

## OPTIMIZATION OF DESULFURIZATION PROCESS THROUGH STUDYING THE LADLE REFINING FURNACE PARAMETERS

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### ABSTRACT

*This research aims to optimize of the desulfurization process through the ladle-refining furnace in the melting shop of Abu Zaabal for Industrial Engineering Company. The Optimization of desulfurization process has been studied in the Ladle Refining Furnace of the melting shop with respect to the amount of desulfurizing agent, deoxidation power of Silicon, Stirring energy, and the temperature as well as The composition and the sulfur content of slag have been determined to calculate the partition coefficient of sulfur at different deoxidizer content, and different content of desulfurizing agent. Y. Yang and Sosinsky-Sommerville modelshave been used to determine the deviation between the measured and computational method for sulfur partition coefficient. The results refer tothe desulfurization efficiency of lime is entirely dependent on the oxygen content. On the other hand, the desulfurizing rate has its maximum value at 0.25% Si. The stirring energy has a linear relationship with the desulfurizing rate, as well as the desulfurizing rate has its ultimatum at 1893K. Eventually, the measured sulfur partition coefficient has closed values to that have been calculated from the Oxygen activity considered model.*

*Keywords:ladle refining furnace, desulfurization, deoxidation, and sulfide partition coefficient*

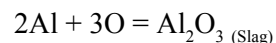
### 1. INTRODUCTION

Over the past few decades, the demand for steel around the world has been increasing at a rapid rate, coupled with an increase in steel quality. Steel producers are required to maximize throughput, minimize production outages and maintain high quality standards while all the time minimizing costs. The modern metallurgy of iron and steel is first of all oriented in quality improvement, effectiveness and competitiveness of its production. One major technique for improving the quality of steel is to reduce its sulfur content. Sulfur is one of the most detrimental impurities in the steelmaking process, affecting both internal and surface quality.

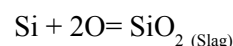
#### *Effectof SulfuronSteel*

- Forming of undesirable sulfides which promote granular weaknesses and cracks in steel during solidification.
- It lowers the melting point and intergranular strength.
- Sulfur contributes to the brittleness of steel and thus acts as stress concentration site in steel. [1]
- Hot shortness.

It seems clear that the oxygen is the intensive barrier to the sulfur segregation into the slag/metal interface because the oxygen has higher surface activity than sulfur [2]. Thereby,the low oxygen content in molten steel enhances the desulfurizing rate during the desulfurization process. deoxidation is carried out through ladle refining furnace by using strong deoxidizers such as aluminum and silicon; their oxides have a low value free energy as stated in equation1,2.



$$\Delta G^\circ = -1205115 + 386.714T \text{ (1)}$$



$$\Delta G^\circ = -580541 + 220.655T \text{ (2)}$$

However,silicon is widely used as a deoxidizer for steel, in particular the structure steel as a result of production cost consideration, but the remaining Oxygen in steel deoxidized by silicon is still higher than steel deoxidized by Aluminum[3].The worse effect of the aluminum on the nozzle clogging, and the skyrocketed price of aluminum lead to using Silicon instead of it in the production of the most structure steel. In Abu Zaabal steel plant,the regime of production is commonly started by melting in electric arc furnace , flowed by refining process ( deoxi-

ation , desulphurization )in ladle refining furnace. Thereafter, the molten metal is poured in water-cooled ingots through Continuous Casting Process.

The escalating of energy crisis in Egypt led the team of Abu Zaaba industrial company to find out the most consumable process in Abu Zaabalsteel industry plant. Therefore, the aim of this research is detecting the most significant parameters that have a great impact on the desulfurization process in term of energy and efficiency.

## 2. Experimental Work

Tens of heats required for producing structure steel were used as a pattern for optimization the desulfurization process in ladle refining furnace. Samples were collected from ladle refining furnace at different silicon content and at different amount of desulfurizing agent, and subjected for Emission Spectrophotometer chemical analysis machine. The slag has been determined chemically for each heat by the using X-ray fluorescence (XRF). On the other hand, sulfur content in the slag was determined by using CS-444LS Lecco equipment. Samples collected from certain heats for observing the effect of deoxidation process on the morphology of manganese sulfide inclusions. Afterward, specimens collected from the same heats and submitted for tensile test, impact test at different temperature. The measured Sulfur partition coefficient has been compared with Y. Yang, and Sosinsky-Sommerville computational models. The studying several heat of steel with different wide range of sulfur and silicon content, and closed range of the other alloying elements as shown in table 1.

**Table 1 Basic composition of investigated steel**

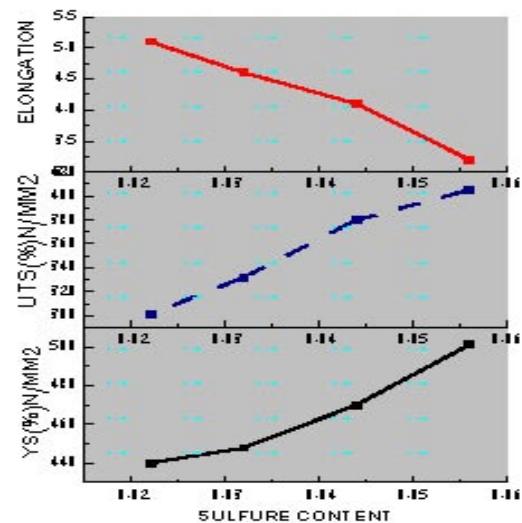
Heats	C	Mn	Si	P	S
12450-12495	0.25	0.65	0.05	0.042	0.070
	0.25	0.65	0.32	0.042	0.020

## 3. RESULTS & DISCUSSION

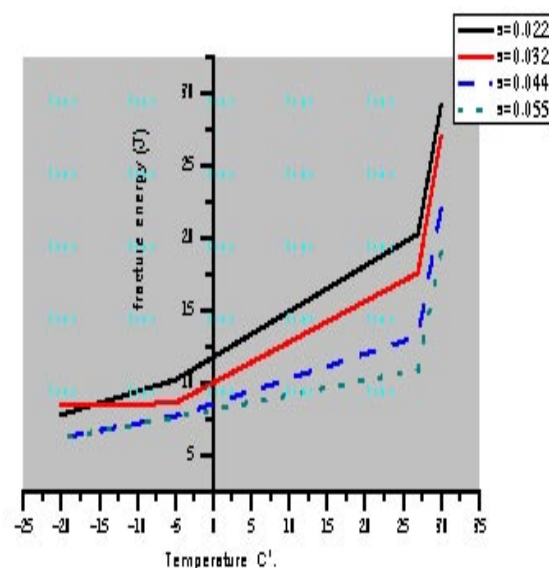
### 3.1 The effect of sulfur content on the mechanical properties

It is well known that the sulfur content has a great deteriorative effect on the toughness of the

structure steel ensued from the precipitation of manganese sulfide on the ferrite grain boundary [4, 5]. On the other hand, it is expected that the opposite effect will be observed in the strength. The effect of sulfur on the strength and toughness has been studied in the ordinary ingots produced in the melting shop of Abu Zaabal steel plant. Figure 1 confirms the deterioration effect of sulfur on the toughness, as well as its positive effect on strength. This can be explained by the



**Fig.1: Effect of the Sulfur content on the tensile properties** Sub: UTS is the ultimate tensile strength and YS is the yield strength



**Fig.2: Effect of sulfur content on Impact toughens at different temperature**

interaction between the dislocation and manganese sulfide inclusions will lead to the strength enhancement [ 6,7 ]. However, the ductile brittle transition temperature remains unchanged with sulfur content, but the impact value is entirely affected by the sulfur content as shown in Figure 2. This fact is attributed to the precipitation of manganese sulfide on the ferrite grain boundaries.

### 3.2 The effect of deoxidation on the morphology of sulphide inclusions

Many researchers have dedicated in studying the effect of deoxidation process on the morphology of manganese sulfide inclusions. It can be concluded from the literature survey that the sulfide inclusion is susceptible to nucleation on either aluminum or silicon oxides[8,9]. The modification of the morphology of sulfide inclusions consequently leads to the enhancement of the mechanical properties of the structure steel. By using E-45 ASTM for determining the inclusions morphology, it has been proved that silicon content has the main effect on the distribution and the morphology of sulfide inclusions. As shown in Fig.3, the number of inclusions is sharply decreased with silicon addition [10]. which can be explained by the nucleation phenomenon of sulfide inclusions as increasing the silicon content. Moreover, the heavy sulfide inclusions are sharply decreased with the increment of silicon content as shown in Fig.4. This observation should be attributed to the role of silica inclusion in steel acting as nucleus site for manganese sulfide nucleation [11]. The optical observations on the polished surface of steel specimen have ensured the role of silica as a nucleation site for manganese sulfide inclusions as shown in Fig.5a, b.

### 3.4 The effect of deoxidation on the desulfurization processes.

It was well established that the activity of sulfur is inversely proportional to the oxygen activity in the molten steel [2]. As increasing the oxygen content in molten steel, the oxygen is being enriched in the interphase layer between the molten metal and slag, which obstacles the sulfur segregation to the molten metal and slag interphase [3]. Thereby, the desulfurization rate is tremendously affected by the oxygen content

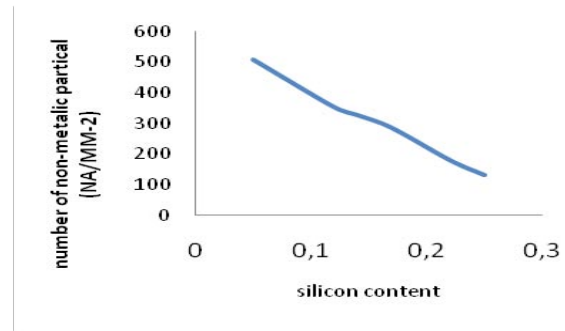


Fig. 3: Effect of silicon content o Number of non-metallic particles (NA) / mm-2

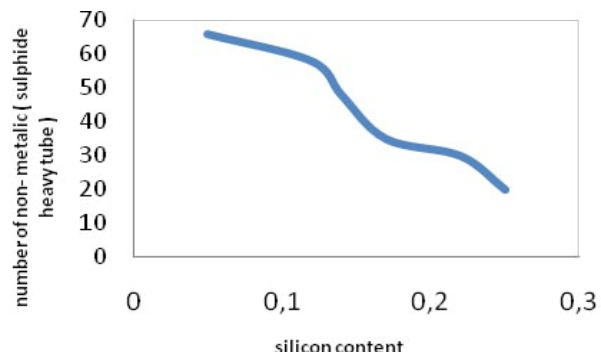


Fig. 4: Effect of silicon content on Number ) of non-metallic sulfides heavy tube

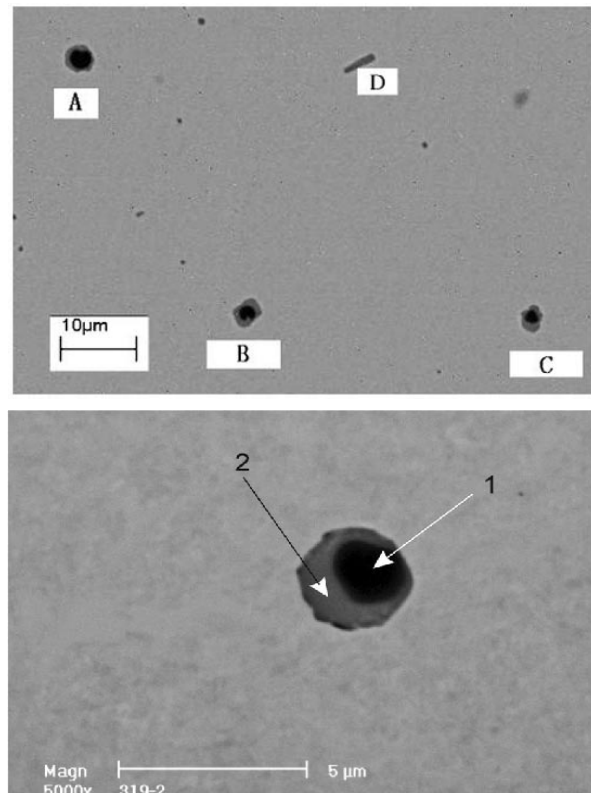


Fig.5 a: Typical duplex oxide–sulfide inclusion  
 Fig .5 b: theoxy sulphide inclusion; 1 –SiO<sub>2</sub>, 2 – MnS.  
 (Particle A, B and C) and plate-like MnS (particle D) In conventional continuous casting silicon steel.

in steel. It is well known that Aluminum considers as the most powerful deoxidizer agent in the steel making process. However, the nozzle clogging, as well as the cost of aluminum promotes the using of silicon as deoxidizer, in particular in manufacturing of structure steel. The desulfurizing rate as well as the oxygen content of the molten steel bath has been determined in the ladle-refining furnace of abu zaabal engineering company for producing construction steel, using different percentage of silicon as a deoxidizer. Figure 6 represents that the silicon content has a significant effect on either the desulfurizing rate, or the oxygen content of steel. On the other hand, the desulfurizing rate of steel at optimum silicon content (0.25%) has been enhanced 40 times more than the non-deoxidizer steel. In addition, the sulfur partition coefficient between metal and slag is sharply increased with the silicon content as shown in figure 7. These results can be explained by the reducing of oxygen con-

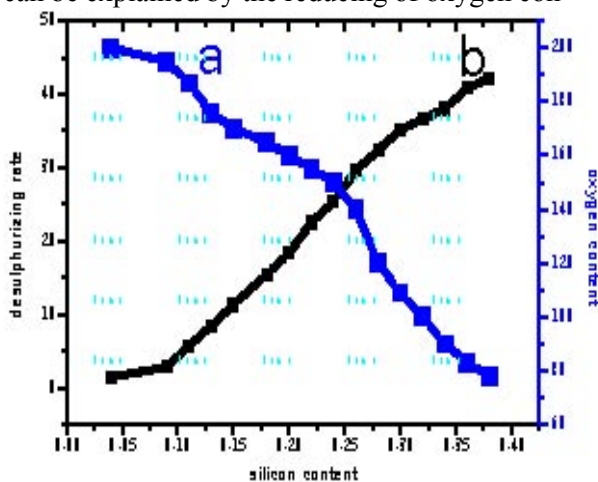


Fig.6: relationship explains effect of silicon content On desulfurization rate and oxygen percent.

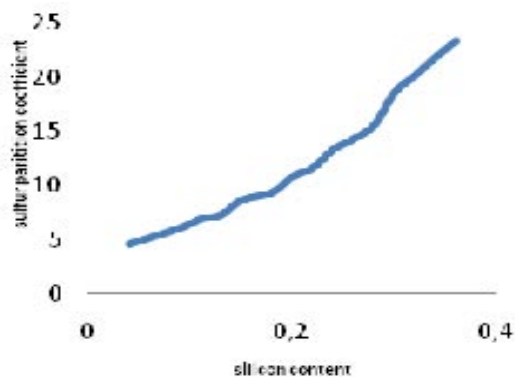


Fig.7: effect of different silicon content on sulfur partition coefficient.

centration in molten bath promote the sulfur activity in the slag/metal interphase layer.

$$\text{Sub: desulfurizing rate} = \left( \frac{50 - 5f}{50} \times 100 \right)$$

### 3.5 The effect of desulfurizing agent on the desulfurization processes

The lime stone is ordinary used as a desulfurizing agent in ladle refining process in the steel plant of abu zaabal engineering company. It is commonly used as a source of lime, which improves the desulfurizing reaction in term of forming CaS, or increasing the apparent basicity of the slag layer. As shown in equation (3, 4).



$$\text{Basicity} = \frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} \quad (4)$$

Referring to the aim of study in reducing the energy consumption in steel plant of abu zaabal engineering Company, the lime stone considers as the most intensive energy consumer through its dissociation as shown in equation (5).



$$\Delta G^\circ_r = 177,100 - 158 T (\text{J/mol}) \quad (5)$$

The ordinary amount of lime stone that is being used in ladle refining furnace of abu zaabal engineering company has been compared with the stoichiometric amount of lime stone required for desulfurization process at different silicon content as shown in Figure 8 a, b. The results indicate that the amount of lime that must have been used for complete desulfurization can be achieved by using stoichiometric computation method at steel deoxidized with Si (0.27%), which means that the amount of lime stone that is required for complete desulphurization is explicitly fit to the stoichiometric calculation at Si (0.27%). Thereby, the amount of lime stone is reduced 50% much less than the ordinary amount of lime stone. Certainly, these results will reflect on the energy consumption through ladle refining furnace of abu zaabal engineering company. Where, it was found that 1kg of lime stone actually consumed about 10KW/h.



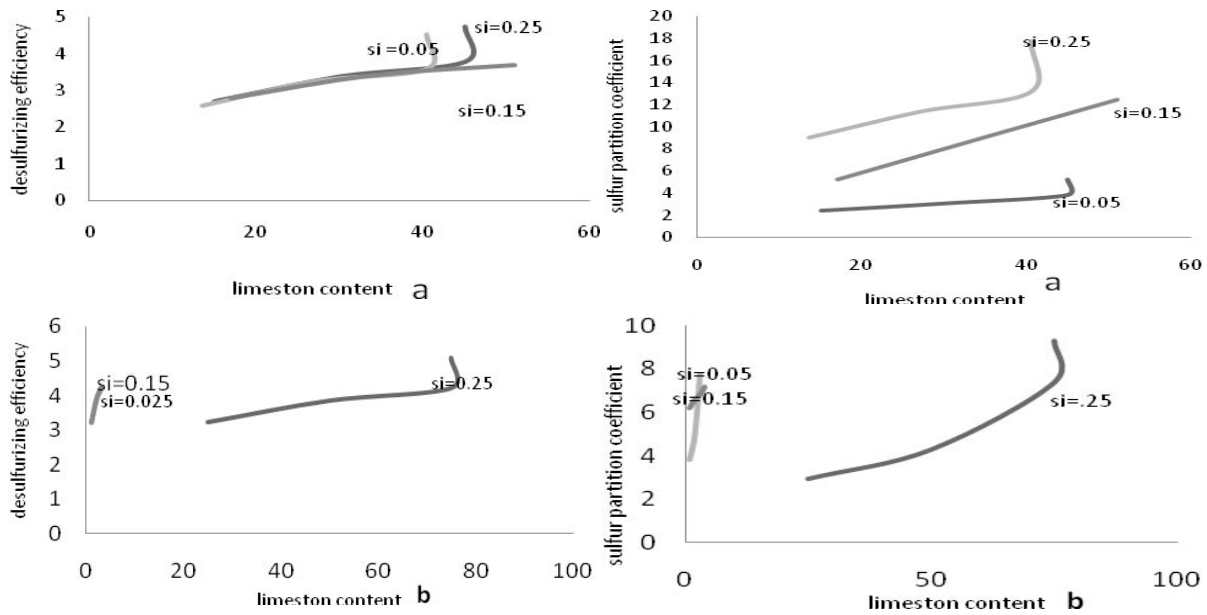


Fig. 8 a, b:relationship between [stoichiometric (a), ordinary (b)] limestone content and desulfurizing efficiency and sulfur partition coefficient Percent at different silicon content(0.05, 0.15, 0.25-%)

**3.6 The effect of temperature on the sulfur removal.**

The temperature of the molten steel bath consider as a crucial parameter in the desulfurizing process [12]. The main source of heat in Ladle refining furnace is the electric current passed across the graphite electrode, the ordinary temperature used for obtaining an optimum desulfurizing rate is 1923°k. Thereby, it is expected that the optimizing of the desulfurizing temperature must have reduced the energy consumption in the desulfurization process. The instantaneous desulfurizing rate  $\delta S/\delta T$  of different silicon containing steels has been determined through wide range of temperatures (1860° – 1930° k), as shown in figure 9.

This figure depicts that instantaneous desulfurizing rate is reduced as increasing the temperature of steel containing 0.25% Si. On the contrary, the instantaneous desulfurizing rate is linearly increased as increasing the temperature of the non-deoxidized steel 0.05 Si %. However, the steel containing 0.15 % Si is unchanged pending to 1890° k, followed by sharply descending with increasing temperature. These results should have been explained by the activity of oxygen is entirely dependent on the temperature. Thus, the increasing of temperature of deoxidized steel improves the oxygen activity at

the expense of sulfur activity. V.Kudrin, found that the oxygen activity is completely dependent on the temperature[13]. Then, the temperature required for attaining to an optimum desulfurizing rate, should be reduced from 1923° to 1870°k.

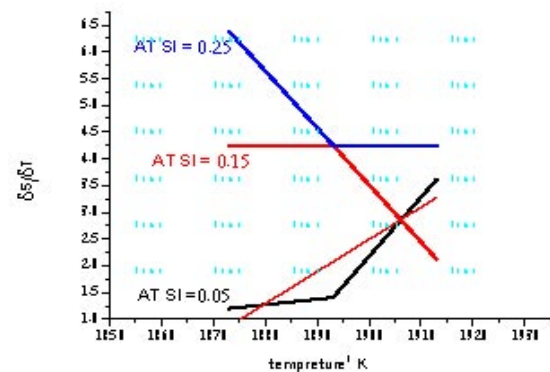


Fig. 9: relation between instantaneous desulfurizing rate and temperatures Sub: $\delta S/\delta T$  change of desulfurizing rate per temperature

**3.7 The effect of stirring on the sulfur removal**

The downward blowing of argon into the molten steel bath at the ladle-refining furnace of abu zaabal engineering company has been studied at constant silicon, amount of limestone, as well as temperature in Term of energy as seen in equation (6). The results indicate that the desulfurizing rate is linearly dependent on the stirring energy as shown in figure 10. This can be attributed to the role of stirring energy in the progress of the interaction between sulfur ion and slag /

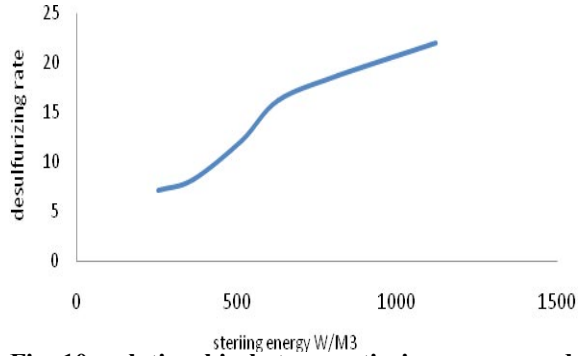
metal inter face, and consequently promote the desulfurizing rate. The results concord with the previous research [14].

$$e = 6.18 * F * T * \left[ 1 + \ln \left( 1 + \frac{\rho * g * h}{1.013 * 10^5} \right) \right] \quad (6)$$

F: Argon flow rate (Nm<sup>3</sup>/h)

$\rho$  : Specific density of liquid steel (7,000 kg/m<sup>3</sup>)

T: Temperature (°K)                      g: 9.81 (m/s<sup>2</sup>)



**Fig. 10: relationship between stirring energy and desulfurization rate**

### 3.7 Comparison between measured and computational sulfur partition

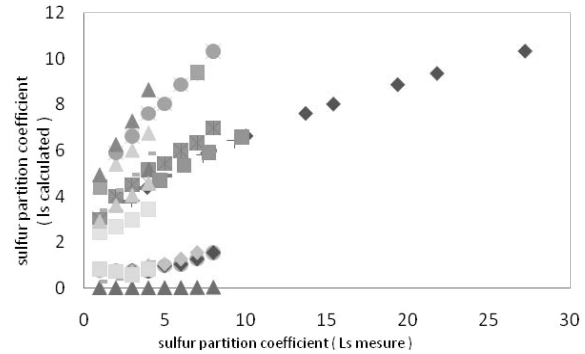
Sulfur partition coefficient considers as the main indication for the desulfurization process, where  $L_s = (S)_{\text{slag}} / [S]_{\text{metal}}$ . Then, the measured sulfur partition coefficient has been determined through tens of heats, and compared with the computational sulfur partition coefficient, using two models [15]. The first model considered the oxygen activity (Y. Yang model), as shown in equation (7).

$$C_s = (\%S) [a_o] / [a_s] \quad (7)$$

While, the second considers the optical basicity (The Sosinsky-Sommerville optical basicity model), as seen in equation(8).

$$\log C_s = \frac{22690 - 54640 A}{T} + 43.6A - 25.2$$

It is clear from Figure 11 that the computational values from the first model are much closed to the measured sulfur partition coefficient than the second model. Certainly, this ensure sensitive dependence of desulfurizing process on the deoxidation power of the steel deoxidized with silicon. The low deviation between  $L_s$  measured and the first model has been proved in the previous work [16, 17].



**Fig. 11: Comparison of the relationship between measured and calculated sulfur partition ratio  $L_s$  for the different calculated values of Log  $C_s$  and  $[a_o]$  of oxygen activities**

## CONCLUSIONS

- The desulfurizing rate through LRF of the Abu-Zaabal Steel plant completely dependson the percentage of silicon.
- The morphology of sulfide inclusions transformed into globular shape with increasing of silicon content.
- The stoichiometric amount of limestone is applicable at silicon 0.25%.
- The energy consumption has been reduced ensuing from the reduction of the limestone amount.
- The stirring energy has a positively effect on the desulfurizing rate.
- The measured  $L_s$  are much fit to the oxygen activity considering Y. Yang, model rather than the Sosinsky-Sommerville optical basicity model.

## REFERENCES

- [1]Margareta A.ndersson, Pär G. Jönsson, Mselly M. Nzotta; Application of Sulphide Capacity Concept on High basicity Ladle Slags Used in Bearing Steel Production. ISIJ International, Vol 39 (1999) No 11, pp 1140-1149.
- [2]Margareta A. Andersson, Lage T.I. Jonsson, Pär G. Jönsson, A thermodynamic and Kinetic Modelling of Reoxidation and Desulfurization in the Ladle Furnace; ISIJ International Vol. 40 (2000), No. 11, pp. 1080–1088
- [3]K.W. Lange" Thermodynamics and kinetic aspects of secondary steelmaking" International Materials Reviews, (1988), vol. 33 p 53
- [4]S. Mizoguchi: "A study on segregation and oxide inclu-

- sions for the control of steel properties”, Ph. D. thesis, The University of Tokyo, (1996)
- [5] P.J. Paduch" Modification of non-metallic inclusions in steels with enhanced machinability" Archives of Metallurgy 48 (2003) 285-307.
- [6] F. Ishikawa, T. Takahashi and T. Ochi: Metall. Trans. A, 25A (1994), 929
- [7] Lis T., Róañski P.: Hutnad 75 (2005) 5, 259-264.
- [8,9] J. Whitbread, A. Cubero and L. Zampetti: Draft Final Report "Improved Deoxidation Practices for Ultra Clean Steel Production", ECSC sponsored project, Jan. (1999), British Steel plc. Sidenor I & D and Centro Sviluppo Materiali.
- [10] ASTM Standard E45-97, (2004), "Standard test methods for determining the inclusion content of Steel," Annual Book of ASTM Standards, Vol. 03.01, pp. 187-199
- [11] von M. Eng. Zhongting Ma" Control of nonmetallic inclusions in continuously cast steels in view of macro-cleanliness, castability, precipitation modification and grain refinement" geboren am 04.09.1964 in Anhui, V. R. China, (2001), vol.2 p4-17
- [12] Pär Jönsson, Lage T.I. Jonsson" The Use of Fundamental Process Models in Studying Ladle Refining Operations" ISIJ International, Vol 41 (2001), No. 11, pp1289-1302.
- [13] V.Kudrin, Steelmaking, (1981), vol.3 p89
- [14] SC Koria and K S Rao: Mathematical model for powder injection refining of steel melt. Ironmaking and steelmaking 25 (6), (1998) 453-459
- [15] I. D. Sommerville, Y. Yang, Optical basicity for control of slags and Fluxes, Steel Technology International, (1994), 117
- [16] Hao N, Li H., Wang H, Wang X. And Wang W. (2006), Application of the sulphide Capacity theory on refining slags during LF treatment, Journal of University of Science and Technology Beijing, Vol 13, Number 2, April, pp. 112- 116.
- [17] Uday PAL"Estimation of Sulfide Capacities of Multi-component Slags using Optical Basicity" ISIJ International, Vol. 53 (2013), No. 5, pp. 761-767