Kaolinite and hematite flotation separation using etheramine and ammonium quaternary salts

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ABSTRACT

Clay minerals are widespread in various types of mineral deposits. When present, they contribute to the high content of certain parameters such as silica, aluminium, and magnesium. This study aimed to find selectivity windows to separate hematite from a clay mineral (kaolinite) to allow reduction of the levels of silica and alumina in iron ore. The collectors used were: etheramine Flotigam EDA (EDA) and the ammonium quaternary salts: dodecyltrimethylammonium bromide (DTAB) and Tomamine Q-14-2 PG (AQ142). The depressant used was corn starch. The separation selectivity was achieved using DTAB in the pH range between 4 and 10. Using the collectors EDA and AQ142, the selectivity was obtained only in the presence of starch, at pH 10. Laboratory scale tests showed that as far as the particles size is concerned, better selectivity was achieved with finer particles. Circuit configurations including cleaner and scavenger stages, and pilot scale tests, will be required prior to a possible industrial implementation of the separation.

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1. Introduction

In most of the countries in the world one can observe the increase of industrial segments, like automotive, manufacturing, and civil construction. To maintain this growth, it is necessary to supply the demand of steel, consequently, of iron ore.

Clay minerals are widespread in various types of mineral deposits. When present, they contribute to the high content of certain parameters such as silica, aluminium and magnesium. The presence of kaolinite, a clay mineral, has contributed to increase the grade of silica and aluminium in Brazilian and Australian iron ores (Ma et al., 2009).

Kaolinite $(Al_2Si_2O_5(OH)_4)$ is the main mineral in kaolin ores and is very common, as gangue mineral, in bauxite ores. In the current literature, there are many articles addressing the removal of kaolinite from bauxite ores. Amines and ammonium quaternary salts are the types of collector mostly used to float kaolinite from bauxite ores (Wang et al., 1999; Cao et al., 2009; Hu et al., 2003, 2008; Xu et al., 2004; Zhaohui and Gallus, 2007; Jiang et al., 2011). However, information on removing kaolinite from iron ores is scarce.

Kaolinite is the most common clay mineral in Brazilians iron ores. Most of the beneficiation plants remove kaolinite (and other aluminosilicates) in the desliming stage. This is a consequence of the size of kaolinite particles. Despite using the desliming stage, the presence of a high Al_2O_3 grade is common. In these cases, the removal of kaolinite in the concentration stage may be a good alternative. Due to the small size of kaolinite particles, their removal via flotation is more indicated than through magnetic separation.

There is a wide knowledge about separation of quartz from iron ore. Despite the fact that quartz and kaolinite belong to the silicates class, they do not present similar behaviours in an industrial flotation process, probably due to the face-edge structure present only in the kaolinite structure (Ma et al., 2009). According to Araujo et al. (2003) it is not trivial to separate kaolinite from iron ores. In most of the cases kaolinite particles are not amenable to flotation concentration, in the other words the kaolinite content is just partitioned according to the pulp flow. Rodrigues (2009) stated that the kinetics of flotation is a critical point to achieve selective flotation of kaolinite. She showed that two amines (dodecylamine and Flotigam EDA) and two ammonium quaternary salts (cetylpiridinium choride and cetyltrimetylammonium bromide) are efficient as collector of both, kaolinite and quartz, however the span of time required to float kaolinite was approximately 5–10 times longer than that necessary to float quartz (depending on the collector type). Also, the author discussed the influence of increasing the

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flotation time in an industrial process, what can cause many problems, for instance, the flotation of hematite resulting in selectivity losses.

Ma (2010, 2011a and b) discussed aspects related to kaolinite separation in iron ore processing. Ma (2011a) showed that when hydrolysable metal cations such as Ca and Mg are present in the process water they cause a strong coagulation of kaolinite particles and sodium silicate cannot effectively disperse this pulp, resulting in selectivity losses. Furthermore, in an anterior paper, Ma (2010) showed that, considering concentration of cations above 0.001 mol/L, the presence of starch in low dosages intensifies the coagulation phenomenon, but the corn starch re-disperses the kaolinite in higher dosages. The presence of cations renders the zeta potential of kaolinite particles less negative at pH 10.5, consequently it favours the coagulation. High dosage of starch causes the opposite effect due to steric forces between the kaolinite particles coated with starch. In a third article, Ma (2011b) suggested a low-molecular-weight polyacrylic acid (MW1800 by Sigma) as good dispersant for kaolinite under typical conditions of iron ore flotation and selective flocculation.

In a general scenario there were some advances concerning this issue, but the background in the academic group should be further improved. This study aimed to find selectivity windows, using microflotation experiments, to separate hematite from kaolinite to allow reduction of the levels of silica and alumina in iron ores when kaolinite is present as gangue. Also, laboratory scale tests were done to check if the conditions observed in microflotation could be reproduced in bench scale.

2. Methodology

Microflotation tests were conducted with the use of a Hallimond tube using pure minerals (kaolinite and hematite) to evaluate the performance of collectors and depressants in the system.

The samples were carefully milled, avoiding fines production and contamination, using an agate mortar and pestle. The particles size of the samples was adjusted between 75 μm and 212 μm.

The agitation in the Hallimond tube causes further comminution of the already fine kaolinite particles, so an extension was adapted to the apparatus to prevent entrainment. N_2 was the gas used to produce the bubbles, at a flow rate of 50 mL/min.

Throughout this study four amines and four ammonium quaternary salts were tested. This article presents just the results with the collectors that showed selectivity at the microflotation stage. The best collectors were: the etheramine Flotigam EDA (EDA); and the ammonium quaternary salts: dodecyltrimethylammonium bromide (DTAB) and Tomamine Q-14-2 PG (AQ142). EDA and AQ142 are commercial collectors produced by, respectively, Clariant and Pietsch Chemicals. DTAB is a pure reagent produced by Aldrich Chemistry. Gelatinised corn starch was used as depressant.

The collectors performance was evaluated at three concentrations: 1×10^{-4} mol/L, 5×10^{-5} mol/L, and 1×10^{-5} mol/L. The collectors conditioning time was one minute. The performance of corn starch was checked at a concentration range between 10 mg/L and 400 mg/L. The depressant conditioning time was 2 min. The froth collection time was determined after kinetic experiments, and established at 5 min for the tests using EDA and DTAB, and 2 min for the tests using AQ142. These experiments were done at pH values close to 4, 6, 8 and 10.

Laboratory scale flotation tests were conducted to verify the reproducibility of the results indicated in the microflotation stage. The sample consisted of a blend of iron ore (90%) and kaolin (10%). These tests were done in a Denver machine using a 900 mL cell.
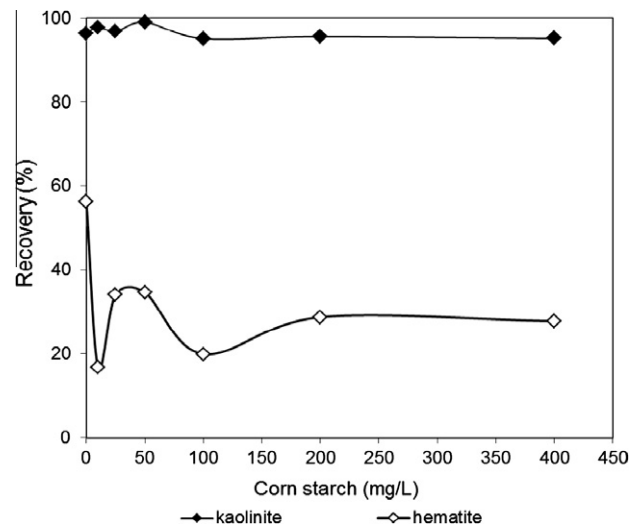

Fig. 2. Floatability of kaolinite and hematite, as a function of starch concentration, with EDA (1×10^{-4} mol/L) at pH = 10.
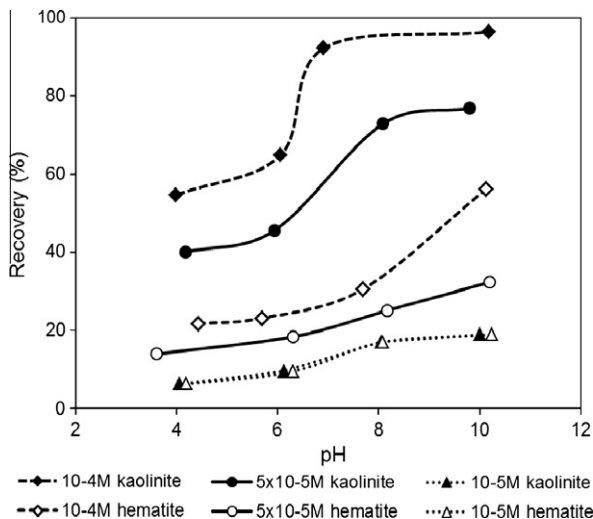

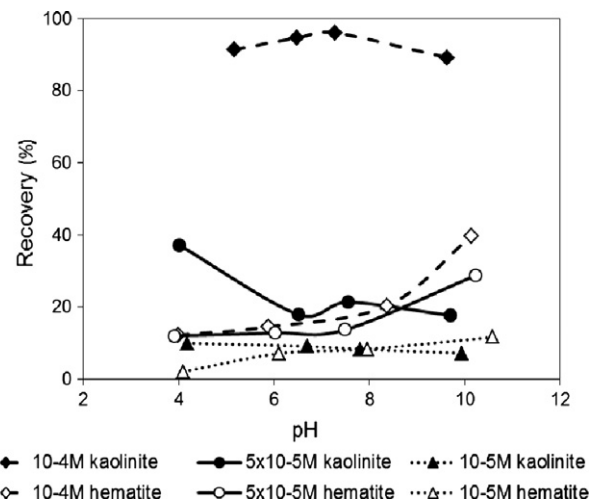**Fig. 1.** Floatability of kaolinite and hematite as a function of pH and EDA concentration.

Fig. 3. Floatability of kaolinite and hematite as a function of pH and DTAB concentration.
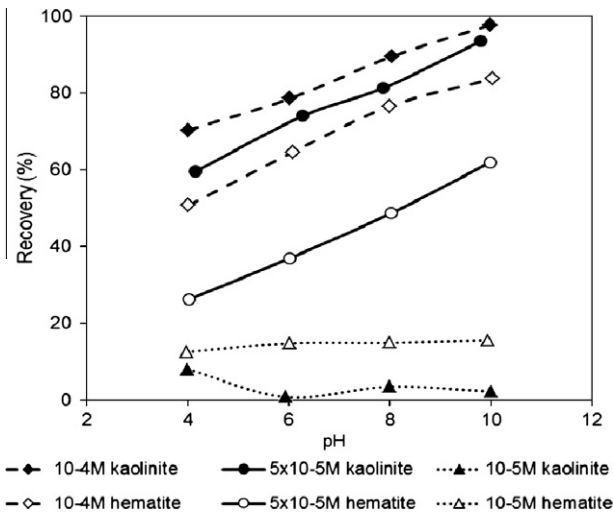
Fig. 4. Floatability of kaolinite and hematite as a function of pH and AQ142 concentration.
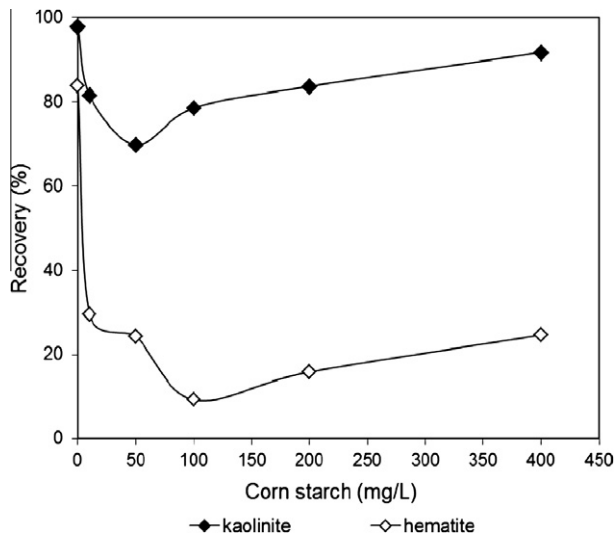

Fig. 5. Floatability of hematite and kaolinite, with AQ142 (1×10^{-4} mol/L), as a function of starch concentration, at pH = 10.

Each test was fed with 270 g of iron ore, 30 g of kaolin and 700 mL of water. The gas flow rate was 6 NL/min. A strong agitation stage (2 min) was used to homogenise the feed prior to the reagents conditioning (5 min for depressant and 2 min for collector). These experiments were done at pH values close to 7 and 10. Bench scale

tests were conducted in two size ranges: −150 μm deslimed and −45 μm.

Both stages, microflotation and laboratory scale, were conducted with distilled water.

3. Results and discussion

3.1. Microflotation experiments

Fig. 1 presents the floatability of kaolinite and hematite as a function of pH, considering the three concentrations of EDA tested. The separation of these two minerals is not possible in the absence of depressant. Fig. 2 shows the results of adding corn starch to the system, at pH = 10. The presence of depressant resulted in selective separation. One can verify a selectivity window of approximately 65% in, practically, every condition investigated. These conditions are similar to those used in the industrial process, in terms of reagents and pH. Many Brazilian plants use the etheramine EDA as a collector of quartz, sometimes mixed with other amines.

Fig. 3 shows the recovery of kaolinite and hematite, using the collector DTAB, as a function of pH considering the three concentrations tested. The results showed that the separation between kaolinite and hematite is possible in the full range of pH, just for the concentration of collector equal to 1×10^{-4} mol/L. Zhao et al. (2007), using an ammonium quaternary salt (cetyltrimtylammonium bromide – CTAB) as a collector of aluminosilicate (including kaolinite), reached similar result, floatability of kaolinite were between 80% and 90% at pH range between 4 and 10. CTAB and DTAB differ from each other in that the first has carbon chain composed by 16 carbons and the second has 12 carbons. Also, it was observed that the selectivity decreases with the increase of pH due to the increase in the hematite recovery. The selectivity windows is, approximately, 80% at pH = 4 and decreases to, approximately, 50% at pH = 10.

Fig. 4 illustrates the recovery of kaolinite and hematite, using the collector AQ142, as a function of pH considering the three concentrations tested. The results shown in Fig. 4 indicate that the separation is not possible. However, the Fig. 5 shows that the addition of corn starch results in a selectivity window of, approximately, 60%. As AQ142 is a new collector this result represents a significant contribution to the literature.

3.2. Laboratory scale experiments

The Al$_2$O$_3$ and SiO$_2$ grades of the iron ore were, respectively, 0.34% and 1.04%. Due to the low Al$_2$O$_3$ content, this parameter was chosen to evaluate the kaolinite separation from the feed blend (3.78% Al$_2$O$_3$). This stage was conducted in two size ranges: (i) coarse, particles size less than −150 μm and deslimed (ii) fine, particles size −45 μm. In the first case aggregates of kaolinite were present (this alternative simulates the feed of common industrial

Table 1
Results of laboratory scale flotation tests with feed size −150 μm deslimed.

Test	pH	Collector	Depressant	Product	Fe (%)	SiO$_2$ (%)	Al$_2$O$_3$ (%)	Fe Rec (%)	Al$_2$O$_3$ Rec (%)	Mass Rec (%)
3	7	DTAB 400 g/t	X	Reject	59.95	6.25	4.60	33.60	6.51	30.80
				Concentrate	68.13	1.20	0.72			
				Feed	62.47	4.69	3.41			
12	10	EDA 400 g/t	Corn starch 600 g/t	Reject	54.94	9.58	7.26	67.37	31.79	63.56
				Concentrate	65.02	2.90	1.94			
				Feed	61.35	5.33	3.88			
20	10	AQ142 400 g/t	Corn starch 400 g/t	Reject	58.47	7.54	5.40	46.36	17.79	42.98
				Concentrate	67.03	1.95	1.55			
				Feed	62.15	5.14	3.75			

Table 2
Results of laboratory scale flotation tests with feed size −45 μm.

Test	pH	Collector	Depressant	Product	Fe (%)	SiO$_2$ (%)	Al$_2$O$_3$ (%)	Fe Rec (%)	Al$_2$O$_3$ Rec (%)	Mass Rec (%)
24	7	DTAB 400 g/t	X	Reject	59.22	6.96	5.04	23.83	4.21	21.47
				Concentrate	67.76	1.02	0.81			
				Feed	61.05	5.68	4.13			
33	10	EDA 400 g/t	Corn starch 600 g/t	Reject	57.55	8.06	5.92	41.72	10.53	37.94
				Concentrate	67.40	1.56	1.14			
				Feed	61.29	5.59	4.11			
38	10	AQ142 400 g/t	Corn starch 400 g/t	Reject	58.58	7.37	5.23	34.34	8.83	31.52
				Concentrate	66.58	1.70	1.12			
				Feed	61.10	5.58	4.00			

flotation of iron ore). The second case simulates the condition of slimes flotation. Tables 1 and 2 present the bests results with each collector. These tables differ from each other in that Table 1 shows the results of tests with feed size −150 μm deslimed and Table 2 shows the results of tests with feed size −45 μm.

Two differences may be observed. Firstly, with the decrease of feed size, the selectivity increases, as shown by the lower contaminants grades in the concentrates of tests using feed size −45 μm. This enhanced selectivity of the fines is desirable, for the kaolinite low hardness causes the production of fines in the comminution stages.

Secondly, the finer size caused a decrease in the mass recovery in all situations, consequently, yielding decreased recovery of Fe. Also, the reject fraction iron grade was still high (approximately 50%), well above the grade acceptable in industrial scale. This high iron content is partially due to the high iron feed grade (61%). Circuit configurations including cleaner and scavenger stages, and pilot scale tests, will be required prior to a possible industrial implementation of the separation. On the other hand, silica grades in the concentrate in the range from 1.0% to 1.5% were achieved, figures compatible with iron ore concentrates specifications.

It is important to stress that the kaolinite content in the synthetic ore feeding the laboratory scale flotation tests represents an ultimate condition, being much higher than the content in ores that are processed in actual plant practice.

4. Conclusion

The separation selectivity between kaolinite and hematite was achieved using DTAB at the pH range between 4 and 10. In the presence of the collectors EDA and AQ142, the selectivity was obtained only in the presence of starch, at pH 10. Laboratory scale tests showed that as far as the particles size is concerned, better selectivity was achieved with finer particles. Circuit configurations including cleaner and scavenger stages, and pilot scale tests, will be required prior to a possible industrial implementation of the separation.

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