Evaluation of slag regime in ladle during utilization of briquetted synthetic slag in VHM a.s.

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ABSTRACT

Purpose: The paper focuses on evaluation of slag regime by the help of synthetic slags based on Al₂O₃. The comparison of influence of synthetic slags on the production of two chosen grades of steels focused on evaluation of effectivity of created refining slag during treatment in the secondary metallurgy was the objective of plant experiments.

Design/methodology/approach: During evaluation of slag regime in the ladle, steel samples for assessment of desulphurization degree were taken under the plant conditions. Slag samples were also taken for evaluation of chosen parameters: basicity, content of easily reducible oxides, proportion of CaO/Al₂O₃ and Mannesmann’s index. The temperature and oxygen activity in steel was continuously measured too.

Findings: From plant experiments, it was found out that during using of two different types of synthetic slags during production of steel grades St52-3 and S34MnV similar values of desulphurization degree were achieved. Chosen parameters of ladle slag were monitored and it was demonstrated that the developed synthetic slag B reaches the results comparable with the standard used synthetic slag A.

Research limitations/implications: Plant experiments were made under conditions of VÍTKOVICE HEAVY MACHINERY a.s. Obtained results are limited by the testing during production of two different steel grades St52-3, S34MnV and by the specific technology of production formed by EAF→LF→VD/VCD.

Practical implications: The research results made it possible to realize the optimization of slag regime under the plant conditions of VÍTKOVICE HEAVY MACHINERY a.s. plant. It was proved that developed synthetic slag B from the company JAP TRADING s.r.o. can adequately replace the common synthetic slag A.

Originality/value: Results mentioned in this paper are intended for steel producers and they represent basic information about possibilities of slag regime optimization in the ladle.

Keywords: Steel; Secondary metallurgy; Synthetic slag; Slag regime; Desulphurization

Reference to this paper should be given in the following way:
1. Introduction

In steelmaking industry, the requirements to quality and service properties of steel are continuously increasing. One of the possibilities for fulfillment of these requirements within the secondary metallurgy is optimisation of the slag regime by the help of synthetic slags with the aim of creation of effective refining slag.

Slags in the ladle are formed by slag-making additions presenting lime and fluxing additions (CaF₂ or synthetic slags). The slag composition is influenced by products of steel deoxidation (Al₂O₃, SiO₂, MnO), lining corrosion (abrasion) of ladle (MgO) as well as certain amount of slag passed from furnace. These components have i.a. different melting temperatures and some of them have melting temperatures overlapping working temperature at steel production and refining. During steel treatment within secondary metallurgy, gradual blending and solution of separate components (presenting e.g. slag-making additions, ferro-alloys, carburizers, deoxidation additions, passed through furnace slag etc.) under the creation of oxides mixture happens. This mixture has generally lower melting temperature than pure oxides until partial or total slag melting is achieved. After melting of separate slag components, modification by the help of slag-making additions with the aim of achievement of optimal chemical composition of slag, so called refining slag, happens [1,2].

Usage of synthetic slags based on Al₂O₃ presents one of the possibilities to influence the slag properties during secondary metallurgy desulphurization. Their task is to reduce the melting point and also the viscosity of basic steel slags with a view of increasing of slag reactivity. In this way, desulphurization effectivity will be improved and physical chemical interaction proceeding on slag metal interface will be accelerated [3, 4]. Presently, fluxing agents based on Al₂O₃ are routinely used. They are produced from pure oxides or various secondary raw materials, namely by using of both types of synthetic slags. During treatment in secondary metallurgy units, samples of steel and slag were taken, namely in following technological places: in the ladle after tapping from EAF (sample LADLE), at the beginning and at the end of treatment in ladle furnace (sample LFSTART and LFEND) and at the end of treatment in vacuum unit (sample VDSTART or VDCDEND). In case of steel, the attention was devoted especially to the sulfur content, in the slag samples analysis aimed on sulfur content and basic types of oxides was made. Except taking steel and slag samples, temperature and oxygen activity in steel were continuously measured, namely especially at the beginning of treatment in the ladle furnace (LF) and at the end of treatment in the vacuum station (station VD/VCD).

3. Basic parameters of synthetic slags

Two different types of synthetic slags based on Al₂O₃ were chosen for evaluation of slag regime under plant conditions. These synthetic slags differ in their chemical composition, used technology of their production, basic raw materials and grain size:

- **synthetic slag A** – it is standard slag used especially in the past in plant conditions of VHM a.s. for liquefying and creation of refining slag. This synthetic slag is produced from natural raw materials, such as bauxite, lime or dolomite. The main component is Al₂O₃. Proper production is made in the rotary furnace where sintering happens and porous granular synthetic slag with grain size from 5 to 15 mm is a result.

- **synthetic slag B** – represents the slag developed by the JAP TRADING, s.r.o. company. Mentioned slag is produced from secondary corundum raw materials, which are by-products from production of electro-melted corundum (such as for example dust and sludge), in combination with dolomitic lime and various types of binding agents (water glass or organic binder). The main components are Al₂O₃ and CaCO₃ which is a source of CaO. This type of slag is made by briquetting. In standard manner, it is delivered as briquettes with dimensions 60×50×30 mm.
Photos of separate synthetic slags for plant experiments are shown in Figure 1 and their basic chemical composition is given in Table 2 [5].

4. Evaluation and discussion of achieved results

Evaluation of slag regime by using synthetic slags A and B in the ladle during production of steels St52-3 and S34MnV was made in a few steps. At first, evaluation of influence of synthetic slags on refining capabilities of slag in the ladle by the help of achieved desulphurization degrees of separate steels was made. Degree of desulphurization is defined by following relation:

\[
\eta_s = \frac{[S_{\text{START}}]-[S_{\text{END}}]}{[S_{\text{START}}]} \cdot 100
\]

where:
- \( \eta_s \) – degree of desulphurization, %
- \([S_{\text{START}}]\) – starting content of sulfur in steel, wt. %
- \([S_{\text{END}}]\) – ending content of sulfur in steel, wt. %

Proper evaluation of desulphurization degree \( \eta_s \) (ETA S) was made for chosen technological operations proceeding during steel treatment in secondary metallurgy units:
- **ETA S LADLE** – desulphurization degree from tapping from EAF into the ladle until transport to the ladle furnace LF,
- **ETA S LF-VD/VCD** – desulphurization degree from treatment beginning at the ladle furnace LF until the end of treatment in the vacuum station VD/VCD,
- **ETA S VD/VCD** – total degree of desulphurization from tapping into ladle until the end of treatment in the station VD/VCD.

Results of desulphurization degree for steels St52-3 and S34MnV by the help of synthetic slags A and B are shown in Figure 2 and Figure 3. Achieved values represent results of separate technological operations which were processed by a statistic method box plot and added with average values.

It follows from Figure 2 during the first technological operation ETA S LADLE that in case of steel St52-3 at using synthetic slag A, desulphurization degree ETA S LADLE ~ 19%
was achieved from tapping from EAF until transport to ladle furnace (LF). In case of usage of developed synthetic slag B, the desulphurization degree ETA S LADLE ~ 23% was achieved in ladle. Similar values of desulphurization degree were obtained by the steel S34MnV (see Figure 3). At steel tapping from EAF until transport to ladle furnace (LF) was achieved desulphurization degree ETA S LADLE ~ 21% for synthetic slag A whereas for synthetic slag B a higher value, namely ETA S LADLE ~ 28% was obtained.

In case of operation ETA S LF-VD/VCD, desulphurization degrees are comparable for both steel grades and tested synthetic slags A and B. Strong growth of desulphurization degree in ladle furnace and vacuum station (LF and VDVD/VCD) can be explained with the total solution of slag-making additions. Modification of chemical composition of slag by the help of the second dose of slag-making additions (lime, synthetic slag, material for lining protection, Al and CaC2 intended for reduction of slag composition) presents another influence. Slag mixture created during synthetic slag using can be defined as a liquid slag that participates in reactions between slag and metal in an important way.

By comparison of resulting desulphurization degrees ETA S LF-VD/VCD (see Figure 2 and Figure 3), it was found that in case of steel St52-3 the same degree of desulphurization for both synthetic slags A and B was achieved, namely ETA S LF ~ 92%. A slight difference was found at steel S34MnV when the desulphurization degree ETA S LF ~ 89% was obtained at using synthetic slag A. At using synthetic slag B the desulphurization degree ETA S LF ~ 92% was achieved. This is an insignificant difference.

It is evident from the resulting degrees of desulphurization ETA S LF-VD/VCD that during production of two grades of steels St52-3 and S34MnV with a different technology by using synthetic slags A and B in effect the same desulphurization degree (89 to 92%) was achieved. It is proper to point out that each type of synthetic slag is produced from different raw materials and with different technology of production.

In the second part of evaluation of slag regime in the ladle chosen parameters of slag and their influence on desulphurization degree were monitored. Basicity, content of easily reducible oxides, proportion of CaO/Al2O3 and Mannesmann’s index belong to the monitored parameters. Except that also influence of oxygen activity on desulphurization degree of steel was qualified. Chosen parameters of ladle slag were defined by the help of following relations [6,7]:

\[
B_1 = \frac{(CaO)}{(SiO_2)}
\]

(2)

where:

- \(B_1\) – basicity
- \((CaO)\) – content of CaO in slag, wt. %
- \((SiO_2)\) – content of SiO2 in slag, wt. %

\[
B_2 = \frac{(CaO) + 2/3(MgO)}{(SiO_2) + (Al_2O_3)}
\]

(3)

where:

- \(B_2\) – basicity
- \((CaO)\) – content of CaO in slag, wt. %
- \((MgO)\) – content of MgO in slag, wt. %
- \((SiO_2)\) – content of SiO2 in slag, wt. %
- \((Al_2O_3)\) – content of Al2O3 in slag, wt. %

\[
ERO = (FeO) + (Fe_2O_3) + (MnO) + (Cr_2O_3) + (V_2O_5) + (P_2O_5)
\]

(4)

where:

- \(ERO\) – content of easily reducible oxides, wt. %
- \((FeO)\) – content of FeO in slag, wt. %

Fig. 2. Achieved degrees of desulphurization for steel St52-3

Fig. 3. Achieved degrees of desulphurization for steel S34MnV

From the comparison of separate degrees of desulphurization for both steel grades it is possible to state that in case of both types of synthetic slags A and B a similar low degree of desulphurization ETA S LADLE ~ cca 19 to 28% occurred. It can be explained with the gradual, only beginning, solution of separate slag-making additions (representing lime and synthetic slag), namely in a short time interval running cca 8 to 11 minutes.

During following technological operation ETA S LF-VD/VCD (treatment in LF to VD/VCD) multiple growth of desulphurization degree happens (see Figure 2 and Figure 3). In case of steel St52-3, the same desulphurization degree ETA S LF-VD/VCD ~ 90% was achieved by using synthetic slag A and B during treatment in secondary metallurgy units (LF to VD). Lower values of desulphurization degree were achieved by steel S34MnV during treatment in secondary metallurgy units (LF to VCD). The desulphurization degree ETA S LF-VD/VCD ~ 87% was obtained in case of synthetic slag A and desulphurization degree ETA S LF-VD/VCD ~ 88% in case of synthetic slag B.
The monitored parameters of slags that influence the desulphurization capabilities in an important way such as basicity, content of easily reducible oxides, proportion of CaO/Al2O3 and Mannesmann's index are shown in Figure 4 to Figure 9. Except influence of oxygen activity in steel on desulphurization degree for both steel grades is given here too.

Figure 4a presents the influence of basicity – B1 on desulphurization of steel St52-3. It is obvious from the figure that the starting slag basicity in the ladle achieves the values 6.3 and 6.9. Modification of chemical composition of slags occurs after the addition of the second dose of slag-making additions which was shown with the growth of basicity to the values 8.79 and 8.71. Figure 4b presents the basicity for steel S34MnV. In this case it was determined that the starting basicity after the first dose of slag-making additions reaches the values 5.66 and 7.70. The next growth to the values 8.13 and 9.24 occurs with the second dose of slag-making additions. These slags can be identify as high basicity slags, namely already at the beginning of treatment within the secondary metallurgy.

Thereafter the so-called wide basicity - B2 was defined that deals with another oxides in the slag. Figure 5a presents the influence of basicity for steel St52-3. In this case the starting basicity of slag reaches the values 1.50 and 1.71. A slight growth of basicity occurs after the addition of the second dose of slag-making additions, namely to the values 1.98 and 1.90. Figure 5b shows the results for steel S34MnV. The starting slag achieves here the basicity 1.54 and 1.78. A slight growth of basicity to values 1.99 and 1.89 occurs in this case too, namely after the addition of the second dose of slag-making additions in the ladle furnace LF.

It is also evident from Figure 4 and Figure 5 for both steel grades that a gradual fall of desulphurization degree during basicity growth occurs. This tendency can be explained with the influence of higher contents of CaO in the slag which leads to its thickening, decrease of refining capabilities and achievement of lower degrees of desulphurization. It is evident from Figure 4 and Figure 5 that the total solution of slag mixtures together with modification of chemical composition occurs with the treatment in the ladle furnace LF which was shown with the growth of basicity B1 and B2 and it helped to the higher degree of steel desulphurization. This tendency is also evident from the achieved desulphurization degree for both steel grades (see Figs. 2 and 3).

The last monitored parameter was the content of easily reducible oxides - ERO. The starting appearance of oxides in the steel St53-3 was in contents 1.68 and 1.22 wt.% for both synthetic slags (see Figure 6a). The results for steel S34MnV presents Figure 6b and the starting contents achieved the values 2.74 and 1.08 wt.%. It is possible to suppose that the certain amount of mentioned oxides is made by the passed through furnace slag of CaO/Al2O3 and Mannesmann's index are shown in Figure 4 and Figure 5 for both steel grades. Enormous desulphurization degree for both synthetic slags A and B using.

$$C/A = \frac{(CaO)}{(Al_2O_3)}$$

where:

- $C/A$ – calcium-aluminium ratio
- $(CaO)$ – content of CaO in slag, wt. %
- $(Al_2O_3)$ – content of Al2O3 in slag, wt. %

$$MM = \frac{(CaO)((SiO_2))/(Al_2O_3)}$$

where:

- $MM$ – Mannesmann's index (sulphide factor)
- $(CaO)$ – content of CaO in slag, wt. %
- $(SiO_2)$ – content of SiO2 in slag, wt. %
- $(Al_2O_3)$ – content of Al2O3 in slag, wt. %

The content of easily reducible oxides - ERO. The starting appearance of oxides in the steel St53-3 was in contents 1.68 and 1.22 wt.% for both synthetic slags (see Figure 6a). The results for steel S34MnV presents Figure 6b and the starting contents achieved the values 2.74 and 1.08 wt.%. It is possible to suppose that the certain amount of mentioned oxides is made by the passed through furnace slag from EAF (FeO, MnO, P2O5) and a part of these oxides are products of deoxidation. The cases of increased contents of easily reducible oxides were found in both steel grades. However, this tendency is strong in case of steel S34MnV and during usage of synthetic slag A.

However, decrease of content of easily reducible oxides is evident from Figure 6 for both steel grades and synthetic slags. It is possible to explain by their aluminium reduction and by CaC2 added in the ladle furnace LF during treatment. In this case, reduction of mentioned oxides to contents 1.14 wt.% and 0.67 wt. % for steel S52-3 and to contents 1.40 and 0.77 wt. % for steel S34MnV was achieved. This modification of chemical composition of slags in the ladle furnace LF made it possible to achieve the high degree of desulphurization ETA SLF-V/D/VCD (87 % to 90 %) and it supported the deep steel desulphurization (SMax, 0.005 wt. %) for both steel grades during both synthetic slags A and B using.
The influence of basicity for steel St52-3. In this case the starting highly basic slags, namely already at the beginning of treatment dose of slag-making additions. These slags can be identify as next growth to the values 8.13 and 9.24 occurs with the second of slag-making additions reaches the values 5.66 and 7.70. The was shown with the growth of basicity to the values 8.79 and 6.9. Modification of chemical composition of slags occurs after the starting slag basicity in the ladle achieves the values 6.3 and degree for both steel grades is given here too. Mannesmann's index are shown in Figure 4 to Figure 9. Except content of easily reducible oxides, proportion of CaO/Al₂O₃ and desulphurization capabilities in an important way such as basicity,

\[
\text{MM} = \frac{3 \times \text{SiO}_2}{2 \times \text{CaO}}
\]

where:

- \(\frac{\text{SiO}_2}{\text{CaO}}\) – content of SiO₂ in slag, wt. %
- \(\frac{\text{CaO}}{\text{Al}_2\text{O}_3}\) – content of CaO in slag, wt. %
- \(\text{Cr}_2\text{O}_3\) – content of Cr₂O₃ in slag, wt. %
- \(\text{Fe}_2\text{O}_3\) – content of Fe₂O₃ in slag, wt. %
- \(\text{MnO}\) – content of MnO in slag, wt. %
- \(\text{P}_2\text{O}_5\) – content of P₂O₅ in slag, wt. %
- \(\text{Al}_2\text{O}_3\) – content of Al₂O₃ in slag, wt. %

Thereafter, the so-called wide basicity - \(B_2\) was defined that Figure 4a presents the influence of basicity – \(B_1\) on the monitored parameters of slags that influence the desulphurization degree for both steel grades (see Figs. 2 and 3). The cases of increased contents of easily reducible oxides - ERO. The starting appearance of oxides in the products of deoxidation. The cases of increased contents of easily reducible oxides for both steel grades during both synthetic ETA S LF-VD/VCD optimum proportion CaO/Al₂O₃ (C/A) supporting the refining and secondary metallurgy units (at station LF to VD/VCD) targeted technological operation similar values 1.94 and 2.11 were achieved. These values represent the bottom limit of the optimum ratio (C/A) which was created with the first dose of slag-making additions. However, the separate component doesn’t need to be totally dissolved yet.

It is also evident from Figure 7 that these values go up to 2.42 and 2.28 for steel St52-3 and to 2.50 and 2.25 for steel S35MnV at the end of treatment in secondary metallurgy units. This growth is caused by the second dose of slag-making additions and by the solution of separate components of slag in the ladle furnace LF. From this development, it is obvious that during steel treatment in secondary metallurgy units (at station LF to VD/VCD) targeted modification of chemical composition of slags for achievement of optimum proportion CaO/Al₂O₃ (C/A) supporting the refining and desulphurization capabilities of slag mixtures occurred.

Following monitored parameter is Mannesmann's index (so-called sulphide factor). The optimum value of mentioned parameter should be within the limits 0.15 and 0.30. From Figure 8 for both steel grades, it is evident that with the partial solution of the first dose of slag-making additions in the ladle the synthetic slags reach values 0.22 and 0.26 for steel St52-3 and values 0.21 and 0.29 for steel S34MnV. These values respond to the bottom limit of the optimum range. However, it is obvious from Figure 8 that the addition of next slag-making additions during the beginning of treatment in the ladle furnace (LF) shown with the values growth to 0.35 and 0.34 for steel S52-3 and to 0.34 and 0.35 for steel S34MnV. These values present the upper limit of the Mannesmann's index. At monitoring of this parameter (see Figure 8) decrease of desulphurization degree came out with the increasing Mannesmann's index. It is related to the increased thickening of refining slag.

The last monitored parameter is oxygen activity in steel which presents an important thermodynamic parameter influencing the steel desulphurization. From the achieved results on Figure 9, it is evident that at tapping and during transport to the ladle furnace LF values of oxygen activity in steel 5.8 and 4.4 for steel St52-3 and values 10.5 and 5.4 for steel S34MnV were achieved. It is also obvious from Figure 9 that certain dispersion of values of oxygen activity in steel occurs, higher values point up the insufficient deep steel deoxidation. These cases were realized in both steel grades, however, in case of steel S34MnV and during usage of slag A this tendency is strong.
However, it is evident from Figure 9 that for both steel grades and synthetic slags, the decrease of oxygen activity to values 3.9 and 3.5 ppm for steel St52-3 and to values 9.0 and 5.7 ppm for steel S34MnV. This decrease can be explained by the use of deoxidation agents added in the ladle furnace LF at the treatment beginning. In this case, weaker decrease of oxygen activity in steel grade S34MnV should be noticed which is caused by production technology EAF→LF→VCD when deep cogulative steel deoxidation is not made.

It may be stated from the obtained plant results in the VHM a.s. plant that the developed synthetic slag B from the JAP TRADING s.r.o. company is comparable with the synthetic slag A which is used in a standard manner, namely on the bases of evaluation of slag regime in the ladle by the help of steel desulfurization degree according to the desulfurization degree ETA S LF-VD/VCD during the technological operation of tapping and transport to the ladle furnace LF, low degree of desulfurization achievement of deep steel desulfurization.

Acknowledgements


References


Fig. 7. Dependence of desulfurization degree on calcium-aluminium ratio – C/A

Fig. 8. Dependence of desulfurization degree on Mannesmann’s index – MM (sulphide factor)

Fig. 9. Dependence of desulfurization degree on oxygen activity in steel – a_{O2}
desulphurization results according to the desulphurization degree and other monitored parameters. It can be deduced that the synthetic slag B presenting briquetted mixture of secondary corundum raw materials can adequately replace the synthetic slag A formed by the sintered mixture of natural raw materials. These plant results also proved the possibilities of developed slag B using during the different technology of steel production under the conditions of VHM a.s.

5. Conclusions

In plant conditions of VHM a.s. plant series of experimental heats using two types of synthetic slags during production of steel grades St52-3 and S34MnV was made. The aim was to assess the effectivity of steel desulphurization for slag regime optimization in the ladle. From the obtained results of plant experiments following findings can be defined:

• during the technological operation of tapping to the ladle furnace LF, low degree of desulphurization ETA S LADLE was found out. Values 19 % (synthetic slag A) and 23 % (synthetic slag B) were achieved for steel St52-3. Values 21 % (synthetic slag A) and 28 % (synthetic slag B) were achieved for steel S34MnV which is caused by the relatively short run period of this operation and by the situation that no all slag-making additions are dissolved enough.

• during following operations between the LF station and VD/VCD, the desulphurization degree ETA S LF-VD/VCD multiple growth compared to the desulphurization during tapping into the ladle was determined. Values 90 % (synthetic slags A and B) were achieved for steel St52-3. Values 87 % (synthetic slag A) and 88 % (synthetic slag B) were obtained for steel S34MnV.

• total degree of desulphurization ETA S for steel St52-3 achieved the values 92 % (synthetic slag A and B) and values 89 % (synthetic slag A) and 92 % (synthetic slag B) for steel S34MnV were obtained.

• based on obtained values of basicity B1, it is possible to include the created slags in the ladle into the group of highly basic slags and according to the basicity B2 to the medium basic slags. The next growth of basicity and modification of chemical composition of slag in the ladle occurs with the second addition of slag-making additions which helps to the achievement of deep steel desulphurization.

• according to the results of content of easily reducible oxides ERO, penetrations of furnace slag into the ladle were determined. Except that, positive influence of reduction of mentioned oxides with the additions of aluminium and CaC2 in the ladle furnace LF was ratiffed which shown with the content decrease of monitored oxides.

• based on results of calcium-aluminum ratio, it was found out that with the first dose of slag-making additions (lime and synthetic slag) values cca 2.0 for both steel grades were achieved. The achieved value 2.0 can be considered as the bottom limit of the optimum range of proportion C/A. With the addition of the second dose (lime and aluminium) the value was further increased in range of 2.2 to 2.5.

• it follows from the achieved values of Mannesmann's index that synthetic slags used for two different steel grades move in the optimum interval 0.15 to 0.30. The upper optimum limit 0.35 is reached with the second dose of slag-making additions.

• it was found from the results of oxygen activity in steel that decrease of oxygen activity occurs with the first dose of dezoxidation additions during tapping, namely from values cca 400 - 800 ppm measured in EAF just before tapping to values cca 5 to 10 ppm measured during the beginning of steel treatment in LF. The next decrease happens with the addition of dezoxidation agents for achievement of deep steel desulphurization (SMax. 0.005 hm %) in the following treatment in secondary metallurgy units, namely for both steel grades and at usage of both synthetic slags A and B.

• synthetic slag B presenting the briquetted mixture of secondary corundum raw materials can adequately replace the synthetic slag A formed by sintered mixture of natural raw materials.

• in the next stage of research of synthetic slags and optimization of slag regime, the attention will be focused on confirmation of these plant results during production of different grades of steel.

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