



# Utilization of Fine Fraction of Converter Slag in the Form of an Addition to Copper Concentrate Briquettes

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**Abstract:** During the copper matte converting process, slag is produced. Owing to its valuable components, it is returned to the shaft furnace, where copper concentrates are smelted. Recycled slags should not contain excessive amounts of fine fractions, which reduce the permeability of the furnace charge and may be entrained with the gas stream. This study aimed to investigate the possibility of using a fine fraction of converter slag as an addition to copper concentrate briquettes. The results indicate that the optimal addition, in terms of briquette strength, is 6 % converter slag with a particle size of (0–1) mm. The presence of fayalite in the slag causes even such a small addition to reduce the final melting temperature by approximately 30 °C compared with the slag-free charge. Consequently, copper concentrates can be smelted with reduced coke consumption, while the resulting shaft slag exhibits lower viscosity and, therefore, reduced copper losses.

**Keywords:** converter slag; briquettes; melting point; slag recycling

## 1. Introduction

Copper sulphide concentrates are typically smelted in shaft furnaces. The main sulphide minerals include chalcopyrite ( $\text{CuFeS}_2$ ), bornite ( $\text{Cu}_5\text{FeS}_4$ ), chalcocite -  $\text{Cu}_2\text{S}$  and covellite -  $\text{CuS}$ . Copper sulphide concentrates contain various minerals, which mainly contain copper and iron. The purpose of the shaft process is to transfer copper compounds into copper matte and to separate them from the slag phase, into which the gangue components pass. The input to the shaft furnace is Cu concentrates in the form of briquettes and fluxes enabling faster melting of charge materials and regulating slag and matte separation [1,2]. For the production of briquettes, a specific binder addition is used, whose task is to combine all the concentrate ingredients and ensure appropriate strength parameters. The above-mentioned additive is often a sulphite lye, water glass as well as it is possible to use other available and cheap substances [3,4] ensuring compliance with the conditions for obtaining durable briquettes.

Fluxes are added to the stock depending on the concentrate composition. They primarily affect the process of melting the charge [5] but can also intensify the removal of such harmful components from the charge such as arsenic compounds [6,7]. The content of silica in concentrate is very important for the slag formation process in the shaft furnace. It is the main component of slag, it creates an ionic structure that facilitates the separation of products. The basic flux used in the shaft process is converter slag, which is one of the products of copper matte processing in the converter. Converter slag is added to the shaft furnace because of the relatively high copper content, but also as it has a low melting point of (1100–1150) °C and low viscosity [8,9]. It first melts and facilitates the melting of copper concentrate - it is also a solvent for gangue components.

Available studies [10–12] have shown that an increase in the Fe/SiO<sub>2</sub> ratio in the molten material results in a significant decrease in its viscosity. In pure fayalite, this ratio is approximately 1.1 - therefore, it is several times higher than the values typically observed in concentrates fed into shaft furnaces. Slag supplied to the shaft furnace should not contain excessive fine or oversized fractions. The optimal particle size range of slag is (20–125) mm. The fraction above 125 mm is crushed to achieve the optimal size; management of slag fractions with particle sizes below 20 mm remains a problem. Such fine grains reduce the gas permeability of the charge column, as well as can be largely carried away with the gas stream from the shaft furnaces and only increase the load on the furnace de-dusting system.

The purpose of this work was to attempt to determine the possibility of using a fine fraction of converter slag as an addition to briquettes. The impact of slag addition on the strength properties of briquettes and their melting point was determined.

## 2. Materials and Methods

### 2.1. Grain size composition of converter slag

The research described in this paper began with an estimation of the share of slags with (0–20) mm particle size in the total mass of converter slag obtained during the process of converting copper matte. For this purpose, a sieve analysis of a sample of converter slag from KGHM Polska Miedz S.A. was carried out. A preliminary sieve analysis showed that approximately (25–30) % of the slag consisted of particles in the (0–20) mm size range. In the next stage, an attempt was made to divide the (0–20) mm fraction of the blend of converter slag (fayalite slag from the first stage of the converting process and the oxide slag from the second stage) into (0–6) mm and (6–20) mm fractions. To this end, a sieve analysis of 10 kg of slag was performed, and the results are presented in Table 1.

**Table 1.** Distribution of (0–20) mm converter slag fraction

Particle size/mm	Mass/kg	Mass fraction/%
0–6	4.83	48.3
6–20	5.17	51.7

Detailed sieve analysis of fine fraction (0–20) mm obtained from the screening of converter slag is presented in Table 2.

**Table 2.** Results of sieve analysis of converter slag

Particle size range mm	Mass fraction %
20.0–6.0	51.7
6.0–2.0	10.2
2.0–1.25	8.2
1.25–0.8	5.5
0.8–0.5	4.2
0.5–0.315	2.3
0.315–0.16	7.0
0.16–0.08	0.8
0.08–0.071	5.1
0.071–0.00	5.0

In order to examine the possibility of crushing thicker fractions of converter slag under laboratory conditions, an attempt was made to grind a specific amount of slag with a particle size of (6–20) mm. The results of this test were to provide a qualitative answer to the question about the susceptibility of this material to comminution processes. For this purpose, 4 kg of converter slag with a grain size of (6–20) mm was crushed in a LM-1

laboratory mill. After 20 minutes of crushing, the material was subjected to a sieve analysis which showed that 2.1 kg of slag had a particle size below 6 mm (52.5 %) and 1.9 kg of slag above 6 mm (47.5 %). It can therefore be concluded that slag with a particle size of (6–20) mm is susceptible to comminution.

## 2.2. Chemical analysis of slag

Tested slags were subjected to chemical analysis. In the case of a blend of converter slag, the content of Cu and Pb in samples of different particle sizes was determined. The results are presented in Table 3.

Table 3. Cu and Pb content in converter slag fractions of different particle sizes

Converter slag	(0–6) mm	(6–20) mm
Cu	18.12 %	13.99 %
Pb	6.62 %	7.23 %

Copper in the converter slag samples was determined by AAS (atomic absorption spectrometry), while lead was determined by ICP-OES (inductively coupled plasma optical emission spectrometry). Since separate samples of fayalite and oxide slags were also available, their chemical compositions were also determined. The analyses were performed using an ARL9900 X-ray fluorescence spectrometer. The results are presented in Table 4.

Table 4. Chemical composition of fayalite and oxide slags (wt.%)

Element	Fayalite slag	Oxide slag
Fe	35.52	8.32
Si	15.16	12.24
Zn	3.01	0.55
S	0.26	0.002
Pb	5.95	7.42
Cu	2.71	39.55
Ag	0.002	0.019
Cr	0.11	0.08
Cl	0.01	0.01
Ca	0.51	0.14
Al	0.93	0.49
Mn	0.20	0.032
Cd	0.0034	0.0064
Sn	0.0260	0.013
As	0.01	0.26
K	0.77	0.32
Mg	0.19	0.19
Na	1.25	0.19
Sb	0.016	0.071
Ni	0.071	0.87
Co	1.260	0.55

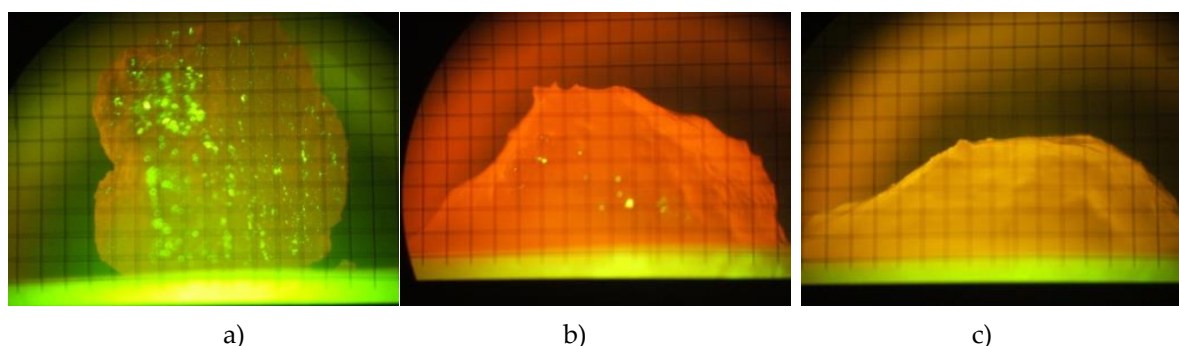
As shown above, oxide slag contains significantly higher concentrations of copper, silver, and nickel compared to fayalite slag. The high copper content in the (0–6) mm and (6–20) mm fractions (18.12 % and 13.99 %, respectively) indicates that in the fine fraction of converter slag mixture, oxide slag dominates, in which the copper content is much higher than in fayalite slag. The chemical form of copper differs between these slags. In fayalite slag, copper occurs as  $\text{Cu}_2\text{S}$ , and in oxide slag we deal with  $\text{Cu}_2\text{O}$  and metallic copper [13]. The masses of fayalite slag and oxide slag obtained in the converting process are in the proportion of about 3:1 [14,15].

### 2.3. Melting tests

As part of the research on the physicochemical properties of slag, it was decided to carry out an analysis of the melting temperature of converter slag [16]. For this purpose, Leitz high-temperature microscope was used to observe the slag samples placed in the furnace heating field. Samples were made of slag by pressing with a force of 1000 kg to form a cube with a side of 1 cm. The furnace temperature was increased at a rate of about 0.3 °C/s while observing the changes taking place in the slag sample. Due to the inability to unambiguously determine the slag melting temperature, three temperatures were determined during the tests, in which they took place in sequence:

- softening of the slag sample,
- settlement and decrease in height to approx. 50 % of the original height,
- complete melting of the slag.

For each of the slags, two series of tests were performed and the results obtained were averaged. Figure 1 shows a view of a slag sample during temperature testing.



**Figure 1.** Converter slag, a – 1108 °C, softening of the slag sample; b – 1202 °C, sample settlement; c – 1302 °C, sample melting

Table 5 summarizes the characteristic temperatures recorded during both series of measurements and the arithmetic means of these values for converter slag. Temperatures were determined with an estimated uncertainty of  $\pm 10$  °C.

**Table 5.** Temperatures recorded during melting of converter slag

	1st series	2nd series	Mean value
softening temperature/°C	1108	1102	1105
settling temperature/°C	1202	1192	1197
melting temperature/°C	1302	1306	1304

### 2.4. Briquetting of a mixture of copper concentrates with the addition of fine fractions of converter slag

The research was aimed at assessing the possibility of briquetting in a roller press a mixture of copper ore concentrates and a binder in the form of a sulphite lye along with the addition of various fractions of fine-grain

converter slag and fayalite slag. Sulphite lye is a by-product of the cellulose production process based on conifers by the sulphite method. It is a thick liquid of brown color with an intense sweetish smell. The sulphite lye used contained more than 50 % of dry matter, which had a sugar content of (5–10) %; calcium oxide (- 0.3–10) % and sulfur (- 0.3–0.5) %. The lye density was (1270–1300) kg/m<sup>3</sup>, and the relative viscosity was (3–5) °E (Engler degrees), a conventional industrial measure of relative viscosity.

The following materials were used for laboratory tests:

- copper ore concentrates mixture
- converter slag with a fraction of (0–1) mm
- fayalite slag with a fraction of (0–6) mm
- sulphite lye as a binder.

The chemical composition of the concentrate mixture used for briquetting is presented in Table 6.

**Table 6.** Content of basic components of the copper concentrate mixture used for briquetting

	Cu	Ag	Fe	Pb	SiO <sub>2</sub>	MgO	CaO	Al <sub>2</sub> O <sub>3</sub>	S	Zn	C <sub>org</sub>	C	Cl	As
	%	ppm	%	%	%	%	%	%	%	%	%	%	%	%
content	26.0	636	3.4	1.55	17.77	4.27	8.16	6.22	9.7	0.4	6.56	9.38	0.2	0.2

It was found that its moisture content was about 8 %. To the concentrate mixture 2 % of fayalite slag (0–6) mm fraction as well as 3 % or 6 % of converter slag (0–1) mm was added, followed by the addition of 11 % sulfite lye relative to total weight of the concentrate and slag. For averaging and drying the material, a laboratory Z-mixer was used with a heated jacket to a temperature of about 80 °C.

The relative moisture content was determined by the weight method. A sample of the blend prepared for briquetting was dried at 105 °C until its constant weight was obtained. The relative moisture content of the mixture was calculated from the following formula:

$$w = \frac{m_w - m_s}{m_w} \cdot 100 \% \quad (1)$$

where:

w - relative moisture content of the mixture/%

m<sub>w</sub> - sample mass before drying/g

m<sub>s</sub> - sample mass after drying/g.

The average moisture content of two determinations was considered representative.

The mixture prepared for briquetting was fed into a compaction zone of the laboratory roll press LPW 450. A roller work surface allowed obtaining drop-shaped briquettes (briquettes with a division plane) with a volume of approx. 13 cm<sup>3</sup>. Briquettes were collected in a special container from where they were taken to assess the effects of briquetting. The mechanical resistance was tested immediately after consolidation. The testing of briquette strength under laboratory conditions was carried out dropping 20 randomly selected briquettes from a height of 2.0 m onto a steel plate 120 mm thick. The briquette strength was assessed as the number of briquettes that remained in total after three tests. For each prepared mix, the drop test was carried out twice. According to literature data [17–19], the minimum required briquette resistance to drop test is 90 %. The results of laboratory tests of briquetting of a mixture of copper ore concentrates together with a binder in the form of a sulfite lye and addition of fine-grain converter slag and a fraction of (0–6) mm fayalite slag is presented in Table 7. The addition of 2 % fayalite slag means full use of slag from the grain range (0–6) mm appearing in the current production of converter, and 3 % of converter slag corresponds to the addition to the briquettes of the entire slag with granulation (0–6) mm with simultaneous milling of this material to grain size (0–1) mm.

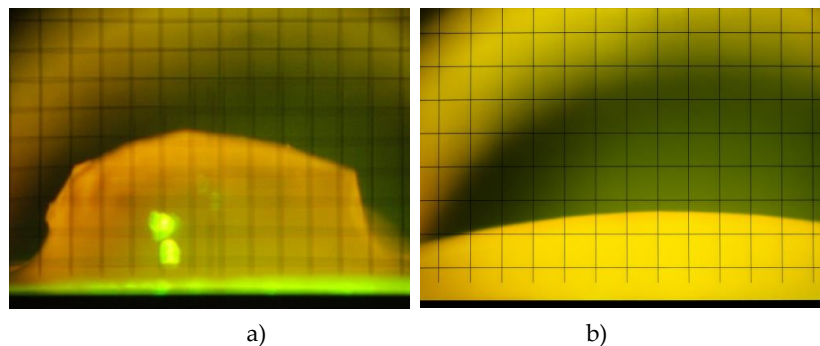
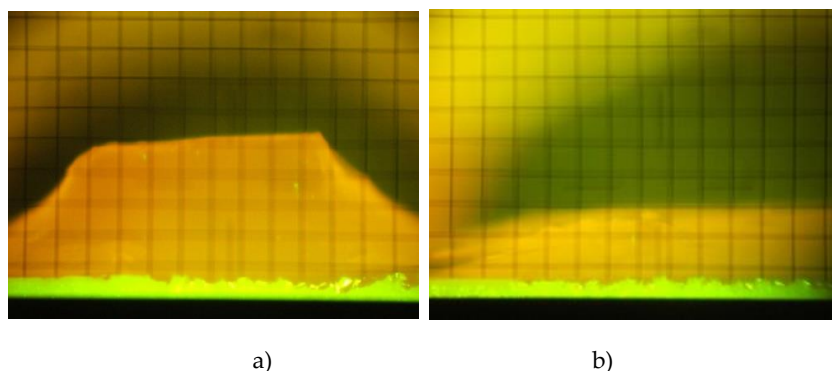
**Table 7.** Research results of the briquetting process of copper ore concentrate with the addition of converter slag (slag mixture), fayalite slag and sulphite lye

Addition	Addition amount	Moisture content	Drop test I	Drop test II	Mean value
	%	%			
Converter slag (0–1) mm	3	4.5	18 (90 %)	18 (90 %)	18 (90 %)
Converter slag (0–1) mm	6	4.1	20 (100 %)	20 (100 %)	20 (100 %)
Fayalite slag (0–6) mm	2	4.5	15 (75 %)	17 (85 %)	16 (80 %)

Using a high-temperature microscope, the melting behaviour of briquettes without slag addition and with 6% converter slag was investigated. The briquettes were formed into cubes with a side length of 1 cm and placed in the furnace to determine the characteristic temperatures. The final melting temperature decreased by approximately 30 °C, although the initial softening temperature slightly increased (Table 8). Figures 2 and 3 show the shrinkage and melting behaviour of the tested samples.

**Table 8.** Temperatures recorded during the melting of copper concentrates without addition and with 6 % addition of converter slag

	Without slag addition	6 % slag addition
Softening temperature/°C	1101	1123
Settling temperature/°C	1217	1222
Melting temperature/°C	1259	1230

**Figure 2.** Briquette sample without the addition of slag, a – 1217 °C, sample settlement; b – 1259 °C, sample melting**Figure 3.** Briquette sample with 6 % addition of converter slag, a – 1222 °C, sample settlement; b – 1230 °C, sample melting

### 3. Results and discussion

The analysis carried out in this work provided valuable information on the physicochemical properties and chemical composition of converter slag from KGHM Polska Miedz S.A. Separately analyzed fayalite and oxide slags showed copper content 2.71 % and 39.55 %, respectively. Hence, the copper content in the converter slag (a mixture of fayalite and oxide slag) can usually be in the range of about (12–14) %. The form of copper occurrence in these slags is completely different, which is due to the moment of the formation of individual slags during copper matte converting process. Copper in fayalite slag occurs in the form of  $\text{Cu}_2\text{S}$ , and in oxide slag in the form of  $\text{Cu}$  and  $\text{Cu}_2\text{O}$ . At the same time, the slag from the 1st stage of converting process is characterized by the presence of fayalite ( $2\text{FeO}\cdot\text{SiO}_2$ ) in it, which, as demonstrated during the research presented in the paper, reduces the liquefaction temperature of briquettes of copper concentrate melted in shaft furnace. Strength tests of briquettes made with the addition of slag indicate that even a 2 % addition to briquettes of fayalite slag with a grain size of (0–6) mm leads to decrease in briquette strength and failure to meet the requirements of the drop test. Adding converter slag with a grain size of (0–1) mm to briquettes improves their strength properties. This material is characterized by better particle packing, better binder distribution, and reduced porosity.

The melting tests of a mixture of copper concentrates with a 6 % addition of the fine fraction of converter slag indicated that the final melting temperature decreased by about 30 °C, which is very beneficial from an industrial point of view. Fayalite phases act as low-melting components, promoting early liquid formation and lowering the melting temperature [20,21]. The above-mentioned results clearly lead to the conclusion that it is necessary to process the converter slag in lump form as a direct addition to the charge for shaft furnace, and its fine phase could be used successfully as an addition to briquettes.

### 4. Conclusions

The research carried out in this work and the subsequent analysis of the results obtained allow the following conclusions to be drawn regarding how to deal with the fine fraction of converter slag:

- 1) About 50 % of the converter slag fraction with a grain size of (0–20) mm is a (0–6) mm fraction, which can be added to the briquettes.
- 2) Processing the (6–20) mm fraction of converter slag would require crushing to a particle size of (0–6) mm.
- 3) In a roller press, a mixture of copper ore concentrates and a binder in the form of a sulfite lye along with the addition of various fractions of fine-grain converter and fayalite slag can be briquetted while maintaining the moisture content of the mixture in the range of (4.0–4.5) %.
- 4) An increase in the diameter of the fayalite slag grains added to the concentrate mixture causes an increase in porosity and a decrease in the smoothness of the external surface of the briquettes.
- 5) The addition of a 6 % fine fraction of converter slag (0–1) mm improves the mechanical strength of briquettes, compared to briquettes made with the addition of 2 % fayalite slag with (0–6) mm grain size and 3 % addition of converter slag with (0–1) mm grain size.
- 6) Agglomerated copper concentrates with a 6 % addition of converter slag with a particle size of (0–1) mm, due to the presence of fayalite, melt completely at temperatures about 30 °C lower than briquettes without this addition.

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