UPOREDNA ANALIZA PIROMETALURŠKIH I HIDROMETALURŠKIH PROCESA ZA RECIKLAŽU ŠTAMPANIH PLOČA - TEORIJA I PRAKSA

COMPARATIVE ANALYSIS OF PYROMETALLURGICAL AND HYDROMETALLURGICAL PROCESSES FOR PCB RECYCLING - THEORY AND PRACTICE

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Elektronski otpada od starih računara povećala se za oko pet puta, a sa odbačenih mobilnih telefona gotovo 20 puta za 2020. Godinu u odnosu na 2007. E-otpad (elektronski otpad) je jedna od najbrže rastućih vrsta otpada na svetu sa oko 40-50 miliona tona godišnje u poslednjoj deceniji, što predstavlja 2-3% ukupnog otpada koji se godišnje generiše širom sveta. Štampane ploče (PCB) su najvrednije komponente E-otpada. Cilj ovog rada je uporedna analiza pirometalurških i hidrometalurških procesa za reciklažu plemenitih metala iz PCB na osnovu eksperimentalnih istraživanja i rezulta

***Ključne reči:** Reciklaža; pirometalurgija;, hidrometalurgija; analiza*

The production of e-waste from old computers increased by about five times, and from discarded mobile phones almost 20 times by the year 2020 compared to the year 2007. E-waste (electronic waste) is one of the fastest growing types of waste in the world, about 40-50 million tons per year in the last decade, representing 2-3% of the total waste generated annually worldwide. Printed circuit boards (PCBs) are the most valuable components of E-waste. The aim of this paper is a comparative analysis of pyrometallurgical and hydrometallurgical processes for the recycling of precious metals from PCBs based on experimental research and results.

1 Introduction

In the last few decades KSKS century, as the amount of e-waste grows because animals age device and product shortens processing e-waste is updated. The importance of these technologies is reflected in obtaining the valuable materials and solving the environmental problems. Technologies for the process usually include a combination of methods due to the complexity of processed materials [1, 2].

In the period of the 1970s and early to mid-1980s, the main method for recycling the electronic scrap was the blast furnace smelting with secondary copper or lead smelters. Since the mid-1980s, this trend has been shifted toward the hydrometallurgical processing.

Recovery of metals from e-scrap by pyrometallurgical processing, include the incineration, smelting in a plasma arc furnace or blast furnace, drossing, sintering, melting and reactions in a gas phase at high temperatures [3-4] became a traditional method to recover the non-ferrous metals and precious metals from electronic waste in the past two decades.

The most active research area on recovery of metals from electronic scraps is recovering the precious metals using the hydrometallurgical techniques [5-6]. Comparing with the pyrometallurgical processing, the hydrometallurgical method is more exact, more predictable, and more easily controlled [7].

The solutions, obtained by a series of acid or caustic leaches of solid material, are the subject of separation and purification procedures such as precipitation of impurities, solvent extraction, adsorption and ion-exchange to isolate and concentrate the metals of interest.

In recent times, the recovery of metals by biotechnology has been one of the most promising technologies [7-9]. Biometallurgy has been the subject to growing investigations for the last 20

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years. A number of metals such as copper, nickel, cobalt, zinc, gold, and silver [10] are the aim of investigation.

E-scrap processing of based metal production in the Mining and Metallurgy Institute Bor, Serbia was investigated by a group of authors [11-18] based on the actual trends in related technology and economy fields. These investigations included the recycling of various secondary raw materials with the primary goal to obtain silver, gold and platinum group of metals (PGMs). It should be noted that copper was a significant product of recycling. Economy of copper recovery is based on high content of copper in the e-waste, and the ease of obtaining high grade by electrorefining [13]. The additional goal of research was to obtain the materials of higher value than pure metals, such as the micro sized silver powder for electrical contacts [16], cadmium free environmentally friendly silver brazing alloys [17] and gold organic complex for electroplating [18].

2 Experimental part

In the aim to keep step with the actual trends and the situation in the field, Mining and Metallurgy Institute Bor, with its reach R&D experiences, qualified staff and equipments capacities (Figure 1), has undertook approximate investigations and framed the project of e-scrap processing and metal production as a part of its medium-term development plan. The project is planned to be realized and is expected to be important from both economical and ecological aspects.

a) Electrolytic arc furnace *b) Plant for electrolytic refining of copper* *c) Glass reactor for dissolving*

Figure 1. *Pilot plant equipment*

The first stage for both processing methods (pyrometallurgical and hydrometallurgical) was manual disassembling of computers, liberation of PCB and removal the batteries and capacitors. Preparation was done by mechanical processing, i.e. by rejecting the parts without gold, for the purpose of less acid consumption required for dissolution. The average composition of PCB boards is shown in Table 1.

Content of metallic and non-metallic components of PCB determined using a Roentgen Thermo Scientific Niton XL3t- 900 (Producer: Niton, Palomar, Model: Niton XL3t- 900 Series) is presented in Table 1.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Produced by: Spectro, Model: Ciris Visio, Detection limit: < 0.0001 g/dm^3) and Atomic Absorption Spectrophotometer (AAS, Produced by: Perkins & Elmer, Model: 403, Detection limit: < 0.0001 g/dm^3) in order to obtain the exact chemical composition of PCB, were used for the analyzed solution after leaching (Table 2).

Table 1. *Composition of PCB boards*

No.	Part of PCB	Mass fraction of PCB (%)
1.	Phenol formaldehyde resins (PF), "black plastic"	42.25
2.	FR-4 glass epoxy board with printed connections	33.91
3.	Metal contacts	17.02
4.	Metal solder	2.55
5.	Others	2.47
6.	Technological losses	1.80
Σ		100.00

Table 2. *Chemical composition of PCB*

Element	%	Element	%	Element	%
Ag	0.0151	Cr	0.0025	Mg	0.0141
Cu	22.3021	Ba	0.0072	Bi	$6.79x10^{-6}$
Sn	3.6252	Si	0.0142	As	0.0021
Pb	1.2551	Mo	0.0003	Ag	0.0159
Ni	0.2433	Zr	0.0015	Ti	0.0076
Au	0.0069	Sr	0.0002	Se	0.00032
Mn	0.0041	Co	0.0015	Fe	0.9552
Sb	0.0213	Al	0.0084	Zn	1.8823
Cr	0.0022	Mg	0.0145	Ca	0.1225
Ba	0.0095	Cd	$6.79x10^{-6}$	Insoluble residue	69.4777

2.1 Pyrometallurgical process

The pyrometallurgical process includes melting metal parts plates with copper in a Birlac furnace (Figure 1a). After melting, the anodes dimension 480x380 mm are cast. Cathode copper with a purity of 99.99% (Figure 2) and anode sludge are obtained by electrolytic refining process in the semi-industrial plant (Figure 1b). In the final phase of processing, by hydrometallurgical treatment of anode sludge (Figure 1c) are obtained in high purity noble metals.

Figure 2. *Cathode (99.99% Cu)*

2.2 Hydrometallurgical process

Previous disassembled computer components are leached in three different ways:
- direct leaching in aqua regia
- two-phase leaching (nitric acid/aqua regia)
- three-phase leaching (hydrochloric acid/nitric acid/aqua regia)

Table 1. Metal extraction efficiency for the three-phase leaching

Element	Direct leaching in aqua regia	Two-phase leaching (nitric acid/aqua regia)	Three-phase leaching (hydrochloric acid/ nitric acid/aqua regia)
Au	97.95	97.91	98.17
Ag	96.44	98.25	98.08
Cu	95.66	97.33	94.31
Ni	94.71	95.61	93.28
Sn	91.21	90.09	97.07
Mn	90.01	91.32	93.25
Sb	92.29	93.12	93.16
Mg	91.03	94.22	96.35
Si	92.61	91.07	90.47
V	93.59	92.28	91.87
Cr	96.24	95.51	94.88
Mo	95.03	94.31	94.21
Se	96.12	95.19	94.38
Ti	92.12	91.81	92.28
Al	96.39	98.25	97.36

By all hydometallugical procedures, it is possible to obtain gold and silver powder of 99.95% quality. A purity of 99.99% can be achieved by a second successive deposition. Gold obtained from recycling can be used for the production of gold salts as well as for the synthesis gold complexes based on mercaptotriazole (Figure 3), from which it is possible to obtain decorative coatings that fully meet the requirements of decorative coatings (Figure 4).

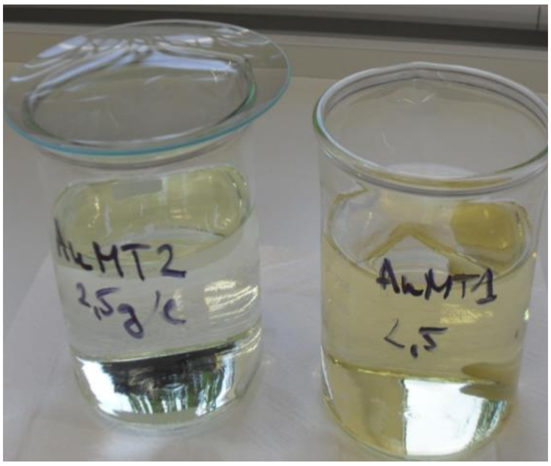

Figure 3. *Gold complex based on mercaptotriazole*

Figure 4. *Gold coating*

From silver obtained by the recycling process by additional processing, it is possible to obtain super fine Ag powder with a micro particle size of 0.1 to 1.0 μm and a purity of 99.999% (Figure 5).

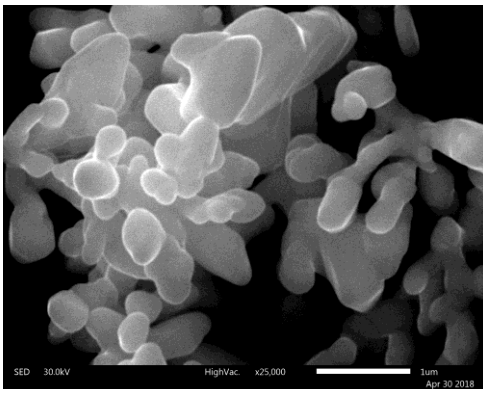

Figure 5. *Nanoparticles of silver obtained from the recycling process*

3 Conclusion

This paper presents a review of the literature on electronic waste processing as well as a comparative analysis of pyrometallurgical and hydrometallurgical processing of E-scrap. Using pyrometallurgical, hydrometallurgical and electrometallurgical processes, high pure metals as well as micro sizes were obtained silver powder as well as gold coatings.

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