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The Use of Coffee Waste in the Reduction of Metallurgical Slags

T. Matuła [a,] *, Ł. Kortyka [b], Ł. Myćka [b], J. Łabaj [a], T. Wojtal [a]
[a] Silesian University of Technology, Faculty of Materials Engineering,
Krasińskiego 8, 40-019 Katowice, Poland
[b] Łukasiewicz Research Network - Institute of Non-Ferrous Metals
Sowińskiego 5, 44-100 Gliwice, Poland
* Corresponding author. E-mail address: tomasz.matula@polsl.pl

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Abstract

Coffee is grown in over 50 countries around the world, and its sale is the largest in the world trade after crude oil. In the case of coffee beans, after consumption remains a solid waste in the form of a waste plant extract. At present, coffee waste is not fully managed, which means that it is often deposited in landfills. Taking into account their availability on the market and the content of significant amounts of carbon in them, it was proposed to use them as a reducing agent in the processing of copper slags. The use of Solid Coffee Grounds (SCG) as an alternative reducing agent for coke and coke breeze can be beneficial in two aspects. The first is the reduction of carbon dioxide emissions in the process, and the second is due to the possible release of hydrocarbons from these wastes at high temperatures, which, apart from participating in the reduction process itself, causes also mixing of the bath in the melting unit, which facilitates the process of copper sedimentation in the slag. The experiments carried out on a laboratory scale showed the possibility of reducing the copper content in the slag after the reduction process from 10.3 to 0.41 % by mass. The obtained values of the relative degree of copper splashing for all experiments ranged from 88.4 to 96.0 %. The presented solution is an innovative approach to the use of SCG in the processing of copper slags.

Keywords: Solid coffee grounds, Reduction, Copper slag, Calorimeter

1. Introduction

Coffee is one of those drinks with a very high daily consumption. Annual coffee production in the last decade has a growing tendency, and so in 2010/2011 it amounted to 140,076,000 pieces of 60 kg bags and in the years 2021/2022 the amount was 167,500,000 bags. (Fig. 1). It is assumed that about 15 million cups of coffee are consumed in the world every week, which is associated with the generation of 175,000 Mg of waste. Unfortunately, most of them end up in landfills, and only a small percentage is used.

In Poland, 94.4 million kg of coffee were sold in 2019, worth 4.03 billion PLN. In terms of coffee consumption, Poland ranks on 11th place in the world, and the average Pole drinks approx. 95 litres of coffee per year (approx. 2.5 kg of beans) [1].

The chemical composition of coffee is varied. Both before and after the grain firing process, they contain: folic acid, vitamin E and B vitamins. Minerals account for about 4 % of the grain composition. Coffee mainly contains: magnesium, phosphorus, calcium and potassium. In smaller amounts there are: iron, sodium, nickel, zinc, copper, cobalt, chromium, fluorine and iodine. Raw coffee, before roasting, contains: proteins, carbohydrates and significant amounts of sugar. The former are about 13 % and are decomposed during the grain burning process. The sugar content is on average about 40 %. The sugar compounds remain in the form of solids - waste during the preparation of a coffee drink. Heat-treated coffee beans may also contain numerous organic acids, e.g. lactic acid, acetic acid, formic acid, glycolic acid, polyphenols and fatty acids. Insoluble coffee waste accounts for almost 65% of the weight of roasted coffee. As previously mentioned, due to their large amounts, they are collected in landfills or used in composting processes for the production of fodder. Research are also conducted on the use of the discussed waste (Solid Coffee Grounds) for the production of biofuels [3-6] and in the extraction of organic acids [7, 8]. Moreover, SCG can be used as: a sorbent to remove metals from solutions, to remove pollutants from wastewater [9, 10], as a precursor for the production of activated carbons or as a source of sugars [11, 12]. The examples of using SCG presented above do not allow for full management of all this type of waste. This makes it necessary to conduct further research towards their use in other branches of the economy.

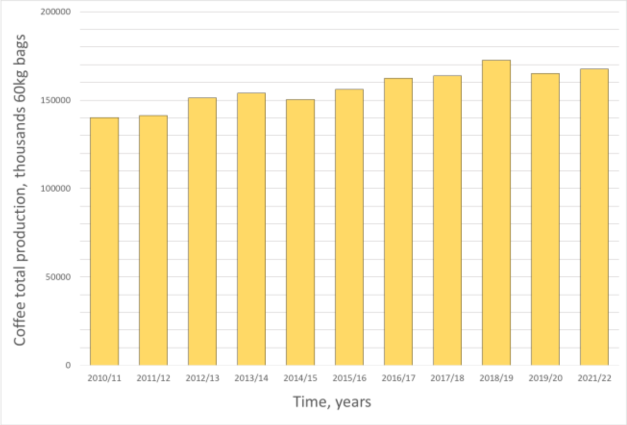

Fig. 1. World coffee production in the years 2010-2021 [2]

The article presents the results of the research undertaken on the possibility of using SCG for the reduction of slags generated in the copper production processes. The concept of using SCG waste in the slag reduction process results from the decline in coal extraction observed in recent years in EU countries, and thus the reduction in the production of coke and coke breeze. The two carbon-bearing materials, as well as graphite and anthracite, are the basic carbon-bearing materials used in pyrometallurgical processes of copper recovery from slags [13-16]. It should be mentioned that there are also studies on the use of fine-grained coal fractions in these processes, generated in coal enrichment or processing [16-18], as well as waste oils and biomass [19-25].

2. Research

In order to investigate the suitability of SCG for use in the pyrometallurgical process, including the copper slag reduction process, a number of tests were carried out to determine the basic physicochemical parameters. The research cycle, of which the results are presented below, included:

1. Calorimetric tests to determine the heat of combustion of coffee waste,
2. Research on degassing coffee waste carried out with the thermogravimetric method,
3. Research on slag reduction with the use of SCG.

2.1. Research materials

Slag from the copper production technology was used in the research, as well as coffee waste after the drying process. The chemical composition of the slag is presented in Table 1.

Table 1.
The composition of the copper slag used in the research

Component of the slag	Cu	Pb	Fe	SiO2	CaO
Component content, % wt.	10.3	2.25	11.1	34.5	14.1

2.2. Equipment and research methodology

The basic parameter characterizing the SCG in the form of the heat of combustion was determined with the use of the KL-12 Mn calorimeter by Precyzja-BIT. The schematic diagram of the calorimeter is shown in Fig. 2. The measurement of the temperature rise was carried out with an accuracy of 0.001 °, and the accuracy of the mass measurement of the samples was 0.0001 g.

The measurement consisted in the complete combustion of a coffee waste sample (SCG) in an oxygen atmosphere in a calorimetric bomb submerged in water and the measurement of the water temperature rise. The heat of combustion of the sample after the measurement was completed was calculated automatically by a computer program according to the formula:

$$Q = K \cdot (T_3 - T_2 - k) \quad (1)$$

where:
Q - The heat of fuel combustion
K - Calorimeter constant
k - correction for heat exchange with the environment

The value of the constant K was determined from the dependence:

$$K = 0.5 \cdot [0.2 \cdot (T_2 - T_1) + 0{,}2 \cdot ((T_4 - T_3)] + 0.2 \cdot (n - 1) \cdot (T_4 - T_3)] \quad (2)$$

where:
T_x - Characteristic temperatures of the heat balance for given measurement moments
n - number of minutes in cycle 2

The test sample was placed in a calorimetric bomb, then the device was started and thermally stabilized. In next step the T_1 temperature values were recorded in equal time steps - 300 s. The T_2 and T_3 temperature values were determined based on the maximum temperature value during the tests. The last parameter determined was the value of the T_4 temperature, which was determined after the end of the test. The diagram of the combustion heat measurement system is shown in Fig. 2, while Fig. 3 shows an example of recording temperature changes with the characteristic temperatures marked: T_1, T_2, T_3 and T_4.

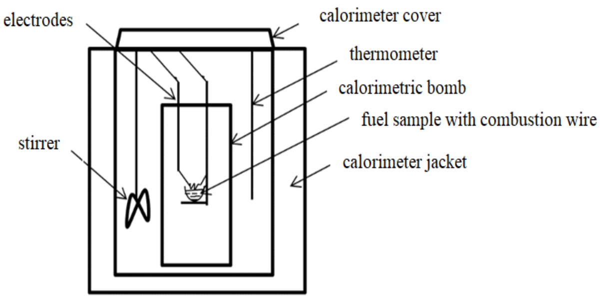

Fig. 2. Schematic diagram of the calorimeter used in the research

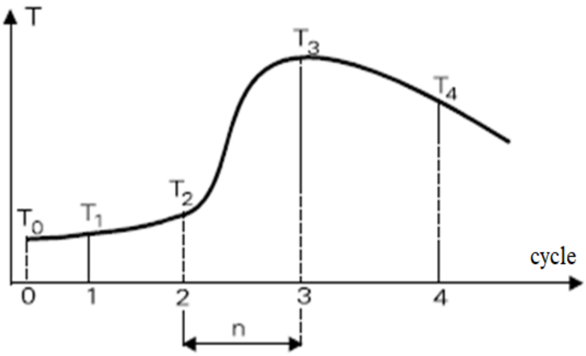

Fig. 3. An example of a graph from the measurement of the heat of combustion obtained with a calorimeter

Calorimetric measurements of the heat of combustion of coffee waste (SCG) were carried for three samples weighing about 1.5 g. Due to the rapid course of the combustion reaction, an undesirable effect was observed in the form of ejection of some ashes from the quartz crucible, which made it impossible to determine the mass of ashes contained in the samples in individual experiments.

In thermogravimetric tests, a thermal analyzer, model STA 449 F3 Jupiter by Netzsch was used. The diagram of this device and the view of the test stand are shown in Fig. 4 and 5, respectively.

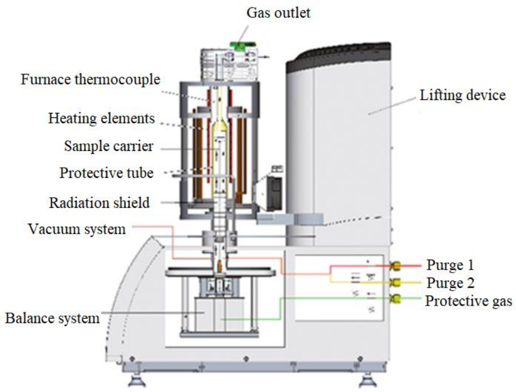

Fig. 4. Schematic diagram of the thermal analyzer STA 449 F3 Jupiter

Fig. 5. Overview of the STA 449 F3 Jupiter thermal analyzer

The F3 Jupiter analyzer is a device that allows to carry out a number of measurements including thermal analysis methods. The basic operating parameters of the device are presented in Table 2. The carriers/heads included allow for thermogravimetric measurements (TG) and differential thermal analysis (DTA) of the tested materials. The analyzer is equipped with a graphite furnace operating in a protective atmosphere (argon, helium), and enables measurements to be carried out at temperatures up to 2000 °C. Thermal analysis can take place in the presence of a selected gas or a gas mixture.

Table 2.
Operating parameters of the STA 449 F3 Jupiter thermal analyzer

Operating temperature	1200 °C
Work atmosphere	Ar + H_2
Gas flow rate	Ar = 95 ml/min, H_2 = 5 ml/min
Crucible material	Al_2O_3
Heating rate	20 °C/min
Type of measurement	TG, DTG

Before the experiment, a material sample of a certain mass (approx. 200 mg) was placed in a DTA/TG crucible made of Al$_2$O$_3$. The crucible was attached to the measuring head in the analyzer's working chamber (Fig. 6).

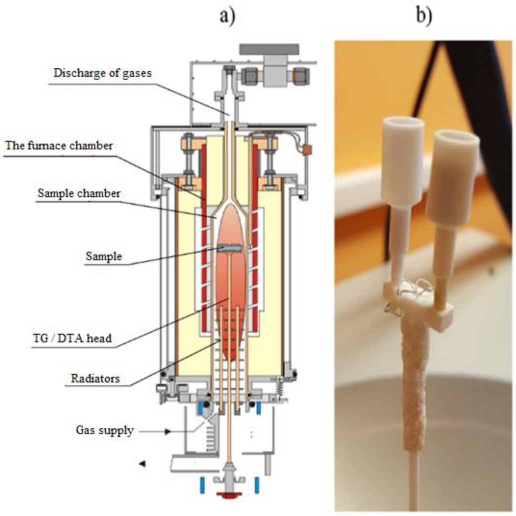

Fig. 6. The method of placing the sample in the device: a) diagram of the working chamber of the thermal analyzer, b) Al$_2$O$_3$ crucible

The weight loss of the sample recorded during the experiment was assumed as the content of volatile parts in the tested material. The measurements were carried out in an argon atmosphere with the addition of hydrogen. The adopted sample heating program consisted of three main stages:

- heating the sample to the temperature of 1200 °C at the rate of 20 °C / min,
- isothermal heating of the sample at the temperature of 1200 °C for 30 minutes,
- cooling the sample to a temperature of 800 °C.

The research of the slag reduction smelting process was carried out with the use of the resistance pit furnace PT 40/1300 by Czylok. The operating parameters of this unit are summarized in Table 3. The use of this type of furnace during laboratory tests allowed for easy loading of the charge, as well as the possibility of controlling and observing the processes taking place in the crucible during the experiment.

Table 3.
Working parameters of a resistance pit furnace

Work temperature	to 1250 °C
Work atmosphere	Air
Rated power	13.5 kW
Rated current	19.57 A

The reduction process was carried out at a temperature of 1300 °C. in alundum crucibles. This temperature was considered optimal on the basis of the results of the preliminary tests. The mass of the tested slag sample was 100 g. The variable parameters in the tests were:

- weight of the reducer - SCG (5.67 g, 7.56 g)
- duration of the reduction process (1 i 2 h)

The general view of the PT 40/1300 furnace as well as the schematic diagram of the test stand for the reduction process are shown in Fig. 7 and 8.

Fig. 7. General view of the PT 40/1300 resistance pit furnace

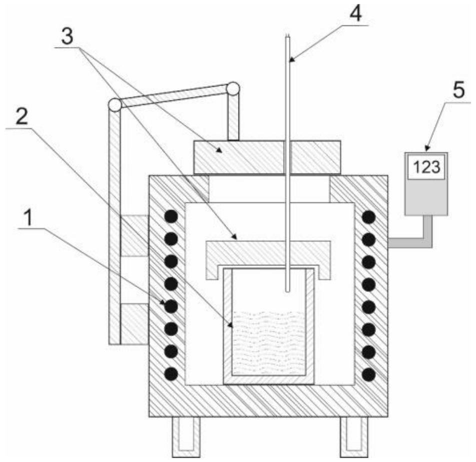

Fig. 8. Schematic diagram of the stand for the slag reduction process
1 - Electric resistance furnace, 2 - Crucible with the tested sample, 3 - Ceramic cover, 4 - Thermocouple, 5 - Device controlling the furnace operation

After each experiment, the mass of molten metal was determined, and the slag was analyzed for its chemical composition for copper content. Before the chemical analysis, the slag sample was completely ground in a planetary mill whose grinding chamber was made of zirconium oxide (ZrO2). The final grain size of the sample was <0.2 mm, which was an analytical sample. The mass of 2.0000 g (+/- 0.0001 g) of the sample prepared in this way was transferred in to a weighing vessel, where it was mixed with 2.0000 g (+/- 0.0001 g) of a binder, which was anhydrous crystalline cellulose with purity p.a. In the next stage, the entire sample was pressed in a hydraulic press from Herzog, model HTP 40. The pellet obtained in this way was analyzed for its elemental composition using a Primus II X-ray fluorescence spectrometer from Rigaku. Measurements were carried out using analytical programs used in the laboratory for quantitative and semi-quantitative SQX analyzes, which is part of the analytical software of the spectrometer.

3. Research results and their discussion

3.1. Calorimetric research

Table 4 summarize the values of the heat of combustion of the SCG samples determined on the basis of experimental tests. For comparison, it also includes the determined values of the combustion heat of coke breeze, which is the main reducer in the processing of copper slag. The Q_{av} value for SCG was 21.09 kJ/kg and for coke breeze was 27.42 kJ/kg. It should be noted that the heat of combustion obtained for coffee waste was higher than the heat of combustion of most types of biomass [26].

Table 4.
Summary of measurement results for the heat of combustion of coke breeze and coffee waste

Sample determination	Heat of combustion, Q	Heat of combustion, Q	Average heat of combustion, $Q_{śr}$
	J/g	MJ/kg	MJ/kg
Coffee sample 1	21 167	21.17	21.09
Coffee sample 2	21 010	21.01	
Coffee sample 3	21 102	21.10	
Coke breeze sample 1	27 375	27.38	27.42
Coke breeze sample 2	27 393	27.39	
Coke breeze sample 3	27 479	27.48	

Despite the difference in the Q_{av} values, the use of SCG seems to be in favor of the target coke breeze in the analyzed technological process. It should be remembered that the processing of copper slags takes place mainly in electric furnaces, where the primary role of coal in the charge is to participate directly or indirectly in the reduction reactions of metal oxides contained in the slag. Its role as a factor indirectly supplying heat to the process is smaller. As previously mentioned, the use of SCG may enable the reduction of carbon dioxide emissions in the process. In addition, the hydrocarbons released from these wastes at high temperatures also act as reducing agents and at the same time intensify the mixing of bath components. The latter is of particular importance for improving the sedimentation of metallic copper in the liquid slag.

3.2. Thermogravimetric studies

The results of thermogravimetric tests are presented graphically in Fig. 9 and 10. Fig. 9 shows the TG curve of the degassing process obtained for the SCG sample, while Fig. 10 shows the DTG curves for this process, respectively.

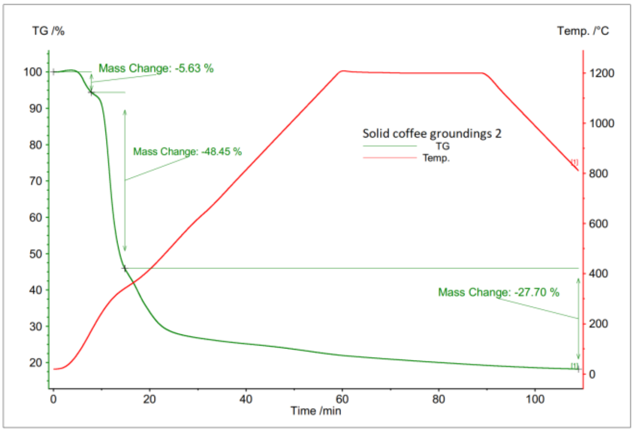

Fig. 9. TG curve of the degassing process of the SCG coffee waste sample

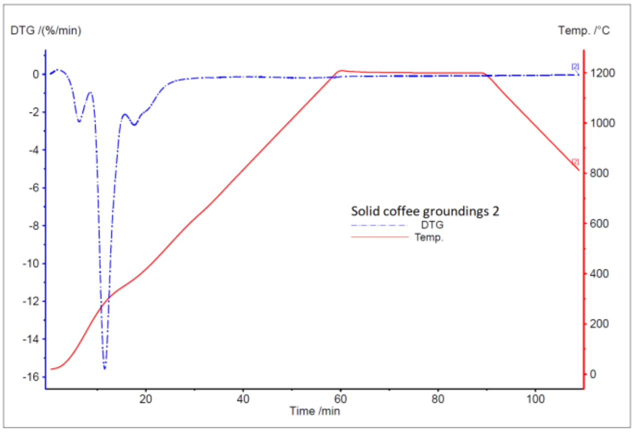

Fig. 10. DTG curve of the degassing process of the SCG coffee waste sample

By analyzing the curve of weight loss of the SCG sample as a function of time (Fig. 9), it was found that there were three distinct temperature ranges, significantly different in the value of the weight loss. Their characteristics are summarized in Table 5. Based on the analysis of the chemical composition of the tested material and the temperature range for individual mass losses in the sample, the possibility of the course of characteristic reactions during the heating of the sample was determined. The first mass loss recorded in the sample was related to the evaporation of moisture contained in the tested material. Another reduction in weight was associated with the loss of the so-called volatile components contained in the sample. The last, occurring at the highest temperatures, weight loss of the samples was related to the thermal decomposition of chemical compounds included in the SCG. The total weight loss of the SCG sample was 81.78 % and the average rate of weight loss of the sample was 0.019 mg/s.

Table 5.
Recorded weight losses of individual samples

Mass change	I	II	III
	%		
	5.63	48.45	27.70
Temperature range for a given weight loss, °C	20 - 200	200 - 340	340 - 1200
The rate of weight loss, mg/s	0.0131	0.1254	0.0062

3.3. Slag reduction process

Table 6 summarizes the exemplary results of copper slags reduction with the use of SCG as a reducer. Apart from the basic data concerning the experiments, this table also includes the mass of the melted alloy as well as the copper content in the slag after the reduction process. Additionally, it includes estimated values of the so-called the relative degree of copper removal of the S_{Cu} slag. It was estimated from the equation:

$$S_{Cu} = (C^0_{Cu} – C^k_{Cu}) / C^0_{Cu} \cdot 100 \ \% \qquad (3)$$

where:
C^0_{Cu} ; C^k_{Cu} - the initial copper content in the slag and the copper content in the slag after the reduction time, respectively, % wt.

Table 6.
Results of the slag reduction process with the use of SCG

No	Slag mass, g	SCG additive weight, g	Temp., °C	Time, h	Mass of obtained metal, g	C^k_{Cu} % wt.	S_{Cu} % wt.
1	100	5.67	1300	1	5.64	1.19	88.4
2		7.56		1	11.89	0.50	95.1
3		5.67		1.5	8.42	0.91	91.1
4		7.56		1.5	12.09	0.45	95.6
5		5.67		2	10.65	0.79	92.3
6		7.56		2	12.05	0.41	96.0

The data presented in Table 6 show that for the copper slag reduction process with the use of SCG as a reducing agent, carried out at a temperature of 1300 °C for a period of 2 hours, a significant degree of copper removal was achieved. Already after 1 hour of the process, the copper content in the slag was reduced from 10.3 wt.%. up to 0.50 wt.% Cu. Extending the duration of the reduction process to 2 h allowed for further reduction of the copper content in the slag to the level of 0.41 % by mass of Cu. Increasing the reductant addition (SCG) also increases the degree of copper slag copper removal. In the case of an increase in the used SCG additive from 5.67 g to 7.56 g, it causes an increase in the copper recovery at the level of approx. 3.7 to approx. 6.7 %.

4. Conclusions

On the basis of the research carried out on the reduction of copper slags with the use of the coffee waste (SCG) as a reducer, it can be concluded that:

- The use of SCG coffee waste makes it possible to replace the standard reducer - coke, in the process of reducing copper slags.
- As a result of the copper slag reduction process carried out at the temperature of 1300 °C and during 2 hours, the copper content in the slag was reduced from 10.3 % to 0.41 % by weight.
- The obtained results of the change in the concentration of copper in the slag during the copper removal process made it possible to determine the S_{Cu} loss index, ranging from 88.4 to 96.0 %.
- Increasing the amount of reducer additive (SCG) by 25 % and extending the duration of the reduction process to 2 hours allowed to increase the degree of copper slag removal from approx. 4 to approx. 7 % for individual tests.

Acknowledgments

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