PHOSPHIDE AND SULPHIDE CAPACITIES OF FERROMANGANESE SMELTING SLAGS

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ABSTRACT

This study consists of experimental measurements of the phosphide and sulphide capacities of MnO-CaO-SiO_2-MgO-Al_2O_3-CaS-Ca_3P_2 *slags. The measurements of phosphide and sulphide capacities of the ferromanganese smelting slag system was carried out by equilibrating slags with the* Fe-Mn-Si-C_{sat}-S-P *alloys at 1773 K in graphite crucibles under carbon monoxide atmosphere. The experimental results indicated that CaO and* SiO_2 *are the main influencing parameters for controlling the phosphide and sulphide capacities of slag system. Thermodynamic models were developed by using the linear relations among the logarithm of sulphide, phosphide capacities of slags and the binding energy of* O^{-2} *ion in above mentioned slag system.*

INTRODUCTION

A major problem in ferromanganese production is the quality of raw materials. It is a key issue which impacts the sulphur and phosphorus behaviour in ferromanganese smelting. Ferroalloys with low sulphur and phosphorus contents are required in the production of high quality steel.

Most of the phosphorus tends to transfer to metal phase during the smelting process of ferromanganese due to the very reducing atmosphere and high temperatures which exist in the smelting furnace. Mineral processing techniques have had limited success reducing the phosphorus content of manganese ores due to technical and economical obstacles [1, 2].

Sulphur mostly enters ferromanganese production from the carbon based reducing agents such as anthracite, coal and metallurgical coke. The sulphur content of metallurgical grade cokes might vary between 0.5 to 1.5 percent [3, 4]. Generally the smelting conditions in ferromanganese production favours the transfer of sulphur from metal to slag phase.

In this study a further extension of previous study [5] is conducted for. understanding the main factors that influence phosphide and sulphide capacities of ferromanganese smelting slags and to develop simple models for the prediction of these capacities for the ferromanganese smelting slag system. Such models can be used as an important tool for optimization of the slag chemistry, maximizing phosphorus and sulphur transfer from metal to slag.

The Concept of Phosphide Capacity

The ability of a slag to contain phosphorus is expressed by phosphate or phosphide capacity as phosphorus can be in either $PO4^{-3}$ or P^{-3} form in slags depending on the existing oxygen partial pressure and temperature. Slag chemistry can also play a part, and for high chromium and manganese steels, due to the oxidation states of these alloying elements (Mn,Cr) in the slag, dephosphorization can be achieved by forming Ca_3P_2 in the slag. [6]

The thermodynamic behaviour of phosphide in $CaO\text{-}CaF_2$ melts under low partial pressures of oxygen has been investigated in a previous study [7]. Their results show that the phosphide capacity for the melt increased with increasing CaO concentration and was constant after about 20 mass percentage of CaO. By increasing the temperature from 1673 K to 1823 K, the critical partial pressure of oxygen which defined the stability regions of phosphate and phosphide in $CaO\text{-}CaF_2$ system increased from 1.4×10^{-18} to 1.1×10^{-16} atm.

The phosphide capacity values can be determined by measuring by the phosphorus content of the slag and metal phases under controlled partial pressure of oxygen, with replacement of partial pressure of phosphorus in the gas by phosphorus activity in the of metal.

The reaction between phosphorus and oxygen in metal and slag phases can be expressed as reaction (1).

$$[P]+\frac{3}{2}\left(O^{-2}\right)\Leftrightarrow\left(P^{-3}\right)+\frac{3}{4}\{O_2\} \qquad (1)$$

where [ ], ( ) and { } shows a species in metal, slag and gas phases, respectively. By using equation 2, phosphide capacity (C_p) can be defined as follows:

$$C_P = \frac{(P^{-3}).\,P_{O_2}^{\;3/4}}{[P].\,f_P} \qquad (2)$$

where (P^{-3}) and [P] are the weight percentages of phosphide in the slag and the weight percentage of phosphorus in the metal respectively; f_P is the activity coefficient of phosphorus in manganese for 1 weight percentage standard state; P_{O_2} is the partial pressure of oxygen.

The Sulphide Capacity Concept

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 [8]. Sulphur can be stable either as SO_4^{-2} or S^{-2} species in slags depending on the existing oxygen partial pressures. CaS is the stable species when the partial pressure of oxygen is less than 10^{-5} atm at 1773 K in calcium-alumina-silicate melts [9]. Fincham and Richardson show that the sulphur can exist 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. [10, 11].The partial pressures of oxygen in the ferromanganese smelting process is far below then this value, so it can be presumed that the sulphur is stable in ferromanganese slags as a sulphide.

The equilibrium of sulphur between metal and slag phases can be expressed as follows. [12]

$$[S] + \left(O^{-2}\right) \Leftrightarrow (S^{-2}) + \frac{1}{2}\{O_2\} \tag{3}$$

The equilibrium constant for reaction (3) is given by

$$K_3 = \frac{(a_{s^{-2}}).(P_{o_2})^{1/2}}{[a_s].(a_{o^{-2}})} = \frac{(f_{s^{-2}}).(S^{-2}).(P_{O_2})^{1/2}}{[f_s].[S].(a_{o^{-2}})} \tag{4}$$

By using Equations 3 and 4, the sulphide capacity (C_s) can be defined as follows:

$$C_s = \frac{K_3.(a_{o^{-2}})}{(f_{s^{-2}})} = \frac{(S^{-2}).(P_{o_2})^{1/2}}{[f_s][S]} \tag{5}$$

where a_S^{-2}, P_{S_2}, f_S^{-2}, f_S represent activity of sulphide in the slag, partial pressures of sulphur, sulphide ion activity coefficient in the slag at 1 weight percentage standard state, activity coefficient of sulphur in manganese for 1 weight percentage standard state respectively.

Iron and manganese are chemically similar elements with similar atomic sizes. Fe-Mn liquid solutions at temperatures around 1773 K behave almost ideally [12] The first and second order interaction coefficients of the Mn-Fe alloy system are not needed and it was assumed the interaction coefficients of liquid iron can be used for the calculation of the activity coefficient of sulphur (fs) and phosphorus (fp) in the infinitely dilute solution of manganese. Several researchers have applied similar approaches for different alloy systems [14, 15, 16]. The interaction coefficient parameters were derived from Sigworth and Eliott, adjusted to a temperature of 1773 K. [17]

In the present study basicity of the slag system is expressed as follow:

$$Basicity = \frac{(CaO) + (MgO)}{(SiO_2)} \tag{6}$$

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

METHODOLOGY

The master slags were prepared as the homogeneous mixtures of CaO, MgO, Al_2O_3, SiO_2 and $Ca_3(PO_4)_2$ powders (Laboratory reagent grade) which were dried at 125°C for 24 hours. The required amounts of the slag components were weighed and mixed in the agate mortar under acetone. The dried mixtures were pressed into pellet forms and sintered at 1100ºC for 36 hours for achieving a homogeneous slag phase formation. The sintered slag pellets were ground and mixed with MnO powder to have the required compositions.

Ferromanganese alloys were prepared from powders of electrolytically pure Fe, Mn, Si and spectrographic grade graphite. Chemically pure grade of FeS was used for addition of an equivalent amount of sulphur into the alloy. The required amounts of the metal components were dried, weighed and mixed homogeneously in the agate mortar. The reactants consisting of 6 g alloy and 6 g slag were placed at the bottom of the graphite crucible.

According to previous studies, a reaction time of 18 hours was sufficient to attain equilibrium [18, 19]. Blank experiments with graphite powder were conducted periodically for checking for oxygen leaks into the furnace tube the mass loss of graphite powder was negligible. Hence atmosphere was maintained thoughout this study.

The reaction tube was flushed with argon for 30 minutes after to placing the cruciblein the cold zone of the furnace tube. After slowly lowering into the hot zone, CO was introduced into the furnace tube at 200 cc /min. The Ar was purified by flowing through a deoxidizing furnace containing Cu-chips at 500ºC, and the carbon monoxide gas was dried by passing it through magnesium perchlorate and silica gel. The experiments were conducted under carbon monoxide atmosphere and the oxygen potential was controlled by C-CO equilibrium where the activity of carbon was unity due to graphite crucible. The partial pressure of carbon monoxide was taken as 0.83 atm.; equal to the atmospheric pressure in Johannesburg. The oxygen partial pressure was determined as 1.21 x 10^{-16} atm. at 1773 K according to reaction (7) and its standard free energy change given in Equation 8.

$$C_{(Solid)} + \frac{1}{2}O_{2\ (gas)} \Leftrightarrow CO_{(gas)} \tag{7}$$

$$\Delta G^{o} = -112877 - 86.514T \text{ (J/mol) [7]} \tag{8}$$

The graphite crucibles containing the equilibrated slag and alloy were taken to the cold end of the reaction tube, removed from the furnace and quenched in water after 18 hours reaction. After quenching, the crucible contents were carefully separated which were then grounded into the powder form for chemical analysis. The alloy was analyzed first by ICP for Fe, Mn , Si and P contents and then by LECO analyzer for C and S content. The slags was analyzed by ICP for MgO, CaO, SiO_2 , MnO, Al_2O_3 , FeO and P contents, and sulphur was determined by LECO analyzer.

RESULTS AND DISCUSSION

Table 1 and 2 list the mass percentages of SiO_2, Al_2O_3, CaO, MgO, CaS, Ca_3P_2 and MnO in the slag, and Fe, C, Mn, Si, S and P in the metal phase from the equilibration experiments, respectively. The calculation of slag compositions assumed that the molecular species which contains the P^{-3} and S^{-2} ions are Ca_3P_2 and CaS, respectively due to the lower formation free energy of Ca_3P_2 and CaS compared to the other phosphides and sulphides [20, 21]. The calculated logarithm of phosphide and sulphide capacity are represented in Table 1. E_o (the binding energy of O^{-2} ion in the mixture) values for the slags were calculated from the available data in a previous study [22].

Table 1: Slag phase compositions in mass percentage

Experiment Code	SiO_2	Al_2O_3	MgO	MnO	CaO	Ca_3P_2	CaS	E_o	Log Cp	Log Cs
1	45.92	6.50	11.60	14.80	18.16	0.003	1.599	5521.35	-14.624	-8.112
2	41.61	9.14	18.70	4.42	22.34	0.012	2.382	5374.46	-14.177	-7.920
3	38.44	6.64	13.20	3.00	34.84	0.029	2.362	5254.80	-13.486	-7.427
4	38.47	6.50	15.00	3.02	33.40	0.003	2.196	5248.09	-13.761	-7.520
5	44.48	7.54	19.30	9.22	16.42	0.003	1.811	5450.62	-14.715	-8.064
6	37.13	7.95	8.34	1.73	40.88	0.015	2.513	5229.79	-13.437	-7.554
7	43.25	5.86	13.20	17.90	17.29	0.003	0.956	5443.66	-14.598	-8.048
8	44.04	5.78	13.10	17.40	16.53	0.006	1.908	5472.38	-14.212	-8.028
9	40.66	5.83	14.60	6.88	29.20	0.018	1.710	5315.78	-13.744	-7.877
10	43.06	5.69	10.30	13.40	24.21	0.003	1.872	5430.32	-14.237	-7.863
11	42.49	5.86	15.80	10.10	22.81	0.009	1.753	5385.68	-14.112	-7.741
12	42.43	6.15	16.40	8.07	23.61	0.021	1.984	5380.38	-14.145	-7.750
13	44.68	7.31	18.40	8.22	18.32	0.012	1.685	5451.32	-14.326	-8.022
14	39.20	6.35	13.40	4.78	32.84	0.012	2.133	5277.49	-14.005	-7.666
15	39.92	6.27	13.20	4.44	32.61	0.015	2.149	5298.60	-13.923	-7.702
16	41.67	6.58	15.10	6.93	25.90	0.015	2.531	5366.99	-14.222	-7.903

Table 2: Metal phase compositions in mass percentage

Experiment Code	*Mn*	*Si*	*Fe*	*C*	*P*	*S*
1	66.1	11.2	18.6	3.309	0.016	0.038
2	75.9	12.9	6.55	3.273	0.017	0.024
3	70.7	6.29	17.7	5.258	0.017	0.017
4	68.6	7.41	18.5	4.72	0.003	0.019
5	65.9	12.2	18.2	3.01	0.018	0.034
6	66.7	10.4	18.5	3.943	0.005	0.016
7	79.4	7.25	7.51	4.6	0.022	0.030
8	72.3	8.29	13.1	4.99	0.013	0.039
9	68.8	4.18	18.4	6.48	0.02	0.030
10	74.4	6.42	13.4	5.03	0.01	0.038
11	73.7	6.38	14.5	4.84	0.024	0.030
12	68.1	7.76	18.9	4.72	0.047	0.027
13	65.6	12.3	18.5	2.88	0.03	0.029
14	81	4.29	7.34	6.31	0.025	0.025
15	74.2	5.39	13.6	6.06	0.022	0.024
16	79.1	7.49	7.11	5.16	0.037	0.043

The Change of Phosphide and Sulphide Capacities with Basicity

According to the results higher phosphide and sulphide capacities can be achieved when the slags have high basicity. The variation of the logarithm phosphide capacity with basicity, at 1773 K under carbon monoxide atmosphere where the partial pressure of oxygen is around 1.22×10^{-16} atm., can be seen in Figure 1. The logarithm of C_p increased from -14.624 to -13.437 when the slag basicity increased from 0.648 to 1.325. The similar influence of basicity on the phosphide capacities values of ferromanganese smelting slags was reported in a recent study [16].

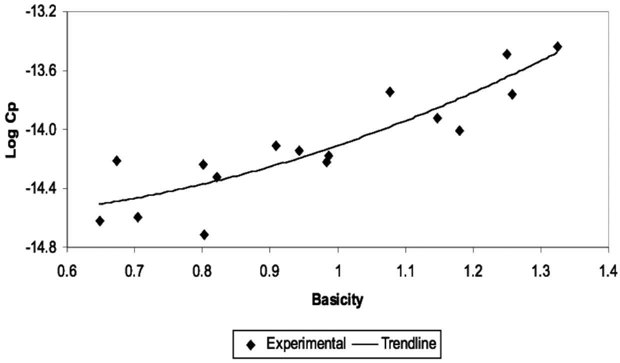

Figure 1: The effect of basicity on the phosphide capacity of slag at 1773 K

Figure 2 shows that the sulphide capacity for the slag system as a function of slag basicity at 1773 K under carbon monoxide atmosphere. When basicity increased from 0.648 to 1.325, the logarithm of C_s increased sharply from -8.112 to -7.554.

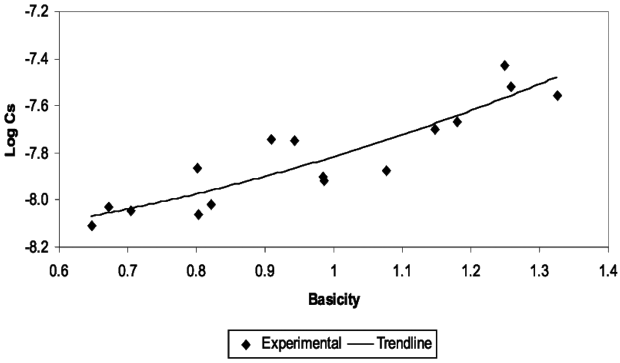

Figure 2: The effect of basicity on the sulphide capacity of slag at 1773 K

The strong affect of basicity on the phosphide and sulphide capacities values can be explained by the modern slag theory. Almost 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 at low basicity. The increase of network modifying oxides which can be classified as basic oxides cause a breakdown in the three dimensional network of silica structure. A decrease in the acidity of slag will cause an increase in the concentration of free O^{-2} ions helping the reactions (1) and (3) to proceed to the right [23].

The Change of Phosphide and Sulphide Capacities with CaO

The amount of CaO in the ferromanganese smelting slags is the one main factor which determines the transfer of phosphorus and sulphur from the metal to slag by forming Ca_3P_2 or CaS in the slag phase. Figure 3 and 4 show that the affect of CaO content of the slag system on the phosphide and sulphide capacities, respectively.

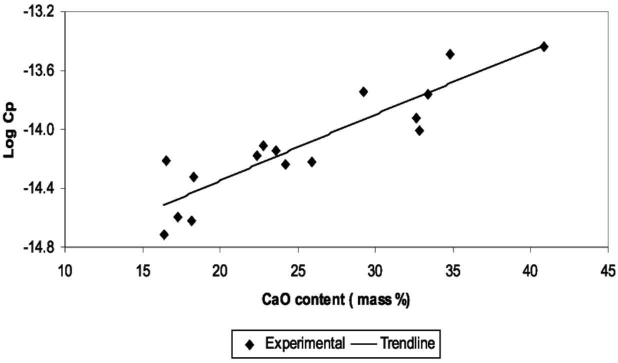

Figure 3: The effect of CaO content on the phosphide capacity of slag at 1773 K

As basic oxides are added to pure silica, the network structure (initially containing all bridging oxygens; n_{O^0}) is broken down, initially forming various mixtures of silicate polymers (terminating with non-bridging oxygen ions; n_{O^-}) which , which decrease in chain length as more basic oxide is added. The concept assumes that there is equilibrium between the various polymers and free O^{-2} ions are also present in the slag. With further base addition, at a certain composition, most of the silicate polymers may have broken down to SiO_4^{-4} anions with the number of free oxygen ions (0^{-2}) close to zero. Addition of further basic oxides then increases the number of free oxygen ions($n_{O^{-2}}$). Sulphur and phosphorus increase in concentration in the slag as they probably interact strongly with the basic cation, and decrease the effective concentration of free oxygen ions in the slag.

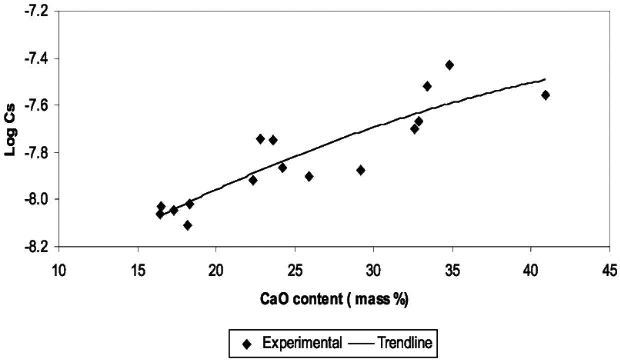

Figure 4: The effect of CaO content on the sulphide capacity of slag at 1773 K

The Change of Phosphide and Sulphide Capacities with MnO

MnO content of the slag system is another critical factor on the sulphide and phosphide capacities of the ferromanganese smelting slags. Figure 5 and 6 illustrate the affect of MnO content on the phosphide and sulphide capacities of the slag system when the basicity kept in certain ranges.

In Figure 5 the basicities are kept in certain ranges and the experimentally determined log C_p values are plotted as functions of MnO content at 1773 K. The results show that the increase in MnO content of the slag system causes higher phosphide capacities. Since the phosphide capacities increase with with increasing a_O^{-2} or basicity of the slag, the basic oxide nature of MnO will improve the dephosphorisation capacity of the slag.

As can be seen in Figure 6, MnO has a positive impact on the sulphide capacity of the slag system. This can be explained on the basis of high affinity of MnO to sulphur in the slag. Nilsson *et al.* [24] applied a mathematical model for the estimation of sulphide capacities. The calculations and experimental data show that MnO-SiO_2 (Cs=-2.75 at X MnO =0.5, T=1773 K) system has higher sulphide capacity value compared to CaO-SiO_2 (Cs=-4 at X CaO =0.5, T=1773 K) and CaO-Al_2O_3 (Cs=-3.75 at X Al_2O_3 =0.5, T=1773 K) systems. When MnO replaced CaO in CaO-SiO_2-MnO slag system, the results show that the higher MnO content slag has significantly higher slag capacity. This can be explained on the basis of high affinity of MnO to sulphur in the slag. Also an increase in the activity of MnO in the slag as will increase the basicity of slag system and resulting a higher sulphur power of slag. It is also known that the reaction of mangnase orthosilicate has the lowest Gibbs energy change compared to calcium and manganese orthosilicate therefore the formation of 2 MnO.SiO_2 should be supported. This approach can be extended to metasilicates formation cases. [25]

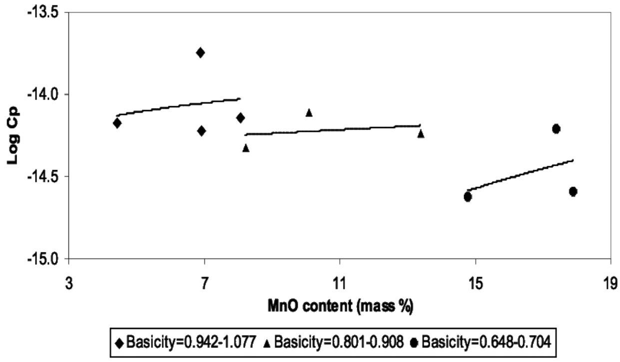

Figure 5: The effect of MnO content on the phosphide capacity of slag at 1773 K

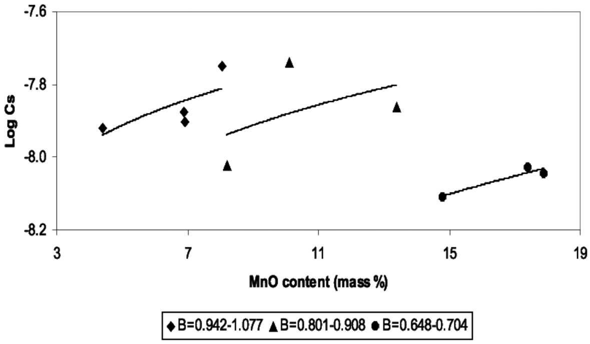

Figure 6: The effect of MnO content on the phosphide capacity of slag at 1773 K

The Change of Phosphide and Sulphide Capacities with MgO

Figure 7 and 8 show that the affect of MgO content on the phosphide and sulphide capacities of ferromanganese slags when the ratio of CaO/SiO_2 kept between certain ranges. Figure 7 and 8 show that an increase in the MgO content will improve the phosphide and sulphide capacities of the ferromanganese smelting slags. 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. 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 [20].

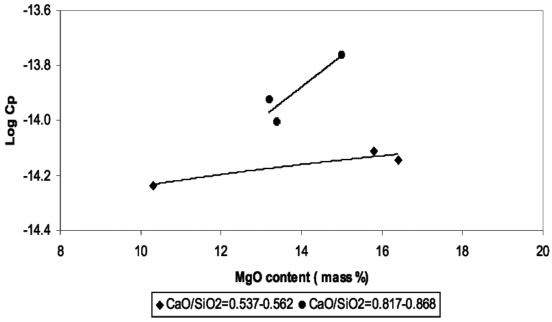

Figure 7: The effect of MgO content on the phosphide capacity of slag at 1773 K

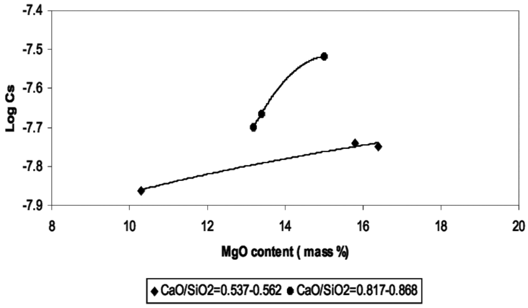

Figure 8: The effect of MgO content on the sulphide capacity of slag at 1773 K

Relation between Lattice Energy and Phosphide and Sulphide Capacity

Ichise and Moro-Oka evaluated the interaction energy between anion and cation of an oxide from the lattice energy of the oxide by applying the Born-Haber cycle to the thermal data and ionization energy of elements. In this model, it is also assumed that no rigid combinations have been occurred between cations and anions. The interaction energy of an oxide anion is determined. The binding energy of O^{-2} ion in the mixture is expressed in terms of lattice energy per mole of O^{-2} of an oxide mixture and related to the sulphide capacity. It was found that the logarithmic value of the activity coefficient of oxide anion in slag ($\gamma_{O^{-2}}$) has a linear relation with the averaged lattice energy obtained from the lattice energy of the component oxides(E_o). Their results show that the lattice energy per mole of O^{-2} ion of an oxide mixture (E_o) which is another way for expressing the binding energy of O^{-2} ion in the mixture, has a linear relationship with the logarithmic sulphide capacities in CaO-MgO-Al_2O_3, CaO-MgO-SiO_2, CaO-Al_2O_3-SiO_2, CaO-MgO, Al_2O_3-SiO_2 slags at 1773 K [22].

A similar approach was applied to this study to investigate the relation between binding energy of O^{-2} ion in the mixture and phosphide and sulphide capacities. Equations 11 and 12 can be used for the prediction of phosphide and sulphide capacities of the ferromanganese smelting slags. Figure 9 and 10 show linear relationships between E_0 values of the slags and phosphide, sulphide capacities of the slags.

$$LogCp = -0.00374E_o + 5.972345 \tag{10}$$

for which R^2 (correlation coefficient) = 0.801

$$LogCs = -0.00214E_o + 3.684051 \tag{11}$$

for which R^2 (correlation coefficient) = 0.830

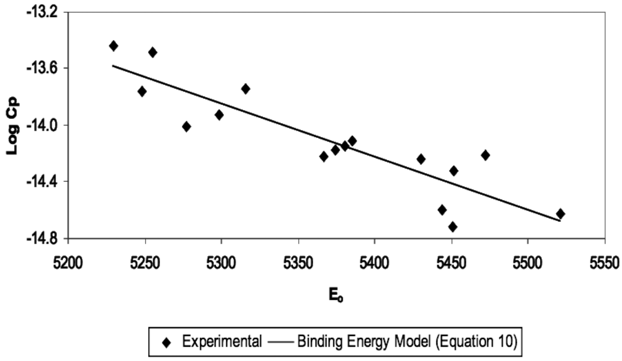

Figure 9: The relationship between E_o and phosphide capacity of slag at 1773 K

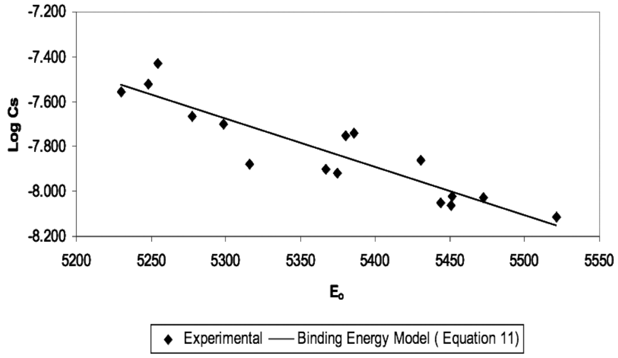

Figure 10: The relationship between E_o and sulphide capacity of slag at 1773 K

The high correlation coefficients showing that if the slag compositions fall within the range as given in this study, these models can be confidently used to determine the phosphide and sulphide capacity for slags at 1773 K under carbon monoxide atmosphere.

CONCLUSIONS

The study was carried out to determine the sulphide and phosphide capacities of ferromanganese smelting slags. The results show that the transfer of sulphur and phosphorus from metal phase to the slag phase increases with increasing basicity and CaO content of slags. The positive influence of MnO content on sulphide and phosphide capacities of the slags are seen when basicity is keep in a narrow range. The enhancenment of MgO content in the slag system causes an increase on the phoshide and sulphide capacities when the CaO/SiO_2 ratio is keep in a certain range. Two linear relationship model derived by using binding energy O^{-2} ion in the mixture. These simple models which are combination of regression and thermodynamic approaches can be used in industrial ferromanganese smelting operations. But it should be kept in the mind that these models were obtained under equilibrium conditions which may not be entirely representative of the actual industrial conditions.

ACKNOWLEDGEMENTS

The authors wish to acknowledge Ferro Alloy Producers Association, for providing the financial assistance for this study.

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