SULPHUR BEHAVIOUR IN FERROMANGANESE SMELTING

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ABSTRACT

In the present study, the measurement of sulphur distribution ratios between the slag and metal phases encountered in the ferromanganese smelting has been carried out at 0.83 atm of partial pressure of CO at 1773 K by using classical gas-slag-metal equilibrium quenching technique as a function of composition. The distribution results were employed in calculating the sulphide capacities of SiO_2-Al_2O_3-*CaO-MgO-MnO slags in equilibrium with the* Mn-Fe-Si-$C_{satd.}$-S *metal phase. It is shown that the sulphur transfer from metal to slag phase increases with increasing the basicity of the slag. As expected, the sulphur distribution ratio decreases by increasing the silica content of the slag system. The effect of metal composition on the sulphide capacities of the slag as well as on the sulphur distribution ratios between the slag and metal phases have been discussed. Emprical relationships were developed to express the sulphur distribution ratios and sulphide capacities of the above slag system.*

1. INTRODUCTION

Manganese is a crucial alloying metal in the production of iron and steel. During the iron and steel production, manganese is mostly added to the molten steel in the form of ferromanganese or silicomanganese alloy. Sulphur is introduced into the ferromanganese smelting process by the carbonaceous reducing agents such as metallurgical coke, anthracite and coal. In metallurgical coke, sulphur may exist in the form of organic compounds, sulphides and sulphates. The sulphur content of metallurgical cokes varies between 0.5 to 1.5 per cent [1,2,3,4].

In ferromanganese production, the sulphur removal can be achieved by maintaining high slag basicity, low activity of dissolved oxygen in the metal phase and high operation temperatures. During ferromanganese smelting process in order to prevent the excess oxidation of manganese from the melt the application of strongly reducing conditions is essential. The results of Fincham and Richardson show that the sulphur can be held in the slag entirely as sulphide when the partial pressure of oxygen is less than 10^{-5} atm and as sulphate when the partial pressure of oxygen is greater than 10^{-5} atm [5,6].

The slag-metal equilibrium in terms of sulphur and oxygen can be written as follows:

$$[S] + \left(O^{-2}\right) \Leftrightarrow (S^{-2}) + [O] \tag{1}$$

where round bracket indicates a species in the slag and square brackets indicates a species in the metal phase.

The partition ratio of sulphur between slag and metal phases can be expressed as:

$$\frac{(pctS)}{[pctS]} = K_1 \frac{a_{o^{-2}}}{a_o} \frac{\gamma_s}{\gamma_{s^{-2}}} \tag{2}$$

where K_1, a_o, a_o^{-2}, (pct S), [pct S], γ_s and γ_s^{-2} represent the equilibrium constant for Eq. (1), activity of oxygen in the metal, the activity of oxygen ions in the slag, weight percent of sulphur in the slag phase and metal phases, the activity coefficients of sulphur in the metal and sulphide ions in the slag respectively.

Richardson and Withers suggested that under reducing conditions the sulphide capacity can be defined by using the transfer reaction of sulphur between slag and gas phases [7].

$$\frac{1}{2}S_2 + (O^{-2}) \Leftrightarrow \frac{1}{2}O_2 + (S^{-2}) \tag{3}$$

The equilibrium constant (K_3) of Reaction (3) can be represented by the following equation:

$$K_3 = \frac{(a_{S^{-2}})}{(a_{o^{-2}})} . \frac{P_{o_2}^{1/2}}{P_{S_2}^{1/2}} = (pctS) . \frac{f_{s^{-2}}}{a_{o^{-2}}} . \frac{P_{o_2}^{1/2}}{P_{S_2}^{1/2}} \tag{4}$$

where a_s^{-2}, P_{O2}, P_{S2} and f_S^{-2} represent activity of sulphide in the slag, the partial pressures of oxygen and sulphur in atmosphere and the sulphide ion activity coefficient in the slag at 1 weight per cent standard state, respectively.

The sulphide capacity (C_s) can be defined for a given slag by using following equation,

$$C_S = (pctS)\frac{P_{O_2}^{1/2}}{P_{S_2}^{1/2}} = K_3 . \frac{a_{O^{-2}}}{f_{S^{-2}}} \tag{5}$$

Elliott J. F. expressed the Eq. (3) in a different way to represent the equilibrium of sulphur between metal and slag phases as given in the Eq. (6) [8]

$$[S] + \left(O^{-2}\right) \Leftrightarrow (S^{-2}) + \frac{1}{2}O_{2(g)} \tag{6}$$

The equilibrium constant for Eq. (6) is given by

$$K_6 = \frac{(a_{s^{-2}}).(P_{o_2})^{1/2}}{[a_s].(a_{o^{-2}})} = \frac{(f_{s^{-2}}).(pctS^{-2}).(P_{O_2})^{1/2}}{[f_s][pctS].(a_{o^{-2}})} \tag{7}$$

By using Eq. (6) and (7), the sulphide capacity can be redefined as follows:

$$C_s = \frac{K_6 .(a_{o^{-2}})}{(f_{s^{-2}})} = \frac{(pctS^{-2}).(P_{o_2})^{1/2}}{[f_s][pctS]} \tag{8}$$

The sulphide capacity describes the potential ability of an arbitrary homogeneous molten slag to absorb sulphur and could be used for defining the desulphurization characteristics of a particular slag [9].

The solution of manganese in liquid iron is assumed as ideal. Also iron and manganese are chemically similar elements and their atomic sizes are approximately the same. Due to the lack of data available for the first and second order interaction coefficients which are related to the Mn-Fe alloy system, the interaction parameters reported for liquid iron may be used to calculate the activity coefficient of sulphur [f_s] in the dilute solution of manganese. Similar methods have been applied for different alloy systems [10,11].

The ratio between the sulphur contents in the slag and the metal phases is defined as the partition ratio or distribution ratio of sulphur (L_s) which can be expressed as follows:

$$Ls = \frac{(pct.S)}{[pct.S]} \tag{9}$$

In this study, the basicity ratio of the slag is defined as follows:

$$\text{Basicity} = \frac{(\text{pct.CaO}) + (\text{pct.MgO})}{(\text{pct.SiO}_2)} \tag{10}$$

where (pct. CaO), (pct. MgO) and (pct. SiO_2) are the mass percentages of CaO, MgO and SiO_2 in the slag, respectively.

2. EXPERIMENTAL PROCEDURE

The gas-slag-metal equilibrium-quenching method was used in order to study the sulphur behaviour related to Mn-Fe-$C_{satd.}$-Si-S alloys and MnO-CaO-MgO-Al_2O_3-SiO_2 slag system.

The slags were prepared as the homogeneous mixtures of pure CaO, MgO, Al_2O_3, and SiO_2 . The desired amounts of the slag components were weighed and mixed in an agate mortar under acetone. The dried slag mixtures were pressed into pellet form and sintered at 1200°C for 48 hours to obtain a homogeneous structure. The sintered slag pellets were ground and mixed with pure MnO powder to have the required compositions.

The ferromanganese alloy samples were prepared by using electrolytically pure Mn,Fe, Si and spectrographic grade of graphite. The chemically pure grade of FeS was used for addition of equivalent amount of sulphur into the alloy. The required amounts of the metal components were dried, weighed and mixed homogeneously in an agate mortar and placed into pure graphite crucibles with the corresponding slag samples. The alloy sample of 6 g was placed at the bottom of the crucible and 6 g of slag sample was placed above the alloy sample in the same crucible.

A vertical molybdenum wire resistance furnace with an alumina work tube was used for the gas-slag-metal equilibration experiments. Molybdenum wire was protected from the oxidation by decomposition of anhydrous ammonia. Eurotherm Thyristor 0703 25 A power pack was used as the power control unit of the furnace by using S-type thermocouple (Pt10Rh-Pt) placed to be in contact with the winding tube. The temperature of the furnace was controlled to be in the range of ± 2°C at 1500°C at the hot zone. The hot zone temperature of the reaction tube was measured with another S-type thermocouple (Pt10Rh-Pt) placed under the crucible.

According to the results of previous studies, the equilibration time for the experiments was chosen as 18 hours [12,13,14]. Experiments with graphite only were conducted periodically for checking the gas tight condition of the system which indicated negligible loss in the mass of graphite in each case.

The flow rate of CO was 200 cm^3/min as calibrated by Bunsen Tower. The oxygen partial pressure of the system was calculated as 1.21×10^{-16} atm. at 1773 K according to Eq. (11) and its standard free energy change given in Eq. (12). The partial pressure of carbon monoxide was taken as 0.83 atm to be equal to the atmospheric pressure in Johannesburg and the activity of carbon was unity due to the presence of graphite crucible.

$$C_{(Solid)} + \frac{1}{2}O_{2(gas)} \Leftrightarrow CO_{(gas)} \tag{11}$$

$$\Delta G^{o} = -112877 - 86.514T \quad \text{(J/mol)} \qquad (12)$$

The graphite crucibles containing the samples were introduced into the reaction tube by using an alumina pedestal. The reaction tube was flushed for 20 minutes with purified argon prior to each run and purified CO was introduced into the reaction tube. After equilibration and quenching, the slag and metal phases were separated and ground into the powder form for analysis. The alloy phases were analyzed first by ICP method for their Fe, Mn and Si contents and then by LECO analyzer for their C and S contents. The slag phases were analyzed by ICP method for their MgO, CaO, SiO_2, MnO, Al_2O_3 , FeO and S contents.

3. RESULTS AND DISCUSSION

According to the analytical results, the slag and metal constituents varied in the following ranges: Slag Phases : MnO; 2.21-10.5 %, CaO; 19.4-40.4 %, SiO_2; 36.3-44.7%, MgO; 11.6-18.6%, Al_2O_3; 5.86-7.44%, S;0.749-1.191%, the amount of FeO is negligible. The basicity ratio varied between 0.851 to 1.302.

Metal Phases : Mn; 65.6-81.9%, Si; 2.29-12.3%, Fe; 6.77-18.9%, C; 2.88-7.25 %, S; 0.021-0.036%.

3.1 The Effect of Slag Composition On Sulphur Behaviour

Figure 1 illustrates the strong effect of basicity change on the sulphide capacity values of the MnO-MgO-SiO_2-Al_2O_3-CaO multicomponent slag system at 1773 K. As shown in the figure, the sulphide capacity increases with the increase in the basicity of the slag such as the logarithm of sulphide capacity increases from -8.022 to -7.631 when the slag bacity increases from 0.85 to 1.433.

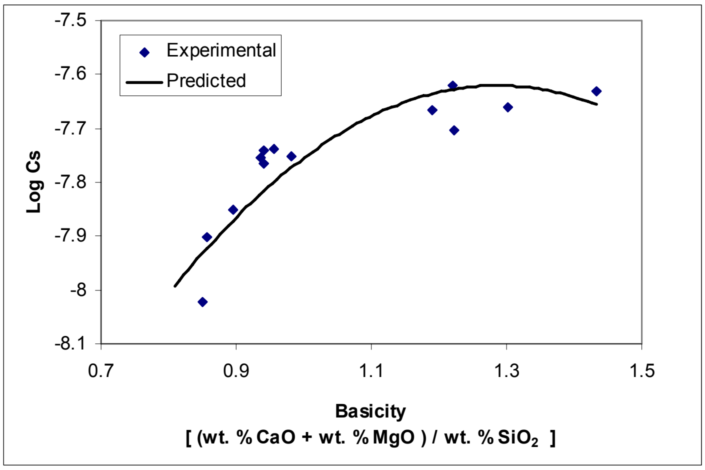

Figure 1: The effect of basicity ratio on the sulphide capacity of slag at 1773 K

The influence of basicity ratio change on the sulphide capacity values can be explained by the modern slag theory. At low basicities, nearly all the metal cations such as Ca^{+2}, Mg^{+2} and Mn^{+2} are linked with the large silica anionic groups which make very few free O^{-2} ions available [15]. As the amount of basic oxides increases in the slag system, the silica network starts to break down which causes an increase in the concentration of free O^{-2} ions assisting the reaction (1) to proceed to the right direction [16]. It is quite clear from Eq. (2) that the partition ratio of sulphur between slag and metal can be increased by increasing the activity of oxygen ions in the slag phase. A similiar assumption can be applied for the sulphide capacity values of slags.

Quadratic multivariable regression model equations have been derived from the experimental results which have high correlation coefficients ($R^2 = 0.975$ for the logarithm of sulphide capacity and $R^2=0.907$ for the logarithm of partition ratio of sulphur between slag and metal phases) indicating that if the slag compositions fall within the range as given above, these models can be confidently used in order to determine the sulphide capacity of slags and partition ratio of sulphur between slag and metal phases at 1773 K. The weight percentage of CaO, SiO_2, MgO, MnO, Al_2O_3 and basicity ratio are the independent variables of the model equations.The regression model equations have been calculated by using Statistical Analysis Software (SAS) system. The quadratic multivariable regression model equations are:

$$\begin{aligned}\mathrm{Log}_{10}\, C_s = {} & 18.077 - 0.028\,(\%Al_2O_3).(\%MnO) - 0.023\,(\%CaO) - 0.409(\%SiO_2) \\ & - 6.578\,(Basicity) - 0.004\,(\%MgO)\end{aligned} \tag{13}$$

$$\begin{aligned}\mathrm{Log}_{10}\, L_s = {} & 11.737 - 0.171\,(\%SiO_2) - 1.709\,(Basicity) - 0.007\,(\%MgO) - 0.066\,(\%MnO) \\ & - 0.028\,(\%CaO)\end{aligned} \tag{14}$$

The dominant influence of CaO of the slag system on the sulphur partition ratio can be seen in Figure 2. When the amount of CaO increases from 19.6 to 40.4 per cent, the partition ratio of sulphur also increases from 25.82 to 56.71. As the CaO content of the slag increases, more free O^{-2} anions are supplied to the slag phase which cause an increase in the activity of oxygen anion in the slag. The dissociation reaction of CaO can be expressed as:

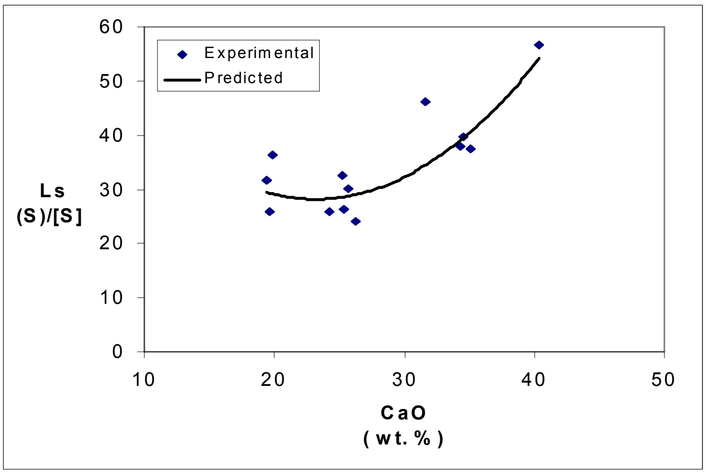

Figure 2: The effect of the CaO content on the sulphur partition ratio (L_s) at 1773 K

$$(CaO) \Leftrightarrow (Ca^{+2}) + (O^{-2}) \tag{15}$$

CaO in the slag system is the main factor which determines the transfer of sulphur from the metal to slag by forming CaS sulphide in the slag phase. This assumption can be supported by comparing the Gibbs free-energy values of CaS, FeS, MnS and MgS for the reactions between sulphur in the metal and the oxides in the slag. CaS has the lowest Gibbs free-energy values compared to other sulphides and it is estimated that the desulphurising power of the basic oxides declines slightly in the sequence of CaO, FeO, MnO and MgO [17]

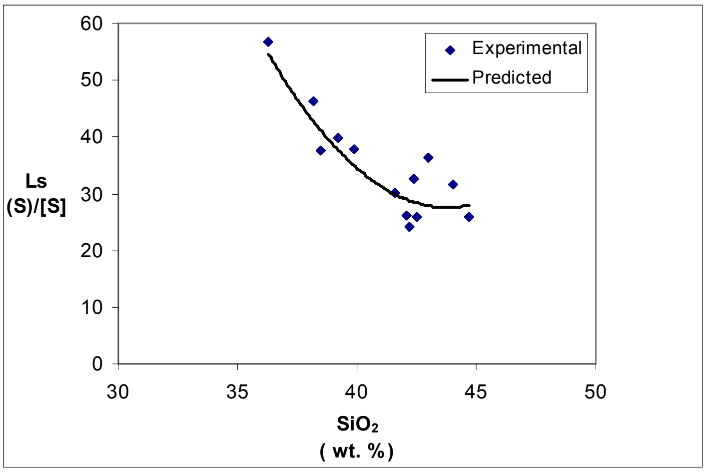

Figure 3: The effect of SiO_2 content on the sulphur partition ratio (L_s) at 1773 K

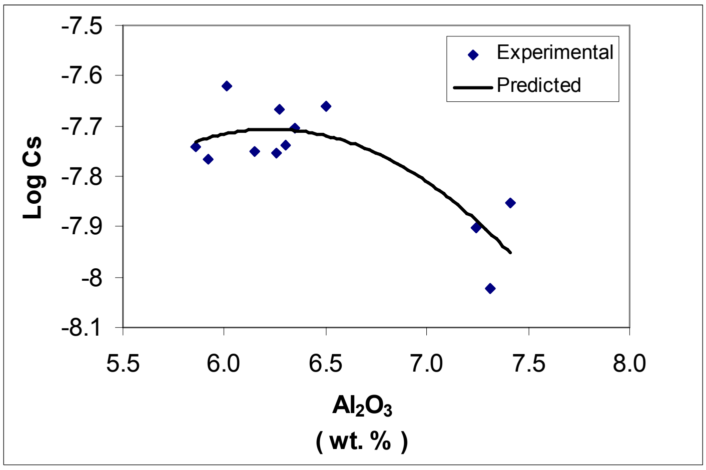

Figure 4: The effect of the Al_2O_3 content on the sulphide capacity of slag at 1773 K

The effect of SiO_2 on the partition ratio of sulphur is given in Figure 3. The partition ratio of sulphur decreases from 56.71 to 26.33 by increasing the amount of SiO_2 in the slag from 36.3 to 44.7 per cent.

Figure 4 illustrates that the logarithm of sulphide capacity decreases from -7.74 to -8.02 by increasing the alumina concentration of the slag from 5.8 to 7.31 per cent.

According to the modern slag theory, the oxides such as SiO_2 and Al_2O_3 that accept oxygen ions form anion complexes in the slag structure and this structural occurence causes a decrease in the partition ratio of sulphur between slag and metal phases. The oxygen ion-consuming reactions for SiO_2 and Al_2O_3 can be written as follows:

$$(SiO_2) + 2(O^{-2}) \Leftrightarrow (SiO_4^{-4}) \tag{16}$$

$$(Al_2O_3) + 3(O^{-2}) \Leftrightarrow 2(AlO_3^{-3}) \tag{17}$$

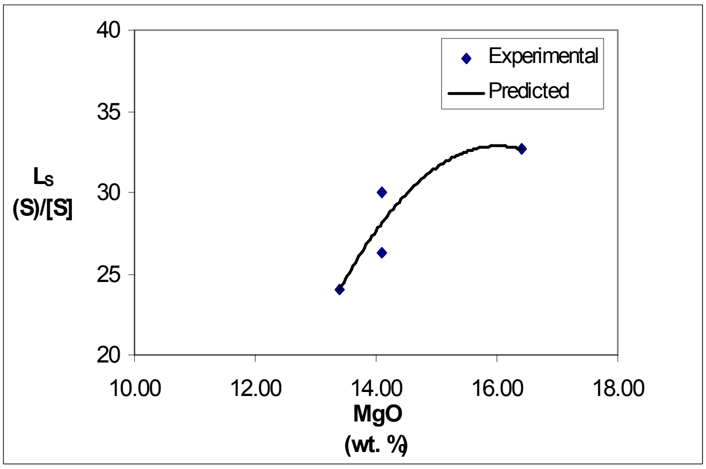

Figure 5: The effect of the MgO content on the sulphur partition ratio (L_s) of slag at 1773 K with CaO/SiO_2= 0.59-0.62, Al_2O_3= 5.92 %-6.3 %

When oxygen ions are consumed, reactions (1) will not shift to right causing a decrease in the desulphurization capacity of the slags, hence increasing alumina and silica will decrease the sulphide capacity of the slag.

The increase in the concentration of O^{-2} anions resulting from the oxygen ion-producing dissociation reactions of CaO and MgO cause a breakdown in the Si-O bonds and the network of silicate structure is broken. According to Bodsworth C. and Bell H.B. [17], when magnesia is added to the melt, while holding the ratio of CaO/SiO_2 constant, the activity of oxygen ions in the slag system is raised and this causes an increase in the partition ratio of sulphur between slag and metal phases. Figure 5 shows that the partition ratio of sulphur between slag and metal phases increases from 24.055 to 32.66 when MgO content in the slag phase increases from 13.4 to 16.4 when the ratio of CaO/SiO_2 is kept between 0.59 and 0.62.

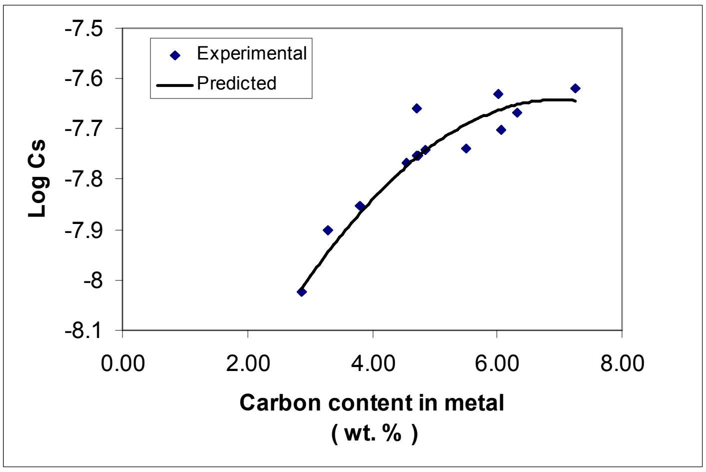

Figure 6: The effect of the carbon content of the metal phase on the sulphide capacity of slag at 1773 K

3.2 The Effect of Metal Composition on Sulphur Behaviour

Figure 6 shows that the sulphide capacity of the slag can be enhanced by increasing the carbon solubility in the metal phase.

In metal phase, increasing the amount of carbon decreases the activity of oxygen which enhances the activiy coefficient of sulphur in the metal phase hence results in an increase in the desulphurization of the metal melt. The effect of carbon thus can cause a raise in the partition ratio of sulphur between slag and metal phases as expressed in Eq.(2). The sulphide capacity of the slag will then be increased by increasing the concentration of carbon in the melt.

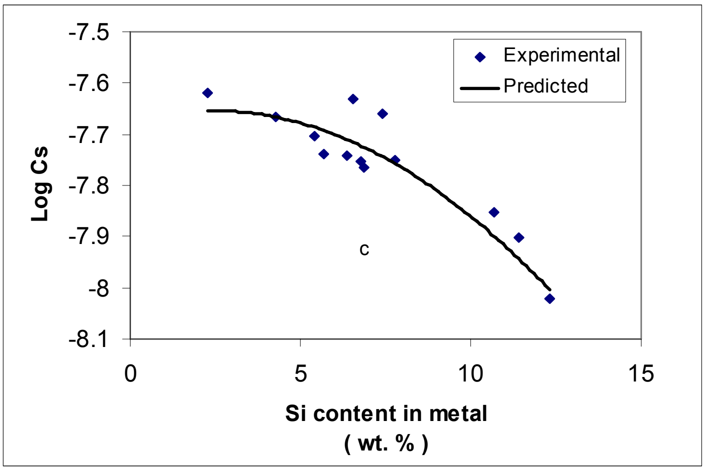

Figure 7: The effect of the silicon content of the metal phase on the sulphide capacity of slag at at 1773 K

The sulphide capacity and silicon concentrations of the metal phase are inversely proportional to each other which can be observed in Figure 7. According to Fulton and Chipman [18], when the concentration of silicone in the metal phase increases, the concentration of silica in the slag phase in equilibrium with silicon is also enhanced, the reaction can be expressed as follows:

$$\frac{1}{2}[\mathrm{Si}]+[\mathrm{O}] \Leftrightarrow \frac{1}{2}(\mathrm{SiO_2}) \tag{18}$$

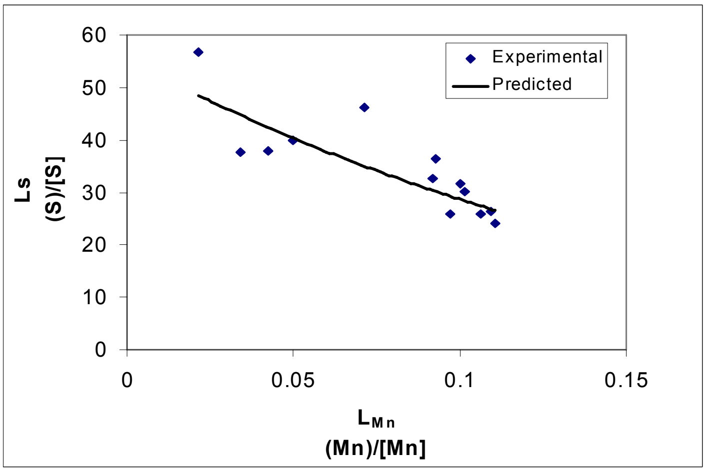

Figure 8: The effect of the manganese distribution ratio on the sulphur partition ratio (Ls) at 1500 °C

The increase in the amount of SiO_2 lowers the available free oxygen anions in the slag phase according to Eq.(16) resulting in a decrease of the sulphide capacity.

Figure 8 indicates that the partition ratio of manganese increases from 0.02 to 0.11,when the sulphur distribution between slag and metal phases decreases from 56.71 to 24.61. The partition ratio of manganese between slag and metal phases is mainly related to the basicity ratio of the slag. The decrease in the basicity of the slag causes a decrease in the partition of manganese between slag and metal. Therefore it is assumed that the main factors which control the manganese distribution between slag and metal phases also contribute to the partition ratio of sulphur between slag and metal phases.

4. CONCLUSION

This study was carried out in order to investigate the sulphur behaviour in the ferromanganese smelting process. The results indicate that the transfer of sulphur from metal phase to the slag phase increases with increasing basicity ratio and CaO content of the slag system. Also the partition ratio of sulphur decreases with the increase of SiO_2 content in the slag phase. The increase of the concentration of Al_2O_3 in the slag also lowers the partition ratio of sulphur between slag and metal phases. The enhancenment of MgO content in the slag system causes an increase on the partition ratio of sulphur between slag and metal phases when the CaO/SiO_2 ratio is fixed. The results show that the sulphide capacity and silicon concentrations of the metal phase are inversely proportional to each other. The increase in the content of carbon in the metal phase will also increase the sulphide capacity of slags.

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