Environmental impact of an etheramine utilized as flotation collector

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Abstract: Flotigam EDA is an etheramine with dodecyl radical and neutralization degree, with acetic acid, of 50%, manufactured by Clariant. This species is a common collector for quartz in the concentration of iron ores via the cationic reverse flotation technique. The scarcity of information on the presence of amines in effluents of iron concentration plants operating reverse cationic flotation and on toxicity and biodegradability of etheramines lead to the need of laboratory studies including: (i) determination of residual Flotigam EDA in samples collected in mining companies and in water from filtering concentrate and tailings of bench scale flotation; (ii) toxicity for *Eisenia foetida*; (iii) acute toxicity for *Daphnia magna*; (iv) oral medium lethal dose for rats; (v) biodegradability test. The results led to the conclusions that the collector Flotigam EDA utilized in the reverse cationic flotation of iron ores adsorbs tightly onto quartz particles in the conditioning stage of the reagent with the pulp; desorption is not significant and is not enough to cause negative environmental impacts; the collector is biodegradable at the concentrations assayed in industrial effluents and at these levels it does not present risks to species that are usually employed for toxicity assays.

1 INTRODUCTION

Iron ores may be concentrated by gravity and magnetic techniques and by flotation. The choice of the concentration method depends essentially on the definition of the mesh of grind for the liberation of the iron minerals from the gangue species. The so-called physical methods of concentration (gravity and magnetic) do not require the addition of reagents, but their application is restricted to coarse size ranges and the concentrates are less pure. The production of concentrates with high iron grades and low impurity levels from ores that require fine comminution for the liberation of the iron minerals from the gangue makes necessary the use of the "froth flotation" or, simply, flotation technique.

Flotation is a physico-chemical technique based on differences of surface characteristics among the mineral species present in the pulp, the most important being hematite (Fe_2O_3) and quartz (SiO_2).

Flotation may be performed either in sub-aeration mechanical cells or in columns. The selectivity in the process requires the addition of chemical reagents to induce the differential property. At their natural condition particles of hematite and quartz are both avid for water. The hematite particles are rendered even more water eager (hydrophilicity) by the action of starch and those of quartz become

water averse (hydrophobicity) by the action of amine. Amine plays also the roles of stabilizing the froth generated by the addition of air to the system and facilitating the kinetics of quartz particles-air bubbles interaction. Hydrophobic particles are air avid and are carried by the froth phase while those hydrophilic remain in contact with water, rendering possible the selective separation among species or concentration.

The phenomenon of a chemical species concentration on a mineral surface (or else, at the solid-liquid interface) is designated as adsorption. Amine species adsorbed onto the quartz surfaces cause these particles to leave the system with the froth, being removed from the top of the flotation machine, constituting the floated fraction or tailings. Due to the presence of adsorbed starch molecules, hematite particles follow the water flow, being removed at the bottom part of the flotation machines, constituting the non floated fraction or concentrate. In most flotation systems the particles of the useful mineral are removed by the froth, characterizing the direct flotation. The remotion of gangue particles by the froth, the concentrate being collected as the unfloated fraction, leads to the so-called reverse or inverse flotation.

The amine addition level is normally between 20 and 200 g/t (grams of amine per ton of feed), depending on the ore composition and the desired concentrate quality.

Amines are organic compounds that contain the group NH_2 bound to an alkyl or aromatic radical (example: aniline). Only alkylamines are employed in ores flotation.

A primary alkylamine RNH_2 may be visualized (equation 1) from the substitution of a hydrogen of the ammonia molecule by an alkyl radical:

$$NH_3 \Rightarrow RNH_2 \quad (1)$$

The replacement of a second and, eventually, a third hydrogen leads to the formation of secondary and tertiary amines, which are not employed in flotation.

A primary amine may be changed into an etheramine by means of the introduction, between the alkyl radical and the nitrogen atom, of a $O\text{-}(CH_2)_3$ group, as shown in equation 2:

$$RNH_2 \Rightarrow R\text{-}O\text{-}(CH_2)_3\text{-}NH_2 \quad (2)$$

All amines employed in the flotation of iron ores are etheramines.

The alkylamines with more than 5 carbon atoms in the alkyl radical present very low solubility in water. The solubility may be increased by means of partial neutralization with acetic acid. The solubility increases with the neutralization degree at the expense of the flotation performance.

Flotigam EDA is an etheramine with dodecyl radical and neutralization degree, with acetic acid, of 50%.

The main property of etheramines employed in flotation, in aqueous environment, is hydrolysis or dissociation:

$$R\text{-}O(CH_2)_3\text{-}NH_2+H^+ \Leftrightarrow R\text{-}O(CH_2)_3\text{-}NH_3^+ \quad (3)$$

Equation 3 shows that acidity favors the dissociated species and alkalinity stabilizes the molecular species. The equilibrium condition for the concentration of the two species stays at pH 10.5. For pH 9.5 the cation concentration approaches 100%, the same happening with the molecular species from pH 11.5. The ionic species is water soluble and adsorbs easily onto the quartz surface, by an electrostatic attraction mechanism, considering that the mineral surface is negatively charged at pH values above 2.5. With the increase of the adsorption density of the amine cations, the hydrocarbon chains approach each other and establish van der Waals bonds, creating high stability configurations known as hemi-micelles. For the pH value 10.5, molecular species of amine interpenetrate between ionic species, eliminating the repulsive electrostatic component in the hemi-micelle, rendering the configuration even more stable. The molecular species also act as frother, imparting elasticity to the interlamelar film in the froth, enhancing the selectivity of the separation. The particle-bubble attachment causes the interpenetration of collector and frother layers, stabilizing the adsorption onto quartz of the frother acting species. The stability of the adsorption bond does not suggest the possibility of amine desorption in the tailings pond.

2 STATE OF ART

A review of the state of art on amines in mining effluents revealed a lack of specific legislation (definition of standards) in Brazil and overseas.

In the state of Minas Gerais Copam's rule nº 10, 16/12/1986, published in the official newspaper Jornal Minas Gerais in 10/01/1987, defines maximum contents for some potentially harmful substances, such as:

(i) nitrate: 10 mg/L
(ii) nitrite: 1.0 mg/L
(iii) ammoniacal nitrogen: 1.0 mg/L.

In all the three cases the content refers to contained nitrogen.

In the United States of America there are standards for the concentration of certain amines (Table 1), distinct from these employed as flotation collectors, established by the US Environmental Protection Agency - EPA - Water Quality Criteria:

(i) Documents 1980 EPA - 440/5 - 80 - 015 a 079
(ii) Federal Register, Part V. Friday, November 28, 1980 - Volume 45, nº 231

It is relevant stressing that these amines are by far more toxic than the fatty etheramines employed in flotation.

In Canada there are no standards regarding amines. In general EPA standards are utilized.

In the United Kingdom, fatty amines are employed in the production of silvite concentrate (KCl) at the Boulby concentrator, Cleveland Potash Ltd, in North Yorkshire. The liquid effluents and the flotation tailings are disposed directly into the ocean. There are no environmental standards for the reagent amine.

Since January 1st 1998 the European Community adopted the concentration 28 mg/L as the maximum limit for NH_4^+ in effluents.

The literature search on toxicity brought few specific pieces of information.

Saube (1986) mentions toxicity data for distearyldimethylammonium chloride:
(i) fishes: LC_{50} 1.5 – 40 mg/L (LC_{50} ou TL_m is the concentration that causes the death of 50% of the organisms, under the test conditions, for a 24 hours period);
(ii) daphniae (still water crustacean): LC_{50} 4 – 100 mg/L.

The data are vague, the ranges are fairly wide and the amine is different from these employed in flotation.

Ritcey (1989) states that the value of LC50 for fathead minnow varies from 3.2 to 32 mg/L in the presence of Aeromine 3037, a primary amine 50% neutralized with acetic acid, manufactured in the past by Cyanamid, today Cytec. The company's catalogue does not inform the number of carbon atoms in the radical.

The biodegradability of surfactants is also discussed by Saube (1986). The minimum biodegradability level required by the European community legislation is 80% in the OECD confirmatory test. The figures mentioned for cationic surfactants are:
(i) cetyltrimethylammonium bromide: 98%
(ii) dodecylbenzyldimethylammonium: 96%
(iii) distearyldimethylammonium: 94%.

A study from the mid seventies on flotation reagents biodegradability (Read & Manser, 1975) presents the following results for a tallow primary amine acetate (Armac T - Armour Hess Chemicals Ltd):
(i) BOD mg/L after 5 days: 0.5 [C] 1 mg/L; 0.2 [C] 10 mg/L
(ii) -BOD mg/L after de 10 days: 1.7 [C] 1 mg/L; 1.6 [C] 10 mg/L.

Table 1 EPA standards for the concentration of certain amines

Parameter	Concentration ng/L in water for human consumption*	Concentration ng/L in effluents*
N-nitrosodimethylamine	14	160000
N-nitrosodiethylamine	8	12400
N-nitrosodi-n-butylamine	64	5868
N-nitrosodiphenylamine	49000	161000

* the values refer to risk of cancer 10E-5

The reagent is biodegradable at low concentrations, the action being inhibited at concentrations higher than 3 mg/L.

3 LABORATORY STUDIES

The scarcity of information on the presence of amines in effluents of iron concentration plants operating reverse cationic flotation and on toxicity and biodegradability of etheramines lead to the need of laboratory studies including:
(i) Determination of residual Flotigam EDA in samples collected in mining companies and in water from filtering concentrate and tailings of bench scale flotation.
(ii) Toxicity for **Eisenia foetida**.
(iii) Acute Toxicity for **Daphnia magna**.
(iv) Oral Medium Lethal Dose for Rats.
(v) Biodegradability Test.

3.1 Determination of Residual Flotigam EDA

The determination was performed in samples collected in mining companies and water resulting from filtering concentrate and tailings of bench scale flotation.

The residual content of FLOTIGAM EDA was determined in samples collected in different points of the industrial facilities of mining companies located in the Iron Quadrangle and in products of bench scale flotation with ore from CVRD's Conceição mine (Table 2). The determinations were performed, via chromatography (CG/FID), after extraction with chloroform, at the Technical Application Mining Laboratory - Clariant. The detection limit of the method is 0.5 mg/kg.

The method was sensitive enough for quantifying the collector concentration in samples collected in two tailings ponds, the values being slightly above the detection limit.

The assays of the liquid phase from filtering the products of laboratory scale flotation tests confirmed the almost total adsorption of the collector.

3.2 Toxicity for Eisenia Foetida

The assays were performed at Instituto Tecnológico do Paraná - TECPAR, with brood stock supplied by the Biological Assay Laboratory of CETESB/SP. The presence of animals was verified for collector concentrations several orders of magnitude higher than the levels assayed in the samples collected in industrial environments.

3.3 Acute Toxicity for Daphnia Magna

The assays were performed at Instituto Tecnológico do Paraná - TECPAR, with brood stock supplied by Instituto Ambiental do Paraná. The results indicated that FLOTIGAM EDA presents EC_{50} = 0.791 mg/L in 48 hours of incubation, with confidence limits (95%) between 0.63 e 0.99 mg/L. The statistical method employed was Trimmed Spearman - Karber. The lower limit of the confidence

interval is higher than the largest concentration of collector assayed in industrial environment. The reason for choosing Daphnia was the fact that this species is more sensitive to reagents than fishes.

Table 2 Results of assays of concentration of Flotigam EDA performed in samples collected in companies that utilize the reagent. The method was chromatography (CG/FID), after extraction with chloroform. The detection limit is 0.5 mg/kg

Sample	Flotigam EDA (mg/kg)
Campo Grande tailings pond– SAMITRI 24/05/99 **	0.62
Recirculated water – SAMITRI 24/05/99	nd* < 0.5
Tailings pond feed – MBR 06/05/99	nd < 0.5
Tailings pond – MBR 06/05/99	nd < 0.5
Final effluent (tailings pond overflow) – MBR 06/05/99	nd < 0.5
Tailings pond feed – CVRD-Cauê 14/05/99	nd < 0.5
Tailings pond – CVRD-Cauê 14/05/99	nd < 0.5
Final effluent (tailings pond overflow) – CVRD-Cauê	nd < 0.5
Rio do Peixe tailings pond – CVRD-Conceição 26/05/99	0.58
Tailings pond – CVRD-Conceição 26/05/99	nd < 0.5
Itabiruçu tailings pond– CVRD-Conceição 6/05/99	nd < 0.5
Tank feed – CSN 06/05/99	nd < 0.5
Tank – CSN 06/05/99	nd < 0.5
Final effluent – CSN 06/05/99	nd < 0.5
Recirculated water – CVRD-Timbopeba 25/05/99	nd < 0.5
Laboratory test – RDC294*** 26/04/99	nd < 0.5
Laboratory test – RDC296 26/04/99	nd < 0.5

* nd: not detected

** sample collection date

*** laboratory tests. Liquid phase resulting from filtering concentrate and tailings.

3.4 Oral Medium Lethal Dose for Rats

The assays were performed at Instituto Tecnológico do Paraná - TECPAR, aiming at determining the oral medium lethal dose for albino rats, Wistar strain. The LD_{50} was calculated by means of the Litchfield-Wilcoxon's statistical method. The results showed LD_{50} = 1536 mg/kg for males (higher 1722 mg/kg; lower 1370 mg/kg) and LD_{50} = 1425 mg/kg for females (higher 1684 mg/kg; lower 1205 mg/kg). These values are several orders of magnitude higher than the concentrations of collector assayed in industrial environments.

3.5 Biodegradability Assay

The biodegradability assays were performed at the Technical Application Laboratory / Microbiology - Clariant, recognized by the Brazilian Health Ministry. The immediate biodegradability is measured by means of the soluble COD decay with the use of the Inherent Biodegradability Modified Zahn Wellens Test (OECD). The following samples were assayed: FLOTIGAM EDA as a concentrate solution; FLOTIGAM EDA 7%, final effluent from CSN's Casa de Pedra concentrator and SAMITRI's tailings pond overflow. FLOTIGAM EDA concentrate solution presented, after 28 days, 20% degradability, being characterized as a non biodegradable product. Degradation levels assayed for FLOTIGAM EDA 7% solution, CSN's final effluent and Samitri's overflow were, respectively, 94%, 93% and 90%. All these samples presented, in a period of 28 days, degradability levels higher than 80%, so they are characterized as biodegradable products.

4 CONCLUSION

The collector FLOTIGAM EDA utilized in the reverse cationic flotation of iron ores adsorbs tightly onto quartz particles in the conditioning stage of the reagent with the pulp. Desorption is not significant and is not enough to cause negative environmental impacts. The collector is biodegradable at the concentrations assayed in industrial effluents and at these levels it does not present risks to species that are usually employed for toxicity assays.

REFERENCES

Read A. D. & Manser R.M., 1975. Residual flotation reagents: Problems in effluent disposal and water recycle. In: *Proceedings XI Mineral Processing Congress.*, 1323-44.

Ritcey G.M. 1989. *Tailings management: Problems and solutions in the mining industry*, Elsevier, Amsterdam, 970 pp.

Saube J. 1986. *Surfactants in consumer products: Theory, technology and applications*, Springer-Verlag, Berlin, 536 pp.

Wpływ na środowisko eteraminy używanej jako kolektor flotacyjny

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Streszczenie: Flotigam EDA, produkowany przez Clariant, jest eteraminą z rodnikiem dodecylowym i 50%-towym stopniem neutralizacji z kwasem octowym. Ta substancja jest popularnym kolektorem kwarcu przy koncentracji rud żelaza poprzez technikę odwrotnej flotacji kationowej. Znikoma ilość informacji na temat występowania amin w odciekach z koncentracji żelaza w zakładach wykorzystujących odwrotną flotację kationową oraz na temat toksyczności i biodegradacji eteraminy stwarza konieczność prowadzenia badań laboratoryjnych w zakresie określenia pozostałości Flotigam EDA w próbkach zebranych w kopalniach i w wodzie z koncentratu filtrującego oraz stawów poflotacyjnych; (ii) toksyczności dla *Eisenia foetida*; (iii) toksyczności dla *Daphnia magna*; (iv) śmiertelnej średniej dawki doustnej dla szczurów; (v) wykonania testu biodegradacji. Wyniki badań doprowadziły do wniosków, że kolektor Flotigam EDA używany w koncentracjach rud żelaza poprzez technikę odwrotnej flotacji kationowej, adsorbuje się ściśle na cząsteczkach kwarcu w stadium przygotowywania odczynnika. Natomiast desorpcja nie jest znaczna i jest niewystarczająca, aby mieć negatywny wpływ na środowisko. Kolektor ulega biodegradacji w roztworach pobranych w wyciekach przemysłowych i na tych poziomach nie przedstawia ryzyka dla gatunków, które zwykle wykorzystywane są w pomiarach toksyczności.