained with the Araxá and Catalão phosphates in this study, it could be said that these two minerals are very suitable for the manufacture of wet process phosphoric acid by the dihydrate process.

In actual industrial conditions, they can be regarded as phosphates easy to process. As regards hydrofluoric acid corrosion, it would be desirable to take precautions to minimise the risk of this. For example, reactive silica could be added during the attack to compensate for the lack of this constituent in these phosphates.

The products obtained are of good quality. The shape of the gypsum crystals, needles rather than plates, did not prevent the slurry from having good filtration characteristics for both Araxá and Catalão. This accords with the conclusions drawn by Robinson (8) and is shown by the good figures obtained in this study for filterability.

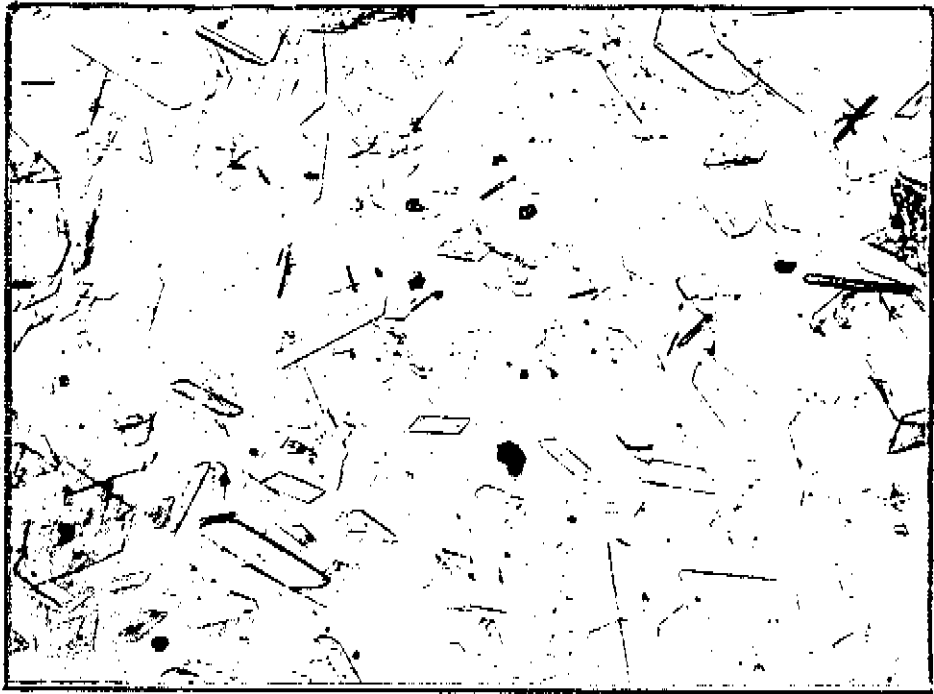


Figure 3 - Photographie (60X). Cristaux de gypse produits avec le phosphate d'Araxá.



Figure 4 - Photographie (60X). Cristaux de gypse produits avec le phosphate de Catalão.

Table 3 - Technical results of the phosphoric acid manufacture

Phosphate		<u>Araxá</u>	<u>Catalão</u>
Solid by-product (gypsum) tonnes/tonne P ₂ O ₅ (dry basis)		4.22	3.86
P ₂ O ₅ losses	unattacked P ₂ O ₅	0.45	0.34
% (with respect	co-crystalline P ₂ O ₅	0.33	0.27
to dry gypsum-	water soluble P ₂ O ₅	0.16	0.24
60°C	total P ₂ O ₅	0.94	0.85
Chemical yield,	Attack	96.7	97.6
%	Filtration	99.3	99.1
	total	96.0	96.7
Sulphuric acid consumption, tonnes 100% H ₂ SO ₄ /tonne P ₂ O ₅ produced		2.41	2.37
Phosphate consumption Tonnes dry phosphate/tonne P ₂ O ₅ produced		2.95	2.56
Filterability tonnes P ₂ O ₅ /m ² /day		5.7	6.8

Table 4 - Chemical analysis of the products

Phosphate	<u>Araxá</u>		<u>Catalão</u>	
	<u>Acid</u>	<u>Gypsum (a)</u>	<u>Acid</u>	<u>Gypsum (a)</u>
Constituent, %				
P ₂ O ₅	27.73	0.94	27.69	0.86
CaO	0.27	30.31	0.31	33.10
SO ₃	1.53	43.25	1.53	46.53
SiO ₂	0.72	0.29	0.80	0.18
F	1.50	0.05	1.64	0.04
Cl	-	-	-	-
Al ₂ O ₃	0.27	0.06	0.11	0.09
Fe ₂ O ₃	2.73	0.39	0.33	0.19
MgO	0.08	0.02	0.02	0.08
K ₂ O	0.015	< 0.01	0.18	0.07
Na ₂ O	0.19	0.05	0.02	0.01
BaO	0.01	3.66	-	-
Loss at 250°C	-	47.3	-	47.2
Density at 20°C	1.317	-	1,300	-

(a) Results for gypsum expressed on dry product at 60°C to constant weight.

- Figure 1 - Photograph (x130). Catalão phosphate (crude sample)
Fraction 63 . Ap = Apatite; Qz = Quartz; Op = Opaque
- Figure 2 - Photograph (x35). Araxá phosphate (concentrated)
Fraction 149 . Ap = Apatite; Op = Opaque
- Figure 3 - Photograph (x60). Gypsum crystals produced with
Araxá phosphate
- Figure 4 - Photograph (x60). Gypsum crystals produced with
Catalão phosphate.

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TA/80/4 Bench-scale studies on the use of Brazilian phosphate concentrates in the production of wet process phosphoric acid by M.A.C. Bruno, CEFER, Brazil.

DISCUSSION : (Rapporteur J.D. Crerar, Fisons Ltd, United Kingdom)

In reply to questions from Mr. P. BECKER (Cofaz, France), Mr. BRUNO said that for the laboratory scale test, phosphate rock and acid are added simultaneously and continuously by hand over a period of 15 min. The mixture is then left to digest for a period giving a total reaction time of 2 1/2 hours. The filtration test is carried out in two parts - filtration and washing - and the total cycle time for Araxa rock is 40 seconds and for Catalao rock 36-37 seconds.

Dr. S.L. PENG (Fertilizantes Uniao, Brazil) asked whether the rock samples tested were the same as those commercially available. Mr. BRUNO pointed out that tests were carried out 18 months ago on samples requested from the rock producers. One would expect start-up problems from the rock producing plants but there were no great differences between samples and current production. For Catalao, the P_2O_5 content was currently about 37%.

Mr. P. BALDWIN (Cremer & Werner, United Kingdom), asked how the concentrates were obtained from Run of Mine material. Unfortunately, CEFER were not involved in ore treatment so that Mr. BRUNO could not give an answer.

Mr. M. GAURON (Cofaz, France) mentioned that the high iron level of Araxa acid had been mentioned but pointed out that in Table 4 the iron in the acid exceeded that in the rock. Mr. BRUNO felt that this was an analytical problem and, although the material balances had been done, he did not have them with him. Nevertheless, the overall conclusion stands, that the majority of the iron stays in the acid.

Mr. M. BARLOY (CERMI, France) pointed out that the silica content of Catalao rock, if it is completely reactive, would react with only 60% of the fluorine. He asked about the corrosion caused by free HF. Mr. BRUNO replied that no corrosion tests had been done.

Mr. T.R. BOULOS (National Research Centre, Egypt) stated that the phosphoric acid from Araxa rock seemed to contain about 3% total iron and aluminium, content which should increase during concentration of the acid, and asked whether CEFER had studied this. Mr. BRUNO replied that no tests had been done in the laboratory but both Araxa and Catalao rocks were being used commercially and information should be available from the processors. He had no information on the composition of precipitated solids.