A Review of Modeling Hot Metal Desulfurization

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Hot metal desulfurization serves as the main unit process for removing sulfur in blast-furnace-based steelmaking. The available body of literature on modeling hot metal desulfurization is reviewed to provide an in-depth analysis of the approaches used and results obtained. The mathematical models for reaction kinetics have evolved from simplistic rate equations to more complex phenomenon-based models that provide useful information on the effect of physicochemical properties and operating parameters on desulfurization efficiency. Data-driven approaches with varying levels of phenomenological basis have also been proposed with the aim of achieving better predictive performance in industrial scale applications. Bath mixing has been studied using physical and numerical modeling to optimize mixing conditions in ladles and torpedo cars. The coupling of gas-particle jets and their penetration into the liquid have been a focal point of physical and numerical modeling. In recent years, the fluid flow phenomena in mechanically stirred ladles has been studied extensively using physical and numerical modeling. These studies have focused on the fluid flow field, reagent dispersion, and bubble dispersion.

1. Introduction

Hot metal desulfurization serves as the main unit process for removing sulfur in blast-furnace-based steelmaking. Hot metal desulfurization is commonly conducted in a ladle or a torpedo car,[1] using a desulfurization reagent that is either injected into the metal bath or added on top of it.[2] From the thermodynamic point of view, the fundamental requirement for the desulfurization reagent is to be able to donate electrons and form a new sulfide-binding phase.[3] Typical reagents used in the industry are calcium carbide (CaC$_2$), lime (CaO), magnesium (Mg), soda (Na$_2$CO$_3$), and mixtures of them.[4]

Following the advent of injection metalurgy in plant practice, studies devoted to practical aspects of hot metal desulfurization using lance injection started appearing from the late 1960s onward.[5–12] In lance injection, the desulfurization reagent is delivered pneumatically through a submerged lance.[11,13] A distinction can be made between mono- and co-injection of reagents.[14,15] Although it is more common to use an inert carrier gas (e.g. nitrogen or argon), hydrocarbons such as natural gas[6,7] or propane[16] have also been used on an industrial scale. Initially, lance injection practice used to use torpedo cars, but nowadays it is more common to use ladles, which enable longer reagent residence times and easier removal of the slag.[15] The lance injection practice is common in Europe, America, and India.[17] Magnesium mono-injection (MMI) is a process developed at the Ukrainian Academy of Sciences between 1969 and 1971 and is operated mainly by Russian, Ukrainian, and a few Chinese steelmakers.[18] In this process, the tip of the submerged lance is often fitted with a separate evaporation chamber.[14]

Hot metal desulfurization methods with mechanical stirring were introduced in Germany[18,19] and Japan[20] in the 1960s. The Demag–Östberg Reaction Accelerator (DORA) features a Y-shaped stirrer, which first absorbs hot metal from the bottom of the vertical tube and then discharges the hot metal through the horizontal tubes by centrifugal forces.[18,21] The RheinStahl stirrer features a paddle-type stirrer, which is submerged only partially in the metal bath to provide turbulent mixing of desulfurization fluxes in the upper part of the metal bath.[21,22] The Kanbara reactor (KR) process was developed by Nippon Steel in 1965 and represents a hot metal desulfurization practice, which makes use of a rotating submerged lance equipped with four rotor blades.[14,15,23,24] The reagent is usually added on top of the metal bath, but the reagent can also be injected through the rotating lance with a carrier gas.[2,14] The KR process excels at achieving low sulfur contents consistently, but is characterized by greater metal losses[2,17] and higher refractory wear.[2] The KR process is widely used nowadays in Asia, especially in Japan.[15,17,23]

The theoretical foundations of the kinetics and thermodynamics associated with different reagents and carrier gases have been studied exhaustively.[25–30] Furthermore, plenty of literature has been published on the experimental aspects of the KR process, e.g. impeller practice,[31,32] flux additions,[31,33] probe blowing,[16] and powder blasting.[34] Similarly to other steelmaking processes, various modeling methods have been applied to

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circumvent the difficulty of obtaining direct measurements from the vessels during operation. Relatively early on there were attempts\cite{25,35} to predict the overall desulfurization kinetics on the process scale with the help of mathematical modeling. In addition to thermodynamic-kinetic aspects, research has been directed at studying different physical aspects of hot metal desulfurization, including fluid flows,\cite{36,37} bath mixing\cite{36–42} reagent injection,\cite{37,43–51} and reagent dispersion.\cite{52–54}

Despite the importance of modeling studies in establishing a fundamental understanding of the hot metal desulfurization process, a comprehensive review of these studies has not yet been made. Consequently, the aim of this article is to provide an in-depth analysis of the available studies, categorize the approaches used, and summarize the results obtained. As for the kinetic models, the focus is on modeling the hot metal desulfurization process with mechanistic and data-driven modeling approaches. In addition, a review of studies on numerical and physical modeling of hot metal desulfurization is presented. Here, the focus is on the fluid flow field, bath mixing, particle dispersion, and particle penetration.

### 2. Mathematical Modeling of Hot Metal Desulfurization Process

The mathematical models were categorized following their main modeling principles. Here, an earlier proposed categorization principle\cite{56} was used as a basis for a new categorization, which extends the original categorization with subcategories for data-driven modeling approaches. A schematic illustration of the proposed categorization is shown in Figure 1. The main line of division is between fundamental and data-driven models.

The fundamental models aim to describe the process dynamics using physico-chemical fundamentals and can roughly be divided into three subcategories depending on how the kinetics are described. System free energy minimization models assume that the whole observed volume is in thermodynamic equilibrium at any given instant. Reaction volume models approximate heterogeneous reactions by considering mass exchange between bulk and one or more reaction volumes, which reach their thermodynamic equilibrium at any given instant. In reaction equilibrium models, the conservation of momentum is not considered and the mass flows between the volumes are considered arbitrary. Finite volume reaction models solve the momentum equation in a specified geometry and thus provide a physical basis for the mass flows between the observed volumes; these are essentially computational fluid dynamics (CFD) models coupled with kinetic descriptions. The third main category of fundamental models are reaction interface models, which describe heterogeneous reactions at phase interfaces using the boundary layer theory.\cite{56} Key parameters of such reactions are the size of the interfacial area, efficiency of mass transfer to and from the interface, and the rate of interfacial reaction. For metal–slag reactions, it can usually be assumed that the rate of interfacial reaction is much faster than the mass transfer steps. In simple reaction interface models, the mass transport terms are incorporated into a time constant, which is held constant for certain operating conditions. Reaction interface models, which aim to describe relation of the mass transfer rates and interfacial areas to operating and technological parameters, are labeled process mechanism models. In these models, the overall mass transfer resistance is often calculated using the Lewis–Whitman two-film model.\cite{57}

Data-driven models differ from fundamental (i.e., mechanistic) models such that for models of this kind, the model identification has been conducted to some extent based on the process data. The extent depends on the level of expert knowledge available from the system. Further categorization of data-driven models can be made based on model structure, which is either derived from physico-chemical phenomena (parametrized reaction models) or has a generic mathematical form (linear regression models and artifi-
attributes of the process. First, hot metal desulfurization is dominated by kinetics rather than thermodynamics, which makes purely thermodynamic calculations unfeasible. Second, the system is characterized by two reaction mechanisms (transitory and permanent) that are distinctly different in their kinetic behavior. Differentiating between these two mechanisms requires some sort of phenomenon-based description for reagent injection and the transitory nature of the metal–reagent reactions. Data-driven modeling techniques for modeling hot metal desulfurization have been studied to a lesser extent than have mechanistic models. For this reason, the repertoire of data-driven approaches used is relatively narrow, with the most common category being parametrized reaction models. It is likely that the relative unpopularity of data-driven modeling approaches is related to limited volume of data available from the process, which can be further associated with the harsh process conditions.

2.1. Fundamental Models

The model proposed by Oeters et al.\(^\text{[25]}\) focused on the desulfurization reaction at the surface of the injected reagent particles. The model accounted for both boundary layer diffusion and solid-state diffusion in the reaction product layer. The overall rate was expressed as

\[
\frac{d[S]}{dt} = -\frac{m_{\text{CaO}}}{m_{\text{bath}}} \rho_{L} \frac{D_S}{\delta r_p} \left( [S] - [S]^* \right)
\]

where \(m_{\text{CaO}}\) is the CaO injection rate, \(m_{\text{bath}}\) is the bath mass, \(\rho_{L}\) is the density of hot metal, \(\rho_{\text{CaO}}\) is the density of CaO, \(r_p\) is the average particle radius, \(D_S\) is the mass diffusivity of sulfur, \(\delta\) is the thickness of the diffusion boundary layer, and \(t_{\text{res}}\) is the residence time of the particles in the metal bath. The thickness of the diffusion boundary layer was determined using the Ranz–Marschall correlation\(^{[95,96]}\)

\[
\text{Sh} = \frac{\beta d_p}{D} = 2 + 0.6\text{Re}^{1/2}\text{Sc}^{1/3}
\]

where \(\beta\) is the mass transfer coefficient, \(d_p\) is the particle diameter, \(D\) is the mass diffusivity, \(\text{Re}\) is the Reynolds number, and \(\text{Sc}\) is the Schmidt number. The interfacial sulfur content \([S]^*\) was solved numerically by setting the molar flux of sulfur transport in the boundary layer equal to the solid-state diffusion of sulfur in the CaS layer. The thickness of the CaS layer was assumed to follow a parabolic time law

\[
\xi = \sqrt{2\tilde{V}_{\text{CaS}} k_r t}
\]

where \(\tilde{V}_{\text{CaS}}\) is the molar volume of CaS, \(k_r\) is the molar apparent rate of reaction in the CaS layer, and \(t\) is the time, which is taken to be equal to the residence time of the particles in the metal bath. Equation (3) is equivalent to the more commonly used expression, where the product \(\tilde{V}_{\text{CaS}} k_r\) is replaced by the parabolic rate constant \(K_r\).\(^{[29,97]}\) For hot metal with approximately 0.5 wt% Si at 1300°C (1573.15 K), the value of \(k_r\) in a natural gas atmosphere was calculated according to the following expression\(^{[25]}\)

\[
k_r = 2.60 \times 10^{-9} \cdot (4.92 + \log_{10} [S]^*)
\]

The CaS layer thicknesses obtained from Equation (4) are close to those reported by Mitsuo et al.\(^{[98]}\) but two orders of magnitude lower than those reported by Lindström and Sichen.\(^{[29]}\) Oeters et al.\(^{[25]}\) suggested that in the case of desulfurization with lime and natural gas at 1300°C (1573.15 K), the boundary layer...
diffusion formed the rate limiting step at sulfur contents of less than 500 ppm, whereas above this value the rate was limited mainly by solid state diffusion. However, due to the coupling of the two mechanisms, the sulfur removal rate had no distinct turning point, but rather a gradual convergence from the rate limited by solid-state diffusion toward the rate limited by boundary layer diffusion. An increase in temperature was predicted to shift the turning point in the rate-controlling mechanisms to

Table 1. Summary of studies on the mathematical modeling of hot metal desulfurization.

| Year   | Study                  | Type(s) | Vessel          | Reagent(s) | Gas          |
|--------|------------------------|---------|-----------------|------------|-------------|
| 1973   | Oeters et al.[25]      | PMM     | Ladle           | CaO        | CH₄         |
| 1981/82| El-Kaddah and Szekely[35,38]| FVRM    | Ladle           | 80% CaO–20% CaF₂ | NA          |
| 1984   | Ohguchi et al.[59]     | SRIM    | Crucible        | CaFCl or CaF | Ar          |
| 1985   | Oeters[60]             | PMM     | NA              | CaO or CaC₂ | Ar or N₂    |
| 1986   | Sawada et al.[81]      | PMM     | Ladle           | CaO–FeO–CaF₂ | O₂          |
| 1988   | Deo and Grieveson[82]  | PMM     | Crucible        | CaO–CaF₂–Al₂O₃ | Ar          |
| 1990/91| Chiang et al.[83,64]   | PMM     | Ladle           | CaC₂       | Ar          |
| 1990   | Kitamura et al.[52]    | PMM     | Ladle           | CaO–CaO₂–CaO₃ | NA          |
| 1993   | Deo and Boom[66]       | PMM     | Ladle           | CaC₂       | NA          |
| 1994   | Zhao and Irons[67]     | PMM     | Induction furnace | CaO₂-based | N₂ or CO₂  |
| 1994   | Datta et al.[88]       | ANNM    | Torpedo car     | CaO        | NA          |
| 1994   | Rastogi et al.[89]     | PRM     | Torpedo car     | CaC₂       | NA          |
| 1994   | Deo et al.[90]         | ANNM    | Torpedo car     | CaC₂       | NA          |
| 1997   | Seshadri et al.[71]    | PMM     | Ladle           | CaO-based  | NA          |
| 2001   | Vargas-Ramirez et al.[72]| PMM     | Induction furnace | CaO–SiO₂–CaF₂–FeO–Na₂O | N₂ |
| 2001   | Zou et al.[73]         | PMM     | Ladle           | CaC₂, Mg or CaC₂ + Mg | NA          |
| 2002   | Pirker et al.[74]      | FVRM    | Ladle           | None       | N₂          |
| 2002   | Quinn and Vaculik[75]  | LRM     | Torpedo car     | CaC₂, Mg or CaC₂ + Mg | NA          |
| 2004   | Bhattacharya et al.[76]| LRM     | Torpedo car     | CaC₂, Mg or CaC₂ + Mg | NA          |
| 2006   | Jin et al.[77]         | PMM     | Crucible        | CaO- and Mg-based | N₂        |
| 2006   | Scheepers et al.[78]   | PMM     | Ladle           | CaC₂       | N₂          |
| 2007   | Visser and Boom[79]    | PMM     | Ladle           | CaO + Mg   | NA          |
| 2007   | Vinoo et al.[80]       | LRM     | Ladle           | CaC₂-based | NA          |
| 2008   | Ochoterena et al.[81]  | SRIM    | Ladle           | CaO- and CaC₂-based | NA        |
| 2008   | Dan et al.[82]         | ANNM    | Kanbara reactor | NA         | –           |
| 2009   | Da Silva et al.[83]    | PMM     | Kanbara reactor | CaO-based fluxes | –          |
| 2012   | Rodríguez et al.[84]   | FVRM    | Ladle           | CaC₂       | NA          |
| 2012   | Huang et al.[85]       | FVRM    | Torpedo car     | NA         | N₂          |
| 2015   | Barron et al.[86]      | SRIM    | Ladle           | CaC₂ or CaO + CaC₂ | Ar          |
| 2016   | Visser[87]             | PMM     | Ladle           | CaO + Mg   | N₂          |
| 2017   | Ma et al.[88]          | PMM     | Ladle           | CaO + Mg   | N₂          |
| 2018   | Fan et al.[89]         | FVRM    | Kanbara reactor | CaO        | NA          |
| 2018   | Moosavi-Khoonsari et al.[90]| REM| Ladle           | CaO + Mg   | N₂          |
| 2018   | Vuolio et al.[91]      | PRM     | Ladle           | CaO-based  | N₂          |
| 2019   | Vuolio et al.[92]      | PRM     | Ladle           | CaO-based  | N₂          |
| 2019   | Vuolio et al.[93]      | PRM     | Ladle           | CaO-based  | N₂          |
| 2019   | Vişeri et al.[94]      | PMM     | Ladle           | CaO-based  | N₂          |
| 2019   | Feng et al.[95]        | PRM     | Kanbara reactor | CaO-based  | NA          |

a) FVRM = finite volume reaction model, LRM = linear regression model, PMM = process mechanism model, PRM = parametrized reaction model, REM = reaction equilibrium model, SRIM = simple reaction interface model; b) CaD = calcium diamide (CaC₂ + CaCO₃ + CaO); CaFCl = 30CaO–20CaF₂–20CaCl₂; CaF = 30CaO–40CaF₂–30Fe₂O₃; CaFCl = 30CaO–20CaF₂–20CaCl₂–30Fe₂O₃; NA = not available.
higher sulfur contents. This was attributed to the higher activation energy of boundary layer diffusion in comparison to boundary layer diffusion.

Later, Oeters[60] proposed a simplified model for desulfurization with CaO or CaC₂ in a boundary layer diffusion-controlled case. In this model, the desulfurization rate was assumed to be controlled by external mass transfer

\[
\frac{[\%S]}{[\%S]_0} = \exp \left( -\frac{m_{p}}{m_{\text{bath}}} \beta \left( \frac{A}{V} \right) \tilde{t}_{\text{p,rest}} \right)
\]  

(5)

where \( \beta \) is the mass transfer coefficient and \( \tilde{t}_{\text{p,rest}} \) is the average residence time of the particles. As for CaO-based desulfurization, it was suggested that when using inert carrier gas, the silicon contained by the metal bath reacts with the oxygen brought by CaO injection to form Ca₂SiO₄. As the molar volume of Ca₂SiO₄ is roughly twice that of CaO, half of the reaction surface area was assumed to be covered by Ca₂SiO₄ thus reducing the active reaction area available for desulfurization to half of the nominal surface area. This was treated mathematically by setting the surface-area-to-volume-ratio equal to \( (A/V)_p = 3/d_p \) for CaO and \( (A/V)_p = 6/d_p \) for Ca₂SiO₄.

An early attempt to create a model combining the thermodynamic-kinetic description of desulfurization with the velocity field induced by reagent injection was published by El-Kaddah and Szekely.[35,58] Their model consisted of three components: 1) solution of 2D turbulent Navier–Stokes equations, 2) dynamic balance of the sulfur content, and 3) thermodynamic equilibrium relationships.

The dynamic balance of the sulfur content was formulated by making use of a first-order rate expression based on boundary layer theory. The mass transfer coefficient was described using the model of Sano et al.[99] which describes mass transfer of suspended particles in agitated vessels and in bubble columns

\[
Sh = \frac{\beta d_p}{D} = \left[ 2 + 0.4 \left( \frac{\varepsilon d_p}{\nu} \right)^{1/4} \left( \frac{Sc}{C} \right)^{1/3} \right] \phi_p
\]

(6)

where \( \varepsilon \) is the rate of energy dissipation, \( \nu \) is the kinematic viscosity, and \( \phi_p \) is the surface factor of the injected particle (\( \phi_p = 1 \) for a sphere). The reaction model of El-Kaddah and Szekely[35,58] was validated against experimental measurements from a 6-ton pilot unit and a 40-ton industrial scale vessel. The results suggest that the vessels are relatively well-mixed and that the overall rate is controlled by mass transport of sulfur to the reaction interface at the metal–slag interface and in the three-phase region. The simulations for the 6-ton ladle under highly deoxidized conditions suggested that desulfurization in the three-phase region accounted for most of the sulfur removal. However, in the case of the less deoxidized 40-ton ladle most of the sulfur removal was attributed to the metal–slag reaction.

Ohguchi et al.[105] proposed a model for combined dephosphorization and desulfurization of hot metal. Their model focused on the permanent reaction mechanism and assumed that the reactions were controlled by both metal and slag phase mass transfer. The rate expressions were formulated in terms of a 1 wt% driving force. The mass fraction at the interface is obtained from effective equilibrium constants derived from reaction quotients of the reactions studied. For sulfur, the flux-density equation and effective equilibrium constant were expressed as follows

\[
f_S = \frac{\rho_{\text{CaS}}}{M_{\text{CaS}}} \left( \frac{[\%S] - [\%S]^*}{[\%S]_0} \right) = \frac{\rho_{\text{CaS}}}{M_{\text{CaS}}} \left( \frac{([\%S] - ([\%CaS] - ([\%CaS]^*)))}{[\%S]_0} \right)
\]

(7)

\[
f_S = \frac{\rho_{\text{CaS}}}{M_{\text{CaS}}} \left( \frac{([\%S] - ([\%CaS] - ([\%CaS]^*))}{[\%S]_0} \right) = \frac{\rho_{\text{CaS}}}{M_{\text{CaS}}} \left( \frac{([\%S] - ([\%CaS] - ([\%CaS]^*)))}{[\%S]_0} \right)
\]

(8)

where \( \beta_s \) is the mass transfer coefficient of sulfur, \( \rho_l \) is the density of hot metal, \( M_s \) is the molar mass of sulfur, \( \rho_{\text{CaS}} \) is the mass transfer coefficient of CaS, \( \rho_s \) is the density of slag, \( M_{\text{CaS}} \) is the molar mass of CaS, \( \rho_{\text{CaS}} \) is the Henrian activity coefficient (1 wt% basis) at the interface, \( f_{\text{CaS}} \) is the Henrian activity coefficient for both transitory and permanent reaction mechanisms.[61,65,72] All three models accounted for both transitory and permanent reaction mechanisms.[61,65,72] The models of Sawada et al.[61] and Vargas-Ramirez et al.[72] represent different development stages of the same model and thus share many similarities. In both models, the mass transfer rates in the metal and slag phases were described using empirical equations.[61,65] However, in the model of Kitamura et al.,[65] the thermodynamic treatment is improved by the use of Wagner–Lupis–Elliott (WLE) formalism[106] and regular solution model[107] to describe the activities of metal and slag species, respectively. Furthermore, Kiramura et al.[65] derived the activity coefficient of sulfur from the sulfide capacity calculated using the model proposed by Sosinsky and Sommerville.[108] The model of Vargas-Ramirez et al.[72] focused on desulfurization with CaO–SiO₂–CaF₂–FeO–Na₂O reagents at 1400–1500°C (1673–1773 K). Similar to Kitamura et al.,[65] the model of Vargas-Ramirez et al.[72] featured activity models for both metal and slag species, although it was not mentioned explicitly which models were used. In contrast to Sawada et al.[61] and Kitamura et al.,[65] Vargas-Ramirez et al.[72] assumed that the transitory reaction proceeds only through the fraction of reagent particles.
that come into contact with the metal bath. The average share of particles remaining at the gas–liquid interface calculated based on physical properties was reported to be 77% of the overall mass of the injected reagent.

Deo and Grieveson\cite{62} proposed a mathematical model for crucible experiments on desulfurization of aluminium-containing molten pig iron by injection of 40% CaO – 40% CaF$_2$ – 20% Al$_2$O$_3$ powder. In their model, the overall desulfurization rate was defined as the sum of the rates of the transitory and permanent reactions. The rates were formulated on the basis of boundary layer theory assuming that the area of the transitory reaction corresponds to the surface area of the particles and that the area of the permanent reaction corresponds to the nominal metal–slag contact area. The partition coefficient of sulfur was estimated based on the results of the crucible experiments, whereas the mass transfer coefficients were calculated using the approach of Engh et al.\cite{109} They reported that the calculated mass transfer coefficients of the transitory and permanent reactions were nearly the same, and that the principal advantage of powder injection is the increase in interfacial area available for the desulfurization reaction.

Chiang et al.\cite{63,64} proposed a model for CaC$_2$-based hot metal desulfurization. Following a careful analysis of potential rate controlling steps, the rate of transitory metal–particle reaction was assumed to be controlled by two consecutive steps, termed “pumping control” and “contact control”. Pumping control denotes the mass transport of sulfur to plume due to entrainment, while contact control refers to mass transfer in the diffusion boundary layer surrounding the particles, which is different for penetrated particles and those located on the bubble interfaces. A schematic illustration of these processes is shown in Figure 2.

In the model of Chiang et al.,$^{63,64}$ the sulfur balance in the plume was expressed as

$$\frac{1}{A_{\text{plume}}} \frac{dC_{[S],\text{plume}}}{dZ} U_L A_{\text{plume}} \theta_L = \frac{C_{[S],\text{bath}}}{A_{\text{plume}}} \frac{d\theta_L}{dZ} U_L A_{\text{plume}}$$

sulfur in the plume

$$-6 \theta_L \beta_p (1 - f_{p,b}) \left( C_{[S],\text{plume}} - C_{[S],p}^{*} \right)$$

desulfurization by particles on the metal bath

$$-6 \theta_L \beta_b \left( C_{[S],\text{plume}} - C_{[S],b}^{*} \right)$$

desulfurization by particles on bubble surfaces

where $A_{\text{plume}}$ is the plume area, $C_{[S],\text{plume}}$ is the sulfur concentration in the plume, $U_L$ is the rising velocity of liquid, $\theta_L$ is the liquid volume fraction, $Z$ is the vertical distance from bottom of plume, $C_{[S],\text{bath}}$ is the sulfur concentration in the metal bath, $\theta_p$ is the particle volume fraction, $\beta_p$ is the mass transfer coefficient to particles, $f_{p,b}$ is the fraction of particles on the bubble surfaces, $d_b$ is the particle diameter $C_{[S],p}^{*}$ is the sulfur concentration at the metal–particle interface, $\beta_b$ is the mass transfer coefficient to bubbles, $\theta_C$ is gas volume fraction, $d_b$ is the bubble diameter, and $C_{[S],b}$ is the sulfur concentration at the particle–bubble interface. Similar to El-Kaddah and Szekely,\cite{35,36} the turbulent mass transfer in the diffusion boundary layer of the particles was described using Equation (6). The gas bubbles were assumed to be spherical caps and the related mass transfer to them was described using the equation of Baird and Davidson\cite{110}

$$\beta_b = 0.951 g^{1/4} d_b^{-1/4} D^{1/2}$$

Figure 2. Schematic illustration of the physico-chemical phenomena in the gas plume. Reproduced with permission.\cite{64} Copyright 1991, Association for Iron & Steel Technology.
where \( g \) is the standard gravity. The results of their simulations suggest that the rate of particles in the liquid depends strongly on the mass flow rate of particles and weakly on gas flow rate, whereas the rate of particles residing at the bubble interface depends weakly on the mass flow rate of particles and strongly on the gas flow rate. The rate of sulfur entrainment into the plume did not affect the desulfurization rate significantly.

The fundamental model proposed by Deo and Boom\(^{[66]}\) focuses on desulfurization with CaC\(_2\) in a torpedo car. The overall desulfurization rate is assumed to be the sum of permanent (metal–slag) and transitory (metal–reagent) reactions. Assuming good mixing in the metal bath, the rate of permanent reaction was formulated according to a first-order rate expression in which the mass transfer rate was assumed to be controlled by mass transfer in the diffusion boundary layer of the metal phase. As for the transitory reaction, a further distinction was made between particles that penetrated into the metal bath and those that remained entrapped in the gas bubbles. The overall expression for sulfur removal was thus formulated as

\[
\frac{d[\%S]}{dt} = -\frac{1}{V_{\text{bath}}}(a + b + c)
\]

where

\[
a = A_{\text{slag}} \beta_1
\]

\[
b = \frac{L_h \rho_p}{\rho_s} \left(1 - f_{p,b}\right) \left[1 - \exp \left(-\frac{6\rho_p f_{p,res} g t_{p,b}}{d_b T_{\text{bath}} \rho_b} \right)\right]
\]

\[
c = \frac{L_h \rho_p}{\rho_s} f_{p,b} \left[1 - \exp \left(-\frac{2.38 m T_{\text{bath}} \rho_b t_{p,\text{res}} V_{G,\text{STP}} \rho_s}{298 m_p f_{p,b} L_b} \right)\right]
\]

where \( A_{\text{slag}} \) is the nominal metal–slag interfacial area, \( \beta_1 \) is the metal-side mass transfer coefficient of the permanent reaction, \( m_p \) is the particle feed rate, \( \rho_s \) is the slag density, \( f_{p,b} \) is the fraction of CaC\(_2\) particles which reside inside the bubbles at the metal–bubble interface, \( \rho_b \) is the mass transfer coefficient of the penetrated particles, \( t_{p,\text{res}} \) is the residence time of the penetrated particles, \( d_b \) is the diameter of the particles, \( L_b \) is the partition ratio of sulfur, \( d_b \) is the bubble diameter, \( m \) is the (dimensionless) effective area factor, \( T_{\text{bath}} \) is the bath temperature, \( \beta_0 \) is the mass transfer coefficient of the entrapped particles, \( t_{b,\text{res}} \) is the residence time of bubbles, and \( V_{G,\text{STP}} \) is the volumetric carrier gas injection rate in STP conditions. In an example calculation with a CaC\(_2\) reagent, the contributions of the permanent (\( a \)), particle (\( b \)), and bubble (\( c \)) mechanisms were shown to be 30.6\%, 41.8\%, and 27.6\%, respectively. Consequently, the transitory reaction (mechanisms \( b \) and \( c \)) is expected to account for over two-thirds of the desulfurization. Different values have been reported for other reagents. For example, Hara et al.\(^{[111]}\) reported that the transitory reaction accounted for only 25\% of the sulfur removal in their process experiments with a CaCO\(_3\)-based reagent.

Zhao and Irons\(^{[49,67]}\) studied hot metal desulfurization with CaC\(_2\)-based reagents in an induction furnace. A mathematical model was proposed for describing the simultaneous desulfurization and deoxidation observed in the experiments.\(^{[67]}\) The coupled differential equations for the bulk sulfur and oxygen concentrations were written as follows

\[
\frac{dC_{[S]}}{dt} = -\left(\frac{k_{\text{CaC}_2} + k_{\text{CaO}}}{K_{\text{eq}} + 1}\right) C_{[S]} + \frac{k_{\text{CaO}}}{K_{\text{eq}} + 1} K_{\text{eq}} C_{[O]} + k_{\text{CaC}_2} C_{[O],\text{CaC}_2}
\]

(16)

\[
\frac{dC_{[O]}}{dt} = \frac{k_{\text{CaO}}}{K_{\text{eq}} + 1} C_{[S]} - \left(\frac{k_{\text{CaC}_2} + k_{\text{CaO}}}{K_{\text{eq}} + 1}\right) C_{[O]} + k_{\text{CaC}_2} C_{[O],\text{CaC}_2}
\]

(17)

where \( k_{\text{CaC}_2} \) is the rate constant of CaC\(_2\), \( k_{\text{CaO}} \) is the rate constant of CaO, \( C_{[S]} \) is the sulfur concentration in equilibrium with CaC\(_2\), and \( K_{\text{eq}} \) is the equilibrium constant, which is defined as

\[
K_{\text{eq}} = \frac{C_{[O],\text{CaC}_2}}{C_{[S]} C_{[O],\text{CaC}_2}}
\]

For the sake of simplicity, the rate constants \( k_{\text{CaC}_2} \) and \( k_{\text{CaO}} \) were assumed to be equal to the overall rate constant \( k_{\text{tot}} \) proportional to their weight-fractions in the reagent, i.e., \( k_{\text{CaC}_2} = f_{\text{CaC}_2} k_{\text{tot}} \) and \( k_{\text{CaO}} = f_{\text{CaO}} k_{\text{tot}} \). Making use of Equation (2), it was deduced that \( S_h = 2 \) due to the low slip velocity of the particles.

Seshadri et al.\(^{[71]}\) proposed a model, which describes the overall rate of desulfurization as a sum of the contributions of the top slag, dispersed particles, and bubbles. The sulfur mass transfer coefficient at the metal–particle interface was described using Equation (6), whereas the sulfur mass transfer coefficient at the metal–slag boundary layers was defined according to Riboud and Olette\(^{[112]}\)

\[
\beta_S = k \left(\frac{D_{S}}{A_{\text{adl}}}ight)
\]

(18)

where \( k \) is a constant with a value of \( k = 500 \text{ m}^{-0.5} \), \( D_S \) is the mass diffusivity of dissolved sulfur, \( V_G \) is the volumetric gas flow rate at the temperature and pressure of the metal–slag interface, and \( A_{\text{adl}} \) is the cross-sectional area of the ladle. As for the metal–bubble interface, the mass transfer coefficient of sulfur in contact with spherical cap bubbles was calculated according Equation (11), whereas the correlation available in ref. [113] was used for other bubble types. The residence time of particles was estimated to be equal to the residence time of the gas bubbles. The sulfur partition coefficient was calculated using the correlation of Sosinsky and Sommerville.\(^{[108]}\)

Zou et al.\(^{[73]}\) proposed a model for hot metal desulfurization with CaC\(_2\), Mg, or mixtures of them. The overall rate of plain CaC\(_2\)-based desulfurization was assumed to consist of transitory and permanent reactions, whereas the reactions of magnesium with dissolved sulfur were divided into a first-order heterogeneous reaction with solid Mg and an apparent second-order homogeneous reaction with dissolved Mg. One of the novel features of the model is that it incorporates the effect of bath mixing on hot metal desulfurization without solving the momentum equation. The overall desulfurization rate for co-injection of CaC\(_2\) and Mg was thus expressed as
where \( V_{\text{G, tot}} \) is the total volumetric flow rate of carrier gas and magnesium vapor, \( \beta_b \) is the mass transfer rate to bubbles, \( t_{\text{mix}} \) is the mixing time, \( t_{\text{inj}} \) is the total injection time, \( f_{p,b} \) is the fraction of particles which have penetrated into the metal bath, \( y_{\text{CaC}_2} \) is the mass fraction of \( \text{CaC}_2 \) in the reagent mixture, \( \beta_L \) is the mass transfer coefficient in hot metal, \( \beta_k \) is the mass transfer coefficient in slag, and \( K \) is a constant, which is defined as follows

\[
K = \frac{A_s \beta_{\text{Mg}} p_{\text{Slag}}}{V_{\text{bath}} (\beta_{\text{Mg}} p_{\text{Slag}} + \beta_{\text{S}})}
\]  

(20)

where \( A_s \) is the total area for \( \text{MgS} \) precipitation, \( \beta \) denotes mass transfer coefficient, and \( C \) denotes concentration. Regarding the co-injection of \( \text{CaC}_2 \) and Mg, the modeling results of Zou et al.\[73\] suggest that their contributions to the overall desulfurization rate vary over time. In the case studied, the desulfurization rate of \( \text{CaC}_2 \), decreased almost linearly as a function of injection time, whereas the desulfurization curve attributable to Mg had a roughly parabolic trajectory, which surpassed that of \( \text{CaC}_2 \) at 2 min of injection and reached its peak value at \( \approx 2.5 \) min. The reaction model by Zou et al.\[73\] was later implemented by Huang et al.\[83\] as a user defined function in their CFD model for hot metal desulfurization in a torpedo car.

The reaction modeling of a two-step technology, which consists of a desulfurization step with bottom stirring of nitrogen followed by a slag regeneration step with submerged lance injection of oxygen, was studied by Pirker et al.\[74\] using a CFD-based reaction model. The model was based on the solution of Reynolds-averaged Navier–Stokes (RANS) equations in the metal and slag phases using a standard \( k-\varepsilon \) model for turbulence. The removal of sulfur with nitrogen stirring was described using a scalar transport equation with convective and diffusive terms. The desulfurization via permanent contact during bottom stirring of nitrogen was assumed to be controlled by metal-side mass transfer at the slag–metal interface

\[
\frac{d[S]}{dt} = M_{L,c} \beta_L \left( |S|_{\text{f-str}} - \frac{\left( S_C^{\text{L}} \right)^{\rho}}{L_S} \right)
\]  

(21)

where \( M_{L,c} \) is the molar mass of hot metal in a cell \( c \), \( \beta_L \) is the metal-side mass transfer coefficient, \( A_k \) is the area in the cell \( c \), and \( |S|_{\text{f-str}} \) is the sulfur content in the free-stream. The temperature field in the ladle was solved by accounting for the reaction enthalpy of desulfurization, through the refractories, and the heat loss to atmosphere due to convection and radiation. The cooling effect of nitrogen was not taken into account.

Jin et al.\[77\] proposed a kinetic model for desulfurization with powder injection. The desulfurization was assumed to take place via permanent and transitory reactions, i.e., via the top slag and the reagent powder. The transitory metal–reagent reaction was assumed to be controlled by mass transport of sulfur in the metal phase. The thickness of the diffusion metal–slag boundary layer was solved using the expression proposed by Geters\[19\] whereas the thickness of the metal–particle boundary layer was calculated using Equation (2). The residence time of the particles was related to the carrier gas flow rate via the equation proposed by Zhu and Hsiao.\[114\] Based on model calculations, it was suggested that the desulfurization rate of Mg-based fluxes is significantly higher than that of CaO-based fluxes. Furthermore, the calculated desulfurization rates with CaO–CaF\(_2\) flux and calcium aluminous flux were found to be comparable.

Scheepers et al.\[78\] derived a 1D steady state model which accounts for momentum, heat, and mass transfer in the plume formed by gas, liquid and reagent particles, as well as the contribution of the top slag. The heat balance was formulated according to Farias and Irons.\[115\] The rate equations for calcium carbide particles were adapted from Chiang et al.\[64\] whereas the contribution of the top slag was calculated similar to Seshadri et al.\[71\] The fraction of particles inside gas bubbles \( f_{p,b} \) was used as a tuning parameter. As for the predicted average utilization of the Ca\(_2\) particles, the best agreement with industrial data was obtained by using \( f_{p,b} = 0.7 \). The sulfur mass transfer coefficients at the metal–slag and metal–particle boundary layers were described using Equation (6) and (18), respectively. The mass transfer correlation for bubbles was taken from Szekely and Themelis\[116\]

\[
\beta_b = 1.08 g_1^{1/4} d_b^{-1/4} D_s^{1/2}
\]  

(22)

where \( g \) is the gravity constant, \( d_b \) is the bubble diameter, and \( D_s \) is the mass diffusivity of dissolved sulfur. It should be noted that Equation (22) deviates from Equation (11) only with respect to the prefactor and can be derived by substituting the bubble rise velocity by Haberman and Morton\[117\] into the mass transfer correlation by Calderbank\[118\] for spherical cap bubbles. The main advantage of the model of Scheepers et al.\[78\] in comparison to other models listed in Table 1 is that it relates the desulfurization kinetics to the velocity and temperature of bubbles and particles in the three-phase plume.

Visser and Boom\[79\] proposed a model based on the description for the bubble plume generated by injected carrier gas and reaction kinetics of the desulfurization agents. In their model, it was assumed that the carrier gas and Mg vapor form a plume, the velocity of which determines the residence time of the reagent. Moreover, Mg was assumed to dissolve upon injection and to react with sulfur by a homogeneous reaction on nucleates. Ochoitena et al.\[81\] studied desulfurization using CaO- and Ca\(_2\)C\(_2\)-based reagents. As for the CaO-based reagent, they accounted for both the resistances of the chemical reaction and external mass transfer. It was suggested that with CaO-based reagent the desulfurization rate is controlled by chemical reaction at high sulfur contents, but that the rate-controlling
mechanism changes to sulfur diffusion at lower sulfur contents. The shift from one mechanism to another was suggested to occur at a sulfur content of ≈0.01 w% (100 ppm). Desulfurization with a CaC₂-based reagent was assumed to take place only at a transitory bubble–metal site.

The model by da Silva et al.[83] describes desulfurization in a KR with CaO-based fluxes. Their model accounts for two reaction mechanisms: 1) reactions between the metal bath and slag droplets detached from the carry-over slag, and 2) reactions between the metal bath and reagent particles. The mathematical treatment of the two reaction mechanisms was simplified by assuming that the interfacial area and mass transfer coefficient of the metal–slag reaction mechanism are equal to those of the metal–particle reaction. The mass transfer coefficient of the particles was calculated using Equation (6) and the sulfide capacity of the slag was described using the model by Sosinsky and Sommerville.[108] The model was applied to simulate roughly 600 heats and performed reasonably well in comparison to the measured data. The model predictions suggest that the initial rate of desulfurization has a quadratic relationship with the particle diameter. However, due to the simplifications of the model, it is not meaningful to differentiate between the relative contributions of the metal–particle and metal–slag reaction mechanisms.[83]

Rodríguez et al.[84] proposed a thermodynamic–kinetic model for desulfurization with CaC₂ based on first-order kinetics. Both cylindrical and spherical coordinates were tested for discretization of the differential rate equations. The cylindrical model was found to be in reasonable agreement with the spherical model. Furthermore, the predictions of both models were in reasonable agreement with experimental values.

The CFD-based reaction model proposed by Barron et al.[86] was developed for simulating hot metal desulfurization with mono-injection (CaC₂) and co-injection (CaC₂ and CaO) practices. In both cases, the rate of desulfurization was assumed to be determined by mass transfer in the liquid phase. Their CFD simulations suggest that the assumption of a well-stirred tank holds well in the case of hot metal desulfurization in a ladle.

Visser[87] proposed a model for hot metal desulfurization with co-injection of CaO and Mg. In the model, the desulfurization due to CaO injection is attributed entirely to the transitory metal–reagent reaction. The injected Mg was assumed to vaporize and dissolve in to the metal bath, where it reacts on the surface of MgS seeds, whereas the undissolved Mg vapor was assumed to end up in the gas plume formed by the carrier gas. The overall mass balance was written as

$$\frac{d\%S}{dt} = \left(\frac{d\%S}{dt}\right)_{CaS} + \left(\frac{d\%S}{dt}\right)_{MgS}$$

(23)

where the first term on the right denotes the desulfurization rate due to CaO particles, whereas the second term denotes the desulfurization rate due to Mg particles

$$\left(\frac{d\%S}{dt}\right)_{CaS} = -\frac{m_{CaO \cdot f_{res \cdot CaO}}}{m_{bath}} \frac{\rho_{CaO}}{\rho_{MgS}} \beta_{S, CaO} \left(\frac{6}{d_{p, CaO}}\right) f_{p, CaO} \%S - \%S_{CaS}$$

(24)

where $\beta_{S, CaO}$ is the mass transfer coefficient to CaO particles, $f_{p, CaO}$ is the fraction of penetrated CaO particles, $\beta_{S, MgS}$ is the mass transfer coefficient to MgS particles, and $a_{MgS}$ is the specific surface area of the MgS particles in hot metal, for which a value of 10 m² m⁻³ was estimated. For both the CaO and Mg particles, the mass transfer coefficient was calculated using the Ranz–Marshall correlation.[95,96] Due to the small size of the particles, their slip velocity was assumed to be zero, and consequently the Ranz–Marshall correlation (Equation (2)) reduced to $Sh = 2$.[87]

Ma et al.[88] proposed a kinetic model for desulfurization with injection of Mg–CaO powder. In their model, the total rate of desulfurization was calculated as the sum of the contributions of the top slag, as well as CaO- and Mg-based reagents. The mathematical expressions used for these mechanisms are the same as those used by Zou et al.[73] and consequently the overall rate can be expressed according to Equation (19). An example of the predicted sulfur content curve is shown in Figure 3. Based on the results obtained, Ma et al.[88] proposed that the desulfurization process can be considered to consist of three stages: an incubation stage, a rapid desulfurization stage, and a slow desulfurization stage.

The model proposed by Moosavi-Khoonsari et al.[89] uses what they term an effective equilibrium reaction zone (EERZ) approach, in which the process is divided into a finite number of reaction zones, which have mass and heat exchange with bulk volumes. The thermodynamic equilibrium in the reaction volumes was calculated using the FactSage database. The model considered a total of nine reaction zones, four of which were used to describe the transitory reaction: 1) reaction between gas plume and dissolved Mg, 2) first homogenization in the gas plume, 3) reactions between gas plume and CaO particles, and 4) second homogenization in the gas plume.

![Figure 3. Predicted and measured change of sulfur content in hot metal desulfurization with co-injection of Mg (60%) and CaO (40%). Reproduced with permission.[88] Copyright 2017, the Iron and Steel Institute of Japan.](https://www.advancedsciencenews.com)
The remaining five zones were used to describe the permanent reaction: 5) first homogenization in the top slag, 6) reactions between plume and top slag, 7) homogenization in metal bath, 8) second homogenization in the top slag, and 9) gas exit. In zone 1, the reaction between metal bath and magnesium was assumed to proceed to equilibrium. The reactions in zones 3 and 6 were treated with expressions for effective reaction volumes, which were calculated based on the mass transfer correlations of Kitamura et al.[6] As for the homogenization zones for top slag (zones 5 and 8), it was assumed that the temperature and composition of the slag is fully homogenized. In zones 2 and 4, the metal in the gas plume was assumed to fully homogenize with the metal bath. Conversely, the homogenization of the metal bath (zone 7) incorporated the effect of the mixing and dead zones.

Visuri et al.[93] proposed a model for lime-based hot metal desulfurization in a ladle. Their model accounted for both metal–reagent and metal–slag reactions. The overall rate of the transitory metal–reagent reaction was calculated by summation of the rate of each particle size class. To determine the rate of individual size classes, the model accounted for the resistances of bath mixing, boundary layer diffusion, and steady-state diffusion in the CaS layer. The external resistances (bath mixing and boundary layer diffusion) were coupled to the rate of the CaS layer growth similar to Oeters et al.[63] by solving a molar balance at the metal–particle interface. The resistance of bath mixing was derived from the mixing time measurements of Usui et al.[38] whereas the rate of boundary layer diffusion was calculated according to the Ranz–Marschall correlation.[95,96] The description of the critical Weber number proposed by Oeters[3] was used as the penetration criterion. The model assumed that only the particles that penetrated into the metal bath participate in the metal–reagent reaction. The metal–slag reactions were assumed to take place not only between bulk metal and slag but also between metal droplets and slag. Making use of the mathematical formulation of Feiterna et al.,[119] it was assumed that metal droplets are generated by the bubble-bursting phenomenon, and follow the Rosin–Rammler–Sperling size distribution function.

The internal and external mass transfer related to the droplets was described using the Newman solution[120] and Ranz–Marschall correlation,[95,96] respectively. The activities of species in metal were calculated using the unified interaction parameter formalism,[121] which provides a thermodynamically consistent description for dilute and nondilute solutions. The activities of the slag species were described using the regular solution model.[122] Based on a preliminary validation with two CaO reagents, it was suggested that the overall rate controlling step changes from solid-state diffusion to boundary layer transport as the sulfur content decreases. The turning point was found to be affected by the metal bath temperature and size distribution of the reagent.

### 2.2. Data-Driven Models

Data-driven approaches for modeling and control of hot metal desulfurization offer a tempting alternative to mechanistic models. Data-driven approaches are well-suited for modeling if the mechanisms of the system are poorly known, but there is enough data available. Pre-trained data-driven models can also be applied online due to less intensive computational procedures. A certain downside of these methods is that the models are poorly generalizable to other similar processes, even if the fundamentals of the process are the same. One benefit of the data-driven techniques is that they enable the quantification of the uncertainties regarding the phenomena occurring during reagent injection.

When considering prediction of the state of hot metal desulfurization, a very common variable of interest is the sulfur content in hot metal. This highlights the dominance of regression problems in the field. The basic principle of a data-driven regression model is to predict the expected value of the output variable based on a set of independent variables and identified model parameters. This can be mathematically expressed as follows

\[
E(y|X) = f(X, b) + \varepsilon
\]

where \(E(y|X)\) is the expected value of a dependent variable \(y\) for a given data matrix \(X\), \(f(X, b)\) is a linear or nonlinear function, \(b\) is the parameter vector, and \(\varepsilon\) is the modeling error. The identification of such a prediction model can be roughly divided into the following steps: 1) model structure selection, 2) variable or feature selection, 3) model parameter identification, and 4) model validation and testing.

For the first step, there are numerous alternatives for \(f(X)\), each of which has its own demands, benefits, and restrictions. The alternatives in the literature concerning the modeling of hot metal desulfurization include multiple linear regression (MLR), nonlinear regression, and ANN. However, a much wider variety of methods exists, and have been applied in a wider metallurgical context, especially for the modeling of converter and blast furnace processes. Popular examples of these include support vector machines (SVM)[122] and Random Forests (RF).[123]

The variable or feature selection means the selection of proper input variables or features for a generic model structure.[124] A simple example of a generic model structure is the MLR model, which is given as

\[
E(y|X) = b_0 + \sum_{j=1}^{k} b_jx_j + \varepsilon
\]

This particular step is important especially in the context of metallurgy, where the data is often noisy and contains a limited number of observations. The problem of variable selection can be stated to be the selection of a variable subset from a larger set of candidate variables that minimizes the modeling error or some other selection criteria.[124] It is common that the complexity of the model is also taken into account in evaluation of the suitability of the model, for which Akaike Information Criterion (AIC),[125] Bayesian Information Criterion (BIC)[126] and Mallow’s \(C_p\)[128] are commonly used criteria. However, the metallurgical examples of these are limited to the work of Saxén and Pettersson.[129]

To avoid a biased model output, a proper selection criteria would be based on cross-validation. Cross-validation in its most simple form means testing the model error to a randomly selected external data set once. In the literature, this is also referred as the holdout method.[130] In this case, the external data set means that the model is completely independent of the data.
i.e., no decisions concerning the model structure and parameters have been made based on this criterion. However, to avoid an optimistically biased estimate and the selection result being dependent on the data split, a sophisticated approach is to use repeated cross-validation. In repeated cross-validation, such as Leave-One-Out (LOO), k-fold, and Leave-Multiple-Out (LMO) cross-validation, the data is repeatedly split into training and validation sets and the validation error is taken as the average of the splits. However, there are fundamental differences between approaches to data splitting. The variable or feature selection can be carried out either manually or automatically. Manual selection often corresponds to using expert knowledge on system mechanisms in selection without any error criteria. For automatic selection, there are numerous alternatives, including forward selection, backward elimination, Tabu search, genetic algorithms (GAs), and many more.

In modeling hot metal desulfurization, the selection is often carried out manually, and the literature concerning automatic variable selection in the context of mathematical modeling of hot metal desulfurization is scarce.

The model by Quinn et al. was based on a partial least squares (PLS) regression. Their model had 14 input variables and was used to improve the controllability of desulfurization in a torpedo car. The study by Bhattacharya et al. applied principal component analysis (PCA) to the analysis for an input variable selection. The selection criteria were based on a k-fold cross-validated sum of squared errors, referred to in the study as the predicted residual error sum of squares (PRESS). The variables that explained the most variance in the reagent consumption were the initial, final, target, and turn-down sulfur content. The PLS regression was selected to be used for the prediction, as it performed slightly better than the MLR and PCR. The number of latent variables that minimized the PRESS of the PLS model was 4. In the study of Vuolio et al., a GA was proposed as a variable selection method for prediction of the transitory desulfurization reaction. The algorithm applied repeated LMO cross-validation as the objective function in the variable selection phase in MLR model identification. In the study, it was observed that the objective function studied resulted in parsimonious models and sufficiently high repeatability of the selection. The authors suggested that the most relevant variables were the diameter of the reagent, total gas flowrate, mass flowrate of the reagent, and initial mass of the hot metal. Vinoo et al. applied a MLR model to predict the calcium carbide consumption and the evolution of sulfur during the process. The authors carried out the model identification with manual selection based on the MLR model. The chosen criterion was the sum of squared errors for the training set. Prior to the model selection, the authors classified the data based on the initial temperature. This was assumed to increase the predictive power of the model, as it was based on linear interactions only, and thus ignored the nonlinear behavior that is characteristic of mass-transfer related control of the reaction mechanism. Despite ignoring the nonlinear behavior, the modeling error is relatively small (MAE = 15.3 ppm).

The objective of the third step, i.e., model parameter identification (also known as model training), is to identify the weights that are associated with the independent variables used. This procedure is carried out via optimization, in which the objective function, i.e., the expression of the modeling error is minimized. If the model is linear with respect to its parameters, for example, MLR, an analytical solution for the parameters can be obtained. In a nonlinear case, the parameters need to be solved iteratively with a suitable minimization algorithm. The most usual objective function is the least-squares cost function, in which the sum of squared prediction residuals is minimized. This is mathematically expressed as:

$$\min \text{SSE} = \min \sum_{i=1}^{k} (\hat{y}_i - \hat{y}_i)^2$$

where SSE is the sum of squared errors, $\hat{y}_i$ is the measured output of an observation $i$, and $\hat{y}_i$ is the model output for observation $i$. It should be noted that the sum of squared errors or the mean squared errors is often used as a variable selection criterion too. If cross-validation is used, the objective function is referred as the sum of squared errors for cross-validation (SSE$_{CV}$).

A typical example of a model parameter identification for a nongeneric model structure is the study by Rastogi et al. In this study, the authors applied a GA to fit the model of Deo and Boom to process data concerning CaC$_2$-based desulfurization in a torpedo car. The authors stated that the GA gave more realistic prediction results than the analytical solution of the least-squares problem. Based on the identification, they suggested that the contribution of the reagent particles entrapped in the gas plume to the overall rate of reaction is negligible. A second example of this type of modeling was published by Vuolio et al., who derived a parametrized model based on surface-area approximation. The objective of their study was to identify the effect of particle size distribution on the rate of reaction using a lime-based reagent. The model used a GA for identification of the model parameters based on the plant data from hot metal desulfurization with lime-based reagents in a ladle. The authors suggested that the effective surface area of the particles is much less than the nominal surface area of the reagent particles. All the authors presented applied a simple cross-validation for model evaluation.

Among simple regression or MLR models, ANN based models have been used for modeling hot metal desulfurization. Neural network models consist of artificial neurons that are connected to each other using connective weights, i.e., model parameters, in the form of layers. The neurons are a set of mathematical functions, which modify a given input to produce an estimate of the desired output. It should be noted that the field of research concerning ANN is very wide, so the reader is encouraged toward more comprehensive literature concerning the subject.

Neural networks are considered as universal approximators, which means that they can map any given function with arbitrary accuracy, provided that there is a suitable number of neurons in the network. However, the interpretation of neural networks is rather difficult, as the network structure usually consists of a large number of neurons and consequently a large number of model parameters. Neural network models are identified based on a generic structure in which the information flows through the layered structure. A crucial part in applying neural networks for modeling is network training, in which the network parameters are identified such that the error between the network
output and the corresponding measurement value is minimized. However, more interest is focused on the optimization of the network structure with respect to its input variables and structure. Training is usually carried out using a backpropagation algorithm and its variations, of which more detailed descriptions can be found, for example, in refs. [135–137]. The large number of network parameters makes training the neural network a computationally very intensive process.\(^{136}\) Due to the large number of network connective weights to be optimized, a large amount of input data is usually needed for training ANN models, which is rarely possible in the case of metallurgical systems due to the difficult process conditions. As the neural network can deduce complex nonlinear, input–output relations of the training data, it allows the identification of totally black-box systems, where no information on the mechanistic behavior of the process is available.

Datta et al.\(^{68}\) and Deo et al.\(^{70}\) used ANN for modeling hot metal desulfurization in a torpedo car. The final sulfur content of the hot metal was predicted based on five input variables: treatment time, hot metal weight, initial sulfur content, carrier gas flow rate, and reagent injection rate. The authors managed to obtain adequate prediction accuracy with respect to final sulfur content \((R^2 = 0.39–0.60; \text{MAE} = 27–27.8 \text{ ppm})\) with this set of variables and relatively complex network architectures. Both studies observed that a relatively large amount of input data is needed for an ANN to learn the input–output relations properly. In addition, in the study of Deo et al.,\(^{70}\) it was observed that by optimizing the learning rate of the backpropagation algorithm, the training result for a sparse data set can be improved. Coupling mechanistic and data-driven modeling was suggested by Vuolio et al.,\(^{92}\) who studied the possible resulfurization of hot metal via an inverse permanent contact reaction at laboratory-scale by coupling a simple mechanistic model with ANN. In the study, it was observed that the sulfide capacity of the slag contributed the most to the potential for resulfurization. By making use of meta-analysis of their experimental data along with those of earlier studies,\(^{138–141}\) an ANN model was proposed to predict the sulfur partition ratio to obtain an estimate of the magnitude of the thermodynamic driving force.

There have been only a few attempts to use data-driven approaches for modeling the KR. Dan et al.\(^{82}\) applied three ANN configurations to predict the consumption of the reagent, stirring speed, and the stirring time. The variable selection was carried out manually and the suggested input variables for prediction were the weight, temperature and sulfur content of the hot metal, operation cycles of hot metal ladle, output reagent weight, stirring velocity, operation cycles of stirring bar, and the stirring time. The number of neurons was selected using an empirical relation. A drawback of the approach by Dan et al.\(^{82}\) is that the proper architecture of the network is dependent on the characteristics of the data, which usually makes the empirical relations designed for architecture selection poorly generalizable to other problems. Instead, it would be better to use cross-validation as it usually performs better in the model selection.\(^{142}\) An interesting attempt to combine parametrized modeling with a case-based reasoning model (CBRM) in the modeling of a KR was carried out in the study by Feng et al.\(^{94}\) The approach in the study was referred to as the corrected model. In the approach, the end sulfur content was predicted separately with the CBRM and a parametrized model (PRM). The overall prediction result was corrected based on the following expression\(^{94}\)

\[
[S]_{t,\text{corr}} = a + \sqrt{b[S]_{t,\text{CBRM}}^2 + c[S]_{t,\text{PRM}}}^2
\]

where \([S]_{t,\text{corr}}\) is the corrected sulfur content at time \(t\), \([S]_{t,\text{CBRM}}\) is the sulfur content at time \(t\) predicted by the CBRM, \([S]_{t,\text{PRM}}\) is the sulfur content at time \(t\) predicted by the PRM, and \(a\), \(b\), and \(c\) are fitting parameters that are identified based on the data. It was found that the corrected model performed slightly better, determined with the hit rate of the prediction, than ANN and PMR individually.\(^{94}\)

2.3. Summary and Prospects of Process Modeling

The development of mathematical models for hot metal desulfurization kinetics is likely to benefit from the increasing computational capacity that permits more and more complex calculations to be carried out within a reasonable time, whereas the interest toward data-driven models is expected to be interrelated with the amount of available data. In addition to the amount of data, novel measurement techniques would allow more advanced feature generation, i.e., enrichment of data sets with computational variables.

Nevertheless, there are still many uncertainties with respect to the phenomena taking place in the vessel thus necessitating many simplifications. A fundamental inconvenience concerns the effect of surface area of the reagent used in the process. In particular, a comprehensive description on the role of different rate-limiting factors, including both physical and chemical properties, is missing. Although metal losses to slag can reach 0.6–1.1% of the total amount of the hot metal,\(^{143}\) very little is known about the residence time and contribution of metal droplets to desulfurization rate. Yang et al.\(^{144}\) have suggested that fine metal droplets originate from bubble bursting, whereas larger droplets are due to splashing in the open eye zone. Their suggestion agrees well with the notion that the droplet size distribution reported by Chiang et al.\(^{63,64}\) is coarser than that reported by Feiterna et al.\(^{119}\) for mere bubble bursting. It can be summarized that the presented modeling approaches still need additional information particularly on the following aspects: 1) fraction of noncontacted particles, 2) residence of individual particles and the contact time available for mass transfer, 3) residence time and contribution of metal droplets to desulfurization, 4) heterogeneity of metal and slag phases in terms of composition and temperature, 5) effect of gas-forming additives on the effective contact area, and 6) adhesive behavior of the reagent.

Based on the literature, the applicability of data-driven models in quantifying the aforementioned effects is evident. In addition to parametrized models, the fully generic black-box models offer an interesting alternative as a modeling strategy. It is seen in the literature that the development of data-driven models has benefited from advanced computational techniques such as GA. In addition, the increased number of data and computational resources has allowed the use of repeated cross-validation. Further steps could be taken toward the application of complex
data-driven models, such as ANNs and regression trees, in modeling hot metal desulfurization. As there are several examples of the applicability of ANN in process modeling,[144] interest toward the application of ANN models is expected to increase in the metallurgical industry as well. However, for small and noisy data sets, the generalization ability of the network should be critically evaluated.[145] It should be kept in mind that the reaction data sets, the generalization ability of the network should be critically evaluated. The momentum was assumed to be changed only by buoyancy, which was determined using single-particle drag coefficients. Despite its simplicity, some useful results were obtained with respect to the effect of powder on the fluid flow in the gas plume. Figure 4 shows an example for hot metal desulfurization with CaC₂ using N₂ as carrier gas. For this case, it is evident that the liquid velocity in the gas plume is governed by gas flow rate at low gas flow rates only if the particle injection rate is low enough, whereas at high gas flow rates, the fluid flow is controlled by gas flow rate irrespective of particle injection rate.

Recently, Tripathi et al.[37] used physical modeling and a multiphase CFD model to study the effect of seven different lance port designs on mixing time in the case of desulfurization with CaC₂ in a ladle. As for simulations for a real ladle, hot metal, gas, and particles were considered as continuous phase, dispersed gas phase, and dispersed solid phase, respectively. Turbulence was described using the k-ε model. The gas bubbles were found to rise mostly adjacent to the lance due to the surface tension effect. Figure 5 shows that the commonly used straight lance that provides a considerably lower dispersion of bubbles compared with more complex lance designs.

The flow fields calculated for reagent injection with a submerged lance in ladles[35,37,58,149] are qualitatively similar to the results of the CFD simulations by Pirker et al.[74] for slag regeneration using an injection of oxygen with an eccentrically positioned submerged lance. Similar to El-Kaddah and Szekely,[58] Pirker et al.[74] reported that the bath movement was more vigorous using deeper position of the lance.

Table 3 shows a compilation of physical modeling studies on ladles and torpedo cars with lance injection. It can be seen that the main aspect studied using physical modeling is bath mixing. Lance injection in ladles and torpedo cars represents a fairly complex multiphase system for numerical modeling. A compilation of numerical modeling studies on ladles and torpedo cars with lance injection is shown in Table 3. These studies have focused mainly on studying the effect of the lance position on desulfurization, bath mixing, and particle penetration. The increasing computational resources have made more complex multiphase approaches feasible and virtually all the studies published in the 2010s are transient 3D simulations. Nevertheless, the authors are not aware of any studies in which all the phases present in hot metal desulfurization (hot metal, slag, gas, reagent) would have been accounted for. This highlights the need for further studies.

### 3.1. Fluid Flow Field

Relatively little information exists on the detailed fluid flow field in hot metal desulfurization. An early attempt to simulate the flow field was published by El-Kaddah and Szekely.[55] In their model, they treated the gas plume as a homogeneous three-phase region, the dimensions of which were extracted from visual observation of the open eye in the slag layer. Except for the quiescent bottom of the ladle, the modeling results exhibited a circulating pattern roughly similar to gas-stirred ladles. In a follow-up study[58] using the same model, a deeper lance position was reported to significantly increase the surface velocity. Despite an increase in the size of the gas plume, an increase in gas flow rate was found to have a significant effect on velocities at the surface of the metal bath.

Farias and Irons[107,115] proposed a simplistic 1D numerical model for the gas plume. In this model, all variables were averaged across the plume diameter, which was determined experimentally. The momentum was assumed to be changed only by buoyancy, which was determined using single-particle drag coefficients. Despite its simplicity, some useful results were obtained with respect to the effect of powder on the fluid flow in the gas plume. Figure 4 shows an example for hot metal desulfurization with CaC₂ using N₂ as carrier gas. For this case, it is evident that the liquid velocity in the gas plume is governed by gas flow rate at low gas flow rates only if the particle injection rate is low enough, whereas at high gas flow rates, the fluid flow is controlled by gas flow rate irrespective of particle injection rate.

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The residence time of reagent particles affects their microkinetic efficiency to a great extent. In the study by Tripathi et al.,[37] the longest particle residence times were achieved with a lance with two spiral ports in mutually opposite directions (H-45),

| Year | Study     | System          | Measurements                          | Focus of the study            |
|------|-----------|-----------------|---------------------------------------|-------------------------------|
| 1969 | Berner and Müller[46] | Ladle | H₂O | Air | No | Mechanical velocity measurements, fumigation of the bath with NH₃ | Bath velocities and mixing |
| 1980 | Usui et al.[138] | Ladle | H₂O-liquid paraffin | Air | No | Electrical conductivity | Mixing time |
| 1984 | Carsson et al.[39] | Torpedo car | H₂O | Air | No | Electrical conductivity (NaCl solution) | Mixing time |
| 1989 | Irons[40] | Torpedo car | H₂O | Air | Hollow glass particles | Electrical conductivity (HCl) | Mixing time |
| 2011 | Nadif et al.[147] | Torpedo car | H₂O | Air | No | Electrical conductivity | Pulsed gas injection |
| 2017 | Tripathi et al.[37] | Ladle | H₂O | Air | No | Electrical conductivity (NaCl solution) | Flow visualization (KMnO₄ solution) | Mixing and residence times |
followed by a using a lance with two curved ports in mutually opposite directions (C-45). The residence times associated with straight and T-lances used in typical operating practice were 25 and 23 s, respectively. These values are roughly an order of magnitude higher than that expected on the basis of the velocities in the gas plume, but much smaller than the estimates of Oeters et al.,[25] who assumed that the desulfurization rate is attributable entirely to transitory reaction and calculated that the residence time would need to be 39 s if the overall rate is limited by external mass transfer and 78 s if the overall rate is controlled by product layer resistance. Clearly, more information on the residence times of reagents is still needed.

So far, the possible emulsification of slag during hot metal desulfurization has not been studied. However, it is likely that the mechanisms of slag droplet detachment around the gas plume are similar to gas-stirred ladles, for which there is an abundance of studies involving physical modeling,[150–152] numerical modeling,[153–156] and plant experiments.[157] It is uncertain whether this mechanism contributes to the desulfurization rate in hot metal desulfurization.

### 3.1.2. Bath Mixing

Several studies have addressed bath mixing related to lance injection in ladles[36,38,158] and torpedo cars[39–41] using different lance types. Experiments with gas injection using centered and eccentric

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**Table 3.** Studies on the numerical modeling of ladles and torpedo cars with lance injection.

| Year | Study | System | Vessel | Liquid(s) \(^{[a]}\) | Gas injection | Particle injection | Modeling assumptions | Focus of the study |
|------|-------|--------|--------|-----------------|---------------|-------------------|---------------------|-------------------|
| 1981 | El-Kaddah and Szekely[35] | Ladle | HM | Unknown gas | CaO + CaF₂ | 2D SS | Drift flux (L–G–P) | Scalar transport equation, mass transfer correlation \(^{[29]}\) | Desulfurization |
| 1982 | El-Kaddah and Szekely[38] | Ladle | HM | Unknown gas | CaO + CaF₂ | 2D SS | Drift flux (L–G–P) | Scalar transport equation, mass transfer correlation \(^{[29]}\) | Desulfurization |
| 2002 | Pirker et al.[74] | Ladle | HM–slag | O₂/N₂ | No | 3D T | Couette (L–S) | Scalar transport equation | Desulfurization |
| 2010 | Sun et al.[39] | Ladle | HM | Ar | Mg | 1D SS | None | None | None | Gas and particle heat-up, particle penetration |
| 2011 | Nadif et al.[147] | Ladle | HM | N₂ | No | 3D T | NA | NA | NA | Pulsed gas injection |
| 2012 | Huang et al.[85] | Torpedo car | HM | N₂ | No | 3D T | Euler-Euler (L–G) | User defined function for kinetic model \(^{[73]}\) | Desulfurization |
| 2012 | Zhang et al.[41] | Torpedo car | HM | N₂ | No | 3D T | VOF (L–G) | REA | k–ε | None | Mixing time |
| 2017 | Tripathi et al.[77] | Ladle | HM | N₂ | CaC₂ | 3D T | Inhomogeneous model (L–G–P) | k–ε | None | None | Optimal lance type |
| 2019 | Ma et al.[148] | Ladle | HM | N₂ | No | 3D T | VOF (L–G) | STD k–ε | None | Clogging behavior |

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\(^{[a]}\)HM = hot metal; \(^{[b]}\)SS = steady-state; \(^{[c]}\)G = gas, L = liquid; \(^{[d]}\)P = particles, VOF = volume of fluid; \(^{[e]}\)NA = not available, REA = realizable, STD = standard.
Submerged lances conducted by Berner and Müller\[36\] suggest that the centric position is more suitable for hot metal desulfurization, as it provides more bath movement in the upper part of the ladle and is thus beneficial for the metal–slag reactions.\[36\] The efficiency of bath mixing in a ladle with gas injection using submerged lances was studied by Usui et al.\[38\]. Using physical modeling, they compared the mixing of a water bath (95% criterion) stirred with four gas-injection methods: straight lance, T-type lance, Y-type lance, and bottom gas injection with one nozzle. Usui et al.\[38\] reported that the shortest mixing times with a given stirring energy were achieved with the T-type lance, followed by Y-type, straight pipe, and bottom gas injection with one nozzle. The T-type lance was also the most efficient in experiments, in which liquid paraffin oil was used to simulate the slag layer. It was suggested that the better performance of T- and Y-type lances in terms of mixing time was attributable to higher efficiency of energy dissipation due to higher dispersion of the gas injected.

Combined gas-injection from both a submerged lance and bottom nozzle has also been studied. Nadif et al.\[147\] investigated the use of pulsed gas injection using physical and CFD modeling. The physical model was based on injection of air into liquid water using a submerged lance. The CFD simulations were conducted as a two-phase simulation (argon and hot metal) without reagent particles or slag. The surface of the bath was found to fluctuate more aggressively than in the case of continuous stirring, and it was hypothesized that this behavior would promote the emulsification of slag. Based on an industrial campaign, it was reported that using pulsed stirring the treatment time could be reduced by 1 min, whereas consuming 29% less argon compared with continuous gas injection.

In the study by Tripathi et al.\[37\], the shortest mixing times were achieved using a four port T-lance (TT) and a lance with two curved ports in mutually opposite directions (C-45), whereas the use of a straight lance was the least efficient in this regard, yielding the longest mixing times of the lances studied. The results of Tripathi et al.\[37\] support the reasoning of Usui et al.\[38\] that a shorter mixing time is associated with a higher dispersion of the gas injected. The numerical results for the industrial ladle were found to be in good agreement with the mixing times measured from a physical model, in which water and air were used to describe hot metal and nitrogen, respectively, and the residence and mixing times were measured using the electrical conductivity method with NaCl as the tracer. In an industrial experiment, the desulfurization rate constant was roughly 20% higher with a lance with two curved ports in mutually opposite directions (C-45) than with a regular T-lance.

As for torpedo cars, Carlsson et al.\[39\] conducted water-modeling experiments to study the effect of lance design on bath mixing. In their model, the dynamic similarity was established based on a modified Froude number

$$ F_{r_{\text{mod}}} = \frac{\rho_G u_C^2}{g \left( \rho_L - \rho_G \right)} $$

where $$ \rho_G $$ is the gas density, $$ u_C $$ is the gas velocity, $$ L $$ is the characteristic length, $$ g $$ is the standard gravity, and $$ \rho_L $$ is the liquid density. The mixing time was determined by measuring the change in electric conductivity of water using NaCl as the tracer. The tracer was injected close to the bath surface, whereas the conductivity was measured as far away from the nozzle as possible. By comparing five difference lance types (straight,
crossed, hockey-stick, T-hole, and 4-hole) they found that the shortest mixing time was associated with T- and 4-hole lances positioned asymmetrically in the vessel. The effect of the lance position and gas flow rate on bath mixing was studied using CFD modeling by Zhang et al.[41] The best mixing characteristics were obtained when the immersion depth of the lance was 4/5 of the bath height and a further improvement in mixing could be achieved by increasing the gas flow rate.[41] However, even in the best case, the mixing time (95% criterion) was 230 s.[41] As expected, the ends of the torpedo vessel were reported to be low velocity areas.[41]

In view of the available information, it seems that ladles have a characteristically higher mixing efficiency than the torpedo cars.[39,40,159] This is likely to be attributed to the fact that the relative size of the gas plume in torpedo cars is smaller than in ladles. To study the rate-controlling steps, Irons[40] established a simple mathematical model of the effect of carrier gas flow on resistances in CaC\textsubscript{2}-based desulfurization in a torpedo car. The study concluded that metal bath mixing is likely to have little effect on the overall desulfurization rate in torpedo cars, and is likely to play an even smaller role in desulfurization with lance injection in ladles.[49] This conclusion agrees well with the numerical simulations of El-Kaddah and Szekely[35] for desulfurization in 6 and 40 ton ladles.

### 3.1.3. Modeling of Gas-Particle Jets

The behavior of the gas-particle jet is closely coupled with the performance of hot metal desulfurization, and consequently, plenty of research has been dedicated to studying different aspects of the associated phenomena ranging from heat-up of the jet in the lance to its penetration into the metal bath. A summary of studies on injection of powders into liquid metals is presented in Table 4.

An excellent synthesis of the fluid flow behavior of gas-particle jets relevant for hot metal desulfurization has been given by Farias and Irons.[46] They noted that with high particle loadings fine particles generally travel at velocities corresponding to that of the gas flow and labeled this behavior as coupled flow.[46] An uncoupled flow was described as a flow in which the particle loading is low and the boundary layers of the particles no longer overlap.[46] A further distinction was made to describe the penetration behavior.[46] When a coupled gas-particle flow penetrates into a liquid, the resulting flow regime is called jetting, whereas in the case of an uncoupled flow, the resulting fluid flow regime is labeled as bubbling.[46] The term transition regime refers to a fluid flow regime that has characteristics of both jetting and bubbling regimes.[46]

**Heat-up of gas-particle jets:** Along with the change in pressure, the heat-up of the gas can have a significant effect on the carrier gas velocity, and thereby affect the velocity of the particles conveyed by the carrier gas. Due to the difficulties in direct measurement, virtually no experimental information exists on the heat-up of the gas-particle mixture in the lance. Consequently, physical and numerical modeling has been used for estimating the heat-up in industrial ladles. Irons[46] studied heat transfer during submerged injection by injecting silica particles into liquid lead using nitrogen as the carrier gas. In these experiments, the inner heat transfer coefficient was found to be dependent on the particle loading, but the outer heat transfer coefficient was not affected by it. By making use of a 1D two-phase heat-up model,

**Table 4.** Modeling studies on the injection of powders into liquid metals.

| Year  | Study                | Physical | Numerical | Liquid(9)       | Lance(9) | Particles(9)          | Carrier gas |
|-------|----------------------|----------|-----------|-----------------|----------|-----------------------|-------------|
| 1979  | Engh et al[41]       | Yes      | No        | H\textsubscript{2}O | S        | Polystyrene, polythene, | Ar          |
| 1982  | Ghosh and Lange[46]  | Yes      | No        | H\textsubscript{2}O, ethanol; glycerine, glycerine + 20% H\textsubscript{2}O, 1,1,2,2-tetrabromoethane | S        | Na\textsubscript{2}CO\textsubscript{3}, SiO\textsubscript{2}, graphite powders | Ar          |
| 1983  | Irons and Tu[45]     | Yes      | No        | Pb              | S        | Coarse sand, SiO\textsubscript{2} flour | N\textsubscript{2} |
| 1985  | Farias and Irons[46] | Yes      | No        | H\textsubscript{2}O | S        | SiO\textsubscript{2} sand, hollow glass particles | N\textsubscript{2} or He |
| 1986  | Irons and Farias[47] | Yes      | No        | Pb or HS        | S        | Al(OH)\textsubscript{3}, SiO\textsubscript{2} | N\textsubscript{2} |
| 1987  | Irons[48]            | Yes      | No        | Pb              | S        | SiO\textsubscript{2} sand, SiO\textsubscript{2} flour | N\textsubscript{2} |
| 1994  | Zhuo and Irons[49]   | Yes      | No        | HM              | S        | CaD                   | N\textsubscript{2} or CO\textsubscript{2} |
| 2010  | Sun et al[50]        | No       | Yes       | HM              | S        | Granulated Mg         | Ar          |
| 2016  | Nakano and Ito[51]   | Yes      | Yes       | H\textsubscript{2}O(7) / Fe\textsuperscript{+}     | –        | Polystyrene\textsuperscript{9} / CaO\textsuperscript{+} | –          |
| 2017  | Tripathi et al[57]   | Yes      | Yes       | H\textsubscript{2}O(7) / HM\textsuperscript{+}     | S, T, T-4S, T-1S, TT, C-4S, H-4S | None\textsuperscript{9} / CaC\textsubscript{2} \textsuperscript{+} | Ar\textsuperscript{+} / N\textsubscript{2}\textsuperscript{+} |
| 2018  | Matsuzawa et al.[140] | Yes     | No        | H\textsubscript{2}O | S        | Polypropylene         | Ar          |
| 2019  | Ma et al.[148]       | No       | Yes       | HM              | T        | 60% Mg + 40% CaO      | N\textsubscript{2} |

\textsuperscript{9}HM = hot metal; \textsuperscript{10}C-4S = two curved ports in mutually opposite directions, HS = hockey-stick, H-4S = two spiral ports in mutually opposite directions, S = straight, T = T-lance, T-1S = two ports at 15º angle in mutually opposite directions, T-4S = two ports at 45º angle in mutually opposite directions, TT = four ports in mutually perpendicular directions; \textsuperscript{11}CaD = calcium diamide (commercial CaC\textsubscript{2} powder); \textsuperscript{12}In physical model; \textsuperscript{13}In CFD model.
Irons [48] estimated that under industrial conditions the temperature of the gas–particle mixture should be less than 500 °C at the lance exit.

Efforts to study the heat-up experimentally were continued by Zhao and Irons [49] using an induction furnace, in which calcium carbide powder was injected into hot metal along with nitrogen or carbon dioxide gas. As for plain gas injection, the first-order rate constant for heat loss increased linearly with the gas flow rate.

As computational resources have increased, the use of CFD to study the behavior of gas-particle jets has become feasible; examples of applications include studies on penetrability [50] and clogging [148] of particles. Sun et al. [50] analyzed the injection of Mg particles using a 1D mathematical model which accounted for the effect of the gas heat-up on particle motion in the lance and during penetration. As shown in Figure 6, the carrier gas was predicted to heat up to 307 °C (580 K) when reaching the lance tip, whereas the particles were hardly heated at all, reaching only 31 °C (304 K) at the lance tip. At the lance tip, the velocities of the carrier gas and particles were predicted to be 83 and 54 m s⁻¹, respectively.

Tendency to clogging can constitute a significant problem in plant practice. Irons [48] reported that with injection of silica particles into liquid lead, clogging occurred in the bubbling regime when the inner temperature of the lance dropped below the liquidus temperature of the lead. Recently, Ma et al. [148] studied clogging of a T-shaped lance by simulating a situation in which one of the openings is clogged. Based on an SEM–EDS analysis, it was determined experimentally that the clogging was due to deposition of the reagent. To study the effect of the clogged lance on the fluid flow pattern, a numerical model based on RANS equations together with the k–ε turbulence model was set up. The interfaces, including the shape and coalescence of the particles, were tracked using the volume of fluid (VOF) model. The results of the numerical simulations suggest that the clogging of one lance opening induces a large “dead zone” on side the clogged opening of the T-lance. The predicted surface velocities on the side of the clogged opening were much lower than in the case of a nonclogged lance.

Some numerical estimates on the heat-up of the gas and particles after the penetration zone are also available. Using a 1D model for the gas plume, Farias and Irons [48,51] provided estimates for the heat-up of the gas-particle jet under industrial conditions. In their simulations, the reagent particles heat-up almost instantaneously to bath temperature upon injection. This is mostly attributable to the small size of the particles. The carrier gas reached the bath temperature only after 1 m of vertical rise.

**Penetrability of gas-particle jets**: A lot of research interest has been directed at studying the penetration behavior of particles. Matsuzawa et al. [160] divided experimental studies on penetration behavior into two categories: 1) experiments with fine powder with the aim of providing information on the macrosopic behavior of the system, and 2) experiments with relatively large single particles to provide detailed information on microscale phenomena.

As for the first category of experiments, Engh et al. [43] studied the penetration of gas-particle jets into liquids using a physical model. Both downward and horizontal lances were tested for injection of polystyrene, polythene, iron spikes, and sugar particles into water using air as the carrier gas. By equating the buoyancy of the liquid displaced by the solid particles with the momentum of the gas jet, they derived an equation to predict the penetration length of the particles

$$L = \left[ \frac{3\pi^2 u_p \sin \alpha}{\sigma \tan^2 \left( \frac{2}{3} \pi / 2 \right) \rho g} \right]^{1/2} L_0$$

where $m_p$ is the injection rate of the particles, $u_p$ is the velocity of the particles, $\alpha$ is the angle between the lance axis and the horizontal, $\theta$ is the jet cone angle, and $L_0$ is the slope distance of the lance tip from the surface of the liquid. Equation (31) was found to be in reasonable agreement with the penetration depths recorded in the case of downward injection. Depending on the particles used, the velocity of the particles was determined either by optical methods (still camera and high-speed cine-camera) or by mechanical measurement. In the cases studied, the particle velocity measured was approximately 40% of the velocity of the gas jet.

Ghosh and Lange [44] conducted physical modeling of powder injection with a submerged lance using a 1:25 scale physical model of a 280 ton ladle. In their experiments, SiO₂, Na₂CO₃, and graphite particles were injected into various liquids (water, ethanol, glycerine, glycerine + 20% water, and 1,1,2,2-tetrabromoethane) using argon as the carrier gas. The gas injection rate was chosen based on the similarity of the ratio of energy supplied by the gas injection to the mass of the liquid bath. The viscosity of the liquid was not found to influence the depth of penetration. The increase in liquid density decreased penetration only up to 1500 kg m⁻³; above this value, penetration was found to be insensitive to liquid density. The particle velocities measured were approximately 50% of the gas velocity, which falls between the value of 40% reported by Engh et al. [43] and the value of 65% predicted by Sun et al. [50] using numerical modeling.

On the basis of a fluid dynamic analysis of a coupled gas-particle jet, Farias and Irons [48,51] suggested that for a given entrainment constant $K$, the maximum dimensionless penetration $x_{\text{max}}^*$ is determined by the liquid to mixture density ratio $\Upsilon$ and the modified Froude number $F_{\text{mod}}$ [46].

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**Figure 6.** Simulated temperature profiles in the vertical direction of a straight submerged lance using Mg as reagent and argon as the carrier gas. Reproduced with permission [50]. Copyright 2010, Taylor & Francis.
where $z$ is the vertical penetration depth, $d_{\text{nuzzle}}$ is the nozzle diameter of the lance, $\rho_{M,\text{tip}}$ is the density of the mixture at the nozzle tip, and $u_{M,\text{tip}}$ is the mixture velocity at the nozzle tip. It is worth noting that for gas injection without reagent particles, the density and velocity of the mixture at the nozzle tip correspond to those of the carrier gas ($\rho_{M,\text{tip}} = \rho_{G,\text{tip}}$ and $u_{M,\text{tip}} = u_{G,\text{tip}}$) and Equation (34) reduces to Equation (30) i.e., the form used by Carlsson et al.\cite{49} for mixing in a torpedo car. Figure 7 shows the dimensionless penetration $z_{\text{max}}$ as a function of the modified Froude number (shown here as $N_{Fr}$) for different liquid to mixture density ratios. It is apparent that the liquid to mixture density ratio has a relatively strong influence on the penetrability so that heavier jets penetrate deeper (low value of $\gamma$) than lighter jets (high value of $\gamma$).

Continuing with the experiments on injection of silica particles into liquid lead initiated by Irons,\cite{48} Irons and Farias\cite{161} found that the cooling rate of the metal bath was only 30% of the cooling potential of the reagent in the case when it heated up to bath temperature. The deviation was suggested to be related to the penetration of the injected reagent being only partial.\cite{161} Irons and Farias\cite{161} suggested that because the penetrated particles are likely to reach the temperature of the metal bath very quickly, the fraction of the penetrated particles should be equal to 30%. The almost immediate heat-up to bath temperature seems plausible in view of the numerical simulations conducted by an earlier study by Farias and Irons.\cite{115} Although slightly higher values have been reported in later studies (see Table 5), it is apparent that a significant share of the particles does not penetrate into the metal bath irrespective of the reagent or carrier gas used.

As argued by Lee and Morita,\cite{163} the penetration of a single reagent particle into hot metal is affected by physical properties of the liquid, particularly the surface tension and the contact angle. As the surface tension of hot metal increases as a function of decreasing sulfur content,\cite{163} it is likely that the penetrability of the reagent changes to some extent during hot metal desulfurization. Different critical conditions for the penetration of a single particle have been derived based on force balance. Ozawa and Mori\cite{164} proposed a critical Weber number for penetration based on force balance

$$W_{Ec} = \frac{4A}{C_d} \left\{ 1 - \exp \left( \frac{3C_d}{2\rho_a^*} \right) \left[ \frac{4\rho_a^*}{3C_d} - 1 + \cos \theta + \frac{2G}{3A}\rho_b^* \right] + 2 \right\}$$

(35)

where $A$ is the correction factor, $C_d$ is the drag coefficient, $G$ is a dimensionless constant representing the relation between the buoyancy force and the surface tension force, whereas $\rho_a^*$ and $\rho_b^*$ are dimensionless densities. It was reported that a good match with experimental results for penetration of different materials in liquid mercury was obtained by setting $A = 2.5$. $\rho_a^*$ and $\rho_b^*$ were defined as follows

$$G = \frac{\rho_g \rho_b \sigma}{\rho_a^* C_L}$$

(36)

$$\rho_a^* = \rho_a^* + \frac{1}{4}$$

(37)

### Table 5. Estimates for the share of particles penetrating.

| Study | Liquid\(^a\) | Particles or powder\(^b\) | Carrier gas | Particles penetrating [%] | Basis of deduction |
|-------|---------------|-----------------|-------------|------------------|------------------|
| Irons and Farias\cite{161} | Pb | Al(OH)\(_3\), SiO\(_2\) | N\(_2\) | 30 | Heat losses |
| Chiang et al.\cite{162} | HM | CaC\(_2\) | Ar | 30–50 | Reaction rates |
| Zhao and Irons\cite{49} | HM | CaD | N\(_2\) or CO\(_2\) | 30\(^*\), 50\(^*\) | Heat losses |
| Vargas-Ramirez et al.\cite{72} | HM | CaO-SiO\(_2\)-CaF\(_2\)-FeO-Na\(_2\)O | N\(_2\) | 23 | Fitting of a mathematical model |
| Jin et al.\cite{77} | HM | CaO- and Mg-based | N\(_2\) | 98.05 | Force balance |
| Scheepers et al.\cite{78} | HM | CaC\(_2\) | N\(_2\) | 30 | Fitting of a mathematical model |
| Ma et al.\cite{88} | HM | CaO + Mg | N\(_2\) | 36.39 | Fitting of a mathematical model |

\(^a\)HM = hot metal; \(^b\)CaD = calcium diamide (commercial CaC\(_2\) powder); \(^*\) Loading below 60 kg Nm\(^{-2}\); \(^{**}\) Loading above 60 kg Nm\(^{-2}\).
\[ \rho_b^* = \rho^* - \frac{1}{2} \] (38)

where \( \sigma_L \) is the surface tension of the metal phase and \( \rho^* \) is the density ratio \( \rho^* = \rho_p / \rho_l \). Later, a slightly different variation of Equation (35) was proposed by Oeters,\(^1\), who showed that the alternative formulation typically yields higher critical Weber numbers than that proposed by Ozawa and Mori\(^{[164]}\). Ogawa and Matsumoto\(^{[165]}\) suggested that the critical velocity should be larger in the case of low wettability and proposed an expression in which the critical Weber number is modified using the ratio of the associated film thickness to the particle diameter (\( \alpha \))

\[ \text{We}_c = 1 \left(1 - \exp\left(\frac{0.66}{\rho^*} \left(1 + \cos \theta \right) + 2\right) \right) \] (39)

\[ \rho^*_0 = \frac{\rho_L^*}{4} \] (40)

\[ \rho_p' = \frac{W_p}{(V_p + V)} \] (41)

\[ \alpha = \Delta r / d_p \] (42)

where \( \rho^*_0 \) is the density ratio, \( \rho_p' \) is the apparent density of the particle, \( \rho_L^* \) is the density of the liquid, \( W_p \) is the weight of the particle, \( V_p \) is the volume of the particle, \( V \) is the volume of the associated film, \( \Delta r \) is the thickness of the associated film, and \( d_p \) is the particle diameter.

Nakano and Ito\(^{[51]}\) used 2- and 3D models to study the penetration of solid particles into liquid. The simulation model was based on the smoothed particle hydrodynamics (SPH) method. The authors first studied the injection of polystyrene particles into water and after successful validation with a water model, went on to simulate the injection of CaO particles into liquid iron at 1600 °C (1873 K). For a single CaO sphere with a diameter of 1 mm in molten iron, the numerical result of dense injection of solid particles into liquid. The simulation model was published using the smoothed particle hydrodynamics (SPH) method, went on to simulate the injection of CaO particles into liquid iron at 1600 °C (1873 K). For a single CaO sphere with a diameter of 1 mm in molten iron, the numerical result of particle penetration was found to be in reasonable agreement with the value of 2.3 m s\(^{-1}\) derived from the equation for the critical Weber number proposed by Ozawa and Mori\(^{[164]}\) with the equation by Ogawa and Matsumoto\(^{[165]}\) for nonwettable particles than with the equation by Ozawa and Mori\(^{[164]}\) for wettable particles. Despite the efforts to study penetration of individual particles, more research is required for the penetration of desulfurization powders under industrial conditions.

### 3.2. Modeling of Ladles with Mechanical Stirring (Kanbara Reactor)

The fluid flow phenomena in KRs has been studied extensively using physical (see Table 6) and numerical modeling (see Table 7). In the last 10 years, far more studies have been published on modeling fluid flows in KRs than on modeling fluid flows in ladles and torpedo cars with lance injection. In the

| Year | Study | System | Gas injection | Particles* | Measurements | Focus of the study |
|------|-------|--------|---------------|------------|--------------|-------------------|
| 1978 | Nakanishi et al.\(^{[42]}\) | H\(_2\)O–liquid paraffin | N\(_2\) | Alumina | Electroconductivity measurements (KCl) | Mixing time |
| 2009 | Liu et al.\(^{[160]}\) | H\(_2\)O | Air | No | High speed video camera | Bubble disintegration and dispersion |
| 2009 | Seshadri et al.\(^{[167]}\) | H\(_2\)O, H\(_2\)O–ZnCl\(_2\) | No | Plastic | Dispersion sampling | Particle dispersion |
| 2010 | Nakai et al.\(^{[172]}\) | H\(_2\)O | No | Styrene foam | Video camera | Particle dispersion |
| 2013 | Liu et al.\(^{[178]}\) | H\(_2\)O | CO\(_2\) | No | pH measurements | Bubble disintegration and dispersion |
| 2014 | Horiuchi et al.\(^{[148]}\) | H\(_2\)O–liquid paraffin, H\(_2\)O–tetradeacane | No | No | Video camera | Liquid-liquid mixing pattern |
| 2014 | Horiuchi et al.\(^{[149]}\) | Ion-exchanged H\(_2\)O | No | No | Electroconductivity measurements (benzoic acid) | Liquid-liquid mass transfer, liquid-gas mass transfer |
| 2014 | Shiba et al.\(^{[170]}\) | HCl (aq.) | No | Perlite | Electroconductivity measurements (HCl) | Solid-liquid mass transfer |
| 2015 | Nakai et al. \(^{[171]}\) | H\(_2\)O | N\(_2\) | Teflon | Video camera | Flux dispersion and aggregation |
| 2017 | Ji et al.\(^{[172]}\) | H\(_2\)O | N\(_2\) | None | Video camera | Bubble size distribution |
| 2017 | de Menezes Torres et al.\(^{[173]}\) | H\(_2\)O | No | Polypropylene | Electroconductivity measurements (KCl), pH measurements (CO\(_2\)) | Mixing time, gas-liquid interaction particle dispersion |
| 2018 | Song and Park\(^{[27]}\) | H\(_2\)O–paraffin oil | N\(_2\) | None | Concentration measurements (thymol) | Mass transfer between liquid bath and top phase |
| 2019 | Li et al.\(^{[174]}\) | H\(_2\)O | No | EVA | Torque measurements | Drawdown mechanism of particles |

*EVA = ethylene-vinyl acetate copolymer.
following, the modeling studies related to the fluid flow field, reagent dispersion, and bubble dispersion are discussed in detail.

### 3.2.1. Fluid Flow Field and Mixing Patterns

The fluid flow field in the KR is characterized by the bath motion induced by the rotating impeller. CFD simulations of physical models\(^{[53,158,172,175]}\) and actual KRs\(^{[34]}\) suggest that although KRs have relatively good mixing characteristics, the bottom of the bath directly below the impeller is typically a low velocity region. Various means to improve the fluid flow conditions have been studied using numerical modeling. As for the impeller, the studied aspects include the effect of the impeller geometry,\(^{[158]}\) the impeller depth,\(^{[54]}\) the impeller rotation rate,\(^{[175]}\) and the variable impeller rotation direction.\(^{[172]}\)

Physical modeling has been applied successfully to study the liquid–liquid mixing patterns\(^{[168]}\) and related mass transfer in mechanically stirred ladles.\(^{[169,170]}\) As shown in Figure 8, Horiuchi et al.\(^{[169]}\) suggested that there are three types of mixing patterns in a mechanically stirred ladle: Region I: no dispersion of liquid phases; Region II: the vortex of the top phase reaches the impeller position and begins to disperse; Region III: both the top phase and the gas phase reach the impeller position and heavy dispersion of the top phase occurs.

The transfer from region I to region II is promoted by increases in the impeller rotation speed, the ratio of the top phase volume to the liquid phase volume, the density of the top phase, the impeller diameter and the vessel diameter, and by a decrease in the impeller depth, whereas the transition from region II to region III is affected by the same parameters except for the vessel diameter and the ratio of the top phase volume to the liquid phase.\(^{[168]}\)

Horiuchi et al.\(^{[169]}\) studied the related liquid–liquid mass transfer in a physical model by following the transfer of benzoic acid between liquid paraffin and water, whereas the liquid–gas mass transfer was studied by following the absorption of CO\(_2\).\(^{[169]}\) The liquid–liquid mass transfer rate follows an S-shape curve so that it is virtually constant in region I, increases rapidly as the system moves to region II, but increases more slowly near region III and in region III.\(^{[169]}\) The liquid–gas mass transfer rate increases slowly as a function of the impeller rotation rate in regions I and II, but increases sharply as a function of the impeller rotation rate in region III.\(^{[169]}\)

Later, Shibata et al.\(^{[170]}\) extended the analysis to solid–liquid mass transfer by conducting physical modeling experiments, in which the rate of an ion-exchange reaction between pearlite particles and HCl aq. was determined using electroconductivity measurements. The increase of the solid–liquid mass transfer rate as a function of impeller rotation rate was moderate in regions I and III and strong in the region II. The impeller depth did not have much effect in region I, but had a strong effect in region II and a moderate effect in region III. For a given stirring energy, mechanical stirring was reported to result in a higher...
solid–liquid mass transfer rate than with gas injection. The aforementioned findings are in qualitative agreement with the results by Nakai et al.\[52\] who conducted high-temperature experiments using a 70 kg furnace and found that the rate of desulfurization reaction followed first-order kinetics and that the rate constant increased considerably when the system moved from “non-dispersion” (i.e., region I) via transitory dispersion (i.e., region II) to complete dispersion (i.e., region III).

3.2.2. Particle Dispersion

In a KR, the reagent is usually added from the top and is coarser than that used in lance injection. Several authors have studied means to improve the dispersion of particles and fluxes in the KR process.\[52,53,171\] Nakai et al.\[52\] studied the effect of the impeller rotation rate and immersion depth on particle dispersion using physical modeling and found that the particle dispersion increased strongly by increasing the rotation rate of the impeller. The positive effect of a higher impeller rotation rate on the desulfurization rate has been confirmed by high-temperature experiments in an induction furnace.\[52\] The numerical calculations by Fan et al.\[54\] suggest that the effect of the impeller geometry on the bubble dispersion is secondary compared with the impeller rotation rate and reagent particle size. Ji et al.\[53\] conducted simulations using a Euler–granular model which suggest that the entrainment and dispersion of the particles is increased when a variable-velocity stirring mode is used.

As the density of the reagent particles is typically much lower than that of hot metal, an important aspect of the particles dispersion is their drawdown into the metal bath. Recently, the drawdown mechanism of the particles was investigated in detail by Li et al.\[174\] by modeling the particles in a Lagrangian framework. Their results indicate that the drawdown of the particles is dominated by axial circulation at shallow impeller depths and by eddies at deep impeller depths.\[174\]

Aggregation of the flux reduces the interfacial area available for reactions and consequently, methods to avoid the agglomeration of flux in the KR process have been studied. Using physical modeling, Nakai et al.\[171\] showed that more flux aggregation is observed in the case of batch addition than in the case of continuous addition or powder blasting.

3.2.3. Bubble Dispersion

The injection of gas has been studied as a way to increase the dispersion of the reagent particles. De Menezes Torres et al.\[173\] studied the effect of the rate and position of gas injection in a 1:7 scale model of a 315 ton mechanically stirred vessel. In their study, the criteria for the impeller rotation velocity and liquid viscosity were derived from Froude and Reynolds numbers and are expressed by Equation (43) and (44), respectively, whereas the criterion for dynamic similarity of gas injection was derived from the modified Froude number as shown in Equation (45).

\[
\frac{N_P}{N_M} = \left( \frac{D_M}{D_P} \right)^{1/2}
\]

(43)

\[
\frac{\nu_{L,P}}{\nu_{L,M}} = \left( \frac{D_P}{D_M} \right)^{1/2}
\]

(44)

\[
\frac{\rho_{G,P}V_{G,P}^{2}}{\rho_{L,M}d_{nozzle,M}^{2}D_M} = \frac{\rho_{G,M}V_{G,M}^{2}}{\rho_{L,P}d_{nozzle,P}^{2}D_P}
\]

(45)

where the subscripts P and M denote a prototype and model, respectively, and N is the rotation velocity of the impeller, D is the impeller diameter, \(\nu_L\) is the kinematic viscosity of the liquid phase, \(\rho_G\) is the density of the gas phase, \(V_G\) is the volumetric gas injection rate, \(\rho_L\) is the density of the liquid phase, and \(d_{nozzle}\) is the nozzle diameter. The results of de Menezes Torres et al.\[173\] indicate that the presence of gas injection reduced the mixing time by 20% and increased the particle dispersion up to 40%. Furthermore, gas injection from the base center of the impeller or from the ladle bottom was found to be more efficient than gas injection from the center of the lateral faces of the impeller.

The effect of the impeller geometry of the bubble dispersion and disintegration was studied by Liu et al.\[158\] using a water model. The liquid–gas mass transfer coefficients were determined by measuring the absorption of CO\(_2\) in an aqueous...
NaOH solution. Their results indicate that the geometry of the impeller has a significant effect on the bubble dispersion and disintegration, gas–liquid mass transfer and power consumption. Ji et al.\textsuperscript{[172]} coupled a Euler–Euler model with a bubble population model to study the bubble size distribution and the related break-up and coalescence effects in a physical model of a KR. The results suggest that increasing the rotation speed of the impeller increased the bubble disintegration and dispersion in clockwise–anticlockwise and clockwise variable-speed rotation modes.\textsuperscript{[172]} Increasing the gas flow rate was reported to be a disadvantageous way to increase the disintegration of bubbles as it worsened the hold-up and bubble size distributions.\textsuperscript{[172]}

4. Conclusions

The aim of this article was to provide an overview of experimental and modeling studies on hot metal desulfurization. Based on the analysis of the available literature, the following conclusions were drawn.

As for desulfurization with lance injection, the main reaction mechanisms established by mathematical models are the transitory (metal–particle) and permanent (metal–slag). These reaction mechanisms differ in terms of kinetic behavior and thermodynamic driving force. The main resistances of the transitory reaction are the resistance of the diffusion boundary layer surrounding the particles and the resistance of the product layer. As for the permanent reaction, it has been suggested that the desulfurization rate is controlled by mass transfer in the metal phase. The main reaction mechanisms in the Kanbara process are similar in principle to desulfurization with lance injection, albeit the reaction areas and kinetics differ from those of a lance injection in a ladle or a torpedo car.

In recent years, as more data has continuously become available, there has been increasing interest in applying data-driven methods to improve the predictive accuracy. A common methodology in modeling hot metal desulfurization is to apply efficient search methods, for example GAs, in model identification tasks. The data-driven models have been proven effective especially in hot metal desulfurization, as some of the process phenomena cannot be accurately quantified with current technologies.

With the help of modeling it has been established that ladles with lance injection exhibit—except for the quiescent bottom—a circulating pattern roughly similar to gas-stirred ladles. Bath mixing is dominated by the gas flow instead of reagent particles and the efficiency of mixing is affected greatly by the type of lance tip used. For a given specific mixing energy, mixing in ladles is more efficient than in torpedo cars. However, bath mixing is not likely to have much effect on the overall desulfurization rate.

In mechanically stirred ladles, the fluid flow field is dominated by the operating practice of the impeller. Three main mixing patterns can be identified on the basis of the vertical position of the vortex. These patterns differ in terms liquid–liquid, liquid–gas, and liquid–solid mass transfer as well as in the resulting mass transfer behavior. Aside from the way the impeller is operated, the dispersion and agglomeration of the reagent particles can also be affected by the method of particle injection. Penetration studies suggest that the coupling of the gas and particles affects the penetration behavior to a great extent. The coupling is affected by loading, particle size as well as heat-up and acceleration of the gas in the submerged lance. However, in the light of the available information, no significant heat-up of the reagent particles takes place prior to exiting the lance. The available information regarding the effect of particle size on penetration under industrial conditions remains limited. More information is required also regarding the residence times of the reagent particles.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

fluid mechanics, hot metal desulfurization, modeling, powder injection

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[1] W. Meichsner, K. H. Peters, W. Ullrich, H. Knahl, J. Met. 1974, 26, 55.
[2] F. Schrama, B. Van den Berg, Millenium Steel India 2014, 4, 26.
[3] F. Oeters, Metallurgie der Stahlherstellung, Verlag Stahleisen mbH, Düsseldorf, Germany 1989, p. 503.
[4] S.-Y. Kitamura, Treatise on Process Metallurgy, Volume 3: Industrial Processes (Eds: S. Seetharaman, A. McLean, R. I. L. Guthrie, S. Sridhar), Elsevier, Oxford, United Kingdom 2014, pp. 177–221.
[5] H. Pohl, W. Maschlinka, Stahl Eisen 1967, 87, 190.
[6] F. Oeters, U. Pückoff, R. Scheel, P. Strohmenger, Hoesch Ber. Forsch. Entwickl. unserer Werke 1969, 4, 71.
[7] U. Nölle, U. Pückoff, P. Strohmenger, Stahl Eisen 1972, 92, 1085.
[8] A. S. Zubrev, M. F. Sidorenko, V. A. Kudrin, Izvest. Akad. Nauk SSSR 1972, 10.
[9] H. Sandberg, Ironmaking Steelmaking 1977, 4, 230.
[10] J. C. Niedringhaus, Ph.D. Thesis, Carnegie Mellon University, Pittsburgh, PA, USA 1986.
[11] H.-M. Delhey, E. Schürmann, W. Fix, L. Fiege, Stahl Eisen 1989, 90, 1207.
[12] C. Brodrick, in Proc. of the 7th Int. Heavy Minerals Conf. “What next, Southern African Institute of Mining and Metallurgy, Drakensberg, South Africa 2009.
[13] E. Schürmann, R. Bruder, K. Nürnberg, E. Schulz, Stahl Eisen 1979, 99, 181.
[14] F. Schrama, B. van den Berg, G. van Hattum, in Proc. of the 6th Int. Congress on the Science and Technology of Steelmaking, The Chinese Society for Metals, Beijing, China 2015, pp. 61–66.
[15] F. N. H. Schrama, E. M. Beunder, B. Van den Berg, Y. Yang, R. Boom, Ironmak. Steelmak. 2017, 44, 333.
[168] S. Horiuchi, M. A. Uddin, Y. Kato, N. Kikuchi, ISIJ Int. 2014, 54, 82.
[169] S. Horiuchi, M. A. Uddin, Y. Kato, Y. Takahashi, Y. Uchida, ISIJ Int. 2014, 54, 87.
[170] R. Shiba, M. A. Uddin, Y. Kato, S.-Y. Kitamura, ISIJ Int. 2014, 54, 2754.
[171] Y. Nakai, Y. Hino, I. Sumi, N. Kikuchi, Y. Uchida, Y. Miki, ISIJ Int. 2015, 55, 1398.
[172] J.-H. Ji, R.-Q. Liang, J.-C. He, ISIJ Int. 2017, 57, 453.
[173] F. de Menezes Torres, C. A. da Silva, I. A. da Silva, P. H. Resende Vaz de Melo, M. A. Lourenço, Tecnol. Metal. Mater. Miner. 2017, 14, 204.
[174] M. Li, Y. Tan, J. Sun, D. Xie, Z. Liu, Chin. J. Chem. Eng. 2019, 27, 247.
[175] R. Liang, J. Ji, F. Yan, J. He, Appl. Mech. Mater. 2012, 130–134, 3050.
[176] L. Xiao, K. Chen, B. Dan, Z. Rong, Int. J. Simulat.: Syst. Sci. Technol. 2016, 17, 61.
[177] L. Xiao, K. Cheng, B. Dan, Z. Rong, R. Wang, Adv. Mech. Eng. 2016, 8, 1.