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Comparative studies on hydrometallurgical treatment of smelted low-grade electronic scraps for selective copper recovery

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Abstract: A comparison of three hydrometallurgical methods for selective recovery of copper from low-grade electric and electronic wastes was reported. Scraps were smelted to produce Cu−Zn−Sn−Ag alloy. Multiphase material was analyzed by SEM−EDS and XRD. The alloy was dissolved anodically with simultaneous metal electrodeposition using ammoniacal and sulfuric acid solutions or leached in ammonia−ammonium sulfate solution and then copper electrowinning was carried out. This resulted in the separation of metals, where lead, silver and tin accumulated mainly in the slimes, while copper was transferred to the electrolyte and then recovered on the cathode. The best conditions of the alloy treatment were obtained in the sulfuric acid, where the final product was metal of high purity (99% Cu) at the current efficiency of 90%. Ammoniacal leaching of the alloy led to the accumulation of copper ions in the electrolyte and further metal electrowinning, but the rate of the spontaneous dissolution was low. Anodic dissolution of the alloy in the ammonia−ammonium sulfate solution led to the unfavorable distribution of metals among the slime, electrolyte and cathodic deposit.

Key words: copper alloy; leaching; electrolysis; recovery; waste electric and electronic equipment

1 Introduction

The recovery of metals from waste electric and electronic equipment (WEEE) is a necessary operation nowadays. It is mainly driven by fast growing amounts of obsolete devices displaced by saving energy innovative products, which are more attractive for users. It corresponds to the increased e-waste quantities collected in the individual countries. For example, based on the Eurostat data [1] solely, collection of used IT and telecommunications equipment (computers, laptops, mobile phones, smartphones, etc.) in the European Union increased from approximately 61.400 t in 2005 to approximately 714.700 t in 2010, while total recycling and reuse reached approximately 48.400 t in 2005 and 402.600 t in 2010. It not only showed better assortment ranges, but also declined effectiveness of such electronic waste treatment from 79% to 56%, caused mainly by various advances in the development of the recycling technologies in particular member countries. A large volume of used WEEEs are also shipped out of the European Union as well as United States, Canada, Japan and Australia to West Africa or South Asia [2,3]. Most of them are falsely classified as used goods though they are non-functional, in fact. General estimations of this illegal trade shows that at least 250.000 t of WEEEs were sent annually from the EU [2], while 50%−80% of e-wastes collected for recycling in US can be exported to the developing countries [3]. Although some African or Asian destination regions banned importation of second-hand electronic and electric equipment, it is still continued in practice due to a lack of control by local governments [4].

WEEEs are classified in several categories, among them large household appliances (49%), consumer (21%), IT and telecommunications (16%) equipment represent dominating fractions [4]. These multicomponent materials are a mixture of metals, ceramics and plastics. Electronic waste containing precious metals is the most economically attractive [5,6], but a low-value scrap (i.e., below 1×10^{-4} Au [6]) with low content or no gold,

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palladium or platinum still remains useful for recycling due to the presence of other elements like copper or tin.

Metals are recovered mainly by hydrometallurgical or pyrometallurgical routes [5−8] and the latter is currently the dominating way of e-waste recycling in the industry [8]. Bioleaching of the metals is also introduced, although only on a laboratory scale [9]. Hydrometallurgical treatment of the electronic scraps offers a variety of advantages over thermal processes, including relatively low capital costs, profitability of a small scale plants, high metal recovery and reduced environment pollution. Extraction of precious metals directly from the scraps is usually carried out using aqua regia, alkaline cyanide or thiosulfate solutions, resulting over 90% recovery of gold and silver [7−9]. Low grade wastes are leached mainly in hydrochloric and sulfuric acids or ammoniacal solutions to recover tin and copper, respectively [7,10].

A combination of thermal (e.g., smelting, pyrolysis) and hydrometallurgical procedures gives a new practice for the recovery of metals. It allows removing polymers, plastics and non-metallic elements from the origin material with simultaneous concentration of metals during pyrometallurgical stage (Table 1). The obtained alloys [11] are then dissolved in acidic or ammoniacal solutions [12−14]. GROOT and LINDE [12] reported results of cyclic voltammetry applied for the identification of the most soluble phases from the alloy immersed in HCl and H_2SO_4 solutions. LIM et al [13] presented comparative research on the behavior of some metals (Cu, Zn, Ni, Pb, Sn, Au, Ag) dissolved from pure powders and an alloy obtained from smelting reduction process of mobile phone and printed circuit boards, using sulfate and chloride ammoniacal baths. Enhanced extraction of copper from thermally pretreated (burning, pyrolysis) printed circuit boards in HCl solution was also studied and 98% efficiency instead of 6% for non-burned scrap was obtained [14].

The aim of the current work was to investigate the dissolution of an alloy obtained after pyrometallurgical treatment of low grade electronic scraps. Three methods were used: anodic dissolution in sulfuric acid or ammoniacal−sulfate solutions and spontaneous leaching in ammoniacal solution with addition of cupric ions. A comparison of the results allowed determining the behavior of the individual metals in various baths and selection of the most suitable system for the recovery of copper from smelted e-waste.

2 Experimental

Low-grade mixed electronic waste (mainly computer boards and printed circuit boards from mobile phones) from an urban scrap heap was collected, then crushed and directly thermally treated (without any additives or any special atmosphere) for a few hours in an industrial chamber furnace to remove non-metallic elements and organic compounds. Obtained alloy ingot was cut into rectangular samples (~17 cm^2). Structure of the alloy was observed under scanning electron microscope (Hitachi), while the analysis of the chemical composition was performed by energy dispersive spectroscopy (EDS).

Samples of the alloy were dissolved anodically (J_A = 3 A/dm^2) in acid (1 mol/L H_2SO_4) and ammoniacal (0.5 mol/L NH_{3aq} with 1 mol/L $(NH_4)_2SO_4$) solutions or leached in ammoniacal electrolyte with Cu(II) ions addition (50 mmol/L, added as sulfate). Platinum plate (50 cm^2) was used as a cathode (J_C = 1 A/dm^2). Solution (400 mL) was agitated with a magnetic stirrer at a rotation rate of 300 r/min. Process was carried out for 24 h.

Solution after ammoniacal leaching was used for further recovery of copper. It was diluted to 1 L and then portions of 400 mL were used for the electrolysis. The process was carried out at the current density of 1 A/dm^2 using two platinum electrodes (each 50 cm^2) and magnetic stirring (300 r/min).

All measurements were performed at ambient temperature (~ 20 °C). Before and after measurement, all samples were weighed. Slimes produced on the alloy surface as well as cathodic deposits were collected, washed, dried at the temperature of 60 °C for 4 h and then weighed.

Samples (2.5 mL) of the solutions were taken during the alloy dissolution and electrowinning, then diluted with 2 mol/L H_2SO_4 and analyzed by atomic absorption spectrometry (AAS Solaar M5, Thermo Elemental) to determine concentrations of metal ions. Weighted portions of the slimes and cathodic deposits were dissolved in hot 2 mol/L H_2SO_4 with H_2O_2 addition and then analyzed by means of AAS. X-ray diffractometry (Rikagu) was used for identification of the phase composition of the alloy and obtained solids.

Stationary potential of the dissolved samples was monitored every 5 min using saturated calomel electrode as a reference. Obtained results were subsequently converted versus standard hydrogen electrode (SHE).

3 Results and discussion

3.1 Alloy composition

The alloy obtained from low-grade electronic scraps was a polymetallic and multiphase material with a general composition shown in Table 1. It contained 72.6% Cu, 16.4% Zn and 6.4% Ag, comparable amounts of Fe and Sn (~1.6%) as well as some other metals (each below 1%). Comparison of the data with the results of