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An advanced study on the hydrometallurgical processing of waste computer printed circuit boards to extract their valuable content of metals

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ABSTRACT

This study refers to two chemical leaching systems for the base and precious metals extraction from waste printed circuit boards (WPCBs); sulfuric acid with hydrogen peroxide have been used for the first group of metals, meantime thiourea with the ferric ion in sulfuric acid medium were employed for the second one. The cementation process with zinc, copper and iron metal powders was attempted for solutions purification. The effects of hydrogen peroxide volume in rapport with sulfuric acid concentration and temperature were evaluated for oxidative leaching process. 2 M H_2SO_4 (98% w/v), 5% H_2O_2, 25 °C, 1/10 *S/L* ratio and 200 rpm were founded as optimal conditions for Cu extraction. Thiourea acid leaching process, performed on the solid filtrate obtained after three oxidative leaching steps, was carried out with 20 g/L of $CS(NH_2)_2$, 6 g/L of Fe^{3+}, 0.5 M H_2SO_4, The cross-leaching method was applied by reusing of thiourea liquid suspension and immersing 5 g/L of this reagent for each other experiment material of leaching. This procedure has lead to the doubling and, respectively, tripling, of gold and silver concentrations into solution. These results reveal a very efficient, promising and environmental friendly method for WPCBs processing.

1. Introduction

The treatment of wastes coming from electronic and electric equipments (EEE) exhibits two main advantages: (i) reduction of land filling, avoiding in this way the environment pollution with the hazardous content of these kinds of wastes and (ii) reutilization of the recovered materials in the manufacturing of the new EEEs. For their processing, many researchers have studied and proposed various processes, e.g. physico-mechanical, hydrometallurgical, pyrometallurgical, biometallurgical or by combination of thereof as there are present in the reviews of Cui and Zhang (2008), Tuncuk et al. (2012) and Pant et al. (2012). As all the EEEs have in their structure a motherboard, component which has a high amount of valuable metals, most of scientific papers were focused on their treatment. Beside their valuable metals content, the WPCBs have about 70% nonmetals which mainly consist in epoxy resins, glass fibers and brominated flame retardants. The mechanical–physical processes for the separation of elements by their physical properties have been performed by various researches, but these have as main drawback the fact that a complete liberation cannot be realized, this resulting in a considerable loss of valuable metals. Therefore, the mechanical–physical process is generally used prior to pyro-, bio- or hydro-metallurgical processes as a pretreatment. The pyrometallurgical process consist in a very high working temperature, i.e. 1200 °C, thereby this kind of process always requires high investments (Flandinet et al., 2012). Beside this, the required high temperature leads to the releases of dioxins into atmosphere (Tsydenova and Bengtsson, 2011). As is shown in literature, the bio-metallurgical methods, e.g. biological leaching is slower and more toxic than the chemical leaching (Pant et al., 2012). Thus, the hydrometallurgical processes, which consist in a first step of metals extraction into solution by chemical leaching in acid or alkaline medium, and then a second step that consists of solution purification by various methods such as precipitation, cementation, absorption, ion exchange, electrowinning and solvent extraction, are considerate environmental friendly and more easily to be controlled due to their moderate working conditions.

For metals recovery from waste printed circuit boards, most of the scientific papers present as main steps the following

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operations: dismasting of hazardous components (i.e. capacitors, resistor, batteries), comminuting, in some cases a thermal treatment, chemical leaching, solution purification and metals recovery. Reagents like the inorganic acids (sulfuric acid, hydrochloric acid and nitric acid), organic acids (citric acid, oxalic acid) or solution with alkaline character (ammonium and sodium hydroxide) have been used for base metals leaching, afterwards a subsequent leaching on the solid suspension has been applied with chemicals such as cyanide, thiosulfate, thiourea and halides for the precious metals recovery (Birloaga et al., 2013; Jianfeng et al., 2009; Kim et al., 2011; Lee et al., 2011; Oishi et al., 2007; Kamberović et al., 2011; Zhou and Qiu, 2010; Zhu et al., 2011; Fogarasi et al., 2013; Fogarasi et al., 2014; Yang et al., 2011a,b). Many hydrometallurgical attempts were tried to extract copper from the composition of WPCBs, this "red gold" being considerate the major metallic element in the composition of these wastes. The sulfuric acid is a cheap reagent and was widely used at industrial level for metals recovery from ores and presents good efficiency on Cu dissolution in the presence of hydrogen peroxide; therefore this system was considered by many authors a very suitable chemical leaching system for Cu dissolution from waste printed circuit boards (Yang et al., 2011a,b). This system presents the advantage of a lower toxicity and the possibility to be used at industrial scale due to its less corrosive nature. Conversely, for precious metals recovery there are still problems in the development of a reliable and less poisonous hydrometallurgical route. As a conscience of accidents produced in the gold mining industry (e.g. Mine from Los Frailes, Spain in 1998; Mine from Baia Mare, Romania in January 2000) (European Commission, 2010), the use of cyanide, reagent with a high level of toxicity, was tried to be replaced by less poisonous reagents. The leaching with thiosulfate could be considerate a good way for precious metals but with the issues of high cost raised in the purification step this method cannot be considered suitable for application at large scale. Application of halides can be regarded efficient as they present high leaching rates, but as the use of an oxidant (usually the halogen of the halide itself) is required, this would lead to high costs for the prevention of corrosion and the use of a bound system; therefore, there is no economy for their use at industrial level (Yang et al., 2011a,b; Zhang et al., 2012; Syed, 2012). The precious metals leaching with thiourea could be regarded as a suitable method due to its high rate of leaching, lower toxicity and eco-efficiency. Beside these advantages, this process has as main drawback the fact that a lot of reagent is consumed.

Therefore, the present study complement the previous work (Birloaga et al., 2013) with the core to obtain a total extraction of copper, gold and silver from waste computer printed circuit boards and also to reduce the consumption of reagents during the thioureation process. For both reduction of reagent consumption and improving of precious metal content into solution, three-stage thiourea acid cross-leaching process was applied. The paper shows new data for the application of the thiourea cross leaching procedure for precious metals extraction, this method not being until now studied or applied on WPCBs treatment and the obtained results are considered helpful for a possible application at industrial scale.

2. Materials and methods

2.1. Materials

Experimental tests were performed on a sample of waste computer printed circuit board. This was preliminary subjected to manual removal of some electronic components (e.g. capacitors, batteries, relays) and then crushed to a certain particle size (less than 2 mm). The chemical attack with aqua regia and hydrofluoric acid was performed on a certain amount of the material obtained after preliminary roasting for 1 h at 600^0C in a muffle furnace (Humboldt, H-30204F) and milling in a planetary ball mill (Fritsch Pulverisette Mod. 06 102/2045) (more details are shown elsewhere (Birloaga et al., 2013)). According to Atomic Absorption Spectrometry, which was used for determination of elements concentration in the solution obtained after chemical attack, the sample contained 305.7 g/kg of Cu, 116.9 g/kg of Al, 152.1 g/kg of Fe, 73.6 g/kg of Sn, 15.8 g/kg Ni, 18.6 g/kg of Zn, 67 g/kg of Pb, 238 mg/kg of Au and 688 mg/kg of Ag. In the case of thiourea leaching two samples of waste CPU and CPU connection pins manually removed from their surfaces were used as control experiments to test the leaching efficiency of the thiourea approach. Chemicals used in the experiments were of analytical reagent grade. The leaching solutions were prepared by dissolving the proper chemicals in distilled water to the required concentration.

2.2. Methods

2.2.1. Oxidative leaching

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 three hours. 10 g of ground waste printed circuit boards (<2 mm particle size) were immersed in 100 ml solutions that contains sulfuric acid as leaching reagent and hydrogen peroxide as oxygen source. As was observed in our previous work, in two steps oxidative leaching not all copper was extracted, leading to a efficiency of about 70% of gold extraction (Birloaga et al., 2013). For a complete removal of copper, 3 consecutive leaching tests were performed by the following process conditions: 2 M H_2SO_4, 5% H_2O_2, 25 and 30 °C and three hours of stirring. Process conditions were: 2 M H_2SO_4, 5% H_2O_2 (20 mL of 30% H_2O_2), 30 °C and three hours of mechanical stirring (200 RPM). The effect of different procedures of H_2O_2 addition to the solution containing 2 M H_2SO_4 and WPCB was estimated and summarized below. The addition was performed either (A) in one step (20 mL at $t = 0$); (B) in two steps of 10 mL ($t_1 = 0$, $t_2 = 90$ min); (C) in four steps of 5 mL ($t_1 = 0$, $t_2 = 45$, $t_3 = 90$, $t_4 = 135$ min); (D) in eight steps of 2.5 mL at every 22.5 min.

At the end, the leaching suspensions were filtered under vacuum and the cakes washed, then the pH of pregnant solutions was measured. A sample of 5 ml of each solution was withdrawn for XRF (Semi-Quantitative X-ray florescence spectrometry, Spectro Xepos) and AAS (atomic absorption spectrometry, VARIAN AA240FS). The solid material was further used for acid thiourea leaching.

2.2.2. Acid thiourea leaching

Thiourea leaching tests were performed on the solid residues of oxidative leaching. Leaching conditions adopted were: 100 ml (1/10 S/L ratio) of solution containing 20 g/L of thiourea, 6 g/L of ferric ion and 0.5 M H_2SO_4 (pH = 1) and continuous stirring at room temperature. An Innova 2000 (New Brunswick Scientific) open air shaker was used for the experiments and the stirring rate was 500 RPM.

The chemical analyzes of all samples generated in the various leaching tests were also performed by flame atomic absorption spectroscopy (AAS) and Semi-Quantitative X-ray florescence spectrometry (XRF).

3. Results and discussion

3.1. Base metals recovery

3.1.1. Three step oxidative leaching

The extraction yields (% of the total amount in the WPCB sample) for the metals are summarized and plotted in Table 1