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Study of multi-step hydrometallurgical methods to extract the valuable content of gold, silver and copper from waste printed circuit boards

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ABSTRACT

In this work, hydrometallurgical methods like counter and cross current chemical leachings and cementation have been studied and applied for copper, gold and silver recovery from waste printed circuit boards. 1.7 M H_2SO_4 (98% wt./vol.), 17% (V/V) H_2O_2 (30 wt./vol%.), solid/liquid ratio of 15 g/L, room temperature, with a continuous stirring rate of 200 rpm for 1 h have been the optimal conditions for Cu dissolution by the two-step counter current leaching procedure. The cross current leaching procedure with thiourea as reagent and triferric ion as oxidizing agent in diluted acid sulfuric media were involved for the dissolution of gold and silver. About 90% of Au and 75% of Ag extraction yield were obtained in the first step with 20 g/L of thiourea, 6 g/L of ferric ion, 0.1 M of sulfuric acid with a vigorous agitation of 200 rpm of 1 h at ambient temperature. In the solutions purification step, high recovery rates of both Cu and precious metals have been achieved by applying cementation process with Zn powder. This procedure can be considered of interest and is under continuously development for a further application on a small hydrometallurgical pilot plant.

1. Introduction

In the last decade the treatments of printed circuit boards (PCBs) gained great interest from both economic and environmental. As is shown in literature data, about 70% of the PCB's composition consists of ceramic and plastic materials, the rest being made up of mainly copper (concentration of 16–20%), solder (concentration of 4–5%), zinc (concentration of 1–3%), iron (concentration of 2–3%), nickel (concentration of 1–2%) and precious metals (concentration of Au of 150–300 ppm, of Ag of 600–1000 ppm and of Pd of 80–150 ppm) [7,18]. Therefore, for the recovery of copper, gold and silver, many processes involving different technologies such as physical separation and metallurgical (pyrometallurgical, hydrometallurgical and bio-metallurgical) processing or their pooling have been experimented by many researchers [6,9]. The biometallurgical process, even this was successfully used in the treatment of minerals, for waste printed circuit boards treatments is still in its infancy [15]. The pyrometallurgical process is highly dependent on investments, therefore, the metals recovery through hydrometallurgical technique has gained much more attention as is cost effective and affable to the environment [10].

The chemical leaching of metals from waste printed circuit boards, can be carried out separately for base metals by the precious one or not, by the use of aqua regia. Then, for the solution purification, according to solution media, various procedures like precipitation, cementation, ion exchange, solvent extraction, electrowining and carbon absorption may be applied [4,5,14,16]. The chemical leaching of copper with sulphuric acid under the action of various oxidants such us oxygen, ferric chloride, dichromate, chlorine and hydrogen peroxide was intensively investigated [11,20,21]. As the hydrogen peroxide has a high oxidation potential (1.78 V), this is considerate a suitable oxidation agent. Its capacity of oxidation is based on the reduction potential (Eq. (1)), this can play also the role of reduction agent (Eq. (2)) [2,17].

$$H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O \quad (1)$$

$$H_2O_2 \leftrightarrow O_2 + 2H^+ + 2e^- \quad (2)$$

The recovery of precious metals by leaching with thiourea as chemical reagent in acidic media is considered a conveyable alternative to cyanide as this presents less toxicity and a higher speed of reaction. For the dissolution of gold with thiourea various oxidants like hydrogen peroxide, oxygen, ozone, and ferric ion etc., are required. Many studies on the kinetics of gold dissolution with these oxidants in acidic thiourea media have revealed that triferric

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ion is the most effective, especially when the process is carried out in sulfuric acid solution [13]. Waste printed circuit boards using these two leaching systems, have been tested and have provided good results on the recovery of Cu, Au and Ag. However, large consumption of chemicals was required. Therefore, in this paper, reduction of both system chemicals is undertaken by performing the solubilisation procedure using counter and cross current leaching procedures.

The cementation process is preferred to all the others technologies of metals extraction from solution due to ultrahigh purity metals that can be obtained and to the less consumption of materials and energy [8]. The typical reaction of a cementation process is of electrochemical nature and consists in the following equation [1]:

$$mM^{n+} + nN^{\circ} \rightarrow nN^{m+} + mM^{\circ} \quad (3)$$

where M^{n+} and M° are the ionic and metallic forms of noble metals and N° and N^{m+} represent the same entities for reductive metals.

To recover the ionized copper from acid solutions, cementation process with metals like iron, aluminium and zinc has been intensively studied. The cementation reactions of Cu with these elements in acidic media are shown below.

$$Cu^{2+} + 3Al \rightarrow Al^{2+} + 2Cu \quad (4)$$

$$Cu^{2+} + Fe \rightarrow Fe^{2+} + Cu \quad (5)$$

$$Cu^{2+} + Zn \rightarrow Zn^{2+} + Cu \quad (6)$$

Cementation with aluminium presents a good technique for the displacement of copper within solution, but this has as main drawback the very slow kinetics of reaction. The use of iron was presented in many investigations and has been noticed that a complete precipitation of copper could not be achieved with this reducing agent. Therefore, zinc cementation is preferred as this presents very efficient speed of reaction and high purity of the final product.

The recovery of precious metals from acid thiourea solution by cementation with lead, iron, aluminum and zinc was examined. Between all these metals, the use of zinc metal as cementing agent is the best chose as it presents the highest deposition rate of precious metals [12]. In most of experimental works performed for gold recovery from acid solution with thiourea and triferric iron contents was noticed that oxidant presence leads to a high consumption of cementation agent and low recovery rates for the noble metal. To avoid this deleterious effect, cysteine and oxygen were involved for gold cementation with lead and was observed that these substances cannot extract all precious metal from solution [3]. Wang et al. [19] have proposed the use of tri-sodium citrate during the cementation of Au with iron. Moreover, its application at industrial scale can posoin the environment as the citrate contained in the residual solution presents a large sensitivity due to its complexation with heavy metals when this solution is discharged.

The core of this work is to establish the optimum dissolution parameters for the leaching of copper, gold and silver from PCBs of computers waste using two kinds of leaching system: one oxidative for copper extraction according to a multi-stage counter-current procedure and another one fitted to a cross-leaching procedure which makes uses of an acidic thiourea solution for precious metals dissolution of the solid residue obtained in the first leaching system. Cementation with zinc metal powder was chosen for purification of both reach solutions. This hydrometallurgical approach can be considered an eco-friendly and sustainable technology for the treatment of waste printed circuit boards coming from obsolete electronic devices.

2. Materials and methods

2.1. Reagents and materials

Distilled water was used throughout. All chemical reagents such as H_2SO_4, H_2O_2, $CS(NH_2)_2$, $Fe_2(SO_4)_3$ and NaOH were of analytical reagent grade. After the removal of some components (electrolytic aluminium capacitors, resistors, heat sinks, connection peripherals) from the surface waste printed circuit boards, grinding to a particle size of about 300 μm was carried out and then the acid attack with aqua regia was performed; the resulted solution was analyzed in terms of Cu, Au and Ag content by Varian spectrometer SpectrAA 200Atomic Absorption Spectrometry (AAS). A content of 204.6 g/kg of Cu, 136 mg/kg of Au and 689 mg/kg of Ag was determined in the composition of the grounded waste printed circuit board sample.

2.2. Methods

All the leaching experiments were performed in Erlenmeyer flasks with a total volume of 250 mL, these being mounted on an open air shaker Innova 2000 (New Brunswick Scientific). The solid materials of various weights were immersed in 100 mL of solution with diluted sulfuric acid (98 wt.%) and hydrogen peroxide (30 wt. %); in order to extract all Cu from WPCB and to have a less consumption of reagents, this first process has been performed according to a two and three-step counter current leaching procedure. For this, a pretreatment of sample with certain amounts of sulfuric acid and hydrogen peroxide for one hour was performed. Consequently, the resulted solid was leached with a fresh solution of various concentrations of H_2SO_4 and of H_2O_2. Afterwards, the leaching solution was makeup with other 10 mL of H_2O_2 and used for leaching of a new sample; thus, the obtained sample's acid leaching solution was used for application of the cementation process.

After each leaching tests, the leaching residues were separated from leach solution by vacuum filtration and the cakes have been washed with distilled water. Then, the resulted solid residues were leached in diluted sulfuric acid solution by using thiourea as leaching reagent and ferric ion as oxidant for gold and silver extraction. It is worth to mention that all experiments have been carried out at room temperature with a stirring rate of 200 rpm. The cementation process with zinc metal powder has been used for metals extraction from their solutions. All cementation tests were carried on a plate with a magnetic stirring rate of 450 rpm for 15 min. Prior to cementation of gold and silver from thiourea acid solution, neutralization with 30 wt./vol.% NaOH solution was performed on the leaching solution. Analysis of copper and precious metals within leach solution was done via AAS (Varian spectrometer SpectrAA 200). The semi-quantitative analysis of Cu cements was performed with X-ray fluorescence spectrometry (XRF).

3. Results and discussions

3.1. Multi-step counter-current oxidative leaching process (CCOLP) for Cu recovery: optimization on sulfuric acid concentration, pulp density and stages number of the process

In our previous studies, it has been found that three steps of oxidative leaching process were required to extract all copper content of waste printed circuit boards (WPCB). For each step fresh solutions and three hours of leaching time were used. Therefore,