Short Communication Metals Content in Printed Circuit Board Waste

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> Received: 20 June 2013 Accepted: 24 October 2014

Abstract

This paper an presents analysis of metals in waste of printed circuit boards (PCB) covering types of PCB, segregated from PC computers, mobile phones, and mixed. The presented data identifies metals and other substances found in PCB waste based on elemental and technical analysis of PCBs. PCB categorization based on gold concentration is presented, resulting in two groups: electric and electronic PCBs. Then mass of PCBs in waste of electric and electronic equipment (WEEE) is presented, and annual PCB mass is calculated for collection in Polish WEEE. Finally, I present an analysis of metals values in PCBs pointing to gold, palladium, and copper as the three the most valuable metals for recovery. This study presents an overview of resources present in printed circuit boards.

Keywords: PCBs, printed circuit boards, WEEE, waste, recovery, recycling, metals

Introduction

The increasing digitalization of appliances and machines equips them with electronic circuit boards. These boards, after the end of an appliance's life, become hazardous waste that needs to be handled adequately. Mass production of electric and electronic equipment requires huge amounts of non-renewable resources, including precious metals. That is why it is important to develop new effective ways of recycling electric and electronic printed circuit board (PCB) waste, as they become a "renewable" resource that can supply recycled metals for new production. By processing the waste of electronic circuit boards it is possible to recover metals, energy, and decrease their hazardous effect on the environment.

The waste of electrical and electronic equipment (WEEE) is a global concern. In the 27 EU countries it is estimated that the weight of produced WEEE in 2005 was 8.3-9.1 million Mg (tones), 25% of which is collected and processed, while the remaining 75% is not registered and does not occur at collection points [1, 2].

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Electric and Electronic Printed Circuit Boards

Electric and electronic printed circuit boards are essential parts of electric and electronic equipment. Circuit boards are built on the flat base of an electrical insulator most commonly an epoxy resin reinforced with fiberglass. The laminate allows fixing all of electric and electronic components and interconnections between them through copper paths. Examples of electric and electronic circuit boards are presented in Fig. 1. Fig. 1A presents an electronic circuit board (from a computer hard disk drive) with SMD components, and the large electronic chips and golden connector pins are visible. Fig. 1B shows an electric PCB. Electric and electronic PCBs differ from each other due to huge electric components like capacitors, transistors, and transformers used on electric ones, and electric PCBs are commonly not SMD devices, which means that the components are mounted and soldered through holes in the laminate plate.

PCBs are separated from WEEE in preprocessing steps, with the application of two main technologies: manual dismantling of devices or mechanical treatment [19, 20]. In mechanical treatment PCBs are separated from milled

	РС	CB 1		PCB 2	PCB 3	PCB 4	PCB 5
Material	Element	Content (%) mass	Overall mass	Content (%) mass	Content (%) mass	Content (%) mass	Content (%) mass
Organic Epoxy resign	С	18.1	31.8%	n/a	24.69	41	26.36
	Н	1.8		n/a	1.38		2.8
	Ν	0.32		n/a	0.85		1
	O Org	6.03		n/a	n/a		15.58
	Br	5.07		n/a	4.94		6.5
	Sb	0.45		1.97	n/a		n/a
Nonmetals Glass fibers	SiO ₂ /Si	24.7	37.6%	n/a	n/a	n/a	11.3
	Al ₂ O ₃	9.35		n/a	n/a	n/a	n/a
	CaO/Ca	3.36		3.2	1.9	n/a	6.7
	MgO/Mg	0.081		0.096	0.22	n/a	n/a
	BaO/Ba	0.0022		0.16	n/a	n/a	n/a
	NaO/Na	0.09		0.002	n/a	n/a	n/a
	SrO/Sr	0.035		0.02	n/a	n/a	n/a
Metals . Solder	Cu	14.6	30.1%	24.69	13.79	13	11.09
	Sn	5.62		2.31	n/a	1	n/a
	Pb	2.96		0.63	n/a	0.6	n/a
Construction Elements	Fe	4.79		0.22	1.97	7	n/a
	Ni	1.65		0.11	0.17	1.5	n/a
	Cr	0.356		0.025	0.003	n/a	n/a
	Мо	0.016		n/a	n/a	n/a	n/a
Connectors	Ag	0.045		0.0242	n/a	0.363	n/a
	Au	0.0205		0.0076	n/a	0.0347	n/a
	Pd	0.022		< 0.0027	n/a	0.0151	n/a

Table 1. The content of metals and organic substances present in printed circuit boards from: PC computers (PCB 1 [11], PCB 2 [16],
PCB 3 [17]), mobile phones without battery (PCB 4 [18]), mixed (PCB 5 [3]).

WEEE in automated segregation of resources. In manual dismantling technology complete boards are segregated manually.

but on the other hand contains considerable amounts of valuable metals that can be recovered [6].

The Amount of PCBs in WEEE

PCBs occur in WEEE in various amounts. Some devices contain up to 22% of their mass, and others contain 2% or less. The literature data indicates that the average PCB amount in collected WEEE is 3% [3, 4].

To quantify the overall PCB mass in WEEE collected in Poland, the overall mass of WEEE in 2011 was used, which is 143,339 Mg [5], and average PCB content in WEEE was assumed to be 3%. The calculation indicates that each year in Poland 4300 Mg of PCB can be segregated from collected WEEE. This amount on one hand requires processing,

PCB Composition

PCB waste can contain up to 60 elements [7], some of which are valuable and some hazardous. This variety of elements can be classified into three groups: metals, nonmetals, and organic. Their composition in overall PCB mass varies depending on the kind of PCB (electric or electronic), type of the device, year of manufacture, and other factors. Each of these groups represents approximately 1/3 of PCB mass. The example of elemental analysis of electronic PCB from PC computers, grouped by metals, organics, and nonmetals, is presented Table 1 in column PCB 1 [11]. The main metals in PCBs are copper used as an electric current conductor (paths on laminate and parts of electric connectors and electronic elements), and tin used in solder for connections between elements and tracks on the board. Before 2006 solders containing lead were allowed (Sn 65%, Pb 37% [8]), but since 2006 the RoHS directive [9] took effect and use of Pb in solder decreased, but Ag content increased. The new lead-free solders mainly composed of Sn 95.5%, Ag 3.8%, Cu 0.7%; Sn 96.1%, Ag 2.6%, are now used [10].

The precious metals are also found in PCBs, mostly in electronic ones. The silver is mainly used in solder and contacts, whereas gold is in electronic components and is a protective later on contacts. Also, palladium is being used in contacts and multilayer ceramic capacitors.

Other metals like Fe, Ni, and Cr occur in PCBs as construction elements for contacts on the board, or magnetic cores of transformers and chokes. Also, some metal oxides (Al₂O₃, CaO, MgO) are being used as fillers for epoxy resin [21].

Nonmetals in PCBs occurs mainly as glass fibers (SiO₂, CaO), fillers in epoxy resin, ceramic packages of electric and electronic devices, and insulators of electronic components, capacitors, resistors [21].

Organic substances in PCBs are mainly epoxy resin in PCB laminate and other materials containing C, H, O, Br, and Cl atoms such as paint, rubber, or PVC electric insulation. For PCB production FR-4 laminate is commonly used (epoxy resin reinforced with ceramic fibers), and filled with brominated fire retardants to decrease its flammability. Widely used for this purpose is Tetrabromobisphenol A (TBBPA) [22]. In addition, Sb is being used in PCBs due to its capability to further decrease flammability [11].

In PCB waste management practice the PCB waste is categorized into three groups (A, B, C) based on precious metals concentrations. This categorization is not a strictly defined selection system, but it is commonly used in WEEE Those categories identify each PCB batch. Category A printed circuit boards contain more than 400 ppm of gold (mainly electronic printed circuit boards, Fig. 1A). Category B contains PCBs with 100-400 ppm of gold. Category C covers PCBs with less than 100 ppm of gold, mostly segregated from devices like CRT displays, power supply, radios, and TV (Fig. 1B).

Chemical Elements and Substances in PCBs

From the point of view of metals recovery (in the smelting process) most important is the elemental analysis of PCBs that corresponds to available metals for recovery, the composition of the slag, and the heating value of waste, including emissions from the process. Characterization of chosen PCB groups is presented below.

Printed Circuit Boards from PC Computers

Table 1 – column PCB 1 [11] presents elemental analysis of PCB segregated of 20 PC computers manufactured in Japan in 2007. Also, columns PCB 2 [16] and PCB 3 [17] in Table 1 present results of analysis of PCBs from PC computers.

The presented data show a vide variety of examined samples. Despite the fact that each sample was segregated from PC computers the content of metals is different. Cu concentration ranges from 13.8% to 24.6%, Fe ranges from 0.2% to 4.79%, and Au ranges from 0.0076% to 0.02%. Also, each data set covers a slightly different range of results. In PCB 1 and PCB 3 bromine content is available at about 5%. In PCB 2 bromine content is not available.

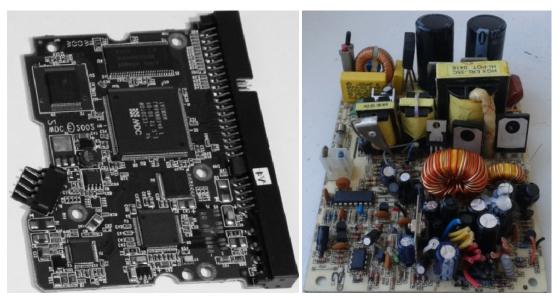


Fig. 1. A) Example of electronic printed circuit board (from hard disk drive). B) Example of electric printed circuit board (from PC power supply).

Printed Circuit Boards from Mobile Phones

PCBs from mobile phones are special due to the very high content of precious metals. The mobile phones can contain up to 40 different elements (Cu, Sn, Co, In, Sb, Ag, Au, Pd, and others), on average 23% of phone mass are metals [12]. Table 1 column PCB 4 presents amounts of metal elements and organic substances in PCBs from mobile phones in a sample of 100 Mg of complete mobile phones without battery. Au concentration is 0.0347% and is almost two times higher than in PCB from PC computers. Chemical energy available in mobile phones equals 10.65 MJ/kg, and the energy required for processing this waste is 7.43 MJ/kg [18]. This means that the chemical energy of the organic substances in mobile phones can cover energy demand of the metals recovery process from this waste in the smelting process.

The Other Printed Circuit Boards

Table 1 column PCB 5 presents results of analysis of waste of PCBs collected from 6 different sources (shops, service) at 10 kg each. Collected samples were mainly FR-4 PCB containing TBBA. Analyzed samples indicated that their heating value is 11.368 MJ/kg [3]. Unfortunately, the authors focused their study on organic substances present in PCBs, thus the metals analysis in this sample was limited to copper concentration, which is 11%, slightly lower than in other PCB types.

The Calculation of Market Value of Metals Present in PCBs

In order to verify that the recovery of metals from PCBs is economically feasible, the market value of metals present in PCBs should be estimated. For this calculation, an averaged metals concentration in PCBs based on data from Table 1 and pries of metals in 2013-03-29 from the London Metal Exchange were used.

Based on the above assumptions and my own calculations, the highest calculated values of five metals present in an average one Mg of PCB are:

- Au 8736 USD
- Pd 1977 USD
- Cu 1296 USD
- Sn 778 USD
- Ag 589 USD

This data reveals that despite the large amount of copper in a PCB (171 kg/Mg of PCB) and its high market value (7,582 USD/Mg), the market value of copper in a PCB is smaller than gold or palladium, whose mass in a PCB is 1,700 times smaller than copper. This means that those two metals, together covering 0.025% (0.25 kg in one Mg of PCB) of PCB mass, create 79% of overall metals market value.

In spite of the economical point of view concerning the recycling and recovery of precious metals from PCB waste, the environmental aspects of these actions should be taken into account. Each amount of metals recovered from waste decreases the need of their production from natural ore. The environmental footprint of metals production from waste is much smaller than from primary resources that require large-scale ore mining and processing. Additionally the comparison of gold concentration in natural ores (1.4-8.3 g of gold in one Mg of ore) [13, 14] to gold concentration in PCB (17-81 g of gold in one Mg of electric PCB, and 100-1,300 g of gold in one Mg of electronic PCB) justifies that PCB waste is an important gold and other metals resource.

Conclusions

The current situation in PCB processing in Poland is deficient. Besides processing of PCBs using mechanical methods and exporting segregated PCBs to western countries for recovery, no PCBs are being processed for gold and other metals recovery. To change this technological gap, a research project was undertaken to design and investigate new technology allowing PCB neutralization and metals recovery using plasma smelting technology in the Industrial Research Institute for Automation and Robotics [24]. A team of researchers (including the author of this work) developed a new process while carrying out the the research project: "High temperature plasma technology of waste utilization, of electrical and electronic equipment (WEEE), allowing recovery of precious and rare earth metals" [6, 15]. The developed technology allows for neutralization of PCB waste to form vitrified slag, and recovery of metals molded to casts. Preliminary results indicate that 76% of metals from PCBs can be recovered in metallic form using this process.

The data presented in this paper confirms the high variety of PCBs. On the other hand, they consist of similar substances and elements, but occure in highly variable amounts. Those differences and similarities need to be taken into account in designing and exploiting the PCB recovery process, regardless of the focus on recovery of precious, technical, or other metals. Moreover, every recovery process needs to anticipate the occurrence of every possible element in processed PCBs. Next to metals, also elements like bromine, chlorine, antimony, and other organic compounds.

Despite the variety of printed circuit boards, this special waste is becoming a newly renewable resource, and it is important to develop effective ways suitable for recovery of valuable metals and substances.

Acknowledgements

This work was carried out within a research project financed by the Ministry of Science and Higher Education, No. NR03008310.

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