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Floatability studies of wavellite and preliminary results on phosphorus removal from a Brazilian iron ore by froth flotation

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ABSTRACT

Along with other deleterious elements, phosphorus is an extremely harmful element found in iron ores used as a raw material in the steel making process. It is responsible for increasing its hardness and brittleness while decreasing its ductility. Reducing the phosphorus content in ores when the apatite is the main phosphorous mineral can be easily achieved through reverse flotation making use of anionic collectors to float the apatite and sodium silicate to depress the iron oxides. However, the phosphorus removal from iron ores other than igneous formations has been a challenge for most of the iron ore operations. This research aims to make a preliminary study of wavellite's floatability and to evaluate the reduction of phosphorus content by froth flotation from a Brazilian iron ore with a P content of 0.82%. Microflotation experiments of wavellite using anionic, cationic and amphoteric collectors were carried out in the basic pH range. Sodium silicate was evaluated as a depressant, and the presence of this reagent did not change significantly the wavellite's floatability. Dodecylamine showed the best floatability results, which were around 100% above pH 8. Bench flotation experiments confirmed the results of the microflotation experiments. During the bench experiments, flotation with amine as collector gave the lowest phosphorus content at the final iron concentrate. A concentrate containing 0.201% P with a mass recovery of 62.31% was achieved when a 150 g/t dosage of Flotigam EDA (an amine type collector) was used. In a bench experiment with Flotigam 2835 2L as collector led to a concentrate containing 0.312% P with a mass recovery of 90.24%. The collector Flotigam 2835 2L appeared to be more selective onto phosphates and aluminum silicates than the other amine.

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1. Introduction

The iron ore deposits have been exhibited an increasingly complex mineralogical composition. Minerals carrying phosphorus, aluminum and sulfides are becoming even more widespread in the deposits. Amongst these deleterious elements, the phosphorus is an extremely harmful element in the steel making process, causing detrimental effects on the product, such as increased hardness and brittleness and decreased ductility (Chiaverini, 2008).

The phosphorus in iron ore deposits may occur primarily as apatite, or in the form of secondary phosphates originated from the weathering of apatite, or in the crystal structures of hydrated iron oxides, especially in the goethite (Couto, 2009; Ler and Stanforth, 2003; Barbour, 1973). Apatite occurs more frequently

in Kiruna magmatic hydrothermal deposits type (Romer et al., 1994; Frietsch, 1978), whereas secondary phosphates are more often found in deposits that were submitted to a supergene enrichment process. The wavellite [Al₃(PO₄)₂(OH)₃·5H₂O] is one of the most common secondary phosphates present in high phosphorus content iron deposits.

The reduction of phosphorus content at the concentrate of some iron ore mines in Mexico, Sweden and Iran, where the apatite is the main phosphorous mineral, can be easily reached through anionic flotation with fatty acids collectors to float the apatite when sodium silicate is used to depress the iron oxides (Subramanian et al., 2002; Ranjbar, 2002; Rao et al., 1999; Pyatt, 1990; Siirak and Hancock, 1990). However, the phosphorus removal from iron ore other than of magmatic origin has been a challenge for most iron ore operations. Several researchers have studied hydrometal-lurgical process to reduce phosphorus content from sedimentary and magmatic iron ores; however the high costs, low efficiency, and the high environmental impact (high production of the red dusty) limit their industrial application (Jin et al., 2006; Cheng et al., 1999; Kokal, 1990; Araujo et al., 1994).

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Characterization studies have showed that the occurrence form of phosphorus will directly influence the efficiency of the concentration methods (Couto, 2009; Ler and Stanforth, 2003; Nunes, 2009). If the phosphorous minerals present a good liberation degree, phosphorus separation could be accomplished by flotation and magnetic separation. Such combination shows a great potential for minimizing the final concentrate phosphorous content of sedimentary iron ores.

With the objective of initiating studies about the froth flotation potential for producing concentrates with low phosphorous content, microflotation experiments of wavellite, the most common secondary phosphate that occurs in the iron ores and bench flotation experiments with a high-P iron ore were carried out. The experiments made use of collectors currently used in apatite and iron ores flotation plants. The experiments were performed in the basic pH range with absence and presence of sodium silicate as depressant.

2. Experimental

2.1. Sample preparation and characterization

The wavellite sample originated from Mauldin Mountain Quarries, Mauldin Mt., Montgomery Co., Arkansas, USA, was comminuted in a porcelain mortar and the size fraction +75 μ m $-300~\mu$ m was used in the microflotation experiments.

The high phosphorus content iron ore sample was acquired from a mine located at the Iron Quadrangle (Minas Gerais – Brazil) for using in the bench flotation experiments. This sample was comminuted in a ball mill to the size fraction $-106~\mu m$ followed by a desliming stage, eliminating particles under $10~\mu m$. Quantitative chemical analysis of the bench flotation experiments feed and the flotation products were performed by X-ray fluorescence (XFR).

Helium pycnometry analyses of wavellite and the iron ore sample were accomplished by using Quantachrome NOVA 1200. The wavellite's density was established as $2.34\,\mathrm{g\,cm^{-3}}$ and the iron ore sample's density as $4.87\,\mathrm{g\,cm^{-3}}$. Both samples, the wavellite mineral and the iron ore, were submitted to a qualitative chemical analysis using an X-ray diffractometer model PHILIPS PW 1710, Cu K α radiation and a graphite monochromator crystal. The results were analyzed by comparing the peaks intensities displayed in the diffractograms of the analyzed sample to a reference sample from the standard data base PDF-2 of the ICDD – International Centre for Diffraction Data. The software XPert HighScore version 2.1-2004 was also used in this analysis.

2.2. Microflotation experiments

The microflotation experiments were carried out in a modified Hallimond tube at selected pH values varying from 8 to 12. The solution volume in the tube was 180 mL with 1 g of wavellite sample. The air flow rate was set to 30 mL min⁻¹. The reagents used in the microflotation experiments are presented in Table 1. All the reagents, with the exception of sodium silicate and dodecylamine,

were prepared at the concentration of 10 mg L^{-1} . With regard to the sodium silicate, the concentrations used in the experiments were $5 \times 10^{-2} \text{ M}$, $5 \times 10^{-3} \text{ M}$, $5 \times 10^{-4} \text{ M}$, and $5 \times 10^{-5} \text{ M}$. The dodecylamine concentration evaluated was $1 \times 10^{-4} \text{ M}$. The pH was adjusted with hydrochloric acid (HCl) and sodium hydroxide (NaOH).

For the experiments with depressants, the mineral was conditioned for 5 min in 90 mL of depressant solution. Immediately after conditioning 90 mL of a 20 mg $\rm L^{-1}$ collector solution (resulting in 10 mg $\rm L^{-1}$ final concentration) were added. The wavellite's floatability with dodecylamine was not evaluated in the presence of depressant.

The reagents tall oil, fatty acid, and rice bran oil were saponified using sodium hydroxide at the ratio of 3:1 (by weight). The sodium sulfosuccinate solution was prepared at 60 °C and the dodecylamine was 100% neutralized with acetic acid. All the reagents were conditioned for 5 min. The flotation time in all experiments went on for 3 min.

2.3. Zeta potential measurements

The zeta potential measurements were carried out in the basic pH range using the microelectrophoretic technique (Zeta-Meter System 3.0 + ZM3-D-G) with direct video imaging. Samples of 0.025 g of the mineral under 38 μm were added into 200 mL of the electrolyte solution to prepare the suspensions. The suspensions were then settled down for a period of 24 h in such a way that the supernatant particles size was under 5 μm . Sodium nitrate (NaNO3) at the concentration of 5×10^{-3} mol L $^{-1}$ was used as supporting electrolyte. The experiments were also performed in the presence of dodecylamine (1 \times 10 $^{-4}$ mol L $^{-1}$). The pH values were adjusted with hydrochloric acid (HCl) and sodium hydroxide (NaOH).

2.4. Milling and desliming experiments

The iron ore sample was comminuted, first in a jaw crusher and afterward in a roll crusher to achieve the size range of 95% under 2.36 mm. A preliminary study of liberation was carried out by SEM/EDS analysis (scanning electron microscope/energy-dispersive spectrometer) for the fractions +150 µm and +75 µm.

After the crushing stage, the sample was transferred to a ball milling under the following conditions: 68 rpm; 2400 mL of pulp with 60% of solids and 30 min of grinding time. The final size of the sample was 94% under 106 μm , with about 15% of slimes (particles smaller than 10 μm). Desliming experiments were performed considering two different conditions: directly after the grinding or adding a scrubbing stage. The flotation experiments were carried out in pH 10.5. Effects of number of steps, sedimentation time, and stirring velocity were evaluated. Desliming experiments were carried out in a 2 L of pulp with 600 g of material. Besides eliminating slime particles, desliming stages would be able to reduce the phosphorus content from ores.

Table 1Reagents used in the microflotation experiments.

Reagent	Comercial name	Producer	Chemical formula
Tall oil	FA 01	Akzo Nobel	CH ₃ -(CH ₂) _n -COOH
Sodium sarcosinate	Berol 867A	Akzo Nobel	R-CH(CH ₃ NH)(COOH)
Sodium sulfosuccinate	Emulgin MC 711	Cognis	ROOC-CH ₂ -CH(COONa)(SO ₃ Na)
Rice bran oil	=	Igorvel	$CH_3-(CH_2)_n-COOH$
Fatty acid	Hidrocol	Hidroveg	$CH_3-(CH_2)_n-COOH$
Dodecylamine	=	Sigma-Aldrich	$CH_3-(CH_2)_{10}CH_2-NH_2$
Sodium silicate	-	Clariant	Na_2SiO_3

2.5. Bench flotation experiments

The bench flotation experiments were accomplished in a CDC flotation cell with a rotor stirring velocity of 1200 rpm and an air flow rate of 10 m³ min⁻¹. The cell pulp volume was 1100 mL and the ore sample weighted 500 g. The anionic and amphoteric collectors and the depressant were conditioned for 5 min, while the amines collectors were conditioned for 1 min.

All the reagents used in the microflotation experiments (shown in Table 1), with exception of dodecylamine, were also used in the bench flotation experiments. Some amines employed in industrial flotation processes were used as cationic collectors. The reagents are depicted in the Table 2 that also includes the corn starch, a universal iron oxides depressant.

3. Results and discussion

3.1. Mineral characterization

Wavellite was the only phase identified in the mineral sample diffratogram, based on comparison with the standard number 74-2250 of the ICDD data base PDF-2. Amorphization domes were not observed, indicating the absence of amorphous phases.

Concerning the iron ore, X-ray diffraction showed that the sample is essentially constituted by hematite, with wavellite and senegalite as main gangue minerals. Quartz and aluminum–silicate minerals did not appear in the diffratogram. X-ray fluorescence (XFR) chemical analysis revealed a high Fe content of 61.92%, 1.28% of SiO₂ and 3.3% of Al₂O₃. Phosphorus content of 0.82% is by far the most difficult contaminant to remove.

3.2. Microflotation experiments and zeta potential measurements

The results of wavellite floatability with anionic and amphoteric collectors, at basic pH conditions, are presented in Fig. 1. The highest values of floatability were achieved in the presence of fatty acid and its derivative compounds (tall oil and rice bran oil).

In the presence of fatty acid, the wavellite floatability was higher than 80% for all pH values evaluated. Above pH 11, the tall oil showed the same efficiency of fatty acid, with 100% of floatability, whereas the maximum value achieved with rice bran oil was 80% at pH 11.

The adsorption of fatty acids and its derived compounds onto the wavellite surface, in the alkaline pH, may occur essentially by chemisorption. According to the acid oleic species distribution diagram, neutral molecules (RCOOH) prevail in the acidic region whereas dissociated species (RCOO $^-$, (RCOO) 2_2 and (RCOO) $_2$ H $^-$) are predominant in the basic region (Ananthapadmanabhan and Somasundaran, 1988). The interaction between the dissociated ions of these acids with the surface Al cations may lead to the formation of aluminum oleate as insoluble salt onto the surface of the mineral. This mechanism has been suggested by several authors (Young and Miller, 2000; Hanumantha Rao et al., 1990; Chander and Fuerstenau, 1984; Antti and Forssberg, 1989).

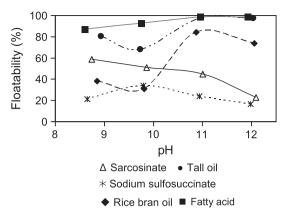


Fig. 1. Floatability of wavellite with anionic and amphoteric collectors. Collectors concentration: 10 mg L^{-1} .

The sodium sulfosuccinate was the least effective collector. A hypothesis to explain its poor efficiency would be the interaction of only one polar group, most probably the carboxyl group, with the aluminum sites at the wavelite surface. The sulfonate groups would, then, be free to interact with the solubilized species, providing, to a certain degree, a hydrophilic character to the wavellite. The adsorption of only one of the anionic groups would also be favored as the mineral solubility increases in the alkaline pH leading to an insufficient number of Al cations surface present at the wavellite surface.

In the alkaline pH range sarcosinates act as an anionic collector and its carboxyl group is the dissociated species ready to be adsorbed. The intermediate floatability achieved with sarcosinate can be partially explained by the fatty acid like behavior of this reagent in the alkaline pH range, providing a better floatability compared to the wavellite floatability when sulfosuccinate is used as a collector. Despite the negligible dissociation of the N-H groups in this pH range, they might present some polar character, leading to the interaction between the partially adsorbed molecules of the collector and the aqueous species allowing some hydrofilicity to the particles.

The Fig. 2 shows that the use of sodium silicate did not substantially modify the wavellite floatability in the basic pH range. Even in the presence of sodium silicate in the concentration of $5\times 10^{-3}\, \text{M},$ the fatty acid and its derived compounds displayed the best results of floatability. Sodium sulfosuccinate and sarcosinate were, again, the least effective collectors in the presence of sodium silicate.

The effects of the concentration of sodium silicate in the wavellite floatability at pH 10 are shown in Fig. 3. The sodium silicate did not substantially modify the wavellite floatability. As the sodium silicate concentration was increased from $5\times 10^{-4}\,\text{M}$ to $5\times 10^{-3}\,\text{M}$ the wavellite floatability also increased from 60% to 80% when using fatty acid. When tall oil was used as a collector the wavellite floatability reached the upper limit for a sodium silicate concentration of $5\times 10^{-4}\,\text{M}.$

 Table 2

 Cationic collectors and depressant reagents used in the bench flotation experiments.

Reagent	Comercial name	Producer	Chemical formula
Ether mono-amine	Flotigam EDA 3	Clariant	CH ₃ -(CH ₂) ₈ -O-(CH ₂) ₃ -NH ₂
Ether di-amine	Flotigam 2835 2L	Clariant	$CH_3-(CH_2)_{11}-O-(CH_2)_3-NH-(CH_2)_3-NH_2$
Vegetal fatty amine	Gemul NCD	Quimigel	=
Tallow amine	Gemul NSD	Quimigel	=
Corn starch	=	Maisena	$(C_6H_{10}O_5)_n$

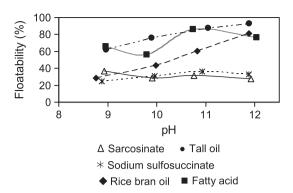


Fig. 2. Floatability of wavellite with anionic and amphoteric collectors in the presence of sodium silicate at concentration of 5×10^{-3} M. Collectors concentration: 10 mg L⁻¹.

The results of wavellite floatability when the dodecylamine was used as the cationic collector under basic pH conditions are presented in Fig. 4. The high floatability values obtained may be attributed to both chemical and electrostatic adsorption mechanisms of the amine dissociated species onto the wavellite surface. The strength of these interactions can explain the highest effectiveness of amine compared to the other collectors.

Since related by Laskowski et al. (1986), for a concentration of 1×10^{-4} M of dodecylamine hydrochloride precipitation will occur from pH 10.5 to 12. So, the high floatability values obtained in this pH range may be due to amine precipitation at the wavellite surface. At pH 8-10, dodecylamine is soluble for this concentration and the adsorption may be due to electrostatic forces. However, adsorption of amine onto wavellite may also be considered as result of precipitation of insoluble salt of aluminum onto wavellite surface. This adsorption would be result of ion-exchange reactions between the mineral anion and the collector cation. The contribution of electrostatic forces can be supported by the zeta potential measurements obtained in the presence of this reagent (Fig. 5). Wavellite surface is negatively charged in the pH range studied and the amine addition reverses the negative surface to positive from pH 7 to 11. The zeta potential reversion from negative to positive values can be explained by the dodecylamine adsorption onto the wavellite surface.

The zeta potential measurements rule out the possibility of anionic collectors' adsorption through electrostatic interaction, since both are negatively charged. However they do not clarify the degree of contribution of both electrostatic and chemical interactions for the amine adsorption. Based on these results, one can expect that bench flotation with cationic collectors would present better results than with anionic and amphoteric collectors.

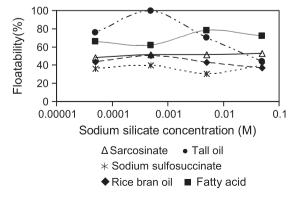


Fig. 3. Floatability of wavellite as a function of sodium silicate concentration at pH 10. Collectors concentration: 10 mg L^{-1} .

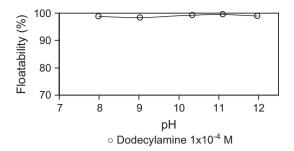


Fig. 4. Floatability of wavellite with cationic collector.

3.3. Desliming

According to the results showed in Table 3, the desliming experiments were not efficient to reduce the phosphorus content significantly. Nevertheless the slimes displayed high concentrations of Al₂O₃ and SiO₂. These high grades in the slimes can be attributed to aluminum silicates and aluminum phosphates in the finer granulometric fractions.

Scrubbing stages seem not to affect phosphorus reduction in the product. The decreasing in the scrubbing time from 6 to 2 min, for the same stirring velocity and sedimentation time caused a slight decrease of phosphorus content and distribution in the product. The increasing in the stirring velocity from 1800 to 2000 rpm led to an increase in the phosphorus distribution in the product.

Particles of phosphates with good degree of liberation in the coarser granulometric fractions might be responsible to the low efficiency of desliming concerning phosphorus reduction. Moreover, the presence of iron oxides and phosphates mixed particles may also contribute to the inefficiency of the process. The initial morphological analysis by SEM/EDS demonstrated that in the fractions over 150 μ m the phosphates particles already showed good degree of liberation, as can be seen at the Fig. 6a. Nevertheless, some mixed particles were detected in the fraction +75 μ m (Fig. 6b).

3.4. Bench flotation

Based on the results of the microflotation experiments, bench flotation experiments were carried out at pH 10.5 varying the concentrations of depressants and collectors. The different products of desliming experiments were used as the bench flotation experiments feed. Taking into account the final concentrate phosphorus content, the best results for anionic and amphoteric collectors are presented in Table 4.

According to the microflotation experiments, the sodium sulfossuccinate would be the least effective collector. In fact, fatty acid showed the best result considering the phosphorus content at

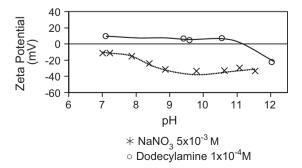


Fig. 5. Zeta potential curves of wavellite with cationic collector and sodium nitrate.

Table 3Results of desliming experiments in pH 10.5.

Condition	Products	Grade (%)				P distribution (%)	Mass recovery (%)
		Fe	SiO ₂	Al_2O_3	P		
No scrubbing; 4 steps; sedimentation time: 8 min	Feed (calc.)	62.93	1.46	3.25	0.996	100.00	100
	Product	64.96	1.14	1.95	0.691	47.93	69.08
	Slimes	58.40	2.19	6.14	1.677	52.07	30.92
Scrubbing: 6 min; 1600 rpm; 3 steps; sedimentation time: 10 min	Feed (calc.)	62.47	1.59	3.74	0.932	100.00	100
	Product	64.10	1.32	2.81	0.731	63.60	81.07
	Slimes	55.47	2.74	7.73	1.791	36.40	18.93
Scrubbing: 2 min; 1600 rpm; 3 steps; sedimentation time: 10 min	Feed (calc.)	63.47	1.35	2.82	0.815	100.00	100
	Product	65.24	1.07	1.84	0.571	59.30	84.60
	Slimes	53.74	2.86	8.22	2.153	40.70	15.40
Scrubbing: 2 min; 1800 rpm; 2 steps; sedimentation time: 12 min	Feed (calc.)	63.33	1.43	2.67	0.720	100.00	100
	Product	64.79	1.18	1.92	0.549	69.78	91.51
	Slimes	47.50	4.18	10.75	2.564	30.22	8.49
Scrubbing: 2 min; 2000 rpm; 2 steps; sedimentation time: 12 min	Feed (calc.)	63.28	1.08	3.28	0.761	100.00	100
	Product	64.64	0.83	2.53	0.597	72.15	91.95
	Slimes	47.70	3.93	11.86	2.632	27.85	8.05

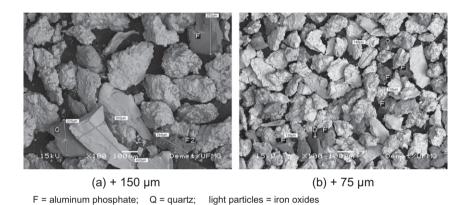


Fig. 6. Analysis of fractions +150 μm and +75 μm by SEM/EDS.

Table 4Best results of bench flotation with anionic and amphoteric collectors using sodium silicate as depressant.

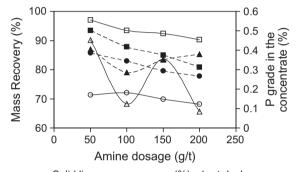
Condition	Products	Grade (%)				P distribution (%)	Mass recovery (%)
		Fe	SiO ₂	Al ₂ O ₃	P		
Sodium silicate 700 g/t; sodium sulfosuccinate 500 g/t	Feed (calc.)	65.39	1.05	1.84	0.535	100.00	100
	Tailings	61.60	1.22	4.14	1.139	42.87	20.15
	Concentrate	66.34	1.01	1.26	0.383	57.13	79.85
Sodium silicate 350 g/t; fatty acid 500 g/t	Feed (calc.)	64.54	1.15	2.15	0.670	100.00	100
	Tailings	61.57	1.14	3.71	1.163	63.41	36.51
	Concentrate	66.25	1.15	1.25	0.386	36.59	63.49
Sodium silicate 350 g/t; rice bran oil 300 g/t	Feed (calc.)	65.03	1.08	2.02	0.625	100.00	100
	Tailings	62.59	1.40	3.36	0.838	24.85	18.55
	Concentrate	65.59	1.01	1.71	0.577	75.15	81.45
Sodium silicate 350 g/t; sarcosinate 300 g/t	Feed (calc.)	65.05	1.15	2.00	0.560	100.00	100
	Tailings	63.67	1.20	2.86	0.755	23.47	17.41
	Concentrate	65.34	1.14	1.82	0.519	76.53	82.59
Sodium silicate 500 g/t; tall oil 300 g/t	Feed (calc.)	65.01	0.80	2.32	0.593	100.00	100
	Tailings	63.03	1.17	3.46	0.884	37.61	25.24
	Concentrate	65.68	0.68	1.94	0.495	62.39	74.76

the concentrate and its rejection to the tailings. With the same sodium silicate dosage of $700 \, \text{g/t}$, other collectors did not achieve good reduction of phosphorus. Rice bran oil and sodium sarcosinate were the least effective collectors, since the final phosphorus contents at the concentrate were 0.577% and 0.519% respectively. The phosphorus recovery to the concentrates was 75.15% and 76.53% respectively.

As expect, amine collectors yielded better results than anionic and amphoteric collectors, as can be observed in Table 5. Flotigam EDA at a dosage of 150 g/t led to a concentrate with 0.201% of phosphorus and mass recovery of 62.31%. The phosphorus recovery to the concentrate was 22.30%, emphasizing its better selectivity. Despite of the less reduction on the phosphorus grade, Flotigam 2835 2L showed the major mass recovery.

Table 5Best results of bench flotation with amine collectors using corn starch as depressant.

Condition	Products	Grade (%)			P distribution (%)	Mass recovery (%)	
		Fe	SiO ₂	Al_2O_3	P		
Corn starch 500 g/t; Flotigam EDA 150 g/t	Feed (calc.)	65.08	0.85	2.28	0.562	100.00	100
	Tailings	60.73	1.52	5.02	1.158	77.70	37.69
	Concentrate	67.71	0.44	0.63	0.201	22.30	62.31
Corn starch 500 g/t; Gemul NCD 100 g/t	Feed (calc.)	64.71	0.77	2.35	0.642	100.00	100
	Tailings	59.73	1.77	5.17	1.410	69.59	31.70
	Concentrate	67.02	0.30	1.04	0.286	30.41	68.30
Corn starch 500 g/t; Gemul NSD 200 g/t	Feed (calc.)	64.16	0.78	2.68	0.756	100.00	100
	Tailings	58.11	1.93	6.34	1.799	75.93	31.89
	Concentrate	66.99	0.24	0.96	0.267	24.07	68.11
Corn starch 500 g/t; Flotigam 2835 2L 200 g/t	Feed (calc.)	64.58	0.84	2.26	0.654	100.00	100
	Tailings	45.59	4.18	12.64	3.810	56.92	9.76
	Concentrate	66.64	0.48	1.14	0.312	43.08	90.24



Solid line: mass recovery (%); short dash: P grade at the concentrate (%). Squares: Flotigam 2835 2L; circles: Gemul NSD; triangles: Gemul NCD.

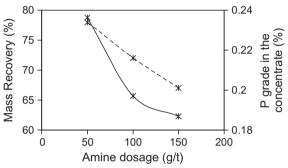
Fig. 7. P grade at the concentrate and mass recovery as a function of amine dosage. Corn starch dosage: 500 g/t.

Concerning P and Al₂O₃ grades in the tailings and concentrates, Flotigam 2835 2L appears to be more selective to phosphates than the other amines. While the phosphorus grade in the tailings is 1.158% using Flotigam EDA, these values reach 3.810% with Flotigam 2835 2L. However, due to the higher mass recovery, the phosphorus recovery to the concentrate was higher using Flotigam 2835 2L. An increase in the Al₂O₃ grade can also be observed in the tailings with the last collector, achieving 12.64% compared to 5.02% for Flotigam EDA. These results may also be related to the higher selectivity of Flotigam 2835 2L onto aluminum silicates.

The effects of amine dosage on the final concentrate phosphorus content and in the mass recovery were also evaluated. As can be seen in Fig. 7, Flotigam 2835 2L showed the best results considering mass recovery, while Gemul NSD was the least effective collector. In general, the increase in the amine dosage results in decreasing both mass recovery and phosphorus grade at the concentrate.

As can be seen in Fig. 8, amine Flotigam EDA showed the worst results considering mass recovery, despite of the best result concerning phosphorus content at the iron concentrate. Mass recovery decreases abruptly when amine dosage is increased from 50 to 100 g/t.

The usage of amines as collectors in bench flotation led to a moderate reduction of phosphorus grade, indicating that reverse cationic flotation of secondary phosphates in the alkaline pH range may be an attractive route for this sample. The liberation degree may be a relevant factor in the process selectivity, since an initial study indicated the existence of some mixed particles in the iron



Solid line: mass recovery (%); short dash:
P grade at the concentrate (%).

Fig. 8. P grade at the concentrate and mass recovery as a function of Flotigam EDA dosage. Corn starch dosage: $500 \, \text{g/t}$.

ore sample used in this study. Even though the final phosphorous grades are higher than the specifications of the iron ore market, the products obtained could be blended with other iron ores with low phosphorus contents, rendering concentrates appropriated to the steel industry.

4. Conclusions

The primary studies of microflotation demonstrated that wavellite presents a higher floatability with fatty acids and its chemical derivatives. The surface formation of aluminum oleate through the interaction between the carboxyl groups of the fatty acids and the surface aluminum hydroxides seems to be the most probable hypothesis for the adsorption mechanism and the likely high floatability of wavellite in alkaline pH. Sulfosuccinate was the least effective collector. The amphoteric reagent was not an efficient collector for wavellite. Its poor performance can be ascribed to the interaction of only one polar group with the surface species while the other polar group would be available to interact with aqueous species providing some hydrophilic character to the mineral. Likewise, sodium silicate was not an effective depressant for wavellite.

The wavellite floatability with dodecylamine was around 100% above pH 8. The adsorption of amine onto wavellite might be attributed to both chemical and electrostatic interactions. The high floatability values obtained from pH 10.5 to 12 may be due to amine precipitation at the wavellite surface. At pH 8–10, the adsorption may be due to electrostatic forces. The adsorption of amine onto wavellite may also be considered as result of precipitation of insoluble salt of aluminum onto wavellite surface.

According to the results of the bench flotation with anionic and amphoteric collectors, fatty acid showed the best result considering the phosphorus content and its recovery at the final concentrate. Rice bran oil and sodium sarcosinate were the least effective collectors, since the final phosphorus grades were 0.577% and 0.519% and the phosphorus recoveries at the concentrate were 75.15% and 76.53%, respectively. Supporting the microflotation results, the anionic and amphoteric collectors were less effective than amines.

Flotigam EDA at dosage of 150 g/t led to a 0.201% phosphorus concentrate and mass recovery of 62.31%. The final concentrate of bench experiment with Flotigam 2835 2L presented a phosphorous content of 0.312% and mass recovery of 90.24%. Despite the less reduction on the phosphorus grade, Flotigam 2835 2L showed the higher mass recovery and appeared to be more selective onto phosphates than other amines. While the phosphorus grade in the tailings is 1.158% using Flotigam EDA, such values reach 3.810% when Flotigam 2835 2L is used as the collector. Desliming experiments were not efficient to significantly reduce the phosphorus content.

The bench flotation results with amines indicate that reverse cationic flotation of secondary phosphates in the alkaline pH range may be an attractive route for this sample. Products with grades of phosphorus higher than market specifications could be blended with other iron ores with low phosphorus contents. Higher liberation degrees could increase the selectivity of flotation, rendering concentrates with lower phosphorus contents.

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