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Separation between silicon and aluminum powders
contained within pulverized scraped silicon-based waste
solar cells by flotation method

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Abstract:

There are few study examples on the separation of metals by floating method. In this study, separation of silicon and aluminum, which are the main components of silicon-based solar cell module, was carried out by floating method in order to purify silicon from waste solar cell module. The selection of surfactant, control of electric charge, wettability of the solid particles, surface tensions and bubble surface area are important for separation of solids by floating method. Sodium dodecyl sulfate (SDS) can increase the hydrophobicity of aluminum powder due to the difference of surface potential between silicon and aluminum. SDS behaves as a collector of aluminum as well as a frothing agent to decrease the bubble size. At a SDS concentration of 2 g/L and sample dipping time of 10 min and, 80.1 mass% of aluminum was floated and separated, and the sedimentary silicon reached a purity of 90.7 % from a mixture of 50 mass% aluminum and 50 mass% silicon. Finally, at a pH value of 7.0, SDS concentration between 1.0 and 2.5 g/L and air flow rate of 2.5 L/min (STP) were suitable experimental conditions to purify silicon from a mixture of silicon and aluminum by flotation separation method.

Key words:

Flotation, Floating separation, Waste solar cell module, Silicon, Sodium dodecyl sulfate

“Main text”

1. Introduction

Photovoltaic power is one of the most promising renewable energy due to sustainability and cleanness. The world capacity of photovoltaic installation has been dramatically escalated since the 1970s and amounted to 402.5 GW in 2017 [1]. There are variety kinds of solar cells [2], and the most prevailing crystalline silicon solar cell modules are said to have a life-span of only 20 to 30 years and estimated to be sharply scrapped hereafter [3,4]. They contain valuables such as silver, copper, silicon and tin in addition to lead of hazardous element [5]. The recycling of valuables and proper disposal of harmful agents are technically desired from a standpoint of sustainability [6,7].

The WEEE (Waste Electrical and Electronic Equipment) directive on EU (European Union) was revised in 2012 so as to make recycling and reusing of the waste solar cell modules compulsory [8] and a guideline on recycling of the waste photovoltaic facility was announced from the Japanese government in 2016 [3]. According to these policies, many studies on the recycling process of the solar cell modules have been done by means of Ethylene Vinyl Acetate (EVA) dissolution using organic solvent [9] and chemical etching with acid or alkali solution [10-15]. However,

these approaches are quite difficult to handle a large amount of waste solar cell modules because of a volume of waste liquid treatment.

The pulverized powder of crystalline solar cells was focused in this study. Toho Kasei Co., Ltd, reported this powder in the project entitled “Development project for photovoltaic (PV) recycling technology” [16] carried out under New Energy and Industrial Technology Development Organization (NEDO) in Japan. Figure 1 shows the schematic recycling flow of waste photovoltaic modules described in terms of the project [16]. After separating frame, glass and cells from the module, the cell pieces were pulverized by a grinding process. About 7 mass % of EVA and about 93 mass % of inorganic element were involved in the cell powder. The typical chemical composition of the inorganic element was as follows: silicon of 87.5 mass%, aluminum of 9.5 mass%, silver of 1.2 mass%, copper of 0.5 mass%, tin of 0.8 mass%, lead of 0.3 mass%. Silicon powder and the other valuable metal products are obtained from purifying pulverized cells below a given impurity concentration by flotation separation and/or chemical etching [7]. In other words, a single or multiple flotations is selected and sequential process of flotation and chemical etching is occasionally required for a purification target.

As a new approach, we tried floating separation method to collect a high purity of

silicon. It has put into practical use for concentrating valuable components in a raw mineral for a long period [17-21]. Recently, the recycling of waste plastics [22-25], water treatment [26] and removal of fly ash [27] became the target for the floating separation.

In this study, the direct separation between silicon and aluminum contained in large amounts in silicon-based waste solar cell powders was investigated by the flotation method. It needs use of multiple of flotation reagents as follows: a collector to adsorb some materials selectively, a frother to control bubble size, a regulator for pH adjustment etc. The selection of the collector is especially important because it affects the separation target selectively and changes the surface property, that is, the collector has polar and non-polar groups in a molecule and the polarity causes the hydrophobicity of the target surface [28]. There are many researches [29] on the collector. For example, the recoveries of precious metals from the polishing process of dental alloy [30,31] and heavy metals from incinerated automobile shredder residuals [32]. However, the collector affects metal oxide in the former and sulfurization on the metal surface in the latter and the study of the collector which behaves directly on the metal surface was not carried out. After selecting the proper collector, the suitable flotation conditions must be found by changing controllable factors.

Thus, the objectives of this study are to select a preferable collector to separate between silicon and aluminum, and to determine the optimal purification condition of silicon by examining the effects of floating time, pH, collector concentration, dipping time of sample in a collector solution before the separation experiment, contact angle of sample, air flowrate and mass ratio of silicon to aluminum.

2. Experimental

2.1 Sample preparation

The mixture of aluminum (Fujifilm Wako Pure Chemical Corporation) and silicon (Junsei Chemical Co., Ltd.) were used for the experiment. The purities of aluminum and silicon were 99.0 and 99.5 %, respectively. The original flake silicon was pulverized by a grinder mill (Osaka Chemical Co., Ltd, WB-1). Both powders were screened between 100 – 212 μm , pickled with 0.1 M nitrate acid and cleaned with ion-exchanged water.

Sodium dodecyl sulfate (SDS, FUJIFILM Wako Pure Chemical Corporation) known as an anionic surfactant and dodecyltrimethylammonium bromide (DTAB, Tokyo Chemical Industry Co., Ltd.) recognized as a cationic surfactant were examined as a collector so as to compare the flotation ability between them. The purities of SDS and DTAB were 98.5 and 98.0 %, respectively. Ion-exchanged water was used as a

solvent for floating separation method.

2.2 Preparation of sample-contained solution

A given amount of collector was dissolved with 500 mL of ion-exchanged water and the pH value was adjusted by 0.1 M NaOH and HCl. Total 5.0 g of sample was mixed with a given mass ratio, dipped in the prepared collector solution of 250 mL and kept for a given hour in the room temperature. Another 250 mL of collector solution was used as the compensating liquid during the flotation experiment as shown in the next section.

2.3 Experimental method of floating separation

The schematic diagram of an experimental apparatus is shown in Fig. 2 The glass cylinder of 0.08 m in inner diameter and 0.320 m in height was used as a separation part. A porous glass filter was set at a lower part.

The suspending solution of 5.0 g sample and 250 mL ion-exchanged solution after a given time of dipping was put into the vessel and air was blown through the porous filter. The part of floating substance (Al + Si) adhered to the air bubbles and it was removed from the system as the froth (air and floating substance). To compensate the

froth, another SDS solution was supplied from the upper part of the vessel as shown in Fig. 2.

After the experiment, the froth and residual were collected respectively, and washed by ion-exchanged water and dried in the room temperature. Each mass was measured before and after the aluminum dissolution by HCl solution. The flotation recovery ratio, $R_{i,j}$ [%], and purity, $P_{i,j}$ [%], of i -component (= silicon or aluminum) and j -part (= float or sediment) in mixed sample was calculated from the following equations.

$$R_{i,j} = \frac{M_{i,j}}{M_{Si,0} + M_{Al,0}} \quad (1)$$

$$P_{i,j} = \frac{M_{i,j}}{M_{Si,j} + M_{Al,j}} \quad (2)$$

Here, $M_{Si,0}$ and $M_{Al,0}$ are the initial mass of silicon and aluminum, respectively, and $M_{i,j}$ is the mass of i -component and j -part after separation.

The experimental conditions are shown in Table 1. Concentrations of SDS, C_{STB} , and DTAB, C_{DTAB} , were varied to 0.1 – 4.0 and fixed to 2.5 [g/L], respectively, and pH was between 2 and 12. The sample dipping time, t_{dip} , in collector solution before the floating separation treatment was changed to 10, 60 and 120 min, whereas the floating separation time, t_{flo} , 2 – 20 min. The mass ratio of silicon to aluminum, $M_{Si,0}/M_{Al,0}$, was varied to 9/1, 7/3 and 5/5 and air flowrate, mass of sample, Q_{air} , 1.0, 2.5 and 4.0 L/min

(STP) and mass of sample, M_{sam} , was fixed to 5 g. Here, the underlined figures such as pH of 6.8, t_{dip} of 10 min, t_{flo} of 5 min, $M_{\text{Si},0}/M_{\text{Al},0}$ of 5/5, M_{sam} of 5.0 g, and Q_{air} of 2.5 L/min (STP) indicate the standard conditions and they were kept constant except that the effect of each factor is examined.

2.4 Characterization test

The surface electric charge of sample was evaluated by a device for the measurement of ζ potential (Malvern Panalytical, Zetasizer Nano ZS). The wettability of metal piece (1 cm x 1 cm) was used in place of metal powder and studied by a contact angle measuring device (Kyowa Interface Science Co., Ltd, Drop Master 300).

3. Results and discussion

3.1 Selection of collector

The selected operating collector needs to be used to separate each material by flotation method. In this study, ionic collectors were chosen to change the surface properties of metal sample. They lead to an efficient separation with a single agent as they also take a role as a frothing agent.

When the physical adsorption by electrostatic interaction is used to separate one

material from another by flotation method, the ionic collector has to be selected on the condition that each material has the opposite electric charge [33]. The relationship between ζ potential and pH for silicon or aluminum powder is shown in Fig. 3. There was neither DTAB nor SDS in the solution. The ζ potential of silicon powder indicated the negative value in the total pH range, whereas that of aluminum became positive in the acid and slightly negative in the neutral and alkaline range. That indicates either a cationic DTAB or an anionic SDS collector can separate aluminum and silicon.

The effect of the collector on the separation of aluminum and silicon was compared between cationic DTAB and anionic SDS solutions as shown in Fig. 4. DTAB concentration was 2.5 g/l (8.1×10^{-3} M) and SDS 2.0 g/L (7.0×10^{-3} M), that is, both had similar molar concentration values. In the case of DTAB, silicon floated on the surface and its purity was 99 % from Fig. 4 (b), but the silicon recovery was only 38 % from Fig. 4 (a). On the other hand, SDS floated aluminum on the surface and the silicon recovery ratio and the silicon purity at the non-floating zone reached about 98 and 90 %, respectively. From these results, the anionic SDS solution was examined further to maximize the separation recovery and purity of silicon at the non-floating zone.

3.2 Effect of operating factors on floating separation

3.2.1 Change in floating ratio with time

The temporal change in flotation ratio of the sample without silicon is shown in Fig. 5. The flotation recovery ratio became almost constant after 5 min. Thus, each experiment was carried out for 5 min of floating separation in the latter section.

3.2.2 Effects of pH and surface potential

The surfactant concentration as a collector and surface charge characteristics affect the separation conditions of different kind of material. As seen in Fig. 3, the pH value changed the ζ potential of the powder. In this section, the effect of pH on the separation behavior of the sample was explained under the conditions of SDS concentration of 1.5 g/L, Si/Al mass ratio of 5/5 and air flowrate of 2.5 L/min (STP). The relationships between flotation recovery ratio, purities of silicon and aluminum, and pH value are shown in Fig. 6. Silicon almost remained on the bottom at any pH ranges as indicated in Fig. 6 (a). An excess of 80 % of aluminum was floated and recovered until the pH 9 and then decreased with the increasing pH. The hydrophobic property of aluminum decreases with the increase in pH due to the larger negative charge on the surface as seen in Fig. 3 and less extraction of SDS on the surface. This caused the decrease in the flotation recover ratio of aluminum. Thus, the larger negative charge or dissolution of the aluminum surface is considered to be the reason

of lower floating behavior at the high pH value. The subsequent experiment was carried out in the neutral pH range.

3.2.3 Effects of SDS concentration and contact angle

The relationship between the separation behavior of silicon and aluminum, and SDS concentration is shown in Fig. 7. The sample dipping time in SDS solution was 10 min. As recognized in Fig. 7 (a), silicon powders almost accumulated on the bottom regardless of SDS concentration, whereas aluminum floating ratio became a lower level until SDS concentration of 0.5 g/L, indicated about 80% between 1.0 and 2.5 g/L and decreased gradually 2.5 g/L. The maximum silicon purity at the non-floating region reached 90 % at the SDS concentration of 2.0 g/L as seen in Fig. 7 (b) and the aluminum purity at the floating zone was kept above 95.8 % for all SDS concentrations. Figure 8 shows the relationship between the separation behavior of silicon and aluminum, and SDS concentration. The sample dipping time in SDS solution was 120 min. The floating behavior had the almost same tendency as that shown in Fig. 7. These results denote that the aluminum surface was hydrophobized before 10 min of the sample dipping time in SDS solution.

The contact angles of polished pieces of silicon and aluminum (1cm x 1 cm) instead of powders were measured to examine the change in wettability with dipping

time in SDS solution. The temporal change in the contact angle is shown in Fig. 9. The initial contact angles of silicon and aluminum without dipping in SDS solution became 55 and 65 deg, respectively, that is, hydrophilic nature. After 10 min of sample dipping, the contact angle of silicon decreased to about 47 deg and then kept constant, whereas that of aluminum increased to about 100 deg at 10 min of dipping and continued to slightly increase. The aluminum piece changed to hydrophobic property and silicon heightened hydrophilic one. Next, the contact angle of silicon and aluminum pieces with surface asperity was measured after 10 min dipping into SDS solution. Figure 11 shows the contact angle and SDS concentration. The initial contact angles of the surface roughness were about 40 deg in silicon (Fig. 10 (a)) and about 30 deg in aluminum (Fig. 10 (b)). The silicon piece had hydrophilicity property for the different SDS concentration, whereas the hydrophilicity of aluminum changed from hydrophilic to hydrophobic property by adding SDS. Both contact angles of silicon and aluminum after dipping in SDS solution decreased with the increase in SDS concentration, which is going to be explained later. Compared with the contact angles under SDS concentration of 2.0 g/L and dipping time of 10 min in Figs. 9 and 10, the contact angle of polished silicon was slightly larger than that of silicon with surface roughness, however, the contact angle of aluminum was almost independent from the surface

roughness.

The relationship between ζ potential of silicon or aluminum powder and SDS concentration is shown in Fig. 11. Here, the sample dipping time in SDS solution and pH value were kept to 10 min and 8.0, respectively. The ζ potential of aluminum decreased to the negative range with the increasing SDS concentration.

In previous studies on the adsorption of ionic surfactant on the powder [29,34,35], Somasundaran proposed a reverse orientation model. The low concentration of anionic surfactant ion adsorbs on the target with positive surface charge electrostatically (a), and hemimicelle is formed with an increase in the surfactant concentration and the hydrophilic group with negative charge adsorbs on the target (b). In this case, the target behaves as a hydrophobic group because the hydrophobic hydrocarbon chain of the surfactant faces the liquid side. The further increase in anionic surfactant begins to form patches of surfactant bilayers called admicell whose hydrophilic group faces the liquid due to the adsorption between hydrocarbon chains by action of mutual hydrophobic property (c). The admicell generation occurs at the critical micelle concentration (CMC) of the surfactant [36] and the CMC value of SDS was between 1.7 and 2.3 g/L [37]. Above the CMC, the separation target increases the hydrophilic group and decreases contact angle. These explanations were schematically shown in Fig. 12. Here, (a), (b)

and (c) correspond to the symbol in the above statements. The decrease in ζ potential of Fig. 11 agreed well with Fig. 12, although there was no reduction of contact angle (Fig. 10) at SDS concentration of 4.0 g/L in (c) range. The increase in SDS concentration above 2.0 g/L decreased the flotation recovery ratio of aluminum in Figs. 7 and 8 and it was also explained by this discussion.

On the other hand, the floating ratio in Figs. 7 and 8 became smaller at the lower SDS concentration below 0.5 g/L in spite of the fact that aluminum hydrophobicity indicated the higher value. Thus, the role of SDS as a frother was examined by observing the shifting of bubble size while changing the SDS concentration. The video camera (SONY, HDR-CX700) was used and the mean diameter of number of 10 bubbles was calculated when air flowrate, pH and amount of SDS solution were fixed to 2.5 L/min (STP), 6.8 and 250 mL, respectively. The relationship between the mean bubble diameter and SDS concentration is shown in Fig. 13. The bubble diameter decreased with the increasing SDS concentration, especially until 1 g/L of SDS concentration due to the reduction of surface tension. As the larger bubble diameter decreases the total surface area of bubbles, the floating ratio of aluminum became small at the lower SDS concentrations.

3.2.4 Effect of air flowrate and bubble surface area

The effects of air flowrate and SDS concentration on the flotation separation behavior are shown in Fig. 14. The flotation recovery ratio of aluminum and sedimentary silicon purity of sediment increased with the increase of air flowrate and reached the highest values at SDS concentration of 2.0 g/L for all air flowrate. However, compared with air flowrate between 2.5 and 4.0 L/min (STP), their increases became moderate or plateau, which meant 2.5 L/min (STP) was sufficient for the separation between silicon and aluminum. Silicon did not float for any air flowrate and SDS concentration ranges.

3.2.5 Effect of mass ratio of silicon to aluminum

The relationship between the flotation separation behavior and mass ratio of silicon to aluminum is shown in Fig. 15. Air flowrate and pH were fixed to 2.5 L/min (STP) and 6.8, respectively, and SDS concentration was varied to 0.5, 2.0 and 4.0 g/L. For each SDS concentration, aluminum flotation ratio was roughly decreased with the increase in mass ratio of silicon to aluminum, whereas silicon was almost kept sedimented regardless of SDS concentration from Fig. 15 (a). On the other hand, the sedimentary silicon purity promoted with increasing silicon ratio to aluminum as seen in Fig. 15 (b) due to the decrease in the initial aluminum amount. Both of aluminum recovery ratio and silicon purity at SDS concentration of 2.0 g/L indicated largest values

between 0.5, 2.0 and 4.0 g/L as well as Fig. 14.

3.3 Relationship between controllable factors and controlled properties for separation between silicon and aluminum

According to Sections 3.1 to 3.2, the relationship between controllable factors and controlled properties for the separation between silicon and aluminum by flotation method is schematically summarized in Fig. 16. There were pH, SDS concentration and air flowrate as the controllable factors, whereas electric charge, wettability, surface tension and surface area of bubbles as the controlled properties. pH made the electric charge positive or negative, SDS concentration made the wettability hydrophilic or hydrophobic as a collector and reduced the surface tension as a frother, and air flowrate controlled the surface area of bubbles as well as the surface tension. Powder size also affects the flotation efficiency as a controllable factor, although it was kept constant in this study. The effect of powder size will be investigated in the future.

Higher separation efficiency between silicon and aluminum was caused by the difference of the electric charge and wettability, smaller surface tension and larger surface area of bubbles. In this study, the pH value of about 7.0 from Fig. 3, SDS concentration between 1.0 and 2.5 g/L from Figs. 7, 8 and air flow rate of 2.5 L/min

(STP) from Fig. 14 became preferable conditions to purify silicon from the mixture of silicon and aluminum by flotation separation method.

The separation between silicon and aluminum mainly composed in silicon-based solar cells was a target in this study. The next step is the separation of silicon from the other grinded elements in solar cells. When the other elements have a different charge of ζ potential from silicon as shown in Fig. 3, one or multiple flotation processes enhance the purity of silicon. However, the separation of the elements with the same ζ potential charge as silicon is difficult and the other purification like a chemical etching [7] must be used. In this situation, the sequential process of flotation and chemical etching is considered to be effective in terms of low-cost and more eco-friendly recycling process.

The above purification process does not guarantee the reusing for solar-grade silicon [38] due to a small amount of metal contamination. It seems to be safe to use this separated silicon as a starting material of a practically used purification process for solar grade silicon.

4. Conclusions

The flotation separation between aluminum and silicon which contained in the waste crystalline solar silicon cells was examined by semi-batch typed experiments.

- 1) Sodium dodecyl sulfate (SDS) permitted to hydrophobize only aluminum powder due to the difference of surface potential between silicon and aluminum.
- 2) SDS behaved as a collector of aluminum and a frothing agent and made it possible to purify silicon.
- 3) At sample dipping time in SDS solution for 10 min and SDS concentration of 2.0 g/L, 80.1 mass% of aluminum was floated and eliminated from the system, and sedimentary silicon purity reached 90.7 %.
- 4) The pH value of about 7.0, SDS concentration between 1.0 and 2.5 g/L and air flow rate of 2.5 L/min (STP) became preferable conditions to purify silicon from the mixture of silicon and aluminum by flotation separation method.

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Caption List

Fig. 1 Schematic recycling flow of waste PV modules.

Fig. 2 Schematic diagram of flotation equipment.

Fig. 3 Relationship between ζ potential and pH for aluminum and silicon powder.

Fig. 4 Comparison of separation behaviors of silicon and aluminum between collectors of DTAB and SDS..

Fig. 5 Temporal change in flotation ratio of aluminum powder.

Fig. 6 Effect of pH value on flotation recovery ratio and purity of silicon and aluminum.

Fig. 7 Effect of SDS concentration on separation behavior of silicon and aluminum at sample dipping time of 10 min.

Fig. 8 Effect of SDS concentration on separation behavior of silicon and aluminum at sample dipping time of 120 min.

Fig. 9 Relationship between contact angle of silicon and aluminum pieces and dipping time in SDS solution.

Fig. 10 Effect of SDS concentration on contact angles of silicon and aluminum pieces at dipping time of 10 min.

Fig. 11 Relationship between ζ potential of silicon and aluminum powders and SDS concentration at dipping time of 10 min in SDS solution.

Fig. 12 Schematic illustration of SDS adsorption on aluminum surface.

Fig. 13 Relationship between the mean bubble diameter and SDS concentration at air flowrate of 2.5 L/min (STP).

Fig. 14 Effects of air flowrate and SDS concentration on separation behavior of silicon and aluminum.

Fig. 15 Effects of mass ratio of silicon to aluminum and SDS concentration on flotation separation behavior.

Fig. 16 Schematic diagram of relationship between controllable factors and controlled properties for separation floating method of silicon and aluminum.

Table 1 Experimental conditions

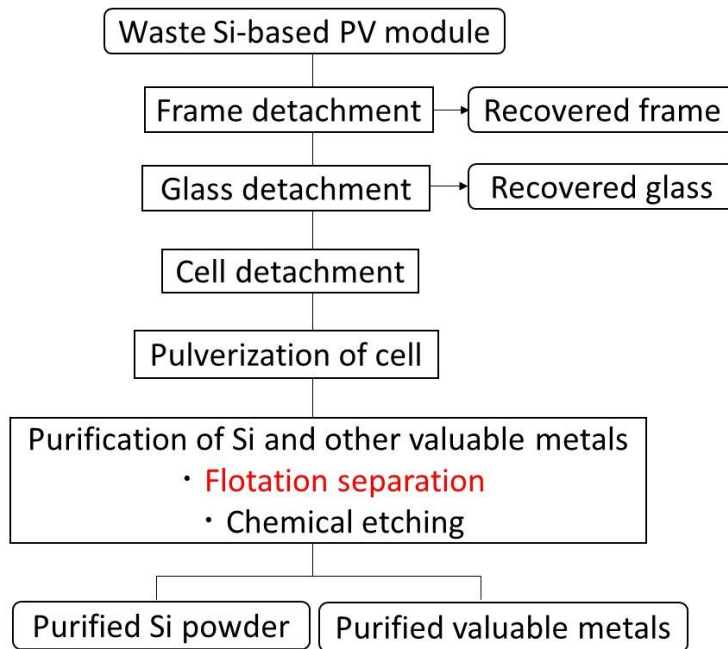


Fig. 1 Schematic recycling flow of waste PV modules.

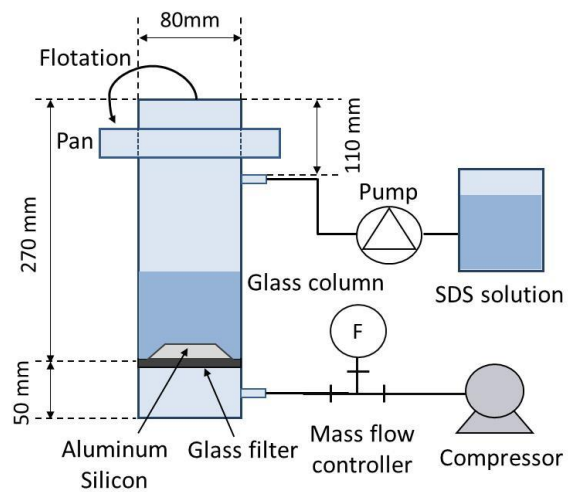


Fig. 2 Schematic diagram of flotation equipment.

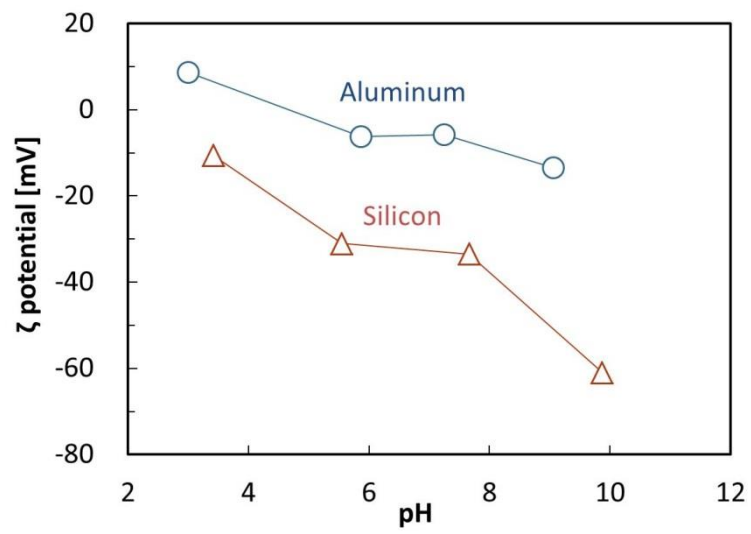


Fig. 3 Relationship between ζ potential and pH for aluminum and silicon powder.

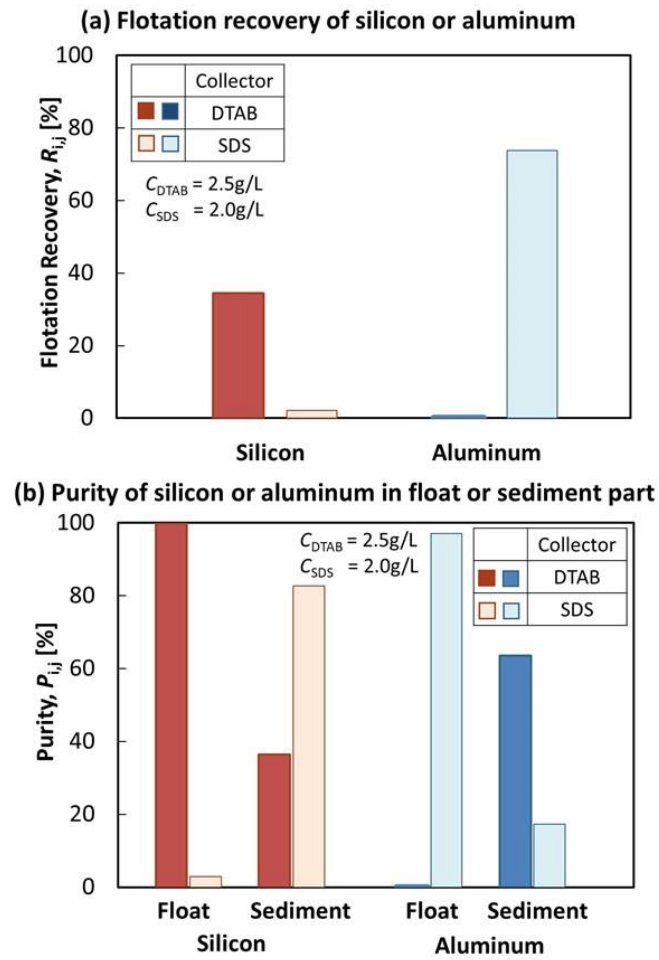


Fig. 4 Comparison of separation behaviors of silicon and aluminum between collectors of DTAB and SDS.

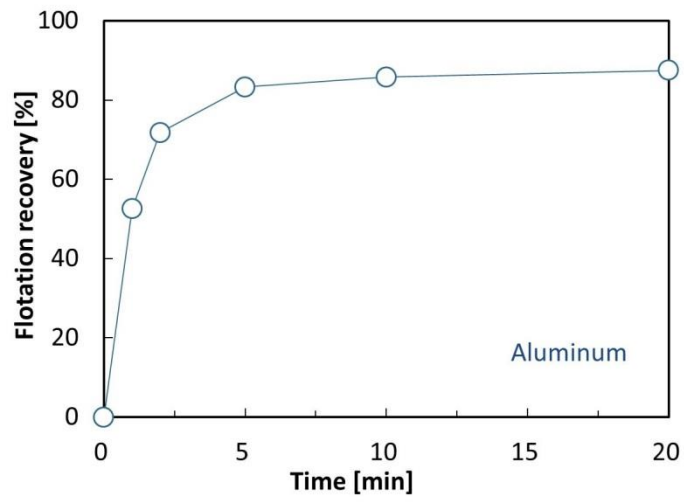


Fig. 5 Temporal change in flotation ratio of aluminum powder.

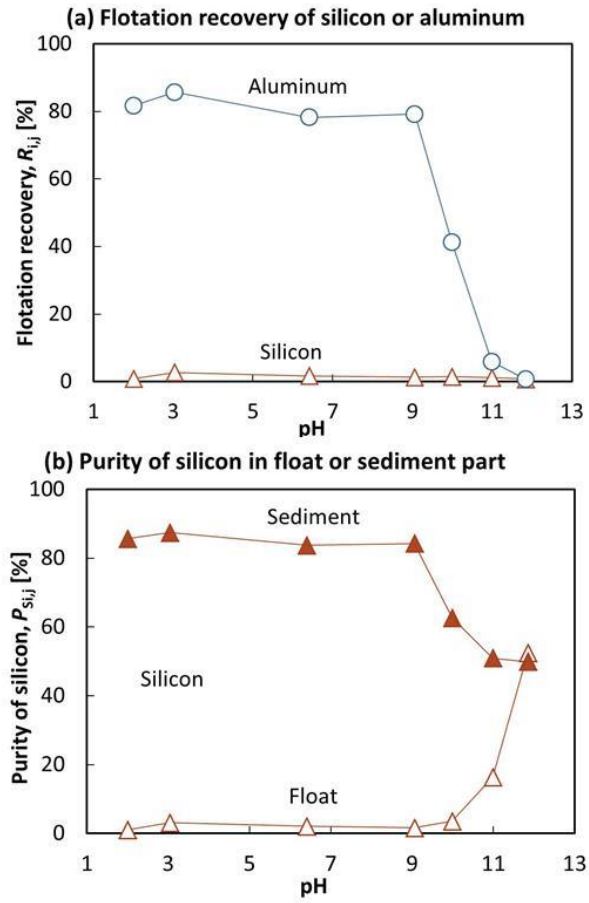


Fig. 6 Effect of pH value on flotation recovery ratio and purity of silicon and aluminum.

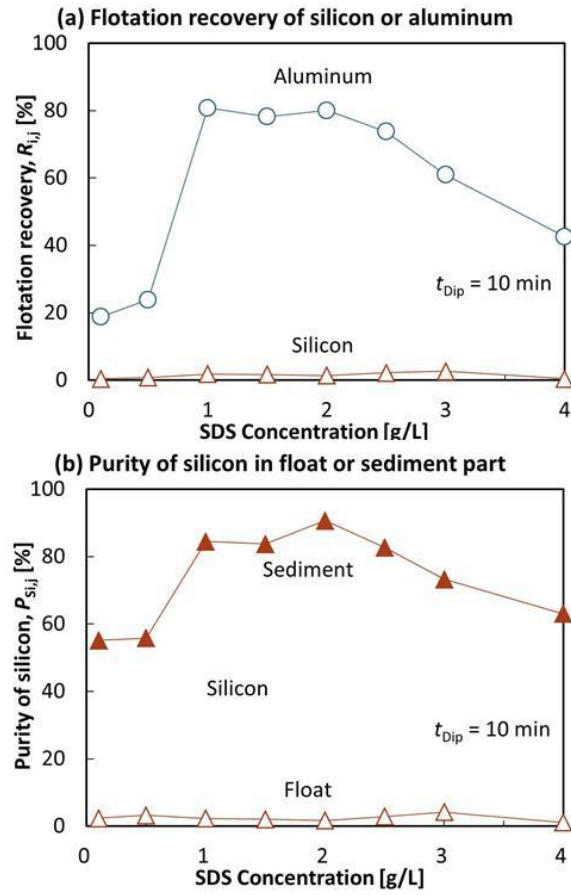


Fig. 7 Effect of SDS concentration on separation behavior of silicon and aluminum at sample dipping time of 10 min.

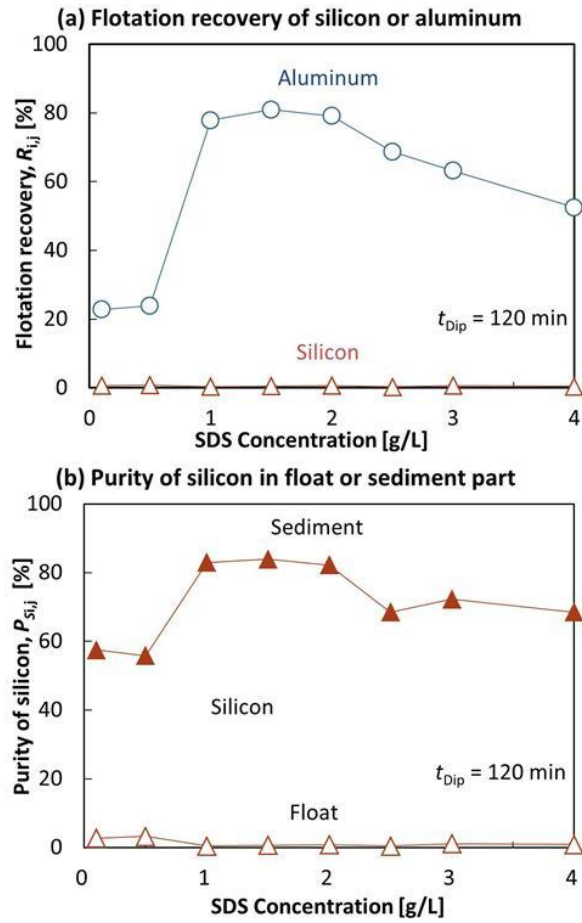


Fig. 8 Effect of SDS concentration on separation behavior of silicon and aluminum at sample dipping time of 120 min.

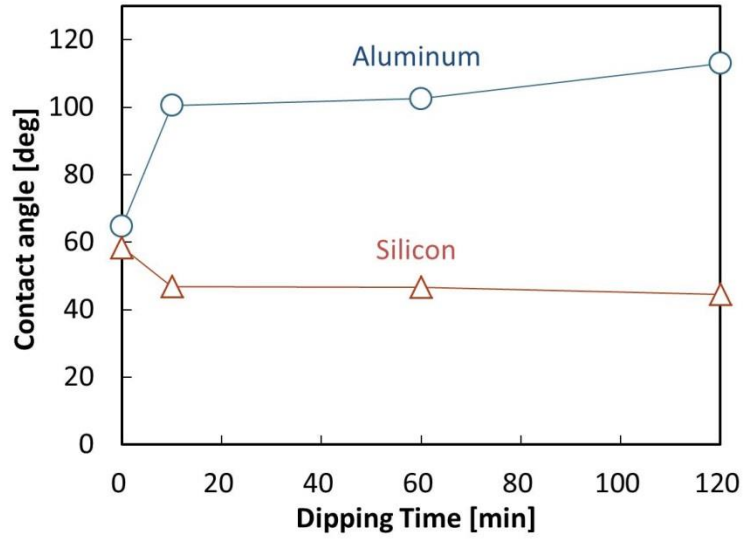


Fig. 9 Relationship between contact angle of silicon and aluminum pieces and dipping time in SDS solution.

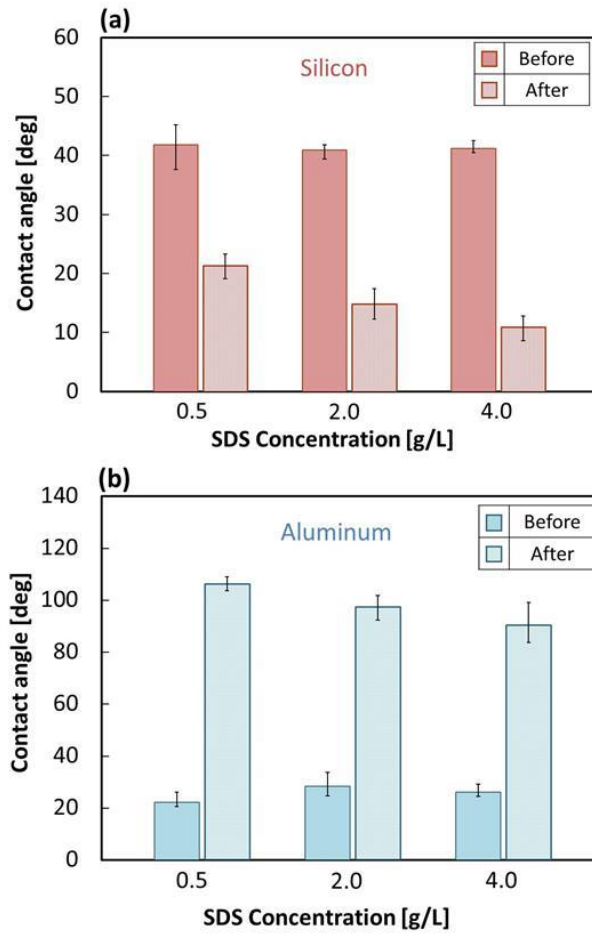


Fig. 10 Effect of SDS concentration on contact angles of silicon and aluminum pieces at dipping time of 10 min.

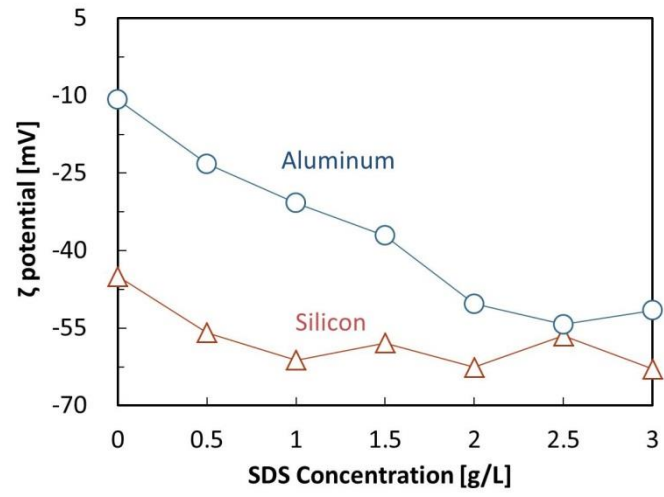


Fig. 11 Relationship between ζ potential of silicon and aluminum powders and SDS concentration at dipping time of 10 min in SDS solution.

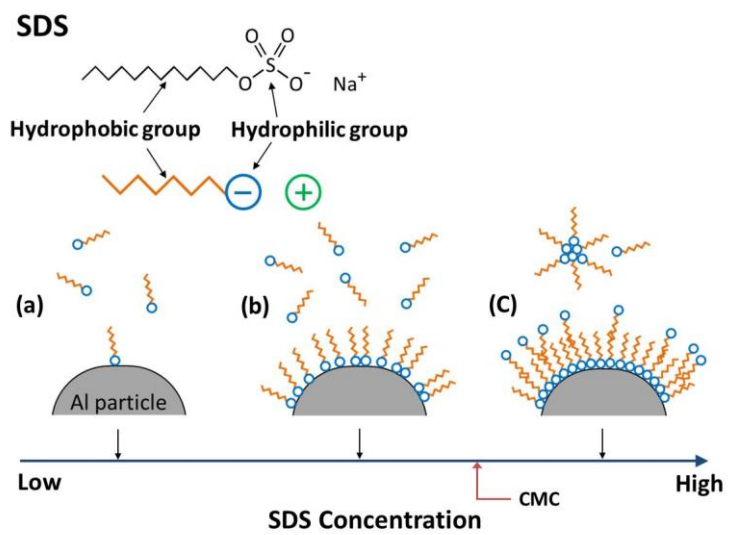


Fig. 12 Schematic illustration of SDS adsorption on aluminum surface.

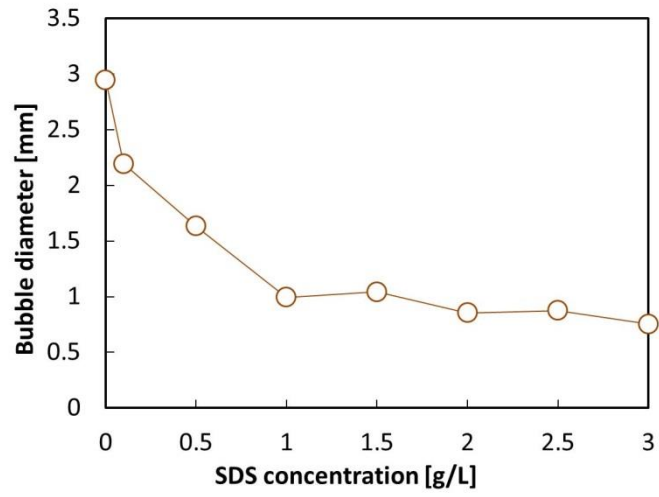


Fig. 13 Relationship between the mean bubble diameter and SDS concentration at air flowrate of 2.5 L/min (STP).

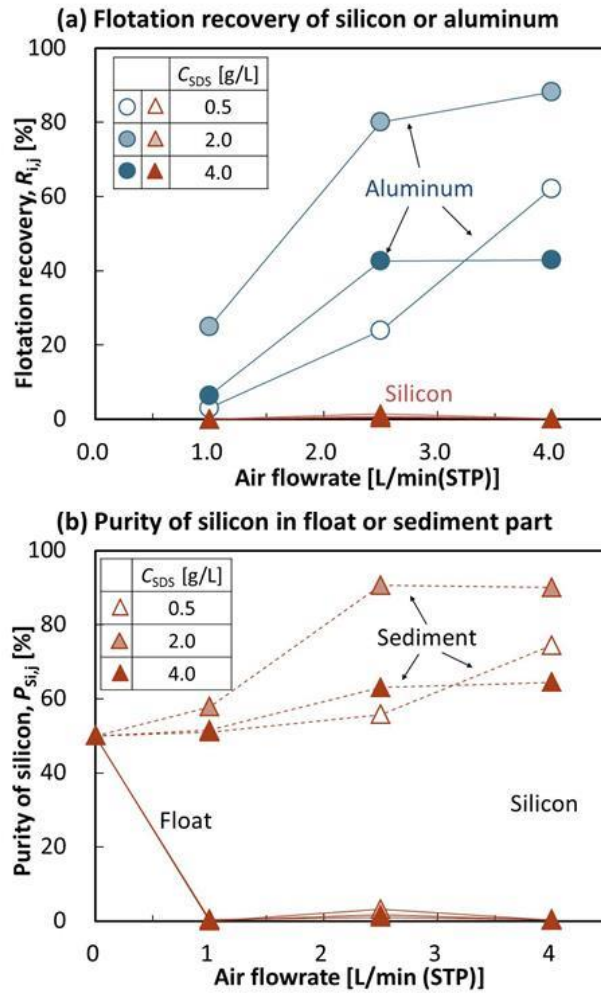


Fig.14 Effects of air flowrate and SDS concentration on separation behavior of silicon and aluminum.

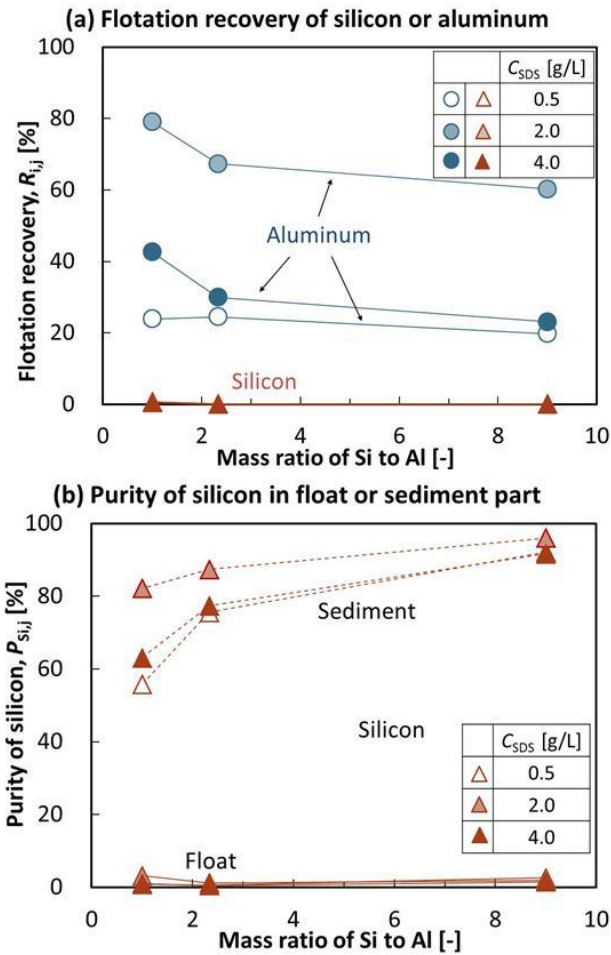


Fig.15 Effects of mass ratio of silicon to aluminum and SDS concentration on flotation separation behavior.

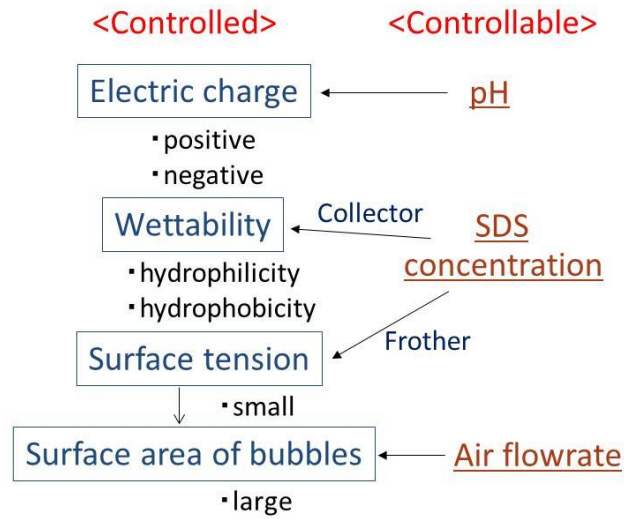


Fig. 16 Schematic diagram of relationship between controllable factors and controlled properties for separation floating method of silicon and aluminum.

Table 1 Experimental conditions

SDS concentration, C_{SDS} [g/L]	0.1 - 4.0 <u>2.0</u>
DTAB concentration, C_{DTAB} [g/L]	2.5
pH	2 - 12 <u>6.8</u>
Dipping time, t_{dip} [min]	10, 60, 120 <u>10</u>
Floating separation time, t_{flo} [min]	2 - 20 <u>5</u>
Mass ratio of Si to Al, $M_{\text{Si},0}/M_{\text{Al},0}$ [-]	9/1, 7/3, <u>5/5</u>
Mass of sample, M_{sam} [g]	<u>5.0</u>
Air flowrate, Q_{air} [L/min (STP)]	1.0, <u>2.5</u> , 4.0