

## EVALUATING SLAG-METAL EQUILIBRIUM IN SECONDARY STEELMAKING\*

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### Resumo

Steel-slag reactions are of paramount importance in steelmaking, in special in secondary steelmaking. Currently, desulfurization, deoxidation and inclusion removal are mostly performed during ladle processing. The extent to which these reactions proceed is governed by the initial state of the material reaching the ladle, the additions made to the ladle and by undesired interactions such as reoxidation and steel-refractory reactions. In this work fundamental thermodynamic aspects involved in ladle refining of Al-killed and Si-Mn deoxidized steel are briefly reviewed. Using thermodynamics, the extent to which equilibrium is approached for the different deoxidation reactions is evaluated. These results are compared to measurements performed in industrial ladle furnaces. Based on this comparison, observations are made with respect of the efficiency of the refining process. It is concluded that the relationship between agitation and reoxidation by air play a key role on the ability to reach low and controlled oxygen in steel. It is also concluded that relatively long treatments with controlled agitation are needed to achieve steel-slag equilibrium..

**Palavras-chave:** ladle furnace, deoxidation, reoxidation, thermodynamics .

### AVALIAÇÃO DO EQUILÍBRIO METAL-ESCÓRIA EM METALURGIA SECUNDÁRIA

#### Abstract

Reações metal-escória são fundamentais no refino do aço, em especial no refino secundário. A maior parte das operações de desoxidação, desulfuração e remoção de inclusões são realizadas na metalurgia de panela. A possibilidade de atingir o equilíbrio nestas reações é definida pelo estado inicial do aço na panela, pelas adições realizadas e pelas interações indesejadas, tais como reoxidação e interações com os refratários. Neste trabalho a termodinâmica básica da desoxidação por Al e por Si-Mn é brevemente revista. Aplicando a termodinâmica computacional, avalia-se o desvio em relação ao equilíbrio, para as diferentes práticas de desoxidação, comparando os resultados com medidas industriais. Com base nesta comparação, a eficiência dos processos de desoxidação é avaliada. Conclui-se que a relação entre agitação e reoxidação pelo ar tem um papel importante na capacidade de se atingir valores baixos e controlados de oxigênio no aço. Conclui-se ainda que tempos longos sob agitação controlada são necessários para atingir o equilíbrio metal-escória.

**Keywords:** forno panela, desoxidação, reoxidação, termodinâmica.

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## 1 INTRODUCTION

Steel-slag reactions are of paramount importance in steelmaking, in special in secondary steelmaking. Currently, desulfurization, deoxidation and inclusion removal are mostly performed during ladle processing (1). The extent to which these reactions proceed is governed by the initial state of the material reaching the ladle, the additions made to form slag and adjust the chemical composition of the steel and by undesired interactions such as reoxidation and steel-refractory reactions.

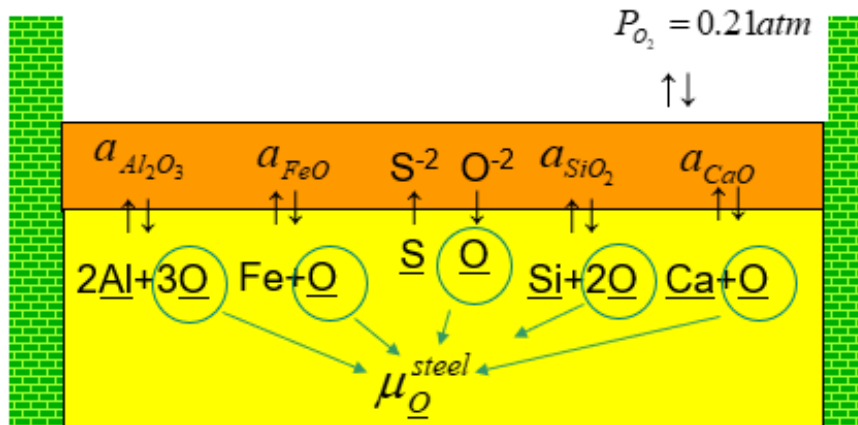
While equilibrium is achieved under some processing conditions, this is not a general rule. When equilibrium is attained, determining the expected composition is not an excessively complex task if one has access to computational thermodynamics facilities. If, however, equilibrium is not achieved, the final state is dependent on many process variables and, in principle, a complex kinetic model would be needed. In the present work the fundamental thermodynamic and kinetics aspects involved in ladle refining of aluminum killed and silicon-manganese deoxidized steel are briefly reviewed, with focus on deoxidation- reoxidation. Furthermore, the extent to which equilibrium is approached for the different deoxidation processes is evaluated, using computational thermodynamics. Two different thermodynamic databases were used (2): a database originally derived from the IRSID model, that uses the Kapoor-Frohberg-Gaye cell model (3,4) and another one, using the ionic liquid model, developed at KTH (5,6). These results are compared to experimental measurements performed on industrial ladle furnaces. Based on this comparison, observations are made with respect of the efficiency of the refining process and recommendations for process improvements and further testing are made. .

### 1.1 Deoxidation Thermodynamics and Kinetics

The thermodynamics of deoxidation of steel has been well reviewed in many publications (e.g.(7,8)). Although there are still some doubts concerning thermodynamic data for Al (9), Ca and Mg (10), in special, the present knowledge is sufficiently good to perform good predictions in the range of commercial steels. It is generally agreed that the deoxidations reactions involving Al and Si are not limited by nucleation and that the oxygen in solution in steels approaches the equilibrium values with the dissolved deoxidants very rapidly (11), at least when the pure oxide is formed. If, however, equilibrium must be attained with an oxide that is not pure, but dissolved in the slag, kinetics may play an important role (e.g. (12-15)).

While ladle stirring is critical for the kinetics of the metal-slag reactions, it is well established that judicious control must be exercised to avoid reoxidation and slag entrainment (11,16). For steel processed in LF under ideal conditions of agitation and with due care to prevent reoxidation, it has been observed that the final composition is very close to equilibrium (e.g. (2,15)). In this case, the equilibrium of all possible oxidation reactions should prevail and a single value of oxygen in solution should satisfy all the calculated equilibria, as indicated in Figure 1.

If processing time is short, agitation is inadequate (either too weak or too strong (11)) and if reoxidation is not properly controlled, this condition, however, is not fulfilled. In this case, the observed values of the chemical composition of the steel and of the slag will indicate how the process is evolving. This has been demonstrated, for instance, by (17), who tried to understand the reasons for the observed deviations. As the problem is complex, efficient kinetic models for the LF are still being developed (e.g. (12,18)).



**Figure 1.** When metal-slag equilibrium prevails in the ladle, the soluble oxygen content is such that it satisfies all metal-oxide equilibria (19). Here  $\mu_O^{steel}$  is the oxygen chemical potential in the steel, directly related to the oxygen content in solution in the steel.

## 2 EXPERIMENTAL

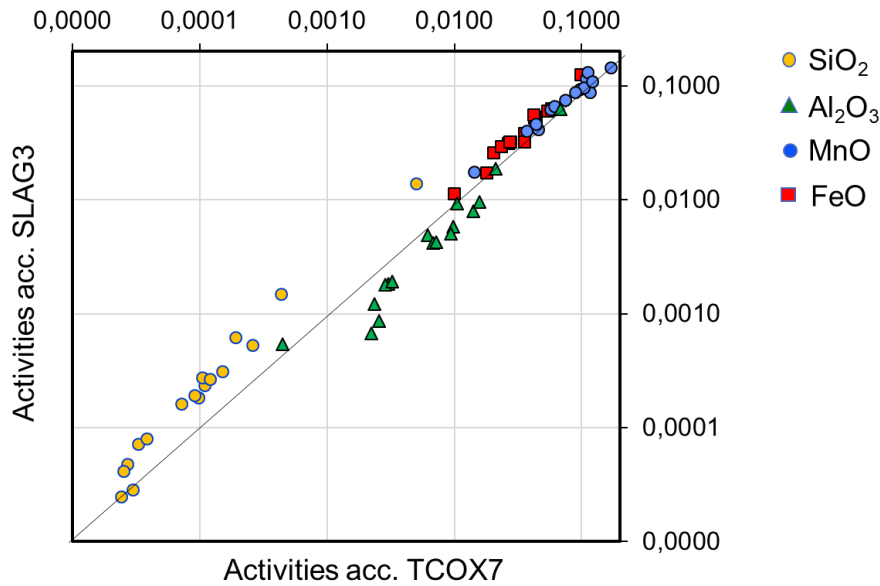
Several heats made both in an oxygen converter (BOF) and in an electric arc furnace (EAF) were processed in ladle furnaces (LF) without vacuum protection. During LF processing slag and metal were sampled at defined points of the process. Furthermore, oxygen dissolved in steel was measured using commercial, disposable electrolytic cells, and temperature was measured.

All experiments performed in BOF steel were in heats of the same low-sulfur HSLA steel containing around 1% Mn and 0.1% C. This steel was aluminum deoxidized and calcium treatment. All sampling was done in the ladle furnace before the calcium treatment. All experiments performed in EAF steel were heats of the same engineering bar steel containing around 0.25% C. The steel was silicon-manganese deoxidized. Sampling was performed in the ladle and in the tundish.

Computational thermodynamics calculations were performed using Thermo-calc (20) in conjunction with the SLAG3 and TCOX7 databases (21,22). The application of these databases to steelmaking is described and discussed elsewhere (2,4).

## 3. EVALUATING THE DEVIATION FROM METAL-SLAG EQUILIBRIUM

In order to evaluate the deviation from equilibrium, the following strategy was adopted. Using the composition of the slag and temperature at the end of the LF process the activity of the oxides in the slag was calculated using computational thermodynamics. In the case of aluminum deoxidation, the alumina activity was also calculated using Ohta and Suito's empirical formula (23,24). There agreement of the results of Ohta and Suito's formulas with those calculated using computational thermodynamics was reasonable. The agreement of the activities calculated using the two different databases mentioned in 2, above, was also reasonable, as shown in Figure 2.



**Figure 2.** Comparison of the calculated activities of oxides in slag in LF using two different databases and Thermo-calc. Reference states are pure oxides at the calculation temperature, and 1atm.

For each oxide-metal reaction (Equations 1 to 4) applicable, equilibrium was calculated considering the metal activity determined from the steel chemical analysis (Al, Si, Mn and Fe) and the oxide activities, to determine the oxygen content in equilibrium with these conditions. If equilibrium had been achieved, all calculations should result in the same value for the oxygen content dissolved in the steel, which should agree with the experimental measurements. The difference between these values indicate the extent of deviation from metal-slag equilibrium.



This can also be expressed by recalling, from Figure 1, that equilibrium must fulfill equation 5, since there is only one value for the dissolved oxygen content in the steel.

$$\text{O}_{\text{Al}} = \text{O}_{\text{Si}} = \text{O}_{\text{Mn}} = \text{O}_{\text{Fe}} = \text{O} \quad (5)$$

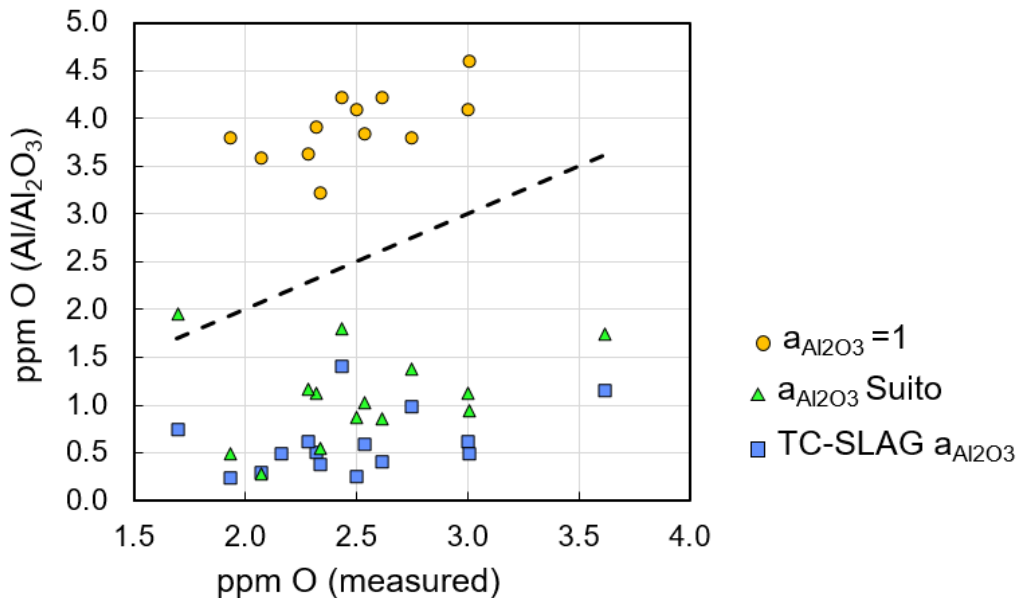
Thus, when the calculated values of oxygen in equilibrium with each metal and oxide are compared among each other and with the measured oxygen content, an estimate of the deviation from equilibrium is obtained as well as insight into the effectiveness of the deoxidation process.

### 3.1 Aluminum killed steel

In the case of aluminum killed steels, the oxygen content that would be in equilibrium with the elements and the oxides (according to reactions 1-4) were calculated for Al, Mn and Fe. As observed in a previous work (25) with other flat product steels, the deviation between the measured oxygen and the Fe/FeO equilibrium was very large. For this reason, the comparison between these calculations and the measured values is not presented in the following figures.

Figure 3 presents the comparison of the measured oxygen content with the oxygen calculated according to the Al/Al<sub>2</sub>O<sub>3</sub> equilibrium. This calculation was performed for three different values of alumina activity:

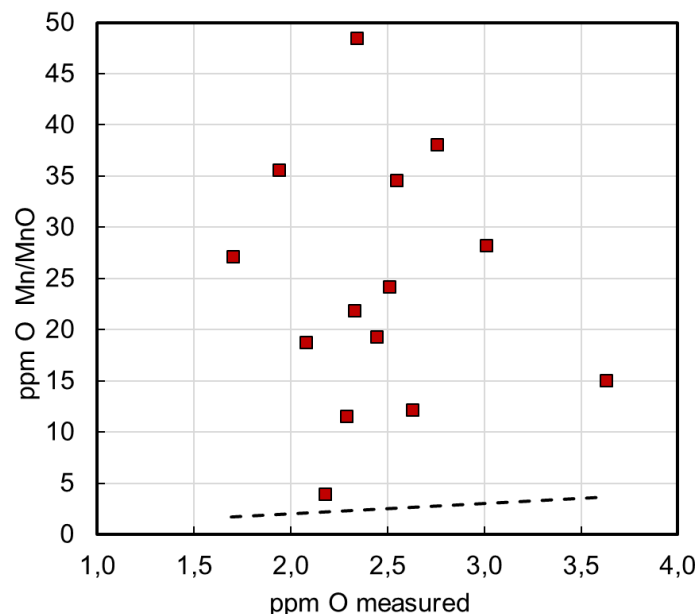
- (a) Pure alumina, ( $a_{Al_2O_3} = 1$ ) which is the condition prevailing right after the aluminum addition to the liquid metal;
- (b) Alumina activity calculated based on the LF slag composition at the sampling moments, using Ohta and Suito's formula and
- (c) Alumina activity based on the same slag composition and temperature, calculated using SLAG3 and Thermo-calc.



**Figure 3.** Calculated values of oxygen concentration in equilibrium with different alumina activities. Pure alumina, alumina activity calculated according to Ohta and Suito's formula and alumina activity calculated using computational thermodynamics. Dashed line shows measured values for each heat.

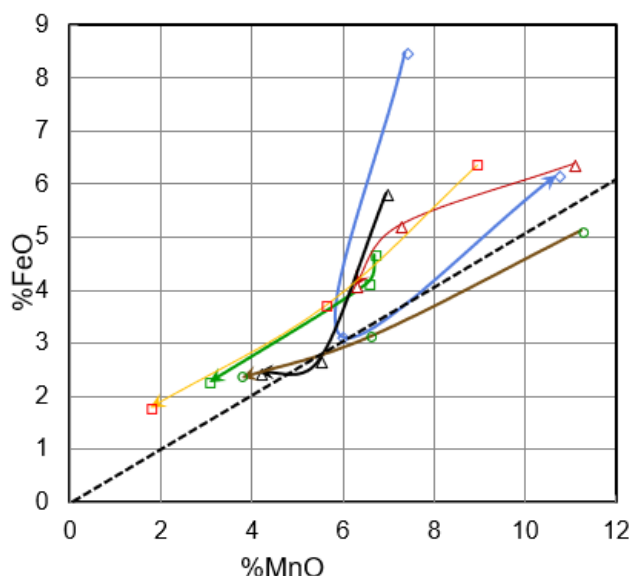
The results in Figure 3 show that the oxygen content in the steel is lower than that which would be in equilibrium with pure alumina. This indicates that the dissolution of alumina and lowering of its activity is having some effect on the aluminum deoxidation. However, the calculated oxygen in equilibrium with conditions (b) and (c) above are lower than the measured oxygen content.

Figure 4 presents the oxygen content in equilibrium with Mn/MnO. It is clear that there is no equilibrium between Mn and MnO, the slag content of MnO being substantially higher than that, which would be in equilibrium.



**Figure 4.** Calculated values of oxygen concentration in equilibrium with Mn and MnO. Oxide activity calculated using computational thermodynamics. Dashed line shows measured values for each heat.

Among the oxides considered in the calculations, MnO and FeO are part of the passing slag from the BOF tapping operation. In order to follow the evolution of MnO and FeO in the LF, their values during the LF treatment were compared. The values of MnO and FeO along the treatment in the LF are presented in Figure 5.



**Figure 5.** Evolution of FeO and MnO during the treatment in the LF for various Al-killed heats. Dashed line indicates equilibrium FeO/MnO relation proposed by Turkdogan (8)

Most heats consistently approach lower values of FeO and MnO and the MnO/FeO equilibrium relationship. At least in one heat the approach is interrupted during the process. The final contents, however, are still high for the level of deoxidation of the steel, as seen in Figure 4.

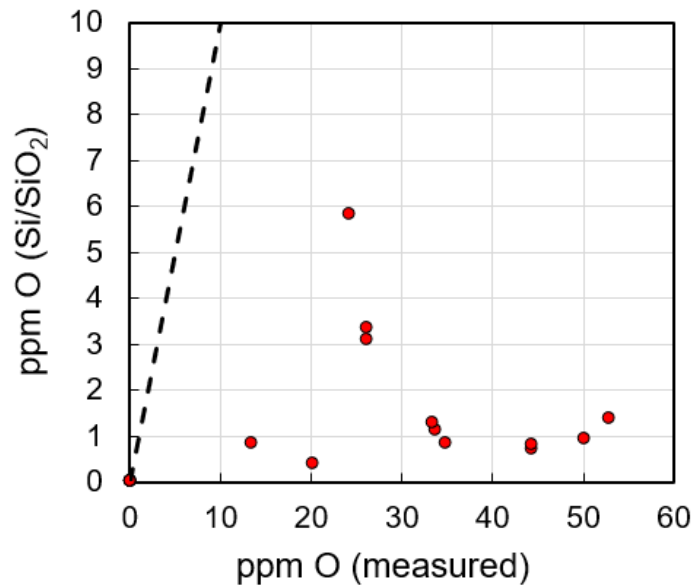
The results in Figures 3 to 5 indicate that indeed aluminum is the element controlling the lowering of the soluble oxygen in the process. Nonetheless, it is clear that

equilibrium is not attained. This could be caused either by reoxidation of the liquid metal by the atmosphere (“open eye” due to excessive agitation) or by the difficulty in lowering the FeO and MnO contents in the slag.

### 3.1 Silicon manganese killed steel

In the case of silicon manganese killed steels, the oxygen content that would be in equilibrium with the elements and the oxides (according to reactions 1-4) were calculated for Si, Mn and Fe.

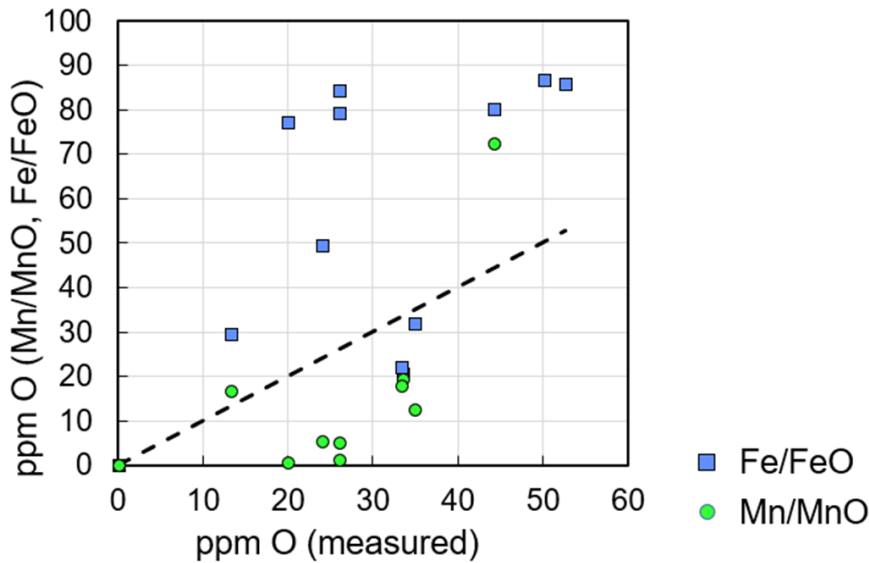
Figure 5 presents the comparison of the measured oxygen content with the oxygen calculated according to the Si/SiO<sub>2</sub> equilibrium. As the silica activity in the slag is very low, silicon becomes an excellent deoxidant.



**Figure 6.** Calculated values of oxygen concentration in equilibrium with Si and silica. Silica activity calculated using computational thermodynamics. Dashed line shows measured values for each heat.

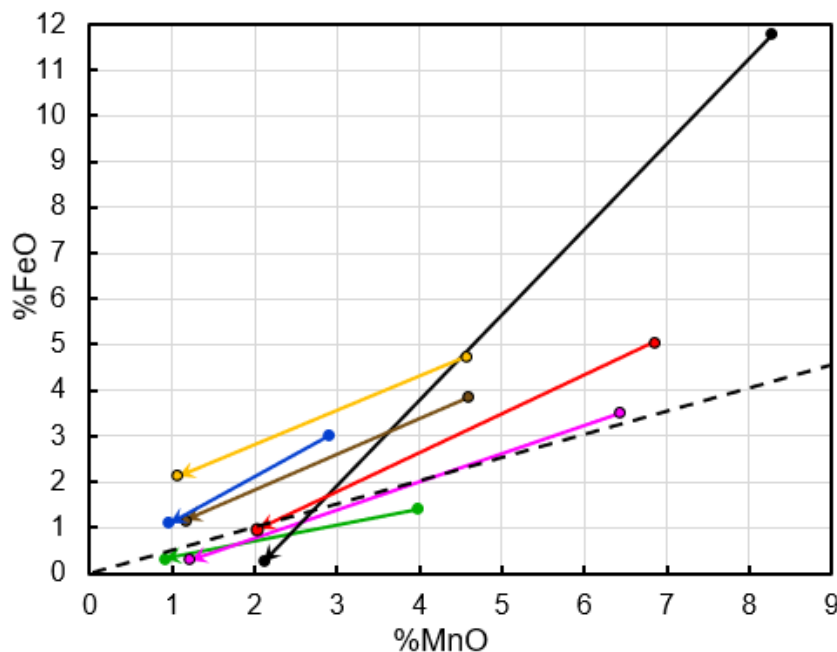
However, the actual oxygen values achieved in the LF deoxidation process are significantly higher than those calculated from the Si/SiO<sub>2</sub> equilibrium.

The values for the Fe/FeO and Mn/MnO calculated equilibria are presented in Figure 7.



**Figure 7.** Calculated values of oxygen concentration in equilibrium between Mn and MnO and Fe and FeO. Oxide activities calculated using computational thermodynamics. Dashed line shows measured values for each heat.

The expected values for the oxygen in equilibrium with Mn/MnO and with Fe/FeO are of the same order of magnitude as the experimental values of oxygen content. Furthermore, evaluating the evolution of the content of MnO and FeO in the LF slag (Figure 8) indicates that the heats approach the FeO/MnO equilibrium and reach lower values than those shown in Figure 5, for Al-killed steel. This may be due to the strong slag deoxidation performed with CaC<sub>2</sub> during tapping from EAF, in these Si-Mn steels. Direct slag deoxidation seems to be quite effective in lowering its content of the less stable oxides.



**Figure 8.** Evolution of FeO and MnO during the treatment in the LF for various Si-Mn deoxidized heats, using CaC<sub>2</sub> additions during tapping of the EAF. Dashed line indicates equilibrium FeO/MnO relation proposed by Turkdogan (8)



### 3.2 Summary of the observations

In both cases (Al-killed and Si-Mn deoxidation), the expected equilibrium oxygen contents would be significantly lower than the values measured at the end of the LF process. In the case of Al-killed steels, much lower soluble oxygen contents were reached than in the case of Si-Mn steels. This is reasonable as the equilibrium with a lower oxide activity (in the slag) is not critical to an effective deoxidation with Al. The measured values would be in equilibrium with an alumina activity somewhere between 1 (no effect of the slag) and the calculated value for the slag composition.

In the case of the Si-Mn deoxidized steel, the measured soluble oxygen content deviates significantly from what would be expected. It is, however, much lower than the value expected if equilibrium was established with pure silica, that would be in the range of 120-140 ppm. There are two plausible explanations to the observed phenomena. First, it could be postulated that the processing time was not enough to achieve metal-slag equilibrium. However, during the processing of the Al-killed heats, for instance, many heats required further additions of aluminum to keep this concentration within the specified range. Furthermore, times as long as 30-40 minutes were used in some Al-deoxidized heats, which should approach equilibrium based on information acquired elsewhere in similar conditions, but under vacuum (e.g.(11)). This seems to indicate that the reduction of less stable oxides is not effective in the process and/or reoxidation by air is playing a relevant role in the process. While FeO and MnO are reduced during the processing of both steels, it seems that the practice of directly deoxidizing the slag used in the Si-Mn steel is positive for oxygen control. However, in the processing of both steels, the deviations suggest that reoxidation due to exposure to air may be playing a relevant role. This indicates that the formulation of a kinetic model for the LF process is of paramount importance for the further development of the understanding of the deoxidation-reoxidation process. This understanding will have a significant impact on quality of steel and cost control in the melt shop.

## 4. CONCLUSIONS

Contrary to steels processed for longer times and under vacuum, equilibrium between deoxidants in the steel and oxides in the slag was not achieved during the regular ladle furnace processing of Al-killed BOF steel and Si-Mn EAF steels. In the case of Al-killed steels aluminum clearly controls the oxygen potential in the steel and levels of oxygen close to that expected by equilibrium are achieved. In the case of Si-Mn steels, with somewhat shorter LF processing times the deviation is quantitatively larger. The use of direct slag deoxidation with CaC<sub>2</sub> in the Si-Mn steels was shown to be effective in reducing the content of less stable oxides in the slag but was not sufficient to make possible slag-metal equilibrium at the end of the process.

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