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Generation of positively charged bubbles by dissolved air flotation in aluminum electrolysis solution

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ABSTRACT

The collision efficiency between bubbles and negatively charged particles in a dissolved air flotation (DAF) system can be enhanced by generating positively charged bubbles. In this paper, we aim to generate bubbles that are already positively charged by using a new DAF-Al electrolysis solution system based on the mechanisms for the generation of such bubbles. A microelectrophoresis method was introduced to measure the zeta potential of the bubbles. Upon adding Al electrolysis solutions of varying concentrations into the saturator of a DAF, positively charged bubble was observed, and the zeta potential of the bubbles changed from –35.37 to 28.64 mV, depending on the concentration of Al ions, as follows: The zeta potential of the bubbles increased as the Al-ion concentration increased but did not change once the Al-ion concentration exceeded 15 mg/L in the pressurized water. Compared with the result obtained using an electroflotation system in $AlCl_3$ solution, in the DAF-Al electrolysis solution system, positively charged bubbles can be generated with a lower Al injection concentration.

Keywords: Aluminum electrolysis; Dissolved air flotation; Positively charged bubble; Microelectrophoresis

1. Introduction

The most important factors affecting the collision efficiency of particles and bubbles during the flotation process are the zeta potentials of the bubbles and particles [1]. However, little research has addressed the changes in the zeta potentials of bubbles for use in water treatment processes, such as dissolved air flotation (DAF) [2]. To enhance the collision efficiency between bubbles and particles that are negatively changed in water, positively charged bubbles must be generated. Although several studies [3,4] have investigated the generation of positively charged bubbles, the exact mechanism has not been elucidated. According to Han et al. [5], when bubbles are generated in a solution with added metal ions, such as Al^{3+} and Mg^{2+}, through electroflotation (EF), the surface potentials of the bubbles will become positively charged through a complicated mechanism, such as the interfacial precipitation of hydroxide precipitate by a metal salt and the chemical adsorption of the formed ionic hydroxylated species in a limited pH range. However, the generation of positively charged bubbles by this method has a limitation: both the particles and bubbles generated by EF are charged because of the addition of metal ions to the aqueous solution. Handerson et al. [6] demonstrated the indirect generation of positively charged bubbles by adjusting the zeta potential of the bubbles with surfactants and improving the algae removal efficiency.

The purpose of this study is to generate bubbles that are already positively charged by using a new DAF-Al electrolysis solution system based on the mechanisms for the generation of such bubbles. Thus, the aims of this study are to measure the zeta potentials of bubbles generated by the DAF-Al electrolysis solution, compare them with the values

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measured by other researchers under a variety conditions, and analyze the effects of the injected concentration of Al electrolysis solution on the zeta potentials of the bubbles.

2. Materials and methods

2.1. Measurement of the bubble zeta potential

Currently available measurement methods for the zeta potential of microbubbles can be divided into three types: methods using a spinning cylinder [7,8], methods using the Dorn potential or streaming current methods using the Dorn effect [9], and electrophoresis methods [10–12].Among these methods, the electrophoresis methods has been determined to be the most appropriate way to measure the zeta potential of microbubbles and has continued to evolve [13]. In this study, the measurement device shown in Fig. 1 was constructed to measure the zeta potential of bubbles, with improvements based on microelectrophoresis studies. In particular, the accuracy and ease of measurement were improved through computational image analysis using special software.

2.2. Measurement equipment configuration

The EPM set-up consists of three functional parts: electrophoresis, microscopy, and image analysis systems.

The electrophoresis system consists of an electrophoresis cell (such as that shown in Fig. 2a) and a DC constant-voltage power supply. The electrophoresis cell has a rectangular cross section with internal dimensions of L65 × H15 × W10 mm. A pair of platinum wires (Ø 0.5 mm) is inserted into the center of each side of the cell. The DC constant-voltage power supply is connected to the Pt electrodes to generate an electric field in the cell. Holes (Ø 1 mm) are drilled at the bottom and top of the cell to be used as bubbled water injection and withdrawal in to and out of the cell.

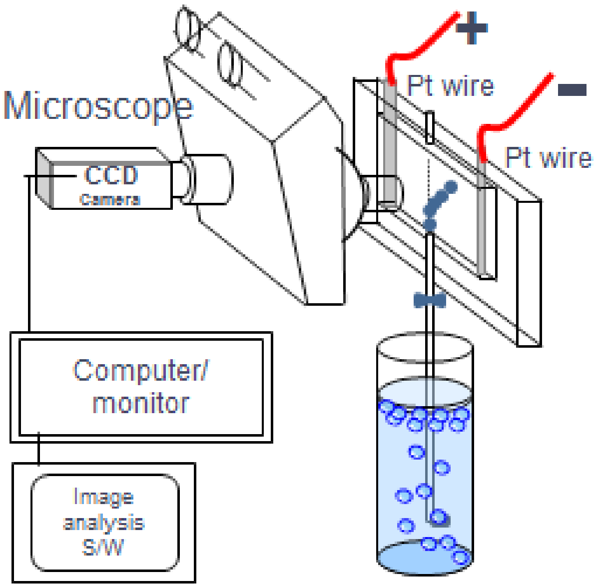


Fig. 1. Schematic diagram of the electrophoresis measurement (EPM) set-up.

In the microscopy system, an optical microscope (Nikon Optiphot, Japan) is positioned horizontally and connected to a charge-coupled device (CCD) camera (Artcam 150III, Sometech). This microscope system is used to observe the rising bubbles.

The image analysis system consists of a computer, monitor, and image analysis software. Computational image analysis using image analysis software (i-solution 5.0, Sometech) is conducted on images captured by the CCD camera, which can record pictures automatically at intervals as short as 1/1000 s.

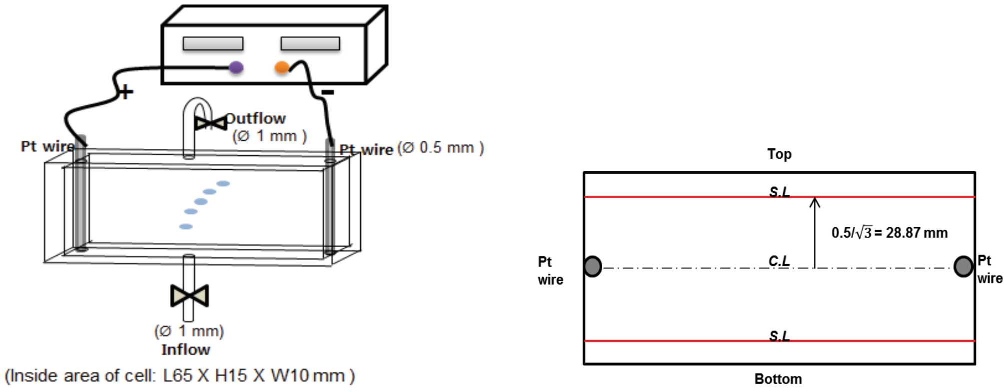
2.3. Measurement procedure

The measurements were conducted using the following protocol. Before an experimental run, the electrophoresis cell was filled with distilled water (58.5-mg/L NaCl) at pH 7. Subsequently, the stationary layer was identified (Fig. 2(b)). During the measurements, the microscope must be focused on the stationary layer. The narrow width of the electrophoresis cell leads to the occurrence of electrical osmosis. Measurements should be taken at the stationary layer where the electro-osmotic velocity is zero to obtain the pure electrophoretic mobility. The stationary layer can be calculated by the following equation: $y = \pm h/\sqrt{3}$ [14], where y is the distance from the centerline of the width, and h is the distance between the vertical cell walls. When the microscope was focused on the stationary layer, microbubbles were injected into the injection hole (Ø 1 mm) in the middle of the bottom of the electrophoresis cell. To eliminate the vortex phenomenon, valves were installed both below and above the cell and were closed after the bubbles were injected into the cell. When the bubbles rose to the stationary layer, an electric field was applied to the cell. While the DC voltage was supplied on both sides of the cell, the rising bubbles could continue to rise and move horizontally in the opposite direction to the electrode surface charge. The movement of the microbubbles was tracked by the microscope, which was oriented perpendicularly, and images were captured with the CCD camera connected to the microscope. The horizontal displacement of bubbles was measured through computational image analysis using image analysis software, which could perform measurements automatically in increments as short as 1/1000 s. Thus, the accuracy and measurement time were improved relative to previous methods. Then, the measured horizontal displacement was used to calculate the zeta potential of the bubbles by substituting it into the Smoluchowski Eq. (1).

$$\varsigma = \frac{\mu V_e \lambda_0 A}{\varepsilon_0 \varepsilon_r i} \tag{1}$$

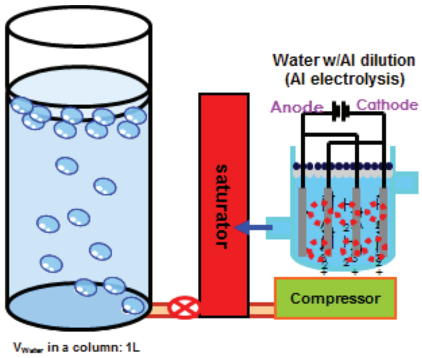
Here, ζ: zeta potential (V); μ: viscosity (0.89×10^{-3} kg m^{-1} s^{-1}) at 25°C; ε_0: permittivity of a vacuum (8.854×10^{-12} kg^{-1} m^{-3} s^4 A^2); ε_r: relative permittivity of a vacuum; i: electric current (A); λ_0: electrical conductivity of the solution (Ω^{-1} m^{-1}); A: cross-sectional area of the cell (m^2); V_e: velocity (m s^{-1}).

The measurements were repeated nine times under the same conditions and following the same procedure.



(a) **(b)**

Fig. 2. Schematic diagram of the electrophoresis cell (a) and the stationary layer (b).



Coagulant type	Al electrolysis
Coagulant dosage	0-, 5-, 10-, 15-, and 30-mg/L poly-Alchloride
Pressure	6 atm
Recycle ratio	30%
NaCl concentration	1.0 mM
pH	7

Fig. 3. Schematic diagram of the DAF-Al electrolysis solution batch system and its operational conditions.

2.4. DAF-Al electrolysis solution system

The batch system of the DAF-Al electrolysis solution system consists of an Aluminum (Al) electrolysis system and a DAF system.

The Al electrolysis system consists of four Al electrodes with dimensions of L7 × W4 × T0.5 cm, a column with dimensions of D20 × H50 cm, and a DC power supply (SEJIN 30V 3A, Korea). Four Al electrodes are set with a 0.5-cm gap in an aqueous solution of NaCl (1.0 mM).The DC power supply is operated in constant-current mode. The eluted Al concentration in the solution is controlled by the current supply time (0–268 s) and can be calculated by Faraday's law (2) [15].

$$w = \frac{itM}{nF} \qquad (2)$$

Here w: quantity of electrode material dissolved (g/M cm^{-2}); i: current density(A cm^{-2}); t: time(s); M: relative molar mass of the electrode (g) n: number of electrons in the oxidation/reduction reaction; F: Faraday's constant (96,500 C mol^{-1}).

The DAF system consists of a saturator (1-L volume), an air compressor, and a column with dimensions of D5 × H50 cm. Various concentrations of Al electrolysis solution (0–30 mg/L) are used to fill the saturator, which is pressurized by the air compressor. Bubbles are generated in a column of 1.0-mM aqueous NaCl (1L) adjusted to pH 7 under the same operational conditions (pressure: 6 atm; recycling ratio: 30%). The bubbles (20–40 mm) generated at that time are used for the measurement of the zeta potential by the EPM set-up.

3. Results and discussion

In this study, bubbles were generated in distilled water containing 1-mM NaCl (pH 7)using the DAF-Al solution system. The DAF-Al solution system presented in Fig. 3 differs from other electro floatation processes. In this case, the electrolysis unit is used to produce Al^{3+} ions via the dissolution of the Al electrode in the NaCl electrolyte [16].Chlorine (Cl) plays an important role in the dissolution of Al^{3+} by pitting from the Al anode. This dissolved Al^{3+} is then pumped into the saturator for the production of positively charged bubbles. The air bubbles generated by a conventional saturator in the absence of an electrolysis unit are negatively charged [5]. The addition of Al^{3+} ions to the saturator via the dissolution of the Al electrode in the electrolysis unit facilitates the formation of positively charged bubbles because of the adsorption of Al^{3+} ions on the negatively charged air bubbles. In addition to the generation of positively charged bubbles, which is difficult in most DAF systems, this system is also able to produce a relatively high amount of these bub-

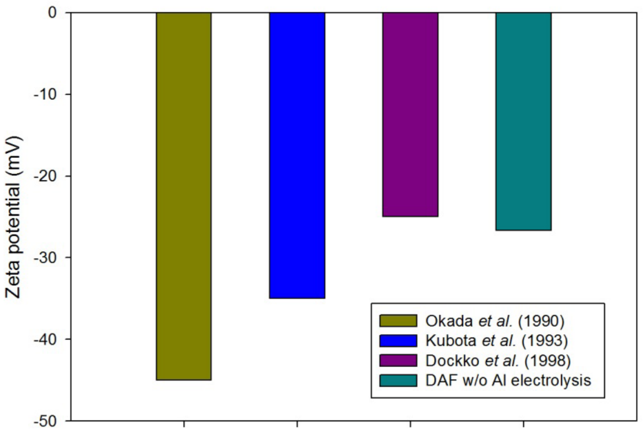


Fig. 4. Comparison of the zeta potential of bubbles generated by DAF without a coagulant.

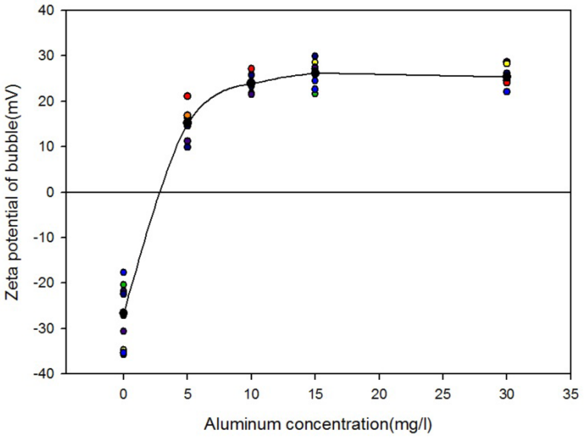


Fig. 5. Zeta potentials of bubbles produced by DAF-Al electrolysis dilution.

bles compared to other electrofloatation systems. Indeed, the design of this system allows it to take advantage of both saturator-based DAF units to generate large quantities of bubbles and an electrolysis unit to dissolve the Al electrode and generate Al^{3+} for the production of positively charged bubbles. The other advantage of this system is its ability to overcome the challenges associated with the direct addition of Al-based chemical coagulants into DAF systems.

The zeta potential of the bubbles was measured at various Al electrolysis solution concentrations (0–30 mg/L). The zeta potential values measured by other researchers under various conditions were analyzed and compared with the results of this study.

Fig. 4 compares the zeta potentials of bubbles measured in this study and those obtained by other researchers. Measuring the zeta potentials of bubbles generated by DAF without a coagulant at pH 7 yielded values of approximately –50 mV [11], –35 mV [12], and –25 mV [13]. Comparing the zeta potentials of bubbles generated in the DAF-Al electrolysis solution system without Al electrolysis to the other referenced values revealed that the values obtained here were similar to those reported in Dockko's most recent research. This supports the fact that the bubbles produced by the proposed system in the absence of electrolysis are negatively charged, consistent with the results of other researchers.

When the electrolysis unit was used, the charge of the bubbles gradually increased as the concentration of Al^{3+} dissolved in the system was increased by applying different voltages. Fig. 5 shows that the zeta potential of the bubbles changed from –35.37 to 28.64 mV as the Al-ion concentration changed. Upon the injection of the Al electrolysis solution into the DAF saturator, the bubbles became positively charged. The generation of positively charged bubbles via Al electrolysis may follow a mechanism similar to that described in [5]. However, in this case, this phenomenon is attributable to the precipitation of poly-Al chloride on the bubble surfaces at neutral pH (pH 7).The zeta potential increased as the Al-ion concentration increased but remained constant once the Al-ion concentration exceeded 15 mg/L in the pressurized water.

In this research,the zeta potential measurements of bubbles in aqueous solution were similar to those obtained using Al ions produced via EF. Similarly, in this study, we also investigated the possibility of generating positively charged bubbles by the DAF-Al electrolysis solution system [5]. In the experiment, positively charged bubbles were observed when the Al concentration exceeded 5 mg/L in the pressurized water. However, when the recycle ratio was 30%, the required Al concentration in the entire aqueous solution was decreased to 1.15 mg/L. Comparing the bubble charges shown in Fig. 6 revealed that the possibility of generating positively charged bubbles at lower Al concentrations is greater in the DAF-Al electrolysis solution system than in the EF system using $AlCl_3$ solution, as reported in [5].

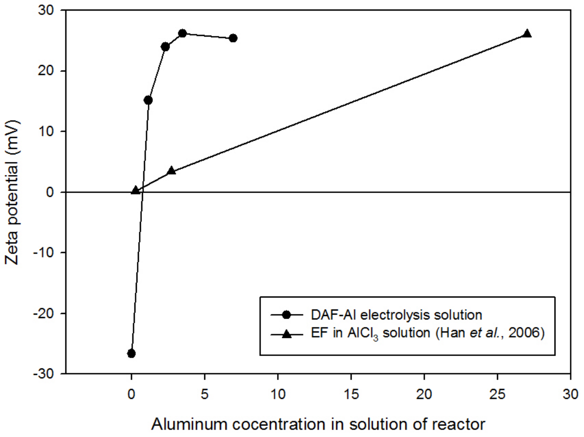


Fig. 6. Comparison of the effect of the Al concentration on bubbles produced by EF in $AlCl_3$ solution and DAF-Al electrolysis solution.

4. Conclusions

In this study, positively charged bubbles were generated by using the DAF-Al electrolysis solution system. To confirm the production of positively charged bubbles, an EPM set-up that was improved compared to existing measuring devices, was used to measure the zeta potential of the bubbles. The results obtained with this device were similar to those reported by other researchers. The bubbles were generated in an aqueous solution at pH 7 using DAF via the injection of Al electrolysis solution from the electrolysis process in pressurized water. The zeta potential of the resulting bubbles was measured.

The results showed that positively charged bubbles were generated with a very small concentration of metal ions (5 mg/L). When the typical recycle ratio was considered to be 10%, the 5-mg/L concentration in pressurized water corresponded to a concentration of 0.5 mg/L in the reactor column. In addition, the EPM results obtained for bubbles prepared with different Al concentrations in pressurized water confirmed that the zeta potential of the bubbles can be changed by controlling the injected Al concentration. Therefore, using this new generation system (i.e., the DAF-Al electrolysis solution system), which is based on the mechanism of generating positively charged bubbles through the adsorption of trivalent Al ions, positively charged bubbles can be produced. This is achieved by injecting a lower Al concentration compared to that required in the EF system with $AlCl_3$ solution. Furthermore, the Al^{3+} concentration in the pressurized water can be easily controlled by varying the voltage of the electrolysis system.

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