DESULPHURIZATION OF THE HIGH-ALLOY AND MIDDLE-ALLOY STEELS UNDER THE CONDITIONS OF AN EAF BY MEANS OF SYNTHETIC SLAG BASED ON CaO-Al₂O₃

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The article deals with the results of the experimental heats performed in the electric steel plant of TŘINECKÉ ŽELEZÁRNY, a. s. (TŽ, a. s.). The aim was to verify the possibility of deep desulphurization of steel in the basic 10-t electric arc furnace. Experimental procedures making use of the industrially produced synthetic slag were applied in the production of the high-alloy chrome steels and the middle-alloy tool steels, where the desulphurization, in terms of thermodynamics, is a more demanding process than the chrome-nickel steel desulphurization. With the use of the technological processes it is possible to achieve low contents of sulphur in steel, below mass fraction 0.003 %. Achieving these contents depends on a suitable slag basicity, and, in particular, on the ratio of CaO/Al₂O₃. Based on the analysis of the results, a critical factor significantly affecting the final content of the sulphur and thus the efficiency of the desulphurization of steel, the content of FeO in the reduction slag, is carefully considered. A higher MgO content in slag (up to w = 25 %) has no significant influence on the results of the steel desulphurization.

Keywords: steel, desulphurization, synthetic slag, basicity of slag

1 INTRODUCTION

Options for steel desulphurization primarily depend on managing the technology itself, as well as on the metallurgical processes of desulphurization. In particular, the optimization of the slag regime, and the compliance with the basic thermodynamic and kinetic parameters of slag and metal have to be considered.

The possibility of using a high-quality, industrially produced synthetic slag¹² is a significant advantage, which guarantees balanced and high-quality results, and brings a number of metallurgical, and, subsequently, economic benefits. These can be seen not only in achieving the desired cleanliness of steel, but also in compensating for the lack of modern and also expensive technological equipment for the production and secondary metallurgy. Using the production technology with synthetic slag, the high parameters of desulphurization with the final sulphur content in mass fractions being as high as 0.002 % in an electric arc furnace (EAF), and the subsequent tapping of the steel in the ladle can be achieved.

2 BASIC FACTORS INFLUENCING THE DESIRED DEGREE OF STEEL DESULPHURIZATION

In the steel production in an EAF, one of the limiting factors for achieving the desired degree of desulphurization is the sulphur contained in the basic composition of the metal-bearing batch of an external steel waste, or of an internally occurring metal (alloying additives, solid pig iron, slag-forming substances, etc.). Unlike the pure-oxygen production processes, where, in terms of desulphurization, inappropriate oxidation conditions dominate, the process of melting in an EAF is much
more variable, with a choice of heat-melting conditions and the associated slag regime. An EAF can create the standard oxidation conditions that are necessary for the decarburization process, the oxidation of the accompanying elements, the dephosphorization process, and also the reduction conditions that, in turn, provide the possibility of a successful desulphurization of steel.

The thermodynamics of desulphurization shows that, in order to achieve a low sulphur content in the metal, it is necessary to achieve, in particular, the following:

- a high level of activity of free oxygen anions in the slag, i.e., a high alkalinity of the slag with a high proportion of alkaline oxides and a low proportion of acidic oxides;
- a low activity of the oxygen $a_o$ in the steel, i.e., a low content of the dissolved oxygen and a low value of an activity coefficient $f_o$.

Another negative factor affecting the degree of steel desulphurization is the presence of the "easily reducible" oxides in the refining slag - in addition to FeO there are also MnO, P$_2$O$_5$ and Cr$_2$O$_3$. The sum percentage content of the aforementioned elements for a well-working refining slag is usually recommended to be up to the mass fraction 3%.

From the kinetic point of view, an increased temperature has a positive effect on the steel desulphurization. Increasing the temperature helps decrease the viscosity of the slag and metal; it also increases the sulphur-diffusion coefficient and reduces the surface tension, so that the chemical reaction more quickly reaches a state of equilibrium. However, the effect of the appropriate kinetics of the ongoing processes is closely connected with meeting the basic thermodynamic conditions.

3 CURRENT TECHNOLOGICAL AND METALLURGICAL PROCESSES IN THE PRODUCTION OF THE LOW-SULPHUR STEEL IN THE CONDITIONS OF THE ELECTRIC STEEL PLANT TRINECKE ZELEZARNY, a. s.

The production technology of steel with a low sulphur content, below 0.005 %, is, in terms of the electric steel plant of the TŽ, a. s. EAF, is currently based on the use of the calcium slag containing CaF$_2$ (calcium fluoride - fluorspar).

In the slag with a low silica content a positive effect of CaF$_2$ can be explained with a lowered melting point of the slag resulting from the formation of the eutectic, easily melttable phases CaO–CaF$_2$, or CaO–Al$_2$O$_3$–CaF$_2$ with a low liquidus temperature and a low viscosity, which are shown in Figure 1. CaF$_2$ also affects the reduction of the sulphur activity in the slag, leading to an increased ability of the slag to bind sulphur.

Disadvantages of using technologies with fluorspar can be seen in two major aspects:

In the contact of fluorspar with the liquid metal or liquid slag, environmentally harmful fluorides are released, which worsen the working and living environment. Fluorides concentrate in the bone tissue in a bond with Ca and Mg, thereby preventing these elements from performing their biochemical function.

Fluorspar in the slag causes an increased wear of the furnace lining and casting ladles, particularly in the slag lines, thus significantly reducing the overall durability of the furnace linings.

The use of fluorspar as a slag-forming additive is currently undergoing significant restrictions in many foreign and domestic metallurgical plants, and some economically acceptable replacements in the form of industrially produced homogeneous synthetic slag is being sought.

Currently, reputable companies provide high-quality industrially produced synthetic slag with different Al$_2$O$_3$/CaO proportions and in the form of, e.g., granules, pellets, little briquettes, crushed pieces, etc. The primary advantage is the guarantee of the exact required chemical composition with a high homogeneity.

Another group of slag-forming materials are the mixtures prepared from differently treated waste materials or
other technological products. Mixtures of this type can also be named "diluents" or "flux" for liquefaction of the ladle slag; however, they cannot themselves significantly activate the conditions for deep desulphurization.

4 SELECTION OF SUITABLE, INDUSTRIALLY PRODUCED SYNTHETIC SLAG FOR OPERATIONAL TESTING

The synthetic slag manufactured by the REFRA-TECHNIK company under the name REFRAFLUX 4842 was purposefully selected for the operational testing in the electric steel plant at TZ, a.s.

The material in the form of pellets and their fragments with a granulometry from 5 mm to 15 mm is shown in Figure 2. Although it is part of the 2008 supply, the granulometry has remained unchanged and with no dust proportion.

The basis for the chemical composition of the synthetic slag was based on a mixture of two oxides (in mass fractions) – 41.1 % Al₂O₃ and 46.2 % CaO, including 4.9 % SiO₂, 1.2 % MgO, 0.2 % FeO and 1.9 % TiO₂.

Figure 3 shows the chemical composition of the tested, industrially produced synthetic slag in a ternary chart Al₂O₃–CaO–SiO₂. It is a synthetic slag designed to be used with lime, for which it provides a high rate of assimilation and a subsequent liquefaction of the entire slag system.

5 PRODUCTION CONDITIONS OF EXPERIMENTAL HEATS

The production processes of desulphurization have been tested on the 10-ton-EAF when manufacturing the heat-resisting, high-alloyed steel of P91-grade (X10CrMoVNb9-1) and also the medium-alloyed tool steel of 19569-grade (X63CrMoV5.1). Table 1 shows the internal-release chemical composition of both steels.

The production technology for reduction slag with a high refining effect was based on the use of a mixture of burnt lime and synthetic slag REFRAFLUX, where both components were added into the EAF using an alternating dosing on the bath surface. The proportion of both components was chosen in such a way that the composition of the slag, after the melting, ranged in optimal amounts suitable for the desulphurization of the steel in the values of 50 % to 55 % CaO, 18 % to 25 % Al₂O₃, ≤ 10 % SiO₂, and ≤ 12 % MgO. In terms of good fluidity of the slag and its sulphidic capacity, the task was to maintain an optimal proportion of CaO/Al₂O₃ and its basicity.

Table 1: Internal-release chemical composition of P91 steel and 19569 in mass fractions, w/%

<table>
<thead>
<tr>
<th>Composition w/%</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Nb</th>
<th>V</th>
<th>W</th>
<th>N</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>P91 X10CrMoV Nb9-1 1.4903</td>
<td>0.06–0.12</td>
<td>0.30–0.60</td>
<td>0.06–0.10</td>
<td>8.00–9.50</td>
<td>0.85–1.05</td>
<td>0.06–0.18</td>
<td>0.015</td>
<td>0.8–1.2</td>
<td>0.06</td>
<td>0.030–0.070</td>
<td>max.</td>
<td>0.040</td>
<td></td>
</tr>
<tr>
<td>19569 X63CrMoV5.1</td>
<td>0.58–0.68</td>
<td>0.7–1.1</td>
<td>0.25–0.55</td>
<td>4.5–5.5</td>
<td>0.8–1.2</td>
<td>0.2–0.4</td>
<td>max.</td>
<td>0.6</td>
<td>0.040</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3: Area of the chemical composition of the tested synthetic slag REFRAFLUX 4842 S in the ternary chart Al₂O₃–CaO–SiO₂.

Slika 3: Področje kemijske sestave preizkušene sintetične žlindre REFRAFLUX 4842 S v ternarnem diagramu Al₂O₃–CaO–SiO₂.
In terms of the composition of the metal bath it was very important to maintain, in compliance with the theory of steel desulphurization, a low activity of the oxygen in the metal. In the EAF, this requirement was ensured with the higher levels of deoxidising elements in the liquid metal (especially Al) during the entire desulphurization process.

For a successful completion of the required chemical reactions, it is necessary, in addition to ensuring the thermodynamic conditions, to provide appropriate kinetic conditions. Mutual mixing of the slag and metal was carried out in the EAF by blowing argon through the porous block in the furnace bottom, with the 15–50 l.min⁻¹ volumetric flows according to the individual production stages. The subsequent thermal and chemical homogenization was performed by argon blowing through the porous block at the bottom of the ladle.

6 RESULTS

It should be noted that the course of each experimental heat was, to some extent, unique. A total of 14 heats were carried out in order to achieve the desired composition of the reduction slag and the other metallurgical and technological parameters, thus achieving the desired desulphurization of steel. Comparisons of the basic chemical analyses of the slag and the steel from the selected tested P91- and 19569-grade heats are shown in Table 2 and in Table 3.

From both tables it is evident that in the composition of the reduction slag, even with the same dosage of REFRAFLUX, the synthetic slag and the burnt lime showed differences. The CaO/Al₂O₃ ratio in most heats ranged from 1.8 to 2.1, while the basicity (CaO/SiO₂) ranged from 5 to 8.

6.1 Effect of the MgO content in the reduction slag on the parameters of steel desulphurization

Some heats showed a higher MgO content in the reduction slag (in some cases up to w = 25 %), whose source can be seen in the wear of the furnace lining, and, especially, in the lower-quality repairing material used for the patch-type repairs of the lining. The slag with this MgO content showed a higher viscosity, which complicated the course of desulphurization. However, it should be stated that even with these higher MgO contents, the final sulphur content in steel has been, in some cases, up to w = 0.002 %. A comparison of the effect of the increased MgO in the reduction slag is shown in the following charts.

Figure 4 and Figure 5 show the development of the chemical composition of steel and slag during the reduction period for the heat No. 686 (19569, X63CrMoV5.1).

![Figure 4: Development of the chemical composition of steel and slag during the reduction period for the heat No. 686 (19569, X63CrMoV5.1)](image)

Table 2: Selected chemical analyses of the final reduction slag and steel of the heats No. 716 and 731 (P91), w/%

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>SiO₂</th>
<th>FeO</th>
<th>Cr₂O₃</th>
<th>MnO</th>
<th>Ssteel</th>
<th>Tap temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>716</td>
<td>47.8</td>
<td>25.5</td>
<td>11.5</td>
<td>8.5</td>
<td>0.5</td>
<td>0.47</td>
<td>0.36</td>
<td>0.0020</td>
<td>1642 °C</td>
</tr>
<tr>
<td>731</td>
<td>43.1</td>
<td>21.2</td>
<td>12.6</td>
<td>7.2</td>
<td>5.57</td>
<td>5.70</td>
<td>1.35</td>
<td>0.0110</td>
<td>1688 °C</td>
</tr>
</tbody>
</table>

Table 3: Selected chemical analyses of the final reduction slag and steel of the heats No. 649 and 686 (19569), w/%

<table>
<thead>
<tr>
<th>Heat No.</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>SiO₂</th>
<th>FeO</th>
<th>Cr₂O₃</th>
<th>MnO</th>
<th>Ssteel</th>
<th>Tap temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>649</td>
<td>45.6</td>
<td>23.0</td>
<td>19.4</td>
<td>6.0</td>
<td>1.5</td>
<td>0.71</td>
<td>0.45</td>
<td>0.0020</td>
<td>1653 °C</td>
</tr>
<tr>
<td>686</td>
<td>36.5</td>
<td>20.8</td>
<td>25.7</td>
<td>9.2</td>
<td>3.0</td>
<td>1.13</td>
<td>0.72</td>
<td>0.0070</td>
<td>1630 °C</td>
</tr>
</tbody>
</table>
Figure 5: Development of the chemical composition of steel and slag during the reduction period for the heat No. 731 (P91, X10CrMoVNb9-1)

Slika 5: Razvoj kemijske sestave jekla in žlindre med trajanjem redukcije v talini št. 731 (P91, X10CrMoVNb9-1)

Figure 6: Areas of the chemical composition of the final reduction slag of the tested steel grades for the heats No. 686 (19569, X63CrMoV5.1) and No. 731 (P91, X10CrMoVNb9-1) in the quaternary chart Al2O3-CaO-MgO-SiO2 at w = 20 % Al2O3

Slika 6: Področja kemijske sestave končne redukcijske žlindre preizkušenih jekel, talina št. 686 (19569, X63CrMoV5.1) in št. 731 (P91, X10CrMoVNb9-1) v kvaternarnem diagramu Al2O3-CaO-MgO-SiO2 pri w = 20 % Al2O3

Figure 7: Development of the chemical composition of steel and slag during the reduction period for the heat No. 649 (19569, X63CrMoV5.1)

Slika 7: Razvoj kemijske sestave jekla in žlindre med trajanjem redukcije taline št. 649 (19569, X63CrMoV5.1)

Figure 8: Development of the chemical composition of steel and slag during the reduction period for the heat No. 716 (P91, X10CrMoVNb9-1)

Slika 8: Razvoj kemijske sestave jekla in žlindre med trajanjem redukcije taline št. 716 (P91, X10CrMoVNb9-1)
(\(w = 26\%\) and \(w = 12\%\)), at comparable temperatures and ratios of \(\text{CaO}/\text{Al}_2\text{O}_3\), a similar, though a low-grade, steel desulphurization (30\% to 40\%) was achieved, together with the final sulphur contents of \(w = 0.007\%\) and \(w = 0.011\%\).

The areas of the chemical composition of the final reduction slag No. 686 and No. 731 are shown in Figure 6 in the quaternary diagram \(\text{Al}_2\text{O}_3–\text{CaO–MgO–SiO}_2\) at 20\% \(\text{Al}_2\text{O}_3\).

Similarly, Figure 7 and Figure 8 show a development of the chemical composition of steel and slag during the reduction period for the heats No. 649 and No. 716.

Again, if we disregard different levels of chromium in the steel, at different steel grades, and focus solely on the \(\text{MgO}\) content in the slag, it can be stated that under the conditions of the very different \(\text{MgO}\) contents in the reduction slag in both heats (\(w = 19\%\) and 11\%), at comparable temperatures and ratios of \(\text{CaO}/\text{Al}_2\text{O}_3\), a similar, but high, degree of desulphurization (from \(w = 78\%\) to 87\%) was achieved, which corresponds to very low final sulphur contents, i.e., \(w = 0.002\%\).

The areas of the chemical composition of the final reduction slag in the heats No. 649 and No. 716 are shown in Figure 9 in the quaternary diagram \(\text{Al}_2\text{O}_3–\text{CaO–MgO–SiO}_2\) at \(w = 20\%\) \(\text{Al}_2\text{O}_3\).

When comparing the areas shown in Figure 6 and Figure 9, it is possible to conclude that the negative effect of the increased content of \(\text{MgO}\) in the reduction slag was not always associated with a higher content in the given areas proven in the experimental heats. The deterioration of the kinetic conditions in the case of a higher \(\text{MgO}\) content due to an increase in the viscosity of the reduction slag was not significant enough to substantially affect the thermodynamics of the chemical reactions observed.

6.2 Effect of the \(\text{FeO}\) content in the reduction slag on the parameters of steel desulphurization

Of all the monitored parameters, which influenced the desulphurization process and the overall degree of desulphurization, a very negative impact was shown by the content of \(\text{FeO}\) in the reduction slag. An example of this is the course of sulphur behaviour in the reduction period for the heat No. 731 (steel P91) – see Figure 5.

At the beginning of the reduction period the sulphur content in the bath was \(w = 0.018\%\). Upon the reduction refining it was \(w = 0.006\%\). However, at the end of the reduction period the sulphur content in steel was re-increased to \(w = 0.009\%\) (before tapping), and to \(w = 0.011\%\) (analysis of steel in the ladle).

The cause for this behaviour can be derived from the courses of the slag and metal compositions. As shown in Figure 5, the reoxidation and the increase in the \(\text{FeO}\) content in the slag to the values of approximately up to \(w\)
= 5.5 % took place in the final phase of the melting process and during the final heating of the melt to the tap temperature using arches. Simultaneously, the content of CaO significantly decreased (down to \( w = 43 \% \)), and, at the same time, the content of MgO increased, probably from wear or the lining, or from the loose repair material. The main cause for the sulphur-content increase can be considered the "reverse" transition from slag into the metal at an increased temperature, and with an increasing content of FeO in the slag. The mechanism of the reverse transition of sulphur from the slag to the metal is confirmed even by the simultaneous reduction of the sulphur content in the slag.

The behaviour of sulphur in steel during the reduction period is common for all heats, in which the content of FeO was increased. As shown in Figure 10, more significant degrees of desulphurization can only be achieved in the cases of very low contents of FeO in the slag (below \( w = 1 \% \)). The degree of desulphurization is significantly reduced in relative terms when these values are exceeded. Furthermore, if they increase to \( w = 3 \% \) or 4 \%, the FeO content only reaches values of approximately 30 to 40 wt. %. This observation is entirely consistent with the theory and practice of desulphurization by the reduction slag.

6.3 Achieved degree of desulphurization in the EAF

As shown in Figure 11 and Figure 12 the achieved degrees of desulphurization, when using the Refralfux-lime mixture, are totally comparable with the heats that use classic technology (lime + fluorspar), and in some cases significantly better results were achieved.

7 CONCLUSION

The steel desulphurization process involving the use of synthetic slag REFRAFLUX 4842 S with the final sulphur-content requirement below \( w = 0.005 \% \) was optimized for the heats in the EAF at the electric steel plant of TŽ, a. s.

The technology of the operational experimental heats was focused on the desulphurization of the two main steel brands, the high-alloy steel P91 (X10CrMoVNb9-1), and the medium-alloy steel 19569 (X63CrMoV5.1) with a chromium content of \( w = 9.5 \% \) and 4.5 \%.

It was found that even with a deterioration of the kinetic conditions in the cases of higher contents of MgO in the reduction slag (up to \( w = 26 \% \)), due to a higher slag viscosity, very low sulphur contents, i.e., up to \( w = 0.002 \% \) in the steel produced can be achieved.

The results of the experimental heats confirmed that a higher degree of desulphurization can be achieved only with a very low FeO content in the slag, preferably below \( w = 1 \% \).

Based on the results achieved, the changes in the EAF production technology were recommended, which enabled the final sulphur content in steel to be below \( w = 0.005 \% \). The basis for the technology recommended includes not only an application of the new synthetic slag, but also the provision of the necessary thermodynamic and kinetic conditions so that the melted slag showed the declared desulphurization efficiency.

Acknowledgements

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