

Fundamental characteristics of bubbles and ramifications for the flotation process

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Abstract Flotation processes involve the use of very small bubbles (micro-bubbles) to separate particles from water. The process has become a good alternative to sedimentation, especially where the particles are small or of low density. Although the flotation process commences with a collision between particles and bubbles, most research has been focused only on the characteristics of the particles. In this paper, recent theoretical and experimental research on the characteristics of bubbles is summarized. The effect on the collision efficiency of the size and charge of bubbles is calculated through trajectory analysis. The size and charge of bubbles are measured under different conditions and the ramifications of the results are discussed. The results may lead to a better understanding and optimization of the existing process. In particular, we discuss an idea that a new advanced flotation process might be possible by the modification of the characteristics of the bubble alone or of both bubble and particle.

Keywords Bubble charge; bubble size; DAF; electroflotation; flotation; trajectory analysis

Introduction

The flotation process involves using micro-bubbles for separating particles from water. The process has become a good alternative to the sedimentation process, being especially suitable for the removal of particles with low density, such as algae and alum floc. Dissolved-air flotation (DAF) is the most widely used flotation process. Electroflotation (EF), which uses micro-bubbles generated during electrolysis, is also considered an effective flotation process. Although the flotation process is widely used in many applications, its fundamental characteristics have not been fully understood.

Considering that the flotation process involves collisions between particles and bubbles, the characteristics of both the particles and the bubbles are important and both should be considered in the understanding of the process and in optimization of design and operation. However, most research and practice have been focused only on the characterization and modification of the particles. The characterization of bubbles is made possible by the development of computerized methods and state-of-the-art measuring techniques.

In this paper, we focus on the characterization of bubbles, and summarize recent research carried out in the author's research group. The sensitivity of the process to bubble size and charge is described. The development of methods to measure bubble size and charge is also described and some of our results are presented. The significance of this point of view in relation to current design and operation of the flotation process is discussed. We suggest some possible improvements to the process by modifying the characteristics of the bubble alone or of both the bubble and the particle.

Modelling

The movement and collision of rising bubbles and settling particles can be well described by equations that include those from hydrodynamics and interparticle forces (van der Waal's forces and electrostatic forces). Details of the method used to quantify the collision efficiency in DAF are described elsewhere (Han, 2002). In that paper, the collision

efficiency (α_{bp}) is defined as a function of the sizes of the bubble and the particle, which can be calculated from a trajectory analysis that includes all the short-range and long-range forces. The result of a sensitivity analysis of bubble characteristics and the significance and ramifications of this result are discussed.

The conditions for the calculation are as shown in Table 1. The particle size and density were chosen for those particles that may exist in water within a water treatment plant, a wastewater treatment plant or a natural system. Two values of particle zeta potential are chosen to simulate the conditions of stable and destabilized particles. A wide range of both bubble size and bubble zeta potential was chosen from the literature and experimental data.

Effect of bubble size

The effect of bubble size on α_{bp} is shown in Figure 1. The effect on the coagulation status is dramatic. For a stable condition ($\zeta_p = -30$ mV) the collision efficiency is very low, but the collision efficiency for a destabilized condition ($\zeta_p = 0$ mV) is one to two orders of magnitude higher than for a stable condition. The optimum bubble size that results in the highest collision efficiency depends on the size of the particles. For smaller particles, smaller bubbles are required to achieve a higher efficiency. Similarly, larger bubbles are required for larger particles. The optimum ratio of particle to bubble size is around 2:1 for the calculated conditions.

Effect of bubble zeta potential

The effect of bubble zeta potential on α_{bp} is shown in Figure 2 for three particle sizes ($d_p = 15 \mu\text{m}, 60 \mu\text{m}, 150 \mu\text{m}$), and for both stable and destabilized particles with all other conditions as noted in Table 1. A small particle size ($15 \mu\text{m}$) was used to represent

Table 1 Parameters used in the calculation of α_{bp}

Effect of	Bubble		Size	Particle Zeta	Density
	Size	Zeta (mV)			
1) Bubble size	20 ~ 120 (μm)	-25 (mV)	15, 60, 150 (μm)	0, -30 (mV)	1.2 (g/cm^3)
2) Bubble zeta potential	60 (μm)	-150 ~ -10 (mV)			

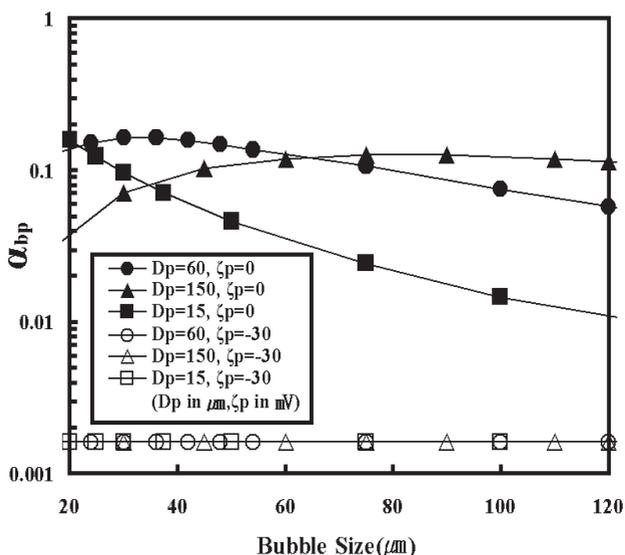


Figure 1 α_{bp} : Effect of bubble size

non-flocculated or less well flocculated particles, while a large particle size (150 μm) was used to represent flocculated particles.

In a destabilized condition ($\zeta_p = 0$ mV), the collision efficiency is high and does not change with the sign and magnitude of the bubble's zeta potential except where the bubble zeta potential is near zero. Electric attraction is induced between the negatively charged bubble and an uncharged particle, whereas no electric interaction is expected between uncharged bubbles and particles. For the conditions used in this calculation, the value of α_{bp} for 60 μm particles is greater than for the other sizes, although it depends on the size of bubble used in the calculation, as can be seen in Figure 1.

For stable particles ($\zeta_p = -30$ mV), there is a dramatic change of collision efficiency with change of the sign of the bubble zeta potential. The collision efficiency of a negatively charged particle with a negatively charged bubble is very low, but it increases abruptly when the charge of the bubble is changed to positive. This is due to the electric attraction between particles of opposite charge. It is interesting to note that α_{bp} is constant when the bubble zeta potential is in the negative range reported by others ($\zeta_b = -10$ mV to -150 mV), regardless of its value. This is because the electric repulsion in this region is so strong that it dominates the other two forces: hydrodynamic and van der Waals attraction forces.

Discussion

Although a range of optimum bubble sizes in DAF has been suggested and recommended in the literature or by manufacturers, there is little scientific basis for their suggestions or for the conditions to which their suggestion applies. Considering the wide variation in the collision efficiency, an optimum condition for a certain case may not be optimum for other conditions. Therefore, the optimum design of nozzle and pressure systems should be selected carefully so that bubbles of an optimum size can be produced. Also, the degree of flocculation or the flocculation time required to create particle flocs of a certain size could be considered in relation to the size of the bubbles.

Judged on the theoretical prediction of the effect of bubble charge, it can be postulated that the electrostatic characteristics are the most important to achieve high removal efficiency in DAF. In the design and operation of the DAF process, it has been emphasized that pre-treatment is important. If pre-treatment is considered as being a process that changes the zeta potential of the particles, current theory supports the practice. In the operation and

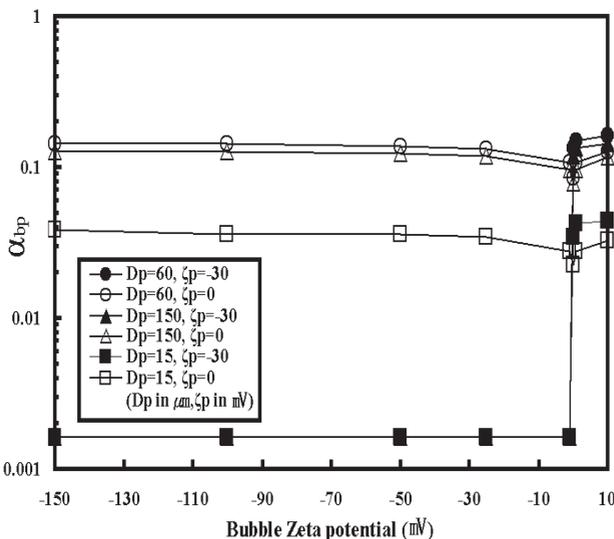


Figure 2 α_{bp} : Effect of bubble zeta potential

design of the DAF process, the zeta potential of the bubbles has not been considered as a controlling parameter, nor has any attempt been made to change it. However, if positive bubbles can be utilized, then higher collision efficiency with little or no pre-treatment can be expected.

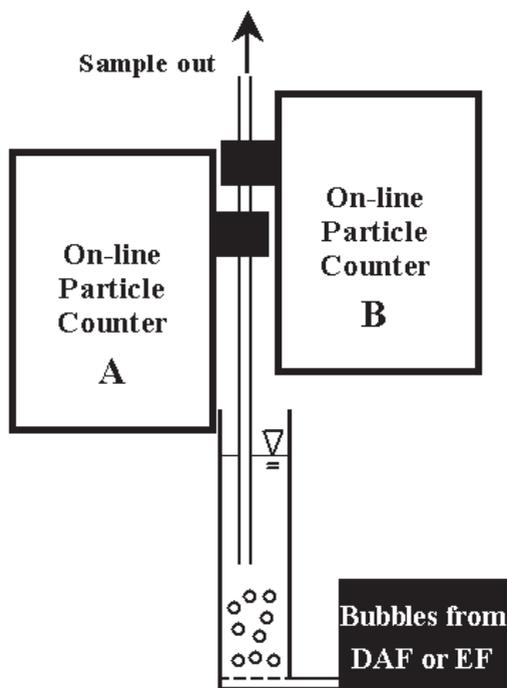
Bubble size measurement

A new measurement technique for bubble size and some of the results obtained with it have been reported by the author's group (Han *et al.*, 2002). In this research, two identical particle counters (Chemtrac Model PC2400 D, USA) were used to increase the number of channels, resulting in measurements that are more accurate. This method has an advantage over the traditional image analysis because of continuous on-line monitoring. The experimental set-up is as shown in Figure 3.

The size of bubbles

The size of bubbles generated in DAF and EF experiments has been measured, and the results are shown together in Figure 4. In this figure, the bubble size distributions and the average bubble size under different generation conditions are presented.

For DAF, the effect of pressure on the bubble size was investigated. The left-hand plot clearly shows that the bubble size decreases as the pressure increases until a critical pressure is reached, after which the size is constant. However, the critical pressure in this study is 3.5 atmospheres, which is lower than the value of 5 atmospheres that was suggested in the literature (Haarhoff and Vuuren, 1995; Edzwald, 1995). Also, the average size of the bubbles produced in this work is less than those reported in the literature. The reason for this may be a difference in the time and position of measurement. In this study, the bubbles sizes were measured immediately after release from the pressure vessel. Literature values might have been delayed because the time-consuming image analysis method was used. It is possible that the bubbles might have been observed in a contact zone in an operating DAF



plant where the pressures are reduced by passage through piping, valves, and orifices. Lower pressures tend to increase the size of the bubbles. In addition, the opportunity for bubble coalescence increases with the time between generation and measurement, and literature values reflect this fact.

For EF, the bubble size is not a function of pressure, so the average bubble size is marked at the axis of 0 atmospheres in the graph. The size of hydrogen bubbles generated from both gold and stainless electrodes were investigated and proved to be a function of the type of metal. The average bubble sizes from gold electrodes and stainless steel electrodes are 20 and 27 μm , respectively. These are much smaller than for bubbles generated in DAF.

Discussion

During practical operation of DAF processes, the nozzle pressure is generally in the range of 4–6 atmospheres, or even higher, in an attempt to generate bubbles that are as small as possible. However, according to these experimental results, bubble size is not a function of pressure when it is over 3.5 atmospheres. Therefore, it is not only costly but also unnecessary to maintain a pressure above 3.5 atmospheres if the goal is only to generate smaller bubbles. However, improved treatment efficiency might be expected under the higher pressure conditions but only because this results in a greater volume of bubbles rather than smaller bubble size. Another factor that should be considered is that the pressure conditions measured in this work were the pressure around the nozzle system. In real plants, this is greater than the pressure in the saturation tank because pressure is lost while saturated water passes through a pipeline from the saturation tank to the nozzle system. Therefore, it is important in DAF plant design to make the pipelines as short as possible and keep the pressure constant at all nozzles in operation.

Bubble zeta potential measurement

The method and experimental set-up for measuring the zeta potential of bubbles are reported elsewhere by the author's group (Dockko *et al.*, 1998). It is based on the principle of electrophoresis measurement (EPM), using equipment comprising an electrophoresis cell, microscope, CCD camera, and a video image analyser. The electrophoresis cell is made up of two slide glasses, with inner dimensions of 50 mm (length) \times 40 mm (width) \times 2 mm (depth). A potential difference was applied across the platinum electrodes on each side of the cell. While both hydrogen and oxygen gas bubbles are formed during electrolysis at the platinum wires, we measured the zeta potential of only the hydrogen gas bubbles because their size, and therefore the rising velocity, are small. It needs careful technique to locate the bubbles rising in a stationary layer in the cell. Instead, the horizontal velocity is measured and substituted in the Smoluchowski Equation to yield the zeta potential.

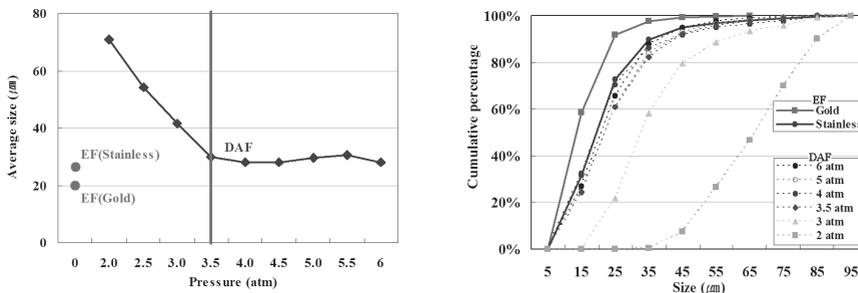


Figure 4 Bubble size distribution and average bubble size of DAF and EF

Results of zeta potential measurement

The bubbles are produced from the dissolved air tank in a medium of distilled water. The zeta potential of bubbles was measured over a wide range of pH, adjusted by addition of H_2SO_4 or NaOH . The zeta potential of bubbles from pH 2 to 12 is shown in Figure 5.

The zeta potential of bubbles is negative throughout the range of pH investigated. The highest negative value is about -25 mV near pH 7. The absolute value of zeta potential decreases as the pH is varied from pH 7. The results from previous research projects that used the electrophoretic method are also shown in Figure 5. The current result is similar to the previous research in the sense that the charge of a bubble is negative over a wide range of pH and that it is pH dependent. However, the previous research results are over a narrower range of pH values. Okada *et al.* (1990) presented his research only in the pH range of 2–8. Kubota and Jameson (1993) published results over a wider pH range. He observed a trough near pH 7–8 and obtained results that are broadly similar to ours. The zeta potential values measured in our work are smaller than those of the others. The difference might be due to the method of measuring the moving bubbles at the stationary level.

In EF, the zeta potential of bubbles is a function of the ions in solution. Results from separate research are summarized in Figure 6. Five metal species (Na, K, Ca, Mg, and Al) were selected, because they are mostly ions that occur in natural waters. To exclude the effect of the anion, the chloride salts were used throughout. Experimental conditions are as shown in Table 2. The zeta potential of hydroxide precipitates was measured using a Zetaphometer II (Sephy, France) in order to examine the relationship between the zeta potential of bubbles and metal ions, including their hydrolysis products.

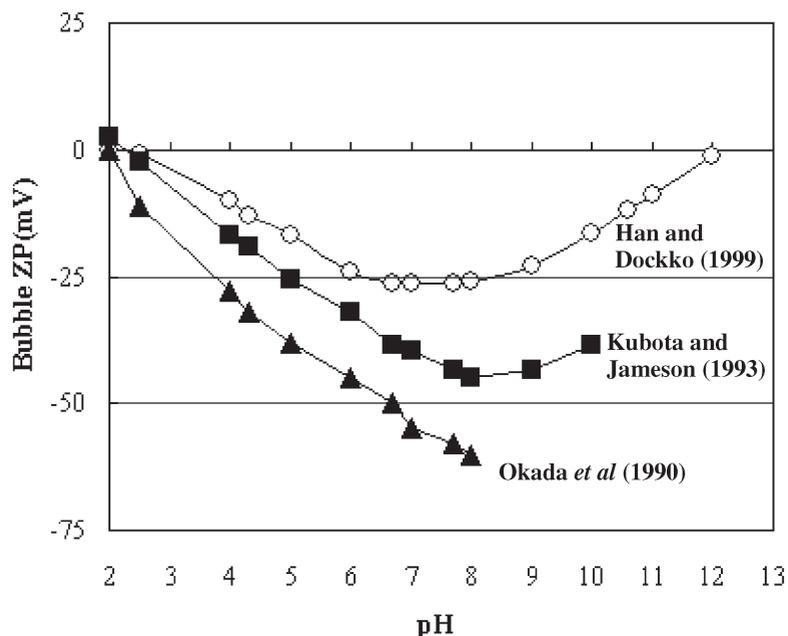


Figure 5 Bubble zeta potential as a function of pH

Table 2 Solution conditions for measuring the ζ -potential of bubbles

Valency of ion	Metal species	Metal conc.	pH	Background electrolyte
Monovalent	Na, K	10^{-2} mol l^{-1}	3–12	NaCl 0.01 mol l^{-1}
Multivalent	Divalent Trivalent	Mg, Ca Al		
		10^{-3} mol l^{-1}		

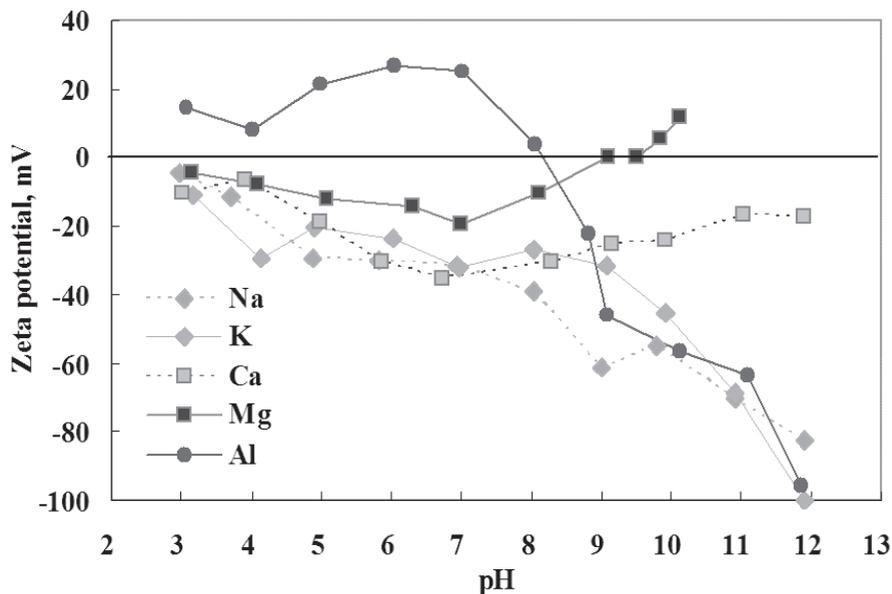


Figure 6 Zeta potential of bubbles

Zeta potential–pH curves obtained for solutions of five different metal ions are shown in Figure 6. Except for aluminium ion, we used all metal ions at a concentration of $10^{-2} \text{ mol l}^{-1}$. At a concentration of aluminium of $10^{-2} \text{ mol l}^{-1}$, the solution becomes a gel and so we used AlCl_3 $10^{-3} \text{ mol l}^{-1}$ solution.

Figure 6 shows that the zeta potential of bubbles varies according to the valency of the ion. In the case of Na and K, which are monovalent ions, bubbles are negatively charged over the entire pH range studied. The magnitude of the zeta potential decreased with a decrease in the pH value. In the case of Ca and Mg (which are divalent ions), it was found that bubbles are negatively charged in CaCl_2 solutions, whereas, under certain conditions, they become positively charged in MgCl_2 . Charge reversal of bubbles was observed above $10^{-2} \text{ mol l}^{-1}$ Mg, especially above pH 9. When Al (a trivalent ion) was used, the bubbles were more positively charged until pH 8.2, with a maximum of about +30 mV. These results clearly show the marked effect of aluminium ions on the electrokinetic behaviour of the bubbles, compared to monovalent and divalent metal ions.

Consequently, the zeta potential of bubbles is a function of the type and concentration of metal ion and the pH of the solution. A probable principle that can be used to explain the process of charge reversal would be a combined mechanism, with both specific adsorption of hydroxylated species and formation of a hydroxide precipitate. It may be possible, therefore, to create solution conditions under which bubbles with positive charges can be formed. This leads on to the possibility of removing particles from water by flotation methods where there is a reduced requirement, perhaps even no requirement at all, for the use of a coagulant.

Conclusions

Fundamental characteristics of micro-bubbles in the flotation process (both dissolved air flotation and electroflotation) have been investigated, both theoretically and experimentally. From modelling of the collision efficiency in flotation, it is noted that the characteristics of the bubble, such as the size and zeta potential, are as important as those of the particles. The size of the bubble on DAF is a non-linear function of pressure. The size of bubbles in EF is smaller than those from the DAF process. The zeta potential of bubbles in

the flotation process is dependent on the pH and the method of bubble generation. Under some conditions, we can generate positively charged bubbles.

The results of this study can explain the current practice of design and operation of the DAF process. The importance and the goal of pre-treatment can be suggested in terms of particle size and charge. Through a better understanding of the characteristics of both bubbles and particles, we can either optimize the existing process or be able to develop a new process that utilizes the characteristics of both particles and bubbles.

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