Separation and Purification Technology 205 (2018) 302–307

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Completely separating metals and nonmetals from waste printed circuit boards by slurry electrolysis

Deze Yang[a], Yingying Chu[a], Jianbo Wang[a], Mengjun Chen[a,*], Jiancheng Shu[a], Furong Xiu[b], Zhonghui Xu[a], Shuhui Sun[c], Shu Chen[a]

[a] Key Laboratory of Solid Waste Treatment and Resource Recycle (SWUST), Ministry of Education, Southwest University of Science and Technology, 59 Qinglong Road, Mianyang 621010, China

[b] College of Geology & Environmental, Xi'an University of Science and Technology, Xi'an 710054, China

[c] Institut National de la Recherche Scientifique-Énergie, Matériaux et Télécommunications, Varennes, QC J3X 1S2, Canada

ARTICLE INFO

Keywords:
E-waste
WPCBs
Metal and nonmetal
Recovery
Separation
Suspension electrolysis

ABSTRACT

Completely separating and recovering metals and nonmetals from waste printed circuit boards (WPCBs) is key to e-waste recycling. Here we proposed a novel approach, slurry or suspension electrolysis, to separate metals and nonmetals from WPCBs. The factors that impact the separation rate during the slurry electrolysis were discussed in detail. The results indicate that $CuSO_4 \cdot 5H_2O$, NaCl, H_2SO_4, WPCBs dosage, current and time could impact metals separating from WPCBs. Increasing NaCl and H_2SO_4 concentration and extending electrolysis time could effectively increase the metal and nonmetal separation rate, while increasing WPCBs dosage and current have negative impacts on the metal and nonmetal separation rate. Slurry electrolysis could directly and completely separate and recover metals from WPCBs with a separation rate up to 97.79% under the conditions of 3 g WPCBs dosage in 100 mL electrolyte, 30 g/L $CuSO_4 \cdot 5H_2O$, 40 g/L NaCl, 150 g/L H_2SO_4, 0.5 A and 9 h. The separated micro-metal powders are mainly Cu, about 86.6%, without any nonmetal powders. Copper recovered is dendritic, with a copper recovery rate up to nearly 99%. Thus, slurry electrolysis shows a prospective future in e-waste reutilization, providing a way to enrich metals for all kinds of urban mines.

1. Introduction

Rapid technology innovation in information communication technology that leads to a shorter and shorter lifespan or an accelerated upgrading of household appliances and electronic products, electronic waste (e-waste) is growing globally [1–3]. In 2014, the global production of e-waste ran up to 42 million tons [4] with an average annual growth of 5–10%, which is 3–5 times higher than that of municipal solid waste [5,6]. In the coming years, China will enter the scraping peak period of waste electrical and electrolytic equipment.

Printed circuit boards (PCBs) are the basic building blocks for almost all electronic products. PCBs of desk computers composed of composite materials containing about 40% resin, 30% glass fiber and 30% metals [7,8]. Virtually, waste PCBs (WPCBs) recycling is the core of the e-waste recycling because it is resource-rich but hazardous. It is famous for urban mine since metals contained in WPCBs is 10 times more abundant higher than that in minerals [9,10]. On the other hands, it is also notorious because of the hazardous material composition. The contained heavy metals and persisted organic pollutants could be emitted when WPCBs are treated or disposed of improperly [11,12]. Therefore, we should pursuit profit during the recycling of WPCBs with a more environmentally friendly way.

In order to identify cost-effective and environmentally sustainable ways of recycling WPCBs, number of methods based on mechanical-physical approach [13], pyrometallurgy [14,15], hydrometallurgy [16], biometallurgy [17,18], electrolysis [19–22], supercritical fluid [23–26], have been developed aiming to recycle copper and precious metals present. The achievements are remarkable. For example, a process based on mechanical-physical method [27], including two-step crushing, magnetic separation, corona separation, and cyclone air separation course, has been developed, and industrial applied in several factories in China. Besides, pyrolysis method which belongs to the category of pyrometallurgy is also employed to recover metals from WPCBs [28,29]. However, the products of above processes are almost metallic and nonmetallic mixtures. As a matter of fact, complete separation of metals and nonmetals is crucial for further refining of each metal from the viewpoints of both eliminating the residue and elevating the purity of metal recovered. Therefore, can a process that realize

* Corresponding author.
E-mail address: kyling@swust.edu.cn (M. Chen).

https://doi.org/10.1016/j.seppur.2018.04.069
Received 23 January 2018; Received in revised form 9 April 2018; Accepted 25 April 2018
Available online 26 April 2018
1383-5866/

complete separation of metals from nonmetals of WPCBs with a shorter procedure, a lower cost, less energy consumption, and less secondary contamination? Slurry electrolysis, also named suspension electrolysis, may be a potential method to solve the above problem.

Slurry electrolysis, which combines leaching, solution purification and electrowinning within one single procedure in one reactor, was firstly put forward by E. C. Brace via a U.S. patent about a new copper electrolytic deposition device in 1969. Now many researches have employed this method to extract Cu, Zn, Pb, Mn, Fe, and other metals from their ores of sulfides or oxides. Then could it be used in separating metals from nonmetals in WPBCs effectively and environment-friendly? In order to testify this hypothesis, WPCBs powders without further pretreatment were directly used as the raw materials for slurry electrolysis, and the factors that would affect metals and nonmetals separation efficiency during the electrolysis process were examined in detail. The success of this technology may provide a new method to separate metals from nonmetals in WPCBs and, facilitate further purification and refinement of metals.

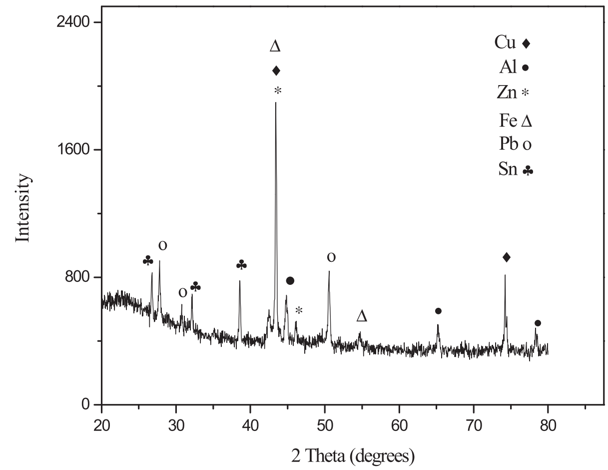

Fig. 1. XRD patterns of WPCBs.

2. Materials and methods

2.1. Sample preparation

WPCBs, from desktop computers without disassembling the attached electronic components, were first cut to small pieces and then shred to smaller than 0.5 mm. The obtained WPCBs powders were then dried at 105 °C for 24 h, and analyzed by an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Optima 8000, PerkinElmer, America) after digested by HNO_3-HF-H_2O_2 system [30]. The results are shown in Table 1. The sum of the concentrations of these metals gives a total metal concentration of WPCBs, which is 38.64%. The X-ray diffraction indicated that the concentration of Cu is highest, and other metals, such as Fe, Al, Pb, Sn, and Zn, could also be identified, which agreed with the result of ICP-OES (Fig. 1).

2.2. Slurry electrolysis

All the experiments were carried out in a self-made cylinder-shaped slurry electrolyser. The slurry electrolyser was separated to anode zone and cathode zone by an installed porous ceramic (50 μm). Graphite stick and titanium mesh were used as anode and cathode, respectively. At the bottom of the anode zone, an inlet pipe was linked to an ozonizer (3S-A10, Tonglin Technology, Beijing, China) to introduce ozone with a flow rate of 1.5 L/min to provide an oxidation environment and to make the WPCBs powders to be suspended. WPCBs powders were added into the anode zone. Six factors, $CuSO_4·5H_2O$ concentration, NaCl concentration, H_2SO_4 concentration, WPCBs dosage, current, and time, were examined in detail.

After each experiment, the metal powder in the cathode zone were collected, and ultrasonic washed with absolute ethanol for several times, then dried in vacuum. After that it was digested by HNO_3-HF-H_2O_2 system and analyzed by ICP-OES. XRD and scanning electron microscope (SEM, SUPRA 55, Zeiss) was also used to character the phases and morphology of the obtained metal powders. Metal and nonmetal separation rate was calculated according to the following Eq. (1):

$$\text{Separation rate} = \frac{M_1 + M_2 - M_3}{\text{Metals contained in WPCBs powders}} \times 100\% \quad (1)$$

where M_1 is the mass of metal powders obtained at the cathode zone, g; M_2 is the metals contained in the electrolyte, g; and M_3 is the mass of Cu in $CuSO_4·5H_2O$ that added at the beginning of each experiment, g. Energy efficiency was represented by current efficiency of copper due to copper is the main metal in WPCBs, which was calculated according to Eq. (2):

$$\text{Current efficiency of copper} = \frac{M_4}{M_5} \times 100\% = \frac{M_4}{I\bullet t\bullet C} \times 100\% \quad (2)$$

where M_4 is the mass of copper that is actually deposited on the cathode as it passes a certain charge, g; and M_5 is the theoretical electrodeposition mass of copper calculated by Faraday's law at the same amount of charge as M_4, g; I is the current value during electrodeposition, A; t is the electrodeposition time, h; C is the electrochemical equivalent of Cu^{2+}, 1.186 g/(A·h).

3. Results and discussion

3.1. Effect of $CuSO_4·5H_2O$ concentration

The effect of $CuSO_4·5H_2O$ concentration on metal and nonmetal separation rate and current efficiency of copper is given in Fig. 2. Metal and nonmetal separation rate first increase from 70.91 to 87.77% with $CuSO_4·5H_2O$ concentration increasing from 10 to 30 g/L, and it then slightly decreases to 72.45% as further increasing $CuSO_4·5H_2O$ concentration to 50 g/L. Simultaneously, the current efficiency of copper increases from 23.30 to 63.23% when $CuSO_4·5H_2O$ concentration increases from 10 to 50 g/L. During this process, $CuSO_4·5H_2O$ plays as copper ion resource for the initiation of slurry electrolysis to enhance electron transfer, accelerate metals oxidation, and inhibit H_2 generation. As a consequence, the cathode diffusion current of the solution is elevated with the increasing of $CuSO_4·5H_2O$ concentration, meaning that more Cu^{2+} can reach and deposit on the cathode easier [31]. Hence, the current efficiency of copper continuously increases with the increasing of $CuSO_4·5H_2O$ concentration. However, excessive $CuSO_4·5H_2O$ in the electrolysis system would saturate copper ions in the electrolyte and inhibit metals in WPCBs (mainly copper) oxidation, leading to the decreasing of metal and nonmetal separation rate. Therefore, $CuSO_4·5H_2O$ concentration of 30 g/L is used for experiments carried out subsequently.

Table 1
Chemical compositions of waste printed circuit boards by ICP-OES.

Element	Cu	Pb	Sn	Zn	Fe	Al	Cr	Sb	Ni
Content	20.14%	1.97%	1.4%	3.2%	8.1%	2.7%	0.12%	0.24%	0.32%