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Concentration of manganese tailings via reverse flotation in an acid medium

Helder Silva Souza
Mestre em Engenharia Mineral
Escola Politécnica - Universidade de São Paulo
Departamento de Engenharia de Minas e de Petróleo
São Paulo - SP - Brasil
heldersilva@usp.br

Andre Soares Braga
Pesquisador
Escola Politécnica - Universidade de São Paulo
Laboratório LFQI - Departamento de Engenharia de Minas e de Petróleo
São Paulo - SP - Brasil
andre.braga@usp.br

Arildo Henrique de Oliveira
Ph.D, Gerente de Reservas e Planejamento Longo Prazo Fertilizantes
Belo Horizonte - MG - Brasil
arildo.oliveira@valefert.com

Laurindo de Salles Leal Filho
Ph.D, Diretor Científico
Instituto Tecnológico Vale e Professor do Departamento de Engenharia de Minas e de Petróleo
Escola Politécnica - Universidade de São Paulo
Ouro Preto - MG - Brasil
laurindo.leal@itv.org, lauleal@usp.br

Abstract

Beneficiation of manganese ores has been conducted around the world by circuits composed basically of crushing, screening and spiral classifier. Therefore, solely the coarse size fractions (and commonly the richest) are actually recovered: "lump" (-75+9mm) and "sinter feed" (-9+0.15mm). In the industrial plant which processes the ore from the Azul Mine-PA, the overflow of the spiral classifier (- 0.15mm) is disposed of in a tailings dam because it bears a low Mn content (<10%) and high kaolinite content (70%). This paper reports the findings of a process development conducted on laboratory scale with the aim of concentrating Mn-bearing minerals from the tailings of the Azul Mine-PA (7% of Mn and 70% of kaolinite). The process is composed of desliming (-10µm), followed by reverse cationic flotation of kaolinite (rougher, scavenger) at pH~5. Results indicate that the reverse cationic flotation in the acid medium, when utilizing amide amine as collector and in the presence of a silicate activator and a dispersing agent could be a possible route for the concentration of tailings that had previously been deslimed at 10µm.

The results yielded a mass recovery of 18%, a metallurgical recovery of 50% and a 32% Mn concentrate which may be mixed with current high grade products, increasing the overall recovery of the plant.

Keywords: Manganese tailings, froth flotation, reverse flotation, cationic collector.

1. Introduction

Manganese ore is a mineral resource of great prominence in Brazil, owing to the large existing reserves (53.5 million tons in 2012) and concentrated production (3.5 million de tons in 2012). Furthermore, it is a strategic mineral due to its widespread use in the production of ferroalloy (DNPM, 2013).

Azul is the biggest Brazilian manganese mine and has been in operation since 1985. It is located in the north of Brazil in the Carajás mineral province and operates in synergy with other mines in the region.

The manganese ore in the Azul mine is processed in a plant composed of crushers, scrubbers, screens and a spiral classifier. The coarse fractions are naturally rich in manganese, and the products from the unit are lump ore (particle size of more than 9mm) and sinter feed (size of more than 0.15mm), the fines are discarded in a tailings dam.

The development of an appropriate technology to concentrate manganese fines will enable a production upgrade by processing the tailings as they are discharged from the plant, as well as, any that are already in the tailings dam. In addition to enhancing production, the recovery of manganese fines will also reduce the environmental impact of this mining activity, since it minimizes the disposal of tailings. Therefore, the reverse flotation of kaolinite was evaluated for the recovery of manganese from the tailings (Souza, 2015).

The relevance of kaolinite flotation study is due to its presence in various kinds of ores, therefore studies of complementary concentration routes have become relevant. The number of articles relating to the flotation of kaolinite in manganese ores is relatively small in relation to bauxite and iron ore. This study investigated the separation of kaolinite in the reverse flotation of the concentration of manganese tailings (Rodrigues, 2009).

According to Xu *et al.* (2004) the amide amine is the best collector for kaolinite flotation, therefore the amide amine collector was adopted in the experiments.

According to Neder (2005) the collector amide amine is an amine condensate characterized by having an amide group and an amine group combined in one molecule, usually synthesized from a reaction with fatty acid short chain polyamines.

2. Methodology

The sample of tailings was obtained from the industrial plant after the ore had been subjected to the steps of crushing, scrubbing, screening and classification. The spiral classifier fines (overflow) were collected and subsequently, dried and homogenized for the characterization and flotation tests.

Mineralogy studies were conducted in order to provide important information from the laboratory scale flotation studies in the definition of the concentration route. A scanning electron microscope with energy-dispersive X-ray spectroscopy (SEM/EDS) and a Mineral Liberation Analyzer (MLA) were used to determine the minerals present in the tailings. The textures, grain sizes, mineral associations and liberations were analyzed.

Following the above procedures, flotation tests were carried out on a laboratory scale, in which, the samples had previously been deslimed at 10μm in order to prepare them for the concentration tests (Leal Filho *et al*. 2012).

The collector conditioning time in both cases was one minute and the silicate activator conditioning time was 3 min. The froth collection was carried out until exhaustion, and established at 6.5 min for the tests using Flotigam 5530 , and 4.5 min for the tests using Custamine UU13. The flotation tests were done at 30% solids.

Laboratory scale flotation studies were conducted so as to understand the behavior of the sample in relation to the cationic reagent in the acid medium. Tests were performed according to the operating conditions presented in Table 1.

Test	Conditioning	Dosage Collector
PETB05	H_2SiF_6= 2,108 g/t (pH=3.0)	Flotigam 5530 =300 g/t pH=3.0
PETB06	H_2SiF_6=1,240 g/t (pH=4.0)	Flotigam 5530 =300 g/t pH=4.0
PETB07	H_2SiF_6=1,116 g/t (pH=4.8)	Custamine UU13 = 300g/t pH=4.7
PETB08	H_2SiF_6= 1,240 g/t (pH=4.8)	Custamine UU13 = 600g/t pH=4.8
PETB09	H_2SiF_6=1,240 g/t (pH=5.0)	Custamine UU13 = 450g/t pH=4.9
PETB10	H_2SiF_6= 1,240 g/t Na_2SiO_3= 500g/t (pH=4.3)	Custamine UU13 = 450g/t pH=4.3
PETB11	H_2SiF_6=1,240 g/t Na_2SiO_3 =1,000g/t (pH=4.3)	Custamine UU13 = 450g/t pH=4.3
PETB47	H_2SiF_6=1,127g/t (pH=3.8) $NaPO_3$=2,000 g/t (pH=4.5)	Flotigam 5530 = 252 g/t pH=4.7
PETB48	H_2SiF_6 =1,124g/t (pH=3.7) $NaPO_3$=2,000 g/t; pH=4.2	Flotigam 5530 = 3,000 g/t pH=5.3

Table 1
Experimental conditions in the flotation tests

In tests PETB-05 to PETB-11, conditioned pulp, together with H_2SiF_6 in 30% of solids, were utilized with the intention of activating the silicates (kaolinite) and sodium hexametaphosphate/sodium silicate for the dispersion of the pulp in sequence and then added to the cationic collector (amide amine) at the rougher and scavenger stages. In tests PETB47/48, conditioned pulp together with H_2SiF_6 in 50% of solids and sodium hexametaphosphate in sequence were added to the cationic collector (amide amine) at the rougher/scavenger stages, as presented in the schematic flowsheet in Figure 1.

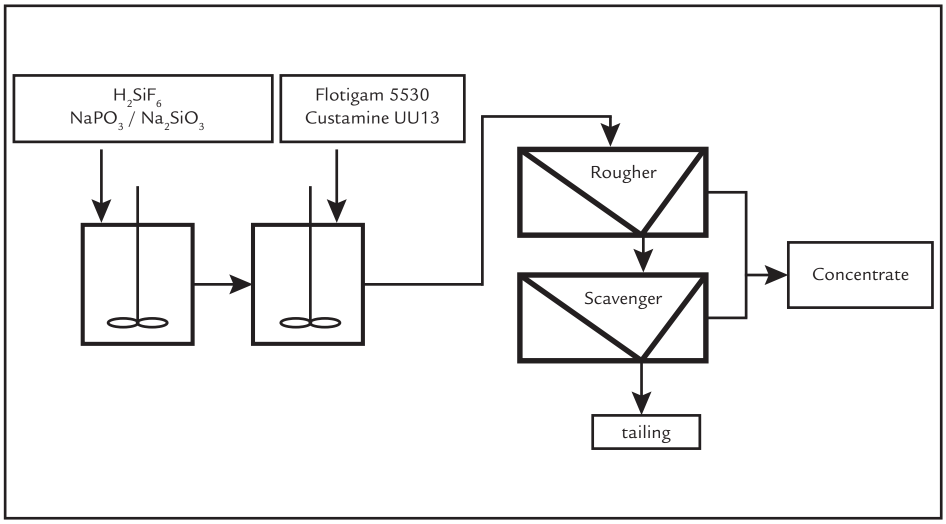

Figure 1
Schematic Flowsheet of the reverse flotation in the acid medium

3. Results and Discussion

Initially, studies of mineralogy were conducted in order to provide important information in the definition of the concentration route, in which, the tailings were mainly composed of kaolinite and smaller proportions of manganese oxides. Kaolinite presented a global liberation of 88%, whilst manganese oxides presented a global liberation level of 52% and an increase in the fines (Kahn *et al*. 2011).

According to Table 2, the sample of tailings has a Mn content of only 7.1% a silica content of 34.2% and an alumina content of 29.7% together with a high volatile content (12.5% loss on ignition) , followed by 7.3% Fe and 1.1% TiO_2.

Table 2
Chemical composition of the tailings used in the laboratory study (%)

Mn	Fe	P	SiO_2	Al_2O_3	TiO_2	LOI
7.1	7.3	0.1	34.2	29.7	1.1	12.5

According to Table 3 the mineralogical composition confirms the chemical composition, given that the sample is composed mainly of kaolinite (71 wt %), accompanied by cryptomelane/hollandite (17%), goethite (3.7%) and bixbyite (3.1%).

Table 3
Mineralogical composition of the sample used in the study

Minerals	Percentage of the mass	Minerals	Percentage of the mass
Cryptomelane / hollandite	17.0	Ilmenite	1.8
Kaolinite	71.0	Lithiophorite	1.0
Goethite	3.7	Quartz	0.7
Bixbyite	3.1	Other	1.7

Figure 2 shows the comparison of the global liberation between the Mn-bearing minerals and the principal gangue mineral (kaolinite) by fraction.

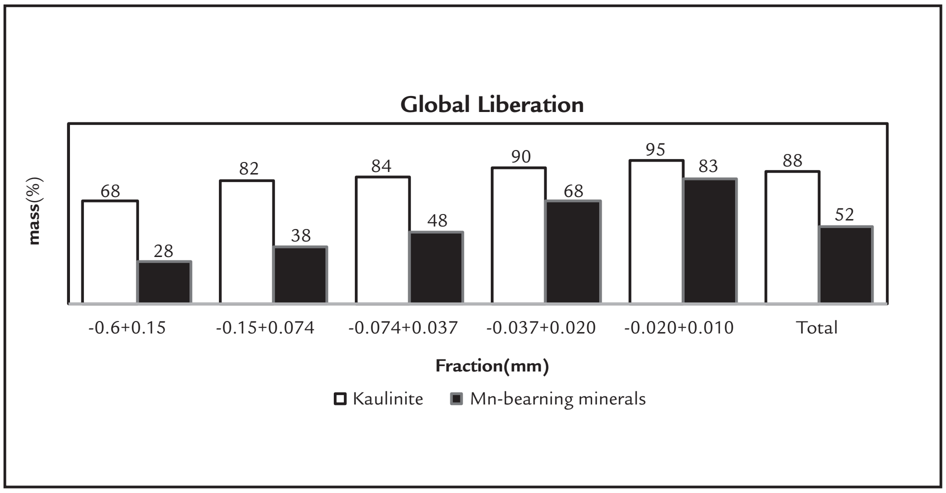

Figure 2
Global liberation between the Mn-bearing minerals and kaolinite by fraction

Owing to the fact that the kaolinite particles (the main gangue mineral) present a greater degree of liberation than the manganese minerals particles, the reverse cationic flotation of the gangue is more recommendable.

Table 4 shows the results of desliming where the flotation feed (underflow) presents an 11% Mn content.

Products	Grade (%)			Recovery (%)			
	Mn	SiO_2	Al_2O_3	Mass	Mn	SiO_2	Al_2O_3
Feed	6.94	35.94	30.11	100.00	100.00	100.00	100.00
Underflow	10.90	30.00	26.70	55.13	87.40	48.34	48.89
Overflow	1.93	39.40	34.30	44.87	12.6	51.66	51.11

Table 4
Metallurgical and mass balances of desliming

The mass of the metal recoveries and desliming were 55% and 87%, respectively. The overflow were poor in Mn (1.93%) and rich in SiO_2 (39.4%) and Al_2O_3 (34.3%), indicating the elimination of a significant amount of gangue mineral (kaolinite).

Table 5 shows the results of the particle size distribution in the flotation feed where it can be observed that the sample is very fine and shows values of F80 ~ 0.056mm.

particle size (mm)	+ 0.210	- 0.210 + 0.149	- 0.149 + 0.105	- 0.105 + 0.074	- 0.074 + 0.044	- 0.044 + 0.037	- 0.037 +0.020
% Passing	90.2	88.6	86.1	84.3	77.3	75.4	72.9

Table 5
Particle size distribution the feed flotation

Table 6 shows the results of flotation in an acid medium (pH ~ 5) with the collector and conditioned with H_2SiF_6 and sodium hexametaphosphate.

Table 6
The reverse flotation performance with a cationic collector in an acid medium

Test	Grade (%)			Recovery (%)			
	Mn	SiO_2	Al_2O_3	Mass	Mn	SiO_2	Al_2O_3
PETB05	12.6	28.9	25.3	76.9	92.5	71.1	71.7
PETB06	11.7	29.7	26.2	80.9	93.9	76.1	76.8
PETB07	9.7	31.9	28.6	80.9	90.9	78.1	78.4
PETB08	15.1	26.9	23.5	64.8	86.2	57.1	57.5
PETB09	13.9	27.3	24.2	72.5	87.9	66.2	66.8
PETB10	15.3	26.3	23.3	59.7	82.6	51.3	51.9
PETB11	14.3	27.1	23.9	68.4	87.9	60.9	61.5
PETB47	12.3	31.0	27.4	88.5	95.6	85.6	85.9
PETB48	32.0	12.7	14.1	17.6	50.5	6.9	8.7

It can be observed in Table 6, that the best result was obtained using the collector (amide amine) with a flotation concentrate of 32% manganese and 13% SiO_2. The mass recovery was 18% and metallurgic recovery 50%.

There is a need to use a high collector dosage collector possibly due to the fine characteristics of the tailings.

The best result obtained with the flotigam 5530 collector was possibly because this collector is an amine condensate which probably increases the adsorption of the collector molecules in clay minerals possibly through two adsorption mechanisms: by electrostatic attraction and hydrogen bonding. More fundamental research is therefore necessary in order to verify this hypothesis.

The Mn grade of 32% in the concentrate is an indication that the reverse cationic flotation in the acid medium, with amide amine and in the presence of a silicate activator and dispersing agent, is a possible route for the concentration of tailings that had previously been deslimed.

4. Conclusion

Within the scope of this research, one can conclude that:

The studies of mineralogy showed that the tailings were mainly composed of kaolinite and smaller proportions of manganese oxides. Kaolinite presented a global liberation of 88%, whilst manganese oxides presented a global liberation level of 52% and an increase in the fines.

The study carried out in the laboratory scale showed that it is technically feasible to produce a concentrate with a 32% Mn content from a tailing sample, taken from the Azul plant, with a7% Mn content, using desliming and cationic reverse flotation in an acid medium and in a circuit of rougher and scavenger stages together with an amide amine collector and in the presence of an activator of silicates and dispersing agent.

The results yielded a mass recovery of 18%, a metallurgical recovery of 50% and a 32% Mn concentrate which may be mixed with current high grade products, increasing the overall recovery of the plant.

Therefore the results in this project confirm the research carried out by Xu *et al.* (2004) who also demonstrated that amide amine is a good collector for kaolinite flotation.

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