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ALTERNATIVE REAGENTS IN PHOSPHATE ORE FLOTATION

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Abstract: To meet the growing demand for fertilizers, strategic in food production, efficient ways of concentrating its main raw material, phosphate rock, are essential. Moreover, when the phosphate ore has carbonated gangue, such as the mineral deposit of Araxá-MG, there is a selectivity difficulty in separating the mineral species, impairing the flotation performance. The search for reagents that present selectivity, low cost and high availability has been the subject of research. Thus, the objective of this work was to evaluate a depressor reagent (starch residue) and collector reagents (Amazon oil from Andiroba and Hydrocol) in the flotation of phosphate ore. For this, the previously characterized ore was subjected to flotation tests in a bench mechanical cell. The independent variables evaluated were type of collector, collector dosage and depressant dosage, with two levels and central point, according to the factorial design. The results revealed that Hydrocol, at minimum dosage levels, provided concentrates with higher P₂O₅ content (17.78%) and metallurgical recovery (66.29%). However, the Amazonian oil, at maximum dosage levels, presented similar contents, but with lower recovery values, indicating that it is a selective reagent and showing promise, considering that the oil is a residue of industrial processes.

Keywords: Flotation; Reagents; Phosphate.

INTRODUCTION

Brazil, over time, achieved a prominent place in the world in the agricultural sector. This is because there was an increase in food production that was made possible by the use of fertilizers in agriculture. However, despite the great demand for fertilizers in crops, around 80% of this input is obtained via imports, leaving the country in a situation of external dependence. Given this context, initiatives have been developed to increase

domestic production. One of these initiatives is linked to sustainable mining, seeking the maximum use of mineral deposits. Mining is the main source of raw material for the production of fertilizers (EPE, 2019; BENITE, 2015, REETZ, 2017).

The Araxá mineral deposit originated in a magmatic environment, with an alkaline-carbonatite complex. Due to weathering, the oxidized ore concentrates in the upper part of the deposit, as the mine deepens the ore becomes less oxidized towards fresh rock. However, the fresh rock has a lower ore content and changes in chemical and physical characteristics, causing low flotation yields, thus affecting the production of phosphate concentrate (GRASSO, 2015, CRUZ et al., 2011).

This scenario led to the development of technologies, so that it would be possible to make better use of this more complex ore. Thus, there are studies seeking to optimize concentration routes, which allow the production of phosphate concentrates within the market specifications for fertilizer production (SOUZA et al., 2014; GUIMARÃES et al., 2004).

These studies are often linked to the concentration stage due to the difficulty of separating the mineral-ore (apatite) from the carbonated gangue minerals (calcite and dolomite), due to the surface similarity existing between them. To work around this situation, reagents have been developed so that flotation presents selectivity. Studies such as those performed by Souza et al. (2014), Oliveira (2007), Carneiro (2018), Carneiro et al. (2021), Guimarães et al. (2004), Martins et al. (2019), Oliveira et al. (2019), among many others presented in the literature, bring fundamental studies, in addition to analyzing the performance of collectors and depressants. They show this scientific initiative in the search for optimal conditions

in phosphate ore flotation operations.

The variety of plant species of Amazonian origin, especially in Brazil, provides resources for obtaining alternative reagents for flotation systems. These fatty sources, such as Andiroba oil (*Carapas guianensi*), have a high potential for application due to their wide technical and economic availability, as they are endemic species in the region where they are found. Still, for some of them, it is possible to extract oils and fats from the residue of their use by other industries, reinforcing their importance (SILVA et al., 2018).

Paiva (2019) and Santos et al. (2022) developed fundamental studies using Andiroba oil in the flotation of apatite and carbonates. In the microflotation tests developed by the authors, the reagent proved to be very promising in the selective flotation of apatite. Therefore, this work is characterized as initial tests, for the attempt to transfer the fundamental study to bench flotation tests. Furthermore, it is one of the first initiatives to use the Andiroba oil-based collector in the flotation of a complex phosphate ore.

Therefore, this work aimed to evaluate the performance of collector reagents (Andiroba oil and Hydrocol) and a depressor reagent (starch residue), in the flotation of phosphate ore, from fresh rock, from Araxá-MG. For this, factorial design was used as a tool for planning tests and data analysis, evaluating the content and recovery of P₂O₅ from flotation products.

MATERIAL AND METHODS

In this study, a sample of phosphate ore from an outcrop of bebedourite was used, consisting of fresh rock, called BEB 01, from the Barreiro Carbonatite Complex, Araxá-MG. The sample was provided by the partner company, previously prepared, with adequate granulometry for the flotation tests. The sample preparation steps were crushing, grinding, magnetic separation and desliming.

Chemical analysis of the feed and products was performed by X-ray fluorescence spectroscopy. The BEB 01 sample had an initial P₂O₅ content of 6.55%, a value consistent with complex phosphate ores, such as the one studied by Carneiro (2018), who worked with a silico-carbonated phosphate ore, with an initial content of 6.08%. The CaO/P₂O₅, Fe₂O₃/P₂O₅ and Al₂O₃/P₂O₅ ratios were 3.24; 1.44 and 0.27, respectively. Since the chemical composition of the sample is shown in Table 1. The ore density was equal to $3,14 \pm 0,06 \text{ g/cm}^3$, obtained by pycnometry, as described by Sampaio and Silva (2007).

The granulometric analysis was carried out via wet sieving, in a suspended sieve. For this, the sieves used were 48# (0.296mm), 65# (0.209mm), 100# (0.148mm), 150# (0.105mm), 200# (0.074mm), 270# (0.052mm), 325 # (0.044mm) and 400# (0.037mm).

Particle size analysis revealed that 27.45% of the particles were below 37 μm .

	P₂O₅	Fe₂O₃	MgO	CaO	Al₂O₃
(%)	6,55	9,45	13,51	21,21	1,76
	TiO₂	SiO₂	BaO	SrO	Nb₂O₅
(%)	3,33	26,86	0,24	0,67	0,10

Table 1: Chemical composition of BEB 01.

Another important observation is that 80% of the particles (d_{80}) were below 120 μm , indicating that the sample had the appropriate granulometry for the flotation tests, considering that apatite presents a satisfactory degree of release in a granulometry below 212 μm .

REAGENT PREPARATION

For flotation tests and reagent preparation, methodologies from previous work carried out by Santos (2017) and Carneiro (2018) were followed. The collector reagents selected were Andiroba oil (A1), an Amazonian oil, chosen based on the work of Paiva (2019) and, for comparison purposes, a conventional reagent was used, a partially hydrogenated soybean oil, known as Hydrocol. The selected depressant was residual potato starch, based on the results obtained by Carneiro (2018).

As for the preparation of these reagents, oil A1 and Hydrocol were saponified to obtain the collector. Thus, 5 g of oil, 7.85 g of water, 7.15 g of NaOH and 180 g of water were weighed for dilution. After that, the oil, water and NaOH were mixed in a magnetic stirrer for 10 minutes. Then, dilution water was added and stirred for another 10 minutes. The solutions prepared with a concentration of 2.5% (m/m) of oil, and an oil:soda ratio of 7:1. Figure 1 shows the two collector solutions after saponification.

For the depressant, gelatinization was carried out, weighing 5 g of starch, 45 g of water, 12.5 g of NaOH, and 104.16 g of dilution water. After that, the starch, water and NaOH were mixed in a mechanical stirrer at 500 rpm for 10 minutes. Then, dilution water was added and stirred for another 10 minutes. The solutions were prepared at 3% (m/m) and a starch:soda ratio of 4:1.



Figure 1: Hydrocol (left) and Oléo A1 (right) collector solutions.

FLOTATION TESTS

The flotation tests were carried out in a Denver mechanical cell, with a 1.5 L tank (useful volume of 1.25 L). Figure 2 illustrates the equipment. The mass percentage of solids during conditioning and flotation was 50% and 25%, respectively. The ore conditioning time with the collector and with the depressant was equal to 5 minutes. After conditioning, air was introduced through the depression created by the impeller. Flotation time was about 2 min, foam collection time. The floated and sunken products were dried in an oven, then weighed, quartered and sent for chemical analysis.



Figure 2: Denver mechanical cell.

During conditioning and flotation, it was observed that the pH remained between 9.4 to 9.6, thus, no pH regulator was used.

TEST PLANNING

Regarding the planning of the tests, the factorial design was used. 2^k , with $k=3$, where the independent variables were collector type, collector dosage and depressant dosage, in two levels and with 8 central points, totaling 16 tests. The response variables analyzed were P₂O₅ content and metallurgical recovery.

The metallurgical recovery (or P₂O₅ recovery) was calculated by Equation 1, using the mass of the feed (A), concentrate (C) and the levels of

P₂O₅ in the feed (a) and in the concentrate (c), for each test.

$$R = \frac{c.C}{a.A} * 100 \quad (1)$$

For statistical analysis, Minitab software was used. The experimental planning matrix is presented in Table 2 and the conversion of the levels used in Table 3. As the variable type of collector is qualitative, 4 tests were proposed at the central point using the Hydrocol collector and 4 tests with Andiroba oil (A1).

11	1	0	0
12	-1	-1	-1
13	-1	0	0
14	-1	1	-1
15	-1	-1	1
16	-1	0	0

Table 2: Factorial planning matrix.

Levels	Type of Collector	Collector Dosage	Depressor Dosage
1	Hydrocol	500	350
0	Hydrocol or A1 oil	350	225
-1	A1 oil	200	100

Table 3: Levels of independent variables.

RESULTS AND DISCUSSION

The results of content of P₂O₅ and metallurgical recovery of each test are presented in Table 4. The Table shows, in general, that the Hydrocol collector (tests 1, 3, 4, 5, 7, 9, 10 and 11) provided higher metallurgical recoveries when compared to oil of Andiroba, under the same conditions. Both reagents are based on fatty acids, adsorb on the apatite surface by a chemical mechanism (Oliveira, 2007 and Santos et al., 2022) however, the composition of the acids is different. According to Santos et al. (2022), Andiroba oil is rich in oleic, palmitic, stearic and linoleic acids. This diversity of carbon chains affects the conformation of the hydrophobic film on the mineral particles and promotes packing on the lower surface (less compact) to a more homogeneous reagent, due to differences in size and conformation of the hydrocarbon chains of the fatty acids present in the oil. What can justify different recovery results for different types of vegetable oils.

Essay	Type of collector	Collector Dosage	Depressant Dosage
1	1	1	1
2	-1	0	0
3	1	-1	1
4	1	-1	-1
5	1	0	0
6	-1	0	0
7	1	1	-1
8	-1	1	1
9	1	0	0
10	1	0	0

EEssay	Type of collector	Collector Dosage (g/t)	Depressor Dosage (g/t)	Content P ₂ O ₅ (%)	Recovery P ₂ O ₅ (%)
1	Hydrocol	500	350	10,04	97,92
2	A1	350	225	16,63	13,86
3	Hydrocol	200	350	15,02	79,54
4	Hydrocol	200	100	17,78	66,13
5	Hydrocol	350	225	11,81	94,12
6	A1	350	225	13,65	3,12
7	Hydrocol	500	100	10,09	95,27
8	A1	500	350	16,93	34,03
9	Hydrocol	350	225	11,71	99,01
10	Hydrocol	350	225	11,97	95,49
11	hydrocol	350	225	15,66	83,23
12	A1	200	100	11,48	1,42
13	A1	350	225	15,23	17,72
14	A1	500	100	15,21	37,99
15	A1	200	350	8,58	1,27
16	A1	350	225	15,29	15,06

Table 4: Flotation results.

Table 4 also shows that the highest P₂O₅ content, 17.78%, was reached in test 4, when minimum dosages of reagents were used (200 g/t of Hydrocol collector and 100 g/t of depressant). The highest recovery, 99.01%, was obtained in test 9, with intermediate level reagent dosages (350 g/t of Hydrocol collector and 225 g/t of depressant). The lowest P₂O₅ content, 8.58%, and the lowest metallurgical recovery (1.27%) were for the conditions of test 15, with Andiroba oil (A1), minimum collector dosage and maximum depressant dosage. However, despite the metallurgical recoveries presented by oil A1 being lower, in tests 2 and 8 the concentrate showed P₂O₅ contents of 16.93% and 16.63%, respectively. In these cases, reagent dosing conditions ranged from intermediate to maximum. Which confirms the results of Santos et al. (2022), who achieved maximum apatite recovery and better selectivity in the apatite/carbonate system at Andiroba oil concentrations higher than those reported in the literature when comparing with pure sodium oleate.

In the flotation tests with the saponified Hydrocol, the foam presented small and mineralized bubbles, as can be seen in figure 3. However, using Andiroba oil, a smaller amount of bubbles was observed, being larger and less mineralized, as illustrated in the figure 4. Indicating absence of foaming action in the Andiroba oil collector, for the tested conditions.

This difference in the bubbles obtained with the reagents may be related to the flotation pH. The microflotation results performed by Santos et al. (2022) with the Andiroba oil collector showed that the pH of maximum apatite floatability was equal to 7.5. At more alkaline pH, they observed a drop in apatite floatability. In this study, the pH remained between 9.4 and 9.6, probably due to the sodium hydroxide added in the

preparation of the reagents, the alkalinity of the medium may have affected the speciation of the reagent, which was predominantly in the ionic form, impairing foaming.



Figure 3: Floated with Hydrocol.

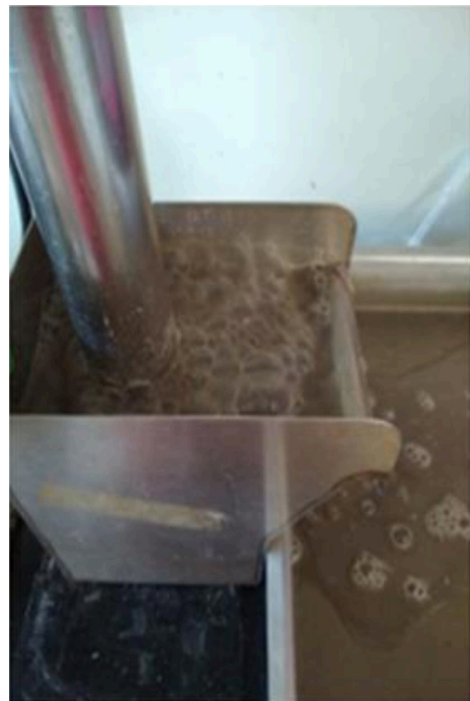


Figure 4: Floated with oil A1.

For the metallurgical recovery, it was observed that the type of collector (A) and its dosage (B) also have significance on the operation, however, they appear as significant main effects, different from the previous analysis, as shown in figure 6. positive effect for variables A and B indicate that moving from level -1 (oil A1) to level +1 (hydrocol) increased metallurgical recovery, as previously discussed. Likewise, increasing the collector dosage leads to greater surface hydrophobization and greater collection of particles by air bubbles.

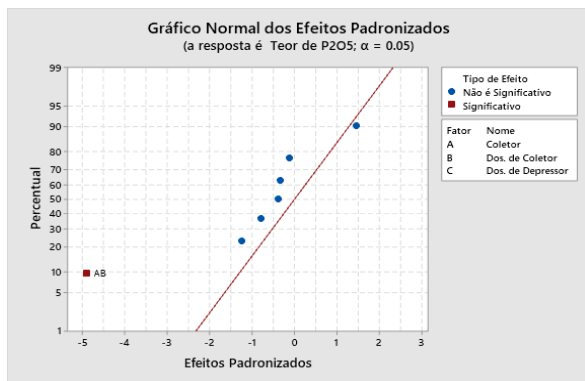


Figure 5: Significance of the independent variables on the content of P_2O_5

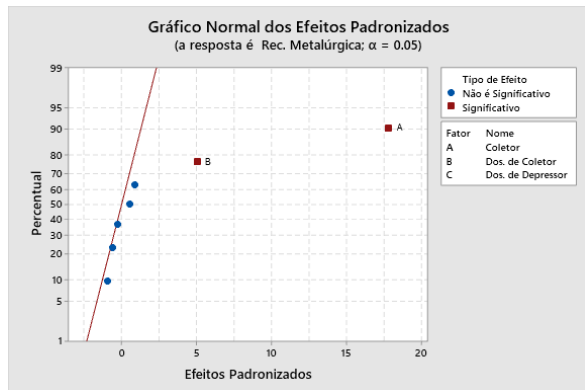


Figure 6: Significance of the independent variables on the recovery of P_2O_5 .

Figure 7 illustrates this behavior for P_2O_5 recovery. When moving from the minimum collector dosage to the intermediate dosage, there is an increase in recovery. This behavior is maintained when increasing the dosage

even more, going from level 0 to +1. This shows that increasing the collector dosage can influence the hydrophobization of the gangue minerals, since the P_2O_5 content also decreases in these cases. The fact that the dosage of the depressant is not a significant variable may be linked to its lower range of variation, and in future work, a larger dosage range of this reagent may be tested.

In an optimization scenario, the statistical analysis also confirmed what was observed in the previous results. An optimal scenario would be obtained using saponified Hydrocol, with the minimum dosages of reagents, with a P_2O_5 content of 17.13% and a metallurgical recovery of 69.75%. All these observations of the variation of reagent dosages on the P_2O_5 content are also presented in figure 8.

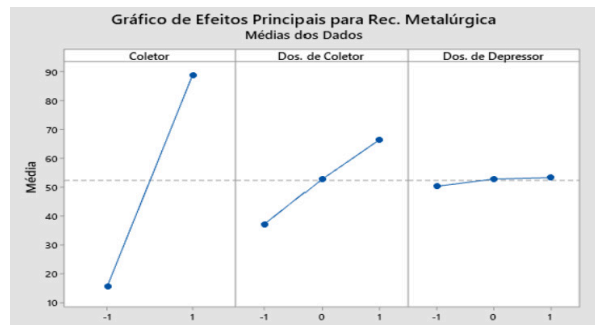


Figure 7: Analysis of main effects on metallurgical recovery.

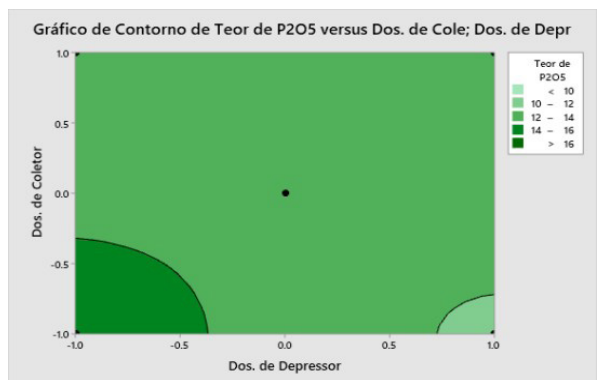


Figure 8: Outline of P_2O_5 content versus reagent dosages.

Another optimal scenario, using Andiroba oil as collector, contemplates the highest dosages, that is, 500 g/t of collector and 350 g/t of depressant, returning a P₂O₅ content of 17.58% and metallurgical recovery of 30.41%.

Finally, the CaO/P₂O₅, Al₂O₃/P₂O₅ and Fe₂O₃/P₂O₅ ratios generally decreased. In the case of the CaO/P₂O₅ ratio, it was greater than 1.6. The Fe₂O₃/P₂O₅ ratio remained below 0.095. The Al₂O₃/P₂O₅ ratio also remained below 0.095, with the exception of tests 1, 12 and 15. Although they did not reach the values specified by Oliveira (2007), as market parameters, there was a decrease in the values of these ratios in relation to the initial values. This selectivity gain indicates that Andiroba oil has high potential as a renewable resource for the production of selective flotation collectors as alternatives to those traditionally used in phosphate concentration circuits.

CONCLUSIONS

Flotation tests revealed different characteristics of the reagents used. When using Hydrocol, the flotation showed a large number of bubbles, small and well mineralized. When using Andiroba oil, the flotation showed a small number of bubbles, large and little mineralized. Consequently, a drop in metallurgical recovery was observed when the oil was used as a collector, due to the lack of foam. This may be related to the pH, which remained between 9.4 and 9.6 during conditioning and flotation.

Regarding the P₂O₅ levels obtained, the tests showed levels, in general, above 10% (except test 15) and the metallurgical recovery remained between 1.27% and 97.92%. The results of the chemical analysis, together with the statistical analysis, showed that the type of collector and its dosage have significance in the process. In an optimal scenario, saponified

Hydrocol must be used as a collector with minimum collector and depressant dosages. If saponified Andiroba oil is fixed, higher dosages of these same reagents would be necessary for apatite flotation.

In general, despite the metallurgical recovery values obtained by the A1 oil being lower than the values obtained in the tests using hydrocol saponified, the chemical and statistical analyzes showed that this collector presented selectivity against carbonates. This indication indicates that it is a promising reagent. Furthermore, it is interesting because it is a reagent derived from a residual substance, originating from a plant species endemic to the Amazon. This fact is very important in the search for alternative, selective, low-cost, readily available reagents that can be applied in the mineral industry.

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