THERMODYNAMICS OF MANGANESE OXIDE IN $CaO-SIO_2-MgO_{SAT.}-Cr_2O_3-MnO$ SLAGS FOR THE PRODUCTION OF HIGH MN STAINLESS STEEL

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ABSTRACT

The manganese equilibria between a manganese rich stainless steelmaking slag ($CaO-SiO_2-MgO_{sat.}-MnO-Cr_2O_3$) and Fe-Cr-Mn stainless steel were investigated in a temperature range from 1823 to 1873 K under Ar atmosphere. The partition ratios of manganese between the molten slag and the liquid steel were determined as a function of slag composition and temperature. The thermodynamics of MnO in the slag were studied by combining experimental results and thermodynamics theory. It was found that, as basicity increases, the manganese partition ratio, $L_{Mn} = (wt\% \ Mn)_{slag}/[wt\% \ Mn]_{steel}$, decreases. The elevated basicity leads to a high MnO activity coefficient. The influence of MnO contents on the activity coefficients was also considered. It can be concluded that in order to maximize Mn recovery during high Mn stainless steel production, a basic slag with a high MnO activity coefficient must be employed whereas high temperatures should be avoided.

Key Words: *Thermodynamics; $CaO-SiO_2-MgO_{sat.}-MnO-CrO_{1.5}$ system; Fe-Cr-Mn alloy; equilibrium partition ratios; manganese.*

INTRODUCTION

In order to reduce the manufacturing cost of austenitic stainless steel, attempts are being made to substitute expensive Ni with a base alloying material. A Ni substitute must provide the new stainless steel with sound mechanical properties, high wear resistance, and at least the same corrosion resistance as traditional stainless steel (304 and 316 grades). Mn, one of the most widely used alloying elements in modern steel production, has been found to satisfy these requirements when used in combination with N, C and Cr [6, 12]. It is thus being considered as a substitute for Ni in austenitic stainless steel production. Of major concern to high-Mn stainless steel producers, however, is the substantial loss of Mn through oxidation and volatilization. It is therefore of fundamental as well as practical importance to evaluate to what extent the recovery of Mn can be optimized in high-Mn stainless steelmaking [2].

Since Mn distributes itself between the slag and metal phases in the refining process, Mn recovery depends on the thermodynamic properties of the slag and metal phases through the activities of MnO in the slag and that of Mn in the steel. Mn losses can be minimized by the use of slags with a high MnO activities at low concentrations of MnO. With respect to non-stainless steel slag, there are sufficient data available on the MnO activity [1, 4, 7, 9]. However, for the combination of MnO and CrO_x in a slag, few studies have been made. Nevertheless, Garbers-Craig and Dippenaar [2] measured activity-composition relations of MnO in $MnO\text{-}CrO_x\text{-}CaO\text{-}SiO_2$-containing melts at 1773 K under an oxygen partial pressure of $10^{-8.99}$ atm by equilibrating slag samples with a Pt-Cr-Mn alloy. Their work is very useful for a better understanding of the behavior of MnO in slags containing both MnO and CrOx. However, their experimental conditions, i.e., absence of MgO, low slag basicity (wt%CaO/wt% SiO_2 = 0.2~1.0), relatively low temperature (1773 K) and Pt-2.9~8.5 wt% Mn-0.7~4.1 wt% Cr as reference metal phase, are quite different from the high Mn stainless steelmaking practice. These measured data are therefore of limited applicability for the production of high Mn stainless steel in conditions similar to current stainless steelmaking practice.

In the present study, the Mn distribution between $CrO_{1.5}$ and MnO containing slags and Fe-18 wt% Cr-12 wt% Mn stainless steel are determined under an Ar atmosphere at temperatures ranging from 1823 to 1873 K. The goal is to establish a suitable slag composition and provide operational guidelines for the maximization of Mn yields in the high Mn stainless steel refining process. Thermodynamics of MnO in the high Mn stainless steelmaking slag ($CaO\text{-}SiO_2\text{-}MgO_{sat.}\text{-}MnO\text{-}CrO_{1.5}$) were studied based on the combination of experimental results and thermodynamic calculations.

THERMODYNAMIC BACKGROUND

The reaction of Mn between molten slags and liquid stainless steel can be expressed as:

$$Mn(l) + \underline{O}_{Fe} = MnO(l) \tag{1}$$

$$\Delta G_1^0 = -229589 + 63.74T\left(J/mole\right)) \text{ [11]} \tag{2}$$

with equilibrium constant

$$K_1 = \frac{a_{MnO}}{a_{Mn} \cdot a_{\underline{O}_{Fe}}} \tag{3}$$

where a_{MnO} and a_{Mn} are the activity of, respectively, MnO in the slag and Mn in the high

Mn stainless steel. The standard states for MnO and Mn are taken as pure liquid MnO and pure liquid Mn at the experimental temperature. $a_{\underline{O}_{Fe}}$ is the activity of oxygen in liquid steel relative to the 1 wt% standard state. The oxygen activity coefficient with reference to the 1 wt% standard state ($f_{\underline{O}_{Fe}}$) can be calculated from available thermodynamic data [8] by the equation:

$$\log f_{\underline{O}_{Fe}} = e_O^{Cr}[wt\% Cr] + e_O^{Mn}[wt\% Mn] + e_O^O[wt\% O] \tag{4}$$

where $e_O^{Cr} = -0.09$, $e_O^{Mn} = -0.021$ and $e_O^O = -0.20$ are the first-order interaction coefficients. Considering that $a_{\underline{O}_{Fe}} = f_{\underline{O}_{Fe}}\left[wt\% O\right]$, $a_{\underline{O}_{Fe}}$ can be obtained by performing chemical analysis of the dissolved elements in the steel. The activity coefficient of MnO, γ_{MnO}, is obtained by writing Equation (3) as a function of the oxygen and Mn activity coefficients in the high Mn stainless steel melt:

$$\gamma_{MnO} = \frac{K_1 f_{\underline{O}_{Fe}}[wt\% O]\cdot a_{Mn}}{X_{MnO}} \tag{5}$$

where X_{MnO} is the mole fraction of MnO in the slag, and K_1 is the equilibrium constant of Equation 1. The latter can be calculated from the standard reaction free energy of Reaction 1:

$$K_1 = \exp\left(-\frac{\Delta G_1^0}{RT}\right) \tag{6}$$

Due to the high concentration of Mn in the steel, a_{Mn} does not obey Henry's law; and the second order parameters and cross product terms in the Wagner formula [13] for γ_{Mn} may not be neglected. Therefore, the relationship $a_{Mn} = \gamma^0_{Mn} X_{Mn}$ (X_{Mn}: mole fraction of Mn in the steel; γ^0_{Mn} : the activity coefficient of Mn at infinite dilution) does not apply, and no straightforward calculation of a_{Mn} is available. In the present study, a_{Mn} was obtained by using Thermo-Calc software the TCFE4 database [5].

The Mn partition ratio, L_{Mn}, is defined as the ratio of Mn (as MnO) in the slag to Mn in liquid steel:

$$L_{Mn} = \frac{(wt\%\ Mn)_{slag}}{[wt\%\ Mn]_{steel}} \tag{7}$$

This ratio can provide a practical way to evaluate the Mn distribution between slag and steel, and hence the Mn recovery during stainless steel refining. L_{Mn} can be experimentally obtained by measuring the Mn contents of slag and steel.

EXPERIMENTAL

A vertical tube furnace (GERO HTRV 100-250/18), which is heated by six U-shaped Super Kanthal 33 (MoSi$_2$) heating elements, was employed for the equilibration experiments. The temperature profile in the furnace ensured a hot zone, around 4 cm in length, in which the temperature varies by less than ± 1 K. An Ar atmosphere, at a flow rate of 200 cm^3/min, was maintained throughout the experiments.

In the experiments, 15 grams of CaO-SiO$_2$-MgO$_{sat.}$-MnO-CrO$_{1.5}$ slag was equilibrated with 25 g of the high Mn stainless steel in a MgO crucible (29 mm ID, 35 mm OD and 50 mm height). The experimental temperature was in the range of 1823 to 1873 K.

The master alloy (cast Ni-free austenitic stainless steel) employed in the present experiments was prepared by melting Fe, Mn and Cr alloys with impurities such as C, Si, Ni, N and Al in a vacuum induction furnace. The chemical composition of this steel is shown in Table 1. The initial slags were prepared from a mixture of reagent-oxide SiO_2, MnO, MgO, Al_2O_3, $CrO_{1.5}$ and CaO, which were dried at 1273 K for 12 hours. The initial slag compositions for each experimental run are listed in Table 2. 10 wt% MgO is added to each slag to protect the MgO crucible from excessive slag attack. This is the MgO level which corresponds to a typical stainless steel slag composition. The content of MnO in the initial slags varies from 10 to 20 wt%, that of $CrO_{1.5}$ from 2 to 10 wt%, and wt%CaO/wt% SiO_2 ratios from 0.5 to 2.0.

Table 1: Chemical composition of stainless steel charged in the experiments (in wt%)

Mn	Cr	C	Ni	Si	N	Al
11.76	17.54	0.15	0.53	0.32	0.262	0.0077

Table 2: Experimental conditions and initial slag compositions (in wt%)

Exp. No	Equilibration time (h)	Temp. (K)	MgO	MnO	Cr_2O_3	CaO	SiO_2	C/S
1-1	10	1873	10	10	10	42.0	28.0	1,5
1-2	15					42.0	28.0	1,5
1-3	20					42.0	28.0	1,5
1-4	2					42.0	28.0	1,5
2-1	30	1873	10	10	10	23.3	46.7	0,5
2-2						35.0	35.0	1
2-3						42.0	28.0	1,5
3-1	20	1873	10	10	5	25.0	50.0	0,5
3-2						37.5	37.5	1
3-3						45.0	30.0	1,5
3-4						50.0	25.0	2
4-1	20	1873	10	20	5	25.0	50.0	0,5
4-2						32.5	32.5	1
4-3						39.0	26.0	1,5
4-4						43.3	21.7	2
5-1	20	1873	10	10	2	26.0	52.0	0,5
5-2						46.8	31.2	1,5
6-1	20	1823	10	10	5	45.0	30.0	1,5
6-2		1853				45.0	30.0	1,5

After equilibration, the MgO crucible was withdrawn from the furnace and the slag and steel were quenched in water. Slag and steel samples were collected. The Cr and Mn contents of the steel samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), after dissolution of the steel in a mixture of hydrochloric acid and nitric acid (3:1). The total oxygen content in the steel was analyzed by a LECO combustion analyzer. Considering the long slag/metal equilibration time under an Ar atmosphere, it is reasonable to assume that the total oxygen content of the steel equals the dissolved oxygen content (i.e., no remaining oxidic inclusions in the steel). The contents of Ca, Mg, Si, Mn and Cr in the slag phase were determined with ICP-AES after dissolution of samples by an oxidizing fusion method. The salt, consisting of 0.2 g of slag mixed with 1 g NaOH and 2 g Na_2O_2, was fused in a glassy carbon crucible. The molten material was then dissolved in HCl (3:5).

Preliminary experiments were performed for the determination of the required equilibration time. Equilibrium was approached by transfer of Mn from steel to slag and Cr from slag to steel. A mixture of 42 wt% CaO-28 wt% SiO_2 -10 wt% MgO-10 wt%

MnO-10 wt% $CrO_{1.5}$ was equilibrated with stainless steel for various durations (2 to 20 hours) at 1873 K, and subsequently quenched to room temperature. The results indicated that equilibrium was attained within 15 hours. On the basis of this observation, an equilibration time of 20 hours was chosen for all equilibration runs reported in this paper.

RESULTS AND DISCUSSION

The equilibrium compositions of slag and steel, and the distribution ratios L_{Mn} as determined after the equilibration experiments are summarized in Table 3. The L_{Mn} at 1873 K is shown in Figure 1 as a function of slag basicity. The latter is defined as B = {(wt% CaO) + (wt% MgO)}/(wt% SiO_2). The value of L_{Mn} decreases with increasing slag basicity, indicating that the Mn content in the steel phase increases as the basicity of the slag increases. This observation is in agreement with the data reported by Morales and Fruehan [7], and Jung *et al.* [3] on the Mn equilibrium between molten iron and $CaO-SiO_2-MgO_{sat.}-MnO-FeO_t-P_2O_5$ slags at 1873 K, which reveal a similar trend. The influence of B on L_{Mn} indicates that MnO behaves as a basic oxide under the present conditions. The a_{Mn} was calculated with Thermo-Calc. Figure 2 shows the dependence of a_{Mn} on X_{Mn} in liquid steel at 1873 K in the concentration range 4.2 ≤ [wt% Mn] ≤ 10.6. A slightly positive departure from Raoultian solution behavior was found for Mn in the molten Fe-Mn-Cr alloys. Apparently, Mn shows a similar thermodynamic behavior as in the Fe-Mn binary system.

Table 3: Chemical compositions of steel and slag phase, and distributions of chromium and manganese between steel and slag after experiments

Exp. No	Contents in steel			Contents in slag (wt%)						LMn
	wt% Mn	wt% Cr	ppm O	MgO	MnO	Cr_2O_3	CaO	SiO_2	B*	
1-1	7.8	18.1	-	11.8	14.8	5.3	40.4	26.0	2.01	1.47
1-2	7.2	17.6	126.2	13.8	14.5	4.3	39.0	26.2	2.02	1.56
1-3	6.9	19.2	134.7	15.2	13.7	5.7	39.2	24.6	2.21	1.54
1-4	9.9	17.5	154.1	12.1	14.5	9.0	41.5	27.1	1.98	1.13
2-1	5.8	20.2	103.0	36.7	11.2	1.8	10.8	37.7	1.26	1.50
2-2	4.2	20.0	60.6	8.9	8.7	0.6	33.2	48.6	0.87	1.60
2-3	4.8	20.1	119.7	12.6	9.4	1.1	38.8	37.9	1.36	1.52
3-1	5.1	20.2	67.5	25.3	8.2	0.7	28.5	37.3	1.44	1.25
3-2	5.7	20.7	80.7	23.0	10.3	1.6	27.6	36.6	1.38	1.40
3-3	7.3	19.4	100.3	12.2	10.6	2.1	43.3	29.2	1.90	1.12
3-4	8.3	19.8	68.3	13.4	8.7	2.5	46.9	27.7	2.18	0.81
4-1	6.1	19.6	92.8	22.2	11.5	1.8	26.8	37.7	1.30	1.46
4-2	7.7	19.5	95.2	16.8	13.0	1.7	30.3	36.8	1.28	1.31
4-4	8.7	19.6	140.2	15.9	12.6	3.0	43.1	24.9	2.37	1.12
5-1	6.5	19.2	51.3	24.7	8.4	0.6	26.6	39.6	1.30	1.00
5-2	10.6	18.6	47.0	10.7	7.5	0.9	48.2	31.9	1.85	0.55
6-1	9.2	19.8	98.2	11.4	8.0	1.4	46.6	31.4	1.85	0.67
6-2	8.4	19.5	141.0	12.2	8.8	1.8	44.5	30.8	1.84	0.81

* B = (wt%MgO + wt%CaO)/wt% SiO_2

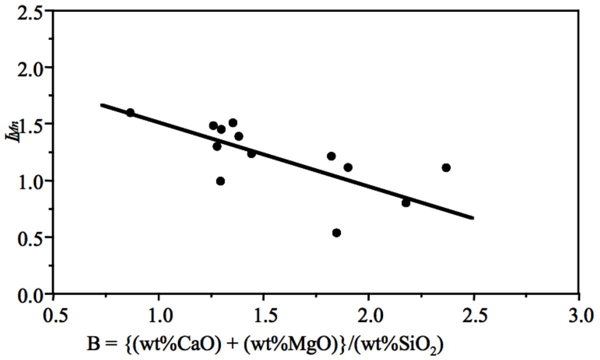

Figure 1: L_{Mn} as a function of slag basicity B (see also Table 3)

By inserting the calculated a_{Mn} in Equation 5, γ_{MnO} and a_{MnO} (= $\gamma_{MnO} X_{MnO}$) could be obtained for each experimental run. Figure 3 shows the variation of a_{MnO} as a function of X_{MnO} in the slags. Data from Morales and Fruehan [7] for CaO-SiO$_2$-MgO$_{sat.}$-MnO-FeO$_t$-P$_2$O$_5$ slags, and from Ding and Eric [1] for CaO-SiO$_2$-MgO.-MnO slags are also shown in this Figure. It is clear that a_{MnO} increases with increasing X_{MnO}. This observation can be attributed to an increase in both the concentration of free oxygen and Mn ions, which are not associated with the silicate ions, when X_{MnO} increases. The increase in Mn^{2+} ions in the slag breaks down the silicate network structure, causing an increase in the number of free oxygen ions. The latter is reflected as an increase in a_{MnO}. As seen in Figure 3, the data obtained in the present work do not strongly depart from ideal behavior. This is in general agreement with Ding and Eric [1], who found a slightly positive departure from ideal behavior. In the case of Morales and Fruehan, the values of a_{MnO} are higher than in this work, most likely owing to different composition of the investigated slag systems. At higher MnO concentrations, they observed a considerable positive deviation of a_{MnO} from ideal behavior. For $X_{MnO} > 0.2$, a_{MnO} is close to unity, indicating that the slags they studied were nearly saturated with MnO or another solid phase.

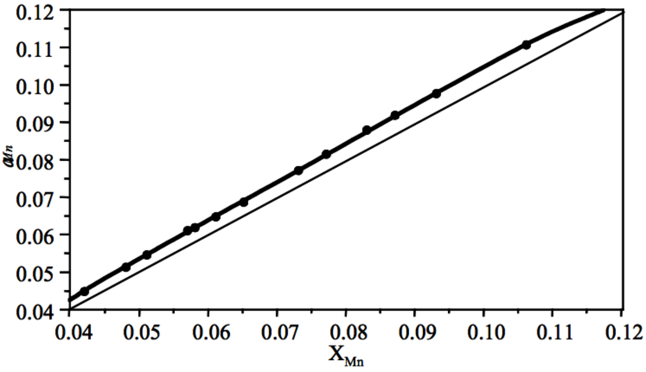

Figure 2: Variation of a_{Mn} with X_{Mn} in the Fe-Mn-Cr melt at 1873 K.
This is calculated with th TCFE4 database of Thermo- Calc.

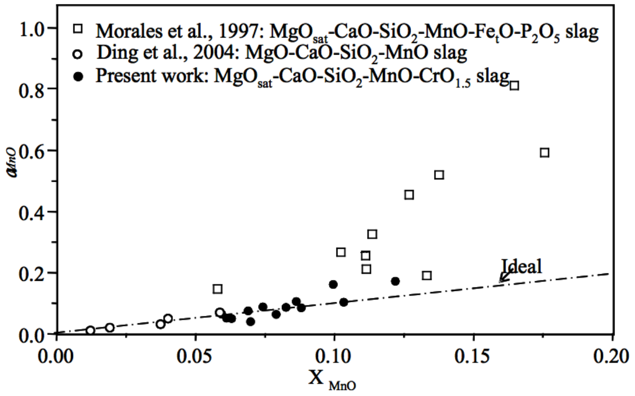

Figure 3: Relation between a_{MnO} with X_{MnO} at 1873 K. Our results are shown together with those of Morales (Ar atmosphere) and Ding ($p_{O2} = 7.89 \cdot 10^{-7}$ atm)

It was found, similar to the behavior of MnO in ferromanganese slags, that the concentration of MnO in the present slag system (CaO-SiO$_2$-MgO$_{sat.}$-MnO-CrO$_{1.5}$) influences its own activity coefficient as depicted in Figure 4. In the MnO concentration range under investigation (7.5 ≤ (wt%MnO) ≤ 15), γ_{MnO} increases as the concentration increases. This observation is in agreement with the results reported by Craig and Dippenaar [2] for CaO-SiO$_2$-MnO-CrO$_x$ slags and by Ding and Eric [1] for CaO-SiO$_2$-MgO-MnO slags. The results of Suito *et al.* [10] and Morales *et al.* [7] for ferromanganese slags are also plotted. There is considerable scatter in those data. The value of γ_{MnO} in the present work lies just below the lower limit of the other data. Activity coefficients of MnO are shown in Figure 5 as a function of slag basicity *B* at 1873 K together with a line obtained using linear regression. There is some scatter in Figure 5. However, it is clear that γ_{MnO} increases as the basicity increases. According to slag theory, the reason is attributed to the preferential association of Ca^{2+} and Mg^{2+} ions with silicate anions [1, 2], compared to metal ions, such as Mn^{2+} ions. As a result, an increase in the amount of Ca^{2+} and Mg^{2+} ions due to a higher slag basicity decreases the degree of association of Mn^{2+} ions and increases the proportion of free O^{2-} anions. Hence, the activity coefficient of MnO increases.

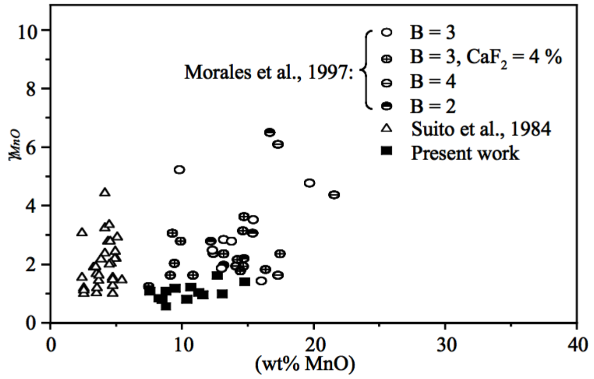

Figure 4: Variation of γ_{MnO} with the MnO content in the slag at 1873 K

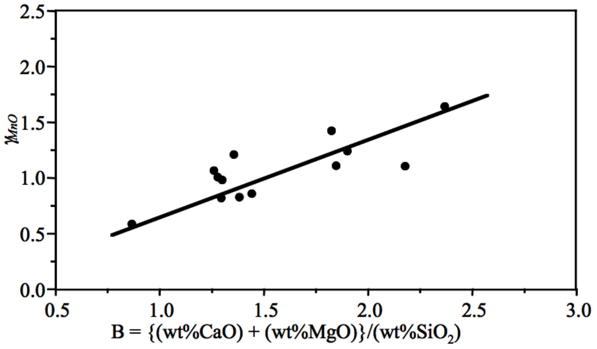

Figure 5: Variation of γ_{MnO} with the basicity B of CaO-SiO_2-MgO_{sat}-MnO-$CrO_{1.5}$ slags at 1873 K

In the case of ferromanganese slags, other authors [1] suggested that the increase continues until reaching a maximum value at certain basicity, after which the value of γ_{MnO} remains constant. In order to prevent the oxidation loss of Mn from steel to slag, a_{MnO} must be maximized without increasing the concentration of MnO in the slag. Consequently, it is a key point that basic slags in which γ_{MnO} is high, should be used to optimize the Mn yield during high Mn stainless steel production.

The effect of temperature on L_{Mn} at more or less constant basicity (B = 1.84~1.90) is shown in Figure 6. As temperature increases from 1823 to 1873 K, the value of L_{Mn} increases considerably. This can be understood by the fact that reaction (1) is highly exothermic. Hence the operational temperature is critically important for the manganese recovery. Manganese losses can be minimized by limiting the steel refining temperature.

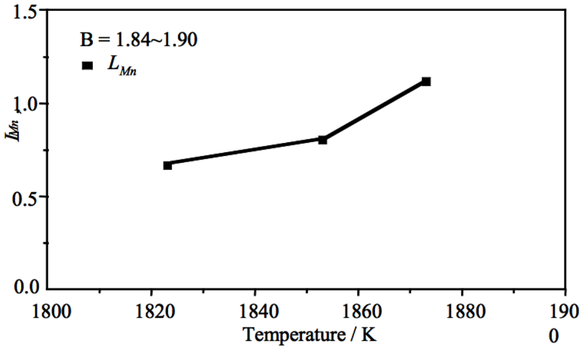

Figure 6: Influence of temperature on L_{Mn}

SUMMARY AND CONCLUSIONS

The Mn and Cr equilibria between high Mn stainless steelmaking slag (CaO-SiO_2-$MgO_{sat.}$-MnO-$CrO_{1.5}$) and Fe-Cr-Mn stainless steel were investigated under an Ar atmosphere at temperatures ranging from 1823 to 1873 K. L_{Mn} was determined as a function of slag composition. The behavior of MnO in the slag was studied based on the combination of experimental observations and thermodynamic calculations. The findings in this work are summarized as follows:

1. With increasing slag basicity, L_{Mn} decreases. This is because the elevated slag basicity leads to higher values of γ_{MnO} in the slags.
2. MnO behaves as a basic oxide in the CaO-SiO_2-$MgO_{sat.}$-MnO-$CrO_{1.5}$ slags. a_{MnO} shows a slightly positive departure from ideality. Similar to the behavior of MnO in ferromanganese slags, γ_{MnO} increases as the MnO concentration increases in the present concentration range ($7.5 \le$ (wt%MnO) ≤ 15). An increase in slag basicity would lead to an increase in the concentration of (Mn^{2+}) ions not associated with the silica network, thereby increasing γ_{MnO} in the slag.
3. Mn oxidation loss from steel to slag inevitably occurs under the present experimental conditions. To optimize the Mn recovery in the high Mn stainless steel production, a basic slag is recommended, with a high value of γ_{MnO}.
4. As temperature increases from 1823 to 1873 K, the value of L_{Mn} increases considerably. Therefore, the operational temperature is of critical importance for the Mn recovery. High manganese losses can be minimized by limiting the steel refining temperature.

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