

Original Article

Reverse cationic flotation of iron ore by amide-amine: bench studies



Geriane Macedo Rocha ^a, Marcus Vinicius Macedo da Cruz ^a, Neymayer Pereira Lima ^b, Rosa Malena Fernandes Lima ^{c,*}

^a School of Mines, Federal University of Ouro Preto, Minas Gerais, Brazil

^b Vale S.A, Minas Gerais, Brazil

^c School of Mines, Federal University of Ouro Preto, CEP.: 35.400-000, Ouro Preto, Minas Gerais, Brazil

ARTICLE INFO

Article history: Received 29 August 2021 Accepted 7 February 2022 Available online 24 February 2022

Keywords: Iron ore Quartz Hematite Amide-amine Etheramine acetate

ABSTRACT

This study evaluated the performance of a new collector amide-amine compared with a traditional etheramine in conventional reverse cationic flotation of a siliceous itabirite sample of the Quadrilátero Ferrífero ($d_{80} = 116 \mu m$, 40% Fe and 41.2% SiO₂). Statistical design of experiments was used to determine the influence of pH, collector and starch dosages on mass and Fe recoveries, Fe and SiO₂ grade in the concentrate, Fe grade in the tailings and Gaudin's selectivity index (S.I). For the amide-amine, starch had no significant effect on mass recovery and in the Fe and SiO₂ grade in the concentrate. For the same dosages, it was found that amide-amine was less selective than etheramine. However, at higher dosages, at pH 8 and without starch, concentrates with Fe >65% and SiO₂ <5% grades were obtained, similar to the grades obtained with etheramine and starch at pH 10.5. The mass and Fe recoveries were higher and consequently, the Fe grades in the tailings were lower. These results indicate that, despite the higher dosage required, amide-amine is selective without starch, which is very interesting from the economic point of view and simplification of the process route, implying a great potential for its industrial application.

© 2022 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

The depletion of the hematite iron ore reserves (>63% Fe) of the Quadrilátero Ferrífero-Brazil, in parallel to the growing demand for this commodity by the world market, led to the use of siliceous itabirites (~30%–45% Fe) by the mines located in this region. Usually, physical methods of gravity (jig, Humphrey's spiral) and magnetic (medium and high field) concentration are applied to size fraction >75 μ m for production of sinter feed (4%–6% SiO₂). For size fractions $<75 \,\mu$ m, reverse cationic flotation is widely used for pellet feed production ($<2\% SiO_2$) [1–7].

In cationic reverse flotation of iron ore at alkaline pH (9–10.5), the starch gelatinized with NaOH is used as an iron minerals depressant. Recent studies, made with alternative sources of starch such as sorghum and residues from the food industry (sugar cane bagasse and cassava wastewater) have shown promising and more economical results than corn and cassava

* Corresponding author.

E-mail address: rosa@ufop.edu.br (R.M.F. Lima).

https://doi.org/10.1016/j.jmrt.2022.02.039

^{2238-7854/© 2022} The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creative commons.org/licenses/by-nc-nd/4.0/).

starches, used in industrial plants [2,8–10]. Ethermonoamine and etherdiamine, partially neutralized (30%-50%) with acetic acid, are used as siliceous gangue collectors. These reagents have a polar group $[O-(CH_2)_3]$ between the hydrocarbon chain and the polar group NH₂, which provides greater solubility compared to primary amines originally used [1,2,10].

For a satisfactory performance of the reverse cationic flotation of Brazilian itabirites with etheramines, a previous desliming step is necessary for removal of particles $<10 \mu m$, resulting in considerable losses of valuable minerals, which are deposited in the tailings dams. These losses are even higher for ores with high grade of LOI (loss of ignition) > 5%, associated with goethite which are usually quite friable [1,11,12]. Another factor for loss of selectivity of etheramines is the presence of polyvalent ions in aqueous medium, which are electrostatically attracted by the surfaces of iron minerals and quartz, providing the adsorption of starch on the sites containing the previously adsorbed ions. This presence also avoids the adsorption of the cations of the collector in the quartz due to the competition of these polyvalent ions with the etheramine ions since electrostatic attraction is the main mechanism of adsorption of amines onto the negatively charged mineral species [1,2,13]. For this reason, some studies of synthesis and application of new cationic reagents of the amide-amine type were carried out, aiming at replacing the etheramines for: i) iron ores, using depressant, including the investigation of the influence of Ca in aqueous medium and ii) slimes from desliming step of iron ores by column flotation, without depressant. See the summary of these studies in Table 1.

As observed in Table 1, the studies carried out, with tailings from the desliming process of iron ore flotation plants of the Quadrilátero Ferrífero [16–18], using amide-amine, were very promising in the concentration of slimes without starch. However, until recently there was no detailed study of characterization of these reagents and their effect on the surface properties of quartz and hematite, the main contaminant and iron mineral presented in siliceous itabirites. Those data would give some predictability of their performance both for slime flotation and for flotation of size fractions of ores usually fed in industrial plants.

Due to the aforementioned reasons, Rocha et al. [19] carried out studies of characterization of an amide-amine

Sample (characteristics)	Conditions of flotation tests	Comments	References
Main minerals (quartz and hematite); SiO ₂ = 30.8%, Fe = 45.2%, and d_{80} = 139 μ m.	Rougher tests in mechanical bench cell:50% solids; ground corn (600 g/t). Variables: pH (9.5 and 11); 8 different amide-amines (300, 400 and 500 g/t SiO ₂); etheramine (180 g/t SiO ₂).	Best result obtained with 500 g/t at pH 11 with N-(2-(2-aminoethyl- amino)ethyl)-dodecanamide: ~4% SiO ₂ in the concentrate, similar to etheramine; and ~6% Fe ₂ O ₃ in the tailings.	[14]
Friable itabirite (hematite, quartz, goethite and kaolinite); SiO_2 = 34%, Fe = 44%; LOI = 0.6% and $d_{80}=92~\mu m$	Tests in mechanical bench cell (rougher/cleaner) with the ore previously deslimed with and without addition of lime (50% solids); 500 g/t corn grits. Variables: dosages from 101 to 242 g/t of different amide-amines (AkzoNobel) and etheramines (Clariant) and pH (8.5, 9.5 and 10.5).	Similar performance of amide- amine (MDB 1521) and etheramine (Flotigam EDA-C). Best result at pH 8.5 in the presence of Ca^{2+} (<2% SiO ₂ in the concentrate and ~20% Fe in tailings).	[15]
Slime (hematite, quartz, goethite and kaolinite): Slime 1: SiO ₂ = 28.6%, Fe = 45.2%, and $d_{90} = 34 \ \mu m$; Slime 2: SiO ₂ = 33.4%, Fe = 39.6, and $d_{90} = 38 \ \mu m$.	Pilot tests in column flotation. Rougher (slime 1) and rougher/cleaner (slime 2) stages. Percentage of solids = 20%–30%; starch (0, 493–1273 g/t); amide-amine (Flotinor 5530) and etheramine (Flotigam EDA-C) (53–678 g/t); pH: 8.5, 9.5 and 10.5.	Best results for slime 1 (no starch, amide-amine > 150 g/t, $pH = 10.5$): Fe >62% and SiO ₂ <4% in the concentrate, and a Fe recovery >90%. Increase of the percentage of SiO ₂ in the concentrate with starch. For slime 2: Fe <55% in the concentrate, with both collectors and the presence or absence of starch.	[16]
Brucutu slime (hematite, quartz, goethite and kaolinite); SiO ₂ = 24.3%, Fe = 41.2%, LOI = 7.7% and d ₈₀ = 45 μm .	Amide-amine (Flotinor 16939 - Clariant) without starch. Mechanical bench flotation: 20% solids; pH (9.5,10.5, and 11), 250–700 g/t collector. Column flotation (rougher) with high intensity conditioning (HIC) at pH 10.5, 20–25% solids, 500 –700 g/t of collector.	Best results in mechanical flotation (concentrate >48% Fe, recovery of Fe >80%, >15% Fe in the tailings) at pH 10.5 and collector >300 g/t. In the column the best results (%Fe in concentrate = 49% and tailings = 10%, recovery of Fe = 90%) was obtained with 500 g/t of collector.	[17]
Slime from Vargem Grande 2 mine – Vale (hematite, goethite, quartz, kaolinite, muscovite and chlorite), $SiO_2 = 31.1\%$, Fe = 44.3%, LOI = 2.2% and $d_{80} = 20 \ \mu m$.	Pilot tests with column flotation (rougher stage) operated in series with the industrial plant. Amide-amine (Flotinor 5530 – Clariant) (160 g/t) in the absence of depressant and pH 10.5.	High selectivity in the absence of starch. On average, 53% Fe in the concentrate was obtained, recovery of 91.5% Fe and silica recovery in foam of 53.1%.	[18]

Table 2 – Factors studied in the benc	n flotation tests.		
Collector type	Factors	Lev	<i>v</i> els
		Low	High
Amide-amine (Flotinor 10118)	рН	8	10.5
	Collector dosage (g/t)	50	100
	Starch dosage (g/t)	0	200
Etheramine (Flotigam 7100)	Collector dosage (g/t)	50	100
	Starch dosage (g/t)	0	200

(Flotinor 10118 – synthesized by Clariant do Brazil) and the effect of this reagent on the surface properties of quartz and hematite. In those studies, selectivity windows from 47% to 80% were found in the separation of quartz from hematite in the pH range 6–10.5, without starch. In order to confirm the results obtained in the previous study of Rocha et al. [19], bench flotation tests using the same amide-amine (Flotinor 10118) were performed with a typical feed sample for the conventional flotation stage (size fraction <150 μ m). In addition, were carried out comparative tests with an ethermono-amine acetate (Flotigam 7100 – synthesized by Clariant do Brazil), normally used in industrial circuits of iron ore flotation in Brazil. The results of these studies are following presented.

2. Materials and methods

2.1. Characterization of the iron ore sample

This study used a sample (~60 kg) of iron ore from a mine located in the western region of the Quadrilátero Ferrífero-Brazil. This sample was provided by Vale S.A. with the granulometry used in conventional flotation. Then, it was submitted to homogenization and quartering processes to obtain aliquots, which were used in the characterization of the ore (physical, mineralogical and chemical) and for flotation tests.

The specific mass of the sample studied (average of the values obtained in 3 scans) was determined by helium pycnometer, model Quantachome Ultrapyc 1200e (medium sample holder), operating under the following conditions: target pressure of 17 psig, automatic equilibrium time, purge time of 4 min and temperature of 23 °C. The size distribution was determined by wet sieving, using the Tyler series of sieves from 300 μ m to 38 μ m and by the laser granulometer (CILAS 1064) for the size fraction <38 μ m.

The main mineralogical constituents of the iron ore were determined by X-ray diffractometry (total powder method). For this, a PanAlytical X 'Pert 3 Powder X-ray diffractometer was used equipped with copper tube ($\lambda_{Kz} = 1.5406$ Å), operated at 45 kV, 40 mA. The diphratograms were collected by the Data Collector software, with scan range 2 Θ (5°–90°) and collection time of 15 min. The interpretation of the dilphrograms obtained was performed with HighScorePlus software, using the PDF-2 database of ASTM.

The chemical composition of the iron ore sample and flotation test products (Fe, SiO₂, P, Al₂O₃, Mn, TiO₂, CaO, MgO) were determined by X-ray fluorescence (Thermo Fisher Scientific Nilton XL3t XRF Analyser). LOI was determined through gravimetry, calculating the percentage of sample mass loss when compared to a known initial mass, after remaining for 1 h in a muffle oven at 1000 °C. Both the determinations of the chemical composition and the LOI were carried out in the Chemical Laboratory of Timbopeba-Vale.

2.2. Flotation tests

Bench flotation tests were performed using mechanical cell CDC model CFB-1000-EEPNBA, operating at 1100 RPM and 1.5 L vat. The reagents used were: Flotinor 10118 (amide-amine) and Flotigam 7100 (ethermonoamine acetate) with concentration of 1% w/v, both supplied by Clariant of Brazil, as collectors; corn starch (maisena-Duryea) gelatinized in the ratio 4:1 (starch:NaOH), with a concentration of 1% w/v, as depressant; NaOH and HCl (Synth) as pH regulators. Collector

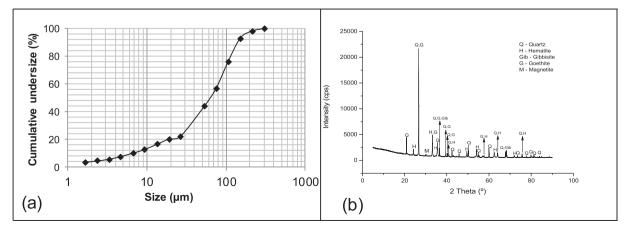


Fig. 1 — - Size distribution curve (a) and X-ray diphratogram (b) of the iron ore sample.

Table 3 – Chemical composition by fraction size of the stuc	omposition by frac	ttion size of	the studied	iron ore san	nple.							
Size fraction (µm)	Weight (%)					Grade (%)					Distribu	Distribution (%)
		Fe	SiO_2	Ρ	Al_2O_3	Mn	TiO_2	CaO	MgO	IOI	Fe	SiO_2
+150	7.2	61.0	11.6	0.021	0.14	0.011	0.019	0.059	0.023	0.28	11.0	2.0
-150 + 75	35.8	39.2	42.6	0.021	0.17	0.002	0.008	0.030	0.001	0.21	35.1	37.0
-75 + 38	34.4	30.3	56.8	0.021	0.21	0.003	0.007	0.018	0.027	0.02	26.1	47.5
-38	22.6	49.3	24.6	0.100	2.25	0.105	0.053	0.048	0.081	2.35	27.8	13.5
Global	100	40.0	41.2	0.039	0.65	0.026	0.019	0.032	0.030	0.63	100	100

and starch solutions were prepared daily. Based on published iron ore flotation studies, some conditions were kept constant: pulp with 45% solids, conditioning time of 5 min with starch and 3 min with collector. The collection time of the floated was fixed at 3 min. During this time, the pulp volume was supplemented with tap water at pH previously adjusted at the same pH value of the assay being performed [7,13,20].

The MINITAB 17[®] software was used for the two-level design of experiments with replication and analysis of the results obtained for both collectors studied. In a previous microflotation study, with concentration of 5 mg/L of amideamine, the floatability of quartz and hematite at pH values 8 and 10.5, without starch, was 82%, 94%, 35%, and 14%, respectively. Under these same conditions, the zeta potential was 9 and -5 mV for quartz and 9 and -15 mV for hematite. In the absence of reagent, the zeta potential of quartz was -23 mV and -32 mV, and of hematite was -13 mV and -17 mV, at pHs 8 and 10.5, respectively. These values showed a change in the zeta potential of minerals more significant at pH 8 than at pH 10.5. The pK_a of the reagent is equal to 8.2 [19]. For these reasons, in addition to collector and depressant dosages, pH was also evaluated in the factorial design of experiments only for amide-amine (planning 2^{3).} In the case of etheramine (planning 2²), the pH was set at 10.5, which is common in the mining industry [1,2,11,13,20]. The dosages of collectors (50 and 100 g/t) were based on values compatible with industrial practice and studies reported in the literature [7,13,20]. Table 2 summarizes the factors and levels studied. The variables analyzed were mass and Fe recoveries, Fe and SiO₂ grades in the concentrate, Fe grade in the tailings and selectivity index of Gaudin (S.I.). Later, based on the analysis of the results obtained from the experimental planning's, complementary tests were performed to optimize the best conditions for the amide-amine collector applicability.

3. Results and discussion

3.1. Characterization of the iron ore sample

The specific mass of the iron ore studied is 3.67 g/cm³, which is consistent with specific masses of ores from Quadrilátero Ferrífero [11,20]. This result was used to calculate the ore mass used in bench flotation tests (1003.5 g).

Figure 1 shows the size distribution curve (a) and the X-ray diphratogram (b) of the iron ore sample used in this study, whose chemical composition and LOI by size fraction is presented in Table 3. As can be seen in Fig. 1(a), the sample presents a $d_{80} = 116 \ \mu\text{m}$, 7.3% of the particles above 150 $\ \mu\text{m}$ and 12% smaller than 10 $\ \mu\text{m}$ (slime), which is consistent with the size distribution of siliceous itabirites usually fed in conventional industrial flotation process [1,7,20].

As can be seen from Table 3, the global Fe grade of the sample is 40% and the main contaminant is SiO₂ (41.2%). It is observed that the coarser fraction (>150 μ m) presents high Fe grade (61.0%) and the SiO₂ grade (11.6%) is much lower than in others size ranges. Fe is evenly distributed through the particle size fractions <150 μ m, while SiO₂ is in greater proportion (47.5%) in the size fraction $-75 + 38 \,\mu$ m. When observing the others components, it can be noted that, although in low

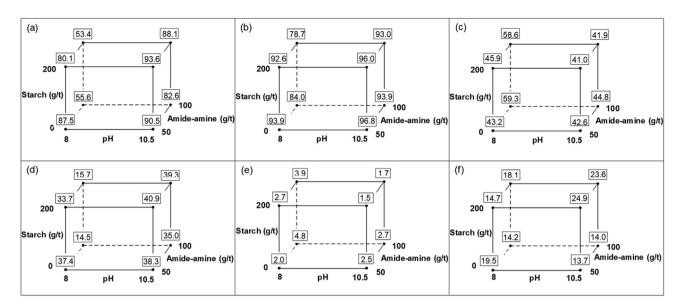


Fig. 2 – Influence of pH, starch and amide-amine dosages on mass recovery (a), Fe recovery (b), Fe grade in the concentrate (c), SiO₂ grade in the concentrate (d), selectivity index – S.I. (e) and Fe grade in tailing (f).

grades, they are major in the fraction $<38 \mu$ m, mainly Al₂O₃ (2.25%) and LOI (2.35%), which are associated with the presence of gibbsite (Al(OH)₃) and goethite (FeO.OH) (Fig. 1(b)), which commonly occur in the finer particle fractions [11,12]. By means of stoichiometric calculations, using the global grades of SiO₂, Al₂O₃ and LOI, and the theoretical chemical formulas of some minerals identified in the X-ray diphratogram, it can be concluded that the sample studied consists of 41.2% quartz (SiO₂), 2.8% goethite (FeO.OH) and 1% gibbisite (Al(OH)₃). Although it is not possible to determine the proportion of magnetite and hematite by the results of chemical analyses (absence of FeO grade), it can be inferred that this sample has a high proportion of hematite (Fe₂O₃), since the magnetite peaks (Fe₂O₃.FeO) were very small (Fig. 1(b)). In studies of mineralogical semi-quantification by optical microscopy performed with an iron ore sample from the same deposit, a proportion of approximately 12% of magnetite was determined in it [20].

3.2. Flotation tests

Figures 2 and 3 present the cube graphs for the mean values of the design of experiments results for amide-amine and etheramine, respectively. Table 4 summarizes the estimated effects and coefficients on the response variables studied for a 95% confidence level.

Higher mass and Fe recoveries are observed for amideamine (Fig. 2(a) and (b)) than for etheramine (Fig. 3(a) and (b)). Inverse effect was observed for selectivity indexes (Figs. 2 and 3(e)) and Fe grades in the tailings (Figs. 2 and 3(f)). At pH 8

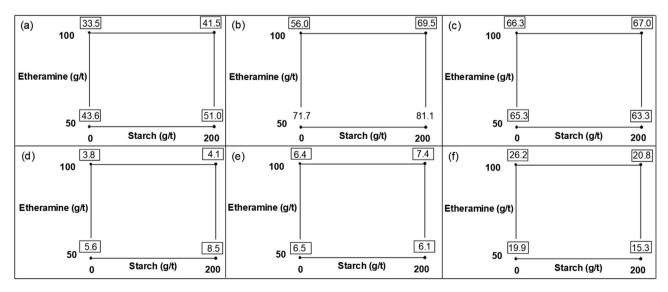


Fig. 3 – Influence of starch and amine dosages on mass recovery (a), Fe recovery (b), Fe grade in the concentrate (c), SiO₂ grade in the concentrate (d), selectivity index – S.I. (e) and Fe grade in tailing (f).

	Concentrate grade (%) Tailing grade (%)	Concentrate grade (%) Tailing grade (%) S.I.
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	SiO ₂ Fe	
789 91.1 47.1 31.8 31.9 31.1 31.1 65 0.00 7 -11.4 -5.7 0.00 2.3 0.00 7 -11.4 -5.7 0.00 2 0.000 Y 1.12 0.00 Y -11.4 -5.7 0.00 2 3 0.000 Y 1.12 0.00 Y 2.3 1.2 0.00 2 0.000 Y 1.12 0.00 Y 2.3 1.2 0.00 2 <th>b</th> <th><i>p</i> S Ef. Coef <i>p</i></th>	b	<i>p</i> S Ef. Coef <i>p</i>
78.9 91.1 47.1 31.8 31.8 15 9.8 0.00 Y 7.6 3.8 0.00 Y -9.2 -4.6 0.00 Y 11 0.5 0.00 18.0 -9.0 0.00 Y -0.7 -0.3 0.33 N 1.1 0.5 0.00 18.0 -9.0 0.00 Y -0.7 -0.3 0.33 N 1.1 0.5 0.00 18.0 -9.0 0.00 Y -1.6 -0.8 0.03 Y -11.4 -5.7 0.00 5.5 0.00 Y -1.6 -0.8 0.03 Y 2.3 0.00 9 0.9 0.1 N -1.6 -0.8 0.03 Y 2.3 0.00 9 0.9 N -1.16 -0.15 0.00 Y 2.3 1.14 5.7 0.00 9 0.9 N -1.12 0.05 0.01 <td></td> <td></td>		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	31.8 17.8	2.7
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.00 Y 2.4 1.2	0.04 Y -1.2 -0.6 0.00
	0.29 N 5.0 2.5	0.00 Y -0.5 -0.3 0.00
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.00 Y -0.7 -0.4	0.49 N 1.1 0.5 0.00
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.04 Y 5.4 2.7	0.00 Y -0.4 -0.2 0.01
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.00 Y 0.2 0.1	0.82 N -0.9 -0.5 0.00
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.12 N 1.8 0.9	0.11 N -0.4 -0.2 0.02
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.45 N -2.6 -1.3	0.03 Y 0.4 0.2 0.02
42.5 69.6 65.5 5.5 7 3.8 0.00 Y 11.4 5.7 0.00 S -0.6 -0.3 0.17 N 1.6 0.8 0.02 3.8 -4.9 0.00 Y -13.6 -6.8 0.00 S 2.4 1.2 0.00 Y -3.1 -1.5 0.00 3 0.1 0.44 N 2.1 1.0 0.00 S 1.4 0.7 0.02 Y -1.4 -0.7 0.04	$\sigma = 2.0$	$\sigma = 0.25$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		
3.8 0.00 Y 11.4 5.7 0.00 S -0.6 -0.3 0.17 N 1.6 0.8 0.02 -4.9 0.00 Y -13.6 -6.8 0.00 S 2.4 1.2 0.00 Y -3.1 -1.5 0.00 0.1 0.44 N 2.1 1.0 0.00 S 1.4 0.7 0.02 Y -1.4 -0.7 0.04	5.5 20.6	6.6
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	0.02 S -5.0 -2.5	0.00 Y 0.4 0.2 0.36
0.1 0.44 N 2.1 1.0 0.00 S 1.4 0.7 0.02 Y -1.4 -0.7 0.04	0.00 S 5.9 2.9	0.00 Y 0.6 0.3 0.16
	0.04 S -0.4 -0.2	0.00 Y 0.7 0.4 0.10
$ \alpha = 0.5 \qquad \qquad \alpha = 0.5 \qquad \qquad \alpha = 0.5 \qquad \qquad \alpha = 0.6 \qquad \qquad$	$\sigma = 0.1$	$\sigma = 0.5$

and 100 g/t of amide-amine, concentrates were obtained with ~59% Fe and ~15% SiO₂, both with and without prior conditioning with starch. Table 4 shows that the starch dosage (B) has no significant effect on the response variables Fe and SiO₂ grades in the concentrates obtained. That is consistent with the results of the hematite and quartz microflotation tests, where the possibility of selective separation between the two minerals in the pH values 8 to 10.5 was verified using only amide-amine without starch [19]. As reported in the literature, the extra NH group in the secondary amide in the amideamine molecule favors the formation of hydrogen bonds with the ionized silanol groups (Si-O) on the quartz surface, in addition to the electrostatic attraction of the positive ion. Another factor is the effect of steric impediment, due to the higher volume of the molecule, which probably affects the reagent adsorption on the hematite [17,21,22]. In addition, the best performance of amide-amine (pka = 8.2) at pH 8 may also be related to concentration of ionic (~50%) and molecular (~50%) species of the reagent. The molecular species, between two ionic species of the reagent, when adsorbed on the quartz surface (IEP = 1.8) avoids electrostatic repulsion between the polar heads of the cations. There is also the tendency of hematite coagulation, due to the predominance of van der Waals's attractive forces for pH near its isoelectric point (pH ~7) [1,23-25].

Table 4 shows that for etheramine, differently than what was observed for amide-amine, starch had a significant effect for all response variables analyzed, except for S.I. The effect was more pronounced on mass and Fe recoveries, which is consistent with several studies reported in the literature using etheramine as a collector [2,7,10]. As can be seen in Fig. 3, the quality of the concentrates obtained with etheramine without starch can also be considered satisfactory (Fe grade in concentrate >64% and SiO₂ <6.0%). However, both mass and Fe recoveries were lower, especially for the 100 g/t collector dosage. Based on the best results obtained for amide-amine (pH 8 and without starch) and the higher values of mass and Fe recoveries when compared to etheramine (compare Figs. 2 and 3), complementary tests were performed with increasing dosages of amide-amine under these conditions. The results are shown in Fig. 4, which also presents the best result obtained with etheramine acetate used as a comparison standard (pH 10.5, starch = 200 g/t and etheramine = 100 g/t).

Figure 4 shows that the best result obtained was for the dosage of 150 g/t of amide-amine (Flotinor 10118), as there is an increase of ~5% in the Fe grade and a decrease of ~9% in the SiO₂ grade in the concentrate obtained when compared to the dosage of 100 g/t of this collector. Both the Fe and SiO₂ grades in the concentrate, as well as the selectivity index for the condition described above, are similar to those obtained in the standard assay with etheramine (Flotigan 7100). However, there is an increase of ~6% and ~9% in the mass and Fe recoveries, respectively. The Fe grade in the tailing is 4% lower. The dosage of 250 g/t of amide-amine for pulp with 45% solids corresponds to 203 mg/L, which is higher than the critical micellar concentration (CMC) between 100 mg/L and 150 mg/L of this reagent, determined through the Du Nouy method by Rocha et al. [19]. Therefore, the worsening of the results of the response variables may be related to the formation of micelles, which are colloidal particles precipitating as slime coating on

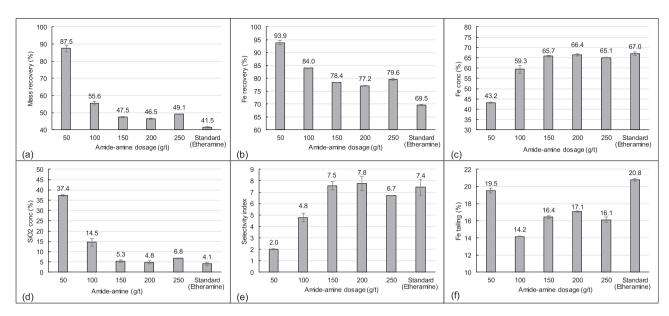


Fig. 4 – Influence of increased amide-amine dosage on mass recovery (a), Fe recovery (b), Fe grade in the concentrate (c), SiO_2 grade in concentrate (d), selectivity index (e) Fe grade in the tailing (f). Standard (Etheramine = 100 g/t, pH = 10.5 and starch = 200 g/t).

the surface of minerals, thus decreasing the selectivity of the process [24]. Despite the dosage of amide-amine being 50% higher than the etheramine, it was evident the possibility of the iron ore flotation (coarse feed of conventional industrial flotation as the sample here studied: $d_{80} = 116 \ \mu\text{m}$) without starch, in addition to greater mass and Fe recoveries than the levels obtained with etheramine. Recent studies have also shown promising results with the application amide-amine collector for flotation of iron ore slimes [16–18].

4. Conclusions

Based on the results of bench flotation tests performed with the sample studied, when using amide-amine and etheramine as collectors at the same dosages, it was verified that the mass and Fe recoveries with amide-amine were considerably higher than with etheramine, but with higher SiO₂ grade in the concentrate. For dosage of 150 g/t of amide-amine, at pH 8, without starch, it was obtained a concentrate with Fe >65% and SiO₂ ~5%, compatible with the levels obtained with 100 g/t of etheramine, 200 g/t of starch and at pH 10.5. Despite the 50% higher dosage of amide-amine, the mass and Fe recoveries were respectively 6 and ~9% higher than those obtained with etheramine, clearly making viable the possibility of flotation of iron ore without starch as a depressant. Hence, the data obtained in this study is very interesting, from both the economic and flotation management point of view, due to the decrease of a process variable.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors are grateful to CAPES, FAPEMIG, CNPq, Universidade Federal de Ouro Preto (UFOP) and Vale S. A. for funding the project and for their fellowship grants in the research and scientific initiation and to Clariant Brazil for providing the collectors.

REFERENCES

- [1] Zhang X, Gu X, Han Y, Parra-Álvarez N, Claremboux V, Kawatra SK. Flotation of iron ores: a review. Miner Process Extr Metall Rev 2019;42:184–212. https://doi.org/10.1080/ 08827508.2019.1689494.
- [2] Nakhaei F, Irannajad M. Reagents types in flotation of iron oxide minerals: a review. Miner Process Extr Metall Rev 2018;39:89–124. https://doi.org/10.1080/ 08827508.2017.1391245.
- [3] Dauce PD, de Castro GB, Lima MMF, Lima RMF. Characterisation and magnetic concentration of an iron ore tailings. J Mater Res Technol 2018;8:1052–9. https://doi.org/ 10.1016/j.jmrt.2018.07.015.
- [4] José FDS, Barcelos HO, Pereira CA. Combination of gravity concentration variables to increase the productivity of the Brucutu mineral processing plant. J Mater Res Technol 2018;7:158–64. https://doi.org/10.1016/ j.jmrt.2017.06.002.
- [5] Silva MSS, Lima MMF, Graça LM, Lima RMF. Bench-scale calcination and sintering of a goethite iron ore sample. Int J Miner Process 2016;150:54–64. https://doi.org/10.1016/ j.minpro.2016.03.008.
- [6] Rosière CA, Chemale Jr F. Itabiritos e minérios de ferro de alto teor do Quadrilátero Ferrífero – Uma visão geral e discussão. Geonomos 2013;8:27–43.
- [7] Lima NP, Valadão GES, Peres AEC. Effect of amine and starch dosages on the reverse cationic flotation of an iron ore. Miner

Eng 2013;45:180-4. https://doi.org/10.1016/ j.mineng.2013.03.001.

- [8] Silva EMS, Peres AEC, Silva AC, Florêncio DL, Caixeta VH. Sorghum starch as depressant in mineral flotation: Part 2 – flotation tests. J Mater Res Technol 2019;8:396–402. https:// doi.org/10.1016/j.jmrt.2018.04.002.
- [9] Marins TF, Rodrigues OMS, Reis ÉL, Beltrão JG. Utilising starches from sugarcane and cassava residues as hematite depressants. Miner Eng 2020;145. https://doi.org/10.1016/ j.mineng.2019.106090.
- [10] Araujo AC, Viana PRM, Peres AEC. Reagents in iron ores flotation. Miner Eng 2005;18:219–24. https://doi.org/10.1016/ j.mineng.2004.08.023.
- [11] Gonçalves GMC, Lima RMF. Proposal for an environmentally sustainable beneficiation route for the amphibolitic itabirite from the Quadrilátero Ferrífero-Brazil. Minerals 2020;10:1–13. https://doi.org/10.3390/min10100897.
- [12] Lima RMF, Abreu FPVF. Characterization and concentration by selective flocculation/magnetic separation of iron ore slimes from a dam of Quadrilátero Ferrífero – Brazil. J Mater Res Technol 2020;9:2021–9.
- [13] da Cruz DG, Gonçalvez PSM, Lelis DF, Lima RMF. Effect of Ca²⁺ and Mg²⁺ ions on the reverse cationic flotation of itabiritic iron ore. Holos 2021;3:1–11. https://doi.org/ 10.15628/holos.2021.9000.
- [14] Budemberg G. Síntese de coletores para flotação de minério de ferro. Lorena:Universidade de São Paulo; 2016. M.Sc. dissertation.
- [15] Mamed CRS. Mitigação dos efeitos de cátions Ca²⁺ na flotação catiônica reversa de minério de ferro. Belo Horizonte: Universidade Federal de Minas Gerais; 2016. M.Sc. dissertation.
- [16] Matiolo E, Couto HJB, Lima N, Silva K, de Freitas AS. Improving recovery of iron using column flotation of iron ore slimes. Miner Eng 2020;158. https://doi.org/10.1016/ j.mineng.2020.106608.

- [17] Araujo VA, Lima N, Azevedo A, Bicalho L, Rubio J. Column reverse rougher flotation of iron bearing fine tailings assisted by HIC and a new cationic collector. Miner Eng 2020;156. https://doi.org/10.1016/j.mineng.2020.106531.
- [18] Filippov LO, Silva K, Piçarra A, Lima N, Santos I, Bicalho L, et al. Iron ore slimes flotation tests using column and amidoamine collector without depressant. Minerals 2021;11:699.
- [19] Rocha GM, Silva JA, Ramos KS, Lima RMF. Selective flotation of quartz from hematite by amide-amine: fundamental studies. Mining, Metall Explor 2021;38:2195–207. https:// doi.org/10.1007/s42461-021-00470-3.
- [20] Lima RMF, Lopes GM, de Figueiredo Gontijo C. Mineralogical, physical and chemical aspects on cationic inverse flotation of low-grade iron ores from Quadrilatero Ferrífero - MG. Tecnol Em Metal Mater e Mineração 2011;8:126–31. https:// doi.org/10.4322/tmm.2011.020.
- [21] Liu W, Liu W, Zhao Q, Peng X, Wang B, Zhou S, et al. Investigating the performance of a novel polyamine derivative for separation of quartz and hematite based on theoretical prediction and experiment. Sep Purif Technol 2019;237. https://doi.org/10.1016/j.seppur.2019.116370.
- [22] Liu W, Liu W, Zhao Q, Shen Y, Wang X, Wang B, et al. Design and flotation performance of a novel hydroxy polyamine surfactant based on hematite reverse flotation desilication system. J Mol Liq 2020:301. https://doi.org/10.1016/ j.molliq.2019.112428.
- [23] Alexandrino JS, Peres AEC, Lopes GM, Rodrigues OMS. Dispersion degree and zeta potential of hematite. Rev Esc Minas 2016;69:193–8. https://doi.org/10.1590/0370-44672014690073.
- [24] Somasundaran P, Moudgil BM. Reagents in mineral technology. New York: Marcel Dekker; INc 1987.
- [25] Mhonde NP. Investigating collector and depressant performance in the flotation of selected iron ores. Cape Town: University of Cape Town; 2016 [M.Sc]. thesis.