A New Approach to Using Modelling for On-line Prediction of Sulphur and Hydrogen Removal during Ladle Refining

M. HALLBERG, T. L. I. JONSSON and P. G. JÖNSSON
Div. of Metallurgy, Royal Institute of Technology, SE-100 44 Stockholm, Sweden.

(Received on December 19, 2003; accepted in final form on May 10, 2004)

A simplified model has been developed for on-line determination of sulphur and hydrogen contents in the steel during vacuum degassing in an ASEA-SKF ladle furnace at Ovako Steel in Hofors, Sweden. The simplified model was developed based on results from fundamental mathematical model simulations of hydrogen and sulphur refining for a number of cases representing normal production situations. More specifically, mass-transfer coefficients were determined from the simulations and thereafter used to develop separate simplified models for sulphur and hydrogen refining. Predictions from using the simplified process models agreed well with sulphur and hydrogen data from full-scale plant trials. It was therefore concluded that the main purpose of the study, namely to achieve a less time-consuming model suitable for production applications, was fulfilled. The final part of the paper presents how the simplified models can provide engineers or operators with off-line or on-line guidelines on performing the vacuum degassing operation such that quality requirements regarding sulphur and hydrogen contents in the steel product are met.

KEY WORDS: sulphur; hydrogen; ladle; vacuum degassing; refining; model.

1. Introduction

Today, it is very difficult to take samples during the vacuum degassing operation in a typical ASEA-SKF ladle furnace. Therefore, a model would be of use for the operator to determine when to stop the treatment in order to reach the required hydrogen and sulphur contents in the steel. The authors earlier developed Computational Fluid Dynamics (CFD) models in which fundamental transport equations, turbulence equations, and thermodynamic equations were solved in order to simulate sulphur and hydrogen refining during vacuum degassing in a ladle furnace.1,2) The three-dimensional fluid-dynamics model takes 3 phases into account, i.e. steel, slag and gas (argon). Verification of the degassing model was carried out at Ovako Steel for both gas stirring and combined stirring using a ladle with two porous plugs.2) Plant trials revealed that the modelling approach has the full potential to predict sulphur and hydrogen refining during degassing at a level of accuracy normally suitable for industrial practices.

The fundamental model is, however, far too computer-resource intensive to be used on line in production. This would be needed in order to provide operators with advice regarding process changes that should be made. Therefore, a simplified model has been developed for on-line control of sulphur and hydrogen content in the steel during vacuum degassing in the ladle furnace. In order to develop the simplified process model, a great number of model simulations with the complex CFD model were performed for a number of cases that represent normal production situations in the ladle furnace at Ovako Steel. The results from these model calculations were then used to calculate mass-transfer coefficients for each standard production case. A brief description of this method of developing a simplified model based on fundamental modelling results was recently presented at the Wolf Symposium.3) The authors have not been able to find any publications in international journals reporting earlier utilisation of this method. From this perspective one can say that this is a novel approach, developing simplified models based on fundamental models to be used for process control.

In the first part of the paper, a short description of the fundamental mathematical CFD model of hydrogen and sulphur refining in an ASEA-SKF ladle furnace during vacuum degassing is given. Thereafter follows a detailed description of how a simplified process model for prediction of hydrogen and sulphur refining was derived based on the CFD simulations. Next, the verification results of the simplified process model are discussed. The final part of the paper provides examples of how the simplified models for hydrogen and sulphur refining can be used on-line as well as off-line in production.

2. Fundamental Mathematical Model

The three-phase mathematical model of a vacuum-degassed ladle takes into account the gas (argon injection), slag and steel phases. The layout of the model is shown in Fig. 1. The model is based on fundamental transport equations and concentration equations for each of the dissolved elements. In addition, it is necessary to solve the thermodynamic equations related to sulphur and hydrogen refining. It
Conservation of momentum in all three dimensions for Conservation of steel, argon and total mass

Transport equations need to be solved:

2.2. Transport and Turbulence Equations

There are no reactions between liquid and gas within the
due to the ladle bottom.

The gas bubbles are introduced through two porous plugs
located at the ladle bottom.

The gas bubbles are uniformly distributed in each
phase at the start of a calculation.

The slag depth is uniform and the slag composition is ho-

A static force field (independently calculated) is suitable
for modelling the influence of the inductive stirrer.

There are no temperature gradients at the start of a cal-

The dissolved elements are uniformly distributed in each
phase at the start of a calculation.

The slag depth is uniform and the slag composition is ho-

An interfacial friction coefficient is used to describe the
force between the gas and the steel.

The free surface of the slag/air interface is frictionless.
An allowance is made for the escape of gas bubbles at
the interface.

There are no reactions between liquid and gas within the
slag phase.

2.2. Transport and Turbulence Equations

The following governing transport and turbulence equa-
tions need to be solved:

Transport equations

- Conservation of steel, argon and total mass
- Conservation of momentum in all three dimensions for
- Conservation of thermal energy for steel, slag and argon
- Concentration equations for dissolved elements in each of the three phases

Turbulence equations

- Turbulent kinetic energy
- Dissipation rate of turbulent energy

2.3. Thermodynamic Considerations

The thermodynamic considerations of sulphur and hy-

drogen refining within the present model have been pub-
lished earlier.1,2,4 However, the most important consider-
as are covered below in this report. Thermodynamic data
such as the activity of alumina, sulphide capacities, interac-
tion coefficients and Gibbs free energies are identical with
the ones published earlier.2 The calculations were made for
a bearing-steel grade with the following component con-
centrations: 1.0 wt% C, 1.4 wt% Cr, 0.28 wt% Mn and 0.22
wt% Si. The aluminium content in the steel before starting
the degassing operation was set to 0.065 wt% for the whole
melt.

2.3.1. Sulphur Refining

Local thermodynamic equilibrium is expected to estab-
lish dynamically in the slag–metal mixing zone. In the pre-
sent study, the desulphurisation of an aluminium-killed
metal bath by a slag initially containing 53 wt% CaO, 32
wt% Al2O3, 7 wt% MgO and 8 wt% SiO2 is considered.
It has been assumed that the slag behaves like a liquid
phase during the process and consequently solid-phase pre-
cipitation in the slag is neglected. This assumption allows
for both the application of the sulphide-capacity concept in
the model and formulation of the different oxide activities.
In order to formulate the chemical process, the following
simplifications have been made:

1. The sulphide capacity of the slag is constant for any
given temperature during the ladle treatment.
2. The oxygen activity (ao) in the bulk of the metallic
melt is determined by the activity of aluminium by the reaction:

\[ 2[\text{Al}]_{\text{metal}} + 3[\text{O}]_{\text{metal}} = \text{Al}_2\text{O}_3(\text{solid}) \]  

However, the oxygen activity in the liquid metal phase, 
\( a_o \), in the slag–metal mixing zone is determined as de-
scribed in Sec. 3.2.

3. The concentrations of dissolved aluminium, oxygen and

The first assumption may be justified by the fact that the
slag composition does not change significantly during the
sulphur refining period. As for the second assumption, it is
reasonable to expect that reaction (1) is dominant in the
bulk of the metallic melt, since aluminium is used as the
deoxidiser and alumina particles are always found in the
liquid metal. The steel bulk is here defined as liquid metal
containing less than 1% top slag (by weight). The assump-
tion that changes in the contents of other dissolved ele-
ments, except for Al, O or S, have a minor effect on desul-
phurisation is based on the assumption that the concentra-
tions of elements like C, Mn, and Si do not change considerably during ladle treatment.

The desulphurisation process can be expressed by the equation:

\[ [S]_{\text{Metal}} + (O^2^-)_{\text{Slag}} = [O]_{\text{Metal}} + (S^2)_{\text{Slag}} \]  

This is based on the slag-metal reaction. The ability of a slag to absorb sulphur from a metallic phase is often expressed as sulphide capacity, \( C_s \), a measurable quantity, which is defined by \( (3) \):

\[ C_s = \frac{(\text{wt}\%S)_{\text{Slag}}}{P_{O_2}} \]  

where \( P_{O_2} \) and \( P_{S_2} \) are the partial pressures of oxygen and sulphur gases, respectively, prevailing adjacent to the slag phase. In the case of slag-metal reactions, \( P_{O_2} \) and \( P_{S_2} \) are related to the activities of oxygen and sulphur in the liquid metal through the following reactions:

\[ \frac{1}{2} O_2 (\text{gas}) = [O]_{\text{Metal}} \]  
\[ \frac{1}{2} S_2 (\text{gas}) = [S]_{\text{Metal}} \]

The sulphur partition ratio, \( L_s \), is related to the sulphide capacity by the relationship:

\[ L_s = \frac{(\text{wt}\%S)_{\text{Slag}}}{(\text{wt}\%S)_{\text{Metal}}} = C_s f_s \cdot \frac{K_{C4}}{a_s \cdot K_{C5}} \]  

where \( a_s \) and \( f_s \) denote the activity of oxygen and the activity coefficient of sulphur in the liquid metal, respectively. \( K_{C4} \) and \( K_{C5} \) in Eq. (6) stand for the equilibrium constants of reactions (4) and (5), respectively. The equilibrium constants \( K_{C4} \) and \( K_{C5} \) are well established for liquid steel and can be found in the literature. For any appropriate length of time step, a sufficient mixing of slag and metal at their interface will locally allow thermodynamic equilibrium to be reached before the end of the time step. If \( a_s \) and \( f_s \) at a given instant and at a given position in the slag/metal mixing zone are known, the partition of sulphur between the slag and metal can be evaluated at that position on the basis of the sulphide capacity of the slag using Eq. (6). However, \( a_s \), \( f_s \), and the activity of aluminium, \( a_{Al} \), are all functions of the contents of the dissolved elements in the liquid slags. In order to deal with this, the dilute-solution model is applied to the liquid metal together with a separate transport equation for each of the dissolved elements. According to the dilute-solution model, the activity coefficient of element \( i \) (\( f_i \) in the logarithm) is expressed as:

\[ \log f_i = \sum_{j=2}^{\infty} e_{ij} \cdot [\text{wt}\%j] \]  

where \( e_{ij} \) represents the interaction coefficient of \( j \) on \( i \).

To sum up, for any given slag composition, measuring \( C_s(T) \) makes it possible to calculate desulphurisation using Eq. (6) and first principles by a model which considers the slag phase, given the assumptions above. However, the concentration profiles for each of the dissolved elements Al, O and S must be known at each instant, meaning that a separate time-dependent transport equation needs to be solved for each of the dissolved elements in the metal and for sulphur in the slag as well.

### 2.3.2. Hydrogen Refining

During vacuum treatment, hydrogen is transferred between liquid metal and bubbles as well as between slag and liquid metal. While the argon bubbles provide a vacuum for hydrogen and carry it away, slag picks up hydrogen from the atmosphere and transfers it to the steel. A number of studies have been carried out to better understand the behaviour of slags in the hydrogen pick-up of steel. It has been found that the dissolved hydrogen is independent of the partial pressure of \( H_2 \) in the gas phase, and depends only on the partial pressure of water vapour present. In industrial practice, water is adsorbed by the raw materials of the synthetic slag, like limestone and dolomite. Although a great portion of the adsorbed water will be driven away during pre-melting of the slag, some water is dissolved in slag through the following reaction:

\[ H_2O(gas) + O^2^- (slag) = 2OH^- \]  

It is well agreed upon that the solubility of hydrogen, or rather \( OH^- \), in a slag is proportional to the square root of the water vapour pressure. If the initial content of hydrogen in the slag was known, the slag/metal reaction regarding the transfer of hydrogen could be formulated using the partition coefficient for hydrogen. Unfortunately, it is very difficult to estimate the content of \( OH^- \) in the slag for each ladle treatment, as this very much depends on the sources and history of the raw materials. In the present work, the effect of hydrogen content in the slag on hydrogen refinement is therefore not considered. However, it is noted that the partition of hydrogen between slag and metal could be far from thermodynamic equilibrium at the start of vacuum degassing, even though the degassing at Ovako Steel usually takes place 20 min after the addition of synthetic slag. A small amount of hydrogen could be transferred from the slag to the liquid steel during the degassing process.

The hydrogen pick-up by the argon bubbles can be considered to take place in three steps, namely the mass transfer of dissolved hydrogen in the liquid metal, the chemical reaction

\[ 2[H]=H_2(gas) \]  

at the surface of the bubbles, and the mass transfer of \( H_2 \) in the bubbles. At the temperatures used during ladle treatment, the chemical reactions are usually very fast. It can be expected that reaction (9) at the bubble/liquid interface occurs at a much higher rate compared to the hydrogen transfer in the liquid metal. Furthermore, if the mass transfer in the bubble is the rate-controlling step, given a certain hydrogen content, the rate of hydrogen refinement will be constant and irrespective of time. Hence, it is probable that the mass transfer in the liquid steel is the rate-controlling process.

Based on the aspects mentioned above, the following model simplifications were made:

1. The gas is assumed to be ideal.
2. Thermodynamic equilibrium for hydrogen is locally established dynamically between the gas bubbles and the liquid metal in each calculation node under considera-
According to the dilute-solution model, for reaction (9) reported by Engh\(^6\) has been employed. In using Eq. (9), the hydrogen activity in the liquid metal is calculated using the dilute-solution model. The transfer of hydrogen between the slag and liquid steel is not considered.

5. The mass transfer of hydrogen in the liquid metal controls the hydrogen refinement process.

6. In the calculation of the gas density, the gas bubbles are assumed to consist only of argon and hydrogen, as the contents of CO and N\(_2\) in the gas phase are moderate and their molecular weights are at the same level as argon. The initial hydrogen concentration in the argon gas is calculated from the content of CH\(_4\) by considering the following reaction:

\[
\text{CH}_4(\text{gas}) = C + 2H_2(\text{gas}) \quad \text{..................(10)}
\]

In order to calculate the thermodynamic equilibrium at a given instance for a given node, the standard Gibbs energy for reaction (9) reported by Engh\(^6\) has been employed. According to Engh,\(^6\) the standard Gibbs energy change for reaction (9) can be expressed as:

\[
\Delta G^\circ = -2(36,480 + 30.46T_f) \quad (\text{J} \cdot \text{mol}^{-1}) \quad \text{........(11)}
\]

where \(T_f\) is the absolute temperature of steel.

Hence, the ratio of the hydrogen pressure in the gas phase, \(P_{H_2}\), over the square of the hydrogen activity in the metal can be expressed as:

\[
\frac{P_{H_2}}{f_{H_2}[\text{wt}\%H]^2_{\text{metal}}} = \exp \left( \frac{-2(36,480 + 30.46T_f)}{RT_f} \right) \quad \text{........(12)}
\]

where \(f_{H_2}\) is the activity coefficient of hydrogen, \([\text{wt}\%H]\) is the hydrogen concentration and \(R\) is the gas constant. According to the dilute-solution model, \(f_{H_2}\) can be expressed by using Eq. (7).

### 2.4. Method of Solution

The Phoenics commercial code was used to obtain the solutions to the governing equations, concentration equations, boundary conditions and source terms. It is a finite-difference code that uses the algorithm IPSA to solve two-phase problems.\(^{10,11}\) The calculations were made in the transient-solution mode. A typical calculation that employed 1-s time steps and a 31\(\times\)31\(\times\)41 non-uniform grid required about 100 h of computational time on a Sun Enterprise 4000 with six 350 MHz CPUs.

### 3. Simplified Model for Process Control

#### 3.1. General Equations for Refining Rates

Traditionally, the kinetics of the refining operation have been described by the boundary-layer theory. This theory assumes that a concentration boundary layer exists for the element that will be refined. If mass transport in the steel bath is the rate-limiting step for refining of a contamination element, the concentration boundary layer in the steel phase determines the refining process. On both sides of the concentration boundary layer, \(i.e.\) in the steel phase and in the refining phase (gas phase for hydrogen refining and slag phase for sulphur refining), perfect stirring conditions are assumed (homogenous concentration profiles) during the whole process. Based on these simplifications, the refining rate for a contamination element in the steel can be described by\(^{12}\):

\[
\frac{d[\text{wt}\%x]}{dt} = -\frac{k_pA}{M}([\text{wt}\%x] - [\text{wt}\%x]_\text{eq}) \quad \text{........(13)}
\]

where \(x\) is the contamination element (S or H), \(k\) is the total mass-transfer coefficient, \(p\) is the steel density, \(M\) is the steel mass and \([\text{wt}\%x]_\text{eq}\) is the concentration of the contamination element. The parameter \([\text{wt}\%x]_\text{eq}\) is the hypothetical concentration of the refined element in the steel phase in equilibrium with the current concentration in the refining phase. The interface area between the steel phase and the refining phase is specified as \(A\).

One disadvantage with the model described by Eq. (13) is that coefficient \(k\) must be determined empirically. Furthermore, \(k\) depends on the prevailing conditions for each specific heat. For example, \(k\) varies with prevailing stirring conditions, slag weight, slag composition, temperature, \(\text{etc.}\) Sometimes the mass-transfer coefficient is expressed as\(^{13}\):

\[
k = \frac{D}{\delta} \quad \text{...............................(14)}
\]

where \(D\) is the diffusivity for the refining element and \(\delta\) is the thickness of the boundary layer. Taking sulphur refining as an example, \(\delta\) depends on the position along the slag/metal boundary layer (approximately the distance from the wall to an open eye) and the velocity of the steel melt at this point. Therefore, it is very difficult to calculate a hypothetical \(\delta\) without knowledge about the fluid-flow conditions in each specific situation.

#### 3.2. Sulphur Refining

The solution to Eq. (13) for sulphur can be written as follows:

\[
\text{wt}\%S = (\text{wt}\%S_0 - \text{wt}\%S) e^{-k_A V/A} + \text{wt}\%S_\text{eq} \quad \text{........(15)}
\]

where \(k\) is the mass-transfer coefficient for sulphur, \(A\) is the surface area and \(V\) is the volume of the steel melt. For all calculations the quotient \(V/A\) has been set to 2.3, which corresponds to the conditions at Ovako Steel. The value of \(V/A\) is set to 2.3 for both desulphurisation and dehydrogenation to render a consistent treatment for the parameter \(k\) in both Eqs. (15) and (22), although the value of \(A\), thought of as the actual area for reaction, is different for desulphurisation and dehydrogenation. This means that the difference in the actual areas for hydrogen and sulphur refining will be embedded in the numerical value of \(k\) when this value is determined from the CFD model calculations. The term \(\%S\) is the sulphur content at treatment time \(t\), \(\text{wt}\%S_\text{eq}\) is the sulphur content at equilibrium between steel and slag and \(\text{wt}\%S_0\) is the sulphur content at the start of the treatment.

In this work, the thermodynamic equation system below has been solved to determine \(\text{wt}\%S_n\) when calculating the mass-transfer coefficients for sulphur for each specific standard case. Equations (16) to (20) were also used to calculate the oxygen activity at each calculation node at the slag/metal interface.
is the oxygen activity in the steel and actual area for hydrogen refining will be embedded in the ladle at Ovako Steel. The deviation compared to the volume/area ratio was set to 2.3, which corresponds to the volume/area ratio able for the studied slag composition and temperature. The vari-

Other thermodynamic data used in the calculation of $\%S_{eq}$ was found that the best results were obtained with the calculated analysis at the end of the treatment. Therefore, this approach was taken throughout the study. The three parameters vacuum pressure, amount of slag to steel by weight (slag weight/steel weight).

### 3.3. Hydrogen Refining

The solution to Eq. (13) for hydrogen can be written as follows:

$$\text{wt}\%H_2 = e^{-k \cdot \frac{\Delta t}{Y} + \text{wt}\%H_{eq}}$$

where $k$ is the mass-transfer coefficient for hydrogen. In calculating the mass-transfer coefficient, the quotient $V/A$ was set to 2.3, which corresponds to the volume/area ratio of the ladle at Ovako Steel. The deviation compared to the actual area for hydrogen refining will be embedded in the value of $k$ when this parameter is determined from the CFD model calculations, compare Sec. 3.2. The variable wt%$H_2$ is the hydrogen content at the treatment time $t$, wt%$H_{eq}$ is the hydrogen content at equilibrium between the steel and gas and wt%$H_0$ is the hydrogen content at the start of the treatment.

$$\text{wt}\%H_2 = \frac{\text{wt}\%H_{eq}}{1 + L_0 T}$$

where $L_0$ is the equilibrium sulphur distribution between slag and metal and $C_s$ is the sulphide capacity of the slag for the studied slag composition and temperature. The variable $a_{eq}$ is the oxygen activity in the steel and $Y$ is the ratio of slag to steel by weight (slag weight/steel weight).

For the sake of completeness, it should be mentioned that an alternative to determining wt%$S_{eq}$ is to use the following expression:

$$\text{wt}\%S_{eq} = \frac{\text{wt}\%S_{eq}}{1 + L_0 T}$$

where $L_0$ is the equilibrium sulphur distribution between slag and metal and $C_s$ is the sulphide capacity of the slag for the studied slag composition and temperature. The variable $a_{eq}$ is the oxygen activity in the steel and $Y$ is the ratio of slag to steel by weight (slag weight/steel weight).

In this work, Eq. (21) and Eqs. (16) to (20) were used to determine wt%$S_{eq}$. It was found that the best results were obtained when the thermodynamic equation system, Eqs. (16) to (20), were used with the calculated analysis at the end of the treatment. Therefore, this approach was taken throughout the study.

### 4. Results and Discussion

#### 4.1. CFD Simulations of Standard Production Cases

In order to develop a simplified process model, a great number of model simulations with the complex CFD model were performed for normal production situations from the ladle refining at Ovako Steel. These production cases are described below. Results from these model calculations were then used to calculate mass-transfer coefficients and equilibrium values for sulphur and hydrogen in contact with slag and gas, respectively, for each standard case. With this knowledge, traditional kinetic boundary layer theory was applied in order to in a fast and easy manner predict the sulphur and hydrogen contents in the steel as a function of treatment or refining time. The approach to introduce a process model is schematically described in Fig. 2.

The model simulations were performed for a 100 t ASEA-SKF ladle furnace equipped with an electromagnetic stirrer (1 000 A, upward direction) and argon injection through two bottom porous plugs. In order to cover standard production, a high-carbon chromium bearing steel (1.0 wt% C, 1.4 wt% Cr, 0.28 wt% Mn and 0.22 wt% Si) was chosen for the simulations. The aluminium content in the steel before starting the degassing operation was set to 0.065 wt% for the whole melt. The initial slag composition was kept constant, as mentioned above, with component concentrations of 53 wt% CaO, 32 wt% Al$_2$O$_3$, 7 wt% MgO and 8 wt% SiO$_2$. The FeO content before vacuum degassing is typically 0.5 wt% and was therefore assumed to have a minor effect on the results in this study. The steel temperature before degassing was 1600°C.

Model simulations with these kinds of complex models are very time consuming. Because it took almost a week to perform one single simulation of a standard case, the number of parameters permitted to vary was limited within this study. The three parameters vacuum pressure, amount of top slag and argon gas flow rate, were considered to be the most important and were therefore varied in such a way that they addressed different normal production situations in the ladle furnace. The selection of these parameters was based on the experience of ladle-furnace operators as well as earlier modelling and plant studies performed at Ovako Steel. Results from one of these publications revealed that slag composition to some extent especially affects the sulphur refining process. However, from a practical point of view, it is almost impossible in plant production to adjust the slag composition so precisely (0.5–1 wt%) that a resulting difference in the sulphur refining rate can be detected. Therefore, the decision was made to keep the initial slag composition constant for the model simulations in this work.

In order to later develop a simplified process model, the three parameters were varied as presented in Table 1 during the CFD simulations. As can be seen from the table, a total
number of 32 (2×2×8) simulations were performed. The vacuum pressure was set to 2.0·10⁻² bar (good) or 6.7·10⁻³ bar (poor), the slag amount to “normal” or “normal/400 kg” and the argon gas flow rate through each of the two porous plugs was set to 10 L/min (low), 100 L/min (medium) or 175 L/min (high). Actually, the total number of model simulations were 36 (2×2×9). But, it is not realistic to perform the vacuum degassing operation with an insufficient argon gas flow rate (low) through both the porous plugs. Therefore, the cases having a flow rate through both porous plugs of 10 L/min were excluded.

The model simulations with the complex CFD model were later complemented by a calculation where the pressure in the vacuum chamber was lowered to 0.27·10⁻² bar. This simulation was done after modification of the vacuum pump in the plant which made it possible to reach pressure levels in the region of 0.27·10⁻² bar. Two calculations were also made where the temperature before degassing was changed from 1600 to 1555°C and 1615°C to observe the effect of initial temperature on the removal of S and H. In order to study the effect of prolonged degassing (>25 min) on sulphur and hydrogen removal, yet three more calculations were made for a treatment time of 40 min. This had to be done since a prolonged treatment time affects the final steel temperature and slag composition, resulting in a changed mass-transfer coefficient. These additional six calculations are also presented in Table 1 (a total of 38 simulations).

### 4.2. Determination of Mass-transfer Coefficients

Based on Eqs. (15) and (22), the mass-transfer coefficient, k, for sulphur and hydrogen could be determined by making a plot of:

\[
kt = -\ln \left( \frac{\text{wt}\% X_t - \text{wt}\% X_{eq}}{\text{wt}\% X_0 - \text{wt}\% X_{eq}} \right) \frac{V}{A} \quad \text{(24)}
\]

where X is either sulphur or hydrogen content. If the expression kt is plotted as a function of time, the result should be a straight line, because k is expected to be constant. Thus, plotting the right hand side of Eq. (24) as a function of treatment time t makes it possible to determine the value of k as the time derivative (inclination) of the expected straight line. By doing that, the derivation from the pre-set value of V/A (=2.3) will be embedded in the value of k, see Secs. 3.1 and 3.2. However, actually inserting the CFD calculated values of S and H into the right-hand side of Eq. (24) does not render a perfectly straight line, as can be seen in Fig. 3. Therefore, an adoption of the line describing the product kt to the calculated values was done. Typical adoptions, or linear regressions, are also shown in Fig. 3 for S and H. More specifically, Figs. 3(a) and 3(b) illustrate the calculated value of (k·t) as a function of time for each element, i.e. sulphur and hydrogen. Here, a priori knowledge of the process should be used to make the line representing
the product $k_t$ cross the calculated curve at a point corresponding to a time near but not yet at the end of ladle treatment by weighing calculated values near the expected end of the treatment. This way the analytical model (process model) can be made very accurate when accuracy is most needed, i.e. when the decision to end the refining process must be made.

It should be noted that this investigation has focused on obtaining knowledge regarding the end of the refining process. That is why the straight lines have been drawn to coincide with the curve at longer treatment times. It is, of course, possible to let the straight line coincide with the simulation curve at shorter treatment times if the earlier stages of ladle refining are more of interest. Furthermore, it is possible to evaluate two or more different mass-transfer coefficients which pertain to different times of the vacuum degassing process. Thus, it would be possible to obtain better agreement between the results from the numerical simulation and the analytical model for the whole refining time on the expense of the complexity and flexibility of the process model.

### 4.3. Verification of the Simplified Process Model

The process model was verified through plant trials performed at Ovako Steel (see Tables 2 and 3 and Fig. 4). In Tables 2 and 3, process model results are also compared with CFD simulation results regarding prediction of sulphur and hydrogen contents during vacuum degassing. A comparison of results from these two models can also be seen in Figs. 5 and 6. In Table 2, both predicted and measured sulphur and hydrogen values are given for 5 heats performed with combined stirring (gas stirring + inductive stirring). The gas flow rate values given in Table 2 for the process model and the CFD model are those within the available range for the process model (Low: 10, Medium: 100, High: 175 L/min). Even if it was possible to use the real argon gas flow rates in the CFD model, as was done in the simulations presented in Table 3, these values were anyhow in order to be able to compare the results from the two models. However, it should be noted that this simplification results in a less good agreement between simulation results and plant data than possible to achieve.

#### 4.3.1. Comparison of Simulation results from process model (combined stirring), CFD model (gas stirring) and plant data (gas stirring) for 2 additional heats.

![Fig. 3. Determination of mass-transfer coefficients from numerical simulation results for a) sulphur refining and b) hydrogen refining.](image-url)
In Table 3, the process model is compared with plant trials and simulation results from the CFD model for 2 heats conducted with gas stirring only. However, the process model could only be used for combined stirring, since it was developed to simulate a process using combined stirring. Therefore, the comparison in Table 3 should only be looked upon as a test to evaluate the influence from electromagnetic stirring on the sulphur and hydrogen removal rates. For the simulation results in both Tables 2 and 3, samples were taken and predictions were made at the start and at the end of degassing. For heats 1 and 2, the operation was interrupted after 3 min at vacuum pressure and an extra sample was taken. Heat data such as argon flow rates and vacuum pressure are also provided in these tables. Simulations and plant trials were performed with a normal slag amount and with the same steel and slag composition as was specified in Sec. 4.1.

The process model results were generally in fairly good agreement with production plant data and simulation results from the CFD model regarding sulphur and hydrogen removal within the limits of what can be classified as a normal heat (see Table 2). Regarding hydrogen removal, Table 2 presents rather poor agreement between plant measurements and predicted values for heat No. 2 for both models after 3 min at vacuum pressure. In this case it was not possible to take a hydrogen sample and therefore a default total hydrogen value was set to 3.8 ppm (typical hydrogen value before degassing) in order to perform the simulations. This can be one explanation as to why the models predicted a
too high hydrogen value in comparison to plant data only 3 min after starting the operation.

In Table 3, process model simulation results are compared to CFD results and measurements carried out with gas stirring only. As mentioned earlier, the simplified model simulates only combined stirring. But, it was also of interest to know how the use of the electromagnetic stirrer influences especially the hydrogen removal rate. The Table 3 information indicates that the process model with combined stirring predicts higher hydrogen contents for both the heats. One probable explanation of this result may be that the use of inductive stirring (1000 A, upward direction at the wall) reduces the retention time for argon gas bubbles in the steel bath. Jauhainen et al. found that when combined stirring was used and the induction stirrer was working upwards, it took a shorter time for the argon gas bubbles to reach the surface compared to a case where the induction stirrer was working downwards and gas stirring was carried out simultaneously. This results in less time for hydrogen to diffuse to the gas bubbles which renders a lower hydrogen removal rate. Regarding sulphur removal, as can be seen in Table 3, there is almost no difference between measurements and CFD-simulation results performed with gas stirring only and process model results using combined stirring. The data from these two heats implies that the inductive stirrer does not contribute to the desulphurisation operation under the prevailing stirring conditions (Table 3). Rephased, the inductive stirrer does not appear to influence the hydrogen and sulphur removal processes in a positive way. However, effective removal of non-metallic inclusions during the degassing operation is greatly dependent on the use of the electromagnetic stirrer.

In Fig. 4, the deviation between model predictions and plant data after degassing is presented for heats 1–5. The resolution of the measured sulphur analysis is 0.001 wt% and the accuracy in the determination of the analysis is 0.0003 wt% (LECO CS-244, ASTM 1019-94). The relative resolution for hydrogen is 0.01 ppm and the accuracy value is 0.05 ppm (ESK method) which corresponds to a relative uncertainty of 4.3%. If all heats were included, the average deviation for the process model would be 26% and 12% for sulphur and hydrogen, respectively. These values should be compared with 18% and 13% for the CFD model and with the relative uncertainty of 12% and 4% in the figures representing the measured values. It is worth noting that beyond earlier mentioned uncertainties the reproducibility of the sampling should be added which reflect the appearance of gradients in the melt. This sample is later compared with model predictions which represent an average value for the whole ladle.

However, results reveal poor agreement between predictions and measurements for heat No. 3 regarding sulphur and for heat No. 5 regarding hydrogen. For both heats 3 and 5, these results may be explained by uncertain argon gas flow rate values due to difficulties in measuring the flow rates through the porous plugs. Experience from the trials indicates that the argon gas flow rate has a greater influence on the sulphur refining process than the dehydrogenation process, which could be an explanation why a poor agreement is reached between predictions and measurement with respect to sulphur but not for hydrogen for heat No. 3. If heats No. 3 and No. 5 are excluded in calculating the average deviation for sulphur and hydrogen, respectively, the average deviation values are then 16% and 8% for the process model and 11% and 6% for the CFD model. These deviation figures are acceptable for a simplified process model in the light of the fact that simplifications such as a constant initial slag composition and fixed values for argon gas flow rates most likely also affect the hydrogen and sulphur removal rate to some extent.

In Fig. 5, wt%S/wt%S 0 is plotted versus the degassing time in a similar way as for sulphur. A comparison of the process model and model simulation with the CFD model (numerical simulation) with respect to sulphur removal indicates good agreement for treatment times shorter than 10 min. The sulphur content predictions, however, show better agreement for treatment times between 10 and 25 min. This is due to the way in which the mass-transfer coefficients were determined (see Sec. 4.2 above). In Fig. 6, wt%H/wt%H 0 is plotted versus the degassing time in a similar way as for sulphur. A comparison of the process model and model simulation with the CFD model with respect to hydrogen removal indicates good agreement for treatment times of 6 to 25 min.

If the simplified model is to be applied for treatment times considerably longer than 25 min, a new mass-transfer coefficient value needs to be calculated. This is because the equilibrium values used in the calculation of mass-transfer coefficients are influenced by the final temperature and slag composition.

4.4. Use of the Process Model

The process model can be used as a tool to predict the sulphur and hydrogen content in the steel either on-line by operators in the plant or by engineers in further developing the refining operation. To be able to initialise a model calculation, the user needs to provide the model with appropriate heat data such as:

- Argon gas flow rates (for each porous plug)
- Top slag amount (synthetic slag + carry-over slag)
- Steel temperature
- Vacuum pressure
- Sulphur and hydrogen contents (in the steel)
- Treatment time

The calculation is performed in less than a second and the user receives information about sulphur and hydrogen removal as a function of treatment time under the stated conditions. In Fig. 2, a calculation sheet for an on-line calculation with the simplified process model is shown. As mentioned previously, the model can be used on-line (dynamic modelling) or off-line (static modelling).

- On-line (Dynamic Modelling)

Process-model guidelines help the operator to choose the appropriate measures that will ensure that required quality specifications are met for the steel grade after the degassing operation. If, for example, predictions show that the limits for S and H will be reached in a shorter amount of time than normal, the operator can choose to decrease the vacuum treatment time. This action results in earlier ingot casting or more time for inclusion removal regarding continuous casting. Especially if the operator is new and has little experience, some guidelines on performing the vacuum de-
gassing operation can be valuable in tricky situations.

- Off-line (Static Modelling)
  An engineer may utilise the information from the model to test new ideas or ways to perform the degassing operation in order to speed up the process or improve steel cleanliness. One task for off-line simulation arises when planning for a new steel grade. The model can determine if operational parameters need to be set differently to maintain final sulphur and hydrogen contents within specification limits. Predictions indicating that limits for S and H will be reached in a shorter amount of time than normal can result in casting being carried out sooner with ingot casting, or more time for inclusion removal in the ladle furnace with continuous casting.

4.5. Motives for Developing a Process Model

The most important motive for developing a process model is to avoid the alternative, i.e. time- and cost-consuming plant trials. Performing plant trials requires taking numerous steel and slag samples. Conducting the subsequent different chemical and microscopic sample analyses can take a lot of time and is expensive. Furthermore, full-scale plant trials can also involve a certain amount of risk for plant personnel. Model simulations can be a powerful complement to plant trials in developing the refining operation.

5. Conclusions

In this investigation a process model was developed for on-line prediction of sulphur and hydrogen removal during vacuum degassing in the ladle furnace at Ovako Steel. The following conclusions have been drawn from the work.

- The main purpose of the study was fulfilled, namely to develop a less time-consuming model suitable for production applications.
- A comparison between the process model and CFD model results revealed good agreement for sulphur removal between 10 and 25 min and for hydrogen removal between 6 and 25 min.
- Verification trials indicate that process model predictions generally are in fairly good agreement with production plant data regarding sulphur and hydrogen removal within the limits of what can be classified as a normal heat.
- The average deviation between model predictions and plant data after degassing was 26% and 12% for sulphur and hydrogen contents, respectively, for the process model with gas flow rates set to closest production cases. The corresponding measured figures for sulphur and hydrogen are given a relative uncertainty of 12% and 4.3%, respectively.
- Results indicate that combined stirring, in comparison with gas stirring, renders lower hydrogen removal rates. One reason for this may be that the use of inductive stirring reduces the retention time for argon gas bubbles in the steel bath which in turn reduces the time for hydrogen to diffuse to the gas bubbles, resulting in a lower hydrogen removal rate.
- On-line simulations: the process model can be used to determine if final specification limits will be met or not, thus during production providing operators with information that helps them select appropriate adjustments to the process to meet specified requirements.
- Off-line simulations: the process model can be used to determine if other operational parameters need to be set differently in order to keep final sulphur and hydrogen contents within specification limits.

The simplified process model has been employed at Ovako Steel for a couple of years, both on-line in the steel plant and by engineers working on further development of the ladle refining process. Precisely how the model has been used in optimising desulphurisation and dehydrogenation during vacuum degassing at Ovako Steel will be covered in another publication by the authors.

Acknowledgements

The authors wish to thank Anders Tenebäck and Patrik Undvall of Ovako Steel AB for their permission to publish the research results as well as for their input on the manuscript.

REFERENCES