A Mathematical Model for Reactions during Top-Blowing in the AOD Process: Derivation of the Model

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Abstract

In earlier work, a fundamental mathematical model was proposed for side-blowing operation in the argon-oxygen decarburization (AOD) process. The purpose of this work is to present a new model, which focuses on the reactions during top-blowing in the AOD process. The model considers chemical reaction rate phenomena between the gas jet and the steel bath as well as between the gas jet and metal droplets. The rate expressions were formulated according to a law of mass action based method, which accounts for the mass transfer resistances in the liquid metal, gas and slag phases. The generation rate of the metal droplets was related to the blowing number theory. This paper presents the description of the model, while validation and preliminary results are presented in the second part of this work.

Keywords: stainless steelmaking, AOD process, top-blowing, mathematical modelling.

1 Introduction

The argon-oxygen decarburization (AOD) process is the most common process for the refining of stainless steel.[1] Owing to violent agitation caused by the high blowing rates, the AOD vessel has very good mixing characteristics.[2–5] Nowadays, top-blowing is employed in conjunction with side-blowing in the early part of the decarburization stage in order to maximize oxygen delivery into the melt.[6] As illustrated in **Figure 1**, two main reaction areas can be identified during combined blowing: 1) inside the gas plume, and 2) on the surface of the bath, including metal droplets.[7,8]

Figure 1

Numerous reaction models have been proposed for the decarburization[8–37] and nitrification[7,38–40] of steel in an AOD vessel. The majority of the models applicable for side-blowing decarburization have been reviewed elsewhere[21,41]. Despite the vast number of reaction models available, there are only a few models that explicitly address the reactions during top-blowing in the AOD process. Arguably the most relevant examples found in the literature are those proposed by Watanabe and Tohge[9], Tohge *et al.*[17], Kikuchi *et al.*[23,42] and Wei *et al.*[8,21,22,26,28]. Some similarities in the modelling setting can be found in the reaction models proposed for the VOD process[41,43]. To summarize, it can be stated that the top-blowing models proposed so far are capable of predicting the decarburization with a reasonable degree of accuracy and have laid the basic foundations for further investigations. However, more research is required along these lines in order to obtain information on the related reaction interfaces and chemical reaction rate phenomena.

In our previous work,[29,30] a fundamental model was proposed and validated for the reactions inside the bath during side-blowing in the AOD process. Consequently, the aim of this work was to extend the original model by developing a mathematical model for reactions during top-blowing. In order to provide more information on the controlling mechanisms and dynamics of decarburization during top-blowing, the model combines the transient solution of multicomponent equilibria with a description of the constraining mass transfer. This paper presents the description of the model, while validation and preliminary results are presented in the second part of this work[44].

2 Derivation of the model

The model was programmed using C++ and its main assumptions can be summarized as follows:

1. The top-blown oxygen may react with iron and species dissolved in iron, dissolve in the steel

bath, or escape through the gas exit.

2. Reactions between gas, metal and slag species take place simultaneously at the surface of the cavity as well as at surface of the metal droplets generated due to top-blowing.
3. Owing to the high temperature, the reaction rates are assumed to be limited by mass transfer onto and from the reaction interfaces and hence the reaction interfaces are able to reach their constrained thermodynamic equilibrium at any given moment.
4. Conservation of mass and heat are solved successively.

The liquid metal phase is assumed to consist of Fe as the solvent and Cr, Mn, Si, C, O, N, Ni, Al and S as solutes. The gas phase consists of O_2, CO, CO_2, N_2 and Ar. The slag phase consists of FeO, Cr_2O_3, MnO, SiO_2, CaO, MgO, Al_2O_3, CaF_2 and MeO_x, which is a generic oxide and depicts the residual species. The reaction system considered is defined by the following reactions:

$$\{O_2\} \rightleftharpoons 2[O] \ , \tag{1}$$

$$[C] + \frac{1}{2}\{O_2\} \rightleftharpoons \{CO\} \ , \tag{2}$$

$$[C] + \{O_2\} \rightleftharpoons \{CO_2\} \ , \tag{3}$$

$$Fe_{(l)} + \frac{1}{2}\{O_2\} \rightleftharpoons (FeO) \ , \tag{4}$$

$$2[Cr] + \frac{3}{2}\{O_2\} \rightleftharpoons (Cr_2O_3) \ , \tag{5}$$

$$[Mn] + \frac{1}{2}\{O_2\} \rightleftharpoons (MnO) \ , \tag{6}$$

$$[Si] + \{O_2\} \rightleftharpoons (SiO_2) \ . \tag{7}$$

The rate expressions were formulated as reversible according to a modified Law of Mass Action, a method that has been discussed more comprehensively in our earlier work[45,46]. More specifically, the rate expressions are defined so that concentrations are replaced with activities and partial pressures, as illustrated below for the oxidation of dissolved carbon to carbon monoxide:

$$R'' = k_f \left(a_{[C]} p_{O_2}^{1/2} - \frac{p_{CO}}{K} \right) \ , \tag{8}$$

where k_f is the forward reaction rate coefficient, $a_{[C]}$ is the activity of dissolved carbon, p_{O_2} is the partial pressure of gaseous oxygen and K is the equilibrium constant.

2.1 Conservation of mass

The observed system consists of gas input, gas exit, two reaction interfaces and three bulk volumes, as shown in **Figure 2**. It should be noted that the reaction interfaces have neither thickness nor mass.

Figure 2

It has been proposed that during simple side-blowing, post-combustion takes place in the off-gas flue, but not in the AOD vessel itself.[47] However, during combined top- and side-blowing a part of the top-blown oxygen may be consumed in the post-combustion of CO to CO_2 before the gas jet impacts the bath surface.[8] In order to simplify the modelling setting, the model proposed in this paper considers post-combustion only at the reaction interfaces. Because the entrainment of cold air from the atmosphere outside the vessel can be neglected under normal operating conditions,[48] the top-lance and the tuyères can be taken as the only gas inputs of the system. More specifically, it was assumed that the side-blown gas exits the metal bath through the plume eye and becomes in contact with the top-blown gas. The mass flow of gaseous species through the top lance into the observed system is given by

$$\dot{m}_{\mathrm{G,in,lance}} = \dot{V}_{\mathrm{G,lance}} \rho_{\mathrm{G,STP}} \,, \tag{9}$$

where $\dot{V}_{\mathrm{G,lance}}$ is the volumetric gas flow rate through top lance (in Nm^3/s) and $\rho_{\mathrm{G,STP}}$ is the density of the gas mixture under standard temperature and pressure according to the DIN 1343 standard[49]: 273.15 K (0 °C) and 101325 Pa. The model is coupled with the earlier-proposed model for side-blowing decarburization[29], which calculates the mass flow of gaseous species from the plume eye (into the observed system. In the case of inert gases, the mass flow rate of gas from the plume eye is equal to the mass flow rate of gas from the tuyères. Preventing the suction of atmospheric gas, the mass flux of gas exiting the system is obtained from

$$\dot{m}_{\mathrm{G,out}} = \max\left(\underbrace{\dot{m}_{\mathrm{G,in,lance}} + \dot{m}_{\mathrm{G,in,plume}}}_{\text{gas injection}} \underbrace{-\dot{m}_{\mathrm{G,cav}} - \dot{m}_{\mathrm{G,md}}}_{\text{gas consumption}} , 0 \right), \tag{10}$$

where $\dot{m}_{\mathrm{G,in},plume}$ is the mass flow of gas from the plume eye, $\dot{m}_{\mathrm{G,cav}}$ is the mass flow of gas from the cavity interface and $\dot{m}_{\mathrm{G,md}}$ is the mass flow of gas from the metal droplet interface. In order to avoid the mathematical complexity of the Maxwell-Stefan equations and the generalized Fick's law, an effective diffusion model was employed[50]. The conservation of species at the two reaction

interfaces is defined by the reaction rates and mass transfer onto and from the reaction surfaces. Employing a first-order upwind scheme for the Stefan flow, the conservation of species i in phase ψ at reaction interface ω is given by

$$\underbrace{\beta_{i,\psi,\omega}\rho_{\psi,\omega}\left(y_{i,B}-y_{i,\omega}^{*}\right)}_{\text{mass transport}}\underbrace{+\max\left(m_{\psi,\omega}'',0\right)y_{i,B}-\max\left(-m_{\psi,\omega}'',0\right)y_{i,\omega}^{*}}_{\text{Stefan flow}}+\underbrace{\sum_{k=1}^{r}R_{k,\omega}''\bar{\nu}_{i,k}}_{\text{chemical reactions}}=0\,, \tag{11}$$

where β is the mass transfer coefficient, ρ is the density, $y_{i,B}$ is the mass fraction of species i in the bulk phase (*i.e.* steel bath, gas jet or top slag), $y_{i,\omega}^{*}$is the interfacial mass fraction of species i, m'' is the total mass flux, R'' is the reaction rate and $\bar{\nu}$ is the mass-based stoichiometric coefficient. It should be noted that all properties are specific to the reaction interface in question. In order to account for conservation of mass within the metal droplets, the following expression is employed for species in the metal phase at the metal droplet interface:

$$\underbrace{\left(\frac{m_{\mathrm{md}}}{A_{\mathrm{md}}\bar{t}_{\mathrm{md}}}-m_{\mathrm{L,md}}''\right)\bar{\eta}_{i,\mathrm{M,md}}\left(y_{i,\mathrm{bath}}-y_{i,\mathrm{md}}^{*}\right)}_{\text{mass transport}}\underbrace{+m_{\mathrm{L,md}}''y_{i,\mathrm{bath}}}_{\text{Stefan flow}}+\underbrace{\sum_{k=1}^{r}R_{k,\mathrm{md}}''\bar{\nu}_{i,k}}_{\text{chemical reactions}}=0\,, \tag{12}$$

where m_{md}, A_{md} and $\bar{t}_{\mathrm{md}}$ are the mass, surface area and average residence time of the metal droplets, respectively, and $\bar{\eta}_{i,\mathrm{M,md}}$ is the average microkinetic efficiency for mass transfer of species i in the metal droplets. The total mass flux of the metal phase is subject to constraint $m_{\mathrm{L,md}}''\leq\frac{m_{\mathrm{md}}}{A_{\mathrm{md}}\bar{t}_{\mathrm{md}}}$. The average microkinetic efficiency was calculated based on the average residence time of the metal droplets:

$$\bar{\eta}_{i,\mathrm{M,md}}=\frac{y_{i,\mathrm{bath}}-y_{i,\mathrm{md}}}{y_{i,\mathrm{bath}}-y_{i,\mathrm{md}}^{*}}=1-\exp\left(-\beta_{i,\mathrm{L,md}}\frac{A_{\mathrm{md}}}{V_{\mathrm{md}}}\bar{t}_{\mathrm{md}}\right), \tag{13}$$

where $y_{i,\mathrm{md}}$ is the composition of species i in the metal droplets. The mass-based stoichiometric coefficients $\bar{\nu}_{i,k}$ are defined in relation to key components:

$$\overline{\nu}_{i,k} = \nu_{i,k}\frac{M_i}{M_{K,k}}, \tag{14}$$

where $\nu_{i,k}$ is the stoichiometric coefficient of species i in reaction k, $M_{K,k}$ is the molar mass of the key component of reaction k and M_i is the molar mass of species i. The key components of the reactions shown in Eqs. 1–7 are O_2, C, C, Fe, Cr, Mn and Si, respectively. The total mass flux of phase ψ at reaction interface ω is given by:

$$m''_{\psi,\omega} = -\sum_{i=1}^{n}\sum_{k=1}^{r}\Gamma_{i,\psi}R''_{k,\omega}\overline{\nu}_{i,k}\ , \tag{15}$$

where $\Gamma_{i,\psi}$ is a binary operator, which is defined as 1 if species i is in phase ψ and 0 otherwise. The total mass flows $\dot{m}_{\psi,\omega}$ are obtained by multiplying the mass flux $m''_{\psi,\omega}$ by the corresponding interfacial area A_ω. Employing the implicit Euler method for time integration, the conservation of species i in the steel bath, top-blown gas and top slag is defined by Eqs. 16, 17 and 18, respectively.

$$\begin{aligned}
&-\beta_{i,\mathrm{L,cav}}\rho_{\mathrm{L,cav}}A_{\mathrm{cav}}\left(y_{i,\mathrm{bath}} - y^*_{i,\mathrm{cav}}\right) - \max\left(m''_{\mathrm{L,cav}}, 0\right)A_{\mathrm{cav}}y_{i,\mathrm{bath}}\\
&+ \max\left(-m''_{\mathrm{L,cav}}, 0\right)A_{\mathrm{cav}}y^*_{i,\mathrm{cav}}\\
&-\left(\frac{m_{\mathrm{md}}}{\overline{t}_{\mathrm{md}}} - m''_{\mathrm{L,md}}A_{\mathrm{md}}\right)\overline{\eta}_{i,\mathrm{M,md}}\left(y_{i,\mathrm{bath}} - y^*_{i,\mathrm{md}}\right)\\
&-m''_{\mathrm{L,md}}A_{\mathrm{md}}y_{i,\mathrm{bath}} - \frac{m_{\mathrm{bath}}y_{i,\mathrm{bath}} - m^{\mathrm{t-\Delta t}}_{\mathrm{bath}}y^{\mathrm{t-\Delta t}}_{i,\mathrm{bath}}}{\Delta t} = 0\ ,
\end{aligned} \tag{16}$$

$$\begin{aligned}
&\sum_{\omega}\left[-\beta_{i,\mathrm{G},\omega}\rho_{\mathrm{G},\omega}A_\omega\left(y_{i,\mathrm{jet}} - y^*_{i,\omega}\right) - \max\left(m''_{\mathrm{G},\omega}, 0\right)A_\omega y_{i,\mathrm{jet}}\right.\\
&\left.+ \max\left(-m''_{\mathrm{G},\omega}, 0\right)A_\omega y^*_{i,\omega}\right] + \dot{m}_{\mathrm{G,in,lance}}y_{i,\mathrm{in,lance}} + \dot{m}_{\mathrm{G,in,plume}}y_{i,\mathrm{in,plume}}\\
&- \dot{m}_{\mathrm{G,out}}y_{i,\mathrm{jet}} - \frac{m_{\mathrm{jet}}y_{i,\mathrm{jet}} - m^{\mathrm{t-\Delta t}}_{\mathrm{jet}}y^{\mathrm{t-\Delta t}}_{i,\mathrm{jet}}}{\Delta t} = 0\ ,
\end{aligned} \tag{17}$$

$$\begin{aligned}
&\sum_{\omega}\left[-\beta_{i,\mathrm{S},\omega}\rho_{\mathrm{S},\omega}A_\omega\left(y_{i,\mathrm{slag}} - y^*_{i,\omega}\right) - \max\left(m''_{\mathrm{S},\omega}, 0\right)A_\omega y_{i,\mathrm{slag}}\right.\\
&\left.+ \max\left(-m''_{\mathrm{S},\omega}, 0\right)A_\omega y^*_{i,\omega}\right] - \frac{m_{\mathrm{slag}}y_{i,\mathrm{slag}} - m^{\mathrm{t-\Delta t}}_{\mathrm{slag}}y^{\mathrm{t-\Delta t}}_{i,\mathrm{slag}}}{\Delta t} = 0\ ,
\end{aligned} \tag{18}$$

where m_{bath}, m_{jet} and m_{slag} are the masses of the steel bath, gas jet and top slag, respectively, and Δt is the time step. The conservation equations for the total mass of the bulk phases (for the steel

bath, gas jet and top slag) are defined correspondingly by summation of the mass transport terms and fluxes of species that are relevant to the bulk phase in question. Metal losses to dust were not accounted for as their effect on the composition of the steel bath is negligible.

2.2 Conservation of heat

Temperature increase is defined by the difference in heat generation and heat losses. While heat is generated by exothermic reactions, it is consumed by endothermic reactions as well as heat losses through the refractory lining, and top slag and exiting gas. The conservation of heat at the cavity interface is defined according to

$$\underbrace{\alpha_{\mathrm{L,cav}}(T_{\mathrm{bath}}-T^{*}_{\mathrm{cav}})+\alpha_{\mathrm{G,cav}}\left(T_{\mathrm{jet}}-T^{*}_{\mathrm{cav}}\right)+\alpha_{\mathrm{S,cav}}\left(T_{\mathrm{slag}}-T^{*}_{\mathrm{cav}}\right)}_{\text{heat transport}} \underbrace{-\sum_{k=1}^{r} R''_{k,\mathrm{cav}}\,\Delta h_k = 0}_{\text{chemical reactions}}, \tag{19}$$

where α is the heat transfer coefficient, T_{bath} is the temperature of the steel bath, T^{*}_{cav} is the temperature of the cavity reaction interface, T_{jet} is the temperature of the gas jet and Δh_k is the specific reaction enthalpy of reaction k. The conservation of heat at the metal droplet interface was defined according to

$$\underbrace{\frac{m_{\mathrm{md}}}{A_{\mathrm{md}}\bar{t}_{\mathrm{md}}}c_{\mathrm{p,L}}\bar{\eta}_{\mathrm{H,md}}(T_{\mathrm{bath}}-T^{*}_{\mathrm{md}})+\alpha_{\mathrm{G,md}}\left(T_{\mathrm{jet}}-T^{*}_{\mathrm{md}}\right)+\alpha_{\mathrm{S,md}}\left(T_{\mathrm{slag}}-T^{*}_{\mathrm{md}}\right)}_{\text{heat transport}} \underbrace{-\sum_{k=1}^{r} R''_{k,\mathrm{md}}\,\Delta h_k = 0}_{\text{chemical reactions}} \tag{20}$$

where T^{*}_{md} is the interfacial temperature of the metal droplets and $\bar{\eta}_{\mathrm{H,md}}$ is the average microkinetic efficiency of heat transfer in the metal droplets:

$$\bar{\eta}_{\mathrm{H,md}}=\frac{T_{\mathrm{bath}}-T_{\mathrm{md}}}{T_{\mathrm{bath}}-T^{*}_{\mathrm{md}}}=1-\exp\left(-\alpha_{\mathrm{L,md}}\frac{A_{\mathrm{md}}}{m_{\mathrm{md}}c_{\mathrm{p,L}}}\bar{t}_{\mathrm{md}}\right), \tag{21}$$

where T_{md} is the temperature of the metal droplets. Employing the implicit Euler method for time integration, the conservation of heat in the steel bath, in the top-blown gas and in the top slag can be

expressed according to Eqs. 22, 23 and 24, respectively.

$$-\alpha_{\mathrm{L,cav}} A_{\mathrm{cav}} (T_{\mathrm{bath}} - T^*_{\mathrm{cav}}) - \frac{m_{\mathrm{md}}}{\bar{t}_{\mathrm{md}}} c_{\mathrm{p,L}} \bar{\eta}_{\mathrm{H,md}} (T_{\mathrm{bath}} - T^*_{\mathrm{md}})$$
$$- \sum_{\omega} \sum_{i=1}^{n} \sum_{k=1}^{r} \Gamma_{i,\mathrm{L}} R''_{k,\omega} \bar{v}_{i,k} A_{\omega} c_{\mathrm{p},i} (T_{\mathrm{bath}} - T^*_{\omega}) - q_{\mathrm{lining}} A_{\mathrm{lining}} \tag{22}$$
$$- m_{\mathrm{bath}} c_{\mathrm{p,bath}} \frac{T_{\mathrm{bath}} - T^{\mathrm{t-\Delta t}}_{\mathrm{bath}}}{\Delta t} = 0 ,$$

$$\sum_{\omega} \left[-\alpha_{\mathrm{G},\omega} A_{\omega} (T_{\mathrm{jet}} - T^*_{\omega}) - \sum_{i=1}^{n} \sum_{k=1}^{r} \Gamma_{i,\mathrm{G}} R''_{k,\omega} \bar{v}_{i,k} A_{\omega} c_{\mathrm{p},i} (T_{\mathrm{jet}} - T^*_{\omega}) \right]$$
$$- \dot{m}_{\mathrm{G,in,lance}} \int_{T_{\mathrm{in}}}^{T_{\mathrm{jet}}} c_{\mathrm{p,lance}} \, \mathrm{d}T - \dot{m}_{\mathrm{G,in,plume}} \int_{T_{\mathrm{plume}}}^{T_{\mathrm{jet}}} c_{\mathrm{p,plume}} \, \mathrm{d}T \tag{23}$$
$$- m_{\mathrm{jet}} c_{\mathrm{p,jet}} \frac{T_{\mathrm{jet}} - T^{\mathrm{t-\Delta t}}_{\mathrm{jet}}}{\Delta t} = 0 ,$$

$$\sum_{\omega} \left[-\alpha_{\mathrm{S},\omega} A_{\omega} (T_{\mathrm{slag}} - T^*_{\omega}) - \sum_{i=1}^{n} \sum_{k=1}^{r} \Gamma_{i,\mathrm{S}} R''_{k,\omega} \bar{v}_{i,k} A_{\omega} c_{\mathrm{p},i} (T_{\mathrm{slag}} - T^*_{\omega}) \right]$$
$$- q_{\mathrm{slag}} A_{\mathrm{slag}} - m_{\mathrm{slag}} c_{\mathrm{p,slag}} \frac{T_{\mathrm{slag}} - T^{\mathrm{t-\Delta t}}_{\mathrm{slag}}}{\Delta t} = 0 , \tag{24}$$

where q_{lining} is the heat flux through the refractory lining, A_{lining} is the surface area of the refractory lining, q_{slag} is the heat flux through the slag and A_{slag} is the cross-sectional surface area of the top slag. The values of A_{lining} and A_{slag} are calculated based on the geometry of the simulated converter. The heat flux through the refractory lining was set to q_{lining} = 12500 W/m^2 as in our previous work[29]. The heat losses through the slag were determined on the basis of radiative heat transfer through the mouth of the vessel. Neglecting back-radiation, the radiative heat flux can be calculated as follows:[51]

$$q_{\mathrm{slag}} = \frac{\sigma T^4_{\mathrm{slag}}}{\left[\frac{A_{\mathrm{slag}} + A_{\mathrm{mouth}} - 2A_{\mathrm{slag}} F}{A_{\mathrm{mouth}} - A_{\mathrm{slag}} F^2} + \left(\frac{1}{\varepsilon_{\mathrm{S}}} - 1 \right) \right]} , \tag{25}$$

where σ is the Stefan-Boltzmann constant, F is the view factor between the top slag and the converter mouth, A_{mouth} is the cross-sectional area of the vessel mouth and ε_{S} is the emissivity of the slag phase, which was assumed to be ε_{S} = 0.95. The view factor for the top slag in relation to the vessel mouth is determined by[51]

$$F = \frac{1}{2r_{\text{slag}}^2}\left[z^2 + r_{\text{slag}}^2 + r_{\text{mouth}}^2 - \left\{\left(z^2 + r_{\text{slag}}^2 + r_{\text{mouth}}^2\right)^2 - 4r_{\text{slag}}^2 r_{\text{mouth}}^2\right\}^{1/2}\right] \quad (26)$$

where z is the distance between the top slag and the vessel mouth, r_{slag} is the radius of the top slag and r_{mouth} is the radius of the vessel mouth. The cooling effect of the side-blown gas on the steel bath temperature is calculated separately by the earlier-proposed model for side-blowing decarburization[29] and is not repeated here.

2.3 Geometry of the cavity

The gas jet exits the lance nozzle at a supersonic velocity, but starts to spread and lose its velocity after the supersonic core. The entrainment of gases from the ambient atmosphere affects the gas jet not only by decreasing its velocity, but also by increasing its mass flow and – if the ambient temperature is higher than that of the gas jet – by increasing its temperature.[52] Considering that the length of the supersonic region is typically 20–30 times the nozzle exit diameter at steelmaking temperatures[53] it is apparent that the gas jet impacts the surface of the steel bath at subsonic velocity. Upon impact, the momentum of the gas jet forms a cavity on the bath surface,[53] while the liquid steel outside the cavity is pushed towards the refractory walls of the vessel in the radial direction[5].

Molloy[54] distinguished three cavity modes, namely *dimpling*, *splashing* and *penetrating*. Dimpling refers to mere depression of the surface without droplet formation, while outwardly directed splashes start to form the edges of the depression when the mode changes to splashing. In the penetrating mode, the penetration depth is deeper and outwardly directed splashes are reduced. The different modes can also be distinguished based on the frequency and amplitude of the cavity oscillation.[55] **Figure 3** presents a schematic illustration of the gas jet impact area with a one-hole lance in the splashing mode.

Figure 3

In this work, the modelling setting was simplified by defining the reaction area between the gas jet and the steel bath as the surface area of the cavity. Because the surface of the cavity is in oscillating motion, the analysis must be based on quasi-steady state flow conditions.[53,56] It has been suggested that chemical reactions[57,58] and the interference of top slag[57] do not affect the geometry of the cavity to a significant extent and on this account their effect was excluded in this work. In accordance with Cheslak *et al.*[59], it was assumed that the geometry of the cavity follows the form of a paraboloid of revolution with an impact radius of r_{cav} and an impinging depth of h_{cav} (see **Figure 3**). The surface

area of the paraboloid of revolution, excluding its base, can be calculated as follows:[60]

$$A_{\mathrm{cav},1} = \frac{\pi\, r_{\mathrm{cav}}}{6\, h_{\mathrm{cav}}^2}\left[(r_{\mathrm{cav}}^2 + 4h_{\mathrm{cav}}^2)^{3/2} - r_{\mathrm{cav}}^3\right]. \quad (27)$$

For a three-hole lance, the geometry is slightly more complicated. Depending on the inclination angle of the gas jets, the gas jets may either coalesce and form only one large cavity, or penetrate the bath surface as three separate jets, whereupon each gas jet will form its own cavity.[61,62] Even if the gas jets do not coalesce, the cavities may still coalesce provided that they are sufficiently close to each other[63] as shown in **Figure 4**. Observations with high-speed cameras[64] suggest that the cavities remain non-coalescing when the inclination angle is greater than 10°. In this work, it is assumed that the gas jets do not coalesce and that the number of cavities is equal to the number of the gas jets (see **Figure 4A**). Therefore, the total surface area of the cavities caused by a multi-hole lance can be calculated simply by multiplying the surface area of a single cavity with the number of exit ports in the top lance:[52,65]

$$A_{\mathrm{cav}} = n_{\mathrm{lance}} \times A_{\mathrm{cav},1}\,. \quad (28)$$

Figure 4

The effects of various factors on the depth and form of the cavity have been studied extensively. In this work, the correlations for the geometry of the cavity were taken from Koria and Lange[63]. The equations required for calculating the depth and radius of the cavity are given in **Table 1**. These are based on a dimensional analysis of experimental data on the penetration of oxygen jets in molten pig iron and pure iron-carbon alloys with both single- and multi-hole lances.[63]. It should be noted that Eq. 35 is applicable only for diatomic ideal gases (*e.g.* O_2 or N_2) and their mixtures. For other gas mixtures, a more general expression for $\dot{m}_t$ can be derived based on the equations presented by Koria[66].

Table 1 Ref.[63]

Eq. (29)
Eq. (30)
Eq. (31)
Eq. (32)
Eq. (33)
Eq. (34)
Eq. (35)

2.4 Droplet generation

The generation of metal droplets during top-blowing is important for steelmaking processes, because it brings about a considerable increase in the interfacial area available to chemical reactions.[67] The contribution of metal droplets to the decarburization rate during top-blowing in the AOD process has been acknowledged likewise[7,8,23,42,68–70]. However, foaming of the AOD slag does take place under typical operating conditions. Considering the high blowing rates and high viscosity of the slag, the behavior of slag should be somewhere between a void-free and an expanded slag. In such case the gas void fraction would depend on the gas velocity.[71]

Different mechanisms contribute to generation of metal droplets. If the momentum flux of the top-blown gas jet is sufficiently high, the liquid surface becomes unstable and the splashing of metal droplets occurs.[72] Standish and He[73] identified two regions of droplet generation: *dropping* and *swarming*. In the dropping region, single droplets are gradually formed and ejected. This is the mechanism of droplet generation when the gas flow rate is relatively low. When the gas flow rate is increased past a certain limit, the system reaches the swarming region and the mechanism of droplet generation changes so that not only single droplets but also large tears of liquid phase are ejected from the bath. Formation of metal droplets is also caused by side-blowing through a mechanism referred to as bubble bursting.[74–77] This phenomenon occurs when a rising gas bubble reaches the surface of the steel and bursts creating very small metal droplets from the thin film of steel around the bubble.[74–77] A related mechanism is the entrainment of large droplets due to jet formation, which is caused by the collapsing of the cavity after the rupture of the iron film.[76]

The secondary break-up of the metal droplets can occur due to various reasons, *e.g.* due to the aerodynamic forces of the gas jet[78], impact on the slag layer[79] or bursting resulting from spontaneous CO nucleation within the droplet[80]. In the absence of suitable quantitative descriptions for the break-up mechanisms and due to uncertainties related to the trajectories of the droplets, the effect of the various break-up mechanisms on the droplet size distribution was not accounted for.

Based on the available knowledge, the lifespan of the metal droplets was assumed to consist of three successive steps. At first, the metal droplets are generated at the vicinity of the cavity, from which they are ejected onto a gas–metal–slag emulsion. This also includes metal droplets, which have been ejected into the atmosphere and land on the emulsion. Thereafter, the metal droplets pass though the emulsion layer, reacting simultaneously with gas and slag species. Finally, the metal droplets return to the steel bath, where they mix with the steel bath immediately. Based on experimental findings[81] it was assumed that the initial composition of the metal droplets corresponds to the bulk composition.

Furthermore, the metal droplets were assumed to be spherical in geometry. This assumption should hold well for small droplets,[82] which are expected to form the majority of the surface area. Considering the distribution of emulsified metal droplets residing in the emulsion, their mass and surface area are obtained from the following equations:

$$m_{\mathrm{md}} = \sum_i m_{\mathrm{md},i}\,, \tag{36}$$

$$A_{\mathrm{md}} = \sum_i \frac{6m_{\mathrm{md},i}}{d_{\mathrm{md},i}\rho_{\mathrm{L}}}\,, \tag{37}$$

where $m_{\mathrm{md},i}$ and $d_{\mathrm{md},i}$ are the mass and diameter of the droplet size class i, respectively. As a practical matter, the droplet distribution was calculated from a diameter of 0.1 mm up to the diameter corresponding to the largest 99.9% by weight using a step size of 0.1 mm. The mass of droplets in the size class i residing in the emulsion can be solved from

$$m_{\mathrm{md},i} = f_{\mathrm{md},i}\dot{m}_{\mathrm{md}}\min\left(t_{\mathrm{md},i}, t\right), \tag{38}$$

where $f_{\mathrm{md},i}$, $\dot{m}_{\mathrm{md}}$ and $t_{\mathrm{md},i}$ are the mass fraction of size class i at place of birth, the metal droplet generation rate and the residence time of size class i, respectively, and t is the time. The Sauter mean diameter of the metal droplets residing in the emulsion at a given moment is obtained from

$$d_{32,\mathrm{md}} = \frac{6m_{\mathrm{md}}}{\rho_{\mathrm{L}}A_{\mathrm{md}}}. \tag{39}$$

2.4.1 Droplet generation rate

The blowing number, which relates the intensity of the jet momentum to the properties of the liquid steel, is defined by[67]

$$\mathrm{N_B} = \frac{\rho_{\mathrm{G}}u_{\mathrm{G}}^2}{2\sqrt{\sigma_{\mathrm{L}}g\rho_{\mathrm{L}}}} = \frac{\eta^2 p_{\mathrm{d}}}{\sqrt{\sigma_{\mathrm{L}}g\rho_{\mathrm{L}}}} \qquad \text{where} \quad \eta = \frac{u_{\mathrm{G}}}{u_{\mathrm{j}}}, \tag{40}$$

where u_{G} denotes the critical gas velocity, σ_{L} is the surface tension of the steel, η is a constant, p_{d} is the dynamic pressure of the gas jet and u_{j} is the axial velocity of the gas jet. The criterion for the Kelvin–Helmholtz instability, and thus the onset of droplet formation, is represented with a value of $\mathrm{N_B} = 1$.[67] The experimental results of other studies suggest that η is not independent of the lance

height[83–85] or the gas jet angle[86]. Here, the variation of η as a function of the gas jet angle was treated in a similar fashion as by Alam *et al.*[86]. Making use of the concept of blowing number, Subagyo *et al.*[67] proposed an empirical expression for droplet generation rate ($\dot{m}_{\mathrm{md}}$) in the splashing cavity mode:

$$\frac{\dot{m}_{\mathrm{md}}}{\dot{V}_{\mathrm{G,lance}}} = \frac{(\mathrm{N_B})^{3.2}}{[2.6\times10^{6} + 2.0\times10^{-4}(\mathrm{N_B})^{12}]^{0.2}} \qquad R^2 = 0.97\,, \tag{41}$$

where $\dot{V}_{\mathrm{G,lance}}$ is the volumetric gas flow rate through the top lance (Nm^3/s). As noted by Sarkar *et al.*[87] and Rout *et al.*[88], Eq. 41 yields droplet generation rates which are considerably below the values estimated from plant data. According to Rout *et al.*[88], one reason for the discrepancy is the fact that Eq. 41 has been derived for conditions corresponding to room temperature. Similar to Rout *et al.*[88], Eq. 41 was modified such that the blowing number $\mathrm{N_B}$ and the volumetric gas flow rate $\dot{V}_{\mathrm{G,lance}}$ are temperature corrected for the conditions at the point of impact:

$$\frac{\dot{m}_{\mathrm{md}}}{\dot{V}'_{\mathrm{G,lance}}} = \frac{(\mathrm{N'_B})^{3.2}}{[2.6\times10^{6} + 2.0\times10^{-4}(\mathrm{N'_B})^{12}]^{0.2}}\,, \tag{42}$$

where $\mathrm{N'_B}$ is the modified blowing number and $\dot{V}'_{\mathrm{G,lance}}$ is the modified volumetric gas flow rate. The modified blowing number $\mathrm{N'_B}$ is obtained from Eq. 40 by employing the dynamic pressure at the point of impact. In this work, the dynamic pressure at the point of impact was calculated according to an experimental relationship proposed by Deo and Boom[52]:

$$p_{\mathrm{d}} = 230\, p_0 \left(\frac{h_{\mathrm{lance}}}{d_{\mathrm{t}}}\right). \tag{43}$$

The modified gas flow rate is calculated as follows:[88]

$$\dot{V}'_{\mathrm{G,lance}} = \frac{p_{\mathrm{G,STP}}}{p_{\mathrm{G}}}\frac{T_{\mathrm{G}}}{T_{\mathrm{G,STP}}}\dot{V}_{\mathrm{G,lance}}\,, \tag{44}$$

where $p_{\mathrm{G,STP}}$ is the standard pressure, p_{G} is the total pressure of the gas at the impact point, T_{G} is the temperature of the gas at the impact point and $T_{\mathrm{G,STP}}$ is the standard temperature. Rout *et al.*[88] suggested also that due to low lance height, the experiments conducted by Subagyo *et al.*[67] did not actually correspond to splashing mode, but rather the penetrating mode of jet interaction, which is

characterized by a lower droplet generation rate than the splashing mode. For this reason, a dimensionless parameter J_{eff} was introduced similar to Sarkar *et al.*[87] in order to calculate the effective droplet generation rate:

$$\dot{m}_{\text{md,eff}} = J_{\text{eff}} \times \dot{m}_{\text{md}} \,. \tag{45}$$

It should be noted that J_{eff} is essentially a fitting parameter, which is evaluated based on plant data.

2.4.2 Droplet size distribution

The size distribution of the metal droplets at their place of birth was determined according to Koria and Lange[89], who proposed a formulation based on the Rosin-Rammler-Sperling (RRS) function:

$$RF = (0.001)^{\left(\frac{d_{\text{md},i}}{d_{\text{limit}}}\right)^n}, \tag{46}$$

where RF is the cumulative weight-fraction, d_{limit} is the limiting droplet diameter (which corresponds to RF = 0.001) and n is the distribution exponent. Experimental studies indicate that the parameter n is independent from the limiting diameter[89], maximum impact pressure of the gas jet[89] and the blowing number[67]. The reported values for the parameter n vary in a relatively wide range from 1.0 to 1.828.[89,90] In this work, a value of n = 1.26 was taken from Koria and Lange[89], because it represents an arithmetic mean for a relatively large amount of data. For non-coalescing jets, the limiting diameter (in m) can be obtained from[91]

$$d_{\text{limit}} = 5.513 \times 10^{-6} \times \left[10 \left(\frac{d_{\text{t}}^2}{h_{\text{lance}}^2}\right) p_{\text{amb}} \left(1.27 \frac{p_0}{p_{\text{amb}}} - 1\right) \cos\theta\right]^{1.206}, \tag{47}$$

where p_0 and p_{amb} are the lance supply pressure (in Pa) and the ambient pressure (in Pa), respectively. This expression suggests that droplet sizes increase with increasing lance supply pressure and decreasing lance height, and thus it appears to be in accordance with other studies[67,90,92]. Modifying the expression presented by Deo *et al.*[93] to a more general form, the mass fraction of size class i at place of birth can be obtained from

$$f_{\text{md},i} = -\ln(0.001)\, n\, RF \frac{d_{\text{md},i}^{n-1}}{d_{\text{limit}}^{n}} \,. \tag{48}$$

2.4.1 Residence time

The average residence time of the metal droplets is obtained from

$$\bar{t}_{\mathrm{md}} = \frac{m_{\mathrm{md}}}{\dot{m}_{\mathrm{md}}}. \tag{49}$$

According to the results available in the literature, the average residence time of the droplets increases with an increasing top gas flow rate[94] and decreasing droplet size[94,95]. As shown by Urquhart and Davenport[96], the size distribution of the metal droplets in the emulsion is shifted towards smaller droplets than the distribution of the generated droplets. The residence time of an individual droplet in the emulsion can be defined as the ratio of the trajectory length to the average velocity.[67] However, for the simplified setting considered in this work, it is more convenient to define the residence time of size class i through a constant κ as follows:[67]

$$t_{\mathrm{md},i} = \kappa \frac{h_{\mathrm{em}}}{u_{\mathrm{md},i}}, \tag{50}$$

where h_{em} is the height of the emulsion layer and $u_{\mathrm{md},i}$ is the terminal velocity of size class i. Because the residence time approaches infinity as the droplet diameter approaches zero, the residence time was limited to $t_{\mathrm{md},i} \leq 60$ s in order to avoid computational problems. The terminal velocity of the metal droplets in the emulsion was defined in three Reynolds ranges according to the equations proposed by Subagyo and Brooks[97]. In the absence of suitable values, κ was taken here as unity. Moreover, it was assumed that all droplets of the same size class have the same residence time. The average thickness of the emulsion layer can be approximated from:

$$h_{\mathrm{em}} = \frac{m_{\mathrm{em}}}{A_{\mathrm{slag}}\rho_{\mathrm{em}}} = \frac{m_{\mathrm{em}}}{(A_{\mathrm{bath}} - n_{\mathrm{lance}} \times \pi r_{\mathrm{cav}}^2)\rho_{\mathrm{em}}}, \tag{51}$$

where m_{em} is the mass of the emulsion, A_{slag} is the surface area of the top slag layer residing around the cavities, ρ_{em} is the density of the emulsion and A_{bath} is the cross-sectional area of the steel bath. The density of the slag-metal-slag emulsion is calculated according to:[97]

$$\rho_{\mathrm{em}} = \rho_{\mathrm{L}}\phi_{\mathrm{L}} + \rho_{\mathrm{S}}(1 - \phi_{\mathrm{L}}), \tag{52}$$

where ϕ_{L} denotes the volume fraction of metal droplets in emulsion, and is obtained from

$$\phi_{\mathrm{L}} = \frac{V_{\mathrm{L}}}{V_{\mathrm{L}} + V_{\mathrm{G}} + V_{\mathrm{S}}} \quad \text{where} \quad V_{\mathrm{G}} = \frac{\phi_{\mathrm{G}}}{1 - \phi_{\mathrm{G}}}(V_{\mathrm{L}} + V_{\mathrm{S}}), \tag{53}$$

where V_{L}, V_{G} and V_{S} denote the volumes of metal, gas and slag phases in emulsion, respectively. The volume-fraction of gas in the emulsion was solved numerically from the correlation proposed by Gou *et al.*[98]:

$$\frac{\phi_{\mathrm{G}}^2}{1 - \phi_{\mathrm{G}}} = 0.91 u_{\mathrm{s}}^{0.57}, \tag{54}$$

where u_{s} is the superficial velocity. The superficial velocity was defined as the ratio of gas flow rate from the plume and cross sectional area of the slag layer, *i.e.* $u_{\mathrm{s}} = \dot{V}_{\mathrm{G,plume}} / A_{\mathrm{slag}}$.

2.5 Mass and heat transfer coefficients

The mass and heat transfer coefficients were defined according to Eqs. 55 and 56, respectively.

$$\beta = \mathrm{Sh}\frac{D}{L}, \tag{55}$$

$$\alpha = \mathrm{Nu}\frac{\lambda}{L}, \tag{56}$$

where Sh is the Sherwood number, D is the mass diffusivity, L is the characteristic length, Nu is the Nusselt number and λ is the heat conductivity. A detailed treatment of these parameters is provided in the following subsections.

2.5.1 Cavity interface

At the cavity interface, the cavity radius (r_{cav}) was employed as the characteristic length. The mass transfer correlations employed for the gas jet were taken from Oeters[99]. These correlations are based on the experimental data published by Lohe[100] and can be represented as follows:

$$\mathrm{Sh} = \begin{cases} 1.41\,\mathrm{Re}^{0.51}\mathrm{Sc}^{0.33} & \text{when} \quad 2 \times 10^3 \leq \mathrm{Re} \leq 3 \times 10^4 \\ 0.41\,\mathrm{Re}^{0.75}\mathrm{Sc}^{0.33} & \text{when} \quad 3 \times 10^4 \leq \mathrm{Re} \leq 2 \times 10^5 \end{cases}, \tag{57}$$

where Re is the Reynolds number and Sc is the Schmidt number. Similarly to Dogan *et al.*[101], the

values of Re and Sc were defined in relation to the properties of the gas film at the impact surface:

$$\mathrm{Re} = \frac{u_\mathrm{G} r_\mathrm{cav} \rho_\mathrm{G}}{\mu_\mathrm{G}}, \tag{58}$$

$$\mathrm{Sc} = \frac{\mu_\mathrm{G}}{\rho_\mathrm{G} D_\mathrm{G}}, \tag{59}$$

where u_G is the critical gas velocity, μ_G is the dynamic viscosity of the gas film and ρ_G is the density of the gas film. The critical gas velocity (u_G) is calculated from the free axial velocity of the gas jet (u_j). For the metal phase in contact with gas jet, the turbulent diffusion boundary layer thickness and the corresponding Sherwood number were defined according to Eqs. 60 and 61, respectively.[99]

$$\delta_\mathrm{N} = \sqrt{\frac{D_\mathrm{L} \sigma_\mathrm{equiv}}{0.41 \rho_\mathrm{L} u_\tau^3}}, \tag{60}$$

$$\mathrm{Sh} = \frac{r_\mathrm{cav}}{2\delta_\mathrm{N}}, \tag{61}$$

where u_τ is the turbulent shear stress velocity and σ_equiv is the equivalent surface tension. The thickness of the thermal boundary layer (δ_Pr) can be obtained from Eq. 60 by replacing the mass diffusivity D_L with the ratio $\mu_\mathrm{L}/\rho_\mathrm{L}$, *i.e.* kinematic viscosity. As a first approximation, the mass transfer coefficients of the slag species were calculated similarly to the metal species, but using the properties of the slag species. Similar to Memoli *et al.*[102], the turbulent shear stress velocity was calculated on the basis of momentum transfer between the gas jet and the metal bath. Assuming that the axial velocity of the gas jet is zero at the bottom of the cavity, the turbulent shear stress velocity can be calculated as follows:

$$u_\tau = \sqrt{\frac{\rho_\mathrm{G}}{\rho_\mathrm{L}}} u_\mathrm{j}. \tag{62}$$

The heat transfer coefficients for gas, metal and slag phases were derived from the mass transfer correlations according to the analogue of heat and mass transfer by replacing the Sherwood number (Sh) and the Schmidt number (Sc) with the Nusselt number (Nu) and the Prandtl number (Pr), respectively.

2.5.2 Metal droplet interface

At the metal droplet interface, the mass and heat transfer coefficients were calculated by employing the Sauter mean diameter of the metal droplets ($d_{32,\mathrm{md}}$) as the characteristic length. The mass transfer coefficient mass of the gas phase in contact with the metal droplets can be calculated from the Steinberger and Treybal[103] correlation, which accounts for the effects of both natural and forced convection:

$$\mathrm{Sh} = \mathrm{Sh}_0 + 0.347\left(\mathrm{ReSc}^{1/2}\right)^{0.62}, \tag{63}$$

$$\mathrm{Sh}_0 = \begin{cases} 2 + 0.569\left(\overline{\mathrm{Gr}}\mathrm{Sc}\right)^{1/4} & \text{for} \quad \overline{\mathrm{Gr}}\mathrm{Sc} < 10^8 \\ 2 + 0.0254\left(\overline{\mathrm{Gr}}\mathrm{Sc}\right)^{1/2}\mathrm{Sc}^{0.244} & \text{for} \quad \overline{\mathrm{Gr}}\mathrm{Sc} > 10^8 \end{cases}, \tag{64}$$

where $\overline{\mathrm{Gr}}$ is the mean Grashof number. The mean Grashof number ($\overline{\mathrm{Gr}}$), the Reynolds number (Re) and the Schmidt number (Sc) were defined as follows:

$$\overline{\mathrm{Gr}} = \mathrm{Gr}_\mathrm{M} + \mathrm{Gr}_\mathrm{H}\left(\frac{\mathrm{Sc}}{\mathrm{Pr}}\right)^{1/2}, \tag{65}$$

$$\mathrm{Re} = \frac{u_\mathrm{G} d_{32,\mathrm{md}} \rho_\mathrm{G}}{\mu_\mathrm{G}}, \tag{66}$$

$$\mathrm{Sc} = \frac{\mu_\mathrm{G}}{\rho_\mathrm{G} D_\mathrm{G}}, \tag{67}$$

where Gr_M is the Grashof number for mass transfer, Gr_H is the Grashof number for heat transfer and Pr is the Prandtl number. Here, Gr_M, Gr_H and Pr were defined according to Eqs. 68, 69 and 70, respectively. It should be noted that the value of Gr_M depends on the species in question.

$$\mathrm{Gr}_{\mathrm{M},i} = \frac{g\rho_\mathrm{G} d_{32,\mathrm{md}}^3 \left(y_{i,\mathrm{md}}^* \rho_{\mathrm{G,md}} - y_{i,\mathrm{jet}} \rho_{\mathrm{G,jet}}\right)}{\mu_\mathrm{G}^2}, \tag{68}$$

$$\mathrm{Gr}_\mathrm{H} = \frac{g\rho_\mathrm{G}^2 d_{32,\mathrm{md}}^3 \left(T_\mathrm{md}^* - T_\mathrm{jet}\right)}{T_\mathrm{G}\mu_\mathrm{G}^2}, \tag{69}$$

$$\mathrm{Pr} = \frac{c_{\mathrm{p,G}}\mu_\mathrm{G}}{\lambda_\mathrm{G}}, \tag{70}$$

where $c_{\mathrm{p,G}}$ is the specific heat capacity of the gas phase and λ_G is the heat conductivity of the gas phase. The heat transfer coefficient was calculated with the help of Eqs. 63 and 64 by replacing Sh,

$\overline{\mathrm{Gr}}$ and Sc with Nu, $\mathrm{Gr_H}$ and Pr, respectively. It is known that mass transfer within small metal droplets takes place almost entirely by diffusion, while larger droplets may exhibit uninhibited circulatory flow.[99,104] In this work, it was assumed that only creeping laminar circulation takes place within the metal droplets. Therefore, the mass transfer coefficient can be calculated according to the Kronig and Brink[105] solution, which can be expressed in terms of the Sherwood number as follows:[106]

$$\mathrm{Sh} = \frac{32}{3}\frac{\sum_{i=1}^{\infty} A_i^2 \lambda_i \exp(-16\lambda_i \mathrm{Fo_M})}{\sum_{i=1}^{\infty} A_i^2 \exp(-16\lambda_i \mathrm{Fo_M})}, \tag{71}$$

where $\mathrm{Fo_M}$ is the Fourier number for mass transfer. The first seven values for the parameters A_i and λ_i were taken from the literature[107] and provide a sufficient convergence. Despite its limited range of theoretical applicability, experimental studies have shown that the Kronig and Brink solution gives a reasonably good prediction of the mass transfer coefficient even at Reynolds numbers well above those corresponding to creeping flow.[108] Employing the average residence time of the metal droplets ($\bar{t}_{\mathrm{md}}$) as the characteristic time, the Fourier number for mass transfer can be defined according to

$$\mathrm{Fo_M} = \frac{4 D_{\mathrm{L}} \bar{t}_{\mathrm{md}}}{d_{32,\mathrm{md}}^2}. \tag{72}$$

The corresponding Fourier number for heat transfer ($\mathrm{Fo_H}$) is obtained from Eq. 72 by replacing mass diffusivity with thermal diffusivity. Thus the heat transfer coefficient for the metal droplets is obtained by replacing Sh and $\mathrm{Fo_M}$ with Nu and $\mathrm{Fo_H}$, respectively. The mass transfer in the slag phase surrounding the metal droplets was calculated according to Eq. 73, which is valid for fluid spheres in creeping flow.[109]

$$\begin{aligned} \mathrm{Sh} &= 0.65 \left(\frac{\mu_{\mathrm{S}}}{\mu_{\mathrm{S}} + \mu_{\mathrm{L}}}\right)^{1/2} \mathrm{Re}^{1/2} \mathrm{Sc}^{1/2} \\ &= 0.65 \left(\frac{\mu_{\mathrm{S}}}{\mu_{\mathrm{S}} + \mu_{\mathrm{L}}}\right)^{1/2} \left(\frac{\rho_{\mathrm{S}} \bar{u}_{\mathrm{md}} d_{32,\mathrm{md}}}{\mu_{\mathrm{S}}}\right)^{1/2} \left(\frac{\mu_{\mathrm{S}}}{\rho_{\mathrm{S}} D_{\mathrm{S}}}\right)^{1/2}, \end{aligned} \tag{73}$$

where $\bar{u}_{\mathrm{md}}$ is the average terminal velocity of the metal droplets in the emulsion. The heat transfer coefficient for the slag phase in contact with the metal droplets was obtained using the analogue of heat and mass transfer by replacing Sh and Sc with Nu and Pr, respectively.

2.6 Thermodynamic properties

All the thermodynamic properties were defined at the composition and temperature of the reaction interface in question. The equilibrium constants are defined by

$$K = \exp\left(-\frac{\Delta G^\circ}{RT^*}\right) \quad \text{where} \quad \Delta G^\circ = \Delta H^\circ - T^*\Delta S^\circ\,, \tag{74}$$

where R is the gas constant, T^* is the temperature of the reaction interface, and ΔG°, ΔH° and ΔS° are the changes in Gibbs free energy, enthalpy and entropy of reaction, respectively. The reaction enthalpy and reaction entropy were calculated according to Eqs. 75 and 76, respectively.

$$\Delta H^\circ = \sum_{i=1}^{n} \nu_i H_i^\circ, \tag{75}$$

$$\Delta S^\circ = \sum_{i=1}^{n} \nu_i S_i^\circ\,, \tag{76}$$

where ν_i, H_i° and S_i° are the stoichiometric coefficient, enthalpy and entropy of species i. The values of H_i° and S_i° at temperature T were calculated as follows:

$$H^\circ(T) = H^\circ_{298.15} + \int_{298.15}^{T} C_\mathrm{p}\,\mathrm{d}T + H^\circ_{\mathrm{tr},T} + H^\circ_\mathrm{dis}, \tag{77}$$

$$S^\circ(T) = S^\circ_{298.15} + \int_{298.15}^{T} \frac{C_\mathrm{p}}{T}\,\mathrm{d}T + S^\circ_{\mathrm{tr},T} + S^\circ_\mathrm{dis}, \tag{78}$$

where $H^\circ_{298.15}$ is the enthalpy at 298.15 K (25 °C), C_p is the molar heat capacity, H°_tr is the total enthalpy of phase transformations from 298.15 K (25 °C) to T, H°_dis is the enthalpy of dissolution, $S^\circ_{298.15}$ is the entropy at 298.15 K (25 °C), S°_tr is the total entropy of phase transformations from 298.15 K (25 °C) to T, and S°_dis is the entropy of dissolution. The enthalpies $H^\circ$and entropies S° correspond to the following standard states: the Henrian standard state for the species dissolved in the steel bath and the Raoultian standard state for the gas and slag species. For the dissolved species, the relevant values of H°_dis and S°_dis were obtained from Sigworth and Elliott[110], while for the gas and slag species H°_dis and S°_dis were set to zero. The molar heat capacity at temperature T is solved from the Shomate equation[111]:

$$C_\mathrm{p} = A + B \cdot 10^{-3} T + C \cdot 10^{5} T^{-2} + D \cdot 10^{-6} T^{2}, \quad (79)$$

where A, B, C and D are fitting parameters applicable to a certain temperature interval. A comprehensive database of the Shomate equation parameters was taken from HSC Chemistry[111]. The partial pressures of the gaseous species can be calculated from the ideal gas law based on the total gas pressure at the reaction interface. The Henrian activity coefficients of the species in the liquid metal phase were calculated with the Unified Interaction Parameter (UIP) formalism[112]:

$$\ln \gamma_i^\mathrm{H} = \ln \frac{\gamma_i^\mathrm{R}}{\gamma_i^\circ} = -0.5 \sum_{j=1}^{n} \sum_{k=1}^{n} \varepsilon_j^k x_j^* x_k^* + \sum_{j=1}^{n} \varepsilon_i^j x_j^* \,, \quad (80)$$

where γ_i^H is the Henrian activity coefficient of species i, γ_i^R is the Raoultian activity coefficient of species i, γ_i° is the activity coefficient of species i at infinite dilution, ε is the first-order molar interaction parameter and x^* is the molar fraction at the reaction interface. The employed first-order molar interaction parameters are given in **Table 2**.

Table 2 Refs. [113] [114] [115] [116] [110]

The activity coefficients of the slag species were calculated according to the model employed by Wei and Zhu[21]. The Raoultian activity coefficients of FeO, Cr_2O_3, MnO and SiO_2 are given by Eqs. 81, 82, 83 and 84, respectively.

$$\log_{10} \gamma_\mathrm{FeO}^\mathrm{R} = \frac{\varepsilon_1}{T^*}\left(x_\mathrm{CaO}^* + x_\mathrm{MgO}^*\right)\left(x_{\mathrm{SiO_2}}^* + 0.25 x_\mathrm{AlO1.5}^*\right) + \frac{\varepsilon_2}{T^*} x_\mathrm{MnO}^* \left(x_{\mathrm{SiO_2}}^* + 0.45 x_\mathrm{CrO1.5}^*\right) + \frac{\varepsilon_3}{T^*} x_\mathrm{AlO1.5}^* x_{\mathrm{SiO_2}}^* + \frac{\varepsilon_4}{T^*} x_\mathrm{MnO}^* x_\mathrm{AlO1.5}^* + \frac{\varepsilon_5}{T^*} x_\mathrm{CrO1.5}^* x_{\mathrm{SiO_2}}^* \,, \quad (81)$$

$$\log_{10} \gamma_{\mathrm{Cr_2O_3}}^\mathrm{R} = \log_{10} \gamma_\mathrm{FeO}^\mathrm{R} - \frac{\varepsilon_6}{T^*}\left(x_\mathrm{CaO}^* + x_\mathrm{MgO}^*\right) - \frac{\varepsilon_7}{T^*} x_\mathrm{MnO}^* - \frac{\varepsilon_5}{T^*} x_{\mathrm{SiO_2}}^* \,, \quad (82)$$

$$\log_{10} \gamma_\mathrm{MnO}^\mathrm{R} = \log_{10} \gamma_\mathrm{FeO}^\mathrm{R} - \frac{\varepsilon_2}{T^*}\left(x_{\mathrm{SiO_2}}^* + 0.45 x_\mathrm{CrO1.5}^*\right) - \frac{\varepsilon_4}{T^*} x_\mathrm{AlO1.5}^* \,, \quad (83)$$

$$\log_{10} \gamma_{\mathrm{SiO_2}}^\mathrm{R} = \log_{10} \gamma_\mathrm{FeO}^\mathrm{R} - \frac{\varepsilon_1}{T^*}\left(x_\mathrm{CaO}^* + x_\mathrm{MgO}^*\right) - \frac{\varepsilon_2}{T^*} x_\mathrm{MnO}^* - \frac{\varepsilon_3}{T^*} x_\mathrm{AlO1.5}^* - \frac{\varepsilon_5}{T^*} x_\mathrm{CrO1.5}^* \,, \quad (84)$$

where $\varepsilon_1 \ldots \varepsilon_7$ are the interaction coefficients of the model. **Table 3** shows the interaction coefficients

reported by Wei and Zhu[21] for early and later periods of refining. In this work, the coefficients applicable for the early period of refining were employed. Similar to Wei and Zhu,[21] it was assumed that $a^{\mathrm{R}}_{\mathrm{Cr_2O_3}} = 1$ if the interfacial Cr_2O_3 content is greater than the maximum solubility of Cr_2O_3 in the slag.

Table 3 Ref. [21]

2.7 Physical properties

The physical properties of the steel and slag phases were estimated at the temperature of the reaction interface, while the properties of the gas phase were defined at gas film temperature, which was approximated as[117]

$$T_{\mathrm{G}} = 0.5 \times \left(T^{*} + T_{\mathrm{jet}}\right), \tag{85}$$

where T^{*} is the temperature of reaction interface and T_{jet} is the temperature of the gas jet. The effective mass diffusivity was defined for each species in the metal phase as the interdiffusivity in liquid iron, while only one effective diffusivity value was assigned for the gas and slag phases. Where possible, the temperature dependency of the mass diffusivity of solutes in liquid iron was described by an Arrhenius type relationship[118]. In order to account for the effect of pressure and temperature, the mass diffusivity of the gaseous species was treated according to[29]

$$D_{\mathrm{G}} = D_{\mathrm{G,eff}} \times \left(\frac{T_{\mathrm{G}}}{T_{\mathrm{ref}}}\right)^{1.5} \left(\frac{p_{\mathrm{ref}}}{p_{\mathrm{G}}}\right), \tag{86}$$

where $D_{\mathrm{G,eff}}$ is the effective mass diffusivity at T_{ref} and p_{ref}, T_{ref} is the reference temperature, p_{ref} is the reference pressure and p_{G} is the total gas pressure. The pressure changes in the gas jet are small enough to be neglected[72] and hence the total gas pressure was taken as equal to the atmospheric pressure at both reaction interfaces. The treatment of other physical properties is summarized in **Table 4** along with their corresponding references.

Table 4 Refs. [119] [120] [121] [122–124] [125] [126] [118] [127] [128] [119] [130] [129]

During decarburization, the top slag consists of a molten slag phase saturated with chromium oxide and a solid chromium oxide phase.[131] For this reason, it is necessary to consider the effect of solid

particles on the viscosity of the top slag. The viscosity of the liquid part ($\mu_{S(l)}$) was calculated using the viscosity model proposed by Forsbacka *et al.*[125], which is an extension of the modified Urbain model[132] for the Al_2O_3-CaO-CrO-Cr_2O_3-'FeO'-MgO-SiO_2 system. The effective viscosity of the top slag was determined as relative to the viscosity of the liquid slag phase:

$$\mu_S = \mu_{S(l)}\mu_{S,rel} \,. \tag{87}$$

The relative viscosity $\mu_{S,rel}$ was calculated according to the equation proposed by Thomas[126]. **Figure 5** provides a comparison of the Thomas[126] equation with other relative viscosity equations available in the literature[133–139]. With the exception of the Einstein equation[133], the equations produce similar results up to a solid volume fraction of 0.3, but begin to diverge as the solid volume fraction approaches unity. The solid volume fraction was calculated as a function of Cr_2O_3 content as shown in the second part of this work[44].

Figure 5 Refs. [126,133–139]

2.8 Numerical solution

The objective of the numerical solution routine is to minimize the error in free variables, while minimizing the error in thermodynamic equilibrium at the reaction interfaces. The thermodynamic equilibrium at the reaction interface and the mass transfer onto and from the interface are solved simultaneously. However, conservation of mass and heat are solved successively. Using small time steps, this does not cause significant inaccuracy, but greatly improves the numerical stability. The flowchart of the model is shown in **Figure 6**.

Figure 6

The numerical solution of both iteration loops is obtained with Newton's method, which approximates the solution by its tangent line.[140] For a set of non-linear equations the Newton's method can be expressed as follows:[50]

$$\mathbf{J} \times \boldsymbol{\partial}\mathbf{x} = -\mathbf{f} \,, \tag{88}$$

where $\mathbf{J}$ is the Jacobian matrix of the system with respect to all free variables, $\boldsymbol{\partial}\mathbf{x}$ is the correction vector and $\mathbf{f}$ is the residual vector, which approaches zero asymptotically during the iteration. The

system of linear equations defined by Eq. 88 is solved by Gauss–Jordan elimination. During iteration, the vector of free variables is updated similar to the relaxed Newton's method. The calculation procedure is repeated until the numerical error is sufficiently small or the maximum number of iterations is exceeded. The error in the residual vector **f** is measured using the l^2-norm, which is the Euclidian length of the correction vector:

$$\|\mathbf{\Delta x}\|_2 = \sqrt{\sum_i \Delta x_i^2}\,. \tag{89}$$

As stated earlier, one of the main assumptions of the model is that the reaction interfaces reach their mass-transfer constrained equilibrium composition at every instant. During the numerical solution, the interfacial composition asymptotically approaches the composition dictated by the equilibrium constants, provided that the forward reaction rate coefficients (k_f) are sufficiently large. In order to assess the fulfilment of the equilibrium assumption, the concept of *equilibrium number* is introduced:

$$\mathrm{E} = \left| 1 - \frac{Q}{K} \right|, \tag{90}$$

where Q and K denote the reaction quotient and the equilibrium constant, respectively. The reaction quotient is defined as follows:

$$Q = \frac{\sum_p a_p^{\nu_p}}{\sum_r a_r^{\nu_r}}, \tag{91}$$

where p and r denote reaction products and reactants, respectively. By definition, $Q = K$ at equilibrium. Because $Q \to K$ as $k_\mathrm{f} \to \infty$, it follows that $\mathrm{E} \to 0$ as $k_\mathrm{f} \to \infty$. Owing to these properties, the equilibrium number provides a practical measure of the relative fulfilment of the equilibrium assumption. As a preliminary setting the maximum allowed error was set to E = 0.1% for all the studied reactions. During numerical solution, the forward reaction rate coefficients are increased periodically until the equilibrium numbers of all the reactions are below the maximum allowed error. A typical calculation time per time step is in the order of few seconds using a desktop PC (3.4 GHz).

3 Conclusions

The objective of this work was to develop a fast numerical model for the reactions that occur during top-blowing in the AOD process. More specifically, the aim was to create a model that considers

reactions both between the top-blown gas and the steel bath and between metal droplets and top slag. Employing the categorization proposed by Ding *et al.*[41], the model derived in this work can be classified as a *complex process mechanism model*, because it emphasizes the local thermodynamic equilibrium and local heat and mass transfer characteristics. In the second part of this work,[44] the model is validated with heats from a full size AOD vessel. In the future, the combined top- and side-blowing stage of the AOD process can be simulated as a combination of the top-blowing model derived in this work and the side-blowing model proposed earlier by Järvinen *et al.*[29].

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Nomenclature

Symbols

a	Activity
A	Surface area [m^2]
A_i	Parameter of the Kronig-Brink solution
C_p	Molar heat capacity at constant pressure [J/(mol·K)]
c_p	Specific heat capacity at constant pressure [J/(kg·K)]
d_t	Nozzle throat diameter [m]
d_limit	Fineness parameter of the RRS distribution [m]
$d_{32,\mathrm{md}}$	Sauter mean diameter of the metal droplets [m]
D	Diffusion coefficient [m^2/s]
f_i	Mass fraction of size class *i* at place of birth
$\mathbf{f}$	Residual vector
g	Standard gravity [m/s^2]
$\Delta G°$	Change in standard Gibbs free energy of reaction [J/mol]
ΔG_tot	Change in total Gibbs free energy [J/mol]

650	h_{cav}	Depth of the cavity [m]
651	h_{lance}	Distance of the top lance from the surface of the steel bath [m]
652	$H°$	Standard enthalpy [J/mol]
653	$\Delta H°$	Change in standard reaction enthalpy [J/mol]
654	$\mathbf{J}$	Jacobian matrix
655	J_{eff}	Droplet generation rate multiplication factor
656	k_{f}	Forward reaction rate coefficient
657	K	Equilibrium constant
658	L	Characteristic length [m]
659	m	Mass [kg]
660	$\dot{m}_{\mathrm{md}}$	Metal droplet generation rate [kg/s]
661	$\dot{m}_{\mathrm{md,eff}}$	Effective metal droplet generation rate [kg/s]
662	M	Molar mass [kg/mol]
663	n_{lance}	Number of exit ports in a nozzle
664	n	Distribution exponent of the RRS distribution
665	p	Partial pressure
666	p_{cav}	Arc length of the cavity [m]
667	p_{amb}	Ambient pressure [Pa]
668	p_0	Stagnation pressure at upstream part of the top lance [Pa]
669	r_{cav}	Top radius of the cavity [m]
670	R	Gas constant [J/(mol·K)]
671	R''	Reaction rate [kg/(m^2·s)]
672	R^2	Correlation coefficient
673	RF	Cumulative weight-fraction
674	$S°$	Standard entropy [J/(mol·K)]
675	$\Delta S°$	Change in standard reaction entropy [J/(mol·K)]
676	$t_{\mathrm{md},i}$	Residence time of metal droplet size class *i* [s]
677	$\bar{t}_{\mathrm{md}}$	Average residence time of the metal droplets [s]
678	T	Temperature [K]
679	T^*	Interfacial temperature [K]
680	u_{G}	Critical gas velocity [m/s]
681	u_{j}	Axial velocity of the gas jet [m/s]
682	$u_{\mathrm{md},i}$	Terminal velocity of metal droplet size class *i* [m/s]
683	$\bar{u}_{\mathrm{md}}$	Average terminal velocity of the metal droplets [m/s]

u_τ	Turbulent shear stress velocity [m/s]
$\dot{V}_G$	Volumetric gas flow rate [Nm^3/s]
$\dot{V}'_G$	Modified volumetric gas flow rate [Nm^3/s]
x	Molar fraction
X	Cation fraction
$\partial\mathbf{x}$	Correction vector
y	Mass fraction
y^*	Interfacial mass fraction
$\|\|\Delta\mathbf{x}\|\|_2$	l^2-norm

Greek symbols

α	Heat transfer coefficient [$W/(m^2K)$]
α	Interaction energy between cations [J]
β	Mass transfer coefficient [m/s]
γ	Activity coefficient
γ°	Activity coefficient at infinite dilution
δ_N	Thickness of the diffusion boundary layer [m]
δ_{Pr}	Thickness of the thermal boundary layer [m]
ε	First order molar interaction parameter
η	Constant
$\overline{\eta}_H$	Average microkinetic efficiency of heat transfer
$\overline{\eta}_M$	Average microkinetic efficiency of mass transfer
θ	Inclination angle of each nozzle relative to lance axis [°]
κ	Constant
λ	Heat conductivity [W/(m·K)]
λ_i	Parameter of the Kronig-Brink solution
μ	Dynamic viscosity [Pa·s]
ν	Stoichiometric coefficient
$\overline{\nu}$	Mass-based stoichiometric coefficient
π	Mathematical constant
ρ	Density [kg/m^3]
σ	Surface tension [N/m]
ϕ	Volume fraction

Dimensionless numbers

E	Equilibrium number
Fo_H	Fourier number for heat transfer
Fo_M	Fourier number for mass transfer
$\overline{Gr}$	Mean Grashof number
Gr_H	Grashof number for heat transfer
Gr_M	Grashof number for mass transfer
N_B	Blowing number
N_B'	Modified blowing number
Nu	Nusselt number
Sc	Schmidt number
Sh	Sherwood number
Pr	Prandtl number
Re	Reynolds number

Subscripts and superscripts

cav	Cavity
bath	Steel bath
em	Gas-metal-slag emulsion
G	Gas phase
H	Henrian standard state
in	Gas flow into the system
jet	Gas jet
L	Liquid metal phase
md	Metal droplet
out	Gas flow out of the system
plume	Gas plume
R	Raoultian standard state
rel	Relative
S	Slag phase
STP	Standard temperature and pressure according to the DIN 1343 standard[49]: 273.15 K (0 °C) and 101325 Pa.
slag	Top slag
(l)	Liquid state

(s)	Solid state

Indices

i	Size class
i	Species
n	Number of species
r	Number of reactions
ψ	Phase
ω	Reaction interface

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