

P. MADEJ*, M. KUCHARSKI*#

INFLUENCE OF TEMPERATURE ON THE RATE OF COPPER RECOVERY FROM THE SLAG OF THE FLASH DIRECT-TO-BLISTER PROCESS BY A SOLID CARBON REDUCER

WPLYW TEMPERATURY NA SZYBKOŚĆ ODMIEDZIOWANIA ŻUŻLA Z PROCESU ZAWIESINOWEGO ZA POMOCĄ REDUKTORA WĘGLOWEGO

The aim of the work was to investigate the influence of temperature on the rate of copper removal from the obtained slag from the flash direct-to-blister process by means of a carbon reducer. The slag used in this work was taken from the direct-to-blister Outokumpu flash furnace at the smelter in Głogów, and graphite penetrators were used as the slag reducers. The experiment was carried out at 1573 K, 1623 K and 1673 K. It was found that the rate of the de-coppering process of the "Głogów" slag increased with the increase of temperature.

Keywords:

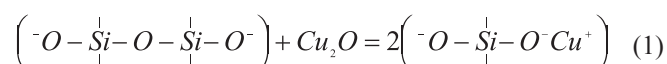
Celem pracy było określenie wpływu temperatury na kinetykę procesu odmiędziowania żużla z procesu zawiesinowego za pomocą reduktora węglowego. Do badań użyto żużel pobrany z procesu zawiesinowego realizowanego w HM „Głogów”, przy czym reduktorem były penetratory grafitowe zanurzone w badanym żużlu. Badania przeprowadzono w temperaturach 1573 K, 1623 K i 1673 K. Uzyskane wyniki wskazują, że szybkość procesu zwiększała się ze wzrostem temperatury ale tylko w pierwszym okresie.

1. Introduction

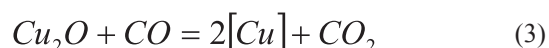
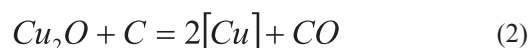
The Outokumpu direct-to-blister process was put into operation in 1978, in Głogów, Poland. The process requires high oxygen pressure and therefore is restricted to those smelting concentrates which mainly consist of minerals without iron (Cu_2S , CuS , Cu_9S_5) or those with a low iron content (Cu_5FeS_4). As a consequence of the high oxygen pressure in the Outokumpu flash smelting furnace, the slag produced contains 12-16% Cu in the Głogów case. This is accounted for by the approximately 1/3 of the copper content in the smelting concentrate. Therefore, a 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 the 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. Despite of many papers [1-6], copper recovery from the slag of direct-to-blister process at Głogow smelter is still away from satisfactory.

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 [7-9] and the copper in the slags exists

mainly as Cu_2O and Cu^+ , associated with the silicate anions, according to the reaction:



Cu_2O is a basic oxide and the oxygen ion in 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, and the silicate anions undergo polymerization. This model [10] suggests that the dissolved copper is almost entirely in the form of $(-\text{Si}-\text{O}^--\text{Cu}^+)$, for the slags containing about 1 wt-% of copper. As such a slag contains a small amount of Cu_2O , it causes sluggishness of the copper recovery process when it is close to completion, because the copper reduction by carbon can proceed only according to the following reactions:



The addition of the limestone to the slag causes some

* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, DEPARTMENT OF METALLURGY OF NON-FERROUS METALS, AL. MICKIEWICZA 30, 30-019 KRAKÓW, POLAND

Corresponding author: markuch@neostrada.pl

of the copper ionic Cu^+ to be replaced by Ca^{2+} , and therefore, the concentration of Cu_2O increases, which fasters copper reduction from the slag.

There are a number of papers [11-22] devoted to the study on the kinetics of the reduction of FeO and Fe_2O_3 oxides from slags, but only few deal with the reduction of non-ferrous metals from slags. Therefore, an extensive study on the kinetics of copper recovery from industrial slags was undertaken to improve effectiveness of the copper recovery in Głogów smelter. In this study the influence of the temperature on the rate of the copper recovery from the slag of the direct-to-blister flash smelting process was investigated.

Kondakov et al. [11] reported the kinetics measurements of the reduction of molten pure iron oxide by means of solid graphite at the temperature range of 1723K-1923K. They conducted their experiments in a closed system, measuring the CO gas pressure as a function of time. Under their experimental conditions, the mass transport was very fast, and not rate limiting. They concluded that the rate limiting stage was the carbon gasification reaction. Grieveson and Turkdogan [12] reduced of pure FeO in an iridium crucible at 1823K. They used a CO-CO₂ mixture as the reducing agent. For the selected CO₂/CO ratio, they held a sample in the furnace for 17 hrs, to establish the equilibrium between the melt and the gas phase, and then the CO₂/CO ratio was changed, to oxidize or reduce FeO . The authors found out that diffusion in the slag was rate-limiting step of the reduction/oxidation process.

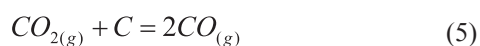
Krainer et al. [13] reduced the SiO_2 - FeO and SiO_2 - FeO - CaO slags with the use of graphite and coke crucibles in a thermobalance. They concluded that the reduction process was controlled by the Boudouard reaction.

Fun [14], has found that the kinetics of the reduction of FeO from the SiO_2 - CaO - FeO slag cannot be explained either by the diffusion or by the carbon gasification limiting stage. He concluded that the reduction rate is proportional to the FeO concentration to power 1.77, and he interpreted this fact in the way that the reduction process can be described by convective mechanisms.

Shalimov et al. [15] have reduced the SiO_2 - FeO slag with a graphite sphere at the temperature range of 1573K-1723K. They discovered that the activation energy for the reduction was 190 kJ/mol and that the process is controlled by the chemical reaction. The reduction process proceeds in two consecutive stages in the gas phase. The graphite/slag reaction produces the initial amount of CO molecules, which form a small bubble. The CO gas reacts at the slag/gas interface with the slag:



and then, at the gas/graphite interface, CO is reproduced by the Boudouard's reaction:

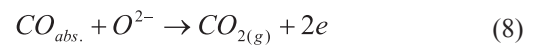
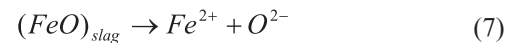


The bubbles grow as the reactions proceed, and when it reaches a certain size, the majority of it floats away from the graphite surface.

Sato et al. [16] reduced the pure liquid FeO with solid graphite and with carbon dissolved in liquid iron. The reduction rates were determined from the amount of CO generated

during the reduction processes. These authors found that the reduction rate in the case of solid carbon is much lower than in the case when the carbon dissolved in the molten iron reduces the iron oxide. They found that the activation energy for the reduction with solid carbon was 313 kJ/mol. In the case when the carbon dissolved in the molten iron was the reducing agent, the activation energy decreased to 183 kJ/mol.

Utigard et al. [17] reduced the copper from the industrial slag (El Teniente converter slag) by using two different CO containing gases. They found that the reduction is controlled by the CO pressure. They suggested that the reduction follows the Min and Fruehan's model [18] for the gas/ slag reaction:



Warczok and Utigard [19] reduced the synthetic fayalite slags in the temperature range of 1523K-1723K using a floating graphite disc or an immersed graphite rod. They found that the reduction rate per unit area of graphite is significantly higher for the immersed rod than for the floating graphite disk. They suggested that the reduction process is controlled by the Boudouard reaction.

El-Rassi and Utigard [20] have studied the reduction kinetics of the nickel smelting and converting slags under the conditions when alternating or direct current was passing through these slags. They observed that the reduction rate increases with the increasing electric power input and the slag temperature. They also found that the converter slag reduction was much faster than the reduction of the smelting slag. The authors suggested that the reduction process is controlled by the Boudouard reaction.

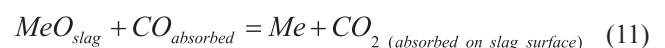
Mróz [21] employed a rotating graphite disc for the reduction of FeO from the SiO_2 - CaO - FeO liquid slags in the temperature range of 1623K-1693K. He found that the process is controlled by the FeO diffusion.

Barti and Coley [22] investigated the kinetics of the CO-CO₂ reaction with the CaO - SiO_2 - FeO - Fe_2O_3 slags, with the CaO/SiO_2 ratio varying between 0.3 and 2. They found that the rate constant increases with the iron oxide content, and with the decreasing of the oxygen partial pressure. They found that the rate constant increases with temperature and follows the Arrhenius relationship.

As can be seen from this literature review, there is a common understanding that the reduction process is initiated by the direct contact of the carbon and the slag:



In the next step, the carbon monoxide absorbed on the slag surface reacts with the metal oxide in the slag:



After the desorption of CO₂ from the slag surface, it diffuses towards the gas-carbon interface and then absorbs on the carbon surface, where the reaction proceeds:



The desorbed CO diffuses towards the gas/slag interface, closing the loop. The overall process can be controlled by:

1. the carbon gasification reaction;
2. the reduction reaction;
3. the metal cation and the associated oxygen anion transport from the bulk of the slag into the slag/gas interface.

2. Experimental

2.1 Apparatus

The aim of these investigations was to determine the influence of temperature on the rate of the copper recovery from the slag of the direct-to-copper process at Glogów with carbon as a reducer agent. The experimental set up used in this work is to some extent similar to those ones utilized in paper [23, 24]. Graphite penetrators were used as the reducers in this study, and their dimensions can be seen in Fig 1.

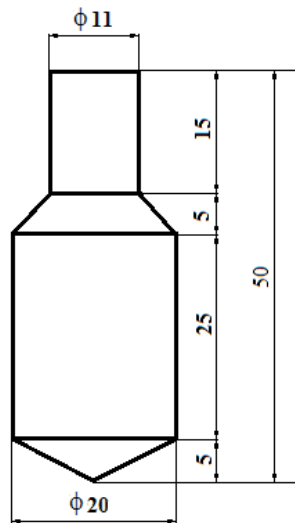


Fig. 1. Graphite penetrator

The graphite penetrator was joined with an alumina tube, and next the alumina tube was fixed into the upper cap of the reaction tube, as is shown in Fig. 2

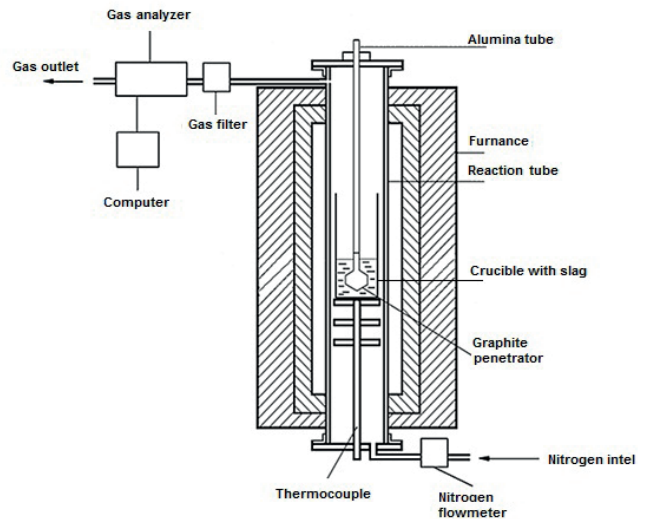


Fig. 2. Schematic diagram of the experimental apparatus

The apparatus consists of a furnace with Kanthal heating elements, powered by means of a transformer controlled by a Eurotherm controller, which is also connected to a controlling thermocouple Pt-PtRh10. The furnace temperature was maintained at $\pm 2 K$ and the maximum temperature variation in the hot zone was $\pm 3 K$. The 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 penetrator was placed under the upper cap of the reaction tube. A sample of 160 g of the slag was put in the crucible, which was then placed in the reaction tube. The composition of this slag is given in Table 1.

Purified nitrogen of 25 Ndm³/h flowrate was admitted to the reaction tube just after the sample was situated in it, and the system was closed. The nitrogen flow rate was maintained throughout the whole experimental run. The nitrogen flow rate was controlled with the use of an electronic flowmeter manufactured by Brooks. The experiment started when the graphite penetrator was transferred into the slag. During the experiment, 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 CO₂ were analyzed by a gas analyzer for CO and CO₂ in every 5 seconds, and the results were recorded by the computer. A typical variation of the CO and CO₂ concentration in the N₂-CO-CO₂ gas mixture is given in Fig.3.

TABLE 1

Main components of the investigated slag.

Components	SiO ₂	CaO	MgO	Al ₂ O ₃	Na ₂ O	K ₂ O	Cu	Pb	Fe	Zn	As
wt. %	33.94	15.60	4.94	10.00	0.75	2.39	12.45	3.05	8.06	1.13	0.192

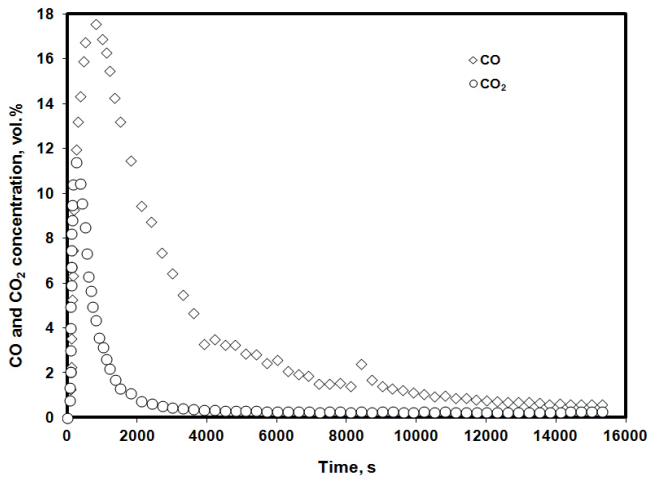


Fig. 3. Typical changes of the CO and CO₂ concentrations in the process gases during the slag reduction with a graphite penetrator at 1573 K. For the sake of these graphs clarity only about 1/10 of experimental points are shown. All experimental data in Excel format are available on request

A negligible slag foaming was observed at 1573 K and 1623 K, and a little bigger one - at 1673 K.

2.2 Calibrations of the gas analyzer and experimental set up

The flow rates (in Ndm³/h) of the CO and CO₂ formed during the reduction process were calculated from the relations:

$$V_{CO} = \frac{26.11 \times (vol.\%CO)}{100 - 1.041 \times (vol.\%CO) - 0.956 \times (vol.\%CO_2)} \quad (13)$$

$$V_{CO_2} = \frac{23.98 \times (vol.\%CO_2)}{100 - 1.041 \times (vol.\%CO) - 0.956 \times (vol.\%CO_2)} \quad (14)$$

These relations were established from the gas analyzer calibration procedure, which has been described in details elsewhere [23,24].

When the penetrator is immersed in the investigated slag, the reduction reactions take place, which generate CO and CO₂. However, the first gas analyzer readings were detected after about 50-60 seconds from the moment of the graphite penetrator immersion into the slag. A part of these gases was cumulated in the reaction tube, and this fraction should be taken into consideration. In order to estimate the real volumes of these gases, the calibration of the reaction tube was carried out [24]. According to this calibration, the volume of accumulated CO and CO₂ can be calculated from the relations:

$$\Delta V_{CO}^i (Ndm^3) = 0.0219 \cdot V_{CO}^i (Ndm^3 / h) \quad (15)$$

$$\Delta V_{CO_2}^i (Ndm^3) = 0.0219 \cdot V_{CO_2}^i (Ndm^3 / h) \quad (16)$$

where: *i* – number of experimental points *i* = 1,2,3,4,... etc.

Therefore, the real flowrate of CO and CO₂ passing through the reaction tube after *t* = 5 · *i* seconds can be calculated from the relations:

TABLE 2

The compositions of the slag(*) after the experiments at 1573 K, 1623 K and 1673 K.

	Temperature 1573 K			Temperature 1623 K			Temperature 1673 K		
	# 1	#2	# 3	# 1	# 2	# 3	# 1	# 2	#3
SiO ₂	38.2	38.9	36.50	38.5	35.0	37.5	38.50	37.20	40.20
CaO	21.05	20.80	21.48	21.17	21.77	21.34	21.59	21.74	21.92
Al ₂ O ₃	12.80	12.80	13.35	15.58	15.48	14.58	20.90	21.76	21.47
MgO	7.41	7.54	7.59	7.53	7.75	7.55	7.66	7.72	7.79
K ₂ O	3.33	3.30	3.50	3.35	3.50	3.38	3.38	3.50	3.51
Na ₂ O	0.71	0.74	0.73	0.74	0.75	0.75	0.75	0.74	0.85
Fe	10.67	10.78	11.29	9.09	11.01	10.14	5.05	5.19	5.21
Zn	0.74	0.50	0.51	0.12	0.19	0.18	0.02	0.02	0.02
Pb	0.24	0.21	0.23	0.01	0.03	0.02	0.01	0.01	0.01
Cu	0.22	0.29	0.22	0.10	0.15	0.13	0.12	0.20	0.25

(*) Analyzed with a spectrometer OPTIMA 7300DV produced by PerkinElmer.

TABLE 3

Composition of the alloys obtained during the slag reduction at 1573 K, 1623 K and 1673 K.

Component	Temperature 1573 K			Temperature 1623 K			Temperature 1673 K		
	# 1	# 2	# 3	# 1	# 2	# 3	# 1	# 2	# 3
% Cu	85.92	84.41	85.74	82.19	82.25	82.63	80.68	65.96	77.16
% Pb	13.53	15.38	14.16	14.09	16.10	14.42	16.87	10.72	13.69
% Fe	0.56	0.92	0.62	3.46	1.63	2.19	2.38	23.31	9.28
Sum	100.0	100.7	100.53	99.75	99.99	99.44	99.93	99.99	100.13

$$V_{CO(A)}^i = V_{CO}^i + (\Delta V_{CO}^i - \Delta V_{CO}^{i-1}) \cdot \frac{3600}{5} \quad (17)$$

$$V_{CO_2(A)}^i = V_{CO_2}^i + (\Delta V_{CO_2}^i - \Delta V_{CO_2}^{i-1}) \cdot \frac{3600}{5} \quad (18)$$

where $V_{CO_2}^i$ and V_{CO}^i are the flowrates of CO and CO₂ respectively estimated with Eqs.(13) and (14).

The second terms of Eqs. (17) and (18) have to be multiplied by the 3600/5 term, to reconcile the units with V_{CO}^i and $V_{CO_2}^i$. As the analyzer readings were adjusted to 273 K, so the numbers of the CO and CO₂ moles per one second could be calculated from the relations:

$$n_{CO} = \frac{V_{CO(A)}}{22.4 \times 3600} \quad (19)$$

$$n_{CO_2} = \frac{V_{CO_2(A)}}{22.4 \times 3600} \quad (20)$$

The number of the oxygen moles reduced from the slag during a period of 5 seconds (5 seconds was the time between two consecutive measurements) was determined from the relation:

$$n_{[O]} = \frac{n_{CO}^i + n_{CO}^{i+1}}{2} \cdot 5 + 2 \cdot \frac{n_{CO_2}^i + n_{CO_2}^{i+1}}{2} \cdot 5 \quad (21)$$

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 CO₂ moles formed during the reduction process per one second, recorded in two consecutive measurements.

2.3 Results

By the summation of the $n_{[O]}$ values, calculated from Eq. 21, the $\sum_{i=1}^n n_{[O]}(t)$ describing a number of the oxygen moles removed from the slag as a function of the reduction time was determined. The results of these computations are presented in Fig. 4, 5 and 6.

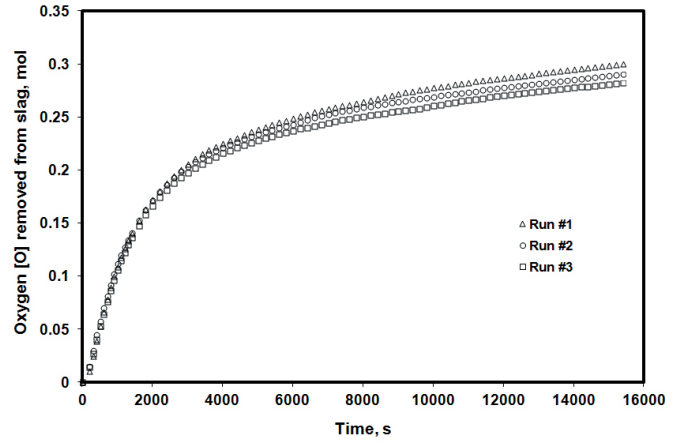


Fig. 4. A relation between the number of moles of the oxygen removed from the slag as a function of the reduction time at 1573 K. For the sake of these graphs clarity only about 1/10 of experimental points are shown

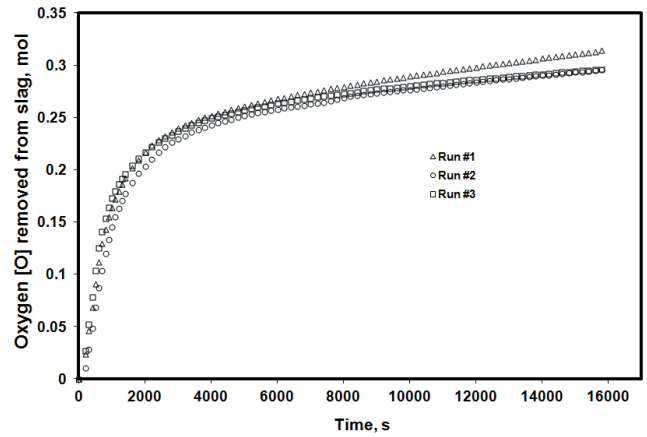


Fig. 5. A relation between the number of moles of the oxygen removed from the slag as a function of the reduction time at 1623 K. For the sake of these graphs clarity only about 1/10 of experimental points are shown

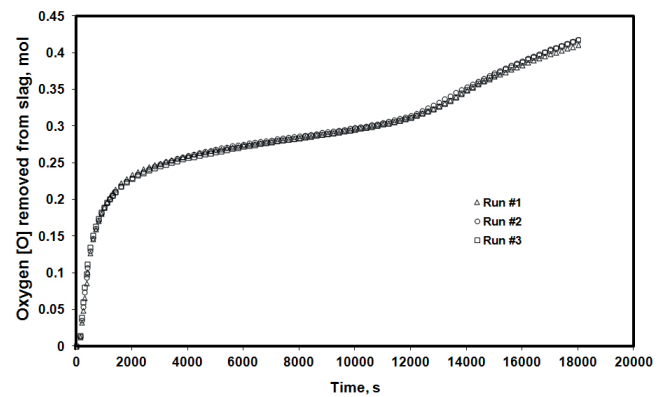


Fig. 6. A relation between the number of moles of the oxygen removed from the slag as a function of the reduction time at 1673 K. For the sake of these graphs clarity only about 1/10 of experimental points are shown

At 1673 K, the function $n_{[O]} = f(t)$ is very similar to the analogical functions at 1573 K and 1623 K, up to the moment when the number of moles of the oxygen removed from the slag exceeds approximately 0.3. From this point, one can observe some increase of the oxygen being removed from the slag. It was assumed that the copper and lead are reduced preferentially up to this point, and then the iron is reduced at a higher rate. This assumption is supported by the chemical analyzes of the slag performed after the experiment. Table 2 encloses the results of the chemical analyzes of the slag from after the experiment.

The iron concentrations in the slags after the experiment at 1573 K and 1623 K are approximately higher than those in the slag after the experiments at 1673 K, as can be seen in Table 2. At the same time, the iron content in the Cu-Pb-Fe alloys obtained during the slag reduction at 1573 K and 1623 K is, in general, lower than that in the alloy obtained at 1673 K (see Table 3). These facts legitimate the above thesis.

In order to support this thesis once again, three additional experiments were conducted at 1673 K, which, however, ended after 8000 seconds, just before the oxygen increase took place. Utilizing these results made it possible to remove and calculate the number of the oxygen moles from the slag, which is presented in Fig. 7.

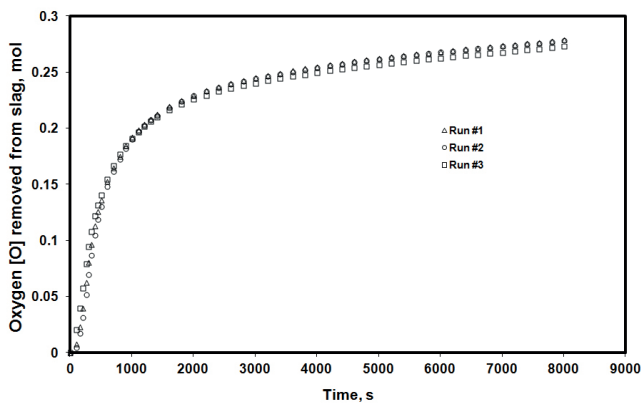


Fig.7. Relation between the number of moles of the oxygen removed from the slag as a function of the reduction time at 1673. The experiments were brought to end after 8000 seconds. For the sake of this graph clarity only about 1/10 of experimental points are shown

After these experiments, the reduced slags were analyzed, and the results are given in Table 4.

TABLE 4
Composition of the slag after the experiments at 1673 K limited to 8000 seconds.

Slag components	Run #1	Run #2	Run#3
SiO ₂ , wt. %	39.90	40.20	40.10
CaO, wt. %	20.13	19.77	20.06

Al ₂ O ₃ , wt. %	13.48	13.59	13.56
MgO, wt. %	7.34	7.05	7.13
K ₂ O, wt. %	3.34	3.42	3.32
Na ₂ O, wt. %	0.71	0.72	0.70
Fe, wt. %	10.11	10.24	10.05
Zn, wt. %	0.26	0.30	0.28
Pb, wt. %	0.05	0.05	0.05
Cu, wt. %	0.16	0.15	0.15

The slag reduced for 8000 seconds contains almost twice as much iron than the slags reduced for 16 000 seconds, while the copper contents in both series of slags are equal (please, compare data in Table 3 and Table 4), within the experimental error. In addition, the chemical analyzes of the obtained Cu-Pb-Fe alloys contained much less iron (see Table 5) than the alloys obtained during the processes lasting 16000 seconds. Once again, this proves the thesis that, in the first step, the copper and lead are reduced preferentially, followed by the iron - with a noticeable rate.

TABLE 5
Chemical composition of the Cu-Pb-Fe alloys obtained during the slag reduction at 1673 K and for a time period limited to 8000 seconds.

Components	Temperature 1673 K		
	Run #1	Run #2	Run #3
Cu, wt. %	84.50	83.98	83.79
Pb, wt. %	12.80	13.24	14.50
Fe, wt. %	2.30	2.26	2.09
Sum	99.60	99.47	100.38

3. Discussion

The attempts to describe the obtained results with a kinetic equation of the first, second or nth order failed. However, the rate of the process reduction can be determined directly with the utilization of the experimental data:

$$\frac{dn_{[O]}}{dt} \approx \frac{\Delta n_{[O]}}{\Delta t} = \frac{n_{[O]}^i - n_{[O]}^{i-1}}{5} \tag{22}$$

where: $n_{[O]}^{i+1}, n_{[O]}^i$ - the numbers of the oxygen moles removed from the slag after $5 \cdot i$ and $5 \cdot (i + 1)$ seconds of the reduction time, $i = 1, 2, 3, \dots, n$ - the numbers of the experimental points.

The example of the calculated values of $dn_{[O]}^i/dt$ for the experimental temperatures are illustrated in Figs. 8-10.

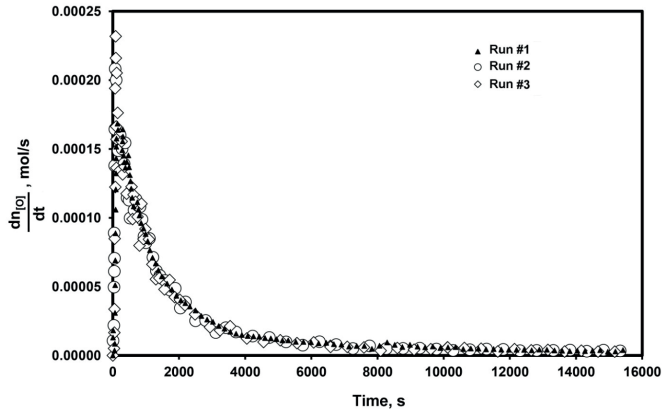


Fig. 8. The rate of the oxygen removal $dn_{[O]}/dt$ from the reduced slag at 1573 K as a function of time. For the sake of the graph's clarity, only about 1/10 of the experimental points are shown

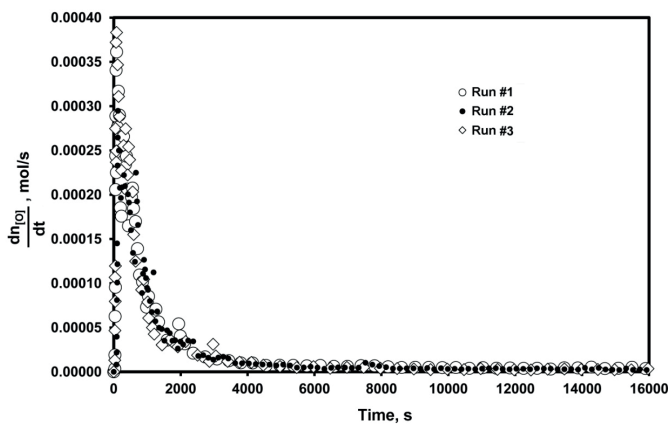


Fig. 9. The rate of the oxygen removal $dn_{[O]}/dt$ from the reduced slag at 1623 K as a function of time. For the sake of the graph's clarity only about 1/10 of the experimental points are shown

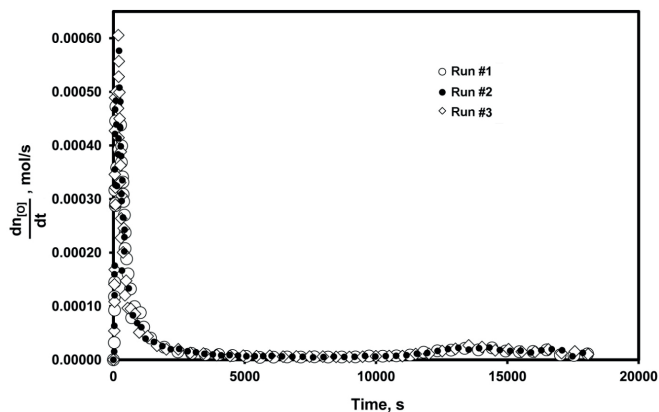


Fig. 10. The rate of the oxygen removal $dn_{[O]}/dt$ from the reduced slag at 1673 K as a function of time. For the sake of the graph's clarity only about 1/10 of the experimental points are shown

It was assumed that the rate of the reduction process can be described by the equation:

$$\frac{d(n_{[O]}^0 - n_{[O]}(t))}{dt} = S \cdot k' \cdot (n_{[O]}^0 - n_{[O]}(t))^n \quad (23)$$

Where: $n_{[O]}^0$ – the number of the oxygen moles which could be removed from the slag,

$n_{[O]}(t)$ – the number of the oxygen moles removed from the slag within the time “t”,

S – the surface on which the reduction take place (It was assumed that it is equal to a penetrator area $S = 22.5 \text{ cm}^2$),

k' – the process rate „constant”,

n – the reaction order.

To estimate the k' and n values, the equation (23) has to be expressed in the logarithmic form:

$$\ln\left(\frac{d(n_{[O]}^0 - n_{[O]}(t))}{dt}\right) = \ln(S \cdot k') + n \ln(n_{[O]}^0 - n_{[O]}(t)) \quad (24)$$

In Fig 11, an example of the relation (24) is graphically presented.

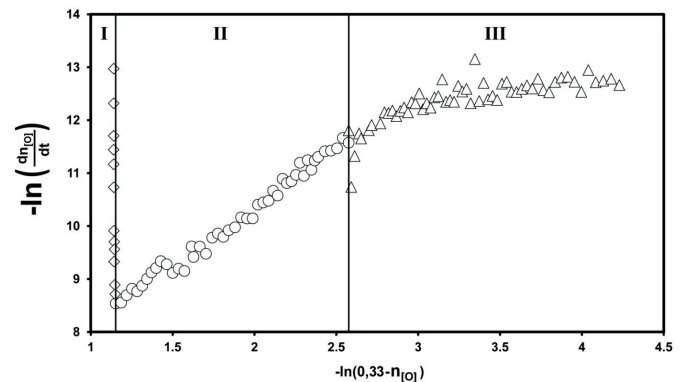


Fig. 11. Graphical representation of the relation (24) for temperature 1573 K

As can be seen in Fig 11, the copper recovery process could be split up into three stages, where, in the first one, an increase of $dn_{[O]}/dt$ is observed, as can be seen in Fig. 12.

There is a probability that, in this stage, the penetrator surface is activated. However, in the same time, the concentrations of Cu_2O , PbO and Fe_2O_3 species in the reduced slag decrease very fast. Consequently, due to these two opposite tendencies, maxima on the $dn_{[O]}/dt = f(t)$ curves can be observed.

In the second stage, a monotonic slowdown of the reduction rate is observed, as can be seen in Fig. 12. It is worth mentioning that, regardless of the temperature of the reduction process, the observed rates are practically equal in the second and third - stages (see Fig. 12).

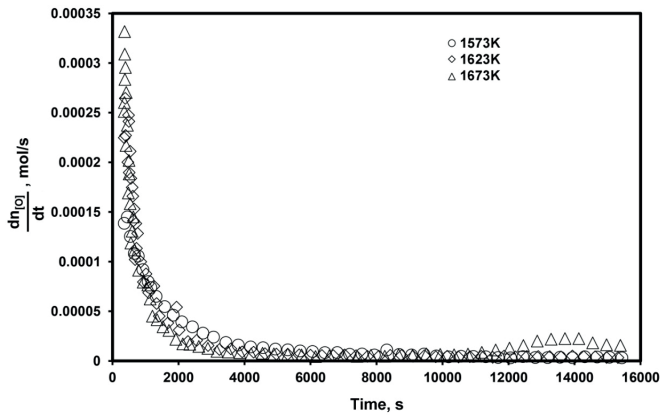


Fig. 12. Dependence of dn_{O1}/dt as a function of time at 1573 K, 1623 K, and 1673 K in the second and third stages of the reduction process. For the sake of the graphs' clarity, only about 1/10 of the experimental points are shown

The third stage starts with an increase of the process rate, which can be connected with the intensification of the iron reduction. The process rate decreases in this stage very fast approaching values close to zero.

Making use of the data obtained in the second stage and by the least square method, the parameters k' and n were calculated. Table 6 contains these calculated parameters.

TABLE 6

The parameters of Eq. 24 for the experimental points obtained at 1573 K, 1623 K and 1673 K ($S = 22.5 \text{ cm}^2$)

T/ K	$\ln\left(\frac{d(n_o^0 - n_o(t))}{dt}\right) = \ln(S \cdot k') + n \ln(n_o^0 - n_o(t))$	$10^4 \cdot k'$
1573	$-6,1994 + 2,029 \cdot \ln(0,33 - n_o(t))$	0,902
1573	$-5,7834 + 2,297 \cdot \ln(0,33 - n_o(t))$	1,368
1573	$-5,7023 + 2,398 \cdot \ln(0,33 - n_o(t))$	1,483
1623	$-4,2072 + 2,830 \cdot \ln(0,33 - n_o(t))$	6,616
1623	$-4,4600 + 2,875 \cdot \ln(0,33 - n_o(t))$	5,138
1623	$-4,1626 + 2,921 \cdot \ln(0,33 - n_o(t))$	6,918
1673	$-3,2252 + 3,191 \cdot \ln(0,33 - n_o(t))$	14,020
1673	$-3,4563 + 3,112 \cdot \ln(0,33 - n_o(t))$	17,665
1673	$-3,2179 + 3,268 \cdot \ln(0,33 - n_o(t))$	17,795
1673*	$-3,0964 + 3,319 \cdot \ln(0,33 - n_o(t))$	20,096
1673*	$-2,8486 + 3,513 \cdot \ln(0,33 - n_o(t))$	25,774
1673*	$-2,7554 + 3,559 \cdot \ln(0,33 - n_o(t))$	28,259

*- The experiments were brought to the end after 8000 seconds.

Unfortunately, the exponent value changes with temperature, as can be seen in Fig. 13.

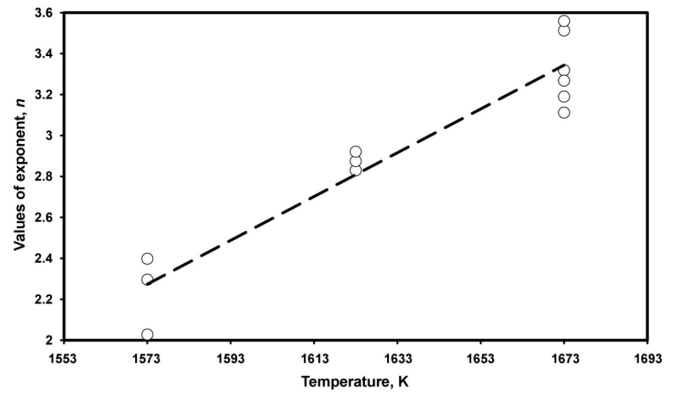


Fig. 13. Dependence of the exponent n on temperature

As the exponent n changes with temperature, we cannot speak about the process rate k' in a rigorous sense. In consequence the parameter k' does not have a defined unit. However, parameter k' exhibits the same dependence as the real rate process constant, as can be seen in Fig. 14.

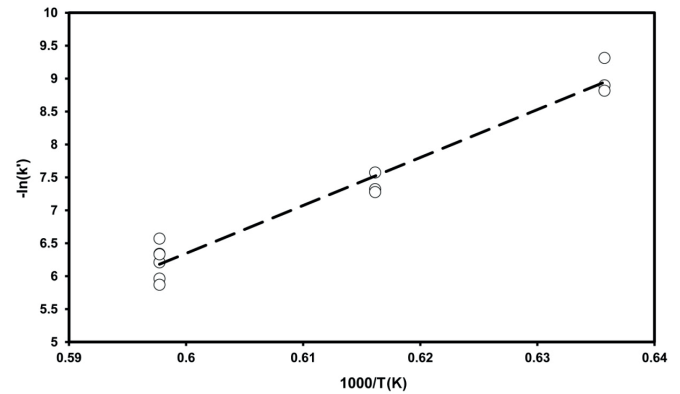


Fig. 14. The correlation between $\ln(k')$ and temperature (in Kelvin degree)

The experimental results allow us to determine the amount of the carbon consumption for 1 Mg of the reduced slag. Figure 14 shows the carbon consumption in the copper recovery process referred to 1 Mg of the reduced slag as a function of the temperature process. It can be seen that the carbon consumption increases sharply as the process temperature achieves 1673 K.

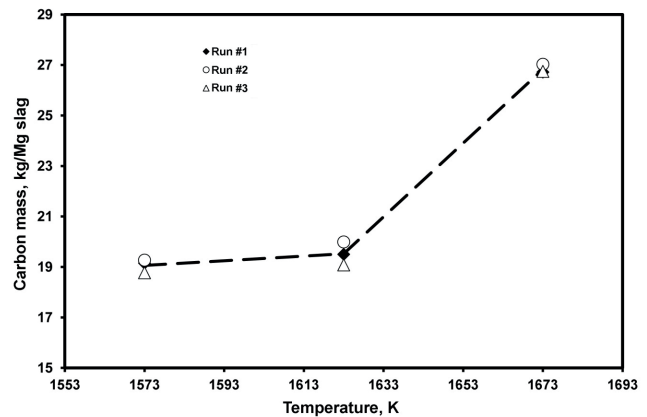


Fig. 14. Carbon consumption in the copper recovery process

Acknowledgment

We would like to thank the Polish National Center Research and Development (NCBiR) for the financial support – grant Nr 07-0022-10

REFERENCES

- [1] M. Kucharski, Solubility of copper in Outokumpu slag, *Metals Technology*, 354-356, September 1979
- [2] M. Kucharski, Copper Reduction from Commercial Slag by Solid Iron, *Arch. Hutn.* **26**, 3-10 (1981).
- [3] B. Szafirska, M. Król, A. Warczok, The role of electrokinetic phenomena in copper recovery from flash-smelter slag, *Arch. Hutn.* **28**, 11-25 (1983).
- [4] M. Kucharski, Solubility of Copper in SiO₂-CaO-Al₂O₃ Slags, *Arch. Metall.* **32**, 1, 27-32 (1987).
- [5] J. Czernecki, Z. Śmieszek, J. Botor, R. Wojciechowski, Decopperizing of slag from flash smelting of sulphide concentrates, "Pyrometallurgy '87" Symposium organized by The Institution of Mining and Metallurgy in association with The Institute of Metals, London 21-23 September, 1987, pp. 265-283.
- [6] J. Czernecki, Z. Śmieszek, S. Gizicki, J. Dobrzański, M. Warmuz, Problems with Elimination of the Main Impurities in the KGHM Polska Miedź S.A. Copper Concentrates from the Copper Production Cycle (Shaft Furnace Process, Direct Blister Smelting in a Flash Furnace) *Sulfide Smelting '98: Current and Future Practices* Edited by J.A. Asteljoki and R.L. Stephens, The Minerals, Metals & Materials Society, 1998, pp. 315-343.
- [7] G.W.Toop, C.S. Samis, *Trans. TMS-AIME* **224**, 878-887 (1962).
- [8] C.R.Masson, *Proc. Roy. Soc.* **A287**, 201-221 (1965).
- [9] D.R. Gaskell, *Met. Trans.* **4**, 185-192 (1973).
- [10] M. Kucharski, *Metals Technology*, 354-356 (1979).
- [11] V. V. Kondakov, D. I. Ryzhonkov, D.M. Golenko: *Izv. VUZ Chern. Met.* **4**, 23-28 (1960).
- [12] P. Grievesson, E.T. Turkdogan, *AIME Trans.* **230**, 1609-1614 (1964).
- [13] H. Krainer, H.P. Beer, H. Brandl, *Techn. Mitt. Krupp Forsch.-Ber* **24** (3), 139-146 (1966).
- [14] Fay Fun, *Metall. Trans.***1**, 2537- 41 (1970).
- [15] M.P. Shalimov, V.N. Boronenkov, S.A. Lyamkin, *Metally* **6**, 32-6 (1980).
- [16] A. Sato, G. Aragane, K. Kamihira, S. Yoshimatsu, *Transactions of ISIJ* **27**, 789-96 (1987).
- [17] D.J. Min, R.J. Fruchan, *Metall. Trans. B* **23B**, 29-37 (1992).
- [18] T. Utigard, G. Sanchez, J. Manriquez, A. Lurashi, C. Diaz, D. Cordero, E. Almendras, *Metall. Trans.B* **28B**, 821-26 (1997).
- [19] A.Warczok, T.A. Utigard, *Can. Metall. Q.* **37** (1), 27-38 (1998).
- [20] K.P. El-Rassi, T.U. Utigard, *Metall. Mater. Trans. B.* **31B**, 1187-1194 (2000).
- [21] J. Mróz, *Metall. Mater. Trans.B.***32B** (5), 821-30 (2001).
- [22] M. Barati, K. Coley, *Metall. Mater. Trans.B* **36B**, 169-178 (2005).
- [23] K. Rogóż, M. Kucharski, The rate of metal oxides reduction from the slag of the direct-to-blister flash smelting process, *Arch. Metall. Materials* **55**, 317-323 (2010).
- [24] M. Kucharski, T. Sak, P. Madej, M. Wędrychowicz, W. Mróz, A study on the copper recovery from the slag of the Outokumpu direct-to-copper process, *Metall. Mater. Trans. B* **45B**, 590-602 (2014).

Received: 20 October 2014.

