The Use of Fundamental Process Models in Studying Ladle Refining Operations

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Existing fundamental models of ladle refining operations have been reviewed. No fundamental model that takes all the individual parts of ladle refining into account has been found in the open literature. Nor does a model exist which considers all refining in only one part of a refining step such as vacuum treatment. However, separate fundamental models for prediction regarding alloying, temperature, hydrogen, sulfur, re-oxidation, and inclusion growth and removal do exist. In one case, a reoxidation model has also been combined with a sulfur-refining model. Predicted values from the separate models for alloying, temperature, sulfur and hydrogen have been found to agree well with corresponding measured data. The verification of the models for reoxidation and the growth and removal of inclusions is currently lacking and separate models for refining operations such as nitrogen or carbon removal need to be developed. Also, more complex models of parts of ladle refining such as vacuum treatment need to be developed, incorporating the sulfur, hydrogen, reoxidation and inclusion growth and removal models. The ultimate goal is, of course, one overall model that can predict desired parameter values for all steps of ladle refining. Even though such a model does not exist today, the usefulness of existing fundamental models is exemplified. This is to illustrate the potential of more complex and more realistic ladle models in process optimization.

KEY WORDS: secondary refining; ladle; modeling; fundamental; steel; slag and gas.

1. Introduction

Developments in ladle metallurgy have contributed a lot to the quality of steel in the last decades in terms of control of chemistry through improved alloying techniques and the reduction of dissolved elements, as well as better control of inclusion distribution in terms of size, frequency, composition and morphology. The purpose of this paper has been to review how fundamental models have contributed to these developments and additionally to give the reader an idea of how these models are built and can be applied in the future development of ladle refining operations. Here, a fundamental model is seen as a mathematical model that consists of i) transport equations of mass, momentum and enthalpy, ii) turbulence equations, and iii) thermodynamic equations. Related reviews on the kinetics of fundamental reactions and alloying, refining and quality issues by, for example, Mori1) and Guthrie,2) respectively, can also be found.

Knowing that the appropriate temperature and inclusion characteristics at the end of ladle treatment ensures a successful casting operation, it is extremely important to optimize ladle refining so that the correct alloy amounts can be used and the desired inclusion characteristics can be obtained in the final product. This way the material properties for each specific product can be met. In order to optimize the ladle refining process it is necessary to know the status of the process while in progress. In practice, too many “unknowns” remain for a static control strategy to be reliable. One way to receive feedback from the process is to sample steel and slag as well as measure the steel temperature. After the results are obtained, adjustments to the process can be made in order to meet specifications. The response time for the temperature measurement is fast, but the response time for receiving feedback on slag and steel samples is usually more than 5 min. Therefore, in addition to sampling, it is necessary to be able to predict how the steel and slag compositions change. This need for model predictions is even more obvious if one looks at inclusion characteristics. Today, the majority of steel companies have no means of getting on-line feedback of inclusion characteristics during ladle refining due to the lack of rapid analysis methods. Thus, model predictions of changes in inclusion characteristics during the different stages of ladle refining are very helpful in optimizing the process. Even companies that have reported access to on-line methods to determine micro-inclusion characteristics have a need for model predictions. The reason, similar to the delay for steel samples, is the response time (approximately 7 min).

In order to optimize steel refining ladle operations, it is necessary to have a very good understanding of the thermodynamics of the refining reactions. It is also necessary to understand the kinetics of the refining reactions, as this has a strong impact on the productivity of the process, which, in turn is a key factor in lowering production costs and increasing product competitiveness. The stirring of steel is commonly used, for example, to improve the kinetics of desulfurization.

From a theoretical point of view, the kinetics of the refining of impurity elements has often been described using the classic two-film theory. Here, it is assumed that a concen-
tration gradient of the element exists at the interface between two phases. This can, for example, be in the steel phase, if the diffusion of the solutes to be removed or added in steel is the rate controlling step. Furthermore, it is assumed that the phases on each side of the concentration boundary layer, the steel phase and the refining phase (gas for hydrogen removal and slag for sulfur removal), are steadily and completely mixed. Therefore, the removal rate of an impurity elements from steel can, for example, be described as follows:5

\[
d\text{[%x]} = -\frac{k\rho A}{M} \left(\text{[%x]}_2 - \text{[%x]}_1\right) \quad \text{........................(1)}
\]

where \(x\) is the element to be refined (i.e. S or H), \(k\) is the total mass-transfer coefficient, \(\rho\) is the steel density, \(M\) is the steel mass, and \(\text{[%x]}\) is the actual concentration of the element to be refined. The parameter \(\text{[%x]}_1\) is the hypothetical concentration of the refined element in the steel phase in equilibrium with the actual concentration in the refining phase. “\(A\)” is the interface area between the steel and the phase to which the element is refined. In the cases of hydrogen refining and sulfur refining, this is the gas phase and slag phase, respectively.

One disadvantage with this traditional approach is that due to the assumptions mentioned, more often than not the coefficients in Eq. (1) can only be valid for one specific case at a time. Therefore, this equation tends to be of limited usefulness in prediction for refining processes in general. For example, the interfacial area \(A\), to be used in prediction of desulfurization during gas stirring, is highly underestimated if it is assumed to be a horizontal and flat interface area between the slag and metal. Many authors have studied the dispersion of the slag phase into steel using physical modeling.5-12 It has been found that in reality, slag and metal droplets are dispersed, causing a much larger interfacial area than an assumed flat interface between the slag and steel.

Another drawback with Eq. (1) is that the mass-transfer coefficient, \(k\), is specific for different stirring conditions as well as varies along the slag/steel interface. This mass-transfer coefficient can, for example in the case of the two-film theory, be expressed as:13

\[
k = \frac{D}{\delta} \quad \text{.................................(2)}
\]

where \(D\) is the diffusivity of the refined element in steel and \(\delta\) is the boundary layer thickness. The latter is in turn, in the example of sulfur refining, dependent on the position along the steel/slag interface and the steel velocity at that position. Thus, it is difficult to specify the boundary layer thickness without having a good knowledge of the fluid flow at the steel/slag interface. On the other hand, models capable of predicting the flow conditions in the slag phase and around the slag/metal interface can be used to estimate when slag droplets might be entrapped for different stirring conditions and slag compositions, for example by calculating the Weber number. The Weber number is the ratio of the inertial force to the interfacial tension.

\[
We = \frac{18 \rho u \delta^2}{\eta}
\]

\(u\) is the bulk flow velocity and \(\eta\) is the viscosity for the two slag compositions in the figure can be found in Table 1 (Figure from Ref. 14). Gas open eye located in the upper left corner and the region consisting of only slag is located above the marked area with a high Weber number.

**Table 1.** Calculated viscosities of some \(\text{Al}_2\text{O}_3-\text{CaO}-\text{MgO}-\text{SiO}_2\) slags.10

| Slag Composition (wt-%) | Viscosity (Pa \(\text{s}^2\)) |
|-------------------------|--------------------------|
| \(\text{Al}_2\text{O}_3\) | 1773K | 1823K | 1873K | 1923K |
| 25 | 55 | 7.5 | 12.5 | 1.634 | 1.134 | 0.812 | 0.599 |
| 30 | 50 | 7.5 | 12.5 | 0.245 | 0.168 | 0.120 | 0.089 |

The figure indicates that more of the slag of lower viscosity is entrapped in the steel, thus affecting the reaction zone. The inertial force, i.e. the radial steel velocity, increases when the viscosity is lowered. This causes an increase in the Weber number and consequently slag entrapment. The viscosity for the two slag compositions in the figure can be found in Table 1.14 Using the traditional theories these consequences of different refining conditions must be handled by altering the mass-transfer coefficients, while the solution is inherent in the fundamental approach.

By using mathematical models based on fundamental theories, empirically determined mass-transfer coefficients for the bulk of each phase, etc. are not necessary. Therefore, this paper is focused on discussing mathematical models based on fundamental theories. In the first part of the paper the basic principle of a fundamental model is given. Thereafter, a review of the different fundamental ladle refining models reported in the open literature is given. Next, the verification of reported model results is presented. Finally, the current status of modeling ladle refining is summarized.

## 2. Mathematical Modeling

In the fundamental mathematical model, the conservation of a general variable \(\phi\), for example the density, momentum, enthalpy or species, within a finite control volume can be expressed as a balance among the various processes, which tend to increase or decrease it. This balance leads to a transport equation which has the following general form according to Patankar:15

\[
\frac{\partial}{\partial t} (\rho \phi) + \frac{\partial}{\partial x_j} (\rho \phi u_j) = \frac{\partial}{\partial x_j} \left( r_{\phi,j} \frac{\partial \phi}{\partial x_j} \right) + r_S \phi \quad \text{..............(3)}
\]
where $\phi$ is the variable to be solved, $r$ is the volume fraction of the phase (i.e., gas, slag or steel), $\rho$ is the density of the phase, $u$ is the velocity, $\Gamma_\phi$ is the exchange coefficient, $t$ is time and $S$ is the source term given per unit time and volume. The indexes $\phi$ and $i$ represent a specific variable and phase, respectively. The first term in Eq. (3) expresses the rate of change in $\phi$ with respect to time. The second term expresses the convection (transport due to fluid flow). The third term expresses the diffusion (transport due to the variation in $\phi$ from point to point) where $G_{\phi,i}$ is the exchange coefficient of the variable $\phi$ in the phase. Finally, the fourth term expresses the source terms (associated with the creation or destruction of $\phi$ within the phase).

“Macromodels” are thought of as describing some aspects of the reality in a whole metallurgical operation or furnace. An integrated part of these macromodels are “reaction models”, such as a model of sulfur refining between the slag and steel phases. The reaction models in turn are made out of “micromodels”, describing for example the sulphide capacity. To facilitate better understanding of how fundamental phenomena influence the process as well as to make the process description more comprehensive, the authors recommend that these reaction models and micromodels be implemented as building blocks (Fig. 2) in the overall process model.16,17)

The micromodels use and influence concentration profiles of species. To facilitate calculation of the different resulting concentration profiles, a separate differential equation of the same type as Eq. (3) is solved for each of the dissolved elements and reaction products.

The overall fundamental model can now be seen as a system of equations, where every variable has its own row in the system and where every equation is expressed in the form of a “transport equation” (3). In order to solve the resulting system of equations it is necessary to supply the following additional information:

- Thermodynamic properties (i.e., sulfide capacity, activity coefficients, etc.)
- Thermophysical properties (i.e., viscosity, thermal conductivity, etc.)
- Source terms (creation or destruction of $\phi$ due to chemical reactions, etc.)
- Transport phenomena between different phases
- Boundary conditions for all variables

The combination of this mathematical description of the problem with a method that numerically solves the equations is conventionally called a computational fluid dynamics (CFD) model. However, used in this way, it is really a macromodel based on the combination of thermochemical and thermophysical relationships and macro kinetics calculated from first principles. As an example of the structure of this type of process model, the different parts of a model describing hydrogen and sulfur refining including reoxidation16) are outlined in Fig. 3. Details regarding the heat and fluid-flow model assumptions, transport equations, boundary conditions, property variations, gas hold-up, and incorporation of the slag phase into the model can be found in earlier publications.14,18–24) The structure of the process model in Fig. 3 helps to illustrate how fundamental phenomena influence the process. In addition, the use of this process model structure makes it easy to include new and upcoming research in the model without requiring substantial reprogramming.

### 3. Alloying

Numerous investigations have been done on the topic of mixing which address alloying in gas-stirred ladle systems. Mazumdar and Guthrie published a comprehensive review on the subject25) and Zhang and Oeters compiled most of the classical theories on modeling the melting and mixing of alloying agents in steel.26)

In the alloying procedure the melt is heated and/or stirred in one or more ways to homogenize and yield a desired temperature. Meanwhile, the fluid-flow and temperature conditions within the steel melt greatly affect the motion, melting and mixing of alloying additives, which in turn affect the flow and temperature. Fundamental models incorporating micromodels for the melting process, i.e., the shell period, particle core melting, alloy distribution, alloy disso-

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**Fig. 2.** Structure of process models based upon “micromodels” (Figure from Ref. 16)).

**Fig. 3.** Structure of a CFD macromodel of refining operations in the ladle that reflects the combined micromodel approach (Figure from Ref. 16).
solution, etc., can be used to perform detailed studies on all these interrelated phenomena and provide a good view of the entire process.

Neifer et al. reported a fundamental model approach together with an experimental study on the subject using FeMn lumps and gas stirring. In their model a separate melting model for alloying material (micromodel) was incorporated and used together with the Lagrangian method to track the melting of FeMn particles. From a modeling point of view, it is interesting to compare the concentration vs. time-response curves with the corresponding curves in the reference by Grip et al., where the addition of tracer elements was studied during the teeming process.

Focusing on the efficiency of a specific stirring method, the mixing time has been the most widely used concept. It has been found in experimental research that the mixing time is not only affected by the process parameters, but also by the experimental conditions, for example the tracer addition position, addition method (pulse or continuous), sampling position, etc. Therefore, fundamental models are very useful for analyzing the mixing behavior of alloys added to the steel in ladles. The possibilities for studying different ways to add the alloy are virtually unlimited and there are also few limitations in expressing and presenting predicted mixing results.

In a recent investigation Jauhiainen et al. studied the way in which different porous plug arrangements influence fluid flow and the mixing of alloys into steel in a 110 ton gas-stirred production ladle (Table 2). In Fig. 4 the local minimum concentrations for the different stirring cases are provided as a function of time. The authors found that for batch additions, centric gas stirring (case D) was predicted to be the most favorable to avoid dead rooms in the ladle. However, it was noted that a centrally stirred ladle was very sensitive regarding alloy addition location. If the alloy were not added precisely in the center of the plume, the mixing results were much worse. A case where the two porous plugs were placed at a distance of 1/3 radius from the wall and such that their radii formed a 60° angle (case B) showed the second best mixing results when studying minimum concentration values. The nearness of the wall to the plumes resulted in a strong flow field, improving the alloy mixing into steel. The greatest differences in local minimum concentration values were observed during the first

| Case  | Porous plug location                      | Figure of ladle bottom |
|-------|------------------------------------------|-------------------------|
| A     | Distance of 1/2 r from center, 60° angle formed | ![Fig. 4. Minimum concentration as a function of time for cases A–D, alloy addition in the beginning of the stirring (Figure from Ref. 46)](image) |
| B     | Distance of 1/3 r from wall, 60° angle formed | ![Case B](image) |
| C     | Distance of 1/2 r from center, 180° angle formed | ![Case C](image) |
| D     | Porous plugs in the middle of the ladle bottom | ![Case D](image) |

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Temperature control during ladle refining is important in many aspects. First, all chemical reactions are temperature dependent. Second, it is necessary to consider temperature losses when adding alloys and slag. Third, the temperature must be optimized at the end of ladle treatment in order to ensure optimum casting conditions.

Several models describing the heat and fluid-flow conditions in casting ladles have been developed in the past. Tomazin et al. used a transient thermal model to simulate the temperature distribution in the ladle refractory, ladle cover and the slag. The steel temperature was assumed to be constant. Ilegbusi and Szekely presented a model for temperature stratification of steel for a ladle holding molten steel based on equations of continuity, motion, thermal energy, and the $k-\varepsilon$ model for describing turbulence. Transient conduction of heat into the slag and the refractory wall was assumed. Significant stratification was found to take place due to natural thermal convection caused by the thermal gradient in the vicinity of the refractory wall. The model could also take induction stirring into account by solving Maxwell’s equations. The authors showed that gentle stirring was enough to minimize stratification.

Kim et al. used the same transport equations as Ilegbusi and Szekely to solve stratification for ladles containing molten steel. The heat losses to refractory were based on one-dimensional non-steady-state heat conduction in the radial direction. The top surface was assumed to be insulated. Argon bubbling was simulated in a simplified manner by adding an extra buoyancy source term to the axial momentum equation. Similar to Ilegbusi and Szekely, they found that without stirring the temperature stratification was significant, but with stirring (for example by gas bubbling) the stratification was easily removed.

Castillejos et al. also modeled thermal homogenization using gas stirring of a ladle holding steel. The two-phase zone of gas and steel was included in a simplified manner in the mathematical model by defining the gas distribution, based on experimental data from physical modeling, and using these values to calculate a modified density. They found that complete homogenization was reached within 3 min after the start of gas stirring.

Austin et al. were the first to report modeling results on the temperature stratification during ladle teeming. Their model contained basically the same equations as the model of Ilegbusi and Szekely. An additional feature, however, was that during draining, the top free surface was replaced by a uniform inflow surface that had a normal enthalpy gradient of zero. A constant uniform heat flux to the refractory at the wall and bottom was used during the calculations. The predicted temperature of the steel leaving the ladle during teeming was compared with temperature measurements of the pouring stream and a good agreement was found. The authors showed that the drainage behavior is heavily dependent on the outlet flow rate.

Chakraborty and Sahai modeled the effect of the slag cover on heat loss and liquid steel flow in a 250 ton ladle before and during teeming. A thin slag layer was found to result in a heat loss of 45 degrees for 47 min of casting compared to 5 to 10 degrees for a thick slag layer.

In summary, it is possible to model the temperature distribution in ladles during stirring, holding and teeming. One future model development needed is a more accurate description of the heat transfer between the liquid slag and the liquid steel.
to the two-film theory. In fundamental models a quite new approach to modeling slag–metal reactions in ladles can be used. This is discussed above in Secs. 1 and 2 and has been described more in detail in other publications relevant to sulfur refining.\(^{16,17,47}\) That approach considers the volume of mixing between the slag and metal and the thermodynamic equilibrium in the two-phase zone in order to predict the combined effect of fluid-flow and thermodynamic conditions. This means that when the metal and slag phases are transported in the ladle as governed by the fluid flow, thermodynamic equilibrium between the phases is expected to establish dynamically, in each elementary volume. This being the case, the calculations of interfacial area and mass-transfer coefficients for different elements are not required, though numerical values for mass-transfer coefficients corresponding to any simulated case might be determined.

5.1 Sulfur Refining

Figure 6 illustrates results from using the fundamentally based approach to studying slag–metal reactions\(^ {48}\) in sulfur refinement. It shows the calculated sulfur distribution in a 100 ton steel ladle after 1, 4 and 6.5 min of vacuum degassing. It is obvious that sulfur is removed from the steel in the slag/metal mixing region, i.e. reaction zone, where the lowest sulfur concentrations are naturally predicted. The steel volume that has been refined in the reaction zone grows in the direction of the main fluid-flow pattern, that is to say towards the ladle wall and down into the bulk region of the steel. In the initial stage of the degassing process, large concentration gradients of sulfur are predicted. The predicted difference in sulfur concentration after 1 min in different parts of the ladle is \(\geq 90\%\) of the initial concentration. After 4 min, these large concentration gradients are reduced to \(\sim 70\%\) of the initial concentration. The highest remnant sulfur concentrations are predicted to exist close to the bottom and close to the lower parts of the wall. After 10 min, the distribution of sulfur in the ladle has approached uniformity, showing concentration differences in the magnitude of \(10^{-3}\%\) [S] by weight.

5.2. Reoxidation Reactions

In the slag/metal mixing zone there are several equilibrium reactions which take place during the process besides the above-described sulfur refining reaction. These reactions influence the oxygen activity and thus the sulfur and aluminum contents in the steel melt. In the work by Andersson et al., four slag–metal reactions were considered besides the desulfurization reaction.\(^ {49}\) It was assumed that no oxides besides FeO, MnO, SiO\(_2\) and Al\(_2\)O\(_3\) are involved in these reactions and further that thermodynamic equilibrium is established dynamically in the slag/metal mixing zone. To calculate the activities of these oxides in the slag phase the empirical expressions suggested by Ohta and Suito\(^ {50}\) were used. Ohta and Suito\(^ {50}\) expressed the activity coefficients of FeO and MnO and the activities of Al\(_2\)O\(_3\) and SiO\(_2\) at 1600°C as functions of the slag composition using multiple-regression analysis. The empirical expressions should only be applied within the following slag composition ranges: 10–60\% CaO, 10–50\% SiO\(_2\), 0–50\% Al\(_2\)O\(_3\) and 0–30\% MgO by weight. Therefore, in the work by Andersson et al.\(^ {49}\) the composition range was limited in

| Table 3. Gibbs free energy of reactions considered in Ref. 49) |
|---------------------------------|
| Reaction | \(\Delta G^\circ_n\) (J/mol) | References |
|---------------------------------|
| \(\text{Fe}_2\text{O}_3(s) = 2\text{FeO} + \text{O}_2\) | \(\Delta G^\circ_n = 116100 - 48.4\cdot T\) | \(4.9\) |
| \(\text{MnO}(s) = \text{Mn} + \frac{1}{2}\text{O}_2\) | \(\Delta G^\circ_n = 288150 - 128.3\cdot T\) | \(4.9\) |
| \(2\text{SiO}_2(s) = \text{Si} + 2\text{O}_2\) | \(\Delta G^\circ_n = 581900 - 221.8\cdot T\) | \(4.9\) |
| \(2\text{Al}_2\text{O}_3(s) = 2\text{Al} + 3\text{O}_2\) | \(\Delta G^\circ_n = 1202050 - 396.3\cdot T\) | \(4.9\) |
| \(\text{O}_2(g) + \text{O} = \text{O}_3\) | \(\Delta G^\circ_n = -117150 - 2.89\cdot T\) | \(35p\) |
| \(\text{SiO}_2(g) = \text{Si} + \frac{1}{2}\text{O}_2\) | \(\Delta G^\circ_n = -135080 + 23.43\cdot T\) | \(35p\) |

where \(n\) stands for reaction number, \(\Delta G^\circ_n\) is the change of Gibbs free energy for reaction \(n\), \(R\) is the gas constant and \(T\) is the temperature in Kelvin. The expressions for the change of the Gibbs free energy for the different reactions in Ref. 49) are listed in Table 3.

In the work by Andersson et al., a separate transport equation was solved for each of the dissolved elements (sulfur, oxygen, aluminum, silicon and manganese) at every instant and for each calculation node in the steel phase.\(^ {49}\) In the same way, separate transport equations in the slag phase were solved for the different slag components (Al\(_2\)O\(_3\), CaO, MgO, SiO\(_2\), MnO, FeO and S). In doing this, concentration profiles for the dissolved elements in the steel phase as well as for oxides and sulfur in the slag phase were determined.

Some results from the work of Andersson et al.\(^ {49}\) are shown in Figs. 7 to 9. The initial slag and steel composition data was set according to Tables 4 and 5. One important feature of the model is the dynamic calculation of the activities of Al\(_2\)O\(_3\), SiO\(_2\), FeO and MnO in the slag. The predicted activities of Al\(_2\)O\(_3\) and SiO\(_2\) and the activity coefficients of FeO and MnO halfway through the simulation are shown in Fig. 7. It can be seen that the values of the activities and activity coefficients vary throughout the slag phase.

In Fig. 8 the concentration profile of dissolved silicon in steel after 6.5 min is illustrated. Since the initial content of Si at the start of the calculation was 0.22\% (Table 5), it is obvious that the average silicon content in steel increased. In Fig. 9 the manganese concentration profile in the molten steel after 30 sec is shown as iso-contours. Similar to the results for silicon in Fig. 8, the manganese content is higher than the initial content of 0.28\%.

A parameter study was made to determine the influence of initial FeO content in the slag on desulfurization and aluminum loss. The initial FeO contents in the slag were assumed to be 0, 2 and 6\%.\(^ {52}\) The initial steel composition was the same as in Ref. 49) (see Table 5). The initial slag compositions in the parameter study are shown in Table 6. The initial slag and steel weights were 1116 kg and 90.8 tons, respectively, at 1600°C. The calculated final steel and slag compositions are shown in Tables 7 and 8.

Figures 10 and 11 show how the average compositions...
Fig. 6. Sulfur concentration in a vertical cross-section of the ladle through both porous plugs at three different times: 1.5, 4 and 6.5 min. Combined Ar and inductive stirring. \( Q_1 = 110 \text{ l/min}, \quad Q_2 = 50 \text{ l/min}, \quad I_0 = 1000 \text{ A}, \quad T_0 = 1579^\circ \text{C}, \quad [S]_0 = 0.019 \text{ wt%}. \) The inductive stirrer is located at the right hand side and the stirring is directed upwards. (Figure from Ref. 16).

Fig. 7. Activities of \( \text{Al}_2\text{O}_3 \) and \( \text{SiO}_2 \) and activity coefficients of \( \text{MnO} \) and \( \text{FeO} \) in the slag after 9.5 min (Figure from Ref. 49)).

Fig. 8. Concentration profile of silicon in the steel melt after 6.5 min (Figure from Ref. 49)).

Fig. 9. Concentration profile of manganese in the steel melt after 30 sec (Figure from Ref. 49)).

Table 4. Initial slag component concentrations for the basic case.49)

| \%Al\text{O}_3 | \%CaO | \%MgO | \%SiO\text{2} | \%FeO | \%MnO | \%S |
|----------------|-------|-------|---------------|-------|-------|-----|
| 28.4           | 48.9  | 9.0   | 11.0          | 2.0   | 0.2   | 0.5 |

Table 5. Initial steel component concentrations for the basic case.49)

| %C  | %Si | %Mn | %Al | %S  |
|-----|-----|-----|-----|-----|
| 1.02| 0.22| 0.28| 0.052| 0.023|

Table 6. Initial slag compositions in the parameter study.52)

| %FeO | %Al\text{O}_3 | %CaO | %MnO | %SiO\text{2} | %S  |
|------|---------------|-------|-------|---------------|-----|
| 0    | 29.0          | 50.0  | 9.2   | 0.0           | 0.0 |
| 2    | 28.4          | 48.9  | 9.0   | 0.2           | 11.0| 0.5 |
| 6    | 27.2          | 46.9  | 8.6   | 0.2           | 10.5| 0.5 |

Table 7. Final steel compositions in the parameter study.52)

| Temperature °C | Initial FeO | wt-% Al | wt-% C | wt-% Mn | wt-% S | wt-% Si |
|----------------|-------------|---------|--------|---------|--------|---------|
| 1600           | 0           | 0.029   | 1.0    | 0.28    | 0.013  | 0.24    |
| 1600           | 2           | 0.023   | 1.0    | 0.28    | 0.014  | 0.23    |
| 1600           | 6           | 0.019   | 1.0    | 0.28    | 0.020  | 0.20    |
of the steel and slag changed with time for the case where the initial FeO content in the slag was 2% and the temperature 1600°C. It can be seen that the model predicted a rapid decrease in FeO and MnO in the beginning of the vacuum treatment. This should be due to the low oxygen potential of the molten steel, which was determined by the equilibrium between Al₂O₃ in the top slag and dissolved aluminum in steel. Initially the dissolved aluminum content was 0.052%, which resulted in a low oxygen potential at the slag/metal interface with favorable conditions for reduction of FeO and MnO. It can also be seen that SiO₂ has been reduced in the top slag in the beginning since the content of silicon increased somewhat in the steel melt.

Figure 12 shows how the model predicted the influence of different initial FeO contents in the top slag on the desulfurization rate at 1600°C assuming constant sulfide capacity (Figure from Ref. 52)).

5.3. Summary
Slag–steel reactions play important roles during secondary refining operations carried out in ladles. The development of models has just begun. Today, models of sulfur refining and reoxidation have been reported on. Future models would need to consider a wide range of other important slag–steel reactions such as phosphorus refining or alloy recovery from slags. In developing these new models it is important to have access to thermophysical properties such as slag viscosity and thermodynamic properties such as the activity of oxide components in slags.

6. Gas–Steel Reactions
The usual way to describe gas–steel reactions is to rely on a total mass-transfer resistance consisting of contributions from the melt boundary layer, chemical reaction, and mass transfer in the gas boundary layer. In those cases where the interface reaction and mass transfer in the gas phase are fast, the overall mass-transfer resistance could be expressed by the mass-transfer coefficient in the melt. This depends on the fluid flow, the bubble velocities, and the elements under consideration. Traditional models use the assumption of perfect mixing and mass-transfer coefficients to describe the mass transport. If the model is based on fundamental transport equations, the use of empirical parameters can be reduced.

6.1. Hydrogen Refining
A fundamental model for the prediction of hydrogen refining in steel ladles during vacuum treatment was developed by the authors. In Fig. 13, some results are shown. The calculated hydrogen distribution after 1, 5, and 10 min of vacuum degassing is plotted. Argon was injected through two porous plugs at a flow of 101 l/min in one and 117 l/min in the other. Large hydrogen concentration gradients can be observed in the beginning of vacuum treatment. However, after 10 min, the hydrogen concentration in the ladle is more uniformly distributed. As also is clear from the figure, the hydrogen concentration is dependent on the...
gas flow in the ladle. The hydrogen content is lower close to the gas plume, where hydrogen can be picked up by the argon bubbles, and at the steel surface in the open-eye region. However, at the lower part of the ladle, far away from the gas plume and the open eyes, the hydrogen concentration is higher. Thus, the rate of hydrogen removal appears to depend on how fast steel of a higher hydrogen content can be transported to the gas plume. The rate of hydrogen refining also increased with a lowering of the vacuum pressure.24

6.2. Nitrogen Refining

Until now nitrogen removal has been carried through in the EAF melting process by carefully selecting the different scrap grades (charging with DRI/HBI or pig iron reduces the nitrogen level to some extent) and carbonizing products in the charge. However, with this practice it is not possible to obtain the low levels of [N] required for some products. For example, the steel usually has a nitrogen level of about 65 ppm just after EAF tapping. (This level can vary significantly from one heat to another.) To obtain a [N] level less than or equal to 50 ppm, the nitrogen must be removed during secondary metallurgical operations, and more specifically, by vacuum treatment.

There are at this time, to the knowledge of the authors, no fundamental models reported using calculated flow fields from first principles put into established thermodynamic relationships for the prediction of nitrogen concentration profiles that are useful to study nitrogen removal/absorption in industrial processes. However, several studies have been reported that include a mathematical formulation of the thermodynamics involved, although no calculation of the resolved fluid flow in the vessel.53,55,56) In addition, a fundamental model for analysis of the nitrogen absorption rate accompanied by Maragoni convection has recently been reported.57)

Kitamura et al. presented a comprehensive modeling work on nitrogen removal covering several reaction sites such as the bath surface and the surfaces of injected gas bubbles and formed CO bubbles.55) In their model, both mass transfers in the steel and the chemical reaction rate at interfaces were assumed to control the reaction rate. The rate constant of the reaction was determined by Kiyose’s equation58) for chrome-containing steel grades and by Harashima’s equation59) for other steel grades. Working with the VOD de-gassing process, Kitamura et al. concluded that, in the early stage of the operation when CO formation in the melt is the predominant decarbonization mechanism, nitrogen desorption mainly occurred at the surfaces of CO bubbles.55) Thereafter, when CO-bubble formation decreased, as well as in all cases without decarbonization, approximately 70% of the nitrogen desorption reaction occurred at the bath surface and only roughly 30% at the surface of injected Ar bubbles.

As an illustrative example, possible augmentation of the model reported by Kitamura et al.55) such that it conforms to the fundamental approach, is discussed below. For example, it could be used to study the influence of different ladle geometries, stirring conditions, slag amounts, vacuum pressures, and slag and steel compositions on the nitrogen refining rate.

In order to supplement the model to be in line with a fundamental approach, the local heat and fluid-flow conditions and their variation in time should be calculated for every specific industrial reactor and operational practice. This could be done in a similar manner as to what has been done for the model of hydrogen refining during vacuum treatment.24,48,54) If this is done, the mass transfer rate of nitrogen in steel could be determined by fluid-flow calculation by solving an additional transport equation for dissolved nitrogen. The mass-transfer coefficient of nitrogen in the steel would consequently not be needed in the extended model and thus would not need to be determined. Furthermore, the fluid-flow calculation would predict the size of the slag-free area above the steel, facilitating determination of the reaction area of the bath surface. Thus, this modification of the already useful model of Kitamura et al.55) could result in an excellent research and analysis tool based entirely on fundamental theories.

6.3. Carbon

If the objective is to produce ultra-low carbon grades, the steel normally passes a vacuum treatment route (RH, RH-OB, VOD, etc.). Here, deoxidation is not done at the time of tapping because dissolved oxygen is required later to react with carbon. Purging with argon gas, possibly in combination with vacuum treatment, makes decarbonization feasible in this situation due to the initially low partial pressure.
of CO, which favors the formation of CO gas at the gas/steel interface. The rate controlling step(s) for this decarbonization reaction can be:

- the transport of [C] from steel bulk to gas/steel interface;
- the transport of [O] from steel bulk to gas/steel interface;
- chemical reaction at the gas/steel interface;
- the transport of CO gas from the gas/steel interface into the bulk of the gas;
- a combination of two or more of the steps above.

A detailed theoretical analysis of the various possible rate controlling steps in the carbon–oxygen reaction can be found in the literature.\(^{60-62}\) By comparison with experimental data from induction-stirred steel baths Suzuki and Mori found that:\(^{60}\)

- for carbon greater than 0.03 wt%, oxygen mass transfer in metal solely controls the rate;
- for oxygen greater than 0.06 wt%, carbon mass transfer in metal solely controls the rate;
- the changeover from oxygen mass-transfer control to carbon mass control occurs at a proportion between the two contents \([C]/[O]\) of 0.69, which is close to that between the two mass-transfer coefficients \(k_{O} / k_{C}\).

Later, Kitamura et al. reported an updated decarbonization model for the VOD process incorporated with the same reaction sites as for nitrogen (discussed above in Sec. 6.2).\(^{55}\) In addition, the hot spot in which the reaction takes place was determined using a refining index proposed by Miyamoto et al.\(^{55}\) The CO gas bubble formation was taken into account as suggested by Kuwabara et al.\(^{54}\) with a bubble evolution pressure estimated as 2 670 Pa from experiments. The rate constant for the carbon–oxygen reaction was evaluated by the Harashima equation.\(^{55}\) By comparing a significant number of predictions with the corresponding measurements in a 130 ton VOD, Kitamura et al. found that the contents calculated and observed were in close agreement, thus validating their modeling.\(^{55}\) From their work they concluded that decarbonization at an early stage of operation is mainly achieved by CO gas formation in the bulk. Thereafter, when the CO gas formation decreases, decarbonization mainly occurs at the bath surface and to some extent at the surfaces of injected argon gas bubbles.

Among other researchers,\(^{56,66-69}\) Stouvenot et al.\(^{70}\) also reported a model of the kinetics of decarbonization of ultra-low carbon steels in a vacuum tank degasser using a similar concept as Kitamura.\(^{55}\) However, Stouvenot determined the thickness of the boiling zone by assuming that spontaneous nucleation of CO bubbles is possible wherever the dynamically calculated partial pressure of CO in equilibrium exceeds the ferrostatic pressure.\(^{70}\) The CO-gas flow rate by boiling was determined by stoichiometric extraction of the amounts of carbon and oxygen in excess. Quite recently, Saint-Raymond et al. also reported a further developed version of their model used to study the mechanisms of liquid steel decarburization below 10 ppm C in RH reactors.\(^{71}\) Unlike Kitamura et al.\(^{55}\) they considered the degassing of metal droplets splashed by bubble bursting in the atmosphere under vacuum. Here, droplets exposed to vacuum were thought to be decarburized similarly as for the CO boiling mechanism, with a linear relationship between the splashed metal and the gas flow rate. Their results indicated that CO boiling is responsible for the largest part of decarbonization for carbon contents above 10 ppm, but droplets projected in the vacuum vessel for lower carbon contents. The model by Saint-Raymond et al. was successfully verified by plant experiments.\(^{71}\) Thereafter, it was used to define standard treatment conditions and to define new equipment characteristics of RH-OB reactors in SOLLAC plants based on measurements of reaction rates deduced from exhaust-gas analysis.

The finding of Suzuki and Mori,\(^{60}\) i.e. that the decarbonization rate seems to be controlled by mass transfer in the metal, points to favorable conditions for the use of a fundamental modeling approach in predicting decarbonization. To the knowledge of the authors, this has not yet been done. It could be carried out in much the same way as discussed in Sec. 6.2 for nitrogen refining, rendering comparable benefits in the analysis of the decarbonization process. This would provide useful information in addition to the results reported by Saint-Raymond et al.\(^{71}\)

### 6.4. Summary

Models for prediction of hydrogen removal have been developed. In the future, these models need to be extended to include the interaction between slag and steel. This requires data of hydroxyl capacities of slags. Contrary to hydrogen refining, fundamental models of carbon and nitrogen refining do not exist. However, it is possible to develop such models following the same approach used in the modeling of hydrogen refining.

### 7. Growth and Removal of Inclusions

In the mid 1970s fluid modeling started to be used for calculating the growth and removal of inclusions in ladles. Table 9 lists the published studies that are based on fundamental transport equations. One of the first of these publications was by Nakaniishi and Szekely.\(^{72}\) A population balance equation was used and turbulent collisions were taken into account using an expression suggested by Saffman and Turner.\(^{73}\) Using the average energy dissipation from a mathematical fluid model for a 50 tonne ASEA-SKF ladle, they calculated the deoxidation kinetics and compared the results with experimental data from a production ladle.
discrepancy between the calculated and the experimental data were handled by introducing a coagulation coefficient ranging between 0.27–0.63 in their experiments. Later, Shirabe and Szekely74 made a fluid-flow model including turbulence with an inclusion coalescence model for an R-H vacuum degasser. Navier–Stoke’s equations were used in combination with the well-known \( k-\varepsilon \) model to calculate the turbulent flow. The spatial size distributions of the inclusions were presented in the results. In 1986, Johansen et al.75 also modeled the fluid flow in steel and inclusion behavior in a similar manner as Shirabe and Szekely, but for a gas-stirred ladle. In addition, they modeled the gas phase using a Lagrangian approach. They also took into account the separation of inclusions to the slag and refractory and the dissolution of the refractory.

Today, three-dimensional models have become more common. In the late 1990s some more comprehensive models were made. In 1997 Miki et al.76 presented a model of inclusion removal in a R-H vacuum degasser. They considered the effect of argon using a volume-fraction-of-fluid model. However, they used the average value of the energy dissipation when calculating the growth and separation of inclusions. With a simple model, the removal of inclusions due to gas bubble flotation was also considered. The model of Miki et al. also included the flotation of clusters in addition to single inclusions. Cluster formation was likewise considered by Wakoh et al.,77 Tozawa et al.78 and Miki and Thomas.79 In addition, Wakoh et al. also considered slag dispersion into the steel.79

Hallberg80 used a static modeling approach to study inclusion growth and removal. A mathematical model of a gas-stirred ladle and one of an induction-stirred ladle were used to predict velocity and turbulence data. These were used as input into a separate model for the growth and separation of inclusions. The change in total oxygen content and size distribution with time was calculated for different stirring situations. Sheng et al.81 also studied the dynamic change of inclusion density with stirring time for a gas-stirred ladle. Using a dynamic modeling approach the growth and removal of inclusions were solved as an integrated part of the fluid-flow simulation. The calculations showed that concentration gradients of all three studied classes of inclusion sizes existed even after stirring for 5 min.

Söder et al.82 also used a static modeling approach to compare different suggested mechanisms for the separation of inclusions due to bubble flotation in gas-stirred ladles. The authors noted that very different results were obtained when predicting the removal rates using different theories. Furthermore, up until then all theories presented in the literature were for spherical bubbles. Söder et al. presented a model of their own describing the removal rate of inclusions due to bubble flotation by spherical cap bubbles. From these modeling results it was concluded that spherical cap bubbles rendered a higher inclusion removal rate than spherical bubbles.

In summary, modeling inclusion behavior during ladle treatment is very difficult. Today, no model exists that takes all important growth and removal mechanisms as well as the effect of reoxidation on inclusion formation into account. Most models consider the most important growth mechanisms, turbulent and Stoke’s collisions. However, it should be pointed out that it is difficult to accurately consider the collision efficiency. More work is needed to cover the removal mechanisms. As an example, it has recently been shown that several models for inclusion removal by bubble flotation exist and that they produce very different removal rates. The effects of reoxidation from both slag and refractory on the formation of new inclusions also need to be included in the models.

8. Verification of Model Predictions
   • Alloying

Neifer et al. modeled the mixing of a tracer substance (ferromanganese) in a ladle during gas stirring and verified the results with plant data.27 They found that time-related tracer concentration curves determined experimentally agreed very well with the numerical predictions. Grip et al.29 also modeled the addition of tracer elements during the teeming process and compared with experiments. The agreement between plant measurements and predictions was also good in that study.

   • Temperature Control

Experimental stratification studies in a 7 ton ladle by Wester83 confirmed the earlier-mentioned theoretical results of Ilegbusi and Szekely,42 Koo et al.,53 and Castillejos et al.44 that suggested that gas stirring quickly homogenizes the melt. He found that a stratified ladle quickly became homogeneous with respect to temperature within less than one minute if the ladle was stirred with a gas flow of 25 l/min-t, and that the ladle became stratified again when the stirring ended.83 Similar experimental results were also reported by Rieche et al.46

   • Slag–Steel Reactions

In the study by Hallberg et al. fundamental model predictions of sulfur refining were compared to industrial data.49 In Fig. 14, the experimentally determined and the predicted sulfur contents in steel are plotted as a function of time. Data are given only for gas stirring and for combined gas and induction stirring. Other reported predictions and corresponding measured sulfur contents are specified in Table 10.24,48,49 As can be seen from Fig. 14 and Table 10, the overall agreement between the predictions and the measurements was satisfactory.

In the study by Andersson et al.49 predictions of dynamically varying slag compositions were heuristically compared to plant data. It was concluded that the fundamental model could be used to predict the loss of aluminum and desulfurization in the steel as well as the reduction of FeO and MnO in the slag.

   • Gas–Steel Reactions

In Fig. 15 the predicted average hydrogen concentration in the steel as given in a study by Hallberg et al. is shown as a function of time.49 Both model predictions and experimentally determined values are shown. Table 11 is a compilation of all comparisons made between measured and predicted hydrogen contents.24,48 As can be seen from Fig. 15 and Table 11, the agreement between predictions made by the fundamental modeling approach and measurements
was in general quite good.

- Inclusion Growth and Removal

Hallberg compared model predictions of total oxygen contents at different times with experimentally determined data. The agreement between model predictions and experimental data was found to be fairly good for both induction-stirred and gas-stirred ladles.

- Summary

Verifications of model predictions of alloy, temperature, sulfur and hydrogen behavior during ladle refining have been carried out. In general, model predictions have agreed well with corresponding experimental data. For both the modeling of reoxidation and inclusion behavior experimental verification is required. This is difficult to carry out in plant trials, but must be done in order to ensure the model predictions’ reliability.

9. Concluding Remarks

The review of the literature shows that no complete overall ladle refining model based on fundamental theories which consider all refining operations exists. Also, even fundamental models describing separate refining operations such as nitrogen and carbon removal are lacking. However, fundamental models for predicting alloy behavior after addition to steel, temperature, sulfur removal, hydrogen removal, reoxidation, and the growth and removal of inclusions have been developed.

The extent to which these fundamental model predictions have been verified with experimental data varies for different refining operations. Predictions of alloy concentrations during additions and temperature distributions have been.
found to agree well with measurements. Furthermore, predictions of sulfur and hydrogen refining rates have also been found to agree well with experimentally determined sulfur and hydrogen concentrations in steel. However, predictions of the effect of reoxidation of steel due to high FeO contents in the slag or the growth and removal of inclusions have not been verified. In the case of the prediction of inclusion behavior, it has been shown that concentration gradients of inclusions exist during stirring. These gradients are similar to those found for hydrogen and sulfur in steel, but in the case of inclusions the predictions need to be verified before further conclusions can be drawn.

A fundamental model that has been carefully verified is quite useful, being inherently suitable for process optimization and for evaluation of new process procedures, as well as for refinement of treatment strategies and more. The reason is that fundamentally based models can be used for a wide range of ladle geometries, stirring conditions, steel and slag compositions, etc. As an example, developed treatment strategies for the CAS-OB process based on model predictions regarding the use of thick or thin slag layers are presented in Fig. 16. In the lower left part of Fig. 16, streamlines indicating the flow field are shown for one case with a thick slag, high argon gas flow rate and a deep immersion depth of the bell. In the lower right part of Fig. 16 streamlines are shown for a case with a thin slag, low argon gas flow rate and a moderate immersion depth of the bell. In neither of the two cases representing different combinations of slag thickness, bell immersion depth and argon gas flow rate are recirculation loops (turbulent regions) predicted in the slag region outside the bell. Turbulent regions in the slag outside the bell should be avoided because such flow situations might, for example, cause reduction of vanadium oxide and wear of the bell. In the upper part of Fig. 16 the corresponding treatment strategies obtained are shown. A thick slag is seen to require a longer total treatment time, Al addition at a later timepoint and a higher argon gas flow rate than a thinner slag. Another example is illustrated in Fig. 17, where predictions show how much more sulfur can be removed during stirring when the amount of slag is increased by 50%.

In the future it will be necessary to develop fundamental models of nitrogen and carbon removal in ladle operations as well as for other important ladle operations not already covered. To create a complete model of each refining step during ladle treatment it is also necessary to couple the required reaction models. A step in that direction was demonstrated in the case of when reoxidation was taken into account in the modeling of desulfurization. A next step could be to extend this model to include inclusion behavior. Thereafter, these three models could be introduced in a model for vacuum treatment that could further be coupled to a model for hydrogen prediction. In doing this, a complete model for the vacuum-treatment part of ladle refining would be created. Similarly, coupled models of the other parts of the refining operations could be created. Finally, these could be put into one overall model of the complete ladle refining process.

Of course, all future models of each individual part of ladle refining or the final overall model must be verified. This must be done through carefully performed plant trials and laboratory trials when possible. It would be highly beneficial if companies, universities and other research organizations cooperated in developing such models. This might lower the cost for model development as well as reduce the time required for completion.

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