A R C H I V E S O F M E T A L L U R G Y A N D M A T E R I A L S
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USE OF INDUSTRIALLY PRODUCED SYNTHETIC SLAG AT TŘINECKÉ ŽELEZÁRNY, A.S.

WYKORZYSTANIE PRZEMYSŁOWYCH ŻUŻLI SYNTETYCZNYCH W HUCIE TŘINECKÉ ŽELEZÁRNY, A.S.

The paper summarises experience with using synthetic slags on the CaO – Al_2O_3 oxide basis in the technological flow of the oxygen converter steelworks in TŘINECKÉ ŽELEZÁRNY, a.s. These slags are used as an alternative to slags containing fluorspar which unfavourably affects both the service life of ladle linings and the steelwork's working environment. The content gives the first knowledge of using the Refraflux type synthetic slag to desulphurize steel, and it also provides a basic statistical evaluation of the heat produced.

Keywords: oxygen converter, secondary metallurgy, steel desulphurization, synthetic slag

W pracy podsumowano doświadczenia z użyciem żużli syntetycznych bazujących na tlenkach CaO – Al_2O_3 w technologii dmuchu tlenu w konwertorze stalowni TŘINECKÉ ŽELEZÁRNY, a.s. Żużle te są stosowane jako alternatywa dla żużli zawierających fluoryt, które niekorzystnie wpływają zarówno na żywotność wyłożenia kadzi i środowisko pracy stalowni. Artykuł przedstawia pierwsze doświadczenia z wykorzystaniem syntetycznych żużli typu Refraflux do odsiarczania stali, a także podstawowe dane statystyczne wytopu.

1. Introduction

Methods for the use of high quality industrially produced homogeneous synthetic slag in the metallurgical plants bring a number of metallurgical and economic benefits. These can be seen not only in achieving the desired cleanliness of steel, but also as a possible compensation for the lack of advanced (and expensive) technological equipment for not only the steel production, but as well as for the outside-of-furnace steel processing. Production technology using synthetic slag can achieve some excellent parameters in desulphurization with the end sulphur contents as low as 30 ppm. The positive aspect is the time for steel processing, which not only results in the possibility to increase the performance of individual production units, but also in reducing the total cost, including energy consumption, flux, ferro-alloy, alloying elements, refractories, and others.

For the conditions of oxygen steelworks TŘINECKÉ ŽELEZÁRNY, a.s. (TŽ, a.s.) the proposal for service testing, evaluation of results, and recommendation of metallurgical-technological measures to achieve the levels of sulphur in steel produced as low as 0.012, respectively to 0.005 wt.% was submitted using industrially produced synthetic slag (fluorspar-free), including laboratory evaluation of their physical and chemical properties.

In terms of the product range, the Al-killed steel with carbon content up to 0.25 wt.%, manganese content up to 1.5 wt.%, carbon content to 0.45 wt.% and manganese one up to 1.2 wt.% has been tested. The steel processing in a vacuum was not required, and heat produced was consequently cast on the continuous casting machine No. 1 (hereafter referred to as CCM No. 1).

2. Primary factors affecting the desired level of steel desulphurization

In the area of a production unit – the LD-type oxygen converter is one of the limiting factors for achieving the required degree of desulphurization, not only the sulphur content in raw iron, but also in the scrap charge. Although there is desulphurization equipment with the iron desulphurization options up to 0.003 wt.% avail-

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able, when using all the common scrap charge resources (internal and external), the achieved sulphur content values after completing the blowing process in the converter are relatively high and usually around 0.025 wt.%. Other ingredients set into an oxygen converter are also significant sources of sulphur (slag formers, carbon materials used for the chemical reheating, raw materials used for refractory linings to protect the converter from erosive and corrosive effects of the steel and slag etc.). These are followed by other, relatively important sources of sulphur present in metallic and non-metallic additives, that are added to the liquid bath during steel deoxidation and alloying during its tapping into ladles, and consequently during the further secondary metallurgy steel processing.

Technological and metallurgical options for the desulphurization of steel are given not only by the technological device for secondary metallurgy, but also by the management and control of technology and metallurgy of desulphurization processes. These include optimizing of the slag regime and compliance with the basic thermodynamic and kinetic parameters of slag and metal [1].

The ionic theory of desulphurization shows that to achieve low sulphur content in metal the following needs to be reached:

• high activity levels of free oxygen anions in the slag, i.e. high basicity of slag with high proportion of basic and low proportion of acidic oxides,

• low activity of oxygen a_o in the steel, i.e. low content of dissolved oxygen as well as low activity coefficient f_O values.

Another negative factor affecting the degree of steel desulphurization is the presence of "slightly reducible" oxides in the refining slag – beside FeO, those also include MnO, P_2O_5 and Cr_2O_3. Their summary percentage content in case of well-operating refining slag in the secondary metallurgy steel processing in ladle furnaces is generally recommended to be as low as possible, preferably to 3 wt.%.

From the kinetic point of view, the steel desulphurization is positively affected by the temperature increase. Increasing the temperature helps to reduce the viscosity of slag and metal, increasing the diffusion coefficient of sulphur and reduction of surface tension which results in a faster approximation of the reaction to the equilibrium.

3. Current technology-metalurgical processes for production of steel with low-sulphur content under TŽ, a.s. conditions

The secondary metallurgy steel processing in the TZ, a.s. is equipped with a homogenization station with argon blowing function (HS), ladle furnace (LF) and degassing unit by the RH process. After completion of steel tapping the steel is processed by argon using a blow lance introduced through the top surface of steel. At temperatures around 1580°C, and in addition to the thermal and chemical homogenization, the steel desulphurization occurs as well. Another transfer to the ladle furnace facility results in a gradual steel cooling in the ladle and thus to a deterioration of thermodynamic and in particular kinetic conditions of the ongoing reactions between the slag and metal. The process renewal of desired reactions does not occur in the ladle until the gradual heating of the steel in a ladle furnace. Also, this final area of steel processing must consider some of the sulphur carriers.

Production technology of steel with low sulphur content below 0.005 wt.% in the oxygen converter steel plant, TRINECKE ŽELEZÁRNY, a.s., currently uses mostly slag containing CaF_2 (calcium fluoride – fluorspar). During the tapping of steel or also in the ladle furnace the CaF_2 additive is carried into the ladle, and thus allowed reach relatively very high quality kinetics of the desulphurization process using alkaline slag of the desired composition.

In metallurgical practice, the CaF_2 beneficial effect in molten slag set for desulphurization is broadly known. For the slags with a low content of silica, the affirmative beneficial effect of CaF_2 could be explained by slag dilution, in which the slag melting temperature is reduced due to formation of the highly meltable CaO-CaF_2 phases with lower viscosity. CaF_2 has been also promoting a reduction of the sulphur activity in the slag, leading to an increased capacity of the slag to bind sulphur.

Disadvantages of using the fluorspar technologies may be viewed from two main aspects:

a) fluorspar in contact with liquid metal and/or liquid slag releases environmentally unfriendly fluorides (e.g. SiF_4), which worsen the working and living environment,

b) fluorspar in the ladle slag increases lining wear, especially in the area of the ladle slag line, and thus significantly reduces the overall life of the ladle lining

That is why both many foreign and domestic steelworks are starting to abandon the use of fluorspar for a slag forming additive and seek compensation in the form of industrially produced synthetic slag that is economically affordable. The current proposals in top companies include a quality, industrially produced synthetic slag, which is provided in different proportions between Al_2O_3/CaO as well as in the form of, for example, granules, pellets, little briquettes, crushed pieces, etc. Their advantage is mostly a guarantee of an exact desired chemical composition along with high homogeneity. The slag is typically designed for use with a lime additive in

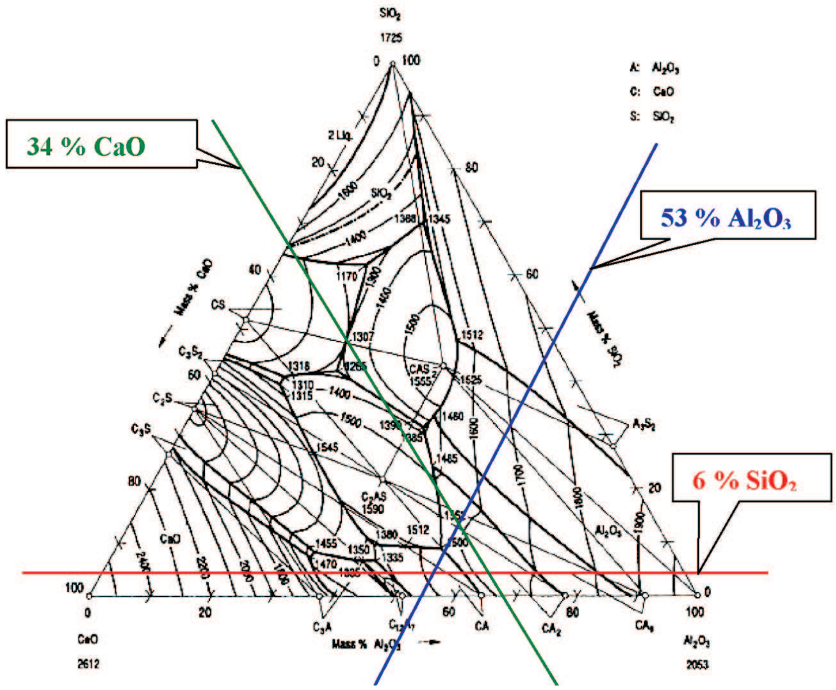

Fig. 1. Area of chemical composition of tested synthetic slag in the Al_2O_3– CaO – SiO_2 ternary diagram

the ladle, while creating the final slag system with the desired flow properties and basicity.

Another group of slag forming materials is the mixtures prepared from differently treated waste materials or other technical products. Mixtures of this type could be also named "solvents" for making the ladle slag liquid; however, those cannot significantly activate the conditions for deep desulphurization; for example, a waste product generated during the production of ferrovanadium using the aluminothermic method. Its disadvantage is also that it contains about 3.5 wt.% V_2O_5.

4. Service test proposal using refraflux 3452s synthetic slag

Based on the analysis of available scientific data and the investigators' personal experience, the synthetic slag produced by the REFRATECHNIK company under the name REFRAFLUX 3452 S has been purposely selected for operational testing [2].

This material is in the shape of pellets and their fractions with granulometry from 5 to 20 mm. The chemical composition is a mixture of two basic oxides – the slag contains about 53 wt.% of Al_2O_3 and 34 wt.% of CaO. In addition, the slag also contains 6.8 wt.%. of SiO_2 and about 2 wt.% of Fe_2O_3 and TiO_2 [3].

Figure 1 shows the chemical composition of the tested industrially produced synthetic slag in the Al_2O_3 – CaO – SiO_2 ternary diagram. It therefore concerns synthetic slag, which is designed for use with lime, which provides for better assimilation and the consequent liquidity process of the entire slag system.

The nature of synthetic slag service testing consisted of a targeted change in dosage of slag during steel tapping and processing on individual units for the secondary metallurgy processing together with the change of other influential parameters such as quantity of lime, CaC_2, aluminium, processing time, oxygen activity in steel etc. So far, 45 operational heats have been produced.

5. Achieved results

For the scientific assessment of individual parameters and their impact, the method of statistical analysis was used. The data file contained more than 100 variables sorted facing the flow direction of steel processing on the units introduced (tapping from LD, HS, LF, RH). It was not only the quantitative parameters determining the amount of additives, the chemical composition of slag, and steel, but also categorical variables such as the occurrence of "re-blows" after completing the main blowing process, slag-free tapping code etc.

Given the starting statistical analysis, the need to obtain quick results, and (so far) as well as a low range of the data, only a paired linear regression (for quantitative regressors) and a single-factor ANOVA (for qualitative regressors) were conducted. The exploratory analysis, time series analysis and paired non-linear and multiple regression are yet to be performed.

Suitability of the desulphurization technology options was evaluated based on the achieved *degree of steel desulphurization* η, which is defined in agreement with the practice by the following dependence: $(S_{init}-S_{final})/S_{init}*100$ [%]. The degree of desulphurization has been evaluated for each technological operation:

▶ *etaS_o* – degree of desulphurization during tapping, respectively from the start of steel tapping from the oxygen converter through the casting ladle to transfer into the homogenization station

▶ *etaS_HS* – degree of desulphurization at homogenization station (HS)

▶ *etaS_LF* – degree of desulphurization during processing in the ladle furnace (LF),

▶ *etaS_RH* – degree of desulphurization during processing of steel at RH station,

▶ *etaS_celk* – overall degree of desulphurisation.

See Figure 2 for a summarized box diagram that shows the degree of desulphurization for each technical operation during molten steel processing. The graph shows that the desulphurization during tapping and processing at HS is characterized by low efficiency (with an average degree of desulphurization equalling to 8.3 and 12.1%, respectively). Regarding processing in LF and RH, the efficiency is then already significantly higher (34 and 41%, respectively). As also shown at the graph referred to, the overall degree of desulphurization reaches 75% of mean value.

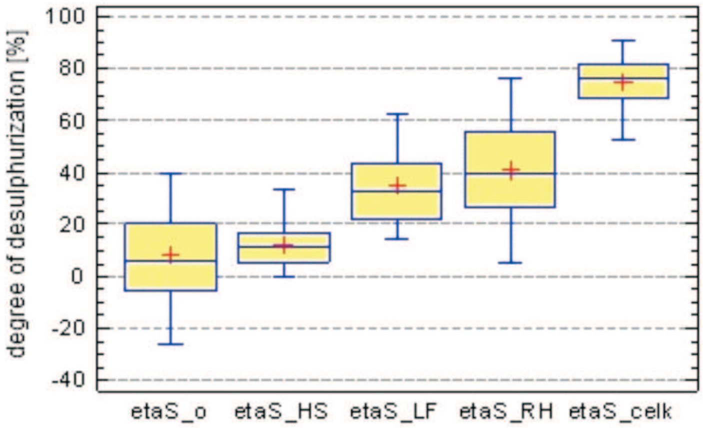

Fig. 2. Box diagram of desulphurization degrees in molten steel processing

TABLE 1

Paired regression results for the total degree of steel desulphurization – etaS_celk

Object	Parameter	Sign	R^2 [%]	Evaluation, Recommendation–the better is/are
LPp (ladle)	vapno (lime)	+	21.3	Higher amount (very significant)
	REC2	–	11.8	Lesser amount
	CaC_2	+	28.1	Higher amount (very significant)
	AlG	+	19.4	Higher amount (very significant)
	Refr2	+	11.6	Higher
HS	Alp (Al init)	+	10.3	Higher
	Alk (Al final)	+	19.0	Higher amount (very significant)
HSs	·	·	·	Effect of HSs parameters is not practically shown
LFp	Refr2	+	9.9	Higher weight of additive
LF	doba (period)	+	32.9	Longer time period of steel in LF (very significant)
	Alp (Al init)	+	26.2	Higher initial Al content
	aktOp	–	16.7	Lower initial activity of oxygen < 3
	Pp (Pinit)		17.3	Initial lower phosphorus content
LFs	Al_2O_3	+	14.8	Higher
	baz	+	12.7	Higher than 5
	MnO	–	11.3	Lower
	P_2O_5		20.2	Lower (very significant)
	SiO_2		14.3	Lower
RHp	Rec1	–	20.2	Lower (very significant)
RH	(period)	·	·	Effect of period in RH is not practically shown

Statistical analysis was focused on assessing the parameters that have a more significant impact on the overall degree of steel desulphurization between the initial state (sulphur content in steel during tapping) and the final state (resulting sulphur content in steel – final heat analysis). The results brought by paired regression are statistically significant regressors (at significance level α = 0.05 or 0.10) shown in Table 1. For better understanding Fig. 3 – Fig. 12 show the paired regression graphs of significant regressors.

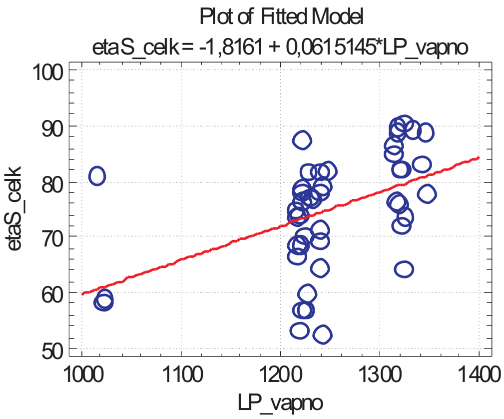

Fig. 3. etaS_celk ← LP_lime regression

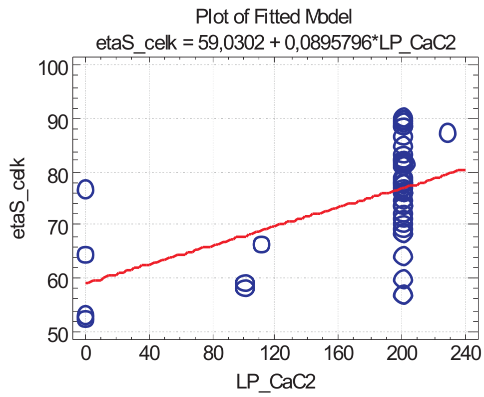

Fig. 4. etaS_celk ← LP_CaC$_2$regression

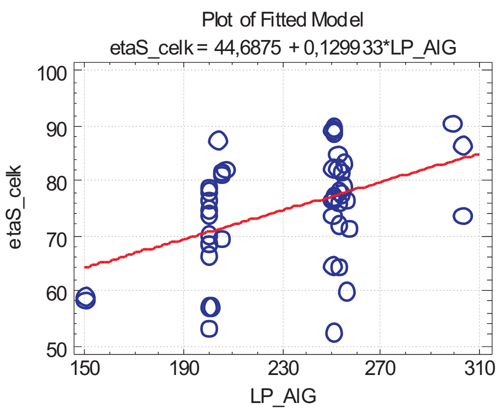

Fig. 5. etaS_celk ← LP_AlG regression

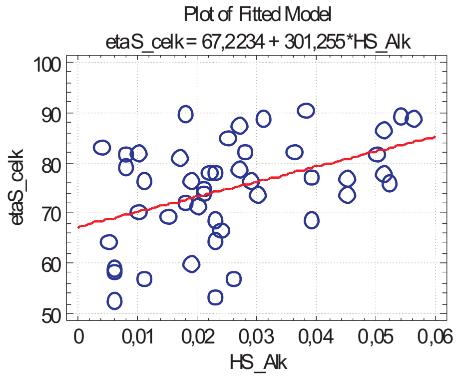

Fig. 6. etaS_celk ← HS_Alk regression

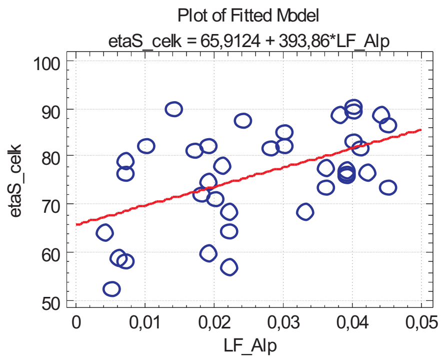

Fig. 7. etaS_celk ← LF_Alp regression

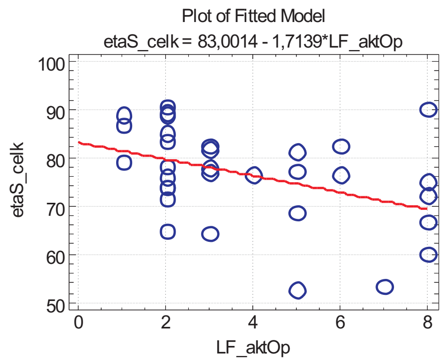

Fig. 8. etaS_celk ← LF_aktOp regression

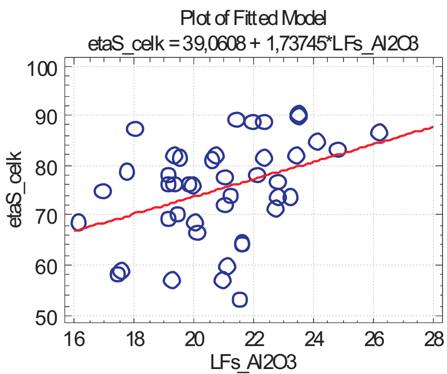

Fig. 9. etaS_celk ← LFs_Al$_2$O$_3$ regresion

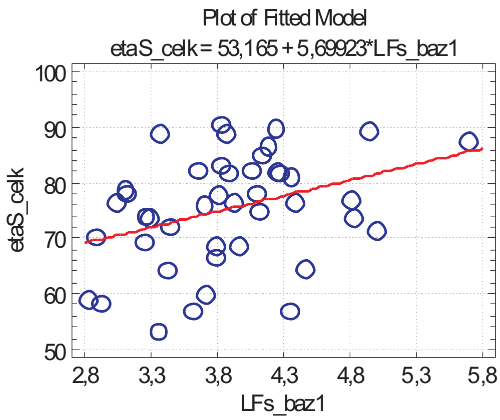

Fig. 10. etaS_celk ← LFs_baz1 regression

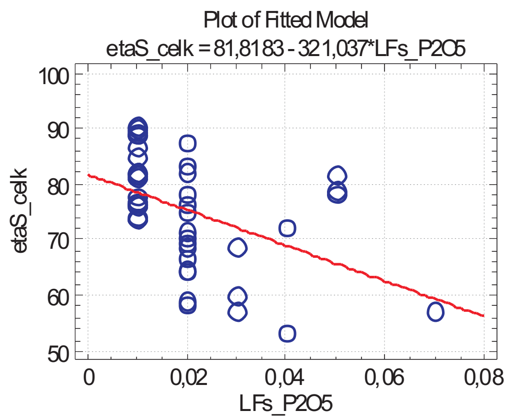

Fig. 11. etaS_celk ← LFs_P_2O_5 regression

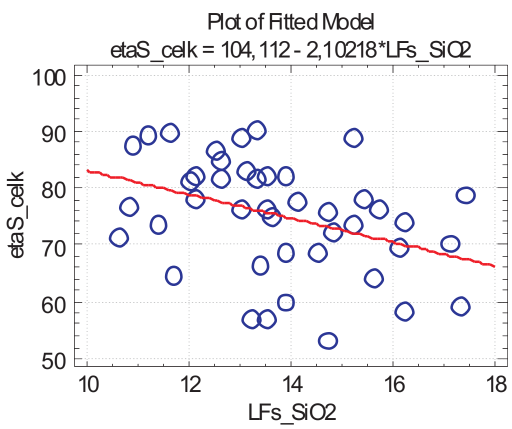

Fig. 12. etaS_celk ← LFs_SiO_2 regression

From the statistical evaluation of the experimental heat data file using the paired regression method, it can be concluded that the resulting degree of steel desulphurization throughout the entire technological cycle of tapping, followed by homogenization, LF, RH, incl. transfer to the CCM is positively affected by the following parameters:

- higher amounts of lime additives, CaC_2, Refraflux, AIG into the casting ladle during tapping,
- higher content of aluminium and related lower activity of oxygen in molten steel (>0.035 wt. % Al, <5 ppm oxygen) during the entire secondary metallurgy steel processing,
- higher slag basicity during the entire secondary metallurgy steel processing (above 4.5),
- higher contents of Al_2O_3 content in refining slag (>25 wt. %), respectively optimum ratio between CaO/ Al_2O_3,
- low content of MnO, P_2O_5 and SiO_2 in the refining slag (¡0.4 wt. % MnO, <0.01 wt. P_2O_5%, <12% wt. SiO_2),
- more time needed to process steel for LF.

In addition, when evaluating the partial degrees of desulphurization process for each metallurgical machine of the secondary metallurgy processing it was found that:

- increased argon flow rate into a bath positively affects the partial degree of desulphurization during tapping (etaS_o),
- low Fe (or FeO) values in slag significantly affect desulphurisation during steel processing at the homogenization station,
- there is a link between the lower degree of steel desulphurization and the chemical content as well as between the higher content of SiO_2 and MnO in converter slag, which is apparently related to the fact that during tapping, despite using the method of ”slag-free tapping” a certain proportion of converter slag gets into the ladle,
- processing in LF was conducted with the knowledge of the subsequent completion of the heat on RH with a potential further sulphur decrease. If it were the non-vacuum heats, it would be possible to further optimize the course of desulphurization in LF just like in the final production unit with a higher degree of desulphurization.

6. Conclusion

A series of experimental heats using the synthetic slag under the trade name REFRAFLUX 3452S was carried out under operating conditions of the oxygen converter steel mill in TŽ, a.s. in order to optimize the process of desulphurization using ”fluorspar-free” technology with the requirement of target sulphur levels being below 0.012, respectively 0.005%.

Service tests with the said synthetic slag consisted of a purposeful change in the slag dosage during steel tapping and processing in the individual units for the secondary metallurgy processing together with a change of other raw materials as well as influential parameters, such as the amount of lime, CaC_2, aluminium, processing time, activity of oxygen in steel etc.

From the statistical evaluation of the data file, which contained more than 100 variables, the basic parameters that may significantly increase the efficiency of desulphurization using this slag were defined. Optimization interventions that were carried out and built on the results achieved resulted in the increase of desulphurization of a degree up to 90%, with final sulphur contents starting from 0.003 up to 0.005%.

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