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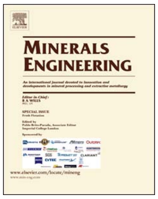

Short communication

Comment on “Aqueous dispersions of nanobubbles: Generation, properties and features“ by A. Azevedo, R. Etchepare, S. Calgaroto, J. Rubio [Miner. Eng. 94 (2016) 29–37]

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Dear Editor

I recently read, with great interest, a paper from Prof. Rubio's group entitled “Aqueous dispersions of nanobubbles: Generation, properties and features“ [Miner. Eng., 94 (2016) 29–37]. The authors should be congratulated on their detailed research related to nanobubble generation by hydrodynamic cavitation in air-supersaturated systems. To fully appreciate their work some of the results are discussed below (Azevedo et al., 2016), which have revealed some striking findings.

1. Critical bubble diameter, d_c

The most incredible finding from the paper is that the sizes of nanobubbles generated can be even smaller than the critical equilibrium bubble size calculated from the classical nucleation theory (CNT). Based on the theory, for a given gas saturation pressure, there is a corresponding critical bubble diameter, d_c (calculated from Young-Laplace equation), so that any bubbles with diameter larger than d_c expand to burst, and that any bubbles with diameter smaller than d_c diminish to disappear, being forced to dissolve in water (Sahu et al., 2006; Zhou et al., 1994, 2009). The data present in Figure 7 of the paper were copied below (Fig. 1), and used as an example for discussion.

Since the saturation pressure was 2.5 bar, the calculated d_c for de-ionized water was about 1160 nm (or 1.16 μm), and 784 nm (or 0.784 μm) for frother solution. However, the measured sizes were about 180 nm for de-ionized water, and 120 nm for frother solution, respectively, immediately after the sample collection. In other words, the generated nanobubbles were more than 6.5 times smaller than the critical bubble diameter predicted from the theory (The work reported by Ushikubo et al. (2010) showed similar trend, but their system was slightly different, by continuously recirculating water through a pressure tank). Such a large difference cannot be attributed to the measurement errors. Would this mean that the classical nucleation theory cracked? or the Laplace equation invalid for the nano-sized objects, due to the surface tension greatly affected by the interface curvature, and by the internal gas pressure at nano scale, as has been questioned by many academics (Attard, 2003; Hemmingsen, 2004)? Based on the information provided in the experimental part, the possible reasons were discussed below.

Assume that virtually no pre-existing gas nuclei present in the tested de-ionized water. The water was air saturated for 30 min. at air saturation pressures of 2.5–5 bar. Since there was no turbulence or agitation during air saturation, there should be no any nanobubbles created in water (Zhou et al., 2010). The saturated air is in the state of molecules dissolved in water. When releasing the water from the pressure chamber via a needle valve (2 mm internal diameter), the resultant turbulence and pressure reduction within the needle valve zone initiated cavities in the releasing water stream. The pressure inside the stream passing through the valve would be lower than the saturation pressure (2.5 bar in Fig. 1), based on Bernoulli equation, by considering energy loss during water release. In other words, the absolute pressure difference between the saturation pressure and the pressure in the water stream passing through the needle valve was greater than 2.5 bar, i.e., the water was stretched, or under tension. Based on the measured sizes of nanobubbles (120–180 nm), and assume no nanobubble

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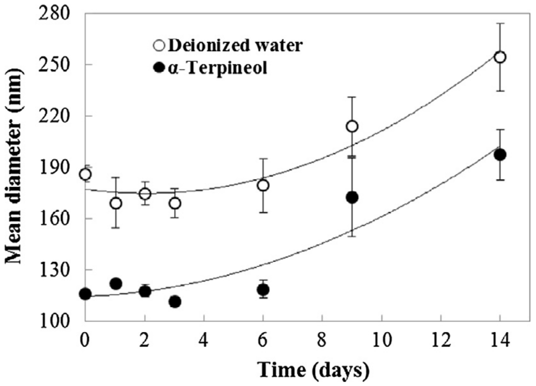

Fig. 1. Stability of aqueous dispersion of NBs: Mean bubbles diameter as a function of storage time (life time). Point 0.0 in the abscissa refers to the test (obtained size) 10 min after the NBs generation. Conditions: pH 7; Psat = 2.5 bar; [a-Terpineol] = 100 mg/L (surface tension = 49 mN/m); deionized water (surface tension = 72.5 mN/m). Measurements were performed with the NTA technique (Fig. 7 in the original paper).

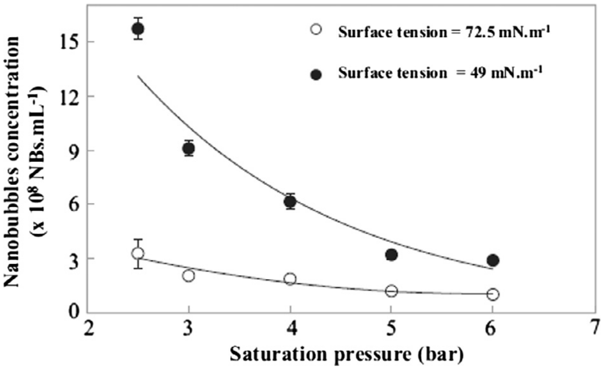

Fig. 2. NBs concentration (density) as a function of saturation pressure at two aqueous surface tension values. Conditions: pH = 7; surface tension of 49 mN/m obtained using 100 mg/L α-Terpineol; surface tension of 72.5 mN/m obtained using DI water. Measurements were performed with the NTA technique (Fig. 4 in the original paper).

coalescence after sample collection and measurement, the estimated water tensile strength in this case would be equivalent to around: −16 bar, if ignoring energy losses during water release.

Of course, such calculations and assumptions are over-simplified. In addition, there is no quantitative correlation established between dissolved air content and the critical diameter of cavity bubbles generated by hydrodynamic cavitation. It is also possible that the classical nucleation theory based on thermodynamic equilibrium conditions is not applicable to dynamic situations such as hydrodynamic cavitation. On the other hand, the obtained results indeed demonstrated that hydrodynamic cavitation, or dynamic bubble nucleation in air supersaturated systems, could produce nanobubbles with the sizes much smaller than those predicted from the classical nucleation theory under static and equilibrium conditions. The results further support the claims that nanobubble generation by hydrodynamic cavitation could occur at much milder conditions than the homogeneous bubble nucleation and prediction from the established theories (Zhou et al., 1994, 2009). In other words, although the generated nanobubbles are thermodynamically unstable, kinetically, they could still last for a few days, because of gas supersaturation, even without adding any chemicals. The generated nanobubbles with such a long life span are more than sufficient to fully play their roles in assisting flotation processes.

2. Effect of air saturation pressure on nanobubble population

The second interesting finding from the paper is that increasing air saturation pressure reduced the population of nanobubbles, which seemed to be contrary to conventional wisdom. It is known that a higher air saturation pressure could be used to produce more bubbles (50–300 μm) in dissolved air flotation. Also based on cavitation principle, a higher dissolved air content should intensify cavitation and generate more tiny bubbles, as has been demonstrated (Zhou, 1996; Zhou et al., 2009). In addition, based on Eq. (1), the minimum energy required for bubble formation, ΔF, is given by:

$$\Delta F = \frac{16\pi\gamma^3}{3(P_{sat}-P_o)^2} \tag{1}$$

Increasing saturation pressure would reduce the energy barrier, ΔF, for bubble formation, thereby producing more smaller bubbles.

In their experiments, a higher saturation pressure would result in faster water release through the needle valve, producing more cavities, other conditions being the same. More cavities could be survived and stabilized with a higher dissolved air content. Therefore, there should have had more nanobubbles formed at a higher saturation pressure. To reconcile such conflicting observations, it appeared that a higher dissolved air content and the formed more nanobubbles enhanced their coalescence to form more relatively larger microbubbles, thereby leading to a higher air holdup (Zhou, 1996; Zhou et al., 2009). In other words, the formed larger microbubbles and higher air holdups were achieved by sacrificing more smaller nanobubbles, which is thermodynamically favorable. As has been claimed, the waters mostly suitable for flotation should contain an abundance of tiny bubbles or nanobubbles (Wrobel, 1952; Zhou et al., 1994). Such nanobubbles act partly as the source for forming flotation size bubbles in flotation, and also as a link in the attachment of nanobubble-activated mineral particles to flotation size bubbles (Wrobel, 1952; Zhou et al., 1994). The results appeared to suggest that nanobubble generation by directly releasing air saturated water through a needle valve may not be effective.

To evaluate the nanobubble generation efficiency, a theoretical value of nanobubble population under air saturation conditions can be calculated for comparison. The actual amount of air dissolved in water at 21.1 °C (70 °F) and 2.5 bar at equilibrium is about: $V_{air}/V_{water} = 0.0622$, or an air holdup of 6.22% under the given test conditions (Rishel, 2002; The Engineering ToolBox). Assume all the dissolved air molecules are present inside the generated nanobubbles, the actual number of nanobubbles (with a diameter of 1160 nm for de-ionized water, and 784 nm for frother solution), generated by dynamic bubble nucleation is about 7.6×10^{10}/mL for de-ionized water, and 2.5×10^{11}/mL for frother solution. It can be noted from Fig. 2 that the surviving nanobubbles generated was < 1% of the theoretical value for both cases. In other words, either almost all the generated nanobubbles coalesced to form larger microbubbles, or not all the dissolved air molecules participated in nanobubble generation, with some remaining molecular dispersion in water. This observation suggested that air-saturated water released from the vessel via a needle valve did not generate sufficient amounts of cavities to accommodate all the dissolved air molecules. It could be partly because of this reason that this research group used similar methods to Ushikubo et al. (2010), by continuously recirculating the air saturated water through a pressure tank (Etchepare et al., 2017). Instead of using compressed air, the air was drawn from atmosphere on the suction side of the pump to accelerate air dissolution in water (Zhou, 1996; Zhou et al., 2009) (but the issue was reduced pumping efficiency, and potential pump damage by cavitation erosion). Although the reported nanobubble population increased from 1.6×10^9 to 2.5×10^9/mL (2.5 Bar) (Etchepare et al., 2017), such an increase was still much lower than the theoretical values, even after recirculation of 29 cycles. However, the role of raising saturation pressure (from 2.5 to 5 bar) in increasing nanobubble generation was verified (from 2.5 to 4.5×10^9/mL), although the amount of nanobubble increase was not directly proportional to the pressure increase. More work remains to be done to boost nanobubble generation efficiency by increasing cavity creation, especially in the absence of