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Effect of slag control on steel process optimization and on environment

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Abstract

Through slag control it is possible to modify the inclusion quality in steels and it is well known that inclusions, when not properly controlled, are harmful to the mechanical properties of every kind of steel. In fact it is well known in steelmaking that inclusions are naturally absorbed by slag when flotation is sufficient. However, separation and dissolution may define the inclusion absorption capacity of slag. In this study an evaluation of the slag optimization has been performed by means of an approach involving both experimental data and theoretical calculations. The theoretical approach s based on the use of thermodynamic calculations and physical models. All the activities are aimed to optimize the slag composition. In particular, by means of a "tailoring" of CaO and CaF_2 concentrations in the slag it is possible to achieve good results in terms of inclusions capture and environmental benefits, too. Based on the results it can be assumed that the target composition formulated for each type of deoxidation allows achieving the benefits both in economic and environmental terms due to the reduced use of fluorine while ensuring adequate process characteristics.

1. Introduction

The objective of the steel producers is to obtain clean steel, that is, with low amounts of inclusions harmful to the performance of the finished product [1-3]. The slag performs various functions of considerable importance during the refining process; its chemical-physical characteristics determine the success or otherwise of the fundamental metallurgical operations, such as the desulfurization and the inclusions capture [4]. The formation of non-metallic inclusions is inevitable and when they are not carefully controlled, it can cause problems in terms of quality and product characteristics. In steel industry it is known that inclusions are absorbed by the slag [5-7] under certain thermodynamic conditions and adopted raw material. For the success of such process is required, however, an adequate inclusions flotation and also an appropriate chemical/physical characteristics of the slag. The genesis of non-metallic inclusions is influenced by various process parameters during the steel production. The study purpose is a better understanding of the refining process in the ladle relatively steel-slag and inclusions interaction.

2. Experimental details

In AcciaiSpeciali Terni S.p.A., carbon steels are tapping by an Electric Arc Furnace (EAF) and transferred to ASEA-SKLB plant to be refined until the analysis desired. The ASEA-SKLB is one of the most complete of secondary refining plant, in terms of metallurgical functions that can fulfill. A peculiar characteristic of ASEA-SKLB is the simultaneous presence of two systems for the bath agitation: electromagnetic stirring and inert gas induction stirring (argon). The bath is agitated mainly to accelerate the homogenization and allows the most of the reactions among surfaces (bath-slag) and the removal of non-metallic inclusions. During the refining process, lollypops (liquid steel samples) are taken to analyze the inclusion panorama. Therefore, the control of slag absorbing capacity with respect to the inclusions type found in the samples is carried out. For this purpose, the use of thermodynamic models is a useful method to assess of the slag ability to absorb inclusions absorb by chemical point of view. The thermodynamic calculations have been done using the slag composition in terms of concentration of its main constituent oxides (CaO, MgO, Al_2O_3, SiO_2, MnO, FeO) as input. Other species that are in low quantities (Cr_2O_3 and TiO_2) are not included in the calculations as their relevance on the slag properties can be considered negligible. In this work, Thermo-Calc software was used [8]. The other aspect concerns the physical aspects related is the slag ability to capture the inclusions. In a simplified point of view, an evaluation of the feasibility of the passage of the oxide inclusions from liquid steel to slag has been studied. Viscosity and surface tension were used as reference slag physical. The reference temperature is 1650 °C, the one typically that achieved before the vacuum stage. The evaluation was made for two different types of reduction, Al-killed and Si-killed [9, 10]. For each of these systems the approach is summarized as follows:

- thermodynamic approach: considering the solid and liquid phases present in the typical operating range, the desulfurizing capacity of the slag and its capacity to inclusions absorb from the point of view of chemical affinity are evaluated;
- chemical-physical approach: the ability of the slag to capture the inclusions is evaluated on the basis of its viscosity and surface tension. The evaluation is done using a method developed by CSM (Centro SviluppoMaterialiS.p.A.) that allows the calculation of capture index of inclusions.

3. Results and Discussion

In AcciaiSpeciali Terni S.p.A. the study was conducted for two cases: Al-killed steels and Si-killed steels.

3.1. Al-killed steels

In a first phase, the typical compositions of the ASEA slags are used as input for the thermodynamic calculations. It must be noticed that CaF_2 is not included in the calculations due to the lack of this species in the used database. Therefore, the calculations have been done by subtracting the equivalentCaO quantity attributed to the fluorine present from the total CaO (measured by chemical analysis of the slag). Theformer has been estimated as 3.6% on a total slag mass of 2500 kg. The thermodynamic calculations performed in such a way show that about 10% of the total mass of slag system is separated as solid phases of CaO (Figure 1a) and MgO (Figure 1b).

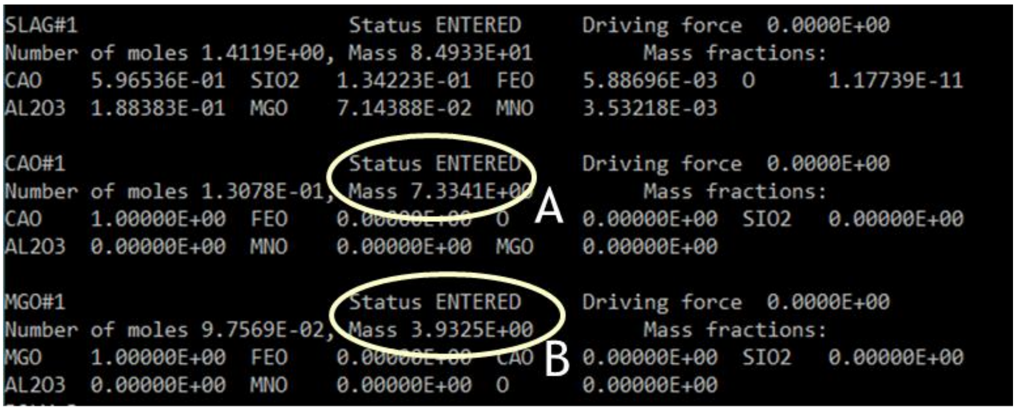


Figure 1: Masses of phases present at equilibrium calculated with Thermocalc (slag system in Al-killed steel case)

The separation of solid CaO is explained by the use of an excessive quantity of such species for the slag formation. The separation of solid MgO is explained by an enrichment of that species in the slag until reaching the saturation. Such enrichment is due to refractory wear. The use of fluorine allows us obviating the CaO problem, thus maintaining the slag with acceptable fluidity. However, the use of fluorine increases the corrosion of MgO based refractories used in ladle. In a second phase, thermodynamic calculations are used to define an ideal composition of the slag. The ideal slag should have a high chemical activity of CaOto ensure a good desulfurizing ability avoiding at the same time the separation of solid phases due to the saturation in CaO. For this reason, the ideal slag has been designed so to have a CaO chemical activity of at least 0.85 at the reference temperature. The subsequent need of less fluorine quantities to be added in such slag has obvious advantages for what concerns both a lower refractory wear and a lower environmental impact. Figure 2 shows the range of composition obtained for the slag objective through calculations performed on the basis of what said above. On the right side of the figure the results related to the expectations inclusions for the typical Al-killed steel produced in ASEA plant are also reported. Such inclusions are calculated from the steel composition and by the measured value of oxygen at the reference operating temperature.

SLAG AIM Al-killed steels	
Species	[%]
MgO	7-8
Al_2O_3	18-19
SiO_2	12.5-13.5
CaO	54-56
CaF_2	0.5-1.5
MnO	0.2-0.3
Cr_2O_3	0.2-0.3
TiO_2	0.01
FeO	0.9-1

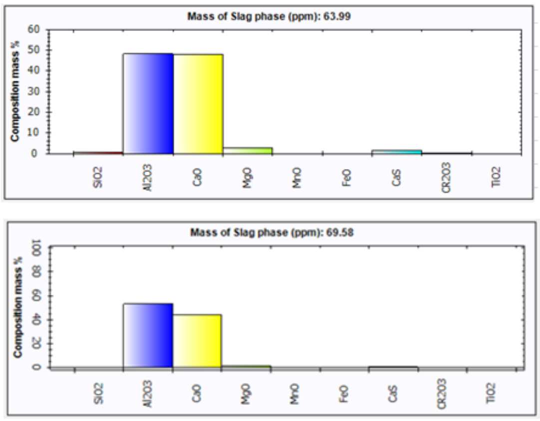


Figure 2: Composition aim slag (left) obtained from thermodynamic calculations (using ThermoCalc). Composition and mass inclusions in Al-killed steel computed using software developed by CSM utilizing a "thermodynamic core" based on Thermo-Calc

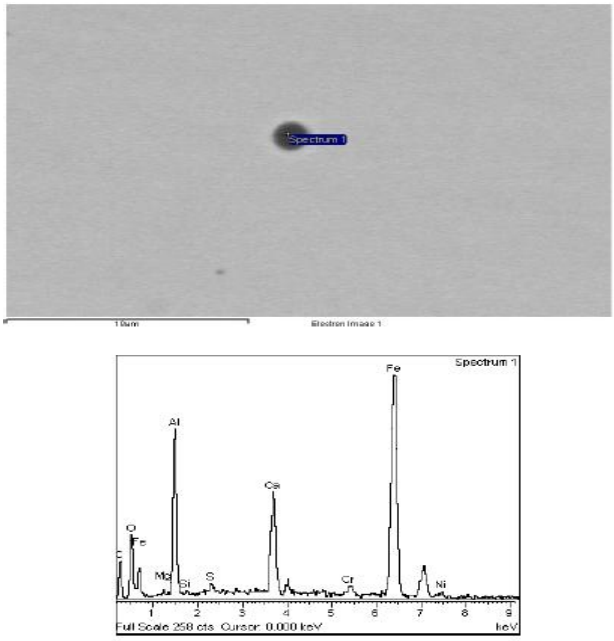


Figure 3: Typical inclusion of refining phase (calcium aluminate) [11]

The calculated inclusions are in very good agreement with the real ones found through microscopic analysis (see Figure 3) as an indication of the good representativeness of the system modelled by the calculations respect to the real one.With such slag composition, it is estimated that the amount of fluorine could be halved.

Once established the ideal chemical composition for the slag, the attention has been focused on the theoretical assessment of its capacity for absorbing inclusions. It is known from plant experiences that a slag with a good absorbing capacity has a consistency that can be defined as "creamy" [12].

The basicity index IB_5 can be used for an initial evaluation of slag creaminess:

$$IB_5 = \frac{\%CaO+\%MgO}{\%SiO_2+\%Al_2O_3+\%CaF_2+(\%FeO+\%MnO)} \quad (1)$$

It is also common to add FeO and MnOas acidic components in IB_5 ratio, provided that the sum of (FeO + MnO) is less than 5%. Then the slag aims at having an IB_5 of 1.8-1.9. This value is within the optimal range of creaminess for a slag type alumino-calcic with low fluorine amount. A further method has been used to estimate the capturing capacity of the slag. This method was developed by the CSM as part of projects for industrial clients.Basically, starting from approaches described in the literature [13-17], CSM has developed a calculation system to define of an index. This index (defined as inclusions “capture”) is calculated taking into account the viscosity and the surface tension of the slag and the appropriate correction coefficients. Comparisons between this calculated index and a corresponding experimental index (obtained by laboratory tests) allowed the determination of an optimal range (practically feasible) for the index in the range 50-70%, where 100% represents the absolute absorbing capacity. The capture inclusions index of the slag aim is positioned in the medium/high area (red point in Figure 4) of the optimum range.

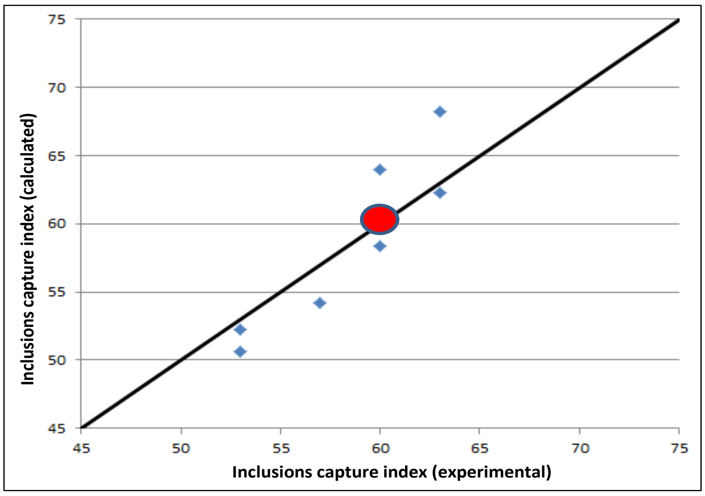
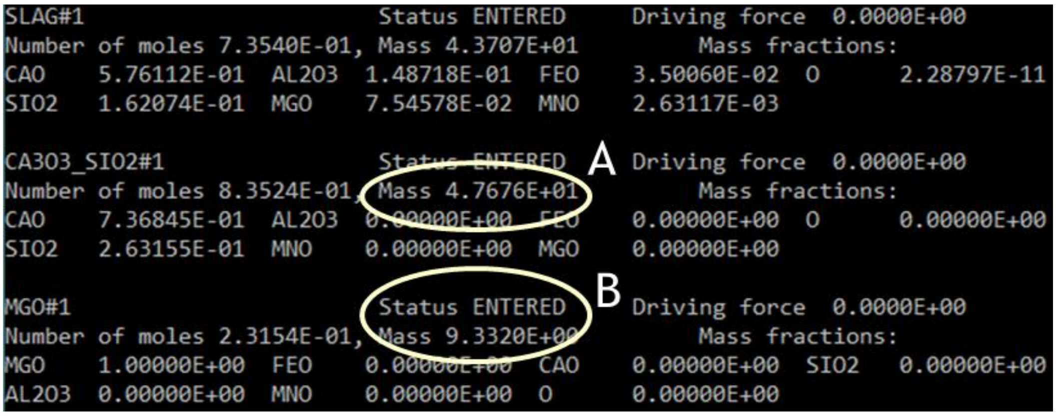


Figure 4: Representation of inclusions capture index for the aim slag (Al-killed)

In this study the Riboud model about slag viscosity [18, 19] has been used. This model was developed to estimate the viscosity of the mold powders but showed a wide range of enforceability.

3.2. Si-killed steels

A similar approach is done for the case of silicon killed steels. At the typical temperature pre-vacuum (1650 °C) the slag presents an excess of solid phases in this case, too. The presence of Ca-silicate (Figure 5a), is explained by an excess of CaO.


```
SLAG#1                         Status ENTERED      Driving force  0.0000E+00
Number of moles 7.3540E-01, Mass 4.3707E+01             Mass fractions:
CAO     5.76112E-01  AL2O3  1.48718E-01  FEO     3.50060E-02  O        2.28797E-11
SIO2    1.62074E-01  MGO    7.54578E-02  MNO     2.63117E-03

CA3O3_SIO2#1                   Status ENTERED    A Driving force  0.0000E+00
Number of moles 8.3524E-01, Mass 4.7676E+01             Mass fractions:
CAO     7.36845E-01  AL2O3  0.00000E+00  FEO     0.00000E+00  O        0.00000E+00
SIO2    2.63155E-01  MNO    0.00000E+00  MGO     0.00000E+00

MGO#1                          Status ENTERED    B Driving force  0.0000E+00
Number of moles 2.3154E-01, Mass 9.3320E+00             Mass fractions:
MGO     1.00000E+00  FEO    0.00000E+00  CAO     0.00000E+00  SIO2     0.00000E+00
AL2O3   0.00000E+00  MNO    0.00000E+00  O       0.00000E+00
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Figure 5: Output of ThermoCalc simulation for silicon killed steels

Also for silicon killed steels the fluorine is used to assure a good fluidity of the slag. The amount of used CaF_2 is estimated at 6-7% considering 2500 kg of total slag amount.Similar to Al-killed steels, the calculations were made considering a composition of the slag where the CaO equivalent of fluorine present is subtracted from the total CaO. Summarising, in the refining process a CaO excess is used, so a larger amount of CaF_2 is needed to maintain the slag more liquid causing increased refractory wear (excess of MgO in the slag).
Therefore, the less use of fluorine would have a double advantage:

- cheap (less refractories wear);
- environmental (phytotoxic effects of fluorides).

The thermodynamic calculations were made with the objective of maintaining the CaO activity sufficiently high but to prevent the formation of Ca-silicate phase (the formation of this phase takes place at 1650 °C for a chemical activity of CaO about 0.6).Thus it would lead to a slag with a tendency to formation of separate solid phases and a consequent need to use more fluorine quantities.The slag proposal is appropriate for the absorption of typical inclusions from a chemical affinity point of view (Figure 6, 7).

SLAG AIM Si-killed steels	
Species	**[%]**
MgO	6-7
Al_2O_3	6.5-8
SiO_2	22-23
CaO	52-54
CaF_2	3.5-4.5
MnO	0.1-0.2
Cr_2O_3	0.1-0.2
TiO_2	0.01
FeO	0.9-1

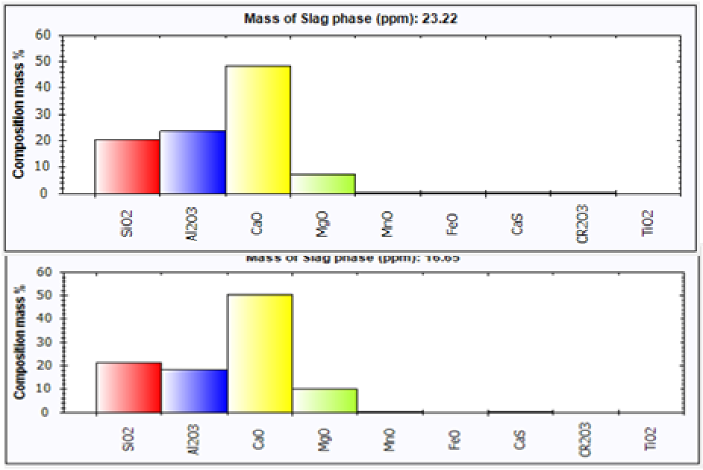

Figure 6: Slag aim composition (left) obtained from thermodynamic calculations (using Thermo-Calc). Composition and mass inclusions in Al-killed steels calculated using software developed by CSM employing a "thermodynamic core" based on Thermo-Calc

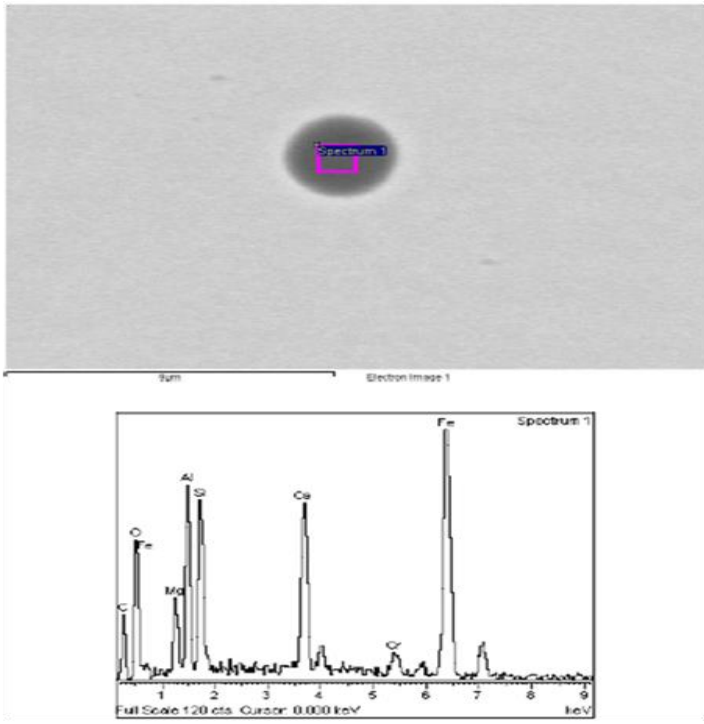

Figure 7: Typical inclusion on the refining phase (calcium-silicate) [20, 21]

As can be seen in Figure 8, the inclusions capture index of the aim slag calculated at 1650 °C taking into account the viscosity and surface tension expected for the liquid phase, is positioned in the medium/low area of the optimum range.

However, this situation is believed to be perfectly normal to a calcium-silicate slag, for which the slag itself can be regarded as adequate. This aspect is also confirmed by the IB_5 1.6-1.7 value calculated for the slag goal. In this case, in fact, the minimum recommended value is 1.5.

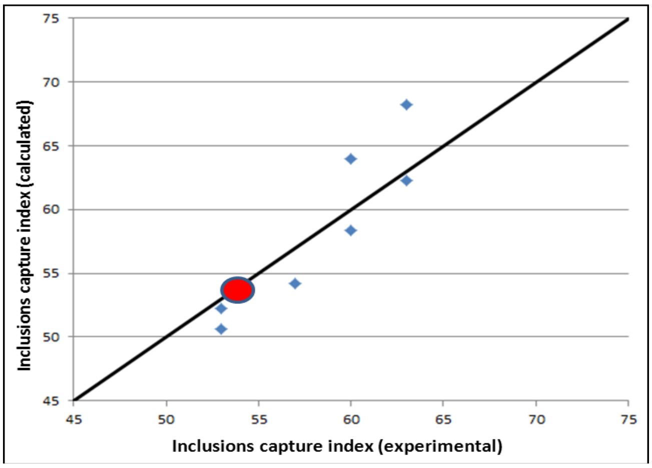

Figure 8: Representation of inclusions capture index for the aim slag (Si-killed)

Conclusions

In this work, the characteristics of the slag ladle ASEA-SKLB have been critically analyzed through a synergistic approach of theoretical/experimentalsynergistic approach. The evaluation was conducted for Al-killed and Si-killed types of deoxidation. A thermodynamic study revealed a possible improvement of slag composition with respect the actual that allows reducing the fluorine amount to be used while still maintaining adequate characteristics of the slag itself in terms of fluidity and desulfurizing capacity. This make possible defining a target composition suitable for each type of killing.In particular, the amount of used CaF_2 is estimated at 6-7% considering 2500 kg of total slag amount in the case of Si killed steels, and about 3.6% in the case of Al killed steels. The application of theoretical/experimental models, previously developed by the CSM for the evaluation of the slag capacity to capture the inclusions process, has allowed the verification of the adequacy of the objective composition also for this purpose. On the basis of the considerations above, it can be assumed that the target composition formulated for each type of deoxidation allowing the benefits both in economic and environmental terms due to the reduced use of fluorine while ensuring adequate process characteristics.

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