Study of Clogging Deposit Build-up in Al-killed and Ca-treated High Sulfur Steels with Focus on the Steel/Refractory Interface

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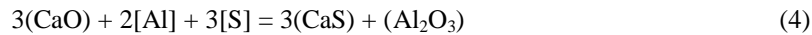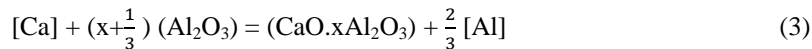
INTRODUCTION

Since the beginning of calcium treatment in the 1960s, it has become the most important tool to prevent clogging in the submerged entry nozzle (SEN) during the continuous casting of Al-killed steel grades. The massively improved castability is a consequence of the modification of pure alumina inclusions with Ca and the formation of calcium aluminate inclusions, which are liquid at process temperatures.[1, 2] In general liquid inclusions have a much lower tendency to get stuck on the inner surface of the SEN compared to solid inclusions like Al_2O_3, $MgO.Al_2O_3$ and CaS and thus hardly cause the build-up of solid

deposits in the nozzle.[3] Especially Al-killed steel grades with demands on machinability and therefore with elevated sulfur contents above 0,02 % are well known for their critical casting behavior towards clogging. Beside the formation of calcium aluminates due to the Ca-addition, solid or semi-solid CaS can be formed, depending on the thermodynamic conditions in the steel melt, causing the build-up of deposits on the inner nozzle wall.[4] The worst case will end up in an early shutdown of the caster.

Several casting sequences from the steel plant of voestalpine Stahl Donawitz GmbH of resulfurized steels have been evaluated with focus on non-metallic inclusions, casting parameters and deposits on the nozzle wall. The inclusion landscape in tundish samples was determined by means of automated SEM/EDS inclusion measurements and compared to particles in the clogging material. Moreover the interaction between liquid steel, deposits and refractory material has been studied. Additionally density measurements of residual composite material attached to the nozzle wall have been performed to quantify the amount of non-metallic phases and solidified steel. The purpose of this study is a detailed investigation of the mechanisms leading to sulphide clogging.

BACKGROUND

Several authors have studied the thermodynamic constraints of the formation of inclusions in high sulfur steels by using computational modeling, focusing on the influences of the concentrations of Al, S, Ca and O, respectively O_{total}. The main reactions governing the inclusion formation are as follows:

$$[Ca] + [O] = (CaO) \qquad\qquad\qquad (1)$$

$$[Ca] + [S] = (CaS) \qquad\qquad\qquad (2)$$

$$[Ca] + (x+\tfrac{1}{3}) \, (Al_2O_3) = (CaO.xAl_2O_3) + \tfrac{2}{3} \, [Al] \qquad\qquad\qquad (3)$$

$$3(CaO) + 2[Al] + 3[S] = 3(CaS) + (Al_2O_3) \qquad\qquad\qquad (4)$$
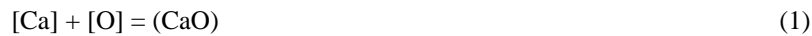
The calculation of the saturation lines of calcium aluminates and CaS have shown that an increasing content of Al and S leads to strong shrinking of the "liquid window" and therefore a more precise adjustment of the Ca-content is demanded to keep the inclusions liquid. The same effect can be observed when O_{total} and the temperature are decreased.[5-8] Excessive Ca-treatment with respect to the thermodynamic conditions does not only result in the formation of CaS. Moreover the highly modified form of calcium aluminates ($12CaO.7Al_2O_3$) gets transformed into the lower modification according to equation (5), which is solid at process temperatures and hence will promote nozzle clogging.[9-11]

$$\tfrac{4}{5}(12CaO.7\,Al_2O_3) + 2[Al] + 3[S] = \tfrac{33}{5}(CaO.\,Al_2O_3) + 3(CaS) \qquad\qquad\qquad (5)$$
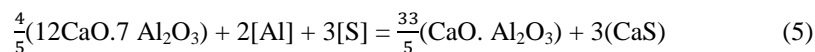
Microscopic analyses have revealed that the deposits found in the SENs mainly consist of spherical CaS and in some cases $MgO.Al_2O_3$-particles surrounded by a matrix of $CaO.2Al_2O_3$ and $CaO.Al_2O_3$.[12, 13] The role of solidified steel within the coral-shaped structure of the clogging deposits has been discussed by Fix et al.[14] They have shown that steel entrapments in the clogging material solidify due to the occurrence of a heat sink on the nozzle wall and therefore stabilize the build-up of the inclusion/steel composite.[14]

Another consequence of elevated concentrations of Ca and highly modified calcium aluminates is the erosion of the SEN material, especially in case of alumina-based refractories. The erosion of the refractory material enables steel infiltration, which will again promote clogging deposit build-up.[14, 15]

Nevertheless several authors give guidelines for an optimized processing of Al-killed, high S containing steel grades to avoid CaS-clogging resulting in longer casting sequences. The most effective measure is a proper Ca-treatment with respect to the thermodynamic conditions in the steel to avoid the formation of solid CaS in the casting system.[3, 4, 16]

INDUSTRIAL EXPERIMENTS

In this work three casting sequences of Al-killed and Ca-treated steels with sulfur levels between 0.02 % and 0.03 % have been analyzed with respect to their clogging behavior. The heats were produced in a 67 tons BOF. While tapping into the ladle the steel was killed with aluminum. Afterwards the ladles were transferred to the ladle furnace for final alloying and temperature adjustment. The last step in processing was the Ca-treatment by feeding CaSi cored wire for the purpose of inclusion modification. Finally the heats with an average weight between 63 to 65 tons were casted on a 5-strand bloom caster using a tundish with a capacity of 29 tons.

Sequence 1 (S1) consists of 4 heats, which were treated with an increased amount of CaSi cored wire compared to the heats of sequence 2 (S2). The submerged entry nozzles used for casting were made of alumina-based refractory material. The casting system consisting of the tundish and the SENs was preheated prior to casting. The aimed temperature of the tundish was 1250°C. The SENs were heated by the off-gas of the burners in the tundish and reach a temperature of 850°C to 900°C. Sequence 3 (S3) was processed according to the standard procedure but with the application of two different types of SENs.

ANALYSING METHODS

For determining the steel chemistry of the heats including total oxygen and nitrogen content, standard steel samples (lollipop sample) were taken out of the tundish and analyzed by means of optical emission spectrometry. Lollipop samples from the tundish were also used for the determination of the inclusion landscape of the steel. The measurements were done in the middle of the sample's surface after grinding and polishing, removing approximately 0,2 mm to 0,4 mm of steel.

Beside the lollipop samples additional cylindrical samples (TOS - Total Oxygen Sample) with 4 mm in diameter and 60 to 70 mm in length were taken. This sample geometry leads to accelerated cooling and solidification, resulting in a lower amount of sulfidic precipitations. As a consequence the results of the SEM/EDS measurements will be less influenced by secondary precipitations, giving a better correspondence with the intrinsic inclusion landscape of the steel.

After cutting the TOS-sample into pieces with 20 mm in length, they were mounted and grinded to the centerline of the cylinder. Inclusion characterization is performed by manual and automated SEM/EDS measurements using a FEI Quanta 200 MK2 scanning electron microscope (SEM), equipped with an energy dispersive X-ray spectrometer (EDS) system of Oxford Instruments. The standard procedure of automated inclusion measurements is explained elsewhere.[17] Additional calculations with the "Equilib"-module of the thermodynamic software tool FactSage™ 7.0 were made to validate the results gained by SEM/EDS. The databases used were FToxid and FSmisc. A detailed explanation for calculating inclusion diagrams can be found elsewhere.[7]

Studies of the SENs, clogging deposits and the interface between them were done in several ways. In a first step the SENs were cut into sections as shown in Figure 1. The thickness of the composite attaching the refractory was measured at eight positions for each cross section (see Figure 2) resulting in a mean value for a certain position of the SEN. In a second step samples of the refractory with attached deposits from the zone above the mould slag were prepared. Special attention was turned to the preservation of the interface between refractory and clogging material. For the optimization of EDS results the samples were sputtered with carbon. Microstructure and phase analysis in the interfacial region were conducted.

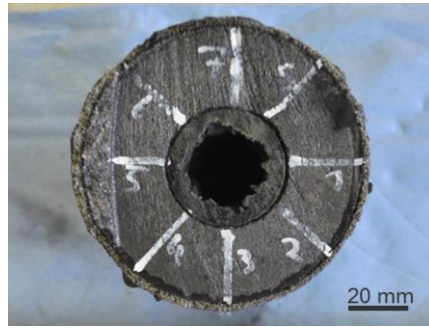Figure 1: SEN of Strand 4 – Sequence 1 after cutting.

Figure 2: SEN cross section of Strand 4 – Sequence 1.

In a third step density measurements applying Archimedes´ principle were conducted to calculate the ratio of volume of non-metallic components and solidified steel in the composite. The erratic distribution of the components causes significant errors when using 2D image analysis for the estimation of the volume-ratio. Due to the small differences in density of the non-metallic particles (Table 1) present in the clogging material and the rather high density of steel, a mean density for the non-metallic phases can be applied. With this assumption the shares of volume in the deposits can be easily calculated, which can give indications for the prevalent mechanism of clogging. Despite the solubility of CaS, water had been used for density measurements. The water-resistant matrix of calcium aluminates and steel protects the sulfides from dissolution.
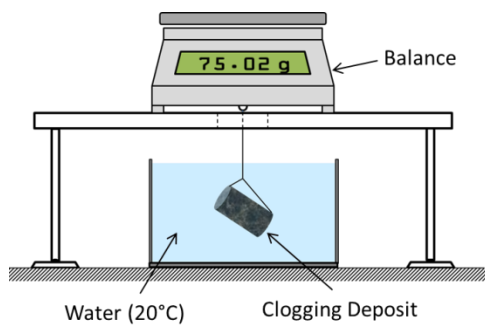

Figure 3: Application of Archimedes' principle for density measurements.

Table 1: Densities of different components present in deposits.

Substance	Density ρ, [g/cm^3]
CA	3.67 [18]
CA$_2$	2.90 [18]
CaS	2.59 [19]
Fe	7.87

To determine the amount of steel in the clogging deposits, parts of the composite were removed from the SEN and density measurements were performed. Following assumptions are made for the calculation:

- The densities of the CaS and calcium aluminates are varying in literature. For calculations the values in Table 1 are used.
- The share in volume of CaS, CA and CA2 is assumed to be 50:25:25 %, resulting in a mean density of 2.937 g/cm^3. Pure CaS has a density of 2.59 g/cm^3. A mixture of 50 % CA and 50 % CA2 has a density of 2.92 g/cm^3. The maximum possible error within these boundaries will be approximately 0.34 g, which is only 11 % of the assumed density.
- The density of pure iron is applied for the steel.
- By checking the surfaces of clogging material for residual material of the refractory or of steel, which solidified after the shutdown of the caster, the influence of these components on the result can be neglected.

RESULTS AND DISCUSSION

S1 vs. S2: Consequences of excessive Ca-recovery for inclusion landscape

The mean chemical composition calculated from the analysis of tundish samples from the sequences S1 (4 heats) and S2 (6 heats) are shown in Table 2. Total oxygen values for these heats typically lie between 15 to 30 ppm. The calculated liquidus temperature (T_{liq}) for the steel is 1498°C. As can be seen from Table 2 the Ca-content of both sequences is highly stable but approximately 12 ppm higher in the heats of sequence S1. Furthermore Al and S concentrations show similar values for both sequences. Even the levels of deviation in Al-concentration are the same.

Table 2: Mean chemical composition of the investigated casting sequences.

		C [%]	Mn [%]	Si [%]	Al [ppm]	S [ppm]	Ca [ppm]
S1 (L1-L4)	μ	0.373	0.745	0.258	281	273	29
	σ	0.004	0.005	0.008	55	11	1
S2 (L1-L6)	μ	0.378	0.765	0.238	257	289	17
	σ	0.007	0.013	0.007	55	6	2

Tundish samples of heat 4 of sequence 1 (S1-L4) and heat 6 of sequence 2 (S2-L6) were analysed using an automated SEM/EDS inclusion measurement. For a maximum of 5000 inclusions, size and morphology were determined by the SEM. Additionally, the chemical composition had been measured by means of the EDS-system. The results of the measurements are displayed in Figure 4 a. The graphic shows a negligible amount of pure Al-based inclusions, including alumina, calcium aluminates and MA-spinels. In S2-L6 the numbers of Al-based oxides with attached sulfidic phases is significantly higher than in sample S1-L4. Considering pure sulfidic inclusions, S1-L4 contains a detrimental amount of CaS-particles. To clarify the influence of cooling and precipitation on the amount of CaS in the lollipop sample, an automated inclusion measurement was performed on a TOS-sample of S1-L4. The size distribution of detected CaS-particles in the samples can be seen in Figure 4 b.
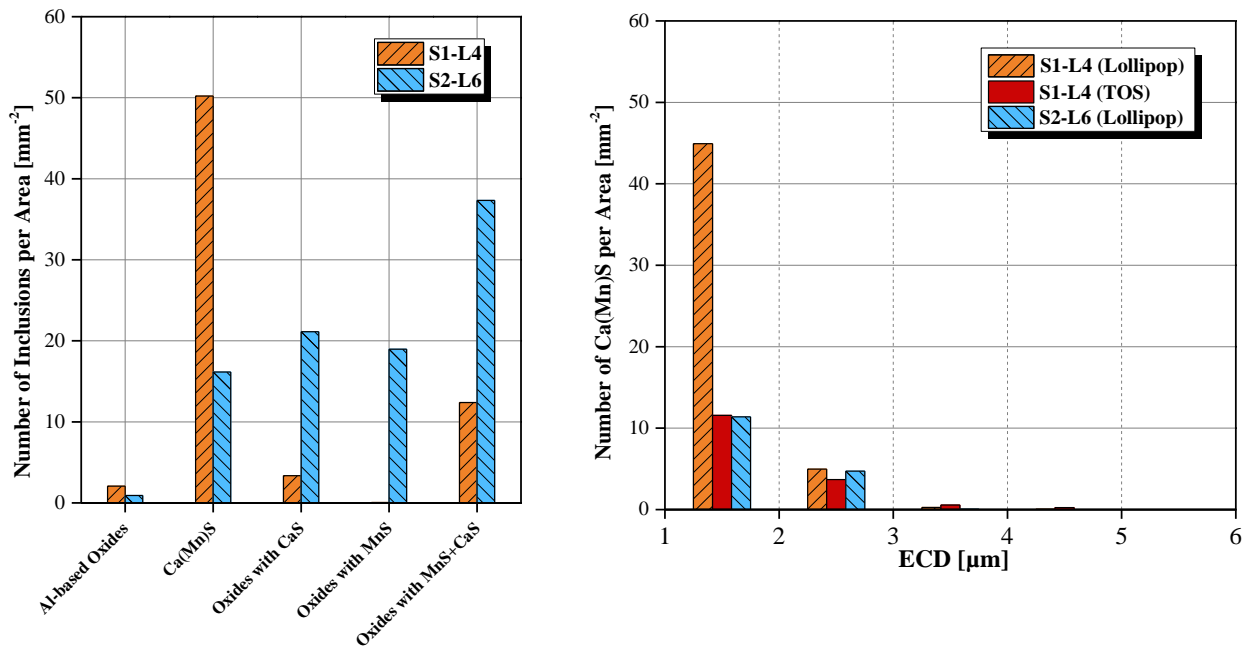

Figure 4: Comparison of numbers of inclusion per area (a) and size distribution of Ca(Mn)S-particles in the last samples of the sequences (b).

From the comparison of the Ca(Mn)S size distribution of the samples, it is evident that accelerated cooling of the TOS-sample reduces the number of precipitated sulphides by 68 %. Despite the cooling conditions of the lollipop sample of S2-L6

the lower Ca-content results in a similar amount of Ca(Mn)S particles compared to the TOS-sample. Considering chemistry and the different cooling conditions of the samples, the majority of sulphides found in the Lollipop sample of S2-L6 precipitate and grow during cooling. This indicates that hardly any solid sulphides were expected at casting temperature (1535-1540°C).

Based on the mean chemical composition of S1 and an estimated O_{total} of 25 ppm, stable inclusion phases were calculated with varying Ca-content at 1540°C. The results are shown in Figure 5. Based on the Ca-content of S2, hardly any solid sulfidic particles should be present in the liquid steel. Assuming 30 ppm of Ca in the steel like in S1, calculations reveal that around 12 % of the total mass of inclusions is CaS. Considering the results of the inclusion measurements and the thermodynamic calculations, it´s evident that the steel S1 contains a decisive amount of solid CaS inclusions at casting temperature, whereas the calcium sulphides found in the lollipop sample of S2 originate in the precipitation during cooling and solidification and therefore will not be present in the liquid steel.
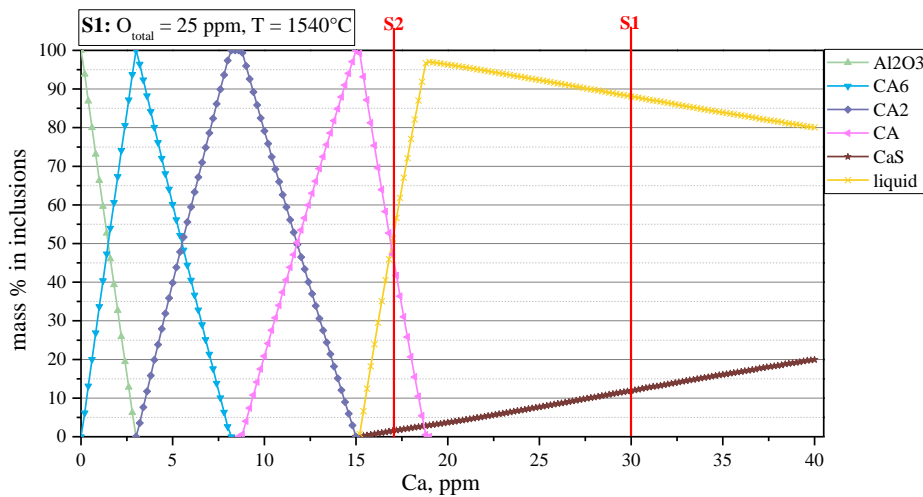

Figure 5: Mass fraction of oxides and CaS in inclusions based on the chemical composition of S1 and varying calcium content.

S1 vs. S2: Consequences of excessive Ca-recovery for nozzle clogging and erosion of refractory
After casting, the thicknesses of residual clogging deposits in the SENs of S1 and S2 were evaluated. The results are displayed in Figure 6. The attaching deposits in the SENs of casting sequence S2 have thicknesses of around 1 mm measured at positions above the slag level. Positions at steel or slag level show a higher thickness due to the solidified steel and slag, which remain after casting. In strand 4 of S1 the build-up of deposits with a mean diameter of 6.5 mm causes a reduction to 46 % of the original cross section, resulting in a blockage of steel flow and shut down of the caster. A maximum of residual material in the SEN could be found approximately 100-150 mm above the slag level which is in contrast to the SENs of S2. In case of S1 the liquid steel surrounding the bottom part of the nozzle prevents a significant amount of steel from solidification. Hence, the residual steel and slag after casting do not lead to an increase of the thickness of the deposits.

Samples from that position were investigated by means of SEM/EDS. Figure 7a shows composite material sticking on the SEN refractory. It is obvious that solidified steel is a major component of the clogging deposit, thus it plays an important role in deposit build-up and stabilization. The density of a single piece of composite (50.15 g) was measured and calculated applying Archimedes principle, resulting in 6.08 g/cm³. According to this, the share in volume of nonmetallic inclusions within the deposit is 36 % and that of steel 64 %.
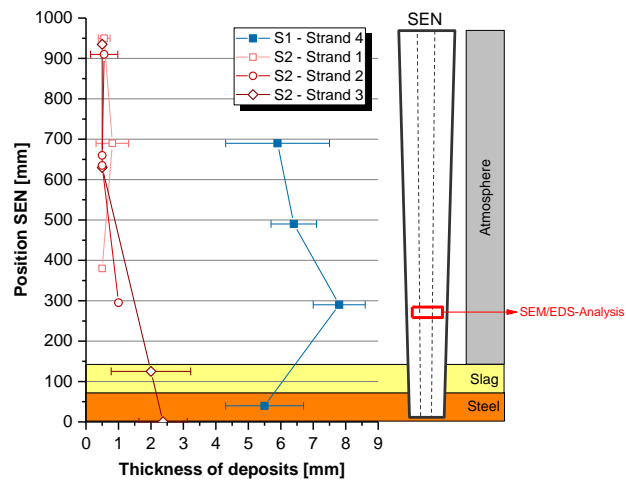
Figure 6: Thickness of clogging deposits in SENs of casting sequences S1 and S2.
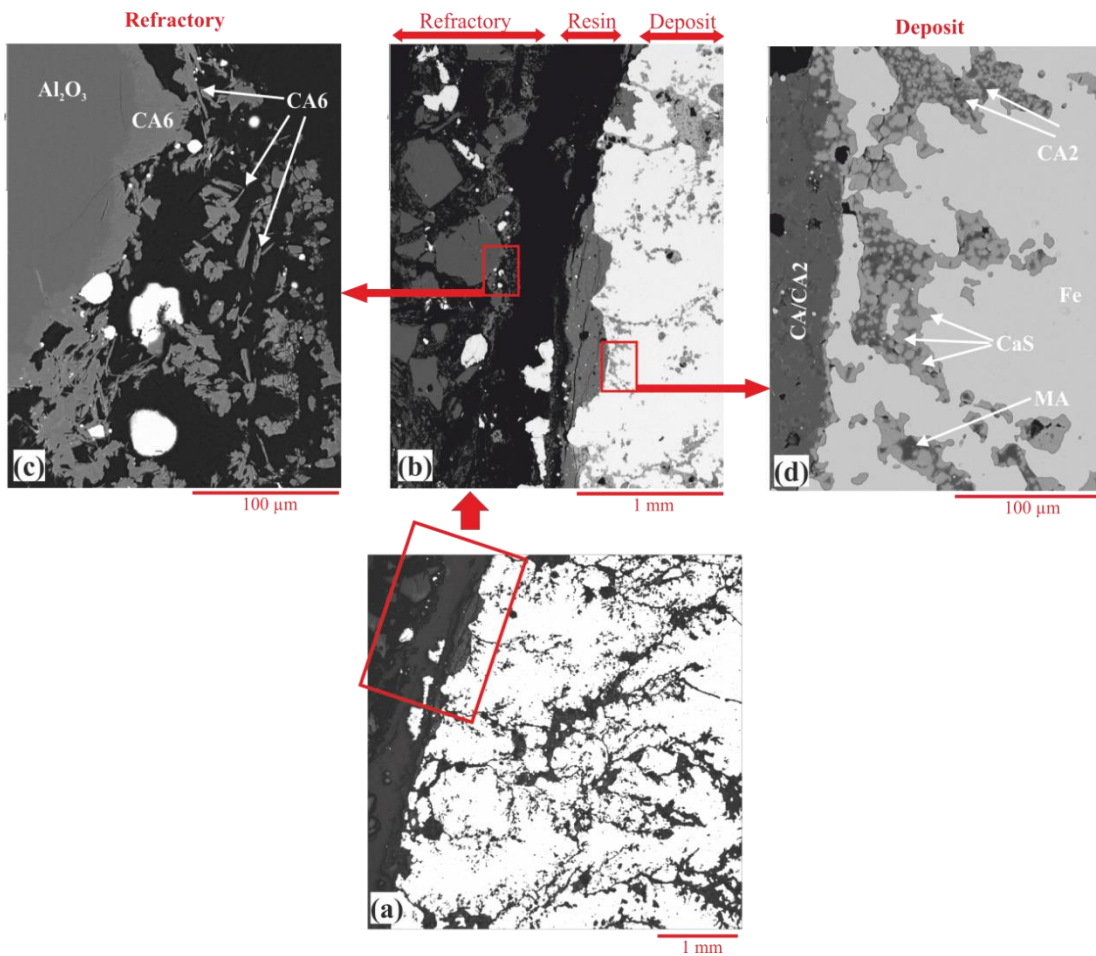

Figure 7: Clogging deposits on refractory material (a+b) with a close up view of composite (d) and Ca-attack on refractory (c).

The nonmetallic components in the deposits were identified as spherical CaS-particles surrounded by a matrix of calcium aluminates. EDS-measurements of the single phases revealed Ca/Al-ratios (weight) of mainly Ca/Al=0.37, which indicates $CaO.Al_2O_3$ inclusions and Ca/Al=0.72, which is close to Ca/Al=0.74 of $CaO.2Al_2O_3$. These findings have also been reported by several other authors.[9-11]. For the mean composition of S1 with a calcium content of 30 ppm the thermodynamic calculation would also predict liquid inclusions, but calcium aluminates with Ca/Al-ratios above 1.0 were not found. Within the CA/CA2-Matrix scattered $MgO.Al_2O_3$ inclusions were detected, originating most probably in refractory material of previous process steps.

At several distances from the refractory material the size distribution of CaS-particles was analyzed manually (Figure 8). Particles with diameters below 3 μm seem to appear less often than bigger ones. The most frequent class of size are sulfides between 5 μm and 6 μm in diameter. Around 65-70 % of inclusions have got diameters between 4 μm and 7 μm. A relation between the size of the particles and the distance to the refractory material could not be found, indicating that the residence time of the particles within the clogging material plays hardly a role in the growth of the sulfides. Due to this, growth of the sulfides may happen during cooling of the steel melt after entering the SEN; probably leading to different size distributions in upper and lower parts of the SEN. Investigations on particle sizes along the SEN are part of ongoing research.
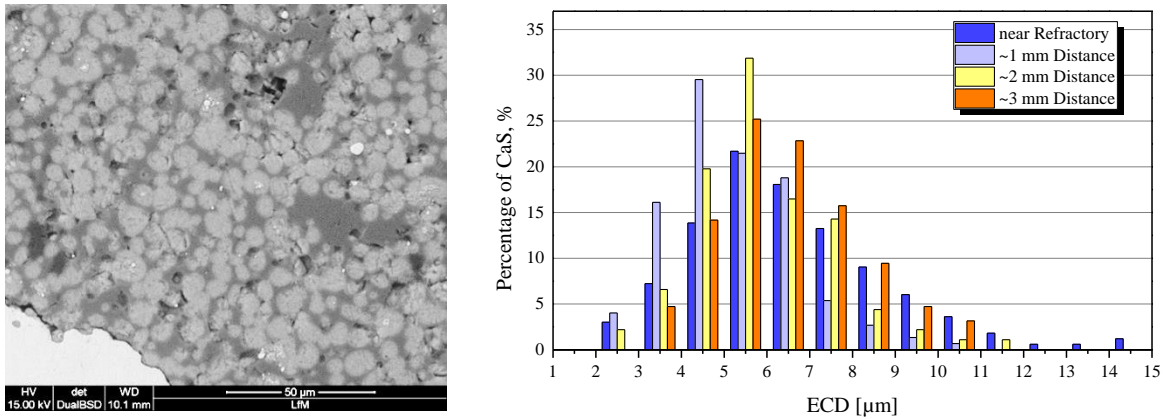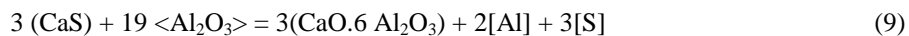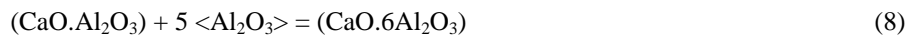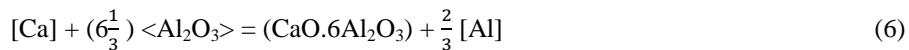

Figure 8: Size distribution of CaS-particles within the clogging material in several distances from the nozzle wall.

As seen in Figure 7c excessive amounts of Ca do not only lead to the formation of CaS particles but also cause modification of refractory. The alumina of the refractory reacts with Ca resulting in the formation of $CaO.6Al_2O_3$ and the alumina grain gets fragmented. Similar results were reported by Son et al.[20] The source of Ca cannot get determined exactly, but the following reactions may occur:

$$[Ca] + (6\tfrac{1}{3}) <Al_2O_3> = (CaO.6Al_2O_3) + \tfrac{2}{3}[Al] \tag{6}$$

$$(12CaO.7Al_2O_3) + 35 <Al_2O_3> = 6 (CaO.Al_2O_3) + 6 (CaO.6Al_2O_3) \tag{7}$$

$$(CaO.Al_2O_3) + 5 <Al_2O_3> = (CaO.6Al_2O_3) \tag{8}$$

$$3 (CaS) + 19 <Al_2O_3> = 3(CaO.6 Al_2O_3) + 2[Al] + 3[S] \tag{9}$$

Most likely reactions (7) and (8) will occur, when liquid calcium aluminates and solid CA-particles attach on alumina particles of the refractory. Due to the low temperatures and the amount of O_{total} and [S] in the melt, dissolved [Ca] will not be available in the SEN for reaction (6). Reaction (9) is based on the dissociation of CaS and the dissolution of [Al] and [S] in surrounding steel. As long as there are highly modified calcium aluminates present, this reaction will not occur.

Build-up mechanism of CaS-Clogging Deposits

The build-up of clogging material in the nozzle is strongly related to the occurrence of solid nonmetallic inclusions in the liquid steel. In case of Ca-treated resulfurized steels, CaS and solid calcium aluminates tend to get trapped at the refractory wall. SEM-investigations revealed the formation of nonmetallic dendritic structures on the inner surface of the clogging material, which grow against the direction of steel flow, as shown in Figure 9.
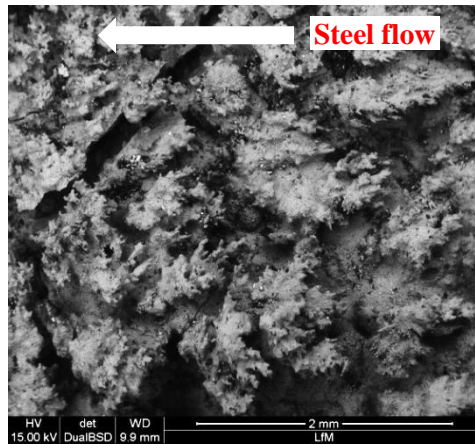

Figure 9: Dendritic build-up on the inner surface of clogging deposits.

To explain the microscopic structure of nonmetallic particles and solidified steel within the composite, sketches are shown in Figure 10. Assuming proper preheating of the SEN and appropriate steel temperature, no steel will solidify stably on the refractory. Cavities are formed at the boundary layer of the refractory due to gasification of graphite lamellas while preheating, enabling the steel to infiltrate. At several positions solid CaS accompanied by partly liquid calcium aluminates get stuck on the refractory. The continuous formation of CaS-agglomerates leads to the development of zones with hardly any steel flow and the creation of heat sinks between the dendrites. The solidification of steel within the structures stabilizes the deposits and offers new liquid/solid interfaces for the attachment of solid CaS particles. By the use of refractory material with different thermal properties, the development of the heat sink can be affected, resulting in a decrease of volume fraction of solid steel and clogging material build-up.
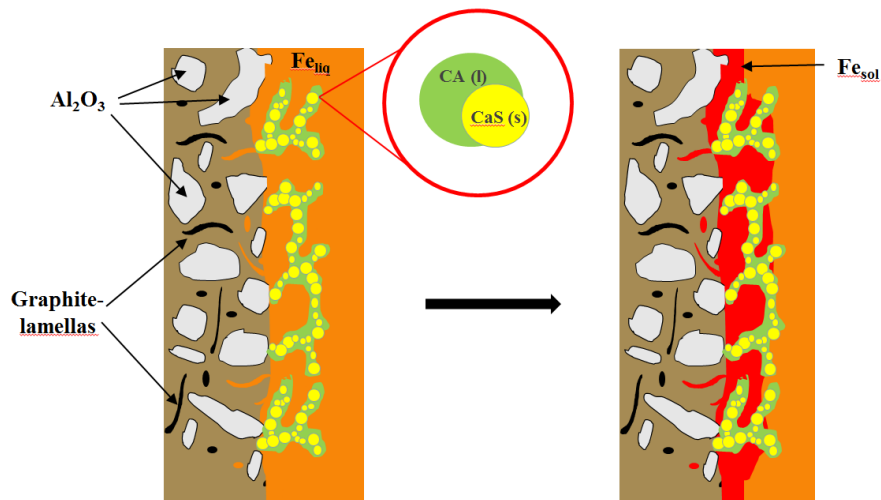

Figure 10: Model concept of composite build-up.

S3: Application of different refractory materials for SEN

A third casting sequence (S3) consisting of four Ca-treated and resulfurized heats (L1-L4) was produced by using two different types of alumina-based SENs. Strand 3, 4 and 5 were equipped with standard SENs, like they were used for S1. For the SENs of strand 1 and 2 a different type was chosen. Due to the different material, changes in the thermal conditions on the steel/refractory interface can be expected. By using different nozzle materials in one tundish, influences of varying chemical composition, inclusion landscape and steel/refractory temperature are eliminated. All SENs were preheated to a temperature of 850°C to 900°C before start of casting. The mean chemical composition of the melts is shown in Table 3. The occurrence of clogging material within the SEN was evaluated. The results are displayed in Figure 11.

Table 3: Mean chemical composition of the heats of sequence 3.

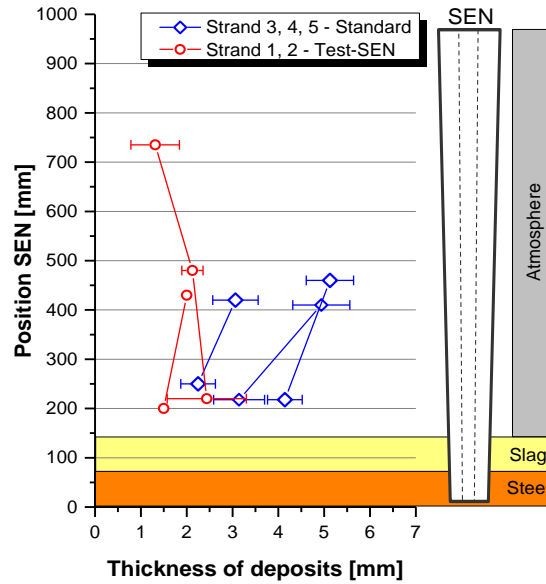|		C [%]	Mn [%]	Si [%]	Al [ppm]	S [ppm]	Ca [ppm]	O_{total} [ppm]
S3 (L1-L4)	μ	0.48	0.77	0.21	275	233	15	26
	σ	0.01	0.00	0.01	21	15	2	6

Figure 10: Thickness of clogging deposit build-up depending on SEN-type.

The SENs of strand 3, 4 and 5 obviously show a higher clogging tendency. For the standard material, the composite has got a thickness between 2 and 5 mm in contrast to the test material, which is just covered by a layer of 1 to 2 mm. Several pieces of the clogging material were removed and their density was determined. Table 4 contains the outcome of the calculations.

Table 4: Results of density measurements.

SEN-Type	Nr.	Weight [g]	Density [g/cm^3]	Vol.-% NMI	Vol.-% Fe
Standard	1	26.71	6.16	35	65
Standard	2	90.74	6.12	35	65
Standard	3	108.06	6.10	36	64
Standard		**Mean:**	**6.13**	**35.4**	**64.6**
Test	1	43.52	5.63	45	55
Test	2	72.04	5.94	39	61
Test	3	46.91	5.62	46	54
Test	4	28.36	5.87	40	60
Test		**Mean:**	**5.77**	**42.7**	**57.3**

The results show that the composite densities of the two SEN-types differ significantly. Deposits in standard SENs have got a mean density of 6.13 g/cm^3, while deposits attaching to the other SEN-type have got 5.77 g/cm^3. The shares of solid steel within the composite are estimated to be 64.5 % and 57.3 % in volume. This indicates that less steel solidifies due to the heat sink, resulting in a slower growth of the composite. Nevertheless influences of the different refractory materials on the formation of the first phases, which get stuck on the wall, cannot get excluded completely.

CONCLUSION

In this study three casting sequences of Ca-treated steels (Al-killed and containing high sulfur levels) were investigated, regarding causal relations for clogging in the submerged entry nozzle. The findings are as follows:

- The heats of sequence 1 show higher concentrations of Ca (29 ppm) compared to the heats of sequence 2 (17 ppm) resulting in significant amounts of solid CaS-inclusions at casting temperature. This is revealed by automated SEM/EDS measurements of samples as well as thermodynamic calculations.
- Sequence S1 shows severe nozzle clogging over the full length of the SEN due to the amounts of CaS present in the steel, whereas the heats of sequence 2 cause just minor residual clogging deposits in the SENs (Figure 6).
- 65-70 % of CaS particles within the clogging deposits are in a size range of 4 to 7 μm in diameter. No significant differences in size could be found in certain distances from the refractory wall, giving the indication that growth of the particles may happen between tundish and final attaching position.
- It was found that solidified steel plays a major role in clogging deposit build-up by stabilizing CaS-networks and providing additional solid/liquid interfaces for further deposition of particles.
- By using different refractory material, the share of solid steel in the deposits can be reduced, which leads to less clogging in the investigated cases.

From these findings it can be concluded, that a proper Ca-treatment with respect to the thermodynamic conditions and temperature control is essential for the prevention of clogging in the submerged entry nozzle. Accompanying measures like improved SEN-refractory materials can alleviate these problems.

ACKNOWLEDGMENT

REFERENCES

1. G. Davies, P. C. Morgan, "Secondary-steelmaking developments on engineering steels at Stocksbridge Works, BSC", Ironmaking and Steelmaking, Vol. 12 (1985), No.4, pp 176.
2. H. K. Tönshoff, W. Kästner, R. Schnadt, " Metallurgische Auswirkungen der Calciumbehandlung von Stahlschmelzen auf das Stranggießen", Stahl und Eisen, Vol. 109 (1985), No.16, pp 39.
3. A. Hamoen, W. Tiekink, "Are Liquid Inclusions Necessary to Improve Castability", Steelmaking Conference Proceedings, ISS, 1998, pp 229.
4. T. Bolender, J. Cappel, K. Wünnenberg, W. Pluschkell, "Metallurgical process engineering for castability-improvement in steel with elevated sulfur contents", steel research, Vol. 72 (2001); No. 11+12, pp 477.
5. L. Holappa, M. Hämäläinen, M. Liukkonen, M. Lind, "Thermodynamic examination of inclusion modification and precipitation from calcium treatment to solidified steel", Ironmaking and Steelmaking, Vol. 30 (2003), No. 2, pp 111.
6. W. V. Bielefeldt, A. C. F. Vilela, C. A. M. Moraes, P. C. Fernandes, "Computational Thermodynamics Application on the Calcium Inclusion Treatment of SAE 8620 Steel", steel research int., Vol. 78 (2007), No. 12, pp 857.
7. W. V. Bielefeldt, A. C. F. Vilela, "Study of Inclusions in High Sulfur, Al-Killed Ca-Treated Steel via Experiments and Thermodynamic Calculations", steel research int., Vol. 86 (2015), No. 4, pp 375.
8. R. Heinke, K. Takahama, „Kinetic model for the formation of CaO and CaS in aluminium deoxidized steels by calcium treatment", steel research int., Vol. 58 (1987), No. 4, pp 162.
9. S. K. Choudhary, A. Gosh, "Thermodynamic Evaluation of Oxide-Sulfide Duplex Inclusions in Steel", ISIJ International, Vol. 48 (2008), No. 11, pp 1552.
10. K. Ahlborg, R. J. Fruehan, M. S. Potter, S. R. Badger, G. S. Casuccio, "Inclusions in Aluminium-Killed Steel with varying Calcium Additions", ISSTech 2003 Conference Proceedings, Vol. 2, pp 177.
11. D. Janke, Z. Ma, P. Valentin, A. Heinen, "Improvement of Castability and Quality of Continuously Vast Steel", ISIJ International, Vol. 40 (2000), No. 1, pp 31.
12. W. Tiekink, B. Santillana, R. Kooter, F. Mensonides, B. Deo, R. Boom, "Calcium: Toy, Tool or Trouble?", AISTech 2006 conference proceedings, Vol. 2, pp 395.
13. F. Fuhr, C. Cicutti, G. Walter, G. Torga, "Relationship Between Nozzle Deposits and Inclusion Composition in the Continuous Casting of Steels", Iron Steelmaker, Vol. 32 (2003), pp 53.
14. W. Fix, H. Jacobi, K. Wünnenberg, "Collision-controlled growth of composites in casting nozzles", steel research, Vol. 64 (1993), No. 1, pp 71.
15. F. Tehovnik, J. Burja, B. Arh, M. Knap, "Submerged Entry Nozzle Clogging During Continuous Casting of Al-Killed Steel", Metalurgija, Vol. 54 (2015), No. 2, pp 371.
16. S. R. Story, T. J. Piccone, R. J. Fruehan, M. Potter, "Inclusion Analysis to Predict Casting Behavior", Iron & Steel Technology, Vol. 1 (2004), No. 9, pp 163.
17. S. K. Michelic, G. Wieser, C. Bernhard, "On the Representativeness of Automated SEM/EDS Analyses for Inclusion Characterisation with Special Regard to the Measured Sample Area", ISIJ International, Vol. 51 (2011), No. 5, pp 769.
18. I. J. McColm, "Dictionary of Ceramic Science and Engineering", 3rd edition, Springer Netherlands, 2013.
19. A. F. Holleman, E. Wiberg,"Inorganic Chemistry", Academic Press, San Diego, 2001.
20. J.-H. Son, I.-H. Jung, S.-M. Jung, H. Gaye, H.-G. Lee, "Chemical Reaction of Glazed Refractory with Al-deoxidized and Ca-treated Molten Steel", ISIJ International, Vol. 50 (2010), No. 10, pp. 1422.