Characterization of a complex carbonate-silicate apatite ore and its concentration by a two-stage anionic flotation method

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Abstract

A carbonate-silicate low weathering phosphate ore from an igneous origin deposit in Southeastern Brazil presents a challenge mainly for apatite flotation from its gangue minerals, calcite and dolomite, plus the presence of phlogopite, diopside, magnetite, richterite, ilmenite, vermiculite, quartz and many other minor impurities. Recently, selectivity has been greatly enhanced by using CO_2 instead of air, so in this study a variant process was used. In a first stage, carbonate minerals were floated with the use of CO_2 as bubble gas; the collector was a saponified fatty acid, medium hydrocarbon chain. Then, the depressed minerals were floated using a sulfosuccinate collector and air as the froth gas. A significant improvement in the apatite concentration has been achieved: the initial 5.28% P_2O_5 tenor was raised to 21.58%. The overall P_2O_5 recovery was 61.8% and 12.0% of the global mass recovery. However, the amount of impurities was still significant with the presence of carbonates, phlogopite and minor magnetite. Therefore, the processing route presented herein is quite viable, but further research is necessary to improve the whole method.

keywords: phosphate ore, apatite, flotation, calcite, dolomite, sulfosuccinate, fatty acids soaps, carbon dioxide.

1. Introduction

Fertilizer is one of the basic inputs used to increase agricultural production due to the continuous growth of the agricultural sector in recent decades in Brazil. This country needs to import a significant part of the phosphate input, since its domestic production is unable to supply the national demand. Apatite group minerals and calcium-bearing carbonates (calcite and dolomite) represent the main challenge of selective flotation. In addition, difficulties encountered in this process go beyond the similarities of the chemistry of the surface because the electrokinetic and dissolution properties of these minerals also tend to respond similarly to anionic and cationic collectors (Somasundaram, 1985).

In Brazil, the Igneous Province of Alto Paranaíba is well known for possessing deposits of strategic commodities, such as phosphate, niobium and rare earths. They are mineral deposits associated with carbonatites, which, by definition, are igneous rocks composed of more than 50% of carbonates and can occur alone or together with silicate rocks forming alkaline-carbonate complexes (Ribeiro *et al*., 2014). The best-known deposits in this province are Catalão, Salitre, Tapira, Serra Negra and Araxá. Besides the carbonatites, other petrological suites occur, such as bebedourites and phoscorites (Brod *et al*. 2004).

In all the rocks, the mineralogical and chemical compositions are usually very complex. The degree of weathering tends to increase this complexity. But even in relatively fresh ores, the number of gangue minerals is high. Therefore, a concentration process is necessary, in order to produce an apatite concentration

(Avelar *et al*., 2019; Avelar *et al*., 2021). In ores with a significant presence of the carbonates, calcite and dolomite, and micas as well, the selective flotation of apatite is very difficult to achieve and practically impossible with the use of fatty acid soaps and starch as depressants.

An attempt to reach selectivity was in the use of sulfosuccinates alone or in the presence of carbon dioxide in conditioning and as the flotation gas (Rezende *et al*., 2011; Wang *et al*., 2013).

In this study, a typical phosphate ore with a very low degree of weathering, therefore having a complex mineralogical composition, was characterized, followed by bench scale flotation tests using conventional fatty acid collectors, along with the employment of a sulfosuccinate surfactant, among other flotation parameters. The aim was to achieve a suitable apatite concentrate, following a thorough assessment of the difficult mineralogical end chemical conditions.

2. Materials and methods

The sample was collected in a mine pit and represented a quite fresh bebedourite lithotype ore. Then, it was subjected to the homogenization, crushing, milling, desliming and flotation steps. The feed to flotation was below 0.210mm screen size.

Chemical assays were conducted using an ICP-OES instrument for all elements, with the exception of S and C, which were analyzed in a LECO device. Loss of ignition (LOI) was assayed by gravimetry. The size analysis used 10 screens (Table 1); the fraction smaller than 45µm was separated in the Cyclosizer, with the lowest cut at 10.0µm.

Mineralogical composition was determined by powder X-ray diffraction in a PW3710 Panalytical instrument, with the following analytical conditions: scan range: 3.030 to 79.91 °2θ; step size: 0,020 °2θ; scan step time: 1.000 s; Cu anode tube, K-Alpha1: 1.5406 Å, graphite monochromator, and detector: photomultiplier tube.

Microstructure analyses were conducted with a QEMSCAN automated SEM with EDS analyzer; further studies were complemented in a FEI-INSPECT F50 scanning electron microscope (SEM) with an EDAX-GENESIS attached energy-dispersive X-ray spectrometer (EDS).

The samples for the flotation tests were ground to 80% passing in the 106µm screen. Excess magnetic minerals were removed using a laboratory scale, low intensity magnetic separator, in a field intensity from 800 to 1000 Gauss. The non-magnetic fraction was deslimined by cycloning to remove particles below 20µm. This material was the feed to the flotation tests. These tests were carried out using a bench scale Denver cell. In the first stage, a carbonates concentrate was produced, using fatty acids soap and CO_2 as the bubble gas. The non-floated fraction, containing apatite, silicates and iron oxides, was then submitted to flotation, with the use of a sulfosuccinate collector and air for bubble generation. A similar approach with different ores and treatment sequence was proposed by others (Matiolo *et al*., 2015; Freitas *et al*., 2021).

3. Results

The raw ore sample was submitted to characterization with the following results.

Table 1 – Size and chemical analyses (in mass %) of the raw ore.

Screen sizes (µm)	% retained	C	Al_2O_3	CaO	Fe_2O_3	MgO	P_2O_5	SiO_2	TiO_2	K_2O	LOI
1000	19.18	3.07	1.43	17.22	15.15	12.38	3.59	27.38	3.99	2.48	11.95
840	11.07	3.24	1.42	17.28	15.29	12.25	3.98	25.80	3.78	2.47	12.64
500	16.62	3.12	1.75	18.17	14.99	12.40	4.55	25.65	3.71	2.60	12.15
300	8.47	2.96	1.74	20.41	15.07	11.64	6.49	23.42	3.49	2.47	11.50
212	10.63	2.94	2.03	20.56	13.73	12.00	6.90	23.62	3.13	2.61	11.51
180	2.80	3.15	1.58	22.51	13.74	11.15	7.76	21.38	2.91	2.42	12.22
150	1.75	3.13	1.62	23.42	14.09	11.06	8.68	19.86	2.79	2.37	12.22
130	2.10	3.40	1.47	23.17	12.66	11.52	7.60	21.76	2.59	2.40	13.49
106	3.21	3.30	1.35	22.42	13.69	11.57	7.26	22.03	2.74	2.40	12.79
74	4.96	3.39	1.16	22.41	13.29	11.77	6.77	22.52	2.57	2.46	13.33
44	7.05	3.59	0.98	22.29	11.99	12.26	6.02	24.00	2.34	2.48	14.29
34	1.28	3.09	0.37	21.22	20.55	8.79	7.14	17.72	6.15	1.36	10.97
25	1.96	4.23	0.62	23.65	10.41	11.47	5.57	22.72	2.25	1.99	16.71
18	2.60	4.23	0.65	23.46	10.27	11.80	5.26	23.44	2.05	2.04	16.74
13	1.95	4.21	0.61	23.86	10.56	11.59	5.63	22.87	2.30	1.99	16.69
10	1.00	4.19	0.79	23.02	9.77	12.02	4.80	24.65	1.76	1.79	17.30
< 10	3.78										
Sum	100.00	3.33	1.38	19.84	14.13	11.74	5.28	23.98	3.26	2.55	12.80

Minor elements: head sample (%): S 0.23; BaO 0.23; Na_2O 0.34; Nb_2O_5 0,10.

The chemical and size compositions of the raw ore sample (ROM – run of mine) is shown in Table 1. On the average, SiO_2, CaO and MgO are the dominant components; this is consistent with a major presence of silicates and carbonates as the major minerals, followed by iron oxides/hydroxides. The P_2O_5 content is only 5.28 on the average, thus demonstrating that this is a low-grade apatite ore.

Chemical and mineral composition of the feed to the flotation concentration sample

The important effect of the pre-treatment of the raw ore was the decrease in the iron oxides value, from 14.13% to 9.07% (Table 2).

Table 2 – Chemical composition of the flotation feed.

Elements	Al_2O_3	BaO	CaO	Fe_2O_3	MgO	P_2O_5	SiO_2	TiO_2	K_2O	LOI
Mass %	1.50	0.22	21.26	9.07	12.51	5.65	25.52	2.98	2.51	14.13

Obviously, this is a consequence of the partial removal of magnetite, due to the magnetic separation; this also has affected ilmenite, since the TiO_2 content decreased a little. However, the pre-treatment had little effect on the contents of CaO, MgO, SiO_2 and P_2O_5.

The mineral composition of the flotation feed is shown in Table 3. The percentages of the minerals were calculated by a combination of X-ray diffraction with the Rietveld-based method, QEMSCAN and chemical assays.

Table 3 – Minerals in the flotation feed sample.

Major minerals	Mass %	Minor minerals	Below 1.0% each
Phlogopite/vermiculite	26.2	Barite	
Diopside/richterite	17.5	Pyrochlore	
Calcite	15.2	Zirconium minerals	
Apatite	10.9	Manganese minerals	
Iron oxy/hydroxides*	8.2	Olivine/serpentine	
Dolomite**	6.9	Titanite	
Ilmenite	4.7	Pyrite	
Quartz	2.9	Crandallite	
Anatase	1.7	Monazite	
Perovskite	1.0	K-feldspar	
		Magnesite	
Sum	95.2		4.8

* The magnetite content is much higher than the amounts of hematite and goethite.

**Includes a small amount of ankerite.

Microstructure study

The following abbreviations are used to indicate the minerals present in the scanning electron microscope images: apatite: Ap; calcite: Ca; dolomite: Do; phlogopite: Ph; diopside: Di; richterite: Ri; magnetite: Ma; ilmenite: IL; quartz: Q; impregnation resin: Re.

Several particles making up the feed of the flotation tests are displayed in Figures 1, 2 and 3, in an increasing order of magnification. The several minerals portrayed show a quite coarse grain size (Figure 1), usually above 200µm, which is consistent with the magmatic origin and very low weathering degree of the rock ore. The minerals appearing in the SEM images are consistent with the chemical and mineralogical compositions determined by instrumental techniques (Tables 2 and 3).

Apatite occurs in subhedral and anhedral grains, either as single or in locked particles. The apatite grains usually do not have inclusions, therefore being quite limpid, as e.g. in Figure 3. Dolomite also appears in relatively inclusion-free grains (Figure 2). Calcite, on the contrary, frequently contains minor and numerous inclusions of magnetite and ilmenite (Figures 2 and 3). Similar complex chemical, mineralogical and microstructure aspects have been reported for other low weathering apatite ores having similar origins, but from different sites (Chula *et al.*, 2004; Avelar, 2018;).

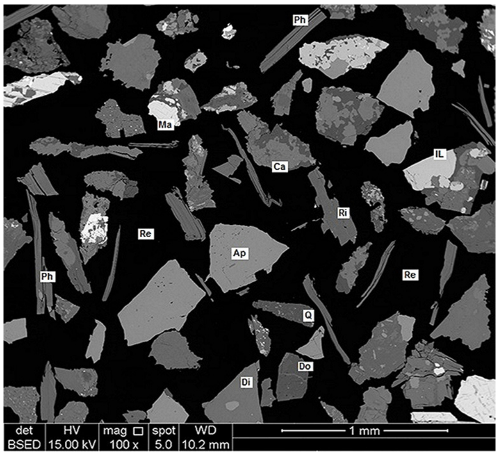

Figure 1 – Scanning electron microscope, backscattered electrons image (SEM, BEI). Particles of the flotation feed sample, in the < 0.300mm fraction. This image illustrates the variety of minerals in the sample. A few free apatite particles are seen; they have small and rare phlogopite and quartz inclusions.

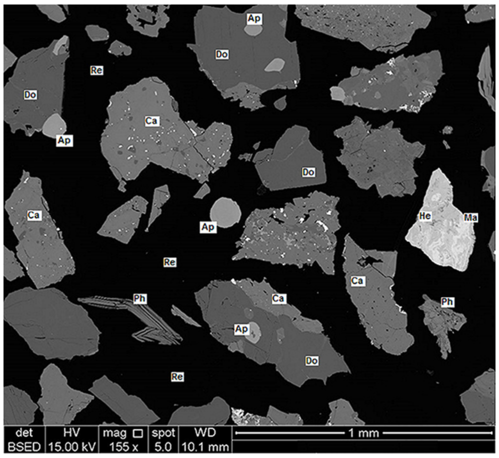

Figure 2 – Scanning electron microscope, backscattered electrons image (SEM, BEI). Particles of the flotation feed sample, in the < 0.300mm fraction. Area with many gangue particles; apatite appears in locked grains; only one free apatite particle is located near the image center.

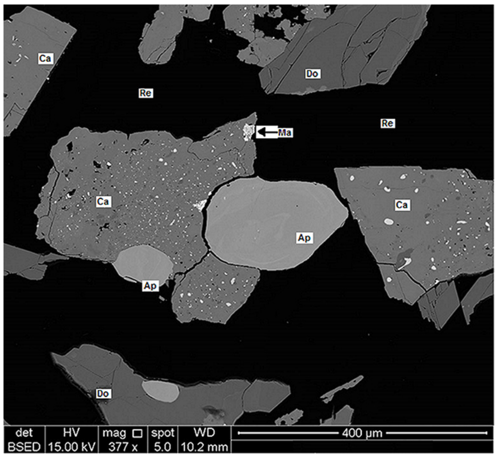

Figure 3 – Scanning electron microscope, backscattered electrons image (SEM, BEI). Particles of the flotation feed sample, in the < 0.300mm fraction. Mixed particles: apatite associated to calcite at the center; apatite locked in dolomite, at the bottom. Calcite has minor magnetite inclusions.

Apatite liberation

With regards to the degree of liberation, the apatite already had a liberation of about 86% in the particle size fractions smaller than 210µm, considering only particles composed of 100% by weight of apatite (this is Gaudin's liberation concept). Now, if one considers a percentage between 80% and 100% of apatite in the locked particles, the liberation reaches values slightly below 90% (Figure 4).

Within the locked particles, apatite is associated mainly with calcite (8%), phlogopite (5%), pyroxene/amphibole (3%), and dolomite (2%). Associations of 1% and below were determined with quartz, magnetite, ilmenite and anatase.

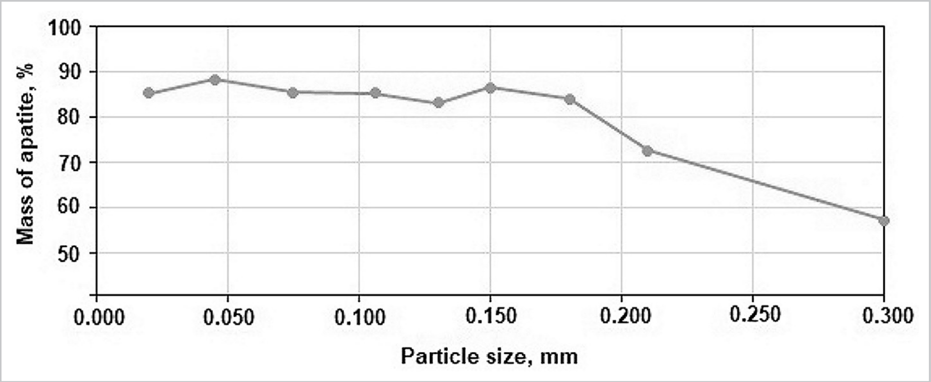

Figure 4 – Liberation of apatite, in function of size, for particles smaller than 0.500mm.

Flotation tests

The flotation tests were carried out in rougher, cleaner and recleaner stages. In a first stage, carbonate minerals were floated with the use of carbon dioxide. For this stage, the collector Liacid 1218 was used. This reagent is a fatty acid produced from medium-chain coconut oil and for its application as a collector, it was submitted to a previous saponification step with caustic soda (Carvalho, 2013).

Then, the feed was conditioned with the collector Liacid 1218, at the following dosages: 300g/t, 380g/t and 500g/t. Solids percentage was 60% in conditioning; afterwards it was lowered to 35% and the flotation tests with CO_2 gas were carried out, at the pH value of approximately 5.0. The floated product in this step fed the cleaner flotation, which was carried out until foam exhaustion. After the end of the carbonate flotation, the non-floated products were joined, and sent to the apatite flotation stage. The final carbonate concentrate (cleaner one) was filtered, dried, weighed and analyzed.

In the apatite flotation tests, corn starch, gelatinized with soda, was used as a depressant, at the 1000g/t dosage. The collector was a sodium sulfosuccinate, Lupromin 721. Conditioning was carried out with a solid percentage of 60%. The conditioning times were 5 minutes for each reagent, depressant and collector. The pH was maintained at 9.5, with the addition of sodium hydroxide, when necessary. After conditioning, the pulp was diluted to 35% and the apatite was floated with air in the rougher, cleaner and recleaner stages; the collector concentrations varied from 200g/t to 250g/t.

The overall P_2O_5 recovery was 61.8% and 12.0% the global mass recovery.

The compositions of the products of the flotation process are displayed in Tables 5 and 6 and Figures 5 and 6.

Table 5 – Chemical composition of the final apatite concentrate.

Elements	C	S	Al_2O_3	BaO	CaO	Fe_2O_3	MgO	P_2O_5	SiO_2	TiO_2	K_2O	LOI
Mass %	3.46	0.07	0.48	0.23	34.59	6.27	7.32	21.58	12.02	3.27	2.05	8.32

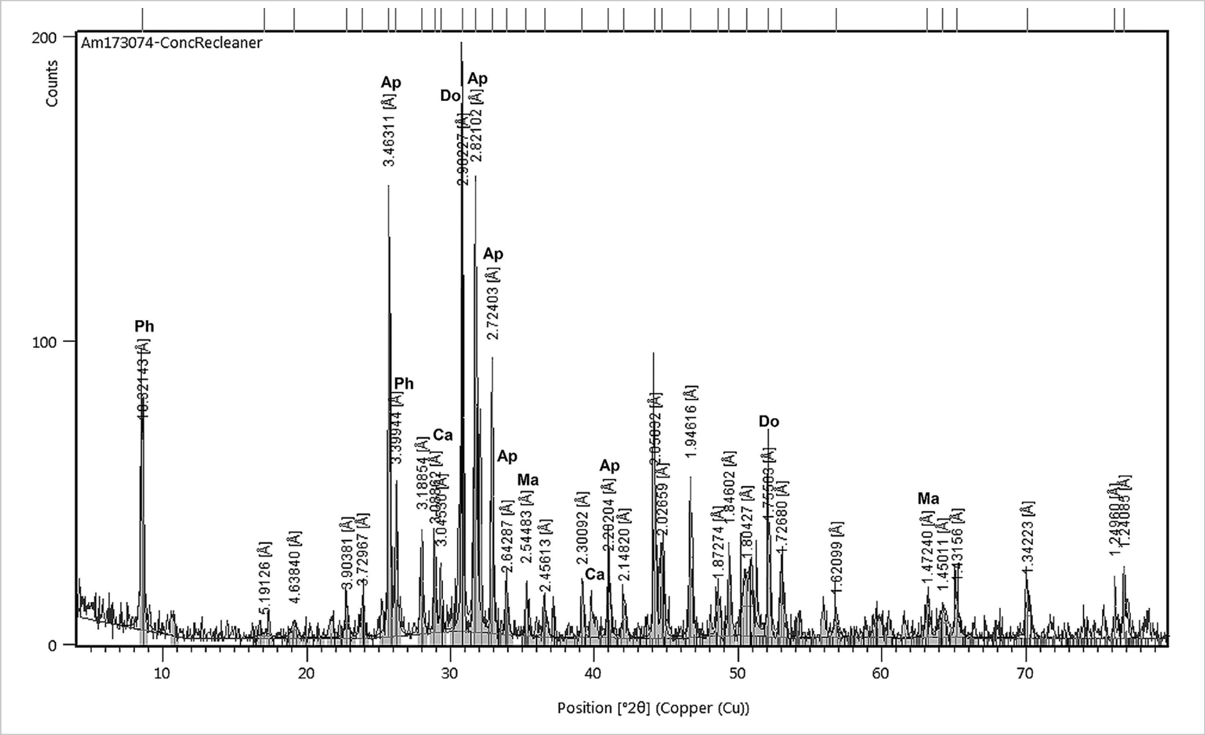

Figure 5 – X-ray diffractogram of the final apatite concentrate.

The minerals identified by X-ray diffraction in the final apatite concentrate were apatite (major), dolomite, phlogopite, magnetite and calcite (low concentration).

Table 6 – Chemical composition of the carbonates concentrate.

Elements	C	S	Al_2O_3	BaO	CaO	Fe_2O_3	MgO	P_2O_5	SiO_2	TiO_2	K_2O	LOI
Mass %	7.20	0.20	0.30	0.40	34.65	5.32	7.59	7.08	10.12	2.24	1.78	22.71

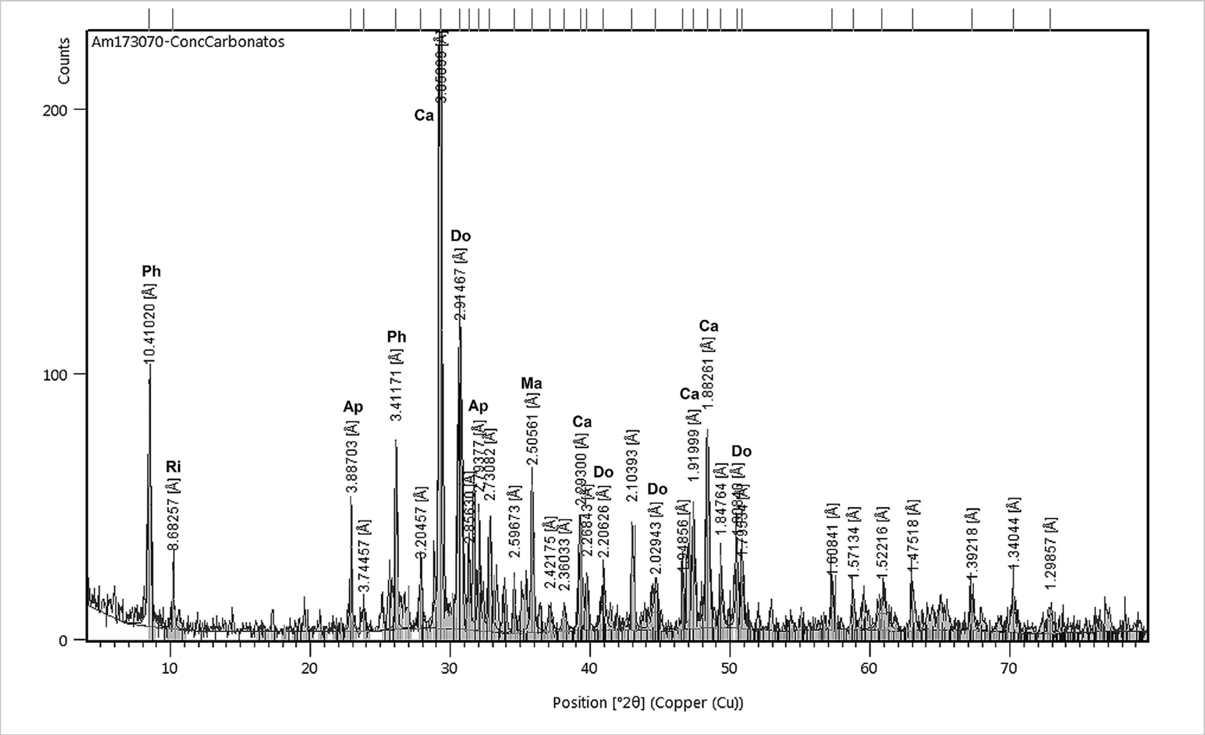

Figure 6 – X-ray diffractogram of the final carbonates concentrate.

X-ray diffraction has detected the following minerals: calcite (major), dolomite and phlogopite (medium concentration), richterite and apatite (low concentration), magnetite and hematite (traces).

From the data obtained in the characterization of the final apatite concentrate, although the P_2O_5 has increased substantially in relation to the original ore, it still contains significant amounts of impurities, mainly as carbonates, phlogopite and some minor iron oxides.

4. Conclusions

The ore studied proved to be really a fresh rock, with minor presence of secondary minerals. Accordingly, the mineral composition was very complex. Apatite, calcite, phlogopite and magnetite were the dominant minerals; dolomite, diopside, richterite, ilmenite, vermiculite and quartz occurred as middle-class minerals. The mineral grain sizes were rather coarse, usually greater than 200μm. Thirteen other minor and trace amount minerals have been identified.

A complex flotation scheme was used to produce separate carbonate and apatite concentrates. Two different anionic collectors and pH values, air and carbon dioxide as froth gases, starch depressant, pre-treatment with magnetic separation and desliming were the process operations and parameters used.

A significant improvement in the apatite concentration has been achieved: the initial 5.28% P_2O_5 tenor was raised to 21.58%. The overall P_2O_5 recovery was 61.8% and 12.0% the global mass recovery. However, the number of impurities was still significant with the presence of carbonates, phlogopite and minor magnetite.

Also, there was a considerable loss of apatite in the carbonate's concentration. The main problem was really selectivity, since the apatite liberation was relatively high, near 90%. Another issue to be improved would be the lowering of the silica content in the apatite concentrate. A search for a specific depressant for silicates, mainly for phlogopite, pyroxene/amphibole and quartz would be important.

The main conclusion is that the processing route presented herein is quite viable, but further research is necessary to improve the overall method.

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