A study on copper recovery from the slag of Outokumpu direct-to-copper process

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Abstract: The work was aimed at the investigation of the influence of the carbon reducer's surface on the rate of the de-coppering of the slag from the flash direct-to-blister process at the Głogów II smelter, Poland. It was found that, for the experimental conditions, the copper recovery from the slag increases as the interface of the slag/carbon increases; however this is the case only to some extent. It is very likely that this limit would depend on the geometry of the investigated system. Further increase of the slag/carbon interface does not noticeably change the final copper content in the slag. The obtained results do not follow any of the reaction rate equations, so it can suggest that the transport phenomena play the key role in the de-coppering process. The investigated slag has probably a higher viscosity, which hampers the mass transfer in this slag. This hypothesis is supported by the fact that the slag layer situated below the penetrator is of a different colour than the slag in the vicinity of those penetrators where it was agitated by the CO, and CO_2 gases generated by the reactions of the slag reductions. The slag in the layer under the penetrator contained more copper than the slag above this layer.

Key words: copper recovery, Outokumpu direct-to-copper process

1. Introduction

The Outokumpu direct-to-blister process was commercially implemented in 1978, in Głogów, Poland. The process requires a high oxygen potential and therefore is restricted to those smelting concentrates which mainly consist of minerals without iron (e g Cu_2S, CuS, Cu_9S_5) or with a small iron content (Cu_5FeS_4). As a consequence of the high oxygen potential in an Outokumpu flash smelting furnace, the produced slag contains 12-16% Cu in the Głogów case. The copper in the slag is accounted for the approximately 1/3 of the copper content in the smelting concentrate. Therefore, the recovery of the copper from this slag has a practical importance and heavily influences the operational costs. A part of the copper in the slag is in form of fine inclusions suspended in the slag; however, the majority of the copper is dissolved in it. The slag cleaning process is carried out in an electric furnace with coke and limestone additions. The limestone modifies the reduced slag in order to facilitate the process. Slags are ionic liquids [1-3], and the copper in the slags exists as Cu_2O and Cu^+ associated with the silicate anions, according to the reaction:

$$\left({}^{-}O - \overset{|}{\underset{|}{Si}} - O - \overset{|}{\underset{|}{Si}} - O^{-} \right) + Cu_2O = 2\left({}^{-}O - \overset{|}{\underset{|}{Si}} - O^{-}Cu^{+} \right) \qquad (1)$$

Cu_2O is a basic oxide and the oxygen ion from it breaks the bridge in the Si-O network structure, which leads to the dissociation of the silicate anion complexes. During the reduction process, the situation becomes reverse. This model [4] suggests that the dissolved copper is almost entirely in the form of (-Si-O-Cu^+), for slags containing about 1 wt-% of copper. This can be taken as an explanation of the sluggishness of the copper recovery process, when it is close to completion, as the slag reduction proceeds according to the reactions:

$$Cu_2O + C = 2[Cu] + CO \quad (2)$$

$$Cu_2O + CO = 2[Cu] + CO_2 \quad (3)$$

The addition of metal oxides (CaO, FeO,…) to the slag causes some of the copper ionic Cu^+ to be replaced by Ca^{2+} ionic and therefore, the number of (Cu_2O) increases. In this paper, the influence of the coal/slag interface on the rate of the copper recovery from the slag of the direct-to-blister flash smelting process was investigated.

2. Apparatus

A schematic diagram of the apparatus used in this study is shown in Figure 1. It consists of a furnace with Superkantal heating elements, powered by means of a transformer controlled by a Eurotherm controller, which is also connected to a controlling thermocouple Pt-PtRh10.

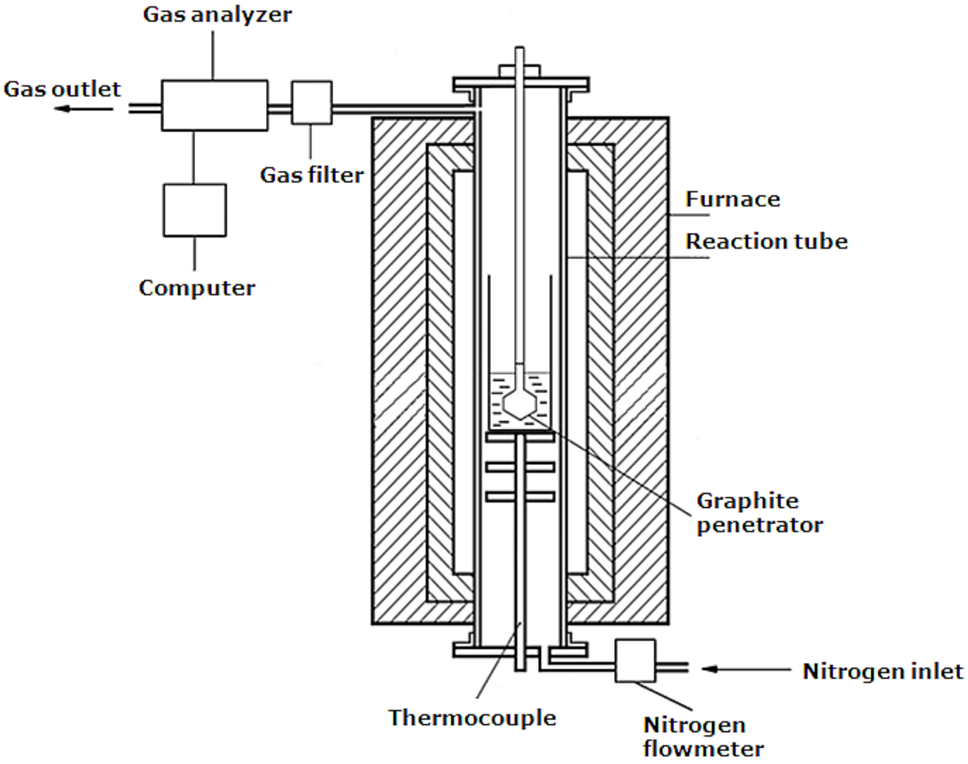

Fig. 1. Experimental apparatus

The furnace temperature was maintained at ± 2 K and the maximum temperature variation in the hot zone was ± 3 K. An alumina reaction tube was sealed at the top and the bottom by means of water cooled brass caps and with the use of rubber O-rings. The measuring thermocouple Pt-PtRh10 was situated close to the crucible with the investigated slag, and it measured the temperature of the sample with a Keithley’s multimeter 2000. The graphite penetrators were placed under the upper cap of the reaction tube. The experiment started when the graphite penetrator was transferred into the slag. In this study four kinds of penetrators of different surfaces were used, as can be seen in Fig. 2.

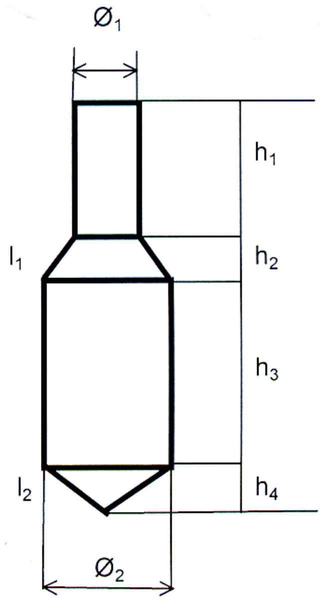

Fig. 2. Shape of the graphite penetrators used in this study

The dimension of these penetrators and their surfaces are enclosed in Table 1.

Table 1. Dimensions of the penetrators and their surfaces

	Penetrator 1	Penetrator 2	Penetrator 3	Penetrator 3
ϕ_1, [mm]	11	11	11	11
ϕ_2, [mm]	15	20	25	30
h_1, [mm]	15	15	15	15
h_2, [mm]	5	5	5	5
h_3, [mm]	25	25	25	25
h_4, [mm]	5	5	5	5
S, [cm^2]	**16.1**	**22.5**	**29.8**	**37.9**

Purified nitrogen of 25l/h flow rate was admitted to the reaction tube just after the sample was put into the reaction tube and during the experimental run. The nitrogen flow rate was controlled with the use of an electronic flow meter manufactured by Brooks. The gas train was made by means of steel tubing connected to Hoke's fittings and valves. During the experiments, a gas composed of nitrogen, carbon monoxide and carbon dioxide was formed as a result of the reactions between the graphite and the slag. The CO and CO_2 were determined by a gas analyzer for CO and CO_2 every 5 seconds and the results were recorded by the computer.

3. Calibrations of the gas analyzer

An infrared gas analyzer was used in this study to analyze the CO and CO_2 in the N_2-CO-CO_2 mixture. To speed up the passage of the reaction gas through the reaction tube, nitrogen of 25 dm^3/h flow rate was admitted. For this reason, the gas analyzer had to be calibrated. The calibration was carried out by allowing a passage of a gas mixture containing nitrogen of 25 dm^3/h flow rate with additions of predetermined flow rates of CO, CO_2, and CO - CO_2. The flow rates of these gases were controlled by Brooks flow meters and corrected to 273 K. In consequence, the gas analyzer showed some readings for CO and CO_2 and the results were recorded by the computer. If the obtained reading of %CO and %CO_2 did not change with time, then these values were taken as true values. Figure 3 shows the relation between the gas analyzer reading for CO and the fraction of CO in the gas mixtures admitted into the reaction tube.

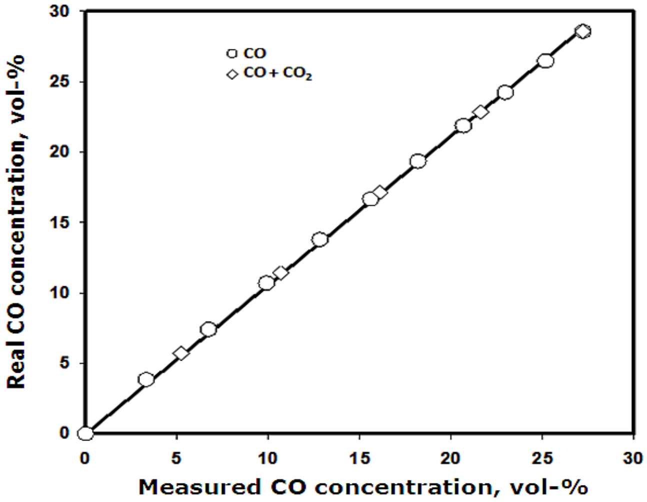

Fig. 3. Correlation between the reading of the gas analyzer for CO and the carbon oxide fraction in the gas mixture N_2-CO-CO_2 passing through the reaction tube of the furnace

A similar correlation was obtained for CO_2. It was assumed that these correlations can be described by the following relations:

$$(\%CO)_{real} = A \cdot (\%CO)_{measured} \tag{4}$$

$$(\%CO_2)_{real} = B \cdot (\%CO_2)_{measured} \tag{5}$$

where:

A – the slope of the calibration straight line for CO,

B – the slope of the calibration straight line for CO_2,

$$(\%CO)_{real} = \frac{100 \cdot V_{CO}}{V_{N_2} + V_{CO} + V_{CO_2}}$$

$\%CO,\ \%CO_2$ - the analyzer readings for CO and CO_2, respectively,

$V_{CO},\ V_{CO_2}$ - the flow rates of CO and CO_2 in [dm^3/h].

With the least squares methods and the calibration results, the “A” and “B” coefficients were determined:

$$(\%CO)_{real} = 1{,}058 \cdot (\%CO)_{measured} \tag{6}$$

$$(\%CO_2)_{real} = 0{,}978 \cdot (\%CO_2)_{measured} \tag{7}$$

Relations (6) and (7) were used for the determination of the flow rates of the CO and CO_2 formed during the reduction process between two consecutive readings of the gas analyzer.

$$V_{CO} = \frac{25 \times (\%CO)}{94{,}48 - (\%CO) - 0{,}942 \times (\%CO_2)} \tag{8}$$

$$V_{CO_2} = \frac{25 \times (\%CO_2)}{102{,}25 - (\%CO_2) - 1{,}08 \times (\%CO)} \tag{9}$$

As the analyzer readings were adjusted to 273 K, the numbers of the CO and CO_2 moles per one second could be calculated from the relations:

$$n_{CO} = \frac{V_{CO}}{22.4 \times 3600} \tag{10}$$

$$n_{CO_2} = \frac{V_{CO_2}}{22.4 \times 3600} \tag{11}$$

The number of the oxygen moles reduced from the slag during a period of 5 seconds was determined from the relation:

$$n_O^i = \frac{n_{CO}^i + n_{CO}^{i+1}}{2} \times 5 + 2 \times \frac{n_{CO_2}^i + n_{CO_2}^{i+1}}{2} \times 5 \tag{12}$$

where:

n_{CO}^{i}, n_{CO}^{i+1} - the number of the CO moles formed during the reduction process per one second, recorded in two consecutive measurements,

$n_{CO_2}^{(i)}$, $n_{CO_2}^{i+1}$ - the number of the CO_2 moles formed during the reduction process per one second, recorded in two consecutive measurements.

4. Experimental procedure

A slag produced by the Głogów direct-to-blister flash smelter was used in this study. The main constituents of this slag are listed in Table 2.

Table 2. Composition of the Głogów direct-to blister flush smelter slag used in this work

Components	Cu	Pb	Fe	Zn	SiO_2	MgO	CaO	Al_2O_3
wt-%	14.31	1.52	7.81	0.87	44.7	3.85	9.0	5.52

The crucible with the slag of 160 g was placed in the reaction tube of the furnace. In the upper cap of the reaction tube a graphite penetrator was situated. A nitrogen stream of 25 dm^3/h flow rate was introduced to the reaction tube of the furnace through its bottom cap. After about 5 hrs, the furnace was switched on and the temperature controller adjusted to 573 K. The furnace was kept in these conditions for approximately 12 hours. Next, the temperature of the furnace was elevated to 1573 K . The sample was kept at this temperature for one hour and then the aluminous tube with the graphite penetrator was transferred into the slag. The immersion of the graphite penetrator in the slag was taken as the beginning of the reduction process. However, the first signal of the reduction process was detectable after about 60 seconds following that moment. The gas living the reaction tube was analyzed for the CO and CO_2 content every 5 seconds by the gas analyzer and the results were recorded by the computer. It was assumed that the reduction would take place on the graphite/slag interface and that it was equal to the surface of the graphite penetrator. An example of the obtained results is shown in Figure 4. In the first stage, the temperature of the penetrator was equalizing with the temperature of the slag, and the reduced slag was foaming, because of the noticeable increase of the CO_2 content observed in the gas phase. It resulted from the reaction:

$$(MeO)_{slag} + CO = [Me]_{alloy} + CO_2 \tag{13}$$

Then the height of the slag foam decreased and this fact was indicated by CO_2 decreases and a simultaneous increases of the CO content. In the next stage, the foam decayed and the reduction took place on the slag/penetrator interface. When the reaction came to an end, the CO and CO_2 content decreased steadily diluted by the incoming nitrogen.

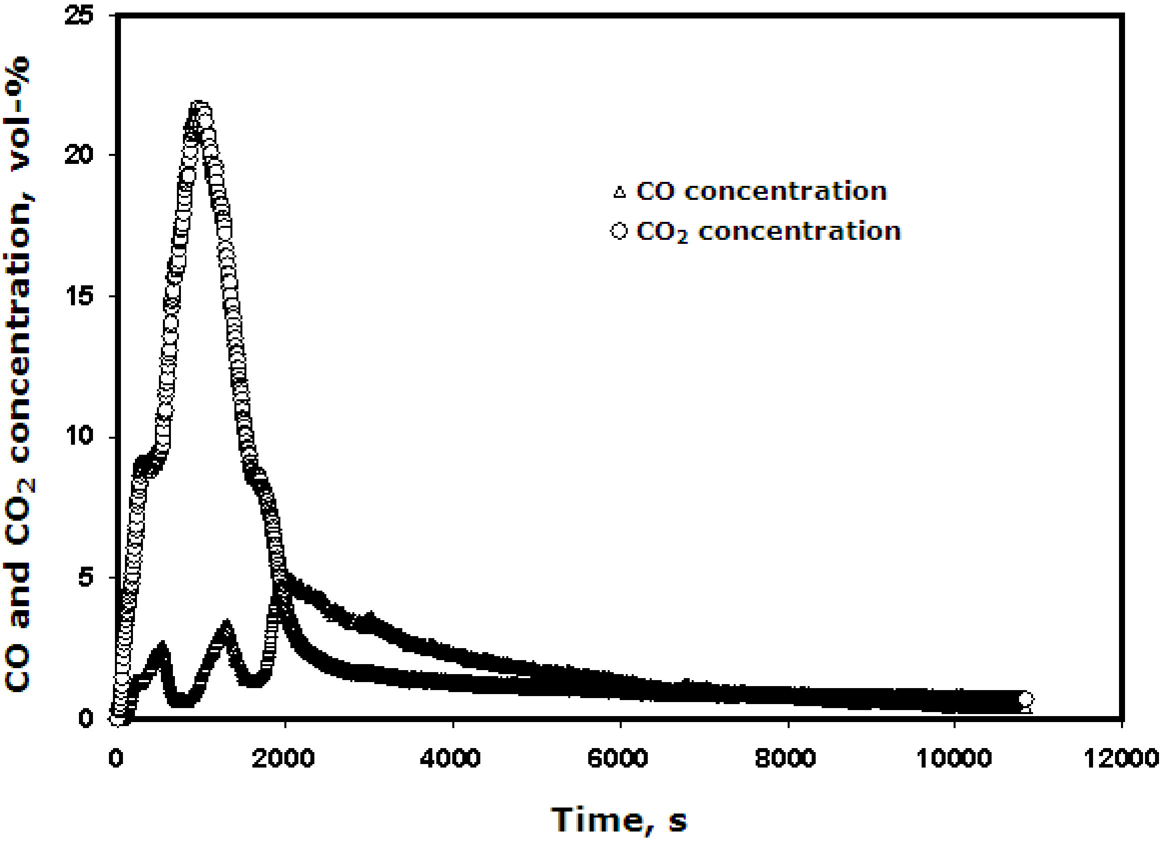

Fig. 4. Gas analyzer readings for the reduction of the slag

By a summation of the n_O^i values with the relation (12), the equation $n_O(t)$ describing the oxygen removed from the slag as a function of the reduction time was determined. Figure 5 shows an example of such functions.

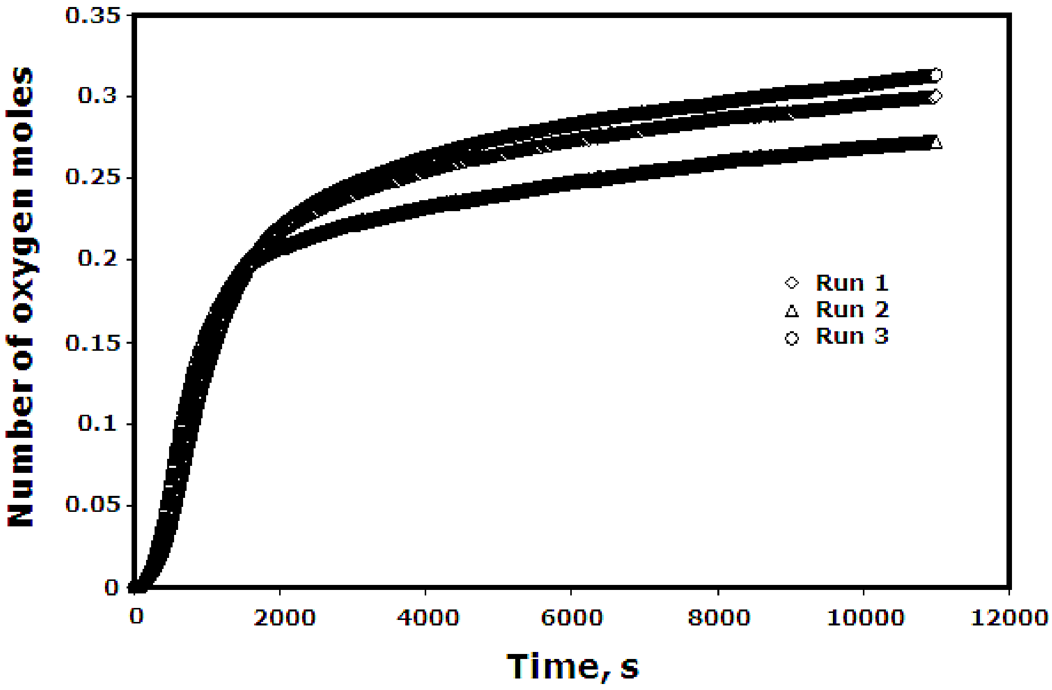

Fig. 5. Relation between the removed oxygen from the slag for the case when penetrator no 4 was employed

Table 3. Results of the chemical analyzes of the slags before and after the reductions process by means of different graphite penetrators.

Components, wt-%	Slag before experiments	Penetrator no 1			Penetrator no 2		
		Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
Na_2O	0.40	0.66	0.63	0.62	0.67	0.65	0.65
K_2O	2.28	3.48	3.43	3.45	3.53	3.61	3.57
CaO	9.00	12.70	12.25	12.34	12.77	12.75	14.26
MgO	3.85	5.13	4.92	4.67	5.05	5.09	5.18
SiO_2	44.70	47.10	46.90	47.50	48.10	47.00	44.60
Al_2O_3	5.52	13.18	13.91	14.36	13.28	13.94	14.67
Fe	7.81	9.54	9.07	8.58	9.01	9.36	9.80
Zn	0.87	0.94	0.78	0.82	0.84	0.72	0.78
Pb	1.52	1.27	1.05	0.94	0.80	0.76	0.63
Cu	14.31	0.69	1.50	0.58	0.45	0.37	0.38

Table 3 (continued). Results of the chemical analyzes of the slags reduced by means of different graphite penetrators.

Components, wt-%	Penetrator no 3			Penetrator no 4		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
Na_2O	0.64	0.63	0.62	0.64	0.65	0.64
K_2O	3.33	3.52	3.46	3.47	3.62	3.52
CaO	12.49	14.12	14.37	14.59	14.40	14.03
MgO	5.03	5.10	4.82	4.97	5.01	5.18
SiO_2	48.9	46.20	48.30	47.30	48.30	46.80
Al_2O_3	13.36	13.90	14.64	14.36	14.03	13.84
Fe	9.41	9.35	8.89	9.00	8.95	9.23
Zn	0.65	0.76	0.68	0.64	0.63	0.61
Pb	0.69	0.62	0.42	0.33	0.38	0.40
Cu	0.97	0.35	0.34	0.35	0.43	0.28

The obtained results are partially similar to those reported in paper [5], however there are very distinguished differences, which are manifested by the fact that the process of the oxygen removal from the investigated slag was a reaction of the first order. For every size of the penetrator, three experiments were conducted, and the obtained results are enclosed in Table 3.

The reduced Cu-Pb-Fe alloys were chemically analyzed and the obtained results are given in Table 4. Despite the fact that the samples of these alloys were taken from their different places, quite big differences are observed. This is because the Cu-Pb-Fe system exhibits limited solubility in the liquid and solid state.

Table 4. Results of the chemical analyzes of the Cu-Pb-Fe alloys obtained during the slag reduction by means of different graphite penetrators.

Element, wt-%	Penetrator no 1			Penetrator no 2		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
Cu	98.78	96.04	97.89	99.14	99.22	92.75
Fe	0.03	0.01	0.02	0.04	0.01	0.145
Pb	1.31	0.75	1.77	0.49	0.84	7.35

Table 4 (continued). Results of the chemical analyzes of the Cu-Pb-Fe alloys obtained during the slag reduction by means of different graphite penetrators.

Element, wt-%	Penetrator no 3			Penetrator no 4		
	Run 1	Run 2	Run 3	Run 1	Run 2	Run 3
Cu	97.78	94.61	93.17	94.11	94.10	97.73
Fe	0.01	0.00	0.11	0.01	0.00	0.03
Pb	2.08	5.49	6.65	5.26	5.68	1.69

5. Discussion

It was found that the results cannot be described by the equation for the reaction of the first order. However, this relation was successfully applied also for the slag from the direct-to-blister process in paper [5]. The comparison of the compositions (see Table 5) of these slags, reveals that the slag used in this work contains more silica. This suggests that the investigated slag has a higher viscosity which hampers the mass transfer in this slag. This hypothesis is supported by the fact that the slag layer of about 5 mm in thickness situated below the penetrator is of different colour than the slag in the vicinity of those penetrators where it was agitated by the CO, and CO_2 gases generated by reactions (2) and (3). This part of the slag contained more copper than the slag above this layer.

Table 5. Main constituents of the slags used in these investigations and in paper [5].

	%Cu	%Pb	%Fe	%Zn	%SiO_2	%MgO	%CaO	%Al_2O_3
This work	14.31	1.52	7.81	0.87	44.7	3.85	9.0	5.52
Paper [5]	11.41	2.62	11.4	0.85	33.22	4.13	12.87	9.22

The viscosity of a slag depends on its temperature and degree of depolymerization. The degree of depolymerization of the slag can be determined with the parameter D:

$$D = \frac{\sum q \cdot N_{Me_pO_q}}{2 \cdot N_{SiO_2}} \tag{14}$$

where:

$N_{Me_pO_q}$ - number of metal oxides moles in 100 g of the slag,

N_{SiO_2} - number of silica moles in 100 g of the slag.

The numerator of the expression (14) is equal to the number of the oxygen moles [O] associated with basic metal oxides, while the denominator of this expression is equal to the number of the oxygen moles [O] which can be joined to all the silica atoms to form exclusively SiO_4^{4-} anions. The computed values of the parameter D for the investigated slag equals 0.511, while for the slag investigated in paper [5], it is almost twice higher and is equal to 0.962. This can explain the difference in behavior of these slags during the reduction process. The influence of the reducer surface on the rate of the slag de-coppering process is demonstrated by the relation between the time in which all the oxygen associated with the copper dissolved in the slag (Cu_2O) is removed and the surfaces of the penetrators. Fig. 6 shows this relation.

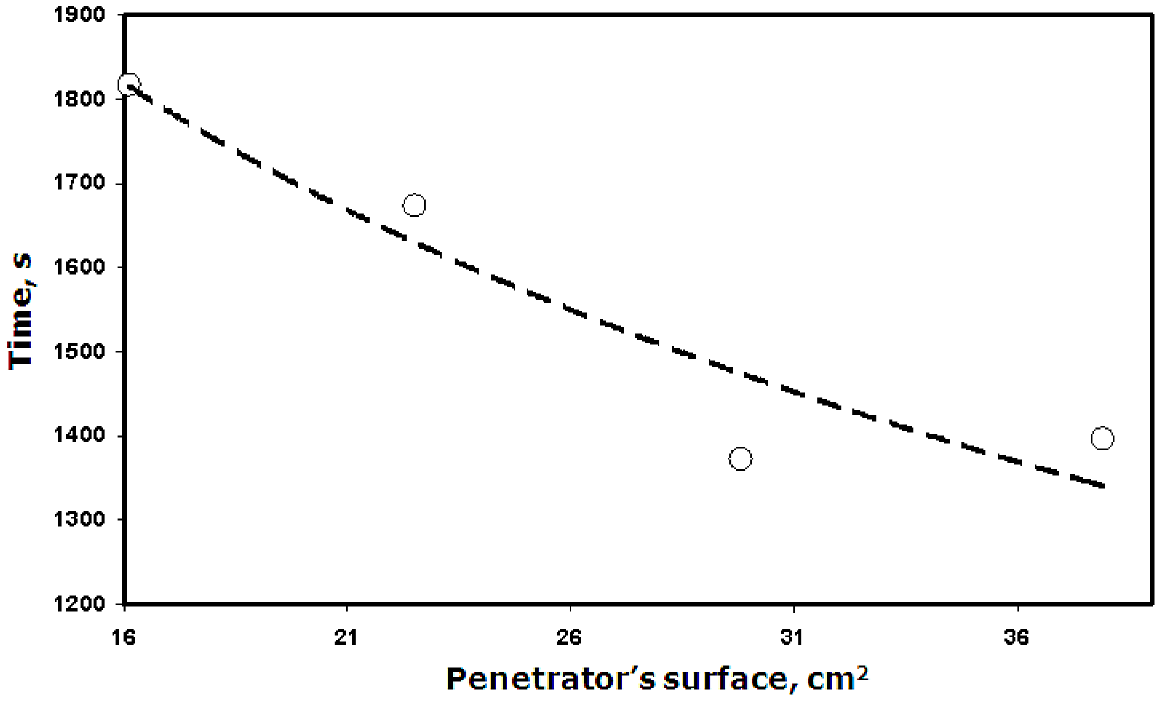

Fig. 6. Relation between the time required for the removal the oxygen associated with the copper dissolved in the slag in form of Cu_2O.

However, it is clear that during the de-coppering proces, copper, lead and iron are reduced simultaenously, but with diffrent rates forming Cu-Pb-Fe alloy. The employed experimental technique is unable to determine the reduction rates of the particular metals.

Figure 6 suggests that the rate of the slag de-coppering process increases with increase of the penetrator's surface, yet to a certain limit. This limit would depend on the geometry of the investigated system. A similar dependence is observed between the final copper content in the slag and the penetrators surface, as can be seen in Fig 7.

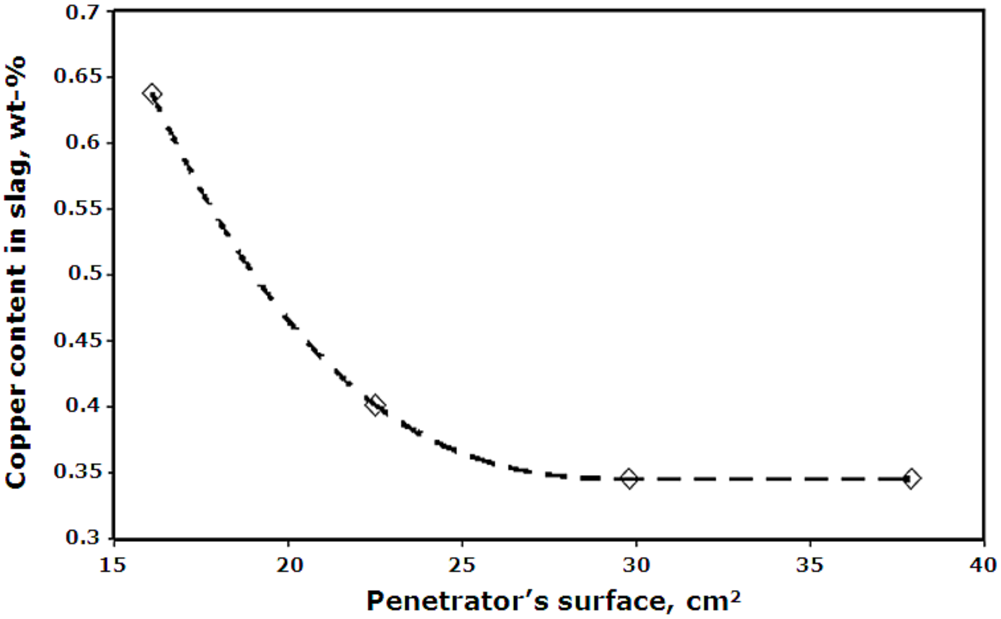

Fig. 7. Relation between the copper final content (mean value from three measurements) and the penetrator's surface.

Figure 7 suggests that the effectiveness of the slag de-coppering process increases with the increase of the penetrator's surface, yet again only to some extent. Further increase of the slag/carbon interface does not result in the lowering of the copper content in the slag after the reduction process.

Acknowledgments

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