Development of a comprehensive model for oxygen steelmaking

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INTRODUCTION

One of the main goals in oxygen steelmaking process is to reduce the carbon concentration of the liquid iron effectively. It is understood that the majority of the carbon removal reaction occurs in the emulsion phase via the reaction between metal droplets and the slag phase. An improved understanding of this reaction and the factors controlling the overall rate should provide better control of the process and increase the productivity. In the literature, there is limited knowledge on how to relate the carbon removal rate within the droplets to the overall kinetics of the process under full scale operating conditions. A global model of oxygen steelmaking including the kinetics of scrap melting, flux dissolution, slag chemistry, temperature profile of the system, formation and residence of metal droplets in the emulsion, kinetics of decarburization reaction in different reaction zones has been developed. This paper will focus on the development of one sub-model on the decarburization reaction in the emulsion phase. This paper critically evaluates the current knowledge on the kinetics of decarburization reaction in the emulsion phase and discusses the repercussions of the new model for industrial practices. The model, in conjunction with the industrial data, suggests that approximately 70% of the decarburisation takes place in the emulsion phase during the main blow.

Emulsification behaviour in Steelmaking

The formation of metal droplets and carbon monoxide bubbles in the emulsion has a crucial impact on extending the interfacial area and promoting the bath circulation that will affect the overall kinetics of the process. There are experimental studies based on the plant measurements that pointed out the importance of emulsification behaviour in steelmaking processes. Meyer et al. further quantified the amount of metal droplets generated in the emulsion and analysed the chemistry of metal droplets using experimental technique for an industrial practice. Cicutti et al. analysed the overall decarburization reaction including the emulsion behaviour based on the bath sampling. The findings from the industrial data lead the researches mainly focus on understanding the kinetics of decarburization in emulsion phase thoroughly. Lin and Guthrie investigated the emulsification behaviour generated by gas bubbles rising through oil/aqueous and oil/mercury analogues at low temperatures. They suggested a relationship to quantify the rate of droplet generation and mean residence time of droplets for top blowing steelmaking process. Molloseau and Fruehan studied the rate of decarburization reaction in metal droplets for slags containing 3 and 35 mass% FeO at high temperatures. They suggested that decarburization reaction of metal droplets in oxidizing slags significantly affects the motion of droplets through rapid evolution of gas from metal droplets. Brooks et al. developed a mathematical model to calculate the residence time of droplets in oxygen steelmaking processes. From the literature, it has been found that metal droplets are “bloated” with CO gas, become less dense and spend longer time in the emulsion. However metal droplets maintain their original density if the decarburization reaction is weak. As a result, it has been concluded that decarburization rate is strongly dependent on the residence time of droplets in the emulsion and that the bloating of droplet is critical to understand the overall kinetics of steelmaking.
Decarburization reaction in the emulsion phase takes place via FeO reduction. There are numerous studies on the mechanism and kinetics of decarburization reaction by FeO reduction in the oxygen steelmaking slags. Some of these investigations used carbon dissolved in iron whereas some of those using solid carbon. There are also studies focusing on decarburization of a metal droplets with oxidizing gas. The majority of these studies are limited with low FeO content (e.g. <15 mass %) of the slag. Laboratory experiments are limited with theoretical basis with regard to the chemical similarity between real and model systems.

When Fe-C metal droplet containing high carbon content (approximately 4 mass %) reacts with the oxygen steelmaking slag containing low level of FeO (14 mass % at maximum), there is a CO gas halo formation surrounding the metal droplet. Mulholland et al. first observed the gas halo surrounding Fe-C-S droplets in slag using x-ray fluoroscopy technique. There are also other researchers who give supporting evidence of the formation of gas halo. This phenomenon may occur due to high rate of external nucleation of CO gas compared to the internal nucleation. In such case, energy barrier for nucleation is reduced due to the sufficient amount of C and O available at slag-metal interface, which is called external nucleation. When oxygen diffuses into a droplet, CO pressure increases with time. And if CO pressure exceeds the ambient pressure, metal droplet become supersaturated and the reaction of oxygen and carbon becomes possible.

When internal pressure of CO exceeds the surface energy of the metal droplet, CO gas formation occurs inside metal droplet. CO pressure depends on the carbon and oxygen concentration, temperature and concentration of other impurities inside the metal droplet. The build up rate of bulk oxygen depends on the difference between the oxygen absorption rate and rate of consumption of this oxygen at the surface due to the decarburization and iron oxide formation.

As the internal nucleation started, metal droplet becomes bloated and surface area increases therefore reaction kinetics increases since the turbulence caused by the generation of CO bubbles inside the metal droplet promotes the diffusivities. The bloating behaviour of metal droplets is suggested due to the generation of CO bubbles inside the metal droplet. On the basis of X-ray transmission photographs and the analysis of the experimental results, it is believed that the reaction takes place in two steps via bubble formation. As the metal droplets are ejected from the liquid metal, they react with FeO in slag. FeO diffuses to the slag-gas interface towards a bubble sitting on the metal-gas interface to supply oxygen. CO reduces FeO at slag-gas interface and followed by reaction at the metal-gas interface with CO2 diffusion through the gas halo. CO2 provides oxygen to react with carbon in the melt. These reactions involve the sequence as below:

\[
CO_{(g)} + FeO \rightarrow Fe + CO_{2(g)} \quad \text{(slag surface)} \tag{1}
\]
\[
CO_{2(g)} + [C] = 2CO_{(g)} \quad \text{(metal surface)} \tag{2}
\]

The overall reaction is

\[
(FeO) + [C] = Fe + CO_{(g)} \tag{3}
\]

These sequential reactions continue until the bubble leaves the slag-metal interface. As a result, carbon content of metal droplets will decrease and numerous CO gas bubbles will be formed. The reaction product, CO gas provides stirring to the emulsion phase. It is believed that the reaction is responsible for the majority of decarburization in oxygen steelmaking process and this reaction provides information about the slag foaming to avoid slag sloping during the process since bubble formation will promote slag foaming significantly.

**MODEL DEVELOPMENT**

In the current study, the global model focuses on the overall decarburization of the process and includes the new bloated droplet theory. The model, which utilizes numerical computational technique, has enabled us to calculate the change in carbon content of bulk metal and metal droplets in the emulsion. Two main reaction zones are considered including the impact zone and emulsion zone.
At the impact zone, the dissolved carbon reacts with gaseous oxygen and carbon dioxide. It is suggested that gaseous diffusion controls the decarburization rate down to the critical level of carbon, where carbon diffusion in liquid phase becomes rate-limiting step. Sain and Belton and Manion and Fruehan studied the reaction decarburization kinetics of liquid iron by CO\textsubscript{2} under high gas flow rates to reduce the effects of mass transfer. They suggested that CO\textsubscript{2} dissociation on the surface controls the reaction rate. In this study, the model for decarburisation in the impact zone of the furnace was based on a mixed control kinetic model including gas phase mass transfer and chemical kinetics over a large range of temperature and fluid flow conditions and the concentration of surface active elements. The development of the impact zone model will be the subject of a future paper.

In the emulsion zone, reaction (3) takes place between metal droplets and slag. Total decarburization rate in the emulsion zone is obtained by the summation of decarburization rates of individual metal droplets. The generated droplets, whose residence time is smaller than given time-step, are returning from the emulsion zone. Based on this boundary condition, decarburization rate can be calculated using:

\[
M \frac{dC}{dt} = \sum_{i=1}^{n} \frac{m_i}{100} \left( C_{i\text{in}} - C_{i\text{eq}} \right) / \Delta t
\]

where the number of the droplets in the emulsion zone is represented by \( n \), \( m_i \) is weight of a single droplet (kg) and \( C \) is the carbon content of droplet (mass\%). Transport of oxygen through the slag phase or through bubbles surrounding the metal droplet, transfer of carbon in the metal, interface chemical reaction, nucleation and removal of CO gas bubbles from the reaction site may all be important in determining the rate of decarburization reaction. However, there is no agreement on description of the mechanism of this reaction and also the rate controlling step of this reaction under various operating conditions.

**Rate Determining Step**

Chemical reactions at the interface are predicted to be relatively rapid at high temperatures (above 1500°C). The dissociation of CO\textsubscript{2} in the gas halo is valid for only low FeO concentration in the slag (above 10 mass %). Transfer rates based on different reaction mechanisms were compared to decide the rate determining step for decarburization in the emulsion phase given in Table I. These studies were compared since they were developed for slags containing high FeO concentrations, which are valid for oxygen steelmaking slags. The input data for this comparison was taken from the previous experimental study\(^9\) since experimental conditions were well defined and valid for oxygen steelmaking operating conditions. For this reason, the change in carbon content of a single droplet was calculated using the rate equations proposed by previous researchers.

<table>
<thead>
<tr>
<th>Studies</th>
<th>Rate Equation</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molloseau and Fruehan(^9)</td>
<td>( \text{Rate} \left( \frac{\text{moles}}{s} \right) = \frac{k \cdot A \cdot \rho}{100 m_{\text{FeO}}} \left( \text{mass}% \text{FeO} - \text{mass}% \text{FeO'} \right) )</td>
<td>mass transfer of FeO through slag phase</td>
</tr>
<tr>
<td>Brooks et al.(^10)</td>
<td>( \text{Rate} \left( \frac{\text{mass} %}{s} \right) = \frac{k_{\text{eff}} \cdot A_{\text{app}}}{V_{\text{app}}} \left( \text{mass} % \text{C} - \text{mass} % \text{C}_{\text{eq}} \right) )</td>
<td>mass transfer of carbon through metal phase</td>
</tr>
<tr>
<td>Chen and Coley(^17)</td>
<td>( \text{Rate} \left( \frac{\text{moles}}{s} \right) = J \cdot \frac{n_x(V_o)}{N_{\Lambda}} )</td>
<td>chemical reaction of C and O in the metal droplet</td>
</tr>
</tbody>
</table>

In reaction rate equation proposed by Molloseau and Fruehan\(^9\), \( k \) refers to mass transfer coefficient in the slag phase; \( m_{\text{FeO}} \) is molecular weight of FeO; mass\% FeO is FeO content of bulk slag; mass\% FeO' is FeO content at the surface of a droplet; \( A \) refers to the surface area of emulsified droplet determined by observation of X-ray videos. In reaction rate equation suggested by Brooks et al.\(^10\), \( k_{\text{eff}} \) is mass transfer coefficient in the metal droplet; \( A_{\text{app}} \) is the apparent surface area of the droplet; \( V_{\text{app}} \) is the apparent volume of the droplet; mass\% C is the carbon content in the droplet; mass\% C\(_{\text{eq}} \) is the
equilibrium carbon content. In Chen and Coley equation\textsuperscript{17),} \( n_e \) is the number of molecules in an embryo; \( N_A \) is Avogadro number; \( V_0 \) is the original droplet volume. \( J_s \) is the nucleation rate and can be found using:\textsuperscript{17)

\[
J_s = N_e \exp \left\{ -\frac{\Delta H}{kT} \left[ \frac{\beta (\psi \sigma \pi)}{\pi m} \right]^{1/2} \right\} \exp \left[ \frac{-16 \pi (\psi \sigma)^2}{3kT \left( P_v - P_L \right)} \right]
\]

(5)

where \( N_0 \) is the number concentration of CO embryos in the liquid; \( \sigma_0 \) is the surface tension at liquid gas interface; \( \Delta H \) is the heat of formation of one CO molecule; \( m \) is the mass of one molecule; \( T \) is temperature; \( k \) is Boltzman constant; \( P_v \) is the pressure in the vapour bubble at equilibrium; \( P_L \) is the liquid pressure; \( \psi \) is the reduction magnitude of surface tension.

Figure 1 presents the changes in carbon content of metal droplet as a function of time. The kinetic model proposed by Brooks et al., based on a simple surface renewal model of carbon diffusions, follows closely the measured values for carbon content in the droplet. It is important to note that the Brooks et al. model used empirical data from the Molloseau and Fruehan study for some of their parameters in their model, so in effect, “fitted” their model to the data, and they only claim that this model is useful for global kinetic calculations and not necessarily the “correct” kinetic model. Further work is required to fully understand the mechanism at the individual droplet level.\textsuperscript{10) This approach has been successfully applied to experimental results\textsuperscript{9) and we have incorporated this approach into our global model.

Assumptions

The following assumptions have been made in the model based on the industrial data available for a 200-ton oxygen steelmaking vessel.

1) The global model is validated against the industrial data reported by Cicutti et al. The operating conditions are given in Table II.

2) The factors affecting the path of decarburization are the temperature profile of hot metal and scrap, the amount of hot metal charged, hot metal and scrap compositions, scrap and flux additions, and blowing practice, which are considered as system inputs for this model. The input data for the calculations were taken from the industrial data reported by Cicutti et al.\textsuperscript{6, 41) The outcome of other refining reactions such as FeO concentration was entered as known variables.
Table II. Data for numerical calculation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot metal charged</td>
<td>170 t</td>
</tr>
<tr>
<td>Scrap charged</td>
<td>30 t</td>
</tr>
<tr>
<td>Oxygen flow rate</td>
<td>620 Nm³/min</td>
</tr>
<tr>
<td>Supply pressure</td>
<td>10 atm</td>
</tr>
<tr>
<td>Number of nozzle</td>
<td>6</td>
</tr>
<tr>
<td>Throat diameter of nozzle</td>
<td>33 mm</td>
</tr>
<tr>
<td>Exit diameter of nozzle</td>
<td>45 mm</td>
</tr>
<tr>
<td>Inclination angle</td>
<td>17.5°</td>
</tr>
<tr>
<td>Lance height</td>
<td>1.8-2.5 m</td>
</tr>
<tr>
<td>Initial hot metal temperature</td>
<td>1350°C</td>
</tr>
<tr>
<td>Tapping temperature</td>
<td>1650°C</td>
</tr>
</tbody>
</table>

3) The simultaneous decarburization reactions at the impact zone and in the emulsion zone, temperature profile of the bath, the dissolution process of flux, the melting process of scrap, the behaviour of gas flow at the impact zone and the generation of off-gases above the bath have been considered in this model. The calculation procedure for flux dissolution and droplet generation that form the global model have been published. 42, 43)

4) The carbon content of metal droplet ejected from the bath has been measured and is lower than carbon content of the liquid metal. However, there is no calculation technique available to predict the initial carbon concentration of metal droplets. Therefore, carbon content of the metal droplet is assumed that it is equal to the bulk carbon content of liquid metal. Bulk carbon content is calculated using mass balance, which includes scrap melting, the decarburization reaction at the impact zone and the emulsion zone, and is given in Eq 6.

\[
W_b \times \frac{\text{mass}\% C}{100} = W_s \times \frac{\text{mass}\% C}{100} + W_{sc} \times \frac{\text{mass}\% C}{100} + \left( \frac{\text{dC}}{\text{dt}} \right)_b + \left( \frac{\text{dC}}{\text{dt}} \right)_{em} \ (6)
\]

where \( W_b \) represents the weight of metal in the bath, \( W_{sc} \) is weight of scrap melted in the bath. The subscripts b and em refer to the corresponding decarburization rates.

5) The decarburization rate of individual droplets is calculated using the rate equation proposed by Brooks et al. given in Table I.

6) The effect of size distribution is not included and the diameter of a metal droplet is assumed to be 2.5 mm. A more complicated picture of droplet size may later be included but this assumption was used for the development of the concept.

RESULTS AND DISCUSSION

The Decarburization Rate

The decarburization rate was calculated based on the assumption that decarburization reaction only takes place in the emulsion zone. The model predictions for decarburization rate in the emulsion zone as a function of various time steps are given in Figure 2. The rates predicted by the model are converging as the time step is decreased. This demonstrates that the model predictions are relatively independent of the numerical calculations below 10 second step internals. These results are compared with the overall decarburization rate taken from the study of Cicotti et al. 5) The industrial data for decarburization rate was measured in the top-blown oxygen steelmaking process. During the blow, decarburization rate increases at 4 min then 7 min. At this point, the rate reaches peak level during the main blow and decreases back towards the end of the blow. The increase in the decarburization rate is due to the variations in the lance height. The variations in lance height were given in Figure 2. As the lance is decreased, more droplets are ejected through the emulsion zone and more decarburization reaction takes place in the emulsion zone.
Figure 2. Model predictions for decarburization rate for various time-steps were compared to the overall decarburization rate reported by Cicutti et al.\textsuperscript{6)}

After verification, this model was further used to predict the decarburization reaction at the impact zone and emulsion zone. The results for decarburization reaction at impact zone and emulsion zone and overall decarburization reaction predicted by the global model are compared in Figure 3. In the early blow, the decarburization rates in different zones are relatively close to each other. During the main blow, the majority of the refining takes place in the emulsion zone. Toward the end of the blow, the metal droplets contain less carbon and the driving force for the reaction between metal droplets and slag is decreased. The bloated droplets began to collapse in a shorter time due to the weak decarburization. So, overall decarburization of the process begins to decrease as decarburization in the emulsion decreases.

Figure 3. The comparison of decarburization rates in oxygen steelmaking process calculated by the global model and based on the operating conditions described by Cicutti et al.\textsuperscript{6)}

The proportion of decarburization via emulsion as a function of bulk carbon content is given in Figure 4. The refining rate decreases as the carbon content of the metal decreases. However, there variations away from these trends as the carbon concentration decreases, reflecting changes in blowing conditions (shown in Figure 2), in particular, more droplets reacting...
in the emulsion due to a decrease in lance height. This study suggests that approximately 70% of the carbon was removed via emulsified droplets, the remaining 30% being removed principally in the impact zone during the main blow.

Figure 4. Carbon removal via emulsion calculated by the model and based on the operating conditions described by Cicutti et al.6)

The Residence Time

Figure 5 illustrates the evolution of residence time of droplets as a function of carbon concentration in the bath. In the early part of the blow, the residence time of droplets is around 60 seconds. Towards the end of the blow, it decreases to 20 seconds. As seen, the residence time of droplets is much higher in the presence of high carbon concentrations. Towards the end of the blow, the residence time is low due to the weak decarburization rates. This implies that metal droplets are “bloated” with CO gas, generated during the active decarburization period, become less dense and spend longer time in the emulsion.11) However, towards the end of the blow, metal droplets maintain their original density due to the weak decarburization. As a result, it has been concluded that decarburization rate is strongly dependent on the residence time of droplets in the emulsion and that the bloating of droplet is critical to understand the overall kinetics of steelmaking. The relative consistency between the predicted overall rate in Figure 2 and the measured overall rate in Figure 2, provides further evidence for the bloated droplet model. Running the model without the bloated droplet included (every droplet is dense) results in a vastly under predicted overall de-carburisation rate.

Figure 5. Residence time of droplets as a function of initial carbon content in the metal droplets

Carbon Concentration
The global model can predict the change in carbon concentration of metal droplets ejected at each time-step. The predicted values vary in a great range due to their presence in the emulsion zone. The metal droplets may be generated, be circulating in the emulsion or be fallen back to the metal bath. Figure 6 compares the averaged carbon concentration of the metal droplets predicted by the global model with the measured values of carbon content of metal droplets taken from the study of Cicuitti et al. The predicted values were lower than the measured values because the carbon concentration of metal droplets decreases to the equilibrium concentrations.

Figure 6. Comparison of averaged carbon content in metal droplets with the measured carbon content of metal droplets reported by Cicuitti et al.

Droplet Size

Table III lists FeO concentrations of the slag taken from the industrial data by Cicuitti et al. and C concentrations of metal droplets predicted from the model with same initial diameter ejected at various blowing time. Figure 7 illustrates the change in the size of a droplet ejected from the bath as a function of residence time during the blow. There is a significant increase in droplet diameter (three times larger than initial diameter) of a droplet due to the bloating behaviour of a droplet regardless of the blowing period. However, the increase in the size of the droplet decreases as the carbon and FeO concentrations decreases towards the end of the blow. It is most likely due to the decrease in the carbon concentration since decarburization rate decreases with a decrease in the difference in carbon concentration of the droplets. This indicates that the maximum decarburization will be achieved initially, followed by an eventual decrease in rate. The carbon content of the droplet and FeO concentration are important to determine the change in the size of the droplet. Therefore, a more robust understanding of how FeO varies during the blow will be important to improve the models described in this paper, as the FeO values used in our calculation come directly from the industrial data.

Table III. FeO and C concentrations of metal droplets ejected from the bath at different time

<table>
<thead>
<tr>
<th>Droplet</th>
<th>mass% FeO</th>
<th>mass% C</th>
<th>Ejection time from start of the blow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>sec</td>
<td></td>
</tr>
<tr>
<td>Droplet 1</td>
<td>34</td>
<td>3.9</td>
<td>2 00</td>
</tr>
<tr>
<td>Droplet 2</td>
<td>25</td>
<td>2.25</td>
<td>7 00</td>
</tr>
<tr>
<td>Droplet 3</td>
<td>15</td>
<td>1.17</td>
<td>12 00</td>
</tr>
</tbody>
</table>
CONCLUSIONS

A mathematical model has been developed to study the decarburization reaction in the slag-metal-gas emulsion for industrial practice. A numerical calculation technique was used to predict the residence time of the droplets and decarburization rates of individual droplets during the blow. As a result of global model, the following conclusions can be drawn.

1. The bloated droplet theory is successfully applied to the industrial data. A global model including the bloated droplet theory can predict decarburization rates of individual droplets under full-scale operating conditions for oxygen steelmaking process. Decarburization rate in the emulsion zone increases as the lance height is decreased.

2. The global model provides information about the variation in the residence time of the ejected metal droplets. For bloated droplets, it is predicted that the residence time of droplets in emulsion is around 60 seconds during the blow. Towards the end of the blow, the residence time of droplets decreases to 20 seconds.

3. The models predict that approximately 70% of decarburisation occurs in the emulsion zone during the main part of the blow, though this decreases as droplets become denser towards the end of the blow.

REFERENCES


