

Slag/metal reactions during ladle treatment

with focus on desulphurisation

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Abstract

Within several co-operative projects, KTH (Royal Institute of Technology), Ovako Steel AB and MEFOS have investigated the desulphurisation of bearing steel during vacuum degassing. The work covers thermodynamic calculations of the slag/metal equilibrium, CFD modelling of slag/metal reactions, plant trials, etc. Results from the different studies are presented and discussed in this paper. Models for predicting slag properties (sulphide capacity, viscosity and oxide activities) in liquid slags as functions of slag composition and temperature have been used for the calculation of data, which have been used in static and dynamic modelling of sulphur refining. The results from static modelling show that the method allows fast and easy evaluation of the theoretical desulphurisation conditions during degassing at Ovako Steel AB as well as theoretical determination of the parameters that have the greatest influence on the equilibrium sulphur distribution. The conclusion from dynamic modelling is that the vacuum-degassing operation can be described dynamically with the present knowledge of sulphide capacity, sulphur distribution, viscosity and oxide activities of ladle slags if this knowledge is combined with fluid-flow modelling to derive the overall kinetics. The presented model approaches have been found useful in understanding the sulphur refining process at Ovako Steel AB. The dynamic modelling concept is also believed to have potential for dynamic descriptions of other slag/metal reactions in steelmaking.

1. INTRODUCTION

At Ovako Steel AB, attention has been focused on producing clean steel with respect to non-metallic inclusions and tramp elements for many years. This has resulted in a significantly reduced average total oxygen content from 11 ppm in 1985 to 5 ppm in 1999 in bearing steel¹⁾. However, to be able to survive in the future new applications for clean special steels must be found which means that the improvement of the steel quality has to continue. Sulphides in steel may also act as crack initiators (similar to calcium aluminate oxides) when there is a high load in different directions. Consequently the sulphur control during the ladle treatment increases in importance. Increasing demands on productivity in the steel plant mean that further improvement of the processes that determine the quality of the steel, is even more vital.

Today, 100 % of the steel being produced at Ovako is vacuum degassed. Vacuum degassing is performed in order to reduce the sulphur and hydrogen contents as well as the amount of non-metallic inclusions in the molten steel. By controlling the ladle treatment, especially the vacuum degassing operation, the quality of the steel is controlled. Within several co-operative projects,^{2, 3, 4)} KTH (Royal Institute of Technology), Ovako Steel and MEFOS have therefore investigated the desulphurisation of bearing steel during vacuum degassing. Since the top slag acts as a recipient for sulphur, an optimisation of the degassing operation will result in an optimisation of the top slag with respect to thermodynamics, kinetics and fluid dynamics. The present paper focuses on vacuum degassing and covers basic thermodynamic and thermophysical research of the slag/metal equilibrium, CFD modelling of slag/metal reactions and plant trials.

In section 2, top slag-properties such as sulphide capacity, viscosity and oxide activity are described theoretically along with measurements and modelling results. Section 3 focuses on the plant trials performed at Ovako Steel. It includes a process description, the experimental procedure for carrying out the plant trials and results from the trials. Thereafter, in section 4, results from static and dynamic modelling of the sulphur distribution between the slag and metal are presented. Finally, in section 5, the results are discussed and summarised.

2. SLAG PROPERTIES

The ability to describe critical thermodynamic and thermophysical properties of the participating phases as functions of slag composition and temperature is of utmost importance when developing models for simulation and control of different metallurgical processes. In the present paper the authors have chosen to highlight some of the slag properties which have been modelled and measured at the Division of Metallurgy, KTH.

2.1. Sulphide Capacity

When calculating slag/metal reactions with respect to desulphurisation, the sulphide capacity is most important. The sulphide capacity, CS, for a liquid slag was defined by Richardson and Fincham⁵⁾ as

$$C_s = \frac{K_1 \cdot a_{O^{2-}}}{f_{S^{2-}}} = (\%S)_{slag} \cdot \sqrt{\frac{p_{O_2}}{p_{S_2}}} \quad (1)$$

where $a_{O^{2-}}$ is the activity of oxygen in the slag phase, p_{S_2} and p_{O_2} are the partial pressures of

$S_2(g)$ and $O_2(g)$, $f_{S^{2-}}$ is the activity coefficient of sulphur in the slag phase and $(\%S)_{slag}$ is the sulphur content in the slag in wt%. K_1 is the equilibrium constant for the reaction



The sulphide capacity is a property of the slag, which is dependent only on the temperature and the slag composition. It describes the potential ability of an arbitrary homogeneous molten slag to remove sulphur and it could be used to compare the desulphurisation characteristics of different slags.

A model for calculation of the sulphide capacity for multicomponent slags at different temperatures has been developed at the Division of Metallurgy, KTH.⁶⁾ The model enables the prediction of the sulphide capacities of multicomponent slags from the data of lower-order systems. The expression of sulphide capacity from equation (1) is represented by the following relationships:

$$K_1 = \exp\left(-\frac{\Delta G^0}{R \cdot T}\right) \quad (3)$$

and

$$\frac{a_{O^{2-}}}{f_{S^{2-}}} = \exp\left(-\frac{\sum (X_i \cdot \mathbf{x}_i) + \mathbf{x}_{mix}}{R \cdot T}\right) \quad (4)$$

where, in equation (3), ΔG^0 is the Gibbs free energy of reaction (2), R is the gas constant and T is the thermodynamic temperature. In equation (4), i stands for component i and X_i is the molar fraction of component i in the multicomponent system. The term \mathbf{x}_i is expressed as a linear function of the temperature for each component in the slag in the absence of interaction between different species. The term \mathbf{x}_{mix} represents the mutual interaction (binary and ternary) between different species in the slag and is dependent on slag composition and temperature. In order to express the mixing, the liquid slag is described by a modified Temkin⁷⁾ approach, which considers the mixing of cations and anions within each of their subgroupings. More details regarding the equations and the assessed parameters necessary for the calculation have been presented elsewhere.⁶⁾

Pure liquid FeO is chosen as the standard in the model, for which the ratio $\frac{a_{O^{2-}}}{f_{S^{2-}}}$ is taken as unity. The standard Gibbs free energy ΔG^0 is calculated from sulphide capacity measurements of pure liquid FeO as

$$\Delta G^0 = 118535 - 58.815 \cdot T \quad (\text{J/mol}) \quad (5)$$

In Figure 1 the calculated sulphide capacity is shown as function of Al_2O_3 content and temperature for an Al_2O_3 -CaO-7%SiO₂-8%MgO slag. Saturation of CaO or MgO in the slag was considered. The predictions were done using the KTH model⁶⁾.

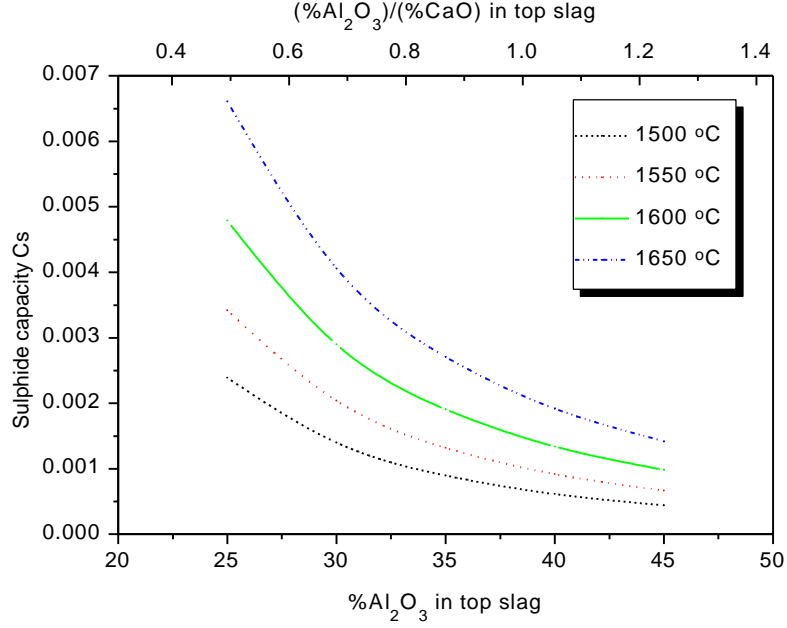


Figure 1: Calculated sulphide capacity of an $\text{Al}_2\text{O}_3\text{-CaO-8\%MgO-7\%SiO}_2$ slag. Solidification of the slag was not considered

2.2. Viscosity

Viscosity is a thermophysical property that affects the kinetic conditions during ladle treatment. It is essential that the viscosity of both liquid slag and metal be known for modelling of the process. While viscosity values of liquid iron at different temperatures have been reasonably well established⁸⁾, accurate data of viscosities of ironmaking and steelmaking slags are still lacking. At KTH viscosity measurements of different metallurgical slag systems have been incorporated into a slag model⁹⁾ which enables extrapolation of slag viscosities as functions of temperature as well as composition in the case of multicomponent systems. A set of model parameters is optimised based on the experimental data up to ternary systems.

In the KTH model the dynamic viscosity, η , is expressed by an Arrhenius relation

$$\mathbf{h} = \frac{h \cdot N \cdot \mathbf{r}}{M} \cdot \exp\left(\frac{\Delta G^*}{R \cdot T}\right) \quad (6)$$

where h is the Planck's constant, N is the Avagadro's number and \mathbf{r} and M are the density and molecular weight of the liquid slag, respectively. The term ΔG^* in equation (6) is the Gibbs energy of activation for viscosity, which is considered to be a function of both temperature and composition of the liquid slag. In the case of multicomponent systems the Gibbs activation energy can be represented by

$$\Delta G^* = \sum X_i \cdot \Delta G_i^* + \Delta G_{mix}^* \quad (7)$$

where ΔG_i^* is the Gibbs energy of activation of the pure component i in liquid state. The second term in equation (7) is due to the mutual interactions between different species and is expected to be a function of composition and temperature. In the case of ionic solutions (slags), the Temkin description is adopted. More detailed information concerning the

viscosity model can be found in published literature⁹⁾.

In Figure 2 the measured viscosity as a function of temperature for a 40%Al₂O₃-45%CaO-9%SiO₂-6%MgO slag is shown together with the calculated viscosity. The viscosity was measured using the rotating cylinder method⁹⁾. The model calculation is an extrapolation from lower order systems. The results show that the model calculation gives a lower viscosity (about 10-15%) than the measured value.

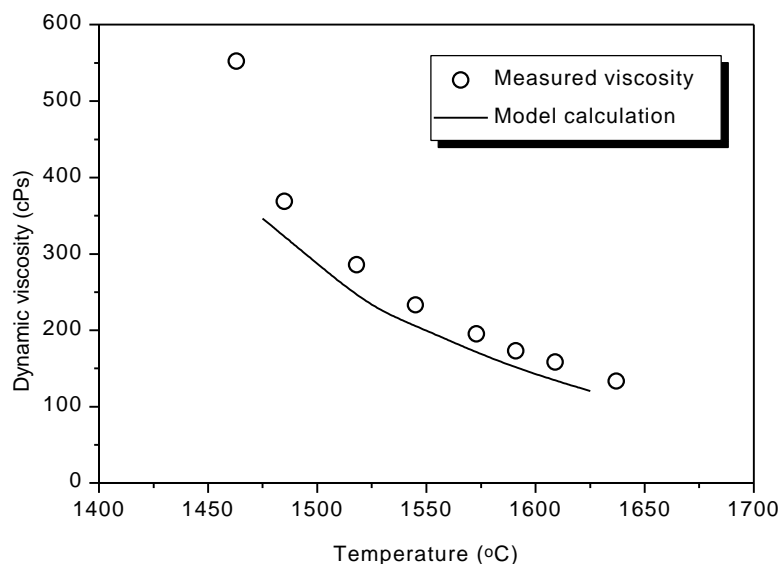


Figure 2: Measured and calculated (KTH-model) dynamic viscosity of a slag of the composition 40% Al₂O₃, 45% CaO, 6% MgO and 9% SiO₂

2.3. Oxide Activities

Thermodynamic properties of metallurgical multicomponent slags are of great importance when studying slag/metal reactions and developing models for process control. The activities of oxides in the molten slag and alloying elements in the molten metal together with the process temperature determine the equilibrium oxygen potential in the system. Many measurements of oxide activities in different slag systems have been made, but it is very difficult to determine properties for all compositions that are encountered in practice. The thermodynamic modelling of silicate melts has thus become one way of providing metallurgists with necessary activity data for multicomponent slags within wide composition ranges.

Several empirical or semi-empirical models for the prediction of thermodynamic properties of slags have been developed over the years. Among them are the IRSID model¹⁰⁾ (based on Kapoor and Froberg's work¹¹⁾) and the two-sublattice model by Hillert¹²⁾. At the Division of Metallurgy, KTH, a mathematical model has recently been developed¹³⁾ which predicts the oxide activities in liquid multicomponent slags. The model uses only experimental information from the corresponding binary subsystems. Furthermore, the model applies Temkin's description of entropy of ionic melts⁷⁾ coupled with Lumsden's description of silicate and aluminate melts¹⁴⁾. Lumsden considered the ionic melt as an oxygen-ion matrix with the cations, including Si⁴⁺, distributed in it. A hypothetical standard state for silica is

adopted, where the SiO_2 network is dissociated into Si^{4+} and O^{2-} ions. More details on the model can be found in published literature¹⁵⁾ on the subject.

Another approach was taken by Ohta and Suito¹⁶⁾, who used measured activity data to derive expressions by multiple regression analysis for activities of Al_2O_3 and SiO_2 and activity coefficients for FeO and MnO . The slag system considered was Al_2O_3 - CaO - MgO - SiO_2 at 1600 °C. Their work resulted in equations by which activities and activity coefficients were easily calculated using the slag composition of interest. In the present work, the expressions by Ohta and Suito were adopted for the calculation of oxide activities except in section 4.2.1, where activity data calculated by the IRSID slag model were used. However, in future work the aim is to test the use of the KTH model for calculation of oxide activities in the slag phase.

In Figure 3 a comparison between the calculated activity of Al_2O_3 using data from the KTH model¹⁵⁾ and Ohta and Suito's equation, is shown. The results show a discrepancy, which decreases when the basicity increases. It should also be pointed out that basicity above 5 corresponds to SiO_2 contents in the slag below 10%. Ohta and Suito's equation¹⁶⁾ for alumina activity was not verified below 10% SiO_2 , which means that extrapolation above basicity 5 should be observed with care. The present authors have, however, used Ohta and Suito's equation¹⁶⁾ at SiO_2 contents below 10% (see section 4).

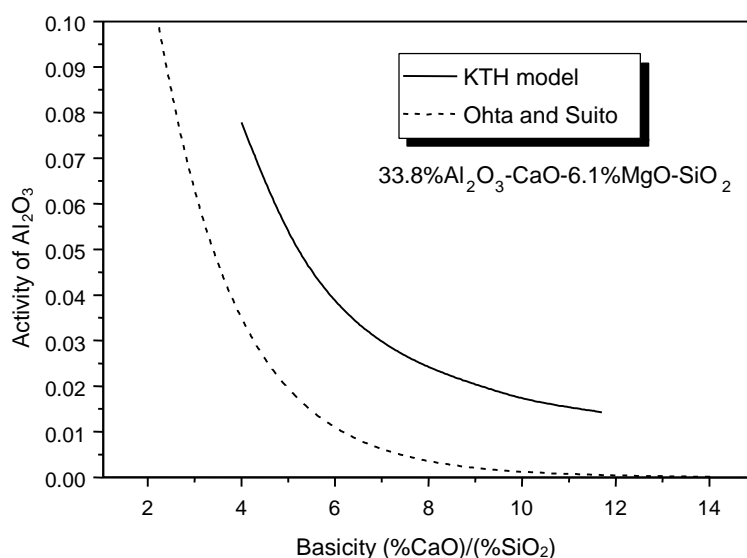


Figure 3: Comparison of Al_2O_3 activities for a typical ladle furnace slag¹⁵⁾ calculated using the KTH model⁶⁾ and Ohta and Suito's equation¹⁶⁾

3. PLANT TRIALS AT OVAKO STEEL AB

3.1. Process Description

Ovako Steel manufactures bearing steels and low-alloyed speciality steels for highly stressed applications. The scrap-based steel plant is situated in Hofors. The annual raw-steel production capacity is 475 000 tonnes of steel for the year 2000.

The scrap is melted in a 100-tonne oval bottom-tapped (OBT) electric arc furnace. After adjusting the steel to the desired phosphorous, carbon, and temperature levels, the steel is tapped into a ladle while undergoing predeoxidation. The ladle is then transported by an overhead crane to the deslagging station. Afterwards, the steel enters the ASEA-SKF furnace from a ladle car. The LF station (see Figure 4) is equipped with graphite electrodes for heating, a vacuum chamber for degassing, wire injection, an electromagnetic stirrer and porous plugs (Ar-gas) for bottom stirring. It has one position for heating and alloying (position 1) and one for vacuum degassing (position 2).

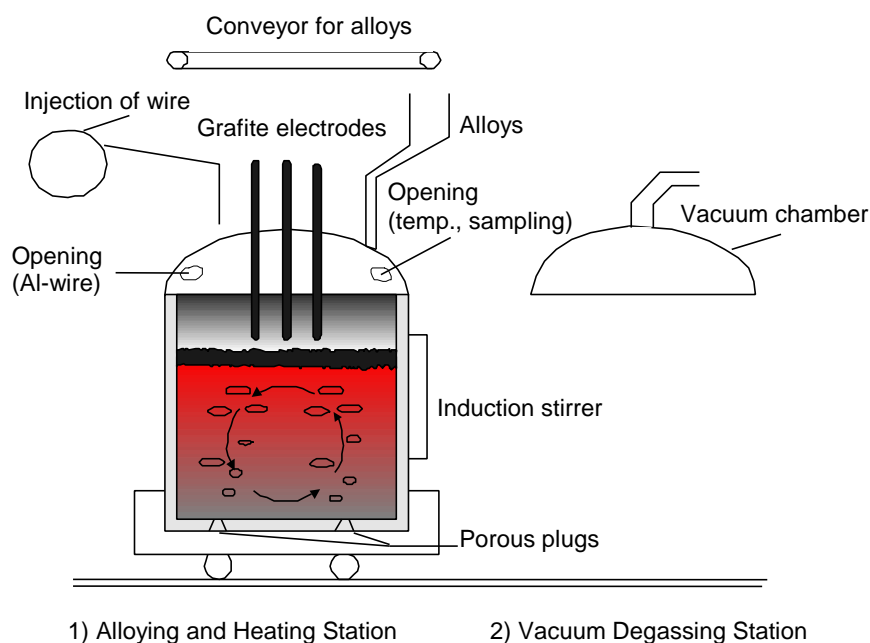


Figure 4: The ASEA-SKF Ladle Furnace at Ovako Steel

The secondary refining process consists of three main steps. Firstly, induction stirring is used during the alloying, deoxidation, and melting of the synthetic top slag. Secondly, gas stirring enhances the vacuum degassing operation, where hydrogen and sulphur refining are done. Argon gas is injected through two porous plugs during vacuum degassing. Thirdly, induction stirring is used again, after the vacuum degassing operation is completed, in order to further promote the separation of inclusions from the steel. Upon completion of ladle treatment the steel is cast using up-hill teeming into twenty-four 4.2-tonne ingots.

Full-scale trials have been carried out at Ovako Steel. The trials presented in section 3.2 were carried out in order to investigate the influence of slag properties such as sulphide capacity, viscosity and oxide activity on desulphurisation. The results were used in the static modelling work covered in section 4.2. The following plant trials (section 3.3) were made to verify the dynamic modelling work described in section 4.3.

3.2. Static Modelling Work Trials

Experiments were conducted for a high-carbon chromium bearing steel grade (1 wt% C and about 1.4 wt% Cr) with the objective to evaluate how different slag properties affect the desulphurisation during ladle treatment³⁾. The top-slag constituents varied during the trials as follows: 39-58 wt% CaO, 27-44 wt% Al₂O₃, 3-16 wt% MgO and 4-11 wt% SiO₂. A

commercial synthetic slag mixture was used together with lime. In some cases (for investigating high-alumina slags) pure alumina was also added to the slag. Note that these slag compositions do not correspond to the ones used in the normal production.

Slag and steel samples were collected during ladle treatment corresponding to the three main steps of the secondary refining operation, which are illustrated in Figure 5.

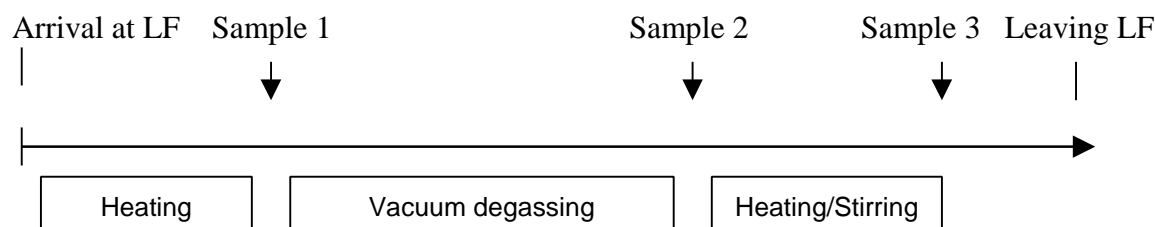


Figure 5: Schematic figure showing the sampling procedure for the trials

The temperature of the molten steel was measured at each sampling occasion. Slag samples were collected manually with a slag spoon. The temperature was measured and steel samples were taken using the automatic sampling equipment installed at the ASEA-SKF ladle furnace. A dual-thickness (lollipop) sampler from Rescon-Electro Nite was used to sample the liquid steel to determine the amount of sulphur as well as other elements that dissolved in the steel. The sulphur content was determined using a LECO CS244 (ASTM 1019-94).

The results are shown in Tables 1a and 1b.

Table 1a - Interval of analysis slag compositions of normalised oxide composition

Sample	%Al ₂ O ₃	%CaO	%MgO	%SiO ₂	%S
1	27-42	45-58	3-11	6-11	0.30-0.74
2	30-44	39-54	5-16	4-11	1.2-2.7
3	30-44	40-54	5-14	4-11	1.2-2.7

Table 1b - Intervals of analysis steel compositions (1 wt% C and 1.4 wt% Cr) and measured temperatures

Sample	%Al	%Mn	%Si	%S	Temperature (°C)
1	0.039-0.086	0.26-0.33	0.24-0.29	0.028-0.016	1565-1618
2	0.021-0.051	0.26-0.33	0.24-0.29	0.007-0.014	1497-1552
3	0.025-0.050	0.26-0.33	0.24-0.29	0.007-0.015	1530-1544

3.3. Dynamic Modelling Work Trials

Experiments were conducted for five heats, A, B, C, D and E, of high-carbon, chromium bearing steel (1 wt % C, 1.4 wt % Cr) in order to verify the model with respect to desulphurisation during vacuum degassing²⁾. A synthetic top slag with a normalised composition of 53 wt % CaO, 32 wt % Al₂O₃, 7.5 wt % MgO and 7.5 wt % SiO₂ was used. Trials were performed during vacuum degassing for both stirring with only argon (heats A-C) and argon stirring in combination with inductive stirring (heats D and E) in order to compare

gas stirring by itself with combined stirring.

Sampling was carried out before and after vacuum degassing for all the heats (samples 1 and 3 in Figure 6). However, in order to study the variation of the sulphur concentration with time, the degassing practice was interrupted after 3 minutes for heats B-E and an additional sample was taken, sample 2 in Figure 6. After sample 2 was taken, the chamber was again evacuated and the degassing process continued.

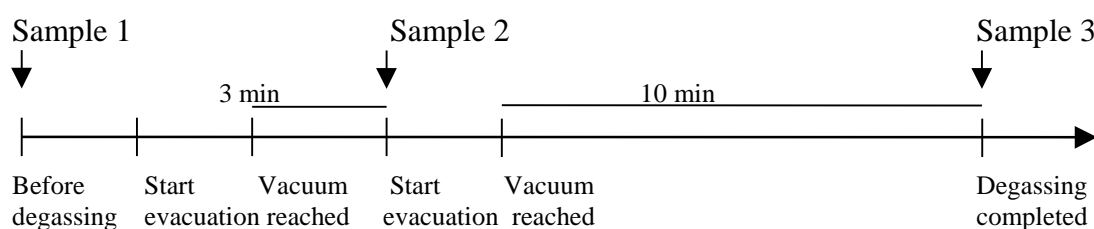


Figure 6: Sampling procedure for the trials (sample 2 was excluded for heat A)

Vacuum was reached within 2 to 3 minutes (with a pressure in the chamber below 5 torr). Separate calculations indicate that this period with continuously decreasing pressure approximately corresponds to 30 seconds under vacuum evacuation. To be able to compare heat A, which was not interrupted, with heats B-E, the period from when vacuum was reached to when degassing was completed was prolonged from 10+3 minutes to 14.5 minutes for this heat. The total vacuum time then became 15 minutes (0.5+14.5 min) for heat A and 14 minutes (0.5+3+0.5+10 min) for heats B-E. In Table 2, total vacuum time is given together with the gas flow rate for porous plugs 1 and 2 and sulphur results from the analysis. It should be mentioned that the vacuum pressure in the chamber varied between 1.3 and 1.8 torr for the heats.

Table 2 - Sampling and sulphur content of the steel melts for heats A, B and C (gas stirring only) and heats D and E (combined stirring) during vacuum treatment

Heat	Total time at vacuum pressure [min] and [s] Approx. Used in model		Samples Before 3min After			Gasflow rate[Nl/min] Ar(1) Ar(2)		Sulphur content [%] Before 3min After		
A(G)	15 min	900 s	X		X	200	130	0.023		0.007
B(G)	14 min	848 s	X	X	X	130	140	0.023	0.015	0.012
C(G)	14 min	840 s	X	X	X	150	50	0.022	0.018	0.012
D(C)	14 min	840 s	X	X	X	110	50	0.019	0.014	0.009
E(C)	14 min	816 s	X	X	X	130	130	0.022	0.014	0.010

(G)=Gas stirring, (C)=Combined stirring

4. RESULTS FROM MODELLING OF THE SULPHUR DISTRIBUTION BETWEEN SLAG AND METAL

4.1. Sulphur Distribution

In order to relate the sulphide capacity to the equilibrium sulphur distribution between the

slag and metal phases the following reaction should be considered:



The equilibrium constant K_8 is expressed as¹⁷⁾:

$$\log K_8 = -\frac{935}{T} + 1.375 \quad (9)$$

The equilibrium constant K_8 can also be written as:

$$K_8 = \frac{a_O}{a_S} \cdot \sqrt{\frac{p_{S_2}}{p_{O_2}}} = \frac{(\%S)_{slag}}{[\%S]_{metal}} \cdot \frac{a_O}{f_S \cdot C_S} \quad (10)$$

where a_O and a_S are the activities of oxygen and sulphur in the metal phase, f_S is the activity coefficient for sulphur in the metal phase and $[\%S]_{metal}$ is the sulphur content in the metal phase.

By combining equations (1), (9) and (10), the following expression for the equilibrium sulphur distribution L_S between the slag and metal phases is obtained¹⁷⁾:

$$\log L_S = \log \frac{(\%S)_{slag}}{[\%S]_{metal}} = -\frac{935}{T} + 1.375 + \log C_S + \log f_S - \log a_O \quad (11)$$

The activity coefficient of a dissolved element in the steel bath can be calculated by using Wagner's equation provided that the molten metal can be treated as a dilute solution. Wagner's equation is written as:

$$\log f_j = \sum (e_j^i \cdot [\%i]) \quad (12)$$

where f_j is the activity coefficient for element j in the molten steel, i represents the dissolved elements in the molten steel and e_j^i is the interaction parameter for element j .

The oxygen activity in the steel bath, a_O , can be calculated by solving the equilibrium reactions between slag and metal with respect to dissolved alloying elements in the steel melt and oxides in the slag phase. The general form of the reactions determining the oxygen activity is:



To simplify the calculation it can be assumed that the equilibrium between dissolved aluminium and oxygen in the steel bath and alumina in the top slag controls the oxygen activity. Except for the dynamic modelling where reoxidation is considered (section 4.3.2.), this assumption has been used in the study documented in this report. It is a reasonable simplification since the oxygen affinity of aluminium is very high compared to other alloying elements. The equilibrium reaction is:



$$\Delta G^o = -1205115 + 386.714 \cdot T \quad (\text{J/mol}) \quad (15)$$

The data for the change of standard Gibbs free energy, equation (15), were taken from Hayes.¹⁸⁾ Solid alumina was chosen as the standard state. The equilibrium constant, K_{14} , for equation (14) could be written as:

$$K_{14} = \exp\left(\frac{-\Delta G^o}{R \cdot T}\right) = \frac{a_{Al_2O_3}}{a_{Al}^2 \cdot a_O^3} \quad (16)$$

where $a_{Al_2O_3}$ is the activity of alumina in the slag phase and a_{Al} is the activity of aluminium in the metal phase.

In order to calculate the oxygen activity (a_O) from the above equation, the activities of aluminium in the molten steel and alumina in the top slag need to be estimated. The activity coefficient of aluminium in the molten steel, f_{Al} , can be calculated using Wagner's equation (12). The aluminium activity is the product of f_{Al} and the aluminium content in the molten steel.

The activity of alumina in the top slag is estimated by using the expression for activity of Al_2O_3 in an Al_2O_3 -CaO-MgO-SiO₂ slag at 1600 °C by Ohta and Suito¹⁶⁾:

$$\log a_{Al_2O_3} = \frac{\{-0.275(\%CaO) + 0.167(\%MgO)\}}{(\%SiO_2)} + 0.033(\%Al_2O_3) - 1.560 \quad (17)$$

where the slag composition is given in wt%.

The composition range, where equation (17) is suggested to be employed, is for CaO: 10-60%, SiO₂: 10-50%, Al₂O₃: 0-50% and MgO: 0-30%. The slag compositions in the present paper were within this range except for SiO₂, which in some cases was below 10%. However, it was assumed that equation (17) could be extrapolated below 10% SiO₂ in order to get an estimation of the activity of Al₂O₃ for the studied slag system. Furthermore, literature data¹⁵⁾ have indicated that there is almost no temperature dependence for the activity coefficient of alumina in slags. Therefore, it was assumed that the expression of Ohta and Suito¹⁶⁾ could be used in the present work, since the studied temperatures were close to 1600 °C.

4.2. Static Modelling

4.2.1. Parameter study – influence of slag properties on desulphurisation

The effect of the following parameters on the equilibrium sulphur distribution was calculated: %Al and %C in the molten steel, temperature and (%Al₂O₃)/(%CaO) ratio in the top slag³⁾. It was concluded from an earlier investigation¹⁹⁾ that the SiO₂ and MgO components in the top slag usually changed very little during the ladle refining operation. Thus, suitable contents of SiO₂ and MgO were chosen and kept constant during the calculations of the whole parameter study. A typical bearing steel composition was chosen for the calculation, with the following major alloying elements: 1.4 %Cr, 1 %C, 0.28 %Si and 0.28 %Mn. Results from the parameter study are shown in Figure 7.

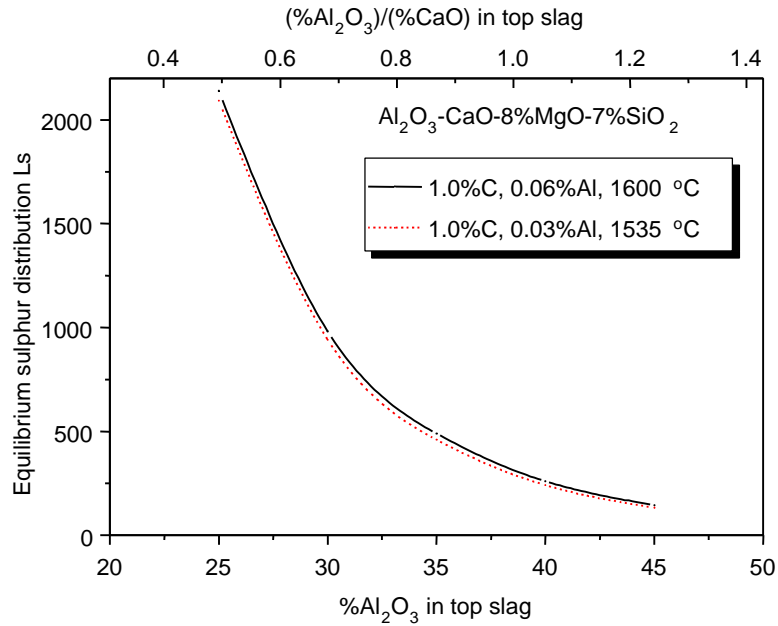


Figure 7: The calculated equilibrium sulphur distribution as a function of %Al₂O₃ in the top slag³⁾

Figure 7 indicates that when the temperature and the dissolved aluminium content in the molten steel both decrease at the same time, as they do in the parameter study, there is a minor effect on the equilibrium sulphur distribution between slag and metal. However, if the slag composition changes at the same time, the influence on the equilibrium sulphur distribution could be substantial. For example an increase in the Al₂O₃ content in the top slag from 30 to 35% would theoretically decrease the equilibrium L_S by about 50%. (Note that the values represent equilibrium calculations.)

4.2.2. Evaluation of Plant Trial Results

As mentioned earlier, the main conclusion from the parameter study³⁾ was that a change in the Al₂O₃/CaO ratio has the largest influence of the studied parameters on the sulphur distribution ratio (see Figure 7). Therefore, specific plant trials were performed³⁾ as described in section 3.2., where the alumina content before vacuum treatment was allowed to vary between 27 to 44%.

The equilibrium sulphur distribution L_S was estimated for all heats by using sulphide capacities calculated by the KTH model for the different slag samples. The oxygen activities were estimated as described in section 4.1. The results are shown in Figure 8, where the estimated equilibrium sulphur distributions are plotted against the sulphur distributions from analysis of the slag and steel samples. It can be seen that there was no equilibrium between the top slag and the molten steel with respect to sulphur content, before degassing. Just after degassing, the estimated equilibrium sulphur distributions agreed reasonably well with the analysis-determined sulphur distributions. The agreement even somewhat improved after the final heating and stirring period at the end of ladle treatment. It should be noted that this comparison is equilibrium based. In reality the experimental data at the end of vacuum degassing may not represent an equilibrium situation. Moreover, a previous study¹⁹⁾ showed that slag sampling affects the experimentally determined slag sulphur content and consequently also the sulphur distribution. However, the results in Figure 8 show that the equilibrium sulphur distribution tends towards an equilibrium value during vacuum

degassing.

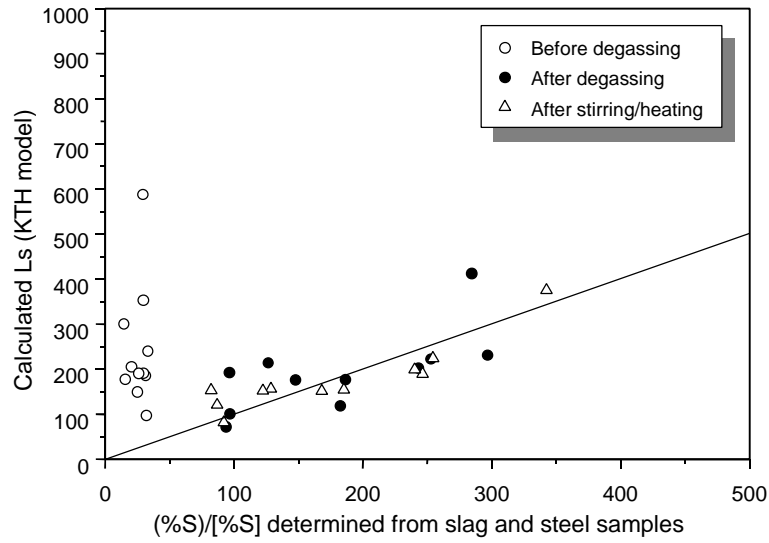


Figure 8: The calculated equilibrium sulphur distribution plotted against the sulphur distribution determined from slag and steel analyses³⁾

In Figure 9 the heats were divided into two groups: basicity < 6.0, and basicity > 6.0. Basicity is defined here as the ratio of %CaO to %SiO₂. The estimated equilibrium L_S values were plotted against the analysis sulphur distributions after the final stirring and heating period at the end of ladle treatment. The heats with lower top-slag basicity generally showed lower sulphur distributions compared to the high-basicity slags, except for one heat. This heat also had the lowest Al₂O₃ content of all heats and also the lowest (%Al₂O₃)/(%CaO) ratio, including heats of both high and low basicity.

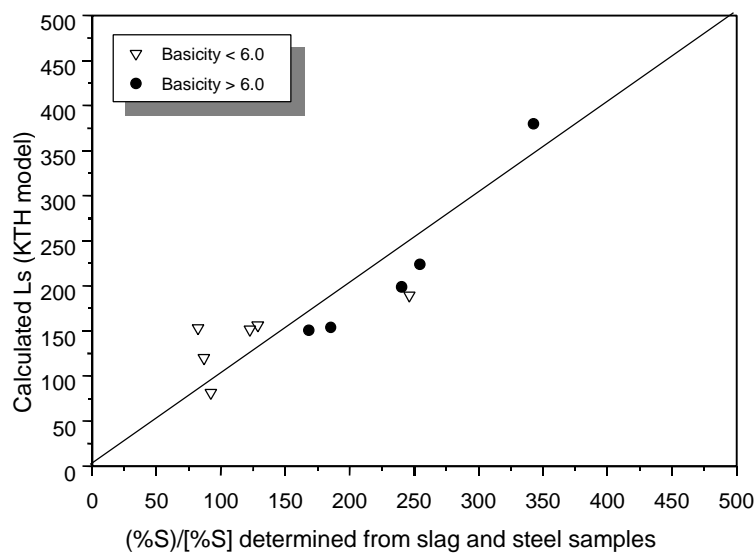


Figure 9: The calculated equilibrium sulphur distribution as a function of the analysis-determined sulphur distribution after the final heating and stirring period³⁾

It can also be noted that the demands of Ovako Steel on the limits of sulphur content in the steel were always fulfilled during the trials although in many cases the slag composition was not optimal for sulphur refining.

4.3. Dynamic Modelling

The driving force for developing a dynamic model of the vacuum degassing operation is basically a lack of production information (actually tools) for determination of steel cleanliness during treatment. Today, it is very difficult to take samples during the degassing operation. A model would help the operators to decide on the required treatment time with respect to the prevailing operational conditions.

Figure 10 shows a schematic layout of the dynamic vacuum degassing model. In the bottom there are thermodynamic models describing for example sulphide capacity and activities along with thermophysical models describing physical properties such as diffusion constants and viscosity. Together with transport equations for the different phases, reaction models for reactions influencing the sulphur refining can be implemented. In this way the dynamic model rests on a scientific foundation and is able to capture dynamical changes in temperature and composition due to the different reactions. The thermodynamic and thermophysical models described earlier in this paper have been used in the dynamic model, except when specified otherwise in the following sections.

The oxygen activity in the bulk of the steel melt is calculated by using the activity of aluminium in the reaction:



In the bulk of the steel melt it is assumed that the activity of alumina is unity.²⁾ The steel bulk is defined as liquid metal containing less than 1% top slag (by weight). In the slag/metal mixing zone however, the activity of oxygen is determined by the equilibrium reactions between the liquid slag and steel. It is further assumed that the effect of changes in slag composition on the sulphide capacity is negligible during degassing. The KTH model⁶⁾ has been applied to obtain values of the sulphide capacity of the slag phase. In this model, besides the temperature, only Al₂O₃, CaO, MgO and SiO₂ in the slag phase are assumed to influence the value of the sulphide capacity.

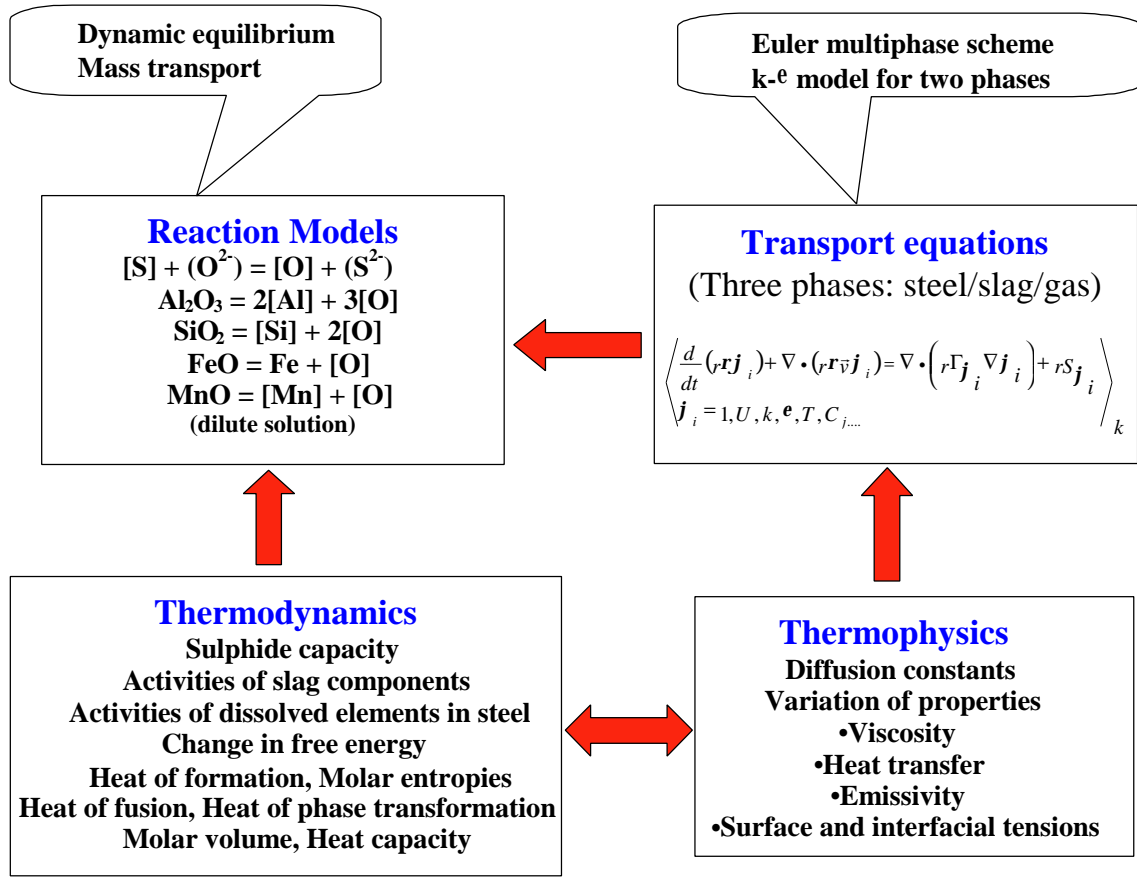


Figure 10: Sketch showing the vacuum-degassing model

4.3.1. Results from Verification Trials of the Three-dimensional Model

The three-dimensional model is a description of the ladle used at Ovako Steel AB, with bottom gas stirring through two porous plugs and an electromagnetic stirrer. The oxygen activity in the slag/metal-mixing zone is calculated according to the equilibrium reaction



The activity of Al_2O_3 as a function of temperature was obtained from the TDCALC database for a slag containing 32% Al_2O_3 , 53% CaO , 7.5% MgO and 7.5% $SiO_2^{(2)}$. Any influence from variations of the slag composition on the activity of Al_2O_3 was neglected. Variations of any other elements but Al, O and S in the molten steel were neglected in the model calculation.

In order to compare the model predictions for sulphur refining with industrial data (Figure 11) the calculated average sulphur concentration for heat B is plotted as function of time. The experimentally determined sulphur concentration is also presented in the same figure for comparison. From the results, it is evident that the sulphur content in the steel drops rather fast during the initial stage (3-5 minutes) of degassing, after which the slope declines. The rather prompt drop of the refining rate is usually caused by the decreasing ability of the slag to absorb sulphur from the melt. The overall agreement between the predictions and the measurements is good, but closer inspection reveals some systematic deviations.

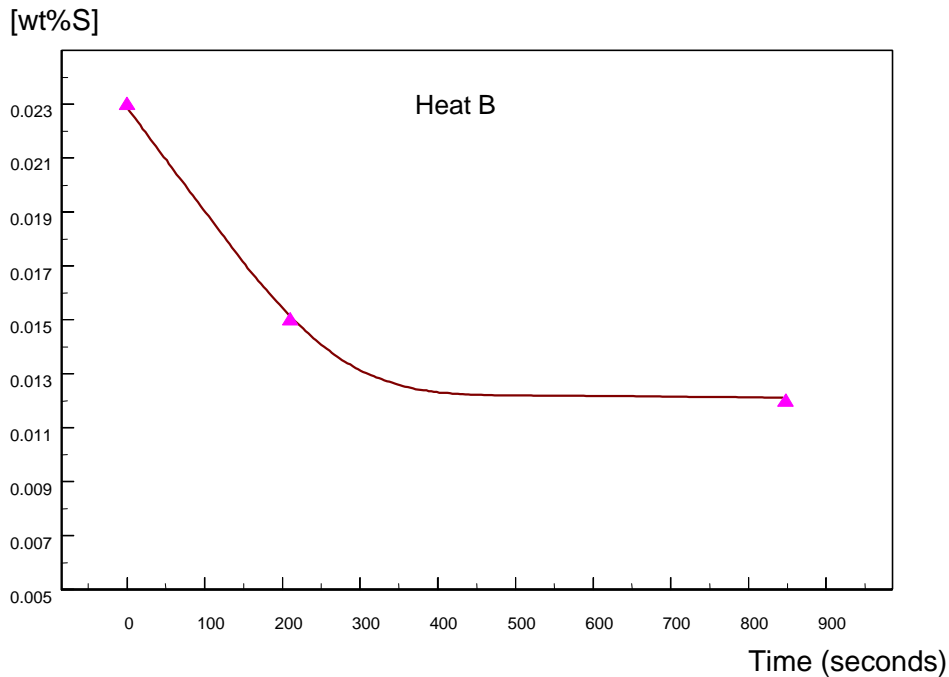


Figure 11: Comparison between the predicted sulphur content and the results from the plant trials for heat B²⁾

According to the results in Table 3, the model predicts somewhat too high sulphur-refining rates in the initial stage of the degassing process (heats C-E).

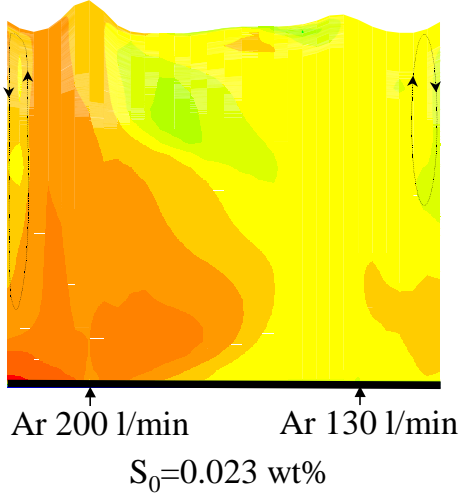
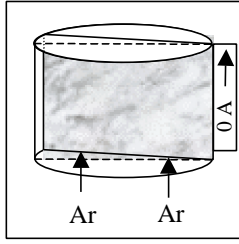
Table 3 - Comparison between predicted and calculated sulphur content in the steel

Heat	[%S] (t=0) Sample	[%S] (t=0) Model	[%S] (3 min) Sample	[%S] (3 min) Model	[%S] (final) Sample	[%S] (final) Model
A	0.023	0.023	-	0.014	0.007	0.008
B	0.023	0.023	0.015	0.015	0.012	0.012
C	0.022	0.022	0.018	0.014	0.012	0.012
D	0.019	0.019	0.014	0.013	0.009	0.010
E	0.022	0.022	0.014	0.012	0.010	0.010

This may be caused by the fact that the model does not take reoxidation from top slag or refractory into consideration, thus using too low oxygen potentials. The predicted sulphur level at the end of the operation is also a little bit too high (all heats). One reason for this may be solid precipitation of calcium sulphide in the top slag during the vacuum degassing, which results in higher sulphide capacity than was anticipated. Another reason for deviations at the end of the operation might be the weight of the top slag input to the model. A higher amount of top slag would, given a certain value of the sulphide capacity, be able to capture a larger amount of sulphur from the steel.

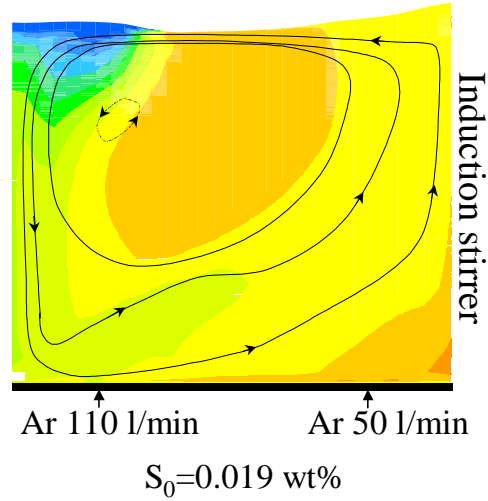
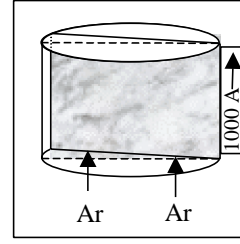
Figure 12 demonstrates calculated concentration profiles of sulphur after 3 minutes of vacuum treatment for two heats (A and D in Table 3). In the first heat only inert gas injection was used as the stirring method. In the second heat, combined gas stirring and inductive stirring was used.

Gas stirring only



a)

Combined stirring



b)

Figure 12: Concentration profiles of sulphur in steel after 3 minutes of vacuum treatment with a) only gas stirring (heat A) and b) combined gas and inductive stirring (heat D)

The results clearly demonstrate the feasibility of the modelling approach for the operating conditions existing at Ovako Steel. The model predictions are in agreement with the experimental data almost to the level of measurement error, but rely on accurate input data. From experience in the project, the parameters causing the greatest errors in the predictions are the oxygen activity and the slag weight at the start of the operation (used as input to the model). Therefore, for accurate prediction of sulphur concentration during vacuum degassing, a rigorous deslagging practice is required together with sufficient knowledge of the thermodynamic and physical properties of the synthetic slag. With these conditions met, the presented modelling approach has the full potential to predict sulphur refining during degassing with the accuracy normally needed in industrial practice.

4.3.2. A Dynamic Model Simulation Study Including Reoxidation Reactions

To investigate the influence of reoxidation on desulphurisation the simultaneous consideration of the following slag/metal reactions, besides the sulphur-oxygen exchange reaction, is necessary⁴⁾:





These reactions, together with equation (11), influence the oxygen activity and the sulphur and aluminium contents in the steel melt. In order to calculate the activities of these oxides in the slag phase the empirical expressions suggested by Ohta and Suito¹⁶⁾ have been adopted. Ohta and Suito¹⁶⁾ expressed the activity coefficients of FeO and MnO and the activities of Al₂O₃ and SiO₂ at 1600 °C as functions of slag compositions using a multiple-regression analysis. These functions have provided the authors of this paper with the relationships needed in the development of the model.

To be able to solve the thermodynamic equations for the transfer of sulphur, oxygen, aluminium, silicon and manganese at every instant and for each calculation node, a separate transport equation is solved for each of the dissolved elements in the steel phase. In the same way, separate transport equations for the slag phase are solved for the different slag components (Al₂O₃, CaO, MgO, SiO₂, MnO, FeO and S). This means that the concentration profiles for the dissolved elements in the steel phase as well as for oxides and sulphur in the slag phase can be determined at each instant. A more detailed description of the differential equations can be found in the literature²⁾.

However, when including the above reactions, the model was simplified to two dimensions due to the need of extensive computer resources. Only gas stirring is considered and the inert gas is injected through a centrally placed porous plug in the bottom of the ladle with a flow rate of 130 Nl/min. The total pressure above the melt is held constant during the calculation at 1.8 torr (240 Pa) in order to simulate vacuum degassing²⁾. The slag density is a function of slag composition and temperature²⁰⁾. The slag is assumed to be a completely liquid layer, initially without concentration gradients. Time zero is defined as the time when the open eye in the slag layer had been established according to the fluid-flow calculation. The simulated process time is 14.1 minutes. Each simulation is isothermal; i.e. the temperature remains constant.

In Figure 13 streamlines of the calculated fluid flow are illustrated. Where the gas is injected, high upwardly directed velocities develop in the centre of the ladle due to the drag force the gas exerts on the steel. At the steel surface the flow of steel is directed towards the ladle wall, where it is diverted downwards along the wall towards the bottom. Thus, a circulation loop in the steel bulk develops. Furthermore, the calculation for this case also shows a circulation loop in the slag. A small, nearly stagnant zone in the slag can be found very close to the ladle wall.

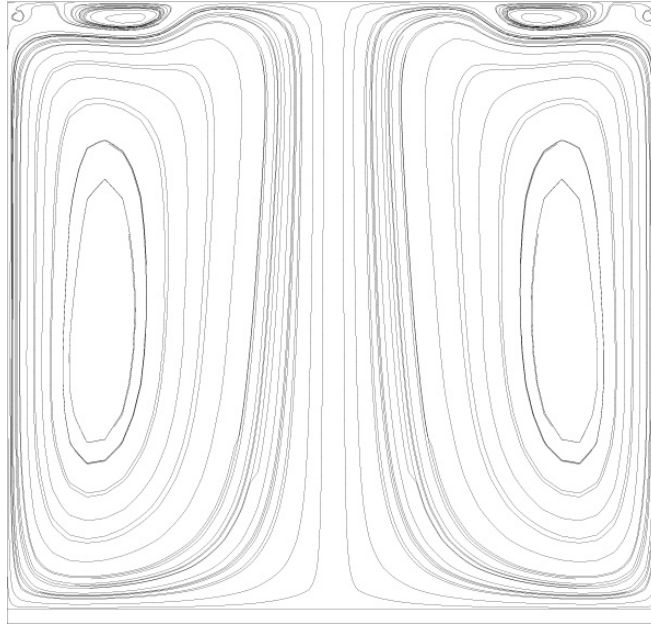


Figure 13: Streamlines in a vertical plane through the centre of the ladle during vacuum treatment (heat size 100t, isothermal temperature 1600°C, and gas stirring 130 Nl/min)

At the left in Figure 14 is a depiction of distribution of sulphur in the slag. Here, the fluid-flow pattern in the slag is also clearly reflected by the concentration profile. The recirculation loop can be seen in the sulphur profile as well as the stagnant zone. The slag absorbs sulphur, which is transported towards the stagnant zone. After 9.5 minutes of vacuum treatment there is a build-up of sulphur in the slag close to the ladle wall (the stagnant zone) with a local maximum sulphur content of about 2%. In the recirculation loop there is also an increased sulphur content, the value being around 1.1%.

At the right side in Figure 14 is a photo of an industrial slag sample investigated by Scanning Electron Microscopy. The slag sample was taken immediately when the vacuum treatment was finished. In this particular heat the normalised slag composition was 55.5% CaO, 32.1% Al₂O₃, 7.6% MgO and 4.3% SiO₂. The sampling temperature was 1509 °C. Precipitated particles of CaS were identified in the slag sample, as indicated in Figure 14. If it is assumed that the CaS particles were precipitated during the vacuum treatment, some explanations as to why this would occur should be proposed. It is possible that local enrichment of sulphur in the slag (as seen to the left in Figure 14) together with a decrease in temperature causes a supersaturation of sulphur in the slag, which could produce the precipitation. The CaO content in this particular heat was also rather high.

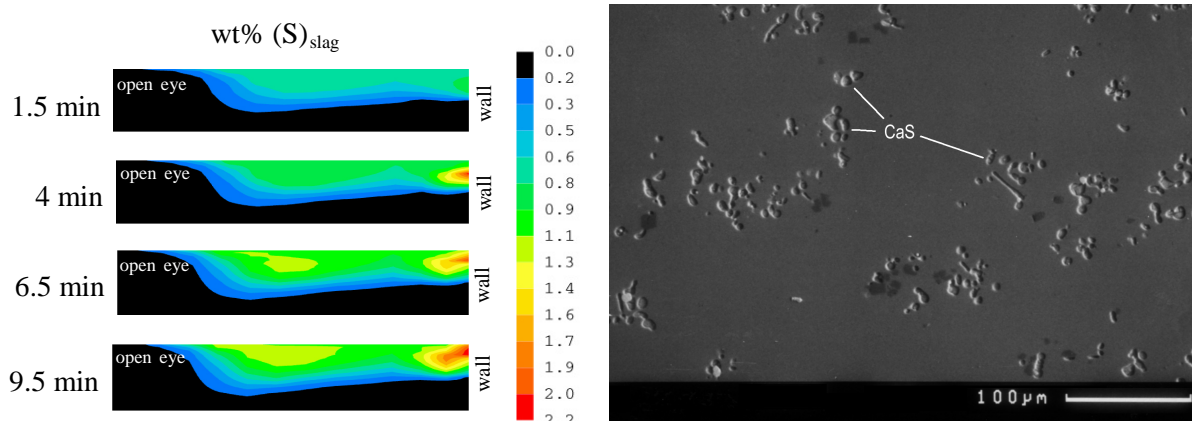


Figure 14: To the left: Calculated sulphur concentration profiles in the slag phase at different points of vacuum treatment time (heat size 100 t, isothermal temperature 1600 °C, gas stirring 130 NL/min). To the right: Precipitation of CaS in sample from top slag after vacuum treatment

In order to evaluate the influence of the initial FeO content in the slag on desulphurisation and aluminium loss, a parameter study was made⁴⁾ for three different slag compositions where the initial FeO content in the slag was 0, 2 and 6%. The different initial slag compositions in the parameter study are specified in Table 4.

Table 4 - Initial slag compositions used in the dynamic parameter study

%FeO	%Al ₂ O ₃	%CaO	%MgO	%MnO	%SiO ₂	%S
0	29.0	50.0	9.2	0.0	11.2	0.5
2	28.4	48.9	9	0.2	11.0	0.5
6	27.2	46.9	8.6	0.2	10.5	0.5

Figure 15 (to the left) shows how the model predicted the influence of different initial contents of FeO in the top slag on desulphurisation at an isothermal temperature of 1600 °C. At 0% initial FeO the average sulphur content decreased from 0.023 to 0.013 within 10 minutes. When the initial FeO content increased, the desulphurisation rate decreased. At 2% initial FeO the average sulphur content was 0.015% after 10 minutes of vacuum treatment. When the initial FeO content was increased even further to 6%, the average sulphur content was 0.020% after 10 minutes.

At the right in Figure 15, two calculated concentration profiles of sulphur in the steel melt at 1600 °C are illustrated. The results are presented as plots in a vertical plane through the centre of the ladle. After 4 minutes of vacuum treatment very different concentration profiles were observed when comparing 0% and 6% initial FeO in the top slag. For the case of 6% initial FeO content the sulphur refining was rather slow, (which also can be observed in Figure 15 to the left). The average sulphur content was calculated to be 0.021% after 4 minutes of vacuum treatment and it was observed that the concentration gradients of sulphur were small in the steel bulk. When the initial FeO content was decreased to 0%, the sulphur concentration gradients in the steel bulk after 4 minutes were significant and the desulphurisation reaction rate was higher. The average sulphur content at this point was 0.016%.

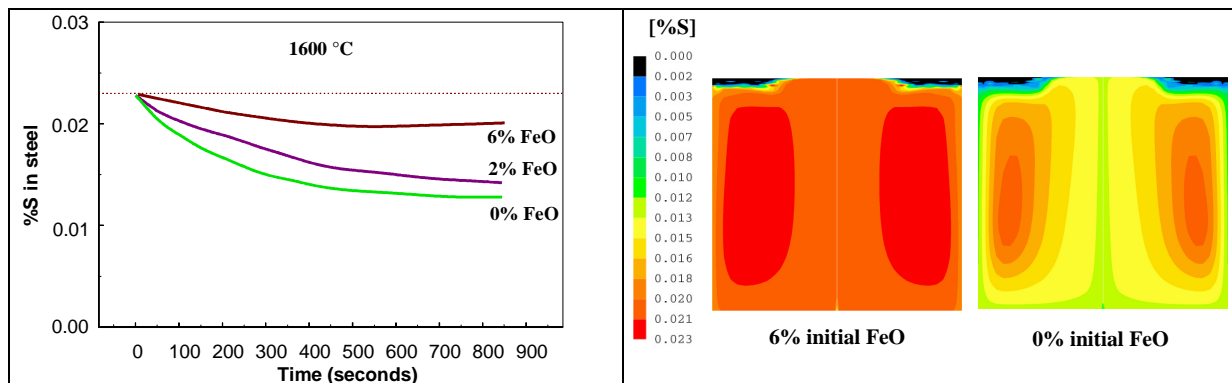


Figure 15: Influence of different initial FeO contents in the top slag on desulphurisation. To the right the predicted sulphur concentration after 4 minutes can be seen. Heat size 100 t. Isothermal temperature 1600 °C. Gas stirring 130 Nl/min. $S_0 = 0.023\%$.

5. DISCUSSION AND CONCLUSIONS

Desulphurisation during vacuum degassing was investigated and reported on in the present paper. The influence of some slag properties on desulphurisation has been discussed. Furthermore, the use of these slag property data in static and dynamic modelling has also been presented and compared with experimental plant data obtained at Ovako Steel.

Slag properties

Models for predicting the sulphide capacity⁶⁾, viscosity⁹⁾ and oxide activities^{13), 16)} in liquid slags as functions of slag composition and temperature have been presented briefly. New results from viscosity measurement for an Al_2O_3 -CaO-MgO-SiO₂ synthetic slag (representing a typical ladle furnace slag) have been shown. The data have also been compared with predictions using the KTH model and the agreement was found to be good.

In order to improve the general understanding of the effect of slag properties on desulphurisation additional information is needed. Information is available regarding the sulphide capacity of ladle slags. Additional viscosity measurements on industrial slag samples are required and these should be compared with, and used for model predictions. However, the slag property for which information is most lacking is the activity of oxide components. Measurements, model predictions and the implementation of the oxide activity in models are necessary. This is especially important for ladle slag compositions nearing CaO and MgO saturation.

Static modelling

The overall conclusion from the static modelling and the corresponding plant trials is that the suggested method of calculating the sulphur distribution ratio (using the KTH model⁶⁾ to calculate the sulphide capacity and Ohta and Suito's expression¹⁶⁾ to calculate the alumina activity) has two important practical applications:

1. It allows for fast and easy determination of the theoretical desulphurisation conditions for the current refining praxis. This is possible to do even for ladle slags with up to six components, since that is the present limit of the KTH model for prediction of sulphide capacities.
2. It makes it possible to theoretically determine the parameters that have the greatest

influence on the equilibrium sulphur distribution ratio. Thereafter, the top-slag composition can be optimised with respect to sulphur refining for each major steel grade that is produced.

In the future, static modelling of desulphurisation could be used as means of predicting near optimal slag composition for vacuum treatment. However, it is important to consider the slag weight, since it has a large influence on the model predictions. Also, the presented static model does not take the effects of FeO and MnO in the top slag on desulphurisation into account.

Dynamic modelling

Dynamic modelling based on first principles and the presented thermodynamic relations can be used to predict the time dependency of the desulphurisation process for any specific ladle and stirring method. The effect of slag and steel composition and weight on sulphur refining can be studied using static as well as dynamic modelling. In addition, dynamic modelling also takes into account the simultaneous interaction between these quantities and other physical conditions like different stirring strengths/methods, varying temperature and heat loss, etc. on the sulphur refining process.

The predicted final sulphur contents in the molten steel are in good agreement with plant data for the operating conditions at Ovako Steel AB. The predicted sulphur content though was somewhat lower in the beginning of vacuum treatment. It was also found that the model was sensitive to the thermodynamic models used to calculate the oxygen activity and the input value of slag weight.

The dynamic modelling of desulphurisation during degassing including reoxidation (two-dimensional model) indicated that a local accumulation of sulphur in the slag could occur, when a recirculation flow pattern is present. This could cause a precipitation of calcium sulphide, especially if the CaO content is high and the temperature drop is large enough. Investigation of a slag sample by Scanning Electron Microscopy revealed precipitated particles of CaS. The model results also showed that an increase in the initial FeO content in the top slag significantly lowered the desulphurisation rate.

From the dynamic modelling results it has been concluded that the presented modelling concept is promising and will be used for future research on slag/metal modelling. Furthermore, the comparison of model predictions with plant data shows that the model also has the potential to be used as a production tool for process control in the near future. However, as also mentioned earlier, access to reliable thermodynamic and thermophysical data of the reacting phases is of utmost importance.

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