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

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A R T I C L E   I N F O

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A B S T R A C T

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 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
Typical component and economic value of the di-
Table 1

<table>
<thead>
<tr>
<th>Type of e-waste</th>
<th>Metal content in wt. %</th>
<th>Metal content in ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe Cu Al Pb Sn Ni</td>
<td>Pd Au Ag</td>
</tr>
<tr>
<td>Metal price (USD/1)</td>
<td>515 6583 2100 2377 20950 11234</td>
<td>2.95 × 10^7 4.16 × 10^7 5.44 × 10^7</td>
</tr>
<tr>
<td>PC mainboards</td>
<td>4.5 14.3 2.8 2.2 – 1.1</td>
<td>124 566 639</td>
</tr>
<tr>
<td>Mobile phone</td>
<td>5 (0) 13 (0) 1 (0) 0.3 (0) 0.5 (0) 0.1 (0)</td>
<td>210 350 1380</td>
</tr>
<tr>
<td>TV boards</td>
<td>28 (5) 10 (25) 10 (8) 1 (1) 1.4 (11) 0.3 (1)</td>
<td>10 (11) 20 (31) 280 (6)</td>
</tr>
<tr>
<td>Typical Cu-Au ore</td>
<td>16 (0) 0.4 (25) 4.5 (8) 0.1 (1) 0.002 (11) 0.001 (1)</td>
<td>– (11) 5.7 (31) 22.9 (6)</td>
</tr>
<tr>
<td>Typical Cu-Au concentrate</td>
<td>2.9 (5) 0.97 (25) 0.5 (8) 0.03 (11) – 0.02</td>
<td>– (11) 490 (31) 100 (6)</td>
</tr>
</tbody>
</table>

“–” 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 Data 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 (Sjöberg 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 cellulosic 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).
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).

<table>
<thead>
<tr>
<th>Types of PCB</th>
<th>Characteristics</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single layer</td>
<td>Single layer of printed wiring or substrate, easily to design and manufacture, low-cost.</td>
<td>General electronic devices, e.g. calculators, radio, printers, etc.</td>
</tr>
<tr>
<td>Double layer</td>
<td>Printed wirings on both sides of substrate.</td>
<td>Instrumentation, computers, LED lighting, automotive dashboards, etc.</td>
</tr>
<tr>
<td>Multi-layer</td>
<td>3 – layers of printed wirings, with metallized holes connecting different layers</td>
<td>For complicated designs like medical equipment, satellite systems, computers, etc.</td>
</tr>
<tr>
<td>Rigid PCB</td>
<td>With rigid substrate preventing the board from twisting.</td>
<td>With single-, double- or multi-layer, application same as them.</td>
</tr>
<tr>
<td>Flexible PCB</td>
<td>Free bending, folding and easily coiled.</td>
<td>With single-, double- or multi-layer, used for special requirements, e.g. complicated shape, waterproof, shockproof</td>
</tr>
<tr>
<td>Flex-rigid PCB</td>
<td>Suitable for streamlined design, reducing overall board size and weight</td>
<td>Used in the case when space or weight are prime concerns, e.g. cellphone, digital cameras, automobiles</td>
</tr>
</tbody>
</table>
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
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., H2O2 and Sn4+) or using oxidizing acid (e.g., HNO3) 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 NOx 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-
methylimidazolium tetrafluoroborate ([EMIM]+ [Br4−]), 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 H2SO4, HCl and HNO3, 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, cannot be recovered economically, can be prevent any commercial and industrial implementation.

(1) Using mineral acid only, including H2SO4, HNO3, HCl and aqua regia (HCl: HNO3 = 3:1, v/v). Bas et al. (2014) reported that the leaching rates of Cu and Ag rise with the increase of HNO3 concentration (1–5 M), and the concentration ≥ 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 HNO3 concentration 1–5 M due to its high standard reduction potential (0.80 V for Ag+/Ag vs. 0.34 V for Cu2+/Cu), indicating that higher concentration of HNO3 is required for a high leaching rate of precious metals like Ag. Generally, dilute H2SO4 under atmospheric pressure cannot significantly leach Cu, with 1 M H2SO4 leaching only 8.8% Cu at room temperature for 96 h (Jadhav and Hocheng, 2015). However, ~1 M H2SO4 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)2Cl6. 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 H2SO4 and H2O2, by which complete leaching of Cu can be achieved (Birloaga and Vegliò, 2016). Other oxidants, such as Cu2+, Fe3+ and air/O2, have also been reported. For example, Yazici and Deveci (2013) reported that Cu2+ 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/O2 for the in situ regeneration of Cu2+, the leaching of Pd could be increased to > 82% (Yazici and Deveci, 2013).

\[ \text{Cu}^0 + \text{Cu}^{2+} \rightarrow 2\text{Cu}^+ \]  
\[ \text{Cu}^+ + n\text{Cl}^- \rightarrow \text{CuCl}_n \] (1)  
\[ \text{Cu}^0 + \text{Cu}^{2+} + 2\text{Cl}^- \rightarrow 2\text{CuCl}_2 \] (2)  
\[ \text{Cu}^0 + \text{Cu}^{2+} + 4\text{Cl}^- \rightarrow 2\text{CuCl}_2 \] (3)

(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 CuCl2 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 CuCl2 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 HNO3 while Sn remained un-leached by forming SnO2 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 HNO3, 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 NOx 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−), hydrocyanide (HCN), complexes and some simple compounds, depending on different pH. It is suggested that cyanidation should happen at a pH ≥ 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 + 8SCN⁻ + O₂ + 2H₂O → 4Au(CN)₂⁻ + 4OH⁻  (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 H₂SO₄ 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 H₂O₂. 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 thiourea, 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, thiourea (thiosulfate, thiourea and thiocyanate), halide leaching and ammonia-ammonium leaching have been actively investigated. Among them, thiourea or 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 ((NH₂)₂CS, TU) used as lixiviant for precious metals is less toxic and more eco-friendly, and it can achieve a high leaching rate (~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[NH₂]₂)₂+ and Ag(SC[NH₂]₂)⁺). To oxidise native Au and Ag in WPCBs, oxidant, mostly Fe³⁺, is used in the system (Eqs. (6) and (7)). It is reported that, with the addition of Fe³⁺, Au extraction efficiency can be increased up to four times higher than that without Fe³⁺ 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 Fe³⁺ in solution at pHs greater than around 3.5 (Mohan and Chander, 2006). High concentration of Fe³⁺ 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, Fe³⁺ can also complex with thiourea forming (Fe₅O₆CS(NH₂)₂)⁺, reducing the leaching efficiency and increasing thiourea consumption (Akcil et al., 2015).

\[
\begin{align*}
\text{Au} + 2\text{SC(NH}_2\text{)}_2 + \text{Fe}^{3+} & \rightarrow \text{Au(SC[NH}_2\text{)]}_2^2 + \text{Fe}^{2+} + \\
\text{Ag} + 2\text{SC(NH}_2\text{)}_2 + \text{Fe}^{3+} & \rightarrow \text{Ag(SC[NH}_2\text{)]}_2^2 + \text{Fe}^{2+} + \\
2\text{SC(NH}_2\text{)}_2 + \text{Fe}^{3+} & \rightarrow (\text{SC[NH}_2\text{]}_2 + 2\text{Fe}^{2+} + 2\text{H}^+ \\
\end{align*}
\]

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 careful control of pH, redox potential, leaching time and the concentrations of thiourea and oxidant (Fe³⁺⁻). 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 out with Au and Ag, whereas most of Pb and Pt remained in the residue. Besides, they also found that the presence of Fe³⁺⁺ had no beneficial effect for Ag leaching which happens much 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 H₂SO₄ and H₂O₂ 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[NH₂]₂)⁺). However, Fe³⁺⁺ 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 Na₂S₂O₅ and K₂Fe(CN)₆ (Zheng et al., 2006). In order to enhance the stability of thiourea in alkaline environment, some stabilizers, i.e. Na₂S₂O₇, Na₂S₂O₅ and (NaPO₃)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 Na₂S₂O₅. 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 (~79% for Au).
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. Thioulate leaching of precious metals

Thioulate (S₂O₂⁻) 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 thioulate leaching for WPCBs recycling have been carried out. Thioulate 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 thioulate solution very slowly with the oxidation of O₂ as oxidant. To enhance the leaching efficiency, Cu²⁺ and ammonia are usually used as additives, making the cuprous ammonia (Cu(NH₃)₄²⁺) act as a “catalyst” with the leaching of Au represented by Eqs. (9) and (10) (Cui and Zhang, 2008).

\[
\begin{align*}
Au + 5S₂O₅²⁻ + Cu(NH₃)₄³⁺ & → Au(S₂O₄)²⁻ + 4NH₃ + Cu(S₂O₃)³⁻ \\
2Cu(S₂O₃)³⁻ + 8NH₃ + \frac{1}{2}O₂ + H₂O & → 2Cu(NH₂)S₂O₃⁺ + 2OH⁻ + 6S₂O₅²⁻
\end{align*}
\]

(10)

In the case of direct leaching of WPCBs or size-reduced WPCBs by thioulate 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 Na₂S₂O₃ or (NH₄)₂S₂O₃, CuSO₄ or H₂O₂ and NH₃ co-existing as Eqs. (11) and (12) (Mpinga et al., 2015). Similar results obtained from the size-reduced WPCBs, Petter et al. (2014) used 0.1 M Na₃S₂O₅, 0.2 M NH₄H₂O₂ and 0.015–0.03 M CuSO₄ 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 H₂O₂ 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 for size-reduced WPCBs for a long leaching time (48 h) (Ficeriová et al., 2011). In order to pre-separate base metals, some researchers employed H₂O₂ and H₂O₂ for selective leaching of base metals from WPCBs, followed by (NH₄)₂S₂O₃-CuSO₄-NH₃OH 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 thioulate leaching are the high consumption of thioulate 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 (Mpinga et al., 2015; Zhang and Xu, 2016). Thiocyanate works in acidic environment at a pH of 1–2 which enables Fe³⁺ to act as an oxidant (Syed, 2012), and the dissolution of Au can be simplified as Eqs. (11) and (12) (Mpinga et al., 2015).

\[
\begin{align*}
Au + 2SCN⁻ + Fe³⁺ & → Au(SCN)₂ + Fe²⁺ \\
Au + 4SCN⁻ + 3Fe³⁺ & → Au(SCN)₃ + 3Fe²⁺
\end{align*}
\]

(11)

(12)

Instead of using thiocyanate as lixiviant alone, various research investigations have been conducted employing dual lixiviants, such as thiourea-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 Fe₃(SO₄)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 ((NH₃)₂CS)SCN. 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 predate 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 Au³⁺ complexes with chloride, bromide and iodide (Cui and Zhang, 2008). Their complexing principles are similar, as indicated as follows (Wu et al., 2017):

\[
\begin{align*}
2M + L₂ + 2L⁻ & → 2ML³⁻ \\
2M + L₂ + 2L⁻ & → 2ML⁴⁻
\end{align*}
\]

(13)

(14)

Where M and L stand for precious metals and halide elements, respectively. L₂ is the oxidizing agent, and L⁻ is the complexing agent.

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 I₂ 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., 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 H₂O₂, 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(NH₃)₂L²⁻), as indicated by Eq. (16).

\[
\begin{align*}
2Cu + O₂ & → 2CuO \\
CuO + 2NH₃H₂O + 2NH₃ & → Cu(NH₃)₂L⁺ + 3H₂O
\end{align*}
\]

(15)

(16)

In addition to Cu, it is reported that ammonia-ammonium also shows leaching ability to other base metals, which is generally dependent 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 (NH₄)₂CO₃ and NH₃H₂O 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 (i.e., IL leaching) and sub-/supercritical leaching. Although the theory and technology behind them already exist and some of them have 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 lixiviant (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 lixiviant 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 H2SO4 to the leaching 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-chelating happens in acidic environment (pH 2–3).

Except for EDTA, other potential chelators, such as Polyethyleneimine (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 H2O2 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. [BSO4H]Py, [BSO4HMIm][H2SO4], [BSO4HMIm][HSO4], [BSO4HMIm][OTf], [BSO4HMIm][OTf] and [BSO4H]Py[OTf] associating with H2O2 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 (Tc) and critical pressure (Pc) having gas-like diffusion rate, viscosity and liquid-like density (Sanyal et al., 2013). Of that, supercritical CO2 has been widely investigated since it has a relatively low critical point (Pc = 7.38 MPa, Tc = 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 CO2 has amazing dissolving capacity, diffusion ability and the penetration capacity. When it comes to metal extraction, supercritical CO2 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 CO2 with H2SO4 and H2O2 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 CO2 modified with acetone and KI-I2 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 CO2 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: +H₃NCH₂COOH (cation), °H₂NCH₂COO⁻ (zwitterion) and H₂NCH₂COO⁻ (anion) depending on different pH (Eq. (17)). The zwitterion and anion can form complexes with both Ca²⁺ and Cu²⁺ to make them soluble in solution.

\[
\begin{align*}
\text{H}_2\text{NCH}_2\text{COOH} \rightarrow & \text{H}_2\text{NCH}_2\text{COO}^{-} + \text{H}^+ \\
\text{H}_2\text{NCH}_2\text{COO}^{-} \rightarrow & \text{H}_2\text{NCH}_2\text{COO}^{-} + \text{H}^+ \\
\text{H}_2\text{NCH}_2\text{COO}^{-} \rightarrow & \text{H}_2\text{NCH}_2\text{COO}^{-} + \text{H}^+ \\
\end{align*}
\]

(17)

Recently, a novel technology employing glycine as lixiviant in alkali environment (pH = 10.5–11) with different oxidants (O₂, H₂O₂ and/or Cu²⁺) 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% H₂O₂, 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 0.322μmol/(m²s) 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 chalcolphile metals such as Ni, Co, Zn, Pb, etc. in a more recent patent (Eksteen and Oraby, 2016).

\[
2\text{Au} + 4\text{NH}_2\text{CH}_2\text{COOH} + 2\text{NaOH} + 1/2\text{O}_2 \rightarrow 2\text{Na}[\text{Au(CH}_2\text{NH}_2\text{COO})_2] + 3\text{H}_2\text{O}
\]

(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 Na₂SO₄, 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⁺/H₂. 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
of CuSO₄ and CuCl₂, has also been intensively investigated as oxidant. It is recyclable, but can be quite expensive, de
not bring any impurities to the system and is considered one of the most environmentally friendly oxidant, but can be quite expensive, de
not bring any impurities to the system and is considered one of the most environmentally friendly oxidant, but can be quite expensive, de
not bring any impurities to the system and is considered one of the most environmentally friendly oxidant, but can be quite expensive, de
not bring any impurities to the system and is considered one of the most environmentally friendly oxidant, but can be quite expensive, de
enjoyable in iodine-iodide leaching system (Table 3).

### 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).

<table>
<thead>
<tr>
<th>Leaching methods</th>
<th>Environmental impact</th>
<th>Economic feasibility</th>
<th>Research level</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Toxicity&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Safety&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Leaching rate&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Aqua regia</td>
<td>Medium</td>
<td>Low</td>
<td>Fairly high</td>
</tr>
<tr>
<td>Cyanide-based leaching</td>
<td>High</td>
<td>Low</td>
<td>Medium</td>
</tr>
<tr>
<td>Thiourea (in acidic solution)</td>
<td>Low, probable carcinogen</td>
<td>Medium, poor stability</td>
<td>Fairly high</td>
</tr>
<tr>
<td>Thiosulfate</td>
<td>Low</td>
<td>High</td>
<td>Medium</td>
</tr>
<tr>
<td>Thiocyanate</td>
<td>Medium</td>
<td>Low</td>
<td>Medium</td>
</tr>
<tr>
<td>Chlorine/chloride</td>
<td>Medium</td>
<td>Low</td>
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<tr>
<td>Bromine/bromide</td>
<td>Medium</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Iodine/iodide</td>
<td>Nontoxic</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Ammonia-ammonium</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>Chelation (EDTA)</td>
<td>Nontoxic</td>
<td>High</td>
<td>Fairly high</td>
</tr>
<tr>
<td>Ionic liquid</td>
<td>Low</td>
<td>High</td>
<td>Medium</td>
</tr>
<tr>
<td>Supercritical technology</td>
<td>Nontoxic</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Glycine</td>
<td>Nontoxic</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>

<sup>a</sup> Referred to Anand et al. (2013), Kaya (2016), Zhang et al. (2012b).
<sup>b</sup> Safety refers to the safety levels (low, medium and high) during the transportation and store of reagents, and the operation of the leaching process.
<sup>c</sup> Reagent costs (low, medium and high) are based on the unit price and consumption of reagents without the consideration of recyclability.
<sup>d</sup> Referred to Cui and Anderson, 2016; Cui and Zhang, 2008; Kaya, 2016.
<sup>e</sup> 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.

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Electro-pair</th>
<th>E°, V</th>
<th>Example</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂/air</td>
<td>O₂⁻/H₂O</td>
<td>1.23</td>
<td>HL and AAL</td>
<td>Liu et al. (2009), Yazici and Deveci (2015)</td>
</tr>
<tr>
<td>O₃/OH⁻</td>
<td>0.40 AAL</td>
<td></td>
<td></td>
<td>Calgaro et al. (2015), Huang et al. (2014), Kumar et al. (2014), Melo Halmenschlager (2015), Sahin et al. (2015), Xiao et al. (2013)</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>H₂O₂/H₂O</td>
<td>1.76</td>
<td>MAL, TL, AAL, III and SL</td>
<td>Behnafard et al. (2013)</td>
</tr>
<tr>
<td>ClO⁻</td>
<td>ClO⁻/Cl⁻</td>
<td>0.89</td>
<td>HL</td>
<td>Behnafard et al. (2013)</td>
</tr>
<tr>
<td>Cl₂</td>
<td>Cl₂/Cl⁻</td>
<td>1.40</td>
<td>HL</td>
<td>Kim et al. (2011a)</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>Cu²⁺/Cu⁺</td>
<td>0.34</td>
<td>MAL, TL, AAL</td>
<td>Lim et al. (2013), Tripathi et al. (2012), Yazici and Deveci (2013, 2015)</td>
</tr>
<tr>
<td>Cu²⁺/CuCl</td>
<td>0.16</td>
<td>HL and AAL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu²⁺/CuBr</td>
<td>0.56</td>
<td>AAL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu²⁺/CuBr</td>
<td>0.65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu²⁺/Cul</td>
<td>0.86</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu²⁺/I⁻</td>
<td>1.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I₂</td>
<td>I₂/I⁻</td>
<td>0.62</td>
<td>HL and SL</td>
<td>Liu et al. (2016), Xiu et al. (2015)</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>Fe³⁺/Fe²⁺</td>
<td>0.77</td>
<td>MAL</td>
<td>Yazici and Deveci (2014)</td>
</tr>
<tr>
<td>Fe(CN)₆³⁻</td>
<td>Fe(CN)₆³⁻ / Fe(CN)₆⁺</td>
<td>0.36</td>
<td>CL (for Au-Ag ore)</td>
<td>Calgaro et al. (2015), Huang et al. (2012), Yazici and Deveci (2014, 2015), Xiao et al. (2013)</td>
</tr>
</tbody>
</table>

### 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 recycling. Among them, O₂/air has low solubility in aqueous solution (about 8 ppm for O₂ from air at 25 °C), which largely limits the leaching efficiency. H₂O₂, with a fairly high standard reduction potential (1.76 V), has been widely reported in WPCBs recycling. It will not add impurities since Cu is already present in WPCBs. I₂ has shown well oxidizing ability in iodine-iodide leaching system (Table 3). 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 I₂ can be used in more leaching systems. The use of Fe³⁺, in the forms of Fe₂(SO₄)₃, as oxidant is restricted in acidic environment, another novel oxidant, Fe(CN)₆³⁻, 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.
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 reoxidation reaction. In addition, in acidic environment, the large consumption of cementing metal and the generation of H₂, 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)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: \[ \text{Au(CN)}_n \rightarrow \text{Zn} + 2\text{CN}^- + \text{e}^- \quad (19) \]

Anode: \[ \text{Zn(CN)}_2 \rightarrow \text{Zn} + 4\text{CN}^- + \text{e}^- \quad (20) \]

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 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 (1) 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.

\[ \text{Ag(NH}_3\text{)}_2^+ + \text{Cu} \rightarrow \text{Cu(NH}_3\text{)}_2^+ + \text{Ag} \quad \Delta G^\circ_{\text{mix}} = -45.8\text{kJ/mol} \quad (21) \]

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 SO₄²⁻/Pb²⁺ molar ratio of 1.4 for the precipitation of Pb as PbSO₄. In addition, Yazici et al. (2014) suggested that pH of 4–7.5 and 9.5 were suitable for the removal of ferrous-ferrous ions 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 sulfates, Na₂SO₄ in particular, remained in mother solution needs to be recycled even not much profitable.

Behnamfard et al. (2013) used sodium borohydride (NaBH₄) 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 NaBH₄ 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 HNO₃ 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 lixiviant 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-lead (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 iodide-leaching solution of WPCBs (with base metals previously
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. Taugtsile 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 in-situ 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. Taugtsile 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.

Another adsorption gel, bisthiourea modified persimmon tannin gel (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% Au3+ 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 CPT gel over other precious and base metals.

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 electrodeposition 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/KCl3M) with competitive Cu2+ reduced to soluble CuCl2−. 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 Cu2+ and Pb2+ deposited as Cu and PbO2 onto cathode and anode respectively from HNO3 leaching solution of WPCBs (with Sn previously removed).

Besides, some researchers also used direct electrodeposition for the Sn and Cu recovery from the acidic stripping 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. Fe3+) (Silva-Martinez and Roy, 2013) and unsatisfactory recovery of Sn (Li et al., 2014).

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 Fe3+ (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 Fe3+ 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, manufacturers, 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 focus 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 inter-disciplinary 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

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