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Study on Recycling of Galvanic Sludge containing Copper for Pure Copper Production

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Abstract

Metal containing waste sludge from electronic industrial has been rapidly accumulating due to the surge of global demands for electronic components. This study looks into the feasibility of recycling copper from galvanic waste through hydrometallurgy combining with electrometallurgy process. The parameters of copper selective leaching including types of leaching solution, acid concentrations, and liquid-solid ratios were systematically studied. The optimum selective leaching conditions were 1 M and 2 M sulfuric acid with 24 h leaching duration, 100/1000 g/cc solid-liquid ratio offering copper leach recovery of 42,540 and 45,850 mg/l, respectively. Copper purification was successfully obtained from electrolytic refining process. The effects of electrolysis voltage to the amount and purity of copper cathode were studied. It was found that the optimum parameters for copper purification were using 2 M sulfuric acid with electrolytic voltage of 2.2 V. Under these conditions, the recovery of pure copper was raised up to 92%.

Keywords: Hydrometallurgy; Electrometallurgy; Electrowinning; Galvanic copper sludge; Copper cathode

Introduction

Currently, metal resources can be in the natural mineral form and recycled wastes. Natural copper resource for example from Chalcopyrite ($CuFeS_2$) is still under production, However, recycling of valuable copper containing wastes is more of great interest, due to high return and environmental regulation. From the statistics of the Department of Industrial Works, Ministry of Industry, Thailand, about the import-export of hazardous waste according to the Basel Convention since 1998-2011, it appears to be a widespread cross-border waste movement across the continents. Thailand has since an average of 200 to 5,000 tons of hazardous waste per year, including electrical and electronic scraps, galvanic sludge, metal finishing wastes, and waste catalysts. The amount of import-export of hazardous waste according to the Basel Convention of Thailand during 2008-2011 is shown in Figure 1 [1].

In present, galvanic copper sludge occurring in the electronics industry is one of the most valuable wastes that contain a high content of copper, potentially feasible for recycling. To extract the high-valued metal from galvanic copper sludge, metal recovery can be carried out by:

1. Pyrometallurgical method as a metal extraction process by smelting to separate the impurity from the desired metal,

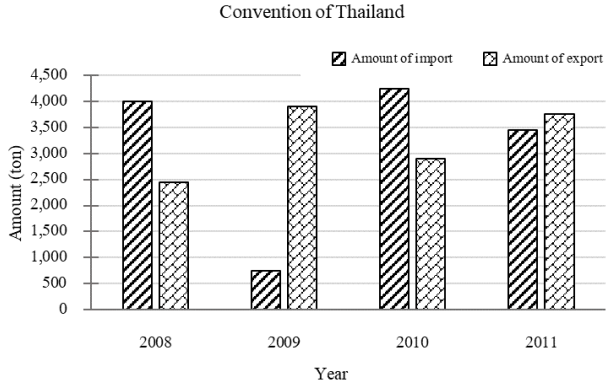

Figure 1: The amount of hazardous waste that has been trans bound since 2008-2011 [1].

2. Hydrometallurgical method as to extract the metal by means of solvent leaching of metal into the solution

3. Electrometallurgy as an extraction process of metals via electrolytic process to selectively purify metal.

Generally, electrometallurgy can be divided into electrowinning and electrorefining to give pure metal deposited at the cathode.

The combination of hydrometallurgy and pyrometallurgy treatment has been studied by Rossini G and Bernardes [2] to recover copper from galvanic sludge. A copper recovery of 50% was obtained with nickel and zinc as the main recycled product. Research by Huyen et al. [3] investigated electrochemical copper recovery from galvanic sludge and suggested the use of a combination of leaching and electrowinning, which the latter employed a batch recirculation electrochemical reactor using a 3-D carbon felt cathode. The technique used could offer the current efficiency as high as 0.90 with higher than 99% of copper recovery within 2 h.

For the leaching of the galvanic sludge prior to electrometallurgy, much research indicated productive recovery of copper after electrowinning in a laboratory scale [4-6], mostly used H_2SO_4 as the leachate agent though some also used ammonical alkaline solution. H_2SO_4 was found to be more attractive to give the optimum results. Studies of leaching in printed circuit boards [7] and the galvanic sludge [3-5,8,9] using H_2SO_4 also confirmed its effective to provide better copper deposited at cathode, % recovery, % current efficiency and purity of copper.

Experimental Section

Galvanic copper sludge

The galvanic copper sludge used in this research obtained from an

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electronic industry located in the middle region of Thailand contains high amount of copper. The sludge was a waste solution from the precipitation process of heavy metals in PCBs manufacturing. Oven dry at 105°C was operated to give a dried sludge ready for leaching. WD-XRF (Wavelength Dispersive X-Ray Fluorescence; Model: Rigaku, ZSXPrimusIV) was selected to analyze the chemical composition of the galvanic sludge as detailed in Table 1.

Extraction of copper from galvanic copper sludge

The extraction technique used for recovery of copper from galvanic copper sludge started with leaching by sulfuric acid, filtration and electrowinning of the leached solution to achieve the copper cathode as illustrated in Figure 2.

Acid leaching by sulfuric acid was carried out at concentrations of 1 M and 2 M for 24 h using an S/L ratio at 1:10. The dried galvanic copper sludge of 1,000 g was leached in an HDPE gallon using 10 l of acid solution. Magnetic stirring was introduced at a speed of 250 rpm to ensure identical leached solution for further electrowinning process.

After acid leaching, a copper sulfate solution was obtained and then filtrated to separate the leached solution from residual, which was later analyzed by ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy; model: Perkin elmer/Optima8000) and WD-XRF techniques respectively. The filtered copper sulfate solution became an appropriate electrolyte solution for further copper extraction in the electrowinning process as described in Figure 2. The electrolytic cell was set up for electrowinning process using the electrolyte solution of 500 ml and by applying DC power supply to vary electrical voltage at 2.2, 2.4 and 2.6 V. Pb-1wt.%Ag alloy of 5x5x0.1 cm^3 dimensions was used as an anode and was set at 4 cm apart from the pure copper cathode of 5x5x0.03 cm^3 dimensions. Magnetic stirring was introduced at a speed of 250 rpm to assure homogeneity of the solution at all time. The condition adopted for each set of experiments is listed in Table 2. In addition, the reaction in the electrolysis process is shown in equations (1-3). The obtained copper cathode was digested by microwave before elemental analysis by ICP-OES to evaluate the purity of copper. However, the current efficiency and recovery of copper were calculated according to the equations (4-6) (Figure 3).

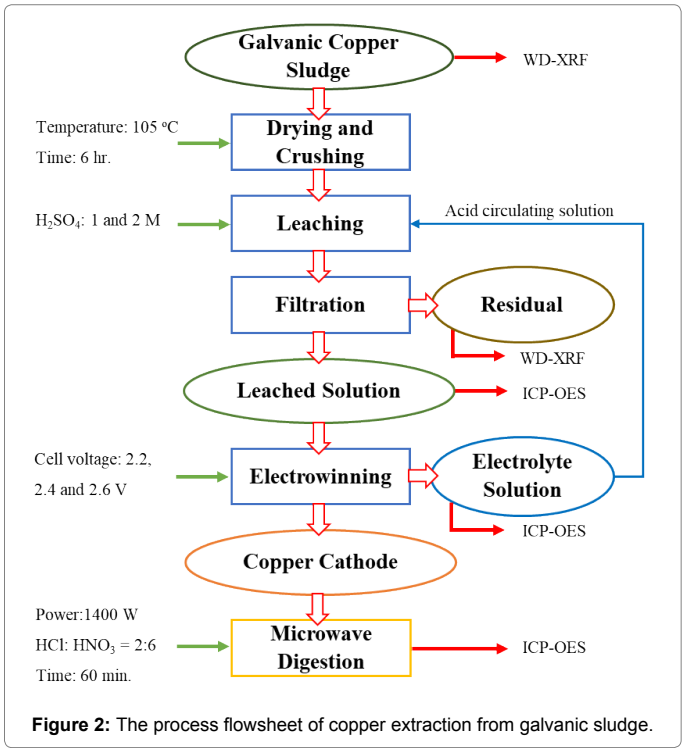

Figure 2: The process flowsheet of copper extraction from galvanic sludge.

Anodic reaction: $H_2O=2H^+ + 2e^- + ½O_2$ (1)

Cathodic reaction: $Cu^{2+} + 2e^- = Cu^o$ (2)

Overall reaction: $Cu^{2+} + H_2O = Cu^0 + 2H^+ + ½O_2$ (3)

Theoretical weight gains: $W_{th} = (ItAw)/zF$ (4)

Current Efficiency: $\%CE = W_{de}/W_{th} \times 100$ (5)

Recovery of copper: $\%Re = M_{re}/M_{in} \times 100$ (6)

Results and Discussion

Leaching

The chemical analyses for the leached solution concentrations of 1 M and 2 M by ICP-OES and WD-XRF are presented in Table 3. In a condition using 2 M H_2SO_4, the leached solution contained higher concentration of copper (45.85g/l) in comparison to that obtained from of a condition using 1 M H_2SO_4, due to greater effect of acidity. It is confirmed by the lower copper content of 4.96 wt.%, left in the residual obtained by using 2 M H_2SO_4 after leaching, as compared with 7.36 wt.% of copper measured from the residual obtained by using 1 M H_2SO_4, as shown in Table 4.

Electrowinning

The leached solutions were used as the electrolyte in the electrowinning and the pure copper was attained at cathode as depicted in Figure 4a-4c. The oxidation reaction at anode gives electrons received at the cathode where by the copper ions from the copper sulfate solution are reduced to form pure copper. The leached solution previously appeared as dark solution then turned into light blue as seen in Figure 4d for a comparison of electrolyte solutions before and after electrowinning process, with their chemical composition analyses by ICP-OES summarized in Table 5.

In Figure 5, in the case of using 1 M leached solution, a higher

Element	Cu	O	S	C	B	Na	P	Fe	Zn	Si	Mn
wt.%	46.85	38.35	5.26	4.21	2.58	1.97	0.62	0.07	0.04	0.02	0.02

Table 1: Chemical composition of galvanic copper sludge by WD-XRF analysis.

Condition	Test number					
	1	2	3	4	5	6
H_2SO_4 (M)	1	1	1	2	2	2
Voltage (V)	2.2	2.4	2.6	2.2	2.4	2.6
Time (h)	24	24	16	20	11	7

Table 2: Experimental conditions for recycling of pure copper by electrowinning process.

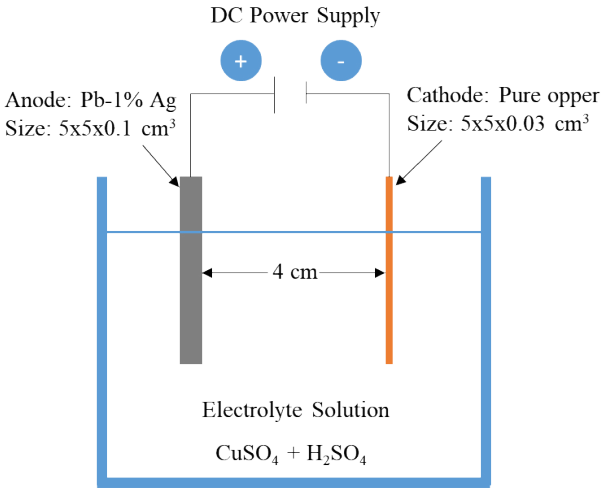

Figure 3: Schematic showing the set up for electrolytic cell of electrowinning process.

Acid concentration	Concentration (mg/l)						
	Cu	Fe	Mn	Ni	Zn	Ca	Pb
1 M H_2SO_4	42,540	24.800	9.800	8.800	35.000	1.297	0.143
2 M H_2SO_4	45,850	56.300	9.600	8.400	32.300	1.203	0.101

Table 3: Chemical composition analysis of leached solution by ICP-OES.

Element	wt.%													
	Cu	Fe	C	O	S	P	Na	Mg	Al	Si	Cl	K	Ca	Mn
1 M H_2SO_4	7.36	7.25	19.09	51.80	9.14	4.52	0.41	-	0.09	0.18	0.04	0.01	0.03	0.02
2 M H_2SO_4	4.96	11.18	26.87	46.37	4.36	5.57	0.34	0.03	0.08	0.13	-	0.01	0.04	0.02

Table 4: Chemical composition analysis of residuals by WD-XRF.

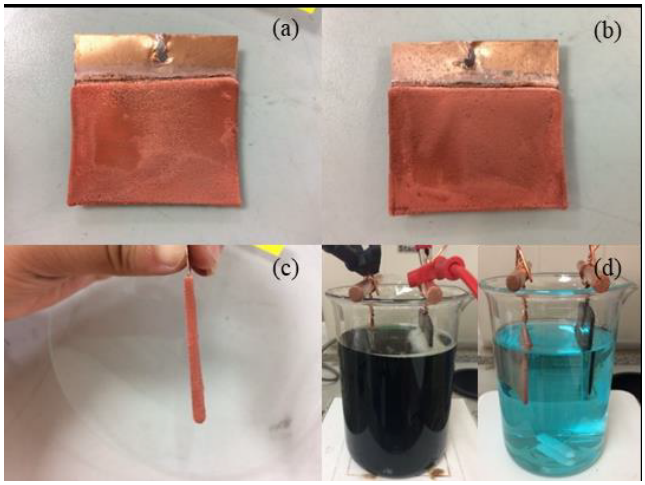

Figure 4: Copper cathode obtained after electrowinning process (a) front (b) back (c) side, and (d) electrolyte solution before (left) and after (right) electrowinning.

amount of copper deposited at the cathode and greater recovery of copper were obtained as the cell voltage was increased from 2.2 to 2.6 V, due to increasing current with increasing electrical voltage. Conversely, in the case of using 2 M leached solution, the amount of copper deposited at cathode reached the optimum value of 21.57 g after 20 h prior to the electrolyte solution turned into a clear solution. This is to prevent impurities from depositing at the cathode. For this reason, the current efficiency and purity of copper for both acid concentrations decreased with increasing cell voltage as illustrated in Figure 6.

Finally, it was considered in this work that copper could be recovered from the galvanic copper sludge up to 92%, with the highest current efficiency of 99.45% when using 2 M leached solution at 2.2 V. However, to obtain the highest copper purity of 99.92%, the electrowinning condition would be 1 M leached solutions at 2.2 V are shown in Table 6. The recovered copper could, therefore, be used

Tests number	Concentration (mg/l)						
	Cu	Fe	Mn	Ni	Zn	Ca	Pb
1	21,600	26.4	6.367	5.778	38.5	1.520	2.232
2	2,560	25.6	7.373	6.941	40.5	1.561	2.758
3	2,140	29.6	6.911	7.083	40.4	1.550	2.850
4	3,940	59.2	6.999	6.587	41.3	1.603	1.903
5	4,250	62.6	6.6.37	6.444	41.4	1.698	1.889
6	19,770	60.3	6.585	6.043	37.3	1.582	2.035

Table 5: Chemical composition analysis of electrolyte solution by ICP-OES.

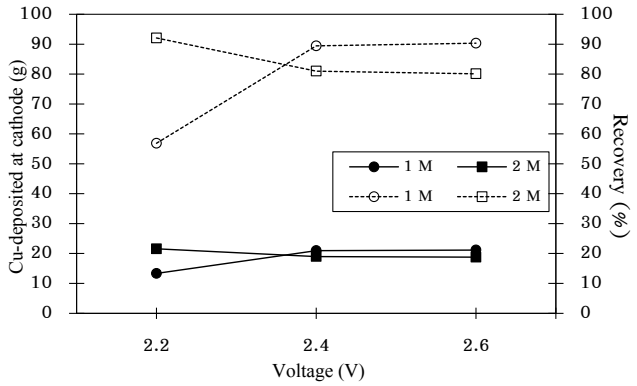

Figure 5: Effect of the cell voltage on Cu-deposited at cathode and recovery of copper (solid line: Cu-deposited at cathode; dotted line: recovery).

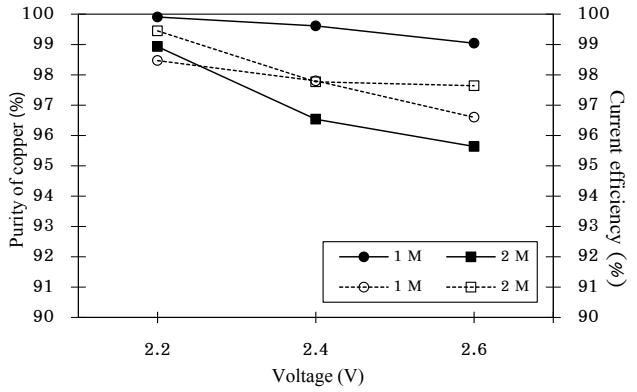

Figure 6: Effect of the cell voltage on purity and current efficiency of copper (solid line: purity; dotted line: current efficiency).

Conditions	Cell voltage (V)	Cu-deposited at cathode (g)	Recovery (%)	Purity (%)	Current Efficiency (%)
Electrowinning of 1 M leached solution	2.2	13.32	56.86	99.91	98.47
	2.4	20.95	89.44	99.61	96.73
	2.6	21.16	90.33	99.04	98.76
Electrowinning of 2 M leached solution	2.2	21.57	92.08	98.93	99.45
	2.4	18.97	80.99	96.54	98.01
	2.6	18.76	80.09	95.64	96.42

Table 6: Summary results of recycling copper from galvanic copper sludge.

as the raw material for the copper and copper alloys productions, etc. In addition, it could be possible to increase the purity of copper by adjusting the parameters in the extraction process which will be included in future work. This study can be made as a guideline for the recycling of electronic industrial waste for pure copper production, which can lead to further research in the pilot and commercial scales. Additionally, this research might be in benefit of promoting environmentally industrial electronic waste management suitable for Thailand and reducing harmful wastes due to landfill.

Conclusions

The recycling of galvanic copper sludge for pure copper production was studied. It was found that it is possible to recover copper, using a combination of leaching by sulfuric acid and electrowinning. According to the result, it can be concluded that the highest amount of copper cathode of 21.57 g., recovery of 92.08% and current efficiency of 99.45% can be obtained by using 2 M H_2SO_4 at 2.2 V. The highest purity

of more than 99.91% of copper purification can be achieved when using 1 M H_2SO_4 with a cell voltage of 2.2 V.

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