Waste Management 33 (2013) 935–941

Contents lists available at SciVerse ScienceDirect

Waste Management

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

Study on the influence of various factors in the hydrometallurgical processing of waste printed circuit boards for copper and gold recovery

Ionela Birloaga [a,*], Ida De Michelis [b], Francesco Ferella [b], Mihai Buzatu [a], Francesco Vegliò [b,*]

[a] Department of Engineering and Management of Metallic Materials, Materials Science & Engineering Faculty, University “Politehnica” of Bucharest, Bucharest 060032, Romania
[b] Department of Chemistry, Chemical Engineering and Materials, University of L'Aquila, 67040 Monteluco di Roio, L'Aquila, Italy

ARTICLE INFO

Article history:
Received 8 August 2012
Accepted 2 January 2013
Available online 29 January 2013

Keywords:
Printed circuit boards
Oxidative leaching
Thiourea
Gold
Copper

ABSTRACT

The present lab-scale experimental study presents the process of leaching waste printed circuit boards (WPCBs) in order to recover gold by thioureation. Preliminary tests have shown that copper adversely affects gold extraction; therefore an oxidative leaching pre-treatment was performed in order to remove base metals. The effects of sulfuric acid concentration, hydrogen peroxide volume and temperature on the metal extraction yield were studied by analysis of variance (ANOVA). The highest copper extraction yields were 76.12% for sample A and 18.29% for sample D, after leaching with 2 M H_2SO_4, 20 ml of 30% H_2O_2 at 30 °C for 3 h. In order to improve Cu removal, a second leaching was performed only on sample A, resulting in a Cu extraction yield of 90%. Other experiments have shown the negative effect of the stirring rate on copper dissolution. The conditions used for the process of gold extraction by thiourea were: 20 g/L thiourea, 6 g/L ferric ion, 10 g/L sulfuric acid, 600 rpm stirring rate. To study the influence of temperature and particle size, this process was tested on pins manually removed from computer central processing units (CPUs) and on waste CPU for 3½ h. A gold extraction yield of 69% was obtained after 75% of Cu was removed by a double oxidative leaching treatment of WPCBs with particle sizes smaller than 2 mm.

1. Introduction

By intensive exploitation of resources at global level, the obtaining of gold and silver from ores has begun to be exhausted because of the insufficient amount of raw materials to supply the high demand of electric and electronic manufacturers. The continuous yearly generation of waste electrical and electronic equipment causes serious environmental problems as it is disposed in landfills, because of their hazardous content. In most of the electronic equipment, waste PCBs (WPCBs) are important components which contain the largest amount of metals, especially copper and precious metals (Tuncuk et al., 2012). According to Takanori et al. (2009), WPCBs contain approximately 30% metallic material (Cu in circuitry; Sn, Fe and Pb in the soldering and lead frames; Au, Ag and Pd in the integrated circuits), approximately 40% organic resin materials, and about 30% glass materials used as resin reinforcing fibers. Thus, their special physical and chemical characteristics make their recycling very difficult. Therefore, a certain number of pyrometallurgical, hydrometallurgical, bio-hydrometallurgical, physical–mechanical processes have been proposed for the recycling of WPCBs. Their recycling generally starts from the pre-treatment stage, which includes the dismantling of the reusable and toxic parts by using a process of shredding/separation and physical recycling. Methods as gravity, magnetic, electrostatic, density and pneumatic separation have been used in order to recover metals from WPCBs, but as metal losses of 10–35% usually occur because of insufficient liberation, they are performed prior to the pyrometallurgical or the hydrometallurgical processes, as pre-treatments (Cui and Zhang, 2008).

The pyrometallurgical process consists in melting the solid waste, resulting in a molten slag as a pool into which precious metals are dissolved and accumulated. This metallic melt is named collector metal; the most commonly used collector metals are Fe, Cu, Ni, Pb–Cu and Ni matte (Hagelüken, 2006). By this process only a partial separation of metals can be achieved, hydrometallurgical methods or electrochemical processing being subsequently required (Cui and Zhang, 2008).

Hydrometallurgical processes involve the dissolution of metals in alkaline or acid medium. Scientific literature surveys of hydrometallurgical technologies for WPCBs treatment indicate that a double oxidizing-acid leaching treatment using complex agents is effective for the selective leaching of base and precious metals (Huang et al., 2009; Tuncuk et al., 2012). Leaching processes of base metals from this sort of wastes by using sulfuric acid and hydrogen peroxide as oxygen source have been performed by

---

* Corresponding authors. Tel.: +40 730 614 162 (I. Birloaga), tel.: +39 0862 434236; fax: +39 0862 434203 (F. Vegliò).

E-mail addresses: ionela_birloaga@yahoo.com (I. Birloaga), francesco.veglio@univaq.it (F. Vegliò).

0956-053X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.wasman.2013.01.003

several authors (Quinet et al., 2005; Deveci et al., 2010; Kamberovic et al., 2011; Yang et al., 2011). Besides this system, the use of nitric acid and hydrochloric acid has been widely studied, but due to stringent environmental regulations and because of the corrosive nature of these reagents, they cannot be considered appropriate, whereas sulfuric acid is less hazardous (Jha et al., 2011). Reagents like cyanide (Parga et al., 2007; Jeffrey and Breuer, 2000), halide (Kim et al., 2011; Dönmez et al., 2001), thiosulphate (Ha et al., 2010; Navarro et al., 2002), and thiourea (Örgül, 2002; Hiskey, 1984) were commonly used for the recovery of precious metals. Cyanide is the most used reagent for gold extraction from ores, but it is characterized by lethal toxicity and a high chemical consumption. For this reason cyanidation processes were gradually replaced by thiourea or thiosulfate leaching. The thiourea leaching process has a fast kinetic reaction with gold and silver, as well as a low impact on the environment as compared to cyanide; furthermore, it involves lower operating costs as compared to the thiosulfate method which consumes a large amount of leaching reagent (Jing-Ying et al., 2012).

Thiourea is a chemical compound whose crystals can be dissolved in water or acid solution and its aqueous form can react with gold (I) to produce a stable cationic complex or aurous ion (Kulenov et al., 1983):

$$\mathrm{Au} + 2\mathrm{SC(NH_2)_2} \rightarrow \mathrm{Au[SC(NH_2)_2]_2^+} + e^- \tag{1}$$

The kinetics of gold leaching using different oxidants such as sodium peroxide, hydrogen peroxide, ferric iron, oxygen (pure oxygen or air), ozone, manganese dioxide, manganate, and dichromate has shown that the most convenient is iron, since iron ions ensure greater gold dissolution rate in acid sulfate solution than in chloride or nitrate solutions (Plaskin and Kozhukhova, 1960; Songina et al., 1971). Gold reaction in sulfuric acid solution, with thiourea and ferric ion, can be expressed as follows:

$$\begin{aligned} &2\mathrm{Au} + 2\mathrm{Fe^{3+}} + 4\mathrm{SC(NH_2)_2} + \mathrm{SO_4^{2-}} \\ &\quad \rightarrow \mathrm{[Au(SC(NH_2)_2)_2]_2SO_4} + 2\mathrm{Fe^{2+}} \end{aligned} \tag{2}$$

The kinetics of gold dissolution during leaching with thiourea in sulfuric acid solution, using ferric sulfate as oxidant was studied by Li and Miller (2007) in order to measure the system variables (disk rotational speed, ferric concentration, thiourea concentration, pH and temperature) and to determine the most important parameters which determine the kinetic response of gold extraction. They concluded that under surface reaction control, the dissolution rate is approximately at a one-fourth order with respect to the thiourea concentration, a zero order with respect to ferric concentration, and a minus one-fifth order with respect to hydrogen ion concentration within a pH range from 1 to 2; the leaching system depends significantly on the agitation speed.

Ficeriová and Balaž (2010) conducted a study on gold recovery from goldsmith's waste using mechanical (milling in water) and mechanochemical activation (milling in thiourea solution) followed by leaching in sulfuric acid solution using thiourea and ferric ion as oxidant with a stirring rate of 600 rpm at room temperature. After leaching without any preliminary treatment 78% gold dissolution was obtained, whereas after mechanical and mechanochemical activation the gold dissolution was 98% and 99%, respectively; physical–chemical changes produced during the pre-treatment had a pronounced influence in the subsequent gold extraction.

After comminuting and preliminary mechanical pre-treatments, Kamberovic et al. (2011) performed an acid leaching on concentrated materials with a particle size range of −1 + 0.071 mm, in order to recover base metals such us copper, tin and zinc. Afterwards, acid thiourea leaching with ferric ion as oxidant was applied on the solid residue for precious metals recovery. More than 90% of gold and 85% of silver dissolution was obtained.

A study of gold recovery from waste mobile phones by thiourea acid leaching process with ferric sulfate as oxidant showed gold extraction around 90%. This process was applied on PCB materials with a size range of 100 mesh: this characteristic resulted in well disintegrated degrees and large exposure areas of gold and silver, which noticeably improved leaching results (Jing-Ying et al., 2012).

The goals of this experimental work were the optimization of copper recovery by oxidative leaching using ANOVA and the examination of the influence of different factors which can affect gold dissolution during thiourea leaching. This study revealed important data to design a less toxic and more sustainable process for precious metals recovery from waste computer PCBs.

2. Materials and methods

2.1. Materials

Experimental works were performed using the following materials: two samples of WPCBs, preliminary comminuted and separated by size as previously described by authors (Birloaga et al., 2012), used for base and precious metals leaching procedures; two samples of waste CPUs for direct thiourea leaching and CPU connection pins manually removed from their surface to study the influence of factors during gold leaching. The chemical composition of all samples was determined by X-ray fluorescence spectrometry analysis (XRF) and the results are reported in Table 1. To ensure the homogeneity of the XRF solid samples, all materials were thoroughly hand mixed in advance, and then samples of 5 g each were taken to be milled with a planetary ball mill (Fritsch Pulverisette Mod. 06 102/2045 in a stain less steel jar) for approximately 15 min. Their elements concentration has also been confirmed by performing a roasting of 20 g of ground PCBs and CPU in a muffle furnace (Humboldt, H-30204F) for 1 h at 600 °C. To estimate the loss of materials, all samples were weighted on an analytical balance (Mettler PE 600); the weight loss was 11% for PCB and 4% for CPU. Subsequently, all residues were ground in the planetary ball mill and sampled to be analyzed by XRF and AAS. For AAS analysis, approximately 0.3 g from each residues were digested in a mixture of aqua regia ($\mathrm{HNO_3}$: HCl = 3:1) and HF, then immersed in a microwave for 1 h. After cooling, the solutions were filtered and diluted using deionized water at a proper concentration level. The Cu, Fe, Pb, Au and Ag concentrations have been determined using a Varian spectrometer SpectrAA 200. The results of these analyses (not presented here) revealed almost the same concentration of the elements in the ground materials previously measured by XRF (Table 1).

2.2. Leaching tests

2.2.1. Oxidative leaching

A 2^3 full factorial design (Montgomery, 1991) was performed in the leaching study, involving eight treatment combinations and three replications of the central point. The investigated variables were the sulfuric acid concentration, hydrogen peroxide volume and temperature. Factors and levels are given in Table 2. Leaching tests were performed in 250 ml Erlenmeyer flasks and placed in a Dubnoff water bath (BSD/D, ISCO, Italy) with a mechanical stirring rate of 200 rpm for 3 h. A 10 g of ground PCBs (<3 mm particle size) were immersed in 100 ml solutions of sulfuric acid as leaching reagent and hydrogen peroxide as oxygen source (reagent concentrations are reported in Table 2). For a complete removal of copper a second leaching test was performed on solid residues of sample A. The experimental conditions, chosen taking into account the