

MnO ACTIVITIES DETERMINATION FOR BASIC MANGANESE ORES IN THE COKE BED ZONE

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Abstract

During ferromanganese production, the manganese ores transit in different zones before reaching the coke bed zone called prerreduction and reduction zone. The transition higher to lower oxides manganese oxides occurs reaching MnO. The reduction of MnO liquid by carbon producing Mn liquid was considered to be at equilibrium while empirical data and previous calculated data were used to determine activity of Mn in the alloys considered saturated with carbon. The MnO activities calculated based on the manganese recovery using FactSage and the calculated MnO activity using HSC (Rea 9) were stacked up against the calculated values using FactSage. It was found that the calculated values using using HSC (Rea 9) and the FactSage were apart.

Keywords: Metallurgy, MnO activities, basic manganese ores, coke bed

1. INTRODUCTION

The ferromanganese industry has made remarkable progress in different areas of challenge. Although many data have been generated for acidic manganese ores, the full understanding of different mechanisms or reactions especially when using basic manganese ores is prone to continuous investigations. The measurements of MnO activity at 1400 °C, 1500 °C and 1600 °C in MnO-SiO₂ melts and measurements obtained at 1500 °C in MnO-CaO-SiO₂ have demonstrated a deviation in MnO activities in the MnO-SiO₂ system between the two measurements although the same data were used [1, 2]. Therefore, it is not appropriate to assess MnO activities in different systems. Phase equilibrium describing five components namely MnO, CaO, SiO₂, MgO and Al₂O₃ are not well known. However, for lower order systems, although some systems were proposed [3], a relativization is required to adapt to a specific combination of parameters. However, the correlation between the activity of MnO and some oxides originating from fluxes used in the multicomponent system MnO-CaO-SiO₂-MgO-Al₂O₃ with less than 30% MnO including the influence of the substitution of basic oxides for acidic oxides impacting on the formation of the slag. The effect of fluxes, not only on reduction kinetics of the MnO in the slag [4, 5]. The effect of fluxes, not only on reduction kinetics of the MnO in the slag [6], but also on Mn and Si activities [7-10] is relatively complex. In this study, the model was based on pure MnO as state of reference as restriction to calculate MnO activity.

2. EXPERIMENTAL

2.1 Materials and equipments

The materials for the experiments used were:

- Different basic manganese ores from South Africa were used in this project namely Nchwaneng 1, Nchwaneng 2 and Nchwaneng 3 respectively referred to as NC1, NC2 and NC3.
- Metallurgical Coke.
- Quartz was used as flux to decrease the basicity to unity.

Different analytical equipments were used to characterize the materials (feed) and products generated from the experiments. The following techniques were used:

- 1) XRD was used for mineralogical characterization of different phases present in different manganese ores.
- 2) XRF essentially for elemental characterization.
- 3) It is important to mention that the coke used for reduction was characterized using proximate analysis.

3. RESULTS AND DISCUSSION

Table 1 provides the XRD-Topaz Rietveld results of the three manganese ores used in the investigations.

Table 1 Mineralogical analysis of the three manganese ores used in this study (wt%) [11]

Mineral	NC1	NC2	NC3
Braunite 1 $Mn^{2+}Mn^{3+}_6[O_8]SiO_4$	44	48	38
Braunite 2 $Ca(Mn,Fe)_{143}SiO_{24}$	25	10	24
Bixbyite $Mn^{3+}_2O_3$	7	5	12
Hausmannite	1.8	9.8	6
Wollastonite $CaSiO_3$	0	0	0
Calcite $CaCO_3$	9.4	9.9	7.9
Hematite Fe_2O_3	9.6	9	7
Barite $BaSO_4$	1	2	3
Kutnahorite $Ca(Mn,Mg,Fe)(CO_3)_2$	0	0	1
Manganite $MnO(OH)$	1.7	6	1

The results revealed that braunite 1 and 2, hematite, hausmannite, jacobsonite, pyrolusite, kutnahorite and manganite are the main manganese oxide minerals present in the ores. Pyrolusite and jacobsonite are not present in the three ores. It was observed that in all basic South African manganese ores analysed, braunite 1 is the most predominant manganese mineral. Although braunite 2 was present, its amount was considerably lower than that of braunite 1.

Table 2 below provides the XRF results of the analyses performed on the manganese ores used in this project.

Table 2 Chemical composition of the manganese ores using X-Ray fluorescence

Element	Mn _{tot}	MnO ₂	Fe _{tot}	P	SiO ₂	CaO	Al ₂ O ₃	MgO	K ₂ O	Mn/Fe	Basicity (CaO+MgO/Al ₂ O ₃ +SiO ₂)
NC1	44	32	8.78	0.03	5.6	8.92	0.28	1.2	0.02	5.0	1.72
NC2	42.8	28.9	13	0.05	6.6	7.2	0.42	0.98	0.02	3.23	1.17
NC3	45.5	33	8.9	0.04	4.8	7.2	0.32	0.47	0.02	5.1	1.5

Table 3 provides results of the proximate analysis performed on the coke used for the reduction of ferromanganese.

Table 3 Proximate and ultimate results of coke used [11]

Parameter	Proximate analysis (wt%)			
	Fixed-C	Volatile	Ash	Moisture
Coke	83%	3.9%	11.7%	1.8%

As Received, CV: Calorific value, Fixed carbon by difference [100 - (Volatile matter + Moisture + Ash content)]

3.1 Determination of MnO activity using FactSage

The determination of MnO activities in the slag containing MnO was conducted using different tools, assumptions, empirical data, experimental data and equations. FactSage, HSC 9 were used as tools to determine the MnO activity at different temperatures in this project. To calculate MnO activities, in this work, a restriction was adopted. Pure MnO was considered as the point of reference because Mn is the driving force of the carbothermic reduction since the amount of MnO available to react is very critical. The MnO activities were calculated using FactSage tool by assuming 100g of manganese ores were used. The input data were based on the chemical composition of different manganese ores used in this work. The carbon amount in the input was calculated as per the stoichiometry. A more productive juxtaposition was established between different manganese ores. **Figures 1, 2 and 3** depict the calculated MnO activities at 1400 °C, 1450 °C and 1475 °C respectively against theoretical recovery of Mn in the alloy.

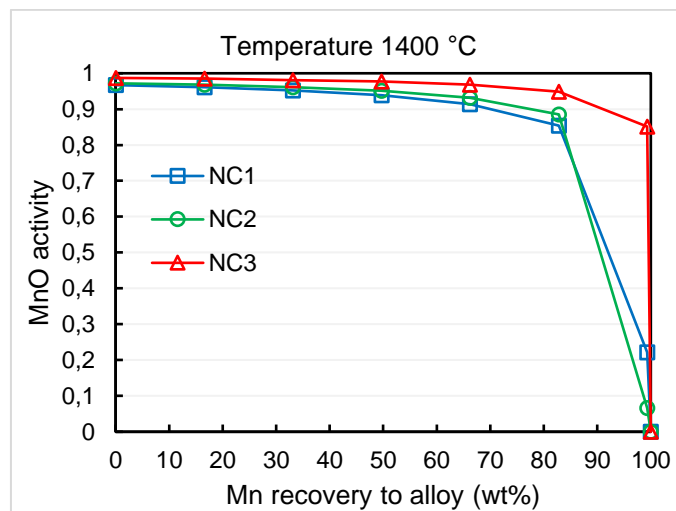


Figure 1 Calculated MnO activity versus Mn recovery for three Nchwaning manganese ores at 1400 °C using FactSage [11]

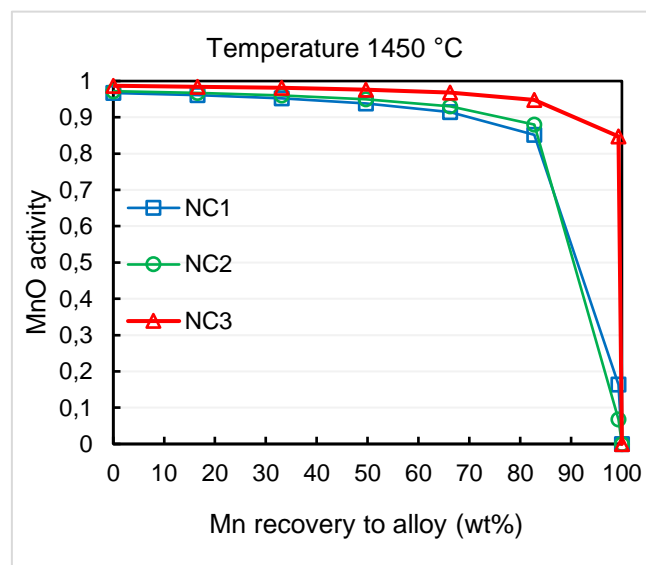


Figure 2 Calculated MnO activity versus Mn recovery for three Nchwaning manganese ores at 1450 °C using FactSage [11]

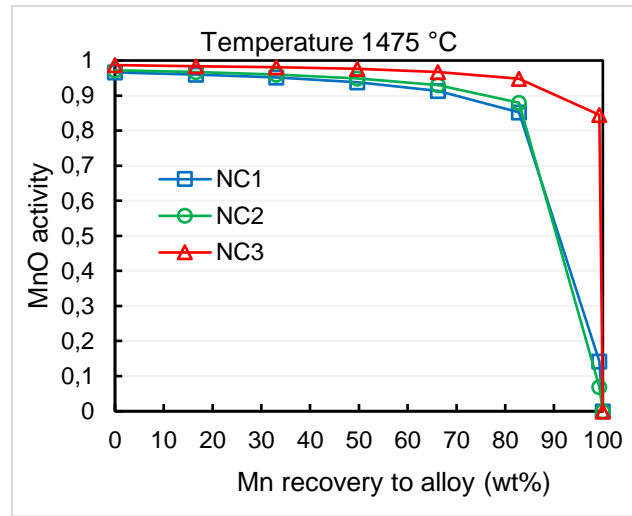


Figure 3 Calculated MnO activity versus Mn recovery for three Nchwaning manganese ores at 1475 °C using FactSage [11]

It transpired from **Figures 1, 2** and **3** that MnO activity is inverse proportional to Mn recovery for different temperatures investigated in this work. Also, for all the three types of basic manganese ores, the trend of MnO activity is the same. However, an abrupt decrease in MnO activity is vivid from 66.6% Mn recovery for all manganese ores. This has always been attributed to the change in reduction kinetics.

3.2 Determination of activities of MnO in the slag using HSC 9

The activities were calculated assuming the system is at equilibrium. Reaction (1) describes the equilibrium between the slag and the metal while equation (2) responds to equilibrium assumptions.

At equilibrium, we have:



The equilibrium constant of the reaction is given by:

$$K = \frac{[(a_{\text{Mn}}) \cdot (p_{\text{CO}})]}{[(a_{\text{MnO}}) \cdot (a_{\text{C}})]} \quad (2)$$

From empirical data, the percentage of Mn is averaging 79 wt%. The assumption is that the mass percentage of Mn is equivalent to its activity. This means f_{Mn} is close to unity. Consequently, the activity of Mn is around 0.7. Using empirical Mn percentages in the HCFeMn, and using equation (3) below, the activity coefficient of Mn in the Mn-C system in the temperature region of 1673 K was determined and remain an acceptable assumption since previous works have confirmed the validity of the equation in the temperature region of the current investigation.

$$\ln \gamma_{\text{Mn}} = 5.47 X_{\text{C}}^2 - 46.8 X_{\text{C}}^3 \quad [1] \quad (3)$$

where:

X_{C} - the mole fraction of carbon

As per HSC9 (Rea module), K and a_{MnO} values were calculated at 1400, 1450 and 1475 °C. Results are presented in **Table 4**.

Table 4 Calculated K and MnO activity at 1400, 1450 and 1475 °C using HSC (Rea 9)

Temperature (°C)	K value	a_{MnO} (Katnelson)	a_{MnO} (HSC9)
1400	0.972	0.772	1.03
1450	1.774	0.441	0.564
1475	2.366	0.330	0.423

Since calculated $a_{\text{Mn}} = 0.75$; 0.78 and 0.79 (from empirical data, private communication with the plant in [12] at 1400, 1450 and 1475 °C respectively in the alloy, $p_{\text{CO}} = 1$ atmosphere as assumed and $a_{\text{C}} = 1$ (at saturation), a_{MnO} in the slag was calculated. The calculated a_{MnO} values presented in **Table 4** from equation (3). a_{Mn} was rounded up to 1 (unity), from 0.7; to find the highest a_{MnO} in order to look at a certain range of values. It should, however, be noted that the metal is not pure Mn, but this has been assumed to find the highest a_{MnO} values. Since $a_{\text{Mn}} = 1$, $p_{\text{CO}} = 1$ atmosphere as assumed and $a_{\text{C}} = 1$, a_{MnO} in the slag was calculated. Therefore, $K = 1/a_{\text{MnO}}$. This implies $a_{\text{MnO}} = 1/K$. Using HSC 9, a_{MnO} was calculated assuming that $a_{\text{Mn}} = 1$ whereas values of a_{MnO} from Katsnelson a_{Mn} calculations.

4. CONCLUSION

Since MnO is the driving force of the carbothermic reduction, to calculate MnO activities for the chemical equilibrium, pure MnO is the restriction and MnO was the state of reference. Therefore, MnO activity is critical. FactSage and HSC (Rea 9) were used to calculate MnO activities at different temperatures for different basic manganese ores. It was found, with FactSage; that MnO activities decreased abruptly at around 66,2 per cent Mn recovery in the metal. This was an indication of change in kinetics. However, results have shown that MnO did not disappear from the slag regardless of temperature and residence time which means the unreduced MnO was always present during the reduction of high carbon ferromanganese. It was, therefore, concluded that at all temperatures the system contained unreduced MnO and MnO activity away from zero, therefore the system was far from equilibrium. Since little has been published on basic manganese ore carbothermic reduction the current paper has incorporated only references, although applied to acidic and specific conditions; were close to the current research project.

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