WASM: Minerals, Energy and Chemical Engineering

Sustainable recovery of base and precious metals from waste printed circuit boards using alkaline glycine processes

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Declaration

To the best of my knowledge and belief, this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

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Abstract

Waste printed circuit boards, as a typical type of electric and electronic waste (e-waste), represent considerable metal values and pose significant risks to human health and the environment. Conventionally, waste printed circuit boards have been transferred to developing economies through transboundary e-waste movement. As dedicated by the Basel Convention, e-waste should be recycled domestically to avoid additional hazards and costs, reflected by the recent bans on foreign e-waste by traditional waste-importing countries. Pyrometallurgy has been applied in Europe and Asia, where a significant amount of e-waste can be transported to a centralised location for smelting. However, due to the limited e-waste generation and the vast geography, Australia's scenario does not contribute to an economical pyrometallurgical process, which brings the need for a de-centralised, scalable and environmentally benign hydrometallurgical approach.

In recent years, the simplest amino acid, glycine (NH_2CH_2COOH), has been actively reported in the hydrometallurgy of natural resources, owing to its high affinity to the base and precious metals, and has been considered as a "green" lixiviant. In contrast, the application of glycine for e-waste recycling has not been reported yet. The present thesis, consisting of five peer-reviewed journal papers and one additional unpublished chapter, proposes sustainable hydrometallurgical processes for metals recovery from waste printed circuit boards using glycine as a key lixiviant. Various alkaline glycine-based leaching systems have been proposed and investigated. Different options for copper recovery from glycine leachates have been studied.

Firstly, the exploratory study shows that alkaline glycine solution could selectively leach copper, zinc and lead over precious metals from powdered metallic fractions of waste printed circuit boards (>72% metals). The precious metals of gold and silver could be leached in a subsequent stage using alkaline glycine solution but in the presence of a starved level of NaCN (300 mg/L). The two-stage leaching system showed higher or similar metal extractions than the conventional cyanidation (6.5 g/L NaCN), ammonia leaching and single-stage glycine-NaCN leaching. This study proved the feasibility of using a glycine-only and cyanide-starved glycine leaching system to extract base and precious metals from waste printed circuit boards.

The detailed investigation of base metals' first-stage leaching from simply pre-treated waste printed circuit boards (100%≤ 2 mm) was then carried out. The results show that glycine solution presented high selectivity to copper and zinc (>90%) while the extraction of other base metals (lead, aluminium, nickel, tin and cobalt) varied to a different extent and was significantly affected by initial pH, glycine concentration and

solid content. Solution pH was found progressing automatically and was greatly influenced by other variables. Under the optimised conditions (0.5 M glycine, initial pH 10, 2% solid, ≤2 mm particle size, room temperature, 72 h and using ambient oxygen as an oxidant), 96.5% copper, 92.5% zinc and 46.8% lead were extracted, and the extraction of other base metals remained at <20%. Precious metals of gold and silver were almost un-leached, while palladium extraction of 12.6% was recorded. SEM-EDS analysis found the remaining copper and nickel were locked in inert metal layers. Kinetic study showed that the copper extraction was mainly controlled by internal diffusion with an activation energy of 6.62 kJ/mol.

To recover copper from glycine leachate, the methods of hydrazine reduction, sulfide precipitation and solvent extraction were investigated and compared. For hydrazine reduction, copper recovery was sensitive to solution pH, and the rise of initial pH, copper concentration and temperature contributed to the higher copper recovery. At the copper/hydrazine molar ratio of 1:0.7 and 1:1, the products were cuprite and metallic copper with 96.9% and 98.6% recoveries, respectively, with noticeable lead and tin co-precipitations. When using sulfide to recover copper, ≥99.5% copper was easily precipitated in only 5 min. >65% lead, tin and zinc were also co-precipitated, but aluminium and nickel co-precipitation was limited (≤3%). Covellite (CuS) was identified as a product by XRD analysis with a purity of 87.9%. During solvent extraction, the extractant Mextral 84H showed better performance than Mextral 54-100 but needed higher H_2SO_4 concentration for stripping. Mextral 84H also showed higher selectivity than Mextral 54-100. The overall copper recoveries of 91.6% for 15% Mextral 84H extraction followed by 200 g/L H_2SO_4 stripping, and 86.7% for 30% Mextral 54-100 extraction followed by 80 g/L H_2SO_4 stripping were achieved.

During the detailed investigation on the second-stage leaching of precious metals from the residue of first-stage leaching using cyanide-starved glycine leaching system, 90.1% gold, 89.4% silver and 70.1% palladium were extracted with 81.0% copper and 15.0% zinc under the optimised conditions (4× stoichiometric amount of glycine (170 kg/t), 250 mg/L cyanide, initial pH 11, 2% solid, sample pulverised, room temperature and 96 h). The extraction of other base metals remained low at <10%, indicating the system's selectivity. The system showed comparable or better performance on precious metals extraction than stoichiometric and intensive cyanidation, but cyanide consumption was reduced by about 70–90%. At the optimal 250 mg/L cyanide dose, no free cyanide presented in leaching solution after 4 h, which minimised safety and health risks significantly in comparison to traditional cyanidation (>3500 mg/L cyanide). Leaching

kinetics was found to be controlled by glycine and cyanide dose, pH, and particle size, while staged addition of cyanide did not enhance the extractions.

A preliminary study on a non-NaCN glycine leaching system showed that using glycine solution in the presence of additional oxidant, permanganate or ferricyanide (non-hazardous reagent), could leach more than 75% gold from the residue of first-stage leaching. Increasing oxidant concentration resulted in a higher final gold extraction for both ferricyanide and permanganate. However, the rise of temperature ($\sim 55^{\circ}C$) and glycine concentration (0.5–1 M) did not show obvious benefit for gold extraction for both oxidants. Controlling E_h at a specific range did not enhance gold extraction for permanganate. In contrast, by controlling E_h, the ferricyanide consumption was reduced by more than 50%. Under optimised conditions, 86.1% and 76.5% gold extraction were achieved for glycine-permanganate and glycine-ferricyanide leaching system, respectively, with the potential of a higher extraction at an extended time. However, the oxidant consumption was considerable, with 632.1 kg/t permanganate and 610.1 kg/t ferricyanide consumed under the optimised conditions. Further studies are required to develop these non-NaCN glycine leaching systems but were not deemed within the scope and time frame of this thesis.

Acknowledgements

List of Publication included as part of the thesis

The following peer-reviewed journal publications form the main body of the thesis:

I.   **Li, H.,** Eksteen, J., & Oraby, E. (2018). Hydrometallurgical recovery of metals from waste printed circuit boards (WPCBs): Current status and perspectives – A review. *Resources, Conservation and Recycling*, 139, 122–139.

II.   Oraby, E. A., **Li, H.,** & Eksteen, J. J. (2020). An alkaline glycine-based leach process of base and precious metals from powdered waste printed circuit boards. *Waste and Biomass Valorisation*, 11 (8), 3897–3909.

III.   **Li, H.,** Oraby, E., & Eksteen, J. (2020). Extraction of copper and the co-leaching behaviour of other metals from waste printed circuit boards using alkaline glycine solutions. *Resources, Conservation and Recycling*, 154, 104624.

IV.   **Li, H.,** Oraby, E., & Eksteen, J. (2021). Recovery of copper and the deportment of other base metals from alkaline glycine leachates derived from waste printed circuit boards (WPCBs). *Hydrometallurgy*, 199, 105540.

V.   **Li, H.,** Oraby, E., & Eksteen, J. (2021). Cyanide consumption minimisation and concomitant toxic effluent minimisation during precious metals extraction from waste printed circuit boards. *Waste Management*, 125, 87–97.

Author contribution statement

As the primary author of four out of five publications forming the body of this thesis, the PhD candidate conceived, planned and conducted all the experiments, collected, organised, processed and interpreted all the experimental data, and took the lead in writing and revising the manuscript of all the four publications. Prof Jacques Eksteen and Dr Elsayed Oraby provided constructive design, critical comments and insightful feedback throughout and assisted in data analysis and interpretation, edition and revision of the manuscripts.

For the fifth publication, the PhD candidate is the second co-author from a total of three authors. The candidate conducted a part of the experiments, contributed to the data analysis and interpretation, writing and revision of the manuscript.

Co-authors of all five publications have permitted the published papers to be included in this thesis. Two signed statements of contribution to the published works from this thesis are attached in Appendix B.

Dedication

To my grandfather who encouraged me to become a scientist.

"May you rest in peace."

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Abbreviations and glossary

AAS	Atomic absorption spectrometry
BMs	Base metals
Cyanide-starved glycine leaching system	A leaching system including glycine, pH modifier and starved level of cyanide with ambient air/oxygen ingress
DO	Dissolved oxygen
EEE	Electric and electronic equipment
E-waste	Waste electric and electronic equipment
Gly	Glycine
Glycine-oxidant leaching system	A leaching system including glycine, pH modifier and added oxidant. Such oxidant is not ambient oxygen
Glycine-only leaching system	A leaching system including glycine, pH modifier with ambient air/oxygen ingress
Glycine processes	Hydrometallurgical processes using glycine as a lixiviant
ICP-OES	Inductively coupled plasma- optical emission spectroscopy
ICP-MS	Inductively coupled plasma- mass spectroscopy
MFs	Metallic fractions
NMFs	Non-metallic fractions
Non-cyanide glycine leaching system	Any leaching system that includes glycine as a lixiviant and does not contain sodium cyanide (NaCN)
PCBs	Printed circuit boards
PMs	Precious metals
SEM-EDS	Scanning electron microscopy- energy dispersive spectroscopy
UV-Vis	Ultra violet-visible
WAD	Weak acid dissociable
WEEE	Waste electric and electronic equipment
WPCBs	Waste printed circuit boards
XRD	X-Ray diffraction
XRF	X-Ray fluorescence

Chapter 1 Introduction and overview

1.1 General background

Electric and electronic equipment (EEE), as defined by European Directive 2012/19/EU, is the equipment dependent on electric currents or electromagnetic fields and the equipment for the generation, transfer and measurement of such currents and fields, used at a specific voltage range (European Union, 2012). It includes a wide range of products from almost any household or business equipment (home appliances, toys and tools, etc.), to ICT items (mobile phones, computers, etc.) (Forti et al., 2020), which has become ubiquitous in people's daily life. When EEE is abandoned and not reused, it becomes end-of-life and is considered a waste, commonly referred to as e-waste or waste EEE (WEEE).

In the last decade, with the fast-technological advancement and market penetration, the amount of e-waste generated worldwide has been growing rapidly, at an annual rate of about 2 million tonnes (Mt)/year (Baldé et al., 2015; Forti et al., 2020; Hao et al., 2020). In 2019, 53.6 Mt of e-waste was produced worldwide, representing a material value of USD 57 billion, and the amount is projected to reach 74.7 Mt by 2030 (Forti et al., 2020). However, only a limited portion of it has been formally collected and recycled, being 17.4% in 2019 (Forti et al., 2020).

Currently, e-waste produced worldwide is mostly from developed (USA, Germany and Japan) and populous developing (China, India and Russia) countries (Islam et al., 2020). However, most of it has gone into domestic landfills or been exported to developing economies, where industrial capability is limited, which has caused severe health and environmental issues (Petridis et al., 2020; Song and Li, 2014b). In recent years, with the implementation of e-waste importing bans and restrictions by the traditional waste-importing countries, the domestic recycling of e-waste is becoming more urgent and essential for advanced economies (Lin et al., 2020; Tan et al., 2018). As dedicated by the Basel Convention, e-waste should be treated domestically, and its transboundary movement should be avoided to eliminate the hazardous consequences (Patil and Ramakrishna, 2020).

Printed circuit boards (PCBs) can be found in almost all the EEE, accounting for 4–7% by weight (Wang et al., 2017). When it comes to the recycling of e-waste, waste PCBs (WPCBs) represent one of the most challenging parts for their complicated composition and structure. WPCBs, with electronic components mounted, can contain more than 40 types of metals and nearly ten types of non-metals (Lu and Xu, 2016). Of them, various base and precious metals are of considerable economic interest, such as copper (Cu), cobalt (Co), nickel (Ni), zinc (Zn), gold (Au), silver (Ag) and palladium (Pd), and many of the

others (e.g. mercury (Hg), lead (Pb), arsenic (As) and cadmium (Cd)) are toxic which need to be recycled or disposed of appropriately (Song and Li, 2014a). Besides, hazardous organic substances, such as brominated flame retardants, also need to be recycled for environmental protection (McGrath et al., 2018). However, many of the metals and plastics are associated together by forming alloys or laminations, which has made the separation and recovery of them challenging. For example, size reduction by crushing, grinding, and milling has been a crucial step of recycling used to liberate metals from plastics. At the same time, intensive energy is required to achieve a complete liberation, and some metals are often lost in tailings (Duan et al., 2015).

Currently, mechanical-physical (Cui and Forssberg, 2003), pyrometallurgical (Wang et al., 2017), and hydrometallurgical (Cui and Anderson, 2016) processing approaches have been used, together or separately, to recycle WPCBs (Awasthi and Li, 2017). Different approaches have presented different advantages and drawbacks, and, therefore, their application is often case-specific.

The mechanical-physical processing approach is often used for the pre-treatment of WPCBs, such as dismantling, size reduction (shredding, crushing, grinding and milling) and the separation/metal enrichment utilising the difference of physical properties (e.g. gravity, magnesium, electric conductivity and density). As the approach cannot achieve a complete separation and recovery of each part of WPCBs (Cui and Forssberg, 2003), it is often followed by pyro-/hydro- metallurgical treatment.

The pyrometallurgical processing approach has been effectively used to recycle WPCBs with high recovery of precious metals (>95%). At the same time, it requires a large capital investment to achieve economy of scale and, hence, a high volume of WPCBs should be constantly fed into the smelter to achieve profitability (Islam et al., 2020). This may not be practical for sparsely populated regions, such as Oceania and North Americas, where the amount of e-waste is small (554 kilotons (kt) for Australia vs 10,129 kt for China in 2019). Furthermore, their geography (cities, towns and islands are far from each other) does not lead to the economical transportation of e-waste to a centralised location.

A hydrometallurgical process commonly includes leaching, separation, purification and recovery steps conducted in an aqueous medium. It should be noted that bio-metallurgy, the method employing microorganisms to leach metals, is also considered a hydrometallurgical approach. However, many works still need to be done to achieve a satisfactory leaching rate and metal extraction for its industrial application (Lee and Pandey, 2012). The hydrometallurgical process (except bio-metallurgy) could often achieve high purity of products and has been shown flexible in scalability and associated capital investment required (Diaz et al., 2016), making it suitable for small and fit-for-purpose recycling facilities. Hence, it is considered to be economically friendly for small and

medium enterprises (SMEs) and particularly favourable to Australia's scenario. Taking Western Australia as an example:

(1) The large state has only around 2.5 million residents scattered in the coastal and inland cities and towns, generating a limited volume of e-waste.

(2) The capital city, Perth, is about 2,000 km from another large city (Adelaide, South Australia), making the road transportation of e-waste costly.

This situation makes the pyrometallurgical processing of e-waste uneconomical. It creates the need for a sustainable and safe hydrometallurgical process that can be operated in the proximity of living areas, namely through "urban mining". Therefore, in this thesis, hydrometallurgy is considered for recycling WPCBs and is expected to be de-centralised, modularised, and scalable.

In a hydrometallurgical process used for WPCBs recycling, the lixiviant, utilised at the appropriate pH and E_h, plays a significant role in dissolving metals into a solution that is to be further separated and recovered. In recent years, a new lixiviant of glycine has been intensively reported to dissolve metals, chalcophile metals in particular, by complexation in an alkaline environment (Oraby and Eksteen, 2014; Oraby et al., 2019; Tanda et al., 2018a; Tanda et al., 2017). Various studies have shown the effectiveness of using glycine (with/without synergist and catalyst) to extract Cu, Au and Ag from their metallic foils and oxide/ sulfide minerals (Eksteen and Oraby, 2015; Oraby and Eksteen, 2015; Tanda et al., 2018a; Tanda et al., 2018b). Among the studies, different glycine leaching systems have been reported, including glycine-only, glycine-cyanide and glycine-oxidant (adding oxidant into glycine-only solution) systems. An alkaline environment has been employed in all the glycine processes, in which high extraction of targeted metals could be achieved and impurities, iron (Fe) in particular, could be reduced.

Glycine (NH_2CH_2COOH, H(Gly)), with amino and carboxylic groups attached to a carbon atom, is the simplest amino acid. It is naturally derived from microbes (Oraby and Eksteen, 2015) and is the first amino acid isolated from hydrolysis of protein in 1820 by Henri Braconnot (Aliyu and Na'Aliya, 2012). Currently, glycine is mainly used as an additive in food and animal feeds. It is a crystalline, non-toxic, non-volatile, recyclable (through de-complexation) reagent and is available by mass production (Tanda et al., 2017). Therefore, using glycine as a lixiviant can be considered a "green" approach in hydrometallurgy and is selected as the major lixiviant in this thesis.

1.2 Objective and significance of the thesis

Although there have been various investigations on the hydrometallurgy of natural resources, the employment of glycine for the recycling of such complicated secondary resource, WPCBs, has not yet been reported. This thesis, for the first time, reports the use

of glycine in the proposed recycling processes to recover base and precious metals from WPCBs.

In this thesis, glycine is used as a key lixiviant, and the hazardous effects of other additives (starved level of cyanide, sodium hydroxide, potassium permanganate, potassium ferricyanide, etc.) are minimised. The leaching of WPCBs can be operated in a mildly alkaline environment and ambient temperature and pressure. It is hence less harmful and minimises safety and health risks compared to conventional processes. It also does not require high capital investment and could be used with light industrial facilities near urban areas.

The processes developed in this thesis are expected to be particularly beneficial for the developed countries with strict environmental regulations and countries with a relatively small amount of e-waste generated that cannot be economically processed by pyrometallurgy. Given the recent e-waste importing bans and restrictions launched by the traditional waste-importing countries, this thesis provides developed economies, which used to landfill or export e-waste, with potentially feasible processes to treat e-waste domestically. Australia is a country with less e-waste generation and with several large cities which are far from one another and numerous remote towns. The employment of glycine processes also gives the country a fit-for-purpose approach to treat e-waste locally. Consequently, the transportation costs of e-waste and the safety risks during transportation can be avoided.

Overall, this thesis is expected to develop sustainable, decentralised, scalable and cost-effective processes for the base and precious metals recovery from WPCBs. Moreover, given the complicated composition of WPCBs, the studies of this thesis can also be referred to in more broad areas, including the recovery of corresponding metals from natural resources and other solid wastes.

The thesis mainly aims to (1) investigate the current status of hydrometallurgical recycling of WPCBs in literature; (2) explore the leaching behaviours of the various base (Cu, Zn, Ni, aluminium (Al), Fe, Pb, tin (Sn) and Co) and precious (Au, Ag and Pd) metals in different glycine leaching systems from WPCBs; and (3) investigate the recovery of Cu and the deportment of other metals from glycine-containing leachates. To be more specific, the objectives of the thesis are listed below.

- To comprehensively investigate and evaluate the current technologies in the hydrometallurgical recycling of WPCBs, including both leaching of metals and the recovery of metals from leachates;
- To develop multi-stage alkaline leaching processes, using glycine as the key lixiviant, for the extraction of base and precious metals from WPCBs;

- To investigate the behaviour and mechanism of different glycine leaching systems that serve the extraction of a different group of metals from WPCBs, such as glycine-only, glycine-oxidant and cyanide-starved glycine leaching systems;
- To investigate different options of technology for the recovery of base metals from the resulted leachates of WPCBs.
- To summarise the research gaps perceived in this thesis and give recommendations for future study for further development of alkaline glycine processes for the recycling of WPCBs.

1.3 Scope of the thesis

Figure 1.1 illustrates the scope of this thesis. As shown, this thesis is trying to develop comprehensive hydrometallurgical processes for the base and precious metals recovery from WPCBs. All the experiments were performed in lab/bench scales. The metals of interest in the processes cover most of the metal contents and economic values, including base metals of Cu, Zn, Ni, Al, Fe, Pb, Sn and Co, and precious metals of Au, Ag and Pd. Two types of WPCB samples were used in the thesis, i.e. 1) the metallic fractions (MFs) of WPCBs (obtained after a series of physical treatments, used in Chapter 3) the WPCBs that were simply dismantled, crushed and shredded, as used in Chapters 4–7. The metallic fractions of WPCBs were used for exploratory tests to evaluate the potential of using glycine as a lixiviant for WPCBs recycling. Once the potential was confirmed on the metallic fractions, the simply pre-treated (i.e. crushed and shredded) WPCBs were used for the more comprehensive and detailed studies, as they are considered to be more representative of the original stream of WPCBs and do not come with the losses of mechanical/physical preconcentration as all of the material contained in the WPCBs is treated hydrometallurgically. Such studies include the following:

(1) Leaching of base metals using glycine solutions (first-stage leaching, Chapter 4);
(2) Recovery of base metals from the glycine leachates, using three options: solvent extraction, sulfide precipitation and chemical reduction (Chapter 5);
(3) Leaching of precious metals from the residue obtained from first-stage leaching, using cyanide-starved glycine leaching system and non-cyanide glycine leaching system, respectively (Chapter 6–7).

Given that the precious metals recovery from glycine media have been intensively reported and well investigated (Deng et al., 2020; Eksteen and Oraby, 2015; Oraby and Eksteen, 2015; Tauetsile et al., 2018a; Tauetsile et al., 2018b; Tauetsile et al., 2019a; Tauetsile et al., 2019b), the recovery of precious metals from leachates is not included in the scope of this thesis. However, it is still discussed and included in the process development (Chapter 3, 5–6) based on the currently known technologies.
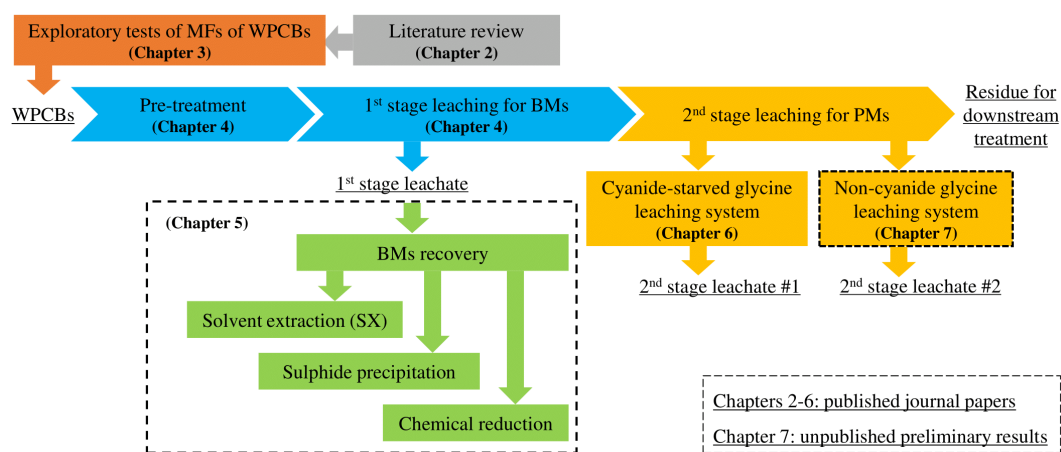
Figure 1.1 Illustration of the scope of this thesis (MFs denote metallic fractions; BMs and PMs denote base and precious metals, respectively).

1.4 Thesis organisation

This thesis is written in compliance with the specific guidelines for the "Thesis by Publication" and copyright policies of Curtin University. The experimental designs, including materials and methods for the studies, were demonstrated and explained in each chapter. The thesis consists of 8 chapters. Among them, chapters 3–7 are based on lab works, as shown in Figure 1.1. The overview of each chapter is given below.

Chapter 1 Introduction and overview

Chapter 1 covers an introduction and overview of this thesis. It includes background, objective and significance, scope and thesis overview. The chapter points out the motivation of the thesis and the research gaps in scientific knowledge and gives the readers a general outline of the thesis.

Chapter 2 Literature review

To enter into the area of WPCBs recycling, it is necessary to review the previous studies and investigate the current status. Chapter 2 (published paper #1, Li et al. (2018)) provides a comprehensive literature review of the hydrometallurgical processes used for metals recovery from WPCBs. It gives information about WPCBs in regards to the structure, types, and materials of manufacture. This information is considered necessary for the design and development of a hydrometallurgical process. Moreover, it investigates and evaluates the current hydrometallurgical approaches (including both metal leaching and recovery steps) used for WPCBs recycling and points out their merits and barriers and future study trends. Notably, based on the comprehensive review and evaluation, this chapter perceives the knowledge gaps that pave the way to this thesis.

Chapter 3 Exploratory tests using metallic fractions of WPCBs

Experimental investigations of the proposed glycine processes were first started using metallic fractions of WPCBs. Chapter 3 (published paper #2, Oraby et al. (2020a)) is a preliminary work to show the feasibility of using glycine as a lixiviant for the leaching of metals from the preconcentrated metallic fractions of WPCBs (>72% metals). A two-stage alkaline leaching process was proved effective to leach most of the base (Cu, Zn, Al and Pb) and precious (Au and Ag) metals. In the first-stage leaching, glycine was used as the only lixiviant, while in the second-stage leaching, glycine was used with a starved level of cyanide. Comparison tests were conducted, including leaching by direct cyanidation, ammonia and glycine-cyanide in a single stage.

Chapter 4 Leaching of base metals using glycine-only leaching system

When the feasibility study was done, leaching of base metals was carried out in-depth using original WPCBs. Chapter 4 (published paper #3, Li et al. (2020)) elaborates the mechanism and kinetics of Cu extraction and the behaviours of other metals (Zn, Pb, Al, Ni, Co, Fe, Sn, Au, Ag and Pd) using glycine solutions in an alkaline environment (glycine-only leaching system). Various parameters, including initial pH, glycine concentration, solid content, temperature, oxidant (ambient air and hydrogen peroxide) and particle size of WPCBs, were evaluated.

Chapter 5 Recovery of copper from glycine leachates

When the base metals are leached into solutions, they will need to be further recovered. Chapter 5 (published paper #4, Li et al. (2021a)) presents three methods to recover Cu and investigate the behaviours of other base metals from glycine leachates of WPCBs. They are chemical reduction using hydrazine, sulfide precipitation using hydrosulfide and solvent extraction using two types of extractant (Mextral 54-100 and 84H). For the chemical reduction, more attention was given to the fundamental study as it was not reported in glycine media of WPCBs before. Synthetic Cu glycinate solution was first used to investigate the mechanism and effect of variables, followed by using actual glycine leachate of WPCBs. In contrast, for solvent extraction and sulfide precipitation, as previous studies have shown their feasibility in glycine leachates of natural resources (malachite and chalcopyrite), directly using real glycine leachates of WPCBs was considered. Finally, the three options were evaluated and compared, and a process flowsheet was proposed.

Chapter 6 Leaching of precious metals using cyanide-starved glycine leaching system

When base metals, mainly Cu and Zn, were removed from WPCBs, precious metals were leached in a second stage. Chapter 6 (published paper #5, Li et al., (2021b)) investigates the leaching of precious metals (Au, Ag and Pd) from the residue obtained from the first-stage leaching of WPCBs (Chapter 4) using glycine in the presence of starved level of

cyanide. The behaviours of other metals (Cu, Zn, Pb, Sn, Al, Ni, Co and Fe) were studied during the leaching. The mechanism in terms of thermodynamics of Cu, Au and Ag in the system was investigated. The variables, including cyanide concentration, glycine amount, initial pH, the particle size of feed sample and the method of cyanide addition, were evaluated.

Chapter 7 Leaching of precious metals using non-cyanide glycine leaching system: A preliminary study on gold

This chapter has not been published yet upon the submission of this thesis. It is a preliminary and exploratory study for precious metals extraction from the residue of first-stage leaching (Chapter 4). Only the extraction and behaviour of Au were focused as it represents the highest economic value of WPCBs. A non-cyanide glycine leaching system, i.e. glycine-oxidant leaching system, was used in this chapter, which is in pursuit of a safer approach and of avoiding the use of sodium cyanide that has been banned in some countries. More detailed studies were envisaged based on the preliminary results of this chapter.

Chapter 8 Conclusions and recommendations

Chapter 8 gives the overall and enumerated conclusions based on the results obtained in this thesis. Recommendations for future research are also outlined at the end of the chapter.

1.5 Reference

Aliyu, H.N. and Na'Aliya, J., 2012. Potentiometric studies on essential metal (II) amino acid complexes. International Research J. Pharm. Pharmacol., 2(2): 76–80.

Awasthi, A.K. and Li, J., 2017. An overview of the potential of eco-friendly hybrid strategy for metal recycling from WEEE. Resour. Conserv. Recy., 126 (Supplement C): 228–239.

Baldé, C.P., Wang, F., Kuehr, R. and Huisman, J., 2015. The global e-waste monitor - 2014. United Nations University (UNU), IAS-SCYCLE, Bonn, Germany. Available at https://i.unu.edu/media/unu.edu/news/52624/UNU-1stGlobal-E-Waste-Monitor-2014-small.pdf

Cui, H. and Anderson, C., 2016. Literature Review of Hydrometallurgical Recycling of Printed Circuit Boards (PCBs). J. Adv. Chem. Eng., 6(1): 142–153.

Cui, J. and Forssberg, E., 2003. Mechanical recycling of waste electric and electronic equipment: a review. J. Hazard. Mater., 99(3): 243–263.

Deng, Z., Oraby, E.A. and Eksteen, J.J., 2020. Gold recovery from cyanide-starved glycine solutions in the presence of Cu using a molecularly imprinted resin (IXOS-AuC). Hydrometallurgy, 196: 105425.

Diaz, L.A., Lister, T.E., Parkman, J.A. and Clark, G.G., 2016. Comprehensive process for the recovery of value and critical materials from electronic waste. J. Clean. Prod., 125: 236–244.

Duan, C.L., Diao, Z.J., Zhao, Y.M. and Huang, W., 2015. Liberation of valuable materials in waste printed circuit boards by high-voltage electrical pulses. Miner. Eng., 70: 170–177.

Eksteen, J. and Oraby, E., 2015. The leaching and adsorption of gold using low concentration amino acids and hydrogen peroxide: Effect of catalytic ions, sulphide minerals and amino acid type. Miner. Eng., 70: 36–42.

European Union, 2012. Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on waste electrical and electronic equipment (WEEE). Off. J. Eur. Union (OJEU), 197: 38–71.

Forti, V., Baldé, C.P., Kuehr, R. and Bel, G., 2020. The global e-waste monitor - 2020. United Nations University (UNU)/United Nations Institute for Training and Research (UNITAR) – co-hosted SCYCLE Programme, International Telecommunication Union (ITU) & International Solid Waste Association (ISWA), Bonn/Geneva/Rotterdam. Available at https://www.itu.int/myitu/-/media/Publications/2020-Publications/Global-E-waste-Monitor-2020.pdf

Hao, J., Wang, Y., Wu, Y. and Guo, F., 2020. Metal recovery from waste printed circuit boards: A review for current status and perspectives. Resour. Conserv. Recy., 157: 104787.

Islam, A., Ahmed, T., Awual, M. R., Rahman, A., Sultana, M., Aziz, A. A., Monir, M. U., Teo, S. H. and Hasan, M., 2020. Advances in sustainable approaches to recover metals from e-waste-A review. J. Clean. Prod., 244: 118815.

Lee, J.-c. and Pandey, B.D., 2012. Bio-processing of solid wastes and secondary resources for metal extraction–a review. Waste Manage., 32(1): 3–18.

Li, H., Eksteen, J. and Oraby, E., 2018. Hydrometallurgical recovery of metals from waste printed circuit boards (WPCBs): Current status and perspectives – A review. Resour. Conserv. Recy., 139: 122–139.

Li, H., Oraby, E. and Eksteen, J., 2020. Extraction of copper and the co-leaching behaviour of other metals from waste printed circuit boards using alkaline glycine solutions. Resour. Conserv. Recy., 154: 104624.

Li, H., Oraby, E. and Eksteen, J., 2021b. Cyanide consumption minimisation and concomitant toxic effluent minimisation during precious metals extraction from waste printed circuit boards. Waste Manage., 125: 87–97.

Li, H., Oraby, E. and Eksteen, J., 2021a. Recovery of copper and the deportment of other base metals from alkaline glycine leachates derived from waste printed circuit boards (WPCBs). Hydrometallurgy, 199: 105540.

Lin, S., Man, Y.B., Chow, K.L., Zheng, C. and Wong, M.H., 2020. Impacts of the influx of e-waste into Hong Kong after China has tightened up entry regulations. Crit. Rev. Env. Sci. Tec., 50(2): 105–134.

Lu, Y. and Xu, Z., 2016. Precious metals recovery from waste printed circuit boards: a review for current status and perspective. Resour. Conserv. Recy., 113: 28–39.

McGrath, T., Morrison, P.D., Ball, A.S. and Clarke, B.O., 2018. Spatial distribution of novel and legacy brominated flame retardants in soils surrounding two Australian electronic waste recycling facilities. Environ. Sci. Technol., 52: 8194–8204.

Oraby, E.A., Li, H. and Eksteen, J.J., 2020a. An alkaline glycine-based leach process of base and precious metals from powdered waste printed circuit boards. Waste Biomass Valori., 11(8): 3897–3909.

Oraby, E.A. and Eksteen, J.J., 2014. The selective leaching of copper from a gold–copper concentrate in glycine solutions. Hydrometallurgy, 150: 14–19.

Oraby, E.A., Eksteen, J.J., Karrech, A. and Attar, M., 2019. Gold extraction from paleochannel ores using an aerated alkaline glycine lixiviant for consideration in heap and in-situ leaching applications. Miner. Eng., 138: 112–118.

Oraby, E.A. and Eksteen, J.J., 2015. The leaching of gold, silver and their alloys in alkaline glycine–peroxide solutions and their adsorption on carbon. Hydrometallurgy, 152: 199–203.

Patil, R.A. and Ramakrishna, S., 2020. A comprehensive analysis of e-waste legislation worldwide. Environ. Sci. Pollut. Res., 27(13): 14412–14431.

Petridis, N.E., Petridis, K. and Stiakakis, E., 2020. Global e-waste trade network analysis. Resour. Conserv. Recy., 158: 104742.

Song, Q. and Li, J., 2014a. Environmental effects of heavy metals derived from the e-waste recycling activities in China: A systematic review. Waste Manage., 34(12): 2587–2594.

Song, Q. and Li, J., 2014b. A systematic review of the human body burden of e-waste exposure in China. Environ. Int., 68: 82–93.

Tanda, B., Eksteen, J. and Oraby, E., 2018a. Kinetics of chalcocite leaching in oxygenated alkaline glycine solutions. Hydrometallurgy, 178: 264–273.

Tanda, B., Oraby, E. and Eksteen, J., 2018b. Kinetics of malachite leaching in alkaline glycine solutions. Miner. Process. Extr. Metall.: 1–9.

Tanda, B.C., Eksteen, J.J. and Oraby, E.A., 2017. An investigation into the leaching behaviour of copper oxide minerals in aqueous alkaline glycine solutions. Hydrometallurgy, 167: 153–162.

Tan, Q., Li, J. and Boljkovac, C., 2018. Responding to China's Waste Import Ban through a New, Innovative, Cooperative Mechanism. Environ. Sci. Technol., 52: 7595–7597.

Tauetsile, P.J., Oraby, E.A. and Eksteen, J.J., 2018a. Adsorption behaviour of copper and gold glycinates in alkaline media onto activated carbon. Part 1: Isotherms. Hydrometallurgy, 178: 202–208.

Tauetsile, P.J., Oraby, E.A. and Eksteen, J.J., 2018b. Adsorption behaviour of copper and gold Glycinates in alkaline media onto activated carbon. Part 2: Kinetics. Hydrometallurgy, 178: 195–201.

Tauetsile, P.J., Oraby, E.A. and Eksteen, J.J., 2019a. Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper. Part 1: Isotherms. Sep. Purif. Technol., 211: 594–601.

Tauetsile, P.J., Oraby, E.A. and Eksteen, J.J., 2019b. Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper. Part 2: Kinetics. Sep. Purif. Technol., 211: 290–297.

Wang, H., Zhang, S., Li, B., Pan, D., Wu, Y. and Zuo, T., 2017. Recovery of waste printed circuit boards through pyrometallurgical processing: A review. Resour. Conserv. Recy., 126: 209–218.
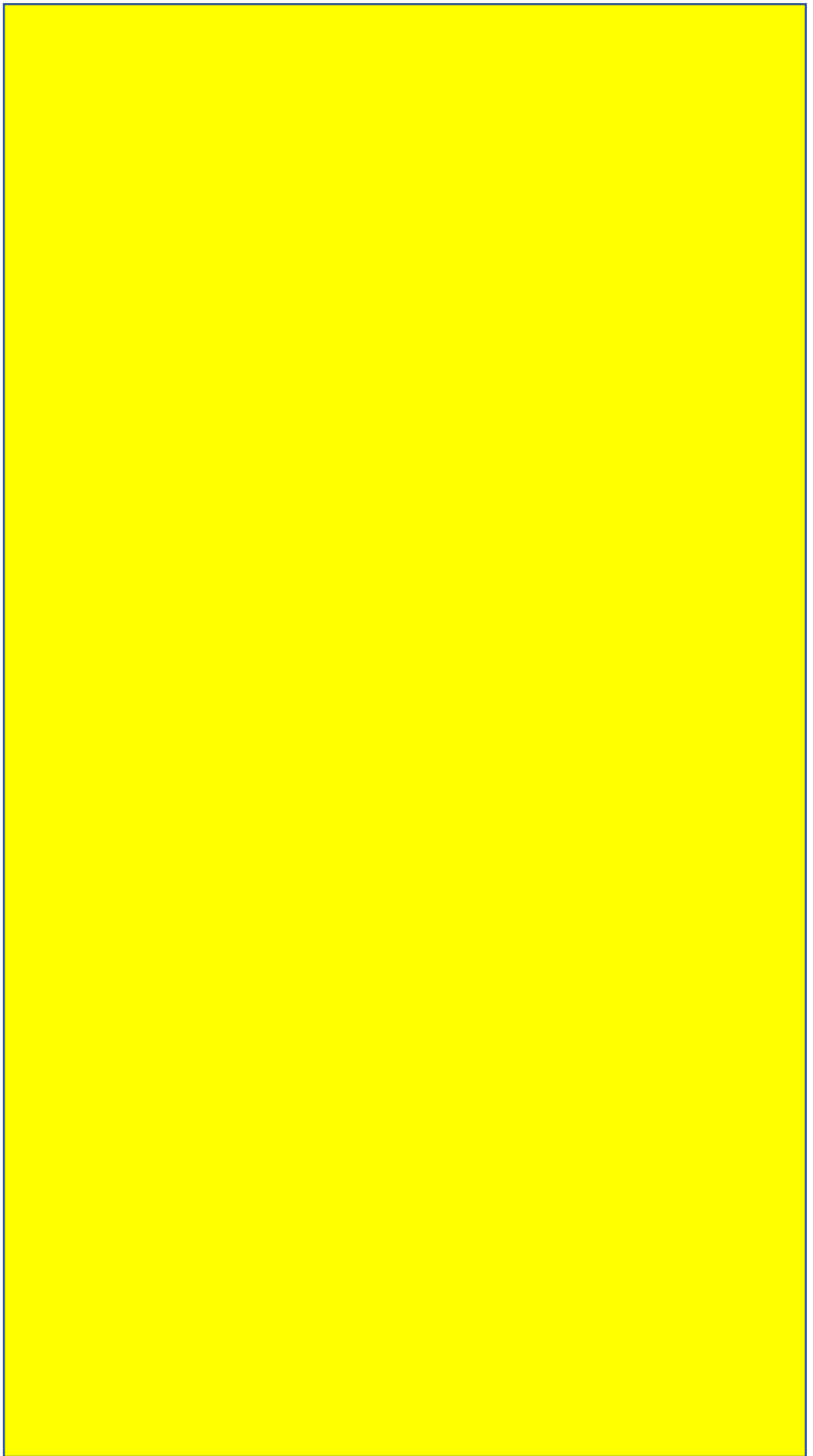
Chapter 2 Literature review

Li Huan, Eksteen Jacques and Oraby Elsayed, 2018.

Summary

This chapter reviews and compares the reported hydrometallurgical approaches in the area of WPCBs recycling. Based on the observed knowledge gaps, the glycine processes were introduced for the first time.

Review

Hydrometallurgical recovery of metals from waste printed circuit boards (WPCBs): Current status and perspectives – A review

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ABSTRACT

Printed circuit boards (PCBs) represent one of the most complicated and valuable components in electric and electronic equipment (EEE). Waste PCBs (WPCBs) contain more than 40 kinds of metals with a wide and variable range of concentrations, such as environmentally harmful metals (*e.g.* Pb, Cr, As, Cd and Hg) and others of economic value (*e.g.* Cu, Sn, Au, Ag and Pd). Recovery of metals from WPCBs is of great importance for both environmental protection and resource re-utilization. In contrast to metal recovery from natural resources, these secondary resources have to be essentially stripped completely of its harmful metallic content before the remaining plastic substrate can be disposed, charred or incinerated. Hydrometallurgy has been successfully used for metals recovery from primary and secondary resources around the world, owing to its easily controlled process and high recovery rates at relatively low costs, and a number of researches using various hydrometallurgical methods for metals recovery from WPCBs has been published each year since 2002. This study provides an up-to-date review of the hydrometallurgical recovery of metals from WPCBs and gives perspectives of this particular area, which is expected to provide an insight for the selection of suitable hydrometallurgical leaching and purification methods and to point out the novel and potential technologies that would be the future focuses of this area.

1. Introduction

Printed circuit boards (PCBs), also known as printed wiring boards (PWBs), are an integral component of almost all electric and electronic equipment (EEE) (Ning et al., 2017). Generally, PCBs make up 4–7% of the total mass of EEE. The proportion is usually much higher in consumer electronic products, ranging from mobile phones (20–30%), computers (~20%) to televisions (~10%) (Wang et al., 2017). In the past two decades, with the rapid technology advancement and fast market penetration, a large amount of waste electric and electronic equipment (WEEE) has been generated around the globe and the amount still continues to increase at an alarming rate (Ghosh et al., 2015; Ning et al., 2017; Ogunseitan et al., 2009). Particularly, driven by the unprecedented replacement rate of small consumer electronic products, the annual amount of WEEE has reached 44.7 million t/year worldwide in 2016 and is forecasted to be 52.2 million t/year by 2021 (Baldé et al., 2017).

According to Wang et al. (2016b), most of the WEEE in the world is produced from developed countries and rapidly developing countries, with the U.S. and China ranking first and second, respectively.

Meanwhile, 50–80% of the WEEE finally ends up in developing countries, where relevant regulation is lacking. In 2012, about 70% of WEEE in the world was disposed in China, and the rest went to India, Pakistan, and some countries in Southeast Asia and Africa (Zhang et al., 2012a). However, most of the recycling activities in these developing countries are of a primitive and limited nature. They are often conducted in labour-intensive workshops, mainly focusing on the profitable metals, Cu and Au in particular. The remaining toxic metals (*e.g.* As, Cd, Cr, Pb, Hg) and hazardous organic substances are often simply disposed by landfill or incineration, which are harmful to human bodies, animals and environment (Awasthi et al., 2016; Li et al., 2017; Nnorom and Osibanjo, 2009). According to the latest statistics conducted by United Nations University (UNU), International Telecommunication Union (ITU) and International Solid Waste Association (ISWA), only 20% WEEE generated in the world was documented to be collected and recycled in 2016, and the recycle rates in different countries vary greatly (Baldé et al., 2017), which implies our global society is still far from a closed-loop system for the manufacture-use-recycle of EEE. For example, Reuter et al. (2018) has shown that, for the few mobile companies (such as Fairphone) that are willing to make their bill of

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Normal metals:

Ca, Cu, Fe, Al, Sn, Ba, Zn, Ti, Sb, Ni, Mg, Na, Mn, Sr, K, Bi, Zr, Mo, Co, Se, Li, Ga, V, Hf, Th, U, Be, Te

$7.5×10^4$ $6.2×10^3$ $1.2×10^3$ 41   1

Precious metals: **Rare earth metals (REMs):**

Ag, Au, Pd, Pt   La, Ce, Sc, Y

849   5.3   91.5   9.7

Heavy metals: **Non-metals:**

Pb, Cr, As, Cd, Hg   Si, C, Cl, B, Br, S, P, F, I   (All the contents are in ppm)

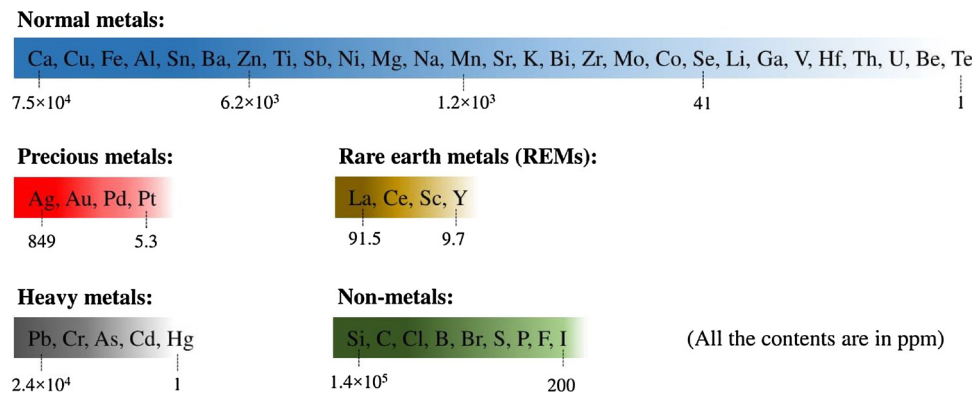$2.4×10^4$ 1 $1.4×10^5$ 200

Fig. 1. Contents of metallic and non-metallic elements in typical WPCBs, adapted from Lu and Xu (2016) (metal contents decrease with the colour becoming light).

materials public, simulated recycling rates varied from 31 to 36% depending the process route with a wide variation in the individual metal yields (and energy from plastic incineration). It is therefore clear that, even in advanced economies, recovery rates can be poor and may also be dependent on the design for recycling.

WEEE contain a wide range of organic and inorganic substances (> 1000) with contents largely depending on the equipment's type, manufacture and age (Tuncuk et al., 2012). As an indispensable component of EEE, PCBs represent the most complicated fraction. It is reported that there are up to 60 kinds of elements contained in waste PCBs (WPCBs) (Szałatkiewicz, 2014). Fig. 1 summarises the contents of metallic and non-metallic elements in typical WPCBs. As shown in the figure, there are more than 40 kinds of metals, including a significant amount of base (e.g. Cu, Fe, Al, Sn) and precious (Ag, Au, Pd, Pt) metals, and nearly 10 kinds of non-metals contained in WPCBs. Metal contents in different types of WPCBs, comparing with typical minerals are listed in Table 1. It shows that some of the metal contents in WPCBs are even much higher than those in ore and could be comparable with concentrate, indicating vast economic potential, mainly dominated by precious metals such as Au, Ag, Pd and some base metals such as Cu. It is estimated that the recovery of metals from WPCBs in China reached 3 billion USD in 2007, with around 85% of them contributed by precious metals (Lu and Xu, 2016), and the material value of global WEEE has reached 56 billion USD in 2014 (Baldé et al., 2015).

Therefore, for both environmental and economic reasons, recovery of metals from WPCBs are greatly significant. Since 2002, the year Europe launched Directive 2002/96/EC as a WEEE legislation, the recycling of WEE has been becoming an active area, with numerous

research articles and reviews published each year (Marques et al., 2013; Pérez-Belis et al., 2015). To date, most of the reviews focus on the generation and management of WEEE (Kiddee et al., 2013), environmental and social impacts (Awasthi et al., 2016; Song and Li, 2014), policy and legislation (Bandyopadhyay, 2008; Zhou and Xu, 2012) or materials (metals or non-metals) recovery (Wang and Xu, 2014; Zhang and Xu, 2016). The term of "WEEE recycling" can cover the recycling of every component contained in WEEE, mainly including the recycling of waste screen display, spent LIBs, WPCBs and plastics which are often disassembled from WEEE to be recycled respectively (Li et al., 2015). As one of the most important and difficult parts of WEEE recycling, the recycling of WPCBs should accordingly be reviewed solely as a reference to this particular area.

So far, the existing processes for the recycling of WPCBs can be divided into mechanical (physical), pyro-metallurgical, hydrometallurgical and bio-metallurgical process, as well as some hybrid processes. Although some reviews of these processes have been published in recent years, only very few of them are specialized in the recovery of metals from WPCBs in hydrometallurgical technology (Akcil et al., 2015; Cui and Anderson, 2016; Lu and Xu, 2016; Marques et al., 2013; Ning et al., 2017; Wang et al., 2017; Zhang et al., 2012b). The hydrometallurgical process, with a long history of the recovery of metals from materials (primary and secondary resources), has been intensively investigated in the case of WPCBs recycling, with a number of advances updated each year. Cui and Anderson (2016) presented a review on the hydrometallurgical recovery of metals and plastics from WPCBs, however, the latest and emerging technologies were not fully included, and the challenges of the conventional processes and future

Table 1
Typical component and economic value of the different types of WPCBs in comparison to typical minerals.

Type of e-waste	Metal content and economic value (%, in brackets)								
	Metal content in wt. %						Metal content in ppm		
	Fe	Cu	Al	Pb	Sn	Ni	Pd	Au	Ag
Metal price (USD/t)[a]	515	6583	2100	2377	20950	11234	$2.95 × 10^7$	$4.16 × 10^7$	$5.44 × 10^5$
PC mainboards[b]	4.5	14.3	2.8	2.2	–	1.1	124	566	639
	(0)	(3)	(0)	(0)		(0)	(13)	(82)	(1)
Mobile phone[b]	5	13	1	0.3	0.5	0.1	210	350	1380
	(0)	(4)	(0)	(0)	(0)	(0)	(27)	(65)	(3)
TV boards[b]	28	10	10	1	1.4	0.3	10	20	280
	(5)	(25)	(8)	(1)	(11)	(1)	(11)	(31)	(6)
Typical Cu-Au ore[c]	16	0.4	4.5	0.1	0.002	0.001	–	5.7	22.9
Typical Cu-Au concentrate[d]	2.9	0.97	0.5	0.03	–	0.02	–	490	100

"–" denotes not reported.
[a] Data extracted from the official prices of London Metal Exchange (LME) (price for cash seller & settlement on 4th October 2017).
[b] Date from Cui and Zhang (2008).
[c] Date from Lacoste-Bouchet et al. (1998).
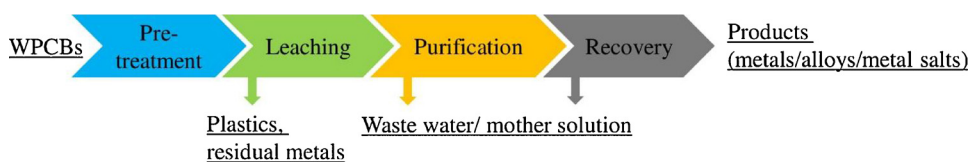[d] Data from Oraby and Eksteen (2016).

opportunities in this area were not presented in depth. Zhang et al. (2012b), Akcil et al. (2015) and Lu and Xu (2016) summarised the leaching and/or recovery of precious metals from WPCBs, but other metals like base and toxic metals were not presented. Although the precious metals (Au, Ag and Pd) represent the major profitability of WPCBs recycling, attention to other metals, such as base metals (Cu, Fe, Al, Sn, Zn, *etc.*) and heavy metals (Pb, Cr, As, Cd and Hg) should also be paid for the environmental perspective. It is also clear that simulation based tools to model the variability in recycle rates, such as proposed by Reuter et al. (2018) is seldom covered in reviews, and the maximum extent of recycling is often ignored.

Generally, as presented in Fig. 2, the process for the hydrometallurgical recycling of WPCBs can be divided into pre-treatment, complete/selective leaching of metals, purification of metals from leaching solution and recovery of metals as final products. While the emphasis of this review is on hydrometallurgical approaches, the use of pyrometallurgy in pyrometallurgy-hydrometallurgy hybrid processes are not precluded, but are viewed outside the scope of this work. In this study, we try to provide a comprehensive review of the whole hydrometallurgical process, including the basic information of PCBs, pre-treatment, leaching, purification and recovery of metals. Particularly, the state-of-the-art technologies in this area and potential alternatives from other related areas, *e.g.* mining industry, are also introduced. Moreover, the comparison of different methods in economic, ecological and technical perspectives and outlook of the future trend are also presented.

2. Printed circuit boards (PCBs)

As the major component inside EEE, PCBs mechanically support the electronic components (ECs) and connect them together to function properly. The intrinsic properties and complicated compositions make the WPCBs recycling challenging and much different from the metals recovery from natural minerals (Lu and Xu, 2016). Therefore, prior to recycling WPCBs, it is necessary to investigate their structure and manufacturing materials.

2.1. Materials

Although different EEE use different kinds of PCB, as presented in Fig. 3, all the PCBs generally comprise ECs, silkscreen (optional), solder mask, joining materials, metal coatings and layers, and polymer substrate (Li et al., 2004; Marques et al., 2013; Wang et al., 2017).

ECs (resistors, capacitors, chips, *etc.*), with a high content of metals, are usually first dismantled and classified for separate recycling (Wang et al., 2017). On the top of a bare PCB, silkscreen with part outline and text (mostly in white colour) is usually printed by non-conductive epoxy inks to make the board readable, but it is not an indispensable option for today's products (Sjoberg et al., 2016). Below the silkscreen is the solder mask, commonly in green colour, consisting of epoxy resin to prevent the leakage of solder and protect the circuit from corrosion (Jadhav and Hocheng, 2015; Tang et al., 2001).

Most of the joining materials, which are used for connecting ECs and boards, are made up of Pb-Sn alloy, dominated by the traditionally used 63%Sn-37%Pb solder material with low-costs, good properties and a melting temperature (a key factor for dismantling ECs by melting) of 183 °C. Due to the hazardous influence to humans and environment brought by Pb use, some Pb-free solders, such as 91%Sn-9%Zn, 77.2%

Sn-20%In-2.8%Ag and 85%Sn-10%Bi-5%Zn, have been proposed in recent years (Marques et al., 2013). Another kind of joining material is electrically conductive adhesives (ECAs), consisting of polymeric binder and metal fillers (Ag, Au, Cu, or Ni), which is considered to be more environmentally friendly than Pb solder (Li and Wong, 2006). However, ECAs are only restricted to certain applications as an alternative to Pb solder (Marques et al., 2013). The metals in PCB substrate are in the forms of the laminating of Cu layers (10–20% of PCB mass) and the coatings (Sn, Ni, Au, Ag, *etc.*) on the surface of Cu layers, pins and holes that increase conductivity and oxidation resistance (Li et al., 2004; Wang et al., 2017).

The polymer substrate that provides support for ECs and insulates different Cu layers is composed of flame retardant (FR), thermosetting resin, reinforcing material as well as some other additives (Wang et al., 2017). The substrate represents the most complicated organic compositions of a PCB and is the main source of organic pollutants during the recycling process. Among the flame retardants (FRs), brominated flame retardants (BFRs), including polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD), have been most important and popular (Hadi et al., 2015; Herat, 2008). However, their environmental impact has aroused wide concerns, especially the PBDEs and PBBs that are likely to bio-accumulate (Chen et al., 2012).

Currently, the most widely used substrate is glass fibre reinforced epoxy resin which is commercially called FR-4 type with high thermal resistance and infinitesimal water absorption and is common in high-value EEE, such as computers and mobile phones (Hadi et al., 2015; Li et al., 2004; Zhou et al., 2010). Another widely used substrate is cellulose paper reinforced phenolic resin, also called FR-2 type, mainly used in home electronics and TVs (Guo et al., 2009).

According to Guo et al. (2009) and Marques et al. (2013), WPCBs mounted with ECs are generally composed of around 40% of metals, 30% of plastics and 30% of ceramics. While, for the substrate of WPCB (without ECs), 30–50% of metals and 50–70% of non-metals are contained (Wang et al., 2017). The metal and non-metal contents of typical WPCB have been presented in Fig. 1. It should be noted that these values of contents should be referred with caution since they are much dependent on the specific type of study (Hadi et al., 2015).

2.2. Structure and types of PCB

PCBs can be divided into different types according to different physical properties. Table 2 and Fig. 4 present the classification of PCB and their simplified structures, respectively. Based on the number of layers, PCBs can be divided into single layer, double layer and multi-layer. The forms of the board can be rigid, flexible or flex-rigid (Xu and Liu, 2015). Different types of PCB have their particular application, they can be sorted and classified after the WEEE are disassembled. PCBs with different layer and board form can significantly affect the leaching of metals in a hydrometallurgical recycling process since different types have a different degree of association between metals and other materials. As can be seen from Fig. 4, Cu is laminated inside of a PCB. In order to leach Cu, it has to be exposed to make it contactable with lixiviant. In most hydrometallurgical recycling routes, the solution is to comminute the PCB into small particles (Birloaga et al., 2014; Long Le et al., 2011) using various crushing, shredding and grinding technologies. In other cases researchers have used approaches that lead to board swelling and exfoliation to expose Cu from laminates (Jha et al., 2011).
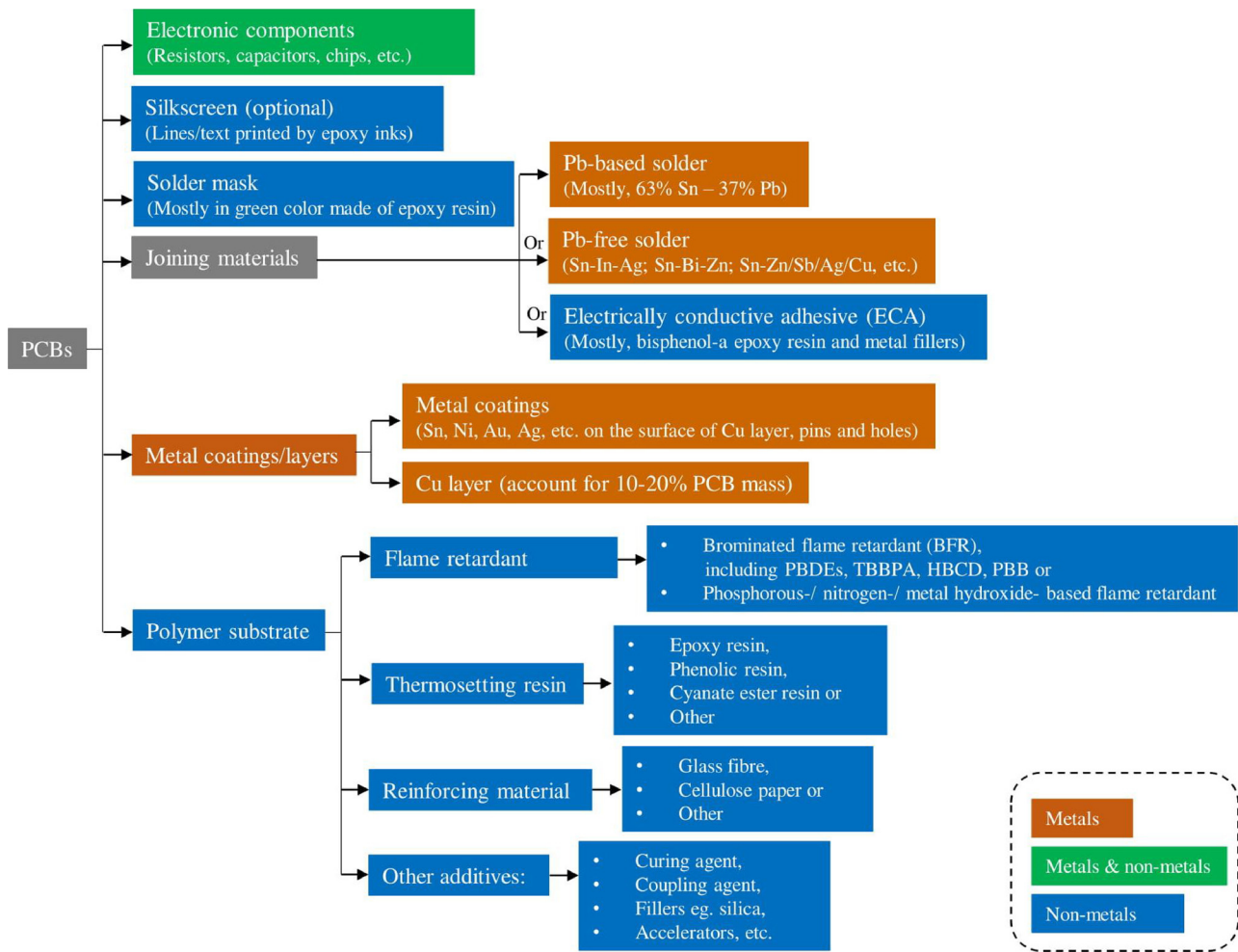
Fig. 3. Components and materials of PCBs.

3. Pre-treatment

3.1. Mechanical-physical methods

Mechanical-physical methods are considered to be the most environmentally friendly approach for metals recovery (Cui and Anderson, 2016). However, due to the poor separation of metals and low recycle rates, it is often restricted to pre-treatment and mostly for metals enrichment. As presented in Fig. 5 mechanical-physical pre-treatment can be divided into three major stages: (1) disassembly for the separation of electronic components (ECs, *e.g.* cell batteries,

capacitors, resistors, chips) from base boards, and sorting out the hazardous and valuable components, which is an indispensable stage; (2) size reduction of the boards by shredding, crushing and/or grinding (optional); and (3) separation and enrichment of metals/non-metals based on the differences of physical properties (optional) (Cui and Forssberg, 2003; Luda, 2011). It should be noted that the pre-treated materials from each stage can be further treated by a hydrometallurgical process for metals recovery (Tuncuk et al., 2012).

- Stage (1) disassembly. As the first step in WPCBs recycling chain, disassembly is essential to a successful recycling process. In the

Table 2

Classification of PCB based on the number of layers and board forms, adapted from Xu and Liu (2015).

Types of PCB	Characteristics	Applications
Based on the number of layers		
Single layer	Single layer of printed wiring or substrate, easily to design and manufacture, low-cost.	General electronic devices, *e.g.* calculators, radio, printers, *etc.*
Double layer	Printed wirings on both sides of substrate.	Instrumentation, computers, LED lighting, automotive dashboards, *etc.*
Multi-layer	3 ~ layers of printed wirings, with metallized holes connecting different layers	For complicated designs like medical equipment, satellite systems, computers, *etc.*
Based on board forms		
Rigid PCB	With rigid substrate preventing the board from twisting.	With single-, double- or multi-layer, application same as them.
Flexible PCB	Free bending, folding and easily coiled.	With single-, double- or multi-layer, used for special requirements, *e.g.* complicated shape, waterproof, shockproof
Flex-rigid PCB	Suitable for streamlined design, reducing overall board size and weight	Used in the case when space or weight are prime concerns, *e.g.* cellphone, digital cameras, automobiles
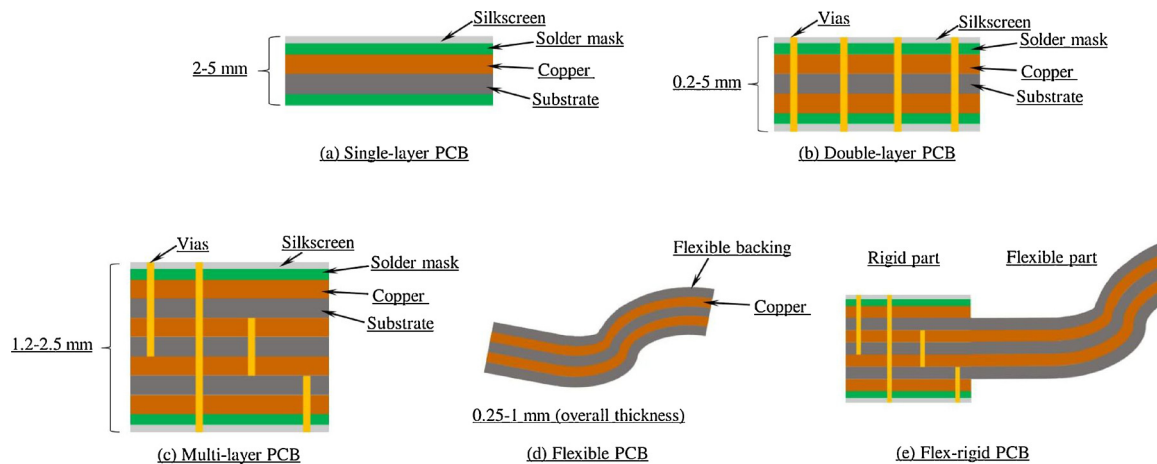
Fig. 4. Simplified structures of typical types of PCB.

informal recycling cases, the WPCBs are disassembled manually, which is labour-intensive and highly unsafe. In recent years, some studies have been performed to disassemble WPCBs using greener and more automatic methods, which are based on destroying solder joints between ECs and boards and then separating them by an external force (Wang and Xu, 2015). Melting of the solder has been reported to be an effective way. Currently, the most widely used solder material is 63%Sn-37%Pb alloy with a melting temperature of 183 °C. It is suggested that a heating temperature 40–50 °C higher than the melting temperature of solder material can be used for an effective dismantling (Duan et al., 2011). However, the possibility of generating harmful substances, dioxin in particular, during the heating at 270–280 °C has aroused concerns (Duan et al., 2011). Wang et al. (2016a) designed an automatic system, including ECs disassembly and off-gas purification, in which solders from both TV and computer WPCBs was completely removed at heating temperature 265 ± 5 °C, rotating speed of disassembling cylinder 10 rpm and incubation time 8 min. After disassembly, ECs can be classified to be further recycled individually (Wang and Xu, 2015).

- Stage (2) size reduction. Since the metals are laminated in resins layer by layer, to enhance the contact of metals with lixiviants, most of the researchers employ mechanical machines to shred, crush and/ or grind the bare boards for size reduction, which is a process similar with ore processing in mining industry. Fig. 6 presents a typical machine (Retsch Cutting Mill SM 200) that is commonly used in laboratory for the preparation of powdered WPCB samples.
- Stage (3) enrichment. Another scenario is the further treatment of the ground board particles for the enrichment of metals based on the physical differences of different materials (Cui and Forssberg, 2003). Then, the metal and non-metal fractions can be crudely separated and metal contents can be enriched. After enrichment, the materials can be purified or further treated for the recovery of metals by the hydrometallurgical process (Li et al., 2015; Tuncuk et al., 2012).

3.2. Chemical methods

Chemical methods refer to the pre-treatment of WPCBs employing chemicals, which is based on the dissolution of different components of
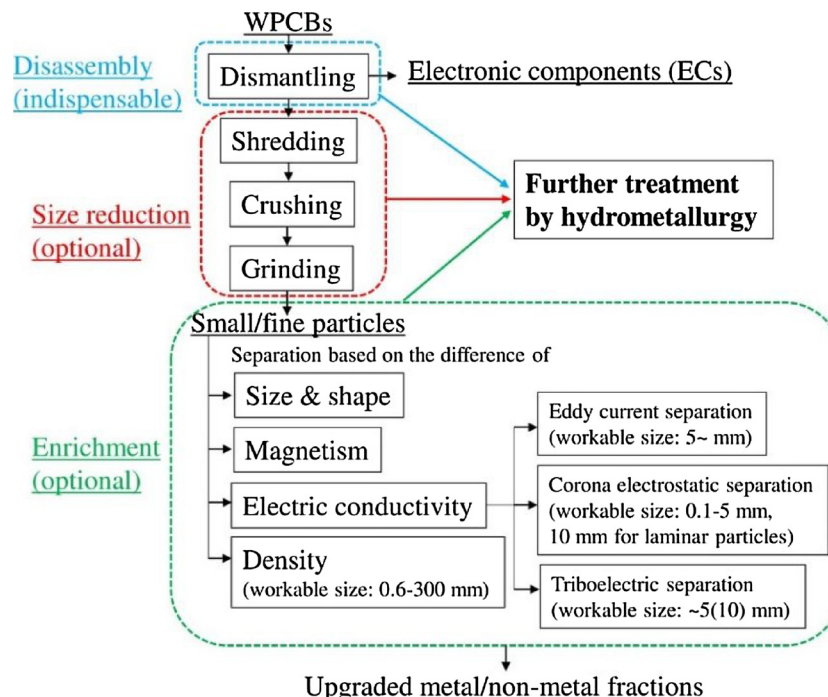
Fig. 5. Mechanical-physical pre-treatment of WPCBs, information source from (Cui and Forssberg, 2003).
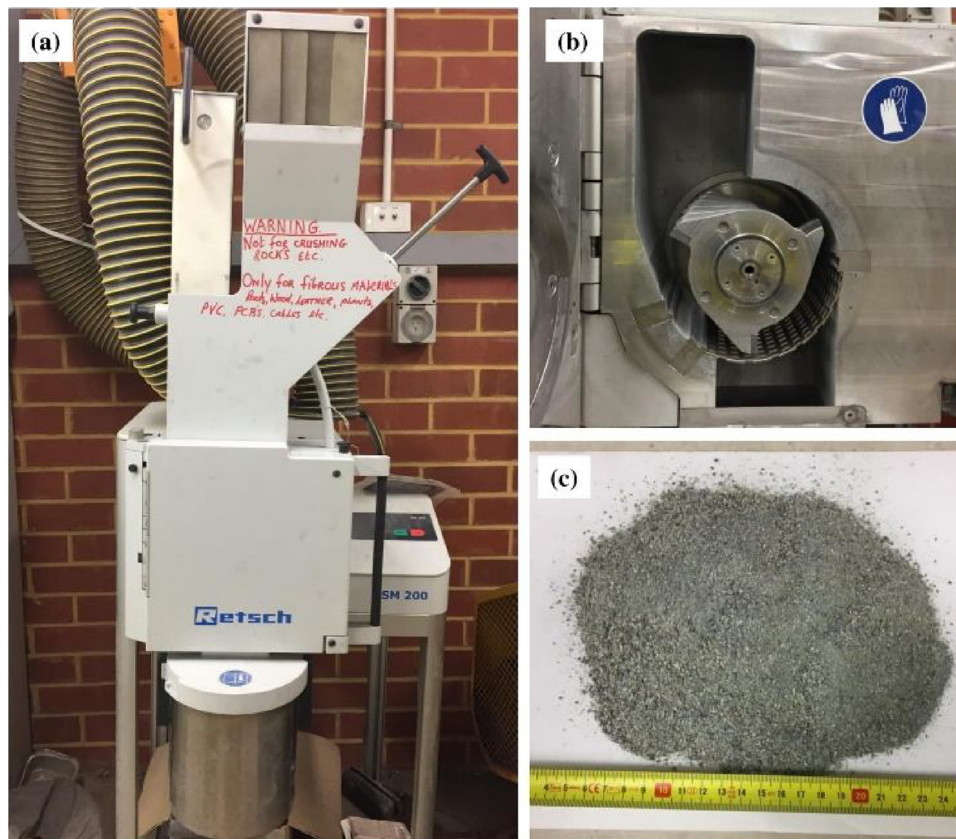
Fig. 6. Size reduction of WPCBs in laboratory, (a) Retsch Cutting Mill SM 200; (b) inside of the mill with 6-disc rotor; (c) milled WPCBs by using 2 mm screen.
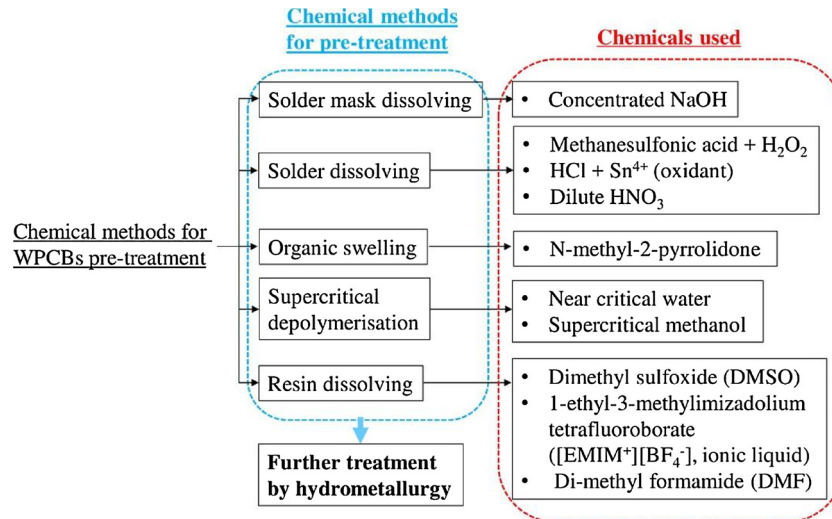
Fig. 7. Chemical method for the pre-treatment of WPCBs.

WPCBs (solder mask, solder, adhesive and/or resin) to favour the downstream leaching process. Fig. 7 summarises the chemical methods in different categories and the chemicals used (details given in Table S1). Jadhav and Hocheng (2015) used high concentration (10 M) NaOH solution to dissolve solder mask, a layer of chemical coating on the surface of WPCBs, to enhance the following leaching of metals. In order to dismantle ECs from substrate, some researchers used acids (e.g. methanesulfonic acid (MSA) and HCl) associating with oxidants (e.g. H_2O_2 and Sn^{4+}) or using oxidizing acid (e.g. HNO_3) to selectively dissolve Sn-Pb solder based on redox reaction (Jung et al., 2017; Yang et al., 2011a; Zhang et al., 2017), thus, making the ECs fall off from

substrate. In some cases the use of acids may lead to the release of toxic fumes (such as NO_x gases). Jha et al. (2012) used N-methyl-2-pyrrolidone solution to dissolve the adhesive and other chemicals presented with the resin resulting in the WPCBs swelled, which makes the leaching of metals easier. Another way of pre-treating WPCBs is the depolymerisation of resin using sub-/supercritical solvent to make it separated with metals and glass fibres. For example, Yildirir et al. (2015) proposed a novel method to dissolve resin by using water as a solvent in the presence of NaOH under near critical state to depolymerise resin. What's more, researchers have used various organic solvents, such as dimethyl sulfoxide (DMSO), 1-ethyl-3-

methylimizadolium tetrafluoroborate ($[EMIM^+][BF^{4-}]$, ionic liquid) and di-methyl formamide (DMF), to effectively dissolve brominated epoxy resin (BER), resulting in the WPCBs delaminated. Then, Cu sheets and glass fibres can be separated manually and recovered individually (Verma et al., 2016; Zhu et al., 2013a,b, 2012). After pre-treating by chemicals, WPCBs can be further treated by a hydrometallurgical process for metals recovery. Inherent to many of the proposed processes is dealing with the excess reagent (particularly where dangerous and volatile organic solvents are used) and the residual solvent phases. The reagent and consumables cost, particularly if the solvents or reagents cannot be recovered economically, can be prevent any commercial and industrial implementation.

4. Leaching of metals

To transfer metals from solid materials to a solution for further recovery, leaching is an inevitable step in a hydrometallurgical process.

4.1. Traditional leaching methods

Traditional leaching methods employ mineral acids or cyanide-based chemicals as major lixiviant. The mineral acid leaching has been reported for both base and precious (*esp*. aqua regia) metals leaching, while cyanide-based leaching is usually targeted on precious metals.

4.1.1. Mineral acid leaching of base and precious metals

Mineral acids, including H_2SO_4, HCl and HNO_3, with their advantages of low costs, well-investigated leaching mechanism and more flexibility in process control and upscale, have been widely reported for metals leaching from WPCBs (Jadhav and Hocheng, 2015). Table S2 summarises the details of reported studies employing mineral acids for the leaching of WPCBs. Generally, base metals like Zn, Sn, Fe and Al, can be dissolved in dilute mineral acids, however, Cu and precious metals like Au and Pd only significantly dissolve in oxidizing acid (*e.g.* concentrated HNO_3) or non-oxidizing acid in the presence of oxidant (air/O_2, H_2O_2, Cl_2, Cu^{2+}, Fe^{3+}, *etc.*), which can be explained by their standard reduction potentials. In most cases, metals such as Ag and Pb pose particular problems to acid-leach effectively due to the range of insoluble salts that these metals form. Accordingly, the reported mineral acid leaching can be divided into the following aspects according to what kind of leaching agents used:

(1) Using mineral acid only, including H_2SO_4, HNO_3, HCl and aqua regia (HCl: HNO_3 = 3:1, v/v). Bas et al. (2014) reported that the leaching rates of Cu and Ag rise with the increase of HNO_3 concentration (1–5 M), and the concentration $\geq$2-3 M is required for a high leaching rate of Cu (88.5–99.9%) at 6% pulp density and 70 °C, while only 14–68% Ag leached at HNO_3 concent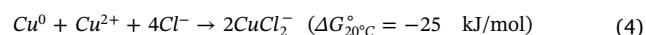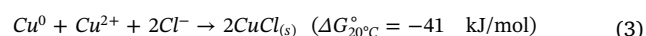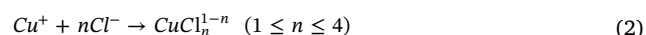ration 1–5 M due to its high standard reduction potential (0.80 V for Ag^+/Ag *vs.* 0.34 V for Cu^{2+}/Cu), indicating that higher concentration of HNO_3 is required for a high leaching rate of precious metals like Ag. Generally, dilute H_2SO_4 under atmospheric pressure cannot significantly leach Cu, with 1 M H_2SO_4 leaching only 8.8% Cu at room temperature for 96 h (Jadhav and Hocheng, 2015). However, ~1 M H_2SO_4 under pressure (2 MPa) and at high temperature (~120 °C) can achieve almost complete leaching of Cu as well as Ni, Zn and Fe (Altansukh et al., 2016; Kumari et al., 2016). Aqua regia, as a traditional lixiviant, can non-selectively and aggressively leach many kinds of base and precious metals (*e.g.* Cu, Pb, Zn, Ni and Au) (Zhang and Xu, 2016). Park and Fray (2009) used aqua regia to selectively leach Au (97%) over Ag and Pd from WPCBs. The results show that Ag has a strong chemical durability in aqua regia, with only 2% Ag leached at L/S ratio 20 mL/g and 20 ± 2 °C for 3 h, in the meantime, Pd formed the precipitate of Pd(NH4)$_2$Cl$_6$. However, the application of aqua regia has been largely restricted since it is easily decomposed, strongly oxidative and highly corrosive to the reactor

(Behnamfard et al., 2013).

(2) Using mineral acid and oxidant. Since precious metals with high reduction potentials are hardly leached by non-oxidizing acids, oxidant is usually used for the leaching of them and accelerating the leaching efficiency. The most common pair of mineral acid and oxidant is H_2SO_4 and H_2O_2, by which complete leaching of Cu can be achieved (Birloaga et al., 2014). Other oxidants, such as Cu^{2+}, Fe^{3+} and air/O_2, have also been reported. For example, Yazici and Deveci (2013) reported that Cu^{2+} as oxidant working with Cl^- in sulphate solution shows satisfactory leaching of Fe, Ni, Cu and Ag (> 90%) and partial leaching of Pd (58%), with the leaching of Cu represented by Eqs. (1) and (2). However, the amount of Cl^- should be maintained at a sufficient level to prevent Cu^+ from forming precipitate CuCl (Ksp = 1.86×10^{-7}) (Eqs. (3) and (4)). It is also reported that by adding air/O_2 for the *in situ* regeneration of Cu^{2+}, the leaching of Pd could be increased to > 82% (Yazici and Deveci, 2013).

$$Cu^0 + Cu^{2+} \rightarrow 2Cu^+ \tag{1}$$

$$Cu^+ + nCl^- \rightarrow CuCl_n^{1-n} \ \ (1 \leq n \leq 4) \tag{2}$$

$$Cu^0 + Cu^{2+} + 2Cl^- \rightarrow 2CuCl_{(s)} \ \ (\Delta G_{20°C}^\circ = -41 \ \ kJ/mol) \tag{3}$$

$$Cu^0 + Cu^{2+} + 4Cl^- \rightarrow 2CuCl_2^- \ \ (\Delta G_{20°C}^\circ = -25 \ \ kJ/mol) \tag{4}$$

(3) Multi-stage leaching. To achieve selective leaching of metals, multi-stage leaching has been reported to be an effective option. Somasundaram et al. (2014) used 0.1 M $CuCl_2$ and 3.0 M HCl at 25 °C to selectively leach Sn (92%) from WPCBs with only slight leaching of Cu, Pb and Ni (< 6.9%). Then, by elevating $CuCl_2$ concentration and temperature to 0.5 M and around 50 °C respectively, Cu, Pb and Ni could be leached out at 2nd stage. According to Jha et al. (2012), Pd and Sn could be leached from the solder of WPCBs separately by a two-stage leaching. In the 1st stage, 99.99% Pd was leached by 0.2 M HNO_3 while Sn remained un-leached by forming SnO_2 which could be further leached by 3.5 M HCl.

Researchers have proved mineral acids can effectively leach many base metals from WPCBs under relatively moderate conditions, while for precious metals, higher requirements for leaching time, temperature, pressure and concentrations of acid and oxidant are needed (Table S2), which may not be economic. The volatile HNO_3, HCl and aqua regia may bring risks for workers and environment, not only because of their inherent volatility, but also due to potential release of harmful gaseous reaction products such as NO_x gas mixtures. Moreover, the corrosive strong acids bring higher requirement for equipment and often accompany with unwanted by-products and large amount of acid waste water needing to be managed properly. In some researches, therefore, a mineral acid is used in the first stage of leaching for base metals, followed by using other lixiviants, *e.g.* cyanide and thiourea, for precious metals leaching (Birloaga and Vegliò, 2016).

4.1.2. Cyanide-based leaching of precious metals

Cyanide leaching for Au and Ag recovery from natural minerals has been commercialized for over 100 years (Behnamfard et al., 2013). Although cyanide is highly toxic, its advantages of high efficiency and lower cost have made it still industrially preferable to other non-cyanide lixiviants for precious metals (Akcil et al., 2015). Cyanide ion (CN^-) can exist in solution as different forms *i.e.* free cyanide (CN^-), hydrogen cyanide (HCN), complexes and some simple compounds, depending on different pH. It is suggested that cyanidation should happen at a pH $\geq$ 10.5, so that the formation and volatilisation of toxic HCN (dominant at pH < 8.5) can be limited. The overall reaction during the leaching of Au in cyanide solution in the presence of oxygen (oxidant) can be represented by Eq. (5) (Akcil et al., 2015).

$$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4Au(CN)_2^- + 4OH^- \qquad (5)$$
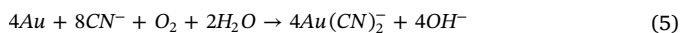
Since a significant amount of Au and Ag, two of the most valuable metals in PCB, are contained in WPCBs (Table 1), using cyanide leaching in the case of WPCB recycling is also viable. However, the dissolution of the high content of Cu (10–20 wt. % in PCB) will cause excessive cyanide consumption when it is used to leach WPCB directly, which will considerably drive cost up and bring higher risk of hazardous impact. Furthermore, the presence of significant content of Cu can also impair the dissolution of precious metals due to copper oxide and copper hydroxide layers on the particle surface (Montero et al., 2012). In addition, the formation of large amounts of residual weak acid dissociable (WAD) cyanide complexes have to be detoxified after precious metal recovery. To solve the problems, a multi-stage leaching may be feasible, in which Cu, as well as some base metals, can be leached in the first stage by mineral acid and proper oxidant prior to leaching precious metals in the second stage. Many researchers have proved that H_2SO_4 in the presence of proper oxidant can effectively leach Cu and other base metals (Fe, Al, Ni, Zn) from WPCBs (Table S2). However, it should be noted that the cyanidation of precious metals should happen in an alkaline environment (pH ≥ 10.5) (Akcil et al., 2015), which means the noticeable amount of alkali may be needed for neutralization of residue after the acid leaching in the first stage.

Another way to reduce the consumption of cyanide is adding other lixiviant that can cooperate with cyanide to complex with metals. A preliminary research reported by Bisceglie et al. (2017) suggests that 3-nitrobenzene-sulphonate (NBS) can act as a synergist in cyanide solution for the leaching of Au from electronic scrap (e-scrap). The possible mechanism was reposted to be as follows: 1) firstly, cyanide complexes with Au to form the soluble $Au(CN)_2^-$; 2) Au from $Au(CN)_2^-$ then attaches to one of the sulphonate oxygen group of NBS, by which cyanide can be free to complex with Au again. NBS is also a mild oxidant that has a longer stability than other oxidants such as H_2O_2. When serving as an oxidant the nitro group is reduced. The reagent is used in intensive cyanidation reactors for the treatment of gravity gold concentrates.
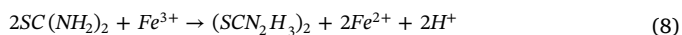
Reaction speed is another concern in the case of WPCB recycling by cyanide leaching. As shown in Eq. (5), the oxidant used in Au cyanidation is oxygen coming from air which will largely restrict the reaction speed to the magnitude of days (Bisceglie et al., 2017). However, unlike the mining operations happening in the remote areas, WPCB recycling (a.k.a. urban mining) is often suggested to be conducted close to the urban area as a way to reduce transport cost (due to low bulk density) and risks. The amount of WEEE or WPCBs in urban areas is rapidly accumulating and is becoming a pressing problem for municipalities. A high recycling efficiency is accordingly required to avoid the collateral hazards brought about by accumulation. Also, the risks of cyanide use in the proximity of urban areas should also be carefully considered. In most cases globally, the use of large quantities of cyanide in urban areas is forbidden. Consequently, there is a need for more environmentally and socially acceptable leaching approaches. Some promising substitutes, such as thiosulfate, thiourea, and halide, have been reported in lab- or pilot-scale, which will be discussed in the following sections.

4.2. Mild leaching methods

Undoubtedly, WPCBs remain as a pressing environmental issue requiring urgent attention. Using environmentally harmful traditional leaching methods to solve another environmental issue may not be advisable. The recent research focus has been very much on finding more benign and milder lixiviants and leach conditions. So far, thio-system leaching (thiosulfate, thiourea and thiocyanate), halide leaching and ammonia-ammonium leaching have been actively investigated. Among them, thio-system and halide are mainly for precious metals leaching, while ammonia-ammonium is reported to leach base metals from WPCBs.

4.2.1. Thiourea leaching of precious metals

4.2.1.1. Acidic thiourea leaching. Compared with traditional leaching methods, thiourea ($(NH_2)_2CS$, TU) used as lixiviant for precious metals is less toxic and more eco-friendly, and it can achieve a high leaching rate ($\sim 99\%$ for Au) (Zhang and Xu, 2016). Initially, thiourea is used in acidic solutions where thiourea dissolves Au and Ag by forming cationic complexes ($Au(SC[NH_2]_2)_2^+$ and $Ag(SC[NH_2]_2)_3^+$). To oxidise native Au and Ag in WPCBs, oxidant, mostly Fe^{3+}, is used in the system (Eqs. (6) and (7)). It is reported that, with the addition of Fe^{3+}, Au extraction efficiency can be increased up to four times higher than that without Fe^{3+} addition (Gurung et al., 2013). However, thiourea is very unstable, especially at pH > 4.3, and easily oxidised and decomposed (Zheng et al., 2006). Moreover, it is difficult to maintain the Fe^{3+} in solution at pH's greater than around 3.5 (Mohan and Chander, 2006). High concentration of Fe^{3+} can oxidise thiourea to formamidine disulphide (FDS) (Eq. (8)), which could be forward oxidised to unwanted sulphur and cyanamide, and the sulphur may cause passivation for the dissolution of Au (Birloaga et al., 2014). In addition, Fe^{3+} can also complex with thiourea forming $[FeSO_4CS(NH_2)_2]^+$, reducing the leaching efficiency and increasing thiourea consumption (Akcil et al., 2015).

$$Au + 2SC(NH_2)_2 + Fe^{3+} \rightarrow Au(SC[NH_2]_2)_2^+ + Fe^{2+} \qquad (6)$$

$$Ag + 2SC(NH_2)_2 + Fe^{3+} \rightarrow Ag(SC[NH_2]_2)_3^+ + Fe^{2+} \qquad (7)$$

$$2SC(NH_2)_2 + Fe^{3+} \rightarrow (SCN_2H_3)_2 + 2Fe^{2+} + 2H^+ \qquad (8)$$

According to Hilson and Monhemius (2006), acidic thiourea leaching is normally conducted at pH of 1–2, and the effective leaching largely relies on the carful control of pH, redox potential, leaching time and the concentrations of thiourea and oxidant (Fe^{3+}). In such acidic environment, base metals, such as Fe, Cu, Ni, Zn and Pb, contained in WPCBs may also be leached out with Au and Ag, resulting in additional consumption of thiourea. Gurung et al. (2013) used thiourea to leach WPCBs directly. The results show that significant amount of Cu as well as small amount of Fe, Ni, Zn and Pb were leached with Au and Ag, whereas most of Pd and Pt remained in the residue. Besides, they also found that the presence of Fe^{3+} had no beneficial effect for Ag leaching which happens more rapidly than Au leaching. To separate base metals prior to leaching Au and Ag, Birloaga and Vegliò (2016) used a two-step leaching method for metals recovery from WPCBs, in which H_2SO_4 and H_2O_2 was used for the selective leaching of base metals, followed by acidic thiourea leaching for Au and Ag, with 90% and 75% extraction yields for Au and Ag, respectively.

4.2.1.2. Alkaline thiourea leaching. In order to overcome the disadvantages in acidic thiourea leaching, such as high thiourea consumption, serious corrosion of equipment and complicated regeneration and purification procedures, alkaline thiourea leaching has been proposed (Chai et al., 1997; Wang et al., 2003; Wei et al., 1999). According to Zheng et al. (2006), in alkaline solution, Au dissolution is also based on the complex with thiourea forming cationic complex ($Au(SC[NH_2]_2)_2^+$). However, Fe^{3+} is not stable in alkaline solution and other oxidant should be carefully selected since thiourea is easily decomposed by oxidation, which is irreversible and will also further cause passivation. It is suggested that the suitable oxidant should have enough solubility and moderate redox potential, such as $Na_2S_2O_8$ and $K_3Fe(CN)_6$ (Zheng et al., 2006). In order to enhance the stability of thiourea in alkaline environment, some stabilizers, *i.e.* Na_2SO_3, Na_2SiO_3 and $(NaPO_3)_6$, have been reported by Wang et al. (2003) and Li et al. (2014b), making the decomposition of alkaline thiourea reduced from 72.5% to 33.8% with the addition of 0.3 M Na_2SiO_3. Although a number of investigations have been performed, the application of alkaline thiourea leaching is still in an early stage since the decomposition of thiourea is still considerable and the leaching performance is not satisfactory ($\sim 79\%$ for Au). In

particular, the current research for alkaline thiourea leaching is aimed at metals extraction from ores and concentrates, the feasibility in WPCBs has not been verified.

4.2.2. Thiosulfate leaching of precious metals

Thiosulfate ($S_2O_3^{2-}$) has been seen as a promising substitute of cyanide for the leaching of precious metals from minerals owing to its reduced environmental risk, high selectivity, low corrosivity and cheap cost (Xu et al., 2017) and some studies using thiosulfate leaching for WPCBs recycling have been carried out. Thiosulfate leaching is conducted in alkaline environment, at a pH range of 9–10.5, since it is easily decomposed in acid solution (Zhang et al., 2012b). In the absence of catalyst, Au dissolves in alkaline thiosulfate solution very slowly with the dissolved O_2 as oxidant. To enhance the leaching efficiency, Cu^{2+} and ammonia are usually used as additives, making the cupric ammonia ($Cu(NH_3)_4^{2+}$) act as a "catalyst" with the leaching of Au represented by Eqs. (9) and (10) (Cui and Zhang, 2008).

$$Au + 5S_2O_3^{2-} + Cu(NH_3)_4^{2+} \rightarrow Au(S_2O_3)_2^{3-} + 4NH_3 + Cu(S_2O_3)_3^{5-} \quad (9)$$

$$2Cu(S_2O_3)_3^{5-} + 8NH_3 + \frac{1}{2}O_2 + H_2O \rightarrow 2Cu(NH_3)_4^{2+} + 2OH^- + 6S_2O_3^{2-} \quad (10)$$
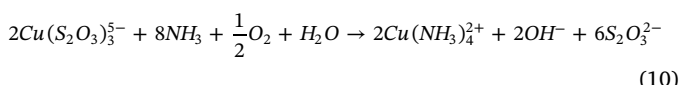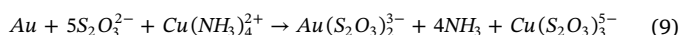
In the case of direct leaching of WPCBs or size-reduced WPCBs by thiosulfate leaching system, negative results have been shown in several studies (Table S3) which implies, for a high leaching rate, the operational conditions can be further optimised and potential additives may be considered. It is reported that $Na_2S_2O_3$ or $(NH_4)_2S_2O_3$, $CuSO_4$ or H_2O_2 and $NH_3 \cdot H_2O$ leaching system did not show considerable leaching effect for both Au and Ag from complete size of WPCBs, with all the rates < 16% (Ficeriová et al., 2011; Melo Halmenschlager Petter et al., 2015). Similar results obtained from the size-reduced WPCBs, Petter et al. (2014) used 0.1 M $Na_2S_2O_3$, 0.2 M $NH_3 \cdot H_2O$ and 0.015–0.03 M $CuSO_4$ to leach Au and Ag from ~1 mm WPCBs of mobile phone with only 15% Au leached out. Moreover, it was found that the addition of H_2O_2 as oxidant did not show significant influence for both Au and Ag leaching. However, > 93% leaching rates for both Au and Ag were also observed from size-reduced WPCBs for a long leaching time (48 h) (Ficeriová et al., 2011). In order to pre-separate base metals, some researchers employed H_2SO_4 and H_2O_2 for selective leaching of base metals from WPCBs, followed by $(NH_4)_2S_2O_3$-$CuSO_4$-NH_4OH leaching for precious metals with > 95% Au and Ag leached out (Oh et al., 2003). According to Cui and Zhang (2008) and Tesfaye et al. (2017), the major problems of thiosulfate leaching are the high consumption of thiosulfate and relatively low leaching kinetics which make the process uneconomic and inefficient, in spite of its potential environmental benefits.

4.2.3. Thiocyanate leaching of precious metals

Thiocyanate (SCN^-) has been known as lixiviant for Au extraction from minerals for a long time, which shows potential for precious metals (Au and Ag) extraction from WPCBs despite very few works have been reported (M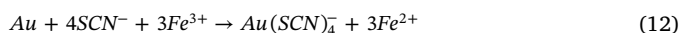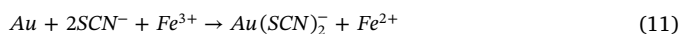pinga et al., 2015; Zhang and Xu, 2016). Thiocyanate works in acidic environment at a pH of 1–2 which enables Fe^{3+} to act as an oxidant (Syed, 2012), and the dissolution of Au can be simplified as Eqs. (11) and (12) (Mpinga et al., 2015).

$$Au + 2SCN^- + Fe^{3+} \rightarrow Au(SCN)_2^- + Fe^{2+} \quad (11)$$

$$Au + 4SCN^- + 3Fe^{3+} \rightarrow Au(SCN)_4^- + 3Fe^{2+} \quad (12)$$

Instead of using thiocyanate as lixiviant alone, various research investigations have been conducted employing dual lixiviants, such as thiorea-thiocyanate leaching (Yang et al., 2011b; Zhang et al., 2014) and iodide-thiocyanate leaching (Barbosa-Filho and Monhemius, 1994). Yang et al. (2011b) used thiourea-thiocyanate in the presence of $Fe_2(SO_4)_3$ as oxidant to leach Au disc. The results show that Au leaching

rate was higher than either ferric-thiorea or ferric-thiocyanate separately, and the explanation was reported to be a synergistic effect attributed to the formation of a mixed ligand complex *Au $((NH_2)_2CS)_2SCN$*. According to Barbosa-Filho and Monhemius (1994), synergistic effect during Au leaching was also observed by leaching with iodide-thiocyanate due to the formation of the relatively stable mixed iodide-thiocyanate species which participate in the dissolution of Au.

4.2.4. Halide leaching of precious metals

Although the use of halide (chlorine, bromine and iodine) leaching for Au-bearing minerals predates cyanidation, as surmised in Table S3, not much attention has been paid to its use for Au extraction from WPCBs (Cui and Zhang, 2008; Ghosh et al., 2015). Au can form both Au^+ and Au^{3+} complexes with chloride, bromide and iodide (Cui and Zhang, 2008). Their complexing principles are similar, as indicated as follows (Wu et al., 2017):

$$2M + L_2 + 2L^- \rightarrow 2ML_2^- \quad (13)$$

$$2M + 3L_2 + 2L^- \rightarrow 2ML_4^- \quad (14)$$

Where M and L stand for precious metals and halide elements, respectively. L_2 is the oxidizing agent, and $L-$ is the complexing agents.

According to Cui and Zhang (2008), chlorine/chloride leaching has been investigated for years, with the traditional aqua regia leaching as an example, and has been industrialised in a significant scale. However, the high requirement for equipment, *i.e.* stainless steel and rubber-lined reactor, and potential health risk hinder its wide application.

In recent years, some researchers used iodine/iodide to leaching precious metals in alkaline environment, mostly as a following step after separation of base metals from WPCBs (Table S3). Iodine/iodide leaching is considered to be non-corrosive and non-toxic, and it has a quick kinetics and good selectivity for precious metals (Zhang et al., 2012b). Moreover, Au-iodide complex is the most stable compound formed by Au and halogen (Ghosh et al., 2015). Altansukh et al. (2016) used 2 g/L I_2 and 12 g/L KI to leach Au from WPCBs pre-treated by incineration and acid leaching, the results indicated that > 99% Au was dissolved in the solution at 40 °C for 120 min. EnviroLeach Technologies Inc. in Canada has recently patented a process to use an iodide-iodate system with reagent recycle and electrolysis to recover precious metals from e-waste (Nelson et al., 2017). However, iodine/iodide leaching also has high reagents consumption and iodine is relatively expensive, which are the main obstacles of this method (Ghosh et al., 2015; Zhang et al., 2012b).

4.2.5. Ammonia-ammonium leaching of base metals

Several studies (Table S3) using ammonia and ammonium for leaching base metals from WPCBs have been reported (Koyama et al., 2006; Lim et al., 2013; Liu and Kao, 2003; Liu et al., 2009; Oishi et al., 2007; Sun et al., 2015). Ammonia-ammonium has demonstrated high selectivity and leaching rate (≥90%) for Cu (Lim et al., 2013; Sun et al., 2015). According to Sun et al. (2015), the Cu dissolution in ammonia-ammonium solution can be divided into two steps: (1) Cu is firstly oxidised by oxidant, such as dissolved oxygen or H_2O_2, at the surface of Cu metal (Eq. (15)); (2) then the CuO is further dissolved by the ammonia-ammonium solution, resulting in the formation of soluble Cu (I)-ammine complex ($Cu(NH_3)_4^{2+}$), as indicated by Eq. (16).

$$2Cu + O_2 \rightarrow 2CuO \quad (15)$$

$$CuO + 2NH_3 \cdot H_2O + 2NH_4^+ \rightarrow Cu(NH_3)_4^{2+} + 3H_2O \quad (16)$$

In addition to Cu, it is reported that ammonia-ammonium also shows leaching ability to other base metals, which is generally depended on the reduction potential of metals and the stability of metal-ammine complex (Wang et al., 2011). For example, both Xiao et al. (2013) and Wang et al. (2011) used $(NH_4)_2CO_3$ and $NH_3 \cdot H_2O$ with different oxidant to leach metals from ICT waste and WPCBs

respectively. The results from both study indicate 70% and 100% Zn were leached together with Cu respectively, since Zn has lower reduction potential and can form more stable ammine complex in comparison to Cu. Thus, purification steps for the leaching solution are required for the recovery of Cu. On the other hand, the decomposition and volatility of ammonia during leaching process also cause risks for human and environment, although it shows advantage for the following recovery of metals from solution by heating (Liu et al., 2009).

4.3. Novel leaching methods

Aiming to overcome the limitations in traditional and mild leaching methods, in recent years, some novel leaching methods for the recycling of WPCBs are proposed, such as chelating leaching, ionic liquid leaching (ionometallurgy) and sub-/ supercritical leaching. Although the theory and technology behind them already exist and some of them has even been commercially applied in other area, they are still at an early stage in the area of WPCBs recycling and need to be further investigated. The details of the novel leaching methods reported in recent years are given in Table S4, which shows the chelating technology and ionic liquid have been used for base metals leaching from WPCBs, and the supercritical technology has been reported for the leaching of both base (Cu) and precious (Ag, Pd) metals from WPCBs.

4.3.1. Chelating leaching of base metals

Chelating leaching is normally referred as the leaching by using the lixivant (chelator) with multi-dentate (inc. bidentate) ligands that get complexed with metals or metal ions to form soluble metal-ligand complexes (Gary et al., 2014). Previously, chelation technology has been applied for the extraction of heavy metals from contaminated soils and industrial waste. Some chelators, especially EDTA, have been wildly used in various applications for many years (Chauhan et al., 2018). Turning to the area of e-waste recycling, a pioneer research employing EDTA as lixivant for the Cu extraction from WPCBs was reported by (Jadhao et al., 2016). The results show that nearly 84% Cu was leached from WPCB powders by leaching with 0.5 M EDTA at 100 °C and pH of 7 for 3 h. Further study reported by Sharma et al. (2017) indicates the potential of the improved leaching performance by employing response surface methodology. The optimum conditions were suggested as follows: EDTA concentration 0.5–0.6 M, S/L ratio 1/ 19–1/23 g/mL, reaction temperature 83–89 °C, reaction time 130–148 min and pH 8–9, under which the Cu extraction of greater than 90% was predicted (Sharma et al., 2017). However, the authors did not address the complexing of EDTA with other metals contained in WPCBs. Due to the relatively high binding strength brought by the multi-dentate ligands, EDTA may also chelate with other metals, such as base metals of Ni, Zn, Sn and Pb and precious metals of Au, Ag and Pd. (House, 2008). When they are complexed and leached into solution, how to separate and recover them will be concerned.

An important advantage of EDTA leaching is the recyclability of chelating agent. According to Jadhao et al. (2016), more than 96% EDTA can be recycled by introducing H_2SO_4 to the chelating solution to form the EDTA precipitate. In this way, the chelator can be reused and its consumption can be largely reduced. Nevertheless, the significant consumption of alkali and acid should also be noted since chelating happens in alkaline environment (pH 8–9) while de-chelation happens in acidic environment (pH 2–3).

Except for EDTA, other potential chelators, such as Polyethylenimine (PEI), and biodegradable EDDS, GLDA and iminodisuccinic acid (IDSA), can also be considered for the leaching of metals from WPCBs (Kobayashi et al., 1987; Perrine and Landis, 1967). The synthesis of new biodegradable chelating agents and the research of their degradation pathways are also future trend of this area (Chauhan et al., 2015). Besides, the separation and recovery of chelated metals from leaching solution also need more attentions in future researches.

4.3.2. Ionic liquid leaching of base metals

Ionic liquids (ILs) are a kind of liquid that only consists of ions at a low temperature (100 °C) or even at room temperature (room temperature ionic liquid, RTIL) (Wasserscheid and Keim, 2000). ILs have at least one ion with delocalized charge and one component is organic, which prevents the formation of a stable crystal lattice, typically consisting of an organic cation and an inorganic or organic anion (Chen et al., 2015b). With the advantages of low melting point (< 100 °C), no measurable vapour pressure, negligible volatility, high thermal stability, high conductivity and wide electrochemical window, ILs have been seen as a promising "green chemistry" replacing the organic solvents (Chen et al., 2015a; Wasserscheid and Keim, 2000). Recently, several researches using ionic liquid acids for the extraction of Cu from WPCBs have been reported. Huang et al. (2014) used [bmim]HSO₄, together with H_2O_2 for Cu extraction from WPCBs and almost 100% Cu extraction was achieved. Chen et al. (2015b) investigated the leaching performances of five typical IL acids, i.e. [BSO₄HPy]HSO₄, [BSO₃HMIm] HSO₄, [BSO₃HMIm]OTf, [BSO₃HMIm]OTf and [BSO₃HPy]OTf associating with H_2O_2 for Cu extraction from WPCBs and the relationship between Pb and Cu during the process. The results indicate that each of the IL acids leached almost 100% Cu and the Pb leaching was below 30%. Although several ILs have been shown high leaching rate of Cu from WPCBs, other metals such as Au, Ag, Sn, Ni, etc. contained in WPCBs have not been investigated yet. Taking into account the complexity of metal contents in WPCBs (Fig. 1), the investigation should not only limited in the metal of Cu with highest content, the co-leaching and interference of other metals, and how to separate them in leaching solution and how to regenerate the ILs should also be focused in the future research of this area. Accordingly, to reduce the solubilisation loss of ILs and favour the metals recovery from solution, options like synthesis of task-specific ionic liquids (TSILs) and the addition of organic ligands have been proposed for heavy metals extraction from aqueous solution (Chauhan et al., 2018), that needs further research in the case of WPCBs recycling.

4.3.3. Supercritical leaching of base and precious metals

In recent years, much attention has been paid to the extraction of metals through supercritical fluid technology. By definition, supercritical fluid (SCF) is a substance that remains as a single phase at above its critical temperature (T_c) and critical pressure (P_c) having gas-like diffusion rate, viscosity and liquid-like density (Sanyal et al., 2013). Of that, supercritical CO_2 has been widely investigated since it has a relatively low critical point (P_c = 7.38 MPa, T_c = 31.1 °C), is environmentally acceptable, can be recycled and reused (Calgaro et al., 2015). Moreover, with the diffusion coefficient 100 times larger than that of liquid, supercritical CO_2 has amazing dissolving capacity, diffusion ability and the penetration capacity. When it comes to metal extraction, supercritical CO_2 is often associated with co-solvents since using it alone cannot meet charge neutralization requirements and weak solute-solvent interactions (Liu et al., 2016). Calgaro et al. (2015) used supercritical CO_2 with H_2SO_4 and H_2O_2 as co-solvents at 7.5 MPa and 35 °C to extract Cu from WPCBs and 88.79% Cu extraction was achieved in only 20 min, which shows fast kinetics. In addition, Liu et al. (2016) reported a two-stage leaching method for Ag and Pd extraction from WPCBs. In the 1st stage, WPCBs were pre-treated by supercritical water oxidation (SCWO) followed by dilute HCl leaching of residue to enrich precious metals grade with enrichment factors of Pd and Ag reached 4.8 and 5.3, respectively. It should be noted that the pre-treatment by sub-/supercritical water has been classified in the pre-treatment section of WPCBs in this study (Section 3.2). In the 2nd stage, supercritical CO_2 modified with acetone and KI-I_2 was used to extract Pd and Ag from the precious metals concentrate with Pd and Ag extraction reached 93.7% and 96.4%, respectively in only 10 min. Although several researches have proved the feasibility of supercritical CO_2 leaching of metals from WPCBs, the operational costs for the pressure leaching and its availability in mass production should also be

evaluated in future research. In addition, novel types of supercritical solvents and co-solvents should be developed (Calgaro et al., 2015) and the co-extraction of other metals should also be concerned.

4.4. Potential leaching methods

4.4.1. Glycine leaching of base and precious metals

Glycine, naturally derived from microbes, is the simplest amino acid and commonly mass produced as food additive. It is eco-friendly, non-toxic, non-volatile and stable in a wide pH-Eh range and has been shown high metal affinities (Oraby et al., 2017). Aksu and Doyle (2001) investigated the electrochemical properties of Cu in glycine solution in the application of chemical mechanical planarization (CMP). They reported that glycine can exist in solution as three forms: $^+H_3NCH_2COOH$ (cation), $^+H_3NCH_2COO^-$ (zwitterion) and $H_2NCH_2COO^-$ (anion) depending on different pH (Eq. (17)). The zwitterion and anion can form complexes with both Cu^+ and Cu^{2+} to make them soluble in solution.

$$^+H_3NCH_2COOH \xleftrightarrow{pKa2=2.350} {}^+H_3NCH_2COO^- \xleftrightarrow{pKa2=9.778} H_2NCH_2COO^- \quad (17)$$

Recently, a novel technology employing glycine as lixiviant in alkali environment (pH = 10.5–11) with different oxidants (O_2, H_2O_2 and/or Cu^{2+}) and catalyst/synergist (for precious metals) for effectively recovering Au, Ag and Cu from their pure foils or minerals has been reported by Eksteen and Oraby, with the leaching system depicted in Fig. 8, and the Au dissolution is represented by Eq. (18) (Eksteen and Oraby, 2014; Oraby and Eksteen, 2015; Oraby et al., 2017). Under their optimised conditions (0.3 M glycine, 1% H_2O_2, t = 48 h, T = 23 °C, pH = 11), 98% Cu could be selectively leached over Au from Au-Cu concentrate (Oraby and Eksteen, 2014). And the Au leaching rate reached 0.322 $\mu mol/(m^2 s)$ when leaching pure Au foils at elevated temperature of 60 °C (Oraby and Eksteen, 2015). In addition, they have also extended the glycine leach approach to a broad range of chalcophile metals such as Ni, Co, Zn, Pb, etc. in a more recent patent (Eksteen and Oraby, 2016).

$$2Au + 4NH_2CH_2COOH + 2NaOH + 1/2O_2 \rightarrow 2Na[Au(CH_2NH_2COO)_2] + 3H_2O \quad (18)$$
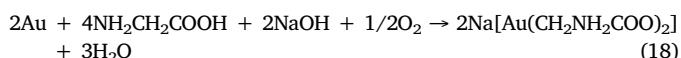
So far, glycine leaching system has not been reported in the case of WPCBs recycling yet. Taking into account the similarity of Au-Cu concentrate, foils and WPCBs, it is potential to extract base and precious metals from WPCBs by using glycine leaching system. However, the relatively low leaching efficiency of glycine solution (lasting about 40–50 h in ore extraction) should be improved since, unlike in mining industry, the space for storing increasing amount of WPCBs in urban areas is limited and the longer store time may bring higher environmental risks. Hence, more efficient oxidant or catalyst should be tested and developed. In addition, the intrinsic structure (Fig. 4) and complicated compositions (Fig. 1) of WPCBs may bring challenges for

leaching WPCBs with glycine solution, which should be focused in future works.

4.5. Summary of various leaching systems

4.5.1. Comparison of various leaching methods

Various leaching and purification methods used for the recovery of metals from WPCBs have been discussed in the foregoing sections. It is believed that the economic, environmental and technic feasibilities are the major factors in deciding the suitable process for metals recovery from WPCBs. Table 3 compares different leaching methods used for metals recovery from WPCBs. It should be noted that the weight of each factors listed in the table will be varied depending on specific situation. However, it can still be forecasted that, with the development of technology and increasing environmental requirement for "urban mining", the factors of toxicity and safety will gain more priority in the future research, and the traditional leaching methods will gradually step out of the area of WPCBs recycling, particularly when the e-waste legislation is becoming sound in developing countries.

In terms of economic feasibility, leaching rate related to kinetics is also increasingly important since, unlike the mining of primary resources, the space for storing increasing e-waste in recycling site of urban areas is limited and the longer store time may bring higher environmental risks. Taking into account the complicated metal compositions of WPCBs (Fig. 1), high selectivity of a leaching method implies less procedures of downstream purification process. Considering the leachability of metals, it is advisable to leach base and precious metals in two stages respectively. However, the leaching environment in the two stages should better both be acidic or alkaline, otherwise large amount of acid/alkali will be consumed for neutralization and unprofitable by-product, such as Na_2SO_4, may be generated.

In addition, the reagent with high recyclability can considerably reduce the costs for the reagent consumed, which makes the leaching based on coordination and chelation advantageous. Considering the low research level, glycine and EDTA leaching could be further investigated, and other complexing agents need to be tested in the near future.

4.5.2. Selection of an oxidant

Basically, most of the base metals (except for Cu) can be leached in acidic environment without the addition of oxidant, explained by their standard reduction potentials compared with H^+/H_2. However, Cu and precious metals can only be significantly leached in the presence of oxidant either in acidic or alkaline environment. Therefore, most of the leaching systems used for the leaching of these metals include at least one kind of oxidant (Tables S2–S4). Accordingly, the selection of suitable oxidant is of great importance for an effective and efficient leaching system. Table 4 lists some common and potential oxidants that have been reported or can be potentially used in the future research of
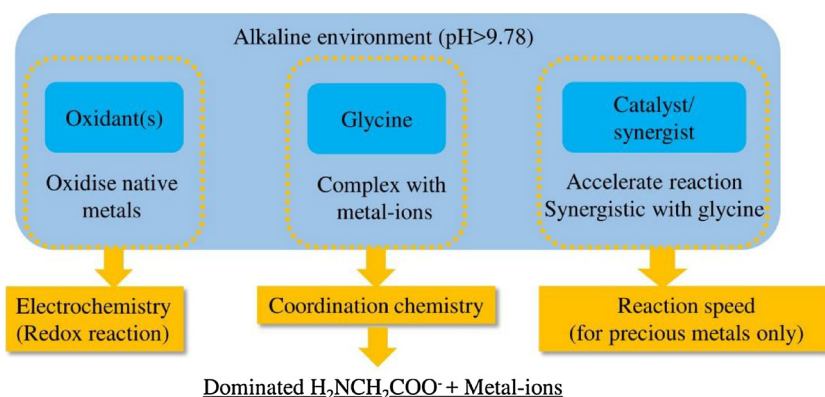

Fig. 8. Glycine leaching system used for metals extraction from foils and minerals.

Table 3

Comparison of various leaching methods used for metals recovery from WPCBs (Anand et al., 2013; Cui and Anderson, 2016; Cui and Zhang, 2008; Kaya, 2016; Pant et al., 2012; Zhang et al., 2012b).

Leaching methods	Environmental impact		Economic feasibility						Research level[d,e]
	Toxicity[a]	Safety[a,b]	Leaching rate[a]	Selectivity	Reagents recyclability	Reagent costs[a,c]	Corrosivity[a]	Special investment[d]	
Aqua regia	Medium	Low	Fairly high	Low	Low	Low	Highly corr.	Anticorrosive equipment	Low
Cyanide-based leaching	High	Low	Medium	High	High	Medium	Least corr.	Wastewater disposal	Low
Thiourea (in acidic solution)	Low, probable carcinogen	Medium, poor stability	Fairly high	Medium	Low	Medium	Fairly corr.	Not specified	High
Thiosulfate	Low	High	Medium	Medium	Medium	Medium	Least corr.	Not specified	High
Thiocyanate	Medium	Low	High	Medium	Medium	Medium	Fairly corr.	Not specified	Low
Chlorine/chloride	Medium	Low	High	Low	Low	Low	Highly corr.	Anticorrosive equipment	Low
Bromine/bromide	Medium	Low	High	Low	Low	Medium	Medium	Not specified	Low
Iodine/iodide	Nontoxic	High	High	High	Medium	Medium	Least corr.	Not specified	Low
Ammonia-ammonium	Medium	Low	High	High	Medium	Low		Absorption system	Medium
Chelation (EDTA)	Nontoxic	High	Fairly high	Medium	High	High	Least corr.	Not specified	Low
Ionic liquid	Low	High	Medium	Lack info.	Lack info.	High	Least corr.	Not specified	Low
Supercritical technology	Nontoxic	High	High	Lack info.	Lack info.	Low	Lack info.	High pressure system (reactor)	Low
Glycine	Nontoxic	High	High (Cu)	High	High	High	Least corr.	Not required	None

[a] Referred to Anand et al. (2013), Kaya (2016), Zhang et al. (2012b).
[b] Safety refers to the safety levels (low, medium and high) during the transportation and store of reagents, and the operation of the leaching process.
[c] Reagent costs (low, medium and high) are based on the unit price and consumption of reagents without the consideration of recyclability.
[d] Referred to (Cui and Anderson, 2016; Cui and Zhang, 2008; Kaya, 2016).
[e] Research level (none, low, medium and high) is based on the research extent in the area of WPCBs recycling only.

Table 4

Potentials of selected oxidants at 25 °C and the leaching examples.

Oxidant	Electro-pair	E^o, V	Example	Ref.
O_2/air	O_2/H_2O	1.23	HL and	Liu et al. (2009), Yazici and
	O_2/OH^-	0.40	AAL	Deveci (2015)
H_2O_2	H_2O_2/H_2O	1.76	MAL, TL, HL, AAL, IIL and SL	Calgaro et al. (2015), Huang et al. (2014), Kumar et al. (2014), Melo Halmenschlager Petter et al. (2015), Sahin et al. (2015), Xiao et al. (2013)
ClO^-	ClO^-/Cl^-	0.89	HL	Behnamfard et al. (2013)
Cl_2	Cl_2/Cl^-	1.40	HL	Kim et al. (2011a)
Cu^{2+}	Cu^{2+}/Cu	0.34	MAL, TL, HL and AAL	Lim et al. (2013), Tripathi et al. (2012), Yazici and Deveci (2013, 2015)
	Cu^{2+}/Cu^+	0.16		
	$Cu^{2+}/CuCl$	0.56		
	$Cu^{2+}/CuBr$	0.65		
	Cu^{2+}/CuI	0.86		
	$Cu^{2+}/Cu(CN)_2^-$	1.12		
I_2	I_2/I^-	0.62	HL and SL	Liu et al. (2016), Xiu et al. (2015)
Fe^{3+}	Fe^{3+}/Fe^{2+}	0.77	MAL	Yazici and Deveci (2014)
$Fe(CN)_6^{3-}$	$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	0.36	CL (for Au-Ag ore)	Xie et al. (2008)

HL: halide leaching; AAL: ammonia-ammonium leaching; CL: cyanide-based leaching; SL: supercritical leaching; MAL: mineral acid leaching; TL: thiosulfate leaching; HL: halide leaching; IIL: ionic liquid leaching.

WPCBs recycling. Among them, O_2/air has low solubility in aqueous solution (about 8 ppm for O2 from air at 25 °C), which largely limits the leaching efficiency. H_2O_2, with a fairly high standard reduction potential (1.76 V), has been widely reported in WPCBs recycling. It does not bring any impurities to the system and is considered one of the most environmentally friendly oxidant, but can be quite expensive, depending on the location of use. However, it is easily decomposed (Galbács and Csányi, 1983), particularly in the presence of Fe^{3+} and Cu^{2+}, and is accordingly unrecyclable. In addition, Cu^{2+}, in the forms of $CuSO_4$ and $CuCl_2$, has also been intensively investigated as oxidant. It

will not add impurities since Cu is already present in WPCBs. I_2 has shown well oxidizing ability in iodine-iodide leaching system (Table S3). It can act as both oxidant and lixiviant, since the reduced form, I^-, can complex with metals, Au in particular (Sahin et al., 2015; Xiu et al., 2015). Compared with other halogens, iodine forms most stable complex with Au and is considered less corrosive and toxic. Hence, in the future research, it is an optimistic hope that I_2 can be used in more leaching systems. The use of Fe^{3+}, in the forms of $Fe_2(SO_4)_3$, as oxidant is restricted in acidic environment, another novel oxidant, $Fe(CN)_6^{3-}$, which has been reported for Au-Ag ore extraction, may be an potential substitute for alkaline environment. Besides, other novel oxidant with higher efficient should also be developed and the combination of different oxidants to make them work synergistically can also be considered.

5. Purification and recovery of metals from leaching solution

Through the leaching process, metals in WPCBs are transferred into solution. To make final metal products, the leaching solution needs to be further treated for purification and recovery. There are various methods have been proposed, including cementation, ion exchange, carbon adsorption, solvent extraction and electrowinning. The selection of downstream purification and recovery method is essentially determined according to the reagents system used for leaching process, the metal contents in leaching solution, and the categories of target metals and impurities (Tuncuk et al., 2012).

5.1. Cementation

Usually, metals exhibiting strong reduction potential can act as reductant to cement those with relatively lower reduction potential. In particular, base metals like metallic Fe, Zn, Al and Cu are used to replace precious metals in solution (Wu et al., 2017). This process includes cathodic cementation of target metals and anodic corrosion of reductant, which occur at the surface of reductant particles.

Concerning the cementation of metals from the leaching solution of

WPCBs, it can happen in acidic solution derived from mineral acid leaching, thiourea leaching, *etc*. or alkaline solution derived from cyanide-based leaching, thiosulfate leaching and ammonia-ammonium leaching. A widely experienced problem during cementation is the passivation of cementing metal surface by forming a layer of metal oxide or hydroxide inhibiting the further redox reaction. In addition, in acidic environment, the large consumption of cementing metal and the generation of H_2, which is hardly avoided, are also significant disadvantages (Gurung et al., 2013). Moreover, the excess addition of cementing metal will also present in the cement residue reducing the grade of target metal. According, the oxidised cementing metal-ion in mother solution also needs to be removed and recycled in the downstream process.

The benefit from the high affinity of Zn for the cyanide-ion and the low standard reduction potential of $Zn(CN)_4^{2-}/Zn$ (-1.34 V), Zn cementation, also known as Merrill-Crowe Process, has been commercially used for recovering Au and Ag from cyanide solutions since the 1890s. It can easily get Au precipitated from the cyanide leaching solution of WPCBs as the reactions shown in Eqs. (19) and (20). It was reported that the Zn cementation is practically constant over the pH 8–11 in cyanide solution. However, practice has shown that when the cyanide concentration is reduced too low, the reactions may get passivated by forming a layer of $Zn(OH)_2$ on the surface of Zn particles. In addition, impurities, such as Pb, Cu, Ni, As, Sb and S, are most deleterious for Au cementation (Cui and Zhang, 2008), which implies a impurities removal step may need to be conducted prior to Zn cementation. Birloaga and Vegliò (2016) used Zn powders to recover Cu from the sulfuric leaching solution of WPCBs. The Cu recovery of 99.76% was achieved by introducing Zn with an amount 50% higher than the stoichiometric ratio, and there was significant proportion of Zn (17%) presented in the cement that needs to be further removed.

$$Cathode: Au(CN)_2^- + e^- \rightarrow Au + 2CN^-, E° = -0.60 \quad V \tag{19}$$

$$Anode: Zn(CN)_4^{2-} + 2e^- \rightarrow Zn + 4CN^-, E° = -1.34 \quad V \tag{20}$$

Deveci et al. (2016) compared the performance of Al, Zn and Cu used for the cementation of Ag from sulfuric leaching solution of WPCBs. High Ag recoveries (> 90%) was achieved using metallic Cu and Zn whereas Al yielded only 40.4% Ag recovery at even 2000-fold stoichiometric excess of dosage possibly due to the passivation of Al surface of oxide film (Deveci et al., 2016). Alam et al. (2007) used Cu powder to selectively cement Ag over Co, Ni, Zn and Cu from ammoniacal alkaline solution simulating the ammonia-ammonium leaching solution of WPCBs, according to Eq. (21). The results indicate more than 99.5% of Ag was selectively cemented at Cu°/Ag (I) molar ratio of 6 for 45 min. It was also found that increasing temperature had a negative effect on the Ag cementation for the possible passivation at high temperature. In addition, Mpinga et al. (2014) evaluated the use of Merrill-Crowe cementation for the recovery of platinum group metals from their cyanide complexes.

$$Ag(NH_3)_2^+ + Cu \rightarrow Cu(NH_3)_2^+ + Ag, \Delta G_{298K}^O = -45.8 \text{kJ/mol} \tag{21}$$
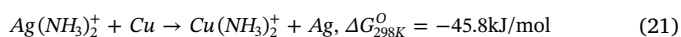
5.2. Chemical precipitation (except cementation)

One of the most common method of precipitating metal-ions from solution is pH adjusting by introducing alkali (NaOH, lime, *etc*.). Yang et al. (2017) used NaOH to stepwise adjust the pH of the acidic leaching solution obtained from the pre-treatment of WPCBs. About 99% of the Sn, Pb, Fe, Cu, and Zn were precipitated at the pH values of 1.5 for Sn, 3 for Fe, 6 for Cu, and 8 for Zn, respectively, and the SO_4^{2-}/Pb^{2+} molar ratio of 1.4 for the precipitation of Pb as $PbSO_4$. In addition, Yazici et al. (2014) suggested that pH of 4–7.5 and 9.5 were suitable for the removal of ferric-ferrous irons and precipitation of Cu^+ from a synthetic leaching solution (with Au and Pd previously removed), respectively. However, the considerable co-precipitation of Cu and Ag also occurred

during the removal of Fe with 41% Cu and 46% Ag co-precipitated along with 100% Fe at pH of 4. Taking into account the complex metal compositions of the WPCBs leaching solution, how to upgrade the precipitated products in economic way will be challenging. Also, this method will inevitably lead to large amount of alkali consumed by the neutralization and the soluble sulphates, $NaSO_4$ in particular, remained in mother solution needs to be recycled even not much profitable.

Behnamfard et al. (2013) used sodium borohydride ($NaBH_4$) to recover Au and Ag from WPCBs thiourea leaching solution (with Cu previously removed) as native forms, with 100% Au and Ag precipitated by 8 g/L $NaBH_4$ at room temperature for only 15 min, which seems to be an promising alternative to Zn cementation. Due to the insoluble property of AgCl (Ksp = 1.77×10^{-10}), Joda and Rashchi (2012) used NaCl to precipitate Ag^+ from HNO_3 leaching solution of WPCBs with 87.3% Ag selectively recovered. Besides, some novel methods, such as oxalate precipitation (Ryu et al., 2014) and solvent displacement crystallisation (Yazici and Deveci, 2016), have also been reported for the recovery of metals from WPCBs leaching solution, which needs to be further studied in terms of viability, selectivity and downstream upgrading process.

5.3. Solvent extraction

Solvent extraction has been widely discussed for the metals recovery from solutions. It has the advantages of good selectivity and mild reaction conditions. While, it also accompanies with high consumption rates particularly in the case of WPCBs that has a significantly high grade of metals, and at the end of the extraction, a reverse extraction process must occur (Wu et al., 2017). Table 5 lists the details of the solvent extraction of metals form WPCBs leaching solution. LIX series (LIX 84, LIX984N and LIX84IC) has been used to extract Cu in acidic environment with a satisfactory extraction rate (> 99%) achieved. Oishi et al. (2007) also used LIX 26 for the impurities removal from ammonia-ammonium leaching solution of WPCBs, and > 95% impurities (Zn, Pb, Mn, Ni and Fe) were removed favouring the following recovery of Cu. As for precious metals recovery, although very few studies have been reported in the case of WPCBs leaching solution, a number of systems has been investigated regarding other sources of solution, including organophosphorus derivatives, guanidine derivations, and mixture of amines-organophosphorous derivatives (Wu et al., 2017), that may also be effective in WPCBs leaching solution. Cui and Zhang (2008) compared the extractants on the aurocyanide complex extraction, and concluded that LIX-79 extractant allowed Au extraction from alkaline cyanide media, which can be potentially used in the cyanide-based leaching solution of WPCBs. Tanda et al. (2017) have shown that diketones and oxime lixiviants can be used effectively to extract copper from alkaline glycinate solutions while leaving the glycinate in the aqueous raffinate after copper extraction.

5.4. Activated carbon adsorption

Activated carbon, as one of the most common adsorbent used for Au and Ag recovery, has been shown fast adsorption rate, large adsorption capacity, relatively high Au selectivity and ease of elution (Bryson, 1995). With such advantages, activated carbon adsorption has been successfully applied in Au and Ag recovery from cyanide leaching solution, typically represented by carbon-in-pulp (CIP) and carbon-in-leach (CIL) technologies (Snyders et al., 2017). The mechanism and kinetics of carbon adsorption haven been extensively investigated by many researchers in terms of different solution media (Adams, 1990; Navarro et al., 2006; Rees and Van Deventer, 2001; Rees et al., 2001; Syna and Valix, 2003; Van Deventer, 1986; Zhang et al., 2004). Since activated carbon can also partially adsorb base metal (*e.g.* Cu, Zn, Fe, and Ni) ions, a previous step is often required before using it for Au and Ag recovery. It is reported that 98% Au could be adsorbed from iodine-iodide leaching solution of WPCBs (with base metals previously

Table 5
Solvent extraction of metals from leaching solution of WPCBs.

Feed solution from WPCBs leaching	Target metal	Extractant	Con.	Diluent	pH	Extraction	Ref.
Chloride leach solution (Pd enriched)	Pd	Diisoamyl sulfide (S201)	10%	N-dodecane	–	99.4%	Zhang and Zhang (2014)
Ammonia-ammonium leach solution	Cu	LIX 84	50%	Kerosene	10	99.6%	Yang et al. (2012)
Ammonia-ammonium leach solution	Impurities (Zn, Pb, Mn, Ni, Fe)	LIX 26	15%	Shellsol D70	–	95~% impurities	Oishi et al. (2007)
HNO_3 leach solution	Cu	LIX 984 N	50%	Kerosene	1.5	99.7%	Long Le et al. (2011)
H_2SO_4 leach solution	Cu	LIX 84IC	10%	Kerosene	2.5	99.99%	Kumari et al. (2016)
HBF_4 leach solution	Cu	CP-150	20%	Kerosene	3	99.99%	Kavousi et al. (2017)
Synthetic solution	Zn, Cu, Ni	Cyanex 272	0.1M	Hexane	2.5, 4.5, 12	96.7%Zn, 99.2%Cu, 97.2%Ni	Bari et al. (2009)

leached) by using 1 g/L–75 μm active carbon at 20 °C for 30 min (Altansukh et al., 2016). Activated carbon is however poorly suited to solutions with high copper (cyanide) concentrations due to copper co-loading and requiring excessive carbon transfer rates between CIL tanks. Tauetsile et al. (2018a,b) have shown that activated carbon can also be effectively used to recover Au and Cu from alkaline glycinate solutions, thereby augmenting the alkaline glycine leach approach used for these metals.

5.5. Ion exchange by resin

Compared with activated carbon, adsorption based on ion exchange often has higher adsorption and Au recovery rates. It's desorption and regeneration can be conducted under ambient pressures and temperatures. Additionally, mechanical strength, breakage rate and abrasion resistance of the resin used for ion exchange are significantly lower than those of activated carbon (Wu et al., 2017). As a potential alternative to activated carbon, Gurung et al. (2013) reported a novel biosorbent, crosslinked persimmon tannin gel (CPT gel), for selective adsorption of Au and Ag from thiourea leaching solution of WPCBs, which showed higher selectivity and better adsorption for Ag compared with activated carbon. Zhang and Dreisinger (2004) tested three gel-type resins including Dowex G51, Dowex 21K and amberlite IRA-410 for Au recovery from ammoniacal thiosulfate solution. The results indicate that, in the absence of Cu, Au can be rapidly loaded and to high loading concentrations, while in the presence of Cu, effective adsorption can only be operated under limited conditions due to the instability of the thiosulfate solution and the possible formation of poisoning polythionates. However, Kim et al. (2011b) used Amberlite XAD-7HP to adsorb Au from chlorine leaching solution of WPCBs. Although a small amount of Cu was also co-loaded with Au, they used different elution conditions to separate them successfully, i.e. 1.0 mol/L HCl in acetone for Au elution and 0.1 mol/L HCl for Cu elution.

Another adsorption gel, bisthiourea modified persimmon tannin (BTU-PT), reported by Gurung et al. (2012) showed outstanding selectivity for precious metals over base metals owing to the coordination/chelation effect by the thiocarbonyl group. Moreover, by combination of CPT gel and BTU-PT gel, they reported that 100% Au^{3+} could be exclusively adsorbed by CPT gel over other precious and base metals from chloride leaching solution of WPCBs, and Pd were then selectively adsorbed by BTU-PT gel from the Au-free solution. In addition, Fırlak et al. (2014) prepared a new thiol-ene hydrogel and tested its adsorption ability to Au^{3+} from aqua regia leaching solution of WPCBs with, however, only 71.4% Au^{3+} adsorbed under the experimental conditions.

Since both base and precious metals are usually presented in the leaching solution of WPCBs, to achieve higher selectivity of ion exchange, other novel or new resin should also be developed, especially with modified by foundational groups.

5.6. Electrodeposition

From the environmental and economic points of view, electrodeposition has overwhelming superiority in comparison to other purification methods mentioned above as it utilizes simple electric device and requires minimal chemical input. Nevertheless, the drawback of this method is the selectivity. It is almost not possible to perform a selective electrodeposition from a solution containing different metals (Lekka et al., 2015), particularly from the leaching solution of WPCBs. A realistic way is taking it as a final step for the manufacture of fairly pure metal with other metals previously removed, usually following solvent extraction or activated carbon adsorption step that has high selectivity (Joda and Rashchi, 2012; Long Le et al., 2011; Oishi et al., 2007).

However, some attention has been paid on the selective electrodeposition of WPCBs leaching solution by controlling electrochemical parameters. Lekka et al. (2015) investigated the feasibility of electrodepositing Au directly from aqua regia leaching solution of WPCBs prior to recovering any other metals. The results show that it was possible to electrodeposit Au selectively at 0.55 V (vs. Ag/AgCl/KCl$_{3M}$) with competitive Cu^{2+} reduced to soluble $CuCl_2^-$. Kasper et al. (2016) reported that 99% Au could be selectively deposited over Cu from ammoniacal thiosulphate leaching solution of WPCBs by controlling potential in a range between −400 and −500 mV (vs Ag/AgCl). In addition, Mecucci and Scott (2002) proved the feasibility of making Cu^{2+} and Pb^{2+} deposited as Cu° and PbO_2 onto cathode and anode respectively from HNO_3 leaching solution of WPCBs (with Sn previously removed).

Besides, some researchers also used direct electrodeposition for the Sn and Cu recovery from the acidic striping solution of WPCBs which has more simple metal compositions (e.g. Sn, Cu and Fe) than the leaching solution of the complete boards, while the results still reveal the interference of impurities (e.g. Fe^{3+}) (Silva-Martinez and Roy, 2013) and unsatisfactory recovery of Sn (Li et al., 2014a).

In recent years, there are also some novel electrochemical processes coupling with leaching of WPCBs or other purification methods which seem to be effective for the electrodeposition of metals. Diaz et al. (2016) packed milled WPCBs into a column bed then leached with acidic Fe^{3+} (as oxidant) solution. The obtained leaching solution was pumped to electro-reactor for the deposition of Cu, Sn, Ni, Fe, Zn and Pb all together, and regeneration of Fe^{3+} for reuse, which implies in situ generation of reagents could be an effective way to reduce materials input by consuming electricity. Zhu et al. (2014) reported a electrochemical process combining in situ chlorine leaching of WPCBs, ion

exchange by membranes, purification of Cu by solvent extraction and electrodeposition of high purity Cu. In the future research, the combination of electrodeposition, *in situ* leaching and other purification methods can be focused, while the balance between the complexity of the process and a high purity product should be carefully considered.

6. Outlook

Primary metal resources are limited and non-renewable. The importance of establishing a global society with closed-loop material streams has been widely recognised. E-waste, as a valuable resource, can be problematic in any country and district where people use electric and electronic products, particularly when the traditional developing countries, the final destination of e-waste, are shrinking their importing regulations and policies (Lee et al., 2018). The current problems existing in e-waste recycling, such as ineffective legislation, low collection rates, active illegal transportation and thriving informal sector, keep reminding us there is still a long way to go in the area of e-waste recycling. WPCBs represent one of the most complicated component of e-waste in terms of structure and compositions, its sustainable recycling is accordingly of great challenge. To achieve a sound recycling system, it is necessary to connect all the parts involved in the WPCBs' material stream, including PCB designers, manufactures, waste collectors, primary recyclers, and professional recovery companies. Accordingly, the recycling-oriented design, extended producer responsibility (EPR), sustainable e-waste management have been intensively discussed in recent years (Hagelüken and Corti, 2010; Institute, 2017) and are expected to be the future focuses of WPCBs recycling. In addition, the latest information technology, such as big data, and internet of things will also play a role in the WPCBs recycling process (Gu et al., 2017).

Among the reported processes of metals recovery from WPCBs, most of them focuses on the profitable metals, including Cu, Sn, Au, Ag and Pd. However, WPCB is a kind of waste containing more than 40 kinds of metals (Fig. 1), other metals with relatively less economic values and tiny contents (in ppm/ppb) are just neglected. As a result, the current recycling process is only a way to make one kind of waste become another one with less hazard, which is obviously not the expectation for a sustainable process. Considering the complexity of WPCBs, it is difficult to achieve a complete recovery by using one kind of leaching or purification method, it can be forecasted that more novel process using hybrid methods will be developed, and new methods involving interdisciplinary technologies could be the future trend of this area. In addition, all recycling processes should be evaluated for their water balances and the practicality of reagent recycle. Leach residues and precipitates need to be evaluated if they are sufficiently benign to be disposed of in landfill. Solid-liquid separation technologies can add large capital costs to enable the required recycling. The use of organic solvent can be particularly problematic as is the use of volatile reagents in the proximity of urban neighbourhoods.

7. Conclusions

The present work reviews the current status of metals recovery from WPCBs in hydrometallurgical process and gives the discussions and perspectives regarding various proposed methods. The general conclusions drawn from this review are as follows:

- PCBs have complicated composition containing various metals and organics, and intrinsic structures laminated in layers, which makes them challenging to be recycled. These information should be referred when a sustainable recycling process is to be developed.
- For a large-scale hydrometallurgical process, the mechanic-physical methods used for disassembly and size reduction will continue being dominantly used in the pre-treatment of WPCBs since it favours the downstream leaching process, has low costs and does not involve harmful chemicals.

- Traditional and mild leaching methods cannot meet the requirements in the environmental, economic and technic aspects. More attention should be paid on developing novel leaching methods using environmentally benign and easily recycled lixiviant and oxidant. Taking into account the complicated metal compositions in WPCBs, to simplify the downstream purification process, selective leaching in multi-stages should be considered.
- Suitable methods for the purification and recovery of metals from leaching solution should be decided based on the specific leaching solution. It is almost not possible to separate and recover metals by one kind of method, hence employing hybrid processes and developing novel processes will be the trend of this area.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.resconrec.2018.08.007.

References

Adams, M., 1990. The mechanism of adsorption of aurocyanide onto activated carbon, 1. Relation between the effects of oxygen and ionic strength. Hydrometallurgy 25 (2), 171–184.

Akcil, A., et al., 2015. Precious metal recovery from waste printed circuit boards using cyanide and non-cyanide lixiviants–a review. Waste Manag. 45, 258–271.

Aksu, S., Doyle, F.M., 2001. Electrochemistry of copper in aqueous glycine solutions. J. Electrochem. Soc. 148 (1), B51–B57.

Alam, M.S., Tanaka, M., Koyama, K., Oishi, T., Lee, J.C., 2007. Electrolyte purification in energy-saving monovalent copper electrowinning processes. Hydrometallurgy 87 (1), 36–44.

Altansukh, B., Haga, K., Ariunbolor, N., Kawamura, S., Shibayama, A., 2016. Leaching and adsorption of gold from waste printed circuit boards using iodine-iodide solution and activated carbon. Eng. J. 20 (4).

Anand, A., Jha, M.K., Kumar, V., Sahu, R., 2013. Recycling of precious metal gold from waste electrical and electronic equipments (WEEE): a review. Proceedings of the XIII International Seminar on Mineral Processing Technology (MPT-2013). pp. 916–923.

Awasthi, A.K., Zeng, X., Li, J., 2016. Environmental pollution of electronic waste recycling in India: a critical review. Environ. Pollut. 211, 259–270.

Baldé, C.P., Wang, F., Kuehr, R., Huisman, J., 2015. The Global e-Waste Monitor – 2014. United Nations University (UNU), IAS-SCYCLE, Bonn, Germany.

Baldé, C.P., Forti, V., Gray, V., Kuehr, R., Stegmann, P., 2017. The Global e-Waste Monitor – 2017. United Nations University (UNU), International Telecommunication Union (ITU) & International Solid Waste Association (ISWA).

Bandyopadhyay, A., 2008. A regulatory approach for e-waste management: a cross-national review of current practice and policy with an assessment and policy recommendation for the Indian perspective. Int. J. Environ. Waste Manag. 2 (1), 26–39.

Barbosa-Filho, O., Monhemius, A.J., 1994. Iodide-thiocyanate Leaching System for Gold, Hydrometallurgy "94". Springer, Netherlands, Dordrecht, pp. 425–440.

Bari, M., Begum, M., Jamaludin, S., Hussin, K., 2009. Solvent extraction separation and recovery of copper, nickel and zinc from printed circuit board by Cyanex 272. Miner. Process. Extr. Metall. 118 (4), 227–234.

Bas, A.D., Deveci, H., Yazici, E.Y., 2014. Treatment of manufacturing scrap TV boards by nitric acid leaching. Sep. Purif. Technol. 130, 151–159.

Behnamfard, A., Salarirad, M.M., Veglio, F., 2013. Process development for recovery of copper and precious metals from waste printed circuit boards with emphasize on palladium and gold leaching and precipitation. Waste Manag. 33 (11), 2354–2363.

Birloaga, I., Vegliò, F., 2016. Study of multi-step hydrometallurgical methods to extract the valuable content of gold, silver and copper from waste printed circuit boards. J. Environ. Chem. Eng. 4 (1), 20–29.

Birloaga, I., Coman, V., Kopacek, B., Vegliò, F., 2014. An advanced study on the hydrometallurgical processing of waste computer printed circuit boards to extract their valuable content of metals. Waste Manag. 34 (12), 2581–2586.

Bisceglie, F., Civati, D., Bonati, B., Faraci, F.D., 2017. Reduction of potassium cyanide usage in a consolidated industrial process for gold recovery from wastes and scraps. J. Clean. Prod. 142, 1810–1818.

Bryson, A.W., 1995. Gold adsorption by activated carbon and resin. Miner. Process. Extr. Metall. Rev. 15 (1–4), 145–151.

Calgaro, C.O., et al., 2015. Fast copper extraction from printed circuit boards using supercritical carbon dioxide. Waste Manag. 45, 289–297.

Chai, L., Zhong, H., Zhang, C., Okido, M., Ichino, R., 1997. Study on selective dissolution of gold in alkaline thiourea media. J. Cent. South Univ. Technol. 4 (2), 79–83.

Chauhan, G., Pant, K., Nigam, K., 2015. Chelation technology: a promising green

approach for resource management and waste minimization. Environ. Sci. Processes Impacts 17 (1), 12–40.

Chauhan, G., Jadhao, P.R., Pant, K.K., Nigam, K.D.P., 2018. Novel technologies and conventional processes for recovery of metals from waste electrical and electronic equipment (WEEE): challenges & opportunities – a review. J. Environ. Chem. Eng. 6 (1), 1288–1304.

Chen, Y., Li, J., Chen, L., Chen, S., Diao, W., 2012. Brominated flame retardants (BFRs) in waste electrical and electronic equipment (WEEE) plastics and printed circuit boards (PCBs). Procedia Environ. Sci. 16, 552–559.

Chen, M., Huang, J., Ogunseitan, O.A., Zhu, N., Wang, Y.-m., 2015a. Comparative study on copper leaching from waste printed circuit boards by typical ionic liquid acids. Waste Manag. 41, 142–147.

Chen, M., Zhang, S., Huang, J., Chen, H., 2015b. Lead during the leaching process of copper from waste printed circuit boards by five typical ionic liquid acids. J. Clean. Prod. 95, 142–147.

Cui, H., Anderson, C., 2016. Literature review of hydrometallurgical recycling of printed circuit boards (PCBs). J. Adv. Chem. Eng. 6 (1), 142–153.

Cui, J., Forssberg, E., 2003. Mechanical recycling of waste electric and electronic equipment: a review. J. Hazard. Mater. 99 (3), 243–263.

Cui, J., Zhang, L., 2008. Metallurgical recovery of metals from electronic waste: a review. J. Hazard. Mater. 158 (2), 228–256.

Deveci, H., Yazici, E., Bas, A., 2016. Cementation of silver from synthetic leach solutions of waste of printed circuit boards (WPCB). IMPC 2016: XXVIII International Mineral Processing Congress Proceedings. pp. 1–9.

Diaz, L.A., Lister, T.E., Parkman, J.A., Clark, G.G., 2016. Comprehensive process for the recovery of value and critical materials from electronic waste. J. Clean. Prod. 125, 236–244.

Duan, H., Hou, K., Li, J., Zhu, X., 2011. Examining the technology acceptance for dismantling of waste printed circuit boards in light of recycling and environmental concerns. J. Environ. Manag. 92 (3), 392–399.

Eksteen, J.J., Oraby, E.A., 2014. A process for copper and/or precious metal recovery. US Patent 20160194734 A1.

Eksteen, J.J., Oraby, E.A., 2016. Process for selective recovery of chalcophile group elements. PCT/AU2016/050171.

Ficeriová, J., Baláž, P., Gock, E., 2011. Leaching of gold, silver and accompanying metals from circuit boards (PCBs) waste. Acta Montan. Slovaca 16 (2), 128.

Fırlak, M., Yetimoğlu, E.K., Kahraman, M.V., 2014. Adsorption of Au (III) ions from aqueous solutions by thiol-ene photoclick hydrogels and its application to electronic waste and geothermal water. J. Water Process Eng. 3, 105–116.

Galbács, Z.M., Csányi, L.J., 1983. Alkali-induced decomposition of hydrogen peroxide. J. Chem. Soc. Dalton Trans. 0, 2353–2357.

Gary, M.L., Paul, S.J., Donald, T.A., 2014. Inorganic Chemistry, 5th edition. .

Ghosh, B., Ghosh, M., Parhi, P., Mukherjee, P., Mishra, B., 2015. Waste printed circuit boards recycling: an extensive assessment of current status. J. Clean. Prod. 94, 5–19.

Gu, F., Ma, B., Guo, J., Summers, P.A., Hall, P., 2017. Internet of things and Big Data as potential solutions to the problems in waste electrical and electronic equipment management: an exploratory study. Waste Manag. 68, 434–448.

Guo, J., Guo, J., Xu, Z., 2009. Recycling of non-metallic fractions from waste printed circuit boards: a review. J. Hazard. Mater. 168 (2), 567–590.

Gurung, M., et al., 2012. Selective recovery of precious metals from acidic leach liquor of circuit boards of spent mobile phones using chemically modified persimmon tannin gel. Ind. Eng. Chem. Res. 51 (37), 11901–11913.

Gurung, M., et al., 2013. Recovery of gold and silver from spent mobile phones by means of acidothiourea leaching followed by adsorption using biosorbent prepared from persimmon tannin. Hydrometallurgy 133, 84–93.

Hadi, P., Xu, M., Lin, C.S., Hui, C.-W., McKay, G., 2015. Waste printed circuit board recycling techniques and product utilization. J. Hazard. Mater. 283, 234–243.

Hagelüken, C., Corti, C.W., 2010. Recycling of gold from electronics: cost-effective use through 'Design for recycling'. Gold Bull. 43 (3), 209–220.

Herat, S., 2008. Environmental impacts and use of brominated flame retardants in electrical and electronic equipment. Environmentalist 28 (4), 348–357.

Hilson, G., Monhemius, A.J., 2006. Alternatives to cyanide in the gold mining industry: what prospects for the future? J. Clean. Prod. 14 (12), 1158–1167.

House, J.E., 2008. Inorganic Chemistry, 1st ed. Academic Press, Burlington, USA.

Huang, J., Chen, M., Chen, H., Chen, S., Sun, Q., 2014. Leaching behavior of copper from waste printed circuit boards with Brønsted acidic ionic liquid. Waste Manag. 34 (2), 483–488.

Institute, C.H.E.A.R, 2017. White Paper on WEEE Recycling Industry in China – 2016.

Jadhao, P., Chauhan, G., Pant, K., Nigam, K., 2016. Greener approach for the extraction of copper metal from electronic waste. Waste Manag. 57, 102–112.

Jadhav, U., Hocheng, H., 2015. Hydrometallurgical recovery of metals from large printed circuit board pieces. Sci. Rep. 5, 14574.

Jha, M.K., et al., 2011. Pressure leaching of metals from waste printed circuit boards using sulfuric acid. JOM 63 (8), 29–32.

Jha, M.K., et al., 2012. Leaching of lead from solder material of waste printed circuit boards (PCBs). Hydrometallurgy 121, 28–34.

Joda, N.N., Rashchi, F., 2012. Recovery of ultra fine grained silver and copper from PC board scraps. Sep. Purif. Technol. 92, 36–42.

Jung, M., Yoo, K., Alorro, R.D., 2017. Dismantling of electric and electronic components from waste printed circuit boards by hydrochloric acid leaching with stannic ions. Mater. Trans. 58 (7), 1076–1080.

Kasper, A.C., Carrillo Abad, J., Garcia Gabaldon, M., Veit, H.M., Perez Herranz, V., 2016. Determination of the potential gold electrowinning from an ammoniacal thiosulphate solution applied to recycling of printed circuit board scraps. Waste Manag. Res. 34 (1), 47–57.

Kavousi, M., Sattari, A., Alamdari, E.K., Firozi, S., 2017. Selective separation of copper over solder alloy from waste printed circuit boards leach solution. Waste Manag. 60, 636–642.

Kaya, M., 2016. Recovery of metals and nonmetals from electronic waste by physical and chemical recycling processes. Waste Manag. 57, 64–90.

Kiddee, P., Naidu, R., Wong, M.H., 2013. Electronic waste management approaches: an overview. Waste Manag. 33 (5), 1237–1250.

Kim, E.-y., Kim, M.-s., Lee, J.-c., Jeong, J., Pandey, B., 2011a. Leaching kinetics of copper from waste printed circuit boards by electro-generated chlorine in HCl solution. Hydrometallurgy 107 (3), 124–132.

Kim, E.-y., Kim, M.-s., Lee, J.-c., Pandey, B., 2011b. Selective recovery of gold from waste mobile phone PCBs by hydrometallurgical process. J. Hazard. Mater. 198, 206–215.

Kobayashi, S., Hiroishi, K., Tokunoh, M., Saegusa, T., 1987. Chelating properties of linear and branched poly(ethylenimines). Macromolecules 20 (7), 1496–1500.

Koyama, K., Tanaka, M., Lee, J.-c., 2006. Copper leaching behavior from waste printed circuit board in ammoniacal alkaline solution. Mater. Trans. 47 (7), 1788–1792.

Kumar, M., Lee, J.-c., Kim, M.-S., Jeong, J., Yoo, K., 2014. Leaching of metals from waste printed circuit boards (WPCBs) using sulfuric and nitric acids. Environ. Eng. Manag. J. 13 (10).

Kumari, A., Jha, M.K., Lee, J.-c., Singh, R.P., 2016. Clean process for recovery of metals and recycling of acid from the leach liquor of PCBs. J. Clean. Prod. 112, 4826–4834.

Lacoste-Bouchet, P., Deschênes, G., Ghali, E., 1998. Thiourea leaching of a copper-gold ore using statistical design. Hydrometallurgy 47 (2), 189–203.

Lee, D., Offenhuber, D., Duarte, F., Biderman, A., Ratti, C., 2018. Monitour: tracking global routes of electronic waste. Waste Manag. 72, 362–370.

Lekka, M., Masavetas, I., Benedetti, A., Moutsatsou, A., Fedrizzi, L., 2015. Gold recovery from waste electrical and electronic equipment by electrodeposition: a feasibility study. Hydrometallurgy 157, 97–106.

Li, Y., Wong, C., 2006. Recent advances of conductive adhesives as a lead-free alternative in electronic packaging: materials, processing, reliability and applications. Mater. Sci. Eng. R Rep. 51 (1), 1–35.

Li, J., Shrivastava, P., Gao, Z., Zhang, H.-C., 2004. Printed circuit board recycling: a state-of-the-art survey. IEEE Trans. Electron. Packag. Manuf. 27 (1), 33–42.

Li, B., et al., 2014a. Recovery of copper and tin from stripping tin solution by electro-deposition. Rare Met. 33 (3), 353–357.

Li, L., et al., 2014b. Optimisation of efficient auxiliary agents of gold leaching in an alkaline thiourea solution for a finely disseminated gold ore. Int. J. Min. Miner. Eng. 5 (4), 315–327.

Li, J., Zeng, X., Chen, M., Ogunseitan, O.A., Stevels, A., 2015. "Control-Alt-Delete": rebooting solutions for the e-waste problem. Environ. Sci. Technol. 49 (12), 7095–7108.

Li, J., He, X., Zeng, X., 2017. Designing and examining e-waste recycling process: methodology and case studies. Environ. Technol. 38 (6), 652–660.

Lim, Y., Kwon, O.-h., Lee, J., Yoo, K., 2013. The ammonia leaching of alloy produced from waste printed circuit boards smelting process. Geosyst. Eng. 16 (3), 216–224.

Liu, J., Kao, T.-H., 2003. Extraction of Cu and Pb from printed circuit board sludge using ammonia solutions. Water Sci. Technol. 47 (1), 167–172.

Liu, R., Shieh, R., Yeh, R.Y., Lin, C., 2009. The general utilization of scrapped PC board. Waste Manag. 29 (11), 2842–2845.

Liu, K., Zhang, Z., Zhang, F.-S., 2016. Direct extraction of palladium and silver from waste printed circuit boards powder by supercritical fluids oxidation-extraction process. J. Hazard. Mater. 318, 216–223.

Long Le, H., et al., 2011. Hydrometallurgical process for copper recovery from waste printed circuit boards (PCBs). Miner. Process. Extr. Metall. Rev. 32 (2), 90–104.

Lu, Y., Xu, Z., 2016. Precious metals recovery from waste printed circuit boards: a review for current status and perspective. Resour. Conserv. Recycl. 113, 28–39.

Luda, M.P., 2011. Recycling of printed circuit boards. Integrated Waste Management-Volume II. InTech.

Marques, A.C., Cabrera, J.-M., de Fraga Malfatti, C., 2013. Printed circuit boards: a review on the perspective of sustainability. J. Environ. Manag. 131, 298–306.

Mecucci, A., Scott, K., 2002. Leaching and electrochemical recovery of copper, lead and tin from scrap printed circuit boards. J. Chem. Technol. Biotechnol. 77 (4), 449–457.

Melo Halmenschlager Petter, P., Veit, H.M., Moura Bernardes, A., 2015. Leaching of gold and silver from printed circuit board of mobile phones. Rem: Rev. Esc. Minas 68 (1).

Mohan, D., Chander, S., 2006. Single, binary, and multicomponent sorption of iron and manganese on lignite. J. Colloid Interface Sci. 299 (1), 76–87.

Montero, R., Guevara, A., dela Torre, E., 2012. Recovery of gold, silver, copper and niobium from printed circuit boards using leaching column technique. J. Earth Sci. Eng. 2 (10), 590.

Mpinga, C.N., Bradshaw, S.M., Akdogan, G., Snyders, C.A., Eksteen, J.J., 2014. Evaluation of the Merrill-Crowe process for the simultaneous removal of platinum, palladium and gold from cyanide leach solution. Hydrometallurgy 142, 36–46.

Mpinga, C., Eksteen, J., Aldrich, C., Dyer, L., 2015. Direct leach approaches to Platinum Group Metal (PGM) ores and concentrates: a review. Miner. Eng. 78, 93–113.

Navarro, P., Vargas, C., Alonso, M., Alguacil, F., 2006. The adsorption of gold on activated carbon from thiosulfate-ammoniacal solutions. Gold Bull. 39 (3), 93–97.

Nelson, D., Scott, S., Doostmohammadi, M., Jafari, H., 2017. Methods, materials and techniques for precious metal recovery. US Patent 2017/0329967 A1.

Ning, C., Lin, C.S.K., Hui, D.C.W., McKay, G., 2017. Waste printed circuit board (PCB) recycling techniques. Top. Curr. Chem. 375 (2), 43.

Nnorom, I.C., Osibanjo, O., 2009. Toxicity characterization of waste mobile phone plastics. J. Hazard. Mater. 161 (1), 183–188.

Ogunseitan, O.A., Schoenung, J.M., Saphores, J.-D.M., Shapiro, A.A., 2009. The electronics revolution: from e-wonderland to e-wasteland. Science 326 (5953), 670–671.

Oh, C.J., Lee, S.O., Yang, H.S., Ha, T.J., Kim, M.J., 2003. Selective leaching of valuable metals from waste printed circuit boards. J. Air Waste Manag. Assoc. 53 (7), 897–902.

Oishi, T., Koyama, K., Alam, S., Tanaka, M., Lee, J.-C., 2007. Recovery of high purity copper cathode from printed circuit boards using ammoniacal sulfate or chloride solutions. Hydrometallurgy 89 (1), 82–88.

Oraby, E.A., Eksteen, J.J., 2014. The selective leaching of copper from a gold–copper concentrate in glycine solutions. Hydrometallurgy 150, 14–19.

Oraby, E.A., Eksteen, J.J., 2015. The leaching of gold, silver and their alloys in alkaline glycine–peroxide solutions and their adsorption on carbon. Hydrometallurgy 152, 199–203.

Oraby, E.A., Eksteen, J.J., 2016. Gold dissolution and copper suppression during leaching of copper–gold gravity concentrates in caustic soda-low free cyanide solutions. Miner. Eng. 87, 10–17.

Oraby, E.A., Eksteen, J.J., Tanda, B.C., 2017. Gold and copper leaching from gold-copper ores and concentrates using a synergistic lixiviant mixture of glycine and cyanide. Hydrometallurgy 169, 339–345.

Pant, D., Joshi, D., Upreti, M.K., Kotnala, R.K., 2012. Chemical and biological extraction of metals present in E waste: a hybrid technology. Waste Manag. 32 (5), 979–990.

Park, Y.J., Fray, D.J., 2009. Recovery of high purity precious metals from printed circuit boards. J. Hazard. Mater. 164 (2), 1152–1158.

Pérez-Belis, V., Bovea, M., Ibáñez-Forés, V., 2015. An in-depth literature review of the waste electrical and electronic equipment context: trends and evolution. Waste Manag. Res. 33 (1), 3–29.

Perrine, T., Landis, W., 1967. Analysis of polyethylenimine by spectrophotometry of its copper chelate. J. Polym. Sci. Polym. Chem. Ed. 5 (8), 1993–2003.

Petter, P., Veit, H., Bernardes, A., 2014. Evaluation of gold and silver leaching from printed circuit board of cellphones. Waste Manag. 34 (2), 475–482.

Rees, K., Van Deventer, J., 2001. Gold process modelling. I. Batch modelling of the processes of leaching, preg-robbing and adsorption onto activated carbon. Miner. Eng. 14 (7), 753–773.

Rees, K., Van Deventer, J., Dunne, R., 2001. Gold process modelling. II. The effect of ore type on leaching and adsorption dynamics at telfer gold mine. Miner. Eng. 14 (8), 887–900.

Reuter, M.A., Vans Schaik, A., Ballester, M., 2018. Limits of the circular economy: fairphone modular design pushing the limits. World Metall. Erzmetall. 71 (2), 68–79.

Ryu, S.-H., Ahn, J.-W., Ahn, H.-J., Kim, T.-Y., 2014. Recovery of tin and copper from waste solder stripper by oxalate precipitation. J. Korean Inst. Resour. Recycl. 23 (3), 37–43.

Sahin, M., et al., 2015. A potential alternative for precious metal recovery from e-waste: iodine leaching. Sep. Sci. Technol. 50 (16), 2587–2595.

Sanyal, S., et al., 2013. Understanding and optimizing delamination/recycling of printed circuit boards using a supercritical carbon dioxide process. J. Clean. Prod. 41, 174–178.

Sharma, N., Chauhan, G., Kumar, A., Sharma, S., 2017. Statistical optimization of heavy metals (Cu^{2+}/Co^{2+}) extraction from printed circuit board and mobile batteries using chelation technology. Ind. Eng. Chem. Res. 56 (23), 6805–6819.

Silva-Martinez, S., Roy, S., 2013. Copper recovery from tin stripping solution: galvanostatic deposition in a batch-recycle system. Sep. Purif. Technol. 118, 6–12.

Sjoberg, J., Nash, C., Sbiroli, D., Qu, W., 2016. High-density assembly and root cause analyses. Pan Pacific Microelectronics Symposium (Pan Pacific), 2016 1–6.

Snyders, C., Akdogan, G., Bradshaw, S., van Wyk, A., 2017. Gold CIP and CIL process optimization in a capital constraint environment. J. South. Afr. Inst. Min. Metall. 117 (8), 819–828.

Somasundaram, M., et al., 2014. Recovery of copper from scrap printed circuit board: modelling and optimization using response surface methodology. Powder Technol. 266, 1–6.

Song, Q., Li, J., 2014. Environmental effects of heavy metals derived from the e-waste recycling activities in China: a systematic review. Waste Manag. 34 (12), 2587–2594.

Sun, Z., et al., 2015. Selective copper recovery from complex mixtures of end-of-life electronic products with ammonia-based solution. Hydrometallurgy 152, 91–99.

Syed, S., 2012. Recovery of gold from secondary sources-a review. Hydrometallurgy 115, 30–51.

Syna, N., Valix, M., 2003. Modelling of gold (I) cyanide adsorption based on the properties of activated bagasse. Miner. Eng. 16 (5), 421–427.

Szałatkiewicz, J., 2014. Metals content in printed circuit board waste. Pol. J. Environ. Stud. 23 (6), 2365–2369.

Tanda, B.C., Oraby, E.A., Eksteen, J.J., 2017. Recovery of copper from alkaline glycine leach solution using solvent extraction. Sep. Purif. Technol. 187, 389–396.

Tang, S., Hui, S.R., Chung, H.-H., 2001. A low-profile power converter using printedcircuit board (PCB) power transformer with ferrite polymer composite. IEEE Trans. Power Electr. 16 (4), 493–498.

Tauetsile, P.J., Oraby, E.A., Eksteen, J.J., 2018a. Adsorption behaviour of copper and gold glycinates in alkaline media onto activated carbon. Part 1: isotherms. Hydrometallurgy 178, 202–208.

Tauetsile, P.J., Oraby, E.A., Eksteen, J.J., 2018b. Adsorption behaviour of copper and gold glycinates in alkaline media onto activated carbon. Part 2: kinetics. Hydrometallurgy 178, 195–201.

Tesfaye, F., Lindberg, D., Hamuyuni, J., et al., 2017. Valuable metals and energy recovery from electronic waste streams. In: Zhang, L. (Ed.), Energy Technology 2017: Carbon Dioxide Management and Other Technologies. Springer International Publishing, Cham, pp. 103–116.

Tripathi, A., et al., 2012. Leaching of gold from the waste mobile phone printed circuit boards (PCBs) with ammonium thiosulphate. Int. J. Metall. Eng. 1 (2), 17–21.

Tuncuk, A., Stazi, V., Akcil, A., Yazici, E.Y., Deveci, H., 2012. Aqueous metal recovery techniques from e-scrap: hydrometallurgy in recycling. Miner. Eng. 25 (1), 28–37.

Van Deventer, J., 1986. Competitive equilibrium adsorption of metal cyanides on activated carbon. Sep. Sci. Technol. 21 (10), 1025–1037.

Verma, H.R., Singh, K.K., Mankhand, T.R., 2016. Dissolution and separation of

brominated epoxy resin of waste printed circuit boards by using di-methyl formamide. J. Clean. Prod. 139, 586–596.

Wang, R., Xu, Z., 2014. Recycling of non-metallic fractions from waste electrical and electronic equipment (WEEE): a review. Waste Manag. 34 (8), 1455–1469.

Wang, J., Xu, Z., 2015. Disposing and recycling waste printed circuit boards: disconnecting, resource recovery, and pollution control. Environ. Sci. Technol. 49 (2), 721–733.

Wang, Y.-y., Chai, L.-y., Min, X.-b., He, D.-w., Peng, B., 2003. Optimization of efficient stable reagent of alkaline thiourea solution for gold leaching. J. Cent. South Univ. Technol. 10 (4), 292–296.

Wang, M., Cao, H., Zhang, Y., 2011. Selective recovery of copper, zinc and nickel from printed circuit boards by ammonia leaching under pressure (In Chinese). Environ. Sci. 32 (2), 596–602.

Wang, J., Guo, J., Xu, Z., 2016a. An environmentally friendly technology of disassembling electronic components from waste printed circuit boards. Waste Manag. 53, 218–224.

Wang, z., Zhang, B., Guan, D., 2016b. Take responsibility for electronic-waste disposal. Nature 536, 4.

Wang, H., et al., 2017. Recovery of waste printed circuit boards through pyrometallurgical processing: a review. Resour. Conserv. Recycl. 126, 209–218.

Wasserscheid, P., Keim, W., 2000. Ionic liquids—new "solutions" for transition metal catalysis. Angew. Chem. Int. Ed. 39 (21), 3772–3789.

Wei, D., Chai, L., Ichino, R., Okido, M., 1999. Gold leaching in an alkaline thiourea solution. J. Electrochem. Soc. 146 (2), 559–563.

Wu, Zebing, Yuan, Wenyi, Li, Jinhui, Wang, Xiaoyan, Liu, Lili, Wang, Jingwei, 2017. A critical review on the recycling of copper and precious metals from waste printed circuit boards using hydrometallurgy. Front. Environ. Sci. Eng. China 11 (5), 8.

Xiao, Y., et al., 2013. Hydrometallurgical recovery of copper from complex mixtures of end-of-life shredded ICT products. Hydrometallurgy 140, 128–134.

Xie, F., Dreisinger, D., Lu, J., 2008. The novel application of ferricyanide as an oxidant in the cyanidation of gold and silver. Miner. Eng. 21 (15), 1109–1114.

Xiu, F.-R., Qi, Y., Zhang, F.-S., 2015. Leaching of Au, Ag, and Pd from waste printed circuit boards of mobile phone by iodide lixiviant after supercritical water pretreatment. Waste Manag. 41, 134–141.

Xu, Y., Liu, J., 2015. Recent developments and perspective of the spent waste printed circuit boards. Waste Manag. Res. 33 (5), 392–400.

Xu, B., et al., 2017. A review of thiosulfate leaching of gold: focus on thiosulfate consumption and gold recovery from pregnant solution. Metals 7 (6), 222.

Yang, H., Liu, J., Yang, J., 2011a. Leaching copper from shredded particles of waste printed circuit boards. J. Hazard. Mater. 187 (1), 393–400.

Yang, X., et al., 2011b. Thiourea–thiocyanate leaching system for gold. Hydrometallurgy 106 (1), 58–63.

Yang, J.-g., Wu, Y.-t., Li, J., 2012. Recovery of ultrafine copper particles from metal components of waste printed circuit boards. Hydrometallurgy 121, 1–6.

Yang, C., Li, J., Tan, Q., Liu, L., Dong, Q., 2017. Green process of metal recycling: coprocessing waste printed circuit boards and spent tin stripping solution. ACS Sustain. Chem. Eng. 5 (4), 3524–3534.

Yazici, E., Deveci, H., 2013. Extraction of metals from waste printed circuit boards (WPCBs) in H2SO4-CuSO4-NaCl solutions. Hydrometallurgy 139, 30–38.

Yazici, E., Deveci, H., 2014. Ferric sulphate leaching of metals from waste printed circuit boards. Int. J. Miner. Process. 133, 39–45.

Yazici, E., Deveci, H., 2015. Cupric chloride leaching (HCl–CuCl 2–NaCl) of metals from waste printed circuit boards (WPCBs). Int. J. Miner. Process. 134, 89–96.

Yazici, E.Y., Deveci, H., 2016. Recovery of copper sulphate from sulphuric acid leach solutions via solvent displacement crystallisation using acetone. International Black Sea Mining & Tunnelling Symposium. pp. 455–460.

Yazici, E., Deveci, H., Ehsani, A., 2014. Recovery of metals from chloride leach solutions of waste of printed circuit boards by adsorption and precipitation, XXVII. Int. Mineral Processing Congress (IMPC 2014) 170–179.

Yildirir, E., Onwudili, J.A., Williams, P.T., 2015. Chemical recycling of printed circuit board waste by depolymerization in sub-and supercritical solvents. Waste Biomass Valori. 6 (6), 959–965.

Zhang, H., Dreisinger, D.B., 2004. The recovery of gold from ammoniacal thiosulfate solutions containing copper using ion exchange resin columns. Hydrometallurgy 72 (3), 225–234.

Zhang, L., Xu, Z., 2016. A review of current progress of recycling technologies for metals from waste electrical and electronic equipment. J. Clean. Prod. 127, 19–36.

Zhang, H., Ritchie, I.M., La Brooy, S.R., 2004. The adsorption of gold thiourea complex onto activated carbon. Hydrometallurgy 72 (3–4), 291–301.

Zhang, K., Schnoor, J.L., Zeng, E.Y., 2012a. E-waste recycling: where does it go from here? Environ. Sci. Technol. 46 (20), 10861–10867.

Zhang, Y., Liu, S., Xie, H., Zeng, X., Li, J., 2012b. Current status on leaching precious metals from waste printed circuit boards. Procedia Environ. Sci. 16, 560–568.

Zhang, J., et al., 2014. Dual lixiviant leaching process for extraction and recovery of gold from ores at room temperature. Hydrometallurgy 144–145, 114–123.

Zhang, X., et al., 2017. Effective dismantling of waste printed circuit board assembly with methanesulfonic acid containing hydrogen peroxide. Environ. Prog. Sustain. Energy 36 (3), 873–878.

Zhang, Z., Zhang, F.-S., 2014. Selective recovery of palladium from waste printed circuit boards by a novel non-acid process. J. Hazard. Mater. 279, 46–51.

Zheng, S., Wang, Y.-y., Chai, L.-y., 2006. Research status and prospect of gold leaching in alkaline thiourea solution. Miner. Eng. 19 (13), 1301–1306.

Zhou, L., Xu, Z., 2012. Response to waste electrical and electronic equipments in China: legislation, recycling system, and advanced integrated process. Environ. Sci. Technol. 46 (9), 4713.

Zhou, Y., Wu, W., Qiu, K., 2010. Recovery of materials from waste printed circuit boards by vacuum pyrolysis and vacuum centrifugal separation. Waste Manag. 30 (11),

30

2299–2304.

Zhu, P., Chen, Y., Wang, L., Zhou, M., 2012. Treatment of waste printed circuit board by green solvent using ionic liquid. Waste Manag. 32 (10), 1914–1918.

Zhu, P., et al., 2013a. A novel approach to separation of waste printed circuit boards using dimethyl sulfoxide. Int. J. Environ. Sci. Technol. 10 (1), 175–180.

Zhu, P., Chen, Y., Wang, L., Zhou, M., Zhou, J., 2013b. The separation of waste printed circuit board by dissolving bromine epoxy resin using organic solvent. Waste Manag. 33 (2), 484–488.

Zhu, P., et al., 2014. Extractive metals from metallic powders recovered from waste printed circuit boards. Can. Metall. Q. 53 (1), 74–81.

Supporting Information (Tables & References)

Hydrometallurgical recovery of metals from waste printed circuit boards (WPCBs): current status and perspectives – A review

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4 tables, 17 pages

Table S1 Chemical methods for the pre-treatment of WPCBs

Methods	Materials	Chemicals used	Temperature	Time	L/S ratio[b]	Results (optimal)	Ref.
Solder mask dissolving	4 × 4 cm dismantled WPCBs[a]	10 M NaOH	Room temperature	24 h	-[c]	Solder mask completely dissolved	(Jadhav and Hocheng, 2015)
Solder dissolving	WPCBs with ECs mounted by Sn-Pd solder	3.5 M methanesulfonic acid (MSA) and 0.5 M H_2O_2	20±2°C	45 min	-	Not specified	(Zhang et al., 2017)
	WPCBs with ECs mounted by Sn-alloy solder	1 M HCl and 13 g/L Sn^{4+} (oxidant)	90°C	30 min	13.4 mL/g	ECs completely dismantled	(Jung et al., 2017)
Organic swelling	7×7 cm dismantled WPCBs	N-methyl-2-pyrrolidone	Heating	Overnight	-	Making WPCBs swelled	(Jha et al., 2012)
Supercritical depolymerisation (of resin)	~2 mm dismantled WPCBs	Near critical water and NaOH	400°C	-	24 mL/g	94% resin removed	(Yildirir et al., 2015)
	~1 mm dismantled WPCBs	Supercritical methanol	300-420°C	30-120 min	10-30 mL/g	Metal contents upgraded to 62%	(Xiu and Zhang, 2010)

Process	Sample[a]	Size	Unit	Solvent	Temperature	Time	L/S ratio[b]	Result	Reference
Resin dissolving	Dismantled WPCBs	16	mm²	Dimethyl sulfoxide (under N_2)	145°C	60 min	7	Brominated epoxy resin (BER) completely separated	(Zhu et al., 2013b)
	dismantled WPCBs	15-20	cm²	Dimethyl sulfoxide	170°C	30 min	2	BER completely separated	(Zhu et al., 2013a)
	dismantled WPCBs	15-20	cm²	1-ethyl-3-methylimizadolium tetrafluoroborate ([EMIM⁺][BF₄⁻], ionic liquid)	260°C	10 min	5	BER completely dissolved	(Zhu et al., 2012)
	dismantled WPCB	1 × 1	cm	Di-methyl formamide	135°C	4 h	10:3 mL/g	Most of the BER dissolved	(Verma et al., 2016)

[a] dismantled WPCBs refer to the WPCBs with electronic components (ECs) removed; [b] L/S ratio denotes liquid-solid ratio; [c] "-" denotes not reported.

Table S2 Details of mineral acid leaching for metals extraction from WPCBs

Materials	Leaching agent	Temperature	Time	L/S ratio (LS)[b] or pulp density (PD)	Leaching rate (optimal)[d]	Ref.
Using mineral acid only						
NaOH pre-treated (for dissolving solder mask) 4×4 cm dismantled WPCBs[a]	1 M HCl, HNO$_3$ and H$_2$SO$_4$ used individually	Room temperature (RT)	22 h, 96 h and 96 h, respectively	-[c]	100% base (Cu, Zn, Sn, Ni, Pb, Fe, Al) and precious (Ag, Au, Pd) metals for both HCl and HNO$_3$; only 8.8% Cu for H$_2$SO$_4$	(Jadhav and Hocheng, 2015)
5 ×5 cm^2 WPCBs	4 M HNO$_3$	65°C	72 min	5 mL/g (LS)	98% Cu, 87% Ag	(Joda and Rashchi, 2012)
2~ mm pyrolysed WPCBs	4 M HNO$_3$	90°C	60 min	30 g/L (PD)	Complete leaching of Cu, Fe, Pb; 57.5% Ni	(Kumari et al., 2016b)
63-1000 µm WPCBs	3.5 M HNO$_3$	50°C	1 h	120 g/L (PD)	99% Cu	(Long Le et al., 2011)
~250 µm dismantled WPCBs from TV	2-3 M HNO$_3$	70°C	120 min	6% (PD)	88.5-99.9% Cu; 14-68% Ag (at 1-5 M HNO$_3$)	(Bas et al., 2014)

Feedstock	Reagent	Temperature	Time	S/L ratio	Results	Reference
90%<0.208 mm metallic fractions of WPCBs	a. 2.18 N H_2SO_4 b. 2.18 N H_2SO_4 and 3.0 N HCl c. 3.0 N HCl d. 3.0 N HCl and 1.0 N HNO_3	60±2°C	120 min	10 mL/g (LS)	a. 2.7% Sn, ~0.01% Cu b. 90.5% Sn, 12.3% Cu (2-stage) c. 89.1% Sn, 33.2% Cu d. 98% Sn, 93% Cu	(Castro and Martins, 2009)
0.5~ mm simulated WPCBs metal fractions without Cu	Fresh aqua regia (HCl: HNO_3=3:1, v/v)	20±2°C	3 h	20 mL/g (LS)	97% Au, about 2% Ag, 5.4% Pd; Most of Ag remained un-leached and Pd precipitated as $Pd(NH_4)_2Cl_6$.	(Park and Fray, 2009)
~2 mm pyrolysed WPCBs	2.4 M H_2SO_4 under 2 MPa pressure	150°C	90 min	100 g/L (PD)	Almost 99% Cu, Ni and Fe	(Kumari et al., 2016a)
~206 μm incinerated WPCBs	1 M H_2SO_4 under 2 MPa pressure	120°C	30 min	100 g/L (PD)	99.3% Cu, 82.3% Al, 61.2% Fe, 96.4% Zn	(Altansukh et al., 2016)
Using mineral acid and oxidant						
2-4 mm WPCBs	a. 3 M HNO_3 b. 1.2M H_2SO_4 and 10 vol.% H_2O_2	a. 90°C b. 50°C	a. 5 h b. 4 h	100 g/L (PD)	a. 96% Cu b. 75.5% Cu	(Kumar et al., 2014)
~2 mm dismantled WPCBs	2 M H_2SO_4 and 5% H_2O_2	25°C	3 h	10 mL/g (LS)	100% Cu	(Birloaga et al., 2014)

Feedstock	Reagents	Temperature	Time	Ratio	Recovery	Reference
~1 mm conducting and non-magnetic fractions of WPCBs[e]	2 M H_2SO_4 and 0.2M H_2O_2	85°C	12 h	100 mL/g (LS)	95~% Cu, Fe, Zn, Ni, and Al	(Oh et al., 2003)
7×7 cm organic swelled dismantled WPCBs	2 M H_2SO_4 and 15 vol.% H_2O_2 under oxygen pressure 20 bar	150°C	90 min	30 g/L (PD)	97.01% Cu	(Jha et al., 2011)
~500 μm WPCBs	3.92M H_2SO_4 and 3.93M H_2O_2	RT	3.7 h	6.98% (w/v, PD)	99.2% Cu	(Isildar et al., 2017)
~250 μm dismantled WPCBs	0.5 M H_2SO_4, and $CuSO_4$ and NaCl with Cl^-/Cu^{2+} ratio 21	80°C	-	100 mL/g (LS)	100% Cu; 58% Pd; >90% Fe, Ni and Ag	(Yazici and Deveci, 2013)
~250 μm dismantled WPCBs	0.05-1M H_2SO_4 and 0.05-0.5M $Fe_2(SO_4)_3$ with/without addition of NaCl, air/O_2 and H_2O_2	20-80°C	120 min	1-15% (w/v, solid ratio)	≥98% Cu, 93% Ni, 21.4% Ag and 69.4% Pd	(Yazici and Deveci, 2014)
Multi-stage leaching[f]						
~3 mm dismantled WPCBs	1st stage: 2M H_2SO_4 with H_2O_2 addition; 2nd stage: same with 1st stage	RT	3 h	About 10.4 mL/g (LS)	1st stage: 85.76% Cu; 2nd stage: 99~% Cu	(Behnamfard et al., 2013)

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Material	Reagents	Temperature	Time	L/S ratio	Results	Reference
~1 mm non-magnetic fraction of WPCBs	1st stage: 1M H_2SO_4; 2nd stage: keeping same with 1st stage, then adding H_2O_2 to about 13 vol.%	75°C	4 h	1st stage: 10 mL/g (LS); 2nd stage: not specified	1st stage: 90% Al, 40% Zn and 8.6% Sn; 2nd stage: 100% Cu, 60% Zn and 10% Al.	(Silvas et al., 2015)
WPCBs powders thermally pre-treated	1st stage: 0.1 M $CuCl_2$ and 3.0 M HCl; 2nd stage: 0.5 M $CuCl_2$ and 3.0 M HCl	1st stage: 25°C; 2nd stage: around 50°C	-	12 mL/g (LS)	1st stage: 92% Sn only (5.7% Cu, 6.9% Pb, 1.2% Ni); 2nd stage: leached out Cu, Pb and Ni	(Somasundaram et al., 2014)
7×7 cm organic swelled dismantled WPCBs with Cu pre-separated	1st stage: 0.2 M HNO_3; 2nd stage: 3.5 M HCl	90 °C	120 min	1st stage: 100 mL/g; 2nd stage: 20 mL/g	1st stage: 99.99% Pb; 2nd stage: 98.74% Sn	(Jha et al., 2012)

[a] dismantled WPCBs refer to the WPCBs with electronic components (ECs) removed; [b] L/S ratio denotes liquid-solid ratio (LS); [c] "-" denotes not reported; [d] unless specified, the leaching rate denotes the percentage of the metals leached from the WPCBs; [e] the materials were pre-treated by electrostatic and magnetic separation in sequence; [f] unless specified, the conditions listed for multi-stage are for each single stage.

Table S3 Details of mild leaching methods for metals extraction from WPCBs

Materials	Leaching agent	Temperature	Time	pH	L/S ratio (LS)[b] or pulp density (PD)	Leaching rate[d] (optimal)	Ref.
Thiosulfate leaching							
0.5-3.0 mm dismantled WPCBs from mobile phone (MP)	0.1 M $(NH_4)_2S_2O_3$ and 40 mM $CuSO_4$	RT	8 h	10-10.5	10 g/L (PD)	56.7% Au	(Tripathi et al., 2012)
Complete size of dismantled WPCBs[a] from MP	0.1 M $(NH_4)_2S_2O_3$ and 40 mM $CuSO_4$	RT	8 h	10-10.5	40 g/L (PD)	78.7% Au	(Tripathi et al., 2012)
~1mm dismantled WPCBs from MP	0.1 M $Na_2S_2O_3$, 0.2 M $NH_3 \cdot H_2O$ and 0.015-0.03 M $CuSO_4$	25±2°C	4 h	9-11.5	20:1 (L/S)	15% Au	(Petter et al., 2014)
Complete size of dismantled WPCBs from MP	0.1 M $Na_2S_2O_3$, 0.2 M $NH_3 \cdot H_2O$ and 0.1 M H_2O_2	25±2°C	4 h	9-11.5	20:1 (L/S)	11% Au	(Melo Halmenschlager Petter et al., 2015)
Complete size of dismantled WPCBs from MP	0.1 M $(NH_4)_2S_2O_3$, 0.2 M $NH_3 \cdot H_2O$ and 0.05 M H_2O_2	25±2°C	4 h	9-11.5	20:1 (L/S)	9% Au	(Melo Halmenschlager Petter et al., 2015)

Material	Reagent	Temp	Time	pH	L/S ratio	Recovery	Reference
Mobile phone scrap	0.12 M $(NH_4)_2S_2O_3$, 0.2 M $NH_3 \cdot H_2O$ and 20 mM $CuSO_4$	RT	2 h	10-10.5	- [c]	98% Au	(Ha et al., 2010)
~800 µm dismantled WPCBs	0.5 M $(NH_4)_2S_2O_3$, 1 M $NH_3 \cdot H_2O$ and 0.2 M $CuSO_4$	40°C	48 h	9	45:4 mL/g	98% Au and 93% Ag	(Ficeriová et al., 2011)
Complete size of WPCBs	0.5 M $(NH_4)_2S_2O_3$, 1 M $NH_3 \cdot H_2O$ and 0.2 M $CuSO_4$	40°C	48 h	9	45:4 mL/g	16% Au and 12% Ag	(Ficeriová et al., 2011)
~2 mm dismantled WPCBs from MP with Cu pre-separated by acid leaching	0.13 M $(NH_4)_2S_2O_3$ and 20 mM $CuSO_4$	20°C	2 h	10	20:1 mL/g	70% Au	(Camelino et al., 2015)
~1mm conductive and magnetic fraction of dismantled WPCBs with base metals pre-separated by acid leaching	0.2 M $(NH_4)_2S_2O_3$, 0.02 M $CuSO_4$, and 0.4 M NH_4OH	40°C	-	10	1:5 L/g	95% Au in 48 h; 100% Ag in 24 h	(Oh et al., 2003)

Halide leaching

Material	Reagents/Conditions	Temperature	Time	pH	Pulp/Ratio	Recovery	Reference
~250 μm dismantled WPCBs	1 M HCl, 8-157 mM CuCl₂, 0.7-2.0 M NaCl and 1 L/min air/O₂	20-80°C	120 min	~3	1% w/v	98~% Cu, Ni and Fe	(Yazici and Deveci, 2015)
~4 mm dismantled WPCBs pre-treated by supercritical water and HCl leaching, respectively	I₂/KI mole ratio of 1:5 (1:6 for Ag)	RT	120 min (90 min for Ag)	9	10 g/mL (8 g/mL for Ag)	90~% Au, Ag and Pd	(Xiu et al., 2015)
~212 μm dismantled WPCBs with Cu pre-separated by acid leaching	3% I₂ and 1% H₂O₂	35°C	240 min	7	15% (solid-%)	99.85~% Au	(Sahin et al., 2015)
~300 μm dismantled WPCBs after acid and thiorea leaching, respectively	5 M HCl, 1 V% H₂O₂ and 10 V% NaClO	63°C	3 h	-	10:1 (LS)	Not specified	(Behnamfard et al., 2013)
2-3 cm WPCBs after incineration and acid leaching	2 g/L I₂ and 12 g/L KI	40°C	120 min	-	5 % (PD)	99~% Au	(Altansukh et al., 2016)
Ammonia-ammonium leaching							
WPCBs underneath 200 mesh sieve	Triple amount of stoichiometric quantity	-	2 days	-	5:1 mL/g (LS)	-	(Liu et al., 2009)

Material	Reagents	Temperature	Time	L/S or PD	Results	Reference
	of NH₃ and NH₄HCO₃ with aeration					
≤8 mm ICT waste	120 g/L (NH₄)₂CO₃, 75.5 g/L NH₃·H₂O with air flow rate of 70 L/h	RT	Around 180 min	50 (LS)	90% Cu leached (90 min at 45°C)	(Sun et al., 2015)
≤8 mm ICT waste	200 mL 6M NH₃·H₂O, 45 g (NH₄)₂CO₃ and 100 mL 4M H₂O₂	22°C	3.5 h	6 mL/g (LS)	90% Cu and 70% Zn	(Xiao et al., 2013)
0.5-3 mm WPCBs	5 M NH₃·H₂O, 0.5 M Cu(II), 1 M (NH₄)₂SO₄ and 4 M NH₄Cl under nitrogen	25°C	24 h	About 10	Cu, Zn, Pb, Mn and some Ni were leached	(Oishi et al., 2007)
WPCBs from smelting process	2 kmol/m³ NH₄Cl, 5 kmol/m³ NH₃·H₂O and 0.1 kmol/m³ CuCl₂	30°C	-	1% (PD)	98% Cu leached. No Fe, Au and Ag detected in leaching solution	(Lim et al., 2013)
WPCBs granules	1 M (NH₄)₂CO₃, 4 M NH₃·H₂O and 0.2 MPa O₂	55°C	150 min	10.2-10.6 10:1 mL/g (LS)	100% Zn, >99% Cu and >64% Ni leached; <2% Sn and Pb, and almost 0% Fe leached.	(Wang et al., 2011)

[a] dismantled WPCBs refer to the WPCBs with electronic components (ECs) removed; [b] L/S ratio denotes liquid-solid ratio (LS); [c] "-" denotes not reported; [d] unless specified, the leaching rate denotes the percentage of the metals leached from the WPCBs.

Table S4 Details of the novel leaching methods for metals extraction from WPCBs

Materials	Leaching agent	Temperature	Time	pH	L/S ratio (LS)[b] or pulp density (PD)	Leaching rate[d] (optimal)	Ref.
Chelating leaching							
~150 μm dismantled WPCBs[a]	0.5-0.6 M EDTA	83-89°C	130-148 min	8-9	19-23 mL/g (LS)	>90% Cu	(Sharma et al., 2017)
~150 μm dismantled WPCBs	0.5 M EDTA	100°C	3 h	7	15 mL/g (LS)	84% Cu	(Jadhao et al., 2016)
<2 mm PCB wastewater sludge	0.1 M EDTA or 0.1 M DTPA (diethylenetriaminepentaacetic acid)	25°C	24 h	-[c]	20-5 mL/g (LS)	0.72-0.81 mol Cu/mol EDTA 0.57-0.80 mol Cu/mol DTPA	(Chang et al., 2007)
Ionic liquid leaching							
1 g 0.1-0.25 mm WPCBs mounted with ECs	25 mL 80% (v/v) 1-butyl-3-methyl-imidazolium hydrogen sulfate ([bmim]HSO$_4$), 10 mL 30% H$_2$O$_2$	70°C	2 h	-	25 (LS)	Almost 100% Cu	(Huang et al., 2014)

Feedstock	Reagents/Method	Temperature	Time		L/S	Results	Reference
Shredded WPCBs	Five ionic liquid acids, i.e. [BSO$_4$HPy]HSO$_4$, [BSO$_3$HMIm] HSO$_4$, [BSO$_3$HMIm]OTf, [BSO$_3$HMIm]OTf and [BSO$_3$HPy]OTf together with H$_2$O$_2$ were tested respectively.	40-70ºC	5-480 min	-	1-15 mL/g (LS)	Around 100% Cu and <30% Pb	(Chen et al., 2015)

Supercritical leaching

Feedstock	Reagents/Method	Temperature	Time		L/S	Results	Reference
80 mesh WPCBs powder	1st stage: supercritical water oxidation (SCWO) of WPCBs followed by 0.1 M HCl leaching of residue; 2nd stage: Supercritical CO$_2$ modified with acetone and KI-I$_2$ at I$_2$/KI molar ratio of 1:15 and pressure of 30 MPa	1st stage: 450ºC for SCWO and 25ºC for HCl leaching; 2nd stage: 50ºC	1st stage: 60 min for SCWO and 10 min for HCl leaching; 2nd stage: 10 min	-	1st stage: 16 mL/g (LS) for SCWO and 25 mL/g (LS) for HCl leaching	1st stage: enrichment factors of Pd and Ag were 4.8 and 5.3, respectively; 2nd stage: 93.7% Pd and 96.4% Ag extracted	(Liu et al., 2016)
<2 mm WPCBs	Supercritical CO$_2$ with 20% H$_2$O$_2$ and 2.5 M H$_2$SO$_4$ as co-solvents at 7.5 MPa	35ºC	20 min		20 mL (15% H$_2$O$_2$ +85% H$_2$SO$_4$)/g (LS)	88.79% Cu	(Calgaro et al., 2015)

[a] dismantled WPCBs refer to the WPCBs with electronic components (ECs) removed; [b] L/S ratio denotes liquid-solid ratio (LS); [c] "-" denotes not reported; [d] unless specified, the leaching rate denotes the percentage of the metals leached from the WPCBs.

References

Altansukh, B., Haga, K., Ariunbolor, N., Kawamura, S. and Shibayama, A., 2016. Leaching and adsorption of gold from waste printed circuit boards using iodine-iodide solution and activated carbon. Eng. J., 20(4): 29-40.

Bas, A.D., Deveci, H. and Yazici, E.Y., 2014. Treatment of manufacturing scrap TV boards by nitric acid leaching. Sep. Purif. Technol., 130: 151-159.

Behnamfard, A., Salarirad, M.M. and Veglio, F., 2013. Process development for recovery of copper and precious metals from waste printed circuit boards with emphasize on palladium and gold leaching and precipitation. Waste Manage., 33(11): 2354-2363.

Birloaga, I., Coman, V., Kopacek, B. and Vegliò, F., 2014. An advanced study on the hydrometallurgical processing of waste computer printed circuit boards to extract their valuable content of metals. Waste Manage., 34(12): 2581-2586.

Calgaro, C. O., Schlemmer, D. F., da Silva, M. D. C. R., Maziero, E. V., Tanabe, E. H. and Bertuol, D. A., 2015. Fast copper extraction from printed circuit boards using supercritical carbon dioxide. Waste Manage., 45: 289–297.

Camelino, S., Rao, J., Padilla, R.L. and Lucci, R., 2015. Initial Studies about Gold Leaching from Printed Circuit Boards (PCB's) of Waste Cell Phones. Procedia Mater. Sci., 9: 105-112.

Castro, L.A. and Martins, A.H., 2009. Recovery of tin and copper by recycling of printed circuit boards from obsolete computers. Braz. J. Chem. Eng., 26(4): 649-657.

Chang, F.-C., Lo, S.-L. and Ko, C.-H., 2007. A copper removal process for printed circuit board wastewater sludge applying extraction and cementation with chelating agents recovery. Environ. Eng. Sci., 24(8): 1006-1016.

Chen, M., Zhang, S., Huang, J. and Chen, H., 2015. Lead during the leaching process of copper from waste printed circuit boards by five typical ionic liquid acids. J. Clean. Prod., 95: 142-147.

Ficeriová, J., Baláž, P. and Gock, E., 2011. Leaching of gold, silver and accompanying metals from circuit boards (PCBs) waste. Acta Montan. Slovaca, 16(2): 128.

Ha, V.H., Lee, J.-c., Jeong, J., Hai, H.T. and Jha, M.K., 2010. Thiosulfate leaching of gold from waste mobile phones. J. Hazard. Mater., 178(1): 1115-1119.
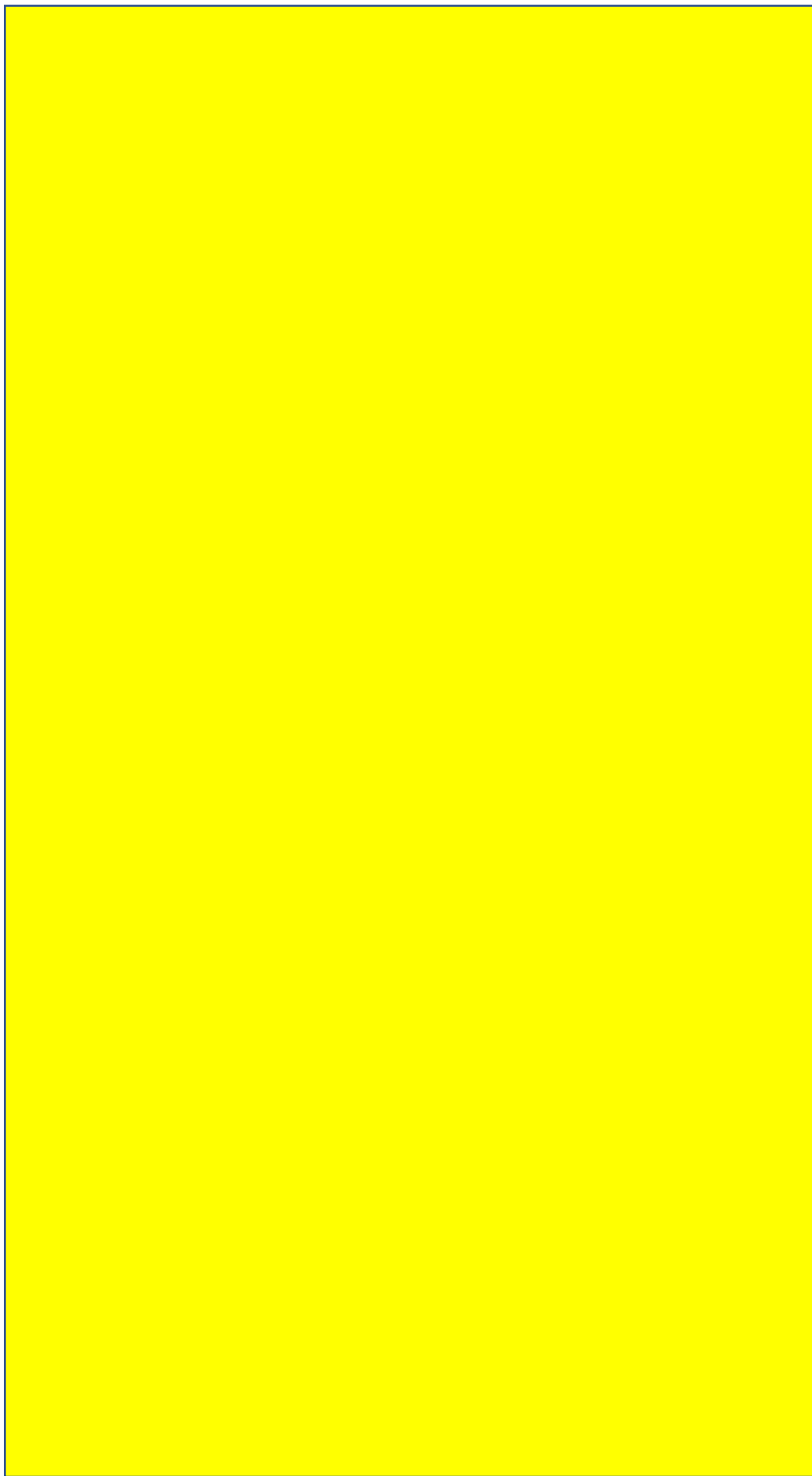
Huang, J., Chen, M., Chen, H., Chen, S. and Sun, Q., 2014. Leaching behavior of copper from waste printed circuit boards with Brønsted acidic ionic liquid. Waste Manage., 34(2): 483-488.

Isildar, A., Rene, E.R., Hullebusch, E.D.v. and Lens, P.N.L., 2017. Two-Step Leaching of Valuable Metals from Discarded Printed Circuit Boards, and Process Optimization Using Response Surface Methodology. Adv. Recycl. Waste Manage., 02(02).

Jadhao, P., Chauhan, G., Pant, K. and Nigam, K., 2016. Greener approach for the extraction of copper metal from electronic waste. Waste Manage., 57: 102-112.

Jadhav, U. and Hocheng, H., 2015. Hydrometallurgical recovery of metals from large printed circuit board pieces. Sci. Rep., 5: 14574.

Jha, M. K., Kumari, A., Choubey, P. K., Lee, J., Kumar, V and Jeong, J., 2012. Leaching of lead from solder material of waste printed circuit boards (PCBs). Hydrometallurgy, 121: 28–34.

Jha, M. K., Lee, J., Kumari, A., Choubey, P. K., Kumar, V and Jeong, J., 2011. Pressure leaching of metals from waste printed circuit boards using sulfuric acid. JOM, 63(8): 29–32.

Joda, N.N. and Rashchi, F., 2012. Recovery of ultra fine grained silver and copper from PC board scraps. Sep. Purif. Technol., 92: 36-42.

Jung, M., Yoo, K. and Alorro, R.D., 2017. Dismantling of Electric and Electronic Components from Waste Printed Circuit Boards by Hydrochloric Acid Leaching with Stannic Ions. Mater. Trans., 58(7): 1076-1080.

Kumar, M., Lee, J.-c., Kim, M.-S., Jeong, J. and Yoo, K., 2014. Leaching of metals from waste printed circuit boards (WPCBs) using sulfuric and nitric acids. Environ. Eng. Manag. J., 13(10).

Kumari, A., Jha, M.K., Lee, J.-c. and Singh, R.P., 2016a. Clean process for recovery of metals and recycling of acid from the leach liquor of PCBs. J. Clean. Prod., 112: 4826-4834.

Kumari, A., Jha, M.K. and Singh, R.P., 2016b. Recovery of metals from pyrolysed PCBs by hydrometallurgical techniques. Hydrometallurgy, 165: 97-105.

Lim, Y., Kwon, O.-h., Lee, J. and Yoo, K., 2013. The ammonia leaching of alloy produced from waste printed circuit boards smelting process. Geosyst. Eng., 16(3): 216-224.

Liu, K., Zhang, Z. and Zhang, F.-S., 2016. Direct extraction of palladium and silver from waste printed circuit boards powder by supercritical fluids oxidation-extraction process. J. Hazard. Mater., 318: 216-223.

Liu, R., Shieh, R., Yeh, R.Y. and Lin, C., 2009. The general utilization of scrapped PC board. Waste Manage., 29(11): 2842-2845.

Long Le, H., Jeong, J., Lee, J.C., Pandey, B.D., Yoo, J.M. and Huyunh, T.H., 2011. Hydrometallurgical process for copper recovery from waste printed circuit boards (PCBs). Miner. Process. Extr. Metall. Rev., 32(2): 90–104.

Melo Halmenschlager Petter, P., Veit, H.M. and Moura Bernardes, A., 2015. Leaching of gold and silver from printed circuit board of mobile phones. Rem: Rev. Esc. Minas, 68(1).

Oh, C.J., Lee, S.O., Yang, H.S., Ha, T.J. and Kim, M.J., 2003. Selective leaching of valuable metals from waste printed circuit boards. J. Air Waste Manag. Assoc., 53(7): 897-902.

Oishi, T., Koyama, K., Alam, S., Tanaka, M. and Lee, J.-C., 2007. Recovery of high purity copper cathode from printed circuit boards using ammoniacal sulfate or chloride solutions. Hydrometallurgy, 89(1): 82-88.

Park, Y.J. and Fray, D.J., 2009. Recovery of high purity precious metals from printed circuit boards. J. Hazard. Mater., 164(2): 1152-1158.

Petter, P., Veit, H. and Bernardes, A., 2014. Evaluation of gold and silver leaching from printed circuit board of cellphones. Waste Manage., 34(2): 475-482.

Sahin, M., Akcil, A., Erust, C., Altynbek, S., Gahan, C.S., Tuncuk, A., 2015. A potential alternative for precious metal recovery from e-waste: iodine leaching. Sep. Sci. Technol. 50(16), 2587–2595.

Sharma, N., Chauhan, G., Kumar, A. and Sharma, S., 2017. Statistical Optimization of Heavy Metals (Cu^{2+}/Co^{2+}) Extraction from Printed Circuit Board and Mobile Batteries Using Chelation Technology. Ind. Eng. Chem. Res.

Silvas, F.P., Correa, M.M.J., Caldas, M.P., de Moraes, V.T., Espinosa, D.C. and Tenório, J.A., 2015. Printed circuit board recycling: physical processing and copper extraction by selective leaching. Waste Manage., 46: 503-510.

Somasundaram, M., Saravanathamizhan, R., Basha, C.A., Nandakumar, V., Begum, S.N. and Kannadasan, T., 2014. Recovery of copper from scrap printed circuit board: modelling and optimization using response surface methodology. Powder Technol., 266: 1–6.

Sun, Z.H.I., Xiao, Y., Sietsma, J., Agterhuis, H., Visser, G. and Yang, Y., 2015a. Selective copper recovery from complex mixtures of end-of-life electronic products with ammonia-based solution. Hydrometallurgy, 152: 91–99.

Tripathi, A., Kumar, M., Sau, D.C., Agrawal, A., Chakravarty, S. and Mankhand, T.R., 2012. Leaching of gold from the waste mobile phone printed circuit boards (PCBs) with ammonium thiosulphate. Int. J. Metall. Eng., 1(2): 17–21.

Verma, H.R., Singh, K.K. and Mankhand, T.R., 2016. Dissolution and separation of brominated epoxy resin of waste printed circuit boards by using di-methyl formamide. J. Clean. Prod., 139: 586-596.

Wang, M., Cao, H. and Zhang, Y., 2011. Selective recovery of copper, zinc and nickel from printed circuit boards by ammonia leaching under pressure (In Chinese). Environ. Sci., 32(2): 596-602.

Xiao, Y., Yang, Y., van den Berg, J., Sietsma, J., Agterhuis, H., Visser, G. and Bol, D., 2013. Hydrometallurgical recovery of copper from complex mixtures of end-of-life shredded ICT products. Hydrometallurgy, 140: 128–134.

Xiu, F.-R., Qi, Y. and Zhang, F.-S., 2015. Leaching of Au, Ag, and Pd from waste printed circuit boards of mobile phone by iodide lixiviant after supercritical water pre-treatment. Waste Manage., 41: 134-141.

Xiu, F.-R. and Zhang, F.-S., 2010. Materials recovery from waste printed circuit boards by supercritical methanol. J. Hazard. Mater., 178(1): 628-634.

Yazici, E. and Deveci, H., 2013. Extraction of metals from waste printed circuit boards (WPCBs) in H2SO4-CuSO4-NaCl solutions. Hydrometallurgy, 139: 30-38.

Yazici, E. and Deveci, H., 2014. Ferric sulphate leaching of metals from waste printed circuit boards. Int. J. Miner. Process., 133: 39-45.

Yazici, E. and Deveci, H., 2015. Cupric chloride leaching (HCl–CuCl 2–NaCl) of metals from waste printed circuit boards (WPCBs). Int. J. Miner. Process., 134: 89-96.

Yildirir, E., Onwudili, J.A. and Williams, P.T., 2015. Chemical recycling of printed circuit board waste by depolymerization in sub-and supercritical solvents. Waste Biomass Valori., 6(6): 959-965.

Zhang, X., Guan, J., Guo, Y., Cao, Y., Guo, J., Yuan, H., Su, R., Liang, B., Gao, G., Zhou, Y. and Xu, J., 2017. Effective dismantling of waste printed circuit board assembly with methanesulfonic acid containing hydrogen peroxide. Environ. Prog. Sustain. Energy, 36(3): 873–878.

Zhu, P., Chen, Y., Wang, L.Y., Qian, G.R., Zhou, M. and Zhou, J., 2013a. A novel approach to separation of waste printed circuit boards using dimethyl sulfoxide. Int. J. Environ. Sci. Technol., 10(1): 175–180.

Zhu, P., Chen, Y., Wang, L. and Zhou, M., 2012. Treatment of waste printed circuit board by green solvent using ionic liquid. Waste Manage., 32(10): 1914-1918.

Zhu, P., Chen, Y., Wang, L., Zhou, M. and Zhou, J., 2013b. The separation of waste printed circuit board by dissolving bromine epoxy resin using organic solvent. Waste Manage., 33(2): 484-488.

Chapter 3 Exploratory tests using metallic fractions of waste printed circuit boards

Summary

This chapter is an exploratory study that aims to prove the feasibility of a two-stage alkaline glycine leaching process for the base and precious metals extraction from metallic fractions of WPCBs.

ORIGINAL PAPER

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

Elsayed A. Oraby[1,2] · Huan Li[1] · Jacobus J. Eksteen[1]

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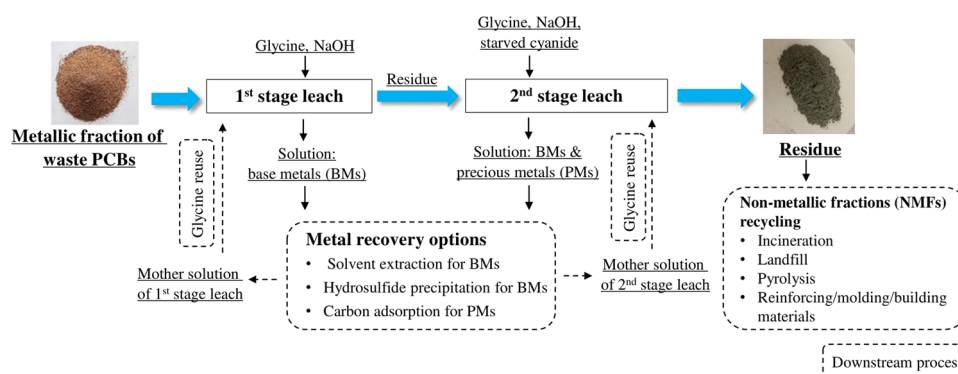
Flowsheet of a two-stage glycine leaching method for metal extractions from waste PCBs proposed in this study

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

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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.
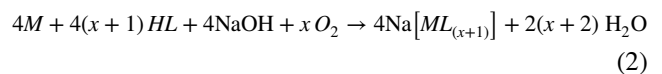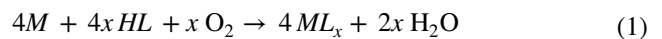
Introduction

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 form 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].

$$4M + 4x\,HL + x\,O_2 \rightarrow 4\,ML_x + 2x\,H_2O \tag{1}$$

$$4M + 4(x+1)\,HL + 4NaOH + x\,O_2 \rightarrow 4Na\left[ML_{(x+1)}\right] + 2(x+2)\,H_2O \tag{2}$$

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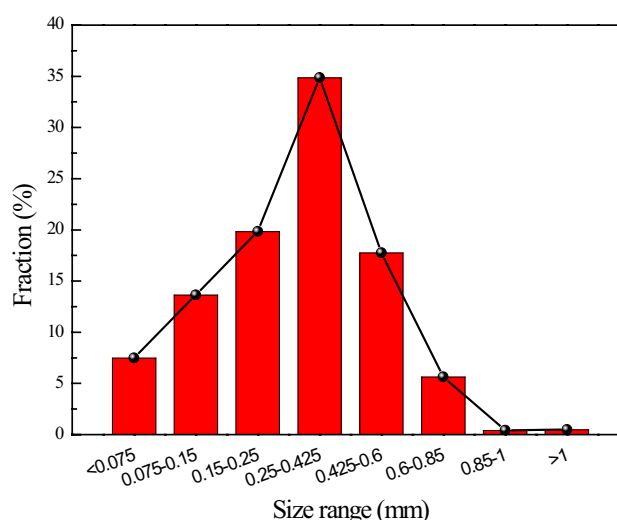
Fig. 2 Size distribution of the metallic powder obtained from the processing line

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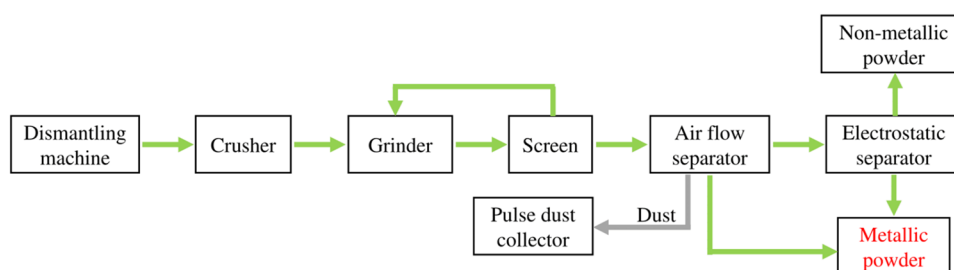
Table 2 Elemental and value analysis of the metallic portion of PCB powder

| | 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

[a]Data extracted from the official prices of London Metal Exchange (LME, https://www.lme.com/) (price for cash seller & settlement on 9th July 2019)

[b]Only the metals specified are taken into consideration
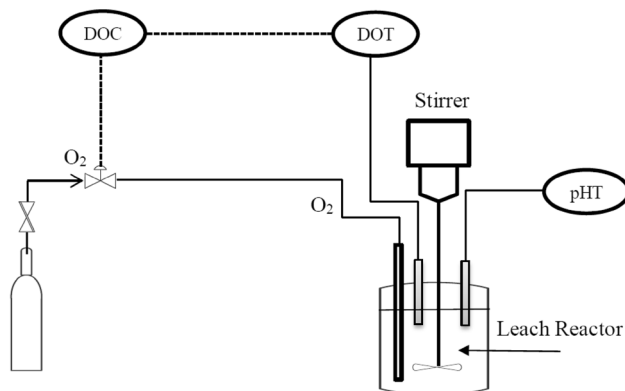
Fig. 3 Schematic diagram of dissolved oxygen controlled tank leach (*DOC* dissolved oxygen controller, *DOT* dissolved oxygen transmitter, *pHT* pH transmitter)

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

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

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	NH₃	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 NH₃ 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 (NaAlO₂) due to the reaction with NaOH as shown in Eq. 4.

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2, \quad \Delta G^o_{25\ °C} = -952.3\ KJ/mol \tag{4}$$
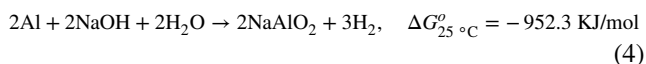
The time profile shows that the extent of Zn leaching reduced over time for the cases where the glycine concentration was 7 or 15 g/L, but not when the glycine was 30 g/L. This is due to the initial rapid leaching of Zn, but after 6 h, Cu present in the PCBs outcompetes the Zn for the available glycine 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
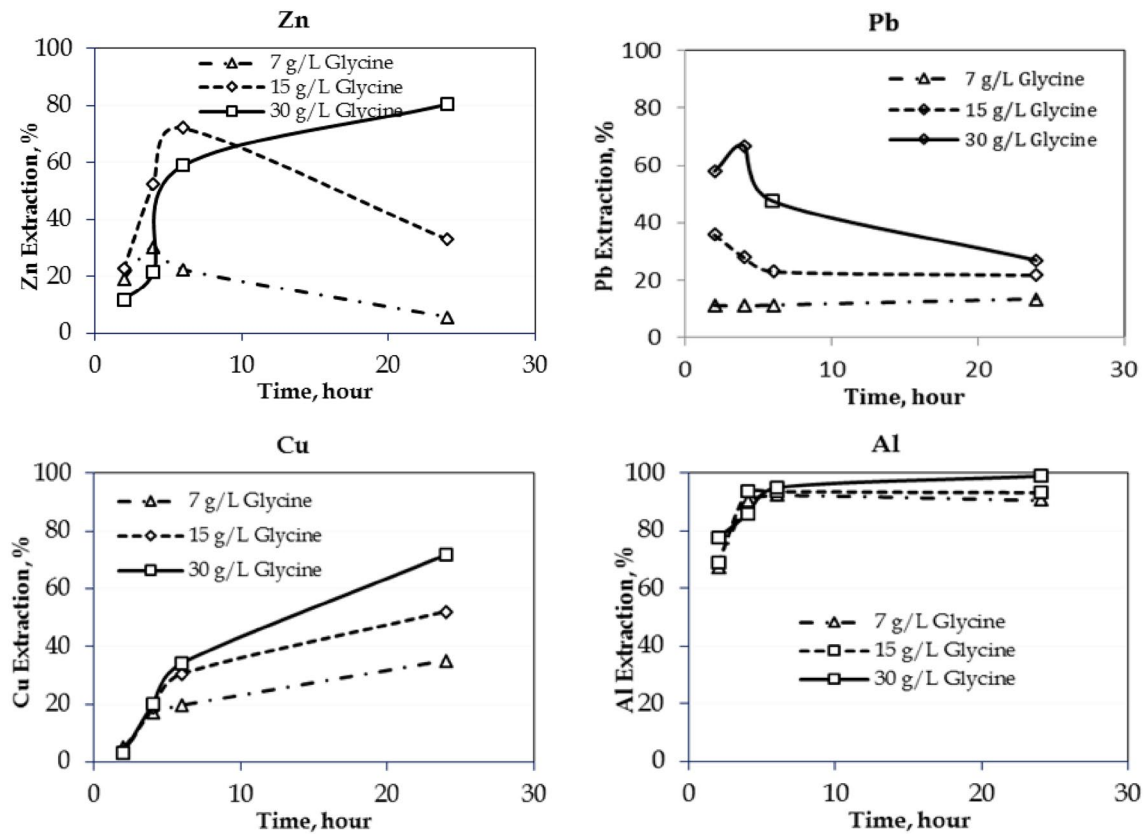
Fig. 4 Effect of glycine concentration on metals (Zn, Pb, Cu, Al) extraction from PCB powder at pH 11.0, room temperature (RT) and 0.4% solids in a bottle roll

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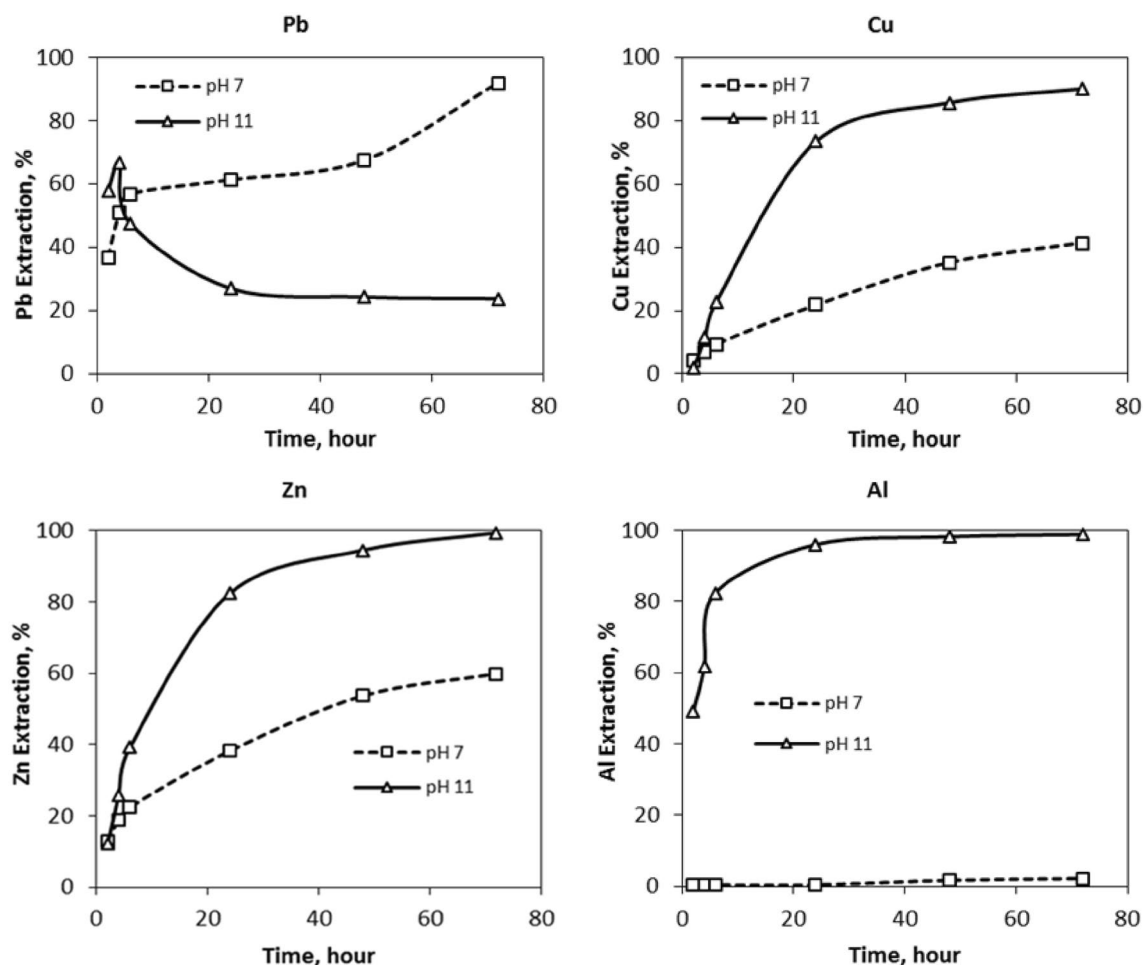
Fig. 5 Effect of leach pH on metals extraction (Pb, Cu, Zn, Al) from PCB powder at 30 g/L glycine, RT and 0.4% solids in bottle roll leach

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 whe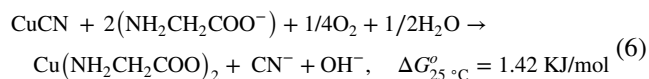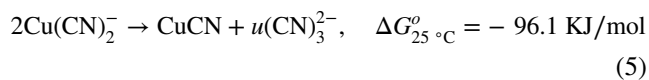n different Au–Cu ores/concentrate are treated [30]. According to Eq. 5 [39], at a starved cyanide concentration, CuCN is precipitated at which glycine play the role to re-dissolve CuCN and regenerate cyanide (Eq. 6). The presence of glycine can also enhance the Au extraction in aqueous solutions

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.

$$2Cu(CN)_2^- \rightarrow CuCN + u(CN)_3^{2-}, \quad \Delta G_{25\,°C}^o = -96.1 \text{ KJ/mol} \tag{5}$$

$$CuCN + 2(NH_2CH_2COO^-) + 1/4O_2 + 1/2H_2O \rightarrow$$
$$Cu(NH_2CH_2COO)_2 + CN^- + OH^-, \quad \Delta G_{25\,°C}^o = 1.42 \text{ KJ/mol} \tag{6}$$

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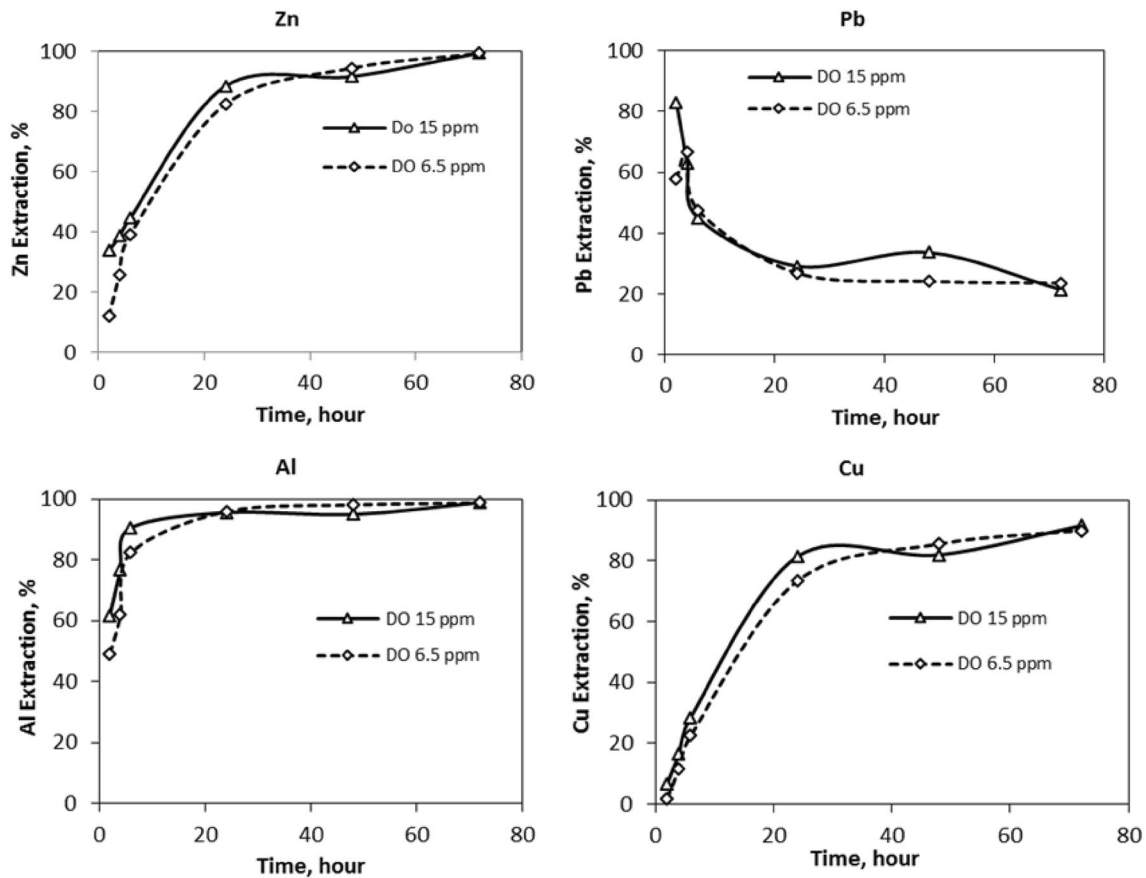
Fig. 6 Effect of dissolved oxygen on metals extraction from PCB powder at 30 g/L glycine, pH 11, RT and 0.4% solids in bottle roll leach

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/m^3 [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
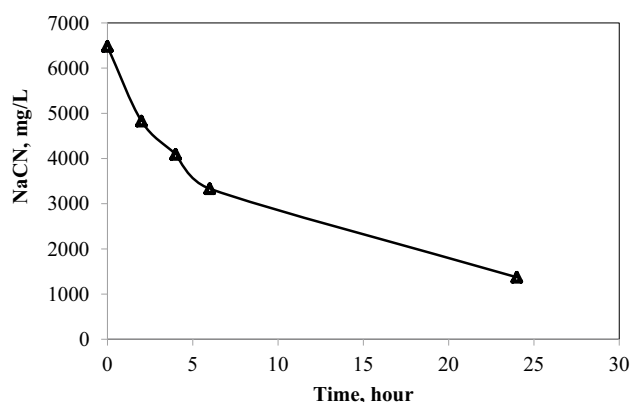
Fig. 7 NaCN concentration during the leaching of PCB powder at 6500 ppm NaCN, pH 11.0, RT and 0.4% solids in bottle roll leach
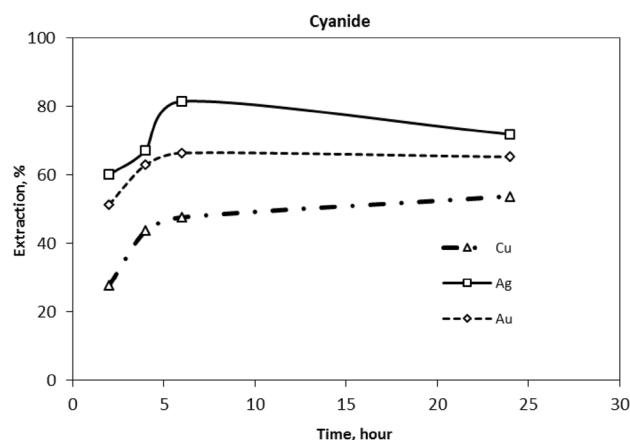
Fig. 8 Au, Ag and Cu extraction during cyanidation at 3500 ppm NaCN and pH 11.0

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 Time, (h)	Au (mg/L)	Ag (µg/L)	Zn (mg/L)	Al (mg/L)	Pb (mg/L)	Cu (mg/L)	Ni (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
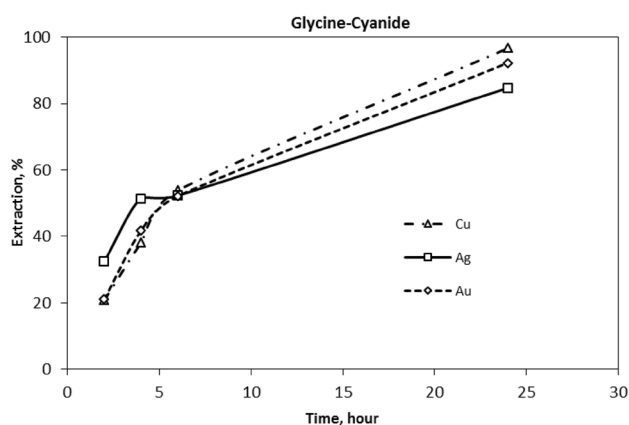
Fig. 9 Total Au, Ag and Cu extraction after glycine leaching at 30 g/L at pH 11 (stage1) and glycine–cyanide leaching (stage 2) at 30 g/L glycine, 300 ppm NaCN at pH 11

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:S^{2-} 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
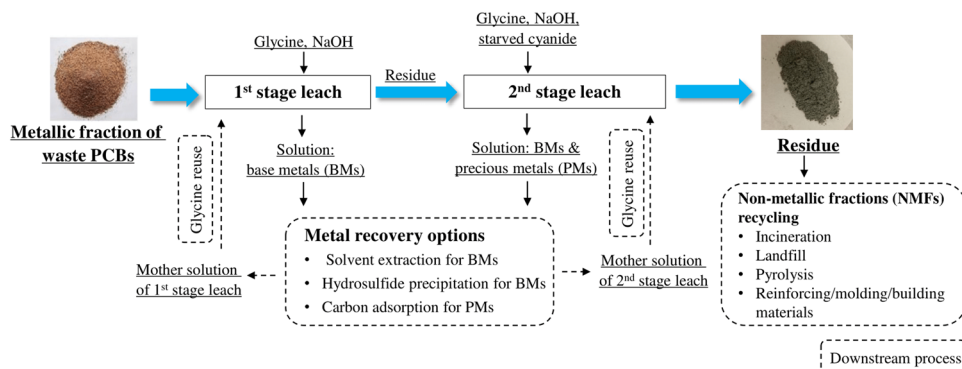
for E-waste under mild operating conditions (room temperature, ambient pressure, low levels of toxic reagents). It was found that glycine leaches most of the base metals such as Pb, Zn and Cu at room temperature. Precious metals (Au, Ag) were then recovered in a consecutive step using glycine and low 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.
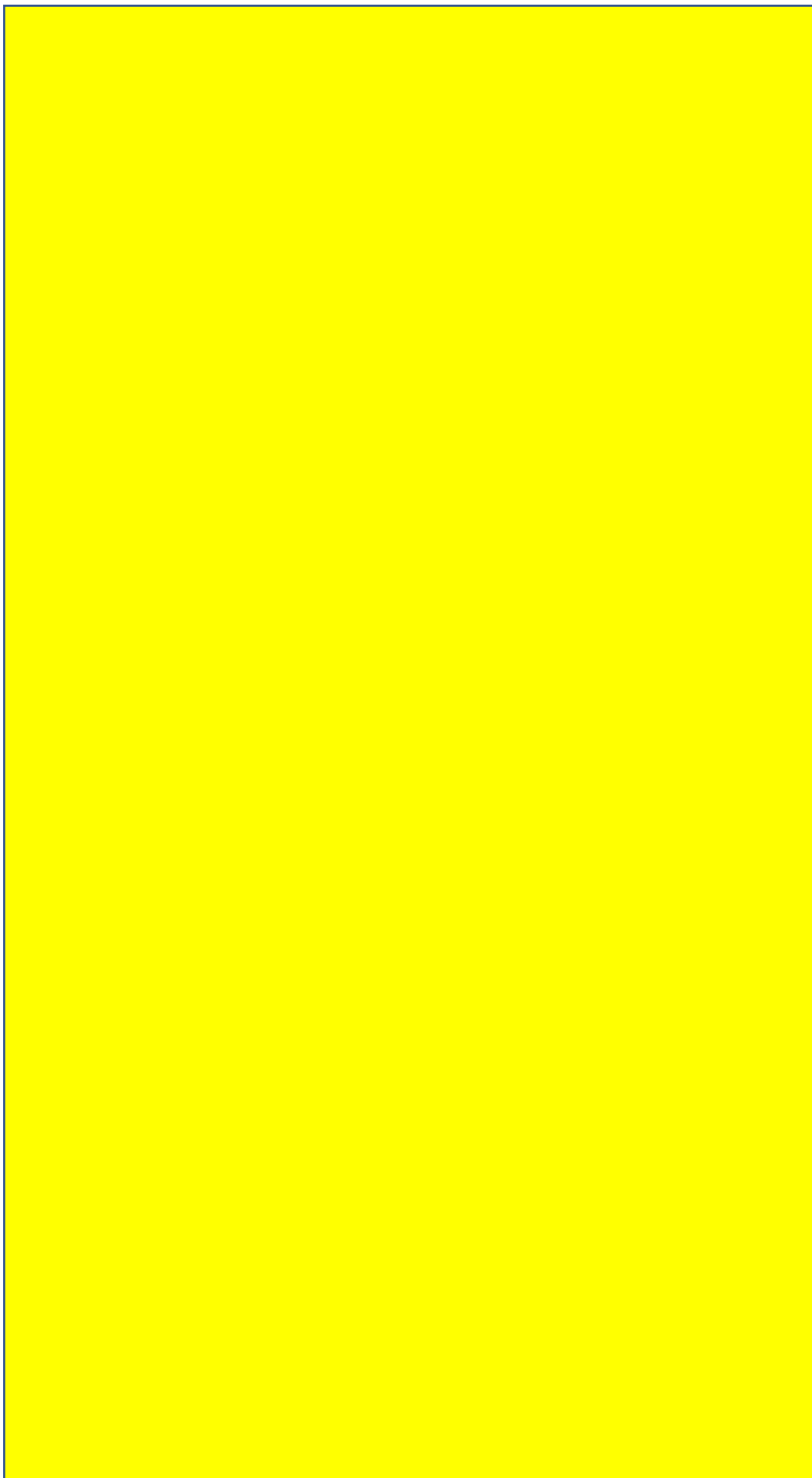
Compliance with Ethical Standards

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.

References

1. Wang, Z., Zhang, B., Guan, D.: Take responsibility for electronic-waste disposal. Nature **536**, 4 (2016)
2. Priya, A., Hait, S.: Feasibility of Bioleaching of Selected Metals from Electronic Waste by Acidiphilium acidophilum. Waste Biomass Valori **9**, 871–877 (2017)
3. Cui, J., Zhang, L.: Metallurgical recovery of metals from electronic waste: a review. J. Hazard. Mater. **158**(2), 228–256 (2008)
4. Lin, C., Chi, Y., Jin, Y.: Experimental study on treating waste printed circuit boards by molten salt oxidation. Waste Biomass Valori. 8:2523–2533 (2017).
5. Baldé, C.P., Forti, V., Gray, V., Kuehr, R., Stegmann, P.: The global e-waste monitor—2017. https://www.itu.int/en/ITU-D/Climate-Change/Documents/GEM%202017/Global-E-waste%20Monitor%202017%20.pdf Accessed 10 June 2018
6. Khaliq, A., Rhamdhani, M.A., Brooks, G., Masood, S.: Metal extraction processes for electronic waste and existing industrial routes: a review and Australian perspective. Resources **3**(1), 152–179 (2014)
7. Williams, P.T.: Valorization of printed circuit boards from waste electrical and electronic equipment by pyrolysis. Waste Biomass Valori. **1**(1), 107–120 (2010)
8. Yildirir, E., Onwudili, J.A., Williams, P.T.: Chemical recycling of printed circuit board waste by depolymerization in sub-and supercritical solvents. Waste Biomass Valori. **6**(6), 959–965 (2015)
9. Shuey, S., Vildal, E., Taylor, P.: Pyrometallurgical processing of electronic waste. In: SME Annual Meeting 2006, pp. 06–037
10. Kim, B.-S., Lee, J.-C., Seo, S.-P., Park, Y.-K., Sohn, H.Y.: A process for extracting precious metals from spent printed circuit boards and automobile catalysts. JOM **56**(12), 55–58 (2004)
11. Sum, E.Y.L.: The recovery of metals from electronic scrap. JOM **43**(4), 53–61 (1991)
12. Puente-Siller, D.M., Fuentes-Aceituno, J.C., Nava-Alonso, F.: An analysis of the efficiency and sustainability of the thiosulfate-copper-ammonia-monoethanolamine system for the recovery of silver as an alternative to cyanidation. Hydrometallurgy **169**, 16–25 (2017)
13. Sharma, N., Chauhan, G., Kumar, A., Sharma, S.: Statistical optimization of heavy metals (Cu^{2+}/Co^{2+}) extraction from printed circuit board and mobile batteries using chelation technology. Ind. Eng. Chem. Res. **56**, 6805–6819 (2017)
14. Liu, K., Zhang, Z., Zhang, F.-S.: Direct extraction of palladium and silver from waste printed circuit boards powder by supercritical fluids oxidation-extraction process. J. Hazard. Mater. **318**, 216–223 (2016)
15. Yang, C., Li, J., Tan, Q., Liu, L., Dong, Q.: Green process of metal recycling: coprocessing waste printed circuit boards and spent tin stripping solution. ACS Sustain. Chem. Eng. **5**(4), 3524–3534 (2017)
16. Li, H., Eksteen, J., Oraby, E.: Hydrometallurgical recovery of metals from waste printed circuit boards (WPCBs): current status and perspectives—a review. Resour. Conserv. Recycl. **139**, 122–139 (2018)
17. Yang, H., Liu, J., Yang, J.: Leaching copper from shredded particles of waste printed circuit boards. J. Hazard. Mater. **187**(1), 393–400 (2011)
18. Tuncuk, A., Stazi, V., Akcil, A., Yazici, E.Y., Deveci, H.: Aqueous metal recovery techniques from e-scrap: hydrometallurgy in recycling. Miner. Eng. **25**(1), 28–37 (2012)
19. Koyama, K., Tanaka, M., Lee, J.-C.: Copper leaching behavior from waste printed circuit board in ammoniacal alkaline solution. Mater. Trans. **47**(7), 1788–1792 (2006)
20. Ficeriová, J., Baláž, P., Gock, E.: Leaching of gold, silver and accompanying metals from circuit boards (PCBs) waste. Acta Montan. Slovaca **16**(2), 128 (2011)
21. Montero, R., Guevara, A., Torre, E.: Recovery of gold, silver, copper and niobium from printed circuit boards using leaching column technique. J. Earth Sci. Eng. **2**(10), 590 (2012)
22. Jing-ying, L., Xiu-li, X., Wen-quan, L.: Thiourea leaching gold and silver from the printed circuit boards of waste mobile phones. Waste Manage. **32**(6), 1209–1212 (2012)
23. Sahin, M., Akcil, A., Erust, C., Altynbek, S., Gahan, C.S., Tuncuk, A.: A potential alternative for precious metal recovery from e-waste: iodine leaching. Sep. Sci. Technol. **50**(16), 2587–2595 (2015)
24. Oraby, E., Eksteen, J.: A process for precious metals recovery. PCT Patent, PCT/AU2014/000877 (2014).
25. Oraby, E.A., Eksteen, J.J.: The selective leaching of copper from a gold–copper concentrate in glycine solutions. Hydrometallurgy **150**, 14–19 (2014)
26. Eksteen, J., Oraby, E.: The leaching and adsorption of gold using low concentration amino acids and hydrogen peroxide: Effect of

catalytic ions, sulphide minerals and amino acid type. Miner. Eng. **70**, 36–42 (2015)

27. Oraby, E.A., Eksteen, J.J.: The leaching of gold, silver and their alloys in alkaline glycine–peroxide solutions and their adsorption on carbon. Hydrometallurgy **152**, 199–203 (2015)

28. Tanda, B.C., Eksteen, J.J., Oraby, E.A.: An investigation into the leaching behaviour of copper oxide minerals in aqueous alkaline glycine solutions. Hydrometallurgy **167**, 153–162 (2017)

29. Oraby, E.A., Eksteen, J.J.: Gold leaching in cyanide-starved copper solutions in the presence of glycine. Hydrometallurgy **156**, 81–88 (2015)

30. Oraby, E.A., Eksteen, J.J., Tanda, B.C.: Gold and copper leaching from gold-copper ores and concentrates using a synergistic lixiviant mixture of glycine and cyanide. Hydrometallurgy **169**, 339–345 (2017)

31. Tauetsile, P.J., Oraby, E.A., Eksteen, J.J.: Adsorption behaviour of copper and gold Glycinates in alkaline media onto activated carbon Part 2: Kinetics. Hydrometallurgy **178**, 195–201 (2018)

32. Aksu, S., Wang, L., Doyle, F.M.: Effect of hydrogen peroxide on oxidation of copper in CMP slurries containing glycine. J. Electrochem. Soc. **150**(11), G718–G723 (2003)

33. Aliyu, H.N., Na'Aliya, J.: Potentiometric studies on essential metal (II) amino acid complexes. Int. Res. J. Pharm. Pharmacol. **2**(2), 76–80 (2012)

34. Eksteen, J.J., Oraby, E.A., Lombard, L., Di Prinzio, L.: Leaching of cobalt bearing nickel sulfide and furnace converter mattes with alkaline glycine, and subsequent SX and IX. Paper presented at the Proceedings of ALTA Hydrometallurgy Conference 2018, Perth, Australia, 19–26 May

35. González-López, J., Rodelas, B., Pozo, C., Salmerón-López, V., Martínez-Toledo, M., Salmerón, V.: Liberation of amino acids by heterotrophic nitrogen fixing bacteria. Amino Acids **28**(4), 363–367 (2005)

36. Kiss, T., Sovago, I., Gergely, A.: Critical survey of stability constants of complexes of glycine. Pure Appl. Chem. **63**(4), 597–638 (1991)

37. Tanda, B., Oraby, E., Eksteen, J.: Recovery of copper from alkaline glycine leach solution using solvent extraction. Sep. Purif. Technol. **187**, 389–396 (2017)

38. Eksteen, J.J., Oraby, E.A., Tanda, B.C.: A conceptual process for copper extraction from chalcopyrite in alkaline glycinate solutions. Miner. Eng. **108**, 53–66 (2017)

39. Breuer, P., Dai, X., Jeffrey, M.: Leaching of gold and copper minerals in cyanide deficient copper solutions. Hydrometallurgy **78**(3), 156–165 (2005)

40. Lewis Sr., R.J.: Hazardous Chemicals Desk Reference. Wiley, New York (2008)

41. Deng, Z., Oraby, E., Eksteen, J.: The sulfide precipitation behaviour of Cu and Au from their aqueous alkaline glycinate and cyanide complexes. Sep. Purif. Technol. **218**, 181–190 (2019)

42. Wang, R., Xu, Z.: Recycling of non-metallic fractions from waste electrical and electronic equipment (WEEE): A review. Waste Manage. **34**(8), 1455–1469 (2014)

43. Buekens, A., Yang, J.: Recycling of WEEE plastics: a review. J Mater Cycles Waste Manage **16**(3), 415–434 (2014)

44. Marques, A.C., Marrero, J.-M.C., Malfatti, C.: A review of the recycling of non-metallic fractions of printed circuit boards. SpringerPlus **2**(1), 521 (2013)

45. Rajarao, R., Sahajwalla, V., Cayumil, R., Park, M., Khanna, R.: Novel approach for processing hazardous electronic waste. Proc. Environ. Sci. 21(Supplement C), 33–41 (2014).

Chapter 4 Leaching of base metals using glycine-only leaching system

Summary

This chapter is a detailed investigation of the leaching behaviours of base and precious metals in alkaline glycine solution (glycine-only leaching system), with an emphasis on copper extraction.

Full length article

Extraction of copper and the co-leaching behaviour of other metals from waste printed circuit boards using alkaline glycine solutions

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A B S T R A C T

Waste printed circuit boards (WPCBs) are a complicated and valuable fraction of electric and electronic waste. The recycling of them is critical to avoid environmental pollutions and to reuse resources. In particular, the e-waste import bans have been implemented in many traditional waste-importing countries in recent years, which is making the sustainable recycling essential and crucial for the advanced economies. In this study, a sustainable approach using alkaline glycine solution for the extraction of copper (Cu) from WPCBs, and the leaching behaviour of other metals (Ni, Al, Fe, Pb, Sn, Co, Zn, Au, Ag and Pd) is presented. Various leaching parameters, including initial pH, glycine concentration, solid content, oxidant, particle size, temperature and time were investigated. A maximum Cu extraction of 96.5 % was achieved, with high co-extraction of base metals (BMs). The extraction of BMs was dependent on the pH of leaching solution, which was highly correlated with other variables. BMs extraction was largely influenced by glycine concentration and solid content, while the sensitivity to H_2O_2, temperature, and particle size was insignificant. SEM-EDS analysis of leaching residue indicated that the unleached Cu may be locked in inert layers, *e.g.* Sn/solder materials. The kinetic analysis showed that the extraction of Cu from WPCBs (100 % < 2 mm) at room temperature with ambient O_2 in air as an oxidant was mainly controlled by internal diffusion.

1. Introduction

In the past two decades, the number of waste electric and electronic equipment (WEEE or e-waste) has been increasing at an alarming rate (Ogunseitan et al., 2009; Wang et al., 2016). According to the recent statistics, the number of WEEE produced around the global has been 44.7 Mt/y (6.1 Kg/inhabitant, Kg/inh) in 2016, and the amount is forecasted to increase to 52.2 Mt/y (6.8 Kg/inh) by 2021 (Baldé et al., 2017). Today, the developed and rapidly developing countries generate majority of WEEE while most of them finally ends up in developing economies (Lee et al., 2018; Li et al., 2018). However, with the restrictions and bans on WEEE import by the traditional developing economies (Janjevic, 2018; Kannan et al., 2016; Lee et al., 2018), WEEE will be increasingly problematic for developed countries due to the hazardous impact to human, animals and the environment. In Australia, only about 10 % of WEEE is now treated with recycling, and more than 50 % was landfilled, stored or incinerated in 2010 (Khaliq et al., 2014). Considering environmental protection, e-waste should better be disposed of in countries where they are generated, which is also what Basel Convention is dedicated to (Ghosh et al., 2016; Tan et al., 2018).

However, the strict environmental regulations and the higher investment and operational costs in developed countries make the domestic recycling challenging, which brings a need for a sustainable and economical recycling approach. Moreover, to avoid transport costs and risks, e-waste should better be recycled in an urban area, where it is generated and collected. Therefore, the recycling approach should meet high safety standards that will secure the urban communities.

As one of the most complicated fractions of WEEE, waste printed circuit boards (WPCBs), with electronic components (ECs) mounted, contain > 40 types of metals and almost 10 types of non-metals (Li et al., 2018). Some of the metals (copper (Cu), gold (Au), silver (Ag), palladium (Pd), *etc.*) even have significantly higher contents in comparison to those in primary resources, indicating significant financial reward from recycling (Zeng et al., 2018). On the other hand, a large fraction of hazardous metals (beryllium (Be), cadmium (Cd), chromium (Cr), mercury (Hg), nickel (Ni), lead (Pb), zinc (Zn), *etc.*) and organic substances, brominated flame retardants (BFRs) in particular, should be appropriately recycled (Chauhan et al., 2018; McGrath et al., 2018). Currently, pyrometallurgical, bio-hydrometallurgical and hydrometallurgical processes have been the most widely reported processes

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for WPCBs recycling (Işıldar et al., 2018; Kumar et al., 2017; Wang et al., 2017). Of these, bio-hydrometallurgy is often considered eco-friendly and has low operational costs, but it is restricted by the low kinetics and is not fully developed for the higher metal complexity of e-waste (Kumar et al., 2017). Pyrometallurgical approaches have been adopted in the industry by a small group of international companies (D'Adamo et al., 2019). To achieve economy of scale required for smelting operations such companies must collect large quantities of e-waste (D'Adamo et al., 2019), which could be feasible in Europe, and the fast-developing countries in Asia. Hydrometallurgical processing has shown much promise since it is flexible, and can reach a relatively high recovery and has the possibilities of eliminating secondary waste (Sun et al., 2016). In addition, hydrometallurgical processing may be more profitable for small and medium enterprises (SMEs), compared with pyrometallurgical approaches that require large scale deployment to be economical with regards to energy efficiency and capital investment. This can make hydrometallurgical processing competitive for remote and inland towns and cities, like many in Australia, Africa and the Americas, which generates a smaller amount of e-waste that may be uneconomic to be transported over long distances to centralised smelters. In the reported hydrometallurgical processes, WPCBs are first dismantled to strip all the ECs off by melting ($250 - 280\,°C$) or dissolving solder materials, which has been an essential step in a whole recycling process (Li et al., 2018). However, the generation of toxic substances, particularly dioxin, during melting of solders has caused worries (Duan et al., 2011). Also, during the dissolution of solders, mineral or organic acids, sometimes together with oxidants, are used, that will add costs for both metal recovery from stripping solution and treatment of the wastewater (Jung et al., 2017; Zhang et al., 2017). After dismantling, the WPCBs without ECs are subjected to size reduction and/or further metal enrichment (Li et al., 2015). Afterwards, the materials are sent to leaching and recovery in aqueous media (Li et al., 2015).

In WPCBs, Cu has significantly higher content (about $10 - 20$ wt. %) than any other metals and represents the major economic values (Li et al., 2018). So far, the methods reported for hydrometallurgical extraction of Cu from e-waste can be categorised as (1) strong mineral acid leaching, including HCl, H_2SO_4 and HNO_3 leaching; (2) ammonia-ammonium leaching; (3) EDTA (ethylenediaminetetraacetic acid) leaching; (4) ionic liquid leaching; and (5) supercritical leaching. Among these, mineral acid and ammonia-ammonium leaching have considerable safety problems due to the corrosive and/or volatile nature of reagent used, especially at elevated temperature (Kumari et al., 2016; Sun et al., 2015a; Yazici and Deveci, 2013). The novel EDTA leaching has been recently reported to extract Cu by chelating reaction at the alkaline environment and elevated temperature ($80 - 100\,°C$) and $96 \sim \%$ EDTA could be recycled through an acidic de-chelation step (Jadhao et al., 2016; Sharma et al., 2017). The leaching using ionic liquid and supercritical technology is considered as a relatively advanced approach with special lixiviant or high-pressure reactor (Calgaro et al., 2015; Chen et al., 2015b), which needs to be further investigated for a practical application. It is clear that, for the "urban mining" of e-waste, a sustainable hydrometallurgical process should avoid collateral environmental problems as much as possible. Therefore, using "green" reagents and mild reaction conditions have been a trend of this area (Li et al., 2018).

1.1. Alkaline glycine leaching system

In recent years, Eksteen and Oraby have reported a novel technology using glycine, the simplest amino acid, as a major lixiviant to effectively leach Cu, Au and Ag from their pure foils and oxide/sulphide minerals (Eksteen and Oraby, 2016, 2014; Oraby and Eksteen, 2015; Oraby et al., 2019a, 2017). According to O'Connor et al. (2018), glycine can exist in solutions as $H_2NCH_2COO^-$ (gly$^-$, glycinate anion), $^+H_3NCH_2COO^-$ (H(gly), zwitterion) and $^+H_3NCH_2COOH$ (H_2(gly)$^+$,
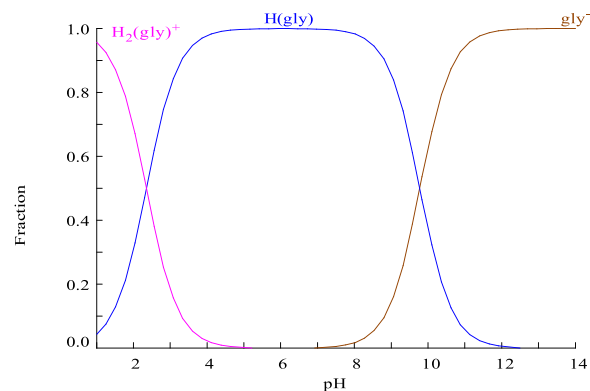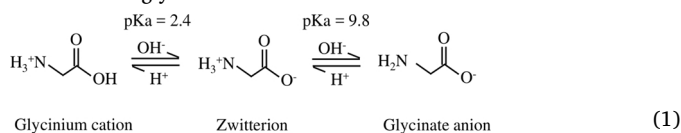

Fig. 1. Fraction of different forms of glycine at different pH in a system comprising waster and glycine (temperature = 25 °C, glycine concentration = 0.5 M, made by Medusa-Hydra software (available at https://www.kth.se/che/medusa/)).

glycinium cation), depending on different pH (Eq. (1)). The species distribution of glycine is depicted in Fig. 1 (Perea and Restrepo, 2018). It is reported that cuprous (Cu$^+$) and cupric (Cu^{2+}) ions can complex with both zwitterion and anion of glycine while the Cu^{2+} complexes show larger stability domain, as indicated by the stability constants in Table 1 (Aksu and Doyle, 2001). In a recent review, the authors of present study have summarised the glycine leaching system for the extraction of Cu, Au and Ag from foils and minerals, in which oxidant (air/O_2, H_2O_2, Cu^{2+}, *etc.*) and glycine are indispensable (Li et al., 2018). They are used to oxidise metals and complex with metal-ions, respectively (Li et al., 2018), with high Cu extraction at even room temperature and ambient environment (Oraby and Eksteen, 2014). However, when it comes to PMs, additional oxidant, catalyst/synergist (*e.g.* cyanide), and/or an elevated temperature ($\sim 60\,°C$) is usually required for a feasible extraction (Eksteen and Oraby, 2015; Oraby et al., 2017), which makes the selective extraction of BMs possible. In addition, an alkaline leaching environment, where glycinate anion is predominant (Eq. (1)), is also necessary for an efficient complexing reaction between glycine and metal ions.

$$\underset{\text{Glycinium cation}}{H_3^+N\!\!-\!\!C(=\!O)\!\!-\!\!OH} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \underset{\text{Zwitterion}}{H_3^+N\!\!-\!\!C(=\!O)\!\!-\!\!O^-} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \underset{\text{Glycinate anion}}{H_2N\!\!-\!\!C(=\!O)\!\!-\!\!O^-} \tag{1}$$

pKa = 2.4   pKa = 9.8

Traditionally used as a food additive, glycine is not toxic, not volatile, mass produced and stable in a wide Eh-pH range (Oraby et al., 2017). Compared with other widely used agent like EDTA, glycine forms less strong complexes through bidentate chelation or monodentate coordination, which makes it more amenable for metal elution (Ortiz-Aparicio et al., 2007). Taking into account the similarity between the previously investigated materials (foils, minerals), there is significant potential to use glycine as a "green" lixiviant for the extraction of BMs from WPCBs selectively. However, the complexities of WPCBs in terms of structure and composition have made the extraction challenging and largely different from the previous studies (Eksteen and

Table 1
Stability constants of copper glycinate species at 25 °C and 1 atm, I denotes ionic strength (Aksu and Doyle, 2001).

Reaction	Stability constant, log K at 25 °C, 1 atm
Cu^{2+} + 2(NH$_2$CH$_2$COO)$^-$ = Cu(NH$_2$CH$_2$COO)$_2$	15.64 ($I = 0$)
Cu^{2+} + (NH$_2$CH$_2$COO)$^-$ = Cu(NH$_2$CH$_2$COO)$^+$	8.57 ($I = 0$)
Cu$^+$ + 2(NH$_2$CH$_2$COO)$^-$ = [Cu(NH$_2$CH$_2$COO)$_2$]$^-$	10.1 ($I = 0.2$)
Cu(NH$_2$CH$_2$COO)$^+$ + H$^+$ = Cu(NH$_3$CH$_2$COO)$^{2+}$	2.92 ($I = 0.1$)

Oraby, 2015; Eksteen et al., 2017; Li et al., 2018). The intrinsic structure of WPCBs is represented by the polymer substrate in which metals (Cu, Sn, Ni, Ag, Au, *etc.*) are coated or laminated in different layers of polymers (Li et al., 2018; Xu and Liu, 2015). This may cause the mechanical lock of metals and hence result in low extraction. Also, many metals (Cu, Ni, Al, Fe, Pb, Sn, Zn, Co, Au, Ag and Pd) are present in WPCBs (with ECs mounted) mostly in a metallic form with significantly varied contents (Lu and Xu, 2016). However, except for Cu, Au and Ag, the leaching behaviour of the rest of metals in alkaline glycine solutions has not been well reported yet.

Recently, the authors of the present study have conducted exploratory tests to extract BMs and PMs in two stages from the metallic fractions of WPCBs (55 % Cu) (Oraby et al., 2019b). In the first stage, an alkaline glycine solution was used to extract Cu, Al, Pb, and Zn over PMs (Au and Ag). While, in the second stage, most of Au and Ag (> 85 %) and the remaining BMs were extracted in glycine solution in the starved cyanide environment. After extraction, downstream process, such as solvent extraction (Eksteen et al., 2017; Tanda et al., 2017b), hydrosulphide precipitation (Deng et al., 2019), carbon adsorption (Tauetsile et al., 2018), *etc.*, could be applied for the metal recoveries (Oraby et al., 2019b). The barren solution containing de-complexed glycine could be recycled back to leaching stages (Oraby et al., 2019b). The residue may be further treated (*e.g.* an acid leaching stage) to be toxic-metal-free that is suitable for landfill, incineration, pyrolysis or other application. However, the materials used in the study was a kind of metal-rich WPCBs (> 72 % metals) obtained after a series of mechanical/physical pre-treatment which lacks representative to the original WPCBs stream. Also, the details of the leaching behaviours of metals, and the leaching kinetics were still remaining unclear. This study, therefore, aims to the extraction of Cu from WPCBs by using glycine solution at alkaline environment. In addition to Cu, the leaching behaviour of various BMs (Ni, Al, Fe, Pb, Sn, Co and Zn) and PMs (Au, Ag and Pd) is investigated and discussed. The WPCBs used in the present study are with ECs mounted (except CPU and RAMs) and simply pre-treated to 100 % < 2 mm that avoids the use of acids/furnace to remove ECs, and avoids the complicated steps for size reduction or metal enrichment. All the reagents during leaching, including lixiviant (glycine) and oxidant (air/O_2 or H_2O_2), are environmentally friendly and non-toxic and have no special requirements for equipment and workplace. The reaction conditions (room or slightly elevated temperature (55 °C)) are mild with low energy costs. Hence, this study is expected to provide a detailed "green" and sustainable approach to extract Cu from WEEE that can be potentially applied in an area where strict environmental requirements apply.

2. Experimental section

2.1. Materials and reagents

In this study, WPCBs were disassembled from end-of-life computers of various brands, supplied by *Total Green Recycling Pty. Ltd.* (Perth, Western Australia). As presented in Fig. 2, around 100 Kg WPCBs were pre-treated prior to the leaching of metals. CPUs and RAMs with high Au values were first dismantled for separate recycling. Then, the WPCBs with ECs (resistors, capacitors, ports, ICs, *etc.*) were shredded into large pieces. The dismantling and shredding were conducted by the supplier. After shredding, the heat sinks, ports and steel fasteners (pure metals with high hardness) were manually selected out for separate recycling, and the large pieces of WPCBs were then milled to 100 % < 2 mm by using a cutting mill (Retsch SM 200, *Retsch Inc.*). The manual selection was performed to favour the following milling; it can be, however, avoided in the industry when appropriate miller is applied. The loss of mass during milling was 0.768 wt. % resulted from the dust collection system and the residue lost in the miller. In practice, the collected dust could be further recovered, but it is excluded in the scope of this study. The major metal contents of pre-treated WPCBs are presented in

Table 2. It indicates that there are a number of BMs and PMs contained in the materials, including 22.60 % Cu, 106.77 ppm Au, 170.50 ppm Ag and 10.37 ppm Pd. The size distribution of the pre-treated WPCBs and the metal grade distribution in different size rages are presented in Figs. S1–S2.

To prepare feed materials for the leaching experiments, the WPCBs comminutions (100 % < 2 mm) were split into small portions (around 12 g each) by using rotary sample divider. All the chemicals, including glycine (NH_2CH_2COOH, 99 %), sodium hydroxide (NaOH) and hydrogen peroxide (H_2O_2, 30 w/v %) were of analytical grade. All the leaching solutions and analytical samples were prepared using deionized (DI) water.

2.2. Experimental setup and procedures

For each experiment, before leaching with alkaline glycine solutions, WPCBs were subjected to a caustic-only leaching step, in which around 12 g WPCBs were mixed with DI water in a 2.5 L Winchester plastic bottle at 5 % solid content and pH 13 (adjusted by solid NaOH). The bottle was then put vertically in a fume cupboard with the lid open for 1 h (until no bubbles are observed). This step was done for safety consideration to avoid the potential ignition/explosion of hydrogen gas (H_2) generated by the reactions between NaOH and amphoteric metals, Al in particular (Eq. (2)) (Aleksandrov et al., 2003). However, this is not necessary in the industry when appropriate H_2 collection system is in place.

$$2Al\ (s) + 2NaOH\ (aq) + 6H_2O\ (l) \rightarrow 2NaAl(OH)_4\ (aq) + 3H_2\ (g) \quad (2)$$
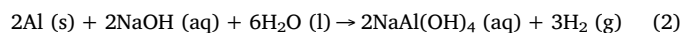
Following the caustic-only leaching, a certain amount of glycine solution was added into the same bottle at different glycine concentrations, initial pH and solid content (g/mL, %). For the supply of ambient oxygen (O_2, acting as an oxidant), the bottle was vented by a 5 mm hole through the lid to allow for O_2 ingress from surrounding air. The bottles were then put in an enclosed, controlled speed, incubator bottle roller with a rotation speed of 100 rpm for up to 72 h, at room (23 ± 2 °C) or elevated (55 °C) temperature. To investigate the leaching kinetics, solution samples with 5 mL each were taken at 2, 4, 6, 24, 48 and 72 h. Meanwhile, the pH and Eh (mv, *vs* Ag/AgCl) of leaching solution were measured with a pH meter (90-FLMV Field Lab Analyser, *TPS Pty Ltd.*) at each sampling time. After leaching with alkaline glycine solution, the mixture was separated by using a pressure filter (ESSA Pressure Filter Unit), and the residue was washed with DI water and then dried at 70 °C overnight. To investigate the effect of particle size on the metals extraction, the WPCBs with different size ranges, *i.e.* < 75 μm, 425−600 mm, < 1 mm, and < 2 mm, were tested. Among them, < 75 μm and 425−600 mm were obtained by screening of the pre-treated WPCBs (100 % < 2 mm) while < 1 mm was obtained by further milling of the pre-treated WPCBs. In some experiments, different concentrations of peroxide (H_2O_2) were added as an additional oxidant in comparison to ambient O_2.

2.3. Analytical methods

The Cu concentrations in the sub-samples at 2, 4, 6, 24, 48 and 72 h were analysed by atomic absorption spectrometer (AAS, 55B AA, *Agilent Technologies Inc.*) for kinetic investigation. The extraction of Cu (E_{Cu}, %) was calculated as shown in eq 3.

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

where m_t and m_f are the mass of metal in the leachate at time t and in the final solution at 72 h, respectively; m_{s1} and m_{s2} are the mass of metal in the samples sampled before time t and before 72 h, respectively; m_r is the mass of metal in the final residue.

The concentrations of other BMs (Ni, Al, Fe, Pb, Zn, Sn, Co) and PMs (Au, Ag, Pd) in the final leaching solutions (at 72 h) were analysed by
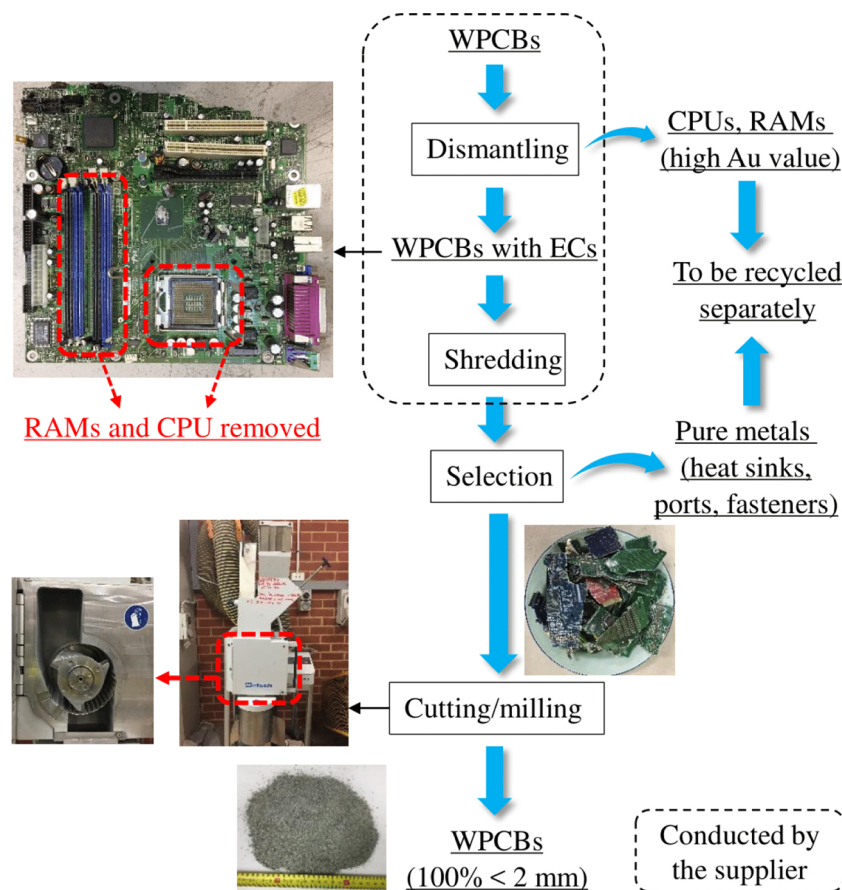
Fig. 2. Scheme of the pre-treatment of WPCBs with electronic components (ECs) mounted.

inductively coupled plasma - optical emission spectrometry (ICP-OES, for Al, Cu, Fe, Ni, Zn) and inductively coupled plasma - mass spectrometry (ICP-MS, for Au, Ag, Pd, Pb, Sn, Co), and independently done by Bureau Veritas, Perth, Australia. The extraction of these metals (E_m, %) was calculated as shown in eq 4.

$$E_m = m_t/(m_f + m_r) \times 100\% \qquad (4)$$

where m_t and m_f are the mass of metal in the leachate at time t and in the final solution at 72 h, respectively; m_r is the mass of metal in the final residue.

The metals in feed materials and final leaching residues were analysed by Ash Aqua Scan and independently done by Bureau Veritas. In the method, leaching residues were ashed and then digested in aqua regia, followed by ICP-OES/MS analysis. The feed materials and leaching residues were analysed to determine their morphology and general compositions by using scanning electron microscope coupled with energy dispersive X-ray spectroscopy (SEM-EDS, Zeiss Evo 40XVP SEM).

2.4. Kinetic model of Cu leaching

Cu represents the highest metal content and major economic value in WPCBs (Table 2). The leaching behaviour of Cu could also affect the leaching of other BMs by competition or synergy (Oraby et al., 2019b). Therefore, there is a necessity to investigate the leaching kinetics of Cu during the process. In this study, shrinking core model (SCM), a kinetic model widely used for e-waste leaching, is used to illustrate the leaching kinetics of Cu in glycine solution at alkaline environment with ambient O_2 (from air) as an oxidant (Chen et al., 2015a; Jadhao et al., 2016; Jha et al., 2011). According to SCM, the leaching of Cu from WPCBs can be described as the following steps: (1) reactant A diffusing from the bulk of the leaching solution to the fluid film surrounding solid phase (WPCBs); (2) diffusion of reactant A from the fluid film to the surface of solid; (3) reaction on the surface (reaction zone) between the reactant A and solid; (4) generation of products from the reaction and their diffusion from the surface to the fluid film; and (5) diffusion of products to the bulk of leaching solution (Chen et al., 2015a). As the

Table 2
Major metal contents of WPCBs (100 % < 2 mm) used in this study, and their economic values.

	Metal price, content and economic value										
	Metal content in wt. %						Metal content in ppm				
	Cu	Fe	Al	Sn	Pb	Zn	Ni	Co	Au	Ag	Pd
Metal price (USD/t) [a]	5710	–	1756	16805	2050	2265	16090	31500	4.41×10^7	5.01×10^5	4.22×10^7
Metal content	22.60	1.83	3.18	2.81	0.34	0.69	865.50	59.72	106.77	170.50	10.37
Metal value (%) [b]	18.2	–	0.8	6.7	0.1	0.2	0.2	0.03	66.4	1.2	6.2

[a] Data taken from the official prices of London Metal Exchange on 19th August 2019.
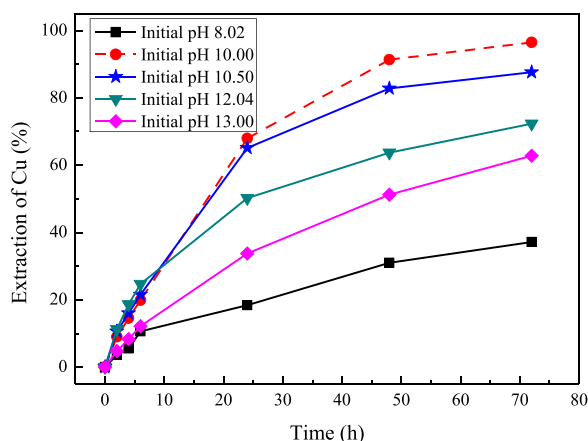[b] Only the metals specified are considered.

Fig. 3. Effect of initial pH on the extraction of Cu (glycine concentration = 0.5 M, solid content = 2 %, particle size = < 2 mm, RT and ambient O_2).

Fig. 4. Eh-pH diagram of Cu-glycine system at 0.5 M glycine, 0.05 M Cu, and 25 °C, made by Medusa-Hydra software (https://www.kth.se/che/medusa/).

reaction proceeds, glycine complexes with Cu (in the presence of dissolved O_2) in the reaction zone, and the complexes transport to fluid film and further to the bulk of solution. With the increase of leaching time, the reaction zone keeps shrinking until only inert solid (without Cu) is left behind. To determine the rate controlling step of Cu leaching, the equations of chemical reaction and diffusion control in SCM are given as Eqs. (5) and (6) (Chen et al., 2015a; Jadhao et al., 2016). Therefore, if the Cu leaching is controlled by diffusion or chemical reaction, there will be a linear relationship will occur between the left side of Eqs. (5) and (6) and time (t), and the regression correlation coefficient will be close to 1.

$$1 - \frac{2}{3}x - (1-x)^{2/3} = kt, \quad \text{diffusion control} \tag{5}$$

$$1 - (1-x)^{1/3} = kt, \quad \text{chemical reaction control} \tag{6}$$

where x is the extraction percentage of Cu, t is the reaction time (h), and k is the apparent rate constant (h^{-1}).

$$\tag{8}$$
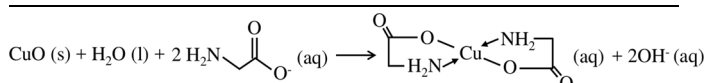
3. Results and discussion

3.1. Effect of variables

3.1.1. Effect of initial pH

As indicated in Fig. 1, pH directly affects the predomination of different forms of glycine in solution, with glycinate anion predominant at pH > 9.8. It has been reported that the Cu dissolution is strongly correlated to the concentration of glycinate anion, and is only affected slightly by the zwitterion (Aksu and Doyle, 2001; O'Connor et al., 2018). In this study, therefore, several experiments were conducted at different initial pH to investigate its effect on the extraction of metals. Other conditions were kept at 0.5 M glycine concentration, 2 % solid content, room temperature (RT) and < 2 mm particle size of WPCBs with ambient O_2 as oxidant. Although the initial pH is controlled, it should be noted that the pH of leaching solution was also progressing with the increase of leaching time (Fig. S3). As shown in Fig. 3, when the initial pH increased from about 8 to 10, Cu extraction increased by 60 % at 72 h, due to the predomination of glycinate anion (Fig. 1). According to Aksu and Doyle (2001), glycinate anion is capable of forming complexes with Cu ions through bidentate chelation,
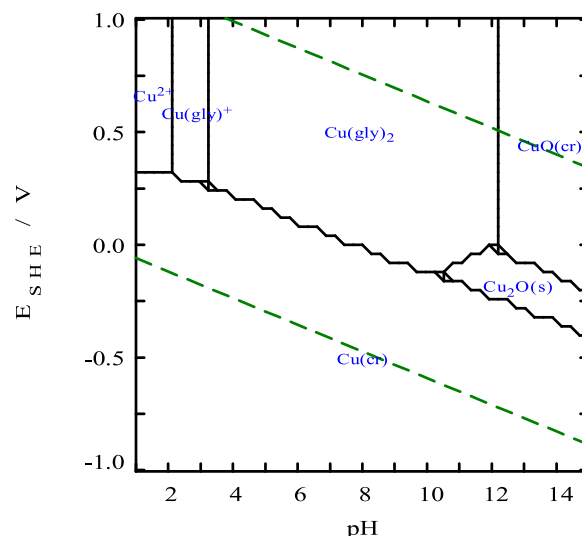
which is considered more stable than those formed by zwitterion through monodentate coordination (by the carboxylate group). The reactions of Cu leaching in alkaline glycine solutions, where glycinate anion is predominant, is represented by Eqs. (7) and (8) (Gary et al., 2014; Tanda et al., 2017a). Among them, Eq. (8) explains the increase of pH during the leaching process (Fig. S3). In addition to ambient O_2, the Cu^{2+} leached into solution could also play as an additional oxidant. However, with the further rise of initial pH up to 13.0, the Cu extraction dropped significantly. This is due to the formation of insoluble Cu_2O or CuO at high pH, as shown by the Eh-pH (Pourbaix) diagram of the glycine-Cu system (Fig. 4). The highest Cu extraction of 96.5 % was achieved after 72 h at the initial pH of 10.0, with a pH progression from 10.0–10.7. According to the SEM-EDS analysis of residue (Fig. 5), the unleached Cu may be locked in the Sn/solder materials. Further pre-treatment, such as nitric acid leaching (Yang et al., 2011), to remove solder materials may be feasible to extract the rest of Cu.

$$2Cu\ (s) + O_2\ (g) \rightarrow 2CuO\ (s) \tag{7}$$
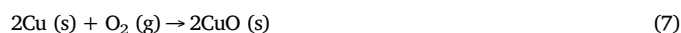
The extraction of other metals for a leaching time of 72 h is shown in Fig. 6. According to Sundaresan et al. (1968), Zn^{2+} can form complexes with glycinate anion as $Zn(gly)^+$, $Zn(gly)_2$ and $Zn(gly)_3^-$, as indicated by the Eh-pH diagram (Fig. S4). However, a pH interval occurs for ZnO precipitation beyond the pH at which $Zn(gly)_3^-$ forms, and the interval enlarges with the increase of Zn^{2+} concentration (Fig. S4), which is explainable for the decrease of Zn extraction (Fig. 6). In contrast, the extraction of both Al and Sn increased continuously to around 55 % with the rise of initial pH. It has been known that Al and Sn can be dissolved in NaOH solution, and the dissolution efficiencies increase with the rise of alkalinity, as the possible reaction represented by eqs. 2 and 9 (Aleksandrov et al., 2003; Kékesi et al., 2000). The increase of Pb extraction can be explained by the formation of $Pb(gly)_2$, $Pb(gly)OH$ and/or $Pb(OH)_4^{2-}$ in an alkaline environment (Hotea, 2013) (Fig. S5). According to Rodriguez-Torres et al. (2000), Ni^{2+} forms complexes with glycine in alkaline environment as $Ni(gly)^+$, $Ni(gly)_2$ and $Ni(gly)_3^-$ (Fig. S6). However, Ni extraction fluctuated in the investigated pH range, which may be caused by the lock of Ni underneath inert Au layers as indicated in Figure S9. Slight increases of extractions
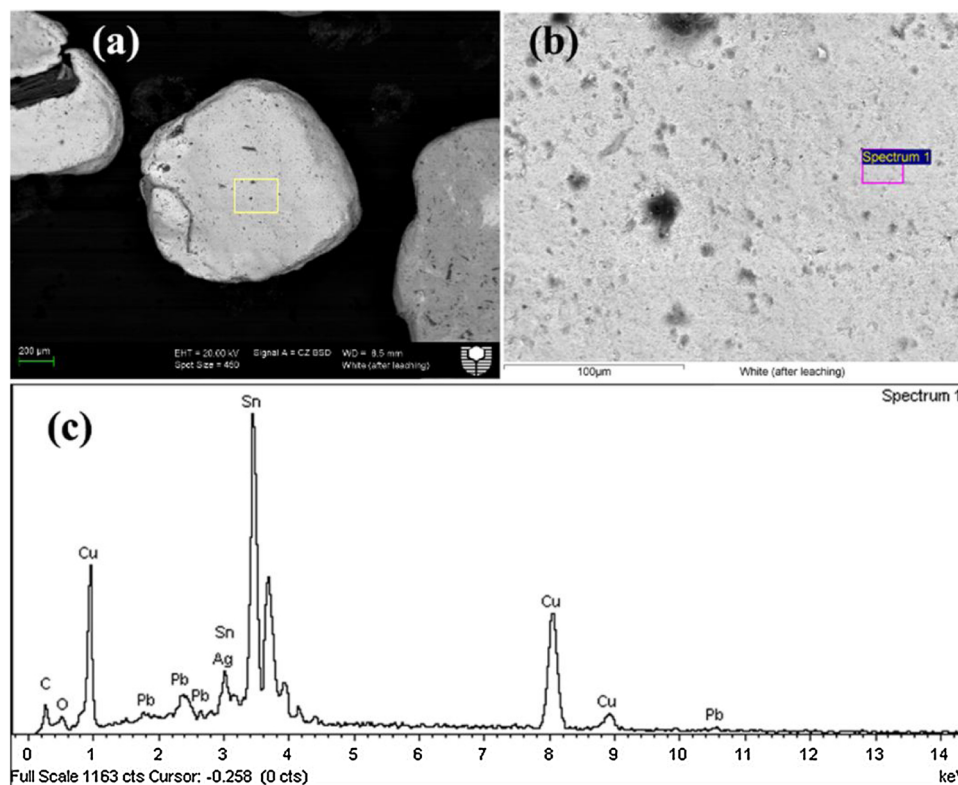
Fig. 5. SEM-EDS analysis of the particles of leaching residue under the conditions with the highest Cu extraction ((b) is from the selected area in (a), (c) is the EDS analysis of the selected area in (b)).
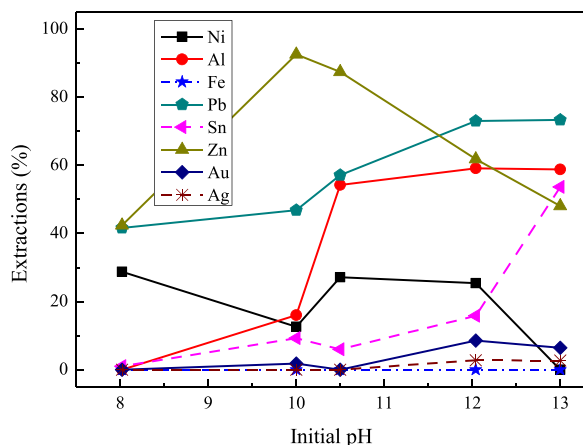

Fig. 6. Effect of initial pH on the extraction of other metals (glycine concentration = 0.5 M, solid content = 2 %, particle size = < 2 mm, RT and ambient O_2).
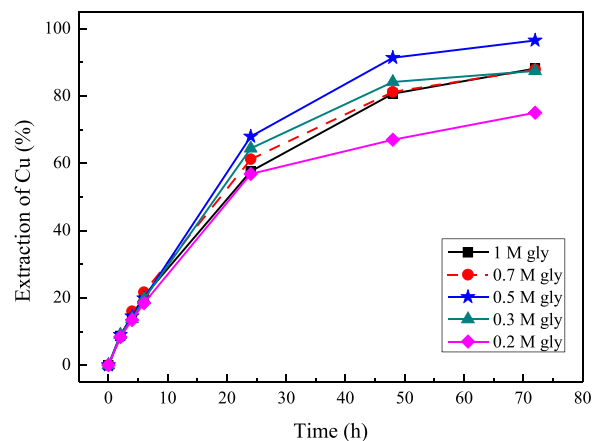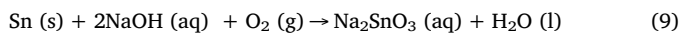

Fig. 7. Effect of glycine (gly) concentration on the extraction of Cu after 72 h (solid content = 2 %, initial pH = 10, particle size = < 2 mm, RT and ambient O_2).

for Au and Ag were also observed at pH > 12, which agrees well with Oraby and Eksteen (2015) and Oraby at al. (2019a) indicating that Au and Ag only dissolve in glycine solution at high pH. However, no Fe was extracted at all the pH values (below detection limit of 0.2 ppm). As indicated in the Eh-pH diagram of Fe-glycine system (Fig. S7), the complexes between glycine and Fe ions in alkaline environment occur with only small windows. As recorded, the Eh values during leaching for 72 h were always between 192 and 326 mV (*vs* SHE), implying that Fe may exist as insoluble Fe_3O_4 as shown in Fig. S7.

$$Sn\ (s) + 2NaOH\ (aq)\ + O_2\ (g) \rightarrow Na_2SnO_3\ (aq) + H_2O\ (l) \qquad (9)$$

3.1.2. Effect of glycine concentration

Several studies have shown that glycine concentration has an obvious effect on the extraction of Cu from its oxide/sulphide ores and concentrates (Eksteen et al., 2017; Oraby and Eksteen, 2014; Oraby et al., 2017). In this study, some experiments at different glycine concentrations (0.2 − 1 M) were performed to investigate its effect on the extraction of metals. All other conditions were fixed at a solid content of 2 %, initial pH of 10, particle size of < 2 mm, room temperature, and with ambient O_2 as oxidant. Fig. 7 presents the Cu extraction as a function of leaching time at different glycine concentrations. It indicates that the increase in glycine concentration from 0.2 to 0.5 M
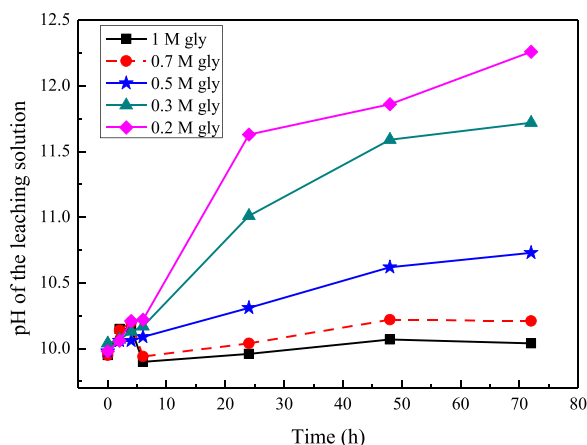
Fig. 8. pH progression of the leaching solution as a function of time at different glycine concentration (solid content = 2 %, initial pH = 10, particle size = < 2 mm, RT and ambient O_2).

enhanced Cu extraction and its kinetics considerably. However, when the concentration increased to 0.7 M, the Cu extraction reduced obviously and remained relatively unchanged when it further increased to 1 M. The highest Cu extraction of 96.5 % was achieved at 0.5 M glycine for 72 h, representing 3.8 times of the stoichiometric glycine amount required for Cu (Eq. (8)). Due to the buffering effect of glycine, the pH progression of leaching solution at different glycine concentrations varied greatly as shown in Fig. 8. Not surprisingly, when the initial pH was fixed, the higher glycine concentration resulted in, the lower pH values developed over 72 h. Therefore, the lower Cu extraction at glycine concentration ≥ 0.7 M may be caused by the lower pH values developed over time, at which the amount of glycine anion was decreased (Fig. 1).

Fig. 9 presents the effect of glycine concentration on the extraction of other metals for a leaching time of 72 h. The increase of glycine concentration from 0.2 to 1 M had a significant effect on the extraction of Pb, Zn and Ni. As shown in Table 3, Cu^{2+} glycinate complexes occur with high stability compared with other BMs, and Cu will hence be dominantly complexed by glycine ligand (gly^-) at a low glycine concentration (available gly^- was limited). With the increase of glycine concentration, more glycine will be available for the complexation with Zn, Ni and Pb, resulting the increase of their extraction. About 25 % decrease of extraction was observed for both Al and Sn with the increase of glycine concentration, explained by the decreasing of pH at which Al and Sn precipitates (Fig. 8). The concentrations of Fe and Ag
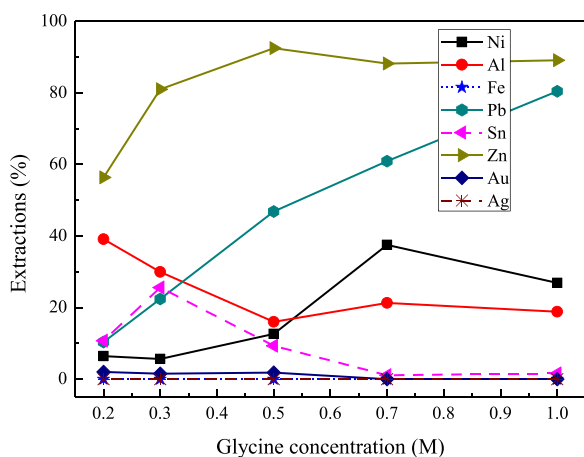
Fig. 9. Effect of glycine (gly) concentration on the extraction of other metals for 72 h (solid content = 2 %, initial pH = 10, particle size = < 2 mm, RT and ambient O_2).

Table 3
Cumulative formation constants for selected metal complexes with glycine at 25 °C, data from Dean, 1999; Kiss et al. (1991) (*M* stands for metal ion specified, *L* standards for glycine ligand, ionic strengths (*I*), unless specified, are approaching zero).

Metal ion	Cu^{2+}	Zn^{2+}	Ni^{2+}	Pb^{2+}	Co^{2+}	Fe^{2+} [a]	Ag^+	Pd^{2+}
log K_{ML}	8.60	5.52	6.12	5.53	5.23	4.13	3.43	9.12
log K_{ML2}	15.54	9.96	11.15	9.98	9.25	7.65	6.86	17.55
log K_{ML3}	16.27	–	–	–	10.76	–	–	–

[a] Ionic strength for Fe^{2+} is 0.1; "-" denotes not reported.

Table 4
Cu concentration in final leaching solution and final pH (at 72 h) at different solid content.

Solid content, %	1	1.4	2	3	10
Gly/WPCBs mass ratio	3.75	2.62	1.88	1.12	0.38
Final pH	11.12	11.88	11.52	12.22	12.22
Cu concentration, g/L	2.23	3.13	4.24	5.99	8.43
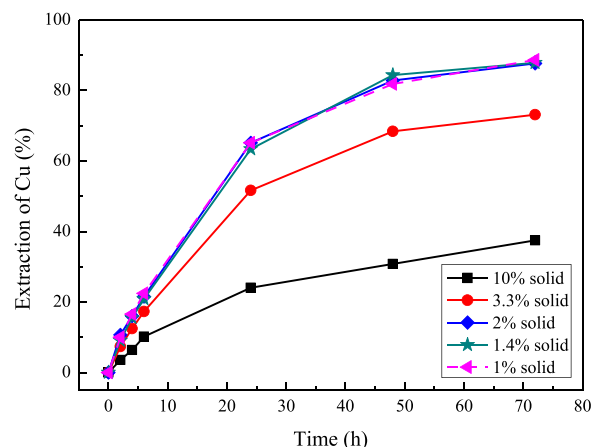
Fig. 10. Effect of solid content on the extraction of Cu (glycine concentration = 0.5 M, initial pH = 10.5, particle size = < 2 mm, RT and ambient O_2).

in the leaching solution were always below their analysis detection limit (< 0.2 ppm for Fe, < 1.0 ppb for Ag).

3.1.3. Effect of solid content

A series of solid contents (1–10 %) is selected to investigate its effect on the extraction of metals. The experiments were conducted at 0.5 M glycine, initial pH of 10.5, room temperature and < 2 mm particle size of WPCBs at ambient O_2. It should be noted that since glycine concentration was constant, the glycine amount used, *i.e.* glycine/WPCBs mass ratio, had been decreasing with the increase of solid content (Table 4). As can be seen from Fig. 10, the solid content below 2 % presented similar Cu extractions while a solid content higher than around 3 % resulted in considerable decrease in the extraction due to the high pH developed during leaching (Eq. (8), Fig. S10) and/or the less glycine added (Table 4). The Cu concentration in the final leaching solution is shown in Table 4. Not surprisingly, when the solid content was rising, Cu concentration increased accordingly. To improve the production capacity in industrial practice, a high solid content, *e.g.* ≥ 10 %, can be maintained and in the meantime, leaching solution with high Cu concentration (> 8 g/L) can be taken out for recovery and replenished by barren mother solutions containing free glycine. In this way, both high Cu extraction and high production capacity can be achieved, and glycine could be reused to reduce the reagent costs. According to Eksteen et al. (2017), the recycled barren mother solution
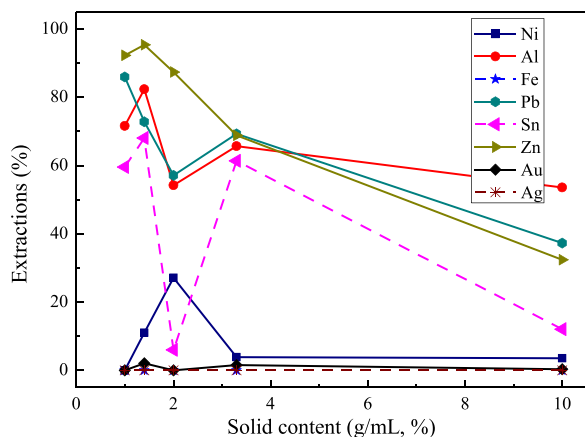
Fig. 11. Effect of solid content on the extraction of other metals for 72 h (glycine concentration = 0.5 M, initial pH = 10.5, particle size = < 2 mm, RT and ambient O$_2$).

Fig. 13. Effect of temperature on the extraction of other metals for 72 h (glycine concentration = 0.5 M, initial pH = 10, solid content = 2 %, particle size = < 2 mm, and ambient O$_2$).

containing recycled free glycine indicated similar rates of Cu extraction compared with the fresh glycine solution, in the case of leaching chalcopyrite. This reveals the feasibility of glycine reuse while further study is still needed to investigate the details of glycine consumption during leaching and recovery steps.

Fig. 11 shows the effect of solid content on the extraction of other metals for a leaching time of 72 h. Zn and Pb extraction decreased overall when solid content increased up to 10 %, explained by the decrease of available glycine (Table 4). The extraction of Al and Sn fluctuated markedly with the increase of solid content, which could be caused by the change of final pH and/or solid content. Slight extraction of Au (< 2.5 %) was also observed while Fe and Ag were still below their detection limit in the leaching solution.

3.1.4. Effect of temperature

To investigate the effect of temperature on the extraction of BMs, experiments at room (RT) and elevated (55 °C) temperature were performed at 0.5 M glycine, 2 % solid, initial pH of 10 and < 2 mm particle size of WPCBs at ambient O$_2$. As shown in Fig. 12, the selected temperatures had no significant influence on the Cu extraction over 72 h of leaching. It was recorded that the pH of leaching solution at 55 °C had been decreasing from 10.00–9.12 with the increase of leaching time (Fig. 12). This could be caused by the decomposition of glycine through deamination and decarboxylation at elevated temperature (O'Connor et al., 2018; Ogura et al., 1998; Sato et al., 2002). The decomposition is irreversible, and the products are mainly formic acid (H$_2$CO$_2$), ammonia (NH$_3$) and carbon dioxide (CO$_2$, or carbonic acid (H$_2$CO$_3$)) as

represented by Eq. (10) (O'Connor et al., 2018), which is confirmed by the obvious smell of ammonia during the leaching at 55 °C.

$$NH_2CH_2COO^- \ (aq) + OH^- \ (aq) \rightarrow HCOOH \ (aq) + NH_3 \ (g) + CO_2 \ (g) + 2e^- \quad (10)$$
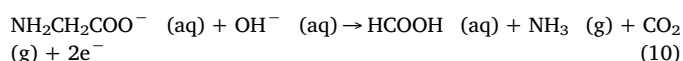
Fig. 13 shows the effect of temperature on the extraction of other metals after 72 h. The increase of temperature to 55 °C had no considerable increase (< 10 %) on the extraction for BMs except around 20 % rise of Pb extraction. On the contrary, the extraction of Zn decreased by about 10 %, due to the decrease of pH (to 9.12) or the decomposition of glycine. Further study with staged addition of alkali to maintain a pH at 10–10.7 (Section 3.1.1) may enhance the extraction of BMs. However, the leaching at elevated temperature (≥ 55 °C) will also increase the operational costs by reducing the recyclability of glycine due to the side reaction (Eq. (10)).

3.1.5. Effect of oxidant

At room temperature and ambient pressure, the solubility of O$_2$ in water is only around 8.2 ppm (Xing et al., 2014). As previously reported, oxidant is essential for the leaching of native metals in glycine leaching system (Li et al., 2018). Hence, to investigate the effect of oxidant on the extraction of BMs, experiments with H$_2$O$_2$ additions were carried out to compare with ambient O$_2$ results. The reason of selecting H$_2$O$_2$ is its environmentally friendly nature and high oxidizing ability (Dean, 1999). Other conditions were kept fixed at 0.5 M glycine,

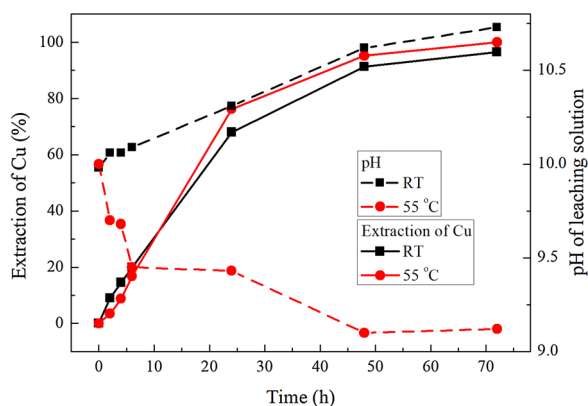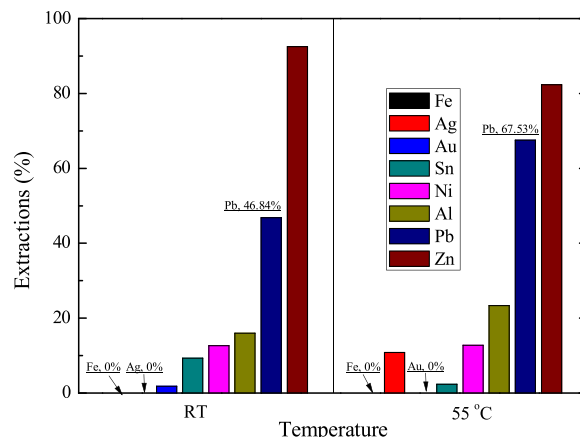**Fig. 12.** Effect of temperature on the extraction of Cu (glycine concentration = 0.5 M, initial pH = 10, solid content = 2 %, particle size = < 2 mm, and ambient O$_2$).

Fig. 14. Effect of peroxide concentration on the extraction of Cu (glycine concentration = 0.5 M, initial pH = 10.5, solid content = 1 %, particle size = < 2 mm, and RT).

Fig. 15. Effect of oxidant on the extraction of other metals for 72 h (glycine concentration = 0.5 M, initial pH = 10.5, solid content = 1 %, particle size = < 2 mm, and RT).

Fig. 16. Effect of particle size on the extraction of Cu (glycine concentration = 0.5 M, initial pH = 10, solid content = 2 %, RT, and ambient O_2).

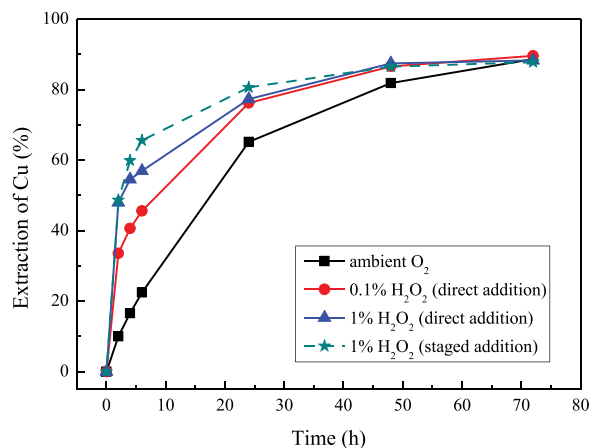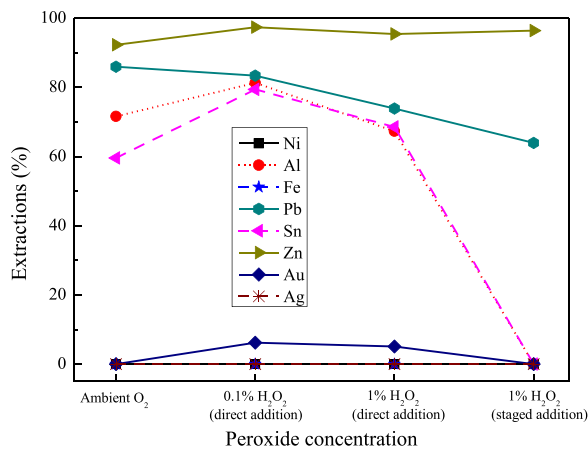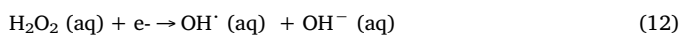initial pH of 10.5, 1 % solid, room temperature and < 2 mm particle size of WPCBs. As shown in Fig. 14, the addition of H_2O_2 had a considerable effect on the kinetics of Cu extraction. At the first 6 h, the additions of 0.1 % and 1 % H_2O_2 with direct and staged (4–4.5 mL 30 % H_2O_2 added at 0, 1, 2, 4, 6 h respectively) addition increased the Cu extraction by around 23 %, 35 % and 43 % respectively, compared with using ambient O_2. According to Oraby and Eksteen (2014), the cathodic reaction of H_2O_2 in alkaline glycine solution can be written as eqs. 11-12. The presence of hydrogen radical (OH·) offers high standard reduction potential (2.38 V). In addition, it has been known that H_2O_2 could be slowly decomposed into O_2 in alkaline environment as indicated in Eq. (13) (Galbács and Csányi, 1983), which also acts as an additional oxidant. However, after 72 h, the extraction of Cu at different peroxide levels reached at an almost same level (88 ± 2 %). This means that the leaching with a vented bottle could provide enough oxidant for Cu leaching

$$H_2O_2 \text{ (aq) } + 2 \text{ e-} \rightarrow 2OH^- \text{ (aq)} \quad (11)$$

$$H_2O_2 \text{ (aq) } + \text{ e-} \rightarrow OH^· \text{ (aq) } + OH^- \text{ (aq)} \quad (12)$$

$$2H_2O_2 \text{ (aq)} \rightarrow 2H_2O \text{ (l) } + O_2 \text{ (g)} \quad (13)$$

The extraction of other metals for a leaching time of 72 h is depicted in Fig. 15. The addition of H_2O_2 had no obvious effect on the extraction of Zn while a continues decrease in the Pb extraction was observed. As shown in Table 5, a decrease in the pH of final solution was observed at the leaching with 1 % H_2O_2, possibly due to the oxidation of glycine by H_2O_2 (Eq. (10)). Slight increase of Au extraction was also observed with 0.1 % and 1 % direct H_2O_2 addition. As reported by Eksteen and Oraby (2015), Au dissolution in alkaline glycine solution is very sensitive to temperature, pH and H_2O_2 concentration. The higher H_2O_2 concentration (0.1–2 %) results in higher Au extraction (Eksteen and Oraby, 2015).
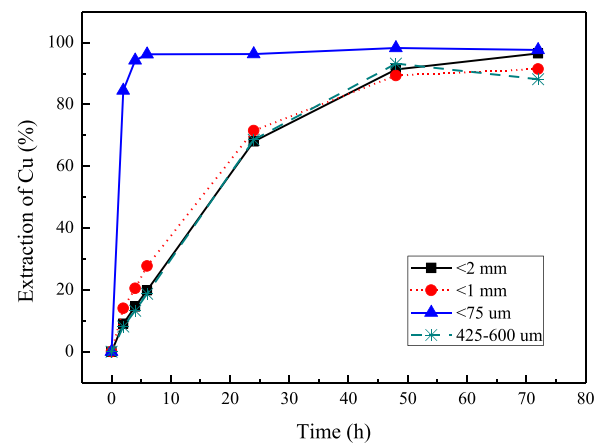
3.1.6. Effect of particle size

The particle size of WPCBs directly affects energy consumption during pre-treatment. To investigate the effect of particle size, four size

Table 5
pH of final leach solution after 72 h of leaching at different peroxide concentration (initial pH = 10.5).

Oxidant	Ambient O_2	0.1 % H_2O_2, direct add.	1 % H_2O_2, direct add.	1 % H_2O_2, staged add.
pH of final leach solution	11.12	10.84	10.26	9.99

ranges, *i.e.* < 75 μm, 425−600 μm, < 1 mm and < 2 mm, were selected. It should be noted that the sizes of < 75 μm and 425−600 μm were obtained from the screening of the originally pre-treated WPCBs (< 2 mm), indicating different metal contents contained in them (Fig. S2). By comparison, the < 1 mm size was obtained by milling of the original WPCBs (< 2 mm). Hence the metal contents in them could be considered the same (Table 2). Except for the particle size, all the other experimental conditions were fixed at 0.5 M glycine, initial pH of 10, 2 % solid content and room temperature with ambient O_2. As shown in Fig. 16, the milling of WPCBs to < 1 mm seems to be not necessary since only a marginal increase (3–8 %) of extraction was observed in the first 24 h. However, the screening of WPCBs to < 75 μm enhanced the extraction dramatically with 94.2 % Cu extracted in the first 4 h. By contrast, the sample with 425–600 size range, representing the fraction with highest Cu content (31.8 %, Fig. S2), did not experience an obvious increase of extraction compared with the original WPCBs (< 2 mm). As shown in Figs. S1–S2, the < 75 μm WPCBs represents a fraction as high as 18 % of total WPCBs mass and has low metal contents. To increase production capacity and efficiency in a real practice, a screening is suggested to separate this fraction of WPCBs before or during leaching. A similar study has been reported by Sun et al. (2015b) who installed a screen at the bottom of the leaching reactor to continuously separate the fine and coarse residues.

Fig. 17 shows the effect of particle size on the extraction of other metals for a leaching time of 72 h. Not as expected, the WPCBs
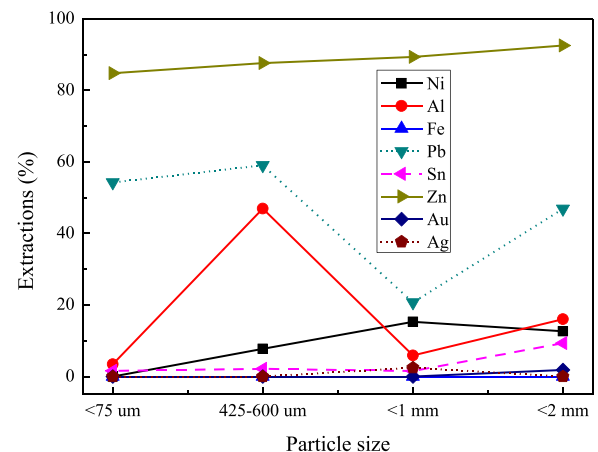
Fig. 17. Effect of particle size on the extraction of other metals for 72 h (glycine concentration = 0.5 M, initial pH = 10, solid content = 2 %, RT, and ambient O_2).

Table 6

pH of final leaching solution developed after 72 h of leaching with different particle size.

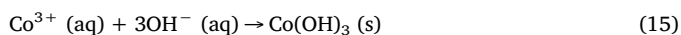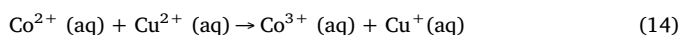| Particle size	< 75 μm	425–600 μm	< 1 mm	< 2 mm
pH of final leaching solution	10.08	11.75	10.54	10.73

with < 75 μm size did not reach higher extraction of BMs compared with those with 425−600 μm size due to the low final pH developed (Table 6, Fig. S11). Also, the milling to < 1 mm size did not result in obviously higher extraction of BMs compared with < 2 mm size, which again confirms that the milling to < 1 mm was not feasible.

After the optimisation of various variables, the leaching conditions of WPCBs at the highest Cu extraction are suggested to be: glycine concentration of 0.5 M, initial pH of 10, solid content of 2 %, leaching time of 72 h, room temperature, < 2 mm particle size at ambient O_2. Under the selected optimum leach conditions, the extraction of BMs and PMs are listed in Table 7. As shown in the table, 96.5 % Cu, 92.5 % Zn and 46.8 % Pb were extracted while the extractions of Al, Ni, Co and Sn were limited and less than 20 %. According to the variable investigations in Section 3.1, further increase of initial pH or glycine concentration could increase the extraction of Pb, Al and Sn considerably. Therefore, another glycine leaching stage with high initial pH could be applicable for these metals. The low level of Co extraction (3.1 %) could be resulted from the oxidation of Co^{2+} by the abundant Cu^{2+} in solution, and the subsequent precipitation of $Co(OH)_3$ as the reactions represented by Eqs. (14)–(15), and the Eh-pH diagram shown in Fig. S8. Among PMs, no obvious extraction of Au and Ag (< 2 %) was recorded while around 12.6 % Pd was extracted. This low extraction of Au and Ag is anticipated given the low levels of free residual glycine, low (ambient) temperature and low oxygen. Given the alkaline nature of the process, this base metals step may be followed by a cyanide-catalysed or starved cyanide system with glycine, which makes use of very low levels of cyanide to catalyse gold and silver dissolution, whilst keeping Weak Acid Dissociable (WAD) cyanide levels below environmental limits that would trigger cyanide detoxification (Eksteen et al., 2018; Oraby et al., 2019b). During this step, the remaining Cu and other BMs from glycine leaching could also be extracted (Oraby et al., 2019b).

$$Co^{2+} (aq) + Cu^{2+} (aq) \rightarrow Co^{3+} (aq) + Cu^+ (aq) \quad (14)$$

$$Co^{3+} (aq) + 3OH^- (aq) \rightarrow Co(OH)_3 (s) \quad (15)$$

3.2. Leaching kinetics of Cu

To determine the rate controlling step during the leaching of Cu from WPCBs, the experimental data of Cu extraction at different leaching time (Section 3.1) were fitted into Eqs. (5) and (6). Table 8 shows the correlation coefficient values for the chemical reaction and diffusion control models. As can be seen, the diffusion control model fits well with the Cu extraction investigated, and shows higher coefficient values than chemical reaction control model for most of the variables (except particle size of 425−600 μm and temperature of 55 °C). Therefore, it can be concluded that the Cu leaching from WPCBs (< 2 mm) in alkaline glycine solution with ambient O_2 is mainly

Table 8

Correlation coefficient values for kinetic models (unless specified, leaching time of 0, 2, 4, 6, 24, 48 and 72 h was investigated).

Variables	Coefficient of variation for the investigated models: R^2	
	Chemical reaction control $1-(1-x)^{1/3}$	Diffusion control $1-(2/3)x-(1-x)^{2/3}$
Initial pH		
8.02	0.9690	0.9897
9.98	0.9755	0.9869
10.51	0.9406	0.9760
12.04	0.9392	0.9949
13.00	0.9860	0.9917
Glycine con, M		
0.2	0.9210	0.9749
0.3	0.9354	0.9657
0.5	0.9755	0.9869
0.7	0.9602	0.9896
1.0	0.9723	0.9917
Solid content, %		
1.0	0.9510	0.9869
1.4	0.9421	0.9696
2.0	0.9406	0.9760
3.3	0.9329	0.9757
10	0.9390	0.9957
Temperature		
RT	0.9755	0.9869
55 °C	0.9954	0.9950
Particle size		
425−600 μm [a]	0.9980	0.9840
< 1 mm	0.9250	0.9549
< 2 mm	0.9755	0.9869

[a] For particle size of 425−600 μm, only the initial 48 h was investigated since no increase of Cu extraction was achieved after 48 h.

controlled by internal diffusion at room temperature. The conclusion is justified by the higher coefficient when particle size was reduced from < 2 mm to 425−600 μm (Table 8). Moreover, the apparent activation energy calculated from Arrhenius equation is 6.62 KJ/mol (Section 7 of SI), verifying that the Cu leaching was controlled by diffusion (4–12 KJ/mol) (Ma et al., 2017). To enhance the internal diffusion, further reduction of particle size to < 425 μm or increase of bottle rolling speed to > 100 rpm may be an effective way.

4. Conclusions

A sustainable approach for the extraction of Cu from WPCBs, and the co-leaching behaviours of other metals in alkaline glycine solution are presented in this study. Under the optimum leach conditions (0.5 M glycine, initial pH 10, 2 % solid, < 2 mm particle size, room temperature, 72 h, and ambient O_2) the highest Cu extraction was 96.5 %, however the extraction for the other BMs were recorded as 92.5 % Zn, 46.8 % Pb, 16.0 % Al, 12.6 % Ni, 9.3 % Sn and 3.1 % Co. Meanwhile, the extractions of Au and Ag were less than 2 % under the investigated leach conditions. Pd extraction of 12.6 % was achieved at the optimum leach conditions. It was found that the pH of leaching solution affected

Table 7

Extraction percentages of BMs and PMs under the optimum conditions (glycine concentration = 0.5 M, initial pH = 10, solid content = 2 %, particle size = < 2 mm, RT, 72 h, and ambient O_2).

	Base metals								Precious metals		
	Cu	Zn	Pb	Al	Ni	Co	Fe	Sn	Au	Ag	Pd
Extraction, %	96.5	92.5	46.8	16.0	12.6	3.1	BDL[a]	9.3	1.8	BDL	12.6

[a] BDL denotes below detection limit of 0.2 ppm for Fe and 1.0 ppb for Ag.

the extraction of BMs considerably, and the pH progression was highly correlated with other parameters (glycine concentration, solid content, temperature and oxidant). It was also found that glycine concentration and solid content had a significant effect on the extraction of BMs. However, temperature (RT-55 °C) and oxidant of H_2O_2 (0.1–1 %) had relatively slight influences. A significant enhancement on the Cu extraction was reached when the size reduced to < 75 μm. The SEM-EDS analyses showed that the unleached Cu and Ni were locked in the inert layers, including Sn/solder materials and Au layer. The Cu leaching kinetic from WPCBs (< 2 mm) in alkaline glycine solution at ambient O_2 was mainly controlled by internal diffusion with an activation energy of 6.62 KJ/mol. This study provides guidance for the extraction of Cu and other BMs from e-waste or any materials bearing these metals using environmental-friendly alkaline glycine solutions, which has the potential to be applied in areas where strict environmental regulations apply.

Author attribution and contributions

Huan Li, the lead author, is a PhD student with Prof Jacques Eksteen as Main Supervisor and Dr Elsayed Oraby as co-supervisor.

Mr Huan Li performed the design and execution of the experiments and compiled the results presented in this manuscript and prepared the draft document for review.

Dr Elsayed Oraby and Prof Jacques Eksteen are the inventors of patents that is utilised in Mr Huan Li's Research and supported Mr Li in the scoping of the PhD research.

The supervisors reviewed and edited the manuscript and contributed with further reference additions and advice.

Declaration of Competing Interest

None.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.resconrec.2019.104624.

References

Aksu, S., Doyle, F.M., 2001. Electrochemistry of copper in aqueous glycine solutions. J. Electrochem. Soc. 148 (1), B51–B57.

Aleksandrov, Y.A., Tsyganova, E.I., Pisarev, A.L., 2003. Reaction of aluminum with dilute aqueous NaOH solutions. Russ. J. Gen. Chem. 73 (5), 689–694.

Baldé, C.P., Forti, V., Gray, V., Kuehr, R., Stegmann, P., 2017. The Global e-waste Monitor - 2017, United Nations University (UNU). International Telecommunication Union (ITU) & International Solid Waste Association (ISWA). Available at https://www.itu.int/en/ITU-D/Climate-Change/Documents/GEM%202017/Global-E-waste%20Monitor%202017%20.pdf (Accessed on 01 July 2019).

Calgaro, C.O., et al., 2015. Fast copper extraction from printed circuit boards using supercritical carbon dioxide. Waste Manage. 45, 289–297.

Chauhan, G., Jadhao, P.R., Pant, K.K., Nigam, K.D.P., 2018. Novel technologies and conventional processes for recovery of metals from waste electrical and electronic equipment: challenges & opportunities – a review. J. Environ. Chem. Eng. 6 (1), 1288–1304.

Chen, M., Huang, J., Ogunseitan, O.A., Zhu, N., Wang, Y.-m., 2015a. Comparative study on copper leaching from waste printed circuit boards by typical ionic liquid acids. Waste Manage. 41, 142–147.

Chen, M., Zhang, S., Huang, J., Chen, H., 2015b. Lead during the leaching process of copper from waste printed circuit boards by five typical ionic liquid acids. J. Clean. Prod. 95, 142–147.

D'Adamo, I., et al., 2019. Towards sustainable recycling processes: wasted printed circuit boards as a source of economic opportunities. Resour. Conserv. Recy. 149, 455–467.

Dean, J.A., 1999. Lange's Handbook of Chemistry, 15th edition. McGraw-Hill Inc.

Deng, Z., Oraby, E., Eksteen, J., 2019. The sulfide precipitation behaviour of Cu and Au from their aqueous alkaline glycinate and cyanide complexes. Sep. Purif. Technol. 218, 181–190.

Duan, H., Hou, K., Li, J., Zhu, X., 2011. Examining the technology acceptance for dismantling of waste printed circuit boards in light of recycling and environmental concerns. J. Environ. Manage. 92 (3), 392–399.

Eksteen, J., Oraby, E., 2015. The leaching and adsorption of gold using low concentration amino acids and hydrogen peroxide: effect of catalytic ions, sulphide minerals and amino acid type. Miner. Eng. 70, 36–42.

Eksteen J. and Oraby, E., 2016. Process for selective recovery of chalcophile group elements. PCT Patent WO2016141438A1.

Eksteen, J.J. and Oraby, E.A., 2014. A process for copper and/or precious metal recovery. US Patent 20160194734 A1.

Eksteen, J.J., Oraby, E.A., Tanda, B.C., 2017. A conceptual process for copper extraction from chalcopyrite in alkaline glycinate solutions. Miner. Eng. 108, 53–66.

Eksteen, J.J., Oraby, E.A., Tanda, B.C., Tauetsile, P.J., Bezuidenhout, G.A., Newton, T., Trask, F., Bryan, I., 2018. Towards industrial implementation of glycine-based leach and adsorption technologies for gold-copper ores. Can. Metall. Q. 57 (4), 390–398.

Galbács, Z.M., Csányi, L.J., 1983. Alkali-induced decomposition of hydrogen peroxide. J. Chem. Soc. Dalton Trans. 0, 2353–2357.

Gary, M.L., Paul, S.J., Donald, T.A., 2014. Inorganic Chemistry, 5th edition. .

Ghosh, S.K., et al., 2016. Waste electrical and electronic equipment management and Basel Convention compliance in Brazil, Russia, India, China and South Africa (BRICS) nations. Waste Manag. Res. 34 (8), 693–707.

Hotea, V., 2013. Clean technology of lead recovery from spent lead paste. In: Chania, Crete Island, Greece. WSEAS Conference Program 2. pp. 263–269.

Işıldar, A., Rene, E.R., van Hullebusch, E.D., Lens, P.N.L., 2018. Electronic waste as a secondary source of critical metals: management and recovery technologies. Resour. Conserv. Recycl. 135, 296–312.

Jadhao, P., Chauhan, G., Pant, K., Nigam, K., 2016. Greener approach for the extraction of copper metal from electronic waste. Waste Manage. 57, 102–112.

Janjevic, D., 2018. Thailand Moves to Ban Importing e-waste and Plastic. Avaliable at https://www.dw.com/en/thailand-moves-to-ban-importing-e-waste-and-plastic/a-45103610 (Accessed on 01 July 2019). .

Jha, M.K., et al., 2011. Pressure leaching of metals from waste printed circuit boards using sulfuric acid. JOM 63 (8), 29–32.

Jung, M., Yoo, K., Alorro, R.D., 2017. Dismantling of electric and electronic components from waste printed circuit boards by hydrochloric acid leaching with stannic ions. Mater. Trans. 58 (7), 1076–1080.

Kannan, D., Govindan, K., Shankar, M., 2016. India: formalize recycling of electronic waste. Nature 530 (7590) 281-281.

Kékesi, T., Török, T.I., Kabelik, G., 2000. Extraction of tin from scrap by chemical and electrochemical methods in alkaline media. Hydrometallurgy 55 (2), 213–222.

Khaliq, A., Rhamdhani, M.A., Brooks, G., Masood, S., 2014. Metal extraction processes for electronic waste and existing industrial routes: a review and Australian perspective. Resources 3 (1), 152–179.

Kiss, T., Sovago, I., Gergely, A., 1991. Critical survey of stability constants of complexes of glycine. Pure Appl. Chem. 63 (4), 597–638.

Kumari, A., Jha, M.K., Singh, R.P., 2016. Recovery of metals from pyrolysed PCBs by hydrometallurgical techniques. Hydrometallurgy 165, 97–105.

Kumar, A., Holuszko, M., Espinosa, D.C.R., 2017. E-waste: an overview on generation, collection, legislation and recycling practices. Resour. Conserv. Recycl. 122, 32–42.

Lee, D., Offenhuber, D., Duarte, F., Biderman, A., Ratti, C., 2018. Monitour: tracking global routes of electronic waste. Waste Manage. 72, 362–370.

Li, H., Eksteen, J., Oraby, E., 2018. Hydrometallurgical recovery of metals from waste printed circuit boards (WPCBs): current status and perspectives – a review. Resour. Conserv. Recycl. 139, 122–139.

Li, J., Zeng, X., Chen, M., Ogunseitan, O.A., Stevels, A., 2015. "Control-Alt-Delete": rebooting solutions for the e-waste problem. Environ. Sci. Technol. 49 (12), 7095–7108.

Lu, Y., Xu, Z., 2016. Precious metals recovery from waste printed circuit boards: a review for current status and perspective. Resour. Conserv. Recycl. 113, 28–39.

Ma, J.-y., et al., 2017. Kinetics on leaching of potassium from phosphorus–potassium associated ore in HCl–H3PO4 media. Trans. Nonferrous Met. Soc. China 27 (8), 1870–1877.

McGrath, T., Morrison, P.D., Ball, A.S., Clarke, B.O., 2018. Spatial distribution of novel and legacy brominated flame retardants in soils surrounding two Australian electronic waste recycling facilities. Environ. Sci. Technol. 52, 8194–8204.

O'Connor, G.M., Lepkova, K., Eksteen, J.J., Oraby, E.A., 2018. Electrochemical behaviour of copper in alkaline glycine solutions. Hydrometallurgy 181, 221–229.

Ogunseitan, O.A., Schoenung, J.M., Saphores, J.-D.M., Shapiro, A.A., 2009. The electronics revolution: from e-wonderland to e-wasteland. Science 326 (5953), 670–671.

Ogura, K., Kobayashi, M., Nakayama, M., Miho, Y., 1998. Electrochemical and in situ FTIR studies on the adsorption and oxidation of glycine and lysine in alkaline medium. J. Electroanal. Chem. 449 (1), 101–109.

Oraby, E.A., Eksteen, J.J., 2014. The selective leaching of copper from a gold–copper concentrate in glycine solutions. Hydrometallurgy 150, 14–19.

Oraby, E.A., Eksteen, J.J., 2015. The leaching of gold, silver and their alloys in alkaline glycine–peroxide solutions and their adsorption on carbon. Hydrometallurgy 152, 199–203.

Oraby, E.A., Eksteen, J.J., Karrech, A., Attar, M., 2019a. Gold extraction from paleochannel ores using an aerated alkaline glycine lixiviant for consideration in heap and in-situ leaching applications. Miner. Eng. 138, 112–118.

Oraby, E.A., Eksteen, J.J., Tanda, B.C., 2017. Gold and copper leaching from gold-copper ores and concentrates using a synergistic lixiviant mixture of glycine and cyanide. Hydrometallurgy 169, 339–345.

Oraby, E.A., Li, H., Eksteen, J.J., 2019b. An alkaline glycine-based leach process of base and precious metals from powdered waste printed circuit boards. Waste Biomass Valori. https://doi.org/10.1007/s12649-019-00780-0. (in press).

Ortiz-Aparicio, J., et al., 2007. Electrodeposition of zinc–cobalt alloy from a complexing alkaline glycinate bath. Electrochim. Acta 52 (14), 4742–4751.

Perea, C., Restrepo, O., 2018. Use of amino acids for gold dissolution. Hydrometallurgy 177, 79–85.

Rodriguez-Torres, I., Valentin, G., Chanel, S., Lapicque, F., 2000. Recovery of zinc and nickel from electrogalvanisation sludges using glycine solutions. Electrochim. Acta 46 (2), 279–287.

Sato, N., Daimon, H., Fujie, K., 2002. Decomposition of Glycine in high temperature and high pressure water. Kagaku Kogaku Ronbunshu 28 (1), 113–117.

Sharma, N., Chauhan, G., Kumar, A., Sharma, S., 2017. Statistical optimization of heavy metals (Cu2 + /Co2 +) extraction from printed circuit board and mobile batteries using chelation technology. Ind. Eng. Chem. Res. 56, 6805–6819.

Sun, Z., et al., 2015a. Selective copper recovery from complex mixtures of end-of-life electronic products with ammonia-based solution. Hydrometallurgy 152, 91–99.

Sun, Z., Xiao, Y., Sietsma, J., Agterhuis, H., Yang, Y., 2015b. A cleaner process for selective recovery of valuable metals from electronic waste of complex mixtures of end-of-life electronic products. Environ. Sci. Technol. 49 (13), 7981–7988.

Sun, Z., et al., 2016. Toward sustainability for recovery of critical metals from electronic waste: the hydrochemistry processes. ACS Sustain. Chem. Eng. 5 (1), 21–40.

Sundaresan, R., Saraiya, S., Radhakrishnan, T., Sundaram, A., 1968. Polarography of zinc in presence of glycine. Electrochim. Acta 13 (3), 443–447.

Tauetsile, P.J., Oraby, E.A., Eksteen, J.J., 2018. Adsorption behaviour of copper and gold glycinates in alkaline media onto activated carbon. Part 1: isotherms. Hydrometallurgy 178, 202–208.

Tan, Q., Li, J., Boljkovac, C., 2018. Responding to China's waste import ban through a new, innovative, cooperative mechanism. Environ. Sci. Technol. 52, 7595–7597.

Tanda, B.C., Eksteen, J.J., Oraby, E.A., 2017a. An investigation into the leaching behaviour of copper oxide minerals in aqueous alkaline glycine solutions. Hydrometallurgy 167, 153–162.

Tanda, B., Oraby, E., Eksteen, J., 2017b. Recovery of copper from alkaline glycine leach solution using solvent extraction. Sep. Purif. Technol. 187, 389–396.

Wang, Z., Zhang, B., Guan, D., 2016. Take responsibility for electronic-waste disposal. Nature 536, 4.

Xing, W., et al., 2014. 1- Oxygen solubility, diffusion coefficient, and solution viscosity. In: Xing, W., Yin, G., Zhang, J. (Eds.), Rotating Electrode Methods and Oxygen Reduction Electrocatalysts. Elsevier, Amsterdam, pp. 1–31.

Xu, Y., Liu, J., 2015. Recent developments and perspective of the spent waste printed circuit boards. Waste Manag. Res. 33 (5), 392–400.

Yazici, E., Deveci, H., 2013. Extraction of metals from waste printed circuit boards (WPCBs) in H2SO4-CuSO4-NaCl solutions. Hydrometallurgy 139, 30–38.

Zeng, X., Mathews, J.A., Li, J., 2018. Urban mining of E-waste is becoming more cost-effective than virgin mining. Environ. Sci. Technol. 52 (8), 4835–4841.

Zhang, X., et al., 2017. Effective dismantling of waste printed circuit board assembly with methanesulfonic acid containing hydrogen peroxide. Environ. Prog. Sustain. Energy 36 (3), 873–878.

Supporting Information (SI)

Extraction of copper and the co-leaching behaviour of other metals from waste printed circuit boards using alkaline glycine solutions

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The contents provided in this attachment is supporting information and covers:

1. The size distribution of the waste printed circuit boards after pre-treatment
2. The grade of metals by size fraction
3. The pH progression of the leach solution with different initial pH
4. E_h-pH diagrams for Zn, Pb, Ni, Fe and Co
5. SEM-EDS analysis of selected particles of WPCBs before leaching
6. The pH progression of the leach solution with varied solids % and crush size
7. Calculation of apparent activation energy

1. Size distribution of the waste printed circuit boards after pre-treatment
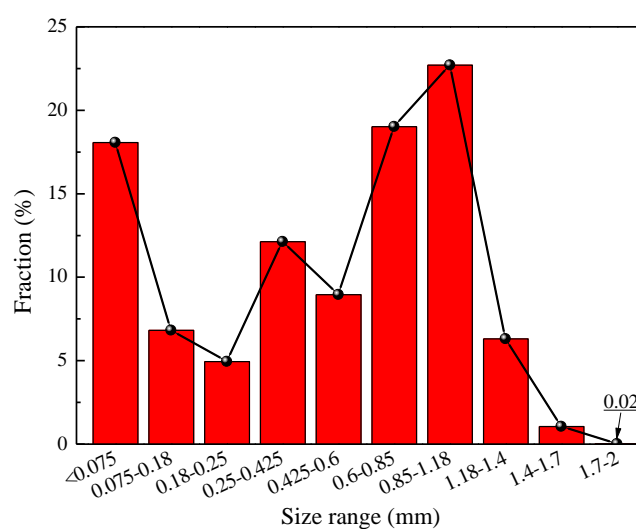
Figure S1. Size distribution of WPCBs (100% < 2 mm) used in this study.

2. Grade of metals by size fraction
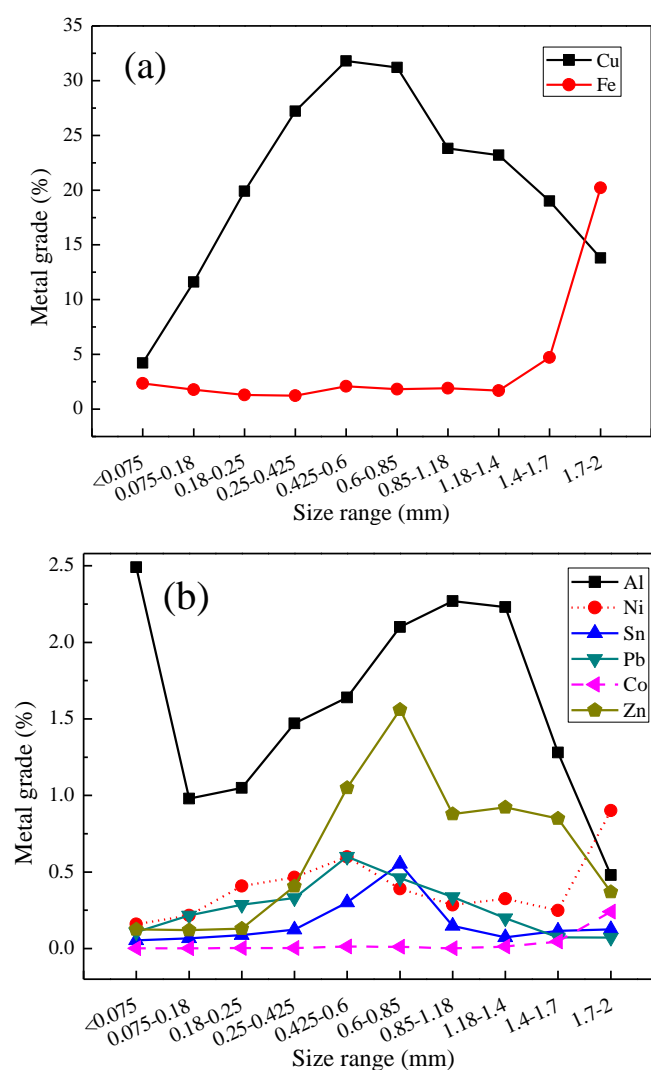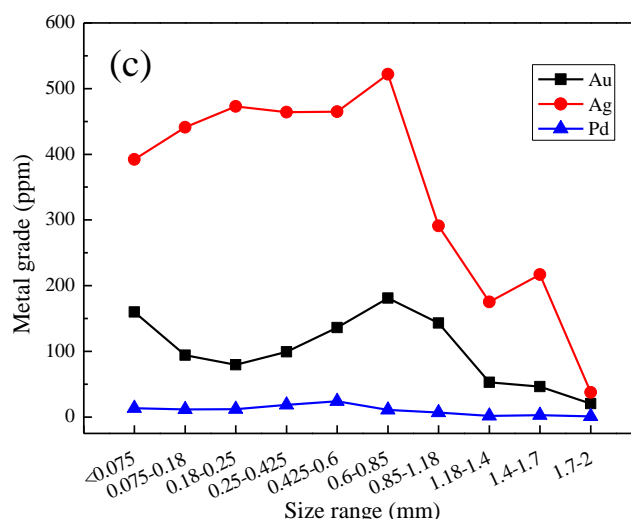
Figure S2. Metal grade distribution of (a–b) base and (b) precious metals in WPCBs (100% < 2 mm) used in this study.

As shown in the Figure S1–2, most of the WPCBs (62.8%) were distributed in a range from 0.25 to 1.18 mm with most of the BMs contained. Among them, the highest Cu grade of 31.8% was found in 0.425–0.6 mm WPCBs. Most of the Au and Ag were found in a smaller size, i.e. <0.85 mm. Considerable amount of WPCBs (18.1%) had a size of less than 75 μm with relatively low grade of BMs, including only 4.2% Cu, and high grade of Au (160 ppm) and Ag (392 ppm).

3. pH progression of leach solution with different initial pH
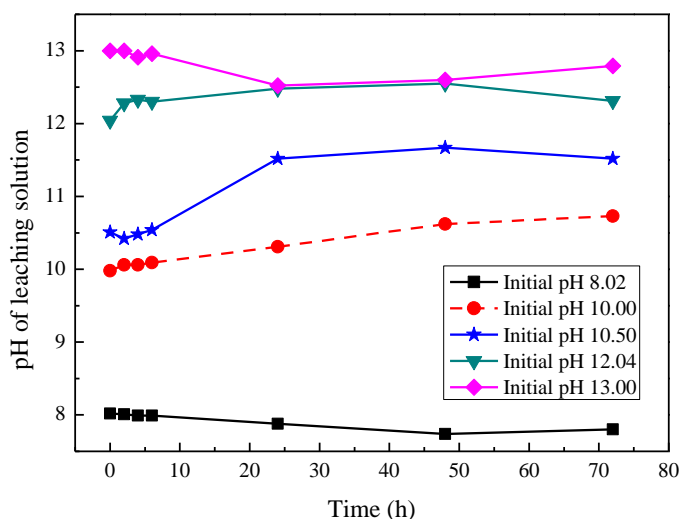
Figure S3. pH progression of the leaching solution as a function of time at different initial pH (glycine concentration = 0.5 M, solid ratio = 2%, particle size = <2 mm, RT and ambient O_2).

4. Eh-pH diagram for Zn, Pb, Ni, Fe and Co
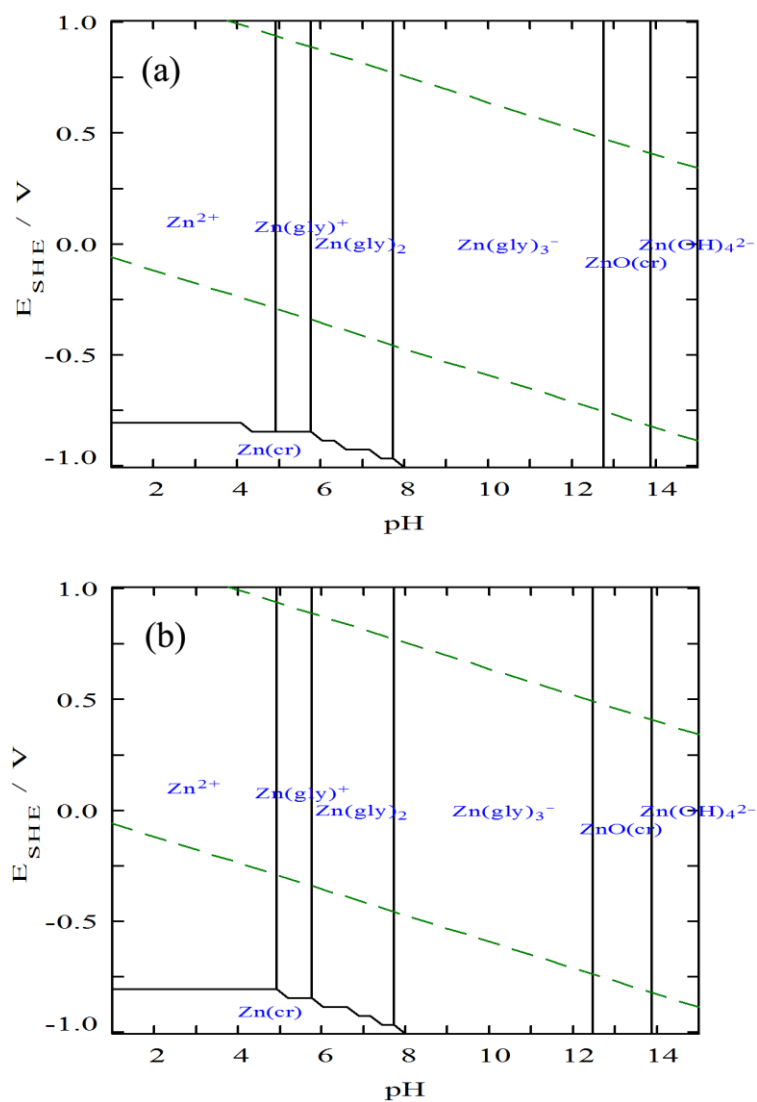
Figure S4. Eh-pH diagram for Zn-glycine system at 0.5 M glycine, 25°C, and (a) 2 mM Zn; (b) 5 mM Zn, made by Medusa-Hydra software (https://www.kth.se/che/medusa/, same below).
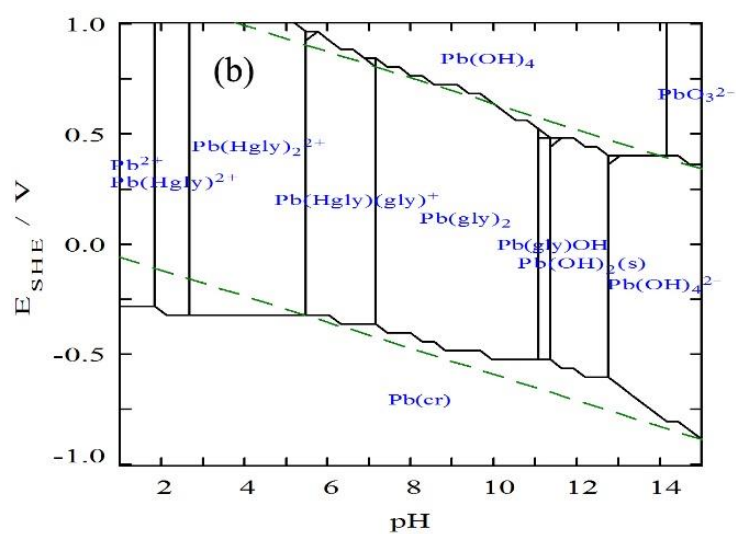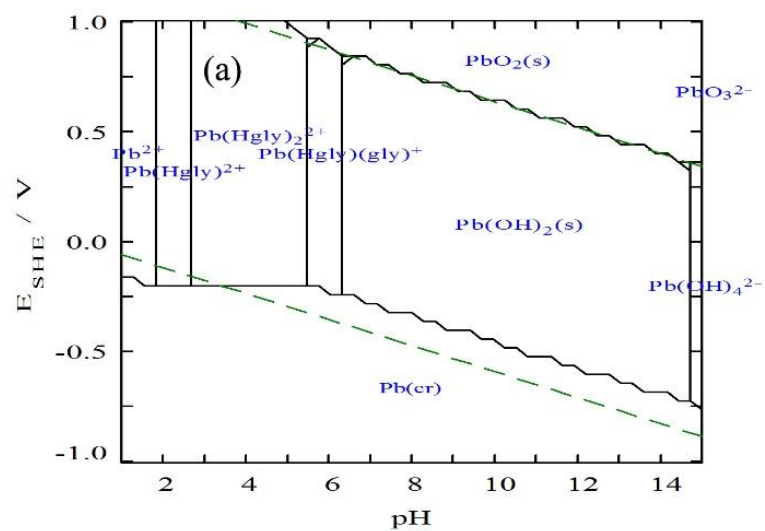
Figure S5. Eh-pH diagram for Pb-glycine system at 0.5 M glycine, 25°C, and (a) 5 mM Pb; (b) 1 μM Pb.
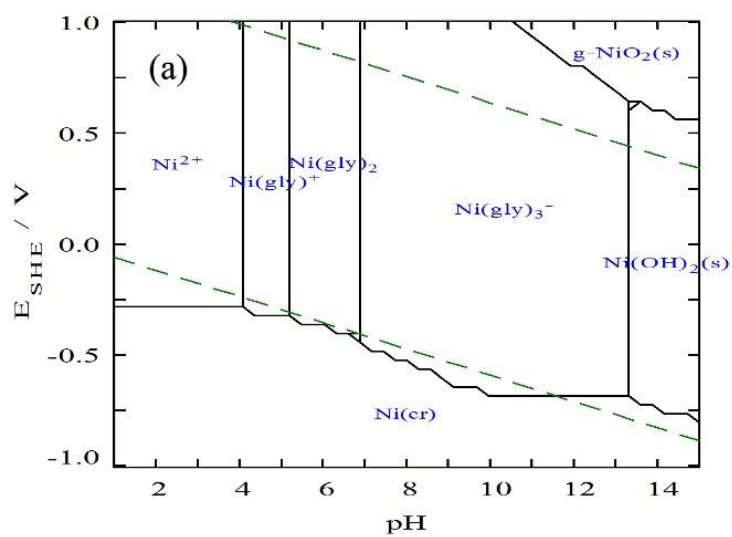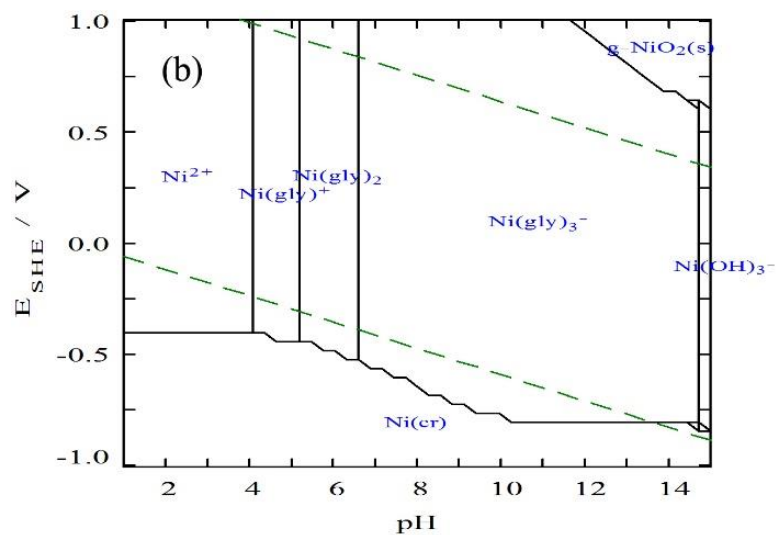
Figure S6. Eh-pH diagram for Ni-glycine system at 0.5 M glycine, 25°C, and (a) 5 mM Ni; (b) 1 μM Ni.
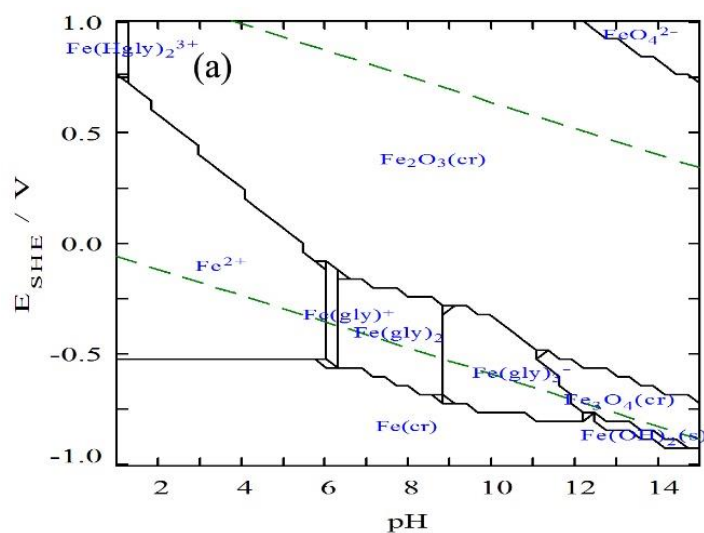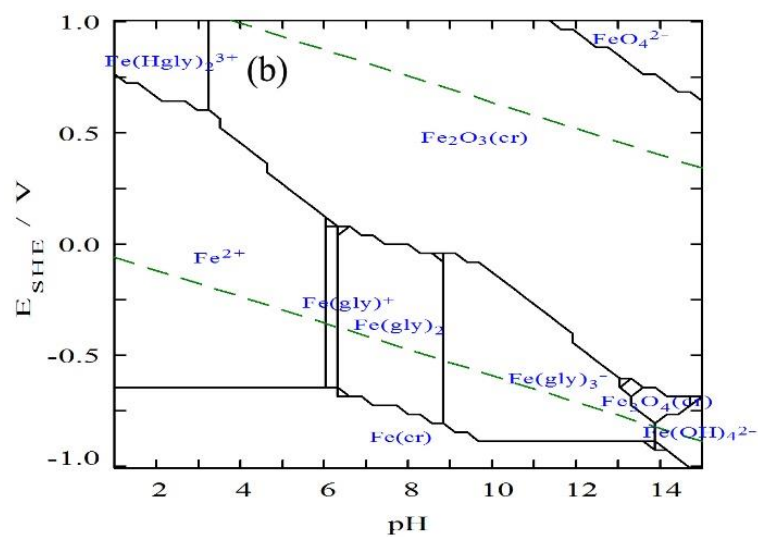
Figure S7. Eh-pH diagram for Fe-glycine system at 0.5 M glycine, 25°C, and (a) 5 mM Fe; (b) 1 μM Fe.
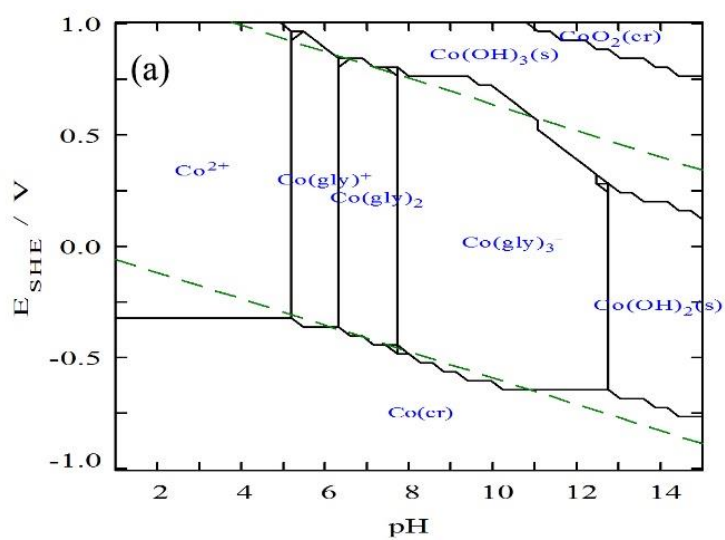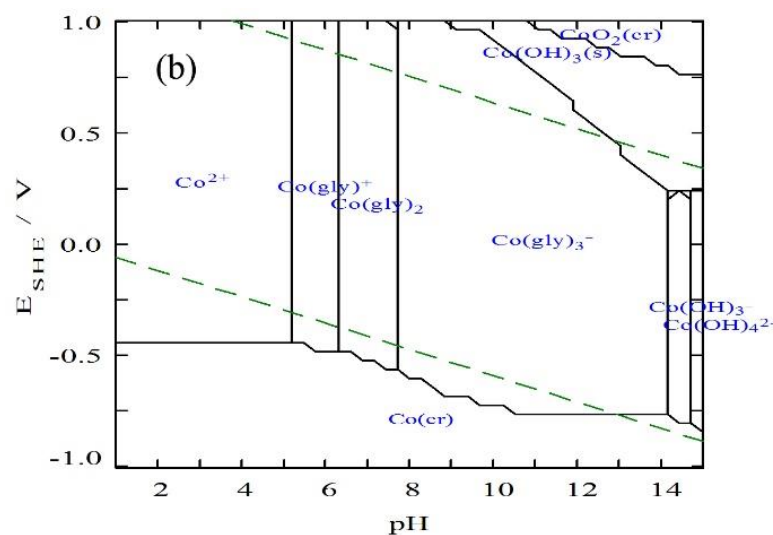
Figure S8. Eh-pH diagram for Co-glycine system at 0.5 M glycine, 25°C, and (a) 5 mM Co; (b) 1 μM Co.

5. SEM-EDS analysis of selected particles of WPCBs before leaching
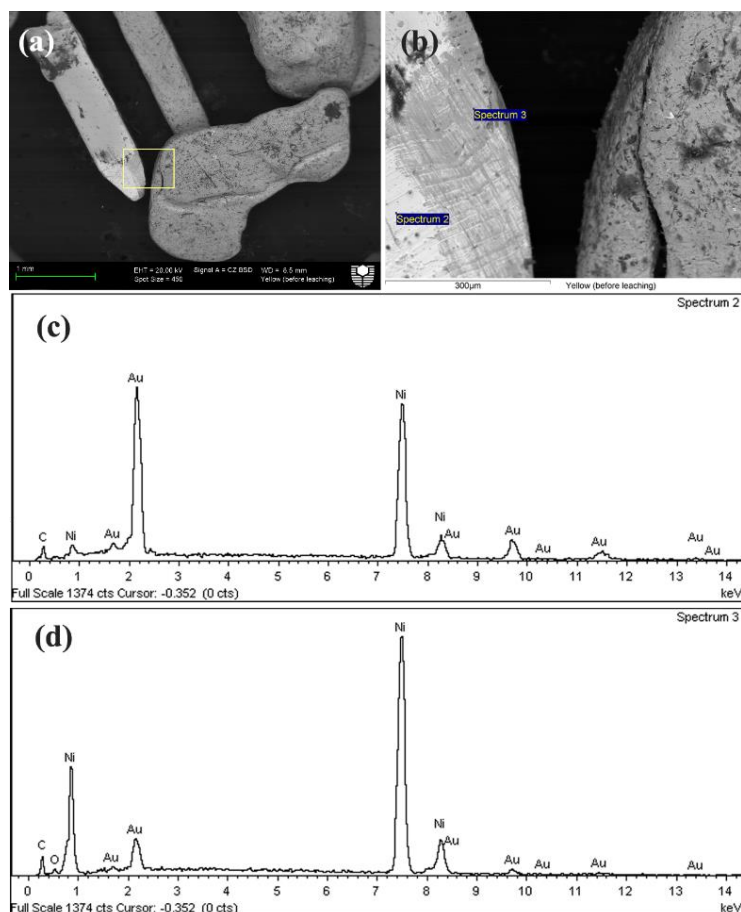
Figure S9. SEM-EDS analysis of selected particles of WPCBs before leaching ((b) is from the selected area in (a), (c) and (d) are the EDS analyses of the selected dots labelled as Spectrum 2 and Spectrum 3 in (b), respectively).

6. pH progression of leach solution with varied solids % and crush size
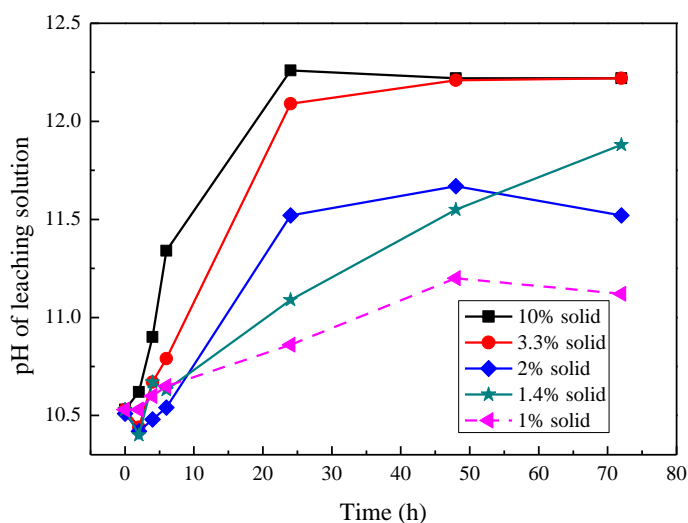
Figure S10. pH progression of the leaching solution as a function of time at different solid ratio (glycine concentration = 0.5 M, initial pH = 10.5, particle size = <2 mm, room temperature and ambient O_2).
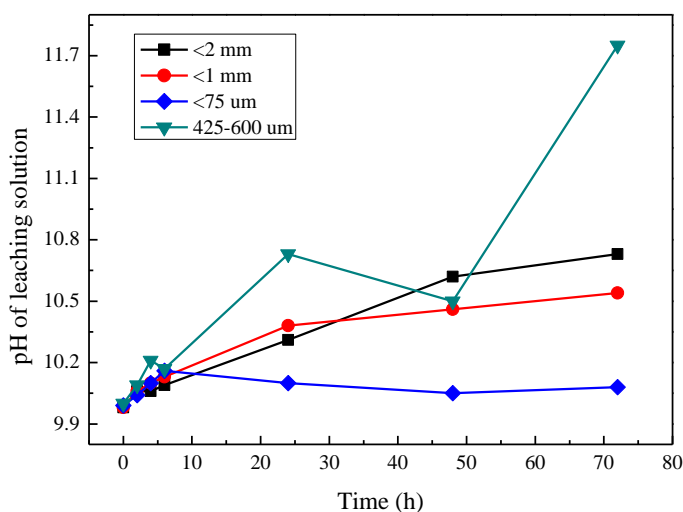
Figure S11. pH progression of the leaching solution as a function of time with different particle size of WPCBs (glycine concentration = 0.5 M, initial pH = 10, solid ratio = 2%, room temperature, and ambient O_2).

7. Calculation of apparent activation energy

During the leaching of Cu from WPCBs (<2 mm) in alkaline glycine solution with ambient O_2 as oxidant, the apparent activation energy under diffusion control is estimated according to Arrhenius equation:

$$k = Ae^{-E_a/RT} \tag{S1}$$

where k represents the rate constant; E_a is the apparent activation energy (J/mol); R is the gas constant with a value of 8.314 J/mol/K; A is the pre-exponential factor, a constant for each chemical reaction; and T is the temperature (kelvin, K).

Alternatively, the equation can be written as:

$$\lg k = -\frac{E_a}{2.303RT} + \lg A \qquad (S2)$$

In this study, two temperatures, i.e. T_1 = room temperature (23°C), and T_2 = 55°C, were tested. Therefore, eq. S2 can be written as:

$$\lg k_1 = -\frac{E_a}{2.303RT_1} + \lg A \qquad (S3)$$

$$\lg k_2 = -\frac{E_a}{2.303RT_2} + \lg A \qquad (S4)$$

S4 – S3:

$$E_a = \frac{2.303RT_1T_2}{T_2 - T_1} \lg \frac{k_2}{k_1} \qquad (S5)$$

Therefore, the apparent activation energy (E_a) can be estimated by eq. S5. Under diffusion control, the k values at 23°C and 55°C can be estimated by plotting $1-(2/3)x-(1-x)^{2/3}$ vs. t according to eq. 5. As shown in Figure S12, k_1 and k_2 are estimated as 0.003759 and 0.004886 respectively. Therefore, the apparent activation energy is calculated as 6.62 kJ/mol.
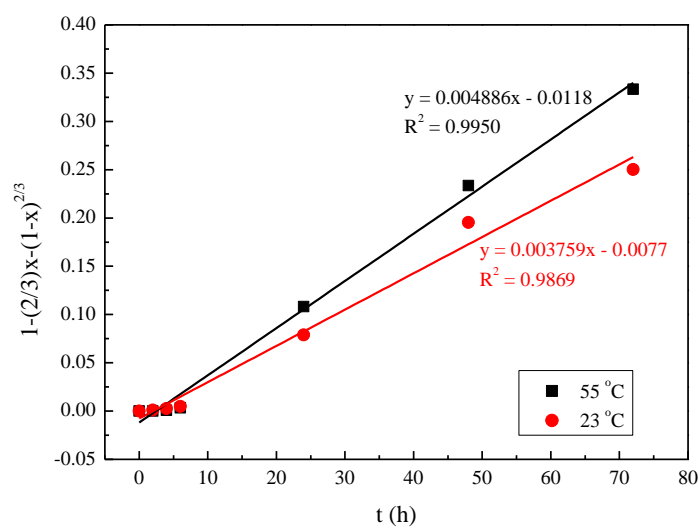
Figure S12. Plot of $1-(2/3)x-(1-x)^{2/3}$ vs. t at different temperature.
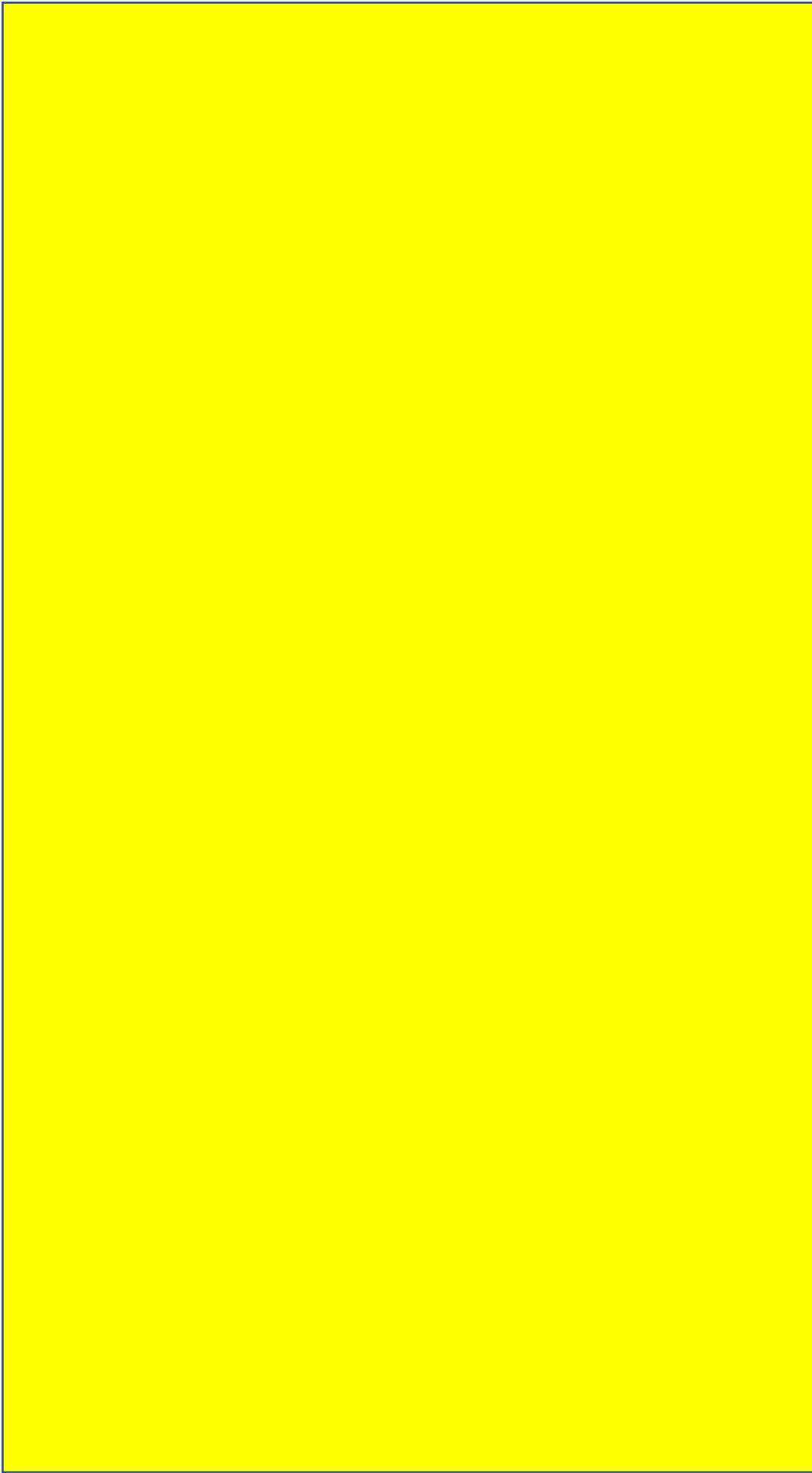
Chapter 5 Recovery of copper from glycine leachates

Summary

This chapter is a follow-up study of Chapter 4. It investigates copper recovery and the behaviours of other base metals from glycine leachates. It focuses on the feasibility of three options, i.e. hydrazine reduction, sulfide precipitation and solvent extraction, for copper recovery.

Recovery of copper and the deportment of other base metals from alkaline glycine leachates derived from waste printed circuit boards (WPCBs)

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ARTICLE INFO

ABSTRACT

E-waste has become a global risk to the environment and humans due to the improper disposal. Recently, a novel approach has been reported to effectively extract copper (Cu) from waste printed circuit boards (WPCBs) using environmentally friendly glycine solutions, with the co-extraction of other base metals. This process step is ideally positioned after the bulk of the aluminium, copper and iron is removed using conventional dry physical processes, but before hydrometallurgical recovery of precious metals. To recover Cu and other minor base metals from glycine leachate of WPCBs and release the glycine for reuse, this study investigates three options, i.e. hydrazine reduction, sulphide precipitation, and solvent extraction. During the hydrazine reduction, it was found that Cu recovery was sensitive to the leachate pH, and copper recovery increases with the increase of initial pH, Cu concentration and temperature. The obvious co-precipitation of lead and tin was also found while no co-precipitation of nickel, zinc and aluminium was observed. At the Cu/hydrazine molar ratio of 1:0.7 and 1:1, the products were identified as cuprite (Cu_2O) and native Cu with 96.9% and 98.6% recoveries, respectively. During sulphide precipitation, $\geq$99.5% Cu could be easily precipitated at Cu/HS^- molar ratio $\leq$ 1:1.2 in only 5 min. Lead, tin and zinc in the alkaline glycinate leachate also precipitated to a significant extent (>65%), whereas aluminium and nickel co-precipitation was limited ($\leq$3%) in the sulphide. XRD analysis of precipitates verifies that Cu was recovered as covellite (CuS). During solvent extraction from the polymetallic leachate, Mextral 84H showed better performance than Mextral 54–100 but requires higher H_2SO_4 concentration for stripping. Mextral 84H also showed higher selectivity than Mextral 54–100 with no zinc, aluminium and nickel co-extractions detected. The overall Cu recoveries of 91.6% for 15% Mextral 84H extraction followed by 200 g/L H_2SO_4 stripping, and 86.7% for 30% Mextral 54–100 extraction followed by 80 g/L H_2SO_4 stripping were achieved. Finally, discussion and comparison of the three methods were made with a suggested conceptual process of WPCBs recycling.

1. Introduction

Electric and electronic waste (e-waste) poses high risks to environment, animal, and humans due to the potential hazards by improper disposal. In the last decade, the amount of e-waste generated globally has been increasing at an alarming rate (Baldé et al., 2015; Forti et al., 2020). The metal resources contained in e-waste indicate significant economic potential, with the contents of major base and precious metals being significantly higher than those in natural resources (Li et al., 2018). In addition, with the implementations of e-waste import bans in many of the traditional waste-importing countries (Janjevic, 2018; Lee et al., 2018; Tan et al., 2018), the recycling of e-waste in sustainable and

economic ways is becoming urgent for advanced economies. It is therefore not only important to recover metals from an economic perspective, but to sufficiently remove the heavy metals from the plastic residue in order to repurpose the remaining plastic or utilise it in waste-to-energy systems. While some metals, such as the bulk of the aluminium (Al), iron (Fe) and some larger copper (Cu) pieces can be recovered by mechanical means, most of the metals remains intimately intergrown into the plastic substrate, even after shredding below 2 mm. The low apparent density of e-waste often makes long distance road transport of the waste infeasible, and smaller quantities of waste needs to be treated closer to source, rather than shipping waste over large distances to centralised smelters (smelting (with appropriate flue gas treatment)

being highly effective means of processing if material can be brought to such a centralised location). This invariably requires smaller, fit-for-purpose recycling facilities that can be operated in light industrial facilities in the proximity of urban areas. Invariably, this requires the use of hydrometallurgical approaches with benign chemicals, or at least minimising the use of hazardous or toxic chemicals. In addition, internal recovery and recycling of reagents at site would be necessary. Furthermore, operation at ambient temperature and atmospheric pressure would significantly reduce the localised risk.

1.1. Glycine leaching system used in urban mining

Recently, an alkaline leaching system, comprising the amino acid glycine (as a lixivant) and an oxidant (e.g. Air, O_2, H_2O_2), has been reported by the authors of the present study to extract metals from e-waste (Li et al., 2018; Li et al., 2020; Oraby et al., 2019). The leaching system has been proven effectiveness for Cu extraction by forming soluble cupric glycinate ($Cu(NH_2CH_2COO)_2$, $Cu(Gly)_2$) at only room temperature with ambient air ingress (Li et al., 2020; Oraby et al., 2019)). In the studies, 72.5% Cu was extracted from the metallic fraction of waste printed circuit boards (WPCBs, >72% metals) by leaching with 0.4 M glycine at room temperature for 24 h (Oraby et al., 2019), and in further work Li et al. (2020) has shown that 96.5% Cu could be extracted from the simply pre-treated WPCBs (100 < 2 mm) by leaching with 0.5 M glycine at room temperature for 72 h. In addition to Cu, other base metals, including zinc (Zn), lead (Pb), nickel (Ni), aluminium (Al), tin (Sn) and cobalt (Co), were also co-extracted with varied degrees by forming soluble complexes with glycine or metal- hydroxyls with hydroxyl in alkaline environment (Li et al., 2020). Oraby et al. (2019) has also shown how the precious metals can be leached in a subsequent leaching step that also involves alkaline glycine with catalysts. Glycine, the simplest amino acid, is traditionally used as an additive in food and animal feeds. It is a crystalline, non-toxic, non-volatile, recyclable reagent and it is currently mass produced (Oraby et al., 2017). Therefore, using a glycine solution may be considered as a more environmentally benign approach for the urban mining of e-waste that may have the potential to be implemented near urban communities (Li et al., 2020).

1.2. State-of-the-art of Cu recovery from glycine leachate

After leaching with glycine, Cu present in leachate should hence be recovered. Currently, the methods commonly used for Cu recovery from solution could be categorised as (1) chemical precipitation (e.g. using sulphide); (2) solvent extraction; (3) ion exchange; and (4) electro-winning (Li et al., 2018). In particular, chemical precipitation (as sulphide) and solvent extraction have been previously reported for Cu recovery from glycine leachates of natural ores and concentrates (Deng et al., 2019a, 2019b; Eksteen et al., 2017; Tanda et al., 2017a). However, the solutions used in previous studies were synthetic (comprising Cu and/or gold (Au) only), or the leachate of natural minerals (malachite and chalcopyrite). Additionally, Deng et al. (2020) studied the use of chelating resins to recover Cu from glycinate leachates in the presence of Au and traces of cyanide at starvation levels. Tauetsile et al. (2018a, 2018b) looked at Cu and Au adsorption from alkaline glycine leachates onto activated carbon. However, the carbon movement logistics would be impractical to remove Cu, while it remains suitable for precious metals in a second stage leach once the base metals have been mostly removed. Tauetsile et al. (2019a, 2019b) identified that Au adsorption can be maximised in alkaline glycine solutions with cyanide at starvation levels when Cu is mostly removed in prior steps. Separating the base metal and precious metals leach and recovery steps are therefore quite appropriate for alkaline glycine-based systems. By controlling, temperature, pH and redox conditions, differential leaching of the base and precious metals becomes possible (Oraby et al., 2019).

Direct electro-winning from leachate requires high Cu concentration (>10–20 g/L) in the pregnant leaching solution (PLS) in order to achieve

an industrially economical practice (Sun et al., 2015). O'Connor et al. (2018) studied the electrochemistry of Cu in alkaline glycine systems as it would pertain to both leaching, reduction and electrowinning processes. It was shown that passivation was only observed at pH's greater than 10.5, and then only at potentials above 0.4 V (vs SHE) for quiescent solutions and that this passivation potential increased with the rotation speed of the Cu electrode. Potential-step and capacitance measurements supported the hypothesis that a duplex oxide passivation layer of Cu_2O and CuO formed that thickens with increasing potential. The Cu glycinate complex itself also acts as an oxidizing agent, the effectiveness is increased with its concentration and the concentration of free glycine. Free glycine is oxidised irreversibly above 1.2 V (vs SHE). This is important in our understanding of Cu leaching and reduction and the limits of direct reduction. Conventionally, Cu electro-winning is conducted in acidic sulphate medium, coupled with other recovery methods, e.g. solvent extraction. Contrary to acidic electrowinning practice, the Cu concentration reached during glycine leaching of WPCBs was much lower (Li et al., 2020), implying that direct electrowinning may not be economical.

Apart from the commonly used methods, chemical reduction may also be a potential way for the recovery of Cu^{2+} as low-valence (e.g. Cu_2O) or native Cu. This method has been widely used to prepare Cu nano/micro-particles from synthetic Cu solutions (Khanna et al., 2007; Liu et al., 2006; Songping and Shuyuan, 2006; Zhang et al., 2010). In the method, glycine is sometimes used as capping agent to stabilise Cu ions in alkaline solution and to control the shape/ size of the particles (Yu et al., 2015). Among the reported various reductants, hydrazine (NH_2NH_2), normal as its hydrate, hydrochloride or sulfate salt, has been shown a strong reducing ability in alkaline environment, and represents a relatively clean approach since the reduction products are nitrogen gas and water, as indicated in the anode reaction (Eq. (1)) (Chen and Lim, 2002). However, the recovery of Cu using hydrazine reduction from glycine leachate of e-waste has not been reported yet.

$$N_2H_4(aq) + 4OH^-(aq) \rightarrow N_2(g) + 4H_2O + 4e^-,$$
$$E^o = 1.16 \text{ V (alkaline environment)} \tag{1}$$
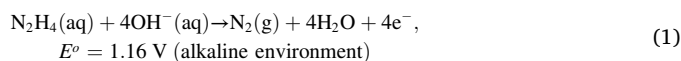
Given the complex metal compositions in the glycine leachate of e-waste (Li et al., 2020), the behaviours of other metals during Cu recovery should also be investigated. Therefore, this study aims to investigate the feasibility of Cu and associated base metal recovery from glycine leachate of e-waste with three recovery options, i.e. sulphide precipitation, solvent extraction, and hydrazine reduction. Given that sulphide precipitation and solvent extraction have already been investigated in synthetic solution, and from glycine leachate of malachite and chalcopyrite (Deng et al., 2019a; Tanda et al., 2017a), the emphasis of this study is on the behaviour of other base metals (Al, Zn, Pb, Ni, Sn). However, since hydrazine reduction has not been reported in the case of glycine leachate, more attention was given to investigate the effect of a range of variables during hydrazine reduction in both synthetic solution and glycine leachate. It is hoped that this study can provide guidance for the recovery of Cu using different options from glycine leachate of e-waste.

2. Experimental section

All the solutions used in this study were prepared using deionized (DI) water. The pH of solutions was adjusted by sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4). Unless specified, all the chemicals are of analytical grade.

2.1. Recovery of Cu by hydrazine reduction

To clearly investigate the effect of variables (initial pH, Cu concentration, temperature and time) on Cu recovery, experiments were first conducted using synthetic solutions (Cu-glycine solutions) as a baseline. The solutions were prepared by dissolving $CuSO_4 \cdot 5H_2O$ and glycine

(≥99%, HPLC grade) in DI water at 0.5 M glycine concentration, different initial pH (9.0–12.8) and different Cu concentrations (0.5–5 g/L). The glycine concentration of 0.5 M was determined by the optimum concentration obtained during glycine leaching of WPCBs in our previous study (Li et al., 2020). The hydrazine solution used in this study was prepared by dissolving hydrazine monohydrochloride (NH₂NH₂·HCl) in DI water at 3 M hydrazine concentration and different pH (kept the same with Cu-glycine solutions). Experiments were then performed by adding a certain amount of 3 M hydrazine solution into the synthetic solutions at different initial pH, Cu concentration, and temperature, with a stirring speed of 300 rpm. The Eh (mV, vs. Ag/AgCl) and pH of solution was monitored over the reduction time with a pH meter (90-FLMV Field Lab Analyser, *TPS Pty Ltd.*). Subsequently, the real solution, i.e. glycine leachate of WPCBs, was used to recover Cu at different Cu/hydrazine molar ratios. The real solution was prepared by leaching WPCBs (100% <2 mm) with 0.5 M glycine at 10% (g/mL) solid content and room temperature for 24 h to reach the required Cu concentration. The major metal concentrations in the glycine leachate are shown in Table 1.

2.2. Recovery of Cu by sulphide precipitation

Sulphide precipitation of Cu was conducted using glycine leachate of WPCBs directly. The leachate was prepared by leaching WPCBs with 0.5 M glycine at 2% solid content and room temperature for 72 h, and the major metal concentrations are presented in Table 2. Experiments were then conducted by adding a certain amount of 5.19 M sodium hydrosulphide (NaHS) solution into the glycine leachate at room temperature and different Cu/HS⁻ molar ratios with a stirring speed of 300 rpm for up to 30 min.

2.3. Recovery of Cu by solvent extraction

Two extractants, Mextral 84H and Mextral 54–100 (Hallochem, China), which have been previously investigated by Tanda et al. (2017a) to recover Cu from glycine leachate of malachite and chalcopyrite, were selected. Mextral 84H is composed of 2-hydroxy-5-nonylacetophenone oxime with a high flash point hydrocarbon diluent, and Mextral 54–100 is a β-diketone 1-benzoyl-2-nonyl ketone in a mixture with high flash point hydrocarbon diluent (Tanda et al., 2017a). Kerosene (pure grade, Sigma-Aldrich) was used as a diluent for the two extractants. To extract Cu, the extractant with different concentrations was mixed with glycine leachate of WPCBs, prepared in section 2.2, in a volumetric flask at 1:1 organic: aqueous phase (O:A) ratio, and then placed in a thermostatic shaker at 250 rpm for 10 min. Subsequently, the mixture was transferred into a separating funnel for phase separation. The pH of aqueous before and after extraction was measured. The organic phase was then subjected to a stripping step in a volumetric flask using different concentrations of sulfuric acid (H₂SO₄) at 1:1 O:A ratio, and room temperature for 20 min.

2.4. Analytical methods

The Cu concentrations in solution were analysed by atomic absorption spectrometer (AAS, 55B AA, *Agilent Technologies Inc.*). The concentrations of other metals, including Ni, Zn, Pb, Al and Sn, were analysed by inductively coupled plasma - optical emission spectrometry (ICP-OES, for Al, Ni and Zn) and inductively coupled plasma - mass

Table 1
Concentration of major metals in the glycine leachate of WPCBs (leaching conditions: 0.5 M glycine, 10% solid content, room temperature and 24 h leach time).

Metal	Cu	Al	Zn	Pb	Ni	Sn
Concentration	In g/L		In ppm			
	5.42	1.41	188.0	75.0	12.0	53.0

Table 2
Concentration of major metals in the glycine leachate of WPCBs (leaching conditions: 0.5 M glycine, 2% solid content, room temperature and 72 h).

Metal	Cu	Al	Zn	Pb	Ni	Sn
Concentration	In g/L	In ppm				
	4.18	225.0	180.0	75.0	30.0	5.0

spectrometry (ICP-MS, for Pb and Sn) conducted by *Bureau Veritas*, Perth, Australia. To identify the products, the precipitates from hydrazine reduction and sulphide precipitation were analysed by X-ray powder diffraction (XRD), X-Ray Fluorescence Spectrometry (XRF), conducted by *Bureau Veritas*, Perth, Australia, and/or scanning electron microscope (SEM, Zeiss Evo 40XVP SEM).

3. Results and discussion

3.1. Recovery of copper by hydrazine reduction

3.1.1. Investigation of variables using synthetic solution

3.1.1.1. Effect of initial pH. Hydrazine can easily undergo hydrolysis in water as represented by Eq. (2) (Chen and Lim, 2002; Patil and Rattan, 2014). The disassociation constant indicates that the proportion of N₂H₄ reaches 100% at pH ≥ 11 (Chen and Lim, 2002). Serov and Kwak (2010) reported that hydrazine can serve as reductant in both acidic and alkaline environment (Eqs. (1) and (3)). It can be seen that the redox potential of Eq. (1) is almost 1 V higher than Eq. (3). This indicates a more powerful reducing ability of hydrazine in alkaline environment, which especially fits with the alkaline glycine leaching solution. Fig. 2 presents the Eh-pH diagram of Cu-glycine-H₂O system in alkaline environment. With the increase of pH, it can be seen that lower Eh is required for Cu being reduced as native Cu. Interestingly, Cu₂O could be more easily produced than native Cu when pH is over about 10.5.

$$N_2H_4(aq) + H_2O = N_2H_5^+(aq) + OH^-(aq),$$
$$K = \frac{[N_2H_5^+] \times [OH^-]}{[N_2H_4]} = 8.5 \times 10^{-7} \tag{2}$$

$$N_2H_5^+(aq) \rightarrow N_2(g) + 5H^+(aq) + 5e^-,$$
$$E^o = 0.23 \text{ V (acidic environment)} \tag{3}$$
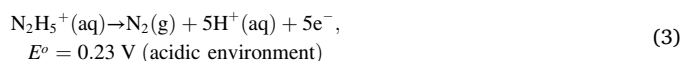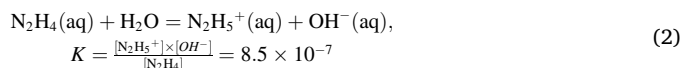
Therefore, to investigate the effect of initial pH on the recovery of Cu, experiments were performed in alkaline environment with the pH ranging from 9.0 to 12.8, at Cu concentration of 3 g/L, Cu/hydrazine molar ratio of 1:1, and room temperature for 30 min. As shown in Fig. 1,
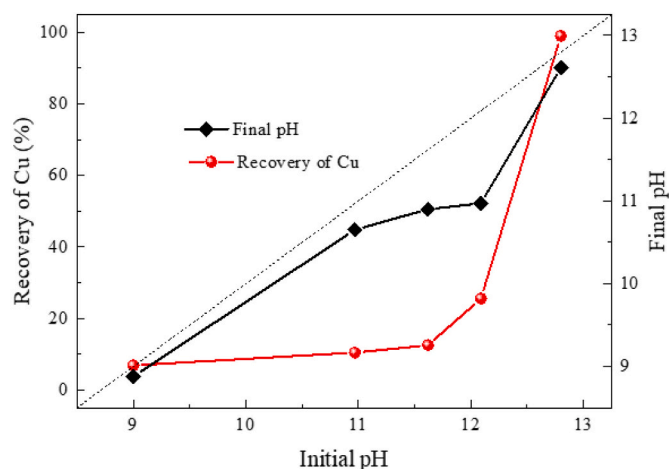
Fig. 1. Effect of initial pH on the recovery of Cu and final pH of solution (Cu concentration = 3 g/L, glycine concentration = 0.5 M, Cu/hydrazine molar ratio = 1:1, room temperature, and 30 min).

the reduction of Cu increased continuously with the rise of initial pH. When the initial pH increased from 12.1 to 12.8, the Cu recovery jumped significantly by about 75%, indicating that the Cu recovery was sensitive to pH under the experimental conditions. As shown in Eq. (1), the hydrazine reduction proceeds by consuming hydroxyl, explaining the pH decrease in the final solution (Fig. 1). The higher pH of the solution will provide the reaction with more hydroxyl. The effect of initial pH on the final Eh of solution is plotted in Fig. 2 (red dots and line). It shows that the pH rise continuously led to lower Eh, resulting in a more reducing environment, which also accounts for the increase of Cu recovery. It is noticeable that Cu_2O could possibly be a product when the initial pH was over 11.6.

According to Songping and Shuyuan's (2006) study, which uses hydrazine to recover Cu from ammonium-ammonia solution, the overall reactions of recovering Cu^{2+} as native Cu and Cu_2O from glycine solutions are proposed as Eqs. (4) and (5), respectively. As is clear from the reaction, the glycinate anion is regenerated and can be reused (after separation from the precipitated copper metal) in the leach reaction after appropriate pH reestablishment. In addition, it can be seen that, to recover same amount of Cu, the hydrazine required for native Cu is doubled than that required for Cu_2O. The highest Cu recovery of 99.1% was recorded at the initial pH of 12.8.

Fig. 3. Effect of Cu concentration on the recovery of Cu (glycine concentration = 0.5 M, initial pH = 12.1, Cu/hydrazine molar ratio = 1:1, room temperature, and 30 min).

$$2Cu(Gly)_2 \ (aq) \ + N_2H_4 \ (aq) + 4OH^- \ (aq) = N_2 \ (g) + 4H_2O + 2Cu \ (s) \ + 4Gly^- \ (aq),$$
$$\Delta G^o \ (25°C) = -399.7 \ KJ/mol \tag{4}$$

$$4Cu(Gly)_2 \ (aq) \ + N_2H_4 \ (aq) + 8OH^- \ (aq) = N_2 \ (g) + 6H_2O + 2Cu_2O \ (s) + 8Gly^- \ (aq),$$
$$\Delta G^o \ (25°C) = -493.0 \ KJ/mol \tag{5}$$

3.1.1.2. Effect of Cu concentration. Experiments with different Cu concentrations were performed to investigate its effect on Cu recovery. Other conditions were fixed at initial pH of 12.1, Cu/hydrazine molar ratio of 1:1, room temperature and a reaction time of 30 min. As shown in Fig. 3, the increase in initial Cu concentration led to the increase of the copper recovery. At Cu concentration of 5 g/L, about 75.1% Cu was recovered from alkaline glycine solutions. Therefore, to reach a reasonable Cu recovery, the Cu concentration in the solution is suggested to be more than 5 g/L. Table 3 presents the effect of solid contents on the Cu extraction, final pH and Cu concentration during glycine leaching of WPCBs conducted in previous study (Li et al., 2020). It reveals that, to reach a satisfactory Cu concentration (≥5 g/L) for the downstream hydrazine reduction, a solid content of at least 3% is required, at which the final pH of leachate was 12.2 indicating a Cu recovery of higher than 75% when no additional alkali added (Fig. 3). However, at this solid content, the single stage Cu extraction from WPCBs was only 73.1% implying that a multi-cycle of glycine leaching

Fig. 2. Eh-pH diagram of Cu-glycine (gly) -H_2O system at 3 g/L Cu, 0.5 M glycine and 25 °C (generated using Medusa-Hydra software), and the effect of initial pH on the final Eh of solution (red dots and line, manually added by Adobe Photoshop CS4, Cu/hydrazine molar ratio = 1:1, room temperature, and 30 min). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3
Cu extraction, final pH and Cu concentration in glycine leachate at different solid contents (glycine concentration = 0.5 M, initial pH = 10.5, particle size ≤2 mm, room temperature and ambient O_2) (Li et al., 2020).

Solid content, %	1.0	1.4	2.0	3.0	10.0
Cu extraction, %	88.7	87.9	87.7	73.1	37.4
Final pH	11.1	11.9	11.5	12.2	12.2
Cu concentration, g/L	2.23	3.13	4.24	5.99	8.43
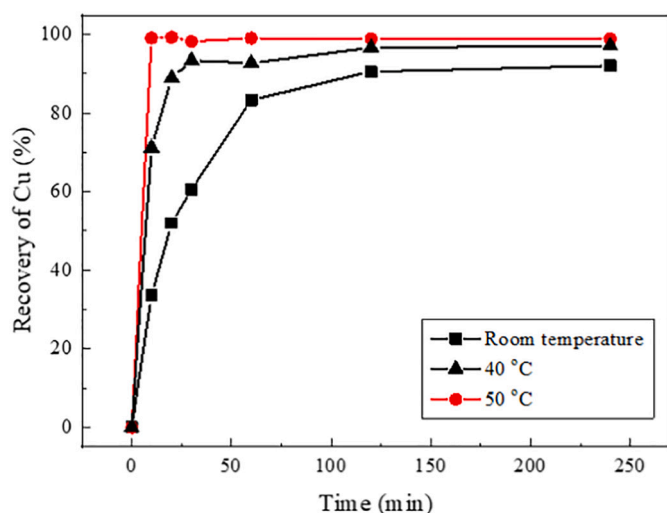
Fig. 4. Effect of temperature over time on the recovery of Cu (glycine concentration = 0.5 M, Cu concentration = 5 g/L, initial pH = 12.1, Cu/hydrazine molar ratio = 1:1).

Table 4
Standard Gibbs free energy of Eqs. (4) and (5) at different temperature calculated by HSC Chemistry 10.0 software with Reaction Equations module.

Temperature, °C	25	30	40	50
ΔG^o of Eq. (4), KJ/mol	−399.7	−401.9	−406.5	−411.8
ΔG^o of Eq. (5), KJ/mol	−493.0	−496.4	−504.0	−513.2

and hydrazine reduction may be required. To increase the production capacity and efficiency in an industrial practice, the solid content of no less than 10% is recommended in a locked cycle glycine leaching and hydrazine reduction process.

3.1.1.3. Effect of temperature on reduction kinetics. The effect of temperature and reaction time on the Cu recovery was investigated at room temperature (RT), 40 °C and 50 °C, respectively, for up to 4 h, at a fixed Cu concentration of 5 g/L, initial pH of 12.1 and Cu/glycine molar ratio of 1:1. The results plotted in Fig. 4 showed that by increasing the temperature, the reduction kinetics significantly accelerated. As can be seen, the reaction equilibrium was reached in around 4 h, 2 h and 10 min for room temperature, 40 °C and 50 °C, respectively. At 50 °C, 99.1% Cu was recovered in only 10 min, which is a significant improvement from the 71.2% recovery at 40 °C and the 33.6% recovery at room temperature for the same reaction time. Table 4 shows the standard Gibbs free energy (ΔG^o) of the Eqs. (4) and (5). It is clear that the increase of temperature results in a lower ΔG^o value, which verifies that higher temperature favours the reduction of Cu to either native Cu or Cu₂O. Considering both the energy consumption and recovery efficiency, reaction temperature of 40 °C and time of 2 h are selected for the following experiments using leachate from leaching WPCBs.

Table 5
Recovery of Cu and other metals at different Cu/hydrazine molar ratio (Cu concentration = 5.42 g/L, initial pH = 12.8, 2 h and 40 °C).

Cu/ hydrazine molar ratio	Final Eh of solution, V vs SHE	Final pH of solution	Recovery, %					
			Cu	Ni	Zn	Pb	Al	Sn
1:0.7	−0.333	12.5	96.9	0	0	25.3	0	34.6
1:1	−0.358	12.5	98.6	0	0	31.5	0	38.0
1:2	−0.452	12.4	99.8	0	0	86.0	0	30.4

3.1.2. Recovery of Cu and other base metals from glycine leachate from polymetallic WPCBs

3.1.2.1. Effect of cu/hydrazine molar ratio. According to Eqs. (4)–(5), the stoichiometric molar ratios of Cu/hydrazine for producing native Cu and Cu₂O are 1:0.5 and 1:0.25, respectively. To investigate the effect of the actual molar ratio on Cu recovery and the behaviours of the other metals, experiments were conducted with the ratio ranging from 1:0.7 to 1:2 by using glycine leachate of WPCBs (Table 1). As shown in Table 5, the Cu recovery reached 96.9% at the ratio of 1:0.7, and continuously increased with more hydrazine added. Simultaneously, Pb and Sn also precipitated with the Cu, although no Ni, Zn or Al precipitation were detected. Fig. S1-3 plot the Eh-pH diagram of Zn, Pb, Ni -glycine-H₂O system at the experimental concentrations (Table 1), respectively. It can be seen that Ni and Zn could not be precipitated or reduced as solid under the experimental conditions of Eh and pH (Table 5) while Pb may be precipitated as hydroxides. Table S1 shows the electrode potential of the possible half-reactions during hydrazine reduction. However, it can not explain the behaviours of all the metals in Table 5, indicating a necessity of further detailed investigation. Table 5 also implies that the unrecovered Pb and Sn (typically from dissolved solder materials) will require other methods to recover their trace concentrations from the alkaline glycine solution. While Pb is known to forma stable glycinate complex, a mix of glycinate and plumbate anions may exist in solution, leading to different precipitation behaviours due to different speciation in solution.

3.1.2.2. Analysis of precipitates. Fig. 5 presents the XRD analysis of the precipitates from the hydrazine reduction at Cu/hydrazine molar ratio of 1:0.7 and 1:1 (Section 3.1.2.1). The XRD pattern at the ratio of 1:0.7 fits well to the standard pattern of cuprite (Cu₂O), which means Cu²⁺ in glycine leachate was mainly reduced to Cu₂O rather than native Cu. By contrast, the XRD analysis of the precipitate at a ratio of 1:1 (with other conditions kept the same) indicates that the product was mainly composed of native Cu (Fig. 5b). This may imply that cupric glycinate is first reduce to cuprous glycinate, which is labile and which, in the presence of hydroxyl anion forms hydrated cuprous oxide. Fig. 2 and Table S1 also confirms that Cu₂O will be more easily produced than native Cu at the experimental pH. However, no crystal phases of Pb and Sn were observed in Fig. 5, as they would have been below the detection limit of X-Ray Diffraction. Therefore, to produce native Cu as a saleable product, the Cu/hydrazine molar ratio of 1:1 is suggested to minimise excessive reagent costs. The SEM images of the precipitates are shown in Fig. 6. As revealed in the figure, the particles from both Cu/hydrazine molar ratios are spherical-like but in agglomerated states.

3.2. Recovery of copper by sulphide precipitation

3.2.1. Effect of cu/HS⁻ molar ratio

Deng et al. (2019a) showed that Cu/HS⁻ molar ratio affected the Cu precipitation considerably from synthetic Cu-Au-CN-glycine solutions. In this study, Cu/HS⁻ molar ratios ranging from 1:1 to 1:1.3 were selected to investigate their effect on Cu precipitation from glycine leachate of WPCBs. As shown in Fig. 7, at the stoichiometric Cu/HS⁻ ratio of 1:1 (Eq. (6)), the Cu precipitation was limited at around 88%. The presence of other cations, which will consume HS⁻ during co-precipitations, could account for the low Cu precipitation.

The high Cu precipitation of 99.5% was achieved at the ratio of 1:1.2 and remained stable with further HS⁻ addition. In addition, it is also shown that the sulphide precipitation kinetics is fast, with the reaction being complete
within around 5 min (Eq. (6)). This agrees well with previous studies (Chung et al., 2015; Deng et al., 2019a; Estay, 2018a, 2018b) which have shown that the sulfidation of Cu in either acidic (SART process) or alkaline environment nearly reached equilibrium in 5–10 min.
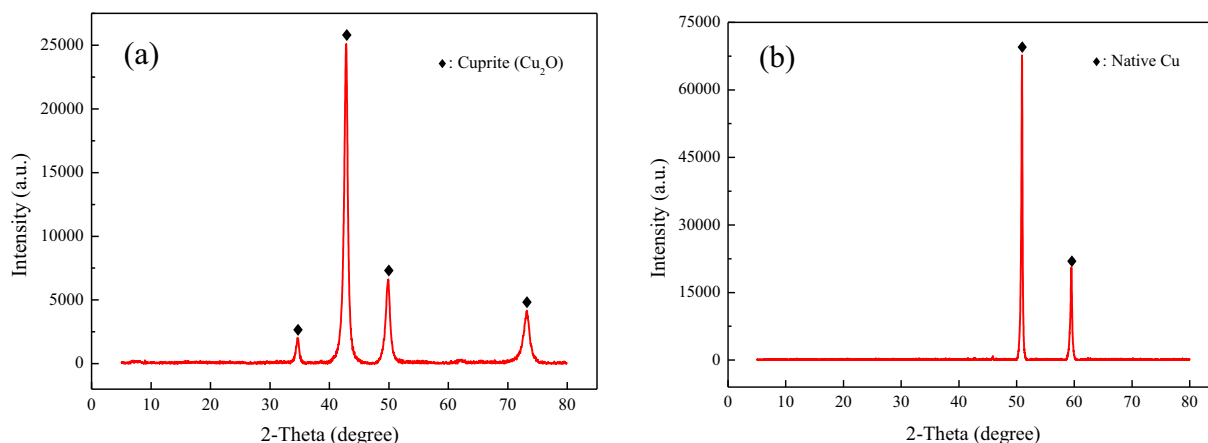
Fig. 5. XRD analysis of precipitate obtained at Cu/hydrazine molar ratio of (a) 1:0.7 and (b) 1:1.
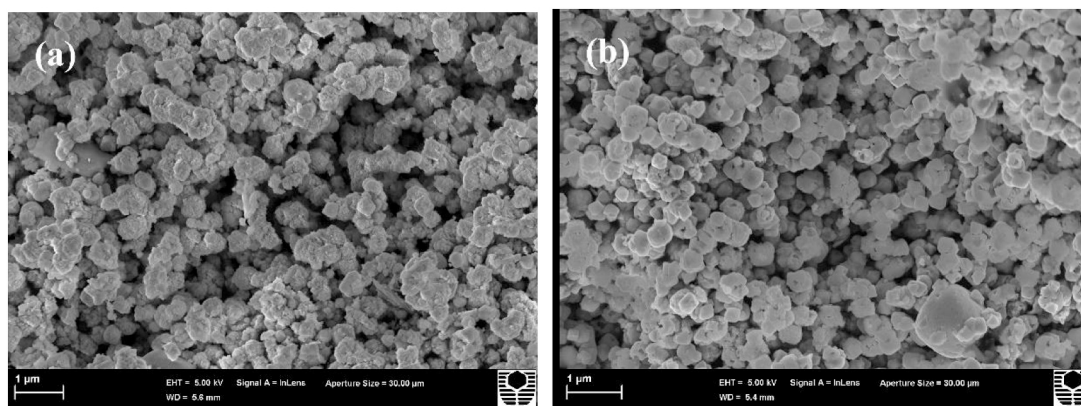
Fig. 6. SEM images of precipitates obtained at Cu/hydrazine molar ratio of (a) 1:0.7 and (b) 1:1.

$$Cu(Gly_2) \, (aq) + HS^- \, (aq) + OH^- \, (aq) = CuS \, (s) + 2Gly^- \, (aq) \quad + H_2O,$$
$$\Delta G^o \, (25°C) = -121.9 \, KJ/mol$$
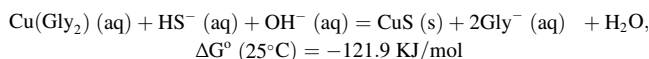
(6)

As before, the glycinate anion is regenerated and can be reused in the leach. A comparison to reaction Eq. (4), shows that, in the case of HS^- precipitation of Cu, half the molar quantity of hydroxyl anions are used,
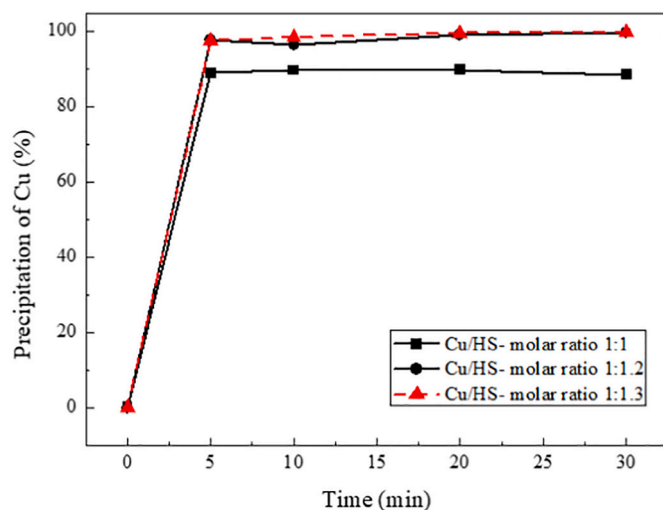
Fig. 7. Effect of Cu/HS$^-$ molar ratio on the precipitation of Cu from alkaline glycine leachate of WPCBs.

Table 6
Solubility product constant (K_{sp}) of metal sulphides and precipitation behaviours of other metals during Cu recovery at Cu/HS$^-$ molar ratio of 1:1.2 (Ksp values taken from Dean (1999)).

	Cu	Ni	Zn	Pb	Al	Sn
Corresponding sulphide	CuS	NiS (α)	ZnS (α)	PbS	Al$_2$S$_3$	SnS$_2$
K_{sp} of the sulphide	6.3×10^{-36}	3.2×10^{-19}	1.6×10^{-24}	8×10^{-28}	2×10^{-7}	1×10^{-46}
Precipitation, %	99.3	3.0	67.7	100	BDL[a]	100

[a] BDL denotes below detection limit of 0.5 ppm for Al.

and half the amount of water is generated. As a result, the pH of solution decreased slightly from 10.6 to 10.2 at Cu/HS$^-$ molar ratio of 1:1.2. This naturally influences the process water balance and reagent consumption. On the positive side, the hydrazine can yield a metal whereas HS$^-$ yields a sulphide that has to be converted to metal.

3.2.2. Precipitation behaviours of other metals
Table 6 shows the precipitation of Cu and other metals at Cu/HS$^-$ molar ratio of 1:1.2, and the K_{sp} of the corresponding sulphides. Along with Cu precipitation, the complete precipitations of Pb and Sn, and 67.7% precipitation of Zn were also reached. Whereas, the precipitation of Ni and Al were in a low level ($\leq$3%) implied by their higher free Gibbs energy required compared with others (Table S2).

Given the complete removal of Sn and Pb from solution, and a significant portion (>67%) of the Zn, the sulphide precipitation has a higher metal removal efficiency than the hydrazine approach. While Pb
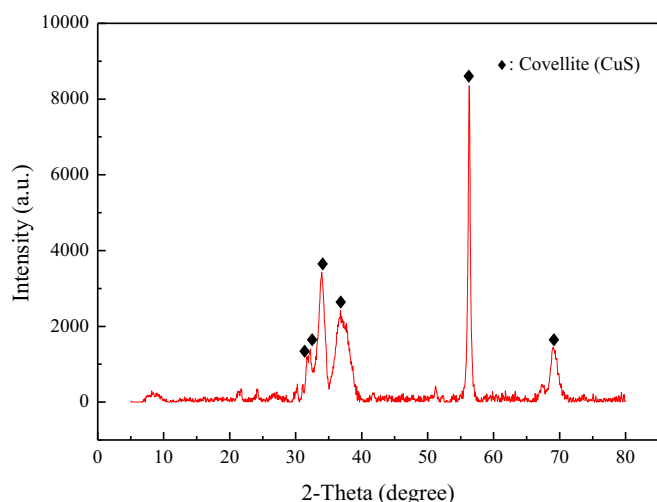
Fig. 8. XRD analysis of precipitates at Cu/HS- molar ratio of 1:1.2.

Fig. 9. Effect of extractant concentration on Cu extraction (Cu concentration in aqueous phase = 4.18 g/L, pH of aqueous phase = 10.6, O/A ratio = 1:1, contact time = 10 min, RT).

recovery is important from an environmental perspective (it must be removed at some stage), Sn has a price of between 3× and 4× that of Cu and is therefore a valuable by-product should it be credited by a downstream metal refiner.

3.2.3. Analysis of the precipitates

The XRD analysis of the precipitates obtained at Cu/HS⁻ molar ratio of 1:1.2 is presented in Fig. 8. It verifies that the Cu was mainly precipitated as CuS (covellite) comprising the majority of the product. The XRF analysis of major elements (Table 7) indicates that the impurities are mainly Pb, Zn and Sn. According to the Cu content, the purity of the CuS in the precipitate is 87.9%. Further refining is hence required to produce a high-purity Cu product, such as using conventional Cu smelting process (Davenport et al., 2002). However, the crude CuS precipitate is of high density and can be accumulated on site and shipped to a refiner in batches when convenient.

3.3. Recovery of copper by solvent extraction

3.3.1. Effect of extractant concentration on cu extraction

The effect of the concentration of selected extractants, Mextral 54–100 and Mextral 84H, was investigated by varying their content in diluent. As shown in Fig. 9, Mextral 54–100 required higher concentration than Mextral 84H to reach a high Cu extraction (>85%). At 20% Mextral 84H, 95.2% Cu could be extracted from glycine leachate of WPCBs while only 88.6% Cu was extracted at concentrations as high as 35% Mextral 54–100, when an aqueous / organic ratio of 1:1 is used. It was also found that the Cu extraction increased slowly with the increase of the extractant concentration (Fig. 9). To reach a high extraction and reduce the amount of extractant used, the concentrations of 15% for Mextral 84H and 30% for Mextral 54–100 were used for the following stripping experiments.

According to (Tanda et al., 2017a), glycine lost in the organic phase during Cu extraction by the same two extractants was negligible. This indicates the high recyclability of raffinate for reuse in leaching step. It was also noted that the pH of raffinate decreased from 10.6 to 9.7 for both the extraction tests with 15% Mextral 84H and 30% Mextral 54–100. This was due to the ion-exchange between Cu from Cu-

glycinate and H⁺ from extractants. In theory, to extract one mole Cu, 2 mol H⁺ will be brought to raffinate, which has caused a lower pH of solution than sulphide precipitation, indicating higher reagent consumption for further pH modification. Application in a process would require a minimum of two stages of extraction with Mextral 84H and 3 stages with Mextral 54–100 in industrial mixer-settler systems.
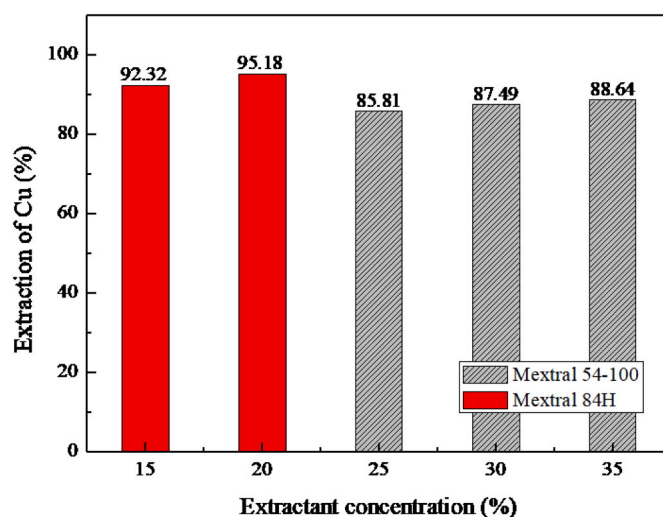
3.3.2. Stripping of cu and the behaviour of other metals (except Pb and Sn)

Stripping of Cu was conducted following the extraction at 15% Mextral 84H and 30% Mextral 54–100, respectively. As shown in Table 8, to reach >99% Cu stripping, Mextral 84H required 2.5 times higher H_2SO_4 concentration compared with Mextral 54–100. Calculated from both extraction and stripping, the overall Cu recovery was 91.6% for 15% Mextral 84H and 86.7% for 30% Mextral 54–100. Mextral 84H showed high selectivity to Cu with no Zn, Al, and Ni extracted while 50% Ni extraction was reached when using Mextral 54–100, but none of it was stripped.

3.4. Discussion and comparison

Based on forgoing results, comparisons of the three methods can be made as follows:

Table 8
The extraction and stripping of metals from glycine leachate of WPCBs using 15% Mextral 84H or 30% Mextral 54–100.

Metal	Cu	Zn	Al	Ni
Using 15% Mextral 84H				
Extraction, %	92.3	0	0	0
Stripping using 200 g/L H_2SO_4, %	99.3	–	–	–
Using 30% Mextral 54–100				
Extraction, %	87.5	0	0	50.0
Stripping using 80 g/L H_2SO_4, %	99.1	–	–	0

Table 7
XRF analysis of major elements in precipitates obtained at Cu/HS- molar ratio of 1:1.2.

Element	Cu	Ni	Al	Ca	Mg	P	S	Zn	Pb	Sn
Content, %	58.4	0.02	0.03	0.02	0.13	0.013	31.2	1.18	1.08	0.065

(1). The hydrazine reduction method can recover nearly all the Cu, and some of the Pb and Sn from the glycinate leachate as metals. The residual Sn and lead would require further removal steps. It requires a higher addition of caustic soda and generates more water, influencing the water balance more. Glycine could be regenerated during the reduction process and made available for reuse (Eqs. (4)–(5)), which needs to be confirmed in future work. However, the excess hydrazine remaining in the solution should be removed before the reuse, as it may affect the glycine leaching step. This can be easily done by aeration since autoxidation of hydrazine can easily occur in the presence of atmospheric oxygen (Patil and Rattan, 2014) (Eq. (7)). Hydrazine is also a more expensive reagent compared to NaHS. Metallic copper is dense and allows shipping in small volumes, if required. It allows the production of either cuprite (Cu_2O) or metallic copper depending on the amount of hydrazine used, thereby allowing less reagent to be used, but the economics would depend on the payments received for the precipitated product from the downstream refiner.

$$N_2H_4 \text{ (aq)} + O_2 \text{ (g)} = N_2 \text{ (g)} + 2H_2O,$$
$$\Delta G^o \text{ (25°C)} = -602.5 \text{ KJ/mol} \tag{7}$$
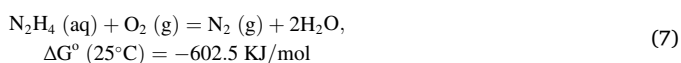
(2). Sulphide precipitation produces a metal sulphide precipitate that quantitatively recovers the Cu, Pb, Sn and most of the Zn form the alkaline glycinate leachate. Reagent usage is less than hydrazine reduction and the product would require further conversion to obtain metal. However, the product is in a form conveniently handled by base metal smelters, and can be shipped as dense, small volume packages. The use of NaHS does however introduce sodium into the decopperised solution, that needs to be taken into account in the overall material balance and requirements for bleed streams in the glycine solution is to be recycled back to leach. The recyclability of barren solution from sulphide precipitation has been shown feasible by (Eksteen et al., 2017).

(3). Solvent extraction left Zn, Al and Ni in aqueous raffinate which should be removed by other methods prior to recycling the glycine reagent, after appropriate pH adjustment as the raffinate becomes acidified during solvent extraction. The recycling of glycine has been shown possible by Tanda et al. (2017b)'s study,

in which the glycine loss was negligible when using the same extractants. A minimum of two stages of extraction is required, or more, depending on the efficiency of liquid-liquid extraction equipment (e.g. continuous mixer-settlers). While this method doesn't produce a directly saleable product, but rather a pure copper sulphate solution after stripping, it does allow the production of pure copper using conventional electrowinning from the stripped solution, or alternatively the copper sulphate can be directly crystallised if the market supports it.

In industry, to limit reagent costs and downstream equipment size, dry physical separation to remove the bulk of the larger and exposed aluminium, iron and copper is prudent. Particularly, when bulk Cu in WPCBs is physically separated, the remaining interlocked Cu in the board is then leached and chemically recovered prior to precious metals recovery, which is the way to minimise the amount of harmful and expensive reagents used in precious metals (Au, Ag and Pd) recovery.

However, residual base metals are worthwhile to recover from WPCB's to 1) strip the plastic substrate from dangerous heavy metals, 2) recover further economic value and 3) further expose the precious metals for subsequent leaching, and 4) reduce the reagent requirements associated with precious metals leaching. Fig. 10 suggests a conceptual process of WPCBs recycling, based on our previous and present studies (Oraby et al., 2019; Li et al., 2018 and 2020). As shown, the hydrometallurgical copper (and other base metals) recovery process can therefore be positioned in-between the dry physical recovery processes and the hydrometallurgical precious metal recovery processes, such the environmentally more benign and cyanide-starved (i.e. zero free cyanide) "GlyCat" glycine leach process as discussed by Oraby et al. (2019) to produce a crude Cu & base metals fraction that would require further refining.

4. Conclusions

In this study, the feasibilities of recovering Cu from glycine leachate of WPCBs using hydrazine reduction, sulphide precipitation and solvent extraction were investigated and discussed, respectively. During the hydrazine reduction, Cu recovery was found to be sensitive to the pH of solution, and the recovery increases with the rise of initial pH, Cu concentration and temperature. The Cu/hydrazine molar ratio affected the

Fig. 10. Conceptual process flow block diagram indicating the positioning of the base metal purification section and the processes discussed in this research (within the dotted line system boundary).

co-precipitation of Pb and Sn considerably. The more hydrazine used caused the more Pb and Sn co-precipitation while no co-precipitation was observed for Ni, Zn and Al. The XRD analysis indicates t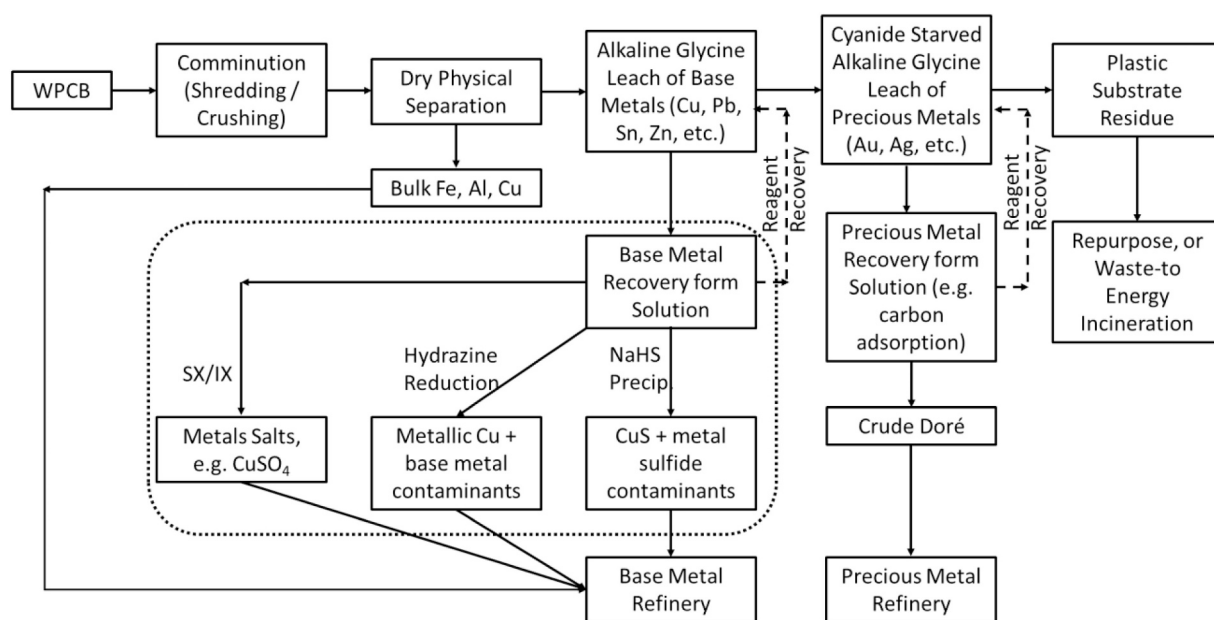hat cuprite (Cu_2O) and native Cu were present with 96.9% and 98.6% recoveries at the Cu/hydrazine molar ratio of 1:0.7 and 1:1, respectively.

During the sulphide precipitation, high Cu precipitation ($\geq$99.5%) could be easily achieved in only 5 min when Cu/HS^- molar ratio was no more than 1:1.2. Along with the Cu precipitation, a co-precipitation of other metals, i.e. 100% Pb, 100% Sn and 67.7% Zn were also observed. However, the co-precipitation of Al and Ni was limited ($\leq$3%). The XRD analysis of precipitates verifies that Cu was recovered as covellite (CuS). The XRF analysis indicates a CuS purity of 87.9%, showing the necessity of further refining.

During the solvent extraction, Mextral 84H showed better performance than Mextral 54–100 but requires higher H_2SO_4 concentration for the stripping of Cu. In addition, Mextral 84H also showed higher selectivity than Mextral 54–100 with no Zn, Al and Ni co-extractions detected. The overall Cu recoveries of 91.6% for 15% Mextral 84H extraction followed by 200 g/L H_2SO_4 stripping, and 86.7% for 30% Mextral 54–100 extraction followed by 80 g/L H_2SO_4 stripping were achieved.

The comparisons of the methods showed that each of them has its own advantages and disadvantages. It is expected that this study can provide guidance for the selection of a suitable method that is co-considered with specific requirements of an application.

Declaration of Competing Interest

The authors hereby declare:

1. Huan Li, the lead author, has no conflict of interest and is a PhD student supported by Curtin University and the China Scholarship Council.
2. Dr. Elsayed Oraby and Prof Jacques Eksteen are the supervisors of Mr. Huan Li.
3. Messrs. Oraby and Eksteen are the listed inventors of a number of patents that utilises glycine as a lixiviant for numerous precious and base metals from various materials such as ores, wastes, concentrates, etc., and which is background Intellectual Property to the research presented in this paper.
4. Should processes be commercialised that utilises the patents mentioned in Point no. 3 above, Messrs. Oraby and Eksteen may be eligible to receive royalty income.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.hydromet.2020.105540.

References

Baldé, C.P., Wang, F., Kuehr, R., Huisman, J., 2015. The Global e-Waste Monitor - 2014. United Nations University (UNU), IAS-SCYCLE, Bonn, Germany. Available at. https://i.unu.edu/media/unu.edu/news/52624/UNU-1stGlobal-E-Waste-Monitor-2014-small.pdf.

Chen, J.P., Lim, L.L., 2002. Key factors in chemical reduction by hydrazine for recovery of precious metals. Chemosphere 49 (4), 363–370.

Chung, J., et al., 2015. Factors affecting crystallization of copper sulfide in fed-batch fluidized bed reactor. Hydrometallurgy 152, 107–112.

Davenport, W.G., King, M.J., Schlesinger, M.E., Biswas, A.K., 2002. Extractive metallurgy of copper. Elsevier Sci. Technol. 452 eBook ISBN: 9780080531526.

Dean, J.A., 1999. Lange's Handbook of Chemistry (15th Edition). McGraw-Hill Inc.

Deng, Z., Oraby, E., Eksteen, J., 2019a. The sulfide precipitation behaviour of cu and au from their aqueous alkaline glycinate and cyanide complexes. Sep. Purif. Technol. 218, 181–190.

Deng, Z., Oraby, E.A., Eksteen, J.J., 2019b. Sulfide precipitation of copper from alkaline glycine-cyanide solutions: precipitate characterisation. Miner. Eng. 145 (Article 106102).

Deng, Z., Oraby, E.A., Eksteen, J.J., 2020. Cu adsorption behaviours onto chelating resins from glycine-cyanide solutions: isotherms, kinetics and regeneration studies. Sep. Purif. Technol. 236 (Article 116280).

Eksteen, J.J., Oraby, E.A., Tanda, B.C., 2017. A conceptual process for copper extraction from chalcopyrite in alkaline glycinate solutions. Miner. Eng. 108, 53–66.

Estay, H., 2018a. Designing the SART process – a review. Hydrometallurgy 176, 147–165.

Estay, H., 2018b. Designing the SART process – a review. Hydrometallurgy 176, 147–165.

Forti, V., Baldé, C.P., Kuehr, R., Bel, G., 2020. The Global e-Waste Monitor - 2020. United Nations University (UNU)/United Nations Institute for Training and Research (UNITAR) – Co-Hosted SCYCLE Programme. International Telecommunication Union (ITU) & International Solid Waste Association (ISWA), Bonn/Geneva/Rotterdam. Available at. https://www.itu.int/myitu/-/media/Publications/2020-Publications/Global-E-waste-Monitor-2020.pdf.

Janjevic, D., 2018. Thailand Moves to Ban Importing E-Waste and Plastic. Avaliable at. https://www.dw.com/en/thailand-moves-to-ban-importing-e-waste-and-plastic/a-45103610 (accessed on 01/07/2019).

Khanna, P.K., Gaikwad, S., Adhyapak, P.V., Singh, N., Marimuthu, R., 2007. Synthesis and characterization of copper nanoparticles. Mater. Lett. 61 (25), 4711–4714.

Lee, D., Offenhuber, D., Duarte, F., Biderman, A., Ratti, C., 2018. Monitour: tracking global routes of electronic waste. Waste Manag. 72, 362–370.

Li, H., Eksteen, J., Oraby, E., 2018. Hydrometallurgical recovery of metals from waste printed circuit boards (WPCBs): current status and perspectives – a review. Resour. Conserv. Recycl. 139, 122–139.

Li, H., Oraby, E.A., Eksteen, J.J., 2020. Extraction of copper and the co-leaching behaviour of other metals from waste printed circuit boards using glycine solution. Resour. Conserv. Recycl. 154 (Article 104624).

Liu, M.-S., Lin, M.C.-C., Tsai, C.Y., Wang, C.-C., 2006. Enhancement of thermal conductivity with Cu for nanofluids using chemical reduction method. Int. J. Heat Mass Transf. 49 (17), 3028–3033.

O'Connor, G.M., Lepkova, K., Oraby, E.A., Eksteen, J.J., 2018. Electrochemical behaviour of copper in alkaline glycine solutions. Hydrometallurgy 181, 221–229.

Oraby, E.A., Eksteen, J.J., Tanda, B.C., 2017. Gold and copper leaching from gold-copper ores and concentrates using a synergistic lixiviant mixture of glycine and cyanide. Hydrometallurgy 169, 339–345.

Oraby, E.A., Li, H., Eksteen, J.J., 2019. An alkaline glycine-based leach process of base and precious metals from powdered waste printed circuit boards. Waste Biomass Valori. 11 (8), 3897–3909.

Patil, K., Rattan, T.M., 2014. Inorganic Hydrazine Derivatives: Synthesis, Properties and Applications. John Wiley & Sons.

Serov, A., Kwak, C., 2010. Direct hydrazine fuel cells: a review. Appl. Catal. B Environ. 98 (1–2), 1–9.

Songping, W., Shuyuan, M., 2006. Preparation of micron size copper powder with chemical reduction method. Mater. Lett. 60 (20), 2438–2442.

Sun, Z., Xiao, Y., Sietsma, J., Agterhuis, H., Yang, Y., 2015. A cleaner process for selective recovery of valuable metals from electronic waste of complex mixtures of end-of-life electronic products. Environ. Sci. Technol. 49 (13), 7981–7988.

Tan, Q., Li, J., Boljkovac, C., 2018. Responding to China's waste import ban through a new, innovative, cooperative mechanism. Environ. Sci. Technol. 52, 7595–7597.

Tanda, B., Oraby, E., Eksteen, J., 2017a. Recovery of copper from alkaline glycine leach solution using solvent extraction. Sep. Purif. Technol. 187, 389–396.

Tanda, B.C., Eksteen, J.J., Oraby, E.A., 2017b. An investigation into the leaching behaviour of copper oxide minerals in aqueous alkaline glycine solutions. Hydrometallurgy 167, 153–162.

Tauetsile, P.J., Oraby, E.A., Eksteen, J.J., 2018a. Adsorption behaviour of copper and gold glycinates in alkaline media onto activated carbon. Part 1: isotherms. Hydrometallurgy 178, 202–208.

Tauetsile, P.J., Oraby, E.A., Eksteen, J.J., 2018b. Adsorption behaviour of copper and gold glycinates in alkaline media onto activated carbon. Part 2: kinetics. Hydrometallurgy 178, 195–201.

Tauetsile, P.J., Oraby, E.A., Eksteen, J.J., 2019a. Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper. Part 1: isotherms. Sep. Purif. Technol. 211, 594–601.

Tauetsile, P.J., Oraby, E.A., Eksteen, J.J., 2019b. Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper. Part 2: kinetics. Sep. Purif. Technol. 211, 290–297.

Yu, J.-C., Zhao, F.-G., Shao, W., Ge, C.-W., Li, W.-S., 2015. Shape-controllable and versatile synthesis of copper nanocrystals with amino acids as capping agents. Nanoscale 7 (19), 8811–8818.

Zhang, Q.-L., Yang, Z.-M., Ding, B.-J., Lan, X.-Z., Guo, Y.-J., 2010. Preparation of copper nanoparticles by chemical reduction method using potassium borohydride. Trans. Nonferrous Metals Soc. China 20 (1), s240–s244.

Supporting Information (SI)

Recovery of copper and the deportment of other base metals from alkaline glycine leachates derived from waste printed circuit boards (WPCBs)

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3 figures and 2 tables
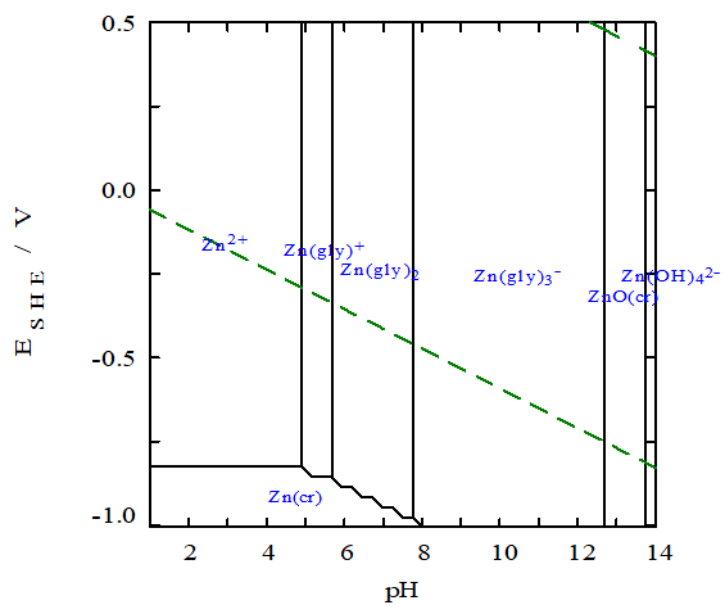
Figure S1. Eh-pH diagram of Zn-glycine (gly)-H$_2$O system at 0.5 M glycine, 188 mg/L Zn and 25°C (as shown, Zn starts to precipitate as ZnO when pH is over about 12.7).
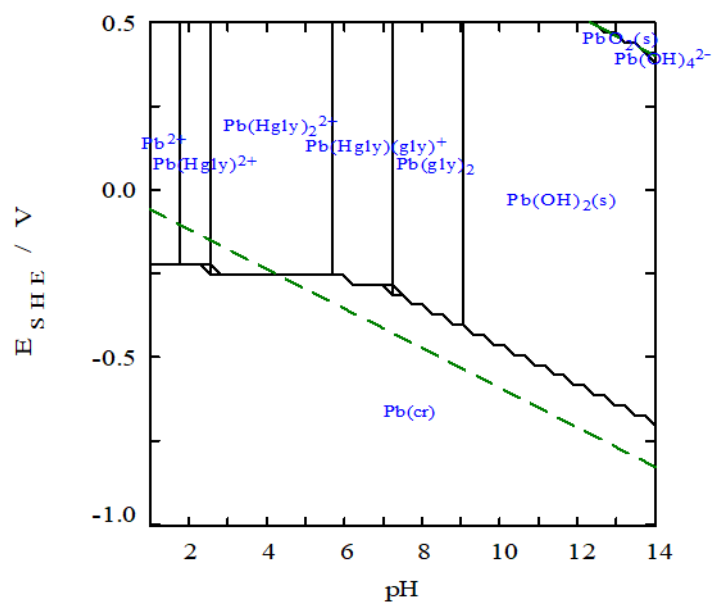
Figure S2. Eh-pH diagram of Pb-glycine (gly)-H$_2$O system at 0.5 M glycine, 75 mg/L Pb and 25°C (as shown, Pb starts to be reduced as native Pb at Eh of lower than about −0.63 V when pH is 12.8).
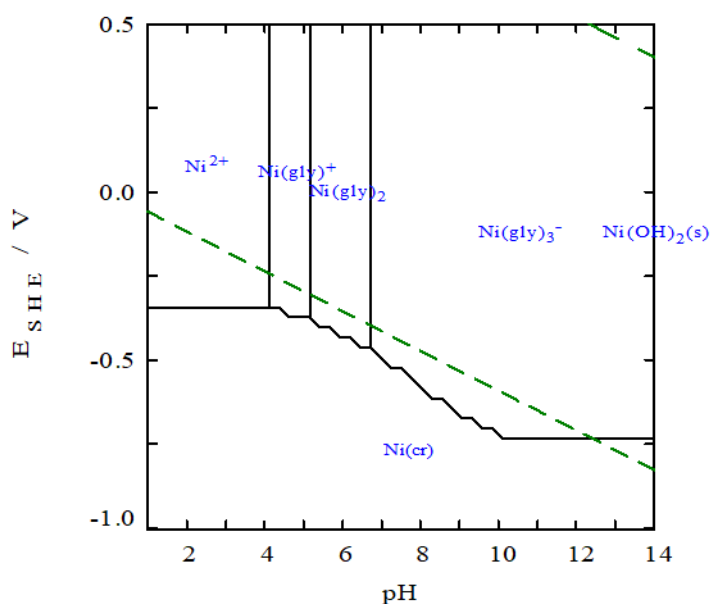
Figure S3. Eh-pH diagram of Ni-glycine (gly)-H_2O system at 0.5 M glycine, 12 mg/L Ni and 25°C (as shown, Ni starts to be reduced as native Ni at Eh of lower than about -0.73 V when pH is 12.8).

Table S1. Possible half-reactions of metals during hydrazine reduction, and their standard free Gibbs energy and electrode potential at 40°C, calculated by HSC Chemistry 10.0 software with Reaction Equations module (only native metals are considered as product for Pb, Sn, Ni, Zn and Al).

Reaction [a]	ΔG^o, kJ/mol	E, V vs SHE
$Cu(Gly)_2$ (aq) + 2e⁻ = Cu (s) + 2Gly⁻ (aq)	25.5	−0.132
$2Cu(Gly)_2$ (aq) + 2OH⁻ (aq) + 2e⁻ = Cu_2O (s) + 4Gly⁻ (aq) + H_2O	−23.3	0.121
$Pb(Gly)_2$ (aq) + 2e⁻ = Pb (s) + 2Gly⁻ (aq)	78.4	−0.407
$Ni(Gly)_2$ (aq) + 2e⁻ = Ni (s) + 2Gly⁻ (aq)	109.5	−0.568
$Zn(Gly)_2$ (aq) + 2e⁻ = Zn (s) + 2Gly⁻ (aq)	−7.3	0.038
$Al(OH)_4^-$ (aq) + 3e- = Al (s) + 4OH⁻ (aq)	664.8	−2.298
$Sn(OH)_6^{2-}$ (aq) + 4e⁻ = Sn (s) + 6OH⁻ (aq)	363.0	−0.941

[a] For Al and Sn, only their hydroxides are considered present in the solution.

Table S2. Standard Gibbs free energy of the possible equations for metal precipitation during sulphide precipitation at 25°C, calculated by HSC Chemistry 10.0 software with Reaction Equations module.

Reaction [a]	ΔG^o, kJ/mol
$Cu(Gly)_2$ (aq) + HS^- (aq)+ OH(-a) = CuS (s) + $2Gly^-$ (aq)+ H2O	−121.9
$Ni(Gly)_2$ (aq) + HS^- (aq)+ OH(-a) = NiS (s) + $2Gly^-$ (aq)+ H2O	−74.8
$Zn(Gly)_2$ (aq) + HS^- (aq)+ OH(-a) = ZnS (s) + $2Gly^-$ (aq)+ H2O	−299.3
$Pb(Gly)_2$ (aq) + HS^- (aq)+ OH(-a) = PbS (s) + $2Gly^-$ (aq)+ H2O	−116.4
$2Al(OH)_4^-$ (aq)+$3HS^-$ (aq)+$5H^+$ (aq)=Al_2S_3 (s) +$8H_2O$	6.6
$Sn(OH)_6^{2-}$ (aq)+$2HS^-$ (aq)+$4H^+$ (aq)=SnS_2 (s) +$6H_2O$	−282.1

[a] For Al and Sn, only their hydroxides are considered present in the solution.
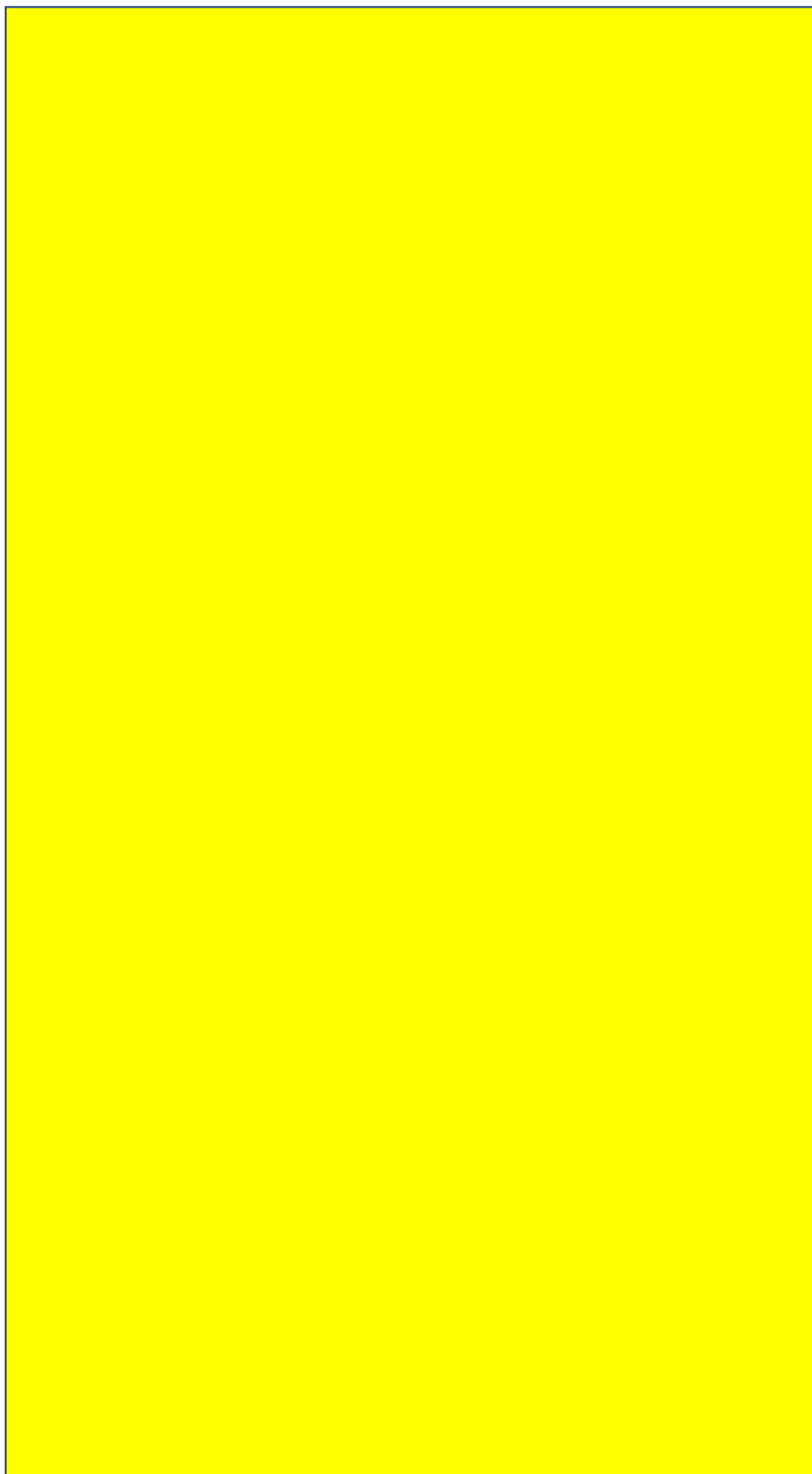
Chapter 6 Leaching of precious metals using cyanide-starved glycine leaching system

Summary

This chapter provides an in-depth study of the leaching of precious metals using cyanide-starved glycine solution from the residue of glycine-only leaching of WPCBs. The cyanide consumption was reduced significantly, compared with stoichiometric and conventional cyanidation.

Cyanide consumption minimisation and concomitant toxic effluent minimisation during precious metals extraction from waste printed circuit boards

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A B S T R A C T

Waste printed circuit boards (WPCBs) constitute a hazardous material with up to 40 different metals, including numerous many heavy metals and environmentally harmful metals. Most hydrometallurgical processing approaches use high concentrations of toxic reagents and generate significant amounts of harmful effluents. This research investigates the use of cyanide-starved glycine solution containing no free cyanide in the leachate to extract precious metals from WPCBs, with most of copper and base metals pre-removed by upstream glycine-only leaching. Under the optimised conditions, 90.1% Au, 89.4% Ag and 70.1% Pd were extracted together with 81.0% Cu and 15.0% Zn. The extraction of other base metals remained low at 8.3% for Al and <5% for Pb, Ni, Co, Fe and Sn, indicating a fairly good selectivity of the leaching system. By comparing with stoichiometric and intensive cyanidation, the cyanide-starved glycine system showed comparable or better performance on precious metals extraction, but cyanide use was reduced by >70% whereas the glycine can be reused. Analysis indicates that with an initial cyanide dose of 250 ppm, the leaching solution was starved of cyanide after 4 h with no free cyanide, which minimises safety and health risks significantly compared with traditional intensive cyanidation ([CN] > 3500 ppm). Glycine and cyanide dose, pH, and particle size dominated leaching kinetics, while staged addition of cyanide did not enhance the extractions. A significant (70–90%) reduction in required cyanide use and cyanide-bearing effluents can be achieved while performing polymetallic metal removal and allowing reagent recycling.

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1. Introduction

Printed circuit boards (PCBs) are the core components of most electric and electronic equipment (EEE) (Zhou et al., 2011). PCBs contain significant amounts of base and precious metals, compared with natural resources (Otsuki et al., 2019a). It also contains several hazardous substances, making proper recycling a necessity (Qiu et al., 2020). The amount of e-waste has increased considerably in recent decades, driven by high consumption rates, short life cycles and few repair options (Forti et al., 2020; Lee et al., 2018). Forti et al. (2020) mentions that e-waste amount has reached 53.6 million tons (Mt) worldwide in 2019, representing a value of about $57 billion USD, and the amount is projected to increase to 74.4 Mt by 2030. As shown in Table 1, China generated the highest amount of e-waste (10.1 Mt) in 2019, and the figure is forecast

to be 27.2 Mt in 2030 and 51.6 Mt in 2050 (Zeng et al., 2020). In Australia, e-waste generation has reached 21.7 kg/inhabitant in 2019, ranking the fifth highest in the world (Table 1), and the non-regulated e-waste (outside national recycling scheme) is projected to reach 461 kt in 2030 (Islam and Huda, 2020). Conventionally, a significant amount of e-waste has been transported from developed to developing countries (Kiddee et al., 2013). However, due to the bans and restrictions on e-waste transborder movement, domestic recycling is becoming more urgent for advanced economies (Li et al., 2020; Tan et al., 2018). Compared with the populous countries and regions, Australia generated less e-waste in total, but generated a significant amount of e-waste per person (5th overall), and has one of the poorer collection and recycling efficiencies (just slightly>10%, compared to Norway that collects and recycles>70% of its e-waste (Table 1)). Australia has a few large cities that are far from another and many remote towns, making road transport of waste expensive. The traditional pyrometallurgical approaches currently adopted by large international companies

Table 1
E-waste statistics of top 5 countries in generation per capita, and of countries with total generation > 2000 kt in 2019, adapted from Forti et al. (2020).

| Rank by e-waste generation/capita	Country	Region	E-waste generated in 2019, kg/capita	E-waste generated in 2019, kt	E-waste documented to be collected and recycled, kt
1	Norway	Europe	26.0	139	99 (2017)
2	The U.K.	Europe	23.9	1,598	871 (2017)
3	Switzerland	Europe	23.4	201	123 (2017)
4	Denmark	Europe	22.4	130	70 (2017)
5	Australia	Oceania	21.7	554	58 (2018)
8	The U.S.	Americas	21.0	6,918	1020 (2017)
9	Japan	Asia	20.4	2,569	570 (2017)
62	Brazil	Americas	10.2	2,143	0.14 (2012)
88	China	Asia	7.2	10,129	1546 (2018)
138	India	Asia	2.4	3,230	30 (2016)

may not suit Australia because it requires a high level of e-waste input for a profitable scale (D'Adamo et al., 2019). To reduce transportation costs and risks, e-waste should also be disposed of near where it is collected. This will require a recycling process that can meet safety and health requirements in urban or rural areas.

Most hydrometallurgical recovery operations occur in a multi-step process that may include preconcentration and physical separation to remove the bulk of the aluminium and iron and some of the copper (Koyanaka et al., 2006; Otsuki et al., 2019b). Subsequent hydrometallurgical steps typically vary pH, temperature, and redox potential to achieve selective metal dissolution, with precious metals commonly removed last in the processing sequence. Li et al. (2018) mentions in their review that the hydrometallurgical methods commonly reported for the extraction of precious metals from e-waste can be categorised as (1) aqua regia leaching, (2) cyanidation, (3) thiourea leaching, (4) thiosulfate leaching, (5) thiocyanate leaching, (6) iodine/iodide leaching, and (7) supercritical leaching. Among them, aqua regia, thiourea and thiocyanate effectively work in acidic environment where most reagents are either dangerous and toxic, and/or unstable leading to poor ability to recycle reagents, adding significant effluent treatment costs. Thiourea is also easily oxidised and decomposed in an acidic environment and a potential carcinogen (Akcil et al., 2015). Iodine/iodide and thiosulfate have low toxicity and work in alkaline environment (pH > 9) but the reagent consumption and costs are relatively high (Kaya, 2016) and recycling is expensive or infeasible due to reagent instability and speciation. Supercritical leaching refers to the method of using supercritical fluid. It has been shown promising but research is still at a low level and more studies are needed for its development (Liu et al., 2016). Cyanidation (pH $\geq$ 10.5) has been traditionally used to extract precious metals from natural resources for over 100 years, owing to the high affinity between cyanide and gold and silver (Bisceglie et al., 2017). However, due to the relatively high residual contents of Cu (1–3%) and other cyanide consuming base metals that remain in the first stage leaching residue (Li et al., 2020), the cyanide consumption will increase significantly. The high cyanide concentration required for precious metals recovery is problematic for "urban mining" in the proximity of urban environments and will make the safe disposal through detoxification of effluent that contains week acid dissociable (WAD) cyanide expensive. Detoxification costs range from USD $1.5/kg_{WAD\ CN}$ to USD $4.5/kg_{WAD\ CN}$ (reagents only (Adams, 2016b)).

Recently, the authors have reported an alkaline leaching system, comprising of glycine as a lixivant and with an oxidant (*e.g.* Air, O_2, H_2O_2), to extract base metals from WPCBs (Li et al., 2018; Li et al., 2020; Oraby et al., 2019). As shown in eq. (1), glycine can exist in solution in three forms: cation, zwitterion and anion, depending on different pH (O'Connor et al., 2018). It has been shown that > 95% copper (Cu) could be effectively extracted by an alkaline glycine solution, with soluble cupric glycinate

$(Cu(NH_2CH_2COO)_2, Cu(Gly)_2)$ formed at ambient temperature and pressure and at a pH of 10.0–10.8. Other base metals, such as zinc (Zn), lead (Pb), nickel (Ni), aluminium (Al) and tin (Sn), were also co-extracted with varied extents by forming soluble metal-glycine complexes or metal- hydroxyls (Li et al., 2020). In contrast, precious metals (gold (Au) and silver (Ag)) remained almost un-leached with both extractions < 2% (at room temperature). Recently, the authors have also shown the feasibility of using three methods, i.e. sulphide precipitation, solvent extraction and chemical reduction, to recover copper and other base metals from glycine leachate of WPCBs (Li et al., 2021). Glycine, the simplest amino acid, is conventionally used as an additive in food and animal feeds. It is a crystalline, non-toxic, non-volatile, recyclable reagent and is currently mass produced (Oraby et al., 2017). Therefore, using a glycine solution is perceived to be a more environmentally benign approach that may have the potential to be implemented in areas close to urban communities (Li et al., 2020). In addition, compared with the pyro-metallurgical process, the hydrometallurgical process using a glycine solution shows potential in small and medium enterprises (SMEs) with higher flexibility and efficiency that may be applied in remote and inland towns and cities of Australia (Li et al., 2020; Diaz et al., 2016).

$$^+H_3NCH_2COOH \xleftrightarrow{pKa=2.350} {}^+H_3NCH_2COO^- \xleftrightarrow{pKa=9.778} H_2NCH_2COO$$
(1)
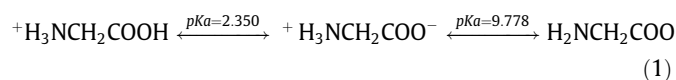
After Cu and base metal extraction, the remaining precious metals in the residue could subsequently be extracted in a second leaching stage. The authors have explored a novel alkaline method that integrates glycine and starved-cyanide (i.e. no "free" cyanide) to extract precious metals from a preconcentrated metallic fraction of WPCBs (>72% metals) (Oraby et al., 2019). The exploratory research has shown that 92.1% Au and 85.1% Ag were extractable using 30 g/L glycine and 300 ppm cyanide from the residue obtained from the first-stage glycine leaching of WPCBs (Oraby et al., 2019). With this method, the consumption of cyanide was considerably lower than traditional cyanidation, and the free cyanide remaining in solution was expected to be minimal as it was mostly complexed with precious metals and Cu. The cyanide-starved glycine system poses advantages over previous methods as (1) glycine can be recycled and reused after the recovery of metals from leachate (through de-complex of metal-glycine species), (2) cyanide use is at a minimal level that minimises the safety risks and (3) the alkaline leaching environment reduces the dissolution of other base metals, resulting in a better selectivity than acidic leaching methods. However, our precious study (Oraby et al., 2019) was an exploratory work and many details were not investigated. Moreover, the materials used in the study were the metallic fraction of WPCBs only, as obtained from a series of physical treatment and recovery steps which may not be representative to the original WPCBs stream.

When precious metals are extracted into glycine-containing solution, they will need to be separated and recovered. Eksteen et al. (2018) has studied copper–gold systems in alkaline glycine and has investigated the recovery of precious metals using activated carbon. Further studies by Deng et al. (2020a, 2020b, 2019a, and 2019b) have looked at selective separation of copper and gold glycinates and cyanides using precipitation and ion exchange approaches and Tauetsile et al. (2019a, 2019b, 2018a, and 2018b) investigated the mechanisms of copper and gold glycinates and cyanides from solutions in which they occur as mixed species. These authors have shown that the selective separation and recovery of these base and precious metals from solutions containing them as cyanide and glycine complexes are technically feasible. The metal recovery from solution is, therefore, not discussed again in present study, except for noting that feasible methods already exist for their separation and purification.

Figure S1 (see Supporting Information) shows the conceptual flowsheet for the management of WPCBs the author proposed. As shown, base and precious metals are expected to be extracted in two stages and eventually, non-metallic fractions (NMFs) are expected as end-output. In this way, the hazards of this typical waste can be managed properly and its economic value can be exploited. Therefore, as shown in Figure S1, this study aims to further investigate the use of glycine in the presence of starved cyanide to extract precious metals from WPCBs without physical separation of the metals (e.g. magnetic and electrostatic separations) which simplifies the process. The samples used in the study are the residue obtained from the first-stage glycine leaching of WPCBs with > 95% Cu extracted. The leaching behaviour, especially the interactions between metals, glycine and cyanide, is studied in detail. Other than precious metals, the deport of base metals is also investigated. This study is expected to provide a deeper understanding of cyanide-starved glycine system used for precious metals extraction from materials of not only e-waste but also relevant primary resources, e.g. Cu bearing Au/Ag ores/concentrates, and other secondary resources.

2. Experimental Section

2.1. Preparation of WPCB samples

The WPCB samples used in this study is the residue obtained from the first-stage glycine leaching of WPCBs. The original WPCBs, containing around 22.6% Cu, was from end-of-life computer mother boards with high-value CPUs and RAMs removed, supplied by *Total Green Recycling Pty Ltd* (Perth, Western Australia), and the original WPCBs were shredded to 100% ≤ 2 mm (Li et al., 2020), i.e. without preconcentration of the metallic portion. The WPCB samples used in this study were prepared by leaching the original WPCBs (100% ≤ 2 mm) with 0.5 M glycine at 5% solid, initial pH 10, and room temperature for 72 h, followed by another stage of leaching under same conditions but for 7 days. The total Cu

extraction from the two stages of glycine leaching was calculated as 93.8%. The major metal contents of the prepared WPCBs samples used in this study are presented in Table 2. As shown, the samples contain 119.91 ppm Au, 412.39 ppm Ag, and 1.28% Cu. The economic value is dominated by Au (88.9%). According to (Otsuki et al., 2020); L i et al., 2018), Au and Ag should be presented in WPCBs as native or alloy form, mostly coated on the pins and holes of electronic components and board, or inside the microprocessors. To prepare for each experiment, the samples were split into small portions (around 9.0 g each) using a rotary sample divider. To investigate the effect of particle size on metal extractions, some samples were further pulverised for about 4 min by Essa LM5 Pulverising Mill. The mill is commonly used for size reduction or mechanical activation of minerals in mining industry. It allows sample to be grinded in a steel bowl by mechanical forces. It was found that 3.1% mass of sample was lost after pulverisation. Therefore, the major metal contents of the pulverised sample was also analysed and is shown in Fig. 4. Another sample size, referred as ≤ 1 mm, was prepared from the two-stage glycine leaching of 100% ≤1mm original WPCBs.

2.2. Reagents

Glycine used in this study was of HPLC grade (≥99%), supplied by Sigma-Aldrich. Sodium hydroxide (NaOH) and sodium cyanide (NaCN) were of analytical reagent grade, supplied by Rowe Scientific Pty Ltd. Unless specified, cyanide or CN mentioned in the following sections refers to NaCN. All the leaching solutions and analytical samples were prepared using deionized (DI) water.

2.3. Experimental setup and procedures

All the leaching experiments were conducted in 2.5 L plastic Winchester bottles. For each experiment, unless specified otherwise around 9.0 g of WPCB sample was mixed with a solution at 2% solid (g/mL), a different particle size, initial pH (±0.1, adjusted by NaOH) and concentrations of glycine and cyanide. A ~ 5 mm hole was left on each bottle lid to allow air ingress, providing the leaching reactions with oxygen. No further oxygen was added. For safety considerations, the cyanide was added after the addition of glycine and NaOH with the pH adjusted to ≥ 10.5, unless otherwise specified. The bottle containing the mixture was then put on a bottle roller at room temperature and rotated at a speed of 100 rpm for up to 96 h. Solution samples of 5 mL each were taken at 2, 4, 6, 24, 48, 72 and 96 h. At each sampling time, the pH and Eh (mV, *vs* Ag/AgCl) of leaching solution were measured by using a pH meter (90-FLMV Field Lab Analyser, TPS Pty Ltd). Upon completion of leaching, the solid and liquid were separated with a vacuum filter, the solid was washed with DI water and then dried at 70 °C overnight.

Table 2
Major metal contents of the feed materials used in this study, prepared from glycine leaching of WPCBs (100% ≤2 mm), and their economic values.

	Metal price, content and economic value										
	Metal content in wt. %						Metal content in ppm				
	Cu	Fe	Al	Sn	Pb	Ni	Zn	Co	Au	Ag	Pd
Metal price (USD/t) [a]	6339	–	1659	17,455	1817	13,425	2132	28,500	5.79×10^7	5.99×10^5	6.29×10^7
Metal content	1.28	1.52	0.67	0.10	0.15	0.19	535.00	56.53	119.91	412.39	7.57
Metal value, USD/t materials	81.1	–	11.1	17.5	2.7	25.5	1.1	1.6	6942.8	247.0	476.2
Metal value (%) [b]	1.0	–	0.1	0.2	<0.1	0.3	<0.1	<0.1	88.9	3.2	6.1

[a] Data taken from the official prices of London Metal Exchange on 10th July 2020. [b] only the metals specified are considered.

2.4. Analytical methods

The Au, Ag and Cu concentrations in the solution samples were analysed by inductively coupled plasma - optical emission spectrometry (ICP-OES, for Cu) and inductively coupled plasma - mass spectrometry (ICP-MS, for Au, Ag), and were independently done by *Bureau Veritas* (Perth, Australia). The extractions of Au and Ag ($E_{Au/Ag}$, %) were calculated as eq. (2) (Li et al., 2020).

$$E_{Au/Ag} = (m_t + m_{s1})/(m_f + m_{s2} + m_r) \times 100\% \qquad (2)$$

where m_t and m_f are the mass of metal in the leachate at time t and in the final solution at 72 h, respectively; m_{s1} and m_{s2} are the mass of metal in the samples sampled before time t and before 72 h, respectively; m_r is the mass of metal in the final residue.

The concentrations of base metals (Ni, Al, Fe, Pb, Zn, Sn and Co) and other precious metals (Pd) in the final leaching solutions (at 72 or 96 h) were analysed by ICP-OES (for Al, Fe, Ni, Zn and Co) and ICP-MS (for Pd, Pb, Sn), and independently done by *Bureau Veritas*. The extraction of these metals (E_m, %) was calculated as eq. (3) (Li et al., 2020).

$$E_m = m_t/(m_f + m_r) \times 100\% \qquad (3)$$

where m_t and m_f are the mass of metal in the leachate at time t and in the final solution at 72 h, respectively; m_r is the mass of metal in the final residue.

It should be noted that, due to the heterogeneous nature and the relatively large sizes (~2 mm) of PCBs material used in this study, the extraction of metals shown in eqs. 2–3 are based on metals in solution sample and leaching residue (referred as "solution-residue"), instead of on feed samples. The mass balance of metals was conducted to validate the results of extractions in latter section.

The metal contents in feed samples and leaching residues were analysed by aqua regia digestion followed by ICP-OES/MS and analysed by *Bureau Veritas*. The feed samples and leaching residues were also analysed by scanning electron microscope coupled with energy dispersive X-ray spectroscopy (SEM-EDS, Mira 3 VP-FESEM) to determine their morphology and general compositions (Pereira Gonçalves and Otsuki, 2019).

To investigate the interaction of glycine, cyanide, and metals, the concentrations of cupric ions in some solution samples were tracked by Ultraviolet–visible spectroscopy (UV–Vis spectroscopy, Varian Cary 50) at a wavelength of 625 nm. This method was previously developed and reported by Tanda et al. (2017a,b).

3. Results and discussion

3.1. Theoretical consideration

In the present leaching system, the major species are glycine, cyanide, various native metals and their oxidised/coordinated cyanide/glycinate states, which makes the system complex. Partial cyanide oxidation to cyanate also takes place during the overall leach process. The metals of interest in this study are mainly Cu, Au, and Ag, representing > 90% economic value of the materials (Table 2). To better understand and explain the leaching behaviours, the interactions among the species of interest need to be investigated first. Other metals are also discussed in latter sections, but a detailed investigation is beyond the scope of this study. To contextualise results, it is worthwhile to consider the thermodynamic drivers and stabilities of the complexes during this leach process, in particular the copper, gold and silver with glycine-cyanide system.

3.1.1. Cu-glycine-cyanide-H₂O system

Tables 3 presents the cumulative formation constants for selected complexes of metal and glycine or cyanide. As shown, cupric ion has a high affinity with glycine compared with other metal ions. A number of previous studies (Li et al., 2020; Oraby and Eksteen, 2014; Tanda et al., 2017) have shown that cupric glycinate ($Cu(NH_2CH_2COO)_2$, $Cu(Gly)_2$) is the dominant form of complex when using glycine to leach Cu in alkaline environment. However, when cyanide is present, cuprous ion can also form a strong complex with cyanide, as shown by the high formation constants in Table 3. Figure S2 presents the E_h-pH diagram of Cu-glycine-cyanide-H₂O system at 25 °C. It can be seen that cuprous ion forms $Cu(CN)_2^-$ and $Cu(CN)_3^{2-}$ with cyanide at E_h from −0.44 to 0.40 V and a wide alkaline pH range, while cupric glycinate forms at higher E_h values. The possible reactions can be written as eqs. 4–6. At the proposed cyanide concentrations, $Cu(CN)_4^{3-}$ is not dominant in the Eh-pH diagram.

$$2Cu\ (s) + O_2\ (g) + 4Gly^-\ (aq) + 2H_2O \rightarrow 2Cu(Gly)_2\ (aq)$$
$$+ 4OH^-(aq), \Delta G^o(25\,°C) = -202.6 KJ/mol \qquad (4)$$

$$2Cu\ (s) + 1/2O_2\ (g) + 4CN^-\ (aq) + H_2O \rightarrow 2Cu(CN)_2^-\ (aq)$$
$$+ 2OH^-(aq), \Delta G^o(25\,°C) = -161.1 KJ/mol \qquad (5)$$

$$2Cu\ (s) + 1/2O_2\ (g) + 6CN^-\ (aq) + H_2O \rightarrow 2Cu(CN)_3^{2-}\ (aq)$$
$$+ 2OH^-(aq), \Delta G^o(25\,°C) = -308.9 KJ/mol \qquad (6)$$
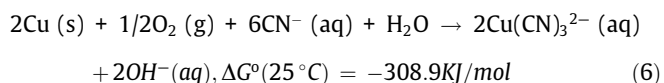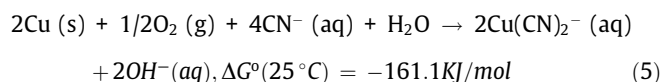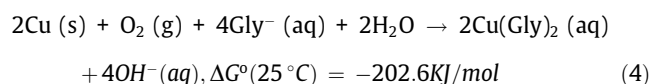
3.1.2. Au-glycine-cyanide-H₂O system

It is well known that $Au(CN)_2^-$ is the dominant and most stable form between gold and cyanide (Figure S3, Theodor et al., 2006), and the cyanidation of gold can be represented by eq. (7). According to Oraby et al. (2017), glycine can also complex with Au with the reaction represented as eq. (8). Adams (2016a) indicated that the standard reduction potential of $Au(Gly)_2^-/Au$ is 0.632 V (*vs* SHE). This reveals that $Au(Gly)_2^-$ may form in glycine-cyanide solution when the system is in appropriate oxidizing environment.

$$2Au\ (s) + 1/2O_2\ (g) + 4CN^-\ (aq) + H_2O \rightarrow 2Au(CN)_2^-\ (aq)$$
$$+ 2OH^-(aq), \Delta G^o(25\,°C) = -196.2 KJ/mol \qquad (7)$$

$$2Au\ (s) + 1/2O_2\ (g) + 4Gly^-\ (aq) + H_2O \rightarrow 2Au(Gly)_2^-\ (aq)$$
$$+ 2OH^-(aq), \Delta G^o(25\,°C) = 195.8 KJ/mol \qquad (8)$$
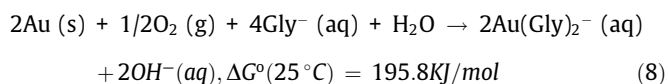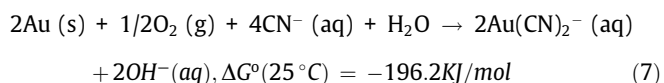
WAD Cu-cyanide could promote the leaching of Au in cyanide-only solutions when no free cyanide is present. The explanation is that the weakly bound Cu-cyanide complexes could dissociate to release free cyanide that can form more stable complexes with Au (Table 3). The possible reactions are proposed as eq. 9–11, but the final speciation of Cu is highly dependent on pH (Rees and Van Deventer, 1999). However, when glycine is added into the system, the precipitated CuCN (eq. (10)) could be dissolved to further release free cyanide (eq. (12), Oraby et al., 2017).

In addition, Eksteen and Oraby (2015) have shown that the addition of cupric ions (as additional oxidant) into a glycine-peroxide solution could significantly accelerate the dissolution of Au from Au foils. This implies that the $Cu(Gly)_2$ may also act as additional oxidant in the glycine-cyanide system when leaching WPCBs.

$$2Au\ (s) + 1/2O_2\ (g) + 4Cu(CN)_3^{2-}\ (aq) + H_2O \rightarrow 2Au(CN)_2^-\ (aq)$$
$$+ 4Cu(CN)_2^-\ (aq) + 2OH^-(aq), \Delta G^o(25\,°C) = 99.4 KJ/mol \qquad (9)$$
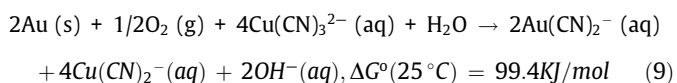
Table 3
Cumulative formation constants of selected complexes between metal and glycine or cyanide at 20–25 °C (*M* stands for metal ion specified, *L* standards for glycine or cyanide ligand).

Metal-ion	Cu+	Cu2+	Zn2+	Ni2+	Pb2+	Co2+	Fe2+	Fe3+	Au+	Au3+	Ag+	Pd2+
Complexing with glycine												
log K_{ML}	–	8.60	5.52	6.18	5.53	5.23	4.13	–	–	7.05	3.41	9.12
log K_{ML2}	10.0	15.54	9.96	11.14	9.98	9.25	7.65	–	18	10.57	6.89	17.55
log K_{ML3}	–	16.27	–	15	–	10.76	–	–	–	–	–	–
Ref. [a]	1	2	2	2	1	2	1	–	3	1	2	2
Complexing with cyanide												
log K_{ML}	s [b]	–	5.4	5.3	–	–	–	–	18	–	s	–
log K_{ML2}	24.0	–	s	s	–	–	–	–	38.3	–	21.1	s
log K_{ML3}	28.59	–	16.0	–	–	–	–	–	–	–	21.7	–
log K_{ML4}	30.3	22.6	19.6	31.3	–	–	–	–	–	–	20.6	42.4
log K_{ML5}	–	–	–	–	–	–	27.4	34.8	–	–	–	–
log K_{ML6}	–	–	–	–	–	–	35.4	42.3	–	–	–	–
Ref. [a]	2	4	4, 5	2, 5	–	–	4	4	2, 4	–	2	6

[a] the reference numbers applicable to this table only; [b] "s" denotes solid; "-" denotes not reported; ref. 1: Kiss et al. (1991); ref 2: Dean (1999); ref 3:Adams (2016a); ref. 4: Kyle (1997); ref. 5: Wang and Forssberg (1990); ref. 6: Schoeman et al. (2017).

$$2Au\ (s) + 1/2O_2\ (g) + 4Cu(CN)_2^-\ (aq) + H_2O \rightarrow 2Au(CN)_2^-\ (aq)$$
$$+ 4CuCN(s) + 2OH^-(aq), \Delta G^o(25\,^\circ C) = -284.9 KJ/mol \quad (10)$$

$$2Au\ (s) + O_2\ (g) + 2Cu(CN)_2^-\ (aq) + 2H_2O \rightarrow 2Au(CN)_2^-\ (aq)$$
$$+ 2Cu(OH)_2(s), \Delta G^o(25\,^\circ C) = -306.2 KJ/mol \quad (11)$$

$$2CuCN\ (s) + 4Gly^-\ (aq) + 1/2O_2\ (g) + H_2O \rightarrow 2Cu(Gly)_2\ (aq)$$
$$+ 2CN^-(aq) + 2OH^-(aq), \Delta G^o(25\,^\circ C) = 2.8 KJ/mol \quad (12)$$

3.1.3. Ag-glycine-cyanide-H_2O system

Ag forms weak complexes with glycine, with the constants 2–3 times less than that of cupric glycinate (Table 3). Conversely, Ag forms moderately strong complexes with cyanide, and the constants are similar with that of cuprous cyanides (Table 3). Figure S4 illustrates the E_h-pH diagram of Ag-glycine-cyanide-H_2O system at 25 °C. In an alkaline environment (pH > around 9.8), $Ag(CN)_2^-$ can be easily formed with the reaction represented by eq. (13). At the E_h beyond 0.65 V (451 mV, *vs* Ag/AgCl), $Ag(Gly)_2^-$ can be formed but may be further precipitated if the pH and E_h continue increasing. It has been shown by previous studies that the presence of Ag could enhance/assist Au dissolution in cyanide-only, glycine-only and thiosulfate solutions (Oraby and Eksteen, 2015b). In cyanide-only solutions, Rees and Van Deventer (1999) indicated that silver was rapidly dissolved from a copper concentrate, but was then precipitated, possibly as native Ag and/or AgCN (eq. (14)). Like the case for copper, it is due to the dissociation of the weakly bound silver-cyanide species to release free cyanide that can complex with gold, when cyanide is starved in the solution. Whether AgCN can be dissolved again by glycine (like copper) remains unclear.

$$2Ag\ (s) + 1/2O_2\ (g) + 4CN^-\ (aq) + H_2O \rightarrow 2Ag(CN)_2^-\ (aq)$$
$$+ 2OH^-(aq), \Delta G^o(25\,^\circ C) = -155.0 KJ/mol \quad (13)$$

$$2Au\ (s) + 4Ag(CN)_2^-\ (aq) + 1/2O_2\ (g) + H_2O \rightarrow 2Au(CN)_2^-\ (aq)$$
$$+ 2OH^-(aq) + 4AgCN(s), \Delta G^o(25\,^\circ C) = -102.1 KJ/mol \quad (14)$$

3.2. Effect of variables

3.2.1. Effect of cyanide (CN) concentration

Based on our precious exploratory study (Oraby et al., 2019), cyanide concentrations of 100 to 350 ppm were selected to investigate its effect on metal extractions, and the results are plotted in Fig. 1a-b and Figure S9. Other conditions were kept at the initial pH

of 11 and particle size of ≤ 2 mm, and the glycine addition was 4 times of the stoichiometric requirement (4 ×). As a comparison, leaching at stoichiometric amount of cyanide-only (897.5 ppm) was also performed. The required stoichiometric additions are determined by the coordination number shown in Table S1, which is based on the analysis in Section 3.1. However, it should be noted that the stoichiometry used in this study is rather a reference of reagent amount but not an intention to precisely indicate the stoichiometry in real-time leaching system.
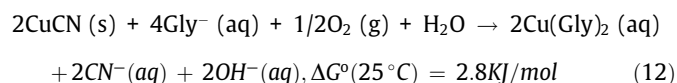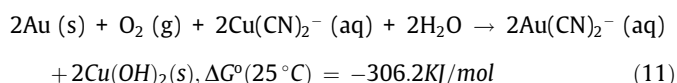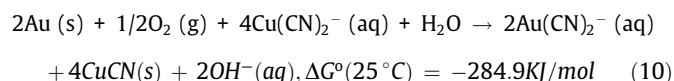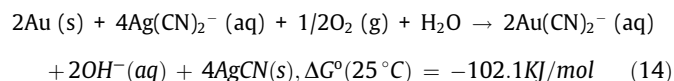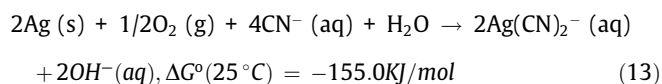
Not surprisingly, the increase of cyanide concentration resulted in the rise of Au extraction (Fig. 1a). This is due to the increased cyanide amount available to complex with Au and the strength and stability of the gold cyanide complex. Fig. 2 plots species concentrations of Cu as a function of cyanide concentration. From Section 3.1.1, it can be concluded that Cu presented in leachate as Cu^{2+} and/or Cu^+, and in the experimental pH range (10.6–11, Figure S5), their complexes are $Cu(Gly)_2$, $Cu(CN)_2^-$ and/or $Cu(CN)_3^{2-}$ (Figure S2). Therefore, the Cu^+ concentration (Fig. 2) can be calculated from the difference between total Cu from ICP-MS, and Cu^{2+} from UV–Vis spectroscopy. With the increase of cyanide concentration, more Cu speciated as Cu^+ complexed with cyanide. When the cyanide concentration reached 350 ppm, there was no Cu^{2+} detected in leachate. This confirms that Cu has higher preference to complex with cyanide than with glycine in this leaching system. It is foreseen that should oxygen be sparged into a stirred vessel (instead of air ingress through a bottle lid), this equilibrium will be shifted towards the formation of cupric glycinate rather than cuprous cyanide complexes. By comparing eqs. 5–6, 9–10 and 12, the role of cyanide during the dissolution of Cu could be seen as a "catalyst". However, higher cyanide concentrations will leave more Cu complexed with cyanide, reducing the catalysing effect. In addition, to reduce safety risks, cyanide use should be reduced at a low level (Mudder and Botz, 2004), and ideally, free cyanide could be maintained at zero or a marginal level. Cu should hence present in the leachate as $Cu(Gly)_2$ as much as possible. To achieve this, the starved 250 ppm cyanide dosage is recommended. At this concentration, Au extraction reached 78.5% at 72 h (Fig. 1a) which is close to that at stoichiometric amount of cyanide-only (81.4% at 897.5 ppm, Fig. 1a), with around 72% reduction of cyanide concentration.

The extractions of Ag in cyanide-starved glycine solutions experienced a sharp increase in the first 6 h with ≥ 99% Ag extraction achieved, indicating a much faster kinetics than Au, but further decreased dramatically with time extending to 72 h (Fig. 1b). However, this trend did not occur when using stoichiometric cyanide only. The decrease of Ag extraction could be due to the dissociation of the weak Ag-glycine complex (Table 3). The possible reactions
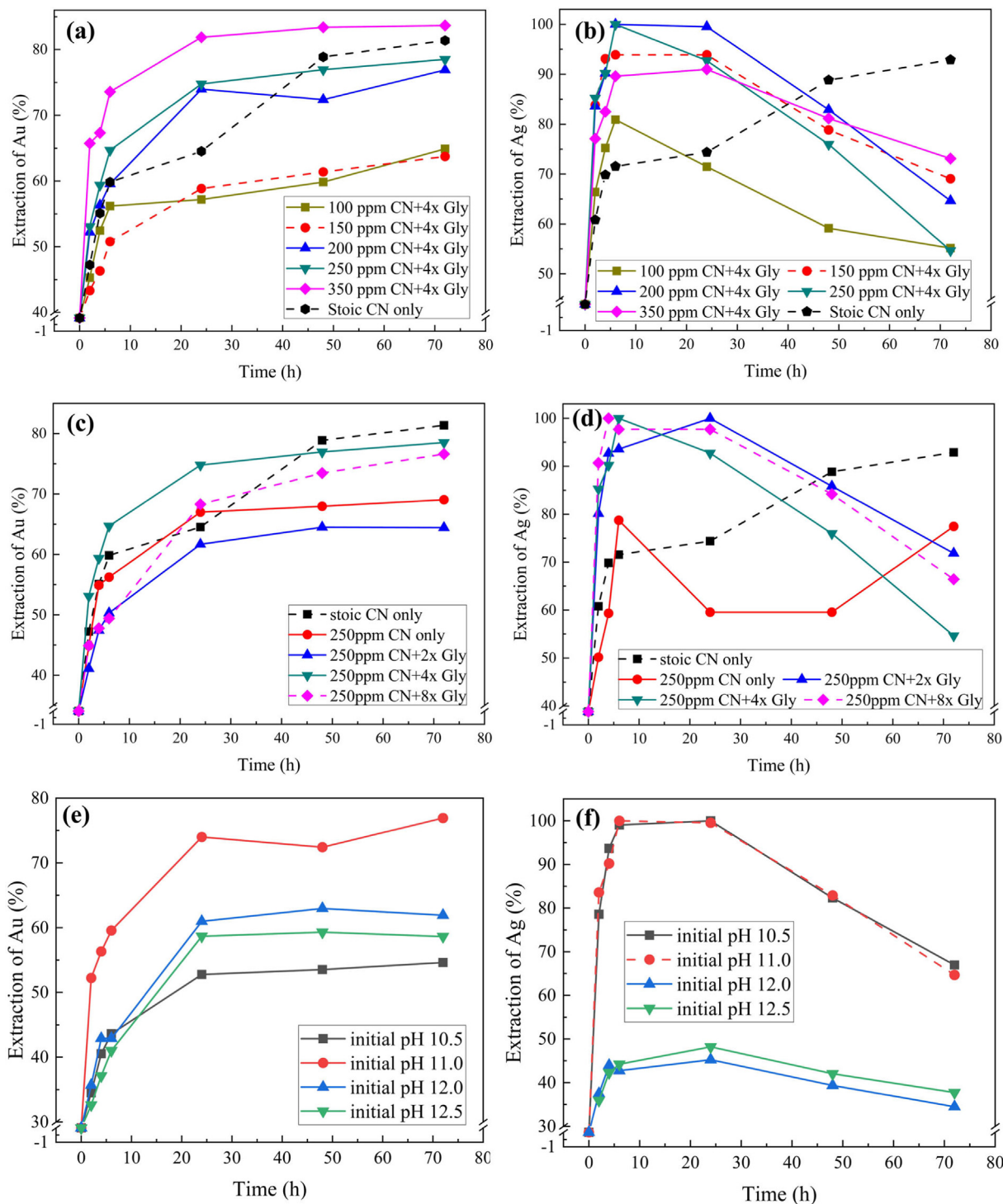
Fig. 1. Effect of (a-b) cyanide concentration, (c-d) glycine addition, (e-f) initial pH, (g-h) particle size and (i-j) the method of cyanide addition on the extractions of gold and silver.

during Ag leaching and precipitation are shown in eqs. 13–16. The speciation of the Ag precipitates could not be verified by SEM-EDS since the quantity was too small to be found. The Ag extraction increased with increasing cyanide concentration from 100 to 200 ppm in the first 48 h, but was noted to decrease when the concentration rose to over 250 ppm. In industry, carbon in leach (CIL) or resin in leach (RIL) technologies to simultaneously remove leached Ag could be considered.

$$AgCN \ (s) + 2Gly^- \ (aq) \rightarrow Ag(Gly)_2^- \ (aq) + CN^- \ (aq) \qquad (15)$$

$$2Ag(Gly)_2^- + 2OH^- \ (aq) \rightarrow Ag_2O \ (s) + 4Gly^- \ (aq) + H_2O \ (l) \qquad (16)$$
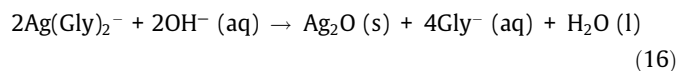
Figure S9 shows the effect of cyanide concentration on the extraction of other metals. The extraction of Pd peaked at 75.6% with 250 ppm cyanide. This figure is higher than that of using a
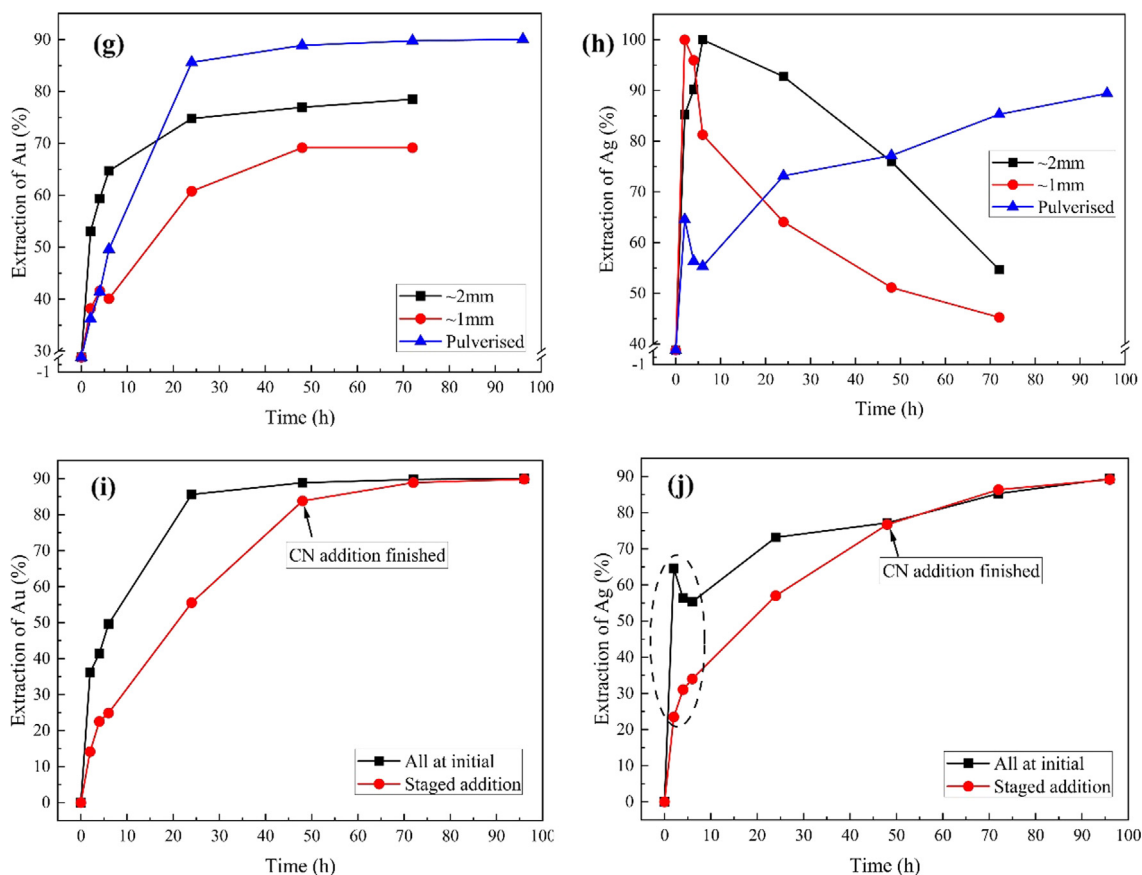
Fig. 1 (*continued*)
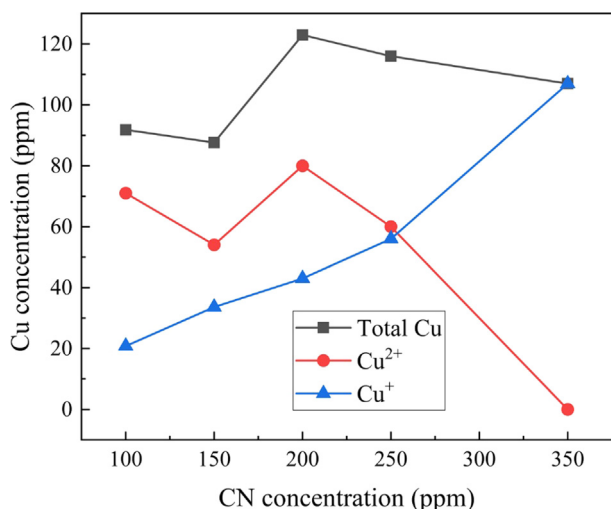
Fig. 2. Cu concentration in final leachate (at 72 h) as a function of CN concentration (Glycine addition = 4x stoichiometric, initial pH = 11, particle size ≤ 2 mm).

stoichiometric amount of cyanide-only (46%). Moreover, our previous study has shown that Pd could be extracted at only a limited level (<15%) in glycine-only solutions (Li et al., 2020). Therefore, it can be concluded that the cyanide-starved glycine leaching enhanced the Pd extraction significantly above cyanide-only and glycine-only systems. By increasing cyanide concentration, the extractions of Ni and Zn increased by about 15% and 7% respectively, but still remained at low levels (<25%). In contrast, those of Cu, Al, Pb, Fe and Sn remained relatively stable. Among them,

Fe, Sn and Pb posed a minimal extraction of ≤ 5%. The relatively low extractions of base metals are expected to reduce the amount of WAD cyanide in leachate.

3.2.2. Effect of glycine (gly) addition

To investigate the effect of glycine on the extraction of metals, experiments were carried out at different multiples of the stoichiometric amount of glycine (8×, 4×, 2 × and none). Other conditions remained constant at the initial pH of 11, cyanide concentration of 250 ppm and particle size of ≤ 2 mm. As can be seen from Fig. 1c, the addition of glycine at 4 × and 8 × enhanced the Au extraction, compared with using same concentration of cyanide-only. However, the 8 × glycine did not lead to any further increase of Au extraction.

As presented in Fig. 1d, the addition of glycine enhanced Ag extraction considerably in the first 24 h, compared with both using 250 ppm and stoichiometric cyanide-only. Moreover, more glycine addition led to faster kinetics in the initial leaching hours but was detrimental to the leaching after 24 h. The leaching at 250 ppm cyanide-only had fast kinetics in the first 6 h but the leached Ag precipitated, while this did not happen to using stoichiometric cyanide-only. Thus, at a starvation level, cyanide will not preferably complex with Ag, but most possibly will with Au (eq. (14)). In addition, given the similar formation constant of cuprous cyanides and Ag-cyanides (Table 3), there is also possible competition between Ag and Cu for the available cyanide in real-time leachate. In contrast, the glycine introduced into the system formed a Ag-glycine complex, i.e. Ag(Gly)$_2^-$, resulting in higher Ag extractions (eq. (15)). Our previous study has already shown that Ag almost could not be leached in a glycine-only solution at room temperature (Li et al., 2020). This reveals that cyanide played an

indispensable role for Ag extraction in the cyanide-starved glycine solution, which can be seen as a "catalyst" from eq.13–15. Again, the synergy between the reagents (cyanide and glycine) leads to improved extractions, whilst allowing to minimise overall cyanide requirement.

The effect of glycine addition on the extraction of other metals is shown in Figure S10. Considering the effect on all the extractions of Au, Ag, Pd and Cu, a glycine addition of 4 × stoichiometric is therefore considered optimum for this study. At this dose, the glycine used was around 170 kg/ton feed materials, and its concentration in solution was around 0.045 M. Using the separation and recovery technologies suggested by Tanda et al. (2017b), Deng et al. (2019a, 2019b, 2020a, 2020b) using ion exchange and and Tauetsile et al. (2018a, 2018b, 2019a, 2019b) the metals can be recovered from solution while leaving the glycine in solution for recycling back to the leach stage.

3.2.3. Effect of initial pH

As shown in the Eh-pH diagrams (Fig. S2-4), pH directly affects the existing form of metals in solution. Experiments were performed at different initial pH values (10.5–12.5) to investigate its effect on metal extractions. It should be noted that although the initial pH was controlled, the pH of leaching solution was progressing slightly due to the redox reactions (Figure S7). Other conditions were fixed as follows: glycine addition of 4x, cyanide concentration of 200 ppm and particle size of ≤ 2 mm. As obviously shown in Fig. 1e, the optimum initial pH for Au extraction was 11, with a further increase of pH to 12.5 the extraction decreased by about 20%. A similar trend was observed by Oraby and Eksteen (2015a). In their study, Au dissolution from pure Au-foil in cyanide-starved glycine solution increased and further decreased with the increase of pH from 10 to 13, while the optimum pH was recorded as 12.

Fig. 1f indicates that the Ag extraction was greatly sensitive to initial pH from 11 to 12, but no considerable changes of extraction were observed for the pH range of 10.5–11 and 12–12.5. As implied in eq. (16), Ag may be precipitated at high pH (high OH^- concentration) as Ag oxides. Therefore, for a high Ag extraction, the initial pH of cyanide-starved glycine solution should preferably not be ≥ 12.

Figure S11 plots the effect of initial pH on the extraction of other metals. Both the extraction of Pd and Cu peaked at the initial pH of 11. The decrease of Cu extraction could also account for the decrease of Au extraction at pH ≥ 12 (Fig. 1e) given that less Cu^{2+} ($Cu(Gly)_2$) was present in leachate to oxide Au. In contrast, the extraction of Al, Pb and Sn increased with pH rising from 10.5 to 12.5. This result is consistent with that of glycine-only leaching (Li et al., 2020). It has been well known that the amphoteric metals, Al, Pb and Sn, could be dissolved in highly alkaline solution and the dissolution increases with the rise of alkalinity (Hotea, 2013; Li et al., 2020), which explains the rise of their extractions in cyanide-starved glycine solution. Aiming at a high extraction for the metals of interest, Au, Ag, Pd and Cu, the initial pH of 11 is hence considered optimum.

3.2.4. Effect of particle size

3.2.4.1. Intensive cyanidation. In the forgoing variable investigations, the Au and Cu extractions were always restricted to < 85% and < 50%, respectively. The intrinsic structure of the WPCB substrate is metal-polymer laminations (Kaya, 2016), which may cause the locking of metals, accounting for the low extractions. To confirm this, leaching by intensive cyanidation was first carried out at different particle sizes. To be clear, the ≤ 2 mm and ≤ 1 mm sizes refer to the WPCBs samples obtained from glycine leaching of original 100% ≤2 mm and 100% ≤1 mm WPCBs respectively, while the pulverised size refers to the samples obtained by pulverising the ≤ 2 mm sample for 4 min (Section 2.1).
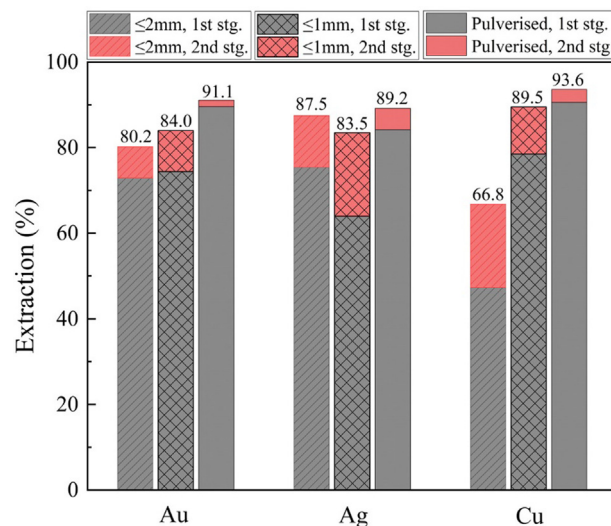
Fig. 3. Extractions of Au, Ag and Cu at different particle sizes (3500 ppm CN and 48 h at each stage, pH maintained at 11).

The intensive cyanidation was conducted in two stages, with 3500 ppm cyanide and 48 h of leaching time in each stage, and the pH was always maintained at 11 ± 0.5. As shown in Fig. 3, when the particle size became smaller, more Au and Cu were extracted in two stages. The relatively lower Ag extraction at ≤ 1 mm size may be due to precipitation after leaching. A lower metal extraction was achieved in the 2nd stage for pulverised materials. This indicates that the locking of metals accounts for the low extractions of Au and Cu, and the extraction has almost reached its maximum limit by the intensive cyanidation with pulverised samples.

3.2.4.2. Cyanide-starved glycine leaching. Leaching experiments in cyanide-starved glycine solution were then performed at different particle sizes of the feed materials. Other conditions were kept at 4 × glycine addition, 250 ppm cyanide and initial pH of 11. As indicated in Fig. 1g, after pulverising, Au extraction was enhanced by about 10% from the ≤ 2 mm size. It almost reached equilibrium in the first 24 h (85.6%) but slowly increased to 90.1% until 96 h of leaching. This figure is comparable with 91.1% obtained from the intensive cyanidation (Fig. 3), showing the high performance of the cyanide-starved glycine leaching.

As shown in Fig. 1h, reducing the particle size to 1 mm led to faster kinetics of Ag extraction, but also caused faster rate of reprecipitation. However, it is interesting that the extracted Ag from pulverised samples experienced a small window of precipitation (2–6 h), but further an almost linear rate of extraction until 96 h was obtained which is opposite in behaviour compared to other sizes. Given the polymetallic nature of the materials, leading to a complicated interaction of the leachate with the solids, the mechanism behind this phenomenon remains unexplained and further investigation is required but excluded in present study. One potential reason may be the possible agglomerates of ductile metals in the pulverised samples (same to Fig. 1g) (Otsuki et al., 2019b). In addition, competition and re-equilibration amongst the various cyanide and glycinate species may causes delayed interchanges between the various metal complexes based upon differences in chemical thermodynamics and kinetics.

3.2.5. Effect of the method of cyanide addition

In the cyanidation of primary resources, it has been seen that cyanide is often added in different stages to control and enhance the process (Lotz et al., 2009). The staged addition is also expected
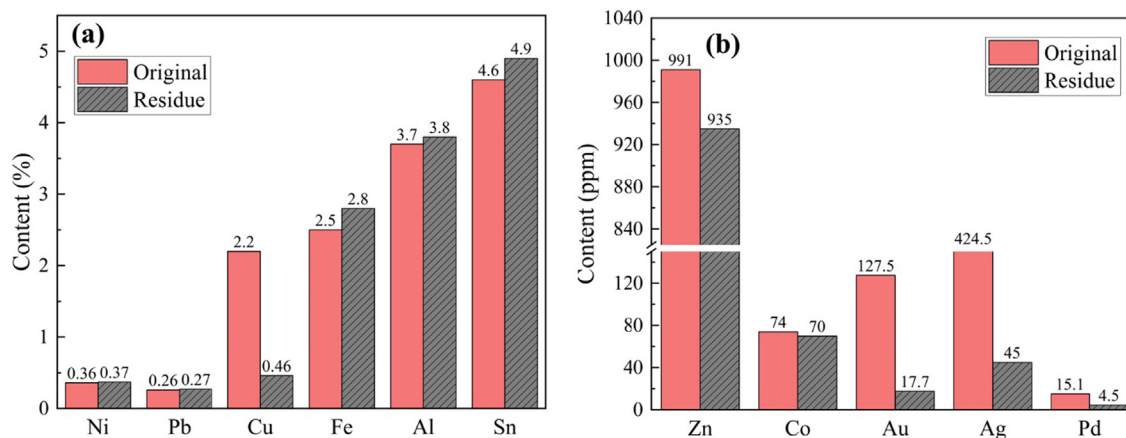
Fig. 4. Metal contents of pulverised PCBs before and after leaching under the recommended conditions.

Table 4
Extraction (%) of precious and base metals under the recommended conditions (4× glycine, 250 ppm cyanide all added in a single initial dose, initial pH 11, 96 h and pulverised sample).

	Precious metals			Base metals							
	Au	Ag	Pd	Cu	Zn	Pb	Al	Ni	Co	Fe	Sn
Extraction, %	90.1	89.4	70.1	81.0	15.0	1.9	8.3	2.9	BDL[a]	BDL	0.3

[a] BDL denotes below detection limit of 0.2 ppm.

to reduce the amount of free cyanide in real-time leaching solution that could reduce safety and health risks. Therefore, the comparison between a single initial cyanide addition and addition in different stages (Table S2) is made in this study. As shown in Fig. 1i-j, the staged addition slowed the rate of Au and Ag extraction in the first 48 h with no further enhancement of extraction. It is noticeable that there was no precipitation of Ag in the first 6 h with staged addition of cyanide (Fig. 1j). It appears that the relatively high level of cyanide caused Ag precipitation in the non-staged test where all cyanide was added in one initial dose. Conversely, the way of cyanide addition made no difference on Cu extraction (Figure S13). Since Cu preferably complexes with cyanide as cuprous forms, the presence of Cu^{2+} (as $Cu(Gly)_2$) theoretically indicates no free cyanide is generated in the leaching solution. As shown in Figure S14, cyanide all added as an initial dose made all the Cu present as Cu^+ in the first 2 h. Consequently, cyanide addition in a single initial dose is recommended.

3.2.6. Reaccommodated conditions and mass balance

Under the recommended conditions, the extractions of precious and other metals were calculated and are shown in Table 4. It is clear that precious metals of Au and Ag were extracted by cyanide-starved glycine solution, at a percentage very competitive to the two-stage intensive cyanidation (Fig. 3). The fairly high extraction of Pd (70.1%) can also contribute the economics of the process. Base metals, except Cu and Zn (15.0%), were only extracted at a low level of < 10%, which will facilitate the downstream recovery of precious metals and reduce the WAD cyanide amount in wastewater.

Given the heterogeneous nature of PCBs materials, calculations for mass balance were done to validate the extraction (%) of metals, with the results shown in Table S3-4. Slight deviations (<5%) were found between the extractions calculated from solution-residue (Table 4) and feed-residue. However, it should be noted that the main purpose of present study is not to provide a set of constant conditions as, in real industry, the composition of e-waste is always varying in different batches. Rather, the mechanism, feasibility, and the extent of the effect of different variables are more important information for future studies.

3.3. Analysis of leaching residue

3.3.1. Metal contents

Fig. 4 shows the metal contents of original pulverised PCBs and the leaching residue. It can be seen that the copper content decreased to 0.46% after leaching under recommended conditions (Section 3.2.6). By contrast, other base metals still remained at a high level of contents that need to be further removed before the utilization of non-metallic fraction (NMFs). It is obvious that the contents of precious metals in residue were still at high levels, including 17.7 ppm Au and 45 ppm silver (Fig. 4b). This portion of precious metals may be locked in alloys and plastics which needs to be verified by instrumental analysis, such as SEM-EDS.

3.3.2. SEM-EDS analysis

Figure S15-23 present the SEM-EDS analysis of the leaching residue obtained under the recommended conditions (4x glycine, 250 ppm cyanide all added in a single initial dose, initial pH 11, 96 h and pulverised sample). It can be seen that a number of un-leached metals is presented as alloys with or without partial oxidization, dominated by Sn, Fe and Al (Figure S16, 19, 21 and 23). This agrees well with Fig. 4 that show the major metals in residue are Sn, Al and Fe. Large pieces of metal were also identified as Sn, Al and Fe or their alloys after oxidation. A large number of small particles were found dispersed on the material surface which turned out to be Sn-containing phases. Ag was also identified most likely associated with Sn as an alloy (Figure S19). However, gold was not found due to its low content (17.7 ppm). It can be reasonably expected that a step of washing with dilute mineral acid can further remove these easily-accessible base metals, before leaching the rest of precious metals and before the production of non-metallic fraction for further re-purpose (Qiu et al., 2021).

4. Conclusions

The research focussed on the second step, after most of the base metals have been leached earlier by alkaline glycine leaching, which is aimed at removing precious metals and the remaining base metals from waste PCBs, while replacing most of the cyanide that would have been used in a cyanide-only leach with glycine and also mostly eliminating the production of weak acid dissociable cyanide effluent.

The study investigated the leach behaviour of various base (Cu, Zn, Pb, Fe, Al, Sn, Ni, Co) and precious (Au, Ag, Pd) metals, with emphasis on the dominant metals (Au, Ag and Cu). The role of glycine dose, cyanide concentration, initial pH, particle size and the way of cyanide addition were evaluated. The use of cyanide-starved glycine system achieved comparable or better performance on Au, Ag, Pd and/or Cu extractions than using either stoichiometric or intensive cyanidation, with the cyanide consumption being reduced by about 72% and 93%, respectively. It was found that cyanide concentration (100–350 ppm), glycine dose (2-8×, 1650–6600 ppm in solution), initial pH (10.5–12.5) and particle size played a major role during Au, Ag and Cu extraction, while the staged addition of cyanide did not affect the extractions noticeably except slowing initial kinetics for Au and Ag. Under the optimised conditions (4 × stoichiometric amount of glycine, 250 ppm cyanide added all at initial, initial pH 11, pulverised feed), the extractions of precious metals reached 90.1% for Au, 89.4% for Ag and 70.1% for Pd, with 81.0% Cu co-extracted at only room temperature and ambient environment for 96 h. Other base metals returned a low extraction of < 10%, except 15% for Zn, which demonstrates the selectivity of the system to precious metals and Cu. At the optimised cyanide concentration (250 ppm), the theoretical and experimental analyses indicate that the cyanide amount was starved and zero free cyanide should be generated under the conditions after 4 h, which minimises safety and health risks significantly compared with traditional cyanidation, implying a potential of application in urban or rural areas. SEM-EDS analysis shows dominant Sn, Fe and Al in the leach residue that could be further removed by a step of acid washing, to generate NMF (with minimal metal levels) for further application. This study is expected to provide guidance for using cyanide-starved glycine solutions to extract precious metals from e-waste.

CRediT authorship contribution statement

Huan Li: Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing - original draft. **Elsayed Oraby:** Conceptualization, Formal analysis, Methodology, Validation, Writing - review & editing. **Jacques Eksteen:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2021.02.033.

References

Adams, M.D., 2016a. Gold ore processing: project development and operations. Elsevier, 447–484.

Adams, M.D., 2016b. Comparison of the MMS CN-DTM Cyanide destruction process with Caro's Acid, SMBS/Air and hydrogen peroxide options. ALTA 2016 Conference. 7, p.

Akcil, A. et al., 2015. Precious metal recovery from waste printed circuit boards using cyanide and non-cyanide lixiviants–a review. Waste Manage. 45, 258–271.

Bisceglie, F., Civati, D., Bonati, B., Faraci, F.D., 2017. Reduction of potassium cyanide usage in a consolidated industrial process for gold recovery from wastes and scraps. J. Clean. Prod. 142, 1810–1818.

D'Adamo, I. et al., 2019. Towards sustainable recycling processes: Wasted printed circuit boards as a source of economic opportunities. Resour. Conserv. Recy. 149, 455–467.

Dean, J.A., 1999. Lange's handbook of chemistry. McGraw-Hill Inc..

Deng, Z., Oraby, E.A., Eksteen, J.J., 2019a. The sulfide precipitation behaviour of Cu and Au from their aqueous alkaline glycinate and cyanide complexes. Sep. Purif. Technol. 218, 181–190.

Deng, Z., Oraby, E.A., Eksteen, J.J., 2019b. Sulfide precipitation of copper from alkaline glycine-cyanide solutions: precipitate characterisation. Miner. Eng. 145, 106102.

Deng, Z., Oraby, E.A., Eksteen, J.J., 2020a. Cu adsorption behaviours onto chelating resins from glycine-cyanide solutions: Isotherms, kinetics and regeneration studies. Sep. Purif. Technol. 236, 116280.

Deng, Z., Oraby, E.A., Eksteen, J.J., 2020b. Gold recovery from cyanide-starved glycine solutions in the presence of Cu using a molecularly imprinted resin (IXOS-AuC). Hydrometallurgy 196, 105425.

Diaz, L.A., Lister, T.E., Parkman, J.A., Clark, G.G., 2016. Comprehensive process for the recovery of value and critical materials from electronic waste. J. Clean. Prod. 125, 236–244.

Eksteen, J.J., Oraby, E.A., 2015. The leaching and adsorption of gold using low concentration amino acids and hydrogen peroxide: Effect of catalytic ions, sulphide minerals and amino acid type. Miner. Eng. 70, 36–42.

Eksteen, J.J., Oraby, E.A., Tanda, B.C., Tauetsile, P.J., Bezuidenhout, G.A., Newton T. Trask, F., Bryan, I., 2018. Towards Industrial Implementation of Glycine-Based Leach and Adsorption Technologies for Gold-Copper Ores. Can. Metall. Q., 57(4), 390-398

Forti, V., Baldé, C.P., Kuehr, R. and Bel, G., 2020. The global e-waste monitor - 2020. United Nations University (UNU), International Telecommunication Union (ITU) & International Solid Waste Association (ISWA). Available at https://www.itu.int/en/ITU-D/Environment/Documents/Toolbox/GEM_2020_def.pdf (accessed on 01/07/2020)

Hotea, V., 2013. Clean technology of lead recovery from spent lead paste, WSEAS Conference program, Chania, Crete Island, Greece, pp. 263-269.

Islam, M.T., Huda, N., 2020. Assessing the recycling potential of "unregulated" e-waste in Australia. Resour. Conserv. Recy. 152, 104526.

Kaya, M., 2016. Recovery of metals and nonmetals from electronic waste by physical and chemical recycling processes. Waste Manage. 57, 64–90.

Kiddee, P., Naidu, R., Wong, M.H., 2013. Electronic waste management approaches: An overview. Waste Manage. 33 (5), 1237–1250.

Kiss, T., Sovago, I., Gergely, A., 1991. Critical survey of stability constants of complexes of glycine. Pure and applied chemistry 63 (4), 597–638.

Koyanaka, S., Endoh, S., Ohya, H., 2006. Effect of impact velocity control on selective grinding of waste printed circuit boards. Advanced Powder Technology 17 (1), 113–126.

Kyle, J., 1997. Stability of metal-cyanide and hydroxide complexes, World Gold'97. Singapore, 163–169.

Lee, D., Offenhuber, D., Duarte, F., Biderman, A., Ratti, C., 2018. Monitour: Tracking global routes of electronic waste. Waste Manage. 72, 362–370.

Li, H., Eksteen, J., Oraby, E., 2018. Hydrometallurgical recovery of metals from waste printed circuit boards (WPCBs): Current status and perspectives – A review. Resour. Conserv. Recy. 139, 122–139.

Li, H., Oraby, E., Eksteen, J., 2020. Extraction of copper and the co-leaching behaviour of other metals from waste printed circuit boards using alkaline glycine solutions. Resour. Conserv. Recy. 154, 104624.

Li, H., Oraby, E., Eksteen, J., 2021. Recovery of copper and the deportment of other base metals from alkaline glycine leachates derived from waste printed circuit boards (WPCBs). Hydrometallurgy 199: 105540, 9 p.

Liu, K., Zhang, Z., Zhang, F.-S., 2016. Direct extraction of palladium and silver from waste printed circuit boards powder by supercritical fluids oxidation-extraction process. J. Hazard. Mater. 318, 216–223.

Lotz, P., Janse van Rensburg, S., Swarts, A., 2009. Kinetic gold leach monitoring including cyanide speciation. J. South. Afr. Inst. Min. Metall. 109 (10), 635–639.

Mudder, T.I., Botz, M.M., 2004. Cyanide and society: a critical review. ejmp & ep (European Journal of Mineral Processing and Environmental Protection) 4 (1), 62–74.

O'Connor, G.M., Lepkova, K., Eksteen, J.J., Oraby, E.A., 2018. Electrochemical behaviour of copper in alkaline glycine solutions. Hydrometallurgy 181, 221–229.

Oraby, E.A., Eksteen, J.J., 2014. The selective leaching of copper from a gold–copper concentrate in glycine solutions. Hydrometallurgy 150, 14–19.

Oraby, E.A., Eksteen, J.J., 2015a. Gold leaching in cyanide-starved copper solutions in the presence of glycine. Hydrometallurgy 156, 81–88.

Oraby, E.A., Eksteen, J.J., 2015b. The leaching of gold, silver and their alloys in alkaline glycine–peroxide solutions and their adsorption on carbon. Hydrometallurgy 152, 199–203.

Oraby, E.A., Eksteen, J.J., Tanda, B.C., 2017. Gold and copper leaching from gold-copper ores and concentrates using a synergistic lixiviant mixture of glycine and cyanide. Hydrometallurgy 169, 339–345.

Oraby, E.A., Li, H., Eksteen, J.J., 2019. An alkaline glycine-based leach process of base and precious metals from powdered waste printed circuit boards. Waste Biomass Valori. 11 (8), 3897–3909.

Otsuki, A., Gonçalves, P.P., Stieghorst, C., Révay, Z., 2019a. Non-destructive characterization of mechanically processed waste printed circuit boards: X-ray fluorescence spectroscopy and prompt gamma activation analysis. Journal of Composites Science 3 (2), 54.

Otsuki, A., Pereira Gonçalves, P., Leroy, E., 2019b. Selective milling and elemental assay of printed circuit board particles for their recycling purpose. Metals 9 (8), 899.

Otsuki, A. et al., 2020. Non-destructive characterization of mechanically processed waste printed circuit boards - particle liberation analysis. Waste Manage. 102, 510–519.

Qiu, R., Lin, M., Qin, B., Xu, Z., Ruan, J., 2021. Environmental-friendly recovery of non-metallic resources from waste printed circuit boards: A review. J. Clean. Prod. 279, 123738.

Qiu, R. et al., 2020. Recovering full metallic resources from waste printed circuit boards: A refined review. J. Clean. Prod. 244, 118690.

Pereira Gonçalves, P., Otsuki, A., 2019. Determination of Liberation Degree of Mechanically Processed Waste Printed Circuit Boards by Using the Digital Microscope and SEM-EDS Analysis. Electronics 8 (10), 1202.

Rees, K.L., Van Deventer, J.S.J., 1999. The role of metal-cyanide species in leaching gold from a copper concentrate. Miner. Eng. 12 (8), 877–892.

Schoeman, E., Bradshaw, S.M., Akdogan, G., Snyders, C.A., Eksteen, J.J., 2017. The extraction of platinum and palladium from a synthetic cyanide heap leach solution with strong base anion exchange resins. Int. J. Miner. Process. 162, 27–35.

Tan, Q., Li, J., Boljkovac, C., 2018. Responding to China's Waste Import Ban through a New, Innovative, Cooperative Mechanism. Environ. Sci. Technol. 52, 7595–7597.

Tanda, B.C., Eksteen, J.J., Oraby, E.A., 2017a. An investigation into the leaching behaviour of copper oxide minerals in aqueous alkaline glycine solutions. Hydrometallurgy 167, 153–162.

Tanda, B.C., Oraby, E.A., Eksteen, J.J., 2017b. Recovery of copper from alkaline glycine leach solution using solvent extraction. Sep. Purif. Technol. 187, 389–396.

Tauetsile, P.J., Oraby, E.A., Eksteen, J.J., 2018a. Adsorption Behaviour of Copper and Gold Glycinates in Alkaline Media onto Activated Carbon. Part 1: Isotherms. Hydrometallurgy 178, 202–208.

Tauetsile, P.J., Oraby, E.A., Eksteen, J.J., 2018b. Adsorption behaviour of Copper and Gold Glycinates in Alkaline Media onto Activated Carbon. Part 2: Kinetics. Hydrometallurgy 178, 195–201.

Tauetsile, P.J., Oraby, E.A., Eksteen, J.J., 2019a. Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper. Part 1: Isotherms. Sep. Purif. Technol. 211, 594–601.

Tauetsile, P.J., Oraby, E.A., Eksteen, J.J., 2019b. Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper. Part 2: Kinetics. Sep. Purif. Technol. 211, 290–297.

Theodor, V., Klaus, W., Brent, H., Gerd, B., 2006. Liquid-Solid Extraction, Ullmann's Encyclopedia of Industrial. Chemistry. https://doi.org/10.1002/14356007. b03_07.pub2.

Wang, X., Forssberg, K.S.E., 1990. The Chemistry of Cyanide-Metal Complexes in Relation to Hydrometallurgical Processes of Precious Metals. Miner. Process. Extr. Metall. Rev. 6 (1–4), 81–125.

Zeng, X., Ali, S.H., Tian, J., Li, J., 2020. Mapping anthropogenic mineral generation in China and its implications for a circular economy. Nat. Commun. 11 (1), 1–9.

Zhou, Y., Wu, W., Qiu, K., 2011. Recycling of organic materials and solder from waste printed circuit boards by vacuum pyrolysis-centrifugation coupling technology. Waste Manage. 31 (12), 2569–2576.

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Supporting Information (SI)

Cyanide consumption minimisation and concomitant toxic effluent minimisation during precious metals extraction from waste printed circuit boards

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The contents provided in this attachment is supporting information and covers:

1. Flowsheet for the management of waste PCBs
2. E_h-pH diagrams
3. pH progression of leachate
4. Coordination numbers considered between metals and glycine or cyanide.
5. Effect of variables on the extraction of other metals
6. Additional information for cyanide staged addition and all added at initial
7. Mass balance of metals in pulverised sample before and after leaching
8. SEM-EDS analysis of leaching residue

23 figures and 4 tables

1. A conceptual flowsheet for the management of waste PCBs (WPCBs)
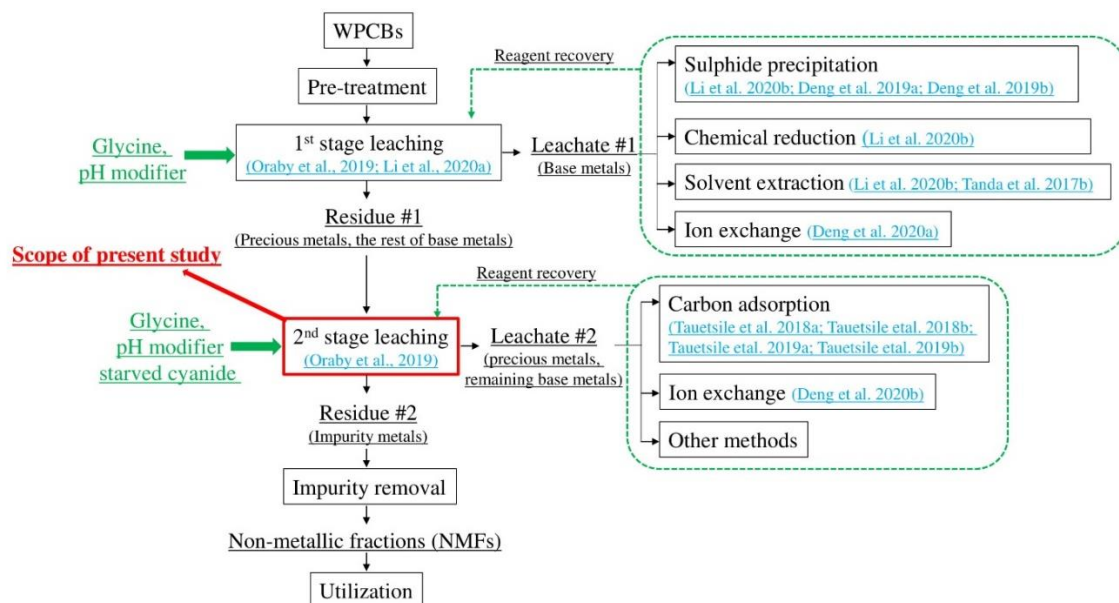
Figure S1. A conceptual flowsheet for the management of waste printed circuit boards with the scope of present study highlighted in red (previous arts are highlighted in blue and the references are listed in manuscript context).

2. Eh-pH diagrams of copper, gold and silver in glycine-cyanide solution
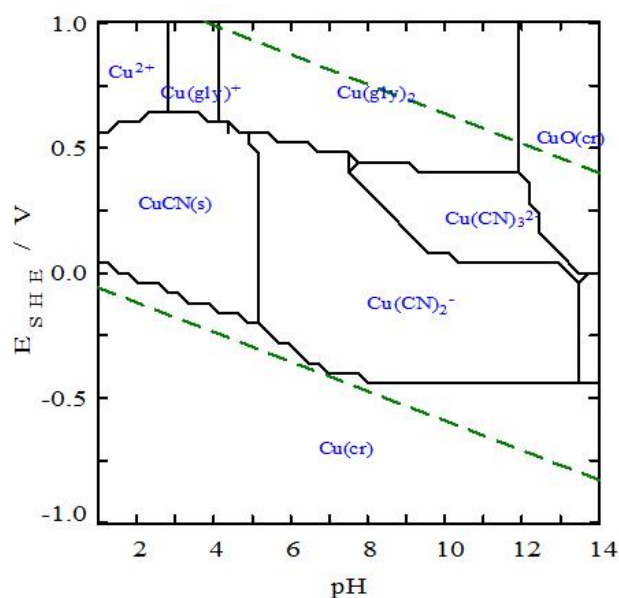
Figure S2. Eh-pH diagram of copper-glycine-cyanide-H_2O system at 2 mM Cu, 5 mM cyanide, 50 mM glycine and 25°C (made by Medusa-Hydra software, https://www.kth.se/che/medusa, same below)
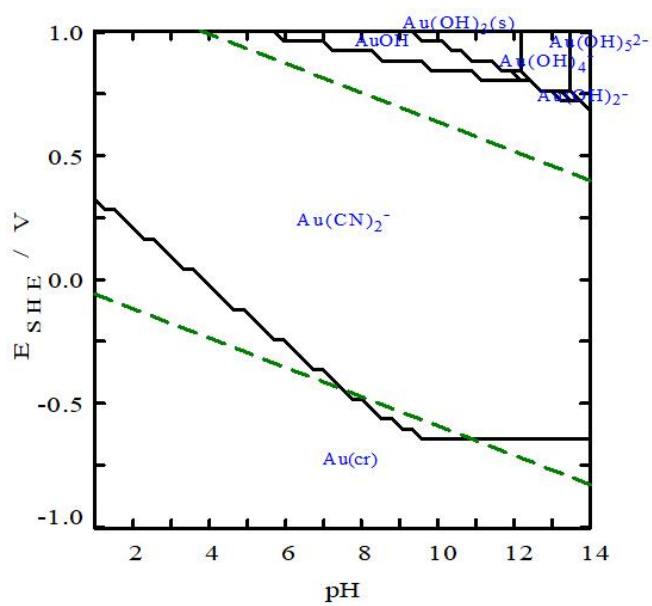
Figure S3. E_h-pH diagram of gold-cyanide-H_2O system at 0.01 mM Au, 5 mM cyanide and 25°C.
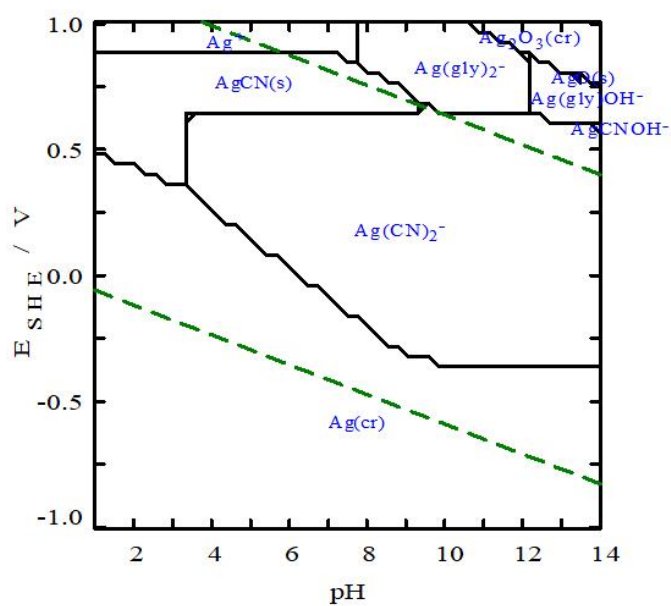
Figure S4. E_h-pH diagram of silver-glycine-cyanide-H_2O system at 0.08 mM Ag, 5 mM cyanide, 50 mM glycine and 25°C.

3. pH progression of leachate

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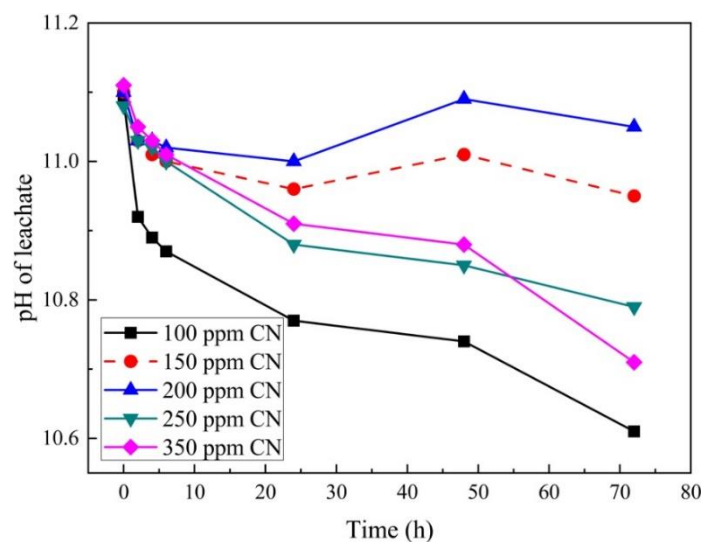
Figure S5. pH progression of the leachate as a function of time at different CN concentration (gly amount = 4x, initial pH = 11±0.1, particle size ≤2 mm)
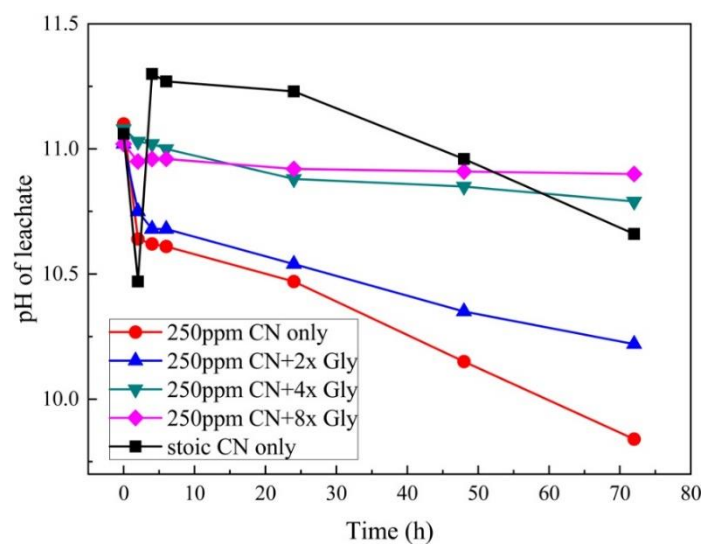
Figure S6. pH progression of the leachate as a function of time at different glycine amount (initial pH = 11±0.1, particle size ≤2 mm, pH for stoic CN only at 2 h was manually adjusted to 11.47 after sampling)
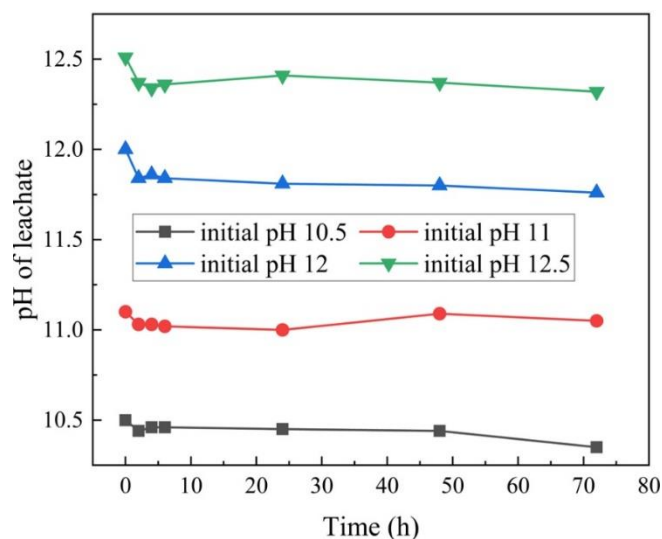
Figure S7. pH progression of the leachate as a function of time at different initial pH (gly amount = 4x, CN concentration = 200 mg/L, particle size ≤2 mm)
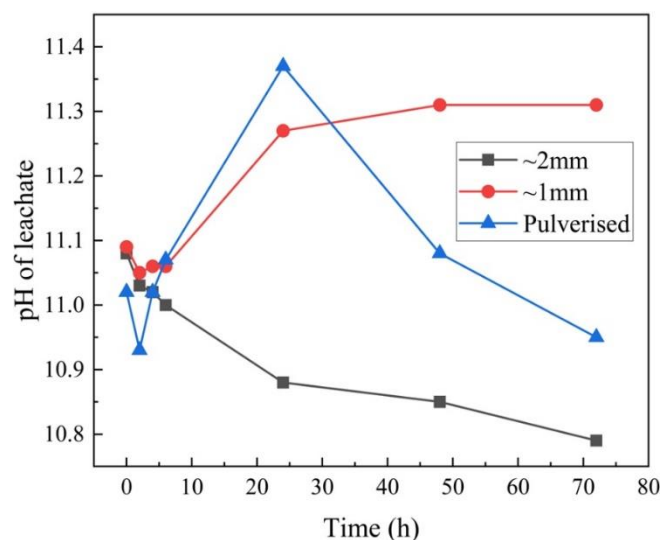
Figure S8. pH progression of the leachate as a function of time at different particle size (gly amount = 4x, CN concentration = 250 mg/L, initial pH 11±0.1, pH for pulverised samples at 2 h was manually adjusted to 11.0 after sampling)

4. Coordination numbers considered between metals and glycine or cyanide.

Table S1. Coordination number considered to determine the stoichiometric amounts of glycine and cyanide used in this study.

Metal		Cu	Au	Ag	Pd	Ni	Co	Pb	Zn
Coordination number	Glycine/Gly⁻	2	2	2	2	3	3	2	3
considered	Cyanide/CN⁻	4	2	3	4	2	2	2	2

5. Effect of variables on the extraction of other metals
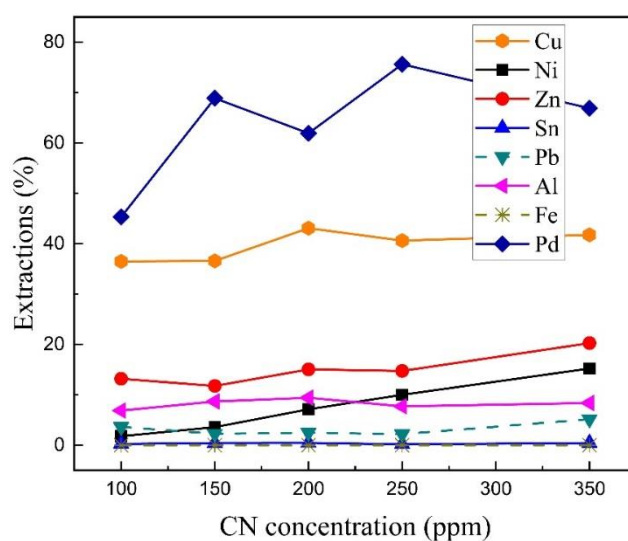
Figure S9. Effect of cyanide concentration on the extraction of other mortals (gly amount = 4×, initial pH = 11±0.1, particle size ≤2 mm)
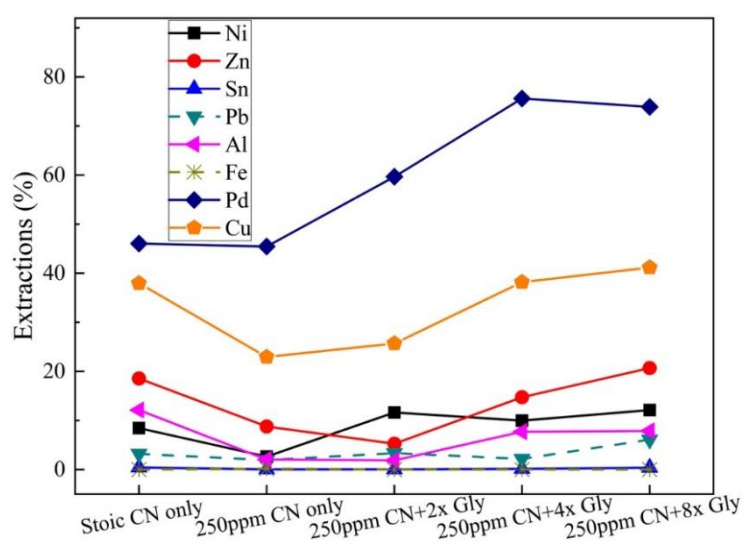
Figure S10. Effect of glycine addition on the extraction of other mortals (initial pH = 11±0.1, particle size ≤2 mm)
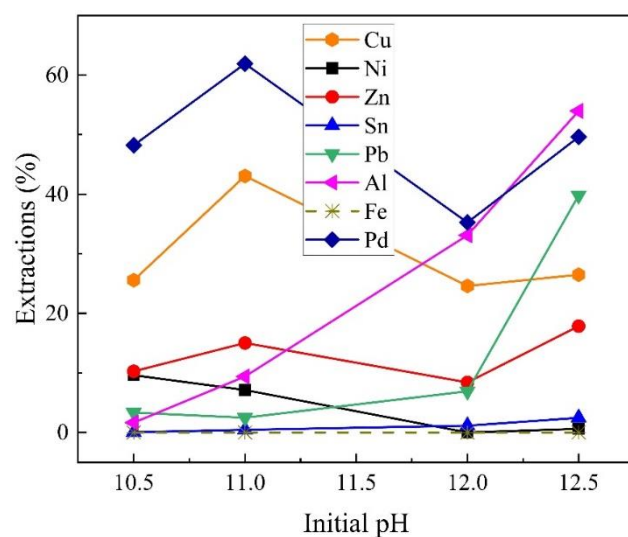
Figure S11. Effect of initial pH on the extraction of other mortals (gly amount = 4x, CN concentration = 200 mg/L, particle size ≤2 mm)
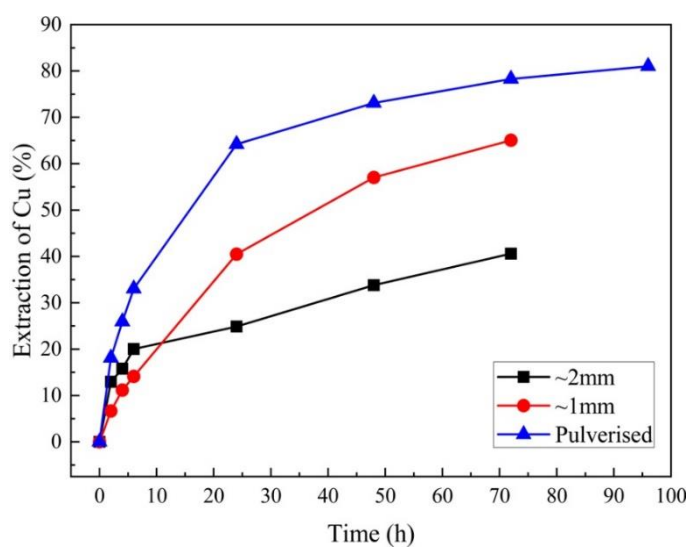
Figure S12. Effect of particle size on Cu extraction (gly amount = 4x, CN concentration = 250 mg/L, initial pH = 11±0.1)
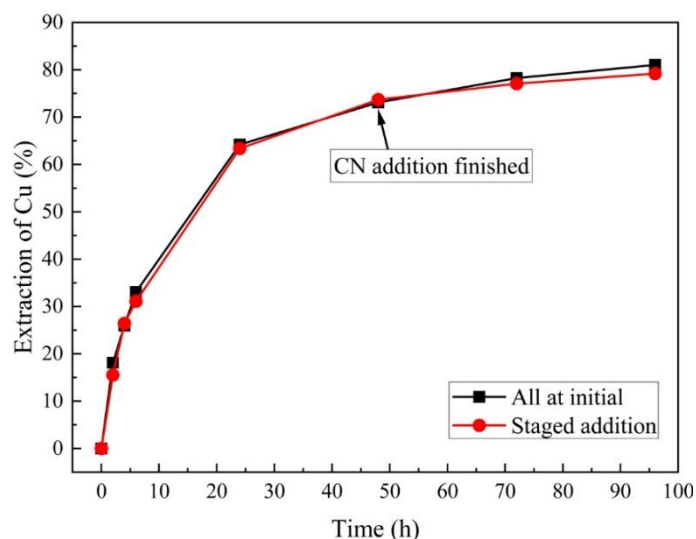
Figure S13. Effect of the way of CN addition on Cu extraction (gly amount = 4x, CN concentration = 250 mg/L, initial pH = 11±0.1, pulverised samples)

6. Additional information for cyanide staged addition and all added at initial

Table S2. Proportion of cyanide added during staged addition test (gly amount = 4x, CN concentration = 250 mg/L, initial pH = 11±0.1, pulverised samples)

Time, h	0	1	2	3	4	5	6	24	48	72	96
Proportion of cyanide added, %	15	5	5	5	5	5	20	25	15	0	0
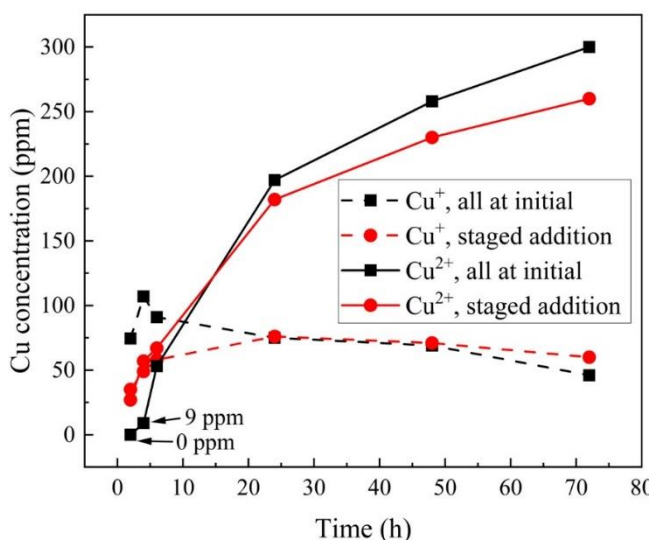
Figure S14. Cu concentration as a function of time with different way of cyanide addition (gly amount = 4x, CN concentration = 250 mg/L, initial pH = 11±0.1, pulverised samples).

7. Mass balance of metals in pulverised sample before and after leaching

Table S3–4 show the mass balance of metals in the pulverised samples before (original) and after leaching. For the test, 13.9005 g pulverised sample was used for leaching and 12.6149 g residue was collected, which indicates a mass reduction of 9.25%.

Table S3. Mass balance of metals, with content in %, in pulverised materials before and after leaching.

	Content, %		Extraction on solution-residue [a]	Extraction on feed-residue [b]	Deviation of extraction [c]
	Original	Residue	%	%	%
Ni	0.36	0.37	2.9	6.73	3.8
Pb	0.26	0.27	1.9	5.76	3.9
Cu	2.2	0.46	81.0	81.02	0.02
Fe	2.5	2.8	BDL [d]	-	-
Al	3.7	3.8	8.3	6.80	1.5
Sn	4.6	4.9	0.3	3.33	3.0

[a] denotes the extraction calculated based on metal mass in solution sample and leaching residue; [b] denotes the extraction calculated based on metal mass in feed sample and leaching residue; [c] denotes the difference between "[a]" and "[b]"; [d] BDL denotes below detection limit of 0.2 mg/L.

Table S4. Mass balance of metals, with content in ppm, in pulverised materials before and after leaching.

	Content, ppm		Extraction on solution-residue [a]	Extraction on feed-residue [b]	Deviation of extraction [c]
	Original	Residue	%	%	%
Zn	991	935	15.0	14.38	0.6
Co	74	70	BDL [a]	-	-
Au	127.5	17.7	90.1	87.40	2.7
Ag	424.5	45	89.4	90.38	1.0
Pd	15.1	4.5	70.1	72.95	2.9

[a] denotes the extraction calculated based on metal mass in solution sample and leaching residue; [b] denotes the extraction calculated based on metal mass in feed sample and leaching residue; [c] denotes the difference between ""[a]" and "[b]"; [d] BDL denotes below detection limit of 0.2 mg/L.

8. SEM-EDS analysis of leaching residue

To make sure the SEM-EDS analysis is representative, the leaching residue obtained from the optimised experiment was sorted by eyes into different categories: (1) fine particles, (2) silver-colour particles, and (3) other paticles, inluding white, red, green and black particles, etc. The three categories of particle were then coated by carbon and tested by SEM-EDS, and below figures show the typical imiges and compositions of the tests.
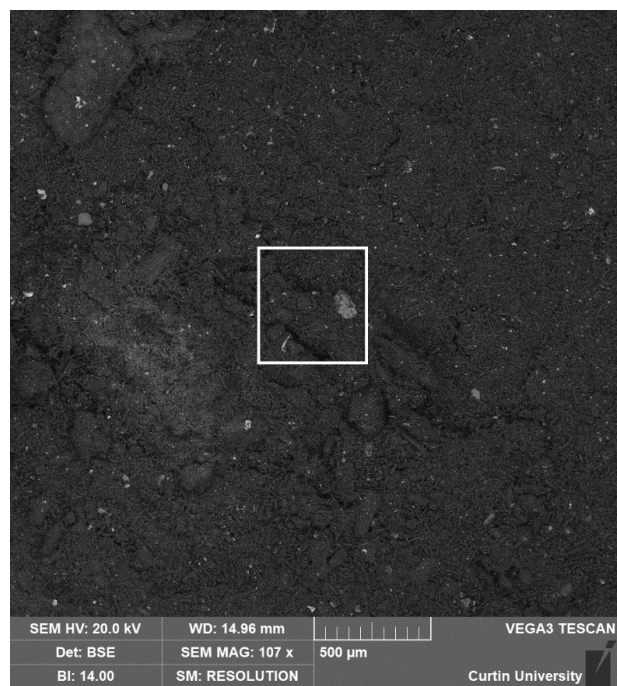
Figure S15. SEM image of fine particles
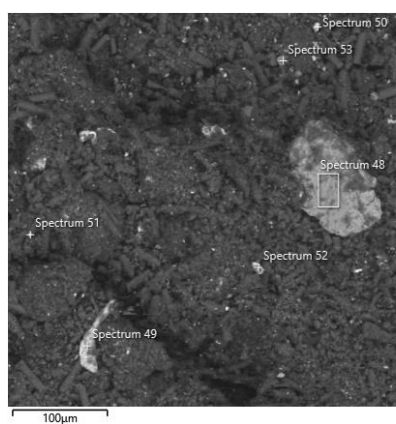
Spem. 48: Fe-Al-Si-O
Spem. 49: Sn-Ni-Cu-Al-O
Spem. 50: Sn-Ca-Br-Si-O
Spem. 51: Sn-Br-Si-O
Spem. 52: Sn-Br-O
Spem. 53: Fe-Mn-Zn-Br-Si-O

Figure S16. SEM-EDS analysis of the marked rectangle in Figure S8
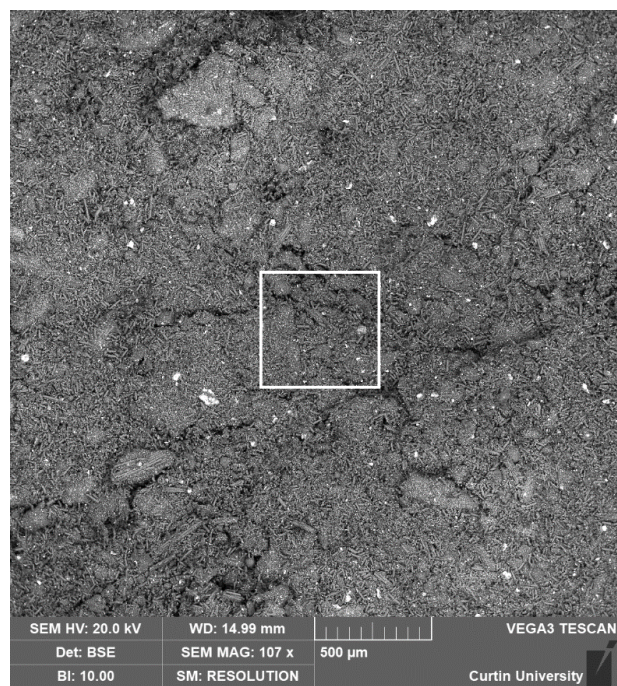
Figure S17. SEM image of fine particles

Spem. 55: Ba-Ti-Ca-Si-O

Spem. 56: Sn-Br-O

Spem. 57: Ni-O

Spem. 58: Sn-Ca-Ba-Ag-Br-Si-O

Spem. 59: Sn-Br-Si-O

Spem. 60: Ca-Br-Si-O
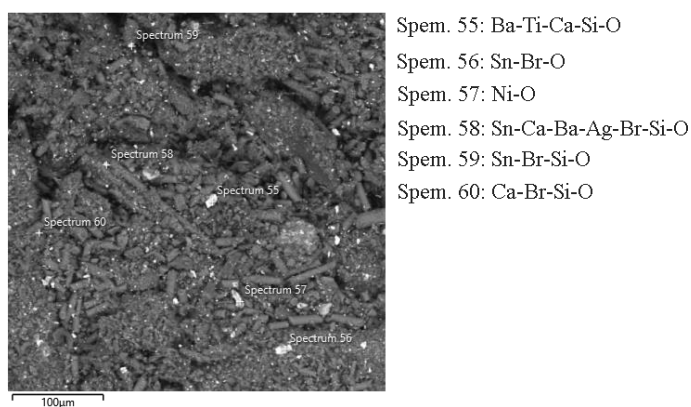
Figure S18. SEM-EDS analysis of the marked rectangle in Figure S10

Spem. 61: Sn-Ag-O

Spem. 62: Sn-Al-Ag-O

Spem. 63: Sn-Ca-Al-Si-O

Spem. 64: Sn-Ca-Al-Si-O

Spem. 65: Sn-Ca-Al-Si-O
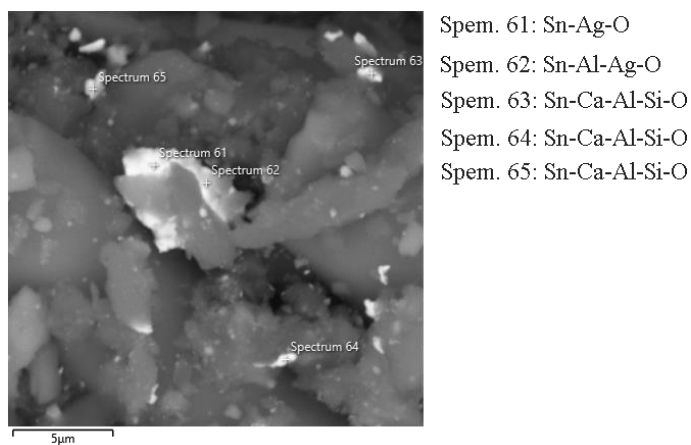
Figure S19. SEM-EDS analysis of Spem. 58 in Figure S10
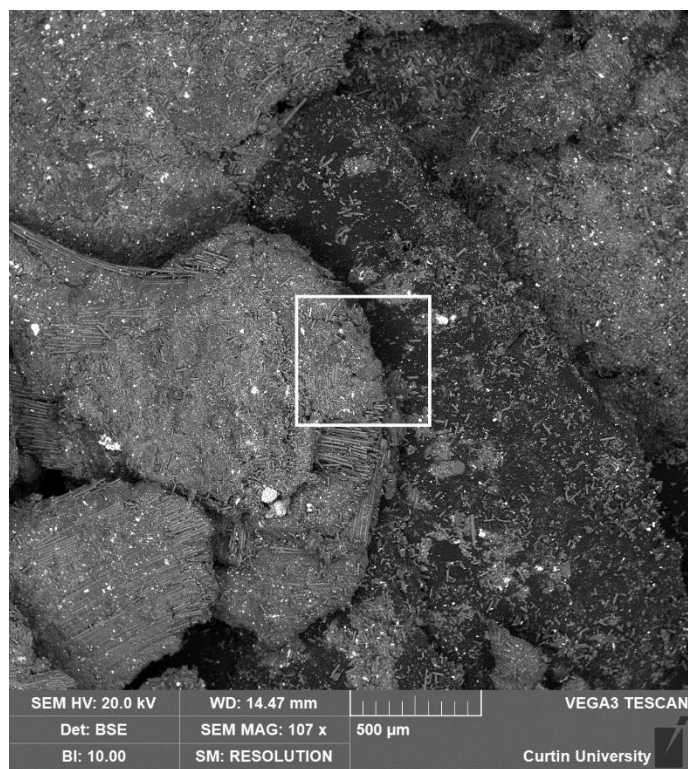
Figure S20. SEM image of the other particles

Spem. 66: Sn-O
Spem. 67: Sn-O
Spem. 68: Fe-Cr-Ni-O
Spem. 69: Sn-O
Spem. 70: Sn-Al-Si-O
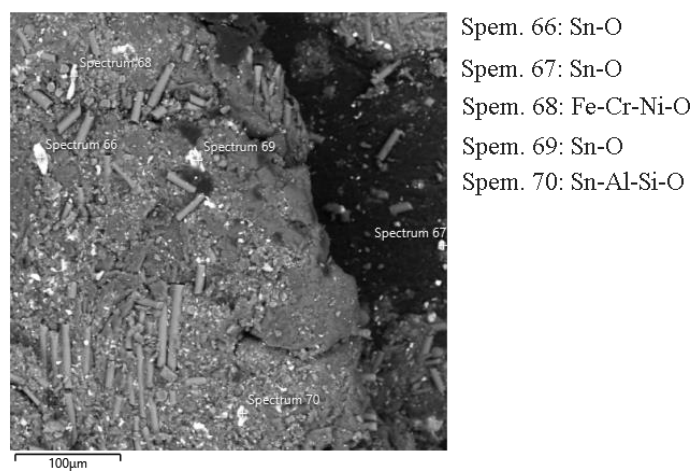
Figure S21. SEM-EDS analysis of the marked rectangle in Figure S13
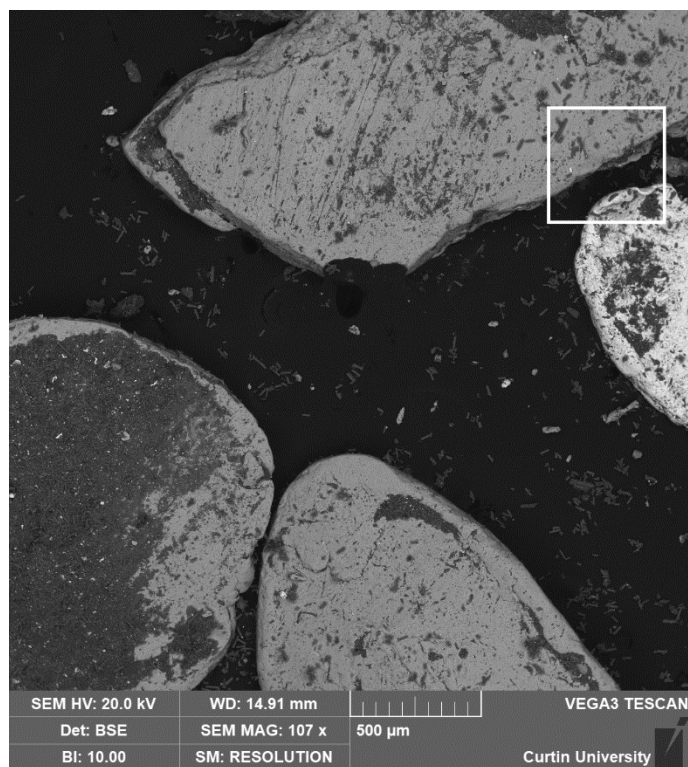
Figure S22. SEM image of silver-colour particles

Spem. 71: Sn-Al-O
Spem. 72: Fe-O
Spem. 73: Pb-Sn-Al-Fe-O
Spem. 74: Fe-Sn-O
Spem. 75: Fe-Sn--O
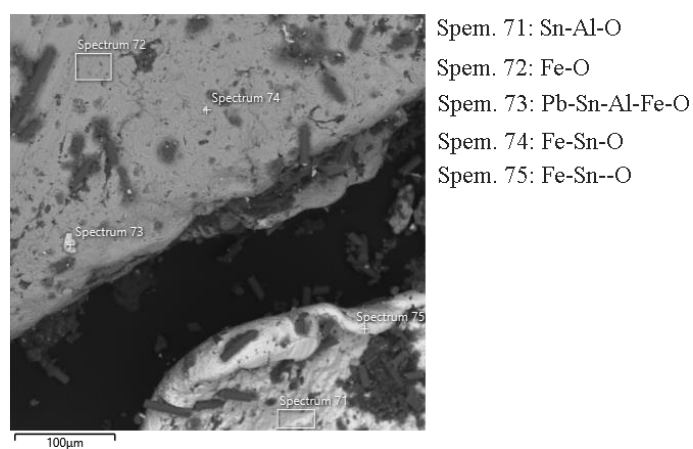
Figure S23. SEM-EDS analysis of the marked rectangle in Figure S15
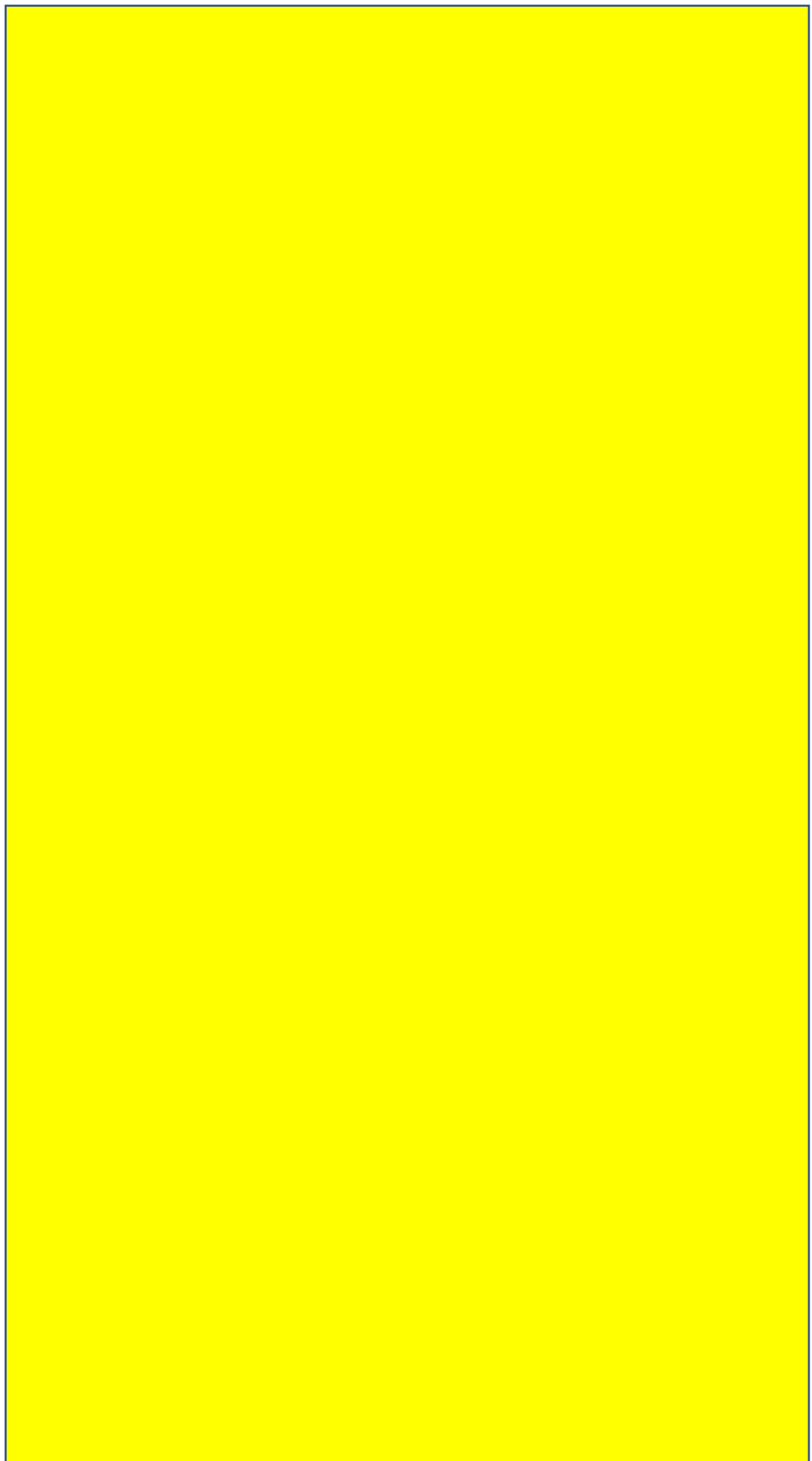
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Chapter 7 Leaching of precious metals using non-cyanide glycine leaching system: A preliminary study on gold

7.1 Introduction

As presented in Chapter 6, the cyanide-starved glycine leaching system has shown promising leachability of precious metals (>90% Au, >85% Ag and >70% Pd). The cyanide use was reduced to a minimal level (250 mg/L), and no free cyanide was present in the leaching solution after four hours, which significantly reduced the safety risks. However, the industrial use of sodium cyanide (NaCN) in many countries and regions, especially near urban communities, is strictly prohibited, such as Germany, the Czech Republic, Greece and Montana of USA (Laitos, 2013). This makes the application of the cyanide-starved glycine leaching system inappropriate. In efforts to achieve a safer and more environmentally benign process, a non-NaCN leaching system is always of interest to academia and industry.

It has been shown that glycine ligand (as the anionic glycinate ion or $NH_2CH_2COO^-$, or Gly^-) can complex with precious metal ions, such as Au (I) and Ag (I) (Table 3 of Chapter 6). However, since the metals exist in WPCBs as native forms, they will need to be oxidised for the complexation. Due to their highly unreactive nature, additional oxidant, except ambient oxygen, may be required to provide a stable and consistent oxidising environment and to achieve practical leach kinetics. An example is that, as shown in Section 3.1 of Chapter 4, glycine solution was used to leach WPCBs, with oxygen coming from ambient air, while only 1.8% Au extraction was recorded in 72 h.

Recently, Oraby et al. (2020b) have used glycine solution in the presence of potassium permanganate to extract precious metals from natural resources. They have shown that 85.1% Au could be removed from Au oxide ore using 1.5 kg/t glycine and 3 kg/t potassium permanganate at 30% solids, pH of 10.5 and room temperature. This study suggests the potential of using a non-NaCN glycine leaching system with an environmentally benign strong oxidant to dissolve precious metals from WPCBs, which may be an alternative to NaCN-based systems.

Another oxidant, ferricyanide ($[Fe(III)(CN)_6]^{3-}$), may also be feasible for use in the extraction of precious metals from WPCBs. Studies have already shown the effectiveness of using ferricyanide as an additional oxidant during traditional cyanidation or thiosulfate leaching of natural resources (Putnam, 1950; Xie et al., 2008; Xie and Dreisinger, 2007; Zi et al., 2012). Ferricyanide, common as potassium salt, is a strong metal-cyanide complex with a cumulative formation constant as high as 42.3 (Dean, 1999). Its half-lives vary from 1 year (reducing environment) to 1000 years (oxidising environment) at pH 4, indicating

that a strongly acidic environment is required for disassociation and release of free cyanide (Chen et al., 2019). It is, hence, commonly considered non-hazardous with an oral rats-LD_{50} value of about 2970 mg/kg, which is close to that of sodium chloride (about 3000 mg/kg). Ferricyanide also has a high solubility in water (464 g/L for potassium ferricyanide vs 8.2 mg/L for ambient oxygen) (Dean, 1999). Therefore, using a glycine-ferricyanide leaching system can be a potential environmentally benign approach for precious metals extraction from WPCBs. However, unlike natural resources, WPCBs have various metals contained, intrinsic structure (laminations and coatings) and complex materials of manufacture, which will inevitably make the leaching complicated.

Therefore, this chapter aims to investigate the use of glycine-oxidant leaching systems to extract precious metals from WPCBs. Same as Chapter 6, the feed samples used in this chapter are the residue of the glycine-only leaching of WPCBs, referred to as first-stage leaching, with most of the base metals pre-leached out by glycine-only solutions (Section 2.1 of Chapter 6). It should hence be noted that the study of this chapter is ideally positioned as a second stage of leaching for precious metals (Figure 1.1 of Chapter 1). Two environmentally benign oxidants, i.e. potassium permanganate and potassium ferricyanide, are focused and compared. Experimentally controlled parameters affecting the leaching of Au are investigated. It is hoped that this chapter can provide a preliminary investigation of a greener approach for the extraction of precious metals that eliminates the use of NaCN.

7.2 Possible reactions during Au leaching

Gold represents the major economic value of WPCBs (Table 2 of Chapter 4). To understand the leaching behaviour of Au in WPCBs, it is necessary to summarise and analyse the chemical reactions between oxidant and various species in the leaching system. First of all, due to the strong oxidising environment, glycine may be oxidised and decomposed into different products. Second, the glycinate ligand ($NH_2CH_2COO^-$, Gly^-) can complex with Au in the presence of ambient oxygen (but at a slow rate) and additional oxidant (permanganate or ferricyanide). This explains the dissolution of Au in the leaching system. Third, the decomposition products of glycine may also react with metals in WPCBs, which remains complex and unclear.

Additionally, other metals, mainly Cu, may also act as an additional oxidant when they are complexed with glycine (e.g. $Cu(Gly)_2$) or, possibly, with glycine's decomposition products (e.g. cupric ammonia). In this section, only the major reactions during Au leaching are presented. Due to the complexity of the system, the side reactions between metals and glycine's decomposition products are excluded in the scope of this chapter.

7.2.1 Glycine-permanganate leaching system

Several early studies have claimed that glycine can be oxidised by permanganate in an acidic or slightly alkaline environment, with the products being formaldehyde (HCHO), ammonia and carbon dioxide (Eq. 7.1) (Insausti et al., 1996; Perez-Benito et al., 1987). The generation of MnO_2 in Eq. 7.1 is backed by the brown precipitates observed during experiments. However, with excess permanganate, HCHO may be oxidised to formic acid (HCOOH) or further to carbon dioxide (CO_2), especially in the presence of a catalyst of noble metals (Au, Ag, Pd etc.) and manganese dioxide (MnO_2) (Eq. 7.2–4) (Issa and Issa, 1954; Yusuf et al., 2017). This agrees with Yusuf et al. (2017) and Zhang et al. (2012), who mentioned the general sequence of catalytic HCHO oxidation is $HCHO \rightarrow HCOO^- \rightarrow CO_2$.

$$2MnO_4^- + 3NH_2CH_2COO^- + 4H_2O \rightarrow 2MnO_2 \text{ (s)} + 3HCHO + 3NH_3 \text{ (aq)} + 3CO_2 \text{ (g)} + 5OH^-, \Delta G^o \text{ (25}^o\text{C)} = \text{-534.5 kJ/mol} \tag{7.1}$$

$$3HCHO + 2MnO_4^- + OH^- \rightarrow 2MnO_2 \text{ (s)} + 3HCOO^- + 2H_2O, \Delta G^o \text{ (25}^o\text{C)} = \text{- 1092.8 kJ/mol} \tag{7.2}$$

$$3HCOO^- + 2MnO_4^- + H_2O \rightarrow 3CO_2 \text{ (g)} + 2MnO_2 \text{ (s)} + 5OH^-, \quad \Delta G^o \text{ (25}^o\text{C)} = \text{- 729.0 kJ/mol} \tag{7.3}$$

$$HCOO^- + 2MnO_4^- + OH^- \rightarrow CO_2 \text{ (g)} + 2MnO_4^{2-} + H_2O, \Delta G^o \text{ (25}^o\text{C)} = \text{-250.3 kJ/mol} \tag{7.4}$$
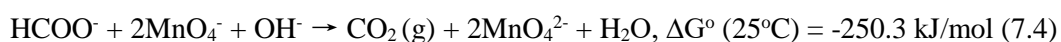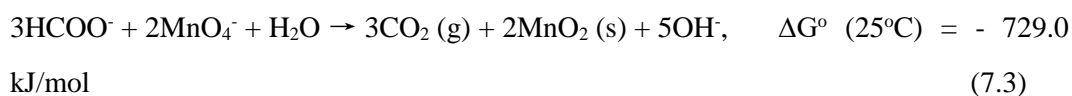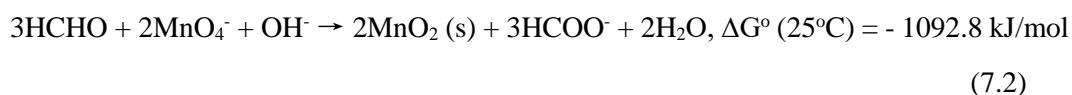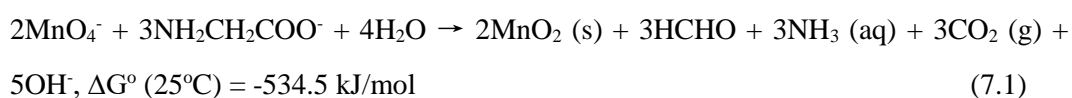
In the experimental alkaline environment (pH = 11), glycinate anion (Gly$^-$) will be dominant among the three forms of glycine (HGly, (H$_2$Gly)$^+$ and Gly$^-$) (Figure 1 of Chapter 4). As proven in Chapter 4, some base metals, the remaining Cu in particular, will be dissolved by glycine solution represented by Eq. 7.5. Previous studies, including Chapter 6 of this thesis, have indicated that Cu(Gly)$_2$ could act as an additional oxidant during Au dissolution (Eksteen and Oraby, 2015). It has also been reported that Gly$^-$ complexes with Au as Au(Gly$_2$)$^-$ (log β_2 = 18, E^o = 0.63 V (SHE)) (Aylmore, 2016). Therefore, the anode dissolution of Au and the possible cathode reactions can be written as Eq. 7.6–9. Eq. 7.7, oxygen reduction, should contribute to Au dissolution at a limited degree at room temperature, due to its lower reduction potential and limited solubility in water. The overall reaction of Au dissolution can be written as Eq. 7.10–12.

$$2Cu + O_2 \text{ (aq)} + 4Gly^- + 2H_2O \rightarrow 2Cu(Gly)_2 + 4OH^-, \Delta G^o \text{ (25}^o\text{C)} = \text{-219.0 kJ/mol} \tag{7.5}$$

Anode reaction:

$$Au + 2Gly^- \rightarrow Au(Gly_2)^- + e^-, E^o = 0.63 \text{ V} \tag{7.6}$$

Cathode reactions:

$$O_2 \text{ (from ambient air)} + 2H_2O + 4e^- \rightarrow 4OH^-, E^o = 0.40 \text{ V} \tag{7.7}$$

$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 \text{ (s)} + 4OH^-, E^o = 0.60 \text{ V}$ (7.8)

$Cu(Gly)_2 + e^- \rightarrow Cu(Gly)_2^-$ (7.9)

Overall reactions:

$2Au + 4Gly^- + 1/2O_2 \text{ (aq)} + H_2O \rightarrow 2Au(Gly_2)^- + 2OH^-, \Delta G^o \text{ (25}^o\text{C)} = 187.6 \text{ kJ/mol}$
(oxygen as oxidant) (7.10)

$3Au + 6Gly^- + MnO_4^- + 2H_2O \rightarrow 3Au(Gly_2)^- + MnO_2 \text{ (s)} + 4OH^-, \Delta G^o \text{ (25}^o\text{C)} = 229.9$
kJ/mol (permanganate as oxidant) (7.11)

$Au + Cu + 1/2O_2 + 4Gly^- + H_2O \rightarrow Au(Gly_2)^- + Cu(Gly)_2^- + 2OH^-$ (Cu(Gly)$_2$ as
oxidant) (7.12)
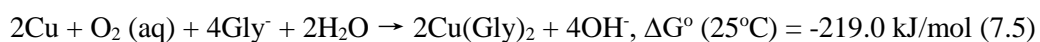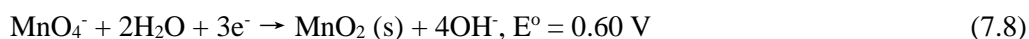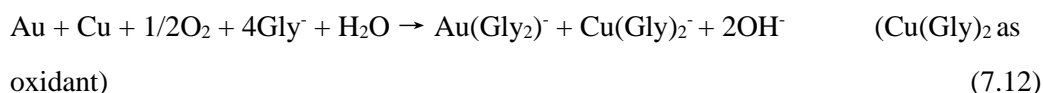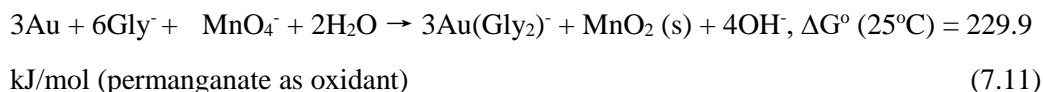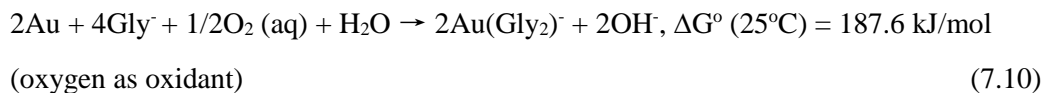
7.2.2 Glycine-ferricyanide leaching system

As an oxidant, ferricyanide can be reduced to ferrocyanide ($[Fe(II)(CN)_6]^{4-}$) as the cathodic reaction shown in Eq. 7.13. Although its reduction potential is slightly lower than that of oxygen (Eq. 7.7), a stronger oxidising environment can still be maintained due to its high solubility in glycine solution (Xie et al., 2008). In analogy to ferricyanide oxidation of glycine in acidic medium (Pd(II) as a catalyst) (Yerneni et al., 2017), the possible reaction in alkaline medium is proposed as Eq. 14 while the reaction rate remains unclear. Likewise, whether formate can be further oxidised to CO_2 in the glycine-ferricyanide leaching system remains unanswered. Other reactions, including Eq. 7.5–7, Eq. 9, 10 and 12, will also occur in the glycine-ferricyanide leaching system. The overall reaction of using ferricyanide as an oxidant can be proposed as Eq. 15.

$[Fe(III)(CN)_6]^{3-} + e^- \rightarrow [Fe(II)(CN)_6]^{4-}, E^o = 0.36 \text{ V}$ (7.13)

$4[Fe(III)(CN)_6]^{3-} + NH_2CH_2COO^- + 4OH^- \rightarrow 4[Fe(II)(CN)_6]^{4-} + HCOO^- + NH_3 \text{ (aq)} + CO_2$
(g) + 2H$_2$O, ΔG^o (25°C) = - 440.8 kJ/mol (7.14)

$Au + 2Gly^- + [Fe(III)(CN)_6]^{3-} \rightarrow Au(Gly_2)^- + [Fe(II)(CN)_6]^{4-}, \Delta G^o \text{ (25}^o\text{C)} = 102.1 \text{ kJ/mol}$
(7.15)
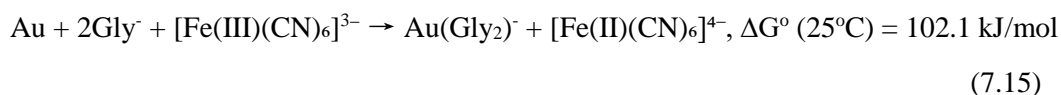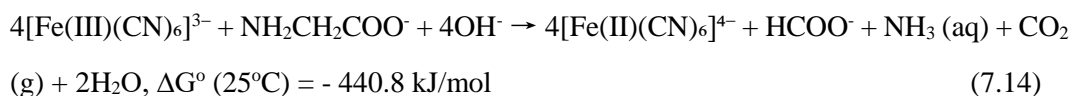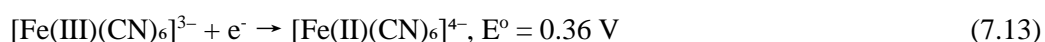
Both ferricyanide and ferrocyanide are highly strong metal-cyanide complexes that can hardly disassociate at a considerable rate unless they are exposed to strong UV light (Arellano and Martínez, 2010; Chen et al., 2019). Figure 7.1 plots the E_h-pH diagram of Fe-CN-H$_2$O system at 25°C. As shown, a highly reducing environment (-1.32 V vs SHE at pH 7) is required for the disassociation of ferri/ferro-cyanide to native Fe in alkaline solution under the conditions specified, as a result, toxic free-cyanide (CN$^-$) may be released. In the study of this chapter, the pH of the leaching solution was fixed at about 11,

therefore, the effect of ferri-/ferro-cyanide dissociation on metal extraction is not investigated.
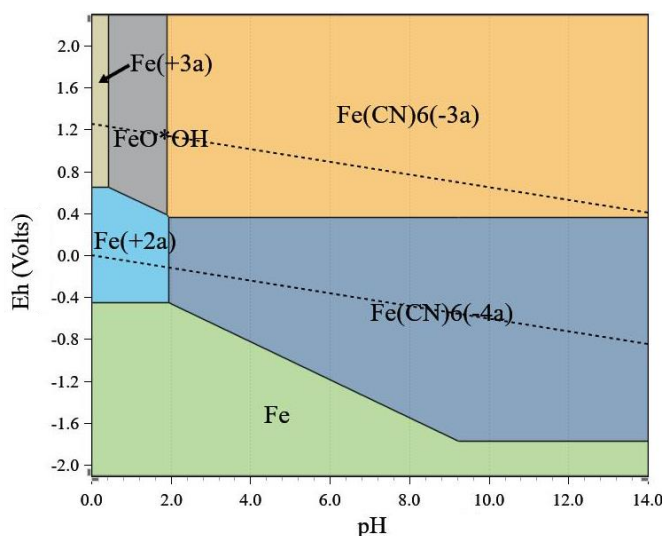
Figure 7.1 E_h-pH diagram of Fe-CN-H_2O system at 0.08 M Fe, 0.48 M CN$^-$ and 25°C (generate by HSC Chemistry 10.0)

7.3 Experimental section

7.3.1 Preparation of feed samples

Unless specified otherwise, the feed samples used in this chapter is the pulverised residue obtained from the first-stage glycine leaching of pre-treated WPCBs. The pre-treated WPCBs (22.6% Cu, 100% ≤ 2 mm) was from spent computer motherboards with CPUs and RAMs removed (high-value), supplied by Total Green Recycling Pty Ltd (Perth, Western Australia). The procedures for preparing the feed samples are detailed in Section 2.1 of Chapter 6. The major metal contents of the pulverised sample are shown in Table 7.1.

Table 7.1 Major metal contents of the prepared samples used in this study.

	in wt. %				in ppm				
	Cu	Fe	Pb	Ni	Zn	Co	Au	Ag	Pd
Metal content	2.20	2.50	0.26	0.36	991.0	74.0	127.5	424.5	15.1

7.3.2 Reagents

Glycine (NH_2CH_2COOH, GlyH) used in this chapter was of HPLC grade (≥99%), supplied by Sigma-Aldrich. Sodium hydroxide (NaOH), potassium permanganate ($KMnO_4$) and potassium ferricyanide ($K_3[Fe(CN)_6]$) were of analytical grade, supplied by Rowe Scientific Pty Ltd. "Permanganate" and "ferricyanide" mentioned in this chapter refers to $KMnO_4$ and $K_3[Fe(CN)_6]$, respectively. All the leaching solutions and analytical samples were prepared using deionised (DI) water.

7.3.3 Experimental setup and procedures

7.3.3.1 Leaching in rolled bottles without E_h control

The batch leaching experiments, without E_h control, were conducted in 2.5 L plastic Winchester bottles. For each experiment, unless specified otherwise, around 9.0 g of feed sample was mixed with a solution at 2% solid (g/mL), initial pH of 11 ($\pm$0.1, adjusted by NaOH) and different concentrations of glycine. Subsequently, a different amount of oxidant, potassium permanganate or potassium ferricyanide, was added into the mixture. The addition of oxidant was done in various stages, as detailed in Table 7.2, until its concentration reaches a pre-set value. A ~5 mm hole was left on each bottle lid for the ingress of ambient air. The bottle containing the mixture was then put on a bottle roller at different temperatures and rotated at a speed of 100 rpm for up to 96 h. Solution samples of 5 mL each were taken at 2, 6, 24, 48, 72 and 96 h. At each sampling time, the pH and E_h (mV, vs Ag/AgCl) of leaching solution were measured by using a pH meter (90-FLMV field lab analyser, TPS Pty Ltd), and the pH was maintained at 11 by adding NaOH. Upon completion of leaching, the solid and liquid were separated with a vacuum filter. The solid was washed with DI water and then dried at 70°C overnight.

Table 7.2 Proportion of oxidant (potassium permanganate or potassium ferricyanide) added during leaching in rolled bottles.

Time, h	0	2	4	6	24	48	72	96
Proportion of oxidant added, %	15	10	10	25	25	15	0	0

7.3.3.2 Leaching in a stirred reactor with E_h control

To control the E_h (vs Ag/AgCl) value during leaching, some experiments were done in a stirred reactor. Figure 7.1 shows the schematic diagram of the experimental setup. The E_h of the leaching solution was controlled by an ORP controller ($\pm$25 mV, HI 504 Hanna Instruments) connected with an ORP probe and a pump. For each experiment, around 9 g feed sample was mixed with 0.5 M glycine solution at pH 11 ($\pm$0.1, adjusted by NaOH), 2% solid and room temperature. The leaching mixture was then put on a magnetic stirrer at 400 rpm for up to 72 h. A stock solution of oxidant was automatically added by the E_h controller to maintain a specific E_h range, which inevitably resulted in the change of solution volume. It should, therefore, be noted that the solid content of the leaching solution was not constant at the initial 2% value. The concentrations of the prepared stock solution were 0.1 M for $KMnO_4$, and 0.1 M and 0.6 M for $K_3[Fe(CN)_6]$. Unless specified otherwise, the sampling schedule and other procedures remained the same with the leaching in rolled bottles (Section 7.3.3.1).
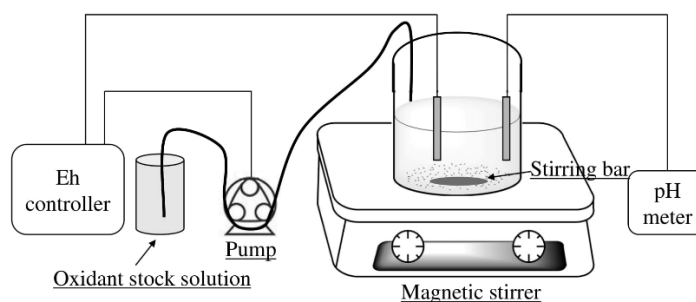
Figure 7.2 Schematic diagram of the experimental setup for leaching in a stirred reactor.

7.3.4 Analytic method

The analytic method for gold (Au) remained the same as that in Section 2.4 of Chapter 6. It is, therefore, not specified in this chapter. The Gibbs free energy of the equations in this chapter was calculated using the Reaction Equations module in HSC Chemistry 10.0.

7.4 Results and discussion

7.4.1 Effect of particle size

To investigate the effect of particle size of feed samples on Au extraction, two experiments were done using unpulverised and pulverised residue, respectively, obtained from the first-stage leaching of ≤ 2 mm WPCBs. Both of the tests were done at 0.5 M glycine, 0.08 M ferricyanide (staged addition, Table 7.2) and room temperature. As indicated in Figure 7.3, considerable enhancement of Au extraction was achieved for pulverised sample after 24 h of leaching. At 72 h, the Au extraction for pulverised sample was 78.0%, indicating about 20% points increase from that of unpulverised sample. This result agrees well with that in Section 3.2.4.1 of Chapter 6 where intensive cyanidation was used to leach both samples, revealing that the lock of metals accounted for the lower extractions. Therefore, in the following investigations, only pulverised samples were used.
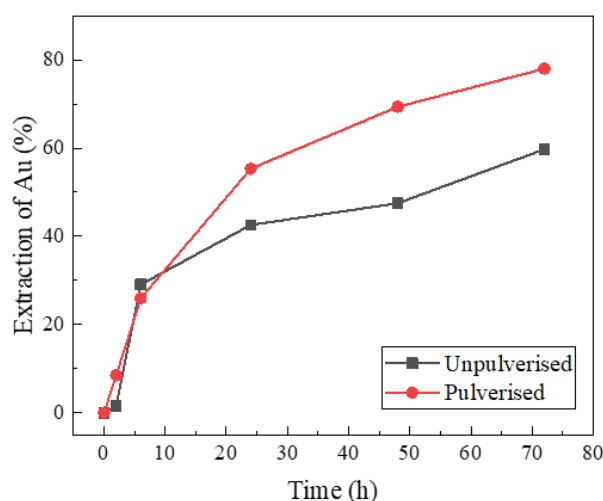
Figure 7.3 Effect of particle size on the extraction of Au (0.5 M glycine, 0.08 M ferricyanide, RT)

7.4.2 Effect of oxidant

The effect of oxidant was investigated using permanganate or ferricyanide at different concentrations. Other conditions were kept at 1 M glycine and 35°C. As shown in Figure 7.4, the addition of both permanganate (0.04–0.16 M) and ferricyanide (0.08–0.16 M) resulted in a considerable increase of Au extraction, compared with the test without additional oxidant. By comparing Eq. 7.8 and 7.13, the same molar amount of permanganate could provide a more oxidising environment than ferricyanide. However, it can be noticed that the leaching with permanganate (0.08 M and 0.16 M) had slower kinetics and a similar or lower Au extraction at 72 h than that with the same concentration of ferricyanide. This may be due to the side reactions between permanganate and glycine (Eq. 7.1–4) that consumed both oxidant and lixiviant for Au leaching. To reduce oxidant consumption, a concentration of 0.08 M was used for both permanganate and ferricyanide in the following tests.

Figure 7.5 shows the change of solution E_h recorded at each sampling time before the oxidant was added (Table 7.2). It can be seen that ferricyanide led to a much higher E_h of solution in the first several hours than permanganate. This explains the higher extraction of Au for ferricyanide in Figure 7.4. However, due to the addition scheme (Table 7.2), solution E_h with ferricyanide decreased and remained between −50 and −80 mV (vs Ag/AgCl) after 24 h. This implies the possibility of enhancing Au extraction by automatically controlling E_h at a constant high value. By contrast, the E_h for permanganate always remained below zero, which may be caused by its quick side reactions (Eq. 7.1–4).
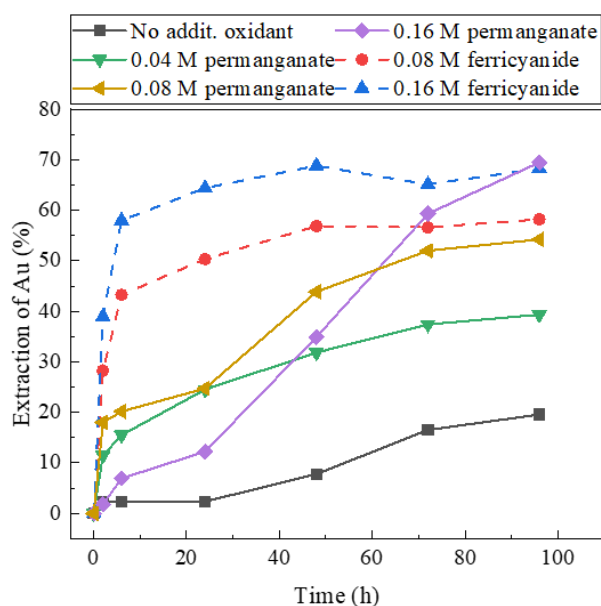
Figure 7.4 Effect of oxidant on the extraction of Au (1 M glycine, 35°C).
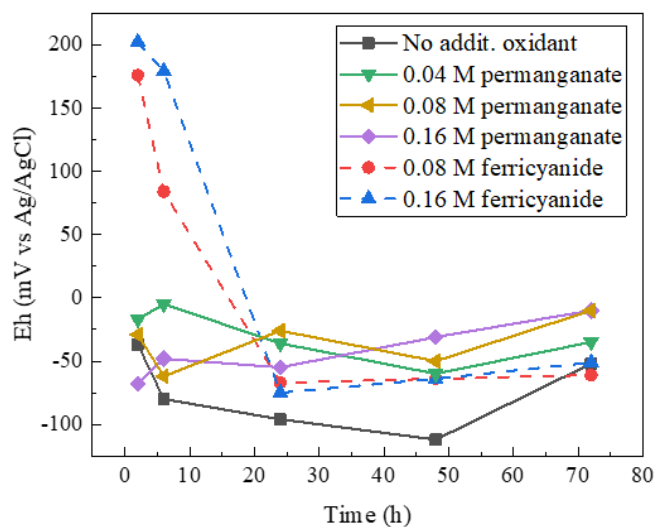
Figure 7.5 Effect of oxidant on the E_h of leaching solution (E_h measured at each sampling time before adding oxidant).

7.4.3 Effect of temperature

To study the effect of temperature on Au extraction, several experiments were carried out at room temperature, 35°C and 55°C, respectively. Other conditions were glycine concentration of 1 M and oxidant concentration of 0.08 M. As shown in Figure 7.6, in general, ferricyanide showed better Au extraction compared with permanganate at the same temperature. For permanganate addition, the increase of temperature to above 35°C resulted in faster leaching kinetics but not a considerably higher extraction at the end of leaching (72 h). Whereas, in the case of ferricyanide addition, temperature increase to above 35°C seemed to be detrimental to Au extraction, which is indicated by the lower E_h of solution in Figure 7.7. Overall consideration, room temperature is recommended for leaching with both ferricyanide and permanganate.
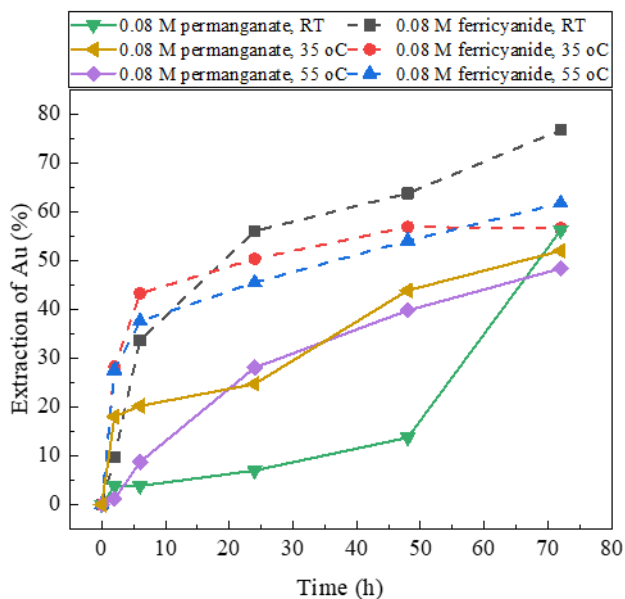
Figure 7.6 Effect of temperature on the extraction of Au (1 M

glycine).

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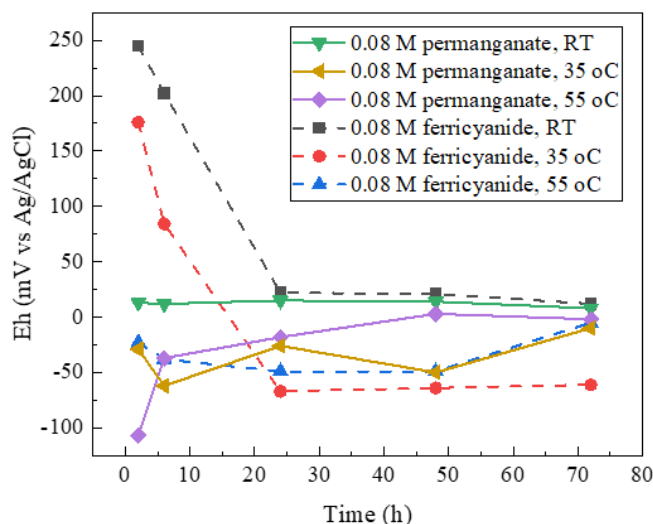
Figure 7.7 Effect of temperature on the E_h of leaching solution (E_h measured at each sampling time before adding oxidant).

7.4.4 Effect of glycine concentration

The effect of glycine concentration on Au extraction was investigated from 0.5 M to 1.0 M at room temperature. The results (Figure 7.8) show that the rise of glycine concentration resulted in a significantly lower Au extraction with permanganate addition, with 30% points of decrease obtained at 72 h. This may be explained by the lower E_h of leaching solution recorded for the 1.0 M glycine test (Figure 7.9). However, the glycine concentration did not obviously affect Au extraction with ferricyanide addition, although the 0.5 M glycine overall presented a higher E_h of the leaching solution. In addition, it is interesting that the same concentration of permanganate reached a higher Au extraction than ferricyanide at 0.5 M glycine, which is different from that at 1.0 M glycine in Section 7.4.3. More investigations are required to explain this phenomenon, such as the reactions between glycine and oxidants and the behaviour of other metals (e.g. Cu). For a higher Au extraction, a glycine concentration of 0.5 M was recommended for using both oxidants in the following tests. The challenge with these stronger oxidants is that the overall reaction chemistry is complicated by sacrificial reactions wherein the glycine itself is partially oxidised, which is not the case for oxygen or air oxidation. The action of reaction products themselves on the overall leach chemistry has not been determined. The net availability of "free" glycine and dissolved oxidant has yet to be established.
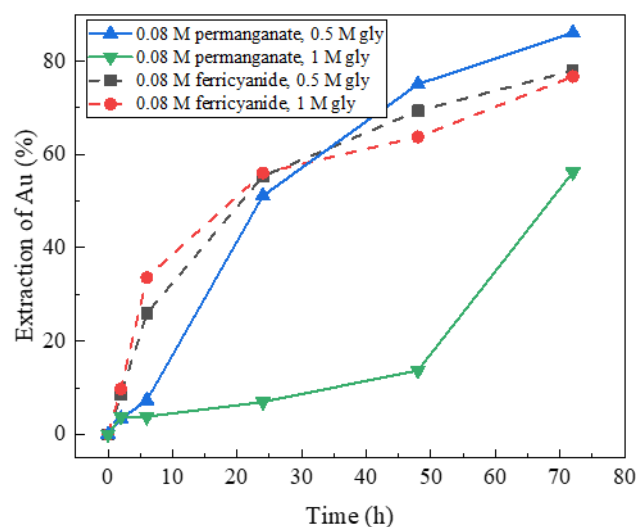
Figure 7.8 Effect of glycine concentration on the extraction of Au (RT).
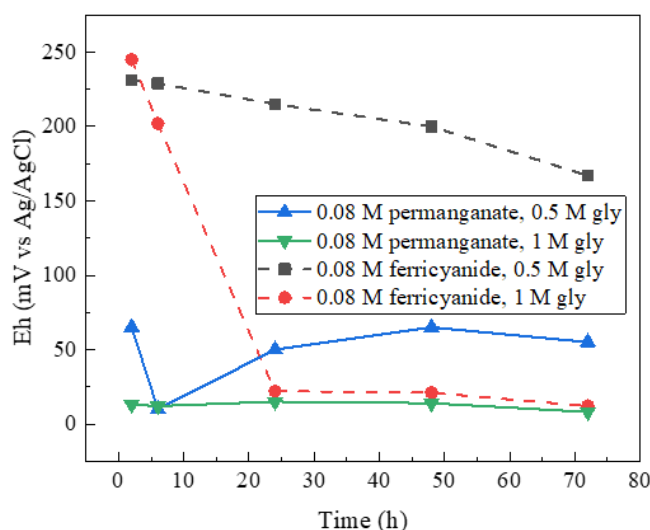
Figure 7.9 Effect of glycine concentration on the E_h of leaching solution (E_h measured at each sampling time before adding oxidant).

7.4.5 Effect of E_h

Effect of E_h on Au extraction was studied at 0.5 M glycine, pH 11 and room temperature. Table 7.3 shows the tests with different ranges of controlled E_h (mV, vs Ag/AgCl) and their consumption of oxidant (kg/t). Due to the apparent decomposition of glycine (observed by many precipitates while mixing glycine and permanganate), the E_h higher than 150 mV was not used for permanganate addition. As revealed in Figure 7.10, an increase of E_h resulted in a significant rise in Au extraction. Although a similar amount of permanganate was added in total (Table 7.3), E_h controlled at 50–100 mV experienced much lower Au extraction than the manual staged addition. It should be noted that during the E_h control test, permanganate was automatically added gradually and slowly to maintain a specific E_h range. By contrast, the manual addition test is expected to have an E_h pulse after each time of addition (Table 7.2), although the E_h measured before each addition time was also

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between 50–100 mV (except 6 h, Figure 7.11), which may contribute to the higher Au extraction. At 72 h, the highest Au extraction of 86.1% was achieved by manual staged addition with permanganate consumption of 632.1 kg/t.

Table 7.3 Amount of oxidant consumed in total during each test.

Test	Staged manual addition	$E_h = 50–100$ mV	$E_h = 100–150$ mV	$E_h = 150–250$ mV	$E_h = 250–350$ mV
Oxidant consumption, kg/t	**Using potassium permanganate (WM = 158.0 g/mol)**				
	632.1	607.5	1028.2	-	-
	Using potassium ferricyanide (WM = 329.2 g/mol)				
	1317.7	281.6	610.1	1028.3	2658.7
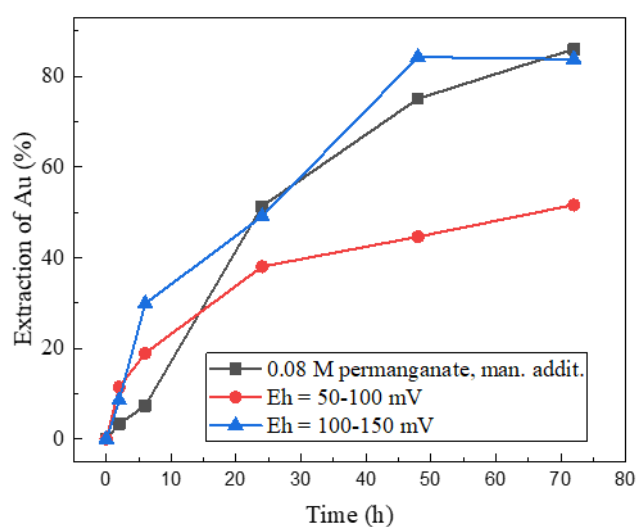
Figure 7.10 Effect of E_h, controlled by adding permanganate, on the extraction of Au (0.5 M glycine, RT).

Figure 7.11 presents the effect of E_h on Au extraction for ferricyanide addition tests. It can be seen that the rise of E_h led to a higher Au extraction while E_h more than 100 made no obvious increase of extraction at 72 h. To reduce oxidant consumption, E_h 100–150 mV may be suitable which only consumes less than half of ferricyanide in manual addition test (610.1 kg/t vs 1317.7 kg/t). At this E_h range, the highest Au extraction of 76.5% was obtained at 72 h.
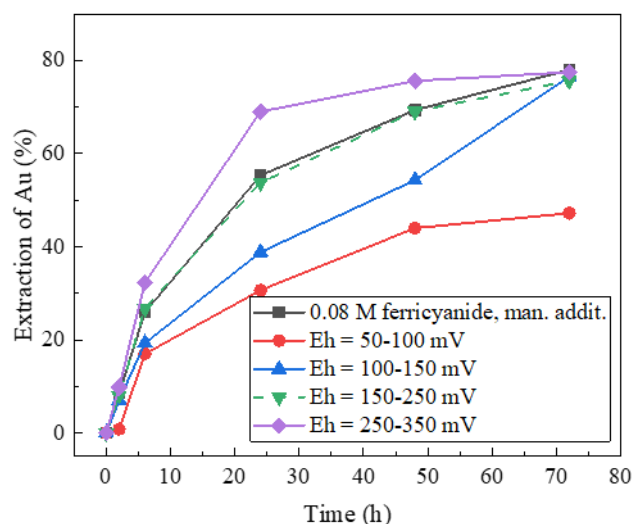
Figure 7.11 Effect of E_h, controlled by adding ferricyanide, on the extraction of Au (0.5 M glycine, RT).

Up to now, the parameters that affected Au extraction have been optimised and shown in Table 7.4. It should be noted that the conditions were obtained from the scope of this chapter, which may still have the potential to be further optimised. For example, as implied in Figure 7.8, <0.5 M glycine concentration may also achieve a higher or similar Au extraction that was not in the range of investigation. Moreover, as shown in Figure 7.10 and Figure 7.11, reaction equilibrium seemed not to be reached at 72 h under the optimised conditions. Therefore, a higher Au extraction may be achieved when leaching time is extended.

Table 7.4 Optimised conditions for Au extraction using glycine-permanganate or glycine-ferricyanide leaching system.

System	Sample size	Gly. conc., M	T	Oxidant addition /E_h	Oxidant consump., kg/t	Au ext. at 72 h, %
GP [a]	Pulv.[b]	0.5	RT[c]	Staged addition to 0.08 M	632.1	86.1
GF [d]	Pulv.	0.5	RT	E_h controlled at 100–150 mV	610.1	76.5

[a] refers to glycine-permanganate leaching system; [b] denotes the pulverising specified in Section 7.3.1 of this chapter; [c] denotes room temperature; [d] refers to glycine-ferricyanide leaching system.

7.5 Conclusions

This Chapter presents the potential of using glycine-oxidant leaching systems to extract precious metals from WPCBs, which may be an alternative to NaCN-based systems. Two

oxidants, i.e. potassium permanganate and potassium ferricyanide, have been tested and compared. The conclusions from the preliminary results are shown as follows:

- To achieve a reasonably high Au extraction, pulverising of samples was needed to avoid any lock of metals in plastics.
- Both glycine-permanganate and glycine-ferricyanide leaching systems enhanced Au extraction significantly, with the percentage jumped by about 40% at 0.08 M oxidant (ferricyanide or permanganate) from glycine-only leaching system.
- The rise of oxidant concentration resulted in a higher final Au extraction for both ferricyanide (0.08–0.16 M) and permanganate (0.04–0.16 M).
- However, the increase of temperature (room temperature – 55°C) and glycine concentration (0.5–1 M) seemed not to be beneficial for Au extraction for both oxidants.
- E_h controlled test did not enhance Au extraction for permanganate. To consume a similar amount of permanganate, the staged manual addition showed considerably higher Au extraction than the addition by E_h controlled at 50–100 mV.
- In contrast, by controlling E_h, the ferricyanide consumption was reduced by more than half when similar Au extraction was achieved. In addition, increasing E_h to ≥150 mV led to higher extracting kinetics but not a higher Au extraction at the final time of leaching (72 h).
- Under optimised conditions (Table 7.4), 86.1% and 76.5% Au extraction were achieved for glycine-permanganate and glycine-ferricyanide system, respectively, with the potential of a higher extraction at an extended time.

7.6 Future study

As this chapter only presents preliminary results of Au extraction, more questions still remain outstanding, such as the extraction of other precious metals (Ag, Pd), deportment of base metals, etc. Below the recommendations for future study are listed.

7.6.1 Optimisations

More work on the optimisation of variables can still be done to reduce oxidant consumption or to increase metal extractions. This includes (1) the investigating range of variables that can be expanded, such as temperature >55°C, glycine concentration <0.5 M and leaching time >72 h; (2) a more systematic optimisation using experimental design methods, such as orthogonal and response surface tests. The extraction of Ag and Pd should be focused on in future optimisations. However, it should be noted that e-waste is heterogeneous material, and different batches of samples (by brand /category) may have very different metal compositions. Therefore, in the industry, optimisation should be done on each particular e-waste material.

7.6.2 Glycine's fate

Glycine is the major lixiviant in the leaching system. As analysed in Section 7.2 of this chapter, glycine could be decomposed by introducing a strong oxidant. However, more studies on glycine's fate should be carried out to verify decomposition products, rate and extent (%). Such research may use instrumental analysis, e.g. Ultra-Performance Liquid Chromatography, to determine the amount of glycine that remained in leachates. This will be crucial information for the recyclability of glycine. Another method is to recover precious metals from leachates and then reuse barren solutions for the leaching step. By continuously recycling barren solutions, the recyclability of glycine can be indicated.

The interaction between metals and glycine's decomposition product also need to be investigated. For example, if glycine is decomposed to ammonia, how the metals interact with it and how this affects the extraction of precious metals still remain unanswered. The possible reactions proposed in Section 7.2 of this chapter also need to be verified experimentally.

7.6.3 Behaviours of other metals

WPCBs residue (obtained from the first stage glycine-only leaching) still have various base metals present (Table 7.1). The behaviour of these metals during precious metals extraction also need to be investigated. The reasons are (1) base metals may affect the extraction of precious metals, especially Cu (by acting as an additional oxidant); (2) the deportment of base metals determine the concomitant effluent, downstream metal recoveries and final residue treatment/disposal.

7.6.4 Regeneration of ferricyanide

As shown in Table 7.4, even under optimised conditions, ferricyanide consumption was still high at 610.1 kg/t. Ferricyanide may be regenerated by chemical or electrochemical oxidation of barren solution (when precious metals are recovered) to reduce reagent costs. Xie et al. (2008) and Rice and Browning (1980) respectively mentioned that ferricyanide added in conventional cyanidation process or remained in photographic bleach (already commercialised) can be regenerated through re-oxidization of ferrocyanide using ozone (O_3), as represented by Eq. 7.16. In addition, Adaikkalam et al. (1993) have shown that ferricyanide in photographic bleach can be regenerated by electrochemical oxidation in a certain range of potential. Further studies are required for the regeneration of ferricyanide from WPCBs leachate that contains glycine.

$$2[Fe(II)(CN)_6]^{4-} + O_3 \, (aq) + H_2O \rightarrow 2[Fe(III)(CN)_6]^{3-} + 2OH^- + O_2 \, (aq), \; \Delta G^o \, (25^oC) = -166.0 \; kJ/mol \tag{7.16}$$
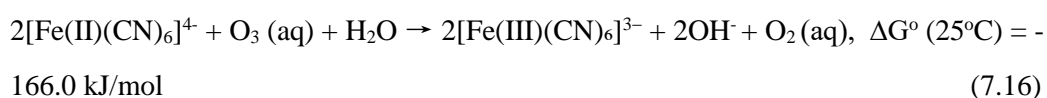
This regeneration of ferricyanide with ozone (made by passing oxygen of a corona discharge device) therefore allows a self-regenerating system, the equivalent of which cannot be conveniently achieved with the permanganate system.

7.7 References

Adaikkalam, P., Sathaiyan, N. and Visvanathan, S., 1993. Electrolytic regeneration of bleach solution in the motion picture industry. J. Chem. Technol. Biotechnol., 56(4): 389–392.

Arellano, C.A.P. and Martínez, S.S., 2010. Effects of pH on the degradation of aqueous ferricyanide by photolysis and photocatalysis under solar radiation. Sol. Energy Mater. Sol. Cells, 94(2): 327–332.

Aylmore, M., 2016. Alternative lixiviants to cyanide for leaching gold ores, Gold Ore Processing (Second Edition). Elsevier, pp. 447–484.

Chen, W.D., Kang, S.-K., Stark, W.J., Rogers, J.A. and Grass, R.N., 2019. The light triggered dissolution of gold wires using potassium ferrocyanide solutions enables cumulative illumination sensing. Sens. Actuators B Chem., 282: 52–59.

Dean, J.A., 1999. Lange's handbook of chemistry (15th edition). McGraw-Hill Inc.

Eksteen, J. and Oraby, E., 2015. The leaching and adsorption of gold using low concentration amino acids and hydrogen peroxide: Effect of catalytic ions, sulphide minerals and amino acid type. Miner. Eng., 70: 36–42.

Insausti, M.J., Mata-Pérez, F. and Alvarez-Macho, M.P., 1996. Kinetic study of the oxidation of glycine by permanganate ions in acid medium. Collect. Czechoslov. Chem. Commun., 61(2): 232–241.

Issa, I.M. and Issa, R.M., 1954. Formic acid as a reagent for alkaline permanganate: Potentiometric determination of formate. Anal. Chim. Acta, 11: 192–199.

Laitos, J.G., 2013. Cyanide, mining, and the environment. Pace Environ. Law Rev., 30(3): 869.

Oraby, E.A., Eksteen, J.J. and O'Connor, G.M., 2020b. Gold leaching from oxide ores in alkaline glycine solutions in the presence of permanganate. Hydrometallurgy: 105527.

Perez-Benito, J.F., Mata-Perez, F. and Brillas, E., 1987. Permanganate oxidation of glycine: Kinetics, catalytic effects, and mechanisms. Can. J. Chem., 65(10): 2329–2337.

Putnam, G., 1950. A laboratory study of the influence of ferricyanide on the extraction of gold. J. South. Afr. Inst. Min. Metall., 50(9): 228–230.

Rice, R.G. and Browning, M.E., 1980. Ozone for industrial water and wastewater treatment: A literature survey. United States Environmental Protection Agency.

Xie, F., Dreisinger, D. and Lu, J., 2008. The novel application of ferricyanide as an oxidant in the cyanidation of gold and silver. Miner. Eng., 21(15): 1109–1114.

Xie, F. and Dreisinger, D.B., 2007. Leaching of silver sulfide with ferricyanide–cyanide solution. Hydrometallurgy, 88(1): 98–108.

Yerneni, K. K., Cholkar, K., Guin, M., Nayak, A. N., Ananda, S. and Gowda, N. M. M., 2017. Palladium (II) Catalyzed Oxidation of Glycine by Ferricyanide in Acid Medium: Kinetics and Mechanism. Curr. Phys. Chem., 7(1): 63–70.

Yusuf, A., Snape, C., He, J., Xu, H., Liu, C., Zhao, M., Chen, G. Z., Tang, B., Wang, C. and Wang, J., 2017. Advances on transition metal oxides catalysts for formaldehyde oxidation: A review. Catal. Rev., 59(3): 189–233.

Zhang, C., Liu, F., Zhai, Y., Ariga, H., Yi, N., Liu, Y., Asakura, K., Flytzani‐Stephanopoulos, M. and He, H., 2012. Alkali‐metal‐promoted Pt/TiO2 opens a more efficient pathway to formaldehyde oxidation at ambient temperatures. Angew. Chem. Int. Ed, 51(38): 9628–9632.

Zi, F.T., Hu, X.Z., Zhang, W.B. and He, S.Q., 2012. Thiosulfate leaching of middle-refractory gold ore with ferricyanide as oxidant, Adv. Mat. Res., 548: 309–314.
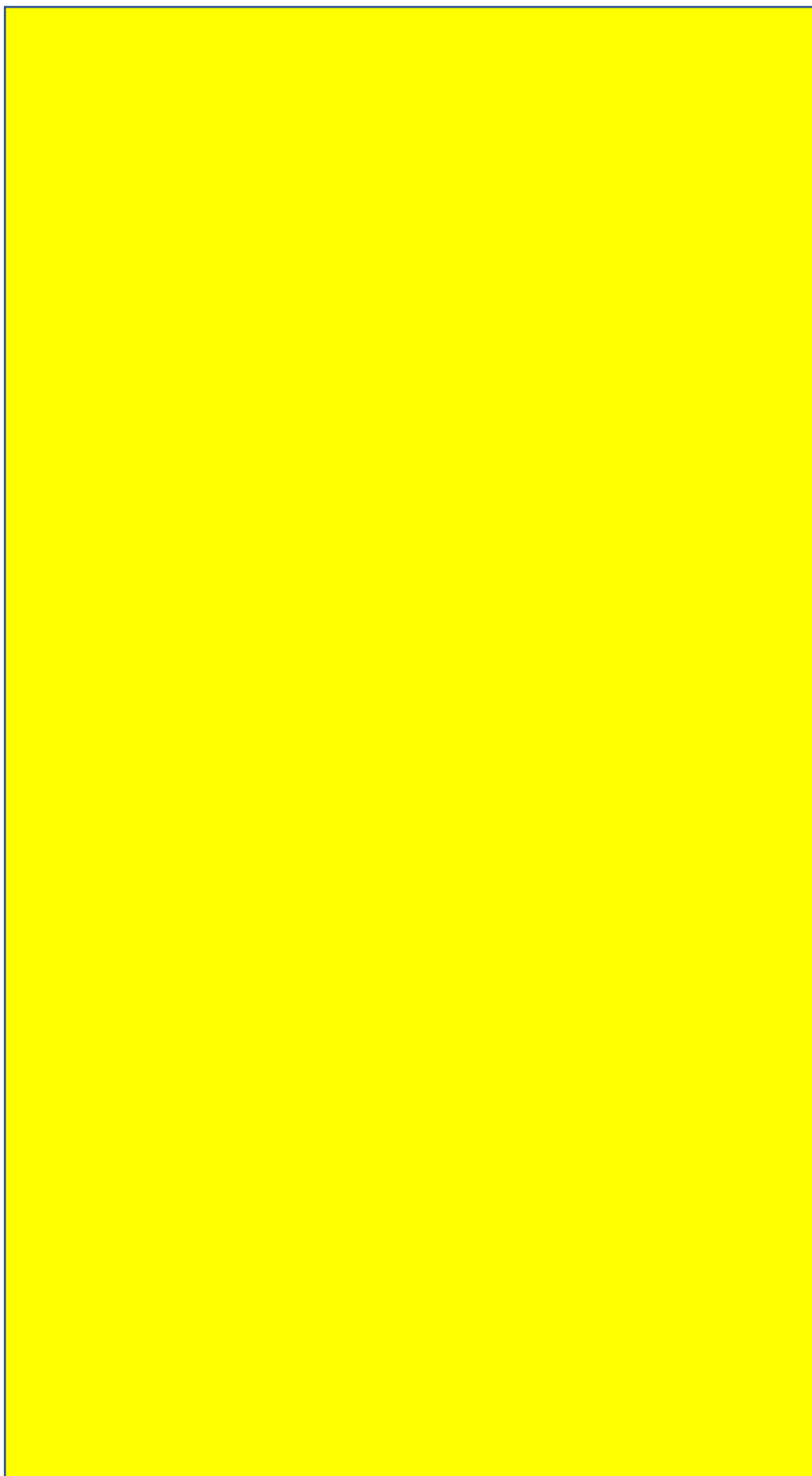
Chapter 8 Conclusions and recommendations

8.1 General conclusions

In this thesis, the recovery of base and precious metals from WPCBs, a typical portion of e-waste, using alkaline glycine-based processes has been investigated. The thesis is trying to develop sound hydrometallurgical processes from pre-treatment of WPCBs to metal extractions and recoveries (Figure 1.1 of Chapter 1). The processes have been shown advantages in operational conditions (room temperature, ambient pressure, mildly alkaline environment) and the use of reagents (nontoxic glycine, starved level of cyanide, and cyanide-free in the presence of nontoxic and mild oxidants). This makes the processes particularly beneficial for applying near urban areas where strict safety requirements apply, with flexible scale and low capital and operational costs. The thesis has covered background investigation (literature review), exploratory study and in-depth investigations of the process proposed. It is the conclusion of the author that a multistage alkaline process has been technically demonstrated that can recover the predominant base and precious metals from WPCBs. Due to the nature of the work, error sources regarding the results may be from the standard instrumental analyses and the heterogeneity of the WPCBs sample.

Below the general conclusions are listed.

(1) A review on the background of this thesis, i.e. recycling of WPCBs using hydrometallurgy, has summarised the current status and pointed out the opportunity of the glycine-based process in this area. The review has provided vital information on WPCBs' properties (components, materials and structure), previous approaches of pre-treatment, metal extraction and recovery. The information has helped design the following experiments and has been frequently referred to in the following chapters.

(2) An exploratory study has proved the feasibility of using a two-stage glycine-based leaching system to extract base and precious metals from metallic fractions (MFs) of WPCBs. The two-stage system comprises the extraction of base metals using glycine solution and the extraction of precious metals using cyanide-starved glycine solution.

(3) A detailed and in-depth investigation of the first-stage extraction of base metals from original WPCBs has been performed. Not only the primary metal of Cu was targeted, the behaviours of various other metals, including Ni, Al, Fe, Pb, Zn, Sn, Co, Au, Ag and Pd, were also investigated. The alkaline glycine-only leaching system presented high selectivity to Cu and Zn (>90%), with minimal extraction of Fe and precious metals (<2%) at the redox, glycine concentration, pH and temperature conditions studied.

(4) A feasibility study of Cu recovery from first-stage leachates and the deportment of other base metals (Zn, Al, Ni, Pb and Sn) was conducted. Three recovery options, i.e. hydrazine reduction, sulfide precipitation and solvent extraction, were studied and compared. This study shows the advantages and disadvantages of the options that can help select a suitable method for base metals recovery from glycine-containing leachates.

(5) Detailed and in-depth investigation of the second-stage extraction of precious metals (Au, Ag and Pd) using a cyanide-starved glycine leaching system was performed. Along with the precious metals extraction, the behaviours of various metals (Cu, Zn, Pb, Al, Ni, Co, Fe and Sn) were also investigated. The cyanide consumption was significantly reduced from traditional cyanidation, and the leaching solution was starved of cyanide with no free cyanide presence after 4 h of leaching. The cyanide-starved glycine leaching system showed fairly good selectivity to Cu and precious metals, with the extraction of base metals less than 10% (except 15% for Zn).

(6) To avoid using NaCN, another leaching system, i.e. glycine-oxidant leaching system, was proposed for the second-stage precious metals extraction. Preliminary results on Au extraction show the promising potential of the system as an alternative to the NaCN-containing system. However, more works are still needed to explain the experimental phenomenon and to develop the system.

8.2 Enumerated conclusions

8.2.1 Literature review

- WPCBs have complicated composition and intrinsic structure, which has made the recycling challenging. The composition and structure also vary among the different categories of products. This information must be referred to when a sustainable recycling process is to be developed.

- Mechanical-physical treatment of WPCBs owns the merits of lower costs and fewer hazards compared with chemical treatments. Ideally, the bulk of metals should be separated by the mechanical-physical process, while the lower impurity of the product may require further treatment by hydrometallurgy.

- Traditional leaching methods, including mineral acid and cyanide (NaCN)-based leaching, are highly toxic or corrosive and pose high safety and environmental risks. Mild leaching methods, including thiourea, thiosulfate, thiocyanate, halide, ammonia-ammonium leaching, also have their disadvantages, such as high reagent consumption and costs and the use of highly volatile and harmful reagents. More attention should be paid to develop a more environmentally benign leaching method with easily recycled lixiviant and a suitable oxidant.

- Various downstream purification and recovery methods, including cementation, chemical precipitation, solvent extraction, carbon adsorption, ion-exchange by resin and electrodeposition, are reviewed while a suitable method should be determined by the specific scenario of leachates. Given the complicated metal contents in WPCBs, multiple methods may be employed to achieve the high purity of the product.

8.2.2 Exploratory study on preconcentrated metallic fractions

- Glycine solution could leach most of the base metals, including 72.5% Cu, 80.9% Zn, 85.6% Pb, 99.1% Al and 6.5% Ni, at room temperature and pH 11 in 24 h from a metallic portion (>72% metals, about 100% ≤ 1 mm) of WPCBs. Meanwhile, the extractions of Au and Ag were below 2%. The dissolution of Zn, Pb, Cu and Al increased with the rise of glycine concentration (7–30 g/L), pH (7–11) and dissolved oxygen in solution (6.5–15 mg/L).

- Second-stage leaching using cyanide-starved glycine solution could leach >85% Ag and Au and most of the remaining base metals at room temperature and pH 11 in 24 h.

- Overall, 85.3% Ag, 92.1% Au, 99.1% Cu, 98.5% Zn, 98.1% Al, 89.8% Pb and 19.5% Ni could be extracted under the optimised conditions of the two-stage leaching steps. Both stages were conducted at room temperature, pH 11 and 30 g/L glycine for 24 h. In the second stage, NaCN concentration was starved at 300 mg/L. No other oxidant or lixiviant was required.

- The two-stage glycine-based system showed better or similar performance on metals extraction in comparison to direct cyanidation, single-stage glycine-cyanide leaching and ammonia leaching.

8.2.3 First-stage leaching of base metals

- The WPCBs from the mixed brand of computer motherboards were simply pre-treated to 100%< 2mm. The major base metals were Cu (22.6%), Fe, Al, Sn, Pb, Zn, Ni and Co. The major precious metals were Au (106.8 ppm), Ag (170.5 ppm) and Pd (10.4 ppm). Cu, Au, Ag and Pd contributed to about 92% of the total economic value.

- The conditions for the highest Cu extraction of 96.5% were obtained as glycine concentration of 0.5 M, initial pH of 10.0, solid content of 2%, WPCBs size of 100% <2 mm, room temperature and 72 h. Except for ambient oxygen, no additional oxidant was added. In the meantime, the extraction of other base metals varied as follows: 92.5% Zn, 46.8% Pb, 16.0% Al, 12.6% Ni, 3.1% Co and 9.3% Sn. In particular, a glycine solution was almost inert with Fe throughout all the range of

conditions. Importantly, the extraction of precious metals of Au and Ag remained below 2%.

- In general, the solution pH was increasing with leaching going on, due to the redox reactions during metal dissolution. Initial pH (8–13) affected the extraction of base metals considerably, and its progression was highly related to other experimental variables.

- Glycine concentration (0.2–1 M) and solid content (1–10%) affected base metals extraction significantly. In contrast, temperature (room temperature – 55°C) and the concentration of additional oxidant (H_2O_2, 0.1–1%) had relatively slight effects.

- Fine (<75 µm) WPCBs showed significantly faster Cu leaching than the coarse ones (425–600 µm, <1 mm and <2 mm). Grinding of WPCBs to 100% <1 mm was found to be unnecessary as no apparent enhancement of Cu extraction was achieved.

- The SEM-EDS analysis indicated that the remaining Cu and Ni were locked in inert layers of WPCBs, including Sn-Pb solder and Au layers. It was also expected that Cu could be locked in the lamination of plastics.

- The kinetic study revealed that Cu leaching from 100% < 2 mm WPCBs in alkaline glycine solution with ambient ingress was mainly controlled by internal diffusion with an activation energy of 6.62 kJ/mol.

8.2.4 Recovery of Cu and the deportment of other metals from first-stage leachates

8.2.4.1 Method #1: hydrazine reduction

- In the case of hydrazine reduction, Cu recovery was found sensitive to solution pH. To reach a reasonably high Cu recovery, the pH should preferably be more than 12, which can be satisfied by the natural first-stage leachate (without pH adjustment). The increase of initial pH (9.0–12.8), Cu concentration (0.5–5 g/L) and temperature (room temperature – 50°C) led to the rise of Cu recovery.

- The increase of hydrazine addition amount resulted in higher Sn and Pb co-precipitations. In contrast, no obvious co-precipitation of Ni, Zn, and Al was noted in the investigated range of Cu/hydrazine molar ratio (1:0.7 – 1:2).

- XRD analysis revealed that at the Cu/hydrazine molar ratio of 1:0.7 and 1:1, cuprite (Cu_2O) and metallic Cu were obtained at 96.9% and 98.6% recoveries, respectively.

8.2.4.2 Method #2: Sulfide precipitation

- Sulfide precipitation of Cu had fast kinetics with ≥99.5% Cu precipitated in only 5 min at Cu/HS⁻ molar ratio of ≤ 1:1.2 and room temperature.

- At the optimal Cu/HS⁻ molar ratio of 1:1.2, 100% Sn, 100% Pb, and 67.7% Zn were co-precipitated. Whereas the co-precipitation of Ni and Al were found limited at ≤ 3%.

- XRD analysis verified that the precipitates were mainly composed of covellite (CuS) at the optimal Cu/HS⁻ molar ratio. XRF analysis indicated a covellite purity of 87.9%, which made the necessity of further refining.

8.2.4.3 Method #3: Solvent extraction

- Mextral 84H demonstrated higher Cu extraction than Mextral 54-100, while it required higher H_2SO_4 concentration to strip Cu off from the extractant.

- Mextral 84H also had higher selectivity than Mextral 54-100 with no Al, Ni and Sn co-extracted.

- Overall Cu recoveries of 91.6% for extraction using 15% Mextral 84H followed by stripping using 200 g/L H_2SO_4, and 86.7% for extraction using 30% Mextral 54-100 followed by stripping using 80 g/L H_2SO_4.

Comparisons of the three methods indicated the merits and drawbacks of each. The selection of a suitable way should be based on the specific conditions of an application.

8.2.5 Second-stage leaching of precious metals using cyanide-starved glycine leaching system

- By employing a cyanide-starved glycine system, a better or similar leaching performance on Au, Ag, Pd and/or Cu were achieved, compared with using either stoichiometric or intensive cyanidation, and significantly, the cyanide consumption was reduced by around 72% and 93% respectively.

- Glycine amount (2–8× stoichiometric amount), cyanide concentration (100–350 mg/L), initial pH of solution (10.5–12.5) and particle size of feed sample affected Au, Ag and Cu leaching considerably. By contrast, adding cyanide in multiple stages did not enhance the extractions.

- The conditions for precious metals extraction were optimised as glycine amount of 4× stoichiometry, cyanide concentration of 250 mg/L (all added at initial), initial solution pH of 11 and feed sample being pulverised. Under the conditions, 90.1% Au, 89.4% Ag and 70.1% Pd were extracted from the pulverised residue of first-stage leaching, with co-extraction of 81.0% Cu, at only room temperature for 96 h.

- The system presented a reasonably good selectivity to precious metals and Cu. The extraction of other base metals (Pb, Al, Ni, Co, Fe and Sn) was at a low level of less than 10%, except for 15% for Zn.

- The optimal cyanide concentration of 250 mg/L was found starved in solution, and no free cyanide was present after 4 h of leaching. This indicates a significant reduction in safety and health risks compared with conventional cyanidation.
- SEM-EDS analysis revealed that Sn, Fe and Al were dominant in leaching residue, which may be removed by a step of acid washing.

8.2.6 Second-stage leaching of precious metals using non-cyanide glycine leaching system: A preliminary study on gold

- The introduction of an additional oxidant, i.e. potassium permanganate or potassium ferricyanide, enhanced Au extraction significantly, with the extraction increased by around 40% from the glycine-only system.
- Oxidant concentration of both ferricyanide (0.08–0.16 M) and permanganate (0.04–0.16 M) had a positive effect on final Au extraction while increasing temperature (room temperature – 55°C) and glycine concentration (0.5–1 M) did not enhance Au extraction obviously for both oxidants.
- Controlling E_h did not enhance Au extraction for permanganate. To consume a similar amount of permanganate, E_h controlled test posed significantly lower Au extraction than the test by staged manual addition of permanganate. On the contrary, by controlling E_h, ferricyanide consumption was reduced by more than 50% when similar Au extraction was achieved.
- Conditions for Au extraction during glycine-oxidant leaching were optimised as follows.
  - Using permanganate as additional oxidant: Feed sample pulverised, 0.5 M glycine, room temperature, 0.08 M permanganate added in stages at consumption of 632.1 kg/t which 86.1% Au were extracted in 72 h.
  - Using ferricyanide as additional oxidant: Feed sample pulverised, 0.5 M glycine, room temperature, E_h controlled at 100–150 mV with a ferricyanide consumption of 610.1 kg/t, under which 76.5% Au extraction was achieved in 72 h.
- Kinetics of leaching showed the potential of a higher Au extraction at a longer leaching time.

8.3 Recommendations for future study

The present thesis is by no means an exhaustive study but should establish a sound foundation for further work and process optimisation. Based on the identified gap of research, the following recommendations are proposed for future research.

(1) Improving production efficiency

As shown in Chapter 4 of this thesis, the leaching kinetics of Cu using alkaline glycine-only solution was still quite slow compared with conventional mineral acid leaching. For example, it required 72 h (3 d) to reach the highest Cu extraction of >95%, while similar Cu extraction could be achieved by sulfuric acid – oxidant leaching within 12 h. Therefore, improvement of Cu leaching kinetics in glycine medium will be substantial in the view of production efficiency and can be a focus of future study. Potential methods could be adding synergistic lixiviant, catalyst and additional oxidant.

(2) Improving solid content (production capacity)

Waste printed circuit boards are significantly high-grade Cu materials (about 10–20 wt.%). However, as observed in experiments, cupric glycinate ($Cu(Gly)_2$) has limited solubility in water and was most likely precipitated when it becomes saturated, which restricted the solid content during Cu leaching using a glycine-only system. This will bring a low production capacity and high consumption of water in actual industrial applications. How to improve the solid content of Cu leaching will hence be critical in a practical application. Adding a leaching synergist may be an option that is expected to stabilise cupric ions in the leaching solution.

In addition, the leaching behaviour of precious metals at high solid content (e.g. >10%) also needs to be investigated.

(3) Development of non-cyanide glycine leaching system

To avoid using cyanide, even at the starved levels, a non-cyanide glycine system can be developed based on the preliminary results from Chapter 7 of this thesis. Much research still needs to be done, as shown in Section 7.6 of Chapter 7.

(4) Recovery of precious metals from leachates

As shown in Chapter 6, Ag was first leached into the solution but further precipitated due to the instability of corresponding complexes. To solve this, one may need to separate and recover Ag during the leaching step, such as using carbon-in-leach (CIL) and resin-in-leach (RIL). However, how the various species (e.g. cyanide, glycine and cupric complexes) will behave during CIL /RIL will need to be investigated.

(5) Glycine recycling and reuse

To reduce reagent costs, glycine from barren solution needs to be recycled back to leaching stages when metals are recovered from the pregnant leaching solution (PLS). To achieve this, recommended focuses are (1) instrumental analysis of glycine to determine glycine's decomposition (%) during each step of the process; (2) a locked-cycle test to show the effect of recycled glycine on metals leaching.

(6) Residue utilization

Even after cyanide-starved glycine leaching, the final residue still contains a relatively high grade of precious metals (17.7 ppm Au and 45 ppm Ag), compared with natural resources. How to extract and recover this portion of precious metals will need to be addressed in a future study. Moreover, the remaining toxic base metals need to be removed before utilising non-metallic fractions (NMFs).

(7) Scale-up of process

All the experimental work in this thesis were done on a lab/bench scale, and all the steps of the process were done separately. Further validation of the whole process by scaling up and the continuous test will supplement the study. Fully integrated flowsheet and process simulation would be required for design and scale-up, as a basis for techno-economic assessment. Mass balance based on the test of the whole process, in which each step is done continuously, is suggested.

(8) Alternative process

It is well known that mineral acid (e.g. sulfuric acid) in the presence of oxidant (e.g. peroxide or ferric ions) is capable of leaching base metals, including copper. Moreover, it presents much faster leaching kinetics (completion within 24 h) and, sometimes, higher extractions than the glycine-only leaching system. Also, the mineral acid-oxidant leaching system could have lower reagent costs than the glycine-only leaching system if glycine recycle is not considered. Therefore, the investigation of alternative process, i.e. mineral acid -oxidant leaching of base metals followed by alkaline glycine-based leaching of precious metals, is recommended. A detailed comparison between this process and the completely alkaline glycine process should be made in such investigation.

(9) Techno-economic assessment

When the studies mentioned above are adequately addressed, the techno-economic assessment can be done to show the economic profitability of the process. Such an assessment is suggested to be based on the data from the scaled-up continuous run of the process.

Appendices

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Appendix B Statements of the contribution of co-authors

Appendix C Tabulation of experimental data

Appendix A Copyright permission from journal publishers

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STATEMENT OF CONTRIBUTION OF CO-AUTHORS

To whom it may concern

I, **Huan Li**, the primary author of the following four publications forming the parts of this thesis, contributed to the conception, design, data collection, analysis and interpretation and wrote the manuscript of all the four publications. These are:

- **Li, H.,** Eksteen, J., & Oraby, E. (2018). Hydrometallurgical recovery of metals from waste printed circuit boards (WPCBs): Current status and perspectives – A review. *Resources, Conservation and Recycling*, 139, 122-139.
- **Li, H.,** Oraby, E., & Eksteen, J. (2020). Extraction of copper and the co-leaching behaviour of other metals from waste printed circuit boards using alkaline glycine solutions. *Resources, Conservation and Recycling*, 154, 104624.
- **Li, H.,** Oraby, E., & Eksteen, J. (2021). Recovery of copper and the deportment of other base metals from alkaline glycine leachates derived from waste printed circuit boards (WPCBs). *Hydrometallurgy*, 199, 105540.
- **Li, H.,** Oraby, E., & Eksteen, J. (2021). Cyanide consumption minimisation and concomitant toxic effluent minimisation during precious metals extraction from waste printed circuit boards. *Waste Management*, 125, 87-97.

Signature of Candidate:

I, as a co-author, endorse that this level of contribution by the candidate indicated above is appropriate.

Dr Elsayed Oraby

Signature:

Prof Jacques Eksteen

Signature:

STATEMENT OF CONTRIBUTION OF CO-AUTHORS

To whom it may concern

I, **Huan Li**, the second co-author of the following publication forming the part of this thesis, conducted a part of the experiments, and contributed to the data analysis and interpretation, writing and revision of the manuscript. The publication specified is:

- Oraby, E. A., **Li, H.,** & Eksteen, J. J. (2020). An alkaline glycine-based leach process of base and precious metals from powdered waste printed circuit boards. *Waste and Biomass Valorization*, 11 (8), 3897-3909.

Signature of Candidate:

I, as a co-author, endorse that this level of contribution by the candidate indicated above is appropriate.

Dr Elsayed Oraby

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Prof Jacques Eksteen

Signature:

Appendix C Tabulation of experimental data

Appendix C1 Leaching of base metals using glycine-only leaching system

C1.1 Size distribution of the WPCBs after pre-treatment

Size range, mm	Fraction, wt.%
<0.075	18.07
0.075–0.18	6.82
0.18–0.25	4.94
0.25–0.425	12.13
0.425–0.6	8.95
0.6–0.85	19.01
0.85–1.18	22.70
1.18–1.4	6.30
1.4–1.7	1.06
1.7–2	0.02

C1.2 Grade of metals by size fractions

Size range, mm	Metal grade, %							
	Cu	Fe	Al	Zn	Ni	Sn	Pb	Co
<0.075	4.22	2.34	2.49	0.126	0.160	0.0544	0.107	0.00252
0.075–0.18	11.6	1.78	0.98	0.120	0.217	0.0672	0.217	0.00220
0.18–0.25	19.9	1.30	1.05	0.131	0.409	0.0876	0.287	0.00342
0.25–0.425	27.2	1.23	1.47	0.407	0.465	0.124	0.330	0.00318
0.425–0.6	31.8	2.08	1.64	1.05	0.599	0.301	0.601	0.0134
0.6–0.85	31.2	1.83	2.10	1.56	0.391	0.553	0.461	0.0113
0.85–1.18	23.8	1.90	2.27	0.879	0.285	0.148	0.337	0.0013
1.18–1.4	23.2	1.69	2.23	0.922	0.326	0.0732	0.198	0.0129
1.4–1.7	19.0	4.72	1.28	0.850	0.249	0.116	0.0725	0.0456
1.7–2	13.8	20.2	0.48	0.370	0.902	0.126	0.0721	0.241

Size range, mm	Metal grade, ppm		
	Au	Ag	Pd
<0.075	160	392	13.4
0.075–0.18	94.2	441	11.7
0.18–0.25	79.6	473	11.8
0.25–0.425	99.1	464	18.3
0.425–0.6	136	465	24.1
0.6–0.85	181	522	10.9
0.85–1.18	143	291	6.9
1.18–1.4	52.8	175	1.51
1.4–1.7	46.4	217	2.58
1.7–2	20.3	37.3	1.1

C1.3 Effect of initial pH

Experimental conditions: glycine concentration = 0.5 M, solid content = 2%, particle size = <2 mm, RT and ambient oxygen.

t, h	Extraction of Cu, %				
	Initial pH 8.02	Initial pH 10.00	Initial pH 10.50	Initial pH 12.04	Initial pH 13.00
0	0	0	0	0	0
2	3.59	9.02	10.64	11.27	4.78
4	5.56	14.55	16.02	18.68	8.33
6	10.60	19.87	21.54	24.69	12.16
24	18.43	68.00	65.13	50.20	33.75
48	30.99	91.34	82.79	63.72	51.29
72	37.18	96.54	87.65	72.32	62.85

Initial pH	Extractions at 72 h, %							
	Ni	Al	Fe	Pb	Sn	Zn	Au	Ag
8.02	28.78	0.00	0.00	41.64	1.04	42.41	0.00	0.00
10.00	12.64	15.99	0.00	46.84	9.30	92.51	1.84	0.00
10.50	27.15	54.20	0.00	57.12	5.99	87.38	0.00	0.00
12.04	25.44	59.08	0.00	72.99	15.83	61.79	8.59	2.78
13.00	0.00	58.77	0.00	73.28	53.64	48.06	6.45	2.69

t, h	pH of leaching solution				
	Initial pH 8.02	Initial pH 10.00	Initial pH 10.50	Initial pH 12.04	Initial pH 13.00
0	8.02	9.98	10.51	12.04	13.00
2	8.01	10.06	10.42	12.28	13.00
4	7.99	10.06	10.48	12.33	12.91
6	7.99	10.09	10.54	12.30	12.96
24	7.88	10.31	11.52	12.48	12.52
48	7.74	10.62	11.67	12.55	12.60
72	7.80	10.73	11.52	12.31	12.79

C1.4 Effect of glycine concentration

Experimental conditions: initial pH = 10, solid content = 2%, particle size = <2 mm, RT and ambient oxygen.

t, h	Extraction of Cu, %				
	1 M gly	0.7 M gly	0.5 M gly	0.3 M gly	0.2 M gly
0	0	0	0	0	0
2	8.66	8.37	9.02	9.01	8.40
4	14.80	15.99	14.55	13.71	13.44
6	20.44	21.71	19.87	19.65	18.49
24	57.63	61.24	68.00	64.46	56.87
48	80.72	81.22	91.34	84.18	66.98
72	88.13	87.92	96.54	87.43	75.01

Gly conc., M	Extractions at 72 h, %							
	Ni	Al	Fe	Pb	Sn	Zn	Au	Ag
0.2	6.40	39.14	0.00	10.39	10.70	56.36	2.01	0.00
0.3	5.61	29.93	0.00	22.37	25.60	81.01	1.53	0.00
0.5	12.64	15.99	0.00	46.84	9.30	92.51	1.84	0.00
0.7	37.53	21.30	0.00	60.95	1.08	88.20	0.00	0.00
1	26.90	18.84	0.00	80.47	1.56	89.12	0.00	0.00

t, h	pH of the leaching solution				
	1 M gly	0.7 M gly	0.5 M gly	0.3 M gly	0.2 M gly
0	9.95	9.95	9.98	10.04	9.98
2	10.15	10.14	10.06	10.07	10.06
4	10.15	10.2	10.06	10.13	10.21
6	9.90	9.94	10.09	10.17	10.22
24	9.96	10.04	10.31	11.01	11.63
48	10.07	10.22	10.62	11.59	11.86
72	10.04	10.21	10.73	11.72	12.26

C1.5 Effect of solid content

Experimental conditions: initial pH = 10.5, glycine concentration = 0.5 M, particle size = <2 mm, RT and ambient oxygen.

t, h	Extraction of Cu, %				
	10% solid	3.3% solid	2% solid	1.4% solid	1% solid
0	0	0	0	0	0
2	3.56	7.32	10.64	9.07	9.97
4	6.35	12.42	16.02	15.51	16.57
6	10.16	17.26	21.54	20.85	22.43
24	24.03	51.65	65.13	63.37	65.16
48	30.77	68.39	82.79	84.37	81.81
72	37.44	73.11	87.65	87.86	88.67

Solid content, %	Extractions at 72 h, %							
	Ni	Al	Fe	Pb	Sn	Zn	Au	Ag
1	0.00	71.57	0.00	85.95	59.56	92.27	0.00	0.00
1.4	11.05	82.37	0.00	72.84	68.03	95.34	2.11	0.00
2	27.15	54.20	0.00	57.12	5.99	87.38	0.00	0.00
3.3	3.87	65.69	0.00	69.26	61.34	68.80	1.54	0.00
10	3.57	53.59	0.00	37.29	12.05	32.40	0.32	0.00

t, h	pH of leaching solution				
	10% solid	3.3% solid	2% solid	1.4% solid	1% solid
0	10.53	10.53	10.51	10.53	10.53
2	10.62	10.44	10.42	10.40	10.53
4	10.90	10.67	10.48	10.67	10.60
6	11.34	10.79	10.54	10.63	10.65
24	12.26	12.09	11.52	11.09	10.86
48	12.22	12.21	11.67	11.55	11.20
72	12.22	12.22	11.52	11.88	11.12

C1.6 Effect of temperature

Experimental conditions: initial pH = 10, glycine concentration = 0.5 M, solid content = 2%, particle size = <2 mm, and ambient oxygen.

t, h	Extraction of Cu, %	
	RT	55ºC
0	0	0
2	9.02	3.45
4	14.55	8.79
6	19.87	16.85
24	68.00	76.23
48	91.34	95.23
72	96.54	100.00

Temperature	Extractions at 72 h, %							
	Fe	Ag	Au	Sn	Ni	Al	Pb	Zn
RT	0.00	0.00	1.84	9.3	12.64	15.99	46.84	92.51
55ºC	0.00	10.85	0.00	2.35	12.74	23.36	67.53	82.30

t, h	pH of leaching solution	
	RT	**55ºC**
0	9.98	10.00
2	10.06	9.70
4	10.06	9.68
6	10.09	9.45
24	10.31	9.43
48	10.62	9.10
72	10.73	9.12

C1.7 Effect of oxidant

Experimental conditions: initial pH = 10.5, glycine concentration = 0.5 M, solid content = %, particle size = <2 mm, and RT.

t, h	Extraction of Cu, %			
	Ambient O_2	**0.1% H_2O_2 (direct addition)**	**1% H_2O_2 (direction addition)**	**1% H_2O_2 (staged addition)**
0	0	0	0	0
2	9.97	33.53	47.96	48.65
4	16.57	40.57	54.52	59.87
6	22.43	45.59	56.94	65.55
24	65.16	76.17	77.31	80.62
48	81.81	86.58	87.45	86.53
72	88.67	89.57	88.30	87.81

Peroxide concentration	Extractions at 72 h, %							
	Ni	**Al**	**Fe**	**Pb**	**Sn**	**Zn**	**Au**	**Ag**
Ambient O2	0.00	71.57	0.00	85.95	59.56	92.27	0.00	0.00
0.1% H2O2 (direct addition)	0.00	81.27	0.00	83.38	79.38	97.36	6.14	0.00
1% H2O2 (direction addition)	0.00	67.26	0.00	73.84	68.51	95.42	5.08	0.00
1% H2O2 (staged addition)	0.00	0.00	0.00	63.89	0.00	96.36	0.00	0.00

C1.8 Effect of particle size

Experimental conditions: initial pH = 10, glycine concentration = 0.5 M, solid content = 2%, RT, ambient oxygen.

t, h	Extraction of Cu, %			
	<2 mm	<1 mm	<75 um	425–600 um
0	0	0	0	0
2	9.02	14.04	84.51	8.09
4	14.55	20.49	94.25	13.23
6	19.87	27.72	96.23	18.74
24	68.00	71.51	96.29	68.57
48	91.34	89.39	98.24	93.20
72	96.54	91.49	97.64	88.16

Particle size	Extractions at 72 h, %							
	Ni	Al	Fe	Pb	Sn	Zn	Au	Ag
<75 um	0.00	3.39	0.00	54.21	1.55	84.77	0.00	0.00
425–600 um	7.72	46.92	0.00	59.03	2.11	87.57	0.00	0.00
<1 mm	15.30	5.87	0.00	20.70	1.50	89.33	0.00	2.41
<2 mm	12.64	15.99	0.00	46.84	9.30	92.51	1.84	0.00

t, h	pH of leaching solution			
	<2 mm	<1 mm	<75 um	425–600 um
0	9.98	9.98	9.99	10.00
2	10.06	10.06	10.04	10.09
4	10.06	10.10	10.10	10.21
6	10.09	10.13	10.16	10.17
24	10.31	10.38	10.10	10.73
48	10.62	10.46	10.05	10.50
72	10.73	10.54	10.08	11.75

Appendix C2 Recovery of Cu from glycine leachates

C2.1 Recovery of Cu by hydrazine reduction

C2.1.1 Effect of initial pH on Cu recovery

Experimental conditions: Cu concentration = 3 g/L, glycine concentration = 0.5 M, Cu/hydrazine molar ratio = 1:1, room temperature and 30 min.

Initial pH	Final pH	Final E_h, mV vs Ag/AgCl	Recovery of Cu, %
9.00	8.88	−286	6.88
10.97	10.65	−369	10.46
11.62	10.90	−376	12.50
12.09	10.97	−382	25.57
12.8	12.61	−420	99.06

C2.1.2 Effect of Cu concentration on Cu recovery

Experimental conditions: glycine concentration = 0.5 M, initial pH = 12.1, Cu/hydrazine molar ratio = 1:1, room temperature and 30 min.

Cu concentration, g/L	Final pH	Final E_h, mV vs Ag/AgCl	Recovery of Cu, %
0.5	11.93	−392	4.35
2	11.32	Recording missed	19.29
3	10.97	−382	25.57
5	10.42	−371	75.14

C2.1.3 Effect of temperature on reduction kinetics

Experimental conditions: glycine concentration = 0.5 M, Cu concentration = 5 g/L, initial pH = 12.1, Cu/hydrazine molar ratio = 1:1.

t, min	Recovery of Cu, %		
	Room temperature	40ºC	50ºC
0	0	0	0
10	33.56	71.20	99.14
20	52.07	88.90	99.31
30	60.62	93.45	98.27
60	83.35	92.77	99.09
120	90.57	96.71	98.93
240	92.14	97.15	98.95

C2.2 Recovery of Cu by sulfide precipitation

C2.2.1 Effect of Cu/HS- molar ratio on Cu precipitation

Experimental conditions: room temperature, stirring speed = 300 rpm.

t, min	Precipitation of Cu, %		
	Cu/HS- molar ratio 1:1	Cu/HS- molar ratio 1:1.2	Cu/HS- molar ratio 1:1.3
0	0	0	0
5	88.92	97.80	97.55
10	89.66	96.55	98.43
20	89.84	99.15	99.56
30	88.49	99.54	99.67

Appendix C3 Leaching of precious metals using cyanide-starved glycine leaching system

C3.1 Effect of cyanide (CN) concentration on metal extractions

Experimental conditions: glycine amount = 4× stoichiometric amount (except the stoichiometric CN only test), initial pH = 11, particle size of feed sample = ≤ 2mm.

t, h	Extraction of Au, %					
	Stoic CN only	100 mg/L CN+4x Gly	150 mg/L CN+4x Gly	200 mg/L CN+4x Gly	250 mg/L CN+4x Gly	350 mg/L CN+4x Gly
0	0	0	0	0	0	0
2	47.24	45.28	43.32	52.22	53.09	65.75
4	55.10	52.46	46.33	56.32	59.37	67.33
6	59.85	56.18	50.78	59.56	64.70	73.60
24	64.54	57.19	58.85	73.99	74.79	81.86
48	78.87	59.83	61.39	72.40	76.95	83.39
72	81.37	64.90	63.75	76.92	78.51	83.66

t, h	Extraction of Ag, %					
	Stoic CN only	100 mg/L CN+4x Gly	150 mg/L CN+4x Gly	200 mg/L CN+4x Gly	250 mg/L CN+4x Gly	350 mg/L CN+4x Gly
0	0	0	0	0	0	0
2	60.82	66.39	83.87	83.60	85.25	77.10
4	69.85	75.25	93.11	90.20	90.20	82.51
6	71.56	80.92	93.89	100.00	100.00	89.63
24	74.38	71.49	93.89	99.53	92.73	91.00
48	88.85	59.14	78.86	82.90	75.97	81.14
72	92.89	55.16	69.05	64.66	54.67	73.12

CN concentration, mg/L	Extractions at 72 h, %							
	Cu	Ni	Zn	Sn	Pb	Al	Fe	Pd
100	36.47	1.77	13.19	0.24	3.63	6.86	0.00	45.32
150	36.59	3.58	11.75	0.43	2.27	8.68	0.00	68.88
200	43.07	7.13	15.04	0.44	2.49	9.41	0.00	61.92
250	40.61	9.99	14.74	0.16	2.18	7.72	0.00	75.63
350	41.76	15.23	20.27	0.42	5.16	8.38	0.00	66.88

CN concentration, mg/L	Cu concentration at 72 h, mg/L		
	Total Cu	Cu^{2+}	Cu^+
150	87.6	54.0	33.6
200	123.0	80.0	43.0
250	116.0	60.0	56.0
350	107.0	0.0	107.0

t, h	pH of leachate				
	100 mg/L CN	150 mg/L CN	200 mg/L CN	250 mg/L CN	350 mg/L CN
0	11.09	11.10	11.10	11.08	11.11
2	10.92	11.03	11.03	11.03	11.05
4	10.89	11.01	11.03	11.02	11.03
6	10.87	11.00	11.02	11.00	11.01
24	10.77	10.96	11.00	10.88	10.91
48	10.74	11.01	11.09	10.85	10.88
72	10.61	10.95	11.05	10.79	10.71

C3.2 Effect of glycine addition on metal extractions

Experimental conditions: CN concentration = 250 mg/L (except the stoichiometric CN only test), initial pH = 11 (pH for stoichiometric CN only at 2 h was manually adjusted to 11.47 after sampling), particle size of feed sample = ≤ 2mm.

t, h	Extraction of Au, %				
	stoic CN only	250 mg/L CN only	250 mg/L CN+2x Gly	250 mg/L CN+4x Gly	250 mg/L CN+8x Gly
0	0	0	0	0	0
2	47.24	44.90	41.12	53.09	44.91
4	55.10	54.91	47.44	59.37	47.79
6	59.85	56.23	50.31	64.70	49.41
24	64.54	66.99	61.69	74.79	68.30
48	78.87	67.96	64.50	76.95	73.47
72	81.37	69.05	64.43	78.51	76.61

t, h	Extraction of Ag, %				
	stoic CN only	250 mg/L CN only	250 mg/L CN+2x Gly	250 mg/L CN+4x Gly	250 mg/L CN+8x Gly
0	0	0	0	0	0
2	60.82	50.17	80.12	85.25	90.69
4	69.85	59.36	92.68	90.20	100.00
6	71.56	78.73	93.57	100.00	97.70
24	74.38	59.58	100.00	92.73	97.70
48	88.85	59.58	85.84	75.97	84.21
72	92.89	77.46	71.85	54.67	66.43

Gly addition	Extractions at 72 h, %							
	Cu	Ni	Zn	Sn	Pb	Al	Fe	Pd
Stoic CN only	37.96	8.45	18.56	0.44	3.24	12.14	0.00	46.05
250mg/L CN only	22.96	2.65	8.79	0.03	1.95	2.05	0.17	45.46
250mg/L CN+2x Gly	25.71	11.65	5.28	0.04	3.36	1.89	0.00	59.69
250mg/L CN+4x Gly	38.18	9.99	14.74	0.16	2.18	7.72	0.00	75.63
250mg/L CN+8x Gly	41.19	12.13	20.69	0.41	6.11	7.88	0.00	73.92

t, h	pH of leachate				
	stoic CN only	250 mg/L CN only	250 mg/L CN+2x Gly	250 mg/L CN+4x Gly	250 mg/L CN+8x Gly
0	11.06	11.10	11.02	11.08	11.02
2	10.47	10.64	10.75	11.03	10.95
4	11.30	10.62	10.68	11.02	10.96
6	11.27	10.61	10.68	11.00	10.96
24	11.23	10.47	10.54	10.88	10.92
48	10.96	10.15	10.35	10.85	10.91
72	10.66	9.84	10.22	10.79	10.90

C3.3 Effect of initial pH on metal extractions

Experimental conditions: glycine amount = 4× stoichiometric amount, CN concentration = 200 mg/L, particle size of feed sample = ≤ 2mm.

t, h	Extraction of Au, %			
	initial pH 10.5	initial pH 11.0	initial pH 12.0	initial pH 12.5
0	0	0	0	0
2	34.49	52.22	35.69	32.63
4	40.53	56.32	42.89	37.12
6	43.61	59.56	42.89	41.02
24	52.76	73.99	60.97	58.67
48	53.51	72.40	62.96	59.30
72	54.62	76.92	61.90	58.63

t, h	Extraction of Ag, %			
	initial pH 10.5	initial pH 11.0	initial pH 12.0	initial pH 12.5
0	0	0	0	
2	78.57	83.60	37.50	35.93
4	93.66	90.20	43.96	42.29
6	99.06	100.00	42.75	44.24
24	100.00	99.53	45.26	48.20
48	82.31	82.90	39.37	42.05
72	66.97	64.66	34.48	37.74

Initial pH	Extractions at 72 h, %							
	Cu	Ni	Zn	Sn	Pb	Al	Fe	Pd
10.5	25.59	9.62	10.28	0.05	3.34	1.66	0.00	48.24
11	43.07	7.13	15.04	0.44	2.49	9.41	0.00	61.92
12	24.60	0.00	8.41	1.15	6.92	33.11	0.00	35.25
12.5	26.50	0.62	17.85	2.46	39.83	53.98	0.00	49.63

t, h	pH of leachate			
	initial pH 10.5	initial pH 11	initial pH 12	initial pH 12.5
0	10.50	11.10	12.00	12.51
2	10.44	11.03	11.84	12.37
4	10.46	11.03	11.86	12.34
6	10.46	11.02	11.84	12.36
24	10.45	11.00	11.81	12.41
48	10.44	11.09	11.80	12.37
72	10.35	11.05	11.76	12.32

C3.4 Effect of particle size on metal extractions

C3.4.1 Intensive cyanidation

Experimental conditions: CN concentration = 3,500 mg/L, 48 h for each stage, pH maintained at 11.

Metal	Extraction, %	
	≤2 mm, 1st stg.	≤2 mm, 2nd stg.
Au	72.9	7.3
Ag	75.4	12.1
Cu	47.3	19.5

Metal	Extraction, %	
	≤1 mm, 1st stg.	≤1 mm, 2nd stg.
Au	74.4	9.6
Ag	64.0	19.5
Cu	78.5	11.0

Metal	Extraction, %	
	Pulverised, 1st stg.	Pulverised, 2nd stg.
Au	89.6	1.5
Ag	84.2	5.0
Cu	90.6	3.0

C3.4.2 Cyanide-starved glycine leaching

Experimental conditions: glycine amount = 4× stoichiometric amount, CN concentration = 250 mg/L, initial pH = 11, pH for pulverised sample at 2 h was manually adjusted to 11.0 after sampling.

t, h	Extraction of Au, %		
	~2 mm	~1 mm	Pulverised
0	0	0	0
2	53.09	38.21	36.21
4	59.37	41.59	41.42
6	64.70	40.10	49.60
24	74.79	60.79	85.62
48	76.95	69.17	88.89
72	78.51	69.17	89.77
96	N/A	N/A	90.06

N/A: experiments were stopped at 72 h, the 96 h data were therefore not applicable, same below.

t, h	Extraction of Ag, %		
	~2 mm	~1 mm	Pulverised
0	0	0	0
2	85.25	100.00	64.56
4	90.20	95.95	56.35
6	100.00	81.25	55.33
24	92.73	64.08	73.18
48	75.97	51.15	77.16
72	54.67	45.25	85.29
96	N/A	N/A	89.41

t, h	Extraction of Cu, %		
	~2 mm	~1 mm	Pulverised
0	0	0	0
2	12.95	6.66	18.10
4	15.79	11.15	25.95
6	20.01	14.10	33.04
24	24.88	40.49	64.21
48	33.81	57.03	73.11
72	40.61	65.04	78.27
96	N/A	N/A	81.02

t, h	pH of leachate		
	~2 mm	~1 mm	Pulverised
0	11.08	11.09	11.02
2	11.03	11.05	10.93
4	11.02	11.06	11.02
6	11.00	11.06	11.07
24	10.88	11.27	11.37
48	10.85	11.31	11.08
72	10.79	11.31	10.95

C3.5 Effect of the method of cyanide addition

Experimental conditions: glycine amount = 4× stoichiometric amount, CN concentration = 250 mg/L, initial pH = 11, pulverised sample.

t, h	Extraction of Au, %	
	All at initial	Staged addition
0	0	0
2	36.21	14.16
4	41.42	22.52
6	49.60	24.88
24	85.62	55.53
48	88.89	83.83
72	89.77	88.89
96	90.06	89.84

t, h	Extraction of Ag, %	
	All at initial	Staged addition
0	0	0
2	64.56	23.48
4	56.35	31.04
6	55.33	33.99
24	73.18	57.04
48	77.16	76.70
72	85.29	86.34
96	89.41	89.15

t, h	Extraction of Cu, %	
	All at initial	Staged addition
0	0	0
2	18.10	15.51
4	25.95	26.41
6	33.04	31.07
24	64.21	63.37
48	73.11	73.70
72	78.27	77.10
96	81.02	79.20

t, h	Cu concentration, mg/L			
	Cu^+, all at initial	Cu^+, staged addition	Cu^{2+}, all at initial	Cu^{2+}, staged addition
2	74.4	35	0	27
4	107	49	9	57
6	91	58	53	67
24	75	76	197	182
48	69	71	258	230
72	46	60	300	260

Appendix C4 Leaching of precious metals using non-NaCN glycine leaching system

C4.1 Effect of particle size

Experimental conditions: glycine concentration = 0.5 M, Ferricyanide concentration = 0.08 M, room temperature.

t, h	Extraction of Au, %	
	Un-pulverised	Pulverised
0	0	0
2	1.55	8.50
6	29.08	25.94
24	42.57	55.35
48	47.51	69.35
72	59.72	78.01

C4.2 Effect of oxidant

Experimental conditions: using pulverised sample, glycine concentration = 1.0 M, 35°C.

t, h	Extraction of Au, %					
	No addit. oxidant	0.08 M ferricyanide	0.16 M ferricyanide	0.04 M permanganate	0.16 M permanganate	0.08 M permanganate
0	0	0	0	0	0	0
2	2.35	28.24	38.97	11.47	1.85	18.03
6	2.35	43.26	58.00	15.51	6.93	20.19
24	2.35	50.34	64.42	24.55	12.24	24.73
48	7.80	56.87	68.81	31.85	34.92	43.87
72	16.54	56.63	65.11	37.41	59.32	52.01
96	19.58	58.20	68.26	39.35	69.46	54.23

t, h	E_h, mV vs Ag/AgCl					
	No addit. oxidant	0.08 M ferricyanide	0.16 M ferricyanide	0.04 M permanganate	0.16 M permanganate	0.08 M permanganate
2	−37	176	202	−17	−68	−29
6	−80	84	179	−5	−48	−62
24	−96	−67	−75	−36	−55	−26
48	−112	−64	−64	−60	−31	−50
72	−52	−61	−51	−35	−10	−10

Note: E_h measured at each sampling time before adding oxidant.

C4.3 Effect of temperature

Experimental conditions: using pulverised sample, glycine concentration = 1.0 M.

t, h	Extraction of Au, %					
	0.08 M ferricyanide, RT	0.08 M ferricyanide, 35ºC	0.08 M ferricyanide, 55ºC	0.08 M permanganate, RT	0.08 M permanganate, 55ºC	0.08 M permanganate, 35ºC
0	0	0	0	0	0	0
2	9.71	28.24	27.53	3.80	1.14	18.03
6	33.63	43.26	37.58	3.80	8.71	20.19
24	56.02	50.34	45.47	6.97	28.04	24.73
48	63.76	56.87	54.04	13.73	39.77	43.87
72	76.72	56.63	61.75	56.23	48.34	52.01

t, h	E_h, mV vs Ag/AgCl					
	0.08 M ferricyanide, RT	0.08 M ferricyanide, 35ºC	0.08 M ferricyanide, 55ºC	0.08 M permanganate, RT	0.08 M permanganate, 55ºC	0.08 M permanganate, 35ºC
2	245	176	−23	13	−107	−29
6	202	84	−38	12	−37	−62
24	22	−67	−49	15	−18	−26
48	21	−64	−49	14	3	−50
72	12	−61	−5	8	−2	−10

Note: E_h measured at each sampling time before adding oxidant.

C4.4 Effect of glycine concentration

Experimental conditions: using pulverised sample, room temperature.

t, h	Extraction of Au, %			
	0.08 M ferricyanide, 0.5 M gly	0.08 M ferricyanide, 1 M gly	0.08 M permanganate, 0.5 M gly	0.08 M permanganate, 1 M gly
0	0	0	0	0
2	8.50	9.71	3.36	3.80
6	25.94	33.63	7.28	3.80
24	55.35	56.02	51.15	6.97
48	69.35	63.76	75.09	13.73
72	78.01	76.72	86.10	56.23

t, h	E_h, mV vs Ag/AgCl			
	0.08 M ferricyanide, 0.5 M gly	0.08 M ferricyanide, 1 M gly	0.08 M permanganate, 0.5 M gly	0.08 M permanganate, 1 M gly
2	231	245	65	13
6	229	202	10	12
24	215	22	50	15
48	200	21	65	14
72	167	12	55	8

Note: E_h measured at each sampling time before adding oxidant.

C4.5 Effect of E_h

Experimental conditions: using pulverised sample, glycine concentration = 0.5M, room temperature.

t, h	Extraction of Au, %		
	0.08 M permanganate, man. addit.	E_h = 50–100 mV	E_h = 100–150 mV
0	0	0	0
2	3.37	11.45	8.56
6	7.30	18.94	29.88
24	51.34	38.03	49.09
48	75.09	44.64	84.29
72	86.05	51.64	83.82

t, h	Extraction of Au, %				
	0.08 M ferricyanide, man. addit.	E_h = 50–100 mV	E_h = 100–150 mV	E_h = 150–250 mV	E_h = 250–350 mV
0	0	0	0	0	0
2	8.50	0.82	7.05	8.07	9.82
6	25.94	16.98	19.31	26.73	32.27
24	55.35	30.65	38.83	53.80	69.03
48	69.35	44.01	54.31	69.06	75.61
72	78.01	47.20	76.54	75.65	77.51

Bibliography

Adaikkalam, P., Sathaiyan, N. and Visvanathan, S., 1993. Electrolytic regeneration of bleach solution in the motion picture industry. J. Chem. Technol. Biotechnol., 56(4): 389–392.

Adams, M., 1990. The mechanism of adsorption of aurocyanide onto activated carbon, 1. Relation between the effects of oxygen and ionic strength. Hydrometallurgy, 25(2): 171–184.

Adams, M.D., 2016a. Gold ore processing: project development and operations. Elsevier, pp.447–484.

Adams, M.D., 2016b. Comparison of the MMS CN-D^{TM} Cyanide destruction process with Caro's Acid, SMBS/Air and hydrogen peroxide options. Proceedings of ALTA Conference 2016, Perth, Australia, 21–28 May.

Aliyu, H.N. and Na'Aliya, J., 2012. Potentiometric studies on essential metal (II) amino acid complexes. International Research J. Pharm. Pharmacol., 2(2): 76–80.

Akcil, A., Erust, C., Gahan, C. S., Ozgun, M., Sahin, M. and Tuncuk, A., 2015. Precious metal recovery from waste printed circuit boards using cyanide and non-cyanide lixiviants–a review. Waste Manage., 45: 258–271.

Aksu, S. and Doyle, F.M., 2001. Electrochemistry of copper in aqueous glycine solutions. J. Electrochem. Soc., 148(1): B51–B57.

Aksu, S., Wang, L., Doyle, F.M., 2003. Effect of hydrogen peroxide on oxidation of copper in CMP slurries containing glycine. J. Electrochem. Soc. 150(11), G718–G723.

Alam, M.S., Tanaka, M., Koyama, K., Oishi, T. and Lee, J.C., 2007. Electrolyte purification in energy-saving monovalent copper electrowinning processes. Hydrometallurgy, 87(1): 36–44.

Aleksandrov, Y.A., Tsyganova, E.I. and Pisarev, A.L., 2003. Reaction of Aluminum with Dilute Aqueous NaOH Solutions. Russ. J. Gen. Chem., 73(5): 689–694.

Altansukh, B., Haga, K., Ariunbolor, N., Kawamura, S. and Shibayama, A., 2016. Leaching and Adsorption of Gold from Waste Printed Circuit Boards Using Iodine-Iodide Solution and Activated Carbon. Eng. J., 20(4).

Anand, A., Jha, M.K., Kumar, V. and Sahu, R., 2013. Recycling of Precious Metal Gold from Waste Electrical and Electronic Equipments (WEEE): A review, Proceedings of the XIII International Seminar on Mineral Processing Technology (MPT-2013), pp. 916–923.

Arellano, C.A.P. and Martínez, S.S., 2010. Effects of pH on the degradation of aqueous ferricyanide by photolysis and photocatalysis under solar radiation. Sol. Energy Mater. Sol. Cells, 94(2): 327–332.

Awasthi, A.K. and Li, J., 2017. An overview of the potential of eco-friendly hybrid strategy for metal recycling from WEEE. Resour. Conserv. Recy., 126 (Supplement C): 228–239.

Awasthi, A.K., Zeng, X. and Li, J., 2016. Environmental pollution of electronic waste recycling in India: A critical review. Environ. Pollut., 211: 259–270.

Aylmore, M., 2016. Alternative lixiviants to cyanide for leaching gold ores, Gold Ore Processing (Second Edition). Elsevier, pp. 447–484.

Baldé, C.P., Forti V., Gray, V., Kuehr, R. and Stegmann, P., 2017. The global e-waste monitor - 2017, United Nations University (UNU), International Telecommunication Union (ITU) & International Solid Waste Association (ISWA). Available at https://www.itu.int/en/ITU-D/Climate-Change/Documents/GEM%202017/Global-E-waste%20Monitor%202017%20.pdf

Baldé, C.P., Wang, F., Kuehr, R. and Huisman, J., 2015. The global e-waste monitor - 2014. United Nations University (UNU), IAS-SCYCLE, Bonn, Germany. Available at https://i.unu.edu/media/unu.edu/news/52624/UNU-1stGlobal-E-Waste-Monitor-2014-small.pdf

Bandyopadhyay, A., 2008. A regulatory approach for e-waste management: a cross-national review of current practice and policy with an assessment and policy recommendation for the Indian perspective. Int. J. Environ. Waste Manage., 2(1): 26–39.

Barbosa-Filho, O. and Monhemius, A.J., 1994. Iodide-thiocyanate leaching system for gold, Hydrometallurgy "94". Springer Netherlands, Dordrecht, pp. 425–440.

Bari, M., Begum, M., Jamaludin, S. and Hussin, K., 2009. Solvent extraction separation and recovery of copper, nickel and zinc from printed circuit board by Cyanex 272. Miner. Process. Extr. Metall., 118(4): 227–234.

Bas, A.D., Deveci, H. and Yazici, E.Y., 2014. Treatment of manufacturing scrap TV boards by nitric acid leaching. Sep. Purif. Technol., 130: 151–159.

Behnamfard, A., Salarirad, M.M. and Veglio, F., 2013. Process development for recovery of copper and precious metals from waste printed circuit boards with emphasize

on palladium and gold leaching and precipitation. Waste Manage., 33(11): 2354–2363.

Birloaga, I., Coman, V., Kopacek, B. and Vegliò, F., 2014a. An advanced study on the hydrometallurgical processing of waste computer printed circuit boards to extract their valuable content of metals. Waste Manage., 34(12): 2581–2586.

Birloaga, I. and Vegliò, F., 2016. Study of multi-step hydrometallurgical methods to extract the valuable content of gold, silver and copper from waste printed circuit boards. J. Environ. Chem. Eng., 4(1): 20–29.

Bisceglie, F., Civati, D., Bonati, B. and Faraci, F.D., 2017. Reduction of potassium cyanide usage in a consolidated industrial process for gold recovery from wastes and scraps. J. Clean. Prod., 142: 1810–1818.

Breuer, P., Dai, X., Jeffrey, M., 2005. Leaching of gold and copper minerals in cyanide deficient copper solutions. Hydrometallurgy 78(3), 156–165.

Bryson, A.W., 1995. Gold adsorption by activated carbon and resin. Miner. Process. Extr. Metall. Rev., 15(1–4): 145–151.

Buekens, A., Yang, J., 2014. Recycling of WEEE plastics: a review. J. Mater. Cycles Waste Manag. 16(3), 415–434.

Calgaro, C. O., Schlemmer, D. F., da Silva, M. D. C. R., Maziero, E. V., Tanabe, E. H. and Bertuol, D. A., 2015. Fast copper extraction from printed circuit boards using supercritical carbon dioxide. Waste Manage., 45: 289–297.

Chai, L., Zhong, H., Zhang, C., Okido, M. and Ichino, R., 1997. Study on selective dissolution of gold in alkaline thiourea media. J. Cent. South Univ. Technol., 4(2): 79–83.

Chauhan, G., Jadhao, P.R., Pant, K.K. and Nigam, K.D.P., 2018. Novel technologies and conventional processes for recovery of metals from waste electrical and electronic equipment: Challenges & opportunities – A review. J. Environ. Chem. Eng., 6(1): 1288–1304.

Chauhan, G., Pant, K. and Nigam, K., 2015. Chelation technology: a promising green approach for resource management and waste minimization. Environ. Sci.: Process. Imp., 17(1): 12–40.

Chen, J.P. and Lim, L.L., 2002. Key factors in chemical reduction by hydrazine for recovery of precious metals. Chemosphere, 49(4): 363–370.

Chen, M., Huang, J., Ogunseitan, O.A., Zhu, N. and Wang, Y.-m., 2015a. Comparative study on copper leaching from waste printed circuit boards by typical ionic liquid acids. Waste Manage., 41: 142–147.

Chen, M., Zhang, S., Huang, J. and Chen, H., 2015b. Lead during the leaching process of copper from waste printed circuit boards by five typical ionic liquid acids. J. Clean. Prod., 95: 142–147.

Chen, Y., Li, J., Chen, L., Chen, S. and Diao, W., 2012. Brominated flame retardants (BFRs) in waste electrical and electronic equipment (WEEE) plastics and printed circuit boards (PCBs). Procedia Environ. Sci., 16: 552–559.

Chen, W.D., Kang, S.-K., Stark, W.J., Rogers, J.A. and Grass, R.N., 2019. The light triggered dissolution of gold wires using potassium ferrocyanide solutions enables cumulative illumination sensing. Sens. Actuators B Chem., 282: 52–59.

China Household Electric Appliances Research Institute (CHEARI), 2017. White Paper on WEEE Recycling Industry in China - 2016. Available at https://bcrc.tsinghua.edu.cn/col/1357523858259/2017/10/11/1507709623374.html

Chung, J., Jeong, E., Choi, J. W., Yun, S. T., Maeng, S. K. and Hong, S. W., 2015. Factors affecting crystallization of copper sulfide in fed-batch fluidized bed reactor. Hydrometallurgy, 152: 107–112.

Cui, H. and Anderson, C., 2016. Literature Review of Hydrometallurgical Recycling of Printed Circuit Boards (PCBs). J. Adv. Chem. Eng., 6(1): 142–153.

Cui, J. and Forssberg, E., 2003. Mechanical recycling of waste electric and electronic equipment: a review. J. Hazard. Mater., 99(3): 243–263.

Cui, J. and Zhang, L., 2008. Metallurgical recovery of metals from electronic waste: A review. J. Hazard. Mater., 158(2): 228–256.

D'Adamo, I., Ferella, F., Gastaldi, M., Maggiore, F., Rosa, P. and Terzi, S., 2019. Towards sustainable recycling processes: Wasted printed circuit boards as a source of economic opportunities. Resour. Conserv. Recy., 149: 455–467.

Dean, J.A., 1999. Lange's handbook of chemistry (15th edition). McGraw-Hill Inc.

Deng, Z., Oraby, E. and Eksteen, J., 2019a. The sulfide precipitation behaviour of Cu and Au from their aqueous alkaline glycinate and cyanide complexes. Sep. Purif. Technol., 218: 181–190.

Deng, Z. Oraby, E.A., Eksteen, J.J. 2019b. Sulfide precipitation of copper from alkaline glycine-cyanide solutions: precipitate characterisation. Miner. Eng., 145, 106102.

Deng, Z., Oraby, E.A. and Eksteen, J.J., 2020a. Gold recovery from cyanide-starved glycine solutions in the presence of Cu using a molecularly imprinted resin (IXOS-AuC). Hydrometallurgy, 196: 105425.

Deng, Z., Oraby, E.A., and Eksteen, J.J., 2020b. Cu adsorption behaviours onto chelating resins from glycine-cyanide solutions: Isotherms, kinetics and regeneration studies. Sep. Purif. Technol., 236, 116280.

Deveci, H., Yazici, E. and Bas, A., 2016. Cementation of silver from synthetic leach solutions of waste of printed circuit boards (WPCB), IMPC 2016: XXVIII International Mineral Processing Congress Proceedings, pp. 1–9.

Davenport, W.G., King, M.J., Schlesinger, M.E. and Biswas, A.K., 2002. Extractive metallurgy of copper. Elsevier Science & Technology.

Diaz, L.A., Lister, T.E., Parkman, J.A. and Clark, G.G., 2016. Comprehensive process for the recovery of value and critical materials from electronic waste. J. Clean. Prod., 125: 236–244.

Duan, H., Hou, K., Li, J. and Zhu, X., 2011. Examining the technology acceptance for dismantling of waste printed circuit boards in light of recycling and environmental concerns. J. Environ. Manage., 92(3): 392–399.

Duan, C.L., Diao, Z.J., Zhao, Y.M. and Huang, W., 2015. Liberation of valuable materials in waste printed circuit boards by high-voltage electrical pulses. Miner. Eng., 70: 170–177.

Du, X.L., Qin, Y.H., Wu, Z.K., Chi, R.A. and Wang, C.W., 2017. Kinetics on leaching of potassium from phosphorus–potassium associated ore in HCl–H_3PO_4 media. Trans. Nonferrous Met. Soc. China, 27(8): 1870–1877.

Eksteen, J.J. and Oraby, E.A., 2014. A process for copper and/or precious metal recovery. US Patent 20160194734 A1.

Eksteen, J. and Oraby, E., 2015. The leaching and adsorption of gold using low concentration amino acids and hydrogen peroxide: Effect of catalytic ions, sulphide minerals and amino acid type. Miner. Eng., 70: 36–42.

Eksteen, J. and Oraby, E., 2016. Process for selective recovery of chalcophile group elements. PCT Patent WO2016141438A1.

Eksteen, J.J., Oraby, E.A., Lombard, L., Di Prinzio, L., 2018. Leaching of cobalt bearing nickel sulfide and furnace converter mattes with alkaline glycine, and subsequent SX and IX. Proceedings of ALTA Conference 2018, Perth, Australia, 19–26 May.

Eksteen, J.J., Oraby, E.A., Tanda, B.C., 2017. A conceptual process for copper extraction from chalcopyrite in alkaline glycinate solutions. Miner. Eng. 108, 53–66.

Eksteen, J.J., Oraby, E.A., Tanda, B.C., Tauetsile, P.J., Bezuidenhout, G.A., Newton T. Trask, F., Bryan, I., 2018. Towards Industrial Implementation of Glycine-Based Leach and Adsorption Technologies for Gold-Copper Ores. Can. Metall. Quart., 57(4), 390–398.

Estay, H., 2018. Designing the SART process – A review. Hydrometallurgy, 176: 147–165.

European Union, 2012. Directive 2012/19/EU of the European Parliament and of the Council of 4 July 2012 on waste electrical and electronic equipment (WEEE). Off. J. Eur. Union (OJEU), 197: 38–71.

Ficeriová, J., Baláž, P. and Gock, E., 2011. Leaching of gold, silver and accompanying metals from circuit boards (PCBs) waste. Acta Montan. Slovaca, 16(2): 128.

Forti, V., Baldé, C.P., Kuehr, R. and Bel, G., 2020. The global e-waste monitor - 2020. United Nations University (UNU)/United Nations Institute for Training and Research (UNITAR) – co-hosted SCYCLE Programme, International Telecommunication Union (ITU) & International Solid Waste Association (ISWA), Bonn/Geneva/Rotterdam. Available at https://www.itu.int/myitu/-/media/Publications/2020-Publications/Global-E-waste-Monitor-2020.pdf

Fırlak, M., Yetimoğlu, E.K. and Kahraman, M.V., 2014. Adsorption of Au (III) ions from aqueous solutions by thiol-ene photoclick hydrogels and its application to electronic waste and geothermal water. J. Water Process Eng., 3: 105–116.

Galbács, Z.M. and Csányi, L.J., 1983. Alkali-induced decomposition of hydrogen peroxide. J. Chem. Soc. Dalton Trans., 0: 2353–2357.

Gary, M.L., Paul, S.J. and Donald, T.A., 2014. Inorganic Chemistry (5th Edition).

Ghosh, B., Ghosh, M., Parhi, P., Mukherjee, P. and Mishra, B., 2015. Waste printed circuit boards recycling: an extensive assessment of current status. J. Clean. Prod., 94: 5–19.

Ghosh, S. K., Debnath, B., Baidya, R., De, D., Li, J., Ghosh, S. K., Zheng, L., Awasthi, A. K., Liubarskaia, M. A. and Ogola, J. S., 2016. Waste electrical and electronic equipment management and Basel Convention compliance in Brazil, Russia, India, China and South Africa (BRICS) nations. Waste Manage. Res., 34(8): 693–707.

González-López, J., Rodelas, B., Pozo, C., Salmerón-López, V., Martínez-Toledo, M., Salmerón, V., 2005. Liberation of amino acids by heterotrophic nitrogen fixing bacteria. Amino Acids 28(4), 363–367.

Gu, F., Ma, B., Guo, J., Summers, P.A. and Hall, P., 2017. Internet of things and Big Data as potential solutions to the problems in waste electrical and electronic equipment management: An exploratory study. Waste Manage., 68: 434–448.

Guo, J., Guo, J. and Xu, Z., 2009. Recycling of non-metallic fractions from waste printed circuit boards: a review. J. Hazard. Mater., 168(2): 567–590.

Gurung, M., Adhikari, B B., Kawakita, H., Ohto, K., Inoue, K. and Alam, S., 2012. Selective recovery of precious metals from acidic leach liquor of circuit boards of spent mobile phones using chemically modified persimmon tannin gel. Ind. Eng. Chem. Res., 51(37): 11901–11913.

Gurung, M., Adhikari, B B., Kawakita, H., Ohto, K., Inoue, K. and Alam, S., 2013. Recovery of gold and silver from spent mobile phones by means of acidothiourea leaching followed by adsorption using biosorbent prepared from persimmon tannin. Hydrometallurgy, 133: 84–93.

Hadi, P., Xu, M., Lin, C.S., Hui, C.-W. and McKay, G., 2015. Waste printed circuit board recycling techniques and product utilization. J. Hazard. Mater., 283: 234–243.

Hagelüken, C. and Corti, C.W., 2010. Recycling of gold from electronics: Cost-effective use through 'Design for Recycling'. Gold Bull., 43(3): 209–220.

Hao, J., Wang, Y., Wu, Y. and Guo, F., 2020. Metal recovery from waste printed circuit boards: A review for current status and perspectives. Resour. Conserv. Recy., 157: 104787.

Herat, S., 2008. Environmental impacts and use of brominated flame retardants in electrical and electronic equipment. journal article Thesis, 348–357 pp.

Hilson, G. and Monhemius, A.J., 2006. Alternatives to cyanide in the gold mining industry: what prospects for the future? J. Clean. Prod., 14(12): 1158–1167.

Hotea, V., 2013. Clean technology of lead recovery from spent lead paste, WSEAS Conference program, Chania, Crete Island, Greece., 2: 263–269.

House, J.E., 2008. Inorganic Chemistry, 1st ed. Burlington, USA.

Huang, J., Chen, M., Chen, H., Chen, S. and Sun, Q., 2014. Leaching behavior of copper from waste printed circuit boards with Brønsted acidic ionic liquid. Waste Manage., 34(2): 483–488.

Insausti, M.J., Mata-Pérez, F. and Alvarez-Macho, M.P., 1996. Kinetic study of the oxidation of glycine by permanganate ions in acid medium. Collect. Czechoslov. Chem. Commun., 61(2): 232–241.

Işıldar, A., Rene, E.R., van Hullebusch, E.D. and Lens, P.N.L., 2018. Electronic waste as a secondary source of critical metals: Management and recovery technologies. Resour. Conserv. Recy., 135: 296–312.

Islam, A., Ahmed, T., Awual, M. R., Rahman, A., Sultana, M., Aziz, A. A., Monir, M. U., Teo, S. H. and Hasan, M., 2020. Advances in sustainable approaches to recover metals from e-waste-A review. J. Clean. Prod., 244: 118815.

Islam, M.T. and Huda, N., 2020. Assessing the recycling potential of "unregulated" e-waste in Australia. Resour. Conserv. Recy., 152: 104526.

Issa, I.M. and Issa, R.M., 1954. Formic acid as a reagent for alkaline permanganate: Potentiometric determination of formate. Anal. Chim. Acta, 11: 192–199.

Jadhao, P., Chauhan, G., Pant, K. and Nigam, K., 2016. Greener approach for the extraction of copper metal from electronic waste. Waste Manage., 57: 102–112.

Jadhav, U. and Hocheng, H., 2015. Hydrometallurgical recovery of metals from large printed circuit board pieces. Sci. Rep., 5: 14574.

Janjevic, D., 2018. Thailand moves to ban importing e-waste and plastic. Avaliable at https://www.dw.com/en/thailand-moves-to-ban-importing-e-waste-and-plastic/a-45103610 (accessed on 01/07/2019)

Jha, M. K., Kumari, A., Choubey, P. K., Lee, J., Kumar, V and Jeong, J., 2012. Leaching of lead from solder material of waste printed circuit boards (PCBs). Hydrometallurgy, 121: 28–34.

Jha, M. K., Lee, J., Kumari, A., Choubey, P. K., Kumar, V and Jeong, J., 2011. Pressure leaching of metals from waste printed circuit boards using sulfuric acid. JOM, 63(8): 29–32.

Joda, N.N. and Rashchi, F., 2012. Recovery of ultra fine grained silver and copper from PC board scraps. Sep. Purif. Technol., 92: 36–42.

Jung, M., Yoo, K. and Alorro, R.D., 2017. Dismantling of Electric and Electronic Components from Waste Printed Circuit Boards by Hydrochloric Acid Leaching with Stannic Ions. Mater. Trans., 58(7): 1076–1080.

Kannan, D., Govindan, K. and Shankar, M., 2016. India: Formalize recycling of electronic waste. Nature, 530(7590): 281–281.

Kasper, A.C., Carrillo Abad, J., Garcia Gabaldon, M., Veit, H.M. and Perez Herranz, V., 2016. Determination of the potential gold electrowinning from an ammoniacal thiosulphate solution applied to recycling of printed circuit board scraps. Waste Manage. Res., 34(1): 47–57.

Kavousi, M., Sattari, A., Alamdari, E.K. and Firozi, S., 2017. Selective separation of copper over solder alloy from waste printed circuit boards leach solution. Waste Manage., 60: 636–642.

Kaya, M., 2016. Recovery of metals and nonmetals from electronic waste by physical and chemical recycling processes. Waste Manage., 57: 64–90.

Kékesi, T., Török, T.I. and Kabelik, G., 2000. Extraction of tin from scrap by chemical and electrochemical methods in alkaline media. Hydrometallurgy, 55(2): 213–222.

Khaliq, A., Rhamdhani, M.A., Brooks, G., Masood, S., 2014. Metal extraction processes for electronic waste and existing industrial routes: a review and Australian perspective. Resources 3(1), 152–179.

Khanna, P.K., Gaikwad, S., Adhyapak, P.V., Singh, N. and Marimuthu, R., 2007. Synthesis and characterization of copper nanoparticles. Materials Letters, 61(25): 4711–4714.

Kiddee, P., Naidu, R. and Wong, M.H., 2013. Electronic waste management approaches: An overview. Waste Manage., 33(5): 1237–1250.

Kim, E.-y., Kim, M.-s., Lee, J.-c., Jeong, J. and Pandey, B., 2011a. Leaching kinetics of copper from waste printed circuit boards by electro-generated chlorine in HCl solution. Hydrometallurgy, 107(3): 124–132.

Kim, E.-y., Kim, M.-s., Lee, J.-c. and Pandey, B., 2011b. Selective recovery of gold from waste mobile phone PCBs by hydrometallurgical process. J. Hazard. Mater., 198: 206–215.

Kim, B.-S., Lee, J.-c., Seo, S.-P., Park, Y.-K., Sohn, H.Y., 2004. A process for extracting precious metals from spent printed circuit boards and automobile catalysts. JOM 56(12), 55–58.

Kiss, T., Sovago, I. and Gergely, A., 1991. Critical survey of stability constants of complexes of glycine. Pure Appl. Chem., 63(4): 597–638.

Kobayashi, S., Hiroishi, K., Tokunoh, M. and Saegusa, T., 1987. Chelating properties of linear and branched poly(ethylenimines). Macromolecules, 20(7): 1496–1500.

Koyama, K., Tanaka, M. and Lee, J.-c., 2006. Copper leaching behavior from waste printed circuit board in ammoniacal alkaline solution. Mater. Trans., 47(7): 1788–1792.

Koyanaka, S., Endoh, S. and Ohya, H., 2006. Effect of impact velocity control on selective grinding of waste printed circuit boards. Adv. Powder Technol., 17(1): 113–126.

Kumar, M., Lee, J.-c., Kim, M.-S., Jeong, J. and Yoo, K., 2014. Leaching of metals from waste printed circuit boards (WPCBs) using sulfuric and nitric acids. Environ. Eng. Manag. J., 13(10).

Kumar, A., Holuszko, M. and Espinosa, D.C.R., 2017. E-waste: An overview on generation, collection, legislation and recycling practices. Resour. Conserv. Recy., 122: 32–42.

Kumari, A., Jha, M.K., Lee, J.-c. and Singh, R.P., 2016. Clean process for recovery of metals and recycling of acid from the leach liquor of PCBs. J. Clean. Prod., 112: 4826–4834.

Kumari, A., Jha, M.K. and Singh, R.P., 2016. Recovery of metals from pyrolysed PCBs by hydrometallurgical techniques. Hydrometallurgy, 165: 97–105.

Kyle, J., 1997. Stability of metal-cyanide and hydroxide complexes, World Gold'97, Singapore, pp.163–169.

Lacoste-Bouchet, P., Deschênes, G. and Ghali, E., 1998. Thiourea leaching of a copper-gold ore using statistical design. Hydrometallurgy, 47(2): 189–203.

Laitos, J.G., 2013. Cyanide, mining, and the environment. Pace Environ. Law Rev., 30(3): 869.

Lee, D., Offenhuber, D., Duarte, F., Biderman, A. and Ratti, C., 2018. Monitour: Tracking global routes of electronic waste. Waste Manage., 72: 362–370.

Lee, J.-c. and Pandey, B.D., 2012. Bio-processing of solid wastes and secondary resources for metal extraction–a review. Waste Manage., 32(1): 3–18.

Lekka, M., Masavetas, I., Benedetti, A., Moutsatsou, A. and Fedrizzi, L., 2015. Gold recovery from waste electrical and electronic equipment by electrodeposition: A feasibility study. Hydrometallurgy, 157: 97–106.

Lewis Sr, R.J., 2008. Hazardous chemicals desk reference. John Wiley & Sons.

Li, B., Pan, D. A., Jiang, Y. H., Tian, J. J., Zhang, S.G. and Zhang, K., 2014a. Recovery of copper and tin from stripping tin solution by electrodeposition. Rare Metals, 33(3): 353–357.

Li, H., Eksteen, J. and Oraby, E., 2018. Hydrometallurgical recovery of metals from waste printed circuit boards (WPCBs): Current status and perspectives – A review. Resour. Conserv. Recy., 139: 122–139.

Li, H., Oraby, E. and Eksteen, J., 2020. Extraction of copper and the co-leaching behaviour of other metals from waste printed circuit boards using alkaline glycine solutions. Resour. Conserv. Recy., 154: 104624.

Li, H., Oraby, E. and Eksteen, J., 2021a. Recovery of copper and the deportment of other base metals from alkaline glycine leachates derived from waste printed circuit boards (WPCBs). Hydrometallurgy, 199: 105540.

Li, H., Oraby, E. and Eksteen, J., 2021b. Cyanide consumption minimisation and concomitant toxic effluent minimisation during precious metals extraction from waste printed circuit boards. Waste Manage., 125: 87–97.

Li, J., He, X. and Zeng, X., 2017. Designing and examining e-waste recycling process: methodology and case studies. Environ. Technol., 38(6): 652–660.

Li, J., Shrivastava, P., Gao, Z. and Zhang, H.-C., 2004. Printed circuit board recycling: a state-of-the-art survey. IEEE T. Electron. Pack. manuf., 27(1): 33–42.

Li, J., Zeng, X., Chen, M., Ogunseitan, O.A. and Stevels, A., 2015. "Control-Alt-Delete": rebooting solutions for the e-waste problem. Environ. Sci. Technol., 49(12): 7095–7108.

Li J., Xu X., Liu W., 2012. Thiourea leaching gold and silver from the printed circuit boards of waste mobile phones. Waste Manage. 32(6), 1209–1212.

Li, L., Zhu, Z., Liu, Y., Lin, Q., Li, Z. and Fu, J., 2014b. Optimisation of efficient auxiliary agents of gold leaching in an alkaline thiourea solution for a finely disseminated gold ore. Int. J. Min. Miner. Eng., 5(4): 315–327.

Li, Y. and Wong, C., 2006. Recent advances of conductive adhesives as a lead-free alternative in electronic packaging: Materials, processing, reliability and applications. Mater. Sci. Eng. R. Rep., 51(1): 1–35.

Lim, Y., Kwon, O.-h., Lee, J. and Yoo, K., 2013. The ammonia leaching of alloy produced from waste printed circuit boards smelting process. Geosyst. Eng., 16(3): 216–224.

Lu, Y. and Xu, Z., 2016. Precious metals recovery from waste printed circuit boards: a review for current status and perspective. Resour. Conserv. Recy., 113: 28–39.

Lin, S., Man, Y.B., Chow, K.L., Zheng, C. and Wong, M.H., 2020. Impacts of the influx of e-waste into Hong Kong after China has tightened up entry regulations. Crit. Rev. Env. Sci. Tec., 50(2): 105–134.

Lin, C., Chi, Y., Jin, Y., 2017. Experimental Study on Treating Waste Printed Circuit Boards by Molten Salt Oxidation. Waste Biomass Valori., 1–11.

Liu, J. and Kao, T.-H., 2003. Extraction of Cu and Pb from printed circuit board sludge using ammonia solutions. Water Sci. Technol., 47(1): 167–172.

Liu, K., Zhang, Z. and Zhang, F.-S., 2016. Direct extraction of palladium and silver from waste printed circuit boards powder by supercritical fluids oxidation-extraction process. J. Hazard. Mater., 318: 216–223.

Liu, M.-S., Lin, M.C.-C., Tsai, C.Y. and Wang, C.-C., 2006. Enhancement of thermal conductivity with Cu for nanofluids using chemical reduction method. Int. J. Heat Mass Transfer, 49(17): 3028–3033.

Liu, R., Shieh, R., Yeh, R.Y. and Lin, C., 2009. The general utilization of scrapped PC board. Waste Manage., 29(11): 2842–2845.

Long Le, H., Jeong, J., Lee, J.C., Pandey, B.D., Yoo, J.M. and Huyunh, T.H., 2011. Hydrometallurgical process for copper recovery from waste printed circuit boards (PCBs). Miner. Process. Extr. Metall. Rev., 32(2): 90–104.

Lotz, P., Janse van Rensburg, S. and Swarts, A., 2009. Kinetic gold leach monitoring including cyanide speciation. J. South. Afr. Inst. Min. Metall., 109(10): 635–639.

Luda, M.P., 2011. Recycling of printed circuit boards, Integrated Waste Management-Volume II. InTech.

Marques, A.C., Cabrera, J.-M. and de Fraga Malfatti, C., 2013. Printed circuit boards: A review on the perspective of sustainability. J. Environ. Manage., 131: 298–306.

Marques, A.C., Marrero, J.-M.C., de Fraga Malfatti, C., 2013. A review of the recycling of non-metallic fractions of printed circuit boards. SpringerPlus 2(1), 521.

McGrath, T., Morrison, P.D., Ball, A.S. and Clarke, B.O., 2018. Spatial distribution of novel and legacy brominated flame retardants in soils surrounding two Australian electronic waste recycling facilities. Environ. Sci. Technol., 52: 8194–8204.

Mecucci, A. and Scott, K., 2002. Leaching and electrochemical recovery of copper, lead and tin from scrap printed circuit boards. Journal of Chemical Technology and Biotechnology, 77(4): 449–457.

Melo Halmenschlager Petter, P., Veit, H.M. and Moura Bernardes, A., 2015. Leaching of gold and silver from printed circuit board of mobile phones. Rem: Rev. Esc. Minas, 68(1): 061–068.

Mohan, D. and Chander, S., 2006. Single, binary, and multicomponent sorption of iron and manganese on lignite. J. Colloid Interf. Sci., 299(1): 76–87.

Montero, R., Guevara, A. and dela Torre, E., 2012. Recovery of Gold, Silver, Copper and Niobium from Printed Circuit Boards Using Leaching Column Technique. J. Earth Sci. Eng., 2(10): 590.

Mudder, T. I., & Botz, M. M. 2004. Cyanide and society: a critical review. ejmp & ep (European Journal of Mineral Processing and Environmental Protection), 4(1), 62–74.

Mpinga, C.N., Bradshaw, S.M., Akdogan, G., Snyders, C.A. and Eksteen, J.J., 2014. Evaluation of the Merrill-Crowe process for the simultaneous removal of platinum, palladium and gold from cyanide leach solution. Hydrometallurgy, 142: 36–46.

Mpinga, C., Eksteen, J., Aldrich, C. and Dyer, L., 2015. Direct leach approaches to Platinum Group Metal (PGM) ores and concentrates: A review. Miner. Eng., 78: 93–113.

Navarro, P., Vargas, C., Alonso, M. and Alguacil, F., 2006. The adsorption of gold on activated carbon from thiosulfate-ammoniacal solutions. Gold Bull., 39(3): 93–97.

Nelson, D., Scott, S., Doostmohammadi, M. and Jafari, H., 2017. Methods, materials and techniques for precious metal recovery. US Patent 2017/0329967 A1.

Ning, C., Lin, C.S.K., Hui, D.C.W. and McKay, G., 2017. Waste Printed Circuit Board (PCB) Recycling Techniques. Top. Curr. Chem., 375(2): 43.

Nnorom, I.C. and Osibanjo, O., 2009. Toxicity characterization of waste mobile phone plastics. J. Hazard. Mater., 161(1): 183–188.

O'Connor, G.M., Lepkova, K., Eksteen, J.J. and Oraby, E.A., 2018. Electrochemical behaviour of copper in alkaline glycine solutions. Hydrometallurgy, 181: 221–229.

Ogunseitan, O.A., Schoenung, J.M., Saphores, J.-D.M. and Shapiro, A.A., 2009. The Electronics Revolution: From E-Wonderland to E-Wasteland. Science, 326(5953): 670–671.

Ogura, K., Kobayashi, M., Nakayama, M. and Miho, Y., 1998. Electrochemical and in situ FTIR studies on the adsorption and oxidation of glycine and lysine in alkaline medium. Journal of Electroanalytical Chemistry, 449(1): 101–109.

Oh, C.J., Lee, S.O., Yang, H.S., Ha, T.J. and Kim, M.J., 2003. Selective leaching of valuable metals from waste printed circuit boards. J. Air Waste Manag. Assoc., 53(7): 897–902.

Oishi, T., Koyama, K., Alam, S., Tanaka, M. and Lee, J.-C., 2007. Recovery of high purity copper cathode from printed circuit boards using ammoniacal sulfate or chloride solutions. Hydrometallurgy, 89(1): 82–88.

Oraby, E.A. and Eksteen, J.J., 2014. The selective leaching of copper from a gold–copper concentrate in glycine solutions. Hydrometallurgy, 150: 14–19.

Oraby, E.A. and Eksteen, J.J., 2015. The leaching of gold, silver and their alloys in alkaline glycine–peroxide solutions and their adsorption on carbon. Hydrometallurgy, 152: 199–203.

Oraby, E.A., Eksteen, J.J., 2015. Gold leaching in cyanide-starved copper solutions in the presence of glycine. Hydrometallurgy 156, 81–88.

Oraby, E.A. and Eksteen, J.J., 2016. Gold dissolution and copper suppression during leaching of copper–gold gravity concentrates in caustic soda-low free cyanide solutions. Miner. Eng., 87: 10–17.

Oraby, E.A., Eksteen, J.J. and Tanda, B.C., 2017. Gold and copper leaching from gold-copper ores and concentrates using a synergistic lixiviant mixture of glycine and cyanide. Hydrometallurgy, 169: 339–345.

Oraby, E.A., Eksteen, J.J. and O'Connor, G.M., 2020b. Gold leaching from oxide ores in alkaline glycine solutions in the presence of permanganate. Hydrometallurgy: 105527.

Oraby, E.A., Li, H. and Eksteen, J.J., 2020a. An alkaline glycine-based leach process of base and precious metals from powdered waste printed circuit boards. Waste Biomass Valori., 11(8): 3897–3909.

Oraby, E.A., Eksteen, J.J., Karrech, A. and Attar, M., 2019. Gold extraction from paleochannel ores using an aerated alkaline glycine lixiviant for consideration in heap and in-situ leaching applications. Miner. Eng., 138: 112–118.

Oraby, E., Eksteen, J., 2014. A process for precious metals recovery. PCT Patent, PCT/AU2014/000877.

Ortiz-Aparicio, J.L., Meas, Y., Trejo, G., Ortega, R., Chapman, T.W., Chaînet, E. and Ozil, P., 2007. Electrodeposition of zinc–cobalt alloy from a complexing alkaline glycinate bath. Electrochim. Acta, 52(14): 4742–4751.

Otsuki, A., Gonçalves, P.P., Stieghorst, C. and Révay, Z., 2019a. Non-destructive characterization of mechanically processed waste printed circuit boards: X-ray fluorescence spectroscopy and prompt gamma activation analysis. J. Compos. Sci., 3(2): 54.

Otsuki, A., Pereira Gonçalves, P. and Leroy, E., 2019b. Selective milling and elemental assay of printed circuit board particles for their recycling purpose. Metals, 9(8): 899.

Otsuki, A., De La Mensbruge, L., King, A., Serranti, S., Fiore, L. and Bonifazi, G., 2020. Non-destructive characterization of mechanically processed waste printed circuit boards - particle liberation analysis. Waste Manage., 102: 510–519.

Qiu, R., Lin, M., Qin, B., Xu, Z. and Ruan, J., 2021. Environmental-friendly recovery of non-metallic resources from waste printed circuit boards: A review. J. Clean. Prod., 279: 123738.

Qiu, R., Lin, M., Ruan, J., Fu, Y., Hu, J., Deng, M., Tang, Y. and Qiu, R., 2020. Recovering full metallic resources from waste printed circuit boards: A refined review. J. Clean. Prod., 244: 118690.

Pant, D., Joshi, D., Upreti, M.K. and Kotnala, R.K., 2012. Chemical and biological extraction of metals present in E waste: a hybrid technology. Waste Manage., 32(5): 979–990.

Park, Y.J. and Fray, D.J., 2009. Recovery of high purity precious metals from printed circuit boards. J. Hazard. Mater., 164(2): 1152-1158.

Patil, R.A. and Ramakrishna, S., 2020. A comprehensive analysis of e-waste legislation worldwide. Environ. Sci. Pollut. Res., 27(13): 14412–14431.

Patil, K. and Rattan, T.M., 2014. Inorganic hydrazine derivatives: Synthesis, properties and applications. John Wiley & Sons.

Petridis, N.E., Petridis, K. and Stiakakis, E., 2020. Global e-waste trade network analysis. Resour. Conserv. Recy., 158: 104742.

Pérez-Belis, V., Bovea, M. and Ibáñez-Forés, V., 2015. An in-depth literature review of the waste electrical and electronic equipment context: Trends and evolution. Waste Manage. Res., 33(1): 3–29.

Perez-Benito, J.F., Mata-Perez, F. and Brillas, E., 1987. Permanganate oxidation of glycine: Kinetics, catalytic effects, and mechanisms. Can. J. Chem., 65(10): 2329–2337.

Pereira Gonçalves, P. and Otsuki, A., 2019. Determination of Liberation Degree of Mechanically Processed Waste Printed Circuit Boards by Using the Digital Microscope and SEM-EDS Analysis. Electronics, 8(10): 1202.

Perrine, T. and Landis, W., 1967. Analysis of polyethylenimine by spectrophotometry of its copper chelate. J. Polym. Sci. Pol. Chem., 5(8): 1993–2003.

Petter, P., Veit, H. and Bernardes, A., 2014. Evaluation of gold and silver leaching from printed circuit board of cellphones. Waste Manage., 34(2): 475–482.

Puente-Siller, D.M., Fuentes-Aceituno, J.C., Nava-Alonso, F., 2017. An analysis of the efficiency and sustainability of the thiosulfate-copper-ammonia-monoethanolamine system for the recovery of silver as an alternative to cyanidation. Hydrometallurgy 169, 16–25.

Putnam, G., 1950. A laboratory study of the influence of ferricyanide on the extraction of gold. J. South. Afr. Inst. Min. Metall., 50(9): 228–230.

Rajarao, R., Sahajwalla, V., Cayumil, R., Park, M., Khanna, R., 2014. Novel Approach for Processing Hazardous Electronic Waste. Procedia Environ. Sci. 21(Supplement C), 33–41.

Rees, K.L. and Van Deventer, J.S.J., 1999. The role of metal-cyanide species in leaching gold from a copper concentrate. Miner. Eng., 12(8): 877–892.

Rees, K. and Van Deventer, J., 2001. Gold process modelling. I. Batch modelling of the processes of leaching, preg-robbing and adsorption onto activated carbon. Miner. Eng., 14(7): 753–773.

Rees, K., Van Deventer, J. and Dunne, R., 2001. Gold process modelling. II. The effect of ore type on leaching and adsorption dynamics at telfer gold mine. Miner. Eng., 14(8): 887–900.

Reuter, M.A., Vans Schaik, A. and Ballester, M., 2018. Limits of the circular economy: Fairphone modular design pushing the limits. World Metall. – Erzmetall, 71(2): 68–79.

Rice, R.G. and Browning, M.E., 1980. Ozone for industrial water and wastewater treatment: A literature survey. United States Environmental Protection Agency.

Perea, C. and Restrepo, O., 2018. Use of amino acids for gold dissolution. Hydrometallurgy, 177: 79–85.

Rodriguez-Torres, I., Valentin, G., Chanel, S. and Lapicque, F., 2000. Recovery of zinc and nickel from electrogalvanisation sludges using glycine solutions. Electrochim. Acta, 46(2): 279–287.

Priya, A., Hait, S., 2017. Feasibility of Bioleaching of Selected Metals from Electronic Waste by Acidiphilium acidophilum. Waste Biomass Valori., 1–7.

Ryu, S.-H., Ahn, J.-W., Ahn, H.-J. and Kim, T.-Y., 2014. Recovery of tin and copper from waste solder stripper by oxalate precipitation. J. Korean Inst. Resour. Recycl., 23(3): 37–43.

Sahin, M., Akcil, A., Erust, C., Altynbek, S., Gahan, C.S., Tuncuk, A., 2015. A potential alternative for precious metal recovery from e-waste: iodine leaching. Sep. Sci. Technol. 50(16), 2587–2595.

Sanyal, S., Ke, Q., Zhang, Y., Ngo, T., Carrell, J., Zhang, H. and Dai, L.L., 2013. Understanding and optimizing delamination/recycling of printed circuit boards using a supercritical carbon dioxide process. J. Clean. Prod., 41: 174–178.

Sato, N., Daimon, H. and Fujie, K., 2002. Decomposition of Glycine in High Temperature and High Pressure Water. KAGAKU KOGAKU RONBUNSHU, 28(1): 113–117.

Schoeman, E., Bradshaw, S.M., Akdogan, G., Snyders, C.A. and Eksteen, J.J., 2017. The extraction of platinum and palladium from a synthetic cyanide heap leach solution with strong base anion exchange resins. Int. J. Miner. Process., 162: 27–35.

Serov, A. and Kwak, C., 2010. Direct hydrazine fuel cells: A review. Applied Catalysis B: Environmental, 98(1–2): 1–9.

Sharma, N., Chauhan, G., Kumar, A., Sharma, S., 2017. Statistical optimization of heavy metals (Cu^{2+}/Co^{2+}) extraction from printed circuit board and mobile batteries using chelation technology. Ind. Eng. Chem. Res. 56, 6805–6819.

Shuey, S., Vildal, E., Taylor, P., 2006. Pyrometallurgical processing of electronic waste. In: SME Annual Meeting 2006, pp. 06–037

Silva-Martinez, S. and Roy, S., 2013. Copper recovery from tin stripping solution: Galvanostatic deposition in a batch-recycle system. Sep. Purif. Technol., 118: 6–12.

Silvas, F.P., Correa, M.M.J., Caldas, M.P., de Moraes, V.T., Espinosa, D.C. and Tenório, J.A., 2015. Printed circuit board recycling: physical processing and copper extraction by selective leaching. Waste Manage., 46: 503–510.

Sjoberg, J., Nash, C., Sbiroli, D. and Qu, W., 2016. High-density assembly and root cause analyses, Pan Pacific Microelectronics Symposium (Pan Pacific), 2016. IEEE, pp. 1–6.

Snyders, C., Akdogan, G., Bradshaw, S. and van Wyk, A., 2017. Gold CIP and CIL process optimization in a capital constraint environment. J. South. Afr. Inst. Min. Metall., 117(8): 819–828.

Somasundaram, M., Saravanathamizhan, R., Basha, C.A., Nandakumar, V., Begum, S.N. and Kannadasan, T., 2014. Recovery of copper from scrap printed circuit board: modelling and optimization using response surface methodology. Powder Technol., 266: 1–6.

Song, Q. and Li, J., 2014a. Environmental effects of heavy metals derived from the e-waste recycling activities in China: A systematic review. Waste Manage., 34(12): 2587–2594.

Song, Q. and Li, J., 2014b. A systematic review of the human body burden of e-waste exposure in China. Environ. Int., 68: 82–93.

Sum, E.Y.L., 1991. The recovery of metals from electronic scrap. JOM 43(4), 53–61.

Sun, Z.H.I., Xiao, Y., Sietsma, J., Agterhuis, H., Visser, G. and Yang, Y., 2015a. Selective copper recovery from complex mixtures of end-of-life electronic products with ammonia-based solution. Hydrometallurgy, 152: 91–99.

Sun, Z., Xiao, Y., Sietsma, J., Agterhuis, H. and Yang, Y., 2015b. A cleaner process for selective recovery of valuable metals from electronic waste of complex mixtures of end-of-life electronic products. Environ. Sci. Technol., 49(13): 7981–7988.

Sun, Z.H.I., Cao, H., Xiao, Y., Sietsma, J., Jin, W., Agterhuis, H. and Yang, Y., 2016. Toward sustainability for recovery of critical metals from electronic waste: the hydrochemistry processes. ACS Sustain. Chem. Eng., 5(1): 21–40.

Sundaresan, R., Saraiya, S., Radhakrishnan, T. and Sundaram, A., 1968. Polarography of zinc in presence of glycine. Electrochim. Acta, 13(3): 443–447.

Syed, S., 2012. Recovery of gold from secondary sources-a review. Hydrometallurgy, 115: 30–51.

Syna, N. and Valix, M., 2003. Modelling of gold (I) cyanide adsorption based on the properties of activated bagasse. Miner. Eng., 16(5): 421–427.

Szałatkiewicz, J., 2014. Metals content in printed circuit board waste. Pol. J. Environ. Stud, 23(6): 2365–2369.

Tanda, B., Oraby, E. and Eksteen, J., 2017a. Recovery of copper from alkaline glycine leach solution using solvent extraction. Sep. Purif. Technol., 187: 389–396.

Tanda, B.C., Eksteen, J.J. and Oraby, E.A., 2017b. An investigation into the leaching behaviour of copper oxide minerals in aqueous alkaline glycine solutions. Hydrometallurgy, 167: 153–162.

Tanda, B., Eksteen, J. and Oraby, E., 2018a. Kinetics of chalcocite leaching in oxygenated alkaline glycine solutions. Hydrometallurgy, 178: 264–273.

Tanda, B., Oraby, E. and Eksteen, J., 2018b. Kinetics of malachite leaching in alkaline glycine solutions. Miner. Process. Extr. Metall.: 1–9.

Tang, S., Hui, S.R. and Chung, H.-H., 2001. A low-profile power converter using printed-circuit board (PCB) power transformer with ferrite polymer composite. IEEE T. Power Electr., 16(4): 493–498.

Tan, Q., Li, J. and Boljkovac, C., 2018. Responding to China's Waste Import Ban through a New, Innovative, Cooperative Mechanism. Environ. Sci. Technol., 52: 7595–7597.

Tauetsile, P.J., Oraby, E.A., and Eksteen, J.J. (2018a). Adsorption behaviour of copper and gold glycinates in alkaline media onto activated carbon. part 1: isotherms. Hydrometallurgy, 178: 202–208.

Tauetsile, P.J., Oraby, E.A., and Eksteen, J.J. (2018b). Adsorption behaviour of copper and gold glycinates in alkaline media onto activated carbon. part 2: kinetics. Hydrometallurgy, 178: 195–201.

Tauetsile, P.J., Oraby, E.A. and Eksteen, J.J., 2019a. Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper. Part 1: Isotherms. Sep. Purif. Technol., 211: 594–601.

Tauetsile, P.J., Oraby, E.A. and Eksteen, J.J., 2019b. Activated carbon adsorption of gold from cyanide-starved glycine solutions containing copper. Part 2: Kinetics. Sep. Purif. Technol., 211: 290–297.

Tesfaye, F., Lindberg, D. and Hamuyuni, J., 2017. Valuable Metals and Energy Recovery from Electronic Waste Streams. In: L. Zhang et al. (Eds.), Energy Technology 2017: Carbon Dioxide Management and Other Technologies. Springer International Publishing, Cham, pp. 103–116.

Theodor, V., Klaus, W., Brent, H. and Gerd, B., 2006. Liquid–Solid Extraction, Ullmann's Encyclopedia of Industrial Chemistry. Available at https://doi.org/10.1002/14356007.b03_07.pub2

Tripathi, A., Kumar, M., Sau, D.C., Agrawal, A., Chakravarty, S. and Mankhand, T.R., 2012. Leaching of gold from the waste mobile phone printed circuit boards (PCBs) with ammonium thiosulphate. Int. J. Metall. Eng., 1(2): 17–21.

Tuncuk, A., Stazi, V., Akcil, A., Yazici, E.Y. and Deveci, H., 2012. Aqueous metal recovery techniques from e-scrap: hydrometallurgy in recycling. Miner. Eng., 25(1): 28–37.

Van Deventer, J., 1986. Competitive equilibrium adsorption of metal cyanides on activated carbon. Sep. Sci. Technol., 21(10): 1025–1037.

Verma, H.R., Singh, K.K. and Mankhand, T.R., 2016. Dissolution and separation of brominated epoxy resin of waste printed circuit boards by using di-methyl formamide. J. Clean. Prod., 139: 586–596.

Wang, H., Zhang, S., Li, B., Pan, D.A., Wu, Y. and Zuo, T., 2017. Recovery of waste printed circuit boards through pyrometallurgical processing: A review. Resour. Conserv. Recy., 126: 209–218.

Wang, J., Guo, J. and Xu, Z., 2016a. An environmentally friendly technology of disassembling electronic components from waste printed circuit boards. Waste Manage., 53: 218–224.

Wang, J. and Xu, Z., 2015. Disposing and recycling waste printed circuit boards: Disconnecting, resource recovery, and pollution control. Environ. Sci. Technol., 49(2): 721–733.

Wang, M., Cao, H. and Zhang, Y., 2011. Selective recovery of copper, zinc and nickel from printed circuit boards by ammonia leaching under pressure (In Chinese). Environ. Sci., 32(2): 596–602.

Wang, R. and Xu, Z., 2014. Recycling of non-metallic fractions from waste electrical and electronic equipment (WEEE): A review. Waste Manage., 34(8): 1455–1469.

Wang, X. and Forssberg, K.S.E., 1990. The Chemistry of Cyanide-Metal Complexes in Relation to Hydrometallurgical Processes of Precious Metals. Miner. Process. Extr. Metall. Rev., 6(1–4): 81–125.

Wang, Y.-y., Chai, L.-y., Min, X.-b., He, D.-w. and Peng, B., 2003. Optimization of efficient stable reagent of alkaline thiourea solution for gold leaching. J. Cent. South Univ. Technol., 10(4): 292–296.

Wang, Z., Zhang, B., Guan, D., 2016b. Take responsibility for electronic-waste disposal. Nature 536, 4.

Wasserscheid, P. and Keim, W., 2000. Ionic liquids—new "solutions" for transition metal catalysis. Angew. Chem. Int. Ed, 39(21): 3772–3789.

Wei, D., Chai, L., Ichino, R. and Okido, M., 1999. Gold leaching in an alkaline thiourea solution. J. Electrochem. Soc., 146(2): 559–563.

Williams, P.T., 2010. Valorization of printed circuit boards from waste electrical and electronic equipment by pyrolysis. Waste Biomass Valori. 1(1), 107–120.

Wu, S., and Meng, S., 2006. Preparation of micron size copper powder with chemical reduction method.   Mater. Lett., 60(20): 2438–2442.

Xiao, Y., Yang, Y., van den Berg, J., Sietsma, J., Agterhuis, H., Visser, G. and Bol, D., 2013. Hydrometallurgical recovery of copper from complex mixtures of end-of-life shredded ICT products. Hydrometallurgy, 140: 128–134.

Xie, F., Dreisinger, D. and Lu, J., 2008. The novel application of ferricyanide as an oxidant in the cyanidation of gold and silver. Miner. Eng., 21(15): 1109–1114.

Xie, F. and Dreisinger, D.B., 2007. Leaching of silver sulfide with ferricyanide–cyanide solution. Hydrometallurgy, 88(1): 98–108.

Xiu, F.-R., Qi, Y. and Zhang, F.-S., 2015. Leaching of Au, Ag, and Pd from waste printed circuit boards of mobile phone by iodide lixiviant after supercritical water pre-treatment. Waste Manage., 41: 134–141.

Xing, W., Yin, M., Lv, Q., Hu, Y., Liu, C. and Zhang, J., 2014. 1 - Oxygen Solubility, Diffusion Coefficient, and Solution Viscosity. In: W. Xing, G. Yin and J. Zhang (Eds.), Rotating Electrode Methods and Oxygen Reduction Electrocatalysts. Elsevier, Amsterdam, pp. 1–31.

Xu, B., Kong, W., Li, Q., Yang, Y., Jiang, T. and Liu, X., 2017. A review of thiosulfate leaching of gold: Focus on thiosulfate consumption and gold recovery from pregnant solution. Metals, 7(6): 222.

Xu, Y. and Liu, J., 2015. Recent developments and perspective of the spent waste printed circuit boards. Waste Manage. Res., 33(5): 392–400.

Yang, C., Li, J., Tan, Q., Liu, L. and Dong, Q., 2017. Green Process of Metal Recycling: Coprocessing Waste Printed Circuit Boards and Spent Tin Stripping Solution. ACS Sustain. Chem. Eng., 5(4): 3524–3534.

Yang, H., Liu, J. and Yang, J., 2011a. Leaching copper from shredded particles of waste printed circuit boards. J. Hazard. Mater., 187(1): 393–400.

Yang, J.-g., Wu, Y.-t. and Li, J., 2012. Recovery of ultrafine copper particles from metal components of waste printed circuit boards. Hydrometallurgy, 121: 1–6.

Yang, X., Moats, M.S., Miller, J.D., Wang, X., Shi, X. and Xu, H., 2011b. Thiourea–thiocyanate leaching system for gold. Hydrometallurgy, 106(1): 58–63.

Yazici, E. and Deveci, H., 2013. Extraction of metals from waste printed circuit boards (WPCBs) in H_2SO_4-$CuSO_4$-NaCl solutions. Hydrometallurgy, 139: 30–38.

Yazici, E. and Deveci, H., 2014. Ferric sulphate leaching of metals from waste printed circuit boards. Int. J. Miner. Process., 133: 39–45.

Yazici, E. and Deveci, H., 2015. Cupric chloride leaching (HCl–CuCl 2–NaCl) of metals from waste printed circuit boards (WPCBs). Int. J. Miner. Process., 134: 89–96.

Yazici, E., Deveci, H. and Ehsani, A., 2014. Recovery of metals from chloride leach solutions of waste of printed circuit boards by adsorption and precipitation, XXVII. Int. Mineral Processing Congress (IMPC 2014), 20–24 Oct., Santiago, Chile, pp. 170–179.

Yazici, E.Y. and Deveci, H., 2016. Recovery of Copper Sulphate from Sulphuric Acid Leach Solutions via Solvent Displacement Crystallisation Using Acetone, International Black Sea Mining & Tunnelling Symposium, pp. 455–460.

Yerneni, K. K., Cholkar, K., Guin, M., Nayak, A. N., Ananda, S., Gowda, N. M. M., 2017. Palladium (II) Catalyzed Oxidation of Glycine by Ferricyanide in Acid Medium: Kinetics and Mechanism. Curr. Phys. Chem., 7(1): 63–70.

Yildirir, E., Onwudili, J.A. and Williams, P.T., 2015. Chemical recycling of printed circuit board waste by depolymerization in sub-and supercritical solvents. Waste Biomass Valori., 6(6): 959–965.

Yusuf, A., Snape, C., He, J., Xu, H., Liu, C., Zhao, M., Chen, G.Z., Tang, B., Wang, C., Wang, J. and Behera, S.N., 2017. Advances on transition metal oxides catalysts for formaldehyde oxidation: A review. Catal. Rev., 59(3): 189–233.

Yu, J.-C., Zhao, F.-G., Shao, W., Ge, C.-W. and Li, W.-S., 2015. Shape-controllable and versatile synthesis of copper nanocrystals with amino acids as capping agents. Nanoscale, 7(19): 8811–8818.

Zeng, X., Mathews, J.A. and Li, J., 2018. Urban Mining of E-Waste is Becoming More Cost-Effective Than Virgin Mining. Environ. Sci. Technol., 52(8): 4835–4841.

Zeng, X., Ali, S.H., Tian, J. and Li, J., 2020. Mapping anthropogenic mineral generation in China and its implications for a circular economy. Nat. Commun., 11(1): 1–9.

Zebing Wu, W.Y., Jinhui Li, Xiaoyan Wang, Lili Liu, Jingwei Wang, 2017. A critical review on the recycling of copper and precious metals from waste printed circuit boards using hydrometallurgy. Front. Environ. Sci. Eng., 11(5): 8.

Zhang, H. and Dreisinger, D.B., 2004. The recovery of gold from ammoniacal thiosulfate solutions containing copper using ion exchange resin columns. Hydrometallurgy, 72(3): 225–234.

Zhang, H., Ritchie, I.M. and La Brooy, S.R., 2004. The adsorption of gold thiourea complex onto activated carbon. Hydrometallurgy, 72(3–4): 291–301.

Zhang, J., Shen, S., Cheng, Y., Lan, H., Hu, X. and Wang, F., 2014. Dual lixiviant leaching process for extraction and recovery of gold from ores at room temperature. Hydrometallurgy, 144–145: 114–123.

Zhang, K., Schnoor, J.L. and Zeng, E.Y., 2012a. E-Waste Recycling: Where Does It Go from Here? Environ. Sci. Technol., 46(20): 10861–10867.

Zhang, L. and Xu, Z., 2016. A review of current progress of recycling technologies for metals from waste electrical and electronic equipment. J. Clean. Prod., 127: 19–36.

Zhang, Q.-L., Yang, Z.-M., Ding, B.-J., Lan, X.-Z. and Guo, Y.-J., 2010. Preparation of copper nanoparticles by chemical reduction method using potassium borohydride. Trans. Nonferrous Met. Soc. China, 20(1): s240–s244.

Zhang, X., Guan, J., Guo, Y., Cao, Y., Guo, J., Yuan, H., Su, R., Liang, B., Gao, G., Zhou, Y. and Xu, J., 2017. Effective dismantling of waste printed circuit board assembly with methanesulfonic acid containing hydrogen peroxide. Environ. Prog. Sustain. Energy, 36(3): 873–878.

Zhang, Y., Liu, S., Xie, H., Zeng, X. and Li, J., 2012b. Current status on leaching precious metals from waste printed circuit boards. Procedia Environ. Sci., 16: 560–568.

Zhang, Z. and Zhang, F.-S., 2014. Selective recovery of palladium from waste printed circuit boards by a novel non-acid process. J. Hazard. Mater., 279: 46–51.

Zhang, C., Liu, F., Zhai, Y., Ariga, H., Yi, N., Liu, Y., Asakura, K., Flytzani‑Stephanopoulos, M. and He, H., 2012. Alkali‑metal‑promoted Pt/TiO2 opens a more efficient pathway to formaldehyde oxidation at ambient temperatures. Angew. Chem. Int. Ed, 51(38): 9628–9632.

Zheng, S., Wang, Y.-y. and Chai, L.-y., 2006. Research status and prospect of gold leaching in alkaline thiourea solution. Miner. Eng., 19(13): 1301–1306.

Zhou, L. and Xu, Z., 2012. Response to waste electrical and electronic equipments in China: legislation, recycling system, and advanced integrated process. Environ. Sci. Technol., 46(9): 4713.

Zhou, Y., Wu, W. and Qiu, K., 2010. Recovery of materials from waste printed circuit boards by vacuum pyrolysis and vacuum centrifugal separation. Waste Manage., 30(11): 2299–2304.

Zhou, Y., Wu, W. and Qiu, K., 2011. Recycling of organic materials and solder from waste printed circuit boards by vacuum pyrolysis-centrifugation coupling technology. Waste Manage., 31(12): 2569–2576.

Zhu, P., Cao, Z.B., Qian, G.R., Sun, Y., Liu, Q., Fan, Z.Y. and Zhou, M., 2014. Extractive metals from metallic powders recovered from waste printed circuit boards. Can. Metall. Quart., 53(1): 74–81.

Zhu, P., Chen, Y., Wang, L.Y., Qian, G.R., Zhou, M. and Zhou, J., 2013a. A novel approach to separation of waste printed circuit boards using dimethyl sulfoxide. Int. J. Environ. Sci. Technol., 10(1): 175–180.

Zhu, P., Chen, Y., Wang, L. and Zhou, M., 2012. Treatment of waste printed circuit board by green solvent using ionic liquid. Waste Manage., 32(10): 1914–1918.

Zhu, P., Chen, Y., Wang, L., Zhou, M. and Zhou, J., 2013b. The separation of waste printed circuit board by dissolving bromine epoxy resin using organic solvent. Waste Manage., 33(2): 484–488.

Zi, F.T., Hu, X.Z., Zhang, W.B. and He, S.Q., 2012. Thiosulfate leaching of middle-refractory gold ore with ferricyanide as oxidant, Adv. Mat. Res., 548: 309–314.