Modeling of Dephosphorization using Bloated Droplet Theory in Basic Oxygen Steelmaking

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Abstract. A considerable fraction of refining of hot metal in basic oxygen steelmaking is carried out in emulsion layer by interaction between the metal droplets and slag. The top oxygen blowing ejects metal droplets into the slag which then undergo refining reactions and return to the metal bath. During this period, the carbon in metal droplets reacts with available oxygen to form carbon monoxide. Above a certain threshold decarburization rate, the evolved carbon monoxide inside the droplet causes the droplet to bloat which increases its surface area. The bloating affects the residence time and the rate of certain interfacial reactions. Here, efforts have been made to study dephosphorization in metal droplet in emulsion by coupling dephosphorization kinetics with the ‘bloated droplet theory’. As observed in industrial furnaces, the calculated phosphorous concentration in droplet was found to be lower than that of metal bath. Dephosphorization model developed using mixed transport control model was found to fit industrial data. The results obtained were in satisfactory agreement with the available data and a step ahead in improving the understanding of dephosphorization in steelmaking.

1. Introduction
In basic oxygen steelmaking, metal droplets are ejected into the slag due to impingement of supersonic oxygen jet on the hot metal bath which leads to the formation of an emulsion consisting of ejected metal droplets, gas phase and slag. Models have been developed to incorporate this phenomenon for comprehensive understanding of steelmaking process. Researchers have argued that considerable fraction of refining occurs in the emulsion zone as the formation of droplets increase the interfacial area for reactions. Molloseau and Fruehan [1] have studied the bloating or swelling of metal droplets when reacting with slags which further increase the surface area of the reaction. Brooks and co-workers [2] were able to explain this through a model which was subsequently used for developing of a comprehensive model by Dogan [3-5]. However, these works considered only the decarburization reaction but the effect of bloating on the kinetics of oxidation of phosphorous, manganese and silicon is a matter of further study. In current work, efforts have been made to model the dephosphorization in emulsion using bloated droplet theory. Various dephosphorization model is coupled with bloated droplets theory and the results were compared with the experimental data.

2. Model Development
The basic oxygen steelmaking furnace has been divided into two zones, as shown in Fig.1, namely - the emulsion zone and the metal bath. However, the present study is limited to dephosphorization in the emulsion zone only. The model is divided into three subroutines as shown in Fig. 2., namely, i) The
bloated droplet model which calculates the rate of droplet generation, the interfacial area and the residence time, ii) the slag model that calculates the physical properties of the slag, and iii) the dephosphorization model to couple the earlier two models to calculate the phosphorous concentration of metal droplets in emulsion. The important parameters considered for this study are the amount of metal in the emulsion zone at a given time, the residence time of the droplet, the size distribution of the droplets and the total interfacial area between the metal and slag phases.

2.1. Droplet Model

The mechanism of droplet generation by the impinging oxygen jet has been studied earlier. Subagyo et al [6], in their work had related the droplet generation rate with blowing number \( N_B \) and gas flow \( F_G \) rate. The Blowing number \( N_B \) depends on the critical gas velocity \( U_c \), the density of the gas \( \rho_g \), the surface tension of the metal \( \sigma \), the density of the metal bath \( \rho_M \) and acceleration due to gravity \( g \) as given in equation 1. The value of \( N_B \) should be greater than 3 for significan number of droplets formation [7].

\[
N_B = \frac{\rho_g U_c^2}{\zeta \sigma \rho_M g}
\]  

Subagyo et al [6] further proposed an empirical correlation between droplet generation rate \( R_B \), Kg/sec, the blowing number \( N_B \) and the volumetric oxygen input flow rate \( F_G \), Nm\(^3\)/s as expressed in equation 2.

\[
R_B = \frac{(N_B)^{3.2} \times F_G}{[2.6 \times 10^8 + 2.0 \times 10^{-4} (N_B)^{12}]^{0.2}}
\]  

To model the trajectory of the metal droplet in emulsion the initial velocity \( u_i \) and diameter of the droplet \( D \) are required. The model for trajectory has been proposed by Subagyo et al [7] and is referred...
to as “Ballistic Droplet Theory”. The initial velocity is calculated by energy balance between the kinetic energy of droplets (\( KE_{\text{droplets}} \)) and impinging jet (\( KE_{\text{jet}} \)). The kinetic energy of droplets is given by equation 3 and that of impinging jet by equation 4.

\[
KE_{\text{droplets}} = \frac{1}{2} R_B u_i^2 
\]

\[
KE_{\text{jet}} = \frac{1}{2} \rho g R_G U_G^2 
\]

Both of these kinetic energies are co-related by empirical expression as given in equation 5.

\[
KE_{\text{droplets}} = 0.00143 (N_B)^{0.7} KE_{\text{jet}} 
\]

As assumed by earlier models [2-7], the diameter of metal droplet in this study also was taken to be 2 mm. This theory was further extended by Brooks [1] to include decarburization in the droplet which was closer to the actual phenomenon occurring in the steel converter. They co-related the density of the droplet with the decarburization rate as shown in equation 6 where, \( r_c \) is the decarburization rate and \( r_c^* \) is the critical decarburization rate. The modified density is then used to calculate the bloated or swelled diameter of the droplet. The droplet is bloated only when \( r_c \) exceeds \( r_c^* \) otherwise, \( r_c \) is taken equal to \( r_c^*[2] \).

\[
\rho_d = \rho_o \frac{r_c^2}{r_c^*} 
\]

The equation for \( r_c^* \) is given by \( 2.86 \times 10^{-4} \times (\text{FeO}) \), where \( (\text{FeO}) \) is the wt % of FeO in slag [2]. The residence time is also dependent on the density of slag-gas mixture, the gas fraction, the initial size of the droplet and initial velocity of the droplets. All these were used to calculate the residence time of the droplet in the emulsion [2]. Extensive discussion on these parameters can be found in the work of Dogan [4]. Steady state is assumed for calculating the mass of metal droplets in slag. The mass of droplets in slag is given as product of residence time and generation rate of the droplets [6]. The area is taken as the average area of a droplet during its motion in the emulsion. The total area in emulsion is the sum of individual areas of the droplets at a given instant of time. Droplets are also generated by bottom blowing. However, the size of droplet generated by bottom blowing is too small and they have very low residence time [8].

2.2. Slag Model
The slag model was used to calculate the density and viscosity of the slag as a function of temperature and composition. The methodologies outlined in the Slag Atlas [9-10] was followed to calculate these quantities. The slag composition was taken from Millman et al [11] and fed into the model to calculate the viscosity and density.

2.3. The dephosphorization Model
Dephosphorization of metal bath is favoured by high basicity, low temperature, and high FeO in slag [12]. Since, the reaction takes place at high temperatures, the chemical reactions at interface are not considered as rate limiting reactions, instead the mass transfer in slag or metal or both in slag and metal (mixed) is taken as rate controlling step. Mori et al [13] and Wei et al [14] have considered the mass transfer as mixed controlled while Monaghan et al [15] have concluded that the mass transfer in slag phase is the rate controlling step. The equations 7 and 8 were proposed by Monaghan for first order dephosphorization with mass transport in slag and metal as rate controlling step respectively. The subscript ‘b’ is for the bulk concentration, ‘o’ is for initial concentration and ‘e’ is for equilibrium concentration. Here the mass transfer coefficient in slag and metal are \( k_s \) and \( k_m \) respectively, \( W_m \) is the
mass of the metal in emulsion, $W_m$ is the mass of the slag, $\rho_s$ is the density of the slag. In these cases the initial phosphorus concentration in slag was taken as zero.

\[
\ln \left[ \frac{[\text{pct } P]_b}{[\text{pct } P]_o} \right] \left( \frac{W_s}{\rho_{MA}} \right) = -k_s t
\]

\[
\ln \left[ \frac{[\text{pct } P]_b}{[\text{pct } P]_o} \right] \left( \frac{W_m}{\rho_{MA}} \right) = -k_m t
\]

In the current model, mixed mass transport equation proposed by Manning and Fruehan [16] was used. The initial phosphorous concentration of slag was not taken to be zero instead the %P in slag was taken from Millman et al [11] based on $P_2O_5$ evolution with time. Therefore, equation 9 was used,

\[
[pct \ P]_{emulsion} = \frac{(Z4+\exp(-Z1*Z3*t)+Z2)}{Z1}
\]

where $L_P$ denotes the equilibrium phosphorous partition ratio and is discussed in later stage. The area term (A) in Z3 is the average interfacial area of all the droplets during their motion through the slag after ejection. Average area of a single droplet is multiplied by the total number of droplets in emulsion to get the total interfacial area in emulsion. The total number of droplet is calculated by dividing the total mass of droplets generated ($R_B$ x Residence time) by mass of a single droplet. The overall mass transfer coefficient for mixed control dephosphorization, $k_o$, is calculated by equation 10. The values for $k_s$ and $k_m$ were taken from Wei et al[14].

\[
k_o = \frac{1}{k_m \frac{W_m}{W_s L_P} + \frac{1}{k_m}}
\]

As discussed by Monaghan, the equilibrium concentration is difficult to predict and is usually taken equal to the minimum phosphorus content or equal to the concentration at thermodynamic equilibrium. Basu et al [17] has calculated the phosphorous distribution with time in running converter and concluded that after 10 minutes of blow the phosphorous partition is 40-60% of the equilibrium partition ratio. Similar observation were made by Choudhary and co-workers [18] where they have suggested that Turkdogan’s [19] model fits best for end phosphorous calculation for industrial furnaces. However, Manning and Fruehan [16] used the equation of Ide and Fruehan [20] to calculate the $L_P$. This calculated $L_P$ is used in equation 9. In equation 11, the T is the temperature in Kelvin and [%O] is the oxygen concentration calculated from equation 13 where (%FeO) is the FeO wt % in slag. Similarly, in equation 12 and 14, the quantities in parentheses are wt. % of components in slag. Apart from this, in present study, the mixed control of mass transfer was compared with slag controlled mass transfer for the dephosphorization.

\[
\log(LP)_{Turkdogan} = \frac{21740}{T} - 9.87 + 0.071BO + 2.5\log([%O])
\]

\[
BO = (%CaO) + (%CaF_2) + 0.3(%MgO)
\]

\[
\frac{[%O]}{(%FeO)} = (0.17 - 155.3) \times 10^{-4}
\]
\[
\log(L_P)_{ide} = \frac{10^{730}}{T} + 4.11 \log(\%CaO + 0.015\%MgO + \%CaF_2 - 0.05\%Fe_tO) + 2.5 \log(\%FeO) + 0.5 \log(\%P_2O_5) - 13.87
\] (14)

3. Results and Discussion

The residence time and average interfacial area were calculated from the bloated droplet model and the slag model fed the physical properties of the slag in the bloated droplet model to account for changing slag characteristics with time. Fig. 3 shows the variation of density and viscosity with time. The residence time and average interfacial area was then fed in to the dephosphorization model. The dephosphorization model used mixed transport control, along with two methodologies to calculate the equilibrium phosphorous concentration, namely, the Turkdogan’s equation and Ide and Fruehan’s equation. The mechanism and equilibrium equations were clubbed together one by one and compared. Fig. 4 shows the final result obtained from the developed model. The input data for the model was from Millman et al [11]. While comparing the different equations of \( L_P \), Ide and Fruehan’s as well as Turkdogan’s equation gave similar results. However, in initial part, none of the models can be said to be completely successful in predicting the phosphorous in emulsion.

![Figure 3: Variation of Density and Viscosity with blowing time](image)

Fig. 5 is the temporal evolution of phosphorous content in metal droplet in the emulsion zone, which is similar to the results of Gaye [21]. One possible explanation for variation between the results of the model and experiments is the difference in conditions. The models used above had been developed at laboratory scale which were not much close to the industrial process. One more possibility that was not considered was the breakage or bursting of droplets. If evolution of carbon monoxide is sufficiently vigorous, the droplet may break into smaller droplets which should increase the effective surface area of the droplet. The droplets may later coalesce or remain unaffected while continuing their downward motion. This sudden increase of surface area (and diameter) may increase dephosphorization rate and the effective residence time of the droplets which in turn would change the mass of metal in the emulsion. It is difficult to model the breakage and coalescence of metal droplets in emulsion because of high temperature conditions which makes model validation an issue. Efforts are being made in author’s laboratory to model the breakage of droplets using stochastic approaches.
Figure 4: Variation of final Phosphorous content in metal droplet calculated by model in emulsion with blowing time. The bloated droplet theory was coupled with the dephosphorization models mentioned in legend. The experimental data is from Millman et al [11]

Figure 5: Evolution of Phosphorous content of metal with residence time at t=6 minutes, Turkdogan’s Model with mixed transport control.

4. Conclusion
A formal approach of incorporation of interfacial area changes due to bloating of droplet interaction kinetics of dephosphorization has been developed in the study. The result also quantifies the extent of dephosphorization occurring in emulsion of an oxygen steelmaking reactor. Both Turkdogan’s and Ide and Fruehan’s equation for $L_P$ along with the mixed mass transport controlled mechanism are found to fit satisfactorily with the experimental conditions.
5. References

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