

A NUMERICAL ANALYSIS AS A TOOL FOR A PREDICTION OF FINAL SULPHUR STEEL LADLE CONTENT

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Abstract

This work presents the industrial results of sulfur level prediction at the end of vacuum degassing (VD) of low carbon Al-Si killed steels. The effect of plant conditions, such as slag chemistry, temperature, oxygen levels of the molten steel, and slag weight on desulphurization was investigated based on the measured results and thermodynamic calculations. The variables which influence steel desulfurization such as the sulfur capacity, the initial sulfur content, and the amount of ladle slag at the end of the VD process are also defined. The desulfurization procedure was numerically analyzed using the results of 31 heats under real plant conditions in which the measured final sulfur content had been reduced to less than of 10 ppm. A method for prediction of the slag amount based on the material balance of sulfur and aluminum is also presented.

The values of the sulfur capacity were determined according to the well-known KTH and optical basicity based models. The obtained results of the regression equation show a predictive final sulfur level ability of $R=0.911$. This was proved as satisfactory.

Key words: numerical analysis, sulphur prediction, VD degassing, Al-Si killed steels, sulphide capacity

Introduction

Sulfur is an impurity which has a deleterious effect on the steel quality because it has tendency to form sulfides and initiate fatigue cracks [1-2]. Based on this fact, the requirement of improved desulphurization is led to many innovations in steelmaking [3]. The steelmaking technology has always been focused on the removal of sulfur from metal to slag during the steelmaking operation to the lowest possible level. With rising demand for high quality 'clean steel' modern steelmaking technology has been faced with the requirement to produce steel with the fewest ppm of sulfur possible.

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Since the conditions in the primary steelmaking vessels are not favorable for removal of sulfur to the highly oxidized slag, deep desulfurization is carried out after tapping steel into the ladle. Many studies [4-8] of the equilibrium of desulfurization reactions during the last five decades have enabled the development a number of the ladle procedures for tuning and control of the deep steel desulfurization.

Therefore, it becomes an important problem during the refining process of how to decrease the sulphur content. On the other hand, the prediction of final sulfur content can be accompanied with effort to save energy and therefore leading to substantial cost reduction. At present there are many models for sulfur content prediction [3, 9-10]. However, a serious problem is that mechanism models needs to determine many parameters and most of the parameters are difficult to obtain.

This work is an attempt to predict the final sulfur content at the end of the steel refining process in the ladle using some parameters which are very difficult to obtain under real plant conditions. To solve this problem in this study, as an auxiliary tool a numerical analysis, will be used.

Experimental procedure

Steel-desulphurisation

In this study, the results of numerical analysis of the 31 heats in real plant conditions of BOF low carbon Al-Si structural steel in 200 t steel ladles are presented. After BOF tapping, the metal from all heats was directed to VD degassing. During the VD steel treatment, samples of steel and slag were taken namely in the following technological steps: in the ladle after 2 minutes of argon bubbling and at the end of vacuum treatment. The temperature of the steel was measured for each sample that was taken. Afterwards, all the samples of steel were subjected to an analysis, which concerned the content of sulfur.

The schematic diagram of the experimental procedure is presented in Figure 1.

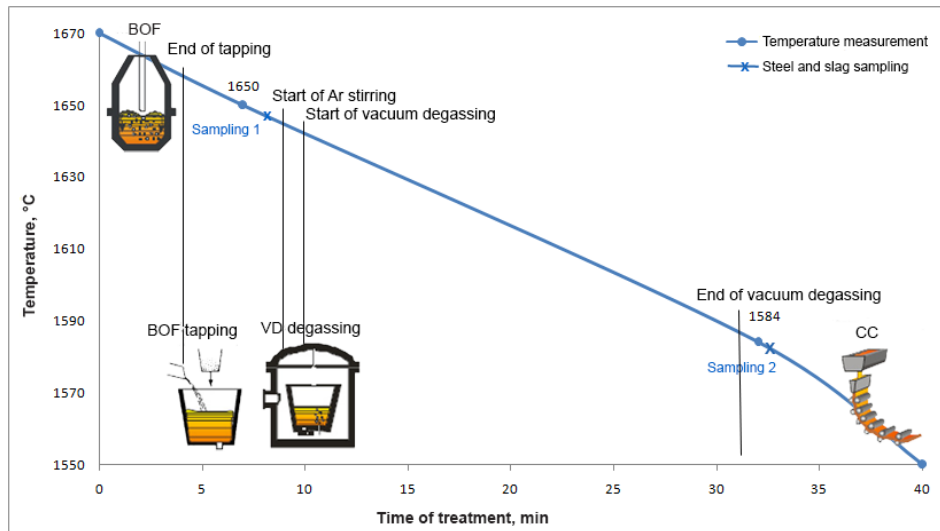


Fig.1. Schematic diagram of the experimental procedure

The samples of slag were subjected to the chemical analysis of the basic elements and oxides. Finally, the steel is cast on the radial casting machines. Due to the fact that the oxygen analyses of the steel samples were not available, a logical method to estimate the oxygen levels in the steel bath was used to estimate the activities of Al_2O_3 and SiO_2 in the slag by thermodynamic calculations from the contents obtained by sampling and chemical analysis. These were then used to estimate the oxygen potential in the steel bath, assuming slag-metal equilibrium.

All additions in the ladle are presented in Table 1, while Tables 2 and 3 show the range of steel and slag composition for the 31 analyzed heats.

Table 1. Additions during tapping, argon stirring and vacuum degassing

Heats	Weight of steel, [t]	At tapping			Vacuum Process				
		Lime, [kg]	Al, [kg]	Dolo-Lime, [kg]	Lime, [kg]	Fireclay, [kg]	Ca-Aluminate, [kg]	Sand, [kg]	Al, [kg]
1	183.9	1020	348	499		60			111
2	189.5	1010	242		299		300		0
3	182.3	1300	267				49		178
4	194.4	1180	403	501					122
5	190.4	1040	326	499	700				309
6	178.2	1010	331	501	252	80			179
7	188.9	980	364	499	150	99			47
8	189.4	1130	389	499	199				173
9	183.9	1000	310	500	300			120	182
10	190.7	1030	293	500	150				141
11	178.7	1030	308	498	497	259		59	202
12	180.4	1010	342	499	397	150			251
13	183.3	970	484	500					72
14	181.7	1200	437	502	100	111			50
15	188.2	1500	364				50		185
16	178.9	1000	349	500		120			109
17	177.5	1020	367	499					201
18	184.8	1160	394	499		69			149
19	181.1	980	479	501		120			132
20	182.6	1320	367				301		80
21	191	1250	452				140		0
22	193.5	1320	339				120		110
23	185.8	1140	367	499	151	61			197
24	193.7	1310	325				150		26

25	185.6	1330	383				130		64
26	188.3	1250	303				138		38
27	175.4	1210	315	498					279
28	181.4	1310	366		150		79		149
29	178.2	1000	356	500	100				169
30	197.1	1270	232				179		129
31	182.5	1040	339	501					139

Table 2. Steel composition, [wt.%]

Composition	%C	%Si	%Mn	%S	%Al	T, [°C]
Minimum	0.03	0.00	1.28	0.0002	0.011	1555
Maximum	0.19	0.47	1.61	0.0010	0.075	1611
Average	0.11	0.32	1.50	0.0006	0.034	1584

Table 3. Slag composition, [wt.%]

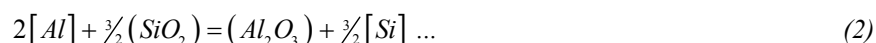
Composition	%CaO	%SiO ₂	%Fe _{tot.}	%MnO	%S	%Al ₂ O ₃	%MgO
Minimum	53.91	4.15	0.12	0.31	0.19	11.31	1.85
Maximum	61.73	13.86	11.84	7.34	0.64	27.69	12.09
Average	58.06	7.95	1.89	1.79	0.36	19.69	6.98

Table 4. Available methods for calculating the parameters used in the sulfur prediction at the end of ladle treatment

Parameters	Formulas	References
Sulphide capacity	Optical basicity-based models	[11-14]
	KTH-models	[15]
Oxygen activity, [a _o]	Ohta-Suito method/Andersson's method/	[16-17]
Activity coefficient of S-f _S , Si-f _{Si} , Al-f _{Al}	Wagner's model	[18]
Initial sulphur content, [%S] _i		[19]
Amount of final slag SLAG ₂		[19]

Activity of oxygen in the slag and steel

It is well known that a control of the desulphurization process is impossible if the oxygen activity is not known. As mentioned earlier, the oxygen activity in steel [a_o] at the end of the VD treatment was not measured. In order to calculate the oxygen activity in the steel the following equations were used:



$$\Delta G_{Al}^0 = -1205115 + 386.7T \dots \quad (3)$$

$$\Delta G_{Al-Si}^0 = -329300 + 53.6T \dots \quad (4)$$

The equilibrium constant of equations (3) and (4) is given by

$$K_{Al} = \exp \frac{-\Delta G_{Al}^0}{RT} = \frac{a_{(Al_2O_3)}}{[a_0]^3 \cdot [a_{Al}]^2} \dots \quad (5)$$

$$K_{Al-Si} = \exp \frac{-\Delta G_{Al-Si}^0}{RT} = \frac{a_{(Al_2O_3)} \cdot [a_{Si}]^{3/2}}{a_{(SiO_2)}^{3/2} [a_{Al}]^2} \quad (6)$$

The oxygen activity in the steel bath $[a_o]$ was calculated by assuming that one of the reactions (1) or (2) was in equilibrium. The detailed process of calculation is presented in earlier published papers [20, 21].

From Equations (5) and (6) of equilibrium constants, it was possible to derive an expression for the oxygen activity.

$$[a_0] = \sqrt[3]{\frac{a_{(Al_2O_3)}}{[a_{Al}]^2 \cdot e^{\frac{-\Delta G^0}{RT}}}} \dots \quad (7)$$

Numerical Analysis Description and Formulation

Numerical analysis was carried out based on the variables which influence on the steel desulfurization such as the sulfur capacity, the initial sulfur content, which have influence, and the amount of ladle slag. The reason for using the numerical analysis is the following:

- The moment when the process of the desulfurization began was unknown. This is because the steel and the slag samples were not taken after the end of the tapping from the BOF converter, but after 2 minutes of argon bubbling in the ladle
- The amount of the slag in the ladle at the end of the vacuum degassing was also unknown

For successful analysis, in conditions when all input data is not available, it is necessary to take in to account an acceptable reliable tool in order to simulate the aforementioned lack of data. Because of this, the mass balance calculations of individual elements are a possible way for their roughly determination.

For this purpose, it was necessary to define the following assumptions and simplifications.

- Estimated content of sulfur and aluminum in all additions in the ladle during tapping from the BOF furnace and the VD vacuum degassing

- Estimated weight of BOF slag carried into the ladle $SLAG_{LD}$ (500 kg), slag coming from ladle glaze and refractory wear during tapping of steel into the ladle $SLAG_{(-1)}$ (500 kg) and the amount of the slag in the beginning $SLAG_1$ and at the end of VD vacuum degassing $SLAG_2$.
- Estimated weight of sulfur content: 0.15% in $SLAG_{LD}$ and 1% in $SLAG_{(-1)}$
- Weights of all mentioned slag can be estimated by the writing of mass balance equations for alumina
- Calculation of the initial sulfur content in the steel and the slag: $[\%S]_i$, $(\%S)_i$ can be estimated by the aluminum and the sulfur balance equation;

Presented in Table 5 and Figure 2 are the steps for prediction of final sulfur content at the end of the VD vacuum degassing refining.

Table 5. Schematic review of the model

The first step	Estimated quantity of slag in the ladle: $SLAG_{LD}$, $SLAG_{(-1)}$, $SLAG_1$, $SLAG_2$;
The second step	Calculation of the initial sulfur content in the steel and the slag: $[\%S]_i$, $(\%S)_i$;
The third step	Estimated values of final sulfur level after ladle treatment $[\%S]_2$

Determination of the ladle slag weight

In the first step the estimation quantity of the slag will be calculated based on input data presented in Table 1. However, neither the slag composition nor the slag amount can be completely calculated from the well-defined slag forming admixtures given in Table 1. Some converter slag carried over into the ladle during the slag cutting operation at the end of tapping, designated as $SLAG_{LD}$, and a fraction of the ladle slag from the preceding heat adhered to the ladle refractory lining, during the emptying of the ladle slag to the slag pot, designated as $SLAG_{(-1)}$, are undesirable but inevitable ladle slag forming components. Unfortunately, the amount of $SLAG_{LD}$ and $SLAG_{(-1)}$ cannot be directly measured and therefore they should be estimated or assumed. According to extensive plant experience and long-term averages the amount of these two mentioned slags are estimated to be 500 kg each.

In such a way the amounts of desulphurizing $SLAG_1$ and $SLAG_2$ are obtained by summing up all slag forming additions from Table 1 and adding to it 1000 kg as a quantity of $SLAG_{LD}$ and $SLAG_{(-1)}$, combined. The data on the amounts of $SLAG_1$ and $SLAG_2$ given in Table 6 is assessed in this way and as such will be used in further considerations.

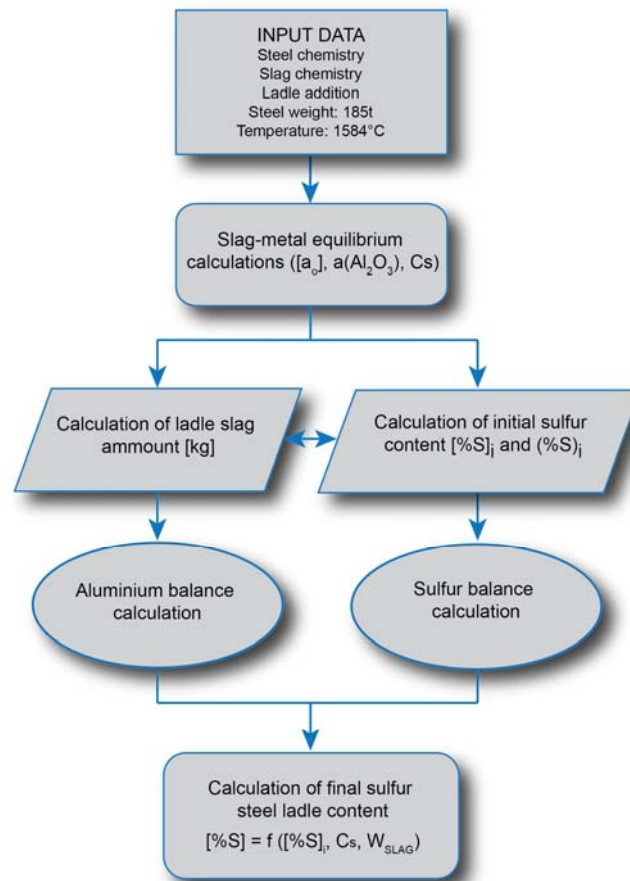


Fig.2. The flow chart for calculating of the final sulfur steel ladle content

On the other hand the assumed same amounts of $SLAG_{LD}$ and $SLAG_{(-1)}$ and of a uniform concentration of sulfur being 0.15%S in $SLAG_{LD}$ and 1%S in $SLAG_{(-1)}$ are first approximations that make these parameters a constant of the same value for each heat. This might not appreciably affect long-term statistical averages, but unnecessarily raises a discrepancy between the estimated and the real quantity of $SLAG_{LD}$ and $SLAG_{(-1)}$ on which the numerical modeling should be based and consequently adversely affects its prediction potential.

This is a strong reason why it is necessary to try to approximate the amounts of these two ladle slag components by a more detailed method that may enable specifying the amount of $SLAG_{(-1)}$ and $SLAG_{LD}$ for every heat. Based on the above assumptions, the following equations were applied to conduct the simulation. In the work [19] is presented the all mentioned steps of calculation in details.

Alumina Balance

The formula of alumina balance for ladle slag is:

$$\sum_{i=1}^n W_{Admn.}^{(i)} \cdot F_{(Al_2O_3)}^{(i)} = W_{SLAG}^{Output} \cdot \frac{(\% Al_2O_3)_{SLAG}^m}{100} \quad (11)$$

where

W is the amount of slag in kg

$F_{(Al_2O_3)}$ is the conversion factor to calculate the amount of Al_2O_3 in kg for each addition.

The left input side of the balance formula can be written taking into account all (Al_2O_3) containing ladle slag forming components as:

$$\sum_{i=4}^n W_{Admn.} \cdot F_{(Al_2O_3)} =$$

$$W_{[Al] \rightarrow (\% Al_2O_3)} \cdot \frac{102}{54} + W_{CaAl_2O_7} \cdot \frac{204}{260} + W_{Fireclay} \cdot 0,4 + W_{SLAG(-1)} \cdot \frac{(\% Al_2O_3)}{100} \quad (12)$$

where on the right side conversion factors for the first two terms are stoichiometric ratios, and for the second two the mass contents of alumina in each. The right output side of the alumina balance equation (11) becomes:

$$W_{SLAG}^{Output} \cdot \frac{(\% Al_2O_3)_{SLAG}^{Output}}{100} = W_{SLAG2} \cdot \frac{(\% Al_2O_3)_{SLAG2}^m}{100} \quad (13)$$

Determination of the initial sulfur content in steel and slag

A consistent sulphur balance is of prime importance for the interpretation of desulphurization results, and for providing reliable data on which a numerical analysis of desulphurization procedure could be based. For making a correct sulphur balance the condition

$$[\%S] + (\%S) + \{\%S\} = "S" = const \quad (14)$$

in any moment of desulphurization should be fulfilled. However, in the desulphurization procedure considered here, because of a short operation time, a transfer of sulphur to the gas phase may be neglected. Thus the condition (14) reduces to

$$[\%S] + (\%S) = "S" = const \dots \quad (15)$$

and consequently the sulphur balance equation for desulphurization between any initial and final state becomes

$$[\%S]_i + (\%S)_i = [\%S]_f + (\%S)_f = const \dots \quad (16)$$

The lacking initial sulfur content, $[\%S]_i$ can be simply calculated from the balance equation (16) by introducing $[\%S]_2$ and $(\%S)_2$ to the output side and $[\%S]_{LD} + (\%S)_{LD} = (\%S)_i$ to the input side of the (16). Then the lacking is estimated as

$$[\%S]_i = [\%S]_2 + (\%S)_2 - (\%S)_i \dots \quad (17)$$

where

$$(\%S)_i = (\%S)_{SLAG(-1)} + (\%S)_{LD} + \sum (\%S)_{LDAddn} \dots \quad (18)$$

$$\sum (\%S)_{LDAddn} = (W_{Lime} + W_{Dolo-Lime}) \cdot \frac{0,03}{100} \dots \quad (19)$$

Both sets of the initial data, where evaluated in this way, $[\%S]_i$ and $(\%S)_i$ are referred to an assumed starting point which could practically only exist if during tapping any deoxidizing or slag forming addition would not have been added into the ladle and/or into the steel stream. Since it was not the case their reliability should be somehow proved. The straightforward way to do it is to compare their values with those of $[\%S]_1$ and $(\%S)_1$ for the same heat.

The values $[\%S]_i$ and $(\%S)_i$ being related to an assumed point in which the desulphurization could begin, and that are derived from the final sulphur contents, $[\%S]_2$ and $(\%S)_2$, while the $[\%S]_1$ and $(\%S)_1$ relate to the state of desulphurization process after the intensive argon stirring during which some transfer of sulphur from the steel to the slag has certainly occurred. The $[\%S]_i$ should be higher than $[\%S]_1$.

Results and Discussion

Prediction of sulfur content in the steel

Multiple regression equations, with $[\%S]_2^{calc.}$ as the dependent variable and earlier mentioned parameters determined as independent variables, will now be used for the prediction of the final sulfur content in the steel at the end of VD treatment in the ladle according to applied numerical analysis.

$$[\%S]_2^{calc.} = 0,000893 - 0,01801C_s + 0,02744[\%S]_i - 0,000018SLAG_2 \dots \quad (20)$$

n=31 heats R=0,911

The scatter diagrams present for the regression equation (20) in Figure 3. It is evident that most of the values lay above or on the regression curve. Some discrepancies are a result of a relatively small number of analysed heats.

For analysed heats, Table 6 shows the results of calculated values of slag amounts before ($SLAG_1$) and after ($SLAG_2$) ladle refining, initial sulphur content $[\%S]_i$ e.g. the moment when the process of desulphurisation begins and the predicted values of final sulphur content $[\%S]_2$ in comparison to the measured values of sulphur content after 2 minutes of argon bubbling in the ladle $[\%S]_1^m$ and the measured values of the final sulphur content at the end of vacuum degassing $[\%S]_2^m$.

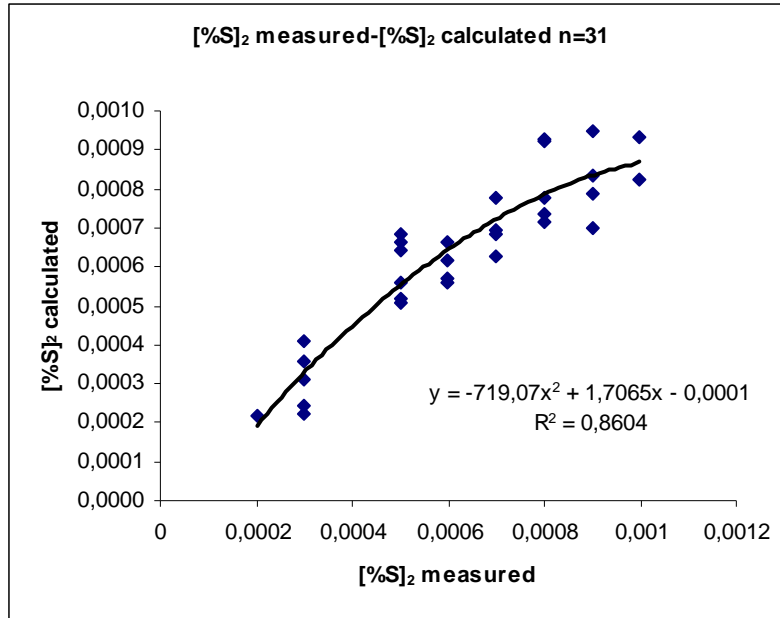


Fig.3. Comparison of calculated [%S]₂ and measured [%S]₂ in [wt.%]

As can be seen in Table 6, in 27 heats [%S]_i is higher than [%S]₁ and only in 4 heats was recorded as lower. In view of the smaller differences between [%S]_i and [%S]₁ values, and allowing for the possible already mentioned wide scatter of [%S]₁, the great majority of heats with [%S]_i > [%S]₁ makes [%S]_i acceptable as a starting point of desulphurization in further considerations.

Table 6: The comparison of calculated values of *SLAG*₁, *SLAG*₂, initial sulphur content [%S]_i and final sulphur content [%S]^c₂ and measured sulfur content [%S]^m₁ and [%S]^m₂

Heats	Slag ₁ [kg]	Slag ₂ [kg]	[%S] _i	[%S] ^m ₁	[%S] ^m ₂	[%S] ^c ₂
1	2880.9	3362.7	0,00870	0.0076	0,0002	0.00023
2	2377.6	3026.6	0,01125	0.0123	0,0003	0.00025
3	2625.5	3062.1	0,00800	0.0091	0,0003	0.00034
4	3185.1	3551.6	0,00690	0.0060	0,0003	0.00031
5	2928.1	4305.3	0,00820	0.0072	0,0003	0.00041
6	2947.5	3745.7	0,00470	0.0047	0,0003	0.00021
7	2792.0	3324.0	0,01500	0.0106	0,0005	0.00069
8	3063.3	3767.0	0,01710	0.0125	0,0005	0.00066
9	2852.8	3793.6	0,01260	0.0107	0,0005	0.00050
10	2845.6	3406.3	0,00970	0.0090	0,0005	0.00064
11	2819.6	4205.1	0,01120	0.0099	0,0005	0.00056
12	2967.6	4114.7	0,00950	0.0076	0,0005	0.00051
13	2916.7	3302.1	0,01520	0.0110	0,0006	0.00058

14	3173.8	3723.0	0,01320	0.0095	0,0006	0.00066
15	2956.4	3462.5	0,01100	0.0103	0,0006	0.00060
16	2888.7	3441.1	0,00790	0.0088	0,0006	0.00055
17	3016.5	3495.6	0,02140	0.0182	0,0007	0.00077
18	3096.1	3655.8	0,01940	0.0141	0,0007	0.00062
19	2930.7	3529.4	0,01770	0.0115	0,0007	0.00070
20	2723.5	3313.7	0,01050	0.0104	0,0007	0.00068
21	2652.7	3070.4	0,02300	0.0160	0,0008	0.00092
22	2697.2	3149.1	0,01870	0.0143	0,0008	0.00093
23	3086.5	3807.7	0,01970	0.0130	0,0008	0.00077
24	2631.3	2962.6	0,01250	0.0133	0,0008	0.00073
25	2720.6	3167.2	0,01245	0.0101	0,0008	0.00071
26	2534.3	2900.6	0,02050	0.0162	0,0009	0.00094
27	3167.2	3753.9	0,02090	0.0142	0,0009	0.00078
28	2655.5	3254.7	0,01660	0.0153	0,0009	0.00083
29	2963.9	3473.8	0,01290	0.0065	0,0009	0.00069
30	2559.2	2972.9	0,02200	0.0184	0,001	0.00093
31	2881.6	3371.4	0,01820	0.0168	0,001	0.00081

Conclusions

Steelmaking desulfurization during ladle refining is a complex and nonlinear process and because of this the prediction of the final sulfur content in the steel is difficult to measure on-line. In order to predict the final sulfur content accurately, a numerical analysis could be a good tool. Simulation results show that the numerical analysis can help in the prediction of final sulfur content in the ladle after VD degassing. The accuracy of the suggested regression equation is acceptable for steelmaking plant conditions and it can provide effective guidance for the final sulphur content prediction. The results could be useful in making further modifications of derived regression equation by updating with a higher number of heats.

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