Minerals Engineering 89 (2016) 24–29

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Separation of amine-insoluble species by flotation with nano and microbubbles

S. Calgaroto[a], A. Azevedo[b], J. Rubio[b,*]

[a] Instituto de Química, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500, Campus do Vale, Prédio 43131 – Setor 1, 91501-970 Porto Alegre, RS, Brazil[1]
[b] Departamento de Engenharia de Minas-DEMIN, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500, Campus do Vale, Prédio 43819 – Setor 6, 91501-970 Porto Alegre, RS, Brazil[1]

ARTICLE INFO

Article history:
Received 16 June 2015
Revised 26 November 2015
Accepted 10 January 2016
Available online 14 January 2016

Keywords:
Amines
Flotation
Nanobubbles
Microbubbles
Environmental

ABSTRACT

Amines (alkylamines–ether amines) are employed on a large scale to separate iron ores by reverse flotation of the gangue particles (mostly quartz and silicates). Quartz gangue particles coated with amine collector are dumped in tailings dams as concentrated pulps. Then, the fraction of the amines that detach from the surfaces and the portion that is soluble in water, contaminate surface and ground-water supplies. This work presents a novel flotation technique to remove decyl-trimethyl-ether-amine (collector employed in Brazilian iron mines) from water. This amine forms precipitates at pH > 10.5 which are removed by flotation with microbubbles (MBs: 30–100 μm) and nanobubbles (NBs: 150–800 nm). Bubbles were generated simultaneously by depressurization of air-saturated water (P_{sat} of 66.1 psi during 25 min) forced through a flow constrictor (needle valve). The flotation by these bubbles is known as DAF-dissolved air flotation, one of the most efficient separation technologies in water and wastewater treatment. Herein, best results (80% amine removal) were obtained only after selective separation of the MBs from the NBs exploring the fact that while the NBs remain dispersed in water, the MBs rise leaving the system. The MBs, because of their buoyancy, rise too rapidly and do not collide and adhere appropriately at the amine colloids/water interface, even causing some precipitates breakage. It was found that the "isolated" NBs attach onto the amine precipitates; aggregate (flocculate) them and entrain inside the flocs before rising by flotation. Because of the low residual amine concentration in water (6 mg L^{-1}), it is believed that this flotation technique have potential in this particular treatment of residual amine-bearing effluents.

1. Introduction

Amines are organic compounds widely used in the industry. The consumption of these reagents as flotation agents (collectors) in iron and potassium mining is growing fast in Brazil (Araujo et al., 2010). In the reverse flotation of iron ore the process consists of a selective separation of quartz/silicates particles (gangue material) from the valuable iron oxides. Thus, the amine collector is adsorbed onto quartz particles surfaces and is removed from the system as a mineralized froth and dumped in tailings dams.

It is estimated that approximately 5500 tons of amine derivatives per year are used in flotation processes only in Brazil, values that will continue to increase in the next few years, due to the more complex (disseminated-locked particles) and low feed grade of values in future ores (Araujo et al., 2010).

The use of amines in mining industry has been a matter of concern because of various environmental problems involved; amines are accumulated in large quantities in tailings dams and present incomplete degradation (Araujo et al., 2010; Chaves, 2001; Baltar et al., 2002). Another problem (at least in Brazil) associated with wastewaters containing amines is the nonexistence of specific protective legislation (Peres et al., 2000; Neder and Leal Filho, 2005).

High levels of fatty amines can be harmful and cannot be directly disposed into aquatic bodies (Newsome et al., 1991; Schultz et al., 1991). More, their toxicity, degradation and byproducts formed are issues which are not completely understood. Studies on amine biodegradation have been reported by Araujo et al. (2010) and Chaves (2001).

Chaves (2001) studied the toxicity of an ether amine (2% by weight concentration – Akzo Nobel®) on *Tenebrio molitor* larvae and found that about 50% of the insect population expired in

---

* Corresponding author.
E-mail address: jrubio@ufrgs.br (J. Rubio).
[1] www.ufrgs.br/ltm.

http://dx.doi.org/10.1016/j.mineng.2016.01.006
0892-6875/© 2016 Elsevier Ltd. All rights reserved.

7 days. The same author evaluated the effect of acute toxicity of these amines to albino Wistar rats, concluding that the absorption of the ether amine orally by the body is low, but the toxicological effects when it is absorbed by the body (intraperitoneal absorption) caused leukopenia, leading to death of 50% of the population. Also, it was concluded that the degradation time of these ether amines in tailings dams would be approximately 12 days. But, the byproducts species are not known and the emission, in large quantities of nitrogen compounds still continues.

DAF-dissolved air flotation is a well-known separation technology for removing colloids, precipitates, flocs, oily drops, fine pollutants and ultra-fines solids (Rubio et al., 2002; Oliveira and Rubio, 2009; Rodrigues and Rubio, 2007; Edzwald, 1995, 2010; Liu et al., 2012; Karhu et al., 2014).

The amines are precipitated in alkaline medium, after a decrease of their solubility at pH > 10.5 (Laskowski, 1989, 2013; Smith and Akhtar, 1976; Fuerstenau et al., 1985). Herein, the amine was precipitated at pH 10.8 and the precipitates or flocs removed by flotation.

This work is a continuation of a series on flotation of pollutants which also explores the properties of nanobubbles (NBs) on flotation systems (Calgaroto et al., 2014, 2015). Recently, our research group discovered and measured the simultaneous generation of microbubbles (MBs) and NBs in DAF, after depressurization of a flux of water containing dissolved air in a flow constrictor (Calgaroto et al., 2014, 2015). The separation of the NBs from the MBs and their flotation properties by deferential rising velocities, in water, was another finding (Calgaroto et al., 2015).

2. Experimental

2.1. Materials and reagents

Solutions (2–500 mg L^{-1}) of a commercial amine: Flotigam EDA 3B (Clariant®), were prepared using deionized water (reverse osmosis) and used throughout the work. This reagent is a cationic decyl-trimethyl-ether-amine with molecular weight of 195 g mol^{-1} (molecular formula: $[R{-}O{-}CH_2)_3{-}NH_3]^+ \ CH_3COO^-$, where R is a hydrocarbon chain of approximately ten carbon atoms; molecular weight).

Solutions of pre-polymerized coagulant Acquafloc 18 ($Al_n(OH)_mCl_{3n-m}$; cationic; Faxon®) and NaCl (supplied by Synth®) were employed for flocculating the amine precipitates.

A buffer solution, composed of bromocresol green, potassium biphthalate and 0.1 M NaOH was used in the colorimetric method for determination of the residual content of amine. Chloroform (Merck®) was used as solvent in the chemical extraction of amine and NaOH and HCl solutions were employed for pH adjustments.

2.2. Methods

2.2.1. Characterization of the amine precipitates

The residual turbidity (NTU) of solutions was measured with a nephelometer (Hach® 2100N) in order to follow the precipitation of the amine Flotigam EDA 3B at pH 10.8. Measurements (triplicated runs) were performed at different amine concentrations and pH 10.8 (standard deviations were <1%). The higher the turbidity, the greater the concentration of the colloidal precipitates.

The amine precipitates were characterized by their size and zeta potential. The particle size distribution and the zeta potential of the nano sized amine precipitates were determined using a Zeta Sizer Nano ZS (red badge) – ZEN3600 – Malvern® Instrument. The particle size distribution of the micrometric precipitates was determined by laser diffraction (Cilas® 1064).

The ZetaSizer Nano employs a Laser Doppler Microelectrophoresis technique whereby an electric field is applied to the precipitates migrating at a velocity that is dependent on zeta potential. This velocity is measured by laser interferometry-M3-PALS (phase analysis light scattering), which enables the calculation of the electrophoretic mobilities, then converted to zeta potential (millivolts) using Smoluchowski's equation (Hunter, 1981). This equipment uses dynamic light scattering (DLS) for size measurements (Berne and Pecora, 2000). Measurements of zeta potential and size were performed at a scattering angle of 90°, a wavelength of 290 nm and a temperature of 296 K. Each zeta potential and size determination corresponded to mean values calculated from 90 measurements (forty-five for two different samples).

The experiments were performed in duplicate with three runs of analysis for each sample and the mean values were calculated with associated errors corresponding to the standard deviation of the data.

2.2.2. Jar test for flocculation of amine precipitates

These studies were carried out in Jar Test® equipment (0.6 L of jars capacity). The solutions of Flotigam EDA 3B, at various concentrations (2–500 mg L^{-1}; pH = 11) were destabilized with an inorganic salt (5 mg L^{-1} NaCl) and flocculant (5 mg L^{-1} Acquafloc 18).

The resulting suspension was submitted to a rapid stirring (120 rpm) for 1 min to promote the diffusion and adsorption of destabilizing reagents. This was followed by slow stirring (50 rpm) for 1 min to build up the flocs of the amine precipitates. This was necessary to strengthen the precipitates and improve their flotation.

2.2.3. Flotation studies

2.2.3.1. Removal of precipitates (flocs) of amine by DAF (flotation with MBs + NBs). Here, DAF will refer to conventional flotation with MBs and NBs and F-NBs will refer to flotation with only NBs, after separation of the MBs. MBs have been measured in our laboratory as having Sauter diameters varying between 30 and 100 μm (Rodrigues and Rubio, 2003) and NBs between 300 and 800 nm, measured in the same ZetaSizer Nano ZS (Calgaroto et al., 2014).

Flotation studies were carried out using the same setup shown as in Calgaroto et al. (2015). The bubbles were generated by depressurizing air-saturated water solutions (flow rate of 0.2 L min^{-1}) forced through a steel needle valve (2-mm internal diameter: Globo 012 – Santi®).

The saturation of pure deionized water in air was achieved in a stainless steel vessel with a height of 15 cm, an inner diameter of 12 cm and a wall thickness of 1 cm. The vessel enclosed an internal glass container of with a height of 14 cm, an inner diameter of 10 cm, a wall thickness of 0.5 cm and a capacity of 0.7 L. The air was dissolved, in batch runs, at 66.1 psi pressure for 25 min. Inline air filters were employed to purify the depressurized air in water.

The flotation of the precipitate flocs followed, using 150 mL of water with bubbles in a micro column (240 mL capacity; h = 280 mm; diameter = 23 mm) containing an air inlet at the base.

2.2.3.2. Removal of precipitates (flocs) of amine by flotation with NBs (F-NBs). Fig. 1 shows the flotation set up, which is similar to that used in Section 2.2.3.1, but includes a glass column (2 L capacity; h = 250 mm; diameter = 100 mm) employed to separate the NBs from the MBs. This column had two air inlets at the base: one entry receiving the depressurized flow (NBs and MBs) and another connected to the flotation column to inject the isolated NBs.

The separation of the bubbles proceeded simply letting the MBs rise (about 4 cm min^{-1}), for 3 min, abandoning the glass column, leaving the NBs dispersed in the water (Calgaroto et al., 2015).