Thermodynamic analysis and experimental study of manganese ore alloy and dephosphorization in converter steelmaking

by G. Chen* and S. He*

Synopsis

In this study, the effects of slag compositions, slag amount, temperature, and carbon content of steel on the manganese and phosphorus distribution ratios during converter steelmaking were analysed using the classical regular solution theory, and industrial tests were performed using two 80 t top-and-bottom combined blown converters (duplex melting process). The results indicate that the slag amount, temperature, and carbon content in steel are the main factors affecting the manganese yield when converter slag compositions remain constant. The FeO content of the slag has a strong impact on the manganese distribution ratio, while the slag basicity and MgO content have no obvious effect. The calculations and experimental results show that the phosphorus distribution ratio increases sharply with increasing slag basicity R, but then decreases with the increase of MgO and MnO contents in the slag. The final slag in converter steelmaking should have the following characteristics: $3.5 < R < 4.5$, $15\% < (FeO) < 20\%$, and $6\% < (MgO) < 8\%$. The slag amount should be controlled appropriately at the same time. The results of this investigation would be useful in deciding on the application of manganese ore in alloying and identifying the slagging regime in converter steelmaking.

Keywords

slag compositions, distribution ratios, classical regular solution theory, slagging regime.

Introduction

The increase in the international iron ore price in recent years has forced Chinese steel companies to seek domestic sources of iron ore in order to reduce costs. The availability of large amounts of phosphorus- and manganese-rich ores in the Three Gorges Reservoir region has made the development of a characteristic metallurgical technology in local steel plants possible (Wang and Dong, 2009). In the conventional steelmaking process, one converter must fulfill several functions, such as dephosphorization, decarburization, and raising temperature. It is unreasonable and uneconomical to decrease the phosphorus content using only one converter when high-phosphorus molten iron is smelted. Separation of the decarburization process from dephosphorization (using De-P and De-C converters) in the duplex melting process is advantageous, as it allows for the use of phosphorus-rich iron ore and relatively lower amounts of slag, as well as direct alloying with manganese ore in the converter. Consequently, iron procurement costs and metal losses are reduced to a considerable extent. For these advantages to be translated into commercial benefits, the dephosphorization converter should be fully exploited to produce low-phosphorus, high-carbon, high-temperature semi-steel, and the semi-steel smelting process should be further optimized by manganese ore alloying and by improving the manganese yield. A number of studies have been carried out on the improvement of the manganese yield and its impact on the converter, both in China and abroad (Suito and Inoue, 1995; Gao, Zhao, and Xing, 2011; Kaneko et al., 1993; Min and Fruehan, 1992; Lv et al., 2010; Soifer, 1958).

In this study, the main factors affecting the manganese yield are systematically investigated by thermodynamic analysis and industrial tests, and the relationship between manganese alloying and dephosphorization in the converter is discussed in detail. Finally, the final slag composition and control ranges for converter steelmaking are proposed.

Thermodynamic calculations

The reaction of manganese ore during the alloying process in the converter is described as follows for a given slag system (Gao, Zhao, and Xing, 2011; Kaneko et al., 1993; Huang, X.H. 2008).

$$(MnO) + [C] = [Mn] + CO \qquad [1]$$

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$$[\%Mn] = K_{Mn-C} \cdot \frac{a_{(MnO)} \cdot f_{[C]} \cdot [\%C]}{p_{CO} \cdot f_{[Mn]}} \qquad [2]$$

The equilibrium constant of the above reaction is

$$\log K_{Mn-C} = -\frac{10903.93}{T} + 7.32 \qquad [3]$$

(Yang and Cao). The effect of [C] content of steel on the manganese distribution ratio (L_{Mn} = (%Mn)/[%Mn]) is given by Equation [1] at $P_{CO} = 1$, $f_{[C]} = 1$, and $f_{[Mn]} = 1$. The activity of (MnO), $a_{[Mn]}$, can be obtained by using the regular ionic solution model (Huang, 2008).

$$\log \gamma_{Fe^{2+}} = \frac{1000}{T} \cdot \left\{ 2.18 \left[x_{(Mn^{2+})} \cdot x_{(Si^{4+})} \right] + 5.90 \right.$$
$$\left. \left[x_{(Ca^{2+})} + x_{(Mg^{2+})} \right] \cdot x_{(Si^{4+})} + 10.50 \left[x_{(Ca^{2+})} \cdot x_{(P^{5+})} \right] \right\} \qquad [4]$$

$$\log \gamma_{Mn^{2+}} = \log \gamma_{Fe^{2+}} - \frac{2180}{T} \cdot x_{(Si^{4+})} \qquad [5]$$

$$\log \gamma_{P^{5+}} = \log \gamma_{Fe^{2+}} - \frac{10500}{T} \cdot x_{(Ca^{2+})} \qquad [6]$$

$$a_{(MnO)} = \gamma_{(Mn^{2+})} \cdot x_{(Mn^{2+})} \qquad [7]$$

where $x_{(i)}$ is the mole fraction of positive ion i.

The (FeO) content plays a critical role in the control of manganese ore reduction during the later stage of blowing in the converter (Suito and Inoue, 1995; Gao, Zhao, and Xing, 2011; Morales and Fruehan, 1997; Takaoka et al., 1993). This reaction is shown in Equation [8].

$$\left(Fe^{2+} \right) + [Mn] = \left(Mn^{2+} \right) + [Fe] \qquad [8]$$
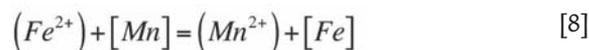
$$[\%Mn] = \frac{1}{K_{Mn-Fe^{2+}}} \cdot \frac{\gamma_{(Mn^{2+})} \cdot x_{(Mn^{2+})}}{x_{(Fe^{2+})} \cdot \gamma_{(Fe^{2+})} \cdot f_{[Mn]}} \qquad [9]$$

Equation [10] is derived from Huang (2008).

$$\log K_{Mn-Fe^{2+}} = \frac{6700}{T} - 3.12 \qquad [10]$$

The effects of slag basicity R = (%CaO)/(%SiO$_2$) and (FeO) and (MgO) contents of the slag on L_{Mn} are studied through the reaction in Equation [8] at $f_{[Mn]} = 1$. Similarly, the activity coefficients of (Fe^{2+}), $\gamma_{(Fe2+)}$ and (Mn^{2+}), $\gamma_{(Mn2+)}$ can be obtained from Equations [4] and [5] respectively.

Moreover, the effects of temperature on L_{Mn} are calculated separately by Equations [1] and [8], and the carbon content in Equation [1] is set as 0.08%.

The major dephosphorization reaction between molten steel and slag in the converter is described by Equation [11] (Basu, 2007; Ikeda and Matsuo, 1982).

$$2[P] + 5\left(Fe^{2+} \right) + 8\left(O^{2-} \right) = 2\left(PO_4^{3-} \right) + 5[Fe] \qquad [11]$$
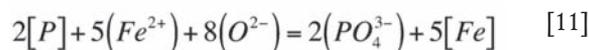
In order to calculate the phosphorus distribution ratio L_p = (%P)/[%P], the activity of the complex ion of phosphorous and oxygen can be expressed by the simplified reaction Huang (2008) :

$$2[P] + 5(FeO) = (P_2O_5) + 5[Fe] \qquad [12]$$
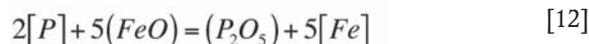
$$a_{(P_2O_5)} = \gamma^2_{(P^{5+})} \cdot x^2_{(P^{5+})} \qquad [13]$$

$$a_{(FeO)} = \gamma_{(Fe^{2+})} \cdot x_{(Fe^{2+})} \qquad [14]$$

$$[\%P] = \frac{1}{K_P^{0.5}} \cdot \frac{x_{(P^{5+})} \cdot \gamma_{(P^{5+})}}{x_{(Fe^{2+})}^{2.5} \cdot \gamma_{(Fe^{2+})}^{2.5}} \qquad [15]$$

where the K_P value is 0.0234 (Huang (2008). The values of $x_{(P5+)}$, $x_{(Fe2+)}$, $\gamma_{(Fe2+)}$, and $\gamma_{(P5+)}$ can also be obtained from the regular ionic solution model (Huang (2008).

Figures 1 and 2 show that R has no obvious effect on L_{Mn}. In addition, compared with (FeO), (MgO) has a less obvious effect on the change in L_{Mn}. L_{Mn} tends to increase with an increase in (FeO) but decrease with an increase in (MgO). Therefore, L_{Mn} is more strongly affected by the (FeO) content rather than R or (MgO) content. Figure 3 shows the variation of the calculated activity coefficient of (MnO) as a function of (FeO) content. When (FeO) content in slag increases from 15% to 35%, the activity coefficient of (MnO) decreases from 1.71 to 1.29, which can also be observed in the results of Jung et al. (1993), Jung (2003), and Suito and Inoue (1984). Obviously, the results obtained in this work are in agreement with the data from the literature. In addition, as can be seen in Figure 4, the activity of FeO in slag increases strongly with an increase of (FeO) in slag over the calculated concentration range, which is in good
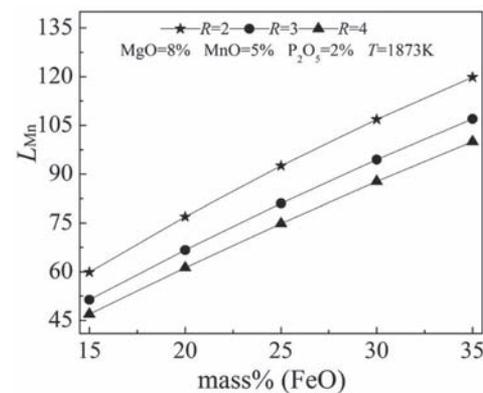

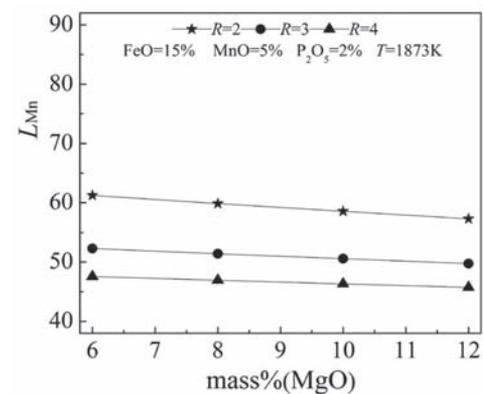Figure 1—Effect of FeO content of slag on L_{Mn}

Figure 2—Effect of MgO content of slag on L_{Mn}

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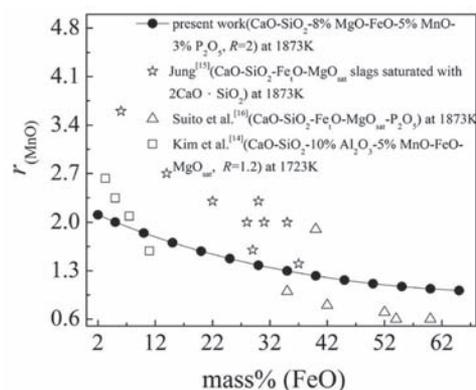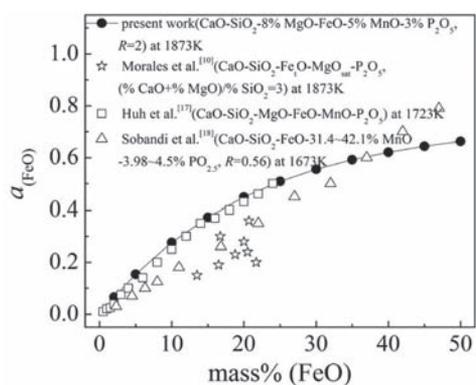

Figure 3—Effect of FeO content of slag on r(MnO)

Figure 4—Effect of FeO content of slag on a(FeO)

accordance with the results of other investigators (Morales and Fruehan, 1997; Huh and Jung, 1996; Sobandi, Katayama, and Momon, 2002). The distribution ratio L_{Mn} thus increases with the increase of (FeO), resulting in a low reduction efficiency of (MnO) when (the FeO) content is increased, as shown by Equation [9]. Hence, in order to improve the manganese yield in the converter, the (FeO) content of the final slag should be maintained at a low level in the alloying process performed using manganese ore. This has been affirmed by previous experiments (Suito and Inoue, 1995; Morales and Fruehan, 1997; Suito and Inoue, 1984; Jung, Rhee, and Min, 2002). However, the dephosphorization in the converter requires a high (FeO) content. As illustrated in Figure 5, the increase in (FeO) content initially enhances L_P, but the trend is reversed beyond a certain level, and the optimal (FeO) content decreases with increasing R. Generally, L_P has already reached the maximum level when the (FeO) content approaches 20% at a relatively high R value. These results are similar to those assessed thermodynamically and experimentally by previous researchers (Basu, 2007; Ikeda and Matsuo, 1982; Sobandi, Katayama, and Momon, 2002; Suito and Inoue, 1995). Therefore, the (FeO) content could be controlled between 15% and 20% to achieve a high manganese yield.

It is well known that slag with higher R and higher (FeO) content is required in the later stage of the smelting process for dephosphorization (Basu, 2007; Jeong et al., 2009; Nozaki et al., 1983). Consequently, the conditions used for

converter steelmaking are suited for dephosphorization. As shown in Figures 5–7, it is obvious that the dephosphorization effect increases sharply as R is increased, which is believed to dramatically reduce the activity coefficient of (P_2O_5) in slag, as recognized (Basu, 2007; Sobandi, Katayama, and Momon, 2002; Suito and Inoue, 1995; Turkdogan, 2000; Suito and Inoue, 1982, 1984; Nakamura, Tsukihashi, and San, 1993). A higher R is thus indispensable for dephosphorization in the converter. Conversely, an excessively high R will worsen the kinetic conditions for manganese ore reduction and dephosphorization. Simultaneously, taking previous studies (Lv et al.,
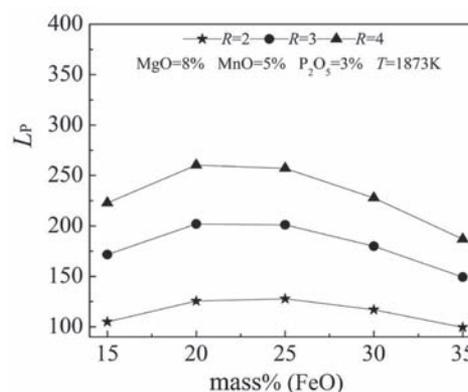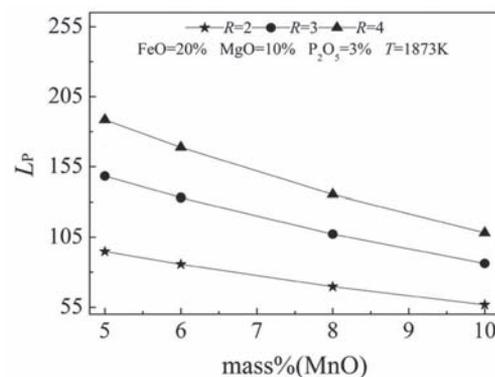

Figure 5—Effect of FeO content of slag on L_P

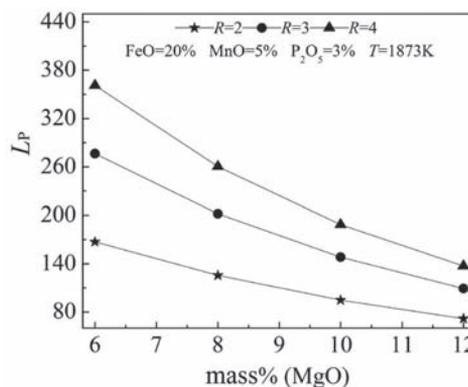Figure 6—Effect of MnO content of slag on L_P

Figure 7—Effect of MgO content of slag on L_P

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2010; Basu, 2007; Tabata *et al*., 1990) into consideration, R should be high when the (FeO) content is relative low and, in general, the R of the final slag should be controlled between 3.5 and 4.5 to achieve a higher degree of dephosphorization.

Furthermore, L_P clearly decreases with an increase in the (MgO) and (MnO) contents of the slag at a given R (Figures 6 and 7). Also, the influences of (MgO) and (MnO) contents on L_P are gradually enhanced with the increase of R from 2 to 4; the effects of R on L_P become progressively weaker with increasing (MgO) and (MnO) contents. Specifically, calculations show that increasing the (MgO) and (MnO) contents of the slag can increase the activity of (P_2O_5), which is detrimental for L_P, as confirmed by Figure 8. Separately, the dephosphorization effects weaken significantly when the slag has a high (MnO) content, as has been reported by many investigators (Suito and Inoue, 1995; Mukherjee and Chatterjee, 1996; Simeonov and Sano, 1985) and observed by previous researchers, all of whom have advised against the addition of manganese oxide to converter slag. As a result, manganese ore alloying during converter smelting would become advantageous when low-phosphorus hot metal is used as raw material. Also, the experiments of Halder and co-workers demonstrated conclusively that $2CaO \cdot SiO_2$ exists under conditions of higher slag basicity, lower steel tapping temperatures, and higher phosphorus contents of the hot metal, which comprised the majority of the solid part of the slag and also had greater solubility for phosphorus than the liquid part of the slag (Deo *et al*., 2004) . In addition, Suito, Inoue, and Takada (1981) also proved that slag containing $2CaO \cdot SiO_2$ had a higher L_P in the MgO-saturated slag of the system $CaO\text{-}MgO\text{-}FeO_x\text{-}SiO_2$, and the same result was also obtained in the $CaO\text{-}CaF_2\text{-}SiO_2$ system by Muraki, Fukushima, and Sano, (1985). However, the increase of (MgO) content in slag could result in a reduction in both the size of the $2CaO \cdot SiO_2$ grains and the dissolution of phosphorus in $2CaO \cdot SiO_2$. Thus, dephosphorization was greatly hindered (Deo *et al*., 2004). Therefore, taking only dephosphorization into consideration, the lower the MgO content the better. However, since (MgO) plays an important role in protecting the furnace lining, it is imperative that the appropriate amount of (MgO) should be present in the slag. We can manipulate this relationship by using slag-splashing protection technology for the converter. In general, the (MgO) content should be controlled between 6% and 8%.
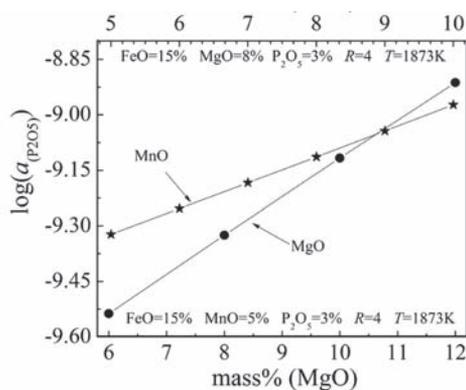
From Equations [1] and [8], the values of L_{Mn} are calculated separately as a function of steel temperature in Figure 9. The results of the authors and of Jung *et al*. (1993) and Jung, Rhee, and Min (2002) are plotted for comparison. It is seen that most values of $\log(L_{Mn})$ in this work are slightly higher compared with previous results. This may be a result of the slightly different components of the slag. In general, $\log(L_{Mn})$ decreases linearly with increasing temperature. Equations [3] and [10] clearly indicate that the reaction in Equation [1] is endothermic and Equation [8] is exothermic. The equilibrium [Mn] content in steel is therefore expected to increase with increasing temperature. On the other hand, many studies indicate that the dissolution reaction $(MnO(s) = MnO_{(slag)})$ of (MnO) in slags is endothermic, so that (MnO) dissolution in slag increases with temperature (Jung *et al*., 1993; Suito and Inoue, 1984; Simeonov and Sano, 1985; Suito and Inoue, 1984. Accordingly, the activity of (MnO) will increase with increasing mole fraction of (MnO) in the slag, and these results are widely accepted in previous studies (Ding and Eric, 2005). Thus, the equilibrium [Mn] content increases naturally.

Figure 10 shows that the final [C] carbon content of the steel has a great influence on L_{Mn}. With a decrease in the final carbon content [C] in steel, L_{Mn} increases distinctly, and this has been experimentally confirmed by previous investigators (Kaneko *et al*., 1993; Yang and Cao, 2009; Tabata *et*
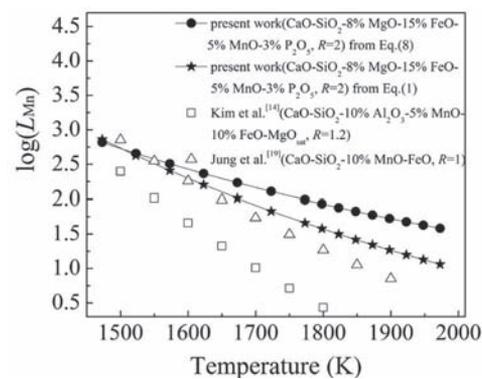
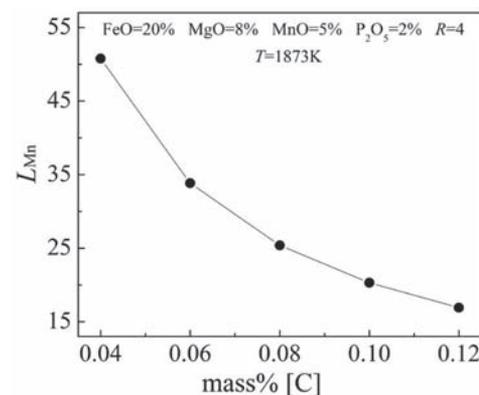**Figure 9—Effect of temperature on log(L_{Mn})**

Figure 8—Effect of MgO and MnO contents of slag on log($a_{(P2O5)}$)

Figure 10—Effect of [C] of steel on L_{Mn}

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al., 1990; Matsuo, Fukagawa, and Ikeda, 1990). Clearly, the [C] in the molten steel can accelerate the reduction of (MnO) and improve the manganese yield. The [C] content of steel acts as a heat source and as well as a reducing agent, and carbon is thus consumed in large amounts. At the same time, carbon reacts with oxygen to form CO gas, which can enhance the fluidity of the entire slag system, which drives the reactions towards equilibrium (Keum *et al.*, 2007).

The effect of the amount of slag on the manganese yield $((W_s * ([Mn]_f - [Mn]_s))/(0.3 * W_{Mn})$, where $[Mn]_f$ and $[Mn]_s$ are the [Mn] content in the final steel and semi-steel respectively; W_s and W_{Mn} are the yield of final steel (tons) and manganese ore charged (tons), respectively) is shown in Figure 11. While the slag amount affects the manganese yield, it does not influence L_{Mn}. The manganese ore yield decreases sharply with an increase in the slag amount, due to the fact that the (MnO) content in the slag will decrease and the balanced [Mn] content in steel also will decline. As can be seen, since the manganese yield is less than 35% when the slag amount exceeds 60 kg/t, the slag amount must be maintained at a value less than 40 kg/t to ensure a high Mn yield (>45%). Similar results have been reported by other researchers (Kaneko *et al.*, 1993; Tabata *et al.*, 1990; Mukherjee and Chatterjee, 1996).

In conclusion, steelmaking by a process that involves manganese ore alloying and the use of low quantities of slag is an effective measure for lowering the consumption of raw materials and raising the manganese yield, which are the typical advantages of the De-P/De-C steelmaking process.

Industrial tests

Industrial process description

To verify the results of the thermodynamic calculations, we carried out industrial tests using two 80 t converters at a steel plant in China. The blast furnace, De-P converter, De-C converter, refining, and continuous casting route has been been adopted. The experimental conditions used for the industrial-scale tests are shown in Table I. Tables II and III show the compositions of the molten iron and manganese ore used in the tests, respectively; the additions of manganese ore and compositions of semi-steel, final steel, and final slag are shown in Table IV. In this exploratory study, only a small

amount of manganese ore (0~810 kg) was added to ascertain the factors affecting alloying, which can provide reference data for further industrial-scale production.

Results and analysis

The values of L_{Mn} obtained from the results are shown against (FeO) contents in Figure 12, where the R values range from 3.0 to 5.5. The values of L_{Mn} change irregularly
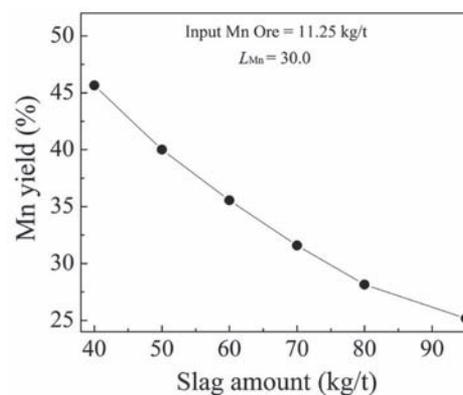

Figure 11—Effect of slag amount on manganese yield

Table II

Compositions of molten iron (mass %)

C	Si	Mn	P	S
4.0–4.2	0.4–0.6	0.2–0.4	0.11–0.45	0.036–0.06

Table III

Compositions of manganese ore (mass, %)

CaO	MgO	SiO$_2$	Al$_2$O$_3$	Mn	TFe	S	P
8–12	4–8	10–15	2–5	28–32	1–3	0.08–0.15	0.01–0.02

Table I

Operating conditions of De-P/ De-C converters

	De-P converter	De-C converter
Molten iron/semi-steel scrap	77~83 t 7~10 t Lime Slagging agent	84~93 t 0 Lime
Slagging elements	Returned slag Fluorite Bauxite	Slagging agent Manganese ore
Flow rate of top gas (O$_2$)	10000–13000 Nm³/h	16000–16500 Nm³/h
Flow rate of bottom gas (N$_2$/Ar)	300–600 Nm³/h	300–600 Nm³/h
Blowing time	7–9 min	10~12 min

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Table IV

Manganese ore additions and compositions of semi-steel, final steel, and final slag (mass %)

	Semi-steel, %				Mn Ore,	Final steel, %				Temp.,	Final slag, %							
	C	Mn	P	S	kg	C	Mn	P	S	°C	SiO$_2$	Al$_2$O$_3$	CaO	MgO	TFe	P$_2$O$_5$	MnO	FeO
1	2.8	0.11	0.13	0.057	0	0.023	0.01	0.011	0.04	1612	8.34	2.05	40.66	8.61	24.02	2.87	2.22	21.7
2	2.8	0.1	0.163	0.046	0	0.047	0.02	0.016	0.043	1638	16.9	2.57	46.09	8.01	18.43	3.61	2.22	16.88
3	2.7	0.1	0.15	0.041	0	0.044	0.02	0.008	0.036	1608	8.12	2.57	43.27	7.4	22.9	3.34	1.93	21.2
4	2.84	0.08	0.14	0.042	0	0.042	0.02	0.01	0.047	1624	8.08	2.05	44.82	6.18	21.5	3.9	1.93	20.19
5	2.82	0.04	0.128	0.046	0	0.037	0.01	0.01	0.042	1630	8.51	1.54	43.41	6.08	23.32	3.52	2.22	21.84
6	2.75	0.07	0.1	0.048	0	0.063	0.02	0.013	0.048	1627	9.52	2.05	42.15	7.9	20.94	3.57	1.93	20.19
7	2.73	0.1	0.12	0.048	0	0.067	0.07	0.01	0.045	1638	8.98	2.05	38.34	8.72	23.04	3.55	3.86	20.98
8	2.8	0.07	0.06	0.05	0	0.15	0.1	0.018	0.06	1666	12.2	1.94	38.76	12.67	20.25	2.52	2.53	19.26
9	2.94	0.08	0.1	0.055	0	0.046	0.06	0.021	0.057	1642	10.58	2.62	44.26	8.82	16.34	1.76	2.97	17.17
10	2.87	0.07	0.077	0.053	0	0.053	0.05	0.018	0.052	1645	10.02	3.05	40.74	11.15	18.71	1.76	2.82	18.75
11	2.7	0.08	0.088	0.048	70	0.078	0.09	0.014	0.048	1632	10.24	3.19	41.72	10.34	18.29	1.51	4.46	17.53
12	2.88	0.09	0.071	0.045	400	0.095	0.12	0.015	0.048	1629	10.78	2.9	41.16	9.12	17.03	1.26	5.94	17.68
13	2.78	0.09	0.08	0.043	480	0.117	0.16	0.015	0.048	1640	11.24	3.2	40.45	8.82	17.87	1.76	6.54	17.89
14	2.85	0.08	0.077	0.049	490	0.048	0.11	0.021	0.058	1646	12.62	3.07	43.7	11.25	14.92	2.01	4.31	14.37
15	2.86	0.1	0.196	0.046	510	0.07	0.06	0.019	0.039	1624	8.84	1.05	41.3	10.95	22.06	2.89	3.4	20.55
16	2.73	0.13	0.152	0.048	510	0.052	0.1	0.015	0.039	1655	8.12	2.05	38.48	7.9	22.06	3.58	4.75	21.77
17	3.01	0.14	0.18	0.051	530	0.083	0.14	0.02	0.044	1653	9.38	2.57	40.88	8.41	17.59	4.07	4.75	17.24
18	2.88	0.11	0.138	0.047	600	0.062	0.11	0.019	0.051	1664	8.14	2.57	34.39	8.92	24.02	3.57	5.2	22.42
19	2.87	0.1	0.101	0.049	600	0.062	0.14	0.021	0.058	1634	11.7	2.88	42.01	8.82	17.45	2.01	5.5	16.96
20	2.86	0.12	0.14	0.045	630	0.08	0.18	0.023	0.044	1645	9.86	1	42.43	7.8	17.45	2.18	6.06	15.45
21	2.74	0.1	0.071	0.046	670	0.082	0.13	0.01	0.038	1622	10.46	2.64	40.45	9.12	18.71	1.51	6.13	19.4
22	2.9	0.16	0.146	0.038	680	0.06	0.16	0.019	0.04	1629	9.12	1	38.9	10.54	18.29	4.04	6.65	16.31
23	2.6	0.18	0.201	0.044	690	0.04	0.11	0.018	0.038	1653	8.42	1.8	39.33	10.84	19.97	3.43	5.02	16.81
24	2.44	0.15	0.18	0.045	700	0.05	0.1	0.015	0.038	1630	8	1.05	40.6	8.82	23.04	3.46	5.62	19.76
25	2.78	0.06	0.05	0.052	710	0.056	0.1	0.012	0.048	1621	9.86	2.01	37.49	9.93	21.78	1.26	6.09	21.12
26	2.88	0.13	0.145	0.048	760	0.07	0.16	0.018	0.04	1656	9.46	1.04	38.9	7.09	18.99	4.13	6.21	15.59
27	2.8	0.18	0.22	0.04	810	0.07	0.17	0.02	0.037	1660	8.5	1.04	42.15	8.61	17.87	4.41	6.35	15.59

with the increase of R at a given (FeO) content, and L_{Mn} increases with an increase in (FeO) content at a given R, which shows a relatively consistent tendency with thermodynamics (Figure 1). This is also confirmed in Figures 13 and 14. L_{Mn} increases as the FeO content increases when [C] content and temperature remain constant. In addition, L_{Mn} shows a rapid increase as the [C] in the steel decreases at the same FeO content (Figure 13), and the temperature has a similar impact on L_{Mn}, as illustrated in Figure 14. In Figure 13, the experimental values of L_{Mn} locate between 25 and 45, indicating that these values agree well with the calculated values (which are between 20 and 47) according to Equation [1] (Figure 10), under the condition of 0.04–0.09% [C] carbon content. However, these experimental values turn out to be somewhat less than the calculated values according to Equation [8] (Figure 10), probably because the reduction of MnO in slag by carbon [C] in steel leads to a significant increase of the [Mn] content of the steel, and in turn, the oxidization of [Mn] by FeO in the slag may not reach a thermodynamic equilibrium. As shown in Figures 12–14, as expected, low L_{Mn} values result when the (FeO) content is less than 25%, the [C] content exceeds 0.06%, and the temperature is higher than 1920K. As is well known, the increase in temperature depends on the oxidization of carbon during blowing in the BOF, and there is a strong negative correlation between [C] carbon content and temperature. On the other hand, the oxidation of [C] carbon will be depressed while the oxidation of [Fe] will be facilitated when the [C] content is less than about 0.05% (Huang, 2008), which will cause excessive (FeO) content in slag. As demonstrated in Figure 15, when the final carbon content is less than 0.06%, the majority of the corresponding (FeO) content in slag
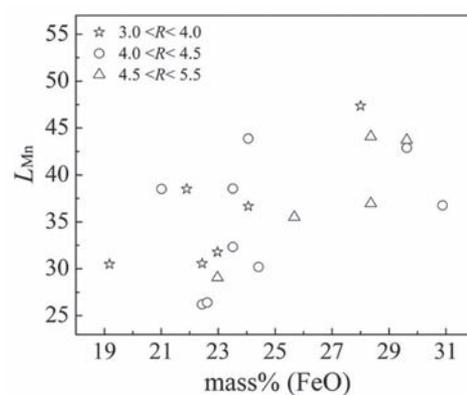

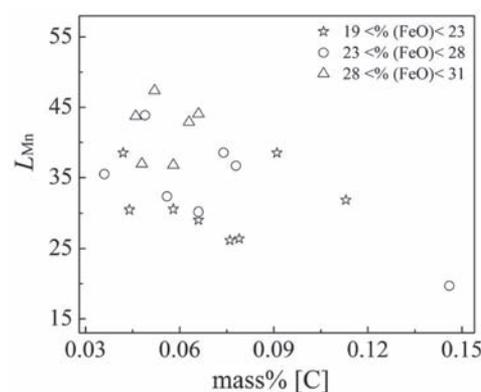Figure 12—Effect of FeO content of slag on L_{Mn}
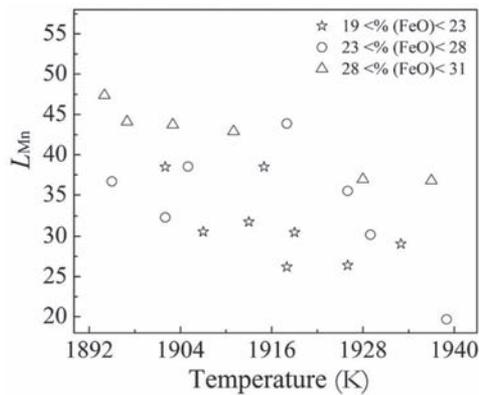

Figure 13—Effect of [C] on L_{Mn}

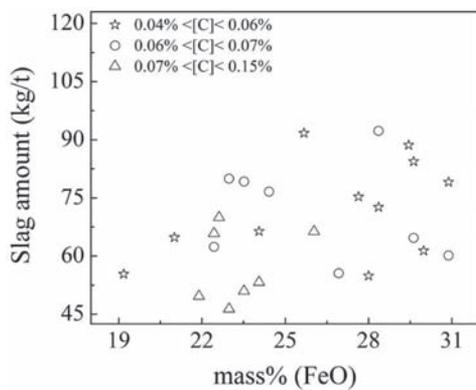Figure 14—Effect of temperature on L_{Mn}

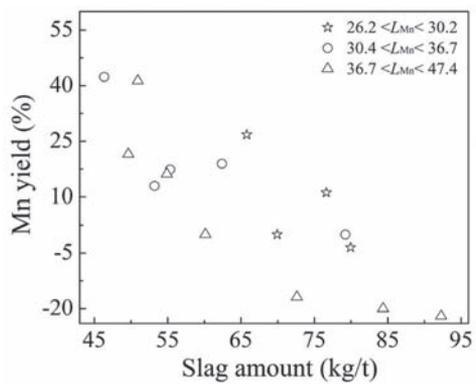Figure 15—Relation between of FeO content and slag amount

Figure 16—Effect of slag amount on manganese yield

exceeds 28%. However, a high [C] carbon content, high temperature, and low (FeO) content are required in order to attain a low L_{Mn}. More intensive research is required to determine the appropriate amount of carbon powder that should be added to the slag when the [C] carbon content of the semi-steel is insufficient to provide adequate heat and reduce the manganese ore to a large extent.

The influence of the slag amount on the manganese yield is shown in Figure 16. The yield of the manganese ore decreases sharply with an increasing slag amount at similar values of L_{Mn}, and it falls below 25% when the slag amount is 60 kg/t. Generally, the manganese yields in the industrial

tests are fairly low (usually below 20%); this is the inevitable consequence of the presence of a large amount of slag. The main reason is that the iron ore used by the aforementioned steel plant is rich in phosphorus, and the [P] content of the semi-steel charged in the De-C furnace is still high and a large amount of time and energy will lost in dephosphorization. Consequently, a large amount of slag is generated. At the same time, a large amount of slag is required for deep dephosphorization, which in turn has an enormous negative influence on manganese yield.

The influences of R and the (FeO), (MnO), and (MgO) contents of the slag on L_P are shown in Figures 17–19. From the experimental results, it is obvious that L_P increases with
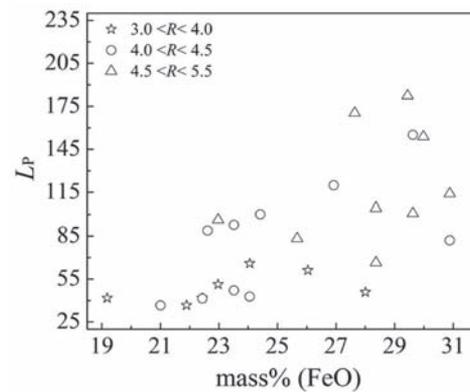

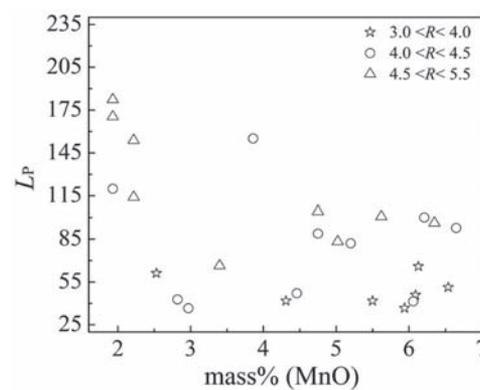Figure 17—Effect of FeO content on L_P
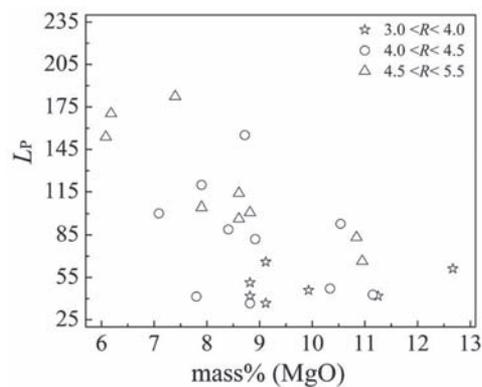

Figure 18—Effect of MnO content on L_P

Figure 19—Effect of MgO content on L_P

Thermodynamic analysis and experimental study of manganese ore alloying

increasing R from 3.0 to 5.5, regardless of whether the (FeO), (MnO), or (MgO) contents are held constant. It is also found that the higher the (FeO) content of slag, the more the L_P increase at a given R. However, the optimum (FeO) content is not observed. This is corroborated by the theoretical calculations and has been reported in previous investigations (Basu, 2007; Ikeda and Matsuo, 1982; Sobandi, Katayama, and Momon, 2002; Suito and Inoue, 1995). It is considered that this phenomenon is due to the increase in the amount of slag, even if the L_P is decreased slightly with an (FeO) content higher than the optimum. As shown in Figure 15, the results confirm a strong positive correlation between (FeO) content and slag amount. In addition, as expected, the dephosphorization effect weakens markedly with increasing (MgO) and (MnO) contents in slag when R is greater than 4. However, when R is less than 4, no regular relationship has been found. Furthermore, the impact of R on L_P is weakened when the (MgO) and (MnO) contents are high, respectively.

From the data pertaining to the smelting test conducted in 27 heats, we can conclude that the average final [P] content of the steel and the average degree of dephosphorization are 0.016% (0.008–0.023%), and 87.4%, respectively, when the average [P] content of the semi-steel charged in the De-C furnace is 0.126% (0.05–0.22%). Since a larger amount of slag (on average, about 68.3 kg/t) with high (FeO) content (mean, 25.6%) is used in the converter to decrease the [P] content to the required steel grade, a relatively good degree of dephosphorization is achieved, but the manganese yield is only 17.2% on average. Hence, for manganese ore alloying to be beneficial, the process in the De-P furnace should be optimized to decrease the [P] content of the semi-steel further.

Obviously, the data obtained in the test work is basically in good agreement with the results of the thermodynamic calculations. This, in turn, shows that the choice of the method of calculation is reasonable.

On the basis of the thermodynamic calculations and the industrial test results, it is concluded that coordinated control between the dephosphorization ability and manganese ore alloying technology in the De-C converter should be considered carefully. The characteristics of the final slag for converter steelmaking should be controlled in the following ranges: 3.5 < R < 4.5, 15% < (FeO) <20%, and 6% < (MgO) < 8%.

Conclusions

A thermodynamic analysis and industrial tests of manganese ore alloying and dephosphorization in converter steelmaking were carried out. The conclusions can be drawn as follows.

(1) The main factors affecting the alloying process performed using manganese ore in the converter are the slag amount, temperature, and the [C] content of the steel with a given slag system

(2) The (FeO) content of the slag has an enormous impact on L_{Mn} but shows no clear relationship with the slag basicity or the (MgO) content of the slag

(3) The L_P increases sharply with increasing slag basicity, but weakens with increasing (MgO) and (MnO) contents in the slag

(4) The characteristics of the final slag for converter steelmaking should be controlled in the following

ranges: 3.5 < R < 4.5, 15% < (FeO) < 20%, and 6% < (MgO) < 8%. The slag amount should be controlled appropriately at the same time.

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