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# PREMISES IN THE DESIGN OF COMPUTATIONAL ALGORITHMS FOR REFINING SLAGS APPLIED IN LADLE TREATMENT OF STEELS. INFLUENCE OF BOF SLAG AND OF OTHER SOURCES OF SLAG

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## ABSTRACT

*In the design of computational algorithms for refining slags for ladle treatment of steels, the evaluation of contributions of different factors is a definitory step, allowing to evaluate the real posibilities and limitations in steel refining practice. Slag carried over from steelmaking converters to the ladle is evaluated from the point of view of contributions of its amount and contents of $SiO_2$ and iron oxides. It is shown in quantitative manner what it happens in conditions of variations of the above mentioned factors, in the ranges of values closed to real industrial practice. It is shown and concluded that quantitative evaluations of the contributions of slag carried over in refining ladle are of outmost importance. It is possible, under the above mentioned conditions, to ensure adequate values of sulphide capacity, low residual values of iron oxides in economical conditions and to save aluminium from the exaggerate loss by oxidation.*

KEYWORDS: BOF slag amount, $SiO_2$ content, iron oxydes content, aluminium consumption

## 1. Introduction

Nowadays, informatics applied in engineering of materials plays an increasing role to achieve reproducible quality indicators of products, to increase their levels and simultaneously to save costs, allowing reaching all these in a friendly interaction with the environment. Steel production in oxygen blowing furnaces (BOF), also known as L-D converters and steel refining in different secondary metallurgy facilities, like process in ladle metallurgy, are permanently the object of different measures directed to fulfill the actual requirements for the above mentioned purposes, including the extension of informatics applied in engineering of steelmaking and refining. In this regard, for accurate results that can be obtained with full knowledge, there is no other way than a correct evaluation of technollogical parameters and requirements from the points of view of their contribution and weight.

Actually, about the whole production of steels obtained at industrial scale in BOF steel plants and electric arc furnaces is treated using slags. Treatment of steels in ladle under slags, applied in various purposes is applied in order to achieve very low and extremely low contents of sulphur and high purity levels in non-metallic inclusions, is from far one of the most advantageous and cheap methods because of some particular features. Low carbon aluminium killed steels (LCAK) are a wide class of steels grades made in BOF and treated with refining slags in ladle, ladle furnace (LF) and other refining plants.

Despite thef act that technology of steel refining based on synthetic slags is not a new one, its efficiency in obtaining advanced refined steels made it a permanent and an indispensable technique to obtain high quantities of refined steels in conditions of low cost of investments and in short times. The simplicity of the method is remarkable due to the fact that in the ladle, the steel must be always covered by a slag layer along its residing period and therefore the problem to have an adequate slag, corresponding to a certain purpose of maximal utility, could be always posed at large. Therefore the refining of steel, using adequate refining slag became almost naturally a real technological plurivalent tool which must be permanently re-evaluated in order to update the knowledge, procedures and working technologies, all those serving to increase the technical and economical performances.

## 2. Current state and requirements

There is usually in steelmaking the tradition and practice of using the so-called general or basic recipes which are used because of the availability only of short time intervals, frequently of orders of few minutes, when different intended actions, in different technological steps, are possible in many cases in critical conditions of time. Such a practice is suitable in conditions when parameters of liquid steel are fully in the ranges of certain previous established values, which are practically the desired final values for the processing step in question but unfortunately these are also frequently far from their optimal values. A certain variability of many other factors, other than the ones before mentioned, contributing the values of different parameters of refining is superposed on the mentioned practice, but only rarely these factors are evaluated with satisfactory precision in the traditional procedure. It results that there are not too many freedom degrees in a such procedure and anything out of the usual range of parameters will affect the efficiency of steel treatment. Finally, it could be mentioned that the traditional practice is still wide spread and intensively used, although this is not always recognized fairly. However many of these difficulties can be avoided, the flexibility of the procedures can be increased and the reproducibility rate of the results could be improved, when adequate computational algorithms for slags are implemented, coupled with the availability of certain technological facilities in the steel refining shop. A good evaluation of particular conditions in the steelmaking practice of the steel grades taken into consideration allows for the design of adequate computational algorithms, flexible enough to be useful in many refining purposes, either simultaneously or separately, according to needs and conditions.

Starting from the above general remarks, fully acceptable as veridicity, a procedure of designing computational algorithms, to obtain a refining slag used mainly in desulphurization process of low carbon and low alloyed steels obtained in blowing oxygen converter (BOF) and treated in ladle, could be realized in the established practical conditions. These algorithms once established, tested and evaluated, can be used directly in steel refining practice as a tool for operators use, or at a superior level of integration in neural networks, making possible the management of steel refining processes based on artificial intelligence, replacing older mathematical methods based only on statistics, in the form of static and dynamic models, even of those implemented in on-line computer management facilities.

The necessity of such an approach, like the one suggested in the present paper, is due also to the fact that, despite the huge amount of reported data on slag refining technologies, there are only formal and often incomplete aboard, the most frequent limited to a narrow target.

## 3. General premises of computational algorithms for refining slags

Starting from necessities, a set of general and preliminary premises have been established, as it follows, in the form of direct and indirect sources:

1. the natural sources of slags during steel refining from starting of tapping to the end of treatment in the ladle, and even later if deleterious actions on quality occur;
2. the external sources of slags-fluxes, introduced in the process to obtain certain numerical values of the edificatory physico-chemical properties in an optimised manner;
3. the physico-chemical properties and their values related to slags in general and to refining slags, in particular;
4. the main refining process taken into account to be performed and the potential possible and desired adjacent refining processes, which can be coupled to the first;
5. the adjacent undesired processes taking place naturally or associated to the desired processes; their actions must be obligatorily known, evaluated and limited in their development.
6. the impact on environment taken into account from various points of view, starting from the possible action on life and work environment, to the impact on social environment and recycling.

All these aspects mentioned above must be carefully evaluated according to their characteristic actions, amounts, and weight from the various points of view which are relevant.

## 4. Contribution of (BOF) slag to the refining slag

Slag resulted from steelmaking process in BOF process, called shortly (BOF) slag, is an important primary source in obtaining the refining slag from the point of view of quantity and as an initial factor of influence acting further and determining technological actions and measures to bring it in the range of requirements. Despite this, in practice the weight of its contribution is not always precisely evaluated and included in computations. Many times the results of treatments under slag are bad, even disastrous, because of this attitude. Unfortunately, it seems that many times the amount of slag transferred in the ladle during tapping of steel not only it is not measured, but even it is not at least evaluated somewhat objectively. In an extensive study dealing also with evaluation of amounts of different sources leading to impurification of steel, the slag carried over to the ladle during tapping is about 3kg/t liquid steel, in a normal practice using different stoppers of slag [1]. Frequently and not only accidentally in the industrial practice the amount of slag carried over to the laddle during tapping is even higher than the amount mentioned above.

At the end of the heat BOF the slag contains high levels of iron oxides according to the carbon content and the temperature at the end point of blowing. In great measure this depends also upon the performing oxygen blowing combined with argon bubbling through nozzle placed on the bottom of the converter when such a facility and practice are used. Some typical chemical compositions of slags, at the end of oxygen blowing presumed to be identical to the transferred slag from converter into the pouring/refining ladle, are presented in table 1.

***Table1.*** *Main chemical compositions (rounded values) of final slags in BOF*

| Ref. No./year | **Chemical composition of slag**, mass % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | CaO | MgO | $SiO_2$ | $Al_2O_3$ | FeO $^{(*)}$ | $Fe_2O_3$ $^{(*)}$ | MnO | $P_2O_5$ | S $^{(**)}$ |
| [2]/1999 | 48 | 1 | 12 | 1 | 26 | - | 0.3 | 3.3 | 0.12 |
| [3]/2004 | 30-35 | 5-15 | 8-20 | 1-6 | 10-35 | - | 2-8 | 0.2-2.0 | 0.07-0.14 |
| [4]/2006 | 52 | 5 | 11 | 1.3 | 17 | 10 | 2.5 | 1.3 | - |
| [5]/2007 | 45 | 10 | 11 | 2 | 11 | 11 | 3 | - | - |
| [6]/2009 | 48 | 6 | 12 | 2 | 23 | - | 2 | 2.7 | - |
| [7]/2010 | 48 | - | 13 | 3 | - | 24 | 2.6 | 1.5 | - |

$^{(*)}$-upon the analysis method; $^{(**)}$-derived from the content of $SO_3$, initially determined

Valuable sources of data are provided in papers published in the adjacent research fields of waste management, recycling and cement industry. From far there are strong evidences that, despite efforts to standardize the technological process of steelmaking in BOF, according to conditions, high variability of final chemical compositions of slags is present. Therefore, once again, high quality algorithms must be applied when refining processes with BOF slag participation take place.

The steelmaking process and refractories contribute in most cases to the chemical composition of slag. The necessity to take into consideration these aspects could result from comments on the chemical composition of slags in table 1. As a general remark, it can be said that there are practically two major tendencies in the use of refractory linings, the first being to use classical lining based on dolomitic blocks and the second to use the lining based on magnesite elements, more or less evoluated, including those in the class MgO-C. In order to decrease the wear of such lining, due to the chemical agresivity when $SiO_2$ content is at high levels [3], also is encountered the practice consisting in increasing MgO content to levels closed to saturation of slag with MgO. Therefore in table 1 the component MgO is present in contents of very high variability [2]-[6]. This fact is frequently associated with the content of silica in slag. Increasing the content of MgO in slag is more efficient in lowering the aggressively of slags at high contents of $SiO_2$ due to the lower molar mass of MgO because of the bigger numbers of moles contained in the same amount, compared to the CaO.

Slags from table 1 ref [3] are the result of modern steelmaking process, in BOF lined with magnesite, therefore they contain 5-15mass % MgO. In the same time in the respective BOF are processed heating based on highly preliminary treated crude liquid iron with desulphurizing reagent up to low contents of sulphur and therefore the sulphur content in the final BOF slag is low, below 0.014 mass%. The relatively high final content of FeO (10-35 mass%) and of MnO (2-8 mass%) proves the heating has been processed with low proportions of iron scrap as cooling materials in favor of oxydic materials, perhaps iron ores.

Silica content in final slags (8-20 mass %) seems to prove that have been processed both de-silicized crude iron and crude iron with normal silicon content were used.

Due to the same mentioned conditions, final slags contain low contents of phosphorus oxyde (0.2-2%) [3].

As a general consideration, heatings must be processed in BOF with the lowest possible amount of slag. In the case of such slags, attention will be paid to contents of FeO and MnO, being known that refing of steels under slags requires extremely low contents of FeO+ MnO, usualy bellow 1-2 mass% [8].

The necesities of the chemistry in BOF determine high contents of iron oxydes in slag along the whole processing route of heatings. Excepting the content of CaO which is the highest in the BOF slag, iron oxydes are on the second place at levels of 22-35 mass % the sum of both two oxydes obtained by chemical analysis (FeO+$Fe_2O_3$).

## 5. Evaluation of effects of BOF slag on some technological parameters and on the estimated performances of refining slags

In the above mentioned conditions, due to their composition, (BOF) slags give a set of limits in what regards the amount of refining slag and even their composition, sometimes limiting also the maximal refining performance to lower levels than the theoretically required highest values.

The refining slags used for advanced desulphurization and advanced removal of oxydic inclusions in low carbon aluminium killed (LCAK) steels are based in the system $CaO$-$MgO$-$Al_2O_3$-$SiO_2$ with some additions of fluorine as fluidizer. In such slags, besides optimal ranges of the major components CaO and $Al_2O_3$, there are severe limitations for $SiO_2$ contents, usually at max. 5mass% in order to limit the increasing of silicon content in LCAK grades where it is limited or prohibited like it is in many grades of high strength low alloyed (HSLA) steels. Many times even more severe restrictions are imposed consisting in limitation of $SiO_2$ to levels below 2.5 mass%.

Another restriction is imposed concerning the sum of contents of FeO and MnO, limited to below 1mass% and admitted sometimes for qualities not so high up to 1.5-2mass%. These contents must be compared to the values from table 1 in order to evaluate the directions to action in order to fulfill the requirements in conditions of the amount of BOF slags carried over in refining ladle.

Particular values of the ($\%SiO_2$) contents in the refining slag could be computed using the following relation:

$$(\%SiO_2)=\frac{\sum_{i=1}^{n} q_i\cdot(\%SiO_2)_i}{\sum_{1=1}^{n} q_i}\cdot 100 \quad \%mass \qquad (1)$$

where:

i - current number of source of slag;
n - total number of sources of slag;
$q_i$ - amount of slag from source i;
$(\%SiO_2)_i$- $SiO_2$ content of source i, in %mass.

but a valuable and fast image on the simultaneous influence of the $SiO_2$ contents and of different sources of slags could be obtained using Figure 1 or a similar figure.

Data presented in Fig. 1 are in the range of interest in the industrial practice; the range of accidental of hazardous data is avoided. It is obvious that only carefully an adequate refining slag could be obtained and that the process of obtaining the slag is a very sensitive one to complex factors as composition and the amount of the converter slag carried over in the refining slag. It is difficult to obtain contents of $SiO_2$ as low as possible, but it is possible to take adequate measures to limit these contents at required values satisfying which meet the requirements.

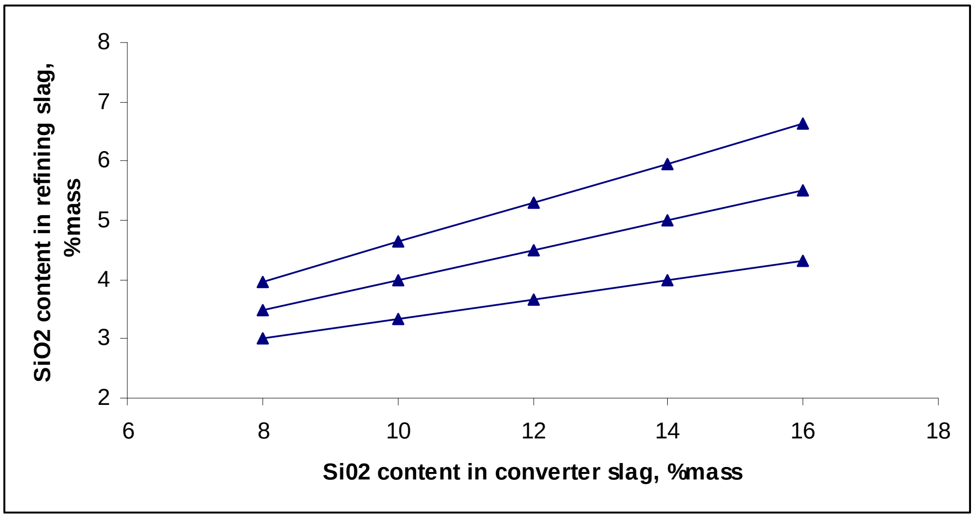

***Fig.1.*** *Influence of the $SiO_2$ content in converter slag and of the amount of slag carried over on the $SiO_2$ of the refining slag in the ladle.*
*Reference steel heat treated under slag - 180t; reference amount of refining slag -2160kg (corresponding to 12kg slag/tone liquid steel). Converter slag carried-over in the ladle:720kg (upper line);540kg (middle line); 360kg (lower line). Contribution of other components added to form refining slag- 2%mass $SiO_2$*

The content of $SiO_2$ in slag acts as a major factor in the activity of $SiO_2$ in slag and the basicity of the refining slag.

Considering a slag in the system $CaO$-$Al_2O_3$-$SiO_2$ where CaO and $Al_2O_3$ represents the base (%CaO+ %$Al_2O_3$ = min.90% mass) at a ratio %massCaO/ %mass$Al_2O_3$=1.4, it results a chemical composition of the $CaO$-$Al_2O_3$- $SiO_2$ shown in Table 2. for various concentration of $SiO_2$ in the refining slag.

***Table 2.*** *Several quality indicators of $CaO$-$Al_2O_3$- $SiO_2$ slags at various contents of $SiO_2$ and ratio $CaO/Al_2O_3$=1.4, compared to the pure $CaO$-$Al_2O_3$ slag at the same ratio*

| Quality indicators of slag | Chemical composition of $CaO$-$Al_2O_3$- $SiO_2$ (C-A-S), %mass | | | |
|---|---|---|---|---|
| | 3% $SiO_2$ | 6% $SiO_2$ | 9%$SiO_2$ | 0% $SiO_2$ |
| Basic composition | A=40.42<br>C=56.58 | A=39.17<br>C=54.83 | A=37.92<br>C=53.08 | A=41.67<br>C-58.33 |
| *Optical basicity, $\Lambda$ | 0.76863 | 0.75587 | 0.74799 | 0.78176 |
| *Sulphide capacity, $C_s$ at 1873.15K | 4.309x$10^{-3}$<br>(72.21%) | 3.1405x$10^{-3}$<br>(52.63%) | 2.58321x$10^{-3}$<br>(43.29%) | 5.967x$10^{-3}$<br>(100%) |

*computed according to ref.[8]:

$$\Lambda = \frac{1.783\%CaO + 1.756\%Al_2O_3 + 1.598\%SiO_2}{1.783\%CaO + 2.943\%Al_2O_3 + 3.33\%SiO_2}; \quad lgC_S = 10.767\,\Lambda - 10.64$$

The deleterious effect of the presence of $SiO_2$ content in slag, exerted on relevant technological properties involved in refining operation, is better shown by the decrease of the sulphide capacity $C_s$. Even a relativelly reduced percentage of $SiO_2$ in slag, despite of an apparently not important decreasing of the optical basicity of slag (1.68-3.38%), exerts very strong effects in decreasing the sulphide capacity of slag of an important magnitude (42.29-72.21%), compared to the similar slag without $SiO_2$ content, further affecting in a negative manner the efficiency in removal of sulphur and the final content of sulphur in steel. These results have been confirmed experimentally in ref. [8], also in many other published papers, here not cited because of economy reasons.

It is extremely obvious that the main source of iron oxides in the refining slag is the slag carried-out from converter in the refining ladle. As it is shown in table 1 in the widest range, considering oxides in the form of FeO, this content is 10-35%mass, but more frequent the sum of iron oxides contents is $\Sigma(FeO+Fe_2O_3)$=20-27%mass and (MnO)=2-3%mass. An important loss of aluminium will be in steel due to the reactions of slag deoxidization, which takes place in the presence of aluminium content from aluminium killed steels:

$$3(FeO)+2[Al]\rightarrow(Al_2O_3)+3[Fe] \qquad (1)$$

$$3(MnO)+2[Al]\rightarrow(Al_2O_3)+3[Mn] \qquad (2)$$

For easiness, the content of MnO will be included in the sum of iron oxides because of the small content of MnO in BOF slag and closed molar mases ($M_{Mn}$ =54.93 and $M_{Fe}$=55.84), also considering only the FeO form.

The quantity of aluminium in liquid steel, consumed directly $q^{c}_{[Al\}}$ in order to reduce the (FeO) content to a final residual value, according to the reaction (1), is given by the following relation:

$$q^{c}_{[Al]} = \left[ q^{'}_{BOF} \cdot (\%FeO)_{BOF} - Q_{slag\ \ ladle} \cdot \frac{(\%FeO)_{residual}}{100} \right] \cdot \frac{2 \cdot M_{Al}}{3M_{FeO}}, \text{ kg/heat} \qquad (3)$$

where:
$q^{'}_{(BOF)}$- is the amount of BOF slag carried over in the ladle ;
$(\%FeO)_{BOF}$- is the FeO content in the BOF slag;
$(\%FeO)_{residual}$-is the residual content of (FeO) in refining slag;
$Q_{slag\ ladle}$- is the amount of refining slag, from all sources;
$M_{Al}$, $M_{(FeO)}$ – are respective molar mass of aluminium (27) and of iron oxyde (72).

Data from Fig. 2 show the necessary amounts of aluminium for reduction of iron and manganese oxides in the slag carried over form BOF in the ladle refining. Reduction starts in industrial conditions from initial contents in the range ($FeO+Fe_2O_3$)=20-35mass% and (MnO)=2-4mass% even less than 1%mass. The refining slag must contain much more lower contents of iron and manganeze oxides in order to be of certified utility. The sum of their contents must be lower than 1-2 %mass. Sometimes, due to requirements to guarantee extra low activity of oxygen and of extra low content of oxide inclusions, this sum must not exceed 0.5- 1.0%.

These extra low contents also favorize a deep removal of sulphur from steel in the refining slag. Unfortunately, this is obtained scarifying a certain content from the aluminium present in the liquid steel, and this must be compensated by re-feeding the corresponding amount of aluminium, usually by immersing wire of Al. From Figure 2 it results that, in the case of a heat of 180 t liquid steel, in conditions of addition 1.5KgAl/tone, important amounts of aluminium are consumed to reduce content of iron oxides below 1%mass and these amounts must be taken into account in algorithms of any mathematical model to ensure the accomplishing of different functions of performance concerning the quality by refining.

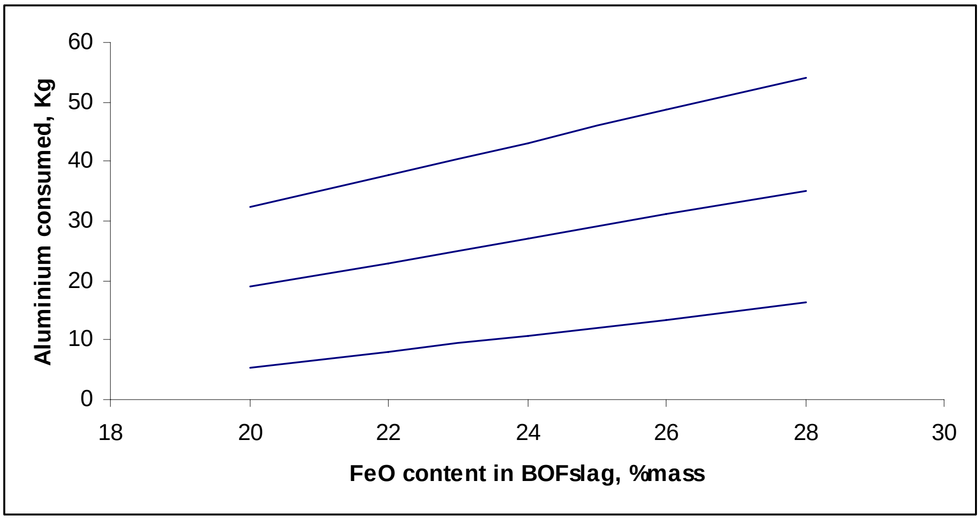

***Fig. 2**. Consumption of [Al] in steel due to reduction of iron oxydes contents in the ladle slag from initial content to 1% FeO residual content in slag, starting from values coresponding to input with various BOF slag amounts.*
*Reference steel heat treated under slag - 180t; reference amount of refining slag ($Q_{slag\ ladle}$) 2160kg (corresponding to 12kg slag/tone liquid steel); Final content in the ladle slag $(\%FeO)_{residual}=1\%$.*
*BOFslag carried-over in the ladle:720kg(upper line);540kg(middle line); 360kg(lower line)*

## 6. Conclusions and comments

From the theoretical approach and the results presented, the final slag in BOF converter contributes the final results of steel refining operations by the following major factors:

a. $SiO_2$ content acting in the sense of decreasing the sulphide capacity of slag which is one of the definitory parameters of slag in desulphurization of steel. The decreasing of the negative influence of $SiO_2$ content is costly and practically it may be performed only by increasing the total amount of slag by supplementing the additions. The possibilities to do this are limited in a narrow range and other performance indicators of steel refining efficiency became worse due to the increasing of slag amount in the ladle.

b. the amount of slag carried-over in the refining ladle, during tapping;

c. the content of iron oxides, whenever this indicator is expressed.

As general conclusions, it might be mentioned that the refining of steel under slags is possible, efficient and might be optimized as performance and costs, only if the amount of transferred slag from converter to the ladle is limited to less than 400-500kg/heat (180tones of steel) and the content of $SiO_2$ in slag to also limited at less than 12% mass. At a such moderate and acceptable amount of BOF slag carried over in the refining ladle, the intake of iron oxides is also moderate and the necessary content for successful refining operation (including FeO<0.5-1%mass) is controllable by usual operations during current operations involved in normal practice and normal duration of the refining period. Reduction of iron oxides in the ladle slag is realized with an important consumption of aluminium (7-54kg/heat of 180t of steel) at a reference amount of slag 2120kg equivalent to 12kg slag/t steel.

These conditions are relatively easy to be accomplished in the normal practice of steelmaking in

BOF, but they are easier to be ensured if the pre-treated liquid iron is used.

A complex treatment of liquid iron consisting in decreasing the content of silicon, sulphur and carbon, combined with steelmaking in BOF equipped with argon bubbling bottom nozzles is the optimal solution to minimize the possible negative effects of converter slag carried – over in the refining ladle.

There is evidence that, if optimal parameters of BOF slag carried over in the ladle refining are not respected, any computational algorithm will give receipts and parameters for treatment with refining slag out of optimal range satisfying technical and economical requirements.

Mainly either due to the necessity to prolong too much the duration of treatment or due to the increasing of the necessary amount of refining slag, refining process will evoluate with difficulty and usual purposes of treatments, i.e. obtaining low contents of oxide inclusions and/or low contents of sulphur, are missed or are random.

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