ASSESSMENT OF ENVIRONMENTAL IMPACTS: RESIDUAL COLLECTORS ANALYSIS IN WATER FROM FLOTATION PROCESS[1]

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Abstract

Amines are compounds that carry one or more nitrogen atoms attached to alkyl group. The alkyl group constitutes the amines hydrophobic portion and has different chains and length. Amine salts are normally used as flotation agents (collectors) and are the most important cationic collectors at reverse iron ore flotation in Brazil. The reverse iron ore flotation basically consists of the selective separation of quartz particles from hematite. The amines, at the froth flotation processes, are added to the system being adsorbed on the quartz surface, and both are removed from the flotation cell as foam. Amines compounds can be released into the tailing dams after industrial flotation processes and still remain in the water left from the process. The present paper describes a new methodology development to analyze the residual amine in water from flotation process to evaluate the water quality in tailing dams besides can be applied to optimize the dosage.

Key words: Flotation; Iron ore; Effluents; Amine salts; “Remaining water”.

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1 INTRODUCTION

The three main techniques to concentrate iron ore comprises gravity and magnetic separation and flotation. An important parameter to define the best method for concentration depends on the granulometric distribution needed for the liberation of iron ore from the gangue species. The gravity and magnetic methods are generally applied for coarse particles, without reagents, producing a poor concentrate. The depletion of current reserves forces the beneficiation of increasingly poor minerals, which have to be ground into fine particles to achieve the liberation degree. The froth flotation is widely apllied for fine particles and needs the reagents use to produce purer concentrate.

Both hematite and quartz particles are hydrophilic and the process to separate them requires the use of chemicals to induce different property between them. The current procedure for purifying iron ore is the reverse cationic flotation. The standard reagents used in it comprise one depressant for hematite (starch) which makes it more hydrophilic and one collector for quartz (fatty amine) which makes it hydrophobic. Adsorption can be defined as the chemical interaction between solid-liquid interfaces. The fatty amine collector adsorbs on quartz surface and attaches to the air bubbles, leaving the froth in the system. The froth will then be removed from its top thus constituting the floated fraction or tailings. The starch depressor adsorbs on hematite surfaces and moves along with the water flow, leaving the system from its bottom, constituting the non-float fraction or concentrate.

Amines are a class of organic chemical compounds derived from ammonia (NH_3) resulting from partial or total substitution of the hydrogen atom per molecule of the hydrocarbon groups (alkyl or aryl - often abbreviated by the letter R). Primary amines ($R\text{-}NH_2$) are formed by the substitution of one hydrogen atom. Secondary (R1R2NH), and tertiary (R1R2R3N) amines are formed by the substitution of 2 and 3 respectively. A primary amine can be changed into an etheramine by introducing an ether group between the fatty chain and the amine group ($R\text{-}O\text{-}(CH_2)_3\text{-}NH_2$). The large amount of amines used in reverse cationic flotation comprises the etheramine type and Flotigam EDA 3® which is a standard product on the market.

Fatty amine high levels(1) have toxic effects for aquatic organisms. Chaves(2) describes the etheramines from industrial flotation process in SAMARCO mine (MG-Brazil) found in the tailing dam are degraded after a period of time by microorganisms. Araujo et al.(3) studied the biodegradation rate against *S. marcescens* for Flotigam EDA 3®, and concluded after 36 h, around 93.8% of all fatty amine had already degraded at 40 mg L^{-1}, while at the concentration of 60 mg L^{-1}, degradation reached 91.3%, after the same period of time.

The adsorption binding stability suggests the highest amount of fatty amine found adsorbed onto quartz surface. Due to the concentration(4), fatty amines can present an unpleasant smell, sensitizers, irritant to skin and eyes, mucosa membrane and respiratory tract. These compounds can be present in the environment, so it raises the need to develop an analytical methodology to quantify the presence of fatty amine in industrial water disposed to the tailing dam after the iron ore flotation.

Araujo, Yoshida e Carvalho(5) relates a quantification method for fatty amine derived from iron ore reverse flotation process effluents and residues using the colorimetric technique. The methods consist in the reaction of the group amine with an organic dye and quantification of the colored substance comparing with the analytical standard curve in a spectrophotometer UV. Araujo, Yoshida e Carvalho(6) also investigated the amine quantification using gas chromatography through amine derivatization reaction using silylating and acylating reagents.

Gas chromatography(7) (CG) has been widely used for amine analysis because of its inherent advantages such as simplicity, high resolving power, high sensitivity, shot analysis time and low cost. Components of a sample are separated as consequence of the partition between the mobile phase and a gas within the column stationary phase and after separation, the compounds obtained are identified by a detector. The flame ionization detector (FID) responds mainly to the presence of organic compounds such as fatty amines, including water sample contaminates with nitrogen and sulfur oxide.

The present paper describes the development of CG-FID method to analyze the residual amine in the reverse iron ore flotation process water.

2 MATERIAL AND METHODS

2.1 Reagent

The reagent used for the analytical curve was Flotigam EDA 3® produced by Clariant S.A (Brazil). Such product is the standard collector used in the mining industry in Brazil. Flotigam EDA 3® comprises a mono alkyl ether propylamine, partially neutralized, with the molecular formulae $R\text{-}O\text{-}(CH_2)_3\text{-}NH_2$.

2.2 Gas chromatography – FID analysis

For the sample quantification the equipment used was C.G. Agilent 789N. The injector splitless condition with T(temperature)=160°C, P(pressure)=19.808psi, purge flow= 3 mL/min. Column stationary phase of melt silica (Varian CP 624), heating ramp from 25° to 120°C (6 minutes), with flame ionization detector (FID), gas sample (comb pal).

2.3 Analytical Curve

To prepare the standard analytical curve, it was necessary to use 105.8 mg of pure Flotigam EDA 3® sample, in a 100mL volumetric flask. After that, 2 drops of concentrated acetic acid were added as well as ultra-pure water to fill up the flask. The solution was diluted three times, using 10 mL aliquots. For each sample, it was added 200µL of internal standard (PI). (PI = 0.08g THF concentrated / 25mL Ultra-pure water).

2.4 Process Water Sample

The process water samples were collected in two different mines located in the Iron Quadrangle (MG-Brazil) named Mine A and Mine B. In both mines A and B samples were collected in two different points: (1) water from the process which feeds the flotation pulp, (before adding the collector) and (2) water from the process, which will be released to the tailing dam (after the flotation). Water from the process, after the flotation, is sampled as pulp. The pulp is left under rest for 12 h for sedimentation and solid-liquid separation is performed by siphoning.

3 RESULTS AND DISCUSSION

3.1 Flotigam EDA 3® Chromatogram

The typical chromatogram for Flotigam EDA 3® is represents at Figure 1. The internal standard (THF) presents a peak retention time of 2.36 min. The etheramine presents a peak retention time of 9.91-12.06 min. The free residual alcohol stemming from Flotigam EDA 3 synthesis, presents a peak of 7.55 – 9.60 min.

The chromatography peaks for the etheramine and free alcohol do not present a single peak, in function of isomers found in the alcohol fatty chain. The isomers remain at the etheramine molecule structure, so a range retention time was used for both.

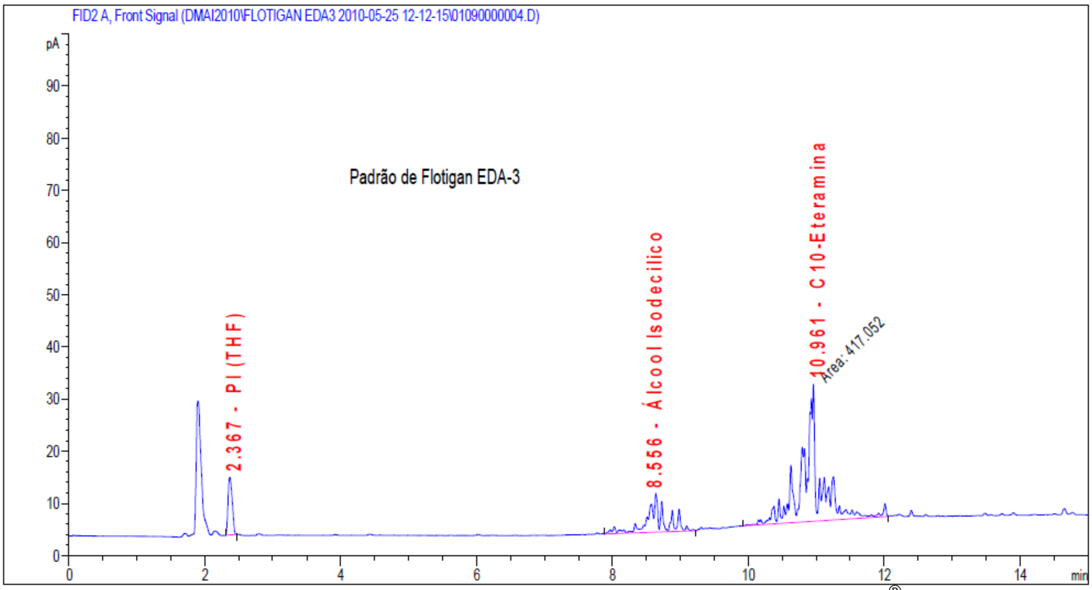

Figure 1. Typical CG-FID chromatogram to Flotigam EDA 3®.

3.2 Analytical Curve

An aliquot was measured from the solution, resulting from Flotigam EDA 3® dilution, and transferred to headspace vial from CG, resulting solutions with different collector concentrations to compose the standard analytical curve (table 1).

Table 1. Aliquot and concentration to compose the analytical curve

Aliquot (mL)	Flotigam EDA 3® (mg/L)
1	1.06
2	2.12
5	5.29
10	10.58

The analytical curve composed by the ratio area between etheramine and the internal standard (PI) is shows in Figure 2.

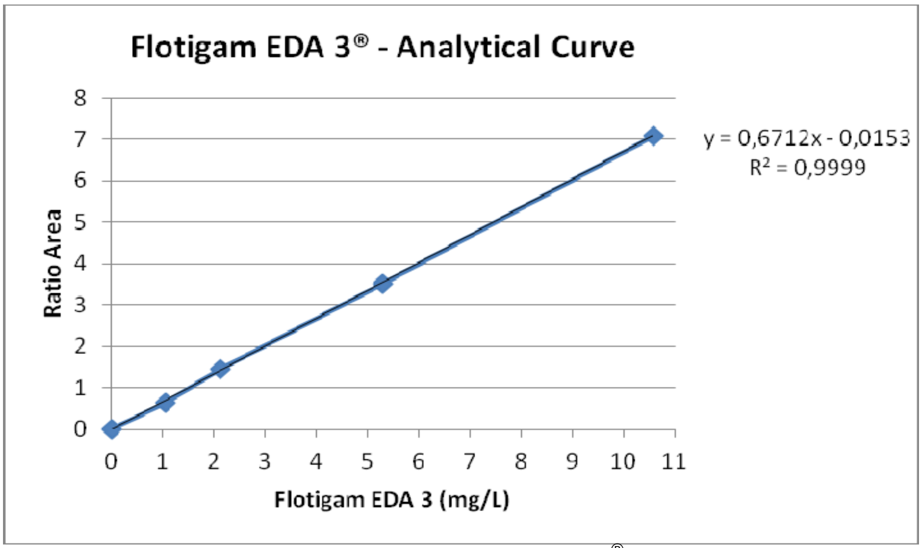

Figure 2. Analytical curve for Flotigam EDA 3® standard product.

3.3 Process Water Sample

Process parameters from flotation process are described at table 2. Flotigam EDA 3 dosage (g/ton) as well as the % SiO_2 (flotation feed) described below represent an average from the period evaluated.

Table 2. Process parameter for Mine A and B.

Process Parameter	Mine A	Mine B
% SiO_2 (Flotation feed)	14.56	36.54
Solid pulp (%)	55-65	65-70
Flotigam EDA 3 (g/ton SiO_2)	316.9	196.6
Flotigam EDA3 (mg/L) *	69.0	145.0

***Note 1:** *The Flotigam EDA 3 (mg/L) estimated concentration into the liquid fraction of flotation pulp (in case of no absorption of collector on quartz surface).*

The samples collected in point 1 (before flotation) and points 2 (after the flotation) are identified in Table 3, as well as, the quantification results.

Table 3. CG-FID analysis results for Mines A and B.

Point	Mine A		Mine B	
	Sample day	Flotigam EDA 3 (mg/L)	Sample day	Flotigam EDA 3 (mg/L)
1	03.03.2010	*ND<1	08.03.2010	*ND<1
2	03.03.2010	1.1	08.03.2010	1.3
2	06.03.2010	1.1	09.03.2010	1.7
2	08.03.2010	1.0	11.03.2010	1.6

**ND= Not Detected < 1 mg/L*

The colorimetric and CG (derivatization) techniques analyze indirectly the fatty amine concentration by reaction before the measurement. The nitrite, nitrate and ammonium found in the water from the process as well as sub-products from synthesis (free alcohol) represent a source of reagents and can lead to a false positive for fatty amine concentration value.

The CG-FID separates the etheramine molecule from other substances including sub- products from synthesis, due to different polarity between the column and the substance which composes the sample.

The values found for the Flotigam EDA 3 for samples from point 1 (Mine A and Mine B) shows values lower than 1 mg/L confirming the absence of etheramine in the waste water.
As for point 2 (Mine A and Mine B) the values are between 1-2 mg/L confirming most part of etheramines, around 98% (in accordance with note 1) found absorbed on quarts surface, not remaining at the liquid part of the pulp.

4 CONCLUSIONS

The CG-FID method to analyze the residual amine in the iron ore reverse flotation water from the process, shows to be adequate for etheramine analysis after the flotation process. The technique is able to separate the chemical compounds present in the water from the process. The values (98%), found by the experiment, confirm that most part of etheramines are found absorbed on quarts surface, not remaining in the water from the process.

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