Recycling of Precious Metals from E-scrap

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ABSTRACT: *Recovery of gold and other valuable metals from electronic scrap involves a complex metallurgical flow sheet and requires state-of-the-art recovery technologies that are available in large-scale, integrated smelter and refinery operations. At the end of their use, electronic and other electrical product scrap offer an important recycling potential for the secondary supply of gold and silver into the market. With gold concentrations reaching 200-250 g/t for computer circuit boards, this scrap is an 'urban mine' that is significantly richer in gold than the sources of the primary ores today. This paper gives methods of gold and silver recovery from printed circular board. The methods of purification are given and they separate gold from the impurities (tin, copper and nickel). The obtained gold and silver have 99.99% quality.*

KEY WORDS: *Gold, Silver, Recovery, Printed Circuit Boards (PCBs), Powder.*

INTRODUCTION

The production of Electrical and Electronic Equipment (EEE) is one of the fastest growing global manufacturing activities. This development has resulted in an increase of Waste Electric and Electronic Equipment (WEEE) [1]. From 20 to 50 million tonnes of waste electrical and electronic equipment (WEEE, e-waste) are generated each year, which is a significant risk to human health and the environment [2]. EU legislative restricts the use of hazardous substances in Electrical and Electronic Equipment (EEE) (Directive 2002/95/EC) such as: lead, mercury, cadmium, chromium and flame retardants: PolyBrominated Biphenyls (PBB) or PolyBrominated Diphenyl Ethers (PBDE) and also promotes the collection and recycling of such equipment (Directive 2002/96/EC). They have been in implementation since February 2003. Despite rules on collection and recycling only one third of electrical and electronic waste in the European Union is reported as appropriately

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treated and the other two thirds are sent to landfills and potentially to sub-standard treatment sites in or outside the European Union. In December 2008 the European Commission proposed to revise the directives on EEE in order to tackle the fast increasing waste stream of these products [3].

The materials contained in scrap electronic equipment are numerous: valuable, toxic and hazardous metals. Typical materials contained in electronic waste are:

1. Precious metals such as gold, silver and palladium, and to a lesser extent, platinum and ruthenium,

2. Non-ferrous metals: iron, copper, aluminium, nickel, zinc, tin, cobalt, indium and gallium.

3. Non-metals and metalloids like: selenium and tellurium,

3. Toxic elements: mercury, beryllium, cadmium, arsenic and antimony,

4. Halogens - bromine, fluorine and chlorine,

5. Other substances like: organics/plastics, glass and ceramics [4].

Printed Circuit Board (PCB) is a key component in the WEEE. PCBs assemblies typically consist of various metals including precious metals such as gold, silver and palladium [5]. In general, waste management preferences are reuse and recycling options. Since no reuse is possible, recycling is the best option for WEEE treatment. There have been several studies on the recycling of materials by mechanical [6, 7], thermal [8] and chemical [9, 10] processes, but they dealt with recovery of one or two specific materials. *Pilone & Kelsall* [11] reported alloy electrodeposition from an electrolyte containing Au, Pd, Ag, Cu, Sn and Pb, followed with a mathematical model. *Young Jun Park & Derek J. Fray* [12] developed a new process for recovery of high-purity metals from a PCB waste.

General approach for the recovery of valuable metals from PCBs is shown in Fig. 1. First step is iron and aluminium separation by magnetic and eddy current, respectively. It is followed with non-metallic separation. Other metals are separated and recovered by hydrometallurgy processes and electrowinning.

A technology for copper separation is well established through ammonium sulphate leaching, solvent extraction, and electrowinning [13]. The last two steps are recovery of precious metals and separation of nickel and zinc.

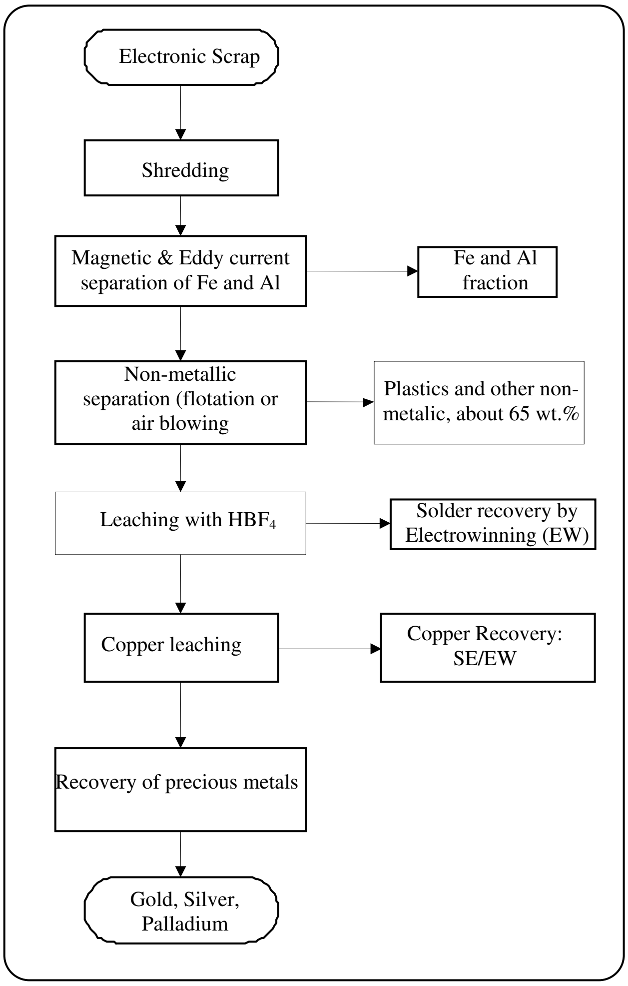

Fig. 1: Block diagram for metal recovery from PCBs.

Goosey & Kellner in their detailed study [14] have defined the existing and potential technologies that might be used for the recycling of PCBs.

Oishi et al. [15] conducted research on recovery of copper from PCBs by hydrometallurgical techniques. *Frey & Park* [12] performed research for recovery of high purity precious metals from PCBs using aqua regia as a leaching agent. *Sheng & Etsell* investigated leaching of gold from computer chips. The first stage was leaching of base metals with nitric acid and the second, leaching of gold by aqua regia due to its flexibility, ease and low capital requirement. Non-metallic materials, mainly plastics and ceramics, also could be recovered by this technology. *Quinet et al.* carried out bench-scale extraction study on the applicability of economically feasible hydrometallurgical processing routes to recover silver, gold and palladium from waste

Table 1: Mass and mass percent composition of PCB parts.

No.	Part of PCB	Mass (g)	Mass fraction of PCB (%)	Mass of parts after dissolving in aqua regia (g)
1.	Phenol formaldehyde resins (PF), "black plastic"	103.4	42.03	103.4
2.	FR-4 glass epoxy board with printed connections	83.8	34.06	68.27
3.	Metal contacts	45.10	17.32	0.14
4.	Metal solder	5.72	2.44	2.25
5.	Others	6.0	2.44	6.0
6.	Technological losses	4.2	1.70	4.2
Σ		246.0	100	184.26

Fig. 2: PCB.

Fig. 3: Parts o PCB after manual disassembling.

mobile phones. Selective extraction of dissolved metals from solution is very difficult and demanding process [15].

EXPERIMENTAL SECTION

Electronic waste is defined as a mixture of various metals, particularly copper, aluminium and steel, attached to different types of plastics and ceramics. This study was performed to recover valuable metals from the Printed Circuit Boards (PCBs) of waste computers. Our research team's aim was development of new process that can recover high purity gold and silver from PCBs waste [16]. Gold and silver recovery from PCB is performed in five stages:

Preparation of gold plated parts for dissolution

The first stage was manual disassembling of computers, separation of PCB (Fig. 2.) and removal of 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. Parts of PCB after manual disassembling are shown in Fig. 3. Mass and mass percentage of parts of PCB are given in Table 1.

Research is done on 10 PCBs with full analyses and details but from practical reasons in this paper results from one representative PCB are given.

Content of metallic and non-metallic components of PCB determined using Roentgen Thermo Scientific Niton XL3t- 900 (Producer: Niton, Palomar, Model: Niton XL3t- 900 Series) is shown in Fig. 4.

Component analysis of the PCB used in this experiments determined the metal component to 37% by weight, mainly base metals (Cu 17.0%, Fe 5.0%, Ni 0.5%, Sn 5.0%, Pb 0.8%, Al 0.2% and Zn 8.0%). Precious metals concentration was low, 10 ppm of gold and 50 ppm of silver. Content of plastic materials were above 60% by weight. Also, metal oxides (oxides of the alkali and alkaline earth metals, alumina and other metals oxides) were determined. In terms of weight, plastic and steel tend to dominate, but in terms of value, gold and the other precious metals dominate. Gold and the other precious metals make more than 80%

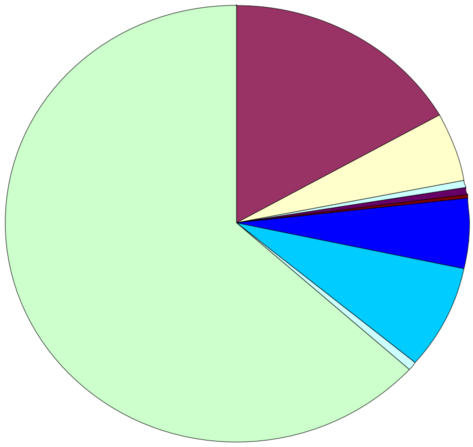

Fig. 4: Chemical composition of the PCB (mass %).

of the value in PCB. Copper is the second valuable material in WEEE after gold.

Metal dissolution (gold, silver, tin, cooper and nickel) from gold plated parts.

Dissolution of gold and associated metals in aqua regia was performed without additional heating. Reactions of metals dissolution in aqua regia are exothermal ones, causing the temperature about 80 °C during the reaction, after initial heating for the reaction accelerating. The disassembled parts were dissolved in aqua regia where all quantities of all present metals entered the solution in the form of chlorides, while all other non-metal parts remained insoluble. Solid non-metallic residue mass is measured after filtration and drying (insoluble residue in Table 2). The present metals are dissolved in aqua regia according to the following reactions:

$$Au_{(s)} + 4HCl_{(aq)} + HNO_{3(aq)} \rightarrow HAuCl_{4(aq)} + 2H_2O_{(aq)} + NO_{(g)} \quad (1)$$

$$3Ag_{(s)} + 3HCl_{(aq)} + HNO_{3(aq)} \rightarrow 3AgCl_{(s)} + 3H_2O_{(aq)} + NO_{(g)} \quad (2)$$

$$Cu_{(s)} + 3HCl_{(aq)} + HNO_{3(aq)} \rightarrow CuCl_{2(aq)} + NOCl_{(aq)} + 2H_2O_{(aq)} \quad (3)$$

$$Ni_{(s)} + 3HCl_{(aq)} + HNO_{3(aq)} \rightarrow NiCl_{2(aq)} + NOCl_{(aq)} + 2H_2O_{(aq)} \quad (4)$$

$$Sn_{(s)} + 4HCl_{(aq)} + HNO_{3(aq)} \rightarrow SnCl_{2(aq)} + NOCl_{(aq)} + 2H_2O_{(aq)} \quad (5)$$

The optimal conditions for leaching were found to by solution of aqua regia and a reaction temperature at 80^0C. 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 ordered to obtain exact chemical composition of PCB were used for analysed solution after leaching in aqua regia. Chemical composition of solution after dissolving parts of PCB (metal part, metal solder and glass epoxy board with printed connections) is shown in Table 2.

Solution purification from tin

Due to tin(II) chloride hydrolysis β-tin acid is formed (Eq. (6)). It is in the form of voluminous deposit and could be separated from solution. Hydrolysis was induced by decreasing of pH value of the solution.

$$SnCl_{2(aq)} + H_2O_{(l)} \rightarrow Sn(OH)Cl_{(s)} + HCl_{(g)} \quad (6)$$

Silver reduction

Generally, aqua regia dissolves most of metals but silver has a strong chemical resistance to aqua regia. Silver stability in aqua regia is based on passivation. This behaviour is due to a spontaneous formation of a thin

Table 2: Chemical composition of the PCB.

Part / Element	Metal part (%)	Metal solder (%)	Vitroplast board with printed connections (%)	PCB (%)
Ag	0.00444	0.003497	0.0102	0.00437
Cu	55.4324	12.06294	15.9196	16.67886
Sn	3.25942	17.95455	8.52952	5.23132
Pb	0.95344	5.944056	1.49553	0.822764
Ni	2.6608	0.006993	0.01	0.49407
Au	0.00444	0.005245	0.00102	0.001283
Mn	0.0133	0.001748	0.00034	0.002596
Sb	0.0133	0.017483	0.0136	0.00748
Cr	0.00044	0.000262	0.00136	0.000551
Ba	0.002	0	0	0.000366
Si	0.00444	0.007867	0.017	0.006789
Mo	0.00022	0.000437	0.0002	0.00012
Zr	0.00022	0.005245	0.00238	0.000974
Sr	0	0	0.00024	0.00E+00
Co	0.00089	0.000874	0	0.000183
Al	0.00089	0.005245	0.0068	0.260231
Mg	0.00022	0.006993	0.02379	0.008313
Cd	0.00067	0	0	0.000122
Bi	0	0	0	0
As	0	0	0.00102	0.000348
Ag	0.00444	0.003497	0.0102	0.00437
V	0	0	0	0
Ti	0.00044	0.000524	0	9.35E-05
Se	0.00155	0	0	0.000285
Fe	2.57206	0.253497	0.2719	4.86707
Zn	34.887	1.748255	0.0136	7.687561
Ca	0	0	0.16655	0.056768
Insoluble residue	0.51	62.01	73.8	63.88
Σ	100.327	100.0392	100.2948	100.0169

protecting layer of AgCl, the passive layer, as a product of the initial silver dissolution. The silver with AgCl surface layer can be refined by conventional purification process, dissolving precipitate in aqueous ammonia followed by reduction with hydrazine hydrate [13].

$$AgCl_{(s)} + 2NH_4OH \rightarrow [Ag(NH_3)_2]Cl_{(aq)} + 2H_2O \quad (7)$$

$$4[Ag(NH_3)_2]Cl_{(aq)} + N_2H_4 \cdot H_2O_{(aq)} \rightarrow \quad (8)$$

$$4Ag_{(s)} + N_{2(g)} + 4NH_{3(g)} + 4NH_4Cl_{(aq)} + H_2O$$

The recovered silver powder had the quality of 99.9% or higher. It is possibly to obtain purity of 99.99% with two consecutive precipitations.

Gold reduction

During the selective reduction of gold a part of dissolved tin and all the quantity of copper and nickel remain in the solution in the form of chlorides. Gold is reduced and precipitated by appropriate reducing agent like: sodium sulphite, sodium nitrite or sulphur dioxide.

$$HAuCl_{4(aq)} + Na_2SO_{3(s)} + H_2O_{(aq)} \rightarrow \quad (9)$$

$$Au + Na_2SO_{4(aq)} + 3HCl_{(g)} + \frac{1}{2}Cl_{2(g)}$$

$$HAuCl_{4(aq)} + NaNO_{2(s)} + H_2O_{(aq)} \rightarrow \quad (10)$$

$$Au + NaNO_{3(aq)} + 3HCl_{(g)} + \frac{1}{2}Cl_{2(g)}$$

$$HAuCl_{4(aq)} + SO_{2(g)} + 2H_2O_{(aq)} \rightarrow \quad (11)$$

$$Au + H_2SO_{4(aq)} + 3HCl_{(g)} + \frac{1}{2}Cl_{(g)}$$

The reducing agent is usually added in amounts slightly in excess of the stoichiometric amount necessary to precipitate substantially 100% of the gold from the aqua regia solution.

The reaction mixture is filtered and gold particles collect as the filter cake. The cake is washed with ethanol (96%) and then water. The filter cake is then dried in laboratory dryer and fine gold powder results. The obtained gold powder had the purity of 99.95%. It is possibly to obtain purity of 99.99% with subsequent reduction and precipitation of gold powder.

Since small quantity of silver and gold their purity are proven on larger sample (recovered from ten PCBs) using ICP-AES and AAS.

CONCLUSIONS

Waste printed circuit boards contain valuable materials such as gold, palladium and silver. In this paper we focused on the silver and gold in high purities. Aqua regia was used as a leaching agent. Silver is relatively stable in aqua regia so it was recovered by dissolving in ammonia. The gold was recovered by reduction with SO_2. Purity of the obtained gold and silver powders by recovery from electronic scrap was 99.99%. According to the difference in commercial price and gold processing cost, it can be concluded that gold recovery from PCB is very profitable.

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