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A Study on Selective Recovery of Silicon from Used Solar Cell using Cavitation Effect

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Abstract

This study was conducted to find the optimum process condition to recover Si selectively from solar cell by removing impurities (Al, Zn, Ag, etc.) on cell surface through the use of cavitation effect of HNO_3 and ultrasonic cleaner. After the impurities were removed using the cavitation effect of HNO_3 and ultrasonic cleaner, solar cell was dried in a drying oven, and the reacted HNO_3 solution was decompression filtered, where the filtered solution was used for ICP-Full Scan analysis. In addition, solar cell was crushed after being dried for XRD and XRF analyses, which determined the purity and recovery of Si. The experiment was conducted with concentration, temperature, reaction time, and ultrasonic intensity as variables to draw the optimum process conditions. The optimum process conditions obtained from above process to recovery Si from solar cell is acid solution concentration of 3M HNO_3, reaction temperature of 60°C, reaction time of 90min, and ultrasonic intensity of 150W, and ultimately, the purity of Si was 99.78% and recovery rate was 98.9%.

Keywords: Used solar cell, Cavitation effect, Silicon, Purity, Recovery rate

1. INTRODUCTION

Recently, new renewable energy is drawing attention due to the resource issues and rising concern of environmental issues caused by rapid industrial development. With the increasing attention in new renewable energy, the use of solar energy is on the rise as it is the most popular eco-friendly energy source. According to the data by IEA (International Energy Agency) in 2017, energy generation status includes thermal and nuclear (67%), hydroelectric (20%), solar (4.4%), etc., and forecasted the reduction of thermal and nuclear power generation to 50%, while increase of solar power generation to 12% in 2040 growth prospect. [2-3)] Installation of solar modules is gradually increasing, which accumulated to approximately 509GW in 2018 worldwide, and this indicates that solar industry is continuously growing.[1)]

However, the disposal of used solar modules after their life cycle (approximately 20~30 years) has become a serious issue. According to IEA's report, about 7,600 million tons of used solar modules are expected to be disposed in 2050.[4-5)] Europe designated solar module as electronic waste through Waste Electrical and Electronic Equipment (WEEE) to be recycled.

Used solar cell module consists of silver (Ag), aluminum (Al), Silicon (Si), lead (Pb), etc.[6-7)] Used solar cell module contains hazardous substances such as lead that it is expected to cause significant environmental pollution when buried or incinerated. However, while the high-priced silicon, copper, silver, etc. in it are worth recycling, most are being buried. Since the high purification process of polysilicon accounts for approximately 50% of the energy consumed in the entire process of solar module manufacturing process, recovery of high-purity silicon from solar cell would bring economic and environmental benefits.[8)]

This study was conducted to attempt selective recovery of silicon from used solar cell using wet process. In order to improve the purity and recovery rate of recovered silicon, the concentration of solution, reaction temperature, reaction time, and ultrasonic intensity were controlled to establish the optimum process conditions.

2. MATERIALS

The raw material powder used in this study is used solar cell. Fig.1 and Table.1 display the result of analysis of used solar cell used in the study. Used solar cell was crushed and analyzed using SRD (X-Ray Diffraction) and XRF (X-Ray Fluorescence), and SEM-mapping analysis was performed on the front and back sides of used solar cell.

XRD result showed that Si and Al existed in solar cell. Based on the result of XRF analysis, 89.75% of Si, 10.18% of Al, and 0.07% of Zn existed. SEM-Mapping analyzed the red circle area marked in Fig.1, which detected Ag that was not detected in XRD and XRF analyses.

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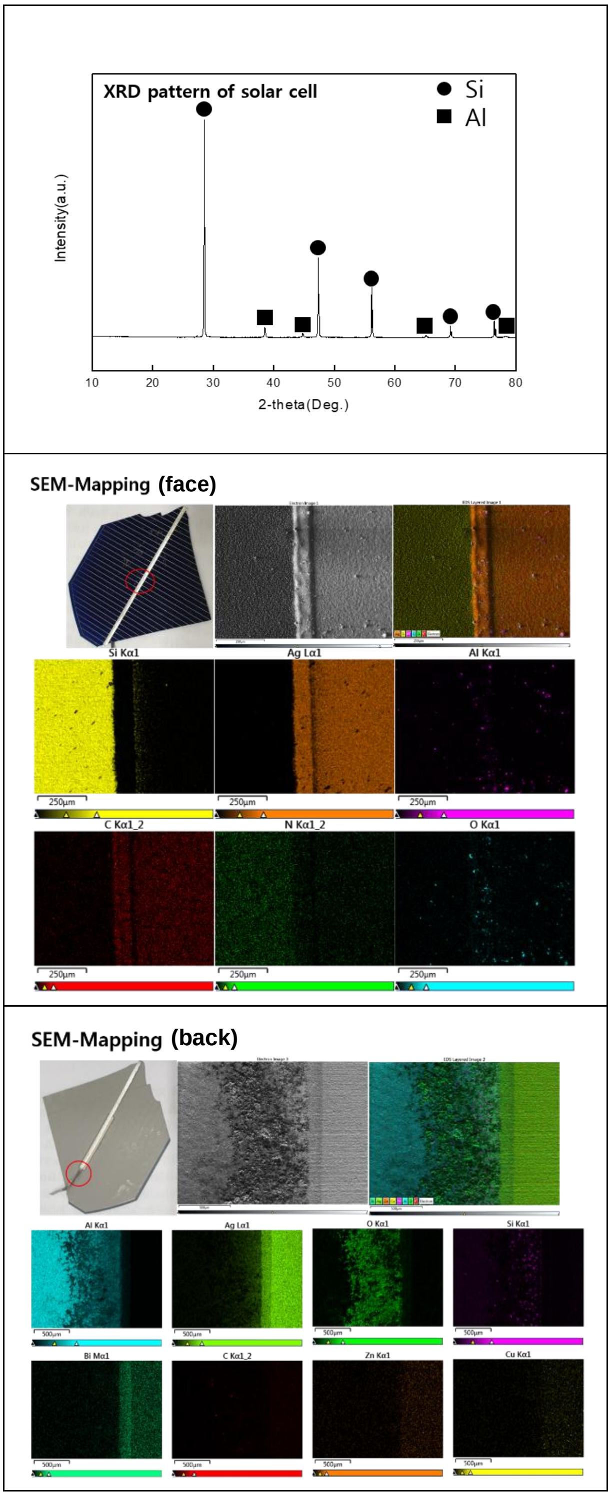

Fig. 1 XRD and SEM-Mapping results of used solar cell

Table 1. XRF result of used solar cell

Element	Si	Al	Zn	Total
Result(%)	89.75	10.18	0.07	100

3. EXPERIMENT METHOD

Result of analysis showed that used solar cell included Al, Ag, Zn, etc. in addition to Si. As seen in Fig.2, under HNO_3 condition, Al dissolves into Al^{3+}, $AlOH^{2+}$, and $Al(OH)_2^+$ at pH 3 or below, Ag dissolves into Ag^+ at pH 8 or below, and Si does not dissolve in acidic region.

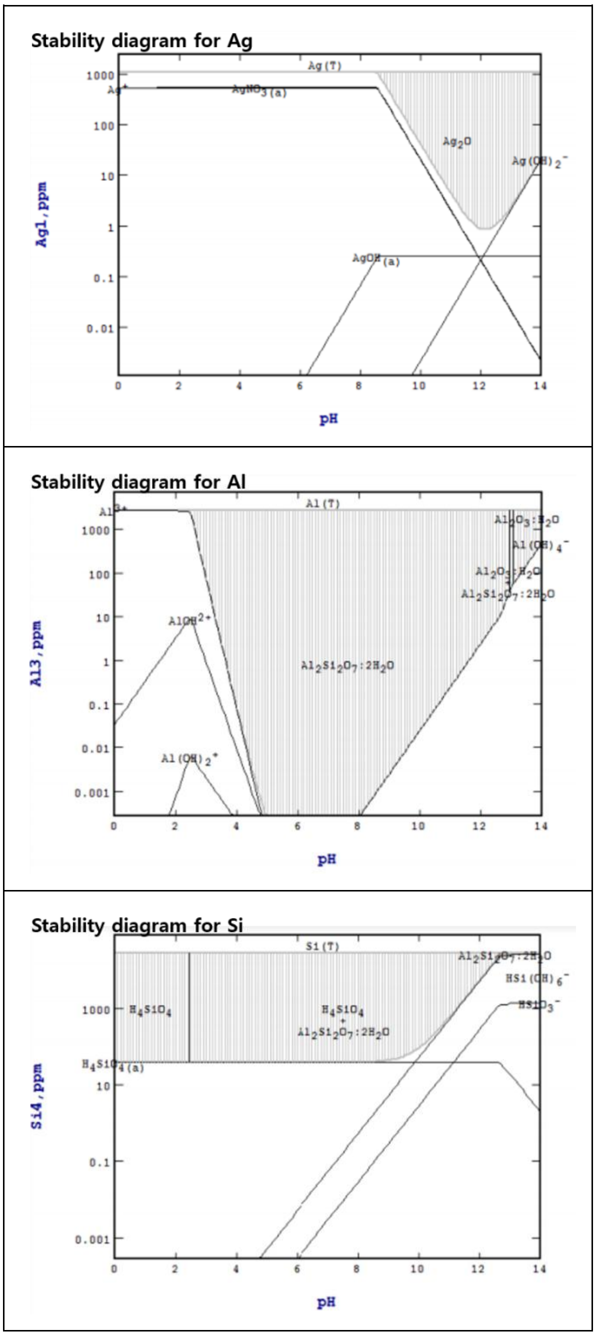

Fig. 2 Stability simulation of HNO_3

Experimental equipment to remove impurities (Al, Ag, Zn, etc.) from used solar cell and recover Si used was an ultrasonic cleaner, and acidic solvent used was 70% HNO_3 solvent.

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In order to increase the purity and recovery rate of Si, conditions such as concentration of acidic solvent, temperature, time, and ultrasonic intensity were diversified to conduct the experiment. After the reaction, solar cell was washed with distilled water and dried in a drying oven. Also, the HNO_3 solution reacted with used solar cell was decompression filtered, and ICP-Full Scan analysis was performed on filtered solution. Dried solar cell was crushed for XRD and XRF analyses.

3-1 Acid solution concentration experiment

10g of used solar cell was placed in a beaker, and the experiment was conducted with 100ml of 1M, 2M, and 3M HNO_3, while keeping temperature, reaction time, and ultrasonic intensity fixed.

3-2 Reaction temperature experiment

10g of used solar cell was placed in a beaker, and the experiment was conducted at 30, 40, 50, and 60℃, while keeping concentration, reaction time, and ultrasonic intensity fixed.

3-3 Reaction time experiment

10g of used solar cell was placed in a beaker, and the experiment was conducted at 30, 60, 90, and 120min, while keeping concentration, temperature, and ultrasonic intensity fixed.

3-4 Ultrasonic intensity experiment

10g of used solar cell was placed in a beaker, and the experiment was conducted at 100, 150, and 200W, while keeping concentration, temperature, and reaction time fixed.

4. RESULT AND DISCUSSION

4-1 Acid solution concentration experiment

XRD and XRF results of dried solar cell based on HNO_3 solution concentrations and ICP-Full Scan analysis result of filtered solution are displayed below.

As seen in Fig.3, Al was not detected in all concentrations, and only Si phase is detected. Also, as seen in XRF analysis result in Table 2, Si content was detected at 100% in 3M HNO_3 solution.

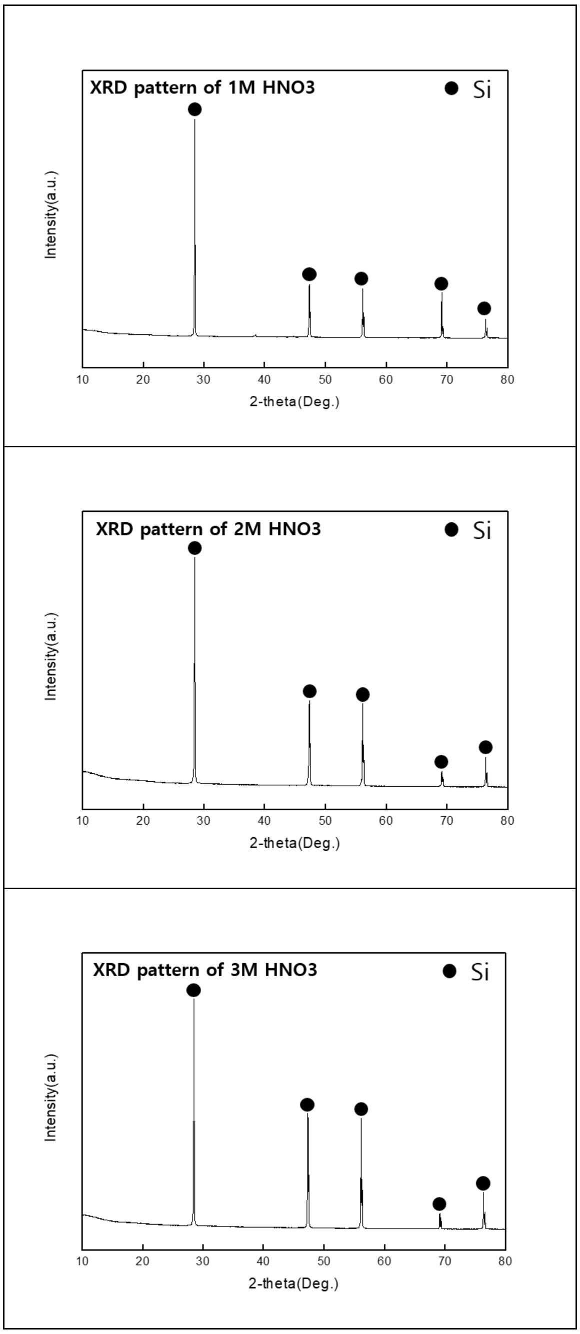


Fig. 3. XRD result of dried solar cell – Concentration

Table 2. XRF result of dried solar cell – Concentration (unit : %)

element / concentration	Si	Al	Total
1M	95.60	4.40	100
2M	99.77	0.23	
3M	100	-	

ICP-Full Scan result of filtered solution is displayed in Table 3. Based on ICP-Full Scan result, impurities (Al, Ag, Zn, etc.) were detected the most in 3M HNO_3 solution. This implies that 3M HNO_3 has the highest impurity removal effect.

Table 3. ICP-Full Scan of filtered solution – concentration

Analyzed element and content (mg/L)			
	1M	2M	3M
Al	830	1,000	1,300
Ag	0.013	280	410
Si	54	58	89
Fe	2.7	3.5	4.2
Zn	12	10	15
Pb	2.3	19	27
Bi	N/D	60	51
Ni	0.38	1.8	8.1
In	0.63	0.93	1.0
Sn	1.3	1.6	6.2
Mg	0.11	0.23	0.22
Mn	0.033	0.068	0.37
Co	0.038	0.10	0.52
Cu	0.11	2.6	0.98

In addition, weight of solar cell before reaction and weight of dried solar cell after reaction were measured, and Si recovery rate was calculated through the Si content obtained from XRF analysis result.

Table 4. Solar cell weight before/after experiment & Si recovery rate - Concentration

	Weight change		Recovery rate(%)
	Before experiment	After experiment	
1M HNO_3			97.28
2M HNO_3			97.65
3M HNO_3			98.3

As seen in Table 4, weight of solar cell was 10.02, 10.19, and 10.10g before experiment, and reduced to 9.15, 8.95, and 8.91g after experiment at 1, 2, and 3M respectively.

Calculation formula of Si recovery rate is as follows.

$$\text{Si recovery rate} = \frac{\text{Recovered Si weight}}{\text{Si weight in module}} \text{X100}$$

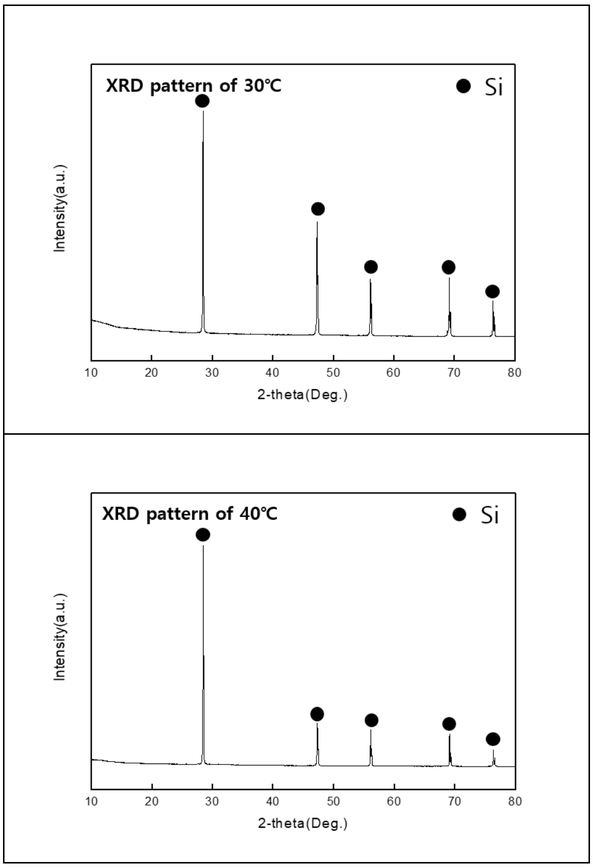
Based on the calculation using above formula, Si recovery rate is 97.28, 97.65, and 98.3% at 1, 2, and 3M respectively, showing the highest recovery rate of 98.3% in 3M HNO3 solution.

Based on the results of XRD, XRF, ICP-Full Scan, and Si recovery rate with the concentration as variable, the optimum concentration was 3M.

4-2 Reaction temperature experiment

In order to determine the optimum temperature to recover Si from used solar cell, experiment was conducted at 30, 40, 50, and 60℃, and concentration was set at 3M HNO_3 solution as determined in previous experiment, while other conditions were maintained identically.

Based on XRD analysis result in Fig. 4, impurity (Al, Zn) phase was not detected and only Si phase was detected at all temperatures, and XRF analysis result, as seen in Table 5, showed that Si purity was measured the highest (100%) at 60℃.



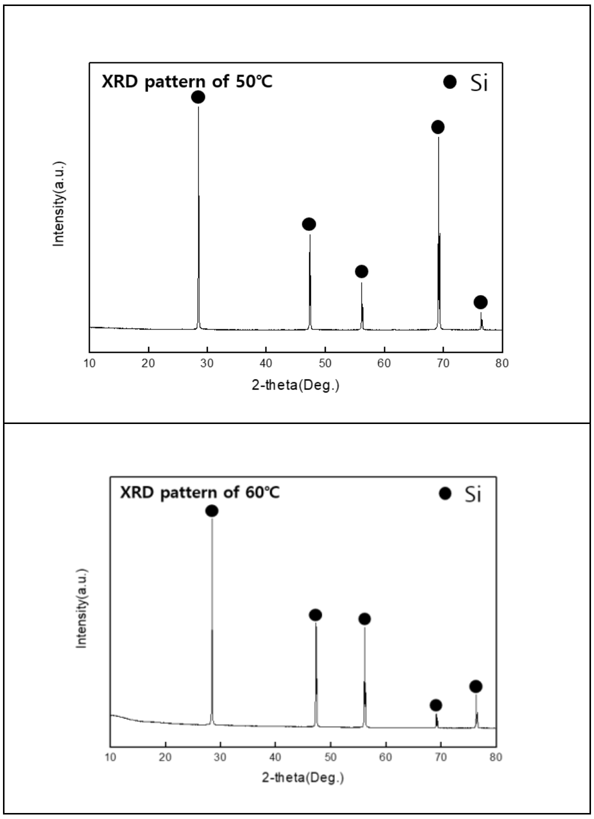


Fig. 4. XRD analysis result of dried solar cell - Temperature

Table 5. XRF analysis result of dried solar cell - Temperature

(Unit : %)

Analyzed element / Temperature(℃)	Si	Al
30	99.84	0.16
40	99.86	0.14
50	99.85	0.15
60	100	-

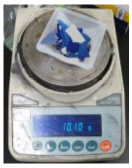
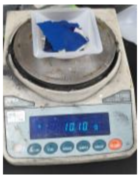
Table 6 presents the ICP-Full Scan analysis result of filtered solution by temperature. Based on ICP-Full Scan result, impurity removal rate is the highest at 60℃.

Table 6. ICP-Full Scan of filtered solution – Temperature

Analyzed element and content (mg/L)				
	30	40	50	60
Al	620	860	1,100	1,300
Ag	240	200	300	410
Si	36	55	51	89
Fe	2.5	2.9	3.2	4.2
Zn	4.2	8.1	13	15
Pb	59	11	14	27
Bi	14	31	56	51
Ni	1.0	2.2	0.4	8.1
In	0.68	0.94	0.5	1.0
Sn	4.7	1.6	1.2	6.2
Mg	0.088	0.086	0.1	0.22
Mn	0.088	0.15	<0.1	0.37
Co	0.065	0.20	<0.1	0.52
Cu	7.9	0.50	2.2	0.98

Table 7 displays the weight change of solar cell before and after the experiment. Weight was 10.10, 10.10, 10.13, and 10.10g before the experiment, and reduced to 8.78, 8.88, 8.88, and 8.91g after the experiment. Recovery rate calculated through XRF analysis result was 96.71, 97.84, 97.5, and 98.3%. The highest recovery rate was at 60℃.

Table 7. Solar cell weight before/after experiment & Si recovery weight - temperature

	Weight change		Recovery rate (%)
	Before experiment	After experiment	
30℃			96.71
40℃			97.84
50℃			97.5
60℃			98.3

Based on the experiment with temperature as variable, XRD analysis result did not show significant differences, but Si purity was the highest at 60℃, as well as impurity removal rate. Accordingly, the optimum temperature of 60℃ to recover Si was drawn.

4-3 Reaction time experiment

In order to determine the optimum time to recover Si from used solar cell, experiment was conducted at 30, 60, 90, and 120min, and concentration and temperature were set at 3M HNO_3 and 60℃ as determined in previous experiments, and ultrasonic intensity at 150W.

Based on XRD analysis result of dried solar cell, as seen in Fig. 5, only Si phase was detected under all 4 conditions (30, 60, 90, 120min).

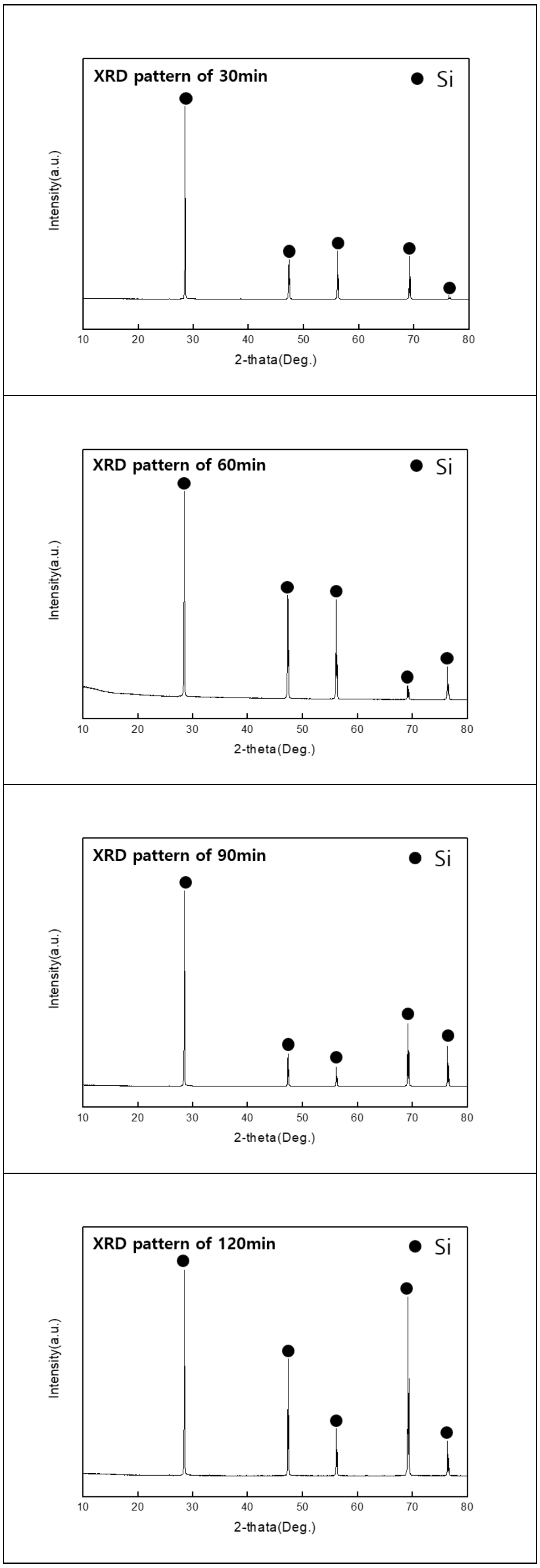


Fig. 5. XRD analysis result of dried solar cell - Time

Table 8 displays XRF analysis result of dried solar cell. Based on the result, Si purity is 99% or above under all 4 conditions (30, 60, 90, 120min). among them, Si purity was the highest at 60 min.

Table 8. XRF analysis result of dried solar cell - Time

Analyzed element / Time(min)	Si	Al
30	98.80	1.20
60	100	-
90	99.81	0.19
120	99.87	0.13

Based on ICP-Full Scan Result, as seen in Table 9, impurity removal is the highest at 30min, followed by 90, 60 and 120min.

Table 9. ICP-Full Scan of filtered solution – Time

Analyzed element and content(mg/L)				
	30	60	90	120
Al	1600	1300	1500	1300
Ag	460	410	430	330
Si	64	89	54	43
Fe	5.1	4.2	3.8	3.1
Zn	12	15	12	4.1
Pb	44	27	27	53
Bi	27	51	21	64
Ni	0.4	8.1	0.6	3.4
In	0.8	1.0	0.6	3.4
Sn	1.6	6.2	1.2	3.4
Mg	0.2	0.22	0.1	0.2
Mn	<0.1	0.37	0.1	0.1
Co	<0.1	0.52	<0.1	0.2
Cu	35	0.98	1.6	1.0

Si recovery rate obtained from experiment results by time is displayed in Table 10. Weight of solar cell went from 10.43, 10.10, 10.42, and 10.33g to 9.15, 8.91, 9.27, and 9.11g at 30, 60, 90, and 120min respectively.

Based on Si recovery rate formula (1), the recovery rate was 96.6, 98.3, 98.9, and 98.2% as seen in Table 10, and the highest at 90min.

Table 10. Weight of solar cell before/after experiment & recovery rate - time

	Weight change		Recovery rate (%)
	Before experiment	After experiment	
30min			96.6
60min			98.3

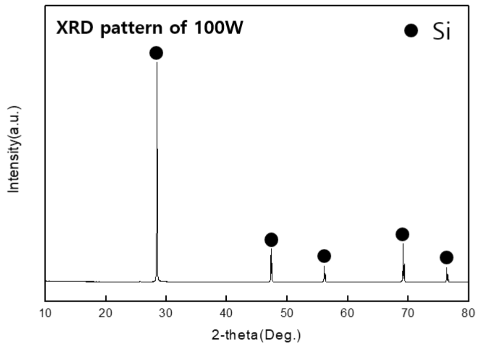
90min			98.9
120min			98.2

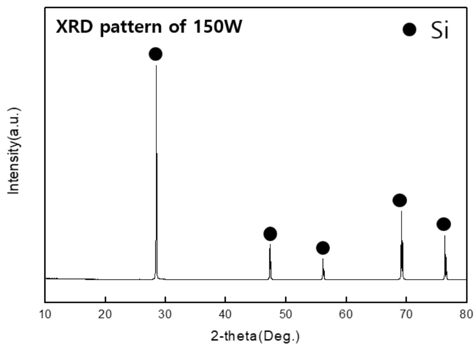
Based on XRD, XRF, ICP-Full Scan analysis and Si recovery rate results, the optimum time to recovery Si was 90 min.

4-4 Ultrasonic intensity experiment

In order to determine the optimum ultrasonic intensity to recover Si from used solar cell, experiment was conducted at 100W, 150W, and 200W. Concentration of solution was set at 3M, reaction temperature 60℃, and reaction time at 90 min to conduct the experiment.

Based on XRD analysis result in Fig. 6, Si phase is only detected at 100W, 150W, and 200W, and impurities (Al, Zn) that were detected in the XRD analysis of original sample were not detected.





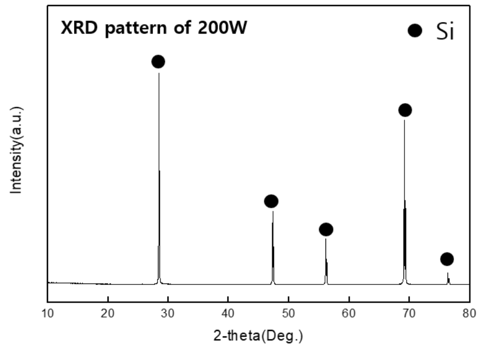


Fig. 6. XRD result of dried solar cell – Ultrasonic intensity

Result of XRF analysis of crushed dried solar cell is displayed in Table 10. As a result, Si purity was 99% or above under all 3 conditions and was the highest (99.92%) at 200W.

Table 10. XRF result of dried solar cell – Ultrasonic intensity

	Si	Al
100W	99.91	0.09
150W	99.81	0.22
200W	99.92	0.08

As seen in ICP-Full Scan result of filtered solution in Table 11, impurity (Al, Ag, Zn, etc.) content is the highest at the ultrasonic intensity of 150W.

Table 11. ICP-Full Scan of filtered solution – Ultrasonic intensity

Analyzed element and content (mg/L)			
	100	150	200
Al	1,600	1500	1,200
Ag	300	430	190
Si	61	54	45
Fe	5.7	3.8	3.1
Zn	13	12	7.5
Pb	14	27	7.2
Bi	56	21	37
Ni	0.4	0.6	0.3
In	0.5	0.6	0.7
Sn	1.2	1.2	0.5
Mg	0.1	0.1	0.1
Mn	<0.1	0.1	0.1
Co	<0.1	<0.1	<0.1
Cu	2.2	1.6	0.5

Table 12 presents the weight of solar cell before and after the experiment and Si recovery rate. Weight was 10.13, 10.28, and 10.01g before the experiment, and reduced to 8.88, 8.70, and 8.73g after the experiment. Si recovery rate obtained using Formula 1 was 94.3, 98.9, and 97.1%, highest at 150W.

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Table 12. Weight change before/after experiment & recovery rate – change of ultrasonic intensity

	Weight change		Recovery rate (%)
	Before experiment	After experiment	
100W			94.3
150W			98.9
200W			97.1

5. CONCLUSIONS

This study used HNO_3 solution and cavitation effect of ultrasonic cleaner to recover Si selectively from used solar cell. The optimum conditions for concentration of HNO_3 solution, reaction temperature, reaction time, and ultrasonic intensity were drawn to recover Si, and the solar cell was dried and crushed after the experiment for XRD and XRF analyses to calculate the purity and recovery rate of recovered Si.

Results of experiment are summarized as follows.

1. Experiment of HNO_3 solution by concentration determined that the optimum concentration to recover Si was 3M, in which the purity of recovered Si was 100% and recovery rate was 98.3%.
2. The optimum reaction temperature to recover Si from used solar cell was 60℃, in which the purity was 100% and recovery rate was 98.3%.
3. The optimum reaction time was 90 min, in which the purity of Si was 99.81% and recovery rate was 98.9%.
4. The optimum ultrasonic intensity was 150W, in which the purity of Si was 99.81% and recovery rate was 98.9%.
5. The Si ultimately recovered through the optimum concentration, reaction temperature, reaction time, and ultrasonic intensity experiment presented 99.81% purity and 98.9% recovery rate.

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