Slag formation during the steel refining process in a ladle furnace combined with the vacuum treatment

Jan FALKUS[1], Katarzyna MIŁKOWSKA-PISZCZEK[1], Lechosław TRĘBACZ[1], Paweł DROŻDŻ[1], Tomasz KARGUL[1]

Jacob LAMUT[2] and   Alojz ROZMAN[3]

1)   AGH University of Science and Technology, Faculty of Metals Engineering and Industrial Computer Science, A. Mickiewicza 30 Ave, 30-059 Kraków, Poland;

2)   Ljubljana University, Ljubljana, Slovenia;

3)   Metal Ravne, ,Koroška cesta 14, 2390 Ravne na Koroškem, Slovenia;

Abstract: The process of slag formation and the change of its chemical composition during the steel refining process is determined by the composition of the slag-forming materials used, the efficiency of the furnace slag cutoff and the kinetics of reactions on the metal – slag interface. It is possible to consider all these factors in theoretical reasoning by using the so-called hybrid model for calculations. A concept for modelling the changes in the chemical composition of metal and slag has been elaborated. The tank theory combined with the thermodynamic model of reactions on the metal bath-slag and metal bath-gas phase interfaces were used to develop a hybrid model of the process. The tank theory was used to describe the stirring of the metal bath, and this made it possible to simulate the process in real time. Some theoretical basis and the verification of the model were presented, inter alia, during the last, IX International Conference on Molten Slags in Santiago.This paper presents a continuation of previous work, additionally including refining processes in a vacuum. Special attention is paid to the reactions on interfaces between metal and slag as well as those between metal and the gas phase. In the hybrid model these reactions are simulated using thermodynamic calculations, taking into account the kinetics of the aforementioned reactions. The processes' kinetics can be determined by the mixing model based on the tank theory. Another important improvement of the hybrid model is the extension of the chemical composition of both metal bath and slag being considered in computations. It enables using the suggested model to simulate the alloy steel refining process. The summary presents the verification based on industrial melts. The verification was conducted for a technological line consisting of a 40-ton ladle furnace working in parallel with a vacuum chamber. The typically stored industrial database was complemented with additional measurements necessary to conduct the verification.

Key words: Process Control, Hybrid Model, Steel Refining Slag

1. Introduction

Nowadays, steel refining processes carried out in the ladle constitute a very important stage in the technological production line. These processes are highly varied and can be divided into two major groups:

- Steel refining processes running under the atmospheric pressure;
- Steel refining processes running in a vacuum.

The subject of this publication is a study of changes taking place in ladle slag during processes running under a reduced pressure. In the majority of cases, vacuum refining is intended to progress without the presence of slag, as this

makes steel degassing much easier. However, a certain number of vacuum processes is carried out in two stages, where vacuum refining represents only a fragment of the technological line for secondary refining. In this case, it is interesting to have information about the impact of reduced pressure on changes in slag contents and the impact of these changes on refining reactions. This is particularly important in the production of alloy steel grades containing a higher number of additives.

The research conducted makes it possible to assess changes to the chemical composition of system phases taking into account the kinetics of the process carried out. Hence the presented results are not traditional calculations of equilibrium states. The hybrid model used for calculations had previously been validated for a ladle furnace. Key parameters of the model were also established in experiments conducted on cold models. This concerns the percentage share of tanks into which the ladle was divided.

The scope of research carried out included two subjects. The first was to verify the proposed model in industrial conditions and assess whether it generated accurate projections. The second was a series of virtual experiments to assess the impact of pressure on changes in the chemical composition of refining slag.

2. Vacuum steel refining process

The proposed solution of the problem of dynamically controlling the vacuum steel refining process is designed for an electric furnace shop producing high-alloy steel grades. In this case, the secondary metallurgy stage is completed at two stands, the first of which works as a traditional ladle furnace, and the second is a vacuum chamber. Both at the first and the second stage, the metal bath is blown with argon. The chemical composition of the bath is mainly adjusted in the early period, when additives are fed in under atmospheric pressure. At that time, samples of metal and slag are collected and oxygen activity is measured. Before vacuum refining starts, the bath composition should be brought very close to the target composition. Refining in the ladle furnace lasts between 40 minutes and 1 hour. Then the bath is refined in a vacuum chamber where it continues to be mixed by argon blown in at the bottom. Vacuum refining influences not only the chemical composition of the metal, but also partly changes the composition of slag. MgO and SiO_2 are the components whose contents in slag may be significantly reduced. This automatically causes the proportion of the remaining constituents, mainly CaO and Al_2O_3, to rise. However, it should be noted that the final composition of ladle slag after vacuum refining probably does not reach the equilibrium state and is greatly dependent on the kinetics of processes running on the metal/slag interface.

3. The hybrid model of vacuum steel refining

The idea of the kinetic model of vacuum steel refining is based on the solution previously used for the ladle furnace. [1,2] The essence of this solution is the assumption that to describe process kinetics, one has to use the mixing model, in which the solution can be achieved within a time shorter than the actual refining duration. The key task is to select the bath mixing model in which, subsequently, a thermodynamic model will be embedded, with the latter enabling the calculation of the local equilibrium that is reached on the metal/slag interface.

In the solution adopted, the selected bath mixing model is based on the tank theory. The idea of this model is based on the assumption that the ladle can be split into so-called tanks, which are assigned the following characteristics: [3]

- The volume of the tank does not change over time;
- There is no concentration gradient within the tank;
- The chemical composition of the tank changes in steps after the pre-defined Δt time expires.

To validate the mixing model based on the described theory, the volume of individual tanks and the value of mass fluxes exchanged between them must be defined. The quality of this verification is of key importance for the precision of the projection generated by the mixing model.

Fig. 1 shows the adopted split of the steel-making ladle into tanks. It is noteworthy that the process of blowing argon into steel is of decisive importance for this split. [4,5]
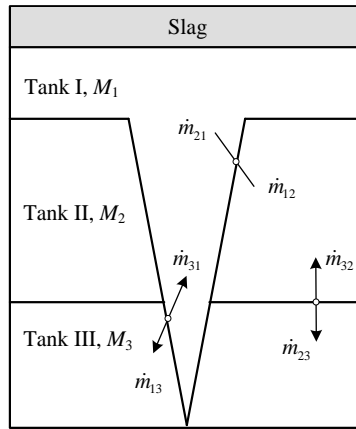

Fig 1. A diagram of splitting the ladle into tanks

For the split defined as above, the system of differential equations describing the mixing process takes the following form:

$$dm_1^i(t) = -\frac{m_1^i(t)}{M_1}\dot{m}_{12}\Delta t + \frac{m_2^i(t)}{M_2}\dot{m}_{21}\Delta t - \frac{m_1^i}{M_1}\dot{m}_{13}\Delta t + \frac{m_3^i}{M_3}\dot{m}_{31}\Delta t$$

$$dm_2^i(t) = \frac{m_1^i(t)}{M_1}\dot{m}_{12}\Delta t - \frac{m_2^i(t)}{M_2}\dot{m}_{21}\Delta t - \frac{m_2^i(t)}{M_2}\dot{m}_{23}\Delta t + \frac{m_3^i(t)}{M_3}\dot{m}_{32}\Delta t \qquad (1)$$

$$dm_3^i(t) = \frac{m_2^i(t)}{M_2}\dot{m}_{23}\Delta t - \frac{m_3^i(t)}{M_3}\dot{m}_{32}\Delta t - \frac{m_1^i}{M_1}\dot{m}_{13}\Delta t + \frac{m_3^i}{M_3}\dot{m}_{31}\Delta t$$

m^i_j mass of component i in tank j, [t]

M_j mass of tank j , [t]

m_{ij} flow intensity of metal between the tank and i and j [t/min]

The thermodynamic model embedded in the mixing model allows a local equilibrium to be determined on the metal/slag interface for freely defined chemical compositions of metal and slag. The tool used to create the thermodynamic model was FactSage©, which allows a subprogram to be generated in the form of a file that can be embedded in a proprietary application.

The essence of the proposed solution is explained by Fig. 2, in which the adjacent metal and slag layers achieving equilibrium are marked. The proper definition of the thickness of both these layers represents the next step determining the accuracy of model calculations.
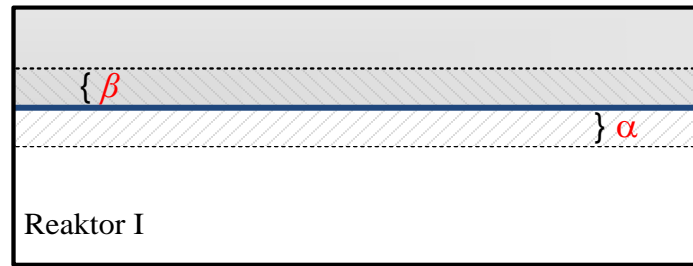

Fig 2. A diagram of the metal/slag interface with the adjacent layers marked [6]

In accordance with the research work completed before, the thickness of the metal and slag layers which achieve equilibrium should be established taking into account the time considered. In the case of numerical calculations, this is the computational time step Δt. The value of the α parameter is determined from relationship (2)

$$\alpha = k \frac{\Delta t \cdot \dot{m}_{12}}{M_I} \times 100\% \tag{2}$$

α the coefficient defining the percentage of the mass of the first tank that is transferred to the thermodynamic model, [%]

k dimensionless coefficient , $0.2 \div 1$

The value of the β parameter was determined based on the precise observation of changes in slag composition during experimental research melts.

Embedding the thermodynamic model in the bath mixing model consists in modifying the first equation of the system of equations (1). Then, the equation takes the following final form:

$$dm_1^i(t) = -\frac{m_1^i(t)}{M_1} \dot{m}_{12} \Delta t + \frac{m_2^i(t)}{M_2} \dot{m}_{21} \Delta t + \Delta m_1^i(t)_{eq} \tag{3}$$

where:

$$\Delta m_1^i(t)_{eq} = m_{eq}^i(t) - \alpha \cdot m_1^i(t) \qquad (4)$$

m_{eq}^i *(t)* - the equilibrium content of component i calculated by the thermodynamic model, [Mg]

At this stage, it should be noted that the hybrid model of steel refining in a ladle, defined above, makes it possible to account for the pressure under which the analysed process runs. As a result, this model is suitable for simulating processes running in a vacuum. This capability is due to the need to define the system pressure in the thermodynamic model. As the thermodynamic model is called up at each time step of the calculation, it is also possible to account for the system pressure variability during the process. This is of major importance for the realistic representation of the conditions in which vacuum steel refining occurs.

4. Validating the steel refining model based on an industrial process

The model presented above has been validated for an electric furnace shop at which the melt weight amounted to 40 tons. A major challenge was the need to account, in the thermodynamic model, for a wide range of elements, due to the broad range of alloy steel grades produced. In a sense, this introduced time restrictions in the model, as the procedure of establishing equilibrium states determines the computation duration. In the final version, the actual duration of computations represented some 30% of the real process time.

For validation purposes, all parameters of the model were determined, and their values are presented in Table 1.

Table 1. Key parameters of the model

Parameter name	Unit	Value
Mass share of tank I	%	25
Mass share of tank II	%	53
Mass share of tank III	%	22
Mass flux between tanks I and II	kg/min	2795
Mass flux between tanks I and III	kg/min	280
Mass flux between tanks II and III	kg/min	894
Coefficient α value	-	0.006
Coefficient β value	-	0.002
Calculation time step Δt	s	25

The values of main model parameters presented in the table allowed the projection accuracy to be checked using the precise recording of the melt progress. Fig. 3 shows a comparison of simulation results with the actual change of alloy element contents in the metal bath. Fig. 4, in turn, presents results of simulations of changes in the slag chemical composition for the same melt and the actual changes during the process. Results presented in Figures 3a,3b and 4 concern one of the randomly selected validation melts. The accuracy achieved is satisfactory and allows the model to be used for virtual experiments.
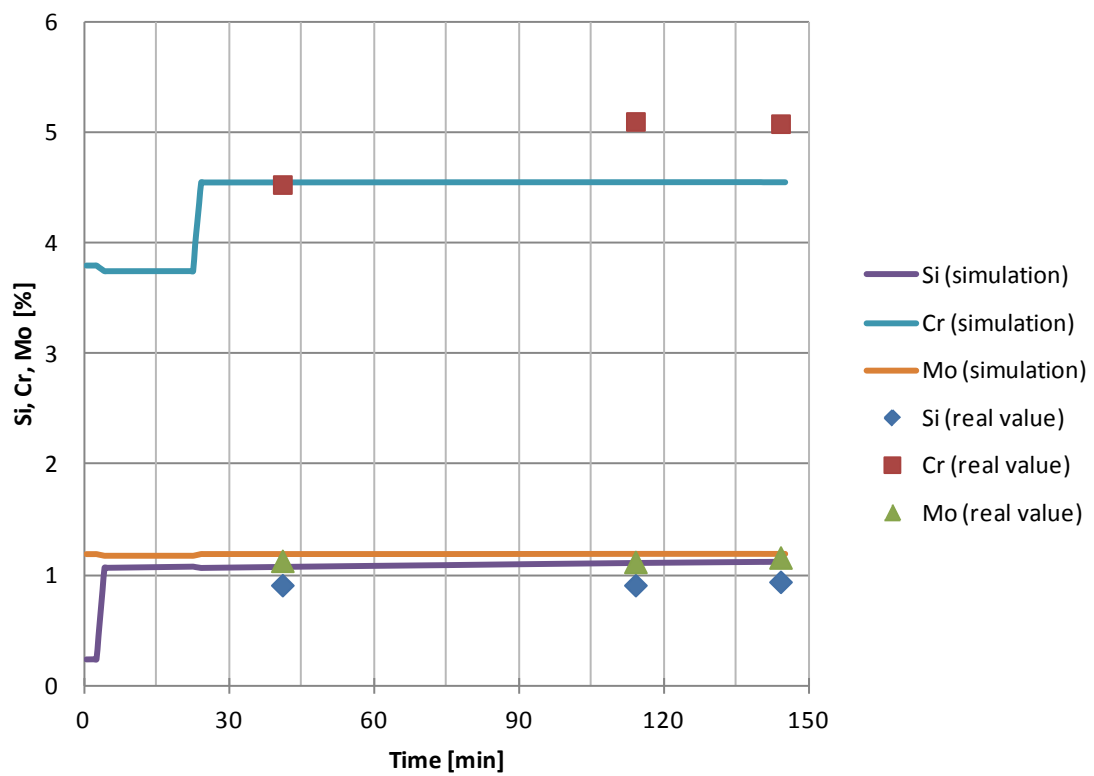
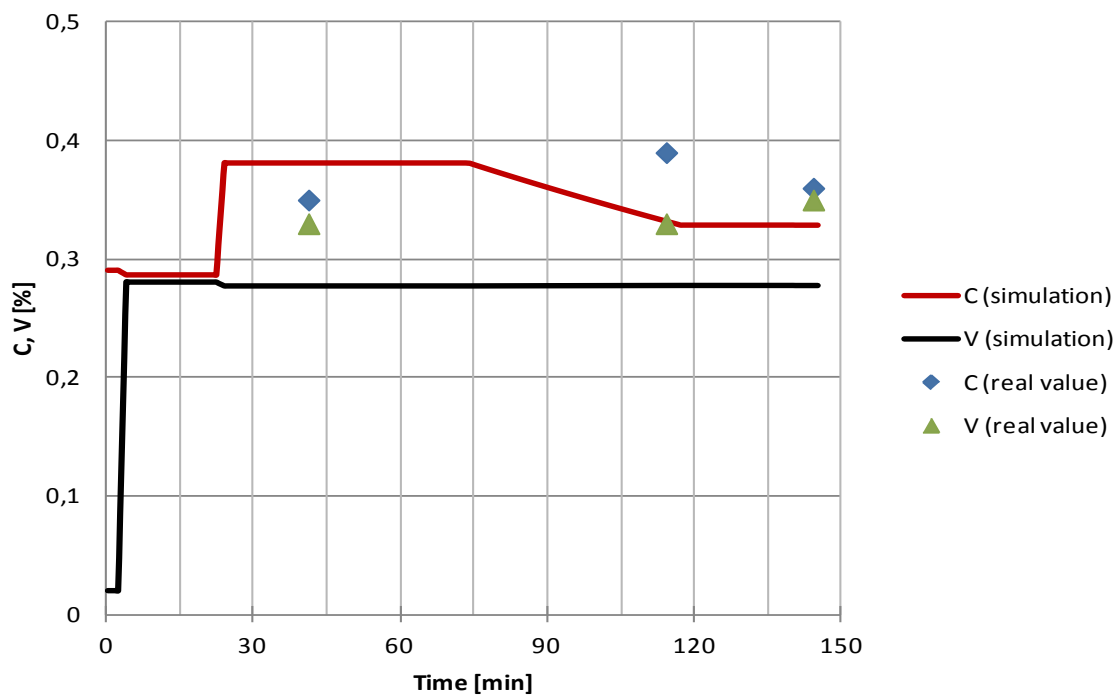Fig 3a. Course of changes Si, Cr, Mo in the chemical composition of the metal bath

Fig 3b. Course of changes C and V in the chemical composition of the metal bath
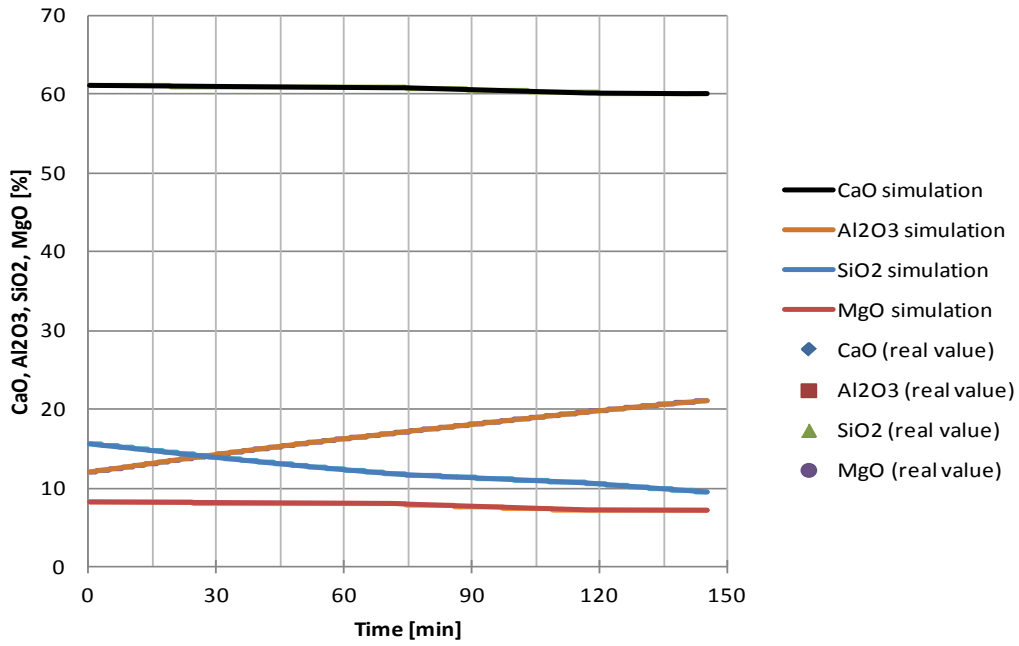
Fig 4. Course of changes in the chemical composition of slag

5. Impact of vacuum on changes in the chemical composition of refining slag

The attempt to assess the impact of vacuum refining on changes in the chemical composition of the slag phase was made using data from the real process. The impact of vacuum on MgO and SiO_2 contents, alkalinity and the Mannesmann's coefficient was evaluated. In each analysed case, two vacuum degrees, i.e. 0.001 and 0.01 bar, were assumed for calculations.

The slag composition change was analysed both for the stage of refining under atmospheric pressure and of refining in a vacuum. Fig. 5 shows changes in the MgO content of slag for various initial quantities of this oxide and two vacuum degrees. Similarly, Fig. 6 shows the same relationships for SiO_2.
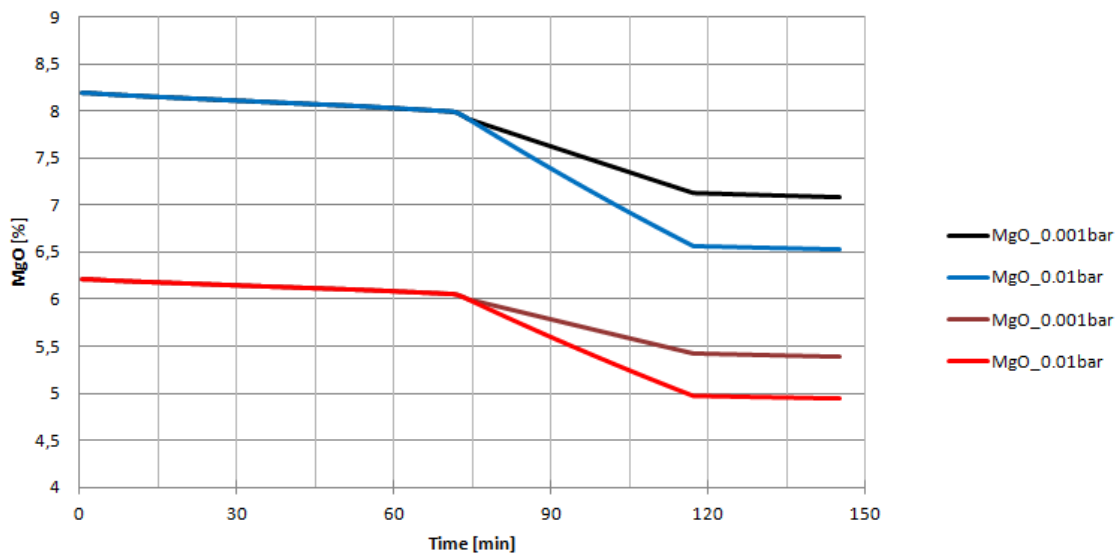

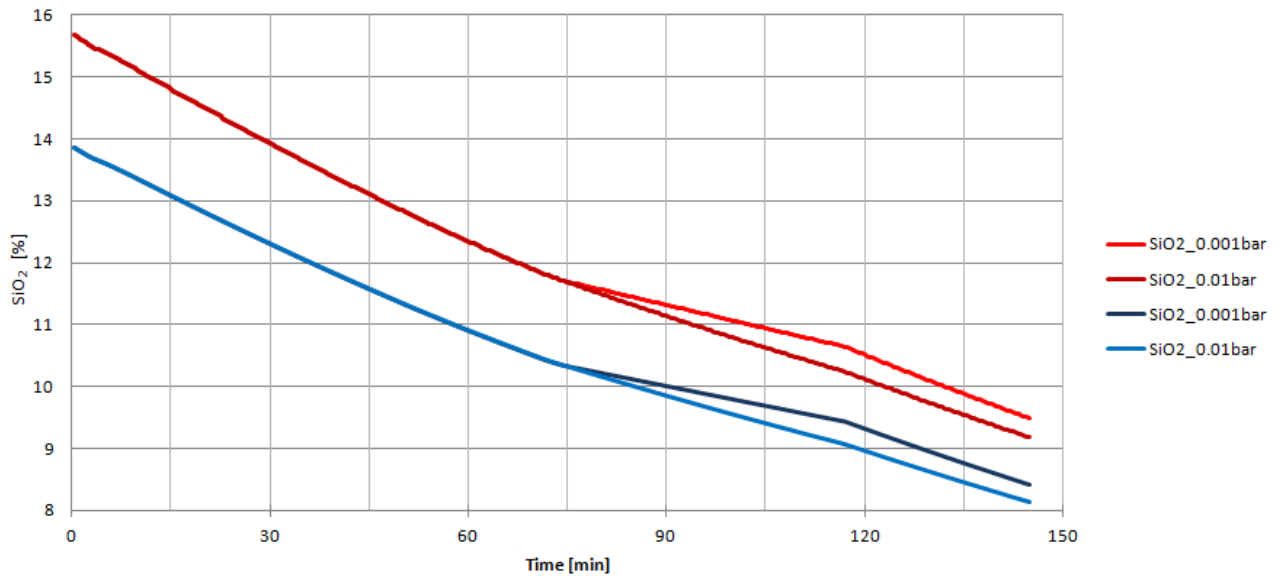Fig. 5 Changes in the MgO content of slag for various initial quantities of this oxide and two vacuum degrees

Fig 6. Changes in the SiO_2 content of slag for various initial quantities of this oxide and two vacuum degrees

The simulation carried out also allows generating the relationship between another two parameters – basicity and so called Mannesmann's coefficient - as a function of time for vacuum refining. It is calculated using the following formula:

$$W_M = \frac{\%\,CaO}{\%\,SiO_2} \bigg/ \%\,Al_2O_3 \qquad (5)$$

Its value should stay within the range of $0,3 \pm 0,4$.

The impact of vacuum on the change in the W_M (Mannesmann's coefficient) is shown in Figure 7.
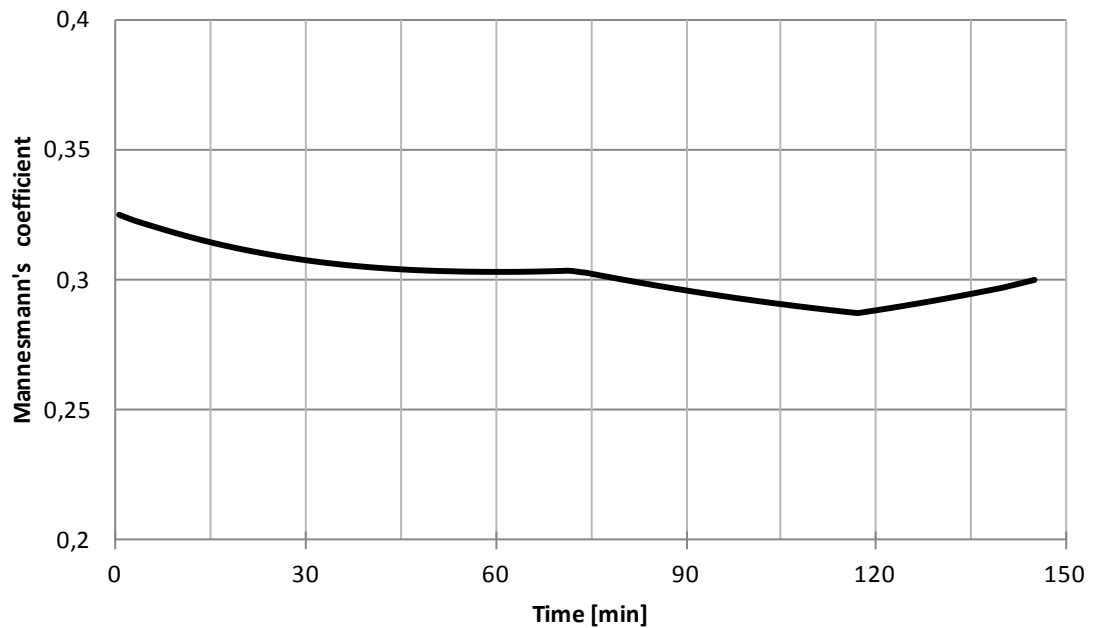

Fig 7. Mannesmann's coefficient

Fulfilling the condition (5) confirms the fact, that the chemical composition of refining slag changes in the selected area in the Figure 8.
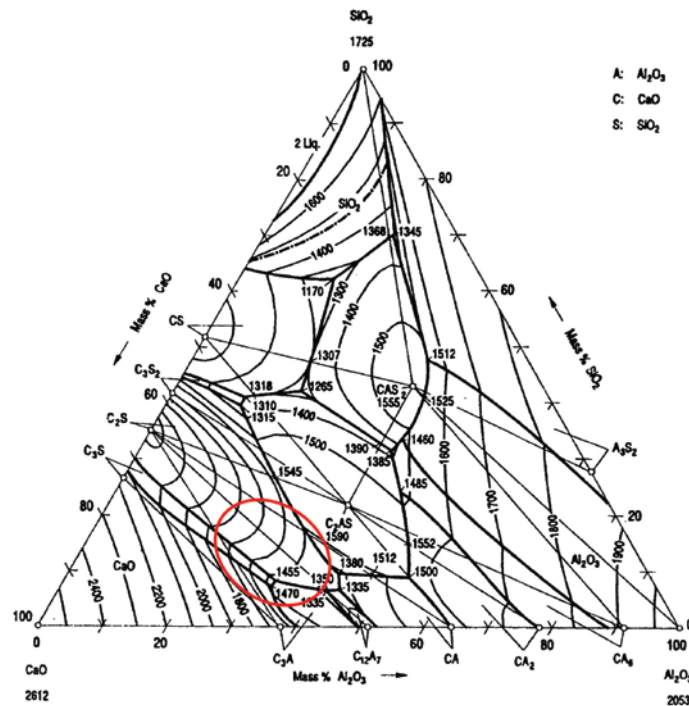

Fig 8. Phase diagram CaO- Al_2O_3- SiO_2

6. **Discussion**

As expected, vacuum steel refining in a ladle also impacts the slag phase, causing its chemical composition to change. Although this impact is not decisive for the course of the steel degassing process, it causes a new metal/slag equilibrium state to be achieved. A very important issue in calculations is to account for the fact that solids precipitate in slag. For obvious reasons the mixing model accounts only for liquid phases. The thermodynamic model, in turn, allows all phases present in the system to be calculated. From the formal perspective, the problem described is numerical in nature. Not accounting for precipitates would cause errors to be generated in the melt mass balance.

We propose solving this problem in the model using a simplified declaration of permissible products of chemical reactions. The error resulting from this is many times smaller than the error caused by ignoring precipitates. In this case, the alternative solution consisting in feeding information about the mass of all component coming from the precipitates into the module calculating the chemical balance would not be efficient. The number of precipitates that can potentially form in slags of alloy steels is very high, so an attempt to develop a universal tool would lengthen the computing time too much. At present, the model computation time averages 25% of the duration of the real process.

The quality of the projection from the proposed model depends on the reliability of input information, such as:
- The initial chemical composition and the mass of slag;
- The initial chemical composition and the mass of the metal bath;

- The control of the argon flow intensity;

- The mass of additives and the time of adding them.

The model correctly projects the MgO and SiO_2 losses as well as the course of changes in the content of Al_2O_3 and CaO. Projections of the chemical composition of the metallic phase are also accurate.

7. Conclusions

The proposed model represents a universal tool allowing ladle processes, whether carried out in a vacuum or under atmospheric pressure, to be simulated. The structure of the model allows it to be validated for very different varieties of the process. The main advantages of the proposed solution include:

1. The model computation time is significantly shorter than the real process time;

2. The model allows accounting for the dynamic change of parameters of the process conducted (pressure, temperature, argon flow intensity);

3. Vacuum refining can significantly impact the final, equilibrium chemical composition of slag;

4. MgO i SiO_2 are the slag constituents most sensitive to loss during vacuum refining. The change in the percentage contents of the remaining components is due to changes in proportions caused by the aforementioned loss and the Al_2O_3 inclusions flowing out.

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