

THE INFLUENCE OF THE SILICATE SLAG COMPOSITION ON COPPER LOSSES DURING SMELTING OF THE SULFIDE CONCENTRATES

Ž. Živković^{*#}, N. Mitevska^{**}, I. Mihajlović^{*} and Đ. Nikolić^{*}

^{*}University of Belgrade, Technical Faculty Bor, 19210 Bor, Serbia

^{**}Institute for Mining and Metallurgy 19210 Bor, Serbia

(Received 10 August 2009; accepted 10 September 2009)

Abstract

This paper presents the results of multi-linear regression analysis (MLRA) of the slag composition (SiO_2 , FeO , Fe_3O_4 , CaO , Al_2O_3) and the content of copper in the matte on resulting copper content in the slag during smelting of the sulfide concentrates in the reverberatory furnace. When comparing results obtained with MLRA model calculations with values measured at industrial level high degree of fitting is obtained ($R^2 = 0.974$). This indicates that slag composition and content of copper in the matte influences the copper losses in the waste slag with the probability of 95 %.

Keywords: smelting, slag, copper, copper losses, multiple linear regression

1. Introduction

During pyrometallurgical copper extraction, smelting is the subsequent operation to the oxidation roasting of the concentrates. In modern pyrometallurgical processes for copper extraction, both

operations are facilitated in the same unit, resulting with development of the two main phases: silicate slag and the copper matte. Those phases are differentiated by gravitational settling according to their specific weights. Partially dissolved copper and unsettled copper drops are presenting the

[#] Corresponding author: zzivkovic@tf.bor.ac.rs

main copper losses in the waste slag [1]. With the stationary smelting processes, such as smelting in reverberatory furnace, this loss is about 0.5% Cu which is permanent because of disposal of such slag to the waste yard. With the dynamic smelting processes such as Flash; INCO ..., copper content in the silicate slag could reach up to 2%, which demands further processing of the slag. Processing of such, copper rich slag, is facilitated using flotation or electro-precipitation of remaining sulfides resulting with about 0.5% Cu in the remaining waste slag [2, 3]. Those copper losses in the waste slag are strongly influencing the economy of the copper extraction process. Also, it is a global problem in copper pyrometallurgy which is solved in each smelter plant according to the locally available resources [4].

Numerous investigations revealed that slag's composition has dominant influence on copper losses with the slag [5-8]. The slag is a silicate solution with SiO_2 and FeO as dominant constituents. Accordingly, the prevailing compound of the slag is fayalite ($2\text{FeO}\cdot\text{SiO}_2$). Silicate solution is able for sustaining of the complex polymeric compounds which, in presence of the basic oxides, dissociate according to the following pattern: $\text{Si}_6\text{O}_{18}^{12-} \rightarrow \text{Si}_4\text{O}_{12}^{8-} \rightarrow \text{Si}_3\text{O}_9^{6-} \rightarrow \text{Si}_2\text{O}_7^{6-} \rightarrow \text{SiO}_4^{-4}$. This is the reason why isolated SiO_2 molecules couldn't be registered in the industrial slag. Instead, polymers with the tetrahedral structure (SiO_4^{-4}) are present in which each oxygen ion is linked with two silicon ions [1,2].

Copper losses in the silicate smelting slag are depending on large number of factors, ranging from objective ones which are

depending on the input materials composition, over physicochemical structure of the smelting products, to subjective factors depending on the management of the process [4]. According to Vanjukov, total copper losses in the slag can be divided as: electrochemical losses (chemical and physical) which present 65-80% of overall losses and mechanical losses (unsettled matte drops) with the ration of 20 – 35% of overall losses [3]. Besides copper distribution among matte and the slag, depending on the slag composition, distribution of the other elements (As, Sb, Bi, Au, Ag...) present in the melt is also depending on the composition of the slag [9-11].

The motive for investigations presented in this paper was to perform statistical analysis of the slag constituents influencing the total copper losses in the smelting slag and accordingly development of the mathematical model describing these influences. Obtained results should be helpful for the copper smelter management during constituting of the input charge that will enable better management of the copper losses in the smelting slag. This is resulting from the fact that regulation of the input charge composition can be used for control of the copper losses in the smelting slag, also the degree of desulphurization obtained during oxidative roasting can be used for control of the copper content in the matte [12-14].

2. Experimental

For the analysis of the slag composition influence on the copper losses, we used the

data obtained from the industrial conditions in the Copper Smelter Company – RTB Bor, (Serbia). The smelting process in this company is facilitated in the reverberatory furnace with the annual capacity of 60 000 tons of anodic copper. The copper extraction technology in this smelter plant is in its final phase of the life cycle, on the other hand, from the technological point of view, it still has satisfactorily production stability [15]. Over many years of practice, in this smelter plant, the sampling of the slag and matte was performed during tapping operation and the analysis of the composition carried out on the daily base on composite sample obtained this way [3]. To receive clear picture of the real conditions in the reverberatory furnace a special experiment was organized which included sampling of the slag and matte from the furnace roof using so-called deep sounding during stable operation of the furnace [10]. The position of the measuring points (MM), the sampling probe shape and the metallographic preview of the captured samples' cross-section are presented in the

Figure 1. The sound is made of steel pipe having inner diameter of 12.7 mm and length of 6000 mm. The plug is positioned at the lower band of the pipe which is connected with the steel wire that goes through the pipe. The sound is slowly lowered down from the furnace roof and sunken in the melt at the location of the measuring points (MM), until reaching the bottom of the furnace. During this, the sound is filled with the melted slag and the matte, entering through the gap between pipe and the plug. During the time of 30 seconds, the sound reaches the bottom of the furnace, the plug is closed under pressure and sound is lifted through the furnace roof. Because the temperature is too high at the measuring points MM1 and MM2 they were omitted and measuring was performed only at the points MM3-MM6. After cooling in the air, the sound is cut down transversely to determine the border between the slag and the matte. From each probe in the sound four slag samples are obtained. Slag samples were collected from the surface of the slag (I); at the distance of

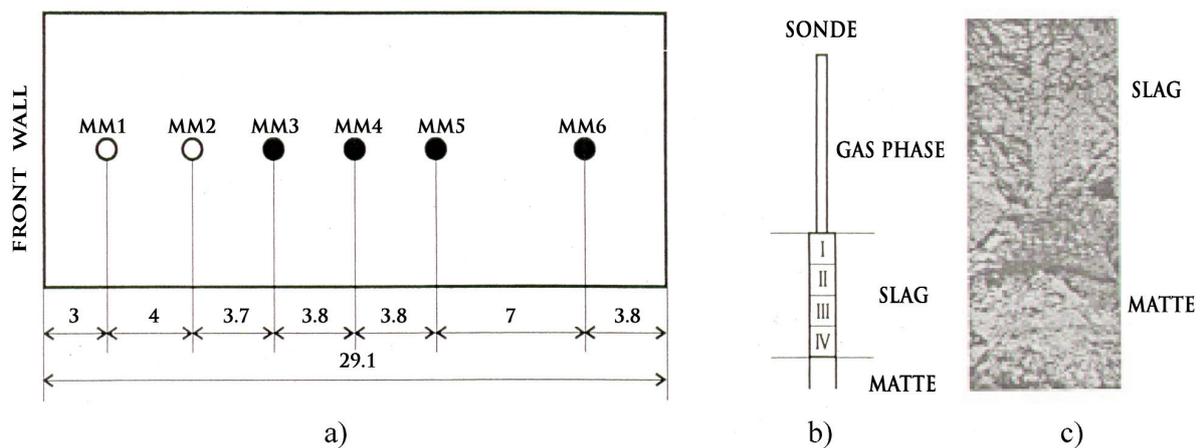


Fig. 1. Schematic presentation of the sampling places (MM=measuring points) in the reverberatory furnace (a), preview of the sampling probe-sound (b) and metallographic presentation of the captured samples' cross-section in the sound (c).

60 mm below the surface of the slag (II); at the distance of 120 mm below the surface of the slag (III) and at the distance of 180 mm below the slag surface. The matte sample was obtained at 10 mm below the border between the slag and the matte. The latitude of each sample for the chemical analysis was 10 mm.

Technological parameters of the furnace operation, for the day in which the sampling was performed, were: 570 tons of produced copper matte with the copper content, in the cumulative sample, 42.12% and 940 tons of slag with 0.49% Cu in the cumulative sample. This indicates the stable furnace operation conditions.

Wet chemical analysis was performed on the samples. For quantitative determination of the elements, with the concentration above 0.1%, optical emission spectrograph

OES JARRELL – Ash 70.000 (SAD) was used, while for the elements with the concentration below 0.1%, mass spectrograph JOEL JMS – 0.1 MB (Japan) with ionic optical system Matauh – Herzog, was used. Concentration of the basic elements contained in the slag and the matte is presented in the Table 1.

For processing of the obtained results with the aim to determine analytical dependence $(Cu) = f(\text{slag composition, matte composition})$, for each particular component and for whole set, Multiple Linear Regression Analysis (MLRA) was used. This method is often used for investigations of this kind. When the fitting level is unsatisfactory, MLRA is usually combined with the Artificial Neural Network (ANN) to obtain credible results [16-19].

Table 1. Concentration of the main slag and matte constituents in the samples collected along the furnace length (measuring points MM3-MM6) and the distance from the slag surface (samples I – IV)

	Sample															
	MM3				MM4				MM5				MM6			
	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV
Copper Slag																
Cusulfide [%]	0.32	0.34	0.40	0.42	0.35	0.38	0.48	0.54	0.46	0.47	0.55	0.62	0.50	0.51	0.59	0.67
Cu _{ox} [%]	0.12	0.13	0.14	0.16	0.13	0.14	0.15	0.17	0.14	0.15	0.17	0.18	0.15	0.16	0.18	0.20
Cu Σ [%]	0.44	0.47	0.54	0.58	0.48	0.52	0.63	0.71	0.60	0.62	0.72	0.80	0.65	0.67	0.77	0.87
SiO ₂ [%]	33.62	33.38	32.78	32.62	33.10	32.70	32.20	32.06	31.94	31.80	31.48	31.02	31.08	30.96	30.78	30.40
FeO [%]	42.26	42.73	43.28	43.56	42.86	43.18	43.69	44.68	44.08	44.28	44.84	46.06	44.75	45.03	45.91	46.69
Fe ₃ O ₄ [%]	7.14	7.29	7.38	7.42	7.31	7.38	7.42	7.49	7.43	7.47	7.53	7.61	7.55	7.57	7.66	7.68
CaO [%]	4.95	4.92	4.87	4.76	4.90	4.84	4.76	4.67	4.73	4.70	4.67	4.63	4.63	4.62	4.60	4.56
Al ₂ O ₃ [%]	3.65	3.59	3.51	3.46	3.55	3.51	3.44	3.42	3.44	3.41	3.39	3.35	3.35	3.31	3.27	3.24
Copper Matte																
Cu [%]	36.31				39.66				40.84				42.12			
Fe [%]	34.91				31.58				30.65				29.44			
S [%]	26.13				25.80				25.67				25.45			

3. Results and discussion

The results presented in the literature indicate that the chemical composition of the slag has strong influence on its copper contents [3-5]. According to the long years of practice of the copper smelter plant in Bor, the content of the main slag constituents is in the following range: SiO₂: 30 – 35%; FeO: 40- 50 %; Fe₃O₄ : 5 – 8 %; CaO : 4 – 6 % and Al₂O₃ : 3 – 6 %. Copper content in the matte is ranging from 30 to 45% [3].

Results obtained in the experiments that are analyzed in this paper, Table 1, are inside these range which indicates that they can be regarded as representative data set for analyses described in the following text.

3.1. The influence of the SiO₂ content in the slag

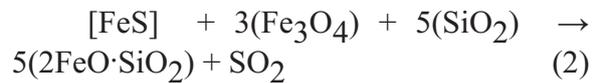
The SiO₂ and FeO are presenting more than 70% of the slag content, in the form of fayalite (2FeO·SiO₂) which is the main compound of the slag and has dominant influence on its physicochemical

characteristics. Figure 2 presents the dependence of the copper content in the slag on SiO₂.

Obtained linear dependency:

$$(Cu) = - 0.116(SiO_2) + 4.357 \quad (1)$$

With the coefficient of determination R²= 0.855 indicate well fitting of the obtained results. Results presented in Figure 2 are suggesting that increase in the SiO₂ content leads to decrease of the copper content in the slag. This dependence is resulting from moving the equilibrium of the reaction, happening at the phase border between slag and matte, to the right:



This way, decrease in oxidation potential of the melt is occurring which leads to decrease in oxidation rate of the copper sulfide oxidizing to Cu₂O and, accordingly, the content of chemically dissolved copper in the slag is then lower [3,4]. Increase of the SiO₂ content in the slag leads to development of Si-O anion complexes,

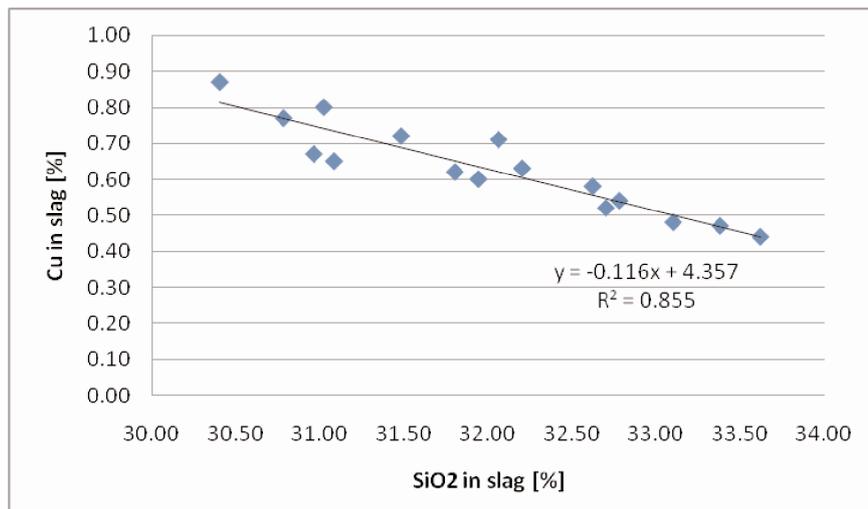
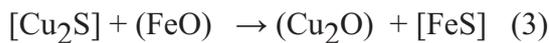


Fig. 2. Dependence between the copper and the SiO₂ content in the smelting slag

which decrease ionic electron exchange through the phase border, which leads to increase of the surface tension at the matte slag bordering layer. Besides, increased SiO_2 content is extensively banding FeO , thus forming fayalite and interrupting silicon net structure, which leads to decrease in the viscosity of the slag. Such conditions improve coalescence of the dispersed copper matte drops in the slag which decrease mechanical copper losses.

3.2. The influence of the FeO content in the slag

Increase of the FeO content in the slag is moving the equilibrium of the equation (3) to the right, which is in the direction of increased copper solubility in the slag [1]:



Besides, increase of the FeO content in

the slag leads to expanding of the ionic – electron areas rich in ferric oxide, whose amount is in direct connection with solubility of the copper sulfides and consequently the electron exchange at the matte-slag phase border. This leads to decrease of the surface tension at the boundary between the copper matte and the slag. Above conditions are worsening the coalescence of the copper drops in the slag, which leads to aggravating stratification in the melt of the copper matte and the slag and, accordingly, increase of the copper losses in the slag. Figure 3 is presenting dependence between the copper content in the slag a FeO content.

Obtained linear dependence (Cu) = $f(\text{FeO})$ is in the form:

$$(\text{Cu}) = 0.094(\text{FeO}) - 3.528 \quad (4)$$

The coefficient of determination $R^2 = 0.946$ for above dependence (4) indicate good fitting of the obtained results.

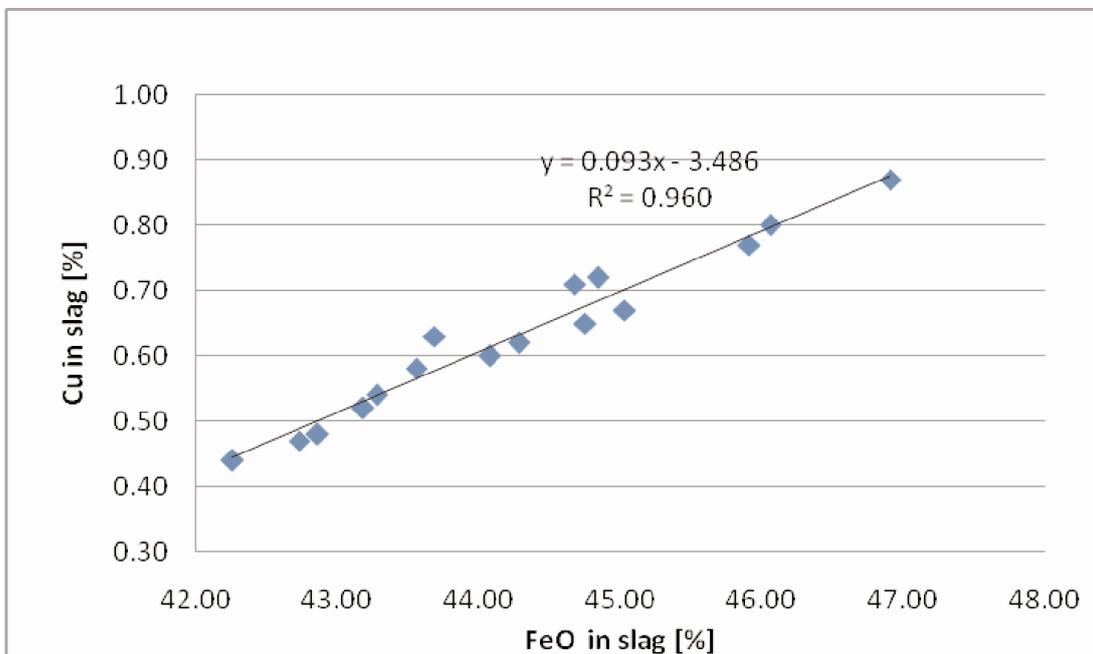
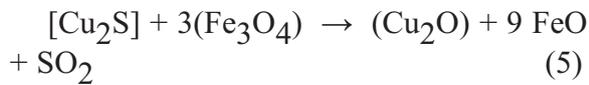


Fig. 3. Dependence between the copper and the FeO content in the slag

3.3. The influence of the magnetite content in the slag

Magnetite is unwanted component in the copper slag which is formed during smelting process but also is added with the returned converter slag [3]. With increase of the Fe₃O₄ in the slag the equilibrium of the reaction (5) is moved to the right, which increases oxidation potential of the slag, this way chemical solubility of the copper in the slag becomes higher.



The dependence between copper and magnetite content in the slag, which indicate increase of the Cu content resulting from the increase in Fe₃O₄, is presented in the fig. 4.

According to the results presented in the Figure 4 and using MLRA, dependence of the copper content on magnetite content in

the slag, is defined in following way:

$$(\text{Cu}) = 0.758(\text{Fe}_3\text{O}_4) - 5.032 \quad (6)$$

The coefficient of determination is $R^2 = 0.87$ which indicate proper fitting of the obtained results.

Increase of the Fe₃O₄ content in the slag, besides movement of the equation's (5) equilibrium to the right, at the same time leads to separation of the magnetite crystals, which causes heterogenization of the silicate melt and sudden increase of its viscosity, and this way increase of the mechanical losses of copper in the slag.

3.4. The influence of the CaO content in the slag

The increase in the CaO content in the slag leads to destruction of the silicate network [1,3], which results in decrease of the slag's viscosity and copper losses in it.

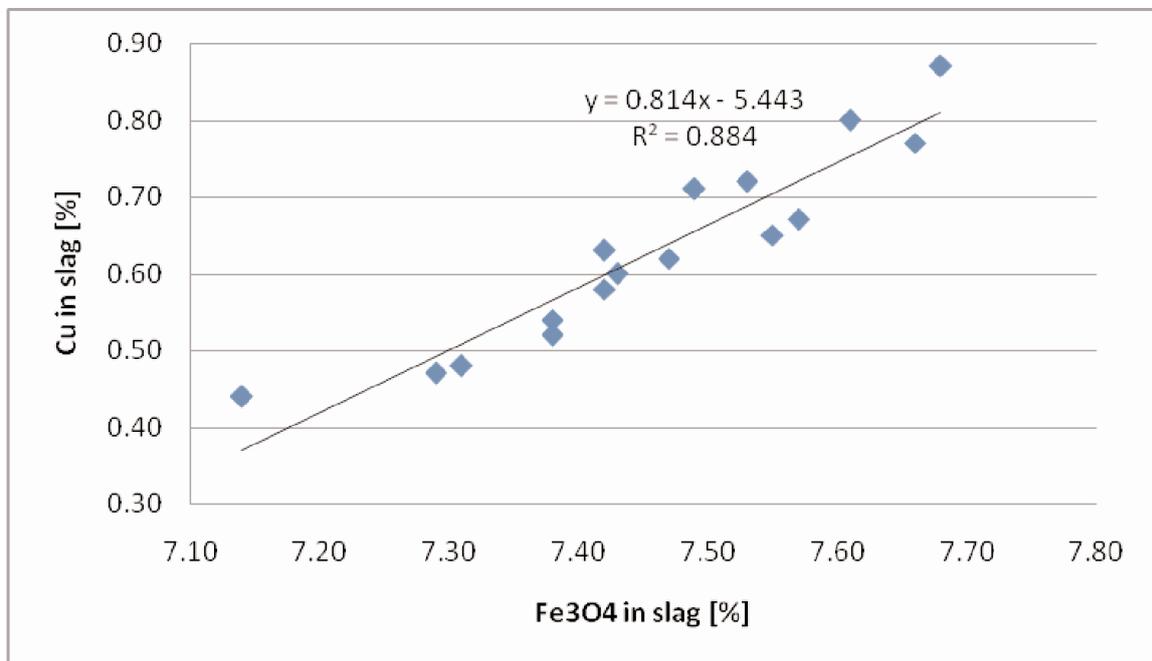


Fig. 4. The influence of the Fe₃O₄ content on Cu losses in the slag

For the case of the system described in this study, Figure 5 presents dependence between the copper and the CaO content in the slag.

Obtained linear dependence $(Cu) = a + b(CaO)$ has following analytical form:

$$(Cu) = - 0.896(CaO) + 4.701 \quad (7)$$

Obtained coefficient of determination $R^2=0.896$, indicates well fitting of the obtained results.

Decrease of the copper content in the slag with increase of the CaO content is happening because CaO is destructing the silicate network structure most easily and this way leads to decrease of its viscosity [4], which enhances stratification of the smelting products and lower mechanical losses of copper in the slag.

3.5. The influence of the Al_2O_3 content in the slag

As principle, the increase of the Al_2O_3 content in the slag leads to formation of the Al-O complexes because of the high ionic

potential of the Al^{3+} ions. This amplifies the effect of the Si-O complex, and this is why its role can be defined as network building compound [3]. Figure 6 is presenting the dependence between copper losses and Al_2O_3 content in the slag.

According to the results, which are presented in Figure 6, and according to the MLRA methodology following analytical dependence $(Cu)=f(Al_2O_3)$ was formulated:

$$(Cu) = - 0.947 (Al_2O_3) + 3.822 \quad (8)$$

The coefficient of determination $R^2 = 0.822$ indicates relatively well fitting of the obtained results.

Increase of the Al_2O_3 content in the slag is leading to creation of the Al-O complexes. Those complexes decrease oxidation potential of the copper melt, and accordingly amount of the copper oxides which are easily dissolved in the slag. At the same time, with development of the Al-O complex, interphasial tension is increasing between matte and the slag which leads to decrease of the mechanical copper losses in the slag.

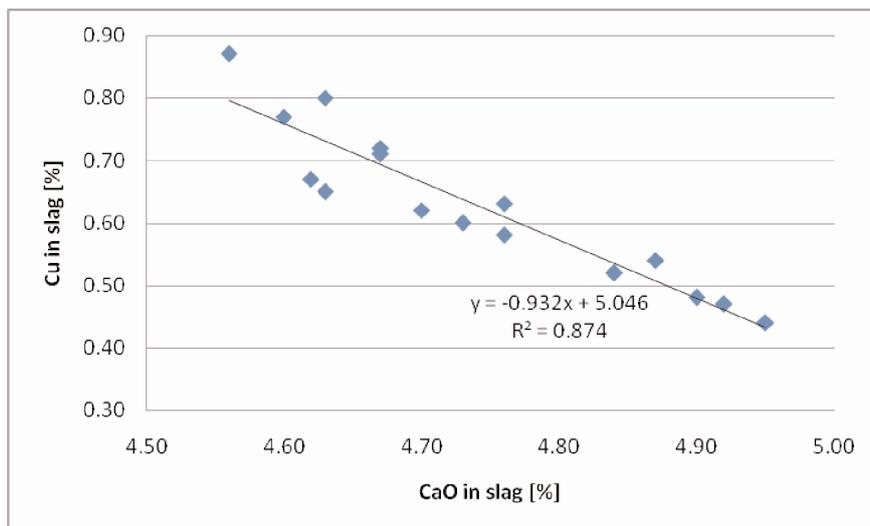


Fig. 5. The influence of the CaO content on copper losses in the slag

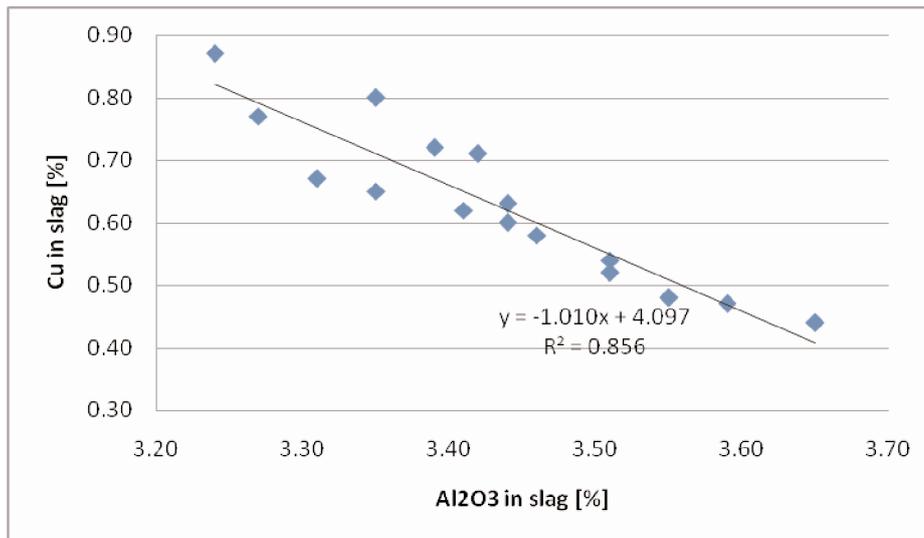


Fig. 6. The influence of Al₂O₃ content on copper losses in the slag

3.6. Influence of the copper content in the matte

Concerning that part of the copper matte is kept in the slag as unprecipitated drops, if these drops have larger copper content, the losses of copper in the slag is also increasing. Figure 7 presents dependence between copper content the matte and the slag, according to the data from the Table 1.

According to the results presented in Figure 7, following analytical form of the dependence (Cu) = f ([Cu]), was formed:

$$(Cu) = 0.04[Cu] - 0.96 \tag{9}$$

Value of the coefficient of determination $R^2 = 0.518$ indicates relatively low fitting. Compared to the previously discussed results, fitting is not that well because of smaller quantity of the data available. Regarding the fact that degree of desulfurization, obtained during roasting, can be used for managing of the copper content in the matte as well as the other components content [9-11], obtained results

should be helpful for the copper smelter management considering the control of the matte and the slag content.

3.7. Determining the copper content in the slag, as the function of its composition and depending on the copper content in the copper matte, using Multiple Linear Regression Analysis

Calculated dependences for the copper content in the slag as the function of the content of individual slag component, while the content of all the other compounds is regarded constant, can result only with approximate information on each compounds' influence. On the other hand, because of the fact that the slag is composed of complex compounds and that the slag composition is changed constantly, even outside the narrow borders defined by the technology of the smelting operation, important information can be obtained using statistical analysis of the content of all compounds in the slag as well as copper

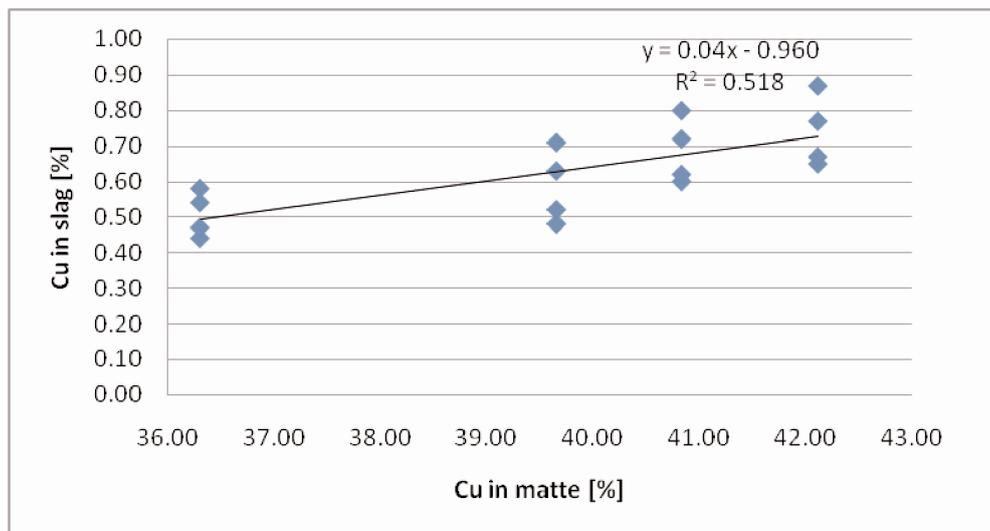


Fig. 7. Dependence between the copper losses in the slag and its content in the matte

content in the matte, considering that the reactions (2), (3) and (5) are happening at the slag-matte phase border. For determination of the quantitative dependence of the copper content in the slag, on slag composition and content of the copper in the matte, Multiple Linear Regression Analysis (MLRA) was used as the part of the SPSS software application. The MLRA is defining the output of the linear correlation of one variable (copper content in the slag) depending on the slag composition (content of slag constituents) and the content of the copper in the matte. This dependence can be presented in the following form:

$$(Cu) = a + b(SiO_2) + c(FeO) + d(Fe_3O_4) + e(CaO) + f(Al_2O_3) + g[Cu] \quad (10)$$

Where: a,b,c,d,e,f and g are coefficients in the linear regression equation, and (), [] are the concentrations of the slag components in %.

Obtained values for the coefficients in the equation (10), according to the MLRA, is defining following dependence of $(Cu) = f$

(slag composition, copper content in the matte):

$$(Cu) = - 4.545 + 0.059(SiO_2) + 0.098(FeO) + 0.093(Fe_3O_4) - 0.446(CaO) + 0.129(Al_2O_3) - 0.002[Cu] \quad (11)$$

This dependence enables prediction of the copper content in the slag according to its composition and according to the copper content in the matte. Using MLRA in the frame of the SPSS software, testing of the above model validity (equation 11) was performed. For the testing operation, calculated values were compared to the experimentally obtained. Dependence between measured and calculated values of the copper content in the slag is presented in Figure 8.

Calculated value of the coefficient of determination ($R^2 = 0.974$) is indicating that the copper content in the waste slag can be predicted with probability above 97%, in case that its composition is known as well as the content of the copper in the matte. Considering that composition of the charge

can be controlled, as well as the degree of desulfurization during oxidation roasting, copper losses in the slag could be managed, using dependence (11), with the accuracy of 97%. This improves overall management of the pirometallurgical copper extraction process at the stage of the silicate smelting. Remaining 3% can be regarded as influence of other parameters, mostly related to the dynamic of smelting operation in the furnace and these are strongly related to the human factor.

4. Conclusions

After examining the influence of the individual constituents of the reverberatory furnace smelting operation: (SiO₂); (FeO); (Fe₃O₄); (CaO), (Al₂O₃) and copper

content in the matte [Cu]; on copper content in the waste slag (Cu) using the MLRA method, following coefficients of determination were obtained: 0.855; 0.946; 0.87; 0.869; 0.822 and 0.518. These results indicate good fitting of the results obtained at the industrial level in the form of defined linear dependences of the copper contents in the slag as the function of individual slag constituents' percentage. Also, these results show that prediction of the influence of each component's concentration on copper content can be accurate above 80%. The prediction of the copper losses in the slag as the function of copper content in the matte has the accuracy of 51%.

At the same time, when considering all the parameters: slag's composition and copper content in the matte, correlation

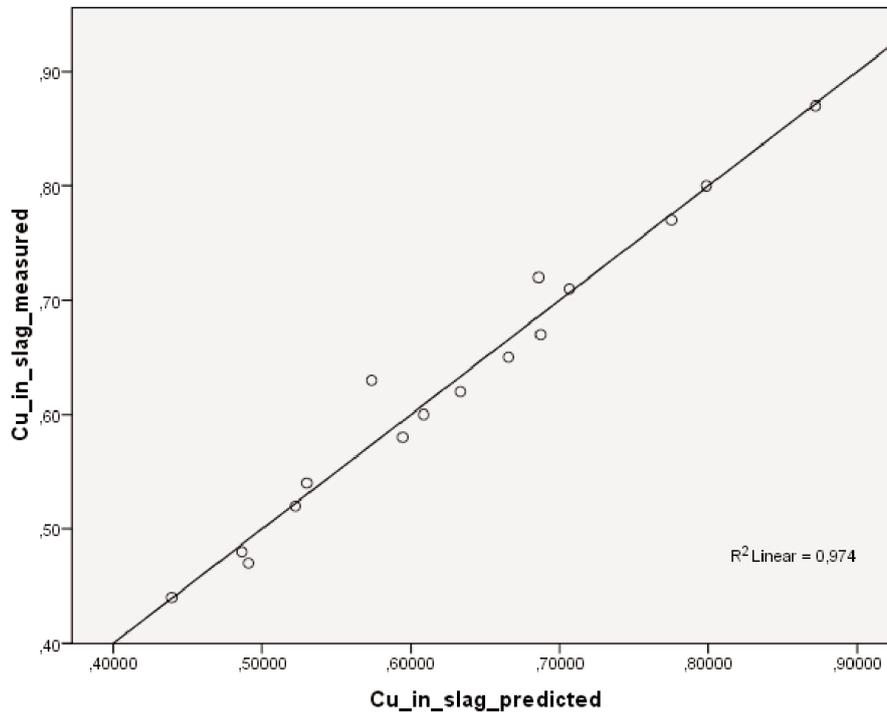


Fig. 8. Dependence between measured and calculated values for the copper content in the slag using MLRA methodology

among measured and calculated values of copper content in the waste slag is obtained with the determination coefficient equal to $R^2 = 0.974$. This indicates that management and control of the copper losses in the slag could be achieved at the level of accuracy over 97% through controlling of the input charge composition and the degree of desulfurization during roasting. Results obtained during regular, real time, control of the process indicate less fitting level which can be explained with higher variation of the technological parameters as the influence of human factor in the management of technological process.

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