

MODEL DEVELOPMENT OF ADDITIVES DISSOLUTION IN THE BOF PROCESS*

*Daniel Augusto Godinho de Carvalho¹
Johannes Schenk²
José Adilson Castro³*

Abstract

Since the beginning of BOF process, slag formation has been subjected to extensive development. During the initial stages of the blow, fast slag formation is primordial for the process performance. This is mainly to allow oxidizing reactions, and also to protect the refractory. A modeling of BOF process for the purpose of process optimization requires precise knowledge concerning the dissolution of CaO and MgO based materials. Using this knowledge, the optimal process conditions can be ensured by a controlling of the slag formation during the converter steelmaking process. Taking into account an application of large amount of different raw materials, as well as location-specific process conditions, the characterization of the dissolution behavior of different additives is an important key to improve the technological process. Thereby, in the frames of this project, an appropriate model for slag formation is established and compared to operational results for a 330t BOF, operating at ThyssenKrupp CSA, Santa Cruz, Brazil.

Keywords: BOF; Slag; Flux; Dissolution; Modeling.

¹ *Metallurgical Engineer, Steel Plant, ThyssenKrupp CSA, Rio de Janeiro, Brazil.*

² *Univ.-Prof. Dipl.-Ing. Dr. techn, Montanuniversität Leoben, Styria, Austria.*

³ *Prof. P.hD, Universidade Federal Fluminense – UFF, Volta Redonda, Rio de Janeiro, Brazil.*

1 INTRODUCTION

BOF slag is created by fluxing the first “FeO”-SiO₂ rich slag with the addition of slag formers as a burnt lime with high contents of CaO and dolomitic lime as MgO source. A good rate of slag formation during the blow, with high contents of CaO and MgO close to saturation is crucial for the process performance and can be governed by the degree of dissolution, a key for understanding the progress of slag-metal reactions in the steelmaking system.

2 MATERIAL AND METHODS

According to experiments conducted by Matsushima [1] the dissolution rate of fluxes, v_r (m/min), into slag systems are controlled by mass transfer, and can be defined, assuming spherical geometry, as the dissolved volume per unit area in a unit of time.

$$v_r = -\frac{1}{S} \frac{dV}{dt} = -\frac{dr}{dt} \quad (1)$$

In a recent research, proposed by Dogan [2], the number of particles (n_i) dissolved in the slag is proportional to the particle concentration, individual calculation for different particle size is calculated, and the results are then; the sum of all particles (Equation 2). The amount of flux dissolved (Equation 3) in emulsion at time t , $M_{d,flux}^t$ is determined by summation of total amount of lime dissolved at time $t - \Delta t$ and amount of lime dissolved at given time step Δt . Subscript d refers to dissolved flux in emulsion.

$$\frac{dW_i}{dt} = -\rho_i S \frac{dr}{dt} n_i \quad (2)$$

$$M_{d,flux}^t = M_{d,flux}^{t-\Delta t} + \frac{dW_L}{dt} \Delta t \quad (3)$$

2.1 Lime Dissolution Mechanism

For stagnant laboratory experiments, irrespective of the lime type, the dissolution mechanism is very fast in the “FeO”-SiO₂ slags, while the reaction became extremely slow in the case of CaO-“FeO”-SiO₂ slags due a di-calcium silicate formation, the main dissolution mechanism of lime is assumed to be controlled by CaO diffusion through a boundary layer according to Matsushima [1].

$$-\frac{dr}{dt} = k \frac{\rho_{slag}}{100 \rho_{Lime}} (\%CaO_{saturation} - \%CaO_{slag}) \quad (4)$$

2.1.1 CaO saturation

The saturation of CaO can be calculated according to Schürmann's [3] research, where the CaO saturation is calculated by the conversion of all oxides contents in a in a simple quasi ternary system CaO*-FeO_i*-SiO₂*. MnO should not be considered into accounts, because has only a diluting (Equation 5) effect and all the other elements should be recalculated without MnO (Equation 6).

$$F_{MnO} = \frac{100}{100 - \%MnO} \quad (5)$$

$$\%(Oxide)' = F_{MnO} \cdot \%Oxide_{Initial} \quad (6)$$

The analytical concentration of each component in the steelmaking slags are normalized by considering the equivalent amount designated in terms of mass;

$$\%CaO^* = \%CaO' + 0.238.\%P_2O_5' + (1 - 0.32 + (\frac{\%FeO_n'}{200}).MgO') + 0.238.\%Al_2O_3' \quad (7)$$

$$\%SiO_2^* = \%SiO_2' + 0.762.\%P_2O_5' + (0.32 - (\frac{\%FeO_n'}{200})).MgO' + 0.762.\%Al_2O_3' \quad (8)$$

$$\%FeO_t^* = FeO_t' \quad (9)$$

CaO saturation for reference temperatures (1600°C), in the quasi-ternary slag system system, CaO*-FeO_t*-SiO₂*, can be calculated according to mathematical description presented below, where $\varphi = \%FeO_n^* / \%SiO_2^*$.

$$\%CaO_s^* = 100 - (1 + \varphi) \left[\frac{\left(\frac{(-0.64\varphi - 1)}{(0.00212\varphi^2)} \right)}{2} - \sqrt{\left(\frac{\left(\frac{(-0.64\varphi - 1)}{(0.00212\varphi^2)} \right)}{2} \right)^2 - \left(\frac{32}{(0.00212\varphi^2)} \right)} \right] \quad (10)$$

In order to consider the influence of temperature on lime saturation, allowing a complete mathematical description of the lime saturation contents in the system CaO*-FeO_t*-SiO₂* dependent on slag composition and temperature.

$$\%CaO_{Sat,T(^{\circ}C)}^* = \%CaO_s^* + 0.0225.(T_{slag} - 1600) \quad (11)$$

2.2 Dolomitic Lime Dissolution Mechanism

Dolomitic lime has a tendency to form a solid product with FeO. Umakoshi [4], suggested that diffusion of dolomitic lime is controlled by CaO dissolution of CaO through a boundary layer when the FeO content in slag is lower than 20% (Equation 12), otherwise MgO is the rate limiting for FeO concentrations higher than 20% (Equation 13).

$$-\frac{dr}{dt} = \left(1 + \frac{M_{MgO}}{M_{CaO}} \right) \cdot k_{dol} \cdot \frac{\rho_{slag}}{100 \rho_{dolime}} \cdot (\%CaO_{saturation} - \%CaO_{slag}) \quad (12)$$

$$-\frac{dr}{dt} = \left(1 + \frac{M_{CaO}}{M_{MgO}} \right) \cdot k_{dol} \cdot \frac{\rho_{slag}}{100 \rho_{dolime}} (\%MgO_{saturation} - \%MgO_{slag}) \quad (13)$$

2.2.1 MgO saturation

In the present study, the MgO saturation levels is calculated according to a mathematical description of magnesia saturation in complex steelmaking slags proposed by Schürmann [5], all steps are similar to the CaO saturation proposed in this study.

$$\%CaO^* = \%CaO + 0.59.\%MnO + 0.37.\%P_2O_5 + 0.21.\%Al_2O_3 \quad (14)$$

$$\%SiO_2^* = \%SiO_2 + 0.63.\%P_2O_5 + 0.79.\%Al_2O_3 + 0.41.\%MnO \quad (15)$$

$$\%FeO_t^* = FeO_t \quad (16)$$

Then, the normalized values for CaO-FeO_t-SiO₂ are.

$$\%CaO^{\Delta} = 100.\%CaO^* / (\%CaO^* + \%SiO_2^* + \%Fe_tO^*) \quad (17)$$

$$\%SiO_2^{\Delta} = 100.\%SiO_2^* / (\%CaO^* + \%SiO_2^* + \%Fe_tO^*) \quad (18)$$

$$\%FeO_t^\Delta = 100 - \%SiO_2^\Delta - \%CaO^\Delta \quad (19)$$

The mathematical descriptions presented below describe the MgO saturation;

$$\%MgO_{s,1600} = a + b \cdot \%SiO_2^\Delta + 0.01354 \cdot (\%SiO_2^\Delta)^2 \quad (20)$$

The factors (a) and (b) are function of normalized total iron oxide, and are described below.

$$a = 7.989 - 0.1547 \cdot \%FeO_t^\Delta + 0.001232 \cdot (\%FeO_t^\Delta)^2 \quad (21)$$

$$b = -0.4374 + 0.01034 \cdot \%FeO_t^\Delta \quad (22)$$

A complete mathematical description of the MgO saturation contents in the system $CaO^*-FeO_t^*-SiO_2^*$ dependent on slag composition and temperature is described below.

$$\%MgO_{sat,T(K)} = (\%MgO_{s,1600}) \cdot e^{\left(5.5478 - \frac{10391}{T(K)}\right)} \quad (23)$$

2.3 Slag Properties

2.3.1 Density of multicomponent slags

An additive method for the estimation of densities in alloys and slags has been widely used. In this method, proposed by Keene [6] the density can be obtained from the following equation.

$$\rho = \frac{M_1x_1 + M_2x_2 + M_3x_3 + \dots}{x_1V'_1 + x_2V'_2 + x_3V'_3 + \dots} \quad (24)$$

Where, ρ = Density (g/cm^3), M = Molecular weight (g/mol), x = Mole fraction, V' = Partial molar volume (cm^3/mol).

Table 1. Recommended values for partial molar volume of slag constituents (Slag Atlas, 1995)

Constituent	V (cm^3/mol)
CaO	20.7
MgO	16.1
MnO	15.6
FeO	15.8
SiO ₂	$19.55 + 7.996x_{SiO_2}$

2.3.2 Viscosity of multicomponent slags

In order to calculate the viscosity of slags, a model proposed by Mills [7] is applied, the slags constituents are divided in three categories; glass formers (Equation 25) modifiers (Equation 26) and amphoteric (Equation 27).

$$X_G = X_{SiO_2} + X_{P_2O_5} \quad (25)$$

$$X_M = X_{CaO} + X_{MgO} + 3 X_{CaF_2} + X_{FeO} + X_{MnO} + X_{TiO_2} \quad (26)$$

$$X_A = X_{Al_2O_3} + X_{Fe_2O_3} + X_{B_2O_3} \quad (27)$$

Normalized values x_G^* , x_M^* , x_A^* are obtained by dividing the mole fractions, x_G , x_M , x_A by the equation 28;

$$1 + X_{CaF_2} + 0.5 X_{FeO} + X_{TiO_2} + X_{K_2O} \quad (28)$$

The viscosity of slag (in poise) can then be determined by using the equation below;

$$\mu_s = AT \exp\left(1000 \frac{B}{T}\right) \quad (29)$$

Parameters A and B can be expressed as detailed below ($\alpha = x_M^* / (x_M^* + x_A^*)$). The parameters for B are available on Table 2.

$$B = B_0 + B_1 x_G^* + B_2 (x_G^*)^2 + B_3 (x_G^*)^3 \quad (30)$$

$$-\ln A = 0.2693.B + 11.672 \quad (31)$$

Table 2. B parameters for calculating the viscosity of slag [11]

$B_i = \alpha_i + b_i \alpha + c_i \alpha^2$
$B_0 = 13.8 + 39.9355\alpha - 44.049\alpha^2$
$B_1 = 30.481 - 117.1505\alpha + 139.9978\alpha^2$
$B_2 = -40.9429 + 234.0486\alpha - 300.04\alpha^2$
$B_3 = 60.7619 - 153.9276\alpha + 211.1616\alpha^2$

As the viscosity of the slag is strongly influenced by the solid fraction (ε) in the slag, the equation proposed (Equation 32) by Einstein-Roscoe is considered by Oeters [8].

$$\mu_{\text{slag}} = \mu_s (1 - \varepsilon)^{-2,5} \quad (32)$$

2.4 Mass Transfer Coefficients

Mass transfer coefficient can be estimated by semi-empirical relationship based on Sherwood, Reynolds and Schmidt numbers. Schmidt number for CaO and MgO can be found as a function of physical properties of slag and diffusivities of lime and dolomite. Dogan [2] suggested that there are two different flow regimes in the slag due to the stirring conditions. The regime near the lance has a higher stirring intensity due to the CO gas generation. The regime far away from the lance and close to the refractory lining is expected to be more stagnant regime. Therefore, dissolution of solid particles in this stagnant regime takes place at a slower rate compared to that in the turbulent regime. As a practical solution to the problem, an empirical correlation for Reynolds Number (Re') was applied.

$$Re' = 10 \left(\frac{u_p d_p \rho_s}{\mu_s} \right) \quad (33)$$

$$Sc = \frac{\mu_s}{\rho_s D} \quad (34)$$

$$Sh = 1 + 0.724 (Re')^{0,48} Sc^{1/3} \quad (35)$$

$$k = \frac{Sh \cdot D}{d_p} \quad (36)$$

It is assumed the diffusivity of 1.6×10^{-5} cm²/s for MgO 1.400°C, for CaO diffusivities, the table below (Table 3) is assumed.

Table 3. Diffusivities of lime available at Matsushima research [1]

T (°C)	D (cm ² /s)	μ_{slag} (Poise)
1500	5.5×10^{-6}	9,2
1400	2.7×10^{-5}	1,2

In order to calculate the diffusivities of CaO and MgO for various temperatures, the equation of Stokes-Einstein and Eyring, $D \propto T_S/\mu_S$, is considered by Dogan [2].

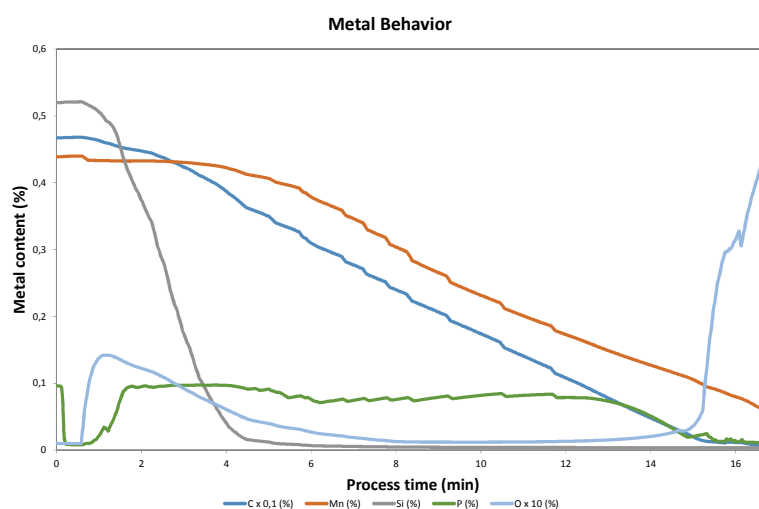
3 RESULTS AND DISCUSSION

Some experimental heats were conducted in order to validate and check the model at ThyssenKrupp CSA (TKCSA), Santa Cruz, Brazil. There are two state of art BOF installed, a nominal capacity of 350t of charge and Thyssen Blowing Metallurgy (TBM) technology available.

An example for one typical chemical composition (Metal and Slag) is available in the table below (Table 4), and also the slag and metal behavior (Figure 1 and 2) for one simulated heat as result of the proposed slag model.

Table 4. Heat 740897 - Hot Metal and EOB steel analysis.

Sample	C (%)	Mn (%)	P (%)	S (ppm)	Si (%)	Oxygen (ppm)
Hot Metal	4,97	0,44	0,096	12	0,52	-
Steel EOB	0,03	0,14	0,013	23	0,00	516 ppm
Sample (%)	CaO	SiO ₂	Fe(T)	MgO	MnO	P ₂ O ₅
Slag EOB (Sample)	48,8	12,5	16,1	7,6	3,3	2,1
Slag EOB (Model)	51,2	12,4	15,9	6,8	4,6	1,9

**Figure 1.** Typical metal behavior during BOF blow - Heat 740897.

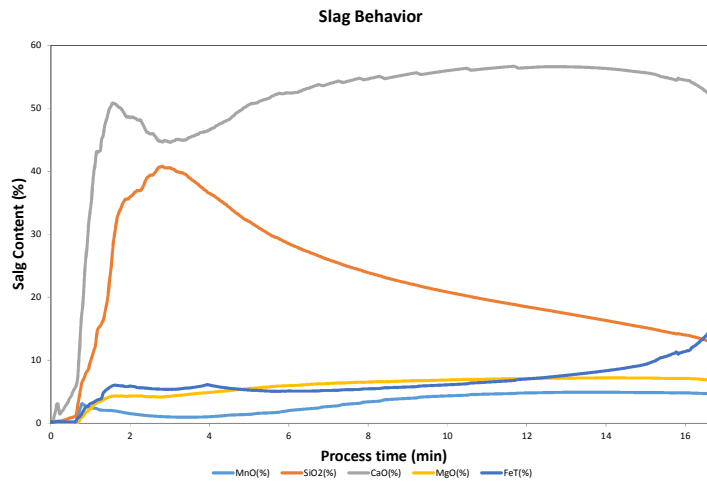


Figure 2. Typical Slag Behavior during BOF blow. Heat 740897.

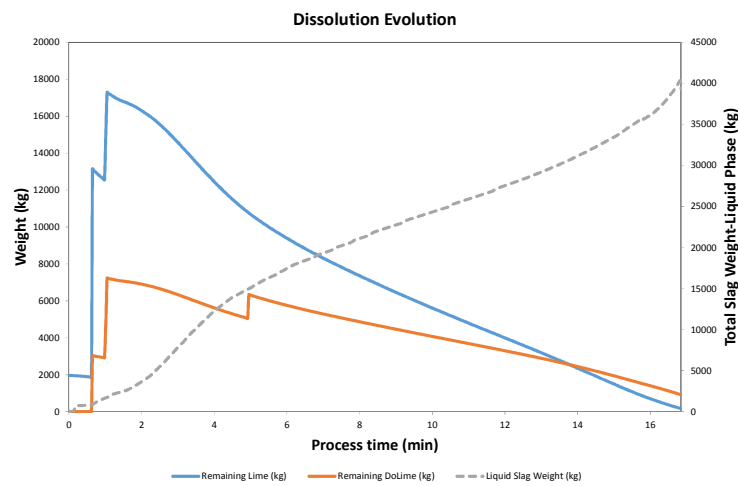


Figure 3. BOF slag mass behavior between liquid and solid phase during blow. Heat 740897.

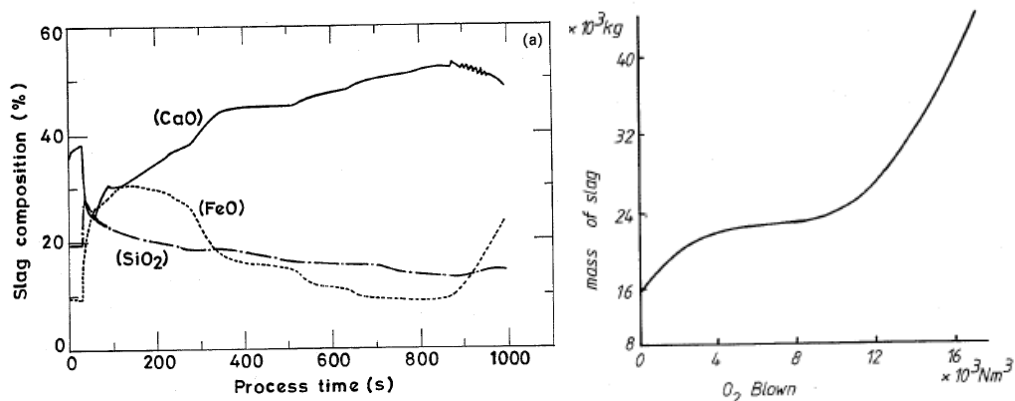


Figure 4. (Left) Evolution of slag composition by dynamic slag-droplet model proposed by Brahma Deo [9]. (Right) Increasing mass of slag with oxygen blown in 300 t converter at Hoogovens Ijmuiden.

According to Figure 2 and 3 for the first step of the blow, an acid slag is formed from oxidized Si and Fe, the lime is only very partially dissolved and the temperature is low, so that part of the phosphorus is oxidized. Then, in the second step, lime is progressively dissolved with enrichment of liquid slag in CaO and decrease in FeO content due to dilution and FeO reduction during full decarburization. It means a heterogeneous slag and non-reactive with respect to phosphorus. At the end, the slag is reactive and suitable for final dephosphorization. as shown in Figure 1 and 2.

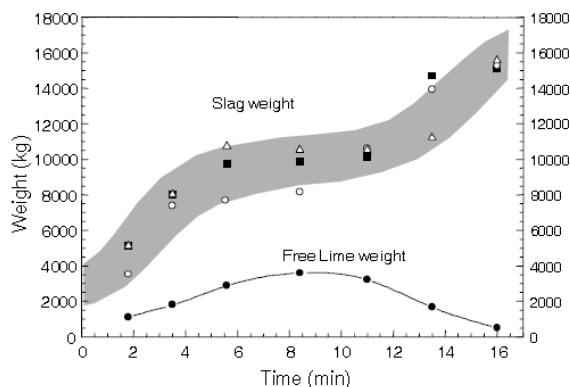


Figure 5. Slag weight and free lime content along the process at Siderar steel plant in a recent study of Cicutti [10] about an analysis of slag foaming.

Establishing a comparison between the proposed model (Figures 3 and 2) and the study developed by Cicutti [10], on Figure 5, and also the models proposed by Brahma Deo [10], on Figure 4, the results of proposed model are in accordance with the literature. The different curve for free lime, is regarding to different additions steps between both plants, at TKCSA 90% of lime addition is made just after the ignition, at Siderar there is an addition of 1000 kg of lime before start the process, and the 6600 kg in first half of the process. All heats simulated below (Figure 6) were carried out in a BOF without slag splashing procedure just before the simulated heat (remaining slag were not considered). Also, the dissolution of BOF lining to slag was not considered.

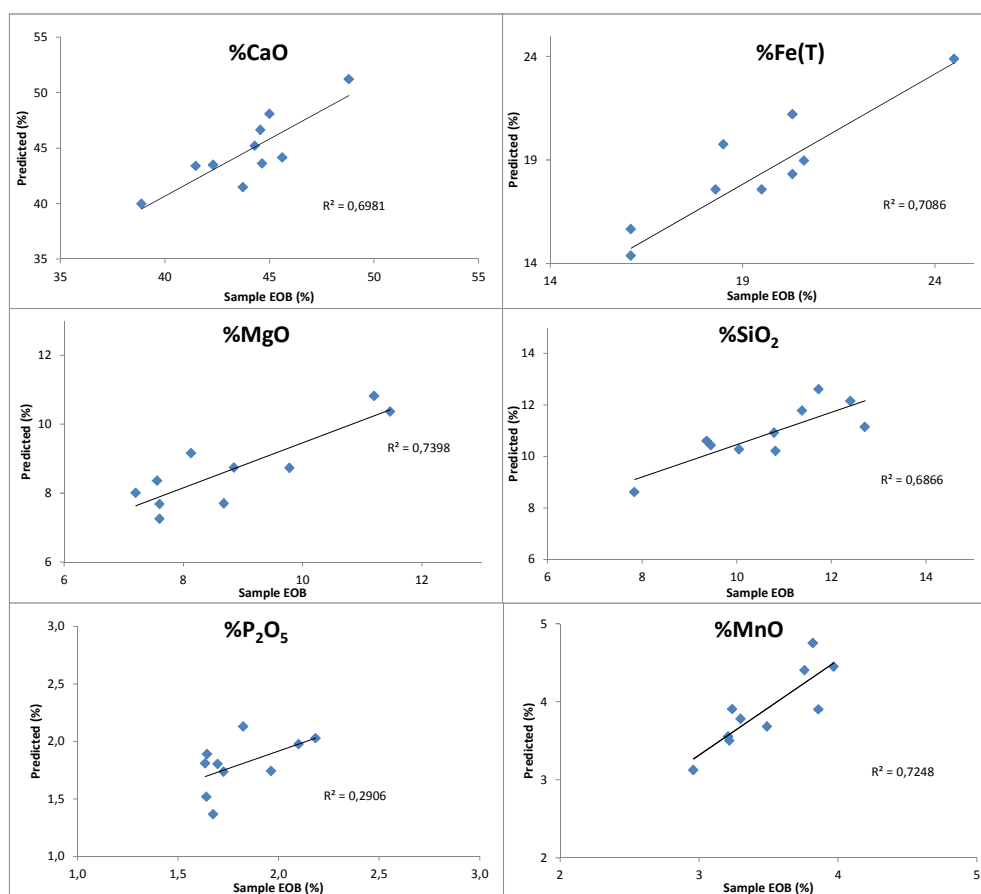


Figure 6. Comparison between slag samples at the end of BOF blow (EOB) X Predicted by current work.

4 CONCLUSION

A suitable model were developed and proposed, a comparison between slag sample and predicted values by the proposed model at BOF end of blow were done (Figure 6), as well literature validation with previously works, as already mentioned before. All of the mentioned comparisons displayed a good consistency. Nevertheless, there is still an opportunity to improve the phosphorous modeling (Figure 6), some other challenging points to be considered are the suction of flux by a primary dedusting system, which is estimated to be around 5-10% in TKCSA regular process. A good technical approach for this issue can be a combination of process data and the modeling of terminal velocity in the presence of buoyancy force. One other important point is the dissolution of BOF lining and slag-splashing “cover” in the subsequent heat. A better comprehension for BOF lining dissolution over the process is a key point not only to improve the slag modeling, but also to improve the BOF lining life time, by reducing the refractory wear.

REFERENCES

- 1 Matsushima, Masaaki, et al. 1977. A Fundamental Study on the Dissolution Rate of Solid Lime into Liquid Slag. Trans. Iron Steel Inst. Jpn. 1977, p. 442.
- 2 Dogan, Neslihan, Brooks, Geoffrey and Rhamdhani, Muhamad. 2009. Kinetics of Flux Dissolution in Oxygen Steelmaking. ISIJ International. 2009, Vol. 49, 10, pp. 1474-1492.
- 3 Schürmann, Eberhard, Schmöle, Peter e Kolm, Ingo. 1985. Verlauf der Kalksättigung im System $\text{FeO-Fe}_2\text{O}_3\text{-CaO-SiO}_2\text{-P}_2\text{O}_5\text{-MgO-MnO}$ beim Gleichgewicht mit einer Eisenschmelze. Steel Research. 56, 1985.
- 4 Umakoshi, M., Mori, K. e Kawai, Y. 1984. Trans. Iron Steel Inst. Jpn. 1984, Vol. 24, p. 532.
- 5 Schurmann, E.; Kolm, I. Mathematical description of magnesia saturation in complex steelmaking slags in equilibrium with liquid iron. Steel Res. 1986, 57, 7-12.
- 6 Keene, B. J. e Mills, K.C. 1995. Densities of Molten Slags. [ed.] Verein Deutscher Eisenhüttenleute (VDEh). Slag Atlas. Düsseldorf : Verlag Stahleisen GmbH, 1995.
- 7 Mills, K. C. 1995. Viscosities of Molten Slags. [ed.] Verein Deutscher Eisenhüttenleute (VDEh). Slag Atlas. 2a. Düsseldorf : Verlag Stahleisen GmbH, 1995, pp. 349-397.
- 8 Oeters, Franz. 1989. Metallurgie der Stahlherstellung. Berlin : Stahl Einsen, 1989
- 9 Deo, Prof. Dr. Brahma, Mazumdar, Dipak e Chakraborti, Nirupam. 1998. Modeling and simulation on iron and steelmaking. s.l. : REM, 1998, pp. 210-216.
- 10 Cicutti C., Valdez M., Pérez T., R. Donayo, J. Petroni. 2009. Analysis of slag foaming during the operation of an industrial converter. Latin America Applied Research. 2009, Vol. 32.
- 11 Slag Atlas. 1995. M. Allibert, et al. [ed.] Verein Deutscher Eisenhüttenleute (VDEh). 2a. Düsseldorf : Verlag Stahleisen GmbH, 1995.