Journal of Metals, Materials and Minerals, 34(4), 2007, 2024

Tin, silver, and copper sulfate compound extraction from lead-free solder dross by reduction with petroleum coke, electrorefining, cementation, and crystallization process

Sakhob KHUMKOA[1, *], Natthicha MA-UD[1], Tapany PATCHARAWIT[1], and Tanongsak YINGNAKORN[1]

[1] *School of Metallurgical Engineering, Institute of Engineering, Suranaree University of Technology, Suranaree, Muang, Nakhon Ratchasima, 30000, Thailand*

***Corresponding author e-mail**: sakhob@sut.ac.th

Received date:
24 March 2024
Revised date:
18 October 2024
Accepted date:
5 December 2024

Keywords:
Metal recycling;
Lead-free solder dross;
Cementation;
Silver precipitation;
Copper sulfate

Abstract

Solder dross, a waste by-product from the electronic component dipping bath, contains significant quantities of valuable metals. This study presents a four-step process for recovering tin, silver, and copper from lead-free Sn-Ag-Cu solder dross. The process involves the initial reduction of the dross using petroleum coke to produce an anode plate, followed by electrorefining to extract tin from the anode plate. Selective leaching of silver and copper from the residual anode slime and cementation techniques are employed to recover silver powder. The rest of the copper solution was used to synthesize copper sulfate crystals. Experimental results demonstrate optimal conditions for the reduction process, resulting in a high tin recovery rate of 92.88%. The electrorefining step yields tin with a purity of 99.94%. Silver and copper are successfully recovered from the anode slime, achieving purities of 99.60% for recovered silver powder and 99.90% for crystallized copper sulfate compounds. This comprehensive study offers insight into the efficient extraction and recovery of tin and other valuable metals from lead-free solder dross.

1. Introduction

Lead-free solder has extensive applications in soldering electronic components and pin-dipping devices like sensors, switches, and relays. Throughout these procedures, solder oxides or solder dross are generated through the interaction of the molten solder surface with oxygen in the atmosphere. This resulting waste material is periodically removed from the surface of the solder bath [1,2]. Recent investigations have revealed that solder dross comprises elements and compounds such as tin (Sn), stannous oxides (SnO, SnO_2), and silver-tin (Ag_2Sn), with variations based on the alloy composition of the solder used. Solder dross typically contains a tin content ranging from 71.6% to 93.1% by weight, along with additional elements incorporated in alloy form. This composition renders it well-suited for recovery as pure metal or compound, facilitating reuse for other relevant industries [3-5]. Various solder types include tin-silver (Sn-Ag series), tin-copper (Sn-Cu series), tin-silver-copper (Sn-Ag-Cu series), tin-silver-bismuth (Sn-Ag-Bi series), and tin-silver-copper-antimony (Sn-Ag-Cu-Sb series), among others. These alloy compositions influence the mechanical properties and melting points of the solder. However, the solder dross used in this study is a Sn-Ag-Cu solder because it has been primarily used in industry for its excellent mechanical properties compared to Pb-Sn solder alloys [6-9].

Drawing upon existing research, technology, and investigations into tin recycling from industrial solder waste, it has been discerned that pyrometallurgy, hydrometallurgy, and electrochemical methodologies emerge as promising avenues for tin extraction. In the pyrometallurgical approach described by Z. Harang and T. Kékesi [4], tin oxide-laden solder dross from electronic parts manufacturing undergoes carbothermic melting. Experimental conditions involved the reduction of solder using carbon powder at temperatures of 800°C and 1000°C with durations ranging from 0.5 h to 2 h. Additionally, I. García-Díaz *et al.* [10] detailed a method for recovering tin and silver from dross generated in wave soldering during circuit board manufacturing. An anode plate was produced by carbothermic reduction with coke and calcium carbonate at 1200°C. Subsequent electrorefining transformed the anode plate, containing 82 wt% tin, into high-purity tin at 99.94 wt% on the cathode region under optimal conditions after 845 h. Researchers have developed hydrometallurgical techniques to recover target metals such as tin, silver, and copper from lead-free solder waste. These processes utilize acidic solutions, such as hydrochloric and nitric acid, often supplemented with oxidizing agents like hydrogen peroxide or iron chloride to extract desired metals [10-13]. For instance, K. Yoo *et al.* [13] focused on recycling solder dross leached with a 2.0 $kmol \cdot m^{-3}$ nitric solution at 75°C and a waste-to-volume ratio of 100 $kmol \cdot m^{-3}$, facilitating the leaching of silver and copper from tin sludge. The subsequent stages involved the precipitation of silver powder using sodium chloride and the extraction of copper through electrowinning. However, optimization of the electrorefining process time, the carbothermic reduction temperature, and the room temperature operation for the leaching process are essential to ensure the economic viability of the metal recovery process.

Cementation, a separation technique that precipitates noble metal ions in solution into solid metal, capitalizes on the potential difference between the noble metal ion and solid metal. This method offers advantages in terms of simplicity, low energy consumption, and cost-effectiveness [14]. For the cementation of silver, the substitution reaction involving silver solution and a copper sheet can be conducted at 80°C within 1 h, utilizing a hydrochloric leaching solution. The size of the recovered silver can be controlled by adding ascorbic acid [15]. Conversely, copper, a prominent component in Sn-Ag-Cu solder waste, is crucial for extraction. In this investigation, we propose the recovery of copper in the form of copper sulfate crystals due to its versatile applications. Copper sulfate is an inorganic compound widely employed in agriculture for fertilizer, pesticide, disinfectant, fungicide, feed, and soil additive. It crystallizes into a bright blue copper sulfate hydrate crystal with the chemical formula $CuSO_4{\cdot}n(H_2O)$ (where n can range from 0 to 7) [16].

As indicated by prior investigations, the pyrometallurgy approach has demonstrated its capacity to generate an anode plate, facilitating the subsequent acquisition of high-purity tin through electrochemical means. However, solder dross melting via reduction with petroleum coke (a by-product of crude oil refining characterized by elevated heat and carbon content) has received limited attention [17]. Specifically, there needs to be more research regarding the reduction temperature for casting anodes from solder dross. A paramount consideration involves implementing a closed-loop process with high recovery efficiency for all metals from the initial waste. Therefore, this study aims to recycle Sn-Ag-Cu lead-free solder dross through a reduction process involving petroleum coke, followed by extracting high-purity tin through electrorefining. Furthermore, the residual silver and copper containing anode slime will undergo nitric solution leaching, enabling the recovery of these metals. The recovered silver will be obtained through cementation with a copper plate. In contrast, the remaining solution containing high copper concentration, derived from both the initial leached solution and the substitution reaction during silver/copper cementation, will be subjected to crystallization to produce copper sulfate crystals.

2. Experimental

2.1 Materials

The lead-free solder dross employed in this investigation originated from the dip soldering of electronic components from an electronic part-producing company in Thailand. This dross was intermittently removed from the surface area of the molten solder during the process. The chemicals used in this study were nitric acid (HNO_3, QReC^{TM}, 65%), sulfuric acid (H_2SO_4, QReC^{TM}, 98%), high-purity tin grade (99.99%, Thaisarco), copper plate (99.99%), and petroleum coke with a carbon content of about 99 wt%.

2.2 Reduction of the solder dross using petroleum coke and tin extraction via electrorefining process

The lead-free solder dross, predominantly composed of tin oxide, underwent reduction using petroleum coke with a carbon content of 99 wt% within a muffle furnace. In this step, 0.025 and 0.05 weight ratios of petroleum coke to solder dross (P/D ratio) were used to evaluate the percentage recovery of tin from solder dross waste by comparison of weight before and after reduction treatment. The experimental setup involved mixing 50 g of lead-free solder dross with 1.25 g (0.025 P/D ratio) and 2.5 g (0.05 P/D ratio) of petroleum coke in an alumina crucible. The reduction process encompassed a temperature range of 450°C to 1050°C at intervals of 100°C, with a fixed holding time of 0.5 and 1 h. Subsequently, the optimal reduction conditions were determined for producing an anode plate by casting the material in an iron mold. A tin anode plate of impure composition (from the optimized condition of the solder dross reduction) was crafted to extract high-purity tin. The anode possessed dimensions of 10 cm × 6.5 cm, with a thickness of about 3 mm to 5 mm, and each plate weighed about 150 g. To establish an electrochemical cell, a high-purity tin grade (99.99% purity) was employed as the cathode, mirroring the size of the anode.

The prepared anode and cathode plates were positioned about 10 cm apart and connected via copper wires and busbars to a voltage source. An electrical potential of 0.2 V was applied to initiate the electrolysis process in a 600 mL solution of 2 $mol{\cdot}L^{-1}$ aqueous sulfuric acid. After 96 h of electrorefining, the deposited tin on the cathode surface was collected for further analysis.

2.3 Recovery of silver and copper from anode slime

The residual anode plate, post-electrorefining, comprised of silver and copper, was hereafter denoted as anode slime. This anode slime underwent leaching with 2.5 $mol{\cdot}L^{-1}$ aqueous nitric acid solution (prepared by diluting roughly 6.5 mL of 65% nitric acid and diluted to 100 mL with water) at a 1:10 weight ratio of anode slime and the aqueous nitric acid solution (S:L ratio) for a duration of 9 h. Subsequently, the leached solution was filtrated to separate from the rest residual. The filtrated solution was then used for silver recovery. The silver precipitation was achieved through cementation with a copper plate (99.99% purity) measuring approximately 5 cm by 5 cm. Following silver powder separation by filtration, the remaining copper-rich solution (50 mL) was combined with approximately 24 mL of 7.5 $mol{\cdot}L^{-1}$ sodium hydroxide and heated to 160°C for 1 h to yield copper oxide. The resulting product was then filtrated and dried at 120°C for 1 h. The copper oxide was further converted into a copper sulfate solution by mixing with 60 mL of 1.5 $mol{\cdot}L^{-1}$ sulfuric acid at 60°C for 1 h, followed by allowing the solution to crystallize the copper sulfate over 24 h. Notably, the acid concentrations were determined with a 20% excess based on chemical reactions outlined in Equations (9-14) and Equation (18-21).

2.4 Characterization and chemical analysis

The solid materials underwent a drying process at 120°C for 1 h and subsequent grinding before being subjected to analysis using X-ray diffraction (XRD) techniques. The XRD patterns were collected using a D2 PHASER X-ray generator operating at 30 kV and 10 mA, controlled by DIFFRAC.SUITE software. All samples were prepared in polymethyl methacrylate (PMMA) specimen holders of 8.5 mm height and 25 mm diameter and were scanned over a range of 10° to 80° 2θ with a step size of 0.02°. Chemical compositions of the solid materials were also determined through energy-dispersive X-ray fluorescence (ED-XRF) employing a Horiba XGT-5200 model, which operated at 50 kV and 1 mA. The purities and chemical compositions of the anode plate, cathode deposit, anode slime, recovered silver powder, copper sulfate compounds, and changing metals concentration in the solutions were analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES) of an Optima 8000 instrument. Before ICP-OES analysis, the solid samples were initially digested in aqua regia (3:1 HCl: HNO_3) at 90°C for 24 h to ensure complete dissolution. The resulting solutions were then cooled to room temperature and diluted to appropriate concentrations for analysis.

3. Results and discussion

The experimental procedure followed the four-step process depicted in Figure 1 for recovering tin, silver, and copper (as copper sulfate crystals). Initially, lead-free solder dross was reduced using petroleum coke as a reducing agent at varying temperatures, ranging from 450°C to 1050°C. After identifying optimal conditions, the molten solder was cast into anode plates. Subsequently, an electrorefining process was implemented to extract high-purity tin from the anode plates within an aqueous sulfuric acid solution. The anode slime generated after the electrorefining process was leached with an aqueous nitric solution and filtered from the residual matter, and the resulting solution was then used to precipitate silver through cementation with a copper plate. Finally, the concentrated copper solution remaining after silver precipitation was subjected to further treatment and crystallization to obtain copper sulfate compounds. The lead-free solder dross, existing in the forms of Sn, SnO, and Ag_3Sn, as illustrated in the XRD pattern shown in Figure 2, serves as the initial material for this study. The chemical composition of the lead-free solder dross comprised 88.67 wt% Sn, 7.19 wt% O, 2.93 wt% Ag, 1.11 wt% Cu, and a small amount of other trace elements (<0.1%).

Figure 1. Experimental diagram of tin, silver, and copper sulfate extraction from the solder dross.

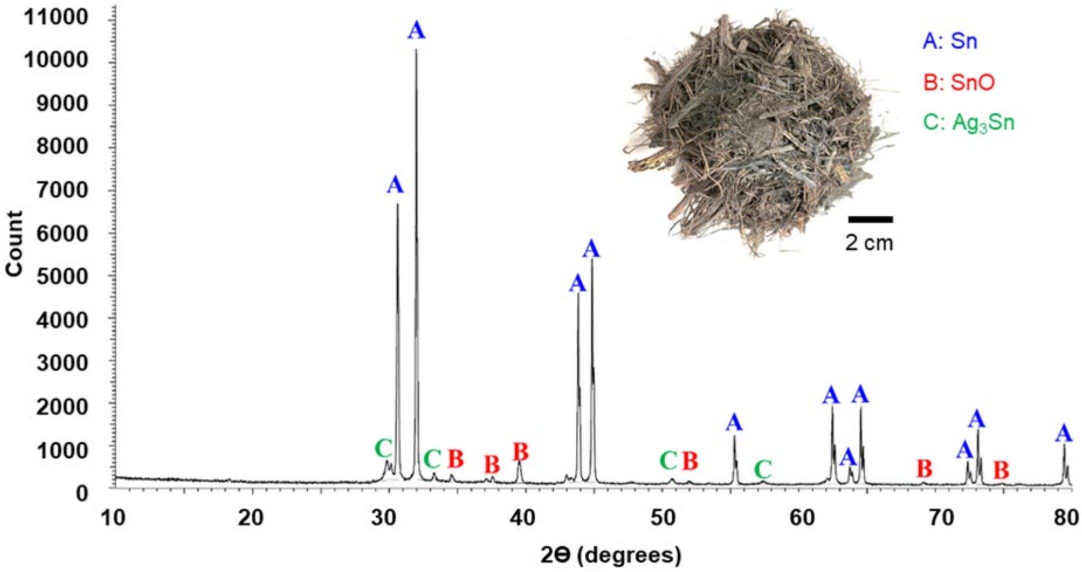

Figure 2. XRD pattern and the image of the initial lead-free solder dross collected from a dip soldering process.

3.1 Lead-free solder dross reduction using petroleum coke

The reduction of SnO_2 by carbon is significantly influenced by temperature. Under standard conditions, the direct reduction is energetically favorable above approximately 700°C [18]. However, an indirect reduction pathway can also occur, with CO (produced by the oxidation of carbon) serving as the effective reducing agent, as illustrated in Equations (1-5) [4]. The specific temperature range for reducing tin oxides depends on the carbon source employed; for instance, coconut charcoal initiates reduction at 800°C, whereas graphite requires a higher temperature of 925°C. The difference may be attributed to minerals in the carbon source that have a catalytic effect [19,20]. The general optimal of tin could achieved within a temperature range of 700°C to 1200°C [18,21]. Therefore, the optimization of the reduction temperature is required due to the difference in the initial SnO_2 raw material (solder dross) and carbon source (petroleum coke) used in this study. In the thermal extraction of tin through the petroleum coke reduction method, P/D ratios of 0.025 and 0.05 were employed. The 0.025 P/D ratio is derived from stoichiometry, while the 0.05 ratio is twice the stoichiometry to account for potential carbon loss factors.

$$C_{(s)} + O_{2(g)} = CO_{2(g)} \tag{1}$$

$$C_{(s)} + CO_{2(g)} = 2CO_{(g)} \tag{2}$$

$$SnO_{2(s)} + CO_{(g)} = SnO_{(s)} + CO_{2(g)} \tag{3}$$

$$SnO_{(s)} + CO_{(g)} = Sn_{(l)} + CO_{2(g)} \tag{4}$$

$$SnO_{2(s)} + C_{(s)} = Sn_{(l)} + CO_{2(g)} \tag{5}$$

The experimental result in Figure 3 elucidates the impact of metal recovery achieved through reduction over periods of 0.5 h and 1 h, employing a P/D ratio of 0.025 and 0.05 at various temperatures. The results indicate a continuous rise in % recovery during the 0.5 h reduction, reaching 65.01% at 1050°C. Similarly, the % recovery during the 1 h reduction significantly increased from 43.97% at 450°C to 78.60% at 1050°C. According to a 0.05 P/D ratio, the % recovery after 0.5 h and 1 h of reduction shows a substantial escalation from 37.69% and 48.33% at 450°C to 92.88% and 91.20% at 1050°C, respectively. Notably, the recovery obtained with a 0.05 P/D ratio surpassed that achieved with a 0.025 P/D ratio, potentially attributable to atmospheric carbon loss.

In accordance with the optimal outcome, the solder dross melted at 1050°C utilizing a 0.05 P/D ratio for 0.5 h for anode plate casting within an iron mold with a yield of 92.88%. The ICP-OES analysis of the anode plate revealed a composition of approximately 96.00 wt% Sn, 2.59 wt% Ag, 1.41 wt% Cu, and trace amounts of other elements (<0.01 wt%). Further purification through electrorefining is deemed necessary for this anode. However, a secondary dross, primarily consisting of SnO and SnO_2 compounds (corroborated by the XRD pattern shown in Figure 4), was generated post-reduction, accounting for approximately 7 wt% of the total mass. The oxidation of the molten metal by atmospheric oxygen is the probable mechanism for forming these oxides. This secondary dross is intended to be reintroduced into the reduction process.

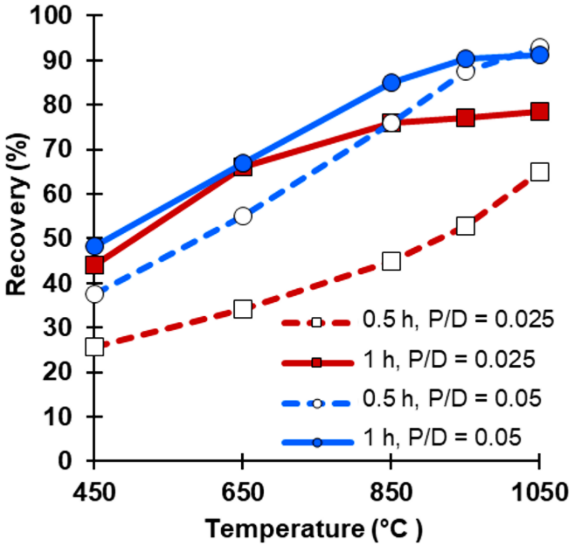

Figure 3. Solder metal recovery at different reduction temperatures at two different P/D ratios of 0.025 and 0.05.

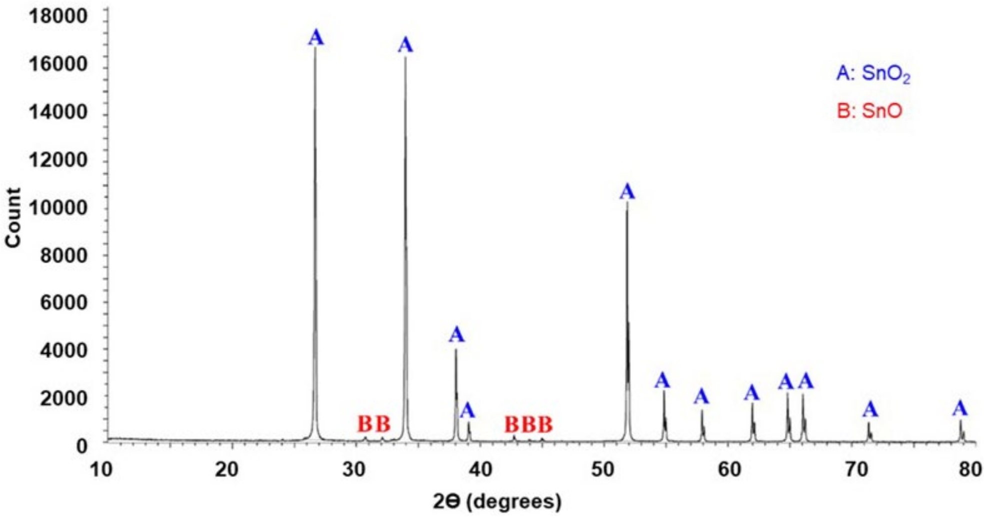

Figure 4. XRD pattern of secondary dross via 1050°C reduction for 1 h (P/D ratio = 0.05).

3.2 Extraction of tin via electrorefining

The cast anode from the optimized condition of solder dross reduction (1050°C and 0.05 P/D ratio) is shown in Figure 5(a). The anode (96.00% purity of tin) was connected to the cathode (99.99% purity of tin) via connected with copper wires and busbars (Figure 5(b)) and a voltage supply. The electrolyte was a 2 mol·L^{-1} aqueous sulfuric acid solution. An external voltage supply was then applied to the anode and cathode at an electric potential of 0.2 V. In the electrorefining process, tin cations migrate from the anode plate through the electrolyte solution and gain electrons at the cathode, resulting in the deposition of highly pure tin dendrites, as depicted in Figure 5(c). Adequate control of the potential during this phase inhibits the dissolution of impurity metals from the anode plate into the solution and their subsequent deposition at the cathode. The chemical reactions involved in the electrolytic process are depicted in Equations (6-8).

Anodic reaction:

$$Sn_{(s)} \rightarrow Sn^{2+}_{(aq)} + 2e^{-} \quad E^{0} = +0.1375\ \text{V} \qquad (6)$$

Cathodicreaction:

$$Sn^{2+}_{(aq)} + 2e^{-} \rightarrow Sn_{(s)} \quad E^{0} = -0.1375\ \text{V} \qquad (7)$$

Overallreaction:impure

$$Sn_{(s)} \rightarrow \text{Pure } Sn_{(s)} \quad E^{0} = 0.00\ \text{V} \qquad (8)$$

Furthermore, the electrorefining process, conducted without mechanical stirring, promotes the preferential deposition of tin [21]. After 96 h of electrorefining, the cathode plate exhibited a significant increase in tin purity from approximately 96.00% to 99.94%, confirmed by the ICP-OES result. Additionally, the recovery of tin, calculated based on the tin content in the anode plate, reached 87.33%.

Figure 5(d) presents the anode slime collected after the electrolytic process. The WD-XRF analysis of this material indicates a composition of approximately 37.07 wt% O, 27.24 wt% Sn, 20.45 wt% Ag, 7.44 wt% Cu, and minor amounts of other contaminants, including C and S. The carbon content is likely a residue from the petroleum coke used in the reduction step, while the sulfur may originate from the sulfuric acid employed in the electrorefining process. Figure 6 presents the XRD pattern of the anode slime, revealing the presence of Ag_3Sn, CuSn, and $CuSO_4(H_2O)_5$ compounds. These compounds encompass high-value metals such as silver and copper, alongside residual tin, slated for extraction through the hydrometallurgical method. The remaining electrolyte solution is anticipated to be recycled in the electrorefining process [22].

3.3 Silver recovery and copper sulfate crystallization

The residual anode slime (after the electrorefining process) contained high amounts of silver and copper. Therefore, these metals are recovered in this step. The anode slime undergoes leaching with a 2.5 mol·L^{-1} aqueous nitric acid solution, resulting in a remarkable 99.55% silver leaching efficiency and an overall 45.75% anode slime leaching efficiency. The acid concentration is calculated from Equations (9-14), delineating the chemical reactions involved in the leaching of silver and copper from the anode slime. In contrast, Equations (13-14) illustrate the formation of a tin oxide compound, resulting in the selective leaching of silver and copper into solution [13]. The residual sludge after leaching, comprising 60.35 wt% Sn, 28.95 wt% O, 3.24 wt% C, 2.26 wt% Cu, and 2.38 wt% Ag (determined and calculated via WD-XRF) is recommended for amalgamation with raw solder dross material

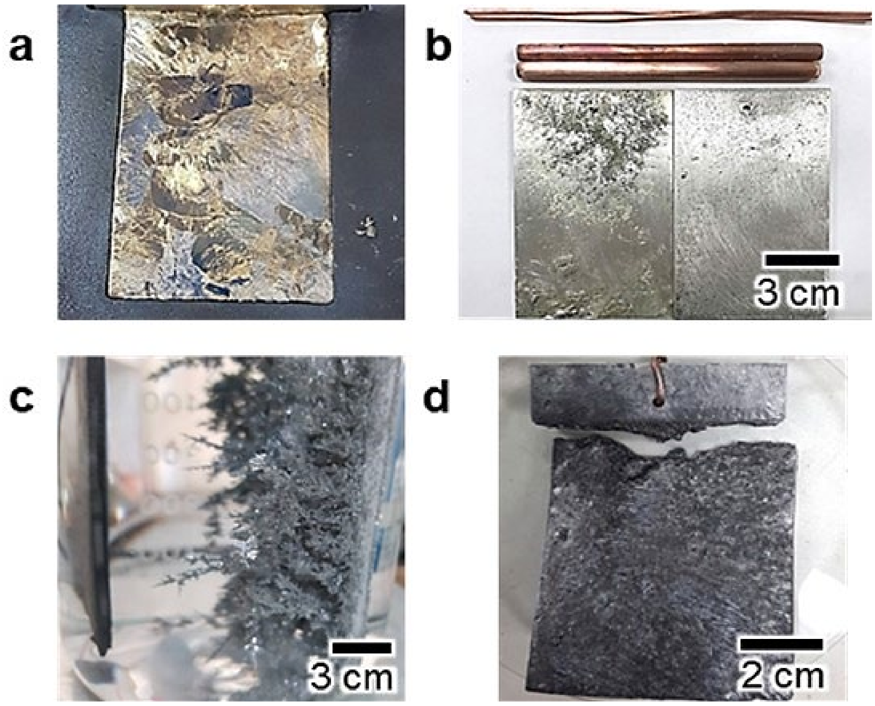

Figure 5. Electrorefining process setup and results: (a) anode casting on an iron mound before cutting into plates, (b) impure tin-based anode plates (left) and high-purity tin cathodes (right) with copper busbars and wires, (c) tin dendrite formation on the cathode during the electrorefining experiment, and (d) anode slime collected after the experiment.

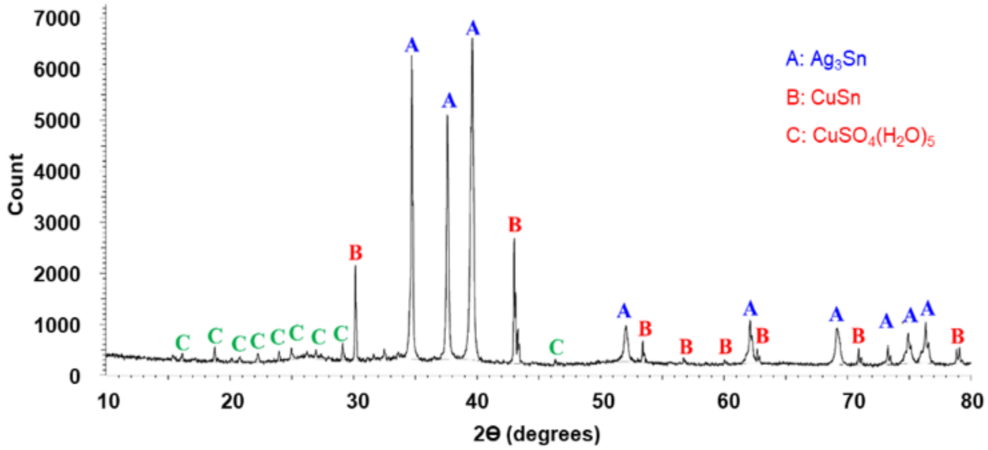

Figure 6. XRD pattern of the anode slime after electrorefining for 96 h.

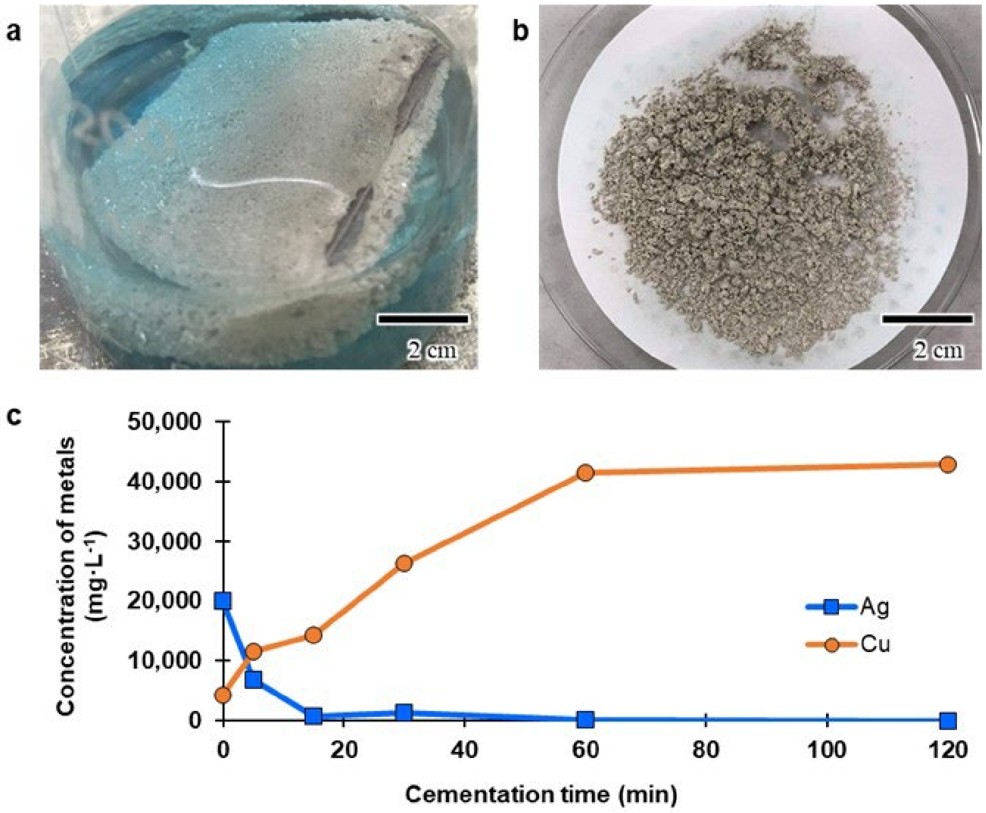

Figure 7. Precipitation of silver by cementation with a copper plate: a) precipitating silver at the surface of the copper plate, b) silver powder after filtration, and c) copper and silver concentration in solution over time (ICP-OES analysis).

$$3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O \tag{9}$$

$$Ag + 2HNO_3 = AgNO_3 + NO_2 + H_2O \tag{10}$$

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O \tag{11}$$

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O \tag{12}$$

$$3Sn + 4HNO_3 + H_2O = 3SnO_2{\cdot}H_2O + 4NO \tag{13}$$

$$Sn + 4HNO_3 = SnO_2{\cdot}H_2O + 4NO_2 + H_2O \tag{14}$$

The ICP analysis of the solution following leaching indicates concentrations of 20110 mg·L^{-1} of silver and 4300 mg·L^{-1} of copper, serving as the initial metal amounts targeted for silver recovery. This investigation selects a copper plate for cementation due to its non-contaminating influence on the system with additional cations, making it an economically viable choice for industrial applications. Upon introducing a copper plate to the silver-rich solution, silver particles precipitate through electron exchange between silver cations and solid copper on the plate's surface, as shown in Figure 7(a). The redox replacement reaction of copper and silver in the silver-rich solution is thermodynamically favorable due to their different standard reduction potentials. The redox replacement reaction, where two silver atoms substitute for each copper atom, can be represented by Equations (15-17) [23]. The precipitated silver powder obtained after filtration, as shown in Figure 7(b), analyzed by the ICP technique, exhibits a purity of 99.60%. The variation of silver ions concentration in the solution with time, as shown in Figure 7(c), experiences a significant reduction within 15 min, achieving approximately 99.99% silver recovery efficiency within 2 h.

$$Cu^{2+} + 2e^{-} \rightarrow Cu_{(s)} \quad E^{0} = +0.34\ V \qquad (15)$$

$$Ag^{+} + e^{-} \rightarrow Ag_{(s)} \quad E^{0} = +0.80\ V \qquad (16)$$

$$Cu(s) + 2Ag^{+}_{(aq)} \rightarrow 2Ag_{(s)} + Cu^{2+} \quad \Delta E^{0} = 1.14\ V \qquad (17)$$

The solution resulting from the silver recovery process contains a significant concentration of copper ions derived from the dissolution of copper from the anode slime and the copper plate employed in the cementation process. This copper-rich solution exhibits potential for copper recovery. This study aims to recover copper as a copper sulfate compound, which finds widespread application in various domains, including agriculture (particularly as a fungicide and algaecide), electronics, water infrastructure, and healthcare (as an intrauterine contraceptive device and antifungal agent) [24,25]. A copper-rich solution was subjected to alkaline precipitation with sodium hydroxide at 160°C, yielding copper oxide as a black precipitate. Subsequent acid dissolution of the copper oxide was achieved by leaching with 60 mL of 1.5 mol·L^{-1} sulfuric acid at 60°C for 1, followed by a 24 h crystallization period to obtain copper sulfate crystals. Equations (18-21) depict the chemical reactions underlying these processes, encompassing the copper-rich solution treatment and the formation of crystallized copper sulfate compounds.

$$Cu^{2+}_{(aq)} + 4HNO_{3(aq)} = Cu(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_{(aq)} \qquad (18)$$

$$Cu(NO_3)_{2(aq)} + 2NaOH_{(aq)} = Cu(OH)_{2(s)} + 2Na(NO_3)_{(aq)} \qquad (19)$$

$$Cu(OH)_{2(aq)} = CuO_{(s)} + H_2O_{(l)} \qquad (20)$$

$$CuO_{(s)} + H_2SO_{4(aq)} = CuSO_{4(aq)} + H_2O_{(l)} \qquad (21)$$

The obtained copper sulfate crystals, as shown in Figure 8(a), demonstrate a 96.95% copper recovery efficiency from the solution and exhibit a remarkable 99.90% purity of copper sulfate, as calculated from the ICP results. The observed blue coloration of the copper crystals can be attributed to copper sulfate pentahydrate. However, the XRD patterns in Figure 8(b) corroborate the successful synthesis of copper sulfate compounds in the forms of $CuSO_4{\cdot}H_2O$ and $CuSO_4{\cdot}3(H_2O)$. Therefore, it is essential to note that potential discrepancies in the XRD results may arise from the drying process involved in sample preparation. This drying step could lead to an inaccurate determination of the number of water molecules within the copper sulfate compounds.

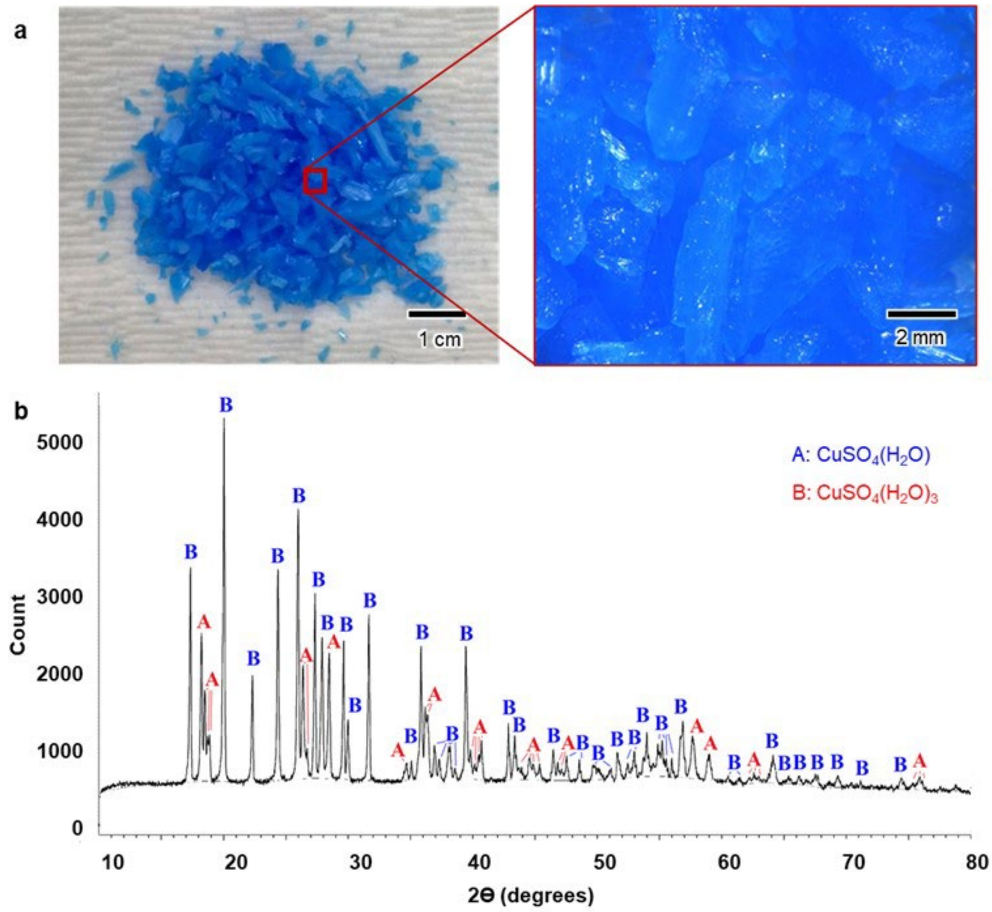

Figure 8. Crystallized copper sulfate characterization: a) images and b) XRD pattern of crystallized copper sulfate compounds.

4. Conclusion

This study presents a comprehensive approach to recovering valuable metals from lead-free solder dross, including high-purity tin, silver powder, and copper in the form of copper sulfate compounds. The experimental methodology combined a petroleum coke reduction process with subsequent hydrometallurgical techniques. The findings reveal that reducing solder dross using petroleum coke at an optimal temperature of 1050°C with a P/D ratio of 0.05 yields a significant tin recovery of 92.88%. The subsequent electrorefining process further enhances tin purity to 99.94%. Subsequent hydrometallurgical processes, such as leaching, cementation, and crystallization, successfully recovered silver and copper from the anode slime, producing high-quality products, including silver powder with 99.60% purity and copper sulfate compounds with 99.90% purity. The overall recovery efficiencies achieved in this study promise the potential for scale-up ability and developing economically viable processes for recycling lead-free solder dross waste from electronic industries.

Acknowledgements

The authors would like to thank the Department of Primary Industries and Mine (DPIM), the Ministry of Industry, Thailand, and the Innovative Processing and Recycling of Metal Research Center (IPRMRC) for funding and technical support under the collaborative recycling technology.

References

[1] B. Lucheva, T. Tsonev, and P. Iliev, "Recycling of lead solder dross, generated from PCB manufacturing," *JOM: the journal of the Minerals, Metals & Materials Society*, vol. 63, no. 8, pp. 18-22, 2011.

[2] H. M. Henao, C. Masuda, and K. Nogita, "Metallic tin recovery from wave solder dross," *International Journal of Mineral Processing,* vol. 137, pp. 98-105, 2015.

[3] P. Kaewboonthong, P. Bunnaul, K. Kooptarnond, and T. Plookphol, "Recovery of metals from Sn-Ag-Cu solder alloy dross," The Proceedings of the International Conference on Mining, Material and Metallurgical Engineering, Prague, Czech Republic, 2014, 79.

[4] Z. Harangi, and T. Kekesi, "Extraction of tin from oxidized soldering dross by carbothermic reduction and acid leaching," *Materials Science and Engineering*, vol. 39, no. 2, pp. 13-22, 2014.

[5] S. A. Ismail, N. H. Jamil, K. Hussin, and M. A. A. Mohd Salleh, "Tin (Sn) recovery from wave soldering lead free solder dross via hydrochloric acid leaching and combustion treatment," *Materials Science Forum*, vol. 857, pp. 535 - 539, 2016.

[6] Y. Kang, J.-J. Choi, D.-G. Kim, and H.-W. Shim, "The Effect of Bi and Zn additives on Sn-Ag-Cu lead-free solder alloys for Ag reduction," *Metals*, vol. 12, no. 8, p. 1245, 2022.

[7] Y. Cui, J. W. Xian, A. Zois, K. Marquardt, H. Yasuda, and C. M. Gourlay, "Nucleation and growth of Ag_3Sn in Sn-Ag and Sn-Ag-Cu solder alloys," *Acta Materialia*, vol. 249, p. 118831, 2023.

[8] J. Wu, G. Huang, Y. Wu, X. Huang, R. Yu, X. Yang, G. Chen, C. Tan, Z. Yu, H. Sun, and Y. Xu, "Applicability evaluation of nano-Al_2O_3 Modified Sn-Ag-Cu solder in high-density electronic packaging subjected to thermal cycling," *Crystals*, vol. 12, no. 12, p. 1736, 2022.

[9] M. Sarkar, F. Gulshan, A. R. M. H. Rashid, and M. Hasanuzzaman, "A Review of TiO_2-nanoparticle reinforced lead-free solder composites used in electronic components soldering," in Encyclopedia of Materials: Electronics, A. S. M. A. Haseeb Ed. Oxford: Academic Press, pp. 456-463, 2023.

[10] I. García-Díaz, F. J. Alguacil, and F. A. López, "Tin and silver recovery from wave soldering dross," *Waste Management & Research*, vol. 36, no. 12, pp. 1201-1209, 2018.

[11] S. Kim, J.-c. Lee, K.-s. Lee, K. Yoo, and R. D. Alorro, "Separation of tin, silver and copper from waste pb-free solder using hydrochloric acid leaching with hydrogen peroxide," *Materials Transactions*, vol. 55, no. 12, pp. 1885-1889, 2014.

[12] S.-h. Lee, K. Yoo, M. K. Jha, and J.-c. Lee, "Separation of Sn from waste Pb-free Sn–Ag–Cu solder in hydrochloric acid solution with ferric chloride," *Hydrometallurgy*, vol. 157, pp. 184-187, 2015.

[13] K. Yoo, K. Lee, M. K. Jha, J.-C. Lee, and K. Cho, "Preparation of nano-sized tin oxide powder from waste Pb-free solder by direct nitric acid leaching," *Journal of Nanoscience and Nanotechnology*, vol. 16, no. 11, pp. 11238-11241, 2016.

[14] C. Daniela Ionela, I. Oana Daniela, and B. Marius, "Studies and research on the recovery of copper from industrial waste solutions by the cementation method," *Test*, vol. 1, no. 1(49), 2022.

[15] W. D. Xing, M. S. Lee, and S. H. Choi, "Separation of Ag(I) by ion exchange and cementation from a raffinate containing Ag(I), Ni(II) and Zn(II) and traces of Cu(II) and Sn(II)," *Processes*, vol. 6, no. 8, p. 112, 2018.

[16] S. Hajimohammadi, S. Gharibi, V. Pourbarkhordar, S. R. Mousavi, and H. Salmani Izadi, "Acute poisoning of copper sulfate: a case report and review literature," *The Egyptian Journal of Internal Medicine*, vol. 34, no. 1, p. 84, 2022.

[17] I. J. Okeke and T. A. Adams, "Life cycle assessment of petroleum coke gasification to fischer-tropsch diesel," in Computer Aided Chemical Engineering, vol. 46, A. A. Kiss, E. Zondervan, R. Lakerveld, and L. Özkan Eds.: Elsevier, 2019, pp. 1495-1500.

[18] F. A. López, I. García-Díaz, O. Rodríguez Largo, F. G. Polonio, and T. Llorens, "Recovery and purification of tin from tailings from the penouta Sn–Ta–Nb deposit," *Minerals*, vol. 8, no. 1, p. 20, 2018.

[19] G. Levêque, and S. Abanades, "Thermodynamic and kinetic study of the carbothermal reduction of SnO_2 for solar thermochemical fuel generation," *Energy & Fuels*, vol. 28, no. 2, pp. 1396-1405, 2014.

[20] Y.-C. Zhang, W.-H. Yu, and S.-M. Xu, "Enhanced leaching of metals from spent lithium-ion batteries by catalytic carbothermic reduction," *Rare Metals*, vol. 42, no. 8, pp. 2688-2699, 2023.

[21] W. Hyk, and K. Kitka, "Selective recovery of tin from electronic waste materials completed with carbothermic reduction of Tin (IV) oxide with sodium sulfite," *Recycling*, vol. 9, no. 4, p. 54, 2024.

[22] A. Ashiq, A. Cooray, S. C. Srivatsa, and M. Vithanage, "Electrochemical enhanced metal extraction from E-waste," in Handbook of Electronic Waste Management, M. N. V. Prasad, M. Vithanage, and A. Borthakur Eds.: Butterworth-Heinemann, pp. 119-139, 2020.

[23] P.-M. Hannula, S. Pletincx, D. Janas, K. Yliniemi, A. Hubin, and M. Lundström, "Controlling the deposition of silver and bimetallic silver/copper particles onto a carbon nanotube film by electrodeposition-redox replacement," *Surface and Coatings Technology*, vol. 374, pp. 305-316, 2019.

[24] S. Naz, R. Hussain, Z. Guangbin, A. M. M. Chatha, Z. ur. Rehman, S. Jahan, M. Liaquat, and A. Khan, "Copper sulfate induces clinico-hematological, oxidative stress, serum biochemical and histopathological changes in freshwater fish rohu (Labeo rohita)," (in eng), *Frontiers in Veterinary Science*, vol. 10, p. 1142042, 2023.

[25] S. Aktas, "A novel purification method for copper sulfate using ethanol," *Hydrometallurgy*, vol. 106, no. 3, pp. 175-178, 2011.