Original Article

Challenges and opportunities in modeling liquid steel processing using computational thermodynamics – the case of secondary metallurgy

André Luiz Vasconcellos da Costa e Silva [1]*

Abstract

The developments in computational thermodynamics (CT) in the last decades have made possible not only the understanding of many aspects of steel behavior during processing and application but also opened the avenue for "Integrated Computational Materials Engineering" which is fast becoming reality. When it comes to the processes that lead to the initial shape and composition of the products, significant advances have also been made on the design of solidification processing, from foundry to continuous and ingot casting as well as additive manufacturing. On the other hand, progress in developing a better understanding of liquid steel processing and of extrapolating this knowledge to design better and more efficient processes has evolved at a relatively slower pace. While most of the thermodynamics needed to understand and control liquid steelmaking operations are well established and consolidated in databases, there is considerable uncertainty on the conditions for mass transfer and their relations to the operational parameters (such as injected gas flow in ladle metallurgy, blow conditions in converter or tapping conditions both in converter and electric furnace) during steelmaking processes and this requires additional investigation and improved sampling. This has led to three main approaches to process control and development: (a) handling of "big data" to derive predictive models (within the bounds of available data) which is extremely useful for process control (b) physico-chemistry based models supported by CT that may be useful for process development and (c) physico-chemistry based models with the use of "big data" for adjustment of some parameters and partially or totally supported by CT which may or may not be useful in process development. In the present paper, we present some recent efforts and results in this area, and highlight the difficulties, limitations and advantages of using models based essentially on physical chemistry fundamentals. We also discuss the possibility of using different approaches, by presenting and comparing selected examples using the three main approaches mentioned above. We try to further the discussion about which would be the more promising approaches both for control and for development of liquid steel processing operations.

Keywords: Steelmaking; Ladle metallurgy; EERZ; Mass transfer; Kinetics.

1 Introduction

In 1876, eleven years after Sir Henry Bessemer patented [1] his converter and started the development of tonnage steel production, JW Gibbs, published a framework adequate to properly predict the equilibrium of substances [2]. Many authors were studying the question of chemical equilibrium at the time (e.g. [3]) and some published their concepts before Gibbs, but the complete formulation of Gibbs is probably the first time the complete problem was faced and solved. Brooklyn bridge, a massive structure hanging from steel cables was inaugurated in 1883 [4], about fourteen years before Sir William Chandler Roberts-Austen published the first reasonable attempt at an Fe-C "phase diagram" (with the title "freezing point curves of carburized iron") [5]. After the work of Gibbs started to be understood, the use of thermodynamics in metallurgy and chemistry evolved very quickly. Around 1910 Howe published the first Fe-C phase diagram that obeyed Gibbs phase rule [6]. In 1913 Lewis formulated the equation we have used for many decades, relating the Gibbs free energy change of a reaction to its change in the "standard states" and the activities (or fugacities) of reactants and products. This has opened a wide avenue of applications of thermodynamics in metallurgy, that will be reviewed elsewhere [7]. Here we briefly focus on the evolution as applied to steelmaking. Concerning this progress, it is sufficient to say that after a considerable volume of very relevant publications, notably by Charles Herty, Jr. [8] at the US Bureau of Mines [9] and also sponsored by the Carnegie Institute [10], the 1944 edition of the AIME classical book "Open Hearth Steelmaking", included a chapter by John Chipman [11] detailing the thermodynamic treatment of compound formation, activities in dilute solutions, deoxidation reactions in steels, among other most relevant topics. During the next decades there were significant developments in understanding slags, measuring

---

[1]*Escola de Engenharia Industrial Metalúrgica de Volta Redonda – EEIMVR, Universidade Federal Fluminense – UFF, Volta Redonda, RJ, Brasil.*

*Corresponding author: andre.costaesilva@gmail.com

and modeling their properties and extending the knowledge about the behavior and interactions of a considerable number of solutes in iron as well as slag-steel equilibrium. This data has been summarized in many accessible and important publications (e.g. [12-14]). During the second half of the XXth Century many important steelmaking questions were solved using thermodynamics, especially in situations where equilibrium is approached. Thus, as reviewed elsewhere [15], many steelmaking and refining processes were understood and improved using thermodynamics. Some examples are: the proper control of deoxidation, in special with aluminum, was established [16,17]; the conditions to produce spring and tire cord wires with highly deformable inclusions, leading to outstanding fatigue life and processability were identified [18-20]; the use of calcium for avoiding nozzle clogging and produce isotropic structural steels [21-24] as well as significant improvements to achieve high cleanliness in bearing steels (e.g. [25]) as well as a number of other improvements in slag and process design were made. Around 1960 Larry Kaufman [26-28] established the foundations of the CALPHAD (Computer Calculation of Phase Diagrams) approach and started computational thermodynamics. Many thermodynamic problems that previously required substantial simplification or difficult calculations became amenable to treatment by this technique. Perhaps not surprisingly, in view of the progress already achieved in the use of thermodynamics in steelmaking, the complexity associated with properly modeling the thermodynamics of slags [29-33] and the importance of especially high accuracy in the dilute solute range, for the liquid metal [34], the method found much faster acceptance and expansion in the area of physical metallurgy [28,35-37]. In any case, soon the application of the CALPHAD method to steelmaking became very important too [34,38-40]. Using either the (modified) associated model for the slag [41,42] as in FactSage [43], or a cell model [38,44] as in CEQCSI [45], that evolved from the IRSID model (e.g. [46]) or the ionic liquid model [47,48] used by Thermo-calc [49], among other software and well developed thermodynamic databases, the applications of computational thermodynamics to steelmaking flourished starting on the beginning of the XXIst Century [46,50-52]. The fundamental aspects of the method, as applied to steelmaking problems, will be briefly presented in the next section.

Thermodynamics lays on a solid foundation and uses sound and consistent methods to solve many important problems in steelmaking while in other cases, by indicating the end state, helps one understand the driving forces and the general trends of the system. One of the reasons why this is true is the fact that the mechanism of the process needs not to be known to properly apply thermodynamics. When one tries to incorporate the changes that the material undergoes with time, during a process, and enter the realm of kinetics, the situation is less well defined. As LS Darken stated in the 1950-60 [53,54] *"the methods of kinetics, however, are step-by-step in which a knowledge of the detailed reaction mechanism is essential. [The thermodynamic] underlying theory rests on a completely solid basis. This is far from the case with kinetic data and even kinetic theory."* In the last decades significant progress has happened in the application of transport phenomena theory to steelmaking. As in chemical engineering [55], metallurgical engineering has opted to treat momentum, heat and mass transfer as one single discipline, in view of the similarities in the mathematical framework for the treatment of these phenomena [55]. In metallurgy, pioneering work on transport phenomena was performed mostly by N Themelis, J Szekely and JK Brimacombe, in the 1970s [56-60]. Mass transfer between two phases, however, continues to be a very complicated phenomenon to handle. All descriptions of kinetic processes happening at interfaces (such as slag-metal) in steelmaking and processing are fundamentally phenomenological. Even when the temperature is high enough that reaction kinetics does not has a significant role in the kinetics of the heterogeneous processes – i.e. those that happen at the interface between phases – that dominate steelmaking and refining, transport phenomena are handled via phenomenological descriptions [15]. These descriptions are frequently used, even if they deviate from our physical observations, provided they are useful in reaching results. Thus, the flux of a given species in phase, across the interface would be given by Equation 1 where k_s is the mass transfer of the species in this phase C_s^{bulk} is the concentration of species s in the bulk of the phase and $C_s^{\text{interface}}$ is the concentration of species s at the interface. It is evident that the units of the mass transfer coefficient will depend on the concentration unit chosen. If one uses mass/volume as a concentration unit, then k_s will be expressed in $\frac{\text{length}}{\text{time}}$ units (e.g. m/s). This is a first complicating issue when comparing mass transfer data from different authors.

$$J_s\left[\frac{\text{mass}}{\text{area time}}\right]=k_s\left(C_s^{\text{bulk}}-C_s^{\text{interface}}\right) \tag{1}$$

Three main theories have been formulated to predict values of the mass transfer coefficient, k_s. The film theory, developed in the 1920s, in which a stagnant film of the fluid would exist at the interface and mass transport through this stagnant film would be controlled by diffusion [61,62] (one should note that the first to formulate this model, remarked in his paper: "*The gas and liquid films at the boundary can be indicated as having a definite thickness, although actually no such sharp demarcation exists"* [61] . Two variations of a model developed in 1935 in which eddies are considered to reach the interface, stay there for a given volume of time and, during this time, exchange matter with the other phase via diffusion [63,64]. All theories modify the specie diffusion coefficient in the phase by a factor: either a hypothetical diffusion distance or a hypothetical time of residence or a hypothetical distribution of residence times. A skeptic might consider that, in most cases, the theories replace one unknown (k_s) by other unknown(s).

If one considers that mass transport in this single phase controls the process and, for simplification, assumes that the interface concentration of the transported species does not change with time a mass balance on the phase under consideration can be performed. The result of the mass balance will depend on the concentration units used, as shown in Equation 2 and Equation 3 (for detailed derivations see one of the cited textbooks, e.g. [15,56,59])

$$\frac{d\%_S(t)}{dt} = -\frac{Ak_s}{100W}\left(\%_S(t) - \%_S^i(t)\right) \tag{2}$$

$$\frac{dC_S(t)}{dt} = -\frac{Ak_s}{V}\left(C_S(t) - C_S^i(t)\right) \tag{3}$$

In both Equation 3 and Equation 2 the mass transfer coefficient appears together with the area. For a considerable time [62,65] it has been observed that the lumped variable Ak_s, the volumetric mass transfer coefficient, may be very useful, in special in situations where the system is agitated, since both the mass transfer coefficient and the effective interfacial area are affected by the agitation and it is usually impossible to separate the individual effects in the kinetics of mass transfer [65,66]. Unfortunately, Ak_s, may also be expressed in different units, depending on the units used in the investigation by different authors.

In the last decades, efforts have concentrated on finding correlations between either the mass transfer coefficient or the volumetric mass transfer coefficients and other parameters related to the process. This includes the use of dimensionless numbers [67-69] or other data calculated from process parameters such as dissipated stirring energy, for instance [70-72]. Some of the important correlations between stirring energy and mass transfer between two liquid phases will be discussed in the next sections.

2 Thermodynamic and kinetic techniques

2.1 Thermodynamic techniques

Beyond the limitations due to the complexity of using Wagner formalism [15,73], thermodynamic solutions that did not involve computational thermodynamic had to rely on some sort of model or equations for the activity of oxides in the slag, which can be very complex. The use of simple models as proposed by Ban-ya [74,75] has given reasonable approximation and many good regression equations are available in systems of interest for steelmaking, most of them developed by Ohta and Suito [76-78] among other. The efficacy of the use of this approach has been demonstrated (see for instance [79]), albeit it involves considerable work and has limitations due to the interpolation characteristics of the equations. The use of computational thermodynamics eliminates most of these difficulties [28], as long as reliable database are available, in special for the oxides, sulfides and fluorides in slag. As discussed above, these databases are available from more than one source. Hence, the calculations of thermodynamic equilibrium can be achieved with little effort with the proper computer, software and database, by the minimization of the Gibbs energy of the system for a set of conditions. The complexity in the use of computational thermodynamics lies in properly identifying the conditions and the correct interpretation of the results in relation to the problem considered. This has been discussed in detail in many previous publications (e.g. [15,50,80]) and will not be discussed here. Equilibrium calculations are needed to determine the final state of systems but also to determine conditions at interfaces, in kinetic problems in which the reaction is sufficiently rapid to maintain equilibrium at the interface [15]. The use of computational thermodynamics software coupled with kinetic models has become a reality in many areas [81] of material and metallurgical engineering, including steelmaking [82]. In most cases, however, specific software had to be written for the kinetic part of the model, which somehow limited the wider application of this approach. Some of the solutions to this problem are discussed in the next section.

2.2 Kinetic modeling techniques

In this section we review selected topics on kinetic modeling techniques, emphasizing information required to highlight what we considered current opportunities and challenges in the area, rather than presenting a complete review.

2.2.1 Interfacial concentrations

Under the premise of equilibrium at interface relatively simple solutions, including analytical solutions, can be formulated when only one element is transported through a two-phase interface [15]. Similarly, when two elements react at the interface forming a compound in the second phase, analytical solutions may be possible too [83]. Robertson and collaborators formulated a model considering the coupling of fluxes of many species reacting or transferring at an interface [84] which has been extensively adapted and used (see the review by Kitamura [85] for uses and evolution). This was an important contribution that made possible the solution of many kinetic modeling problems in steelmaking.

2.2.1.1 Mass transfer coefficient, volumetric mass transfer coefficient and other kinetic parameters

As mentioned in the introduction, the mass transfer coefficient of a given specie is $\mathbf{k_s}$, expressed in $\frac{\text{length}}{\text{time}}$ units. Since the group $\mathbf{Ak_s}$, frequently appears together in kinetic equations, it is frequently called volumetric mass transfer coefficient and should be expressed in $\frac{\text{volume}}{\text{time}}$ units. This is especially useful as agitation, which increases $\mathbf{k_s}$ normally also increases the effective area of an interface between two phases $\mathbf{A}$ and it is not simple to separate these effects.

Furthermore, once the mass balances (expressed similarly to the form of Equations 2 and 3) is integrated, “simple” equations such as shown in Figure 1 can be obtained.

In the Japanese literature the variable K, obtained in the description of the overall integral kinetics (as in Figure 1) is frequently called mass transfer coefficient, and has the units of $\frac{1}{\text{time}}$ [67,87]. The normal result of the integration when the transport in a single phase controls the process would be either Equations 4 or 5 and the density of the phase may need to be included in the equivalent of Equation 5, depending on the units of $\mathbf{k_s}$ in that case.

$$\mathbf{K} = \frac{\mathbf{Ak_s}}{100\mathbf{W}} \tag{4}$$

$$\mathbf{K} = \frac{\mathbf{Ak_s}}{\mathbf{V}} \tag{5}$$

To avoid this confusion, Graham [88] called this coefficient “mass transfer capacity coefficient”. In this paper, we follow the Japanese terminology and use mass transfer coefficient for k_s $\frac{\text{length}}{\text{time}}$ and volumetric mass transport coefficient for K $\frac{1}{\text{time}}$. No “mass transfer” coefficient expressed in $\frac{\text{volume}}{\text{time}}$ is employed, as used, for instance, by Conejo and collaborators [70].

2.2.2 The EERZ (Effective Equilibrium Reaction Zone) model

In recent years, an ingenious approach was developed to couple equilibrium thermodynamics with kinetics in a relatively simple way. By combining the circulation model concept probably first proposed by Hsieh and collaborators [89] and Oeters and collaborators [90] with classical kinetic models such as the one presented in Equation 1 it was possible to use computational thermodynamics to do successive equilibrium calculations to simulate mass transfer. The various contributions to this development are reviewed by van Ende et al. [91] and this type of model was named “Effective Equilibrium Reaction Zone”, or EERZ. The essential point, as will be seen in the next section, is that by using the proper adjustment of the circulation parameters in a model such as Hsieh´s, it is possible to calculate the kinetic evolution of a system by (a) calculating the equilibration of defined volumes of the system that would react at each moment (b) keeping track of the changes of each phase caused by the successive equilibration of these volumes, as will be detailed in the next section. This has made possible the creation of modules or routines in computational thermodynamics that made possible their simpler application to industrial applications, and they proliferated in the last decades (e.g. [91-97]). There are, however, still some important limitations to the modeling of steelmaking processes and that will be discussed next, together with some of the possibilities of circumventing them.

Hsieh and collaborators observed that if a phase p circulates with a given rate q, between a reservoir and a reactor which it leaves, after reaction with composition C_S^i of the specie s, a mass balance of s in the reservoir results in Equation 6.

$$\frac{dC_S(t)}{dt} = -\frac{q}{V}\left(C_S(t) - C_S^i(t)\right) \tag{6}$$

A comparison of Equation 3 and Equation 4 indicates that:

$$\frac{q}{V} = \frac{Ak_S}{V} \tag{7}$$

Thus, Equation 7 indicates that an apparent circulation rate can promote the same changes as mass flux in the conventional kinetic approach using a model as presented schematically in Figure 2. The equilibrated masses at each time interval Δt, indicated by m_s and m_m can be used to

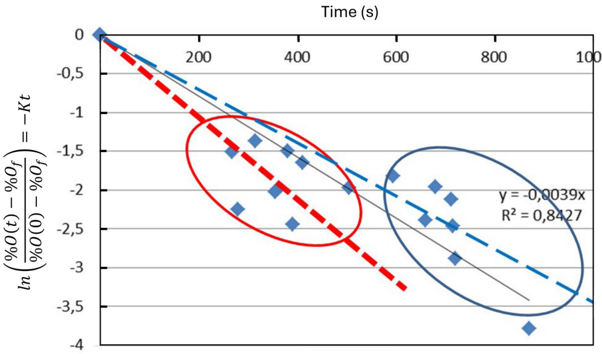


Figure 1. Kinetics of removal of oxygen from ladle during ladle furnace treatment. Three different kinetic constants $K\left(s^{-1}\right)$ were derived by the authors. One to describe the early stages of inclusion removal (red), another for the overall process and one for the final stages of the process (blue). See original reference for discussion. Adapted from [86].

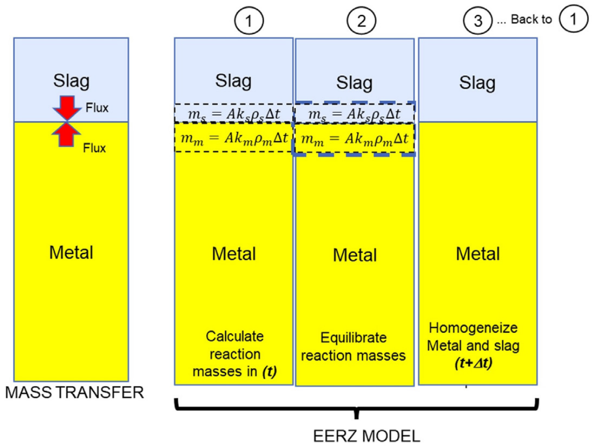


Figure 2. Schematic summary of the EERZ model. (See refs. [15, 93] for detailed discussion).

calculate in according to Equation 5 (using the mass of the phases and their mass concentrations, instead of their volumes). This makes possible to calculate the evolution of the compositions of two phase reacting at an interface with mass transfer control, using precise computational thermodynamic calculations.

2.2.3 Mass transfer coefficients

As discussed in the introduction, the three theories formulated to directly calculate mass transfer coefficients are of limited applicability in real problems and depend on the knowledge of other variables that are difficult to measure. In 1975, Nakanishi and Szekely proposed a correlation between the stirring energy dissipated in a phase and the mixing time in that phase [71] as shown in Figure 3.

In the same work they derived a formulation for calculating the stirring energy of a ladle subjected to gas stirring. It soon became evident that there should be a correlation between stirring energy and mass transfer coefficients as pointed out by Ishida and collaborators [87] who observed that the mass transfer coefficient in ladle desulfurization in gas agitated ladles correlate with gas flow rate, as shown in Figure 4.

Nakanishi proposed one of the first formulas for the stirring energy of a gas injected in a ladle. This was discussed by Mori and Sano [98] who considered the individual contributions of the injected gas on ladle stirring in different parcels of works (expansion due to pressure, due to temperature, transfer of kinetic energy…). Many authors reviewed or presented modified formulations of the stirring energy associated to gas injection, as briefly summarized in a paper by Conejo and coworkers [99] (and more recently in [70]) who compared 12 different formulas and found that six gave very consistent results, as the example of Figure 5 shows.

Attempts to correlate the stirring energy or the gas flow rate in industrial processes with the mass transfer coefficients met with variable success (e.g. [88,102]), however, as the two examples in Figure 6 show.

Observing this information, it seems that relatively good correlations between stirring power or gas flow rate with mass transfer coefficients can be obtained when results represent a limited number of tests or heats (e.g. Figure 4 or the various correlations reviewed by Ogawa [104]). However, when many heats are considered, even in the same equipment,

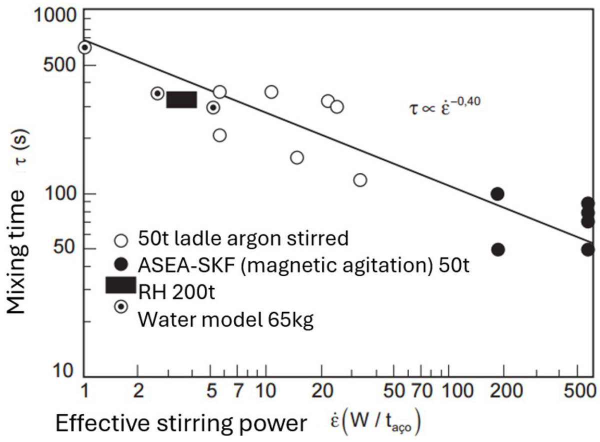


Figure 3. Homogenization time of a steel bath in a vessel as a function of the stirring energy density (Adapted from [71]).

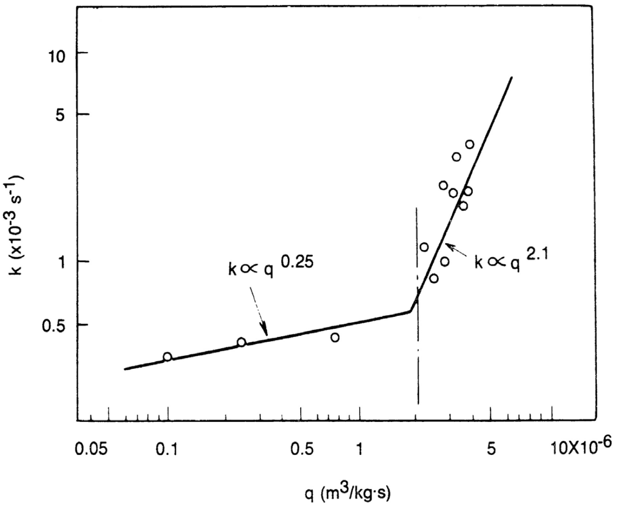


Figure 4. Volumetric mass transfer coefficient during desulfurization trials in a 2.5t laboratory ladle furnace as a function of argon rate of injection at the bottom of the furnace (Adapted from Ishida [87]). Straight lines and slope correlations proposed by [67]. Change of slope is explained as start of slag emulsification in metal, due to strong agitation.

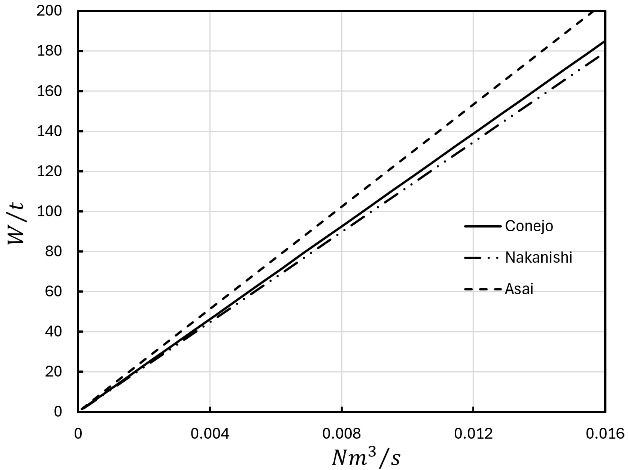
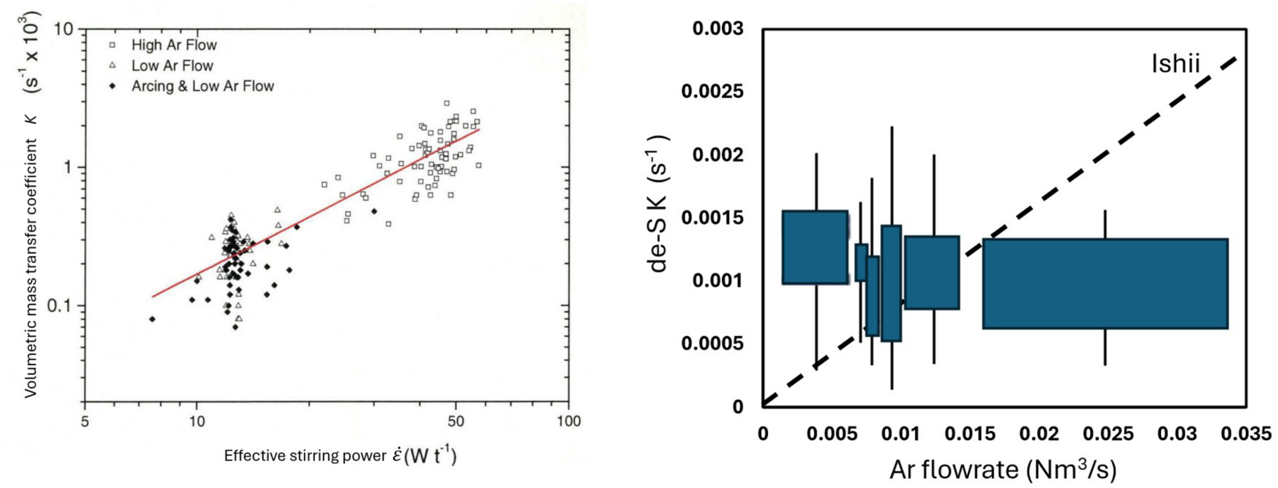


Figure 5. Calculated stirring energy in a 50t ladle, 1.78m deep, as a function of argon rate of injection at the ladle bottom. Calculated with the formulas proposed by Nakanishi et al. [71], Conejo and collaborators [99] and Asai and collaborators [67]. Formulas consider expansion of gas due to pressure change and temperature change (gas kinetic energy is not relevant [98,100]). The reader is cautioned since a significant number of formulas are given in the literature and many are equal (e.g. [71,101]) or have minimum differences between them.



(a)

(b)

Figure 6. De-S volumetric mass transfer as a function of stirring power or argon flow rate in ladle furnace. (a) Values obtained by Graham [88] in 165t ladle. (b) Values reported by Pistorius as box plots [102] for a 250t ladle furnace, compared with correlation proposed by Ishii and coworkers [103].

there seems to be more significant variations and discrepancies (e.g. Figure 6,[105]) and the variations become even more significant when different equipment or processes are considered (e.g. Figure 7, [103,106]).

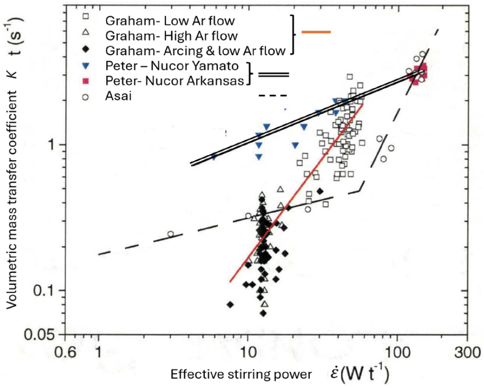


Figure 7. Comparison of volumetric mass transfer coefficients correlated with stirring energy, as determined by various authors (Adapted from [88]). Graham [88], Peter et al. [107], Asai et al. [67] (or Ishida et al. [87], Figure 4).

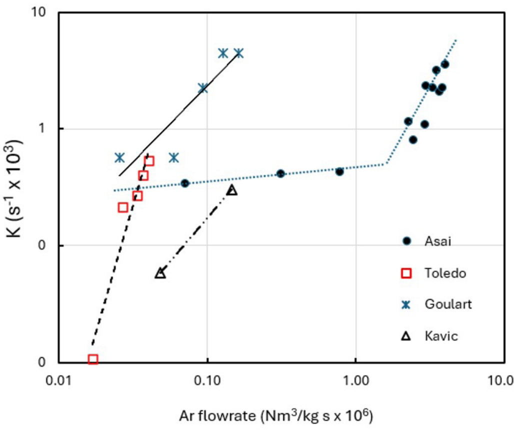


Figure 8. Comparison of volumetric mass transfer coefficients correlated with argon flow rate adjusted in recent studies, compared to the data of Asai et al. [67] (or Ishida et al. [87], Figure 4). Goulart and collaborators [93], Toledo [107] and Kavic and collaborators [97].

3 Discussion

3.1 Mass transfer and stirring correlations

Recent attempts at modeling processes in the ladle furnace using the EERZ indicated reasonable correlations between the volumetric mass transfer coefficients and the argon flow rate for the individual plants, as discussed above. There was, however, considerable variation between the results obtained at different plants and in their comparison with other modeling efforts (Figure 8), as shown in the previous item.

While the measurement or calculation of the stirring energy in electromagnetic stirred ladles is relatively precise when based on the proper data and theory [57,109] the calculation of the stirring energy in gas stirred ladles depends on the correct measurement and control of the Argon flowrate. This measurement is known to be quite difficult, dependent of eventual leakages, plug behavior and other process variables. For this reason, there is intense research on how to properly characterize stirring, eye opening and similar phenomena in gas stirred ladles [110-112]. Currently the most promising techniques appear to be image analysis of the bath surface [111] (which was used in the ladle studied by Graham [88] and ladle vibration monitoring [110]. Thus, while it can be expected that gas flow values will be reasonably consistent within heats of the same plant, when the operating practices are consistent, and reliable in laboratory conditions, it is not unexpected that actual values will vary between different plants, depending on the plant specifics. Furthermore, values on the same plant may be less than completely reliable (see the results in Figure 6b, for instance).

3.2 Model complexity

Many models used to describe the ladle furnace process focus on mass transfer at the slag-metal interface and the effects of heating, stirring and alloy and slag forming additions (e.g. [88,92,95,96]). When using the EERZ model, some software, such as Thermo-calc (Process metallurgy module in version 2025a), have presently limitation of using a single EERZ interface. FACTSAGE allows the definition of more complex representations (e.g. More than one EERZ reaction interface, as in [93] or in [97] who also considered multiple zones, as summarized in Table 1 but using a more complex procedure [113]. A more user friendly interface for multiple EERZ interfaces is currently under development in FACTSAGE [114]. Table 1 focuses only on multiple zones applying the EERZ concept in the two selected examples. Heat losses, heat input, oxygen pickup by open eye, metal or slag homogenization, formation of non-metallic inclusions in equilibrium with the liquid metal and additions to metal or slag are not considered EERZ specific and hence not included in Table 1.

Some models consider alloy addition yield explicitly [96,97]. However, if one considers that most alloys will either dissolve in the steel or oxidize and incorporate to the slag as oxides, one should assume that "yields" should only be considered in the cases of vaporization of additions (e.g. Calcium in some forms of addition) or fine powder loss to the exhaust system depending on the grain size distribution of the material being added. Other considerations of "yield" may behave as extra adjustable parameters of the model that can be relatively complex to evaluate and predict based on metallurgical knowledge.

Table 1. Examples of EERZ interfaces considered in different models

Ladle furnace model by van Ende and Jung [93]	Secondary refining model by Bernhard and collaborators [97]
Slag/steel reaction	Slag/steel reaction
Inclusion/steel reaction	Refractory dissolution into slag
Refractory dissolution into slag	Refractory dissolution into steel
refractory (ladle glaze) interaction with steel	

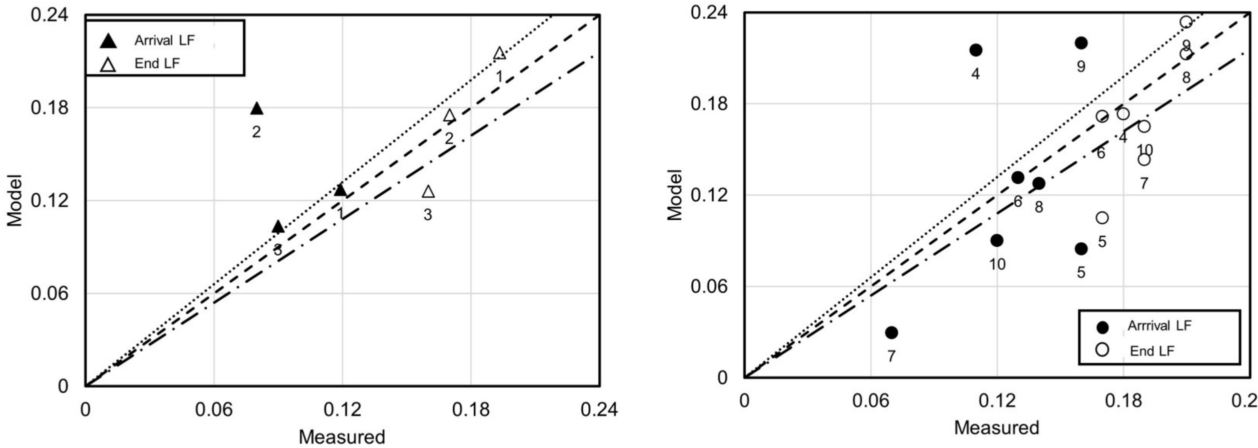
3.3 Reproduction and prediction of actual plant results

A considerable number of publications that present ladle furnace kinetic model compare the model results to a very limited number of actual industrial results (e.g. [93,95,99]). In some cases, even, results used to "validate" one model are repeated in publications of a different model by a different author. Some recent publications [92,108] have attempted to adjust the models (and hence the mass transfer coefficients) using a number of heats and then to test the model using another set of heats (e.g. Figure 9).

The results obtained with a limited number of heats can be promising when it comes to improving and developing practices such as deoxidation sequence and ladle additions [115] without going through extensive industrial tests.

3.4 Process control

Since at least the development of the EERZ model some attempts have been made to develop online versions to aid in process control of the ladle refining operation. Thermo-Calc [116] has reported work in collaboration with Georgsmarienhütte GmbH (GMH) introducing their EERZ model to the ladle furnace (Figure 10). As other authors, they remarked that some of the parameters that must be adjusted (beyond mass transfer coefficients) are complex (e.g. Air pickup [92,108] and seem not to be amenable to a



(a)

(b)

Figure 9. Comparison of the %Si in steel at the arrival at ladle furnace (modeled starting with EAF values and tapping additions) (a) Heats used to adjust the mass transfer coefficients (b) Test heats[92].

treatment based on "purely data-driven approaches such as machine learning".

The information that is currently available, however, does not allow one to evaluate how the model was adjusted to the process or if the adjustment includes any sort of feedback and information from previous heats is not known since the complete work is proprietary [116].

In view of the current limitations of adjusting a model using only predicted or measured process variables and metallurgical theory, Bernhard and collaborators [97] incorporated statistical analysis of the production data in the model. The authors mention "alloy addition yield" and carbon pickup from electrodes as examples of variables that were adjusted using this procedure. Apparently more than 25 variables were included in the statistical analysis which comprised a very extensive analysis of more than 10000 heats selected from one year production at VoestAlpine Stahl GmbH.

One example of results obtained by the model formulated as combination of metallurgical theory using computational thermodynamics databases and the EERZ approach for the description of kinetics and including the statistical analysis of the production data are shown in Figure 11.

3.5 Modeling strategies

3.5.1 Regression, machine learning, "big data"

Results of models using powerful data analysis techniques and educated guesses of the correlated variables produce very good results for process control applications, when mostly interpolation is performed [117]. It is well known that these techniques have limited extrapolation power and may even lead to erroneous results when used with data that is not covered in the range of the "learning" or fitting stage. Furthermore, the ability to gain insights into process improvement is also limited to the use of the model withing the fitting range. Should be population be very large and cover a wide range of conditions, there is a possibility

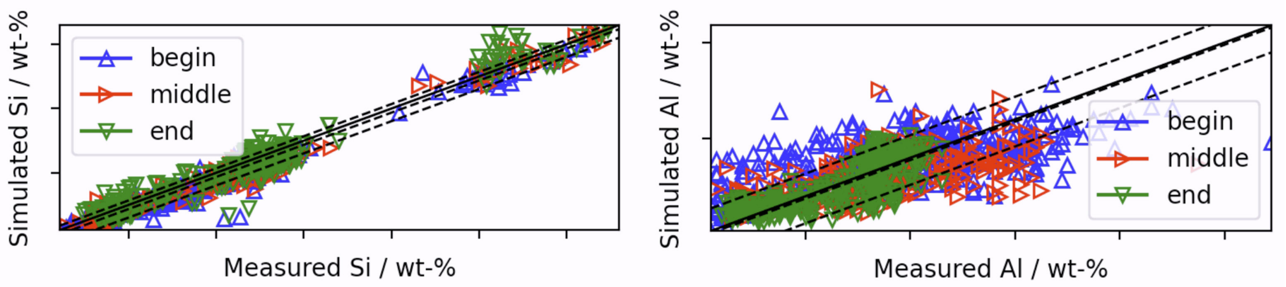


Figure 10. Calculated versus measured values in ladle furnace processing at a German mill, four years in use [116]. "Scales omitted in the publication for proprietary reasons", according to [116].

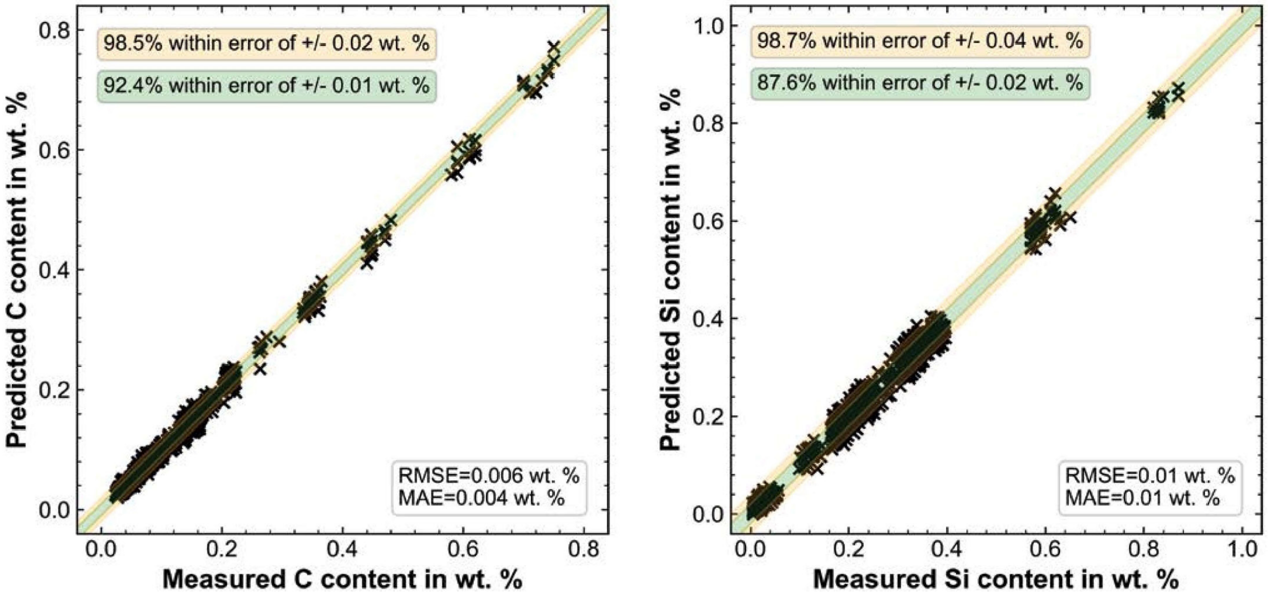


Figure 11. Calculated versus measured values in secondary metallurgy processing at VoestAlpine Stahl GmbH. Figure adapted from [97] (Standard deviations and variations shown do not represent the acceptable range of variation specified by VoestAlpine Stahl GmbH [97]).

that the model may produce insights, provided the variables included in the regression or in the model are, indeed, guessed in an educated way, i.e. there is some fundamental basis to assume that they may indeed be theoretically related to the variables being modeled.

3.5.2 Fundamental models

There are currently very few completely fundamental models. Even the simplest of models that incorporate mass transfer must rely on some regression or correlation to derive some of the important model variables. Assuming that these are kept to a minimum and are used/fitted respecting the physico-chemical aspects that govern them, these models have a good potential to explore "what-if" situations, even extrapolations within reasonable ranges and help prevent an extensive number of trial-and-error experiments in actual plant conditions. They are, however, at this point in time, limited in the extent to which they may be used even to support process control decisions.

3.5.3 Fundamental models with significant adjustments ("learning", fitting last results, etc.)

It seems that fundamental models can have some parameters fitted in order to achieve good or very good descriptions of processes (e.g. [97,116]). However, as these models involve the direct interests of the companies using/developing them as well as the commercial interests of some software houses, in some cases, the exact parameters that are fitted or adjusted are not readily informed in the publications. Furthermore, there may be some doubts about the exact method or mathematical formulations used to perform this adjustment. So, at this point, even with very promised results published, it is somewhat difficult to judge how efficiently the models would be in another situation. It does seem, however, that this technique may have great potential, if sensible and open adjustments are made and are made known to all parties involved in using the model. This would make it possible to judge, for instance, the extrapolation potential of the model. Thus, at this point, it seems like companies are either bound to use the two approaches described above or enter in a partnership with a software house for their model development.

4 Summary and conclusions

Even with a very advanced knowledge of the thermodynamics of steelmaking and refining processes, there are still significant difficulties in modeling the kinetics of these processes. In some cases, the fundamental physico-chemistry of mass transfer may be reasonably established but depends on parameters that are very hard to accurately measure in industrial conditions. Models that use the interpolation, learning or adjustment of a large, properly curated database and try to establish correlations with variables in accordance with metallurgical theory principles have been shown to be extremely effective in process control. They are limited when it comes to extrapolating from the ranges of the database used to adjust the model, however. Models that use sound principles, including computational thermodynamics still rely on some empirical adjustments of factors such as mass transfer coefficients, air pickup, etc. as discussed above. They have a great potential to give good insight to process development but are not accurate enough to be used for process control. This situation may persist for some time. Finally, using sound principles and a more extended number of adjustable parameters may be the most promising solution for process control and development, presently. However, this has to be carefully tested, since most publications of models that follow this approach omit important information, either because of proprietary information from the steelmaker or based in a common decision between user a developer.

Acknowledgements

The author thanks the many professors, colleagues in industry and academia, students and former students for their important contributions, insights and help during the development of the concepts summarized in the present paper.

References

1 Bessemer H. Improvement in machinery for the manufacture of iron and steel. United States Patent 49055. 1865 Jul 25 [cited 2025 May 25]. Available at: https://patentimages.storage.googleapis.com/14/6f/65/fadc30167c498b/US49055.pdf

2 Gibbs JW. On the equilibrium of heterogeneous substances. Transactions of the Connecticut Academy of Arts and Sciences. 1876;3:108-248.

3 von Helmholtz H. Die thermodynamik chemischer Vorgänge. Berlin: Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin; 1882 [cited 2025 May 25]. (3 pt. in 1 vol.). Available at: https://catalog.hathitrust.org/Record/012261709

4 Prentzas GS. The Brooklyn bridge. New York: Chelsea House Publishers; 2009. 120 p. (Building America: then and now).

5 Roberts-Austen WC. Fourth report to the alloys research committee. Proceedings - Institution of Mechanical Engineers. 1897;52(1):31-100.

6 Howe HM. The metallography of steel and cast iron. New York: McGraw-Hill Book Co. Inc.; 1916.

7 Costa e Silva A. Physical chemistry in steelmaking: the giants in this history. Tecnologia em Metalurgia, Materiais e Mineração 2025. In press.

8 Merica PD. Charle Holmes Herty, Jr. A biographical note. Washington DC: National Academy of Sciences; 1958.

9 Herty CH Jr. Fundamental and applied research on the physical chemistry of steel making. Denver: United States Bureau of Mines; 1930. (vol. 3054).

10 Herty CH Jr. The physical chemistry of steel making. Pittsburgh: Mining and Metallurgical Advisory Boards; 1934 [cited 2025 May 25]. Available at: https://catalog.hathitrust.org/Record/005735065

11 Chipman J. The physical chemistry of liquid steel. In: Washburn TS, Larsen BM, Marsh JS; Alloys of Iron Research, editors. Basic open hearth steelmaking. New York: American Institute of Mining; 1944.

12 Hino MK, Ito K, editors. Thermodynamic data for Steelmaking. Sendai: Tohoku University Press; 2010.

13 The Japan Society for the Promotion of Science. Steelmaking data sourcebook. New York: Gordon and Breach; 1988.

14 Stahlinstitut VDEh. Slag Atlas. Dusseldorf: Verlag Stahleisen; 1995.

15 Costa e Silva A. Refino dos Aços: fundamentos e aplicações. São Paulo. Editora Blucher; 2023.

16 Chipman J. Researches in steel. The Japan Institute of Metals and Materials. 1973;14(4):233-241.

17 Darken LS. Role of chemistry in metallurgical research. Transactions of the Metallurgical Society of AIME. 1961;221:653-671.

18 Onoe T, Ito S, Ogawa K, Mimura T, Matsumoto H, Maeda S. Shape control of inclusions for steel tire cord (development in ladle arc refining). Trans ISIJ. 1987;27:B249.

19 Shiwaku K, Yamada Y, Koarai J, Kawaguchi Y. Improvement of fatigue life of valve spring wire by reducing non-metallic inclusions. Warrendale: SAE International; 1985. (SAE Technical Paper; 850364).

20 Gattelier C, Gaye H, Lehmann J, Bellot J, Moncel M. Inclusion control in low-aluminum steel. Rev Metall - CIT. 1992:362-369.

21 Lu DZD. Kinetics, mechanisms and modelling of calcium treatment of steel [thesis]. Hamilton: McMaster University; 1992.

22 Pellicani F, Villette F, Dubois J. The production of clean, isotropic steel by means of calcium treatment with the Affival cored-wired. In: 4th International Conference on Injection Metallurgy - ScanInject 4; 1986 Jun 11-13; Lulea, Sweden. Lulea: MEFOS; 1986.

23 Bannenberg N. Inclusion modification to prevent nozzle clogging. In: 78th Steelmaking Conference Proceedings; 1995 Apr 2-5; Nashville. Warrendale, PA: ISS-AIME; 1995. p. 457-463.

24 Stouvenot F, Gaye H, Gatellier C, Lehmann J. Secondary Steelmaking Slag Treatment for Inclusions Control in Semi-Killed Steels. In: Electric Furnace Conference Proceedings; 1994 Nov 13-16; Nashville. Warrendale, PA: ISS-AIME; 1994. p. 423-428.

25 Beswick J, Gabelli A, Ioannides E, Tripp JH, Voskamp AP. Rolling bearing life models and steel internal cleanliness. In: Mahaney JK Jr, editor. Advances in the production and use of steel with improved internal cleanliness, ASTM STP 1361. West Conshohocken, PA: American Society for Testing and Materials; 1999.

26 Kaufman L. Coupled phase diagrams and thermochemical data for transition metal binary systems-VI. Calphad. 1979;3(1):45-76.

27 Kaufman L. The lattice stability of metals—I. Titanium and zirconium. Acta Metallurgica. 1959;7(8):575-587.

28 Saunders N, Miodownik P. CALPHAD: a comprehensive guide. London: Pergamon Press; 1998.

29 Sano N. Thermodynamics of slags. In: Sano N, Lu WK, Riboud PV, editors. Advanced physical chemistry for process metallurgy. San Diego: Academic Press; 1997.

30 Hallstedt B, Hillert M, Selleby M, Sundman B. Modelling of acid and basic slags. Calphad. 1994;18(1):31-37.

31 Hillert M, Kjellqvist L, Mao H, Selleby M, Sundman B. Parameters in the compound energy formalism for ionic systems. Calphad. 2009;33(1):227-232.

32 Pelton AD. Solution models. In: Sano N, Lu WK, Riboud PV, Maeda M, editors. Advanced physical chemistry for process metallurgy. San Diego, CA: Academic Press; 1997. p. 87-116.

33 Hillert M, Burton B, Saxena SK, Degterov S, Kumar KCH, Ohtani H, Aldinger F, Kussmaul A. Group 4: Modelling of Oxides - 1996 Ringberg Workshop. Calphad. 1997;21(2):247-263.

34 Kattner U, Erickson G, Spencer P, Schalin M, Schmid-Fetzer R, Sundman B, Jansson B, Lee B, Chart T, Costa e Silva A. Group 4 & 5: Process Modeling and applications - 1997 Ringberg Workshop. Calphad. 2000;24(1):55-94.

35 Lukas HL, Weiss J, Henig ET. Strategies for the calculation of phase diagrams. Calphad. 1982;6(3):229-251.

36 Ansara I, Burton B, Chen Q, Hillert M, Fernandez-Guillermet A, Fries SG, et al. Models for composition dependence. Calphad. 2000;24(1):19-40.

37 Lukas HL, Fries SG, Sundman B. Computational Thermodynamics. Cambridge: Cambridge University Press; 2007.

38 Gaye H, Welfringer J. Modelling of the thermodynamic properties of complex metallurgical slags. In: Fine HA, Gaskell DR, editors. Second International Symposium on Metallurgical Slags and Fluxes. Lake Tahoe, Nevada: TMS-AIME; 1984. p. 357-375.

39 Faral M, Gaye H. Metal slag equilibria. In: Fine HA, Gaskell DR, editors. Second International Symposium on Metallurgical Slags and Fluxes. Lake Tahoe, Nevada: TMS-AIME; 1984. p. 159-179.

40 Lehmann J, Gaye H, Yamada W, Matsumiya T. A statistical thermodynamics model of sulphur and fluorine bearing iron and steelmaking slags. In: 6th International Iron and Steel Congress; 1990 Oct 21-26; Nagoya, Japan. Nagoya: ISIJ; 1990. p. 256-263.

41 Pelton AD, Blander M. Thermodynamic analysis of ordered liquid solutions by a modified quasichemical approach-application to silicate slag. Metallurgical Transactions. B, Process Metallurgy. 1986;17B:805-815.

42 Pelton AD, Blander M. Computer assisted analysis of the thermodynamic and phase diagrams of slags. In: Fine HA, Gaskell DR, editors. Second International Symposium on Metallurgical Slags and Fluxes. Lake Tahoe, Nevada: TMS-AIME; 1984. p. 281-294.

43 Bale CW, Bélisle E, Chartrand P, Decterov SA, Eriksson G, Gheribi AE, et al. FactSage thermochemical software and databases, 2010–2016. Calphad. 2016;54:35-53.

44 Kapoor ML, Frohberg MG. Theoretical treatment of activities in silicate melts. In: Kubaschewski O, editor. Chemical Metallurgy of Iron and Steel, Proceedings of a Conference; 1971 Jul 19-21; Sheffield. London: ISI London; 1971. p. 17-22.

45 Lehmann J. Applications of arcelormittal thermodynamic computation tools to steel production. In: Reddy RG, Chaubal P, Pistorius PC, Pal U, editors. Advances in Molten Slags, Fluxes, and Salts: Proceedings of the 10th International Conference on Molten Slags, Fluxes and Salts 2016. Cham: Springer International Publishing; 2016 [cited 2025 May 25]. p. 697-706. Available at: http://link.springer.com/10.1007/978-3-319-48769-4_74

46 Gaye H, Lehmann J, Rocabois P, Ruby-Meyer F. Slag modelling and industrial applications. High Temp Mater Process. 2001;20(3-4):285-292.

47 Hillert M, Jansson B, Sundman B, Agren J. A two-sublattice model for molten solutions with different tendency for ionization. Metallurgical Transactions. A, Physical Metallurgy and Materials Science. 1985;16A:261-266.

48 Sundman B. Modification of the two-sublattice model for liquids. Calphad. 1991;15(2):109-119.

49 Sundman B, Jansson B, Andersson JO. The Thermo-Calc databank system. Calphad. 1985;9:153-190.

50 Costa e Silva A. An overview of the use of CALPHAD methods in steelmaking. Journal of Mining and Metallurgy. 1999;35B(1):85-112.

51 Jung IH. Overview of the applications of thermodynamic databases to steelmaking processes. Calphad. 2010;34(3):332-362.

52 Costa e Silva A. Controle de Inclusões não-metálicas em aços: passado, presente e futuro. São Paulo: ABM; 2005. (Keynote Lecture In: 60 Congresso Anual da ABM, Belo Horizonte, MG).

53 Darken LS. Kinetics of metallurgical processes. In: Philbrook WO, Bever MB, editors. Basic open hearth steelmaking. 2nd ed. Pittsburgh: AIME Pittsburgh; 1951.

54 Darken LS. Kinetics of metallurgical Processes In: Sims C, editors. Electric furnace steelmaking. Pittsburgh: AIME Pittsburgh; 1962.

55 Bird RB, Stewart WE, Lightfoot EN. Transport phenomena. 2nd ed. Weinheim: Wiley; 2005. 895 p.

56 Richardson FD. Physical chemistry of melts in metallurgy. London: Academic Press; 1974.

57 Szekely J. Fluid flow phenomena in metals processing. New York: Academic Press; 1979. 437 p.

58 Poirier DR, Geiger GH. Transport phenomena in materials processing. Cham: Springer International Publishing; 2016 [cited 2025 May 25]. Available at: http://link.springer.com/10.1007/978-3-319-48090-9

59 Themelis NJ. Transport and chemical rate phenomena. Basel: Gordon and Breach; 1995. 369 p.

60 Seetharaman S, editor. Treatise on process metallurgy: Volume 4, Industrial plant design and process modeling. 2nd edition. Amsterdam: Elsevier; 2024.

61 Whitman WG. The two film theory of gas absorption. International Journal of Heat and Mass Transfer. 1962;5(5):429-433.

62 Lewis WK, Whitman WG. Principles of gas absorption. Industrial & Engineering Chemistry. 1924;16(12):1215-1220.

63 Higbie R. The rate of absorption of a pure gas into a still liquid during short periods of exposure. Trans AIChE. 1935;31:365-389.

64 Danckwerts PV. Significance of Liquid-Film Coefficients in Gas Absorption. Industrial & Engineering Chemistry. 1951;43(6):1460-1467.

65 Yoshida F, Akita K. Performance of gas bubble columns: volumetric liquid-phase mass transfer coefficient and gas holdup. AIChE Journal, American Institute of Chemical Engineers. 1965;11(1):9-13.

66 Fruehan RJ. Mass transfer between liquid metals and injected gases. Metals Technology. 1980;7(1):95-101.

67 Asai S, Muchi I, Kawachi M. Fluid flow and mass transfer in gas stirred ladles. In: Katz S, Landefeld CF, editors. Foundry processes. Boston, MA: Springer US; 1988 [cited 2025 May 25]. p. 261-292. Available at: http://link.springer.com/10.1007/978-1-4613-1013-6_9

68 Mazumdar D, Guthrie RI. The physical and mathematical modelling of gas stirred ladle systems. ISIJ International. 1995;35(1):1-20.

69 Fruehan RJ. Kinetics of gas–liquid and liquid–liquid reactions. In: Treatise on process metallurgy. Amsterdam: Elsevier; 2014 [cited 2025 May 25]. p. 143-177. Available at: https://linkinghub.elsevier.com/retrieve/pii/B978008096984800001X

70 Conejo AN. Physical and mathematical modelling of mass transfer in ladles due to bottom gas stirring: a review. Processes. 2020;8(7):750.

71 Nakanishi K, Fujii T, Szekely J. Possible relationship between energy dissipation and agitation in steel processing operation. Ironmaking & Steelmaking. 1975;2(3):193-197.

72 Kim SH, Fruehan RJ. Physical modeling of liquid/liquid mass transfer in gas stirred ladles. Metallurgical Transactions. B, Process Metallurgy. 1987;18(2):381-390.

73 Lupis CHP. Chemical thermodynamics of materials. New York: North-Holland; 1983.

74 Ban-ya S. Mathematical expression of slag-metal reactions in steelmaking process by quadratic formalism based on regular solution model. In: 4th International Conference on Molten Slags and Fluxes; 1992 Jun 8-11; Sendai, Japan. Sendai: ISIJ; 1992. p. 8-13.

75 Oertel L, Costa e Silva A. Application of thermodynamic modeling to slag-metal equilibria in steelmaking. Calphad. 2000;23(3-4):379-391.

76 Ohta H, Suito H. Activities of SiO2 and Al2O3 and activity coefficients of FetO and MnO in CaO-SiO2-Al2O3-MgO slags. Metallurgical and Materials Transactions B. 1998;29(1):119-129.

77 Ohta H, Suito H. Activities in CaO-MgO-Al2O3 slags and Al, Mg and Ca Deoxidation Equilibria of Al, Mg and Ca. ISIJ International. 1996;36(8):983-990.

78 Ohta H, Suito H. Activities in Mno-SiO2-Al2O3 slags and deoxidation equilibria of Mn and Si. Metallurgical and Materials Transactions B. 1996;27B:263-270.

79 Suito H, Inoue R. Thermodynamics on control of inclusions composition in ultra-clean steels. ISIJ International. 1996;36(5):528-536.

80 Costa e Silva A. Descrição termodinâmica de fases e sistemas: objetivos e limitações do método CALPHAD através de exemplos. In: Associação Brasileira de Metalurgia e Materiais. 61 Congresso Anual da ABM; Jul 2006; Rio de Janeiro, Brazil. São Paulo: ABM; 2006. p. 1206-1216.

81 Schmitz GJ, Prahl U, editors. Handbook of software solutions for ICME. Weinheim: Wiley; 2017. 595 p.

82 Haug-Warberg T, Chen L, Kattner U, Hallstedt B, Costa e Silva A, Lee J, et al. Thermodynamics. In: Schmitz GJ, Prahl U, editors. Handbook of Software Solutions for ICME. Weinheim: Wiley; 2016 [cited 2025 May 25]. p. 325384. Available at: https://onlinelibrary.wiley.com/doi/10.1002/9783527693566.ch4

83 Castro RN, Cordeiro NB, Silva ALC, Tokumitsu N. Metodologias para a análise da etapa controladora na cinetica de remocao de carbono do aco durante o tratamento sob vacuo. In: XXVIII Seminário sobre Fusão, Refino e Solidificação dos Aços; 1997 May 12-14; Campinas, Brazil. São Paulo: ABM; 1997. p. 469-487.

84 Robertson DGC, Deo B, Ohguchi S. Multicomponent mixed-transport-control theory for kinetics of coupled slag/metal and slag/metal/gas reactions: applications to desulphurization of molten iron. Ironmaking & Steelmaking. 1984;11(1):41-55.

85 Kitamura SY. Analysis of steelmaking reactions by coupled reaction model. In: Mackey PJ, Grimsey EJ, Jones RT, Brooks GA, editors. Celebrating the megascale. Cham: Springer International Publishing; 2014 [cited 2025 May 25]. p. 317-324. Available at: http://link.springer.com/10.1007/978-3-319-48234-7_28

86 Botelho T, Medeiros GE, de Castro JA, Costa e Silva A. Estudo da taxa de desoxidação e aços desoxidados ao Silício e Manganês. São Paulo: Editora Blucher; 2018 [cited 2025 May 25]. p. 775-786. Available at: http://abmproceedings.com.br/ptbr/article/estudo-da-taxa-de-desoxidao-em-aos-desoxidados-ao-silicio-e-mangans

87 Ishida J, Yamaguchi K, Sugiura S, Yamano K, Hayakawa S, Demukai N. Effects of the stirring by gas blowing on the metallurgical reactions. Denki-Seikoelectric Furn Steel. 1981;52(1):2-8.

88 Graham KJ. Integrated ladle metallurgy control [thesis]. Hamilton: McMaster University; 2008.

89 Hsieh Y, Watanabe Y, Asai S, Muchi I. Effect of recirculating flow rate of molten steel in refining processes. Tetsu To Hagane. 1983;69(6):596-603.

90 Oeters F, Pluschkell W, Steinmetz E, Wilhelmi H. Fluid flow and mixing in secondary metallurgy. Steel Research. 1988;59(5):192-201.

91 van Ende MA, Kim YM, Cho MK, Choi J, Jung IH. A kinetic model for the Ruhrstahl Heraeus (RH) degassing process. Metallurgical and Materials Transactions B. 2011;42(3):477-489.

92 Goulart LLDO, Castro JAD, Costa e Silva A. Development of a computational thermodynamics EERZ model for the improvement of hot rolled light steel profiles steel refining. Calphad. 2023;81:102550.

93 van Ende MA, Jung IH. A kinetic ladle furnace process simulation model: effective equilibrium reaction zone model using factsage macro processing. Metallurgical and Materials Transactions B. 2017;48(1):28-36.

94 Konar B, Miao K, Quintana N, Wang Z. Study of the vacuum degassing process using the effective equilibrium reaction zone model. In: Iron and Steel Technology Conference; 2024 May 6-9; Columbus, Ohio. Warrendale: AIST; 2024 [cited 2025 May 25]. p. 731-745. Available at: https://imis.aist.org/store/detail.aspx?id=PR-388-077

95 Mason P, Grundy AN, Rettig R, Kjellqvist L, Jeppsson J, Bratberg J. The Application of an Effective Equilibrium Reaction Zone Model Based on CALPHAD Thermodynamics to Steel Making. In: Peng Z, Hwang JY, Downey JP, Gregurek D, Zhao B, Yücel O, et al., editors. 11th International Symposium on High-Temperature Metallurgical Processing. Cham: Springer International Publishing; 2020 [cited 2025 May 25]. p. 101-113. (The Minerals, Metals & Materials Series). Available at: http://link.springer.com/10.1007/978-3-030-36540-0_10

96 You D, Bernhard C, Mayer P, Fasching J, Kloesch G, Rössler R, et al. Modeling of the BOF tapping process: the reactions in the ladle. Metallurgical and Materials Transactions B. 2021;52(3):1854-1865.

97 Kavic D, Bernhard M, Roman Rössler R, Bernhard C. Simulation of Secondary Metallurgical Processes Using Computational Thermodynamics and Comprehensive Statistical Learning Methods. Iron & Steel Technology. (Dec 2024):34–46.

98 Mori K, Sano M. Process kinetics in injection metallurgy. Tetsu To Hagane. 1981;67(6):672-695.

99 Conejo AN, Lara FR, Macias-Hernández M, Morales RD. Kinetic model of steel refining in a ladle furnace. Steel Research International. 2007;78(2):141-150.

100 Oryall GN, Brimacombe JK. The physical behavior of a gas jet injected horizontally into liquid metal. Metallurgical Transactions. B, Process Metallurgy. 1976;7(3):391-403.

101 Pluschkell W. Grundoperationen Pfannenmetallurgischer Prozesse. Stahl und Eisen. 1981;101(13–14):97-103.

102 Pistorius C. Modern tools for steelmaking research and optimization. Iron & Steel Technology. 2022;60-65.

103 Ishii A, Tate M, Ebisawa T, Kawakami K. The ladle refining process for alloyed oil country tubular goods steels at NKK. In: 40th Electric Furnace Conference; 1982 Dec 7-10; Kansas City. Warrendale, PA: ISS-AIME; 1982. p. 137-144.

104 Ogawa K. Slag refining for Production of Clean Steel. In: 143rd–144th Nishiyama Memorial Seminar; 1992; Tokyo. Tokyo: ISIJ; 1992. p. 137-166.

105 Lachmund H, Xie Y, Buhles T, Pluschkell W. Slag emulsification during liquid steel desulphurisation by gas injection into the ladle. Steel Research International. 2003;74(2):77-85.

106 Zhang L, Thomas BG. State of the art in evaluation and control of steel cleanliness. ISIJ International. 2003;43(3):271-291.

107 Peter J, Peaslee KD, Robertson DGC. Experimental study of kinetic processes during the steel treatment at two LMF's. Aistech-Conference Proceedings. 2005;1:959.

108 Toledo PVV. Modelamento termodinâmico e cinético da dessulfuração de aços ultrabaixo enxofre [dissertation]. Volta Redonda: Universidade Federal Fluminense; 2024.

109 Lindskog N. Studies of Al deoxidation in ASEA-SKF furnaces using radioactive Zr. Scandinavian Journal of Metallurgy. 1975;4:153-160.

110 Burty M, Pussé C, Bertoletti C, Wetta P, Cariola E. Kettlor: efficient stirring in ladle metallurgy. Revue de Métallurgie. 2006;103(11):493-499.

111 Burty M; Europäische Kommission, editors. Development of advanced methods for the control of ladle stirring process: contract no 7210-PR/330, 1 July 2002 to 30 June 2005; final report. Luxembourg: Office for Official Publ. of the European Communities; 2007. 139 p. (EUR Technical Steel Research).

112 Dannert C; Research Fund for Coal and Steel. Improvement of ladle stirring to minimise slag emulsification and reoxidation during alloying and rinsing (Stimprove). Bruxelles: European Commission; 2012.

113 Bock ML. Elaboração de modelo de desulfuração de aço para forno panela [dissertation]. Belo Horizonte: Universidade Federal de Minas Gerais; 2024

114 Poëti K, Costa e Silva A, Oishi K, Harvey J-P. A new interface for Effective Equilibrium Reaction Zone (EERZ) in FactFlow. In: 52nd CALPHAD Conference; 2025 May 25-30; Busan. State College, PA: CALPHAD Inc.; 2025.

115 Goulart LEP, Silva EP, Alves C, Castro JA, Costa e Silva A. Application of a computational thermodynamics effective equilibrium reaction zone (EERZ) to describe the processes from tapping to arrival at the ladle furnace. In: Anais do Seminário de Aciaria, Fundição e Metalurgia de Não-ferrosos; 2022 Jun 7-9; São Paulo. São Paulo: ABM; 2022 [cited 2025 May 25]. Available at: https://abmproceedings.com.br/ptbr/article/application-of-a-computational-thermodynamics-effective-equilibrium-reaction-zone-eerz-to-describe-the-processes-from-tapping-to-arrival-at-the-ladle-furnace

116 Thermo-Calc Software. GMH Teams up with Thermo-Calc Software to Develop a Physical Model of Secondary Steelmaking Metallurgy [Internet]. [cited 2025 May 25]. Available at: https://thermocalc.com/blog/gmh-teams-up-with-thermo-calc-software-to-develop-a-physical-model-of-secondary-steelmaking-metallurgy/

117 Demuner D, Carvalho H, Castro L, Viana M Jr. BOF process optimization and technology improvements at ternium Brazil. In: Association for Iron and Steel Technology. Proceedings of the Iron and Steel Technology Conference – AISTech 2019; 2019 May 6-9; Pittsburgh, United States. Warrendale: AIST; 2019 [cited 2025 May 25]. p. 897-912. Available at: https://imis.aist.org/store/detail.aspx?id=PR-377-094

Received: 10 Jun. 2025
Accepted: 1 Jul. 2025

Editor-in-charge:
Paula Fernanda da Silva Farina