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Sequential flotation of 4 components in silicon-based waste solar cells

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Abstract:

Si, Al, Cu, and Ag particles mixture which mainly composes pulverized silicon-based waste solar cells were individually separated by the batch flotation experiments with high recovery and content, and then a general flow chart of the sequential flotation procedure of *n*-component was postulated including 2-, 3-, and 4-components. The *n*-component mixture was separated to 1 : *n*-1 or *i* : j (*i* + *j* = *n*) by a flotation procedure and *n*-1 times operation was necessary to divide into the individual component. The first flotation process to separate Al into the froth layer was carried out with a collector of SDS solution after dipping Si, Al, Cu, and Ag mixture into the SDS solution. Si was separated in the froth by the second flotation with a collector of a commercial neutral detergent after Al etching by HCl, and Si, Cu and Ag mixture dipped in the detergent. The Cu and Ag mixture was calcinated at 673 or 773 K and dipped into the detergent, and the third flotation with the collector of the detergent led to Cu in the froth and Ag in the sediment. The 4-component mixture was successfully separated into each component by the 3-consecutive flotation processes.

Key words:

Flotation, Multicomponent, Waste solar cell, Silicon, Recovery

1. Introduction

Material recycling is performed to recover valuable materials and isolate hazardous materials derived from waste products, and it has been addressed in a variety of technical approaches such as physical/mechanical, chemical and metallurgical processes [1]. As the physical/mechanical processes, there are manual or automated disassembly, crushing, sieving, gravity, magnetic, electrostatic and flotation separations. The flotation technology, which has been used for concentrating the valuable components of a raw mineral in the mineral industry for an extended period of time, began to be investigated for separation of waste mixed matter such as hazardous poly (vinyl chloride) [2-4], microplastics recovery [5, 6], water treatment [7], removal of fly ash [8-10], and gold recovery [11-13] as a new separation approach. The combination of the flotation procedure with microwave [14-16], surface modification [17, 18], Fenton pretreatment [19] and jig separation [20, 21] was applied to obtain the higher flotation efficiency of waste plastic mixture.

Photovoltaic (PV) power as a promising renewable energy has been increasing its capacity since the 1970s and the most prevailing crystalline silicon (Si) solar cell modules are estimated to be sharply scrapped before too late. The Waste Electrical and Electronic Equipment (WEEE) directive on European Union (EU) was revised in 2012 to impose the recycling and reusing of waste solar cell modules mandate [22], and a guideline on the recycling of waste PV facility was announced by the Japanese government in 2016 [23]. Metallic frames and glasses to protect the solar cells, which are relatively easy to separate, divided by a manual disassembly. The assembled solar cells including Ethylene Vinyl Acetate (EVA) is detached by a chemical process dissolving the EVA dissolution in the organic solvent [24, 25] or by the thermal decomposition of the EVA alone [26]. The subsequent separation between the pulverized solar cell mixture without EVA is usually carried out by a hydrometallurgical process where targeted substances are etched in acid or basic water solution [27-29]. For example, Matsubara et al. [30] studied the etching rates of copper (Cu) and aluminum (Al) particles derived from waste Si-based solar with a mixed solution of HNO_3 and HCl, and obtained the optimal conditions for achieving high yield Si. The typical chemical compositions of the pulverized mixture of the waste solar cells are indicated as follows: Si/87.5 mass% Al/9.5 mass%, Cu/0.5 mass%, silver (Ag)/1.2 mass%, Tin (Sn)/0.8 mass%, Lead (Pb)/0.3 mass% etc. [30]. Meanwhile, Dias et al. [31] distinguished each component such as Si, Cu, Ag, EVA, and glass in the waste silicon-based PV modules using combining a crushing and electrostatic separator which are classified as a mechanical separation.

Recently, Harada et al. [32] reported that Al- and Si- mixed particles, which constitute the main material of pulverized waste crystalline Si-based solar cells, which were successfully separated into froth and sediment zones, respectively, by the flotation technique described above as one of the physical/mechanical recycling processes. Sodium Dodecyl Sulfate (SDS) solution was mainly used as a collector and frother. Kato et al. [33] analyzed the froth flotation kinetics of fine Al fine particles derived from waste Si-based solar cells and compared the froth recovery between batch, continuous, and column flotation practices according to the rate-determining steps of the gas flowrate and feed rate. However, there is little research on the sequential flotation procedure for the three-component mixture to separate each material, although the other valuable substances besides the Al- and Si particles are contained in the scrapped Si-based solar cells. The ideal sequential flotation of *n*-component is to repeat to completely divide a particle mixture into two groups at a time and finally separate into each component. A flowchart is useful to clarify a process flow and indispensable for facilitating complicated and sequential operations. However, the sequential flotation procedure has been insufficiently discussed on the basis of a flowchart.

In this study, a general flow chart of sequential flotation separation of *n*-component particles was first postulated including 2-, 3-, 4-components, and then for the purpose of simulating the sequential separation of the 4-component mixture of Si, Al, Cu, and Ag particles by the combination of different pretreatment and subsequent flotation, the flotation experiments of 4- (Si, Al, Cu, Ag), 3- (Si, Cu, Ag), and 2- (Cu, Ag) component mixtures were individually carried out and each kind of particle was almost successfully separated into the froth or sediment zone with high recovery and content. The appropriate pretreatment and flotation conditions were also discussed.

2. Flowchart of sequential flotation separation of the n-component mixture

Harada et al. [32] carried out the dipping pretreatment of Al-Si mixed particles into SDS solution, an anionic surfactant, for a predetermined time, and then separated the Al particles to the froth layer and Si ones to the sediment zone by a flotation procedure. Conversely, the Si particles transferred to the froth layer and Al remained on the bottom in dodecyltrimethylammonium bromide (DTAB) solution, a cationic surfactant. The flowchart of flotation separation of 2-, 3-, and 4-component mixtures is shown in Fig. 1. As seen in Fig. 1 (a), a single pretreatment and flotation procedure enabled us to isolate each component due to a binary system. The 3-component mixture is divided into 2- and 1-components by the first pretreatment and flotation procedure as indicated in Fig. 1 (b), and the second procedure for 2-component was needed to separate each other.

In terms of the flotation separation of the 4-component mixture, one is the sequential 1-component separation by the combination of one pretreatment and flotation procedure as denoted in Fig. 1 (c), the other is that two 2-components are initially separated, and then each 2-component mixture is divided into 1-component by each pretreatment and flotation procedure as shown in Fig. 1 (c’). Both numbers of the separation procedure of Fig. 1 (c) and (c’) became 4-1 =3.

The general flowchart of the combination of the pretreatment and flotation to individually separate *n*-component mixture is shown in Fig. 2. It is confirmed that the flowchart of Fig. 2 covers those in Fig. 1. The iteration number, *k*, is easily found to be n-1. While the pretreatment and subsequent flotation proceed continuously, the n-component separation is achieved by (n-1)-cells continuous flotation separation devices with the (n-1)-cells pretreatment vessels. However, a combined application of the continuous and batch operations must be applied when the batch-typed pretreatment such as calcination described in Chapter 3 is needed.

3. Experimental

3.1 Sample preparation

Si (Junsei Chemical Co., Ltd.), Al (Fujifilm Wako Pure Chemical Corporation), Cu

(Fujifilm Wako Pure Chemical Corporation) and Ag (Fujifilm Wako Pure Chemical Corporation) were used for the experiment. The purity of these elements was 99.0% or more. The original flake silicon was pulverized by a grinder mill (Osaka Chemical Co., Ltd, WB-1). The Si, Al, and Cu particles were screened between 100 – 212 µm, whereas the Ag between 212 – 425 µm which was the minimum size available to us in this study. The silicon particles were immersed in 0.1 M nitrate acid solution for 1 min, cleaned with ion-exchanged water and dried in a chamber to prevent contamination by foreign materials in the grinder.

3.2 Pretreatment and flotation procedures and experimental conditions

The schematic diagram of a flotation apparatus is shown in Fig. 3. The glass cylinder of 80 mm inner diameter and 270 mm height was used as separation part. A porous glass filter was set at a lower part. After pretreating and dipping the sample mixture in a given concentration of collector solution with ion-exchanged water for a given time, this suspending solution of 250 mL was put into the vessel. At the same instant, air was blown through the porous filter. The test duration was fixed to 5 min. The same concentration of the collector solution was added from the vessel side through a pump to compensate for the solution in the vessel during the experiment.

The experimental conditions of sequential flotation separation are summarized in Table 1 and each procedure is set forth below. The pH of the collector solution was maintained at 6.8 throughout all stages of flotation separation as with the case of Harada et al. [32].

3.2.1 Procedure 1 for Al separation from Si, Al, Cu, and Ag mixture

The total mass and ratio of Si, Al, Cu, and Ag mixture was 6.0 g and 2: 2: 1: 1, respectively. Here, a simple mass ratio instead of the typical chemical compositions of the waste solar cells was used to conform a flotation procedure functions well. SDS was used as a collector to isolate Al into the froth layer from the sample mixture. The SDS concentration was varied to 0.5, 2.0 and 4.0 g/L, whereas the dipping time of the sample was changed to 10, 120, 240 and 360 min to find the optimal flotation recovery condition. The air flowrate was fixed to 4.0 L/min (STP). The average bubble diameter recorded by a video camera (SONY, HDR-CX700) was 3.0 mm without SDS, reduced to 1.0 mm at 1.0 g/L SDS concentration, and then slightly decreased to 0.8 mm at 3.0 g/L SDS solution.

3.2.2 Procedure 2 for separation of Si, Cu, and Ag mixture

Before the second flotation sequence, 3.0 g of Si, Cu, and Ag mixture was adjusted in equal mass proportion and 0.2 g of Al were etched in 0.1 M HCl solution for 60 min to simulate the removal of a small amount of Al recovered in the froth layer by the first flotation separation procedure. After the Al etching, the Si, Cu, and Ag sample mixture was dried naturally and dipped in a collector solution for 120 min. Here, the second flotation experiments were also carried out by a simple mass ratio of samples instead of the product that sank in the first flotation to check the successful second flotation. The commercial dishwashing neutral detergent named Cucute Masukatto-no-Kaori (Kao Corporation) [34] was used as a collector to recover Si in the froth layer. The main components of the collector were shown in Table 2. There were many kinds of ingredients such as anionic, ampholytic and non-ionic surfactants, stabilizing agents, sequestering agents, etc. The collector concentration was changed to 0.25, 0.5 1.0, and 1.5 g/L. The air flowrate was kept to 3.0 L/min (STP).

3.2.3 Procedure 3 for separation of Cu - Ag mixture

The equal mass of Cu and Ag were used for the third flotation procedure. The total sample mass was 2.0 g. As a pretreatment, the sample mixture was calcinated at 673 and 773 K for 4 h to change the wettability of the metal surface before dipped in the collector solution. The neutral detergent indicated above was used for a collector to recover Cu in the froth layer, and varied to 0.25, 0.5 1.0, and 1.5 g/L. The dipping time of the calcinated samples and air flowrate were fixed to 120 min and 3.0 L/min (STP), respectively.

3.3 Calculation of flotation recovery and content

The froth flotation recovery rate, R_i [%], and content, C_i [%], of the i-component were calculated as Eqs. (1) and (2), respectively, as follows:

$$R_i = (M_i/M_{i,0})\ \mathrm{x}100 \tag{1}$$

$$C_i = (M_i/\textstyle\sum_1^n M_j)\mathrm{x}100 \tag{2}$$

Here, M_i is the mass [g] of the i-component recovered in the froth layer, $M_{i,0}$ is the initial mass [g] of i-component, and $\sum_1^n M_j$ is the total mass [g] recovered in the froth layer.

To measure the mass of each component after the experiment, the sample including Al and Cu were dissolved in HCl and HNO_3 solution [30], respectively, and Si was separated from Ag by a sieve method due to the difference in the particle size distribution.

4. Results and discussion

4.1 1st sequence of pretreatment and flotation separation

4.1.1 Zeta (ζ) potential of Al, Si, Cu and Ag

When physical adsorption caused by electrostatic interaction is used to separate one material from another, ionic collector such as SDS is selected on the condition that each material has the opposite electric charge [35]. The surface electric charge of each sample was evaluated by a device for the measurement of ζ potential (Malvern Panalytical, Zetasizer Nano ZS). The relationship between ζ potential and pH for Al, Si, Cu, and Ag is shown in Fig. 4. There was no surfactant in the solution. The ζ potential of Si, Cu, and Ag indicated the negative value in the total pH range, whereas that of Al became positive in the acid and slightly negative in the neutral and alkaline range. It means that an anionic collector such as SDS has the potential to change only the Al surface to hydrophobic property as shown by Harada et al. [32]. Thus, only Al particles float with bubbles in the SDS solution with Al, Si, Cu, and Ag mixture. Moreover, Si indicated the highest negative values throughout all the pH range.

4.1.2 Effect of SDS concentration and dipping time on 1st flotation separation

The effect of SDS concentration on the froth recovery and content is shown in Fig. 5. The sample dipping time into the SDS solution before the experiment was fixed to 120 min. As expected in the previous section, only the Al particles were recovered in the froth layer and the high content was maintained. However, the Al recoveries at 0.5 g/L and 4.0 g/L of SDS concentration were lower than that at 2.0 g/L. The lower Al recovery at 0.5 g/L is due to the lower amount of hydrophilic group in SDS and at 4.0 g/L results from the admicell generation above the critical micelle concentration of SDS [32, 36].

The effect of the sample dipping time into 2.0 g/L SDS solution on the froth recovery and content is shown in Fig. 6. The Al recovery became more than 80% when the sample was dipped into SDS solution beyond 10 min and the Al content reached 96.3% at a dipping time of 120 min. The Al recovery and content at a dipping time of 10 min were lower because it took insufficient time for the sample to soak in the SDS solution.

Based on the above experimental results, 2.0 g/L SDS concentration and dipping time of 120 min was most suitable for the first flotation condition of Al, Si, Cu and Ag mixture.

4.2 Second sequence of pretreatment and flotation separation

The Si, Cu, and Ag sample including Al was etched and perfectly dissolved in 0.1 M HCl solution. The relationship between the recovery and content of the froth layer, and the commercial dishwashing neutral detergent concentration after the second flotation separation is shown in Fig. 7. Si was stably floated in the froth layer and the maximum recovery achieved 98.9% at the detergent concentration of 0.25 g/L as indicated in Fig. 7 (a). The Si recovery was gradually decreased with the increase in the detergent concentration until 86.7% at 1.5 g/L. It’s difficult to explain the reason, however, the assumption of the admicell generation between 0 and 0.25 g/L detergent concentration might result in the decrease of the Si recovery as the detergent concentration increases. The reason for the Cu entrainment is difficult to interpret at present. Meanwhile, the Si content at 0.25 g/L detergent concentration was 83.9% due to the Cu recovery of 16.1% and increased to 96.6% at 1.5 g/L detergent concentration as shown in Fig. 7 (b). There was no Ag recovery in the froth layer as shown in Fig. 7 (a). In terms of the higher content of Si, the detergent concentration of 1.5 g/L seems to be preferable in the second flotation procedure.

The reason why Si was recovered in the froth layer is assumed as follows. The dish washing detergent ‘Cucute’ contains an ampholytic surface active agent, alkyl hydroxy sulfobetaine (HSB) which exhibits cationic surface active properties in the acid solution as indicated in Table 2. $AlCl_3$, the reaction product of Al and HCl during the second pretreatment, was partially attached to the dried sample after the Al etching, and estimated to acidize the detergent ‘Cucute’ solution as a collector. Since the ζ potential of Si in Fig. 4 becomes the most negative value in the acid region, the HSB in the detergent ‘Cucute’ adsorbed on the Si particles and Si transferred to the froth layer.

4.3 Third sequence of pretreatment and flotation separation

As the third pretreatment, the calcination of the sample mixture of Cu and Ag was done at 673 or 773 K for 4 h and then this sample was dipped in the detergent solution. The possible calcination reactions and Gibbs free energy, ΔG_i, of i (=Cu, Ag) are as follows [37]:

$$4Cu + O_2 = 2Cu_2O \quad \Delta G^{o}_{i} = -334800 + 144.8T$$

$$2Cu + O_2 = 2CuO \quad \Delta G^{o}_{i} = -311700 + 180.34T$$

$$4Ag + O_2 = 2Ag_2O \quad \Delta G^{o}_{i} = -56240 + 121.26T$$

Here, T is the calcination temperature [K]. The critical calcination temperatures of Cu_2O, CuO and Ag_2O were calculated as 2312, 1728, and 463 K, respectively. Thus, Ag is unoxidized under the calcination conditions of 673 and 773 K. The Cu_2O with smaller ΔG^{o}_{i} value is preferentially formed in this experiment. According to the mass measurement of Cu before and after the calcination, 32.9 and 84.1% in Cu was oxidized to Cu_2O at 673 and 773 K, respectively.

The relationship between the recovery and content of the froth layer, and the commercial dishwashing neutral detergent concentration after the third flotation separation is shown in Fig. 8. The calcinated sample was used. It was found that Ag almost remained in the sediment zone. The recovery of Cu corrected to the mass of Cu_2O in the sample, was low at detergent concentration of 0.25 g/L, however above 0.25 g/L it indicated the higher values. The Cu recovery after the calcination at 773 K was higher than at 673 K due to the larger Cu oxidation. The Cu content in the froth layer was kept above 90%.

There are two reasons for the froth flotation of the calcinated Cu. One is the ζ potential difference between Cu and Cu_2O. The relationship between the ζ potentials of Cu and Cu_2O measured by Behera and Giri [38] is shown in Fig. 9. The ζ potential of Cu_2O was larger than that of Cu, which indicates the anionic surfactants in Table 2 float the Cu covered with Cu_2O in the froth layer like Al in Fig. 5. The other reason for the increased floatability of behavior of Cu particles is the activation effect by calcination.

4.4 Overview of sequential flotation of fine particles mixture in silicon-based waste solar cell

As discussed in earlier sections, the 4-component of fine particles mixture was individually separated by three sequential flotation procedures. The froth flotations of the first, second, and third procedures were Al, Si, and Cu, respectively. The flowchart of the 4-component mixture separation is shown in Fig. 10. It was comparable to Fig. 1 (c), however, the flotation does not always separate each material as 1: *n*-1 (*n*: number of components).

In this study, artificial pulverized materials such as Si, Al, Cu, and Ag were used by a simple mass ratio and successfully separated from each other. The real waste of solar cells containing EVA, which is typically composed of 87.5 % Si, 9.5 % Al, 0.5 % Cu, and 1.2 % Ag, will be tried on the next stage. Small amounts of components such as Cu and Ag are generally advantageous to float and separate from the pulverized waste of solar cells. The sequential flotation separation must be chosen by pursuing both the principle of physical chemistry and cost-minimum operations.

Moreover, the froth flotation of each component was mainly explained by the difference of ζ potential. The Ag particle size was different from the Si, Al, and Cu ones as described in Section 3.1. The particle size is also one of the most important factors in flotation. The effects of the ζ potential and particle size in relation to each other on the flotation must be discussed next time around.

5. Conclusions

A general flow chart of sequential flotation procedure of *n*-component particles mixture was first explained including 2-, 3-, 4-components, and then Si, Al, Cu, and Ag particles mixture were individually separated by the sequential flotation experiments with high recovery and content. The results obtained in this study are as follows.

1. *n*-component mixture was separated to 1: *n*-1 or *i* : j (*i* + *j* = *n*) by a flotation procedure and *n*-1 times flotation operation was necessary to divide into individual component.
2. Al and Si had the highest and lowest ζ potential value throughout all the pH ranges, respectively, among Al, Si, Cu, and Ag.
3. After dipping Al, Si, Cu, and Ag mixture in SDS solution as a pretreatment, Al was only separated in the froth layer by the first flotation with a collector of SDS.
4. After the Al etching by HCl treatment and dipping of the Si, Cu, and Ag mixture sample in a commercial dishwashing neutral detergent as a pretreatment, Si was only separated in the froth layer by the second flotation with the detergent.
5. After calcinating Cu and Ag mixture at 673 or 773 K and dipping it in the detergent, Cu transferred in the froth layer and Ag remained in the sediment zone by the third flotation procedure.

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References

1. Kaya, M (2016) Recovery of metals and nonmetals from electronic waste by physical and chemical recycling processes. Waste Manage 57:64-90.
2. Wang C, Wang H, Fu J, Zhang L, Luo C, Liu Y (2015) Flotation separation of polyvinyl chloride and polyethylene terephthalate plastics combined with surface modification for recycling. Waste Manage 45:112-117.
3. Truc NTT, Lee BK (2016) Sustainable and selective separation of PVC and ABS from a WEEE plastic mixture using microwave and/or mild-heat treatment with froth flotation. Environ Sci Technol 50:10580–10587.
4. Wang J, Wang H, Wang C, Zhang L, Wang T, Zheng L (2017) A novel process for separation of hazardous poly (vinyl chloride) from mixed plastic wastes by froth flotation. Waste Manage 69:59-65.
5. Jiang H, Zhang Y, Bian K, Wang H, Wang C (2022) Insight into the effects of aqueous species on microplastics removal by froth flotation: kinetics and mechanism. J Environ Chem Eng 10: 107834.
6. Zhang Y, Jiang H, Bian K, Wang H, Wang C (2021) A critical review of control and removal strategies for microplastics from aquatic environments. J Environ Chem Eng 9: 105463.

7. Eivazihollagh A, Tejera J, Svanedal I, Edlund H, Blanco A, Norgren M (2017) Removal of Cd^{2+}, Zn^{2+}, and Sr^{2+} by ion flotation, using a surface-active derivative of DTPA (C_{12}-DTPA). Ind Eng Chem Res 56(38):10605–10614.

8. Dey S, Paul G. M, Pani S (2013) Flotation behaviour of weathered coal in mechanical and column flotation cell. Powder Technol 246:689-694.

9. Jatav P P, Tajane S P, Mandavgane S A, Gaidhani S B (2019) A process of carbon enrichment of bottom slag ash for value-added applications. J Mater Cycles Waste Manag 21: 539-546.

10. Xie Q, Wang D, Han Z, Tao H, Liu S (2022) Removal of carbon and dioxins from municipal solid waste incineration fly ash by ball milling and flotation methods. J Mater Cycles Waste Manag Published online 06 October.

11. Altansukh B, Burmaa G, Nyamdelger S, Ariunbolor N, Shibayama A, Haga K (2014) Gold recovery from its flotation concentrate using acidic thiourea leaching and organosilicon polymer. Int J Soc Mater Eng Resour 20: 29-34.

12. Burat F, Demirag A, Safak M C (2020) Recovery of noble metals from floor sweeping jewelry waste by flotation-cyanide leaching. J Mater Cycles Waste Manag 22: 907-915.

13. Dinc N I, Tosun A U, Basturkcu, Ozer M, Burat F (2022) Recovery of valuable metals from WPCB fines by centrifugal gravity separation and froth flotation. J Mater Cycles Waste Manag 24: 224-236.

14. Truc, N T T, Lee B-K (2016) Sustainable and selective separation of PVC and ABS from a WEEE plastic mixture using microwave and/or mild-heat treatment with froth flotation. Environ Sci Technol 50: 10580-10587.

15. Mallampati S R, Lee C-H, Park M H, Lee B-K (2018) Processing plastics from ASR/ESR waste: separation of poly vinyl chloride (PVC) by froth flotation after microwave-assisted surface modification. J Mater Cycles Waste Manag 20: 91-99.
16. Qu Y H, Li Y P, Zou X T, Xu K W, Xue Y T (2021) Microwave treatment combined with wetting agent for an efficient flotation separation of acrylonitrile butadiene styrene (ABS). J Mater Cycles Waste Manag 23: 96-106.
17. Wang C, Wang H, Fu J, Zhang L, Luo C, Liu Y (2015) Flotation separation of polyvinyl chloride and polyethylene terephthalate plastics combined with surface modification for recycling. Waste Manage 45: 112-117.
18. Wang J, Wang H, Wang C, Zhang L, Wang T, Zhang L (2017) A novel process for separation of hazardous poly (vinyl chloride) from mixed plastic wastes by froth flotation. Waste Manage 69: 59-65.
19. Li W, Li Y (2022) Selective flotation separation of polycarbonate from plastic mixtures based on Fenton treatment combined with ultrasonic. J Mater Cycles Waste Manag 24: 917-926.
20. Ito M, Takeuchi M, Saito A, Murase N, Phengsaart T, Tabelin C B, Hiroyosshi N, Tsunekawa M (2019) Improvement of hybrid jig separation efficiency using wetting agents for the recycling of mixed-plastic wastes. J Mater Cycles Waste Manag 21: 1376-1383.
21. Ito M, Saito A, Murase N, Phengsaart T, Kimura S, Kitajima N, Takeuchi M, Tabelin C B, Hiroyosshi N (2020) Estimation of hybrid jig separation efficiency using a modified concentration criterion based on apparent densities of plastic particles with attached bubbles. J Mater Cycles Waste Manag 20: 2071-2080.

22. European Union (2012) Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on waste electrical and electronic equipment (WEEE). Official Journal of the European Union 197:38-71.

23. Ministry of the Environment Government of Japan (2016) https://www.env.go.jp/press/102330.html Accessed 20 Dec. 2022.

24. Doi T, Tsuda I, Unagida H, Murata A, Sakuta K, Kurokawa K (2001) Experimental study on PV module recycling with organic solvent. Sol Energy Mater Sol Cells 67:397-403.

25. New Energy and Industrial Technology Development Organization (NEDO) (2019) https://www.nedo.go.jp/content/100901845.pdf Accessed 20 Dec. 2022.

26. New Energy and Industrial Technology Development Organization (NEDO) (2019) https://www.nedo.go.jp/content/100901845.pdf . (accessed 20 June 2022)

27. Park J, Park N (2014) Wet etching processes for recycling crystalline silicon solar cells from end-of-life photovoltaic modules. RSC Adv 4:34823-34829.

28. Klugmann-Radziemska E, Ostrowski P (2010) Chemical treatment of crystalline silicon cells as a method of recovering pure silicon from photovoltaic modules. Renew Energy 35:1751–1759.

29. Takami K, Kobashi M, Shiraga Y, Uddin MA, Kato Y, Wu S (2015) Effect of HF and HNO_3 Concentration on Etching Rate of Each Component in Waste Crystalline Silicon Solar Cells. Mater Trans 56:2047-2052.

30. Matsubara T, Uddin MA, Kato Y, Kawanishi T, Hayashi Y (2018) Chemical treatment of copper and aluminum derived from waste crystalline silicon solar cell modules by mixed acids of HNO_3 and HCl. J Sustain Metall 4:378–387.

31. Dias P, Schmidt L, Gomes LB, Bettanin A, Veit H, Bernardes AM (2018) Recycling waste crystalline silicon photovoltaic modules by electrostatic separation. J Sustain Metall 4:176–186.

32. Harada S, Uddin MA, Kato Y, Kawanishi T, Hayashi Y (2019) Separation between silicon and aluminum powders contained within pulverized scraped silicon‑based waste solar cells by flotation method. J Sustain Metall 5:551–560.

33. Kato Y, Harada S, Nishimura N, Uddin M. A, Uchida Y (2023) Flotation kinetics of aluminum powders derived from waste crystalline silicon solar cells and its comparison between batch, continuous and column flotation practices. J Mater Cycles Waste Manag 25:826-834.

34. https://www.kao.com/jp/products/kyukyutto/inc-common/fabric/4901301288493/ (Accessed 24 Dec. 2022)

35. Matsuoka I (1982) Flotation of oxide minerals. J Min Metall Inst Jpn 98:664–670.

36. Koopal LK, Lee EM, Bohmer MR (1995) Adsorption of cationic and anionic surfactants on charged metal oxide surfaces. J Colloid Interface Sci 170(1):85–97.

37. The Japan Institute of Metals and Materials (1980) Hitetsu Kinzoku Seiren (Non-ferrous smelting). Sendai.

38. M. Behera, G. Giri (2014) Green synthesis and characterization of cuprous oxide nanoparticles in presence of a bio-surfactant. Materials Science-Poland 32(4):702-708.

Caption List

Table 1 Experimental conditions

Table 2 Main ingredients and their functions for ‘Cucutte Muscat-no-Kaori’ [34]

Fig.1 Flotation flowcharts for separation of each component from 2-, 3-, and 4-component particle mixtures

Fig. 2 Flowchart of separation procedure of *n*-component mixture by flotation technique

Fig. 3 Schematic diagram of flotation equipment

Fig. 4 Relationship between ζ-potential and pH

Fig. 5 Relationship between recovery and content of froth layer, and SDS concentration after the first flotation separation between Al, Si, Cu, and Ag

Fig. 6 Relationship between recovery and content of froth layer, and dipping time after the first flotation separation between Al, Si, Cu, and Ag

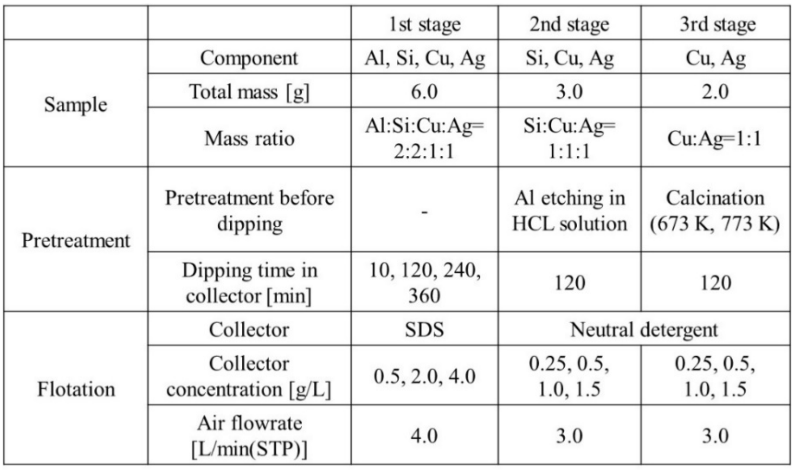
Fig. 7 Relationship between recovery and content of froth layer, and detergent concentration after the second flotation separation between Si, Cu, and Ag

Fig. 8 Relationship between recovery and content of froth layer, and detergent concentration after the third flotation separation between Cu covered with Cu_2O and Ag

Fig. 9 Comparison of ζ-potential between Cu_2O [38] and Cu

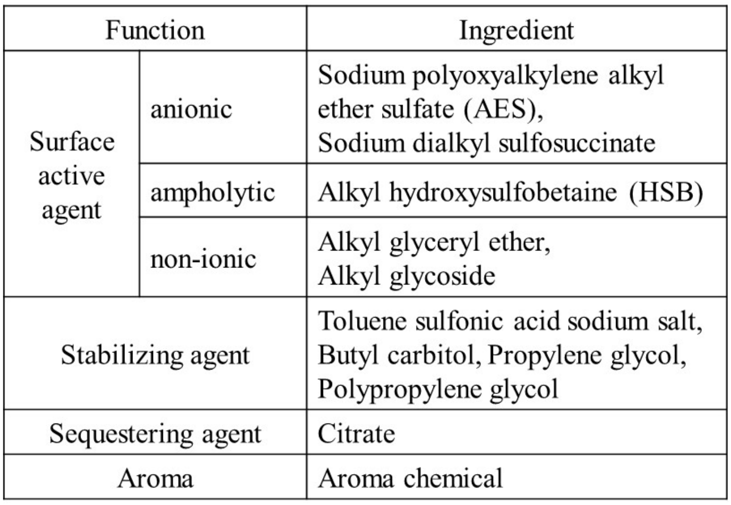
Fig. 10 Flotation separation procedure of Al, Si, Cu, and Ag particle mixture derived from waste Si solar cells

Table 1 Experimental conditions



		1st stage	2nd stage	3rd stage
Sample	Component	Al, Si, Cu, Ag	Si, Cu, Ag	Cu, Ag
	Total mass [g]	6.0	3.0	2.0
	Mass ratio	Al:Si:Cu:Ag= 2:2:1:1	Si:Cu:Ag= 1:1:1	Cu:Ag=1:1
Pretreatment	Pretreatment before dipping	-	Al etching in HCL solution	Calcination (673 K, 773 K)
	Dipping time in collector [min]	10, 120, 240, 360	120	120
Flotation	Collector	SDS	Neutral detergent	
	Collector concentration [g/L]	0.5, 2.0, 4.0	0.25, 0.5, 1.0, 1.5	0.25, 0.5, 1.0, 1.5
	Air flowrate [L/min(STP)]	4.0	3.0	3.0

Table 2 Main ingredients and their functions for ‘Cucutte Muscat-no-Kaori’ [34]



Function		Ingredient
Surface active agent	anionic	Sodium polyoxyalkylene alkyl ether sulfate (AES), Sodium dialkyl sulfosuccinate
	ampholytic	Alkyl hydroxysulfobetaine (HSB)
	non-ionic	Alkyl glyceryl ether, Alkyl glycoside
Stabilizing agent		Toluene sulfonic acid sodium salt, Butyl carbitol, Propylene glycol, Polypropylene glycol
Sequestering agent		Citrate
Aroma		Aroma chemical

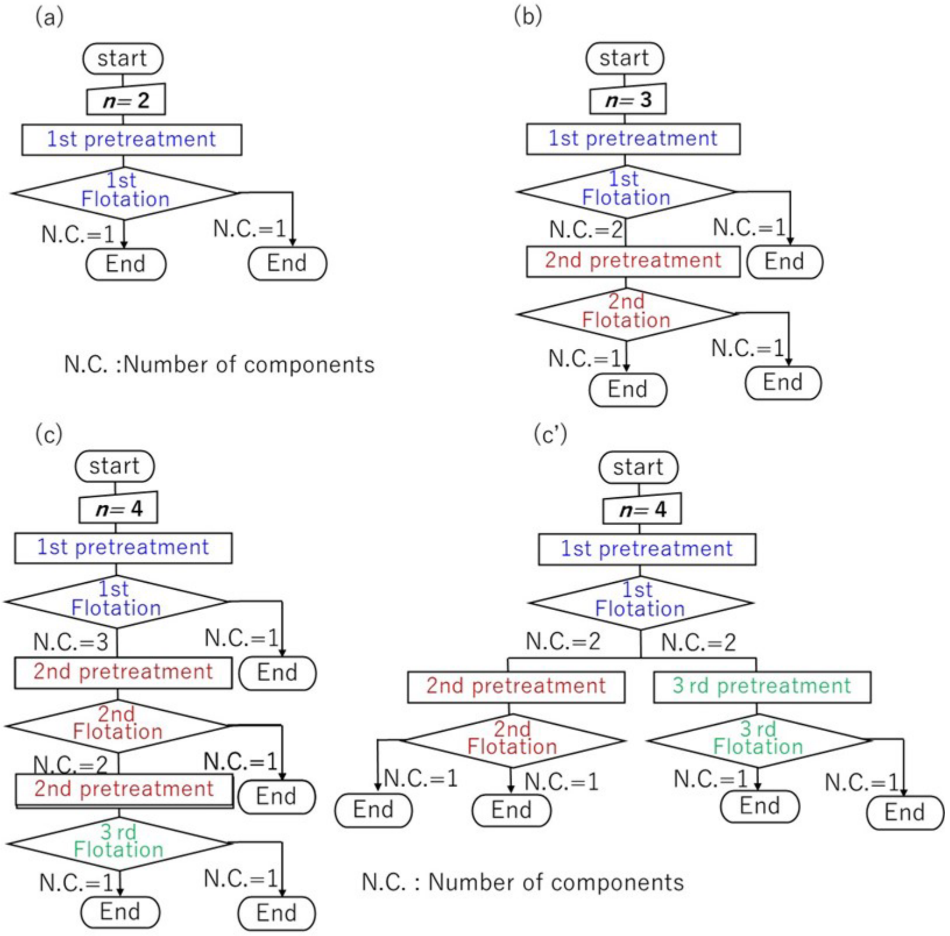


Fig.1 Flotation flowcharts for separation of each component from 2- and 3-, and 4-component particle mixtures

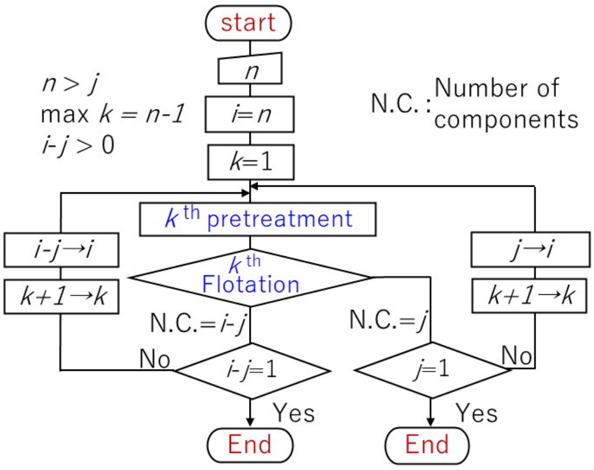


Fig. 2 Flowchart of separation procedure of *n*-component mixture by flotation technique

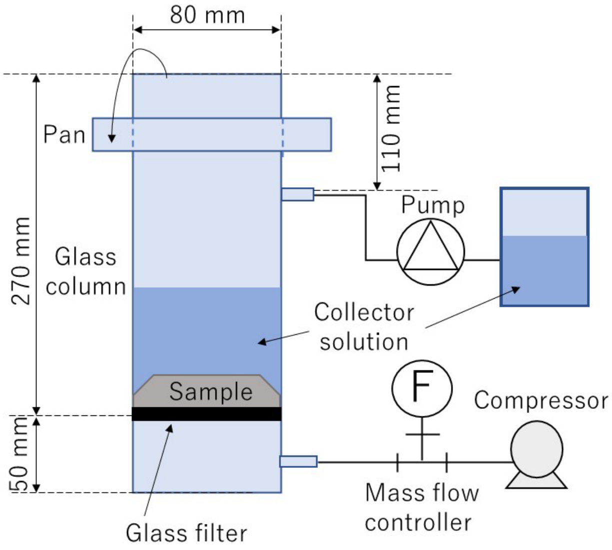


Fig. 3 Schematic diagram of flotation equipment

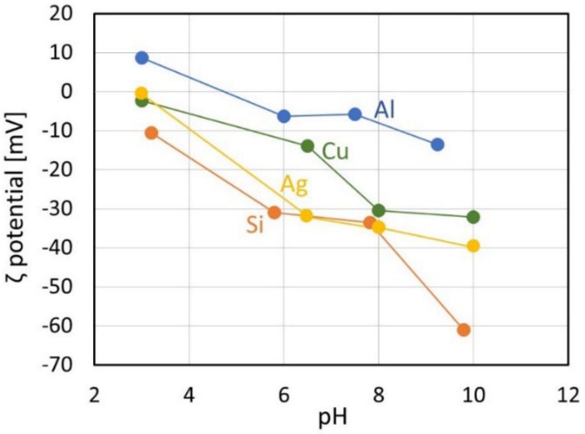


Fig. 4 Relationship between ζ potential and pH

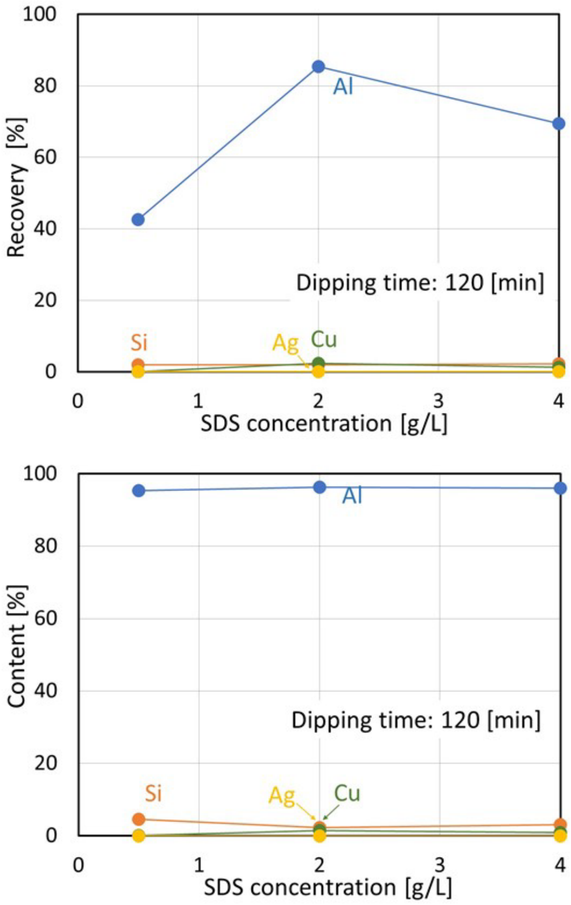


Fig. 5 Relationship between recovery and content of froth layer, and SDS concentration after the first flotation separation between Al, Si, Cu, and Ag

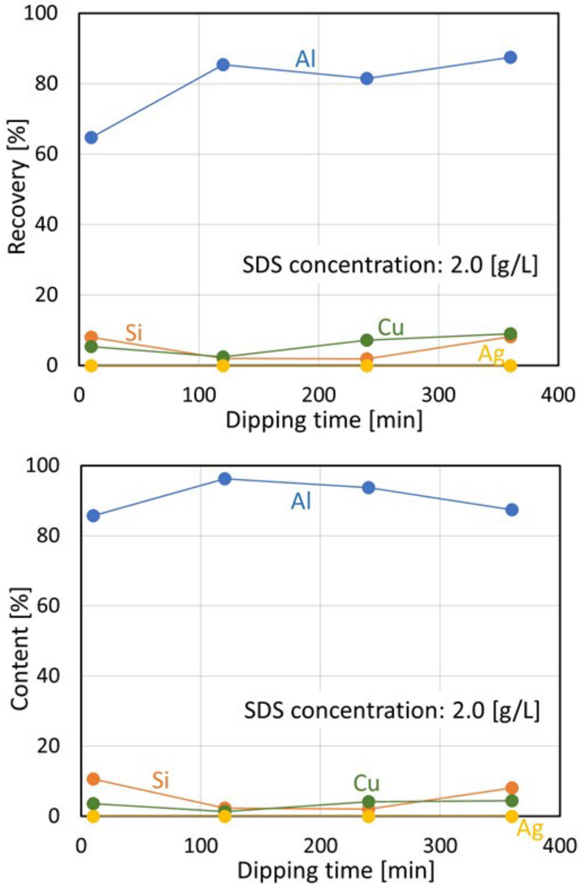


Fig. 6 Relationship between recovery and content of froth layer, and dipping time after the first flotation separation between Al, Si, Cu, and Ag

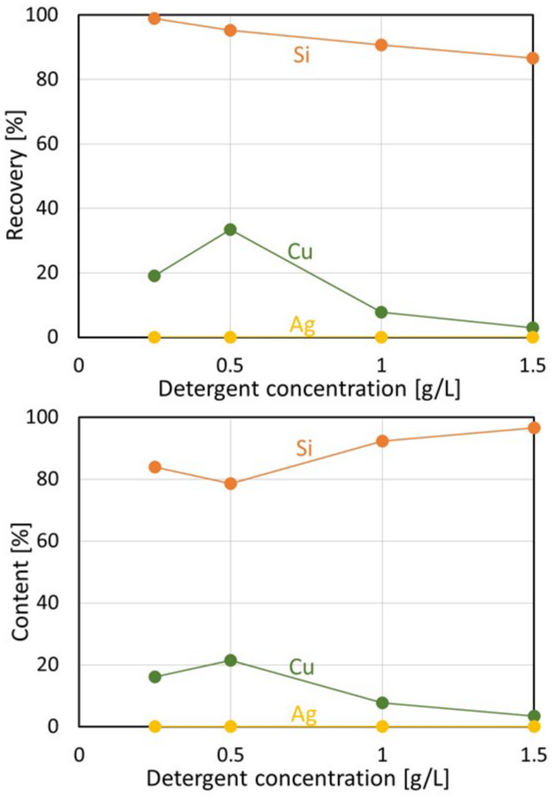


Fig. 7 Relationship between recovery and content of froth layer, and detergent concentration after the second flotation separation between Si, Cu, and Ag

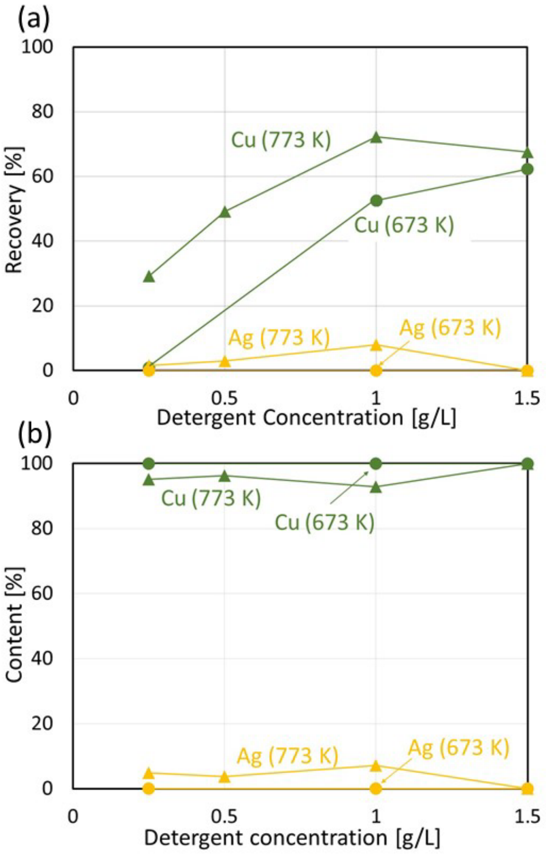


Fig. 8 Relationship between recovery and content of froth layer, and detergent concentration after the third flotation separation between Cu covered with Cu_2O and Ag

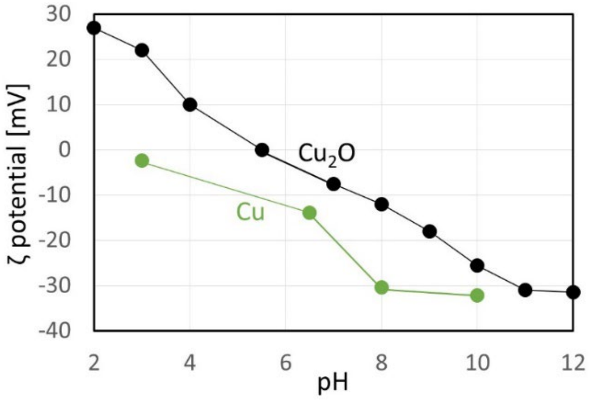
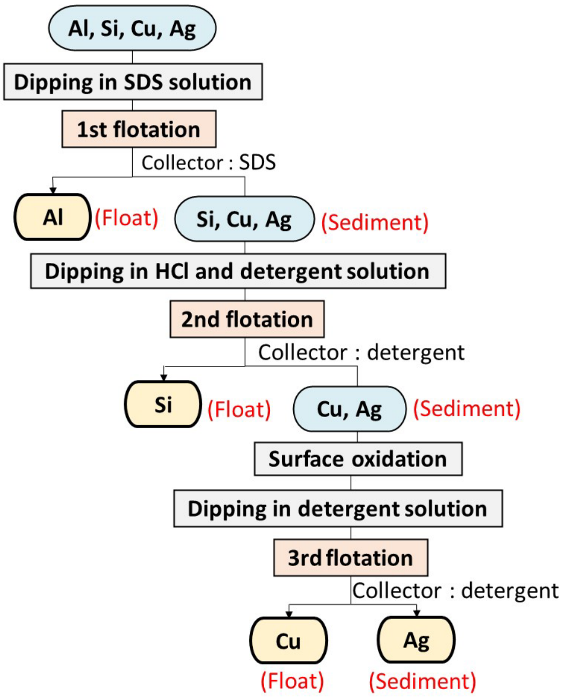


Fig. 9 Comparison of ζ-potential between Cu_2O [38] and Cu



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