Effect of nanoparticles on froth stability and bubble size distribution in flotation

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A B S T R A C T

In order to investigate the usability of nanomaterials as a froth stabiliser in mineral flotation, an experimental study was performed using a froth column and a modified flotation cell. Four different nanomaterials, namely SiO_2, TiO_2, Fe_2O_3 and Al_2O_3, were used in the experiments. The froth column tests were carried out to measure the Sauter-mean bubble size and dynamic froth stability under different operating conditions. Single mineral flotation tests with or without the nanomaterials were performed using a pure barite sample. Results of the froth column tests show that despite of the increasing froth height, the bubble coalescence in the froth or bursting on the surface can be decreased considerably by using the nanomaterials. The effect of the increase in froth height on the Sauter-mean bubble size and the bubble coalescence was found to be negligible by using the nanomaterials in all pH values used. These effects of the nanomaterials could not be attributed to both signs and magnitudes of their surface charges.

It was determined that the nanomaterials used in this study did not contribute to the flotation efficiency at shallow froth. Contrary to this, the nanomaterials, in particular nano-sized Fe_2O_3 and Al_2O_3, provide a significant increase in barite recovery (7–11%) at deep froth, which means that selection of the type of the nanomaterials to be used in flotation is also important. As a result of the use of the nanomaterial, the decrease in the flotation performance at deep froths was found to be negligible.

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1. Introduction

The structure and stability of a froth phase are critical in determining its ability to transport the hydrophobic mineral particles into the concentrate launder. Therefore, the separation efficiency and selectivity of the flotation process relate directly to froth stability, bubble coalescence and bubble size distribution (Schwarz and Grano, 2005; Gupta et al., 2007; Zanin et al., 2009; Farrokhpay, 2011). However, frothers, along with many other physical and chemical factors of the froth flotation, play an important role in flotation rate, grade, recovery, water recovery and bubble size distribution. The most important effect of frothers on flotation comes from their effect on bubble size which results from their ability to prevent bubble coalescence (Laskowski, 1998; Cho and Laskowski, 2002; Grau et al., 2005; Harvey et al., 2005; Nguyen et al., 2006; Wang and Yoon, 2006; Gupta et al., 2007). On the other hand, with increasing froth residence time and froth height, the water films between the bubbles may drain to a critical thickness and film rupture may occur. This process may lead to a decrease in the carrying capacity of the froth and the possibility that some mineral particles may become detached and be lost from the froth (Schwarz and Grano, 2005; Ata,

2012). It can clearly be concluded from these researches that both overall recovery of flotation and froth phase performance are strong functions of froth stability, bubble coalescence, froth mobility, entrainment and drainage of particles (George et al., 2004).

It is well known that froth stability is defined as a function not only of the type and concentration of the frother used in the flotation but also of the characteristics of the particles present in the froth (Nguyen and Schulze, 2004; Pugh, 2005; Grau et al., 2005; Schwarz and Grano, 2005; Nguyen et al., 2006; Gupta et al., 2007; Zanin et al., 2009; Farrokhpay, 2011). Ata et al. (2003) investigated the changes in bubble size in the froth zone of a flotation column and found the bubble growth rate to be sensitive to the degree of hydrophobicity of particles present in the froth zone. Maximum froth stability occurs with moderately hydrophobic particles. In addition, Szatkowski and Freyburger (1985, as cited in Tao et al., 2000) observed that fine quartz particles rendered bubbles to be more resistant to coalescence and promoted the production of the stable froth. Livshits and Dudenkov (1965) believed that only coarse particles are able to act as buffers between bubbles and prevent bubble coalescence, consequently strengthening the stability of the froth. Klassen and Mokrousov (1963) reported that more hydrophobic particles had greater stabilising effects on the froth. Johansson and Pugh (1992) showed that particles of intermediate hydrophobicity (of contact angle ~65°) would enhance froth stability but more hydrophobic

particles ($\theta > 90°$) would destabilise the froth while more hydrophilic particles ($\theta < 40°$) would not influence the froth properties (Tao et al., 2000).

Colloidal (nano-sized) particles act in many ways like surfactant molecules, particularly if adsorbed to a fluid–fluid interface. Therefore, they have been incorporated into surfactant-stabilised aqueous foams for many years, and their influence on the formation and stability of the foam is very dependent on the surfactant type, particle size and concentration (Binks, 2002; Horozov, 2008). The literature review shows that a number of researchers have studied the ability of the nano-sized particles to act as foam/emulsion stabilisers (Binks, 2002; Paunov et al., 2002; Du et al., 2003; Dickinson et al., 2004; Binks and Hozorov, 2005; Horozov, 2008; Liu et al., 2010; Zech et al., 2012). However, majority of these studies are not related directly to the flotation process. In addition, Hunter et al. (2008) and Ata (2012) present reviews and excellent discussions on the effects of particles on the froth/emulsion stability. In these reviews, they highlight the fact that the fine particles creating a steric barrier to coalescence is a major contribution to foam stabilisation, and as with emulsions, smaller particles in high concentrations that form a more complete layer gives the most effective barrier. In other words, the coalescence time (the time required for the two bubbles to merge together) increases with the bubble surface coverage and the bubbles become more resistance to coalescence. In addition, even if very fine particles are hydrophobic or hydrophilic, they can be nonselectively recovered by entrainment, which can be related directly to froth stability. While a more stable froth can recover a greater amount of hydrophobic particles, it also recovers more hydrophilic (gangue) particles, generally due to entrainment (George et al., 2004; Nguyen and Schulze, 2004; Ata et al., 2006; Farrokhpay, 2011; Ata, 2012).

As mentioned previously, sufficiently hydrophobic fine particles irreversibly adsorb to the air–water interface because of their high adsorption energy and they create a strong steric barrier against bubble coalescence. This leads to resistance during froth drainage, allowing very stable froths to be produced. Mineral flotation is effective for particle sizes below about 100–120 μm with a lower-size limit typically of 20 μm (Jameson et al., 2007). The implication of the observation that sub-micron size particles give the most stable foam is that, for the particle size range used in the flotation process, froths can only be stabilised to a certain degree and complete stabilisation is not possible (Ata, 2012).

Abovementioned findings and discussions reveal that in order to prevent bubble coalescence and to stabilise froth phase in a flotation cell, the nanomaterials can be used effectively in mineral flotation. The aim of this study is therefore to evaluate the usability of the nanomaterials in mineral flotation by means of examining their effect on the Sauter-mean bubble diameter, froth stability and flotation performance. If the nanomaterials as a froth stabiliser can be used effectively in the mineral flotation, the froth stability becomes a controllable factor, and it can be adjusted easily to the desired level during the flotation. In this way, the separation efficiency and selectivity of the flotation process could be enhanced considerably using a simple method like this.

2. Experimental

2.1. Materials

Flotation chemicals (frother; Oreprep F-507 and collector; Aero 722) were supplied from Cytec Industries, USA. Hydrochloric acid, sodium hydroxide, sodium silicate and dextrin were purchased from Sigma-Aldrich.

In single mineral flotation tests, a pure barite sample (-0.106 mm) was used. Pure barite particles were handpicked from the Seydisehir barite deposits of Turkey. The lump-sized barite particles in the sample were crushed by a hammer and then ground in a ceramic mill with ceramic balls to produce a sample of -106 μm in size for flotation studies. The chemical analysis of the sample shows that it is composed of 96.4–98.7% $BaSO_4$, 1.2–2.3% SiO_2 and 0.8–1.2% $CaCO_3$.

Table 1
Some properties of the nano-sized particles used in the experiments.

Material	Particle size (nm)	Purity (%)	PZC (pH)
Gamma-Al_2O_3	20	99.99	6.2
Alpha-Fe_2O_3	20–40	99	7.6
SiO_2	15–20	99.9	–
TiO_2	15–30	99.5	3.4

De-ionised water (Milli-Q purification system, Millipore) was used in all experiments. Four kinds of nanomaterials were purchased from SkySpring Nanomaterials Inc., USA. Some properties of these materials used in the experiments are given in Table 1.

2.2. Methods

Several methods can be used to determine froth/foam characteristics (Ata et al., 2003; Du et al., 2003; Neethling et al., 2003; Dickinson et al., 2004; Bailey et al., 2005; Binks and Hozorov, 2005; Schwarz and Grano, 2005; Ata et al., 2006; Gupta et al., 2007; Stevenson, 2007; Giribabu et al., 2008; Kazakis et al., 2008; Farrokhpay, 2011; Zech et al., 2012). Experiments were carried out using a square (50×50 mm), vertical (500 mm), glass froth column, in this study.

0.25 g/L of a nanomaterial suspension was prepared and used in all tests. A required amount of each nanomaterial was dispersed in sodium silicate solution of 25 ppm (of predetermined pH value and frother concentration) by sonicating the mixture for 30 min. A Denver laboratory flotation machine was used in flotation experiments and, two different glass cells were used to obtain constant pulp level with different froth depths (15 and 35 mm) in these tests. Pulp pH was adjusted to 10 ± 0.5 by adding NaOH and conditioned for 10 min. $BaCl_2$, the activator, was added into the pulp at a dosage of 50 g/t and conditioned for a further 10 min. Then, Aero 722 was used as the collector at a dosage of 150 g/t and the pulp was conditioned for a further 5 min. The frother, Oreprep-507, was added into the pulp and air was introduced. These flotation conditions were determined by results obtained from the preliminary flotation tests performed without the nanomaterial. Air flow
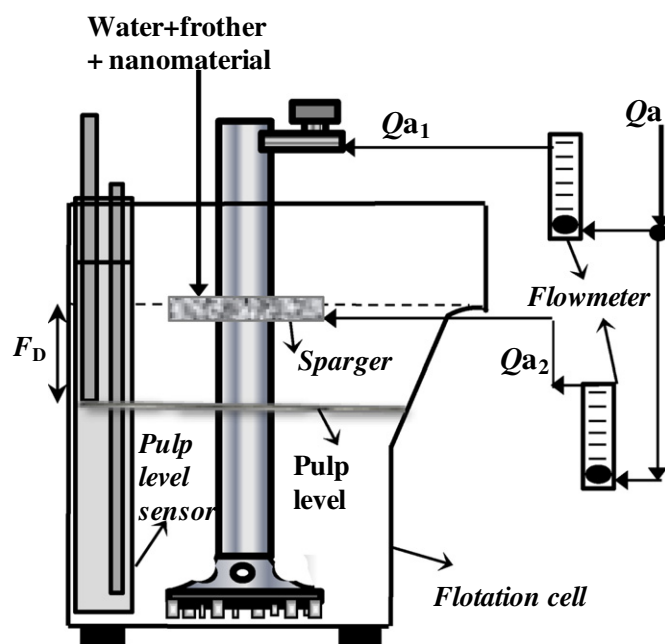

Fig. 1. Schematic illustration of experimental setup.