Minerals Engineering 127 (2018) 178–184

Contents lists available at ScienceDirect

Minerals Engineering

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

On the role of nanobubbles in particle–bubble adhesion for the flotation of quartz and apatitic minerals

A.F. Rosa, J. Rubio*

Laboratório de Tecnologia Mineral e Ambiental (LTM), Departamento de Engenharia de Minas, PPGE3M, Universidade Federal do Rio Grande do Sul, Setor 6-Av. Bento Gonçalves, 9500, 91501-970 Porto Alegre, RS, Brazil

ARTICLE INFO

Keywords:
Flotation
Nanobubbles
Microbubbles
Macrobubbles
Apatitic ore
Quartz

ABSTRACT

This work evaluated the influence of nanobubbles (150–200 nm, mean diameter) on the visual adhesion of microbubbles (70 µm mean diameter) and macrobubbles (1 mm mean diameter) onto selected mineral particles (quartz and apatite) and on the flotation of both minerals, at bench scale. The adhesion of bubbles to high purity grains of quartz and apatite was monitored using a specially designed photographic technique. The results showed that the highest adhesion of bubbles onto the mineral grains occurred only after "conditioning" with nanobubbles. The nanobubbles appear to adhere to hydrophobic surfaces and confined to the rough surfaces of the grains, probably due to the dissipation of the free surface energy of the solids. As a result, the nanobubbles appear to serve as nuclei for enhanced adhesion of micro and/or macrobubbles, assisting the flotation of both minerals. In the case of quartz (D50 = 290 µm), the recovery increase was about 23% compared to a standard test of flotation with macrobubbles only. Furthermore, flotation kinetics was rapid and quartz recovery, at the first min, was double that obtained in the absence of nanobubbles. In the case of a fine apatitic ore (35% < 37 µm particles), best results were obtained with a combination of nano, micro and macrobubbles, with a 500–1000 g t^{-1} saponified soybean oil collector and a 300–600 g t^{-1} gelatinized corn starch depressant of iron bearing minerals. The P_2O_5 recoveries increased about 9% compared to flotation with macrobubbles only, and separation also occurred at a higher rate. The total recovered phosphate (4 min standard test) was obtained in the first 1.5 min, after conditioning with nanobubbles, followed by injection of and microbubbles. Results validated the reported high potential for nanobubbles in "surface conditioning", the first stage of mineral flotation and were explained in terms of the solution and interfacial phenomena involved.

1. Introduction

Froth flotation is believed to be the most efficient and cost-effective unit operation in mineral processing (Fuerstenauet al., 2007). Yet, separation efficiency decreases for particles less than 37 µm and fall sharply for the ultrafines fractions (< 13), due to the low probability of bubble-particle capture (poor attachment). Yet, it has been reported that fine particle recovery in flotation is enhanced by using microbubbles (MBs - 30–100 µm diameter) and/or nanobubbles (NBs of 120–800 nm diameter) (Ahmed and Jameson, 1985; Ralston et al., 1999; Gontijo et al., 2007, Azevedo et al., 2016a,b, Etchepare et al., 2017, Oliveira et al., 2018).

Mechanisms involved while employing microbubbles are related to a higher residence time for bubble-particle adhesion at the film-thinning and disjoining pressure stage (Yoon, 2000; Ralston et al., 1999; Rubio et al., 2003; Fuerstenau et al., 2007; Santana et al., 2012). Yet, microbubbles do not have enough lifting power (carrying capacity) and a combination with coarser bubbles appears to be essential; unfortunately, the practical use of a wide bubbles size distribution poses a serious challenge to flotation machine manufacturers. This occurs mainly because of bubbles interactions themselves, usually leading to coalescence or engulfing of the fine bubbles by the coarser bubbles (Yoon, 2000; Ralston et al., 1999; Azevedo et al., 2016a; Fuerstenau et al., 2007).

Regarding nanobubbles in mineral flotation, recent studies reported advantages regarding the enhancement of the contact angles after their capture by particles, assisting the probability of flotation (and its rate) by larger bubbles (> 1 mm) (Ahmadi et al., 2014; Calgaroto et al., 2015; Fan and Tao, 2008; Fan et al., 2012; Sobhy and Tao, 2013, Azevedo et al., 2016b). In other words, they would act as a conditioner

---

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

https://doi.org/10.1016/j.mineng.2018.08.020
Received 7 May 2018; Received in revised form 6 August 2018; Accepted 8 August 2018

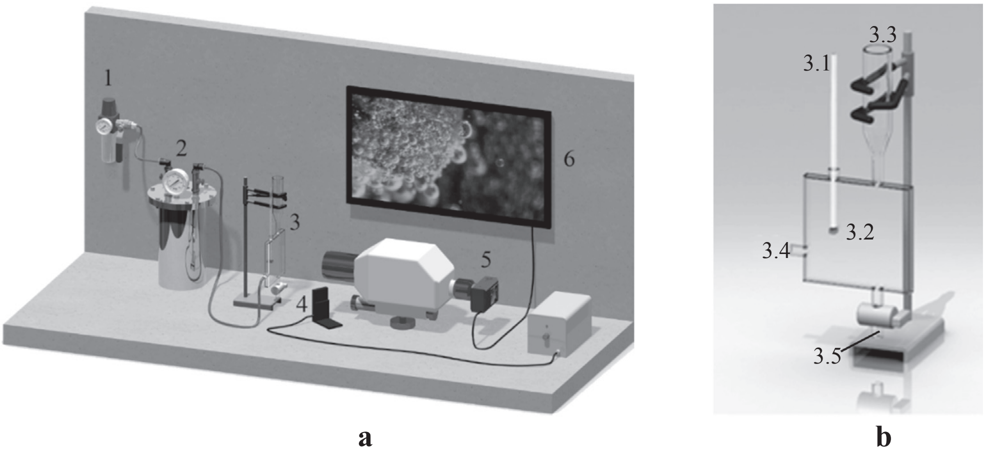

Fig. 1. Experimental setup for image acquisition of the bubble-mineral particle interactions; (a): (1) Compressed-air filter; (2) Saturator vessel; (3) Flat glass cell; (4) White-light source; (5) Stereomicroscope coupled to a digital camera; (6) Monitor for image reproduction. (b): Details of the flat glass cell - (3.1) Mineral grain holder; (3.2) Mineral particle; (3.3) Inlet for injection of aqueous dispersion of NBs and deionized water; (3.4) Inlet for injection of aqueous dispersion of MBs; (3.5) Inlet for generation/injection of MaBs.
Source: Adapted from Azevedo et al. (2016b).

Table 1
Conditions of bubbles-particles (apatite/quartz) interactions. The adhesion of bubbles onto quartz was studied under conditions 1, 2 and 3.

Condition	Bubbles injected
1	MaBs
2	NBs
3	NBs + MaBs
4	MBs
5	NBs + MBs
6	MBs + MaBs
7	NBs + MBs + MaBs

Table 2
Flotation studies conditions at 28% w/w.

Conditions	Reagents dosage [collector][a]; [depressant][b] ($g{\cdot}t^{-1}$)
1	1000; 600
2	500; 300

[a] Fatty acid soap from soybean oil.
[b] Gelatinized corn starch.

or as a “second collector,” because the nanobubbles do not rise (or float) in water, nor do they have lifting power.

Furthermore, recent studies by our research group have revealed two other phenomena:

i. Nanobubbles are able to aggregate particles (ultrafines) and improve their floatability (Azevedo et al., 2016a; Etchepare et al., 2017, Calgaroto et al., 2015). ii. Nanobubbles serve as nuclei (“seeds”) for the adhesion of other bubbles, micro and macro (>1 mm diameter) (Azevedo et al., 2016b). The validation of this phenomenon and its effect on the particle flotation of quartz and phosphate at laboratory scale is the main theme of this work.

2. Experimental

2.1. Materials

Distilled water treated in a reverse-osmosis cartridge and modules of ion-exchange resins and activated carbon was employed for the particle-adhesion studies. The conductivity of the water was $3\ \mu S\ cm^{-1}$; had a surface tension of $72.5 \pm 0.1\ mN\ m^{-1}$ and an equilibrium pH of 5.5. For flotation tests, tap water from the city of Porto Alegre – South Brazil was used. A sulfochromic solution and subsequent abundant rinse with the treated water were used to remove possible organic compounds from all glass materials. Hydrochloric and nitric acids, ammonium metavanadate, ammonium molybdate and monosodium phosphate were the reagents used for the quantitative determination of P_2O_5.

High purity lumps of apatite ($Ca_5(PO_4)_3(OH, F, Cl)$) and quartz (SiO_2), both from southern Brazil, were used to investigate bubble-mineral interactions. Samples of phosphate ore for the flotation studies were collected from Tapira (Vale Fertilizers, South Brazil), from a feed flotation circuit, after comminution, classification, low intensity magnetic separation, attrition and desliming stages. More than 98% of the sample consisted of particles smaller than 200 # (75 µm), with 37% in the 400 # fraction (37 µm). The mean diameter (D50) of the particles was 55 µm, while the D80 was 100 µm. The average sample content was 8.4% P_2O_5. Quartz samples for flotation were prepared from rock crystals from Lajeado (South Brazil). The quartz particles were fractioned using Mesh Tyler sieves, and the particle-size distribution of each fraction was measured in a Cilas 1064 laser particle size analyzer. A $-48 + 100\#$ fraction was used in the flotation studies with a mean diameter (D50) of 290 µm.

Fatty acid soap from soybean oil was used as the collector for phosphate and gelatinized corn starch was used as gangue mineral depressant. A 10% NaOH solution was used for pH adjustment. In the quartz flotation studies, the collector was the commercial reagent Flotigam EDA 3B (Clariant®), an alkyl ether monoamine.

2.2. Methods

2.2.1. Chemical analyses

The P_2O_5 content was determined by molecular absorption spectrophotometry based on the reaction of the phosphate with a solution containing ammonium molybdate and ammonium metavanadate in an acid medium.

2.2.2. Studies of quartz and apatite bubble-adhesion

The experimental setup, shown in Fig. 1, was a modified technique previously reported by our group (Azevedo et al., 2016a) and consisted of a system that allowed the injection of different types of bubbles into a flat glass cell. The visualization was possible using a stereomicroscope (Zeiss Stemi SV 11) and a digital camera (Sony NEX 3). A strip of graph paper, as a size reference for measuring the size of the larger bubbles, was attached at the bottom of the cell. Glass tubing (0.5 cm in diameter and 15 cm in length) containing either quartz or apatite particles adhered to its end was inserted into the cell through a hole at the top. Additionally, the cell contained two more orifices for injecting the bubbles.

Nanobubbles (NBs - mean diameter 150–200 nm) and microbubbles (MBs - mean diameter 40 µm) were generated by the depressurization of DI water, previously saturated with air at various saturation pressures for 30 min (Psat; Psat = 2.5 bar for NBs and Psat = 4.0 bar for