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PROBLEMS OF PROCESSING AND SEPARATION OF MULTI-MATERIAL ELECTRONIC WASTE IN TERMS OF CIRCULAR ECONOMY

The article presents current methods used for the recovery of metals from used electronic equipment. The analysis of the composition and structure of the material was made on the example of one of the most popular and widespread e-waste – used cell phones. The article was address the problems of processing and separation of individual components included in these heterogeneous wastes. The main purpose of the conducted research was to prepare the tested material in such a way that the recovery of metals in the further stages of its processing was as effective as possible.The results of attempts to separate individual material fractions with magnetic, pyrometallurgical or hydrometallurgical methods will be presented. An analysis of the possibilities of managing electronic waste in terms of the circular economy will be made.

Keywords: electronic waste, mobile phone, metals recovery, circular economy

1. Introduction

A circular economy is a concept aimed at the rational use of resources and reducing the negative environmental impact of manufactured products. These materials should remain in the economy for as long as possible and also waste production should be minimized as much as possible [1]. In today's circular economy, it is an important challenge to deal with electronic waste. Constant innovation in electrical and electronic technologies have further reduced the life of electronic equipment and thus increased the amount of generated e-waste [2]. In 2020, it is expected that the waste emission of used cell phones will be almost 18 times higher than in 2007 [3,4]. With the continuous growth of demand for metals and parallel degradation and depletion of primary ores, there is an increasing need for secondary raw materials [5]. Used electronic devices, such as mobile phones, contain substances that are attractive when it comes to recycling, but also those that pose a serious threat to the environment and health [6]. The Global E-Waste Monitor 2017, published by ITU, UN University (UNU) and International Solid Waste Association (ISWA), draws attention to the increasing level of e-waste and its inappropriate and dangerous treatment and disposal by incineration or in landfills [6]. Waste is no longer waste, but tomorrow's resource (Fig. 1) [7-8]. In 2016, 44.7 million tons of electronic waste was generated – the equivalent of 4500 Eiffel towers – including around 435,000 metric tonnes of mobile phones. This trend will continue, due to the continuous increase in the number of these wastes. By 2021, it is predicted that their number will increase to 52.2 million metric tons [6]. Every year, more and more used electronic equipment comes to Poland. This is confirmed by the data of the Main Inspectorate of Environmental Protection. In 2007, the weight of collected waste electronic equipment per capita was 0.71 kg, while in 2016 – 5.58 kg. The latest data also shows that the total mass of collected used equipment of IT and telecommunications equipment in Poland amounted to 31 million kg in 2016 [9]. Four European Union directives [10-13] ((EU) 2018/849, (EU) 2018/850, (EU) 2018/851 and (EU) 2018/852) adopted in May 2018 as a result of inter-institutional negotiations between Parliament and the Council included among others: mandatory extended producer

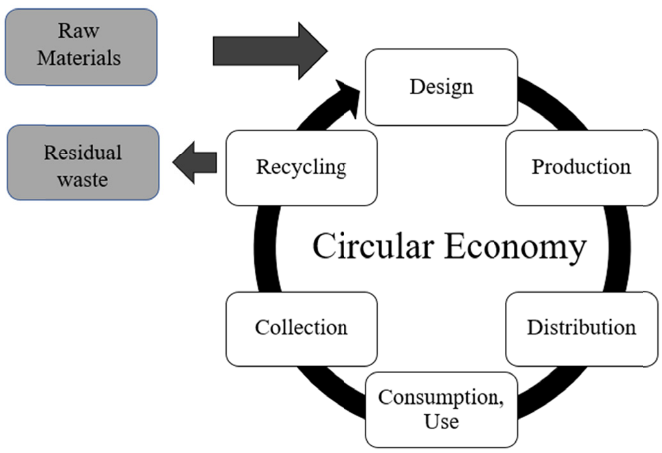

Fig. 1. General scheme of circular economy [7-8]

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responsibility schemes to encourage producers to market more environmentally friendly products and support recovery and recycling schemes (for example, packaging, batteries, electrical and electronic equipment and end-of-life vehicles) [14].

This new concept will transform the way in which whole industries and markets think about the processing of e-waste, and can even change the attitude of people to the recycling of electronic waste. However, if people switch to a more proactive attitude, this would lead to people around the world paying more attention to e-waste. Some company is planning to produce a mobile phone made entirely of recycled materials. A good example of this approach is that during the 2020 Olympic Games in Tokyo medals will be made of precious metals that have been recycled from a mobile phone and 3C products. In addition to launching wearable jewellery products made from recycled materials, another company will also introduce computers made of recycled materials [15].

The transition to a circular economy can bring many benefits, not only related to the environment and health, but also to increasing competitiveness, stimulating innovation, growth and employment (580,000 new jobs in the EU). It can also provide consumers with more durable and innovative products that provide savings and a better quality of life [7]. In spite of the important communication function, the mobile telephone and its structure and composition of the material are very diverse [16]. In mobile phones there are several components: printed circuit board (**PCB**), liquid crystal display (LCD), batteries, plastic housing and other elements such as the antenna, loudspeaker and keyboard, etc. [17]. The basic structure of the PCB (Fig. 2) is a copper-covered laminate consisting of fiberglass reinforced epoxy resin (up to 70%) and many metallic materials, including precious metals (Au, Ag and Cu) – representing the value of PCB in the recycling process (total metal content up to 30%). [18]. A comparison of the precious metals content of typical ores and printed circuit boards is presented in the Table 1. These data show that used PCBs mobile phones are an attractive option for recycling [19-21]. LCD have liquid crystal is embedded between layers of glass and transistors for lighting and electrical charge.

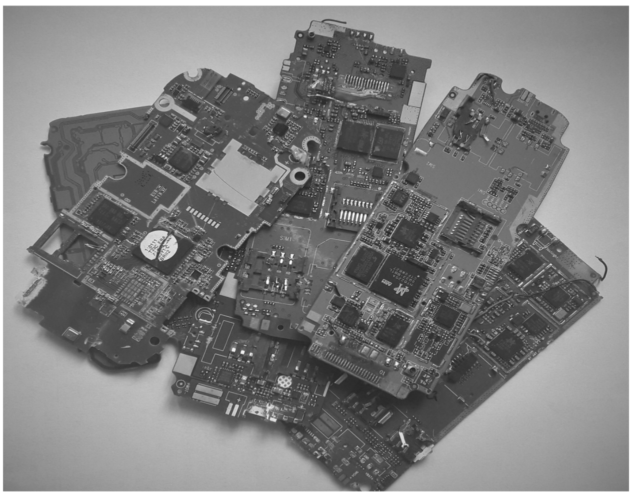

Fig. 2. Printed circuit boards separated from the rest of the mobile phone

The battery is a combination of one or more electrochemical cells, used to convert stored chemical energy to produce electricity.

Due to the heterogeneity of e-waste, its processing is difficult. It includes certain stages of mechanical operations such as disassembly, classification, size reduction – crushing/grinding, and finally separation of metals and non-metals – by magnetic, gravity, electrostatic separation or flotation. After separation, modernized e-waste is processed to recover metals by pyrometallurgical, hydrometallurgical or bio metallurgical method [22].

TABLE 1

Comparison of precious metal content of typical ores and PCB, concentration in % [19-21]

Metal	Ore (%)	PCB (%)
Copper	0.5-3.0	12.0-29.0
Gold	<5 ppm	29-1120 ppm
Silver	<500 ppm	100-5200 ppm

The main purpose of the conducted research was to prepare the tested material in such a way that the recovery of metals in the further stages of its processing was as effective as possible. Attention is paid to copper, because PCBs of used cell phones contain the most of this metal. The research involved the use of basic mechanical operations and separation method for the segregation of non-metallic fraction of the PCB (fiberglass reinforced epoxy resin) material from the metal-bearing fraction. The purpose of the work was to release metals from organic matter, determine the degree of metal dissipation in individual fractions of ground PCB material and obtain the knowledge necessary to determine the minimization of losses of these metals during further processing (pirometallurgy and/or hydrometallurgy).

A preliminary tests of melting of ground and whole PCB material were also carried out to determine the possibility of separating individual fractions, which will facilitate further processing of the material.

2. Experimental methodology

2.1. Preparation of sample: mechanical operations and separation method

The PCB of used cell phones were used as the research material. In the first stage 10 mobile phones were manually dismantled and individual elements (LCD panels, batteries, plastic housing and other elements) were separating from PCB. These pieces of PCB (total weight 124.5 g) were cut and milled (Fig. 3) in the cross beater Retsch SK100 hammer mill equipped with sieves with a diameter of 5 mm, 1 mm and 0.2 mm. Multiple grinding of the PCB material batch using a decreasing mesh size of sieves was used and finally a material <0.2 mm was obtained. The ground material (<0.2 mm) prepared in this way was subjected to sieve analysis with a laboratory shaker (shaker with an electromagnetic drive from MULTISERW-Morek, sieves in the range of 0.2-0.045 mm), to determine the particle size distribution, weight and metals content in the each fractions of the material. In the next step magnetic separation was applied and magnetically susceptible material was extracted from a mixture of each sieved fraction.

Fig. 3. Printed circuit boards after grinding in a mill

2.2. Chemical analysis of samples

The analysis of metal content in each fractions of ground PCB were performed by atomic absorption spectroscopy ASA – UNICAM Solaar 936 M6 model. Samples for analyzing the content of metals were prepared by dissolving 0.5 g of material in hot aquq regia. The present metals are dissolved in aqua regia according to the following reactions [23-24]:

$$2HNO_3 + 6HCl \rightarrow 2NO + 4H_2O + 3Cl_2 \quad (1)$$

$$2Au + 9HCl + 3HNO_3 \rightarrow 2AuCl_4 + 3NOCl + 6H_2O \quad (2)$$

$$3HCl + HNO_3 \rightarrow Cl_2 + NOCl + 2H_2O \quad (3)$$

for metals such as Cu, Ni, and Sn:

$$Me + 3HCl + HNO_3 \rightarrow MeCl_2 + NOCl + 2H_2O \quad (4)$$

and for metals such as Al, Zn, Fe, Ag:

$$Me + 3HCl + HNO_3 \rightarrow MeCl_3 + NO + 2H_2O \quad (5)$$

2.3. Pyrometallurgical treatment

Second part of experiments was dedicated to both fractions after sieve analysis and additionally entire PCBs (pieces 30 mm×30 mm). Samples of entire PCB or material divided according to the sieve analysis were placed in graphite crucibles The pyrometallurgical processing of PCBs was carried out in the Czylok electric furnaces with silite rods by heating samples at 1350°C for 1800s.

3. Results

Table 2 presents results of size distribution of ground PCB fractions from sieve analysis and results of their magnetic separation in the grain range of 0.2-0.045. The magnetic separation process allowed the separation of the metallic fraction from the organic fraction in the ratio of 50/50. However, it can be seen that the metallic fraction separates most easily in the case of the smallest particle size in the range of 0.15-0.045 and <0.045, in which the fraction of metals is 68.5% and 98.1%, respectively.

The content of metals in PCB varies depending on the age of the device, manufacturer or the type of equipment. PCBs contain average about 28% of metals and 23% of plastics, the rest are ceramics and glass materials [25]. The analyzed batch of PCBs has a typical composition for this type of materials. The sample contained analyzed metals (Table 3) of 13% Fe, 7% Cu, 2% Ni, 6% Sn, 0.3% Zn, 420 ppm Ag, 340 ppm Au, respectively, as well as polymers, plastics, glass fibers and iron are dominate components. The small content of precious metals were also present in the material. It should also be noted here that the content of precious metals (in different electronic devices <0.5%) in PCBs is 10 times higher than a typical rich ore. Thus, the content of individual metals in PCBs determines the value of electronic scrap as a source of these materials [26].

From the point of view of further stages of metals recovery, e.g. by hydrometallurgical method, it is important to determine the possible tendency to accumulate/concentrate metals (Ag, Au, Fe, Cu, Al, Zn, Ni, Sn) in each fraction of ground material. It is also important to obtain answers to the question: is the previous division into factions according to the particle size is a key operation and will it facilitate the implementation of further stages of the recovery process? The results of grinding and analysis of metal content in particular grain fractions (Table 3) clearly show that the content of precious metals and basic metals varies in these fractions. Chemical analysis indicate that the content of copper, nickel and tin is the highest at the fraction >0.2 and in the smallest fraction <0.045. Other metals (noble and basic) show a certain tendency to accumulate in finer fractions (grain size <0.2 mm). This tendency is particularly visible in the silver case, which is concentrated in the smallest factions.

TABLE 2

Results of sieve analysis after grinding and magnetic separation the PCBs

Fraction, mm	Weight, g	Magnetic, g	Non-magnetic, g	% of the metallic fraction
>0.2	13.75	2.7	11.05	19.6
0.2-0.15	24.3	1.9	22.4	7.8
0.15-0.045	26.0	17.8	8.2	68.5
<0.045	20.7	20.3	0.4	98.1

In the second experimental part the melting behavior of PCB entire pieces and ground PCB fractions was studied. When the desired temperature was reached, the liquid metals could flow along the surface of the PCB and the droplets of alloys gath-

TABLE 3

Content of metals in ground PCB fractions from sieve analysis and in entire PCB

Fraction mm	Weight g	The content of elements, % mass							
		Ag	Au	Fe	Cu	Al	Zn	Ni	Sn
>0.2	13.75	0.015	0.060	0.771	22.774	0.305	0.179	2.154	2.277
0.2-0.15	24.3	0.003	0.140	1.786	6.451	0.605	0.211	1.353	1.912
0.15-0.045	15.1	0.056	0.090	4.245	9.200	1.201	0.194	0.937	0.770
<0.045	17.85	0.074	0.096	0.028	21.700	1.288	0.653	2.569	8.889
Entire PCB	124.45	0.042	0.034	13.756	6.954	—	0.346	1.825	6.172

TABLE 4

The content of elements and weight of samples after pyrometallurgical treatment

Fraction mm	Weight, g	Content of elements, % mass.							
		Ag	Au	Fe	Cu	Al	Zn	Ni	Sn
>0.2	13.75	0.058	0.034	0.895	19.668	0.300	0.299	5.628	8.109
0.2-0.15	24.3	0.071	0.045	2.321	22.801	0.410	0.086	2.187	1.936
0.15-0.045	15.1	—	0.158	1.950	11.487	0.531	0.039	1.798	0.774
<0.045	17.85	0.016	0.107	2.050	7.386	2.000	0.016	1.064	0.725
entire PCB	124.45	—	—	0.077	7.517	1.148	0.013	1.506	0.086

ered in the bottom of the crucible. The obtained melted entire PCB pieces were characterized by the formed large metal alloy droplets, containing analyzed metals with the dominate copper content (Table 4), while the material of PCB (mostly polymer and glass fibers) was partially charred.

The results of the crushed fraction after pyrometallurgical treatment (Table 4) clearly show that the content of precious and base metals is also different in fractions. Chemical analyzes show that the content of zinc, nickel, tin is the highest at the metal fraction >0.2 and copper and iron in the finer metal fraction 0.2-0.15. The highest silver content is at a residue fraction of 0.2-0.15. Gold is the only metal that accumulates in the metallic fraction 0.15-0.045. Aluminum is concentrated in the finest residue fraction <0.045.

The results in Table 4 show the lack of Au and Ag content after melting whole pieces of PCB, may be due to the fact that the content of these metals is below the accuracy of the determination.

The tests carried out above prove, due to the high heterogeneity of the material, separation processes through the use of high-temperature processes are a desirable operation and can be a preliminary process for main recovery processes. It would enable the preperation for further processes to the processing of a selected fraction rich in a particular metal.

As it is in other metallurgical processes on the industrial scale, hydrometallurgy is used as auxiliary operations (leaching or electrolysis) to purify metals smelted in pyrometallurgical operations [25].

4. Conclusions

E-waste amount is growing at about 4% annually, and has become the fastest growing waste stream in the industrialized world [25]. 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 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.

The complexity of PCBs material complicates their processing and can reduce the efficiency of metal recovery. The results of the conducted research indicate that satisfactory results can be obtained with the fragmentation of the material and the use of magnetic separation at the beginning of the processing processes of used PCBs of mobile phones. This method allows the separation of the metallic fraction of the material from the non-metallic fraction. As a result of the presented experiment of magnetic separation of the metallic fraction, 22.774% Cu was obtained. Metals show a certain tendency to accumulate in the finest fractions (<0.045), which may be beneficial in the further processing of this material by hydrometallurgical treatment for the recovery of these metals.

As a result of initial pyrometallurgical tests, organic matter from the chipped PCBs has not been completely eliminated. The analysis showed that the content of precious and base metals varies in metallic fractions and other fractions. In this case, most metals show a certain tendency to accumulate in larger fractions with granularity 0.2-0.15 mm and >0.2 mm. The attempt to melt whole pieces of tiles and comminute to Au and Ag content gave definitely worse results. The gold and silver content was not detected in the pieces of PCB, this is probably due to the small amounts of these metals in the test material. Silver and gold yields would improve the use of extended process time and increased temperature.

The presented method is a simple and relatively universal way at the initial stage of preparing the material for further processing.

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