

# Thermodynamic Activity of Manganese Oxide in Ferromanganese Slags, and the Distribution of Manganese between the Metal and Slag phases

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A study was made of the MnO–CaO–MgO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> slags that are typical of the production of ferromanganese in submerged-arc furnaces. The Al<sub>2</sub>O<sub>3</sub> content of the slags was kept constant at 5 per cent by mass. The study was directed at the thermodynamic activities of MnO in ferromanganese slags at 1500 °C. The thermodynamic activities of Mn in Pt–Mn alloys were redetermined at 1300, 1400, and 1500 °C for calibration purposes. The equilibrium between carbon-saturated Mn–Si–Fe–C alloys and MnO–CaO–MgO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> slags was studied under a CO atmosphere at 1500 °C.

In the experiments, it was found that  $a_{\text{MnO}}$  values increase with increasing MnO, and tend to increase with an increasing CaO-to-MgO ratio. The  $a_{\text{MnO}}$  values also increase with an increasing basicity ratio. In the slag–metal equilibrium experiments, the carbon and silicon contents of the metal phase were inversely related. At constant silicon contents, as the Mn-to-Fe ratio increases, the carbon solubility in the metal phase increases. The silicon content of the metal increases with increasing SiO<sub>2</sub> content of the slag, and increases as MgO replaces CaO in the slag. An increase in the slag basicity decreases the silicon content of the metal phase.

## Introduction

Manganese is one of the most widely used alloying materials in modern steel production. It is also used in non-ferrous metallurgy. As a strategic and critical material, the optimization of the recovery of manganese in smelting and refining processes is essential. The efficiency of smelting depends, in part, on the distribution of the valuable manganese between the alloy, slag, and gas phases, which, in turn, depends on the thermodynamic properties of the alloy and slag phases and on the phase equilibria among them. Knowledge of these factors, when coupled with information on the viscosity and electrical conductivity, is extremely useful in maximizing the efficiency of the process, and in predicting the changes that may occur owing to the use of different raw materials and to changes in furnace operation.

Literature on the thermodynamic activity of MnO in ferromanganese slags is very limited, although a substantial amount of data has been accumulated on the binary SiO<sub>2</sub>–MnO system<sup>1</sup>, and on MnO activities in blast-furnace slags and in CaO–SiO<sub>2</sub>–MnO and MgO–SiO<sub>2</sub>–MnO ternary systems<sup>2-13</sup>. However, it is felt that the data provided are not accurate enough owing to discrepancies, at the time when these experiments were conducted, in the standard free energies of formation of the MnO and  $x\text{MnO}\cdot y\text{SiO}_2$  compounds. In complex systems similar to ferromanganese slags, only one study, done by Warren<sup>14</sup>, has been carried out on slags with higher basicities than those used in the present study.

According to the work described by Warren<sup>14</sup>, changes in the concentration of MnO in the slag, within the compositional limits of the study, did not affect its own activity coefficient. An increase in the Al<sub>2</sub>O<sub>3</sub> content for a given basicity ratio (mass % (CaO + MgO):mass % SiO<sub>2</sub>) decreased the activity coefficient of MnO, especially in the more basic slags. The main aim of the present study was to determine MnO activities in MnO–CaO–MgO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> slags with basicities ranging from about 0.4 to 1.2 and MnO contents ranging from 5 to 30 per cent.

Activity–composition relations in Pt–Mn binary systems are well established<sup>15-17</sup>. This metallic system was re-investigated in the present study for calibration purposes at 1300, 1400, and 1500 °C. The slags were equilibrated with platinum strips during the determination of MnO activities. The equilibrium between carbon-saturated Mn–Fe–Si–C alloys and MnO–CaO–MgO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> slags was also investigated at 1500 °C under a CO atmosphere in the present work in order to establish slag–metal equilibria pertinent to the smelting of manganese ores.

## Experimental Procedure

The initial compositions of the metal and slag phases are shown in Tables I and II respectively. The slags that were equilibrated with those metal charges were chosen from 55 slags of different compositions. The gas-equilibration technique was used for the determination of activity–composition relations both in Pt–Mn alloys and in ferromanganese slags.

In the slag experiments, the equilibrium runs were carried

TABLE I  
THE INITIAL COMPOSITIONS OF THE METAL PHASES (IN PERCENTAGES)

Phase	Mn	Fe	Si	C
Ferromanganese	82,19	9,34	1,5	7
	79,77	11,73	1,5	7
	74,56	16,94	1,5	7
Silicomanganese	66,64	19,3	12,34	1,7
	62,55	19,3	16,46	1,7
	57,04	19,3	21,94	1,7

TABLE II  
THE INITIAL COMPOSITIONS OF THE SLAGS (IN PERCENTAGES)

Slag	MnO	CaO	MgO	SiO <sub>2</sub>
1	5,0	20,0	11,9	58,1
2	5,0	25,0	6,9	58,1
3	5,0	25,0	15,0	50,0
4	5,0	30,0	10,0	50,0
5	5,0	35,0	5,0	50,0
6	5,0	32,1	15,0	42,9
7	5,0	35,0	12,1	42,9
8	5,0	35,0	17,5	37,5
9	10,0	20,0	10,2	54,8
10	10,0	25,0	5,2	54,8
11	10,0	25,0	12,8	47,2
12	10,0	30,0	7,8	47,2
13	10,0	35,0	2,8	47,2
14	10,0	30,0	14,5	40,5
15	10,0	35,0	9,5	40,5
16	10,0	32,8	16,8	35,4
17	10,0	35,0	14,6	35,4
18	15,0	20,0	8,4	51,6
19	15,0	25,0	3,4	51,6
20	15,0	20,0	15,6	44,4
21	15,0	25,0	10,6	44,4
22	15,0	30,0	5,6	44,4
23	15,0	26,9	15,0	38,1
24	15,0	31,9	10,0	38,1
25	15,0	35,0	6,9	38,1
26	15,0	30,0	16,7	33,3
27	15,0	35,0	11,7	33,3
28	20,0	20,0	6,6	48,4
29	20,0	20,0	13,3	41,7
30	20,0	25,0	8,3	41,7
31	20,0	35,0	3,3	41,7
32	20,0	24,9	15,0	35,7
33	20,0	30,0	9,3	35,7
34	20,0	35,0	4,3	35,7
35	20,0	28,7	15,0	31,3
36	20,0	33,7	10,0	31,3
37	20,0	35,0	8,7	31,3
38	25,0	20,0	4,8	45,2
39	25,0	20,0	11,1	38,9
40	25,0	25,0	6,1	38,9
41	25,0	21,7	15,0	33,3
42	25,0	26,0	10,0	33,3
43	25,0	30,0	6,7	33,3
44	25,0	25,8	15,0	29,2
45	25,0	30,0	10,8	29,2
46	25,0	35,0	5,8	29,2
47	30,0	20,0	3,1	41,9
48	30,0	20,0	8,9	36,1
49	30,0	25,0	3,9	36,1
50	30,0	20,0	14,1	30,9
51	30,0	25,0	9,1	30,9
52	30,0	29,1	5,0	30,9
53	30,0	22,9	15,0	27,1
54	30,0	27,9	10,0	27,1
55	30,0	32,9	5,0	27,1

out with different slag compositions under two different  $P_{O_2}$  values:  $4,76 \times 10^{-7}$  and  $5,80 \times 10^{-8}$  atm. In total, 55 samples of slags of different compositions, containing MnO, CaO, MgO, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> were prepared from analytical-reagent grade oxides. All the oxides, except MnO, were first calcined in an electrical resistance-heated muffle furnace for about 24 hours at 1200 °C. After cooling, the oxides were mixed in the desired proportions to give slags of the desired compositions. The mixtures were pelletized, and the pellets were recalcined for 12 hours at about 1200 °C in order to promote some useful sintering, and thereby homogenization, of the samples. On cooling, the pellets were crushed and ground in an agate mortar and mixed with the required quantities of reagent-grade MnO before every individual run. The rest of the pellets were stored in sealed bottles for re-use. All the mixing procedures were carried out under acetone in order to secure the best possible mixing of the oxide components. The samples were heated for several hours at 110 °C to drive off the acetone, cooled, and charged into the manganese-saturated platinum crucibles.

The platinum specimens for equilibration were prepared as coupons with dimensions of 4 mm by 4 mm, cut from foil 0,025 mm thick. Prior to any experimental run with a platinum specimen, the platinum crucibles were equilibrated with pure MnO at the chosen gas mixture at 1500 °C. The platinum crucibles were made by the welding of platinum sheets 0,125 mm thick. The slag samples for the slag experiments and the pure MnO for the Pt–Mn calibration tests were charged, in 1 g quantities, into MnO-saturated platinum crucibles with the following dimensions: 7 mm in diameter, 25 mm in depth, and a wall thickness of 0,125 mm. Seven platinum strips were immersed in the slag (or pure MnO) sample at different levels. In the case of the slag experiments, the platinum crucibles charged with slags of different compositions were placed in an A1-size Al<sub>2</sub>O<sub>3</sub> crucible surrounded by Al<sub>2</sub>O<sub>3</sub> bubbles, so that it was possible to run four or five different experiments at a time. The Al<sub>2</sub>O<sub>3</sub> crucible was placed on the pedestal and pushed up slowly into the even-temperature region of the furnace over a period of about 40 minutes. The reaction tube of the furnace was flushed for about 15 minutes with spectrographically pure argon before the mixed gases were added. In the Pt–Mn calibration tests, the samples were left in the furnace for 48 hours at 1300 °C and for 24 hours at 1400 and 1500 °C. However, all the slag samples were equilibrated in the furnace at 1500 °C for 24 hours. Previous studies mention an equilibration time of about 8 hours for slag experiments<sup>15</sup>. Profiles obtained by X-ray energy-dispersive analysis using a scanning electron microscope (SEM–EDAX) of manganese on platinum strips verified that equilibrium had been attained in that the profiles were very smooth. At the end of the equilibration, the samples were rapidly withdrawn into the water-cooled end of the furnace and quenched in water.

In the slag–metal distribution experiments, the metal charge was prepared from electrolytic manganese and iron powders, high-purity silicon, and spectrographic-grade graphite powder. From these, a number of master alloys were prepared by melting the elements under an argon atmosphere in graphite crucibles. After the master alloys had been crushed and ground, they were stored in closed bottles in a vacuum desiccator. The compositions of the actual alloys for the experimental runs were adjusted by the addition of the necessary pure elements in powder form to these master alloys. Graphite crucibles, 14 mm in internal

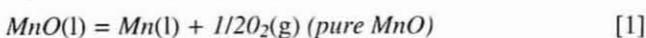
diameter and 44 mm in height, were used for the equilibrium runs. The charge consisted of about 6 g of metal and 4 g of slag of selected compositions. The flowrate of CO was kept at 600 cm<sup>3</sup>/min. After equilibration at 1500 °C for 24 hours, the crucibles with their contents were quenched in water. The slag and metal phases were then removed from the crucible. The graphite that had stuck onto both phases was removed with emery paper or a wire wheel. Afterwards, both phases were kept in sealed bottles until their contents were analysed. A portion of the samples was kept for EDAX work.

The analytical work was done at Mintek. The manganese contents of the equilibrated Pt–Mn coupons were determined by the standard periodate (photometric) method, the final basic constituents of the slag were analysed by X-ray fusion, and the iron content of the slag was determined by the o-phenanthroline colorimetric method. The carbon content of the metal was analysed by means of a Leco analyser, and the other constituents of the metal by the inductively coupled plasma (ICP) method.

In all the activity and slag–metal distribution experiments, the initial Al<sub>2</sub>O<sub>3</sub> content of the slags was kept at around 5 per cent by mass.

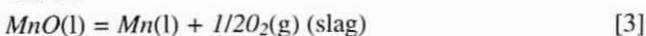
A gas-tight reaction furnace heated electrically with molybdenum wire as the resistance was used. All the gases first passed over drying columns of silica gel and anhydrous magnesium perchlorate. Argon gas was also passed through copper turnings kept at about 500 °C so that as much oxygen as possible was removed. The ancillary equipment thus involved a gas-purifying train and a gas mixer of conventional design. Type B thermocouples were used both for the measurement of sample temperatures and for control of the furnace temperature using Eurotherm controllers. The low oxygen partial pressures were obtained by the mixing of CO and CO<sub>2</sub> gases through capillary tubes connected to flowmeters.

The method adopted for the measurement of MnO activities in ferromanganese slags was similar to that used by Abraham *et al.*<sup>2</sup>: the platinum strips were equilibrated with slag in a platinum crucible, and a partial pressure of oxygen was imposed by gas mixtures of CO and CO<sub>2</sub>. If initially pure MnO is used instead of a slag containing MnO, the equilibrium constant for the reaction will be given by



$$K' = a'_{\text{Mn}} \sqrt{(p'_{\text{O}_2})} / a'_{\text{MnO}} \quad [2]$$

If a slag containing MnO is used, the equilibrium constant will be



$$K = a_{\text{Mn}} \sqrt{(p_{\text{O}_2})} / a_{\text{MnO}} \quad [4]$$

Since activities are used, and not concentration terms, the equilibrium constants given by equations [2] and [4] will be the true constants and will be equal. Equating and rearranging give

$$a_{\text{MnO}} = \sqrt{(p_{\text{O}_2}/p'_{\text{O}_2})} a'_{\text{MnO}} (a_{\text{Mn}}/a'_{\text{Mn}}) \quad [5]$$

and, when  $a_{\text{Mn}} = a'_{\text{Mn}}$ , equation [5] becomes

$$a_{\text{MnO}} = \sqrt{(p_{\text{O}_2}/p'_{\text{O}_2})} a'_{\text{MnO}}$$

Therefore,  $p_{\text{O}_2}$  is the partial pressure of oxygen prevailing at the time of the experiment,  $p'_{\text{O}_2}$  is the pressure of oxygen that would be in equilibrium with pure MnO and an alloy that contains the same amount of manganese as was formed in the slag experiment, and  $a'_{\text{MnO}}$  is the activity of the stoichiometric MnO in the non-stoichiometric oxide that would be in equilibrium with  $p'_{\text{O}_2}$ . Values of  $p'_{\text{O}_2}$  and  $a'_{\text{MnO}}$  have been measured by Richardson *et al.*<sup>15</sup> and by Davies and Richardson<sup>18</sup> respectively.

## Results and Discussion

Activity–composition relations in the Pt–Mn system were re-determined for calibration purposes at 1300, 1400, and 1500 °C and at  $p_{\text{O}_2}$  values between  $5,40 \times 10^{-6}$  and  $4,54 \times 10^{-13}$  atm. In Figure 1, the activity coefficient of manganese is plotted against its mole fraction. The results of the present work are in good agreement with those obtained in a previous study<sup>17</sup>.

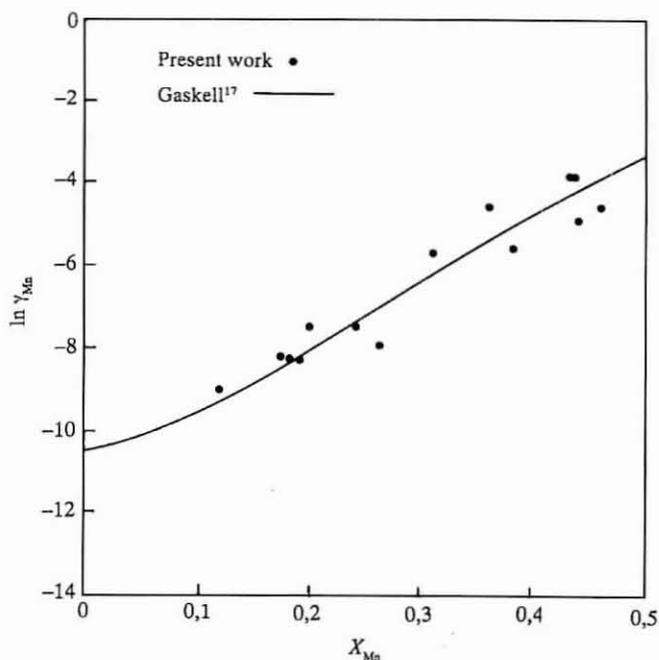


FIGURE 1. The change of the activity coefficient of manganese with composition in Pt–Mn alloys at 1500 °C

Extensive experimental runs were carried out in order to determine MnO activities in slags at 1500 °C. The Al<sub>2</sub>O<sub>3</sub> content of the slags was kept at about 5 per cent by mass. The basicity ratios of the slags varied between 0,41 and 1,18.

A quadratic multivariable regression model was developed to predict the activities of MnO in ferromanganese slags as a function of slag compositions based on the gathered data. The seven independent variables chosen initially were the mass percentages of MnO, CaO, MgO, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> in the slag, as well as the basicity ratio,  $B$ , and the CaO-to-MgO ratio. The regressions were carried out by the use of routines from the SAS (Statistical Analysis Software) system. Initially, the SAS procedure RSREG, which fits a complete quadratic response surface to the data, was used, and the correlation coefficient was found to be 0,982. For a seven-variable model, including quadratic and cross-product terms, the analysis resulted in a model having 36 parameters, which were regarded as too many. The SAS procedure RSQUARE was then used, and the correlation coefficient was found to be 0,979. This procedure selects the optimum combination of independent variables in the model. With this approach, it was found that essentially similar fits could be obtained from a model with far

fewer parameters. The analysis resulted in a model having 16 parameters, and this was referred to as the 'reduced model'. Thus, the equation used to predict the activities of MnO in ferromanganese slags using the reduced model would be written as

$$a_{\text{MnO}} = 0,7265 - 0,0249 (\% \text{SiO}_2) - 2,3115(B)^2 + 0,0619 (\% \text{MnO} \times B) - 0,0003 (\% \text{MnO})^2 + 0,1451 (\% \text{CaO} \times B) - 0,0018 (\% \text{CaO} \times \% \text{MnO}) - 0,0023 (\% \text{CaO})^2 + 0,1439 (\% \text{MgO} \times B) - 0,00019 (\% \text{MgO} \times \% \text{MnO}) - 0,0045 (\% \text{MgO} \times \% \text{CaO}) - 0,0022 (\% \text{MgO})^2 - 0,0506 (\% \text{SiO}_2 \times B) + 0,0005 (\% \text{SiO}_2 \times \% \text{MnO}) + 0,0015 (\% \text{SiO}_2 \times \% \text{CaO}) + 0,0015 (\% \text{SiO}_2 \times \% \text{MgO}).$$

In Figures 2 and 3, the individual data groups with similar basicity ratios and different CaO-to-MgO ratios are superimposed. The curves represent the predicted values calculated from the empirical model, and the symbols represent the experimental values. From a large number of measurements of the optical basicity of glasses<sup>19</sup> using mainly  $\text{Pb}^{2+}$  as probe ion, the optical basicity of an oxide,  $\lambda$ , was found to be related to the Pauling electronegativity,  $x$ , of the cation involved by the expression

$$\lambda = 0,74/(x - 0,26). \quad [7]$$

Hence, by use of the relationship

$$\Lambda = X_A \lambda_A + X_B \lambda_B + \dots, \quad [8]$$

it was possible to calculate the bulk value of  $\Lambda$  (the optical basicity) for a slag of any composition involving these oxides. In equation [8],  $X$  is the equivalent cation fraction based on the fraction of negative charge neutralized by the charge on the cation concerned. For any component,  $X$  was calculated in terms of mole fractions by the equation

$$X = \frac{(\text{mole fraction of component} \cdot \text{number of oxygen atoms in oxide molecule})}{\sum \text{mole fraction of component} \cdot \text{number of oxygen atoms in oxide molecule}} \cdot [9]$$

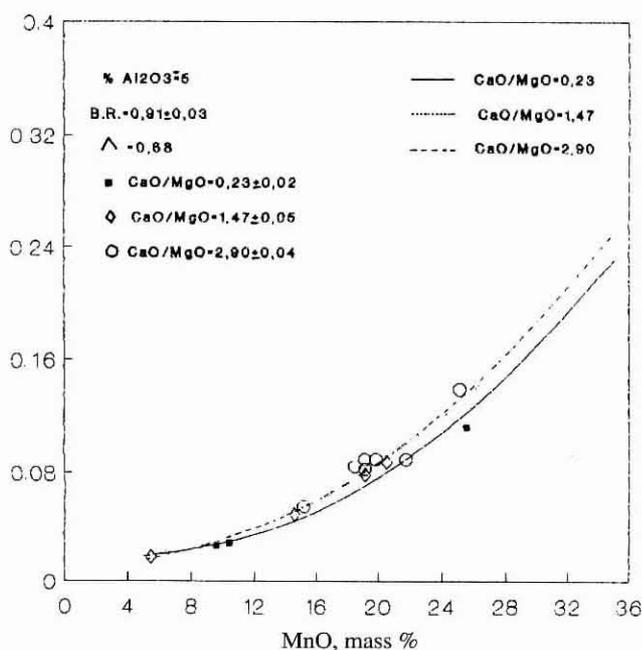


FIGURE 2. Activities of MnO in  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-CaO-MnO}$  slags for various CaO-to-MgO ratios

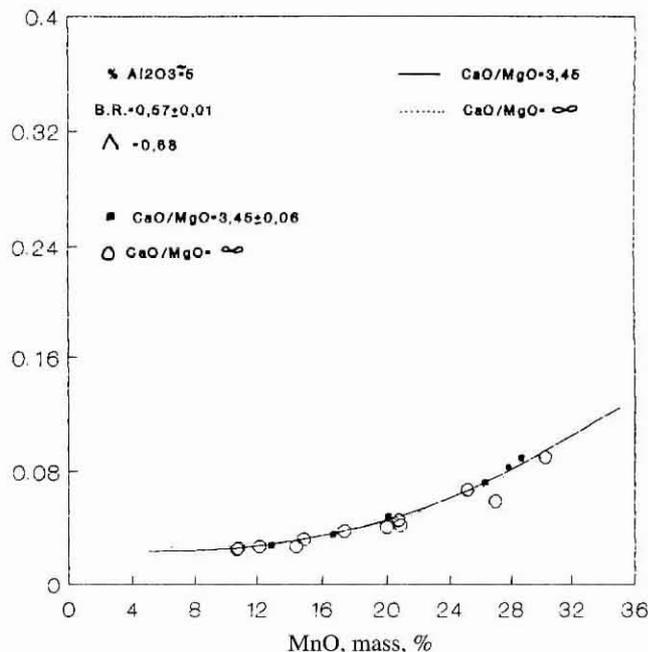


FIGURE 3. Activities of MnO in  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-CaO-MnO}$  slags for various CaO-to-MgO ratios

Normally, an increase in the mass concentration of MnO increases the MnO activities, and an increase in the CaO-to-MgO mass ratio increases the  $a_{\text{MnO}}$  values. The increase in the activity of MnO with increasing concentration can be explained in terms of the principle of the ionic structure in liquid slags. At any one concentration of MnO, a certain number of  $\text{Mn}^{2+}$  ions will be associated with the silicate and aluminate ions, and a certain number only with free oxygen ions. An increase in the MnO content of the slag will cause a simultaneous increase in the number of free oxygen ions and in the number of associated manganese ions. In other words, there will be excess  $\text{Mn}^{2+}$  and  $\text{O}^{2-}$  ions in the molten slag. Hence, the activity of MnO increases with increasing concentration of MnO in the slag.

The result obtained during the runs showed that CaO has a slight effect in increasing the  $a_{\text{MnO}}$  values. This is in agreement with the work of Warren<sup>14</sup>. In the present work, the  $\text{Al}_2\text{O}_3$  content was kept at around 5 per cent by mass in all the experimental runs. When the free energy of the formation of the orthosilicates  $\text{Ca}_2\text{SiO}_4$ ,  $\text{Mg}_2\text{SiO}_4$ , and  $\text{CaMgSiO}_4$  are taken into consideration, it can easily be seen that  $\text{Ca}_2\text{SiO}_4$  has the most negative free energy of formation<sup>20-23</sup>. Furthermore, the free energy of formation of  $\text{CaMgSiO}_4$  is more negative<sup>20-23</sup> than that of  $\text{Mg}_2\text{SiO}_4$ . In other words, the interaction of  $\text{Ca}^{2+}$  ions with  $\text{SiO}_2$  is stronger than those of mixed  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions and  $\text{Mg}^{2+}$ . Thus, one can conclude that an increase in the amount of CaO can lead to an increase in the formation of  $\text{Ca}_2\text{SiO}_4$  orthosilicate, leading to higher  $a_{\text{MnO}}$  values in the slags. Therefore, because of the interaction with  $\text{SiO}_2$ ,  $\text{Mn}^{2+}$  ions become freer, i.e. less associated with the  $\text{SiO}_2$  network, and therefore the  $a_{\text{MnO}}$  values increase.

In Figure 4, the individual data groups with similar CaO-to-MgO ratios and different basicity values are superimposed. The curves represent the predicted values calculated through the empirical model, and the symbols represent the experimental values. An increase in the basicity ratio clearly increases the MnO activity. This can be explained in a

very similar way in terms of modern slag theory. At low basicities, almost all the metal cations are associated with the large  $\text{SiO}_2$  anionic groups, and only a few  $\text{O}^{2-}$  ions exist. The activity of  $\text{MnO}$  in such melts is thus low (high slag viscosity). In other words, at low basicities, the  $\text{SiO}_2$  network is not disrupted. As the concentration of the basic oxides increases, the  $\text{SiO}_2$  network is broken up into smaller anionic groups (lower slag viscosity) and the proportion of free oxygen anions begins to increase. Thus, an equal number of divalent cations, which were associated with  $\text{SiO}_2$  anions, associate with free oxygen anions. At this point, divalent cations like  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ , because of their higher interaction with  $\text{SiO}_2$  ions, are preferentially associated with silicate ions, and thus  $\text{Mn}^{2+}$  ions become freer from association with silicate ions. In other words, the free energy of formation of  $\text{MnSiO}_3$  is less negative than that of  $\text{MgSiO}_3$ ,  $\text{CaSiO}_3$ , etc. Thus,  $\text{Mn}^{2+}$  cannot overcome the interaction between these metal cations and silicate ions, and therefore an increase in basicity increases the  $a_{\text{MnO}}$  values in the slag.

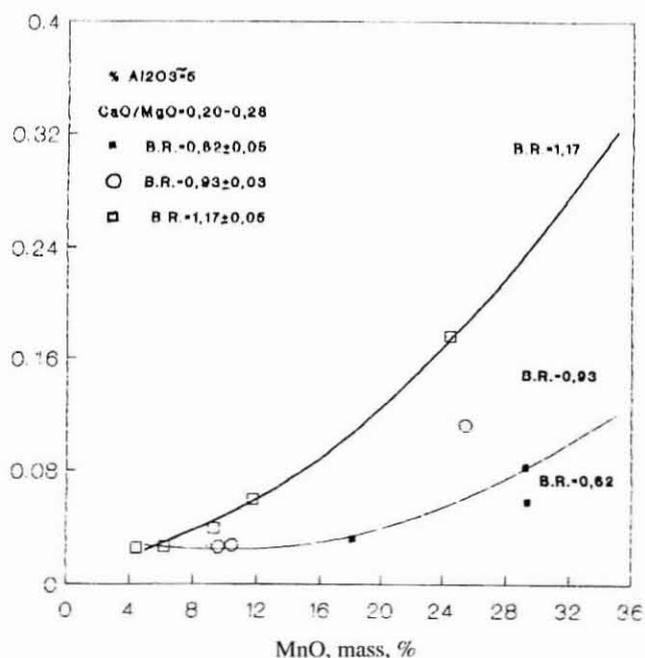


FIGURE 4. Activities of  $\text{MnO}$  in  $\text{SiO}_2$ - $\text{Al}_2\text{O}_3$ - $\text{MgO}$ - $\text{CaO}$ - $\text{MnO}$  slags for various basicity ratios

Extensive experimental runs were carried out on the slag-metal equilibrium at  $1500^\circ\text{C}$ . The metal phase was always saturated with respect to graphite. The actual basicity ratios of the slags ranged between 1,00 and 1,39 for different ferromanganese compositions<sup>24</sup>. For the ferromanganese-metal phase, four different Mn-to-Fe ratios were selected: 3,7, 5,5, 6,7, and 7,4. In Figure 5, three different data groups with different Mn-to-Fe ratios are superimposed, showing the relationship between dissolved carbon and silicon. It can be seen that, at constant silicon contents, as the Mn-to-Fe ratio increases, the carbon solubility in the metal phase increases. The carbon and silicon concentrations in the metal phase are inversely related, as expected,

and this behaviour can be explained in terms of the stability of carbides. As silicon lowers the solubility of carbon, the conditions become less favourable for carbide formation. Thermodynamically, this means that silicon decreases the activity of carbon.

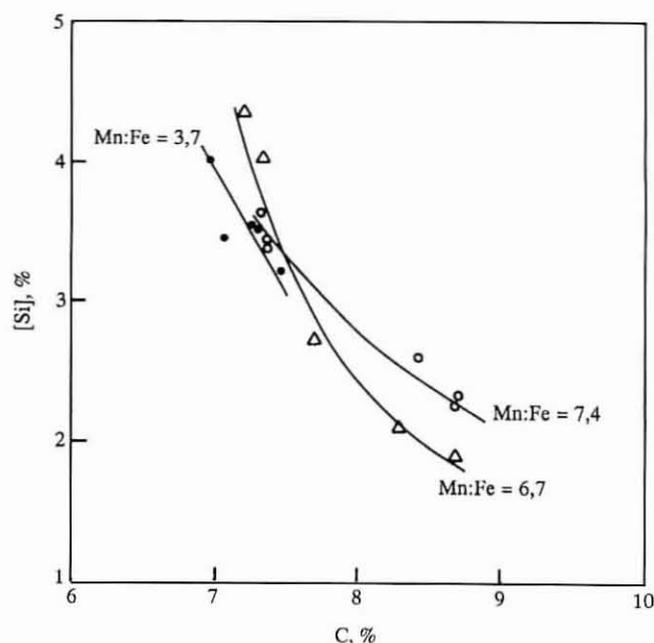


FIGURE 5. The effect of the silicon content on the carbon content of metal at different Mn-to-Fe ratios

Figure 6 shows the effect of the Mn-to-Fe ratio of the metal phase on the relationship between the silicon content of the metal and the  $\text{SiO}_2$  content of the slag. As the  $\text{SiO}_2$  content of the slag increases, the silicon content of the metal increases, and this effect is even more noticeable at the higher Mn-to-Fe ratios. The increase in the  $\text{SiO}_2$  activity in the slag with increasing  $\text{SiO}_2$  concentration results in the transfer of silicon from the slag to the metal.

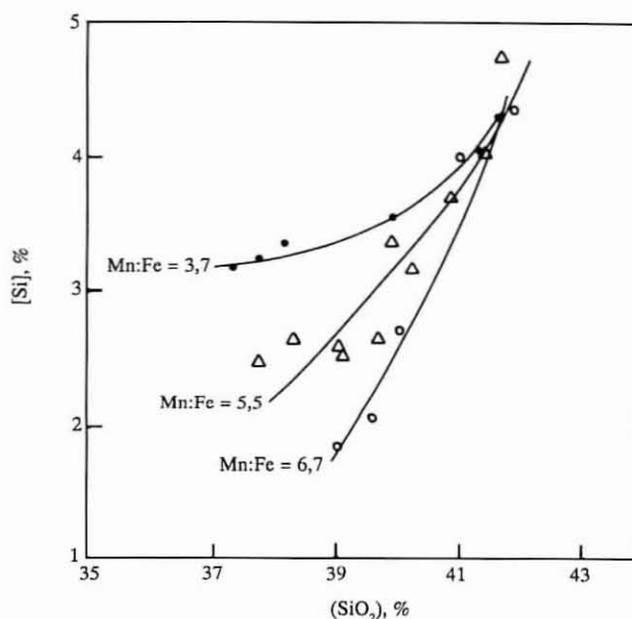


FIGURE 6. The effect of the silica content of the slag phase on the silicon content of the metal phase at different Mn-to-Fe ratios

Figure 7 shows the effect of the CaO-to-Al<sub>2</sub>O<sub>3</sub> ratio on SiO<sub>2</sub> reduction at two different Mn-to-Fe ratios in the metal phase. As the CaO-to-Al<sub>2</sub>O<sub>3</sub> ratio in the slag increases (at constant Al<sub>2</sub>O<sub>3</sub> content), the silicon content of the metal decreases. As the Mn-to-Fe ratio increases, the effect of increasing CaO-to-Al<sub>2</sub>O<sub>3</sub> ratio on the silicon content of the metal is even greater. This indicates that the activity of SiO<sub>2</sub> in the slag is decreased by the substitution of CaO in accordance with the network-modification power of CaO. This result is similar to the findings of Fulton and Chipman<sup>25</sup>. Another study<sup>26</sup> showed that, as Al<sub>2</sub>O<sub>3</sub> was replaced with CaO in slags of low SiO<sub>2</sub> content, the equilibrium silicon content of the metal increased. In the case of slags with a high SiO<sub>2</sub> content, the opposite effect was observed. This is also in agreement with the findings of the present study.

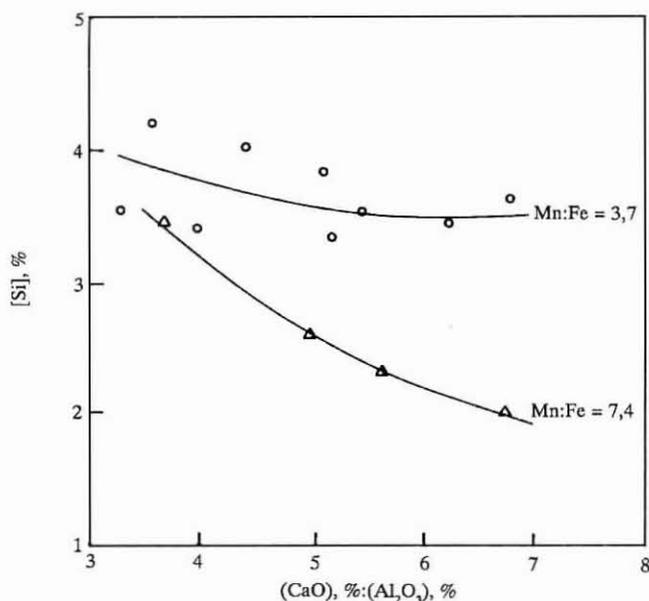


FIGURE 7. The effect of the CaO-to-Al<sub>2</sub>O<sub>3</sub> ratio of the slag on the silicon content of the metal at different Mn-to-Fe ratios

In Figure 8, the effect of the MgO-to-CaO ratio of the slag on the silicon distribution between the metal and the slag phases is analysed at constant Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> levels. As MgO replaces CaO in the slag, the distribution ratio of silicon decreases, and the silicon content of the metal increases relative to that of the slag. This can be explained with reference to the MnO activities. It was observed that CaO had a slight effect in increasing the  $a_{MnO}$  values owing to the different free energies of formation of the complex orthosilicates. As MgO replaces CaO, it causes a decrease in MnO activity, and there is less tendency for Ca<sub>2</sub>SiO<sub>4</sub> species to form in the slag. This may cause an increase in the activity of SiO<sub>2</sub> in the slag, and therefore the silicon content of the metal increases.

In Figure 9, it can be seen that the silicon content of the metal decreases as the basicity ratio of the slag increases. This can also be explained in a very similar way in terms of the breakup of the SiO<sub>2</sub> network on the addition of basic oxides. Because of the strong interaction between divalent cations Ca<sup>2+</sup>, Mg<sup>2+</sup>, and silicate ions, the activity of SiO<sub>2</sub> decreases and the silicon content of the metal decreases with increasing basicity. Figure 10 shows the dramatic decrease of the Mn content of the slag that occurs when the basicity of the slag is increased.

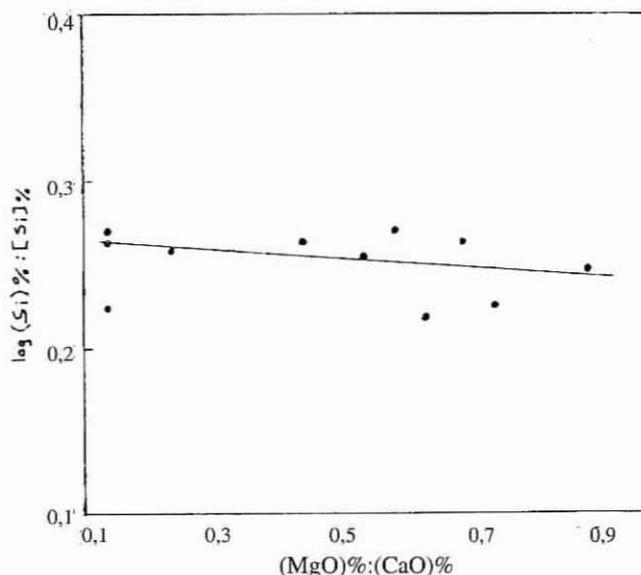


FIGURE 8. The effect of the MgO-to-CaO ratio on the silicon distribution (at 6,7% Al<sub>2</sub>O<sub>3</sub>; 63,1% SiO<sub>2</sub>)

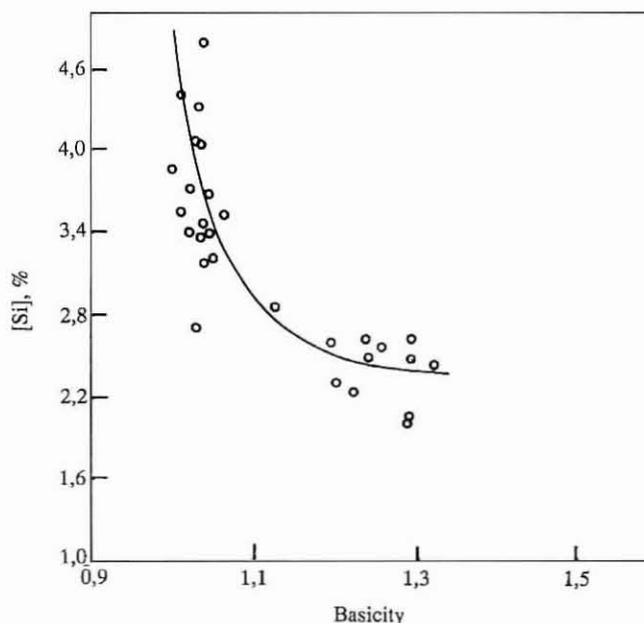


FIGURE 9. The effect of basicity on the silicon content of the metal at 1500 °C under an atmosphere of carbon monoxide

## Conclusions

In the experiments, it was found that  $a_{MnO}$  values increase with increasing concentration of MnO, and tend to increase with an increasing CaO-to-MgO ratio. The  $a_{MnO}$  values increase with an increasing basicity ratio. In the slag-metal equilibrium experiments, the carbon and silicon contents of the metal phase were inversely related. At constant silicon contents, as the Mn-to-Fe ratio increases, the carbon solubility in the metal phase increases. The silicon content of the metal increases with increasing SiO<sub>2</sub> content of the slag, and increases as MgO replaces CaO in the slag. An increase in the slag basicity is associated with a decrease in the silicon content of the metal phase.

As far as the behaviour of slag is concerned, the most important factors are the MnO content and the basicity ratio,

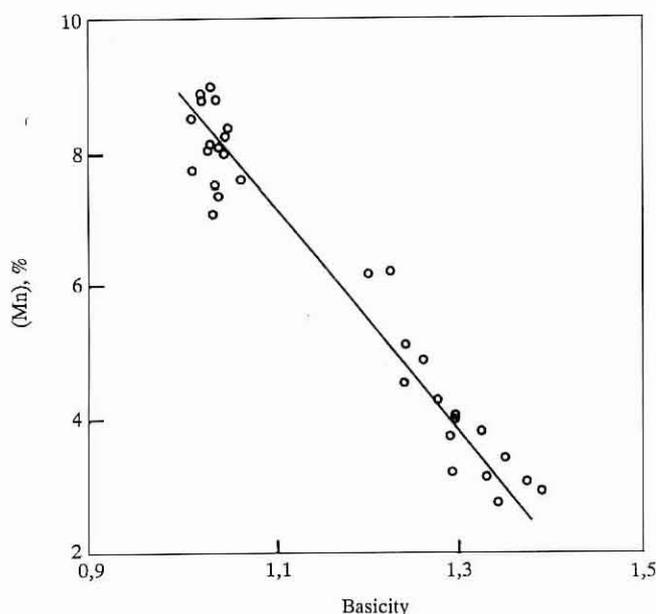


FIGURE 10. The effect of basicity on the manganese content of the slags at 1500 °C under an atmosphere of carbon monoxide

as has been clearly demonstrated in this work. It was shown in recent work<sup>24</sup> that an increase in MnO concentration decreases the viscosity and increases the electrical conductivity. Thus, a lower viscosity implies a greater diffusive mobility of all the components in the slag, in which case the kinetics of the chemical reactions should improve. In order to improve the recovery of manganese, its activity in the slag must be maximized without increasing its concentration. The activity of MnO can be increased by employing slags of higher basicities. However, this also results in higher liquidus temperatures of slag<sup>24</sup>, requiring higher power input in the furnace. Therefore, an optimum must be reached. Both the manganese content of the slag and the silicon content of the metal phase decrease rapidly as the basicity of the slag increases. It appears that a basicity ratio of around 1,0 to 1,2 results in reasonably optimum conditions where the silicon content of the metal is low and the manganese content of the slag is around 9 per cent (about 12 per cent MnO). In the previous work<sup>24</sup>, it was suggested that a slag composition having an optimum around 15 per cent would be the range for furnace operation. In terms of optimum electrical conductivities, viscosities, and liquidus temperatures, this is in excellent agreement with the findings of the present work, where  $a_{\text{MnO}}$  could be maximized without an increase in its concentration in the slag by operating the slags at a basicity ratio of about 1,0 to 1,2 and an MnO content of approximately 12 per cent. When this is done, better recoveries of manganese will be achieved with reasonably high MnO activities in the slag, low viscosity, low liquidus temperature, and reasonable slag resistivity.

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