

Original Article

# A Study to Recover Si and Ag from Solar Cells and PV Ribbons by Utilizing Acid Solutions

Hyun-Jong Kim<sup>1</sup>, Jong-Min Jeong<sup>2</sup>, Jei-Pil Wang<sup>3</sup>

<sup>1</sup> Metallurgical Engineering Major, Department of Convergence Material Engineering, Pukyong National University, Busan, Republic of Korea

<sup>2</sup> Department of Energy Industry Facility, Korea Polytechnics, Republic of Korea

<sup>3</sup> Division of Convergence Materials Engineering, Major of Metallurgical, Department of Marine Convergence Design Engineering (Advanced Materials Engineering), Pukyong National University, Busan, Republic of Korea.

<sup>1</sup>Corresponding Author: [jpwang@pknu.ac.kr](mailto:jpwang@pknu.ac.kr)

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**Abstract** - In this research, a study was conducted to selectively recover Si and Ag from solar cells and PV ribbons, which are elements of solar cell modules, by utilizing acid solutions. To selectively recover Si from spent solar cells and PV ribbon, a leaching process was carried out by using an acid solution ( $\text{HNO}_3$ ). The solar cells in which the reaction had ended were washed with distilled water and dried in a drying oven at  $100^\circ\text{C}$  for 24 hours. After crushing the dried solar cells into a fine powder, Si's purity and recovery rate was found through XRD and XRF analysis. For the solution that had reacted with the solar cells, ICP-OES analysis was carried out after decompression filtration. In addition, to selectively recover Ag from the filtered solution that had reacted with the solar cells, HCl was input to proceed with the sediment formation reaction. The sediment powder that had formed was recovered and reduced by using Hydrazine ( $\text{N}_2\text{H}_4$ ). After the powder in which the reduction reaction had completed was decompression filtered and recovered, it was dried in a drying oven at  $100^\circ\text{C}$  for 24 hours. The purity and recovery rate of Ag for the dried powder was found through XRD and XRF analysis. In addition, ICP-OES analysis was carried out on the filtered solution after recovering the sediment powder. The experiment was conducted with the concentration, reaction temperature, reaction time, and ultrasound intensity of the acid solution ( $\text{HNO}_3$ ) as variables during the leaching process and with the input amount of HCl as the variable during the sediment formation reaction. As the result of the experiment, the optimal process for the leaching reaction using  $\text{HNO}_3$  was derived from being acid solution concentration of 3M, reaction temperature of  $60^\circ\text{C}$ , the reaction time of 30min, and ultrasound intensity of 200W, and the optimal process for the sediment formation reaction was derived from being 1ml of HCl input. At this time, the Si purity and recovery rates were 99.58% and 99.94%, respectively, and the Ag purity and recovery rates were 99.72% and 93.96%, respectively.

**Keywords** - Spent solar cell, Acid solution, Recovery rate, Silicon (Si), Silver (Ag).

## 1. Introduction

While various alternatives are being proposed to solve the global environmental pollution and energy supply and demand problems currently, alternatives to solve the fundamental problems are insufficient. Although developing alternative energy utilization technologies cannot be an underlying solution, it may be established as a partial alternative. Since the portion of electric power generation due to solar cells is the largest among them, it has become established as an alternative energy production technology. Mass manufacturing of solar cell modules is being realized in many countries worldwide, and the rapid occurrence of solar power facilities and spent solar waste modules is expected.[1, 16] Accordingly, the recovery of valuable materials contained in the waste modules and the preparation of alternatives to solve the environmental problems are required.[3] The global solar power generation capacity up to 2017 was 414 GW (domestic solar power generation capacity was 5.7 GW) and has been in a growing trend every year. However, the solar cells installed in the initial stages have reached the end of their life expectancy

of 15-20 years, and some are now being scraped. [4, 5] The global cumulative total solar power generation capacity will reach 1,600 GW (30 GW for the total domestic solar power generation capacity) in 2030 and 6,862 GW (135 GW for the total domestic solar power generation capacity) in 2050. According to the IRENA report, it is expected that about 8 million tons of solar waste modules will be generated in 2030 and about 78 million tons in 2050. [4-9] Among the components of the solar cell module, a solar cell is composed of the front, and rear electrodes made of silver (Ag), aluminum (Al), etc., antireflection coating (Silicon Nitride,  $\text{SiNx}$ ), emitter, and back surface field (BSF) based on silicon, which is a valuable metal. It is reported that Ag in solar cells has the highest global warming index per  $\text{m}^2$ , followed by silicon, when the environmental impact of the raw material collection process during solar cell production is evaluated through a Life Cycle Assessment (LCA).[18] In addition, since Ag is the most expensive material, great economic and environmental value can be created if it is effectively recovered and recycled.[11] Since 2012, the European Union (EU) has revised the Waste Electrical and



Electronic Equipment (WEEE) to recycle solar cells by designating them as waste.[19] Accordingly, the European Union stipulates responsibility for solar waste disposal through the European Parliament and the European Council Directive 2012/19/EC, and Germany, Italy, France, etc. in Europe have actively responded to recycling by building collection facilities for solar waste.[13] However, the possibility that most of the solar waste modules were neglected or scraped is high in Korea. The need to develop solar waste module recycling technology is increasing due to the lack of technologies and systems for recycling.[20] Therefore, in this study, we proceeded with research utilizing acid solutions by considering the impurity behavior characteristics through thermodynamic modeling to effectively recover Si and Ag, which are valuable metals, in solar cell modules. The optimal condition was derived to improve the purity and recovery rate of Si and Ag by utilizing this, controlling the concentration, reaction temperature, reaction time, and ultrasound intensity for an acid solution (HNO<sub>3</sub>) and the HCl input amount.

## 2. Materials

To analyze the element content in solar cells and PV ribbon, XRD and XRF analysis were conducted after the front and back sides of the solar cells used in this study were analyzed by SEM-Mapping and crushed into fine powder. SEM-Mapping analysis was carried out on the PV ribbon after mounting and polishing them. For the analysis, X'Pert3-powder from PANalytical was used for XRD, XRF-1800 from SHIMADZU was used for XRF, Optimas 5300DV by Perkin Elmer was used for ICP, and JSM-7610FF by Jeol was used for SEM. The XRD and XRF analysis results for spent solar cells are shown in Figure 1. The XRD analysis result confirmed that Si and Al's phases are present on the surface of the spent solar cells. From the XRF analysis result, Si and Al were mostly detected. In addition, a small amount of Ag and other impurities was detected.

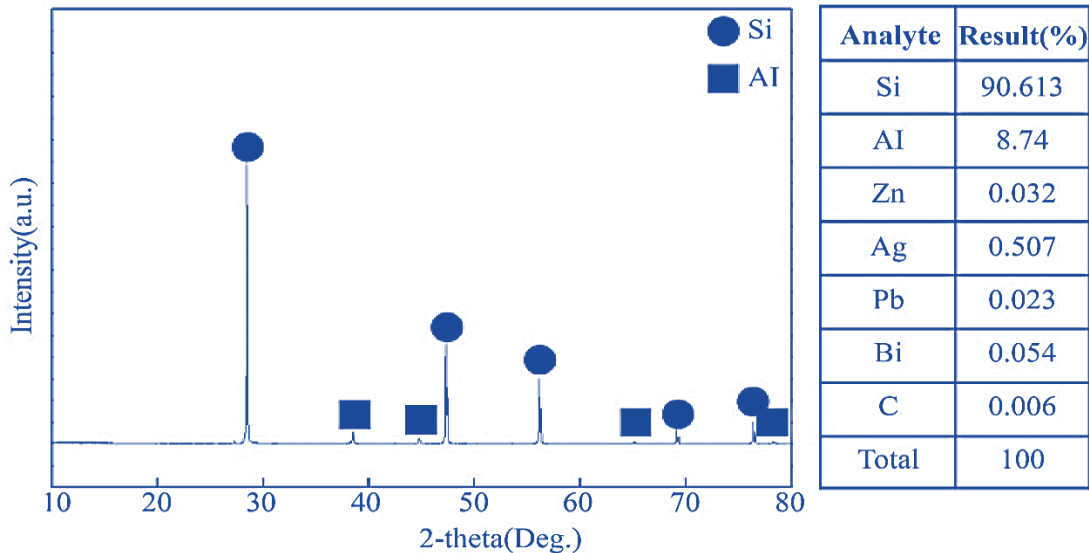
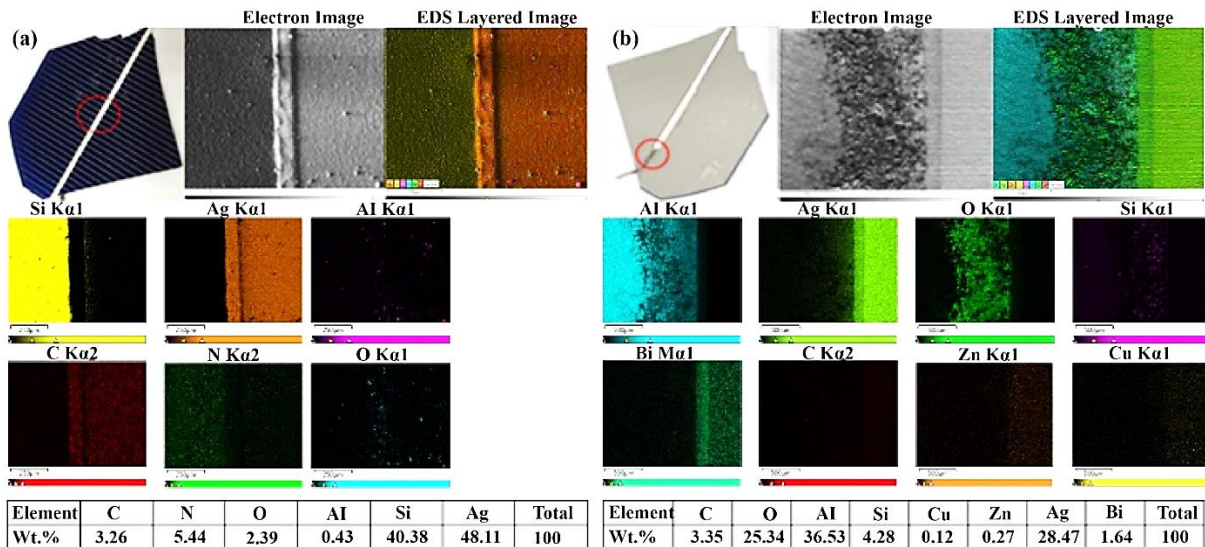


Fig. 1 XRD and XRF analysis results for spent solar cells.



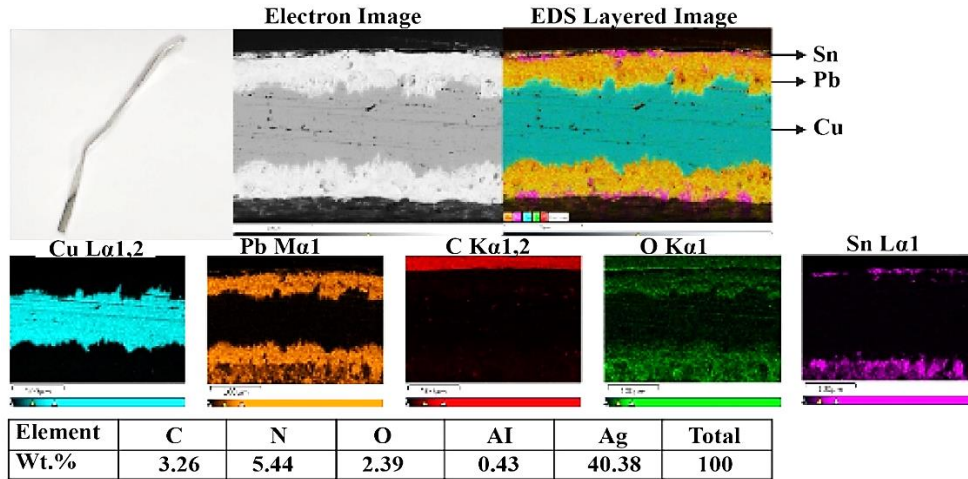


Fig. 2 SEM-Mapping Analysis results for spent solar cells (a) Front side of the solar cell (b) Back side of the solar cell (c) PV ribbon cross-section

In addition, the SEM-Mapping analysis results for the front and back sides of the spent solar cells and PV ribbon are shown in Figure 2. For the SEM-Mapping analysis of the spent solar cells, the parts marked with red circles in Figure 2 (a) and (b) were analyzed for the SEM-Mapping analysis of the PV ribbon, and the exposed cross-section after polishing was analyzed. The SEM-Mapping analysis result confirmed that Si and Ag are mostly present on the front side, and Al and Ag are mostly present on the back side of the spent solar cells. It confirms that the PV ribbon has a structure in which Pb and Sn surround Cu, which is the core, and that Cu and Pb were mostly present.

### 3. Experiment Methods

In this study, the behavior of the impurities in solar cells was identified through thermodynamic modeling for each acid solution by utilizing data from the Stabcal Modeling Program (Montana Tech, USA) to effectively recover Si and Ag from spent solar cells and Cu wires. The data for the Stabcal Modeling Program is shown in Figure 3. Based on this, the selection and experiment design for the optimal acid solution was carried out.

As shown in Figure 3, in HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub>, Al is dissolved in the Al<sup>3+</sup>, AlOH<sup>2+</sup>, and Al(OH)<sub>2</sub><sup>+</sup> states when the pH is lower than 3. While Si does not dissolve in the acid region, the formation of Al and Si compounds between pH 2~10 when H<sub>2</sub>SO<sub>4</sub> is used is expected to be unsuitable for recovering Si. In addition, Ag precipitates into AgCl in all pH regions in HCl when the content is 10 ppm or higher. In H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>, Ag dissolves into the Ag<sup>+</sup> state when pH is lower than pH 10 and pH 8, respectively. Therefore, since Ag in HCl mostly precipitates into AgCl form, it was expected to be unsuitable for recovering Si and Ag since the removal rate from the solar cell surface is low.

Finally, since it was determined using HNO<sub>3</sub> would be suitable for the effective removal of Al, which is an impurity, and recovery of Si and Ag, HNO<sub>3</sub> was selected as the acid solution to be used during leaching. In addition, since it was judged that Ag recovery from the filtered solution after HNO<sub>3</sub> leaching would be possible due to AgCl precipitation, HCl was selected as the acid solution to be used for Ag recovery.

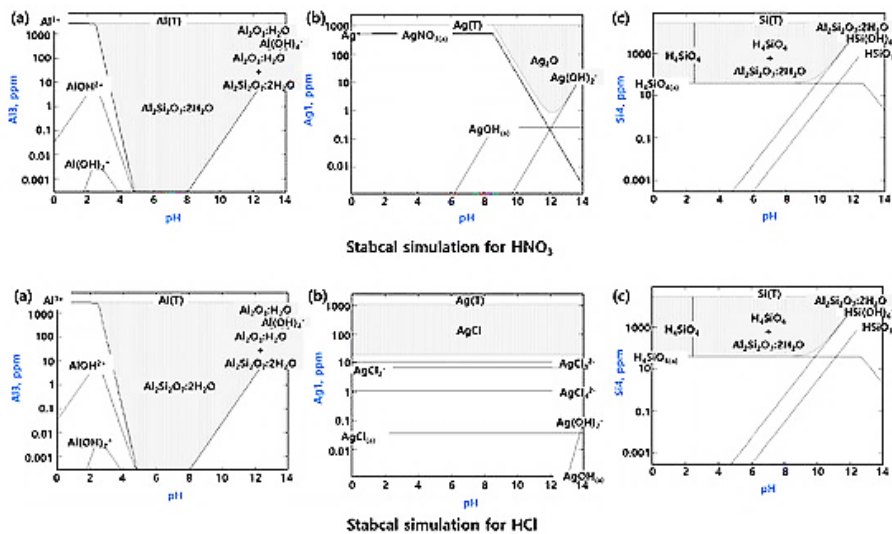


Fig. 3 Stability diagram for (a) Al (b) Ag (c) Si

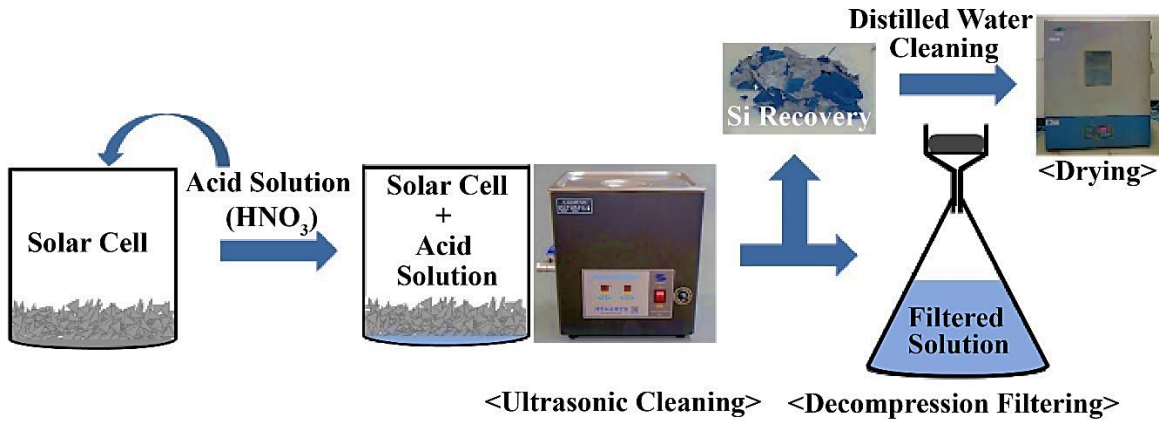


Fig. 4 Si recovery experiment process chart

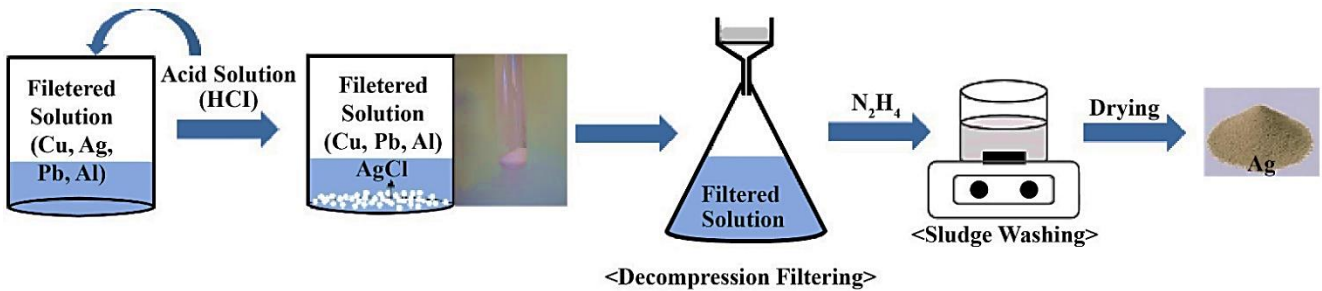
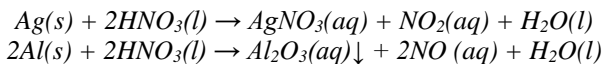


Fig. 5 Ag recovery experiment process chart

### 3.1. Si Recovery Process by Acid Solution Leaching Reaction of Solar Cells and PV ribbon

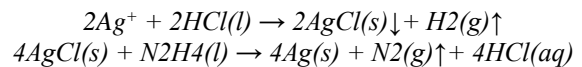
For the experimental condition to selectively recover Si from solar cells and PV ribbon by using an ultrasonic cleaner and an acid solution, an experiment was conducted using the concentration, leaching reaction temperature, reaction time, and ultrasonic intensity of an acid solution (HNO<sub>3</sub>) as the variables. After inserting 13 g of a spent solar cell and 2.5 g of PV ribbon into a beaker containing 100 ml of an HNO<sub>3</sub> solution prepared by mixing HNO<sub>3</sub> and distilled water, leaching was conducted to remove impurities by using an ultrasonic cleaner. After the leaching reaction was completed, the solar cell was washed with distilled water and dried in a drying furnace at 100°C for 24 hours. In addition, decompression filtration was carried out on the acid solution that had reacted with the solar cell and ICP-OES analysis was conducted on the filtered solution. After crushing the dried solar cell into a fine powder, XRD and XRF analyses were conducted. The expected reaction equations of Al and Ag in the solar cell and the acid solution (HNO<sub>3</sub>) are shown below. In addition, the Si recovery experiment process chart is shown in Figure 4.



### 3.2. Ag Recovery Process through Acid Solution-Based Sediment

For the experimental condition to selectively recover Ag from the filtered solution after it had reacted with the solar cell, an experiment was conducted by using the HCl input amount as the variable. The sediment formation reaction experiment was conducted by adding HCl to the filtered solution. Decompression filtration was carried out

to recover the sediment powder formed after adding HCl. A reduction reaction was carried out by adding Hydrazine(N<sub>2</sub>H<sub>4</sub>) to the sediment powder that was recovered after the filtration. The powder in which the reduction reaction had completed was recovered after sludge washing and decompression filtration and dried in a drying furnace at 100°C for 24 hours. In addition, ICP-OES analysis was conducted by recovering the filtered solution after recovering the sediment powder to check the sediment formation reaction rate through the residual quantity of Ag. The dried powder was recovered, and XRD and XRF analyses were conducted. The expected reaction equations of Ag and HCl in the filtered solution and the sediment and Hydrazine(N<sub>2</sub>H<sub>4</sub>) formed are shown below. In addition, the Ag recovery experiment process chart is shown in Figure 5.



## 4. Results and Discussion

### 4.1. Acid Solution Concentration Experiment

An experiment was conducted by changing the concentration of the HNO<sub>3</sub> solution to understand the effect of the acid solution (HNO<sub>3</sub>) in selectively recovering Si from spent solar cells and PV ribbons. After inserting 13 g of a spent solar cell and 2.5 g of PV ribbon into a beaker containing 100 ml of a 1, 2, 3M HNO<sub>3</sub> solution, a leaching experiment was conducted by using an ultrasonic cleaner. At this time, the experiment was conducted by fixing the reaction temperature to 60°C, the reaction time to 60min, and the ultrasound intensity to 125W. After the leaching reaction was completed, the solar cell was washed with distilled water and dried in a drying furnace at 100°C for 24

hours. In addition, decompression filtration was carried out on the acid solution that had reacted with the solar cell. After crushing the dried solar cell into a fine powder, XRD and XRF analyses were conducted. ICP-OES analysis was conducted on the filtered solution.

XRD and XRF analysis results for the solar cell that was recovered after drying are shown in Figure 6 and Table 1.

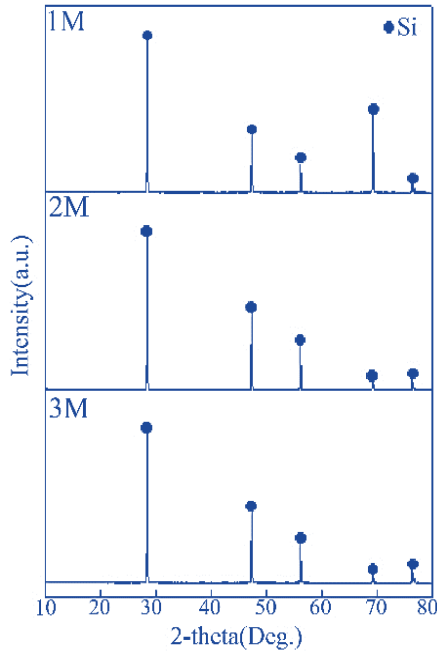


Fig. 6 XRD analysis result of the recovered solar cell after leaching according to the acid solution.

Table 1. XRF analysis results of the recovered solar cell after leaching according to the acid solution (HNO<sub>3</sub>) concentration.

Concentration (M)	Analyzed Element (%)				
	Si	Al	Cu	Pb	Total
1	95.14	4.34	-	0.52	100
2	98.87	0.85	0.28	-	
3	99.17	0.83	-	-	

From the XRD analysis result for the recovered solar cell, only the Si phase was detected in all acid solution concentrations 1, 2, and 3M. From the XRF analysis result, it was confirmed that as the concentration of the HNO<sub>3</sub> solution increases, the purity of Si increases and that the removal of Al, the impurity that is contained the most on the solar cell surface, is effective.

The ICP-OES analysis result for the filtered solution that had reacted with the solar cell for each acid solution (HNO<sub>3</sub>) concentration is shown in Table 2.

Table 2. ICP-OES analysis result of the filtered solution after leaching according to the acid solution (HNO<sub>3</sub>) concentration.

Concentration (M)	Analyzed Element (mg/L)					
	Al	Ag	Si	Cu	Pb	Sn
1	9,397	2	110	55	187	110
2	12,685	21	<1	7,752	1,372	<1
3	12,435	851	<1	26,385	1,213	<1

The ICP-OES analysis result confirmed the impurities removed from the solar cell surface through the element content in the filtered solution. The elements, excluding Si and Sn, were dissolved in the acid solution (HNO<sub>3</sub>). As the concentration of the HNO<sub>3</sub> solution was increased, a tendency for impurities to be removed more effectively from the solar cell surface was shown. For Al, removing 12,000 ppm or more was possible when the acid solution concentration was 2M or higher. For Ag, it was confirmed that the rate of removal from the solar cell was the highest when the acid solution concentration was 3M. In addition, when the concentration of the HNO<sub>3</sub> solution was 1M, 2M, and 3M, the filtered solution was observed to be colorless, light blue, and dark blue, respectively, from the experiment result.

Through this, it was confirmed that the PV ribbon was not completely dissolved when the concentration of the HNO<sub>3</sub> solution was 1M or 2M and that the PV ribbon was mostly dissolved when the concentration was 3M compared with Table 2.

The weight and recovery rate of the solar cell before and after leaching are shown in Table 3. As the result of leaching at the acid solution concentration, the weight of the solar cell decreased from 1M 13g, 2M 13.03g, and 3M 13.10g before leaching to 1M 12.05, 2M 11.65, and 3M 11.7g after leaching. The Si content in the raw sample solar cell was 90.613%. When the Si content in the solar cell was calculated before leaching, it was 1M 11.78g, 2M 11.81g, and 3M 11.87g. After leaching, the Si content in the solar cell was confirmed to be 1M 11.46g, 2M 11.52g, and 3M 11.6g. The recovery rate of Si was calculated from the weight of the solar cell before and after leaching, and the XRF analysis result is in Table 1. The Si recovery rate calculation was done through equation (1) below. The results of the Si recovery rate calculation, which were 1M 97.28%, 2M 97.54% and 3M 97.73%, confirmed that the recovery rate is highest when the HNO<sub>3</sub> solution concentration is 3M.

$$\text{Si recovery rate(\%)} = \frac{\text{Si weight percent (wt\%) that exists in solar cells that were recovered after drying}}{\text{Si weight percent (wt\%) that exists in solar cells}} \times 100(1)$$

**Table 3.** Solar cell weight and Si recovery rate before and after leaching according to the acid solution concentration

Concentration (M) \ Weight (g)	Before leaching	After leaching	Si recovery rate (%)
1	13	12.05	97.28
2	13.03	11.65	97.54
3	13.10	11.7	97.73

#### 4.2. Reaction Temperature Experiment

An experiment was conducted by changing the reaction temperature to understand the leaching reaction temperature's effect in selectively recovering Si from spent solar cells and PV ribbons. After inserting 13 g of a solar cell and 2.5 g of PV ribbon into a beaker containing 100 ml of a 3M HNO<sub>3</sub> solution which was derived from the experiment that was conducted previously, a leaching experiment was conducted by using an ultrasonic cleaner. At this time, the experiment was conducted by fixing the reaction time to 60min, the ultrasound intensity to 125W, and by changing the reaction temperature to 30°C, 40°C, 50°C, and 60°C. After the leaching reaction, the solar cell was washed with distilled water and dried in a drying furnace at 100°C for 24 hours. Decompression filtration was carried out for the acid solution that had reacted with the solar cell. After crushing the dried solar cell into a fine powder, XRD and XRF analyses were conducted. In addition, ICP-OES analysis was conducted on the filtered solution.

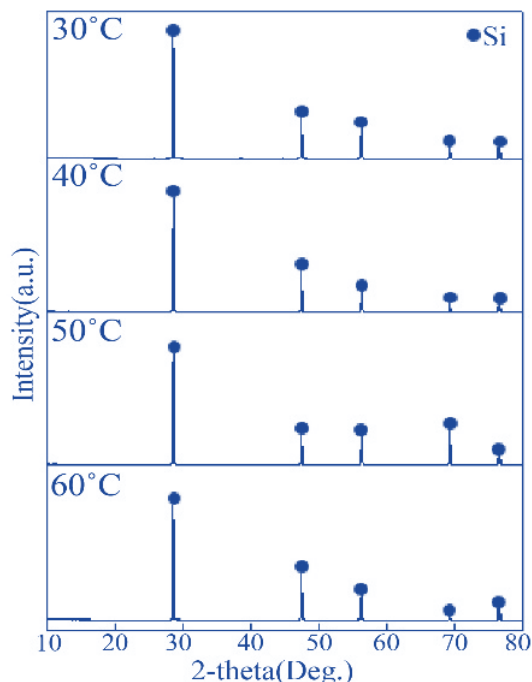
XRD and XRF analysis results for the solar cell that was recovered after drying are shown in Figure 7 and Table 4.

From the XRD analysis result of the recovered solar cell, only Si phases were detected at the leaching reaction temperatures of 30°C, 40°C, 50°C, and 60°C. From the XRF analysis result, Si purity of 99% or higher was shown for all temperatures except the reaction temperature of 30°C. It was confirmed that as the reaction temperature increases, the purity of Si increases and that the removal of Al, which is an impurity, was effective.

**Table 5.** ICP-OES analysis result of the filtered acid solution after leaching in an acid solution (HNO<sub>3</sub>) according to the reaction temperature.

Temperature (°C)	Analyzed Element (mg/L)					
	Al	Ag	Si	Cu	Pb	Sn
30	10,225	551	21	24,455	1,213	<1
40	10,325	414	24	25,975	1,326	<1
50	10,605	433	34	23,845	1,389	<1
60	11,486	811	<1	26,779	1,465	<1

The ICP-OES analysis result confirmed that as the leaching reaction temperature increased, the removal of Al, an impurity on the solar cell's surface, became more effective. While Ag can be removed at all temperatures, the removal rate was confirmed to be highest at the reaction temperature of 60°C. The weight and recovery rate of the solar cell

**Fig. 7** XRD analysis result of the recovered solar cell after leaching in an acid solution (HNO<sub>3</sub>) according to the reaction temperature.**Table 4.** XRF analysis result of the recovered solar cell after leaching in an acid solution (HNO<sub>3</sub>) according to the reaction temperature.

Temperature (°C)	Analyzed Element (%)	
	Si	Al
30	98.62	1.38
40	99.12	0.88
50	99.48	0.52
60	99.65	0.35

ICP-OES analysis result of the filtered solution that had reacted with the solar cell after leaching in an acid solution (HNO<sub>3</sub>) according to the reaction temperature is shown in Table 5.

before and after leaching according to reaction temperature are shown in Table 6. During acid solution leaching according to the reaction temperature, the weight of the solar cell decreased from 30°C 13g, 40°C 13.04g, 50°C 13.03g, and 60°C 13g before leaching to 30°C 11.81g, 40°C 11.90g, 50°C 11.81g, and 60°C 11.68g after leaching. The

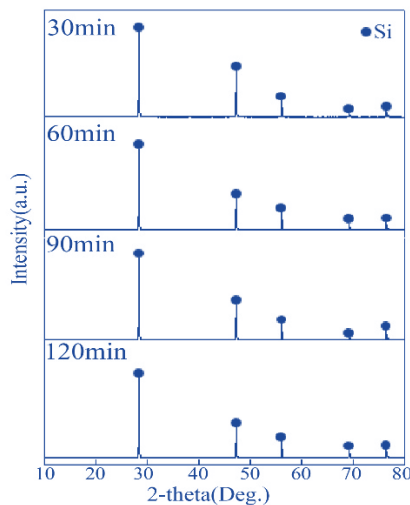
Si content in the raw sample solar cell was 90.613%. When the Si content in the solar cell was calculated before leaching, it was 30°C 11.78g, 40°C 11.82g, 50°C 11.82g, and 60°C 11.78g. The Si content in the solar cell after leaching was confirmed to be 30°C 11.65g, 40°C 11.62g, 50°C 11.64g, and 60°C 11.64g. The result of calculating the Si recovery rate through equation (1) was 30°C 98.89%, 40°C 98.31%, 50°C 98.48%, and 60°C 98.81%, and the recovery rate was confirmed to be highest at the reaction temperature of 30°C.

**Table 6. Solar cell weight and recovery rate before and after leaching in an acid solution (HNO<sub>3</sub>) according to the reaction temperature.**

Weight (g) / Temperature (°C)	Before leaching	After leaching	Si Recovery Rate (%)
30	13.00	11.81	98.89
40	13.04	11.90	98.31
50	13.03	11.81	98.48
60	13.00	11.68	98.81

**4.3. Effect of Reaction Time Experiment**

An experiment was conducted by changing the reaction time to understand the effect the leaching reaction time has in selectively recovering Si from spent solar cells and PV ribbons. After inserting 13 g of a solar cell and 2.5 g of Cu wire into a beaker containing 100 ml of a 3M acid solution (HNO<sub>3</sub>) which was derived from the experiment that was conducted previously, a leaching experiment was conducted by using an ultrasonic cleaner. At this time, the experiment was conducted by fixing the reaction temperature to 60°C and the ultrasound intensity to 125W and changing the reaction time to 30min, 60min, 90min, and 120min. After the leaching reaction was completed, the solar cell was washed with distilled water and dried in a drying furnace at 100°C for 24 hours. Decompression filtration was carried out for the acid solution that had reacted with the solar cell. After crushing the dried solar cell into a fine powder, XRD and XRF analyses were conducted. In addition, ICP-OES analysis was conducted on the filtered solution.



**Fig. 8 XRD analysis result of the recovered solar cell after leaching in an acid solution(HNO<sub>3</sub>) according to the reaction time.**

**Table 7. XRF analysis result of the recovered solar cell after leaching in an acid solution(HNO<sub>3</sub>) according to the reaction time.**

Time (min) / Analyzed Element (%)	Si	Al
30	99.86	0.14
60	99.76	0.24
90	99.77	0.23
120	99.56	0.44

From the XRD analysis result, only Si phases were detected at all reaction times. From the XRF analysis result, a Si purity of 99% or higher was shown for all reaction times and Si purity was confirmed to be highest at the reaction time of 30min.

ICP-OES analysis result of the filtered solution that had reacted with the solar cell after leaching in an acid solution (HNO<sub>3</sub>) according to the reaction time is shown in Table 8.

**Table 8. ICP-OES analysis result of the filtered acid solution after leaching in an acid solution(HNO<sub>3</sub>) according to the reaction time.**

Time (min) / Analyzed Element (mg/L)	Al	Ag	Si	Cu	Pb	Sn
30	16,810	2,053	28	29,045	2,121	<1
60	13,959	1,939	26	26,875	1,845	<1
90	15,134	1,542	27	25,785	1,956	<1
120	1,934	1,934	28	25,695	1,532	<1

From the ICP-OES analysis result, the element content in the filtered solution displayed a tendency for Al and Ag to be removed more effectively from the solar cell surface when the leaching reaction time was shorter. At the reaction time of 30 min, Al and Ag contents were found to be the highest, and the removal of Al and Ag was confirmed to be the most effective.

The weight and recovery rate of the solar cell before and after leaching according to the reaction time is shown in Table 9. During acid solution leaching according to the reaction time, the weight of the solar cell decreased from 30min 13g, 60min 13.04g, 90min 13.03g, and 120min 13g before leaching to 30min 11.67g, 60min 11.61g, 90min 11.59g, and 120min 11.60g after leaching. The Si content in the solar cell, which is a raw sample, was 90.613%. When the Si content in the solar cell was calculated before leaching, it was 30min 11.78g, 60min 11.82g, 90min 11.81g, and 120min 11.78g. The Si content after leaching was confirmed to be 30min 11.65g, 60min 11.58g, 90min 11.56g, and 120min 11.55g. The result of calculating the Si recovery rate through equation (1) was 30min 98.89%, 60min 97.97%, 90min 97.88%, and 120min 98.05%. A recovery rate of 98% or higher was shown at the reaction time of 60min and 120min, and a recovery rate of 97% or higher was shown at the reaction time of 30min and 90min. In addition, the recovery rate was confirmed to be highest when the reaction time was 30 min.

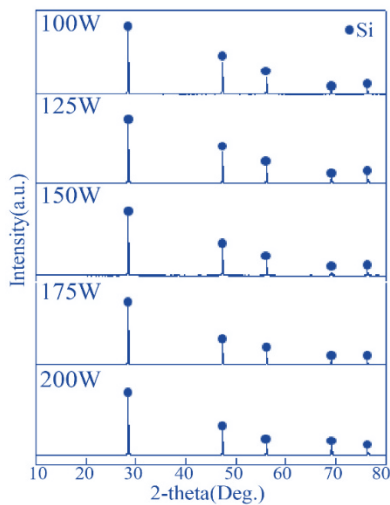
**Table 9. Solar cell weight and recovery rate before and after leaching in an acid solution(HNO<sub>3</sub>) according to the reaction time.**

Weight (g) \ Time (min)	Before leaching	After leaching	Si recovery rate (%)
30	13.00	11.67	98.89
60	13.04	11.61	97.97
90	13.03	11.59	97.88
120	13.00	11.60	98.05

**4.4. Effect of Reaction Time Experiment**

An experiment was conducted by changing the ultrasound intensity to understand the effect ultrasound intensity has in selectively recovering Si during an acid solution leaching reaction using an ultrasonic cleaner to recover Si from spent solar cells and PV ribbon selectively. After inserting 13 g of a solar cell and 2.5 g of PV ribbon into a beaker containing 100 ml of a 3M acid solution (HNO<sub>3</sub>) which was derived from the experiment that was conducted previously, a leaching experiment was conducted by fixing the reaction temperature to 60°C, the reaction time to 30min, and by changing the ultrasound intensity to 100W, 125W, 150W, 175W, and 200W. After the leaching reaction was completed, the solar cell was washed with distilled water and dried in a drying furnace at 100°C for 24 hours. Decompression filtration was carried out for the acid solution that had reacted with the solar cell. After crushing the dried solar cell into a fine powder, XRD and XRF analyses were conducted. In addition, ICP-OES analysis was conducted on the filtered acid solution.

XRD and XRF analysis results for the solar cell that was recovered after drying are shown in Figure 9 and Table 10. From the XRD analysis result, only Si phases were detected for all ultrasound intensities. From the XRF analysis result, it can be confirmed that 99% or higher Si purity is shown when ultrasound intensity is 125W, 150W, and 200W. It can be confirmed that Si purity is highest and removal of Al, which is an impurity, is most effective when ultrasound intensity is 200W.



**Fig. 9 XRD analysis result of the recovered solar cell after leaching in an acid solution(HNO<sub>3</sub>) according to the ultrasound intensity**

**Table 10. XRF analysis result of the recovered solar cell after leaching in an acid solution(HNO<sub>3</sub>) according to the ultrasound**

Analyzed Element (%) \ Ultrasound Intensity (W)	Si	Al
100	98.78	1.22
125	99.33	0.67
150	98.32	1.68
175	99.12	0.88
200	99.58	0.42

ICP-OES analysis result of the filtered solution that had reacted with the solar cell after leaching in an acid solution according to the ultrasound intensity is shown in Table 11.

**Table 11. ICP-OES analysis result of the filtered acid solution after leaching in an acid solution(HNO<sub>3</sub>) according to the ultrasound intensity**

Analyzed Element (mg/L) \ Ultrasound Intensity (W)	Al	Ag	Si	Cu	Pb	Sn
100	11,175	239	24	23,174	1,493	N.D.
125	12,698	1,516	31	27,595	1,522	N.D.
150	12,794	953	33	25,223	1,515	N.D.
175	14,350	724	34	24,475	1,506	N.D.
200	10,784	1,586	25	27,101	1,642	N.D.

From the ICP-OES analysis result, the element content in the filtered solution was most effective in removing Al, an impurity, from the solar cell's surface when the ultrasound intensity was 175W. It can be confirmed that removing Ag is most effective when the ultrasound intensity is 200W.

The weight and recovery rate of the solar cell before and after leaching in an acid solution according to the ultrasound intensity is shown in Table.12. During acid solution leaching according to the ultrasound intensity, the weight of the solar cell decreased from 100W 13.02g, 125W 13.04g, 150W 13g, 175W 13g, and 200W 13g before leaching to 100W 11.71g, 125W 11.49g, 150W 11.65g, 175W 11.48g, and 200W 11.71g after leaching. The Si content in the raw sample solar cell was 90.613%. When the Si content in the solar cell was calculated before leaching, it was 100W 11.79g, 125W 11.82g, 150W 11.78g, 175W 11.78g, and 200W 11.78. The Si content after leaching was confirmed to be 100W 11.57g, 125W 11.41g, 150W 11.45g, 175W 11.38g, and 200W 11.66g. The result of calculating the Si recovery rate through equation (1) was 100W 98.13%, 125W 96.53%, 150W 97.19%, 175W 96.6%, and 200W 98.98%. A Si recovery rate of 98% or higher was shown at the ultrasound intensity of 100W and 200W, and the recovery rate was confirmed to be highest at the ultrasound intensity of 200W.



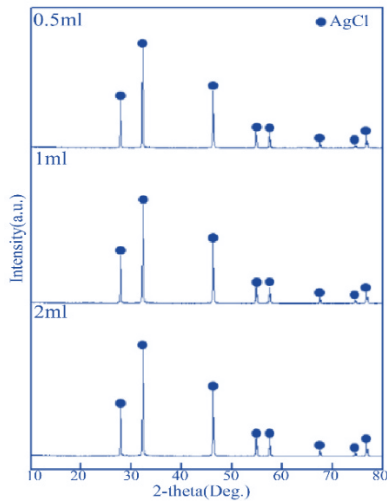
**Table 12. Solar cell weight and recovery rate before and after leaching in an acid solution(HNO<sub>3</sub>) according to the ultrasound intensity**

Weight (g) Ultra sound Intensity (W)	Before leaching	After leaching	Si recovery rate (%)
100	13.02	11.71	98.13
125	13.04	11.49	96.53
150	13.00	11.65	97.19
175	13.00	11.48	96.6
200	13.00	11.71	98.98

**4.5. Ag Recovery Experiment through Sedimentation Reaction**

To selectively recover Ag from solar cells and PV ribbon, the acid solution that had reacted with the solar cell after acid solution (HNO<sub>3</sub>) leaching was decompression filtered. The experiment was conducted by changing the input amount of HCl by 0.5, 1, and 2 ml in the filtered solution. After adding HCl, mixing was carried out at room temperature, mixing speed of 300rpm and a mixing time of 5min. When the mixing was completed, the sediment powder formed in the solution was recovered after filtering and dried in a drying furnace at 100°C for 24 hours. After drying was completed, XRD and XRF analysis was conducted on the sediment powder. After the sediment powder was recovered, ICP-OES analysis was conducted on the filtered solution.

XRD and XRF analysis results of the sediment powder that was recovered after drying are shown in Figure 10 and Table 13.



**Fig. 10 XRD analysis result of the recovered sediment powder after drying according to the HCl input amount.**

**Table 13. XRF analysis result of the recovered sediment powder after drying according to the HCl input amount.**

Analyzed Element (%) HCl Input Amount (ml)	Ag	Cl	Al
0.5	65.63	33.94	0.42
1	66.56	32.94	0.50
2	74.31	25.25	0.43

From the XRD analysis result, only AgCl phases were detected when HCl 0.5, 1, 2ml was added. From the XRF analysis result, it can be confirmed that the purity of AgCl is 99% or higher for all cases. From the XRD and XRF analysis results, it is thought that AgCl sediment was formed when AgNO<sub>3</sub>, which exists in the solution filtered after reacting with the solar cell, reacted with HCl.

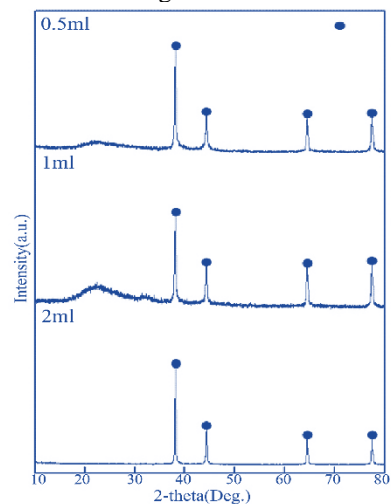
To find out the sediment formation reaction amount according to the HCl input amount, the ICP-OES analysis result of the recovered solution before and after decompression filtration is shown in Table 14.

**Table 14. ICP-OES analysis result of the recovered solution before and after decompression filtration according to the HCl input amount**

Input Amount (ml) Analyzed Element	Before HCl input			After HCl input		
	0.5	1	2	0.5	1	2
Cu	28,226	27,489	27,884	22,043	24,703	23,539
Pb	1,621	1,839	1,930	1,326	1,664	1,679
Sn	0.2	0.3	1,1	<0.1	<0.1	<0.1
Al	11,417	11,216	10,813	9,500	10,148	9,416
Si	11,216	24	21	23	21	18
Ag	10,813	937	1,422	0.5	0.7	1.3

From the ICP analysis result of the recovered solution, it can be confirmed that precipitation of AgCl due to the sediment formation reaction occurred for 99% or higher when HCl 0.5, 1, 2ml was added. To recover Ag from AgCl, 5 ml of Hydrazine(N<sub>2</sub>H<sub>4</sub>) was added to proceed with the reduction reaction. After the reduction reaction was completed, the powder was washed with distilled water, decompression filtered and then dried in a drying furnace at 100°C for 24 hours. XRD and XRF analysis were conducted after the dried powder was recovered.

XRD and XRF analysis results of the recovered powder after drying are shown in Figure 11 and Table 15



**Fig. 11 XRD analysis result of the recovered Ag powder after sediment formation and reduction reaction according to the HCl input amount**

**Table 15. XRF analysis result of the recovered Ag powder after sediment formation reaction and reduction reaction according to the HCl input amount**

Input Amount (ml) \ Analyzed Element (%)	Ag	Si
0.5	99.48	0.22
1	99.72	0.28
2	99.74	0.26

From the XRD analysis result of the recovered powder, only Ag phases were detected after the sediment formation reaction and reduction reaction according to the HCl input amount. From the XRF analysis result, Ag purity of 99% or higher can be confirmed. It can be confirmed that Ag purity is highest when 2ml of HCl is added.

The weight of Ag in the filtered solution after recovering the solar cell and before adding HCl and the weight of the Ag in the recovered powder after the sediment formation reaction and reduction reaction according to the HCl input amount and the recovery rate of Ag are shown in Table 16.

**Table 16. Ag weight in the filtered solution before HCl input according to the HCl input amount and weight of the recovered powder after HCl input and reduction reaction and the Ag recovery rate.**

Input Amount (ml) \ Weight (g)	Before HCl input	After HCl input	Ag Recovery rate (%)
0.5	0.073	0.06	82.18
1	0.068	0.062	91.18
2	0.085	0.07	82.35

The weight of Ag in the filtered solution before adding HCl was calculated from the ICP-OES analysis results in Table 14, and the weight of Ag in the recovered powder after adding HCl and reduction reaction was calculated from the XRF analysis result in Table 15 and the weight of the recovered powder.

The recovery rate was calculated by using equation (2) below.

$$\text{Ag recovery rate} = \frac{\text{Ag weight percent (wt\%) in the powder after adding HCl and reduction reaction}}{\text{Ag weight percent (wt\%) that exists inside the solution before adding HCl}} \times 100 \quad (2)$$

The weight of Ag in the filtered acid solution after the recovered solar cell decreased from 0.5ml 0.073g, 1ml 0.068g, and 2ml 0.085g before adding HCl to 0.5ml 0.06g, 1ml 0.062g, and 2ml 0.07g after adding HCl. The result of calculating the Ag recovery rate through equation (2) was 82.18% for 0.5ml, 91.18% for 1ml, and 82.35% for 2ml of HCl input. It was confirmed that Ag recovered amount was shown to be highest when 1ml of HCl was added.

## 5. Conclusion

In this study, a leaching process utilizing an acid solution was used to selectively recover Si and Ag, which are valuable metals, from spent solar cells and PV ribbons. It was possible to select the acid solution to be used for recovering Si and Ag by identifying the behavior characteristics of the impurities in solar cells for each acid solution through thermodynamic modeling by utilizing data from the Stabcal Modeling Program. The acid solution used in the experiment was 70% HNO<sub>3</sub> and 35% HCl. In addition, the experiment was conducted by using the acid solution concentration, reaction temperature, reaction time, and ultrasound intensity for recovering Si, and the HCl input amount for recovering Ag, as the variables. The purity and recovery rate of the solar cells and the powder recovered after the experiment was calculated through XRD and XRF analysis. The removal effect for Ag and Al, which is an impurity, from the surface of the solar cells was confirmed through ICP-OES analysis by filtering the acid solution after the solar cells were recovered and the solution after the sediment formation reaction.

From the leaching experiment result, according to the acid solution (HNO<sub>3</sub>) concentration, Si's purity and recovery rate increased as the acid solution concentration

increased. It was confirmed that Si purity of 99.17% and recovery rate of 97.73% was highest when the concentration was 3M. In addition, from the ICP-OES analysis result for the filtered acid solution, it can be confirmed that 12,000 ppm or more of Al, which is an impurity, is removed from the surface of the solar cells when the concentration of the solution is 2M or higher and the removal effect for Ag is greatest when the concentration is 3M.

From the leaching test result, according to the reaction temperature, Si purity increased as the reaction temperature increased. It was possible to confirm that the recovery rate was 98% or higher for all reaction temperatures. The purity was highest at 99.76% when the reaction temperature was 60°C. From the ICP-OES analysis result of the recovered acid solution, it can be confirmed that the removal effect of Al and Ag from the surface of the solar cells was greatest when the reaction temperature was 60°C.

From the result of the leaching experiment, the Si purity was confirmed to be 99% or higher for all reaction times according to the reaction time. It was possible to confirm that the purity was highest at 99.86% when the reaction time was 30min. In addition, the Si recovery rate was 97% or higher for all reaction times. When the reaction time was 30min, the Si recovery rate was confirmed to be highest at 98.89%. From the ICP-OES analysis result for the filtered acid solution, it was possible to confirm that the removal of Al and Ag from the surface of the solar cells was most effective.

From the result of the leaching experiment according to ultrasonic intensity, Si purity of 99% or higher was shown for all ultrasound intensities, excluding the ultrasound intensity of 100W. It was possible to confirm that the purity

was highest at 99.58% when the ultrasound intensity was 200W. In addition, the recovery rate was 96% or higher for all ultrasound intensities, and it was possible to confirm that the Si recovery rate was highest at 98.98% when the ultrasound intensity was 200W. From the ICP-OES analysis result of the filtered acid solution, while the removal of Al from the surface of the solar cell was most effective when the ultrasound intensity was 175W, it was possible to confirm that the removal effect for Ag was highest at 200W.

It was possible to confirm that Ag purity of 99% or higher was shown for all HCl input amounts in the powder that was recovered after the reduction reaction, which was carried out by adding Hydrazine (N<sub>2</sub>H<sub>4</sub>) to the sediment that was formed from the result of the sediment formation reaction experiment according to the HCl input, on the acid solution that was filtered after reacting with solar cells. While Ag purity was highest at 99.74% when 2ml of HCl was input, the recovery rate was 91.18% when 1ml of HCl was input, and it is possible to confirm that this was relatively higher compared to the case in which 0.5ml and 2ml were input.

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Therefore, the optimal condition to selectively recover Si from spent solar cells and PV ribbon was derived from an acid solution(HNO<sub>3</sub>) concentration of 3M, a reaction temperature of 60°C, a reaction time of 30min, and an ultrasound intensity of 200W.

The optimal condition to selectively recover Ag was derived from being HCl amount 1ml.

From the result of the experiment for the derived optimal condition,

- purity was 99.58%, the recovery rate was 99.94% for Si,
- purity was 99.72%, and the recovery rate was 88.24% for Ag.

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