MAIN FACTORS AFFECTING THE SIZE OF HYDROGEN AND OXYGEN BUBBLES PRODUCED IN THE ELECTROFLOTATION PROCESS

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ABSTRACT

Understanding the limits of fine particle flotation is fundamental to achieving a significant and selective separation. Conventional flotation processes are not suitable to treat these particles because of their low collision efficiency. This problem can be overcome by decreasing the bubble size or by increasing the apparent particle size. However it is worth noting that the use of small bubbles or micro bubbles also involves some disadvantages such as their low momentum resulting in a slower process comparing with conventional flotation. Electroflotation is an attractive alternative for treating fine particles with small bubbles less than 100 µm, generated by the electrolysis of water. In this sense, this study assesses the effect of current density and pH on bubble size in a binary electroflotation cell. An increase in the bubble generation rate was reported with an increase in current density. In addition, at acid pH values, the size of oxygen bubbles increased and conversely decreased at basic pH values; this may be due to the electrostatic attraction between the oxygen bubbles and the anode resulting in a greater nucleation time. An opposite trend was observed with the hydrogen bubbles. These results are in agreement with their electrokinetic studies, which reported that at acid conditions the bubble surface may be positively charged for both the hydrogen and the oxygen bubbles. Finally the bubble size was slightly affected by the electrolyte concentration, resulting in smaller diameter bubbles at higher concentrations.

KEYWORDS

Electroflotation, flotation, microbubble, fine particle.
INTRODUCTION

Electroflotation is one of the variants of the flotation process, where the gaseous phase is produced by electrolysis of an aqueous solution, generating oxygen and hydrogen bubbles. These smaller size bubbles allow the treatment of fine particles by increasing the collision efficiency. This process is versatile and competitive in relation to other techniques such as dissolved air flotation and dispersed air flotation because the electroflotation units are smaller, more compact and require less maintenance and less operating cost than other flotation units intended for the treatment of fines (Zouboulis & Matis, 1995). The physical process of gas generation from the electrodes can be divided into three phases: nucleation, growth, and release. The oxygen is formed at the anode (equation 1), while hydrogen is formed at the cathode (equation 2). These gases can be used separately or in combination with air.

\[
\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2(g) + 2e^- \quad \text{E}^\circ = 1.23\text{V} \quad (1)
\]

\[
2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2(g) \quad \text{E}^\circ = 0.83\text{V} \quad (2)
\]

Various factors influence the production and size of the bubbles, such as: current density, electrode material, type and concentration of the electrolyte and pH of the system (Glembotskii, Mamakov & Sorokina, 1973; Ketkar, Mallikarjunan & Venkatachalam, 1991; Chen, 2004; Sarkar, Donne & Evans, 2010, Gupta & Ali, 2013). The size of bubbles produced in the water electrolysis process depends on the type of material and position of the electrode. Studies by Venkatachalam (1992) showed that the kind of cathode material influences the size of the hydrogen bubbles. In addition, the curvature of the surfaces of the electrodes influences the distribution of hydrogen and oxygen bubbles, respectively (Jimenez, Talavera Cañizares & Rodrigo, 2010). Ketkar, Venkatachalam & Mallikarjunan (1988) studied the production of hydrogen bubbles from a stainless steel wire mesh of different diameters and polished plates. Another factor that plays an important role in the determination of the bubble size is the solution pH. Janssen & Hoogland (1973) and Glembotskii et al., (1973) observed that the variation in size of the hydrogen gas bubbles follows a trend opposite to the excess of the hydronium concentration; i.e., hydrogen bubbles are smaller in alkaline conditions in comparison with a neutral or acid medium. On the other hand, oxygen bubbles reach a minimum size in acid conditions and increase as the pH turn basic.

Regarding the current density, Landolt, Acosta, Muller & Tobais, (1970); Sides, (1986); Ben Mansour, Ksentini & Elleuch, 2007 reported an increase in the size of the hydrogen bubbles with the current density. They concluded that there is major bubble coalescence at high current densities. However, studies by Ketkar et al., (1991), refuted that conclusion showing that an increase in current density caused a decrease in the bubble size of hydrogen and oxygen, which is consistent with the nucleation theory. Keeping in view the literature cited above, this work sought to understand how factors such as pH and current density influence bubble size in the electrolysis of water.

EXPERIMENTAL

Equipment and Methodology

The bubble size measurements were conducted at room temperature and atmospheric pressure by use of an Anglo Platinum Bubble sizer (Characterization laboratory - Center for Mineral Technology). Figure 1 shows the experimental setup, which consist of a binary electroflotation cell (a modified...
Partridge-Smith flotation cell) made of glass in order to measure bubble sizes and distributions and two platinum meshes electrodes (anode and cathode). The oxygen bubbles were produced on the anode and the hydrogen bubbles on the cathode electrodes. The area of each electrode mesh was 14.3 cm$^2$ (mesh diameter: 40 mm; wire diameter: 0.02 mm). $\text{Na}_2\text{SO}_4$ solution was used as electrolyte. The desire pH value was adjusted by a controller dosing pump (Model: DLXpH-RX-Cl - Etatron) and finally, with the use of the bubble sizer images of hydrogen and oxygen bubbles were captured and processed by the software ImageJ 1.45.

![Experimental setup for bubble size measurements](image)

Figure 1 – Experimental setup for bubble size measurements. 1) Automatic pH controller. 2;3) Electrolytic cell. 4) Bubble sizer. 5) Magnetic stirrer. 6) pH meter. 7) Peristaltic pump. 8) Voltage source. 9) Multimeter. 10) Cathode. 11) Anode. 12) Electrodes of platinum.

**RESULTS AND DISCUSSION**

**Effect of current density on bubble diameter**

Current density is the most important parameter in the electrolysis process, and hence it is going to be the most significant operational input. Bubble images generated under 5.28 mA/cm$^2$, 6.69 mA/cm$^2$ and 8.31mA/cm$^2$ were obtained for comparison. Figure 2 shows the hydrogen bubble size distribution for the three current densities using platinum as the cathode. Note that an increase in current density caused a decrease in the bubble size, thus for a current density of 5.28 mA/cm$^2$ corresponded to a Sauter mean diameter ($d_{32}$) of 76 µm and for a higher current density of 8.31mA/cm$^2$ the diameter decreased to 56.2 µm. According to the literature, the point of zero charge of hydrogen bubbles is between 2 and 3, then at a pH value of 3 the surface charge of the hydrogen bubbles may be negative favoring the electrostatic repulsion with the cathode and hence increasing the detachment of the bubbles. Another consequence is that the nucleation time will decrease because of the quicker detachment of the hydrogen bubbles resulting in an increase in the diameter. These results are in agreement with the works of Ketkar et al., (1991); Wei, Liang, Yuehua, Yanhong & Ganget, (2011); Liuyi, Yimin, Wenqing, Shexu & Peipei, (2014).
Figure 2 – Effect of current density on production and size distribution of hydrogen bubbles. A) 5.28 mA/cm\(^2\), B) 6.69 mA/cm\(^2\), C) 8.31 mA/cm\(^2\). The pH of the system was 3.

Effect of pH on bubble diameter

Figure 3 shows the hydrogen bubble size behavior at different pH values, with a current density of 5.28 mA/cm\(^2\) and a concentration of 0.05M sodium sulfate. It can be seen that the hydrogen bubbles reach
a \( d_{50} \) of 76.1 \( \mu \text{m} \) in acid medium, which is higher than the diameters achieved in neutral and alkaline conditions. This could be attributed to the electrostatic interaction between the hydrogen bubbles and the cathode, as was proposed by Brandon & Kelsall (1985a). At acidic conditions, the attraction between the positively charged hydrogen bubbles and the negatively charged platinum electrode increases the restraining forces, and hence the nucleation time, producing larger diameter bubbles before buoyancy forces cause bubble departure. On the other hand, in the alkaline range, the bubbles and electrode are negatively charged repelling each other by electrostatic forces, and resulting smaller bubbles. In another study, Brandon & Kelsall (1985b) showed that such bubbles can be charged even under surfactant-free conditions and they possess a point of zero charge between 2 and 3.
Figure 3 – Effect of pH on production and size distribution of hydrogen bubbles. Sodium sulfate: 0.05 M., Current density: 5.28 mA/cm². A) pH: 3, B) pH: 5, C) pH: 7, D) pH: 9, E) pH: 11.
Figure 4 – Effect of pH on production and size distribution of oxygen bubbles. Sodium sulfate: 0.05 M., Current density: 5.28 mA/cm². A) pH: 3, B) pH: 5, C) pH: 7, D) pH: 9, E) pH: 11.
Figure 4 shows the oxygen bubble size behavior at different pH values, with a current density of 5.28 mA/cm² and a concentration of 0.05M sodium sulfate. Note that the trend of the oxygen bubble size was opposite to the behavior of the hydrogen bubbles. In this case, the oxygen bubbles reached a $d_{32}$ around 64 µm in acid medium, which was the minimum value. As the pH increased, the oxygen bubble size reached a $d_{32}$ around 67 µm, at basic conditions. Since the point of zero charge of the oxygen bubble is the pH range between 2 and 4, there may be electrostatic repulsion between the oxygen bubbles and the anode in acid it conditions, decreasing the restraining forces and resulting in smaller bubbles before buoyancy forces cause bubble departure. On the other hand, at alkaline conditions, the electrostatic attraction between the bubbles and the anode favors the formation of larger bubbles.

**Effect of electrolyte concentration on bubble diameter**

Figures 5 and 6 show a profile of the hydrogen and oxygen bubble size as a function of pH at different current densities with two concentrations of sodium sulfate as electrolyte (0.05 to 0.1 M). In both figures it a small decrease in bubble size is observed with increasing concentration of the electrolyte which could be attributed to a slight increase in the rate of bubble generation. This can be attributed to the increased in ionic strength of the system caused by an increase in electrolyte concentration, resulting in a thinner electric double layer of the electrode and the bubbles, a phenomena on known as electric compression. This compression favors the bubble detachment rate, decreasing its diameter.

![Figure 5 – Variation of the hydrogen bubble size as a function of pH for different current densities. A) Sodium sulfate: 0.05M. B) Sodium sulfate: 0.1M.](image-url)
CONCLUSIONS

Studies showed a strong influence of current density, pH and electrolyte concentration on the size of hydrogen and oxygen bubbles. The increase in current density caused a decrease in the bubble size, therefore, for decrease in current density corresponded to an increased in bubble size. This trend was observed for both, the oxygen and hydrogen bubbles. Formation of bubbles during electrolysis of water is significantly influenced by pH. It can be seen that the hydrogen bubbles reach a $d_{32}$ of 76.1 µm in acid medium, which is higher than the diameters achieved in neutral and alkaline conditions. The trend of the oxygen bubble size was opposite the behavior of the hydrogen bubbles, reaching a $d_{32}$ of around 64 µm in acid medium. These results are in agreement with electrokinetic studies, showing that at acid conditions there may be electrostatic attraction between the hydrogen bubbles and the cathode, increasing the nucleation time and therefore resulting in an increase in bubble size. The same principle applied to the oxygen bubbles. However, because the anode is positively charged, there could be electrostatic repulsion and hence a lesser nucleation time, resulting in a smaller bubble. Finally, electrolyte concentration caused a small influence on the hydrogen and oxygen bubble size, as the concentration was increased, the bubble size decreased.

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REFERENCES


