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A Study on the Wet Process Conditions That Affect the Selective Recovery of Si from Photovoltaic Cells by Using the Cavitation Effect

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Abstract: In this research, a study to selectively recover Si from end-of-life photovoltaic cells by using acid solutions (HNO_3 and HCl) and the cavitation effect of an ultrasonic cleaner was carried out. To selectively recover Si from an end-of-life photovoltaic cell, after a leaching process was conducted by using an acid solution, the photovoltaic cell that had completed the reaction was cleaned with distilled water and dried in a drying oven (100 °C) for 24 h. The experiment was conducted with acid solution concentration, reaction temperature, reaction time, and ultrasonic intensity as variables. In the results of the experiment, the optimal process was determined to be a concentration of 3M, a reaction temperature of 60 °C, a reaction time of 90 min, and an ultrasonic intensity of 150 W when using the HNO_3 solution and a concentration of 3M, a reaction temperature of 60 °C, a reaction time of 120 min, and an ultrasonic intensity of 150 W when using the HCl solution. At this time, Si purity was 99.78% for HNO_3 and 99.85% for HCl and the Si recovery rate was 98.9% for HNO_3 and 99.24% for HCl.

Keywords: end-of-life photovoltaic cell; recovery rate; purity; cavitation effect; silicon

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1. Introduction

New renewable energy has been attracting attention recently due to the emergence of resource and environmental problems as a result of rapid industrial development. As interest in new and renewable energy increases, the use of solar energy, the representative eco-friendly energy, is also on the rise. According to data from the International Energy Agency (IEA) in 2017, the current status of energy generation is 67% thermal and nuclear power, 20% hydroelectric power, and 4.4% solar power. In the growth outlook for 2040, it has been forecast that solar power generation will increase to 12% while thermal and nuclear power will decrease to 50% of total power generation [1,2]. The number of installed photovoltaic modules has gradually increased, and the accumulated global solar installation in 2018 was about 509 GW, indicating that the solar industry is continuously growing [3].

However, the processing of end-of-life photovoltaic modules, with a life cycle of about 20–30 years, has emerged as a big problem. According to an IEA report, about 76 million tons of end-of-life photovoltaic modules are expected to end up as waste by 2050 [4,5]. An end-of-life photovoltaic module is composed of silver (Ag), aluminum (Al), silicon (Si), lead (Pb), etc. [6,7]. Since end-of-life photovoltaic modules contain harmful substances, such as lead, they are expected to cause a significant amount of environmental pollution if they are buried or incinerated.

Europe has mandated that photovoltaic modules be recycled by designating them as electric and electronic waste in the Waste Electrical and Electronic Equipment (WEEE) regulations. However, while expensive silicon, copper, silver, etc., in end-of-life photovoltaic

modules are worth recycling, most photovoltaic modules are currently being buried in landfills. Since the polysilicon purifying process in the photovoltaic module manufacturing process accounts for about 50% of the energy consumed by the entire module process, economic and environmental benefits can be expected if recovery of high-purity silicon from solar cells becomes possible [8].

In France, the main purpose of the CABRISS project, which was sponsored by the CEA (French Alternative Energies and Atomic Energy Commission) and launched in June 2015 by a consortium of 16 European companies and research institutes to be executed over 3 years, is to develop technology based on the idea of "total recycling (maximum recycling rate of 90%)", with the goal of recycling all materials that have high economic value even if only a small amount is included, rather than technology development oriented toward silicon recycling. It is focused on maximizing economic feasibility through virtuous recycling of resources [9].

Germany dominates the field of solar cell waste module treatment, and Japan has been securing original technology for recovering valuable metals and recycling silicon from solar cell waste modules in response to resource depletion since the 1980s [10,11]. Korea lags behind in solar cell waste module treatment technology, and it is in a situation where it is burying waste rather than recovering resources [12].

In this research, a study to selectively recover silicon from end-of-life photovoltaic cells with a wet process using acid solutions (HNO_3 and HCl) and identify the cavitation effect of ultrasonic waves was carried out. The cavitation effect refers to the decrease and increase in pressure that appear repeatedly when ultrasonic waves are generated in a solution. The air bubbles that are generated contract when pressure is increased and expand when pressure is decreased. When a certain pressure is exceeded, the air bubbles contract and explode, causing a large shock wave that removes contaminants from the surface of the object being cleaned. The cavitation effect of ultrasonic waves can clean even the interior of the object in a short time, and the surface cleaning effect is far superior compared to that of stirring. Since most of the impurity components present in the end-of-life photovoltaic cells are on the surface of the photovoltaic cells, an experiment was conducted by using an ultrasonic cleaner with a more effective surface cleaning effect [13]. To increase the purity and the recovery rate of the recovered silicon, optimal process conditions were established by controlling the concentration, reaction temperature, reaction time, and ultrasonic intensity of the acid solution. The phase of the recovered photovoltaic cells was identified through X-ray powder diffraction (XRD) analysis, and the purity of recovered Si was measured through X-ray fluorescence (XRF) and Inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis. In addition, the impurity content in the solution was measured through ICP-OES analysis to determine the impurity leaching effect of the acid solutions (HNO_3 and HCl).

2. Materials and Methods

2.1. Materials

In this study, a photovoltaic cell after use is shown in Figure 1. The specimens used were broken cells, and the size varied from 2 cm to 4 cm. The inner size of the ultrasonic cleaner used in the experiment was 300 mm × 240 mm × 150 mm, and a 1 L beaker was used for the experiment. XRD and XRF analyses were performed. The XRD used for the analysis was X'Pert3-Powder (Malvern Panalytical, Malvern, United Kingdom) from PANalytical, XRF was XRF-1800 (Shimadzu, Kyoto, Japan) from Shimadzu, and ICP was Optima 5300DV (PrekinElmer Inc., Beaconsfield, United Kingdom) from PerkinElmer. The results of XRD and XRF analyses are shown in Figure 2. As a result of XRD analysis, it was confirmed that Si and Al phases were present on the surface of the end-of-life photovoltaic cells. As a result of XRF analysis, Si, Al, and Zn were detected and the content was 89.75% for Si, 10.18% for Al, and 0.07% for Zn.

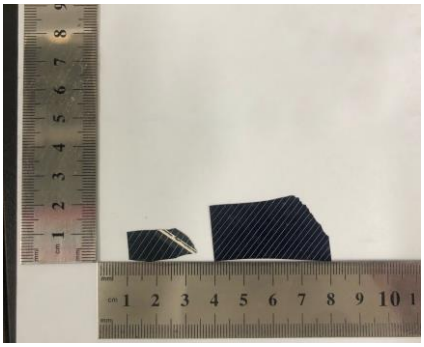

Figure 1. End-of-life photovoltaic cell sample.

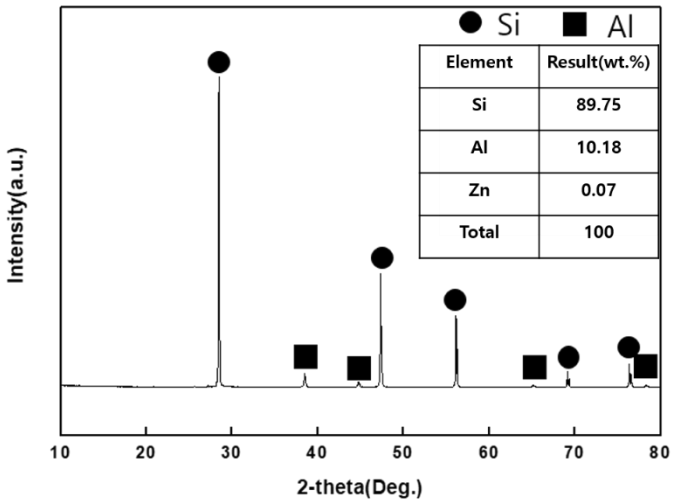

Figure 2. XRD and XRF analysis results for an end-of-life photovoltaic cell sample.

Scanning electron microscope (SEM) mapping analysis results of the front and back side of the photovoltaic cell are shown in Figure 3. The parts circled in red in Figure 3 were analyzed by SEM mapping analysis (JEOL Ltd., Seoul, Korea). Through SEM mapping analysis, it was found that Si, Ag, and Al were mainly present on the front side of the photovoltaic cell and Al and Ag were mainly present on the back side.

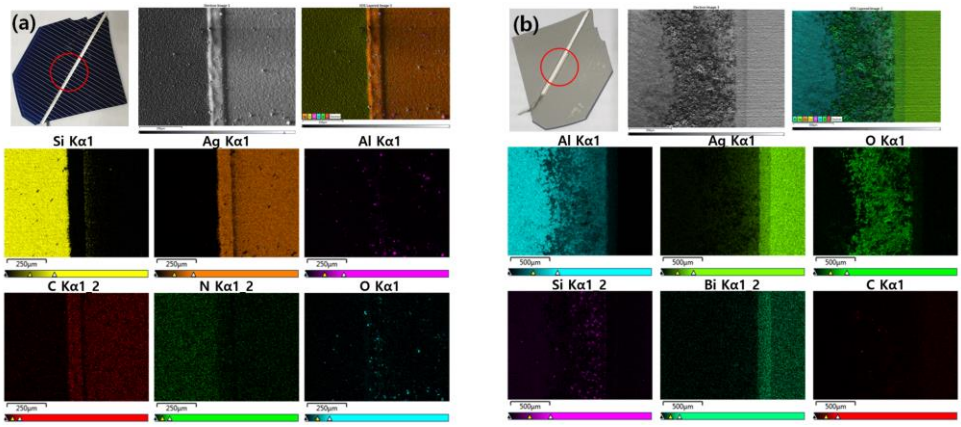

Figure 3. SEM mapping analysis of an end-of-life photovoltaic cell; (**a**) front side of the cell; (**b**) back side of the cell.

In addition, it can be confirmed that Ag, which was not detected in the XRD and XRF analysis results in Figure 2, was detected in the SEM mapping in Figure 3. XRD does not

detect substances with a content of 5% or less, and Ag was not detected during XRD and XRF analyses because the amount of Ag present in the photovoltaic cell is small.

2.2. Methods

On analyzing an end-of-life photovoltaic cell sample, it was found that Al, Ag, and Zn, excluding Si, were present in the photovoltaic cell. To selectively recover Si from a photovoltaic cell, impurities (Al, Ag, etc.) that exist on the surface of the photovoltaic cell need to be removed. To remove impurities, a leaching process was carried out by using the cavitation effect of an ultrasonic cleaner (Sd Ultrasonic Co., Ltd., Seoul, Korea) and HNO_3 and HCl solutions were used during leaching. Figure 4 shows the Stabcal simulation for HNO_3 and HCl for Si, Al, and Ag, which are the components present on the photovoltaic cell surface. The STABCAL program (Dr. Hsin H. Huang, Butte, MT, USA) is a commercial program that can predict and explain the characteristics of chemical reactions by calculating the thermodynamic constants for various chemical reactions in an aqueous solution of the reaction system between substances and aqueous solutions. For the HNO_3 condition, it can be seen that Al is dissolved in Al^{3+}, $AlOH^{2+}$, and $Al(OH)^{2+}$ form at pH lower than 3; Ag is dissolved in Ag^{+} form at pH lower than 8; and Si is not dissolved in the acid region. For the HCl condition, it can be seen that Al is dissolved in Al^{3+}, $AlOH^{2+}$, and $Al(OH)^{2+}$ form at a pH of 3 or less; Ag is precipitated into AgCl over the entire region at 10 ppm or higher; and Si is not dissolved in the acid region. Through the STABCAL simulation results in Figure 3, it can be seen that since HNO_3 and HCl solutions react with Al and Ag and Si does not react, Al and Ag, which are impurities present on the surface of the end-of-life photovoltaic cell, can be removed and Si can be selectively recovered. In addition, Zn present on the solar cell surface is leached together during Ag leaching by HNO_3 and HCl. The experiment was repeated 3 times, and the most optimal experimental result was written in the thesis. In the case of other experimental results, the difference from the optimal experimental results was insignificant, so it was not prepared.

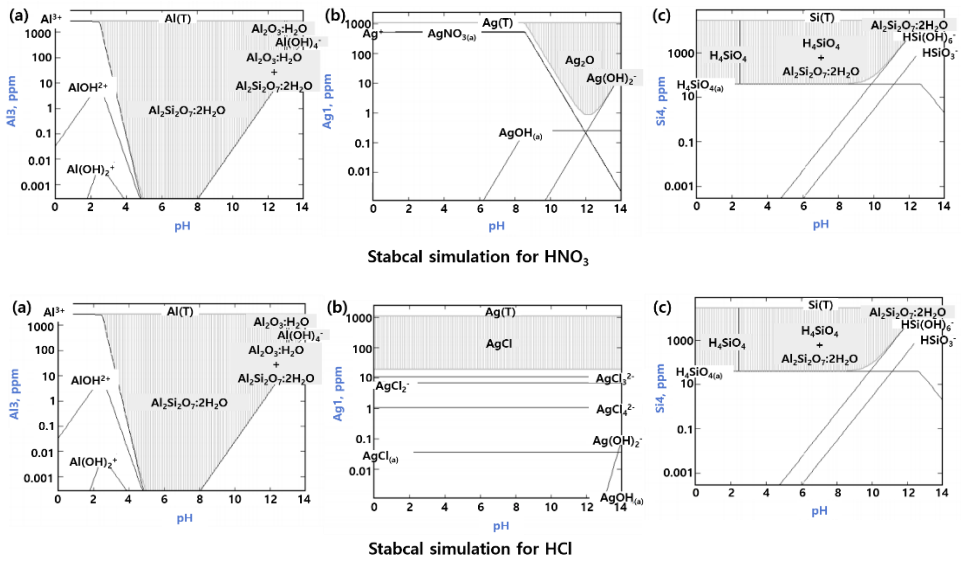

Figure 4. Stabcal simulation for HNO_3 and HCl reaction with Al, Ag, and Si.

As for experimental conditions for selectively recovering Si using an ultrasonic cleaner, the experiment was conducted by varying the conditions of the acid solution concentration, the reaction temperature, the reaction time, and the ultrasonic intensity. After inserting 10 g of an end-of-life photovoltaic cell into a beaker containing 100 mL of an acid solution, it was reacted by using an ultrasonic cleaner to remove impurities. After the reaction, the photovoltaic cell was cleaned with distilled water and dried in a drying oven (100 °C) for 24 h. In addition, decompression filtration was performed on the acid solution that had reacted with the photovoltaic cell and ICP-Full Scan analysis was carried out on the filtered

solution. The photovoltaic cell that had been dried in the drying oven was crushed into fine powder by using a mortar to proceed with the analysis, and then XRD and XRF analyses were performed. The following shows the expected reaction formula for Al and Ag in a photovoltaic cell and the acid solution (HNO_3 and HCl), and Figure 5 shows a process chart of the entire experiment.

$$Ag(s) + 2HNO_3(l) = AgNO_3 + NO_2 + H_2O$$

$$2Al(s) + 2HNO_3(l) = Al_2O_3\downarrow + 2NO + H_2O$$

$$2Ag(s) + 2HCl(l) = 2AgCl\downarrow + H_2\uparrow$$

$$2Al(s) + 6HCl(l) = 2AlCl_3(l) + 3H_2$$

Figure 5. Process chart of the entire experiment.

3. Results and Discussion

3.1. Acid Solution Concentration Experiment

An experiment was carried out by mixing 10 g of an end-of-life photovoltaic cell in 100 mL of 1, 2, and 3M HNO_3 and HCl solutions; placing the mixture in a beaker; and using an ultrasonic cleaner after setting the reaction temperature to 60 °C, the reaction time to 60 min, and the ultrasonic intensity to 150 W. Decompression filtration was performed on the acid solution that had reacted with the photovoltaic cell, and ICP-Full Scan analysis was carried out on the filtered solution. The photovoltaic cell that had reacted with the acid solution was cleaned with distilled water and dried in a drying oven at a temperature of 100 °C. After that, the dried photovoltaic cell was crushed by using a mortar and XRD and XRF analysis were carried out.

Figure 6 shows the results of an XRD analysis of the photovoltaic cell that was recovered after drying. As a result of XRD analysis, it was confirmed that the Al phase was not detected under the concentration conditions of 1, 2, and 3M for both HNO_3 and HCl conditions and only the Si phase was detected.

Table 1 shows the XRF analysis results of the photovoltaic cell that was recovered after drying. As a result of XRF analysis, it can be confirmed that only Si was observed, which was detected only by measuring the front side of Si. As a result of XRF analysis, it was confirmed that the Si purity increases as the concentration of both HNO_3 and HCl solutions is increased. In addition, it was confirmed that Si purity was higher for HNO_3 compared to that for HCl under the same concentration condition.

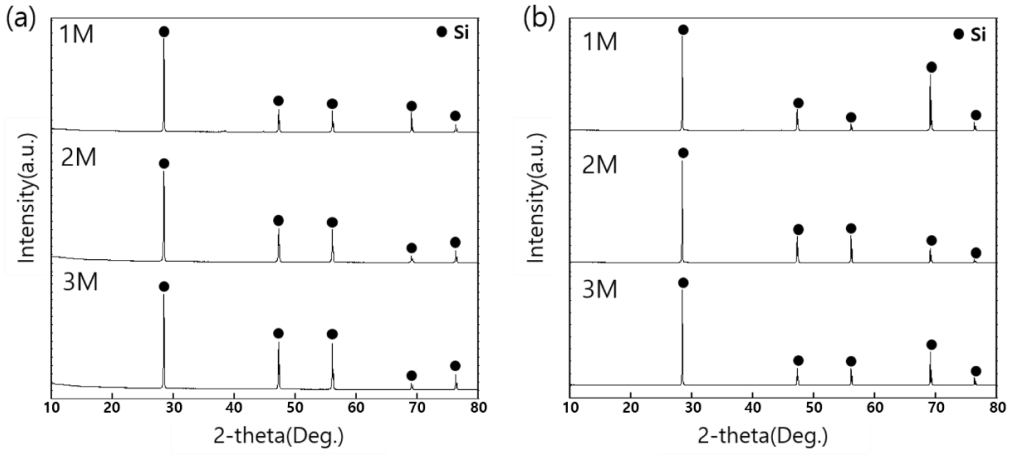

Figure 6. XRD analysis results of a photovoltaic cell after drying—concentration. (**a**) HNO_3 and (**b**) HCl.

Table 1. XRF analysis results of a photovoltaic cell after drying—concentration (unit: wt.%).

Element Analyzed / Concentration (M)	HNO_3		HCl		Total
	Si	Al	Si	Al	
1	95.60	4.40	94.54	5.46	100
2	99.77	0.23	99.66	0.34	
3	100	-	99.85	0.15	

To confirm the effect of removing impurities for each acid solution, ICP-Full Scan analysis was performed on the filtered solution after it had reacted with the photovoltaic cell. The ICP-Full Scan analysis results are shown in Table 2. It was confirmed that the element content of the filtered solution increases as the concentration for both HNO_3 and HCl is increased. In the case of Al, it could be removed effectively at 1000 mg/L for a concentration of 2M or higher for both HNO_3 and HCl solutions. However, in the case of Ag, while a high content was detected because of the HNO_3 experiment, little was detected in the case of HCl. The reason that different amounts of Al and Ag were detected depending on the experimental conditions such as the concentration, time, and temperature of the filtration solution is that the weight of the photovoltaic cell used for each experiment is different and the leaching result is different according to the different experimental conditions for each experiment. Different amounts of Al and Ag present in the solution were detected. Through this, it was found that HNO_3 is more effective in removing Ag.

The Si recovery rate was calculated with the weight of the photovoltaic cell before the experiment, the weight of the photovoltaic cell recovered after drying, and the Si content derived from the XRF analysis results in Table 1. The equation for the Si recovery rate calculation is as shown in Equation (1), below.

$$\text{Silicon recovery efficiency}(\%) = \frac{\text{Weight percent of the recovered silicon}}{\text{Weight percent of silicon inside the module}} \times 100 \quad (1)$$

Table 2. ICP-Full Scan of the filtered solution—concentration.

Element Analyzed and Content (mg/L)							
	HNO_3				HCl		
Element	**1M**	**2M**	**3M**	**Element**	**1M**	**2M**	**3M**
Al	830	1000	1300	Al	1400	1400	1300
Ag	0.013	280	410	Ag	0.4	0.5	4.8
Si	54	58	89	Si	65	48	37
Fe	2.7	3.5	4.2	Fe	6.4	4.0	4.1
Zn	12	10	15	Zn	9.5	8.0	8.0
Pb	2.3	19	27	Pb	4.2	3.5	6.8
Bi	N/D	60	51	Bi	0.6	0.6	1.2
Ni	0.38	1.8	8.1	Ni	0.4	0.4	0.5
In	0.63	0.93	1.0	In	1.0	1.0	0.8
Sn	1.3	1.6	6.2	Sn	1.5	1.0	9.7
Mg	0.11	0.23	0.22	Mg	0.1	0.2	0.1
Mn	0.033	0.068	0.37	Mn	0.2	<0.1	<0.1
Co	0.038	0.10	0.52	Co	<0.1	<0.1	<0.1
Cu	0.11	2.6	0.98	Cu	0.2	0.2	7.7

Table 3 shows the weights of a photovoltaic cell before and after the experiment and the recovery rates. When the HNO_3 solution was used, the weight change decreased from 1M 10.02 g, 2M 10.19 g, and 3M 10.10 g before the experiment to 1M 9.15 g, 2M 8.95 g, and 3M 8.91 g after the experiment. By using Equation (1), the Si recovery rate was calculated to be 1M 97.28%, 2M 97.65%, and 3M 98.3%. When the HCl solution was used, the weight change decreased from 1M 10.13 g, 2M 10.06 g, and 3M 10.21 g before the experiment to 1M 9.21 g, 2M 8.85 g, and 3M 8.95 g after the experiment. The Si recovery rate was calculated to be 1M 95.82%, 2M 97.67%, and 3M 97.93%.

Table 3. Weight of a photovoltaic cell before and after the experiment and Si recovery rates—concentration (unit: wt.%).

Sample Name (M)	HNO_3			HCl		
	Before Experiment (g)	**After Experiment (g)**	**Recovery Rate (%)**	**Before Experiment (g)**	**After Experiment (g)**	**Recovery Rate (%)**
1	10.02	9.15	97.28	10.13	9.21	95.82
2	10.19	8.95	97.65	10.06	8.85	97.67
3	10.10	8.91	98.3	10.21	8.95	97.93

From the result of calculating the Si recovery rate, it was confirmed that the Si recovery rate was 95% or higher for both HNO_3 and HCl solutions. As the concentration of the acid solution was increased, the Si recovery rate also increased and it was found that the recovery rate was the highest at 3M for both HNO_3 and HCl solutions. Under the same concentration conditions, it was confirmed that HNO_3 had a higher Si recovery rate and higher purity compared to HCl. For both solutions, the optimal concentration condition for selectively recovering Si from photovoltaic cells was determined to be 3M.

3.2. Reaction Temperature Experiment

An experiment was conducted under four temperature conditions, 30, 40, 50, and 60 °C, to verify the optimal reaction temperature to selectively recover Si from end-of-life photovoltaic cells. The acid solution concentration that was used in the experiment was 3M, which was derived from the previous experiment, and HNO_3 and HCl solutions were used. The reaction time was set to 60 min, and the ultrasonic intensity was set to 150 W. The photovoltaic cell that had reacted with the acid solution was cleaned with distilled water and then dried in a drying oven at 100 °C. Decompression filtration was carried out on the acid solution that had reacted with the photovoltaic cell. XRD and XRF analyses were carried out on the photovoltaic cells that had been crushed after being recovered and dried, and ICP-Full Scan analysis was performed on the filtered solutions.

Figure 7 shows the results of an XRD analysis of a photovoltaic cell that was recovered after drying. As a result of XRD analysis, it was confirmed that only the Si phase was detected under all temperature conditions, of 30, 40, 50, and 60 °C, for both HNO_3 and HCl solutions. Al, a major impurity element that had been detected in the XRD analysis results for the end-of-life photovoltaic cell sample in Figure 1, was not detected as a result of the experiment.

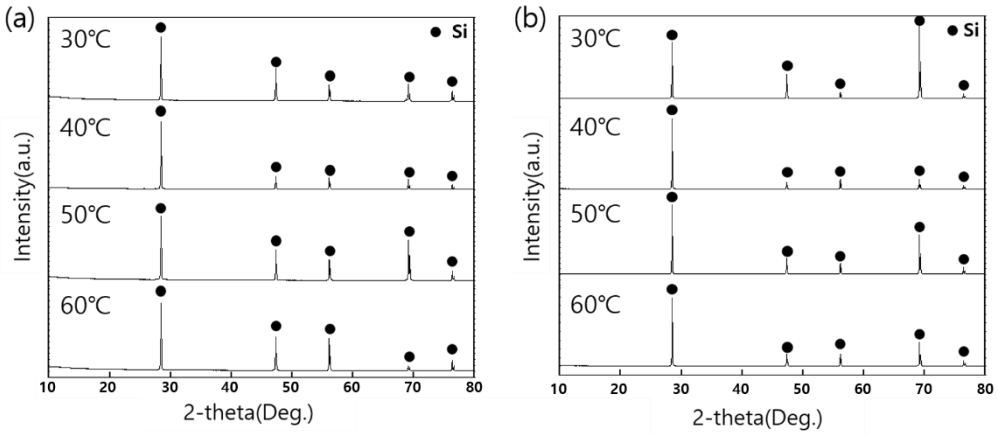

Figure 7. XRD analysis results of a photovoltaic cell after drying—temperature. (**a**) HNO_3 and (**b**) HCl.

Table 4 shows the XRF analysis results of a photovoltaic cell that was recovered after the acid solution reaction. Overall, it was confirmed that as the temperature increased, the purity of Si improved. In the case of HNO_3, Si purity also increased as the temperature increased and it was confirmed that all Al except Si was removed at 60 °C. In the case of HCl, Si purity was similar under all temperature conditions and it was confirmed that the temperature change did not significantly affect the removal of impurities. As a result, it was confirmed that while HCl shows higher purity compared to HNO_3 at temperatures similar to room temperature, HNO_3 shows higher Si purity as the solution temperature increases.

Table 4. XRF analysis results of a dried photovoltaic cell—temperature (unit: wt.%).

Element Analyzed / Temperature (°C)	HNO_3		HCl		Total
	Si	Al	Si	Al	
30	99.84	0.16	99.91	0.09	100
40	99.86	0.14	99.91	0.09	
50	99.88	0.12	99.87	0.13	
60	100	-	99.85	0.15	

Table 5 shows the ICP-Full Scan analysis results of the filtered solution after reacting with the photovoltaic cell. For both HNO_3 and HCl solutions, the content of Al increased as the temperature increased. In the case of HNO_3, it was confirmed that the Al and Ag contents increased as the temperature increased. In particular, the content of Al and Ag was shown to be the highest at 60 °C. Even under the HCl condition, the content of Al and Ag increased as the temperature increased and it was the highest at 60 °C. While the content of Al was similar for the HNO_3 and HCl solutions, the content of Ag was higher in HNO_3 compared to that in HCl. From this, it is confirmed that HNO_3 is more effective in removing Ag.

Table 5. ICP-Full Scan analysis results of the filtered solution—temperature.

Element Analyzed and Content (mg/L)									
	HNO_3					HCl			
Element	**30 °C**	**40 °C**	**50 °C**	**60 °C**	**Element**	**30 °C**	**40 °C**	**50 °C**	**60 °C**
Al	620	860	1100	1300	Al	990	990	1100	1300
Ag	210	215	235	410	Ag	<0.1	<0.1	0.1	4.8
Si	36	55	51	89	Si	23	23	46	37
Fe	2.5	2.9	3.2	4.2	Fe	5.8	5.8	4.9	4.1
Zn	4.2	8.1	8.9	15	Zn	12	12	13	8.0
Pb	59	11	7.5	27	Pb	4.8	4.8	6.9	6.8
Bi	14	31	38	51	Bi	0.8	0.8	0.8	1.2
Ni	1.0	2.2	0.3	8.1	Ni	0.5	0.5	0.5	0.5
In	0.68	0.94	0.6	1.0	In	1.4	1.4	1.4	0.8
Sn	4.7	1.6	0.9	6.2	Sn	0.7	0.7	1.0	9.7
Mg	0.088	0.086	0.1	0.22	Mg	0.1	0.1	0.1	0.1
Mn	0.088	0.15	<0.1	0.37	Mn	0.1	0.1	0.1	<0.1
Co	0.065	0.20	<0.1	0.52	Co	<0.1	<0.1	<0.1	<0.1
Cu	7.9	0.50	5.5	0.58	Cu	0.1	0.1	0.3	7.7

Table 6 shows the weight changes of photovoltaic cells before and after the experiment and the Si recovery rates. The recovery rate was calculated by using Equation (1), and by calculating the Si recovery rate, it was confirmed that both HNO_3 and HCl solutions had Si recovery rates of 96% or higher. While the Si recovery rate also increased as the temperature increased when the HNO_3 solution was used, when the HCl solution was used, it was confirmed that the Si recovery rate was similar.

Table 6. Weight of the photovoltaic cell before and after experiment and Si recovery rates—temperature.

Sample Name (°C)	HNO_3			HCl		
	Before Experiment (g)	**After Experiment (g)**	**Recovery Rate (%)**	**Before Experiment (g)**	**After Experiment (g)**	**Recovery Rate (%)**
30	10.10	8.78	96.71	10.09	8.86	97.68
40	10.10	8.88	97.84	10.02	8.79	97.66
50	10.13	8.88	97.5	10.12	8.81	96.92
60	10.10	8.91	98.3	10.21	8.98	97.93

As a result of calculating the purity and the recovery rate, the optimal reaction temperature condition for selectively recovering Si from photovoltaic cells was determined to be 60 °C for both solutions.

3.3. Reaction Time Experiment

An experiment was conducted under four time conditions, of 30, 60, 90, and 120 min, to confirm the optimal time to selectively recover Si from end-of-life photovoltaic cells. The acid solution concentration that was used in the experiment was 3M, which was derived from the previous experiment, HNO_3 and HCl solutions were used, the reaction temperature was set to 60 °C, and the ultrasonic intensity was set to 150 W. Decompression filtration was carried out on the acid solution that had reacted with the photovoltaic cell and ICP-Full Scan analysis was performed on the filtered solution. The photovoltaic cell that had reacted with the acid solution was cleaned with distilled water and then dried in a drying oven at 100 °C. XRD and XRF analyses were carried out on the photovoltaic cells that had been crushed by using a mortar after being recovered and dried.

Figure 8 shows the XRD analysis results of a photovoltaic cell that was recovered after drying. As a result of XRD analysis, it was confirmed that the Al present in the photovoltaic cell sample was removed through a leaching process and only the Si phase was detected under all-time conditions, of 30, 60, 90, and 120 min, in both HNO_3 and HCl solutions.

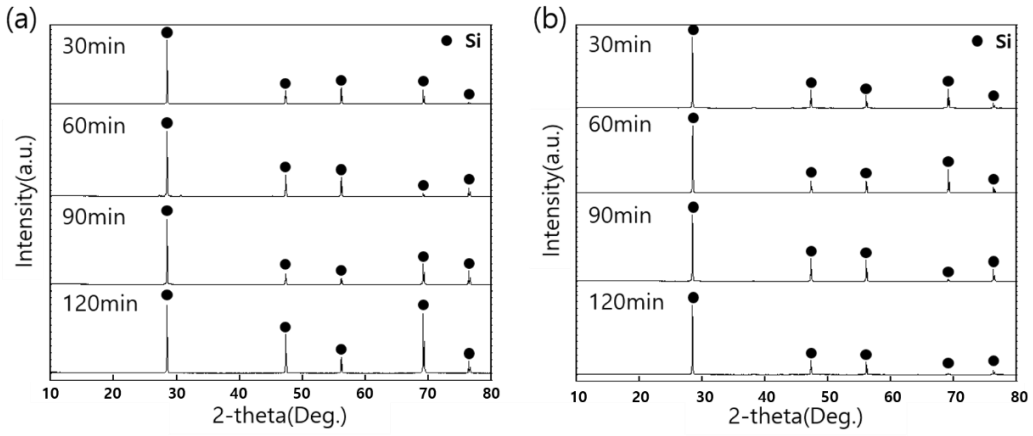

Figure 8. XRD analysis results of a photovoltaic cell after drying—time. (**a**) HNO_3 and (**b**) HCl.

Table 7 shows the XRF analysis results of a dried photovoltaic cell. As a result of XRF analysis, Si purity of 99% or higher was confirmed for both HNO_3 and HCl solutions. For the HNO_3 solution, the Si purity was the highest at 60 min and the HCl solution had the highest purity at 90 min.

Table 7. XRF analysis results of a photovoltaic cell after drying—time (unit: wt.%).

Time (min) \ Element Analyzed	HNO_3		HCl		Total
	Si	Al	Si	Al	
30	99.10	0.9	99.68	0.32	100
60	100	-	99.85	0.15	
90	99.84	0.16	99.92	0.08	
120	99.83	0.17	99.85	0.15	

Table 8 shows the ICP-Full Scan analysis results of the filtered solution. The Al content and the Ag content of the HNO_3 solution were high in the following order: 30 > 60 = 90 ≥ 20. The Al content of the HCl solution was high in the following order:

60 > 90 > 120 > 30. The Ag content was the highest at 60 min, and similar content was detected under other conditions. The Al and Ag contents of the HNO_3 solution actually decrease for times equal to or greater than 90 min. The reason why the Al content in the filtered solution does not increase linearly with the increase in the reaction time is that for the Al present in the dried solar cell, the reaction time between the leaching solution and the solar cell in the beaker increases as the leaching solution increases. The Al present in the solar cell can be adsorbed. In addition, in the case of the filtered solution, distilled water is used to filter all solutions as much as possible when filtering the acid solution reacted with the solar cell. The greater the amount of distilled water used, the lower the concentration of the elements present in the filtration solution. It does not appear linear because the amount of distilled water used is different for each condition.

Table 8. ICP-Full Scan analysis results of the filtered solution—time.

Element Analyzed and Content (mg/L)									
	HNO_3					HCl			
Element	**30 min**	**60 min**	**90 min**	**120 min**	**Element**	**30 min**	**60 min**	**90 min**	**120 min**
Al	1400	1500	1500	1300	Al	900	1300	1200	1100
Ag	412	240	430	330	Ag	0.1	4.8	<0.1	<0.1
Si	64	89	54	43	Si	23	37	35	35
Fe	5.1	4.2	3.8	3.1	Fe	4.0	4.1	3.3	3.4
Zn	12	15	12	4.1	Zn	6.8	8.0	8.9	8.4
Pb	44	27	27	53	Pb	1.6	6.8	1.6	12
Bi	27	51	64	64	Bi	0.3	1.2	0.4	11
Ni	0.4	8.1	0.6	3.4	Ni	0.3	0.5	0.5	0.5
In	0.8	1.0	0.6	0.7	In	0.4	0.8	0.7	0.6
Sn	1.6	6.2	1.2	3.4	Sn	1.0	9.7	0.7	3.2
Mg	0.2	0.22	0.1	0.2	Mg	0.1	0.1	0.1	0.1
Mn	<0.1	0.37	0.1	0.1	Mn	<0.1	<0.1	<0.1	<0.1
Co	<0.1	0.52	<0.1	0.2	Co	<0.1	<0.1	0.1	0.2
Cu	35	0.98	1.6	1.0	Cu	7.1	7.7	<0.1	2.9

Table 9 shows the weight changes of the photovoltaic cell before and after the experiment and the Si recovery rates. The recovery rate was calculated with Equation (1) and the Si content of Table 7. As a result of calculating the Si recovery rate, it was confirmed that both HNO_3 and HCl solutions had Si recovery rates of 96% or higher. It was confirmed that while the recovery rate of the HNO_3 solution increased as the reaction time is increased, the Si recovery rate decreased from 120 min. It was confirmed that the HCl solution had the highest Si recovery rate from 120 min at 99.24%. The optimal reaction time condition for selectively recovering Si from the photovoltaic cell was derived as 90 min, with the highest recovery rate when using the HNO_3 solution, and the optimal reaction time condition for using the HCl solution was derived as 120 min with the highest recovery rate.

Table 9. Change in the photovoltaic cell weight before and after experiment and Si recovery rates—time.

Sample Name (min)	HNO_3			HCl		
	Before Experiment (g)	After Experiment (g)	Recovery Rate (%)	Before Experiment (g)	After Experiment (g)	Recovery Rate (%)
30	10.43	9.15	96.9	10.09	8.95	98.45
60	10.10	8.91	98.3	10.21	8.98	97.93
90	10.42	9.27	98.9	10.14	8.91	97.80
120	10.33	9.11	98.17	10.25	9.14	99.24

3.4. Ultrasonic Intensity Experiment

The cavitation effect refers to the decrease in pressure and the increase in pressure that appear repeatedly when ultrasonic waves are generated in a solution. The air bubbles that are generated contract when pressure is increased and expand when pressure is decreased. When a specific level of pressure is exceeded, the air bubbles contract and explode, causing a large shock wave. This bubble removes the contaminants from the surface of the object being cleaned by exploding. The cavitation effect of ultrasonic waves can clean even the interior of the object in a short time, and the surface cleaning effect is far superior compared to that of stirring. Since most of the impurity components present in the end-of-life photovoltaic cells are present on the surface, an experiment was conducted by using an ultrasonic cleaner with a more effective surface cleaning effect [13].

An experiment was conducted under three ultrasonic intensity conditions, of 100, 150, and 200 W, to verify the optimal ultrasonic intensity for selectively recovering Si from end-of-life photovoltaic cells. The acid solution concentration that was used in the experiment was 3M, which was derived from the previous experiment, and HNO_3 and HCl solutions were used. The reaction temperature was set to 60 °C, and the reaction time was set to 90 min for the HNO_3 solution and 120 min for the HCl solution. Decompression filtration was carried out on the acid solution that had reacted with the photovoltaic cell, and ICP-Full Scan analysis was performed on the filtered solutions. The photovoltaic cell that had reacted with the acid solution was cleaned with distilled water and then dried in a drying oven at 100 °C. XRD and XRF analyses were carried out on the photovoltaic cell that had been crushed with a mortar after being recovered and dried.

Figure 9 shows the results of the XRD analysis of a photovoltaic cell that was recovered after drying. As a result of XRD analysis, it was confirmed that the Al phase in the sample was removed, as in the previous experiments, and only the Si phase was detected under all ultrasonic intensity conditions: 100, 150, and 200 W.

Table 10 shows the results of the XRF analysis of the photovoltaic cell that was recovered after drying. As a result of XRF analysis, it was confirmed that the Si purity was 99% or higher for both HNO_3 and HCl solutions. In addition, it was confirmed that Si purity was the highest, at 99.92% for HNO_3 and 100% for HCl, when the ultrasonic intensity was the highest, at 200 W, for both HNO_3 and HCl solutions.

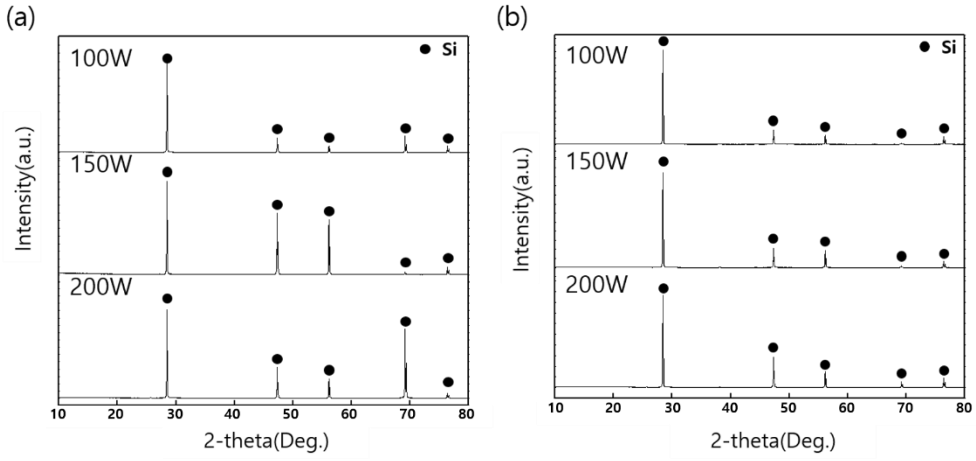

Figure 9. XRD analysis results of a photovoltaic cell after drying—ultrasonic intensity. (**a**) HNO_3 and (**b**) HCl.

Table 10. XRF analysis results of a photovoltaic cell after drying—ultrasonic intensity (unit: wt.%).

Element Analyzed / Ultrasonic Intensity (W)	HNO_3		HCl		Total
	Si	Al	Si	Al	
100	99.91	0.09	99.97	0.03	100
150	99.84	0.16	99.85	0.15	
200	99.92	0.08	100	-	

Table 11 shows the ICP-Full Scan analysis results of the filtered solutions. For the HNO_3 solution, it was confirmed that the Al and Ag contents increased as the ultrasonic intensity increased and had the highest value at 200 W. For the HCl solution, the measured content of Al was similar under all conditions, and it was confirmed that the content of the detected Ag was the highest at 200 W. In addition, it can be confirmed that the Al content is the highest in the XRF analysis result of the solar cell dried under the ultrasonic intensity condition of 150 W using HNO_3 but not the lowest in the filtered solution. In addition, although Al was not detected in the XRF analysis result of the dried photovoltaic cell of 200 W ultrasonic intensity using HCl, it can be seen that the lowest value was found in the analysis result of the filtered solution. This is because the purpose of the ICP Full Scan analysis is to check which elements are present in the material, so there may be errors in the analysis results. Through this, it was confirmed that HNO_3 is more suitable compared to HCl for removing Al and Ag.

Table 12 shows the weight changes of the photovoltaic cell before and after the experiment and the Si recovery rates. It was confirmed that both HNO_3 and HCl solutions had Si recovery rates of 94% or higher. It was confirmed that both HNO_3 and HCl solutions had the highest Si recovery rates at an ultrasonic intensity of 150 W, with 98.9% for HNO_3 and 99.24% for HCl.

The optimal ultrasonic intensity conditions for recovering Si from end-of-life photovoltaic cells were determined to be 150 W for the HNO_3 solution and 200 W for HCl.

Table 11. ICP-Full Scan analysis results of the filtered solution—ultrasonic intensity.

Element Analyzed and Content (mg/L)							
HNO_3				HCl			
Element	**100 W**	**150 W**	**200 W**	**Element**	**100 W**	**150 W**	**200 W**
Al	1000	1400	1500	Al	1100	1100	1000
Ag	220	280	430	Ag	4.1	<0.1	7.4
Si	72	54	46	Si	40	35	35
Fe	5.7	3.8	3.7	Fe	4.8	3.4	11
Zn	16	12	9.3	Zn	8.9	8.4	10
Pb	17	27	9.7	Pb	30	12	20
Bi	62	64	37	Bi	27	11	26
Ni	0.4	0.6	0.4	Ni	0.8	0.5	3.3
In	0.9	0.6	0.7	In	1.0	0.6	1.1
Sn	1.0	1.2	0.7	Sn	34	3.2	3.9
Mg	0.1	0.1	0.1	Mg	0.4	0.1	1.3
Mn	<0.1	0.1	0.1	Mn	0.1	<0.1	0.2
Co	<0.1	<0.1	<0.1	Co	0.1	0.2	0.5
Cu	2.1	1.6	0.4	Cu	0.7	2.9	2.8

Table 12. Change in the photovoltaic cell weight before and after experiment and the Si recovery rate—ultrasonic intensity.

Sample Name (W)	HNO_3			HCl		
	Before Experiment (g)	**After Experiment (g)**	**Recovery Rate (%)**	**Before Experiment (g)**	**After Experiment (g)**	**Recovery Rate (%)**
100	10.28	8.70	94.3	10.15	8.97	98.43
150	10.42	9.27	98.9	10.25	9.14	99.24
200	10.01	8.73	97.1	10.16	9.00	98.68

4. Conclusions

In this research, a study was conducted to selectively recover Si from end-of-life photovoltaic cells by using the cavitation effect of an ultrasonic cleaner. To selectively recover Si, 70% HNO_3 and 36–38% HCl solutions were used as the acid solutions and experiments were conducted by varying the concentration, reaction temperature, reaction time, and ultrasonic intensity conditions of the acid solutions. After the experiment, the photovoltaic cells were crushed using a mortar after drying and XRD and XRF analyses were performed to calculate the purity and the recovery rate of the recovered Si.

As a result of the experiment according to the concentrations of HNO_3 and HCl, it was confirmed that the Si purity and recovery rate increased as the concentrations of both solutions increased. For the optimal concentration conditions, both solutions had the highest Si purity, of 100% for HNO_3 and 99.85% for HCl, and the Si recovery rates were the highest, with 98.3% for HNO_3 and 97.93% for HCl, under the 3M condition. In addition, it was confirmed that HNO_3 has a higher recovery rate and Si purity compared to HCl under the same concentration condition.

As a result of an experiment according to the reaction temperature, it was confirmed that Si purity and recovery rate increased as the temperature of both HNO_3 and HCl solutions increased. The optimal concentration condition was 60 °C for both solutions. Si purity was 100% for HNO_3 and 99.85% for HCl, and Si recovery rates were 98.3% for HNO_3

and 97.93% for HCl. In addition, it can be seen that while HCl has higher Si purity and recovery rate compared to HNO_3 at room temperature, the HNO_3 solution has a higher recovery rate and Si purity compared to the HCl solution at 50 °C or higher temperatures.

From the results of an experiment in accordance with the reaction time, it was confirmed that in the case of HNO_3, the Si purity was high in the order of 60 > 120 > 90 > 30, and the recovery rate was high in the order of 90 > 60 > 120 > 30. In the case of the HCl solution, Si purity was high in the order of 90 > 60 = 120 > 30, and the recovery rate was high in the order of 120 > 30 > 60 > 90. The HNO_3 solution tended to decrease under the time condition of 120 min, and it was most effective at 90 min. The impurity removal effect of the HCl solution was similar for all conditions, but the removal of Ag was the most effective at 60 °C.

For the ultrasonic intensity condition, Si purity increased as ultrasonic intensity increased for both HNO_3 and HCl solutions. However, it was confirmed that the Si recovery rate was the highest at 150 W.

Optimal conditions for selectively recovering Si from end-of-life photovoltaic cells were determined to be a concentration of 3M, a reaction temperature of 60 °C, a reaction time of 90 min, and an ultrasonic intensity of 150 W when using the HNO_3 solution and a concentration of 3M, a reaction temperature of 60 °C, a reaction time of 120 min, and an ultrasonic intensity of 150 W when using the HCl solution. Si purity was 99.78% for HNO_3 and 99.85% for HCl, and the Si recovery rate was 98.9% for HNO_3 and 99.24% for HCl.

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