

SULPHIDE AND PHOSPHIDE CAPACITIES OF FERROALLOY SMELTING SLAGS

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requirements for the degree of Doctor of Philosophy**

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DECLARATION

I declare that this thesis is my own, unaided work. It is being submitted for the Degree of Doctor of Philosophy in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.



(Signature of Candidate)

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ABSTRACT

In this study, the factors affecting sulphur distribution (L_s), phosphorus distribution (L_p), sulphide capacity ($C_{S^{-2}}$) and phosphide capacity ($C_{P^{-3}}$) of ferrochromium smelting slags were investigated under reducing conditions at 1600 °C. Also, sulphur distribution (L_s) and sulphide capacity ($C_{S^{-2}}$) of ferromanganese smelting slags were studied under reducing conditions at 1500 °C.

The results showed that the logarithms of sulphide capacities varied between -7.67 to -9.28 and the logarithms of phosphide capacities were between -15.20 and -12.69 for ferrochromium smelting slags. On the other hand the logarithms of sulphide capacities of ferromanganese slags were found to be change between -7.63 and -8.11.

The experimental results indicated that CaO, SiO₂, MgO and basicity ratio of the slags were the main factors affecting phosphide and sulphide capacities of ferroalloy smelting slags.

According to the results, the transfer of sulphur and phosphorus from metal to slag phase increases with increase in the basicity ratio, calcium oxide and magnesium oxide content of ferroalloys smelting slags. Also, it was found that sulphide and phosphide capacities of ferroalloys smelting slags tend to decrease with increasing concentration of silica in the slag phase.

Structural models based on binding energy of O⁻² ions in the slag systems were developed by using the linear relations among the logarithm of sulphide and phosphide capacities of slags. In addition to these models, easy to use quadratic multivariable regression model equations were developed in order to express sulphide and phosphide capacities of the ferroalloy smelting slags and sulphur and phosphorus partition ratios between slag and metal phases. These simple models which are combination of regression and thermodynamic approaches can be used in industrial ferrochromium and ferromanganese smelting operations. The usage of these models can help ferroalloy smelting process engineers to predict sulphide and phosphide capacities of the relevant slag systems.

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1 INTRODUCTION AND BACKGROUND MOTIVATION

Ferrochromium and ferromanganese are two of the most important ferroalloys which are widely used in the metallurgical industries to produce stainless steel and high quality alloy steels with improved physical and chemical properties.

There are various impurity elements which already exist in the ferroalloy materials. Sulphur and phosphorus can be considered as two critical impurity elements in ferroalloys.

The global competitive steel market forces steel producers to be more responsive to customer demands such as quality, price and delivery times. Steel manufacturing is challenged with high fixed costs as well as expensive and complicated production methods, which are forced to high production rates by efficiencies and economics (Manning and Fruehan, 2001).

The development of steel products in the iron and steel making industry has a significant influence on ferroalloy specifications. Nakamura (1995) mentioned the direct relationship between ferroalloy and steel qualities. The high purity raw materials demand from the steel industry leads to an increase in purity, homogeneity, shape and size distribution of ferroalloys used in the production of quality steel (Dippenaar, 2004).

The elements having the worst influences on steels are phosphorus and sulphur. It is essential to keep sulphur content extremely low in several grades of steel such as X60, X70 and X80 (oil and gas pipeline steel group). There are no means of removing sulphur subsequent to vacuum degassing; any sulphur contamination introduced through ferroalloy additions will lead to a sharp decrease in the fracture toughness of steels (Dippenaar, 2004). For steels used in the production of offshore structures, it is essential to use manganese based ferroalloys with low carbon and phosphorus. Otherwise, the steel cannot fulfil the low temperature toughness requirements in these applications. The concentration of phosphorus

must be less than 0.005 in weight per cent (wt. %) for these applications. The application of a hot metal pre treatment and the dephosphorisation refinement at the converter are not enough to reduce levels of phosphorus. It is more important to minimize the input of phosphorus from the ferroalloy side (Nakamura, 1995). A modern production method of quality steel is to remove silicon, phosphorus and sulphur in the hot metal prior to refining the steel and to add alloying elements late in the secondary operations. With this route of manufacturing cleaner steel, the leading issue is to use higher grade ferroalloys with lower contamination of sulphur, phosphorus, nitrogen, oxygen and hydrogen.

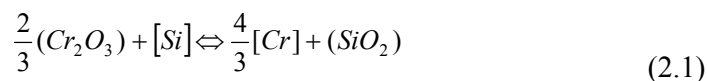
As a result, a solid understanding of the behaviour of sulphur and phosphorus during the smelting of ferroalloys has become an important issue for producing quality steel without increasing the cost. Furthermore, there has been great effort to understand the thermodynamic features of slag-metal systems related to ferroalloy production. However, experimental and theoretical data from existing literature are still insufficient for the slag systems representing the wide range of compositions in the production of ferroalloys. The scope of this research project is to understand the factors that affect sulphide and phosphide capacities of ferroalloys, specifically sulphide and phosphide capacities for ferrochromium and sulphide capacity for ferromanganese smelting slags.

2 LITERATURE REVIEW

A detailed review of relevant studies that have been conducted on slag-metal equilibrium pertinent to ferrochromium and ferromanganese smelting as well as sulphur and phosphorus behaviours in these operations are presented in this chapter. Additionally, previous theoretical and experimental studies on the thermodynamics of phosphorus and sulphur in slag systems with respect to the concept of capacities are reviewed as a part of this chapter.

2.1 Slag-Metal Equilibrium Studies Pertinent to Ferrochromium

Elyutin (1961) defined the optimum operation conditions for the production of ferrochromium. It was concluded that slag must have a liquidus temperature 100°C higher than alloy. High MgO to CaO ratio and low Al₂O₃ contents are the key factors to match with low viscosity requirements of a slag which may contain 45 to 50 wt. % of SiO₂. During the production of ferrochromium, the silica can be partly reduced by the iron and chromium. The reduction of SiO₂ and Cr₂O₃ proceed in parallel and the product of this reaction, silicon can take place in the further reduction of chromium oxides as shown in reaction (2.1).



Furthermore, the phosphorus of the charge is partially carried away with the off-gases, but some remains in the slag and the largest part (60 %) moved into the alloy. Due to the poor desulphurisation capacity of high carbon ferrochromium smelting slags, sulphur in the system is partly moved into alloy and the rest of the sulphur is carried away from the furnace as off-gas. Also sulphur and phosphorus mainly originate from the reducing materials such as coke, coal or char used in the production of ferroalloy (Elyutin, 1961).

Nafziger (1983) investigated high carbon ferrochromium smelting by using chromite concentrates. It was reported that the silicon concentration in the metal varied inversely with the amount of sulphur in the metal. In another study, Nafziger (1988) claimed that the sulphur can be removed as a volatile silicon sulphide gas at higher levels of silicon (4-5 wt. %) in the metal. However, the alloy's phosphorus levels (0.12-0.19 wt. %) were significantly higher than the requirements of ASTM standards. The chromite concentrate was found to be the one of the main sources of phosphorus. The amount of phosphorus was in the range of 0.04-0.08 wt. % in the chromite concentrate. However, quartz was found to contain up to 0.24 wt. % phosphorus and assumed as another major source of phosphorus for ferrochromium alloy. According to the results, 60-80 % of initial phosphorus can be transferred into alloy phase (Nafziger, 1988). Nafziger indicated that to have a highly basic slag in the system with the low bath temperatures can limit the phosphorus transfer from the slag to metal phase. The optimum slag liquidus temperature was found to be in the range of 1550-1575°C. Also, a nominal slag basicity value of 1.04 was determined as optimum slag basicity in order to achieve high carbon ferrochromium smelting. The optimum physicochemical properties of slag such as low liquidus temperature, basicity and fluidity were achieved by the addition of CaO and SiO₂ into smelting process (Nafziger, 1983).

Akyuzlu and Eric (1992) conducted a study on the equilibrium between carbon-saturated Fe-Cr-Si-C alloys and SiO₂-CaO-MgO-Al₂O₃-CrO_x-FeO_y slags under argon and carbon monoxide atmospheres at temperatures of 1500°C and 1600°C. The silica reduction can be explained by using reaction 2.2, where the quantities in the round, square and parenthesis brackets refer to the slag, metal and gas phases, respectively. In the Eq. (2.3); K, a_i and P_i represent the equilibrium constant, activity of the species and the partial pressure, respectively.



$$K_{2.2} = \frac{a_{Si} \cdot P_{CO}^2}{a_{SiO_2} a_C^2} \quad (2.3)$$

The carbon and silicon solubilities in metal phase tend to increase with temperature. The silicon content in the metal phase was found to be directly proportional to the silica content of the slag phase at 1 600°C. This can be a result of increase in $K_{2.2}$. As the temperature increases, reaction moves to right direction. When CaO to Al_2O_3 ratio of the slag increased, the level of silicon in the slag showed a decline due to replacement of alumina by lime which caused a decrease in the activity of silica in the slag phase. With the network modification power of CaO in the slag, the silica network will break down and results an increase in the free oxygen ions which eventually leads to a decrease in the silica activity. According to the results, an increase in the MgO to CaO ratio of the slag causes a decrease in the silicon distribution (partition) ratio (wt. % of Si in the slag / wt. % Si of in the metal). This indicated that the replacement of MgO with CaO causes an increase in the activity of silica which results an increase in the silicon content of the metal phase. Furthermore, experimental results showed that the chromium content of the slag increased with the increase of iron content of the metal phase. On the other hand, at low basicity values, the chromium content of the slag phase decreased sharply as the basicity increased from 0.4 to 0.8 at 1 500°C under argon and carbon monoxide atmospheres, and from 0.7 to 1.0 at 1 600°C under carbon monoxide atmosphere. When the threshold values had been passed, the basicity did not influence the chromium solubility in the slag system which reached to a constant value around 0.15 wt. %. At relatively low oxygen potentials the chromium dissolves in the silicate melts as divalent and trivalent ratio, the concentration ratio $Cr^{+2}:Cr^{+3}$ being dependent on temperature and slag basicity. As the basicity increases the dissolving power of the slag with respect to Cr^{+2} ions decreases which proves that the depolymerisation of the melt with increasing basicity resulting in an increase in oxygen ion activity. Therefore, we can conclude that the chromous capacity (is the concentration of Cr in the slag assumed to be Cr^{+2}) of the slag decreases as the basicity increases. Also, the chromic capacity (is the concentration of Cr in the slag assumed to be Cr^{+3}) of the

slag reduces as the basicity increases. In other words, the slags low in SiO_2 (high basicity slags) can dissolve less chromium. (Akyuzlu and Eric, 1992).

As a summary, the previous studies showed that physicochemical properties of slag such as low liquidus temperature, basicity and fluidity are the critical factors in the control of phosphorus, sulphur and chromium distribution between slag and alloy phases.

2.2 Slag-Metal Equilibrium Studies Pertinent to Ferromanganese

High-carbon ferromanganese is most commonly used raw material in iron and steel making. In recent years majority of high carbon ferromanganese has been produced in submerged electric arc furnaces. Easy and flexible operation conditions with less coke requirements are the main advantages of the production of high carbon ferromanganese in submerged arc furnaces.

Typical high-carbon ferromanganese alloys contain from 74 to 82 wt. % Mn, 6 to 8 wt. % C, not more than 1.25 wt. % Si with the remain being iron. Sulphur should be less than 0.05 wt. % and phosphorus must be less than 0.35 wt. % in the final product (Duke, 1979).

The amount of phosphorus in the final product is significantly influenced by Mn:P ratio of manganese ore. In order to achieve low phosphorus content in the final ferromanganese product, it is essential to start the production with low phosphorus content raw materials (Tangstad et al., 2004).

Olsen et al. (1995) determined the distribution equilibria in the synthetic slag system of $\text{MnO-SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO}$ and the industrial ferromanganese slags were equilibrated with Mn-Fe-Si- C_{sat} alloys. $\text{CaO/Al}_2\text{O}_3$ ratio of the synthetic slag was 1.5 and the $\text{MgO/Al}_2\text{O}_3$ ratio was around 0.8 in this study. The carbon saturated metal with a low silicon content (<1 wt. %) and 10-14 wt. % Fe were used in the experiments. Process temperature and slag basicity are found as main parameters for determining the equilibrium content of MnO in the slag. When the

process temperature was increased from 1350 to 1400 °C, MnO content of the slag tend to reduce from 40 to 33.5 wt. %. Also, MnO content of the slag was found to be reduced from 40 to 30 wt. % by increasing the basicity of the slag ($\text{CaO}+\text{MgO} / \text{SiO}_2$) from 0.75 to 1 at 1350 °C.

Kucukkaragoz and Eric (1998) investigated the equilibria between refined ferromanganese/silicomanganese alloys and silicate slags. The partition ratio of silicon between slag and metal was found to increase by increasing the slag basicity ($\text{CaO}+\text{MgO}/\text{SiO}_2$). In addition to that the partition ratio of manganese between slag and metal showed a decreasing trend with the increase of slag's basicity. A high portion of initial sulphur was transferred to the slag phase by increasing the basicity value over 1.5. CaO present in the slag was probably the main component in transferring sulphur to the slag phase as CaS.

Cengizler (1993) measured the thermodynamic activity of MnO in MnO-CaO-MgO-SiO₂-Al₂O₃ slags pertinent to ferromanganese and silicomanganese production. In the first stage of this study, the activities of Mn in the Pt-Mn alloys at 1300, 1400 and 1500 °C were determined. In addition to that, MnO activities were determined by equilibrating slags of various compositions with Pt-Mn alloys under controlled partial pressure of oxygen in Mn saturated platinum crucibles at 1500 °C. It was found that activities of MnO were increased with increasing basicity and CaO-to-MgO ratio. Also, manganese and silicon distribution between carbon-saturated Mn-Si-Fe-C alloys and MnO- CaO-MgO-SiO₂-Al₂O₃ slags were investigated under one atmosphere of CO gas pressure at 1500 °C. It was found the manganese distribution ratio ($(\text{Mn})/[\text{Mn}]$) increased with increasing the silica content of the slag and and decreasing basicity and CaO-to-Al₂O₃ ratio.

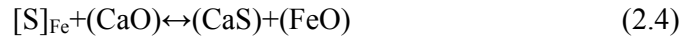
2.3 Slag-Metal Equilibrium Studies Pertinent to Sulphur Behaviour

In this section, slag-metal equilibrium studies pertinent to the behaviour of sulphur in iron, steel, ferrochromium, ferromanganese production will be reviewed. The sulphide capacity concept and previous studies in these fields will also be given.

2.3.1 Behaviour of sulphur in iron and steel making

Sulphur is an undesirable element in steel. During the solidification process of steel, the dissolved sulphur can precipitate and leads to a significant drop in the mechanical properties of the steel (Fischer and Schwerdtfeger, 1977).

Biswas (1981) described the sulphur is transferred from metal to slag in the blast furnace by using following equations (2.4,2.5,2.6,2.7 and 2.8),



The equilibrium constant for reaction 2.4 is,

$$K_{2.4} = \frac{a_{CaS} \cdot a_O}{a_{[S]} \cdot a_{CaO}} \quad (2.5)$$

The choice of the standard state can be rendered mathematically feasible because at low concentrations the weight percent of any solute (in this case sulphur) in a solution is approximately proportional to its mole fraction. In such case, we can redefine the equilibrium constant $K_{2.4}$ (Eq. 2.5) in the form of $K_{2.4}'$ (Eq. 2.6).

$$K_{2.4}' = \frac{(wt.\%S) \cdot a_O}{[wt.\%S] \cdot f_s \cdot a_{CaO}} \quad (2.6)$$

The activity coefficient of sulphur (γ_s) has to be used for the multi-component alloys. The alloying elements influence activity coefficients of one another. Therefore, the activity coefficient of sulphur in pig iron should be calculated by using Wagner's equation (Eq. 2.7)

$$\log \gamma'_s = \log f_s^s + \log f_s^{Si} + \log f_s^{Mn} + \log f_s^{Mn} + \log f_s^P + \log f_s^C \quad (2.7)$$

where γ_s is overall activity coefficient of sulphur in a dilute multi-component alloy at a given concentration of S; f_s^s is the activity coefficient of sulphur in Fe-S binary alloy at the same concentration; $f_s^{Si}, f_s^{Mn}, f_s^P, f_s^C$ coefficients representing the effect of the respective elements on the activity coefficient of sulphur (interaction coefficients).

The sulphur distribution ratio between slag and metal (L_s) can be defined by using Eq. 2.8, where round brackets indicates the slag and square brackets indicates the metal phase. Also, the influence of activity of CaO, oxygen potential and activity coefficient of sulphur can be presented in the same equation.

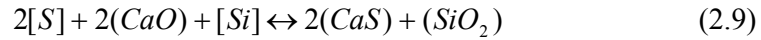
$$L_s = \frac{(S)}{[S]} \alpha K'_{2.4} \frac{a_{(CaO)}}{OxygenPotential} \gamma'_s \quad (2.8)$$

Therefore, the sulphur distribution ratio between slag and metal will be higher,

- Higher CaO content in the slag,
- Higher γ'_s ,
- Lower oxygen potential of the slag.

The equilibrium distribution ratio of sulphur between slag and metal can theoretically be as high as 400 at 1 500°C. However, this value varies between 50 and 100 for industrial applications, which indicates that the system is not in equilibrium state in the industrial smelting process (Biswas, 1981).

For industrial cases, the influence of silica should be included to the desulphurisation reaction (Rosenquist, 1983).



The equilibrium constant for reaction 2.9 can be written as follows:

$$K_{2.9} = \frac{a_{CaS}^2 \cdot a_{SiO_2}}{a_{Si} \cdot a_{CaO}^2 \cdot a_s^2} \quad (2.10)$$

According to reaction and equilibrium constant of Eq. 2.9, high silicon content metal phase can help to decrease sulphur content in steel (Rosenquist, 1983).

Sulphides are also completely miscible with silicates and show extensive solubility at high temperatures such as the solubilities of CaS in CaO.SiO₂, CaO.Al₂O₃.2SiO₂ and 2CaO.Al₂O₃.SiO₂ are 20 to 30 wt. % at 1 500°C and are almost doubled at 1 650°C (Rosenquist, 1983).

Optimisation of slag basicity is an effective method for controlling the sulphur content in pig iron. Gruzdeva et al. (1991) investigated viscosity and desulphurisation capacities of synthetic blast furnace slags. According to their results, a basicity ratio [(wt. % CaO + wt. % MgO) /wt. % SiO₂] equals to 1.23 can be considered as an ideal basicity for effective desulphurisation and the sulphur content can be lowered from 0.028 to 0.022 wt. %. From industrial practice point of view, the optimum slag composition is significantly more basic than typical blast furnace slags and the use of highly basic slags primarily can cause formation of crystals in the slag. This will ultimately results an increase in the viscosity of the slag. Ende and Wigner (1964) concluded that the distribution ratio of sulphur between slag and metal can be increased from 57 to 204 by increasing the basicity ratio [(wt. % CaO + wt. % MgO) / (wt. % Al₂O₃ + wt. % SiO₂)] from 0.9 to 1.18 in blast furnace slags.

It should be noted that blast furnace slags are quite different from steel making slags. Blast furnace slags contain no iron oxide or phosphorus but have very small amounts of iron physically entrapped in their structures.

In steel making process, the principle concern of the operator is to control the carbon, silicon, sulphur, phosphorus and manganese. Figure 2.1 shows the content of elements (Si, Mn, S, C and P) as a function of blowing time.

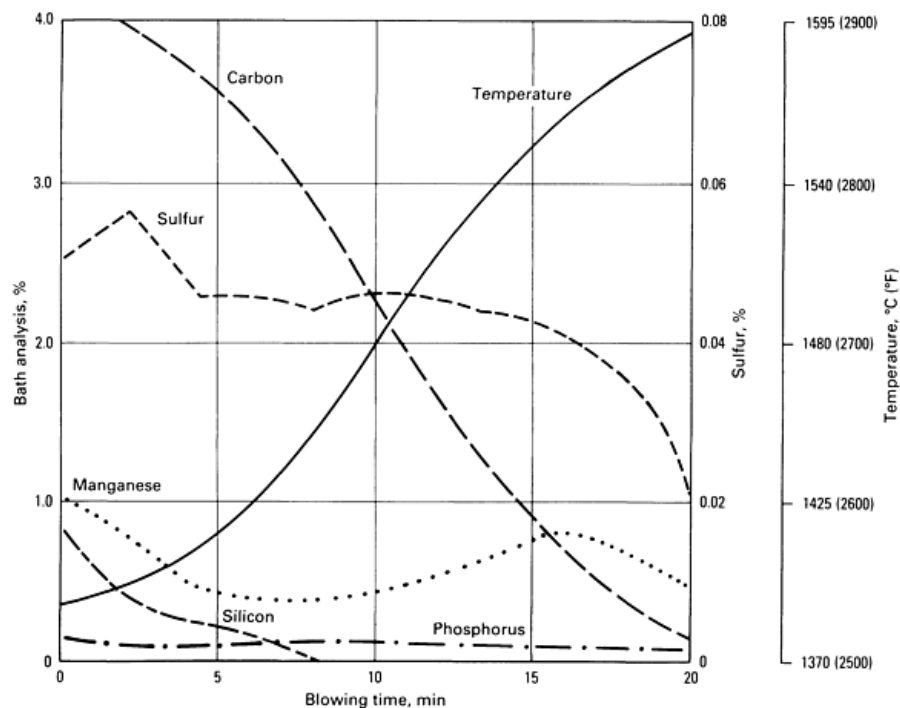


Figure 2.1 Removal of elements during a BOS blow (Guthrie and Jonas, 1990)

As in Figure 2.1, sulphur levels can drop to 0.02 wt. % after 20 minutes oxygen blow, at that time the temperature of the system almost reaches to 1425 °C.

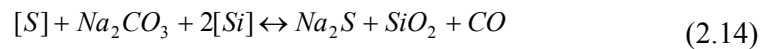
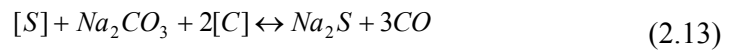
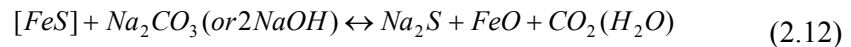
Hassall et al. (1991) investigated the removal of phosphorus and sulphur from liquid steel in the ladle with top flux and injection treatment methods. The liquid steel composition was 0.03 wt. % C, 0.2 wt. % Si, 0.4 wt. % Mn and 0.1 wt. % Al during desulphurisation. According to the results the extent of sulphur removal (R_s) (Eq. 2.11) was found to be between 0.011 and 0.224.

$$R_s = \frac{[\text{wt.\%S}]_{\text{initial}} - [\text{wt.\%S}]_{\text{final}}}{[\text{wt.\%S}]_{\text{initial}}} \quad (2.11)$$

where $[\text{wt.\%S}]_{\text{initial}}$ is the sulphur content of the liquid steel before the desulphurisation treatment and $[\text{wt.\%S}]_{\text{final}}$ is the sulphur content of liquid steel after the desulphurisation treatment.

Several studies were conducted on the desulphurisation of molten steel. The powder injection and blowing treatment are the major techniques applied in desulphurisation of molten steel. Also, the additions of soda ash, calcium carbide or calcium cyanamide have become widely used methods for desulphurisation (Young and Cripps, 1980, Rosenquist, 1983; Wei et al., 2000).

Soda ash has been used as a desulphuriser in iron and steel making practices. Sodium has a great affinity for sulphur which results sodium sulphide (Na_2S) formation (Biswas, 1981). Reaction 2.12 can be facilitated by the removal of FeO by reaction with the carbon and silicon present in the hot metal (2.13 and 2.14) (Rosenquist, 1983).



These reactions indicate that the desulphurisation can be enhanced by low oxygen potential in the melt.

Slag viscosity is another important factor which influences the desulphurisation of steel. It is important to reduce steelmaking slag's viscosity in order to enhance the sulphur transfer from metal to slag. The addition of fluorspar (CaF_2) will help to transform crusty and viscous slag to a fluid nature by lowering the slag's melting point. This addition weakens the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ bonds and results lower viscosities in the slag. In such case, the sulphur transfer from metal to slag will be enhanced. However, this mechanism leads to a significant corrosion on the refractories of the ladle.

In brief, the optimum conditions for desulphurisation in iron and steel making processes can be summarised as:

- Low oxygen potential
- High basicity slag
- Low FeO content slag
- High lime content
- High soda or other alkali oxides content
- Low operation temperature
- High carbon and silicon in metal phase
- Low viscosity slag
- Fluorspar additions
- Stirring in the bath

2.3.2 Behaviour of sulphur in ferrochromium smelting and refining

The sulphur content of ferroalloy products highly depends on the sulphur content of raw materials, slag basicity, slag viscosity, slag-metal mixing, metal composition, temperature and atmosphere conditions (Pickles et al., 1987).

As low carbon ferrochromium becomes less preferred raw material in stainless steel production, the use of high carbon ferrochromium has tremendously increased. However in the high carbon ferrochromium production process, a large

proportion of sulphur in the furnace charge ends in the alloy. On the other hand, the production method for low carbon ferrochromium results extremely low sulphur content in the alloy. The main source of sulphur is the carbonaceous reductant such as coke or charcoal in ferroalloys. The specifications for high carbon ferrochromium have restricted the sulphur content to a maximum of 0.5 wt. % sulphur in the final product (Metcalf and Slatter, 1978). Also, Dai and Shu (1995) indicated that the sulphur content in metallurgical coke can be as high as 1 wt. % in ferrochromium smelting process. According to their statistical treatment on Jilin Ferroalloy Work's (China) production data, 90 % of the total sulphur input was found to be originated from the metallurgical coke used in the production.

Halikia et al., 2001 indicated that ferrochromium producers prefer to use cokes with sulphur contents lower than 0.85 wt. %. However, the sulphur content of commercial coke and coal grades are slightly lower than 0.85 wt. %. Therefore additional mineral processing steps required to achieve such low sulphur content in coke. The sulphur contents of some reductants are given in Table 2.1.

Table 2.1 The average sulphur content of some carbonaceous based reductants.

Reductant	Sulphur (wt. %)
Peak Downs Coal	0.58
Jewell Coal	0.86
Sewell Stroker Coal	0.75
Wawel Coal	0.68
Delmas Coal	1.2
Sumitomo Coke	0.65
Kwangyang Coke	0.55

The influence of the sulphur content and third elements added to Fe-S solutions on the activity coefficient of sulphur at 1600°C is illustrated in Figure 2.2 (Griffing and Healy, 1960). As a rule, the following reactions move from left to right directions when the partial pressure of oxygen decreased in the system.

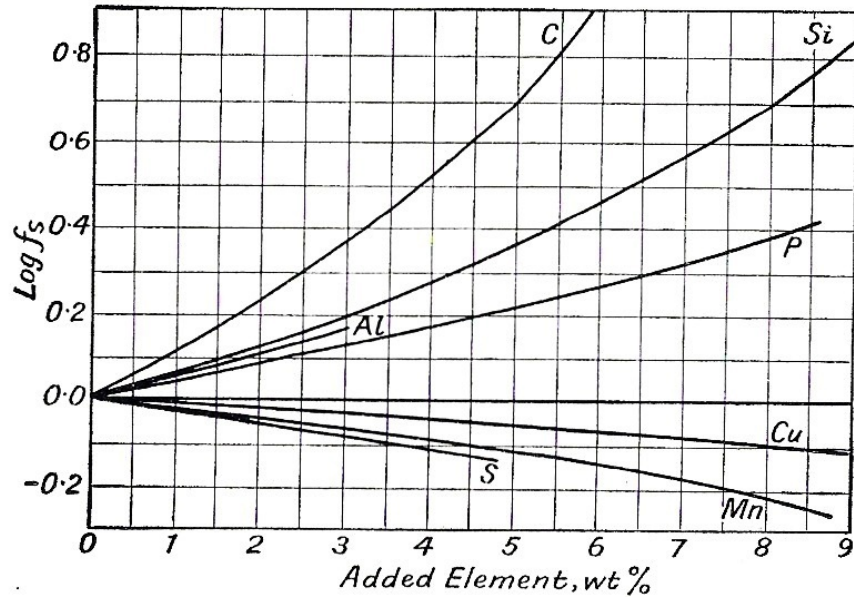
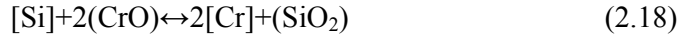
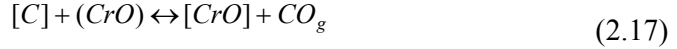
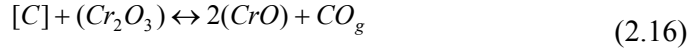
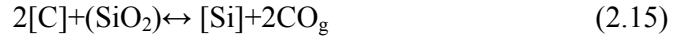


Figure 2.2 The influence of sulphur content and third elements added to Fe-S solutions on the activity coefficient of sulphur at 1600°C (Griffing and Healy, 1960).

According to Metcalfe and Slater (1978), magnesium oxide, aluminium, strontium carbonate and sodium carbonate have been found unsuitable desulphurisation agents in high carbon ferrochromium smelting process. In these cases, desulphurisation was found to be 18 to 33 %, resulting in final sulphur content barely within the specifications. Commercial lime, calcium carbide and calcium cyanamide and a lime-magnesium mixture were considered as highly potential desulphurisation agents in their study.

Contrary to Metcalfe and Slater's (1978) findings, Halikia et al. (2001) showed that desulphurisation beyond 90 % can be achieved by using sodium carbonate in the high carbon ferrochromium smelting. Highly efficient desulphurisation of high carbon ferrochromium with the addition of soda ash can be related to the following parameters:

- The high carbon content of the melt: Na_2CO_3 as an oxidizing agent, low oxygen potential increases the desulphurisation of high carbon ferrochromium carbon.
- The high alkalinity of the slag: The slags of the system $\text{Na}_2\text{O}-\text{SiO}_2$ have higher sulphur capacity compared to CaO based slags; the sulphide capacity of the slags tend to increase with the increasing Na_2O content in the slag (Halikia et al., 2001)

The contradictions between Halikia et al., (2001) and Metcalfe and Slater's (1978) findings can be a result of differences between experimental conditions. The minimum time period required for the completion of FeCr desulphurisation was indicated as 44 minutes in Halikia et al., (2001). However, Metcalfe and Slater (1978) used a maximum 15 minutes as a holding time in their experiments. Also, Halikia et al, (2001) desulphurisation experiments were conducted at 1750°C which is 150°C higher than Metcalfe and Slater's (1978) experimental temperature. From thermodynamic and kinetic points of view, it is highly possible that Halikia et al. (2001) experiments can be considered as much closer to equilibrium conditions compared to Metcalfe and Slater's (1978).

In the case of acid slags, the formation of silicon sulphide results a decrease in the sulphur content of the ferrochromium. The results showed that if the silicon content is kept below 1 wt. % in the ferrochromium alloy, only 40 wt. % of the initial sulphur can be transferred into slag phase (Pickles et al, 1987).

From ferrochromium refining point of view, Pan and Eric (1997) showed that the sulphur transfer from the metal to slag increases with increasing MgO content in

the slag. Also, it was found that increasing silica, alumina and chromium content of slag have negative impacts on the sulphur removal.

The formations of calcium and magnesium compounds favour the desulphurisation of metal phase. Metcalfe and Slater (1978) reported that calcium based reagents helped to generate slags with lower viscosities. From kinetic point of view, the diffusion of reaction species increases in the low viscose slags, which ultimately improves sulphur removal rate from metal (Pickles et al., 1978).

Dai and Shu (1995) investigated sulphur control in high carbon ferrochromium production. According to them, it is possible to reduce the sulphur content of the alloy from 0.028 to 0.013 wt. % by applying a vacuum of 1.0-2.0 mmHg for 3-5 minutes. As a second test, the slag washing method was used for understanding the desulphurisation of high carbon ferrochromium. In this test, the slag of low carbon ferrochromium was tapped into a hot metal ladle. Then, the hot metal of high carbon ferrochromium poured onto it. The basicity of the slag is around 1.8 and slag/metal ratio is 1.5-2. The results (Table 2.2) show a significant drop in the sulphur content of the metal.

Table 2.2 Results of slag washing treatment (Dai and Shu, 1995)

			Slag composition (wt. %)					
	[S]	(S)	SiO ₂	CaO	MgO	FeO	Al ₂ O ₃	Cr ₂ O ₃
1-Before	0.0138	0.0225	27.1	48.78	10.6	0.82	6.34	4.6
1-After	0.0025	0.0513	27.1	47.62	11.8	0.82	6.99	4.12
2-Before	0.0312	0.0275	27.78	47.4	10.6	0.67	7.12	4.95
2-After	0.01	0.055	28.47	42.89	13.1	0.77	8.15	5.01

Dai and Shu (1995) concluded that increase in silicon and carbon contents of the metal phase helps to reduce the sulphur content in the alloy. These elements decrease the activity or the concentration of oxygen in the alloy and promote desulphurisation of the alloy. Also, ferrochromium smelting process shows that the amount of sulphur transferring to the slag varies with temperature and slag physicochemical properties. During this process, it was found that the additions of CaO and MgO oxides favour the formation of high sulphide capacity slag which

will promote the desulphurisation of high carbon ferrochromium alloy. However, researchers indicated that slags's electrical conductivity and furnace operation conditions can be affected in a negative way with the addition of excessive amount of CaO into process. From operation temperature point of view, a high temperature can be considered as a favourable condition for the sulphur removal from the metal. The high temperature conditions will manifest itself as an increase in the silicon content in the metal phase.

2.3.3 Behaviour of sulphur in ferromanganese smelting

Very few studies have been done on investigations of sulphur behaviour in ferromanganese smelting (Elyutin, 1961; Kucukkaragoz and Eric, 1998). Therefore, a further study requires on this subject.

Due to the high operation temperature and reducing atmosphere conditions, most of the sulphur in the charge can be transferred into slag phase during the smelting of ferromanganese. It was concluded that sulphur of the charge is mainly carried away from the alloy with off gases and slag (Elyutin, 1961).

Kucukkaragoz and Eric (1998) found that desulphurisation of alloy increases with increasing slag basicity (Figure 2.3). CaO is found to be the main factor in the transfer of sulphur from alloy to slag phase by association between Ca and S elements (Kucukkaragoz and Eric, 1998). However, this conclusion can be hardly done if the three high basicity data points have significant error bars. In this study, no statistical error analysis was conducted therefore it is hard to make solid comment in this matter.

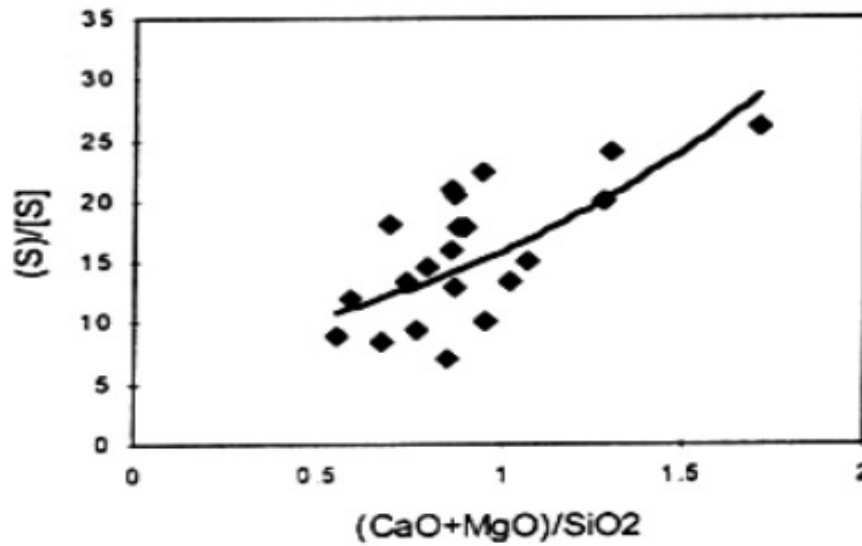


Figure 2.3 Sulphur distribution between slag and alloy phase as a function of basicity ratio (Kucukkaragoz and Eric, 1998)

2.4 Concept of Sulphide Capacity

The impurity capacity describes the potential ability of a slag to absorb impurity and could be used for defining the impurity removal characteristics of a particular slag (Reddy, 2003).

Fincham and Richardson (1954) studied the sulphur behaviour in silicate and aluminate melts and slags. The mixtures of CaO-SiO₂, MgO-SiO₂, FeO-SiO₂, CaO-Al₂O₃ and CaO-SiO₂-Al₂O₃ were brought into equilibrium at temperatures between 1350°C and 1650°C, with gas phases made up of H₂+CO₂ and 1 vol. % SO₂ and 50 vol. % N₂. When partial pressure of oxygen is less than about 10⁻⁵ atm, sulphur is held as sulphides in the slag and its concentration being controlled by reaction 2.19. It was found that if the partial pressure of oxygen is greater than 10⁻³ atm, the sulphur is held as a sulphate in the slag and the corresponding equilibrium reaction can be presented as Eq. 2.20. Figure 2.4 shows the sulphide and sulphate equilibrium constants and the ranges of oxygen pressures over which they are valid. In Figure 2.4, the sulphur is counted as sulphide for the full lines and as sulphate for the broken lines. The results showed that at constant partial

pressure of oxygen and partial pressure of sulphur dioxide gases, raising the temperature increases the amount of sulphide in the slag phase and decreases the amount of sulphate present. Also, it can be concluded that Eq. 2.19 can be applied under reducing and Eq. 2.20 can be used under oxidizing conditions. As it was mentioned early, ferrochromium and ferromanganese smelting process can be achieved under reducing atmosphere conditions without the excessive loss of chromium and manganese into slag phase. Therefore, one can assumed that sulphur can be held as a sulphide form in the ferrochromium and ferromanganese smelting slags. Also, the researchers conducted a different study on sulphur behaviour in silicates, aluminates and iron-and steel-making slags, the results of the study was in good agreement with the previous findings in terms of temperature and partial pressure of oxygen conditions influence on sulphur behaviour (Richardson and Fincham, 1954).

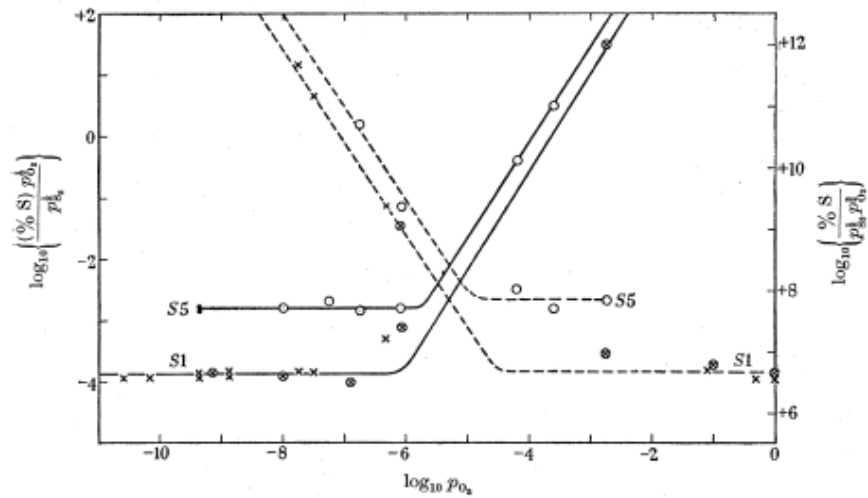
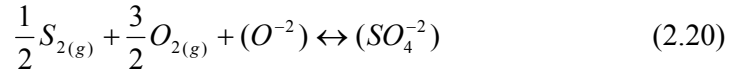
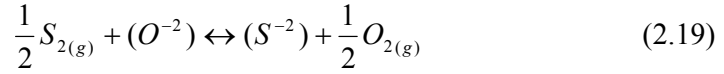
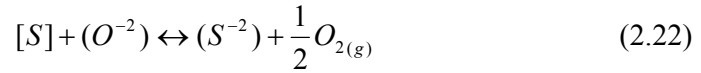


Figure 2.4 The sulphide and sulphate equilibrium constants and the ranges of the oxygen pressures (Fincham and Richardson, 1954).

As described in Finchman and Richardson study (1954), sulphur in the molten slag can be present as either sulphides or sulphates and the exchange of sulphur between gas and melt is controlled by the two equilibrium relations shown in 2.19 and 2.20 (Verein Deutscher Eisenhuttenteute, 1981).



When reaction (2.19) is combined with reaction (2.21), we can reach to reaction 2.22 and represents the dissolution of sulphur in the slag (Rosenquist, 1983).



The equilibrium constant (K) for the reactions (2.19) and (2.20) can be written in these forms (Verein Deutscher Eisenhuttenteute, 1981).

$$K_{2.19} = \frac{(a_{S^{-2}}).P_{O_2}^{1/2}}{(a_{O^{-2}}).P_{S_2}^{1/2}} \quad (2.23)$$

$$K_{2.20} = \frac{(a_{SO_4^{-2}})}{(a_{O^{-2}}).P_{S_2}^{1/2}.P_{O_2}^{3/2}} \quad (2.24)$$

Assuming that Henry's Law is valid for $(a_{S^{-2}})$ and $(a_{SO_4^{-2}})$, $K_{2.19}$ is a constant for the partial pressure of oxygen smaller than 10^{-5} atm. and $K_{2.20}$ is a constant for $P_{O_2} > 10^{-5}$ atm (Fincham and Richardson, 1954; Richardson and Fincham, 1954)

If we considered ferrochromium or ferromanganese smelting slag process, the partition of sulphur between slag and metal can be presented as:



This sulphur-oxygen exchange equilibrium can express in terms of ionic species in the slag phase:



Therefore, reaction 2.26 can be used for describing the partition of sulphur between slag and metal phases. However, the activities of single ions such as O^{2-} and S^{2-} in the slag are not measurable therefore thermodynamic calculation and analysis using Eq. 2.26 becomes impossible to solve. As it was mentioned in the previous part of the thesis, Fincham and Richardson (1954) introduced the concept of sulphide capacity of slag in order to use Eq. 2.22 (for the condition of partial pressure of oxygen is less than 10^{-5} atm) instead of 2.25 and 2.26. As presented in Eq. 2.23, the individual values of a_o^{-2} and a_s^{-2} can't be measureable, therefore it is impossible to determine the equilibrium constant from this description. However, the relevant equilibrium constant value of Eq. 2.21 can be derived by modification of this equation to Eq. 2.27 where (wt. % S) is the weight percentage of sulphur in the slag phase, f_s is the activity coefficient of sulphur as function of the concentration of sulphur and of the concentrations of the other solutes. As equilibrium constant of reaction 2.22 (Eq. 2.23) can't be determined by experimentally, sulphur affinity of the slag can be described as “sulphide capacity” which can be obtained by chemical analysis of the respective phases of slag and metal after equilibration at given partial pressures of sulphur and oxygen in the gas phase (Eq.2.27). “Sulphate capacity” (Eq. 2.28) can be defined in a manner similar to the sulphide capacity.

From Eqs. 2.27 and 2.28, sulphide (C_s^{-2}) and sulphate ($C_{SO_4^{-2}}$) capacities can be defined in accordance with the following expressions (Verein Deutscher Eisenhuttenteute, 1981; Bodsworth and Bell,1972):

$$K_{2.19} \frac{(a_{o^{-2}})}{f_s} = \frac{(wt.\%S).P_{O_2}^{1/2}}{P_{S_2}^{1/2}.f_s} = C_s \quad (2.27)$$

$$K_{2.20} \frac{(a_{o^{-2}})}{f_s} = \frac{(wt.\%S)}{P_{S_2}^{1/2}.P_{O_2}^{3/2}.f_s} = C_{SO_4} \quad (2.28)$$

The right-hand sides of (2.27) and (2.28) are known as the sulphide (C_s) and sulphate (C_{SO_4}) capacities of the melt respectively, where a_o^{-2} is the activity of

oxygen ions in the slag and f_s is the activity coefficient (Henrian) of sulphur in the slag (wt.%) (Bodsworth and Bell, 1972).

Elliott (1997) expressed the reaction 2.22 in a different way to represent the equilibrium of S between metal phase and the slag phase.

The equilibrium constant of reaction 2.22 can be written as follows:

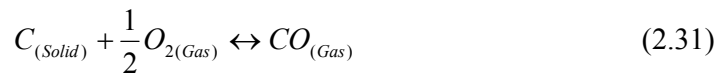
$$K_{2.22} = \frac{(a_{s^{-2}}) \cdot (P_{O_2})^{1/2}}{[a_s](a_{O^{2-}})} = \frac{(f_{s^{-2}}) \cdot (S^{-2}) \cdot (P_{O_2})^{1/2}}{[f_s][S](a_{O^{2-}})} \quad (2.29)$$

where sulphide capacity would be

$$C_s = \frac{K_{2.22} \cdot (a_{O^{2-}})}{(f_{s^{-2}})} = \frac{(S^{-2}) \cdot (P_{O_2})^{1/2}}{[f_s][S]} \quad (2.30)$$

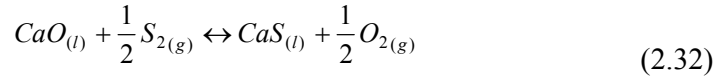
As a note, Eq. 2.30 has been applied to the calculations of sulphide capacity of a slag system in the present study where:

- a) $(\%S^{-2})$ is the wt. % of S^{-2} ions in the slag phase determined by chemical analysis.
- b) P_{O_2} is the partial pressure of O_2 to be calculated from the reaction 2.31



- c) $[\%S]$ is the wt. % S in the metal phase determined by chemical analysis.
- d) $[f_s]$ is the activity coefficient of S in the metal phase to be calculated by using dilute solution treatment.

Another way to define the sulphide capacity is using equilibrium constant of reaction 2.32 (K_{Ca}) and activity of calcium oxide (a_{CaO}). In this method, the sulphide equilibrium reaction can be written as:



When we combine the Eq. 2.27 and 2.33, the following relation then defines the sulphide capacity.

$$C_s = K_{Ca} a_{CaO} \frac{(wt.\%S)}{a_{CaS}} \quad (2.33)$$

where K_{Ca} is the equilibrium constant for reaction 2.32.

According to Young and Cripps (1980), the sulphur partition between slag and metal can be calculated by combining reaction 2.21 and 2.22. The standard Gibbs Energy change for equation 2.21 is equal to $131\,800 - 22.06\,T$ (J) (referred to 1 atm. of S_2 vapour a 1 wt. % solution of S in liquid Fe) (Elliott et al., 1963). The equilibrium constant for 2.21 can be written as:

$$K_{2.21} = \frac{P_{S_2}^{1/2}}{[S].f_s} \quad (2.34)$$

where square brackets indicate wt. % of sulphur in the iron, and f_s is the Henrian activity coefficient of sulphur which can be calculated by Eq. 2.35,

$$\log_{10} f_s = \sum_i e_s^i x_i \quad (2.35)$$

where e_s^i is the first-order interaction coefficient between sulphur and the dilute solute i , and x_i is the weight percentage of the solute i . First and second order interaction-coefficients of sulphur in carbon saturated liquid iron at $1\,600^\circ\text{C}$ are given in Table 2.3 (Sigworth and Elliott, 1974)

Table 2.3 First and second order interaction coefficients of sulphur in carbon saturated iron at 1 600°C (Sigworth and Elliott, 1974).

Interaction Parameter	C	Si	P	S
e_s^j	0.11	0.063	0.035	-0.046
r_s^j	0.0058	0.0017	0.0006	-0.0009

Although the optical basicity concept will be discussed in section 2.7.2, it is important to review several studies that were conducted on the relationship between sulphide capacity of slags and optical basicity.

The optical basicity can be used to develop correlations for the distribution of sulphur and phosphorus between slag and metal (Sosinsky and Sommerville, 1986).

The relationship between optical basicity and sulphide capacity for CaO-based slags are given in Figure 2.5 at 1 500°C and Eq 2.36 for this relationship is expressed as follows (Sosinsky and Sommerville, 1986)

$$\log C_s = 12.6 \Lambda - 12.3 \quad (2.36)$$

where Λ represents the optical basicity of the slag system.

Equation 2.36 is based on data for seven systems, involving four component slag system with a correlation coefficient of (R^2) of 0.965 for 183 data points and permits to calculate the sulphide capacity of 1500 °C for any oxide slag of interest over iron and steelmaking.

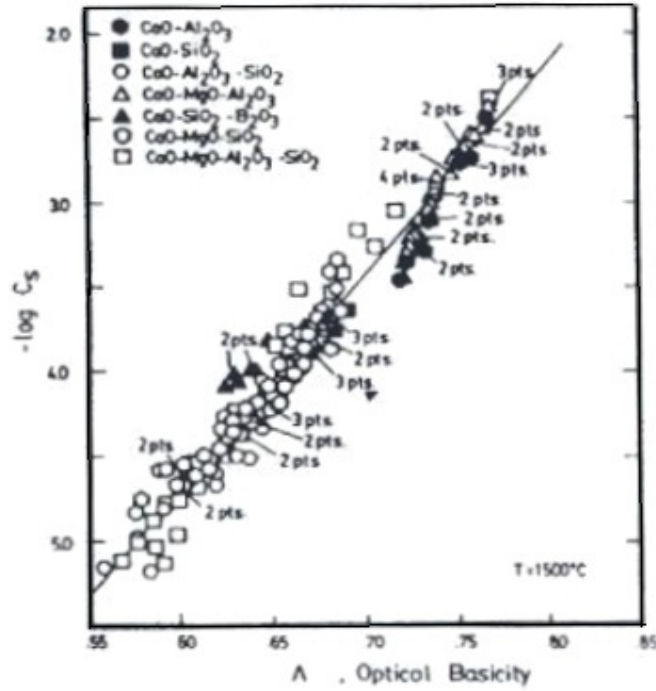


Figure 2.5 Relationship between sulphide capacity and optical basicity at 1 500°C (Sosinsky and Sommerville, 1986)

Another relationship can be used on the determination of sulphide capacities of CaO-MgO-Al₂O₃-SiO₂ slag system is given in Equation (2.37).

$$\log C'_s = \frac{B}{A} + 2.82 - \frac{13300}{T} \quad (2.37)$$

where C'_s , B, and A are represented in Eq. 2.38, 2.39 and 2.40 and T indicates temperature in degree celcius.

$$C'_s = (S) \frac{[a_o]}{[a_s]} \quad (2.38)$$

$$B = 5.623(\text{wt.\%CaO}) + 4.15(\text{wt.\%MgO}) - 1.152(\text{wt.\%SiO}_2) + 1.457(\text{wt.\%Al}_2\text{O}_3) \quad (2.39)$$

$$A = (\text{wt.\%CaO}) + 1.391(\text{wt.\%MgO}) + 1.867(\text{wt.\%SiO}_2) + 1.65(\text{wt.\%Al}_2\text{O}_3) \quad (2.40)$$

Equation 2.37 can only be applied to CaO-MgO-Al₂O₃-SiO₂ system and have limited composition range. However, temperature functionality of Eq. 2.37 can be considered as a major advantage of this equation over Eq. 2.36.

Sosinsky and Sommerville (1986) expressed another equation (2.41) which can be used in the estimation of the sulphide capacity of an oxide slag in the range 1 400°C and 1 700°C. Eq. 2.41 permits us to calculate the predicted sulphide capacity of an oxide slag at any temperature in the range of 1400 °C to 1700 °C. This allows us to cover most of the range of interest for iron and steelmaking slags.

$$\text{Log}C_s = \left(\frac{22690 - 54640\Lambda}{T} \right) + 43.6\Lambda - 25.2 \quad (2.41)$$

where the oxygen potential of the slag-metal system is known, or can be calculated from the deoxidation equilibrium, the equilibrium distribution of sulphur between slag and metal can be determined related to the sulphide capacity according to the Eqs. 2.42 and 2.43 .

$$\log \frac{(S)}{[a_s]} = -\frac{6890}{T} + 1.15 + \log C_s - \frac{1}{2} \log P_{o_2} \quad (2.42)$$

$$\log \frac{(S)}{[a_s]} = -\frac{770}{T} + 1.30 + \log C_s - \log[a_o] \quad (2.43)$$

The equilibrium sulphur distribution ratio can be expressed in terms of temperature and the optical basicity of slag as shown in Eq. (2.44) (Sosinsky and Sommerville, 1986)

$$\log \frac{(S)}{[a_s]} = \left(\frac{21920 - 54640\Lambda}{T} \right) + 43.6\Lambda - 23.9 - \log[a_o] \quad (2.44)$$

Since the activity and activity coefficient of an ionic species can't be measured, activity of oxygen [a_o] can be determined from the thermodynamics of the deoxidation reaction employed and it is a function of temperature and slag composition. Also, the concentration of sulphur in the metal phase can be used

instead of activity of sulphur in the calculations. Therefore, this equation can be applicable to the desulfurisation of hot metal and allows to calculate the equilibrium slag-metal distribution ratio of sulphur by simply using a knowledge of the slag composition and temperature (Sosinsky and Sommerville,1986).

According Young et al. (1992), Sommerville's relationship between optical slag basicity and the sulphide capacity is not accurate, particularly in the high basicity regions (high sulphide capacity) and proposed equations (Eqs. 2.45 and 2.46). Researchers tested Sommerville's relationship and found no simple linear relationship between optical basicity and the log of sulphide capacity. Also, their study showed that Sommerville's relationship has limited power on the prediction of low sulphide capacity values and shows increasing deviation at higher capacities. The adaptation of Λ^2 and including slag concentrations to the regression model provide a better accuracy on the relationship between the log of sulphide capacity and selected parameters. Results showed that a definite change in the relationship sulphide capacity and optical basicity can be seen above an optical basicity value of 0.8. This can be related to changing liquid slag behaviour at basicities beyond the ortosilicate. Therefore, it is necessary to include the slag concentrations in to the equation in order to predict sulphide capacity values.

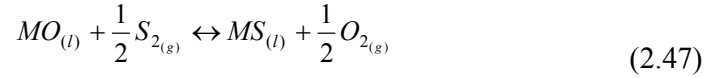
$$\log C_s = -13.913 + 42.84\Lambda - 23.82\Lambda^2 - \frac{11710}{T} - 0.02223(\text{wt.\%SiO}_2) - 0.02275(\text{wt.\%Al}_2\text{O}_3) \quad (2.45)$$

and

$$C_s = -0.6261 + 0.4808\Lambda + 0.7197\Lambda^2 + \frac{1697}{T} - \frac{2587\Lambda}{T} + 0.0005144(\text{wt.\%FeO}) \quad (2.46)$$

Eq. (2.45) can be used when $\Lambda < 0.8$ and Eq. (2.46) can be applied for $\Lambda \geq 0.8$. These equations have shown good results during the calculations of sulphide capacity, as a function of optical basicity Λ and temperature T (in Kelvin).

Reddy and Blander (1987) modelled the sulphide capacities of silicate melts on the basis of the Flory model for polymeric silica chains. According to their theoretical considerations, the sulphide equilibrium reaction can be written as:



and $K_{2.47}$ is given by:

$$K_{2.47} = \left(\frac{P_{O_2}}{P_{S_2}} \right)^{\frac{1}{2}} \frac{a_{MS}}{a_{MO}} \quad (2.48)$$

so the sulphide capacity can be defined as:

$$C_s = K_{2.47} a_{MO} \frac{(wt.\%S)}{a_{MS}} \quad (2.49)$$

The composition range, $0 \leq X_{SiO_2} \leq 0.33$ for MO-SiO₂ system which represents the basic melts, the sulphide capacity can be defined for this composition range:

$$C_s = 100.W_s.K_M a_{MO} \left[\frac{1 - 2X_{SiO_2}}{W_{MO} + X_{SiO_2}(W_{SiO_2} - W_{MO})} \right] \quad (2.50)$$

where W_i and X_i represent molecular weight and mole fraction of species, respectively.

When the composition is $0.33 \leq X_{SiO_2} \leq 0.67$ for MO-SiO₂ system, the authors consider the system as a acidic melt which contain polymeric species and for this assumption the sulphide capacity can be described as:

$$C_s = 100.W_s.K_M a_{MO} \frac{X_{SiO_2}}{W} \left(\frac{\Phi_s}{a_{MS}} \right) \quad (2.51)$$

where a_{MS} can be expressed as:

$$a_{MS} = \frac{(wt.\%S)}{100.W_S} \left[\frac{W_{MO} + X_{SiO_2}(W_{SiO_2} - W_{MO})}{1 - 2X_{SiO_2}} \right] \quad (2.52)$$

and Φ_s is calculated from Eq. 2.53.

$$\Phi_s = \frac{N_s}{N_s + mN_{Si}} \cong \frac{N_s}{N_{Si}} \quad (2.53)$$

where N_s is the number of monomeric sulphur sites, m is the relative volume of an Si unit taken to be one, and N_{Si} is the number of the polymer sites. The relationship between Φ_s and a_{MS} is shown in 2.54.

$$\overline{\Delta G_s} = RT \left[\ln \Phi_s + \left(1 - \frac{1}{m}\right) \Phi_p + x \Phi_p^2 \right] \quad (2.54)$$

$\overline{\Delta G_s}$ is the partial molar free energy of a solution of a monomer (sulphide), x is a very small constant for the expected weak interactions between the anions (sulphide and silicates) and m is an average polymer chain length.

When the melt contains a monomer, m becomes equal to 1 and a_{MS} / Φ_s is equal to 1, but for the melts containing mostly polymers, $m \geq 1$ and $\Phi_p \approx 1$ a_{MS} / Φ_s becomes equal to 2.71.

Figure 2.6 shows the calculated C_s values with the available experimental data. A strong correlation between the sulphide capacity and basicity can be seen from Figure 2.7. The positive impact of increasing basicity can be related to the increase in the activity of CaO (Figure 2.8). Also, for a given composition, the increase in temperature causes a raise in the sulphide capacity values.

As can be seen in Figure 2.7, calculated sulphide capacity values in the FeO-SiO₂ system have less temperature dependence compared to the CaO-SiO₂ slag system. In addition to that the increase in CaO content of slag causes less remarkable increase on the sulphide capacity values of FeO-SiO₂ slag. This can be related to

the relatively small change in a_{FeO} when shifting from acid to basic solutions (Figure 2.9). (Reddy and Blander, 1987)

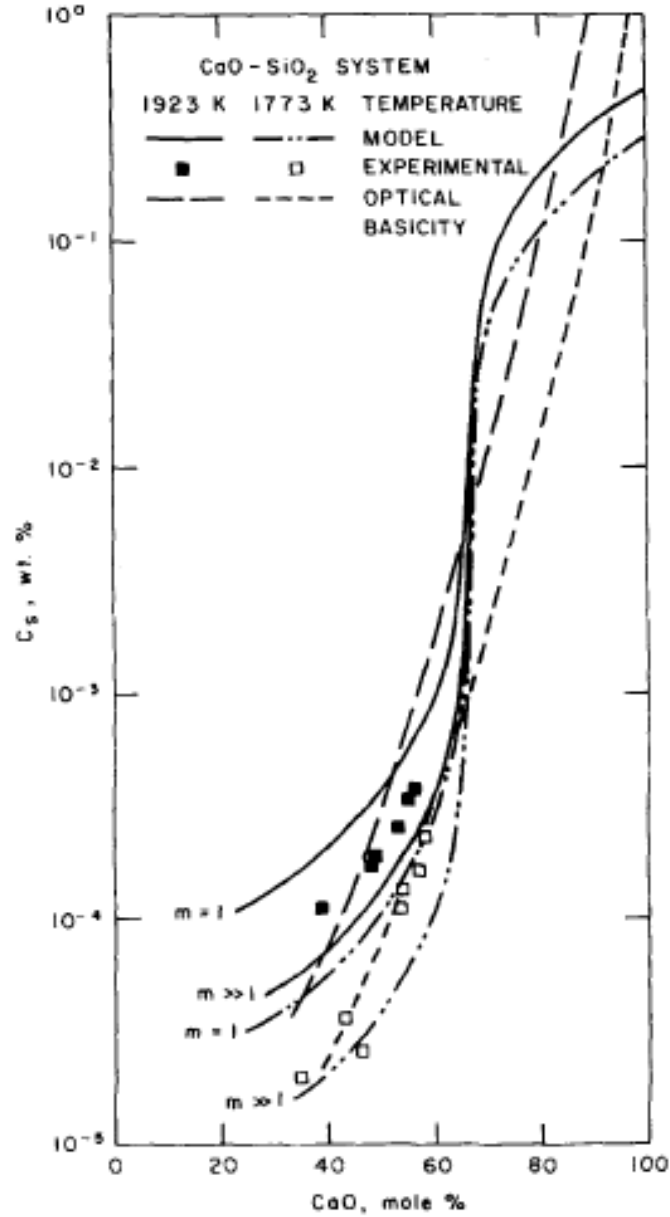


Figure 2.6 Calculated and measured sulphide capacities in the CaO-SiO₂ system at 1 500°C (1 773 K) and 1 700°C (1 923 K) based on the model described by Reddy and Blander (1987) and on the model described by Sosinsky and Sommerville (1986).

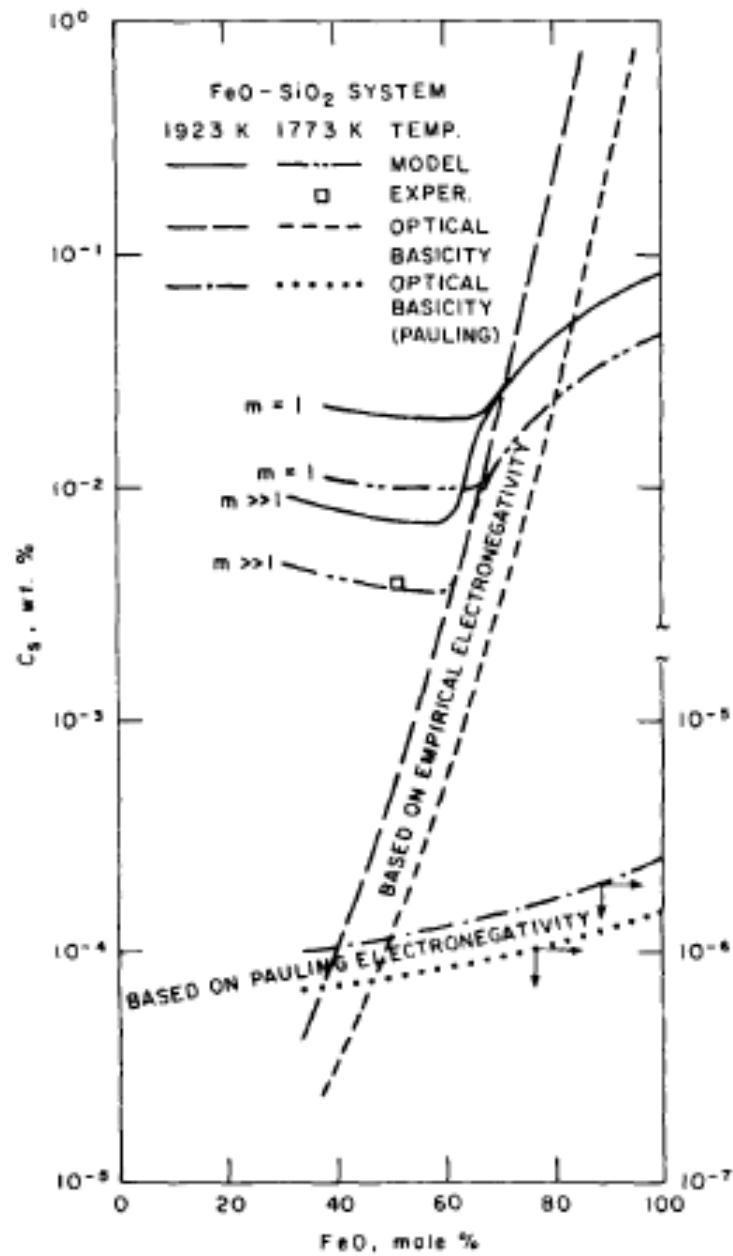


Figure 2.7 Calculated and measured sulphide capacities in the FeO-SiO₂ system at 1 500°C (1 773 K) and 1 700°C (1 923 K) based on the model described in Reddy and Blander (1987) and on the model described by Sosinsky and Sommerville (1986)

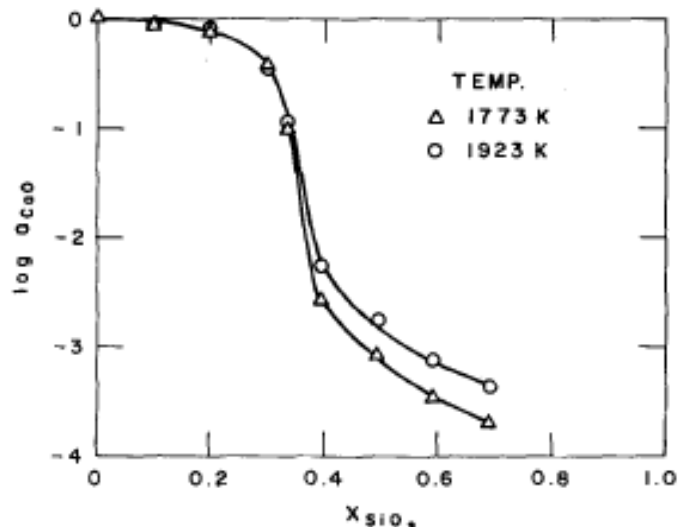


Figure 2.8 Plot of the log a_{CaO} (activity of CaO) in the CaO-SiO₂ system at 1 500°C (1 773 K) and 1 700°C (1 923 K) (Reddy and Blander, 1987)

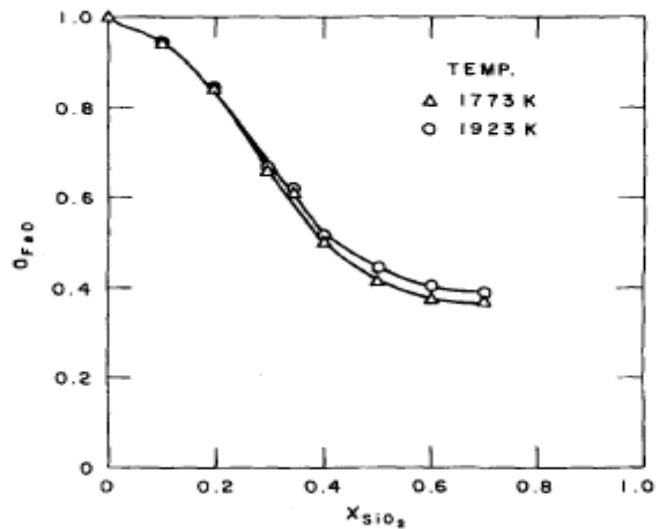


Figure 2.9 Plot of the log a_{FeO} (activity of FeO) in the FeO-SiO₂ system at 1 500°C (1 773 K) and 1 700°C (1 923 K) (Reddy and Blander, 1987)

A good agreement between the experimentally determined and theoretically calculated sulphide capacities in MgO-SiO₂ can be seen in Figure 2.10.

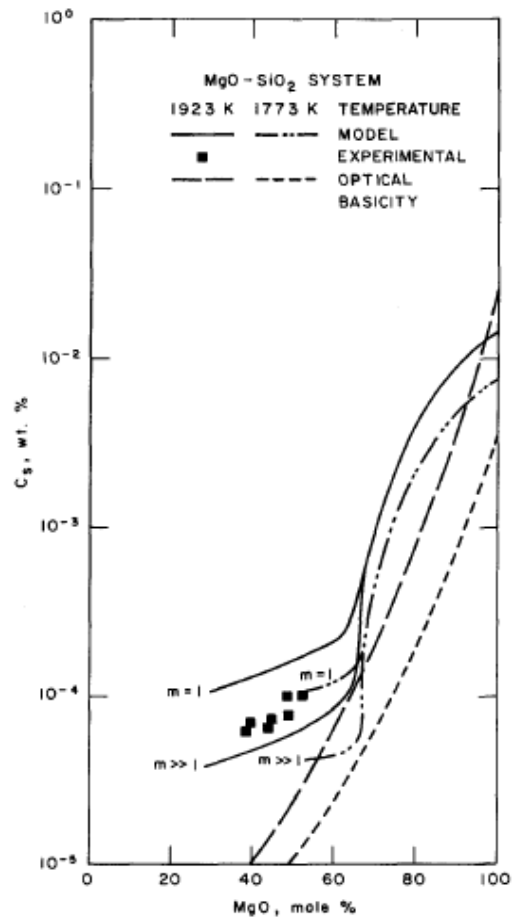


Figure 2.10 Calculated and measured sulphide capacities in the MgO-SiO₂ system at 1 500°C (1 773 K) and 1 700°C (1 923 K) based on the model described in Reddy and Blander (1987) and on the model described by Sosinsky and Sommerville (1986)

The results show that sulphide capacities of the FeO-SiO₂ system are higher than those for the CaO-SiO₂ and MgO-SiO₂ systems in the composition range of XSiO₂ > 0.33. The sulphide capacities of the CaO-SiO₂ slag system tend to decrease with the replacement of CaO by SiO₂. In acid melts, the results are much lower compared to the FeO-SiO₂ system and almost equal to the MgO-SiO₂ system in the concentration range near 40 to 50 mole % of CaO (Reddy and Blander, 1987).

Reddy and Blander (1989) applied same sulphide capacity model to MnO-SiO₂ slags. The calculated values based on the Reddy-Blander model together with results from Abraham et al. (1960) are given in Figure 2.11. Also, the results of an earlier study on the sulphide capacities of the MnO-SiO₂ system are illustrated in Figure 2.12. A good agreement between the Reddy-Blander model calculated and experimentally determined sulphide capacities has been identified in basic melts (X_{SiO_2} up to 0.33). However, when the mole fraction of SiO₂ exceeded 0.5, Reddy-Blander model under predicted the experimental values. For a given temperature, the sulphide capacity tends to rise by increasing the MnO content of the slag. This can be attributed to the increase in the activity of MnO in the MnO-SiO₂ binary slag system with the increasing amount of MnO in the slag phase. Results also indicate that at a given composition, an increase in the temperature will enhance the sulphide capacity of the slag. Hino and Fuwa (1978) mentioned a similar effect on the sulphide capacity with the change of silica concentration in MnO-SiO₂.

Reddy (2003) showed that excellent agreement between Reddy-Blander model predicted sulphide capacities data and laboratory experimental and industrial data for MnO-SiO₂, FeO-CaO-SiO₂, lead and copper slags. However, the major drawback of this model is disregarding of the Lux-Flood reactivity of the system and using of a computation based on rather simple structural models involving oxide activities in binary limiting joins. Therefore, Reddy-Blander model can be considered as a limited tool from structural point of view and has limitations in complex slag systems.

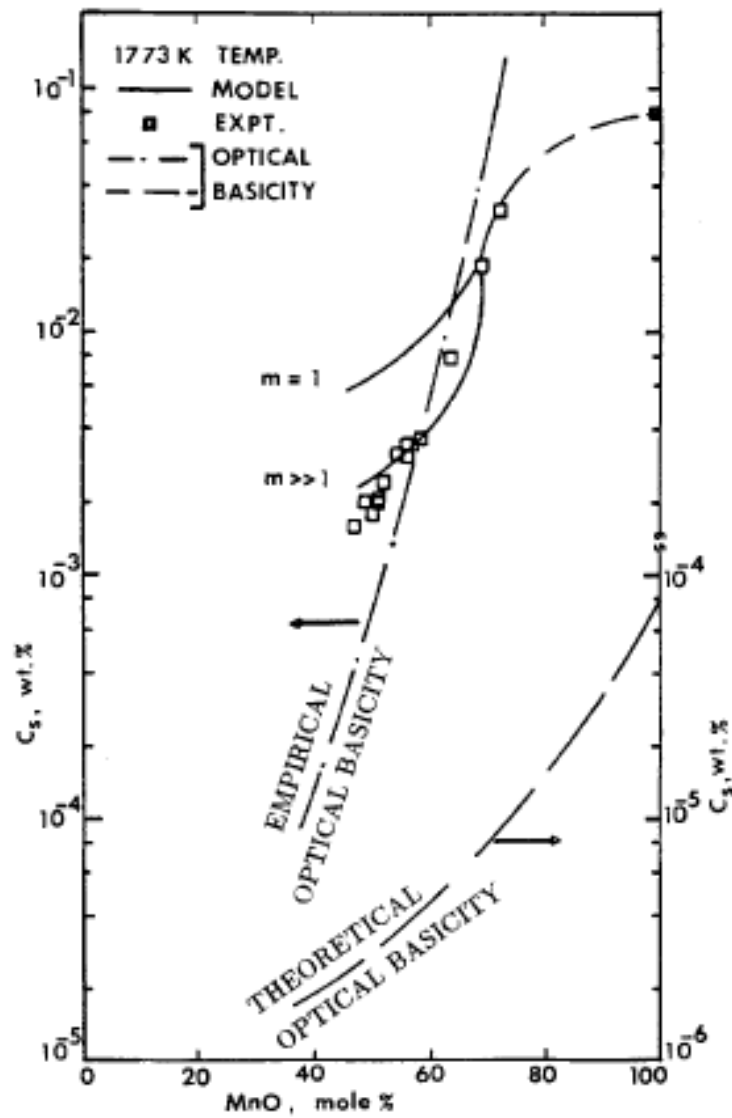


Figure 2.11 Calculated and measured sulphide capacities in the MnO-SiO₂ system at 1700°C (1923 K) – based on experiments from the Abraham et al. (1960) study and calculated by using the model described in Reddy and Blander (1989) and on the model described by Sosinsky and Sommerville (1986).

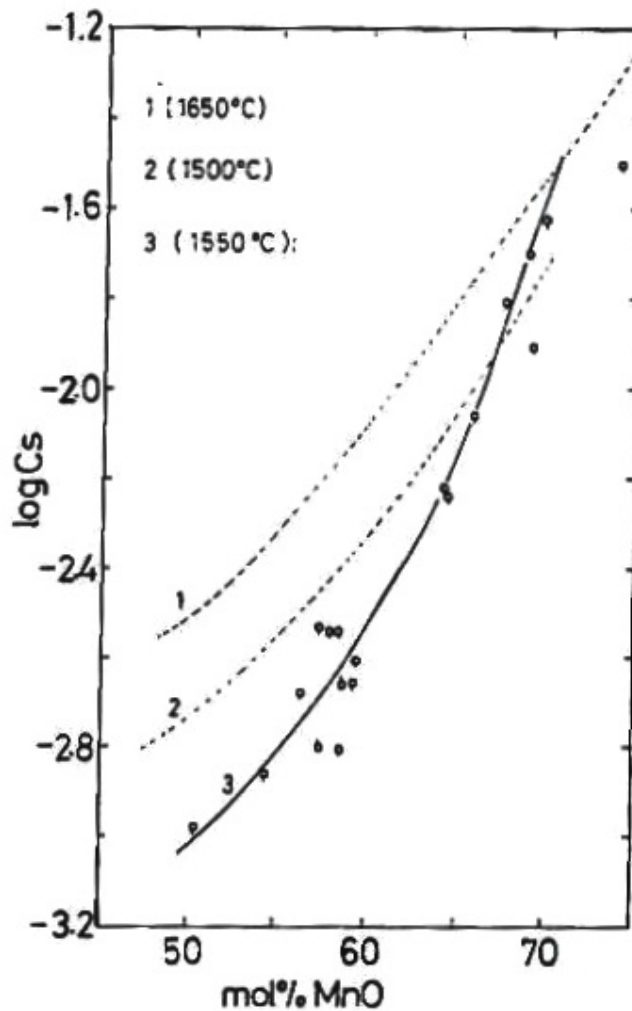


Figure 2.12 The effect of the concentration of MnO on the sulphide capacity of the MnO-SiO₂ system (Hino and Fuwa, 1978).

Hino et al. (1993) investigated the sulphide capacities of CaO-Al₂O₃, CaO-Al₂O₃-MgO and CaO-Al₂O₃-SiO₂ slags in Pt or CaO crucibles at 1 550°C to 1 650°C under Ar-SO₂-CO-CO₂ gas mixtures atmosphere. It is seen that the sulphide capacity of the CaO saturated CaO-Al₂O₃ slags increases with an increase of temperature and concentration of CaO in the slag. In addition to that the sulphide capacities of CaO saturated Al₂O₃-MgO-CaO melts enhance when the alumina concentration decreases in the slag (at a given temperature and for a constant CaO/MgO ratio). When CaO is replaced by MgO in CaO-Al₂O₃-MgO slags,

sulphide capacities tend to decrease. For CaO-Al₂O₃-SiO₂ slag system, the sulphide capacity of the system decreases with the decrease of CaO/SiO₂ ratio at a given Al₂O₃ content. Also the observed results from Gornerup and Wijk (1996) support the trends found in Hino et al. study (1993).

Nilsson et al. (1994a, 1995a) studied the sulphide capacities of CaO-MnO-SiO₂ slags in the temperature range 1 523 to 1 600 °C by equilibrating the slag with a gas-mixture containing CO, CO₂, SO₂ and Ar in Pt crucibles. The results showed that the sulphide capacities of the slags increase with increasing basicity ratio of slag and confirms the active role played by the free oxygen ions in the slag. A comparison of the results indicates that the sulphide capacity values tend to increase when MnO replaced the CaO in the slag system. Figures 2.13 and 2.14 represent the results of these experiments. Nilsson et al. (1994a) explained the basis of a model for predicting the sulphide capacities of the CaO-MnO-SiO₂ slag system as a function of the slag composition and temperature. The values predicted by using KTH sulphide capacity model are indicated in Figures 2.13 and 2.14. The details of KTH's model will be reviewed in this part of thesis based on Drakaliysky et al., 1996; Drakaliysky et al., 1997; Nzotta, 1997a; Nzotta, 1997b; Nzotta et al., 1997c; Nzotta et al., 1998; Nzotta et al., 1999a; Nzotta et al., 1999b; Nzotta et al., 2000 studies.

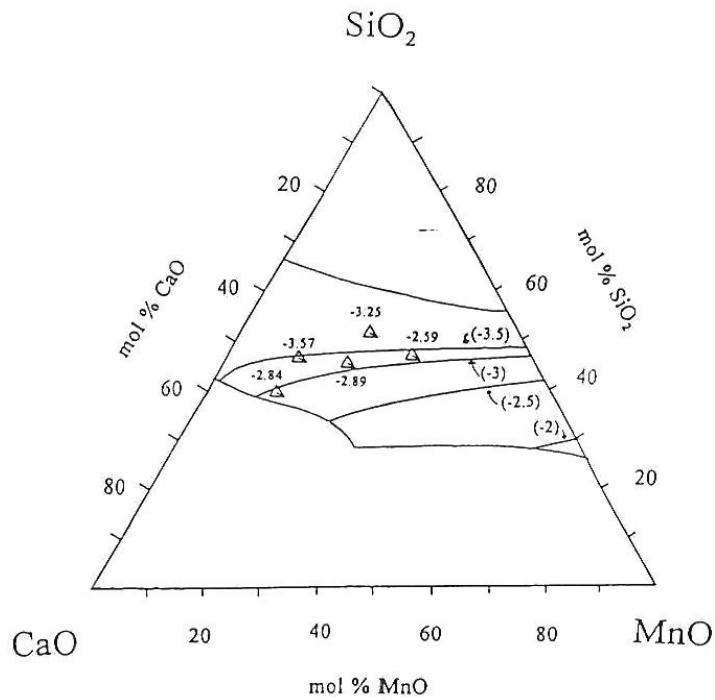


Figure 2.13 Iso- C_S diagram for the system CaO-MnO-SiO₂ at 1524 °C as predicted by model. (Values in log₁₀ C_S) (Nilsson et al., 1994a)

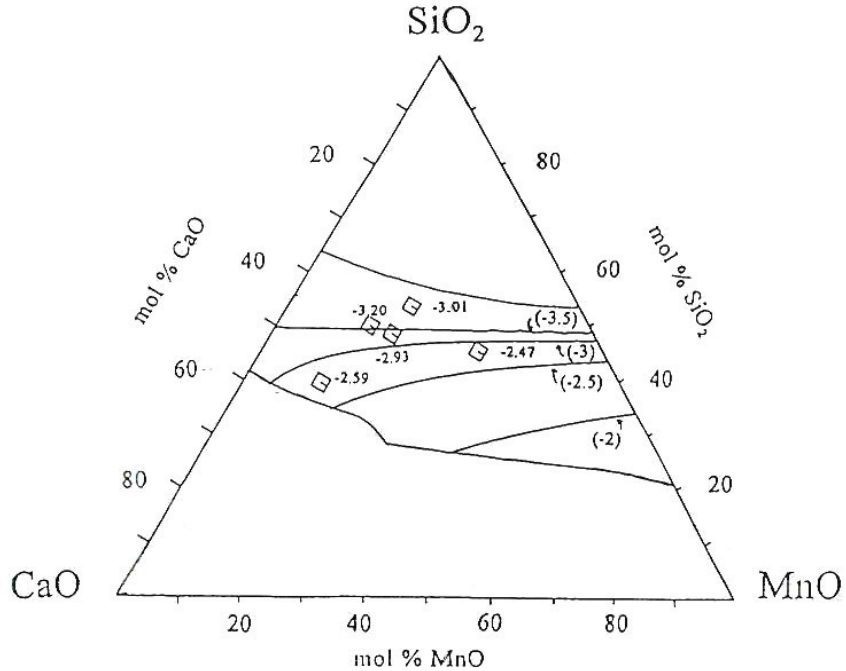


Figure 2.14 Iso- C_S diagram for the system CaO-MnO-SiO₂ at 1600 °C as predicted by the model. (Values in log₁₀ C_S) (Nilsson et al., 1994a)

In Figure 2.15, sulphide capacity and basicity ($X_{\text{CaO}}/X_{\text{SiO}_2}$) chart has been plotted for constant MnO contents ($X_{\text{MnO}} = 0.2, 0.3$ and 0.4). The sulphide capacity increases significantly in high manganese oxide containing slag compares to others. The activity of MnO in the slag increases with the increase of basicity ratio of slag and leads to a higher sulphur holding power slag. The sulphide capacity of $2\text{CaO}.\text{SiO}_2 - 2\text{MnO}.\text{SiO}_2$ as well as $\text{CaO}.\text{SiO}_2 - \text{MnO}.\text{SiO}_2$ at 1600°C are plotted in Figure 2.16. The results show that the sulphide capacity increases with the increase of MnO content. ΔG_0 -T diagram for the reactions between orthosilicates of Ca, Mg, Mn, $\text{S}_2(\text{g})$ to form CaS, MnS and MgS is given in Figure 2.17 which shows that the reaction of manganese orthosilicate has the lowest Gibbs energy change and mostly favoured reaction. A similar trend can be observed for other metasilicates.

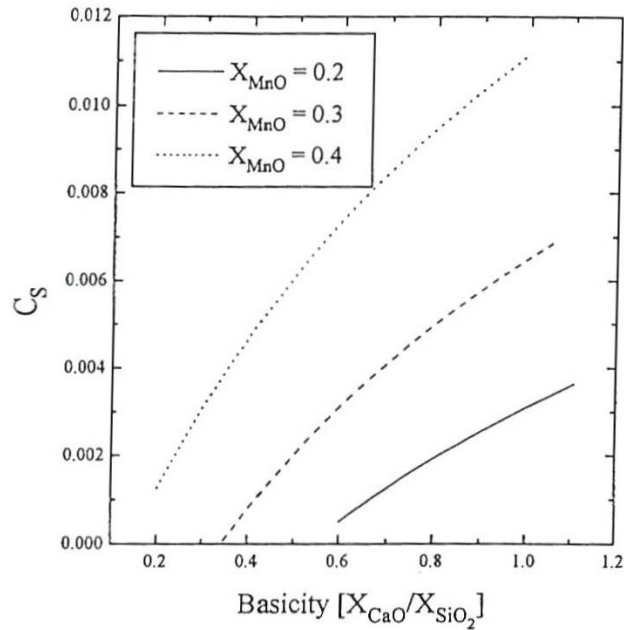


Figure 2.15 Model predictions with respect to the variations of C_S as a function of basicity for a given slag composition (Nilsson et al., 1994a)

According to the analysis of Figure 2.18, the sulphide capacities of slags should reduce when CaO in the slags is replaced by MgO. The influence of Al_2O_3 on the sulphide capacity of Al_2O_3 -CaO- SiO_2 system at 1600°C is presented Figure 2.18. The sulphide capacity increases with increasing Al_2O_3 content when the basicity ratio ($X_{\text{CaO}}/X_{\text{SiO}_2}$) is smaller than 1. However, the trend tends to reverse into opposite direction at higher basicity ratios. This can be related to the amphoteric nature of alumina which can react as either an acid or base depends on the slag basicity (Nilsson et al., 1995b).

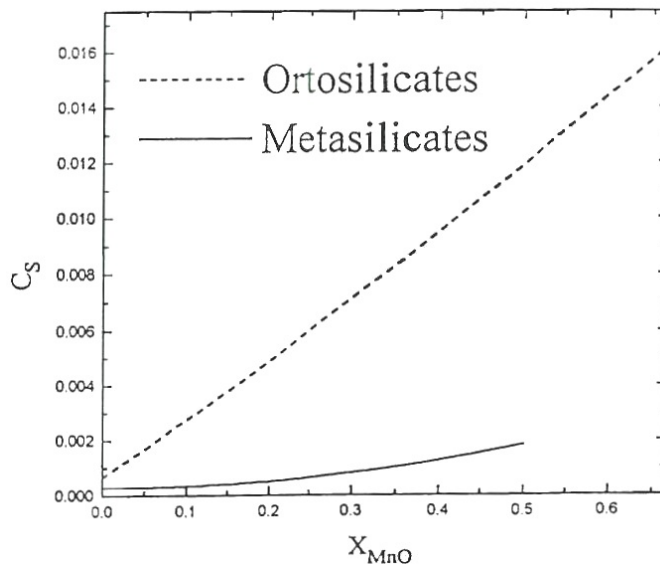


Figure 2.16 The variation of sulphide capacity values calculated by the present model as CaO in the slag is replaced by MnO in the case of ortho-and metasilicates (Nilsson et al., 1994a)

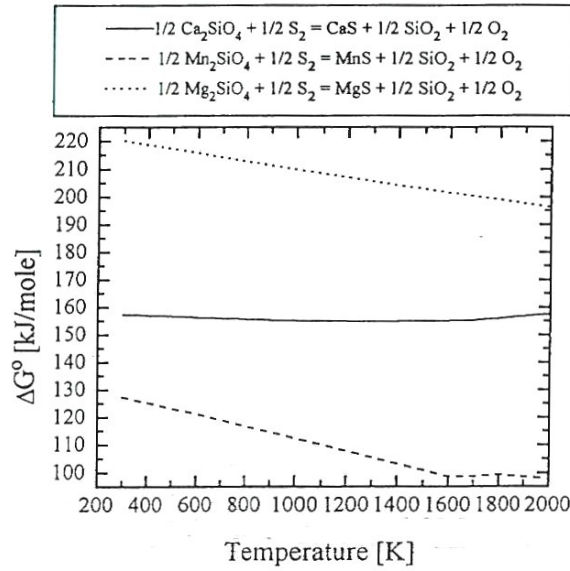


Figure 2.17 ΔG° -T diagram for the reactions between orthosilicates of Ca, Mg, Mn, $S_{2(g)}$ to form CaS, MnS and MgS (Nilsson et al., 1994a)

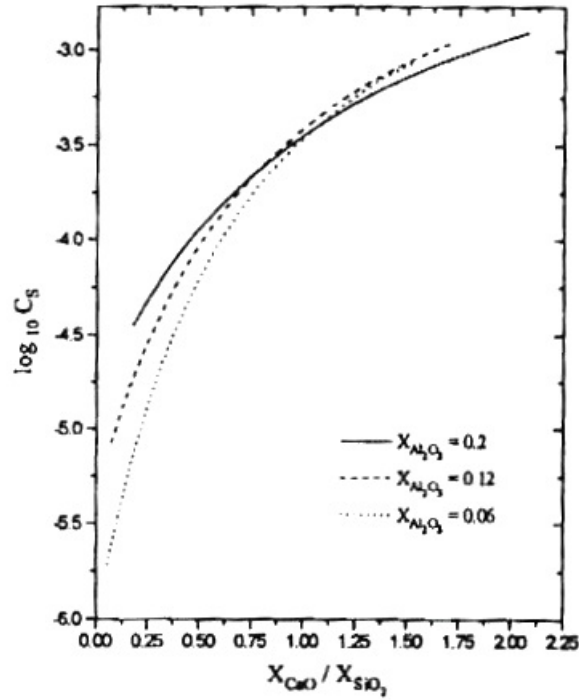


Figure 2.18 Sulphide capacity as a function of basicity at constant $X_{Al_2O_3}$ for different Al_2O_3 contents in the Al_2O_3 -CaO-SiO₂ system at 1600°C (1873 K) (Nilsson et al., 1995b)

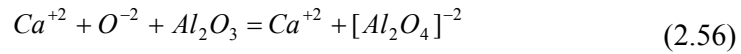
The sulphur-oxygen exchange reaction between gas and slag phase can be described as reaction (Eq. 2.19) and the relevant sulphide capacity of the slag can be defined by using Eq. 2.30 in terms of the partial pressures of sulphur and oxygen in the gas phase. This approach allows determining the sulphide capacity of the slag experimentally by equilibrating the slag with a gas mixture of known partial pressures of sulphur and oxygen and analysing the sulphur content of the same slag. However, comparison of experimental results of different slag system's sulphide capacities can be difficult in view of the fact that experiments have conducted at different conditions such as temperature and partial pressures of sulphur and oxygen. In order to compare different experimental results, an empirical model can be developed. Drakaliysky et al. (1996) used Abraham et al. (1960)'s approach which expressed the sulphide capacities in terms of the mole fractions of sulphide, thus defining the term of molar sulphide capacity (C'_s). This approach avoids considering the differing atomic weights of slag components and gives a better correlation between the structure of the slag and its sulphur capacity (Drakaliysky et al., 1996).

Drakaliysky et al. (1996) determined the sulphide capacities of the CaO-Al₂O₃ binary slag system at 1 500°C (1 773 K) and 1 575°C (1 848 K). Sulphide capacities are defined as molar sulphide capacity, C'_s as:

$$C'_s = \left(\frac{n_s}{n_{CaO} + n_{Al_2O_3}} \right) \left(\frac{P_{O_2}}{P_{S_2}} \right)^{1/2} \quad (2.55)$$

where n_i , represents the number of moles of component i.

Figure 2.19 represents the molar sulphide capacities at 1 500°C and 1 575°C as a function of slag composition. The results show that the molar sulphide capacity increases with the raise of temperature and decreases with the increase of Al₂O₃ content in the melt. This indicates that more O⁻² ions get attached to [Al₂O₄]⁻² units as the Al₂O₃ content increases according to the reaction (2.56). It is reasonable to expect that reaction (Eq. 2.56) would decrease the activities of CaO and Al₂O₃ in the melt.



The effect of temperature on the sulphide capacity is presented in Figure 2.20. Higher degree of dissociation leads to escalate the sulphide capacities of the slag system.

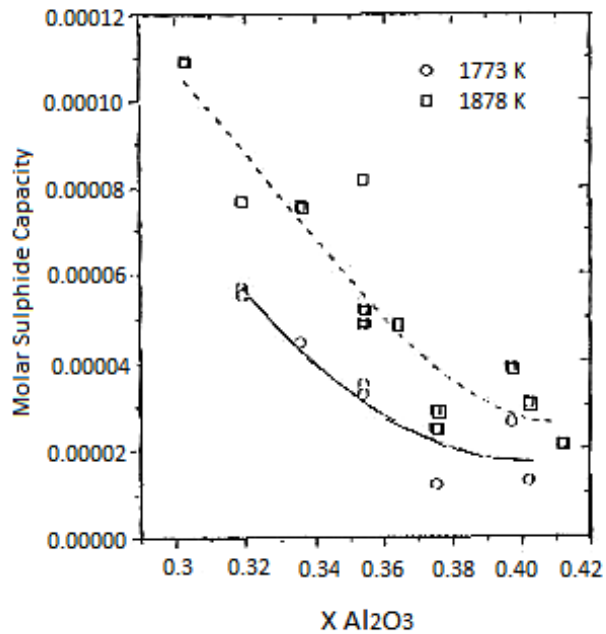


Figure 2.19 Molar sulphide capacity C'_s vs. $X_{Al_2O_3}$ at 1 500 and 1 575 °C . Drakaliysky et al. (1996)

Drakaliysky et al. (1997) conducted experiments to determine the sulphide capacity values of the Al_2O_3 -CaO-SiO₂ between 1 500 and 1 650°C under CO-CO₂-SO₂-Ar gas mixture. Figure 2.21 shows the experimental slag compositions and relevant sulphide capacities of Al_2O_3 -CaO-SiO₂ between at 1 500 °C. A good correlation between experimentally determined sulphide capacity values and model predicted values can be seen in Figure 2.21. As it is seen in this plot, a good correlation between the model and experimental results exist. Results from Young et al. (1992) and Sosinsky and Sommerville (1986) are also included.

Their results indicate considerably lower sulphide capacities compared to the values predicted by the model and experimental sulphide capacities.

As discussed in Drakaliysky et al. (1996) study, it is hard to determine sulphide capacities of complex slag systems. Also, the empirical equations which use optical basicity could often lead to uncertainties in the estimation of sulphide capacity of slag. Therefore, a theoretical model was developed in the Division of Theoretical Metallurgy at the Royal Institute of Technology, Sweden which allows the estimation of the sulphide capacities of complex slags from lower order slag systems. This model is highly empirical and the application of the model requires experimental data for the sulphide capacities of simpler slag systems in order to calculate the complex slag systems.

Nilsson et al. (1997) demonstrates the KTH (Royal Institute of Technology, Sweden) model calculation. Also, Figure 2.22 shows the influence of the replacement of CaO by MgO and MnO at constant Al_2O_3 ($X_{\text{Al}_2\text{O}_3}=0.05$) and SiO_2 ($X_{\text{SiO}_2}=0.47$) contents at 1 600°C (1 873 K). The sulphide capacity increases when CaO is replaced with MnO. This trend is in good correlation with a previous study conducted by Nilsson et al. (1994a).

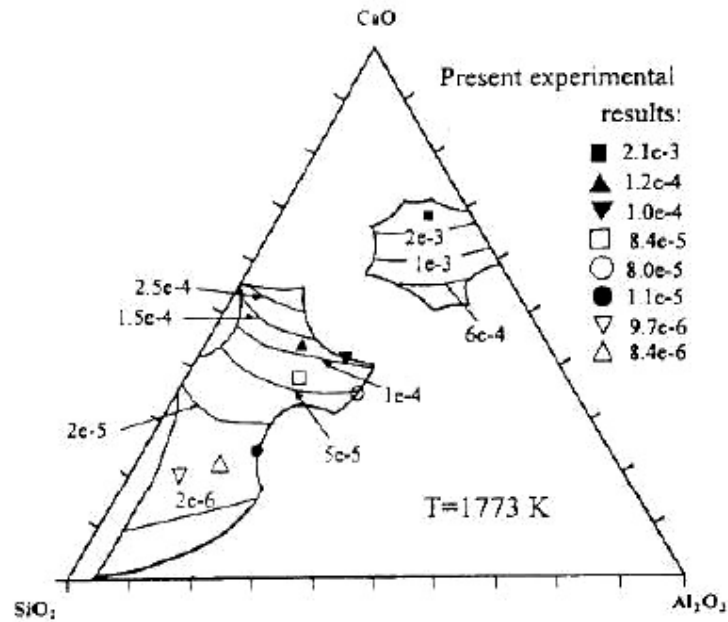


Figure 2.20 Sulphide capacities of Al_2O_3 -CaO-SiO₂ slags at 1500 °C (Drakaliysky et al., 1997)

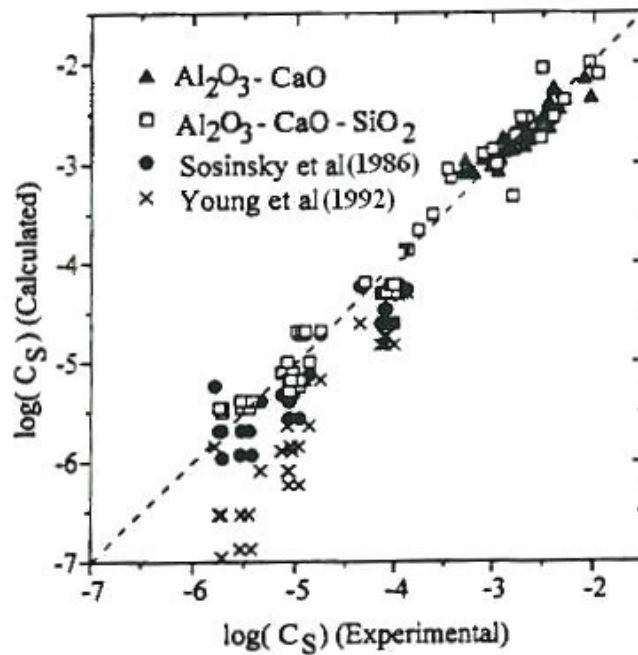


Figure 2.21 A plot of calculated $\log C_S$ against the experimental values of $\log C_S$. (Drakaliysky et al., 1997)

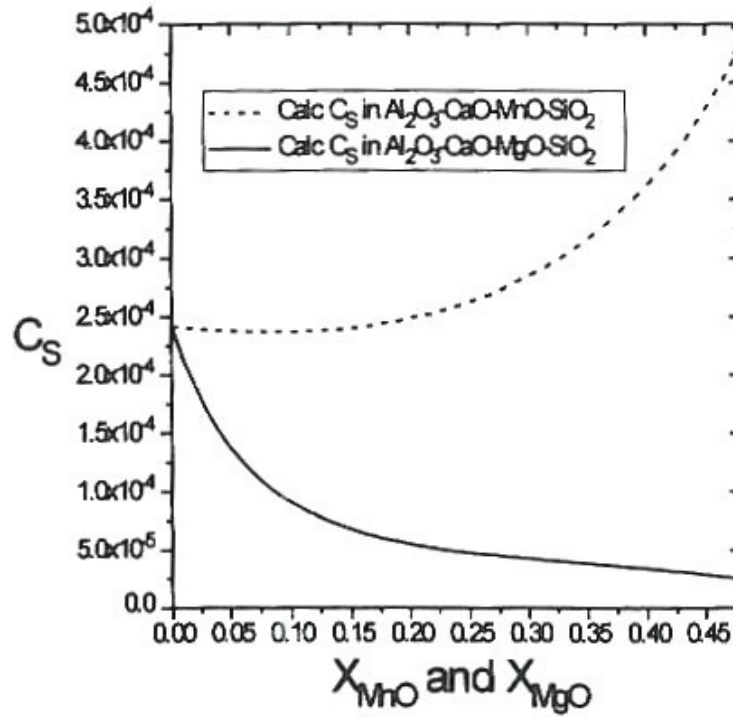


Figure 2.22 Effect of the replacement of CaO by MgO or MnO at constant Al_2O_3 and SiO_2 contents in the four component slags as computed by the KTH model ($X_{\text{Al}_2\text{O}_3}=0.05$ and $X_{\text{SiO}_2}=0.47$) (Nilsson et al., 1997)

In the KTH sulphide capacity model, the sulphide capacity of a slag can be described as:

$$C_s = \exp\left(\frac{-\Delta G^o}{RT}\right) \cdot \left(\frac{a_{\text{o}^{-2}}}{f_s^{-2}}\right) \quad (2.57)$$

where $a_{\text{o}^{-2}}$ is the activity of oxygen ions in the slag, f_s^{-2} is the activity coefficient of sulphide ions in the slag, R is the gas constant, T is the temperature in degree Kelvin and ΔG_o of reaction (2.21) is expressed as:

$$\Delta G_{2,21}^o = 118535 - 58.8157T \quad (\text{J/mol}) \quad (2.58)$$

The ratio of activity of O^{-2} to the activity coefficient of S^{-2} is expressed as

$$\frac{a_{O^{-2}}}{f_{S^{-2}}} = \exp\left(-\frac{\xi}{RT}\right) \quad (2.59)$$

For uniary systems, the parameter ξ is described as a function of temperature (Eq. 2.60) and in the case of multi-component systems, it is a function of both temperature and composition (2.61):

$$\xi = {}^1L + {}^2LT \quad (2.60)$$

$$\xi = \sum X_i \xi_i + \xi_{Mix} \quad (2.61)$$

where X_i is the mole fraction of component i in the multicomponent system. ξ_{Mix} is expressed as polynomials in both composition and temperature. For a given system, the interaction parameters can be optimised using the experimentally determined sulphide capacities. The interaction parameters for several uniary, binary and ternary slag systems were presented in various studies by KTH researchers (Nilsson et al., 1994a; Nilsson et al., 1995a; Nilsson et al., 1995b; Nilsson et al., 1997; Drakaliysky et al., 1996; Drakaliysky et al., 1997; Nzotta, 1997a; Nzotta, 1997b; Nzotta et al., 1997c; Nzotta et al., 1998; Nzotta et al., 1999a; Nzotta et al., 1999b; Nzotta et al., 2000). A summary of the model parameters from these studies is given in Table 2.4.

In KTH model, the modified Temkin (1945) approach has been used to describing the liquid slag that considers the mixing of cations and anions within each of their sub groupings. The ionic solution can be described by the following formula:

$$(C_1, C_2, \dots, C_i, \dots, C_N)P(A_1, A_2, \dots, A_j, \dots, A_M)Q \quad (2.62)$$

P and Q represent the coefficients determined by stoichiometric considerations where $C_1, \dots, C_N$ represent different cations, and $A_1, \dots, A_M$ represent different

anions. The ionic fraction of cation C_i within the cation grouping is expressed as follows:

$$y_{Ci} = \frac{N_{Ci}}{\sum N_c} \quad (2.63)$$

where N is the number of ions and the summation covers all the cations that exist in the system. The ionic fraction of anion A_j within the anion group can be defined as follows:

$$y_{Aj} = \frac{N_{Ai}}{\sum N_A} \quad (2.64)$$

Table 2.4 Summary of KTH Model Parameters

Al ₂ O ₃	1.58E+05			
CaO	-3.31E+04			
MgO	9.57E+03			
MnO	-3.66E+04			
SiO ₂	1.69E+05			
Al ₂ O ₃ -CaO		9.83E+04		
Al ₂ O ₃ -MnO		4.34E+05		2.49E+02
Al ₂ O ₃ -SiO ₂		1.87E+05		
CaO-SiO ₂		9.73E+04	7.29E+01	
MgO-SiO ₂		6.97E+05	-2.24E+02	
MnO-SiO ₂		-3.23E+05	2.12E+02	1.35E+05
FeO-SiO ₂		-3.85E+05	2.09E+02	1.62E+05
FeO-CaO		1.74E+02	9.32E+01	-1.15E+05
FeO-MnO		8.48E+05	-3.48E+02	
Al ₂ O ₃ -CaO -MgO		4.17E+06	-1.07E+03	-3.04E+06
Al ₂ O ₃ -MgO-SiO ₂		1.57E+05		
Al ₂ O ₃ -MnO-SiO ₂		1.57E+06		
Al ₂ O ₃ .CaO-SiO ₂		-2.04E+06		
Al ₂ O ₃ -MgO-MnO		-1.56E+06		
CaO-MgO-SiO ₂		-1.53E+06	6.72E+02	1.48E+06
CaO-MnO-SiO ₂		-1.18E+06	6.21E+02	-1.19E+06
MgO-MnO-SiO ₂		9.10E+06	-4.43E+03	-2.87E+06
FeO-CaO-SiO ₂		-1.22E+06	6.50E+02	-1.51E+06
FeO-MnO-SiO ₂		-8.24E+05	1.64E+02	7.22E+05
FeO-MgO-SiO ₂		1.55E+06	-1.13E+03	1.43E+06
FeO-Al ₂ O ₃ -SiO ₂		-2.62E+06	1.47E+03	-2.77E+06

ξ_{Mix} represents the variation of ξ due to the interactions between different species and can be expressed as:

$$\begin{aligned} \xi_{Mix} = & (\sum \sum \sum y_{Ci1} y_{Ci2} y_{Aj} L_{Ci1, Ci2(Aj)} L_{Ci1, Ci2(Aj)} + \sum \sum \sum y_{Ci} y_{Aj1} y_{Aj2} L_{Aj1, Aj2(Ci)}) + \\ & (\sum \sum \sum \sum y_{Ai1} y_{Ai2} y_{Ai3} y_{Cj} L_{Ci1, Ci2, Ci3(Aj)} + \sum \sum \sum \sum y_{Aj1, y_{Aj2}, y_{Aj3}, y_{Ci} L_{Aj1, Aj2, Aj3(Ci)}) + \dots \end{aligned} \quad (2.65)$$

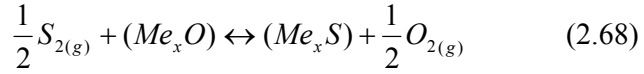
In order to predict the sulphide capacity of multi-component slag systems (FeO-MnO-CaO-MgO-SiO₂-Al₂O₃) binary and ternary interactions between the different species are introduced into the model as can be seen in (2.66):

$$\begin{aligned} RT \ln C_s = & -\Delta G^o - [X_{Al_2O_3} \cdot 157705.28 - X_{CaO} \cdot 33099.43 + X_{MgO} \cdot 9573.07 \\ & - X_{MnO} \cdot 36636.46 + X_{SiO_2} \cdot 168872.59] - \{(\xi_{Al_2O_3-CaO}) + (\xi_{Al_2O_3-SiO_2}) + \\ & (\xi_{Al_2O_3-MnO}) + (\xi_{CaO-SiO_2}) + (\xi_{MgO-SiO_2}) + (\xi_{MnO-SiO_2}) + (\xi_{CaO-FeO}) + \\ & (\xi_{MnO-FeO}) + (\xi_{FeO-SiO_2}) + (\xi_{Al_2O_3-CaO-MgO}) + (\xi_{Al_2O_3-CaO-SiO_2}) \\ & + (\xi_{Al_2O_3-MgO-SiO_2}) + (\xi_{Al_2O_3-MgO-MnO}) + (\xi_{Al_2O_3-MnO-SiO_2}) \\ & + (\xi_{CaO-MgO-SiO_2}) + (\xi_{CaO-MnO-SiO_2}) + (\xi_{MgO-MnO-SiO_2}) \\ & + (\xi_{Al_2O_3-FeO-SiO_2}) + (\xi_{CaO-FeO-SiO_2}) + (\xi_{MgO-FeO-SiO_2}) + (\xi_{MnO-FeO-SiO_2}) \} \end{aligned} \quad (2.66)$$

where X stands for mole fraction, y denotes the cation fraction in the cationic sub-grouping defined as follows:

$$y_i = \frac{N_i}{\sum_{j=1}^n N_j} \quad (2.67)$$

Nilsson et al. (1994a) defined a modified sulphide capacity concept for binary slags with a large difference in the basicity of the oxide components. The modified model suggests that sulphur reacts only with the most basic oxide according to the following reaction where it is a rewritten form of reaction (2.21):



The combination of the equation for the equilibrium constant of reaction (2.68) and Eq. (2.27) gives the following expression

$$K_{2.68} = \left(\frac{k(\text{wt}\%S)\bar{W}\gamma_{Me_xS}}{a_{Me_xO}} \right) \left(\frac{P_{O_2}}{P_{S_2}} \right)^{1/2} = \left(\frac{k\bar{W}C_s\gamma_{Me_xS}}{a_{Me_xO}} \right) \quad (2.69)$$

where γ_{Me_xS} is the activity coefficient of Me_xS , a_{Me_xO} is the activity of Me_xO , k is a constant and $\bar{W}$ is the average molecular mass of slag. Reaction (2.68) indicates that the product $C_s\bar{W}$ should be proportional to the activity of Me_xO when $\gamma_{s^{-2}}$ is independent of the composition. This formulation is easy to apply due to the readily availability of equilibrium constant from standard thermodynamic data for pure liquid sulphide and oxide.

Nzotta et al. (1997c) calculated the product $C_s\bar{W}$ in $MgO-SiO_2$, $CaO-SiO_2$ and $MnO-SiO_2$ systems and these are plotted as functions of the activities of the corresponding basic oxides in Figure 2.23 at 1 650°C. The results show good correlation between activities of oxides and $C_s\bar{W}$. Mg^{+2} has the lowest affinity for sulphur among Mg^{+2} , Ca^{+2} and Mn^{+2} and at constant SiO_2 content, the sulphide capacity decreases when CaO is replaced by MgO . The Gibbs energy changes of sulphide formation reactions for corresponding silicates given in Figure 2.17 (Nilsson et al, 1994a). The higher affinity of Ca^{+2} for sulphur compared with Mg^{+2} can be seen in Figure 2.24 for the ternary slag system. The experimental results illustrated in Figure 2.24 in a good agreement with Nilsson et al. (1994a).

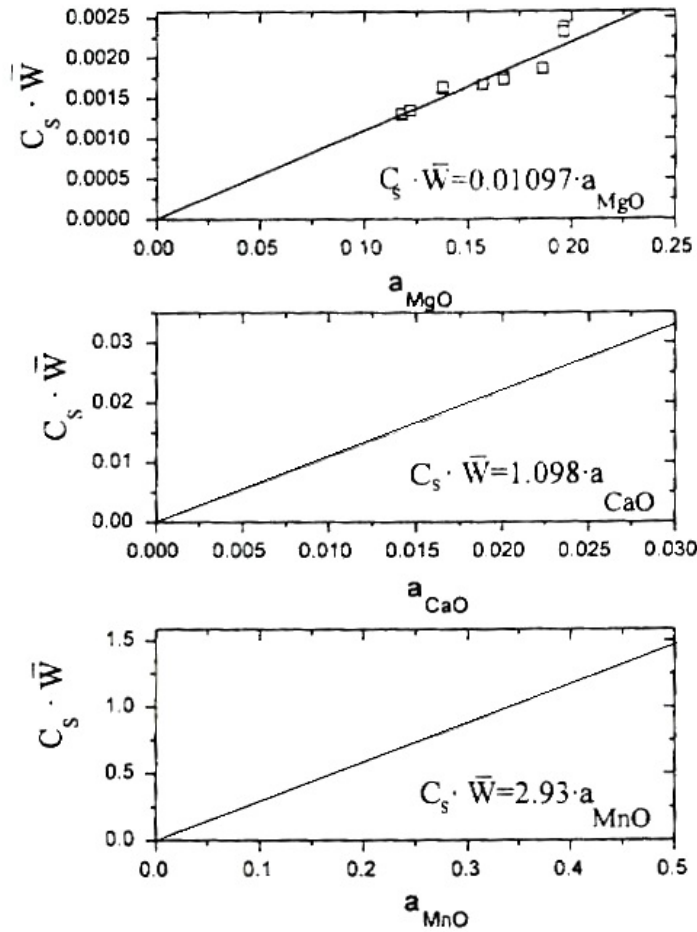


Figure 2.23 Relation between $C_s \cdot \bar{W}$ and oxide activities in MgO-SiO₂, CaO-SiO₂ and MnO-SiO₂ melts at 1 650°C: standard state for basic oxides is a pure solid (Nzotta et al., 1997c).

Nzotta (1997a) investigated the sulphide capacities of MgO-MnO-SiO₂ and MgO-MnO-CaO-SiO₂ slag systems at 1 600 and 1 650°C. Figures 2.25 and 2.26 show sulphide capacity values (experimentally determined, model predicted and previous literature) for the ternary MgO-MnO-SiO₂ system. Figure 2.27 and 2.28 present the iso- C_s curves obtained from previous studies and experimentally determined values in this study. For the similar slag compositions, the previous study results on sulphide capacities are lower than the model predicted values (Figure 2.27). The sulphide capacity values of the previous work at 1 650°C are

considerably different compared to the model predicted results (Figure 2.28). In order to obtain sulphide capacities of ternary MgO-MnO-SiO₂ slag from KTH's model, the binary interactions between Mg⁺²-Si⁺⁴, Mg⁺²-Mn⁺² and Mn⁺²-Si⁺⁴ need to be considered. However, the binary interactions for Mg⁺²-Mn⁺² could not be determined as the liquidus temperatures are very high for this system. Nzotta ignored this interaction for the model calculations as a result of lack of information. Therefore, previous experimental studies results can be different from KTH's model predicted values. All results indicate that the sulphide capacity tends to increase with the increase of MnO content in the slag system. A similar trend has been observed in several other studies (Nilsson et al., 1994a; Nilsson et al., 1995a; Nilsson et al., 1995b; Nilsson et al., 1997).

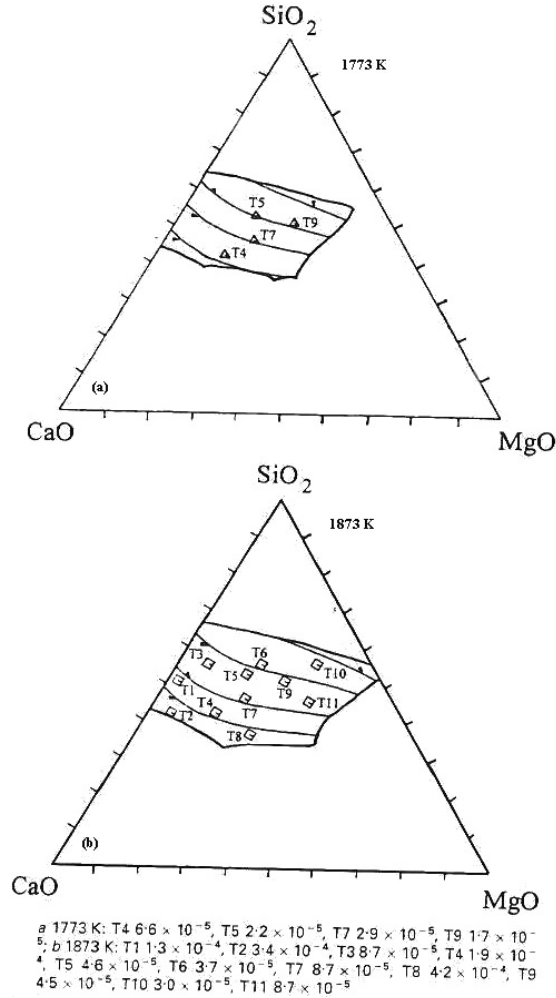


Figure 2.24 Iso-C_S diagrams for CaO-MgO-SiO₂ ternary system at given temperatures (Nzotta et al., 1997c).

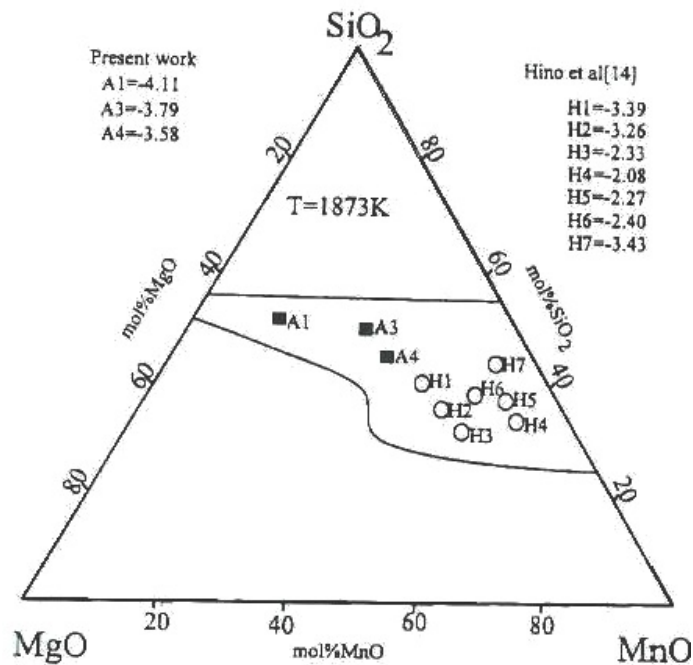


Figure 2.25 The present experimental values (log₁₀Cs) compared with those reported by Hino et al. (1993) at 1 600°C (1 873 K) (Nzotta, 1997a)

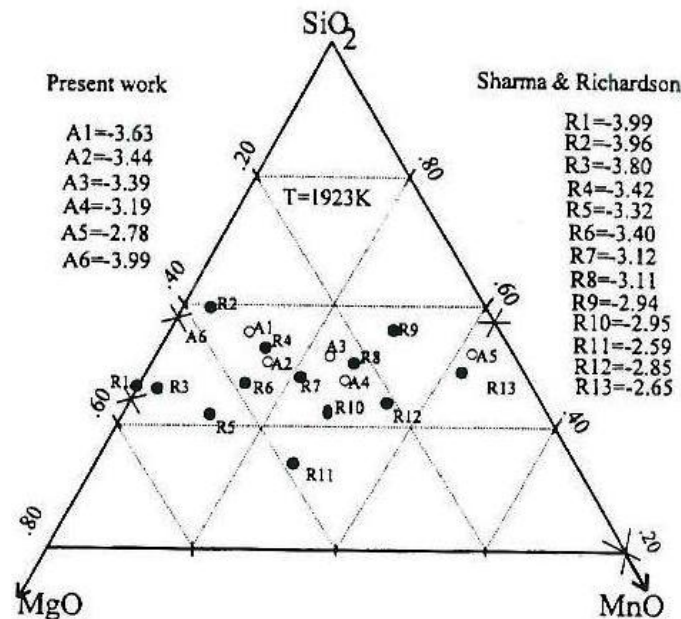


Figure 2.26 The present experimental values (open circles) compared with those reported by Sharma and Richardson (1965) (closed circles) at 1 650°C (1 923 K) (Nzotta, 1997a)

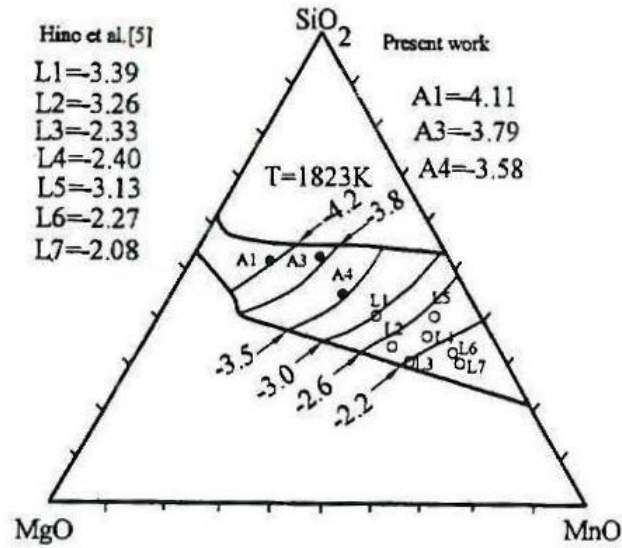


Figure 2.27 The iso-sulphide capacity calculated using the model in the case of MgO-MnO-SiO₂ at 1 550°C (1 823 K) (Nzotta, 1997a)

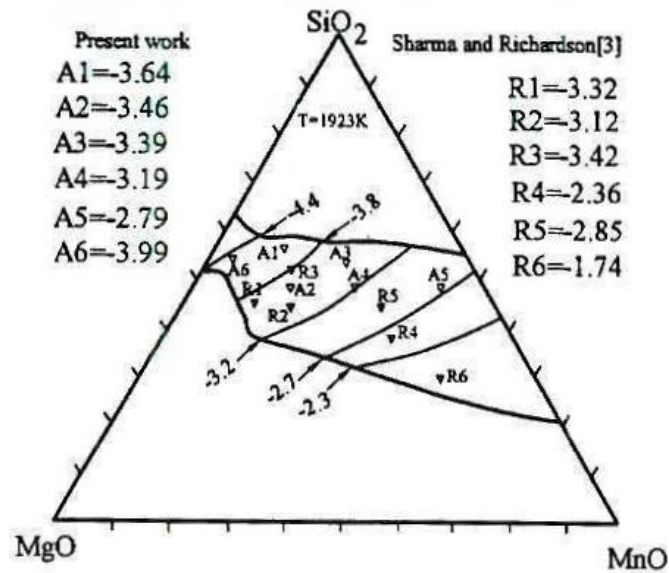
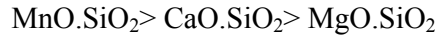


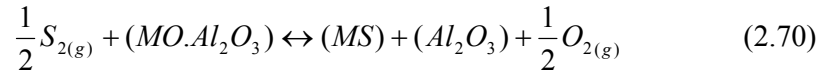
Figure 2.28 The iso-C_s calculated using the model in the case of MgO-MnO-SiO₂ at 1 650°C (1 923 K) (Nzotta, 1997a)

Nzotta (1997b) determined the sulphide capacities of Al₂O₃-MgO-SiO₂, Al₂O₃-MnO-SiO₂ and Al₂O₃-CaO-MgO ternary slag systems between 1 500°C and 1 650°C. Figures 2.29, 2.30 and 2.31 represent the corresponding iso-C_s curves. The sulphide capacity decreases when CaO is replaced by MgO at low Al₂O₃

contents ($X_{Al_2O_3} < 0.3$), whereas at higher Al_2O_3 contents, the replacement of CaO by MgO leads to higher sulphide capacity values for a given slag composition. Figures 2.32 and 2.33 present the iso- C_S curves for Al_2O_3 -MnO- SiO_2 at 1 550°C and 1 600°C, respectively. The sulphide capacity has a tendency to drop when Al_2O_3 replaces MnO. This may be attributed to the high affinity for sulphur by MnO in the slag system. The iso-sulphide capacity contours calculated by using the KTH model for the Al_2O_3 -CaO-MgO ternary slag system at 1 600°C and 1 650°C) are illustrated in Figures 2.34 and 2.35, respectively. In the absence of alumina in the slag system, the sulphide capacities of binary metasilicates follow the order of



This trend can be seen in Figure 2.17. However, when Al_2O_3 is introduced into the slag system to the following reaction prevails:



The standard Gibbs energy changes for the reaction (2.70) are given in Figure 2.36 which indicating higher sulphide capacity of calcium aluminate melts.

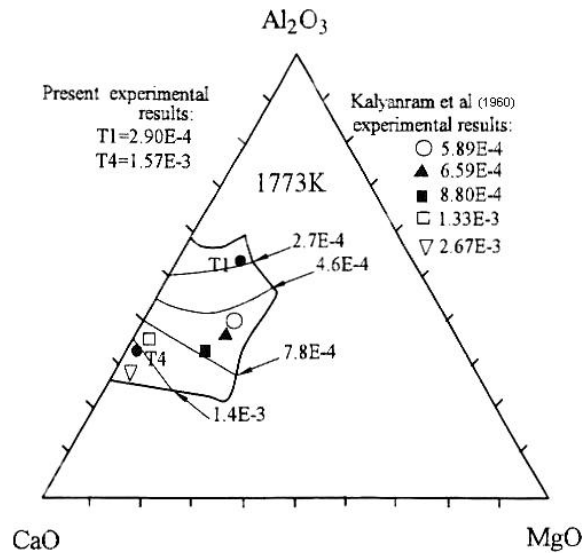


Figure 2.29 Iso- C_S curved for Al_2O_3 -CaO-MgO at 1 500°C (1 773 K) (Nzotta, 1997b)

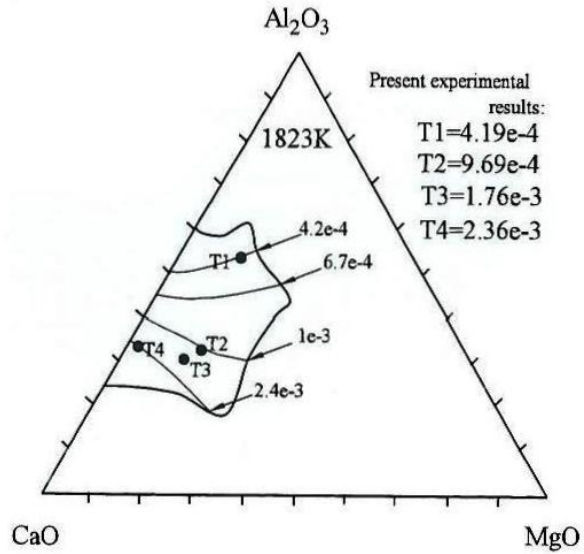


Figure 2.30 Iso- C_s curved for Al_2O_3 -CaO-MgO at 1 550°C (1823 K) (Nzotta, 1997b)

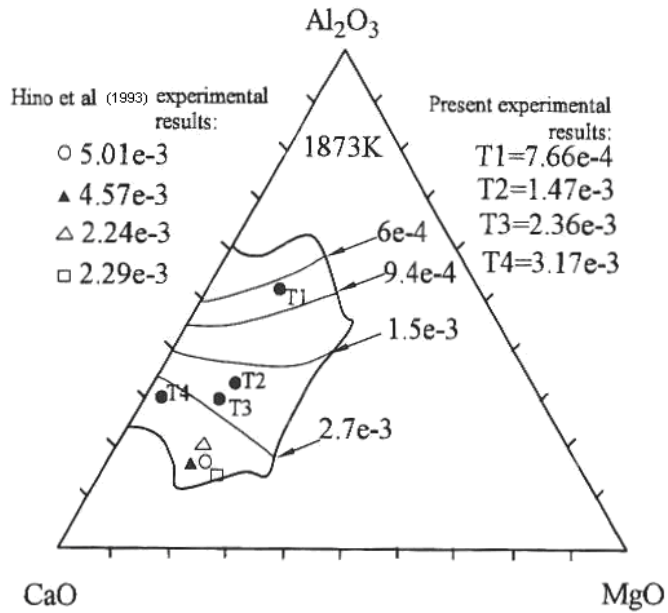


Figure 2.31 Iso- C_s curved for Al_2O_3 -CaO-MgO at 1 600°C (1 873 K) (Nzotta, 1997b)

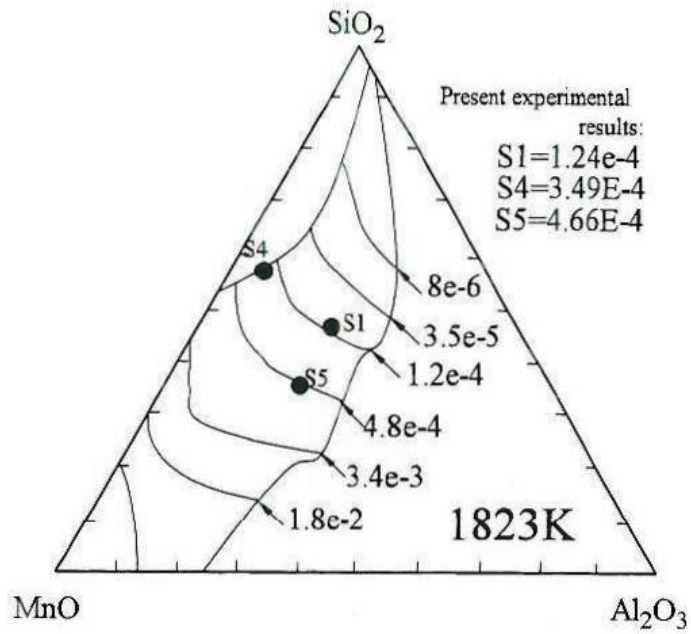


Figure 2.32 Iso- C_S curved for Al_2O_3 - MnO - SiO_2 at $1\ 550^\circ\text{C}$ (1823 K) (Nzotta, 1997b)

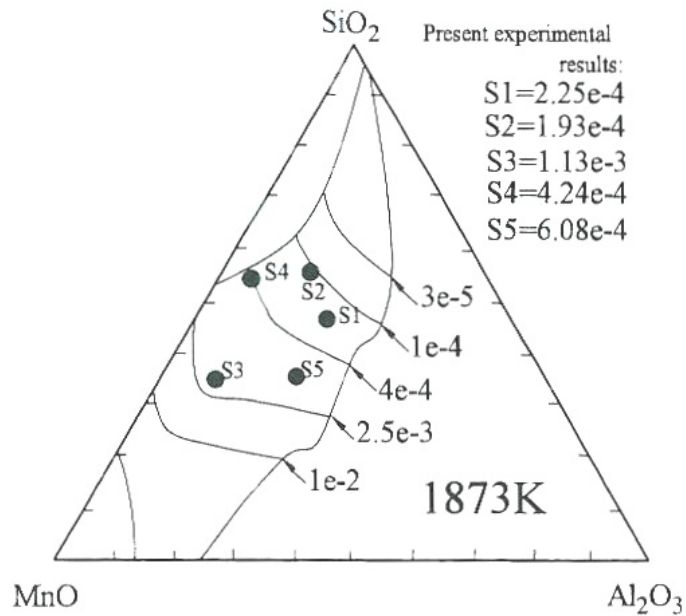


Figure 2.33 Iso- C_S curves for Al_2O_3 - MnO - SiO_2 at $1\ 600^\circ\text{C}$ ($1\ 873\text{ K}$) (Nzotta, 1997b)

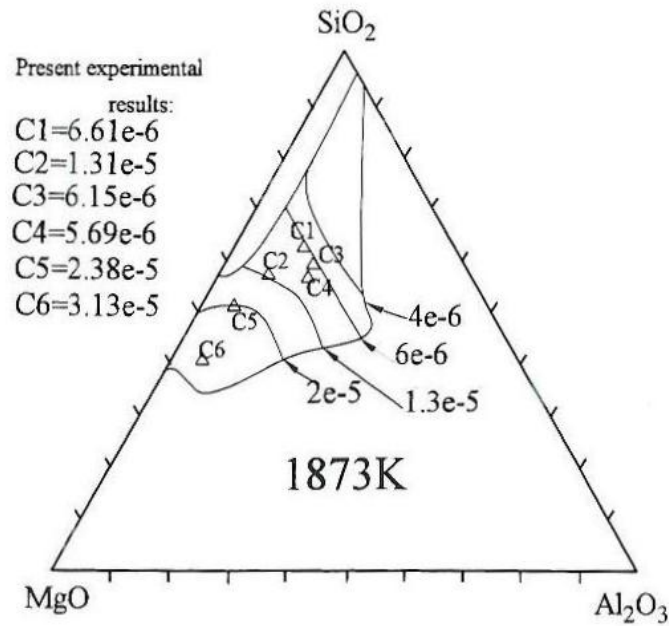


Figure 2.34 Iso-sulphide capacity contours calculated using the KTH model for the Al_2O_3 - SiO_2 - MgO ternary slag system at 1 600°C (1 873 K) (Nzotta, 1997b)

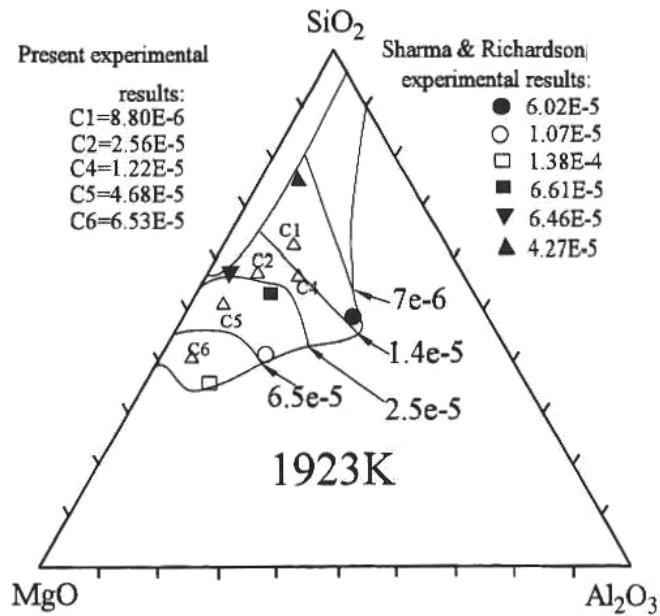


Figure 2.35 Iso-sulphide capacity contours calculated using the KTH model for Al_2O_3 - SiO_2 - MgO ternary slag system at 1 650°C (1 923 K) (Nzotta, 1997b)

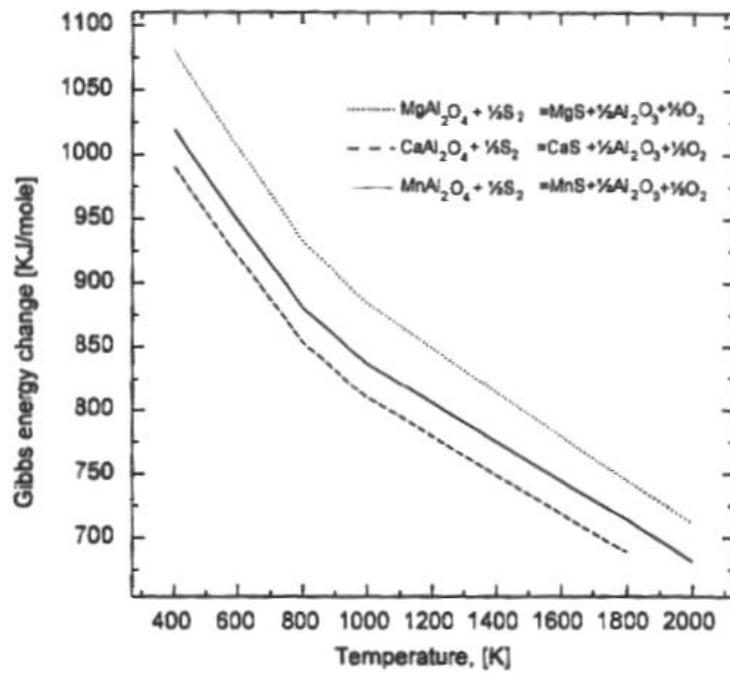
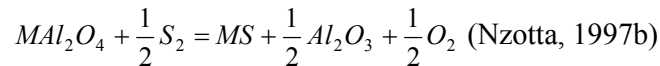


Figure 2.36 The standard Gibbs energy changes for the reaction



Nzotta et al. (1998) measured the sulphide capacities of Al_2O_3 -MnO, Al_2O_3 -MnO-MgO, Al_2O_3 -CaO-MgO-MnO, Al_2O_3 -CaO-MgO-SiO₂, Al_2O_3 -CaO-MnO-SiO₂ and Al_2O_3 -CaO-MgO-SiO₂-MnO systems between 1500°C to 1650°C under the Ar-CO-CO₂-SO₂ gas mixture. For the Al_2O_3 -CaO-MgO-MnO slag system, higher MnO content results a higher value of C_S . Iso- C_S curves of this group of slags (Figure 2.37 and 2.38) show that slags with less than 10 wt. % SiO₂ and 50 wt. % CaO, have higher sulphide capacities. The experimental data showed a slight deviation from the model. The interactions between cations of basic oxides like Ca^{+2} , Mn^{+2} and Mg^{+2} can not be determined due to the high liquidus temperatures in the corresponding binary and ternary slag systems which difficult to measure the sulphide capacities.

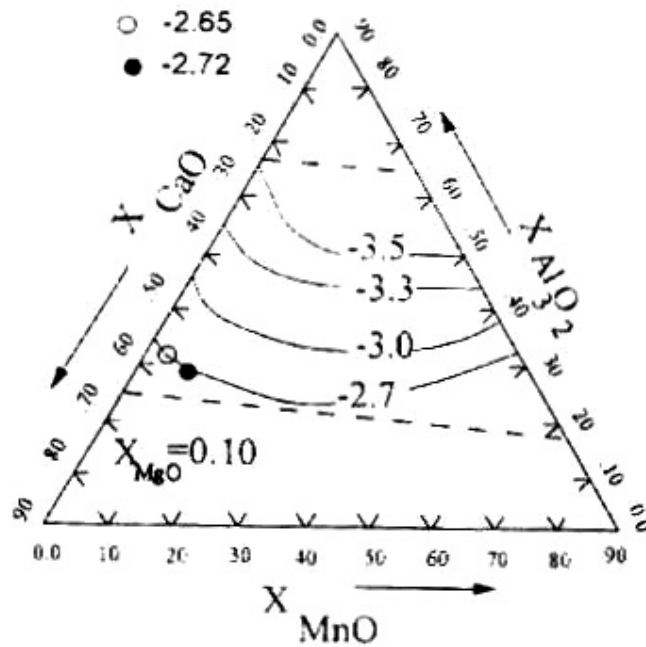


Figure 2.37 Iso- C_S lines for the Al_2O_3 -CaO-MgO-MnO slag system at 1600°C with $X_{\text{MgO}}=0.1$ (Nzotta et al., 1998)

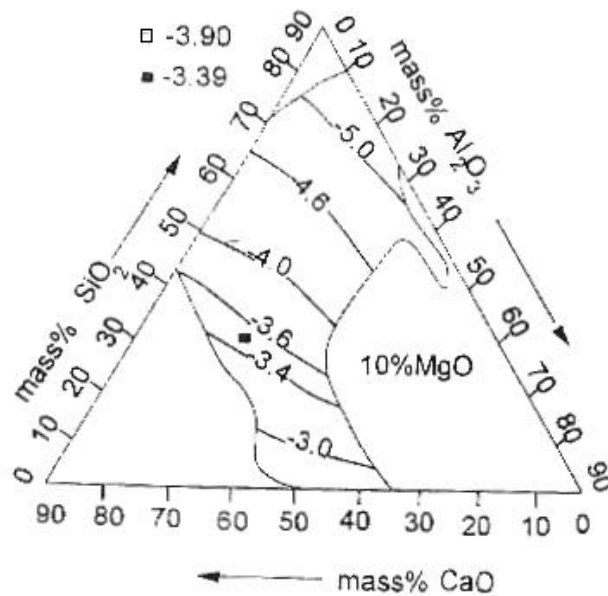


Figure 2.38 Iso- C_S lines for the Al_2O_3 -CaO-MgO-MnO slag system at 1600°C with $X_{\text{MgO}}=0.1$ (Nzotta et al., 1998)

Nzotta et al. (1999a) determined relationships for the sulphide capacities of FeO-SiO₂, FeO-CaO, FeO-MnO melts by equilibrating the melts with a gas mixture of CO, CO₂, SO₂ and Ar in the range of 1 350°C to 1 650°C. $\sqrt{P_{O_2} / P_{S_2}}$ ranged between 0.0022 and 0.0054 in the gas mixture. The investigators expressed the sulphide capacities of the three binary systems as:

a) FeO-SiO₂

$$RT \ln(C_s) = -1.19 \times 10^5 - 58.8T - (1.69 \times 10^5 X_{SiO_2}) - y_{Fe^{-2}} y_{Si^{-4}} (-3.85 \times 10^5 + 210T) + 1.62 \times 10^5 (y_{Fe^{-2}} y_{Si^{-4}}) \quad (2.71)$$

b) FeO-CaO

$$RT \ln(C_s) = -1.19 \times 10^5 - 58.8T - (3.31 \times 10^5 X_{CaO}) - y_{Fe^{-2}} y_{Ca^{-2}} (174 + 93.2T) + 1.15 \times 10^5 (y_{Ca^{-2}} - y_{Fe^{-2}}) \quad (2.72)$$

c) FeO-MnO

$$RT \ln(C_s) = -1.19 \times 10^5 - 58.8T - (-3.66 \times 10^4 X_{MnO}) - y_{Fe^{-2}} y_{Mn^{-2}} (8.48 \times 10^5 - 348T) \quad (2.73)$$

FeO-MnO slags at 1 500°C have higher sulphide capacities compared to FeO-CaO slags ($X_{FeO} > 0.78$) (Figure 2.39). The threshold value of X_{FeO} drops from 0.78 to 0.58 for the same slag systems when temperature raised to 1 600°C (Figure 2.40) (Nzotta et al., 1999a).

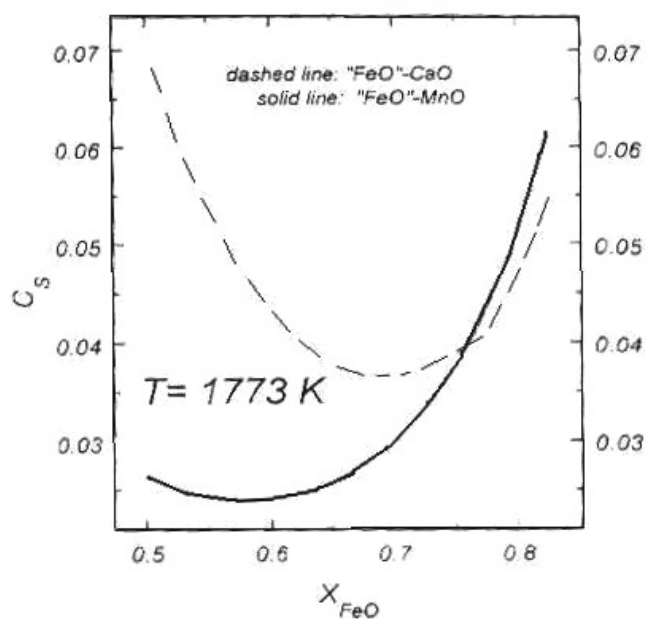


Figure 2.39 Sulphide capacities of the binary systems FeO-CaO and FeO-MnO at 1500°C (1773 K) (Nzotta et al., 1999a).

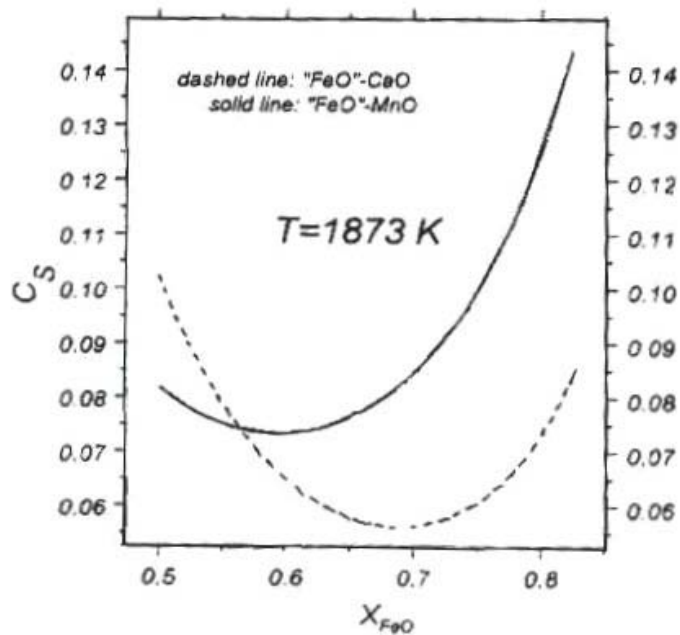


Figure 2.40 Sulphide capacities of the binary systems FeO-CaO and FeO-MnO at 1600°C (1873 K) (Nzotta et al., 1999a).

Nzotta et al. (1999b) determined sulphide capacities of iron oxide containing slags in the FeO-Al₂O₃-SiO₂, FeO-CaO-SiO₂, FeO-MgO-SiO₂ and FeO-MnO-SiO₂ systems between 1 400°C to 1 650°C. $\sqrt{P_{O_2} / P_{S_2}}$ ratios ranged between 107 and 222 in the gas mixture. The experiment results were in a good agreement with the model predicted values.

The KTH model was used to determine the equilibrium sulphur distribution ratio in a specific slag-steel system; the results are close to the predicted values (Figure 2.41). The deviations may be due to the fact that the experimental results are derived from non-equilibrium conditions while the model assumes equilibrium conditions (Nzotta et al., 2000).

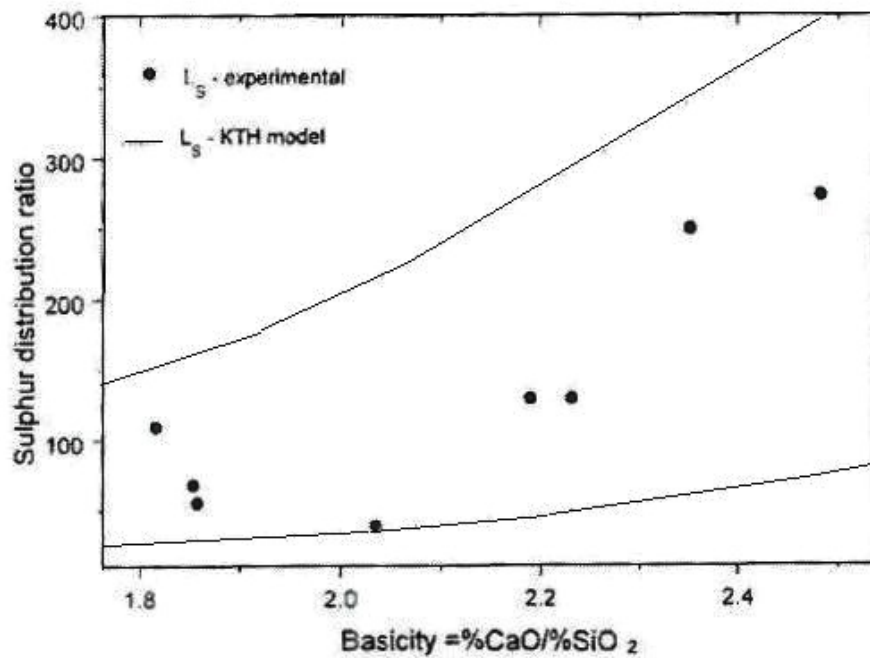


Figure 2.41 Sulphur-distribution ratio as a function of basicity (Nzotta et al., 2000)

Andersson et al. (1999) used the KTH model and the optical basicity approach to predict the sulphur distribution ratio for industrial slags. The results show that the optical basicity approach and KTH model predictions were significantly different

and deviations tend to escalate with increasing slag basicity (Figure 2.42). According to researchers, one parameter would cause these deviations was the oxygen activity in the molten steel. As in their case, KTH's model uses 10^{-5} to 10^{-4} values for oxygen activities. However, the researchers used IRSID model (Gaye et al. 1992) for the estimation of oxygen activities. In order to calculate the sulphur distribution values from the KTH model to agree with the analysis of experimental sulphur distribution values in their case, the oxygen activities must be less than 10^{-4} . The deviation between the measured and calculated sulphur distributions (based on KTH model) is given in Figure 2.43. This figure means that the KTH model calculations predicts higher sulphur distribution values at higher basicities compared to plant data obtained due to implemented oxygen activity. The researchers used a multiple regression equation which was derived from Ohta and Suito (1998) in order to calculate oxygen activities. It is highly possible that the alumina activity might not be appropriate for their slag system which is significantly different from silica content point of view compared to Ohta and Suito's (1998) slag system.

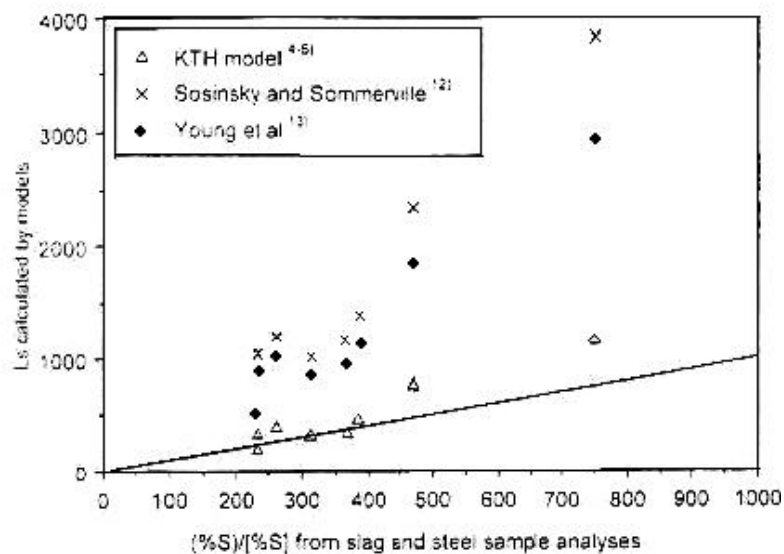


Figure 2.42 Comparison of the KTH model and the optical basicity values at the end of ladle treatment (Andersson et al., 1999)

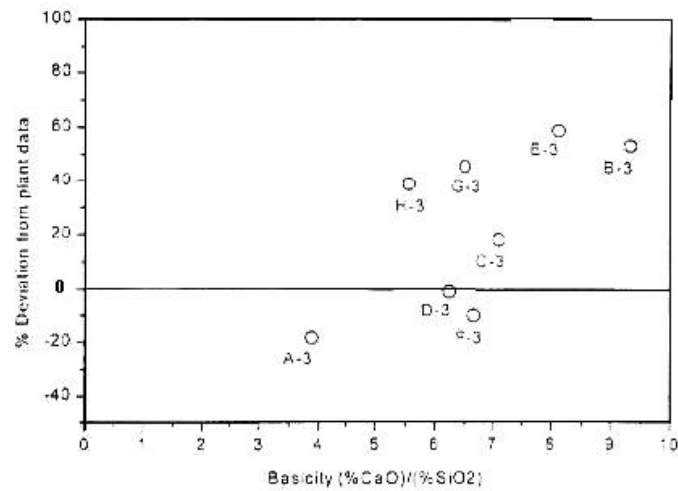


Figure 2.43 Deviation percentage between calculated sulphur distribution ratios (KTH model) and the analysed sulphur distribution ratios as a function of the basicity of the top slag (Andersson et al., 1999)

Andersson et al., (2000) model is used in the prediction of sulphur distribution ratio between slag and metal phases of actual steel plant data (Figure 2.44).

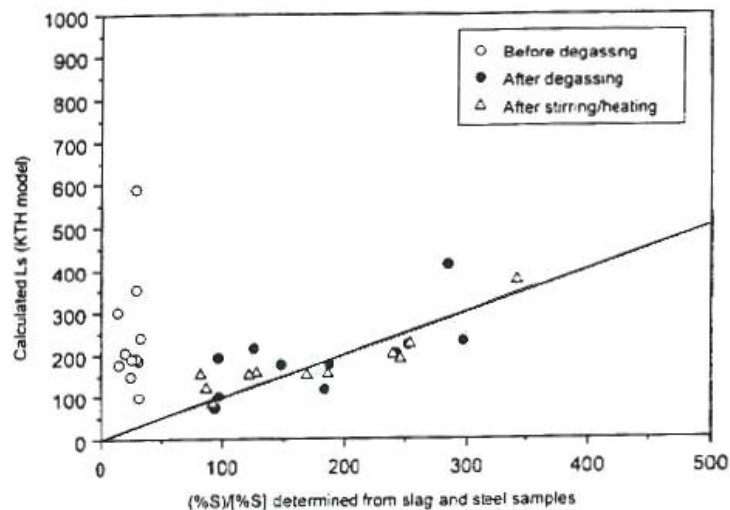


Figure 2.44 Calculated equilibrium sulphur distribution ratio between slag and metal plotted against sulphur distribution determined from slag and steel analysis (Andersson et al., 2000).

Hao et al. (2006) applied the KTH model and optical basicity concept on refining slags in ladle to predict sulphide capacities and sulphur distribution ratios. The predicted L_S from the KTH model agreed well with the measured values.

Shankar et al. (2006) experimentally determined the sulphide capacity of high alumina blast furnace slags in the range of 1 500°C and 1 600°C and derived a linear regression model with the combination of optical basicity and temperature, which is expressed in (2.73). A comparison of experimental and predicted values of sulphide capacity with the estimated values of sulphide capacity by Young's model (1992), Sommerville's model (1994) and the KTH model is given in Figure 2.45. The results show that the proposed linear regression model has better capability for determining the sulphide capacities of high alumina blast furnace slags.

$$C_s = 9.852 \times 10^{-6} (\text{wt.\% Al}_2\text{O}_3) + 0.010574.A - 16.2933 \cdot \frac{1}{T} + 0.002401 \quad (2.73)$$

where T represents temperature in degree Kelvin.

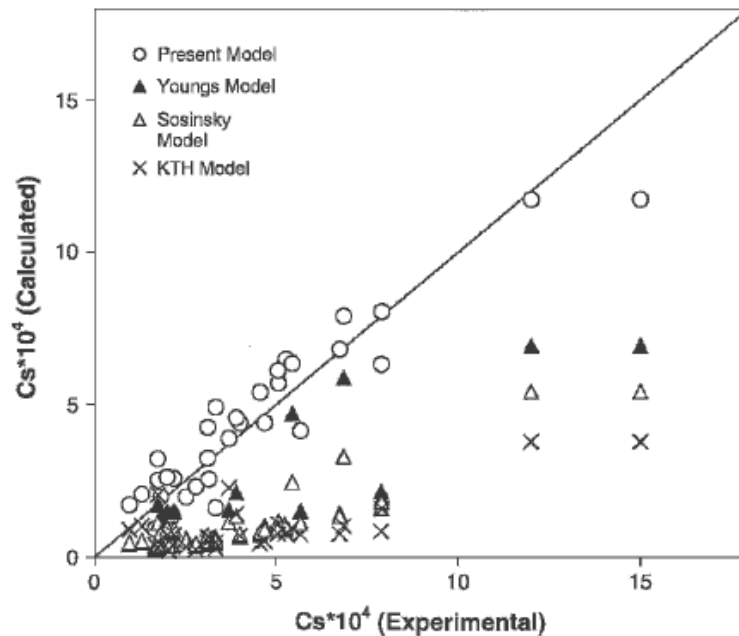


Figure 2.45 Comparison between estimated and measured sulphide capacity for the CaO-SiO₂-MgO-Al₂O₃ system (Shankar et al., 2006)

Korousic (2003) developed a method for predicting sulphide capacities by using a theoretically calculated CaO activity of the slag combined with thermodynamic data for reaction 2.32. Korousic's equation (2003) as follows:

$$K_{2.32} = \frac{a_{CaS}}{a_{CaO}} \sqrt{\frac{P_{O_2}}{P_{s_2}}} \quad (2.74)$$

$$C_s = \frac{K_{2.32} \cdot a_{CaO}}{\frac{a_{CaS}}{(wt.\%S)}} = (wt.\%S) \sqrt{\frac{P_{O_2}}{P_{s_2}}} \quad (2.75)$$

This model was used in the calculation of sulphide capacities of CaO-SiO₂-MgO at different temperatures relevant for ladle slag compositions close to CaO saturation. The predicted values of sulphide capacities of Korousic's model (2003) are in well agreement with experimentally determined data from Gornierup M. and Wijk O. (1996).

Moretti and Ottonello (2003) developed a thermochemical model for the calculation of sulphide capacities of simple and complex silicate melts by combining concept of basicity and polymeric approach. According to the results, the model performs well when the chemical complexity of the system increases such as the SiO₂-Al₂O₃-MgO ternary system. On the other hand, the model deviates from experimental results in the CaO-Al₂O₃ system. The model performance is superior in the tested range when compared to previous models which use empirical correlations of the Lux-Flood oxide basicity approach (Figure 2.46).

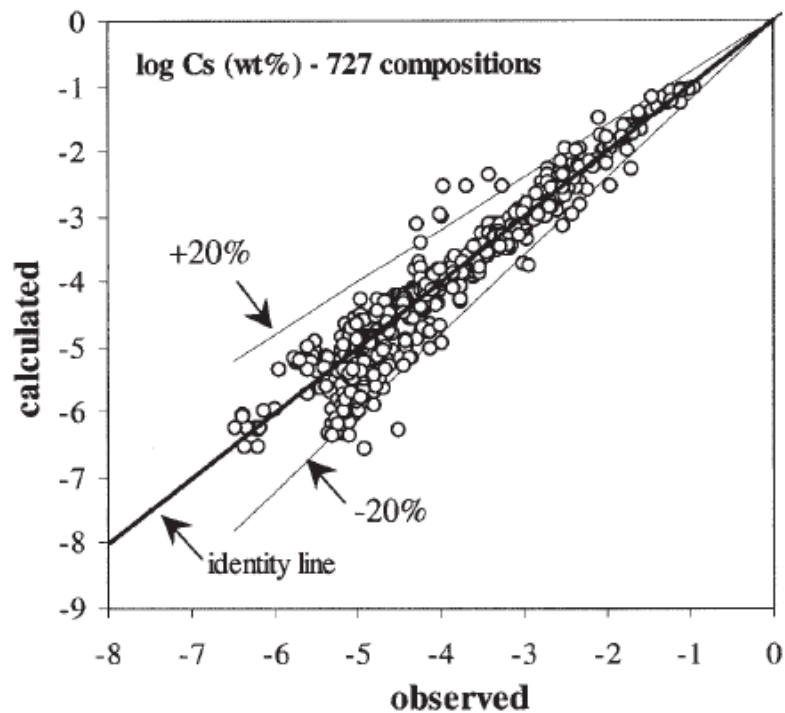


Figure 2.46 Calculated vs. observed sulphide capacity ($R^2=0.92$) (Moretti and Ottonello, 2003)

Ichise and Moro-oka (1990) examined the relation between the affinity of oxide and sulphide ions of the slags and lattice energies of oxide and sulphides by assuming no complex ions formation. A similar approach was applied to this study to investigate the relation between binding energy of O^{2-} ions in the mixture and phosphide and sulphide capacities of the investigated slag systems. The derived models were fitted to the results of the present work by using the equilibrium slag compositions. Therefore, Ichise and Moro-oka's approach will be explained in detail and discussed in section 2.9.

As it can be seen in Sections 2.3 and 2.4, a considerable amount research was conducted in the area of sulphur behaviour of different slag systems. Also, several models were developed by different groups of researchers in order to predict sulphide capacities for different slags. In spite of this, the literature review indicates that there is a lack of experimental data for sulphide capacities of ferrochromium and ferromanganese smelting slags. Beside the lack of

experimental data reported on the sulphide capacities of ferrochromium and ferromanganese smelting slags, there is no model available which can predict the sulphide capacities of these slags. Therefore, understanding of sulphur behaviour in ferrochromium and ferromanganese smelting slags will be a critical outcome of the present work.

2.5 Slag-Metal Equilibrium Studies Pertinent to Phosphorus Behaviour

In this section, slag-metal equilibrium studies pertinent to the behaviour of phosphorus in iron, steel, ferrochromium, ferromanganese production will be reviewed. The phosphide capacity concept and previous studies in these fields will also be given.

2.5.1 Behaviour of phosphorus in iron and steel making

Phosphorus derives mainly from coke, flux, iron ore and manganese ore during the production of pig iron in blast furnace. The low-grade iron ores may contain phosphate minerals such as calcium apatite or tetra-phosphate of calcium. In blast furnace operations, due to existing conditions phosphorus is reduced from phosphates and transfer into the metal. The similar free energies of formation of iron oxide and phosphorus pentoxide cause almost complete reduction of phosphorus pentoxide from the acid blast furnace slag. During the production of pig iron in the blast furnace, silica helps in breaking of phosphate bond and promotes the reduction indirectly, and almost all the mineral phosphate ends in the pig iron. It is almost impossible to control the phosphorus content of the pig iron without lowering the amount of phosphorus in the raw materials (Ward, 1962; Moore and Marshall, 1991; Peters, 1982; Biswas, 1981; Rosenquist, 1983).

The distribution of phosphorus between slag and the metal in the hearth of the blast furnace can be determined from the following reaction:



for which the equilibrium constant is:

$$K_{2.76} = \frac{a_{P_2O_5}}{a_O^5 \cdot a_P^2} \quad (2.77)$$

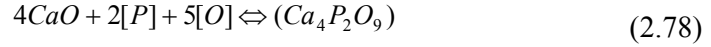
The equilibrium for reaction (2.76) lies far to the left because the activity of oxygen is raised to fifth power in the equilibrium expression. The equilibrium oxygen activity in carbon saturated iron is about 5×10^{-5} at 1 500°C (1 773 K) for $P_{CO}=1$ atm. In other words, the amount of phosphorus in the slag can be assumed negligible due to the extremely small activity of P_2O_5 in the slag. (Bodsworth and Bell, 1972; Rosenquist, 1983).

Dephosphorisation is a function of temperature, the activity of P_2O_5 and high oxygen potentials (Fe_xO activities). The reaction (2.76) indicates that dephosphorisation can be best achieved under strong oxidising conditions but this approach leads to iron oxidation in the process (Ward, 1962). This problem can be solved by lowering the activity of P_2O_5 in the steel making slags, by using a basic slag which dissolves P_2O_5 in the slag (Hoshino and Iwase, 1996). Therefore, the dephosphorisation slag mainly consists of iron oxide which oxidises phosphorus and lime which stabilises the phosphorus pentoxide in the slag. In general, high contents of FeO and CaO are favourable for effective dephosphorisation of steel, but a homogeneous liquid phase can not be established under these conditions. CaO content increase is accompanied by a decrease of FeO content in the slag, this situation partially neutralises the positive effect of lime on dephosphorisation (Turkdogan, 2000). From the practical point of view, no phosphorus is removed in the early stages of refinement where a highly basic slag presents (Tamura et al., 2004).

On the other hand, significant portion of phosphorus can be removed from the metal by using direct smelting processes (such as HIs melt). The formation of highly oxidising slags compared to blast furnace slags is beneficial in direct

smelting processes. These methods allow using high phosphorus iron ores in the production of low phosphorus steels (Lee and Fruehan, 2005).

The reaction for dephosphorisation in the presence of CaO can be written as (Alcock, 1976):

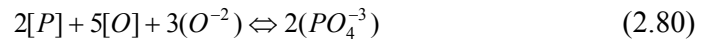


The equilibrium constant for the reaction can be expressed as:

$$K_{2.78} = \frac{a_{Ca_4P_2O_9}}{a_o^5 . a_P^2 . a_{CaO}^4} \quad (2.79)$$

The alternative formulation takes no account of such “compound” formation but uses number of ionic structural units as the basis of the calculation.

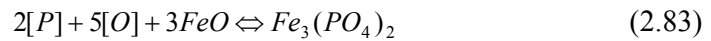
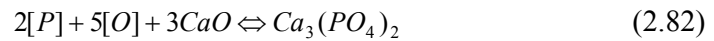
For the alternative formulation, the reaction can be written:



for which the equilibrium constant is:

$$K_{2.80} = \frac{(a_{PO_4^{-3}})^2}{[a_P]^2 [a_O]^5 (a_{O^{-2}})^3} \quad (2.81)$$

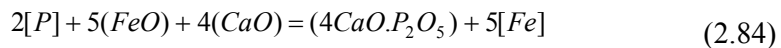
Reactions involving different cations, i.e. Ca^{+2} and Fe^{+2} can be seen in Eqs (2.82) and (2.83) (Alcock, 1976).



In the acid Bessemer converter, the suitable range of metal compositions is very limited for successful dephosphorisation. Phosphorus oxidises readily to phosphorus pentoxide, but this compound is unstable in the presence of carbon, silicon, manganese or other powerful oxide forming elements. The activity of P_2O_5 is also high in the silica-rich slags. Also the acidic refractory lining of converter inhibits the formation of basic nature slags due to the quick formation of dicalcium silicate by reaction of silica lining and basic slag (Bodsworth and Bell, 1972; Peters, 1982).

In the basic Bessemer process, the slag plays an active role in the refinement of phosphorus, therefore the reaction rates become important during the refinement process. Figure 2.47 shows the composition change of hot metal as a function of blowing time in the basic Bessemer converter process. Phosphorus is removed only when the carbon is almost completely oxidised (in the after-blow stage). The activity of oxygen in the metal at the after-blow stage is determined by the amount of phosphorus. The oxidation of phosphorus takes place mainly at the slag-metal interface where slag can absorb the product of oxidation. When slag is saturated with lime, the phosphorus activity coefficient is markedly decreased. With a constant $\gamma_{P_2O_5}$ in the slag phase, the transfer proportion tends to increase with the increase of slag bulk and decrease with the dilution of the slag. However, if the slag is saturated with lime, any further addition of lime remains as solid which can not contribute to the transfer of phosphorus from metal to slag (Bodsworth and Bell, 1972; Ward, 1962).

Schenck and Reiss (1935) suggested that the dephosphorisation reaction should occur according to (2.84) instead of reaction (2.76).



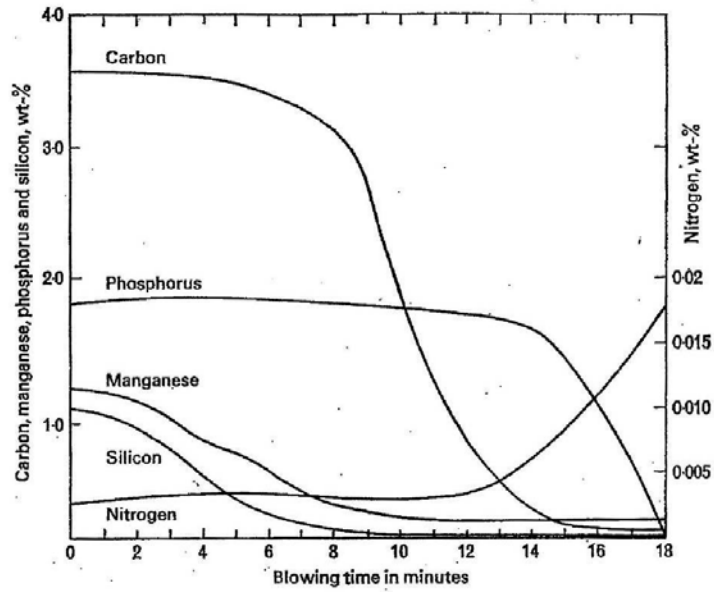


Figure 2.47 Change of carbon, phosphorus, manganese, silicon and nitrogen amounts with blowing time in the basic Bessemer converter process (Bodsworth and Bell, 1972)

If slag is saturated with CaO and $4\text{CaO} \cdot \text{P}_2\text{O}_5$, the equilibrium constant of the reaction (2.84) can be expressed as:

$$K_{2.84} = \frac{a_{\text{Fe}}^5}{a_{\text{FeO}}^5 a_{\text{P}}^2} \quad (2.85)$$

For higher phosphorus transfer from steel to slag, slag composition can be kept within the ranges: 13-20 wt. % FeO , 51-56 wt. % CaO , 0-4 wt. % MgO , 2-5 wt. % MnO , 16-22 wt. % P_2O_5 and 5-8 wt. % SiO_2 . For each slag basicity, there is an optimum ferrous oxide content for higher dephosphorisation rate. If iron oxide content is higher than the optimum, the dephosphorisation power of the slag significantly reduces. Also, any increase in Al_2O_3 concentration will lower the distribution ratio of phosphorus between slag and metal. (Bodsworth and Bell, 1972; Ward, 1962).

LD process is the first commercially successful process to utilize pure (99.5 %) oxygen in converting pig iron to steel. This process produces steel from a charge which contains phosphorus less than 0.3 wt. %. In the first stage, the phosphorus

content of the hot metal drops to 0.2 % by oxidation and then a new slag is formed by addition of lime, fluorspar or bauxite and blow continues till the final slag composition is achieved. Alumina lowers the phosphorus distribution ratio between slag and metal phases but the addition of alumina helps to reduce the viscosity of the slag and accelerates kinetics in the dephosphorisation. In the second stage, a slag contains high level of iron oxide which is used as a raw material to the first slag operation (Bodsworth and Bell, 1972; Moore and Marshall, 1991).

The other methods which allow the use of high phosphorus content charges are the LD-AC and OLP processes. In these methods, powdered lime is injected into the hot metal bath with an oxygen jet. These two processes use two or three stage slags in the refinement of high phosphorus (>0.5 wt. %) containing charges (Bodsworth and Bell, 1972).

Kaldo process is generally preferred when charge contains high level of phosphorus. The major portion of the oxygen is supplied as gaseous state above the slag in Kaldo process. The hot metal contains 2 wt. % carbon and 0.3 wt. % phosphorus in the beginning of the process. Lime and ore are added into the hot metal bath and the converter is blown for a further 10 minutes. The second slag contains about 17 wt. % P_2O_5 and 8 wt. % FeO which indicate the dephosphorisation power of the process. However, this leads to high loss of iron into slag phase. At the end of refinement, the metal bath contains around 0.1 wt % phosphorus and 1 wt. % carbon. The carbon can be considered as a heat source in the process and almost 50 % of the heat is evolved above the surface of the slag due to the combustion of carbon in the oxidising atmosphere (Bodsworth and Bell, 1972, Ward, 1962).

2.5.2 Behaviour of phosphorus in ferrochromium smelting and refining

In the smelting of ferromanganese and ferrochromium, most of the phosphorus in the charge is transferred to the alloy due to reducing conditions. With strong oxidation conditions and high operation temperatures, the removal of phosphorus from the alloy phase becomes extremely difficult without significant loss of manganese and chromium from alloy to slag (Maramba and Eric, 2007).

To obtain a low level of the phosphorus in the ferrochromium alloy, a fluid-high lime content basic slag must be produced during the refinement operations. However, previous results show that about 30 to 40 % of the phosphorus introduced the final product was originally carried into the system by the lime. Therefore a decrease in the slag basicity by taking out the lime from the production cycle can indirectly result in a decrease in the concentration of phosphorus in refined ferrochromium (Pickles et al., 1987).

In order to achieve ultra low levels of phosphorus in ferrochromium alloy without significant loss of chromium as oxides into slag, it is essential to use CaO-CaF_2 , $\text{CaC}_2\text{-CaF}_2$, CaSi-CaF_2 , $\text{BaO-BaCl}_2\text{-Cr}_2\text{O}_3$ and $\text{CaO-BaO-CaF}_2\text{-Cr}_2\text{O}_3$ fluxes during ferrochromium smelting. Calcium fluoride, known as fluorspar is a very good flux in steel making and helps to increase alloy yield. Ferrochromium smelting slags are highly viscous and it is expected that if CaO is partly replaced by CaF_2 , the viscosity of the slag will be decreased. This helps to improve kinetics of the reactions and promotes dephosphorisation of alloy (Pickles et al., 1987; Wrampelmeyer et al., 1984; Li et al., 1999; Jha and Abraham, 1989; Yang and Edstrom, 1992, Behera and Mohanty, 2003).

Kossyrev et al. (2004) conducted a study on removal of carbon, sulphur and phosphorus from high carbon ferrochromium alloy. Ferrochromium alloys were equilibrated with synthetic master slag (30 wt. % CaO -30 wt. % MgO -40 wt. % SiO_2) with the addition of chromium sinter or iron ore pellets in alumina crucibles at 1 600°C for 10, 20, 30 or 40 minutes under argon atmosphere. Results showed

that slag system promotes the desulphurisation without causing chromium loss to slag. It was found that 60 % of the initial sulphur was transferred from metal to slag. Also, phosphorus content of the alloy was dropped significantly under experiments conditions. The degree of dephosphorisation was found to vary between 15 and 40 %. In the first stage of the process, phosphorus transfers to slag phase from the alloy. In the second stage, phosphorus leaves the slag phase as off-gas.

Golev and Zaiko (1962) treated the ferrochromium alloy with a highly basic low alumina-lime slag and managed to produce chromium silicide with low phosphorus content. Calcium phosphides and carbides formations help to remove carbon and phosphorous of the alloy during the treatment. Researchers achieved a factor 10 reduction of the phosphorus content of the alloy by this treatment.

According to Melninhenko et al. (1971), carbon free ferrochromium with an extremely low phosphorus content (0.010-0.015 wt. %) can be produced by using high-chromium containing slags which were derived as by-products of the medium-carbon ferrochromium production process from converters.

The removal of phosphorus from the ferrochromium alloy by using Ca-CaF₂ and deoxidizers was studied by Jha and Abraham (1989). Oxygen in the molten flux leads to formation of CaO which prevents the formation of calcium phosphide. Addition of deoxidation agents was found to be effective for maximization of the removal of phosphorus from ferrochromium alloy. The correlation between the flux's calcium content and the phosphorus partition ratio was found to be in linear form (Figure 2.48).

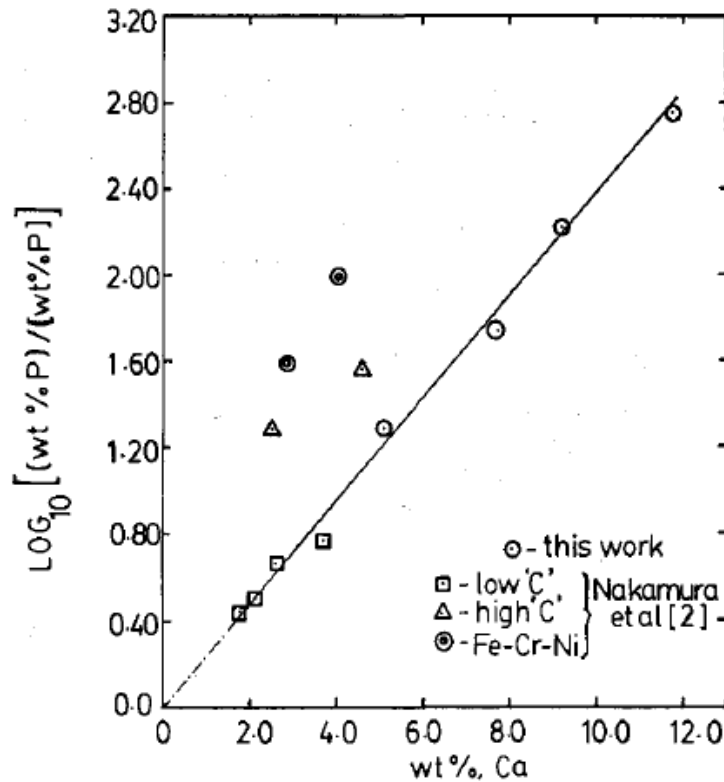


Figure 2.48 Variation of the phosphorus distribution ratio in the flux and alloy phase with calcium content of flux at 1 700°C (Jha and Abraham, 1989)

The influences of additives, such as Al_2O_3 and SiO_2 on the distribution ratios of phosphorus and chromium between slag and metal phases of CaO-CaF_2 slag system was investigated by Yang and Edstrom (1992). Figure 2.49 illustrates the influence of Al_2O_3 addition on phosphorus and chromium distribution ratio between $\text{CaO-CaF}_2\text{-Al}_2\text{O}_3$ slags and $\text{Fe-Cr-C}_{\text{sat}}\text{-P}$ melts at 1 400°C. The distribution ratio of phosphorus is not significantly affected with the Al_2O_3 addition at low concentrations (below 8 wt. %). However, the chromium loss to slag is decreased with increasing Al_2O_3 concentration in the slag. The effect of SiO_2 content on the phosphorus distribution between $\text{CaO-CaF}_2\text{-SiO}_2$ slags and Fe-Cr-C-P melts at 1 400 °C and 1 450 °C are illustrated in Figure 2.50. The phosphorus transfer to the slag phase is higher in the slags with SiO_2 content lower than 5 wt. %. According to their results, the amount of SiO_2 has a remarkable influence on the distribution ratios of chromium between slag and

metal phases. In highly basic slags, $\text{SiO}_2 < 10 \text{ wt. \%}$, $\text{CaO}/\text{SiO}_2 > 4$ and chromium distribution ratio is found to be high. In the low basicity ranges, the distribution ratio of chromium is low and augments with the increase of silica concentration in the slag phase. In the same study, the correlation between the phosphorus distribution ratio and optical basicity of slag is also analysed. As shown in Figure 2.51, the threshold value for optical basicity (Λ) is found to be equal to 0.745. The distribution ratio of phosphorus remains constant when the optical basicity value exceeds 0.745. This point of the curve matches the lime saturation of the slag system and indicates that excessive addition of CaO into the slag system is not effective on the dephosphorisation of metal. Also the results point that the optical basicity of slags should be in the range of 0.75 and 0.8 for achieving maximum phosphorus transfer from metal to slag without any significant loss of chromium from metal to slag. However, the scatter of data on Figure 2.51 is so large that it is hard to say the presence of threshold optical basicity. Also, the correlation between phosphorus distribution ratio and optical basicity is not clear in CaO-CaF₂ slag.

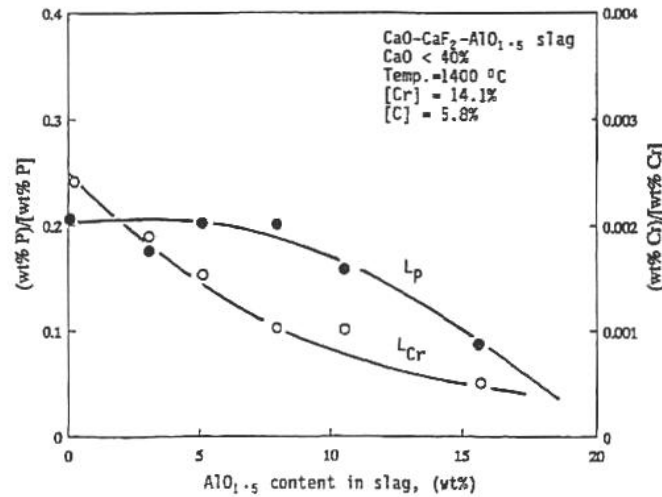


Figure 2.49 Effect of Al_2O_3 addition to CaO-CaF₂ slags on phosphorus and chromium distribution ratios (Yang and Edstrom, 1992)

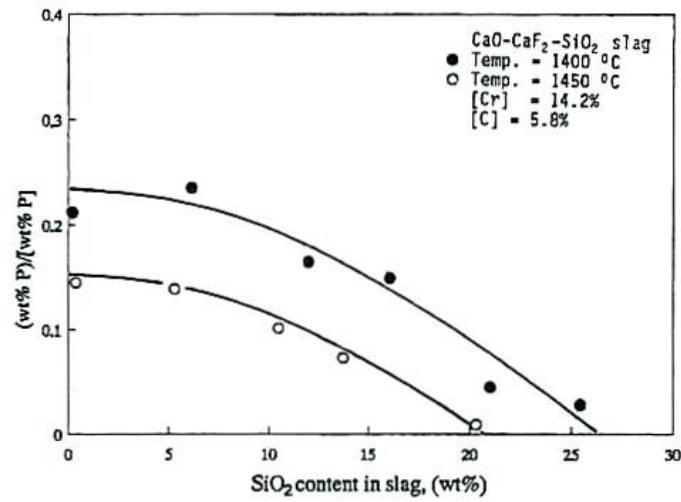


Figure 2.50 Relation between phosphorus distribution ratio and SiO_2 content in slags (Yang and Edstrom, 1992).

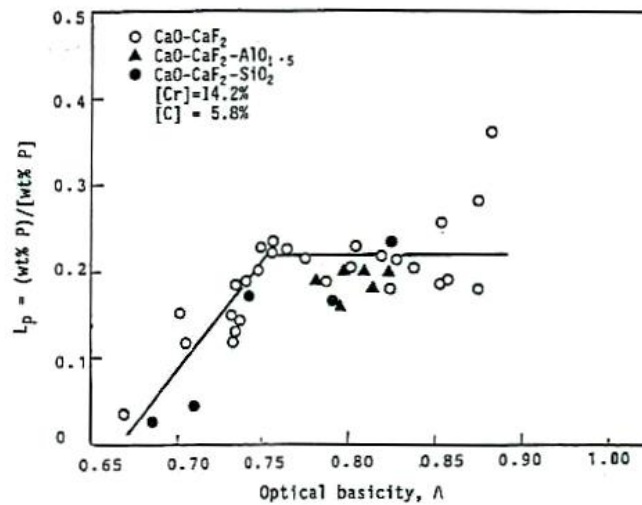


Figure 2.51 Relation between phosphorus distribution ratios and optical slag basicity at 1400°C and $P_{\text{CO}}=1$ atm. (Yang and Edstrom, 1992).

2.5.3 Behaviour of phosphorus in ferromanganese smelting and refining

To date, many research studies have been done on the behaviour of phosphorus in ferromanganese smelting and refining (Zaitsev and Mogutnov, 1992; Maramba and Eric, 2008; Shim and Sano, 1995; Dashevskii et al., 1998a; Liu et al., 1995; Liu et al., 1996; Dashevskii et al., 1998b; Chaudhary et al., 2001; Chaudhary et al., 2007)

Thermodynamic conditions for removing phosphorus from manganese alloys with calcium containing fluxes in reducing conditions have been investigated by Zaitsev and Mogutnov (1992). The removal of phosphorus from the manganese melt is higher at lower temperatures since calcium activity in flux increases but the activity coefficient of Ca_3P_2 decreases as the temperature drops. Moreover, the addition of iron to manganese melt does not affect the equilibrium distribution coefficients of phosphorus. However, silicon and carbon additions result in increases in the equilibrium distribution coefficients of phosphorus. The coefficient of the phosphorus distribution between metal and slag is found to be significantly influenced by the partial pressure of oxygen of the system. High equilibrium distribution coefficients of phosphorus can be achieved at P_{O_2} in the system less than 10^{-28} and 10^{-24} atm at 1 600 and 1 800 K, respectively.

Maramba and Eric (2008) investigated the factors affecting the phosphorus partition ratio between $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO-MgO-MnO-P}_2\text{O}_5$ slags and Mn-Fe-Si- C_{sat} -P alloys at 1 500°C. Also phosphide capacities of the ferromanganese smelting slags were determined in the same study. The results showed that the phosphorus partition ratio was found to be depend on the amount of CaO, SiO_2 and basicity ratio $[(X_{\text{CaO}} + X_{\text{MgO}}) / X_{\text{SiO}_2}]$ and the partial pressure of the oxygen of the slag system. It was found that the change in the amounts of Al_2O_3 and MgO did not significantly affect the phosphorus partition and phosphide capacity of the slag system. Their results indicate that the phosphide capacity of ferromanganese smelting slags increases with increasing oxygen partial pressure. However,

oxidizing atmosphere conditions lead to excessive loss of manganese to slag phases.

It was reported that up to 80 % of phosphorus in liquid stainless steel can be removed by addition of 100 kg BaO-BaCl₂ flux per tonne to liquid metal. The addition of BaO-BaCl₂ flux to liquid metal helps to reduce the viscosity of the slag. However, the high price of BaO and the toxic nature of Ba-containing compounds are the major limitation factors for this application (Yang and Edstrom, 1992). Liu et al. (1995) studied the phosphorus equilibrium between BaO-BaF₂-MnO slags and Mn-Fe-C_{sat}-P melts at 1 300 and 1 400 °C. Low oxygen partial pressure condition was found to be significantly affecting the desulphurisation power and also results a decrease the MnO concentration of the slag. Maximum phosphorus removal can be achieved by BaO-BaF₂-MnO slag system at 1 300 °C (Liu et al., 1996).

Daskevski et al. (1998b) studied the additions of CaF₂, BaO-BaF₂ mixtures into CaO-MnO based slags in order to achieve dephosphorisation of ferromanganese alloys. The obtained L_P values were around 2-2.5 for CaO-CaF₂ treated ferromanganese slags. In BaO-BaF₂ mixtures, the L_P increased to 2.5-6.5. Their findings are in good agreement with Liu et al. (1995, 1996). The results indicate that the partial substitution of CaO with BaO can help to increase the phosphorus removal from alloy.

Chaudhary et al. (2001) determined the optimum slag composition for dephosphorisation of ferromanganese and studied the influence of silicon content on the phosphorus removal. It was found that the high MnO content in the slag can lead to a low degree of phosphorus removal in ferromanganese production (Chaudhary et al., 2007).

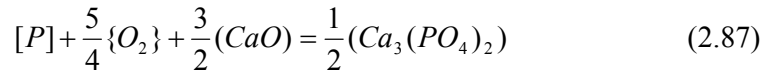
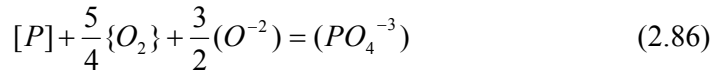
2.6 Concept of Phosphide Capacity

The ability of a slag to contain phosphorus can be named as phosphate or phosphide capacity. Phosphorus can be in either phosphate (PO_4^{-3}) or phosphide (P^{-3}) forms in slags depending on existing oxygen partial pressure and temperature of the system.

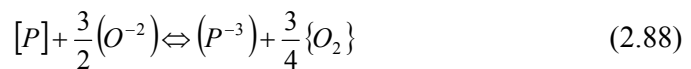
In the conventional refining methods, phosphorus is removed from iron alloys under oxidising atmosphere conditions. However, traditional dephosphorisation methods can be hardly applicable to ferromanganese and ferrochromium smelting due to significant loss of manganese and chromium to slag.

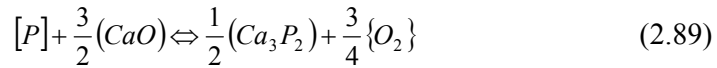
In high chromium and manganese steels, dephosphorisation can be achieved by forming Ca_3P_2 . However, this method requires strongly reducing atmosphere conditions (Sano and Katayama, 1992). Besides, this technique was applied to dephosphorisation of stainless steels by using Ca - CaF_2 or CaC_2 - CaF_2 fluxes (Momokawa and Sano, 1982; Tabuchi and Sano, 1983; Tabuchi and Sano, 1984).

Since the oxygen partial pressure encountered is in the stability region of phosphates rather than phosphide in steel making processes, dephosphorisation can be achieved by forming $Ca_3(PO_4)_2$. Under these conditions, the oxidation of phosphorus can be expressed according to Eq. (2.86) and (2.87):



During ferrochromium or ferromanganese smelting, dephosphorisation can be achieved by forming Ca_3P_2 under highly reducing conditions and relevant reactions are as follows:





Tabuchi and Sano, (1984) investigated the phosphide capacity for CaO-CaF₂ melt. Figure 2.52 shows the relation between phosphate and phosphide capacities against CaO's weight percentages in CaO-CaF₂ system

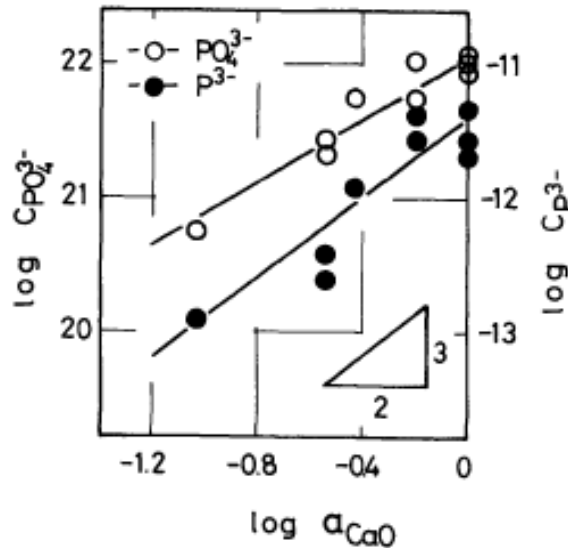


Figure 2.52 Phosphate and phosphide capacities against wt. % of CaO for CaO-CaF₂ system (Tabuchi and Sano, 1984)

The change of the phosphorus content of 41 wt. % CaO-59 wt. % Al₂O₃ slag with the partial pressure of oxygen is presented in Figure 2.53. The critical oxygen potential to divide the stability regions of phosphate and phosphide for this system was determined to be 2.2×10^{-18} atm. at 1550°C (Momokawa and Sano, 1982).

The capacity of a steel making slag to contain phosphorus can be expressed as a phosphate capacity, $C_{PO_4^{3-}}$ (Eq. 2.90) since the oxygen partial pressure prevailing in steel making always favours the formation of phosphates rather than phosphides.

$$C_{PO_4^{-3}} = \frac{(wt.\%PO_4^{-3})}{P_{P_2}^{1/2} P_{O_2}^{5/4}} = K_{2.86} \frac{a_{O_2}^{3/2}}{f_{PO_4^{-3}}} \quad (2.90)$$

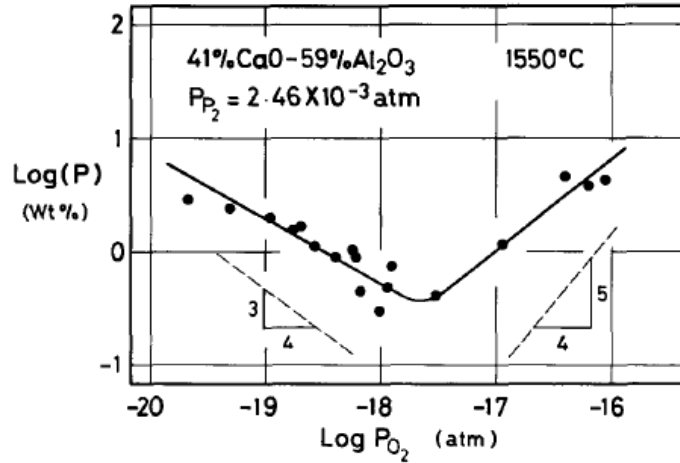


Figure 2.53 The variation of the phosphorus content of a 41 wt. % CaO-59 wt. % Al_2O_3 melt with the partial pressure of oxygen (Momokawa and Sano, 1982)

This value may be calculated by determining the distribution ratio of phosphorus between slag and metal phases under a controlled partial pressure of oxygen, since P_{P_2} in the Eq. 2.90 can be replaced by the amount of phosphorus in the metal phase. In this equation, a_{O_2} represents the activity of free oxide ions and can be assumed as a measure of slag basicity; $f_{PO_4^{-3}}$ is the activity coefficient of PO_4^{-3} and depends on the slag composition; $K_{2.86}$ is the equilibrium constant for reaction (2.86) and tends to increase as the temperature is lowered. According to Eq. (2.90), $C_{PO_4^{-3}}$ increases with increasing a_{O_2} or slag basicity and increasing $K_{2.86}$ or decreasing temperature since reaction (2.86) is exothermic nature.

Figure 2.54 shows $\log C_{PO_4^{-3}}$ as a function of mole fraction basic oxide for a variety of basic slags. As it can be seen in Figure 2.54, slags with higher basicity generally have shown higher phosphate capacity and these slags can be used more effective dephosphorisation purposes (Sano and Katayama, 1992).

The distribution ratios of phosphorus values for the quasi-ternary $\text{CaO-SiO}_2\text{-FeO}$ slag system are given in Figure 2.55. For a fixed CaO/SiO_2 ratio, the phosphorus distribution between slag and metal phases reaches a maximum value with the increase FeO content. FeO acts as an oxidant and a basic oxide in the slag and leads to dephosphorisation of metal. When the partial pressure of oxygen increases, the slag basicity tends to drop significantly and the slag begins to lose its phosphorus absorption capacity. However, the content of FeO is varied between 10 to 20 wt.% in steel making slags, this range can be considered as ideal region for efficient phosphorus removal (Kishitaka, 1977; Sano et al., 1997)

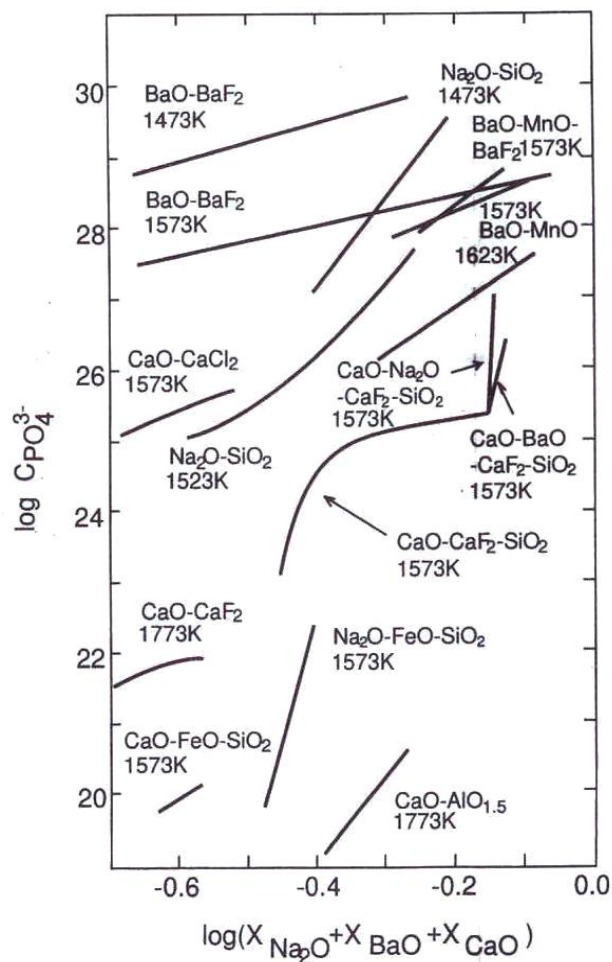


Figure 2.54 Phosphate capacities of various flux systems (Sano and Katayama, 1992)

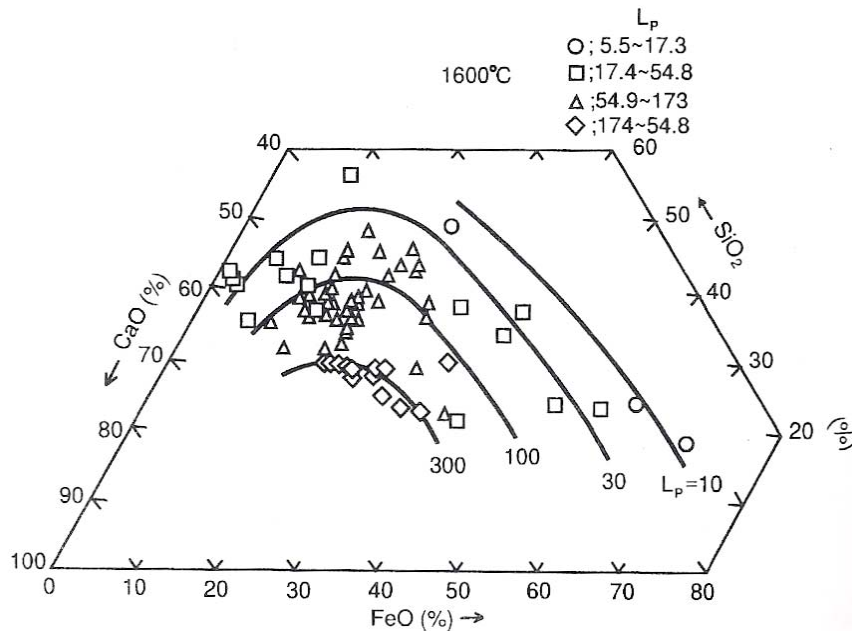


Figure 2.55 Distribution of phosphorus between slag and molten steel at the end of blowing in BOF process (Kishitaka, 1977)

Alkaline metal oxides expected to work as good dephosphorisation agents due to their highly basic nature. However, it was found that the use of Na_2O has a limitation due to the formation of sodium vapour by the reduction of chromium and carbon in the melt (Sano and Katayama, 1992).

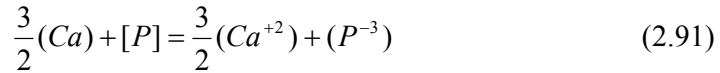
In stainless steel making process, the halides (CaF_2 , CaCl_2 , BaCl_2 , BaF_2 , NaF) can contribute to dephosphorisation by lowering the melting point of the slags, decreasing the activity coefficient of P_2O_5 and increasing the activity coefficient of Cr_2O_3 .

Katayama et al. (1979) states that to achieve high dephosphorisation levels, the refractory should be chosen with the lowest oxygen potential such as magnesia or magdolo. The key to the success of dephosphorisation of stainless steel by high phosphate capacity slags under oxidation conditions requires extremely low

contamination of the slag by refractory materials such as SiO₂ and Al₂O₃ (Sano and Katayama, 1992).

Eiji and Moro-Oka (1988) determined 10^{-18.4} atm as a critical oxygen partial pressure of stabilities of phosphate and phosphide in CaO-SiO₂-MnO-CaF₂ slags at 1300°C. Momokawa and Sano (1982) found 10⁻¹⁸ atm as a critical point between the transition of phosphate and phosphide stability ranges for CaO-Al₂O₃ melt with the partial pressure of oxygen at 1550 °C.

It is believed that reaction (2.91) can occurred at the electrode tip in an Electro-Slag-Remelting Process (E.S.R.) and it was observed that this reaction was dependent only on the amount of calcium in the flux and not dependent on the parameters such as slag volume, melting rate or the amount of phosphorus of alloy (Pickles et al., 1987).



By using Eq. 2.92, phosphide capacity (C_P or C_{P⁻³}) can be defined as follows (Elliott, 1997):

$$C_{P^{-3}} = \frac{(P^{-3}) \cdot P_{O_2}^{3/4}}{[P] \cdot f_P} = K_{2.88} \cdot \frac{(a_{O^{-2}})^{3/2}}{f_P} \quad (2.92)$$

where (P⁻³) and [P] are the weight percentages of phosphide in the slag and the weight percentage of phosphorus in the metal respectively and these values are determined by chemical analysis; f_P is the activity coefficient of phosphorus in the metal phase to be calculated using infinity dilute solution treatment; P_{O₂} is the partial pressure of oxygen to be calculated from the partial oxidation of carbon, reaction 2.31.

As indicated in Sections 2.5 and 2.6, many research studies have been conducted on the phosphorus behaviour in the ferromanganese smelting. However, there has been no considerable research in the area of phosphide capacities of ferrochromium smelting slags. Also, no theoretical or empirical model was developed on the prediction of phosphide capacities of ferrochromium smelting slags. Therefore, it is important to determine and understand the phosphorus behaviour relevant to ferrochromium smelting process.

2.7 Basicity in Metallurgical Slags

Up to this point the term of basicity has been used somewhat loosely and it is necessary to define the concept of basicity. This concept is extremely important during the understanding of the chemical behaviour of slags.

2.7.1 Concept of basicity

As it is defined by Swedish scientist Svante Arrhenius an acid is a compound that contains hydrogen and dissociates in water to produce positive ions. The strength of an acid depends on the extent to which it dissociates, and is measured by its dissociation constant. On the other hand, a base is a compound that reacts with a protonic acid to give water (and a salt) (Verma, 2005; Iwamoto, 1974).

In the Lowry-Brønsted theory, an acid is defined as a substance that is capable of releasing protons and a base is defined as a substance that is capable of accepting protons. Therefore, the acid-base reaction is treated as a competition for protons (Iwamoto, 1974).

A Lewis acid is defined as a compound or atom that can accept a pair of electrons and a base is one that can donate an electron pair. The Lewis theory establishes a relationship between acid–base reactions and oxidation-reduction reactions (Iwamoto, 1974).

In order to understand the concept of basicity, we should define electronegativity and the size of ions.

Electronegativity can be defined as the power of an atom to attract electrons to itself when it is combined in a compound. Elements with an electronegativity difference greater than 1.7 tend to form ionic bonds. On the other hand, those elements with an electronegativity difference of less than 1.7 form mainly covalent bonds. Therefore, the strength of an acid increases as the electronegativity of its negative ions increases (Moore, 1990).

Atomic size tends to decrease with an increase in the atomic number across the same period due to the increased nuclear charge (i.e. protons) which pulls electrons of same and inner shells closer to the nucleus (Moore, 1990).

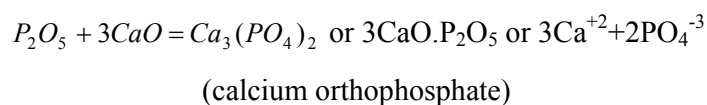
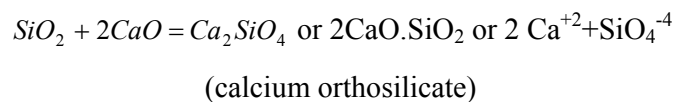
The removal of one or more electrons from the outermost shell of atoms forms a positive ion and often results in a complete removal of the shell with a sharp decrease in the size. On the contrary, negative ions can be formed by adding one or more electrons which results in an expansion of the electron “cloud” and increases the size (Moore, 1990).

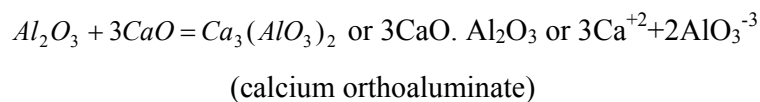
Classification of acid and basic oxides

According to the concept of acid and base given above, we can classify the oxides into two groups (Moore, 1990; Waseda and Toguri, 1998):

1. **Acidic oxides** which receive O^{2-} ions, e.g. SiO_2 , P_2O_5 , Al_2O_3 , and which produce complex anions by reaction with the oxygen anions.
2. **Basic oxides** which are classified as donor oxides and release O^{2-} ions to the slag, e.g. CaO , FeO , MgO , Cu_2O , Na_2O , K_2O .

When the slag is formed by basic and acidic oxides, the following neutralisation reactions can be formulated (Moore, 1990);





The ion-oxygen attraction has been used as a classification tool for oxides by Ward (1962);

$$I = \frac{2Z}{d^2} \quad (2.93)$$

where Z and d represent the valance of cation and ionic radius of cation and oxygen ion, respectively.

It is known that free oxygen ions are unstable and they become stable by bonding with neighbouring cations. In addition, the stability increases with the increase of the field strength. Also, the reacting ability decreases with decreasing basicity (Iwamoto, 1974). As it can be seen in Table 2.5, K₂O and P₂O₅ are the most basic and acidic oxides, respectively (Sano et al., 1997).

Table 2.5 Dependence of the chemical and physical properties of binary silicate melts on the cation-oxygen bond as measured by the ion-oxygen attraction (Sano et al., 1997)

<u>Classification of Oxide</u>	<u>Oxide</u>	<u>Electro-negativity of Cation</u>	<u>Cationic Radius (Å)</u>	<u>Ion-Oxygen Attraction (I)</u>
Basic	K ₂ O	0.8	1.33	0.27
Basic	Na ₂ O	0.9	0.95	0.36
Basic	Li ₂ O	0.95	0.6	0.5
Basic	BaO	0.9	1.35	0.53
Basic	SrO	1	1.13	0.63
Basic	CaO	1	0.99	0.7
Intermediate	MnO	1.4	0.8	0.83
Intermediate	FeO	1.7	0.75	0.87
Intermediate	ZnO	1.5	0.74	0.87
Intermediate	MgO	1.2	0.65	0.95
Intermediate	BeO	1.5	0.31	1.37
Intermediate	Cr ₂ O ₃	1.6	0.64	1.44
Intermediate	Fe ₂ O ₃	1.8	0.6	1.5
Intermediate	Al ₂ O ₃	1.5	0.5	1.66
Acid	TiO ₂	1.6	0.68	1.85
Acid	GeO ₂	1.8	0.53	2.14
Acid	B ₂ O ₃	2	0.2	2.34
Acid	SiO ₂	1.8	0.41	2.44
Acid	P ₂ O ₅	2.1	0.34	3.31

Each oxide has its own specific structure which is governed by its ionic radius, valance and affinity of the metal for oxygen. However, when more than two oxides are mixed, the constituent metallic cations adapt their structure depending on the coordination number of oxygen, relative size and valence. However, it should be kept in mind that the concept of acid and base is relative and it becomes important when they are in the mixtures (Waseda and Toguri, 1998). In the slag melts, acidic oxides have various complex ions forms with various coordination numbers of oxygen atoms, such as SiO_4^{-4} (SiO_2), PO_4^{-3} (P_2O_5), AlO_4^{-5} (Al_2O_3), FeO_4^{-5} (Fe_2O_3), TiO_4^{-4} (TiO_2). There are many forms of SiO_2 and amphoteric Al_2O_3 (Sano et al., 1997);



The equilibrium values of O^{-2} in reactions (2.94), (2.95) and (2.96) decrease in sequence and the more acidic the melt is, the less the number of O^{-2} as well as the non-bridging oxygen atoms per silicon atoms (Waseda and Toguri, 1998; Sano et al., 1997).

When a CaO-network transforming oxide is added to a silicate melt, the bond connecting an oxygen atom with two silicon atoms is broken for forming a smaller unit such as SiO_4^{-4} (2.100) and the viscosity of the slag lowers (Sano et al., 1997).



The negative logarithm of the ion concentration of oxygen can be used in measuring the basicity. For this case, the basicity of a slag (B) can be defined by Eq. (2.101) which is very similar to $\text{pH} = -\log_{10} a_H$ for an aqueous solution (Sano et al. 1997; Verein Deutscher Eisenhüttenleute, 1981).

$$B = \log_{10} a_{O^{2-}} \quad (2.101)$$

2.7.2 Concept of optical basicity

Duffy and Ingram (1976) had a breakthrough development on the basicity concept by proposing “optical basicity”. They measured the energy shift of the ultraviolet absorption spectrum of Pb^{+2} reflected by the trend for an oxygen ion to release electrons toward Pb^{+2} and defined the value of the shift relative to that of CaO as optical basicity (Sano et al., 1997).

It is known that the application of the optical basicity concept can be only done to opaque slags in the ultraviolet. However, Duffy and Ingram (1976) indicated a good empirical correlation between Pauling electronegativity values (with the exception of transition metal oxides such as Co and Ni) and optical basicity. For this purpose, they developed the basicity moderating parameter (γ_B) of each cation which can be expressed as follows:

$$\gamma_B = 1.36(x - 0.26) \quad (2.102)$$

where x represents the electronegativity.

Duffy et al. (1978) extended the use of optical basicity to metallurgical slags. The Lux-Flood concept was applied to acid-base reactions in oxide systems where the basicity is regarded in terms of the electron donor power of the oxygen atoms.

Optical basicity can be described as the “lime character” of the slag, in spite of the fact that some of the slags did not contain calcium oxide in their structure. Although this concept can be applied much better to glass chemistry field than

metallurgical topics, it is still an important tool for forming correlations between different slag systems. The main problem facing the application of optical basicity has been the application of this approach to transition metal oxides such as FeO, MnO, TiO₂ and others (Ghosh, 2001; Masson, 1997).

The optical basicity of an oxide (AO), Λ_A , is related to the Pauling electro negativity, x , of the cation involved by expression (Sosinsky and Sommerville, 1986):

$$\Lambda_A = \frac{0.74}{x - 0.26} \quad (2.103)$$

By using Eq. 2.103, it is possible to calculate the average value of Λ for a slag of any composition involving the non-transition element oxides (Sosinsky and Sommerville, 1986).

$$\Lambda = X_A \Lambda_A + X_B \Lambda_B + \dots + X_N \Lambda_N \quad (2.104)$$

In Eq. 2.104, X is the equivalent cation fraction and can be expressed in terms of mole fraction as shown in Eq. 2.105 (Sosinsky and Sommerville, 1986).

$$X = \frac{[(N) \times (\text{number of oxygen atoms in oxide molecule})]}{\sum [(N) \times (\text{number of oxygen atoms in oxide molecule})]} \quad (2.105)$$

For example in a MgO-Al₂O₃-SiO₂ ternary slag system,

$$X_{MgO} = \frac{N_{MgO}}{N_{MgO} + 3N_{Al_2O_3} + 2N_{SiO_2}} \quad (2.106)$$

$$X_{Al_2O_3} = \frac{3N_{Al_2O_3}}{N_{MgO} + 3N_{Al_2O_3} + 2N_{SiO_2}} \quad (2.107)$$

$$X_{SiO_2} = \frac{2N_{SiO_2}}{N_{MgO} + 3N_{Al_2O_3} + 2N_{SiO_2}} \quad (2.108)$$

The recommended optical basicity values of several slag species is given in Table 2.8 (Young et al., 1992).

The major weak points of the application of optical basicity were indicated by Gouchang et al. (1993).

- The optical basicity utilises various cells such as i-O-j and i-O-i. However, during the calculation of the optical basicity value of a slag, the basicity characteristics of oxide molecules are used instead of that of cells.
- The optical basicity approach is not ideal for clarification of the influence of environment on anion activity.
- The behaviour of Na₂O in the different slag systems is not clear.

Table 2.6 Optical basicity values of several slag species (Young et al., 1992)

Slag Species	Λ
FeO	1
SiO ₂	0.46
P ₂ O ₅	0.4
Al ₂ O ₃	0.6
CaO	1
MnO	0.98
MgO	0.78
K ₂ O	1.4
Na ₂ O	1.15
Fe ₂ O ₃	0.77
BaO	1.15
TiO ₂	0.65
CaF ₂	0.43

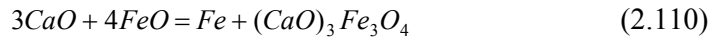
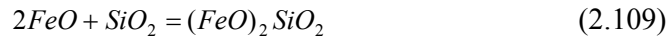
2.8 Structure Theories of Slag

In this section, molecular and ionic slag theories have been reviewed for giving a basic understanding on various reactions with and within slags.

2.8.1 Molecular slag theory

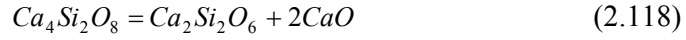
This theory assumes that many complex compounds exist in the molten slag by analogy with the fact that it can be observed by the formation of various compounds in solidified slags (Iwamoto, 1975). In other words, we assume an ideal behaviour for all molecules that exist in the slag; the liquid slags are formed by individual oxides, sulphides or fluorides and these simple individual forms can form complex molecules or remain as non-combined or free compounds rather than ions (Moore, 1990; Verein Deutscher Eisenhüttenleute, 1981).

Thus, the following reactions can be written by using molecular theory (Moore, 1990).



This approach allows for all possible molecule formations that may present in the slag to be considered. For example in a ternary slag system that contains MnO, CaO, SiO₂, the possible molecules can be written as MnO, CaO, CaSiO₃, Ca₂SiO₄, MnSiO₃, Mn₂SiO₄, Ca₂Si₂O₆, Ca₄Si₂O₈. With the existence of eight possible compounds in this case, we should write down eight equations and determine the mole fraction (N) of each compound (Moore, 1990).





As the next step, we should determine the equilibrium constant for each of these reactions:

$$K_{2.112} = N_{MnSiO_3} / (N_{MnO} \cdot N_{SiO_2}) \quad (2.120)$$

$$K_{2.113} = N_{Mn_2SiO_4} / (2N_{MnO} \cdot N_{SiO_2}) \quad (2.121)$$

$$K_{2.114} = N_{CaSiO_3} / (N_{CaO} \cdot N_{SiO_2}) \quad (2.122)$$

$$K_{2.115} = N_{Ca_2SiO_4} / (2N_{CaO} \cdot N_{SiO_2}) \quad (2.123)$$

$$K_{2.116} = N_{Ca_2Si_2O_6} / (N_{CaO} \cdot N_{SiO_2}) \quad (2.124)$$

$$K_{2.117} = N_{Ca_2Si_2O_8} / (4 \cdot N_{CaO} \cdot 2N_{SiO_2}) \quad (2.125)$$

$$K_{2.118} = (N_{Ca_2Si_2O_6} \cdot 2N_{CaO}) / N_{Ca_4Si_2O_8} \quad (2.126)$$

$$K_{2.119} = 2N_{Ca_2Si_2O_4} / N_{Ca_4Si_2O_8} \quad (2.127)$$

We can calculate the number of moles (n) of CaO, MnO and SiO₂ for this ternary slag system by using the following equations:

$$n_{CaO} = n_{CaO(free)} + n_{CaSiO_3} + 2n_{Ca_2SiO_3} + 2n_{Ca_2Si_2O_6} + 4n_{Ca_4Si_2O_8} \quad (2.128)$$

$$n_{MnO} = n_{MnO(free)} + n_{MnSiO_3} + 2n_{Mn_2SiO_4} \quad (2.129)$$

$$n_{SiO_2} = n_{SiO_2(free)} + n_{MnSiO_3} + n_{Mn_2SiO_4} + n_{CaSiO_3} + n_{CaSiO_4} + 2n_{Ca_2Si_2O_4} + 2n_{Ca_4Si_2O_8} \quad (2.130)$$

which can be determined by the chemical analysis of the slag. The mole fractions of the other compounds can be derived from the above-mentioned equations (Moore, 1990).

Although this theory has found several successful applications in ferrous and non-ferrous metallurgy fields, there are several arguments that exist against the molecular theory (Iwamoto, 1975). For example, molecular theory is only valid by

assuming the slag in an ideal state, but it is known that this assumption is not always valid (Moore, 1990). Also, the molecular theory approach gives a formalised description of the slag reactions, but we cannot use the constancy of the equilibrium constant values as a proof of the presence of such molecules and molecular compounds. In addition, the actual molecules formed and the equilibrium constants are not often determined with high accuracy. Furthermore, the experimental data on electrical conductivity, on slag electrolysis and on viscosity measurements have indicated that the slags are composed of ions in the form of cations and anions (Verein Deutscher Eisenhüttenleute, 1981).

2.8.2 Ionic slag theories

With the advance developments in electrochemical and thermodynamic studies on slags, it has been assumed that slags were entirely dissociated structures of ionic species.

Temkin's Theory

The concept of a perfect-ideal ionic solution has been introduced by Temkin (1945) for describing the thermodynamic behaviour of a mixture of fused salts. Temkin assumed that there is mixing only between cations and cation sites and anions and anion sites and also stated that the activity of a salt in a mixture is equal to the product of the ionic fractions of the ions into which the salt decomposes on dissociation. Also, the salts tend to yield v_+ cations and v_- anions during the dissociation, so its activity can be defined by the Eq. (2.131).

$$a = N_+^{v_+} N_-^{v_-} \quad (2.131)$$

where N_+ and N_- represent the ionic fractions of cation and anion, respectively.

Temkin adopted the Lewis Approach to the activity concept and showed that the activity of an ion is equal to its ionic fraction (2.132) (Temkin, 1945).

$$a_+ = N_+ \text{ and } a_- = N_- \quad (2.132)$$

This new expression of “activity” can be related to the concentrations (Verein Deutscher Eisenhüttenleute, 1981). Other assumptions of this theory are as follows (Moore, 1990):

- The slag is entirely dissociated into ions.
- Similar charged ions don't have any interaction.
- Ions are distributed completely random.
- The slag is formed by two ideal solutions of cations and anions.
- All ion species in the slag are known.

By using Temkin's theory, we can calculate the separation of ions in the melt for basic slags. For example, during the calculation of the activity of FeO in a SiO₂-Fe₂O₃-CaO-MnO-FeO slag system. We can write down the following ion-producing dissociation reactions (Moore, 1990).



and the following ion-consuming reactions



The activity of FeO can be calculated by using the following Eq. (2.138):

$$a_{FeO} = N_{Fe^{+2}} \cdot N_{O^{-2}} \quad (2.138)$$

where

$$N_{Fe^{+2}} = \frac{n_{Fe^{+2}}}{n_{Ca^{+2}} + n_{Fe^{+2}} + n_{Mn^{+2}}} \quad (2.139)$$

$$N_{O^{-2}} = \frac{n_{O^{-2}}}{n_{SiO_4^{-4}} + n_{Fe_2O_5^{-4}} + n_{O^{-2}}} \quad (2.140)$$

and

$$n_{O^{-2}} = n_{CaO} + n_{MnO} + n_{FeO} - 2n_{SiO_2} - 2n_{Fe_2O_5} \quad (2.141)$$

One weakness of Temkin's theory is that it assumes that all ions of the slag are known and this makes the application difficult. For example, SiO_4^{-4} , PO_4^{-3} and AlO_3^{-3} ions are formed in strongly basic slags. However, $Si_2O_4^{-6}$ and $Si_3O_{10}^{-8}$ are formed in strong acid slags (Moore, 1990).

Flood's Theory

Flood et al., (1953) used Temkin's theory as a base and considered the equilibrium between elements dissolved in the metallic and slag phases. According to Flood, the slag behaves in an ideal manner but metal behaves in a non-ideal manner. This approach can be applicable to metal-slag reactions like desulphurisation and dephosphorisation reactions in iron and steel making.

$$S_{(metal)} + O_{(slag)}^{-2} = S_{(slag)}^{-2} + O_{(metal)} \quad (2.142)$$

where the equilibrium constant for this reaction can be written as follows:

$$K_{2.142} = \frac{a_{O_{(M)}} \cdot a_{S_{(s)}}^{-2}}{a_{S_{(m)}} \cdot a_{O_{(s)}}^{-2}} \quad (2.143)$$

where (M) and (S) represent metal and slag phases, respectively.

If we assume the slag phase in ideal form and metal phase in real solution form, the activity of sulphur and oxygen can be derived from the following equations, respectively.

$$a_{S_{(s)}^{-2}} = N_{S_{(s)}^{-2}} \text{ and } a_{S_{(m)}} = f_{S_{(m)}} \text{ wt.\%} S \quad (2.145)$$

$$a_{O_{(s)}^{-2}} = N_{O_{(s)}^{-2}} \text{ and } a_{O_{(m)}} = f_{O_{(m)}} \text{ wt.\%} O \quad (2.146)$$

where f represents Henrian activity coefficient, then

$$K = \frac{N_{S_{(s)}^{-2}} \cdot \%O_{(m)} \cdot f_{O_{(m)}}}{N_{O_{(s)}^{-2}} \cdot \%S_{(m)} \cdot f_{S_{(m)}}} = K' \frac{f_{O_{(m)}}}{f_{S_{(m)}}} \quad (2.147)$$

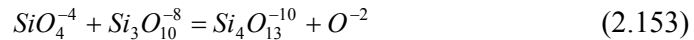
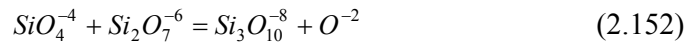
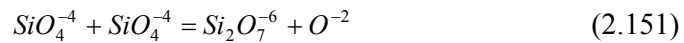
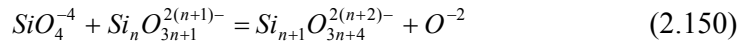
$$K' = \frac{N_{S_{(s)}^{-2}} \cdot \%O_{(m)}}{N_{O_{(s)}^{-2}} \cdot \%S_{(m)}} \quad (2.149)$$

Therefore, K becomes equal to K' when $f_{O(M)} = f_{S(M)} = g(f) = 1$ while Henry's Law is followed (Moore, 1990).

Masson's Theory

Masson's theory treats the distribution of complex ions in terms of ion fraction and calculates the activity of a basic oxide in a silicate slags. However, Masson's approach limited to the silicate anion that has no ring structure (Masson, 1965; Masson et al., 1970).

The reaction (2.150) shows the all polycondensation reactions and the following polymerisation reactions and equilibrium constants represent the equilibria between complex anions (SiO_4^{-4} , $Si_2O_7^{-6}$ and $Si_3O_{10}^{-8}$) (Masson et al., 1970).



Therefore, the equilibrium constant for generalised reaction (2.150) is independent of chain length, equal reactivity if functional groups being assumed. When we consider the multi functional, the number of sites available for growth and degradation by reaction (2.150) tends to vary with n. Therefore, the equilibrium ratios k_{1n} are not identical, but strictly depends on the length of the chain. (Masson et al., 1970)

Hence the sum of the silicate anions can be calculated by the Eq. (2.154) (Moore, 1990).

$$\Sigma N_{(silicateions)} = N_{SiO_4^{-4}} + N_{Si_2O_7^{-6}} + N_{Si_3O_{10}^{-8}} + N_{Si_4O_{13}^{-10}} + N_{Si_nO_{(3n+1)}^{-2(n+1)}} \quad (2.154)$$

$$= N_{SiO_4} + (K_{2.150} \cdot N_{SiO_4} / N_{O^{-2}}) \Sigma N_{(silicateions)} \quad (2.155)$$

The final relation can be defined as follows (Iwamoto, 1975):

$$N_{SiO_4} = 1 - N_{O^{-2}} / 1 + K_{2.150} (1 / N_{O^{-2}} - 1) \quad (2.156)$$

The silica content of the slag can be determined by the chemical analysis of the slag and the mole fraction of SiO_2 , N_{SiO_2} , can be related to $N_{O^{-2}}$ as given by

$$N_{SiO_2} = \frac{n_{SiO_2}}{n_{SiO_2} + n_{MO(free)} + n_{MO(silicates)}} \quad (2.157)$$

Hence, the activity of a basic oxide (a_{MO}) can be derived if we know $N_{O^{-2}}$, $N_{silicate ions}$ and N_{SiO_2} .

Masson's theory has some limitations in the application to slag systems (Moore, 1990; Guochang, 1993):

- Constants, K, for the initial silicates $Si_2O_7^{-6}$, $Si_3O_{10}^{-8}$ are different from the more complex silicates forms.

- Only the formation of linear chains has been taken into consideration which can be applicable to binary silicate structures. It has a limited application zone of mole fraction of SiO₂ is lower than 0.5.
- The ion interaction in the real solutions has not been considered in this approach.

Toop and Samis's Theory

Toop and Samis (1962) applied the theory of polymerisation of silicate anions to ternary slag systems. According to their approach the following equations can be developed (Iwamoto, 1975).

$$2O^- = O^o + O^{-2} \quad (2.158)$$

$$K_{2.158} = \frac{O^o \cdot O^{-2}}{(O^-)^2} \quad (2.159)$$

If we balance the charge,

$$2(O^o) + (O^-) = 4N_{SiO_2} \quad (2.160)$$

$$(O^o) = [4N_{SiO_2} - (O^-)] / 2 \quad (2.161)$$

and when we balance the mass,

$$(O^{-2}) = (1 - N_{SiO_2}) - (O^-) / 2 = (2 - 2N_{SiO_2}) - (O^-) / 2 \quad (2.162)$$

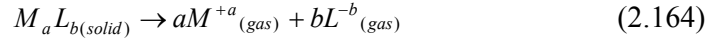
The general equation can be written as follows:

$$4K_{2.158} = [4N_{SiO_2} - (O^-)][2 - 2N_{SiO_2} - (O^-)] / (O^-)^2 \quad (2.163)$$

If we know the values of $K_{2.158}$ and N_{SiO_2} , we can calculate the (O^-) . In addition, Toop and Samis (1962) reported a relationship between (O^-) content and free energy of mixing.

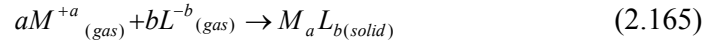
2.9 Relationship between the Sulphide and Phosphide Capacities of Slags and the Lattice Energy of the Component Oxides

Lattice (potential) energy (U) is the amount of energy required to convert a crystalline solid lattice, M_aL_b to its constituent gaseous ions, $aM^{+a}(g)$ and $bL^{-b}(g)$ by the following reaction (2.164).



The required energy for this conversion cannot be experimentally determined. However, it can be estimated by using Hess' Law in the form of Born-Fajans-Haber cycle, which is an enthalpy based-thermodynamic cycle. Also, we can calculate the lattice energy from the electrostatic consideration of its crystal structure (Donald and Jenkins, 2005).

The lattice energy is positive because it is the energy required to separate the ions. On the contrary, the energy requirement for the reverse process will be negative and the energy released is known as the energy of crystallisation (E_{cryst}).



Hence, $U = -E_{cryst}$

By using the Born-Landé equation, we can derive the following equation for the lattice energy.

$$U = -\frac{N_A \cdot A \cdot z^+ \cdot z^- \cdot e^2}{4 \cdot \pi \cdot e_o \cdot r_o} \cdot \left(1 - \frac{1}{n}\right) \quad (2.166)$$

where N_A is Avogadro's number, A is Madelung constant, z^+ is relative cation charge, z^- is relative anion charge, e is electron charge, e_o is permittivity of free space, r_o is sum of the ionic radii and n is the average Born exponent.

As the ionic radius of cations or anions increase, the lattice energies tend to decrease. Also, the solids with monovalent ions have less lattice energies compared to the solids with divalent ions.

For a process at a constant pressure in which ions in gaseous form are generated, the relationship between the lattice enthalpy and lattice potential energy can be defined as follows (Donald and Jenkins, 2005):

$$\Delta H = \Delta U + \Delta nRT \quad (2.167)$$

where H, U, n, R, T represent enthalpy, internal energy, number of moles, gas constant and temperature, respectively.

2.9.1 Relationship between lattice energy and sulphide capacity

Ichise and Moro-Oka (1990) 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 ionisation energy of elements. As described in their work, the Born-Haber cycle can be used during the calculation of the lattice energy of an oxide crystal MO from a variety of disparate factors such as the heat of sublimation of pure metal M, the enthalpy of formation of the oxide and the ionisation energy of M. The Born-Haber cycle calculation of CaO is given in Figure 2.56 (Ichise and Moro-Oka, 1990).

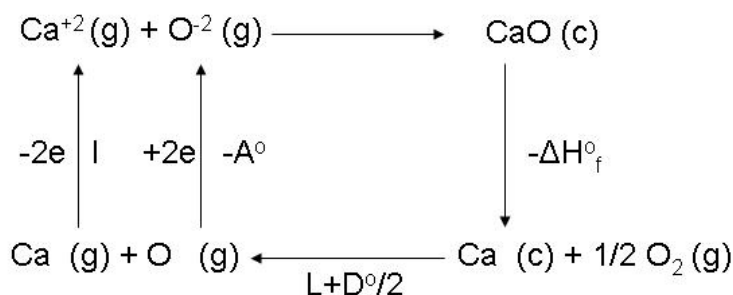


Figure 2.56 Born-Haber Cycle of CaO crystal (Ichise and Moro-Oka, 1990).

$$\oint dE = 0 = -E^0 - \Delta H_f^0 + L + D^0 / 2 + I - A^0 \quad (2.168)$$

where E° , ΔH_f° , L , D° , I , A° are the lattice energy of CaO, enthalpy of formation of CaO, sublimation heat of element Ca, dissociation energy of O_2 molecule, ionisation energy of Ca, electron affinity of O^{2-} , respectively (Ichise and Moro-Oka, 1990).

The sum of energies for the Born-Haber cycle of CaO should be equal to zero. Therefore, the definition of the lattice energy can be written as follows.

$$E^\circ = -\Delta H_f^\circ + L + D^\circ / 2 + I - A^\circ \quad (2.169)$$

If we want to define the lattice energy for an oxide M_xO_y :

$$E^\circ = -\Delta H_f^\circ + x(L + I) + y(D^\circ / 2 - A^\circ) \quad (2.170)$$

The values for energies used in the calculation of lattice energy values are given in Table 2.7 (Ichise and Moro-Oka, 1990)

Ichise and Moro-Oka (1990) assumed the following points for evaluating the binding energy used on the oxide anion in liquid oxide mixture.

- Each ion is surrounded by ions with opposite sign in the liquid oxide mixture.
- Every component of the oxide separated to its elemental ions and no complex rigid combinations have been formed between ionising the liquid oxide mixture.
- The cations mix randomly in the oxide mixture, oxide anions are bound to the cation mixture with the average binding energy of all cations.

Table 2.7 Energies values used in the calculation of lattice energy of selected oxides (Ichise and Moro-Oka, 1990)

MxOy	ΔH_f^0 (kJ/mol)	ΔH_f^S (kJ/mol)	$L_{(298)}$ (kJ/g-atom)	I (kJ/g-ion)	$\bar{E}^o$ (kJ/mol)	$\bar{E}^{os}$ (kJ/mol)
K ₂ O	-363.2	-428.4	90.0	418.8	2 287	231
Na ₂ O	-415.1	-374.5	110.2	495.8	2 536	337
Li ₂ O	-596.7	-446.4	161.5	520.1	2 866	447
BaO	-553.5	-443.5	(192)	1 468.2	3 121	407
SrO	-592.0	-452.3	—	1 613.4	—	436
CaO	-634.3	-476.1	176.1	1 735.1	3 452	455
MnO	-384.9	-213.4	280.7	2 226.3	3 799	468
FeO	-264.4	-100.4	398.3	2 320.9	3 891	461
ZnO	-350.6	-205.2	129.3	2 639.7	4 025	442
MgO	-601.2	-351.5	146.4	2 188.2	3 845	547
BeO	-608.4	-233.5	324.3	2 656.4	4 498	672
Cr ₂ O ₃	-1 129.7	-364.0	396.6	5 231.3	15 108	1 656
Fe ₂ O ₃	-821.3	—	398.3	5 278.5	14 895	—
Al ₂ O ₃	-1 677.4	-723.4	321.7	5 138.8	15 322	1 844
Ti ₂ O ₃	-1 520.9	-618.0	469.0	4 618.7	14 418	1 793
B ₂ O ₃	-1 271.9	-252.3	569.0	6 887.3	18 907	1 910
GeO ₂	-579.9	-156.9	383.7	10 009.8	12 786	1 016
TiO ₂	-944.7	-410.3	469.0	8 789.6	12 019	1 128
SiO ₂	-910.4	-213.4	431.0	9 947.9	13 125	1 291
P ₂ O ₃	-1 505.0	-186.2	316.4	17 055.2	40 786	2 802

$D^o/2(1/2O_2(g) = O(g)) = 249.16 \text{ kJ}$, $A^o(O = O^{2-}) = -658.19 \text{ kJ}$
 $D^S/2(1/2S_2(g) = S(g)) = 215.06 \text{ kJ}$, $A^S(S = S^{2-}) = -395.58 \text{ kJ}$

The following equation can be used for describing the lattice energy (E^o) of an oxide mixture

$$E^o = E_i^o X_i \quad (2.171)$$

The total number of moles of O⁻² ion ($n_{O^{-2}}$) in 1 mol of the oxide mixture is defined by the following equation

$$n_{O^{-2}} = \sum y_i X_i \quad (2.172)$$

Therefore, we have the expression for the binding energy to the O⁻² anion of the oxide mixture, the lattice energy per mole of O⁻², E^o is defined by

$$\overline{E^o} = \frac{\sum E_i^o X_i}{\sum y_i X_i} \quad (2.173)$$

The relationship between the activity coefficient of O^{2-} and the lattice energy per mole of O^{2-} can be written as follows:

$$RT \ln \gamma_{O^{2-}} = \overline{E^o} \quad (2.174)$$

As expressed early, Ichise and Moro-Oka's model 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.

In their approach, first they described the sulphide capacity of the slag system as

$$C_s = (wt.\%S) \left\{ \frac{P_{O_2}}{P_{S_2}} \right\}^{1/2} = K \frac{a_{O^{2-}}}{f_{S^{2-}}} \quad (2.175)$$

where, K , $a_{O^{2-}}$ and $f_{S^{2-}}$ is the equilibrium constant for the reaction 2.21, the activity of O^{2-} and the activity coefficient of S^{2-} , respectively.

We know that the amount of S^{2-} in the slag is extremely low and the ionic fraction of the oxide anion is nearly equal to 1 and if we assume $f_{S^{2-}}$ is constant, we can express the logarithm of sulphide capacity as follows:

$$\log C_s = \log \gamma_{O^{2-}} + \text{constant} \quad (2.176)$$

By combining Eqs. 2.174 and 2.176, we can redefine the logarithm of sulphide capacity

$$\log C_s = \frac{\overline{E^o}}{2.303.R.T} + \text{constant} \quad (2.177)$$

The values of $\overline{E^o}$ for the slag system which contains SiO₂, CaO, MgO, MnO and Al₂O₃ can be calculated by using E^o values from Table 2.9 and Equation 2.173.

$$\overline{E^o} = \frac{3452X_{CaO} + 3845X_{MgO} + 15322X_{Al_2O_3} + 13125X_{SiO_2} + 3799X_{MnO}}{X_{CaO} + X_{MnO} + X_{MgO} + 3X_{Al_2O_3} + 2X_{SiO_2}} \quad (2.178)$$

It was found that the logarithmic value of the activity coefficient of an oxide anion in the slag ($\gamma_{O^{2-}}$) has a linear relation with the averaged lattice energy obtained from the lattice energy of the component oxides ($\overline{E^o}$). Their results show that the lattice energy per mole of O²⁻ ion of an oxide mixture ($\overline{E^o}$) which is another way for expressing the binding energy of O²⁻ ion in the mixture, has a linear relationship with the logarithmic sulphide capacities in CaO-MgO-Al₂O₃, CaO-MgO-SiO₂, CaO-Al₂O₃-SiO₂, CaO-MgO, Al₂O₃-SiO₂ slags at 1 773 K. (Ichise and Moro-Oka, 1990).

Ichise and Moro-Oka (1990) showed that the same approach can be applied to the activity coefficient of S²⁻. For this case, the slag composition dependence of the binding energy to S²⁻ ion in the slag can be calculated by using the following equations.

$$E^s = -\Delta H_f^s + x(L + I) + y(D^s / 2 + A^s) \quad (2.179)$$

Where ΔH_f^s is the enthalpy of formation of the sulphide, D^s is the dissociation energy of S₂ and A^s is the electron affinity of the S²⁻ ion.

The binding energy to the S²⁻ anions in the sulphide mixture can be calculated

$$\overline{E^s} = \frac{\sum E_i^s X_i}{\sum y_i X_i} \quad (2.180)$$

By combining Eqs. 2.177 and 2.180, we can redefine the logarithm of sulphide capacity

$$\log C_s = \log \gamma_{O^{2-}} - \log f_{S^{2-}} + \text{constant} \quad (2.181)$$

Ichise and Moro-Oka indicated that a linear relation can be seen between $\log C_s$ and $(\overline{E}^o - \overline{E}^s)$. Both of oxygen and sulphur are surrounded by the same cation mixture in a slag and they have the same charge -2 in the slag, the values x_i and y_i are common for oxide and sulphide. The difference between $\overline{E}^o - \overline{E}^s$ is equal to $\overline{E}^{OS}$ and can be calculated by the following equation.

$$\overline{E}^{OS} = \frac{\sum (E_i^o - E_i^s) X_i}{\sum y_i X_i} \quad (2.182)$$

Their findings show that a good linear correlation can be achieved between the logarithm of sulphide capacity and the difference of lattice energies of mixed oxide and mixed sulphide in CaO-MgO-Al₂O₃-SiO₂ slags at 1 773 K.

The values of $\overline{E}^{OS}$ for the slag system which contains SiO₂, CaO, MgO, MnO and Al₂O₃ can be calculated by using the following equation.

$$\overline{E}^{OS} = \frac{455X_{CaO} + 547X_{MgO} + 1844X_{Al_2O_3} + 1291X_{SiO_2} + 468X_{MnO}}{X_{CaO} + X_{MnO} + X_{MgO} + 3X_{Al_2O_3} + 2X_{SiO_2}} \quad (2.183)$$

As, it was indicated in Ichise and Moro-Oka 's study (1990), sulphide capacities of different slag systems can be determined by using 2.177. This approach was applied to CaO-MgO-Al₂O₃-SiO₂, CaO-MgO-Al₂O₃-SiO₂-FeO, CaO-MgO-Al₂O₃-SiO₂-FeO-MnO slags systems for a temperature range of 1500 to 1650 °C. Ichise and Moro-Oka's approach (1990) is chosen in order to develop a prediction model for sulphide capacities of ferrochromium and ferromanganese smelting slags in the present study. The simplicity of the model can be considered as an important advantage for industrial applications also it was demonstrated that the model can

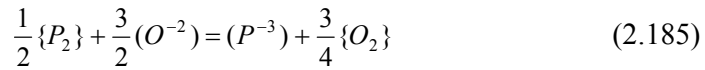
be applicable to the conditions pertinent to ferrochromium and ferromanganese smelting process from slag compositions and temperature point of views.

2.9.2 Relationship between lattice energy and phosphide capacity

A similar approach for developing a correlation between phosphide capacity and lattice energy of the component oxides ($\overline{E^o}$) can be applicable to Ichise and Moro-Oka 's method (1990).

In this approach, first we have to define the phosphide capacity of the slag system (2.184) by using reaction 2.185

$$C_{P^{-3}} = (wt.\%P) \frac{P_{O_2}^{3/4}}{P_{P_2}^{1/2}} = \frac{f_{P^{-3}} (wt.\%P) . P_{O_2}^{3/4}}{P_{P_2}^{1/2} . a_{O^{-2}}^{3/2}} \cdot a_{O^{-2}}^{3/2} \quad (2.184)$$



By assuming that the amount of P^{-3} in the slag is low, the ionic fraction of oxide anion is nearly equal to 1 and if we assume $f_{P^{-3}}$ is constant, we can express the logarithm of phosphide capacity as follows:

$$\log C_{P^{-3}} = \frac{3}{2} \log \gamma_{O^{-2}} + \text{constant} \quad (2.186)$$

We can define the relationship between ($\overline{E^o}$) and the activity of oxygen by using the following equations.

$$RT \ln(a_{O^{-2}})^{3/2} = \overline{E^o} \quad (2.187)$$

$$RT \ln(\gamma_{O^{-2}} . X_{O^{-2}})^{3/2} = -RT \ln K_{3.282} = \overline{E^o} \quad (2.188)$$

$$-RT2.303 \log \frac{1}{\gamma_{O^{2-}}^{3/2}} = -RT2.303 \log \gamma_{O^{2-}}^{-3/2} = \overline{E^o} \quad (2.189)$$

$$\log \gamma_{O^{2-}}^{-3/2} = \frac{\overline{E^o}}{-RT2.303} \quad (2.190)$$

$$\frac{3}{2} \log \gamma_{O^{2-}} = \frac{\overline{E^o}}{RT2.303} \quad (2.191)$$

$$\log C_{P^{-3}} = \frac{3}{2} (\log \gamma_{O^{2-}}) \left[\frac{2}{3} \frac{\overline{E^o}}{RT2.303} \right] + \text{constant} \quad (2.192)$$

$$\log C_{P^{-3}} = \frac{\overline{E^o}}{RT2.303} + \text{constant} \quad (2.193)$$

The derived equation 2.193 can be used in the determination of relationship between phosphide capacity and lattice energy of the component oxides ($\overline{E^o}$). As the equation indicates a linear relation between the logarithm of phosphide capacity and lattice energy of the component oxides ($\overline{E^o}$) can be expected. This approach will be used in the following sections in the prediction of phosphide capacities of ferrochromium smelting slags.

3 EXPERIMENTAL SET-UP AND TECHNIQUE

The measurements of sulphide capacities of the ferromanganese smelting slag system was carried out by equilibrating slags with Fe-Mn-Si-C_{sat}-S alloys at 1500 °C in graphite crucibles under a carbon monoxide atmosphere. Measurements were also made of the sulphide and phosphide capacities of ferrochromium smelting slags which were equilibrated with Fe-Cr-Si-C_{sat}-(S or P) in graphite crucibles under a carbon monoxide atmosphere at 1 600 °C . Slag-metal samples were placed in graphite crucibles and heated in a gas tight vertical molybdenum wound resistance tube furnace at 1500 °C and 1 600 °C under carbon monoxide atmosphere until the equilibrium phases were attained. The samples were quenched after the equilibration. In this chapter, the details of statistical design of experiments, preparation of metal and slag samples, experimental set-up and procedure are given.

3.1 Statistical Design of the Experiments

In this study, slag and metal compositions were chosen to represent the general slag and metal compositions of the high carbon ferrochromium and ferromanganese smelting operations. Typical chemical compositions for slag and metal phases of ferrochromium and ferromanganese studies are listed in Table 3.1 and Table 3.2.

In the actual processes of high carbon ferrochromium production, the slag system contains certain amounts of chromium and iron oxides in the structure. However, in the present study, chromium and iron oxides were not included in the ferrochromium slag composition range. The chromium in the slag phase exists as partially reduced ore or alloy prills. In the reduced ore, the divalent state chromium acts as a modifying cation whereas the trivalent state chromium behaves more acidic (Demir, 1998).

Table 3.1 Examples for slag and metal compositions employed in previous ferrochromium studies.

a) Ferrochromium Slag Compositions (wt. %)

Reference	Al ₂ O ₃	SiO ₂	CaO	MgO	Cr ₂ O ₃	FeO
Pan (1998)	6-45	10-63	0.2-11	0.1-20	1-35	0.2-4
Barcza (1976)	25-27	35-54	1-30	2-24	0.1-1.2	-
Wethmar et al. (1975)	15-20	30-40	5-13	10-20	15-20	5-10

b) Ferrochromium Metal Compositions (wt. %)

Reference	Cr	C	Si	Fe	S
Pan (1998)	65	3-15	1-5	14.5-30.8	0.2-0.5
Wethmar et al. (1974)	50-65	4-8	0-10	17-46	-
Wethmar et al. (1975)	50-55	6-8	2-7	35-40	-
Howat (1986)	47-60	4-6	1-5	30-43	-

Table 3.2 Examples for slag and metal compositions employed in previous ferromanganese studies.

a) Ferromanganese Slag Compositions (wt. %)

Reference	Al ₂ O ₃	SiO ₂	CaO	MgO	MnO
Li et al. (1999)	2.5-7	25-60	4-35	0.5-38	5-40
Cengizler (1993)	15-21	18-22	4-10	-	38-48
Warren (1972)	10-30	18-47	33-46	0.25	0-25
See (1976)	10-14	28-30	14-18	0.5-8	20-27

b) Ferromanganese Metal Compositions (wt. %)

Reference	Mn	C	Si	Fe	S	P
Cengizler (1993)	75-77	7-8	1-2	12.9-16.9	0.02	0.025
See (1976)	74-82.19	6-7	0.1-1.5	9.34-19.9	-	-

The initial slag compositions range employed in the sulphide and phosphide capacity studies of ferrochromium smelting slags are listed in Table 3.3 and 3.4, respectively.

Table 3.3 The initial slag compositions range for the sulphide capacity study of ferrochromium smelting slags (wt. %).

Cr ₂ O ₃	Al ₂ O ₃	CaO	MgO	SiO ₂
0.5-5	20	1.1-5.9	25-45	30-47

Table 3.4 The initial slag compositions range for the phosphide capacity study of ferrochromium smelting slags (wt. %).

Cr_2O_3	Al_2O_3	$\text{Ca}_3(\text{PO}_4)_2$	MgO	SiO_2
0.5-5	20	1.1-10.9	25-45	30-47

Table 3.5 shows the initial slag composition range employed in the sulphide capacity study of ferromanganese smelting slags.

Table 3.5 The initial slag compositions range for sulphide capacity study of ferromanganese smelting slags (wt. %).

MnO	Al_2O_3	CaO	MgO	SiO_2
5-10	5	18-36	10-15	36-54

The statistical method for investigating the properties of multi-component systems as a function of composition was developed by Scheffe (1958). Scheffe's method can be used for making assumptions related to the systems involving composition that the sum of proportions by volume, weight, etc., must be unity. So, the factor space is a regular simplex-for three components, a triangle; for four, a tetrahedron. Factor space is explored at points of composition corresponding to an ordered arrangement known as lattice (Scheffe, 1958).

The lattice method is useful when several properties are of interest. This technique has two main features:

- Properties or responses are measured at lattice composition points.
- Polynomial equations having a special correspondence to the lattice points are calculated. The coefficients in the polynomials then become simple functions of the measured properties (Gorman and Hinman, 1962).

If a response over a wide range of composition is of interest, a possible selection of composition points for measuring responses in one gives a uniform distribution of points over all possible mixtures of the components. Such a distribution is

referred to as cubic or quadratic lattice, depending on the number of points. In addition to these lattices, a modified lattice is made by adding centre points to the two-dimensional face or faces of the quadratic lattice. This modified lattice is called the special-cubic lattice (Gorman and Hinman, 1962).

The extreme vertices design in the present study is formed by the lower and upper boundary constraints of the slag compositions. This approach originally derived from McLean and Anderson (1966) method is described below.

In the experiments dealing with mixtures, the q factors (components) are all represented by a proportion, x_i , of the total mixtures (McLean and Anderson, 1966).

Thus,

$$\sum_{i=1}^q x_i = 1 \quad \text{and} \quad 0 \leq a_i \leq x_i \leq b_i \leq 1 \quad (3.1)$$

where $i = 1, \dots, q$ and the a_i and b_i are constraints on the x_i imposed by the physical conditions involved. First, the constraints placed on the individual factors describe an irregular hyper polyhedron ($q-1$ dimensions). The vertices and centroids of this figure describe a unique set of points (the design of experiment) which may be used to estimate the response surface.

In the case of the quadratic model:

$$y = \sum_{i=1}^q \beta_i \cdot x_i + \sum_{1 \leq i \leq j \leq q} \beta_{ij} \cdot x_i \cdot x_j \quad (3.2)$$

where y is used as a minimum of $\frac{1}{2}q(q+1)$ points are required in this model.

Additional points can be used to estimate the error or the misfit. If an additional point is needed, the mid points of the edges of the hyper-polyhedron can be used or some of the existing points can be repeated (McLean and Anderson, 1966).

Once constraints for each factor are determined, the statistical experimental design can be defined. The definition of the space or region can be achieved by using the parameters range (Demir, 1998; McLean and Anderson, 1966).

The extreme vertices design must fall on the boundary formed by the upper or lower constraints of the $q-1$ factors. So, the vertices of the design may be found by the following rules (McLean and Anderson, 1966):

- a) Write all the possible two level treatment combinations using the a_i and b_i levels for all but one factor which is left, e.g. $(a_1, b_2, a_3, \dots, a_5, b_6)$ for a six factor experiment. This procedure generates $q \cdot 2^{q-1}$ possible treatment combinations with one factor's level blank in each.
- b) Go through all $q \cdot 2^{q-1}$ possible treatment combinations and fill in the blanks that are admissible, i.e., that level (necessary failing within the constraints of the missing factor) which will make the sum of the levels for that treatment combination equal to one. Each of the admissible treatment combinations is a vertex; however, some vertices may appear more than once (McLean and Anderson, 1966).

The hyper-polyhedron is constructed and contains a variety of centroids. There is one located in each bounding 2-dimensional face, 3-dimensional face, ..., r -dimensional face ($r \leq q-2$), and the centroid of the hyper-polyhedron. The next step is to treat the combination obtained by averaging all the factor levels of the existing vertices. The centroids of the 2-dimensional faces are found by isolating all the sets of vertices of which $q-3$ factor levels remains constant within a given set and by averaging the factor levels for each of the three remaining factors. All remaining centroids are found in a similar form using all the vertices which have $q-r-1$ factor levels constant within a set for a r -dimensional face where $3 \leq r \leq q-2$. The assumption given by the researchers is that the dimensionality of the hyper-polyhedron formed by extreme vertices will always be $q-1$ (McLean and Anderson, 1966).

The constraints determine the design and if wrong range of constraints is chosen, there will be too much data in unprofitable regions.

According to Gorman (1966), if some of the extreme vertex points tend to cluster, it might be expedient to see whether slight alterations of the constraints will cause the cluster to collapse to a single point. Also he stated that adding midpoints of the edges to the vertices and centroids gives a design which covers a slightly larger region.

The statistical design approach help the research in the analysis of the joint effects of several factors efficiently on the response. Several metallurgical studies have been conducted by using statistical experimental design method (Demir, 1998; Ding, 2001; Pan, 1998; Kucukkaragoz and Eric, 1998; Maramba, 2007). As the experimental study will be concentrated around the weights of the slag and metal components, Scheffe's approach has been chosen as experimental design method.

3.1.1 Statistical experimental design for the phosphide capacity study of ferrochromium smelting slags

Lower boundary (a_i) and upper boundary (b_i) conditions for the four factors of the system in question are detailed in Table 3.6.

Table 3.6 Lower boundary (a_i) and upper boundary (b_i) conditions for the four variable factors and one fixed factor of the phosphide capacity study of ferrochromium smelting slags.

Component	a_i	b_i
X1= (Cr_2O_3)	0.005	0.05
X2= (SiO_2)	0.3	0.47
X3=(MgO)	0.25	0.45
X4=($\text{Ca}_3(\text{PO}_4)_2$)	0.011	0.109
X5=(Al_2O_3)	0.2 (fixed)	

All the possible combinations of $q-1$ factors are listed by using the a_i and b_i values for all factors except one which is left as blank. a_1, a_2, a_3, a_4 are lower bounds and b_1, b_2, b_3, b_4 are upper bounds for the four factors x_1, x_2, x_3, x_4 . The three level ($q-1$) combinations which are equal to $q.2^{q-1}$ in number are given in Table 3.7.

The design points which are obtained by calculating the blank proportion for all the combinations and by establishing the feasible vertices of the polyhedron which fulfils the boundary conditions are presented in Table 3.8 where the blanks (-) represent the proportion to be filled by the factor which is left out from the combination. As it was mentioned due to the fixed percentage of alumina, it can be represented as $X_5=0.2$ with a constant 20 wt. %. The proportion to be filled into the blank is simply calculated by subtracting the total of the other three from 0.8 (80 wt. %).

At each point that defines the vertex in the polyhedron, the sum of the proportions of the factors must be equal to unity and each factor must be in the region of its boundary values. The rows in the italics represent the vertices and are numbered from 1 to 12.

Table 3.7 All the possible combinations of ($q-1$) factors of the phosphide capacity study of ferrochromium smelting slags.

Group 1	Group 2	Group 3	Group 4
a1,b2,a3,-	a1,b2,a4,-	a1,b3,a4,-	a2,b3,a4,-
a1,a2,a3,-	a1,a2,a4,-	a1,a3,a4,-	a2,a3,a4,-
a1,b2,b3,-	a1,b2,b4,-	a1,b3,b4,-	a2,b3,b4,-
a1,a2,b3,-	a1,a2,b4,-	a1,a3,b4,-	a2,a3,b4,-
b1,b2,a3,-	b1,b2,a4,-	b1,b3,a4,-	b2,b3,a4,-
b1,a2,a3,-	b1,a2,a4,-	b1,a3,a4,-	b2,a3,a4,-
b1,b2,b3,-	b1,b2,b4,-	b1,b3,b4,-	b2,b3,b4,-
b1,a2,b3,-	b1,a2,b4,-	b1,a3,b4,-	b2,a3,b4,-

After the feasible vertices of the polyhedron are defined, next stage is to obtain the points which are located in the centres of the edges, faces and the overall centre of the polyhedron. There is one centroid point located on the bounds of two or more dimensional faces as well as at the overall centroid of the polyhedron. The n-dimensional faces are determined by grouping the vertices where each vertex has the same value X_i for one of the components. The average of these vertices determines the face centroid. There are 8 face centroids and 1 overall centroid which exists in the present system. The overall centroid is defined as the average of the 12 vertices. Co-ordinates of the 21 design points for the slag compositions as defined in Table 3.6 are shown in Table 3.9.

Table 3.8 The design points for the phosphide capacity study of ferrochromium smelting slags.

Group-1						
	X1	X2	X3	X4	X5(Fixed)	Vertices
1	0.005	0.47	0.25	0.075	0.2	1
2	0.005	0.3	0.25	0.245	0.2	
3	0.005	0.47	0.45	-0.125	0.2	
4	0.005	0.3	0.45	0.045	0.2	2
5	0.05	0.47	0.25	0.03	0.2	3
6	0.05	0.3	0.25	0.2	0.2	
7	0.05	0.47	0.45	-0.17	0.2	
8	0.05	0.3	0.45	0	0.2	
Group-2						
	X1	X2	X4	X3	X5(Fixed)	Vertices
9	0.005	0.47	0.011	0.313	0.2	4
10	0.005	0.3	0.011	0.483	0.2	
11	0.005	0.47	0.109	0.215	0.2	
12	0.005	0.3	0.109	0.385	0.2	5
13	0.05	0.47	0.011	0.268	0.2	6
14	0.05	0.3	0.011	0.438	0.2	7
15	0.05	0.47	0.109	0.17	0.2	
16	0.05	0.3	0.109	0.34	0.2	8
Group-3						
	X1	X3	X4	X2	X5(Fixed)	Vertices
17	0.005	0.45	0.011	0.333	0.2	9
18	0.005	0.25	0.011	0.533	0.2	
19	0.005	0.45	0.109	0.235	0.2	
20	0.005	0.25	0.109	0.435	0.2	10
21	0.05	0.45	0.011	0.288	0.2	
22	0.05	0.25	0.011	0.488	0.2	
23	0.05	0.45	0.109	0.19	0.2	
24	0.05	0.25	0.109	0.39	0.2	11
Group-4						
	X2	X3	X4	X1	X5(Fixed)	Vertices
25	0.3	0.45	0.011	0.038	0.2	12
26	0.3	0.25	0.011	0.238	0.2	
27	0.3	0.45	0.109	-0.059	0.2	
28	0.3	0.25	0.109	0.14	0.2	
29	0.47	0.45	0.011	-0.131	0.2	
30	0.47	0.25	0.011	0.068	0.2	
31	0.47	0.45	0.109	-0.229	0.2	
32	0.47	0.25	0.109	-0.029	0.2	

Table 3.9 The co-ordinates of 21 design points for the phosphide capacity study of ferrochromium smelting slags.

Design Point Designation	Type of Boundary	Cr ₂ O ₃ (X1)	SiO ₂ (X2)	MgO (X3)	(Ca ₃ (PO ₄) ₂) (X4)	Al ₂ O ₃ (X5)
1	Vertex	0.005	0.470	0.250	0.075	0.200
2	Vertex	0.005	0.300	0.450	0.045	0.200
3	Vertex	0.050	0.470	0.250	0.030	0.200
4	Vertex	0.005	0.470	0.313	0.012	0.200
5	Vertex	0.005	0.300	0.386	0.109	0.200
6	Vertex	0.050	0.470	0.268	0.012	0.200
7	Vertex	0.050	0.300	0.438	0.012	0.200
8	Vertex	0.050	0.300	0.341	0.109	0.200
9	Vertex	0.005	0.333	0.450	0.012	0.200
10	Vertex	0.005	0.436	0.250	0.109	0.200
11	Vertex	0.050	0.391	0.250	0.109	0.200
12	Vertex	0.032	0.300	0.450	0.012	0.200
13	Face Centroid	0.005	0.385	0.350	0.060	0.200
14	Face Centroid	0.050	0.386	0.309	0.054	0.200
15	Face Centroid	0.028	0.470	0.270	0.032	0.200
16	Face Centroid	0.030	0.300	0.413	0.057	0.200
17	Face Centroid	0.028	0.442	0.250	0.081	0.200
18	Face Centroid	0.016	0.311	0.450	0.023	0.200
19	Face Centroid	0.030	0.375	0.384	0.012	0.200
20	Face Centroid	0.028	0.357	0.307	0.109	0.200
21	Overall Centroid	0.027	0.378	0.341	0.054	0.200

3.1.2 Statistical experimental design for the sulphide capacity study of ferrochromium smelting slags

For the sulphide capacity study, the slag contains the following oxides: Cr₂O₃, SiO₂, MgO, CaO and Al₂O₃. The upper and lower boundaries of the factors are given in Table 3.10.

Table 3.10 Lower boundary (ai) and upper boundary (bi) conditions for the four variable factors and one fixed factor of the sulphide capacity study of ferrochromium smelting slags.

Component	ai	bi
X1= (Cr ₂ O ₃)	0.005	0.05
X2= (SiO ₂)	0.3	0.47
X3=(MgO)	0.25	0.45
X4=(CaO)	0.012	0.059
X5=(Al ₂ O ₃)	0.2 (fixed)	

The design points are listed in Table 3.11. The italic rows represent the defined limits of vertices and are numbered from 1 to 12. 8 face centroids and 1 overall centroid points are defined. Table 3.12 gives the co-ordinates of the 21 design points for the slag compositions in the defined constraints.

Table 3.11 Design points for the sulphide capacity study of ferrochromium smelting slags.

Group-1						
	X1	X2	X3	X4	X5(Fixed)	Vertices
1	0.005	0.47	0.25	0.075	0.2	
2	0.005	0.3	0.25	0.245	0.2	
3	0.005	0.47	0.45	-0.125	0.2	
4	0.005	0.3	0.45	0.045	0.2	1
5	0.05	0.47	0.25	0.03	0.2	2
6	0.05	0.3	0.25	0.2	0.2	
7	0.05	0.47	0.45	-0.17	0.2	
8	0.05	0.3	0.45	0	0.2	
Group-2						
	X1	X2	X4	X3	X5(Fixed)	Vertices
9	0.005	0.47	0.011	0.313	0.2	3
10	0.005	0.3	0.011	0.483	0.2	
11	0.005	0.47	0.059	0.265	0.2	4
12	0.005	0.3	0.059	0.435	0.2	5
13	0.05	0.47	0.011	0.268	0.2	6
14	0.05	0.3	0.011	0.438	0.2	7
15	0.05	0.47	0.059	0.22	0.2	
16	0.05	0.3	0.059	0.39	0.2	8
Group-3						
	X1	X3	X4	X2	X5(Fixed)	Vertices
17	0.005	0.45	0.011	0.333	0.2	9
18	0.005	0.25	0.011	0.533	0.2	
19	0.005	0.45	0.059	0.285	0.2	
20	0.005	0.25	0.059	0.485	0.2	
21	0.05	0.45	0.011	0.288	0.2	
22	0.05	0.25	0.011	0.488	0.2	
23	0.05	0.45	0.059	0.24	0.2	
24	0.05	0.25	0.059	0.44	0.2	10
Group-4						
	X2	X3	X4	X1	X5(Fixed)	Vertices
25	0.3	0.45	0.011	0.038	0.2	11
26	0.3	0.25	0.011	0.238	0.2	
27	0.3	0.45	0.059	-0.009	0.2	
28	0.3	0.25	0.059	0.19	0.2	
29	0.47	0.45	0.011	-0.131	0.2	
30	0.47	0.25	0.011	0.068	0.2	
31	0.47	0.45	0.059	-0.179	0.2	
32	0.47	0.25	0.059	0.02	0.2	12

Table 3.12 The co-ordinates of 21 design points for the sulphide capacity study of ferrochromium smelting slags.

Design Point Designation	Type of Boundary	Cr ₂ O ₃ (X1)	SiO ₂ (X2)	MgO (X3)	CaO (X4)	Al ₂ O ₃ (X5)
1	Vertex	0.005	0.300	0.450	0.045	0.200
2	Vertex	0.050	0.470	0.250	0.030	0.200
3	Vertex	0.050	0.470	0.313	0.011	0.200
4	Vertex	0.005	0.470	0.265	0.059	0.200
5	Vertex	0.005	0.300	0.435	0.059	0.200
6	Vertex	0.050	0.470	0.268	0.011	0.200
7	Vertex	0.050	0.300	0.438	0.011	0.200
8	Vertex	0.050	0.300	0.390	0.059	0.200
9	Vertex	0.005	0.333	0.450	0.011	0.200
10	Vertex	0.050	0.440	0.250	0.059	0.200
11	Vertex	0.038	0.300	0.450	0.011	0.200
12	Vertex	0.020	0.470	0.250	0.059	0.200
13	Face Centroid	0.005	0.374	0.382	0.037	0.200
14	Face Centroid	0.050	0.396	0.319	0.034	0.200
15	Face Centroid	0.029	0.300	0.432	0.037	0.200
16	Face Centroid	0.026	0.470	0.269	0.034	0.200
17	Face Centroid	0.016	0.311	0.450	0.022	0.200
18	Face Centroid	0.040	0.460	0.250	0.049	0.200
19	Face Centroid	0.029	0.374	0.383	0.011	0.200
20	Face Centroid	0.026	0.396	0.318	0.059	0.200
21	Overall Centroid	0.027	0.385	0.350	0.035	0.200

3.1.3 Statistical experimental design for the sulphide capacity study of ferromanganese smelting slags

MnO, SiO₂, MgO, CaO and Al₂O₃ are the slag components chosen for the study of the sulphide capacity of ferromanganese smelting slags. A similar statistical experimental design procedure was applied for determination of the slag compositions. The upper and lower boundaries of the factors for this study are given in Table 3.13.

Table 3.13 Lower (ai) and upper boundary (bi) conditions for the four variable factors and one fixed factor of the sulphide capacity study of ferromanganese smelting slags.

Component	ai	bi
X1= (MnO)	0.05	0.10
X2= (SiO ₂)	0.36	0.54
X3=(MgO)	0.10	0.15
X4=(CaO)	0.18	0.36
X5=(Al ₂ O ₃)	0.05(fixed)	

The design points are listed in Table 3.14. The rows in italic format represent the vertices in the defined boundary limits of the given slag range and are numbered from 1 to 12. 8 face centroids and 1 overall centroid points are defined for the slag system. 21 design points are determined for the slag compositions in the defined constraints (Table 3.15).

Table 3.14 The design points for the sulphide capacity study of ferromanganese smelting slags

Group-1						
	X1	X2	X3	X4	X5(Fixed)	Vertices
1	0.05	0.54	0.1	0.26	0.05	1
2	0.05	0.36	0.1	0.44	0.05	
3	0.05	0.54	0.15	0.21	0.05	2
4	0.05	0.36	0.15	0.39	0.05	
5	0.1	0.54	0.1	0.21	0.05	3
6	0.1	0.36	0.1	0.39	0.05	
7	0.1	0.54	0.15	0.16	0.05	
8	0.1	0.36	0.15	0.34	0.05	4
Group-2						
	X1	X2	X4	X3	X5(Fixed)	Vertices
9	0.05	0.54	0.18	0.18	0.05	
10	0.05	0.36	0.18	0.36	0.05	
11	0.05	0.54	0.36	0	0.05	
12	0.05	0.36	0.36	0.18	0.05	
13	0.1	0.54	0.18	0.13	0.05	5
14	0.1	0.36	0.18	0.31	0.05	
15	0.1	0.54	0.36	-0.05	0.05	
16	0.1	0.36	0.36	0.13	0.05	6
Group-3						
	X1	X3	X4	X2	X5(Fixed)	Vertices
17	0.05	0.45	0.18	0.57	0.05	
18	0.05	0.25	0.18	0.62	0.05	
19	0.05	0.45	0.36	0.44	0.05	7
20	0.05	0.25	0.36	0.44	0.05	8
21	0.1	0.45	0.18	0.52	0.05	9
22	0.1	0.25	0.18	0.57	0.05	
23	0.1	0.45	0.36	0.34	0.05	
24	0.1	0.25	0.36	0.39	0.05	10
Group-4						
	X2	X3	X4	X1	X5(Fixed)	Vertices
25	0.36	0.15	0.18	0.26	0.05	
26	0.36	0.1	0.18	0.31	0.05	
27	0.36	0.15	0.36	0.08	0.05	11
28	0.36	0.1	0.36	0.13	0.05	
29	0.54	0.15	0.18	0.08	0.05	12
30	0.54	0.1	0.18	0.13	0.05	
31	0.54	0.15	0.36	-0.1	0.05	
32	0.54	0.1	0.36	-0.05	0.05	

Table 3.15 The co-ordinates of 21 design points for the sulphide capacity study of ferromanganese smelting slags.

Design Point Designation	Type of Boundary	MnO (X1)	SiO ₂ (X2)	MgO (X3)	CaO (X4)	Al ₂ O ₃ (X5)
1	Vertex	0.050	0.540	0.100	0.260	0.050
2	Vertex	0.050	0.540	0.150	0.210	0.050
3	Vertex	0.100	0.540	0.100	0.210	0.050
4	Vertex	0.100	0.360	0.150	0.340	0.050
5	Vertex	0.100	0.540	0.130	0.180	0.050
6	Vertex	0.100	0.360	0.130	0.360	0.050
7	Vertex	0.050	0.390	0.150	0.360	0.050
8	Vertex	0.050	0.440	0.100	0.360	0.050
9	Vertex	0.100	0.520	0.150	0.180	0.050
10	Vertex	0.100	0.390	0.100	0.360	0.050
11	Vertex	0.080	0.360	0.150	0.360	0.050
12	Vertex	0.080	0.540	0.150	0.180	0.050
13	Face Centroid	0.050	0.477	0.125	0.297	0.050
14	Face Centroid	0.100	0.451	0.126	0.271	0.050
15	Face Centroid	0.076	0.540	0.126	0.208	0.050
16	Face Centroid	0.093	0.360	0.143	0.353	0.050
17	Face Centroid	0.075	0.311	0.100	0.297	0.050
18	Face Centroid	0.076	0.477	0.150	0.271	0.050
19	Face Centroid	0.093	0.451	0.143	0.180	0.050
20	Face Centroid	0.076	0.533	0.126	0.360	0.050
21	Overall Centroid	0.080	0.388	0.130	0.280	0.050

3.2 Experimental Set-Up and Methodology

Details which are related to the furnace, gas-purification system, temperature control, sample preparation, crucibles and procedure are described in this section.

3.2.1 The equilibration furnace

The gas-slag-metal equilibration experiments were conducted in a vertical gas tight molybdenum wound resistance tube furnace with a 460 mm diameter and height. The cylindrical steel shell was water-cooled at the bottom and top. A recrystallised alumina tube with an inside diameter of 48 mm, an outer diameter of 58 mm and a length of 1000 mm was used as a work (reaction) tube. The alumina reaction tube which had a brass cooling system was fitted with two o rings to the steel shell of the furnace at the top and bottom. Silicon sealant and O-rings were used to obtain the gas-tight conditions. An extension bellow was connected on the top of the upper lid which allows the release of the stress occurred due to the thermal expansion of the alumina tube.

Another alumina tube of 450 mm in length and 70 mm inner diameter was wound with the molybdenum resistance elements and used as a heating tube which enclosed the reaction tube. The molybdenum heating wire was protected from oxidation by the decomposition of continuously flushing anhydrous ammonia gas through the furnace into hydrogen and nitrogen at temperatures above 700°C. At high temperatures this reducing atmosphere has enough hydrogen to keep the oxygen potential of the system below the equilibrium level to produce MoO. Due to this reason and to keep away the thermal shocks, the furnace has to be kept at 1200°C when it is not in operation. Anhydrous ammonia was let into the furnace from the bottom end of the furnace through the inlet and passed through the furnace shell. The off-gases were vented to the fume hood through the ammonia outlet at the top of the furnace shell.

The molybdenum elements were covered by alumina cement and placed into the pool of spherical alumina bubbles (diameter range of 1 to 3 mm). The alumina bubbles were used in order to create a thermal insulation. This system was placed

into an alumina-silicate shield tube. Ceramic blankets were filled around the shield tube for covering the gap between the ceramic shield and the furnace steel shell. Two electrically insulated gas-tight terminals connected the molybdenum windings to the electrical power cables.

A 40 mm hot zone was attained with $\pm 5^{\circ}\text{C}$ at $1\,600^{\circ}\text{C}$. The temperature was controlled by Eurotherm Thyristor-0703 25 A, 240 V controller, temperature indicators and thermocouples.

Carbon monoxide gas was introduced by a gas inlet from the bottom end of the reaction tube placed on the bottom brass cap. The off-gases were vented to the fume hood through a gas outlet on the top brass cap. Figure 3.1 and 3.2 represent the cross section of the vertical molybdenum wound resistance furnace and detailed schematic representation of experimental set up respectively which are the same as the one used by Akyuzlu, (1989).

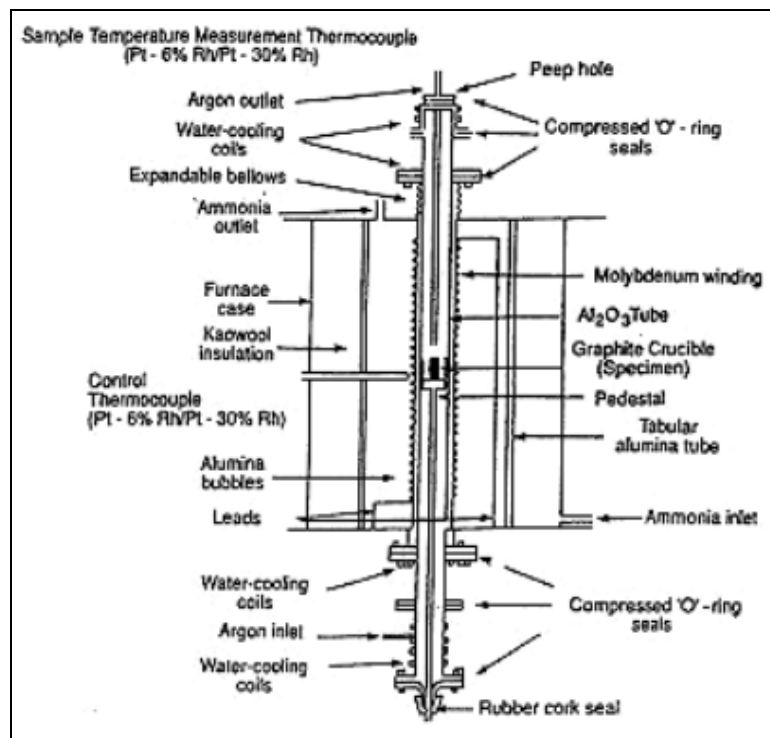


Figure 3.1 The cross section of the furnace (Akyuzlu, 1989).

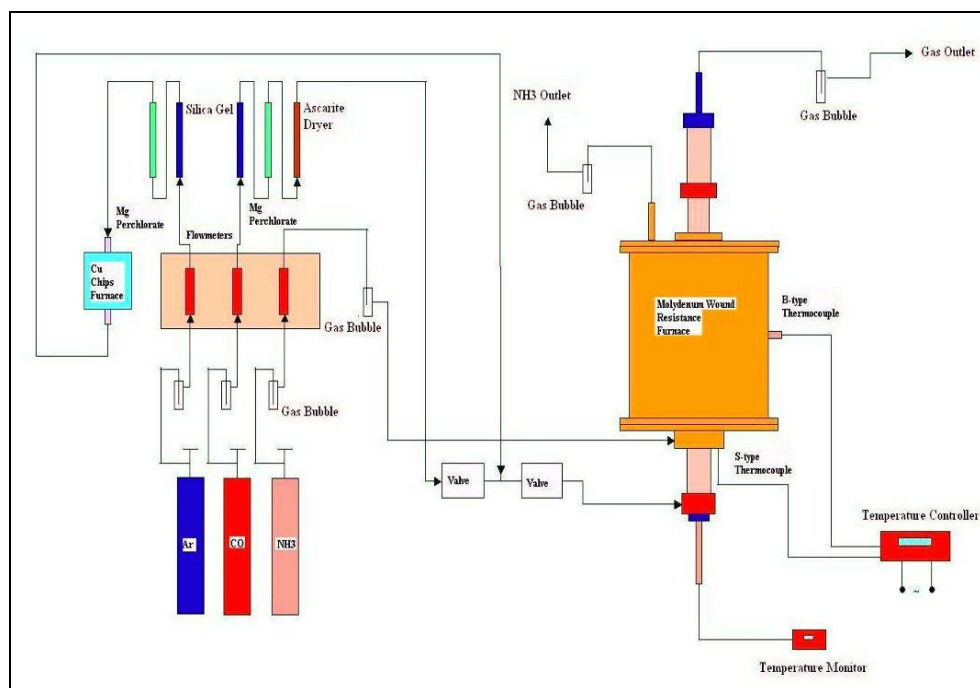


Figure 3.2 The detailed schematic representation of experimental set up.

3.2.2 Gas purification and gas flow control system

The ancillary equipment for controlling the flow of carbon monoxide gas involves flow meters and gas purification unit. The carbon monoxide gas entered the furnace from the bottom end of the reaction tube and left from the top. The gas flow rate was controlled by a pre-calibrated tri-flat flow meter. The flow rate was kept between 340 and 390 cm³/min. During the experiments, the total gas pressure in the furnace was equal to the ambient pressure which is about 0.83 atm in Johannesburg. The flow meter system was calibrated by a using gas-bubble flow meter (Bunson Tower) and the flow rate of carbon monoxide and argon via a tri-flat flow meter. The calibration curves of gas flow rates are presented in Figure 3.3. Carbon monoxide gas was dried by passing through silica gel, anhydrous magnesium perchlorate and ascarid. During the experiments, pure grade CO gas was used. Prior to the experiments, the reaction tube was filled with ultra pure argon which was passed through a deoxidation furnace containing copper chips at 500°C for 15 minutes. The chemical compositions of pure grades carbon monoxide and argon gases are given in Table 3.16 and 3.17. The connections were regularly tested for gas-tightness.

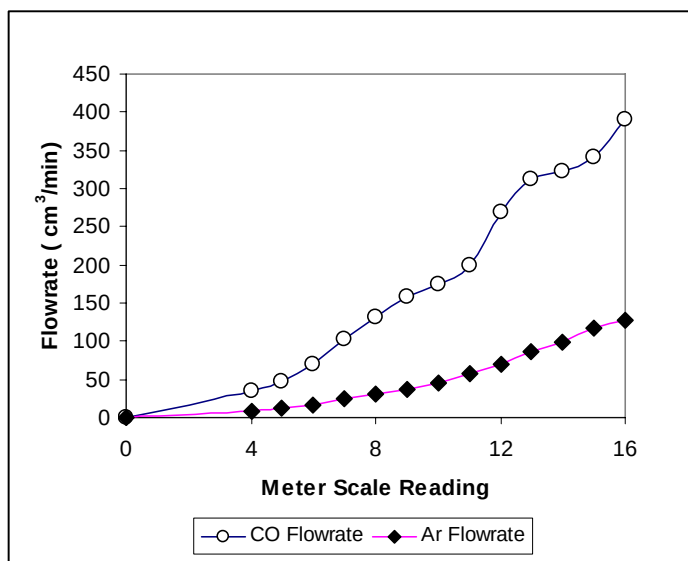


Figure 3.3 Flow rate of carbon monoxide via tri-flat flow meter, calibrated by Bunson Tower.

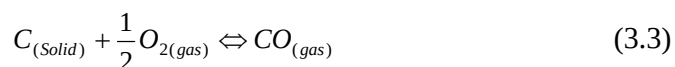
Table 3.16 The chemical composition of pure grade carbon monoxide gas

Minimum Purity	99.97 %
N ₂	< 150 vpm
O ₂	< 20 (including Argon)
H ₂	< 150 vpm
CO ₂	< 30 vpm
THC as CH ₄	< 2 vpm
Moisture	<10 vpm

Table 3.17 The chemical composition of pure grade argon gas.

Minimum Purity	99.999 %
N ₂	< 4 vpm
O ₂	< 2
CO ₂	< 0.5 vpm
THC as CH ₄	< 0.5 vpm
Moisture	<1 vpm
CO	<0.5 vpm

The oxygen partial pressures prevailing in the reaction zone were calculated to be 1.21×10^{-16} atm. at 1 500°C and 2.56×10^{-16} atm. at 1 600°C according to reaction 3.3 and its standard free energy changes given in Eq. 3.4 and 3.5.



$$\Delta G^{\circ} = -112877 - 86.514T \text{ (J)} \quad (\text{Tabuchi and Sano, 1984}) \quad (3.4)$$

$$\Delta G^{\circ} = -26700 - 20.95T \text{ (cal)} \quad (\text{Bodsworth and Appleton, 1965}) \quad (3.5)$$

3.2.3 Temperature control and furnace temperature profile

The hot zone temperature of the reaction tube was measured with a Pt-6 %Rh/Pt-30 %Rh (B-type) thermocouple which was calibrated by using a standard thermocouple of the same composition. Before the experiments, the standard

reference thermocouple was calibrated according to the melting points of gold, silver and copper. First, the thermocouple was placed in a sintered alumina thermocouple sheath and then it was inserted through the mullite support tube which was used as a pedestal during the experiments. The hot zone was closely monitored during the experimental runs by using termocouple. In addition to this, a S-type thermocouple (Platinum –Rhodium Alloy : Wire A- 90 wt. % Platinum- 10 wt % Rhodium/ Wire B- 100 wt. % Platinum) was placed in contact the external surface of heating element tube and connected to Eurotherm Thyristor 0705 25 A, 240 V power pack for controlling the power input of the furnace.

The temperature profiles obtained at 1 500 °C and 1 600 °C can be seen in Figure 3.4 The hot zone lengths were found to be 4 and 3 cm at 1 500°C and 1 600°C, respectively within $\pm 5^{\circ}\text{C}$ range. In each runs, the graphite crucibles containing slag and metal samples were placed completely within the hot zone of furnace. The furnace's temperature profile was monitored regularly during the course of the experimental work and necessary adjustments were made to prevent any changes in the length and position of hot zone.

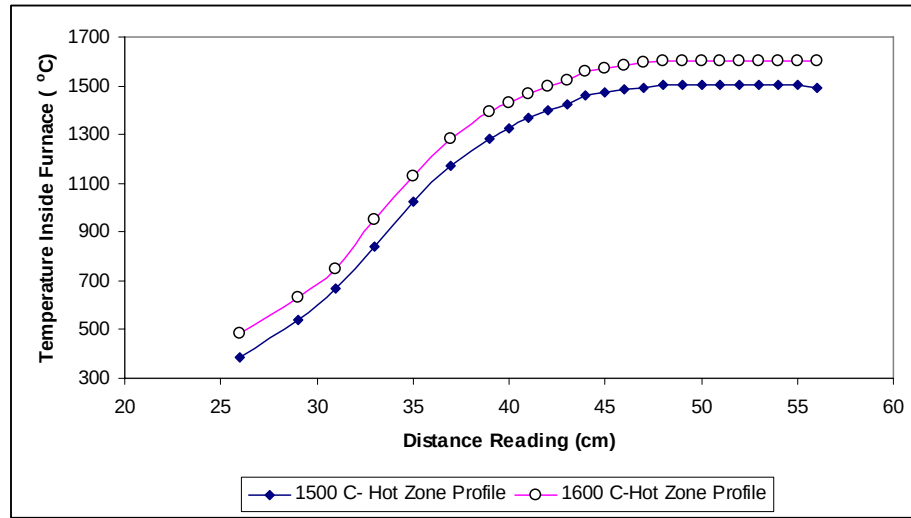


Figure 3.4 Temperature profile inside furnace at 1 500°C and 1 600°C.

3.2.4 Slag sample preparation

Preparation of ferrochromium slag samples for the sulphide capacity study

The master slags were prepared as homogeneous mixtures of CaO, MgO, Al₂O₃ and SiO₂ 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 an agate mortar under acetone. The dried mixtures were pressed into pellet forms and sintered at 1100°C for 36 hours to achieve a homogeneous slag phase formation. A uniaxial hydraulic press at a pressure of 12-15 MPa was used to press the mixtures into the pellets. The sintered slag pellets were ground and mixed with Cr₂O₃ powder to have the required compositions. The compositions of the slag samples for the sulphide capacity study of high carbon ferrochromium smelting slags are given in Table 3.18.

Table 3.18 The compositions of slag samples for the sulphide capacity study of high carbon ferrochromium smelting slags by weight %.

Design Point Designation	Cr ₂ O ₃	SiO ₂	MgO	CaO	Al ₂ O ₃
1	0.50	30.00	45.00	4.50	20.00
2	5.00	47.00	25.00	3.00	20.00
3	5.00	47.00	31.30	1.10	20.00
4	0.50	47.00	26.50	5.90	20.00
5	0.50	30.00	43.50	5.90	20.00
6	5.00	47.00	26.80	1.10	20.00
7	5.00	30.00	43.80	1.10	20.00
8	5.00	30.00	39.00	5.90	20.00
9	0.50	33.30	45.00	1.10	20.00
10	5.00	44.00	25.00	5.90	20.00
11	3.80	30.00	45.00	1.10	20.00
12	2.00	47.00	25.00	5.90	20.00
13	0.50	37.40	38.20	3.70	20.00
14	5.00	39.60	31.90	3.40	20.00
15	2.90	30.00	43.20	3.70	20.00
16	2.60	47.00	26.90	3.40	20.00
17	1.60	31.10	45.00	2.20	20.00
18	4.00	46.00	25.00	4.90	20.00
19	2.90	37.40	38.30	1.10	20.00
20	2.60	39.60	31.80	5.90	20.00
21	2.70	38.50	35.00	3.50	20.00

Preparation of ferrochromium slag samples for the phosphide capacity study

The master slags were prepared as homogeneous mixtures of CaO, MgO, Al₂O₃, SiO₂ and Ca₃(PO₄)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 an agate mortar under acetone. The dried mixtures were pressed into

pellet forms and sintered at 1100°C for 36 hours to achieve a homogeneous slag phase formation. The sintered slag pellets were ground and mixed with Cr₂O₃ powder to have the required compositions. The compositions of the slag samples for the phosphide capacity study of high carbon ferrochromium smelting slags are given in Table 3.19.

Table 3.19 The compositions of slag samples for the phosphide capacity study of high carbon ferrochromium smelting slags by weight %.

Design Point Designation	Cr ₂ O ₃	SiO ₂	MgO	(Ca ₃ (PO ₄) ₂)	Al ₂ O ₃
1	0.50	47.00	25.00	7.50	20.00
2	0.50	30.00	45.00	4.50	20.00
3	5.00	47.00	25.00	3.00	20.00
4	0.50	47.00	31.30	1.20	20.00
5	0.50	30.00	38.60	10.90	20.00
6	5.00	47.00	26.80	1.20	20.00
7	5.00	30.00	43.80	1.20	20.00
8	5.00	30.00	34.10	10.90	20.00
9	0.50	33.30	45.00	1.20	20.00
10	0.50	43.60	25.00	10.90	20.00
11	5.00	39.10	25.00	10.90	20.00
12	3.20	30.00	45.00	1.20	20.00
13	0.50	38.50	35.00	6.00	20.00
14	5.00	38.60	30.90	5.40	20.00
15	2.80	47.00	27.00	3.20	20.00
16	3.00	30.00	41.30	5.70	20.00
17	2.80	44.20	25.00	8.10	20.00
18	1.60	31.10	45.00	2.30	20.00
19	3.00	37.50	38.40	1.20	20.00
20	2.80	35.70	30.70	10.90	20.00
21	2.70	37.80	34.10	5.40	20.00

Preparation of ferromanganese slag samples for the sulphide capacity study

The master slags were prepared as homogeneous mixtures of CaO, MgO, Al₂O₃ and SiO₂ 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 an agate mortar under acetone. The dried mixtures were pressed into pellet forms and sintered at 1100°C for 36 hours to achieve a homogeneous slag phase formation. The sintered slag pellets were ground and mixed with MnO powder to have the required compositions. The compositions of the slag samples for the sulphide capacity study of high carbon ferromanganese smelting slags are given in Table 3.20

Table 3.20 The compositions of slag samples for sulphide capacity study of high carbon ferromanganese smelting slags by weight %.

Design Point Designation	MnO	SiO ₂	MgO	CaO	Al ₂ O ₃
1	5.00	54.00	10.00	26.00	5.00
2	5.00	54.00	15.00	21.00	5.00
3	10.00	54.00	10.00	21.00	5.00
4	10.00	36.00	15.00	34.00	5.00
5	10.00	54.00	13.00	18.00	5.00
6	10.00	36.00	13.00	36.00	5.00
7	5.00	39.00	15.00	36.00	5.00
8	5.00	44.00	10.00	36.00	5.00
9	10.00	52.00	15.00	18.00	5.00
10	10.00	39.00	10.00	36.00	5.00
11	8.00	36.00	15.00	36.00	5.00
12	8.00	54.00	15.00	18.00	5.00
13	5.00	47.70	12.50	29.70	5.00
14	10.00	45.10	12.60	27.10	5.00
15	7.60	54.00	12.60	20.80	5.00
16	9.30	36.00	14.30	35.30	5.00
17	7.50	31.10	10.00	29.70	5.00
18	7.60	47.70	15.00	27.10	5.00
19	9.30	45.10	14.30	18.00	5.00
20	7.60	53.30	12.60	36.00	5.00
21	8.00	38.80	13.00	28.00	5.00

3.2.5 Metal alloy samples preparation

The metal alloy samples prepared for the gas-slag-metal equilibrium experiments had compositions similar to typical industrial ferrochromium and ferromanganese products (Pan, 1998; Wethmar et al., 1974; Wethmar et al., 1975; Howat, 1986; See, 1976; Cengizler, 1993).

Fe-Cr-Si-C-S metal alloys for sulphide capacity study

Ferrochromium alloys were prepared from powders of electrolytically pure Fe, Cr, Si and spectrographic grade graphite. A 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 an agate mortar. The metal alloy compositions employed in the sulphide capacity study of ferrochromium smelting slags are listed in Table 3.21.

Table 3.21 The metal compositions for the sulphide capacity study of ferrochromium smelting slags by weight %.

Code	Cr	Fe	C	Si	S
FCAS1	65	25	7.5	1.5	1
FCAS2	57.5	31	7.5	3	1
FCAS3	50	37	7.5	4.5	1

Fe-Cr-Si-C metal alloys for phosphide capacity study

Ferrochromium alloys were prepared from powders of electrolytically pure Fe, Cr, Si and spectrographic grade graphite. The required amounts of the metal components were dried, weighed and mixed homogeneously in an agate mortar. The metal alloy compositions employed in the phosphide capacity study of ferrochromium smelting slags are listed in Table 3.22.

Table 3.22 The metal compositions for the phosphide capacity study of ferrochromium smelting slags by weight %.

Code	Cr	Fe	C	Si
FCAP1	65	26	7.5	1.5
FCAP2	57.5	32	7.5	3
FCAP3	50	38	7.5	4.5

Mn-Fe-Si-C-S metal alloys for sulphide capacity study

Ferromanganese alloys were prepared from powders of electrolytically pure Fe, Mn, Si and spectrographic grade graphite. A 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 an agate mortar. The metal alloy compositions employed in the sulphide capacity study of ferromanganese smelting slags are listed in Table 3.23.

Table 3.23 The initial metal compositions for the sulphide capacity study of ferromanganese smelting slags by weight %.

Code	Mn	Fe	C	Si	S
FMAS1	84	6	7.5	1.5	1
FMAS2	77	11.5	7.5	3	1
FMAS3	70	17	7.5	4.5	1

3.2.6 Crucibles

Graphite crucibles were used in the gas-slag-metal equilibrium experiments. The graphite electrodes were cut and drilled to the required shape for production of graphite crucibles. Each crucible cylinder had three crucible chambers with the following dimensions: 15 mm crucible chamber inner diameter, 35 mm chamber depth and 40 mm cylinder height. In each experiment, three different samples were equilibrated by using the three-chamber graphite crucibles design.

3.2.7 Experimental procedure

- **Gas-slag-metal equilibrium experimental procedure**

Three groups of experiments were conducted to investigate the gas-slag-metal equilibrium related to the sulphide and phosphide capacities of high carbon ferrochromium and the sulphide capacities of high carbon ferromanganese smelting slags as follows:

Sulphide capacities of high carbon ferrochromium smelting slags: Gas-slag-metal equilibrium in graphite crucibles under a CO atmosphere at 1 600°C for 24 hours.

Phosphide Capacities of high carbon ferrochromium smelting slags: Gas-Slag-Metal equilibrium in graphite crucibles under a CO atmosphere at 1 600°C for 24 hours.

Sulphide Capacities of high carbon ferromanganese smelting slags: Gas-Slag-Metal equilibrium in graphite crucibles under a CO atmosphere at 1 500°C for 24 hours.

According to previous studies, a reaction time of 18 hours was sufficient to attain equilibrium (Akyuzlu and Eric, 1992; Cengizler et al., 1993). However, equilibration time for slag-metal-gas equilibrium experiment was chosen as 24 hours due to practical purposes. The reactants consisting of 6 g alloy and 6 g slag were placed at the bottom of the graphite crucible. In a single experimental run, three different experiments were conducted by using a three chambered crucible. The graphite crucibles containing the samples were placed into the reaction zone of the furnace with an alumina pedestal. The reaction tube was flushed with argon gas for 30 minutes after placing the graphite crucible into the cold zone of the furnace tube. After the samples were slowly raised and located at the hot zone, CO gas was introduced into the furnace tube with a rate of 200 cm³/min. At the end of each experimental run, the samples were lowered to the cold zone of the reaction tube while the system was flushed with argon for 15 minutes. Then the samples were quenched in water. The distinctive metal phase and slag phase were carefully separated, cleaned, crushed and pulverised and sent for the chemical analysis.

3.2.8 Preliminary experiments and determination of equilibration time

Preliminary experiments were conducted in order to check the gas tightness of the furnace system to prevent systematic experimental test errors in case of leak.

The gas tightness of the reaction tube was checked by conducting blank test runs with graphite powder which was placed into an alumina crucible and heated to 1 500°C under argon atmosphere for 24 hours. At the end of the test, the alumina crucible which contained graphite powder was removed from the reaction tube. The graphite powder was weighted for determination the average weight loss percentage. It was found that the weight loss percentage varied between 0.35 and

0.76 at the blank test runs. The weight loss of the graphite powder was found to be insignificant which indicated that a gas tight condition was achieved in the experiments.

The gas flow rate of carbon monoxide was fixed as $200 \text{ cm}^3/\text{min}$ during the experimental study in order to minimise the thermal diffusion of hydrogen molecules to the reaction zone of the furnace. A hydrogen gas atmosphere was formed by cracking of ammonia which was used as a protection shield gas for the molybdenum wires. Although the system was isolated, there is a possibility of light hydrogen molecules to diffuse through the alumina tube at high temperatures which might change the oxygen partial pressure inside the reaction tube. Kubaschewski et al. (1993) reported this situation in their study and mentioned that abnormal activity values can be seen in the experimental results if the gas flow rate was kept lower than 100 ml/min inside the reaction tube. As a last preventing measure for thermal diffusion of hydrogen molecules to the reaction zone a thick alumina tube (6 mm) was used in the experiments.

Under equilibrium conditions, system turns out to be independent from the time. The equilibration time is the minimum time needed to reach the equilibrium state for a given system. The complete gas-slag-metal equilibrium might be difficult to establish. When the equal amounts of slag and metal were used in the experiments, the system hardly reached equilibrium after 24 hours under a carbon monoxide gas atmosphere (Ding and Olsen, 1996a). According to the previous studies, the necessary equilibrium time varied between 1.5 to 24 hours depending on different conditions; mostly determined by the reaction temperature, crucible size, amount of slag/metal phases and gas flow rates (Rait and Olsen, 1999; Ding and Olsen, 1996b). The experiments at higher temperatures required shorter equilibrium times compared to the lower temperature ones.

In a study between Mn-Si-C_{sat} alloys and silicate slags, the equilibrium between the gas-slag-metal phases was attained in 4 hours (Rankin, 1979). Ding and Olsen (1996a) carried out an experimental study on the manganese and silicon

distribution between slag and metal. The required equilibrium time was determined as 3 hours at 1 700°C and 5 hours at 1 600°C. In a different study, 18 hours was found as sufficient time period for reaching the equilibrium between BaO-BaF₂-MnO fluxes and ferromanganese melts under argon atmosphere (Liu et al., 1995). Maramba and Eric (2008) determined the equilibrium time as 18 hours in the phosphide capacity study of the ferromanganese smelting slags. Akyuzlu (1989) reported that a minimum of 10 hours was necessary for establishing the equilibration between Fe-Cr-Si-C alloys and SiO₂-CaO-MgO-Al₂O₃-CrO_x-FeO_y slags under argon and carbon monoxide atmospheres at temperatures of 1 500°C and 1 600°C. The dissolved silicon amount was used as a parameter in the determination of equilibrium time in both studies of Akyuzlu (1989) and Ding and Olsen (1996a). Pan (1998) determined the equilibration time by following the change in carbon of the alloy. Carbon content changed and reached to equilibrium value within the first 10 hours of the equilibrium run and remained unchanged afterwards. Conclusions stated that for gas-metal system experiments 20 hours was sufficient as an equilibrium time. The equilibration time was also determined by looking at the change of all components of the slag, namely Al₂O₃, CaO, Cr₂O₃, Fe₂O₃, MgO, S and SiO₂. Results indicated that a minimum of 13 hours was required in order to reach the equilibrium state in the experiments.

In this study the equilibrium time in the gas-slag-metal system was determined experimentally. Experiments were conducted with 6 g of metal alloy phase (Fe-Mn-Si-C_{sat}-S) and 6 g of slag (SiO₂-MgO-MnO-Al₂O₃-CaO) in a graphite crucible under a carbon monoxide atmosphere at 1 500°C. The samples were taken from the furnace after 8, 12, 24 and 30 hours and subjected to chemical analyses by using ICP-OES for determination of the amount of SiO₂, CaO, Al₂O₃, FeO, TiO₂, MgO, MnO and S in the slag phase. There are no changes in composition after 15 hours. The results are given in Figure 3.5. However, approximately 24 hours was chosen as the experimental duration time in the present study for practical purposes permit two runs per day.

Equilibration times for ferrochromium smelting slag experiments were based on the work of Akyuzlu and Eric (1992) where their experimental conditions were similar to the present study in terms of slag compositions, temperature and atmosphere conditions. However, experimental time was chosen as 24 hours for practical purposes.

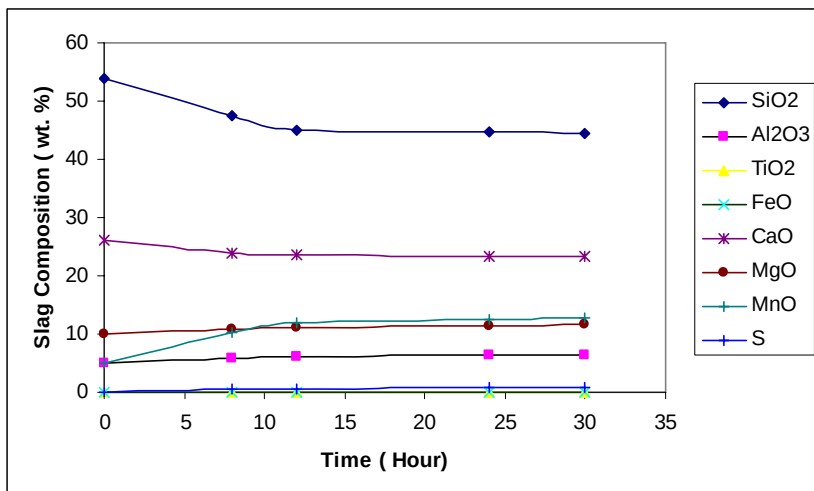


Figure 3.5 Determination of gas-slag-metal equilibration time at 1500°C under carbon monoxide atmosphere

3.2.9 Chemical Analysis

The analytical work was done at UIS Analytical Laboratory – Centurion (RSA). Ferromanganese metal alloy samples were analysed for Mn, Fe, Si, C and S whereas the ferrochromium metal alloy samples were analysed for Cr, Fe, Si, C, S and P elements. The slag samples of ferromanganese slags were analysed for MnO, FeO, SiO₂, MgO, CaO, Al₂O₃ and S whereas ferrochromium slags were analysed for Cr₂O₃, FeO, SiO₂, MgO, CaO, Al₂O₃, S and P. The carbon of the metal alloy phase was analysed by a LECO analyser. The other constituents of the metal and slag phases were analysed by using the inductively coupled plasma (ICP-OES) method. Fusion techniques were used to dissolve both slag and metal phases. The relative error percentage of the chemical analysis was found to be $\pm 2\%$ for each component of slag and metal phases.

4 RESULTS AND DISCUSSIONS

The results of experimental study with the relevant discussion sections are summarised in this chapter.

Firstly all the experimental data gathered is presented in tabular form. Then the empirical quadratic response surface model and the lattice energy capacity relationships derived from the experimental data is presented.

Thereafter using all the above information relevant discussion are presented.

4.1 Experimental Data

4.1.1 Sulphur distribution and sulphide capacity relevant to ferrochromium smelting

In gas-slag-metal equilibrium distribution experiments, 30 successful experiments were done. Some experiments were failed due to the loss of slag due to excessive overflow of slags. In all successful experiments, the slag was found fully molten. The results of final equilibrium composition of slag and metal phases are presented in Table 4.1. The estimated uncertainties from the chemical analysis of slag and metal phase components are included into Table 4.1, as the relative error is around ± 2 for ICP and Leco analysis for each component of slag and metal phases. The amounts of MnO, TiO₂ and Al, Ti, P and Mn were found negligible according to the chemical analysis of slag and metal phases. Therefore, these components of slag and metal phases were excluded from the Table 4.1.

4.1.2 Phosphorus distribution and phosphide capacity relevant to ferrochromium smelting

29 successful experiments were conducted for phosphorus distribution and phosphide capacity study pertinent to ferrochromium smelting. It was found that

the slags were fully molten in successful experiments. The results of final equilibrium composition of slag and metal phases are tabulated in Table 4.2 which includes estimated uncertainties from the chemical analysis of slag and metal components.

4.1.3 Sulphur distribution and sulphide capacity relevant to ferromanganese smelting

In sulphur distribution and sulphide capacity experiments pertinent to ferromanganese smelting, 42 successful gas-slag-metal equilibrium experiments were done. In all successful experiments, the slag was found to be fully molten. The equilibrium composition of slag and metal phases pertinent to sulphur behaviour in ferromanganese process are presented in Table 4.3. Also the estimated uncertainties from chemical analysis of slag and metal components are given in the same table.

Table 4.1 Equilibrium composition of slag and metal phases pertinent to sulphur distribution and sulphide capacity in ferrochromium smelting (1600 °C, CO gas atmosphere) (in wt. %)

	Final Slag Phase Composition(wt. %)										Final Metal Phase Composition (wt.%)													
Experiment Number	SiO ₂		Al ₂ O ₃		CaO		MgO		FeO		Cr ₂ O ₃		S (as CaS)		Cr		Fe		C		Si		S	
1	30.670 ± 0.613		22.513 ± 0.450		10.713 ± 0.214		33.520 ± 0.670		0.176 ± 0.004		0.241 ± 0.005		0.317 ± 0.006		55.315 ± 1.106		30.230 ± 0.605		9.570 ± 0.191		4.611 ± 0.092		0.0245 ± 0.0002	
2	30.674 ± 0.613		22.345 ± 0.447		10.793 ± 0.216		33.637 ± 0.673		0.197 ± 0.004		0.236 ± 0.005		0.354 ± 0.007		54.938 ± 1.099		30.190 ± 0.604		9.676 ± 0.194		4.545 ± 0.091		0.0227 ± 0.0002	
3	35.732 ± 0.715		22.787 ± 0.456		4.792 ± 0.096		35.257 ± 0.705		0.122 ± 0.002		0.245 ± 0.005		0.220 ± 0.004		53.324 ± 1.066		31.250 ± 0.625		7.643 ± 0.153		6.124 ± 0.122		0.0246 ± 0.0003	
4	33.823 ± 0.676		26.738 ± 0.535		5.645 ± 0.113		32.516 ± 0.650		0.127 ± 0.003		0.235 ± 0.005		0.229 ± 0.005		54.118 ± 1.082		28.620 ± 0.572		7.458 ± 0.149		9.074 ± 0.181		0.0193 ± 0.0002	
5	36.756 ± 0.735		24.489 ± 0.490		8.463 ± 0.169		29.289 ± 0.586		0.129 ± 0.003		0.126 ± 0.003		0.231 ± 0.005		51.895 ± 1.038		29.160 ± 0.583		7.157 ± 0.143		10.711 ± 0.214		0.0090 ± 0.0001	
6	30.312 ± 0.606		23.472 ± 0.469		10.823 ± 0.216		32.240 ± 0.645		0.257 ± 0.005		0.519 ± 0.010		0.463 ± 0.009		55.752 ± 1.115		30.070 ± 0.601		9.040 ± 0.181		4.652 ± 0.093		0.0420 ± 0.0004	
7	31.582 ± 0.632		23.280 ± 0.466		9.031 ± 0.181		34.315 ± 0.686		0.125 ± 0.002		0.123 ± 0.002		0.225 ± 0.004		54.330 ± 1.087		30.020 ± 0.600		8.848 ± 0.177		6.082 ± 0.122		0.0219 ± 0.0002	
8	30.680 ± 0.614		24.181 ± 0.484		10.751 ± 0.215		31.353 ± 0.627		0.246 ± 0.005		0.483 ± 0.010		0.442 ± 0.009		55.445 ± 1.109		28.920 ± 0.578		9.460 ± 0.189		4.783 ± 0.096		0.0302 ± 0.0003	
9	34.312 ± 0.686		22.461 ± 0.449		9.007 ± 0.180		32.490 ± 0.650		0.148 ± 0.003		0.244 ± 0.005		0.266 ± 0.005		53.728 ± 1.075		30.880 ± 0.618		8.743 ± 0.175		6.568 ± 0.131		0.0224 ± 0.0002	
10	32.045 ± 0.641		21.632 ± 0.433		12.141 ± 0.243		30.794 ± 0.616		0.217 ± 0.004		0.379 ± 0.008		0.391 ± 0.008		55.930 ± 1.119		31.370 ± 0.627		9.200 ± 0.184		3.414 ± 0.068		0.0182 ± 0.0002	
11	30.380 ± 0.608		22.044 ± 0.441		10.574 ± 0.211		33.384 ± 0.668		0.183 ± 0.004		0.310 ± 0.006		0.329 ± 0.007		55.089 ± 1.102		30.290 ± 0.606		9.271 ± 0.185		4.720 ± 0.094		0.0289 ± 0.0003	
12	30.502 ± 0.610		30.533 ± 0.611		16.876 ± 0.338		20.700 ± 0.414		0.048 ± 0.002		0.006 ± 0.002		0.086 ± 0.002		46.184 ± 0.924		34.101 ± 0.682		5.350 ± 0.107		12.964 ± 0.259		0.0110 ± 0.0001	
13	27.750 ± 0.555		30.946 ± 0.619		13.058 ± 0.261		26.250 ± 0.525		0.036 ± 0.002		0.023 ± 0.002		0.065 ± 0.001		53.187 ± 1.064		31.829 ± 0.637		6.594 ± 0.132		6.830 ± 0.137		0.0190 ± 0.0002	
14	28.024 ± 0.560		30.239 ± 0.605		13.492 ± 0.270		26.070 ± 0.521		0.044 ± 0.002		0.019 ± 0.002		0.079 ± 0.002		48.791 ± 0.976		35.446 ± 0.709		6.950 ± 0.139		7.826 ± 0.157		0.0120 ± 0.0001	
15	29.771 ± 0.595		29.134 ± 0.583		18.296 ± 0.366		19.980 ± 0.400		0.183 ± 0.004		0.562 ± 0.011		0.329 ± 0.007		58.526 ± 1.171		23.392 ± 0.468		6.684 ± 0.134		9.589 ± 0.192		0.0140 ± 0.0001	
16	27.420 ± 0.548		30.050 ± 0.601		14.934 ± 0.299		25.670 ± 0.513		0.427 ± 0.009		0.372 ± 0.007		0.769 ± 0.015		60.086 ± 1.202		24.739 ± 0.495		7.622 ± 0.152		5.942 ± 0.119		0.0220 ± 0.0002	
17	25.858 ± 0.517		32.786 ± 0.656		14.688 ± 0.294		24.730 ± 0.495		0.513 ± 0.010		0.151 ± 0.003		0.924 ± 0.018		54.150 ± 1.083		30.031 ± 0.601		7.243 ± 0.145		6.971 ± 0.139		0.0210 ± 0.0002	
18	27.350 ± 0.547		31.187 ± 0.624		15.442 ± 0.309		23.570 ± 0.471		0.255 ± 0.005		0.176 ± 0.004		0.458 ± 0.009		47.612 ± 0.952		36.929 ± 0.739		5.967 ± 0.119		8.467 ± 0.169		0.0130 ± 0.0001	
19	30.835 ± 0.617		25.584 ± 0.512		10.034 ± 0.201		30.470 ± 0.609		0.136 ± 0.003		0.552 ± 0.011		0.245 ± 0.005		49.118 ± 0.982		37.456 ± 0.749		6.776 ± 0.136		5.830 ± 0.117		0.0440 ± 0.0004	
20	36.047 ± 0.721		28.066 ± 0.561		3.370 ± 0.067		30.560 ± 0.611		0.194 ± 0.004		0.091 ± 0.002		0.350 ± 0.007		58.098 ± 1.162		23.246 ± 0.465		5.804 ± 0.116		11.421 ± 0.228		0.0050 ± 0.0001	
21	36.051 ± 0.721		27.563 ± 0.551		3.176 ± 0.064		31.240 ± 0.625		0.160 ± 0.003		0.070 ± 0.001		0.287 ± 0.006		51.877 ± 1.038		28.411 ± 0.568		5.045 ± 0.101		12.997 ± 0.260		0.0060 ± 0.0001	
22	35.930 ± 0.719		27.852 ± 0.557		3.341 ± 0.067		31.220 ± 0.624		0.127 ± 0.003		0.055 ± 0.001		0.229 ± 0.005		46.208 ± 0.924		34.052 ± 0.681		4.527 ± 0.091		14.189 ± 0.284		0.0040 ± 0.0001	
23	27.100 ± 0.542		20.200 ± 0.404		19.383 ± 0.388		30.900 ± 0.618		0.063 ± 0.001		0.117 ± 0.002		0.113 ± 0.002		62.745 ± 1.255		24.896 ± 0.498		8.916 ± 0.178		2.935 ± 0.059		0.0190 ± 0.0002	
24	33.702 ± 0.674		25.030 ± 0.501		8.710 ± 0.174		30.490 ± 0.610		0.042 ± 0.002		0.046 ± 0.002		0.076 ± 0.002		53.896 ± 1.078		28.720 ± 0.574		6.640 ± 0.133		9.098 ± 0.182		0.0210 ± 0.0002	
25	32.319 ± 0.646		25.524 ± 0.510		8.815 ± 0.176		30.530 ± 0.611		0.048 ± 0.002		0.122 ± 0.002		0.086 ± 0.002		61.016 ± 1.220		24.511 ± 0.490		7.510 ± 0.150		6.391 ± 0.128		0.0550 ± 0.0006	
26	33.037 ± 0.661		24.628 ± 0.493		9.094 ± 0.182		31.110 ± 0.622		0.068 ± 0.001		0.086 ± 0.002		0.123 ± 0.002		54.649 ± 1.093		29.342 ± 0.587		6.979 ± 0.140		7.457 ± 0.149		0.0260 ± 0.0003	
27	32.267 ± 0.645		29.180 ± 0.584		5.498 ± 0.110		31.240 ± 0.625		0.010 ± 0.002		0.027 ± 0.002		0.019 ± 0.002		52.575 ± 1.052		30.269 ± 0.605		5.463 ± 0.109		9.668 ± 0.193		0.0280 ± 0.0003	
28	32.158 ± 0.643		29.355 ± 0.587		5.969 ± 0.119		30.790 ± 0.616		0.041 ± 0.002		0.029 ± 0.002		0.074 ± 0.001		46.838 ± 0.937		35.462 ± 0.709		5.873 ± 0.117		11.122 ± 0.222		0.0098 ± 0.0001	
29	38.667 ± 0.773		27.841 ± 0.557		6.635 ± 0.133		25.200 ± 0.504		0.103 ± 0.002		0.187 ± 0.004		0.185 ± 0.004		52.564 ± 1.051		30.410 ± 0.608		6.349 ± 0.127		7.606 ± 0.152		0.0030 ± 0.0001	
30	36.648 ± 0.733		29.981 ± 0.600		6.476 ± 0.130		24.690 ± 0.494		0.219 ± 0.004		0.328 ± 0.007		0.394 ± 0.008		46.563 ± 0.931		35.934 ± 0.719		5.904 ± 0.118		9.182 ± 0.184		0.0030 ± 0.0001	

Table 4.2 Equilibrium composition of slag and metal phases pertinent to phosphorus distribution and phosphide capacity in ferrochromium smelting (1600 °C, CO gas atmosphere) (in wt. %)

	Final Slag Phase Composition (wt. %)												Final Metal Phase Composition (wt.%)						
Experiment Number	SiO ₂	Al ₂ O ₃	CaO	MgO	FeO	Cr ₂ O ₃	P (as Ca ₃ P ₂)	Cr	Fe	C	Si	P							
1	31.609 ± 0.632	29.486 ± 0.590	7.899 ± 0.158	28.980 ± 0.580	0.515 ± 0.010	0.430 ± 0.009	0.0206 ± 0.0004	57.237 ± 1.145	23.255 ± 0.465	7.205 ± 0.144	11.061 ± 0.221	0.1930 ± 0.0039							
2	31.108 ± 0.622	29.220 ± 0.584	8.861 ± 0.177	29.160 ± 0.583	0.347 ± 0.007	0.092 ± 0.002	0.0235 ± 0.0005	44.429 ± 0.889	34.162 ± 0.683	4.886 ± 0.098	15.853 ± 0.317	0.0920 ± 0.0018							
3	37.237 ± 0.745	23.662 ± 0.473	8.773 ± 0.175	28.280 ± 0.566	0.423 ± 0.008	0.448 ± 0.009	0.0324 ± 0.0006	62.938 ± 1.259	25.019 ± 0.500	8.613 ± 0.172	1.621 ± 0.032	1.4270 ± 0.0285							
4	31.684 ± 0.634	32.100 ± 0.642	7.952 ± 0.159	26.400 ± 0.528	0.418 ± 0.008	0.407 ± 0.008	0.0206 ± 0.0004	57.599 ± 1.152	23.237 ± 0.465	5.967 ± 0.119	10.888 ± 0.218	0.5270 ± 0.0105							
5	32.332 ± 0.647	31.309 ± 0.626	3.373 ± 0.067	31.000 ± 0.620	0.383 ± 0.008	0.313 ± 0.006	0.0353 ± 0.0007	58.223 ± 1.164	23.054 ± 0.461	5.491 ± 0.110	11.295 ± 0.226	0.7850 ± 0.0157							
6	23.100 ± 0.462	25.988 ± 0.520	25.048 ± 0.501	25.100 ± 0.502	0.044 ± 0.001	0.115 ± 0.002	0.0559 ± 0.0011	55.845 ± 1.117	30.292 ± 0.606	7.969 ± 0.159	5.300 ± 0.106	0.0060 ± 0.0001							
7	28.400 ± 0.568	31.006 ± 0.620	14.086 ± 0.282	26.770 ± 0.535	0.036 ± 0.001	0.023 ± 0.000	0.0147 ± 0.0003	54.369 ± 1.087	31.900 ± 0.638	6.594 ± 0.132	6.700 ± 0.134	0.0130 ± 0.0003							
8	29.100 ± 0.582	29.957 ± 0.599	14.489 ± 0.290	26.540 ± 0.531	0.044 ± 0.001	0.019 ± 0.000	0.0118 ± 0.0002	48.842 ± 0.977	35.947 ± 0.719	6.950 ± 0.139	7.400 ± 0.148	0.0100 ± 0.0002							
9	31.000 ± 0.620	29.035 ± 0.581	20.294 ± 0.406	21.530 ± 0.431	0.183 ± 0.004	0.562 ± 0.011	0.0065 ± 0.0001	58.688 ± 1.174	23.554 ± 0.471	6.846 ± 0.137	9.750 ± 0.195	0.0080 ± 0.0002							
10	31.800 ± 0.636	27.949 ± 0.559	19.775 ± 0.395	19.600 ± 0.392	0.223 ± 0.004	0.481 ± 0.010	0.0059 ± 0.0001	52.887 ± 1.058	29.453 ± 0.589	5.838 ± 0.117	11.025 ± 0.220	0.0110 ± 0.0002							
11	26.500 ± 0.530	32.625 ± 0.652	15.292 ± 0.306	24.780 ± 0.496	0.513 ± 0.010	0.151 ± 0.003	0.0088 ± 0.0002	54.299 ± 1.086	30.181 ± 0.604	7.392 ± 0.148	7.120 ± 0.142	0.0070 ± 0.0001							
12	31.600 ± 0.632	24.872 ± 0.497	11.170 ± 0.223	31.870 ± 0.637	0.210 ± 0.004	0.678 ± 0.014	0.0324 ± 0.0006	61.568 ± 1.231	26.004 ± 0.520	8.198 ± 0.164	3.544 ± 0.071	0.4910 ± 0.0098							
13	33.500 ± 0.670	23.049 ± 0.461	11.163 ± 0.223	31.960 ± 0.639	0.126 ± 0.003	0.424 ± 0.008	0.0294 ± 0.0006	55.919 ± 1.118	31.258 ± 0.625	7.532 ± 0.151	4.705 ± 0.094	0.4100 ± 0.0082							
14	32.200 ± 0.644	25.358 ± 0.507	11.268 ± 0.225	31.140 ± 0.623	0.136 ± 0.003	0.552 ± 0.011	0.1000 ± 0.0020	49.154 ± 0.983	37.491 ± 0.750	6.812 ± 0.136	5.865 ± 0.117	0.4030 ± 0.0081							
15	36.800 ± 0.736	28.199 ± 0.564	4.092 ± 0.082	31.258 ± 0.625	0.194 ± 0.004	0.091 ± 0.002	0.0088 ± 0.0002	58.162 ± 1.163	23.310 ± 0.466	5.868 ± 0.117	11.485 ± 0.230	0.7740 ± 0.0155							
16	36.600 ± 0.732	27.943 ± 0.559	4.036 ± 0.081	31.900 ± 0.638	0.127 ± 0.003	0.055 ± 0.001	0.0147 ± 0.0003	46.256 ± 0.925	34.101 ± 0.682	4.575 ± 0.092	14.237 ± 0.285	0.5130 ± 0.0103							
17	27.100 ± 0.542	20.753 ± 0.415	20.976 ± 0.420	31.300 ± 0.626	0.063 ± 0.001	0.117 ± 0.002	0.0265 ± 0.0005	62.796 ± 1.256	24.947 ± 0.499	8.967 ± 0.179	2.986 ± 0.060	0.0130 ± 0.0003							
18	33.900 ± 0.678	24.574 ± 0.491	9.797 ± 0.196	31.358 ± 0.627	0.068 ± 0.001	0.086 ± 0.002	0.0029 ± 0.0001	54.798 ± 1.096	29.491 ± 0.590	7.129 ± 0.143	7.606 ± 0.152	0.0080 ± 0.0002							
19	34.500 ± 0.690	27.523 ± 0.550	6.489 ± 0.130	31.918 ± 0.638	0.062 ± 0.001	0.044 ± 0.001	0.0118 ± 0.0002	60.777 ± 1.216	23.901 ± 0.478	6.271 ± 0.125	8.204 ± 0.164	0.3710 ± 0.0074							
20	32.900 ± 0.658	29.399 ± 0.588	6.384 ± 0.128	31.101 ± 0.622	0.041 ± 0.001	0.029 ± 0.001	0.0176 ± 0.0004	46.866 ± 0.937	35.490 ± 0.710	5.901 ± 0.118	11.150 ± 0.223	0.4110 ± 0.0082							
21	31.743 ± 0.635	23.555 ± 0.471	9.267 ± 0.185	34.205 ± 0.684	0.188 ± 0.004	0.785 ± 0.016	0.2471 ± 0.0049	55.814 ± 1.116	30.680 ± 0.614	7.983 ± 0.160	3.523 ± 0.070	1.2630 ± 0.0253							
22	38.490 ± 0.770	23.014 ± 0.460	7.596 ± 0.152	30.649 ± 0.613	0.114 ± 0.002	0.154 ± 0.003	0.0029 ± 0.0001	53.331 ± 1.067	29.310 ± 0.586	7.909 ± 0.158	7.664 ± 0.153	0.3100 ± 0.0062							
23	40.171 ± 0.803	23.959 ± 0.479	6.567 ± 0.131	28.947 ± 0.579	0.130 ± 0.003	0.147 ± 0.003	0.0029 ± 0.0001	56.033 ± 1.121	29.350 ± 0.587	9.369 ± 0.187	5.869 ± 0.117	0.1140 ± 0.0023							
24	29.984 ± 0.600	24.353 ± 0.487	6.978 ± 0.140	34.684 ± 0.694	1.022 ± 0.020	0.392 ± 0.008	0.0676 ± 0.0014	56.840 ± 1.137	28.970 ± 0.579	6.723 ± 0.134	5.457 ± 0.109	1.1190 ± 0.0224							
25	35.509 ± 0.710	24.703 ± 0.494	8.448 ± 0.169	30.054 ± 0.601	0.292 ± 0.006	0.772 ± 0.015	0.0059 ± 0.0001	52.763 ± 1.055	30.020 ± 0.600	8.801 ± 0.176	5.518 ± 0.110	0.2040 ± 0.0041							
26	38.585 ± 0.772	23.162 ± 0.463	7.880 ± 0.158	29.458 ± 0.589	0.122 ± 0.002	0.142 ± 0.003	0.0029 ± 0.0001	53.324 ± 1.066	30.840 ± 0.617	7.649 ± 0.153	7.627 ± 0.153	0.2630 ± 0.0053							
27	38.609 ± 0.772	22.977 ± 0.460	8.224 ± 0.164	30.071 ± 0.601	0.105 ± 0.002	0.115 ± 0.002	0.0147 ± 0.0003	52.948 ± 1.059	29.010 ± 0.580	8.930 ± 0.179	8.057 ± 0.161	0.2730 ± 0.0055							
28	39.264 ± 0.785	23.142 ± 0.463	9.154 ± 0.183	27.399 ± 0.548	0.121 ± 0.002	0.144 ± 0.003	0.0088 ± 0.0002	54.740 ± 1.095	30.760 ± 0.615	9.455 ± 0.189	4.793 ± 0.096	0.2080 ± 0.0042							
29	40.162 ± 0.803	23.816 ± 0.476	6.714 ± 0.134	28.851 ± 0.577	0.130 ± 0.003	0.129 ± 0.003	0.0029 ± 0.0001	55.814 ± 1.116	29.340 ± 0.587	9.353 ± 0.187	5.794 ± 0.116	0.0980 ± 0.0020							

Table 4.3 Equilibrium composition of slag and metal phases pertinent to sulphur distribution and sulphide capacity in ferromanganese smelting (1500 °C, CO gas atmosphere) (in wt. %)

Experiment Number	Final Slag Phase Composition (wt. %)										Final Metal Phase Composition (wt.%)						
	SiO ₂	Al ₂ O ₃	CaO	MgO	FeO	MnO	S (as CaS)	Mn	Fe	C	Si	S					
1	44.700 ± 0.894	6.310 ± 0.126	22.120 ± 0.442	11.500 ± 0.230	0.0180 ± 0.0004	12.600 ± 0.252	1.629 ± 0.033	77.500 ± 1.550	7.490 ± 0.150	3.850 ± 0.077	9.940 ± 0.199	0.0340 ± 0.0007					
2	45.200 ± 0.904	6.240 ± 0.125	21.770 ± 0.435	11.400 ± 0.228	0.0370 ± 0.0007	12.300 ± 0.246	1.541 ± 0.031	71.000 ± 1.420	13.300 ± 0.266	3.850 ± 0.077	10.800 ± 0.216	0.0289 ± 0.0006					
3	45.800 ± 0.916	6.250 ± 0.125	21.827 ± 0.437	11.400 ± 0.228	0.0500 ± 0.0010	11.500 ± 0.230	1.510 ± 0.030	65.100 ± 1.302	19.000 ± 0.380	2.990 ± 0.060	11.600 ± 0.232	0.0350 ± 0.0007					
4	43.700 ± 0.874	5.600 ± 0.112	16.784 ± 0.336	15.000 ± 0.300	0.0530 ± 0.0011	16.300 ± 0.326	1.179 ± 0.024	78.700 ± 1.574	7.310 ± 0.146	5.200 ± 0.104	7.110 ± 0.142	0.0300 ± 0.0006					
5	45.091 ± 0.902	5.560 ± 0.111	17.269 ± 0.345	14.900 ± 0.298	0.0200 ± 0.0004	15.300 ± 0.306	0.702 ± 0.014	73.500 ± 1.470	13.300 ± 0.266	4.417 ± 0.088	7.710 ± 0.154	0.0230 ± 0.0005					
6	45.920 ± 0.918	6.500 ± 0.130	18.161 ± 0.363	11.600 ± 0.232	0.0360 ± 0.0007	14.800 ± 0.296	1.599 ± 0.032	66.100 ± 1.322	18.600 ± 0.372	3.309 ± 0.066	11.200 ± 0.224	0.0383 ± 0.0008					
7	39.063 ± 0.781	5.850 ± 0.117	28.941 ± 0.579	15.600 ± 0.312	0.0690 ± 0.0014	7.350 ± 0.147	1.899 ± 0.038	77.200 ± 1.544	12.500 ± 0.250	6.678 ± 0.134	2.710 ± 0.054	0.0336 ± 0.0007					
8	39.721 ± 0.794	5.750 ± 0.115	28.655 ± 0.573	15.600 ± 0.312	0.0850 ± 0.0017	6.990 ± 0.140	1.951 ± 0.039	71.500 ± 1.430	17.900 ± 0.358	5.779 ± 0.116	3.790 ± 0.076	0.0305 ± 0.0006					
9	41.614 ± 0.832	9.140 ± 0.183	22.348 ± 0.447	18.700 ± 0.374	0.0300 ± 0.0006	4.420 ± 0.088	2.382 ± 0.048	75.900 ± 1.518	6.550 ± 0.131	3.273 ± 0.065	12.900 ± 0.258	0.0242 ± 0.0005					
10	37.303 ± 0.746	6.760 ± 0.135	35.484 ± 0.710	13.100 ± 0.262	0.1050 ± 0.0021	3.480 ± 0.070	2.340 ± 0.047	80.700 ± 1.614	7.350 ± 0.147	6.267 ± 0.125	4.700 ± 0.094	0.0188 ± 0.0004					
11	37.927 ± 0.759	6.750 ± 0.135	35.526 ± 0.711	13.200 ± 0.264	0.0830 ± 0.0017	2.960 ± 0.059	2.169 ± 0.043	75.100 ± 1.502	12.900 ± 0.258	5.559 ± 0.111	5.750 ± 0.115	0.0182 ± 0.0004					
12	37.439 ± 0.749	6.590 ± 0.132	33.914 ± 0.678	15.000 ± 0.300	0.0440 ± 0.0009	3.140 ± 0.063	2.430 ± 0.049	81.400 ± 1.628	7.160 ± 0.143	5.522 ± 0.110	5.120 ± 0.102	0.0252 ± 0.0005					
13	38.466 ± 0.769	6.500 ± 0.130	33.401 ± 0.668	15.000 ± 0.300	0.1500 ± 0.0030	3.020 ± 0.060	2.196 ± 0.044	68.600 ± 1.372	18.500 ± 0.370	4.720 ± 0.094	7.410 ± 0.148	0.0188 ± 0.0004					
14	38.946 ± 0.779	7.070 ± 0.141	35.936 ± 0.719	10.300 ± 0.206	0.0480 ± 0.0010	2.980 ± 0.060	2.954 ± 0.059	78.100 ± 1.562	7.450 ± 0.149	5.357 ± 0.107	8.050 ± 0.161	0.0282 ± 0.0006					
15	39.619 ± 0.792	7.040 ± 0.141	36.361 ± 0.727	10.400 ± 0.208	0.0590 ± 0.0012	3.010 ± 0.060	2.090 ± 0.042	72.100 ± 1.442	13.300 ± 0.266	4.465 ± 0.089	9.000 ± 0.180	0.0242 ± 0.0005					
16	40.031 ± 0.801	7.090 ± 0.142	36.606 ± 0.732	10.100 ± 0.202	0.0700 ± 0.0014	2.690 ± 0.054	2.036 ± 0.041	65.900 ± 1.318	19.100 ± 0.382	3.916 ± 0.078	10.100 ± 0.202	0.0243 ± 0.0005					
17	44.476 ± 0.890	7.540 ± 0.151	16.423 ± 0.328	19.300 ± 0.386	0.0730 ± 0.0015	9.220 ± 0.184	1.811 ± 0.036	65.900 ± 1.318	18.200 ± 0.364	3.010 ± 0.060	12.200 ± 0.244	0.0337 ± 0.0007					
18	37.046 ± 0.741	7.930 ± 0.159	41.053 ± 0.821	7.810 ± 0.156	0.0430 ± 0.0009	1.780 ± 0.036	2.588 ± 0.052	78.000 ± 1.560	6.660 ± 0.133	4.993 ± 0.100	8.490 ± 0.170	0.0170 ± 0.0003					
19	37.125 ± 0.743	7.950 ± 0.159	40.899 ± 0.818	8.340 ± 0.167	0.0500 ± 0.0010	1.730 ± 0.035	2.513 ± 0.050	66.700 ± 1.334	18.500 ± 0.370	3.943 ± 0.079	10.400 ± 0.208	0.0160 ± 0.0003					
20	37.610 ± 0.752	7.990 ± 0.160	41.025 ± 0.820	8.020 ± 0.160	0.1180 ± 0.0024	1.570 ± 0.031	2.407 ± 0.048	72.700 ± 1.454	12.400 ± 0.248	4.497 ± 0.090	9.260 ± 0.185	0.0170 ± 0.0003					
21	36.344 ± 0.727	7.440 ± 0.149	38.323 ± 0.766	11.600 ± 0.232	0.0980 ± 0.0020	2.210 ± 0.044	2.680 ± 0.054	79.700 ± 1.594	7.280 ± 0.146	6.021 ± 0.120	6.550 ± 0.131	0.0206 ± 0.0004					
22	36.865 ± 0.737	7.290 ± 0.146	37.933 ± 0.759	11.900 ± 0.238	0.0860 ± 0.0017	2.120 ± 0.042	2.437 ± 0.049	72.900 ± 1.458	13.000 ± 0.260	5.409 ± 0.108	7.410 ± 0.148	0.0216 ± 0.0004					
23	36.993 ± 0.740	7.280 ± 0.146	37.834 ± 0.757	11.700 ± 0.234	0.1610 ± 0.0032	2.080 ± 0.042	2.590 ± 0.052	66.800 ± 1.336	19.100 ± 0.382	5.096 ± 0.102	8.260 ± 0.165	0.0216 ± 0.0004					
24	41.600 ± 0.832	6.020 ± 0.120	25.020 ± 0.500	13.300 ± 0.266	0.1250 ± 0.0025	10.700 ± 0.214	1.964 ± 0.039	80.200 ± 1.604	7.380 ± 0.148	4.895 ± 0.098	6.190 ± 0.124	0.0428 ± 0.0009					
25	43.031 ± 0.861	5.870 ± 0.117	24.710 ± 0.494	13.500 ± 0.270	0.2550 ± 0.0051	9.860 ± 0.197	1.530 ± 0.031	66.600 ± 1.332	19.400 ± 0.388	3.653 ± 0.073	7.860 ± 0.157	0.0515 ± 0.0010					
26	42.951 ± 0.859	6.170 ± 0.123	24.013 ± 0.480	13.900 ± 0.278	0.0570 ± 0.0011	9.750 ± 0.195	1.789 ± 0.036	69.100 ± 1.382	18.200 ± 0.364	4.500 ± 0.090	7.560 ± 0.151	0.0411 ± 0.0008					
27	43.255 ± 0.865	5.860 ± 0.117	17.288 ± 0.346	13.200 ± 0.264	0.0390 ± 0.0008	17.900 ± 0.358	0.956 ± 0.019	79.400 ± 1.588	7.510 ± 0.150	4.600 ± 0.092	7.250 ± 0.145	0.0300 ± 0.0006					
28	44.042 ± 0.881	5.780 ± 0.116	16.539 ± 0.331	13.100 ± 0.262	0.0660 ± 0.0013	17.400 ± 0.348	1.908 ± 0.038	72.300 ± 1.446	13.100 ± 0.262	4.990 ± 0.100	8.290 ± 0.166	0.0390 ± 0.0008					
30	45.030 ± 0.901	5.770 ± 0.115	16.613 ± 0.332	13.100 ± 0.262	0.1180 ± 0.0024	16.500 ± 0.330	1.591 ± 0.032	66.500 ± 1.330	19.400 ± 0.388	3.750 ± 0.075	9.350 ± 0.187	0.0460 ± 0.0009					
31	42.194 ± 0.844	5.510 ± 0.110	23.512 ± 0.470	10.200 ± 0.204	0.0980 ± 0.0020	15.500 ± 0.310	1.798 ± 0.036	80.500 ± 1.610	7.380 ± 0.148	5.445 ± 0.109	5.210 ± 0.104	0.0577 ± 0.0012					
32	43.059 ± 0.861	5.690 ± 0.114	24.217 ± 0.484	10.300 ± 0.206	0.0740 ± 0.0015	13.400 ± 0.268	1.872 ± 0.037	74.400 ± 1.488	13.400 ± 0.268	5.030 ± 0.101	6.420 ± 0.128	0.0384 ± 0.0008					
33	43.514 ± 0.870	5.560 ± 0.111	23.757 ± 0.475	10.300 ± 0.206	0.3940 ± 0.0079	13.700 ± 0.274	1.667 ± 0.033	67.600 ± 1.352	18.800 ± 0.376	4.680 ± 0.094	7.350 ± 0.147	0.0446 ± 0.0009					
34	41.851 ± 0.837	6.140 ± 0.123	23.825 ± 0.476	16.400 ± 0.328	0.0490 ± 0.0010	8.990 ± 0.180	1.681 ± 0.034	80.100 ± 1.602	7.330 ± 0.147	5.570 ± 0.111	5.970 ± 0.119	0.0346 ± 0.0007					
35	42.976 ± 0.860	7.410 ± 0.148	17.955 ± 0.359	18.600 ± 0.372	0.0730 ± 0.0015	9.280 ± 0.186	2.538 ± 0.051	77.400 ± 1.548	7.230 ± 0.145	3.810 ± 0.076	10.700 ± 0.214	0.0313 ± 0.0006					
36	43.968 ± 0.879	7.240 ± 0.145	17.847 ± 0.357	18.300 ± 0.366	0.1330 ± 0.0027	9.240 ± 0.185	1.991 ± 0.040	71.600 ± 1.432	12.400 ± 0.248	3.300 ± 0.066	11.400 ± 0.228	0.0280 ± 0.0006					
37	44.682 ± 0.894	7.310 ± 0.146	18.334 ± 0.367	18.400 ± 0.368	0.0480 ± 0.0010	8.220 ± 0.164	1.685 ± 0.034	65.600 ± 1.312	18.500 ± 0.370	2.880 ± 0.058	12.300 ± 0.246	0.0290 ± 0.0006					
38	39.201 ± 0.784	6.350 ± 0.127	32.847 ± 0.657	13.400 ± 0.268	0.0280 ± 0.0006	4.780 ± 0.096	2.133 ± 0.043	81.000 ± 1.620	7.340 ± 0.147	6.310 ± 0.126	4.290 ± 0.086	0.0245 ± 0.0005					
39	39.923 ± 0.798	6.270 ± 0.125	32.623 ± 0.652	13.200 ± 0.264	0.0510 ± 0.0010	4.440 ± 0.089	2.149 ± 0.043	74.200 ± 1.484	13.600 ± 0.272	6.060 ± 0.121	5.390 ± 0.108	0.0242 ± 0.0005					
40	41.667 ± 0.833	6.580 ± 0.132	25.912 ± 0.518	15.100 ± 0.302	0.0210 ± 0.0004	6.930 ± 0.139	2.531 ± 0.051	79.100 ± 1.582	7.110 ± 0.142	5.160 ± 0.103	7.490 ± 0.150	0.0431 ± 0.0009					
41	42.013 ± 0.840	6.560 ± 0.131	26.083 ± 0.522	15.100 ± 0.302	0.0260 ± 0.0005	6.970 ± 0.139	2.086 ± 0.042	73.100 ± 1.462	13.100 ± 0.262	4.350 ± 0.087	8.490 ± 0.170	0.0388 ± 0.0008					
42	44.700 ± 0.894	8.160 ± 0.163	20.571 ± 0.411	19.100 ± 0.382	0.0370 ± 0.0007	4.500 ± 0.090	2.225 ± 0.045	70.200 ± 1.404	14.600 ± 0.292	2.659 ± 0.053	12.300 ± 0.246	0.0300 ± 0.0006					

4.2 Quadratic Response-Surface Models/Equations

Several researchers have used regression models for different metallurgical studies. Pesta et al. (1981) and Eric et al. (1991) obtained good results by creating multi-coefficient quadratic equations which were derived from the experimental study results of ferrochromium and ferromanganese smelting slags.

Huang and Lin (1989) used linear regression analysis for determining the activity of Na_2O as a function of temperature also they indicate the high correlation coefficient (R) which is varied between 0.993 to 0.998. This is a good example of the use of linear regression method for determination of activity in the slag system.

Hejja et al. (1973) also used linear regression to determine the relationship between the desulphurisation efficiency and basicity of basic oxygen furnace slags. In the same study, there are other correlations between MgO , FeO and basicity and they applied linear regression analysis to actual plant data.

Yang and Edstrom (1992) obtained two relations between phosphate capacity of lime saturated slags and optical basicity by using linear regression analysis. In their study, correlation coefficient is used to demonstrate the confidence of the regression models. Also in the same work, they analysed the previous studies results by using regression technique and identified several correlations between phosphate capacity of slags, optical basicity and temperature.

Choi et al. (2004) applied linear regression to determine the sulphide capacity of $\text{CaO-CaF}_2\text{-SiO}_2\text{-MgO}$ slag system.

Turkdogan and Pearson (1954) proposed an empirical relation between the activity coefficient of P_2O_5 and the composition of slags as a function of temperature. This empirical model has been widely used by several researchers such as Niekerk and Dippenaar (1998).

Ding and Eric (2005) derived two quadratic multivariable regression models from the experimental data to determine the activity and activity coefficient of MnO in stainless steel slags. Researchers used square of correlation coefficient value (R^2) as an indicator of a good fitting.

Rao and Gaskell (1981) applied 4th degree polynomial equation to calculate the activity coefficient of Mn in Pt-Mn binary system.

Eric et al. (1991) investigated liquidus temperatures and electrical conductivities of ferromanganese slag. The model equations were in quadratic form with high correlation coefficients (R^2) of 0.800 and 0.897.

Yang (1992) studied carbon solubility in Fe-C-P melts and derived two different regression models. A good linear relationship was found between carbon and phosphorus contents with high correlation coefficient ($R=0.99$) at low phosphorus concentrations whereas the relationship became non-linear at high phosphorus concentrations.

Li et al. (1999) studied the thermodynamic modelling of MnO-containing slags. A regression equation has been proposed to calculate the activity of MnO in the ferromanganese slags. The model was in quadratic form and the MnO activities calculated by the cell model (Kapoor and Frohberg, 1973) were 0.03 to 0.05 lower than those calculated by Cengizler (1993). The difference was considered as acceptable.

Linear regression analysis and fitting a 2nd (or higher) order polynomial is common in the field of metallurgical studies. The basicity ratio has a strong power on the phosphide and sulphide capacities and phosphorus and sulphur distribution values of the multicomponent slag system, which is a cross-product of the system and can be included into the model where the models should be non-linear or specifically quadratic in this case.

In this work, quadratic multivariable regression model equations were derived from the experimental data which have high correlation coefficients indicating that if the slag compositions fall within the range of this study, these models can be confidently used to determine the sulphide and phosphide capacities of slags and sulphur and phosphorus distribution ratio between slag and metal phases at specified experimental conditions. The molar fractions of CaO, MgO, MnO, SiO₂, Al₂O₃ and the basicity ratio are the independent variables of the model. The regression model have been calculated using the Statistical Analysis Software (SAS) package. The degree of accuracy of the predictions in the regression models is measured by Pearson's R² in the bivariate case and by the multiple R² in the multiple regression situations (Dilorio and Hardy, 1996).

In the present work, sulphur and phosphorus distribution ratio between slag and metal are calculated by using following equation:

$$L_x = \frac{(X)}{[X]} \quad (4.1)$$

where round and square brackets surrounding X (S or P) denote components' weight percentages of slag and metal phases, respectively.

The basicity ratio is evaluated by adding together the basic constituents' mole fractions (CaO, MgO) and dividing this by the mole fraction value of SiO₂.

$$\text{Basicity Ratio: } \left(\frac{X_{\text{CaO}} + X_{\text{MgO}}}{X_{\text{SiO}_2}} \right) \quad (4.2)$$

Log and Log₁₀ represent the common logarithm in the present work.

The derived regression models are given below:

$$\begin{aligned} \text{Log}_{10} C_s^{-2} = & -0.942 - 0.833.(X_{\text{MgO}}) - 2.811.(X_{\text{CaO}}) - 32.964.(X_{\text{Al}_2\text{O}_3}) \\ & - 29.611.(X_{\text{SiO}_2})^2 - 5.499\left(\frac{X_{\text{MgO}}}{X_{\text{SiO}_2}}\right) + 75.288(X_{\text{Al}_2\text{O}_3} \cdot X_{\text{MgO}}) + 2.260\left(\frac{X_{\text{CaO}} + X_{\text{MgO}}}{X_{\text{SiO}_2}}\right) \end{aligned} \quad (4.3)$$

for sulphide capacity of ferrochromium slags,

$$\begin{aligned} \text{Log}_{10} L_S = & 1.429 + 13.178.(X_{\text{MgO}}) + 7.039.(X_{\text{CaO}}) - 10.639.(X_{\text{Al}_2\text{O}_3}) \\ & - 23.727(X_{\text{SiO}_2})^2 - 4.527\left(\frac{X_{\text{MgO}}}{X_{\text{SiO}_2}}\right) + 29.036.(X_{\text{Al}_2\text{O}_3} \cdot X_{\text{MgO}}) + \left(\frac{X_{\text{CaO}} + X_{\text{MgO}}}{X_{\text{SiO}_2}}\right) \end{aligned} \quad (4.4)$$

for sulphur distribution ratio between metal and slag phases of ferrochromium smelting,

$$\begin{aligned} \text{Log}_{10} C_p^{-3} = & -41.688 + 41.487.(X_{\text{MgO}})^2 + 8.706.(X_{\text{CaO}}) + 33.254.(X_{\text{Al}_2\text{O}_3}) \\ & + 29.344.(X_{\text{SiO}_2}) + 78.338(X_{\text{Al}_2\text{O}_3} \cdot X_{\text{CaO}}) + 69.142(X_{\text{MgO}} \cdot X_{\text{CaO}}) \end{aligned} \quad (4.5)$$

for phosphide capacity of ferrochromium slags,

$$\begin{aligned} \text{Log}_{10} L_P = & -34.852 + 47.720.(X_{\text{MgO}})^2 + 21.066.(X_{\text{CaO}}) + 47.302(X_{\text{Al}_2\text{O}_3}) \\ & + 37.657.(X_{\text{SiO}_2}) + 38.518(X_{\text{Al}_2\text{O}_3} \cdot X_{\text{CaO}}) + 67.120(X_{\text{MgO}} \cdot X_{\text{CaO}}) \end{aligned} \quad (4.6)$$

for phosphorus distribution ratio between metal and slag phases of ferrochromium smelting,

$$\begin{aligned} \text{Log}_{10} C_S^{-2} = & 0.622 - 18.705.(X_{\text{Al}_2\text{O}_3}) - 11.399.(X_{\text{MgO}}) - 22.420.(X_{\text{MnO}}) \\ & - 10.840.(X_{\text{SiO}_2}) + 16.485(X_{\text{MgO}})^2 + 37.894(X_{\text{SiO}_2} \cdot X_{\text{MnO}}) - 4.925(X_{\text{CaO}}) \end{aligned} \quad (4.7)$$

for sulphide capacity of ferromanganese smelting, and the sulphur distribution ratio between metal and slag phases for ferromanganese smelting is:

$$\begin{aligned} \text{Log}_{10} L_S = & 13.776 - 4.983.(X_{\text{Al}_2\text{O}_3}) - 14.507.(X_{\text{MgO}}) - 37.746.(X_{\text{MnO}}) \\ & - 15.433.(X_{\text{SiO}_2}) + 12.497.(X_{\text{MgO}})^2 + 62.190.(X_{\text{SiO}_2} \cdot X_{\text{MnO}}) - 9.960.(X_{\text{CaO}}) \end{aligned} \quad (4.8)$$

The correlation coefficient and the adjusted correlation coefficient (is a version of R^2 that has been adjusted for degrees of freedom where is equal to 1, if there is an intercept and 0 otherwise) values of the models are high which indicating that the regression models can be confidently used to predict phosphide and sulphide capacities for slags and to determine the equilibrium phosphorus and sulphur

distribution ratios between slag and metal phases for the composition range studied (Table 4.4).

Table 4.4 The correlation coefficient (R^2) and adjusted correlation coefficient values (Adj. R^2) of response surface models.

Equation Number	Model Description	Temperature (°C)	Number of Parameters in Model	Correlation Coefficient (R^2)	Adjusted Correlation Coefficient (Adj. R^2)
4.3	Ferrochromium $\text{Log}_{10} C_S^{-2}$	1600	8	0.914	0.883
4.4	Ferrochromium- $\text{Log}_{10} L_S$	1600	8	0.965	0.924
4.5	Ferrochromium- $\text{Log}_{10} C_P^{-3}$	1600	7	0.913	0.886
4.6	Ferrochromium- $\text{Log}_{10} L_P$	1600	7	0.897	0.862
4.7	Ferromanganese- $\text{Log}_{10} C_S^{-2}$	1500	8	0.915	0.898
4.8	Ferromanganese $\text{Log}_{10} L_S$	1500	8	0.928	0.915

4.3 Relationships between Lattice Energy of the Component Oxides and Sulphide and Phosphide Capacity of Slags

Relationship between sulphide and phosphide capacities of slags and lattice energy of the slag component oxides were discussed in section 2.9. Ichise and Moro-Oka (1990) applied the Born-Haber cycle to the thermal data and ionization energy of elements in order to correlate the interaction energy between anion and cation of an oxide from the lattice energy of the oxide. 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. As it was discussed in section 2.9.2, Ichise and Moro-Oka's model can be used in understanding the relationship between lattice energy of slag component oxides and phosphide capacity of slag.

In an approach applied to investigate the relation between binding energy of O^{2-} ion in the mixture (lattice energy of the oxides) and phosphide and sulphide capacities, Eqs (4.9) and (4.11) can be used to predict the sulphide capacities of ferrochromium and ferromanganese smelting slags, respectively. Eq. (4.10) can also be used to predict the phosphide capacities of ferrochromium smelting slags.

The linear relationship between lattice energy of the slag system's oxides and sulphide and phosphide capacities of slags were derived by using the least square method. Reasonable correlation coefficients (R^2) were achieved for these linear models (Table 4.5). Since the sulphide and phosphide capacities of ferrochromium and ferromanganese smelting slags is related to overall lattice energy of the slag system's oxides, it was decided that the models should be in linear form.

The linear regression model between the lattice energy of ferrochromium smelting slag system's oxides and sulphide capacities of ferrochromium smelting slags is:

$$\text{Log}_{10} C_S^{-2} = -0.004 \overline{E_o} + 14.002 \quad (4.9)$$

The linear regression model between the lattice energy of ferrochromium smelting slag system's oxides and phosphide capacities of ferrochromium smelting slags is:

$$\text{Log}_{10} C_P^{-3} = -0.007 \overline{E_o} + 21.102 \quad (4.10)$$

The linear regression model between the lattice energy of ferromanganese smelting slag system's oxides and sulphide capacities of ferromanganese smelting slags is:

$$\text{Log}_{10} C_S^{-2} = -0.002 \overline{E_o} + 1.902 \quad (4.11)$$

Table 4.5 The correlation coefficient (R^2) and adjusted correlation coefficient values (Adj. R^2) of Equations 4.9, 4.10 and 4.11.

Equation Number	Model Description	Temperature (°C)	Number of Parameters in Model	Correlation Coefficient (R^2)	Adjusted Correlation Coefficient (Adj. R^2)
4.9	Ferrochromium $\text{Log}_{10} C_S^{-2}$	1600	1	0.824	0.818
4.10	Ferrochromium- $\text{Log}_{10} C_P^{-3}$	1600	1	0.808	0.801
4.11	Ferromanganese $\text{Log}_{10} C_S^{-2}$	1500	1	0.892	0.889

It is known that the binding energy of the slag system has a tendency to increase with the decrease of the basicity of the slag. Therefore, the logarithms of sulphide and phosphide capacities of slags are inversely proportional to the lattice energy of component oxides of ferrochromium and ferromanganese slags (Equations 4.9, 4.10 and 4.11).

4.4 Discussion of Results

4.4.1 Sulphur distribution and sulphide capacity relevant to ferrochromium smelting process

Table 4.6 presents the calculated values of molar fraction of components, basicity ratio, optical basicity, lattice energy of component oxides, activity coefficient of sulphur, sulphide capacity, sulphur distribution ratio and regression models pertinent to ferrochromium smelting (1600 °C, CO gas atmosphere). The calculations of activity coefficient of sulphur, sulphide capacity and sulphur distribution ratio includes relative errors in chemical analysis and temperature.

The sulphur distribution ratio (L_s) is calculated by using equation 4.1 by using weight percentages of sulphur in slag and metal phases. The basicity ratio is calculated according to equation 4.2 by using the mole fraction values of CaO, MgO and SiO₂. The slag's optical basicity is determined according to equation 2.104 by using optical basicity values of several slag species in Table 2.8. Equation 2.178 is used in the calculation of lattice energy of component oxides. The calculation methodology of activity coefficient of sulphur related to ferrochromium smelting is presented in Appendix A. The sulphide capacity of ferrochromium slags are calculated according to equation 2.30. Equations 4.3, 4.4 and 4.9 are used in the calculation of regression model values.

Table 4.6 Calculated values of molar fraction of components, basicity ratio,optical basicity, lattice energy of component oxides,activity coefficient of sulphur, sulphide capacity, sulphur distribution ratio and regression models pertinent to ferrochromium smelting (1600 °C, CO gas atmosphere)

	Final Slag Composition in Mole Fraction							Basicity Ratio	Optical Basicity (I)	Lattice Energy of Component Oxides (Eo)	Activity coefficient of Sulphur (f _s)	Log ₁₀ (f _s)	L _s	Log ₁₀ L _s	Cs ⁻²	Log ₁₀ Cs ⁻²	Log ₁₀ L _s (Calculated based on Eq. 4.4)	Log ₁₀ Cs ⁻² (Calculated based on Eq. 4.3)	Log ₁₀ Cs ⁻² (Calculated based on Eq. 4.9)
Experiment Number	X SiO ₂	X Al ₂ O ₃	X MgO	X FeO	X Cr ₂ O ₃	X CaS	X CaO												
1	0.2879	0.1246	0.4691	0.0014	0.0009	0.01284	0.1031	1.987	0.640	5155.37	81.10 ± 9.26	1.909	29.796 ± 0.608	1.474	5.88E-09 ± 9.60E-10	-8.231	1.353	-8.252	-8.166
2	0.2875	0.1234	0.4700	0.0015	0.0009	0.01282	0.1038	1.996	0.640	5153.05	84.58 ± 9.78	1.927	32.130 ± 0.656	1.507	6.08E-09 ± 1.00E-09	-8.216	1.358	-8.253	-8.156
3	0.3331	0.1252	0.4899	0.0010	0.0009	0.00311	0.0467	1.611	0.619	5279.46	42.33 ± 3.96	1.627	7.244 ± 0.148	0.860	2.74E-09 ± 3.88E-10	-8.563	0.983	-8.723	-8.700
4	0.3237	0.1508	0.4639	0.0010	0.0009	0.00286	0.0568	1.609	0.620	5267.96	71.75 ± 7.67	1.856	8.254 ± 0.168	0.917	1.84E-09 ± 2.86E-10	-8.735	1.004	-8.540	-8.650
5	0.3528	0.1385	0.4191	0.0010	0.0005	0.00156	0.0865	1.433	0.618	5324.15	90.30 ± 10.20	1.956	9.654 ± 0.197	0.985	1.71E-09 ± 2.77E-10	-8.767	0.874	-8.709	-8.892
6	0.2883	0.1316	0.4572	0.0020	0.0020	0.01333	0.1055	1.951	0.639	5162.13	62.69 ± 6.67	1.797	17.809 ± 0.363	1.251	4.55E-09 ± 7.06E-10	-8.342	1.344	-8.198	-8.195
7	0.2956	0.1284	0.4788	0.0010	0.0005	0.00793	0.0877	1.916	0.635	5178.14	74.65 ± 8.23	1.873	20.616 ± 0.421	1.314	4.42E-09 ± 7.03E-10	-8.355	1.286	-8.354	-8.264
8	0.2938	0.1365	0.4476	0.0020	0.0018	0.01249	0.1058	1.884	0.636	5179.29	79.15 ± 8.97	1.898	23.056 ± 0.471	1.363	4.66E-09 ± 7.57E-10	-8.332	1.332	-8.189	-8.269
9	0.3233	0.1247	0.4563	0.0012	0.0009	0.00398	0.0895	1.688	0.628	5244.23	77.69 ± 8.63	1.890	10.076 ± 0.206	1.003	2.08E-09 ± 3.32E-10	-8.683	1.216	-8.441	-8.548
10	0.3056	0.1216	0.4378	0.0017	0.0014	0.01212	0.1197	1.824	0.637	5195.87	54.49 ± 5.65	1.736	37.316 ± 0.762	1.572	1.10E-08 ± 1.67E-09	-7.960	1.416	-8.163	-8.340
11	0.2875	0.1229	0.4710	0.0014	0.0012	0.01341	0.1024	1.994	0.640	5153.68	71.16 ± 7.84	1.852	26.145 ± 0.534	1.417	5.88E-09 ± 9.35E-10	-8.231	1.346	-8.264	-8.159
12	0.3120	0.1840	0.3156	0.0004	0.0000	0.00401	0.1835	1.600	0.636	5229.53	71.09 ± 7.56	1.852	19.000 ± 0.388	1.279	4.28E-09 ± 6.62E-10	-8.369	1.319	-8.244	-8.485
13	0.2783	0.1829	0.3924	0.0003	0.0001	0.00876	0.1371	1.903	0.639	5160.52	30.45 ± 2.55	1.484	24.526 ± 0.501	1.390	1.29E-08 ± 1.69E-09	-7.890	1.385	-8.026	-8.188
14	0.2808	0.1785	0.3894	0.0004	0.0001	0.00903	0.1416	1.891	0.640	5162.98	43.17 ± 4.02	1.635	40.083 ± 0.818	1.603	1.49E-08 ± 2.09E-09	-7.828	1.418	-8.002	-8.199
15	0.3063	0.1766	0.3064	0.0016	0.0023	0.00783	0.1989	1.650	0.640	5211.75	57.58 ± 5.78	1.760	29.000 ± 0.592	1.462	8.06E-09 ± 1.20E-09	-8.094	1.454	-8.055	-8.409
16	0.2726	0.1761	0.3805	0.0036	0.0015	0.01025	0.1554	1.966	0.644	5138.89	40.81 ± 3.78	1.611	25.000 ± 0.51	1.398	9.80E-09 ± 1.38E-09	-8.009	1.493	-7.889	-8.095
17	0.2615	0.1954	0.3728	0.0043	0.0006	0.00951	0.1557	2.021	0.644	5123.75	42.14 ± 3.91	1.625	23.905 ± 0.488	1.378	9.08E-09 ± 1.28E-09	-8.042	1.418	-7.944	-8.030
18	0.2783	0.1870	0.3576	0.0022	0.0007	0.00866	0.1653	1.878	0.642	5157.18	32.82 ± 2.79	1.516	34.923 ± 0.713	1.543	1.70E-08 ± 2.26E-09	-7.769	1.481	-7.948	-8.174
19	0.2990	0.1462	0.4404	0.0011	0.0021	0.01065	0.1004	1.809	0.633	5199.57	27.20 ± 2.20	1.435	13.318 ± 0.272	1.124	7.83E-09 ± 1.01E-09	-8.106	1.273	-8.222	-8.356
20	0.3534	0.1621	0.4467	0.0016	0.0004	0.00053	0.0352	1.363	0.609	5348.38	59.18 ± 5.98	1.772	5.800 ± 0.118	0.763	1.57E-09 ± 2.34E-10	-8.805	0.619	-8.872	-8.996
21	0.3515	0.1584	0.4540	0.0013	0.0003	0.00051	0.0330	1.386	0.609	5342.45	64.98 ± 6.74	1.813	4.667 ± 0.095	0.669	1.15E-09 ± 1.75E-10	-8.940	0.654	-8.850	-8.971
22	0.3501	0.1599	0.4535	0.0010	0.0002	0.00047	0.0347	1.394	0.610	5339.48	71.06 ± 7.59	1.852	6.500 ± 0.133	0.813	1.46E-09 ± 2.27E-10	-8.835	0.676	-8.830	-8.958
23	0.2527	0.1110	0.4295	0.0005	0.0004	0.01899	0.1868	2.439	0.665	5027.19	43.62 ± 4.25	1.640	57.211 ± 1.168	1.757	2.10E-08 ± 3.06E-09	-7.678	1.837	-7.620	-7.615
24	0.3250	0.1422	0.4383	0.0003	0.0002	0.00593	0.0879	1.619	0.625	5261.12	51.16 ± 4.97	1.709	15.619 ± 0.319	1.194	4.88E-09 ± 7.09E-10	-8.311	1.128	-8.434	-8.621
25	0.3136	0.1460	0.4416	0.0004	0.0005	0.00956	0.0882	1.689	0.628	5237.92	42.02 ± 3.91	1.623	9.564 ± 0.195	0.981	3.64E-09 ± 5.15E-10	-8.439	1.170	-8.354	-8.521
26	0.3169	0.1392	0.4448	0.0005	0.0003	0.00735	0.0908	1.690	0.628	5239.30	41.90 ± 3.86	1.622	15.731 ± 0.321	1.197	6.01E-09 ± 8.42E-10	-8.221	1.200	-8.367	-8.527
27	0.3158	0.1683	0.4558	0.0001	0.0001	0.00358	0.0564	1.622	0.621	5259.15	34.44 ± 2.97	1.537	6.964 ± 0.142	0.843	3.24E-09 ± 4.33E-10	-8.490	0.990	-8.477	-8.612
28	0.3155	0.1697	0.4503	0.0003	0.0001	0.00197	0.0620	1.624	0.621	5256.48	56.79 ± 5.67	1.754	10.918 ± 0.223	1.038	3.08E-09 ± 4.55E-10	-8.512	1.014	-8.458	-8.601
29	0.3859	0.1637	0.3749	0.0009	0.0007	0.00007	0.0709	1.155	0.605	5415.00	28.00 ± 2.30	1.447	1.167 ± 0.024	0.067	5.72E-10 ± 8.62E-11	-9.243	0.133	-9.370	-9.282
30	0.3717	0.1792	0.3733	0.0019	0.0013	0.00010	0.0703	1.194	0.607	5389.56	33.26 ± 2.86	1.522	1.667 ± 0.034	0.222	4.81E-10 ± 1.07E-10	-9.318	0.248	-9.238	-9.173

- **The variation of C_S^{-2} and L_S with silica (X_{SiO_2}) in ferrochromium smelting slags**

The Gibbs phase rule can be used to analyse the multi-phase equilibria (Pan, 1998; Pan and Eric, 1997) as expressed in Eq. 4.12.

$$F+P=C+2-R \quad (4.12)$$

where F,P,C and R represent the number of degrees of freedom, the number of phases, the number of components and the number of independent restrictions, respectively. For a two-dimensional plot, the number of freedom is limited to one whereas the number of freedom is equal to two for a three-dimensional plot.

For the sulphide capacity study of ferrochromium smelting slags, the system can be defined with the following components.

Phases: slag, metal, gas, crucible; P=4

Slag: SiO_2 , Al_2O_3 , CaO , MgO , FeO , TiO_2 , MnO , Cr_2O_3 , S (CaS)

Metal: Cr, Fe, C, Si, S

Gas: CO

Crucible: Graphite (C)

Since MnO and TiO_2 contents are negligible, they can be removed from the slag system, leaving Al, Ca, Si, Mg, Fe, Cr, S, O, C as the components (C=9).

The Gibbs Phase Rule can be redefined as follows for the system when the pressure and temperature are constant ("2" in equation 4.12 disappears):

$$F=9-4-R \quad (4.13)$$

$$F=5-R \quad (4.14)$$

In designing the experimental runs Al_2O_3 content was kept constant. This was found in good agreement with the alumina contents of the slag samples analyzed which varied between 0.1216 and 0.1954 (in mole fraction). Therefore alumina can be considered as a constant parameter in the slag system. CaO and MgO contents and basicity ratios were kept in a narrow range adding four more restrictions and giving $F=1$ to construct the two-dimensional plots in the present study.

The effect of the silica content (in mole fraction) of ferrochromium smelting slag on the sulphide capacity and distribution ratio of sulphur is illustrated in Figs. 4.1, 4.2 and Figs F 1.1 to F 1.8 in Appendix F1. The logarithm of sulphide capacity decreases from -7.678 to -9.282 as the silica mole fraction increases from 0.2527 to 0.3859 (Fig. 4.1). Also, the logarithm of sulphur distribution between slag and metal phases tends to decrease from 1.757 to 0.066 with the increase of silica mole fraction from 0.2527 to 0.3859 (Fig. 4.2).

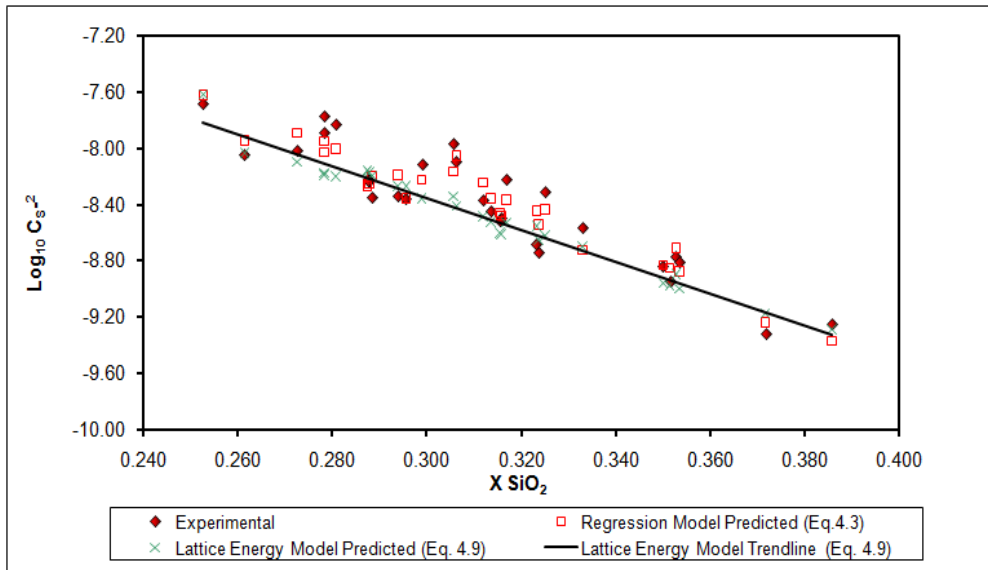


Figure 4.1 The variation of sulphide capacity with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio: 1.433-2.439, X_{CaO} : 0.0330-0.1989, X_{MgO} : 0.3064-0.4899

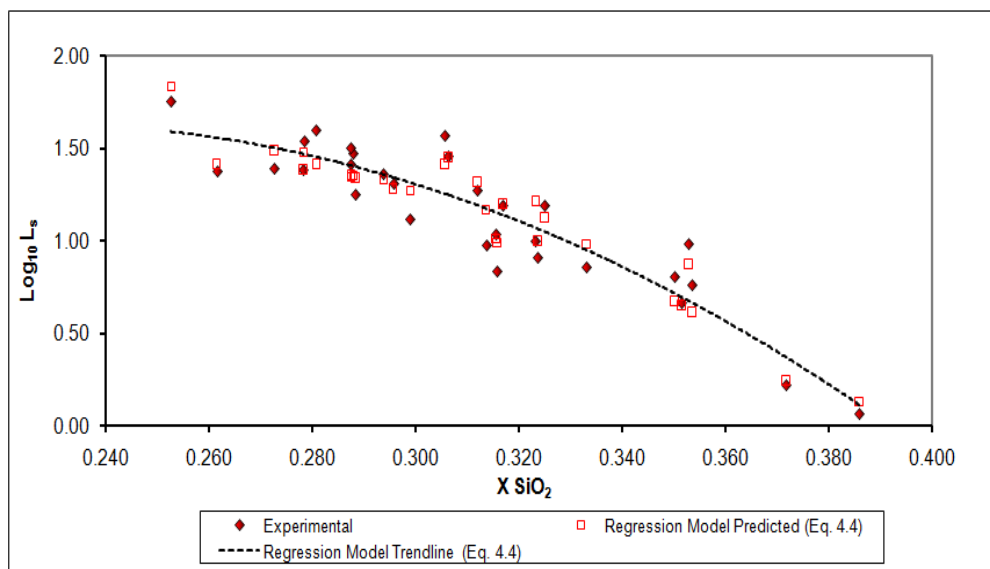
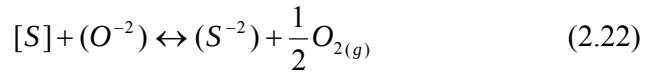


Figure 4.2 The variation of sulphur distribution ratio with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio: 1.433-2.439, X_{CaO} : 0.0330-0.1989, X_{MgO} : 0.3064-0.4899

In the present study, the conditions were highly reducing therefore FeO and other transition metal oxides concentrations were negligible. For this case, SiO_2 can be assumed as the only dominant acidic oxide component of the slag.

The influence of slag basicity on the desulphurisation of ferrochromium has been studied by Dai and Shu (1995). According to them, the elements which can result a decrease on the activity of oxygen in the metal phase may foster desulphurisation of the metal. Their results show that the addition of lime in the charge improved the removal rate of sulphur from metal. The actual sulphur distribution ratios between slag and metal were found to be varying between 5 and 10. Pan and Eric's (1997) study clearly shows the negative impact of SiO_2 on the desulphurisation capacity of low carbon ferrochromium smelting slags. In CaO- SiO_2 binary slag system, sulphide capacity of the slag decreases by a factor of 630 when the mole fraction of SiO_2 enhances from 0.1 to 0.7 at 1650 °C (Fincham and Richardson, 1954). In FeO- SiO_2 slag system, the decrease in the sulphide capacities with the increase of SiO_2 concentration was found to be much smaller compared to CaO- SiO_2 system (Reddy and Blander, 1987). According to the

findings of Derin and Reddy (2002), an increase in the amount of silica results a sharp drop on the sulphide capacities of FeO-CaO-SiO₂, FeO-MgO-SiO₂ and FeO-MnO-SiO₂ ternary slags. For Na₂O-SiO₂ slag system, Susaki et al.(1990) found that the sulphide capacity reduces with increasing silica concentrations in the slag. The strong negative influence of silica content on the 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. An increase in the acidity of slag will cause an decline in the concentration of free O⁻² ions (reaction 2.136) helping the reaction (2.22) to proceed to the left (Verein Deutscher Eisenhuttenteute, 1981). It is quite clear from Eqs. 2.22 and 2.29 that the partition ratio of sulphur between slag and metal can be decreased by decreasing the activity of oxygen ions in the slag phase. In other words, the consumption of free oxygen ions in the slag system will lead a decrease in the sulphide capacity of the slag (Eq. 2.30).



$$K_{2.22} = \frac{(a_{\text{S}^{-2}}).(P_{\text{O}_2})^{1/2}}{[a_{\text{S}}](a_{\text{O}^{-2}})} = \frac{(f_{\text{S}^{-2}}).(S^{-2}).(P_{\text{O}_2})^{1/2}}{[f_{\text{S}}][\text{S}](a_{\text{O}^{-2}})} \quad (2.29)$$

$$C_s = \frac{K_{2.22} \cdot (a_{\text{O}^{-2}})}{(f_{\text{S}^{-2}})} = \frac{(S^{-2}).(P_{\text{O}_2})^{1/2}}{[f_{\text{S}}][\text{S}]} \quad (2.30)$$

Bodsworth and Bell (1972) have explained the sulphur transfer mechanism between metal and slag phases on the bases of slag structure and bond types. The heat of transfer of sulphur from liquid iron into a pure ferrous oxide slag is equal to -50 kJ/g-atom. In the case of ferrous silicate slag, this value decreased to -113 kJ/g-atom. The strong polarization effect of Si⁻⁴ ions on the oxygen ions causes a drop in the repulsive force between charged oxygen and sulphide ions and increases the bonding force between the sulphide and iron ions. Same structural

consideration can be applied to sulphur behaviour in ferrochromium smelting slags.

- **The variation of C_S^{-2} and L_S with calcium oxide (X_{CaO}) in ferrochromium smelting slags**

The effect of calcium content (X_{CaO}) of ferrochromium smelting slag system on the sulphide capacity and distribution ratio of sulphur between slag and metal phases are illustrated in Figures 4.3, 4.4 and Figs F 2.1 to F 2.8 in Appendix F2.

As illustrated in Figure 4.3, the sulphide capacity is enhanced with increasing content of calcium oxide content in ferrochromium smelting slag. Also, the logarithm of sulphur distribution ratio between slag and metal phases is increased from 0.860 to 1.454 with the increase of calcium oxide mole fraction (X_{CaO}) from 0.0467 to 0.1989 in the slag (Figure 4.4).

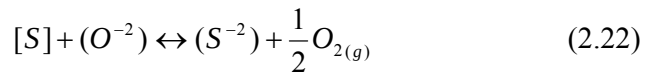
Dai and Shun (1995) showed that the amount of sulphur in high carbon ferrochromium can be reduced from 0.045 to 0.018 wt. % by addition of lime into the charge of high carbon ferrochromium furnace from 1 per cent to 10 per cent by weight. In another study, the sulphur content of high carbon ferrochromium was found to be reduced from 0.037 to 0.028 wt. % with the addition of 1 wt. % of lime into the furnace (Metcalf and Slatter, 1978). Halikia et al. (2001) reported that the desulphurisation of high carbon ferrochromium can be improved by using a high alkaline slag. According to Sassa et al. (1977), the rates of sulphur absorption by $CaO-SiO_2$ and $CaO-Al_2O_3$ binary slags augment with the increase of CaO content in the slag. Their results clearly show that the sulphur absorption rate of the slag system is directly proportional to the activity of lime. According to Sichen et al. (1995), the sulphide capacity changes directly proportional to CaO amount in $CaO-SiO_2$. Gernerup and Wijk (1996) found that a directly proportional relationship between sulphide capacities of $CaO-Al_2O_3-SiO_2$ slags and CaO content of the slags at 1550, 1600 and 1650 °C. The correlation between sulphide

capacity and CaO amount seems to be in exponential form as the slag composition moves from 2CaO.SiO₂ to 3CaO.SiO₂ saturation lines.

For ferrochromium smelting slags, the amount of CaO is the one of main factor to that determines desulphurisation of metal by forming CaS in the slag phase. Basic oxides such as CaO and MgO donate O⁻² ions into the slag and ionise according to reaction 2.133.



As the amount of CaO increases, the silica network is broken up into smaller anionic groups and the proportion of free O⁻² ions increases in the slag structure. Each O⁻² can break one of the four O⁻² bonds between two tetrahedra silica structure. Therefore, the donation of O⁻² ions by CaO break up three dimensional hexagonal network of SiO₂ and result the formation of SiO₄⁻⁴ (Moore, 1990). Thus more cations become available to combine with the sulphur from the metal phase, which eventually results an increase in the sulphide capacity by helping to shift the reaction 2.22 to the right direction. Therefore, the sulphur distribution ratio between slag and metal increases with the increase of activity of oxygen ions in the slag (Eq. 2.29).



$$K_{2.22} = \frac{(a_{s^{-2}}).(P_{O_2})^{1/2}}{[a_s](a_{o^{-2}})} = \frac{(f_{s^{-2}}).(S^{-2}).(P_{O_2})^{1/2}}{[f_s][S](a_{o^{-2}})} \quad (2.29)$$

$$C_s = \frac{K_{2.22}.(a_{o^{-2}})}{(f_{s^{-2}})} = \frac{(S^{-2}).(P_{O_2})^{1/2}}{[f_s][S]} \quad (2.30)$$

Also, further addition of CaO into the liquid silica slags results in an enhancement of the number of common O⁻² bonds broken. For example, when the ratio of O/Si is equal to three, the molecular formula can be written as MO.SiO₂ and the structure will consist of two broken O⁻² bond per tetrahedron with lamellar form. From another point of view, the positive impact of CaO on the sulphide capacity can be supported by comparing the standard Gibbs free energy values of CaS, FeS

and MgS for the reactions between sulphur in the metal and the oxides in the slag. According to Bodsworth and Bell (1972), the standard Gibbs free energies of CaS $[(CaO)_{(slag)} + \underline{S}_{(Fe)} = (CaS)_{(slag)} + \underline{O}_{(Fe)}]$, FeS $[(FeO)_{(slag)} + \underline{S}_{(Fe)} = (FeS)_{(slag)} + \underline{O}_{(Fe)}]$, and MgS $[(MgO)_{(slag)} + \underline{S}_{(Fe)} = (MgS)_{(slag)} + \underline{O}_{(Fe)}]$, at 1600 °C are equal to +53100 J, +61900 J and +140 000 J, respectively. These values indicate that the desulphurisation power of the basic oxides increases in the series of CaO, FeO and MgO. Sulphide ions which have greater ionic size, can be more polarisable than the oxygen ions. In the presence of calcium ions in the slag, $Ca^{+2}-S^{-2}$ bond is relatively more polarised than $Ca^{+2}-O^{-2}$ bond. However, Bodsworth and Bell (1972) mentioned that the difference between metal-oxygen and metal-sulphur bonds is less marked in calcium compared to magnesium.

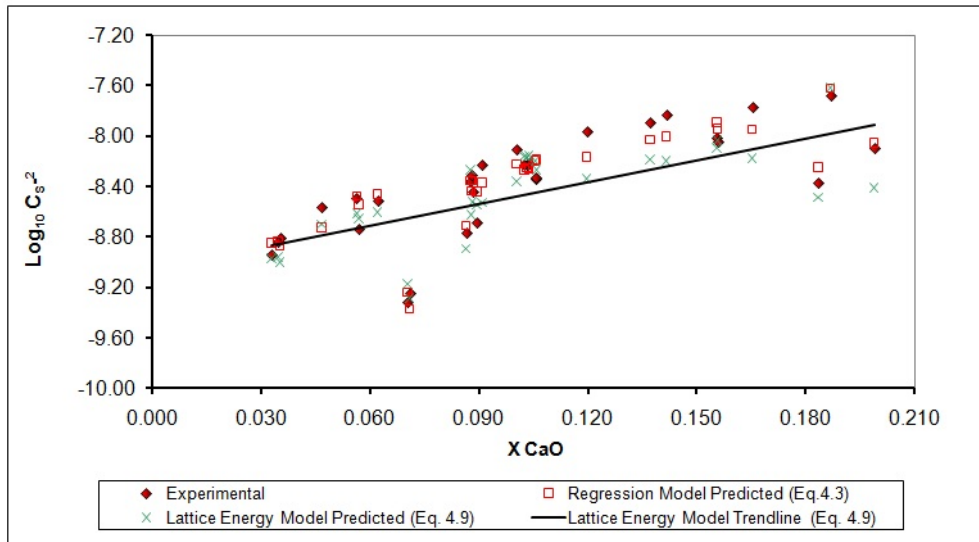


Figure 4.3 The variation of sulphide capacity with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag; Basicity Ratio: 1.433-2.439, X_{SiO_2} : 0.2527-0.3859, X_{MgO} : 0.3064-0.4899

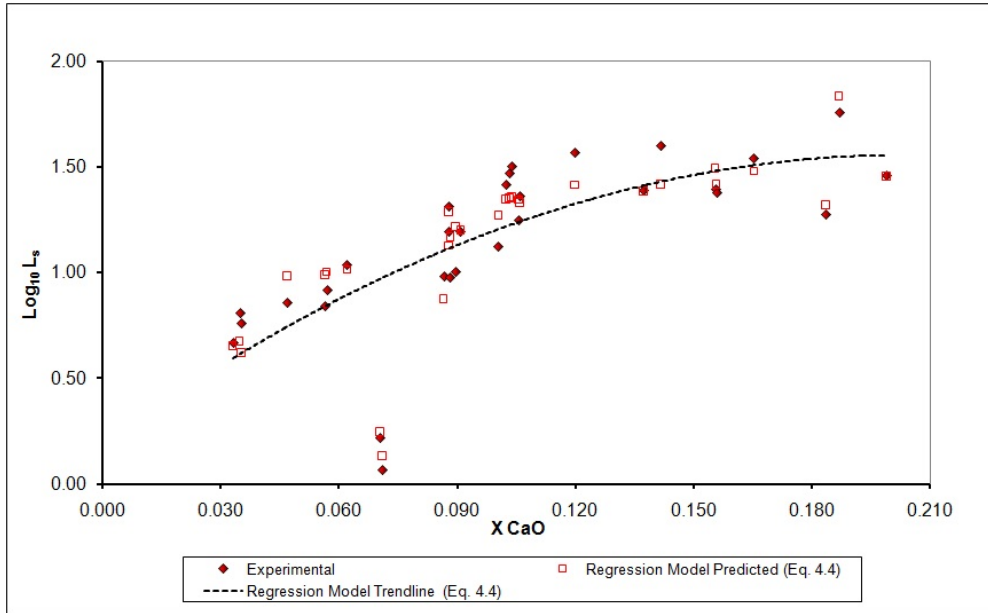


Figure 4.4 The variation of sulphur distribution ratio with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag; Basicity Ratio: 1.433-2.439, X_{SiO_2} : 0.2527-0.3859, X_{MgO} : 0.3064-0.4899

- **The variation of C_S^{-2} and L_S with magnesium oxide (X_{MgO}) in ferrochromium smelting slags**

The influence of magnesium oxide content of ferrochromium smelting slag system on sulphide capacity and sulphur distribution ratio between slag and metal phases are given in Figures 4.5, 4.6 and Figs F 3.1 to F 3.4 in Appendix F3, where CaO and SiO₂ contents have been kept in narrow ranges.

In Figure 4.5, the logarithm of sulphide capacity increases 0.95 per cent with one per cent increase in magnesium oxide content in mole fraction. Based on similar calculations for Figure F 3.1 and F 3.3, it can be observed that the increases are equal to 0.1 and 0.47 for one per cent increase in the magnesium oxide content (in mole fraction).

The results show that the increase of sulphide capacity is not constant and might be significantly influenced by the powerful oxides such as CaO and SiO₂ in the slag system.

MgO in the slag will ionise according to reaction 4.15.



The activity of oxygen ions in the slag system is raised with increase in the MgO content at constant CaO/SiO₂ ratios. As a result of increase in the activity of O⁻² anions, the reaction 2.22 will shift to the right direction which assists the sulphur transfer from metal to slag and eventually result in an increase in the sulphide capacity of the slag.

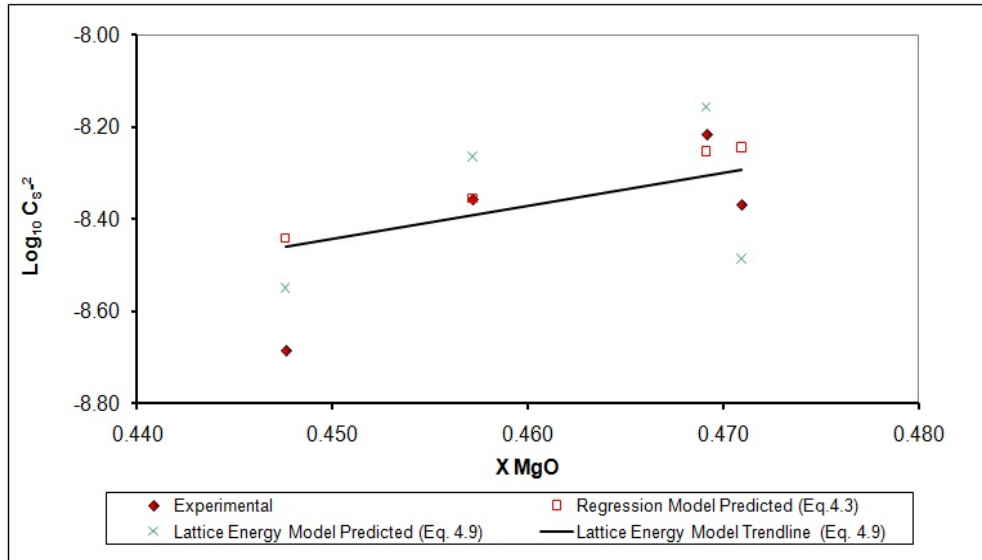


Figure 4.5 The variation of sulphide capacity with magnesium oxide mole fraction (X_{MgO}) of ferrochromium smelting slag; Basicity Ratio: 1.433-2.439, X_{SiO₂}: 0.2875-0.2983, X_{CaO}: 0.1024-0.1058

The sulphur distribution values increase 4.12, 2.88, 4.93 per cent with one per cent increase of magnesium oxide content (in mole fraction) (Fig. 4.6, F 3.2 and F 3.4). When the effects of magnesium oxide and calcium oxide on the logarithm of

sulphur distribution ratio are compared, it seems that the effect of magnesium oxide (range 2.88 to 4.93 per cent for one per cent increase in magnesium oxide content) is much less than that of calcium oxide (range 0.37 to 7.49 per cent for one per cent increase in calcium oxide content).

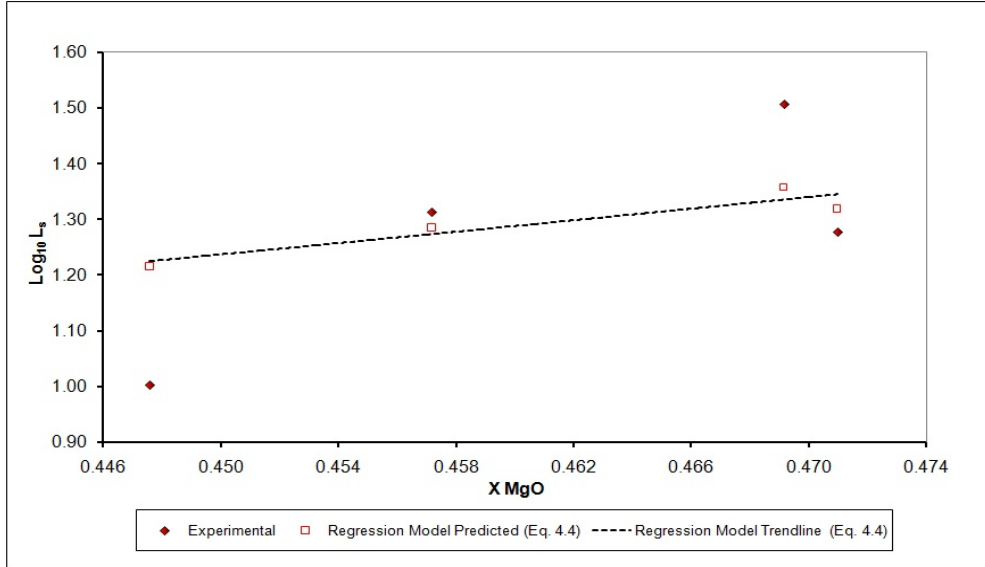


Figure 4.6 The variation of sulphur distribution ratio with magnesium oxide mole fraction (X_{MgO}) of ferrochromium smelting slag; Basicity Ratio: 1.883-1.994, X_{SiO_2} : 0.2875-0.2983, X_{CaO} : 0.1024-0.1058

An increase in the desulphurisation capacity for low carbon ferrochromium smelting slags at 1500 and 1580 °C with increasing MgO content in the slag was observed by Pan and Eric, (1997). Under reducing conditions, the sulphur partition ratio between slag and metal doubled when the MgO content (mol. %) increased from 0.05 to 0.2 at 1500 °C at Cr_2O_3 saturated slags. No substantial influence of MgO on the sulphide capacity of high alumina blast furnace slags has been found when the MgO content increased from 2 to 5 wt. %. Shankar et al. (2006) indicated that the real impact of MgO can be only recognized when its content is above 5 wt. %. According to them, the significant influence of MgO can be only seen when the basicity reaches to certain degree. Bronson and St. Pierre (1981) reported that the replacement of MgO for CaO in CaO-MgO-SiO₂ ternary slag system had negative impact on the sulphide capacities of the slag. As

given in Table 2.4, the equilibrium constant for CaO/CaS equilibrium is higher than the equilibrium constant of MgO/MgS at 1776 K. The replacement of CaO with MgO results in a strong influence on the a_{O-2}/f_{S-2} ratio of silicate melts and the variations in this ratio causes a direct impact on the sulphide capacity (Bronson and St. Pierre, 1981). Hino et al. (1993) found similar results with Bronson and St. Pierre (1981) and reported that the sulphide capacities of CaO-Al₂O₃ slags decreased when MgO was substituted for CaO in the slag. In CaO-MgO-Al₂O₃-SiO₂ slag system, the replacement of CaO with MgO at constant Al₂O₃ and SiO₂ contents caused a decrease in the sulphide capacities. When MgO content increased from 0.075 to 0.225, the sulphide capacity dropped from 1×10^{-4} to 5×10^{-5} (Nilsson et al., 1997).

These earlier results on various slag systems are in accord with the findings of this work, when the effect of MgO is less than that of CaO on desulphurization power of slags of the present work. As it was mentioned early, CaO is the dominant slag component for the slag basicity, therefore the real influence of MgO can be only seen in a small range where CaO content was kept constant.

- **The variation of C_S^{-2} and L_S with basicity ratio $[(X_{CaO}+X_{MgO})/X_{SiO_2}]$ of ferrochromium smelting slags**

The effect of basicity ratio $[(X_{CaO}+X_{MgO})/X_{SiO_2}]$ of ferrochromium smelting slag on the sulphide capacity and distribution ratio of sulphur between slag and metal phases are illustrated in Figures 4.7, 4.8 and Figs F 4.1 to F 4.4 in Appendix F4.

The logarithm of sulphide capacity raises from -9.243 to -7.678 with increasing basicity ratio from 1.155 to 2.439 (Fig. 4.7). Similar influence of basicity ratio on the sulphur distribution ratio has been observed in Figure 4.8. The logarithm of partition ratio of sulphur increases from 0.066 to 2.439 when the basicity ratio increases from 1.155 to 2.439.

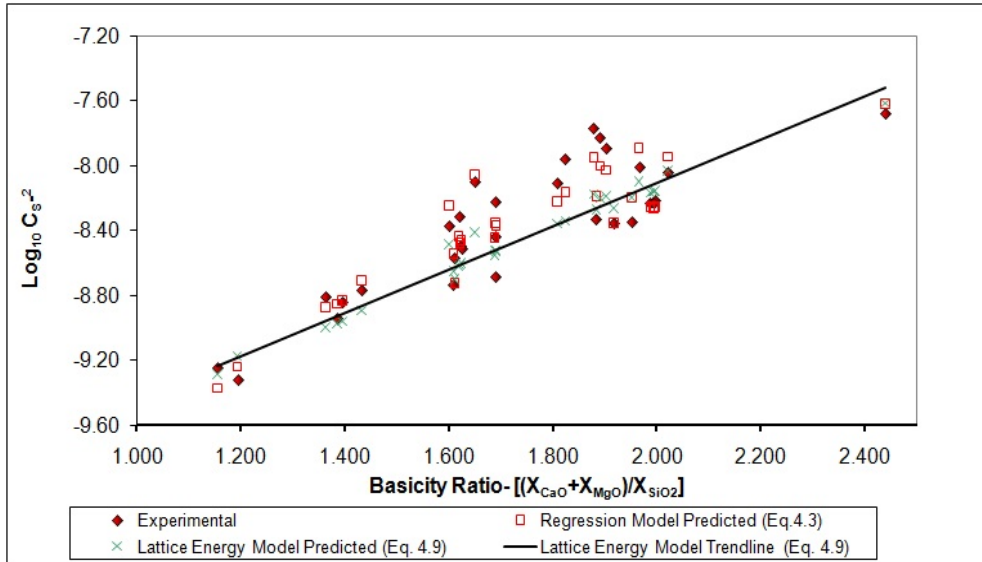


Figure 4.7 The effect of basicity ratio on the sulphide capacity of ferrochromium smelting slag; X_{SiO_2} : 0.2527-0.3859, X_{CaO} : 0.0330-0.1989, X_{MgO} : 0.3064-0.4899

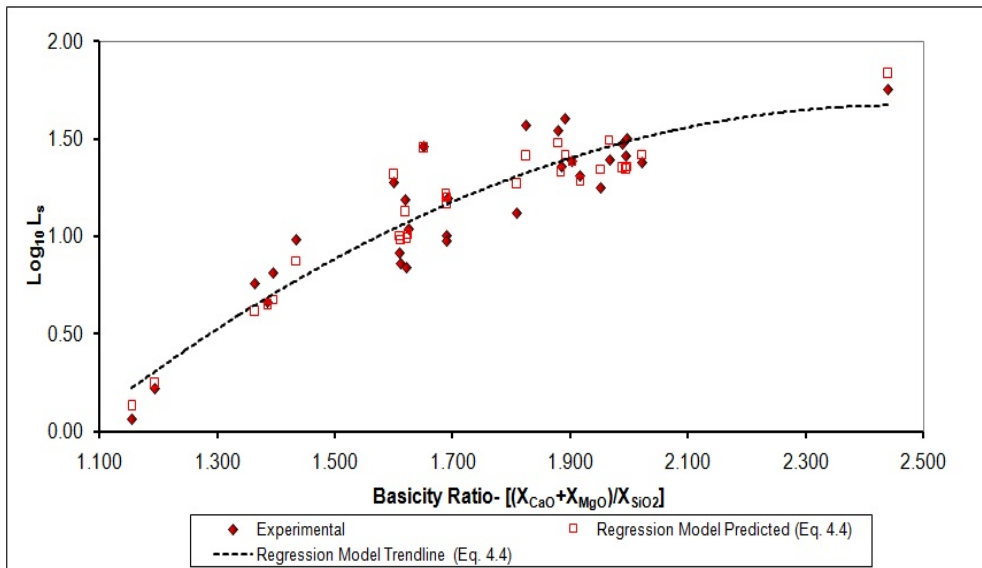


Figure 4.8 The effect of basicity ratio on the sulphur distribution ratio of ferrochromium smelting slag; X_{SiO_2} : 0.2527-0.3859, X_{CaO} : 0.0330-0.1989, X_{MgO} : 0.3064-0.4899

From the slag structure point of view, when a sulphur ion replaces an oxygen ion in the co-ordination shell of a strongly polarising silicon ion, the electron field of silicate group is deformed and broken down. In this case, the sulphur ions will

change their positions with the oxygen ions which are effectively bonded to the basic cations. Based on this structure transformation, the activity coefficient of sulphur in the slag phase increases as the concentration of oxygen ions is decreased which remain unbonded to oxy-acid groups (SiO_4^{-4}) (Bodsworth and Bell, 1972). The degree of breakdown is mainly proportional to the concentration of O^{2-} anions, in other words to the presence of basic and acidic oxides. When the free oxygen anions are consumed by the slag structure, the reaction (2.22) shifts to right side. As a result, the sulphide capacity of the slag system tends to increase. The results of Pickles et al. (1987) and Metcalfe and Slatter (1978) on the desulphurisation of high carbon ferrochromium well agree with the findings of the present study. As pointed in Metcalfe and Slatter's study (1978), the highest desulphurisation of high carbon ferrochromium can be achieved by using commercial lime in the process. The standard heats of formation for CaS and MgS are equal to -460.2 and -347.3 kJ/mol, respectively which indicates that the calcium oxide is the dominant desulphurisation agent in the present slag system. MgO has relatively weaker desulphurisation power compared to CaO in ferrochromium smelting slags, as the desulphurisation power of CaO is 2.41 times higher than MgO in Metcalfe and Slatter (1978)

- **The variation of C_S^{-2} and L_S with optical basicity ratio (Λ) of ferrochromium smelting slags**

As discuss in subsection 2.7.2, the optical basicity concept can be used as a parameter in the analysis of sulphur behaviour in ferrochromium smelting slag. The change of sulphide capacity of ferrochromium smelting slag with optical basicity (Λ) is given in Figure 4.9. As the optical basicity of the slag system increases from 0.604 to 0.665, the logarithm of sulphide capacity raises from -9.243 to -7.678. The logarithm distribution ratio of sulphur between slag and metal goes up from 0.066 to 1.757 with the increase of optical basicity from 0.604 to 0.665 (Fig. 4.10). The change of sulphide capacity and distribution ratio of sulphur with optical basicity is similar to the influence of basicity ratio on these parameters. It appears that the optical basicity offers no advantages over the

basicity ratio formulation. The addition of CaO and MgO oxides into the slag system causes significant improvement in the optical basicity of slag. As indicated in Table 2.8, the optical basicities of CaO and MgO are 1 and 0.78, respectively. MnO can cause a raise in the optical basicity due to its high optical basicity value (0.98). The desulphurisation power of the slags can be enhanced by increasing the optical basicity of the slag system (Figs. F 5.1 to F 5.4).

As discussed earlier, sulphide capacities can be calculated by using Sosinsky and Sommerville (1986) or Young et al. (1992) models. According to Sosinsky and Sommerville (1986), Eq. 2.36 is a practical model for calculating the sulphide capacities of slags between 1400 and 1700 °C. However, Young et al. (1992) reported that Sosinsky and Sommerville's equation has a significant deviation between measured and calculated data at higher sulphide capacity values. Two modified regression models were proposed for the calculation of sulphide capacity by using the optical basicity concept (Eqs. 2.45 and 2.46). On the other hand, Shankar et al. (2006) found that Sosinsky and Sommerville's model (1986), Young et al. model (1992) and Nzotta et al. model (1998) underpredict the values of sulphide capacities for the slag systems with high alumina content and proposed a modified model for slags having CaO: 30 to 46 wt. %, SiO₂ : 30 to 40 wt. %, MgO: 2 to 10 wt. %, Al₂O₃: 12 to 30 wt. %. In the present study, the comparison between estimated and measured logarithm of sulphide capacity for the SiO₂-CaO-Al₂O₃-MgO-CaS-Cr₂O₃ is shown in Figure 4.11. It is clear from Figure 4.11 that three models predict higher sulphide capacity values for the present slag system. The calculated sulphide capacity values of Shankar et al. (2006), Sosinsky and Sommerville (1986), Young et al. (1992) models are given in Appendix I. However, it should be remembered that SiO₂-CaO-Al₂O₃-MgO-CaS-Cr₂O₃ slag system is significantly different compared to the slag systems used for these models. As identified, in Shankar et al.'s study (2006), the estimation of sulphide capacity based on optical basicity requires a level of modification which depends on the slag system components. Sosinsky and Sommerville (1986), Young et al. (1992) model and KTH model had been tuned for the low alumina slags. In the present work, alumina content of the slag phase can be considered as high. In

KTH model, the calculation of the alumina activity and subsequently the oxygen activity is one of the main differences compared to present work approach. Also, KTH model is basically focus on the steelmaking slags where partial pressure of oxygen is extremely higher than the present work atmosphere conditions. In addition to that KTH model includes activity of oxygen as a parameter (which was assumed to be in the range of 10^{-4} to 10^{-5} in steel), therefore we can expect a difference between the present work and KTH model predicted values. Korousic (2003) experienced similar phenomena during the comparison of estimated and experimentally determined sulphide capacities for CaO-Al₂O₃-SiO₂ slag system at 1550, 1600 and 1650 °C. In Korousic's case (2003), Sosinsky and Sommerville's model (1986) overestimated the sulphide capacity values compared to experimentally determined ones. In addition to observed deviations between estimated and experimentally determined sulphide capacities (Shankar et al., 2006; Korousic, 2003), Hao et al. (2006) found that the predicted values by Young et al. (1992) are much higher than the measured values of sulphide capacity.

Based on the findings of previous studies (Shankar et al., 2006; Korousic 2003, Hao et al., 2006), it is possible to explain the disagreement between the experimentally determined and model based estimated values of sulphide capacities. One of the major drawbacks of optical basicity based models is the mutual interactions between different species in the slag system which are not specially considered (Hao et al. 2006). Also, Young et al. (1992) mentioned that the regression model should also include the Al₂O₃ and FeO contents, which clearly indicates the sensitivity of optical basicity models to the slag compositions.

According to the present study, the relationship between optical basicity and the logarithm of sulphide capacity should be in linear nature (Figure 4.12). The multiple regression analysis of the experimental results shows that Eq. 4.16 can define the relationship between optical basicity and the log of sulphide capacity

for $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO-CaS-Cr}_2\text{O}_3$ slag system at 1600 °C under carbon monoxide atmosphere. The correlation coefficient of Eq. 4.16 is 0.82.

$$\text{Log}_{10}C_{S^{-2}} = 26.667\Lambda - 25.176 \quad (4.16)$$

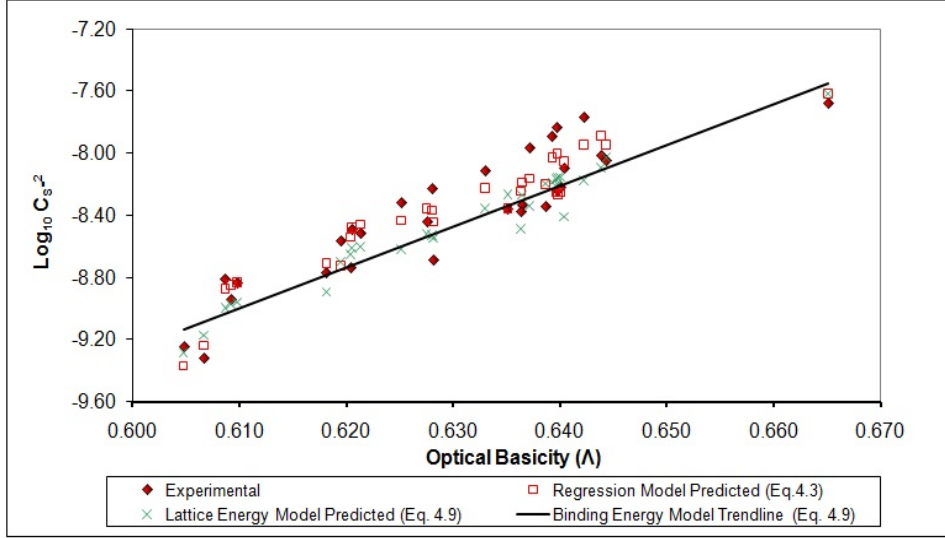


Figure 4.9 The effect of optical basicity on the sulphide capacity of ferrochromium smelting slag; Basicity Ratio: 1.155-2.439, X_{SiO_2} :0.2527-0.3859, X_{CaO} :0.0330-0.1989, X_{MgO} :0.3064-0.4899

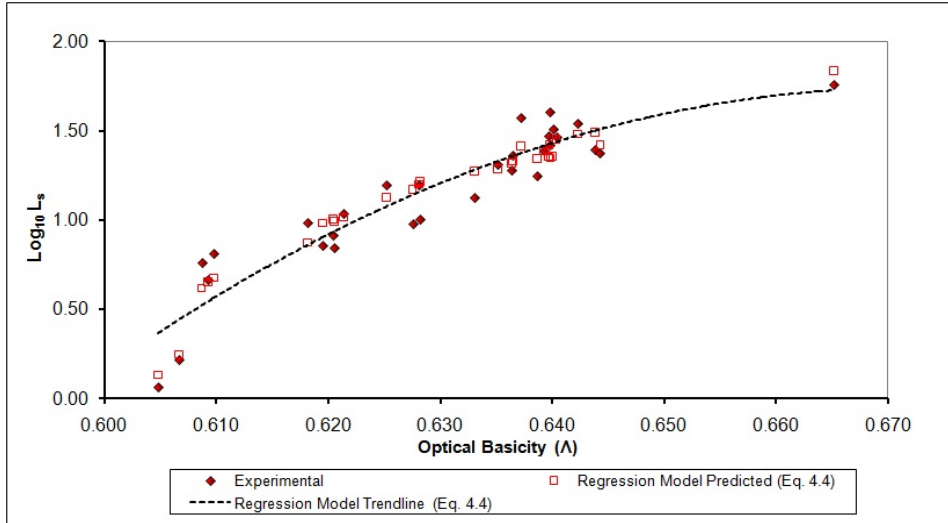


Figure 4.10 The effect of optical basicity on the sulphur distribution of ferrochromium smelting slag; Basicity Ratio: 1.155-2.439, X_{SiO_2} :0.2527-0.3859, X_{CaO} :0.0330-0.1989, X_{MgO} :0.3064-0.4899

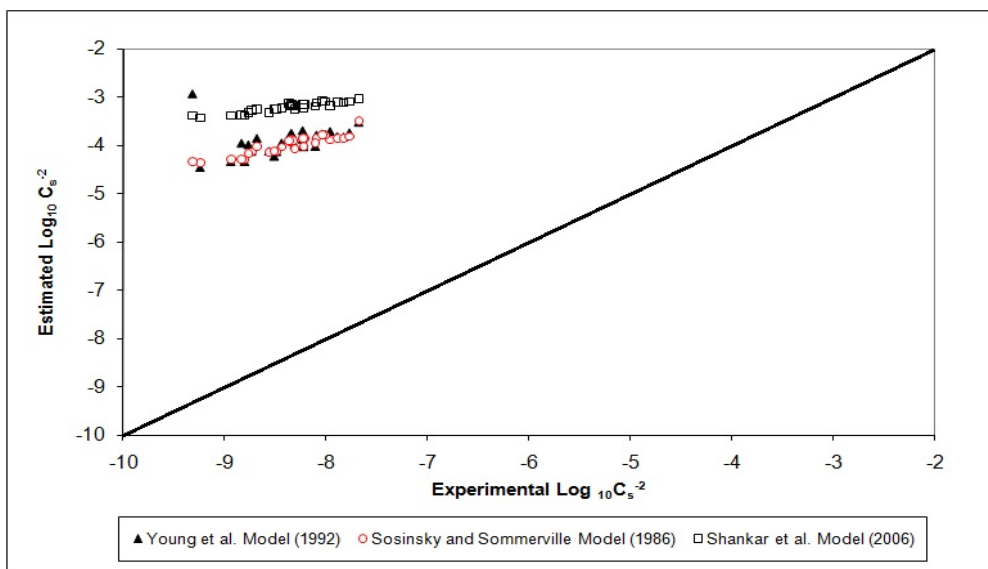


Figure 4.11 Comparison between measured sulphide capacity of the present work and the previous studies' models estimated results.

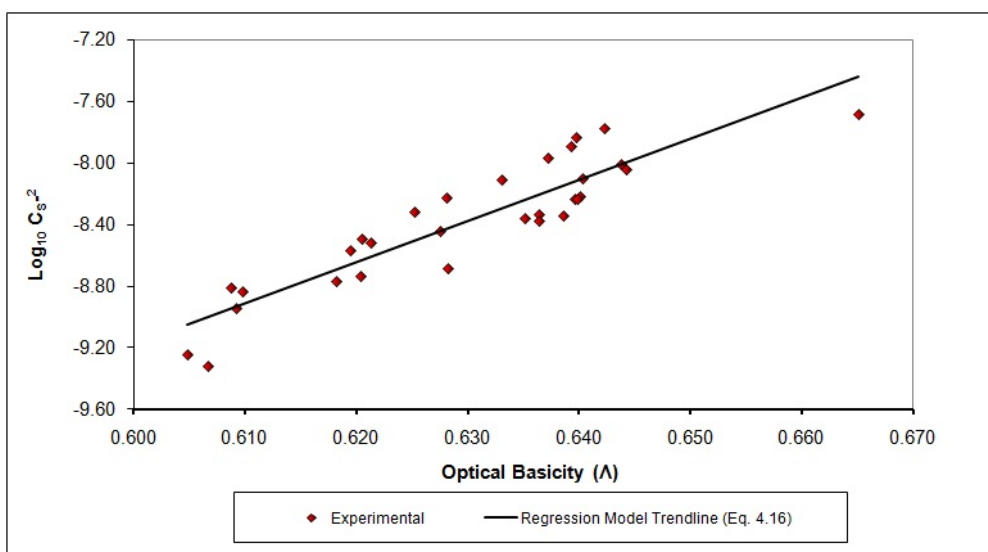


Figure 4.12 The relationship between optical basicity (Λ) and the logarithm of sulphide capacity

- The variation of C_S^{-2} and L_S with CaO-to-MgO ratio (X_{CaO}/X_{MgO}) of ferrochromium smelting slags

The effect of the CaO-to-MgO ratio of ferrochromium smelting slag on the sulphide capacity and distribution ratio of sulphur between slag and metal phases are given in Figures 4.13, 4.14, F 6.1 and F 6.2 (in Appendix F6). This approach will allow us to identify the real influence of CaO and MgO on the sulphur behavior in ferrochromium smelting slags by limiting the influence of SiO_2 .

The logarithm of sulphide capacity increases from -8.939 to -8.093 with the increase in CaO-to-MgO ratio from 0.072 to 0.648 (Fig. 4.13). A similar influence of CaO-to-MgO ratio on the sulphur distribution ratio has been illustrated (Fig. 4.14). The logarithm of sulphur distribution ratio is raised from 0.669 to 1.462 when CaO-to-MgO ratio increases from 0.072 to 0.648. The correlation coefficients between CaO-to-MgO ratio and logarithm of sulphide capacity (Figure 4.13) and sulphur distribution ratio (Figure 4.14) (experimentally determined) are found to be equal to 0.54 and 0.36, respectively which indicates a poor correlation but it should be noted the SiO_2 content is not constant in these cases.

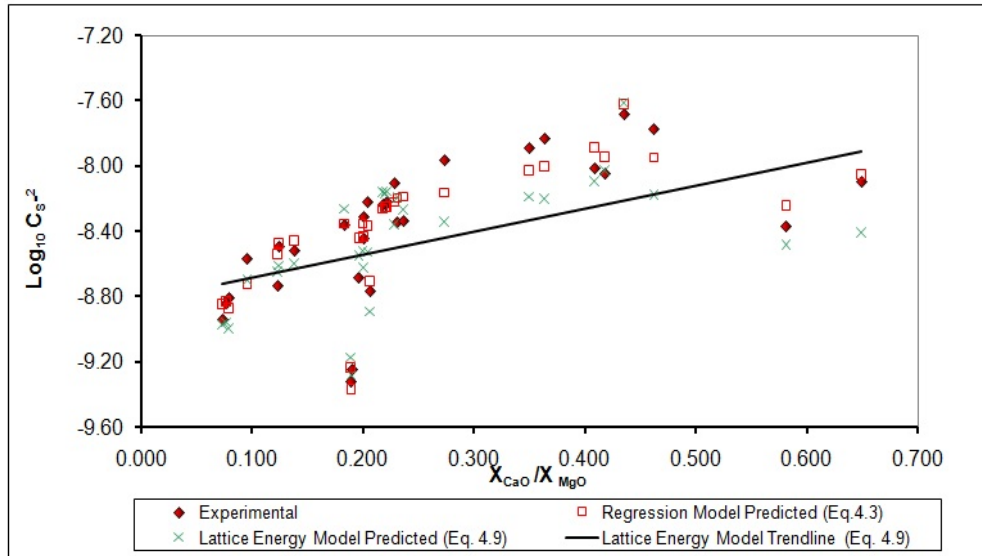


Figure 4.13 The effect of CaO-to-MgO ratio (X_{CaO}/X_{MgO}) on the sulphide capacity of ferrochromium smelting slag; Basicity Ratio: 1.155-2.439, X_{SiO_2} : 0.2527-0.3859, X_{CaO} : 0.0330-0.1989, X_{MgO} : 0.3064-0.4899

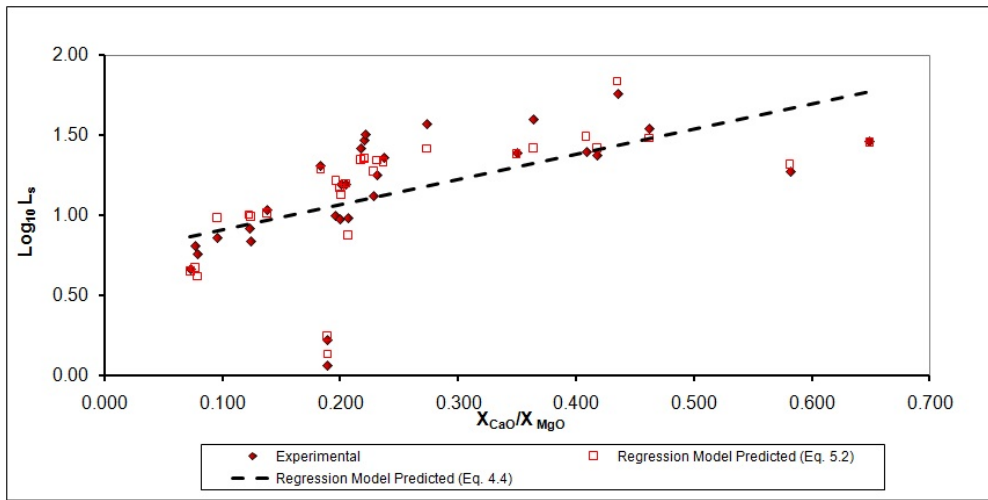


Figure 4.14 The effect of CaO-to-MgO ratio ($X_{\text{CaO}}/X_{\text{MgO}}$) on the sulphur distribution ratio of ferrochromium smelting slag; Basicity Ratio:1.155-2.439, X_{SiO_2} :0.2527-0.3859, X_{CaO} :0.0330-0.1989, X_{MgO} :0.3064-0.4899

As indicated in Shibata et al. (2004), the sulphur removal from metal to slag depended on the liquidus temperature of slags. The sulphide capacity of CaO- Al_2O_3 based flux (CaO: 51.3 wt. %, Al_2O_3 : 43.7 wt. %, MgO: 0.47 wt.%, BaO: 0.03 wt. %, CeO_2 : 0.05 wt. %) is found to be 24 per centage less compared to CaO- Al_2O_3 -BaO- CeO_2 based flux (CaO: 38.2 wt. %, Al_2O_3 : 43.7 wt. %, MgO: 0.35 wt.%, BaO: 8.41 wt. %, CeO_2 : 9.10 wt. %) at 1500 °C. Even though, the amount of CaO content is considerably less in the CaO- Al_2O_3 -BaO- CeO_2 based flux compared to CaO- Al_2O_3 based flux, its liquidus temperature is around 1370°C and thus about 50 °C lower than that of CaO- Al_2O_3 based flux. The fact that the slag liquidus temperatures tend to increase with high slag basicity might cause a decrease in the sulphur transfer from metal to slag. In a previous study, the addition of CaO to MnO-SiO₂ melt in which the silica content is higher than 0.33 (in mole fraction), causes a sharp increase in the sulphide capacity. However, the magnitude of the effect decreases with the further addition of CaO to the slag system (Hino et al. 1978). Also, Zhang and Toguri's model (1987) shows that sulphur distribution equation leads to a positive temperature coefficient which is a

function of slag composition. Therefore, the increasing temperature leads a decrease in the desulphurisation reaction for slags of constant compositions. However, as can be seen in Table 4.7, the desulphurisation process should be enhanced with increasing temperature. This abnormal behaviour can be due to the effect of temperature on the concentration of oxygen in the metal phase which tends to increase with increasing temperature. The decline in the sulphide capacity of the slag in the third region can be attributed to relatively high basicity values which actually push the slag liquidus temperatures to higher values.

Table 4.7 The equilibrium constants for individual exchange reactions (Zhang and Toguri, 1987)

Reaction	Log K
$[S] + (CaO) = (CaS) + [O]$	$\log K_{Ca^{+2}} = -4549/T + 1.23$
$[S] + (FeO) = (FeS) + [O]$	$\log K_{Fe^{+2}} = -6457/T - 2.12$
$[S] + (MnO) = (MnS) + [O]$	$\log K_{Mn^{+2}} = -5456/T - 1.11$
$[S] + (MgO) = (MgS) + [O]$	$\log K_{Mg^{+2}} = -8923/T + 1.73$

As given in Figure F 6.1, the logarithm of sulphide capacity raises from -8.735 to -7.8281 by increasing of CaO-to-MgO ratio from 0.122 to 0.363, which indicates 0.06 per cent increase in the logarithm of sulphide capacity with one per cent increase in CaO-to-MgO ratio. The logarithm of sulphur distribution ratio increases 0.26 per cent with one per cent increase in CaO-to-MgO ratio (Figure F6.2). Figures F 6.1 and F 6.2 prove that as CaO replaces MgO in the slag, the sulphide capacity and sulphur distribution ratio is significantly increased. Also, Hino et al.'s results (1993) agree well with these results. They observed that the value of sulphide capacity decreased with decreasing N_{CaO}/N_{MgO} at a given $N_{Al_2O_3}$ in CaO-Al₂O₃-MgO slag system at 1550, 1600 and 1650 °C. This means that MgO does not have equivalent effect as CaO has on the sulphide capacity. Bronson and St. Pierre (1981) showed that the replacement of CaO with MgO in CaO-MgO-SiO₂ caused a significant drop in the sulphide capacity values. Based on the experimental data, it is found that the sulphur holding power of lime is 1000 times higher than magnesia (Bodsworth and Bell, 1972). According to Figure F 6.1, at a

relative sulphide capacity of MgO taken as unity, the value of CaO is equal to 2.71. Considering the free energy changes for reaction between sulphur in the metal and the CaO and MgO oxides in slags, the ratio between Gibbs free energy values of CaS (+53100 J at 1600 °C) and MgS (+140000 J at 1600 °C) is found to be equal to 2.64. Although not a direct correlation exist on the desulphurisation power ratio between CaO and MgO with the free energy ratio between CaS and MgS, the ratios seem to be close to each other. Metcalfe and Slatter (1978) reported that the desulphurisation power of a laboratory lime and a commercial lime are 2.41 and 2.82 times higher compared to MgO in the desulphurisation process of high carbon ferrochromium and their results agree well with the present findings. The desulphurisation power difference between commercial lime and laboratory lime can be attributed to the high reactivity of the commercial lime due to large surface active area as a result of calcinations process. It is clear that MgO is a weaker basic oxide than CaO therefore its effect on the desulphurisation.

- **The relationship between sulphide capacity (C_s^{-2}) and lattice energy of oxides (binding energy of O^{-2} ion in the mixture) ($\overline{E_o}$) of ferrochromium smelting slag**

The relationship between C_s^{-2} and lattice energy of oxides ($\overline{E_o}$) of ferrochromium slag system is given in Figure 4.15. As explained in subsections 2.9.1 and 4.3 before the lattice (binding) energy of the slag system increases with the decrease in basicity, as the electron clouds of O^{-2} ions are increasingly tightened due to the interaction with polarising cations such as Si^{+4} and Al^{+3} . The linear correlation (Eq. 4.9) between lattice (binding) energy of the slag system and logarithm of sulphide capacity is significant and suggest that this approach can be used for determining the desulphurisation capacities of slag systems even they contain transition metal cations in their structure.

$$\text{Log } C_s^{-2} = -0.0043.\overline{E_o} + 14.002 \quad (4.9)$$

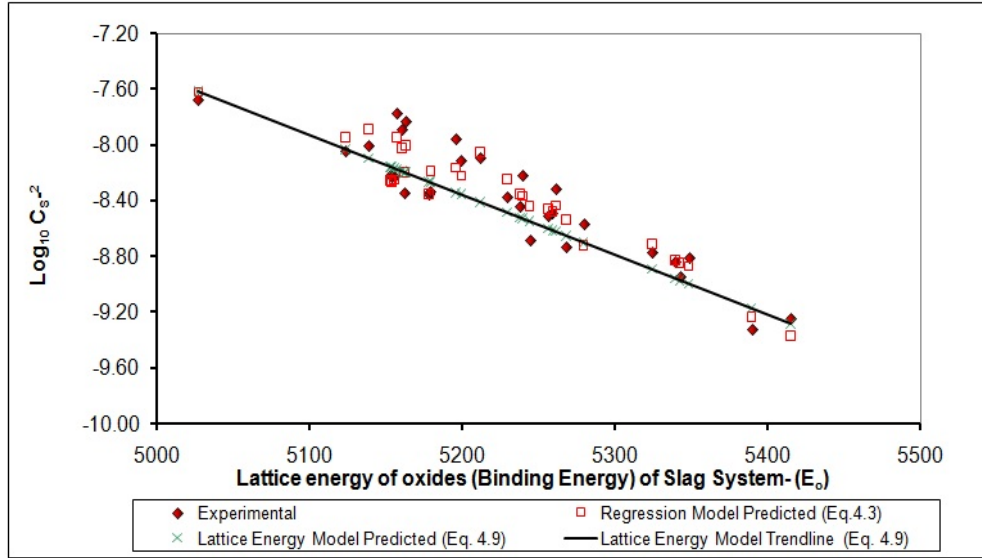


Figure 4.15 The relationship between C_S^{-2} and lattice (binding) energy ($\overline{E_o}$) of ferrochromium smelting slag.

The diagram representing the quaternary MgO-CaO-SiO₂-25 wt.% Al₂O₃ system is given in Fig. 4.16 (Verein Deutscher Eisenhüttenteute, 1981). The solid lines in the liquid region represent iso-sulphide capacity lines determined by using Eq. 4.9 according to the slag compositions. Figure 4.16 shows the potential of the lattice (binding) energy model to predict the sulphide capacity trends of MgO-CaO-SiO₂-25 wt.% Al₂O₃ slag system. It is seen that the sulphide capacities decreases with increasing SiO₂ content of the slag system. On the other hand, the increase in the CaO content results an increase in the desulphurisation power of the given slag system.

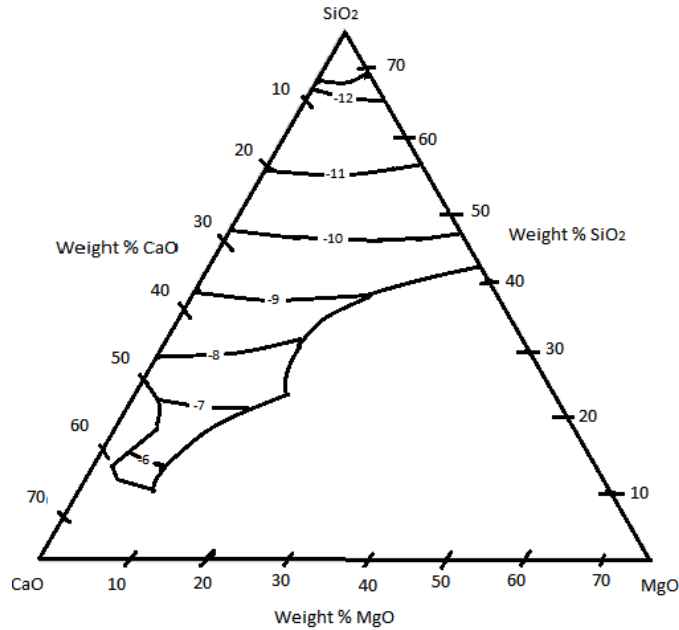


Figure 4.16 Predicted iso-sulphide capacity lines based on lattice (binding) energy model (Eq. 4.9) in MgO-CaO-SiO₂-25 wt.% Al₂O₃ quaternary phase diagram at 1600 °C.

- **The relationship between sulphide capacity (C_s^{-2}) and activity of calcium oxide in ferrochromium smelting slag system at 1600 °C**

Ban-Ya (1993) calculated the activity coefficient of a component in the multi component slag system by using the quadratic formalism based on the regular solution model, even though the silicate melt is not strictly regular.

In this study, the activity of CaO in ferrochromium and ferromanganese smelting slags is likewise calculated.

As described in Ban-Ya's study (1993), the model essentially assumes that all of the cations are randomly distributed in the oxygen anion matrix. The compositions can be expressed with the fractions of cations and also the melt is assumed as to be formed by the oxides. By these assumptions, the activity coefficient of the component, (i), in a multi-component regular solution can be determined as

follows:

$$G_i^E = \Delta \overline{H}_i = RT \ln \gamma_i \quad (4.17)$$

$$RT \ln \gamma_i = \sum_j \alpha_{ij} X_i^2 + \sum_j \sum_k (\alpha_{ij} + \alpha_{ik} - \alpha_{jk}) X_j X_k \quad (4.18)$$

where, X_i and α_{ij} define the cation fraction and interaction energy between cations respectively. The hypothetical pure liquid is taken as the reference state so that the activity coefficient of the component i, can be calculated as a function of slag composition and temperature.

It is well known that the random distribution of cations in the matrix of oxygen anion in silicate melts is a rough assumption in the treatment. Based on the previous experimental studies, Ban-Ya defined the activity coefficient of species of silicate melts which are not strictly regular solution as follows:

$$RT \ln \gamma_i = \sum_j \alpha_{ij} X_i^2 + \sum_j \sum_k (\alpha_{ij} + \alpha_{ik} - \alpha_{jk}) X_j X_k + I' \quad (4.19)$$

where I' represents the conversion factor of activity coefficient between hypothetical regular solution and real solution. Ban-Ya's treatment is similar to quadratic formalism for metallic solutions and the estimated values of activities by this model have been in good agreement with the experimental results. However, it should be considered that the equation is in quadratic form and the minor components with less than 5 mass per cent have been neglected for the approximate calculation.

The activity coefficient of CaO can be calculated for ferrochromium and ferromanganese smelting slags by using the following equations.

$$Ca_{(l)} + \underline{O} = CaO_{(R.S.)} \quad (4.20)$$

$$RT \ln \gamma_{CaO} = RT \ln (X_{CaO} / a_O) + RT \ln \gamma_{CaO} \quad (4.21)$$

$$\begin{aligned}
RT \ln \gamma_{CaO} = & -133890.X_{SiO_2}^2 - 154810.X_{Al_2O_3}^2 - 100420.X_{MgO}^2 - 92050.X_{MnO}^2 \\
& + [(-154810 - 133890 + 127610).X_{SiO_2}.X_{Al_2O_3}] \\
& + [(-133890 - 100420 + 66940).X_{SiO_2}.X_{MgO}] \\
& + [(-133890 - 92050 + 75310).X_{SiO_2}.X_{MnO}] \\
& + [(-154810 - 100420 + 71130).X_{MgO}.X_{Al_2O_3}] \\
& + [(-154810 - 92050 + 83680).X_{MnO}.X_{Al_2O_3}] \\
& + [(-100420 - 92050 - 61920).X_{MgO}.X_{MnO}]
\end{aligned} \tag{4.22}$$

The activity of CaO is there calculated by using the activity coefficient of CaO derived by equation 4.22.

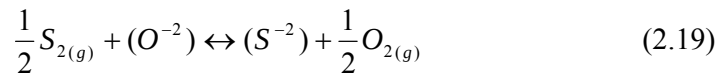
$$a_{CaO} = \gamma_{CaO} . X_{CaO} \tag{4.23}$$

The relationship between $C_{S^{-2}}$ and activity of CaO of ferrochromium smelting slag system is presented in Fig. 4.17. The regression equation between the logarithm of sulphide capacity and logarithm of CaO activity in the slag system under carbon monoxide atmosphere at 1600°C is:

$$\text{Log}C_{S^{-2}} = 0.960.\log a_{CaO} - 6.233 \tag{4.24}$$

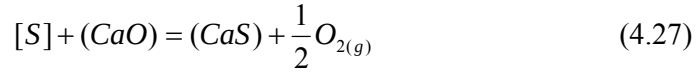
Although the linear regression model has a modest correlation coefficient ($R^2=0.647$), Equation 4.24 can be used to predict the sulphide capacity of ferrochromium smelting slag system by using activity of CaO of the slag system.

The expression ($d(\log C_{S^{-2}})/d(\log a_{CaO})$) should be close to unity for constant γ_{CaS} (Susaki et al. 1990).



$$\frac{1}{2}S_{2(g)} = [S] \tag{4.25}$$

$$C_{S^{-2}} = (S^{-2}) \left(\frac{P_{O_2}}{P_{S_2}} \right)^{1/2} = K_{2.19} \cdot \frac{a_{O^{-2}}}{f_{S^{-2}}} = ((S^{-2})/[S]) \cdot (P_{O_2})^{1/2} \cdot \frac{K_{4.25}}{f_s} \quad (4.26)$$



$$K_{4.27} = ((P_{O_2})^{1/2} \cdot \gamma_{CaS} \cdot X_{CaS}) / (f_s \cdot [S] \cdot \gamma_{CaO} \cdot X_{CaO}) \quad (4.28)$$

The relation between $\log C_{s-2}$ and $\log a_{CaO}$ gives a straight line with a slope close to unity (0.96) which indicates that a_{CaO} is closely related with a_{O-2} . In other words, CaO donates O^{-2} ions in to the slag system and breaks the silica network. Therefore, more cations become available to combine with the sulphur in the metal phase, which will eventually leads to an increase in the sulphide capacity of the slag system. The calculated activity of calcium oxide values are given in Appendix J.

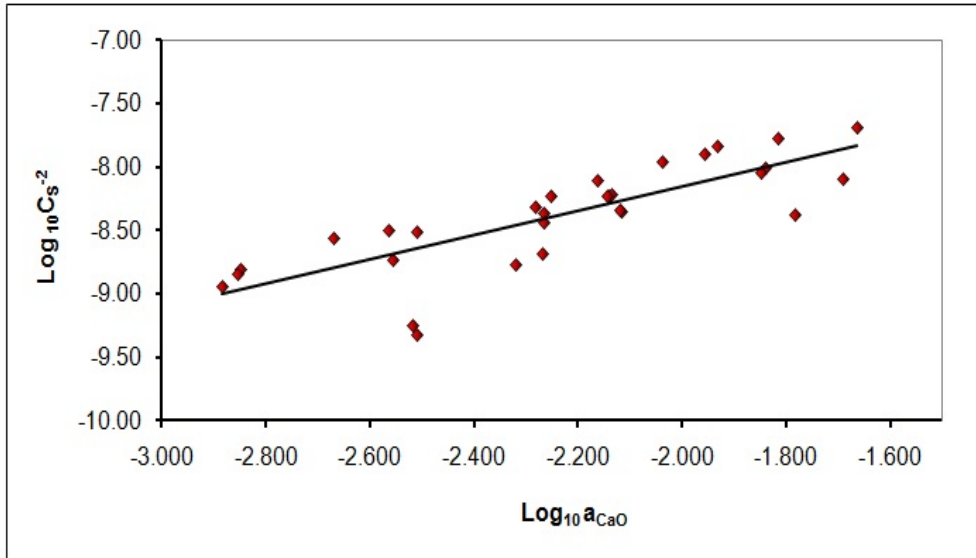


Figure 4.17 The relationship between sulphide capacity and calcium oxide activity in ferrochromium smelting slag.

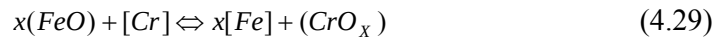
- **Chromium in SiO₂-CaO-Al₂O₃-MgO-CaS-Cr₂O₃ slag system**

In slag systems under reducing conditions, chromium oxide occur in two different oxidation states in such as Cr⁺² and Cr⁺³ (Pan, 1998).

Previous studies have clearly showed that under reducing atmosphere conditions, chromium in the oxide phase can also exist as divalent state (Frohberg and Richter, 1968; Rankin and Biswas, 1978).

A method developed by Muan (1984) was used for analyzing the chromium behaviour in SiO₂-CaO-Al₂O₃-MgO-CaS-Cr₂O₃ slag system in the present study and also by Akyuzlu (1989) and Pan (1998) to study the relationship between the iron and chromium content of chromium oxide containing slags. This approach allows us to determine Cr⁺² to Cr⁺³ ratios in the slag without conducting wet chemical analysis.

The distribution of chromium and iron between slag and metal phases can be defined by using the following slag-metal reaction if iron is assumed to have divalent state:



Since the activity coefficients of all the reactants are not known, it is possible to use the concentrations in the equilibrium. Therefore the apparent equilibrium constant for the reaction 4.29 (K') can be defined as follows:

$$\frac{[wt.\%Fe]^x \cdot (wt.\%CrO_x)}{[wt.\%FeO]^x \cdot [wt.\%Cr]} = K'_{4.29} \quad (4.30)$$

Equation 4.30 can be expressed in the form:

$$LogL_{Cr} = xLogL_{Fe} + LogK'_{4.29} \quad (4.31)$$

where L_{Cr} and L_{Fe} are the distribution of chromium and iron between slag and metal phases, respectively.

$$L_{Cr} = \frac{(wt.\%Cr)_{slag}}{[wt.\%Cr]_{metal}} \quad (4.32)$$

$$L_{Fe} = \frac{(wt.\%Fe)_{slag}}{[wt.\%Fe]_{metal}} \quad (4.33)$$

The value of “x” becomes the slope of a curve representing experimentally determined values of log L_{Cr} versus log L_{Fe} . If the value of slope is close to 1, the chromium in the slag is present as mainly in the divalent state. If the “x” value is close to 1.5, the chromium can be assumed in the trivalent state. By using this approach, the approximate values of CrO and $CrO_{1.5}$ contents of the slag system can be calculated. A study done by Akyuzlu (1989) on the slag-metal equilibrium in the smelting of high carbon-ferrochromium the slope is 0.86 at 1500°C under argon atmosphere decreases to 0.73 and 0.62 at 1500 °C and 1600 °C, respectively under carbon monoxide atmosphere.

Pan (1998) obtained the following slope values under more oxidizing condition:

<u>Slopes</u>	<u>Equilibrium Conditions</u>
1.125	1500 °C-Cr crucible-0.83 atm of CO atmosphere
1.1	1500 °C-Cr crucible-0.05 atm of CO atmosphere
1.07	1600°C-Si crucible-0.034 atm of CO atmosphere

The value of slope is found as 1.09 at experiments done at 1600°C under CO atmosphere (Fig 4.18). Chromium is mainly in divalent state (CrO) in SiO_2 -CaO- Al_2O_3 -MgO-CaS- Cr_2O_3 slag system under carbon monoxide atmosphere. This value indicates approximately that 73.2 percent of the total chromium oxide is CrO and 26.8 percent Cr_2O_3 in the slag. This result is consistent with that proposed by Pan (1998). The amount of chromium in slag is relatively small and presence of metallic chromium due to the entrapment can influence the results significantly. According to the results, most of the chromium is present as CrO in slags, therefore a high basicity slag can be an effective way to minimize the loss of chromium into the slag. A similar method is applied SiO_2 -CaO- Al_2O_3 -MgO- Ca_3P_2 - Cr_2O_3 slag system in the present work.

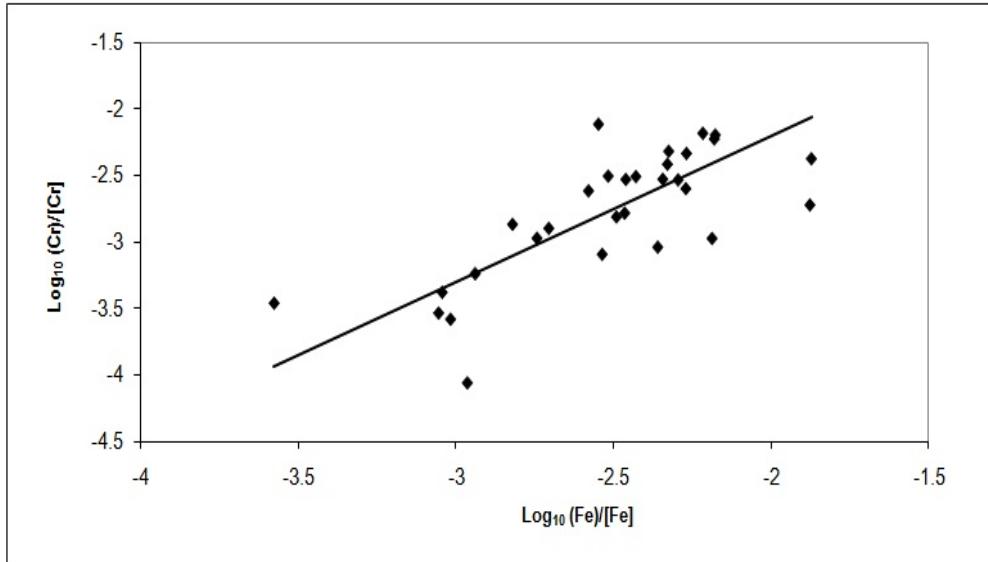


Figure 4.18 The relationship between chromium slag-to-metal distribution ratio and iron slag-to-metal distribution ratio

4.4.2 Phosphorus distribution and phosphide capacity relevant to ferrochromium smelting process

The calculated values of molar fraction of components, basicity ratio, optical basicity, lattice energy of component oxides, activity coefficient of phosphorus, phosphide capacity, phosphorus distribution ratio between slag and metal and regression models pertinent to ferrochromium smelting (1600 °C, CO gas atmosphere) is given in Table 4.8. In this table, the chemical analysis and temperature's relative errors are included into the calculated values of activity coefficient of phosphorus, phosphide capacity and phosphorus distribution ratio.

The phosphorus distribution ratio (L_p) is calculated by using equation 4.1 by using weight percentages of phosphorus in slag and metal phases. The mole fraction of CaO, MgO and SiO₂ values are used in the calculation of basicity ratio (Eq. 4.2). The optical basicity of slag is calculated according to equation 2.104 by using optical basicity values of several slag species in Table 2.8. Lattice energy of component oxides is calculated by using Equation 2.178. The calculation

procedure of activity coefficient of phosphorus relevant to ferrochromium smelting is given in Appendix B. The phosphide capacity of ferrochromium slags is calculated according to Equation 2.92. Equations 4.5, 4.6 and 4.10 are used in the calculation of regression models values related to phosphide capacity, phosphorus distribution ratio between slag and metal phases, lattice (binding) energy, respectively.

Table 4.8 Calculated values of molar fraction of components, basicity ratio, optical basicity, lattice energy of component oxides, activity coefficient of phosphorus, phosphide capacity, phosphorus distribution ratio and regression models pertinent to ferrochromium smelting (1600 °C, CO gas atmosphere)

	Final Slag Composition in Mole Fraction							Basicity Ratio	Optical Basicity	Lattice Energy of Component Oxides	Activity Coefficient of Phosphorus	Log ₁₀ (f _p)	Lp	Log ₁₀ (L _p)	Cp ⁻³	Log ₁₀ (C _p ⁻³)	Log ₁₀ (L _p)	Log ₁₀ (C _p ⁻³)	Log ₁₀ (C _p ⁻³)
Experiment Number	X SiO ₂	X Al ₂ O ₃	X MgO	X FeO	X Cr ₂ O ₃	X Ca ₃ P ₂	X CaO		(A)	(Eo)	(fp)						(Calculated based on Eq. 4.6)	(Calculated based on Eq. 4.5)	(Calculated based on Eq. 4.10)
1	0.3121	0.1716	0.4266	0.0042	0.0017	0.00007	0.0836	1.634	0.625	5243.52	77.63 ± 6.44	1.890	0.036 ± 0.003	-1.440	9.46E-16 ± 1.21E-16	-15.024	-1.597	-14.962	-14.554
2	0.3061	0.1694	0.4277	0.0029	0.0004	0.00008	0.0934	1.703	0.628	5224.41	86.92 ± 6.80	1.939	0.087 ± 0.007	-1.061	2.02E-15 ± 2.60E-16	-14.694	-1.326	-14.670	-14.424
3	0.3604	0.1349	0.4080	0.0034	0.0017	0.00010	0.0910	1.385	0.617	5339.05	18.31 ± 1.26	1.263	0.008 ± 0.001	-2.113	8.52E-16 ± 9.50E-17	-15.070	-2.070	-15.397	-15.204
4	0.3200	0.1910	0.3975	0.0035	0.0016	0.00007	0.0860	1.511	0.621	5272.93	53.98 ± 4.25	1.732	0.013 ± 0.001	-1.877	4.98E-16 ± 6.12E-17	-15.303	-1.484	-14.989	-14.754
5	0.3199	0.1825	0.4572	0.0032	0.0012	0.00012	0.0358	1.541	0.615	5279.45	50.16 ± 3.97	1.700	0.015 ± 0.001	-1.816	6.17E-16 ± 7.39E-17	-15.210	-2.097	-15.608	-14.798
6	0.2246	0.1489	0.3639	0.0004	0.0004	0.00018	0.2610	2.781	0.679	4950.72	31.83 ± 2.16	1.503	3.167 ± 0.253	0.501	2.01E-13 ± 2.58E-14	-12.696	0.338	-12.769	-12.563
7	0.2792	0.1796	0.3923	0.0003	0.0001	0.00005	0.1483	1.937	0.642	5150.82	28.37 ± 1.84	1.453	0.385 ± 0.031	-0.415	2.74E-14 ± 3.50E-15	-13.562	-0.446	-13.740	-13.924
8	0.2855	0.1732	0.3882	0.0004	0.0001	0.00004	0.1523	1.893	0.641	5161.4	36.08 ± 2.49	1.557	0.400 ± 0.032	-0.398	2.24E-14 ± 2.88E-15	-13.649	-0.520	-13.815	-13.996
9	0.3029	0.1672	0.3136	0.0015	0.0022	0.00002	0.2125	1.737	0.645	5187.56	56.45 ± 4.22	1.752	0.275 ± 0.022	-0.561	9.86E-15 ± 1.29E-15	-14.006	-0.525	-13.919	-14.173
10	0.3210	0.1662	0.2949	0.0019	0.0019	0.00002	0.2139	1.585	0.640	5231.11	52.11 ± 3.77	1.717	0.182 ± 0.015	-0.740	7.06E-15 ± 9.18E-16	-14.151	-0.641	-14.124	-14.470
11	0.2662	0.1931	0.3710	0.0043	0.0006	0.00003	0.1645	2.012	0.645	5124.44	39.83 ± 2.79	1.600	0.429 ± 0.034	-0.368	2.18E-14 ± 2.83E-15	-13.662	-0.340	-13.604	-13.744
12	0.2975	0.1380	0.4472	0.0017	0.0025	0.00010	0.1127	1.882	0.637	5178.15	23.97 ± 1.59	1.380	0.022 ± 0.002	-1.650	1.89E-15 ± 2.31E-16	-14.723	-1.225	-14.391	-14.109
13	0.3132	0.1270	0.4454	0.0010	0.0016	0.00009	0.1118	1.779	0.634	5210.94	25.12 ± 1.66	1.400	0.024 ± 0.002	-1.613	1.96E-15 ± 2.42E-16	-14.707	-1.343	-14.519	-14.332
14	0.3037	0.1409	0.4379	0.0011	0.0021	0.00031	0.1139	1.817	0.635	5196.06	25.94 ± 1.72	1.414	0.084 ± 0.007	-1.074	6.58E-15 ± 8.12E-16	-14.182	-1.234	-14.438	-14.231
15	0.3518	0.1588	0.4454	0.0016	0.0003	0.00003	0.0419	1.385	0.610	5340.97	57.38 ± 4.65	1.759	0.004 ± 0.001	-2.412	1.37E-16 ± 2.15E-17	-15.864	-2.230	-15.674	-15.217
16	0.3483	0.1567	0.4525	0.0010	0.0002	0.00005	0.0412	1.417	0.611	5331.75	62.28 ± 4.80	1.794	0.010 ± 0.001	-2.011	3.17E-16 ± 3.91E-17	-15.499	-2.189	-15.612	-15.154
17	0.2496	0.1126	0.4297	0.0005	0.0004	0.00008	0.2070	2.551	0.670	4999.32	26.31 ± 1.70	1.420	0.692 ± 0.055	-0.160	5.32E-14 ± 6.82E-15	-13.274	-0.086	-13.180	-12.893
18	0.3207	0.1370	0.4422	0.0005	0.0003	0.00001	0.0993	1.689	0.629	5238.98	40.83 ± 2.86	1.611	0.125 ± 0.010	-0.903	6.20E-15 ± 8.07E-16	-14.208	-1.408	-14.649	-14.523
19	0.3275	0.1539	0.4516	0.0005	0.0002	0.00004	0.0660	1.581	0.621	5274.13	35.03 ± 2.46	1.544	0.011 ± 0.001	-1.967	6.23E-16 ± 7.77E-17	-15.206	-1.723	-15.066	-14.762
20	0.3179	0.1674	0.4480	0.0003	0.0001	0.00006	0.0661	1.617	0.622	5258.5	53.74 ± 4.14	1.730	0.015 ± 0.001	-1.836	5.50E-16 ± 6.85E-17	-15.260	-1.580	-14.978	-14.656
21	0.2964	0.1296	0.4761	0.0015	0.0029	0.00076	0.0927	1.919	0.636	5175.09	22.88 ± 1.65	1.360	0.067 ± 0.005	-1.177	5.88E-15 ± 6.68E-16	-14.230	-1.368	-14.480	-14.089
22	0.3630	0.1279	0.4309	0.0009	0.0006	0.00001	0.0767	1.398	0.615	5344.57	50.99 ± 4.00	1.708	0.003 ± 0.001	-2.491	1.28E-16 ± 2.46E-17	-15.893	-2.062	-15.360	-15.241
23	0.3839	0.1349	0.4123	0.0010	0.0006	0.00001	0.0672	1.249	0.608	5399.82	53.63 ± 4.23	1.729	0.009 ± 0.001	-2.057	3.31E-16 ± 4.24E-17	-15.480	-2.275	-15.671	-15.617
24	0.2868	0.1372	0.4945	0.0082	0.0015	0.00021	0.0715	1.974	0.634	5159.69	23.77 ± 1.68	1.376	0.021 ± 0.002	-1.687	1.75E-15 ± 2.01E-16	-14.757	-1.633	-14.727	-13.984
25	0.3398	0.1393	0.4288	0.0023	0.0029	0.00002	0.0866	1.517	0.621	5292.64	43.57 ± 3.30	1.639	0.010 ± 0.001	-2.009	4.55E-16 ± 5.75E-17	-15.342	-1.909	-15.189	-14.888
26	0.3683	0.1303	0.4192	0.0010	0.0005	0.00001	0.0806	1.357	0.614	5357.72	46.66 ± 3.56	1.669	0.004 ± 0.000	-2.420	1.65E-16 ± 2.07E-17	-15.783	-2.066	-15.400	-15.330
27	0.3645	0.1278	0.4232	0.0008	0.0004	0.00005	0.0832	1.389	0.616	5346.57	73.56 ± 6.29	1.867	0.018 ± 0.001	-1.737	5.04E-16 ± 6.39E-17	-15.298	-2.013	-15.324	-15.255
28	0.3785	0.1315	0.3938	0.0010	0.0006	0.00003	0.0945	1.290	0.613	5379.46	44.53 ± 3.41	1.649	0.014 ± 0.001	-1.841	6.56E-16 ± 8.29E-17	-15.183	-2.012	-15.407	-15.478
29	0.3841	0.1342	0.4113	0.0010	0.0005	0.00001	0.0688	1.250	0.608	5399.68	52.55 ± 4.12	1.721	0.010 ± 0.001	-1.991	3.93E-16 ± 5.04E-17	-15.406	-2.262	-15.657	-15.616

- The variation of C_P^{-3} and L_P with silica (X_{SiO_2}) in ferrochromium smelting slags

The influence of silica content (in mole fraction) of ferrochromium smelting slag on the phosphide capacity and phosphorus distribution ratio is illustrated in Figs. 4.19, 4.20 and Figs G 1.1 to G. 1.6 in Appendix G1.

The logarithm of phosphide capacity decreases sharply from -12.696 to -15.210 as the amount of silica increases from 0.2246 to 0.3841 (in mole fraction) (Fig. 4.19). The effect of silica content, within the range of 0.2246 to 0.3841 (in mole fraction), on the logarithm of phosphorus distribution ratio between slag and metal is illustrated in Figure 4.20. It is seen from Figure 4.20 that the partition ratio of phosphorus decreases with an increase in the silica content of the slag.

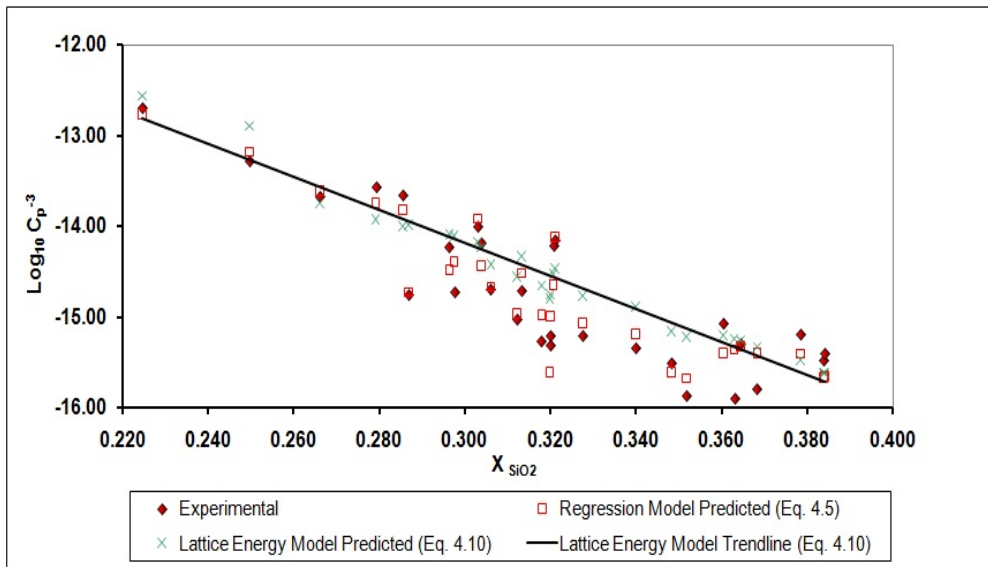


Figure 4.19 The variation of phosphide capacity with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio: 1.250-2.781, X_{CaO} : 0.0358-0.2610, X_{MgO} : 0.2949-0.4945

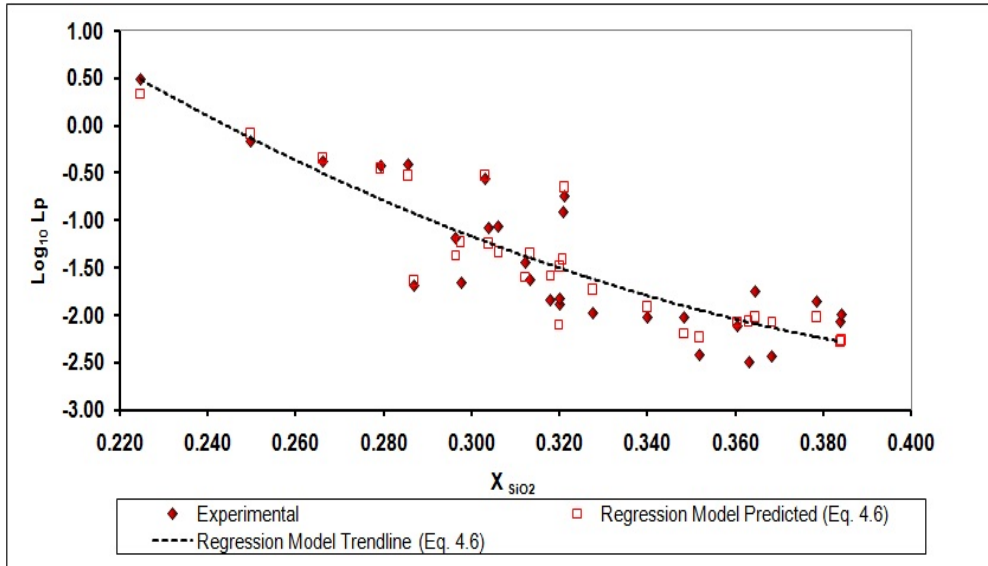


Figure 4.20 The variation of phosphorus distribution ratio with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio: 1.250-2.781, X_{CaO} : 0.0358-0.2610, X_{MgO} : 0.2949-0.4945

The addition of basic oxides (CaO, MgO) donate oxygen ions into the network which can cause a separation of the corners of two SiO_4^{-4} (tetrahedral) in the silicate network. The further addition of basic oxides into the three dimensional arrangement will continuously break down the network and cause the formation of discrete SiO_4^{-4} . As indicated in previous studies, the melts contain primarily monomers at high basicity ($0 \leq X_{SiO_2} \leq 0.33$), where the discrete SiO_4^{-4} units are dominant. The discrete SiO_4^{-4} units are turned into two dimensional chains with N_{SiO_2} in the range 0.33 to 0.50.

Turkdogan and Maddocks (1949) state that the distribution of phosphorus between liquid iron and $FeO-Na_2O-SiO_2$ becomes significantly affected by the silica content of slag. Phosphorus can be removed at higher percentages with decreasing SiO_2 content as given below:

90 % of phosphorus removal at less than 25 wt. % SiO_2

50 % of phosphorus removal between 25 and 40 wt. % SiO_2

15-40 % of phosphorus removal in the range of 50-60 wt. % SiO_2

Similar non-linear nature curve between phosphorus distribution ratio and silica content of ferrochromium smelting slags has been observed in the present work (Figure 4.20). However, it should be noted that the silica content in the slag was not an independent parameter and strongly dependent on the amount of other slag components such as CaO and MgO.

The changes in phosphide capacities and phosphorus distribution ratios with the change of silica content of slag have been illustrated in Figs G 1.1 to G. 1.6 (Appendix G.1). The amounts of CaO and MgO have been kept in a narrow range and alumina almost constant so their influences have been minimized in these figures.

The logarithm of phosphide capacity against the silica content of slag is plotted in Figure G 1.1. As the silica content (in mole fraction) of slag raises from 0.32 to 0.3683, the logarithm of phosphide capacity decreases from -15.309 to -15.783.

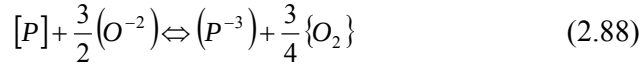
The dephosphorisation power of slag significantly drops with the increase of silica content in the slag (Fig. G 1.2). The logarithm of phosphorus distribution ratio decreases from -1.876 to -2.420 with the increase of silica content (in mole fraction) from 0.32 to 0.3683.

According to the previous studies, an increase in the silica content of ferromanganese smelting slags generally caused a decrease in the phosphorus transfer from metal to slag (Maramba and Eric, 2007).

Yang and Endstrom (1992) reported that the phosphorus distribution ratio between CaO-CaF₂-SiO₂ slag and Fe-Cr-C-P melts at 1450 °C under carbon monoxide atmosphere drops from 0.15 to 0.01 with increasing SiO₂ from 5 per cent to 20 per cent. On the other hand, they did not see any deteriorating influence of silica addition up to 5 wt. % to the CaO-saturated slags on the phosphorus distribution ratio.

The influence of silica content to phosphide capacity and phosphorus distribution ratio correlates well with the above mentioned studies (Maramba and Eric, 2007; Yang and Endstrom (1992). However, the present work showed that the drop in the phosphide capacity and phosphorus distribution ratio can take place only up to a certain level ($X_{SiO_2} = 0.3275$) and beyond this point it becomes almost independent from the silica content of the ferrochromium smelting slag.

Under strongly reducing atmosphere conditions, it is expected that the phosphorus is going to behave according to the reaction 2.88. The equilibrium constant for reaction 2.88 is expressed in Eq. 4.34.



$$K_{2.88} = \frac{f_{P^{-3}} \cdot (P^{-3}) \cdot P_{O_2}^{3/4}}{f_P [P] \cdot a_{O^{-2}}^{3/2}} \quad (4.34)$$

where $f_{P^{-3}}$ is the activity coefficient of phosphide.

The phosphide capacity can be calculated by using Eq. (2.92)

$$C_{P^{-3}} = \frac{(P^{-3}) \cdot P_{O_2}^{3/4}}{[P] \cdot f_P} = K_{2.88} \cdot \frac{(a_{O^{-2}})^{3/2}}{(f_{P^{-3}})} \quad (2.92)$$

Eq 4.35 can define the distribution ratio of phosphorus between slag and metal.

$$\frac{(P)}{[P]} = K_{2.88} \frac{(a_{O^{-2}})^{3/2} \gamma_P}{P_{O_2}^{3/4} \gamma_{P^{-3}}} \quad (4.35)$$

It is evident from Eq. 4.35, the partition ratio of phosphorus is directly proportional to the activity of oxygen anions in the slag. As the SiO_2 content of the slag increases, the activity of free O^{-2} in the slag tends to decrease which

results in a decrease in the phosphorus distribution ratio between the slag and metal.

Highly basic slags contain simple chains, mainly SiO_4^{-4} tetrahedra, while less basic slags contain rings and chains such as $\text{Si}_3\text{O}_{10}^{-8}$, $\text{Si}_2\text{O}_7^{-6}$, $\text{Si}_4\text{O}_{12}^{-8}$. At high silica content in slag, almost all the metal cations such as Ca^{+2} and Mg^{+2} are associated with large silicate anion groups. The acidic oxide SiO_2 can produce complex cations by reacting with the oxygen anions and these reactions consume oxygen anions in the slag system. The breakdown reaction of silica can be demonstrated by reaction (2.136). When the free oxygen anions are consumed in the slag, the reaction 2.136 shifts from left to right direction, this causes an increase in the phosphide capacity of slag system.



- **The variation of C_p^{-3} and L_p with calcium oxide (X_{CaO}) in ferrochromium smelting slags**

The effect of calcium content (in mole fraction) of ferrochromium smelting slag on the logarithm of phosphide capacity and distribution ratio of phosphorus between slag and metal phases are shown in Figures 4.21, 4.22 and Figs. G 2.1 to 2.6 (in Appendix G2).

The variation of the phosphide capacity with the amount of calcium oxide (in mole fraction) is shown in Figure 4.21. However, the amounts of other slag components have not been kept in a narrow range hence the change of phosphide capacity with the change of calcium oxide only can not be determined properly although it is still possible to observe its trend. When CaO content (in mole fraction) is increased from 0.0358 to 0.2610, the phosphide capacity (logarithm) has increased from -15.209 to -12.696 which indicates that larger dephosphorisation power can be achieved by increasing the calcium oxide content in the ferrochromium slags.

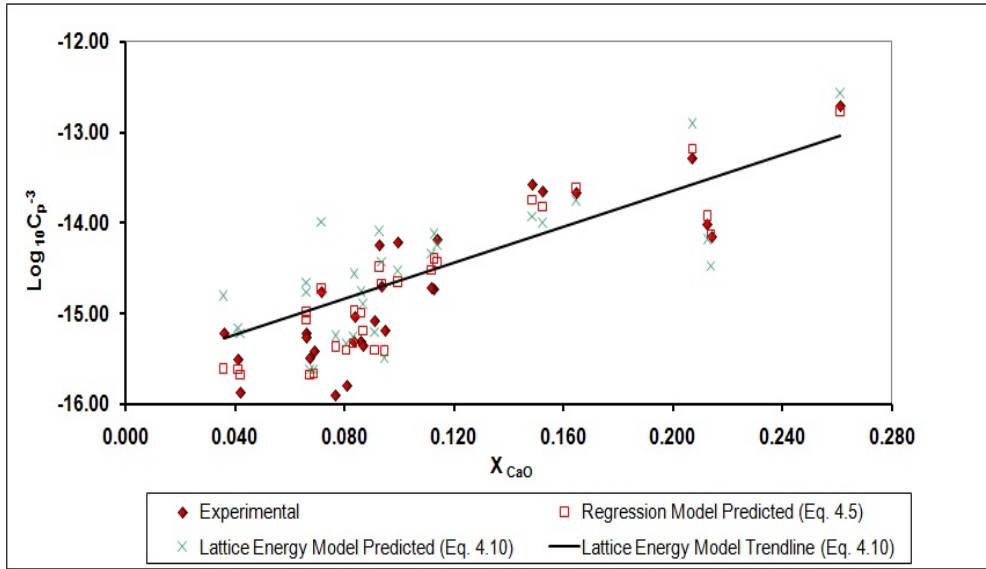


Figure 4.21 The variation of phosphide capacity with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag; Basicity Ratio: 1.250-2.781, X_{SiO_2} : 0.2246-0.3841, X_{MgO} : 0.2949-0.4945

As CaO concentration increases, the silica network is broken up into smaller anionic groups which will result in an increase of the proportion of free oxygen ions in the slag. It is evident from Eqs. 2.133 and 2.92 that the phosphide capacity tends to increase with the increase of activity of oxygen anions in the slag as a result of dissociation reaction of CaO.



$$C_{P^{-3}} = \frac{(P^{-3}) \cdot P_{O_2}^{3/4}}{[P] \cdot f_P} = K_{2.88} \cdot \frac{(a_{O^{-2}})^{3/2}}{(f_{P^{-3}})} \quad (2.92)$$

Silica, alumina and magnesium oxide contents have been kept in a narrow range for eliminating their influences on the relationships between phosphide capacity (logarithm) and calcium oxide content (in mole fraction) of slag in Figures G 2.1, G 2.3 and G 2.5 (in Appendix G). The increase in the calcium oxide content leads to higher phosphide capacities. The logarithm of phosphide capacity is raised from -15.297 to -14.693 when the calcium oxide content (in mole fraction) increases from 0.0832 to 0.0934 (Fig. G 2.1).

It is found that the logarithm of logarithm of phosphorus distribution ratio increases from -1.815 to -1.073 with the increase of calcium oxide content of the slag from 0.0358 to 0.1139 (in mole fraction) (Figure 4.22).

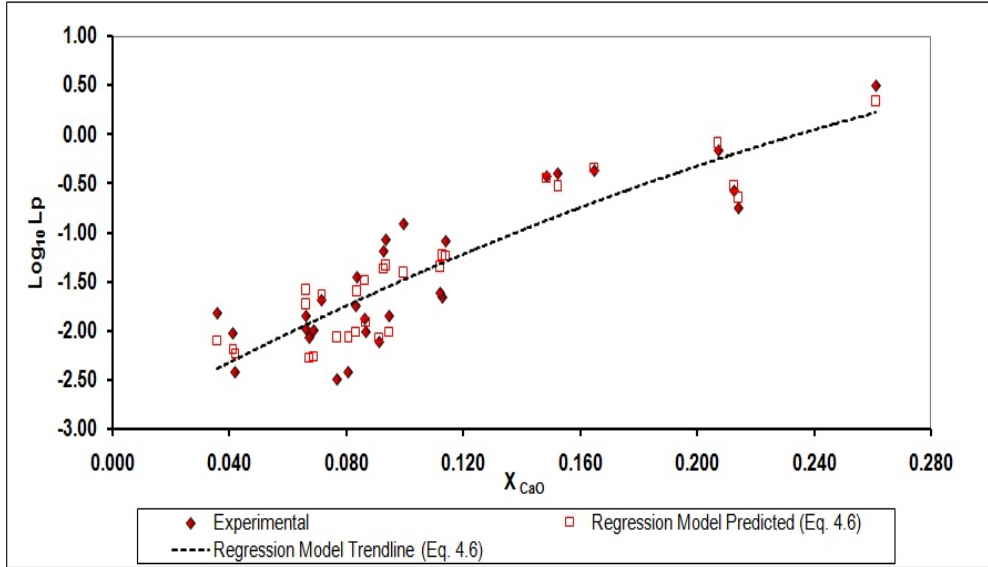
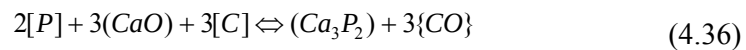


Figure 4.22 The variation of phosphorus distribution ratio with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag; Basicity Ratio: 1.250-2.781, X_{SiO_2} : 0.2246-0.3841, X_{MgO} : 0.2949-0.4945

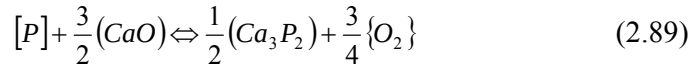
CaO is a strong basic oxide which is the key component for transfer of phosphorus from metal to slag in ferrochromium smelting process. The overall reaction of phosphorus between a carbon-saturated ferrochromium alloy and a slag containing calcium oxide under reducing atmosphere condition can be written as follows,



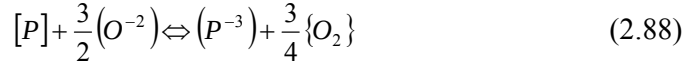
From the standard free energies of formation of metal phosphides, the tendency to form these phosphides decreases (as the free energy of formation increases) in the order (Horn et al., 1998):



The dephosphorisation power of basic oxides decreases slightly in the order CaO, MgO and FeO, thus as the calcium content in the slag increases the phosphorus content of the alloy decreases. Ultimately, the reaction between Ca in the slag and P in the alloy will result in the formation of Ca_3P_2 in the slag (Eq. 2.89).



The partition ratio of phosphorus can be defined by using Eq. 4.35 which is derived from reaction 2.88.



$$K_{2.88} = \frac{f_{\text{P}^{-3}} \cdot (\text{P}^{-3}) \cdot P_{\text{O}_2}^{3/4}}{f_{\text{P}} [\text{P}] \cdot a_{\text{O}^{-2}}^{3/2}} \quad (4.34)$$

$$\frac{(\text{P})}{[\text{P}]} = K_{2.88} \frac{(a_{\text{O}^{-2}})^{3/2} \gamma_{\text{P}}}{P_{\text{O}_2}^{3/4} \gamma_{\text{P}^{-3}}} \quad (4.35)$$

As the CaO amount of slag increases, more free O^{-2} anions are supplied to the slag phase due to the dissociation reaction of CaO (Eq. 2.133). As a result, the activity of oxygen anions in the slag tends to increase. The increase in the activity of oxygen anions in the slag will enhance the phosphorus partition ratio between slag and metal.

Previous study on the phosphorus behaviour in ferromanganese smelting under reducing atmosphere conditions show that the increase in the calcium oxide content of the slag system have positive impact on the dephosphorisation of ferromanganese alloy (Maramba and Eric, 2008). Inoue and Suito (1985) reported that logarithm of phosphate capacity of the pure oxides decrease in the order of $\text{BaO} > \text{CaO} > \text{MgO}$, which indicates that BaO and CaO are more powerful dephosphoriser agents compared to MgO. The results of experiments on CaO-

CaF₂ flux and Ag-P alloy under carbon monoxide/argon gas mixture at 1500 °C clearly indicate that the phosphide capacity of the flux is directly proportional to the activity of calcium oxide or in other words the activity of O⁻² in the flux system (Tabuchi and Sano, 1983). Suito et al. (1981) found that the phosphorus distribution between liquid iron and CaO-SiO₂-FeO_x slag equilibrated in magnesia crucible in the temperature range of 1 550° to 1 650 °C increases with increasing content of CaO in the slag and the relationship between logarithm of phosphorus distribution ratio and logarithm of CaO content can be expressed in either linear or quadratic nature. It is evident that the results of these studies agree well with the present study on the relationship between calcium oxide content of ferrochromium smelting slags and phosphide capacity, partition ratio of phosphorus between slag and metal.

- **The variation of C_P^{-3} and L_P with magnesium oxide (X_{MgO}) in ferrochromium smelting slags**

The change of the logarithm of C_P^{-3} and L_P with magnesium oxide content (in mole fraction) of ferrochromium smelting slag is presented in Figures 4.23, 4.24 and Figs G 3.1 to G 3.4 in Appendix G3.

The influence of MgO content of the ferrochromium smelting slag on the phosphide capacity and phosphorus distribution ratio between slag and metal phases is found to show no clear trend (Figures 4.23 and 4.24). As the magnesium oxide content (in mole fraction) of slag increases from 0.3938 to 0.408, the logarithm of phosphide capacity increases from -15.183 to -15.069 (Fig. 4.23). However, the ranges are both very small and with considering likely errors in the experimental data points, it is not clear direction of the trend.

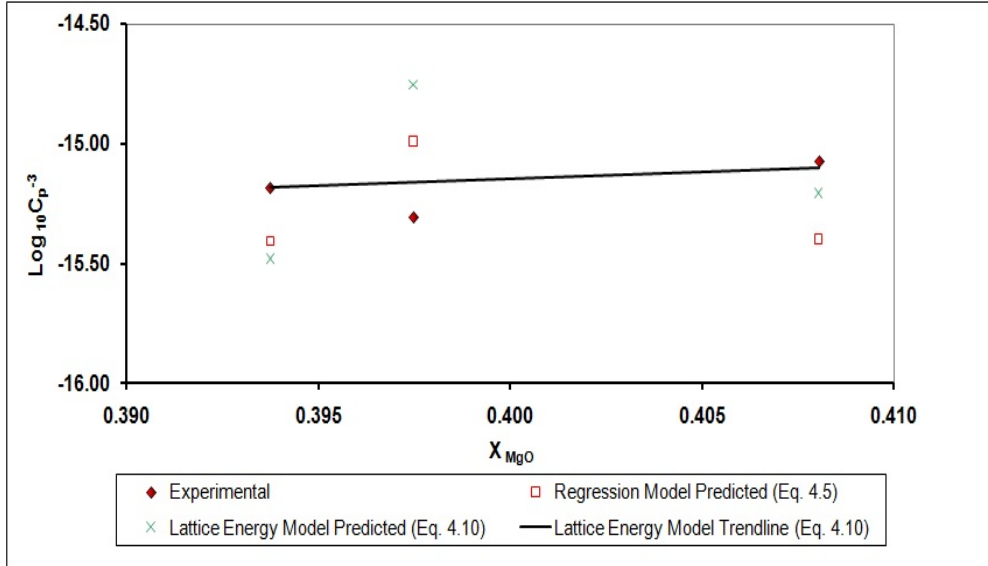


Figure 4.23 The variation of phosphide capacity with magnesium oxide mole fraction (X_{MgO}) of ferrochromium smelting slag; Basicity Ratio: 1.250-2.781, X_{SiO_2} : 0.2246-0.3841, X_{CaO} : 0.2949-0.4945

The variation in the equilibrium phosphorus distribution ratio between slag and metal with change in the MgO content (in mole fraction) from 0.4080 to 0.4288 is given in Fig. 4.24. The logarithm of phosphorus distribution ratio increases from -2.113 to -2.008, when the magnesium oxide content (in mole fraction) of slag increases from 0.4080 to 0.4288. As it was mentioned early, this trend is not clear due to the small range and possible errors related to experimental data.

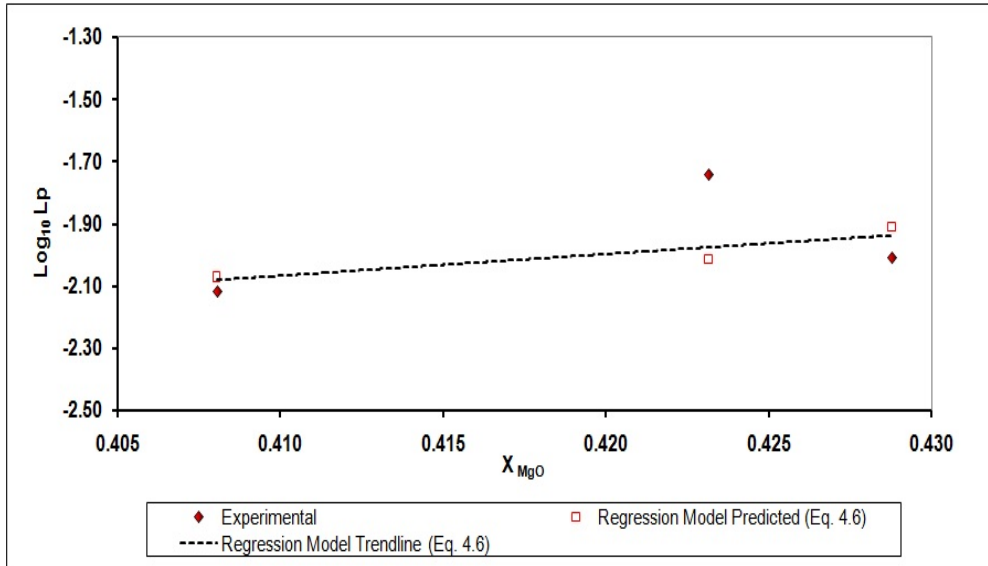


Figure 4.24 The variation of phosphorus capacity with magnesium oxide mole fraction (X_{MgO}) of ferrochromium smelting slag; Basicity Ratio: 1.250-2.781, X_{SiO_2} : 0.2246-0.3841, X_{CaO} : 0.2949-0.4945

Although the addition of magnesium oxide can enhance the slag basicity, we should consider MgO as less powerful basic oxide compared to CaO. Therefore, the observed trend can be due to slight changes in the silica and calcium oxide of the ferrochromium smelting slag.

- **The variation of C_P^{-3} and L_p with basicity ratio $[(X_{CaO}+X_{MgO})/X_{SiO_2}]$ of ferrochromium smelting slags**

The change of phosphide capacity and phosphorus distribution ratio between slag and metal phases with basicity ratio of ferrochromium smelting slag are illustrated in Figures 4.25, 4.26 and Figs G 4.1 to G 4.6 in Appendix G4.

As it can be seen in Figure 4.25, the logarithm of phosphide capacity increases from -15.892 to -12.696 when the slag basicity ratio increases from 1.398 to

2.781. Also, the phosphorus partition ratio between slag and metal increases with the increase of basicity ratio (Figure 4.26)

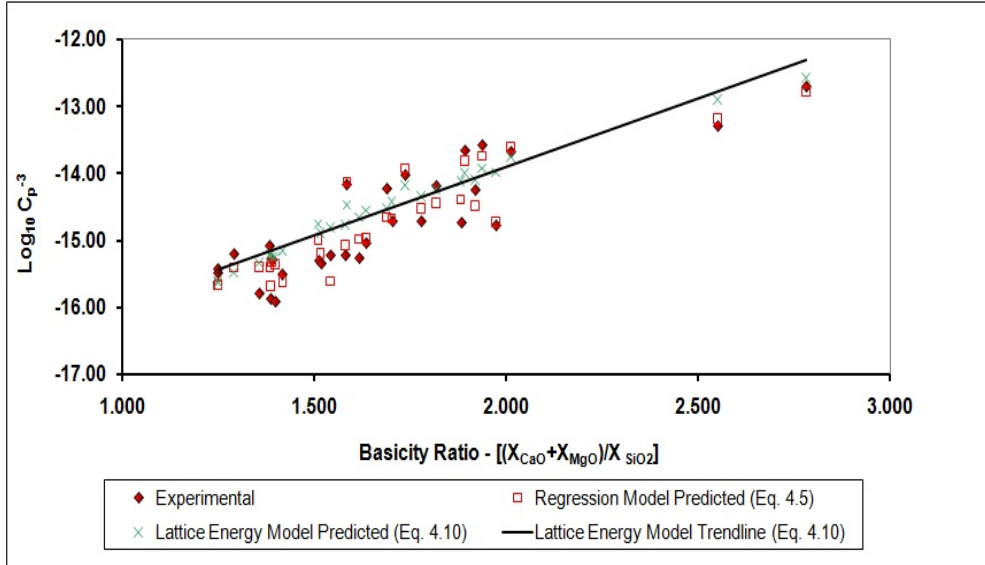


Figure 4.25 The effect of basicity ratio on the phosphide capacity of ferrochromium smelting slag; X_{SiO_2} :0.2246-0.3841, X_{CaO} :0.0358-0.2610, X_{MgO} :0.2949-0.4945

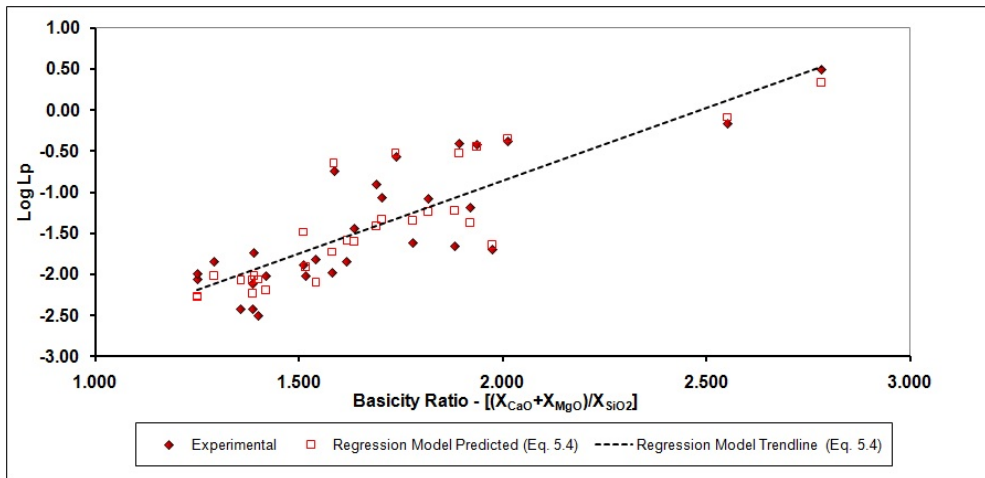


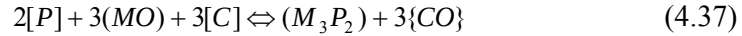
Figure 4.26 The effect of basicity ratio on the phosphorus distribution ratio of ferrochromium smelting slag; X_{SiO_2} :0.2246-0.3841, X_{CaO} :0.0358-0.2610, X_{MgO} :0.2949-0.4945

The influence of slag basicity on the phosphorus distribution ratio has been investigated for different slag systems in detail. Im et al. (1996) pointed out the basicity dependence of phosphorus distribution ratio between $\text{CaO-SiO}_2\text{-FeO}_t$ slags and carbon saturated iron at 1300 °C. Experimental results showed that there has been a good linear correlation between two parameters. The relationship between CaO content of $\text{CaO-CaF}_2\text{-SiO}_2$ melts and phosphorus partition ratio between the melt and carbon saturated iron has been established by Muraki et al. (1985). The phosphorus distribution ratio seems to increase with increasing X_{O}^{-2} as a result of an increase in CaO content of slag. Their study also shows that FeO tends to behave like an acidic oxide in highly basic slags, and therefore causes drop in the phosphate capacity of the slag. Basu et al. (2007) presents a detailed investigation of phosphorus partition ratio between liquid steel $\text{CaO-SiO}_2\text{-FeO}_x\text{-P}_2\text{O}_5\text{-MgO}$ slags containing 15 to 25 wt. % FeO. It was concluded that the phosphorus partition ratio between slag and metal increased with a high slope with the increasing of basicity up to 2. The slope thereafter decreased and became constant at basicity values greater than 2.5. The activity of P_2O_5 decreased continuously as the basicity of slag was increased to 2 and became practically constant when basicity exceeded 2.5 indicating that the slag behaves in heterogeneous nature at a basicity greater than 2.5. Van Niekerk and Dippenaar, (1998) showed that effective removal of phosphorus from liquid iron can be achieved by increasing the basicity of slag from 1.38 to 1.51 at 10 wt. % CaF_2 . Yang (1992) pointed out that a large amount of Cr_2O_3 formed during the dephosphorisation process of ferrochromium under oxidizing atmosphere. Cr_2O_3 coexisting with CaO-based slag will result in the formation of a slag with a high melting point and a low phosphate capacity. Under reducing atmosphere conditions ($\log P_{\text{O}_2} < -17$), it is possible to achieve the dephosphorisation without any significant loss of chromium to slag. Reducing atmosphere conditions also favour the removal of phosphorus from alloy by increasing the phosphorus activity in the ferroalloy. Another study by Yang and Edstrom (1992) clearly shows that effective dephosphorisation of Fe-Cr-C-P melt should be done at an oxygen partial pressure below 2×10^{-14} atm. for preventing the formation of Cr_2O_3 in the slag. The results of Maramba and Eric (2008) on the dephosphorisation of

high carbon ferromanganese under reducing atmosphere indicate that logarithm of phosphide capacity highly depends on the basicity ratio of the slag system which increased from -14.861 to -13.963 when the slag basicity increased from 0.672 to 1.3 under carbon monoxide at 1500 °C.

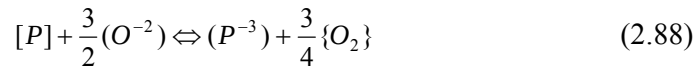
The replacement of silica with other basic oxides in the slags results a decrease in the activity of silicone in the metal phase. As a consequence, the activity of phosphorus in metal tends to reduce with decreasing silicone content in the metal phase due to the positive value of the interaction coefficient between phosphorus and silicone in liquid iron at 1 600 °C (e_P^{Si} : 0.094), which will result in a higher phosphorus transfer from metal to slag (Ward, 1962).

The phosphorus equilibrium between slag and a carbon-saturated ferrochromium alloy under reducing atmosphere condition can be expressed such as:



where M represents Ca or Mg.

The reaction 4.37 can be formulated in a more general form:



The equilibrium constant of this reaction is then:

$$K_{2.88} = \frac{f_P \cdot (P^{-3}) \cdot P_{O_2}^{3/4}}{f_P [P] \cdot a_{O^{-2}}^{3/2}} \quad (4.34)$$

Eq. 2.92 defines the phosphide capacity

$$C_{P^{-3}} = \frac{(P^{-3}) \cdot P_{O_2}^{3/4}}{[P] \cdot f_P} = K_{2.88} \cdot \frac{(a_{O^{-2}})^{3/2}}{(f_{P^{-3}})} \quad (2.92)$$

Since the phosphide capacity of the slag is directly proportional to the activity of oxygen in the slag, the addition of basic oxides such as CaO and MgO into the slag system will result in an increase in the concentration of oxygen anions due to the dissociation reactions (2.133 and 4.15) which causes the reaction 4.15 or 2.88 to move to right.



Eq 4.35 can define the distribution ratio of phosphorus between slag and metal.

$$\frac{(P)}{[P]} = K_{2.88} \frac{(a_{O^{-2}})^{3/2} \gamma_P}{P_{O_2}^{3/4} \gamma_{P^{-3}}} \quad (4.35)$$

Since the partition ratio of phosphorus is directly proportional to the activity of oxygen anions in the slag hence the replacement of silica with basic oxides in the slag results an enhancement in the activity of oxygen anions, which eventually causes an increase in the partition ratio of phosphorus between slag and metal phases (Eq. 4.35).

- **The variation of C_P^{-3} and L_P with optical basicity (Λ) of ferrochromium smelting slags**

The influence of optical basicity (Λ) of ferrochromium smelting slag on the logarithm of phosphide capacity and distribution ratio of phosphorus between slag and metal phases are given in Figures 4.27, 4.28 and Figures G 5.1 and G 5.2 (Appendix G5).

As shown in Figure 4.27, the logarithm of phosphide capacity increases from -15.480 to -12.696 when the optical basicity of the slag system augments from 0.607 to 0.679. The effect of slag optical basicity on phosphorus distribution ratio between slag and metal is presented in Figure 4.28. The phosphorus distribution

ratio between $\text{CaO-CaF}_2\text{-SiO}_2$ slags and Fe-Cr-C-P melts increases with increasing optical basicity of slag up to optical basicity of 0.745 and becomes constant after this breaking point of the curve (Yang and Edstrom, 1992). The curve indicated a linear behaviour in Figure 4.28. Both figures indicate that the dephosphorisation power of the slag can be significantly improved by increasing optical basicity of slag. As given in Table 2.8, optical basicity values of CaO , MgO and SiO_2 are 1, 0.78 and 0.48, respectively which can be enhanced significantly with the addition of CaO and MgO to the slag.

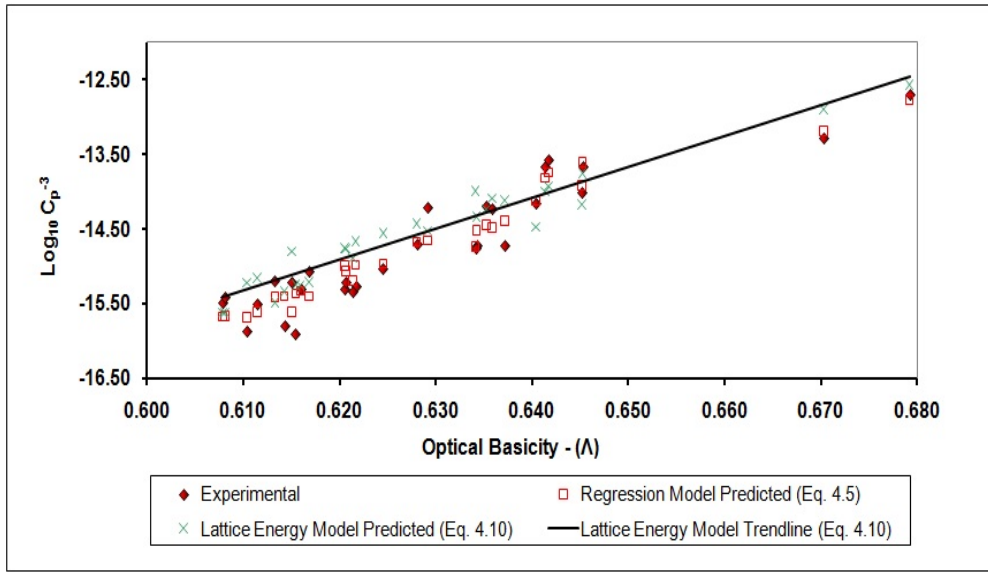


Figure 4.27 The effect of optical basicity on the phosphide capacity of ferrochromium smelting slag; Basicity Ratio: 1.250-2.781, X_{SiO_2} :0.2246-0.3841, X_{CaO} :0.0358-0.2610, X_{MgO} :0.2949-0.4945

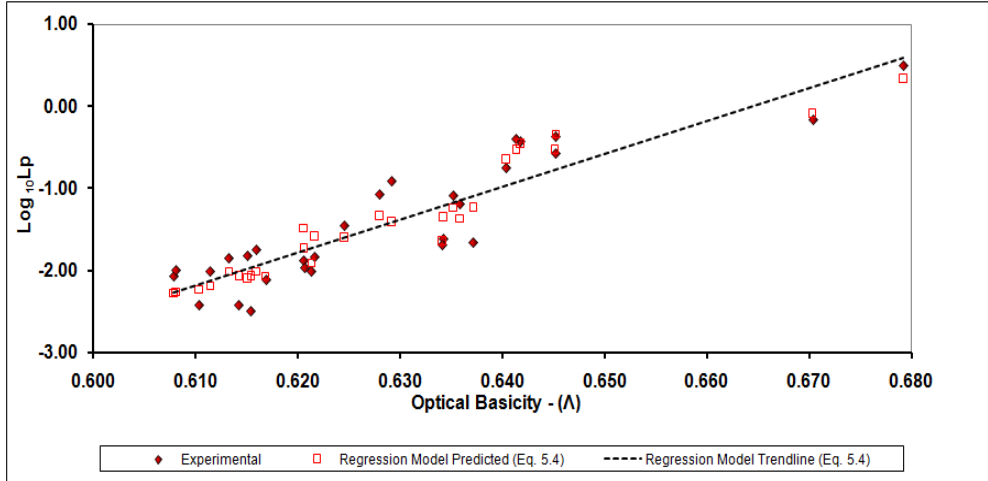


Figure 4.28 The effect of optical basicity on the phosphorus distribution ratio of ferrochromium smelting slag; Basicity Ratio: 1.250-2.781, X_{SiO_2} :0.2246-0.3841, X_{CaO} :0.0358-0.2610, X_{MgO} :0.2949-0.4945

The relationship between optical basicity and the logarithm of phosphide capacity is in linear nature as presented in Figure 4.29. The correlation between optical basicity and the log of phosphide capacity for SiO_2 -CaO- Al_2O_3 -MgO- Ca_3P_2 - Cr_2O_3 slag system at 1600 °C under carbon monoxide atmosphere can be defined by using Eq. 4.38. The correlation coefficient (R^2) of Eq. 4.38 is 0.86 which indicates of reliable fit for regression model.

$$LogC_{P-3} = -44.55\Lambda - 42.747 \quad (4.38)$$

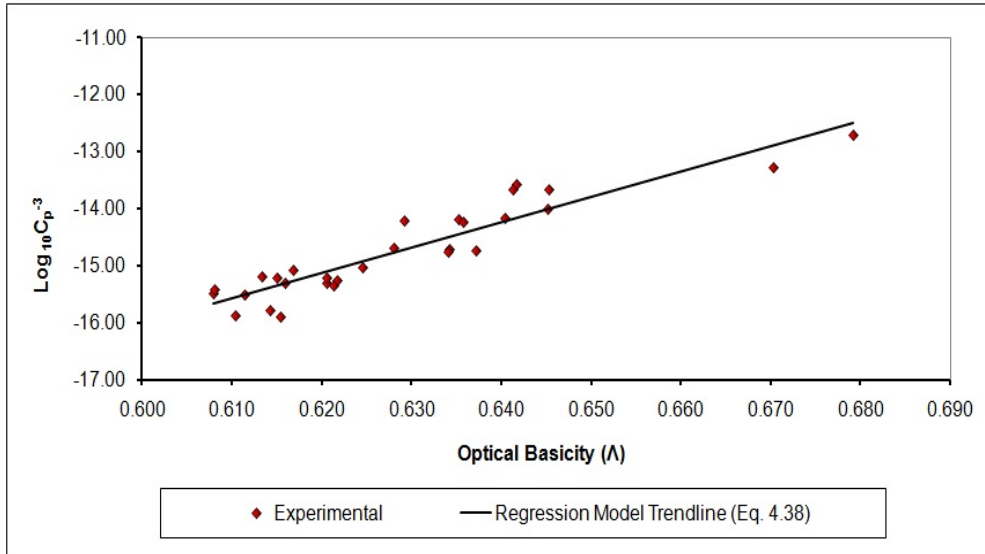


Figure 4.29 The relationship between optical basicity (Λ) and phosphide capacity in ferrochromium smelting process.

- **The variation of C_p^{-3} and L_p with CaO-to-MgO ratio ($X_{\text{CaO}}/X_{\text{MgO}}$) of ferrochromium smelting slags**

The change of phosphide capacity and phosphorus distribution ratio between slag and metal phases of ferrochromium smelting slag with CaO-to-MgO ratio of the slag system is illustrated in Figures 4.30, 4.31 and Figures G 6.1 and G 6.2 in Appendix G6.

The logarithm of phosphide capacity increases from -15.209 to -14.235 with increasing CaO-to-MgO ratio from 0.078 to 0.725 as presented in Figure 4.30. The positive impact of CaO-to-MgO ratio on the logarithm of phosphorus distribution ratio has also been observed in Figure 4.31. However, the amount of SiO_2 is not constant and any change in the silica content of slag can have significant effect on the correlations.

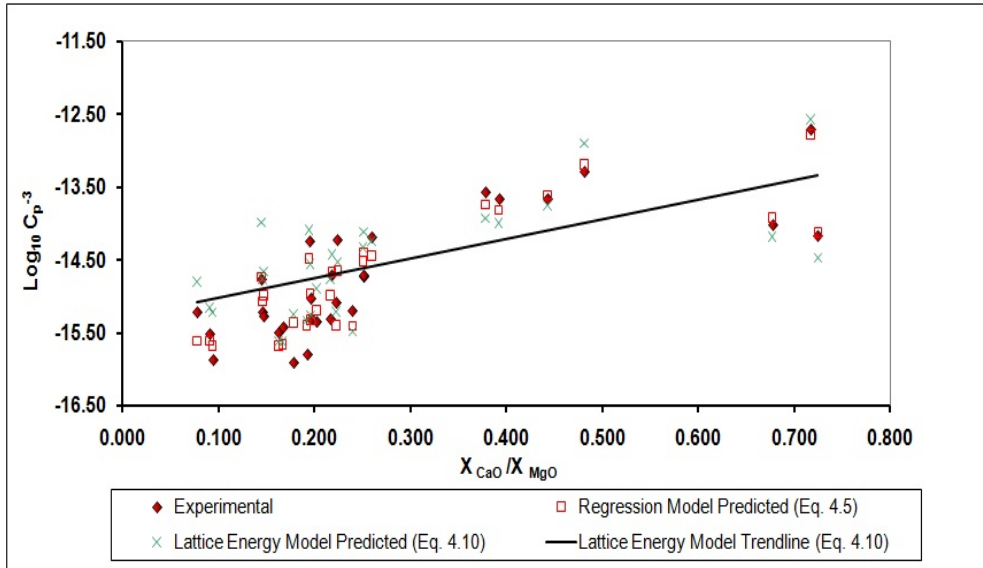


Figure 4.30 The effect of CaO-to-MgO ratio (X_{CaO}/X_{MgO}) on the phosphide capacity of ferrochromium smelting slag; Basicity Ratio: 1.250-2.781, X_{SiO_2} : 0.2246-0.3841, X_{CaO} : 0.0358- 0.2610 X_{MgO} : 0.2949-0.4945

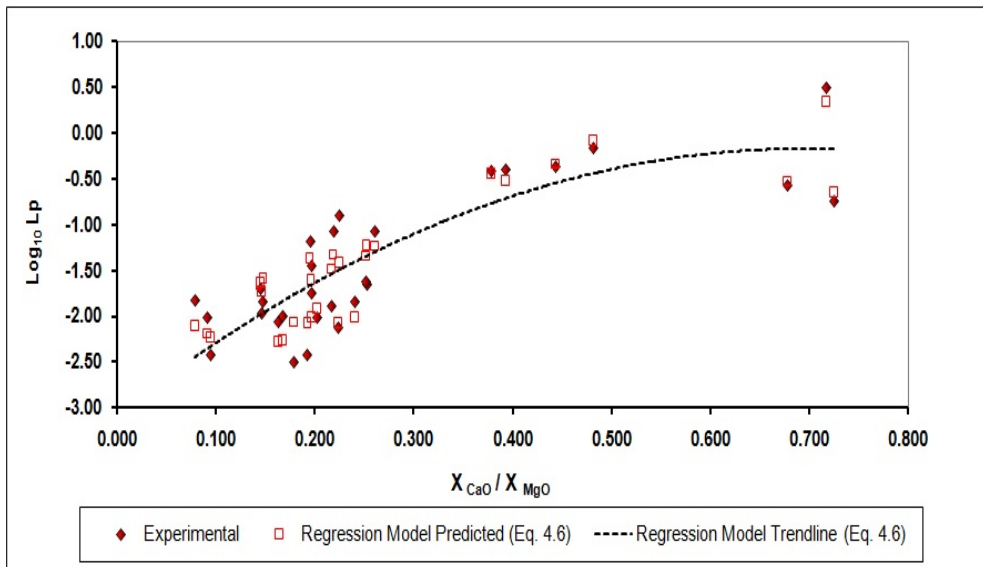


Figure 4.31 The effect of CaO-to-MgO ratio (X_{CaO}/X_{MgO}) on the phosphorus distribution ratio of ferrochromium smelting slag; Basicity Ratio: 1.250-2.781, X_{SiO_2} : 0.2246-0.3841, X_{CaO} : 0.0358- 0.2610 X_{MgO} : 0.2949-0.4945

The real impact of CaO-to-MgO ratio on the phosphorus behaviour can be observed in Figures G 6.1 and G 6.2, where SiO₂ and Al₂O₃ contents kept in narrow ranges.

According to the free energy of formation values, Ca₂SiO₄ is more stable than CaMgSiO₄ which is more stable than Mg₂SiO₄. This shows that the interaction of Ca⁺² with SiO₂ is stronger than that of mixed Ca⁺² and Mg⁺² ions and individual Mg⁺² ions. As the concentration of CaO increases, the silica network is significantly disrupted and broken into the smaller anionic groups which eventually results in lower slag viscosity and the proportion of free oxygen ions increases. These improved conditions ultimately lead higher the phosphide capacity values of the slags which assist the dephosphorisation of metal.

- **The relationship between phosphide capacity (C_p^{-3}) and lattice energy of oxides (binding energy of O⁻² ion in the mixture) ($\overline{E_o}$) of ferrochromium smelting slag**

In Figure 4.32, the relationship between C_p^{-3} and binding energy of O⁻² ion in the mixture (lattice energy of the oxides) ($\overline{E_o}$) of ferrochromium smelting slag system is given.

The binding energies of O⁻² ion in the mixture (lattice energy of the oxides) ($\overline{E_o}$) of the slag system have been calculated by using Eq. 2.178. The derivation of correlation between logarithm of phosphide capacity and binding energy of O⁻² ion in the mixture is explained in subsections 2.9.2 and 4.3. In a previous study, a linear correlation between binding energy of the 1s shell in O⁻² and optical basicity has been observed (Duffy et al., 1978). Therefore, the addition of CaO and MgO based oxides significantly reduces the binding energy. When the cations Si⁺⁴ and Al⁺³ are replaced with Ca⁺² or Mg⁺² cations, the polarisation between the cations and the O⁻² tends to decrease. This results in an increase in the bond length between the cation and O⁻² ion and consequently reduces the bond strength

(Moore, 1990). Based on the arguments raised in section 2.9.2 and 4.3, a linear correlation between binding energy of the slag system and logarithm of phosphide capacity is expected. It is clear from Figure 4.32 and Eq. 4.10 that the logarithm of phosphide capacity decreases with increasing binding energy of O^{2-} in the mixture. The high correlation coefficient value ($R^2=0.801$) of Eq. 4.10 indicates a good curve fitting.

$$\text{Log } C_p^{-3} = -0.007 \cdot \overline{E_o} + 21.102 \quad (4.10)$$

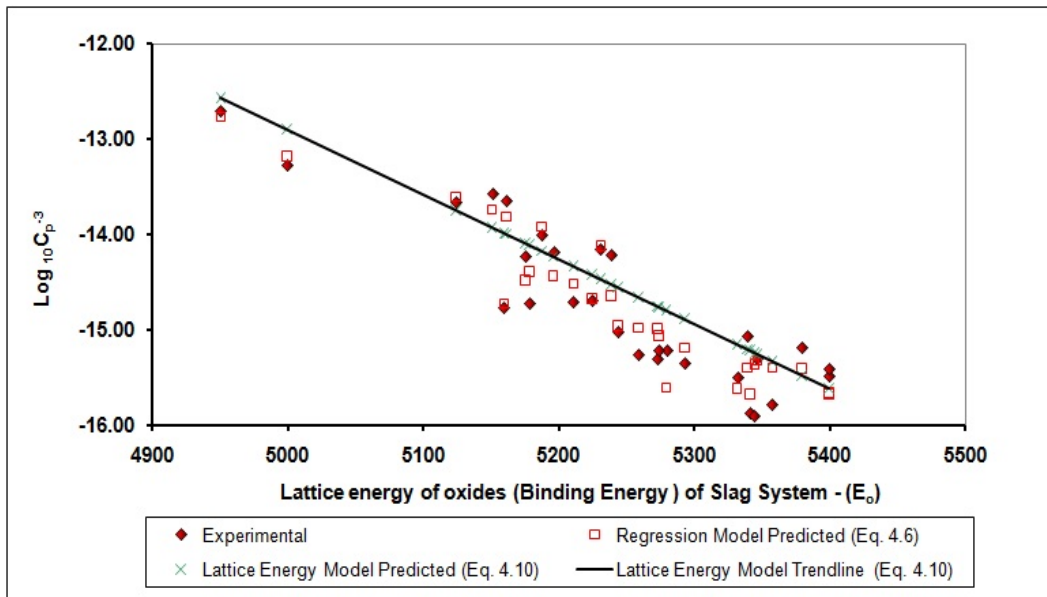


Figure 4.32 The relationship between C_p^{-3} and lattice (binding) energy ($\overline{E_o}$) of ferrochromium smelting slag.

Ternary diagram of quaternary $MgO-CaO-SiO_2-25 \text{ wt.}\% Al_2O_3$ slag system is given in Figure 4.33 (Verein Deutscher Eisenhuttenteute, 1981). The solid lines in the liquid region represent iso-phosphide capacity lines which have been determined by using Eq. 4.10 according to the slag compositions. In Figure 4.33, the lattice (binding) energy model predicted phosphide capacity trends of $MgO-CaO-SiO_2-25 \text{ wt.}\% Al_2O_3$ slag system is illustrated. According to Figure 4.33, the phosphide capacities of the slag system is highly dependant on SiO_2 and CaO

content of the slag. The influence of MgO on the phosphide capacity trends is found in less extent compared to CaO and SiO₂.

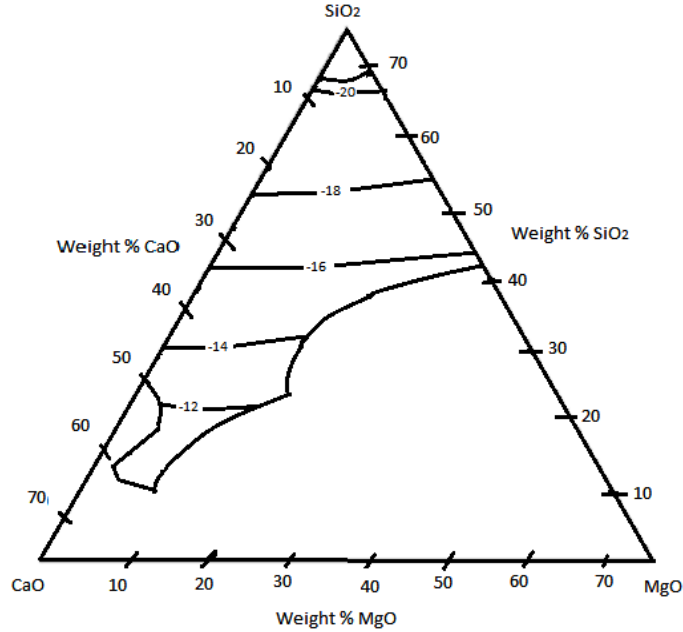


Figure 4.33 Predicted iso-phosphide capacity lines based on lattice (binding) energy model (Eq. 4.10) in MgO-CaO-SiO₂-25 wt.% Al₂O₃ quaternary phase diagram at 1600 °C.

- The relationship between phosphide capacity (C_p^{-3}) and activity of calcium oxide in ferrochromium smelting slag system at 1600 °C

The activity of CaO has been determined by using the equations 4.21, 4.22, 4.23 and 4.24. The relationship between C_p^{-3} and activity of CaO of SiO₂-CaO-Al₂O₃-MgO-Ca₃P₂-Cr₂O₃ slag system is plotted at 1600°C when $P_{O_2} = 2.56 \times 10^{-16}$ atm in Figure 4.34. The regression equation between the logarithm of phosphide capacity and logarithm of activity of CaO in SiO₂-CaO-Al₂O₃-MgO-Ca₃P₂-Cr₂O₃ slag system is given in equation 4.40.

$$\text{Log} C_{p^{-3}} = 1.5268 \log a_{CaO} - 9.9003 \quad (4.40)$$

Equation 4.40 can be used to predict the phosphide capacity of ferrochromium smelting slag system by using calculated CaO's activities in the slag system. The linear nature regression equation has a moderate correlation coefficient ($R^2=0.752$) which can still be used confidently if the slag compositions fall within the range as given in this study.

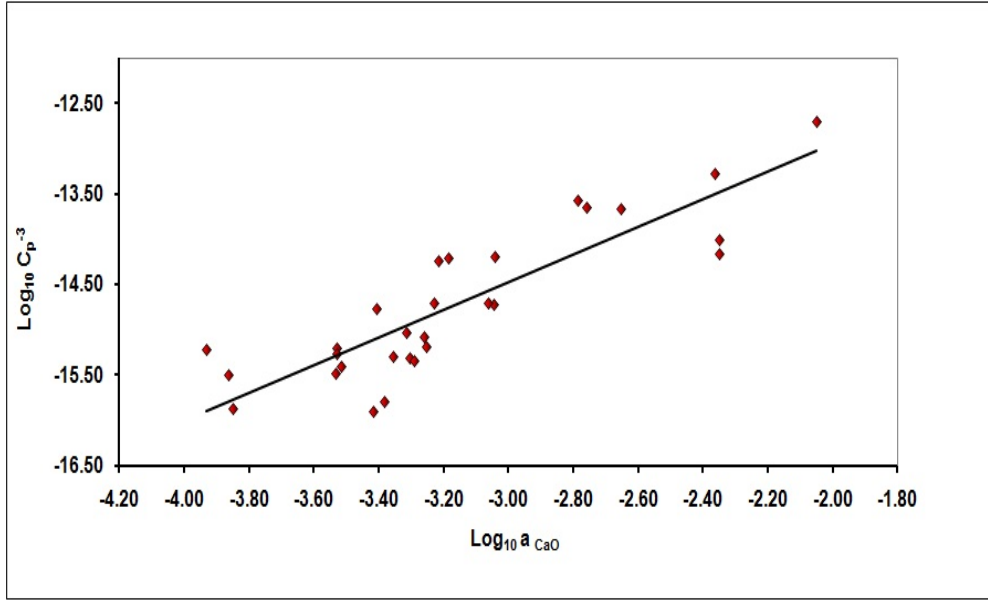
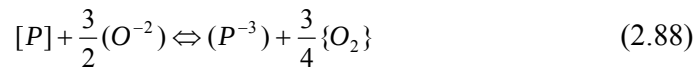


Figure 4.34 The relationship between phosphide capacity and calcium oxide activity in ferrochromium smelting slag.

If the activity of CaO is approximately proportional to the activity of O^{-2} and the composition dependence of f_P^{-3} is small, the slopes of $\log C_P^{-3}$ against $\log a_{CaO}$ are expected to be 1.5 on the basis of Eq. 2.88, 2.92 and 4.34. From this point of view, the experimental results (Slope =1.52) and theoretical assumption (Slope=1.5) are in excellent agreement and also agrees well with the results of Tabuchi and Sano (1983, 1984).



$$K_{2.88} = \frac{f_{P^{-3}} \cdot (P^{-3}) \cdot P_{O_2}^{3/4}}{f_P [P] \cdot a_{O^{-2}}^{3/2}} \quad (4.34)$$

$$C_{P^{-3}} = \frac{(P^{-3}) \cdot P_{O_2}^{3/4}}{[P] \cdot f_P} = K_{2.88} \cdot \frac{(a_{O^{-2}})^{3/2}}{(f_{P^{-3}})} \quad (2.92)$$

- **Chromium in SiO₂-CaO-Al₂O₃-MgO-Ca₃P₂-Cr₂O₃ slag system**

In this part of the study, a method explained in subsection (Chromium in SiO₂-CaO-Al₂O₃-MgO-CaS-Cr₂O₃ slag system) of 4.4.1, has been used to analyze the chromium behaviour in SiO₂-CaO-Al₂O₃-MgO-Ca₃P₂-Cr₂O₃ slag system by calculating the approximate values of CrO and CrO_{1.5} contents of the slag system.

The relationship between chromium and iron distribution ratio has been plotted with a slope of 1.11 as given in Figure 4.35. The chromium is found mainly in divalent state (CrO) in SiO₂-CaO-Al₂O₃-MgO-Ca₃P₂-Cr₂O₃ slag system under carbon monoxide atmosphere at 1600 °C. (If the value of slope is close to 1, the chromium in the slag is present as mainly in the divalent state. If the slope value is close to 1.5, the chromium can be assumed in the trivalent state). This value indicates that CrO in the slag is 74.06 per cent of chromium oxides and 25.94 per cent of the chromium oxides in the trivalent state (Cr₂O₃). This result is consistent with those Akyuzlu (1989), Pan (1998) as well as the results of the present work given in subsection 4.4.1. However, the data is widely scattered and any presence of metallic chromium due to the entrapment might influence the conclusion significantly.

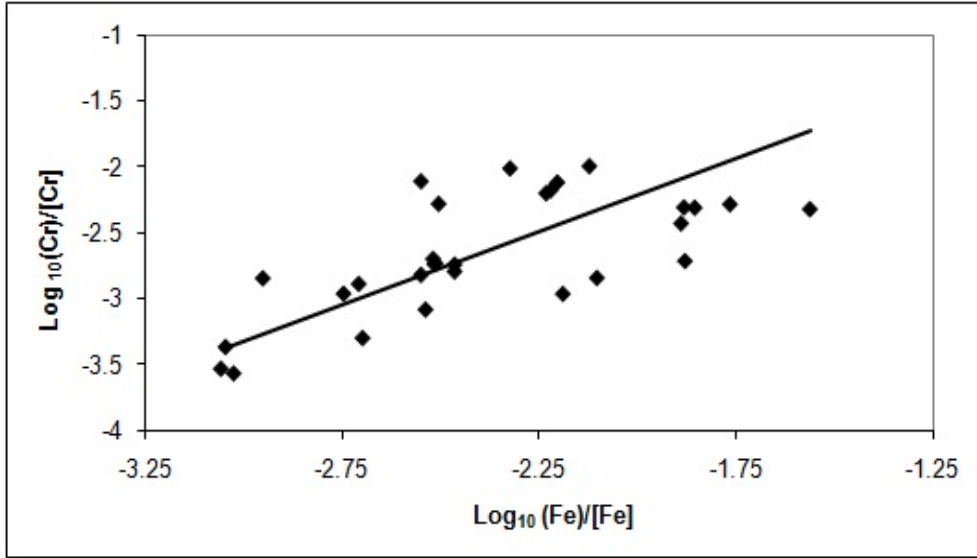


Figure 4.35 The relationship between C_p^{-3} and activity of CaO of SiO_2 -CaO Al_2O_3 -MgO- Ca_3P_2 - Cr_2O_3 slag system.

4.4.3 Sulphur distribution and sulphide capacity relevant to ferromanganese smelting process

The calculated values of molar fraction of components, basicity ratio, optical basicity, lattice energy of component oxides, activity coefficient of sulphur, sulphide capacity, sulphur distribution ratio between slag and metal and regression models pertinent to ferromanganese smelting (1500 °C, CO gas atmosphere) is given in Table 4.9. The chemical analysis and experimental temperature's relative errors are presented in the calculated values of activity coefficient of sulphur, sulphide capacity and sulphur distribution ratio (Table 4.9).

The sulphur distribution ratio (L_s) is calculated by using equation 4.1 by using weight percentages of sulphur in slag and metal phases. Basicity ratio of the slag is calculated by using mole fraction of CaO, MgO and SiO_2 values (Eq. 4.2). The optical basicity of slag is calculated according to equation 2.104 by using optical basicity values of several slag species in Table 2.8. Lattice energy of component oxides is calculated by using Equation 2.178. The calculation procedure of

activity coefficient of sulphur relevant to ferromanganese smelting is given in Appendix C. The sulphide capacity of ferromanganese slags is calculated according to Equation 2.30. Equations 4.7, 4.8 and 4.11 are used in the calculation of regression models values related to sulphide capacity, sulphur distribution ratio between slag and metal phases, lattice (binding) energy, respectively.

Table 4.9 Calculated values of molar fraction of components, basicity ratio, optical basicity, lattice energy of component oxides, activity coefficient of sulphur, sulphide capacity, sulphur distribution ratio and regression models pertinent to ferromanganese smelting (1500 °C, CO gas atmosphere)

Experiment Number	Final Slag Composition in Mole Fraction							Basicity Ratio	Optical Basicity	Lattice Energy of Component Oxides	Activity Coefficient of Sulphur	Log ₁₀ (fs)	Ls	Log ₁₀ (Ls)	C _s ⁻²	Log ₁₀ (C _s ⁻²)	Log ₁₀ (Ls)	Log ₁₀ (C _s ⁻²)	Log ₁₀ (C _s ⁻²)
	X SiO ₂	X Al ₂ O ₃	X MgO	X FeO	X CaO	X MnO	X CaS		(A)	(Eo)	(fs)						(Calculated based on Eq. 4.8)	(Calculated based on Eq. 4.7)	(Calculated based on Eq. 4.11)
1	0.4412	0.0367	0.1692	0.0001	0.2339	0.1053	0.0134	0.914	0.639	5470.90	23.79 ± 1.83	1.376	21.294 ± 0.852	1.328	9.84E-09 ± 1.02E-09	-8.007	1.273	-8.056	-8.055
2	0.4477	0.0364	0.1683	0.0003	0.2310	0.1032	0.0127	0.892	0.637	5487.61	29.23 ± 2.41	1.466	23.702 ± 0.948	1.375	8.92E-09 ± 9.77E-10	-8.050	1.275	-8.065	-8.085
3	0.4538	0.0365	0.1684	0.0004	0.2317	0.0965	0.0125	0.882	0.634	5502.62	26.01 ± 2.09	1.415	19.171 ± 0.767	1.283	8.11E-09 ± 8.67E-10	-8.091	1.276	-8.078	-8.112
4	0.4276	0.0323	0.2188	0.0004	0.1760	0.1351	0.0096	0.923	0.640	5444.82	21.54 ± 1.59	1.333	17.467 ± 0.699	1.242	8.92E-09 ± 8.95E-10	-8.050	1.181	-8.029	-8.007
5	0.4392	0.0319	0.2163	0.0002	0.1802	0.1262	0.0057	0.903	0.636	5469.41	17.87 ± 1.23	1.252	13.565 ± 0.543	1.132	8.35E-09 ± 7.92E-10	-8.078	1.174	-8.047	-8.052
6	0.4573	0.0381	0.1722	0.0003	0.1938	0.1248	0.0133	0.800	0.631	5521.62	26.39 ± 2.12	1.421	18.559 ± 0.743	1.269	7.74E-09 ± 8.28E-10	-8.112	1.310	-8.113	-8.147
7	0.3733	0.0329	0.2222	0.0006	0.2963	0.0595	0.0151	1.389	0.665	5274.07	17.46 ± 1.23	1.242	25.119 ± 1.005	1.400	1.58E-08 ± 1.53E-09	-7.801	1.430	-7.711	-7.696
8	0.3794	0.0324	0.2221	0.0007	0.2932	0.0565	0.0155	1.358	0.662	5292.20	14.24 ± 0.91	1.154	28.426 ± 1.138	1.454	2.20E-08 ± 1.97E-09	-7.658	1.434	-7.714	-7.729
9	0.3979	0.0515	0.2665	0.0002	0.2289	0.0358	0.0190	1.245	0.640	5374.41	40.07 ± 3.69	1.603	43.748 ± 1.751	1.641	1.20E-08 ± 1.44E-09	-7.920	1.655	-7.912	-7.879
10	0.3593	0.0384	0.1881	0.0008	0.3662	0.0284	0.0188	1.543	0.675	5223.18	20.94 ± 1.55	1.321	55.319 ± 2.214	1.743	2.91E-08 ± 2.92E-09	-7.537	1.670	-7.605	-7.604
11	0.3646	0.0382	0.1891	0.0007	0.3658	0.0241	0.0174	1.522	0.673	5236.98	18.92 ± 1.34	1.277	52.967 ± 2.120	1.724	3.08E-08 ± 2.99E-09	-7.512	1.656	-7.620	-7.629
12	0.3574	0.0371	0.2135	0.0004	0.3469	0.0254	0.0193	1.568	0.672	5222.91	16.44 ± 1.11	1.216	42.857 ± 1.715	1.632	2.87E-08 ± 2.67E-09	-7.542	1.700	-7.562	-7.603
13	0.3665	0.0365	0.2130	0.0012	0.3409	0.0244	0.0174	1.512	0.668	5248.18	18.90 ± 1.33	1.276	51.915 ± 2.077	1.715	3.02E-08 ± 2.92E-09	-7.520	1.655	-7.601	-7.649
14	0.3818	0.0408	0.1505	0.0004	0.3775	0.0247	0.0241	1.383	0.667	5290.60	28.17 ± 2.28	1.450	46.560 ± 1.863	1.668	1.82E-08 ± 1.96E-09	-7.740	1.674	-7.679	-7.726
15	0.3863	0.0404	0.1511	0.0005	0.3798	0.0249	0.0170	1.375	0.667	5294.78	24.26 ± 1.87	1.385	38.388 ± 1.536	1.584	1.74E-08 ± 1.80E-09	-7.759	1.583	-7.732	-7.734
16	0.3905	0.0407	0.1469	0.0006	0.3825	0.0222	0.0165	1.356	0.666	5305.43	25.34 ± 1.99	1.404	37.243 ± 1.490	1.571	1.62E-08 ± 1.70E-09	-7.791	1.578	-7.745	-7.753
17	0.4249	0.0424	0.2748	0.0006	0.1681	0.0746	0.0144	1.042	0.630	5450.80	30.47 ± 2.58	1.484	23.887 ± 0.956	1.378	8.62E-09 ± 9.64E-10	-8.064	1.446	-7.965	-8.018
18	0.3666	0.0462	0.1152	0.0004	0.4353	0.0149	0.0213	1.501	0.679	5233.37	26.73 ± 2.13	1.427	67.675 ± 2.708	1.830	2.78E-08 ± 2.96E-09	-7.555	1.824	-7.583	-7.622
19	0.3652	0.0461	0.1223	0.0004	0.4310	0.0144	0.0206	1.515	0.679	5229.66	27.51 ± 2.22	1.440	69.813 ± 2.794	1.844	2.79E-08 ± 3.01E-09	-7.554	1.815	-7.592	-7.616
20	0.3699	0.0463	0.1176	0.0010	0.4323	0.0131	0.0197	1.486	0.677	5242.10	26.08 ± 2.06	1.416	62.941 ± 2.519	1.799	2.65E-08 ± 2.81E-09	-7.576	1.805	-7.606	-7.638
21	0.3519	0.0425	0.1674	0.0008	0.3976	0.0181	0.0216	1.605	0.680	5199.36	27.18 ± 2.19	1.434	57.816 ± 2.314	1.762	2.34E-08 ± 2.51E-09	-7.631	1.808	-7.556	-7.560
22	0.3564	0.0415	0.1715	0.0007	0.3929	0.0174	0.0196	1.584	0.678	5210.87	25.07 ± 1.96	1.399	50.139 ± 2.006	1.700	2.20E-08 ± 2.30E-09	-7.658	1.766	-7.578	-7.581
23	0.3581	0.0415	0.1688	0.0013	0.3923	0.0170	0.0209	1.567	0.677	5217.07	26.49 ± 2.10	1.423	53.287 ± 2.132	1.727	2.21E-08 ± 2.35E-09	-7.655	1.780	-7.574	-7.593
24	0.4055	0.0346	0.1932	0.0010	0.2613	0.0883	0.0159	1.121	0.653	5372.84	15.68 ± 1.03	1.195	20.397 ± 0.816	1.310	1.43E-08 ± 1.31E-09	-7.845	1.301	-7.917	-7.876
25	0.4180	0.0336	0.1955	0.0021	0.2571	0.0811	0.0124	1.083	0.647	5403.40	13.78 ± 0.86	1.139	13.204 ± 0.528	1.121	1.05E-08 ± 9.23E-10	-7.977	1.287	-7.936	-7.932
26	0.4176	0.0353	0.2015	0.0005	0.2501	0.0803	0.0145	1.081	0.646	5407.26	17.86 ± 1.23	1.252	19.343 ± 0.774	1.287	1.19E-08 ± 1.13E-09	-7.924	1.304	-7.955	-7.939
27	0.4286	0.0342	0.1950	0.0003	0.1835	0.1502	0.0079	0.883	0.643	5443.86	17.40 ± 1.19	1.240	14.160 ± 0.567	1.151	8.95E-09 ± 8.42E-10	-8.048	1.143	-8.093	-8.005
28	0.4356	0.0337	0.1932	0.0005	0.1753	0.1458	0.0157	0.846	0.638	5472.60	25.51 ± 2.00	1.407	21.744 ± 0.870	1.337	9.38E-09 ± 9.85E-10	-8.028	1.251	-8.042	-8.058
29	0.4450	0.0336	0.1930	0.0010	0.1759	0.1381	0.0131	0.829	0.635	5493.78	19.96 ± 1.44	1.300	15.372 ± 0.615	1.187	8.47E-09 ± 8.32E-10	-8.072	1.264	-8.051	-8.096
30	0.4196	0.0323	0.1512	0.0008	0.2505	0.1305	0.0149	0.957	0.653	5409.78	16.17 ± 1.08	1.209	13.847 ± 0.554	1.141	9.42E-09 ± 8.72E-10	-8.026	1.217	-7.962	-7.943
31	0.4276	0.0333	0.1525	0.0006	0.2577	0.1127	0.0155	0.959	0.649	5430.51	17.38 ± 1.19	1.240	21.667 ± 0.867	1.336	1.37E-08 ± 1.29E-09	-7.863	1.267	-7.961	-7.981
32	0.4311	0.0325	0.1521	0.0033	0.2522	0.1149	0.0137	0.938	0.647	5438.93	18.33 ± 1.28	1.263	16.614 ± 0.665	1.220	9.97E-09 ± 9.53E-10	-8.001	1.276	-7.952	-7.996
33	0.4005	0.0346	0.2339	0.0004	0.2442	0.0728	0.0134	1.194	0.650	5361.77	19.86 ± 1.43	1.298	21.590 ± 0.864	1.334	1.20E-08 ± 1.18E-09	-7.922	1.346	-7.862	-7.856
34	0.4118	0.0418	0.2657	0.0006	0.1843	0.0753	0.0202	1.093	0.636	5418.61	28.10 ± 2.29	1.449	36.038 ± 1.442	1.557	1.41E-08 ± 1.53E-09	-7.851	1.492	-7.910	-7.959
35	0.4218	0.0409	0.2617	0.0011	0.1834	0.0751	0.0159	1.055	0.633	5439.76	27.65 ± 2.25	1.442	31.607 ± 1.265	1.500	1.26E-08 ± 1.36E-09	-7.901	1.432	-7.956	-7.998
36	0.4276	0.0412	0.2625	0.0004	0.1880	0.0666	0.0134	1.053	0.631	5451.41	29.87 ± 2.52	1.475	25.828 ± 1.034	1.412	9.51E-09 ± 1.06E-09	-8.022	1.409	-7.981	-8.019
37	0.3770	0.0360	0.1921	0.0002	0.3385	0.0389	0.0171	1.407	0.667	5277.46	19.74 ± 1.44	1.295	38.694 ± 1.548	1.588	2.16E-08 ± 2.14E-09	-7.666	1.525	-7.704	-7.703
38	0.3844	0.0356	0.1895	0.0004	0.3365	0.0362	0.0172	1.368	0.663	5298.57	21.86 ± 1.64	1.340	39.463 ± 1.579	1.596	1.99E-08 ± 2.02E-09	-7.702	1.514	-7.721	-7.741
39	0.4013	0.0373	0.2168	0.0002	0.2674	0.0565	0.0203	1.206	0.650	5366.96	22.96 ± 1.74	1.361	26.102 ± 1.045	1.417	1.25E-08 ± 1.28E-09	-7.903	1.453	-7.848	-7.865
40	0.4039	0.0372	0.2164	0.0002	0.2687	0.0568	0.0167	1.201	0.649	5365.78	20.66 ± 1.50	1.315	23.892 ± 0.956	1.378	1.27E-08 ± 1.26E-09	-7.895	1.411	-7.874	-7.871
41	0.4228	0.0455	0.2693	0.0003	0.2084	0.0360	0.0175	1.130	0.630	5440.41	27.67 ± 2.28	1.442	32.967 ± 1.319	1.518	1.31E-08 ± 1.43E-09	-7.882	1.536	-7.943	-7.999

- The variation of C_S^{-2} and L_S with silica (X_{SiO_2}) in ferromanganese smelting slags

The change of sulphide capacity and sulphur distribution ratio with silica content (in mole fraction) of ferromanganese smelting slag at 1500 °C under carbon monoxide atmosphere ($P_{O_2}: 1.21 \times 10^{-16}$ atm) are illustrated in Figures 4.36, 4.37 and Figs H 1.1 to H 1.4 in Appendix H1.

The logarithm of sulphide capacity drops from -7.630 to -8.115 when the mole fraction of silica rises from 0.3519 to 0.4572 (Fig. 4.36). The results shown in Figure 4.37 also demonstrates that the logarithm of sulphur distribution ratio between slag and metal decreases with increasing silica content in the slag. The influence of other slag components on the sulphur behaviour hasn't been included hence the real influence of silica on the sulphur behaviour can be analysed by using the results of Figures H 1.1 to H 1.4 where the contents of other components have been kept in a narrow range.

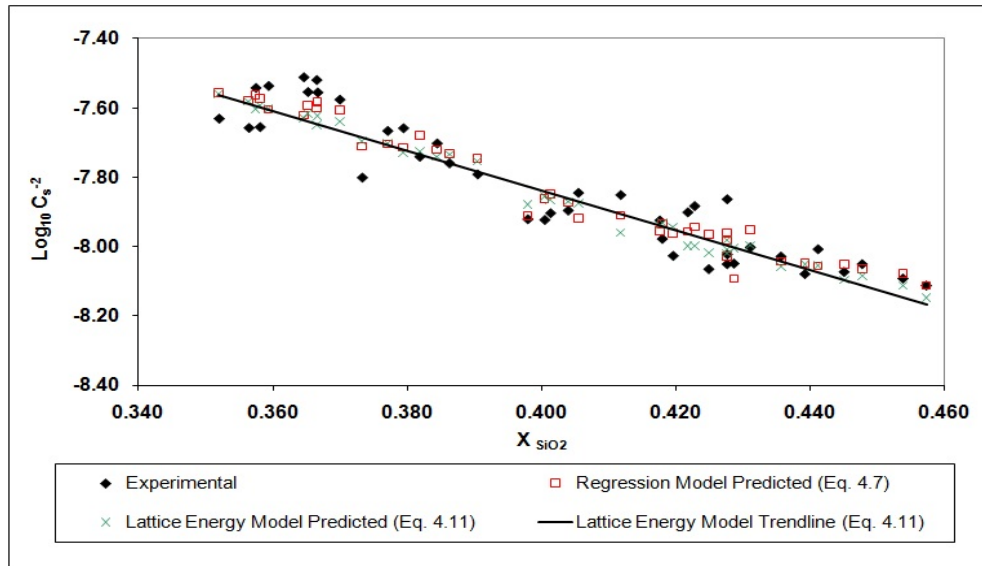


Figure 4.36 The variation of sulphide capacity with silica mole fraction (X_{SiO_2}) of ferromanganese smelting slag; Basicity Ratio: 0.800-1.605, X_{CaO} : 0.1680-0.4352, X_{MgO} : 0.1152-0.2748, X_{MnO} : 0.0130-0.1381

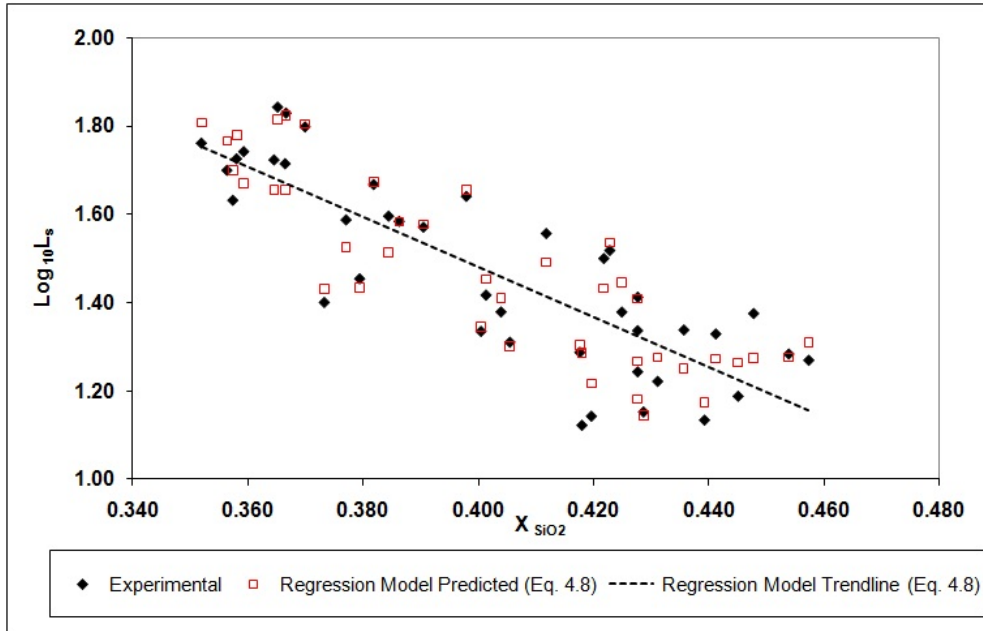


Figure 4.37 The variation of sulphur distribution ratio with silica mole fraction (X_{SiO_2}) of ferromanganese smelting slag; Basicity Ratio: 0.800-1.605, X_{CaO} : 0.1680-0.4352, X_{MgO} : 0.1152-0.2748, X_{MnO} : 0.0130-0.1381

The logarithm of sulphide capacity have been plotted as a function of silica content for constant CaO, MgO contents and basicity ratios (Figures H 1.1 and H 1.3). The sulphide capacity decreases with increasing silica content in the slag. These results exhibit good agreement with the results of previous studies (Nilsson et al., 1994a; Nilsson et al., 1997, Nzotta et al., 1997). The results of Nilsson et al. (1994a) elucidated that the sulphide capacities of CaO-MnO-SiO_2 slags were inversely proportional to the silica content of the slag phase. They also pointed out the similar influence of silica content on the sulphide capacities of $\text{Al}_2\text{O}_3\text{-CaO-SiO}_2$ ternary slag system at 1500 °C. Nzotta et al., (1997) determined the sulphide capacities of MgO-SiO_2 slags at 1600 °C. It is seen that the C_s values decreases from 1.956×10^{-5} to 1.456×10^{-5} when the molar fraction of silica increases from 0.523 to 0.545 in the binary slag system. In a later study conducted on the electric arc furnaces slags clearly demonstrated the negative impact of silica on the sulphide capacities (Nzotta et al, 1999b). This phenomenon can be explained by

considering reaction 2.136 and 2.142. This particular mechanism were explained in subsection (The variation of C_S^{-2} and L_S with silica (X_{SiO_2}) in ferrochromium smelting slags) of 4.4.1.

The influence of silica content of the slag phase on the logarithm of sulphur distribution ratio between slag and metal is illustrated in Figures H.1.2 and H 1.4 which show that the equilibrium distribution of sulphur is inversely proportional to the content of silica in the slag phase. As explained in subsection (The variation of C_S^{-2} and L_S with silica (X_{SiO_2}) in ferrochromium smelting slags) of 4.4.1, the oxygen consuming reaction of silica (2.136) results in a reduction in the activity of oxygen anions in the slag system. The partition ratio of sulphur can be determined by using the equilibrium constant of desulphurisation reaction of metal (2.142). According to equation 2.143, the partition ratio of sulphur is directly proportional to the activity of oxygen anions. A decrease in the activity of oxygen anions leads to a decrease in the partition ratio of sulphur between slag and metal.

Also, the desulphurisation reaction enhance with the increasing Me_xS activity in the slag. The activity coefficient of sulphide ions in $CaO-SiO_2$ and $Al_2O_3-MnO-SiO_2$ slags were found to be inversely proportional to the silica concentration of the slag (Hino et al., 1993). However, at high basicities ($X_{SiO_2} < 0.5$), the trend is reversed and γ_s^{-2} decreases as the concentration of oxygen ions increases (Sharma and Richardson, 1965). In the present study, the slag compositions are within the low basicity regions. Therefore, the replacement of basic oxides with acidic oxides such as silica results in a decrease in the activity of basic oxides in the slag system, which ultimately limit the transfer of sulphur from metal to slag phase.

- The variation of C_S^{-2} and L_S with calcium oxide (X_{CaO}) in ferromanganese smelting slags

The effect of calcium oxide content of the slags on the logarithm of C_S^{-2} and L_S is presented in Figures 4.38, 4.39 and Figures H 2.1 to H 2.4 (in Appendix H2). The results from experiments indicate that the logarithm of sulphide capacity and sulphur distribution ratio increase with increasing amount of the calcium oxide content in the slag.

The relation between logarithm of sulphide capacity and calcium oxide content (in mole fraction) is annotated in Figure 4.38. It is seen that an increase in calcium oxide content of slag from 0.1680 to 0.4352 causes the logarithm of sulphide capacity to rise from -8.064 to -7.556 (Fig. 4.38). However, it should be noted that the other slag constituents haven't been kept in narrow ranges in this figure, the real effect of calcium oxide on the sulphide capacities of slag can be seen in Figures H 2.1 and H 2.3.

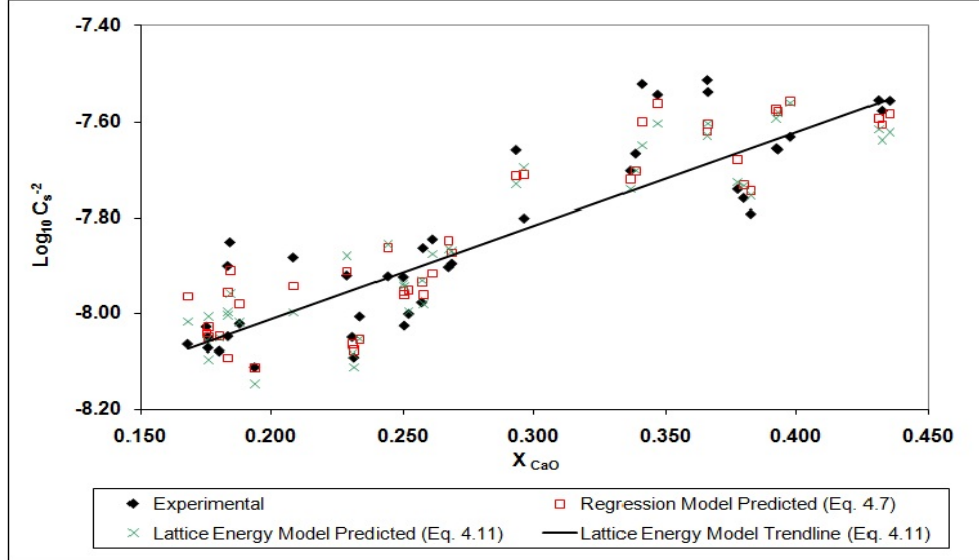


Figure 4.38 The variation of sulphide capacity with calcium oxide mole fraction (X_{CaO}) of ferromanganese smelting slag; Basicity Ratio: 0.800-1.605, X_{SiO_2} : 0.3519-0.4572, X_{MgO} : 0.1152-0.2748, X_{MnO} : 0.0130-0.1381

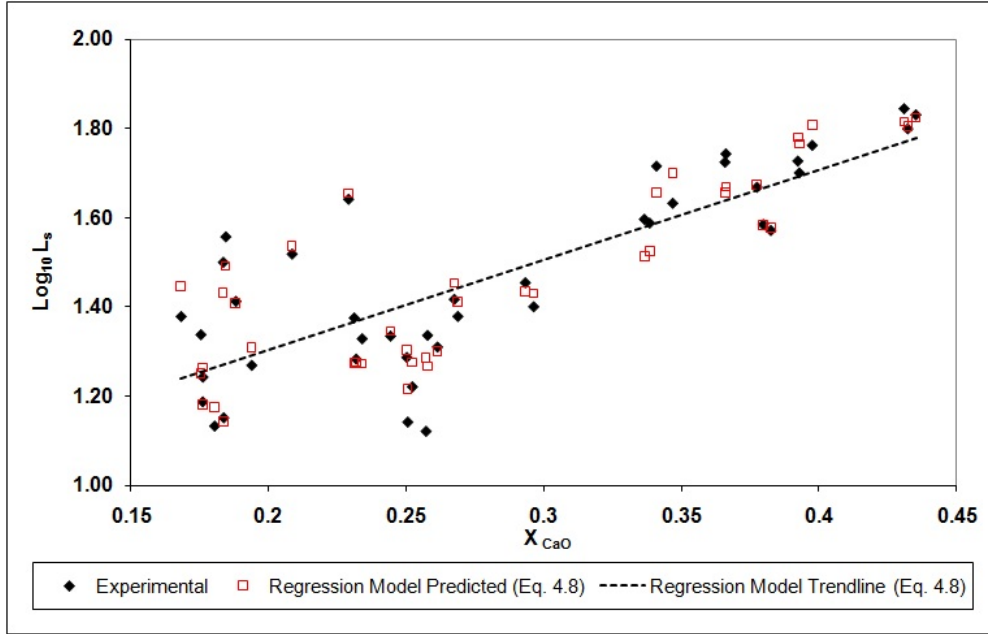
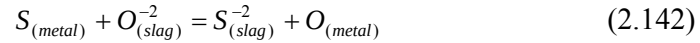


Figure 4.39 The variation of sulphur distribution ratio with calcium oxide mole fraction (X_{CaO}) of ferromanganese smelting slag; Basicity Ratio: 0.800-1.605, X_{SiO_2} : 0.3519-0.4572, X_{MgO} : 0.1152-0.2748, X_{MnO} : 0.0130-0.1381

Based on the results, the sulphide capacity is directly proportional to the mole fraction of calcium oxide in the slag phase. Calcium oxide acts as a network modifier and donates oxygen anions into the slag system. The enhanced oxygen ion concentration results in an improved desulphurisation of metallic phase.

The slag-metal equilibrium in terms of sulphur and oxygen species can be defined by using reaction 2.142.



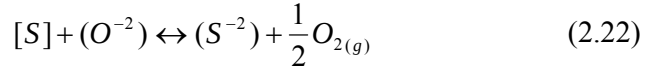
The ionization reaction of calcium oxide is given in equation 2.133.



According to the reaction 2.142, the desulphurisation can be enhanced by increasing the free O^{-2} anions in the slag. The dissociation reaction of calcium

oxide provides the free O^{-2} for the slag system and assists the removal of sulphur from the metal phase.

Richardson and Withers (1950) suggested that the sulphide capacity can be defined by using the transfer of sulphur between slag and metal phases under reducing atmosphere. As it is seen in equation 2.30, the sulphide capacity of slag is directly proportional to the activity of oxygen anions in the slag.



$$K_{2.22} = \frac{(a_{s^{-2}}).(P_{O_2})^{1/2}}{[a_s](a_{O^{-2}})} = \frac{(f_{s^{-2}}).(S^{-2}).(P_{O_2})^{1/2}}{[f_s][S](a_{O^{-2}})} \quad (2.29)$$

$$C_s = \frac{K_{2.22}.(a_{O^{-2}})}{(f_{s^{-2}})} = \frac{(S^{-2}).(P_{O_2})^{1/2}}{[f_s][S]} \quad (2.30)$$

Hino and Fuwa (1978) studied the influence of calcium oxide content of slag on the sulphide capacity of MnO-SiO₂-CaO ternary slag system at 1550 °C. The sulphide capacity was not significantly affected with the addition of CaO to the MnO-SiO₂ melt when the amount of silica was lower than the orthosilicate level ($N_{SiO_2}=0.33$). It was found that the further addition of CaO to the melt caused a significant increase in the sulphide capacity of the slag system. It should be noted that the silica content is higher than the orthosilicate composition in the current study and the similar influence of calcium oxide content can be expected on the sulphide capacity of ferromanganese smelting slag system. Reddy and Blander (1987) confirmed the positive impact of CaO content on the sulphide capacity of CaO-SiO₂ and related it to the large increase in the activity of CaO. The increase in the activity of CaO results in an increase in the concentration of free oxygen ions which increase the desulphurisation power of the slag. The activity of calcium sulphide tends to increase with the increase of calcium oxide content of the slag which eventually leads to higher sulphur removal from metal phase. Therefore, the conclusion of Reddy and Blander (1987) can be used as a supporting argument in the present work.

- The variation of C_S^{-2} and L_S with magnesium oxide (X_{MgO}) in ferromanganese smelting slags

The change of sulphide capacity and sulphur distribution ratio with magnesium oxide content (in mole fraction) of ferromanganese smelting slag are illustrated in Figures 4.40 to 4.43 and Figures H 3.1 and H 3.2 in Appendix H3.

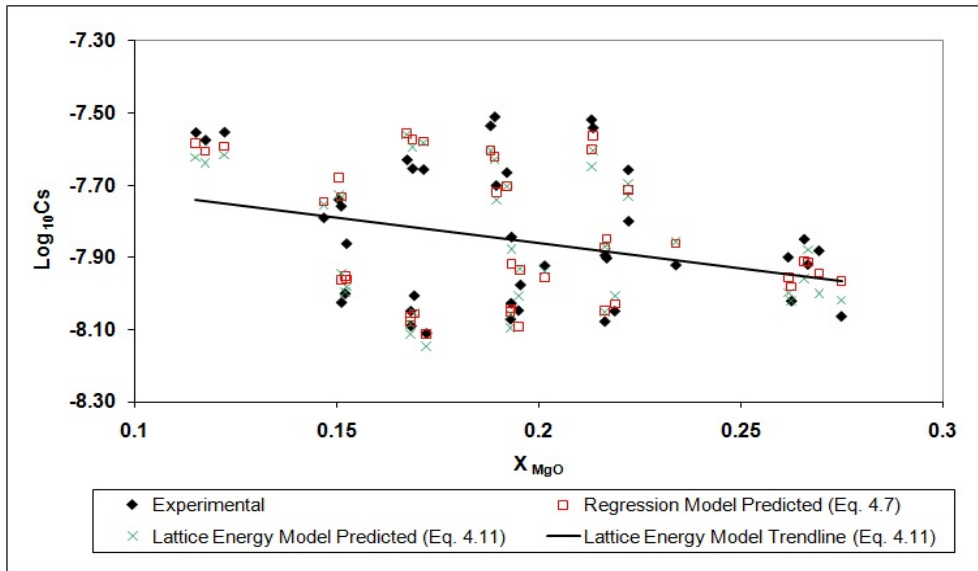


Figure 4.40 The variation of sulphide capacity with magnesium oxide mole fraction (X_{MgO}) of ferromanganese smelting slag; Basicity Ratio: 0.800-1.605, X_{SiO_2} : 0.3519-0.4572, X_{CaO} : 0.1680-0.4352, X_{MnO} : 0.0130-0.1381

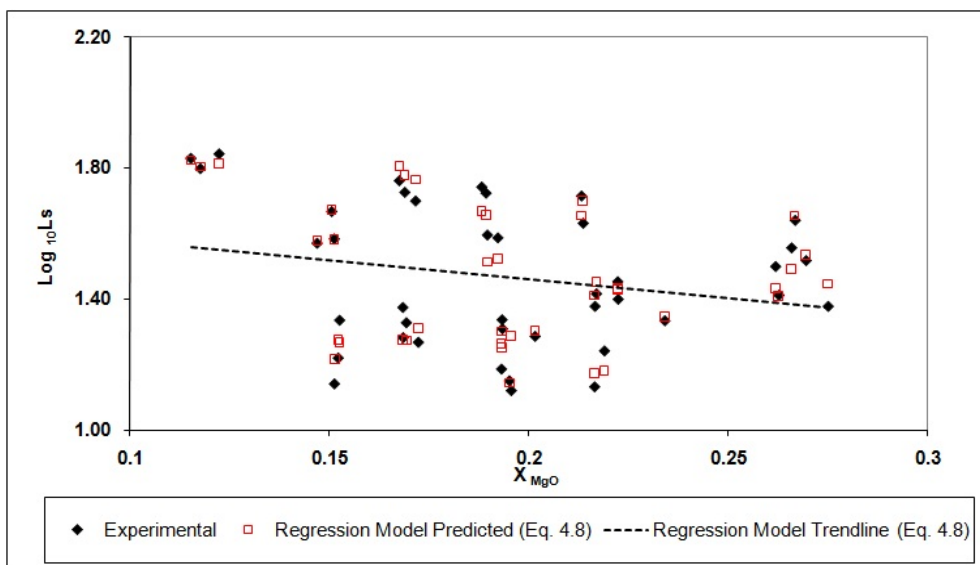


Figure 4.41 The variation of sulphur distribution ratio with magnesium oxide mole fraction (X_{MgO}) of ferromanganese smelting slag; Basicity Ratio: 0.800-1.605, X_{SiO_2} : 0.3519-0.4572, X_{CaO} : 0.1680-0.4352, X_{MnO} : 0.0130-0.1381

Magnesium oxide in the slag is generally considered to have a limited effect on the sulphur removal (Bodsworth and Bell, 1972; Shibata et al., 2004; Hino et al., 1993) as the sulphur distribution ratio between slag and metal is not changed of up to 10 mol. % of magnesia in lime-saturated slags (Bodsworth and Bell, 1972). The comparison of the free-energy changes of reactions between sulphur in the metal and the CaO and MgO in the slags shows that MgO is less powerful compared to CaO in the desulphurisation of metal (Bodsworth and Bell, 1972). The variation of the logarithm of sulphide capacities of ferromanganese smelting slags with the MgO content (in mole fraction) is presented in Fig. 4.40. In contrast to the basicity theory, it is seen that the MgO has a negative effect on the sulphide capacities of ferromanganese smelting slag under the present case. However, it should be noted that the other slag components have not been restricted and their amounts significantly affected the sulphur transfer from metal to slag. The sulphide capacity did not increase with the MgO content due to its weaker basic nature and relatively low content in the slag system. The real influence of MgO content on sulphur behaviour can be observed in Figures 4.42, 4.43, H 3.1 and H 3.2 in which desulphurisation power of the ferromanganese smelting slag

increases with increasing magnesium oxide content of slag. In MgO-SiO₂ slags, similar influence of MgO on the sulphide capacities of slags has been reported in different studies (Sharma and Richardson, 1965; Nzotta et al., 1997c).

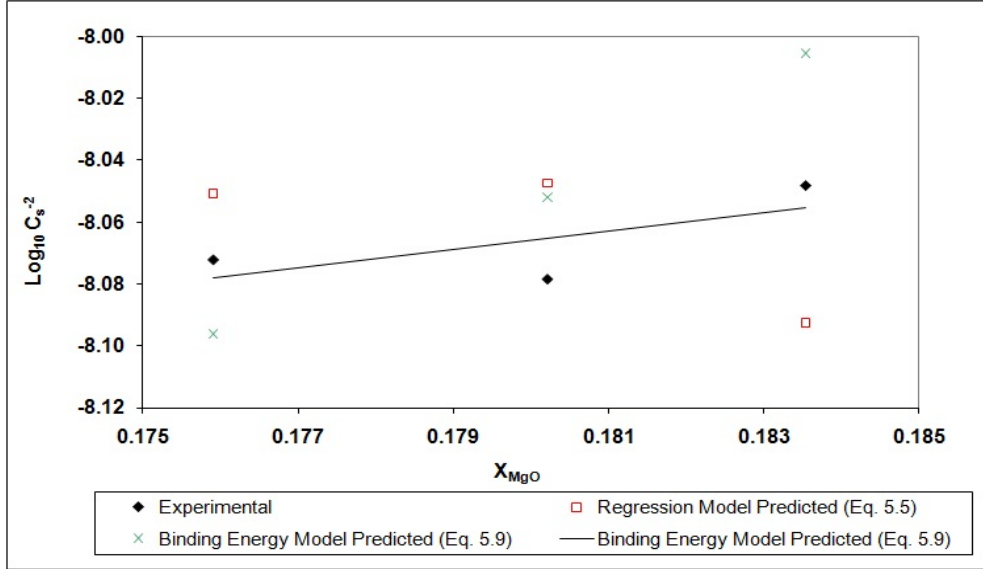


Figure 4.42 The variation of sulphide capacity with magnesium oxide mole fraction (X_{MgO}) of ferromanganese smelting slag; Basicity Ratio: 0.828-0.923, X_{SiO_2} : 0.4276-0.4538, X_{CaO} : 0.1759-0.2317

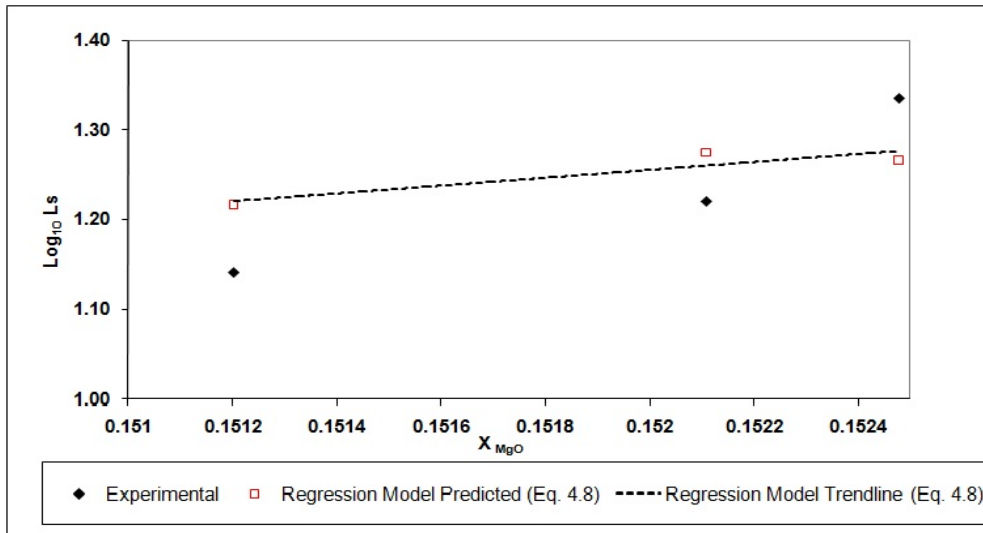
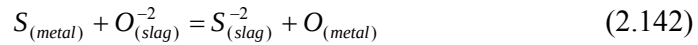


Figure 4.43 The variation of sulphur distribution ratio with magnesium oxide mole fraction (X_{MgO}) of ferromanganese smelting slag; Basicity Ratio: 0.937-0.957, X_{SiO_2} : 0.4195-0.4310, X_{CaO} : 0.2504-0.2576

As discussed in subsection (The variation of C_S^{-2} and L_S with magnesium oxide (X_{MgO}) in ferrochromium smelting slags) of 4.4.1, an increase in MgO concentration of the slag will ultimately enhance the concentration of free O^{-2} anions in the slag and results in an increase in the activity of O^{-2} anions. The increase in the activity of O^{-2} will help to shift reaction (2.19) and (2.22) to the right direction causing an increase in the desulphurisation capacity of slags. It is seen from Equation 2.30 that the sulphide capacity is directly proportional to the activity of O^{-2} in the slag, therefore the addition of MgO into the slag increases the sulphide capacity as expected. Similar influence of MgO content of slag are observed on the sulphide capacities of MgO-SiO₂ slags

According to Bodsworth and Bell (1972) when magnesia is added to the melt while holding the ratio of CaO/SiO₂ constant, the activity of oxygen ions in the slag system is raised which results in an increase in the partition ratio of sulphur between slag and metal phases. The results obtained agree well with those of Bodsworth and Bell (1972).

The equilibrium distribution of sulphur between slag and metal can be expressed by equation (4.41) derived from reaction (2.142). Increasing MgO content of the slag causes an increase in the amount of oxygen anions by the reaction (4.15). As a result, the sulphur removal from metal to slag is encouraged due to high oxygen anion concentration in the slag.



$$K_{2.142} = \frac{a_{O_{(M)}} \cdot a_{S_{(s)}}^{-2}}{a_{S_{(m)}} \cdot a_{O_{(s)}}^{-2}} \quad (2.143)$$



$$\frac{(X_s)}{[X_s]} = K_{2.142} \frac{(a_{O^{-2}}) [\gamma_s]}{[a_O] (\gamma_s)} \quad (4.41)$$

- The variation of C_S^{-2} and L_S with manganese oxide (X_{MnO}) in ferromanganese smelting slags

The effect of manganese oxide (X_{MnO}) on the logarithm of C_S^{-2} and L_S of ferromanganese smelting slags at 1500 °C under carbon monoxide atmosphere are presented in Figures 4.44 to 4.47 and Figures H 4.1 and H 4.2 in Appendix H4.

MnO content of the slag system is another critical factor on the sulphide capacities of the ferromanganese smelting slags. It is seems that from Figures 4.44 and 4.45 that manganese oxide (in mole fraction) display a negative effect on the sulphide capacity and sulphur distribution ratio between slag and metal. This is due to the fact that other slag oxides mask the true effect of MnO on sulphur behavior. The presence of MnO as a basic oxide actually results in an increase in the desulphurisation power of the slag. Therefore, the influence of MnO on the sulphur behaviour of the slag system can be defined better by examining Figures 4.46, 4.47 and H 4.1 where the other slag components compositions have been kept in a narrow range.

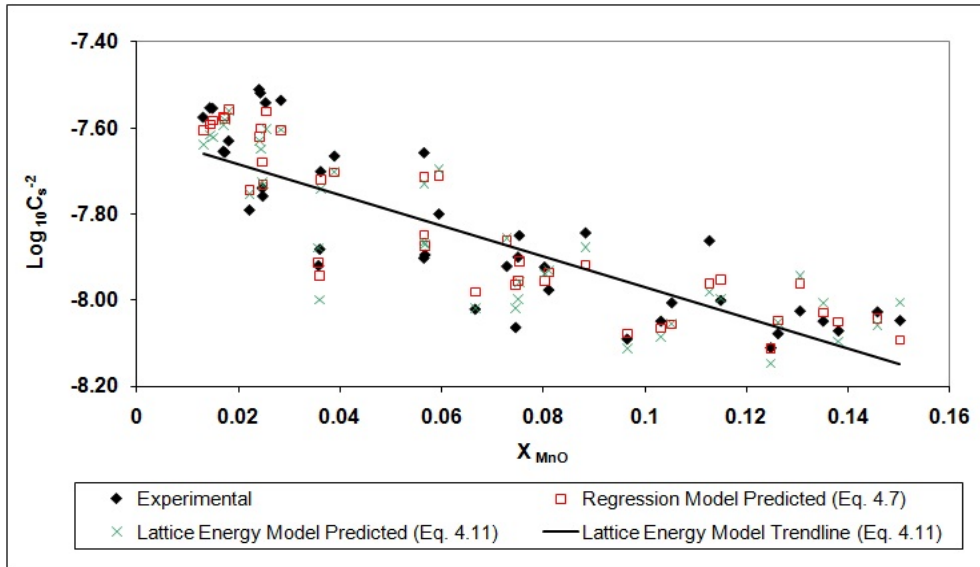


Figure 4.44 The variation of sulphide capacity with manganese oxide mole fraction (X_{MnO}) of ferromanganese smelting slag; Basicity Ratio: 0.800-1.605, X_{SiO_2} : 0.3519-0.4572, X_{CaO} : 0.1680-0.4352, X_{MgO} : 0.1152-0.2748

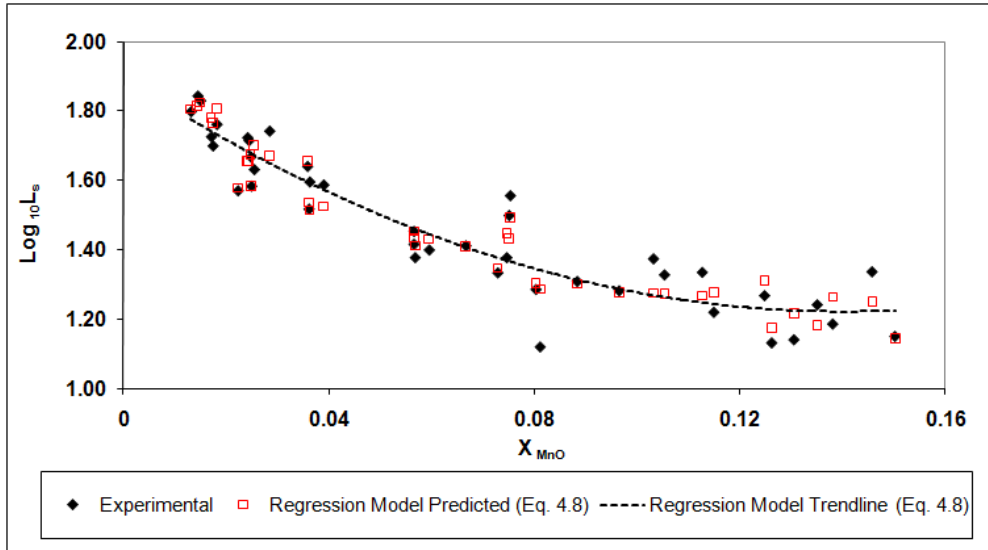


Figure 4.45 The variation of sulphur distribution ratio with manganese oxide mole fraction (X_{MnO}) of ferromanganese smelting slag; Basicity Ratio: 0.800-1.605, X_{SiO_2} : 0.3519-0.4572, X_{CaO} : 0.1680-0.4352, X_{MgO} : 0.1152-0.2748

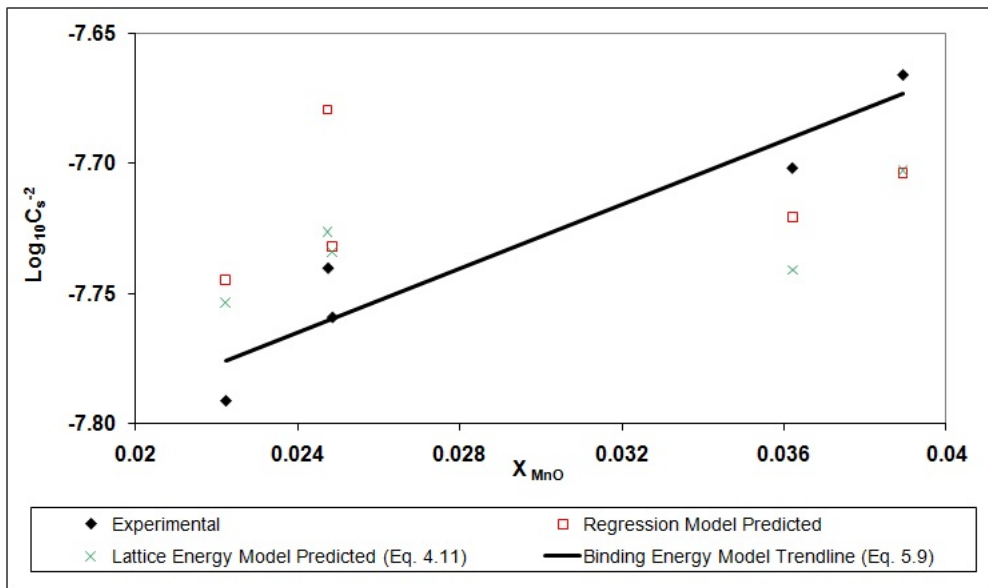


Figure 4.46 The variation of sulphide capacity with manganese oxide mole fraction (X_{MnO}) of ferromanganese smelting slag; Basicity Ratio: 1.355-1.407, X_{SiO_2} : 0.3770-0.3905, X_{CaO} : 0.3365-0.3825, X_{MgO} : 0.1469-0.1921

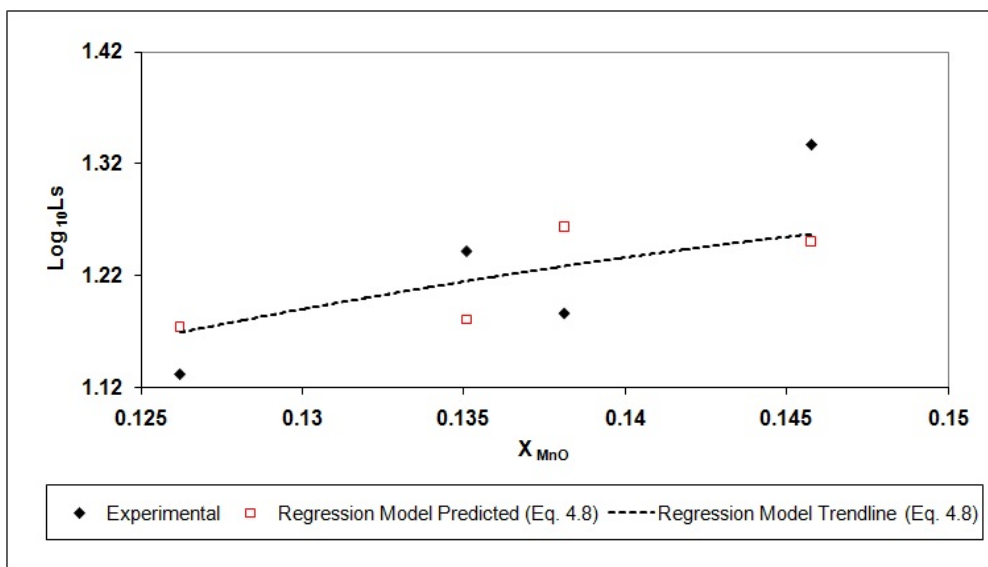


Figure 4.47 The variation of sulphur distribution ratio with manganese oxide mole fraction (X_{MnO}) of ferromanganese smelting slag; Basicity Ratio:0.828-0.923, X_{SiO_2} : 0.4276-0.4392, X_{CaO} : 0.1753-0.1802, X_{MgO} :0.1930-0.2188

It is clear from Figures 4.46 and H 4.1 that the manganese oxide (in mole fraction) of slag has a significant positive impact on the logarithm of sulphide capacity of slag system. These results are in agreement with those of previous studies (Hino and Fuwa, 1978; Reddy and Blander, 1989; Sichen et al., 1995; Nzotta et al., 1998) The logarithm of sulphide capacity increases 0.02 and 0.06 per cent with one per cent increase of manganese oxide concentration (in mole fraction) of ferromanganese smelting slags (Figures 4.46 and H 4.1). The manganese oxide content varies between 0.096 and 0.1146 as observed in Fig. H 4.1. A study done on MgO-MnO-SiO₂ system at 1650 °C, the logarithm of sulphide capacity was found to be increased 0.06 per cent with one per cent increase of manganese oxide (mol.%) (Nzotta,1997). The manganese oxide range (X_{MnO} :0.1-0.15, $\text{Log}C_s^{-2} = -3.68 - -3.57$) in Nzotta (1997) is similar to the present work as shown in Figure H 4.1 in which the rates are the same as in the present study and Nzotta's study where the increase in MnO content of the slag system causes higher sulphide capacities. Since the sulphide capacities increase with increasing a_O^{-2} or basicity of the slag, the basic nature of MnO improves the desulphurisation capacity of the slag. The relationship between manganese oxide content and

sulphide capacity of slag can be explained on the basis of high affinity of MnO to sulphur in the slag. Nilsson et al. (1996) applied a mathematical model to estimate the sulphide capacities. The calculations and experimental data show that MnO-SiO₂ system ($C_s = -2.75$ at $X_{\text{MnO}} = 0.5$, $T = 1773 \text{ K}$) has higher sulphide capacity value compared to CaO-SiO₂ ($C_s = -4$ at $X_{\text{CaO}} = 0.5$, $T = 1773 \text{ K}$) and CaO-Al₂O₃ ($C_s = -3.75$ at $X_{\text{Al}_2\text{O}_3} = 0.5$, $T = 1773 \text{ K}$) systems. When MnO replaced CaO in CaO-SiO₂-MnO slag system, the results show that the higher MnO content slag has significantly higher slag capacity (Nilsson et al. 1994b).

The influence of manganese oxide content of slag on the sulphur distribution ratio between slag and metal are illustrated in Figures 4.47 and H 4.2. The logarithm of sulphur distribution ratio between slag and metal is directly proportional to the manganese oxide (in mole fraction) content of the slag which agrees well with the literature (Zhang and Toguri, 1987). The sulphur distribution ratio equation given by Zhang and Toguri (1987) clearly shows the positive influence of manganese oxide on the desulphurisation capacity of steelmaking slags.

- **The variation of C_s^{-2} and L_s with basicity ratio $[(X_{\text{CaO}} + X_{\text{MgO}})/X_{\text{SiO}_2}]$ of ferromanganese smelting slags**

The effect of basicity ratio $[(X_{\text{CaO}} + X_{\text{MgO}})/X_{\text{SiO}_2}]$ of ferrochromium smelting slag on the logarithm of sulphide capacity and distribution ratio of sulphur between slag and metal phases at 1500 °C under carbon monoxide atmosphere are presented in Figures 4.48, 4.49 and Figs H 5.1 and H 5.2 in Appendix H5.

In Figures 4.48 and 4.49, the desulphurization power of the slag increases with increasing slag's basicity ratio. Similar results were observed by Shankar et al. (2006) for SiO₂-Al₂O₃-CaO-MgO (high alumina blast furnace slags) and by Andersson et al. (1999) for CaO-Al₂O₃-MgO-SiO₂ (ladle) slags.

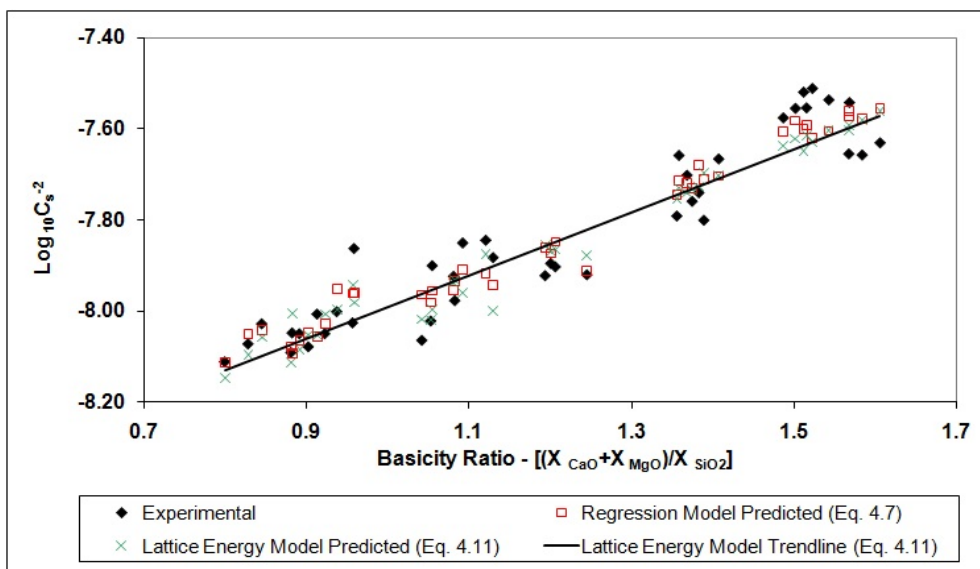


Figure 4.48 The effect of basicity ratio on the sulphide capacity of ferromanganese smelting slag; X_{SiO_2} :0.3519-0.4572, X_{CaO} :0.1680-0.4352, X_{MgO} :0.1152-0.2748, X_{MnO} :0.0130-0.1381

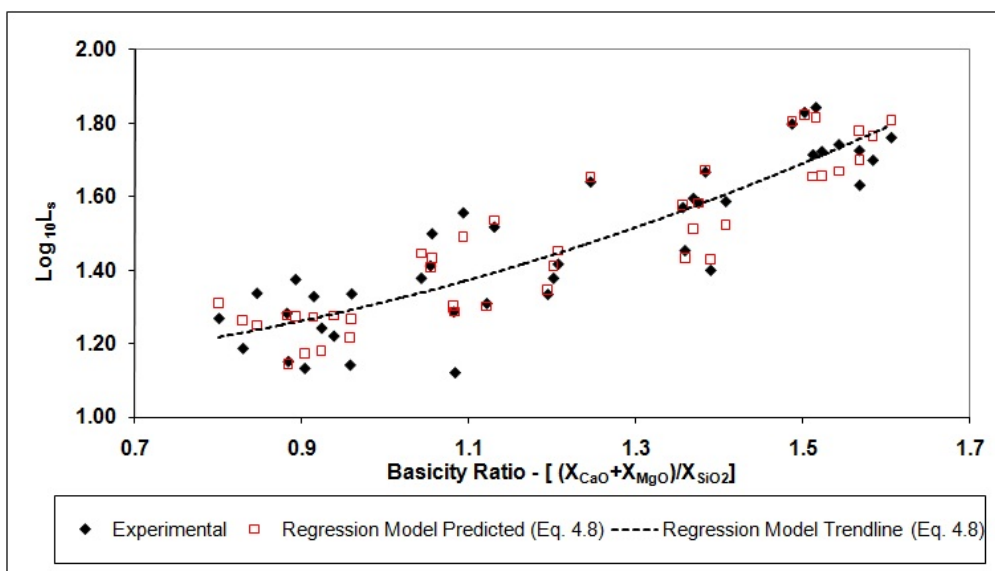


Figure 4.49 The effect of basicity ratio on the sulphur distribution ratio of ferrochromium smelting slag; X_{SiO_2} :0.3519-0.4572, X_{CaO} :0.1680-0.4352, X_{MgO} :0.1152-0.2748, X_{MnO} :0.0130-0.1381

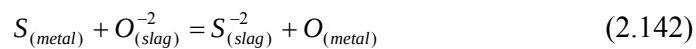
The influence of basicity ratio on the equilibrium sulphur distribution ratio between slag and metal can be examined in Figure 4.49 which indicates that the sulphur partition ratios varied from 18.55 to 57.80 at a slag basicity ratio ranging from 0.80 to 1.60. This is in a good agreement with the observations of Dresler et al. (1992) for $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-CaO}$ (high carbon ferrochromium smelting) slags.

In the present work, the effect of basicity ratio on the sulphide capacities of slags of narrow range compositions was examined in Figure H 5.1. It is found that the sulphide capacities of slags increase with increasing basicity ratio of ferromanganese smelting slag which increase with free oxygen anions due to breaking of SiO_2 network. 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 decrease in chain length as more basic oxide is added. It is assumed that equilibrium prevails between the various polymers and free O^{2-} ions present in the slag. With further basic oxide 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 (O^{2-}) close approaching to zero. Addition of further basic oxides then increases the number of free oxygen ions ($n_{\text{O}^{2-}}$). Sulphur present in the slag interacts strongly with the basic cation and decreases the effective concentration of free oxygen ions in the slag.

Figure H 5.2 demonstrates a strong correlation between the equilibrium sulphur distribution ratio and the basicity ratio of slag. As it was discussed in the subsection of 4.4.1 (The variation of C_S^{2-} and L_S with basicity ratio of ferrochromium smelting slags), at lower basicity ratios where there are less basic oxides (CaO, MgO) in the slag only a limited number of free O^{2-} ions exist which results in low sulphur distribution ratios. As the amount of basic oxides increase, the SiO_2 networks tend to break into smaller anion group and ultimately results in a sharp increase in the free oxygen anions in the slag. As a result, the reaction (2.142) progress as in the right direction and the sulphur distribution ratio is expected to increase according to equation (4.41).

- **The variation of C_S^{-2} and L_S with optical basicity (Λ) of ferromanganese smelting slags**

The changes of logarithm of C_S^{-2} and L_S with the optical basicity of ferromanganese smelting slag at 1500 °C under carbon monoxide atmosphere are given in Figures 4.50, 4.51 and Figures H 6.1, H 6.2 in Appendix H6. The logarithm of sulphide capacity rises from -8.064 to -7.630 by increasing optical basicity value from 0.6296 to 0.6797 (Fig. 4.50) whereas the sulphur distribution ratio between slag and metal varies between 23.88 and 57.80 (Fig. 4.51). The results indicate the positive influence of addition of basic oxides (CaO, MgO and MnO) on the sulphide capacity and sulphur distribution ratio. The higher optical basicity is expected with the replacement of acidic oxides with basic oxides which ultimately leads to an increase in the concentration of free oxygen anions in the slag. When the free oxygen anions are consumed in the slag network, a shift in the right direction is expected for the reaction (2.142) which augments the sulphide capacity of the slag. Hence, the sulphur concentration in the metal phase can be lowered by increasing the optical basicity (or basicity) of the slag.



The models of Young et al. (1992), Sosinky and Sommerville (1986) presented in subsection of 4.4.1 (The variation of C_S^{-2} and L_S with optical basicity ratio (Λ) of ferrochromium smelting slags) have shown significant deviations between the measured and calculated values for sulphide capacities. In fact the models given by Sosinky and Sommerville (1986), Young et al. (1992) and Nzotta et al. (1998) under predicted the values of sulphide capacities for high alumina slags (Shankar et al., 2006). It is clear from Figure 4.52 that both Young et al. (1992), Sosinky and Sommerville (1986) models predict higher sulphide capacity values in the present study. The calculated sulphide capacities based on these models are presented in Appendix K. As mentioned in Shankar et al.'s work (2006), a new model is required for different slag systems to estimate the sulphide capacity

based on optical basicity values. In another study, it is stated that Sosinsky and Sommerville's model (1986) over estimated the sulphide capacity values compared to the measured ones for CaO-Al₂O₃-SiO₂ slag system at 1550, 1600 and 1650 °C (Korousic, 2003). Hao et al. (2006) reported significant deviations between the predicted values and experimental with Young et al.'s model (1992). Young et al. (1992) predicted higher values of sulphide capacity compared the measured values. A new regression model which is sensitive to slag composition should therefore be developed for the present slag system.

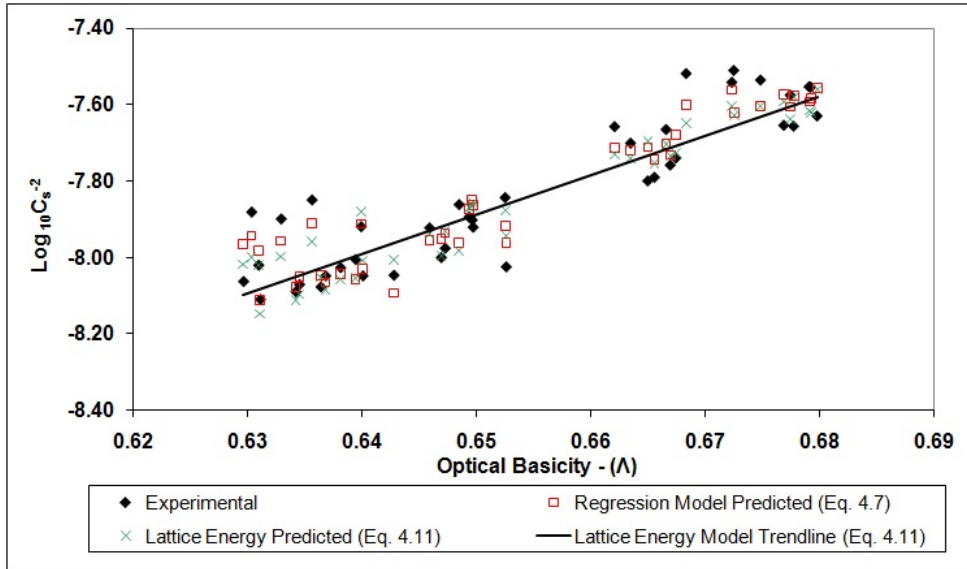


Figure 4.50 The effect of optical basicity (Λ) on the sulphide capacity of ferromanganese smelting slag; Basicity Ratio:0.800-1.605, X_{SiO_2} :0.3519-0.4572, X_{CaO} : 0.1680-0.4352, X_{MgO} :0.1152-0.2748, X_{MnO} :0.0130-0.1381

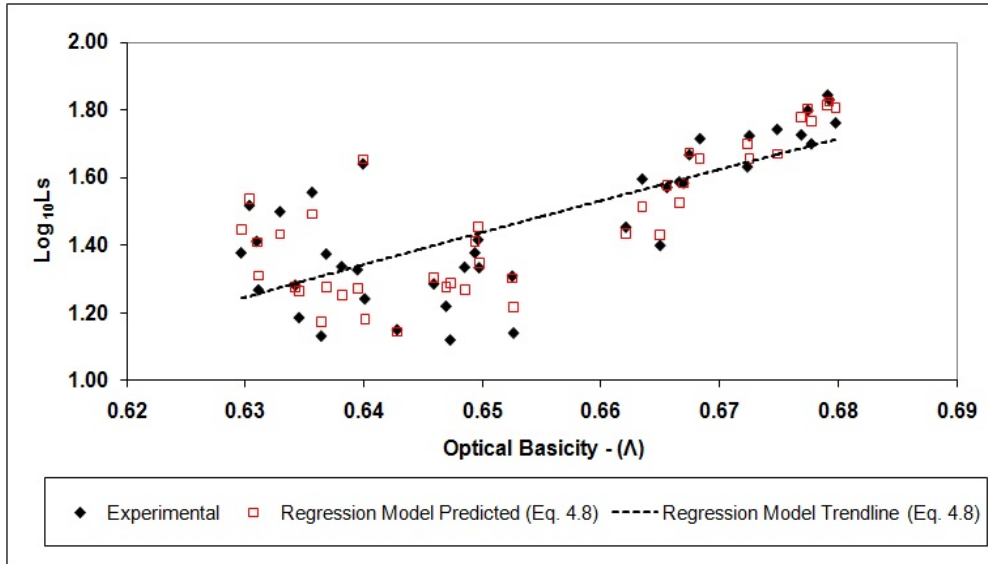


Figure 4.51 The effect of optical basicity (Λ) on the sulphur distribution ratio of ferromanganese smelting slag; Basicity Ratio:0.800-1.605, X_{SiO_2} :0.3519-0.4572, X_{CaO} : 0.1680-0.4352, X_{MgO} :0.1152-0.2748, X_{MnO} :0.0130-0.1381

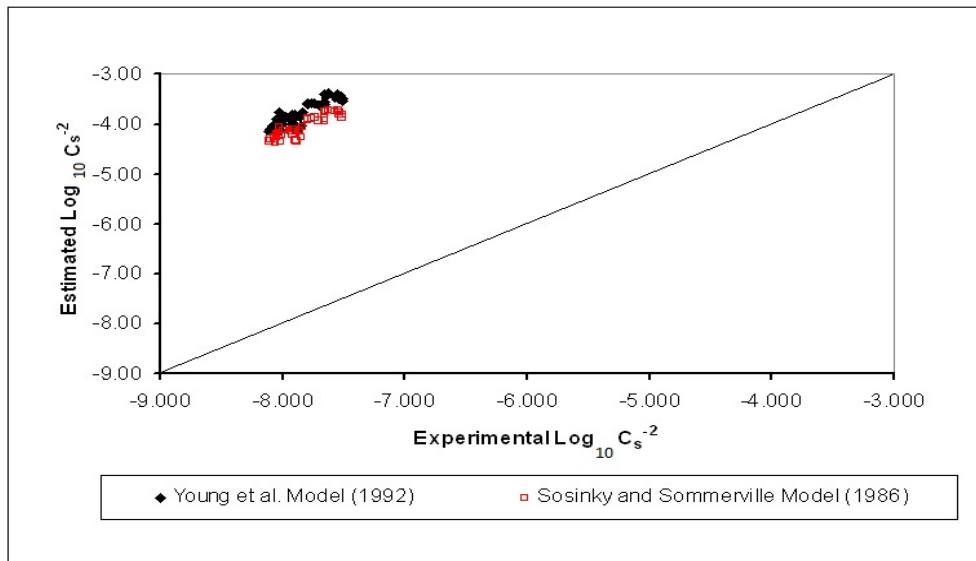


Figure 4.52 Comparison between measured sulphide capacity of the work and the previous studies models estimated results

The relationship between optical basicity and the logarithm of sulphide capacity is a linear type (Fig. 4.50). The multiple regression analysis of the experimental results indicates that Eq. 4.42 can be used as a tool for defining the relationship

between optical basicity and the log of sulphide capacity for $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO-MnO-CaS}$ slag system at 1500 °C under carbon monoxide atmosphere. The correlation coefficient of Eq. 4.42 is equal to 0.81 which indicates that if the slag compositions fall within the range of the current study, this model can be confidently used in order to determine the sulphide capacity of slag system.

$$\text{Log}C_{\text{S}^{-2}} = 10.256\Lambda + 14.54 \quad (4.42)$$

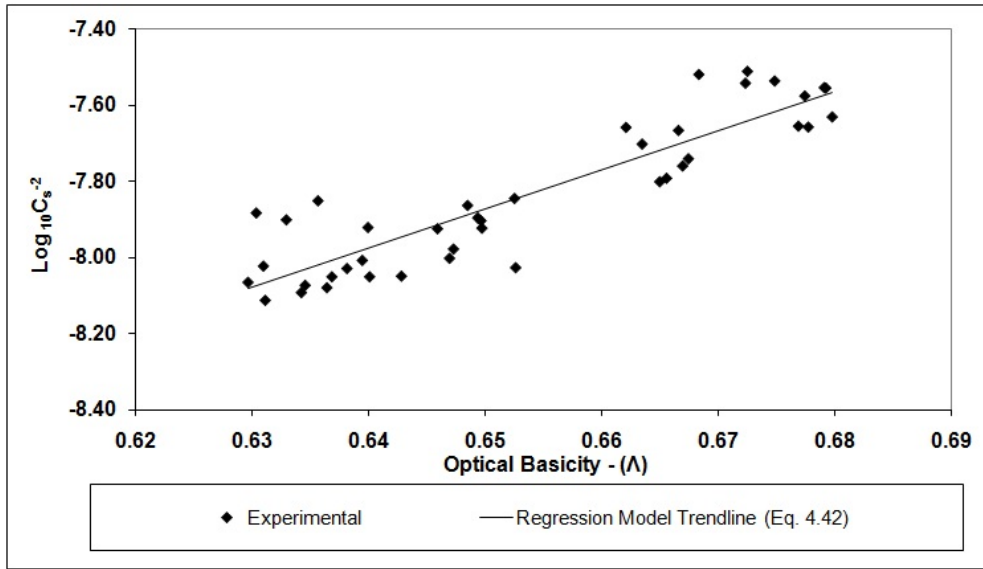


Figure 4.53 The relationship between optical basicity (Λ) and the logarithm of sulphide capacity

It is seen that 1.28 per cent increase in the logarithm of sulphide capacities can be achieved with one per cent increase of optical basicity ratio of slag for the plots of Figure H 6.1 For CaO-MgO-SiO_2 slag system at 1500 °C, Sommerville and Sosinky (1994) showed that the logarithm of sulphide capacity increases from -4.4 to -4.2 with the increase of optical basicity from 0.63 to 0.64 which corresponds to 1.46 per cent increase in the logarithm of sulphide capacities with one per cent increase in the optical basicity ratio of the slag. Their region fits to the present study's plot in Figure H 6.1 and the identified increase rate (1.28) in this plot agrees well with 1.46 given by Sommerville and Sosinky (1994).

- The variation of C_S^{-2} and L_S with CaO-to-MgO ratio (X_{CaO}/X_{MgO}) of ferromanganese smelting slags

The influence of the CaO-to-MgO ratio of ferromanganese smelting slag on the logarithm of sulphide capacity and distribution ratio of sulphur between slag and metal phases are illustrated in Figures 4.54, 4.55 and Figures H 7.1 and H 7.2 in Appendix H7.

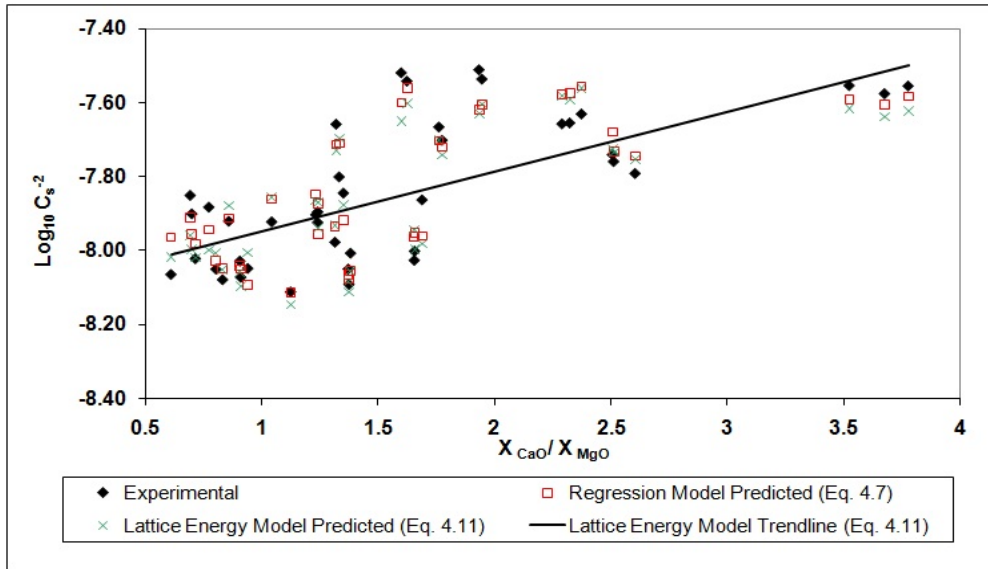


Figure 4.54 The effect of CaO-to-MgO ratio (X_{CaO}/X_{MgO}) on the sulphide capacity of ferromanganese smelting slag; Basicity Ratio:0.800-1.605, X_{SiO_2} :0.3519-0.4572, X_{CaO} : 0.1680-0.4352, X_{MgO} :0.1152-0.2748, X_{MnO} :0.0130-0.1381

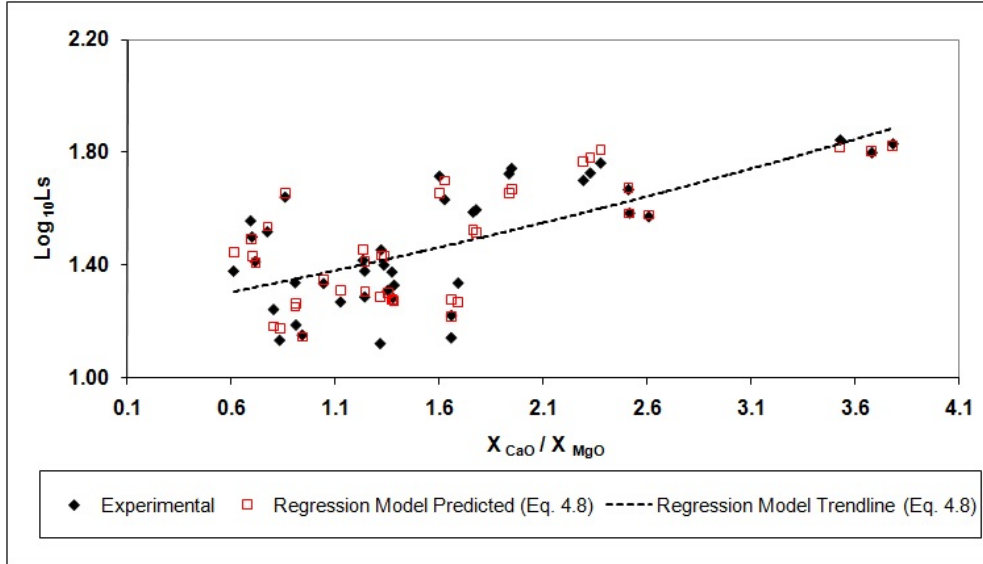


Figure 4.55 The effect of CaO-to-MgO ratio (X_{CaO}/X_{MgO}) on the sulphur distribution ratio of ferromanganese smelting slag; Basicity Ratio:0.800-1.605, X_{SiO_2} :0.3519-0.4572, X_{CaO} : 0.1680-0.4352, X_{MgO} :0.1152-0.2748, X_{MnO} :0.0130-0.1381

Although the SiO_2 and MnO contents haven't been restricted, it is still possible to see the influence of CaO-to-MgO ratio on the desulphurisation power of slag (Figures 4.54 and 4.55). In the absence of Al_2O_3 , the sulphide capacities of binary metasilicates follow the order of $CaO.SiO_2 > MgO.SiO_2$ (Nzotta, 1997b). According to the findings of Hino et al. (1993), the replacement of CaO with MgO at constant Al_2O_3 and SiO_2 leads to lower sulphide capacities in CaO-MgO- SiO_2 - Al_2O_3 slags. Bronson and St. Pierre (1981) reported similar behaviour in CaO-MgO- SiO_2 slags. As mentioned in Bronson and St. Pierre's study (1981), the replacement of MgO for CaO has a strong influence on the a_O^{-2}/f_s^{-2} ratio of silicate melts. It is also known that f_s^{-2} doesn't significantly change; therefore the sulphide capacity is assumed directly proportional to the activity of oxygen anions in the slag. The substitution of MgO for CaO decreases the sulphide capacity by reducing the activity of oxygen anions in the slag which causes the reaction (2.142) to move to the left direction.

$$S_{(metal)} + O_{(slag)}^{-2} = S_{(slag)}^{-2} + O_{(metal)} \quad (2.142)$$

The logarithm of sulphide capacity rises from -8.064 to -7.555 by increasing the CaO-to-MgO ratio from 0.61 to 3.77 (Fig. 4.54). The effect of CaO-to-MgO ratio on the sulphur distribution ratio between slag and metal phases is seen in Figure 4.55. There is a substantial effect of CaO-to-MgO ratio on the logarithm of sulphur distribution ratio between slag and metal (Fig. 4.55). The logarithm of sulphur distribution ratio increases from 1.378 to 1.824 as CaO-to-MgO ratio increases from 0.61 to 3.77.

The MnO, SiO₂ and Al₂O₃ contents have been kept in a narrow range for a better analysis of CaO-to-MgO ratio on the desulphurisation power of slags (Figures H 7.1 and H 7.2). The results clearly indicate the stronger basic oxide nature of CaO compared to MgO which its influence on the desulphurisation of the metal is more substantial than MgO.

- **The relationship between sulphide capacity (C_S^{-2}) and lattice energy of oxides (binding energy of O^{2-} ion in the mixture) ($\overline{E_o}$) of ferromanganese smelting slag**

The relationship between C_S^{-2} and binding energy of O^{2-} ion in the mixture (lattice energy of the oxides) ($\overline{E_o}$) of SiO₂-CaO-Al₂O₃-MgO-MnO-CaS slag system is presented in Figure 4.56.

As discussed in subsection of 4.4.1 (The relationship between sulphide capacity and lattice energy of oxides of ferrochromium smelting slag), the lattice energy (binding energy) of the slag system is reduced with the increase of the basicity of the slag. The relationship between binding energy of the slag system and logarithm of sulphide capacity is in linear form (Eq. 4.11), thus this approach can be assumed as a useful tool for predicting the desulphurisation capacities of slag systems. However, due to the nature of the correlation, this model can only be applicable when the slag compositions fall within the current range.

$$\text{Log } C_S^{-2} = -0.002 \cdot \overline{E_o} + 1.902 \quad (4.11)$$

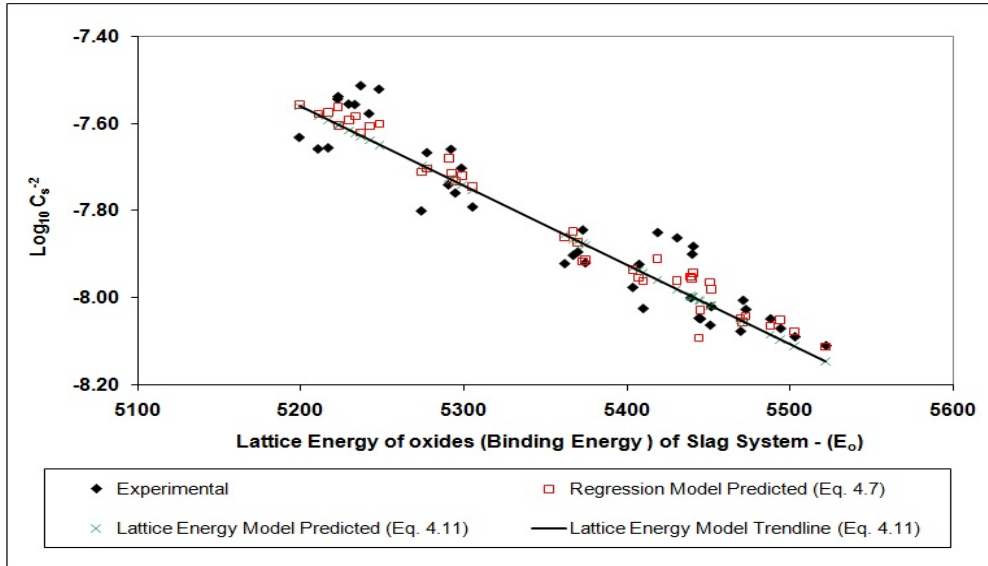


Figure 4.56 The relationship between C_s^{-2} and lattice (binding) energy ($\overline{E_o}$) of ferromanganese smelting slag.

- **The relationship between sulphide capacity (C_s^{-2}) and activity of calcium oxide and manganese oxide in ferromanganese smelting slag system at 1500 °C**

If the activity coefficient of S^{-2} ion in the slag is assumed independent from the oxide composition of the slag, sulphide capacity becomes directly proportional to the activity of O^{-2} anions. Therefore, in a binary slag system M_xO-SiO_2 , the activity of O^{-2} anions is equal to the activity of M_xO (Nilsson et al.,1994b) Although the method is only available for the slags containing one metallic oxide, it is important to analyze the correlation between the activity of CaO and the sulphide capacity of the slag system.

The activity of CaO is determined by using the equations 4.16, 4.17 and 4.18 in subsection of 4.41 (The relationship between sulphide capacity (C_s^{-2}) and activity of calcium oxide in ferrochromium smelting slag system at 1500 °C). The relationship between C_s^{-2} and activity of CaO of ferromanganese smelting slag is

presented in Figure 4.57. The regression equation between the logarithm of sulphide capacity and logarithm of activity of CaO in ferromanganese smelting slag under carbon monoxide atmosphere at 1500°C is presented in equation 4.43.

$$\text{Log}C_{S^{-2}} = 0.3548.\log a_{CaO} - 7.0989 \quad (4.43)$$

The linear nature regression equation has a moderate correlation coefficient ($R^2=0.784$) which may due to the influence of MgO and MnO on a_{CaO} .

The relationship between logarithm of sulphide capacity and logarithm of activity of manganese oxide in CaO of SiO_2 -CaO- Al_2O_3 -MgO -MnO-CaS slag system is given in Fig. 4.58. The activities of manganese oxide have been calculated by using the regression model developed by Cengizler (1993) (Eq. 4.44) where the independent variables are the mass percentages of MnO, CaO, MgO and SiO_2 in the slag and the basicity ratio, B is defined as $B=(\text{CaO}+\text{MgO})/\text{SiO}_2$. It is found that the plot of $\log C_{S^{-2}}$ vs. $\log a_{MnO}$ produces a straight line and the slope of the plot is equal to 1.53. The regression model for this relationship is defined in Eq. 4.45, the correlation coefficient (R^2) of this equation is equal to 0.414 which indicates a rather poor curve fitting.

$$\begin{aligned} a_{MnO} = & 0.7265 - 0.0249(\text{SiO}_2) - 2.3115(B)^2 + 0.0619(\text{MnOxB}) - 0.0003(\text{MnO})^2 \\ & + 0.1451(\text{CaOxB}) - 0.0018(\text{CaOxMnO}) - 0.0023(\text{CaO})^2 + 0.1439(\text{MgOxB}) \\ & - 0.0019(\text{MgOxMn}) - 0.0045(\text{MgOxCaO}) - 0.022(\text{MgO})^2 - 0.0506(\text{SiO}_2\text{xB}) \\ & + 0.0005(\text{SiO}_2\text{xMnO}) + 0.0015(\text{SiO}_2\text{xCaO}) + 0.0015(\text{SiO}_2\text{xMgO}) \end{aligned} \quad (4.44)$$

$$\text{Log}C_{S^{-2}} = 1.5329.\log a_{MnO} - 6.1168 \quad (4.45)$$

These results clearly indicate that both a_{CaO} and a_{MnO} can not be related to $a_{O^{2-}}$ without considering the influence of other slag components on the activity of oxygen anions. The calculated activity of calcium oxide and manganese oxide values are given in Appendix L and M, respectively.

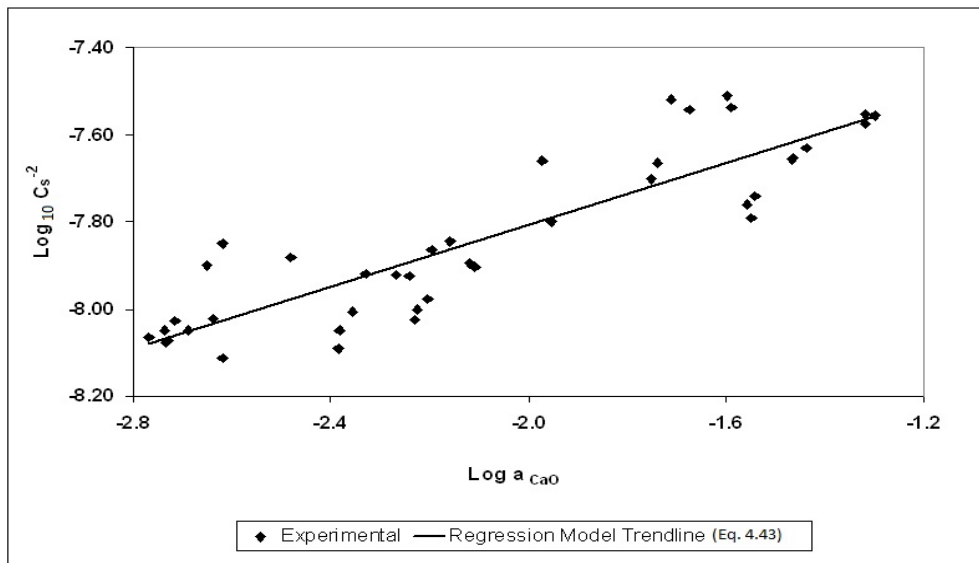


Figure 4.57 The relationship between C_s^{-2} and activity of CaO of ferromanganese slag system.

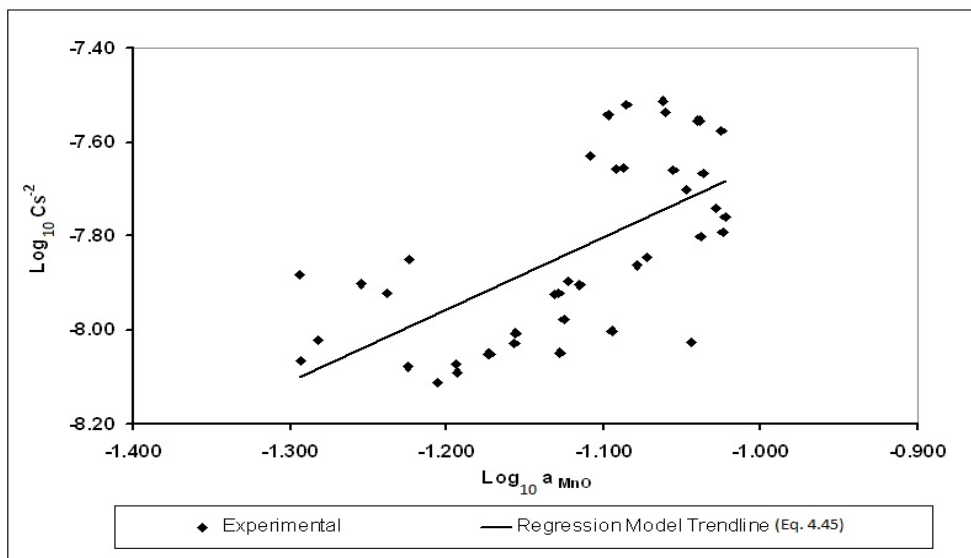


Figure 4.58 The relationship between C_s^{-2} and activity of MnO of ferromanganese slag system.

- **Distribution of manganese between the slag and the metal phases**

The influence of several different parameters on the distribution of manganese between slag and metal phases at 1500 °C under carbon monoxide atmosphere are shown in Figures 4.59 to 4.73. The distribution ratio of manganese (L_{Mn}) is defined as per cent of manganese in the slag divided by per cent of manganese in the metal phase. A regression analysis was performed on the experimental data and a regression equation (Eq. 4.46) given below is used in the prediction of distribution ratio of manganese between slag and metal phase under the experimental conditions.

$$\text{Log}L_{Mn} = 0.715 - 3.872 X_{SiO_2}^2 - 10.927 X_{CaO}^2 - 10.840 X_{MgO}^2 + 0.069 \frac{X_{CaO}}{X_{MgO}} \quad (4.46)$$

The correlation coefficient (R^2) of regression model is equal to 0.975 which indicates a good correlation between the defined parameters and the logarithm of distribution ratio of manganese. Eq. 4.46 can therefore be used for predicting the distribution ratio of manganese between slag and metal phases if the slag compositions are kept within the range of the present experimental work.

The change of distribution ratio of manganese with silica content (X_{SiO_2}) of ferromanganese smelting slag- The effect of silica concentration (in mole fraction) of the slag on the logarithm of manganese distribution ratio are given in Figures 4.59 to 4.61. The manganese distribution ratio shows a tendency to increase with increasing of silica content in the slag.

Under highly reducing atmosphere conditions, the reaction of manganese transfer from metal to slag phase can be written according to reaction 4.47.



and the equilibrium constant of this reaction can be defined as

$$K = \frac{(a_{MnO}) \cdot [a_c]}{[a_{Mn}] \cdot P_{CO}} \quad (4.48)$$

For high carbon ferromanganese smelting conditions, $a_c=1$ and $P_{CO}=1$, and this converts the equation 4.48 to 4.49.

$$K = \frac{(a_{MnO})}{[a_{Mn}]} = \frac{(\gamma_{MnO} \cdot x_{MnO})}{[\gamma_{Mn} \cdot x_{Mn}]} \quad (4.49)$$

The activity coefficients, γ_{MnO} , γ_{Mn} in equation 4.49 change little with MnO and Mn contents, therefore a simplified equation can be derived for manganese distribution ratio between slag and metal phases:

$$K' = \frac{(x_{MnO})}{[x_{Mn}]} \quad (4.50)$$

From the basicity point of view, an increase in the silica content in the slag results in a less basic slag causing more Mn^{+2} ions which associate with the silicate network and consequently leads to an increase in MnO content in the slag .

In high carbon ferromanganese and silicomanganese slags, the manganese distribution ratio between slag and metal is found to be increasing with increasing silica content of slag (Cengizler, 1993). This result is in good agreement with the current findings.

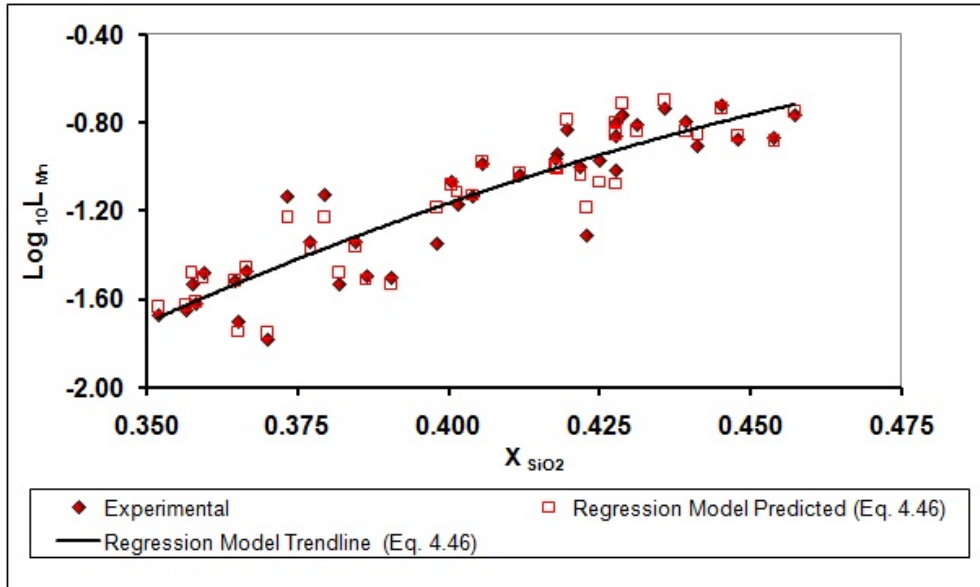


Figure 4.59 The effect of silica (X_{SiO_2}) content ferromanganese slag on the distribution ratio of manganese between the slag and the metal phases;
 Basicity Ratio: 0.800- 1.605, X_{CaO} : 0.1680- 0.4352, X_{MgO} : 0.1152-0.2748

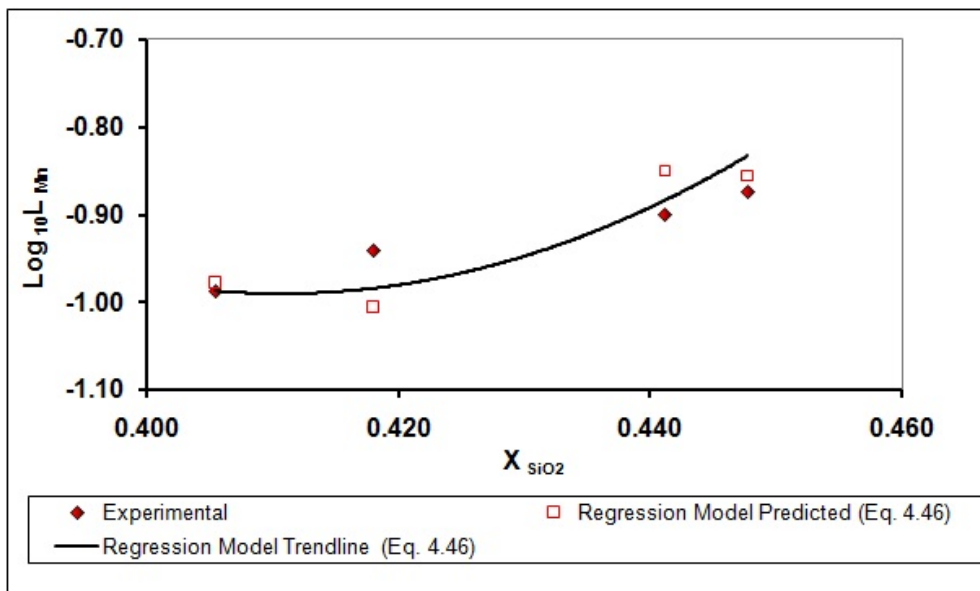


Figure 4.60 The effect of silica (X_{SiO_2}) content ferromanganese slag on the distribution ratio of manganese between the slag and the metal phases;
 Basicity Ratio: 0.891- 1.120, X_{CaO} : 0.2310- 0.2612, X_{MgO} : 0.1683-0.1954

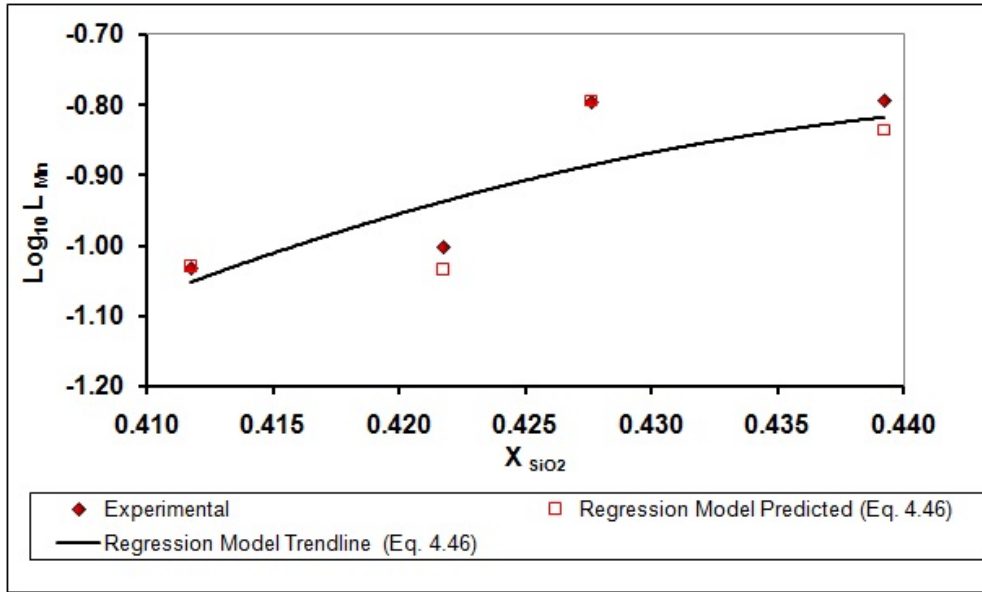


Figure 4.61 The effect of silica (X_{SiO_2}) content ferromanganese slag on the distribution ratio of manganese between the slag and the metal phases;
Basicity Ratio: 0.902- 1.092, X_{CaO} : 0.1759- 0.1843, X_{MgO} : 0.2163-0.2656

The change of distribution ratio of manganese with calcium oxide content (X_{CaO}) of ferromanganese smelting slag- The relationships between calcium oxide concentration (in mole fraction) and manganese distribution ratio between the slag and the metal phases are illustrated in Figures 4.62 to 4.64. The manganese transfer from slag to metal phase increases with increasing CaO content in the slag. This can be attributed to increasing MnO activity due to increase in CaO content in the slag. As given in the literature, manganese equilibrium distribution ratio decreases with increasing lime-silica ratio of the slag (Turkdogan and Hancock, 1957; Cengizler, 1993). Current results are in good agreement with those reported by Turkdogan and Hancock, (1957), Cengizler (1993).

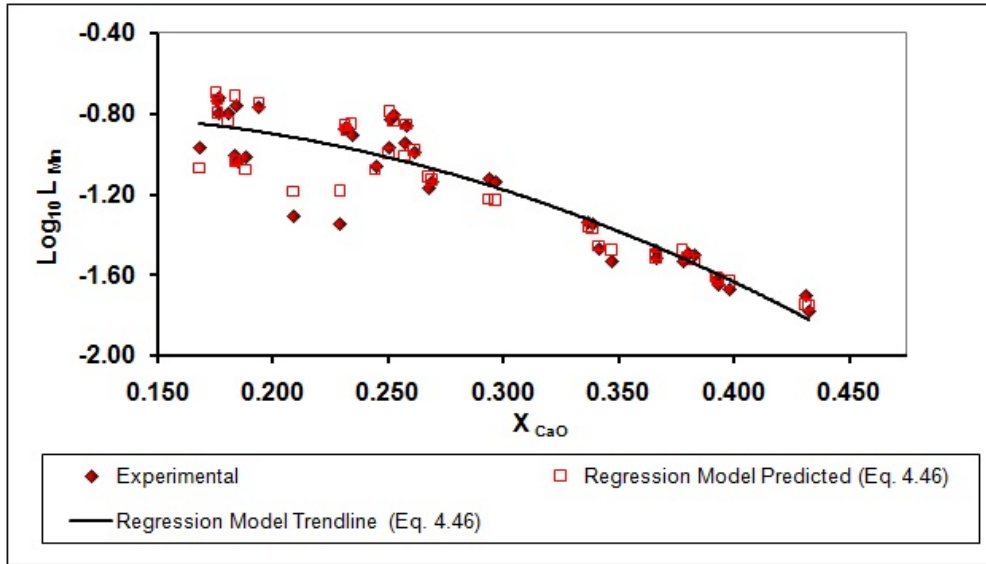


Figure 4.62 The effect of calcium oxide (X_{CaO}) content ferromanganese slag on the distribution ratio of manganese between the slag and the metal phases;
Basicity Ratio: 0.800- 1.605, X_{CaO} : 0.1680- 0.4352, X_{MgO} : 0.1152-0.2748

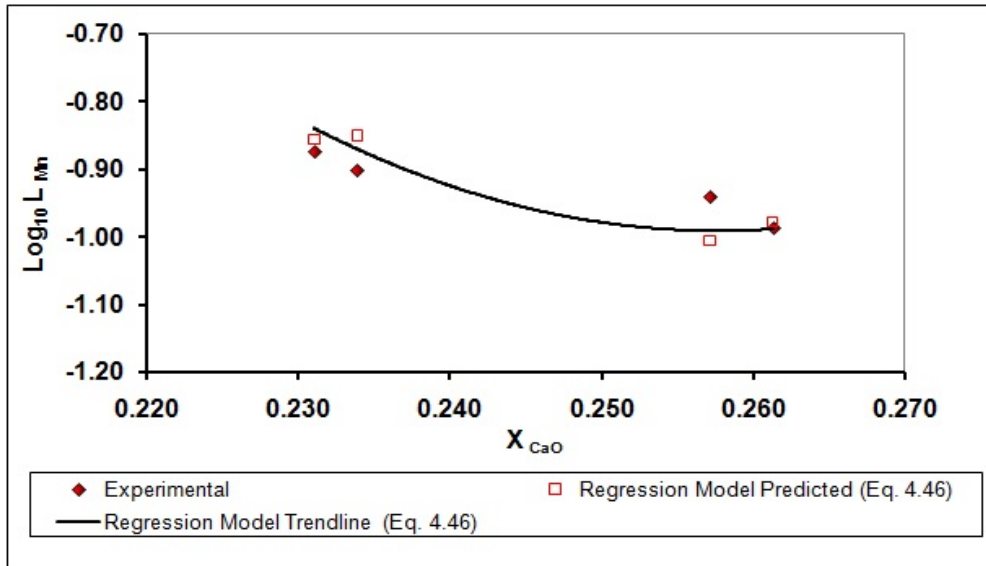


Figure 4.63 The effect of calcium oxide (X_{CaO}) content ferromanganese slag on the distribution ratio of manganese between the slag and the metal phases;
Basicity Ratio: 0.891- 1.120, X_{SiO_2} : 0.4054- 0.4477, X_{MgO} : 0.1683-0.1954

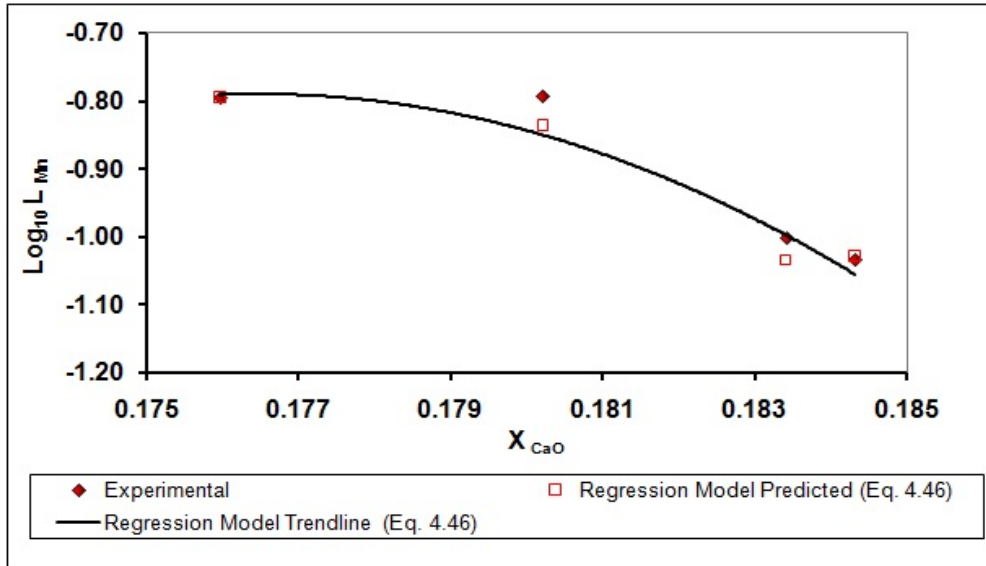


Figure 4.64 The effect of calcium oxide (X_{CaO}) content ferromanganese slag on the distribution ratio of manganese between the slag and the metal phases;
Basicity Ratio: 0.902- 1.092, X_{SiO_2} : 0.4117- 0.4392, X_{MgO} : 0.2163-0.2656

The change of distribution ratio of manganese with magnesium oxide content (X_{MgO}) of ferromanganese smelting slag- The influence of magnesium concentration on the logarithm of manganese distribution ratio is presented without restricting the other slag components composition in Figure 4.65. This result is not expected and does not match with the basicity theory (Cengizler, 1993). It is known that MgO is considered as a basic oxide with its strength being significantly lower than CaO . Therefore, the increase MgO content leads to a limited break-up in the silica network compared to CaO . The actual influence of MgO on the manganese distribution ratio between slag and metal can only be analysed in the plots where the other slag components are kept in a narrow range (Figures 4.66 and 4.67)

The distribution ratio of manganese decreases with the addition of magnesium oxide into the slag in Figures 4.66 and 4.67. A better recovery of manganese in ferromanganese making can be achieved by optimizing the slag compositions. The negative free energy of formation of Mg_2SiO_4 leads to a stronger interaction between Mg^{+2} and silicate anions in the silica network (Barcza, 1976; Barcza

1981). The formation of Mg_2SiO_4 causes disruptions in the silicate network and frees considerable amount of Mn^{+2} ions which results in a higher activity value for MnO , therefore, the amount of manganese in the metal phase tends to increase. The excess addition of MgO causes a decrease in the manganese recovery due to the high liquidus temperature of a high MgO containing slag phase (Barcza, 1976).

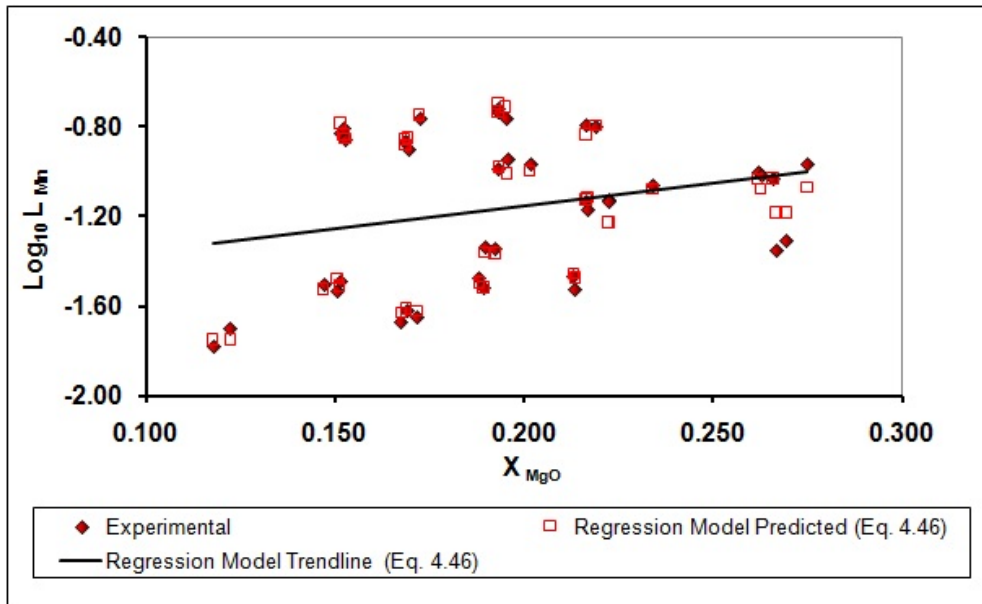


Figure 4.65 The effect of magnesium oxide (X_{MgO}) content ferromanganese slag on the distribution ratio of manganese between the slag and the metal phases; Basicity Ratio: 0.800- 1.605, X_{CaO} : 0.1680- 0.4352, X_{MgO} : 0.1152-0.2748

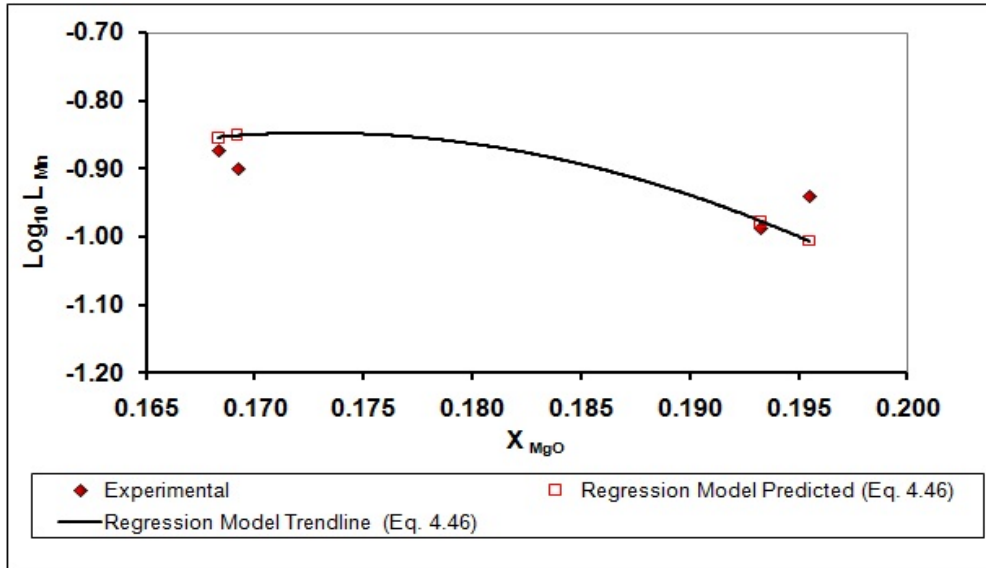


Figure 4.66 The effect of magnesium oxide (X_{MgO}) content ferromanganese slag on the distribution ratio of manganese between the slag and the metal phases; Basicity Ratio: 0.891- 1.120, X_{CaO} : 0.2310- 0.2612, X_{SiO_2} : 0.4054-0.4477

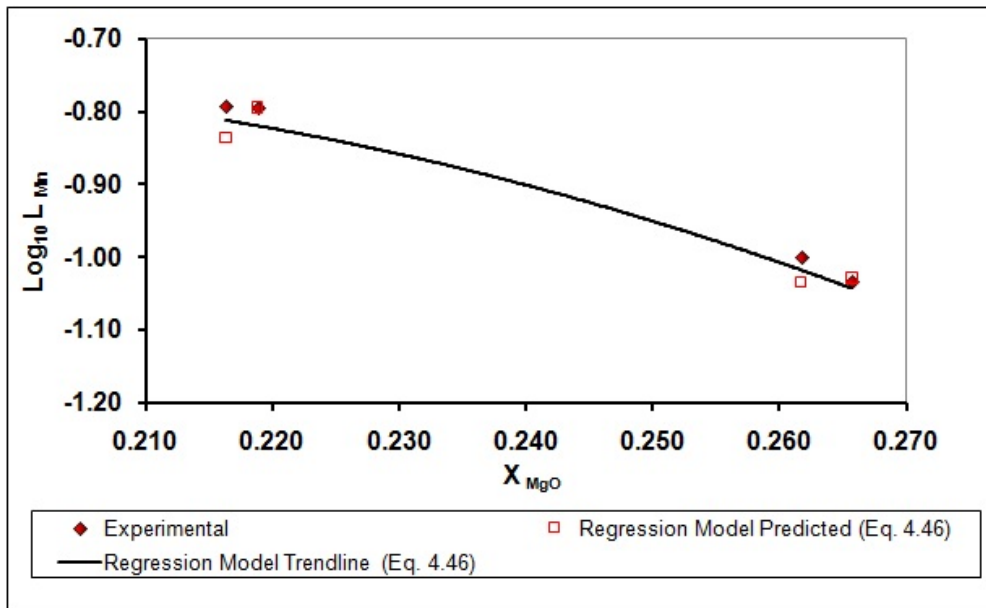


Figure 4.67 The effect of magnesium oxide (X_{MgO}) content ferromanganese slag on the distribution ratio of manganese between the slag and the metal phases; Basicity Ratio: 0.902- 1.092, X_{CaO} : 0.1759- 0.1843, X_{SiO_2} : 0.4117-0.4392

The change of distribution ratio of manganese with basicity ratio of ferromanganese smelting slag- In general slag basicity exerts the most important influence on the manganese distribution ratio between slag and metal phases in ferromanganese smelting. The previous studies clearly demonstrate that the manganese recovery is significantly controlled by the basicity of slags (Barcza, 1976; Cengizler, 1993). The effect of basicity ratio on the logarithm of manganese distribution ratio of $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO-MnO-CaS}$ slags is shown in Figures 4.68 and 4.69. A steady increase in the recovery of manganese has been observed with the addition of CaO and MgO into the slag system. The addition of CaO and to some extent MgO into the slag results in an increase in the activity coefficient of MnO which can be attributed to the disruption of the silica network with the addition of basic oxides (Cengizler, 1993). At low concentrations, basic oxide cations (Ca^{+2} , Mg^{+2} and Mn^{+2}) are mainly connected to larger ionic groups of silica. The strong interaction between divalent cations Ca^{+2} , Mg^{+2} and silicate ions at high basicities results in more free Mn^{+2} ions in the slag whereas the free oxygen anions concentration tend to increase which results in a higher MnO activity in the slag. This clearly assists the transfer of manganese from slag to metal phase. The current results agree well with the results of Barcza (1976) and Cengizler (1993).

The recovery of manganese is extremely limited at low basicity ratios between 0.8 and 0.957 which can be due to insufficient quantity of basic oxides which leads to a decrease in the activity coefficient of the MnO (Fig. 4.68). When the basicity ratio exceeds 0.957, an improvement in the recovery of the manganese can be noticed.

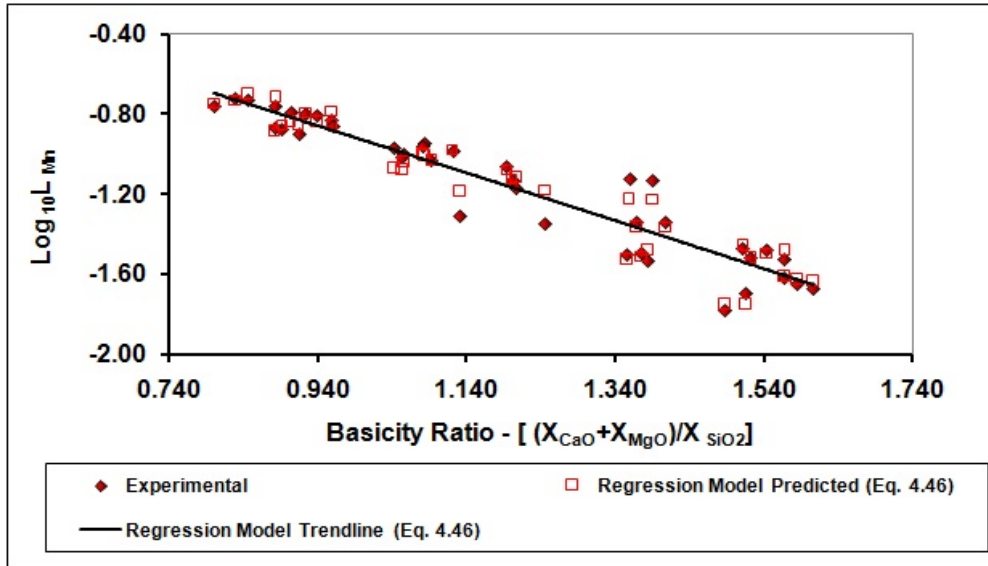


Figure 4.68 The effect of basicity ratio of ferromanganese slag on the distribution ratio of manganese between the slag and the metal phases;
 X_{CaO} : 0.1680- 0.4352, X_{SiO_2} : 0.3519-0.4572, X_{MgO} : 0.1152-0.2748

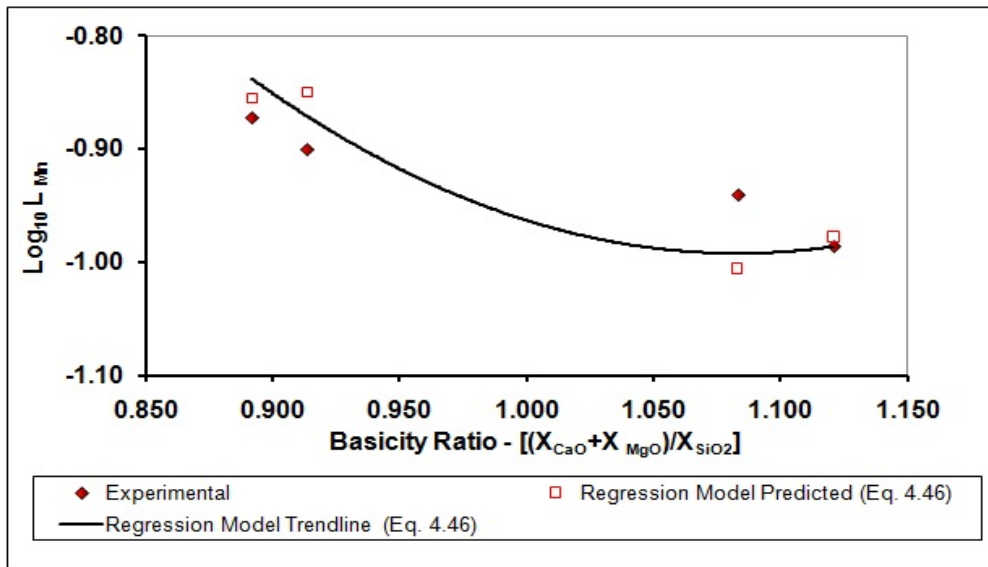


Figure 4.69 The effect of basicity ratio of ferromanganese slag on the distribution ratio of manganese between the slag and the metal phases;
 X_{CaO} : 0.2310- 0.2612, X_{SiO_2} : 0.4054-0.4477, X_{MgO} : 0.1683-0.1954

The change of distribution ratio of manganese with optical basicity (Λ) of ferromanganese smelting slag- In the present study, the relation between optical basicity and logarithm of manganese distribution has been examined. However the expression of optical basicity of transition metal oxides (MnO) is difficult which might causes inaccuracies in the relations.

The influence of optical basicity on the manganese distribution ratio of slags is shown in Figures 4.70 and 4.71 The logarithm of manganese distribution increases with increasing optical basicity. At lower optical basicities ($\Lambda=0.629$ - 0.655), the positive impact of optical basicity on the manganese recovery can not verified clearly due to low CaO and MgO contents in the slag as only a few free O^{2-} ions exist in the slag system which lowers the MnO activity in the slag system subsequently limiting the manganese transfer from slag to metal. The manganese recovery increases when the optical basicity is greater than 0.655. The optical basicity of the slag system increases with increasing basic oxide contents, this results in a break-down in the silica network and the concentration of free oxygen anions increases. Consequently, the manganese recovery from the slag rises as the MnO activity is expected to increase.

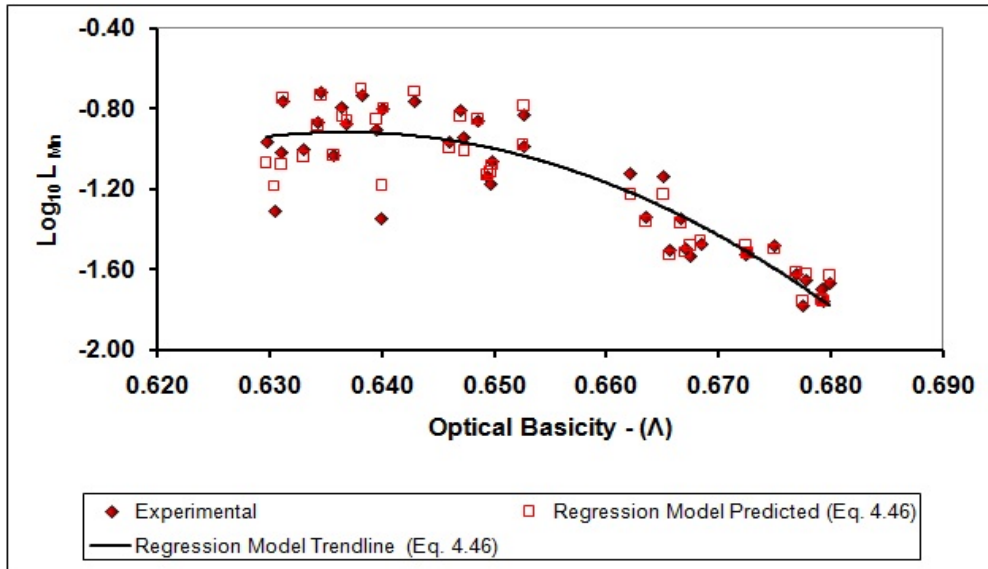


Figure 4.70 The effect of optical basicity of ferromanganese slag on the distribution ratio of manganese between the slag and the metal phases;

X_{CaO} : 0.1680- 0.4352, X_{SiO_2} : 0.3519-0.4572, X_{MgO} : 0.1152-0.2748

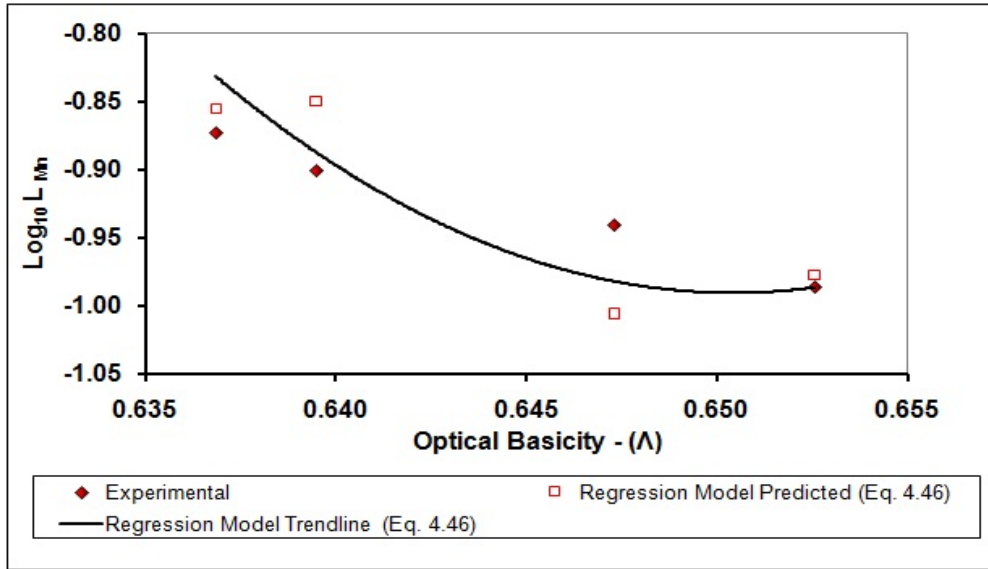


Figure 4.71 The effect of optical basicity of ferromanganese slag on the distribution ratio of manganese between the slag and the metal phases;

X_{CaO} : 0.2310- 0.2612, X_{SiO_2} : 0.4054-0.4477, X_{MgO} : 0.1683-0.1954

The change of distribution ratio of manganese with CaO-to-MgO ratio of ferromanganese smelting slag- The effects of CaO-to-MgO ratio on the logarithm of manganese distribution ratio are given in Figures 4.72 and 4.73. The manganese distribution ratio between slag and metal decreases as CaO replaces MgO (Fig. 4.72). The effect is found to be slight at low CaO-to-MgO ratios (0.61-1.33). However, a significant drop can be seen in the manganese distribution ratio at higher CaO-to-MgO ratios. Since Ca_2SiO_4 is more stable than Mg_2SiO_4 , a stronger interaction between Ca^{+2} and silicate anions can exist which results in a higher MnO activity in the slag and higher manganese content in the metal.

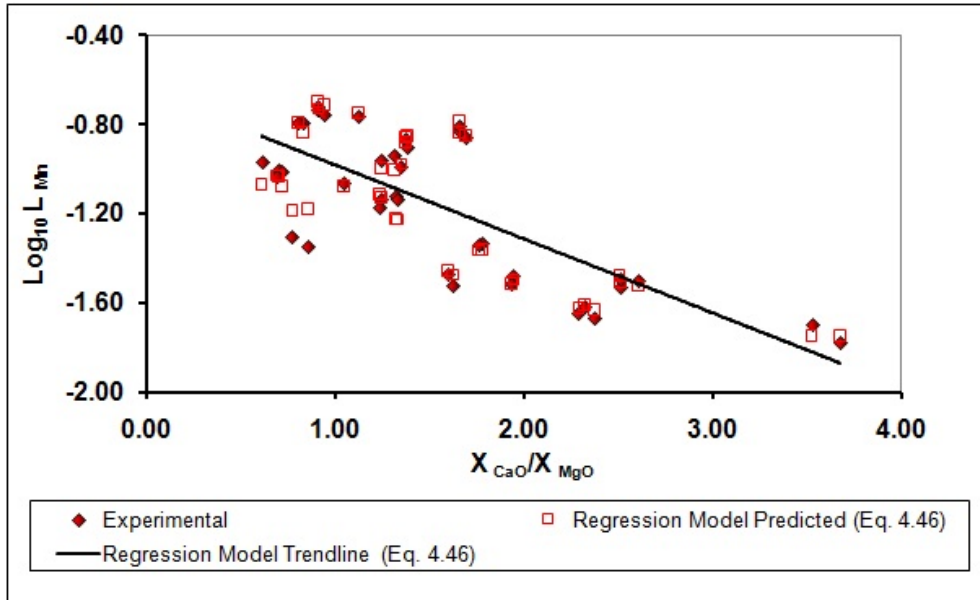


Figure 4.72 The effect of CaO-to-MgO ratio of ferromanganese slag on the distribution ratio of manganese between the slag and the metal phases;
 X_{CaO} : 0.1680- 0.4352, X_{SiO_2} : 0.3519-0.4572, X_{MgO} : 0.1152-0.2748

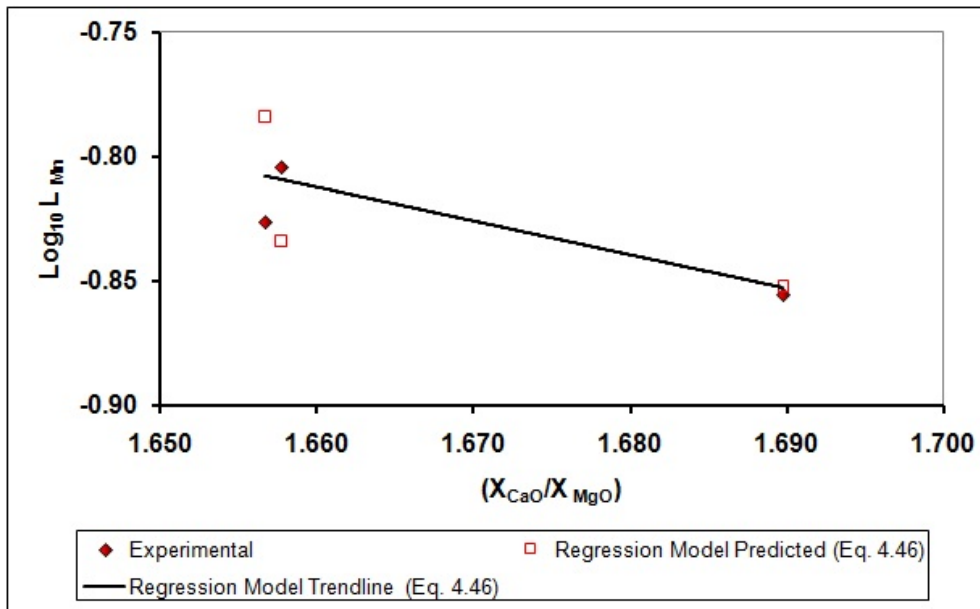


Figure 4.73 The effect of CaO-to-MgO ratio of ferromanganese slag on the distribution ratio of manganese between the slag and the metal phases;
 X_{CaO} : 0.2504- 0.2576, X_{SiO_2} : 0.4195-0.4310, X_{MgO} : 0.1512-0.1524

5 CONCLUSIONS AND RECOMMENDATIONS

The focus of this study has been to understand the influence of slag composition on sulphur and phosphorus behaviour of ferrochromium and ferromanganese smelting slags. The following chapter form a summary of the new information that has been gained from this research study.

The main objectives of this research work were summarized as follows:

- a) To determine sulphide capacities of ferrochromium smelting slags,
- b) To determine equilibrium sulphur distribution ratios between slag and metal phases pertinent to ferrochromium smelting,
- c) To understand slag components influences on the sulphur behavior pertinent to ferrochromium smelting
- d) To determine phosphide capacities of ferrochromium smelting slags,
- e) To determine equilibrium phosphorus distribution ratios between slag and metal phases pertinent to ferrochromium smelting,
- f) To understand slag components influences on the phosphorus behavior pertinent to ferrochromium smelting
- g) To determine sulphide capacities of ferromanganese smelting slags,
- h) To determine equilibrium sulphur distribution ratios between slag and metal phases pertinent to ferromanganese smelting,
- i) To understand slag components influences on the sulphur behavior pertinent to ferromanganese smelting
- j) To determine equilibrium manganese distribution ratios between slag and metal phases pertinent to ferromanganese smelting.
- k) To understand slag components influences on the manganese behavior pertinent to ferromanganese smelting

5.1 Sulphur Behaviour in Ferrochromium Smelting

In the first part of the study, the equilibrium between Cr-Fe-Si-C_(sat)-S alloys and SiO₂-CaO-Al₂O₃-MgO-CaS-Cr₂O₃ slags was studied under carbon monoxide atmosphere (P_{O_2} : 2.56×10^{-16} atm) at 1600 °C in graphite crucibles. 30 successful experiments were conducted. Equilibrium distribution ratios of sulphur between slag and metal phases were determined for different compositions of both phases based on the successful experiments results. In addition to sulphide capacities of SiO₂-CaO-Al₂O₃-MgO-CaS-Cr₂O₃ multi component slag system were determined in this part of the study. The relations between sulphur distribution ratios, sulphide capacities and several parameters (SiO₂ content, CaO content, MgO content, Basicity ratio, Optical Basicity, CaO-to-MgO ratio, Lattice (Binding) Energy of O²⁻ ion in the mixture, activity of calcium oxide) have been analyzed in terms of gas-slag-metal equilibrium. The results and relevant discussions are presented in mainly in the form of figures. Also, the chromium behaviour in SiO₂-CaO-Al₂O₃-MgO-CaS-Cr₂O₃ multi component slag system was examined by using Muan's approach (1984) in the subsection of this study. Two empirical models were developed for expressing the sulphur distribution ratios and sulphide capacities of ferrochromium smelting slag. These two quadratic regression models are suitable for the usage of industrial ferrochromium smelting operations. Another empirical model was produced for understanding the relationship between optical basicity and sulphide capacities of slags. Also, the correlation between activity of calcium oxide and sulphide capacities was analysed on the basis of a regression model. Despite, the development of these models, these are as empirical relations and reliable only for the given slag compositions and experimental conditions. Therefore, "Binding Energy Model" concept has been applied for modeling the sulphide capacities of ferrochromium smelting slags. This approach was derived from a previous study conducted by Ichise and Moro-Oka (1990) and extended to the present slag system. It was found that Binding Energy Model can be successfully applicable for determining sulphide capacities of above-mentioned slag system. Also, a ternary phase diagram which includes iso-sulphide capacity

curves was generated for predicting the sulphide capacities of ferrochromium smelting slags at 1600 °C.

Following points were concluded based on the results of gas-slag-metal equilibrium experiments of sulphide capacities of ferrochromium smelting slags and sulphur distribution ratios between slag and metal phases of ferrochromium smelting at 1600 °C under carbon monoxide atmosphere (P_{O_2} : 2.56×10^{-16} atm)

- 1) It was shown that the silica concentration of slag and sulphide capacities of slags has an opposing effect on each other. In other words, the sulphide capacity of the ferrochromium smelting slag decreases as its silica content increases. Also, the sulphur transfer from metal to slag phase tends to reduce with increasing amount of silica in the slag phase.
- 2) The results revealed that the sulphide capacities of the ferrochromium smelting slags increases with increasing CaO concentration in the slag phase. Secondly, it is seen that the sulphur distribution ratio between slag and metal phases enhances with the increase of CaO content of the slag phase.
- 3) The enhancement of MgO content in the slag system causes an increase on the sulphide capacities of ferrochromium smelting slags when the other slag components compositions is kept in a narrow range. Moreover, the positive impact of MgO addition to the slag phase was found on the sulphur partition ratios between slag and metal phases.
- 4) It is clear that basicity ratio has a significant influence on the sulphide capacity of SiO_2 -CaO- Al_2O_3 -MgO-CaS- Cr_2O_3 multi component slag system. As the basicity ratio increases the sulphide capacity of the slag enhances. In addition to that, an increase in the basicity ratio of the ferrochromium smelting slags results an increase in the sulphur partition ratio between slag and metal phases.
- 5) A linear nature relationship between optical basicity of slag and sulphide capacity was observed. That is, as the optical basicity of the slag increases, the sulphide capacity of the ferrochromium smelting slag tends to enhance.

Again, it was observed that sulphur partition ratios between slag and metal phases tend to enhance with the increase of optical basicity values of the slag.

- 6) An increase in CaO-to-MgO ratio of the slag results an increase on the sulphide capacity of the slag. Also, it is clear from the results that MgO has a limited influence on the sulphide capacities compared to CaO. It was also shown that the sulphur distribution ratios between slag and metal enhances as CaO-to-MgO ratio increases.
- 7) A linear correlation between binding energy of $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO-CaS-Cr}_2\text{O}_3$ multi component slag system and sulphide capacities of the slags was found. As expected, a decrease in the basicity of the slag leads to an increase in the binding energy of the slag system, which ultimately results a drop in the sulphide capacities of the slag.
- 8) A straight line with a slope to unity was observed between logarithm of activity of calcium oxide and sulphide capacities of ferrochromium smelting slags. This indicates that the activity of oxygen ions in the slag is closely related to activity of calcium oxide. In other words, the calcium oxide concentration of the slag system significantly affects the sulphide capacities of $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO-CaS-Cr}_2\text{O}_3$ multi component slag system.
- 9) From chromium behaviour point of view, it was found that the chromium in the slag phase is mainly in its divalent state (CrO). CrO:Cr₂O₃ ratio was calculated as 2.73 based on the experimental results.

5.2 Phosphorus Behaviour in Ferrochromium Smelting

In the second part of the research work, the equilibrium between Cr-Fe-Si-C_(sat)-P alloys and $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO-Ca}_3\text{P}_2\text{-Cr}_2\text{O}_3$ slags was investigated under carbon monoxide atmosphere (P_{O_2} : 2.56×10^{-16} atm) at 1600 °C in graphite crucibles. 29 successful gas-slag-metal equilibrium experiments were conducted. Equilibrium phosphorus distribution ratios between slag and metal phases were determined under these experimental conditions. Also, phosphide capacities

pertinent to ferrochromium smelting were calculated in terms of gas-slag-metal equilibrium. Several figures were generated in the discussion section of this part of the work. The relationships among phosphorus distribution ratios, phosphide capacities and several parameters (SiO_2 content, CaO content, MgO content, Basicity ratio, Optical Basicity, CaO-to-MgO ratio, Lattice (Binding) Energy of O^{2-} ion in the mixture, activity of calcium oxide) were examined in the related discussion parts. The experimental results were used in the development of two empirical models for understanding the phosphorus behaviour (phosphide capacity and phosphorus distribution between slag and metal) in the ferrochromium smelting. A linear regression model was developed for determining the correlation between the optical basicity and phosphide capacities of ferrochromium smelting slags. In addition to that another empirical model was generated for analyzing the relationship between activity of calcium oxide and phosphide capacities. Furthermore, Binding Energy Model was developed for determining phosphide capacities of $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO-Ca}_3\text{P}_2\text{-Cr}_2\text{O}_3$ multi component slag system. The predicted iso-phosphide capacity lines based on binding energy model were plotted in a ternary phase diagram.

For the second part of the study, the following were observed based on the results of gas-slag-metal equilibrium experiments of phosphide capacities of ferrochromium smelting slags and phosphorus distribution ratios between slag and metal phases of ferrochromium smelting at 1600 °C under carbon monoxide atmosphere (P_{O_2} : 2.56×10^{-16} atm)

- 1) An increase in the silica amount of the slag leads to a drop in the phosphide capacities of $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO-Ca}_3\text{P}_2\text{-Cr}_2\text{O}_3$ multi component slag system. Also, it was observed that the phosphorus transfer rate from metal to slag sharply decreases with the increase of silica concentration of the slag.
- 2) It was shown that an increase of CaO content in the slag results an increase of phosphide capacity and phosphorus distribution ratios between slag and metal.

- 3) The addition of MgO content into the slag system leads to an increase on the phosphide capacities ferrochromium smelting slags when the other slag components are kept in a narrow range. Likewise, the phosphorus distribution ratios between slag and metal tend to enhance with increasing MgO concentration in the slag phase.
- 4) The results indicated that the transfer of phosphorus from metal to slag can be enhanced with increasing the basicity ratio. Besides, phosphide capacity of the slag system was found to be directly proportional to the basicity ratio of the ferrochromium smelting slags.
- 5) It was shown that the phosphide capacity and optical basicity of slag are directly proportional to each other. As the optical basicity of the slag increases, the phosphide capacity of the ferrochromium smelting slag tends to increase. Also, the results clearly showed that phosphorus distribution ratios between slag and metal phases tend to augment with the increase of slag's optical basicity.
- 6) The positive influence of CaO-to-MgO ratio of the slags on phosphide capacities of the slags were seen when basicity ratio was kept in a narrow range. Besides, it was observed that the phosphorus transfer from metal to slag tends to increase with increasing CaO-to-MgO ratio of $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO-Ca}_3\text{P}_2\text{-Cr}_2\text{O}_3$ multi component slags.
- 7) The results revealed that an inversely proportional linear correlation between binding energy of $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO-CaS-Cr}_2\text{O}_3$ multi component slag system and phosphide capacities of the slags was exist.
- 8) A straight line with a slope equal to 1.52 was found between logarithm of activity of calcium oxide and phosphide capacities of ferrochromium smelting slags, which clearly indicates the close relation between the activity of oxygen ions and activity of calcium oxide in the slags.
- 9) The $\text{CrO:Cr}_2\text{O}_3$ ratio was found to be equal to 2.85 based on calculations, which shows that the chromium is mainly in divalent form in $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3\text{-MgO-CaS-Cr}_2\text{O}_3$ multi component slag system under these experimental conditions.

5.3 Sulphur Behaviour in Ferromanganese Smelting

In the third part of the research study, the equilibrium between Mn-Fe-Si-C_(sat)-S alloys and SiO₂-CaO-Al₂O₃-MgO-MnO-CaS was studied under carbon monoxide atmosphere (P_{O_2} : 1.21×10^{-16} atm) at 1500 °C in graphite crucibles. 41 successful experiments were conducted. Equilibrium sulphur and manganese partition ratios between slag and metal phases were determined for different metal and slag compositions. Furthermore, the sulphide capacities related to ferromanganese smelting slags were determined in terms of gas-slag-metal equilibrium in graphite crucibles at 1500 °C under carbon monoxide atmosphere. The results and relevant discussions were explained in the form of figures. The relationships between sulphur distribution ratios, sulphide capacities and several parameters (SiO₂ content, CaO content, MgO content, Basicity ratio, Optical Basicity, CaO-to-MgO ratio, Lattice (Binding) Energy of O²⁻ ion in the mixture, activity of calcium oxide) have been analyzed in details in these figures. Also, the correlations between manganese distribution ratios and SiO₂ content, CaO content, MgO content, MnO content, Basicity Ratio, Optical Basicity, CaO-to-MgO ratio, activity of calcium oxide, activity of manganese oxide were derived in this part of the study. Three empirical model were developed for a better understanding the sulphur (sulphide capacity and sulphur distribution ratio) and manganese (manganese distribution ratio) behaviour in ferromanganese smelting. Two different regression models were developed among the activity of calcium oxide, activity of manganese oxide and sulphide capacities. Also, the relationship between optical basicity and sulphide capacities of slags was analyzed by using an empirical model developed during the course of the work. Also, the correlation between activity of calcium oxide and sulphide capacities was analysed on the bases of a regression model. In addition to these models, Binding Energy Model was used for predicting the sulphide capacities of SiO₂-CaO-Al₂O₃-MgO-MnO-CaS multi component slag system at 1500 °C.

The results of gas-slag-metal equilibrium experiments of sulphide capacities of ferromanganese smelting slags and sulphur distribution ratios between slag and

metal phases of ferromanganese smelting at 1500 °C under carbon monoxide atmosphere (P_{O_2} : 1.21×10^{-16} atm) revealed the following conclusions:

- 1) It was evident that the sulphide capacities of ferromanganese smelting slags decreases with increasing silica content of the slag. Also, the results exhibited that the equilibrium distribution ratio of sulphur is inversely proportional to the silica concentration of the slag phase.
- 2) Based on the results, the sulphide capacity was found to be directly proportional to the calcium oxide content of the ferromanganese slag. Furthermore, the sulphur partition ratio between slag and metal tends to increase with increasing calcium oxide concentration in the slag.
- 3) The results showed that an increase in the amount of MgO results an increase on the sulphide capacity of SiO_2 -CaO- Al_2O_3 -MgO-MnO-CaS multi component slag system. In addition to that it was observed that the distribution ratios of sulphur tend to augment with increasing MgO content in the slag phase.
- 4) It was clear that the manganese oxide content of the slag has a significant positive impact on the sulphide capacities of the slag system. Furthermore, it was seen that the sulphur partition ratio between slag and metal rises with the increase of manganese oxide in the slag phase.
- 5) Basicity ratio of slag was found as the main parameter for controlling the sulphur behaviour in ferromanganese smelting process. It was shown that the sulphide capacities of the slags enhance with the increase of the basicity ratio. Moreover, an increase in the basicity ratio of the slag phase leads to enhancement on the sulphur distribution ratio between slag and metal.
- 6) A linear correlation between sulphide capacities and optical basicities of slags were identified in the study. An increase in the optical basicity of the slag results an increase on the sulphide capacities and this effect is more pronounced at the optical basicities lower than 0.66. Also, the sulphur partition ratio tends to augment with the increase of optical basicity of the slag.

- 7) As the CaO-to-MgO ratio of the slag rises the sulphide capacity of the slag increases, that is, as CaO replaces MgO the activity of SiO₂ reduces. Again, it was seen that the replacement of MgO with CaO helps to improve the desulphurisation of the metal phase.
- 8) Based on the experimental results, a moderate correlation between the sulphide capacity and the activity of CaO of SiO₂-CaO-Al₂O₃-MgO-MnO-CaS multi component slag system were observed.
- 9) The results exhibited a presence of poor correlation between the activity of manganese oxide and sulphide capacities can be done. This shows the strong influence of other basic oxides on the activity of oxygen anions in the slag.
- 10) An increase in the silica concentration results an increase on the manganese distribution ratio between slag and metal.
- 11) It was seen that the manganese distribution ratios can be lowered by increasing the calcium oxide concentration of the ferromanganese smelting slag.
- 12) The enhancement of magnesium oxide content of slag phase results a drop in the manganese loss to the slag phase.
- 13) An increase in the basicity ratio of the slag reduces the manganese distribution ratio between slag and metal phases.
- 14) The positive impact of optical basicity on the manganese loss to slag was also observed on the results of experiments. The increased optical basicity leads to drop the manganese transfer from metal to slag.
- 15) As the CaO-to-MgO ratio of the slag enhances the manganese partition ratio between slag and metal phases tends to lower.

In conclusion, the optimum features of slag compositions for minimizing the phosphorus and sulphur problem in the ferroalloy smelting can be stated in broad overall context of the work. It is clear that the slag basicity is the most important tool for effective desulphurisation and dephosphorisation of the ferroalloy smelting slags.

5.4 Recommendations for Future Work

For the future works following recommendations can be done:

- Further gas-slag-metal equilibrium experiments need to be done at elevated temperatures such as 1650 °C for ferrochromium smelting and 1550 °C for ferromanganese smelting.
- It is also recommended that the sulphide and phosphide capacities of ferroalloys smelting slags under argon/carbon monoxide atmosphere need to be determined for understanding the influence of partial pressure of oxygen on the desulphurisation and dephosphorisation of ferroalloys.
- The present work was focused on the high carbon ferroalloy production. Therefore, the future work may include the determinations of sulphide and phosphide of medium and lower carbon ferroalloys.
- The gas-slag-metal equilibrium experiments results need to be integrated into structural and empirical models such as KTH (Nzotta et al., 1999b) and IRSID (Gaye et al., 1992) slag models by using thermodynamic databases. This requires a thermodynamic simulation software preferably FactSage and collaboration with other research centers.

DETERMINATION OF THE ACTIVITY COEFFICIENT OF SULPHUR IN FERROCHROMIUM

The activity coefficient of sulphur in the dilute solution of chromium can be calculated by using the following equation:

$$\begin{aligned} \text{Log } f_s = & e_s^C(\text{wt. \%C}) + e_s^{\text{Si}}(\text{wt. \%Si}) + e_s^{\text{Mn}}(\text{wt. \%Mn}) + e_s^{\text{S}}(\text{wt. \%S}) \\ & + e_s^{\text{Al}}(\text{wt. \%Al}) + e_s^{\text{Ti}}(\text{wt. \%Ti}) + r_s^C(\text{wt. \%C})^2 + r_s^{\text{Si}}(\text{wt. \%Si})^2 \\ & + r_s^{\text{S}}(\text{wt. \%S})^2 + r_s^{\text{Al}}(\text{wt. \%Al})^2 + r_s^{\text{Ti}}(\text{wt. \%Ti})^2 \end{aligned} \quad (\text{A1})$$

The first and second order interaction coefficients of sulphur in carbon saturated iron at 1600 °C (1873 K) are given in Table A1.

Table A1 Values of the interaction parameters (Sigworth and Elliott, 1974)

Interaction Parameter	C	Si	Mn	S	Al	Ti
e_s^J	0.11	0.063	-0.026	-0.046	0.035	-0.072
r_s^J	0.0058	0.0017	-	-0.0009	0.0009	0.0001

APPENDIX B

DETERMINATION OF THE ACTIVITY COEFFICIENT OF PHOSPHORUS IN FERROCHROMIUM

The activity coefficient of phosphorus in the dilute solution of chromium can be calculated by using the following equation:

$$\begin{aligned} \text{Log } f_s = & e_p^C(\text{wt. \%C}) + e_p^P(\text{wt. \%P}) + e_p^{\text{Si}}(\text{wt. \%Si}) + e_p^{\text{Mn}}(\text{wt. \%Mn}) \\ & + e_p^{\text{Al}}(\text{wt. \%Al}) + e_p^{\text{Ti}}(\text{wt. \%Ti}) + r_p^P(\text{wt. \%P})^2 + r_p^{\text{Si}}(\text{wt. \%Si})^2 \end{aligned} \quad (\text{B1})$$

The first and second order interaction coefficients of phosphorus in carbon saturated iron at 1600 °C (1873 K) are given in Table B1.

Table B1. Values of the interaction parameters (Sigworth and Elliott, 1974)

Interaction Parameter	C	P	Si	Mn	Al	Ti
e_p^J	0.126	0.054	0.099	0.002	0.037	-0.04
r_p^J	-	-0.001	-0.001	-	-	-

APPENDIX C

DETERMINATION OF THE ACTIVITY COEFFICIENT OF SULPHUR IN FERROMANGANESE

The activity coefficient of sulphur in the dilute solution of manganese can be calculated by using the following equation:

$$\begin{aligned} \text{Log } f_s = & e_s^C(\text{wt. \%C}) + e_s^{\text{Si}}(\text{wt. \%Si}) + e_s^P(\text{wt. \%P}) + e_s^S(\text{wt. \%S}) + r_s^C(\text{wt. \%C})^2 \\ & + r_s^{\text{Si}}(\text{wt. \%Si})^2 + r_s^S(\text{wt. \%S})^2 + r_s^P(\text{wt. \%P})^2 \end{aligned} \quad (\text{C1})$$

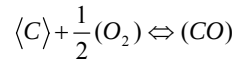
The first and second order interaction coefficients of sulphur in carbon saturated iron at 1500 °C (1773 K) are given in Table C1.

Table C1 Values of the interaction parameters (Sigworth and Elliott, 1974)

Interaction Parameter	Si	P	C	S
e_s^J	0.066	0.03	0.1162	-0.021
r_s^J	0.0017	0.0006	0.0061	-0.0009

APPENDIX D

CALCULATION OF THE PREVAILING PARTIAL PRESSURE OF OXYGEN IN THE REACTION TUBE AT 1600 °C (1873 K) FOR FERROCHROMIUM SMELTING



$$\Delta G^\circ = -26700 - 20.95 T \text{ (cal/mol)} \quad (\text{Bodsworth and Appleton, 1965})$$

$$\Delta G^\circ = -26700 - 20.95 (1873)$$

$$\Delta G^\circ = -26700 - 39239.35$$

$$\Delta G^\circ = -65939.35 \text{ cal}$$

$$-65939.35 \text{ cal} = -RT \ln K_p$$

$$-65939.35 \text{ cal} = -1.9872 \text{ (cal/mol.K)} \times 1873 \text{ K} \times \ln (P_{co}/P_{O_2} \cdot a_c)$$

$$a_c = 1 \text{ (since the graphite crucible was pure solid carbon)}$$

$$P_{co} = 0.83 \text{ atm (since chemically pure carbon monoxide gas was used and the experiments were conducted in Johannesburg)}$$

$$\ln K_p = 17.71598508$$

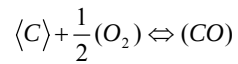
$$K_p = 49425897.27$$

$$P_{O_2}^{1/2} = 0.83 / (49425897.27) = 1.6 \times 10^{-8} \text{ atm.}$$

$$P_{O_2} = 2.56 \times 10^{-16} \text{ atm}$$

APPENDIX E

CALCULATION OF THE PREVAILING PARTIAL PRESSURE OF OXYGEN IN THE REACTION TUBE AT 1500 °C (1773 K) FOR FERROMANGANESE SMELTING



$$\Delta G^\circ = -112877 - 86.514 T \text{ (J/mole)} \quad (\text{Tabuchi and Sano, 1984})$$

$$\Delta G^\circ = -112877 - 86.514 (1773)$$

$$\Delta G^\circ = -266266.322$$

$$-266266.322 = -RT \ln K_p$$

$$-266266.322 = -8.314 \times 1773 \times \ln (P_{CO}/P_{O_2} \cdot a_c)$$

$$a_c = 1 \text{ (since the graphite crucible was pure solid carbon)}$$

$$P_{CO} = 0.83 \text{ atm (since chemically pure carbon monoxide gas was used and the experiments were conducted in Johannesburg)}$$

$$\ln K_p = 18.06331617$$

$$K_p = 69951742.26$$

$$P_{O_2}^{1/2} = 0.83 / (74074548.1) = 1.1 \times 10^{-8} \text{ atm.}$$

$$P_{O_2} = 1.21 \times 10^{-16} \text{ atm}$$

SULPHUR BEHAVIOUR IN FERROCHROMIUM SMELTING

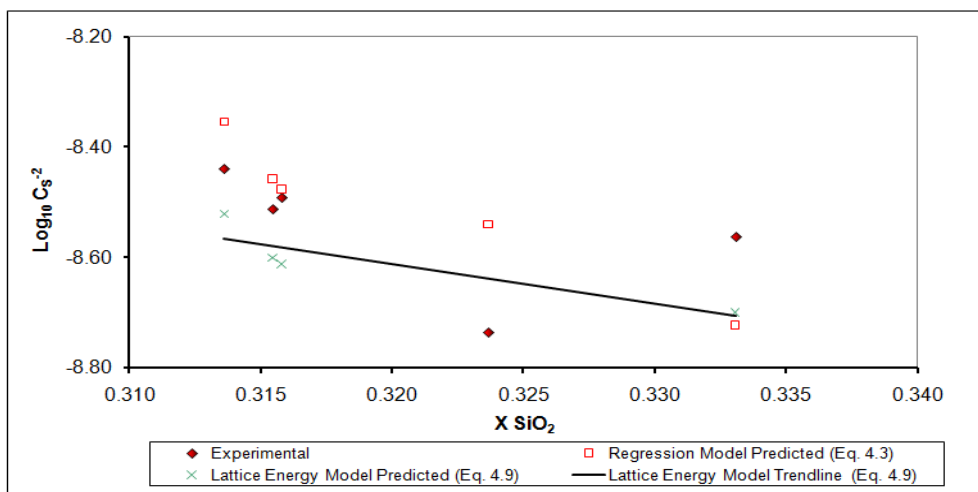
F1 THE VARIATION OF C_S^{-2} AND L_S WITH SILICA (X_{SiO_2}) IN FERROCHROMIUM SMELTING SLAGS

Figure F 1.1 The variation of sulphide capacity with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio:1.689-1.994, X_{CaO} : 0.0882-0.1058, X_{MgO} : 0.4416-0.4710

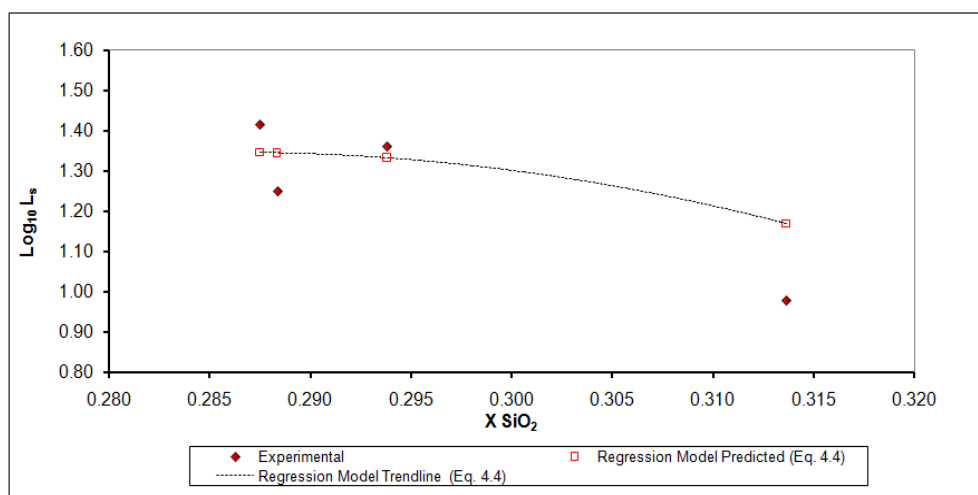


Figure F 1.2 The variation of sulphur distribution ratio with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio:1.689-1.994, X_{CaO} : 0.0882-0.1058, X_{MgO} : 0.4416-0.4710

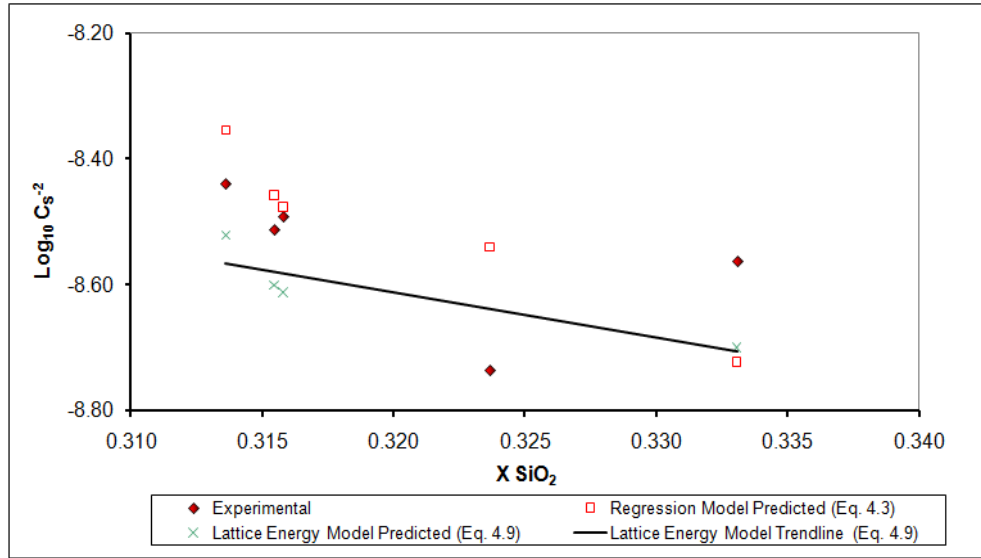


Figure F 1.3 The variation of sulphide capacity with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio:1.608-1.689, X_{CaO} : 0.0467-0.0882, X_{MgO} : 0.4416-0.4899

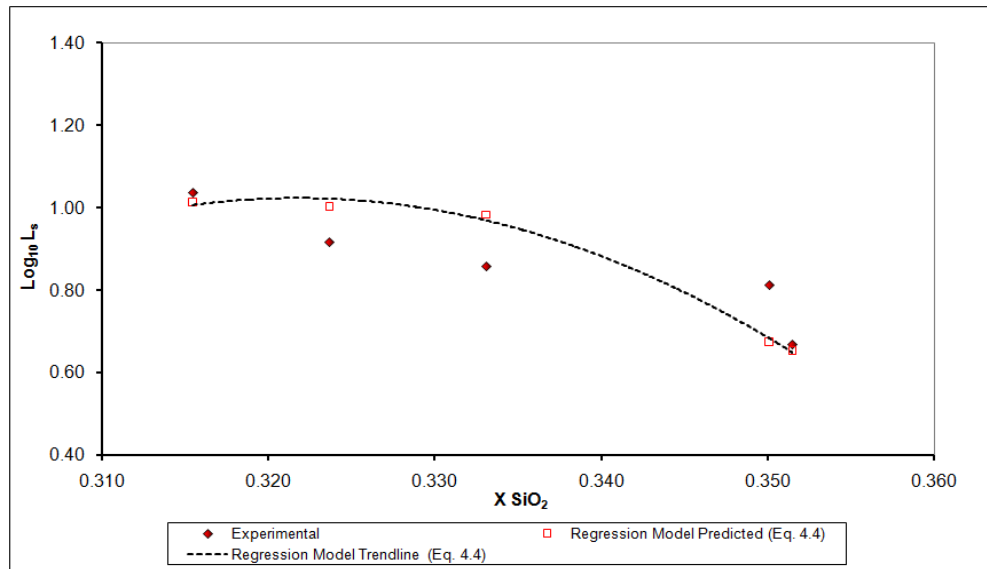


Figure F 1.4 The variation of sulphur distribution ratio with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio : 1.608-1.689, X_{CaO} : 0.0467-0.0882, X_{MgO} : 0.4416-0.4899

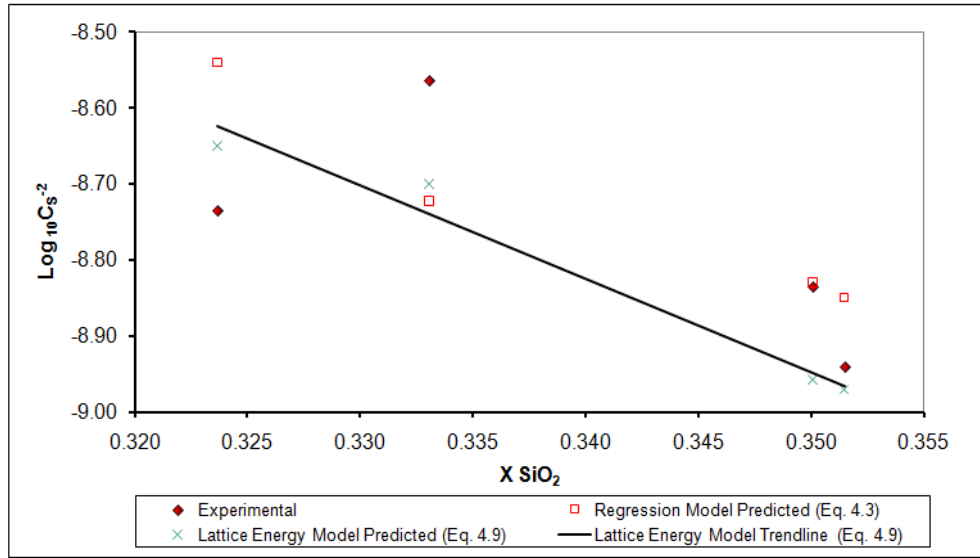


Figure F 1.5 The variation of sulphide capacity with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio : 1.388-1.611, X_{CaO} : 0.0330-0.0568, X_{MgO} : 0.4535-0.4899

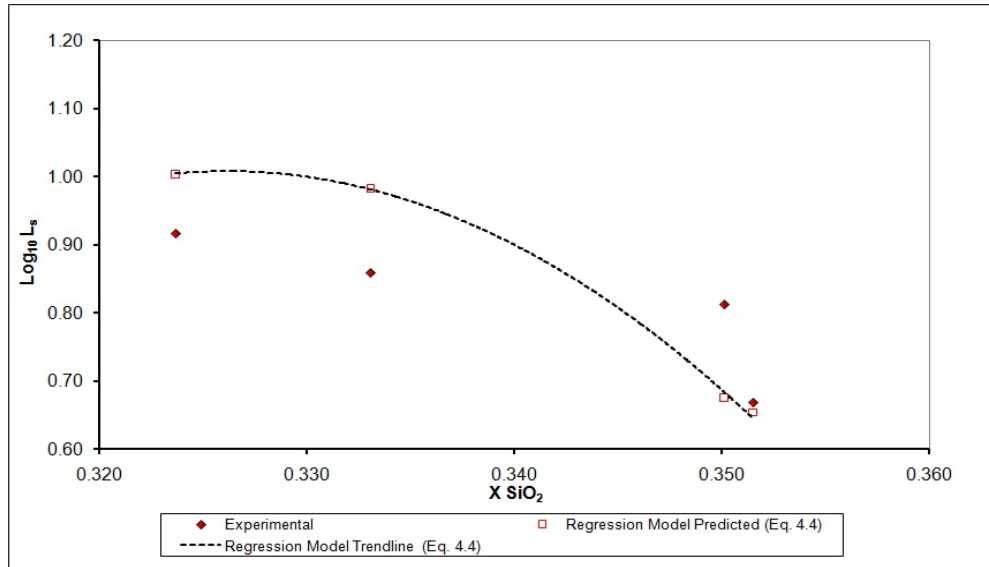


Figure F 1.6 The variation of sulphur distribution ratio with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio: 1.385-1.611, X_{CaO} : 0.0330-0.0568, X_{MgO} : 0.4535-0.4899

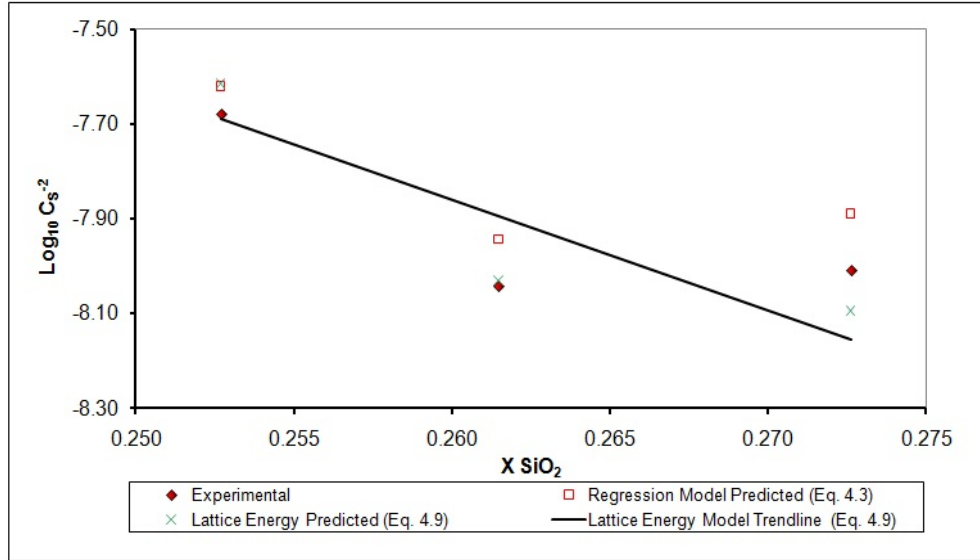


Figure F 1.7 The variation of sulphide capacity with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio: 1.878-2.43, X_{CaO} : 0.1554-0.1868, X_{MgO} : 0.3728-0.4295

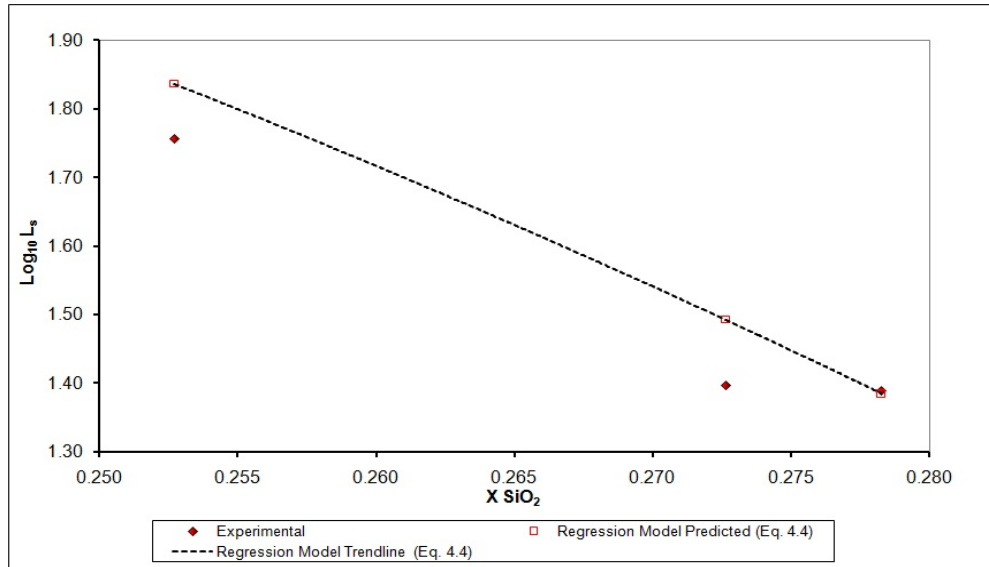


Figure F 1.8 The variation of sulphur distribution ratio with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio : 1.878-2.43, X_{CaO} : 0.1554-0.1868, X_{MgO} : 0.3728-0.4295

F2 THE VARIATION OF C_S^{-2} AND L_S WITH CALCIUM OXIDE (X_{CaO}) IN FERROCHROMIUM SMELTING SLAGS

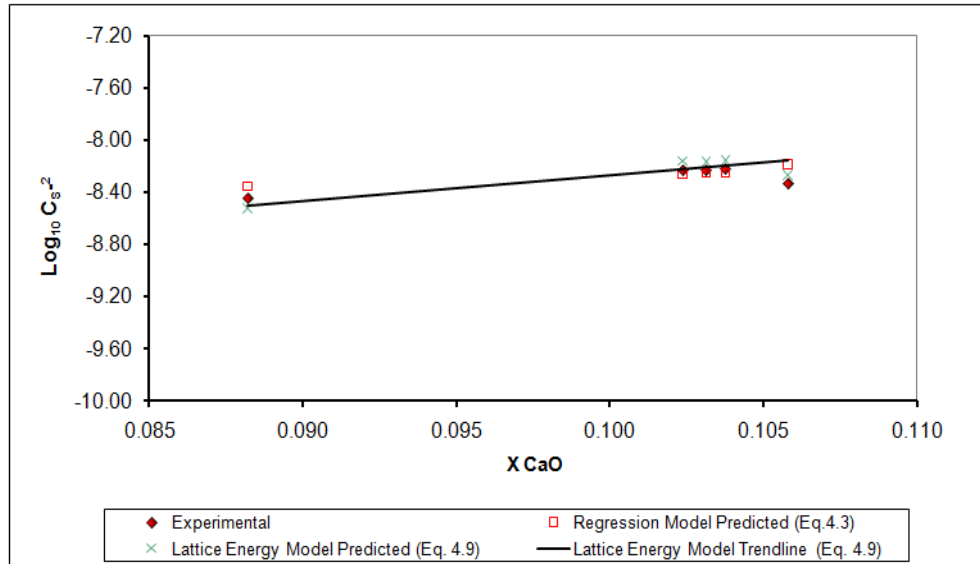


Figure F 2.1 The variation of sulphide capacity with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag; Basicity Ratio: 1.433-2.439, X_{SiO_2} : 0.2527-0.3859, X_{MgO} : 0.3064-0.4899

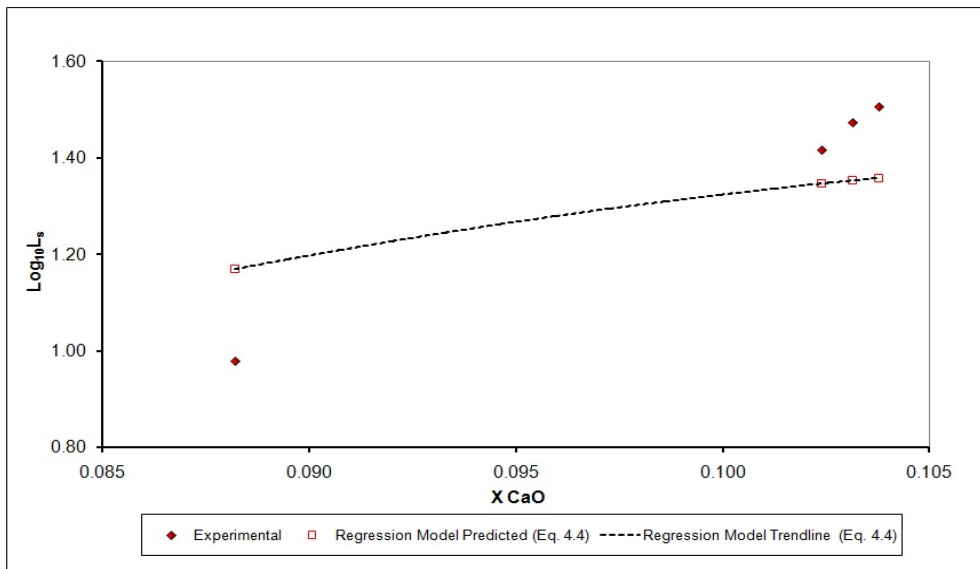


Figure F 2.2 The variation of sulphur distribution ratio with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag; Basicity Ratio : 1.689-1.995, X_{SiO_2} : 0.2875-0.3136, X_{MgO} : 0.4416-0.4710

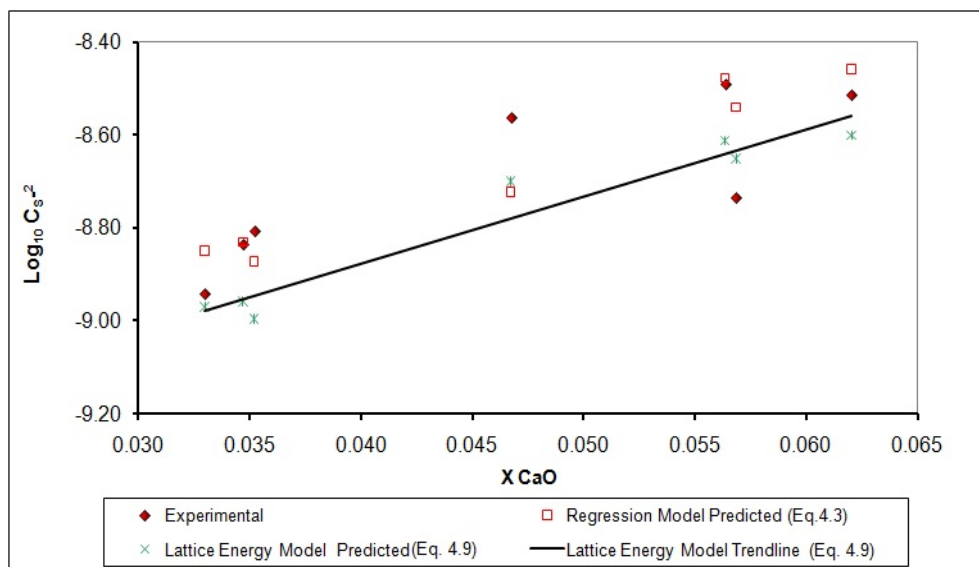


Figure F 2.3 The variation of sulphide capacity with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag; Basicity Ratio: 1.363-1.624, X_{SiO_2} : 0.3155-0.3534, X_{MgO} : 0.4467-0.4899

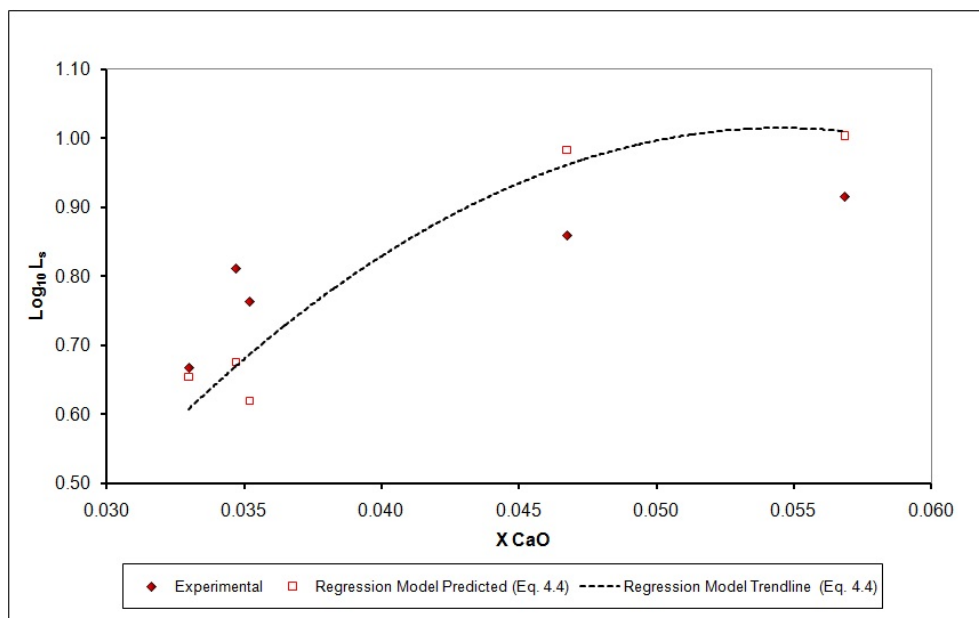


Figure F 2.4 The variation of sulphur distribution ratio with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag; ; Basicity Ratio: 1.363-1.611, X_{SiO_2} : 0.3237-0.3534, X_{MgO} : 0.4467-0.4899

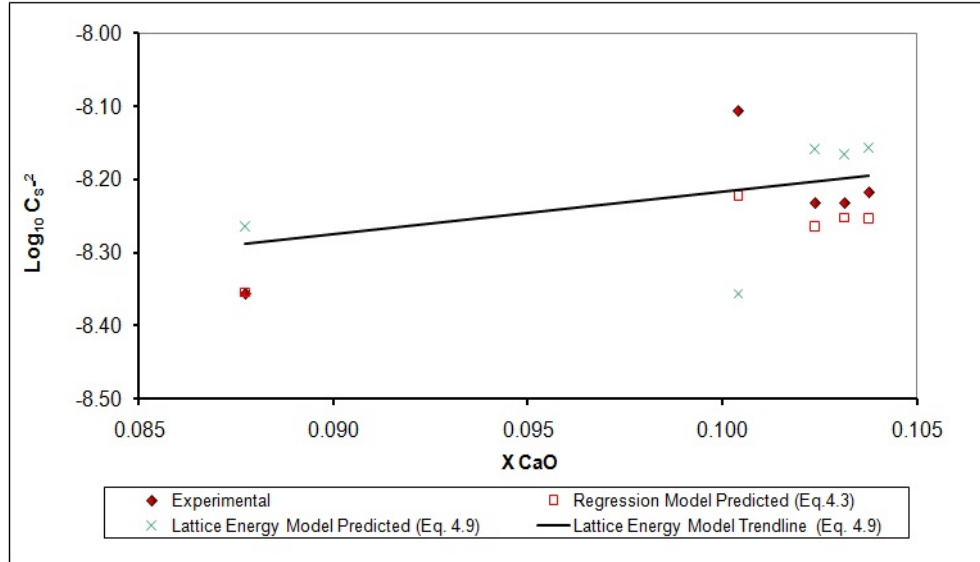


Figure F 2.5 The variation of sulphide capacity with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag; Basicity Ratio: 1.808-1.995, X_{SiO_2} : 0.2875-0.2990, X_{MgO} : 0.4691-0.4788

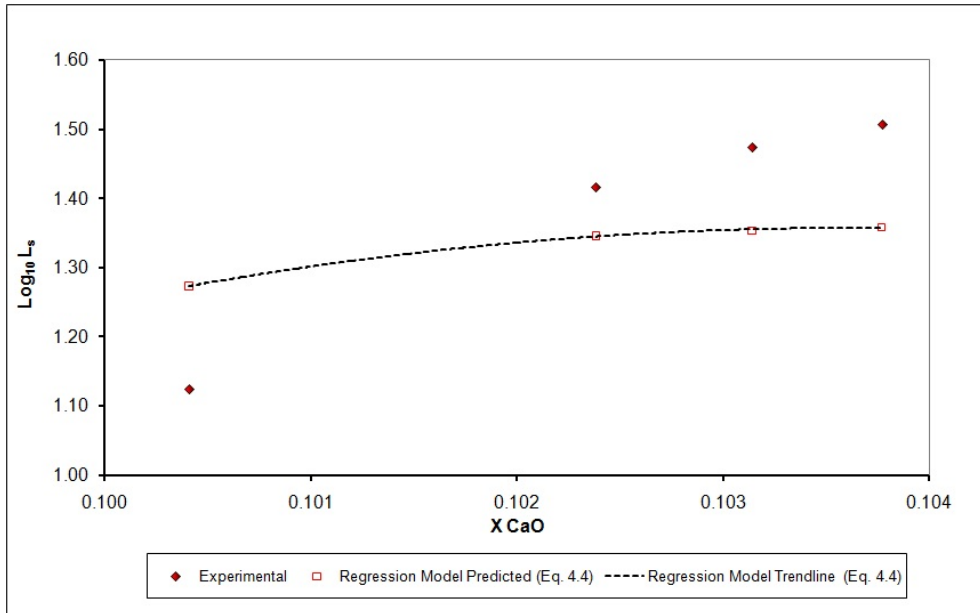


Figure F 2.6 The variation of sulphur distribution ratio with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag ; Basicity Ratio: 1.808-1.995, X_{SiO_2} : 0.2875-0.2990, X_{MgO} : 0.4404-0.4710

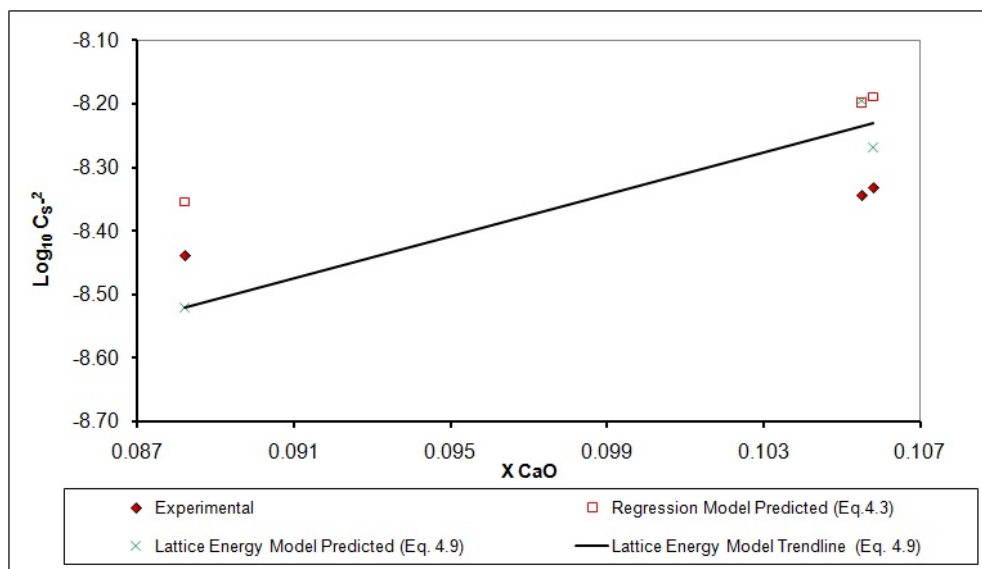


Figure F 2.7 The variation of sulphide capacity with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag; Basicity Ratio: 1.689-1.951, X_{SiO_2} : 0.2883-0.3136, X_{MgO} : 0.4416-0.4572

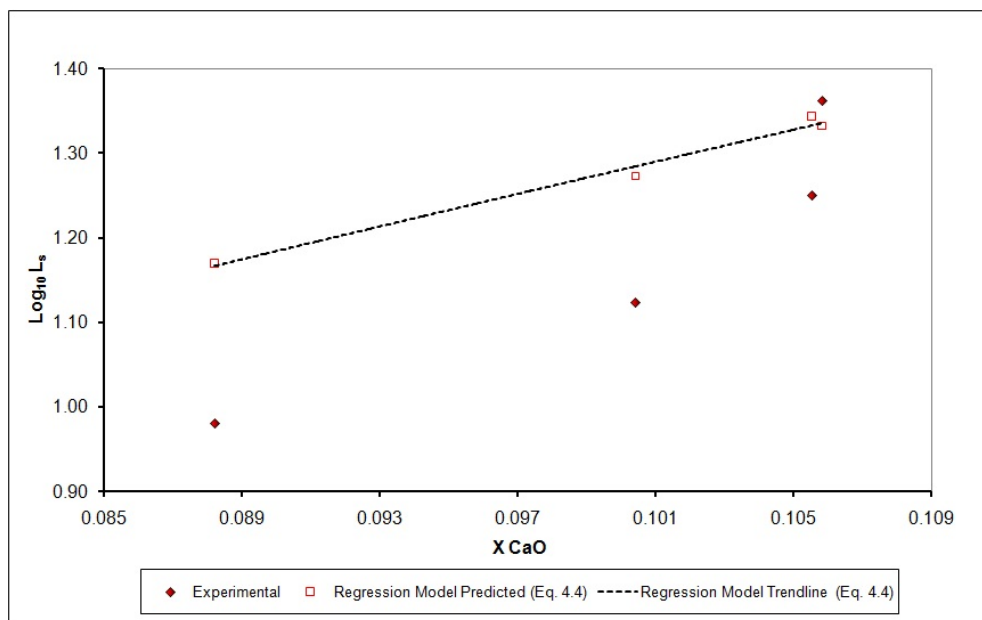


Figure F 2.8 The variation of sulphur distribution ratio with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag ; Basicity Ratio: 1.689-1.951, X_{SiO_2} : 0.2875-0.3136, X_{MgO} : 0.4416-0.4710

F3 THE VARIATION OF C_S^{-2} AND L_S WITH MAGNESIUM OXIDE (X_{MgO}) IN FERROCHROMIUM SMELTING SLAGS

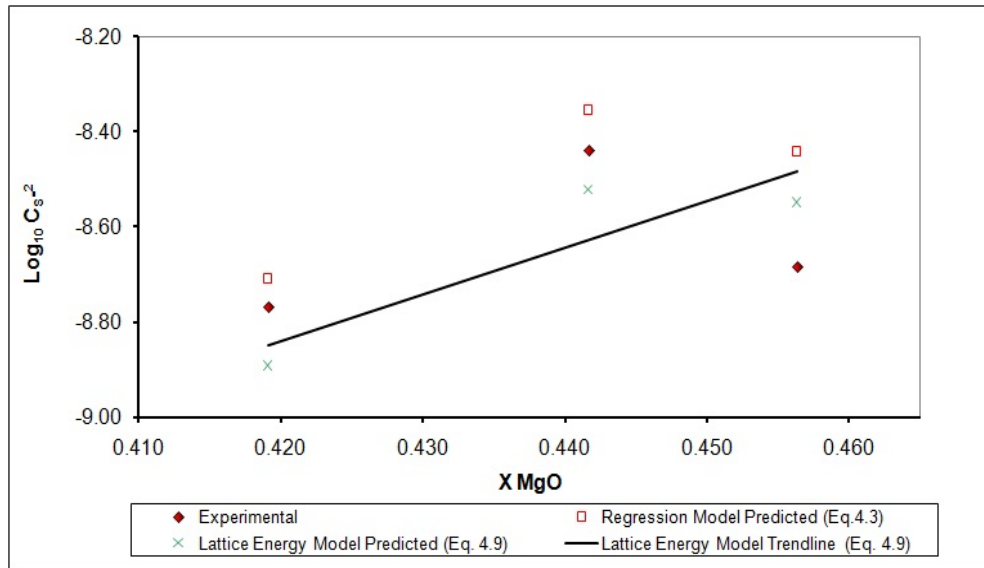


Figure F 3.1 The variation of sulphide capacity with magnesium oxide mole fraction (X_{MgO}) of ferrochromium smelting slag; Basicity Ratio: 1.433-1.689, X_{SiO_2} : 0.3136-0.3528, X_{CaO} : 0.0882-0.0895

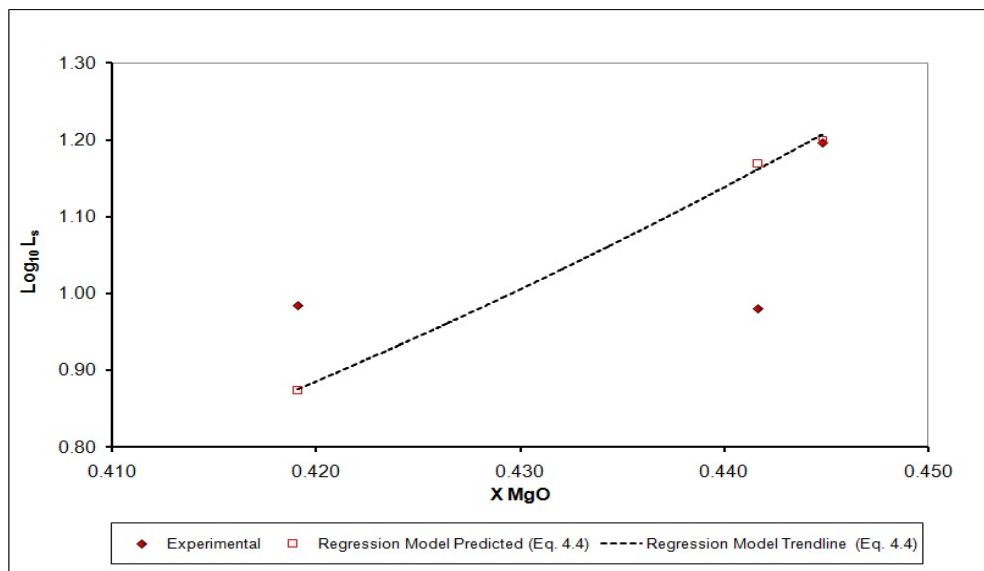


Figure F 3.2 The variation of sulphur distribution ratio with magnesium oxide mole fraction (X_{MgO}) of ferrochromium smelting slag; Basicity Ratio: 1.433-1.690, X_{SiO_2} : 0.3136-0.3528, X_{CaO} : 0.0862-0.0908

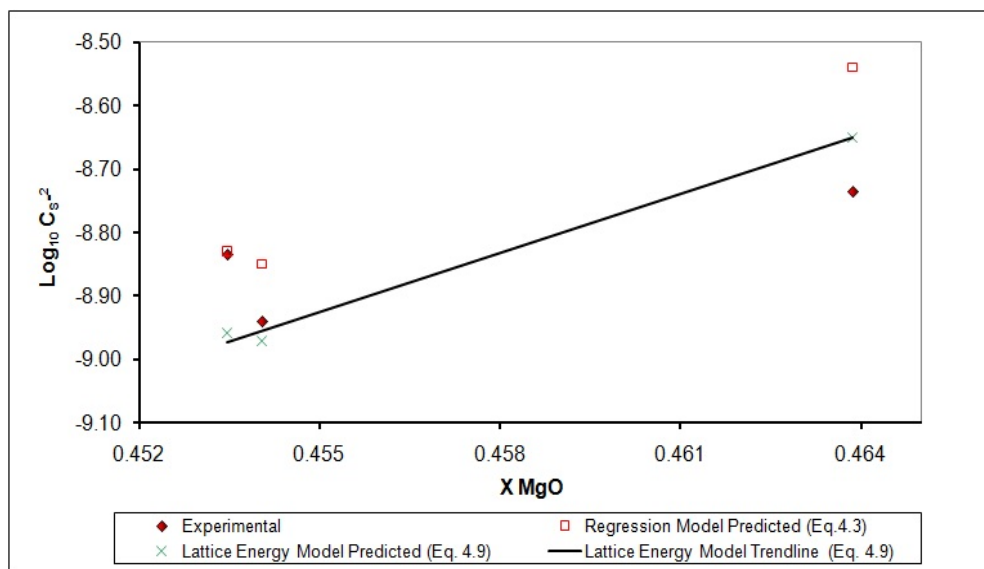


Figure F 3.3 The variation of sulphide capacity with magnesium oxide mole fraction (X_{MgO}) of ferrochromium smelting slag; Basicity Ratio : 1.385-1.608, X_{SiO_2} : 0.3237-0.3515, X_{CaO} : 0.0330-0.0568

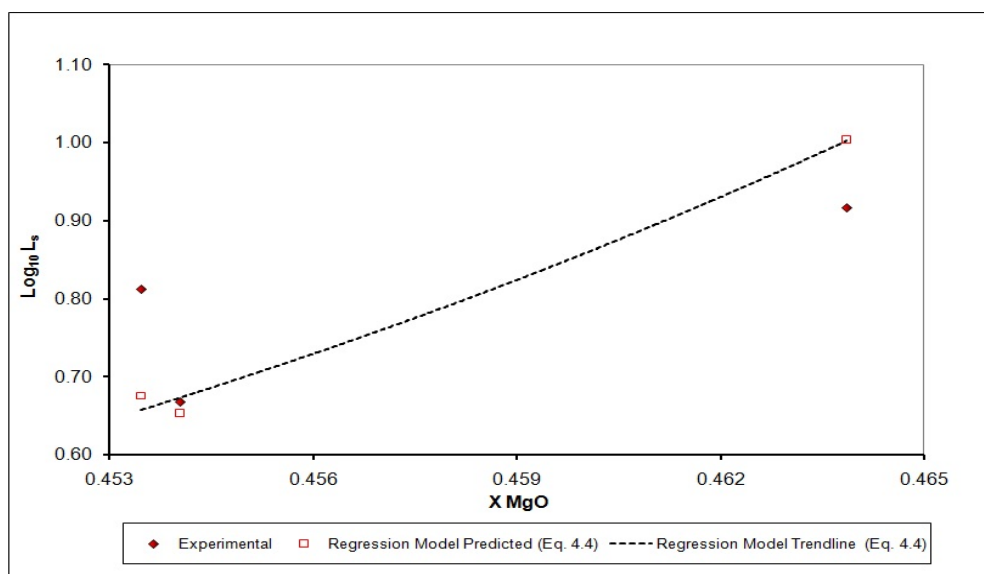


Figure F 3.4 The variation of sulphur distribution ratio with magnesium oxide mole fraction (X_{MgO}) of ferrochromium smelting slag; Basicity Ratio: 1.385-1.608, X_{SiO_2} : 0.3237-0.3515, X_{CaO} : 0.0330-0.0568

F4 THE VARIATION OF C_S^{-2} AND L_S WITH BASICITY RATIO $[(X_{CaO}+X_{MgO})/X_{SiO_2}]$ OF FERROCHROMIUM SMELTING SLAGS

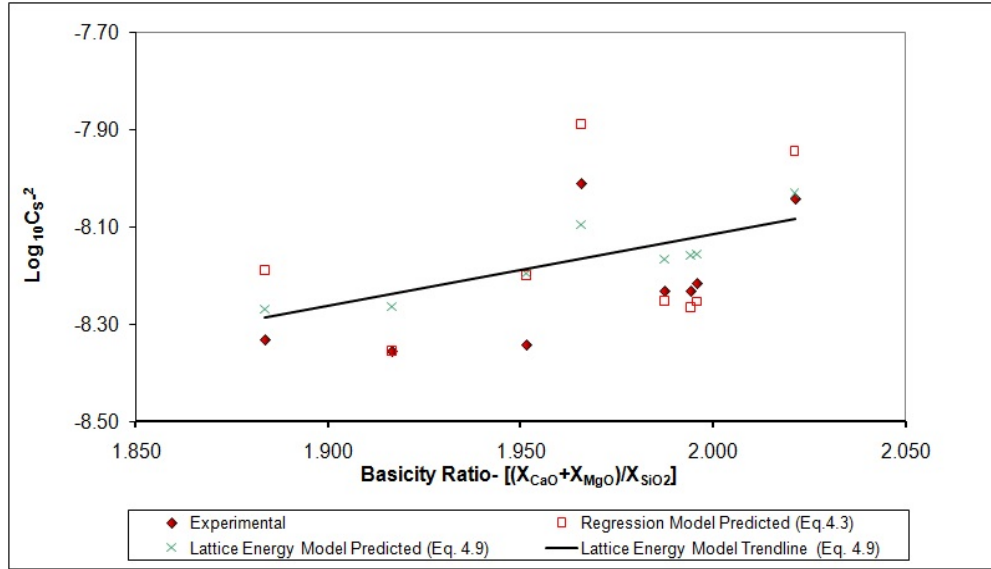


Figure F 4.1 The effect of basicity ratio on the sulphide capacity of ferrochromium smelting slag; X_{SiO_2} :0.2527-0.3859, X_{CaO} :0.0877-0.1557, X_{MgO} :0.3064-0.4899

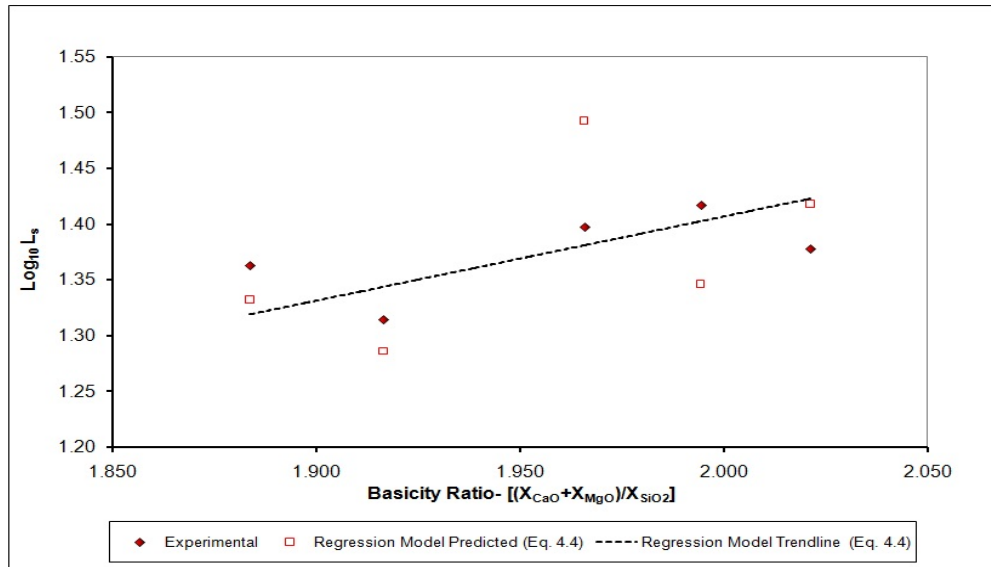


Figure F 4.2 The effect of basicity ratio on the sulphur distribution ratio of ferrochromium smelting slag; X_{SiO_2} :0.2527-0.3859, X_{CaO} :0.0877-0.1557, X_{MgO} :0.3064-0.4899

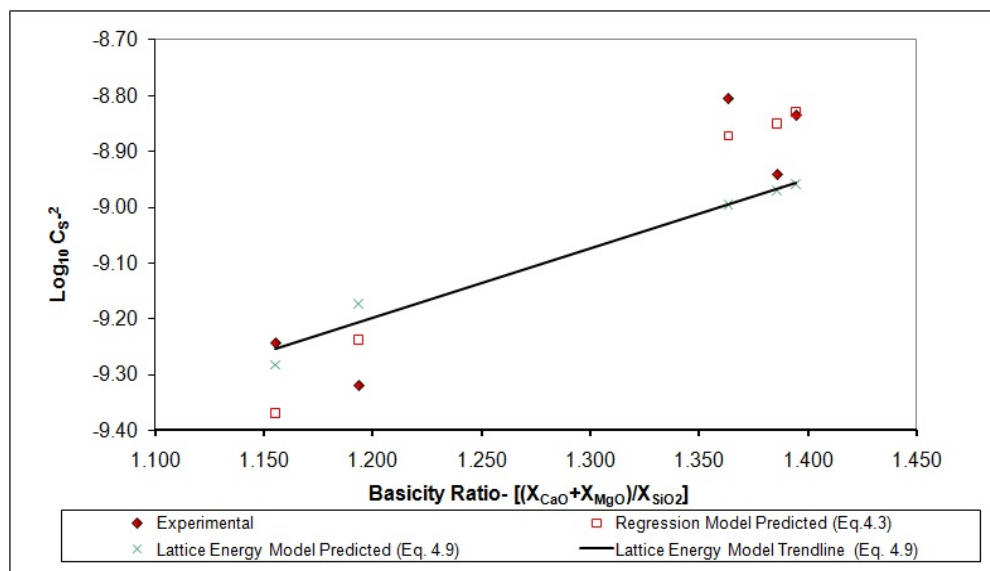


Figure F 4.3 The effect of basicity ratio on the sulphide capacity of ferrochromium smelting slag; X_{SiO_2} :0.3501-0.3859, X_{CaO} :0.0330-0.0709, X_{MgO} :0.3733-0.4540

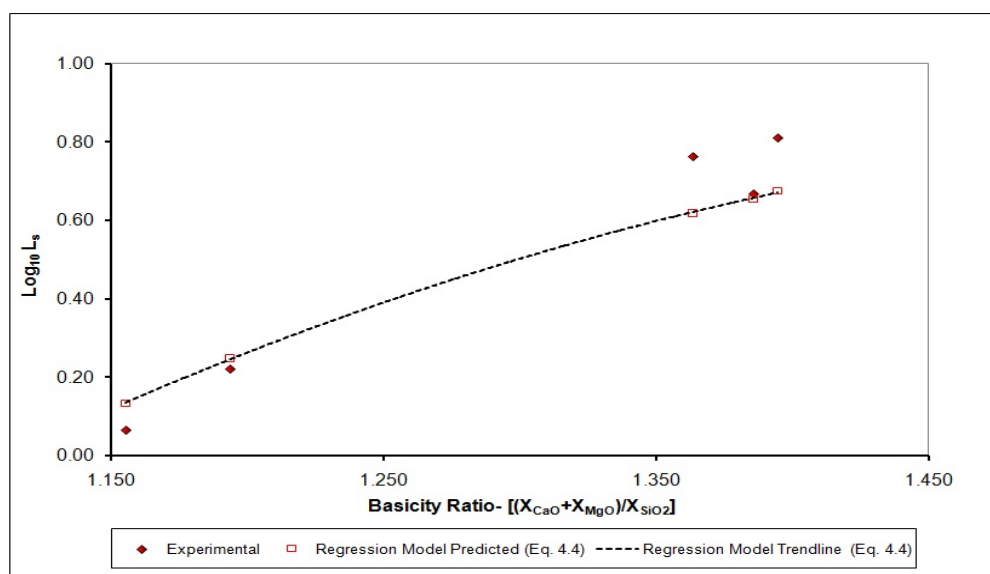


Figure F 4.4 The effect of basicity ratio on the sulphur distribution ratio of ferrochromium smelting slag; X_{SiO_2} :0.3501-0.3859, X_{CaO} :0.0330-0.0709, X_{MgO} :0.3733-0.4540

F5 THE VARIATION OF C_S^{-2} AND L_S WITH OPTICAL BASICITY (Λ) OF FERROCHROMIUM SMELTING SLAGS

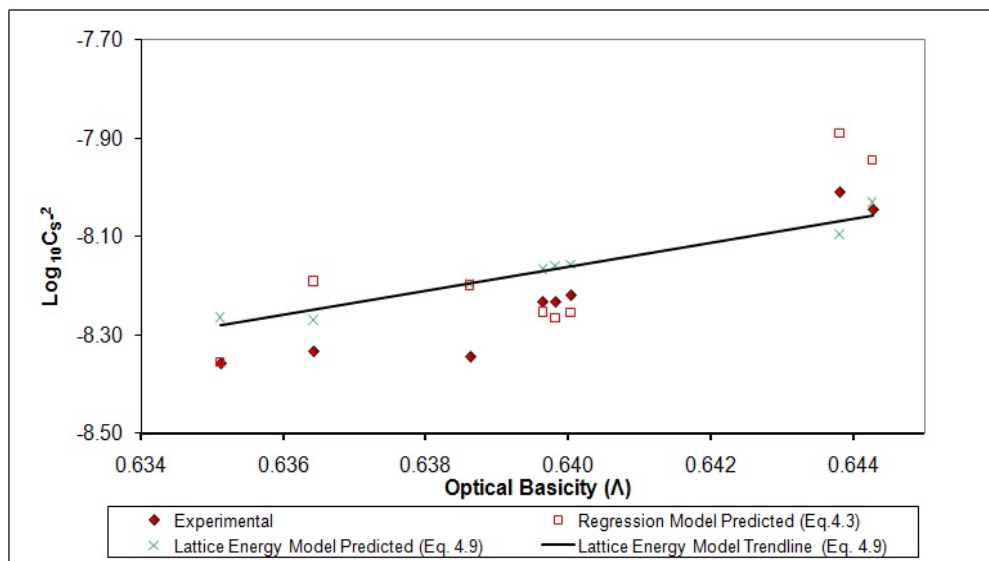


Figure F 5.1 The effect of optical basicity on the sulphide capacity of ferrochromium smelting slag; Basicity Ratio: 1.883-2.021, X_{SiO_2} :0.2615-0.2956, X_{CaO} :0.0877-0.1557, X_{MgO} :0.3728-0.4788

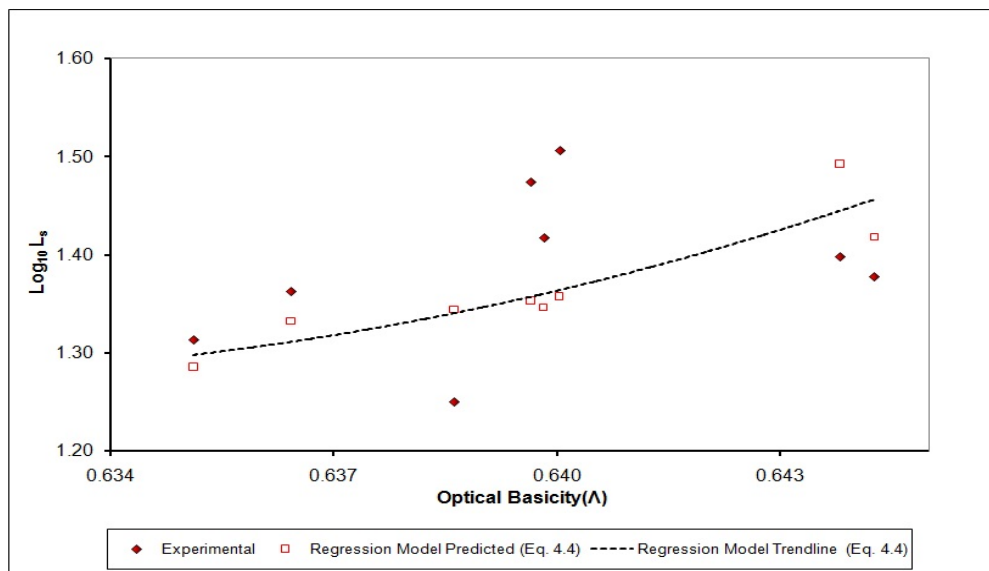


Figure F 5.2 The effect of optical basicity on the sulphur distribution ratio of ferrochromium smelting slag; Basicity Ratio: 1.883-2.021, X_{SiO_2} :0.2615-0.2956, X_{CaO} :0.0877-0.1557, X_{MgO} :0.3728-0.4788

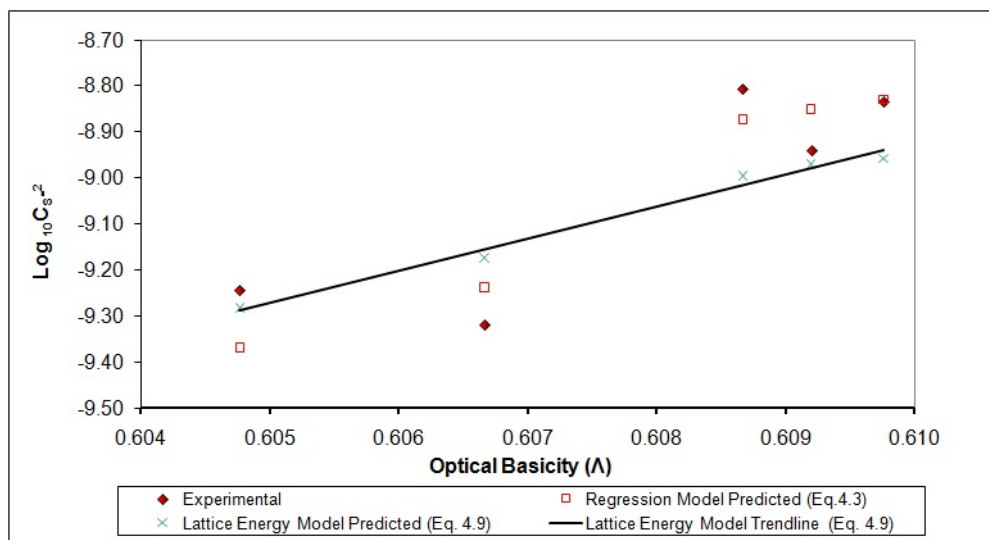


Figure F 5.3 The effect of optical basicity on the sulphide capacity of ferrochromium smelting slag; Basicity Ratio: 1.155-1.394, X_{SiO_2} :0.3501-0.3859, X_{CaO} :0.0347-0.0709, X_{MgO} :0.3733-0.4540

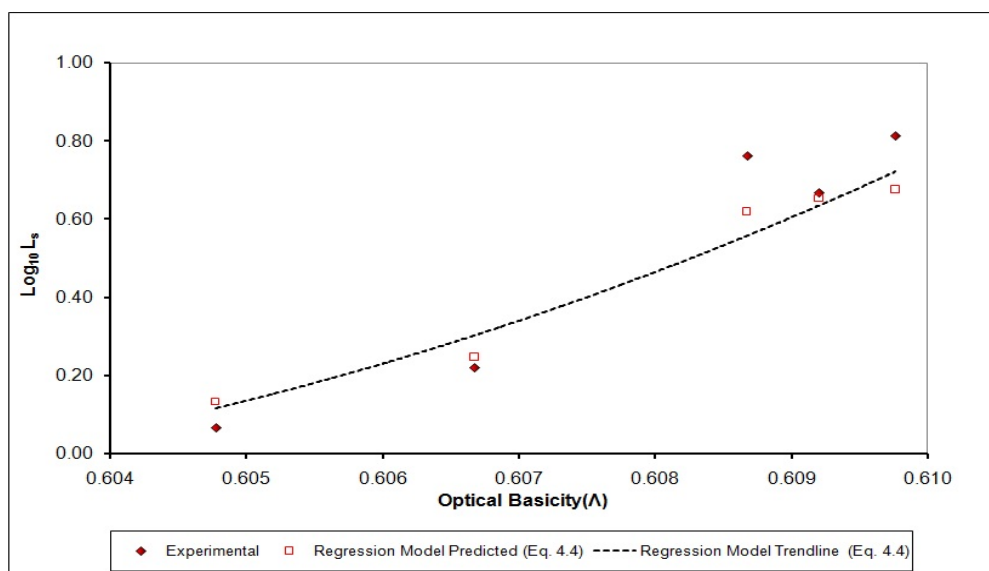


Figure F 5.4 The effect of optical basicity on the sulphur distribution ratio of ferrochromium smelting slag; Basicity Ratio: 1.155-1.394, X_{SiO_2} :0.3501-0.3859, X_{CaO} :0.0347-0.0709, X_{MgO} :0.3733-0.4540

F6 THE VARIATION OF C_s^{-2} AND L_s WITH CaO-to-MgO RATIO (X_{CaO}/X_{MgO}) OF FERROCHROMIUM SMELTING SLAGS

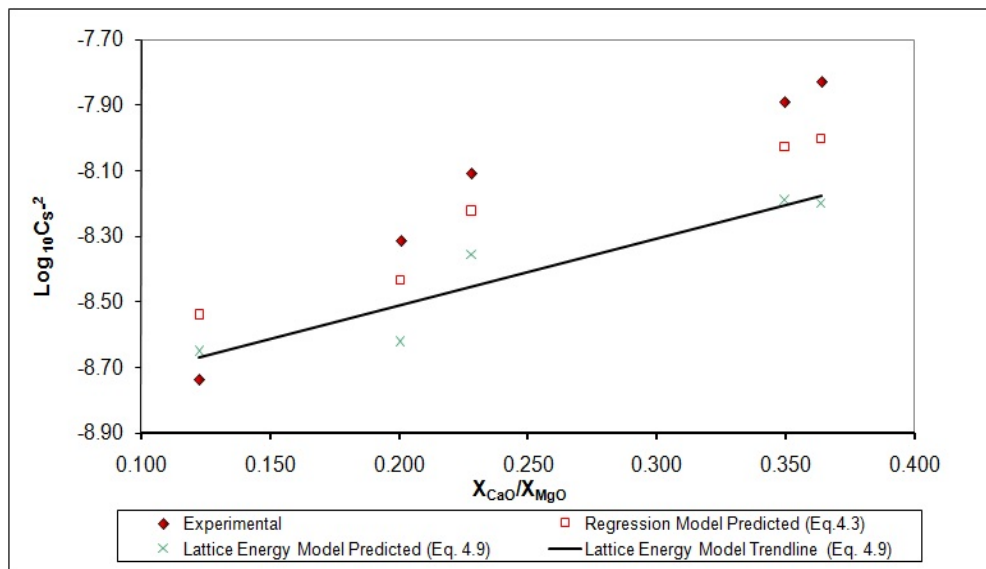


Figure F 6.1 The effect of CaO-to-MgO ratio (X_{CaO}/X_{MgO}) on the sulphide capacity of ferrochromium smelting slag; Basicity Ratio: 1.6087-1.9030, X_{SiO_2} : 0.2783-0.3250, X_{CaO} : 0.0568- 0.1416 X_{MgO} : 0.3894-0.4639

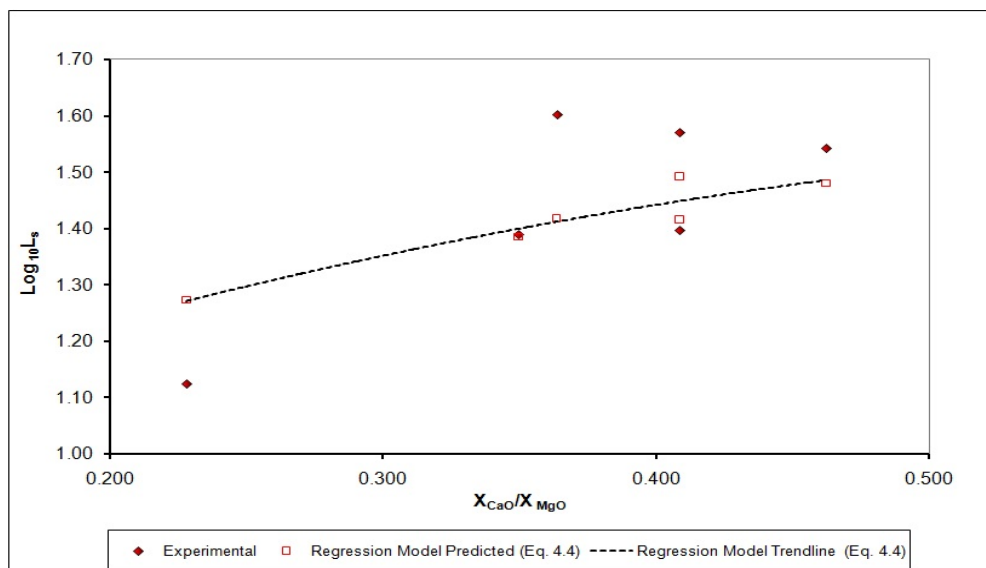


Figure F 6.2 The effect of CaO-to-MgO ratio (X_{CaO}/X_{MgO}) on the sulphur distribution ratio of ferrochromium smelting slag; Basicity Ratio: 1.6087-1.9030, X_{SiO_2} : 0.2783-0.3250, X_{CaO} : 0.0568- 0.1416 X_{MgO} : 0.3894-0.4639

PHOSPHORUS BEHAVIOUR IN FERROCHROMIUM SMELTING

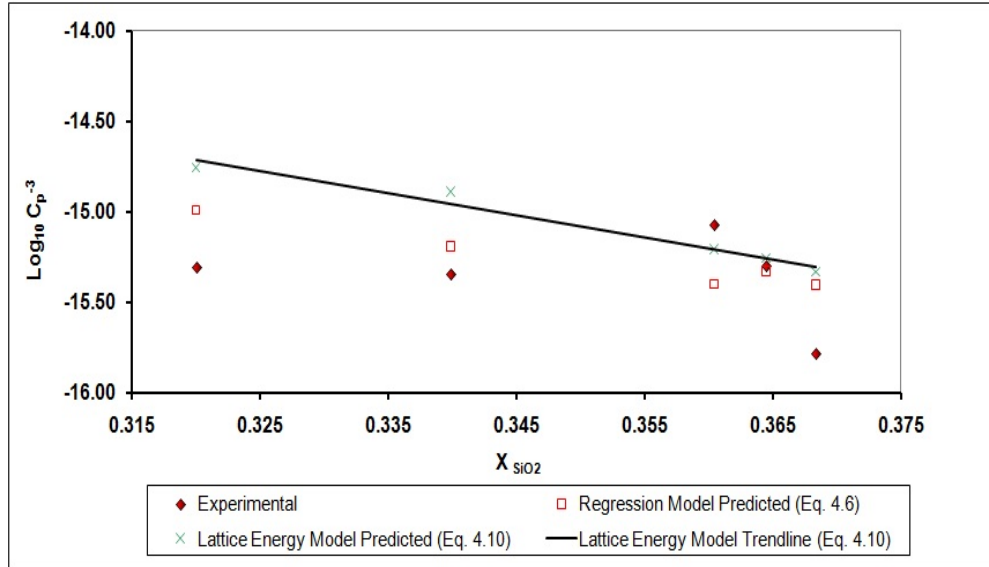
G1 THE VARIATION OF C_P^{-3} AND L_P WITH SILICA (X_{SiO_2}) IN FERROCHROMIUM SMELTING SLAGS

Figure G 1.1 The variation of phosphide capacity with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio: 1.356-1.516, X_{CaO} : 0.0806-0.0910, X_{MgO} : 0.3975-0.4288

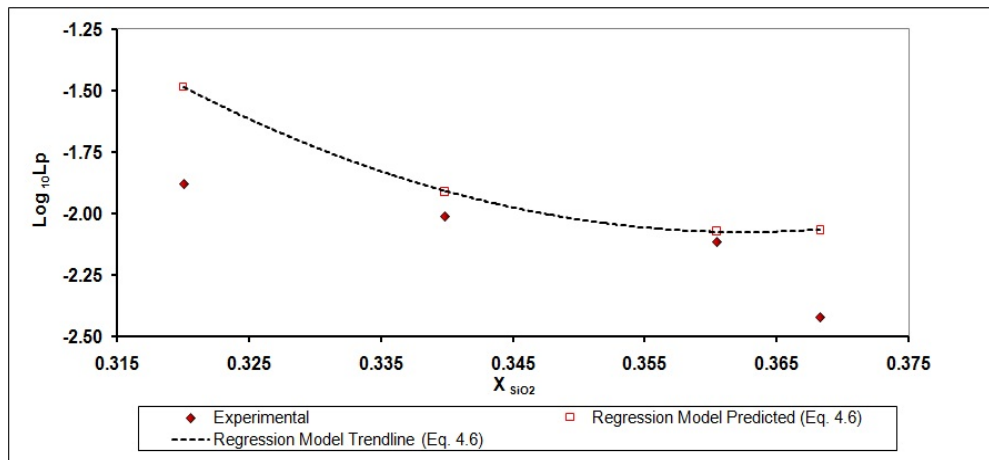


Figure G 1.2 The variation of phosphorus distribution ratio with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio: 1.356-1.516, X_{CaO} : 0.0806-0.0910, X_{MgO} : 0.3975-0.4288

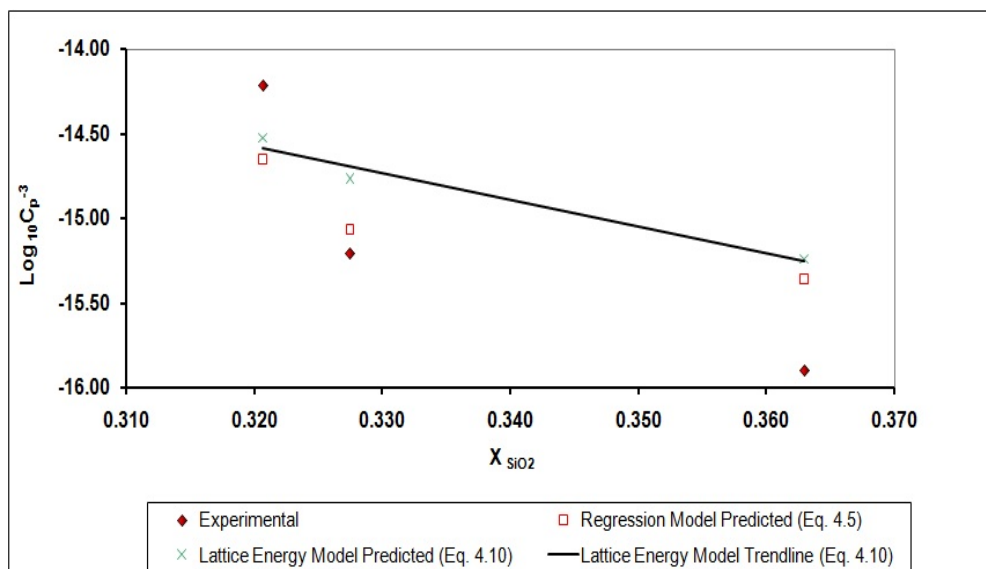


Figure G 1.3 The variation of phosphide capacity with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio:1.398-1.688, X_{CaO} : 0.0660-0.0993, X_{MgO} : 0.4220-0.4516

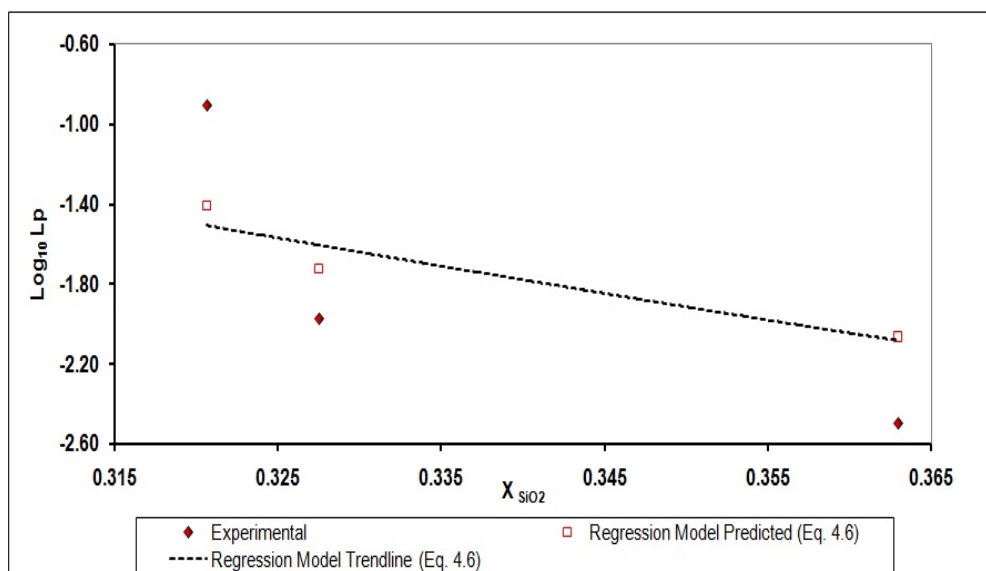


Figure G 1.4 The variation of phosphorus distribution ratio with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio:1.398-1.688, X_{CaO} : 0.0660-0.0993, X_{MgO} : 0.4220-0.4516

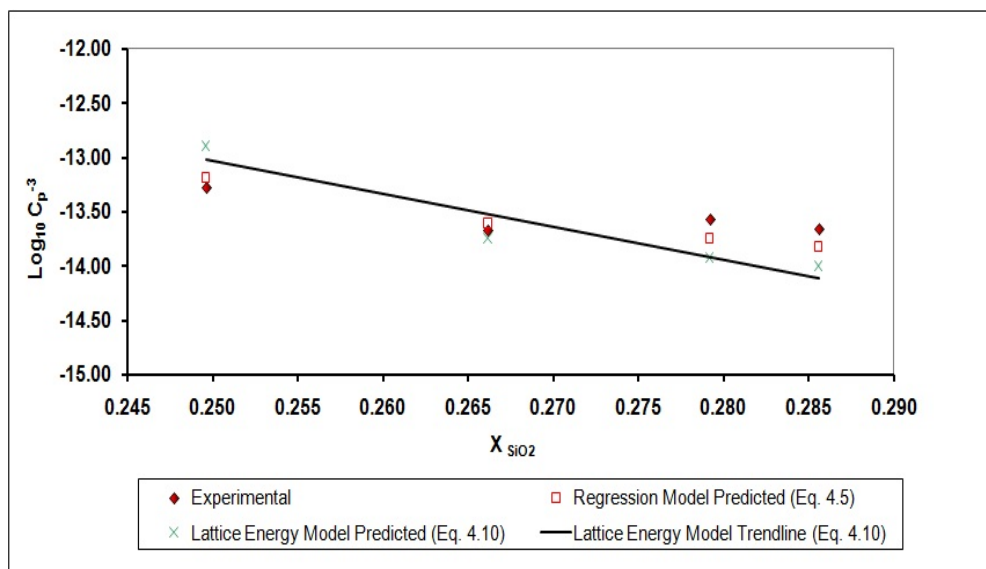


Figure G 1.5 The variation of phosphide capacity with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio:1.893-2.55, X_{CaO} : 0.1483-0.2070, X_{MgO} : 0.3710-0.4297

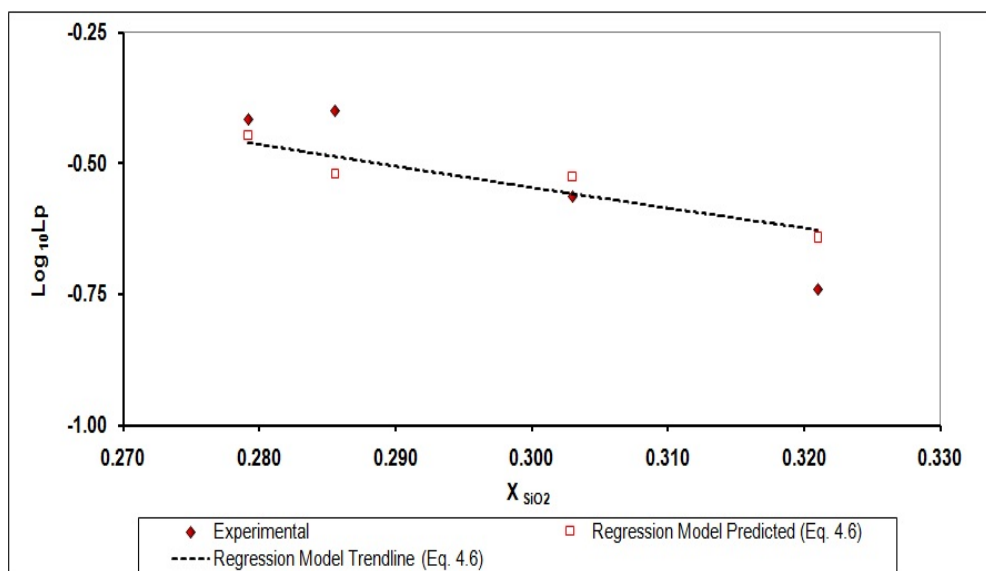


Figure G 1.6 The variation of phosphorus distribution ratio with silica mole fraction (X_{SiO_2}) of ferrochromium smelting slag; Basicity Ratio:1.585-1.936, X_{CaO} : 0.1483-0.2125, X_{MgO} : 0.2949-0.3932

G2 THE VARIATION OF C_P^{-3} AND L_P WITH CALCIUM OXIDE (X_{CaO}) IN FERROCHROMIUM SMELTING SLAGS

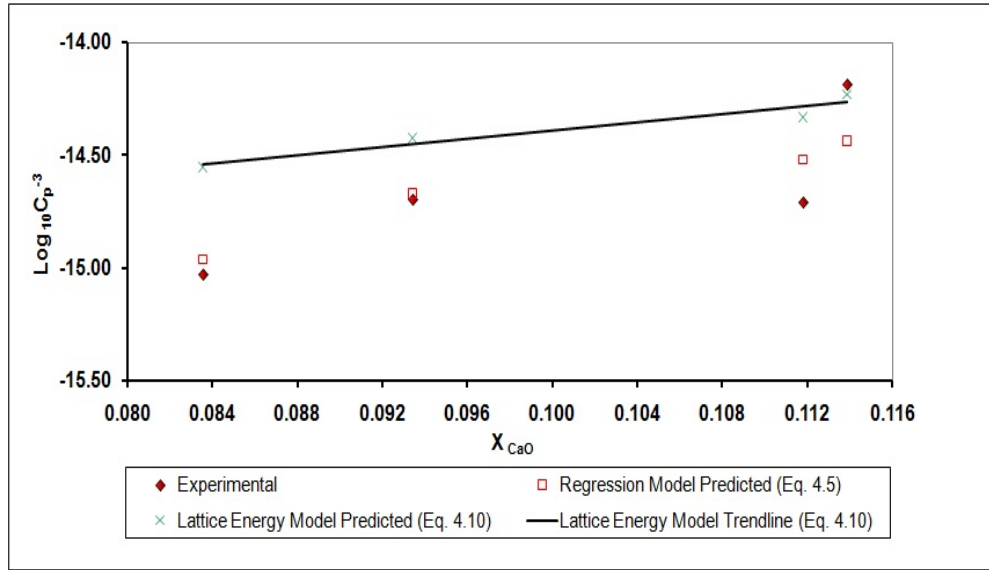


Figure G 2.1 The variation of phosphide capacity with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag; Basicity Ratio:1.634-1.816, X_{SiO_2} : 0.3061-0.3132, X_{MgO} : 0.4266-0.4454

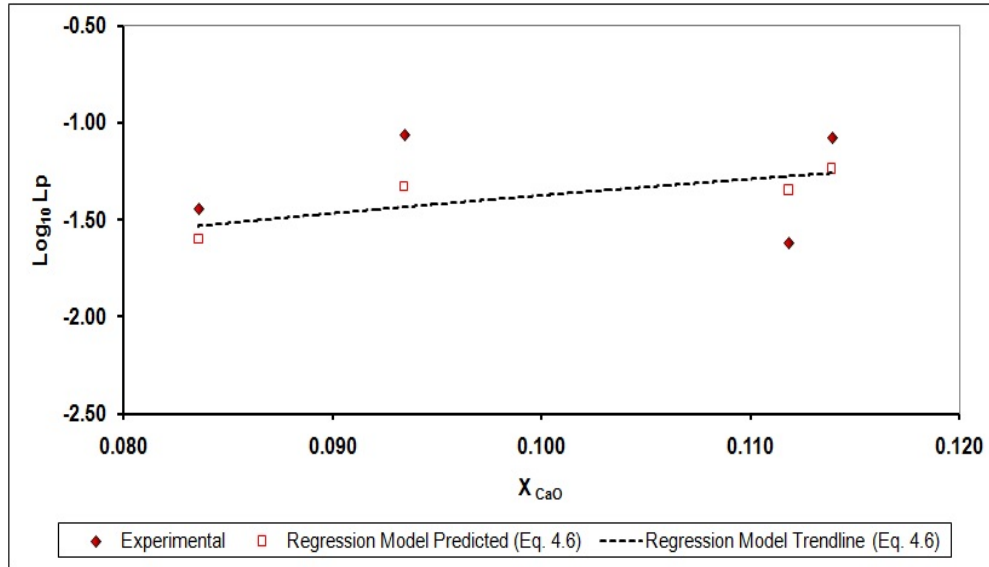


Figure G 2.2 The variation of phosphorus distribution ratio with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag; Basicity Ratio:1.634-1.816, X_{SiO_2} : 0.3061-0.3132, X_{MgO} : 0.4266-0.4454

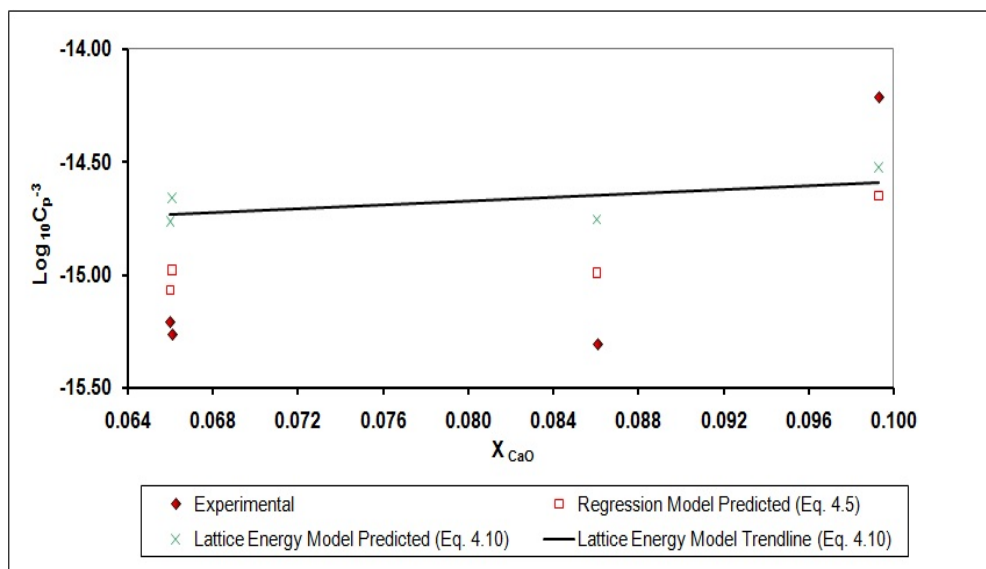


Figure G 2.3 The variation of phosphide capacity with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag; Basicity Ratio:1.511-1.688, X_{SiO_2} : 0.3179-0.3275, X_{MgO} : 0.3975-0.4516

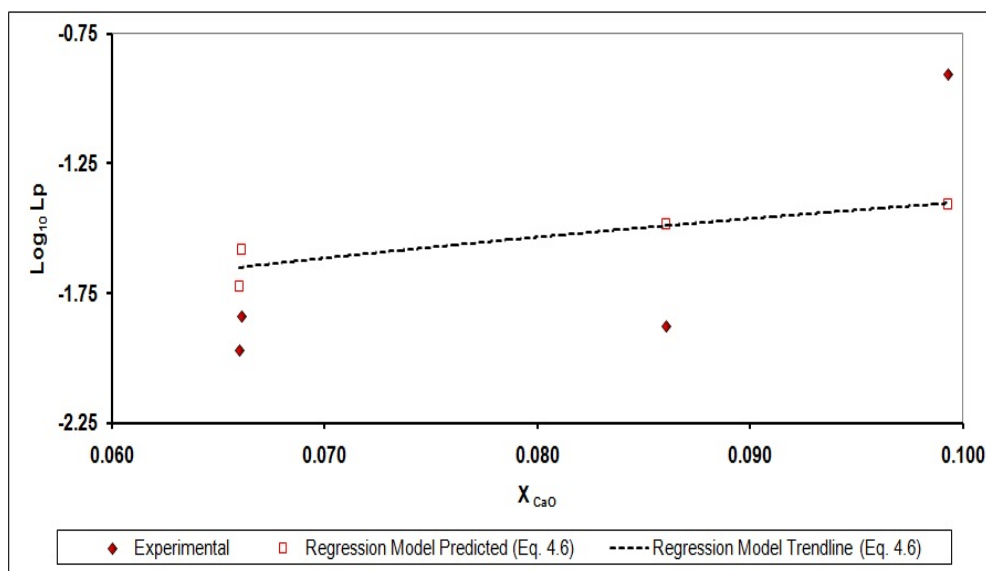


Figure G 2.4 The variation of phosphorus distribution ratio with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag; Basicity Ratio:1.511-1.688, X_{SiO_2} : 0.3179-0.3275, X_{MgO} : 0.3975-0.4516

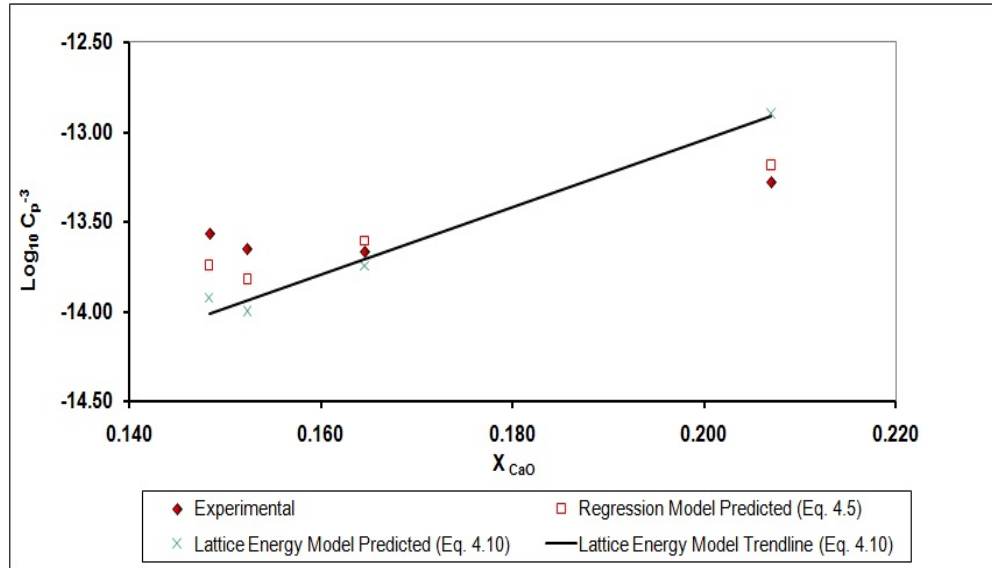


Figure G 2.5 The variation of phosphide capacity with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag; Basicity Ratio:1.893-2.551, X_{SiO_2} : 0.2496-0.2855, X_{MgO} : 0.3710-0.4297

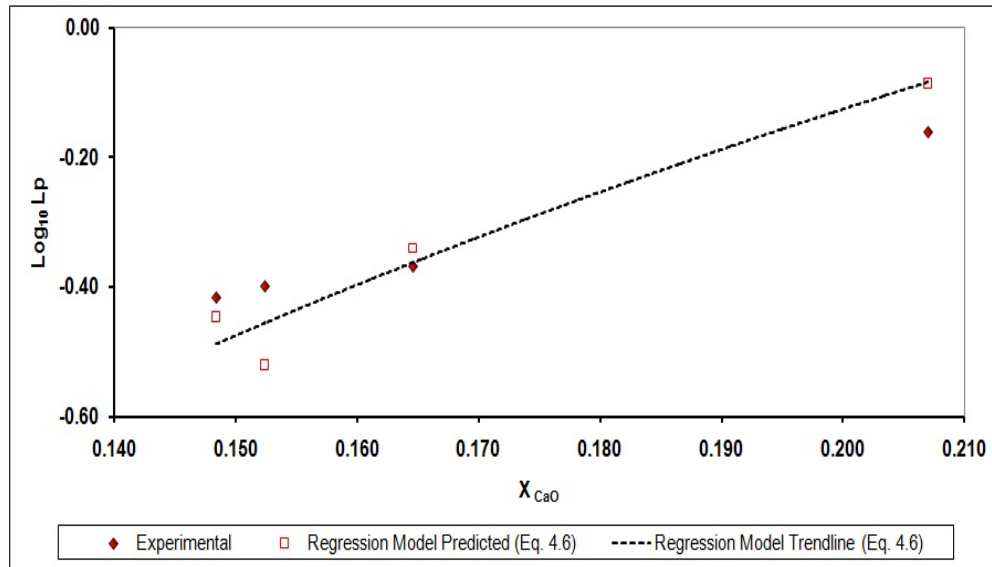


Figure G 2.6 The variation of phosphorus distribution ratio with calcium oxide mole fraction (X_{CaO}) of ferrochromium smelting slag; Basicity Ratio:1.893-2.551, X_{SiO_2} : 0.2496-0.2855, X_{MgO} : 0.3710-0.4297

G3 THE VARIATION OF C_P^{-3} AND L_P WITH MAGNESIUM OXIDE (X_{MgO}) IN FERROCHROMIUM SMELTING SLAGS

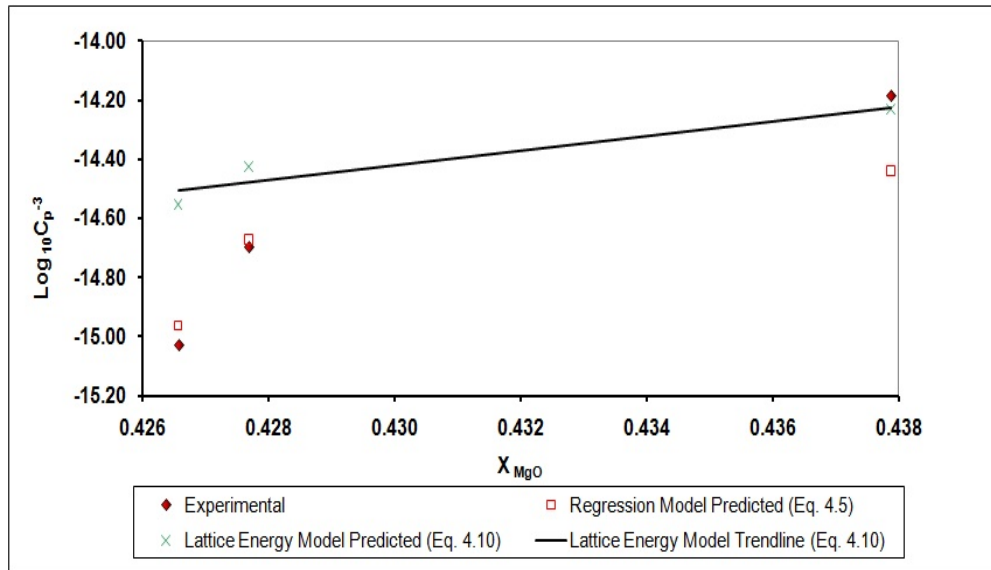


Figure G 3.1 The variation of phosphide capacity with magnesium oxide mole fraction (X_{MgO}) of ferrochromium smelting slag; Basicity Ratio:1.634-1.816, X_{SiO_2} : 0.3037-0.3121, X_{CaO} : 0.0836-0.1139

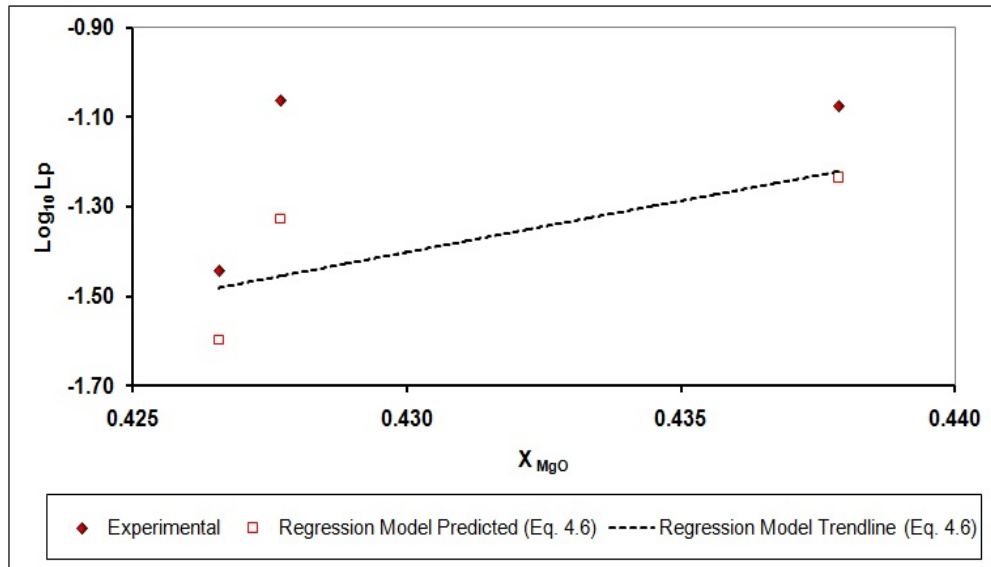


Figure G 3.2 The variation of phosphorus distribution ratio with magnesium oxide mole fraction (X_{MgO}) of ferrochromium smelting slag; Basicity Ratio:1.634-1.816, X_{SiO_2} : 0.3037-0.3121, X_{CaO} : 0.0836-0.1139

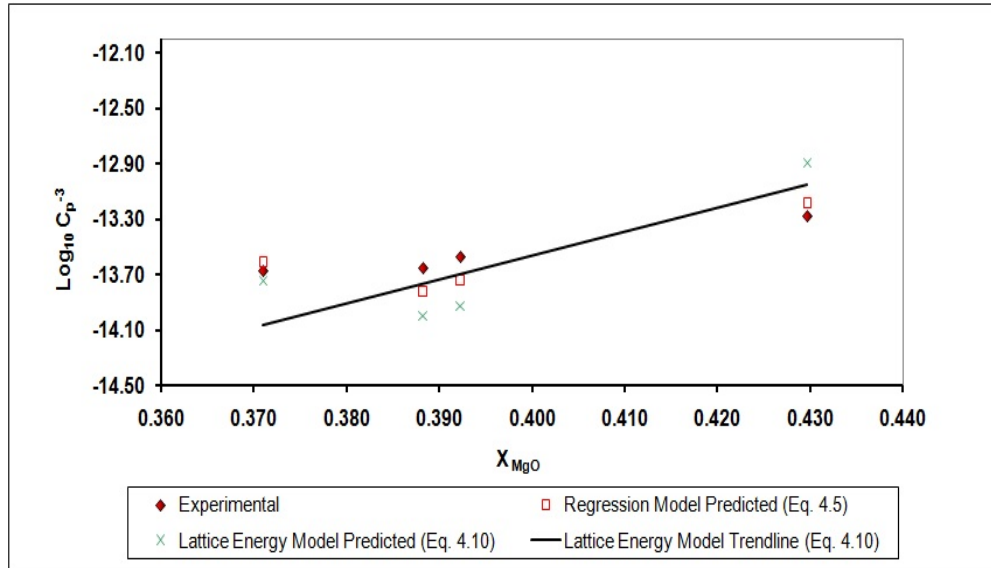


Figure G 3.3 The variation of phosphide capacity with magnesium oxide mole fraction (X_{MgO}) of ferrochromium smelting slag; Basicity Ratio:1.634-1.816, X_{SiO_2} : 0.3037-0.3121, X_{CaO} : 0.0836-0.1139

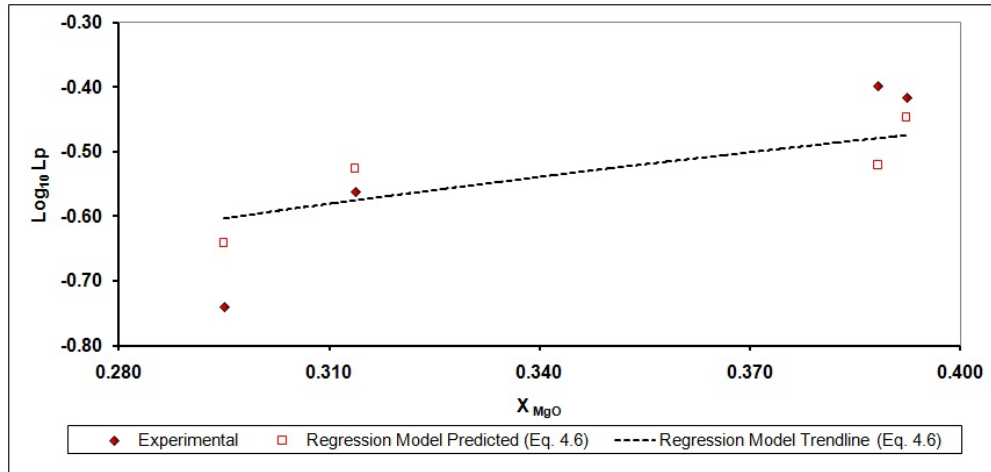


Figure G 3.4 The variation of phosphorus distribution ratio with magnesium oxide mole fraction (X_{MgO}) of ferrochromium smelting slag; Basicity Ratio:1.585-1.936, X_{SiO_2} : 0.2792-0.3210, X_{CaO} : 0.1483-0.2139

G4 THE VARIATION OF C_P^{-3} AND L_P WITH BASICITY RATIO $[(X_{CaO}+X_{MgO})/X_{SiO_2}]$ OF FERROCHROMIUM SMELTING SLAGS

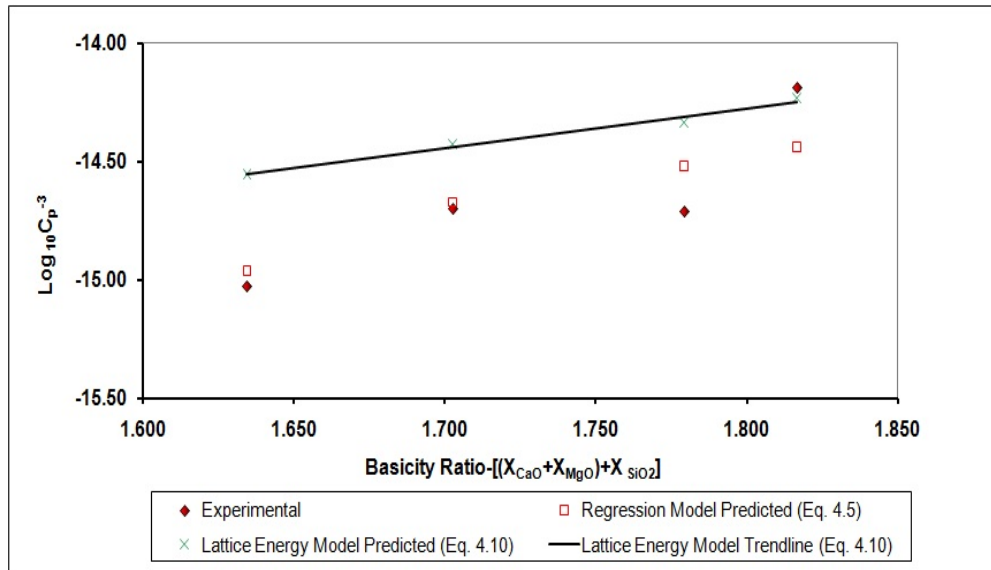


Figure G 4.1 The effect of basicity ratio on the phosphide capacity of ferrochromium smelting slag; X_{SiO_2} :0.3037-0.3132, X_{CaO} :0.0836-0.1139, X_{MgO} :0.4266-0.4454

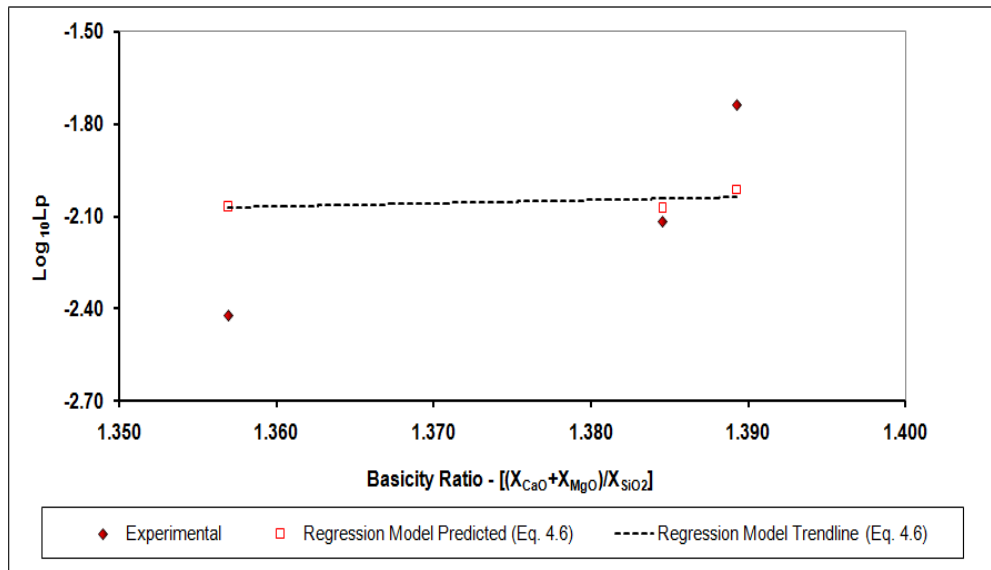


Figure G 4.2 The effect of basicity ratio on the phosphorus distribution ratio of ferrochromium smelting slag; X_{SiO_2} :0.3604-0.3683, X_{CaO} :0.0832-0.0910, X_{MgO} :0.4080-0.4232

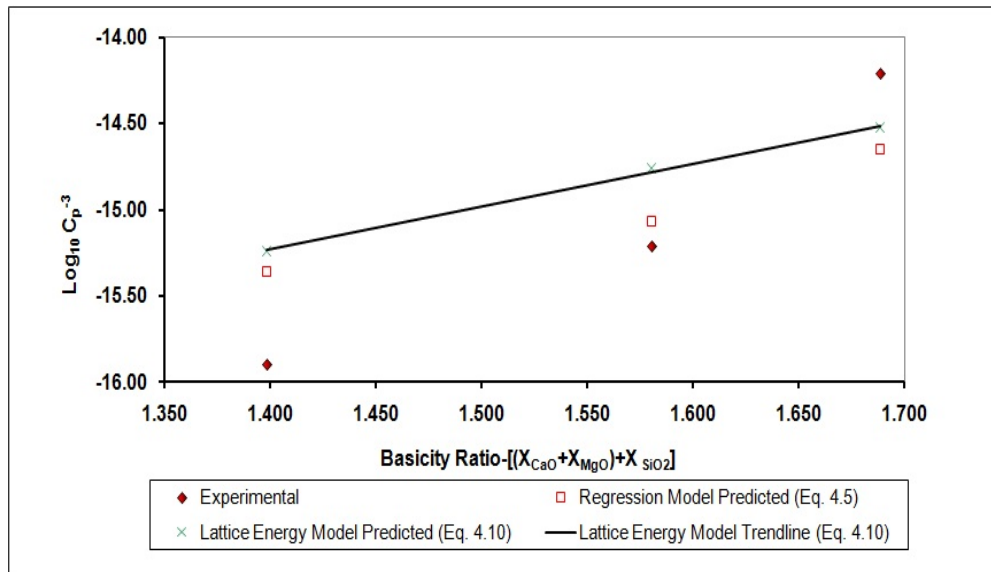


Figure G 4.3 The effect of basicity ratio on the phosphide capacity of ferrochromium smelting slag; X_{SiO_2} :0.3207-0.3630, X_{CaO} :0.0660-0.0993, X_{MgO} :0.4309-0.4516

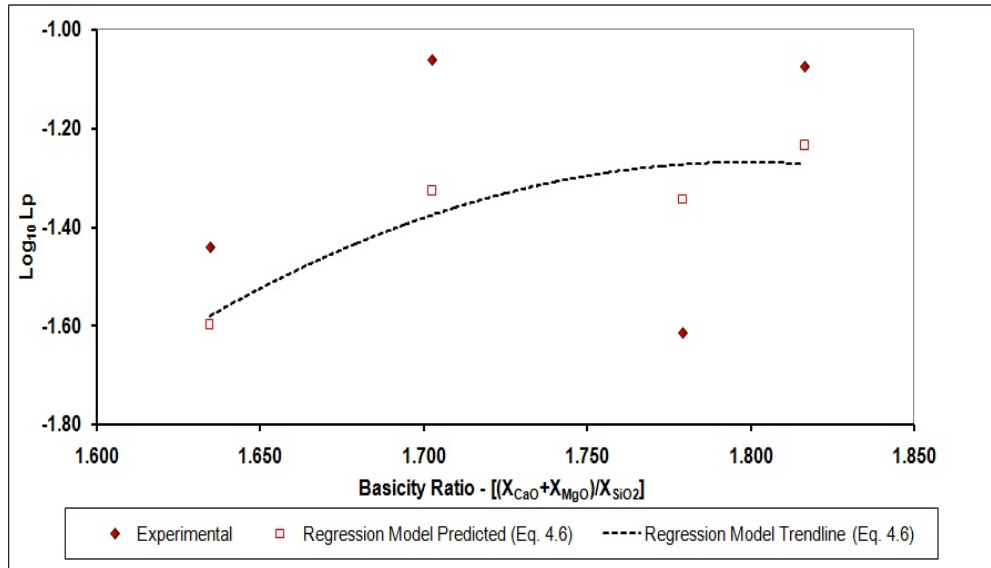


Figure G 4.4 The effect of basicity ratio on the phosphorus distribution ratio of ferrochromium smelting slag; X_{SiO_2} :0.3037-0.3132, X_{CaO} :0.0832-0.1139, X_{MgO} :0.4266-0.4454

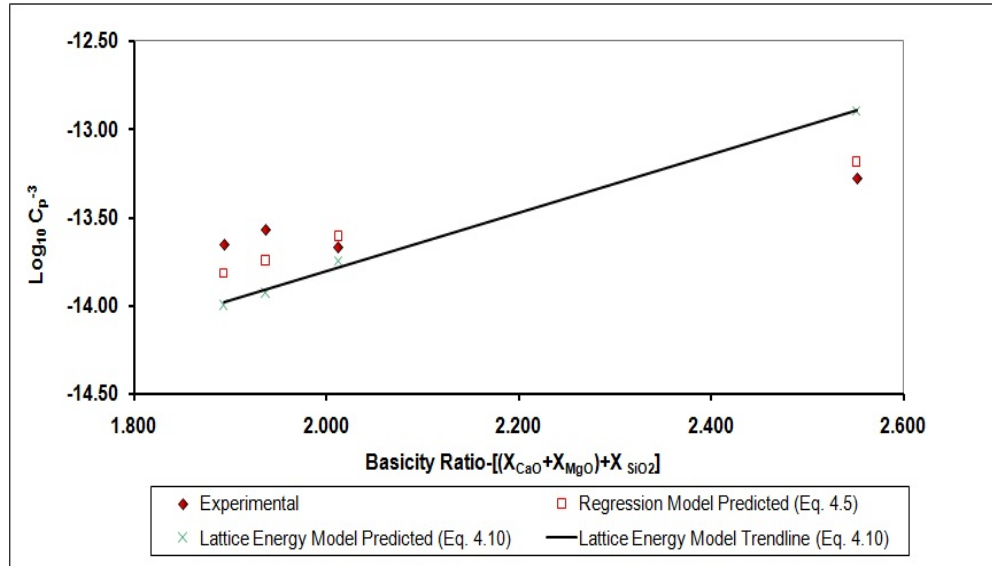


Figure G 4.5 The effect of basicity ratio on the phosphide capacity of ferrochromium smelting slag; X_{SiO_2} :0.2496-0.2855, X_{CaO} :0.1483-0.2070, X_{MgO} :0.3710-0.4297

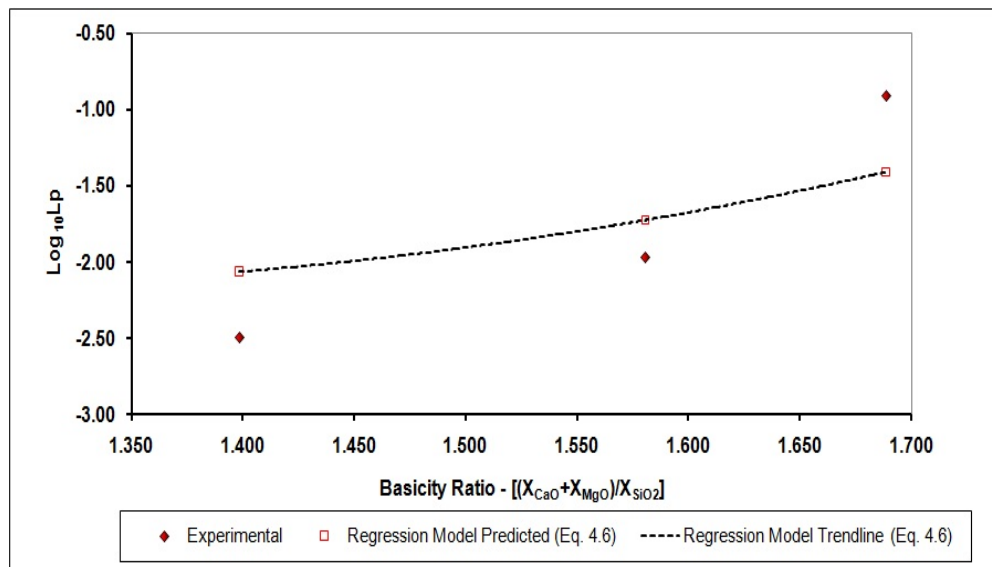


Figure G 4.6 The effect of basicity ratio on the phosphorus distribution ratio of ferrochromium smelting slag; X_{SiO_2} :0.3207-0.3630, X_{CaO} :0.0660-0.0993, X_{MgO} :0.4309-0.4516

**G5 THE VARIATION OF C_p^{-3} AND L_p WITH OPTICAL BASICITY
(A) OF FERROCHROMIUM SMELTING SLAGS**

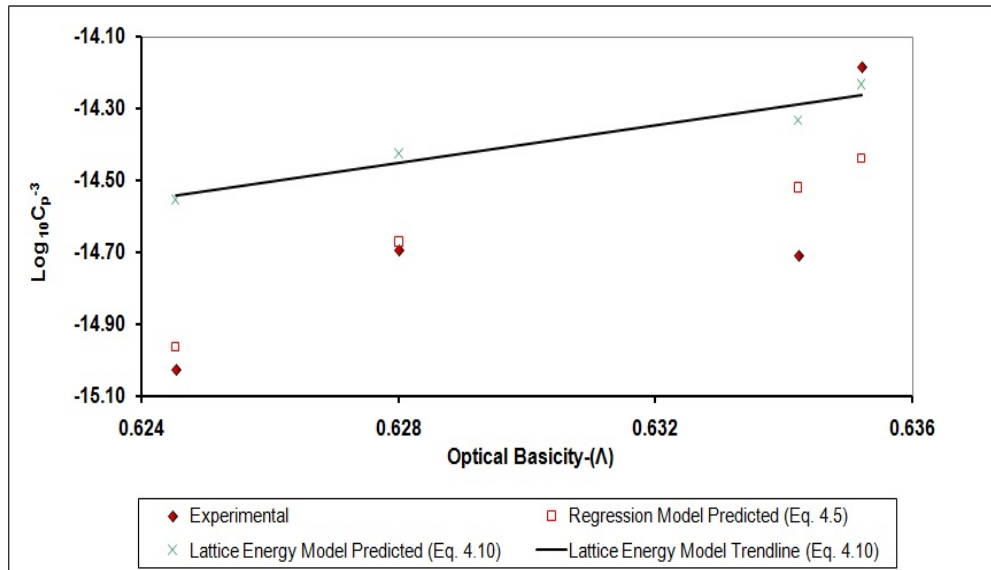


Figure G 5.1 The effect of optical basicity (Λ) on the phosphide capacity of ferrochromium smelting slag; Basicity Ratio:1.155-2.439,

X_{SiO_2} :0.3037-0.3132, X_{CaO} : 0.0836-0.1139, X_{MgO} :0.4266-0.4454

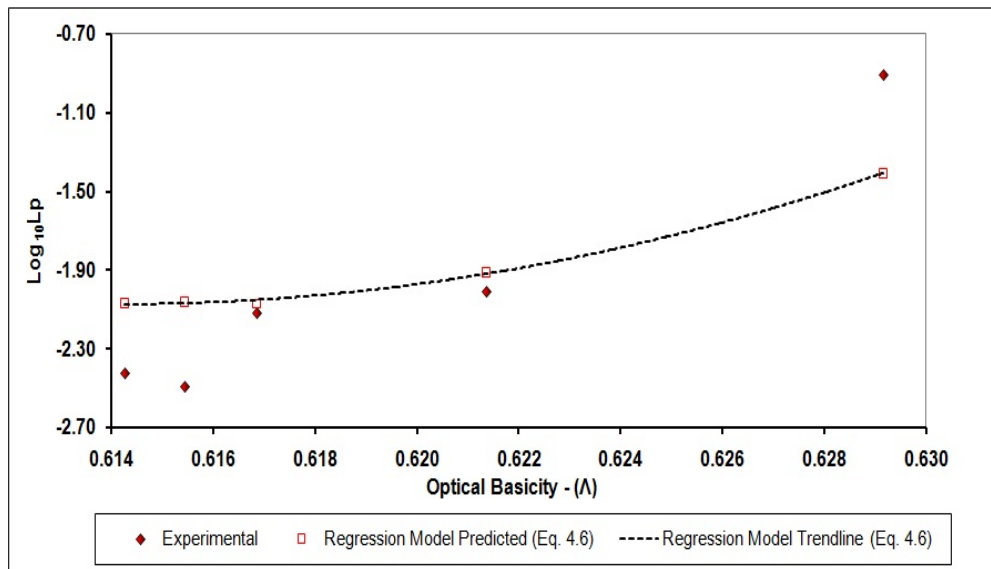


Figure G 5.2 The effect of optical basicity (Λ) on the phosphorus distribution ratio of ferrochromium smelting slag; Basicity Ratio: 1.155-2.439,

X_{SiO_2} :0.3207-0.3630, X_{CaO} : 0.0767-0.0910, X_{MgO} :0.4080-0.4422

G6 THE VARIATION OF C_p^{-3} AND L_p WITH CaO-to-MgO RATIO (X_{CaO}/X_{MgO}) OF FERROCHROMIUM SMELTING SLAGS

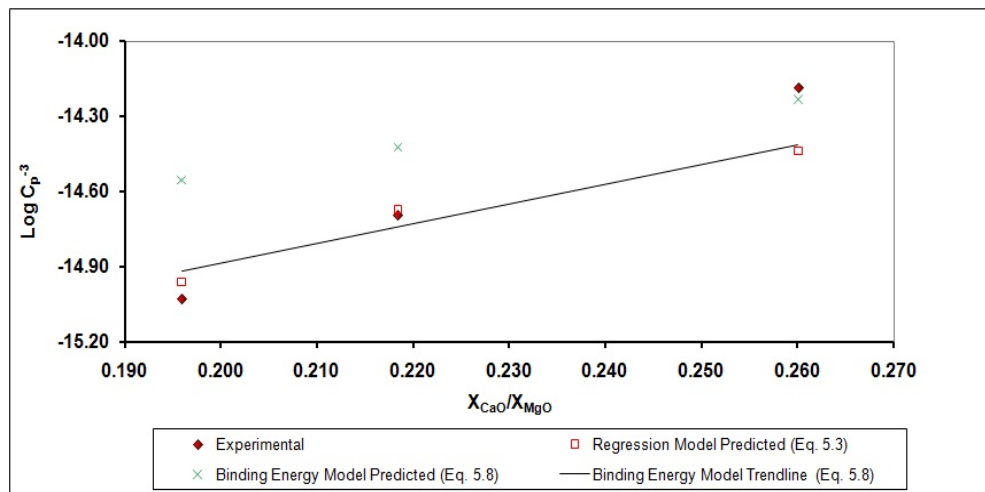


Figure G 6.1 The effect of CaO-to-MgO ratio (X_{CaO}/X_{MgO}) on the phosphide capacity of ferrochromium smelting slag; Basicity Ratio:1.634-1.816, X_{SiO_2} : 0.3037-0.3132, X_{CaO} : 0.0836- 0.1139, X_{MgO} : 0.4266-0.4454

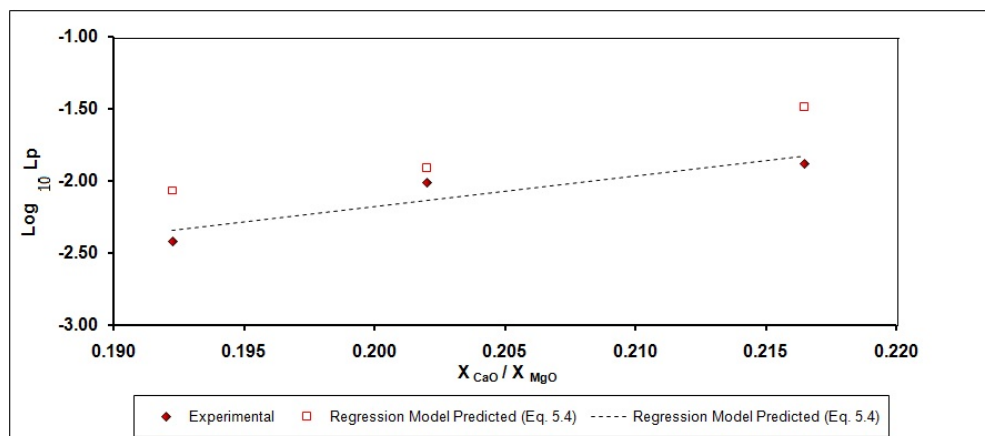


Figure G 6.2 The effect of CaO-to-MgO ratio (X_{CaO}/X_{MgO}) on the phosphorus distribution ratio of ferrochromium smelting slag; Basicity Ratio:1.893-2.551, X_{SiO_2} : 0.2496-0.2855, X_{CaO} : 0.1483- 0.2070, X_{MgO} : 0.3710-0.4297

SULPHUR BEHAVIOUR IN FERROMANGANESE SMELTING

**H1 THE VARIATION OF C_S^{-2} AND L_S WITH SILICA (X_{SiO_2}) IN
FERROMANGANESE SMELTING SLAGS**

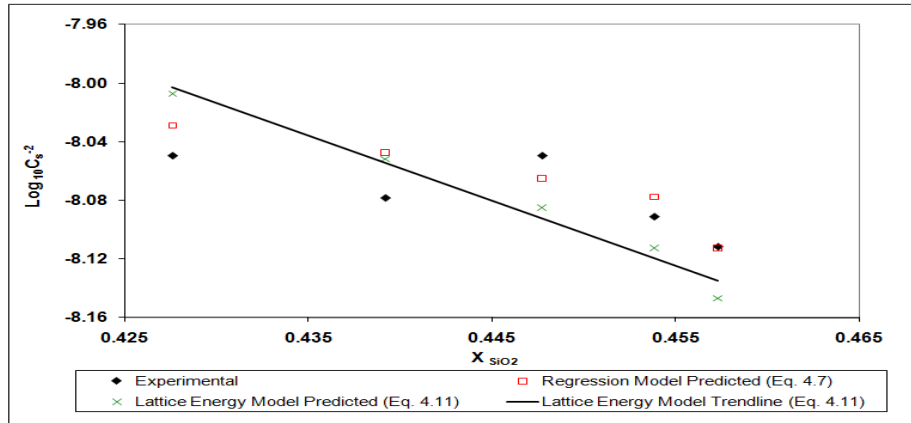


Figure H 1.1 The variation of sulphide capacity with silica mole fraction (X_{SiO_2}) of ferromanganese smelting slag; Basicity Ratio:0.800-0.9231, X_{CaO} : 0.1759-0.2317, X_{MgO} : 0.1683-0.2188

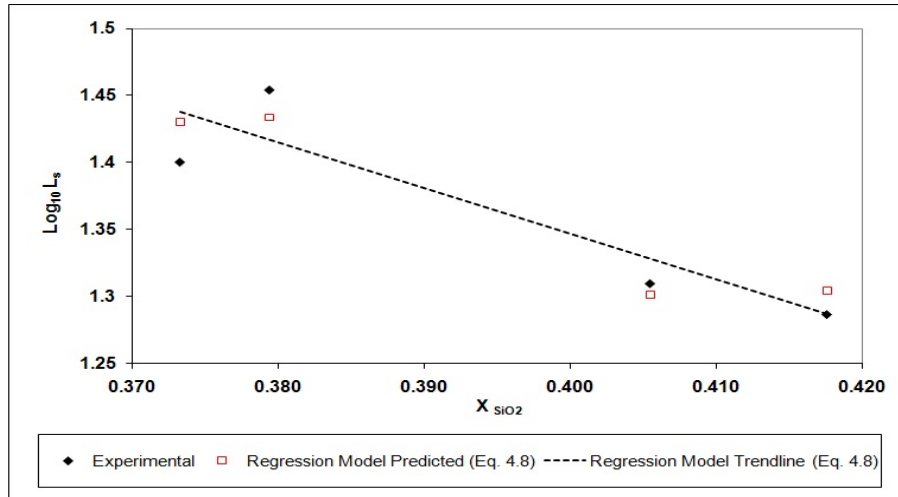


Figure H 1.2 The variation of sulphur distribution ratio with silica mole fraction (X_{SiO_2}) of ferromanganese smelting slag; Basicity Ratio:0.800-0.9231, X_{CaO} : 0.1759-0.2317, X_{MgO} : 0.1683-0.2188

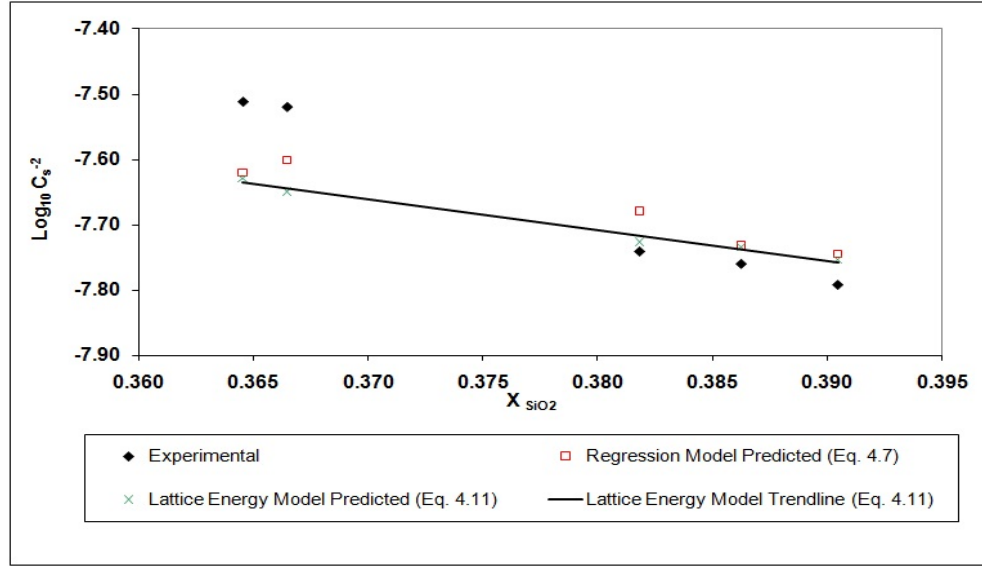


Figure H 1.3 The variation of sulphide capacity with silica mole fraction (X_{SiO_2}) of ferromanganese smelting slag; Basicity Ratio:1.356-1.522, X_{CaO} : 0.3409-0.3825, X_{MgO} : 0.1469-0.2130

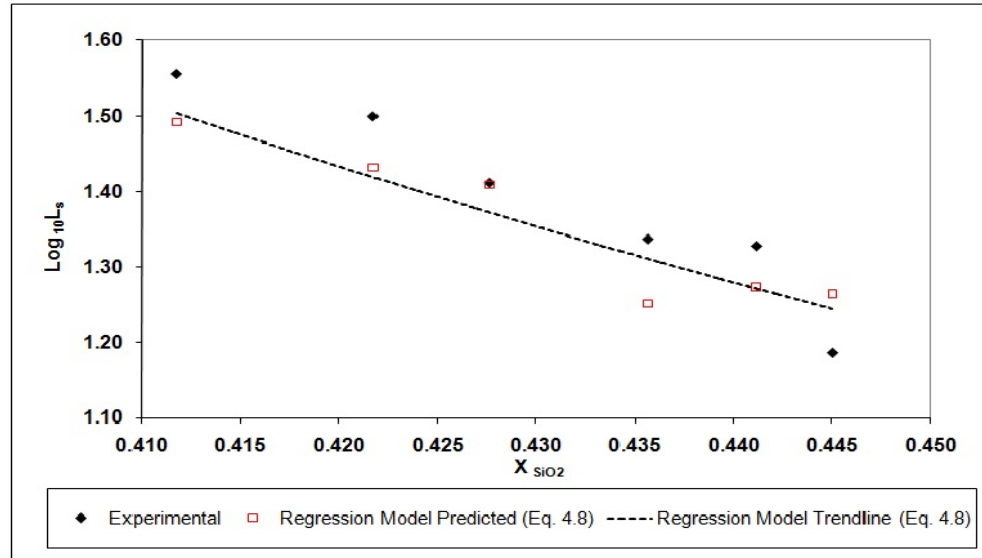


Figure H 1.4 The variation of sulphur distribution ratio with silica mole fraction (X_{SiO_2}) of ferromanganese smelting slag; Basicity Ratio:0.828-1.092, X_{CaO} : 0.1752-0.2338, X_{MgO} : 0.1632-0.2657

H2 THE VARIATION OF C_S^{-2} AND L_S WITH CALCIUM OXIDE (X_{CaO}) IN FERROMANGANESE SMELTING SLAGS

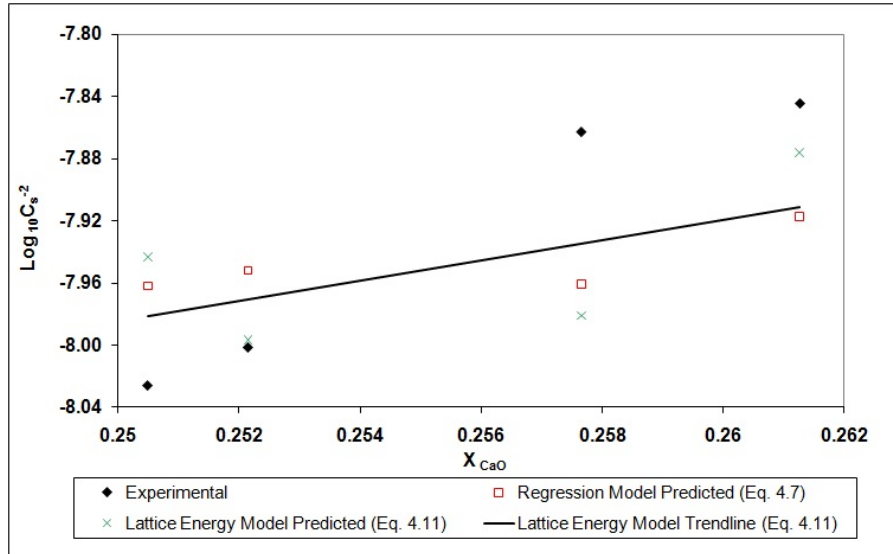


Figure H 2.1 The variation of sulphide capacity with calcium oxide mole fraction (X_{CaO}) of ferromanganese smelting slag; Basicity Ratio: 0.937-1.121, X_{SiO_2} : 0.4055-0.4311, X_{MgO} : 0.1512-0.1955

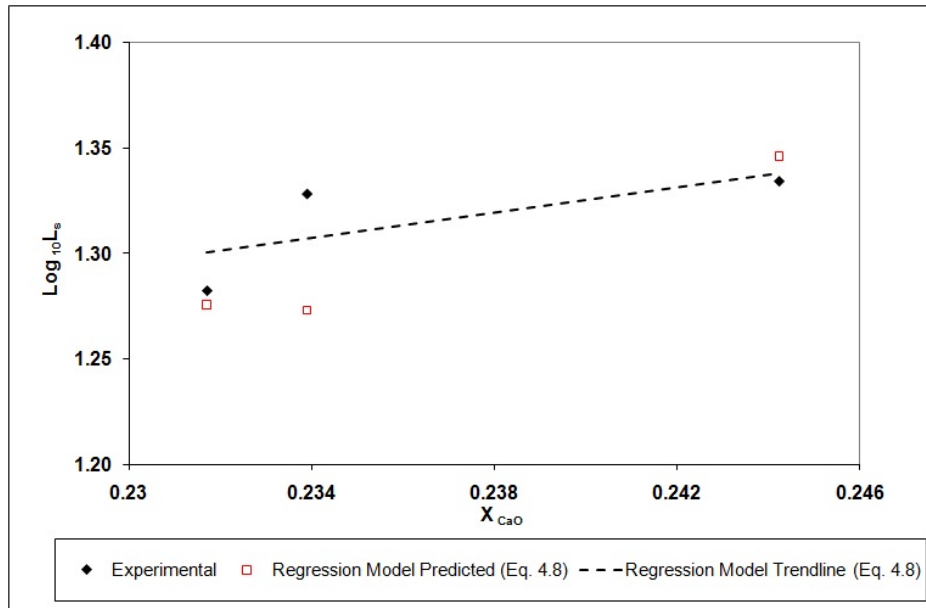


Figure H 2.2 The variation of sulphur distribution ratio with calcium oxide mole fraction (X_{CaO}) of ferromanganese smelting slag; Basicity Ratio: 0.886-1.194, X_{SiO_2} : 0.4004-0.4538, X_{MgO} : 0.1684-0.2339

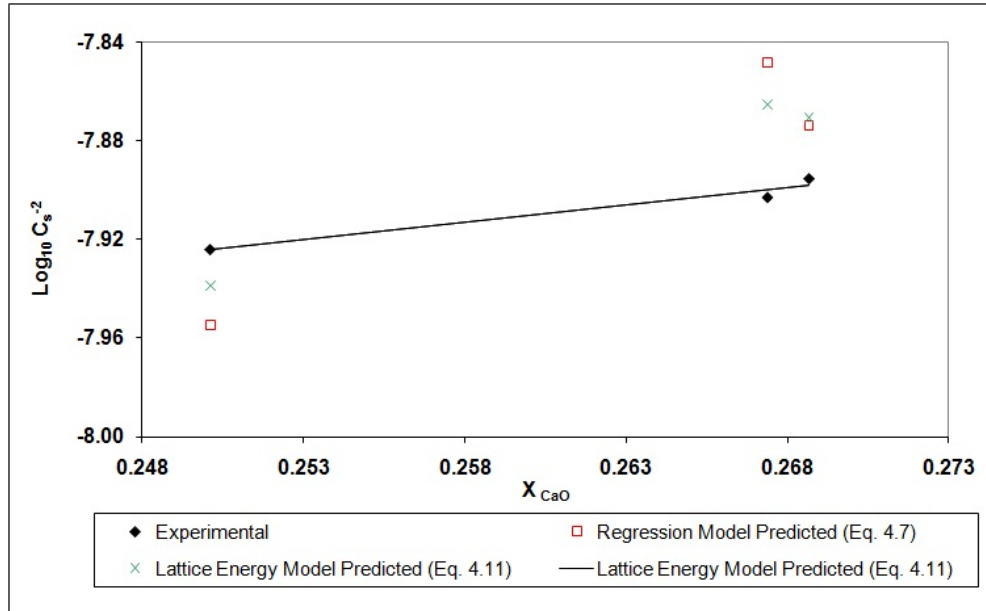


Figure H 2.3 The variation of sulphide capacity with calcium oxide mole fraction (X_{CaO}) of ferromanganese smelting slag; Basicity Ratio: 1.081-1.206, X_{SiO_2} : 0.4013-0.4176, X_{MgO} : 0.1932-0.2168

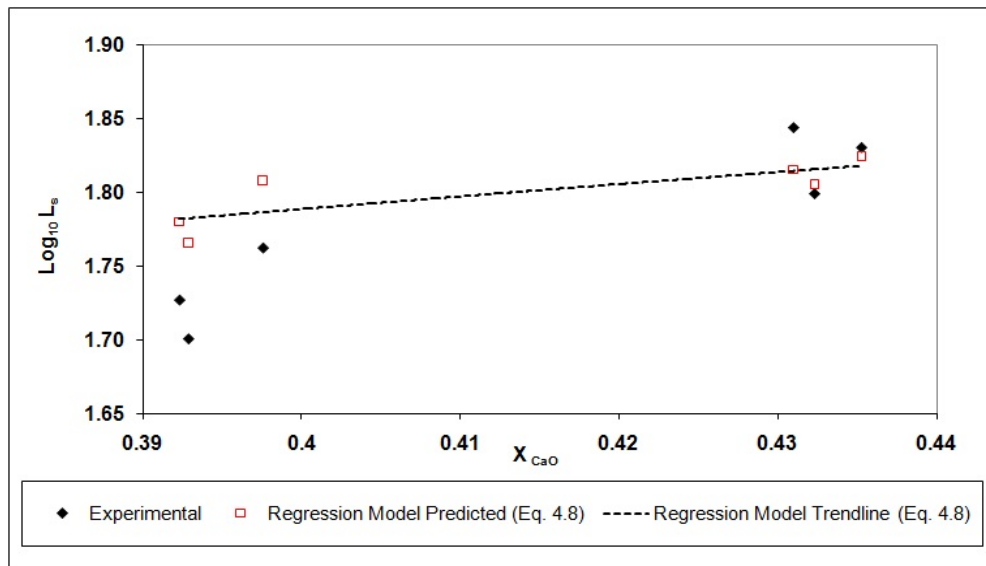


Figure H 2.4 The variation of sulphur distribution ratio with calcium oxide mole fraction (X_{CaO}) of ferromanganese smelting slag; Basicity Ratio: 1.486-1.605, X_{SiO_2} : 0.3519-0.3699, X_{MgO} : 0.1152-0.1715

H3 THE VARIATION OF C_S^{-2} AND L_S WITH MAGNESIUM OXIDE (X_{MgO}) IN FERROMANGANESE SMELTING SLAGS

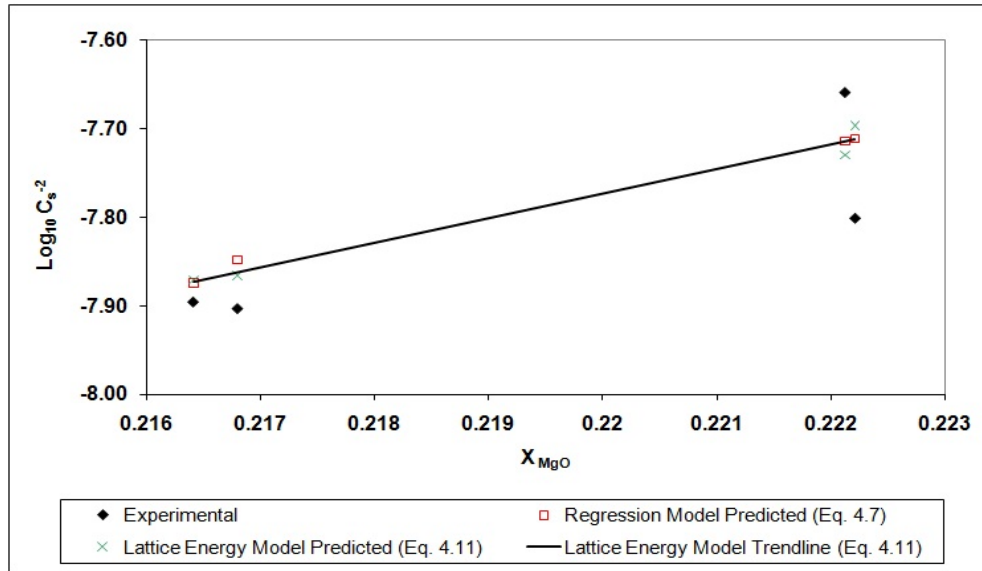


Figure H 3.1 The variation of sulphide capacity with magnesium oxide mole fraction (X_{MgO}) of ferromanganese smelting slag; Basicity Ratio:1.200-1.389, X_{SiO_2} : 0.3733-0.4039, X_{CaO} : 0.2673-0.2962

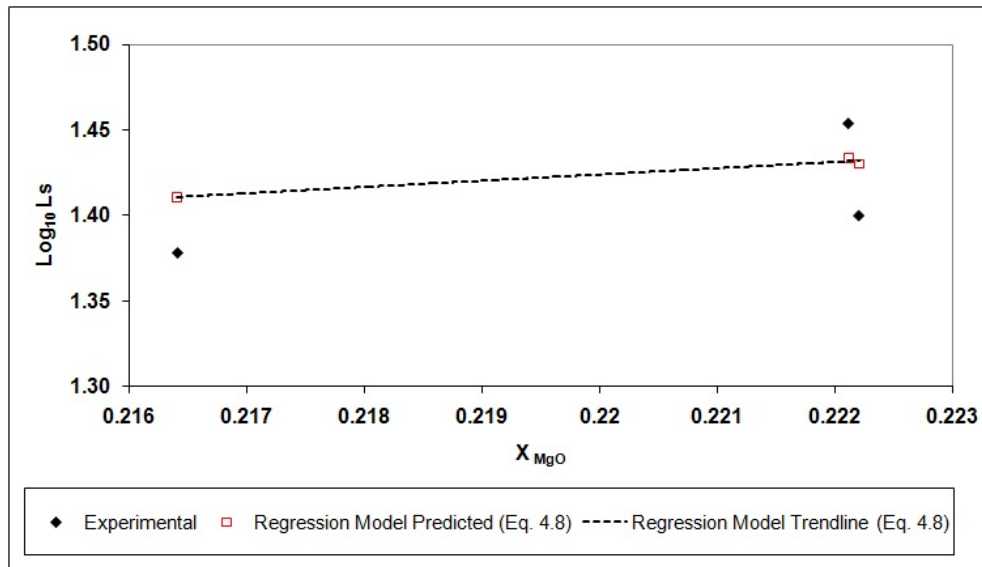


Figure H 3.2 The variation of sulphur distribution ratio with magnesium oxide mole fraction (X_{MgO}) of ferromanganese smelting slag; Basicity Ratio:1.378-1.400, X_{SiO_2} : 0.3732-0.4039, X_{CaO} : 0.2686-0.2962

H4 THE VARIATION OF C_S^{-2} AND L_S WITH MANGANESE OXIDE (X_{MnO}) IN FERROMANGANESE SMELTING SLAGS

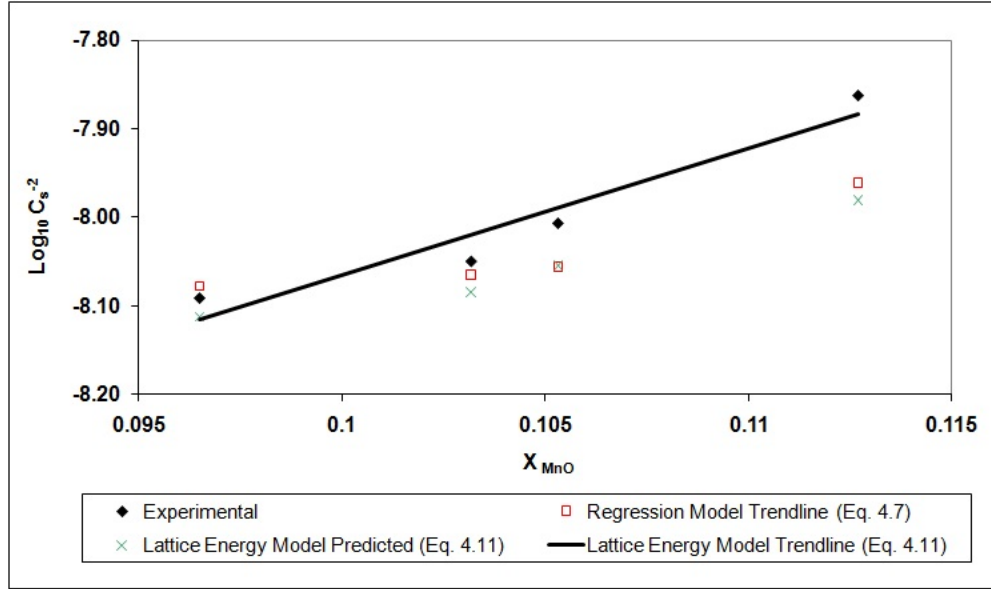


Figure H 4.1 The variation of sulphide capacity with manganese oxide mole fraction (X_{MnO}) of ferromanganese smelting slag; Basicity Ratio:0.881-0.959, X_{SiO_2} : 0.4276-0.4538, X_{CaO} : 0.2310-0.2765, X_{MgO} :0.1521-0.1692

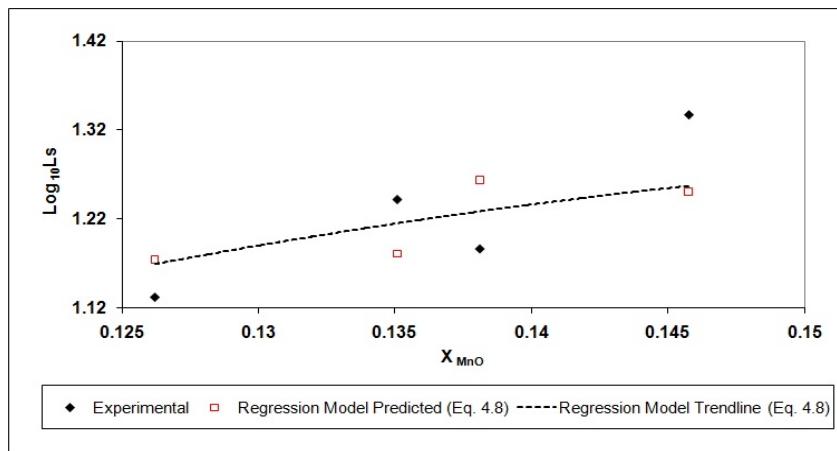


Figure H 4.2 The variation of sulphur distribution ratio with manganese oxide mole fraction (X_{MnO}) of ferromanganese smelting slag; Basicity Ratio:0.828-0.923, X_{SiO_2} : 0.4276-0.4392, X_{CaO} : 0.1753-0.1802, X_{MgO} :0.1930-0.2188

H5 THE VARIATION OF C_S^{-2} AND L_S WITH BASICITY RATIO $[(X_{CaO}+X_{MgO})/X_{SiO_2}]$ OF FERROMANGANESE SMELTING SLAGS

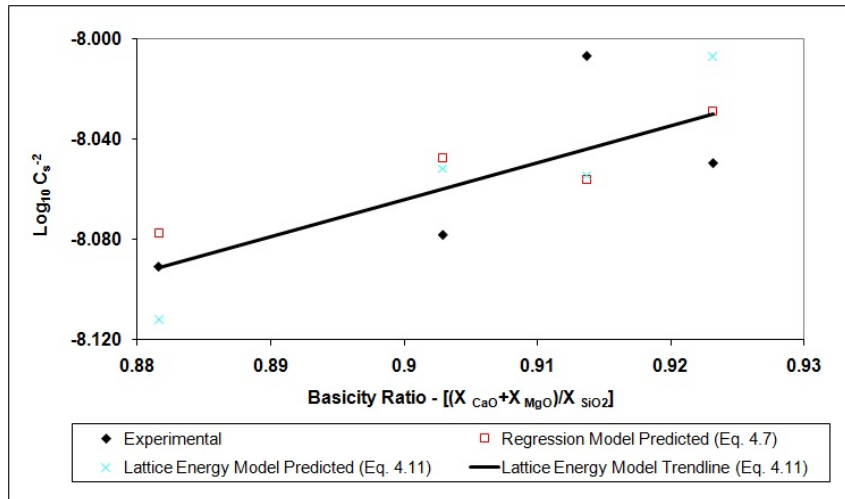


Figure H 5.1 The effect of basicity ratio on the sulphide capacity of ferromanganese smelting slag; X_{SiO_2} :0.4276-0.4538, X_{CaO} :0.1759-0.2338, X_{MgO} :0.1638-0.2188

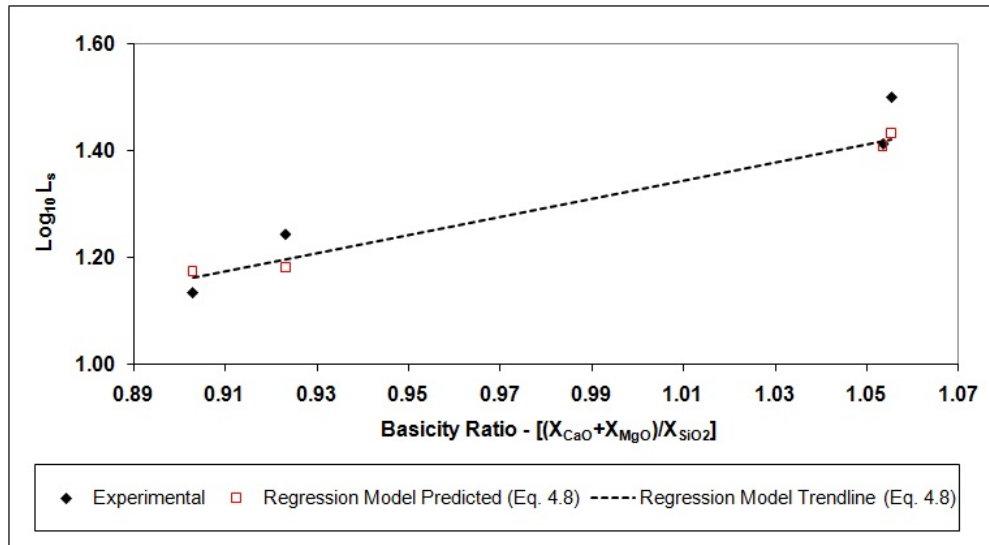


Figure H 5.2 The effect of basicity ratio on the sulphur distribution ratio of ferromanganese smelting slag; X_{SiO_2} :0.4218-0.4392, X_{CaO} : 0.1760-0.1880, X_{MgO} :0.2163-0.2625

H6 THE VARIATION OF C_S^{-2} AND L_S WITH OPTICAL BASICITY (Λ) OF FERROMANGANESE SMELTING SLAGS

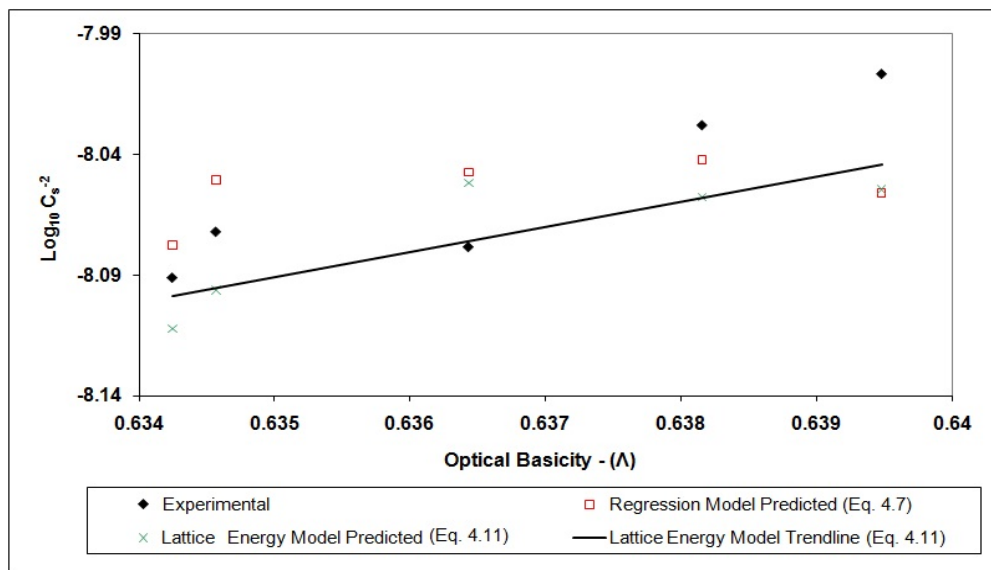


Figure H 6.1 The effect of optical basicity (Λ) on the sulphide capacity of ferromanganese smelting slag; Basicity Ratio: 0.829-0.913, X_{SiO_2} : 0.4356-0.4538, X_{CaO} : 0.1752-0.2338, X_{MgO} : 0.1684-0.2163

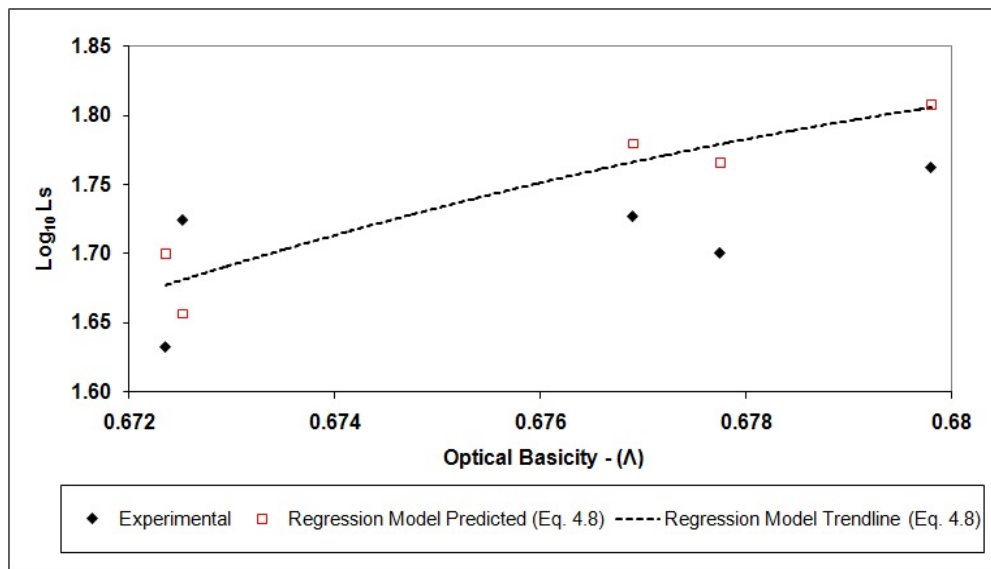


Figure H 6.2 The effect of optical basicity (Λ) on the sulphur distribution ratio of ferromanganese smelting slag; Basicity Ratio: 1.522-1.605, X_{SiO_2} : 0.3519-0.3645, X_{CaO} : 0.3468-0.3975, X_{MgO} : 0.1674-0.2135

H 7 THE VARIATION OF C_s^{-2} AND L_s WITH CaO-to-MgO RATIO (X_{CaO}/X_{MgO}) OF FERROMANGANESE SMELTING SLAGS

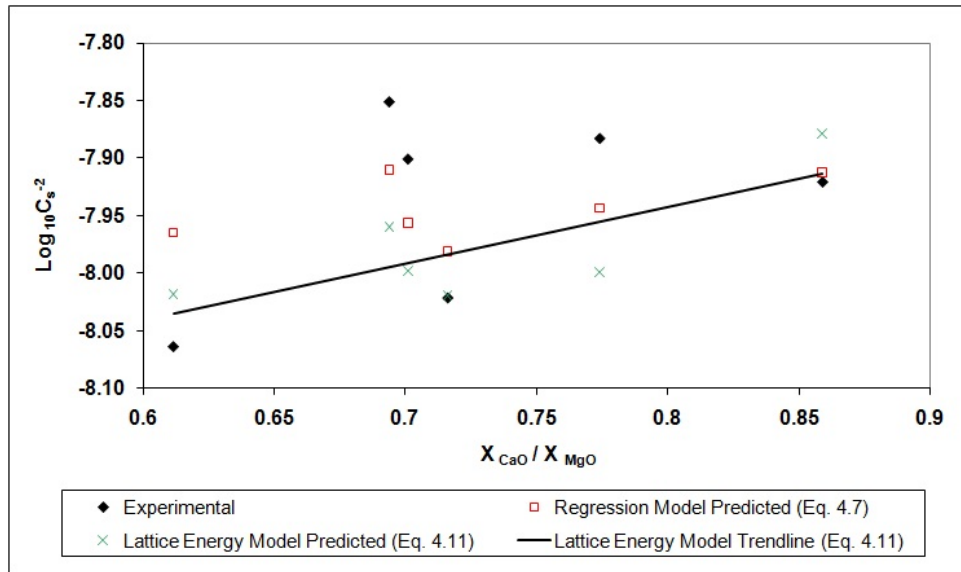


Figure H 7.1 The effect of CaO-to-MgO ratio (X_{CaO}/X_{MgO}) on the sulphide capacity of ferromanganese smelting slag; Basicity Ratio:1.042-1.245, X_{SiO_2} :0.3979-0.4276, X_{CaO} : 0.1680-0.4352, X_{MgO} :0.2617-0.2748

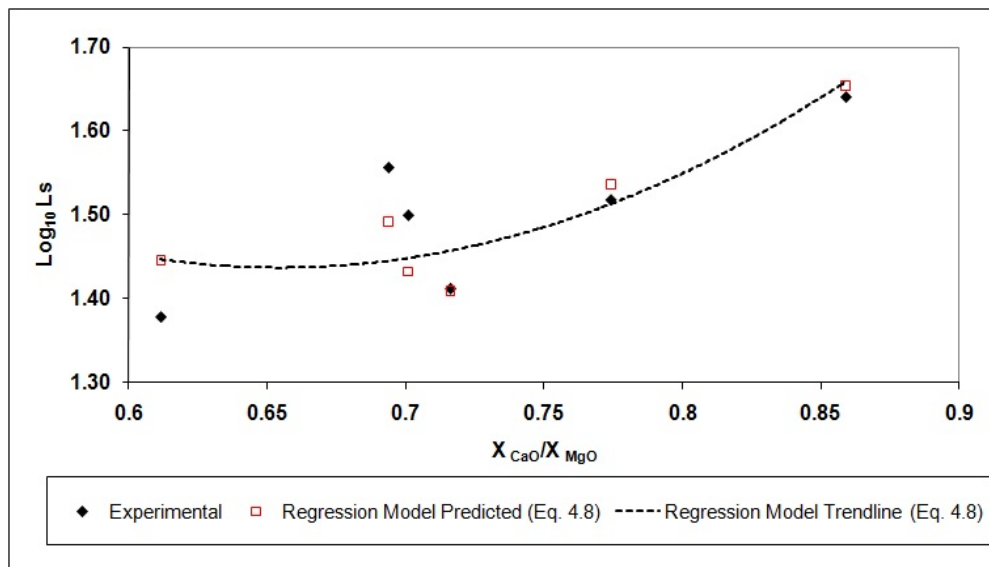


Figure H 7.2 The effect of CaO-to-MgO ratio (X_{CaO}/X_{MgO}) on the sulphur distribution ratio of ferromanganese smelting slag; ; Basicity Ratio:1.042-1.245, X_{SiO_2} :0.3979-0.4276, X_{CaO} : 0.1680-0.4352, X_{MgO} :0.2617-0.2748

APPENDIX I

PREDICTED $\text{Log } C_s^{-2}$ VALUES FOR FERROCHROMIUM SMELTING SLAGS (SULPHIDE CAPACITY) BASED ON YOUNG et al. (1992), SOSINSKY and SOMERVILLE (1986), SHANKAR et al. (2006) MODELS

Table II. Predicted $\text{Log } C_s^{-2}$ values for ferrochromium smelting slags based on Young et al. (1992), Sosinsky and Somerville (1986), Shankar et al. (2006) models

Experiment No.	X SiO_2	X Al_2O_3	X CaO	X MgO	X FeO	X TiO_2	X MnO	X Cr_2O_3	X CaS	Predicted Log Cs (Young et al. Model, 1992)	Predicted Log Cs (Sommerville and Sosinsky Model, 1986)	Predicted Log Cs (Shankar et al. Model, 2006)
1	0.2879	0.1246	0.1031	0.4691	0.0014	0.0001	0.0000	0.0009	0.01284	-3.6987	-3.8573	-3.1628
2	0.2875	0.1234	0.1038	0.4700	0.0015	0.0001	0.0000	0.0009	0.01282	-3.8164	-3.8516	-3.1613
3	0.3331	0.1252	0.0467	0.4899	0.0010	0.0001	0.0000	0.0009	0.00311	-4.1281	-4.1486	-3.3219
4	0.3237	0.1508	0.0568	0.4639	0.0010	0.0000	0.0001	0.0009	0.00286	-4.1293	-4.1347	-3.2793
5	0.3528	0.1385	0.0865	0.4191	0.0010	0.0000	0.0000	0.0005	0.00156	-3.9933	-4.1675	-3.3193
6	0.2883	0.1316	0.1055	0.4572	0.0020	0.0000	0.0000	0.0020	0.01333	-3.7529	-3.8721	-3.1637
7	0.2956	0.1284	0.0877	0.4788	0.0010	0.0000	0.0000	0.0005	0.00793	-3.7971	-3.9226	-3.1891
8	0.2938	0.1365	0.1058	0.4476	0.0020	0.0000	0.0000	0.0018	0.01249	-3.8223	-3.9037	-3.1741
9	0.3233	0.1247	0.0895	0.4563	0.0012	0.0001	0.0001	0.0009	0.00398	-3.8583	-4.0231	-3.2478
10	0.3056	0.1216	0.1197	0.4378	0.0017	0.0001	0.0000	0.0014	0.01212	-3.7162	-3.8931	-3.1855
11	0.2875	0.1229	0.1024	0.4710	0.0014	0.0000	0.0002	0.0012	0.01341	-3.8790	-3.8547	-3.1646
12	0.3120	0.1840	0.1835	0.3156	0.0004	0.0000	0.0004	0.0000	0.00401	-3.8706	-3.9051	-3.1359
13	0.2783	0.1829	0.1371	0.3924	0.0003	0.0001	0.0002	0.0001	0.00876	-3.8240	-3.8627	-3.1155
14	0.2808	0.1785	0.1416	0.3894	0.0004	0.0001	0.0002	0.0001	0.00903	-3.8320	-3.8560	-3.1167
15	0.3063	0.1766	0.1989	0.3064	0.0016	0.0000	0.0001	0.0023	0.00783	-3.7929	-3.8470	-3.1191
16	0.2726	0.1761	0.1554	0.3805	0.0036	0.0000	0.0002	0.0015	0.01025	-3.7781	-3.7972	-3.0939
17	0.2615	0.1954	0.1557	0.3728	0.0043	0.0000	0.0002	0.0006	0.00951	-3.7693	-3.7905	-3.0770
18	0.2783	0.1870	0.1653	0.3576	0.0022	0.0000	0.0003	0.0007	0.00866	-3.7442	-3.8200	-3.0968
19	0.2990	0.1462	0.1004	0.4404	0.0011	0.0001	0.0001	0.0021	0.01085	-4.0314	-3.9529	-3.1888
20	0.3534	0.1621	0.0352	0.4467	0.0016	0.0000	0.0000	0.0004	0.00053	-4.3429	-4.3041	-3.3824
21	0.3515	0.1584	0.0330	0.4540	0.0013	0.0000	0.0010	0.0003	0.00051	-4.3394	-4.2965	-3.3818
22	0.3501	0.1599	0.0347	0.4535	0.0010	0.0000	0.0001	0.0002	0.00047	-3.9613	-4.2884	-3.3727
23	0.2527	0.1110	0.1868	0.4295	0.0005	0.0000	0.0001	0.0004	0.01899	-3.5275	-3.4898	-3.0297
24	0.3250	0.1422	0.0879	0.4383	0.0003	0.0000	0.0000	0.0002	0.00593	-3.9919	-4.0664	-3.2527
25	0.3136	0.1460	0.0882	0.4416	0.0004	0.0000	0.0001	0.0005	0.00956	-3.9566	-4.0322	-3.2300
26	0.3169	0.1392	0.0908	0.4448	0.0005	0.0000	0.0000	0.0003	0.00735	-4.0362	-4.0245	-3.2324
27	0.3158	0.1683	0.0564	0.4558	0.0001	0.0000	0.0000	0.0001	0.00358	-4.1363	-4.1330	-3.2589
28	0.3155	0.1697	0.0620	0.4503	0.0003	0.0000	0.0001	0.0001	0.00197	-4.2359	-4.1215	-3.2510
29	0.3859	0.1637	0.0709	0.3749	0.0009	0.0001	0.0029	0.0007	0.00007	-4.4655	-4.3604	-3.4305
30	0.3717	0.1792	0.0703	0.3733	0.0019	0.0001	0.0021	0.0013	0.00010	-2.9422	-4.3330	-3.3848

APPENDIX J

CALCULATED Log a_{CaO} VALUES FOR FERROCHROMIUM SMELTING SLAGS (SULPHIDE CAPACITY) BASED ON Ban-Ya (1993)

Table J1. Calculated log a_{CaO} values for ferrochromium smelting slags based on Ban-Ya (1993)

Experiment No.	X SiO ₂	X Al ₂ O ₃	X CaO	X MgO	X FeO	X TiO ₂	X MnO	X Cr ₂ O ₃	X CaS	log a_{CaO}
1	0.2879	0.1246	0.1031	0.4691	0.0014	0.0001	0.0000	0.0009	0.01284	-2.140
2	0.2875	0.1234	0.1038	0.4700	0.0015	0.0001	0.0000	0.0009	0.01282	-2.136
3	0.3331	0.1252	0.0467	0.4899	0.0010	0.0001	0.0000	0.0009	0.00311	-2.671
4	0.3237	0.1508	0.0568	0.4639	0.0010	0.0000	0.0001	0.0009	0.00286	-2.556
5	0.3528	0.1385	0.0865	0.4191	0.0010	0.0000	0.0000	0.0005	0.00156	-2.322
6	0.2883	0.1316	0.1055	0.4572	0.0020	0.0000	0.0000	0.0020	0.01333	-2.117
7	0.2956	0.1284	0.0877	0.4788	0.0010	0.0000	0.0000	0.0005	0.00793	-2.267
8	0.2938	0.1365	0.1058	0.4476	0.0020	0.0000	0.0000	0.0018	0.01249	-2.119
9	0.3233	0.1247	0.0895	0.4563	0.0012	0.0001	0.0001	0.0009	0.00398	-2.270
10	0.3056	0.1216	0.1197	0.4378	0.0017	0.0001	0.0000	0.0014	0.01212	-2.038
11	0.2875	0.1229	0.1024	0.4710	0.0014	0.0000	0.0002	0.0012	0.01341	-2.144
12	0.3120	0.1840	0.1835	0.3156	0.0004	0.0000	0.0004	0.0000	0.00401	-1.785
13	0.2783	0.1829	0.1371	0.3924	0.0003	0.0001	0.0002	0.0001	0.00876	-1.956
14	0.2808	0.1785	0.1416	0.3894	0.0004	0.0001	0.0002	0.0001	0.00903	-1.931
15	0.3063	0.1766	0.1989	0.3064	0.0016	0.0000	0.0001	0.0023	0.00783	-1.692
16	0.2726	0.1761	0.1554	0.3805	0.0036	0.0000	0.0002	0.0015	0.01025	-1.841
17	0.2615	0.1954	0.1557	0.3728	0.0043	0.0000	0.0002	0.0006	0.00951	-1.847
18	0.2783	0.1870	0.1653	0.3576	0.0022	0.0000	0.0003	0.0007	0.00866	-1.815
19	0.2990	0.1462	0.1004	0.4404	0.0011	0.0001	0.0001	0.0021	0.01065	-2.164
20	0.3534	0.1621	0.0352	0.4467	0.0016	0.0000	0.0000	0.0004	0.00053	-2.849
21	0.3515	0.1584	0.0330	0.4540	0.0013	0.0000	0.0010	0.0003	0.00051	-2.886
22	0.3501	0.1599	0.0347	0.4535	0.0010	0.0000	0.0001	0.0002	0.00047	-2.855
23	0.2527	0.1110	0.1868	0.4295	0.0005	0.0000	0.0001	0.0004	0.01899	-1.663
24	0.3250	0.1422	0.0879	0.4383	0.0003	0.0000	0.0000	0.0002	0.00593	-2.283
25	0.3136	0.1460	0.0882	0.4416	0.0004	0.0000	0.0001	0.0005	0.00956	-2.266
26	0.3169	0.1392	0.0908	0.4448	0.0005	0.0000	0.0000	0.0003	0.00735	-2.252
27	0.3158	0.1683	0.0564	0.4558	0.0001	0.0000	0.0000	0.0001	0.00358	-2.563
28	0.3155	0.1697	0.0620	0.4503	0.0003	0.0000	0.0001	0.0001	0.00197	-2.511
29	0.3859	0.1637	0.0709	0.3749	0.0009	0.0001	0.0029	0.0007	0.00007	-2.519
30	0.3717	0.1792	0.0703	0.3733	0.0019	0.0001	0.0021	0.0013	0.00010	-2.511

APPENDIX K

PREDICTED $\text{Log } C_s^{-2}$ VALUES FOR FERROMANGANESE SMELTING SLAGS (SULPHIDE CAPACITY) BASED ON YOUNG et al. (1992), SOSINSKY and SOMERVILLE (1986) MODELS

Table K1. Predicted $\text{Log } C_s^{-2}$ values for ferromanganese smelting slags based on Young et al. (1992), Sosinsky and Somerville (1986), models

Experiment No.	X SiO_2	X Al_2O_3	X CaO	X MgO	X FeO	X TiO_2	X MnO	X Cr_2O_3	X CaS	X Ca_3P_2	Predicted $\text{Log } C_s$ (Young et al. Model, 1992)	Predicted $\text{Log } C_s$ (Sosinsky and Somerville Model, 1986)
1	0.4412	0.0367	0.2339	0.1692	0.0001	0.0001	0.1053	0.00002	0.01338	4.7803E-05	-4.000	-4.243
2	0.4477	0.0364	0.2310	0.1683	0.0003	0.0002	0.1032	0.00002	0.01271	1.1515E-04	-4.042	-4.276
3	0.4538	0.0365	0.2317	0.1684	0.0004	0.0002	0.0965	0.00002	0.01245	1.9197E-05	-4.068	-4.308
4	0.4276	0.0323	0.1760	0.2188	0.0004	0.0001	0.1351	0.00003	0.00960	1.8959E-05	-3.954	-4.235
5	0.4392	0.0319	0.1802	0.2163	0.0002	0.0002	0.1262	0.00002	0.00969	6.6050E-05	-4.029	-4.261
6	0.4573	0.0381	0.1938	0.1722	0.0003	0.0002	0.1248	0.00002	0.01326	9.6467E-06	-4.136	-4.348
7	0.3733	0.0329	0.2963	0.2222	0.0006	0.0001	0.0595	0.00001	0.01511	4.5252E-05	-3.564	-3.921
8	0.3794	0.0324	0.2932	0.2221	0.0007	0.0001	0.0565	0.00001	0.01551	1.8505E-05	-3.608	-3.957
9	0.3979	0.0515	0.2289	0.2665	0.0002	0.0001	0.0368	0.00001	0.01896	3.7051E-05	-3.990	-4.237
10	0.3593	0.0384	0.3662	0.1881	0.0008	0.0001	0.0284	0.00001	0.01876	2.7991E-05	-3.438	-3.797
11	0.3646	0.0382	0.3658	0.1891	0.0007	0.0001	0.0241	0.00001	0.01736	5.5867E-05	-3.476	-3.826
12	0.3574	0.0371	0.3469	0.2135	0.0004	0.0001	0.0254	0.00001	0.01931	5.5487E-05	-3.464	-3.828
13	0.3665	0.0365	0.3409	0.2130	0.0012	0.0001	0.0244	0.00001	0.01742	9.2252E-06	-3.528	-3.879
14	0.3818	0.0406	0.3775	0.1505	0.0004	0.0001	0.0247	0.00001	0.02411	2.9492E-05	-3.662	-3.890
15	0.3863	0.0404	0.3798	0.1511	0.0005	0.0001	0.0249	0.00001	0.01836	9.4441E-06	-3.581	-3.896
16	0.3905	0.0407	0.3825	0.1469	0.0006	0.0001	0.0222	0.00001	0.01853	9.4487E-06	-3.607	-3.914
17	0.4249	0.0424	0.1681	0.2748	0.0006	0.0001	0.0746	0.00002	0.01440	9.2541E-06	-4.146	-4.366
18	0.3666	0.0462	0.4353	0.1152	0.0004	0.0000	0.0149	0.00001	0.02133	9.5868E-06	-3.412	-3.741
19	0.3652	0.0461	0.4310	0.1223	0.0004	0.0000	0.0144	0.00001	0.02058	4.7641E-05	-3.416	-3.743
20	0.3699	0.0463	0.4323	0.1176	0.0010	0.0000	0.0131	0.00002	0.01971	2.8595E-05	-3.445	-3.764
21	0.3519	0.0425	0.3976	0.1674	0.0009	0.0000	0.0181	0.00001	0.02160	3.7522E-05	-3.379	-3.795
22	0.3564	0.0415	0.3929	0.1715	0.0007	0.0000	0.0174	0.00001	0.01961	9.3648E-06	-3.409	-3.760
23	0.3581	0.0415	0.3923	0.1688	0.0013	0.0001	0.0170	0.00001	0.02087	2.8128E-05	-3.421	-3.771
24	0.4055	0.0346	0.2613	0.1932	0.0010	0.0001	0.0883	0.00002	0.01594	4.7209E-05	-3.767	-4.078
25	0.4180	0.0336	0.2571	0.1955	0.0021	0.0002	0.0811	0.00002	0.01237	1.4113E-04	-3.857	-4.144
26	0.4176	0.0353	0.2501	0.2015	0.0005	0.0002	0.0803	0.00002	0.01448	1.0360E-04	-3.879	-4.161
27	0.4286	0.0342	0.1835	0.1950	0.0003	0.0002	0.1502	0.00003	0.00788	9.5994E-06	-3.916	-4.200
28	0.4356	0.0337	0.1753	0.1932	0.0005	0.0002	0.1458	0.00003	0.01571	1.9164E-05	-3.969	-4.259
29	0.4450	0.0336	0.1759	0.1930	0.0010	0.0002	0.1391	0.00002	0.01309	4.7870E-05	-4.066	-4.304
30	0.4196	0.0323	0.2505	0.1512	0.0008	0.0001	0.1305	0.00003	0.01488	2.8839E-05	-3.767	-4.077
31	0.4276	0.0333	0.2577	0.1525	0.0006	0.0001	0.1127	0.00002	0.01548	9.6200E-06	-3.839	-4.129
32	0.4311	0.0325	0.2522	0.1521	0.0033	0.0002	0.1149	0.00002	0.01375	5.7580E-05	-3.865	-4.148
33	0.4005	0.0346	0.2442	0.2339	0.0004	0.0001	0.0728	0.00002	0.01339	9.2691E-06	-3.808	-4.113
34	0.4118	0.0418	0.1843	0.2657	0.0006	0.0001	0.0753	0.00002	0.02024	1.7635E-04	-4.034	-4.291
35	0.4218	0.0409	0.1834	0.2617	0.0011	0.0001	0.0751	0.00002	0.01590	6.5045E-05	-4.066	-4.325
36	0.4276	0.0412	0.1880	0.2625	0.0004	0.0002	0.0666	0.00001	0.01343	3.7095E-05	-4.129	-4.349
37	0.3770	0.0360	0.3395	0.1921	0.0002	0.0001	0.0389	0.00001	0.01760	3.7263E-05	-3.560	-3.901
38	0.3844	0.0356	0.3365	0.1895	0.0004	0.0001	0.0362	0.00001	0.01722	4.6638E-05	-3.609	-3.940
39	0.4013	0.0373	0.2674	0.2168	0.0002	0.0001	0.0565	0.00001	0.02030	4.6651E-05	-3.815	-4.114
40	0.4039	0.0372	0.2687	0.2164	0.0002	0.0001	0.0568	0.00001	0.01669	4.6568E-05	-3.825	-4.118
41	0.4228	0.0455	0.2084	0.2693	0.0003	0.0001	0.0360	0.00003	0.01752	9.1622E-06	-4.156	-4.357

APPENDIX L

CALCULATED Log a_{CaO} VALUES FOR FERROMANGANESE SMELTING SLAGS (SULPHIDE CAPACITY) BASED ON Ban-Ya (1993)

Table L1. Calculated log a_{CaO} values for ferrochromium smelting slags based on Ban-Ya (1993)

Experiment No.	X SiO ₂	X Al ₂ O ₃	X CaO	X MgO	X FeO	X TiO ₂	X MnO	X Cr ₂ O ₃	X CaS	XCa ₃ P ₂	Log a_{CaO}
1	0.4412	0.0367	0.2339	0.1692	0.0001	0.0001	0.1053	0.00002	0.01338	4.7803E-05	-2.356
2	0.4477	0.0364	0.2310	0.1683	0.0003	0.0002	0.1032	0.00002	0.01271	1.1515E-04	-2.381
3	0.4538	0.0365	0.2317	0.1684	0.0004	0.0002	0.0965	0.00002	0.01245	1.9197E-05	-2.384
4	0.4276	0.0323	0.1760	0.2188	0.0004	0.0001	0.1351	0.00003	0.00960	1.8959E-05	-2.736
5	0.4392	0.0319	0.1802	0.2163	0.0002	0.0002	0.1262	0.00002	0.00569	6.6050E-05	-2.734
6	0.4573	0.0381	0.1938	0.1722	0.0003	0.0002	0.1248	0.00002	0.01326	9.6467E-06	-2.618
7	0.3733	0.0329	0.2963	0.2222	0.0006	0.0001	0.0595	0.00001	0.01511	4.6282E-05	-1.953
8	0.3794	0.0324	0.2932	0.2221	0.0007	0.0001	0.0565	0.00001	0.01551	1.8505E-05	-1.971
9	0.3979	0.0515	0.2289	0.2665	0.0002	0.0001	0.0358	0.00001	0.01896	3.7051E-05	-2.329
10	0.3593	0.0384	0.3662	0.1881	0.0008	0.0001	0.0284	0.00001	0.01876	2.7991E-05	-1.587
11	0.3646	0.0382	0.3658	0.1891	0.0007	0.0001	0.0241	0.00001	0.01736	5.5867E-05	-1.598
12	0.3574	0.0371	0.3469	0.2135	0.0004	0.0001	0.0254	0.00001	0.01931	5.5487E-05	-1.674
13	0.3665	0.0365	0.3409	0.2130	0.0012	0.0001	0.0244	0.00001	0.01742	9.2292E-06	-1.712
14	0.3818	0.0408	0.3775	0.1505	0.0004	0.0001	0.0247	0.00001	0.02411	2.8492E-05	-1.540
15	0.3863	0.0404	0.3798	0.1511	0.0005	0.0001	0.0249	0.00001	0.01696	9.4441E-06	-1.556
16	0.3905	0.0407	0.3825	0.1469	0.0006	0.0001	0.0222	0.00001	0.01653	9.4487E-06	-1.549
17	0.4249	0.0424	0.1681	0.2748	0.0006	0.0001	0.0746	0.00002	0.01440	9.2541E-06	-2.768
18	0.3666	0.0462	0.4353	0.1152	0.0004	0.0000	0.0149	0.00001	0.02133	9.5868E-06	-1.299
19	0.3652	0.0461	0.4310	0.1223	0.0004	0.0000	0.0144	0.00001	0.02058	4.7641E-05	-1.316
20	0.3699	0.0463	0.4323	0.1176	0.0010	0.0000	0.0131	0.00002	0.01971	2.8585E-05	-1.316
21	0.3519	0.0425	0.3976	0.1674	0.0008	0.0000	0.0181	0.00001	0.02160	3.7522E-05	-1.436
22	0.3564	0.0415	0.3929	0.1715	0.0007	0.0000	0.0174	0.00001	0.01961	9.3648E-06	-1.466
23	0.3581	0.0415	0.3923	0.1688	0.0013	0.0001	0.0170	0.00001	0.02087	2.8128E-05	-1.464
24	0.4055	0.0346	0.2613	0.1932	0.0010	0.0001	0.0883	0.00002	0.01594	4.7209E-05	-2.159
25	0.4180	0.0336	0.2571	0.1955	0.0021	0.0002	0.0811	0.00002	0.01237	1.4113E-04	-2.202
26	0.4176	0.0353	0.2501	0.2015	0.0005	0.0002	0.0803	0.00002	0.01448	1.0360E-04	-2.240
27	0.4286	0.0342	0.1835	0.1950	0.0003	0.0002	0.1502	0.00003	0.00788	9.5994E-06	-2.688
28	0.4356	0.0337	0.1753	0.1932	0.0005	0.0002	0.1458	0.00003	0.01571	1.9164E-05	-2.714
29	0.4450	0.0336	0.1759	0.1930	0.0010	0.0002	0.1381	0.00002	0.01309	4.7870E-05	-2.728
30	0.4196	0.0323	0.2505	0.1512	0.0008	0.0001	0.1305	0.00003	0.01488	2.8899E-05	-2.229
31	0.4276	0.0333	0.2577	0.1525	0.0006	0.0001	0.1127	0.00002	0.01548	9.6200E-06	-2.196
32	0.4311	0.0325	0.2522	0.1521	0.0033	0.0002	0.1149	0.00002	0.01375	5.7580E-05	-2.226
33	0.4005	0.0346	0.2442	0.2339	0.0004	0.0001	0.0728	0.00002	0.01339	9.2691E-06	-2.267
34	0.4118	0.0418	0.1843	0.2657	0.0006	0.0001	0.0753	0.00002	0.02024	1.7635E-04	-2.619
35	0.4218	0.0409	0.1834	0.2617	0.0011	0.0001	0.0751	0.00002	0.01590	6.5045E-05	-2.650
36	0.4276	0.0412	0.1880	0.2625	0.0004	0.0002	0.0666	0.00001	0.01343	3.7085E-05	-2.638
37	0.3770	0.0360	0.3385	0.1921	0.0002	0.0001	0.0389	0.00001	0.01708	3.7269E-05	-1.738
38	0.3844	0.0356	0.3365	0.1895	0.0004	0.0001	0.0362	0.00001	0.01722	4.6638E-05	-1.751
39	0.4013	0.0373	0.2674	0.2168	0.0002	0.0001	0.0565	0.00001	0.02030	4.6651E-05	-2.109
40	0.4039	0.0372	0.2687	0.2164	0.0002	0.0001	0.0568	0.00001	0.01669	4.6568E-05	-2.118
41	0.4228	0.0455	0.2084	0.2693	0.0003	0.0001	0.0360	0.00003	0.01752	9.1622E-06	-2.481

APPENDIX M

CALCULATED Log a_{MnO} VALUES FOR FERROMANGANESE SMELTING SLAGS (SULPHIDE CAPACITY) BASED ON Cengizler (1993)

Table M1. Calculated Log a_{MnO} values for ferrochromium smelting slags based on Cengizler(1993)

Experiment No.	X SiO ₂	X Al ₂ O ₃	X CaO	X MgO	X FeO	X TiO ₂	X MnO	X Cr ₂ O ₃	X CaS	X Ca ₃ P ₂	Log a_{MnO}
1	0.4412	0.0367	0.2339	0.1692	0.0001	0.0001	0.1053	0.00002	0.01338	4.7803E-05	-1.156
2	0.4477	0.0364	0.2310	0.1683	0.0003	0.0002	0.1032	0.00002	0.01271	1.1515E-04	-1.173
3	0.4538	0.0365	0.2317	0.1684	0.0004	0.0002	0.0965	0.00002	0.01245	1.9197E-05	-1.193
4	0.4276	0.0323	0.1760	0.2188	0.0004	0.0001	0.1351	0.00003	0.00960	1.8959E-05	-1.173
5	0.4392	0.0319	0.1802	0.2163	0.0002	0.0002	0.1262	0.00002	0.00569	6.6050E-05	-1.225
6	0.4573	0.0381	0.1938	0.1722	0.0003	0.0002	0.1248	0.00002	0.01326	9.6467E-06	-1.206
7	0.3733	0.0329	0.2963	0.2222	0.0006	0.0001	0.0595	0.00001	0.01511	4.6282E-05	-1.038
8	0.3794	0.0324	0.2932	0.2221	0.0007	0.0001	0.0565	0.00001	0.01551	1.8505E-05	-1.056
9	0.3979	0.0515	0.2289	0.2665	0.0002	0.0001	0.0358	0.00001	0.01896	3.7051E-05	-1.238
10	0.3593	0.0384	0.3662	0.1881	0.0008	0.0001	0.0284	0.00001	0.01876	2.7991E-05	-1.061
11	0.3646	0.0382	0.3658	0.1891	0.0007	0.0001	0.0241	0.00001	0.01736	5.5867E-05	-1.063
12	0.3574	0.0371	0.3469	0.2135	0.0004	0.0001	0.0254	0.00001	0.01931	5.5487E-05	-1.097
13	0.3665	0.0365	0.3409	0.2130	0.0012	0.0001	0.0244	0.00001	0.01742	9.2292E-06	-1.085
14	0.3818	0.0408	0.3775	0.1505	0.0004	0.0001	0.0247	0.00001	0.02411	2.8492E-05	-1.028
15	0.3863	0.0404	0.3798	0.1511	0.0005	0.0001	0.0249	0.00001	0.01696	9.4441E-06	-1.023
16	0.3905	0.0407	0.3825	0.1489	0.0006	0.0001	0.0222	0.00001	0.01653	9.4467E-06	-1.024
17	0.4249	0.0424	0.1681	0.2748	0.0006	0.0001	0.0746	0.00002	0.01440	9.2541E-06	-1.293
18	0.3666	0.0462	0.4353	0.1152	0.0004	0.0000	0.0149	0.00001	0.02133	9.5868E-06	-1.039
19	0.3652	0.0461	0.4310	0.1223	0.0004	0.0000	0.0144	0.00001	0.02058	4.7641E-05	-1.040
20	0.3699	0.0463	0.4323	0.1176	0.0010	0.0000	0.0131	0.00002	0.01971	2.8585E-05	-1.025
21	0.3519	0.0425	0.3976	0.1674	0.0008	0.0000	0.0181	0.00001	0.02160	3.7522E-05	-1.109
22	0.3564	0.0415	0.3929	0.1715	0.0007	0.0000	0.0174	0.00001	0.01961	9.3648E-06	-1.092
23	0.3581	0.0415	0.3923	0.1688	0.0013	0.0001	0.0170	0.00001	0.02087	2.8128E-05	-1.087
24	0.4055	0.0346	0.2613	0.1932	0.0010	0.0001	0.0883	0.00002	0.01594	4.7209E-05	-1.072
25	0.4180	0.0336	0.2571	0.1955	0.0021	0.0002	0.0811	0.00002	0.01237	1.4113E-04	-1.125
26	0.4176	0.0353	0.2501	0.2015	0.0005	0.0002	0.0803	0.00002	0.01448	1.0360E-04	-1.132
27	0.4286	0.0342	0.1835	0.1950	0.0003	0.0002	0.1502	0.00003	0.00788	9.5994E-06	-1.128
28	0.4356	0.0337	0.1753	0.1932	0.0005	0.0002	0.1458	0.00003	0.01571	1.9164E-05	-1.157
29	0.4450	0.0336	0.1759	0.1930	0.0010	0.0002	0.1381	0.00002	0.01309	4.7870E-05	-1.195
30	0.4196	0.0323	0.2505	0.1512	0.0008	0.0001	0.1305	0.00003	0.01488	2.8899E-05	-1.044
31	0.4276	0.0333	0.2577	0.1525	0.0006	0.0001	0.1127	0.00002	0.01548	9.6200E-06	-1.079
32	0.4311	0.0325	0.2522	0.1521	0.0033	0.0002	0.1149	0.00002	0.01375	5.7580E-05	-1.095
33	0.4005	0.0346	0.2442	0.2339	0.0004	0.0001	0.0728	0.00002	0.01339	9.2691E-06	-1.129
34	0.4118	0.0418	0.1843	0.2657	0.0006	0.0001	0.0753	0.00002	0.02024	1.7635E-04	-1.224
35	0.4218	0.0409	0.1834	0.2617	0.0011	0.0001	0.0751	0.00002	0.01590	6.5045E-05	-1.255
36	0.4276	0.0412	0.1880	0.2625	0.0004	0.0002	0.0665	0.00001	0.01343	3.7085E-05	-1.282
37	0.3770	0.0360	0.3385	0.1921	0.0002	0.0001	0.0389	0.00001	0.01708	3.7269E-05	-1.037
38	0.3844	0.0356	0.3365	0.1895	0.0004	0.0001	0.0362	0.00001	0.01722	4.6638E-05	-1.048
39	0.4013	0.0373	0.2674	0.2168	0.0002	0.0001	0.0565	0.00001	0.02030	4.6651E-05	-1.116
40	0.4039	0.0372	0.2687	0.2164	0.0002	0.0001	0.0568	0.00001	0.01689	4.6568E-05	-1.123
41	0.4228	0.0455	0.2084	0.2693	0.0003	0.0001	0.0360	0.00003	0.01752	9.1622E-06	-1.294

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