FLOTATION ROUTES FOR A PHOSPHATE ORE BEARING SILICATE-CARBONATE GANGUE

Rodrigo O. Albuquerque[1], Antonio E. C. Peres[2]*, José A. Aquino[1], Carlos A. Pereira[3]

[1] CDTN/CNEN, Av. Antônio Carlos, 6627, 31270-901 Belo Horizonte, MG, Brazil
[2] Escola de Engenharia UFMG, Av. Antônio Carlos, 6627, 31270-901 Belo Horizonte, MG, Brazil
[3] Escola de Minas UFOP, Campus Morro do Cruzeiro, 35400-000 Ouro Preto, MG, Brazil
*Corresponding author: aecperes@demet.ufmg.br

ABSTRACT

This laboratory scale investigation addressed two different process routes for the concentration of a phosphate ore bearing a silicate-carbonate gangue: (i) bulk apatite and calcite flotation followed by calcite flotation in the presence of phosphoric and citric acids; (ii) calcite flotation in the presence of carbon dioxide followed by apatite flotation. The target of selectively separating apatite from the contaminating silicates and carbonates was achieved. Following the flotation experiments, calcite zeta potential determinations were performed aiming at clarifying the mechanisms that rule the adsorption of the soybean bran oil soap onto the mineral surface in the presence of the modifying agents phosphoric acid, citric acid, and carbon dioxide.

Keywords: flotation; flotation reagents; flotation depressants

1. INTRODUCTION

Ores presenting complex mineralogical associations, such as the Brazilian phosphates bearing silicates and carbonates in the gangue, correspond to a significant fraction of the local reserves and present poor response to concentration via flotation or even lack of a process route for economical recovery. The major Brazilian phosphate reserves of this type are located in Minas Gerais state (Tapira and Araxá), Goiás state (Catalão), and Ceará state (Itataia). Itataia´s deposit outstanding feature is the association between phosphate and uranium, representing the largest Brazilian uranium reserve and the only significant phosphate reserve in the north of the country.

Fundamental studies involving contact angle measurements, zeta potential determinations, Hallimond tube microflotation, laboratory and pilot scale tests have been extensively performed to improve the selectivity between apatite and the sparingly soluble gangue minerals. The poor selectivity in these systems was attributed by Hanna and Somasundaran [1] to similarities in electrokinetic, solubility, and surface chemistry properties of the minerals.

Different process routes for the concentration of phosphate ores bearing silicate-carbonate gangue are mentioned in the literature:

i. bulk apatite/carbonate flotation with fatty acids at alkaline pH, followed by carbonate flotation at pH 5.5 modulated with phosphoric acid [2,3,4,5,6] or citric acid [7,8];

ii. direct apatite flotation with sarcosinate, plant practice at Vale Fertilizantes' Cajati concentrator in Brazil [9], and at Siilinjarvi´s concentrator in Finland [10];

iii. carbonate flotation with oleic acid at pH 5.5 modulated with phosphoric acid followed by silicates flotation with amine at neutral pH [11].

The chemical adsorption of carboxilates onto the surfaces of calcium bearing minerals resulting in the formation of insoluble soaps has been the mechanism proposed by several researchers. French [12] suggested the chemisorption of oleate onto fluorspar. The same mechanism was suggested by Peck and Wadsworth [13] for the system oleate / calcite and fluorspar. Oleate anions replace, respectively, CO^{2-} and F^{2-} in the mineral lattice forming a surface layer of calcium oleate.

The adsorption mechanism is related with the pH. Hanna and Somasundaran [1] showed that the physical adsorption of oleic acid onto fluorspar prevails at low pH values. Under alkaline conditions the mechanism is purely chemical. Mishra [14], based on microflotation experiments of apatite and calcite with sodium oleate, came to the conclusion that the same mechanism rules both adsorption systems. For pH values lower than the isoelectric point physical adsorption occurs changing to chemisorption above the IEP. Maltesh et al [15] proposed the formation of hydrogen bonds between fluor atoms, present in the fluorapatite lattice, and oleate as the adsorption mechanism for the system.

2. MATERIALS AND METHODS

Size analysis was performed by combined screening (Tyler series) and the particles size analyser Sympatec Helos. X-ray fluorescence (EDX-720, Shimadzu) was the analytical technique for P_2O_5 and SiO_2, while $CaCO_3$ content was determined by calcining. The semi-quantitative mineralogical characterization was carried out with the use of the powder method (Rigaku´s X-ray diffratometer, model Geigerflex, semi-automatic, curved graphite crystal monochromator, copper tube).

A laboratory mechanical flotation machine (3 L tank), manufactured by DARMA (model D-1, Sub-A), provided with a mechanical froth scrapper, was used.

Two different process routes were evaluated: (i) bulk apatite and calcite flotation followed by calcite flotation in the presence of phosphoric and citric acids; (ii) calcite flotation in the presence of carbon dioxide followed by apatite flotation.

The reagents scheme for route (i) was based on former worker by Aquino [5,6]. The use of citric acid instead of phosphoric acid as apatite depressant was suggested by Louzada [7]. The use of carbon dioxide in route (ii) was based on investigations by Biswas [16] and Sampat Kumar [17].

The flotation reagents were: saponified soybean bran oil (collector supplied by Óleos Vegetais Pirapora), Flotanol D25 (polyalkylene glycol ether frother, supplied by Clariant S/A), sodium hydroxide, phosphoric acid, citric acid, and carbon dioxide.

Investigation by Albuquerque [18] indicated that the use of depressants for silicates was not required in route (i) and suggested conditions for the bulk flotation: collector 1,200 g/t; frother 25 g/t; pH 9.5.

Zeta potential determinations of a pure calcite sample were performed in the apparatus ZM3-D-G, Zeta Meter System 3.0+.

3. RESULTS

Characterization
The size distribution of the flotation feed is illustrated in figure 1, showing 2.9% retention in 210 μm and 32.7% passing 37 μm. The results of chemical analyses, Bulk flotation followed by calcite flotation.

The addition of depressant for silicates was not required. The bulk flotation stage was followed calcite flotation at pH = 5.5 modulated, respectively, by phosphoric and citric acid. The results of test T1 (pH control with phosphoric acid H_3PO_4) are presented in figure 2. P_2O_5 grade reached only 27.86% at a recovery level of 87.6%.

presented in table I, indicate P_2O_5 content 17.73%, contaminants grades, $CaCO_3$ and SiO_2, 20.78 and 24.14%, respectively. The mineralogical characterization showed that, beyond apatite, calcite and silicates (albite, quartz, biotite, flogopite, montimorillonite, vermiculite, and amphiboles) are present in the flotation feed. The calcite sample used in the zeta potential determinations presented a purity degree of 99% $CaCO_3$.
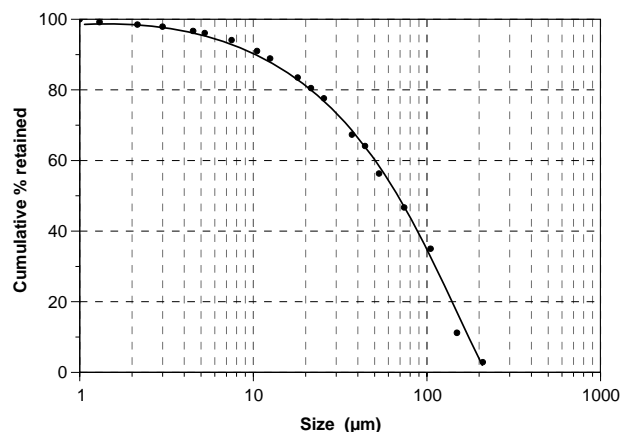

Figure 1 - Size distribution of the flotation feed.

Table 1 - Chemical composition of the flotation feed

Species	Grade (%)
P_2O_5	17.73
Total CaO	34.00
$CaCO_3$	20.78
SiO_2	24.14
Fe_2O_3	3.39
Al_2O_3	9.32
MgO	1.40

Similar recovery, 87.3%, was achieved in test T2 (pH control with citric acid $H_8C_6O_7$), but the P_2O_5 grade was significantly higher reaching 32.46%. The results are illustrated in figure 3. Nevertheless the dosage of citric acid required to set the pH at 5.5 is much higher than that of phosphoric acid.
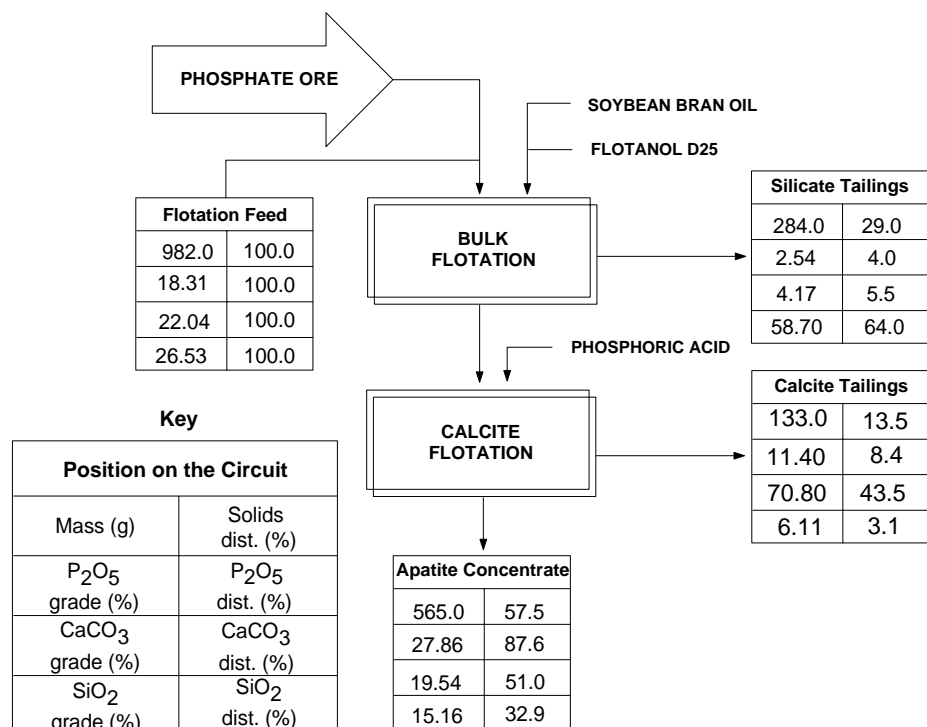
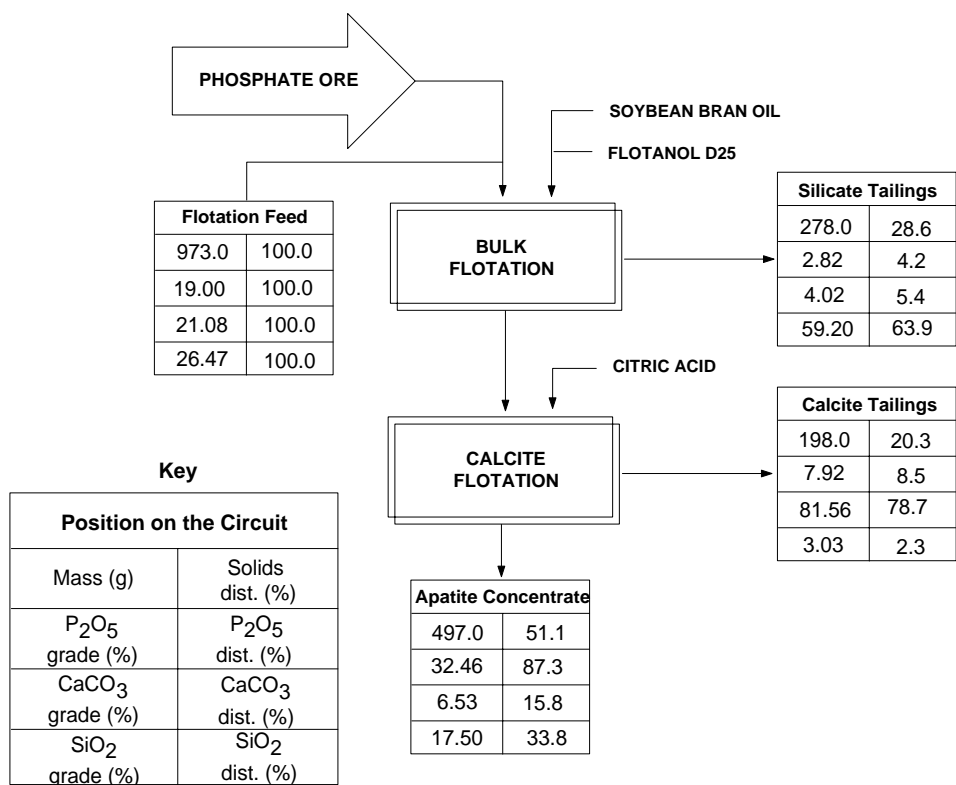Figure 2 - Mass and metallurgical balance test T1.

Figure 3 - Mass and metallurgical balance test T2.

Calcite flotation followed by apatite flotation.

The investigated variables were carbon dioxide (NL/min) flow rate and soybean bran oil and Flotanol D25 dosages. The pH was reduced from its natural value, 8.3, to 6.0 due to carbon dioxide addition. The collector dosage was set at 120 g/t. The $CaCO_3$ recovery was 67%, at the expense of 9% P_2O_5 loss. The next step was the definition of the conditions for the separation between calcite and silicates. P_2O_5 recovery was strongly affected by the system pH, improved results being achieved at 10, in comparison with those obtained at pH 9. The mass and metallurgical balance of the best test using the route calcite flotation followed by apatite flotation, test T3, is illustrated in figure 4. The P_2O_5 grade reached 32.48% at the recovery level of 85.5%, indicating the high selectivity of the proposed route.
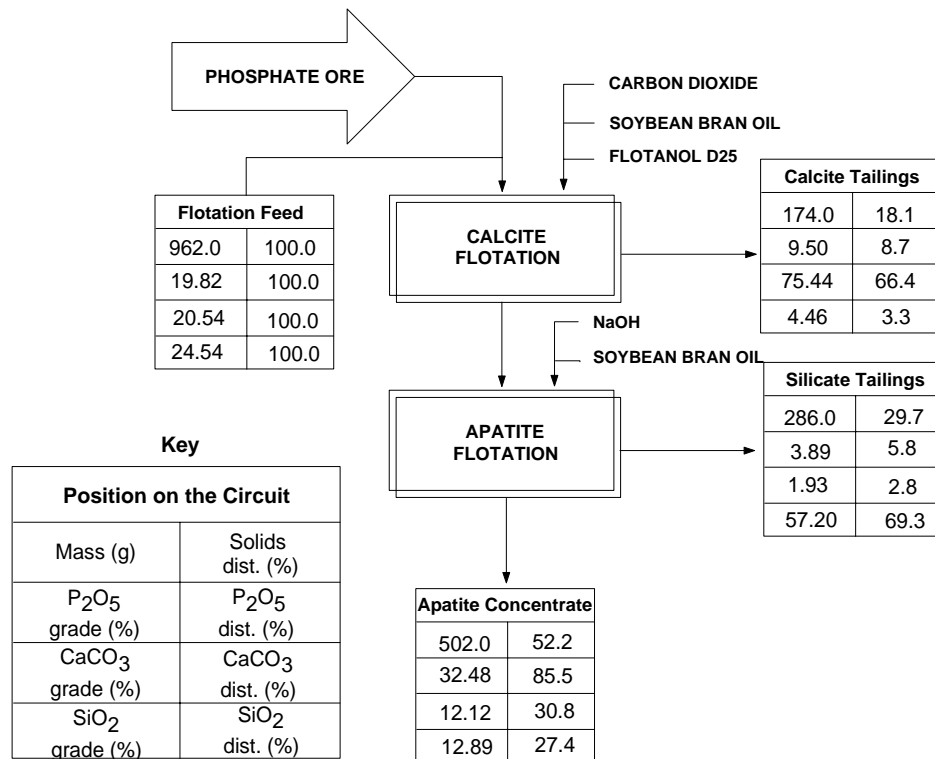

Figure 4 - Mass and metallurgical balance test T3.

Zeta potential determinations.

Different approaches are available in the technical literature explaining the mechanism of apatite depression and carbonates flotation in slightly acidic medium, in the presence of fatty acids. The most plausible mechanism was proposed by Tanaka et al [19] addressing the selectivity in the separation apatite/dolomite with pH modulated by phosphoric acid. Orthophosphate ions adsorb onto both minerals surfaces via hydrogen bonding, rendering them hydrophilic. Under slightly acidic conditions carbon dioxide (CO_2) is formed at the dolomite surface reducing the hydrogen bonds strength and facilitating the collector adsorption onto this mineral while apatite remains hydrophilic.

The results of calcite zeta potential determinations in the presence of modifying agents are presented in table 2. The same zeta potential magnitude order (approximately -15 mV) is achieved in the presence of both acids, in agreement with values reported by Louzada [7], in experiments with calcite from the same deposit.

30

It is likely that the mechanism proposed by Tanaka et al (1988) also explains the calcite/apatite separation in the case of the ore under investigation for both, citric and phosphoric, are week acids and the collector is chemisorbed.

Calcite zeta potential was also determined after previous conditioning with carbon dioxide (CO_2). The gas flow rate was 3.0 NL/min and the injection times were: 5, 10, 30, and 60 seconds. The natural pH, 9.6, was brought down to 5.7. The resulting zeta potential was slightly positive (+4,5 mV) for all injection times. The soybean bran oil soap is an anionic collector. The electrostatic contribution to the collector chemisorption onto calcite is an explanation for the low dosage (120 g/t) used in the experiments. The results agree with those achieved by Biswas [18] and Sampat Kumar [17] who also observed an increase in oleate adsorption due to the presence of carbon dioxide.

Table 2 - Calcite zeta potential as a function of pH ajusted with different modulators

pH	Zeta potencial (mV)
5.5 (phosphoric acid)	-14.0
5.5 (citric acid)	-15.7
5.7 (carbon dioxide)	+4.5

4. CONCLUSIONS

Both flotation routes investigated, bulk apatite and calcite flotation followed by calcite flotation in the presence of phosphoric and citric acids and calcite flotation in the presence of carbon dioxide followed by apatite flotation, resulted in selective separation between apatite and the contaminating mineral calcite.

Citric acid was more effective than phosphoric acid as apatite depressant in calcite flotation after the bulk stage.

The presence of carbon dioxide enhanced the selectivity of calcite flotation with respect to apatite even with the use of low collector dosage due to the suppression of the electrostatic barrier for the anionic collector adsorption.

5. REFERENCES

[1] Hanna, H.S. and Somasundaran, P., Flotation of salt-type minerals. In: Fuerstenau, M.V. (ed.) Flotation A.M. Gaudin Memorial Volume. Baltimore: AIME, v. 1, 1976, pp. 197-272.

[2] Zhang, P., Snow, R., El-Shall, H. and El-Midany, A., Depressants for beneficiation of phosphate/silica/carbonate ores. In: *Froth Flotation: A Century of Innovation. Part 3 - Flotation Chemistry*, ed. M.C. Fuerstenau, G. Jameson, G. and R.H. Yoon, 2007, pp. 555-574.

[3] Zheng, S., Cao, X., Ge, Z. and Song, W., Beneficiation studies on sedimentary siliceous and calcareous phosphate ores in China. In: *Beneficiation of Phosphates – Technology and Sustainability*, ed. P. Zhang, J.D. Miller, H. El-Shall, R. Stana, Chapter 21, SME Inc., Littleton, 2006, pp. 217-222.

[4] Abramov, A. A., Abramov, AL. AL., Onal, G., Atak, S., Celik, M. S. (1993) Mechanism of reverse flotation of calcareous phosphate ores. In: El-Shall, H., Moudgil, B. M., Wiegel, R., *Beneficiation of Phosphate: Theory and Practice*, Cap. 29, AIME.

[5] Aquino, J. A. (1987) Study on the Physical Beneficiation of Itataia´s Phosphorus-Uranium Bearing Ore. *CDTN/CNEN Report DETM CN-012/87*, 228 p. (In Portuguese)

[6] Aquino, J. A. (1991) Study on Column Flotation of Itataia´s Phosphorus-Uranium Bearing Ore. *CDTN/CNEN Report CT3-RT-041/91*, 185 p. (In Portuguese)

[7] Louzada, J.C.G., Calcite and apatite selective flotation with phosphoric and citric acids as depressants. Ms.C. Thesis, COPPE/UFRJ, 2008, 58 p. (in Portuguese)

[8] Sis, H. and Chander, S., Reagents used in the flotation of phosphate ores: a critical review. Minerals Engineering, 2003, 16, 577-585.

[9] Guimarães, R.C., Araujo, A.C. and Peres, A.E.C., Reagents in igneous phosphate ores flotation. Minerals Engineering, 2005, 18, 199-204.

[10] El-Shall, H., Zhang, P., Abdel-Khalek, N.A. and El-Mofty, S., Beneficiation technology of phosphate: challenges and solutions. Minerals & Metallurgical Processing, 21(1), 2004, 17-26.

[11] Abdel-Khalek, N. A. (2000) Evaluation of flotation strategies for sedimentary phosphates with siliceous and carbonates gangues. *Minerals Engineering*, v. 13, No. 7, p. 789-793.

[12] French, R.O., The quantitative application of infrared spectroscopy to studies in surface chemistry. Journal Phys. Chemistry, 1954), 58(10), 805-810.

[13] Peck, A.S. and Wadsworth, M.E., Infrared studies of the effect of F-, SO42- and Cl- ions on chemisorption of oleate on fluorite and barite. In: *Proc. International Mineral Processing Congress*, New York, 1965, pp. 259-267.

[14] Mishra, S.K., Electrokinetic properties and flotation behavior of apatite and calcite in the presence of sodium oleate and sodium metasilicate. Internacional Journal of Mineral Processing, 1982, 9, 59-73.

[15] Maltesh, C., Somasundaran, P. and Gruber, G.A., Fundamentals of oleic acid adsorption on phosphate flotation feed during anionic conditioning. Minerals & Metallurgical Processing, 1996, 156-160.

[16] Biswas, A.K., (1967) Role of carbon dioxide in flotation of carbonate minerals. Indian Journal of Technology, 1967, 5, 187-189.

[17] Sampat Kumar, V.Y. et al, Fundamental studies on the role of carbon dioxide in calcite flotation system. Trans. AIME-SME, 2003, 250, September, p. 182-186.

[18] Albuquerque, R.O., Process alternatives for the flotation of the Itataia´s phosphorous-uraniferous ore. Ph.D. Thesis, CPGEM/UFMG, 2010. 201 p. (in Portuguese)

[19] Tanaka, Y., Katayama, N. and Arai, S., Reagents in phosphate flotation. In: *Reagents in Mineral Technology*, ed. P. Somasundaran and B.M. Moudgil, B. M. Chap. 20, 1988, pp. 645-662.