Hydrometallurgy 156 (2015) 199–205

Contents lists available at ScienceDirect

Hydrometallurgy

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

Technical note

Recovery of metal values from waste printed circuit boards using an alkali fusion–leaching–separation process

Xueyi Guo [a,b,*], Jingxin Liu [a], Hong Qin [a], Yang Liu [a], Qinghua Tian [a,b], Dong Li [a,b]

[a] School of Metallurgy & Environment, Central South University, Changsha, 410083, China
[b] Cleaner Metallurgical Engineering Research Center, Nonferrous Metal Industry of China, Changsha, 410083, China

ARTICLE INFO

Article history:
Received 15 February 2015
Received in revised form 17 June 2015
Accepted 26 June 2015
Available online 2 July 2015

Keywords:
Waste printed circuit boards
Alkali fusion process
Copper
Amphoteric metals

ABSTRACT

An efficient alkali fusion–leaching–separation process is developed to recover metals in crushed metal enrichment (CME) which originated from waste printed circuit boards (PCBs). Impacts of fusion parameters on metals conversions were systematically investigated. In the fusion–leaching process, amphoteric metals such as tin, lead, zinc and aluminum in the CME were leached out, while leaving copper and precious metals in the residue. Subsequently, metals in solution were further extracted via precipitation processes, and metals in the residue were recovered using an acid leaching–electrowinning process. Cathode copper, nano-Cu_2O, $CaSnO_3$/$CaSn(OH)_6$ crystal and mixture of PbS–ZnS were obtained as the final products of this process. By optimizing the experimental conditions, recoveries of 98.66% for Cu, 91.08% for Sn, 91.25% for Zn, 78.78% for Pb were achieved, respectively. And all precious metals were enriched in the final residue with grades of Au 613 g/t, and Ag 2157 g/t.

1. Introduction

Waste electrical and electronic equipment (WEEE) is currently the fastest growing solid waste at an annual growth rate of 3–5% (Afroz et al., 2013). Over the past several decades, concerns have grown regarding the value and hazards presented by WEEE. Of particular interests are the re-utilization and recovery of printed circuit boards (PCBs) which are the essential parts of electronic devices and constitute around 3 wt.% of WEEE (Marques et al., 2013). Unlike normal municipal solid wastes, waste PCBs may lead to tragic health, safety and environmental issues. There are several hazardous materials contained in PCBs, such as lead (in solder), antimony (in solder), beryllium (in connectors), cadmium (in contacts and switches), and brominated flame retardants (in plastics) (Noon et al., 2011). However, PCBs also contain a substantial quantity of valuable metals. It is known that the typical PCBs are made up of non-metal (plastic, resins, glass fibers, etc.) >70%, copper ~16%, solder (mostly tin and lead) ~4%, iron & ferrite ~3%, nickel ~2%, silver ~0.05%, gold ~0.03%, and palladium ~0.01% (Goosey and Kellner, 2003), in which precious metals take up over 70% of the recovery value, while copper about 20% (Flandinet et al., 2012). Waste PCBs are showing promising potential for recovery of metal values.

For recovery of metals from waste PCBs, various treatment options based on conventional mechanical, physical, pyrometallurgical and hydrometallurgical processes are proposed. Most of these treatments can be classified as the following categories:

(1) Pre-treatment;

Since metals in PCBs are often covered with or encapsulated by various nonmetals (plastic or ceramic), a pre-treatment process is first needed to expose metals and to facilitate their extraction in the further treatment (Cui and Zhang, 2008). Mechanical/physical process for separation of nonmetals is established including multiple crushing, magnetic separation, corona electrostatic separation and eddy current separation (Cui and Forssberg, 2003). This process benefits from low capital and operating costs. However, insufficient liberation and loss of metals are the important detractions to it (Tuncuk et al., 2012). On the other hand, pyrolysis is a potential way to separate metals from nonmetals, in which the organic resin is converted to flammable gases and tar, while fiberglass and metals remain as residue of the pyrolytic reaction (Guo et al., 2014). However, particular attention has to be paid to the potential emissions of toxic by-products (Ortuño et al., 2014).

(2) Extraction of base metals;

Pyrometallurgy and hydrometallurgy are both used to extract base metals from waste PCBs/WEEE.

There are several pyrometallurgical plants worldwide, such as Umicore in Belgium (Hagelüken, 2006), Xstrata in Canada and Boliden in Sweden (Cui and Zhang, 2008). In pyrometallurgical processes, waste PCBs/WEEE are smelted with copper concentrate to obtain precious metal-bearing copper bullion, which is subjected to electrolytic

* Corresponding author at: School of Metallurgy & Environment, Central South University, Changsha 410083, China.
E-mail address: xyguo@csu.edu.cn (X. Guo).

http://dx.doi.org/10.1016/j.hydromet.2015.06.011
0304-386X/

refining to produce high purity copper. Slimes collected from copper electrorefining are further refined to recover precious metals. Organic constituents partially/wholly supplant coke as fuel and reducing agent. Environmental impact and scale of operation are the most important factors affecting selection or development of pyrometallurgical processes.

Compared with pyrometallurgical processes, hydrometallurgical processes are more suitable for small scale applications. Acid leaching (Havlik et al., 2010; Yazici and Deveci, 2015), ammonia-based leaching (Oishi et al., 2007; Sun et al., 2015) and bioleaching (Yang et al., 2009) are extensively studied to recover metals from waste PCBs. These processes have advantages on selective and efficient extraction of Cu, however, other base metals (Pb, Zn, Sn, et al.) were removed as impurities, and no recovery scheme was proposed for them.

(3) Leaching and recovery of precious metals.

The most common leaching agents used in recovery of precious metals include cyanide (Quinet et al., 2005), halide (Behnamfard et al., 2013), thiourea and thiosulfate (Syed, 2012). Leaching of precious metals from waste PCBs in these lixiviants is well-established and compared, and precious metal grade is one of the most important factors affecting selection of a treatment process.

This work is focused on selective recovery of base metals from waste PCBs using an alkali fusion–leaching–separation process.

The alkali fusion–leaching process is an efficient method in nonferrous metallurgy, especially for resources bearing amphoteric metals. So far, it has been used to extract metals from low grade ores (Chen et al., 2013; Xue et al., 2009; Yang et al., 2011a, 2011b), and to selectively recover metals from secondary resources (Margulis, 2000; Zhang et al., 2009).

However, as far as we know, few studies were done to recover metals from waste PCBs using this process, even less studies focused on the recovery of amphoteric metals. In this work, an alternative flow-sheet was proposed in Fig. 1 to recover metals from crushed metal enrichment (hereinafter referred to as 'CME') originated from waste PCBs. Parameters of the alkali fusion process were investigated, and further treatments of the leaching solution and residue are also studied to separate and extract metals.

Fig. 2. Photo of the CME.

2. Experimental

2.1. Experimental materials

The CME used in the experiments was supplied by a PCB recycling company in Shenzhen, China, where scrap TV boards were crushed and selected by gravity and magnetism to separate nonmetals (plastic, resins, glass fibers), magnetic metals (Fe, Ni) with the CME. However, the separation could not be absolutely sufficient, especially for resins and glass fibers, which were adhered to the conductive copper foil cohesively. Fig. 2 is a photo of the CME, and Table 1 presents its main chemical compositions. Since metals in waste PCBs present as element and/or as alloys (Ha et al., 2014), a low-cost oxidizing flux of $NaOH–NaNO_3$ was selected as the reaction medium. All reagents used in the experiments were of analytical grade and provided by local suppliers, and distilled water was used to prepare solutions in all experiments.

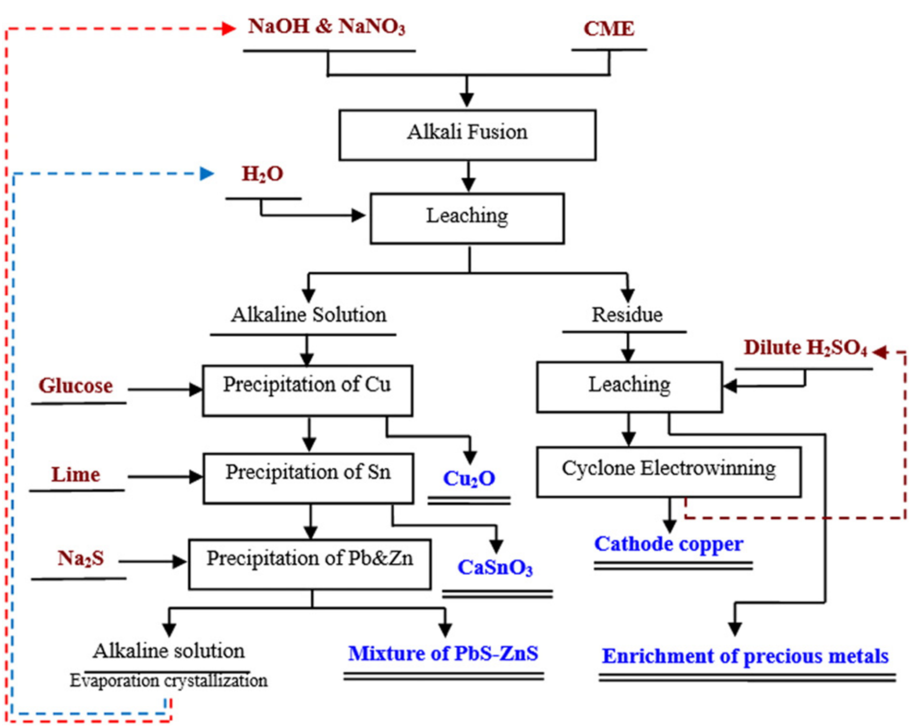

Fig. 1. General flow-sheet of the alkaline fusion–leaching–separation process.