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De-coppering of Metallurgical Slag Using Printed Circuit Boards as a Reducer

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Abstract

In the publication of the results of laboratory tests for decoppering metallurgical slag using a variable addition of "LOW GRADE" PCB scrap as a reducer (dates from 10 to 30% of the slag mass). In practical devices, as well as research on decoppering metallurgical slag using coke - a currently used reducer. The tests involved four measurement series differing in the source of the reducer and the variable process involved. The process was carried out at temperatures of 1350 and 1450°C. Two measurements were taken for each variant analysed.

The conducted research showed the possibility of effective use of printed circuit board scrap in the slag decoppering process. An additional advantage of its use was the introduction of an additional charge of copper into the process at an average level of 10% by mass, which was recovered during the process in the form of a metal alloy. The metal alloy formed during the slag reduction process acted as a collector for the copper contained in the PCB scrap.

Research has shown that as the amount of reducer in the form of PCB scrap increases, the final Cu content in the slag after reduction increases. The highest average degree of slag decopperization was achieved when 10% of PCB scrap was added to the reduction. At the analyzed temperatures it ranged from 95.2 to 97.5%. When coke was used as a reducing agent at a temperature of 1350°C, the average degree of slag decopperization was from about 60 (2 h) to about 75.5% (4 h). Increasing the process temperature to 1450°C resulted in a significant increase in the slag decopperization rate, above 97%, regardless of the process duration.

Keywords: Printed circuit boards, Reduction process, Slag, Recycling

1. Introduction

Coking coal has been included in the EU's list of critical raw materials in 2014, 2017, and 2020 [1, 2]. Like other raw materials on the list, it is of strategic importance for the functioning and economic development of the European Union, and its deficit could have serious economic consequences for the entire European economy. The European Union currently imports about 75% of the coking coal it consumes from countries such as Australia, the United States, Canada, Russia, and Mozambique [3, 4]. Only about 25% of the annual demand for coking coal comes from EU countries, namely Poland and the Czech Republic, which are the only producers of this critical raw material. The European Commission has also recognized this raw material as a material that plays a key role in the process of transforming the steel industry into a climate-neutral economy [5, 6].

Coking coal is a fundamental raw material for coke production, which serves as both a fuel and a reducing agent in metallurgical processes for iron and steelmaking, as well as non-ferrous metal production [1, 7-9].

An analysis of global coal resources reveals a trend, particularly in coking coal mining, towards increasing the number of extraction sites and production levels in regions outside the EU [10]. This necessitates a heightened commitment from EU member states to explore new coking coal deposits and identify alternative materials that can function as reducing agents in metal production processes. Achieving positive outcomes in these endeavors would enable the EU to mitigate the risk of becoming almost entirely dependent on imports of this raw material.

Printed circuit boards (PCBs) could serve as an alternative to the metallurgical coke currently used in metallurgical processes [11, 12].

The growing demand for electrical and electronic devices, driven by technological advancements in Poland, Europe, and globally, has led to a substantial increase in electronic waste. This waste stream, identified as one of the fastest-growing globally by the United Nations Institute for Training and Research, reached 53.7 million metric tons in 2019 [13]. With each person contributing an average of 7.3 kilograms of e-waste, the need for effective recycling solutions is more urgent than ever. Projections suggest that by 2030, global e-waste generation could exceed 82 million metric tons [13].

Global trends in e-waste generation are reflected in the European Union, where electro-waste represents the fastest growing waste stream, of which less than 40% is recycled [14, 15]. The European Union's efforts to achieve a circular economy and a climate-neutral economy place particular emphasis on extending the life cycle of products by recycling existing materials and products. The European Commission's strategy identifies seven key areas necessary to achieve a circular economy. Among these areas is e-waste. Thus, due to the growing stream of e-waste, EU countries are obliged to achieve the recycling levels imposed by the European Commission. This creates the need to develop existing recycling technologies and to search for new alternative methods of processing WEEE, including PCB scrap.

What is e-waste?

Electro-waste, or waste electrical and electronic equipment, means end-of-life, broken or obsolete electrical and electronic equipment, household appliances, computers, etc., in other words any device that requires electricity or batteries to operate. - In other words, any device that requires electricity or batteries to operate. The following groups of WEEE are distinguished according to their use:

- Large household appliances e.g.: fridges, refrigerators, dishwashers,
- Small household appliances e.g. irons, hoovers, mixers,
- ICT equipment e.g.: computers, printers, telephones,
- RTV equipment e.g.: televisions, camcorders,
- Lighting equipment e.g.: fluorescent lamps, chandeliers,
- Electrical and electronic tools e.g.: drills, saws,
- Toys, leisure and sports equipment e.g.: electric trains, token machines.

Printed circuit boards as a specific type of e-waste.

Printed circuit boards (PCBs) are an essential component used in the production of various types of electrical and electronic systems. WEEE waste contains approximately 3 to 5 % by weight of PCBs [16]. In addition to the organic fraction and ceramics, PCBs contain valuable useful metals such as copper, silver and gold. An example of the elemental composition of PCBs according to literature data is presented in Table 1 [17-20].

Their varying chemical composition is mainly due to their use, construction or the number of layers the board is made of.

Table 1.
Approximate elemental composition of printed circuit boards according to literature data [17 - 20].

Metals	Unit	Average metals content			
		[7]	[8]	[9]	[10]
Cu	[% mas.]	30,57	25,06	26	19
Al		11,69	4,65	3,2	4,01
Fe		15,21	0,66	3,4	1,13
Sn		7,36	1,86	4,9	0,69
Ni		1,58	0,0024	1,5	0,17
Zn		1,86	0,4	2,6	0,84
Pb		6,7	0,8	3	0,39
Mn		-	-	0,11	0,04
Sb		-	-	0,16	0,37
Au	[ppm]	238	-	-	130
Ag		588	-	-	704

Among collectors and recyclers of electronic equipment, the most common division is that of circuit boards according to their content of valuable useful metals [21, 22]. Depending on their gold content, three types of groups are distinguished [21, 22]:

- Low grade - with a gold content of up to 50-70 ppm, e.g. plates from domestic appliances (large and small), air-conditioners, refrigerators or dishwashers,
- Medium grade - with gold content ranging from 50÷70 to 120 ppm, e.g. boards from various types of old computers and servers (grade 1; 1a; 1b); boards from printers, decoders and entertainment electronics (grade 2); boards from TV sets, monitors and power supplies (grade 3), as well as parts of printed circuit boards and production discards (dismantled PCBs and frames),
- High grade - with a gold content of more than 120 ppm e.g.: RAM, plug-in cards, most connectors, hard drives, integrated circuits and processors, as well as mobile phone boards.

After decommissioning, PCBs form polymetallic waste with a high plastic content, so-called WEEE, which contains valuable useful metals that play an important role in the technological transformation process.

Recycling methods for scrap printed circuit boards.

Among the currently used PCB recycling methods, the following processing technologies are used [23, 24]:

- Pyrometallurgical,
- Hydrometallurgical,
- Mechanical.

In pyrometallurgical technologies, the processing of this type of material is mainly limited by the content of useful metals and the method of disposal of process gases containing significant amounts of hydrocarbons. PCB scrap is introduced into the copper production process line, where the main copper-bearing product obtained acts as a collector for the precious metals contained in PCBs.

Hydrometallurgical methods mainly involve processes of leaching solid electronic waste with acid or leach. The resulting leaching solutions are subjected to separation and purification (solvent extraction, adsorption and ion exchange).

The mechanical processing technology consists of mechanically reducing the wafers into polymetallic pellets and then using a series of separation processes to recover the metals they contain [25]. The resulting metallic fraction is then remelted into an ingot or anode directed to the electrorefining process [25].

The current state of knowledge on the course of reduction reactions in metallurgical processes in the liquid - gas phase system, indicates that the mass transport of reactants in both the gas and liquid phases is the rate-limiting step in the process. The reduced metal, in the case of a difference in the densities of the resulting phases, may sediment [26]. In order to intensify the mass transport of the components of the system, it is necessary to set it in motion by, among other things, stirring the liquid phase. The movement of the liquid phase also promotes coagulation and sedimentation of the de-reduced metal [26].

Intensification of mixing can be realised, among other things, by a material that will generate a significant amount of gases during the thermal process. Such a role can be played by plastics contained in PCB scrap, of which hydrocarbons are an important component [11].

From the available literature [11], it can be concluded that it is possible to use this type of material for the reduction process of metallurgical slag. Positive results have already been achieved at 1300°C. This publication presents the results of a study of a metallurgical slag de-slagging process using PCB scrap as a reductant, thus extending the temperature range of the process to temperatures of 1350 and 1450°C. 'LOW GRADE' type PCB scrap from Tesla Recycling Sp. z o.o. was used as the reducing material. For comparative purposes, tests were also carried out on the reduction of metallurgical slag using metallurgical coke - a reductant currently used in metallurgical processes.

2. Research methodology

The decopperization process of metallurgical slag was investigated in a laboratory-scale, high-temperature, resistance chamber furnace with a chamber size of 220 x 300 x 350 mm. The furnace operates within a temperature range of 100 to 1600°C and has a heating capacity of 22 kW. A schematic diagram of the laboratory chamber furnace used in the experiments is presented in Figure 1.

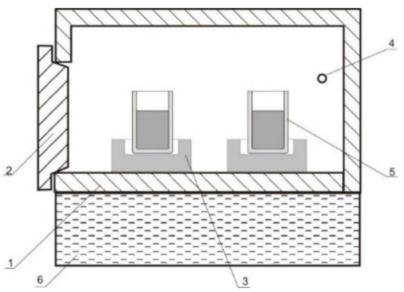

Fig. 1. Schematic of a high-temperature resistance chamber furnace. 1 - resistance furnace, 2 - furnace door, 3 - ceramic stand, 4 - thermocouple, 5 - measurement crucible, 6 - power supply system

For the reduction tests, metallurgical slag containing 9.58% by weight of copper was used. The copper content in the slag was determined using the X-ray fluorescence method using the Axios mAX wavelength dispersive spectrometer. As a reducing agent, "LOW GRADE" PCB scrap (Figure 2), supplied by Tesla Recykling Sp. z o.o., with a fraction size of 28 mm and an average copper content of 10.0% by weight, was used, as well as metallurgical coke.

Fig. 2. LOW GRADE PCB scrap of 28 mm fraction size

In order to obtain as homogeneous a reduction material as possible, the PCB scrap was first subjected to a two-stage shredding process to obtain a 4.5 mm fraction in the first stage, followed by a final fraction of ≤2 mm (Figure 3). The shredding process was carried out using a MOCO slow-shaft shredder (stage I) and a RETSCH SM 300 knife mill (stage II).

Fig. 3. PCB fraction used in slag decopperization studies

In the reduction process, a variable amount of PCB scrap was used as a reducing agent, ranging from 10 to 30% of the slag mass, with a 5% addition of coke as a reference measurement. The slag mass in the experiments was 200 g, and the weighing accuracy of the feed materials and the process products was 0.01 g. The conducted studies included four series of measurements, differing in the type and mass of the reducing agent used:

- Series I - 10% by mass addition of "LOW GRADE" PCB scrap,
- Series II - 20% by mass addition of "LOW GRADE" PCB scrap,

- Series III - 30% by mass addition of "LOW GRADE" PCB scrap,
- Series IV - 5% by mass addition of coke.

A total of 48 melts were carried out, six for each measurement series within the analyzed temperature range. Melts within each measurement series were conducted at temperatures of 1350 and 1450°C for durations of 2, 3, and 4 hours. The furnace heating rate was 10°C/min. After reaching the set temperature, the specified process time was measured. Heating and reduction time control were performed automatically using a Shimaden FP93 programmable PID controller. After cooling the furnace, the crucible was removed and then broken to separate the process products, i.e., metal and slag. The resulting solid products of the melt were subsequently weighed, and samples were taken. After appropriate preparation, these samples were sent for chemical analysis. The copper content in the slag samples was determined using X-ray fluorescence.

3. Results

The average results of the two measurements obtained during the copper removal process from metallurgical slag using PCB scrap and coke are presented in Tables 2 (1350°C) and 3 (1450°C). These tables contain basic data on the experiments, such as: reduction process time, average amount of slag and alloy formed, and the average copper content in the slag after the reduction process.

Table 2.
Results of slag reduction process at 1350°C

Series Name		Process Time	Average Amount of Slag Produced,	Average Amount of Alloy Formed	Average Cu Content in Slag after Reduction
		[h]	[g]		[wt. %]
SERIES I	PCB LG wt. 10%	2	165,65	38,76	0,46
		3	164,55	40,57	0,26
		4	164,92	40,07	0,35
SERIES II	PCB LG wt. 20%	2	165,57	47,49	0,63
		3	164,69	47,89	0,23
		4	163,72	49,11	0,70
SERIES III	PCB LG wt. 30%	2	172,90	48,47	1,80
		3	168,60	51,07	0,80
		4	173,05	51,93	0,74
SERIES IV	COKE wt. 5%	2	178,06	15,33	3,86
		3	175,73	16,36	2,95
		4	172,85	19,46	2,35

Table 3.
Results of slag reduction process at 1450°C

Series Name		Process Time	Average Amount of Slag Produced,	Average Amount of Alloy Formed	Average Cu Content in Slag after Reduction
		[h]	[g]		[wt. %]
SERIES I	PCB LG wt. 10%	2	163,03	39,11	0,26
		3	168,54	35,52	0,42
		4	163,54	39,20	0,24
SERIES II	PCB LG wt. 20%	2	152,28	52,84	0,16
		3	159,21	50,76	0,29
		4	156,37	52,83	0,20
SERIES III	PCB LG wt. 30%	2	152,52	60,87	0,32
		3	150,17	64,96	0,23
		4	152,29	64,78	0,27
SERIES IV	COKE wt. 5%	2	142,94	39,90	0,15
		3	139,26	42,91	0,21
		4	141,82	40,89	0,28

The average degree of copper removal from the metallurgical slag, using the applied reducing agents, was calculated based on the average product masses and chemical analyses (Tables 2-3). The calculation was performed using the following formula:

$$S_{Cuśr.} = (\%Cu_{ż0} - \%Cu_{żk})/\%Cu_{ż0} \times 100\ [\%] \quad (1)$$

gdzie:
$\%Cu_{ż0}$ – initial copper content of metallurgical slag,
$\%Cu_{żk}$ – Cu content of slag after reduction.
The results of these calculations are shown in Figures 4 – 7.

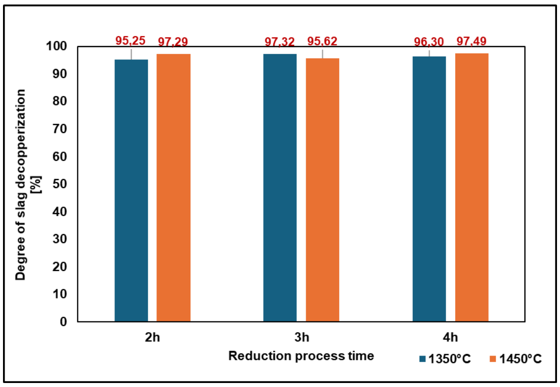

Fig. 4. Average degree of slag decopperization using a 10% addition of PCB scrap to the reduction process

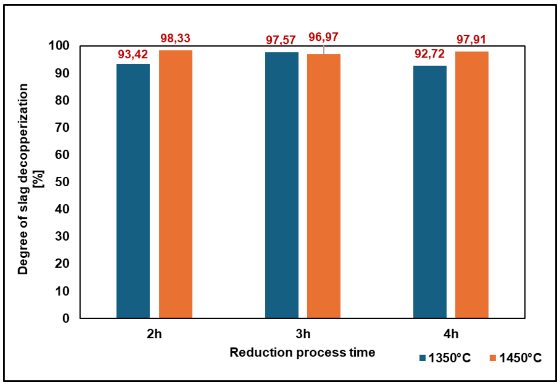

Fig. 5. Average degree of slag decopperization using a 20% addition of PCB scrap to the reduction process

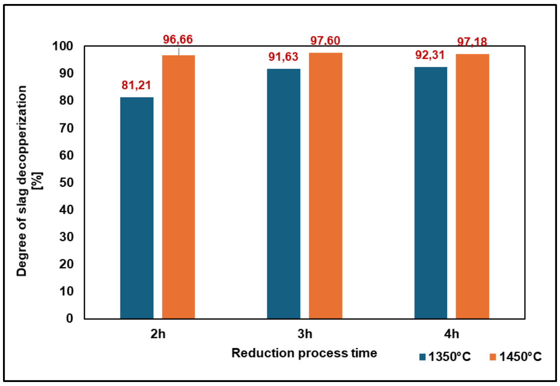

Fig. 6. Average degree of slag decopperization using a 30% addition of PCB scrap to the reduction process

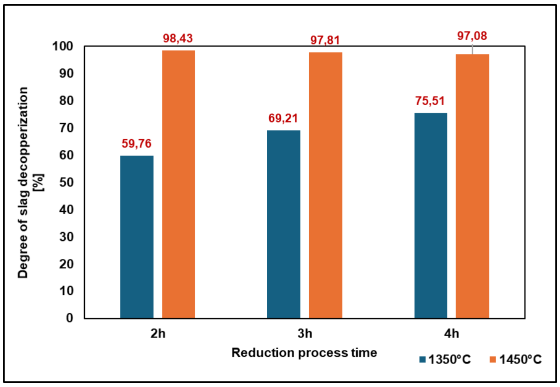

Fig. 7. Average degree of slag decopperization using a 5% addition of coke to the reduction process

The results presented in Tables 2 and 3 demonstrate the influence of time and temperature on the final copper content in metallurgical slag. Regardless of the process duration and temperature, with the addition of 10% PCB scrap for reduction, a final copper content in the slag below 0.5% by mass was achieved. Increasing the temperature to 1450°C for all analyzed series, regardless of the amount, type, and duration of the process, led to a final copper content in the slag below 0.5% by mass. Increasing the addition of PCB scrap for reduction does not positively affect the quality of the results obtained. The results obtained at 1350°C show that as the addition of PCB scrap for reduction increases, the final copper content in the slag after the process increases. However, this content decreases with increasing process time.

4. Conclusions

The conducted research demonstrated the possibility of effectively utilizing printed circuit board scrap in the copper removal process from slag. An additional advantage of its application was the introduction of an additional copper charge at an average level of 10% by mass, which was recovered during the process in the form of a metallic alloy. The metallic alloy formed during the slag reduction process acted as a collector for the copper contained in the PCB scrap.

An analysis of the obtained results indicates that in the applied static system, the use of PCB scrap for reduction at 1350°C allowed for lower copper contents in the slag after reduction compared to coke. This is primarily due to the specific chemical composition of PCB scrap, which contains a significant amount of hydrocarbons that intensify the mixing of the slag during reduction.

The studies showed that as the amount of PCB scrap as a reducing agent increased, the final copper content in the slag after reduction also increased. The highest average degree of copper removal from the slag was achieved with the addition of 10% PCB scrap for reduction. In the analyzed temperatures, it ranged from 95.2 to 97.5%. When coke was used as a reducing agent at a temperature of 1350°C, the average degree of copper removal from the slag ranged from about 60% (2 hours) to about 75.5% (4 hours). Increasing the process temperature to 1450°C resulted in a significant increase in the degree of copper removal from the slag to above 97%, regardless of the process duration.

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