

POSSIBILITIES FOR INCREASING THE PURITY OF STEEL IN PRODUCTION USING SECONDARY-METALLURGY EQUIPMENT

MOŽNOSTI POVEČANJA ČISTOSTI JEKLA PRI PROIZVODNJI Z UPORABO OPREME ZA SEKUNDARNO METALURGIJO

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The possibilities for increasing the purity of steel during the production of the liquid phase using secondary metallurgy mainly relate to affecting the number of emerging occlusions, their size, morphology and chemical composition. The metallographic purity of steel during production in an electric-arc furnace (EAF), in a ladle furnace (LF) and during processing with VD caisson technology was assessed. The steel samples were processed by means of an electron microscope and were simultaneously tested using the single-spark-evaluation (SSE) method.

The aim of this investigation was to find the possibility for an operative steel-quality control and to obtain the desired mechanical properties already while processing the liquid phase.

Keywords: steel purity, secondary metallurgy, occlusions, electron microscope, single-spark evaluation

Možnosti povečanja čistosti staljenega jekla med proizvodnjo z uporabo sekundarne metalurgije so predvsem glede na količino vključkov, njihove velikosti, vrsto morfologije in kemijsko sestavo. Metalografsko je bila ugotavljana čistost jekla med proizvodnjo v elektroobločni peči (EAF), nato v ponovni peči (LF) in po obdelavi v VD. Vzorci so bili pregledani z elektronskim mikroskopom in so bili preizkušeni z metodo plamenskega odžiganja (SSE).

Namen je bil poiskati učinkovito kontrolo jekla in vplive na želene mehanske lastnosti že med obdelavo taline.

Ključne besede: čistost jekla, sekundarna metalurgija, zapore, elektronska mikroskopija, ocena s plamenskim odžiganjem

1 INTRODUCTION

The continuously increasing requirements for achieved levels of mechanical values like ductility, toughness and fatigue properties for steel are increasing the demands put on manufacturers when it comes to searching for new technological processes. One of the main possibilities for achieving higher levels of mechanical properties for steel increases with its metallurgical purity. This can be achieved with the technological processes utilised in secondary metallurgy that can affect the size, the quantity of inclusions and their morphology.¹ Within the conditions existing at the steelworks of Vítkovice Heavy Machinery a.s. (VHM), there are facilities for processing steel in a ladle furnace (LF) and for vacuum steel processing in a caisson (VD).

The objective of the study was to assess the continuous metallographic purity in the course of steel production in an electric-arc furnace (EAF), in a ladle furnace (LF) and during vacuum processing in a caisson using the VD technology. The study was based on the idea that the implemented technological processes (TS No. 1 and TS No. 2) can assist in obtaining metallographic purity.

Metallic disk-pin samples were collected during the steel's production from secondary-metallurgical aggre-

gates of LF and VD. Consequently, they were processed with an optical emission spectrometer, which assesses the analytical signal, while differentiating each individual spark with the single-spark-evaluation (SSE) method. A part of the analytical signal corresponds with the average content of an element in the collected sample (classically in the course of the steel's production process), while the second signal part corresponds with the elemental concentration in the inclusion. The single-spark-evaluation (SSE) method helps us assess information about the amount, the type and the composition of the inclusion. A big advantage of the SSE method is the fact that the sample preparation for the analysis with a spectrometer is identical to the disk-pin sample preparation. Analyses of the standard control sample of the steel's chemical composition were extended by only 20 s. The method took place online. The software for the optical emission spectrometer was set up for an elemental analysis in relation to the chemical composition of the produced steel.²

In order to express certain opinions about the values measured with the SSE method, identical samples, collected in the course of the steel's production, were consequently also processed with a roentgen spectral analysis (using an electron microscope) and subjected to

a metallographic assessment, which was generally recognised within the metallurgical practice. The analyses of the inclusions with the assistance of the roentgen spectral analysis were performed on the basis of the Pirelli Norm No. 18. V. 008 rev. 7 metallographic test of the microstructure and of the defects of the rod wires. The test was slightly modified for the disk-pin measurements. The device scans the image in the BSE mode (reflected electrons); the image size is 1024×1024 pixels at a magnification of 500-times; the field of vision has a size of $0.25 \text{ mm} \times 0.25 \text{ mm}$; and the scanning time for a single pixel is 2800 ns. It looks for inclusions based on the set brightness threshold and then it analyses them. The threshold is set in such a way that all the oxides are recorded, while in the case of sulphides only the partly complex ones (with an oxidative core) are recorded. The analysis is performed for 5 s at about 25 % of the detector's dead time. This corresponds to an intensity of about 4500 impulses per second. The electron beam focuses on the particle's centre of gravity during the analysis. The set of results from the analysed particles passes through a filter that ensures the exclusion of the non-oxidative included particles and, as a result, records them in a ternary diagram with the silicates in one corner, aluminates in the second corner and the remaining oxides (Mn, Ca, and Mg) in the third corner. Particles larger than $1 \mu\text{m}$ are measured. The total assessed area of a sample consisted of 80 fields, i.e., 5 mm^2 , which corresponded to the size of the metallic-sample areas analysed with the SSE method. The measured areas were fully comparable for both measurement techniques.

2 EXPERIMENTAL

The samples were manually collected from the furnace with the assistance of submersible disk-pin samplers and they were identical for both methods of steel purity assessment. The first sample, marked as LF1, represented the beginning of the steel-processing technology in the ladle furnace and, at the same time, the result of the preliminary steel de-oxygenation in the ladle furnace (LP) after the completed tapping, without slag, of the electric-arc furnace. In order to ensure standardisation, a temperature of $1580 \text{ }^\circ\text{C}$ was selected for the LF at the beginning of the collection of each LF1 sample. Considering a certain time delay, related to the necessary heating of the tapped and de-oxygenated melt to that temperature, we assumed a good melt-concentration homogeneity was achieved, including a good liquid, and mixed the newly occurring basic slag. The sample LF2 represents the melt situation at the end of the melt processing in the ladle furnace, where the main stress was put on the creation of the melt slag mode. The LP with the melt was prepared for the subsequent steel vacuuming in the caisson furnace using the VD process. A detailed technological prescription TS 1, prepared by VHM, established the steel temperature before the vacuuming, the steel's chemical composition, the slag parameters, and the oxygen activity. The samples VD1

and VD2 were collected at the beginning and at the end of the steel's vacuum processing in the furnace. The 15 min of homogenisation using porous argon followed after the sample's VD2 collection. The samples were collected from melts processed by following two technological processes. The sample collections from melts No. K58494, K58500, K58507, K58508, K58509, K58555 were performed following the technological process TS No. 1, while the sample collections from melts No. K58489 and No. K58495 followed the technological process TS No. 2 prepared at VHM.

The technological instructions differ, especially in terms of the method of the preliminary steel de-oxygenation in the ladle furnace after the tapping of the electric arc furnace. Other principles of the melt management in the ladle furnace or in the caisson are almost identical.²

TS No. 1

- 2 kg/t of CaC_2 into the ladle furnace (LP) before the tapping,
- FeSi to 0.15 % (steel in the furnace without Si after the oxygenation),
- Calcinated anthracite in the course of carbonaceous steels, e.g., C45,
- Al 0.3–0.6 kg/t into the flow in the course of the first tapping third, depending on the produced steel and according to the melted C content
- Pieces of CaO + synthetic slag + FeMn follow (up to 2/3 of the production composition),
- Possibly FeCr (none in the case of melts monitored by us)
- 0.3–0.6 kg/t of Al, again in the course of the last tapping third

TS No. 2

- 3.0 kg/t CaC_2 + min. of 3.0 kg/t of the calcinated anthracite into the ladle furnace (LP)
- FeMn (up to 2/3 of the production composition) + CaO + synthetic slag during the tapping, before the end of the tapping
- 0.5–0.7 kg/t of Al, according to the melted C

3 DISCUSSION

When assessing the research results, we must consider that the performed analysis could not be identical to the resulting composition of inclusions in the final product. The difference is given especially by the different speeds of cooling for the relatively small metallic sample, when compared with, for example, an ingot of many tons. The analysis does not present the inclusion composition and their quantity in the final product, but the actual inclusion types and the purity of the steel, which are analysed in the course of the technological steps LF and VD.

The following set of figures (**Figures 1 to 6**) summarises the results of the analysis of the number of inclusions performed with a microprobe.

The above-presented figures clearly show that the inclusion density in the individual melts progressively decreased in the course of the technological process. The fundamental decrease in the inclusion density took place in the course of the melt processing in the ladle furnace. This trend is clear for inclusions up to 4 μm in size. The density of the smallest inclusions then changed only a little, or not at all, in the subsequent vacuum steel processing because of their low concentration. In the

case of some melts, even a small increase was noticed. Inclusions larger than 4 μm occur rarely in the samples and their occurrence is thus accidental. No clear trend was noticed. However, we can assume that their occurrence at the end of the technological process in VD is close to zero. The melts 58489, 58495 and 58527, which went through a different de-oxygenation process, differ to some extent from the set. The density of inclusions is lower at the beginning. These melts were produced by TS No. 2.

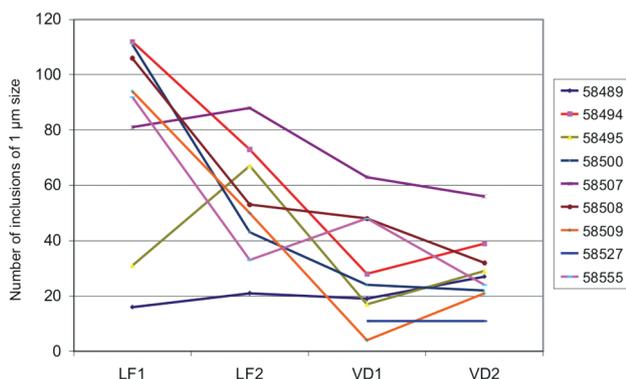


Figure 1: Summary of 1-μm inclusions' density during individual technological operations, in all the monitored melts

Slika 1: Število vključkov velikih 1 μm med posameznimi tehnološkimi operacijami v vseh preiskovanih talinah

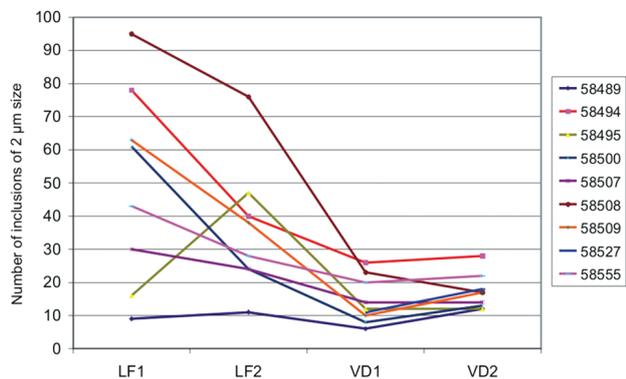


Figure 2: Summary of 2-μm inclusions' density during individual technological operations, in all the monitored melts

Slika 2: Število vključkov velikih 2 μm med posameznimi tehnološkimi operacijami v vseh preiskovanih talinah

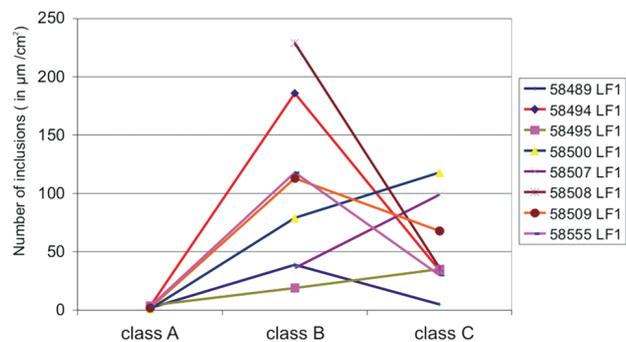


Figure 3: Numbers of inclusions in individual areas of the ternary diagram for the sample LF1 collection

Slika 3: Število vključkov v posameznih področjih ternarnega diagrama za vzorce iz LF1

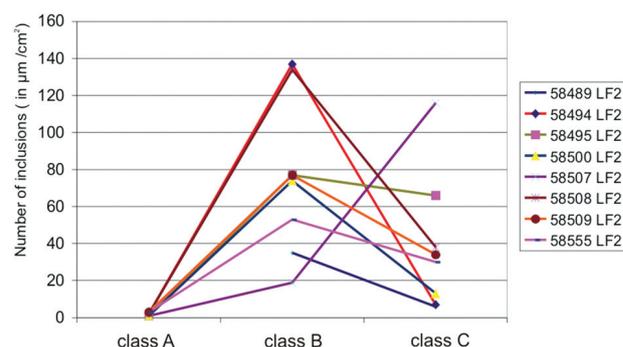


Figure 4: Numbers of inclusions in individual areas of the ternary diagram for the sample LF2 collection

Slika 4: Število vključkov v posameznih področjih ternarnega diagrama za vzorce iz LF2

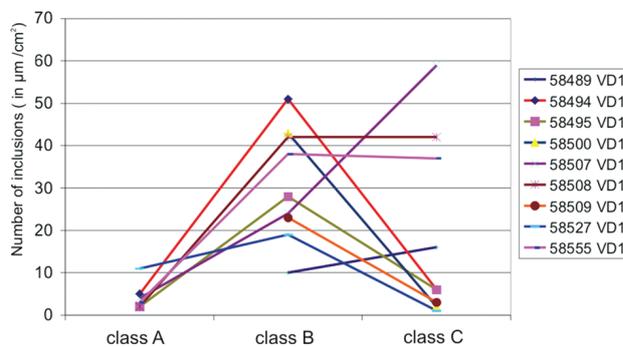


Figure 5: Numbers of inclusions in individual areas of the ternary diagram for the sample VD1 collection

Slika 5: Število vključkov v posameznih področjih ternarnega diagrama za vzorce iz VD1

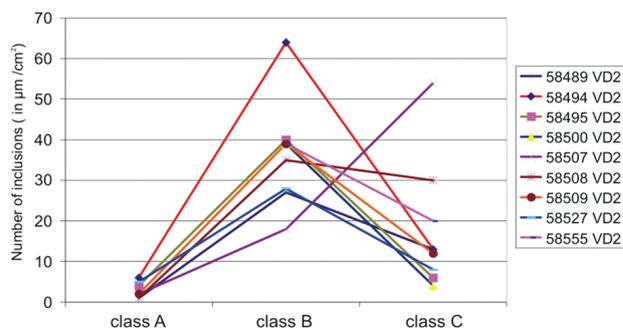


Figure 6: Numbers of inclusions in individual areas of the ternary diagram for the sample VD2 collection

Slika 6: Število vključkov v posameznih področjih ternarnega diagrama za vzorce iz VD2

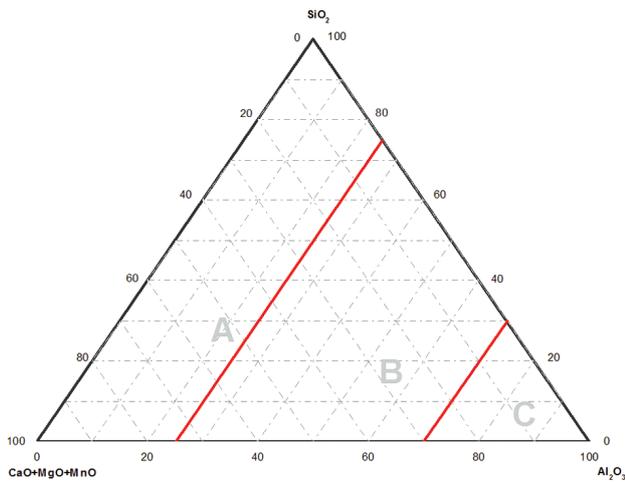


Figure 7: Scheme of the inclusions' division into individual classes
Slika 7: Shematičen prikaz razporeditve vključkov v posamezne razrede

The inclusions were divided into three groups using the following scheme (Figure 7) to monitor their chemical composition.

The inclusion compositions in individual melts and stages were similar. We can claim that:

- Inclusions from Zone A in the ternary diagram are practically absent in LF
- A small number of inclusions from Zone A occur in VD

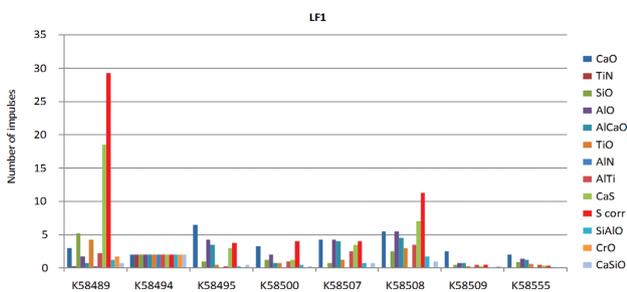


Figure 8: The average number of impulses for the individual elements and melts LF1

Slika 8: Povprečno število impulzov za posamezne elemente iz taline LF1

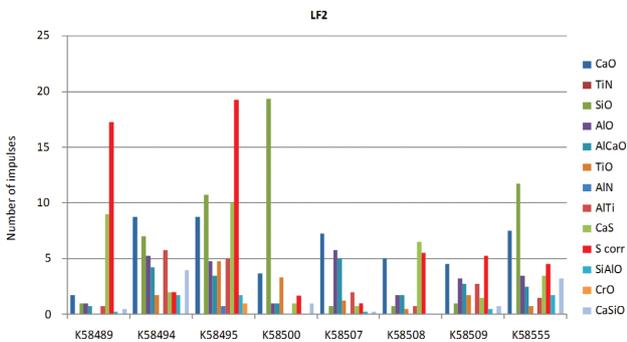


Figure 9: The average number of impulses for the individual elements and melts LF2

Slika 9: Povprečno število impulzov za posamezne elemente iz taline LF2

- The dominant inclusion group consists of the inclusions from Zone B
- The main parts of the individual inclusions are Al, Ca, and O

The measured and presented results suggest that their effects, from the point of view of the number of inclusions in both technologies, TS No. 01 and TS No. 02, are similar. The result of the use of TS No. 02 is only the smaller number of inclusions at the beginning of the technological process in LF. When using TS No. 01

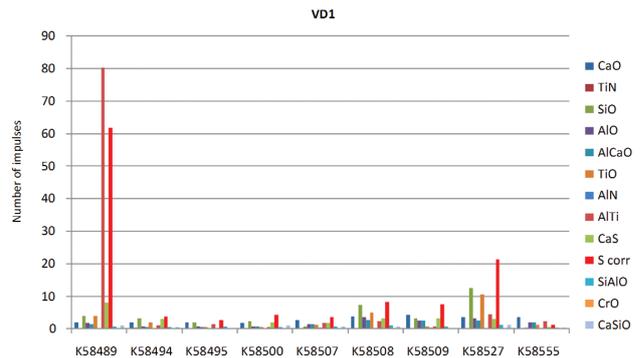


Figure 10: The average number of impulses for the individual elements and melts VD1

Slika 10: Povprečno število impulzov za posamezne elemente iz taline VD1

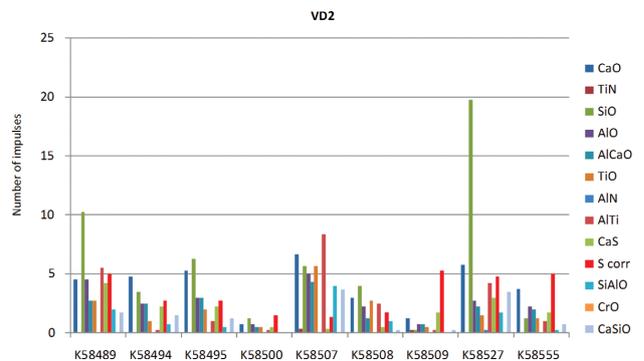


Figure 11: The average number of impulses for the individual elements and melts VD2

Slika 11: Povprečno število impulzov za posamezne elemente iz taline VD2

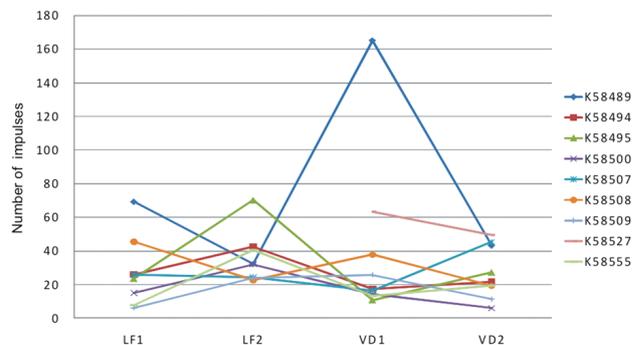


Figure 12: The number of impulses in the course of the steel processing LF1-VD2

Slika 12: Število impulzov med izdelavo jekla (LF1-VD2)

and TS No. 02, the inclusion number and their size become almost equal at the end of the processing in LF. Inclusions larger than 4 μm occur very rarely and accidentally.

The fundamental decrease in the number of inclusions occurs only by 3/4 in the course of steel processing in the LF. The processing in VD does not present a more pronounced change in the number of smaller inclusions, up to 2 μm . The occurrence of inclusions larger than 3 μm is negligible.

From the chemical inclusion composition in the LF point of view, the inclusions from Zone A are not present in any of the tested melts. A slight increase occurs only in the course of the VD technology. The inclusions from Zone B are the dominant ones. Their number from LF1 to VD 2 decreases in accordance with the above-presented conclusions. The Zone C is basically a half of Zone B, where the inclusions of the type $\text{CaO}\cdot\text{Al}_2\text{O}_3$ prevail. Only very fine inclusions of the $\text{CaO}\cdot\text{Al}_2\text{O}_3$ type and pure Al_2O_3 , but also CaO , remain at the end of the VD technology.

The results obtained with the SSE method were based on an analysis of 2000 sparks. If any particles of a different composition than those in the basic metallic matrix, occurred in a given place, they are in the peaks of the present elements and, then, their bonds could be analysed. Each analysis of the relevant sample (disk-pin) was performed in three places, always in such a way that the relevant axis part of the sample was not affected and the measurements were averaged.

The measured values of the analysed samples are summarised graphically in **Figures 8 to 11**. The number of sparks for the melt and the technological step are on the x -axis (2000 for each measurement). The individual colours mark inclusions based on the mentioned elements. The number of impulses is on the y axis.³

The individual analyses and melt graphics, inclusion types and technological steps of the production material flow suggest that the mutual connections in the inclusion volume and number, between individual samples for melting or for individual technological steps LF1, LF2, VD1 and VD2, seem difficult to define. Inclusions based on elements like aluminium and oxygen (AIO) occur more frequently than those based on aluminium, calcium and oxygen (AlCaO). Inclusions based on manganese and oxygen (MnO) or on manganese and sulphur (MnS) were not detected because the optical spectrometer Spectro Lab M10 was not equipped with a photomultiplier for manganese. MnS inclusions were thus derived by calculation from the value S_{corr} . There is a relation $\text{MnS} = S_{\text{corr}} - \text{CaS}$, where (S_{corr}) is the total content of inclusions incorporating sulphur and (CaS) are the inclusions based on calcium and sulphur. The analysis suggests that the number of inclusions (CaS) means a significant amount. We assume that the remaining number of inclusions based on sulphur has got the form of MnS inclusions. The occurrence and the number of inclusions based on aluminium and nitrogen (AlN) and those based on titanium and nitrogen (TiN) is

not important. The occurrence of inclusions based on aluminium and oxygen (CaO) and the sulphur content show mostly the decreasing character. The relatively high and unbalanced contents of inclusions based on silicon and oxygen (SiO) are an oddity.

The graphical presentation of the development in the total number of recorded impulses, in the course of individual technological operations, in all the assessed melts is in **Figure 12**. These data, in the sum of recorded impulses, correspond to the number or, possibly, to the volumes of steel inclusions. The assumption that the curve of recorded impulses would decrease in correspondence to the inclusion analysis made with the assistance of roentgen spectral analysis and the process of steel processing LF1-VD2 has not been quite proved.

Thanks to the graphic assessment in **Figures 8 to 12**, which describe the number of impulses or the relative frequency of the individual elements and melts, we can say in summary that:

- It is very difficult to find any similarity in the number of inclusions in individual samples in a melt and, also, in the technological step
- The similarities of the trends' decreases or increases in individual inclusion types could be followed to a melt or to a technological step
- The occurrence of AlCaO inclusions is not the dominant detected bond
- The occurrence of AIO inclusions is more frequent, when compared with AlCaO inclusions, but the trend after VD2 is relatively balanced in most melts
- The number of AIO and AlCaO inclusions is lower, when compared with $\text{VD1} < \text{VD2}$
- The occurrence of CaO inclusions is a dominant part in all the technological steps and it is lower in $\text{VD1} < \text{VD2}$
- The number of SiO inclusions is a dominant part in all the technological steps
- When the occurrence of AIO inclusions exceeds the value 0.1, the number of SiO inclusions is lower than AIO
- The number of SiO inclusions shows a lower value in $\text{VD1} < \text{VD2}$
- The analysis of the occurrence of the inclusions with the bond MnS or MnO has not been performed because the item for manganese was not purchased for the device and we could not thus analyse it by the SSE method
- The number of S_{corr} inclusions mostly decreases in $\text{VD1} > \text{VD2}$; the number of CaS inclusions logically decreases
- The AlN and TiN inclusions do not practically occur and are not created in the liquid stage
- The CaS inclusions make the dominant sulphur bond, while the remaining sulphur amount was not identified and it will possibly be connected with inclusions of the MnS type

- The number of CaO inclusions occurs in a relatively large number
- The number of TiO inclusions is not negligible and it is lower in VD1<VD2
- Some inclusions show in a relatively larger number after vacuuming

The comparison of the two methods assessing some steel purity factors with the assistance of roentgen spectral analysis and the SSE method is suggested in **Table 1**. In spite of the fact that the testing performance identity of both methods was made as much as possible for individual melts and samples, we have not achieved comparable results. It is probable that the volume of the analysed sample part makes an important difference because the roentgen spectral analysis provides for the relative point character of the detection in an area, while the SSE method examines a larger volume of metal. The comparison of the two methods shows that the difference in the number of Al₂O₃-CaO inclusions, which prevail, and the minimum number of CaO inclusions, detected by the roentgen spectral analysis, is the most important. The occurrence of these inclusions is more probable in every technological step, when compared with the smaller number of AlCaO inclusions and the large number of occurring CaO inclusions detected by the SSE method.

4 CONCLUSIONS

The new method Single Spark Evaluation, or its variant Spark – Data, which are available for modern optical emission spectrometers, performs an analysis of the chemical composition of steel. At the same time, they may identify the inclusion compositions within conditions of the steel production at Vítkovice Heavy Machinery a.s. The advantage of this method is operability, because the inclusion analysis takes place at the same time as the analysis of the steel's chemical composition. The method has already been implemented in the steelworks of VHM, but the correct interpretation of the measured values and their utilisation within the operative influencing of technological process of melts' processing is still discussed. The conclusions of the performed study partly suggested a further verification process and the practice, which might be utilised when interpreting the measured values.

We recommend not comparing the SSE method with the method of the roentgen spectral analysis. The research of the utilisation of the SSE method should continue in various technological production processes, for example, in the condensing or diffusing de-oxygenation technologies. The used de-oxygenation determines the type of an inclusion and its majority share in steel. Similarly, the same should be applied in various technological production processes. For example, in an EAF and in the technology processing melts by facilities of secondary metallurgy with the assistance of the

Table 1: Comparison of some results measured by the Roentgen spectral analysis and the SSE method

Tabela 1: Primerjava med rezultati, izmerjenimi z rentgensko spektralno analizo in SSE-metodo

	Roentgen spectral analysis-	SSE method
Number of inclusions	It decreases in the course of processing in the order LF1-LF2-VD1-VD2	The number of impulses does not depend on the technological step; usually VD1<VD2
Mn	Assessed	Not assessed
MnS	The assessed Mn and S, they occur at the same time	The calculated MnS = S corr – CaS
AlN, TiN	Not assessed	Assessed
AlCaO	The dominant occurrence of Al ₂ O ₃ and CaO at the same time	Not the dominant detected bond
CaO	It does not practically occur	Relatively frequent
Ti	Titanium oxide makes the dominant element in some inclusions	TiO occur practically in all samples

chemical heating by aluminium (VOD), or in production processes in an EAF and when processing in a LF with the shortened heating and in VD, possibly within other tested combinations.

The current idea considers the fact that in such a way the prepared technological processes would require the creation of etalons - the steel status for the specific kind of inclusions and the technological indicator of contaminated steel or pure steel. The number and the probable size of inclusions will be determined by 3 Sigma, 7 Sigma and 9 Sigma. For example, the differential way for the likely occurrence of fine inclusions, classified for an assessment in accordance with the given technological process, should be tested in a similar way and there should be kinds of inclusions specified and determined for the assessment in accordance with the given technological process.

The study results suggest a chance for the Single Spark Evaluation method's utilisation in the steel working practice when determining the inclusions in an online steel production process with secondary metallurgical facilities LF or VD at Vítkovice Heavy Machinery a.s.

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