Physicochemical Problems of Mineral Processing, 41 (2007), 5-11
Fizykochemiczne Problemy Mineralurgii, 41 (2007), 5-11

Jan ZAWALA[*], Jan. DRZYMALA[**], Kazimierz. MALYSA[*]

NATURAL HYDROPHOBICITY AND FLOTATION OF FLUORITE

Received March 15, 2007; reviewed; accepted May 15, 2007

The free ascending bubble–fluorite surface collision test showed that the three phase contact (TPC) was formed and time of the TPC formation was strongly affected by the roughness of the fluorite surface. The time of the TPC formation varied by an order of magnitude, from ca. 20 to 200ms, depending on the fluorite origin and surface roughness. The fact that the TPC was formed shows that fluorite can be considered as a naturally hydrophobic material. The contact angle formed by the bubble attached to fluorite plate was found to be 40° in comparison to 10-25° measured by flotometry and 55° by sessile drop. Thus, the macroscopic contact angle of fluorite depends on the method of measurement as well as its origin and color since colorless fluorites float better. Hydrophobicity of fluorite and the time of the three phase contact formation influence its flotation. The best flotation is observed in Hallimond tubes while flotation is significantly reduced or absent in laboratory flotation machines. This is very likely a result of relatively long time of the TPC formation and/or low hydrophobicity of fluorite, which is not enough to withstand the detachment force during enhanced hydrodynamics of larger flotation devices.

Key words: fluorite, contact angle, bubble-particle attachment, induction time, three phase contact, hydrophobicity, hydrophilicity

INTRODUCTION

Natural flotation of minerals frequently interferes with collectors flotation of useful components of ores. Such difficulties may occur during upgrading by flotation of ores containing chalcopyrite, talc, and graphite. It was mentioned by Barskij (1984) that also fluorite may cause problems due to its native flotation.

Until sixties of the previous century fluorite was considered a hydrophilic mineral, that is material which forms in the water-air-fluorite system contact angle (θ) equal to zero. Gaudin an his coworkers (1957), in their classic paper on native floatability, did not include fluorite in the list of hydropbobic materials. As a result many researchers and technologists have been considering fluorite hydrophilic even today.

---

[*] Institute of Catalysis and Surface Chemistry Polish Academy of Sciences, Cracow, Poland.
[**] Wroclaw University of Technology, Mining Engineering Department, Wroclaw, Poland.

An information on native flotation of fluorite originates from Bakakin in 1960 (Barskij, 1984). They showed that fluorite samples from different sources floated in water, and the flotation of fluorite was reduced in the presence of water glass (Fig. 1a.). The extend of flotation was found to be dependent on the color of fluorite. Since then, there were only sporadic reports on the native hydrophobicity (Busscher et al., 1987; Janczuk et al., 1993) and collectorless flotation (Drzymala and Lekki, 1990; Drzymala, 1994a, 1994b (Fig.1b) of fluorite.

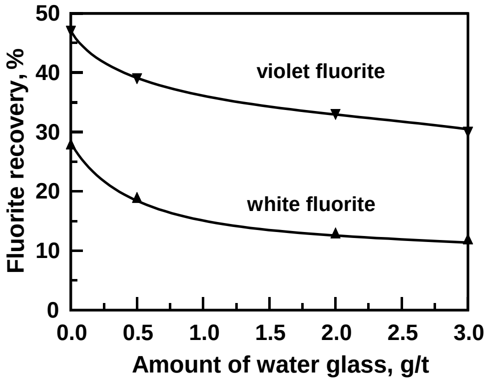


Fig. 1a. Flotation recovery of fluorite in water in presence of water glass (based on Barskij, 1984, original source - Bakakin, 1960)

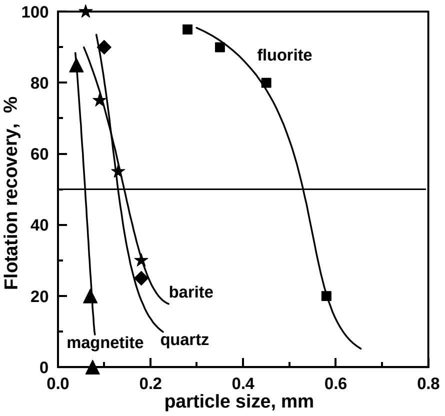


Fig. 1b. Recovery of fluorite and other minerals in water in a Hallimond tube (based on Drzymala and Lekki 1989 and Drzymala, 1994b. Flotation time 30 min. Flotation of each mineral and each fraction separately. Flotometric contact angles: quartz ~0 °, fluorite 25°, barite 5.0 °, magnetite 0 °

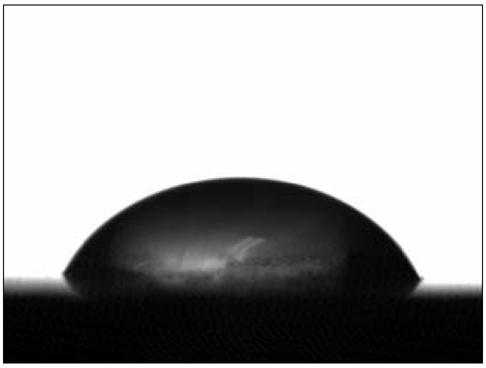


Fig. 1c. A drop of water on fluorite surface (polished with 1600 sand paper) forms contact angle equal to about 55° (Szyszka and Stepien, 2007)

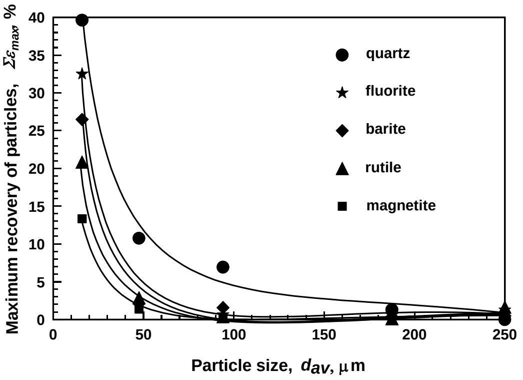


Fig. 1d. Entrainment of minerals in water in a Denver lab. flotation machine after long time of flotation in the presence of fuel oil (0.2 g/kg and 0.05 g/kg α-terpineol. pH natural. Each mineral was tested separately. Sequence of minerals flotation depends on their density (Konopacka, 2005)

Hydrophobicity of fluorite can be demonstrated by putting a drop of water on a polished fluorite surface. This creates non-zero contact angle (Fig. 1c). Most recently, Fa et al., 2006, during investigation of interaction of calcium dioleate colloidal particle and fluorite by atomic force microscope (AFM), found that the density of water at the fluorite surface is low and that fluorite surface is not strongly wetted. This also points to natural hydrophobicity of fluorite.

Micro-flotation tests performed by Drzymala and Lekki (1990) and Drzymala, 1994a,b in a small flotation device called Hallimond tube (Fig. 1b.) confirmed Bakakin's report on natural flotation of fluorite which depends on fluorite samples. Using flotometry, they showed that the contact angle of fluorite is between 10 and 25 degrees. However, trials to float naturally hydrophobic fluorite in laboratory mechanical Denver (5 dm^3) flotation machine by Konopacka (2005) failed. Her investigations on mechanical entrainment of different minerals showed that fluorite does not float. Small amount of fluorite reporting to concentrate was due to mechanical carryover of particles as in the case of hydrophilic quartz or magnetite (Fig.1d).

The presented facts indicate that there is no a simple correlation between natural hydrophobicity and flotation of fluorite and that still more research is needed to understand the fluorite-water-gas system. The present study deals with dynamics of formation of the three phase contact at fluorite surface by a freely ascending bubble using the technique described in details elsewhere (Krasowska et al., 2004; Malysa et al., 2005; Krzan et al, 2006). The technique allows investigating phenomena occurring during bubble collisions with solid surface and time-scale of the three phase contact (TPC) formation. Geometry of the bubble–solid surface contact formed can be monitored as well.

EXPERIMENTAL

METHODS AND MATERIALS

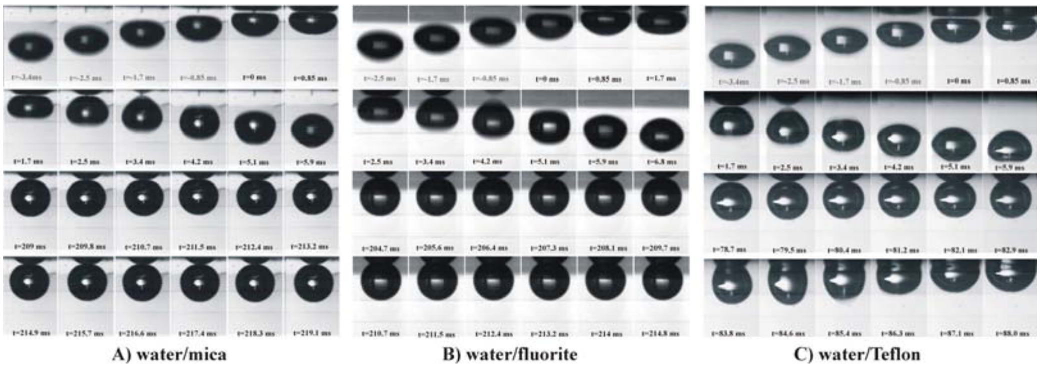
The experimental set-up used in monitoring phenomena occurring during collisions of the rising bubble with fluorite surface was described in details elsewhere (Krasowska et al., 2004; Malysa et al., 2005; Krzan et al., 2006). The main elements of the set-up are the following: i) a square glass column (cross-section 50×50 mm), ii) glass capillary (inner diameter - 0.075 mm), iii) syringe pump with glass high precision syringes, iv) high-speed camera (Weinberger, SpeedCam 512+) and Moticam 2000 CCD camera. The fluorite samples studied were mounted at the distance either ca. 50 mm or 4 mm from the point of the bubble formation (capillary orifice). Distance 50 mm was long enough for the bubble to reach its terminal velocity 34.7 cm/s in water. When the fluorite was placed at the distance 4 mm then the bubble was still at the acceleration stage of its motion and the bubble impact velocity was ca. 17 cm/s (Zawala et al., 2007). For the sake of comparison the experiments were also carried out using the freshly cleaved mica and Teflon plates. Further details about the experimental procedure were described by Krasowska and Malysa (2007).

Fluorite (calcium fluoride, CaF_2) was a fragment of natural high purity, check by X-ray diffraction, mineral originated from East Germany. Fluorite samples were carefully washed with acetone and ethanol and finally rinsed with large quantity of the distilled water, before every experiment. The experiments were carried out at room temperature.

RESULTS AND DISCUSSION

In our tests of the bubble-mineral surface interactions, the free ascending bubble collides with the flat surface and the time of the three phase contact formation as well as bubble attachment is determined. As showed elsewhere (Malysa et al., 2005, Krasowska and Malysa, 2007) even in the case of such hydrophobic solid surface as Teflon, the bubble attachment did not need occur at first collision and in distilled water the bubble can bounce a few times without attachment. Simultaneously, after the first collision the bubble shape started to pulsate rapidly within time intervals of an order of fraction of millisecond. It was showed that roughness of the solid surface and presence of entrapped air at hydrophobic surface (Krasowska et al, 2007) are the factors of crucial importance for the kinetics of the bubble attachment. In the case of hydrophilic glass surface the bubble stayed "arrested" beneath the glass plate without formation of the three phase contact (Malysa et al., 2007). Thus, as a result of the collisions, the bubble either establishes the three phase contact with the solid surface, forming a characteristic constant angle when the surface is hydrophobic enough, or stays entrapped beneath the surface without forming the TPC, when the surface is more hydrophilic and there exists some forces stabilizing the wetting film. For instance repulsive electrostatics between both interfaces of the wetting film can assure its stability (Krasowska et al., 2007b).

Figure 2 presents a comparison of the sequences of photos illustrating phenomena occurring during collision of the rising bubble with freshly cleaved hydrophilic mica ($\theta = 0^o$) (Fig. 2a), highly hydrophobic Teflon ($\theta = 105^o$) (Fig. 2c) and fluorite (Fig. 2b). In the case of mica surface, after the complete dissipation of the kinetic energy, the bubble stayed "arrested" (motionless) beneath the mica plate without formation of the three phase contact (TPC). Thus, in this system the liquid film separating mica and bubble interfaces was stable and did not rupture. In the case of the bubble collision with fluorite surface, the TPC was formed and the bubble was attached to the fluorite surface forming $\theta = 40^o$, indicating its hydrophobicity. Results of quantitative analysis of the velocity variations during the collisions of bubble with mica and fluorite surfaces (sample B) showed that the velocity variations were very rapid and practically identical for the collisions with mica and fluorite surfaces. Moreover, there was at least five distinct "approach-bounce" cycles during which the bubble kinetic energy was dissipated and after sixth approach the bubble stayed practically motionless beneath the plates. Then, in the case of mica there was no TPC formation and the bubble attachment to the mica surface (even after long time of the bubble being entrapped beneath the interface), while in the case of fluorite the TPC was formed at time t_{TPC}=150 ms (time between the first collision and TPC formation) and the bubble was attached. Similarly, the TPC formation was also observed for other fluorite samples (A and C). However, the time of the three phase contact formation and the bubble attachment was different for every of the fluorite samples, which is most probably due to differences in surface roughness and heterogeneity of the samples.



A) water/mica **B) water/fluorite** **C) water/Teflon**

Fig. 2. Free ascending bubble and its collision with flat surfaces of different materials a) mica, b) fluorite, and c) Teflon. The photographs show that mica is hydrophilic (θ =0°, Teflon is highly hydrophobic (θ = 105±2.5°) while fluorite is weakly hydrophobic (θ = 40±2°)

The fact that the surface roughness has a significant effect on the time of the colliding bubble attachment to fluorite can be attributed to the following: i) higher roughness means larger asperices (pillars) at the surface and higher probability that the rupture thickness of the thinning liquid film is locally faster attained, and/or ii) there are larger cavities at rougher surface and larger amount of gas can be present there leading to faster formation of a long enough perimeter of the TPC for the bubble attachment (Krasowska et al., 2007). However, in the case of fluorite we believe that the first factor is the predominant because air entrapment seems to be less important due to rather low hydrophobicity of the fluorite surface.

CONCLUSIONS

The free collision test showed that the three phase contact is formed at fluorite surface and the time of the TPC formation can vary by an order of magnitude (from ca. 20 to 200 ms). Increased roughness of the fluorite surface leads to shortening the time of the TPC formation. Fluorite surface shows some natural hydrophobicity and the measured contact angle values occur between 10 and 55 degrees, depending on the method of measurement. The contact angle is greater for water drops on the surface of fluorite and smaller for air bubble entrapped beneath the fluorite surface. The contact angle of fluorite depends on its origin and the color of the specimen because more colorless fluorites are more hydrophobic. Since fluorite is inherently hydrophobic, it can float in water and aqueous solutions. The flotation of fluorite depends not only on the natural hydrophobicity of fluorite but also on the flotation devices used for flotation. The best flotation is observed for Hallimond tube while flotation is significantly reduced or absent in laboratory flotation machines. This is very likely a result of relatively long time of the TPC formation and/or low hydrophobicity of fluorite, which is not enough to withstand the detachment force during increased hydrodynamics of larger flotation units.

ACKNOWLEDGEMENTS

Partial financial support of the work by the project Scientific Network SURUZ - EC grant INCO-CT-2003-003355 - is gratefully acknowledged.

REFERENCES

BAKAKIN V.V., 1960. *Questions on relation of structure of minerals and their flotation properties,* Journal of Structural Chemistry, v. 1(2), 89-97, in Russian.

BARSKIJ L.A., *Principles of minerallurgy - theory and technology of separation of minerals, Izd. Nauka*, Moscow, 1984, *in Russian*.

BUSSCHER H.J., DE JONG H.P., ARENDS J., 1987. *Surface free energy of hydroxyapatite, fluoroapatite and calcium fluoride,* Materials Chemistry and Physics, 17, 553-558.

DRZYMALA J., 1994a. *Characterization of Materials by Hallimond Tube Flotation. Part 2: Maximum Size of Floating Particles and Contact Angle,* Int. J. Miner. Process., 42, 153-167(1994).

DRZYMALA J., 1994b. *Hydrophobicity and Collectorless Flotation of Inorganic Materials,* Advances in Colloid and Interface Sci., 50, 143-186(1994).

DRZYMALA J., LEKKI J., 1989. *Flotometry-Another Way of Characterizing Flotation*, J. Colloid Interface Sci., 130, 205-210.

DRZYMAŁA, J., LEKKI J., 1990. *Fizykochemia procesów agregacyjnych przetwarzania surowców i odpadów nieorganicznych - V. Fotometryczne badania układu fluoryt oleinian oraz parafinowanych ziaren,* Raport I-11/S-114/90.

Fa, Keqing; Nguyen, Anh V.; Miller, Jan D. 2006, *Interaction of calcium dioleate collector colloids with calcite and fluorite surfaces as revealed by AFM force measurements and molecular dynamics simulation,* Int. J. Miner. Process, 81 (3), 166-177.

GAUDIN A.M., MIAW H.L., SPEDDEN H.R., 1957. *Native floatability and crystal structure. In: Electrical Phenomena and Solid/Liquid Interfaces,* Proc. 2nd Int. Congr. Surface Activity, London, Butterworths, pp. 202-219 .

JANCZUK B.; BRUQUE J.M.; GONZALEZ-MARTIN M.L.; del POZO, J. MORENO, 1993. *Wettability and surface tension of fluorite,* Colloids Surf. Physicochem. Eng. Aspects, 75, 163-168

KONOPACKA Z., 2005, Flotacja mechaniczna, Oficyna Wyd. PWr., 2005, Wrocław.

KRASOWSKA M., KRZAN M., MALYSA K., 2004, *Frother inducement of the bubble attachment to hydrophobic solid surface,* Proceedings of the 5th UBC-McGill Bi-Annual International Symposium of Fundamentals of Mineral Processing, 2004, 121.

KRASOWSKA M., MALYSA K., 2007. *Kinetics of Bubble Collision and Attachment to Hydrophobic Solids: I. Effect of Surface Roughness,* Intern. J. Mineral Process, 81, 205-216.

KRASOWSKA, R. KRASTEV, M. ROGALSKI, K. MALYSA, 2007. *Air facilitated three phase contact formation at hydrophobic solid surfaces under dynamic conditions,* Langmuir, 23 (2) 549-557.

KRASOWSKA M., KOLASINSKA M., WARSZYNSKI P., MALYSA K., 2007b. *Influence of polyelectrolyte layers deposited on mica surface on wetting and bubble attachment,* J. Phys. Chem. C, 111, 5743-5749.

KRZAN M., ZAWALA J., MALYSA K., 2006, *Development of steady state adsorption distribution over interface of the bubble rising in solutions of n-alkanols (C_5, C_8) and alkyltrimethylammonium bromides (C_8, C_{12}, C_{16}),* Colloids & Surfaces A, 42-51, 298.

MALYSA K., KRASOWSKA M., KRZAN M., 2005, *Influence of surface active substances on bubble motion and collision with various interfaces,* Advances Coll. Interface Sci., 205 114-115

SZYSZKA D., STEPIEN P., 2007, unpublished data.

VAGBERG L., STENIUS P., 1988. *ESCA and contact angle studies of the adsorption of aminosilanes on mica Herder, Peter;* Colloids and Surfaces, 34 (2), 117-132.

ZAWALA J., KRASOWSKA M., DABROS T., MALYSA K., *Influence of the bubble kinetic energy on its bouncing during collisions with various interfaces,* Canad. J. Chem. Engin., 2007 (accepted).

Zawala J., Drzymala J., Malysa K., *Naturalna hydrofobowość i flotowalność fluorytu,* Physicochemical Problems of Mineral Processing, 41 (2007), 5-11 (w jęz. ang.).

Badania kolizji swobodnie wznoszącego się pęcherzyka z powierzchnią mineralną zanurzoną w wodze wykazały, że czas tworzenia się kontaktu trójfazowego silnie zależy od chropowatości powierzchni fluorytu. W zależności od chropowatości powierzchni fluorytu, czas kontaktu wynosił od 20 do 200ms. Tworzenie się kontaktu trójfazowego świadczy o naturalnej hydrofobowości fluorytu. Kąt zwilżania tworzony pomiędzy pęcherzykiem powietrza a płaska płytka fluorytową zanurzoną w wodzie wynosił 40^{o} w porównaniu do wartości $10\text{-}15^{o}$ uzyskanych metodą fotometryczną i 55^{o} uzyskaną metodą siedzącej kropli. Zatem makroskopowy kąt zwilżania dla fluorytu zależy od metody pomiaru oraz pochodzenia próbki, a nawet jego koloru, gdyż barwne odmiany flotują lepiej. Hydrofobowość fluorytu oraz czas tworzenia się kontaktu trójfazowego wpływają na flotację. Najlepszą flotację obserwuje się w celce Hallimond, podczas gdy flotacja w mechanicznej maszynce laboratoryjnej jest znacząco zredukowana z powodu względnie długiego czasu tworzenia się kontaktu trójfazowego i/lub słabą hydrofobowością fluorytu, który nie wytrzymuje zwiększonych sił odrywania występujących w większych maszynach flotacyjnych.