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By Abdelrhman Hassan, Mohammed Meraikib & Taha Mattar

Tabbin Institute for Metallurgical Studies (TIMS)

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THERMODYNAMICMODELLINGOFMANGANESEBEHAVIORINOXYGENSTEELMAKING

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Thermodynamic Modelling of Manganese Behavior in Oxygen Steelmaking

Abdelrhman Hassan [α], Mohammed Meraikib [σ] & Taha Mattar [ρ]

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I. Introduction

Bahariya Iron ore which is used for sintering at the Egyptian Iron and Steel Company (EISCO) has relatively high contents of manganese, phosphorous, zinc barium, alkali chlorides and alkali oxides. In the sintering process, manganese oxides remain in the sinter that are used as blast furnace feed. Consequently, the hot metal produced contains relatively high proportions of manganese which should be brought down to the required level in the steel grade to be produced in the LD converter.

The aim of the present work is to investigate the manganese partitioning between slag and molten metal in the LD converter by using the concept of manganate capacity of slag. The effects of the main process parameters, such as temperature and slag basicity, on the factors influencing manganese distribution (i.e. activity of MnO in the slag and manganite capacity) will be studied. The data which was used for this purpose were obtained from three identical 90 ton LD converters of EISCO at Tabbin, Helwan.

II. Experimental

The trial heats were conducted on the three identical 90-ton LD converters at EISCO. At first, steel scrap was charged into the converter. This was followed by pouring the hot metal having the composition given in Table 1.

Table 1: Average composition of EISCO hot metal, weight % [1]

Element	C	Si	Mn	P	S
Composition, %	4.01	0.74	2.25	0.32	0.015

Oxygen was then blown through a water cooled lance (at a rate of 200 to 240 Nm^3/min) in the LD converter. After the start of the oxygen blowing, the first portion of burnt lime (having about 90% CaO and 2% SiO2 and/or dolomite) was fed into the converter; the rest of the fluxes were added during blowing. Due to the high content of impurities in the hot metal, double slagging technique was used. Immediately prior to slag removal, temperature was measured and a slag and corresponding metal

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Author α σ: Tabbin Institute for Metallurgical Studies (TIMS), Tabbin, Cairo, Egypt. e-mails: discover3030@gmail.com, mmeraikib@yahoo.com
Author ρ: Tabbin Institute for Metallurgical Studies (TIMS), Tabbin, Cairo, Egypt. Central Metallurgical Research and Development Institute (CMRDI), Cairo, Egypt. e-mail: tahamattar@yahoo.com

samples were taken for chemical analysis. Following the removal of the first slag, oxygen-blowing was resumed and the required fluxes were added to make a fresh slag. At the conclusion of the second stage of blowing, the temperature was also measured and a slag and the corresponding metal sample were collected for analysis. Finally, the slag was removed and the steel was tapped.

The slag composition was estimated by X-ray Fluorescence technique PL72000 Model and the metal analysis was done by using an Emission Quantometer PL31000 Model. Tapped steel was then deoxidized and brought to the required composition by adding deoxidation materials and ferroalloys in the ladle [2].

III. RESULTS AND DISCUSSION

The average analysis of hot metal used for steel production at EISCO is given in Table 1. For comparison, the range of analysis and optimal composition of hot metal normally used for steelmaking in LD converters is given in Table 2 [3].

Table 2: Range and optimal composition of hot metal for steel making in LD converter, weight% [3]

Element	**C**	**Si**	**Mn**	**P**	**S**
Range, %	3.60-4.60	0.05-2.50	0.30-3.50	≤0.30	≤0.04
Optimum, %	4.20	0.50-0.80	0.60-0.90	≤0.12	≤0.03

It is obvious that both the range and average content of manganese in the hot metal used at EISCO are higher than the average and optimal contents of manganese in the hot metal normally used for steelmaking in LD converters. The high manganese content is attributed to the high concentration of manganese oxide in the ore (MnO= 2.65%) as well as in the sinter (MnO = 2.63%) [4]. The modelling of manganese distribution between slag and metal and the main process parameters affecting the distribution are closely investigated in the present work due to the high level of manganese in the hot metal and the deleterious effect of it’s control in the converter on the yield of steel.

a) *Oxidation of Manganese in LD Process*

The concept of manganate capacity used in this research to study the partition of manganese between slag and metal is based on the oxidation of manganese according to the reaction:

$$[Mn] + \frac{1}{2} O_{2(g)} = (MnO)_{(s)} \tag{1}$$

The equilibrium constant of this reaction, KMn, is

$$K_{Mn} = \frac{a_{(MnO)_s}}{a_{[Mn]} \cdot P_{O_2}^{\frac{1}{2}}} \tag{2}$$

where $a_{(MnO)_{(s)}}$ and $a_{[Mn]}$ are the activities of MnO in the slag and Mn dissolved in the metal respectively; P_{O_2} is the partial pressure of oxygen in the gas phase at the slag/metal interface. The equilibrium constant depends on temperature as follows [5]:

$$\ln K_{Mn} = \frac{43463}{T} - 12.5491 \tag{3}$$

b) *Activity of Manganous Oxide in the Slag*

The activity of manganous oxide can be calculated by using the model of regular ionic solutions developed by Kozheurov [6,7]

$$lg\gamma_{(Fe)} = \frac{1000}{T}\left[2.18x_{Mn}x_{Si} + 5.9x_{Si}\left(x_{Ca} + x_{Mg}\right) + 10.5x_{Ca}x_{P}\right] \tag{4-a}$$

$$lg\gamma_{(Mn)} = lg\gamma_{(Fe)} - \frac{2180}{T} x_{Si} \tag{4-b}$$

The ionic fraction of the cation can be calculated as follows [8]:

$$x_i = \frac{v_1}{\sum v_i \cdot n_i} \tag{5}$$

where n_i is the number of moles of cations i in 100g of the slag and v_i is the number of the cations in a molecule of the oxide.

The activity of manganous oxide can be calculated by multiplying $\gamma_{(MnO)}$ by $x_{(MnO)}$.

$$a_{(MnO)} = \gamma_{(MnO)} \cdot x_{(MnO)} \tag{6}$$

The activity is mainly influenced by temperature and slag composition.

c) *Effect of Temperature on the Activity of Manganous Oxide*

The activity of manganous oxide in the slag changes with the temperature as shown in Figure 1. The regression line resulting from the plotting of ln $a_{(MnO)}$ against the reciprocal of absolute temperature is straight and satisfies the formula:

$$\ln a_{(MnO)}(T) = \frac{18210}{T} - 11.478 \qquad r = 0.6737 \tag{7}$$

The correlation coefficient of equation (7) indicates moderate correlation between the activity of manganous oxide in the slag and the reciprocal of absolute temperature.

The enthalpy of dissolution of manganous oxide in the slag can be obtained from equation (7) as follows: [9,10]

$$\ln a_i = \frac{\Delta \overline{H}_i}{RT} + constant \tag{8}$$

A comparison of equations (7) and (8) leads to the following value for the relative partial enthalpy of solution of MnO in the slag of the Egyptian LD converters:

$$\Delta \overline{H}_{(MnO)} = 151.4\ kJ \cdot mol^{-1} \tag{12}$$

The positive sign of $\Delta \overline{H}_{(MnO)}$ indicates the endothermic nature of the dissolution of MnO in the slag of LD converter. This value is accepted compared with 198 k J mol^{-1} found for $\Delta \overline{H}_{(MnO)}$ in other investigations conducted by S.M.Jung et al on BOF slags[11] and 130 k J mol^{-1} found for the dissolution of MnO in lime based slags containing MnO, BaO and Na_2O [12].

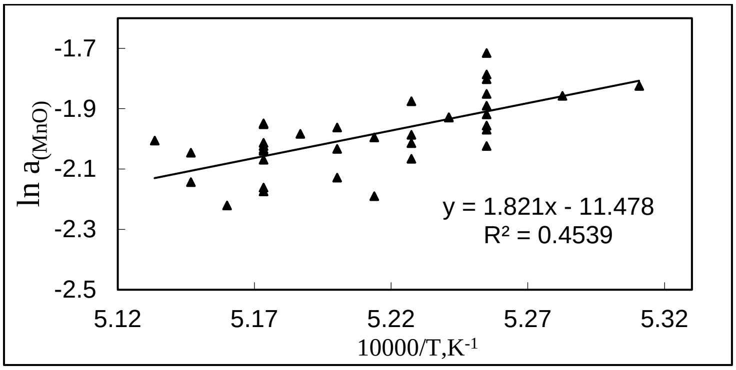

Fig. 1: Variation of the logarithm of the activity of manganous oxide with the reciprocal of absolute temperature in a narrow range of slag composition

d) Effect of Basicity and Temperature on the Activity of Manganous Oxide

In this research, the slag composition is expressed by the basicity defined in the following form:

$$B = \frac{(CaO)}{(SiO_2)} \tag{13}$$

The combined effects of basicity and temperature on the activity of manganous oxide in the slag can be estimated by plotting ln $a_{(MnO)}$ against $^1/_T$ at constant average basicity as shown in Figure 2. The straight lines corresponding to basicity are almost parallel. The slope depends on the temperature, whereasthe intercepts with the ordinate acquire different values at different basicities. The variation of the activityof manganous oxide with both basicity and temperature can be represented by the straight line equation:

$$\ln a_{(MnO)}(B,T) = \frac{A}{T} + b \tag{14}$$

where A is the average slope and b is the intercept of the straight line with the ordinate.

Figure 2 shows that the average slope is equal to 19,043 and the values of the intercept at different basicities are:

b=-12.004 r=0.7910 at B=5.5099 (15)

b=-11.951 r=0.8102 at B=6.4740 (16)

b=-11.961 r=0.9208 at B=7.4693 (17)

Figure 3 illustrates the variation of the intercept with the basicity. The straight line can be defined by the following equation:

$$b(B) = 0.0218B - 12.1132 \qquad r = 0.7579 \tag{18}$$

Substituting the average value of the slope and the intercept $b(B)$ from equation 18 in equation 14, the following equation results for the variation of the activity of manganous oxide with both basicity and temperature:

$$\ln a_{(MnO)}(B,T) = \frac{19043}{T} + 0.0218B - 12.1132 \tag{19}$$

The equation shows the small effect of basicity against the large temperature influence on the activity.

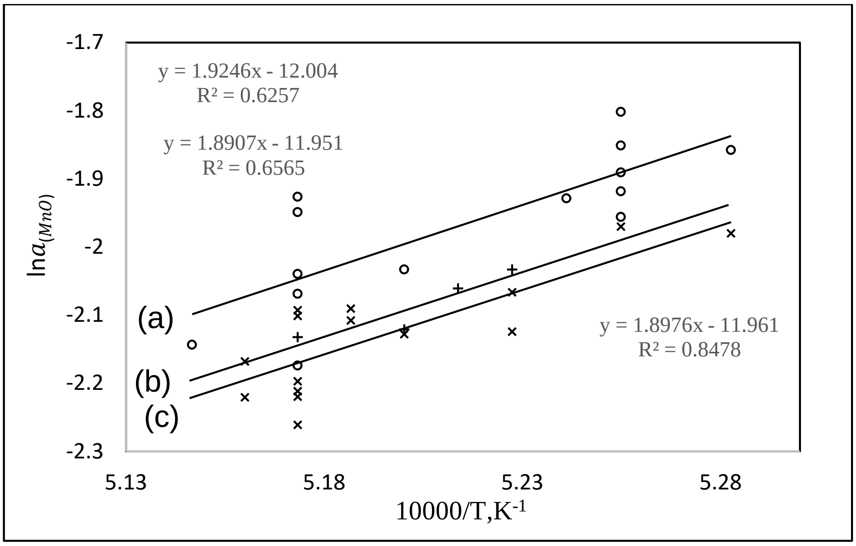

Fig: 2: Variation of the logarithm of manganous oxide activity in the slag with the reciprocal of absolute temperature at the basicity B = (a) 5.5099, (b) 6.4740 (c) 7.4693

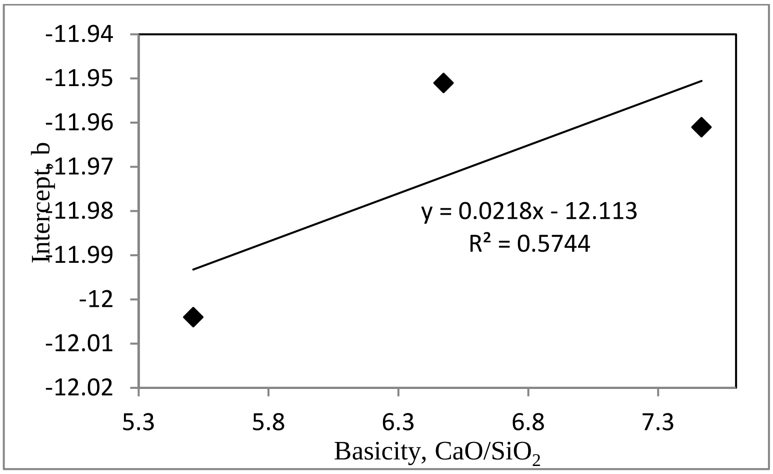

Fig. 3: Variation of the intercept, b, with the basicity, B

e) *Manganate Capacity of Slag*

The manganate capacity of a slag is defined as [12,13]:

$$C_{Mn} = \frac{(Mn)}{a_{Mn} P_{O_2}^{0.5}} \tag{20}$$

It is based on the oxidation reaction of manganese dissolved in the metal as given by equation (1) and it's equilibrium constant in equations (2) and (3). In order to calculate the manganate capacity, the partial pressure of oxygen is estimated from equation (2) and (3) as follows:

$$P_{O_2}^{0.5} = \frac{a_{(MnO)}}{a_{Mn} \cdot exp\left(\frac{43463}{T} - 12.549\right)} \tag{21}$$

The activity of manganous oxide in the slag can be formed by using equations (4-a and 4-b) and (6).

The activity of manganese in the metal $a_{[Mn]}$can be calculated according to the dilute solution model as follows [10,13]:

$$a_{[Mn]} = f_{[Mn]} \cdot [Mn] \tag{22}$$

where $f_{[Mn]}$ is the activity coefficient of manganese in the metal, it can be estimated by:

$$\log f_{[Mn]} = e_{Mn}^{(Mn)}[Mn] \cdot e_{Mn}^{(O)}[O] \cdot e_{Mn}^{(C)}[C] \cdot e_{Mn}^{(S)}[S] \cdot e_{Mn}^{(P)}[P] \cdot e_{Mn}^{(Si)}[Si] \tag{23}$$

The interaction parameters, $e_{Mn}^{(i)}[i]$ are given in table (3).

Table 3: Interaction parameters $e_{Mn}^{(i)}[i]$, [10,13]

Parameter	$e_{Mn}^{(Mn)}$	$e_{Mn}^{(O)}$	$e_{Mn}^{(C)}$	$e_{Mn}^{(S)}$	$e_{Mn}^{(P)}$	$e_{Mn}^{(Si)}$
Value	0	-0.083	-0.07	-0.048	-0.0035	0

The activity coefficient was calculated by substituting the values of the interaction parameters given intable (3) in equation (23) and the activity was found by using equation (22).

f) Effect of Basicity and Temperature on Manganate Capacity

The combined effects of both slag basicity and temperature on the manganate capacity can be estimated by plotting ln C_{Mn} against $^{10000}/_{T}$ at constant average basicity $B = \frac{(CaO)}{(SiO_2)}$ as in the case of the activity of manganous oxide. This is illustrated in Figure 5. The group of straight lines corresponding to basicity are parallel.

Their slope depends on temperature, where the intercepts with the ordinate have different values depending on the basicity. As in the case of activity, the variation of the manganate capacity with both basicity and temperature can be represented by the equation:

$$\ln C_{Mn}(B,T) = \frac{M}{T} + d \tag{24}$$

Where M and d represented the average slope of the straight lines and the intercept of each line with the ordinate, respectively.

The straight lines in Figure 4, relating to the basicity B, have an average slope equal to 37341. The values of intercept, d, at different basicities are as follows:

$d(B) = -4.9307$ r=0.9861 at B=5.5006 (25)

$d(B) = -4.9819$ r=0.9907 at B=6.0162 (26)

$d(B) = -5.0454$ r=0.9628 at B=6.4722 (27)

$d(B) = -5.3705$ r=0.9643 at B=6.9812 (28)

$d(B) = -5.389$ r=0.9565 at B=7.4501 (29)

$d(B) = -5.5102$ r=0.9880 at B=8.0049 (30)

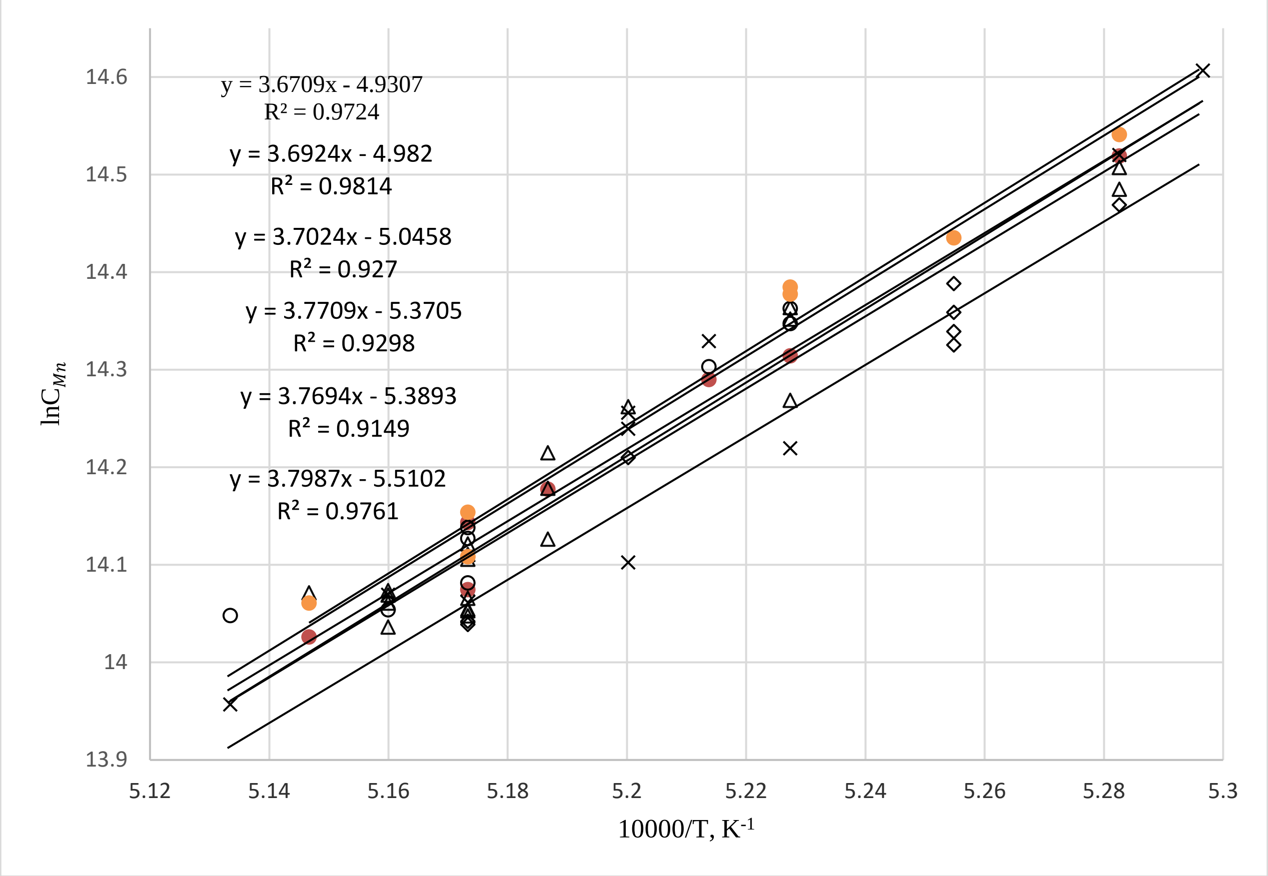

Fig. 4: Variation of the logarithm of manganese capacity in the metal with the reciprocal of absolute temperature at the basicity B = (a) 5.5006, (b) 6.0162, (c) 6.4722, (d) 6.9812, (e) 7.4501, (f) 8.0049

The intercept varies with the corresponding values of basicity as shown in Figure 5, which can be described by the following formula:

$$d(B) = -0.2564B - 3.4774 \qquad r = 0.9621 \tag{31}$$

Substituting the average slope and the intercept from equation (31) in equation (24), therefore thecombined effects of basicity and temperature on the manganate capacity can be expressed as:

$$\ln C_{Mn}(B,T) = \frac{37341}{T} - 0.2564B - 3.4774 \tag{32}$$

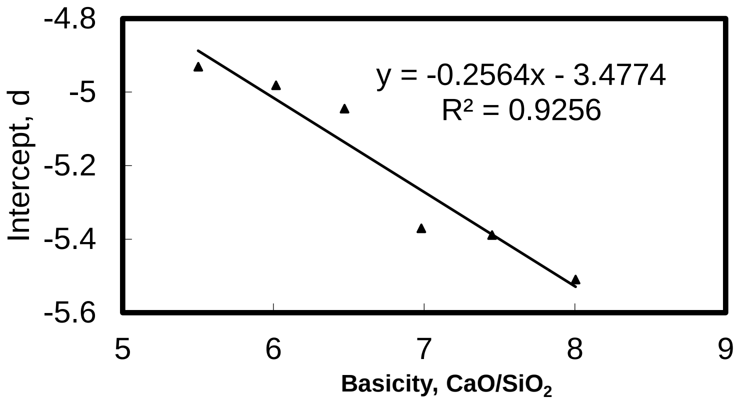

Fig. 5: Variation of the intercept, d, with the basicity, B

g) Manganese Partitioning between Slag and Metal

Substituting the partial pressure of oxygen in equation (21) from equation (2), the definition of manganatecapacity can be defined as:

$$C_{Mn} = \frac{(Mn) \cdot K}{a_{(MnO)}} \qquad (33)$$

The distribution ratio of manganese between slag and metal is defined as:

$$\eta_{Mn} = \frac{(Mn)}{[Mn]} \qquad (34)$$

It follows from equation (33) and (34) that:

$$\eta_{Mn} = \frac{C_{Mn} \cdot a_{(MnO)}}{K \cdot [Mn]} \qquad (35)$$

As in the case of manganate capacity, the distribution ratio is also affected by slag basicity and temperature.

h) Effect of Basicity and Temperature on Manganese Distribution

The combined effects of basicity and temperature on the manganese distribution ratio can be found by substituting the manganate capacity and manganous oxide activity in equation (35) by the corresponding equation showing the combined effects of basicity and temperature. It follows from equations (19) and that:

$$\eta_{Mn}(B,T) = \frac{e^{\left(-0.2346B + \frac{12921}{T} - 3.0415\right)}}{[Mn]} \qquad (38)$$

The results obtained by using this equation to calculate the manganese distribution ratio are illustrated in Figure 6, which are as follows:

$$\eta_{Mn(cal)} = 1.033 \cdot \eta_{Mn(obs)} \qquad r = 0.889 \qquad (39)$$

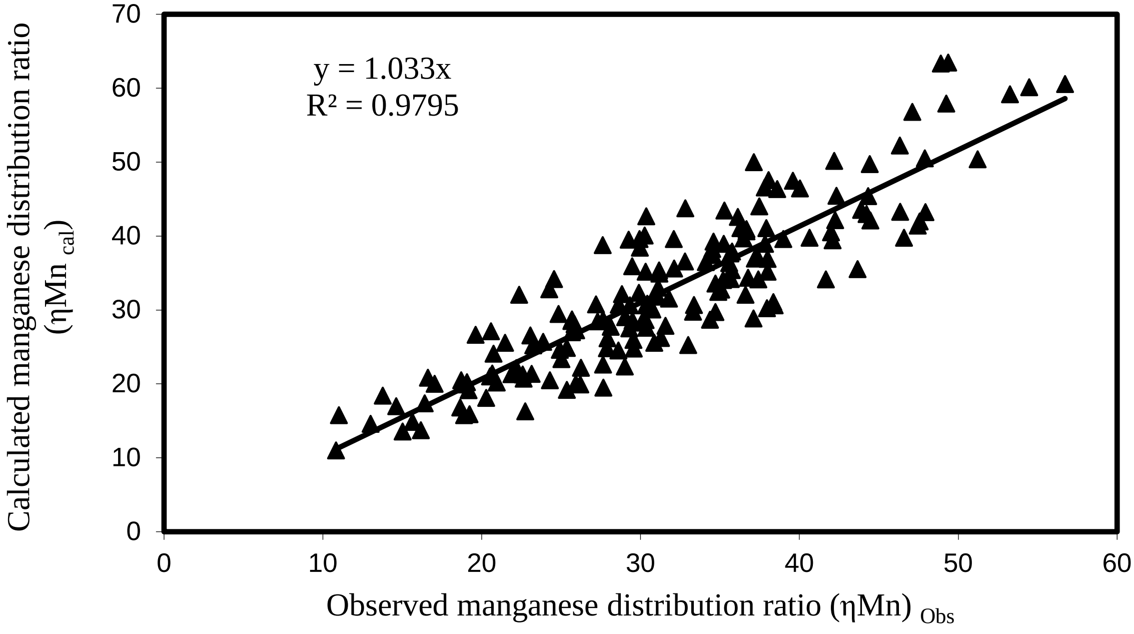

Fig. 6: Relationship between calculated and observed manganese distribution ratio between slag and liquidsteel in oxygen steelmaking processes

IV. CONCLUSIONS

The data were used to investigate the effects of temperature and slag composition on the activity of manganous oxide in the slag and manganate capacity, the data were then utilized for the estimation of the slag/metal distribution ratio of manganese. The following conclusions can be made:

1. The partial molar enthalpy of solution of MnO in the converter slag is 151 k J mol^{-1} and the reaction of dissolution is endothermic.
2. The activity of MnO is largely dependent on temperature and changes only slightly with the basicity of the slag.
3. The manganate capacity is mainly dependent on, and is inversely proportional to, the temperature; it is slightly affected by basicity.
4. The distribution of manganese between slag and metal can be calculated by using the manganate capacity. In addition, it was found that the calculated distribution ratios agree well with the observed data.

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