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MODELLING OF THE SULPHIDE CAPACITY OF STEELMAKING SLAGS

MODELIRANJE SULFIDNE KAPACITETE JEKLARSKIH ŽLINDER

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In this paper the influence of the CaF_2 amount in steelmaking slags on the CaO and Al_2O_3 activities is presented. The new analytical model (RMJ) for determining the sulphide capacity was derived. The aim of this model is to adjust and correct some models, according to Tsao, Daffy and Young, that had limitations regarding the presence of CaF_2 in the slag. Using the RMJ model, the effect of CaF_2 on the sulphide capacity and desulphurisation degree is more precisely defined. Calcium fluoride decreases the negative effect of Al_2O_3 on the sulphide capacity. For an investigation under production conditions, several types of carbon and low-alloy steels were chosen. The steels used for the analysis of specified process parameters were produced using a mixture of CaF_2-CaO and CaO-CaF_2-white bauxite (WB) as the flux. For specified cases, the results obtained with the RMJ model as well as with the Young model, were presented. The RMJ model defines correction factors $k_{1(CaF2)}$ and $k_{2(CaF2)}$. It can be seen that the certainty factor of linear dependence is a bit larger in the case of the RMJ model than the one obtained with the Young model.

Keywords: calcium fluoride, sulphide capacity, RMJ model

V tem članku je predstavljen vpliv vsebnosti CaF_2 v jeklarskih žlindrah na aktivnost CaO in Al_2O_3. Izpeljan je bil nov analitični model (RMJ) za določanje sulfidne kapacitete. Namen modela je prilagoditev in poprava modelov po Tsaoju, Daffyju in Youngu, ki imajo omejitve glede prisotnosti CaF_2 v žlindri. Z uporabo modela RMJ je mogoče bolj natančno opredeliti vpliv CaF_2 na sulfidno kapaciteto in stopnjo razžvepljanja. Kalcijev fluorid zmanjša negativni vpliv Al_2O_3 na sulfidno kapaciteto. Več vrst ogljikovih in malo legiranih jekel je bilo izbranih za industrijski preizkus. Jekla, izbrana za analizo specifičnih procesnih parametrov, so bila izdelana z uporabo mešanice CaF_2-CaO in CaO-CaF_2-beli boksit (WB) kot talilo. Za določene primere so predstavljeni rezultati RMJ-modela, kot tudi Youngovega modela. RMJ-model določa korekcijske faktorje $k_{1(CaF2)}$ in $k_{2(CaF2)}$. Opazi se, da je faktor zanesljivosti linearne odvisnosti nekoliko večji pri RMJ-modelu v primerjavi z dobljenim pri Youngovem modelu.

Ključne besede: kalcijev fluorid, sulfidna kapaciteta, RMJ-model

1 INTRODUCTION

Synthetic-slag practice is employed to obtain clean steels and to desulphurize molten steel (50–60 % of the original sulphur). These slags contain CaO, CaF_2, Al_2O_3 and a small amount of SiO_2. Besides, slag contains insoluble particles (CaO, MgO) and a chemical analysis of the slag gives unrealistic results for the slag basicity. In this case, the calculated basicity is significantly higher than the basicity of fully liquid slags. An important parameter to characterize synthetic slag with respect to its suitability to desulphurize molten steel is the sulphide capacity. On the basis of the ionic theory, the sulphide capacity and sulphur activity must be correlated with the optical basicity because the standard calculation methods neglect the influence of many oxides, except for CaO, MgO and SiO_2.[1] The model by Tsao[2] has been used for defining the chemical-composition influence on the sulphide capacity:

$$\lg C_S = 3.44(X_{CaO} + 0.1X_{MgO} - 0.8X_{Al_2O_3} - X_{SiO_2}) - \\ -\frac{9894}{T} + 2.05 \quad (1)$$

where: X_i is the molar fraction of oxide *i*, *T* is the slag temperature in K.

However, the above correlation is not applicable to the metallurgical slags containing CaF_2 because the effect of CaF_2 must be substituted with an oxide. On the basis of the optical-basicity index, the following correlation was suggested by Gaye[3]:

$$\lg C_S = \frac{B}{D} + 1.445 - \frac{12364}{T} \quad (2)$$

where: *B* = 5.62 (% CaO) + 4.15 (% MgO) – 1.15 (% SiO_2) + 1.46 (% Al_2O_3), *D* = (% CaO) + 1.39 (% MgO) + 1.87 (% SiO_2) + 1.65 (% Al_2O_3).

In this case the amount of CaF_2 is assumed to be part of the CaO amount. Since aluminum was used for steel deoxidation, the activity of Al_2O_3 and the Al amount are considered while calculating the sulphur-distribution coefficient[4]:

$$\lg L_S = \lg C_S - \frac{1}{3}\lg(a_{Al_2O_3}) + \frac{2}{3}(\%Al) + \frac{20397}{T} - 5.482 \quad (3)$$

In the secondary-metallurgy processes Si was used as a deoxidizer. Therefore, the formation of a stable SiO_2, its interaction with the other oxides and its influence on the sulphide capacity should not be neglected. This correlation can be empirically defined with the Young expression[5]:

$$\lg C_S = -13.913 + 48.84\Lambda - 23.82\Lambda^2 - \left(\frac{11710}{T}\right) - \\ -0.02223(\%SiO_2) - 0.02275(\%Al_2O_3) \quad (4)$$

where Λ is the theoretical optical basicity of the slag calculated with the Nakamura method[6]. An experimental analysis of EAF steelmaking slags shows that this model can be used as the basis for further consideration. Young et al.[5] showed that equation (4) can be applied only to the range of $\Lambda < 0.8$, i.e., to the slags examined in the experimental part of this research. Larger values of the CaF_2 amount cause high values of C_s and L_s. In this way, it is possible to obtain a value of L_s that is higher than 1000, and the literature reports show that such large values are indeed obtained in industrial practices[7].

The main aim of this paper is to derive a new model (RMJ) that will more precisely define the impact of CaF_2 on the sulphide capacity of steelmaking slags.

2 EXPERIMENTAL WORK

The first stage of the experimental investigations is a chemical analysis of the slag samples. The chemical compositions of the investigated slags for the two slag mixtures are given in **Table 1**. The steels are produced in a EAF 60 t, while Si and Al are used as deoxidizers. The slag and metal were manually sampled by the EAF operator at the temperature of ≈1570 °C, after a vacuum treatment of the steel, 10–12 min before casting. The mixture for the synthetic slag contains CaO, CaF_2 and white bauxite in the mass ratio of 3 : 1 : 2, with the ratio of 3 : 1 for the CaO-CaF_2 mixture.

For degassing the steel, a vacuum treatment and stirring with argon purging from the ladle bottom are used.

The aim of using a triple slag mixture is to investigate the impact of CaF_2 in the case of an increased presence of Al_2O_3 in white bauxite.

3 RESULTS AND DISCUSSION

A presence of CaF_2 increases the CaO saturation in the slags. For example, at comparable CaO concentrations, activity $a_{(CaO)}$ in the CaO-CaF_2 slag is much higher than in the CaO-Al_2O_3 and CaO-SiO_2 systems. The slags in secondary steelmaking are basically unstable at high temperatures since two or more components in the slag react[8] and the composition changes continuously while the fluorides and oxides react as follows:

$$3CaF_2 + Al_2O_3 = 2AlF_3\,(g) + 3CaO \quad (5)$$

The slag composition shows a steady increase in the CaO concentration and a decrease in Al_2O_3, so that the part of expression (4) that is correlated with Al_2O_3 must be corrected with $k_{1(CaF2)}$. Besides, the effect of moisture when dealing with the slags containing CaF_2 is very important because of the following reaction:

$$CaF_2 + H_2O = CaO + 2HF(g) \quad (6)$$

In this case, CaF_2 increases together with the CaO activity. Therefore, the Young model (equation 4) must be adjusted with the correction factors, $k_{1(CaF2)}$ and $k_{2(CaF2)}$, defining the secondary influence of CaF_2 on C_s as follows:

$$\lg C_S = -13.913 + 48.84\Lambda - 23.82\Lambda^2 - \left(\frac{11710}{T}\right) - \\ -0.02223(\%SiO_2) - 0.02275(\%Al_2O_3)\cdot k_{1(CaF2)} + k_{2(CaF2)} \quad (7)$$

Figure 1 shows sulphide capacities in the CaO-CaF_2-Al_2O_3 ternary system at 1500 °C, as determined by Kor and Richardson[4].

Using the correlations shown in **Figure 1** for the chemical compositions of the investigated slags (**Table 1**), obtained with the regression-analysis method, the following expressions are obtained:

$$k_{1(CaF_2)} = -0.0001(\%CaF_2)^2 + 0.024(\%CaF_2) + 0.031 \quad (8)$$

$$k_{2(CaF_2)} = -0.0002(\%CaF_2)^2 + 0.015(\%CaF_2) + 0.015 \quad (9)$$

Table 1: Chemical compositions of the investigated slags after steel vacuuming (mass fractions, *w*/%)
Tabela 1: Kemijska sestava preiskovanih žlinder po obdelavi jekla v vakuumu (masni deleži, *w*/%)

Slag mixture	Steel (EN)	Amounts of components (*w*/%)								
		CaO	MnO	MgO	SiO_2	Al_2O_3	FeO	Fe_2O_3	CaF_2	S
CaO-CaF_2	1.6582	40.00	1.90	13.70	18.20	16.90	1.77	1.30	5.00	0.27
	1.2714	43.52	0.87	11.31	13.77	21.20	1.14	1.90	4.65	0.50
	1.1181	40.5	0.1	18.1	16.5	15.6	0.6	1.4	6.00	2.50
	1.7147	56.5	0.3	7.8	15.1	6.2	0.9	0.9	8.90	2.30
	1.0503	51.0	0.6	10.6	16.6	7.1	1.1	1.3	9.20	1.20
	1.7005	39.2	1.9	24.3	17.2	9.5	1.5	0.2	5.10	0.30
	1.1191	41.8	3.8	12.3	21.1	20.1	1.9	0.2	5.80	0.30
	1.7225	50.7	0.8	10.1	18.2	13.1	1.2	0.9	4.90	0.50
CaO-CaF_2-WB	1.6582	41.2	0.3	14.7	27.2	12.30	2.30	1.0	2.30	0.40
	1.7225	44.0	0.5	9.2	23.1	9.1	1.8	1.1	2.5	0.32
	1.1141	45.3	0.8	19.1	18.5	18.8	1.33	0.92	3.1	0.41
	1.7147	46.5	0.6	17.8	15.1	9.2	1.4	1.4	3.9	0.39
	1.0503	42.2	0.52	16.8	22.2	13.1	1.21	1.32	2.9	0.35
	1.2714	39.52	0.87	19.31	21.8	20.1	1.94	1.8	2.95	0.33

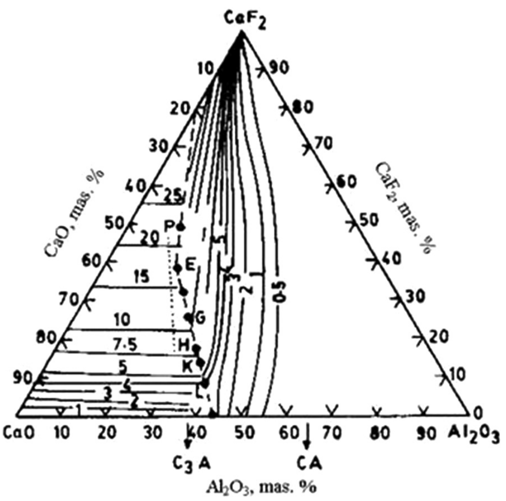

Figure 1: Sulphide capacity for the $CaO-CaF_2-Al_2O_3$ system at 1500 °C
Slika 1: Sulfidna kapaciteta sistema $CaO-CaF_2-Al_2O_3$ pri 1500 °C

Equation 8 shows that CaF_2 decreases the negative effect of Al_2O_3 on CaS and it is defined by $k_{1(CaF2)}$. With a calculation using equations 8 and 9, the effect of CaF_2 on C_s, for the constant amounts of Al_2O_3 and CaO, was examined. Therefore, equations 7, 8 and 9 provide the basis for deriving the RMJ model.

The procedure was repeated for different amounts of these components under the conditions of secondary metallurgy that are analyzed. The values of C_s were analyzed cumulatively so that the influence of Al_2O_3 and CaO was presented indirectly through CaF_2. Equations 8 and 9 show that the $k_{1(CaF2)}$ and $k_{2(CaF2)}$ values are always positive. This is in accordance with the fact that an increase in the CaF_2 amount increases the sulphide capacity. The primary effect of CaF_2 was defined on the basis of the optical-basicity values. However, the secondary effect of CaF_2 can be considered through a decrease in the slag viscosity and an increase in the CaO activity.

Based on the above-mentioned procedure, the $C_{s'}$ values, using the RMJ model (eq.7), and C_s, using the Young model (eq.4), were determined. On the basis of the chemical composition of the slag, optical basicity was calculated with the Nakamura method[4].

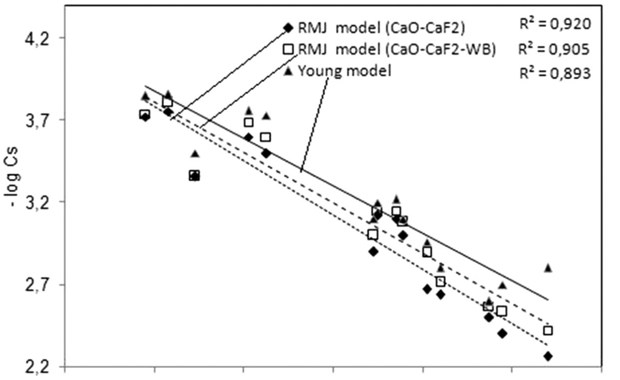

Figure 2: Sulphide capacity as the function of optical basicity
Slika 2: Sulfidna kapaciteta v odvisnosti od optične bazičnosti

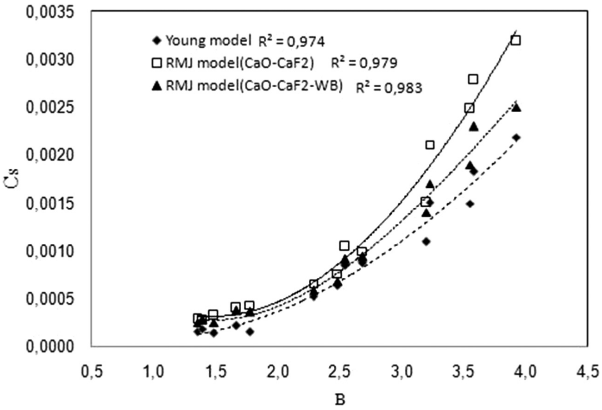

Figure 3: Influence of basicity on sulphide capacity
Slika 3: Vpliv bazičnosti na sulfidno kapaciteto

In all the considered cases, the compared values of $C_{s'}$ are higher than the C_s values. The relationship between the sulphide capacity and the optical basicity for the two above-mentioned models is shown in **Figure 2**.

It is likely that the C_s values increase with an increase in the optical basicity. This is the basis of the CaF_2 effect on the sulphide capacity and desulphurisation. All the values of the sulphide capacity calculated with the new RMJ model are higher than the ones calculated with the Young model. It was noticed that C_s increases faster with the increasing CaF_2 amount when the RMJ model is used because of its effect on $k_{1(CaF2)}$ and $k_{2(CaF2)}$. **Figure 3** shows the variation of C_s as the function of the slag basicity, indicating that the sulphide capacity increases with the increased B values.

For the slag with $B < 2$, the values of C_s obtained with the RMJ and Young models are approximately equal. This is a direct result of the small values of correction factors $k_{1(CaF2)}$ and $k_{2(CaF2)}$ in the RMJ model. In the later stages, for $B > 2$, its values significantly increase and the differences between the C_s values of the two models are higher. The C_s values are higher for the $CaO-CaF_2$ mixture than for the triple $CaO-CaF_2$-WB mixture because of the Al_2O_3 presence in white bauxite.

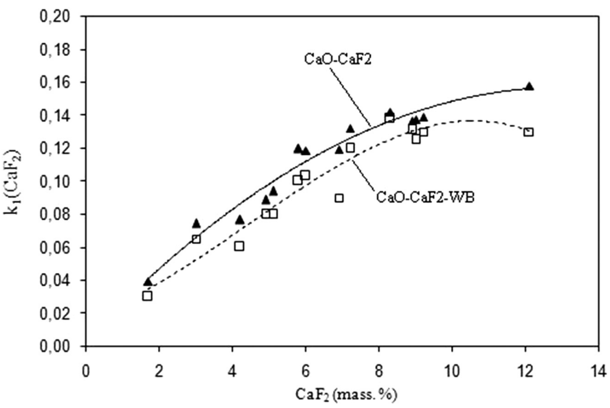

Figure 4: Influence of CaF_2 on the values of $k_{1(CaF2)}$ factor
Slika 4: Vpliv CaF_2 na vrednosti faktorja $k_{1(CaF2)}$

Table 2: Coefficient of sulphur distribution for the investigated slags
Tabela 2: Koeficient razporeditve žvepla pri preiskovanih žlindrah

Slag	1	2	3	4	5	6	7	8
L_s	53.7	73.3	69.1	76.6	80.8	129.3	111.4	99.8
$L_{s'}$(CaO-CaF$_2$)	58.8	79.2	75.6	83.8	88.5	141.6	122.0	109.8
$L_{s'}$(CaO-CaF$_2$-WB)	54.1	75.3	71.1	81.1	85.0	131.2	–	–

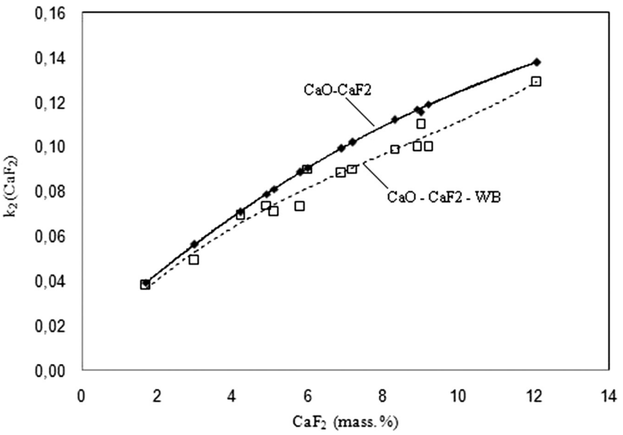

Figure 5: Influence of CaF$_2$ on the values of $k_{2(CaF2)}$ factor
Slika 5: Vpliv CaF$_2$ na vrednosti faktorja $k_{2(CaF2)}$

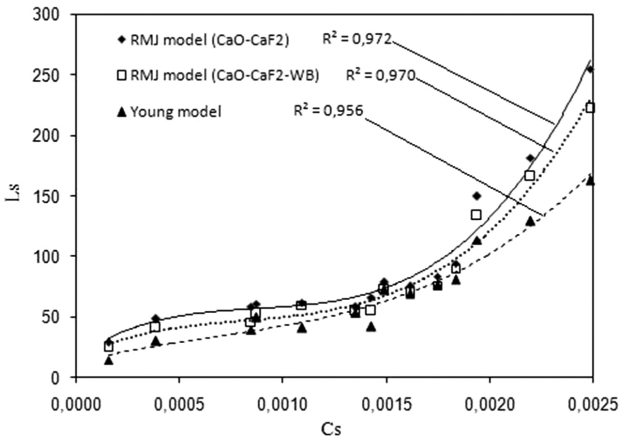

Figure 6: Effect of C_s on sulphur distribution
Slika 6: Vpliv C_s na razporeditev žvepla

The typical values of $k_{1(CaF2)}$ and $k_{2(CaF2)}$, as functions of the CaF$_2$ amount, are shown in **Figures 4** and **5**.

In general, it may be noticed that $k_{1(CaF2)}$ and $k_{2(CaF2)}$ are proportional to the CaF$_2$ amount. Besides, for w(CaF$_2$) < 8 %, the relationship is approximately linear, but for w(CaF$_2$) > 8 %, the intensity of the k_{CaF2} changes is lower. The values of $k_{1(CaF2)}$ and $k_{2(CaF2)}$ are lower for CaO-CaF$_2$-WB than for the CaO-CaF$_2$ slag mixture. It is noticeable that a higher amount of CaF$_2$ and a lower Al_2O_3 amount cause an increase in the correction-factor values. Besides, the results in the case of the CaO-CaF$_2$-WB mixture are more scattered than for CaO-CaF$_2$.

The coefficient of sulphur distribution is calculated with equation 3. The values of L_s (the RMJ model) and $L_{s'}$ (the Young model) are presented in **Table 2**.

The effect of L_s on the sulphide capacity for the two considered models is shown in **Figure 6**. It can be seen that, at the lower C_s values, the relation between L_s and C_s is almost linear.

However, at $C_s > 0.0015$, the L_s values strongly increase, and the results are more scattered in all the cases. It is likely that the degree of desulphurisation is higher for the RMJ model than for the Young model. This is because positive values of $k_{1(CaF2)}$ and $k_{2(CaF2)}$ allow a larger CaO activity that is generally observed in practice. The probability factors of polinomial dependence are higher for the RMJ model ($R^2 = 0.97$ and $R^2 = 0.972$) than for the Young model ($R^2 = 0.956$).

4 CONCLUSION

The results of the new analytical RMJ model, presented in this paper, indicate that a usage of correction factors $k_{1(CaF2)}$ and $k_{2(CaF2)}$ is required. The secondary effect of CaF$_2$ on the degree of desulphurisation is fully defined with these factors. Using white bauxite as a slag component, the values of $k_{2(CaF2)}$ decrease and the degree of desulphurisation is lower. The relative effect of CaF$_2$ on the values of k_{CaF2} and L_s at the basicity of $B > 2$ was indicated. The differences in the values of C_s for the RMJ and Young models increase with the increasing k_{CaF2}. This difference was caused by the secondary effect of CaF$_2$ on the CaO and Al_2O_3 activities as well as the properties of the slag. The presence of Al_2O_3 in white bauxite causes a lower sulphide capacity, and an optimum component amount in the steelmaking slag mixture is a condition for good desulphurisation.

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