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## Surface roughness in bubble attachment and flotation of highly hydrophobic solids in presence of frother – experiment and simulations

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**Abstract:** In this paper, the kinetic of the three-phase contact (TPC) formation and the flotation recovery of highly hydrophobic solids with different surface roughness were studied in pure water and aqueous solutions of n-octanol. The surface roughness varied between 1 to 100  $\mu\text{m}$ . It was found that there was a strong influence of surface roughness on both kinetics of TPC formation and flotation. The time of three phase contact formation and flotation rate were much faster for rough surfaces in both water and aqueous solutions of frother. Irrespective of the surface roughness, at above a certain frother dose, the attachment time increased and the flotation rate decreased. It was related to the presence of air at the hydrophobic solid surfaces. The mechanism of this prolongation of the time of TPC formation at the solid surfaces with different roughness due to the frother overdosage was discussed, and the experimental data were confirmed by numerical simulations.

**Keywords:** surface roughness, attachment, flotation, kinetics, frother

### 1. Introduction

Froth flotation is a widely used physicochemical separation technique based on selective attachment of a gas bubble to a surface of particular mineral in the pulp. It is a complex process involving a large number of factors and numerous elementary phenomena, which have to be taken into account for flotation quantitative and qualitative characterization (Drzymala, 2007; Wills and Finch, 2016). One of the most important sub-process involved in the flotation separation is a bubble collision with a mineral particle and whether or not it results in a successful bubble attachment to the solid/liquid interface via formation of a so-called three-phase contact (TPC - gas/liquid/solid) (Ralston, 1983; Nguyen and Schulze, 2004). Moreover, efficient TPC formation requires favourable chemical environment, usually realized by addition of various reagents to the flotation pulp, mostly surface-active substances (SAS). Frothers are one of the flotation reagents, applied to modify properties of a liquid/gas (bubble) interface by formation of an adsorption layer. Formation of the adsorption layer affects the fluidity of the bubble surface and leads to the hindering of coalescence (increased stability of the foam films formed during the bubbles mutual collisions), enhancement of a gas dispersion degree, formation of a stable froth, and facilitation of the TPC, what improves and accelerates the flotation recovery. Facilitation of the TPC formation results mainly from lowering the bubble motion velocities and longer contact time between liquid/gas and liquid/solid interfaces (longer time available for the wetting films drainage to the rupture thickness) under turbulent flotation conditions.

Generally, the more hydrophobic the surface, the less stable is the wetting film (Laskowski and

Kitchener, 1969). Hydrophobicity is, however, not sole important factor affecting stability of the wetting film. The solid surface roughness is a second one. The solid surfaces of the same chemical and physical properties but of different roughness show different wetting behaviors. It is well known that increase in the surface roughness causes increase of the contact angle (Sedev et al. 2004; Marmur, 2008). Moreover, it decreases stability of the liquid film formed by the colliding bubble at the solid/liquid interface (Anfruns and Kitchener, 1977; Krasowska and Malysa, 2007; Kosior et al., 2013). Single bubble experiments confirmed that the greater hydrophobic surface roughness (even without significant modification of the contact angle) leads to shortening of the time of bubble attachment to the solid surface. This effect was attributed to (Krasowska et al., 2009): (i) variations in the radius of the local liquid film formed at pillars of the rough solid surface, and/or (ii) presence of air entrapped in the scratches, grooves and crevices of the hydrophobic surface, during its immersion into an aqueous phase. The latter mechanism, which in the light of the latest studies prevails, attributes shortening of the time of TPC formation to the presence of previously de-wetted areas – sub-microscopic air bubbles (nanobubbles) entrapped in scratches upon the hydrophobic surface during its immersion into aqueous phase. The presence of tiny bubbles generated by hydrodynamic cavitation in the flotation pulp was found to be significantly advantageous for the flotation efficiency (Zhou et al., 2009; Fan et al., 2010; Calgaoroto et al., 2014). It was reported that the presence of nanobubbles can increase the contact angle of solids, and hence the attachment force, bridge fine particles to form aggregates, minimize slime coating, remove oxidation layers from particle surfaces, and in consequence reduce reagents consumption. Nanobubbles can preferentially attach to the hydrophobic solid particle surfaces, creating de-wetted areas, which improves not only the flotation recovery, but also its selectivity. This is a consequence of the fact that nanometer sized bubbles, attached at a hydrophobic surface, can cause rupture of aqueous wetting films due to the so-called nucleation mechanism (Stockelhuber, 2003; Stockelhuber et al., 2004).

In this paper, we present results on the influence of hydrophobic surface roughness and frother concentration on the flotation kinetics (batch flotation) and time of the TPC formation determined during the colliding (single) bubble experiments. A correlation between time of the TPC formation and flotation kinetics is shown and the proposed mechanism of mutual influence of surface roughness and frother concentration on kinetics of the TPC formation is supported by the results of direct numerical simulations.

## 2. Materials and methods

### 2.1 Single bubble experiments

An experimental set-up used for monitoring a single bubble collision with the liquid/solid interface was described in details elsewhere (Kosior et al., 2011). A single bubble was formed at a thick-walled glass capillary of inner diameter of 0.075 mm at the bottom of glass column of square cross-section (40 x 40 mm). For this capillary diameter, the bubble radius ( $R_b$ ) was equal 0.74 mm. Within the frother concentration studied the difference in detaching bubble  $R_b$  did not exceed 5%. To obtain desired degree of roughness, the surface of the PTFE plates was modified using sand papers of different grid numbers (100, 600, 1200 and 2500). Static advancing contact angles of such prepared surfaces, measured by means of sessile drop method, varied between 100 – 120°. The PTFE plate was positioned horizontally beneath the liquid surface at the distance  $L = 3$  mm above the point of the bubble formation. Bubble motion and collisions with the solid surface were recorded using a high-speed video camera (Weinberger SpeedCam MacroVis, 1000 – 1024 fps). Sequences of recorded bubble images were analyzed frame-by-frame in order to determine the time of TPC formation ( $t_{TPC}$ ), that is the period from the first bubble collision till its attachment to the solid surface, which is a sum of time of a bubble bouncing ( $t_b$ ) and time of a drainage of the intervening liquid film ( $t_d$ ):

$$t_{TPC} = t_b + t_d. \quad (1)$$

Prior to each experimental run the solid plates of PTFE were carefully cleaned using a chromic acid mixture, and then rinsed with Milli-Q® water. N-octanol used in the experiments was purchased from Fluka and was commercial reagents of the highest available purity (≥99.5%). Milli-Q® water was used for solution preparation.

The single bubble experiments were carried out at room temperature (21±2 °C). At least 20 independent experimental runs were performed for each PTFE plate of determined roughness to calculate the influence of surface roughness on the average time of TPC formation.

## 2.2 Numerical simulations of single bubble attachment

The details on the model and computational domain used for numerical simulations of collision of a single bubble, with different degree of liquid/gas interface immobilizations, with a hydrophobic solid surface was described in details elsewhere (Zawala et al., 2016). More details on the computational geometry are described and discussed in this article, after experimental results presentations, where data supporting the proposed mechanism of influence of surface roughness and liquid/gas interface immobilization on the kinetic of the bubble attachment and the flotation recovery are presented. The phenomena occurring during the bubble approach and collision with a solid (no-slip) wall were calculated numerically using the Gerris Flow Solver to solve the governing equations, describing the conservation of momentum and mass of an incompressible viscous liquid, using spatial discretization and a numerical scheme described elsewhere (Popinet, 2003; 2009; Fuster et al., 2009). The contact angle  $\theta$  of the solid surface depended on the level of refinement of the solid boundary and was adjusted to be 100°. To reconstruct and track the bubble interface, the volume-of-fluid algorithm (VOF), based on the idea of fraction function  $f$ , was applied. In such approach,  $f$  changes between 0 and 1. The density ( $\rho$ ) and viscosity ( $\mu$ ) at each point of the system depends on the  $f$  value and, for the bubble in water,  $\mu$  and  $\rho$  are given as:

$$\begin{cases} \rho = \rho_w f + \rho_a(1 - f) \\ \mu = \mu_w f + \mu_a(1 - f) \end{cases} \quad (2)$$

where  $\mu_w$  and  $\mu_a$  are the bulk viscosities of water and air phases, while  $\rho_w$  and  $\rho_a$  are densities of both phases, respectively. The distance between the bubble starting point and the solid surface corresponded to this determined experimentally. In order to take into account gradual decrease in the bubble surface fluidity caused by the surfactant absorption and the presence of adsorption layer at the rising bubble surface (dynamic adsorption layer, DAL) the original VOF approach was modified. It was realized by introducing different viscosity values at the liquid/gas interface, i.e. at two-dimensional plane in the middle of the interfacial region ( $f = 0.5$ ). Different viscosity values of the liquid/bubble interface, implying that there were secondary tangential stresses near the interface, were used in calculations to simulate different degrees of the bubble surface fluidity retardation in surface-active substance solutions of different concentrations. This assumption means applying in computations the following expanded form of Eq. 2

$$\begin{cases} f \neq 0.5, \mu = \mu_w f + \mu_a(1 - f) \\ f = 0.5, \mu = f(\mu_w + \mu_a + \mu_s) \end{cases} \quad (3)$$

In Eq. 3  $\mu_s$  is the value of viscosity at the bubble/liquid interface and is given as:

$$\mu_s = m\mu_w \quad (4)$$

where  $m$  is a liquid/gas interface mobility parameter of value  $\geq 0$  (dimensionless). For the bubble rising in clean water  $m = 0$  and Eq. 3 transfers into Eq. 2, what means that the bubble surface is fully mobile. Higher  $m$  means higher degree of liquid/gas interface immobilization.

Application of Eq. 3 allows reproducing the increased drag, exerted at the rising bubble surface, which was higher for higher  $m$  and reached constant value for  $m \geq 7$ . The drag coefficient varied between values characteristic for the bubble with fully mobile and the fully immobilized interface (Zawala et al., 2016).

## 2.3 Flotation tests

Flotation experiments were carried out using a Denver D12 flotation machine with a cell of volume 1.5 dm<sup>3</sup>. PTFE disks, 2 mm in diameter and 1 mm in thickness, were stamped from a thick PTFE foil. Prior to the discs stamping, both sides of the foil were roughened using sand paper of various grid numbers (220, 600, 1000 and 2500), to obtain similar roughness of both disk surfaces, corresponding to single bubble experiments. The prepared disks (referred further as PTFE particles) were washed in diluted Mucosol® (commercially available cleaning liquid, Sigma Aldrich), and then rinsed with large amount

of warm distilled water. Prior to the tests, the rotor as well as the flotation cell were washed in large amount of distilled water. The PTFE particles were added to the clean flotation cell together with 1.35 dm<sup>3</sup> of frother (n-octanol) solution of known concentration, and then conditioned for 60 s (rotor speed 700 rpm) without air introduction. After 60 s of conditioning the air was introduced to the system with the flow rate oscillating around 30 dm<sup>3</sup>/h. Similarly, as in the case of single bubble experiments, the flotation tests were carried out in distilled water as well as in n-octanol solutions of various, corresponding concentrations. On the basis of ratio between floating particles, skimmed manually after reaching the liquid surface, and the total number of particles used in the experiments (100 - 105 pcs.), the flotation recovery as a function of time ( $t$ ) was determined.

N-octanol used in the experiments was purchased from BDH Chemicals and was commercial reagent of the highest available purity ( $\geq 98\%$ ). The flotation tests were carried out at ambient temperature ( $22 \pm 1^\circ\text{C}$ ). Each flotation test was repeated three times, in order to calculate the average value of first order kinetic constant of the process ( $k$ ), according to the first order kinetics equation:

$$r = r_{\max}(1 - e^{-kt}) \quad (5)$$

where  $r$  is recovery of floating particles,  $r_{\max}$  the ultimate recovery, and  $t$  is the flotation time.

### 3. Results and discussion

#### 3.1 Experiments

Comparison of surface roughness of PTFE plates and discs (particles) used in the single bubble and flotation tests, respectively, is presented in Fig. 1. The photos of surfaces taken using light microscope are presented there. Next to each image, a range of lateral dimensions of the surface scratches, measured using an image analysis software, is given. Due to the fact that the surface modification procedures of the PTFE plates and disks were applied independently by two different persons, and additionally, different sand paper gradations were used in both cases, absolute values of scratches dimensions were slightly different. Nevertheless, the trend of surface roughness variation is identical - the higher the grid number, the smoother the PTFE surface. The PTFE-1 sample has the roughest, while the PTFE-4 sample the smoothest surface.

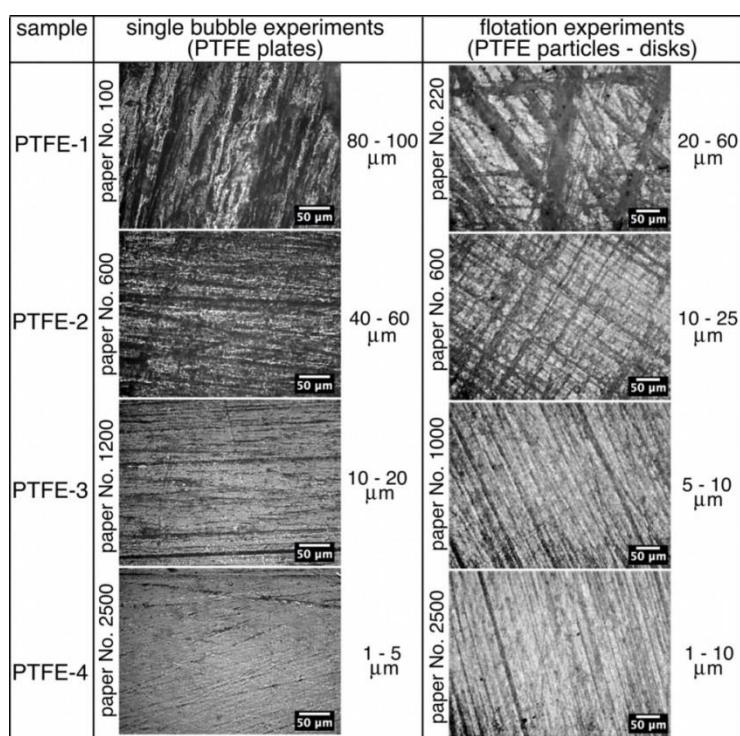


Fig. 1. Microscopic photos of surface of PTFE samples with different (modified) roughness used in single bubble (plates) and flotation (disks) experiments (range of lateral dimensions of the surface scratches is given next to each picture)

The values of time of the three-phase contact formation ( $t_{TPC}$ ) and inversed first order kinetic constant ( $1/k$ ) determined during the single bubble and flotation experiments, respectively, both performed in pure water (no frother, mobile bubble surface) for solid samples of various roughness are presented in Fig. 2. It can be clearly seen that there is a strong influence of the roughness degree on  $t_{TPC}$  and  $1/k$ . The higher the surface roughness, the shorter the  $t_{TPC}$  and smaller values of  $1/k$ . It means that the bubble attachment to the PTFE surface and the recovery of PTFE particles were significantly faster for the solids of rougher surface. Moreover, these results show that stability of the liquid film formed by the colliding bubble is the fundamental step of a flotation process determining its effectiveness. Despite the complexity of the flotation process, which includes vast number of sub-processes, the kinetic of drainage of liquid film separating the bubble and solid surfaces to the critical thickness of rupture is indeed a factor of crucial importance for the final separation outcome (Kowalczyk et al., 2016). As it was recently shown, such correlation can be a useful tool for prediction of the flotation response not only for highly hydrophobic solids, but also minerals of different hydrophobicity degrees in various flotation systems (Kowalczyk and Zawala, 2016; Zawala et al., 2017).

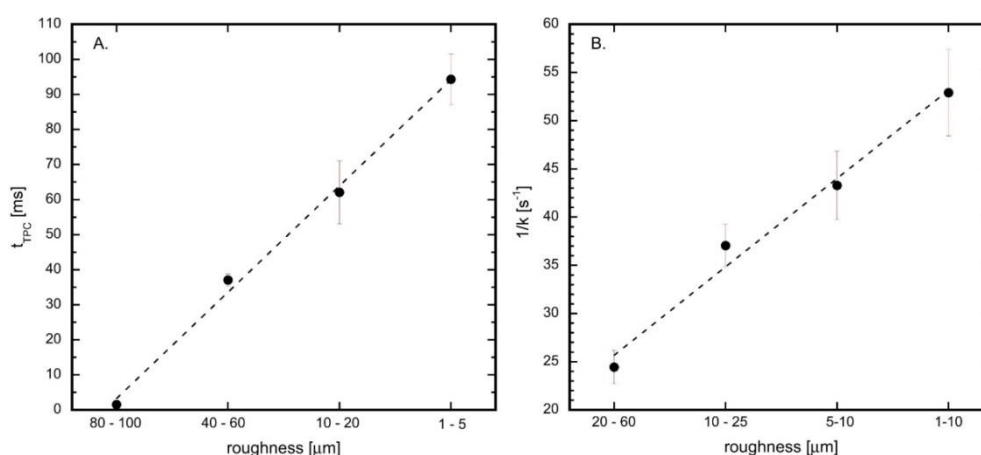


Fig. 2. Influence of PTFE surface roughness on (A) time of TPC formation and (B) values of inversed first order kinetic constant of the flotation process in water (bubble interface fully mobile)

Similar comparison between  $t_{TPC}$  and  $1/k$  is presented in Fig. 3, where respective quantities, determined for PTFE-4 and PTFE-2 samples (see Fig. 1), are presented as a function of frother concentration. There are two general trends, which can be seen in Fig. 3A and 3B. First of all, it can be observed that  $t_{TPC}$  and  $k^{-1}$  values, for each concentration studied are smaller for higher roughness, i.e. in the case of PTFE-2 surface. In turn, for these particular roughness values of the solid samples presented in Fig. 3, this effect is independent on the frother concentration. In addition, initially, for water and low frother concentrations the measured parameters are practically constant, but above some given (threshold) frother concentration (ca.  $0.5 \times 10^{-4}$  M), they start to increase. This value corresponds well to critical coalescence concentration (Zhang et al., 2012; Kowalczyk, 2013). This is rather unexpected effect, as frothers are usually added to the flotation pulp to facilitate the bubble attachment, and hence the flotation recovery. This effect is independent on roughness of the solid surface and indicates that the frother can be overdosed, what significantly hinders the bubble-solid surface attachment.

Results presented in Figs. 2 and 3 clearly show that the surface roughness of the hydrophobic solid has profound influence on the timescale of bubble attachment (TPC formation) and kinetics of flotation. However, depending on the aqueous phase chemical composition, this influence can be quite different. In distilled water, i.e. when the water/air (bubble) interface is fully mobile (clean, without the adsorption layer), there is a linear correlation between the roughness degree and TPC formation. In the frother solution this trend is completely different. Generally, in the presence of frother, the adsorption coverage is formed at the bubble surface, which degree depends on the frother concentration. Existence of the threshold concentration, above which the spectacular increase in the

$t_{TPC}$  and  $k^{-1}$  values can be observed indicates that there is also the threshold for the bubble adsorption coverage, responsible for this effect.

In the case of highly hydrophobic solid surfaces (with  $\theta > 90^\circ$ ) the influence of roughness and frother overdosage on the kinetics of TPC formation by the colliding bubble was attributed to possible presence of air, which can be entrapped in the surface crevices, scratches and holes, during transfer of the solid surface from an ambient atmosphere to an aqueous phase (Snoswell et al., 2003; Krasowska et al., 2007, 2009; Kosior et al., 2011, 2013). Thus, instead of a wetting film formed between the solid and the colliding bubble surfaces there are symmetric (foam) films formed locally between the colliding bubble and de-wetted spots (micro- and/or nano-bubbles) already present at the hydrophobic surface. In distilled water, interfaces of both colliding bubble and submicroscopic bubbles already attached to the solid surface are completely mobile, and therefore the TPC formation occurs as a result of bridging (quick coalescence) between two clean liquid/gas interfaces. As more air can be entrapped at the surface of higher roughness due to larger scratches and cavities dimensions,  $t_{TPC}$  is drastically shortened with the surface roughness increase. It is due to the increased probability of collision, higher de-wetted areas perimeter and size of the TPC hole after the liquid film rupture. In the aqueous solutions of frother the adsorption layer is formed at every solution/gas interface (Zawala et al., 2007), that is, at the colliding bubble surface as well as the surfaces of the interfacial micro- and/or nano- bubbles. It is well known that stability of symmetric foam films increases with the surfactant concentration (Exerowa and Kruglyakov, 1998). Therefore, prolongation of the  $t_{TPC}$ , and thus  $1/k$  at high concentrations of frother solution is rather strong evidence of formation of local foam films of higher stability.

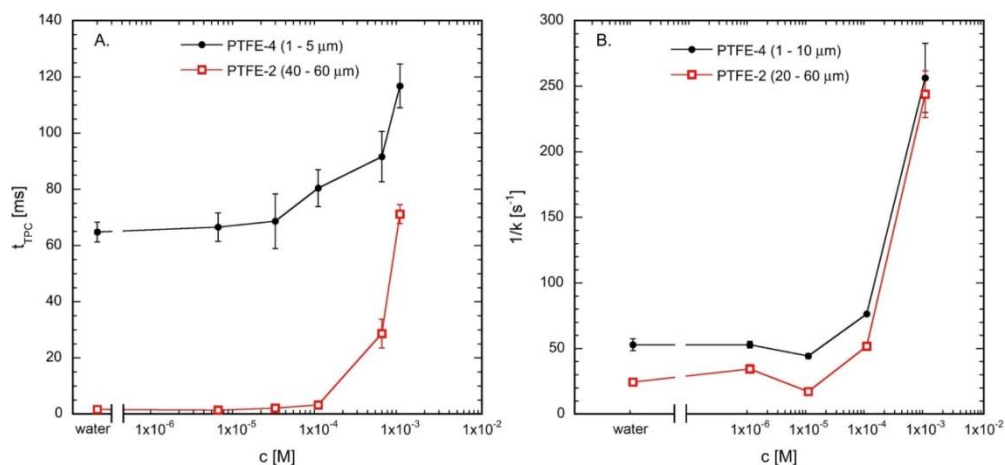


Fig. 3. Influence of frother concentration on (A) time of TPC formation and (B) inverted first order kinetic constant of flotation process for smooth (PTFE-4) and medium rough (PTFE-2) surfaces

### 3.2 Simulations

In order to gain more supporting data about correctness of the mechanism described above, numerical simulations of a single bubble collision with a hydrophobic solid surface were performed. As was already mentioned, due to the developed model, it was possible to take into account gradual immobilization of the bubble surface, i.e. mimics increasing drag exerted at the bubble surface due to increase in the degree of adsorption coverage. Moreover, to include the effect of the surface roughness and the presence of interfacial air in the calculations, two independent simulation series were carried out. In the first one, the hydrophobic surface was set as completely smooth and no-slip (see Fig. 4A), which corresponded to the PTFE-4 surface. In the second series, the presence of air was directly taken into account by introduction a microbubble in the surface pore (Fig. 4B - depth of pore equal to 80 μm, height of microbubble protrusion beneath the solid surface equal to 15.7 μm).

The values of  $t_{TPC}$  as a function of liquid/gas interface mobility parameter ( $m$ ) calculated numerically are presented in Fig. 5. The  $t_{TPC}$  values were calculated from the moment of first collision to the moment of liquid film rupture. As can be seen in Fig. 5, trends obtained by means of numerical simulations are identical to those observed in the experiments (both flotation and single bubble tests).

It is evident that for low  $m$  values, quick coalescence between macro- and micro-bubble was responsible for fast TPC line expansion. Above some specific value of  $m$  (degree of bubble surface immobilization) there is a sharp jump in the  $t_{TPC}$  values, as a result of decreased rate of the liquid film drainage. It is interesting to note that, similarly as already discussed (see Fig. 3), the  $t_{TPC}$  values are higher for smoother surface.

One of the possible reasons of this effect can be related to the variations in radius of the liquid film formed at the surfaces of different roughness. To check correctness of this hypothesis, a simple analysis was performed on the basis of numerically obtained results. Figure 6 illustrates the bubble captured motionless beneath the smooth hydrophobic surface and hydrophobic surface with microbubble protruding from the surface pore (simulation snapshots).

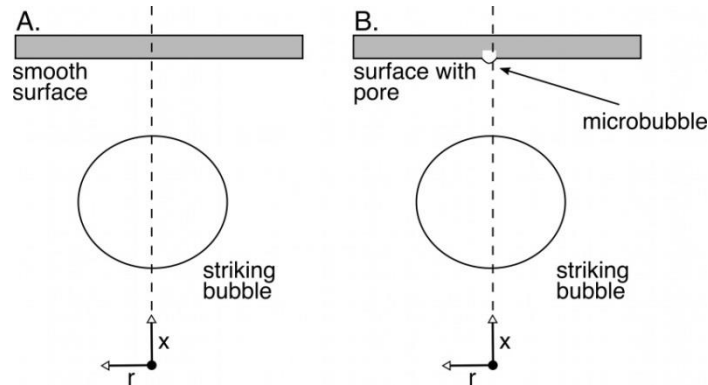


Fig. 4. Schematic presentation of two computational domains used in calculations of the bubble collision with (A) smooth and (B) rough hydrophobic surface (with the air entrapped)

Due to the presence of microbubble, the radius of the local foam film ( $R_f$ ) formed between the colliding bubble and microbubble is much smaller comparing to that formed at smooth hydrophobic solid. From comparison of  $R_f$  values presented in Fig. 6 it can be found that, for the particular dimension of the microbubble used in calculations,  $R_f$  of foam film (formed between two liquid/gas interfaces) is about 4 times smaller than  $R_f$  of wetting film (formed between the solid surface in contact with the liquid/gas interface). Kinetics of drainage of the wetting film can be described using the Scheludko (1967) equation:

$$-\frac{d(1/h)^2}{dt} = \frac{4}{3} n \frac{\Delta p}{\mu R_f^2} \quad (6)$$

where  $h$  is a liquid film thickness,  $n$  is a parameter describing the degree of interfaces fluidity and  $\Delta p$  is a Laplace pressure. Assuming similar values of the rupture thicknesses and the  $n$  parameters for wetting and foam film, the rate of drainage of the liquid film is determined only by magnitude of  $R_f$ . Under this assumption, by comparison of the Eq. 6 for "microbubble" ( $mb$ ) and "smooth" ( $s$ ) cases presented in Fig. 6 it can be written that:

$$t_s = t_{mb} \left( \frac{R_{f(s)}}{R_{f(mb)}} \right)^2 \quad (7)$$

where  $t_s$  and  $t_{mb}$  are the times of drainage of the liquid film formed at the smooth surface and the surface of microbubble. Equation 7 indicates that, if  $R_{f(s)} / R_{f(mb)} = 4$  (see Fig. 6), so  $t_s = 16 t_{mb}$ . The consequences of this effect can be seen in Fig. 7A, where the  $t_{TPC}$  for smooth surface were divided by 16 (according to the calculation). For comparison, this same operation was performed for experimental data, which are presented in Fig. 7B. As seen for numerical data (Fig 7A) the  $t_{TPC}$  value for "s" and "mb" cases initially converge. Beneath the threshold value of  $m$ , the jump in  $t_{TPC}$  is even stronger than this observed in Fig. 5. A similar trend can be observed for the experimental data. Certainly, the data presented in Fig. 6 correspond to some ideal and model situation (Fig. 4), which can be, and most probably is, much more complicated in reality. It has to be underlined that the assumption led to obtaining Eq. (7) is quite a simplification, as similar values of the rupture thicknesses and parameter  $n$  for the foam and wetting film can be justified only for higher concentration of frother ( $c > 1 \times 10^{-4}$  M),

where the liquid/gas interfaces are fully immobilized (Krzan et al., 2007). Nevertheless, this simple analysis shows the strong effect of radius of the liquid film on its drainage and rupture times. A quite good agreement between trends obtained in simulations and experiments indicates that the variations in radius of the liquid film formed at previously dewetted area of the PTFE surfaces of different roughness can be one of the crucial parameters. The PTFE-2 surface is much rougher so the interfacial sub-microscopic bubbles can be higher and wider comparing to those at the PTFE-4 surface. We believe that the nano- and microbubbles can be present also at PTFE-4 surface immersed into the aqueous phase. The amount and sizes of these de-wetted areas, however, are much smaller, causing smaller probability of collision and facilitation of TPC formation.

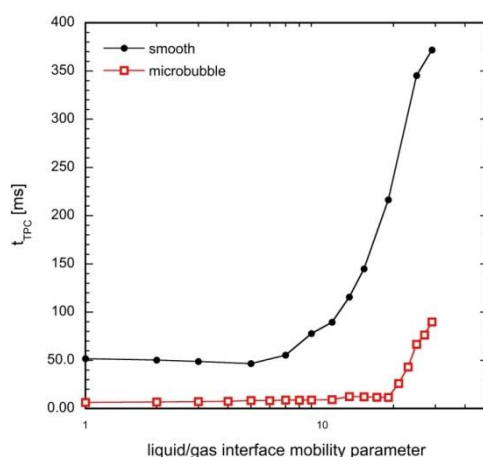


Fig. 5. Influence of degree of bubble (liquid/gas) surface immobilization ( $m$ ) on time of TPC formation at hydrophobic surfaces without (smooth) and with presence of air (microbubble)

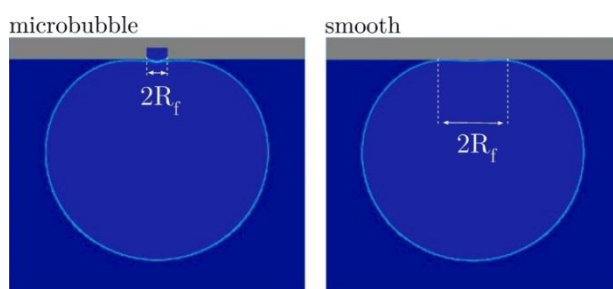


Fig. 6. Diameter of liquid film ( $2R_f$ ) formed at smooth surface (right) and surface with protruding micro-bubble (left). Simulation snapshots

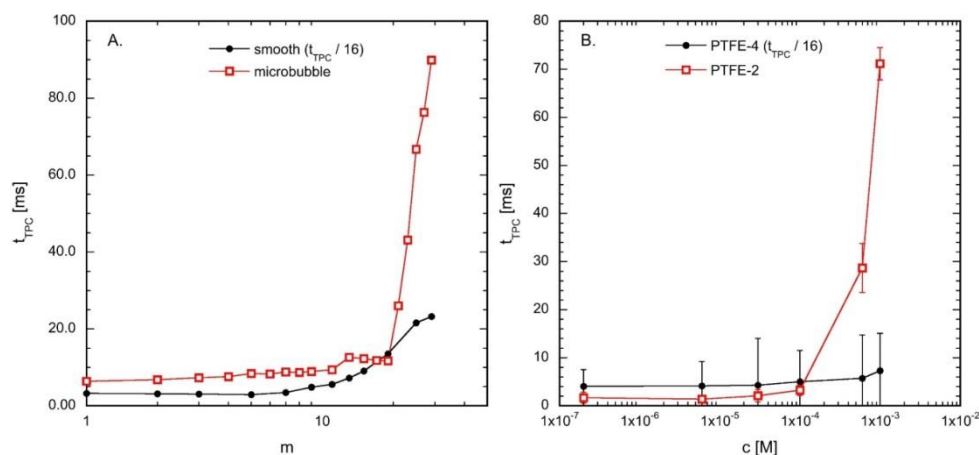


Fig. 7. Data replotted from Fig. 6, where  $t_{TPC}$  for (A) smooth (numerical) and (B) PTFE-4 (experimental) surfaces were divided by 16 to take into account estimated differences in liquid film radius ( $R_f$ )



#### 4. Conclusions

Roughness of solid surfaces and concentration of surface-active substance solutions are the factors strongly affecting the time of the three-phase contact formation by the bubble colliding with hydrophobic surfaces. The effect of surface roughness on the kinetics of the bubble attachment can be attributed to: (i) radii of the local liquid films formed at irregularities of solid surface of different roughness, and (ii) the presence of air entrapped in the scratches, grooves and irregularities of the hydrophobic surface.

Performed numerical simulations show that air, entrapped in irregularities of the hydrophobic surface, can be of crucial importance for kinetic of TPC formation on this surface. Moreover, the mechanism of TPC formation can be tuned by surface-active substances. In case of clean water, foam films formed locally between the micro- and/or nano-bubbles and the colliding bubble are unstable and rupture very quickly facilitating the TPC formation. Stability of the foam films increases with concentration of n-octanol, and therefore at high SAS concentrations the time of the TPC formation is prolonged, that is, the bubble attachment is hindered.

The finding that at high concentrations of various surface-active substances the time of the TPC formation and the bubble attachment to hydrophobic surface are clearly prolonged can have also some important practical implications for flotation process, what is confirmed by presented data. It shows that too high concentrations (overdosage) of surface-active substances (frothers and/or collectors) can be counterproductive, because the flotation kinetics can be slowed down as a result of prolongation (hindrance) of the TPC formation time.

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#### References

- ANFRUNS, J.F., KITCHENER, J.A., 1977, *Rate of capture of small particles in flotation*, IMM Trans. Sect. C Miner. Process. Extra. Metall., 86, 9–15.
- CALGAROTO, S., WILBERG, K.Q., RUBIO, J., 2014, *On the nanobubbles interfacial properties and future applications in flotation*, Min. Eng. 60, 33–40.
- DRZYMALA, J. 2007. *Mineral Processing. Foundations of theory and practice of minerallurgy*, 1st English Edition. Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław.
- EXEROWA, D., KRUGLYAKOV, P.M., 1998, *Foam and Foam Films – Theory, Experiments, Application*, Elsevier, Amsterdam.
- FAN, M., TAO, D., HONAKER, R., LUO, Z., 2010, *Nanobubble generation and its application in froth flotation (part I): nanobubble generation and its effects on properties of microbubble and millimeter scale bubble solutions*, Min. Sci. Technol. 20, 1–19.
- FUSTER, D., AGBAGLAH, G., JOSSERNAD, C., POPINET, S., ZALESKI, S., 2009, *Numerical simulation of droplets, bubbles and waves: state of the art*, Fluid Dyn. Res. 41, 065001.
- KOSIOR, D., ZAWALA, J., KRASOWSKA, M., MALYSA, K., 2013, *Influence of n-octanol and  $\alpha$ -terpineol on thin film stability and bubble attachment to hydrophobic surface*, Phys. Chem. Chem. Phys., 15, 2586–2595.
- KOSIOR, D., ZAWALA, J., MALYSA, K., 2011, *When and how  $\alpha$ -terpineol and n-octanol can inhibit the bubble attachment to hydrophobic surfaces*, Physicochem. Probl. Miner. Process. 47, 169–182
- KOWALCZYK P.B., 2013, *Determination of critical coalescence concentration and bubble size for surfactants used as flotation frothers*. Ind. Eng. Chem. Res., 52(33), 11752–11757.
- KOWALCZYK, P.B., ZAWALA, J., 2016, *A relationship between time of three-phase contact formation and flotation kinetics of naturally hydrophobic solids*, Colloids Surf. A: 506 (2016) 371–377.
- KOWALCZYK, P.B., ZAWALA, J., KOSIOR, D., DRZYMALA, J., MALYSA, K., 2016, *Three-phase contact formation and flotation of highly hydrophobic polytetrafluoroethylene in the presence of increased dose of frothers*, Ind. Eng. Chem. Res. 55, 839–843.
- KRASOWSKA, M., KRASTEVA, R., ROGALSKI, M., MALYSA, K., 2007, *Air-facilitated three-phase contact formation at hydrophobic solid surfaces under dynamic conditions*, Langmuir, 23, 549–557.
- KRASOWSKA, M., MALYSA, K., 2007, *Kinetics of bubble collision and attachment to hydrophobic solids: I. Effect of surface roughness*. Int. J. Miner. Process, 81, 205–216.

- KRASOWSKA, M., ZAWALA, J., MALYSA, K., 2009, *Air at hydrophobic surfaces and kinetics of three phase contact formation*, Adv. Colloid Interface Sci., 147-148 (2009) 155-169.
- KRZAN, M., ZAWALA, J., MALYSA, K., 2007, *Development of steady state adsorption distribution over interface of a bubble rising in solutions of n-alkanols (C<sub>5</sub>, C<sub>8</sub>) and n-alkyltrimethylammonium bromides (C<sub>8</sub>, C<sub>12</sub>, C<sub>16</sub>)*, Colloids Surf. A., 298, 42-51.
- LASKOWSKI, J., KITCHENER, J.A., 1969, *The hydrophilic-hydrophobic transition on silica*. J. Colloid Interface Sci., 29, 670-679.
- MARMUR, A., 2008, *From hydrophilic to superhydrophobic: theoretical conditions for making high-contact-angle surfaces from low-contact-angle materials*. Langmuir 24, 7573-7579.
- NGUYEN, A.V., SCHULZE, H.J., 2004, *Colloidal Science of Flotation*, Marcel Dekker, New York.
- POPINET, S., 2003, *Gerris: a tree-based adaptive solver for the incompressible Euler equations in complex geometries*, J. Comput. Phys. 190, 572-600.
- POPINET, S., 2009, *An accurate adaptive solver for surface-tension-driven interfacial flows*, J. Comput. Phys. 228, 5838-5866.
- RALSTON, J., 1983, *Thin films and froth flotation*, Adv. Colloid Interface Sci. 19, 1-26.
- SCHELUDKO, A., 1967, *Thin liquid films*, Adv. Colloid Interface Sci. 1, 391-464.
- SEDEV, R., FABRETTO, M., RALSTON, J., 2004, *Wettability and surface energetics of rough fluoropolymer surfaces*. J Adhes. 80, 497-520.
- SNOSWELL, D. R. E., DUAN, J., FORNASIERO, D., RALSTON, J., 2003, *Colloid stability and the influence of dissolved gas*, J. Phys. Chem. B, 107, 2986-2994.
- STOCKELHUBER, K.W., 2003, *Stability and rupture of aqueous wetting films*. Eur. Phys. J. E. 12, 431-435.
- STOCKELHUBER, K.W., RADOEV, B.P., WENGER, A., SCHULZE, H.J., 2004, *Rupture of wetting films caused by nanobubbles*, Langmuir, 20, 164-168.
- WILLS, B.A., FINCH, J.A., 2016. *Wills' Mineral Processing Technology, 8th Ed., An introduction to the practical aspects of ore treatment and mineral recovery*. Elsevier Ltd, Amsterdam.
- ZAWALA, J., KOSIOR, D., DABROS, T., MALYSA, K., 2016, *Influence of bubble surface fluidity on collision kinetics and attachment to hydrophobic solids*, Colloids Surf. A., 505, 47-55.
- ZAWALA, J., SWIECH, K., MALYSA, K., 2007, *A simple physicochemical method for detection of organic contaminations in water*, Colloids Surf. A: 302 (2007) 293-300.
- ZAWALA, J., KARAGUZEL, C., WIERTEL, A., SAHBAZ, O., MALYSA, K., 2017, *Kinetics of the bubble attachment and quartz flotation in mixed solutions of cationic and non-ionic surface-active substances*, Colloids Surf. A: 523 (2017) 118-126.
- ZHANG, W., NESSET, J. E., RAO, R., FINCH, J. A., 2012, *Characterizing frothers through critical coalescence concentration (CCC)95-hydrophile-lipophile balance (HLB) relationship*. Minerals 2, 208-227.
- ZHOU, Z.A., XU, Z.H., FINCH, J.A., MASLIYAH, J.H., CHOW, R.S., 2009, *On the role of cavitation in particle collection in flotation - A critical review. II*, Minerals Eng., 22(5), 419-433.