

# Influence of Magnesium Oxide Content on Kinetics of Lime Dissolution in Steelmaking Slags

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The kinetics of lime dissolution containing different amounts of magnesium oxide (4.3–7.6%) in steelmaking slags has been studied in a non-stationary diffusion, at temperatures ranging from 1 300–1 600°C, directly in the hot process. The decrease in solubility of lime with the increasing content of magnesium oxide is due to the formation of high temperature solid chemical compounds ( $\text{Ca}_2\text{SiO}_4$ ,  $(\text{Mg,Fe})_2\text{SiO}_4$ ) and solutions based on MgO like  $(\text{Mg,Fe})\text{O}$  in the volume of lime samples. Formed slightly soluble phases hinder the process of CaO dissolution and slow down the rate of dissolution of lime samples. Based on differential equations of mass balance of the dissolving substance and taking into account its transition into the melt phase, and accumulation in the consistently dissolving layers of solid, values of mass transfer coefficients and diffusion coefficients were calculated. Mass transfer coefficients, despite a decrease in the concentration gradient, increase in the process of slag saturation with lime. Activation energy has been calculated under conditions of non-stationary linear and spatial semi-infinite diffusion. Based on the dependency of the logarithm of diffusion coefficients on the inverse temperature derived value of the activation energy of diffusion is  $230.2 \pm 14.0$  kJ/mol.

KEY WORDS: steelmaking slags; lime; magnesium oxide; saturation; kinetics; mass transfer coefficient; diffusion coefficient; activation energy.

## 1. Introduction

Physico-chemical properties of slag influence the productivity of the steelmaking processes to a great extent. The rapid formation of physically and chemically active slag facilitates removal of sulfur and phosphorus from the melt. It reduces metal loss and formation of *metal-regulus* in the slag; furthermore it decreases wear in the refractory lining. Viscous slag is physically poorly active and has a low refining capacity, thus, reaction processes with metal slow down. Such a viscous slag will lead to an increase in the metal losses due to the regulus formation and slag splashing. It often leads to the lance becoming clogged and formation of skulls on the neck of the vessel. High slag fluidity is also not desirable due to the increased refractory wear of the converter lining. In the process of steelmaking in an oxygen converter it is necessary to obtain at the end of the blowing process a sufficiently flowable, physically and chemically active homogeneous slag with basicity  $\text{CaO}/\text{SiO}_2 = 3.0\text{--}3.5$ . As it is known, the chemical composition of the converter slag and intensity of lining destruction vary in different stages of the converter process. The highest rate of destruction of the lining in the converter is observed during the formation of slag with the basicity  $\text{CaO}/\text{SiO}_2 = 1.0\text{--}1.5$

and a high oxidation state (up to 30% FeO).

Therefore, it is necessary to form a slag with maximum concentration of MgO, closer to the saturation for a desired temperature conditions in the first period of blowing. In order to increase the MgO content in the slag, it is efficient to use Magnesian fluxes. The consumption of slag-forming materials is determined by calculation, in accordance with the raw material composition and the desired slag. During the melting process a slag sample's composition may differ from the calculated value, and pieces of undissolved lime may be present in the sample of slag. Moreover, it can happen that a melting operation is over, slag of the desired composition is not formed and detrimental impurities are not fully removed.

The sources for slag formation are oxides - oxidation products of hot metal components and impurities of scrap loaded into the converter, bulk materials (iron ore, flux materials) and refractory linings.

Study of L. Akselrod *et al.*<sup>1)</sup> on the kinetics of slag saturation with magnesium oxide in simulation process of interaction of the refractory material MgO-C and slag with addition of magnesia flux, showed a significant decrease in the rate of dissolution of magnesium oxide in the slag, in 2.0–2.25 times accordingly.

Industrial research carried out by specialists of the Hamburger Stahlwerke Company, enables the dissolution degree of basic refractory in the slag to be estimated, depend-

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ing on the content of magnesium oxide in the refractory.<sup>2)</sup>

The authors considered the proportion of MgO transiting into the slag from the lining by calculating the material balance of the slag. In the experiment there was a clear tendency towards a decrease in magnesium oxide dissolution from the lining in the slag with the increase of the saturation of slag with MgO.

In industrial conditions there is a problem of even distribution of the dissolving MgO throughout the volume of the slag, which is why the rate of dissolution of magnesia material in the slag plays such an important role. Lime is essential for slag formation. The melting point of lime is 2 570°C, and the temperature of molten slag is 1 250–1 500°C. Therefore, one of the most important tasks of slag formation control is a fairly high assimilation rate of lime into the slag phase.

Dissolution of lime in slag occurs in the following stages:

1. A film of saturated solution with calcium oxide forms on the surface of lime particles with a concentration ( $C_s$ ), which is higher than the CaO concentration in the liquid phase ( $C$ ).

Film formation is accompanied by formation of solid and liquid solutions, as well as chemical compounds of the system CaO–FeO–MnO–SiO<sub>2</sub>. The rate of dissolution is determined by the rate of further mass transport through this film.

2. Penetration of liquid slag through the pores and grain boundaries on the surface of lime.

3. Melting and transition of the remaining surface (film) layers into the slag.

As shown in the experimental studies, the rate of assimilation of lime by slag is limited by the rate of mass transfer of CaO through the film of chemical compounds formed on surface of lime particles.<sup>3)</sup> The impact of the rate limiting step of major metallurgical process of lime dissolution in steelmaking slags provides information about the process' mechanism and methods of its intensification.

Experimental determination of diffusion characteristics in liquid metal solutions in general, in particular with iron, is followed by many difficulties and there is a very small amount of the experimental studies on the following topic.<sup>4)</sup> The main difficulty lies in the suppression or elimination of convective mass transfer, which essentially depends on the viscosity of the melt and the temperature gradient.

T. Deng<sup>5)</sup> studied the dissolution mechanism and rate of lime in converter slag. The author investigated lime dissolution under forced convection using a molybdenum rod for stirring purposes. The experimental equipment allowed the system to be quenched at a high temperature. It was revealed that different lime samples had different dissolution rates, and that CaO dissolution in slag had progressed due to the removal of dicalcium silicate layer.

Nobuhiro Maruoka *et al.*<sup>6)</sup> studied the dissolution rate of different limes into the slag. Authors measured the change in the slag composition after the dissolution test. Procedure was carried out using iron rod for stirring slag, iron crucible and Argon gas to flush the system from the bottom up. XRF method was applied to analyze slag samples. It was found that with the following CaO–FeO–SiO<sub>2</sub> slag a dense dicalcium silicate layer occurred on the lime particles and, therefore, lime porosity had low significance for the dissolution rate due to the formation of the reaction layer.

However, porous lime tends to dissolve faster than a dense lime due to the filling of lime pores with slag.

Huang Fuxiang *et al.*<sup>7)</sup> studied the dissolution rate of oxides in the slag and investigated the effect of the interfacial layer on its dissolution rate. They prepared a mixture of oxides to imitate the interfacial layer from sintered reagents. Prepared sample was immersed in a molten slag stirred with Argon gas. It was found that the thickness and constitution of the interfacial layer affect the dissolution rate.

In the study on the dissolution of MgO from flux and BOF refractory, Nobuhiro Maruoka *et al.*<sup>8)</sup> investigated the dissolution rate of MgO. Authors added different oxides containing MgO into the melt and defined the change in the MgO content. They found that solid formation of MgO and FeO occurred at the interface of the FeO–CaO–SiO<sub>2</sub> slag and sintered MgO.

Nikitin *et al.*<sup>9)</sup> studied the kinetics of the interaction of metal and slag in crucibles made of fused MgO at temperature of 1 580°C. The primary slag contained 9.8–52% CaO, 70.4–6.8% SiO<sub>2</sub>, 19.8–41.2% Al<sub>2</sub>O<sub>3</sub>. A polarizing method was used: an alternating current of small intensity was applied through the cell, consisting of two liquid metal electrodes and molten slag connecting them. By measuring resistivity of melt, diffusion coefficient of ions in the slag was calculated.

This work was performed to investigate the kinetic characteristics of steelmaking processes. The primary kinetic task is a description of the mechanism and rate of metal impurities oxidation, and solid materials transition in the liquid phase, including lime dissolution in the slag. As a result of mixing in steelmaking process turbulent diffusion coefficients increase, so that in each phase concentrations of components are roughly constant. However, at interfaces in the fixed or unstirred boundary layers, the mass transfer is ensured by molecular diffusion. The transfer of matter from one phase to another is a complex process with a limiting step, which is the molecular diffusion in the slag boundary layer. Determination of molecular diffusion coefficients of lime, containing various amounts of magnesium oxide carried out in this paper shows the kinetics of slag formation.

An investigation of the kinetic regime of slag formation helps to achieve a desirable composition of slag, reduces the melting time and refractory wear. This generally leads to greater productivity of the steelmaking converter and lowers the cost of steel production.

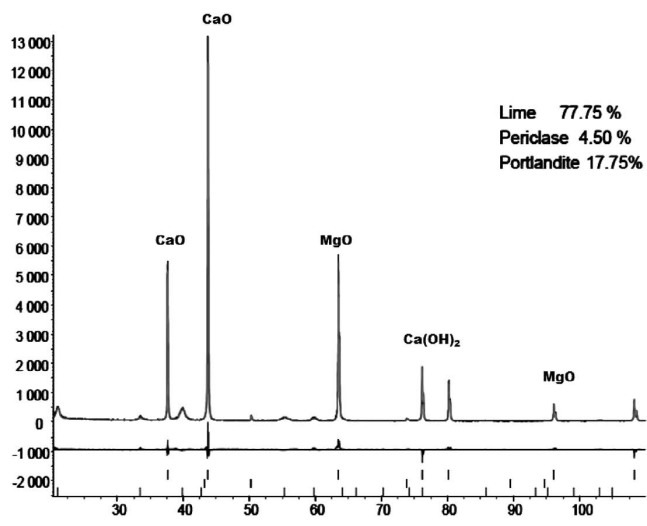
## 2. Experimental Procedure

This procedure is to study the dissolution kinetics of lime containing different amounts of magnesium oxide in the synthetic steelmaking slags, prepared according to the composition of industrial slag with 20% CaO, 35% SiO<sub>2</sub> and 45% FeO. The quantitative composition of lime is presented in **Table 1** and phase composition of lime in **Fig. 1**. A slag sample with a mass of 2 g was placed in a high temperature vertical furnace Gero HTRV 200-250/17 (see **Fig. 2**). Slag melting was performed in resistant to high temperatures up to 1 713–1 720°C synthetic silica crucibles with modification of cristobalite.

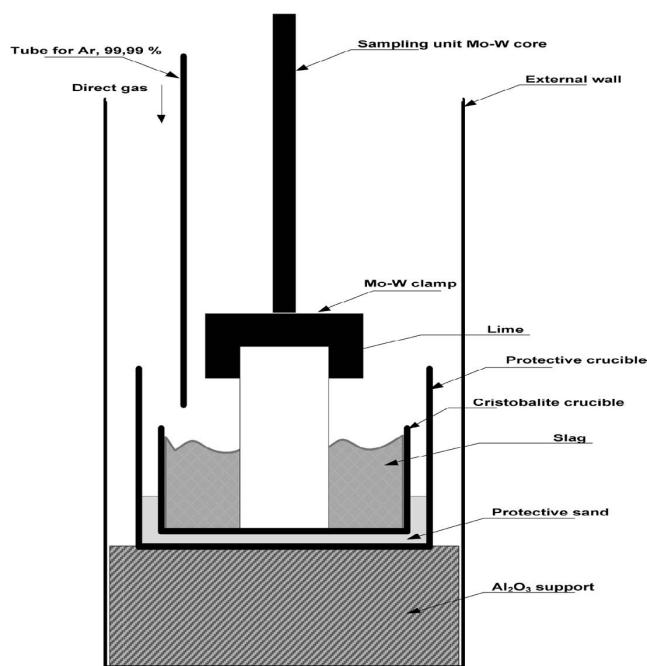
The thermal characteristics of various materials were defined by melting model slag with different compositions

**Table 1.** The composition of the industrial lime.

№	MgO	CaO	LOI	Other
Sample A	4.30%	91.40%	3.90%	0.40
Sample B	5.60%	91.10%	2.94%	0.36
Sample C	6.20%	91.60%	1.82%	0.38
Sample D	7.60%	90.10%	1.93%	0.37



**Fig. 1.** The diffractogram of the industrial lime.



**Fig. 2.** Experimental setup.

in corundum, alundum, iron, boron nitride, electrofused magnesite and silica crucibles. The mass balance of slag performed before and after the dissolution, as well as the results of X-ray fluorescence method and theoretical calculation of SiO<sub>2</sub> concentration in the samples of fused slag, is a confirmation of thermal stability of silica crucibles. The inertness of synthetic quartz material in the range of the

given temperatures, the possibility of extraction the crystallized slag without involvement of special equipment, low cost of the material have defined the use of the crucibles for the experiment.

The melting process was carried out under inert gas argon atmosphere at a predetermined temperature. The maintained heating rate was 400°C per hour. The desired temperature of the process was reached and held for 30 minutes, lime samples heated up to the same temperature in order to limit the thermal buoyancy, respectively, were added into the melt with the density of 2.9 g/cm<sup>3</sup>. Lime samples were prepared in the form of cylinders with height of 1.72–1.75 cm, diameter of 0.5 cm and density of 3.0 g/cm<sup>3</sup> using press machine. To improve strength and reduce porosity of the material all samples were calcined at 1400°C for 20 min before the experiment. The height of the samples was selected to minimize the loss of material when sample is immersed into the melt, possibility of exposure for a certain time and further removal from the melt. In order to eliminate the temperature gradient, lime samples were heated up to chosen temperatures (1300, 1400, 1500 and 1600°C) and immersed into molten slag of same temperature. By limiting the working crucible with protective shell - large size crucible, a stable state of the melt was maintained without temperature fluctuations in the process.

After predetermined time intervals samples were removed, cooled down to the room temperature and weighed on an analytical balance. After removing lime sample from the melt, content of the crucible was quenched; slag saturated with CaO was removed, triturated and analyzed to determine the content of MgO and CaO. The concentration of magnesium and calcium in the slag samples was estimated by X-ray fluorescence method with energy-dispersive X-ray fluorescent spectrometer PANalytical Epsilon 3.

By measuring the mass of dissolved lime in the slag, a change in sample dimensions and the measurement of the concentration of calcium and magnesium oxides in the slag, mass transfer coefficients were calculated.

### 3. Experimental Determination of Mass Transfer Coefficient in Real Reactors and Hot Models

The rate of the complex heterogeneous process at high temperatures in the converter bath is limited by the intensity of diffusion of the reagents to the reaction site.<sup>10)</sup> Accordingly, the mass transfer coefficient of lime dissolution in the melt can be determined by the first order reaction equation Eq. (1):

$$-\frac{dM_{sol}}{dt} = k_{CaO} (C_{sat} - C_{CaO})S, \dots\dots\dots (1)$$

Where  $\frac{dM_{sol}}{dt}$  – is mass rate of the dissolving lime,  $C_{sat}$  – is the saturation concentration of slag with CaO;  $C_{CaO}$  – is the current calcium oxide concentration in the slag phase;  $S$ – is the surface area of the dissolving body,  $k_{CaO}$ – is the mass transfer coefficient, respectively.

Considering recalculation of mass concentration expressed in kg/m<sup>3</sup> into the percent concentration, see Eq. (2) and taking into account the total mass balance of the dissolving body, rate of the dissolution can be defined by the Eq. (3):

$$-\frac{dM_{sol}}{dt} = k_{(CaO)} \frac{\left( \frac{(CaO\%)_{sat}}{100\%} \rho_{liq} - \frac{(CaO)}{100\%} \rho_{liq} \right)}{\frac{(CaO\%)_{sol}}{100\%} \rho_{sol}} \cdot S \rho_{sol} \dots (2)$$

$$= k_{(CaO)} \frac{(CaO\%)_{sat} - (CaO\%)}{(CaO\%)_{sol}} S \cdot \rho_{liq}$$

where  $M_{sol}$  – is the mass of lime;  $(CaO\%)_{sol}$  – is the concentration of CaO in the primary lime,  $(CaO\%)$  and  $(CaO\%)_{sat}$  – CaO concentration in the melt and saturation concentration,  $\rho_{sol}$  – density of lime, kg/m<sup>3</sup>;  $\rho_{liq}$ – density of liquid slag, kg/m<sup>3</sup>.

Accordingly, the mass rate of the lime dissolution would be:

$$-\frac{dM_{sol}}{dt} = \frac{k_{(CaO)} \cdot \{(CaO\%)_{sat} - (CaO\%)\} S \cdot \rho_{liq}}{(CaO\%)_{sol} - (CaO\%)} \dots (3)$$

The contact area of the sample and slag is calculated as the sum of the base and side surfaces of the cylinder, considering its changing linear size (height of the cylinder).

#### 4. Determination of Lime Mass Transfer Coefficients in the Model Slag and Discussion

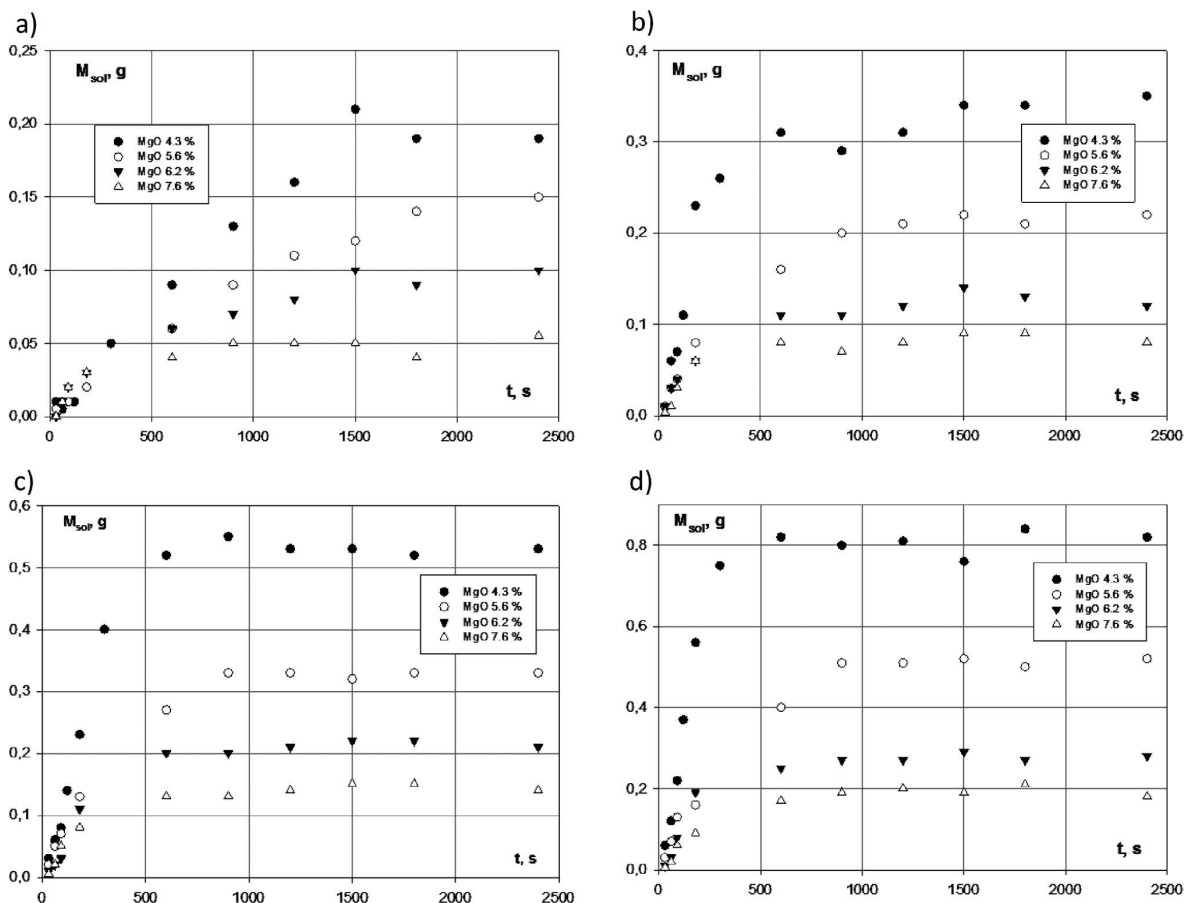
In the experiment the results of the mass change of lime

cylindrical samples containing different amounts of MgO have been obtained as a function of the contact time with slag at temperatures between 1 300–1 600°C as shown in Fig. 3.

It is evident from the experimental data that as model slag becomes saturated with calcium oxide, the mass of the lime samples ceases to change with the increasing contact time. Slag saturation with calcium oxide occurs at any given temperature, wherein the amount of dissolved lime increases with the temperature and, respectively, the equilibrium concentration of calcium oxide in the slag (saturation concentration) raises as well (see Table 2). One of the characteristics of slag saturation with calcium oxide is the formation of dicalcium silicate in the volume of the lime, which prevents further diffusion of CaO in the melt phase.<sup>10-13) Ca<sub>2</sub>SiO<sub>4</sub> is formed due</sup>

**Table 2.** Equilibrium concentration (saturation concentration) of CaO in model slag at different temperatures of lime dissolution process.

№	MgO content in lime, %	Equilibrium concentration of CaO in the slag, % at temperatures °C			
		1 300	1 400	1 500	1 600
1	4.3	26.2–26.5	30.6–30.8	35.4–35.5	41.0–41.2
2	5.6	24.9–25.0	27.1–27.4	30.1–30.3	34.7–34.8
3	6.2	23.4–23.6	24.7–24.8	27.2–27.3	29.1–29.3
4	7.6	21.9–22.0	23.0–23.1	24.9–25.0	26.4–26.5



**Fig. 3.** The dependence of the amount of dissolved lime on contact time with slag. MgO content a) 1 300°C, b) 1 400°C, c) 1 500°C d) 1 600°C.

to the dissolution of lime in the slag with a high concentration of silica, which is contained in the model slag (35% SiO<sub>2</sub>) used in the experiment. Dicalcium silicate is indicated in the diffractogram of the final slag composition (Fig. 4).

There is a correlation between the linear rate of the dissolution of lime with different MgO content and the saturation concentration of calcium oxide in slag at different temperatures, as seen in Fig. 5. With the increasing concentration of CaO in the slag, the rate of the samples' dissolution decreases, which agrees with the Eq. (3) and is explained by the drop in the concentration gradient  $(CaO\%)_{sat} - (CaO\%)$ .

The relationship between the linear rate of dissolution of samples  $\frac{\Delta h}{\Delta t}$  and CaO concentration during saturation of slag is one of the characteristics of the diffusion regime of CaO dissolution in the molten steel slag.

The experiment showed an increase in mass transfer coefficients calculated by the Eq. (3) until the saturation of slag with lime was reached (see Fig. 6).

According to similarity theory, when large particles (greater than 1 cm in diameter) are dissolving, the mass transfer coefficient is dependent on particle size and continuously increases as the dissolution of the lime in the slag progresses at a Reynolds number  $Re > 500$ ; yet still less than a critical value:

$$k = 1,06 \left( \frac{\Delta \rho g}{\rho_{liq}} \right)^{1/4} \frac{D^{2/3}}{h^{1/4} \nu^{1/6}} \dots \dots \dots (4)$$

where  $\Delta \rho$  - is the density difference between solids and liquid melt;  $\rho_{liq}$  - is the density of the melt;  $g$  - is the acceleration of free fall;  $\nu$  - is the kinematic viscosity;  $D$  - is the diffusion

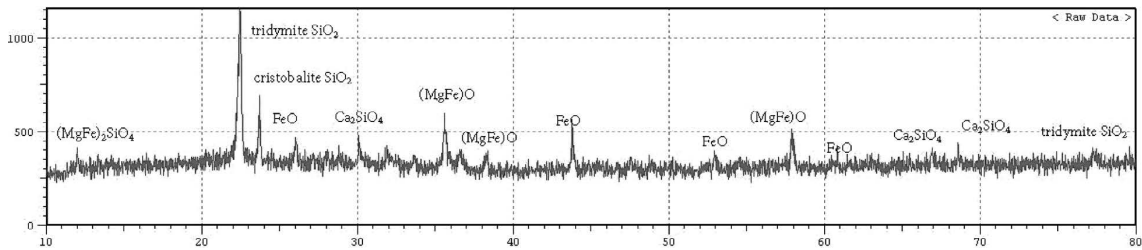


Fig. 4. The diffractogram of the final slag after lime dissolution containing 4.3% of MgO.

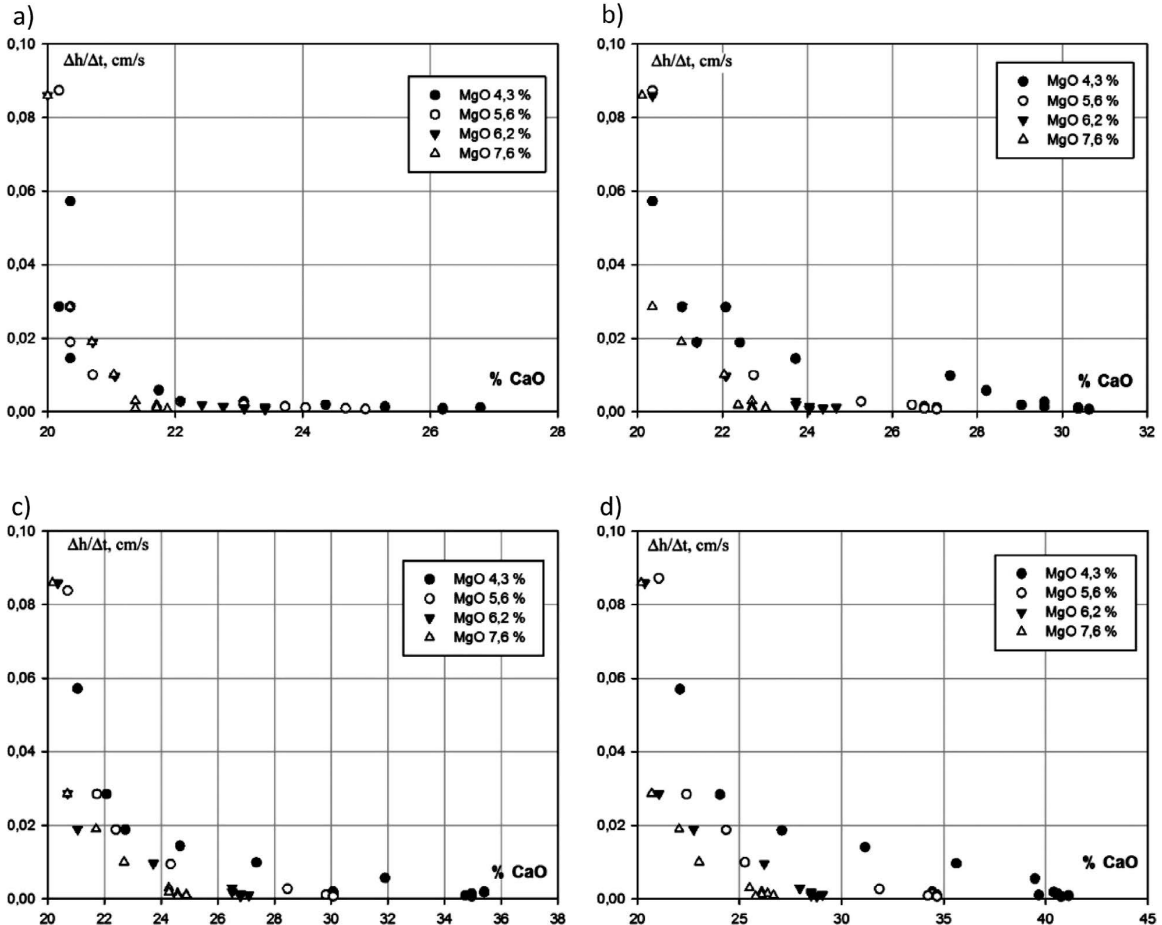


Fig. 5. The dependence of the linear rate of dissolution of lime samples on the CaO content in the slag at a) 1 300°C, b) 1 400°C, c) 1 500°C and d) 1 600°C.

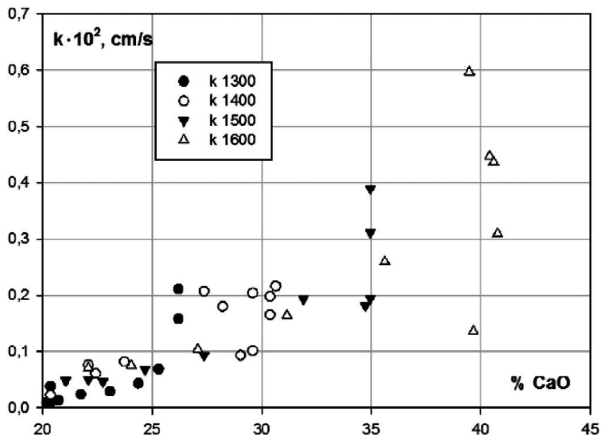


Fig. 6. The values of calculated mass transfer coefficients of lime dissolution containing 4.6% MgO.

coefficient;  $h$  – is the linear size of the dissolving sample. According to B. Baptizmansky<sup>14)</sup> the mass transfer coefficient is greatly influenced by the slag composition and the value of the mass transfer coefficient can increase with the rising basicity of the slag, in spite of the lower concentration gradient.

Therefore, mass transfer coefficients are only of use for an approximate estimation of the dissolution time of large solid lime particles in the melt.

The influence of MgO content in lime on its rate of dissolution should be emphasized. The increase in the concentration of MgO in lime slows down the dissolution rate of the samples. In the work<sup>4,15)</sup> authors measured the rate of calcined dolomite samples  $\text{CaCO}_3 \cdot \text{MgCO}_3$  dissolution in the slag with the composition  $\text{Fe}_x\text{O}-\text{CaO}-\text{SiO}_2$ , containing FeO from 20 to 65%. Authors suggested a limitation of the MgO diffusion in the slag containing FeO more than 20% through the surface layer at the interface.

To prove the limitation of the dissolution rate of samples with the increasing MgO concentration, in this paper, the values of CaO diffusion in the liquid slag are derived from the experimental data.

### 5. The Calculation of the Diffusion Coefficients of Lime Dissolution in the Model Slag

The rate of the heterogeneous process, which is limited by the diffusion, is described by the following equation according to Fick’s first law:

$$w = \frac{1}{(-1)_s} \left( \frac{dm}{dt} \right)_{x=0} = D \left( \frac{\partial c(x,t)}{\partial x} \right)_{x=0}, \dots\dots\dots (5)$$

where  $x=0$  is the origin of the coordinates, which is placed on a surface of solid body and is inwardly directed into the melt (the propagation of the diffusion). The following equation is used to describe a semi-infinite linear diffusion when the substance diffuses along the length of the cylinder, and the reacting surface is the bottom of the cylinder. In terms of non-stationary spatial semi-infinite spherical diffusion Fick’s second law can be represented by the next Eq. (6).<sup>16)</sup>

$$w = D \left( \frac{\partial c(R,t)}{\partial R} \right)_{R=r}, \dots\dots\dots (6)$$

which is expressed in the linear form:

$$w = \sqrt{\frac{D}{\pi}} \frac{c}{\sqrt{t}} + \frac{Dc}{r}, \dots\dots\dots (7)$$

where  $w$  is the rate of diffusion;  $r$  – is the sphere radius;  $C$ – CaO concentration in the slag, expressed in  $\text{mol/m}^3$ .

Taking into account the correlation between the amounts of reacted substance and time, the diffusion coefficient of lime can be determined, as long as the value of the solid surface is known.

The linear dependence of mass change rate of calcium oxide samples  $w = \frac{1}{s} \frac{dM}{dt}$  on the value of  $\frac{c}{\sqrt{t}}$  is evident in

Fig. 7. The lime diffusion coefficient values in the molten slag were calculated using the tangent of the angle.

The values of the calculated diffusion coefficients (spatial semi-infinite diffusion in comparison with the non-stationary linear process) of mass transfer are shown in Table 3.

Derived diffusion coefficient values for the linear and spatial process of mass transfer are in satisfactory agreement with each other. Dependence of the dissolution rate of

samples on the variable  $\frac{c}{\sqrt{t}}$  is approximated by linear correlation with high reliability, which suggests that the chosen spatial model is adequate. It is noteworthy that the calculated from the experimental data  $D$  values are comparable with the value of  $2.7 \cdot 10^{-5} \text{ cm}^2/\text{s}$ , presented by Matsushima *et al.*<sup>11)</sup> for CaO dissolution in slag with the composition: 20% FeO-40%  $\text{SiO}_2$ - 40% CaO at 1400°C.

The difference in the values of the diffusion coefficients is explained by the difference in slag and samples composition. In case when convective fluctuations occur in the high temperature metallurgical system, in the equations of the first and second Fick’s laws’ effective diffusion coefficient,  $D_{\text{ef}}$ , is introduced instead of the molecular diffusion coefficient  $D$ .

The effective diffusion coefficient values are six to eight times higher than the molecular diffusion coefficient and result in 200–1 000  $\text{cm}^2/\text{s}$ , as shown in the study of mass transfer processes in a boiling liquid bath using radioactive indicators.<sup>14)</sup>

In the turbulent medium substance concentration in the volume of each liquid phase is approximately constant. However, in these conditions, the role of molecular diffusion still remains significant, since at the interface there are thin unstirred boundary layers in which the mass transfer is carried out by molecular diffusion.

According to the results derived, the diffusion coefficient values decrease with the increasing content of MgO in lime at the same temperatures and increase with the increasing temperature and constant MgO values. By raising the content of MgO from 4.3 to 7.6% the  $D$  value decreased by a factor of 5 to 8.

An important role in the process of diffusion plays not only the content of MgO in lime, but also the amount of FeO in the original slag. FeO is capable to penetrate into

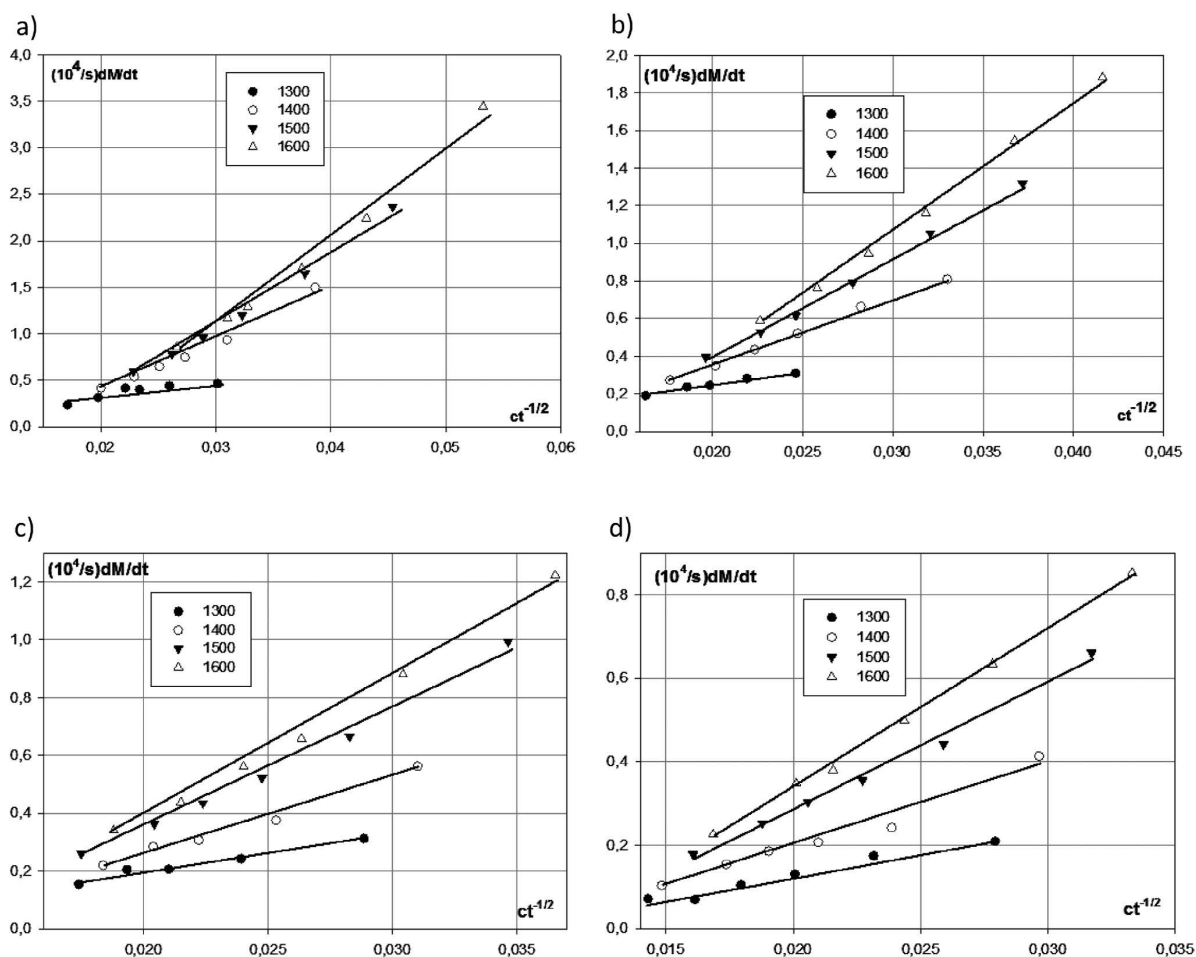


Fig. 7. The dependence of the dissolution rate of lime samples containing a) 4.3% MgO, b) 5.6% MgO, c) 6.2% MgO, d) 7.6% MgO on the value of  $\frac{c}{\sqrt{t}}$ .

Table 3. The values of diffusion coefficients of lime dissolution in slag (SD- spatial diffusion and LD-linear diffusion).

T, °C	D, cm <sup>2</sup> /s							
	SD		LD		SD		LD	
	4.3% MgO		5.6% MgO		6.2% MgO		7.6% MgO	
1 300	1.66·10 <sup>-5</sup>	0.91·10 <sup>-5</sup>	6.15·10 <sup>-6</sup>	4.52·10 <sup>-6</sup>	5.31·10 <sup>-6</sup>	3.14·10 <sup>-6</sup>	3.80·10 <sup>-6</sup>	1.53·10 <sup>-6</sup>
1 400	10.56·10 <sup>-5</sup>	2.83·10 <sup>-5</sup>	4.29·10 <sup>-5</sup>	1.26·10 <sup>-5</sup>	1.81·10 <sup>-5</sup>	1.02·10 <sup>-5</sup>	1.26·10 <sup>-5</sup>	0.38·10 <sup>-5</sup>
1 500	19.60·10 <sup>-5</sup>	5.27·10 <sup>-5</sup>	9.15·10 <sup>-5</sup>	2.83·10 <sup>-5</sup>	5.80·10 <sup>-5</sup>	1.66·10 <sup>-5</sup>	2.80·10 <sup>-5</sup>	0.91·10 <sup>-5</sup>
1 600	30.16·10 <sup>-5</sup>	7.85·10 <sup>-5</sup>	14.95·10 <sup>-5</sup>	5.02·10 <sup>-5</sup>	7.85·10 <sup>-5</sup>	2.29·10 <sup>-5</sup>	4.53·10 <sup>-5</sup>	1.38·10 <sup>-5</sup>

the cracks of poorly soluble dicalcium silicate, and to form with MgO a solid solution of magnesiowustite (Fe, Mg)O with a melting point greater than 1 750°C hindering the process of lime dissolution (Fig. 4).<sup>4)</sup> The observed drop in the equilibrium concentration of CaO in the slag samples with the increasing content of MgO in lime can be explained by an increase in (Mg, Fe and Ca) silicates and magnesiowustite concentration in the volume of lime, which as a consequence, further complicates the process of lime dissolution.<sup>4,8,15,17)</sup>

Figure 8 shows microscopic raster images (SEM Tesla XRAY Oxford) of lime containing 4.3, 7.6 and 80% MgO, after 5 minutes of immersion in the melt at 1 500°C, and the

phase composition of samples carried out with a powder diffractometer “Bruker D2 Phaser”. Sample containing 80% of magnesium oxide was prepared by Voestalpine Stahl Linz consisting of periclase (MgO) and portlandite (Ca(OH)<sub>2</sub>) phases. The sample was prepared in the shape of cylinder according to the methodology described earlier. During kinetic experiment after the contact time up to 2 400 seconds dissolution of sample was not observed. Microscopic investigation of lime containing 80% MgO was carried out for detection of formed solid compounds blocking the dissolution.

Due to the capillary effects after 5 minutes of contact with a melt samples become impregnated with slag. Slag fills the

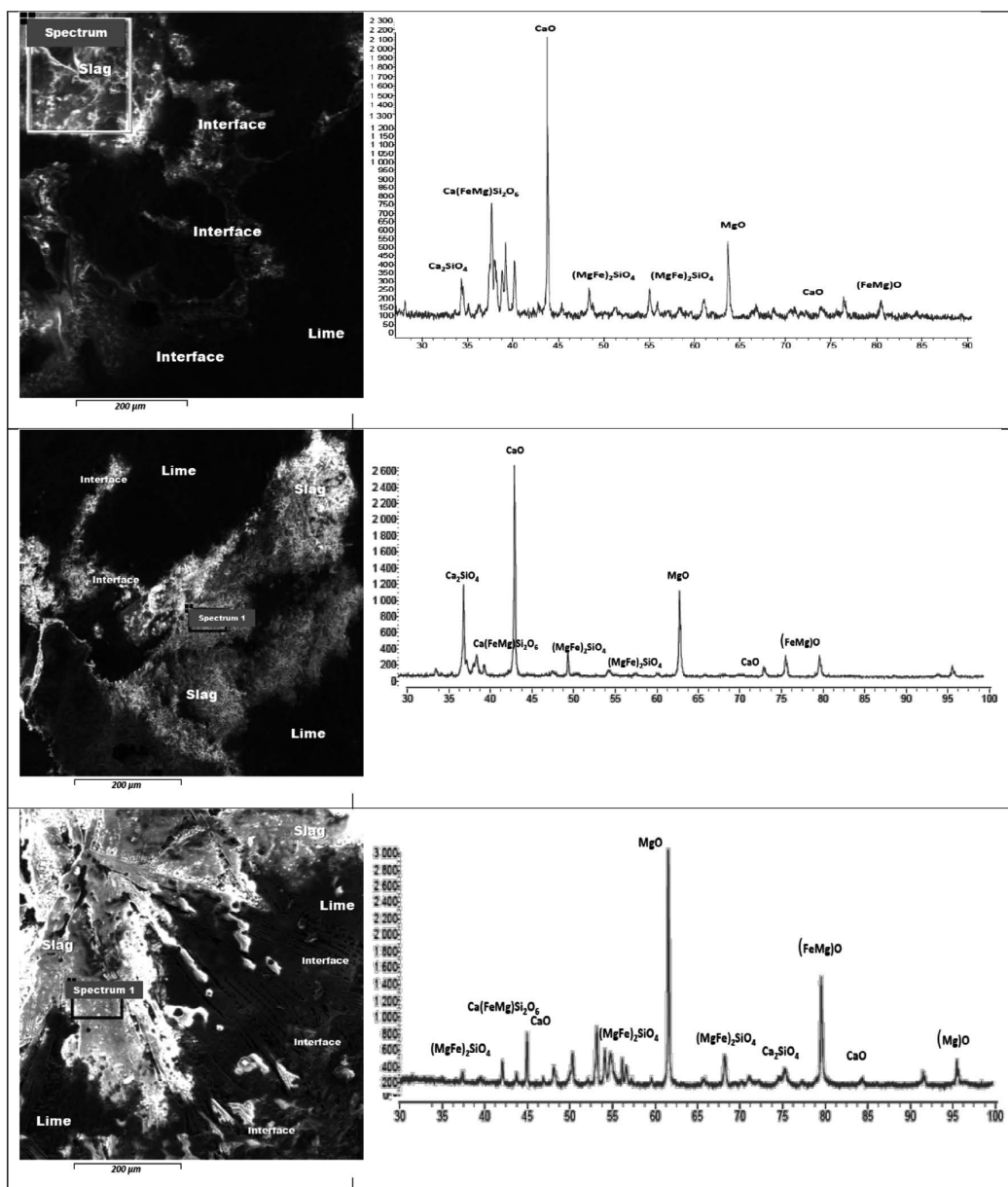


Fig. 8. Microscopic raster images of lime containing 4.3, 7.6 and 80% MgO.

inner and outer pores of lime and is distributed in samples in the form of compounds, consisting of high-temperature silicates of calcium, magnesium and iron, and also magnesiowustite, based on the results of X-ray diffraction analysis. According to the intensities of the characteristic spectral lines, for example of magnesiowustite, it is evident that with the increasing concentration of MgO in lime its concentration increases as well. Chemical compounds formed during the dissolution of the lime in the slag inhibit the diffusion of MgO and CaO in the bulk slag and limit their dissolution in the melt. Growth of the phase formations inhibits the diffusion transport of CaO and MgO in the melt until the complete cessation of diffusion, which leads to the drop of MgO concentration in the slag from 1.38 to 0.71% with the raise of magnesium oxide concentration in lime from 4.3 to 7.6%.

The results obtained are consistent with the conclusions made by Umakoshi. *et al.*<sup>15)</sup> about limitation of lime dissolution process by magnesium oxide in slag systems with FeO content above 20%.

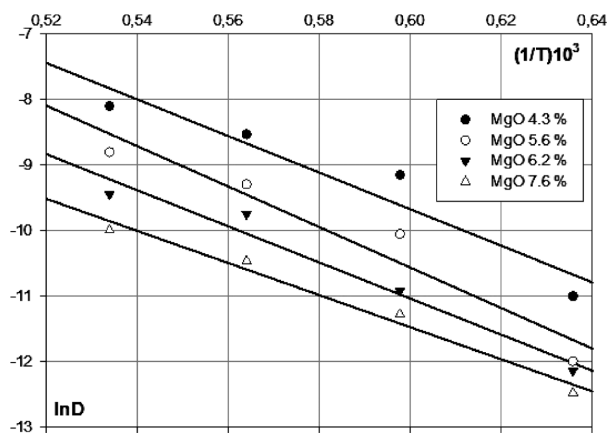


Fig. 9. The dependence of the logarithm of the diffusion coefficient on the inverse temperature.

The experimental data confirms the linear dependence of  $\ln D$  on the inverse temperature  $1/T$  according to the Eq. (8), as shown in (Fig. 9):



$$\ln D = \ln D_0 - \frac{E_D}{R} \frac{1}{T} \dots\dots\dots (8)$$

The calculated mean value of the diffusion activation energy using a tangent of the angle is  $230.2 \pm 14.0$  kJ/mol. High values of diffusion energy are typical for slag systems, for example, the diffusion energy of phosphorus oxide in the silicate slags is 170 kJ/mol. and in the aluminate slags - 200 kJ/mol.<sup>18)</sup>

The elevated levels of diffusion activation energy of calcium oxide in the slag is due to the work that must be applied to bring CaO atoms from the volume of the solid phase onto the interface, where they are in an (e.g. activated) energetically unfavorable state.

Derived kinetic parameters of the lime dissolution process, containing various amounts of MgO, allow for implementing slag formation in the magnesium oxide saturation area.

The slag of this composition have less aggressive effect on the refractory lining of the converter. According to the theory of metallurgical thermodynamics no interaction at the interface of the two phases takes place in case of equality of the concentration of the diffusing component and the saturation concentration.

## 6. Conclusions

(1) The kinetics of slag saturation with lime containing different amounts of MgO in the model process of lime dissolution, in a non-stationary diffusion at temperatures of 1 300–1 600°C has been studied.

(2) To describe the kinetics of dissolution of solid body in the molten slag differential equations derived from the total mass balance of the dissolving substance have been applied. The total mass balance considers the transition of the dissolving substance into the melt phase and its accumulation in the consistently soluble layers of solid.

(3) It was revealed that with the increasing content of magnesium oxide from 4.3 to 7.6% in the technical lime saturation concentration of calcium oxide in the slag decreases 1.2–1.6 times depending on the temperature of the process of lime dissolution.

The equilibrium concentration of CaO in the slag melt is influenced by the FeO content in the slag and MgO content in lime. Magnesium and iron oxides form solid solutions in the form of dense poorly soluble formations in the bulk lime.

(4) It was found that, despite a decrease in the concentration gradient, as the saturation of slag with lime progresses, the mass transfer coefficients are increasing, which value is largely dependent on slag composition and particle size of the lime.

(5) The influence of MgO content in lime on its rate of dissolution has been investigated. The increase in the concentration of MgO in lime results in slower dissolution rates of samples, which indicates the limitation of the process by MgO diffusion in slag. Formation of chemical compounds based on magnesium oxide inhibits diffusive transport of CaO and MgO in the melt and results in the cessation of

diffusion.

(6) Diffusion coefficients were calculated on the basis of the experimental data under the conditions of non-stationary linear and spatial semi-infinite diffusion. The linear dependences of the dissolution rate of samples on the variable

$\frac{c}{\sqrt{t}}$  derived with high reliability consider the chosen spatial model adequate. It was revealed that the diffusion coefficients decrease in approximately 5–8 times with the double increase in the content of MgO (from 4.3 to 7.6%) and increase with the raising temperature (1 300°C to 1 600°C) at constant MgO content by a factor of 15–20.

(7) The linear dependence of diffusion coefficients logarithm on the inverse temperature has been derived. The calculated mean value of the diffusion activation energy is  $230.2 \pm 14.0$  kJ/mol.

The high value of diffusion energy is due to the great degree of viscosity of the slag melt and elevated “energy consumption” of the calcium oxide. This occurs for output through the interface lime-slag, by formation of poorly soluble compounds on the basis of CaO, FeO and MgO.

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## REFERENCES

- 1) L. Akselrod, A. Laptev and V. Ustinov: *Met. Cast. Ukr.*, **1–2** (2009), 9.
- 2) D. Kumar, G. Prasad, S. Vishwanath, P. Ghorui, D. Mazumdar, M. Ranjan and P. Lal: *Iron Steelmaker*, **6** (2007), 521.
- 3) T. Deng, J. Gran and D. Sichen: *Steel Research Int.*, **81** (2010), 347.
- 4) N. Dogan, G. A. Brooks and M. Akbar Rhamdhani: *ISIJ Int.*, **49** (2009), 1474.
- 5) T. Deng and D. Sichen: *Metall. Mater. Trans. B*, **43** (2012), No. 3, 578.
- 6) N. Maruoka, A. Ishikawa, H. Shibata and S.-y. Kitamura: *High Temp. Mater. Process.*, **32** (2013), 15.
- 7) F. Huang, N. Maruoka, A. Ishikawa, J. Liu and S.-y. Kitamura: Proc. Unified Int. Technical Conf. on Refractories, eds. by D. G. Goski and J. D. Smith, John Wiley & Sons, Inc., Hoboken, NJ, (2014), CD-ROM.
- 8) N. Maruoka, A. Ishikawa, H. Shibata and S.-y. Kitamura: Proc. 12th Unified International Technical Conf. on Refractories, Unitecr, Kyoto, (2011), CD-ROM.
- 9) Y. P. Nikitin and O. A. Esin: *Proc. Univ. Ferr. Metall.*, **9** (1959), 3.
- 10) P. Williams, M. Sunderland and G. Briggs: *Ironmaking Steelmaking*, **9** (1982), 150.
- 11) M. Matsushima, S. Yadoomaru, K. Mori and Y. Kawai: *Trans. Iron Steel Inst. Jpn.*, **17** (1977), 442.
- 12) T. Hamano, S. Fukagai and F. Tsukihashi: *ISIJ Int.*, **46** (2006), 490.
- 13) F. Oeters: *Metallurgy of Steelmaking*, Verlag Stahleisen, Düsseldorf, (1994), 219.
- 14) V. I. Baptizmansky and V. B. Okhotskiy: Physico-chemical basis of the BOF process, Vishcha Head Publishing House, Donetsk, (1982), 182.
- 15) M. Umakoshi, K. Mori and K. Kawai: *Trans. Iron Steel Inst. Jpn.*, **24** (1984), 532.
- 16) A. G. Stromberg and D. P. Semchenko: Physical Chemistry, Book for Chemical Special Schools, Vysshaya shkola, Moscow, (2003), 527.
- 17) A. Babenko, L. Krivyh and V. Liauchuk: *Proc. Univ. Ferr. Metall.*, (2010), No. 4, 20.
- 18) M. E. Posin: Research in Inorganic Technology. Salts, Oxides, Acids, Nauka, Moscow, (1972), 361.

## Appendices

Below are the chemical compositions presented as oxides, of the initial and final slag after the dissolution of lime containing 4.3–7.6% MgO at the highest temperature of experiment (1 600°C).

Slag	MgO content in lime, %	Composition, %				
		CaO	SiO <sub>2</sub>	FeO	MgO	other
Initial	–	20.00	35.00	45.00	–	–
Final (XRF), 1 600°C	4.3	40.36	<b>25.93</b>	31.83	1.38	0.50
Final (calculation), 1 600°C		41.84	<b>24.82</b>	31.91	1.30	0.13
XRF, 1 600°C	5.6	35.85	<b>26.20</b>	36.52	1.32	0.11
calculation, 1 600°C		35.16	<b>27.78</b>	35.71	1.28	0.07
XRF, 1 600°C	6.2	31.02	<b>33.90</b>	34.10	0.88	0.10
calculation, 1 600°C		29.10	<b>30.58</b>	39.41	0.82	0.09
XRF, 1 600°C	7.6	26.40	<b>31.28</b>	41.53	0.71	0.08
calculation, 1 600°C		25.79	<b>32.11</b>	41.28	0.75	0.07

The inertness of synthetic quartz material in the range of the experiment temperatures, the possibility of extracting the crystallized slag without involvement of special equipment, low cost of the material have defined the use of the crucibles for the experiment.

### Initial mass of slag = 2 g, after the dissolution of 4.3% lime mass of slag was 2.82 g

	Initial slag Content, %	Initial Mass, g	Slag content after lime dissolution, % (XRF)	Mass after the dissolution, g	M end-M initial, g
Lime 4.3% 1 600°C	CaO	20%	40.36	1.13	0.74
	SiO <sub>2</sub>	35%	25.93	0.73	0.03
	FeO	45%	31.83	0.89	0
	MgO		1.38	0.04	0.04
	Other		0.50	0.01	0.01

Calculation:  $m(\text{SiO}_2)_{\text{primary}} = 0.70 \text{ g}$ ,  $m(\text{SiO}_2)_{\text{final}} = 2.82 - 0.2593 = 0.73 \text{ g}$

### Initial mass of slag = 2 g, after the dissolution of 5.6% lime mass of slag was 2.52 g

	Initial slag Content, %	Initial Mass, g	Slag content after lime dissolution, % (XRF)	Mass after the dissolution, g	M end-M initial, g
Lime 5.6% 1 600°C	CaO	20%	35.85	0.90	0.5
	SiO <sub>2</sub>	35%	26.20	0.66	-0.04
	FeO	45%	36.52	0.92	0.02
	MgO		1.32	0.035	0.035
	Other		0.11	0	0

### Initial mass of slag = 2 g, after the dissolution of 6.2% lime mass of slag was 2.28 g

	Initial slag Content, %	Initial Mass, g	Slag content after lime dissolution, % (XRF)	Mass after the dissolution, g	M end-M initial, g
Lime 6.2% 1 600°C	CaO	20%	31.02	0.70	0.30
	SiO <sub>2</sub>	35%	33.90	0.71	0.01
	FeO	45%	34.10	0.70	0
	MgO		0.88	0.025	0.025
	Other		0.10	0	0

### Initial mass of slag = 2 g, after the dissolution of 7.6% lime mass of slag was 2.18 g

	Initial slag Content, %	Initial Mass, g	Slag content after lime dissolution, % (XRF)	Mass after the dissolution, g	M end-M initial, g
Lime 7.6% 1 600°C	CaO	20%	26.40	0.58	0.18
	SiO <sub>2</sub>	35%	31.28	0.68	0.02
	FeO	45%	41.53	0.91	0.01
	MgO		0.71	0.02	0.02
	Other		0.08	0	0

Confirmation of the inertness of SiO<sub>2</sub> crucibles is a mass balance of slag before and after the dissolution. Due to the complexity of the analysis a certain deviation within the error is appropriate.

The phase composition of sample containing 80%MgO.

