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Hybrid Recovery of Copper and Silver from PV Ribbon and Ag Finger of EOL Solar Panels

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***Abstract*—**Recovery of pure copper and silver from end-of-life photovoltaic (PV) panels was investigated in this paper using an effective hybrid pyro-hydrometallurgical process. In the first step of waste treatment, solar panel waste was first dismantled to obtain a PV sheet to be cut and calcined at 500 °C, to separate out PV ribbon from glass cullet, ash, and volatile while the silicon wafer containing silver finger was collected for recovery. In the second step of metal recovery, copper recovery from PV ribbon was via 1-3 M HCl leaching with $SnCl_2$ and H_2O_2 additions in order to remove the tin-lead coating on the ribbon. The leached copper band was cleaned and subsequently melted as an anode for the next step of electrorefining. Stainless steel was set as the cathode with $CuSO_4$ as an electrolyte, and at a potential of 0.2 V, high purity copper of 99.93% was obtained at 96.11% recovery after 24 hours. For silver recovery, the silicon wafer containing silver finger was leached using HNO_3 at 1-4 M in an ultrasonic bath. In the next step of precipitation, silver chloride was then obtained and subsequently reduced by sucrose and NaOH to give silver powder prior to oxy-acetylene melting to finally obtain pure silver metal. The integrated recycling process is considered to be economical, providing effective recovery of high purity metals such as copper and silver while other materials such as aluminum, copper wire, glass cullet can also be recovered to be reused commercially. Compounds such as $PbCl_2$ and SnO_2 obtained can also be recovered to enter the market.

***Keywords*—**Electrorefining, leaching, calcination, PV ribbon, silver finger, solar panel.

I. INTRODUCTION

PV panels have been increasingly used for decades and in recent years have been recognized world-wide towards circular economy, not only in developed countries but also in developing and undeveloped countries due to energy dependence on economic growth. For renewable electricity generating capacity, solar cell is taking the lead, accounting for 57% of total renewable energy capacity, followed by wind, hydro and bio power. Installation of 22.5% (115 GW) was reported in 2019 [1], due to government support schemes and policies on the grid connection in most countries ranging from self-consumers to large scale systems. Despite the decline in China, India and Japan, Asian countries are the majority for new PV installation around 50% of the global addition. This indicates great amounts of end-of-life (EOL) PV panels piling up in the following 20-25 years.

Directives concerning waste management and recycling of EOL solar panels have become effective across Europe and America, along with Asian countries particularly in Japan and China [2]-[5]. In Europe, first enforced in 2003, the WEEE directive has been the most comprehensive scheme especially in Germany and UK to drive EOL solar waste management through producer responsibility from the take back, recovery and recycling, regardless of manufacturing facility locations, along with environmental impact and public health safety [2]. The policies also encourage product development based on easy recycle with less raw materials used and simpler design for dismantling as well as boosting up awareness of cost factor on collection and recycling of EOL panels. In the USA, regulations for EOL solar wastes have been treated differently depending on each state such as California and Washington in particular [3]. Various schemes have been exercised to promote PV recycling awareness through all stakeholders. Japan's regulations include Specified Home Appliances Recycling Law (SHARL) and Law for Promotion of Effective Utilization of Resources, 2000, raising the awareness to increase recycling ratio of materials used for electrical and electronics devices. Japan's roadmap for PV recycling announced in 2016 [4], concerns guidelines for collection, dismantling, logistics, pretreatment and suitable recycling. In China, Waste Electrical Electronics Product Recycling Management Regulation has been mandatorily effective since 2011 [5] for collection and recycling by qualified institutions coupled with special rules and regulations for EOL PV panel recycling to boost up recycling rates. In Thailand, a new draft WEEE law approved by the cabinet in 2015 is based on a hybrid scheme of Extended Producer Responsibility: EPR and governmental-fund model through the Ministry of Finance [6]. If enacted, that would facilitate collection, dismantling and recycling of the PV waste more systematically by stakeholders involving governmental bodies, private partners and public participation. Besides, the PV waste is not yet clarified as hazardous waste according to the Notification of Ministry of Industry, Subject: List of hazardous substances B.E. 2556 (2013). With the Alternative Energy Development Plan: AEDP2015 to boost up PV installation in the Thailand being 2,983 MW in 2019 and to reach 6,000 MW in 2036, the annual installation since 2011 till 2019 has been fluctuated depending on government support

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policies, giving the average annual installation of approximately 380 MW [7]-[9]. Hence, PV waste of significant value has been collected and accumulated gradually. Measures should therefore be undertaken in order to prevent PV waste to be end up in unauthorized recycle markets.

As the PV panel management and recycling schemes have not yet been fully developed or administrated in most Asian countries (except for Japan and China), it is also unlikely that EOL PV panels will be treated systematically and ecofriendly. Upon unawareness of local communities on solar panel recycling and perhaps related regulations have not yet come into effect, there is more chance of illegal household disposal and later where valuable materials such as aluminum frame is deliberately taken off and sold to the market, leaving behind the solar cell sheet to be ended up in the landfill. This will eventually cause economic-environmental issues within the countries. Therefore, in order to solve the foreseen problems, PV panel recycling scheme adaptable through local social context would help to lead the way towards sustainability, in complied with technological and economical feasibilities. This paper therefore focuses on solar panel recycling via hybrid - metallurgical process in order to obtain valuable metals such as copper and silver to circulate back for re-fabrication or other markets available domestically. The Department of Primary Industry and Mine (DPIM) collaborative with the Innovative Production and Recycling of Metals Research Center (IPRMRC) initiated the first sustainable recycling of EOL PV panels in order to motivate local producers, consumers and collectors involved in the scheme by the recovery of high valued metal such as pure copper and pure silver along with other materials such as aluminum and glass cullet that can enter back to the market. General steps of mechanical dismantling of the PV panel followed by thermal separation of the PV cells [10] have been adopted in order to proceed to the recovery of copper and silver from PV cells. Selective acid leaching of similar kind of wastes from variable sources in many investigations relied on HNO_3, HCl, and H_2SO_4, depending on waste compositions (Ag, Cu, Sn, Pb containing wastes) followed by solvent extraction and precipitation processes [11]-[16], were generally found to be the case. In the purifying step, electrorefining [17]-[19] is considered to be effective to give electrical grade copper where high purity silver can be achieved by means of precipitation. Therefore, in this research, following the mechanical and thermal waste separation, hydrometallurgical process, electrochemical processes and precipitation were selected as the feasible means of metal and materials recycling with potential revenues, and sustainability.

II. EXPERIMENT

A. Waste Pretreatment

As the architecture of PV panel is rather complicated, as simplified in Fig. 1, one of the most important aspects of PV recycling to start with is to effectively dismantle the whole PV structure while still containing highly concentrated valuable wastes for subsequent recovery processes. Recycling of PV panels is known to start from mechanical dismantling to separate aluminum frame and corner joints used for encapsulating the PV cell sheet and these frame and joint can go directly to secondary markets. The cable (junction box) is then detached, leaving a PV cell sheet to be cut and processed in subsequent recycling route. The PV cell sheet consists of PV cells laminated with EVA layer on both sides, which were enclosed with tempered glass on the top layer and attached with protective backsheet on the bottom side.

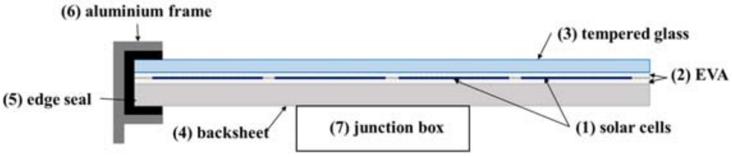
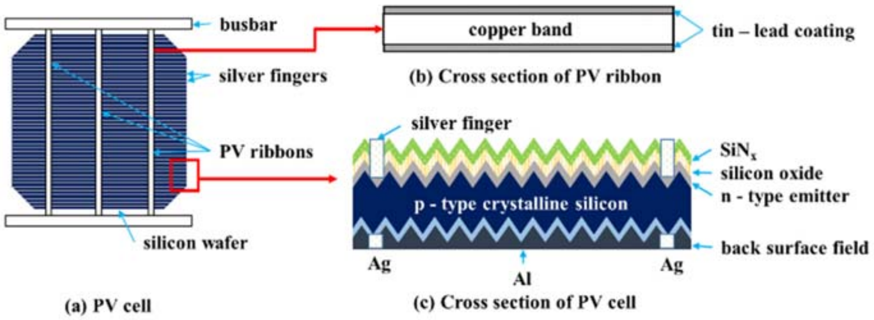


Fig. 1 Simplified architecture of PV panel (crystalline silicon)



(a) PV cell (b) Cross section of PV ribbon (c) Cross section of PV cell

Fig. 2 PV cell architecture showing PV ribbon and Ag finger functioning as electricity harvesting components

According to a previous study [20], the whole EOL solar panel weighed 21.4 kg, for example, giving the laminated PV cell sheet of 19 kg (88.78 wt.%), aluminum frame of 2 kg (9.35 wt.%), aluminum joint of 0.2 kg (0.935 wt.%) and cable of 0.2 kg (0.935 wt.%). On the laminated PV cell sheet of interest, laid PV cells containing high valued metals and materials, having architecture of PV ribbon and silver finger are as illustrated through Figs. 2 (a)-(c). On solar harvesting of electricity, photon reaction at the p-n junction once directing to the sunlight originates electrons traveling through fine parallel line metal finger, then crossed with the PV ribbon and through the bigger bands of busbars, heading for energy storage. The busbars are particularly of similar composition to that of PV ribbon but appears in a bigger size. Both are usually composed of electrical grade copper band coated with thin layer of soldering alloy such as Pb-Sn or lead free Sn-Ag for electrical contacts as shown in Fig. 2#b). Ag finger however appears as very tiny parallel lines running normal to the PV ribbon. The Ag finger is positioned on the spiky surfaces of multi-coated layers of crystalline silicon layer as illustrated in Fig. 2 (c). With the complicated structure of PV cells, each recovery step should be taken with care to conserve these valuable metals in order to achieve final recycling products of high purity and percentage recovery. Table I lists constituents in weight percentage after PV cell sheet calcination giving PV ribbon and busbar of 0.81 wt.%, along with Si wafer debris lined with Ag finger of 4.17 wt.%.

TABLE I
CONSTITUENTS AFTER PV CELL SHEET CALCINATION

Constituent	Weight	Weight %
PV ribbon and busbars	18.77	0.81
Ag containing Si wafer debris	96.41	4.17
Glass cullet	1,824.30	78.95
Ashes	38.48	1.67
Volatile	332.86	14.40
Total	**2,310.82**	**100.00**

The purpose of this research is the recovery of copper and silver of high purity from EOL PV panels through pyro-hydrometallurgical processing or a hybrid process. The EOL PV panels locally and regionally obtained were mechanically dismantled to separate the aluminum frames/joints and junction boxes, leaving the PV sheets to be cut into 15 cm x 15 cm pieces, designated as cut PV cells. The cut PV cells were calcined at 500 °C for 1 hour and the PV ribbon and busbar together with silicon wafer debris were retrieved from glass cullet and ashes. The PV ribbon and busbar are of similar composition, being the first type of waste to be recovered as pure copper. The silicon wafer debris lined with Ag finger are considered as the second type of waste to be recovered as pure silver and silicon fragments.

B. Copper Recovery from PV Ribbon

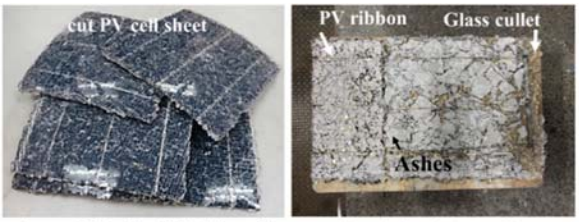
Acid leaching was first applied for Cu recovery, followed by anode melting and electrorefining of pure copper. The calcined PV ribbon obtained was subject to leaching using 1-3 M HCl at 70#C over 15, 30, 45 and 60 minutes, and 400 rpm stirring speed. The S/L ratio remained at 50 g/L, with additions of 2 wt.% H_2O_2 and $SnCl_2$ at 5 g Sn^{2+}/L. After leaching, leached copper was sieved, rinsed with DI water and alcohol and blown dried. The leachate was subject to cooling at 5° C for $PbCl_2$ precipitation. After filtering, the precipitates were dried while the solution was subject to precipitation using NaOH in order to obtain $Sn(OH)_2$ precipitates. Precipitates were heated above 105 °C to obtain tin oxides. Best selected leaching condition was employed for further refining of leached copper through electrorefining. Therefore, the leached copper was melted using oxy-acetylene around 1200#C and cast to prepare copper anode. The electrolytic cell was set up using cast copper as an anode and stainless-steel plate as the cathode while $CuSO_4$ solution was used as electrolyte. The applied voltage was in a range of 0.2-0.3 V for 24 hours to obtain the copper cathode of high purity. Characterization of the calcined, leaching and electrorefining products has been carried out via SEM coupled with EDS and EXD analyses. ICP-OES technique was utilized to obtain wet composition analysis of the leached copper and to confirm the purity of the copper cathode after electrorefining.

C. Silver Recovery from Silver Finger on Silicon cells

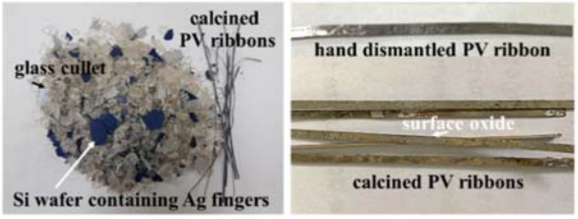
For Ag finger recovery, the silicon wafer debris containing Ag on its surface was subjected to HNO_3 leaching at concentration of 2-4 M with the applications of ultrasonic vibration using solid to liquid ratio at 100 g/L, 40-45 °C for 2 hours. Leaching by using magnetic stirring at 250 rpm, room temperature for 2 hours has also been performed for comparison. Precipitation using NaCl solution prepared at NaCl : H_2O at 300 g/L was carried out to achieve silver chloride (AgCl) prior to reduction using sucrose ($C_nH_{2n}O_n$) and NaOH to obtain silver precipitate. Finally, recovery of pure silver was conducted through melting of the obtained silver precipitate via oxy-acetylene heating. ICP-OES was operated to analyze the purity of leached products, and silver after refining.

III. RESULTS AND DISCUSSION

A. Calcination of PV Cell Sheets



a) cut PV cells (15x15 cm^2) b) calcined PV cells



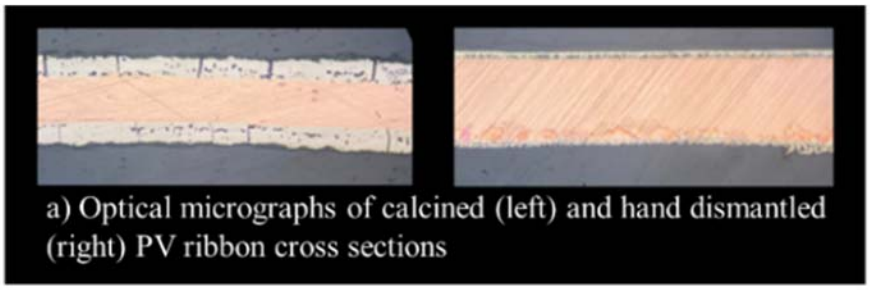
c) calcined PV cell separation d) hand dismantled & calcined PV ribbons

Fig. 3 Calcination of PV cells to obtain PV ribbon and silicon wafer debris lined with Ag finger

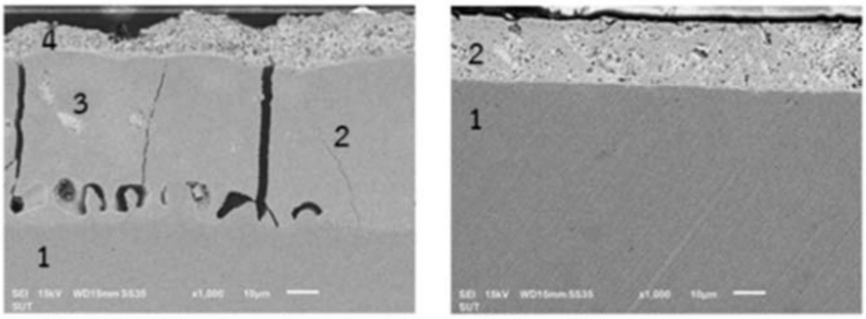
The first step of waste treatment included PV panel mechanical dismantling, PV sheet size reduction and finally, PV cell calcination, to obtain PV ribbon and silicon wafer debris containing Ag finger on its surface as shown in Figs. 3 (a)-(d). The surface of calcined PV ribbon appeared rough and dull due to oxide formation during calcination, as compared with bright surface PV ribbon obtained by hand dismantling.

Cross sections of both calcined and hand dismantled PV ribbon are comparatively shown in Figs. 4 (a) and (b). It can be seen that the cross section of PV ribbon originally contains a thin layer of approximately 20-30 μm with Sn-Pb coating on Cu band of approximately 0.2 mm. Analyzed by SEM coupled with EDS, this section has changed into different interlayers after calcination due to thermal diffusion designated as cracked Cu-Sn layer and Pb oxide at the outmost layer respectively. The thickness of the Cu band has also significantly reduced.

Silver fingers on the Si wafer substrate before and after calcination are compared, according to Figs. 5 (a)-(d). Ag finger underneath the fractured glass on top surface can be seen as very fine deposits lining in a parallel direction and crossing the PV ribbon in Fig 5 (a). Silicon wafer, found as debris after calcination, had the remaining Ag finger on its surface with contamination being observed as shown in SEM and EDS result, while the intact one showed clean surface of both Si wafer and Ag finger, as illustrated in Figs. 5 (b)-(d).



a) Optical micrographs of calcined (left) and hand dismantled (right) PV ribbon cross sections

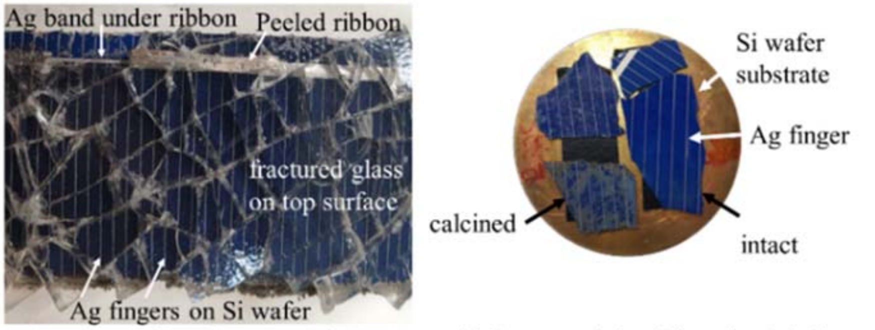


b) SEM micrographs of calcined (left) and hand dismantled (right) PV ribbon cross sections

EDS point analysis at different positions

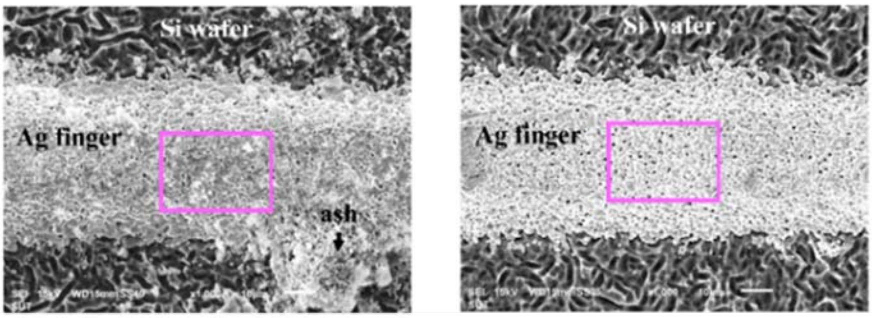
Element	Calcined				Hand dismantled	
	Position 1	Position 2	Position 3	Position 4	Position 1	Position 2
Cu	100	74.26	-	-	100	-
Sn	-	25.74	29.85	-	-	55.70
Pb	-	-	56.89	67.44	-	25.26
O	-	-	-	19.61	-	11.45
C	-	-	13.26	12.95	-	7.59

Fig. 4 Phase analysis of intact and calcined PV ribbon



a) location of Ag fingers on the EOL PV cell.

b) Ag containing Si wafer debris; intact and calcined ones.



c) calcined Si wafer containing Ag finger.

d) intact Si wafer containing Ag finger.

EDS area analysis on Ag fingers

Element	Calcined	Intact
Ag	83.36	95.34
O	11.96	3.18
Si	-	0.87
Pb	-	0.61
Ti	4.68	-

Fig. 5 Structure analysis of intact and calcined Ag finger on Si wafer

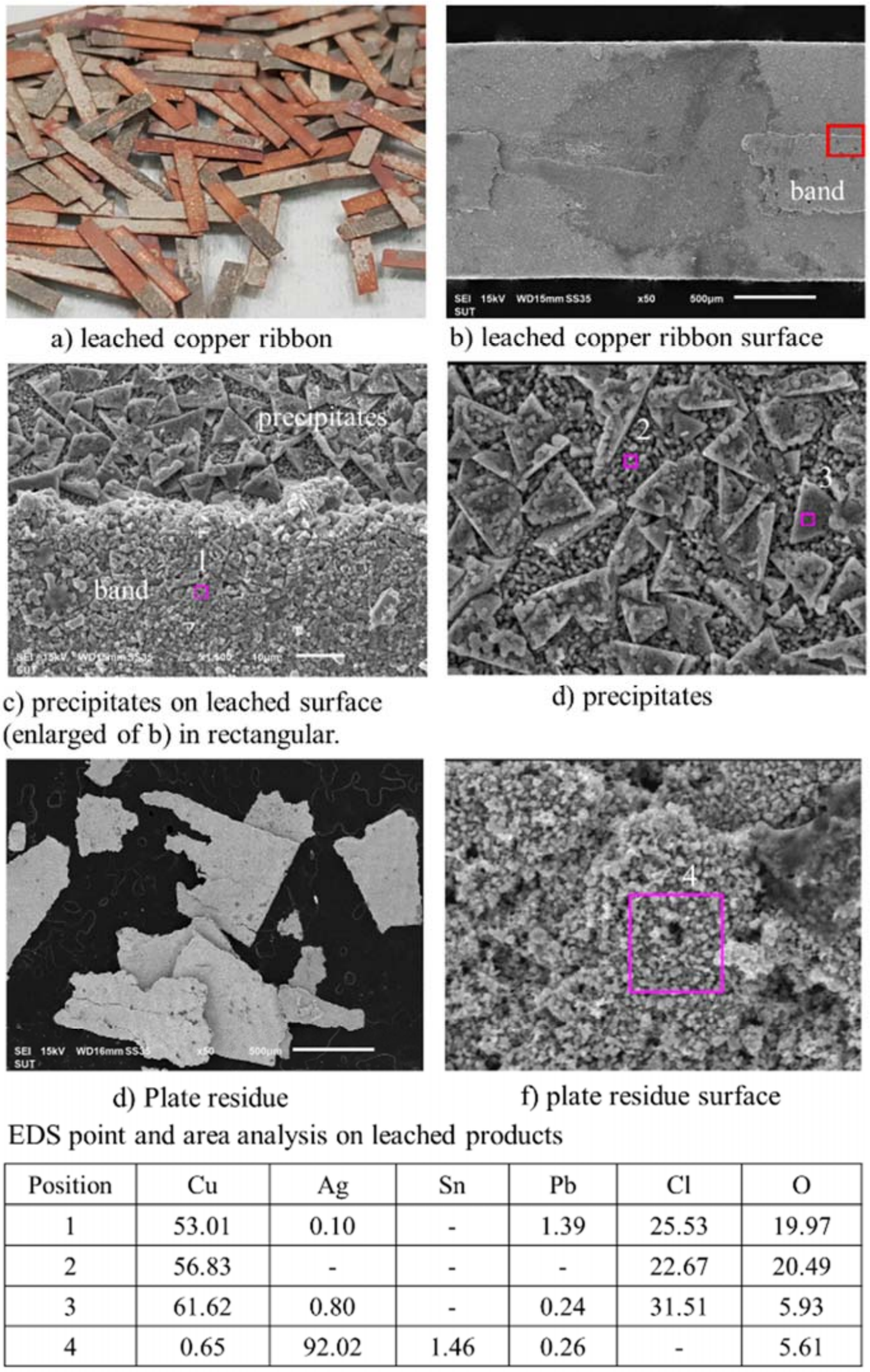
B. Recovery of Pure Copper from Calcined PV ribbon

1. Leaching of Calcined PV Ribbon

The oxide layer of Pb – Sn on the calcined PV ribbon was leached out by using HCl solutions at 0.5-3 M, leaving the Cu bands as shown in Fig. 6 (a), with some precipitate being clearly observed. SEM investigation, as demonstrated in Figs. 6 (b) and (c), shows different structures of precipitates and plate residue. EDS analyses showed spectrums 1-3 consisting of mainly copper with small traces of Sn and Pb. Plate residue as in spectrum 4 revealed composition being mainly of Ag. This silver band attached to the PV ribbon for electrical conduction has not been completely etched by HCl, leaving it in the form of Ag bands, which could be easily filtered out for further recovery.#

Influences of leaching time on leaching efficiency are demonstrated in Figs. 7 (a)-(c) for Pb, Sn and Cu, respectively. According to experimental results, rapid leaching was observed from the first 1-15 minutes and then became stable until 60 minutes. ICP-OES results showed that Cu has been leached out giving the greatest concentration of metal left in the leached solution, followed by Sn and Pb while Ag has also been detected in minor amounts. Higher HCl concentration gave more leaching efficiency, as shown in Fig. 7 (d). However, leaching at the greatest HCl concentration of 3 M resulted in rough surfaces evident on the leached samples. SEM investigation revealed various leached products left as precipitates. Leaching at lower acid concentration offered cleaner copper surfaces. It is therefore appropriate to select 2 M HCl leaching as the optimum condition for further step of electrorefining.

As the leached solution contained Sn and Pb in significant amounts, it was then subjected to a low-temperature precipitation approaching 5 °C to obtain Cu and Pb chlorides in the flake-typed and needle-liked morphologies, respectively, as demonstrated in Figs. 8 (a) and (b). XRD spectra confirmed the existing phases in Fig. 8 (c). The possible precipitation reactions can be explained according to (1)-(3) in the presence of H_2O_2 as an oxidant.



a) leached copper ribbon

b) leached copper ribbon surface

c) precipitates on leached surface (enlarged of b) in rectangular.

d) precipitates

d) Plate residue

f) plate residue surface

EDS point and area analysis on leached products

Position	Cu	Ag	Sn	Pb	Cl	O
1	53.01	0.10	-	1.39	25.53	19.97
2	56.83	-	-	-	22.67	20.49
3	61.62	0.80	-	0.24	31.51	5.93
4	0.65	92.02	1.46	0.26	-	5.61

Fig. 6 Morphology and phase analysis of leached products

$$2Cu_{(s)} + 2HCl_{(l)} \rightarrow 2CuCl_{(pp)} + H_{2(g)} \qquad (1)\#$$

$$Pb_{(s)} + 4HCl_{(l)} \rightarrow H_2(PbCl_4)_{(l)} + H_{2(s)} \qquad (2)\#$$

$$H_2(PbCl_4)_{(l)} \xrightarrow{cooling} PbCl_{2(pp)} + 2HCl_{(l)} \qquad (3)\#$$

After filtering of the leached solution to get rid of precipitates previously mentioned, tin oxide can be further obtained via precipitation using NaOH at pH ~ 2.0-3.0. Other Cu and Ag compounds were also obtained. The related reactions are expressed in (4) and (5) to obtain hydroxides of tin and copper. Tin hydroxide is known to be subsequently heated to finally achieve tin oxide, that is ready for the market.

$$[SnCl_4]^{2-}_{(aq)} + 2OH^-_{(aq)} \rightarrow Sn(OH)_{2(s)} + 2Cl^-_{(aq)} \;\#\#\;\#\; (4)\#$$

$$Cu^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Cu(OH)_{2(s)} \;\#\#\;\#\;\#\;\# \qquad (5)$$

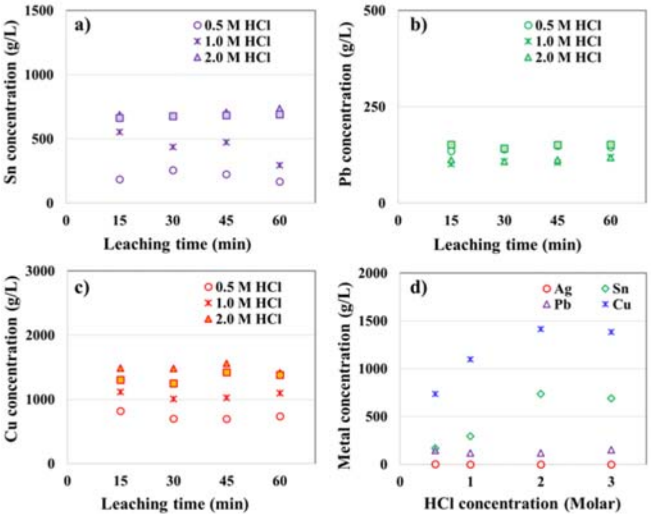


Fig. 7 Concentration of Pb, Sn and Cu in leached solution in (a), (b) and (c) respectively, and (d) effect of acid concentration on leaching of Ag, Pb, Sn and Cu for 60 min of leaching time

2. Electrorefining of Copper

The leached PV ribbon was subjected to melting to make Cu anode for electrorefining and 304 stainless steel is for cathode. Electrolytic cell was set using $CuSO_4$ solution as electrolyte and controlled the potential at 0.2 and 0.3 V for 24 hours. Comparison was made between the calcined and the leached PV ribbon to study the effect of Sn-Pb oxide layer on the recovery and purity of copper in the step of electrorefining.

ICP–OES result of the deposited copper cathode is listed in Table II. Electrorefining of the calcined PV ribbon led to precipitation of $PbSO_4$ in the electrolyte, calling for a halt after proceeded for 20 hours. Recovery defined in (6) is obtained at 94.01%. On the other hand, electrorefining of the leached PV ribbon performed well and no precipitation was obtained, giving 96.11% recovery (%R) according to (6) when the potential was controlled at 0.2 V. Increasing potential to 0.3 V gave a little lower recovery at 96.03%. #

$$\%R = \left[\frac{W_{gc}}{W_{la}}\right] \times 100 \tag{6}$$

where W_{gc} is weight gained at cathode and W_{la} is weight loss at anode.

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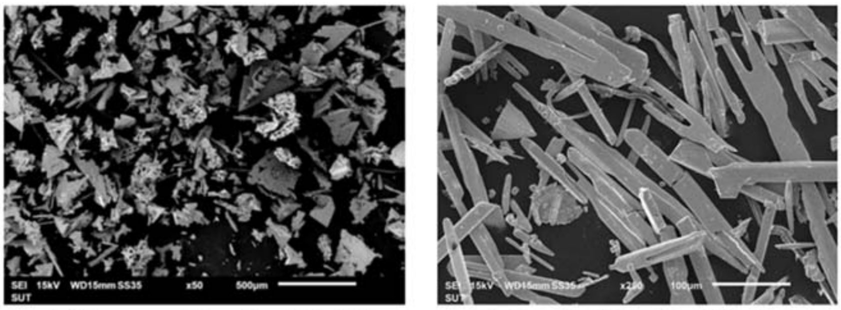
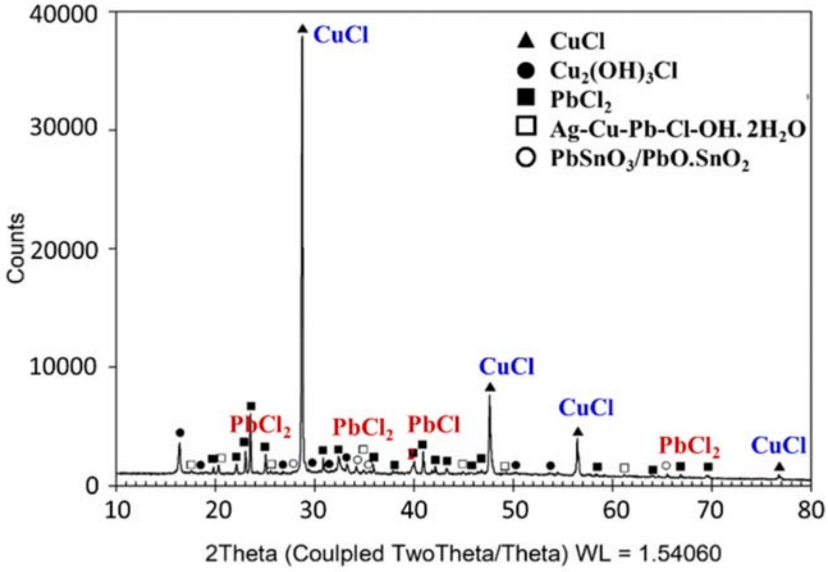


a) Copper chloride (CuCl) b) Lead chloride ($PbCl_2$)



c) XRD spectra of precipitates after HCl leaching

Fig. 8 SEM and XRD analyses of CuCl and $PbCl_2$ precipitated from leached solution

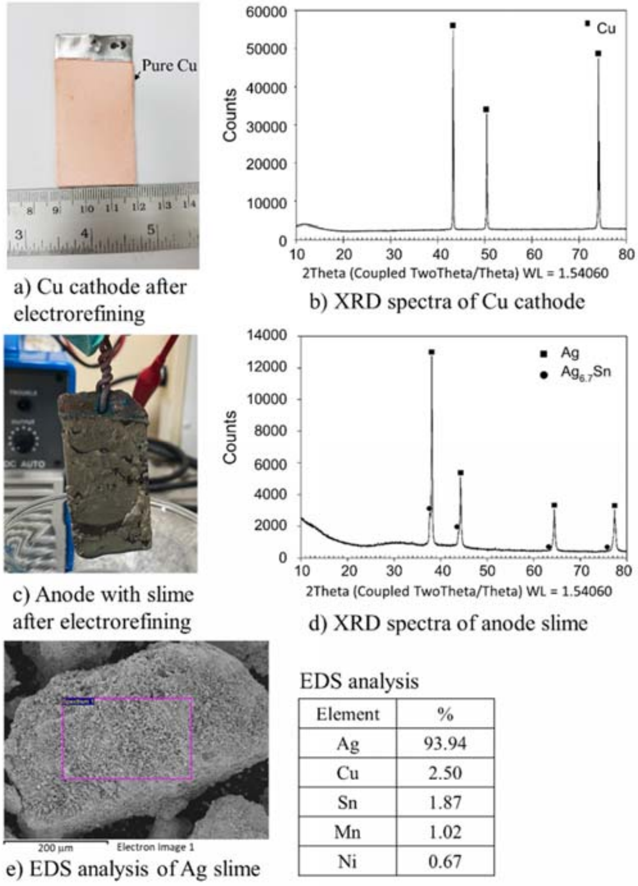
TABLE II
RECOVERY AND PURITY OF COPPER

Condition	Voltage (V)	Time (h)	% Recovery	% Purity
Leached PV ribbon	0.2	24	96.11	99.931
	0.3	24	96.03	99.917
Calcined	0.3	20	94.01	98.580

Purity of Cu deposited at the cathode analyzed by ICP-OES is summarized in Table III. Comparison has been made between the Cu cathodes after electrorefining using the calcined PV ribbons with and without acid leaching. When using cast calcined PV ribbon without leaching as the anode, elements such as Sn and As were found in greater amounts than the composition limit when compared with C10100 grade, yielding lower purity of 98.580%. This indicated that it is necessary to get rid of Sn – Pb oxide layer formed during calcination of the PV sheet via acid leaching prior to electrorefining. In the case of leached PV ribbon, electrorefining at 0.2 V potential gave the maximum copper purity of 99.931% whereas higher potential at 0.3 V led to deposition of Ag at the cathode, giving the purity of 99.917%. XRD and EDS analyses of Cu cathode recovered after electrorefining and anode slime are illustrated in Fig. 9. Only Cu peaks were detected for the obtained Cu cathode. Anode slime contained mainly Ag and Ag-Sn according to XRD results and consisted of around 89-95% of Ag analyzed by EDS. This Ag anode slime could then be subjected to further refining to achieve Ag of higher purity.

TABLE III
COMPOSITION OF COPPER (METAL IMPURITY)

Condition	ICP – OES (% element)								
	Ag	Pb	Sn	Fe	Zn	Mn	As	Sb	Ni
Leached (0.2V)	0.000	0.000	0.011	0.045	-	-	0.000	-	0.013
Leached (0.3V)	0.015	0.000	0.010	0.053	-	-	0.000	-	0.014
Calcined (0.3V)	0.000	0.000	0.200	0.050	-	-	0.017	-	0.000
C10100	0.0025	0.0005	0.0002	0.0010	0.0001	0.0005	0.0005	0.0004	0.001



a) Cu cathode after electrorefining

b) XRD spectra of Cu cathode

c) Anode with slime after electrorefining

d) XRD spectra of anode slime

e) EDS analysis of Ag slime

EDS analysis

Element	%
Ag	93.94
Cu	2.50
Sn	1.87
Mn	1.02
Ni	0.67

Fig. 9 Cu cathode recovered after electrorefining and anode slime with XRD and EDS analyses

C. *Recovery of Pure Silver from Silicon Wafer Containing Silver Finger*

1. Leaching of Ag from Si Wafer Containing Ag Finger

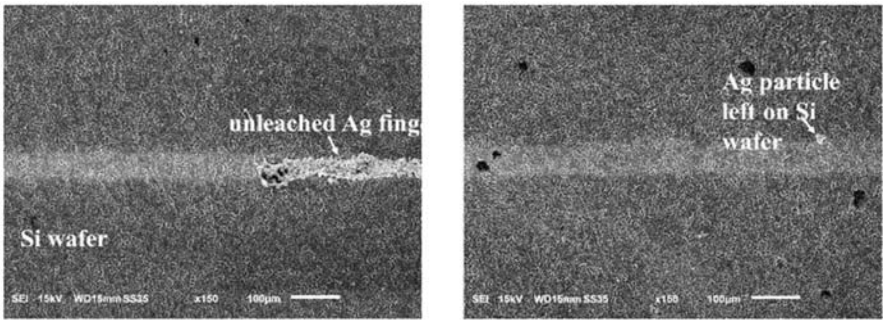
Concentrations of Ag along with other metals in the leached solution are listed in Table III. First, comparison of leaching via mechanical stirring and ultrasonic vibration was discussed when using 2 M HNO_3. Generally, ultrasonic vibration provided superior leaching efficiency to that of mechanical stirring. Greater amount of Ag at 89.23 g/L dissolved in the leached solution using ultrasonic vibration was evident in comparison to a value of 0.720 g/L attained from stir-leaching. Furthermore, ultrasonic vibration leaching showed Ag leaching efficiency dependence on acid concentration. HNO_3 concentration at 4 M gave the greatest amount of Ag in the leached solution at 110.73 g/L, and where Cu, Si and Pb were detected in much lesser amounts in the range of 1.56-4.84 g/L. It is also noted that Cu and Pb were leached out possibly from the remaining PV-ribbon still attached on the Si cell. Amount of Al is quite prevalent in this case as it was used as the back surface shield according to the PV cell architecture previously shown in Fig. 2.

TABLE IV
METAL CONCENTRATION IN NITRIC ACID LEACHED SOLUTION

Leaching technique	HNO_3 concentration	Metal concentration (g/L) by ICP – OES				
		Ag	Al	Cu	Si	Pb
Stirring	2 M	0.720	38.86	1.52	1.62	3.22
Ultrasonic vibration	2 M	89.23	640.58	3.18	3.65	4.18
	3 M	96.28	699.82	3.61	4.84	4.34
	4 M	110.73	722.92	2.80	4.59	4.64

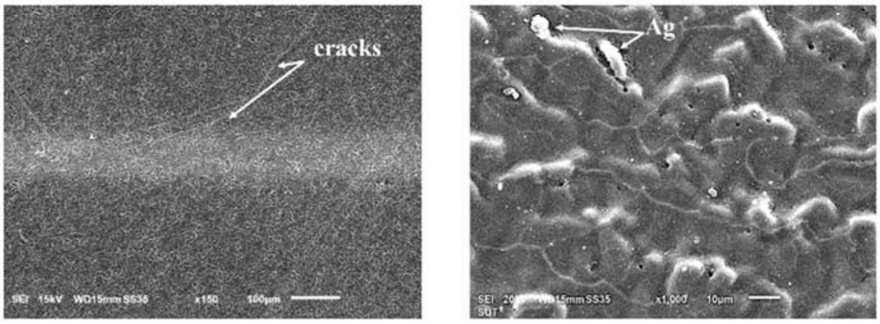
SEM investigation on the leached Si wafer surfaces also confirmed the leaching efficiency dependence on acid concentration mentioned previously, as illustrated in Figs. 10

(a)-(d). Lesser Ag left on the Si wafer was observed when using higher acid concentration. By using 2 M HNO_3, traces of unleached Ag finger were evident, while one using 4 M HNO_3 gave much less Ag left on the Si wafer surface and with very small Ag traces observed at high magnification. It is therefore appropriate to select the acid concentration at 4 M at this leaching step for further Ag recovery through precipitation and reduction.



a) Leached Si wafer at 2 M HNO_3

b) Leached Si wafer at 3 M HNO_3



c) Leached Si wafer at 4 M HNO_3

d) Leached Si wafer using 4 M HNO_3 at higher magnification

Fig. 10 Leached Si wafer using 2 - 4 M HNO_3 under SEM

Fig. 11 Ag recovery; (a) ultrasonic leaching, (b) precipitation of AgCl and (c) Ag metal#

Related reactions are expressed in (7) and (8) for low and high acid concentrations respectively. #

$$4HNO_{3(l)} + 3Ag_{(s)} \rightarrow 3AgNO_{3(l)} + NO_{(g)} + 2H_2O_{(l)} \quad (7)\#$$

$$2HNO_{3(l)} + Ag_{(s)} \rightarrow AgNO_{3(l)} + NO_{2(g)} + H_2O_{(l)} \quad (8)$$

2. Precipitation and Reduction of AgCl

After ultrasonic leaching, the leached solution containing silver nitrate ($AgNO_3$) was then subjected to precipitation using NaCl to produce AgCl appearing as opaque white precipitate, as shown in Figs. 11 (a) and (b) while the solution remained as sodium nitrate ($NaNO_3$). The related reaction is expressed in (9). #

$$AgNO_{3(l)} + NaCl_{(s)} \rightarrow AgCl_{(pp)} + NaNO_{3(l)} \quad (9)\#$$

$$2AgCl + 2NaOH + 2e^{-}(sucrose) \rightarrow 2Ag + O^{2-} + H_2O + 2NaCl \quad (10)\#$$

NaOH together with sucrose ($C_nH_{2n}O_n$) waws used [21] in the later step to reduce AgCl to Ag powder. The reduction reaction is given in (10). Then the obtained NaCl can be reused in the previous step of precipitation. Further melting of Ag powder provided Ag metal of high purity. Composition of the recovered Ag by EDS analysis showed 100% purity.

IV. DISCUSSION

The recycling routes to recover Cu and Ag from PV ribbon and Si wafer containing Ag respectively can be summarized as follows and are illustrated in Fig.#12. In the first step, the process starts from PV panel dismantling to give aluminum frame and junction box for the recycling market. The PV sheet is then cut before calcination at 500 °C. Glass cullet can be separated and reused in small addition in the float glass industry while ash and volatile are collected and neutralized. Then in the later step of recovery, first in the case of copper recovery from PV ribbon (left hand side route), the calcined PV ribbon was leached using 4 M HCl with H_2O_2 and $SnCl_2$ prior to being filtered and cleaned to make anode material for electrorefining purification in the next step. The solution is then through 2-step precipitation; first, cooling to 5 °C to obtain $PbCl_2$ and CuCl, then followed by NaOH addition to precipitate out $Sn(OH)_2$ that requires heating > 105 °C to give SnO_2. The impure Cu is then set as the anode in electrorefining cell and stainless steel is used as the cathode in $CuSO_4$ electrolyte. The potential at 0.2 V was set for 24 hours to finally achieve Cu of 99.92% purity.

For Ag recovery (right hand side route) the Si wafer containing Ag finger is leached in 4 M HNO_3 for 2 hours in the ultrasonic bath. The leached solution is subjected to precipitation using NaCl to give AgCl, which is then reduced using sucrose and NaOH to finally obtain Ag powder. Via melting, the high purity of Ag metal is obtained. The leached Si wafer can be leached with NaOH to remove the remaining element and can be further reused.

Preliminary feasibility study for local investment on pure copper and silver recovery from EOL PV panel of 1,200 tons per year, will arrive at the breakeven point in 2 years with the internal rate of return or IRR of 100.37. By year 2060, local accumulated PV panel waste predicted due to AEDP2015 will be over 700,000 tons [22], [23]. Therefore, it is feasible via the integrated recycling technique employed to recover valuable copper and silver of high purity. The process can be sustained by using accumulated domestic waste within the country and also from neighboring countries. Collection centers should be decided where logistics cost is minimized. Furthermore, panel dismantling can be handled manually by local skilled labors along with automated machines. Metal and material concentration in the waste can be increased and in turn raises the efficiency and recovery of those high valuable metals and materials.

V. CONCLUSION

According to the hybrid pyro-hydrometallurgical process, recovery of pure copper and silver can be achieved via the first step of waste preparation through dismantling and calcination of the PV sheet. In the second step, leaching of the PV ribbon by using 2 M HCl with H_2O_2 and $SnCl_2$ was found effective to recover pure copper of 99.93% via electrorefining. Pure silver was recovered from silicon wafer containing silver finger by HNO_3 leaching followed by AgCl precipitation and reduction to obtain Ag powder, and finally by melting.

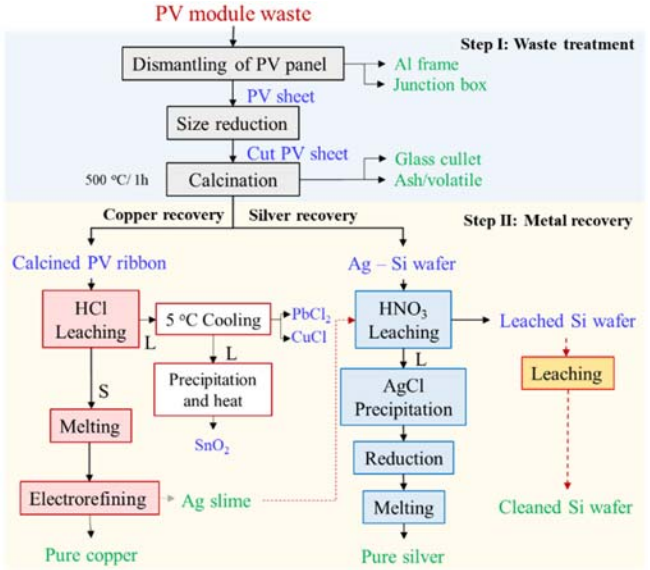


Fig. 12 Flow chart of EOL PV panels recycling to obtain Cu and Ag from PV ribbon and Ag finger

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