



# Physicochemical Properties of Rapeseed Cake and its Potential as a Biomass Reductant of Metallurgical Slags

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## Abstract

The paper presents the results of a study of the basic physical and chemical properties of a reductant traditionally used in the metallurgical industry, i.e. coke, and an alternative biomass reductant, rapeseed cake. The article also presents the results of research into the reduction of smelter slag with a high content of Cu and Pb with rapeseed cake and, for reference purposes, coke. The tests were conducted at 1400 °C and a holding time, 2h. The reductant additions ranged from 2-20 % by weight of the charge (slag) for biomass and 5, 10 and 15 for coke. The results obtained are discussed in the context of several parameters to assess the efficiency of the reduction processes.

**Keywords:** Biomass, Rapeseed cake, Alternative reductors, CO<sub>2</sub> emissions, Slag

## 1. Introduction

The metallurgical industry in Europe and worldwide uses materials with reducing properties (in a chemical context) in the production of metals from ores or secondary raw materials in pyrometallurgical processes. The most widespread reductant used in metallurgy is coal, which is most commonly found under industrial conditions in the form of coke, i.e. a product of the gasification of mined coal [1-4]. In view of the gradually diminishing fossil fuel resources from which coke is produced and the need to meet the provisions of the European Green Deal, such as achieving climate neutrality by 2050, the metallurgical industry is facing the challenge of finding new materials that can replace the currently used reducing agents [5,6]. One possible remedy to the above problems could be the application of

renewable biomass in the metallurgical industry, which, thanks to its neutrality in terms of CO<sub>2</sub> emissions, could be one of the key elements enabling the construction of an efficient metallurgy that is also environmentally friendly [6,7].

The search for alternative materials that can act as reductants in metal production processes is a major creed among global and European producers. This is due to the fact that coking coal, the primary raw material for coke production, is one of the EU's list of critical raw materials [8]. It is, like the other raw materials on the list, of strategic importance for the functioning and economic development of the European Union, and its scarcity could cause serious economic consequences for the entire European economy.

Technologies for the reduction of metal oxides from metal-bearing materials based on alternative reductants such as biomass can make a significant contribution to reducing atmospheric CO<sub>2</sub>



emissions (emission-neutrality of biomass) and reducing the need to extract fossil fuels.

One biomass raw material that can be considered as an alternative reducing agent is rapeseed cake, which is a product of the rapeseed oil production process. It is important to note that this material is widely available on the European market. The largest European producers are Germany, France and Poland. In addition, rapeseed itself is the second most important oilseed crop in the world [9,10].

## 2. Research

In order to determine the potential for the use of rapeseed cake (RC) as a reductant for metallurgical slags, a physico-chemical study of the present material was carried out. These studies included:

- Chemical analysis of the RC and coke
- Calorimetric studies to determine the heat of combustion of the RC and coke
- Studies on the reactivity of rapeseed cake towards an oxidising agent in the form of CO<sub>2</sub>

### 2.1. Research materials

Three materials were used for the study. These were metallurgical slag with a high Cu and Pb content (the composition is reported in Table 1.) and rapeseed cake and coke.

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

Component of the slag	Component content, % wt
O	25.08
Cu	17.25
Pb	14.10
Si	13.15
Fe	11.70
Ca	5.57
C	3.36
Al	2.43
K	1.55
Mg	1.22
As	1.16
Zn	0.92
Co	0.55
Ni	0.29
Other	< 2.0

### 2.2. Equipment and research methodology

Chemical analysis for carbon content in rapeseed cake was carried out using a CS2000 analyser (Eltra), while other elements were analysed using X-ray fluorescence spectrometry (XRF) (spectrometer: ZSX Primus - WDXRF).

The heat of combustion in the analytical and dry state was determined based on three measurements carried out with a Precyzja-BIT KL-12 Mn calorimeter and a moisture measurement carried out with a weigh-dryer. The heat of combustion values were calculated by the calorimeter software.

Reactivity was tested using the mass loss method of a sample exposed to carbon dioxide at 1100 °C for a fixed time of 2h.

The reduction of the metallurgical slag was carried out in an electric resistance furnace. The RC and coke was placed at the bottom of an alundum crucible, successively covered with a layer of slag, placed in the furnace and heated to 1400 °C at a rate of 6 °C/min. From the time the set temperature was reached, the sample in the furnace was held for 2 h and then cooled spontaneously with the furnace. The slag mass was 200 g each time, while the addition of rapeseed cake was variable, ranging from 2-20 %, relative to the slag mass, and coke 5,10 and 15 % relative to the slag mass. Two experiments were conducted for each variable. After each experiment, the sample was weighed, the slag was separated from the metal and the average mass of the products was determined.

For chemical analysis, slags were ground in a planetary mill (P-9 FRITTSCH GmbH). The samples prepared in this way were subjected to chemical analysis in terms of Cu, Pb content using an Innovex XRF spectrometer. Measurements were carried out using software dedicated to the sample types as part of the spectrometer software.

## 3. Research results and their discussion

### 3.1. Chemical composition biomass

Chemical analysis of rapeseed cake determined that this material contained mainly two elements in the form of O and C. Their concentrations were similar to other biomass materials [11]. The results are presented in table 2.

Table 2.  
Composition of RC

Component	O	C	Ca	S	K	Mg	P
Concentration [% wt.]	49	44	1	1	2	1	2

### 3.2 Calorimetric research

The average heat of combustion for rapeseed cake (RC) in the analytical state was 22.725 MJ/kg and in the dry state 24.755 MJ/kg. These values were noticeably higher than for other biomass materials [12, 13]. Compared to coke, RC has a lower heat of combustion value. The results are shown in the Table 3.

Table 3.  
Results for the heat of combustion of RC and coke

Sample	Heat of combustion		Humidity % wt
	analytical Q [MJ/kg].	on dry basis Q [MJ/kg].	
RC 1	22.752	24.785	8.20
RC 1	22.760	24.793	
RC 1	22.663	24.688	
Average	22.725	24.755	1.63
Coke	30.091	30.590	
Coke	30.294	30.797	
Coke	30.300	30.803	
Average	30.228	30.730	

### 3.3 Reactivity

The reactivity of biomass cake towards CO<sub>2</sub> is very high, reaching almost 95 %. For metallurgical coke, this parameter is much lower, at around 33 %. The Table 4 shows the results of the tests carried out. The reactivity of R<sub>CO2</sub> was calculated according to the formula 1.

$$R_{CO_2} = m_0 / m_1 \times 100 \% \quad (1)$$

Where :

m<sub>0</sub> ; m<sub>1</sub> - the initial mass of sample and the mass of sample after experiment.

Table 4.  
Results for the reactivity of RC and Coke

Sample	R <sub>CO2</sub> %
RC 1	95.11
RC 2	94.85
RC 2	94.89
Average	94.95
Coke 1	31.44
Coke 1	31.25
Coke 1	34.99
Average	32.56

### 3.4 Slag reduction

The results of the metallurgical slag reduction are shown in Table 5. It includes data such as the weight of the initial slag, the reductant addition, the weight of the resulting alloys and slags.

Table 5.  
Results of the slag reduction process with the use of RC – mass of products

Reducing agent	mass of slag, g	Reducing agent to mass of slag, %	mass of alloy, g	mass of post-reduction slag, g
Rapeseed cake	200,02	2	19,27	177,59
	200,02	5	35,61	158,21
	200,01	10	52,09	139,3
	200,02	12	56,19	132,88
	200,03	15	58,50	129,98
	200,02	17	59,71	129,82
	200,02	20	58,95	130,60
Coke	200,03	5	29,83	150,9
	200,02	10	37,11	155,41
	200,04	15	48,22	158,77

The most important information contained in the Table 6 was the masses of the alloys obtained. In general terms, they represent an indicator of the efficiency of the reduction. The higher the mass of the alloy, the more effective the reduction process was. Table 6 shows the results of the chemical analyses of the alloys after the processes in terms of Cu and Pb content.

Table 6.  
Results of the slag reduction process with the use of RC – mass of products

Reducing agent	Reducing agent to mass of slag [%]	Concentration of Cu % wt	Concentration of Pb % wt
Rapeseed cake	2	5,47	12,79
	5	1,81	10,65
	10	0,94	3,2
	12	0,84	1,84
	15	0,54	1,29
	17	0,42	0,79
	20	0,36	0,74
Coke	5	2,06	10,01
	10	1,08	6,75
	15	0,59	2,18

For both reductants, the concentration of both Cu and Pb decreased with increasing addition. Cu and Pb concentrations lower than were achieved for 20 % RC addition. At the similar rate, it was observed that for the reference points (coke as reductant) the concentrations of both Cu and Pb were higher than for RC. The exception to this is the 5 % reductant addition for which the Pb concentration in the slag after the process was lower for coke. The results are graphically presented in Figure 1.

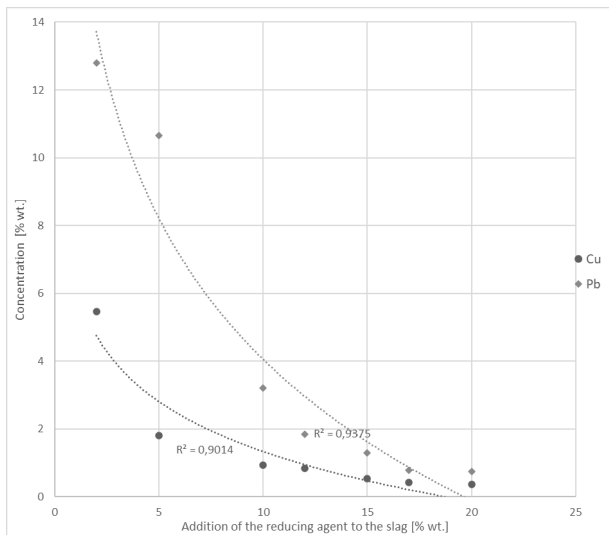


Fig 1. Relationship of Cu and Pb concentrations in slags with regard to reductant addition (RC)

Trend lines were assigned for the points on the graph (Figure 1). The Cu and Pb concentrations in the slag in relation to the reductant addition assume the closest logarithmic relationship.

The following formulae (2) and (3) were used to determine the degree of decopperation and deleadisation. The result is shown in Table 7

$$L_{Cu} = (C_{Cu}^0 - C_{Cu}^1) / C_{Cu}^0 \times 100 \% \quad (2)$$

$$L_{Pb} = (C_{Pb}^0 - C_{Pb}^1) / C_{Pb}^0 \times 100 \% \quad (3)$$

Where:

$C_{Cu}^0$ ;  $C_{Cu}^1$  the initial copper content in the slag and the copper content in the slag after the reduction time, respectively, % wt.

$C_{Pb}^0$ ;  $C_{Pb}^1$  the initial lead content in the slag and the lead content in the slag after the reduction time, respectively, % wt.

Table 7.

Results of the slag reduction process with the use of RC – level of decopperation and deleadisation

Reducing agent	Reducing agent to mass of slag [%]	$L_{Cu}$ %	$L_{Pb}$ %
Rapeseed cake	2	72	19
	5	91	40
	10	96	84
	12	97	91
	15	98	94
	17	98	96
	20	97	97
Coke	5	91	46
	10	95	63
	15	98	89

According to Table 7, the highest levels of decopperation and deleadisation were observed for the RC addition relative to the slag at 17 and 20 %. In the case of coke, the levels of deleadisation were similar to those for the corresponding points for the RC while the deleadisation was noticeably lower with the exception of the 5 % reductant addition.

## 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 RC makes it possible to replace the standard reducer - coke, in the process of reducing copper-lead slags.
- As a result of the slag reduction process carried out at the temperature of 1400 °C and during 2 hours, the copper content in the slag was reduced from 17.25 % to 0.36 % by weight and lead from 14.10 % to 0.74 %.
- The dependence of Cu and Pb concentrations in the slags after the processes for the alternative reductant assumed a character close to logarithmic.
- The obtained results of the change in the concentration of copper and lead in the slag during the metals removal process made it possible to determine the  $L_{Cu}$  index, ranging from 72 % to 98 % and  $L_{Pb}$  from 19 % - 97 %.
- Under the conditions in which the experiments were carried out, considering all the results, it was concluded that RC proved to be a better reductant compared to coke.

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