ASSESSMENT OF INFLUENCE OF BRIQUETTED FLUXING AGENTS ON REFINING SLAGS AT STEEL TREATMENT BY SECONDARY METALLURGY

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Abstract

In steelmaking industry the requirements not only to quality and service properties of steel, but also to environmental indicators of production are continuously increasing. One of the possibilities for fulfilment of these requirements is optimisation of the slag mode. Enhancement of slag properties is routinely made by use of fluxing additions, from which fluorspar (CaF₂) is the best known. This fluxing addition is, however, being preplaced at present. Its detrimental effect on environment and on hygienic conditions is the main reason for this. Its negative impact on service life of basic linings in the slag zone is another unfavourable effect. Fluorspar is replaced by fluxing agents based on Al₂O₃, which are produced from secondary corundum raw materials. At present the company JAP Trading, s.r.o. collaborates with the VŠB-TU Ostrava, FMME, Department of Metallurgy in the field of research and development of briquetting of fluxing agents. These fluxing agents are made from secondary corundum raw materials created at production of electro-melted corundum. Objective of this collaboration consists in research and development of standardised fluxing agents for various operational conditions of those steelworks, which are still using fluorspar. In this manner consumption of fluorspar will be minimised, as well as wear of the lining will be decreased with simultaneous preservation or even improvement of refining and desulphurizing capabilities of slags. The paper presents results of plant experiments aimed at testing of the developed fluxing agents at steelworks Třinecké železárny, a.s. (TŽ, a.s.).

Keywords: fluxing agent, fluorspar, corundum, steel, slag, secondary metallurgy

1. INTRODUCTION

Fluorspar is used for liquefaction of slag at production of more than one tenth of total amount of steel produced in Czech Republic. Main reason for its use is its high efficiency, which satisfies the requirement for rapid liquefaction of slags. However, at present fluorspar is being replaced by fluxing agents based on Al₂O₃, which eliminate its negative impacts. These fluxing agents have at suitable chemical composition lower melting point and therefore also low viscosity for a long time, which contributes also to long-term good refining effects of liquefied slags.

The fluxing agents mentioned above are manufactured from wastes (e.g. from aluminium skimmings), in various forms (for example re-melted, pelletised, lumps or powder mixtures). These types of fluxing agents are, nevertheless, used with certain limitations, which ensue from technology of their production, energy intensity and price.

Objective of the work consisted in obtaining of relevant information on refining capabilities of slags by assessment of the degree of steel desulphurization and its course. The substance of the research consisted
in execution of plant experiments with use of three fluxing agents for steelmaking slags on selected secondary metallurgy unit. During experiments continuous analysis of chemical composition of steel and slag was performed and temperature of steel was measured. At the same time behaviour of fluxing agents and development of their dissolution in steelmaking slags was assessed.

2. COURSE OF PLANT EXPERIMENTS

Plant experiments took place in conditions of the steelworks Třinecké železárny, a.s. (TŽ, a.s.), which is equipped with numerous secondary metallurgy units (such as argon rinsing stations, IR-UT, LF and RH stations). For the evaluation of influence of fluxing agents on refining capabilities of slags the argon rinsing station or homogenization station (hereinafter HS) was chosen, in which homogenization is performed with use of argon, which is blown by top nozzle (700 l·min⁻¹) and bottom nozzle (400 l·min⁻¹).

Altogether 16 heats were performed in plant conditions at treatment of unalloyed structural steel of the grade S355J (ČSN EN 10025-2). Chemical composition of this steel is given in Table 1.

**Table 1**  Chemical composition of the steel grade S355J

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Cr</th>
<th>Ni</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min. content (wt. %)</td>
<td>0.17</td>
<td>1.25</td>
<td>0.15</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.020</td>
</tr>
<tr>
<td>Max. content (wt. %)</td>
<td>0.20</td>
<td>1.45</td>
<td>0.55</td>
<td>0.030</td>
<td>0.030</td>
<td>0.20</td>
<td>0.10</td>
<td>0.20</td>
<td>0.045</td>
</tr>
</tbody>
</table>

The plant experiments were realised in such a manner that after processing of the heat in oxygen converter a slagless tapping into a ladle was performed. The ladle contained prepared slag mixture, comprised of the tested fluxing agent and lime in proportion 1 : 4. During tapping steel was deoxidized by addition of ferroalloys, granulated aluminium and basic alloying of steel was made.

After tapping the ladle containing steel and created slag was transported to the HS, where the experiment itself started. The whole experiment was planned for 18 min. (1080 s). Due to lack of time the experiment was in some heats shortened to 15 min. only (900 s). During treatment of steel in the HS samples of steel and slag were taken, whereas samples of steel were taken in intervals of 3 minutes and slag only at the beginning and at the end of the experiment. Temperature of steel was measured at each taking of the sample. All the samples of steel were afterwards subjected to analysis, which concerned namely the content of sulphur. The samples of slags were subjected to analysis of basic elements and oxides.

3. CHARACTERISTICS OF TESTED FLUXING AGENTS

Three different types of Al₂O₃ based fluxing agents were chosen for optimisation of the slag mode. These fluxing agents differed by their chemical composition, used technology of their production, basic raw materials and grain size. Basic characteristic of the fluxing agents is given below:

- **Fluxing agent A** – represents standard fluxing agent used in plant conditions of TZ. This fluxing agent is formed of crushed slag from production of ferro-vanadium, the main component of which is Al₂O₃. It is routinely supplied with grain size from 2 to 10 mm.

- **Fluxing agent B** – represents the fluxing agent developed by the company JAP, s.r.o. It is produced from secondary corundum raw materials, which are in fact by-products from production of electro-melted corundum (such as for example dust and sludge), in combination with dolomitic lime and different types of binding agents. The main components are Al₂O₃, CaCO₃ (source of CaO) and the binder in the form of water glass (sodium-silica glass). It is made by briquetting and in standard manner it is delivered as briquettes with dimensions 60 × 50 × 30 mm.

- **Fluxing agent C** - represents the second variant of the fluxing agent developed by the company JAP, s.r.o. It contains the same basic components in the same proportion as the previous type, but it
differs by the type of the used binder. In this case an organic binding agent was used. It is also made by briquetting and in standard manner it is delivered as briquettes with dimensions 60 × 50 × 30 mm.

Samples of individual fluxing agents are shown in Fig. 1, and basic chemical composition is given in Table 2.

![Fluxing agent A](image1.png) ![Fluxing agent B](image2.png) ![Fluxing agent C](image3.png)

**Fig. 1** Sample of three types of fluxing agents used in experiments

**Table 2** Basic chemical composition of selected fluxing agents

<table>
<thead>
<tr>
<th>Type of fluxing agent</th>
<th>Basic chemical composition (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>A – standard TZ, a.s.</td>
<td>min. 65.0</td>
</tr>
<tr>
<td>B – developed by JAP, s.r.o.</td>
<td>60 - 70</td>
</tr>
<tr>
<td>C - developed by JAP, s.r.o.</td>
<td>60 - 70</td>
</tr>
</tbody>
</table>

4. **EVALUATION OF THE OBTAINED RESULTS**

During plant experiments samples of steel and slag from each heat were taken at the HS. Moreover continuous measurement of steel temperature and its activity was performed. The samples and measurements were made at the tapping of steel from the oxygen converter into a ladle, and at treatment of steel at the HS.

First evaluation of refining capabilities of slags with use of desulphurization was performed by the desulphurization degree \( \eta_s \). The degree of desulphurization was assessed for two technological operations. The first one represents tapping of steel from the oxygen converter into a ladle, and the second one - treatment of steel in the HS. Results of the degree of desulphurization achieved by slags with different fluxing agents are shown in Fig. 2.

It is evident from Fig. 2 that application of the developed fluxing agents B and C resulted in lower degree of desulphurization at tapping of steel from the converter into a ladle. At this technological step fluxes were already added into a ladle and their progressive dissolution and partial desulphurization occurs. Higher degree of desulphurization (approx. 2 times higher) achieved by the fluxing agent A was apparently caused by technology of its production. The basis of this fluxing agent consists of the crushed slag...
from production of ferro-vanadium. It is therefore possible to assume that individual components of this material have already been partly melted down. Thanks to this focal points of molten slags, which may participate at desulphurization of steel, are created more rapidly.

In the case of the slags with fluxing agents B and C it is appropriate to bear in mind that they are produced by briquetting of individual components (electro-melted corundum, lime and binder). These components have high melting points exceeding the working temperatures of steel (for example tapping temperature is approx. 1640°C). During tapping of steel into ladle individual components are gradually intermixed and dissolved (fluxes, ferro-alloys, carburisers, etc.), which is accompanied by formation of mixture of oxides, which has generally lower melting points than pure oxides. That's why at mixing temperature of liquidus of oxides mixture gradually decreases, till partial or complete melting of the slag is achieved (so called refining slag is formed).

The above mentioned trend of dissolution of fluxes corresponds with an increase of the degree of desulphurization, which is achieved at treatment of steel in the HS. As it can be seen in Fig. 2, all three fluxes with fluxing agents A, B and C show the same high degree of desulphurization. It is therefore possible to assume that in the course of steel treatment in the HS (approx. 18 min.) slag mixture containing individual fluxing agents was dissolved and liquid slag was formed. This liquid slag already significantly participates in reactions between the slag and metal.

Refining capabilities of slags in the HS were furthermore investigated by an analysis of the development of desulphurization and of the selected parameters of slag in this homogenization station. Results of the development of steel desulphurization by slags with different fluxing agents are given in Fig. 3. Table 3 presents the monitored parameters of slags, such as basicity, content of easily reducible oxides, proportion of CaO/Al2O3 and Mannesmann’s index.

Fig. 3 gives the obtained values, including the interposed trend curve, separately for individual slags with fluxing agents A, B and C. It is apparent from these results that drop in content of sulphur in steel is gradual and that efficiency of desulphurization by slags with different fluxing agents is almost identical. It also follows from the results that differences between individual fluxing agents are negligible, whereas average value of desulphurization in the HS within the time interval of 18 minutes varied from 0.009 wt. % (fluxing agent A) to 0.010 wt. % (fluxing agents B and C).

For assessment of the coefficient of agreement a calculation of the variation coefficient for individual slag mixtures was made. Variation coefficient with the values below 0.5 manifests low degree of variability, whereas the values of variation coefficient were the following: 0.165 (fluxing agent A), 0.234 (fluxing agent B) and 0.210 (fluxing agent C). These values confirm achievement of very similar results at repeated experiments carried out with individual fluxing agents, although these experiments were performed in demanding plant conditions.
### Table 3  Investigated parameters of slags in the HS at the start and at the end of experiment

<table>
<thead>
<tr>
<th>Type of fluxing agent</th>
<th>B1&lt;sub&gt;start&lt;/sub&gt;</th>
<th>B1&lt;sub&gt;end&lt;/sub&gt;</th>
<th>B5&lt;sub&gt;start&lt;/sub&gt;</th>
<th>B5&lt;sub&gt;end&lt;/sub&gt;</th>
<th>SO&lt;sub&gt;start&lt;/sub&gt;</th>
<th>SO&lt;sub&gt;end&lt;/sub&gt;</th>
<th>C/A&lt;sub&gt;start&lt;/sub&gt;</th>
<th>C/A&lt;sub&gt;end&lt;/sub&gt;</th>
<th>MM&lt;sub&gt;start&lt;/sub&gt;</th>
<th>MM&lt;sub&gt;end&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>A – standard TŽ, a.s.</td>
<td>3.12</td>
<td>2.80</td>
<td>1.76</td>
<td>1.43</td>
<td>6.55</td>
<td>2.64</td>
<td>3.59</td>
<td>2.83</td>
<td>0.21</td>
<td>0.15</td>
</tr>
<tr>
<td>B – developed by JAP, s.r.o.</td>
<td>2.98</td>
<td>2.17</td>
<td>1.64</td>
<td>1.17</td>
<td>6.13</td>
<td>1.64</td>
<td>3.01</td>
<td>2.00</td>
<td>0.18</td>
<td>0.11</td>
</tr>
<tr>
<td>C - developed by JAP, s.r.o.</td>
<td>2.72</td>
<td>2.61</td>
<td>1.66</td>
<td>1.59</td>
<td>6.99</td>
<td>2.36</td>
<td>3.23</td>
<td>2.92</td>
<td>0.18</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Note:  
- B1 – basicity: B1=(CaO)/(SiO2),  
- B5 – basicity: B5=(CaO+MgO)/(SiO2+Al2O3),  
- SO – easily reducible oxides: SO=(FeO)+(Fe2O3)+(MnO)+(Cr2O3)+(V2O5)+(P2O5),  
- C/A – proportion of C/A=CaO/Al2O3,  
- MM – Mannesmann’s index: MM=(CaO/(SiO2))/(Al2O3).

From comparison of investigated parameters of slags in the HS from Table 3 the following findings may be deduced. It follows from comparison of individual basicities that sufficiently high values were achieved. Slag mixtures with fluxing agents A, B and C can be classified into the group of medium to highly basic slags. These higher values at the beginning and at the end of experiment in individual slag mixtures contribute to desulphurization of steel. This is obvious also from the achieved results of the degree of desulphurization (η<sub>S</sub>), as it may be seen in Fig. 2.

Apart from basicities also content of easily reducible oxides contained in slag mixtures was investigated. In this case their higher content was found. It may be assumed that certain quantity of easily reducible oxides is formed by partial deoxidation and by alloying of steel. Higher contents (FeO) above 3 wt. % indicate that in some cases minimum penetrations of furnace slag into a ladle have occurred. However, at the end of the experiment decrease of easily reducible oxides is evident, which may be explained by their reduction by aluminium.

In the case of calcium-aluminous proportion it is apparent that individual slag mixtures achieve at the beginning of experiment the values > 3. However, at the end of individual experiments these values decrease. It is evident from this development that during treatment of steel in the HS the remaining part of fluxing agents is dissolved in slag. The slag after treatment in the HS is completely dissolved and liquid.

From comparison of the Mannesmann’s index for slag mixtures it is evident that they vary in the mixture with the fluxing agent A within the interval from 0.15 to 0.30. In the case of slag mixtures with the fluxing agents B and C these indexes fluctuate at the bottom limit of the optimum interval. It is therefore appropriate to pay attention at future experiments to the content of basic oxides and to the proposed proportions of fluxes with use of the fluxing agents B and C.

It may be stated on the basis of the obtained results that newly developed fluxing agents B and C are comparable with the fluxing agent A, which is used in a standard manner, as they achieved identical values of desulphurization and slag parameters under similar plant conditions. On the basis of currently achieved results it may be therefore stated that fluxing agents B and C represent briquetted mixture of secondary corundum raw materials and that they may possibly fully replace the fluxing agents used so far in a standard manner.

## 5. CONCLUSIONS

In plant conditions of TŽ, a.s. testing of influence of fluxing agents for steelmaking slags on efficiency of steel desulphurization at secondary refining of steel in the HS was performed. The developed fluxing agents of the type B and C are produced by the company JAP Trading, s.r.o. The following findings may be defined from the achieved results of plant experiments:

- at tapping of steel from the oxygen converter till arrival to the HS (approx. 10 to 15 minutes) partial desulphurization of steel was achieved. The highest degree of steel desulphurization was achieved by the mixture with the fluxing agent A – approx. 18 %. However, in the case of treatment of steel in the
HS for approx. 18 minutes the achieved degree of steel desulphurization was practically the same for all slag mixtures – it was approx. 29%.

- reduction of sulphur content in steel in the HS is gradual and efficiency of desulphurization by slags with different fluxing agents A, B and C is almost identical. Average value of desulphurization for all three types of fluxing agents varied between 0.009 to 0.010 wt. % per 18 minutes.

- slag mixtures with fluxing agents A, B and C may be classified according to their basicity into the group of medium to highly basic slags, by which they contribute to desulphurization of steel.

- penetrations of furnace slag into ladle were detected on the basis of content of easily reducible oxides.

- in the case of calcium-aluminous proportion it was established that in the course of experiment in the HS the remaining part of fluxing agents is dissolved. The slag is after treatment completely dissolved and liquid.

- from the values of the Mannesmann’s index it is evident, that in slag mixtures with fluxing agents B and C its values fluctuate at the bottom limit of the optimum interval (approx. 0.3). That’s why at future experiments it is necessary to pay attention to the proposed proportions of fluxes.

- the developed fluxing agents B and C are comparable with the fluxing agent A, which is currently used in a standard manner. These fluxing agents B and C represent briquetted mixtures of secondary corundum raw materials and they may fully replace routinely used fluxing agents, using different secondary raw material and technology of production.

- in the next stage of research and development of briquetted fluxing agents attention will be focused on confirmation of these primary results, for example at production of different grades of steel, at use of another secondary metallurgy units or under different plant conditions.

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