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E-waste as a source of valuable metals

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ABSTRACT

Purpose: Recovery of metals and precious metals from electronic waste (e-waste) has been an important topic not only for economic aspect but also for recycling rare natural sources and reducing the e-waste to prevent the environmental pollution. The paper presents data concerning material composition of e-waste, with particular attention directed to the precious metals and possibility of their recovery from Printed Circuit Boards (PCBs).

Design/methodology/approach: Material balance, one of the most popular and widespread e-waste in the form of used mobile phones, has been conducted. The results of preliminary leaching of precious metals from ground mass of PCBs derived from used mobile phones have been also shown.

Findings: Main source of precious metals in e-waste are PCBs. In the adopted experimental conditions, when aqua regia was used in the second stage of the leaching, precious metals have not been effectively recovered. Material complexity of PCBs may complicate the hydrometallurgical processes and can reduce the effectiveness of metals recovery.

Research limitations/implications: E-waste consists of several components in the form of metals and multi-material elements. The base metals include iron, copper, aluminum, nickel, zinc, selenium, indium, gallium and precious metals. Hazardous substances that can be found in e-waste, include: mercury, beryllium, lead, arsenic, cadmium, antimony. In addition, the large material group consists of plastics, glass and ceramics. Recovery of desired material with such a diverse group of waste requires the use of complex technology recycling. The biggest problem is a necessity of applying different technologies for the processing of various materials, which are extracted in the subsequent stages of recycling.

Practical implications: This cognitive work provides the basis for further research.

Originality/value: It is a research work.

Keywords: Precious metals; Recycling of electronic waste; Used mobile phone; Leaching

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EDUCATION AND RESEARCH TRENDS IN MATERIALS SCIENCE AND ENGINEERING

1. Introduction

An indispensable part of the civilization development is the development of industries related to electronic devices. Using them makes everyday life easier and more convenient. Modernization of technology and production of electronic and electrical devices, belong to the fastest growing industries in the world. Any spent equipment is a valuable secondary material, which consists of metals and metalloids but also environmentally harmful substances [1]. These are mainly computer equipment, household appliances, television and radio, cell phones. Discarded appliances are not segregated and often all go to the landfill. Among the e-waste in Poland [2]:

- 35-76% is a computer equipment and TV,
- 22-54% is a small electronic equipment,
- 18-25% is a telephone equipment,
- 5-15% is other waste.

2. Material composition of electronic waste

Spent electronic equipment consists of several components in the form of metals and multicomponent elements. The base metals include iron, aluminum, nickel, zinc, selenium, indium, gallium. The noble metals can be divided into copper, palladium or gold, silver. Hazardous substances that can be found in spent electronic equipment, include: mercury, beryllium, lead, arsenic, cadmium, antimony and plastics, glass and ceramics. Depending on many factors, such as the age of the device, manufacturer, the type of equipment, the content of the individual electronic component in the waste is mixed. Table 1 shows selected material composition of the electronic devices. A decisive impact on the value of electronic scrap has the content of PGMs (Precious Group Metals). Although iron and plastic are dominate components (in terms of weight - Table 1), a seemingly small content of precious metals in different electronic devices (<0.5%), constitutes about the electronic scrap value (Table 2) [3]. Analysing only computer equipment and mobile phones, this share is 3% of the world production for Ag, 4% for Au and 16% for Pd.

Table 1.
Selected material composition of electronic devices [4-6]

TYPE OF DEVICE	Contents, %				Contents, ppm		
	Fe	Al	Cu	Plastic	Ag	Au	Pd
TV board	30	15	10	28	280	20	10
PC board	7	5	18	23	900	200	80
Mobile phone	7	3	13	43	3000	320	120
DVD	62	2	5	24	115	15	4
Calculator	4	5	3	61	260	50	5
e-waste	8,3	0,71	8,5	-	290	124	-

Table 2.
The value of selected components in electronic equipment (in terms of prices of 2010) [4]

TYPE OF DEVICE	Value - share, %						
	Fe	Al	Cu	Precious metals (sum)	Ag	Au	Pd
TV board	4	14	35	47	7	33	7
PC board	0	1	13	86	5	69	12
Mobile phone	0	0	6	93	11	71	11
DVD	15	3	30	52	5	42	5
Calculator	1	4	10	85	6	76	3

3. Recycling of electronic waste

The waste electrical and electronic equipment (WEEE) includes diverse equipment in the form of: monitors and TV sets, computers, lighting equipment, household appliances, printers and phones. The raw materials used to produce them are a mixture of metals and their alloys, plastics, glass, paper, wood, ceramics and rubber. Recovery of desired material with such a diverse group of waste requires the use of complex technological recycling. The biggest problem is a necessity of applying different technologies for the processing of various materials, which are extracted in the subsequent stages of recycling. From WEEE it is possible to recover valuable precious metals such as platinum, gold, silver, rhodium or palladium. Steel is most frequently recovered (in amount about 50%) but aluminum so is (from 10 to 30%) and copper and its alloys (from 15 to 45%). The initial stage of WEEE recycling is the manual removal of steel and aluminum as well as a large number of items containing precious metals. In this stage, casings made from plastics, kinescopes and printed circuit boards are separated. The most difficult materials for the processing are plastic casings that contain a mixture of several polymers and substances providing non-flammable parts. Processing of this type of material is limited to grinding [7].

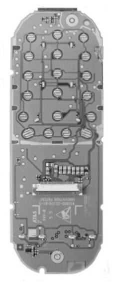
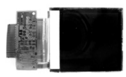
Separated scrap is a mixture of aluminum and steel as well as elements that contain a high concentration of noble metals.

Particularly, rich in these ingredients (precious metals) are printed circuit boards (PCBs). PCBs can be returned to their re-use or subjected to grinding and recovery of non-ferrous and precious metals in traditional metallurgical processes. These technologies consist of a combination of pyro- and hydrometallurgical methods [7,8]. In addition to traditional methods of electronic waste processing, new solutions for the efficient recovery of metals are being sought. Biohydrometallurgical methods using a variety of microorganisms in biological leaching of metals may become a promising method applied in the future [9,10].

3.1. Mobile phone recycling

Over the past 30 years, mobile telephony has become one of the fastest growing technology and currently the cell phone is the most popular and widely used personal communication device in the world. Report of the International Telecommunications Union says that the number of mobile users in 2011 reached 6 billion. This means that the 86 persons per 100 possess the mobile phone [11]. The specific and dominant feature of the mobile phone market is a very fast marketing of the product and its replacement. The estimated life time of a mobile decreased from 3 years in 1991 to 18 months in the year 2006 and it is assumed that the current time may be even shorter [12]. Unfortunately, useless or obsolete mobile is stored by users in drawers. According to the global survey conducted by Nokia in 2008 [13] only 3% of users give away their mobile phones for recycling. Most of the old equipment (44%) is not used any more. Others, however, get a new "life": one per four of the old phones are given to friends and family members, and 16% is sold as spare parts - especially in developing countries.

Table 3.
Mobile phone components [14,15]

Element description	Element view
Printed circuit boards (PCBs) A circuit made mostly of copper is soldered to the board with protective coatings and adhesives. The board is made of epoxy resin or fibreglass and generally coated with gold. Solder joints are made on silver-plated copper contacts. On the PCBs there are plastic, metal and ceramic housing components. Precious metals and other hazardous substances in the PCBs are Pd, Ag, As, Sb, Be, Br, Cd, Pb, Ni, Tl, Zn.	
Liquid Crystal Display (LCD) The LCD contains liquid crystals which are embedded between layers of glass. The liquid crystalline substances can contain toxic substances such as mercury. A typical mobile phone contains several mg of liquid crystal substance.	
Battery The battery enclosed in a sealed plastic housing can belong to one of three types: lithium-ion (Li-ion), nickel-metal-hydride (NiMH), nickel-cadmium (Ni-Cd) batteries - batteries present in the older types of phones, which are still in circulation.	
Plastic Casing The plastic material used to case the phone together is usually polycarbonate (PC), acrylonitrile butadiene styrene (ABS) or a combination of the two.	
Other Components Antenna, speaker, microphone, keypad, accessories - most of these components are very small and contain various elements in terms of material composition: metallic and non-metallic elements.	
Charger The chargers mainly consist of copper wires encased in plastic, but materials such as gold, cadmium and brominated flame retardants may also be present.	

Mobile phone consists of a few basic elements: casing, display, keypad, printed circuit board, antenna, microphone, speaker, battery and charger. Description of the components of a mobile phone is shown in Table 3. In terms of material composition a cell phone does not differ from other electronic devices and contains a number of different elements made of metals, plastics, glass and ceramics. Depending on the design, manufacturer, model and age of the phone the content of these components in the phone may vary. In most cases, phone plastic casing, in certain models could be made from aluminum or magnesium but also different substances and additives may be used by different manufacturers in electronic circuits.

Table 4.
Substances contained in mobile phones [14]

Substance	Conten t [%]	Location in mobile phone
Primary Constituents		
Plastics	~40	Case, PCB
Glass, ceramics	~20	LCD screen, chips
Cu, compounds	~10	PCB, wires, connectors, batteries
Ni, compounds	~2-10*	NiCd or NMH batteries
KOH	<5*	battery, NiCd, NiMH
Co	1-5*	Lithium-ion battery
C	<5	Bateries
Al	~3- 20	Case, frame, batteries
Steel, ferrous metal	~10	Case, frame, charger, batteries
Sn	~1%	PCB
Minor constituents 0.1% - 1%,		
Br, Mg, Ta, W, Zn		PCB
Cd		NiCd batteries
Cr		Case, frame
Pb		PCB; used in a tin-lead solder, which very efficiently bonds components into integrated electronic devices. Small quantities of lead compounds are used in some plastics, although it is gradually phased out. Lead is still used extensively in PVC coated wires (2–5%) and this use of lead is not phased-out yet. Most new mobile phones do not contain lead based solder; however, older end-of-life mobile phones that are sent for material recovery may contain lead based solder.
Li		Lithium-ion battery
Ag		PCB, keypad
Micro or trace constituents < 0.1%		
Sb, Bi, Ca, Ba. Pd, Ru, Sr, S, Y, Zr,		PCB
As		Gallium arsenide LED
Be		Connectors
F		Lithium-ion Battery
Ga		Gallium arsenide LED
Au		Connectors, PCB
Mg		If Mg is used for phone cases, its amount would be much bigger ~20%
Hg		No current use of mercury in mobile phones is known. However, certain old mobile phones may contain mercury oxide or silver oxide button cell batteries with mercury content.

*only if these battery types are used, otherwise minor or micro constituent

Mobile phone can contain more than 40 elements, including the basic metals (Fe, Cu, Al, Ni, Zn, Sn), precious metals (Au, Ag, Pt, Rd) or dangerous ingredients (Be, Cd, As, Sb).

Table 4 shows the typical content of an average mobile phone components, systematized in three categories: primary constituents, minor constituents and micro or trace constituents along with their location in the phone. A statistic mobile phone consists of 40% plastic, 20% glass and 23% of metals. Therefore spent mobile phones are a useful source of metals, including copper, other non-ferrous metals and precious metals like gold, silver and palladium.

Figure 1 shows the general scheme of the recycling chain and material recovery from used mobile phones, including metals.

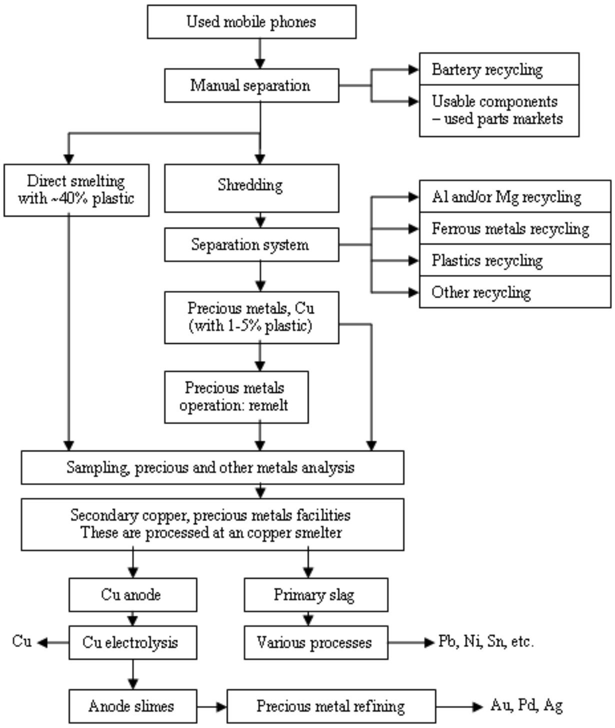


Fig. 1. Flow diagram - recovery of metals and other materials from mobile phones [14]

4. Experiments

4.1. Materials and methods

The study was carried out in the laboratory at the Faculty of Metallurgy, Department of Materials Science and Metallurgy, Silesian University of Technology. In the research, spent mobile phone the Samsung M351, was used. The phone was disassembled. In order to homogenise the structure, the phone was milled in a ball mill-tumbler. Analysis of the content of metals was performed on an atomic absorption spectrometer ASA. The surface of the PCB sample was also analysed by using a scanning electron microscope (SEM) equipped with a Hitachi S 4200 in the X-ray detector.

Accelerating voltage applied during the observation and X-ray microanalysis was 15 kV. Microanalysis of the chemical composition was performed by EDS method (Energy Dispersive Spectrum) (see Figures 2-4 and Table 5).

The weight of each part of the phone is shown in Table 6 and the initial and final results of the analysis of copper, silver and gold in the material of the test are shown in Table 7.

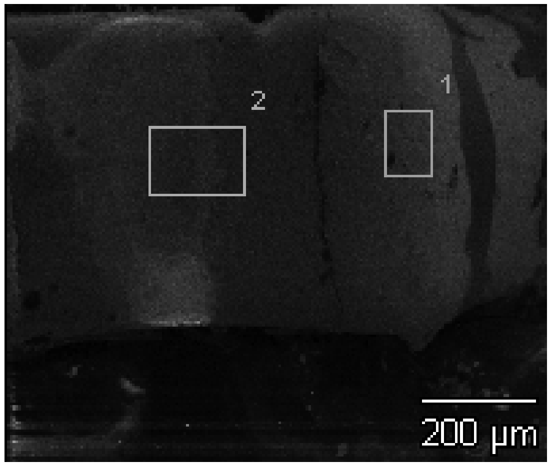


Fig. 2. Structure of PCB with marked selected areas for X-ray energy spectra

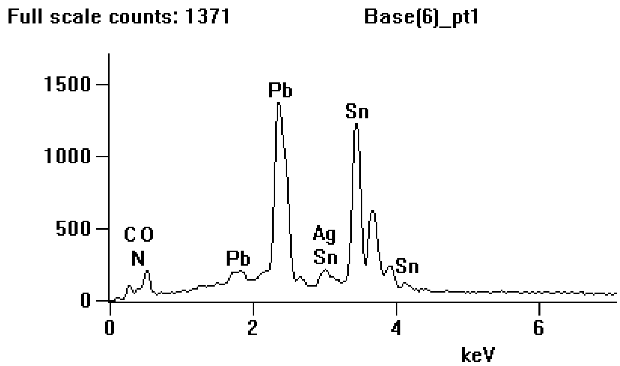


Fig. 3. Microanalysis of the chemical composition by EDS method-pt 1

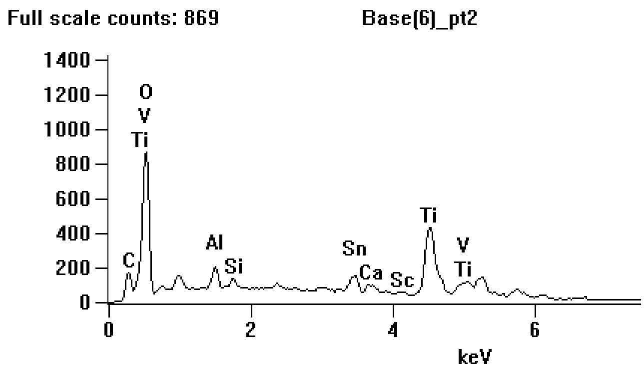


Fig. 4. Microanalysis of the chemical by EDS method-pt 2

Table 5.
The chemical composition of the sample by EDS method

Analysis, No.	Content, % mass						
	C	O	Al	Ti	Ag	Sn	Pb
pt1	1.3	7.5	-	-	2.8	49.9	38.0
pt2	5.7	61.1	1.9	19.4	-	8.8	-

Table 6.
Weight and the percentage of the mobile phone parts [16]

Element	Weight, g	Percentage, %
Casing	14.3	27.13
Battery	2.6	4.93
Keyboard	2.1	3.98
Mainboard	20.8	39.46
Metal parts	3.8	7.21
The connection between a keyboard and screen	9.1	17.26
Weight of phone	52.7	100

In the first stage of the study, milled material was dissolved in concentrated nitric acid (V). In this stage, copper from the spent cell phone was dissolved in acid and changed into solution, giving it a characteristic blue colour. The dissolution process of copper occurred according to the reaction:

$$Cu + 4HNO_3\ conc. \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O \quad (1)$$

$$Ag + HNO3\ conc. \rightarrow AgNO3 + NO2 + H2O \quad (2)$$

The next step was the filtration of the solution. The clear solution ($Cu(NO_3)_2$) was analyzed for copper, silver and gold content. The filtrate was dissolved in aqua regia, the solution took on a yellow colour. The dissolution reaction of Au in aqua regia was:

$$Au + 4Cl- + 3NO3- + 6H+ \rightarrow [AuCl4]- + 3NO2\uparrow + 3H2O \quad (3)$$

This is a two stage process. The first step is the oxidation of gold to Au^{3+} ions by nitric acid (V):

$$Au + 3NO3- + 6H+ \rightarrow Au3+ + 3NO2\uparrow + 3H2O \quad (4)$$

The second stage is creation of $AuCl_4$ ions:

$$Au + NO3 - + 4 H+ \rightarrow Au3+ + NO\uparrow + 2H2O \quad (5)$$

$$Au3+ + 4Cl- \rightarrow [AuCl4] - \quad (6)$$

Consequently, the solution should contain silver and gold. Results of the hydrometallurgical recovery of precious metals from used mobile phones are shown in Table 7.

Table 7.
Results of the hydrometallurgical recovery of precious metals from used mobile phones [16]

Cu		
Initial sample	35.9%	
Initial content in 5 g of a sample	1.8 g	
	Weight	Recovery
After dissolving in HNO_3	1.28 g	71%
Precipitate	0.0018 g	0.1%
After aqua regia adding	0.055 g	3.05%
Precipitate	0.28 g	15.75%
Ag		
Initial sample	0.36%	
Initial content in 5 g of a sample	0.0175 g	
	Weight	Recovery
After dissolving in HNO_3	0.0013 g	7.42%
Precipitate	-	-
After aqua regia adding	0.0007 g	4.11%
Precipitate	-	-
Au		
Initial sample	0.09%	
Initial content in 5g of a sample	0.005 g	
	Weight	Recovery
After dissolving in HNO_3	-	-
Precipitate	-	-
After aqua regia adding	0.0009 g	18%
Precipitate	0.0003 g	5.4%

5. Conclusions

According to presented research, 71% copper was recovered from circuit boards using, at first stage of leaching, the nitric acid V. Slightly inferior results were obtained for silver (7.42%). Silver has leached into solution. Introduction of aqua regia, as a leaching factor, in the second stage of the process, resulted in a low percentage of Cu and Ag recovery but gold was reached 18%. Recovery of silver and gold could be improved by the use of hot aqua regia (in the experiments reagents were used at ambient temperature) and also by the prolonged time of the process. However it should be noted that the material complexity of PCBs complicates the hydrometallurgical processes and can reduce the effectiveness of metals recovery. Tin present in PCBs can form metastannic acid, silver forms silver chloride which hinders gold dissolution. In the adopted experimental conditions, when aqua regia was used, precious metals have not been effectively recovered.

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