

Separation of Valuable Metal from Waste Photovoltaic Ribbon through Extraction and Precipitation[#]

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Abstract

With rapid increasing production and installation, recycling of photovoltaic modules has become the main issue. According to the research, the accumulation of waste modules will reach to 8600 tons in 2030. Moreover, Crystalline-silicon (c-Si) Photovoltaic modules account for more than 90% of the waste. C-Si PV modules contain 1.3% of weight of photovoltaic ribbon inside which contains the most of lead, tin and copper in the PV modules, which would cause environmental and humility problem. This study provided a valuable metal separation process for PV ribbons. Ribbons content 82.1% of Cu, 8.9% of Sn, 5.2% of Pb, and 3.1% of Ag. All of them were leached by 3M of hydrochloric acid in the optimal condition. Ag was halogenated to AgCl and precipitated. Cu ion was extracted and separated from Pb and Sn by Lix984N then stripped by 3M H₂SO₄. The effect of the optimal parameters of extraction was also studied in this essay. The maximum extraction efficiency of Cu ion was 99.64%. The separation condition of Pb and Sn were obtained by adjusting the pH value to 4 thought ammonia to precipitate and separate Pb and Sn. The recovery of Pb and Sn can reach 99%.

Key words : photovoltaic ribbon, hydrometallurgy, leaching, liquid-liquid extraction, Lix984N, recycling

1. General Introduction

The PV technology is one of the greenest and most promoting green energy-generating technologies as it generates electricity directly from the solar energy and therefore avoid fossil energy consumption during energy production process. By the statistic, 106GW of solar PV capacity added in 2018 and the accumulation of PV modules is now increased to 508GW¹⁾. More solar PV was installed than the net capacity additions of fossil fuels and nuclear power combined. However, the rapidly increasing production and installation of PV modules will cause a huge problem in the future due to the life of

PV modules (15-20years)²⁾. According to the research, the accumulation of waste modules will reach to 8600 tons in 2030. Moreover, Crystalline-silicon Photovoltaic modules account for more than 90% of the waste and there is no critical commercial way to recover the valuable metals from the PV modules. The solar module is assembled by tempered glass which allows light penetrates the c-Si cells and protects the cells; EVA resin is the adhesive of glass, solar cells and back sheet. The target of this study, PV ribbon, which looks like the wire what carried the electrical energy produced by c-Si solar cells.

As the importance of recycling PV modules increasing, variable researches were published to purify the valuable

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materials and reduce the mass and volume of the waste. The research from Korea separated PV ribbon by melting the coating layer composed of tin and lead and separate copper layer; then used the thermal process under a low atmosphere with CH₄ to purify Copper, and the purity of Cu was 99.5%³⁾. Another research oxidized the Pb-Sn alloy layer of PV Ribbon and used ball milling to separate copper and oxide layer. The other research leached Pb-free PV ribbon by HCl and HNO₃ then separated it by precipitation and electrochemical⁴⁾. The research from KIGAM showed a recycling process by leaching Sn ions by HCl and separated Cu by adding Sn powder to reductive copper ions to copper metals. After the leaching process, this research used TBP to extract Sn from the leach solution, and <1% of Pb was extracted⁵⁾.

This study provided the leaching process to separated tin, lead and copper from silver by using hydrochloric acid. After the leaching process, this study extracted Cu by Li₉84N and stripped by H₂SO₄. Tin and lead were separated by adjusting pH value and precipitation.

2. Experimental

2.1. Materials

Poly-crystalline silicon PV modules used in this study are from the waste PV modules recycling factory. Table 1 shows that PV modules are composed of aluminum frame (14.7%), tempered glass (68.4%), Ethylene-vinyl acetate resin and back sheet (11.2%), PV cells (3.1%), Ribbon (1.3%), and Junction Box (1.3%), Table 2 shows the chemical composition analyzed by ICP-OES (Inductively

Table 1. Chart of PV modules mass fraction

Aluminum frame	Tempered glass	EVA and backsheets	PV cells	Ribbon
14.7%	68.4%	11.2%	3.1%	1.3%

Table 2. Chart of PV ribbons component

Element	Cu	Pb	Sn	Ag
Mass fraction (%)	82.1%	5.2%	8.9%	3.1%

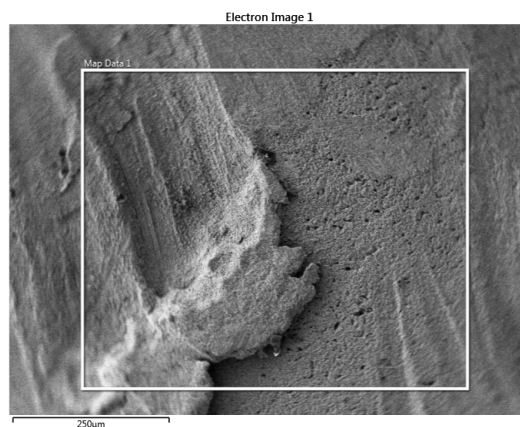


Fig. 1. SEM figure of PV Ribbons.

Coupled Plasma-Optical Emission Spectrometry, PerkinElmer optima 2100DV), and Fig.1 shows the SEM-EDS figure of PV ribbons. The chemical composition of commercial PV ribbons is mainly composed of 83% of Cu, 9% of Sn, 4.5% of Pb and 3% of Ag.

2.2. Pretreatment

PV ribbons were dismantled between the layers of EVA resin and c-Si PV cells. After dismantling, some EVA resin would attach on the surface of the PV ribbon. Pretreatment was employed to eliminate the resin from PV ribbons by heating the resin to evaporation.

2.3. Leaching

Hydrochloric acid was employed to leach PV ribbon. Ag was separated from other metals by halogenating to AgCl. To optimize the experimental condition for effective leaching, this study was made carrying different process parameters viz. time (0.5-4hr), oxidation rate, temperature (25-85°C), liquid-solid ratio, and acid concentration (0.5M-6M).

Leaching efficiency of metal was calculated by the equation below:

$$X\% = \left(\frac{V_c C_x}{Mw_x} \right) \times 100\% \quad (1)$$

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

2.4. Extraction procedure

After the leaching process, the sample was extracted by Lix984N and stripped by H_2SO_4 in the optimal condition. This study also carried the parameters of extraction process viz. pH value (0.5-3), O/A ratio, extractant concentration, stripped solvents concentration, and reaction times.

The extraction efficiency of Lix984N and stripping efficiency were calculated by equations below:

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

$[M]_{org}$ =the concentration of metal in the organic phase after extraction, $[M]_{aq}$ =the concentration of metal in the aqueous phase after extraction.

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

$[M]_{after stripping}$ =the concentration of metal in the aqueous phase after stripping from organic phase, $[M]_{before leaching}$ =the concentration of metal in the organic phase before the stripping process.

2.5. Precipitation

This study provided the separation process to separate Lead and Tin through precipitation. In this process, the concentration of Lead and Tin from the liquid after extraction in different pH value would show. And this study would discuss the difference of concentration between Lead and Tin. After all, this study chose the right point to effectively separate them.

2.6. Analytical method

The sample after leaching, extraction process, and

precipitation were filtered by $0.45\mu m$ of membrane filter and were diluted by 1% HNO_3 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 for eliminating EVA resin

Fig. 2 shows the TG analyst of EVA resin⁶⁾. After heating over $500^\circ C$, the mass decline of EVA resin approach to zero. This study used the thermal process to eliminate EVA resin by heating to $500^\circ C$ for 5 hours in the atmosphere. This process can eliminate 99.97% of EVA resin attaching on PV ribbons.

3.2. Hydrochloric acid leaching process

This study provided an acid leaching process to separate and leach valuable metals into the water as the state of Cu^{2+} , Sn^{4+} , and Pb^{2+} ions.

3.2.1. Effect of the concentration of hydrochloric acid

Fig. 3 shows the leaching efficiency from adjusting the concentration of HCl in 3 hours, 10% of H_2O_2 , 20 of

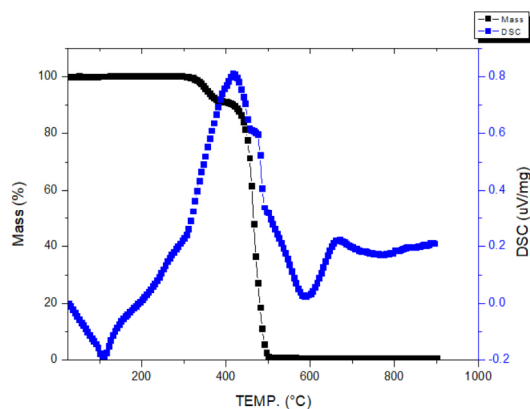


Fig. 2. TGA analysis of EVA resin.

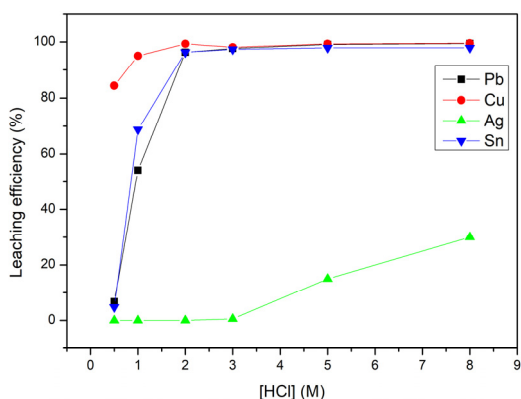


Fig. 3. Leaching efficiency of adjusting [HCl] ($[H_2O_2]=10\%$, $L/S=20$, reaction times=240minute, temperature =60 degrees).

L/S ratio, and 60 degrees of temperature. Lead, Tin and Copper get a good leaching efficiency, up to 97.5% on 3M of hydrochloric acid. After rising the concentration of HCl, the leaching efficiency of silver would gradually increase but not over 30%. To separate silver from the other metals. This study chose 3M as an optimal condition.

3.2.2. Effect of the volume percentage of H_2O_2

Fig. 4 shows the leaching efficiency from adjusting the volume percentage of H_2O_2 to increase the oxidation rate for 3M of HCl, 3hours, 20 of L/S ratio, and 60

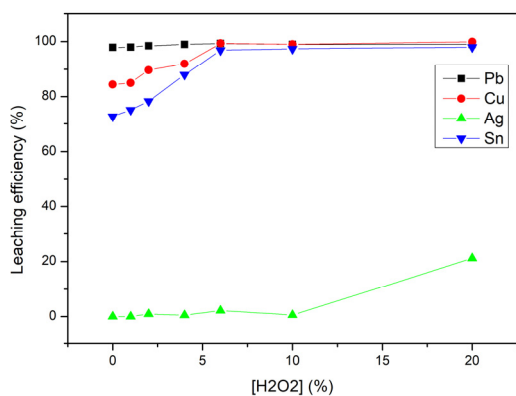
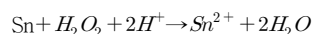


Fig. 4. Leaching efficiency of adjusting $[H_2O_2]$ ($[HCl]=3M$, $L/S=20$, reaction times=240minute, temperature=60 degrees).

degrees of temperature. As the volume percentage of H_2O_2 increased, the leaching rates of Lead, Tin and Copper increased. In the leaching tests, tin was oxidized with hydrogen peroxide as the following equation⁴⁾.



This equation shows the significance of oxidation for tin to increase the leaching efficiency. Because that 6% of H_2O_2 shows effective leaching efficiency (99.3% of lead, 99.35% of copper, and 96.9% of tin) in this experiment and 6%-20% tend to balance, this study set the optimal parameters of H_2O_2 to 6%.

3.2.3. Effect of Liquid-solid ratio

Fig. 5 shows the leaching efficiency from adjusting the liquid-solid ratio. The LS ratio was investigated by verifying the ratio from 10 to 1000. As the result, PV ribbon has effective leaching efficiency (99.5% of lead, 99.85% of copper, and 97% of tin) after 20. Hence, the optimal condition of the L/S ratio was chosen as 20ml/g.

3.2.4. Effect of the reaction times

Fig. 6 shows the leaching efficiency from adjusting the reaction times for 3M of HCl in 20 of LS ratio, and 60 degrees. Reaction times was investigated by verifying

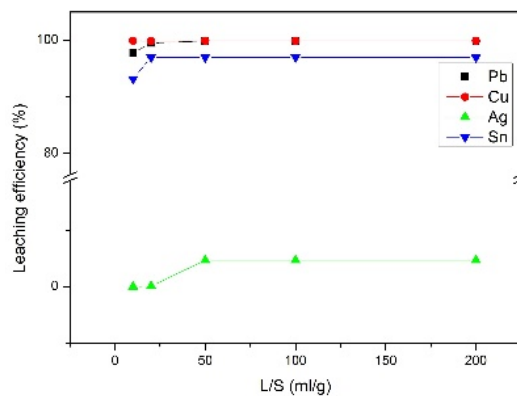


Fig. 5. Leaching efficiency of adjusting L/S ratio ($[HCl]=3M$, $[H_2O_2]=10\%$, reaction times=240minute, temperature =60 degrees).

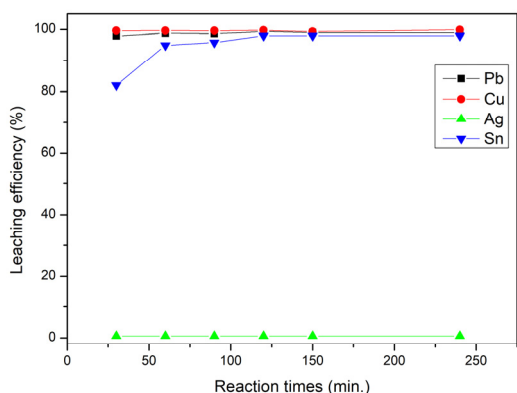


Fig. 6. Leaching efficiency of adjusting Reaction times ([HCl]=3M, [H₂O₂]=10%, L/S=20, temperature=60 degrees).

from 30 minute to 240 minutes. As the result showed, tin needed the time to leach. After 120 minute, PV ribbons has effective leaching efficiency (99.3% of Lead, 99.74% of Copper, and 98.3% of Tin) and tend to balance. Hence, the optimal condition of Reaction times was chosen as 120 minutes.

3.2.5. Effect of the temperature

Fig. 7 shows the leaching efficiency from adjusting temperature. Temperature was investigated by verifying the temperature from 25 degrees to 85 degrees. As the result showed, set the reaction temperature to 60 degrees

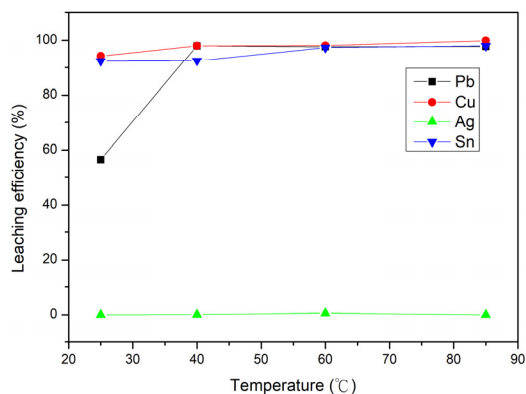
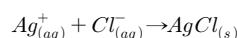


Fig. 7. Leaching efficiency of adjusting Reaction temperature ([HCl]=3M, [H₂O₂]=10%, L/S=20, reaction times=150minute).

has effective leaching efficiency. Hence, the optimal condition of reaction temperature was chosen as 60°C.

Hydrochloric acid can leach most of the metal inside the PV ribbons and nearly no effect on silver due to the reaction equation below.



The solubility product (K_{sp}) of AgCl is 10^{-9.82} at 25°C⁴). That's the reason indicated Ag ion precipitate easily and rapidly as AgCl. This study used this chemical property to separate Ag from other metals.

3.3. Copper extraction by Lix984N

After the leaching process, Lix984N was employed to extract Copper from Lead and Tin. Lix984N was diluted by kerosene.

3.3.1. Extraction efficiency of adjusting initial pH value

Because Tin ion started to precipitate at pH value=2.1, the initial pH value in this study was adjusted within 0.2 to 2 in the condition of A/O=1, 30%(v/v) of Lix984N, shaking frequency of 500 min⁻¹ and reaction times of 10 minute. Fig. 8 shows the effect of aqueous phase pH value on extraction percentage. The optimal parameter was found. The result showed that the extraction percentage of copper and lead increased when

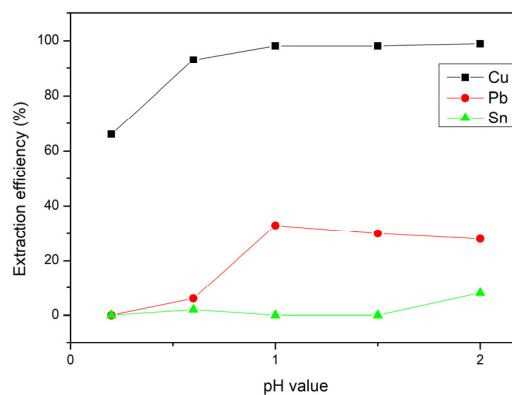
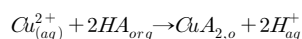


Fig. 8. Extraction efficiency of adjusting pH value ([Lix984N]=30%, A/O=1, Reaction times=10min.).

the aqueous phase pH value increased. Lix984N is an acidic extractant. Extraction reaction of Copper with Lix984N could be represented by^{7,8)}



As the equation above shows, Lix984N in the high acidity of aqueous phase is a disadvantage of releasing hydrogen ion from Lix984N. However, in order to separate copper and lead from extraction, the optimal parameter of pH value was chosen as 0.6. Because the Lix984N exchanges hydrogen ion selectively, the tin and lead ions mostly remain in the water phase. Copper, tin, and lead of extract phase can be separated.

3.3.2. Extraction efficiency of adjusting the concentration of Lix984N

The effect of A/O ratio was examined, and the results are shown in Fig. 9 The result showed that at the v/v(%) =20% has the highest extraction efficiency for copper (99%). The concentration of Lix984N=20% was fixed for subsequent experiment.

3.3.3. Extraction efficiency of adjusting aqueous-oil volume ratio

The effect of A/O ratio was examined, and the results are shown in Fig. 10 The result shows that no significant

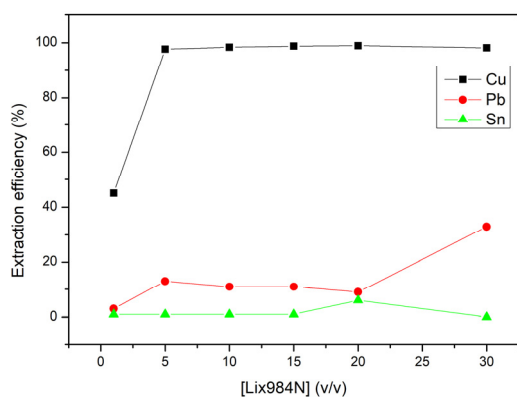


Fig. 9. Extraction efficiency of adjusting [Lix984N] (pH=0.6, A/O=1, Reaction times=10min).

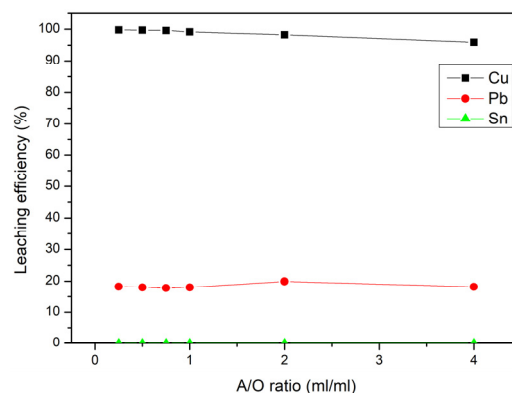


Fig. 10. Extraction efficiency of adjusting A/O ratio (pH value =0.6, [Lix984N]=30%, Reaction times=10min.).

change in the extraction percentage of copper. The A/O ratio=1/1 was fixed for subsequent experiments.

3.3.4. Extraction efficiency of adjusting reaction times

Under the condition of fixed solution pH value=0.6, O/A ratio=1, 20% of Lix984N and shaking frequency of 500min^{-1} , the shake time was changed to 0.5, 1, 3, 5, and 10, respectively. The result is shown in Fig. 11. The results showed that reaction times has less influence the extraction percentage of copper. The extraction efficiency can easily reach to 99% in 1 minute. Hence, the reaction times=1 min. was fixed for the experiments.

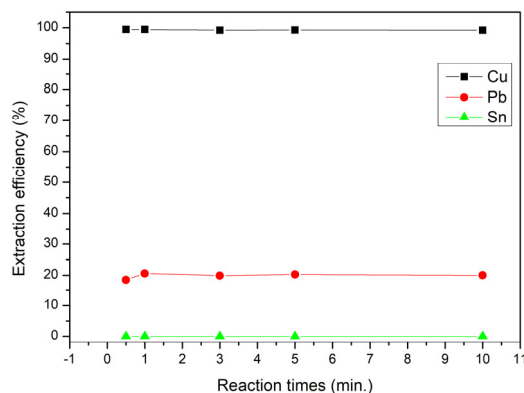


Fig. 11. Extraction efficiency of adjusting Reaction times (pH value=0.6, [Lix984N]=30%, A/O ratio=1).

3.3.5. Stripping experiment

From the extraction experiments, it was observed that Lix984N can extract copper from Cu-Pb-Sn solution. The organic phase with copper was stripped to water phase by different concentration of sulfuric acid, OA ratio and reaction times. The results indicated that 3M H₂SO₄ in the condition of O/A ratio=1 and reaction times=10 minutes can efficiently strip the copper from organic phase.

In terms of extraction, the optimal extraction operating condition of this technique were copper-lead-tin solution with pH 0.6, 20% of Lix984N, oil-aqueous volume ratio of 1/1 and 1minute of reaction time. The extraction efficiency of copper was higher than 99.5% as a result. The copper metal in the organic phase can be stripped by H₂SO₄ successfully.

3.4. Co-precipitation for separating tin and lead

After extraction process, copper was separated from lead and tin. According to the research, Sn²⁺ started to precipitate to Sn(OH)₂ at pH 2.1 and Pb²⁺ started to precipitate to Pb(OH)₂ at pH 7.2 by adding NaOH⁹⁾. Fig.

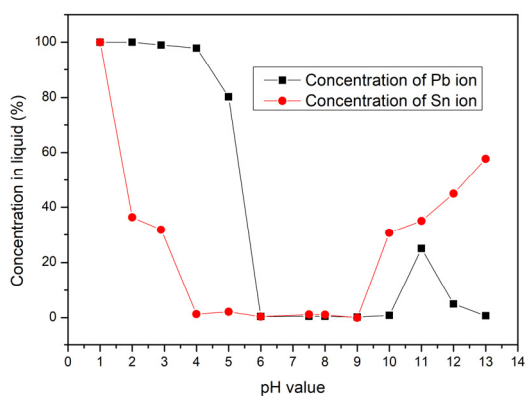


Fig. 12. Concentration percentage of liquid after extraction.

Table 3. Component percentage of precipitate

Element	pH=4	Percentage	pH=8	Percentage
Pb	54 ppm	4.1%	1352 ppm	98%
Sn	1252 ppm	95.4%	21.54 ppm	1.6%
Cu	5.74 ppm	0.4%	5.91 ppm	0.4%

12 shows the concentration of metal in liquid by adding NaOH to adjust pH value. The result showed that tin was totally precipitated at pH 4 and lead ions remained in the liquid. After rising the pH value to 6, lead was totally precipitated. This study separated tin by adding NaOH to pH 4 and filtered the precipitate. Then adjust pH value to 7 to collect Pb(OH)₂. As Table 3 shows, the recovery of lead and tin can reach 99%. The purity of lead was 98% and tin was 95.4%.

4. Conclusion

This study provides several processes to separate valuable metals from PV ribbons. According to the results of this experiment:

- 1) Ag was separated by halogenating to AgCl_(s).
- 2) The leaching efficiency of Pb, Cu, and Sn was 99.5%, 99.8%, and 98%, individually. Cu and Sn need H₂O₂ to rise the Redox value for increasing the leaching efficiency.
- 3) The optimal condition of leaching is 3M HCl, L/S=20, reaction times=120min., [H₂O₂]=6%, and reaction temperature=60 degrees.
- 4) In order to prevent co-extraction of lead and copper, this study chose pH=0.6 as the optimal condition to extract copper. The optimal condition of Lix984N extracting copper is pH=0.6, [Lix984N]=20%, A/O=1, and reaction times=1min. The extraction efficiency is 99.64%
- 5) Copper inside the organic phase was stripped by 3M of H₂SO₄ in O/A=1, reaction times=10 min.
- 6) The solvent extraction can recover low concentration metals selectively, and the separating effect of high distribution coefficient can be obtained by changing parameters. Therefore, this technique provides an effective method for separating and recovering copper metals.
- 7) The precipitation separation process can provide high purity (98%, 95.8%) and recovery of lead and tin.

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요 약*

최근 급격히 증가하는 생산량과 설치로 태양광모듈의 재활용이 주요 이슈가 되고 있다. 연구 결과에 따르면, 폐 태양광모듈의 양은 2030년에는 약 8600톤에 달할 것으로 예상되며, 결정질 실리콘 태양광 모듈은 그 가운데 약 90%에 달할 것으로 예상하고 있다. 결정질 실리콘 태양광 모듈은 중량비로 약 1.3%의 태양광 리본을 함유하며, 이 태양광 리본은 태양광 모듈에 함유된 대다수의 납, 주석, 구리를 포함하는 것으로 알려져 있다. 이에 본 연구는 태양광 리본으로부터 유가금속을 분리하고자 시도되었다. 샘플 분석 결과 태양광 리본은 약 82.1% 구리, 8.9% 주석, 5.2% 납, 그리고 3.1% 은을 포함하는 것으로 확인되었다. 침출 실험은 3M 염산을 사용하였고, 침출된 은 이온은 염화은의 할로겐 화합물로 회수되었다. 구리의 경우, Lix984N을 이용해 납과 주석으로부터 분리되었고, 3M의 황산을 이용해 스트리핑 되었다. 한편, 최적 조건하에서 구리 침출 효율은 약 99.64%이었다. 납과 주석의 경우, 수소이온 농도 조절을 통해 분리될 수 있었으며, 이 경우, 회수율은 약 99%이었다.

주제어 : 태양광 리본, 습식제련, 침출, 용매추출, Lix984N, 재활용

*상기 국문초록은 저자가 작성한 영문초록의 내용을 편집위원회에서 번역, 작성하였습니다.