

Slag-Metal Reactions during the Continuous Casting of Steel

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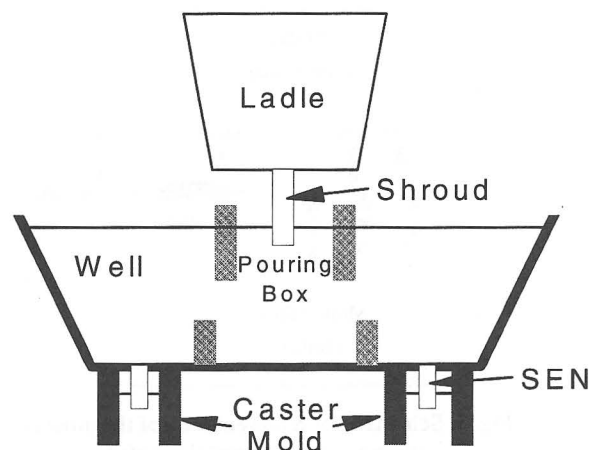


Fig. 1. Schematic of the tundish and continuous caster mold.

ABSTRACT

During continuous casting, steel entering the tundish reacts with fluxes added in the pouring box and then with the mold flux in the mold. The chemistry of the resulting slags determines steel cleanliness and also the performance of the mold. A model based on the first principles of thermodynamics and kinetics has been developed and validated on Inland's casters. The results of the model have been used in developing new powders for the molds and understanding the reactions occurring in the tundish. The paper describes the fundamentals of the model and its application in Inland's casting practice.

1. INTRODUCTION

During continuous casting of steel, molten steel is teemed from a ladle into an intermediate vessel, the tundish, and then flows into the continuous casting mold (Figure 1). Solid flux is added to both the tundish and the mold. In the tundish, the flux is expected to provide thermal insulation, prevent reoxidation and absorb non-metallic precipitates (primarily alumina inclusions); in the mold, the functions are more complex - in addition to the above, the flux should provide lubrication between the mold and solidifying steel and control heat transfer. These aspects are very critical to producing clean steel with no surface defects. In both the tundish and the mold, the performance of the fluxes is determined to a large extent by the chemical changes in the liquid slag resulting from both alumina absorption and slag-metal reactions. A fundamental approach towards understanding the kinetics and thermodynamics of the reactions is essential to optimizing and designing the fluxes and determining the causes for process changes. A general purpose slag-steel chemical interactions model has been developed based on thermodynamic and kinetic considerations. The basic model is then combined with the specifics of the particular reactor - tundish or mold as the case may be. In this paper some details of the model and sample cases of application are discussed.

2. MODEL FORMULATION

The reactions occurring at the slag-steel interface have been classified as follows (1):

- Type I : Reactions between slag and steel phases.

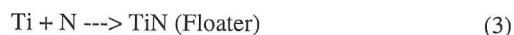


where A is the anion, Sulfur or Oxygen

- Type II : Reactions involving only the slag phase, i.e. the dissolution of non-metallic inclusions.



- Type III : Reactions involving only the steel phase. For example, titanium nitrides precipitating from titanium-bearing steel are not soluble in mold slags and lead to the formation of 'floaters' (2).



Type I and II reactions alter slag composition and are the focus of the present work. The model is based on Robertson's generalized film theory (3).

2.1 Description of the Model

A generalized slag-metal interface is shown in Figure 2. The species [M] stands for elements such as Fe, Mn, Al, Si etc., in steel and (MO_{σ}) for their oxides in the slag (for alumina, $\sigma=1.5$) and (MS_{σ}) for their sulfides in the slag. The description of the reactions is based on the following set of assumptions:

1. The bulk slag and metal are thoroughly mixed such that no concentration gradients exist in the bulk.
2. For reactions to occur, species transfer from the bulk to the interface or vice versa and the rate of transfer is a first order mass transfer process.

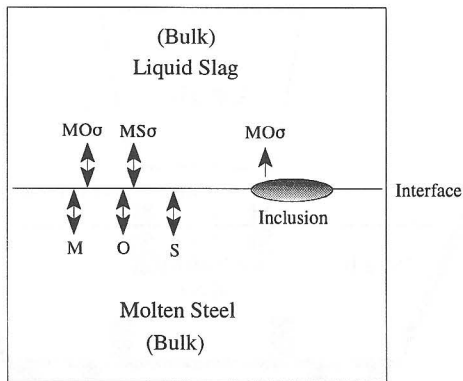


Fig. 2. Schematic of representation of the process occurring at the slag-metal interface.

3. Reactions occur only at the interface where equilibrium is assumed to exist.

The instantaneous concentration of species in the bulk phases is governed by the following mass conservation equation.

$$R_a = R_e - R_o - R_t \quad (4)$$

Where,

R_a = Rate of change of species concentration in the bulk slag or steel

R_e = Rate of species entering with the inlet stream (flux or steel)

R_o = Rate of species exiting with the outlet stream (slag or steel)

R_t = Rate of species transferred from the bulk to the interface

Eq. 4 represents a family of equations, one for each species under consideration. The mathematical representation of Eq. (4) is as follows :

$$dn_{z,j}/dt = X_{z,e} E_j - X_{z,j} P_j - k_{z,j} C_j A_{s/m} [X_{z,i} - X_{z,j}] + A_{inc} C_j k_{z,j} [X_{Al_2O_3,inc} - X_{Al_2O_3,j}] X_{z,inc} / X_{Al_2O_3,inc} \quad (5)$$

where, $A_{s/m} + A_{inc} = A$, the total cross sectional area available for reaction. If Type-II reactions are occurring, the area across which inclusion transfer occurs, A_{inc} , is unavailable for Type-I reactions. The estimation of the area at the interface available for inclusion dissolution (A_{inc}) is discussed subsequently. Also, the last term in the right hand side of Eq. 5 applies only for the slag phase.

In the case of aluminum-killed steels, the inclusions are assumed to be primarily alumina and their rate of dissolution is dependent on the rate of dissolution of the alumina component of the inclusion. Liquid oxide inclusions in steel are assumed not to play an integral part in altering mold slag chemistry.

In order to solve the above equation, the compositions at the interface must be specified. Recalling assumption No. 3, the concentration of the species at the interface are related based on the equilibrium relation for Eq. 1:

$$X_{MA\sigma,i} = [K_M f_{M^A} / \gamma_{MA\sigma}] [\%M_{m,i}] [\%A_{m,i}]^\sigma \quad (6)$$

Furthermore, the rate of change of moles of any species in the steel phase is equal to that in the slag phase:

For oxygen and sulfur,

$$C_m k_{A,m} [X_{A,i} - X_{A,m}] = \sum_M C_S k_{MA\sigma} [X_{MA\sigma,i} - X_{MA\sigma,s}] \quad (7)$$

For each of the M species,

$$C_m k_{A,m} [X_{M,i} - X_{M,m}] = \sum_{A=O,S} C_S k_{MA\sigma} [X_{MA\sigma,i} - X_{MA\sigma,s}] \quad (8)$$

Simultaneous solution of Eqs. 6 - 8 is carried out iteratively in order to determine the interfacial compositions at any given time. The set of differential equations represented by Eq. 5, which is the core of the present model, are then solved using a numerical analysis package based on Gear's algorithm (4) since these equations are stiff.

The application of the above model to tundish and the mold systems differs only in the following - liquid slag remains in the tundish, ladle slag can be entrained in the tundish during ladle exchanges. These are incorporated into the part of the model that deals with reactor specifics.

2.2 Selection of Thermodynamic Data

Thermodynamic data for species in steel are readily available (5). The thermodynamic data for mold slags are not yet well established due to the wide variation in component species. Tundish slags are primarily CaO-MgO-SiO₂-Al₂O₃, but do contain small amounts of other oxides. Sulfur species in slags were assumed to be CaS, MnS and FeS, and thermodynamics of individual species were deduced from available work. In general, it may be stated that thermodynamic data for the systems encountered are not well established. Appropriate models, if readily available, would be very useful for improving the calculations made in this work. In the current work, the optical basicity concept has been used for extrapolation purposes.

2.3 Selection of Mass Transfer Constants

The mass transfer coefficient for all species in the steel phase was set at 0.04 cm/s as suggested by Yamagata (6). Recently, van der Stel (7) suggested values of 10⁻³ to 10⁻⁴ cm/s for Si species in the slag and metal phases. Alumina transport into mold slags was examined by several investigators and values of mass transfer coefficients ranging from 10⁻³ to 10⁻⁵ cm/s have been reported. In view of the variation in the published values of the mass transfer

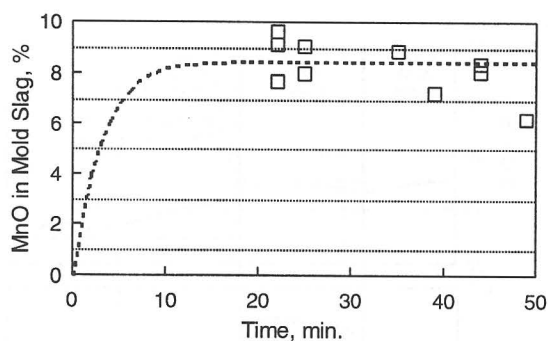


Fig. 3. Measured and predicted MnO pick-up with Flux-B during the casting of free-machining steels.

coefficients, as a first step, the value was estimated as 0.001 cm/s using Kosaka's correlation (8) for flowing films. This value was modified to attain agreement with operational data. It was found that for species that have one atom of the cation in a molecule, e.g. FeO, MnO, SiO₂ etc. a value of 0.002 cm/s satisfactorily described the transfer rate over a wide range of conditions for a large number of data sets obtained from Inland's billet, slab and bloom casters. A value of 0.001 cm/s was retained for species with more than one cation per molecule (such as alumina). Here again, this study points to the need for further understanding of transfer coefficients in slag - metal systems.

3. MODEL VALIDATION AND APPLICATION

In the validation phase of the work, the estimates of the slag phase mass transfer coefficients (described above) and the inclusion-slag interaction area term - A_{inc} - were fine tuned. The latter is dependent on the conditions in the specific reactor and is different for the tundish and the caster mold. Samples obtained in the mold were used first to determine the appropriateness of the kinetic and thermodynamic parameters used in this study. Since the issue of interfacial area is complicated by the probability of turbulence in the pouring region of the tundish, the discussion below is presented in two parts - first application to reactions in the mold and then to reactions in the tundish. Examples of each are described to show how the model has been used.

3.1 Slag - Metal Reaction in the Continuous Caster Mold

3.1.1 Validation of Kinetic parameters

Free machining steels are cast with 30 to 200 ppm oxygen, 0.8 to 1.5% manganese and without the addition of aluminum. Type-II reactions do not occur. Fig. 3 shows the calculated and measured changes in MnO content for a particular flux (B- see Table I). It can be seen that a good agreement exists between the measured and predicted in-mold slag composition using the kinetic parameters stated earlier. As observed in practice, the model also predicts that within a short time from start of cast, the mold slag stabilizes with respect to MnO. The differences seen in Fig. 3 are attributed to variability in oxygen content of steel,

mold flux consumption rate and depth of the liquid flux. These are discussed subsequently.

Additional comparison of changes in in-mold slag MnO levels for various fluxes and FM grades is shown in Table-I. The model provides good prediction of the steady state mold flux composition during the casting of free-machining steels. This provides validation for the mass transfer coefficients and the thermodynamic data used in the model.

3.1.2 Estimation of the inclusion float out term - A_{inc}

Alumina assimilation in the mold slag has been the subject of numerous studies and it has been strongly believed that most of the alumina is picked up through the dissolution of non-metallic inclusions. Typical alumina pick-up at Inland's slab casters is 2-3% for Al-killed (LCAK) steels and 6-7% for high Al cold rolled motor lam (CRML) steels as shown in Table II. Also shown in the same table are predictions from the model for various values of the inclusion-slag interaction area - A_{inc} .

The results in Table II show that if the alumina transfer was essentially by inclusion transfer ($A_{inc} = 95\%$), the predicted pick-up for LCAK grades is much higher than that observed in practice. On the other hand, if the transfer occurred solely by reaction ($A_{inc} = 0\%$), then the transfer during casting of CRML grades is over-predicted. It is found that the best agreement with measured alumina changes is obtained by considering that 20% of the available mold cross section area takes part in inclusion-slag interaction, i.e., $A_{inc} = 0.2 \times$ (total area - cross section of nozzle). This value of A_{inc} was used for all subsequent simulations. Since the sampled mold flux is usually contaminated by unreacted flux, the fact that the predictions with the above value of A_{inc} , are in agreement with the upper end of the measured range, is considered acceptable.

TABLE I
In-mold Slag MnO during casting FM steels

Flux	%MnO in mold flux		
	Initial	Measured Final	Predicted Final
A	5.1	6.3 - 8.5	8.6
B	0.0	6.0 - 9.9	8.6
C	5.0	4.0 - 6.0	6.5
D	2.8	4.1 - 4.3	4.7
E	4.1	3.0 - 4.2	5.7
F	4.0	3.7 - 4.6	5.8
G	5.1	4.7 - 5.7	6.6

TABLE II
Estimation A_{inc} for Al Killed Steels

Flux	Steel	Initial Al_2O_3 %	Measured	Final % Al_2O_3		
				Calculated for $A_{inc} =$		
				0%	20%	95%
H	CRML	0.3	5.0 - 7.5	8.2	7.6	5.2
I	CRML	0.3	4.0 - 7.0	7.9	7.4	5.3
J	LCAK	2.7	4.0 - 5.0	4.9	5.9	9.0

It must be pointed out that in case of air aspiration through the SEN or breakage of the ladle shroud, more alumina is generated and the area across which slag-inclusion reaction (Type-II) takes place increases beyond the value of 20% (of available area) used for the present calculations and consequently that for slag-metal reaction decreases. Table II shows that with the increase in the A_{inc} term, the alumina pick-up in LCAK steels increases. In CRML steels, however, this term decreases due to the reduction in the available area for the dominant slag-metal reaction.

3.2 Application to Practice

3.2.1 Sequence Casting

The model was used to simulate the changes that would occur in the in-mold slag composition during a sequence cast involving a change in mold flux coupled with a change in steel grade (from LCAK grade to CRML grade). Mid-way through the LCAK heat, a flux transition was made (flux-K to flux-H) to accommodate the subsequent CRML heat. Comparisons are shown in Fig. 4. The calculated and measured composition of the steady state in-mold slag correlate well during all stages of the flux transition and steel grade change.

The model is also able to predict the MnO content of the mold slag fairly well, as shown in Fig. 4. Since MnO pick-up occurs only by steel-slag chemical interaction, the accurate prediction of the simultaneous pick-up of MnO and alumina provides further validation for the concept of the A_{inc} parameter and its magnitude stated earlier.

Also shown in Fig. 4, is the excellent agreement between the calculated and actual change in the silica content of the in-mold slag. This clearly demonstrates that aluminum reduction of silica in the mold flux plays a major role in altering the mold flux composition and that the increase in the alumina content of the in-mold slag observed when the Aluminum content of the steel is increased is a result of the slag-metal reaction. It appears that in present-day clean steel practices, the generation, floatation and assimilation of alumina inclusions into the mold slag is limited and therefore the total alumina pick-up is due to both Type-I and Type-II reactions.

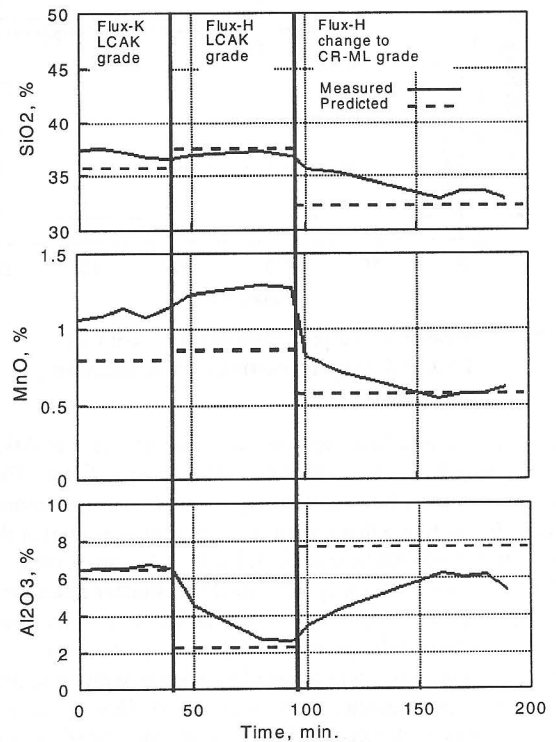


Fig. 4. Changes in Al_2O_3 , MnO and SiO_2 content of the mold slag during a casting sequence.

3.2.2 Development of Mold Fluxes for Aluminum-Killed Steels

As a result of evolution in clean steel practices, alumina pick-up in the mold slag during casting of LCAK steels has been reduced to 2-3 % from 10-12% prevalent in the 70's. Since an increase in the alumina level in the slag increases the viscosity of the mold flux, the starting viscosity of the mold flux has had to be progressively increased so that an in-mold slag viscosity of 2-2.5 poise (@1300°C) is achieved and incidents of longitudinal cracking decreased. In order to identify the important design criteria to minimize alumina pick-up by reactions and therefore produce a predictable and stable in-mold slag, the impact of various parameters was evaluated using the model.

One of the most important parameters was found to be consumption rate, which depends on mold - steel shell gap and the mold flux properties such as viscosity, melting range, surface tension, etc. The impact of consumption rates on alumina pick-up is shown in Fig. 5. Alumina pick-up is strongly influenced by the residence time of the flux in contact with the steel, i.e., the consumption rate. For the fluxes shown, large reductions in alumina pick-up can be achieved by maintaining a consumption rate above 0.8 kg/ton. Ideally, control of consumption rate is the most important design criteria for stabilizing the in-mold slag composition. Alternatively, the flux composition should be such that it is insensitive to the expected alumina change.

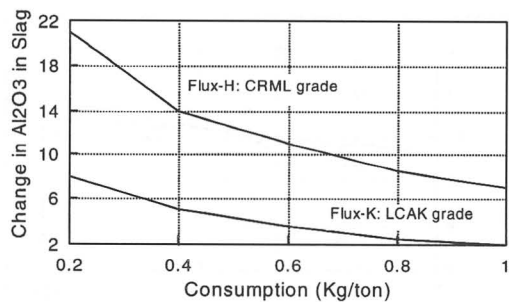


Fig. 5. Effect of consumption rate on alumina pick-up.

Another important aspect of the results shown in Fig. 5 is related to variations in in-mold slag composition at different locations in the mold resulting from varying consumption rates. Due to two-dimensional heat flow at the corners, the mold-shell gap is maximum at the narrow face and minimum at the broad-face of the slab molds. As a result, the consumption rate at the broad-face is also lower and alumina pickup higher. The differential consumption of mold flux will lead to drastic differences in the in-mold slag composition and its properties. This is an important consideration for LCAK steels which are prone to longitudinal cracking at the mid-face. Maintaining a constant liquid slag depth was found to have similar effects on liquid slag properties. This is an important criterion associated with operating procedures. The model hence has helped design both the criteria and necessary practice for optimizing casting of these steels.

3.2.3 Development of Mold Fluxes for Free-Machining Steels

In the past, free - machining steels had been prone to longitudinal mid-face cracks and depressions due to transverse thermal gradients resulting from non-uniform and excessive mold heat transfer. Preliminary analysis of the in-mold slag composition during a series of heats showed that the MnO pick-up in the mold slag fluctuated between 8 and 17% resulting in viscosity change from 1.8 to 3.2 poise (@1300°C) and solidification temperature change from 975°C and 1040°C. It is believed that these variations also exist from one location to the other across the broad faces causing non-uniform heat transfer. The primary design consideration adopted was to suppress the pick-up of MnO by an increase in the optical basicity and MnO level of the flux. As seen in Table I, the change from Flux-B to Flux-A dramatically dropped the MnO pick-up. In practice the incidents of longitudinal cracking were completely eliminated.

A major reason for the success of flux-A is evident in Fig. 6 where the model predictions for the impact of consumption rate on MnO pickup are shown. Clearly, flux-A is much less sensitive to MnO pick-up than flux-B in terms of consumption rate. Therefore, differential consumption at different locations in the mold and that

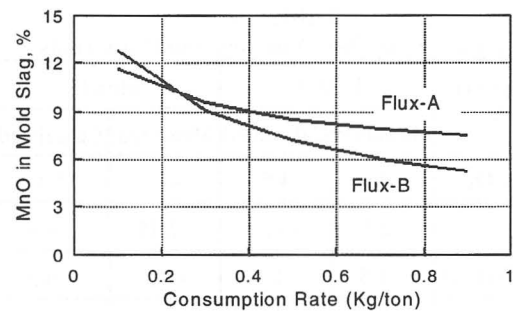


Fig. 6. Effect of consumption rate on MnO pick-up during the casting of free-machining steels.

resulting from fluctuations in casting parameters will lead to a lower magnitude of change in the in-mold slag composition with flux-A. The resultant stabilization of the heat transfer in the mold is considered to be a major contributor to the observed elimination of longitudinal cracking.

3.2.4 Development of high viscosity mold powders for Ti SULC grades.

Recently, work was carried out at Inland to develop higher viscosity mold powders to reduce sliver rejections on Ti added ultra low carbon grades. Trials showed that a 30% reduction in sliver rejections could be achieved by appropriate change in mold flux, indicated here by flux A and flux D. The latter flux had twice the viscosity (3 vs 1.5 poise) as measured at 1300°C. Table III shows the actual and predicted changes in mold slag compositions. Good agreement is observed. It is not entirely clear why the silica changes are more pronounced in the model, whereas the rest of the parameters show a good match. While it is not critical to the current problem, it should be pointed out that the model is also able to predict the TiO₂ pickup - this is an important aspect in designing mold powders for these critical grades. The model results can then be used to compare the results of alumina absorption. Table IV clearly shows that flux D which resulted in 30% lower rejections, did not actually "clean" the steel any better (consumption rate of flux D was slightly lower than that of flux A). An observation that with higher starting viscosity of flux D, more uniform coverage of liquid slag was maintained throughout the cast was therefore considered one of the key reasons. As stated above, non-uniform coverage can lead to variations in slag depth and consumption and hence local gradients in mold slag properties. These effects can be responsible for deterioration in cast slab surface quality.

3.3 Slag - Metal reactions in the Tundish

Analysis of slag-metal interactions in the tundish is complicated by the fact that the pouring region may be subject to significant turbulence and the well region is akin to the mold slag-metal interface - relatively quiet. Reactions in the different parts of the tundish have been studied in the past at Inland Steel for Ti added ultra low

TABLE III
Comparison for High Viscosity Mold Flux Trials

Component %	Flux A		Flux D	
	Measured	Calculated	Measured	Calculated
Al ₂ O ₃	4	4.5	4.3	5.1
SiO ₂	- 2.5	- 4.2	- 2.25	- 4.6
MnO+FeO	- 1.5	- 1.3	- 0.5	- 0.5
C/S start	1.11		0.81	
C/S react	1.21	1.208	0.88	0.88

TABLE IV
Alumina Change - Reaction vs Absorption (from Model)

	Al ₂ O ₃ Change		
	Total, %	By Reaction, %	By Reaction pct. of total
Flux A	4.5	2.0	45
Flux D	5.1	2.5	49

carbon and low carbon Al killed grades (2). High silica fluxes were in use at the time and significant changes in silica, alumina and titania (for Ti ULC grades) in the pouring region slags was found especially during the first two ladles of the sequence when turbulence was high. Steel samples taken in the pouring region also indicated sharp changes in steel chemistry. Preliminary comparison of calculated and actual slags indicated that the observed changes could be understood by a combination of increase in reoxidation products and an increase in surface area for reaction. An order of magnitude increase in surface area is easily understandable when two phases are mixed as is observed in the pouring region. The turbulence is a function of several parameters such as casting rate, nozzle geometry, stream integrity, open/closed pouring etc. The well region reactions can be understood in much the same way as in the mold, i.e., assuming geometrical surface area as that available for reaction.

Here, an example of the application of the model to understand the observation of increases in oxygen concentration during casting leaded free machining grades is described. These grades are open poured and generally have a high oxygen content coming into the tundish. Increases of up to 25 ppm or more were observed on these grades mainly during the latter heats in a cast string. Since these incidences were not tied in to any sharp increase in alumina absorption and were predominant in the latter heats, it was unlikely that ladle stream oxidation by air was the probable cause. It was decided to use the model to understand the changes in the tundish.

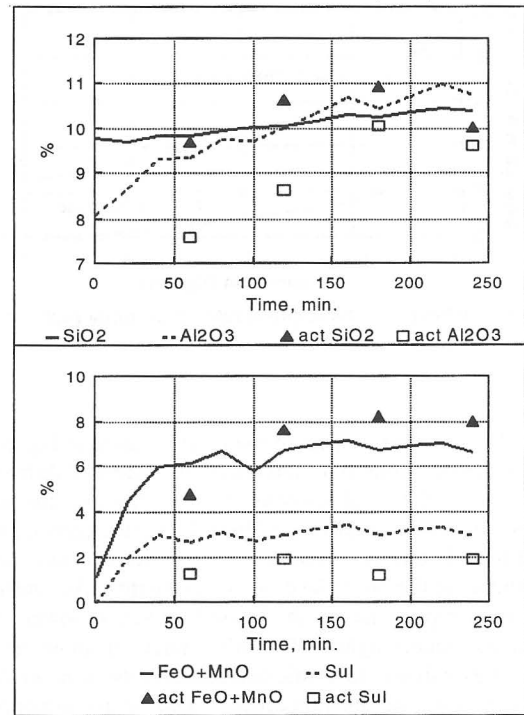


Fig. 7. Change in tundish slag chemistry during a cast string of FM steel.

Figure 7 shows the calculated and measured chemistry changes of the tundish slag in the well region for a cast string where no oxygen increase was observed. In this particular case there is negligible ingress of ladle slag as observed by the low MnO levels. When ladle shut off does not occur properly, MnO levels as high as 25 to 30% have been measured. The figure shows the excellent agreement between measured and calculated results for all the species, including sulfur. This provides the necessary confidence to use the model to understand conditions for oxygen increase. Several sets of simulations were performed as described below :

1. As a test, simulations were performed with a large slag-to-steel ratio for the current system. The model clearly showed that ladle slag was an oxygen source for the steel whereas tundish flux was an oxygen getter.
2. Simulations such as those in Fig. 7 were performed with increased amounts of ladle slag ingress to match the MnO levels found in the latter part of the strings. While silica, alumina and sulfur changes in slag chemistry could be predicted, oxygen ppm in the steel does not generally show much of a change due to the large volume of the steel compared to the slag.
3. The turbulence in the pouring region was simulated by artificially increasing the surface area for reaction. An increase of one order of magnitude along with nominal ladle

slag ingress of 50 kg can account for 15 - 25 ppm increases in oxygen content for the duration when sampling of steel is done following a ladle exchange. Since MnO levels in the well region slag was as high as 30%, clearly, slag carryover is much more than that indicated here. Van der stel et al (7) have suggested values can be as high as 100 kg per ladle exchange.

4. Calculations further showed that the residence time in the tundish well is not sufficient to alter the steel chemistry change occurring in the pouring region due to No. 3 above.

These arguments suggested that the oxygen pickup could not be corrected by tundish flux changes and that the source cause is most likely the enhancement of slag - metal reaction rate due to the changes in the turbulence and mixing in the pouring region. Practices that could lead to the above effect were identified as follows :

- changes in ladle shut off practice leading to a greater ingress of ladle slag
- changes in stream integrity due to nozzle design changes leading to greater turbulence in the pouring region.
- skull etc. in the pouring region during the latter heats in the string causing the ladle stream to breakup and hence increasing slag-metal mixing.

Practice changes instituted to counter the above were instrumental in alleviating the incidents of oxygen pick-up.

4. CONCLUSIONS

A model has been developed based on fundamental concepts of thermodynamics and kinetics and it has been found that with the available data, reasonable simulations of the slag-metal reactions in the tundish and mold can be obtained. The study has identified that additional work in this area will be of great benefit to improving the current simulations. Significant benefits can be derived by using a tool such as this to both analyze changes in practice and to help develop new formulations of fluxes for casting different grades of steels.

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NOMENCLATURE

γ	: Raoultian activity coefficient in the slag phase
A	: Anion, sulfur or oxygen
$A_{s/m}$: Cross sectional area for the reaction
A_{inc}	: Cross sectional area for inclusion dissolution
C	: Molar concentration, moles/m ³
E	: Molar feed rate
f	: Henrian activity coefficient in the steel phase
K_M	: Equilibrium constant
k	: Mass transfer coefficient
P	: Molar exit rate
M	: Metal
n	: Moles of species in the control volume
X	: Mole fraction
z	: Species

subscripts:

i	: Interface
inc	: Composition of the inclusion
int	: Interface
j	: Slag or steel
m	: Steel
s	: Slag

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