Recovery of valuable metal from Photovoltaic solar cells through extraction

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Abstract. The installation of PV modules was 97.9GW and the accumulation volume of PV device was 500GW in 2018. According to the research, the accumulation of waste modules will reach to 8600 tons in 2030 as the result of the life expectancy of PV modules. Moreover, Crystalline-Silicon solar panels account for 90% of the waste. This study recycles photovoltaic solar cells by leaching and extraction. According to the analyst, Silicon cells content 90% of Si, 0.7% of Ag, and 9.3% of Al. Silicon cells were leached by 4M nitric acid at 80°C for 4 hours then 3M sodium hydroxide at 70°C for 3 hours, and the leaching efficiency were 99.7% of Ag, and 99.9% of Al, respectively. Leaching process separated Silicon from others metal. Na-Cyanex 272 in kerosene was employed to separate Al from Ag. The efficiency of extraction is 96%. After the process of extraction, 1M hydrochloride acid was employed to strip Al from the organic solvent. The efficiency of stripping is 99.9%. After extraction process, Ag was remained in the aqueous phase and precipitated to AgCl. In conclusion, this study shows the optimal parameters of the leaching steps, extraction steps, precipitation and vacuum concentration to get the product. The recovery of Si and Ag were 99.5% and 98% respectively.

Keywords: Photovoltaic modules, PV cells, Hydrometallurgy, extraction, recycle

1. Introduction
PV modules is one of the greenest and promoted energy-generator. By the statistic, 106GW of solar PV capacity added in 2018 and the accumulation of PV modules is now increased to 508GW.¹ More solar PV was installed than the net capacity additions of fossil fuels and nuclear power combined. PV modules have an average life of 20-25 years,² which means that at 2030 we will have the great amount of PV waste in the future. According to the statistic in IRENA, the waste of solar panels in 2050 will reach 600,000 tons, which means that we should make effort on recycle PV modules right now.

According to the experiment, Poly-crystalline Silicon solar panels contain Silicon, Aluminum, silver, Lead, and Tin and PV cells contain the most of the Silicon (90%), Aluminum and Silver (1%). This study dismantled PV modules to PV cells and recovered PV cells by leaching and extraction process. Silicon is hard to leach by non-organic acids (HCl, H2SO4, and HNO3). The first step to purify silicon was leaching metals from PV cells and purify silicon. Aluminum is known as easy to separate by precipitate and extraction. This study decided to use extraction process to separate Aluminum from silver to improve the purity of silver. According to the literature review,³⁴⁵⁶⁷⁸⁹, N503, Tributyl Phosphate (TBP), D2EHPA (di-(2-ethylhexyl) phosphoric acid), Cyanex901 and Cyanex272 was used to separate Aluminum from other metals. This study used Cyanex272 for extractant because of the optical pH value 2-3. Cyanex272 and D2EHPA was in the pH range 2-3 for effectively extract Aluminum(III). Therefore, Cyanex272 has higher efficiency and selectivity for Aluminum(III) which
makes Cyanex272 the better agent for selectively extraction.\textsuperscript{[13]} After extraction and stripping process, precipitation was employed to recover Silver to AgCl.\textsuperscript{[14][15]}

This study provided the separation and recovery of Silicon, Aluminum and silver from PV cell via hydrometallurgy to obtain valuable metals. The resources can be recycled and also reduced the wastes of PV modules.

2. Materials and experiment

2.1 Materials

Poly-crystalline silicon PV modules used in this study are from the waste PV modules recycling factory. Table 1 shows the mass fraction of PV modules. PV modules are composed of aluminum frame, tempered glass, Ethylene-vinyl acetate resin and back sheet, PV cells, Ribbon, and Junction Box. This study dismantled PV moduels to PV cells and recovered it by several processes. Table 2 shows the chemical composition of commercial PV cells.

| Table 1. Mass fraction of PV modules |
|-------------------------------------|
| Aluminum frame | Tempered glass | EVA and backsheet | PV cells | Ribbon |
| 14.7% | 68.4% | 11.2% | 3.1% | 1.3% |

| Table 2. The chemical composition of PV cells |
|---------------------------------------------|
| Element | Ag | Al | Si |
| Mass fraction | 0.7% | 9% | 90% |

2.2 Pretreatment

PV cells was dismantled from the PV modules. After removing Aluminum frame and tempered glass, EVA reins still remained on the PV cells. Pretreatment process was employed to eliminate the EVA resin from the PV cells.

2.3 Leaching

Nitric acid was employed to leach Al and Ag from the PV cells. After acid leaching process, Al-Si alloy still remained on the PV cells. In order to purify the Silicon, Sodium Hydroxide leaching was employed to break the boning between Si and Al. To optimize the experimental condition for effective leaching, this study was made carrying different process parameters viz. time (0.5-4hr), liquid-solid ratio, and acid concentration (0.5M-6M).

Leaching efficiency of metal was calculated by the equation below:

\[ X\% = \left( \frac{Vc \cdot Cx}{Mw \cdot x} \right) \times 100\% \]  \hspace{1cm} (1)

\( X\% \) = leaching efficiency (g/L), \( M \) = the weight of the sample (g), \( Vc \) = the volume of the liquid (L), \( Wx \) = target metals weight fraction (wt%).

2.4 Extraction

The metals in the leaching solution is separated through selectively solvent extraction and stripping. Aluminum was extracted by Na-Cyanex272 and silver remained in the solution. Using HCl to strip Aluminum from the organic phase. The metals can be separated. The solution with silver was precipitate by sodium chloride into AgCl. This study also carried the parameters of extraction process
viz. the necessary of saponification, pH value (0.5-3), O/A ratio, extractant concentration, stripped solvents concentration, and reaction times.

The extraction efficiency of Na-Cyanex272 and stripping efficiency were calculated by equations below:

\[
E_0\% = \left( \frac{\sum [M]_{org}}{\sum [M]_{org} + \sum [M]_{aq}} \right) \times 100\% \quad (2)
\]

\[
E_{\text{stripping}}\% = \left( \frac{\sum [M]_{after\,stripping}}{\sum [M]_{before\,stripping}} \right) \times 100\% \quad (3)
\]

\[
Na^+_\text{(aq)} + H^+ \text{ Cyanex272}^{-\text{(aq)}} \rightarrow Na^+_\text{(aq)} \text{ Cyanex272}^{-\text{(aq)}} + H^+ \quad (4)
\]

2.5 Analytical method

The sample after leaching, extraction process, and precipitation were filtered by 0.45 μm of membrane filter and were diluted by 1% HNO3 solution for ICP-OSE (Inductively Coupled Plasma-Optical Emission Spectrometry, PerkinElmer optima 2100DV) analyst. The ICP-OSE analyst was calibrated with ICP multi-element stander and tin standard solutions. Each aqueous solution was analyzed for three times and averaged for the reported.

3. Result and discussion

3.1 Thermal treatment to eliminate EVA resin from PV cells

After dismantling PV modules, EVA resin still remained on the PV cells which might harm to leaching and the process below. Fig. 1 (a) and (b) show the TG/DTA analyst chart of PV cells with EVA resin and pure EVA reasin. Comparing to figures, both of them decline the weight on 300 degree. After heating to 500 degree, the mass changing tend to balance. This study used the thermal process to eliminate EVA resin by heating to 500 Celsius degrees for 5 hours in the atmosphere. This process can eliminate 99.97% of EVA resin from PV cells.

![Fig. 1](a) PV cells with EVA resin layers TG analyst. (b) TG analyst of EVA resin.

3.2 Nitric acid for first leaching process

This study provides the leaching process to leach Ag and Al form PV cells through Nitric acid. Nitric acid can effectively separate Ag and 70% weight of Al from PV cells.

3.2.1 Effect of the concentration of nitric acid
Fig. 3 shows the leaching efficiency from adjusting the concentration of HNO4 in 4 hours, 50 of L/S ratio, and 85 degrees of temperature. Silver and aluminum both get a good leaching efficiency on 4M of nitric acid. After rising the concentration of HNO4, the leaching efficiency of aluminum still not overcome 75%. Al-Si alloy still remained on the PV cells. The optimal condition of the concentration was chosen as 4M.

![Graph of leaching efficiency](image1)

**Fig. 2** Leaching efficiency of adjusting [HNO4] (L/S=50, Reaction times=240min., Temperature=85 degree).

### 3.2.2 Effect of Liquid-solid ratio

Fig. 4 show the leaching efficiency from adjusting the liquid-solid ratio. The L/S ratio was investigated by verifying the ratio from 10 to 400. As the result, PV cells has effective leaching efficiency (99.5% of silver and 70% of aluminum) after 100. Hence, the optimal condition of the L/S ratio was chosen as 100ml/g.

![Graph of leaching efficiency](image2)

**Fig. 3** Leaching efficiency of adjusting L/S ([HNO4]=4M, reaction times=240min., Temperature=85 degree).

### 3.2.3 Effect of the reaction times

Fig. 5 shows the leaching efficiency from adjusting the reaction times for 4M of HNO4 in 100 of LS ratio, and 85 degrees. Reaction times was investigated by verifying from 30 minutes to 240 minutes. As the result, after and hours, both of the leaching efficiency tend to balance. Hence, the optimal condition of reaction times was chosen as 60 minutes.
3.3 Sodium Hydroxide leaching process

After nitric acid leaching process, Al-Si alloy still remained on the PV cells. As the equation showing below:

$$\text{AlSi + 2NaOH + H}_2\text{O} \rightarrow 2\text{Na}^+ + \text{Si}_2\text{O}_3 + \text{Al}^{3+} + \text{H}_2$$ (5)

Sodium Hydroxide has the ability to transfer Al to Al ion. This study set the optimal parameters as 3M of NaOH, L/S ratio=50, 240 minutes, and temperature for 70 degrees. After two leaching processes, the leaching efficiency of Al ion can reach to 99.9%.

3.4 Aluminium extraction through Na-Cyanex272

After leaching process, Na-Cyanex272 was employed to extract Aluminium from Silver. Na-Cyanex272 was diluted by kerosene. Cyanex272 was saponificated by sodium hydroxide into Na-Cyanex272. As Fig. 6 and Fig. 7 show, the extraction efficiency of aluminum with saponification is higher than non-saponification.

3.4.1 Effect of pH value

The pH value was adjusted with nitric acid and ammonia solutions. The pH values were verified from 1 to 4. After the pH value reach 4.2, aluminum started to precipitation into Al(OH)3. According to Fig. 6, the extraction efficiency increased at 2.5. The extraction efficiency was 96% at pH 3.7. Hence, this study set 3.7 as the optimal parameters.

Fig. 4 Leaching efficiency of adjusting reaction times ([HNO4]=4M, L/S=100, Temperature=85 degree).

Fig. 5 The extraction efficiency of Na-Cyanex272 in condition of 0.3M extractant, A/O ratio=1, and reaction times=10min.
3.4.2 Effect of Na-Cyanex272 concentration

The concentration of Na-Cyanex272 was verified from 0.1M to 0.6M. Fig. 8 shows the extraction efficiency of the concentration of Na-Cyanex272. The extraction efficiency increased from 3% to 96% when the concentration of extractant increased from 0.1M-0.6M. After reaching the concentration of extractant to 0.3M, the efficiency tends to balance. Hence, the optimal parameters of the extractant concentration were set as 0.3M.

3.4.3 Effect of extraction aqueous-oil volume ratio

The effect of A/P ratio was investigated and set from 0.1 to 10. Fig. 9 was the extraction efficiency which decreased from 97% to 26.8%. In order to concentrate aluminum in high concentration and reduce the waste of extractant, this study set the optimal parameters of A/O ratio as 3(mL/mL).
3.4.4 Effect of adjusting reaction times

Under the condition of fixed solution pH value=3.7, A/O=3, and [Na-Cyanex272]=0.3M, the shaking time was verified to 1min., 5min., 10min., 15min., 20min., and 30min., individually. Fig. 10 shows the result of verified the reaction times. After the time reach 5min., the efficiency tends to balance. Hence, this study set 5min as the optimal parameters of reaction times.

3.4.5 Stripping experiment

From the extraction experiments, it was observed that Na-Cyanex272 has the ability to extract aluminum from silver-aluminum solution. The organic phase with aluminum was stripped to water phase by different concentration of hydrochloric acid, OA ratio and reaction times. The results indicated that 1M HCl, O/A ratio=0.25, and reaction times=5 min. can efficiently strip the aluminum from organic phase. The efficiency of stripping was 99.9%.

| Table 3. Optimal condition of Al³⁺ stripping |
|---------------------------------------------|
| Optimal condition of Al³⁺ stripping          |
| Reagent          | 1M HCl          |
| O/A ratio        | 0.25            |
| Reaction times   | 5 min           |
| Stripping efficiency | 99.9%          |
3.5 Silver chloride and purified silicon after leaching and extraction processes

After leaching and extraction processes, silicon, aluminum, and silver were separated effectively. Silicon was collected after leaching process due to the selectivity of nitric acid. The composition after leaching process was showed on Table. According to the reaction equation below:

\[
\text{Ag}^{+}_{(aq)} + \text{Cl}^{-}_{(aq)} \rightarrow \text{AgCl(s)}
\]

The standard Gibbs free energies of \( \text{Ag}^{+} \), \( \text{Cl}^{-} \) and \( \text{AgCl(s)} \) are 77.16kJ/mol, -131.0563kJ/mol, and -109.86kJ/mol, respectively. The solubility product (Ksp) of AgCl is 10\(^{-9.82} \) at 25°C.[16] This reason indicated Ag ion precipitated easily and rapidly as AgCl then separated with Al ions. Hence, this study precipitated Ag ion into silver chloride for recovering Silver in the PV cells. The recovery of Si and Ag were 99.1 and 95% individually. Therefore, the purity of silicon after the processes is 99.5%.

![Fig. 10 Silver Chloride after precipitated by Sodium Chloride](image1)

![Fig.11 Silicon after leaching process](image2)

Table 4. Composition of silicon wafer before and after leaching process (Analyst by ICP-OSE)
| Element | Before leaching | After leaching |
|---------|----------------|----------------|
| Ag (mg/kg) | 5701.8 | 22.8 |
| Al (mg/kg) | 78802.8 | 101.4 |
| Na (mg/kg) | 1169.4 | 3850 |
| B (mg/kg) | 75.77 | 74 |
| Cu (mg/kg) | 2.3 | >0.01 |
| Pb (mg/kg) | 6.63 | 6.95 |
| Si (purity %) | 90% | 99.5% |

4. Conclusion
This study proposed a recovery route of silicon and silver from PV cells by hydrometallurgy ways. Two leaching steps (acid and Alkaline) were employed to purify silicon and the purity of silicon was 99.5%. The leaching rate of Al and Ag were up to 99% after two leaching process. Moreover, the recovery of Ag and Si was 98% and 99.5%. This study can provide to the research of recycling PV modules.

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References
[1] T. Doi, I. Tsuda, H.Unagida, A.Murata, K.Sakuta, and K.Kurokawa, “Experimental study on PV module recycling with organic solvent method,” Sol. Energy Mater. Sol. Cells, vol. 67, no. 1–4, pp. 397–403, 2001.
[2] S.Weckend, A.Wade, and G.Heath, End-of-life management: Solar photovoltaic panels. 2016.
[3] Y. K.Yi, H. S.Kim, T.Tran, S. K.Hong, andM. J.Kim, “Recovering valuable metals from recycled photovoltaic modules Recovering valuable metals from recycled photovoltaic modules,” J. Air Waste Manage. Assoc., vol. 64, no. 7, pp. 797–807, 2014.
[4] T.N. Shilimkar, S.S. Kolekar, M.A. Anuse, Rapid extraction separation of aluminium(III) from associated elements with n-octylaniline from succinate media, Sep. Purif. Technol. 42 (2005) 55–63.
[5] W. Hiroshi, K.Yasushi, Extraction of trivalent aluminium and gallium from sodium hydroxide solution containing tartaric acid by trioctylmethylammonium chloride, Solvent Extr. Res. Dev. Jpn. 7 (2000) 118.
[6] I. Toth, E. Brucher, Z. Szabo, Extraction of gallium(III) and aluminium(III) with o,o-dialkyldithiophosphoric acids, Talanta 37 (1990) 1175–1178.
[7] P.E. Tsakiridis, S. Agatzini-Leonardou, Solvent extraction of aluminium in the presence of cobalt, nickel and magnesium from sulphate solutions by Cyanex 272, Hydrometallurgy 80 (2005) 90–97.
[8] M.M. Orive, M.A. Olazabal, L.A. Fernandez, J.M. Madariaga, The recovery of cobalt and nickel from acidic sulphate solutions in the presence of aluminium, Solvent Extr. Ion Exch. 10 (1992) 787–797.
[9] H.S. Ajgaonkar, P.M. Dhadke, Solvent extraction separation of iron(III) and aluminium(III) from other elements with Cyanex 302, Talanta 44 (1997) 563–570.
[10] Cytec, Cyanex 272, Technical Brochure, American Cyanamid Company, 1989.
[11] K. Sarangi, B.R. Reddy, R.P. Das, Extraction studies of cobalt(II) and nickel(II) from chloride solutions using Na-Cyanex 272. Separation of Co(II)/Ni(II) by the sodium salts of D2EHPA, PC88A and Cyanex 272 and their mixtures, Hydrometallurgy 52 (1999) 253–265.
[12] G.M. Ritcey, A.W. Ashbrook, Solvent Extraction Principles and Applications to Process Metallurgy, Part-1, Elsevier Science Publishers B.V., Amsterdam, The Netherlands, 1984, pp. 15–20.
[13] D. Mohapatra, K. Hong-In, C. W. Nam, and K. H. Park, “Liquid-liquid extraction of aluminium(III) from mixed sulphate solutions using sodium salts of Cyanex 272 and D2EHPA,” Sep. Purif. Technol., vol. 56, no. 3, pp. 311–318, 2007.
[14] P. Dias, S. Javimczik, M. Benevit, H. Veit, and A. M. Bernardes, “Recycling WEEE: Extraction and concentration of silver from waste crystalline silicon photovoltaic modules,” Waste Manag., vol. 57, pp. 220–225, 2016.
[15] I. F. F. Neto and H. M. V. M. Soares, “Sequential separation of Ag, Al, Cu and Pb from a multi-metal leached solution using a zero waste technology,” Sep. Sci. Technol., vol. 53, no. 18, pp. 2961–2970, 2018.
[16] Soolyung Kim, J. C. Lee, K. S. Lee, K. K. Yoo, and R. D. Alorro, 2014: Separation of Tin, Silver and Copper from Waste Pb-free Solder Isong Hydrochloric Acid Leaching with Hydrogen Peroxide, Materials Transactions, Vol. 55, No. 12, 1885-1889