



An Alkaline Glycine-Based Leach Process of Base and Precious Metals from Powdered Waste Printed Circuit Boards

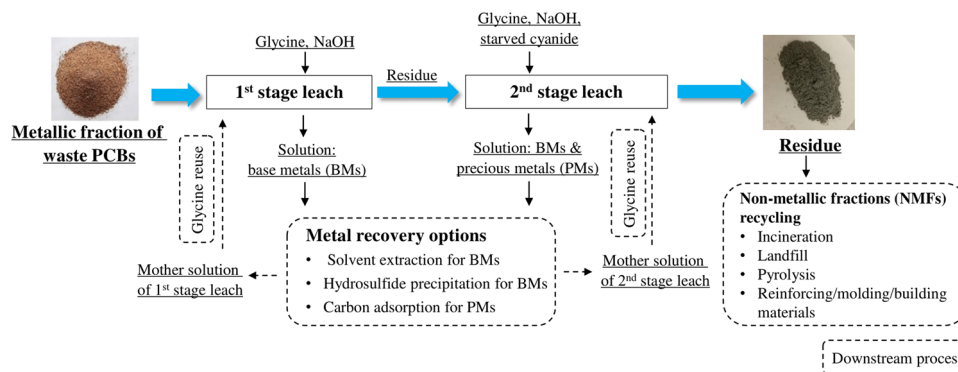
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Abstract

Electronic waste (E-waste) is accumulating rapidly globally and pose a significant environmental challenge. One of the ways to cover the cost of waste processing (in addition to reducing the costs associated with landfill) is through recovery of metals. In addition, toxic and dangerous metals can and must be removed prior to repurposing, incineration or pyrolysis of the plastic substrates. E-waste is usually either transported to landfills or processed by pyrometallurgical and hydrometallurgical processes. Recently, a number of hydrometallurgical approaches have been considered in metals recovery from different electronic components. In this study, glycine (amino acetic acid) or its salts is considered as a lixiviant in an alkaline environment for base and precious metals recovery from shredded and ground printed circuit boards (PCBs). It was found that alkaline glycine solutions selectively dissolve copper, zinc, and lead over precious metals. Gold and silver were then recovered in a subsequent leaching step using glycine and small amounts of cyanide (at starvation levels, implying no free cyanide is present). The leach system remains alkaline throughout both stages of processing. In the two-stage glycine leaching system, gold, silver, zinc, lead and copper recoveries were 92.1%, 85.3%, 98.5%, 89.8%, and 99.1% respectively. The recoveries of precious and base metals by direct cyanidation, single stage glycine–cyanide leaching, and ammonia leaching were lower than the recoveries of these metals using the two-stage glycine and glycine–cyanide systems.

Graphic Abstract



Flowsheet of a two-stage glycine leaching method for metal extractions from waste PCBs proposed in this study

Keywords Glycine · E-waste · Printed circuit boards · Leaching · Metal recovery

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Statement of Novelty

An alkaline glycine leaching system has been evaluated to extract and remove base and precious metals derived from waste printed circuit boards. This leach system has the benefit over other alkaline systems such as pure cyanide-based

or ammonia based leach systems in that it is safer and environmentally friendlier, with no volatile reagents and with the potential to fully recycle and reuse the reagents.

Introduction

Electronic waste (E-waste) is highly diverse in form and composition, e.g.: computers, photocopiers, printers, faxes, monitors, batteries and mobile phones. E-waste contains valuable resources such as precious metals (Au, Ag, Pt and Pd), base metals (Ni, Zn, and Cu), and ceramics (metal oxides). Where appropriate, materials can be physically recovered for repurposing once phase separation was achieved. Some elements in the E-waste can be toxic to human bodies, animals and environment such as Cu, Ni, Pb, Hg, and Cd [1, 2]. Due to the presence of these hazardous materials in E-waste, governments and general public are concerned about the handling of E-waste [3, 4] and its potential to leach in landfill environments. The worldwide E-waste production is dramatically increasing due to the shortened life of electronic devices and equipment as innovation drives continual replacement. It is reported that the annual amount of E-waste generated worldwide has reached 44.7 million tons/year in 2016, with only 20% documented as formally recycled, and forecasted to be 52.2 million tons/years in 2021 [5]. Currently, precious and base metals recovery from E-waste are achieved by the application of pyro-, hydro- and biometallurgical processes. Among these processes, pyrometallurgical processing is the traditional technique for metals recovery from E-waste [3, 6, 7], typically as an initial processing step.

Printed circuit boards (PCBs) are one of the important components of E-waste, due to its high contents of precious and base metals [8]. PCBs contain about 250 to 1000 ppm gold (Au) and about 110 to 3300 ppm silver (Ag) [9–11] which represent more than 70% of the metals value in

E-waste. Recently, many studies have focused on precious and base metals recovery from PCBs by hydrometallurgical routes, rather than the pyrometallurgical one [12–16].

Ideally, extraction of precious and base metals from PCBs can be achieved in two stages of selective base metals extraction followed by leaching and recovery of precious metals in the second stage. The most common reagents used for base metals extraction are ammonia, sulfuric acid and chloride [17–19]. The most common reagents for precious metals extraction from PCBs are halides, thiosulfate, cyanide, thiourea and aqua regia [16, 20–23]. However, most of these reagents have some environmental and technical concerns due to either high toxicity or high reagent consumptions.

Recently, the authors have developed and patented the use of amino acids in alkaline environments, as an environmentally benign alternative lixiviant for precious and base metals recovery [24–29]. It was found that glycine, in particular and amino acids in general, has the ability to dissolve copper (Cu) from different Cu forms such as oxides, sulfides and metal/alloy sources [25, 27, 30]. In addition, the authors have also shown that Au and Ag can be effectively leached from their foil/sheet in alkaline glycine-contained solutions [27]. Glycine acts as a lixiviant for Au, Ag, Cu, zinc (Zn), and lead (Pb) leaching in alkaline environment as the reactions shown in Eqs. 1–2 [31–33]. In addition, nickel (Ni) and cobalt (Co) may also be leached under the appropriate E_h -pH conditions [34]. Glycine is a non-toxic, non-volatile, and low cost reagent with many attractive attributes, as listed and shown in Table 1. It can be easily produced industrially or derived as a by-product from different micro-organisms [35].

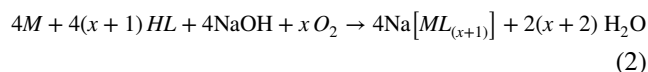
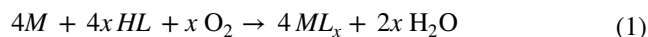


Table 1 Attributes of glycine as a lixiviant for base and precious metals and their minerals

Reagent is non-toxic	Reagent recovery and reuse is easy and cost-effective	It can be operated under dilute and concentrated modes
It is environmentally benign	The reagent cost is low (<USD 2000/tonne)	It is chemically stable (compared to cyanide, thiosulfate, etc.)
It has a high affinity for Au, Ag, Cu, Zn, Pb, Pd, Cd, Ni, Co	It can be used synergistic with cyanide	The precious metal glycinate complexes adsorb well onto activate carbon
Given the alkaline operation, there is no or very limited interaction with acid consuming materials	It can be applied in various leach modes (such as heap, in-situ, vat and agitated tank leaching)	The alkaline operation allows low cost materials of construction
Highly soluble, but non-hygroscopic crystals	No transportability and logistics, trade restrictions	Ease of base metals removal/recovery
Thermally stable	Non-volatile	Simple chemistry
Insignificant Fe, Mn, Mg, Si, Cr dissolution	Cu- glycinate is a good oxidant and acts synergistically with oxygen	No pH changes required between base and precious metals leaching stages

where M stands for Au, Ag, Cu, Zn, Cadmium (Cd), Ni, Co and Pb contained in PCBs, x stands for the valence of the metal ions, L^- stands for glycine anion ($NH_2CH_2COO^-$).

Leaching of base and precious metals from PCBs can be achieved by direct leaching of crushed PCBs or on the metallic portion of the PCB after magnetic, cyclone and/or electrostatic separations. The metallic portion is normally rich in base metals, in particular Cu, which is a high reagent consumer in hydrometallurgical treatment. In addition, the concentrations of toxic and volatile metals such as Pb, Hg, Cd, Sb, and Cd are problematic during the pyrometallurgical treatment of such E-waste powder.

Therefore, the main aim of this work was to evaluate the feasibility of the extraction of base metals such as Cu, Zn, and Pb by glycine leaching in an initial stage followed by precious metals extraction in the glycine–cyanide system. Cyanide concentration in the second stage is very low compared with the direct cyanidation process. A comparison between glycine, ammonia and cyanide leaching of the PCB powder, after most of the non-metal portion has been removed, will be made and options of treating such concentrated E-waste powder will be discussed.

Materials and Methods

Materials

The sample used in this study was a metallic portion of PCB powder supplied by an electronic scrap pre-processing start-up company named Vilytics in Egypt. The metallic portion was produced from a common E-waste processing line, as shown in Fig. 1. In the process, various types of PCBs were dismantled, crushed and ground. Subsequently, the ground PCBs were subjected to two separation steps by air flow and electrostatic force respectively, resulting in the crude products of metallic and non-metallic portions. The metallic portion produced in the processing line represents about 20% of the input mass. The size distribution of the metallic powder is depicted in Fig. 2.

The elemental analysis of the metallic portion of PCB powder by hot acid digestion are shown in Table 2. The metallic portion contains about 55.2% Cu, 368 ppm Au and

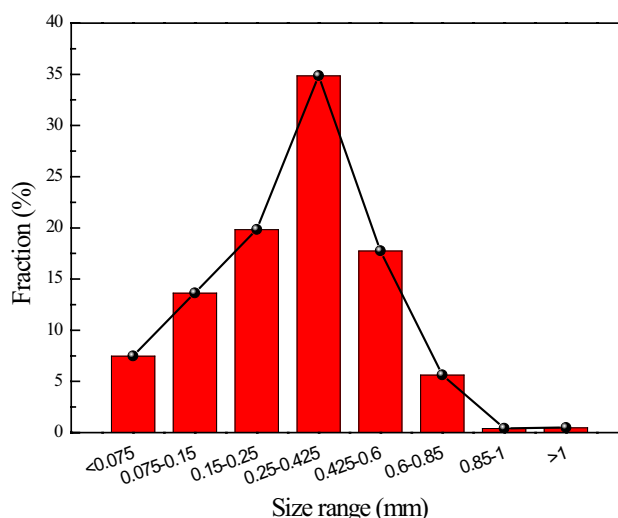


Fig. 2 Size distribution of the metallic powder obtained from the processing line

557 ppm Ag. On a value basis, Au represents about 79.6% of the metal values in the metallic portion followed by Cu (17.3%) and Ag (1.3%). The high contents of Cu and other metal in the metallic portion are caused by the removal of non-metallic portion from PCBs in the processing line (Fig. 1).

Methods: Leaching

All the leaching experiments were carried out using solutions prepared from analytical grade reagents and deionised (DI) water. Two types of leaching reactor were used in this study, i.e. rolled bottle and stirred tank. For the experiments with dissolved oxygen (DO) control, stirred tank reactor was used, and for the rest of experiments, bottle roll was employed. The details of the experiments with the two types of reactor are presented below.

Bottle Roll Tests

For each experiment, 2.000 ± 0.005 g PCB powder was placed in a 2.5 L Winchester bottle containing glycine solution. After pH adjustment to 11.0 with sodium hydroxide, the mix was

Fig. 1 Schematic diagram for the processing line of the PCB powder

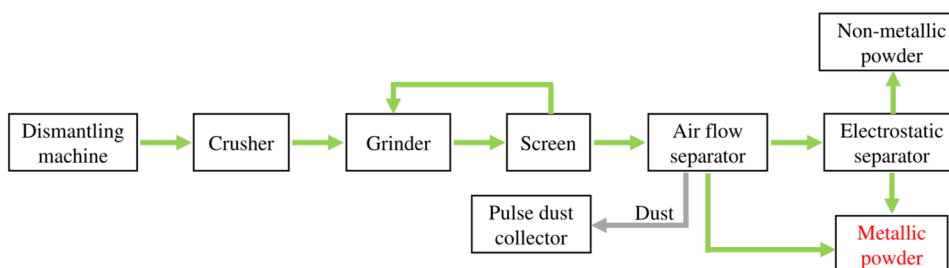
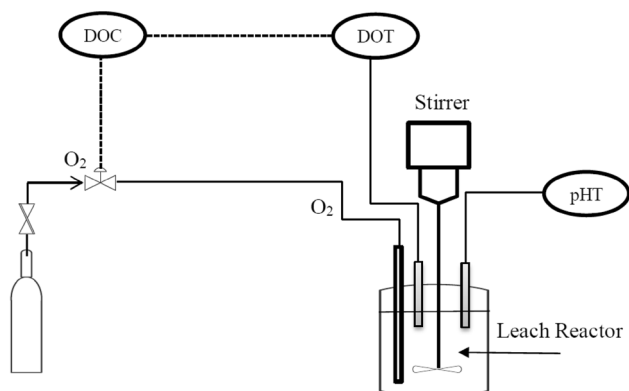


Table 2 Elemental and value analysis of the metallic portion of PCB powder

	Metal price, content and economic value							
	Metal content in wt%					Metal content in ppm		
	Fe	Cu	Al	Pb	Zn	Ni	Au	Ag
Metal price (USD/t) ^a	–	5911	1783	1883	2391	12,520	4.08 × 10 ⁷	4.39 × 10 ⁵
Metal content	2.5	55.2	6.4	2.7	5.8	3560	368	557
Metal value ^b , %	–	17.3	0.6	0.3	0.7	0.2	79.6	1.3

^aData extracted from the official prices of London Metal Exchange (LME, <https://www.lme.com/>) (price for cash seller & settlement on 9th July 2019)

^bOnly the metals specified are taken into consideration

**Fig. 3** Schematic diagram of dissolved oxygen controlled tank leach (DOC dissolved oxygen controller, DOT dissolved oxygen transmitter, pHT pH transmitter)

agitated by rolling the bottle on a bottle roll at 100 rpm. Bottles were vented through a 5 mm hole in the cap to allow for oxygen transfer. At different sampling times, solution samples of the leach solution were obtained after filtration using a 0.45 μm filter paper. The solution samples were then analysed for Au, Ag, Cu, Al, Zn, Ni and Pb by ICP-MS analysis. The residue was collected and analysed for the different elements by acids digestion followed by ICP-MS analysis.

Dissolved Oxygen (DO) Controlled Stirred Tank Reactor

For the leach tests with dissolved oxygen (DO) control, unless specified, the DO level in the leach pulp was controlled at 15 ppm. Leaching experiments were conducted at ambient temperature (23 ± 2 °C) in a 1.25 L leach reactors with agitation at a speed of 300 rpm using overhead stirrers. In these experiments, 2.000 ± 0.005 g of PCB powder was mixed with

500 mL of deionised water before glycine was added to the slurry. The pH of the solution was adjusted to pH 11.0 by the addition of sodium hydroxide. As shown in Fig. 3, the DO level of the leach solution was measured and controlled over the whole leaching time using a Syland DO meter, a mass flow controller, a multifunction data acquisition module (DAQ) and a laptop operating with the LabVIEW program.

Leaching Options

The metal extractions of three different alkaline leaching processes using (1) ammonia; (2) cyanide and (3) direct glycine–cyanide leaching were compared with the two-stage glycine and glycine–cyanide leach developed in this study. Table 3 shows the required stoichiometric amounts of each lixiviant to leach the targeted elements. Table 4 shows the leach conditions and reagent concentration of the different leach systems used to extract precious and base metals from PCB powder. All the lixiviants were added at a mount higher than the required stoichiometric one.

Extraction (%) of Metals

The extraction of metals (E_m , %) investigated in this study was calculated from

$$E_m = (m_t + m_{s1}) / (m_f + m_{s2} + m_r) \times 100\% \quad (3)$$

where m_t and m_f represent the metal mass in the leaching solution at time t and in the final solution, respectively; m_{s1} and m_{s2} represent the cumulative metal mass in the samples taken out before time t and before the final leaching time, respectively; m_r represents the metal mass in the final leaching residue.

Table 3 The stoichiometric amounts of lixiviant to leach the targeted metals at 0.4% solids

Element	Au	Ag	Zn	Al	Pb	Cu	Ni	Total
NaCN, (mg/L)	0.73	2.82	869	–	–	5093	63.4	6029
Glycine (mg/L)	0.91	0.02	0.80	–	750	5201	72.9	6695
Ammonia (mg/L)	0.25	0.98	151	–	–	2356	16.5	2525

Table 4 Leach conditions and reagent concentration of the different leach systems

System	Glycine/Glycine-CN 2- Stages	Glycine-CN Direct	NH ₃	NaCN
Leach conditions	Stage 1: 30 g/L glycine at pH 11 and room temperature (RT) Stage 2: 30 g/L glycine and 300 ppm NaCN at pH 11 and RT	30 g/L glycine and 500 ppm NaCN at pH 11 and RT	1.25 M NH ₃ at pH 11 and RT	6500 ppm NaCN at pH 11 and RT

Results and Discussion

Leaching

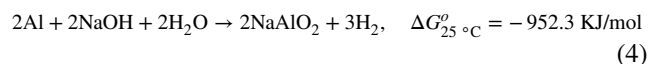
Preliminary experiments were conducted by bottle roll to evaluate the leaching of base and precious metals by glycine, glycine–cyanide, cyanide and ammonia processes. A two-stage leaching process of glycine to recover most of the base metals in first stage followed by glycine–cyanide for precious metal extraction was evaluated. The following sections cover Cu, Zn, Pb, Al, Ni, Au and Ag extraction from PCB powder.

Glycine Leaching (Stage 1)

The metals extraction from leaching PCB powder in solutions containing 30 g/L glycine at pH 11.0 and room temperature (23 ± 2 °C) has been studied. Metals extraction from leaching the PCB powder in glycine solutions for 24 h is shown in Table 5. After 24 h, the results show that glycine selectively dissolves base metals and aluminium (Al) over the precious metals at the leaching conditions. It has been shown by the authors that Au and Ag dissolves slowly in glycine solutions by leaching at room temperature and Cu can be selectively leached over Au [25, 27]. The results shown in Table 5 show that 80.9%, 99.1% 85.6%, 72.5% and 6.5% of Zn, Al, Pb, Cu and Ni were extracted respectively.

Effect of Glycine Concentration

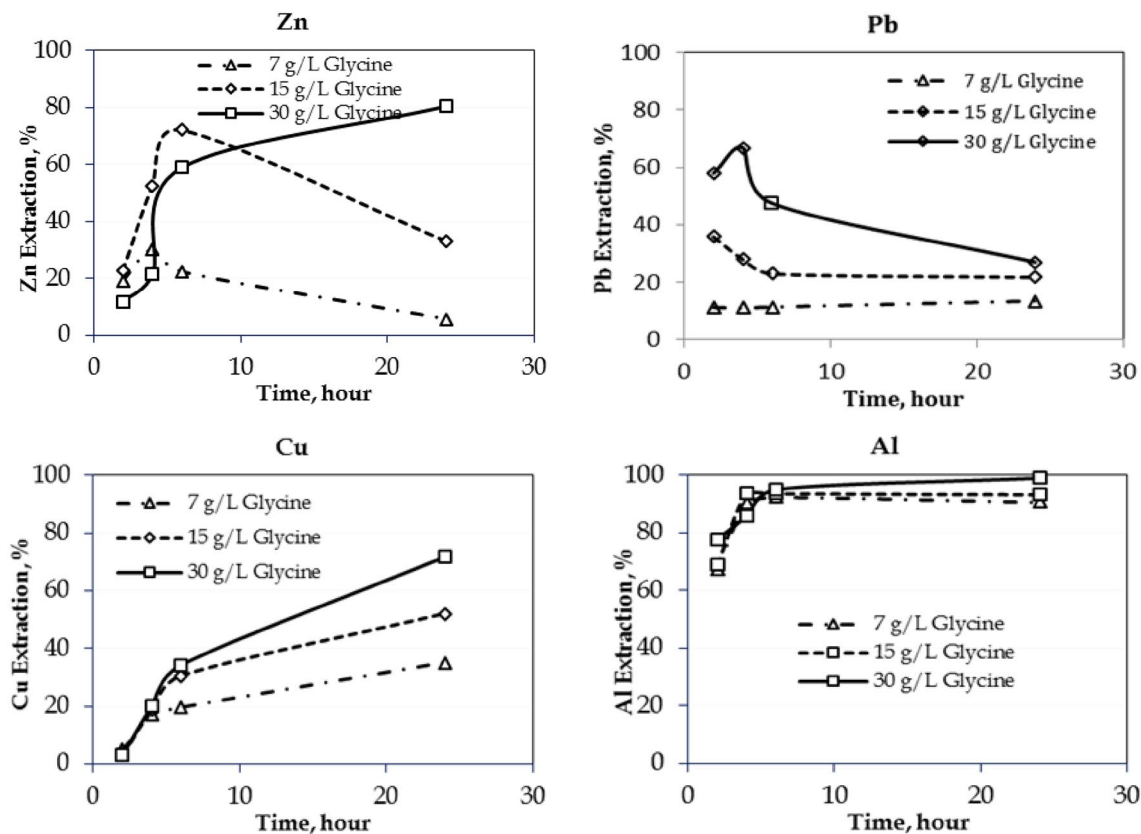
The effects of glycine concentration on metals extraction from leaching the PCB powder is shown in Fig. 4. It can be seen Cu, Pb, Zn extraction depends on the glycine concentration and increasing the glycine concentration enhances the extraction of these metals. To achieve good recoveries of Cu, Pb, and Zn in 24 h leaching, glycine concentration of 30 g/L is necessary. Al is present in the solution as sodium aluminate (NaAlO_2) due to the reaction with NaOH as shown in Eq. 4.



The time profile shows that the extent of Zn leaching reduced over time for the cases where the glycine concentration was 7 or 15 g/L, but not when the glycine was 30 g/L. This is due to the initial rapid leaching of Zn, but after 6 h, Cu present in the PCBs outcompetes the Zn for the available glycine owing to its sheer amount and more stable complexes formed with glycine [36]. Industrially this can be dealt with in staged addition leach circuit. Continuous removal of the leachate and metal recovery from solution (e.g. through solvent extraction [37], ion exchange, carbon

Table 5 Metals extraction in glycine solution from PCB powder

Metal	Au	Ag	Zn	Al	Pb	Cu	Ni
Extraction, (%)	0.3	1.7	80.9	99.1	85.6	72.5	6.5
Extraction (kg/tons)	0.001	0.015	41.229	70.715	84.458	372.314	0.200

**Fig. 4** Effect of glycine concentration on metals (Zn, Pb, Cu, Al) extraction from PCB powder at pH 11.0, room temperature (RT) and 0.4% solids in a bottle roll

adsorption and precipitation [38] will allow continuous recycling of regenerated reagent, although this is not the intent of this investigation. Pb dissolution also experienced the competition with Cu for the available glycine. It is clear that increasing the glycine concentration increases the extraction of Zn Pb and Cu, whereas the change in extraction of Al is insignificant. As the maximum extractions were not 100%, a possible reason is that a certain proportion of each metal was still mechanically locked in an unleachable residues. This can be resolved by either incinerating the matrix prior to leaching or to ultrafine grind the powder to ensure sufficient liberation of the metals.

Effect of pH

The effect of leach solution pH on metals extraction is shown in Fig. 5. It can be seen that high Cu and Zn extractions at

high alkalinity (pH 11.0) were achieved, however Pb shows a better solubility at lower pH (pH 7.0). This finding presents the possibility of selective leaching of Pb over Zn by varying the leaching pH. The data shown in Fig. 5 also confirms that Cu, Zn and Pb are all glycine soluble over a wide pH range, although optimal pH's can be identified. However, Al does not dissolve at lower pH due to the inability to form an aluminate (and it does not form stable glycinate complex either).

Effect of Dissolved Oxygen (DO)

It has been shown in Eqs. 1–2 that oxygen is required for all metals to be oxidised and complexed with glycine. The dissolved oxygen (DO) content in the bottle roll experiments may be limited by oxygen diffusion through the bottle neck, limiting the metal dissolution. Controlled DO leach tests

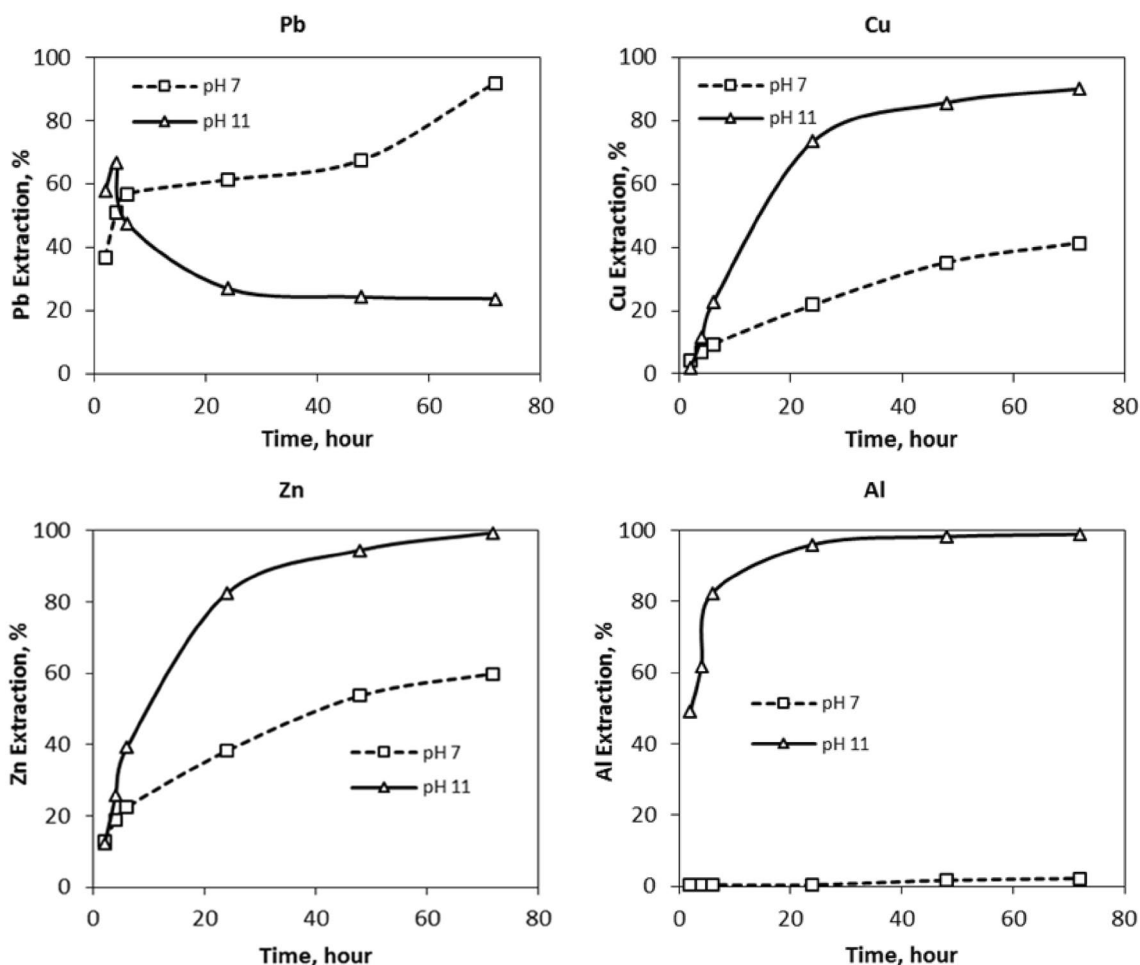


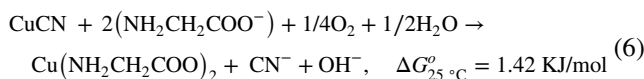
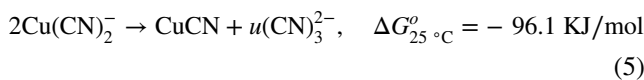
Fig. 5 Effect of leach pH on metals extraction (Pb, Cu, Zn, Al) from PCB powder at 30 g/L glycine, RT and 0.4% solids in bottle roll leach

at 15 ppm were conducted. Metals dissolution at high DO (15 ppm) and low level (6.5 ppm) are shown in Fig. 6. It can be seen that increasing the dissolved oxygen level from 6.5 to 15 ppm had an insignificant effect on the rate of metal dissolution. This implies that oxygen supply was not rate limiting in the experiments. The high concentration of cupric glycinate in the leach solution (~2 g/L) acts here as an additional oxidant for metals dissolution.

Glycine–Cyanide Leaching (Stage 2)

It has been published and shown by the authors [29] that there is a synergistic effect between glycine and low levels of cyanide if Cu is present. Glycine addition to cyanide was found to significantly reduce cyanide consumption when different Au–Cu ores/concentrate are treated [30]. According to Eq. 5 [39], at a starved cyanide concentration, CuCN is precipitated at which glycine play the role to re-dissolve CuCN and regenerate cyanide (Eq. 6). The presence of glycine can also enhance the Au extraction in aqueous solutions

as a main lixiviant for dissolving Au [26, 27]. Glycine acts as an additional lixiviant for Au and Cu as has been shown in Eqs. 1–2.



In this study, to prove the feasibility of glycine–cyanide leaching (Stage 2), a solution containing 30 g/L glycine and 300 ppm NaCN was used to leach PCB residue obtained from the glycine leaching (Stage 1) under the conditions investigated in section “Glycine Leaching (Stage 1)” (30 g/L glycine, pH 11, 0.4% solids, no DO control, 24 h, and RT). It was recorded that the initial PCB mass used in stage 1 was 2.001 g and the residue obtained (to be further leached in stage 2) was 0.781 g, indicating a mass reduction by 60.97%. Table 6 shows the metal extractions in the two-stage

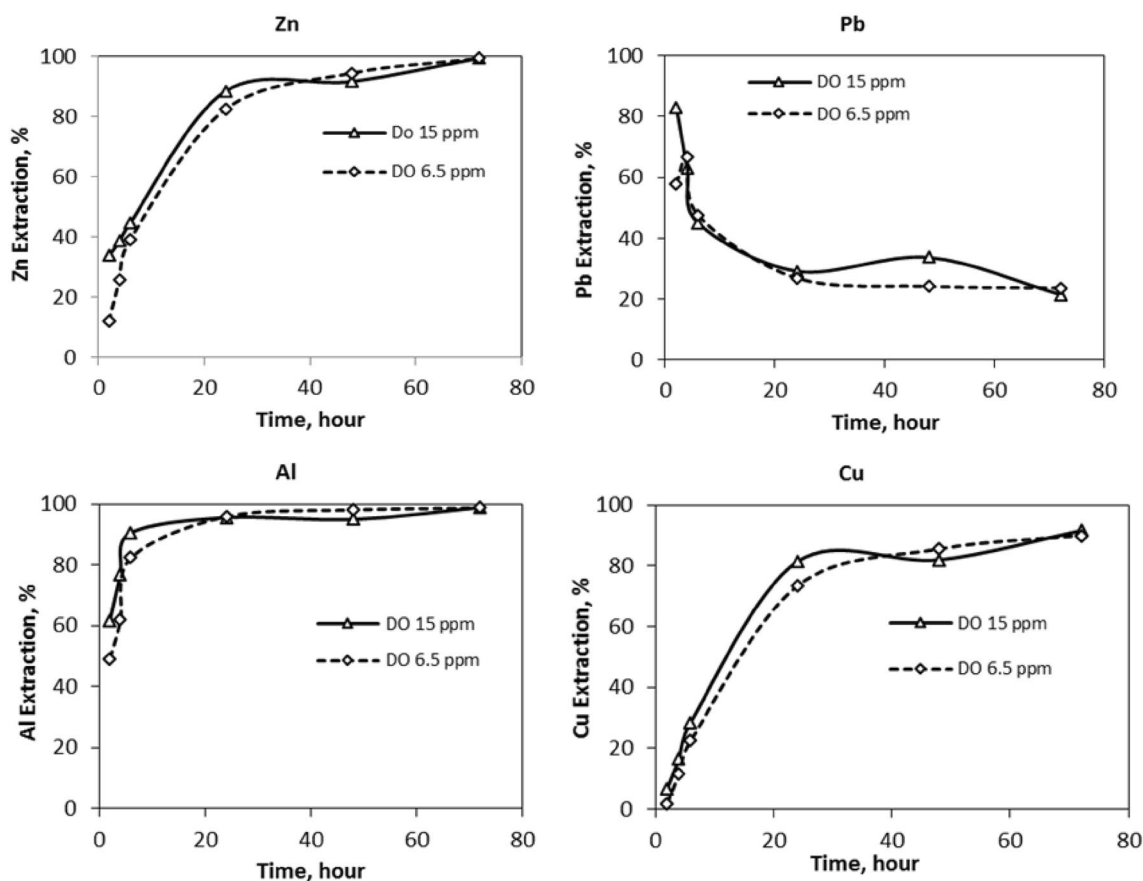


Fig. 6 Effect of dissolved oxygen on metals extraction from PCB powder at 30 g/L glycine, pH 11, RT and 0.4% solids in bottle roll leach

leaching. As shown in the table, most of the precious and remaining base metals were dissolved in stage 2. About 341 g/t Au and 765 g/t Ag were extracted which represent 92.1% and 85.3% extraction of Au and Ag respectively. The extracted Au and Cu values from this rich powder is \$US 13,913/ton and \$US 3,009/ton respectively at Cu price of \$US 5911/ton and Au price of \$US 4.08×10^7 /ton (referred as LME grade metal).

An additional advantage of glycine–cyanide leaching is that most of the Cu in the final leach solution is present as cupric glycinate, while there is no measurable free cyanide after leaching. Cu(II) speciation by UV–Vis spectrometer was conducted at a wavelength of 630 nm and the total Cu in

the leach solution was monitored by AAS. The results show that about 97.5% of Cu was present as cupric glycinate and less than 2.5% of Cu was present as cuprous cyanide in the final leach solution. Tanda et al. [28] discusses the use of UV–Visible spectroscopy to determine the concentration of the Cu–glycinate complex.

The PCB powder has been leaching in solutions containing 300 ppm NaCN which is so far less than the stoichiometric requirement of cyanide. However, this test was conducted to show metals extraction by using the same cyanide addition with and without glycine. Not surprisingly, Au and Cu extractions were only 10.6% and 5.5% respectively by leaching at 300 ppm NaCN without glycine addition (Table 7).

Table 6 Metal extractions after two-stage leaching of glycine (30 g/L glycine, pH 11, 0.4% solids, no DO control, 24 h and RT) followed by glycine–cyanide (30 g/L glycine, 300 ppm NaCN, pH 11, 24 h and RT)

Element	Au	Ag	Zn	Al	Pb	Cu	Ni
Extraction in stage 1 (%)	0.3	1.7	80.9	99.1	85.6	72.5	6.5
Extraction in stage 2 (%)	92.1	85.1	92.6	31.5	59.5	96.9	13.9
Total extraction (%)	92.1	85.3	98.5	98.1	89.8	99.1	19.5
Total extraction (kg/tons)	0.341	0.765	50.725	71.339	101.374	508.995	0.600

Leaching Options

Ammonia

The metals extraction from leaching PCB powder in a solution containing 1.25 M ammonia and 0.4% solids at room temperature and pH 11.0 is shown in Table 8. The ammonia leached 90.1% Zn, 85.3% Cu and 97.1% Al. Au did not dissolve under the leach conditions significantly, however 58.1% of Ag was extracted. It is well known ammonia is not effective to leach Au, so another stage of cyanide-ammonia may be required to dissolve Au. In addition, there are some concerns regarding the environmental, health and safety of ammonia which need attention as the threshold limiting value (TLV in air) for ammonia gas is about 14 mg/m³ [40].

Cyanide

Direct cyanidation of leaching the PCB powder was tested at high cyanide concentration. Metals extraction from the PCB powder by cyanidation at 6500 ppm NaCN and pH 11.0 is shown in Table 9. Natural pH of cyanide solution was 12.2 and adjusted to pH 11 (for comparison to the glycine and glycine–cyanide systems) by adding sulfuric acid.

About 87.9% Au and 86.4% Ag were extracted with direct cyanidation, despite the presence of excess cyanide. Most of the Cu present in the final leach solution (1994 mg/L) as cuprous cyanide plus the free cyanide (1372 mg/L) in the final leach solutions which requires an additional cost of recovery or destruction after leaching. Figure 7 shows the decrease in cyanide concentration over the leaching time due to the base metals extraction. At the end of the leach a very high level of free cyanide was still present, and still it was not able to attain the same metal recoveries as for the starved cyanide (less than 1/20th of the cyanide-only level) with glycine system.

During cyanidation at 6500 ppm cyanide, about 96.5% of Cu was extracted and more cyanide addition is required to get higher metals extraction. The stoichiometric required cyanide concentration, as NaCN to leach Cu, Zn and Ni is 5093, 869 and 63.4 mg/L, respectively. Using such high cyanide concentrations in leaching PCB powder is a public concern, especially when E-waste recovery plant is often built up close to residential areas, or poorly regulated as in some developing countries. Excessive levels of both free and Weak Acid Dissociable (WAD) cyanide is present, which requires a significant investment into cyanide detoxification.

Table 7 Total metals extraction after leaching at 300 ppm NaCN, pH 11.0 and 0.4% solids

Element	Au	Ag	Zn	Al	Pb	Cu	Ni
Total extraction (kg/t)	0.028	0.020	0.050	9.3	0.045	26.5	0.015
Total extraction (%)	10.6	0.7	0.8	16.2	0.1	5.5	0.354

Table 8 Metals extraction from ammonia leaching at 1.25 M ammonia, pH 11.0 and 0.4% solids

Element	Au	Ag	Zn	Al	Pb	Cu	Ni
Time (h)	(mg/L)	(µg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
2	0.002	140	236	249	37.1	1410	1.0
4	0.005	385	326	270	54.0	1810	1.4
6	0.004	422	347	278	60.7	1930	1.4
24	0.002	1240	335	284	50.1	2050	1.6
Extraction (kg/tons)	0.0005	0.3094	83.6	70.9	12.5	511.5	0.4
Extraction (%)	0.4	58.1	90.1	97.1	22.5	85.3	7.3

Table 9 Metals extraction from cyanide leaching at 6500 ppm NaCN, pH 11.0 and 0.4% solids in bottle roll leach

Element	Au	Ag	Zn	Al	Pb	Cu	Ni
Time (h)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
2	0.587	0.08	90.7	153.5	1.9	621	0.81
4	0.623	0.15	144.3	229.1	6.5	1060	1.48
6	0.851	0.66	183.6	261.9	28.4	1387	2.04
24	1.033	1.41	298.6	282.7	111.1	1994	2.41
Extraction (kg/tons)	0.274	0.602	34.5	61.0	29.4	551.0	0.850
Extraction (%)	87.9	86.4	61.8	96.9	46.7	96.5	23.1

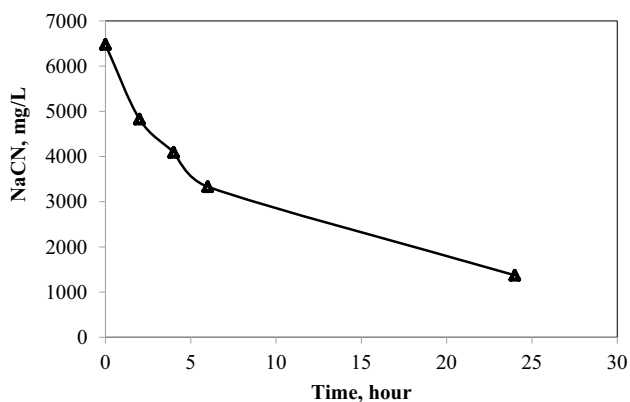


Fig. 7 NaCN concentration during the leaching of PCB powder at 6500 ppm NaCN, pH 11.0, RT and 0.4% solids in bottle roll leach

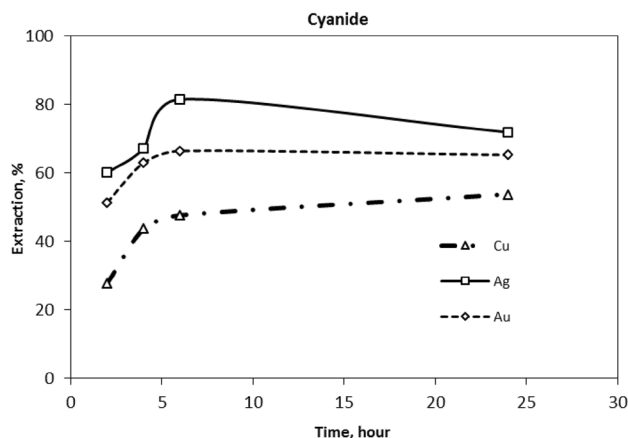


Fig. 8 Au, Ag and Cu extraction during cyanidation at 3500 ppm NaCN and pH 11.0

Direct (Single Stage) Glycine–Cyanide Leaching

Leaching metals from PCB powder in one stage by directly using a glycine–cyanide mixture was evaluated. In solutions containing 30 g/L glycine and 500 ppm NaCN at pH 11 PCB powder was leached. The metals extraction from this test is shown in Table 10. It is not surprising to find the precious metals extraction to be low (37.6% Au and 8.8% Ag). Most of the cyanide is consumed by the high content of cyanide complexing metals, such as Cu, Zn and Ni. The high content of Cu in the PCB powder makes the direct leaching of all metals in a single stage, difficult and highly reagents consuming.

Figure 8 and 9 shows a comparison between direct cyanidation and two-stage of glycine/glycine–cyanide leaching respectively based on Au, Ag and Cu extraction. Au, Ag and Cu extraction during cyanidation were 65.4, 72.0 and 54.6% respectively. Total extractions of Au, Ag and Cu after two-stage leaching of glycine for base metals followed by glycine–cyanide for precious metals were 92.1, 85.3 and 99.1% respectively. In addition to the high metals extraction, glycine leaching has the advantage of environmentally friendly, recyclable and non-toxic reagent.

Table 11 summarises the total metals extraction from leaching the PCB powder by different routes and systems.

The results identify that glycine leaching followed by glycine–cyanide leaching is a suitable and optimum way to deal with such metallic PCB powder which contains high percentages of base metals. Cyanide leaching in two stages would be better to increase the Au and Ag extraction. Glycine is more powerful to dissolve the base metals (Cu, Zn and Pb) than cyanide.

The lower Ni extraction may be due to fact that a significant portion of the Ni may be bound in high chromium stainless steel. The chromium forms a protective and glycine (and cyanide) insoluble oxide layer preventing further reaction. Slightly more reducing conditions and ultrafine grinding may enhance the Ni extraction (as has been shown for Ni-Co extraction from other Ni-Co bearing materials [34].

Discussion of Downstream Treatment

In the foregoing sections, a new two-stage glycine leaching system has been demonstrated and compared with other leaching options. After the two-stage leaching, the metals present in solutions and the residue obtained should be recovered properly. In recent years, the recovery of base and precious metals from glycine-bearing solutions has been actively investigated, particularly by our research group [26,

Table 10 Metals extraction (%) from direct glycine–cyanide leaching at 30 g/L glycine and 500 ppm NaCN and pH 11.0

Element	Au	Ag	Zn	Al	Pb	Cu	Ni
Time. (h)	(mg/L)	(µg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
2	83.7	66	54.5	171	69.7	199	0.5
4	373	168	125	266	99.8	571	1.1
6	380	156	152	286	96.9	739	1.2
24	400	88	258	311	82.2	1620	2.0
Extraction (kg/t)	0.099	0.022	64.4	77.6	20.5	404.3	0.499
Extraction (%)	37.6	8.8	97.7	98.7	24.2	87.6	20.6

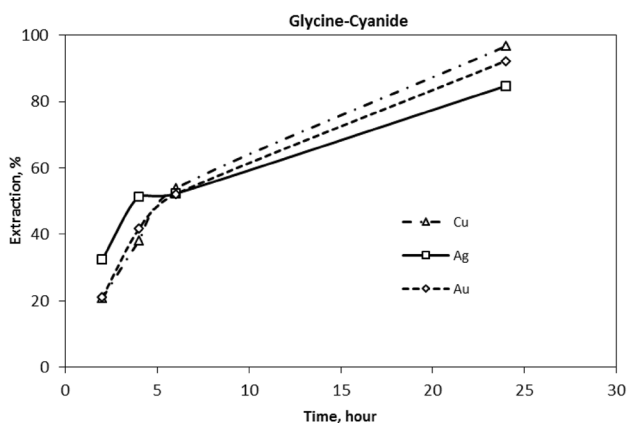


Fig. 9 Total Au, Ag and Cu extraction after glycine leaching at 30 g/L at pH 11 (stage1) and glycine–cyanide leaching (stage 2) at 30 g/L glycine, 300 ppm NaCN at pH 11

Table 11 Metals extraction from leaching PCB powder in different leach systems

Element	Glycine/ Glycine-CN 2-stages	Glycine-CN Direct	NH ₃	NaCN
Metals Extraction, %				
Au	92.1	37.6	0.38	87.9
Ag	85.3	8.8	58.1	86.4
Zn	98.5	97.7	90.1	61.8
Al	98.1	98.7	97.1	96.9
Pb	89.8	24.2	22.5	46.7
Cu	99.1	87.6	85.3	96.5
Ni	19.54	20.6	7.30	23.1

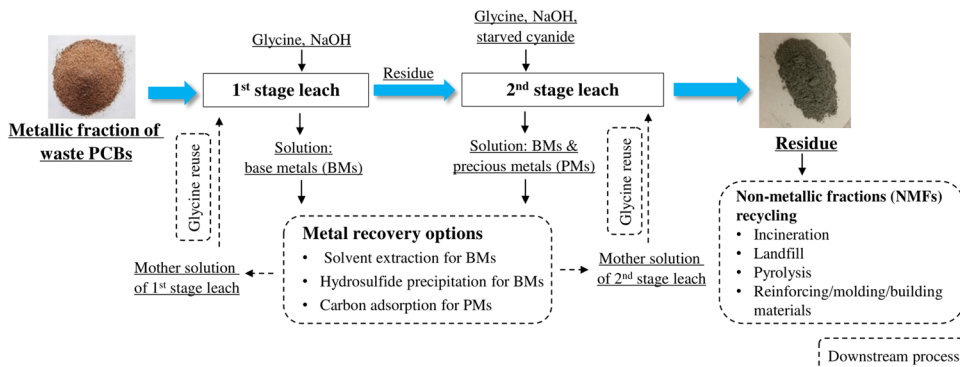
27, 31, 34, 37, 38, 41]. In addition, various methods for the recovery of non-metallic fractions (NMFs) of E-waste have been intensively reported [42–44]. Figure 10 summarises the procedures of two-stage glycine leaching, and the recommended downstream treatment based on the up-to-date research status. As shown in the figure, base metals contained in the solutions from 1st (stage 1) and 2nd (stage

2) stage could be treated by solvent extraction [37] or sulphide precipitation [41], while precious metals contained in the solutions from 2nd stage are recommended to be treated by carbon adsorption [27, 31]. After metal recoveries, glycine contained in mother solutions from the 1st (free of cyanide) and 2nd (with cyanide) stage could be recycled respectively for reuse [38, 41]. For example, Eksteen et al. [38] reported that 99.1% Cu could be precipitated as Cu sulphide (CuS) from glycine leaching solution of chalcopyrite at Cu:S²⁻ molar ratio of 1:1 in only 10 min. The recycled barren solution after sulphide precipitation showed similar rate of Cu leaching compared with fresh glycine solution, indicating the feasibility of glycine reuse [38]. However, it should be noted that the leaching solution of PCBs has more base metals present and higher metal concentrations (Table 11), compared with that of Cu/Au ore/concentrate, which brings complexities during metals recovery. Therefore, more investigations should be carried out in the future to verify the recommended recovery methods. The residue obtained after 2nd stage leach mainly contains plastics, which may be further treated for incineration, landfill, and pyrolysis or as a reinforcing/molding/building materials [44]. In particular, the NMFs after pyrolysis have been shown promising as a reductant, a supplementary carbon source, in ironmaking industries [45]. For environmental and technic considerations, however, some heavy/toxic metals remaining in the residue may need to be removed prior to these downstream treatment.

Conclusions

An exploratory research study on a new leaching system for the metallic portion of PCBs powder has been conducted and a comparison between conventional cyanidation, ammonia and direct glycine–cyanide leaching has been made. PCBs powder containing a high percentage of metals was used to evaluate the leachability of different metals in alkaline glycine solutions. Results show high potential for the use of alkaline glycine as a new hydrometallurgical leach system

Fig. 10 Flowsheet of a two-stage glycine leaching method for metal recoveries from waste PCBs



for E-waste under mild operating conditions (room temperature, ambient pressure, low levels of toxic reagents). It was found that glycine leaches most of the base metals such as Pb, Zn and Cu at room temperature. Precious metals (Au, Ag) were then recovered in a consecutive step using glycine and low cyanide mixture (300 ppm NaCN). The results show metals dissolution increases by increasing glycine concentration, DO and pH. While metal extractions in the 90% levels (except for Ni) were obtained, one should aim for complete metals removal for landfill disposal. This may be facilitated through fine grinding, or slightly raising the heating the leach system to mildly elevated, but still mild, temperatures (e.g. to around 40–50 °C).

The recovery of Au by two-stage glycine, direct cyanidation, direct glycine–cyanide leach, and ammonia was 92.1%, 87.9%, 37.6%, and 0.4% respectively. The total metals value of the extracted Au and Cu by two-stage glycine leaching was about \$US 16,922/ton of the PCB powder (referred as LME grade metal). The advantages of glycine over other leaching options are mainly due to its environmentally-friendly nature, ease of handling, high stability and being an easily recoverable reagent. Continuing further research of metals and residue recovery techniques will supplement the finding from this study.

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Compliance with Ethical Standards

Conflict of interest Messrs Oraby and Eksteen are listed co-inventors on patents that includes the use of glycine in alkaline environments to leach precious and chalcophile metals from materials bearing these metals.

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