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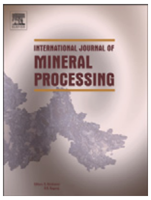

An investigation into the mechanism of the three-phase contact formation at fluorite surface by colliding bubble

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ABSTRACT

Mechanism of the three-phase contact (TPC) formation and phenomena occurring during collisions of the ascending bubble with a solid and flat surface were studied. Three fluorite samples of different origins and surface roughness and smooth mica plates were investigated. It was found that the time-scale and the mode of air bubble/flat fluorite surface bouncing and attachment significantly depended on the surface roughness. For smooth fluorite surfaces the time of the TPC formation and the bubble attachment was over 150 ms while for rough surfaces it was 5 to 45 ms. It was also shown that the TPC formation at fluorite and mica surfaces was determined mainly by the electrical charge of the interacting interfaces. A small amount of cationic surfactant (*n*-octyltrimethylammonium bromide) was used to reverse the sign of electrical charge of the bubble surface. In *n*-octyltrimethylammonium bromide presence there was no TPC formation at the fluorite surface due to repulsions between positively charged interfaces, but the bubble attachment to negatively charged mica surface was observed due to attractive electrostatic interactions. It was also determined that there was no TPC formation at pHs when the signs of zeta potentials of the solution/gas and solution/fluorite interfaces were the same.

1. Introduction

Collisions of bubbles with particles and formation of the bubble–particle aggregates are necessary for separation by flotation. It is rather commonly accepted that the main factors determining the flotation separation are related to hydrophilic–hydrophobic properties of the particle surfaces. However, in flotation cells the formation of bubble–particle aggregates occurs under dynamic conditions. For the aggregate formation a liquid intervening film formed between the colliding bubble and the particle surface needs to be ruptured and the liquid/gas/solid three-phase contact (TPC) must be formed. Thus, the probability of formation of the bubble–particle aggregates is also affected by the stability of the liquid wetting film formed between the bubble and solid surface. Generally, the probability of formation of a stable bubble–particle aggregate can be considered as the product of the probabilities of collision, attachment (formation of the three-phase contact) and detachment (Deryagiun and Dukhin, 1960; Schimmoler et al., 1963; Ralston and Dukhin, 1999). For formation of a stable bubble–particle aggregate due to collisions, the following processes have to occur: i) syneresis and thinning of the liquid layer separating the bubble and particle to a critical rupture thickness, ii) rupture of the liquid film and formation of a “hole” at the three-phase contact, and iii) expansion of the “hole” and formation of the perimeter of the three-phase contact assuring stability of the bubble–particle aggregate. The hydrophilic/hydrophobic property of the solid surface is an important factor of the wetting film stability. Generally, the more hydrophobic the surface, the less stable is the wetting film. The stability of the liquid film is commonly considered in terms of the DLVO theory, which describes the film stability as a result of balance between long-range electrostatic interactions of the electrical double layers of two interfaces (ranging from 1 to 100 nm), and the van der Waals interactions (1–10 nm). In the case of so-called symmetrical systems such as foam films, the van der Waals interactions are always attractive and the electrostatic interactions are repulsive, because both interacting interfaces are identical (Scheludko, 1967). The situation is more complicated in the case of asymmetric wetting films. In this case the van der Waals and electrostatic interactions can be either attractive or repulsive, depending upon signs of the electrical charge and the type of interacting systems (Scheludko, 1967; Israelachvili, 1994; Diakova et al., 2002). In the case of water/air and water/solid interfaces, however, the Hamaker theory always predicts repulsive van der Waals interactions. Interactions of an air bubble and a solid surface in water can be attractive at long separations (Nguyen et al., 2001) but this prediction is beyond the scope of the Hamaker theory.

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During the bubble–solid collision process, the liquid film drains and its thickness decreases with time. When the film thickness reaches a distance of the electrostatic interactions, then the electrical charge of the film interfaces can be decisive for the film stability. If the interfaces are similarly charged, the repulsive interactions (positive disjoining pressure) between the surfaces act as the film stabilizing forces. When the surfaces are oppositely charged, the attractive electrostatic forces do not stabilize the liquid film and the film ruptures.

In the case of naturally hydrophobic particles the wetting films are generally of low stability and are expected to rupture easily and quickly (Sharma and Ruckenstein, 1990; Starov and Churayev, 1999; Ralston et al., 2002). Fluorite is an interesting mineral for which natural hydrophobicity is known but not well established and was not included in the list of naturally hydrophobic materials in the classic work by Gaudin et al. (1957). From time to time there are reports on natural floatability of fluorite (Bakakin, 1960; Barskij, 1984; Busscher et al., 1987; Drzymala and Lekki, 1990; Drzymala, 1994a,b; Janczuk et al., 1993; Fa et al., 2006). However, the natural hydrophobicity of fluorite does not seem to interfere with flotation of other minerals as it happens with chalcopyrite, graphite and talc. It appears that fluorite floats well in the absence of any collectors in small scale flotation cells such as the Hallimond tube. However, it does not float in devices with vigorous hydrodynamics. Therefore, there is a need for more investigations on properties of fluorite under dynamic conditions in the absence and presence of flotation reagents. To find an explanation for differences in fluorite floatation in different cells, the kinetics and mechanism of the three-phase contact formation at fluorite surface has been studied and presented in this work.

This paper presents dynamic phenomena occurring during collisions of a rising bubble with three different fluorite samples and, for comparison purpose, a freshly cleaved mica surface. The effect of the fluorite surface roughness on kinetics of the TPC formation in distilled water and $5 \cdot 10^{-4}$ M *n*-octyltrimethylammonium bromide (OTABr) solutions was also studied. The importance of the electrical surface charge for the TPC formation at fluorite and mica surfaces was determined by: i) pH variations, and ii) addition of a cationic surfactant (OTABr), which should cause a reversal of the bubble surface electrical charge due to its preferential adsorption at the liquid/gas interface.

2. Experimental

2.1. Methods

The experimental set-up used in monitoring the phenomena occurring during collisions of the rising bubble with fluorite surface was described in detail elsewhere (Malysa et al., 2005; Krasowska and Malysa, 2006, 2007). The main elements of the set-up are: (i) square glass column (cross-section 50×50 mm), (ii) a glass capillary (inner diameter — 0.075 mm), (iii) a syringe pump with high precision glass syringes, and (iv) a high-speed Weinberger SpeedCam 512+ and Moticam 2000 CCD cameras. The studied fluorite samples and mica plates were mounted at the distance either ca. 50 mm or 4 mm from the point of the bubble formation (capillary orifice). The distance of 50 mm was long enough for the bubble to reach its terminal velocity equal to 34.7, 33.7 and 33.6 cm/s in water, $5 \cdot 10^{-4}$ M, and $1 \cdot 10^{-3}$ M OTABr solutions, respectively. For fluorite sample placed at the distance of 4 mm, the moving bubble was still at the acceleration stage of its motion and its impact velocity was ca. 17 cm/s (Zawala et al., 2007). It should be noted that in our model experiments the probability of collision and lack of detachment was always 100%.

2.2. Materials

Three fluorites (calcium fluoride, CaF_2) having different surface roughness and freshly cleaved plates of mica were used in the experiments. Fluorite samples A and B were in the form of plates of natural minerals of different origins with very smooth surfaces. Sample A was a polished piece of fluorite from Ural (Russia) while sample B was an optical plate used for IR measurements. The third sample (C) was a fragment of natural mineral with a significantly rougher surface. Fig. 1 presents pictures of the fluorite surfaces, obtained with NIKON EPIPHOT 200 optical microscope.

The surface electrical charge and zeta potential of fluorite and mica were not investigated because such data exist in literature. The acid–base properties and ion exchange reactions on the fluorite surface were determined by Wu and Forsling (1995) while Haas et al. (1999), Miller et al. (2004), Fuerstenau and Bunge (2006) and Assemi et al. (2006) investigated the influence of pH on zeta potential. They found that the maximum values of the fluorite zeta potential of ca. +70 mV occurred at the pH range from 3 to 5 with the isoelectric point at pH from 9 to 10.5. At higher pH values (>10.5) the fluorite surface is negatively charged. Fluorite is weakly hydrophobic because its contact angle determined by flotation (Drzymala, 1994a,b) is 10° to 15°. On the other hand mica, starting from pH 2, has always negative values of

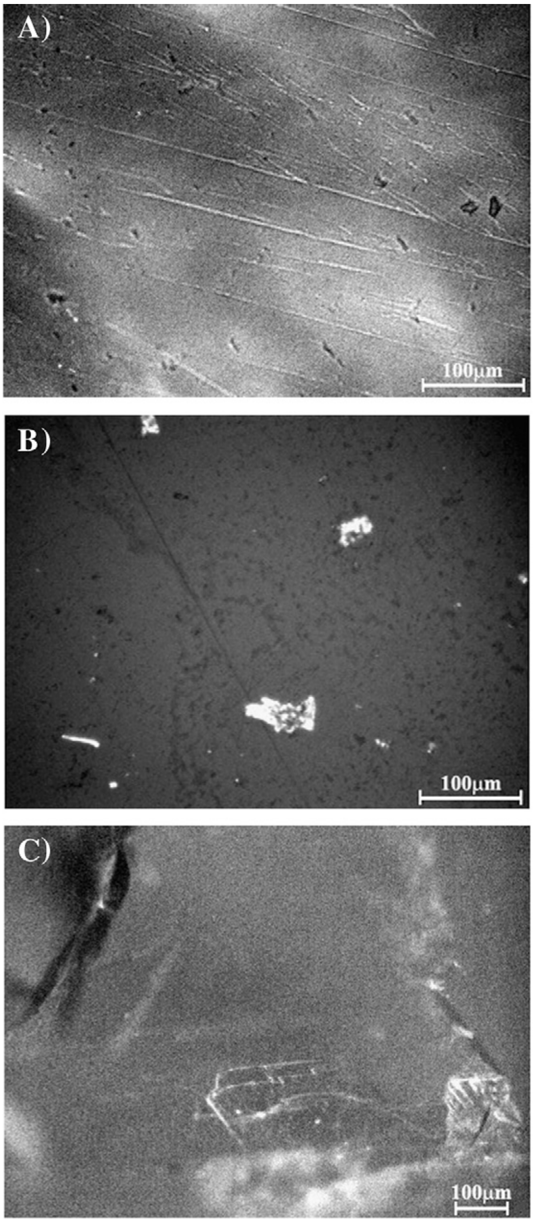

Fig. 1. Microscopic photos of surface of fluorites (A–C) used in the experiments.