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Evaluation of the use of flotation for the separation of ground printed circuit boards

Introduction

Due to the rapid advancement of technology, the global production of electrical and electronic equipment is increasing rapidly (Tuncuk et al. 2012). Along with technological innovations, economic growth and market expansion, a significant increase is observed in waste electrical and electronic equipment (WEEE) and this increase generates environmental problems (He et al. 2006; Khetriwal et al. 2009). If this waste is incinerated in a smelter, it pollutes the air; if it is disposed of in landfill or leached out to recover metals, harmful substances can be released into the soil and contaminate groundwater (Nnorom and Osibanjo 2009).

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The rapidly growing amount of WEEE is becoming a challenge for companies recovering various substances from it. In 2019, the global production of WEEE was 53.6 Mt and is expected to increase to 74.7 Mt in 2030. The estimated value of raw materials contained in e-waste produced in 2019 was 57 billion USD, but considering the current level of WEEE collection and recycling, the potential value for the recovery of raw materials was 10 billion USD (Forti et al. 2020). Increasing the levels of recycling by implementing innovative approaches and technologies allows the reduction of the negative impact on the environment and may bring material benefits to recycling companies.

Printed circuit boards (PCBs), which are an indispensable component of almost all electronic products, can be described as the basis of electronics. PCBs contain large amounts of metals such as Cu, Fe, Al, Sn and rare metals Ta, Ga and other rare metals of the platinum group (PGM) as well as precious metals Au, Ag and Pd (Kaya 2016). They also contain hazardous metals such as Cr, Pb, Be, Hg, Cd, Zn and Ni (Zhang and Forssberg 1997; Kaya 2016). The concentrations of these metals are dozens or even hundreds of times higher than in the mined ores (Yu et al. 2010). The metal concentrations in PCBs and in the corresponding metal ores are presented in Table 1.

Table 1. Metal content in PCBs and in metal ores

Tabela 1. Zawartość metali w PCBs i w rudach metali

Metals	PCBs	Metal ores
	Content (%)	Content (%)
Cu	6–27	0.5–2.0
Fe	1.2–8.0	<65
Al	2.0–7.2	30–60
Sn	1.0–5.6	5–25
Pb	1.0–4.2	–
Ni	0.3–5.4	1–1.5
Zn	0.2–2.2	5–15
Sb	0.1–0.4	5–60
Au (ppm)	250–2,050	0.0001–0.0006
Ag (ppm)	110–4,500	–
Pd (ppm)	50–4,000	–
Pt (ppm)	5–30	–
Co (ppm)	1–4,000	–

Source: Zhang and Forssberg 1997; Kaya 2016; Schwarz 2004; Muwanguzi et al. 2012; Zhou et al. 2004; Haldar 2018; Wang 2016; Anderson 2012.

There are many methods for the recovery of metals from PCBs, including pyrometallurgical, plasma, and (bio)hydrometallurgical separation. However, the use of some of these has some disadvantages. The combustion of non-metal parts by pyrometallurgical methods causes the formation of brominated organic and other toxic compounds (Bidini et al. 2015). Additionally, it produces about 20–25% of ashes containing a large number of heavy metals that require further processing (Long et al. 2010). In hydrometallurgical methods, there is a significant level of high-risk wastewater that can contaminate groundwater and soil (Ma et al. 2018). These methods are also time-consuming.

Physical (or mechanical) and physicochemical processing technologies are considered to be the most environmentally friendly alternative to recovering resources from end-of-life (EoL) products such as PCBs (Goosey and Kellner 2002). Some mechanical processing technologies have advantages with regard to PCB recycling (Zhao et al. 2004; Duan et al. 2009; Zhao et al. 2012) but involve problems in the processing of fine particles (Sarvar et al. 2015). It is scientifically known that froth flotation is an effective technique for fine fraction enrichment (Ogunniyi and Vermaak 2009). This process is based on the selective separation of hydrophobic from hydrophilic materials. It has been used in wastewater treatment, mineral processing, and the paper/waste recycling industries for a long time (Kaya 2019). It has also been employed in the processing of PCBs (Ogunniyi and Vermaak 2009). Flotation technology is widely applied and efficient, especially in the processing of metal ores. However, it requires the use of aqueous solutions. Separation in flotation is achieved by the difference in physicochemical properties of different particles (Farrokhpay 2011; He and Duan 2017). While hydrophilic particles settle down to the bottom of the aqueous medium, hydrophobic particles float due to selective bubble adsorption (Shean and Cilliers 2011). The contact angle, as a parameter that determines the hydrophobic properties of materials, is the angle between the gas and solid phases, through the water phase. This angle is 0° for hydrophilic materials and a maximum of 110° for hydrophobic materials (Drzymala 2007). The ease of separation is directly proportional to the magnitude of the differences in the chemical properties of different particle surfaces (Wills and Finch 2016). For this reason, various reagents called collectors are used to change the hydrophobic properties of the particles. The hydrophobizing power of the collectors is due to their chemical and physical interactions with the surface. The role of frothers is to accelerate flotation, create a stable foam, and disperse the gas. These tasks are accomplished when frothers are preferentially adsorbed at the water-gas interface. A decrease in surface tension accompanies sorption. The reduction in the size of the air bubbles is achieved by adding the frother to the solution. The reduction in the surface tension of the solution is associated with a reduction in bubble size (Drzymala 2007).

The aim of the research was to assess the possibility of recovering metals from ground PCBs by means of flotation. For this purpose, the contact angle of various materials was measured and a series of flotation tests was carried out to select the reagent and its dose, the airflow rate through the flotation tank, and the concentration of the feed. The test results were then compared with the results of electrostatic separation (Suponik et al. 2021) and gravity separation (Franke et al. 2021) used for the same feed.

1. Materials and methods

1.1. Material preparation

The surface of printed circuit boards includes many components that do not contain metals or that can cause considerable problems when grinding. These components can be easily dismantled by simple methods – manual and/or mechanical. These components were first manually separated from the PCBs using basic tools such as screwdrivers and pliers. These manually separated components include resistors (which contain: Ni, Cr, Cd, Al, Pb, and Ta), transistors (Pb and Cu), batteries, chips (Pb, Ni, Sn, Ga, Al, and Ag), capacitors (Sn, Cu, and Zn), electromagnetic interference filters (Fe, Cu, and Zn), connectors (Pb, Ni, and Sn), screws and wrenches (Lee et al. 2012). After manual separation, the pre-cleaned PCBs were cut into 4 × 4 cm pieces due to the limitations of the blade mill.

An LMN-100 blade mill by Testchem (Radlin, Poland) with blades mounted on the chamber body and rotator was used for grinding the material. The mill was also equipped with a sieve to determine the size of the ground material. A perforated sieve with a mesh of 1 mm was used to obtain the finest particle sizes suitable for flotation applications. The rotation speed of the mill was 2815 rpm. Liquid nitrogen was used to reduce the temperature of the previously cut PCB parts to a level of cryogenic temperatures (below –150°C) to avoid the formation of conglomerates (solid metal-plastic-ceramic compounds) that could be formed in the chamber during grinding at high temperatures. An overload of the mill was also prevented for this reason and a load of 20 g/min was applied. The cooling process consisted in placing the feed in a container filled with liquid nitrogen. The feed was cooled until the liquid nitrogen ceased to boil. In this way, the temperature increase in the working chamber of the mill was controlled.

The particle size composition of the feed, which was ensured using Frisch sieves, is presented in Table 2. Most of the feed grains were smaller than 0.5 mm (83 wt%). The rest of the feed consisted of grains up to 0.71 mm (13%) and grains 1.4–0.71 mm (4%). Based on microscopic analysis, it was observed that plastic grains mainly consisted of needle-shaped and fibrous grains, with sizes from less than 50 μm (fiber thickness) to 2000 μm. The less numerous plastic grains were patch-shaped with dimensions up to 1000 μm. This kind of grain

Table 2. Particle size distribution of the feed

Tabela 2. Skład ziarnowy nadawy

Grain classes (mm)	1.4–1.0	1.0–0.71	0.71–0.50	0.50–0.36	0.36–0.25	0.25–0.18	0.18–0.13	0.13–0.09	<0.09
Yield (%)	0.4	3.6	13.0	19.5	17.0	10.6	10.8	8.5	16.6

Source: Suponik et al. 2021.

was characteristic for woven fiberglass. The greatest variation in shape was seen in metal grains. The most numerous shapes were globular (mostly 250 to 500 μm), then patch shape (about 30 μm thick and 500 μm wide) and polyhedral and irregular grains (200–350 μm). In the feed, the conglomerate grains (plastic-metal) were also found. The shape of these grains was mainly patch and globular (approx. 150–1000 μm), which had a layer structure characteristic of PCBs.

1.2. Contact angle measurement

The purpose of measuring the contact angle was to assess the effect of the pH value and the type of reagent on the hydrophobic properties of various materials: metals (copper, molybdenum, niobium, steel, titanium alloy) and poly(tetrafluoroethylene) (PTFE), representing plastics. The greater the difference in the contact angle of metals and PTFE, the better the flotation conditions. PCBs contain roughly 65% of fiberglass and over 30% of hydrophobic materials such as PE, PP, PS, epoxy, PVC, PTFE, and nylon (Kumar et al. 2018; Zhang and Forssberg 1997; Kaya 2016). The assessment of the contact angle on the PCB surface prepared with sandpaper (P5000) was impossible due to the instability of the droplet and its absorption by the PCB structure. This may be due to the deterioration of the fiber structure by polishing. Therefore, PTFE was chosen as the material representing plastics.

The contact angle was measured with a Kernco optical goniometer. Before measurement, each surface was first cleaned with ethanol (30 vol.%), then rinsed with distilled water and quickly dried. For more accurate results for each plate, three drops of the respective solution were spotted onto the surfaces and the contact angles of both the right and left sides of each drop were read. The result was obtained by calculating the arithmetic mean of the six obtained values.

Eleven different aqueous solutions and six different materials were used to measure the contact angle. Plates of copper, PTFE, steel, molybdenum, niobium, and titanium alloys were used for the tests. Solutions of specific concentrations were obtained by dissolving the following reagents in tap water: tannic acid (60 mg/dm^3), 2-octanol (450 mg/dm^3), tannic acid (60 mg/dm^3) + 2-octanol (450 mg/dm^3), dimethoxy dipropyleneglycol (450 mg/dm^3), tannic acid (60 mg/dm^3) + dimethoxy dipropyleneglycol (450 mg/dm^3), calcium oleate (60 mg/dm^3), sodium xanthate (60 mg/dm^3). The given reagents were selected based on the articles by Han et al. Ximei et al. and Langa et al. (Han et al. 2018; Ximei et al. 2017; Langa et al. 2014). The pH values of the presented solutions were 7.57, 7.85, 7.60, 7.83, 7.59, 7.81 and 7.85, respectively. The parameters of tap water were as follows: pH 7.75, redox potential 124 mV, conductivity 0.552 mS, total dissolved solids 323 mg/dm^3, and temperature 16.9°C.

Additionally, the impact of the pH value of tap water on the contact angle was measured in the research. The measurements of the contact angle were made for tap water with different pH values: 2, 4, 7.75 (tap water) and 9. Appropriate pH values were obtained by changing the pH of the tap water with sulfuric acid (0.1 M) or sodium hydroxide (0.1 M).

1.3. Flotation experiments

Flotation experiments were carried out using the laboratory Mechanobr flotation machine produced by "IMN Gliwice; Apparatus Construction Plant of the Institute of Non-Ferrous Metals" using a 1-liter flotation tank. In all tests, the PCB samples were first mixed in tap water for five minutes using a magnetic stirrer. They were then transferred to a flotation tank. The sample doses are given in Table 3. After remixing for two minutes in the flotation tank, if the reagent was not added, the airflow was opened and the test was started (see test number 1 in Table 3). In the case of using one reagent (see tests 2, 3, 6–13 in Table 3), after adding the reagent and mixing for two minutes, the airflow was opened and the test was commenced. In cases where two reagents were used (see tests 4, 5 in Table 3), after the addition of the second reagent, the suspension was stirred for two minutes, then the airflow was opened and the experiment was started. In all tests, the speed of the magnetic stirrer, the rotator speed in the flotation tank and the flotation time remained constant at 100 rpm, ca. 400 rpm and five minutes, respectively.

Table 3. Flotation parameters for different test stages

Tabela 3. Parametry flotacji dla poszczególnych etapów badań

Test No.	Reagent	Solids content	Airflow
First stage: reagent selection			
1	without any reagent	25 g/dm^3	200 dm^3/h
2	tannic acid (60 mg/dm^3)	25 g/dm^3	200 dm^3/h
3	dimethoxy dipropyleneglycol (450 mg/dm^3)	25 g/dm^3	200 dm^3/h
4	tannic acid (60 mg/dm^3), dimethoxy dipropyleneglycol (450 mg/dm^3)	25 g/dm^3	200 dm^3/h
5	tannic acid (60 mg/dm^3) + 2 octanol (450 mg/dm^3)	25 g/dm^3	200 dm^3/h
6	2 octanol (450 mg/dm^3)	25 g/dm^3	200 dm^3/h
Second stage: dose selection			
7	dimethoxy dipropyleneglycol (225 mg/dm^3)	25 g/dm^3	200 dm^3/h
8	dimethoxy dipropyleneglycol (157 mg/dm^3)	25 g/dm^3	200 dm^3/h
9	dimethoxy dipropyleneglycol (60 mg/dm^3)	25 g/dm^3	200 dm^3/h
Third stage: airflow selection			
10	dimethoxy dipropyleneglycol (157 mg/dm^3)	25 g/dm^3	400 dm^3/h
11	dimethoxy dipropyleneglycol (157 mg/dm^3)	25 g/dm^3	600 dm^3/h
Fourth stage: selection of solids content			
12	dimethoxy dipropyleneglycol (157 mg/dm^3)	50 g/dm^3	200 dm^3/h
13	dimethoxy dipropyleneglycol (157 mg/dm^3)	100 g/dm^3	200 dm^3/h

Flotation experiments were divided into four stages (Table 3). The first stage was performed in order to find the best reagent using as a reference the collector and frother doses used in the article by Han et al. (Han et al. 2018) and keeping other parameters constant, with the exception of the reagent types. Additionally, one test was performed with the same parameters without the use of any reagents (test No. 1). The aim of the second stage was to find the optimal dose for the reagent selected in stage 1. The third stage was performed to determine the most effective airflow using the type of reagent and the dose selected in stages 1 and 2. In the fourth stage, the amount of feed was increased by maintaining the most efficient airflow at the optimal dose.

1.4. Methods of analysis

The flotation efficiency (purity of the products obtained) was assessed for all four test stages by means of density measurement. This quick analysis was chosen because PCBs contain plastics with a density below 2.0 g/cm^3, one light metal with a density of 2.7 g/cm^3 (Al, usually at low concentrations in PCBs), and heavy metals with a density above 7 g/cm^3, mainly Cu and ferromagnets (Zhang and Forssberg 1997, 1999). Specific density analysis of flotation products was performed with Gay-Lussac pycnometers based on the PN-EN 1097-7:2001 standard with the use of ethyl alcohol with a density of 0.7893 g/cm^3. There were always three density measurements taken and the result was presented as the arithmetic mean.

The products obtained under optimal flotation conditions (i.e. reagent type – dimethoxy dipropyleneglycol at a concentration of 157 mg/dm^3, airflow and feed concentration of 200 dm^3/h and <50 g/dm^3, respectively) were analyzed using the following analytical techniques:

- Energy dispersive X-ray fluorescence (ED/XRF) by means of a ED-XRF Epsilon 4 Spectofotometer (Malvern Panalytical, Malvern, United Kingdom), equipped with a 10 W X-ray tube with an Ag anode, Silicon Drift Detector type and helium flush system;
- microscopic analysis using Zeiss SteREO Discovery Modular Stereo Microscope (Carl Zeiss AG, Jena, Germany).

2. Results and discussion

2.1. Analysis of flotation tests

The results of the contact angle tests for various pH values of tap water and for various aqueous solutions of the reagents used are presented in Tables 4 and 5, respectively. These values provide rough information on the possibility of separating metals from plastics by flotation.

Table 4. Results of the contact angle tests for different pH values of tap water

Tabela 4. Kąt zwilżania dla wody wodociągowej o różnych wartościach pH

pH	The value of the contact angle (in degrees) for					
	Copper	PTFE	Steel	Molybdenum	Niobium	Titanium Alloy
2	78	107	46	54	50	62
4	78	102	42	59	57	61
7.75 (Tap Water)	62	102	51	57	48	58
9	72	100	52	56	49	58

Table 5. Contact angle test results for various aqueous solutions of the reagents used for different materials

Tabela 5. Kąt zwilżania dla roztworów wodnych reagentów otrzymany dla różnych materiałów

Reagent (concentration)	The value of the contact angle (in degrees) for					
	Copper	PTFE	Steel	Molybdenum	Niobium	Titanium Alloy
tannic acid (60 mg/dm^3)	63	101	54	52	64	58
2 octanol (450 mg/dm^3)	42	95	56	59	54	64
tannic acid (60 mg/dm^3) + + 2 octanol (450 mg/dm^3)	43	93	58	58	66	63
dimethoxy dipropyleneglycol (450 mg/dm^3)	48	109	38	55	48	58
tannic acid (60 mg/dm^3) + dimethoxy dipropyleneglycol (450 mg/dm^3)	55	108	42	50	63	57
calcium oleate (60 mg/dm^3)	69	105	64	58	52	51
sodium xanthate (60 mg/dm^3)	71	104	75	56	43	60

Based on the results of the tests presented in Table 4, displaying the effect of the pH value on the wettability of the samples, it can be concluded that for almost all samples, the contact angle decreased with increasing pH. The best conditions for the separation of plastic grains from metals by the flotation method, i.e. with the greatest difference in the contact angle for PTFE and the analyzed metals, occurred at the pH value of 7.75. These studies concerned the flotation process from aqueous solutions without the use of reagents, i.e. for tap water.

The reagent that generated the greatest difference between the contact angles for PTFE and for the tested metals was dimethoxy dipropyleneglycol at a concentration of 450 mg/dm^3 (this also applies to the lack of reagents, i.e. tap water) (see Table 5). However, the selection of the best reagent was based on laboratory flotation tests with the use of a flotation machine.

The results of these tests are presented in Table 6. They confirm that dimethoxy dipropyleneglycol at a concentration of 450 mg/dm^3 was the best of the tested reagents, generating two products: metals and plastics with densities of 5.6 g/cm^3 and 2.9 g/cm^3, respectively (see first stage – test No. 3 in Table 6). The yield of these products was 42.3% and 57.7%, respectively. Regarding the selection of the best dose for dimethoxy dipropyleneglycol and the best airflow, these parameters were 157 mg/dm^3 and 200 dm^3/h, respectively (both for test No. 8 in Table 6). The metal and plastic densities for these process conditions and their

Table 6. Flotation test results

Tabela 6. Wyniki badań flotacji

Test No.	Yield (%)		Density (g/cm^3)	
	Hydrophobic product (plastics)	Hydrophilic product (metals)	Hydrophobic product (plastics)	Hydrophilic product (metals)
First stage: reagent selection				
1	32.80	67.20	2.9	5.4
2	0.83	99.17	*	4.7
3	57.71	42.29	2.9	5.6
4	19.25	80.75	2.7	4.8
5	16.39	83.61	2.8	4.3
6	53.20	46.80	2.9	5.0
Second stage: dose selection				
3	57.71	42.29	2.9	5.6
7	52.85	47.15	2.8	6.8
8	56.56	43.44	2.7	7.4
9	54.98	45.02	3.0	6.4
Third stage: airflow selection				
8	56.56	43.44	2.7	7.4
10	56.68	43.32	2.9	6.4
11	53.25	46.75	3.1	6.6
Fourth stage: selection of feed concentration				
8	56.56	43.44	2.7	7.4
12	55.08	44.92	2.7	7.2
13	53.92	46.08	2.5	5.4

* No results due to lack of product.

yields were 7.4 g/cm^3, 2.7 g/cm^3, and 43.4 and 56.6%, respectively (second and third stages in Table 6 test No. 8). Based on the research carried out in stage 4, it can be concluded that the flotation efficiency decreases with increasing feed concentration, and is acceptable at the level of 50 g/dm^3. Under these conditions, the metal density decreases from 7.4 g/cm^3 (for feed concentration = 25g/dm^3) to 7.2 g/cm^3. The product yield is very similar, ranging from 43.4% to 44.9%.

2.2. Analysis of products for optimal flotation conditions

The microscopic analysis showed that the hydrophobic product (float fraction) obtained in test No. 8 (see Figure 1a) mainly comprised grains consisting of plastic-ceramic materials of a fibrous and needle shape (< 1100 μm; fiber thickness approx. 150 μm), and less often patch-shaped grains (diameter < 600 μm) with a characteristic PCB composite structure. Individual patch-shaped metal grains with a diameter of up to 230 μm were also observed. Penetration of these grains into the float fraction may be due to their entrapment inside a plastic powder. Moreover, no larger metal grains were found in the float fraction, which may indicate the high purity of this product. The hydrophilic product obtained in test 8 (see Figure 1b) consisted mainly of metal grains of various shapes and sizes, with a fairly large number of plastic-ceramic grains with a specific layered structure. Most of the metals were patch-shaped grains with a diameter of 300 to 700 μm and irregular grains of similar dimensions. Globular grains (diameters from 600 to 800 μm) and polyhedral grains (< 1500 μm; transverse dimensions < 150 μm) were found in smaller numbers. The grains consisting of plastic-ceramic materials visible in the sink fraction were mostly in the patch shape (diameter from 800 to 1000 μm) and, very rarely, the shape of a fiber with a length of 1500 μm and

a) b)

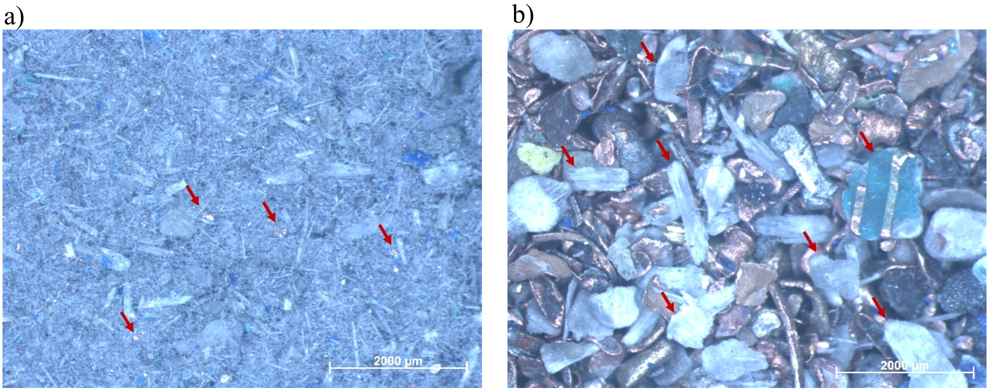

Fig. 1. Microscopic images of a) hydrophobic products (plastics) and b) hydrophilic products (metals) taken for test No. 8 (examples of impurities marked with a red arrow)

Rys. 1. Zdjęcia mikroskopowe: a) produkt górny (produkt hydrofobowy) i b) produkt dolny (hydrofilowy) dla testu nr 8 (zanieczyszczenia oznaczone czerwonym kolorem) a transverse dimension of up to 300 µm. Moreover, grains of metal-plastic conglomerates (800 µm to 1200 µm in diameter) with a layered structure characteristic of PCBs were observed. The penetration of grains consisting of plastic-ceramic materials and metal-plastic conglomerates into the hydrophilic product was undesirable due to the deterioration of the purity of the concentrate. This was probably due to the large size of these grains. This demonstrates the need to improve the grinding in the knife mill. In the case of electrostatic separation, these products went to the middlings.

To evaluate the efficiency of flotation performed for the best option (test No. 8), a chemical composition analysis was carried out using the ED/XRF method (Table 7). The float fraction contained mainly non-valuable elements (29.82%), which are mostly concentrated

Table 7. Chemical composition of the products obtained using Dimethoxy dipropyleneglycol 157 mg/dm^3 (test No. 8)

Tabela 7. Skład chemiczny produktu otrzymanego przy zastosowaniu eteru dimetylowego glikolu dipropylenowego 157 mg/dm^3 (test nr 8)

	Element	Hydrophobic product	Hydrophilic product	Recovery ratio (%)
Valuable elements	Cu	2.33	39.94	93%
	Al	1.71	1.10	33%
	Zn	0.69	0.92	51%
	Ni	0.34	0.64	59%
	Fe	0.49	0.97	60%
	Sn	1.12	7.80	84%
	Cr	0.31	0.05	11%
	Ti	0.52	0.49	42%
	Ag	0.0918	0.5797	83%
	Au	0.0048	0.0140	69%
	Sum	8.01	53.13	84%
Non-valuable elements	Sb	10.40	0.09	–
	Ca	2.89	3.24	–
	Br	0.69	2.16	–
	Ba	0.0065	0.73	–
	Si	15.84	5.02	–
	Mn	0.0014	0.0083	–
	Sum	29.82	11.29	–

in epoxy resins, glass fabrics and flame retardants (Kumar et al. 2018; Muniyandi et al. 2014). The most numerous were Si (15.84%), Sb (10.40%) and Ca (2.89%). About 8% of valuable metals such as Cu (2.33%), Al (1.71%), and Sn (1.12%) were identified in this product. Considering that metals such as Cu and Sn impact the PCB value, their penetration into the float fraction was unfavorable.

53.13% of valuable metals were identified in the chemical composition of the hydrophilic product, mostly Cu (39.91%), Sn (7.80%), and Al (1.10%), and in smaller amounts, Zn, Ti, Cr, Fe and Ni. Significant amounts of precious metals such as Ag (0.5797%) and Au (0.0240%) were also identified in this product. In addition to valuable metals, over 11% of impurities (non-valuable elements) were found in it. The largest share was comprised of Si (5.02%), Ca (3.24%) and, in smaller amounts, Br, Ba, Sb, and Mn. As can be seen from microscopic and ED/XRF analysis, the sink fraction was significantly contaminated with materials from the non-metallic parts of the PCB composite.

The same feed as the one used for flotation has been used for electrostatic separation (Suponik et al. 2021) and gravity separation (Franke et al. 2021). Compared to the above methods of recovering metals from PCBs, flotation is not the most efficient process due to the impurities in both products and their yields. The penetration of the metal grains into the hydrophobic product may be caused by the patch shape of the grains, which tend to float. It mostly concerns Ag grains, but due to the presence of thin tracks in PCBs, it is also true of Cu grains (Allan and Woodcock 2001). This problem was also noticed in the work of Ogunniya and Vermaak (Ogunniya and Vermaak 2009), and is difficult to correct due to the kinetics of the flotation process. The purity of the hydrophobic product is important due to the minimization of metal losses and the production of composites (Mrówka et al. 2021) or concrete (Mohammed and Hama 2022) with specific properties from the obtained plastics.

The presence of significant amounts of fiberglass grains in the hydrophilic product may be due to their large dimensions (above 800 μm). These grains, given their weight, may not have floated to the surface of the tank and may have remained at the bottom of the tank, or been in suspension, despite the fact that fiberglass is hydrophobic (Gallegos-Acevedo et al. 2014). It is therefore necessary to optimize the grinding process to obtain even smaller grains and thus to reduce the amount of impurities in the hydrophilic product. However, much higher efficiency and product purities were obtained, for the same feed, in the case of electrostatic separation.

The recovery ratio (Figure 2) is relatively high for the most valuable metals occurring in PCBs. The highest ratio was obtained for Cu, Sn, Ag, and Au, which amounted to 93%, 84%, 83%, and 69%, respectively. In the work of Han et al. 2018, a similarly high level of copper recovery (90.5%) was achieved, using tannic acid and 2-octanol as flotation reagents. However, in the studies by Ogunniya and Vermaak (Ogunniya and Vermaak 2009), in which no flotation reagents were used, the recovery of Cu was 66%. In this case, such a large loss of this metal can make recovery unprofitable. Therefore, reagents are needed to separate the metals from PCBs by flotation.

The greatest losses of metals (Figure 2) were recorded for Cr, Al, and Ti: 89%, 77% and 58%, respectively. The low Cr recovery may have resulted from the formation of chromium compounds such as nitrides, carbides and oxides in the production process, and thus physicochemical changes, including density (Lynn Davis et al. 1992). On the other hand, in the case of Al and Ti, the grains could be lifted due to their relatively low specific density.

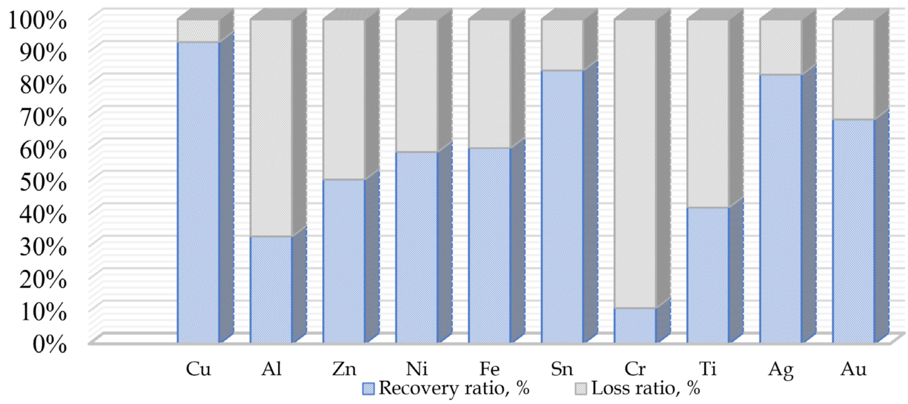

Fig. 2. Recovery and loss ratio for test No. 8

Rys. 2. Wskaźniki odzysku i strat dla testu nr 8

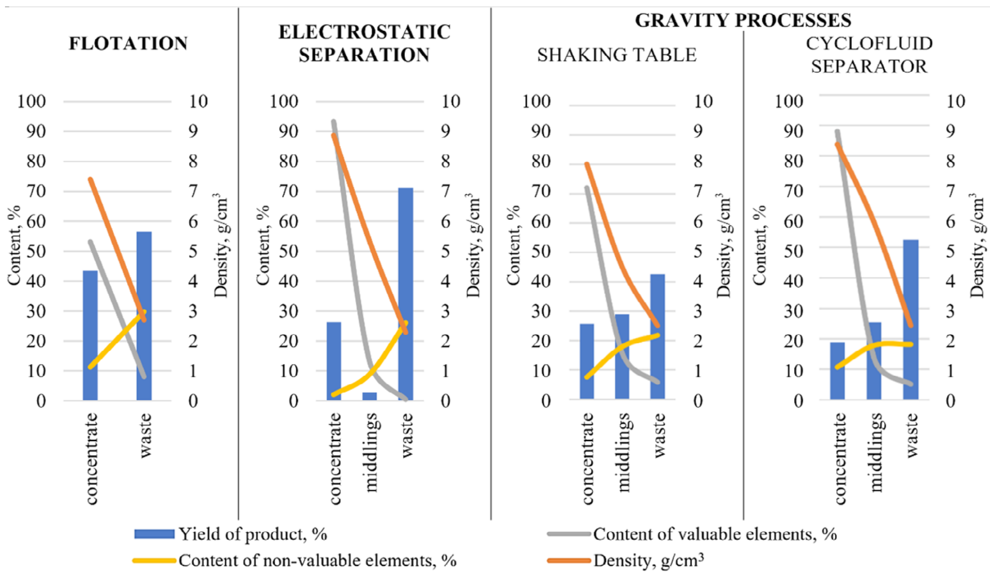

Fig. 3. Yield of separation products as a function of their density and quality parameters (Suponik et al. 2021; Franke et al. 2021)

Rys. 3. Udział produktów separacji w funkcji ich gęstości i parametrów jakościowych

Due to the low values of these metals, their loss should not significantly affect the profitability of the recovery process. New goods generated from the hydrophobic product, due to its content of chromium, should be analyzed in terms of their impact on the environment.

The use of flotation to recover metals from PCBs was an inefficient process compared to electrostatic separation. In this process, the best separation of the metallic product (concentrate) from plastics was obtained (Figure 3). The yield of this product was 26.2%wt., and had the highest amount of valuable elements (above 93.3%, mainly 68.5% Cu, 11.5% Sn, 1074 ppm Ag and 92 ppm Au), and furthermore, it had the lowest amount of impurities (less than 3%). In this method, the yield of plastics product was 71%wt. and had 0.54% valuable elements (mainly Cu). In the case of electrostatic separation, 2.8%wt. middlings were obtained, which mainly consisted of conglomerate grains (plastic-metal) (Suponik et al. 2021). The products obtained by the method of gravity separation were of lower quality. Through use of a shaking table, the following products was obtained: 25.7%wt. metals product (72% valuable elements, mainly 59.2% Cu, 6.3% Sn, 2160 ppm Ag and 72 ppm Au; 8.35% impurities), 28.9%wt. middlings (9.5% Cu), and 45.4%wt. plastics product (5.8% of valuable elements, mainly Cu). The products obtained using a cyclofluid separator were similar to those obtained from the shaking table (Franke et al. 2021).

Conclusions

As a result of the research, optimal conditions were obtained for the flotation process in which the process of metal-plastic separation from ground PCBs achieved the highest efficiency.

This was achieved with the combination of solids content <50 g/dm^3 with the airflow of 200 dm^3/h, and using dimethoxy dipropyleneglycol at a concentration of 157 mg/dm^3. The hydrophilic product thus obtained consisted mainly of copper (39.9%), tin (7.8%), and trace amounts of silver (0.5797%) and gold (0.024%). In addition to valuable elements, over 11% of contaminants were also identified, making the product significantly contaminated.

The flotation efficiency might possibly be improved by using different flotation parameters and the particle composition of the feed. The fact that the measured contact angle given in the material methodology is correlated with flotation efficiency may be helpful in finding better process conditions. The main concern for low efficiency could be the degree of milling and the strongly heterogeneous feed due to various particle size and shapes (from dozens μm to even 2 mm).

As compared to the other methods (specifically, electrostatic separation, gravity separation with the use of a concentration table, and a cyclofluid separator), the hydrophilic product obtained as a result of optimization of the flotation process was characterized by the lowest content of valuable metals and the highest level of contamination. In addition, this process was also associated with a number of other disadvantages, such as:

- relatively high negative impact on the environment caused by high water consumption and the use of chemical reagents,

- higher energy consumption of the process than dry methods resulting from the need to use additional devices for filtration and drying of the obtained products and compressed air installations,
- significant additional workload due to the number of devices used in the process.

In conclusion, the use of a flotation process to recover metals from ground PCBs is possible; however, it is not economically or environmentally viable. Much better results were obtained for the same feed using an electrostatic separator, which is characterized by a higher reliability, its predominantly low energy consumption and environmental impact, as well as its low costs.

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EVALUATION OF THE USE OF FLOTATION FOR THE SEPARATION OF GROUND PRINTED CIRCUIT BOARDS

Keywords

printed circuit boards, recycling, flotation, recovery, metals

Abstract

The paper presents an assessment of flotation efficiency in the separation of plastics from metals derived from printed circuit boards (PCBs). The PCBs were ground in a knife mill prior to flotation. The contact angles of various materials corresponding to the grains from ground PCBs were measured, and a series of flotation tests was carried out to obtain the best product. The impact of the following parameters were investigated: the reagent and its dose, the airflow rate through the flotation tank and the feed concentration. The highest efficiency of metal recovery from PCBs was achieved for Dimethoxy dipropyleneglycol at a concentration of 157 mg/dm^3 and with an airflow of 200 dm^3/h and a feed concentration of <50 g/dm^3. In the hydrophilic product (concentrate), it was mainly Cu (40%) and Sn (7.8%) that were identified by means of XRF, but there were also trace amounts of precious metals such as Au (0.024%), Ag (0.5797%) and Pd (149 ppm). Impurities in the form of Si (5%), Ca (3.2) and Br (2.1) were also identified in this product. Small amounts of metals in their metallic form were identified in the hydrophobic product (waste), mainly Cu (2.3), Al (1.7) and Sn (1.1). As a result of the research, high recovery ratios were obtained for Cu (93%), Sn (84), Ag (83) and Au (69). The purity of obtained metal concentrate with this method was lower in comparison with the other methods of the recovery of metals from ground PCBs for the same feed, i.e. electrostatic or gravity separation. Also considering other factors such as the environmental impact of the flotation process, the number of facilities and their energy consumption, this process should not be used in the developed metal recovery technology. Using electrostatic separation for the same feed obtained much better results.

OCENA ZASTOSOWANIA FLOTACJI W ODZYSKU METALI Z ROZDROBNIONYCH PŁYT OBWODÓW DRUKOWANYCH

Słowa kluczowe

płyty obwodów drukowanych, recykling, flotacja, odzysk, metale

Streszczenie

W artykule przedstawiono ocenę zastosowania flotacji do rozdziału metali od tworzyw sztucznych z rozdrobnionych w młynie nożowym płyt obwodów drukowanych (PCBs). Zmierzono kąty zwilżania różnych materiałów odpowiadających ziarnom zmielonych PCBs oraz określono wypływy odczynników i ich stężeń, wydatków powietrza oraz zagęszczenia materiału na sprawność procesu flotacji. Najwyższą sprawność odzysku metali z PCBs uzyskano przy zastosowaniu eteru dimetylowego glikolu dipropylenowego w stężeniu 157 mg/dm^3, wydatku powietrza 200 dm^3/h i zagęszczeniu materiału poniżej 50 g/dm^3. W produkcie hydrofilowym (metalach), wykorzystując metodę XRF, zidentyfikowano głównie Cu (40%) i Sn (7,8%) oraz śladowe ilości metali szlachetnych takich jak Au (0,024%), Ag (0,5797%) i Pd (0,015%). W produkcie tym rozpoznano również zanieczyszczenia takie jak Si (5%), Ca (3,2%) i Br (2,1%). W produkcie hydrofobowym (tworzywach sztucznych) występowały nieznaczne ilości metali, głównie były to Cu (2,3%), Al (1,7%) i Sn (1,1%). W wyniku przeprowadzonych badań uzyskano wysokie wskaźniki odzysku dla Cu (93%), Sn (84%), Ag (83%) i Au (69%). Niemniej jednak, w porównaniu do separacji elektrostatycznej, która była prowadzona dla tej samej nadawy, czystość produktów uzyskanych za pomocą flotacji była mniejsza. Biorąc pod uwagę również inne czynniki, między innymi takie jak oddziaływanie procesu flotacji na środowisko naturalne, ilość urządzeń oraz ich energochłonność, stwierdzono w konkluzji artykułu, że proces ten nie powinien być stosowany w tworzonej technologii odzysku metali z PCBs. Znacznie lepsze efekty rozdziału uzyskano bowiem dla tej samej nadawy, stosując proces separacji elektrostatyczny, który ma niewielki wpływ na środowisko przyrodnicze, a powstające produkty mogą być w pełni wykorzystywane.