MODELLING OF THE SULPHIDE CAPACITY OF STEELMAKING SLAGS

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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, CaF₂, Al₂O₃ and a small amount of SiO₂. 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 deoxidation degree are correlated with the sulphur activity. On the basis of the optical-basicity index, the following correlation was suggested by Gaye:

\[ \log C_s = \frac{B}{D} + 1.445 \frac{12364}{T} \]  

where: \( B = 5.62 \) (% CaO) + 4.15 (% MgO) – 1.15 (% SiO₂) + 1.46 (% Al₂O₃), \( D = (\% \text{CaO}) + 1.39 \) (% MgO) + 1.87 (% SiO₂) + 1.65 (% Al₂O₃).

However, the above correlation is not applicable to the metallurgical slags containing CaF₂ because the effect of CaF₂ must be substituted with an oxide. On the basis of the optical-basicity index, the following correlation was suggested by Tsao:

\[ \log C_s = -\frac{1}{3} \log(a_{Al_{2}O_{3}}) + \frac{2}{3} \log(a_{Al}) + \frac{20397}{T} \]  

where: \( a_{Al_{2}O_{3}} \) and \( a_{Al} \) are the activities of Al₂O₃ and Al, respectively.

In the secondary-metallurgy processes Si was used as a deoxidizer. Therefore, the formation of a stable SiO₂, 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:

\[ \log L_s = \log C_s - \frac{1}{3} \log(a_{Al_{2}O_{3}}) - \frac{2}{3} \log(a_{Al}) - 5.482 \]  

The model by Tsao has been used for defining the chemical-composition influence on the sulphide capacity:

\[ \log C_s = 3.44(\% \text{CaO}) + 0.1X_{\text{MgO}} - 0.8X_{\text{Al}_{2}O_{3}} - X_{\text{SiO}_{2}} \]  

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

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In this case the amount of CaF₂ is assumed to be part of the CaO amount. Since aluminum was used for steel deoxidation, the activity of Al₂O₃ and the Al amount are considered while calculating the sulphur-distribution coefficient:

\[ \log L_s = \log C_s - \frac{1}{3} \log(a_{Al_{2}O_{3}}) + \frac{2}{3} \log(a_{Al}) + \frac{20397}{T} \]  

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\[
\lg C_s = -13.913 + 48.844A - 2382A^2 - \frac{11710}{T} - 0.02223(\% \text{SiO}_2) - 0.02275(\% \text{Al}_2\text{O}_3)
\]

(4)

where \( A \) is the theoretical optical basicity of the slag calculated with the Nakamura method. 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 \( A < 0.8 \), i.e., to the slags examined in the experimental part of this research. Larger values of the \( \text{CaF}_2 \) amount cause high values of \( L_2 \), i.e., to the slags examined in the experimental part of this research. Therefore, the Young model (equation 4) must be corrected with the correction factors, \( k_{1(\text{CaF}_2)} \) and \( k_{2(\text{CaF}_2)} \), defining the secondary influence of \( \text{CaF}_2 \) on \( C_s \) as follows:

\[
\lg C_s = -13.913 + 48.844A - 2382A^2 - \frac{11710}{T} - 0.02223(\% \text{SiO}_2) - 0.02275(\% \text{Al}_2\text{O}_3) \cdot k_{1(\text{CaF}_2)} + k_{2(\text{CaF}_2)}
\]

(7)

The aim of using a triple slag mixture is to investigate the impact of \( \text{CaF}_2 \) in the case of an increased presence of \( \text{Al}_2\text{O}_3 \) in white bauxite.

### 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 an EAF 60 t, while Si and Al are used as deoxidizers. The slag and metal were manually sampled 10–12 min before casting. The mixture for the synthetic slag contains \( \text{CaO}, \text{CaF}_2 \) and white bauxite in the mass ratio of 3:1:2, with the ratio of 3:1 for the \( \text{CaO-CaF}_2 \) mixture.

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

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### 3 RESULTS AND DISCUSSION

A presence of \( \text{CaF}_2 \) increases the CaO saturation in the slags. For example, at comparable CaO concentrations, activity \( a_{\text{CaO}} \) in the \( \text{CaO-CaF}_2 \) slag is much higher than in the \( \text{CaO-Al}_2\text{O}_3 \) and \( \text{CaO-SiO}_2 \) systems. The slags in secondary steelmaking are basically unstable at high temperatures since two or more components in the slag react and the composition changes continuously while the fluorides and oxides react as follows:

\[
3\text{CaF}_2 + \text{Al}_2\text{O}_3 = 2\text{AlF}_3(\text{g}) + 3\text{CaO}
\]

(5)

The slag composition shows a steady increase in the CaO concentration and a decrease in \( \text{Al}_2\text{O}_3 \), so that the part of expression (4) that is correlated with \( \text{Al}_2\text{O}_3 \) must be corrected with \( k_{1(\text{CaF}_2)} \). Besides, the effect of moisture when dealing with the slags containing \( \text{CaF}_2 \) is very important because of the following reaction:

\[
\text{CaF}_2 + \text{H}_2\text{O} = \text{CaO} + 2\text{HF}(\text{g})
\]

(6)

In this case, \( \text{CaF}_2 \) increases together with the CaO activity. Therefore, the Young model (equation 4) must be adjusted with the correction factors, \( k_{1(\text{CaF}_2)} \) and \( k_{2(\text{CaF}_2)} \), defining the secondary influence of \( \text{CaF}_2 \) on \( C_s \) as follows:

\[
\begin{align*}
\lg C_s &= -13.913 + 48.844A - 2382A^2 - \frac{11710}{T} - 0.02223(\% \text{SiO}_2) - 0.02275(\% \text{Al}_2\text{O}_3) \cdot k_{1(\text{CaF}_2)} + k_{2(\text{CaF}_2)} \\
3\text{CaF}_2 + \text{Al}_2\text{O}_3 &= 2\text{AlF}_3(\text{g}) + 3\text{CaO}
\end{align*}
\]

(5)

### Table 1: Chemical compositions of the investigated slags after steel vacuuming (mass fractions, w/%)

<table>
<thead>
<tr>
<th>Slag mixture</th>
<th>Steel (EN)</th>
<th>Amounts of components (w/%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaO</td>
<td>MnO</td>
</tr>
<tr>
<td><strong>CaO-CaF₂</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.6582</td>
<td>40.00</td>
<td>1.90</td>
</tr>
<tr>
<td>1.2714</td>
<td>43.52</td>
<td>0.87</td>
</tr>
<tr>
<td>1.1181</td>
<td>40.50</td>
<td>0.1</td>
</tr>
<tr>
<td>1.7147</td>
<td>56.50</td>
<td>0.3</td>
</tr>
<tr>
<td>1.0503</td>
<td>51.00</td>
<td>0.6</td>
</tr>
<tr>
<td>1.7005</td>
<td>39.24</td>
<td>1.9</td>
</tr>
<tr>
<td>1.1191</td>
<td>41.83</td>
<td>3.8</td>
</tr>
<tr>
<td>1.7225</td>
<td>50.71</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td><strong>CaO-CaF₂-WB</strong></td>
<td></td>
</tr>
<tr>
<td>1.6582</td>
<td>41.23</td>
<td>0.3</td>
</tr>
<tr>
<td>1.7225</td>
<td>44.00</td>
<td>0.5</td>
</tr>
<tr>
<td>1.1141</td>
<td>45.34</td>
<td>0.8</td>
</tr>
<tr>
<td>1.7147</td>
<td>46.56</td>
<td>0.7</td>
</tr>
<tr>
<td>1.0503</td>
<td>42.25</td>
<td>0.52</td>
</tr>
<tr>
<td>1.2714</td>
<td>39.52</td>
<td>0.87</td>
</tr>
</tbody>
</table>
Equation 8 shows that CaF$_2$ decreases the negative effect of Al$_2$O$_3$ on CaS and it is defined by $k_{1(CaF_2)}$. With a calculation using equations 8 and 9, the effect of CaF$_2$ on $C_s$ for the constant amounts of Al$_2$O$_3$ 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$_2$O$_3$ and CaO was presented indirectly through CaF$_2$. Equations 8 and 9 show that the $k_{1(CaF_2)}$ and $k_{2(CaF_2)}$ 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.

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 $k_{1(CaF_2)}$ and $k_{2(CaF_2)}$. 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 $k_{1(CaF_2)}$ and $k_{2(CaF_2)}$ 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$_2$O$_3$ presence in white bauxite.

Figure 1: Sulphide capacity for the CaO-CaF$_2$-Al$_2$O$_3$ system at 1500 °C
Slika 1: Sulfidna kapaciteta sistema CaO-CaF$_2$-Al$_2$O$_3$ pri 1500 °C

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

Figure 4: Influence of CaF$_2$ on the values of $k_{1(CaF_2)}$ factor
Slika 4: Vpliv CaF$_2$ na vrednosti faktorja $k_{1(CaF_2)}$
The typical values of $k_1(CaF_2)$ and $k_2(CaF_2)$, as functions of the CaF$_2$ amount, are shown in Figures 4 and 5.

In general, it may be noticed that $k_1(CaF_2)$ and $k_2(CaF_2)$ 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 $k_{CaF_2}$ changes lower. The values of $k_1(CaF_2)$ and $k_2(CaF_2)$ are lower for CaO-CaF$_2$ than for the CaO-CaF$_2$ slag mixture. It is noticeable that a higher amount of CaF$_2$ and a lower Al$_2$O$_3$ 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 $k_1(CaF_2)$ and $k_2(CaF_2)$ allow a larger CaO activity that is generally observed in practice. The probability factors of polinomial dependence are higher for the RMJ model ($R^2 = 0.97$) 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 $k_1(CaF_2)$ and $k_2(CaF_2)$ 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 $k_2(CaF_2)$ decrease and the degree of desulphurisation is lower. The relative effect of CaF$_2$ on the values of $k_{CaF_2}$ 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 $k_{CaF_2}$. This difference was caused by the secondary effect of CaF$_2$ on the CaO and Al$_2$O$_3$ activities as well as the properties of the slag. The presence of Al$_2$O$_3$ in white bauxite causes a lower sulphide capacity, and an optimum component amount in the steelmaking slag mixture is a condition for good desulphurisation.

5 REFERENCES

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5. W. Young, A. Duffy, Use of optical basicity concept for determining sulphur slag-metal partitions, Ironmaking and Steelmaking, 19 (1992), 201