A new approach for modelling and control of dephosphorization in BOF converter

S. Khadhraoui, H.-J. Odenthal, S. Das, M. Schlautmann, K. Hack, B. Glaser, R. Woolf

In the BOF process, the accurate control of Phosphorous removal up to ultra-low values is very important to ensure a high quality of the end–product. This has proven to be associated with several challenges, leading to a preferred usage of high priced low P iron ores. Thus, in the scope of the European BOFdePhos project, important thermodynamic and kinetic aspects of the dephosphorisation reaction such as the effect of solid phases on Phosphorous distribution and lime dissolution in a foamy slag were investigated.

It was found that BOF slags are heterogeneous during a large period of the blow and also at the end of blow in most cases. The type and amount of solid phases is strongly affected by temperature and minor oxides content such as MgO-, MnO- and Al_2O_3-content. The consideration of solid phases formation in the slag, especially the P dissolving C2S_C3P phase, is crucial for a successful modelling and control of dephosphorisation. However, most of the Phosphorous distribution equations available in the literature were developed for homogeneous slags. Thus, a new approach for thermodynamic modelling of the P-distribution between a heterogeneous slag and liquid iron covering the total blowing period in converter was developed and incorporated in a kinetic dephosphorisation model. It was found that while the P distribution in a fully liquid slag was a strong function of temperature, CaO- and FeO-content, the P distribution in a heterogeneous slag depended further on temperature but also on the amount of solid phase as well as the basicity of the liquid slag phase. Even though the C2S_C3P phase can dissolve high amount of Phosphorous, the P-dissolution in the solid phase in the industrial process is associated with strong kinetic limitations. New strategies for the enhancement of dephosphorization control in the BOF converter, focusing on using the potential of the solid phase in removing Phosphorous, were developed.

INTRODUCTION

The achievement of ultra-low-P values in steel during oxygen converting of hot metal is crucial for high quality steel production. Lowering the Phosphorous content has become a critical requirement for steels used in thin sheets for deep drawn applications, automobile exteriors and pipelines for transportation of natural gas and petroleum products [1]. The oxygen converter process provides excellent conditions for phosphorous removal from steel. The dominance of a high oxygen potential in the metal-slag interface throughout the blow and the presence of a basic slag cause favored thermodynamic conditions for P removal from the metal phase. Moreover, the high mixing intensity induced by top and/or bottom gas injection at high speed as well as the CO/CO_2 gas generation resulting from the decarburization reaction further contribute to the enhancement of the dephosphorization kinetics. However, the challenges are high for steelworkers especially those with a large variation in hot metal composition and subsequently also in the final slag composition. The non-achievement of final P contents at the end of the oxygen blowing requires a reblowing, that is continuation of oxygen blow instead of the scheduled tapping under addition of fluxing agents, which result in production time loss, decrease in iron yield, excessive lime consumption and increased

refractory wear. Within the scope of the European BOFdePhos project, a comprehensive study of the dephosphorization reaction has been carried out with focus on the thermodynamic

Sabrine Khadhraoui, Hans-Jürgen Odenthal
SMS group GmbH, Germany

Satyajit Das
SMS India Pvt. Ltd, India

Martin Schlautmann
VDEh-Betriebsforschungsinstitut GmbH, Germany

Klaus Hack
GTT Technologies, Germany

Björn Glaser
Royal Institute of Technology, Sweden

Rhian Woolf
Tata Steel Europe, UK

modelling of the state of metal-slag-equilibrium and conside-ration of metal droplets circulating through a metal-slag emul-sion for modelling of transport kinetics. In this paper, the main results with respect to the investigations of thermodynamics and kinetics of dephosphorization will be presented.

Evaluation of the state of BOF slags

The achievement of the aim steel composition at end of the blowing process, especially with respect to P and C-content, depends strongly on controlling the slag evolution. A non-successful slag control may lead to slopping, that is slag over-running from converter mouth with considerable economic withdraws for steelworks. Even though a lot of effort has been made to investigate the thermodynamic state of BOF slags sin-ce the 1930s, their behavior under various process conditions is still not completely understood. This is due to their complex structure, combined with the fact that the slags undergo large variations during the process in terms of composition and tem-perature, mainly as a result of the simultaneous oxidation and reduction processes during the blow. Also, the slag is foamy during a large period of the blow, as a result of CO and CO_2 gas evolution which are the products of the main refining reaction, decarburization. Thus, the state of converter slags as a function of temperature, oxygen partial pressure and minor oxides addi-tion was evaluated within the current project. Some of the main results will be briefly introduced in the current section whereas

a detailed description can be found in [2].

Effect of various process conditions

In order to investigate the thermodynamic behavior of slags in equilibrium with metallic phase under various process conditions, a thermodynamic database for the system CaO-FeO_x-P_2O_5-SiO_2-MnO_x-MgO-Al_2O_3 was developed by GTT. The Gibbs energy of the liquid phase was modelled by the non-ideal associate solution model [3] and the Gibbs energy of non-stoichiometric solid compounds based on the Compound Energy Formalism [4]. Due to the importance of dephosphori-zation reaction, special attention was given to modelling the P-containing phases. The database was critically assessed using all experimental data available, mostly for binary and terna-ry subsystems [2, 5]. The effect of temperature, oxygen par-tial pressure and composition was investigated by means of coupling the database to the thermodynamic software package Factsage ^{TM} [6].

A. Effect of temperature

The effect of temperature on the ternary system CaO-FeO-SiO_2 in equilibrium with liquid iron is illustrated in Fig.1 by means of the isothermals presentation at 1550 °C (Fig.1-a) and 1700°C (Fig.1-b) for the range relevant to the BOF converter slags (low SiO_2 range).
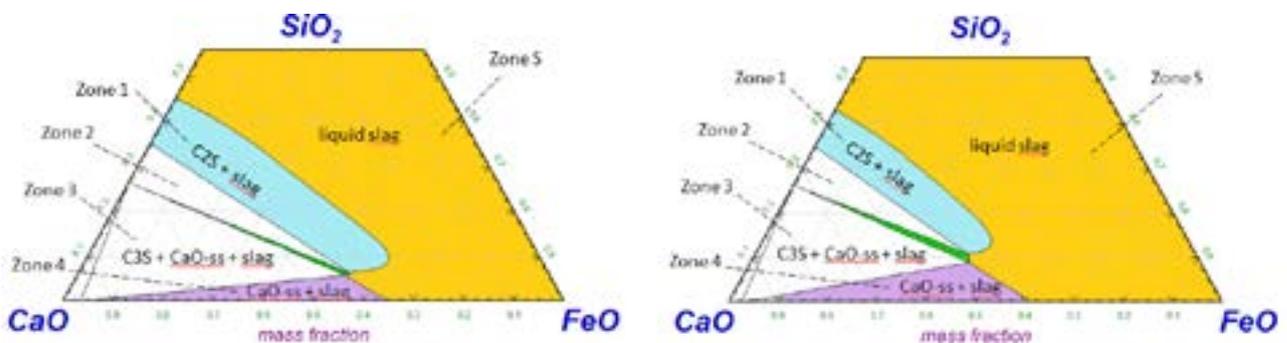
Fig. 1 – Liquidus isothermals of the system CaO-FeO$_x$-SiO_2 in equilibrium with liquid Fe a) 1550°C b) 1700°C

It can be seen that the system is dominated by solid phases precipitation regions: The dominant region is zone 1, which is the saturation region on the $2.CaO.SiO_2$ solid phase, denoted as C2S, followed by zone 2, the double saturation region on both $2.CaO.SiO_2$ and $3CaO.SiO_2$, denoted as C3S. The double satura-tion region on both C3S and the CaO-based monoxide solution is marked as zone 3. It can be seen that the lime only saturation region (zone 4), usually considered as the target zone for opti-mal dephosphorization, has a small stability range in the main oxide system compared to zone 1 and zone 3. For example, at a temperature of 1700°C, the lime saturation only region (zone 4) can be reached only when the SiO_2 contents of the total slag is less than 10 wt. % and this value decreases with a decrease

in temperature. Also, the liquid slag only region (zone S) can be reached only at very high (%FeO)-contents in the total slag: At a temperature of 1700°C, (%FeO) should be higher than 40% to maintain a purely liquid slag, and this value is higher for lower temperatures. Thus, converter slags are expected to be heterogeneous at the end of blowing process, where the typical temperatures are in the range of 1600-1700°C and saturated either on C2S or double saturated on both C3S phase and the CaO-based monoxide solution.

B. Effect of MgO and Al_2O_3

The effect of MgO- and Al_2O_3-addition on the main slag system CaO-FeO$_x$-SiO_2 is illustrated in Fig. 2-a and Fig. 2-b respectively.

The formation of C3S-phase was suppressed for the sake of enhanced readability of the diagrams. Thus, the C2S phase was considered representative of the silicate phases of the system. The addition of Al_2O_3 or MgO resulted in the shrinkage of the C2S-saturation region (marked blue in Fig. 2 and corresponds to zone 1 in Fig. 1) in favor of expansion of both liquid slag and lime only saturation regions (zones S and 4 in Fig. 1), with the effect of Al_2O_3 being stronger than that of MgO in this aspect. One major difference in the effect of both oxides is however the massive change below lime saturation line (for both high and low FeO systems) in case of MgO addition: The saturation regions containing both silicates and monoxide solid solutions (zones 3 and 4 in Fig.1) expanded on the cost of the C2S-only saturation region (marked blue in Fig. 2 and corresponds to zone 1 in Fig. 1). For an MgO-content equal or higher than 7 wt.%, a miscibility gap was observed in the monoxide phase leading to formation of a CaO- and MgO-based monoxide solutions.
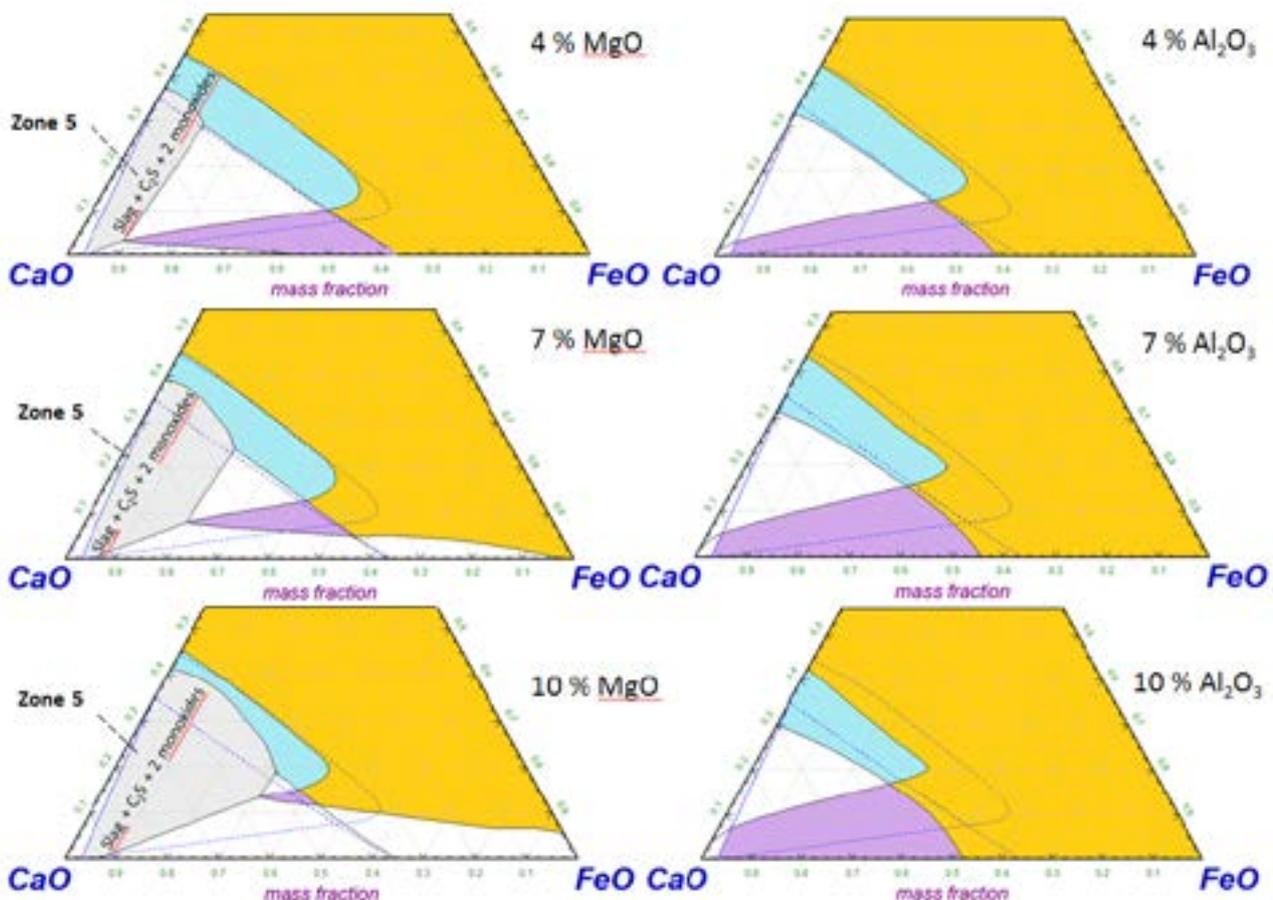

Fig. 2 – Effect of a) MgO b) Al_2O_3 addition at 4% (top), 7% (middle) and 10% (bottom) to the $CaO-FeO_x-SiO_2$ system in equilibrium with liquid Fe at 1600°C: The dashed lines represent the corresponding isothermal in the original $CaO-FeO_x-SiO_2$ system

In conclusion it can be said that the addition of Al_2O_3 and MgO results in more liquid slag formation and less silicates whereas MgO has the additional effect of increasing the amount of monoxide precipitations: For MgO values in the range of 7 % or higher, a lime-saturated slag became saturated on two monoxide phases: an MgO-based and a CaO-based solid solutions.

C. Effect of Oxygen partial pressure
An increase in the Oxygen partial pressure (dashed line in Fig. 3), further noted $p(O_2)$, resulted in a small shrinkage of the silicates saturation regions (zone 1, 2 and 3 in Fig. 1) in favor of more liquid slag compared to the low $p(O_2)$ case (solid lines). A small shift in the lime saturation line towards higher CaO-contents was observed, marking an increase in lime solubility of the slag. The effect of $p(O_2)$ became less significant at higher temperatures, especially for the silicates saturation zones, as can be seen from Fig. 3-b.
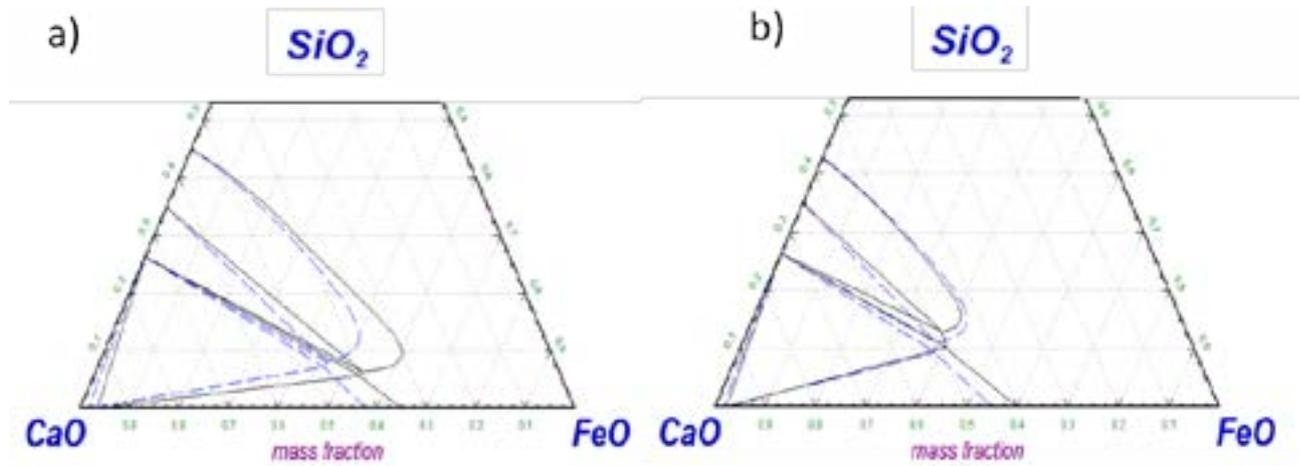
Fig. 3 – Effect of p(O$_2$) on the CaO-FeO$_x$-SiO$_2$ system: The solid lines represent the case of low p(O$_2$) (equilibrium with liquid Fe) whereas the dashed lines represent the case of a high p(O$_2$) = 10^{-5} bar, a) 1550°C b) 1750°C

D. Conclusion

Steelmaking slags are heterogeneous for a large period of the blowing process as well as at the end of blow as long as the final temperatures are equal or less than 1700°C. For low-MgO systems, the final slag is expected to be saturated on C2S or double saturated on C3S and CaO-based monoxide phase, while for the MgO-containing systems, the slag is expected to be either saturated on MgO-based monoxide phase or double saturated on MgO- and CaO- based monoxides. In the industrial process, MgO, Al$_2$O$_3$, MnO and further oxides co-exist in the slag and the resulting effect on slag may be different than in the case of separate addition. For example, while it was found that the addition of MnO does have a considerable effect on the main CaO-FeO$_x$-SiO$_2$ system, it was found that in combination with MgO, MnO stabilizes the monoxide-phase which is formed in the lime saturated part of the system due to its dissolution in both CaO- and MgO-based monoxide phases. As a result, a reduction in the C2S-saturation zone accompanied by an expansion in monoxide saturation zones was observed. Thus, the consideration of minor oxides presence and their combinations is crucial for a proper assessment of the slag state.

Effect of foaming

Slag foaming leads to an increase in the droplets residence time compared to a non-foaming slag [7] which would eventually increase their refining rate, especially with respect to the decarburization reaction [8]. Further experimental investigations of foaming slags within the current project indicated that the foam had considerable effect on the slag structure and the lime dissolution rate. It was found that the gas bubbles are not distributed uniformly in the slag, but rather form a 2-phase-mixture with layers dominated by foam where no liquid film was separating the gas bubbles and bulk slag layers consisting of pure liquid slags [9].

In addition, lime dissolution experiments in foamy slags (see Fig. 4) carried out by KTH showed that the foam slows down the lime dissolution rate by a factor of 0.5 to 0.7, compared to the case of a pure liquid slag. This shows that the contact area between slag and lime is very important and that the presence of the gas phase disturbs lime dissolution. The observed dissolution mechanism was the same for both cases: After reacting with the slag, the lime is peeled off at the edges of the cube with related reduction of the cube side length.
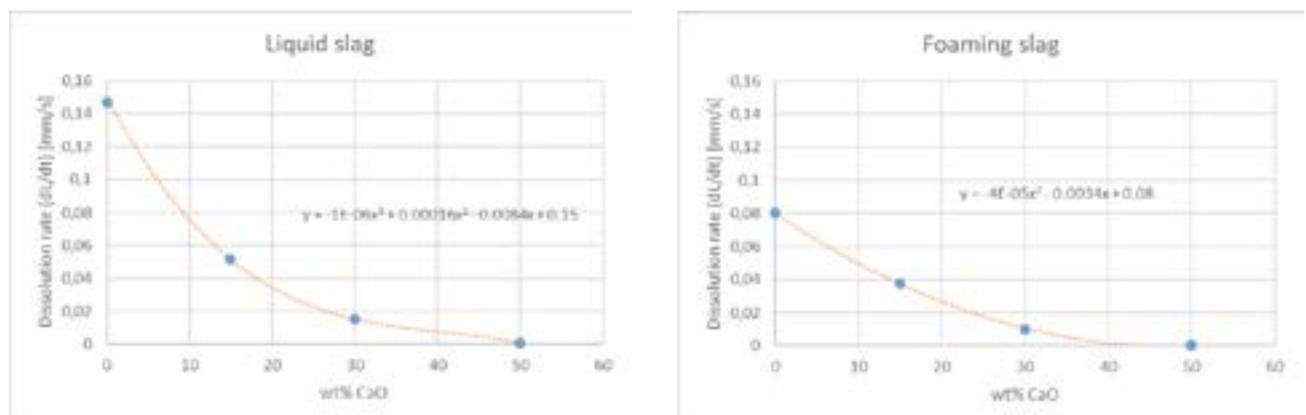
Fig. 4 – Dissolution rate of a lime cube from the Port Talbot Plant at 1600 °C: a) liquid slag b) foamy slag

Consequences for slag sampling in BOF converter

As described in the previous sections, BOF slags have a complex morphology due to the presence of solid phases and gas bubbles. Further contributions to non-homogeneity of the slag are temperature gradients in the slag. It is also possible that the gas dominated parts of a foamy slag would have a lower $p(O_2)$ than the bulk liquid parts since the gas mainly contains CO.

The determination of slag analysis at the end of the blowing process is a common practice for steelworks, as it delivers information about the state of steel-slag equilibrium and, if correlated with the blowing strategy, charge materials input and steel analysis, can be used for optimizing the process especially in terms of enhanced controllability. However, BOF slag sampling is generality carried out by means of immersion of a steel bar into the slag. After taking out, a layer of slag is sticking on the bar which mainly originates from the fluid phase of slag and thus may only represent the liquid slag and not necessarily the total slag based on the current findings. In this context, Fig. 5 shows the comparison between the simulation results of a recently developed dynamic model by Rout and co-workers [10] and industrial measurements of Cicutti et al.

[11]. It can be seen that the simulated FeO-content of the slag increased during the last 2 minutes of the blow, as implied by the oxygen balance due to a decrease in C removal rate. However, the measured FeO-content of the slag remained more or less constant during this period. Considering the main oxide system $CaO-FeO-SiO_2$, it is possible that the slag reached a double saturation zone (zone 2 or zone 3 in Fig. 1) during this period. In such a situation, a change in slag composition while remaining within the same zone would modify the phases amount in the slag but not the phases composition. A further indication is given by the SiO_2 evolution in this period, as the measured value remained constant and did not decrease despite the considerable increase in the total slag mass. Thus, the measured slag evolution, especially during the last 2 minutes, may correspond to the liquid slag composition only, while the total slag contained solid phases (silicates and/or monoxides). It is suggested that during the last 2 minutes of blow, the slag was situated in zone 2 or zone 3 of Fig. 1, with zone 3 being more probable since the final slags in the industrial process are generally lime saturated.
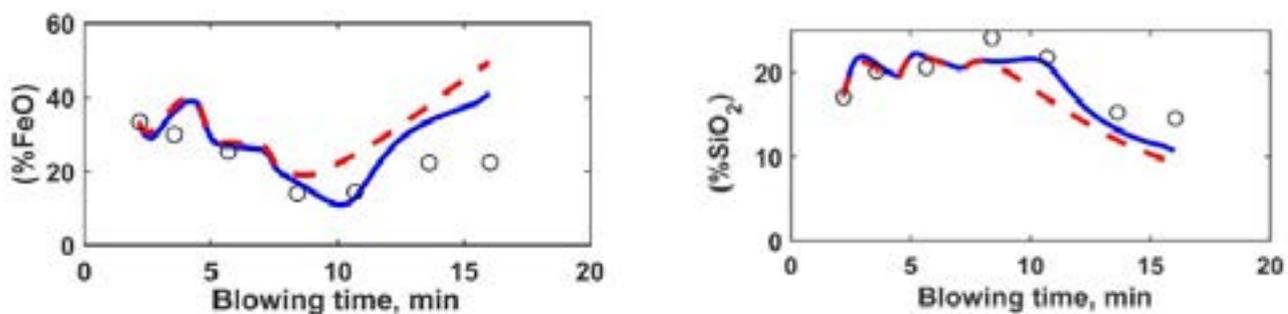
Fig. 5 – Comparison between the measured slag evolution of Cicutti et al. [11] (dots) and simulation results of Rout et al. [10] (solid and dashed lines) for two post combustion profiles (blue: profile 1 , red: profile 2) : a) FeO b) SiO_2

Also, even though it is well-established that the Phosphorus distribution between liquid steel and slag, further noted as Lp, is strongly correlated with the Oxygen potential and thus with the FeO-content of the slag (assuming an FeO-control of the Oxygen potential), the industrial experience showed that the measured Lp-values exhibit a large scatter when represented as a function of the FeO-analysis and slag basicity. This is shown in Fig. 6-a on the example of a large number of heats taken from the Port Talbot Plant in year 2013, which represents the challenges associated with taking representative slag samples.

Interestingly, the correlation between the measured values of [%P]- and [%Mn]-content of the bath, shown in Fig. 6-b is very pronounced. This can be explained by the fact that the Mn-equilibrium between metal and slag phase was governed by Fe/Fe_xO oxygen potential [12]. As a result, [%Mn]-content of the bath was strongly correlated with (%FeO)-content in slag and subsequently with Lp and [%P]-content of the bath. Due to the homogeneity of the steel bath, correlations based on steel analysis were found to be more reliable than those based on slag analysis.
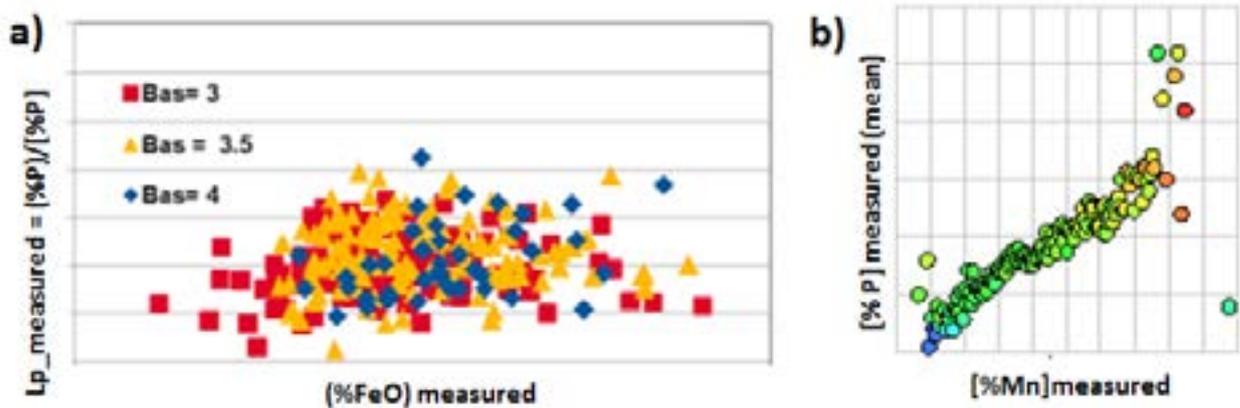
Fig. 6 – Metal-slag-relations based on the analysis of some heats from the TATA Steel's Plant in Port Talbot (UK) (2200 data from year 2013) a) Lp-FeO-basicity relation at a temperature of 1680°C; b) [%Mn]-[%P]-temperature (blue for low Temp. and red for high Temp.) with [%P] averaged for each Manganese value: the average [%P] had a standard deviation σ lower than 40 ppm for 90 % of data

Based on those observations, methods to predict and control the end-Phosphorous content in the steel bath based on monitoring the Manganese content of the bath were developed [13].

Study of P distribution between heterogeneous slag and liquid metal phase
As discussed in the previous section, BOF converter slags are expected to be saturated on silicates for a large period of the blow. Thus, the investigation of the effect of the presence of solid phases and particularly, the effect of silicates on Lp is important for a proper assessment of the equilibrium state of Phosphorous in the industrial process. The simulation results based on the thermodynamic BOFDePhos database revealed

that the presence of P_2O_5 stabilized the C2S phase over the C3S phase. P_2O_5 dissolved in the solid solution under formation of the $2CaO.SiO_2$-$3CaO.P_2O_5$ solid phase, further denoted as C2S_C3P, by substituting some of the silicates with phosphates [2]. As a result, P_2O_5 can be dissolved in the C2S_C3P phase up to its stoichiometric solubility limits of 22 wt. %.
Fig. 7 shows the simulation results for Lp between a C2S-saturated slag containing 2 wt. % P_2O_5 and liquid Iron a function of the mass ratio between C2S_C3P and liquid slag, further denoted as W. It can be seen that Lp-values in the range of 10^3 and higher were calculated when W was equal or higher than 0.3. In all cases, the Lp-values were at least by 2 orders of magnitude higher for slags with a high basicity, which denotes the CaO/SiO_2 weight ratio in the liquid slag part.
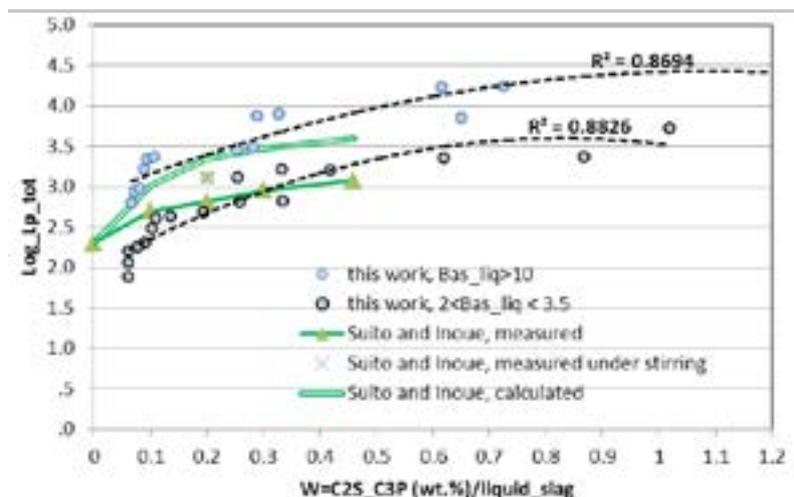
Fig. 7 – Results of the thermodynamic simulations for C2S_C3P saturated slags with 2 % P_2O_5 at a temperature range of 1550-1600°C and comparison with the experimental and calculation results of Suito and Inoue [14] at 1560°C, [%P]= 0.5 wt.% and slag/metal ratio of 1/10

In a series of experiments, Inoue and Suito [14-16] investigated the mechanism of dephosphorization as well as the Phosphorous distribution in C2S_C3P containing slags. The authors reported that by adding C2S particles to liquid slags, Lp increased drastically compared to the case of a fully liquid slag, due to formation of C2S_C3P phase. Some of their results with respect to Lp measurements and calculations (based on their own developed approach) are presented in Fig.7. The results show that the calculated Lp-values by Suito and Inoue [14] were in the same range as those resulting from the simulations for the high basicity case exceeding 10^4 when W was higher than 0.1. The experimental behavior was similar to the simulated behavior with Lp increasing with an increase in W. Even though the experimental values were generally below the simulation results with a maximum of 10^3 reached at a W value of 0.45, they are still considerably higher than in the case of fully liquid slags (case W = 0). The results confirm that the C2S_C3P phase had a strong potential on dissolving P but also suggest that this is associated with kinetic limitations and that a W value exists, above which no further Lp increase occurs. Interestingly, the authors observed that the Lp of a slag which had an W of 0.2 increased by 70% when stirring was used (see Fig. 7). This is an indication of a possible blocking layer removal phenomena, probably similar to that observed during lime dissolution [17]. In a recent work, Gu et al. [18] observed that the overall mass transfer coefficient for dephosphorization in a liquid slag increased by a 2 order of magnitude in the presence of Carbon due to the stirring effect provided by the formation. It is possible that the stirring effect of CO gas may additionally contribute to Lp enhancement in a heterogeneous slag in a similar manner to the increase observed in the experiments of Suito and Inoue. At the same time, the presence of CO gas may decrease the interface between C2S_C3P and liquid slag and thus negatively contribute to dephosphorization. Thus, additional experimental studies are required to clarify the behavior of this phase under foaming conditions.

Finally, the following Lp-equation was developed by regression analysis of the simulation results for C2S_C3P containing slags in the temperature range of 1400-1750°C with a regression coefficient of 0.922:

(1)

$$log(Lp_{C2S-sat.}) = 2.361 * W + 0.1071 \, Basicity_{liq} + 14537.691 * 1/T(K) - 5.938$$

It should be noted that for temperatures below 1550°C, the formation of solid Fe phases was suppressed in the simulations and thus an extrapolation to the case where liquid Fe would be stable at such temperatures was made. In the industrial process, the presence of C lowers the melting point of the metal and thus, the metal phase remains liquid throughout the blow even when the starting temperature is in the range of 1300°C. In the simulations, the addition of C to the liquid phase would lead to FeO-reduction and thus, to a modification of the initial slag composition. This is also the reason behind the non-availability of experimentally established Lp relations below 1550°C : A reduction of a high FeO-slag with Carbon contained in the metal phase and in some cases, also with Carbon contained in the gas phase was observed [19].

Analysis of industrial findings

The industrial analysis of the morphology of BOF slags and the state of P dissolution analyzed by Preßlinger et al. [20] from the Voestalpine plant and DeO et al. [21] from several European and Indian steel plants confirmed that the final slags were C2S-saturated and that a large part of P_2O_5 was present in the solid phase. However, the maximum dissolved value observed was in the range of 5 wt. %, which is much lower than its solubility limit. In general, the Lp values observed in the industrial process are much lower than those predicted by the thermodynamic simulations and experimental measurements in C2S-saturated slags (presented in Fig. 7). This is possibly due to low P_2O_5 contents in industrial slags combined with large C2S precipitation amounts, which cause kinetic limitations to the enrichment process.

Even though industrial observations [20, 21] confirmed that the C2S_C3P phase made a considerable contribution to P removal, little attention was given to the incorporation of the role of this phase in P removal or prediction strategies in conventional oxygen steelmaking. Apart from some few works, such as the work of DeO and al. [21], little effort has been made to incorporate the C2S-formation and dissolution in the derivation of industrial based Lp relations or P control strategies.

It should be noted further that even though the effect of minor oxides on Phosphorous distribution was subject to many experimental and industrial investigations, it has rarely been connected to their effect on the C2S-phase formation and dissolution. Based on the description of the minor oxides effect on the main system CaO-FeO-SiO_2, it is possible that the controversial effect of minor oxides such as MgO, Al_2O_3 and MnO is associated with their effect on solid phases formation and dissolution. For example, MgO was found to have a positive effect on Lp in laboratory based studies, but some steel plants reported a strong negative effect [22]. It is possible that the positive effect of MgO on Phosphorous distribution in the liquid slag would be counteracted by the decreasing effect on the precipitation amount of the P dissolving C2S_C3P phase (see Fig. 2) which results in an overall negative effect. In addition, MgO may lead to high precipitations of the monoxide phase which does not dissolve Phosphorous. As a result, the slag viscosity increases which may contribute to kinetic limitations in the P enrichment in both liquid and C2S phase.

Similarly, Al_2O_3 addition would cause less C2S formation in fa-

vor of more liquid slag (see Fig. 2) and subsequently, decrease the P distribution in a C2S-saturated slag. DeO et al. [21] observed that the presence of Al_2O_3 decreased both the C2S amount and its P content. It was reported at TATA Steel's Plant in IJmuiden (the Netherlands) [23, 24] that Al_2O_3-contents above 3.5 wt. % had a negative effect on dephosphorization. Recently, Drain et al [25] assessed more than 90 Lp-equations based on industrial data and found out that Al_2O_3 had a weak negative effect, except at low Oxygen potential ranges. This can be explained by the fact that at low FeO contents in the slag, excessive C2S precipitations would occur and the optimal C2S/liquid ratio, de-noted as W, would be exceeded. In this case the increasing effect of Al_2O_3 on the liquid slag amount may have a positive effect on Lp in a C2S-saturated slag.

Considered dephosphorization modelling

The results of experiments carried out by Ito and Sato [26] and later by Inoue and Suito [15] showed that Lp_{slag} depended mainly on the liquid slag composition and had maximum values

Thermodynamic approach

Based on the findings introduced in the previous sections, it can be stated that the description of P distribution between a heterogeneous slag and liquid iron should consider the amount, type and composition of the slag phases. However, most Lp-approaches in the literature were developed for fully liquid slags. At the same time, the direct application of the Lp relation given by (1) would lead to an overestimation of Lp since no kinetic limitations on the P enrichment in C2S_C3P are considered in the thermodynamic simulations.

Based on the approach of Inoue and Suito [14, 15], the term Lp_{slag}, describing the P-distribution between the C2S_C3P phase and the liquid slag phase, was introduced:

$$(2)$$

$$Lp_{slag} = \frac{(\%P)_{C2S}}{(\%P)_{liq}}$$

at the nose of C2S_saturation region (zone 1 in Fig. 1). The following relation was developed within the presented work to fit their experimental findings:

$$(3)$$

$$log(Lp_{slag}) = -0.0602 * (\%SiO_2)_{liq} + 2.1652$$

Finally, the P distribution between a heterogeneous slag containing C2S_C3P and monoxide solid phases and liquid iron can be described by the following equation, where $W = C2S/slag_{liq}$ is the ratio of the C2S_C3P and liquid slag phase fractions, $W_{<lim}$ is this ratio with a maximum value of W_{lim} and $f_{monoxide}$, denotes the fraction of the monoxide phase (in case of miscibility gap the sum of both phases is considered) in the heterogeneous slag:

$$(4)$$

$$Lp_{tot} = \frac{Lp_{liq}(1 + Lp_{slag} * W_{<lim})}{1 + W} * (1 - f_{monoxide})$$

The term Lp_{liq} corresponds to the P distribution between the liquid slag and the liquid metal, which was subject to intensive investigations in the literature. Simulation results by of the thermodynamic BOFdePhos database showed that Lp_{liq} was a stong function of temperature, CaO- and FeO-content. The limiting value W_{lim} was introduced into the equation to limit the P transfer from liquid slag to the solid phase when the C2S/$slag_{liq}$ ratio exceeds a certain value, which was found to lie in the range of 0.3-0.45 in the experiments of Suito and Inoue [14]. For application of the equation for Lp_{tot}, the total amount of phases and their composition has to be determined accura-

tely and thus, the thermodynamic database was used for this purpose. Finally it should be noted that even though the description of Lp_{tot} does not explicitly include the effect of minor oxides additions, their effect is indirectly incorporated through the consideration of phases amounts and compositions. For example, if MgO is present and the slag is lime saturated, both liquid slag and C2S phase amounts will decrease in favor of increased monoxide phase formation and lower Lp_{tot} values compared to the MgO-free case will be calculated. The effect of minor oxides on the P distribution between the liquid slag and the metal phase, Lp_{liq}, was not incorporated so far in the

thermodynamic database, mainly due to lack of experimental or industrial data covering the effect of minor oxides additions on the main system $CaO\text{-}FeO_x\text{-}SiO_2$ over a wide range of liquid slag compositions and temperatures.

Kinetic approach

It is a well-established fact that the dephosphorization reaction occurs only as a metal-slag reaction and thus it takes place in the so called emulsion zone in the converter [27], where the ejected metal droplets from the steel bath react with the slag and entrapped gas bubbles. Thus, a 2-zone-modelling approach, similar to that proposed by Schoop et al. [27], was adapted for modelling the dephosphorization reaction, based on the following assumptions:

◦ The droplets ejected from the metal bath to the emulsion zone attain equilibrium with respect to the dephosphorization reaction within their residence time in the emulsion zone. This is based on the fact that high residence time values were reported in a previous work [5].

◦ The droplets returning to the bath from the emulsion zone

have achieved equilibrium. Thus the extent of P removal in the bath depends further strongly on the circulation rate of droplets between bath and emulsion zone.

The circulation rate was calculated based on the blowing number approach suggested by Subagyo et al[28]. However, for the determination of the Oxygen jet impact velocity as a function of lance height, Oxygen flow rate and furnace conditions, a CFD approach was incorporated. Fig. 8 shows the simulation results of the jet axial velocity behavior for a cold and hot ambient temperature and the comparison with corresponding results based on several approaches reported in the literature. It has been found that, in accordance with the results of Alam et al.[29], the approach of Sumi et al. [30] provided the highest accuracy at a hot furnace temperature when the dimensionless axial distance lay below 60 in the BOF converter. At a cold ambient temperature of 20°C however, which is usually the temperature set in most experiments investigating droplets generation and residence time, the equation proposed by Koria et al. [31] followed by that of He and Standish [32] provided the highest accuracies for dimensionless axial distances higher than 15.
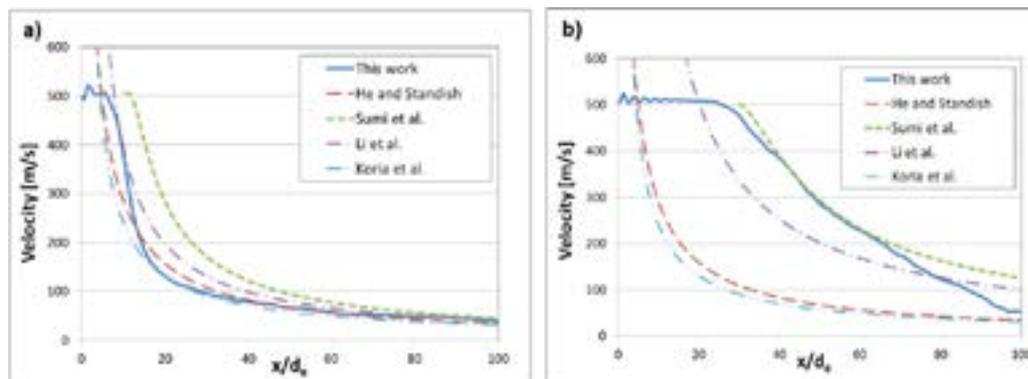
Fig. 8 – LES (Large Eddy Simulation) simulation results of jet axial velocity in cold and hot environment a) T∞ =20°C, b) T∞ =1600°C with x: axial coordinate or lance height, de: nozzle exit diameter

Strategies for enhanced P control

Based on the current findings, the maximum P distribution values in the BOF process are not achieved at lime saturation, but rather at C2S_C3P saturation. The presence of this phase even in small amounts lower than 10 wt. %, would lead to the achievement of ultra-low P values in the metal phase if the enrichment is high. Thus, the focus is on the development of new process control strategies and new technologies to make use of the potential of this phase in removing Phosphorous and overcome the kinetic limitations for its enrichment [33, 34]. An example is presented in Fig. 9. The method consists of blowing powdered lime and, to a lesser extent, also powdered dolomite into the slag (or emulsion zone) through side wall nozzles. It was found that through this technology, the lime consumption can be reduced drastically while high Lp values are achieved as a result of the P dissolution in C2S_C3P. Also, in case powdered dolomite is used, the resulting slags would be high in basicity

and less aggressive to the lining compared to the case where lump dolomite is used as observed in the experiments of Münchberg et al. [35]. By optimizing the lance positions and their blowing angles, the mixing intensity in the slag can be enhanced with minimal carrier gas consumption and thus, the blocking layer formation for both lime dissolution and C2S_C3P enrichment is avoided. Also, an enhanced dephosphorization at low FeO contents and slag amounts would be possible. The cost-effectiveness of the method lies in the possibility of refining high P hot metal in a single step, decreased lime consumption and refractory wear, increased iron yield as well as in the suppression of slopping and skulls formation.

In addition, the new P modelling approach has been implemented into the BOF Design model of SMS used for process design and for supporting the online model [36] as well as into the dynamic online model of BFI [37]. Fig. 10 sketches the implementation scheme with contributions from the thermodynamic

BOFdePhos database regarding amounts and compositions of the involved slag phases, the enhanced Lp model for heterogeneous slags and the transport kinetics based on droplets

generation and circulation between metal bath and metal-slag emulsion zone.
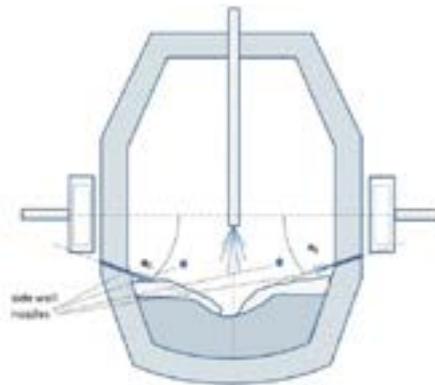
Fig. 9 – Method for refining molten steel for optimal dephosphorisation [33]
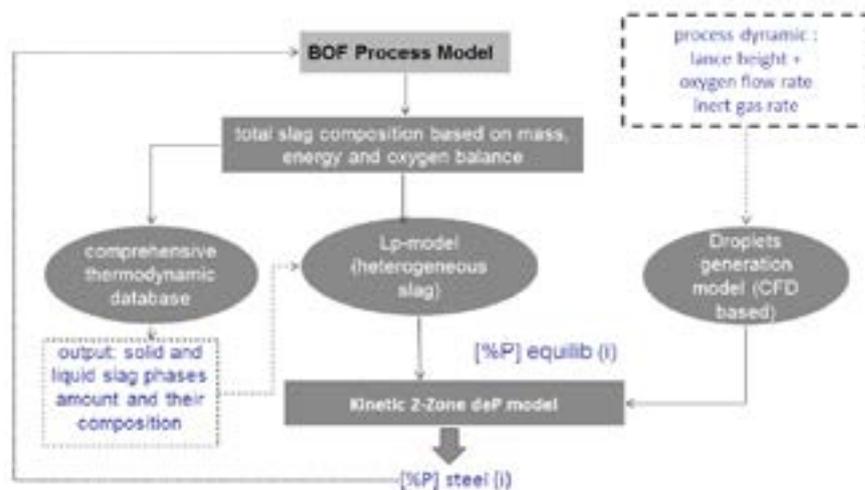
Fig. 10 – Implementation scheme of the new dephosphorization modelling approach into the dynamic process models

The enhanced dynamic online models can be used for continuous monitoring of the actual heat state in the converter as well as for prediction of its further evolution until end of blow. These information can be assessed by dynamic control functions for adaption of the amount of oxygen to be blown, lime to be charged and heating or cooling materials to be added in order to adjust the targets for temperature, carbon and phosphorus content of steel in a time and cost optimal way [37] taking into account the optimal slag conditions for dephosphorization figured out by the presented research work.

CONCLUSION
BOF slags are heterogeneous for a large part of the blowing process. Thus, comprehensive approaches for BOF process modelling as well as control strategies should consider the effect of solid phases from a thermodynamic and also from a kinetic

perspective. The presence of P-dissolving C2S_C3P phase leads to a drastic increase in Phosphorous distribution. An adequate control of this phase formation and providing suitable conditions for its enrichment on Phosphorous hold the key for a successful dephosphorization. In this context, further work is required to understand the behavior of this phase under conditions relevant to the BOF process, such as high stirring and foaming.

REFERENCES

[1]   Tayeb MA, Spooner S, Sridhar S. Phosphorus: the noose of sustainability and renewability in steelmaking. JOM. 2014; 66(9): 1565-71.

[2]   Khadhraoui, S; Hack, K; Janßen, T; Odenthal, H-J : Assessment of the state of P2O5-containing oxide systems relevant to steelmaking slags based on a new thermodynamic database developed for the system CaO- FeO-P2O5- SiO2 -MnO- MgO-Al2O3, submitted for publication, steel research int., December 2018.

[3]   Besmann TM, Spear KE. Thermochemical modeling of oxide glasses. Journal of the American Ceramic Society. 2002; 85(12): 2887-94.

[4]   Sundman B, Ågren J. A regular solution model for phases with several components and sublattices suitable for computer applications. Journal of physics and chemistry of solids. 1981; 42(4): 297-301.

[5]   Schlautmann M, Kleimt B, Khadhraoui S, Hack K, Monheim P, Glaser B, Antonic R, Adderley M, Schrama F. Dynamic on-line monitoring and end point control of dephosphorisation in the BOF converter, Proceedings of the 3rd European Steel Technology and Application Days (ESTAD), 2017, Vienna

[6]   Bale CW, Bélisle E, Chartrand P, Decterov SA, Eriksson G, Gheribi A E, Hack K, Jung IH, Kang YB, Melançon J, Pelton AD, Petersen S, Robelin C, Sangster J, Spencer P and Van Ende M A. FactSage Thermochemical Software and Databases 2010 - 2016. Calphad. 2016; vol. 54(2016), 35-53.

[7]   Martinsson J, Glaser B, Sichen D. Study on apparent viscosity and structure of foaming slag. Metallurgical and Materials Transactions B. 2016 Oct 1;47(5):2710-3.

[8]   Rout BK, Brooks G, Rhamdhani MA, Li Z, Schrama FN, Overbosch A. Dynamic Model of Basic Oxygen Steelmaking Process Based on Multizone Reaction Kinetics: Modeling of Decarburization. Metallurgical and Materials Transactions B. 2018;49(3):1022-33.

[9]   Martinsson J, Glaser B, Sichen D. The structure of foaming BOF-converter slag. Ironmaking & Steelmaking. 2017 Dec 8:1-5.

[10]   Rout BK, Brooks G, Rhamdhani MA, Li Z, Schrama FN, Sun J. Dynamic Model of Basic Oxygen Steelmaking Process Based on Multi-zone Reaction Kinetics: Model Derivation and Validation. Metallurgical and Materials Transactions B. 2018;49(2):537-57.

[11]   Cicutti C, Valdez M, Pérez T, Petroni J, Gómez A, Donayo R, Ferro L. Study of slag-metal reactions in an LD-LBE converter. 6th International Conference on Molten Slags, Fluxes and Salts 2000 (Vol. 367).

[12]   Rout B, Brooks G, Rhamdhani MA, Li Z, Schrama F, van der Knoop W. Dynamic Model of Basic Oxygen Steelmaking Process Based on Multizone Reaction Kinetics: Modeling of Manganese Removal, Metallurgical and Materials Transactions B. 2018; https://doi.org/10.1007/s11663-018-1306-8

[13]   Khadhraoui S, Kemminger A, Krause F, inventors; SMS group GmbH, assignee. Method for monitoring and control of P content during refining of Mn-containing melt. Germany 2018.

[14]   Suito H, Inoue R. Behavior of phosphorous transfer from CaO–FetO–P2O5 (–SiO2) slag to CaO particles. ISIJ international. 2006;46(2):180-7.

[15]   Inoue R, Suito H. Phosphorous partition between 2CaO· SiO2 particles and CaO–SiO2–FetO slags. ISIJ international. 2006;46(2):174-9.

[16]   Inoue R, Suito H. Mechanism of dephosphorization with CaO–SiO2–FetO slags containing mesoscopic scale 2CaO· SiO2 particles. ISIJ international. 2006;46(2):188-94.

[17]   Deng T, Sichen D. Study of lime dissolution under forced convection. Metallurgical and Materials Transactions B. 2012;43(3):578-86.

[18]   Gu K, Dogan N, Coley KS. Dephosphorization kinetics between bloated metal droplets and slag containing FeO: the influence of CO bubbles on the mass transfer of phosphorus in the metal. Metallurgical and Materials Transactions B. 2017 Dec 1;48(6):2984-3001.

[19]   Ek M, Huber JC, Brosse G, Sichen D. Capacities of some CaO–SiO2–FeO–MnO–MgO slags and slag–solid mixtures in capturing phosphorous. Ironmaking & Steelmaking 40. 2013;40(4):305-11.

[20]   Preßlinger H, Fluch J, Apfolterer R. Mikroanalytische Untersuchungen über die Einbindung von Phosphor in LD-Schlacken. BHM Berg-und Hüttenmännische Monatshefte. 2012;157(3):136-43.

[21]   DeO B, Halder J, Snoeijer B, Overbosch A, Boom R. Effect of MgO and Al2O3 variations in oxygen steelmaking (BOF) slag on slag morphology and phosphorus distribution. Ironmaking & steelmaking. 2005;32(1):54-60.

[22]   Chen GJ, He SP. Effect of MgO content in slag on dephosphorisation in converter steelmaking. Ironmaking & Steelmaking. 2015;42(6):433-8.

[23]   Thornton G, D A. Ironmaking and Steelmaking. 1994;21:247.

[24]   Van der Knoop W, Van Unen G, Snoeijer A, Boom R. Steel Times 222:141.

[25]   Drain P, Monaghan B, Zhang G, Longbottom R, Chapman M, J. Chew S. A review of phosphorus partition relations for use in basic oxygen steelmaking. Ironmaking & Steelmaking. 2017;44:721-31.

[26]   Ito K, Sano N. Phosphorus Distribution between CaO-containing Slag and Carbon-saturated Iron at Hot Metal Temperatures. Tetsu-to-Hagane. 1983;69(15):1747-54.

[27]   Schoop J, Resch W, Mahn G. Reactions occurring during the oxygen top blown process and calculation of metallurgical control parameters. Ironmaking Steelmaking. 1978;5(2):72-9.

[28]   Subagyo, Brooks GA, Coley KS, Irons GA. Generation of droplets in slag-metal emulsions through top gas blowing. ISIJ international. 2003;43(7):983-9.

[29]   Alam M, Naser J, Brooks G. Computational fluid dynamics simulation of supersonic oxygen jet behavior at steelmaking temperature. Metallurgical and Materials Transactions B. 2010;41(3):636-45.

[30]   Sumi I, Kishimoto Y, Kikuchi Y, Igarashi H. Effect of high-temperature field on supersonic oxygen jet behavior. ISIJ International. 2006;46:1312-7.

[31]   Koria SC, Lange KW. An experimental study on the behaviour of an underexpanded supersonic gas jet. Archiv für das Eisenhüttenwesen. 1984;55(9):427-32.

[32]   Standish N, He QL. Droplet generation due to an impinging jet and the effect of bottom blowing in the steelmaking vessel. ISIJ International. 1989;29:455-61.

[33]   Khadhraoui S, Das S, Odenthal H-J, Krause F, Kemminger A, inventors; SMS group GmbH, assignee. Method for Refining Molten Metal Using a Converter. India; 2018 Feb 16.

[34]   Khadhraoui S, Defries U, Hofmann A, inventors; SMS group GmbH, assignee. Method for achieving low P-content in steel during refining of molten iron. Germany ; October 2018.

[35]   Münchberg W, Obst K-H, Mahn G, Nolle D. Mikrogefüge von Schlacken aus dem Sauerstoffaufblaskonverter bei Verwendung von dolomitischem Kalk und kaustischer Magnesia. Stahl und Eisen. 1981;101:587-90.

[36]   Hofmann, A, Reichel, J, Loginov, S, Das, S. Stable and optimized performance under suboptimal conditions; Proceedings of the 6th European Oxygen Steelmaking Conference (EOSC), 2011, Stockholm

[37]   Schlautmann M, Kleimt B, Teiter T, Schnabel S, Ponten HJ. Model-based dynamic monitoring and end-point control of converter process, Proceedings of the 6th European Oxygen Steelmaking Conference (EOSC), 2011, Stockholm