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Evaluation of gold and silver leaching from printed circuit board of cellphones

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ABSTRACT

Electronic waste has been increasing proportionally with the technology. So, nowadays, it is necessary to consider the useful life, recycling, and final disposal of these equipment. Metals, such as Au, Ag, Cu, Sn and Ni can be found in the printed circuit boards (PCB). According to this, the aims of this work is to characterize the PCBs of mobile phones with aqua regia; obtaining "reference" values of leaching, to gold and silver, with cyanide and nitric acid, respectively; and study the process of leaching of these metals in alternative leaching with sodium thiosulfate and ammonium thiosulfate. The metals were characterized by digesting the sample with aqua regia for 1 and 2 h at 60 °C and 80 °C. The leaching of Au with a commercial reagent (cyanide) and the Ag with HNO_3were made. The leaching of Au and Ag with alternative reagents: $Na_2S_2O_3$, and $(NH_4)_2S_2O_3$ in 0.1 M concentration with the addition of $CuSO_4$, NH_4OH, and H_2O_2, was also studied. The results show that the digestion with aqua regia was efficient to characterize the metals present in the PCBs of mobile phones. However, the best method to solubilize silver was by digesting the sample with nitric acid. The leaching process using sodium thiosulfate was more efficient when an additional concentration of 0.015 and 0.030 M of the $CuSO_4$ was added.

1. Introduction

Nowadays, there are several models, size, and configuration of electronic devices available. The technology is advancing so fast that in a short period of time, devices that were the best when they were made are becoming obsolete. As a result, electronic devices have to be designed considering their useful life, reuse, and final disposal.

Mobile phones are a big part of these electronic devices that are becoming obsolete faster every day. So, attempts to recycle or reuse mobile phone parts, or to find the right disposal ways are crucial for the safety of the environment.

Electronic waste has precious metals, such as gold, silver, and palladium in its composition. The natural sources of these metals are extremely limited, and the recovery is crucial to have enough raw materials and decreasing environmental impact.

A mobile phone device consists of a polymeric fraction, printed circuit board (PCB), crystal liquid display (LCD), battery, keyboard, and an antenna (Kasper et al., 2011).

PCBs of mobile phones are made of polymers, ceramics, and metals (Yamane et al., 2011 and Hall and Williams, 2007). The metallic fraction consists of several metals, such as copper (Cu), tin (Sn), zinc (Zn), nickel (Ni), gold (Au), silver (Ag), and palladium (Pd).

Silver composition in each mobile phone will probably increase in the coming years, replacing the lead present in welds, due to the European standards – WEEE and RoHS (Kumar et al., 2005).

From an economic perspective, recycling mobile phones is very attractive because each ton has 130 kg of Cu, 3.5 kg of Ag, 0.34 kg of Au, and 0.14 kg of Pd (Schulep et al., 2009) on an average.

Table 1 shows the data about the amount of the main metals present in PCB's of mobile phones, according several authors.

The heterogeneous and complex nature of waste electrical and electronic equipment (WEEE) is the main barrier in the recovery of metals from scraps. There are a few routes, such as mechanical, pyrometallurgical (Hagelüken, 2006a,b), and hydrometallurgical process (Tuncuk et al., 2012) that can be followed to separate and recover metals with great economic interest. The aim of this work is to study the hydrometallurgical process.

Most of the time, hydrometallurgical process is associated with acid or alkaline solutions to solubilize a solid material. This process is called leaching. In this process, PCB's waste is leached using an appropriated leaching. The resulting solution is purified, and then the metals are recovered. The metal elements are often encapsulated by polymer or ceramic materials, so a mechanical process to decrease the size of particles may be necessary to improve the extraction.

The most common leaching agents that are being studied for the recovery of precious metals from PCB of mobile phones are cyanide, thiourea, halide, and thiosulfate (Jeffrey et al., 2003;

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Table 1
Metals concentration (wt%) of printed circuit boards reported in different studies.

Wt%	Sum (2005)	Guo et al. (2009)	Yang et al. (2009)	Park and Fray (2009)	Yamane et al. (2011)	Tuncuk et al. (2012)
Gold	0.1	0.008	–	0.025	0.00	0.035
Silver	0.2	0.33	–	0.100	0.21	0.138
Copper	20	26.8	25.06	16.0	34.49	13
Nickel	2	0.47	0.0024	1	2.63	0.1
Tin	4	1.0	–	3.0	3.39	0.5

Groenewald, 1977; Baláz et al., 1996; Lee et al., 2010). These solutions are submitted to a separation of solid/liquid and a purification process, such as impurities precipitation, solvent extraction, adsorption, cementation, and ionic exchange. So, the recovery of precious metals is possible (Huang et al., 2009).

Although cyanide is a very efficient product in the industry, it is very toxic (Bhat et al., 2012), because of which the cyanide usage as a leaching agent is a major issue (Hilson and Monhemius, 2006), and many studies are being made to substitute this toxic chemical.

The use of thiosulfate ($S_2O_3^{2-}$) instead of cyanide is an alternative. In the recent years, precious metal leaching using thiosulfate has been presented as an alternative to cyanidation (Feng and van Deventer, 2010b). Thiosulfate in presence of ammonia and copper II ion has the ability to form a complex with gold and silver, which makes it a good substitute for cyanide agent (Molleman and Dreisinger, 2002). As thiosulfate is cheaper than cyanide and has a smaller environment impact, the use of this leaching agent is economically and environmentally attractive.

In the tests using thiosulfate as leaching agent, copper ion is added to act as a catalyst to dissolve gold (Alonso et al., 2007), and ammonia to stabilize the system (Briones and Lapidus, 1998) and thereby accelerate the anodic dissolution (Jeffrey et al., 2008). The thiosulfate salt type used as leaching agent can also influence significantly in the dissolution and in the chemical reactions (Feng and van Deventer, 2010a).

Previous studies showed that use a 0.1 M thiosulfate solution was the best condition to leaching precious metals reaching a good solubilization (Briones and Lapidus, 1998; Molleman and Dreisinger, 2002; Ha et al., 2010).

However, the process using thiosulfate as leaching agent is not totally clear, and the leaching mechanism is not well known mainly as thiosulfate is oxidized very easily in an aqueous solution forming others sulfur species including sulfite, sulfate, and polythianates, in function of pH and Eh (Mizoguchi et al., 1976; Webster, 1986). Besides that, metallic thiosulfate complex is decomposed in metallic sulfide easily (Benedetti and Boulegue, 1991). Even with all these uncertainties, the interest of scientific community in thiosulfate as leaching agent of precious metals has increased due to the environmental benefits.

According Tuncuk et al. (2012), usually, acid leaching is used for other metals (non-precious). Acid leaching of metals from electronic waste was investigated with inorganic and oxidants acid (HCl, H_2SO_4, HNO_3/H_2O_2, $HClO_4$, and NaClO). Studies show that the biggest copper extraction from PCB was obtained using HNO_3/HCl (aqua regia).

Acid leaching in presence of an oxidant is also widely used to extract copper from PCBs. According to Sheng and Etsell (2007), there is a rapid dissolution of gold from the computer's PCB in aqua regia. Hydrogen peroxide is a strong oxidant, and it is commonly used along with acids to increase metals extraction.

Nitric acid is a good leaching agent to silver (Petter et al., 2012a,b) from electronic scraps, and it is also efficient in the leaching of minerals from this metal (Holloway et al., 2004).

In this work, the first step was characterizing the PCB from mobile phones, especially the quantity of precious metals present in these boards, using aqua regia. After that, acid leaching process to extract silver, using nitric acid, was made. Another test was made, using a commercial reagent, that is, cyanide-based to extract gold. Following, studies using sodium and ammonium thiosulfate was performed to investigate the possibilities of using these leaching agents to extract gold and silver from PCBs.

2. Materials and methods

In this work, mobile phones from different companies, models, and year of manufacture were used. It was collected randomly in technical assistances to simulate a real situation. Then, the mobile phones were manually disassembled and batteries and polymeric frames were separated from PCBs. Two kilogram of PCBs from about a hundred mobile phones was used in this work. Fig. 1 shows some types of PCBs that are used. Fig. 2 shows a flowchart with the all steps in this work.

First, the PCBs were milled in a hammer mill (Tigre, model A4R) and then milled in a knife mill (Retsch, model SM2000). At knife mill stage, different sizes of sieves were used to gradually decrease the size of particles. The smallest sieve with 16 mesh was used to obtain particles size smaller than 1 mm.

The comminuted fractions of PCB were leaching in aqua regia and after that, they were characterized by atomic absorption spectroscopy. In the leaching test, a closed system with reflow to avoid reagents losses and magnetic agitation were used. A sample of 12.5 g of PCB with a solid/liquid 1/20 ratio was used. The other parameters used to characterize the PCB are described in Table 2. Copper, gold, silver, nickel, and tin were characterized in this work.

After the characterization using aqua regia, tests were made using conventional leaching agent to determination of "reference" values for recovery of gold and silver. To gold was used a leaching agent based in a commercial cyanide (Galvastripper® of Galva, 2013), in order to obtain a typical commercial results to compare with the results of alternative leaching agents. This commercial reagent is a chemical stripper of gold and gold alloys used in a simple immersion. It is a slight yellow liquid having cyanide, and it removes up to 1 mm of gold per minute at ambient temperature (Galva, 2013). This stripper, based in potassium cyanide, with a concentration of 6–8% was used to leach gold. In each test, 10 g of PCB milled was used. The leaching process parameters are presented in Table 3.

After making the chemical characterization of PCB and obtain the results of the leaching with Galvastripper® reagent, leaching tests were performed with acid nitric solution to determine the better leaching for silver.

Nitric acid was prepared in a ratio of 1/3 to deionized water. In each test, 10 g of PCB milled was used. Test parameters are presented in Table 4.

In the next step, the use of alternative reagents was studied. Sodium thiosulfate ($Na_2S_2O_3$) and ammonium thiosulfate ($(NH_4)_2S_2O_3$) were tested. In the leaching tests using thiosulfate, different concentrations of ammonium hydroxide (NH_4OH), copper II sulfate ($CuSO_4$), and hydrogen peroxide (H_2O_2) were added. It is important