EVALUATION OF INFLUENCE OF FLUXING AGENTS Based on Al_2O_3 ON SLAG MODE AND PROCESS OF STEEL DESULPHURIZATION IN EAF

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Abstract

During steel production in EAF, the bath surface is covered with slag that significantly affects the final quality and properties of steel. The use of fluxing agents based on Al_2O_3 is one of the possibilities how to influence the slag properties in the reduction phase. That task is to reduce the melting temperature and thus the viscosity of basic steel slags in order to increase the steel reactivity. This paper presents the operational experience using fluxing agents for slags based on Al_2O_3 during steel treatment in EAF under the conditions of the company UNEX a.s. The aim of the operational experiments was to compare the various additions of fluxing agents focused on assessment of the slag mode in the reduction phase of steel production. Samples of steel and slag were taken in plant conditions to assess the slag mode in particular heats focused on assessment of the desulphurization degree, basicity, content of easily reducible oxides, CaO/Al_2O_3 ratio, sulphur partition coefficient, etc. Operational experience mentioned in this paper represents the basic information about the slag mode in the reduction phase of steel production using fluxing agents based on Al_2O_3.

Keywords: fluxing agents, slag, steel, desulphurization, electric arc furnace

1. INTRODUCTION

The process of steel production in electric arc furnaces (EAF) is more versatile steelmaking process than production in conventional equipment as it allows realisation not only of the standard oxidation phase, which is necessary for the process of decarburization, oxidation of accompanying elements and dephosphorization, but also of the reduction phase with possibility of forming of refining slag, desulphurization and alloying of steel to the required level.

Creation of refining slag in the reduction phase is not easy, because slag is formed not only by slag-forming additives (lime and fluxing agents), but also by products of steel deoxidation (Al_2O_3, SiO_2, MnO), by products from wear of lining and repair material, and also by certain amount of initial oxidation slag (CaO, SiO_2, FeO, MnO, P_2O_5, Cr_2O_3). The final composition of the slag at the end of the reduction phase is therefore significantly different from the expected composition of the added slag-forming additives [1, 2].

Slag in EAF is a poly-component melt, the properties of which are affected by temperature, oxygen activity in the slag and steel, but also by its chemical composition. One of the possibilities how to affect the slag properties at desulphurization during the reduction phase is use of fluxing agents, the function of which is to reduce the melting temperature and thus also the viscosity of the reduction slag in order to increase its reactivity [3]. At present fluxing agents based on Al_2O_3 are commonly used. These fluxing agents are made
from natural oxides or from various secondary raw materials, either by re-melting, sintering, pelletising, briquetting or simply by mixing the individual components [4, 5].

The objective of industrial experiments consisted in evaluation of the slag mode at use of different additives of briquetting fluxing agents based on Al₂O₃. The industrial experiments were aimed at obtaining basic information about the possibilities of steel desulphurization and evaluation of the slag mode in order to optimise the chemical composition of the slag for improvement of kinetic and refining conditions during the reduction phase of steel treatment in conditions of the steel foundry of the company UNEX a.s.

2. CHARACTERISTICS OF INDUSTRIAL EXPERIMENTS

Industrial experiments with briquetted fluxing agents for slags were realised during production of steel in the 8 t EAF in conditions of the foundry of the company UNEX a.s. The influence of fluxing agents on slag mode in the EAF was evaluated at the reduction phase of steel production.

Proper production process at the reduction phase was conducted in the following manner: In the beginning deoxidation of steel and deactivation of slag was performed using aluminium ingots (Al_ingots). Afterwards a new so-called reduction slag was formed by a dose of slag-forming additives consisting of lime and briquetting fluxing agent A55C15BW. At the end of dosing, deactivation of slag was performed by addition of coke. During the reduction phase desulphurization of steel was made, steel was alloyed by addition of ferroalloys and temperature was modified. The process of steel production in EAF is completed by tapping and casting of steel into the moulds [6].

Altogether 17 heats were realised during operating conditions, namely at production of steel grade B50E54D3 designated for castings for wheel hub. The basic chemical composition is shown in Table 1.

Table 1 Basic chemical composition of the steel B50E54D3

<table>
<thead>
<tr>
<th>Range</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Al_Σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min.</td>
<td>0.21</td>
<td>1.25</td>
<td>0.30</td>
<td>×××</td>
<td>×××</td>
<td>×××</td>
<td>0.20</td>
<td>×××</td>
<td>×××</td>
</tr>
<tr>
<td>Max.</td>
<td>0.25</td>
<td>1.45</td>
<td>0.60</td>
<td>0.020</td>
<td>0.015</td>
<td>0.30</td>
<td>0.30</td>
<td>0.05</td>
<td>0.040</td>
</tr>
</tbody>
</table>

Two variants of experiments were proposed for evaluation of the slag mode at the reduction phase of production, which differed by the added amount of the fluxing agent A55C15BW. Characteristics of both variants of the experiments are shown in Table 2.

Table 2 Characteristics of the proposed variants of industrial experiments

<table>
<thead>
<tr>
<th>Experiment variant</th>
<th>Lime</th>
<th>Slag-forming additives (kg)</th>
<th>Ratio A55C15BW/CaO</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100</td>
<td>A55C15BW 20 120</td>
<td>1 : 5</td>
</tr>
<tr>
<td>B</td>
<td>100</td>
<td>A55C15BW 50 150</td>
<td>1 : 2</td>
</tr>
</tbody>
</table>

The used fluxing agent A55C15BW is produced from the secondary corundum raw materials, which are by-products from production of electro-melted corundum in combination with dolomitic limestone and organic binder Binderwar. The basic chemical composition is formed by the following oxides: 55.0 wt. % Al₂O₃, 15.0 wt. % CaO, 4.0 wt. % MgO, 2.0 wt. % SiO₂, 1.5 wt. % Fe₂O₃, 1.0 wt. % Na₂O + K₂O a 0.5 wt. % TiO₂.

3. EVALUATION OF THE OBTAINED RESULTS

Evaluation of the influence of different slag-forming additives on the resulting chemical composition and of the effect of reduction slags was made in several steps. First, an evaluation of the obtained degrees of desulphurization at various technological stages of production in the EAF was performed, as shown in Table 3.
Table 3 Degrees of desulphurization achieved during production in EAF

<table>
<thead>
<tr>
<th>Variant</th>
<th>Achieved degrees of desulphurization of individual phases in EAF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\eta_S$ oxidation</td>
</tr>
<tr>
<td>A</td>
<td>23.05</td>
</tr>
<tr>
<td></td>
<td>Max.</td>
</tr>
<tr>
<td></td>
<td>Min.</td>
</tr>
<tr>
<td>B</td>
<td>28.74</td>
</tr>
<tr>
<td></td>
<td>Max.</td>
</tr>
<tr>
<td></td>
<td>Min.</td>
</tr>
</tbody>
</table>

It is evident from Table 3 that individual degrees of desulphurization reached for both variants similar trends. The overall average degree of desulphurization ($\eta_S$ total) was in both variants 56 %, which is associated with lower initial sulphur contents in the range of approx. 0.021 to 0.032 wt. %, and with the required final content of sulphur in the steel of max. 0.015 wt. %.

The results also show that the main part of desulphurization by addition of slag-forming additives took place during the reduction phase ($\eta_S$ $\sum$ reduction), with an average degree of desulphurization of 42 % for the variant A and 39 % for the variant B.

Desulphurization in the reduction phase can be divided into two parts. The first part of desulphurization is the reduction phase ($\eta_S$ reduction), involving the dosage of slag-forming additives, gradual dissolution and slag formation. During this part the sulphur content was reduced by 0.005 wt. % and the degree of desulphurization varied around the level of 22 % for the variant A and 23 % for the variant B. The second part is then represented by tapping of steel into the pouring ladle ($\eta_S$ tapping). In this case further desulphurization of steel by 0.004 wt. % takes place due to intense mixing of steel with liquid molten slag during tapping. The degree of desulphurization reached 26 % for the variant A and 21 % for the variant B. It also follows from the obtained results represented in Table 3 that the increased content of fluxing agent (A55C15BW) in the variant B didn't affect much the achieved degree of desulphurization.

It can be assumed that the degree of desulphurization at the reduction phase is affected also by the chemical composition of the slag, which is influenced not only by the quantity of slag-forming additives, but also the oxidizing slag, wear of lining or by steel deoxidation technology. For this reason, an evaluation of changes in chemical composition of the reduction slags (variants A and B) on the basis of analysis of the samples taken during the treatment in the EAF was made.

The achieved results of chemical composition of the slag samples are shown in Fig. 1, which represents the results of chemical composition completed by maximal and minimal values achieved in individual experimental heats.

It follows from Fig. 1, that formation of reduction slag by addition of slag-forming additives (CaO and A55C15BW) resulted in an increase of CaO contents in the range from 45 to 46 wt. %, and Al₂O₃ contents to 15 wt. %. It was moreover established that certain quantity of oxidation slag remains in the EAF in spite of slagging during the oxidation phase,

![Fig. 1](image)

**Fig. 1** Achieved chemical composition of reduction slags A and B which was reflected by an increase of SiO₂ content supported by the burn-off of added ferro-alloys. This
oxidation slag contains apart from the increased shares of SiO₂, which reduce the share of free CaO, also some easily reducible oxides (FeO, MnO, P₂O₅ and Cr₂O₃), which negatively influence desulphurization of steel. That's why the formed reduction slag is deactivated by addition of coke and partly also of aluminium (Al ingots) that are designated for deoxidation of steel.

This technological step led to reduction of contents of oxides FeO and MnO to 1.4 to 2.5 wt. %. It also follows from the results of individual heats that deactivation of the initial oxidation slag was not perfect, since in some experimental melts content of the oxides was achieved in the range from 2.3 to 4.7 wt. %.

In addition to these oxides in the slag higher content of MgO was established in the average range from 13 to 16 wt. %. In some extreme cases the contents were achieved in the range from 20 to 25 wt. %. It can be assumed that the increased content of MgO can cause higher slag viscosity and worse desulphurization of steel, and that it may affect the melting temperatures of reduction slags. This trend can be explained by wear of lining and by use of lower quality repair material serving for EAF repairs between individual heats. On the basis of comparison of the chemical composition of the molten slags in the variants A and B it may be stated an optimal composition of reduction slag, which should contain the following percentages of oxides: approx. 50 to 55 wt. % CaO, 25 to 30 wt. % Al₂O₃, ≤ 10 wt. % SiO₂, ≤ 12 wt. % MgO, ≤ 1 wt. % FeO [5, 7] which was not achieved.

The achieved results of chemical composition of reduction slag in the variants A and B were processed into an area of quaternary diagrams of CaO-Al₂O₃-MgO-SiO₂ and they are presented in Fig. 2 [8, 9]. It follows from the quaternary diagrams of CaO-Al₂O₃-MgO-SiO₂ that in the case of the variant A (Fig. 2a), the melting temperatures of slag at the reduction phase of treatment in the EAF vary in the range of 1500-1700 °C. The quaternary diagram shows also the influence of MgO on melting temperatures of slags. When the MgO content is in the slag > 10 wt. % then an increase of melting temperature of slags can occur, which may lead also to the change of viscosity, as well as influence the desulphurization ability of the slag mixture at the reduction phase of steel production in the EAF.

![Quaternary diagram](image)

In the variant B (Fig. 2b) the melting temperatures of slags in the reduction phase of treatment in the EAF varied in the range of 1700-1900 °C. In this case also the non-removed oxidation slag contributes to the high melting
temperature of the slag mixture, but an increased content of MgO in the range from 10 to 18 wt. % had negative effect as well. In the extreme case of two heats the melting temperatures of slags ranged from 2000 to 2100 °C. This phenomenon can be explained by an increased content of MgO, representing approx. 25 wt. % caused by erosion and corrosion of refractory lining of the furnace or by release of the repair material from the soil and from the slag zone of the EAF.

Apart from an evaluation of the changes in chemical composition of reduction slags in the variants A and B an evaluation of the impact of selected parameters of slags on the effective distribution coefficient of sulphur (Ls) was also made. The monitored parameters include: basicity, contents of easily reducible oxides and ratio CaO/Al₂O₃ [8, 10]. The results are shown in Fig. 3 to Fig. 6.

**Fig. 3** Dependence of effective distribution coefficient of sulphur on the basicity - B1  
**Fig. 4** Dependence of effective distribution coefficient of sulphur on the basicity – B2

**Fig. 5** Dependence of effective distribution coefficient of sulphur on the contents of easily reducible oxides - ERO  
**Fig. 6** Dependence of effective distribution coefficient of sulphur on the calcium-alumina ratio – C/A

Basicity of reduction slags is represented in Fig. 3 and Fig. 4. In the case of the basicity (B1) an average value of 2.2 was achieved in the variant A, and the value of 2.6 was achieved in variant B. In the case of the basicity (B2) the values decreased, and a value of 1.6 was achieved in the variant A and a value of 1.9 was achieved in the variant B. In both cases of the basicity (B1) and basicity (B2) the slags in the variants A and B can be characterised as medium basic. We can also see in Fig. 3 and Fig. 4 the increasing trend of the effective distribution coefficient with the increasing basicity, when the highest effective distribution coefficient was reached only in the slag, which can be characterised as strongly basic. For achievement of an optimal chemical composition of reduction slag the basicity (B1) should reach the value of at least 4.5, and the basicity (B2) the value from at least 2.5 to 3.0.
The contents of easily reducible oxides are another monitored parameter. In this case it is apparent from Fig. 5 that the average content for the variant A is 2.6 wt. %, and 4.02 wt. % for the variant B. It can be assumed that certain amount of these oxides is formed by partial deoxidation and by alloying of steel, while higher contents exceeding 3 wt. % indicate that removal of oxidation slag from the EAF was not perfect. This phenomenon was established also in the variant A, but especially in the variant B, as shown in Fig. 5, which is confirmed by the decreasing trend of the effective distribution coefficient of sulphur.

The ratio of calcium-alumina C/A is the last monitored parameter. The optimal value of this parameter should be 1.7 to 2.3, since in the reduction calcium-alumina slag higher contents of Al₂O₃ are required, namely from approx. 25 to 30 wt. % [5, 7]. It is evident form Fig. 6 that both slags in the variants A and B achieve similar average values of 3.1 and 3.0, which can be explained by low Al₂O₃ content of approx. 15 wt. %. The results show also considerable scatter of the achieved values of the C/A ratio, which can be explained by the influence of other oxides in the slag affecting the contents of CaO and Al₂O₃. For optimization of the slag mode it would be suitable to make a targeted modification of the chemical composition of slags in order to obtain the optimum C/A ratio by deactivation of slag and by deep deoxidation of steel.

4. CONCLUSIONS

In industrial conditions of the foundry of the company UNEX a.s. a series of experimental melts with focus on the evaluation of the slag mode and steel desulphurization was performed with use of briquetted Al₂O₃ based fluxing agents. On the basis of the results obtained at industrial experiments it is possible to define the following findings:

- the main part of desulphurisation took place during the reduction phase of steel production in the EAF in the range of 42% for the variant A, and 39% for the variant B, and the overall degree of desulphurization for both variants A and B reached 56%.
- the degree of desulphurization at the reduction phase was affected also by the chemical composition of the slag, which is influenced not only the by quantity of slag-forming additives, but also by residual oxidation slag, by wear of lining and by technology of steel deoxidation.
- addition of slag-forming additives resulted in the variant A in the following average composition of the reduction slag: 47 wt. % CaO, 15 wt. % Al₂O₃, 21 wt. % SiO₂, 13 wt. % MgO and 1 wt. % FeO. In the variant B following average composition of the slag was achieved: 45 wt. % CaO, 15 wt. % Al₂O₃, 17 wt. % SiO₂, 16 wt. % MgO, 1.5 wt. % FeO.
- in all experimental melts an increased MgO content was observed, namely in the reduction slag A and B. It follows from the quaternary diagrams CaO-MgO-Al₂O₃-SiO₂ that at the MgO content in the slag > 10 wt. % the melting temperature of slags increases, which can result in the change of viscosity and also affect the desulphurization ability of the slag mixture at the reduction phase of steel production in the EAF.
- on the basis of comparison of the results achieved in the variants A and B it can be stated that the briquetted fluxing agent A55C15BW can replace the original fluxing agent based on metallurgical fluorspar. Furthermore, it can be stated that the results of both variants are comparable at dosing (fluxing agent : lime) at the ratio of 1: 5 and 1: 2
- in the next stage of research the attention will be focused on confirmation of these operating results in order to optimise the slag mode at the reduction phase by using the following technological steps: removal of oxidation slag supported by deactivation of the slag aluminium skimmings (Al skimmings) or by granulated aluminium (Al granular). Furthermore, it is appropriate to ensure a deoxidation of steel with use of aluminium rod (Al ingots) with an excess of deoxidising agent. This should increase the effectiveness of deoxidising agent (Al ingots), reduce burn-offs of alloying additives FeMn, FeSi and FeSiMn, and also
increase the $\text{Al}_2\text{O}_3$ content, which can be used by lower dosages of the fluxing agent A55C15BW in the ratio of 1: 5.

The obtained results represent data, which made it possible to map the ordinary slag mode in operating conditions. The results will afterwards be used at the next stage of research for an optimization of the slag mode and for modification of the technology in the reduction phase of steel production in the EAF.

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LITERATURE


