Electrostatic and magnetic separations for the recovery of metals from electronic waste

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Abstract. The aim of the study was to recover metals from e-scrap using electrostatic and magnetic separation successively. The type of phases in the four magnetic separation products was determined by X-ray diffraction (XRD). Three grain classes were tested: 2.00 - 0.56, 0.56 - 0.32 and 0.32 - 0.10 mm. Based on the tests, it turned out that the separations were the most efficient for grain class in the range from 0.32 to 0.10 mm. The yields of the products obtained from electrostatic and magnetic separations were as follows: in the case of electrostatic separation, 13.12% metals and 86.88% plastics and glass; and for magnetic separation 1.51% of ferromagnetics, 1.56% of paramagnetics and 10.05 % of diamagnetics. In the diamagnetics Cu was dominant, while in the paramagnetics and ferromagnetics CuSn, γ-Fe and Ni, Fe₃O₄, respectively. Pb, Sn were identified in average amounts in all products of magnetic separation.

1. Introduction

Due to the exhausting deposits of metals, including precious metals and rare earth elements, alternative sources of their acquisition should be sought, among other things by using a closed-circuit economy. In the era of dynamic development of technology (Industry 4.0), there is a need for systematic replacement of electronic equipment components, which results in the creation of a significant amount of electronic waste containing precious and critical metals listed on the European Commission list. Metal recovery is therefore a very important aspect for economic, political and environmental reasons.

Large amounts of valuable metals are needed for production of electric and electronic equipment that are used in many areas of our lives. The amount of metals in these wastes is 60.6%, of which 47.9% is iron and steel, 7.0% copper, 4.7% aluminum, 1.0 non-ferrous [1]. Printed circuit boards (PCBs) are used in many electronic devices, such as personal computers, televisions, mobile phones, hard disks, graphic cards, RAMs, etc. Due to the high content of metals in them, they are particularly interesting in the context of metal recovery [2, 3]. PCBs contain copper 11-14%, iron 4.5-8%, tin 2-4%, aluminum 1.5-3%, lead 1.5-2%, nickel 1-2.5%, zinc 0.5-1% and small amounts of precious metals such as: 0.005% gold, 0.008% silver, 0.002% palladium, 0.004% platinum [4, 5].

The type of metals and their amount in PCBs change each year, depending on the development of technology and current market standards assigned by producers. The metals content is about 20% to 45%, depending on the technology used and the year of production. In 1993, metals such as: Cu, Al,
Pb, Zn, Ni, Fe, Sn, Ag and Au were used for PCB production. Next, other metals were systematically used for the production, such as: Pd, Mg, Sb, Cr, In, Mn, Mg, Co, Ti, Cd, K, Se, and As. The content of metals also varies depending on the purpose of the PCB, eg. PCBs from mobile phones, household appliances, monitors, or stationary computers. It can be seen that the largest contents of expensive metals have cell phones. The reason is the small size of the PCBs of mobile phones, on which elements of electronic components similar to computers must be integrated [6, 7].

As provided by Tuncuk et al. [8] electrostatic and magnetic processes can be used to recover metals from PCBs. These methods have been extensively described in many works [9-14].

The aim of the study was to recover metals from e-scrap using electrostatic and magnetic separation. To assess the type of recovered metals XRD spectroscopy was applied.

2. Methods and materials

2.1. Preparation for electrostatic and magnetic separation

In the study the printed circuit boards (PCBs) from: personal computers (PC), hard disks, graphic cards and RAMs were applied. To separate metals from plastic and glass, the method shown in Figure 1 was used. Before grinding, some parts of PCB i.e. batteries, capacitor, inductors, quartz crystals etc. were removed using basic tools such as screwdrivers, pliers and others. Such prepared PCBs were cut into 4x4 cm pieces. The way of preparing and grinding electronic waste was presented in the paper written by Franke and Suponik [15]. The knife mill manufactured by TESTCHEM [16] was used to grind PCBs. The rotation speed of mill was 2815 rpm. Hardened steel blades and perforated sieve with 2 mm mesh size were used. Four grain classes were separated from the grinded material: 2.00 - 0.56 mm, 0.56 - 0.32 mm, 0.32 - 0.10 mm and <0.10 mm. The last, smallest grain class was not subjected to separation processes. Leaching methods for metals recovery are to be analyzed for this class in subsequent studies.
Figure 1. Research method.
2.2. Electrostatic separation
Boxmag-rapid Ltc separator was applied for electrostatic separation. The main parameters of this separation are: rotational speed of the shaft, voltage flowing through the electrode and its distance from the shaft, and the size of the material and feeding speed [17].

In the separator, the feed was directed to the belt of rotating shaft. The rotational speed of the shaft was 50 rpm. 5 cm from the shaft there was an electrode wire through which high voltage flowed. The voltage flowing through the electrode was 20 kV. As a result of air ionization, the grains of material on the shaft were charged. These with high conductivity quickly lost their charge and were ejected from the rotating shaft by centrifugal forces. The remaining grains that had not lost their charge were removed by a brush at the rear of the shaft.

2.3. Magnetic separation
A disks separator, that ensures heterogeneity of the magnetic field, was used for magnetic separation. In this type of separator, the difference in the magnetic susceptibility of various materials was used. The separator allowed to separate the material by means of two different magnetic forces produced by two electromagnets [18]. The currents supplying two electromagnets were 2 and 2.7 A, respectively. Thus, the magnitude of the magnetic forces in the separator was a parameter that improves the separation of materials. Additionally, at the beginning of the separator there was a permanent magnet that captured the ferromagnetic material.

The grains of material on the moving belt were affected by a magnetic field of varying intensity. Subsequently, the grains from the highest to the lowest magnetic susceptibility were removed from the belt to the four containers. These were successively: ferromagnetics, strong and weak paramagnetics and finally diamagnetics.

2.4. Assessment of products
The qualitative phase analysis of the magnetic separation products was based on X-ray diffraction measurements, performed with the use of a Panalytical X’Pert Pro MPD diffractometer, utilizing filtered radiation of a copper-anode lamp (λ(Ka) = 0.154 nm), and a PIxCell 3D detector on the diffracted beam axis. Diffraction lines were recorded in the angular range of 5-120° (2θ), at step = 0.05° and count time per step = 100 s. Panalytical High Score Plus software with dedicated PAN-ICSD database was used for the identification of phases.

The content of ferromagnetic materials in the samples was carried out using the Satmagan 135 meter by Rapiscan Systems. The density of products was specified using pycnometer method in line with the PN-88/B-04481 standard.

3. Results and discussion
Table 1 shows the granulometric composition of grinded printed circuit boards. Two grain classes represented over 80% of the sample. They are 0.56 - 0.32 mm and 0.32 - 0.10.
Table 1. The results of the screening tests of comminuted PCBs.

| Grain class, mm | Yield of grain class, (in % by mass) |
|-----------------|-------------------------------------|
| 2.00 - 0.56     | 8.4                                 |
| 0.56 - 0.32     | 42.1                                |
| 0.32 - 0.10     | 39.1                                |
| < 0.10          | 10.4                                |

The results of electrostatic and magnetic separation for tested grain classes are presented in table 2. In the grain classes 2.00-0.56 and 0.56-0.32 the yields of conductors (metals) after electrostatic separation were ca. 30%, while in the class of 0.32-0.10 it decreased to 13%. For a smaller grain class, metals were probably much less connected with insulators and thus the separation efficiency was greater. In addition, for larger classes of grains, the force of gravity, on electrostatic separator, acting on larger particles of insulators was probably greater than electrostatic forces, and therefore these particles fell into metallic products. This is evidenced by the higher density of insulators for larger grain classes and much higher yield of diamagnetics for these classes in magnetic separation products (see table 2). In general, the high content of diamagnetics indicates the imperfection of the electrostatic separation process.

Analysis of the content of ferromagnetic materials in the magnetic separation products (table 2) confirmed the correctness of magnetic separation in relation to metals with ferromagnetic properties. The yields of paramagnetics in all analyzed grain classes were the smallest.

Table 2. Results of electrostatic and magnetic separations.

| The grain classes of the feed on the electrostatic and magnetic separators | 2.00-0.56 mm | 0.56-0.32 mm | 0.32-0.10 mm |
|---------------------------------------------------------------------------|--------------|--------------|--------------|
| Electrostatic separation                                                  |              |              |              |
| Type of product after electrostatic separation                            | Conductors   | Insulators   | Conductors   | Insulators   | Conductors   | Insulators   |
| The yield of the products in grain class, in % by mass                    | 33.79        | 66.21%       | 28.47        | 71.53        | 13.12        | 86.88        |
| Density of product, g/cc                                                  | 10.71        | 3.57         | 10.50        | 3.86         | 11.32        | 2.49         |
| Magnetic separation                                                       |              |              |              |              |              |              |
| Type of product after magnetic separation                                 | F⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺ | Pstr⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺ | Pwea⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺ | D⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺ | F⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺ | Pstr⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺ | Pwea⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺ | D⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺ |
| The yield of the products in grain class, in % by mass                    | 2.75         | 3.57         | 1.63         | 25.84        | 3.37         | 2.83         | 1.00         | 21.27        | 1.51         | 1.11         | 0.45         | 10.05        |
Content of ferromagnetics in product, in % by mass

|         | 94.1 % | 0.4 | <0.1 | 82.3 % | 0.4 | <0.1 | 92.4 | 0.2 | <0.1 | <0.1 |
|---------|--------|-----|------|--------|-----|------|------|-----|------|------|

F - ferromagnetics; P_str - strong paramagnetics; P_wea - weak paramagnetics; D - diamagnetics

Based on the diffraction patterns shown in figure 2, the phases presented in table 3 were identified in magnetic separation products. The magnetic properties of these metals are presented in table 4. This table contains information on the use of presented metals in the production of PCBs.

Figure 2. Diffractograms for magnetic separation products for: ferromagnetics (blue), strong paramagnetic (green), weak paramagnetics (pink), diamagnetics (red).

Table 3. Share of identified phases in the separation products.

| Sample           | Identified phases |
|------------------|-------------------|
|                  | Cu    | Sn    | Pb    | CuSn  | Fe γ  | Fe3O4 | PbO   | Ag    | Ni    | Co    |
| Ferromagnetics   | +     | +     | +     | +     | +     | +     | +     | +     | +     | +     |
| Strong paramagnetics | +     | +     | +     | +     | +     | +     | +     | +     | +     | +     |
| Weak paramagnetics | +     | +     | +     | +     | +     | +     | +     | +     | +     | +     |
| Diamagnetics     | +     | +     | +     | +     | +     | +     | +     | +     |

Table 4. Magnetic properties of identified metals (metallic compounds) and examples of their applications in PCB production [5, 8].

| Metal or metallic compounds | Magnetic properties | Application examples         |
|-----------------------------|---------------------|------------------------------|
| Fe3O4 [19]                  | Ferromagnetic       | Data storage                 |
| Ni                          | Ferromagnetic       | Relays, connectors and transformers |
| CuSn  | Contact base material                  |
|-------|--------------------------------------|
| γ-Fe  | Paramagnetic                         |
| Sn    | Paramagnetic                         |
| PbO   | Diamagnetic                          |
| Pb    | Diamagnetic                          |
| Cu    | Diamagnetic                          |
| Ag    | Diamagnetic                          |

The intensity of basic diffraction lines indicated a clear quantitative differentiation of minerals in the samples:

- in diamagnetics Cu dominated, while Pb, Sn were identified in medium and Ag and Al in small quantities,
- in a weak and strong paramagnetics CuSn, Cu and γ-Fe dominated, while Sn and Pb were identified in smaller quantities,
- in ferromagnetics there were Ni, Fe₃O₄, Sn, Pb and CuSn in average amounts.

A relatively large amount of Cu, both in paramagnets and ferromagnetics, indicates that copper as a diamagnetic was probably mechanically bound to other elements or penetrated into paramagnetic and ferromagnetic products as a result of imperfections in the separation process. Also, in this case some fragments of metals may be soldered or covered by others (e.g. Cu or Sn) to increase conductivity.

4. Conclusions

Based on the research, the following conclusions were drawn:

- the yield of grain classes 0.56 - 0.32 and 0.32 - 0.10 mm obtained after grinding PCBs in the knife mill was over 80 %;
- electrostatic separation, and thus also magnetic, is much more efficient for a smaller grain class, in the range of 0.32-0.10 mm. The quantity of metallic products is smaller, but they are much less contaminated with plastics. The yields of the products obtained from electrostatic and magnetic separation were as follows: in the case of electrostatic separation, 13.12% metals and 86.88% plastics and glass; and for magnetic separation 1.51% of ferromagnetics, 1.56% of paramagnetics and 10.05 % of diamagnetics. High content of diamagnetics indicates the imperfection of the electrostatic separation process;
- The yield of magnetic products for the grain class of 0.32-0.10 mm was twice lower than in the case of larger classes. The feed on the magnetic separator for this grain class, i.e. for the conductors of grain class 0.32-0.10 mm, was also twice as small than for larger grains. This proves that magnetic separation worked with similar efficiency for all grain classes;
- In the diamagnetics Cu was dominant, while in paramagnetics and in ferromagnetics CuSn and γ-Fe and Ni, Fe₃O₄, respectively. Pb, Sn were identified in average amounts in all products of magnetic separation. In all magnetic separation products, the most was copper. It appeared even in paramagnets and ferromagnetics. Copper was probably mechanically bound to other chemical substances or penetrated into paramagnetic and ferromagnetic products as a result of imperfections in the magnetic separation process.

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