

DEVELOPMENT AND APPLICATIONS ON COLLECTOR'S AT THE IRON ORE FLOTATION

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ABSTRACT

It's expected for a continuous growth in the demand of iron ore, reaching more than two billion tons per year within the next year. After decades exploiting resources with high content of iron ore, now the industry faces the challenge to exploit and beneficiate more complex ores, low grade ores and also recovering of older tailing dams. The flotation technology is one of the most important and effective beneficiation processes to deal with low grade iron ores around the world, however, it is still necessary to search for new processing routes or relies on the proper selection of flotation chemicals specifically designed for each system, new collectors even to promote the optimization of the existing circuits. Two main routes are applicable for iron ore the direct flotation or the reverse flotation. The reverse iron ore flotation in Brazil, ores mainly constituted by hematite and quartz, uses ether amines as collector for silica minerals and corn starch as depressor for hematite. The process selectivity is highly impacted by the features of the etheramine, such as: mono or di-etheramine, neutralization degree, chain length, branched or linear chain, flotation pH and the size distribution of the flotation feed. This paper describes the experience obtained from laboratory and industrial trials on different ores, conducted to improve the selectivity and recovery in the iron ore flotation by selecting the route and required collector.

Keywords: iron ore flotation; flotation collectors; flotation reagents; etheramines

1. INTRODUCTION

The mining sector was an important player Brazilian industrialization and recently has passed through one of its better moments with the extraordinary international demand for mineral commodities especially iron ore concentrates. Brazil contemplates all types of ores, such as metallic, non-metallic, industrial minerals and the common characteristics of all these mining companies are: large scale installations, intensive use of water, power, natural resources and some chemicals. One of the sustainability challenges is the optimization of chemical inputs along the whole production chain. These actions include natural resource preservation: power, water, materials, emissions and waste, biodiversity, the ecologically efficient use of renewable energy, actions to be taken with suppliers, products, services, transportation, processes and operations. Our efforts in the last years have focused on developing new approaches and technologies in reagents. These efforts have resulted in new reagents for the mineral processing industry. The challenge is understood as a number of actions which will work together to reach a price-performance balance. Not only the price, but also the source of raw material, its toxicity, its biodegradability and other factors play an important role. This gives rise for the need to search for more environmentally friendly chemicals.

In mineral technology, froth flotation is a physical process for the separation of fine grained ores in aqueous suspension in the presence of air bubbles as carrier. Based on the differences in free energy of interfaces involved (solid/liquid, liquid/gas and solid/gas) the valuable minerals are separated from gangue due to the differences in their hydrophobicity. Hydrophobic particles are aerophilic and will be recovered by the froth whereas the more hydrophilic particles are kept suspended in the aqueous pulp (Araujo *et al.*, 2009). The efficiency of the flotation process is significantly determined by the application of collectors which render the surface of specific minerals hydrophobic and therefore increase their affinity to the air bubble. On the other side, the hydrophilicity of particles can be increased by wetting agents. Conclusively, the flotation of a complex ore needs specific adjustment of the collector regime to achieve high selectivity.

Depending on the collector system, the introduction of an air flow is not enough to carry the hydrophobic particles. In this case frothers have to be used in addition to stabilize the froth by reduction of surface tension of the liquid/air interface among other characteristics. The main routes to beneficiate iron ores are reverse cationic flotation of the silica minerals or direct anionic flotation of iron minerals. The route of cationic reverse flotation, in Brazil, is by far the most common process: quartz float with cationic collector's such as etheramines, mono or di, partially neutralized with acetic acid; the degree of neutralization increases the solubility of collectors and is adjusted for each ore, it also affects the flotation performance. The pH of flotation pulp varies from pH 9.5 to pH 10.5.

The development of new chemicals for the anionic flotation of iron minerals is an important route for low grade ores and for the recovery of those stored in tailing dams due to environmental problems, (Li *et al.*, 2010), using soya fatty acids formulations or phosphoric acid esters as collectors. The sodium silicate or fluor sodium silicate have a depressant effect on silicate minerals and are commonly used. The pH of flotation pulp varies from acidic (pH 3.0) to natural (pH 7.0).

The type of collector is an important factor at direct flotation, because it influences the next processing step (agglomeration process). The iron ore concentrates, obtained by direct

flotation, has been recognized as a problem, when used as pellet feed, mainly because it produces weak green pellets besides causing instability in the pelleting circuit. It is attributed, by the fact, the direct flotation is accomplished by using a surface active reagent, so the collector adsorbs on the pellet feed particles, which one, goes to the pelleting process causing the problems. In function of it adjustments and changes on the process flowchart must be implemented. (Forsmo *et al.*, 2008)

Among all concentration processes in Brazil roughly 80 million tons of iron ore concentrate are produced by froth flotation processes only. The flotation is especially employed when the iron ore is characterized by fine grain size below 150 micron and gangue is of siliceous type like quartz. The beneficiation process of iron ore is state to the art and often called “reverse iron ore flotation” because valuable iron mineral is depressed with corn or cassava caustic starch to remain in the pulp and siliceous gangue is recovered by froth. Due to their high affinity to the anionic charged surface of quartz minerals and silicates, cationic collectors are applied to render the gangue more hydrophobic. The activity and selectivity of these amine collectors is mainly defined by their chemical constitution, i.e. composition and number of hydrocarbon substituents attached to the nitrogen as primary, secondary or tertiary amines or quaternary ammonium salts.

Amine collectors typically act also as main collector, co-collector and as a foam stabilizer with sufficient froth performance in the process. Application of frother is therefore exceptional but still objective of research due to economic advantages expected from partial replacement with standard frothers as well as other products who act as a surface cleaner or dispersion agent. In addition, the chemical regime in the reverse iron ore flotation is impacted by the depressant used for iron mineral. Usually, corn starch is the main depressor used at Brazilian mines; it is a natural polymer consisting of amylose and amylopectin in variable proportions and high molecular weight. (Turrer, 2007)

Brazilian concentrator plants are processing itabiritic iron ores. The siliceous gangue, mainly quartz, is commonly floated with ethermonoamine collectors. For minor applications, synergistic mixtures of ethermonoamines and etherdiamines might be used as collector when the siliceous gangue does not contain quartz as majority or the ore contains more fines. The priority of mining companies has shifted to technologies that can not only minimize generation of effluents and wastes, but, above all, recover existing environmental liabilities. The target of the day is sustainability supported by innovative and clean technologies using the minimum natural resources. In this context, the transition between the old and the new mining business models assume a series of implications in supply chain management as a whole particularly on the supply of equipment's, mainly flotation cells like tank cell, pneumatic cell and of course reagents and new technologies.

2. MATERIAL AND METHODS

2.1 Samples

Beneficiation of crude iron ore samples from different Brazilian mines was investigated. The samples of hematite were collected from different deposits of the Quadrilátero Ferrífero area in Minas Gerais State, Brazil and were retained directly from the flotation feed of each concentrator unit. The mine samples are denominated as ore sample A, B, C, D, E, F. The elemental analysis of each ore sample is given in the examples.

2.2 Chemical Reagents

During the flotation test trials various commercial ethermonoamines reagents under Flotigam® trademark were used for the tests, each representing different levels of chain-length, neutralization and branching. The starch (2% aqueous solution) was prepared according to mine specifications in starch/ caustic soda ratios of 5:1 or 4:1 and was used accordingly as depressant. Aqueous solution of sodium hydroxide (7%) was applied as pH modifier. Typical Flotigam collectors and their characteristics are summarized in Table I.

Table I - Clariant Flotigam® collectors for silicate minerals flotation

Collector (ethermonoamines)	Chain Characteristics (length)	Neutralization Degree	Comments
Flotigam EDA	Medium	50	Collectors of silicates such as quartz, micas and feldspars in reverse flotation of iron ore.
Flotigam EDA-3	Medium	30	
Flotigam EDA-C	Short	50	
Flotigam EDA-3C	Short	30	
Collector (etherdiamines)	Chain Characteristics (length)	Neutralization Degree	Comments
Flotigam 2835	Medium	50	Collectors of silicates in reverse flotation of magnetite minerals, fine ores.
Flotigam 2835 -2	Medium	20	
Flotigam 2835 -2L	Long	30	
Flotigam 3135	Short	30	
Flotigam 5442	Long	--	New technology production
Collector (synergic mixtures)	Chain Characteristics (length)	Neutralization Degree	Comments
Flotigam 5925	Medium	30	Synergic mixture for better frother and pulp characteristics
Flotigam 5929	Long	30	

2.3 Experimental Procedure

All flotation tests were made in a Denver cell in a 1.5 liter flotation vat. The ore pulp was prepared from approximately 1.4 Kg of ore sample in 933 mL of tap water at a speed of 1.400 rpm of flotation cell rotor for 1 minute. After measuring the initial pH value caustic starch was added in portions with a total dosage rate of 450 g/t. After conditioning time of 5 minutes the pH was adjusted to pH 10.5 with sodium hydroxide solution. Then the collector was added and conditioned for 1 minute again. Finally air valve was opened to start the flotation and the froth was collected for 3 minutes. The froth fraction (tailing) and the cell fraction (concentrate) were dried in an oven at 100°C for 12 hours. After drying the mass of tailing and the mass of concentrated were weighted and chemically analyzed for silica and iron content. The mass and metal recoveries were calculated. Tree important parameter which could affect the flotation was analysed: the neutralization degree, pH influence, the dosage. The results are presented at topic 3.

3. DISCUSSION AND EXAMPLES

3.1 Influence neutralization degree

Chemically, ethermonoamines are described by the formula $R-O-(CH_2)_3-NH_2$ and are water insoluble liquids. With focus on conditioning times, ethermonoamines are applied in partially neutralized form to improve the availability and partitioning in the aqueous pulp. Nevertheless, high degrees of neutralization deteriorate the flotation performance by limiting the formation of the collector/mineral complex even though solubility is much enhanced. At Figure 1, for higher concentration the neutralization degree has no effect. For usual concentration the optimum neutralization degree is from 30 – 50 %, for ethermonoamines.

3.2 Influence of the neutralization degree and the pH

The significant relevance of neutralization degree on flotation performances is demonstrated by the dissociation equilibrium of the etheramine in aqueous medium depending on pH value. The Figure 2 shows a generic dissociation for ethermonoamine, represents the species formed by increasing pH. (Clariant, 2008)

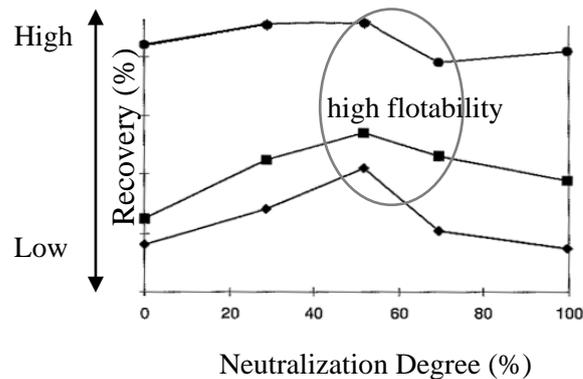


Figure 1 – Neutralization Degree as a function for the recovery. (Clariant, 2008)

The dissociation of a neutralized amine in water is:



$$K_b = \frac{[R-NH_3^+][OH^-]}{[R-NH_2]}$$

Considering the equal concentration of neutral and ionized collector species:

$$[R-NH_3^+] = [R-NH_2], \quad \text{Then the equation above: } [OH^-] = K_b = 10^{-3.5}$$

$$pOH = -\log [OH^-] = -\log 10^{-3.5} = 3.5. \quad \text{If } pH + pOH = 14.0 \text{ Then: } pH = 10.5$$

$$\text{Then: } pH = 10.5 \Rightarrow [R-NH_3^+] = [R-NH_2]$$

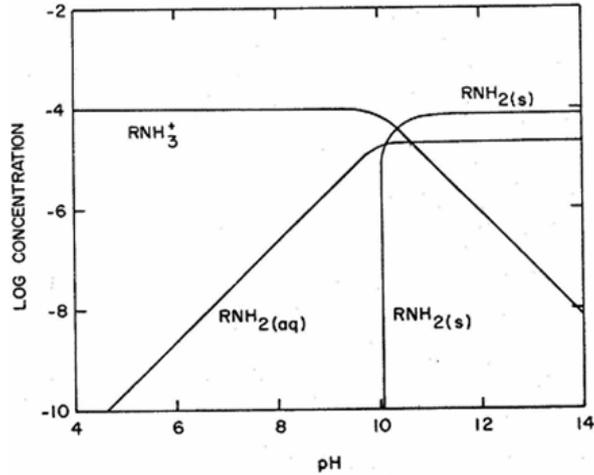


Figure 2 – Ethermonoamine dissociation as function of pH. (Fuerstenau *et al.*, 1985).

Increasing the pH, also increase the amount of neutral species (frother). So around pH 10.5 we have the same amount of collector species and frother species (neutral). The main function of neutral specie is decrease the repulsion between collector micels and act as a frother. Conclusively, the adsorption of the etheramine on the silicate surface is determined by the pH value. Thus the hydrophobic etheramine/silicate complex is formed at pH 8.0. Complete shift of the equilibrium to the complex with coexistent high concentration of dissolved non-neutralized etheramines is achieved in the pH range from 9.5 to 10.5. Conclusively, the pH regime of Brazilian iron ore concentrators is adjusted within this range. (Fuerstenau *et al.*, 1985).

3.3 Optimum dosage of collector

Depending on the ore grade and collector activity the standard consumption of collector is approximately 50g per metric ton of feed. As shown in Figure 3 this dosage level could be confirmed by various industrial trials to be the minimum to achieve an optimum recovery (Clariant, 2008; Castro and Cruz, 2003).

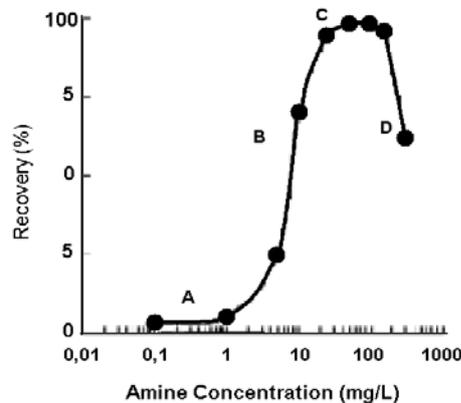


Figure 3 – Influence of amine concentration (mg/L) and the recovery

3.4 Effect of the pH on iron ore recovery

The pH for most of Brazilian's iron ore range from 9.5 to 10.5, as shown in Figure 4. The effect of the pH, for example, the dosage of collector 50g/t the silica content of the iron concentrate stays around 1.6% but the recovery of iron changes around 10% so the pH for each ore must be achieved by flotation test.

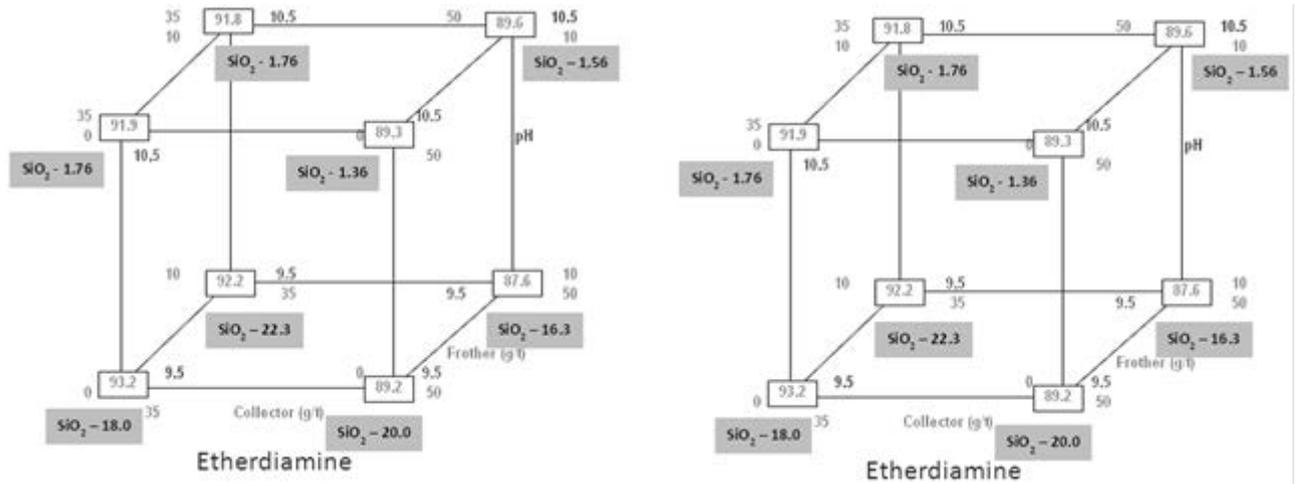


Figure 4 – Influence of the pH on the recovery of iron ore using ethermonoamine or etherdiamine

3.5 New Technology for reagent production

Micellization, a characteristic of hydrocarbon chain surfactants, assumes an important role in flotation systems. Micelles are aggregates of collector ions of colloidal size that form by van der Waal's bonding between hydrocarbon chains of the collectors (Fuerstenau *et al.*, 1985). At the new production system the micelles are smaller. (Table II)

Table II – New Product to improve the iron recovery

	Fe (%)	SiO ₂ (%)	Rec. Fe (%)	pH	Collector etheramines	Depressor Starch (g/t)
Ore A	63.0	9.0				
Test1		0.9	85.5	10.0	Flotigam 5944 (40g/t)	600
Test2		0.9	91.6	10.0	Flotigam 5442 (60 g/t)	400

3.6 Synergic interaction of collectors and additives

A synergic interaction exists between collector and additives as shown in Table III. It is possible to replace 10% of the collector by additives or synergic mixtures between two collector's results in better quality of the iron concentrate.

Table III – Synergic effects on the recovery of iron minerals

	Fe (%)	SiO ₂ (%)	Rec. Fe (%)	pH	Collector etheramines
Ore B	53.0	21.5			
Test 1		1.1	86.7	10.5	Flotigam 5945 (55g/t)
Test 2		0.53	87.3	10.5	Flotigam 5945 (50g/t) + Additive (5 g/t)
Test 3		0.55	86.7	10.5	Flotigam 5945 (35g/t) + Flotigam 3135 (15 g/t)

3.7 Challenges in the ore

Two samples of iron ore from the same mine were evaluated by flotation (table IV). About the Ore C we achieved the specification, however for ore D, it isn't possible. The problem was coarse quartz particles (> 150 micra) at the flotation feed (ore D), which are not collected by traditional etheramines collectors. Then arises the necessity to develop new collectors to overcome the changes in the ore. The results are present in Table V.

Table IV – Flotation comparison between Ore C and Ore D.

		Fe (%)	SiO ₂ (%)	Rec. Fe (%)
Ore C	Test 1	69.1	0.84	79.5
	Test 2	68.9	0.83	77.1
Ore D	Test 3	67.3	3.39	83.4
	Test 4	67.6	3.14	82.3

Table V – Challenges in the ore from the same mine.

Sieve		Mine A- Ore C		Mine A - Ore D	
Mesh	(mm)	Weight Cum (%)	SiO ₂ - Cum distr (%)	Weight Cum (%)	SiO ₂ - Cum distr (%)
+ 48#	0.300	0.75	4.16	1.08	5.52
-48# +65#	0.212	2.76	12.39	4.15	18.26
-65# +100#	0.150	5.49	21.43	7.83	30.26
-100# +150#	0.100	11.34	36.37	14.52	47.08
-150# +200#	0.075	32.55	70.98	33.82	74.61
-200# + 325#	0.044	67.97	94.62	66.80	94.34
-400#	<0.037	100.00	100.00	100.00	100.00

3.8 Direct flotation

In two different ore samples, we have the flotation by the direct route using Ore E (low grade ore). The results suggest that it is possible to achieve a concentrate with the same grade to feed one reverse flotation, with a coarse grain size. Using Ore F (tailing), the same is true. Maybe a regrind should be necessary before the reverse flotation. One important point is that the flotation occurs at natural pH. (Table VI)

Table VI – Flotation test using direct flotation route

	Assay (%)					Rec. Weight (%)	Rec. Fe (%)	Rec. SiO ₂ (%)	pH	Collector
	Fe	SiO ₂	Al ₂ O ₃	P ₂ O ₅	MnO ₂					
Ore E	38.4	41.9	1.56	0.08	0,10					
Test 1	60.0	12.6				47.6	90.5	11.3	Acid	Flotisor 1682
Test 2	51.6	23.7				52.2	87.3	22.9	Natural	Flotigam 5806
Ore F	25.9	55.0	1.29	0.22						
Test 3	50.2	13.8	2.48	0.48		45.2	87.6	13.8	Natural	Flotisor 1682

4.0 CONCLUSION

The collector performance has been evaluated for different Brazilian iron ore mines. It could be demonstrated that the currently used collector regimes of the concentrators can be precisely adapted to the requirements of the mine.

Opportunities to improve the metallic recovery and maintaining the concentrate quality by meeting the requirements of silica grade could be outlined.

It has been demonstrated that maximum collector efficiency can result from achieving the optimum balance between: chain length, hydrophobicity and the degree of neutralization.

For future developments there is space for new collectors for grain coarse quartz.

ACKNOWLEDGEMENTS

We are grateful to the Brazilian mining companies for providing the crude iron ores and for continuous support of development.

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