2 LITERATURE REVIEW

Much work has been done on phosphorus removal in iron and steel making processes, a review of these processes will be given in this section. As will become apparent later most of the processes rely on oxidative dephosphorisation. In the presence of chromium and manganese as alloying elements, for example in the stainless steelmaking processes, due to the high affinity for oxygen of these elements than phosphorus, oxidative dephosphorisation will not be applicable, as it will result in high chromium and manganese losses. The highly reducing atmosphere prevailing inside the submerged arc furnace for ferromanganese smelting reduction process also makes oxidative dephosphorisation not applicable. Because of the difficulty of removing phosphorus in the production of stainless steels and other high alloy special steels it is of paramount importance to remove phosphorus from alloying materials used during their primary production to minimize contamination in down stream processes.

2.1 Partitioning of Phosphorus in the Blast Furnace

Phosphorus is present in most iron ores as mineral phosphates, which are readily reduced in the blast furnace, and the phosphorus is transferred into the iron bath. The partitioning of phosphorus between the slag and metal phases in the hearth can be evaluated from data for reaction (2.1):

\[ 2P_{(\text{in Fe})} + 5O_{(\text{in Fe})} \leftrightarrow P_2O_5_{(\text{slag})} \]  

(2.1)

The equilibrium in this reaction lies far to the left, for the activity of oxygen is raised to the fifth power in the equilibrium expression. When \( P_{co} = 1 \text{atm} \), the equilibrium oxygen activity in carbon saturated iron is about \( 5 \times 10^{-5} \) at 1500°C. It follows that the activity of \( P_2O_5 \) in the slag is vanishingly small, the phosphorus content of the slag is thus negligible, and practically all the phosphorus remains in the metal\(^7\).
2.2 Phosphorus Removal in Steelmaking Processes

2.2.1 The Basic Open-Hearth process - the flush-slag practice

Small quantities of fluorspar (calcium fluoride - CaF$_2$) are added to flux the lime and speed up the rate of slag formation. In basic slags alumina behaves as a very weak acid with a fairly strong fluxing action. When the slag is in “condition” to receive P and S, oxygen additions are made to propagate the carbon boil. The content of P$_2$O$_5$ in the slag will increase during the carbon boil. At the end of refining P$_2$O$_5$ in the slag is in equilibrium with the phosphorus in the metal. The total content of acidic radicals (P$_2$O$_5$ + SiO$_2$) is about 22%. The reduction of oxygen content in the metal resulting from the addition of deoxidants may displace the equilibrium and cause a reversion of phosphorus to the metal. The extent of the reversion is reduced by adding only sufficient deoxidants to the bath to check the elimination of carbon. If the whole cast is to come with the required phosphorus limits, the phosphorus content of the metal at tap must be well below the target to allow for reversion and the slag must be sufficiently basic to minimize its extent$^7$.

At constant temperature and oxygen activity ($a_O$) in the metal, the partitioning of phosphorus can be expressed as:

$$L_p = \frac{(\gamma_{P_2O_5})(X_{P_2O_5})}{[f_p][%P]}$$  \hspace{1cm} (2.2)

From equation (2.2), the residual concentration of phosphorus can be lowered by two methods:

i. Increasing the basicity of the slag so as to lower $\gamma_{P_2O_5}$. This effect however, operates only when the basicity of the liquid slag can be raised.
ii. Increasing the volume of the slag so as to lower $X_{P\text{O}}$ by dilution. This improves the phosphorus partitioning at the expense of a thicker layer of slag and retards heat transfer to the metal.

With moderate amounts of P in the charge the residual concentration can be lowered to acceptable limits with a reasonable volume of slag. As the initial P concentration is increased the production rate must be lowered to allow time for the required large amounts of lime to dissolve in the slag before the start of the carbon boil and for the reduced rate of thermal transfer. In the latter case it is often preferable to operate a Flush-slag (Two-slag) process.

The numerical value of the equilibrium constant for the phosphorus partitioning reaction decreases rapidly as the temperature is raised and for a constant $\gamma_{P\text{O}}$, the residual phosphorus in the metal increases with the temperature. Thus if a basic slag is formed while the metal temperature is still relatively low, a large percentage of the P in the charge can be transferred to the slag before the start of the carbon boil. At this stage the slag is flushed from the furnace and a new slag is formed by additions of lime and a flux. The second slag is required to remove only small amounts of phosphorus and a small volume will suffice, this facilitates thermal transfer during the ensuing carbon boil. Against this advantage though, is the lower metal yield and lower Mn recovery.

### 2.2.2 The removal of phosphorus in top blown oxygen steelmaking processes

For good phosphorus removal the activity of calcium oxide and the oxygen potential of the slag should be high while $P_2O_5$ activity coefficient should be low. The best conditions will be achieved with liquid slags close to saturation with lime or calcium phosphate. Kozakevitch and Ribound (14) have derived from the phase diagram a
formula giving the optimum lime content of steel-slags to achieve these aims, as given below:

\[
\%\text{CaO} = 1.41(\%\text{P}_2\text{O}_5 + \%\text{Al}_2\text{O}_3 + 5\text{TiO}_2) + 2.61\%\text{SiO}_2 \\
+ \%\text{FeO} - 0.005(\%\text{FeO})^2
\]  

(2.3)

The oxygen potential of this slag is higher than that for the FeO/Fe equilibrium and while it may vary to some extent throughout the slag, it is of the order $10^{-5}$ atm, under these conditions dephosphorisation should be very favorable.

### 2.2.3 Phosphorus removal in bottom blown oxygen steelmaking processes
(Basic Bessemer process)

Although this process is extinct, it provides a good example for phosphorous removal. In contact with oxygen, phosphorus in the metal is oxidized readily to form phosphorus pentoxide ($\text{P}_2\text{O}_5$) but this compound is unstable in the presence of C, Si, Mn or other more powerful oxide forming elements. Its stability can be changed by lowering its activity. Phosphorus pentoxide is insoluble in the metal and its activity is high in a silica-rich slag but is lowered markedly in a very basic slag. The optimum conditions for the removal of P occur when the slag in contact with the metal contains only sufficient acidic oxides to give a fluid melt at the operating temperature. Manganese forms a basic oxide which lowers the surface tension of the slag and slightly increases the solubility limit so that more lime can be incorporated in a fluid slag at any given temperature. When operating a basic process the deficiency in heat generated owing to the lower silicon content is compensated by the oxidation of phosphorus which is very exothermic:

\[
2\text{P}(\% \text{ in Fe}) + 5/2\text{O}_2(g) \leftrightarrow \text{P}_2\text{O}_5(g) \quad \Delta H_P = -1200\text{kJ} \]  

(2.4)
During the refining process the actual concentrations of the elements in the alloy decreases in the order: Si, Mn, C, and P as shown in Figure 2.1\(^{(7)}\). As shown the P content does not fall rapidly until the dissolved carbon is almost completely oxidized (approximately 15mins into the refining process). The period during which phosphorus is removed is called the After-Blow and is characterized by the appearance of brown fumes with only a very short reddish flame at the converter mouth\(^{(7)}\). The duration of the after–blow is usually 2 - 2.5mins depending on the phosphorus content of the metal. During the after-blow the oxygen activity in the metal is determined by the P concentration. Since \( \text{P}_2\text{O}_5 \) is unstable and insoluble in the molten iron the oxidation of P occurs mainly at the slag-metal interface, where the oxidation product can be absorbed into the slag. It is therefore expected that phosphorus in the metal approaches equilibrium with the iron oxides in the slag.

The activity coefficient of \( \text{P}_2\text{O}_5 \) is lowered rapidly as the slag approaches saturation with lime. As much as 98% of the phosphorus can be transferred into the slag, hence the \( \gamma_{\text{P}_2\text{O}_5} \) must be very low, such that in the range \( 10^{-15} \) to \( 10^{-20} \) if the metal is at 1600\(^\circ\)C. The amount of phosphorus which is held in the slag is dependent on \( a_{\text{P}_2\text{O}_5} \), which is equal to the product \( \gamma_{\text{P}_2\text{O}_5} \times X_{\text{P}_2\text{O}_5} \). Hence at a constant \( \gamma_{\text{P}_2\text{O}_5} \) in the slag, the proportion of P transferred to the slag is increased as the slag bulk is increased and \( X_{\text{P}_2\text{O}_5} \) is lowered by dilution. But there is a limit to this effect, if the slag bulk is increased by addition of too great a quantity of lime a stage is reached at which the slag becomes saturated with lime and any further addition remains as a solid which makes negligible contribution to the removal of phosphorus. Thus apart from the increase in the thermal load, there is no metallurgical advantage in charging more lime than is required just to saturate the slag.
When the dilute wt % solution is taken as the standard state for the various solutes, the equilibrium constant of dephosphorisation reaction (2.5)\(^7\) is given by:

\[
2\text{P}(%\text{ in Fe}) + 5\text{O}(%\text{ in Fe}) \leftrightarrow \text{P}_2\text{O}_5(\text{l})
\]  

\[(2.5)\]

Therefore

\[
\log K_{2,5} = \log \left( \frac{a_{\text{P}_2\text{O}_5}}{[a_p]^2[a_O]^5} \right) = \frac{35.700}{T} - 30.3
\]  

\[(2.6)\]

Instead of a simple reaction expressed in reaction (2.5) it is possible to assume that the \(\text{P}_2\text{O}_5\) in the slag is combined with lime to form the compound tetracalcium phosphate (4CaO.P\(_2\)O\(_5\)). Thus:

\[
2\text{P}(\text{in Fe}) + 5\text{O}(\text{in Fe}) + 4\text{CaO}(\text{slag}) \leftrightarrow 4\text{CaO}.\text{P}_2\text{O}_5(\text{slag})
\]  

\[(2.7)\]

If the oxygen blow is continued beyond 0.04 wt. % P in the metal to further reduce its level, the oxygen in the metal increases rapidly and the FeO content of the slag is also raised. Thus, the metal yield is lowered and a greater amount of the deoxidizer is required. If lower P contents are required it is preferable to halt the blow when the P content has dropped to about 0.04 wt. % and remove most of the first slag, after which lime is added together with a small quantity of the flux to hasten the formation of a new slag, and the blow is continued. Most of the P is removed with the first slag. The residual P is lower when the second slag is saturated with phosphate than is the case in the one-slag practice, but the total heat time is raised and the production rate is lowered correspondingly.
Figure 2.1 Change of metal composition with time in the “Basic Bessemer process”\textsuperscript{(7)}
2.3 The Removal of Phosphorus from the Metal Phase

2.3.1 Equilibrium conditions

In contrast to the detailed investigations into the distribution between the slag and metal phases of elements like Si, C, S, etc, the factors controlling the partitioning of phosphorus are known only qualitatively. This can be attributed largely to the difficulties associated with the measurement of the thermodynamic properties of phosphorus in solution in the metal and slag at very high temperatures of interest. No direct determination of the activities has been made in multi-component molten iron and steel making slags and ferromanganese smelting slags. The value of the equilibrium constant for phosphorus partitioning between the slag and metal phases is still subject to considerable uncertainty. Nevertheless, conditions, which facilitate the transfer of P into the slag are well established and are listed below:

i. A high slag basicity, particularly high lime content in solution
ii. A high oxygen potential
iii. Low bath temperature

Conditions ii and iii make phosphorus control in ferromanganese (FeMn) smelting challenging due to the highly reducing atmosphere (Po_2 < 10^{-16} atm) and the high operating temperature (T > 1400°C) for the reduction process.

Both the phosphorus element and its oxide P_2O_5 are gaseous in the temperature range of interest. The free energy of formation of P_2O_5 relative to the dilute wt. % standard states of phosphorus and oxygen dissolved in iron is derived as follows:

\[ 2P(g) + \frac{5}{2}O_2(g) \leftrightarrow P_2O_5(l) \]  

(2.8)

\[ \Delta G^\circ = -1514000 + 526T \text{ J/mol} \]  

(2.9)
\[ \Delta G^\circ \] of evaporation of \( \text{P}_2\text{O}_5(l) \) is given by:

\[ \text{P}_2\text{O}_5(l) \leftrightarrow \text{P}_2\text{O}_5(g) \quad (2.10) \]

\[ \Delta G^\circ = 54\,000 - 62.3T \, \text{J/mol} \quad (2.11) \]

Assuming similar heat capacities for the liquid and gaseous \( \text{P}_2\text{O}_5 \), \( \Delta G^\circ \) of formation of \( \text{P}_2\text{O}_5 \) gas is obtained by adding equation (2.9) and (2.11) to get (2.13):

\[ \text{P}_2(g) + \frac{5}{2}\text{O}_2(g) \leftrightarrow \text{P}_2\text{O}_5(g) \quad (2.12) \]

\[ \Delta G^\circ = -1\,460\,000 + 464T \, \text{J/mol} \quad (2.13) \]

At high concentration (>0.1 atom fraction) the activity of \( \text{P} \) dissolved in liquid iron shows positive deviation. The interaction coefficient is given as \( \epsilon_p^\circ = 0.122 \). It is usually assumed that, within the dilute solution range of interest, \( \text{P} \) in liquid iron obeys Henry’s law and the activities are approximately ideal. Assuming ideal behaviour, \( \Delta G^\circ \) of solution of \( \text{P} \) in iron, relative to dilute wt. % standard state, is given by reaction (2.14):

\[ 2\text{P}(\% \text{ in Fe}) \leftrightarrow \text{P}_2(g) \quad (2.14) \]

\[ \Delta G^\circ = 245\,000 + 39T \, \text{J/mol} \quad (2.15) \]

Given that the free energy change of solution of [O] in iron is given by:

\[ \frac{1}{2}\text{O}_2(g) \leftrightarrow \text{O}(\% \text{ in Fe}) \quad (2.16) \]

\[ \Delta G^\circ = -118\,000 - 2.4T \, \text{J/mol} \quad (2.17) \]
Thus combining equations (2.13) and (2.15) with (2.17) gives the standard free energy change for reaction (2.18):

\[
2P(\% \text{ in Fe}) + 5O(\% \text{ in Fe}) \leftrightarrow P_2O_5(g) \tag{2.18}
\]

\[
\Delta G^o = -629\ 000 + 518T \text{ J/mol} \tag{2.19}
\]

and:

\[
\log K_{P_2O_5} = \log \frac{P_{P_2O_5}}{[a_P]^2[a_O]^5} = \frac{33000}{T} - 27.0 \tag{2.20}
\]

At 1600°C \( K_{P_2O_5} = 4 \times 10^{-10} \) (approximately). This shows that the partial pressure of \( P_2O_5 \) gas in equilibrium with the dissolved oxygen and phosphorus is very low. Hence for all practical purposes the possibility of removal of P from the metal as a gas can be neglected. By combining equations (2.9), (2.15) and (2.17) the free energy of formation of liquid \( P_2O_5 \) in the slag can be determined:

\[
2P(\% \text{ in Fe}) + 5O(\% \text{ in Fe}) \leftrightarrow P_2O_5(l) \tag{2.21}
\]

\[
\Delta G^o = -683\ 000 + 580T \text{ J/mol} \tag{2.22}
\]

and:

\[
\log K_{P_2O_5(l)} = \log \frac{(a_{P_2O_5})}{[a_P]^2[a_O]^5} = \frac{35700}{T} - 30.3 \tag{2.23}
\]

At 1600°C \( K_{P_2O_5(l)} = 6 \times 10^{-10} \) (approximately). This value confirms that the activity of the pentoxide in the slag is very small. Equation (2.23) shows that the value of the equilibrium constant decreases with increasing temperature. For example a change of temperature of 100°C changes the value of \( K_{P_2O_5(l)} \) by a factor of 10.
The necessary low activities of the reaction product can be obtained only when it is dissolved in the slag and combines with CaO. Consequently, the phosphorus oxidation reaction occurs at the slag-metal interface. Like other interface reactions, it is expected therefore that, the rate of transfer of phosphorus from the metal to the slag is controlled by transport across an interface boundary layer. Hence a much higher rate of removal into a slag of given composition is obtained when the metal is dispersed as droplets in the slag, as in the LD process, than when the metal and slag are separated by a more or less planar interface as in the open-hearth or submerged electric arc furnace.

2.3.2 The effect of oxygen potential, temperature and slag basicity on dephosphorisation

Goodeve\(^{(48)}\) compared the oxygen potentials for the principal ironmaking and steelmaking processes with those of the formation of calcium phosphate at 1% concentration of \(P_2O_5\) in the slag from a 1% concentration of P in the metal. The results obtained by Goodeve are presented in Figure 2.2 where the broken line represents oxygen potentials in equilibrium with phosphorus pentoxide at activity approximately equal to \(10^{-20}\) in the slag. The line is raised to higher oxygen potentials if the activity of the pentoxide is increased and vice versa. For P transfer into the slag, the activity of the pentoxide must be very much smaller in a low oxygen potential process, such as the blast furnace or the submerged arc furnace, than in the higher oxygen potential refining processes.\(^{(7)}\)
Figure 2.2  Comparison of the oxygen potentials at which phosphorus can transfer from the metal to slag with the oxygen potentials of various iron and steel making processes\textsuperscript{(7)}
Figure 2.2 can also be used to make other qualitative predictions. The oxygen potential lines for the oxidation of C and P intersect at a temperature which depends on the activities of the species in the metal and the slag. Phosphorus may be oxidized in preference to C at all temperatures below this intersection, whilst the converse applies at higher temperatures. Phosphorus exists in a basic slag as $P_2O_5$ or more correctly as the oxy-acid radical $PO_4^{3-}$ at $P_{O_2} > 10^{-15}$ atm. It is evident therefore, that the activity is lowered as the basicity of the slag is increased with the result that the oxygen potential line for P oxidation is lowered and the temperature range over which P is oxidized in preference to C is increased. This feature is demonstrated clearly in various basic converter processes. With the top-blown processes the lime is fluxed rapidly into slag and P can be removed prior to or along with carbon depending on the composition of the slag and temperature of the bath.

### 2.3.3 The activities of phosphorus in the metal and in the slag

Carbon, oxygen, nitrogen, silicon and sulphur raise the activity coefficient of phosphorus in liquid iron, nickel appears to have no marked effect, manganese may have little effect but chromium will cause a decrease in the value. A comparison of the stability of Ca, Mg and Mn phosphates is presented below :\(^\text{(7)}\)

$$3\text{CaO} + 2P\text{(% in Fe)} + 5O\text{(% in Fe)} \leftrightarrow 3\text{CaO}.P_2O_5$$

$$\Delta G^0 = -1 482 000 + 532T \text{ J/mol} \quad (2.24)$$

$$\Delta G^0_{(1873K)} = -496 \text{ kJ/mol} \quad (2.25)$$

$$3\text{MgO} + 2P\text{(% in Fe)} + 5O\text{(% in Fe)} \leftrightarrow 3\text{MgO}.P_2O_5$$

$$\Delta G^0 = -1 269 000 + 548T \text{ J/mol} \quad (2.26)$$

$$\Delta G^0_{(1873K)} = -242 \text{ kJ/mol} \quad (2.27)$$
The stability of calcium phosphate is markedly greater than that of the other two compounds. On this basis, it is suggested that \( a_{P_{2}O_{5}} \) is lowered to a greater extent by lime than by MgO and MnO. These equations are not strictly applicable to steelmaking or ferromanganese-smelting conditions since they apply to the formation of solid phosphate from the solid basic oxides, but the free energy differences are so large that the changes accompanying the alteration to the appropriate standard states would not alter the relative order of the effectiveness of the oxides. It is thought that FeO and MnO have very similar effects on the \( a_{P_{2}O_{5}} \).

The distribution of P between liquid iron and FeO-Na\(_2\)O-SiO\(_2\) slags is such that more than 90% of P in the metal can be transferred to the slag when the silica concentration is less than 25%. The distribution ratio is lowered progressively as the silica content of the slag is raised beyond this level. However, between 50 to 80% of P is removed from the metal into the slag which contains 35 - 40% silica and as much as 15 - 40% of P is removed with a slag containing SiO\(_2\) in the range 50 - 60%. This is very much better than the extent to which phosphorus is removed by normal steelmaking slags and particularly with the more acidic compositions. The most satisfactory explanation is that \( \gamma_{P_{2}O_{5}} \) is lowered markedly by Na\(_2\)O than by lime. However, Na\(_2\)O is reduced by molten iron to form sodium metal vapour:

\[
\text{Na}_2\text{O}(l) + \text{Fe}(l) \leftrightarrow \text{FeO}(l) + 2\text{Na}(g)
\] (2.30)

The effect of BaO addition to the slag on dephosphorisation is very similar to that resulting from Na\(_2\)O addition. Therefore, \( \gamma_{P_{2}O_{5}} \) is lowered much more than by CaO at
constant basicity, but costs prohibit the use of BaO in the bulk steelmaking processes. BaO can be used to facilitate P removal in electro-slag refining.

2.3.4 Ionic and empirical treatments of the phosphorus partitioning

A true thermodynamic treatment of the phosphorus distribution between the slag and the metal is not possible because of the non-existence of reliable free energy and activity data for the reaction. It is therefore useful to examine some of the treatments in which the equilibrium phosphorus distribution is expressed in terms of the ionic theories of liquid slags. In most treatments the reaction is written as:

\[
2P_{(\text{in Fe})} + 5O_{(\text{in Fe})} + 3O^{2-}_{\text{(slag)}} \leftrightarrow 2PO_4^{3-}_{\text{(slag)}} \tag{2.31}
\]

The equilibrium constant for reaction (2.31) is expressed in terms of the ion fractions for the species in the slag and in wt. % or mole fractions for the solutes in the metal:

\[
K_P = \frac{(PO_4^{3-})^2}{[\% \text{P}]^2[\% \text{O}]^5(O^{2-})^3} \tag{2.32}
\]

To determine \(K_P\), Flood et al\(^8\) proposed that:

\[
\log K_P = \sum N_{M^{2+}} \log K_{M^{2+}} \tag{2.33}
\]

Where, \(N_{M^{2+}}\) is the electrically equivalent ionic fraction of a basic oxide cation, and \(K_{M^{2+}}\) is the equilibrium constant for the reaction between phosphorus and the equilibrium cation of the type:

\[
2P_{(\text{in Fe})} + 5O_{(\text{in Fe})} + 3\text{CaO}_{\text{(slag)}} = 3\text{CaO}_7\text{P}_2\text{O}_5_{\text{(slag)}} \tag{2.34}
\]
2P_{(in Fe)} + 5O_{(in Fe)} + 3MgO_{(slag)} = 3MgO.P_2O_5_{(slag)} \quad (2.35)

and so on. Equilibrium constant values were obtained indirectly by fitting the equation to experimental data for the phosphorus distribution under simple slags and equation (2.36) was proposed.

\[
\log K_P = 21N_{Ca^{2+}} + 18N_{Mg^{2+}} + 13N_{Mn^{2+}} + 12N_{Fe^{2+}} \quad (2.36)
\]

Various researchers have modified this relationship to improve the fit of the curve for example Turkdogan and Pearson\(^9\) related the equilibrium constant to the mole-fraction of phosphorus pentoxide in the slag. An interesting feature of these empirical treatments is that in each case a better correlation is obtained when the phosphorus partitioning is related to the ferrous oxide content of the slag than when it is expressed in terms of oxygen content of the bulk metal. This is strong evidence in support of the contention that the oxidation of phosphorus is mainly, if not entirely, a slag-metal interface reaction.\(^7\)

### 2.3.5 Reversion of phosphorus into the metal during casting

A small amount of phosphorus maybe transferred back from the slag into the metal following the addition of deoxidizers to the metal bath. The extent of this reversion is usually greater when the metal temperature is high and/or when the basicity of the slag is low. The addition of deoxidizers lowers the metal oxygen activity both in the bulk phase and at the slag-metal interface. The increase in the rate of phosphorus reversion into the last metal in the ladle can be ascribed to two causes:

i. Firstly the activity of P_2O_5 is not a linear function of the silica concentration and hence it probably increases at a more rapid rate as the neutral composition is approached than in a highly basic slag. Thus the
rate of P reversion would increase more rapidly than the rate at which the acid oxides are dissolving from the lining into the slag.

ii. Secondly, for a constant rate of change of the equilibrium partitioning, the amount of P which reverts from the slag is proportional to the volume ratio of the metal and slag. If the volume ratio is changing more rapidly than the rate of P reversion, then it is possible that the equilibrium partitioning is approached more closely towards the end of teeming when the volume of the metal remaining in the ladle is comparatively small.

From the above considerations it is evident that the extent of phosphorus reversion is reduced as the time the metal is held in contact with the slag in the transfer ladle is lowered and as the basicity of the initial slag is raised. Phosphorus reversion is not encountered when the ladle is lined with a basic refractory.

### 2.4 Basicity in Metallurgical Slags

There are a number of ways to express basicity, most of which are weight or molar ratios of basic and acidic constituents. The V-ratio\(^{(10)}\) is defined by:

\[
V - \text{Ratio} = \frac{\sum \% \text{Metal Oxides}}{\% \text{SiO}_2} \tag{2.37}
\]

and a simplified V\(_1\) - ratio\(^{(15)}\) is defined by:

\[
V_{1} - \text{Ratio} = \frac{\% \text{CaO}}{\% \text{SiO}_2} \tag{2.38}
\]

Equation (2.38) gives a useful first approximate guide of the slag basicity. The B-ratio\(^{(10)}\) is defined by:

\[
B - \text{Ratio} = \frac{\sum \% \text{Metal Oxides}}{\% \text{SiO}_2 + \frac{1}{2} \% \text{P}_2\text{O}_5} \tag{2.39}
\]
Since most blast furnace slags tend to contain significant amounts of MgO and Al₂O₃, the basicity ratio B₁ is given by:

\[ B_1 = \frac{(\%CaO + \%MgO)}{(\%SiO_2 + \%Al_2O_3)} \]  

(2.40)

Basicity ratio B₁ has found some application in industrial practice. Bell et al.⁶ suggested a modified B - ratio (B₂) given by:

\[ B_2 = \frac{\left(X_{CaO} + 0.5X_{MgO}\right)}{\left(X_{SiO_2} + 0.33X_{Al_2O_3}\right)} \]  

(2.41)

Where, X is the mole fraction of the component concerned. When expressed in terms of wt. % of each oxide, the basicity ratio B₂ becomes:

\[ B_3 = \frac{(\%CaO + 0.7\%MgO)}{(0.94\%SiO_2 + 0.18\%Al_2O_3)} \]  

(2.42)

Basicity ratio B₃, has proved a useful measure of basicity for blast furnace type slags. The other approach adopted has been the use of Excess Base expressions of the form:

Excess Base = \( \sum \) basic oxides – \( \sum \) acidic oxides  

(2.43)

Where, the concentration units can be wt. %, mole %, or mole fraction.

Many investigators have espoused the use of the oxygen ion (O²⁻) concentration in a liquid oxide as a measure of basicity because of the ionic character of liquid oxides and slags. According to J. F. Elliott⁵ the concept is attractive because one may write:
(O²⁻) + Al₂O₃(s) ⇌ 2(AlO²⁻) \hspace{1cm} (2.44)

As an acidic reaction because it consumes oxygen ions and conversely:

Al₂O₃(s) ⇌ 2(AlO⁺) + (O²⁻) \hspace{1cm} (2.45)

as a basic reaction because it produces oxygen ions. In equation (2.44) alumina is acting as an acid, and in equation (2.45) as a base. Other examples of such reactions are:

(Na₂O) + Al₂O₃(S) ⇌ 2(NaAlO₂) \hspace{1cm} (2.46)

and

3(Na₂SO₄) + Al₂O₃(s) ⇌ 3(Na₂O) + (Al₂(SO₄)₃) \hspace{1cm} (2.47)

2.4.1 The optical basicity concept

An alternate approach to basicity ratios is the use of Optical Basicity (\(\Lambda\)) which was developed by Duffy and Ingram\(^{17}\). In this approach, basicities are regarded in terms of the electron donor power of the oxygen ions present. Duffy and Ingram discovered that the optical basicity of an oxide (\(\Lambda\)) is related to the Pauling electronegativity (\(x\)) of the cation involved by the expression:

\[\Lambda = 0.74/(x - 0.26)\] \hspace{1cm} (2.48)

Use of this relation allows calculation of the optical basicity for any main group element oxide in a slag. Hence by the use of the relationship:

\[\Lambda = X_A\Lambda_A + X_B\Lambda_B + X_C\Lambda_C + \ldots\ldots\] \hspace{1cm} (2.49)
it is possible to calculate the bulk or average value of $\Lambda$ for a slag of any composition involving these oxides. In equation (2.49) $X$ is the equivalent cation fraction, based on the fraction of negative charge “neutralized” by the charge on the cation concerned. The calculation of $X$ is given in Appendix F. Using this concept Sommerville and Sosinsky$^{(15)}$ were able to establish a correlation relationship between optical basicity of slags and their sulphide capacities at 1500°C given by:

$$\log C_S = 12.6\Lambda - 12.3$$

(2.50)

This relationship permits the calculation of sulphide capacities of a large number of slag systems at 1500°C, including both ironmaking and steelmaking slags. Thus where the oxygen potential is known, the distribution of sulphur between these slags and either iron or steel can be calculated.

2.4.2 Effect of slag basicity

In order to measure and compare the action of various oxides in silicate melts, the modern day slag theory proposes the disintegration of the silica network and the formation of a number of different anionic groups. The extent to which this phenomenon happens has been shown to be dependent upon the free energy of interaction between the metal oxide and silica. At metasilicate composition, the network may not be modified significantly due to the lower free energy of formation of MgSiO$_3$ and CaSiO$_3$ than those of Mg$_2$SiO$_4$ and Ca$_2$SiO$_4$ respectively. This results in a less disrupted silica network. When the free energy of formation of orthosilicates Ca$_2$SiO$_4$, Mg$_2$SiO$_4$ and CaMgSiO$_4$ are taken into consideration, it can be seen that Ca$_2$SiO$_4$ has the most negative free energy of formation. Furthermore, the free energy of formation of CaMgSiO$_4$ is more negative than that of Mg$_2$SiO$_4$. This means that the interaction of Ca$^{2+}$ with SiO$_2$ is stronger than that of mixed Ca$^{2+}$ and Mg$^{2+}$ ions and individual Mg$^{2+}$ ions. Thus, one can conclude that an increase in the amount of
CaO can lead to an increased tendency for the formation of $\text{Ca}_2\text{SiO}_4$, orthosilicate, leading to higher MnO activities in the slags. Because of the interaction of $\text{Ca}^{2+}$ ions with silica, $\text{Mn}^{2+}$ ions gain more freedom that is they become less associated with the silica network and therefore the MnO activities increase. This is explained as follows, at low basicities almost all the metal cations, viz $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Mn}^{2+}$ are associated with the large silicate anionic groups and only very few $\text{O}^2-$ ion exist. Thus at low basicities, the silica network is not disrupted and the activity of MnO in such melts is low. As the concentration of basic oxides increases, the silica network is broken up into smaller anionic groups which result in lower slag viscosity and the proportion of free oxygen ions increases. An equal number of divalent cations associated with silicate anions, now associate with free oxygen anions. Because of their higher interactions with silicate ions divalent cations like $\text{Ca}^{2+}$, $\text{Mg}^{2+}$ are preferentially associated with silicate ions, and thus $\text{Mn}^{2+}$ ions will have a less degree of association with silicate ions. The free energy of formation of $\text{MnSiO}_3$ is less negative than that of $\text{MgSiO}_3$ and $\text{CaSiO}_3$. Thus, $\text{Mn}^{2+}$ ions cannot overcome the interaction between these metal cations and silicate ions, and therefore an increase in basicity increases the MnO activities in the slag. Also at high slag basicity, the slag liquidus temperature tends to increase, which would also result in an increase in MnO activity.\(^{(18,19,37)}\)

### 2.5 Evaluation of Slag-Metal Equilibrium

#### 2.5.1 Oxygen equilibrium

The theoretical oxygen potential values at the slag-metal interface can be obtained from several reactions as given below\(^{(20)}\):

$$\text{[Si]} + 2[\text{O}] \leftrightarrow \text{SiO}_2(\text{S})$$ (2.51)
\[
\log \left( \frac{[a_O]^2 [a_{Si}]}{[a_{SiO_2}]} \right) = -\frac{31040}{T} + 12.0
\]  
(2.52)

\[
[Mn] + [O] \leftrightarrow MnO_{(S)}
\]  
(2.53)

\[
\log \left( \frac{[a_O] [a_{Mn}]}{[a_{MnO}]} \right) = -\frac{15050}{T} + 6.7
\]  
(2.54)

\[
Fe_{(l)} + [O] \leftrightarrow FeO_{(l)}
\]  
(2.55)

\[
\log \left( \frac{[a_O] [a_{Fe}]}{[a_{FeO}]} \right) = -\frac{6320}{T} + 2.73
\]  
(2.56)

The selected values of the equilibrium constants for the reactions are taken from Riboud and Olette\(^{(21)}\). In order to compute the equilibrium oxygen potentials of each of these reactions, it is necessary to evaluate the activities of dissolved elements in the metal phase and the activities of oxides in the slag.

### 2.5.2 Activities of metal phase components

The activities of components in the metal phase are evaluated using the formalism of interaction coefficients given by:\(^{(20)}\)

\[
\log a_i = \log(\%i) + \sum_j e_i^j * (\%j) + ...
\]  
(2.57)

The values of interaction coefficients \(e_i^j\) can be obtained from data compiled by Sigworth and Elliott\(^{(22)}\) and Jacquemot et al\(^{(23)}\).
2.5.3 Activities of oxides in the slag

In order to compute oxide activities in the slag, a statistical thermodynamics model developed by Gaye and Welfringer\(^{(24)}\) can be used. The model describes the thermodynamic properties of the slag in terms of a few binary parameters (2 to 3 per binary system) and has been shown to adequately represent the phase diagrams and oxide activities of silicate systems over a wide composition range from basic to acidic slags (silica saturation). The model provides the phase diagram in addition to liquid phase activities, so that for heterogeneous slags, it computes the actual liquid phase composition and the proportions of solids.

2.6 Slag Systems for Dephosphorisation

2.6.1 The distribution of phosphorus between Na\(_2\)O-SiO\(_2\)-PO\(_{2.5}\) melts and carbon saturated iron\(^{(11)}\)

Tsukihashi et al.\(^{(11)}\) studied the distribution of phosphorus between Na\(_2\)O-SiO\(_2\) melts and carbon-saturated iron. The slag system Na\(_2\)O-SiO\(_2\) is used in steel refining to remove phosphorus and other impurities. The main features of pretreatment by soda ash are high refining capability, lower losses of Mn, Fe, and C and the simultaneous removal of P and S amongst others. Carbon-saturated iron with lead-sodium alloy was equilibrated with Na\(_2\)O-SiO\(_2\)-PO\(_{2.5}\) in a graphite crucible under carbon monoxide atmosphere. The sodium potential was fixed with sodium in the lead. Most of the experiments were carried out at 1200°C but the temperature dependency of the distribution ratio was measured at 1200°C, 1250°C, 1300°C and 1350°C. The Na\(_2\)O content in the slag was varied from 40% to 65% containing PO\(_{2.5}\) of 5% to 25%. The phosphorus distribution ratio between carbon-saturated iron and Na\(_2\)O-SiO\(_2\)-PO\(_{2.5}\) was measured as a function of basicity.
Figure 2.3 shows the phosphorus distribution ratio between the carbon-saturated iron and Na$_2$O-SiO$_2$-PO$_{2.5}$ slag as a function of $X_{Na_{2}O}/(X_{SiO_{2}} + X_{PO_{2.5}})$, which is used as an index of basicity, where $X_i$ is the mole fraction of species $i$. It can be noted that the distribution ratio of P increases with increasing basicity $X_{Na_{2}O}/(X_{SiO_{2}} + X_{PO_{2.5}})$. Interestingly, the distribution ratio of P was independent of the initial concentration of PO$_{2.5}$ in the slag.

Under these experimental conditions, the dephosphorisation reaction was expressed by reaction (2.58) as:

$$[P] + \frac{5}{4}O_2 + \frac{3}{2}O^{2-} \leftrightarrow PO_4^{3-} \quad (2.58)$$

To compare the dephosphorisation capacities of soda slags with those of other flux systems, the slag phosphate capacity was defined by equation (2.59) as:

$$C_{PO_4^{3-}} = \frac{\%PO_4^{3-}}{P_2^{1/2}O_2^{5/4}} = \frac{a_{O^{2-}}^{3/2}K}{f_{PO_4^{3-}}} \quad (2.59)$$

The $\%PO_4^{3-}$ was obtained by chemical analysis of the slag. The $Po_2$ was calculated following reaction (2.60) and was $8.42 \times 10^{-18}$ atm at 1200°C.

$$Cs + 1/2O_2(g) \leftrightarrow CO(g) \quad (2.60)$$

$$\Delta G^o = -27340 - 20.50T \text{ cal/mole} \quad (2.61)$$

The partial pressure of phosphorus ($Pp_2$) was obtained following reaction (2.62).
\[
\frac{1}{2}P_2 = [\%P] 
\] (2.62)

\[
\Delta G^\circ = -29,200 - 4.6T \text{ cal/mole} 
\] (2.63)

The phosphate capacities calculated according to equation (2.59) and shown in Figure 2.4 were used to compare the dephosphorisation capacity of soda slag with those of other flux systems. The calculated phosphate capacities varied from $10^{26}$ to $10^{29}$. As shown in Figure 2.4, it is obvious that the soda slag system has a far higher dephosphorisation capacity than CaO based fluxes. The distribution ratios of P between the slag and metal increased with increasing the slag basicity. Tsukihashi et al\(^{(11)}\) concluded that the low FeO content and low temperature accounted for the high phosphate capacity in this system.
Figure 2.3  The relationship between phosphorus distribution ratio and slag basicity $X_{Na,O}/(X_{SiO_2} + X_{PO_4})$ at $1200^\circ C^{(11)}$
Figure 2.4 A comparison of phosphate capacities of various systems\(^{(11)}\)
2.6.2 Thermodynamics of phosphate and phosphide in CaO-CaF$_2$ melts$^{(13)}$

A new dephosphorisation technique under reducing conditions was proposed using CaO-CaF$_2$ or CaC-CaF$_2$ fluxes. Tabuchi and Sano$^{(13)}$ investigated the thermodynamics of phosphate and phosphide ions in CaO-CaF$_2$ melts under strongly reducing conditions by equilibrating the melts with Ag-P alloys. The investigations were carried out between 1400°C and 1550°C in a graphite boat under CO-Ar gas mixture. After equilibration, the samples were quickly cooled in argon stream and were immediately supplied for chemical analysis to avoid the oxidation of phosphide ion during the treatment.

Under conventional oxidizing conditions, the dephosphorisation reaction can be expressed by reaction (2.64), showing equilibrium between the slag and gas phase:

$$\frac{1}{2}P_2(g) + \frac{3}{2}O^{2-} + \frac{5}{4}O_2(g) \leftrightarrow PO_4^{3-}$$

(2.64)

However, under strongly reducing conditions as in ferromanganese smelting, phosphorous behaves as phosphide ions as follows:

$$\frac{1}{2}P_2(g) + \frac{3}{2}O^{2-} \leftrightarrow P^{3+} + \frac{3}{4}O_2(g)$$

(2.65)

Although the thermodynamic functions for the reactions as formulated above cannot be evaluated because activity coefficients of an individual ion can not be determined experimentally, expressions in terms of ions rather than molecules were used for convenience of theoretical discussions. According to reactions (2.64) and (2.65), the concentrations of phosphate and phosphide ions depend on the partial pressures of phosphorous and oxygen, the slag composition and temperature.

The $Pp_2$ in their system was given by:
\[
\frac{1}{2} \text{P}_2 \leftrightarrow [\text{P}]_{\text{in liquid silver}} \tag{2.66}
\]

\[
\Delta G^o = -RT \ln \left( \frac{a_{P}^{Ag}}{P_{P_2}^{1/2}} \right) = -RT \ln K_{2.66} \tag{2.67}
\]

Where,

\[
\Delta G^o = 15 000 + 3.87T \text{ J/mol.} \tag{2.68}
\]

Since the concentration of P in silver was below 0.2 wt. %, Henry’s law was applicable. Hence, \( P_{P_2} \) can be expressed by reaction (2.69):

\[
\ln P_{P_2} = \frac{2}{RT} \left( \Delta G^o + RT \ln X_{P}^{Ag} \right) \tag{2.69}
\]

Where, \( X_{P}^{Ag} \) is the mole fraction of P in Ag. The \( P_{O_2} \) was calculated according to the following reaction:

\[
\text{C}(s) + \frac{1}{2}\text{O}_2(g) = \text{CO}(g) \tag{2.70}
\]

Where,

\[
\Delta G^o = -112 000 - 87.6T \text{ J/mol,} \tag{2.71}
\]

Because graphite was used as a crucible in this study, \( a_C = 1 \). As the ratio \( \text{CO}/(\text{CO} + \text{Ar}) \) varies from 1.0 to 0.2, the \( P_{O_2} \) decreases from \( 1.82 \times 10^{-16} \text{ atm} \) to \( 7.24 \times 10^{-18} \text{ atm} \) at 1500°C.
The equilibrium constants for reactions (2.64) and (2.65) are expressed by the following equations, respectively:

\[
K_{2.64} = \frac{f_{PO_4^{3-}}(\%PO_4^{3-})}{P_{P_2}^{1/2}P_{O_2}^{5/4}a_{O_2}^{3/2}}
\]  

(2.72)

\[
K_{2.65} = \frac{f_{P^{3-}}(\%P^{3-})P_{O_2}^{3/4}}{P_{P_2}^{1/2}a_{O_2}^{3/2}}
\]  

(2.73)

Where, \( f_{PO_4^{3-}} \) and \( f_{P^{3-}} \) are the activity coefficients of phosphate and phosphide ions respectively. The dependence of dephosphorisation reactions (2.64) and (2.65) on \( P_{O_2} \) is given by:

\[
\log \left( \frac{\%PO_4^{3-}}{P_{P_2}^{1/2}} \right) = \frac{5}{4} \log P_{O_2} + \log \frac{K_{2.64}a_{O_2}^{3/2}}{f_{PO_4^{3-}}}
\]  

(2.74)

\[
\log \left( \frac{\%P^{3-}}{P_{P_2}^{1/2}} \right) = -\frac{3}{4} \log P_{O_2} + \log \frac{K_{2.65}a_{O_2}^{3/2}}{f_{P^{3-}}}
\]  

(2.75)

it was shown that \( (\%PO_4^{3-})/(P_{P_2}^{1/2}) \) increases with \( P_{O_2} \) and the slope is 1.37 and \( (\%P^{3-})/(P_{P_2}^{1/2}) \) decreases with increasing \( P_{O_2} \) and the slope is -0.72 as shown in Figure 2.5.

The slag phosphate capacity and phosphide capacity are defined by the following equations respectively:
These equations are shown in Figure 2.6 with the variation of (wt. %CaO) at 1500°C with Po$_2$ = 4.57x10$^{-17}$ atm. Both phosphate capacity and phosphide capacity increase with increasing CaO concentration and beyond about 20 wt. %CaO in CaF$_2$ at 1500°C they become constant:

\[
\log C_{PO_4^{3-}} = 22.04, \quad \log C_{P^{3-}} = -11.4
\]

The exchange reaction between PO$_4^{3-}$ and P$_3$- is expressed by:

\[
P^3- + 2O_2 \leftrightarrow PO_4^{3-} \quad (2.78)
\]

In addition, the ratio of (%PO$_4^{3-}$) and (%P$_3$-) is given by:

\[
\frac{(%PO_4^{3-})}{(%P^{3-})} = K_{2.78} P_2^2 \frac{f_{P^{3-}}}{f_{PO_4^{3-}}} \quad (2.79)
\]

Therefore, this ratio should be independent of slag composition, only if the ratio $f_{P^{3-}}/f_{PO_4^{3-}}$ does not change.

Figure 2.7\(^{(13)}\) shows the stability of phosphate and phosphide ions for the CaO-CaF$_2$ system saturated with CaO as a function of log Po$_2$. Figure 2.7 shows that as
temperature increases, the critical partial pressure of O$_2$ for the stability of $P^{3-}$ ions increases eg when temperature increases from 1400$^\circ$C to 1500$^\circ$C, the critical partial pressure of oxygen increases from $1.4\times10^{-18}$ atm. to $1.1\times10^{-16}$ atm. Hence with these results Tabuchi and Sano$^{(13)}$ were able to demonstrate the dependence of phosphate and phosphide concentrations in slag melts on the P$\text{p}_2$, P$\text{O}_2$, slag composition and temperature confirming the validity of reactions (2.64) and (2.65).
Figure 2.5  \( \frac{\%PO_3^-}{(P_{O_2}^{1/2})} \) and \( \frac{\%P^3^-}{(P_{O_2}^{1/2})} \) in the CaO\textsubscript{(sat)}-CaF\textsubscript{2} melt as a function of Log Po\textsubscript{2}\textsuperscript{(13)}
Figure 2.6 Phosphate and phosphide capacities against wt. % CaO for the CaO-CaF$_2$ system$^{(13)}$
Figure 2.7  Stability of phosphate and phosphide ions for the CaO-CaF$_2$ system saturated with CaO as a function of log $P$O$_2$\textsuperscript{(13)}
2.6.3 Dephosphorisation equilibria between liquid iron and highly basic CaO-based slags saturated with MgO\(^{25}\)

Ishii and Fruehan\(^{25}\) studied dephosphorisation equilibrium between liquid iron and highly basic CaO-based slags saturated with MgO. Their objective was to examine the ability to remove P using highly basic slags, CaO-MgO\(_{\text{sat}}\)-SiO\(_2\)-Al\(_2\)O\(_3\)-FeO\(_n\) and CaO-MgO\(_{\text{sat}}\)-SiO\(_2\)-FeO\(_n\) by measuring the P distribution ratio between the slag and the metal and determining the phosphate capacities of the slags. The correlation between the phosphate capacity of the slags with the theoretical optical basicity was made in order to determine the effect of Al\(_2\)O\(_3\) and CaF\(_2\) additions on dephosphorisation equilibria. The dephosphorisation reaction between the liquid iron and slag can be represented by:

\[
\frac{5}{2}(\text{FeO}) + [\text{P}] \leftrightarrow (\text{PO}_{2.5}) + \frac{5}{2}\text{Fe} \quad (2.80)
\]

The phosphorous distribution ratio between the slag and metal phases at equilibrium is commonly used, and is defined as:

\[
L_P = \frac{\%\text{P}}{\%\text{P}} \quad (2.81)
\]

However, the \(L_P\) ratio depends on the oxygen potential, which limits the comparison to systems that have the same oxygen potential. The phosphate capacity \(C_{PO_4^{3-}}\) takes into account the oxygen potential. Thus, it can be used to compare different slag systems and is defined by reactions (2.82) and equation (2.83):

\[
\frac{1}{2}\text{P}_2(\text{g}) + \frac{5}{4}\text{O}_2(\text{g}) + \frac{3}{2}(\text{O}^2-) \leftrightarrow (\text{PO}_4^{3-}) \quad (2.82)
\]

\[
C_{PO_4^{3-}} = \frac{\%\text{PO}_4^{3-}}{\frac{\text{P}_{\text{g}}^{1/2}}{\text{P}_{\text{O}_2}^{3/4}} f_{\text{PO}_4^{3-}}} = K_{2.82} \left(\frac{a_{\text{O}^{2-}}}{f_{\text{PO}_4^{3-}}}\right)^{3/2} \quad (2.83)
\]
Where:
i. \( \% PO_{4}^{3-} \) = wt. % of \( PO_{4}^{3-} \) dissolved in the slag

ii. \( Pp_{2} \) = \( P_{2} \) partial pressure in equilibrium with [P] in liquid iron

iii. \( Po_{2} \) = \( O_{2} \) partial pressure at the slag-metal interface

The \( Pp_{2} \) can be evaluated from the P content in the metal and the available thermodynamic data for reaction (2.84):

\[
\frac{1}{2}P_{2}(g) \leftrightarrow [P](1 \text{ wt. } \% \text{ in liquid } Fe) \tag{2.84}
\]

\[
\Delta G^{0} = 122\ 056 - 19.23T \text{ J/mole}^{(25, 26)} \tag{2.85}
\]

\[
K_{2.84} = \frac{f_{p}[\% P]}{P_{P}^{1/2}} \tag{2.86}
\]

Where:
i. [\% P] = wt. % P in the liquid iron

ii. \( f_{p} \) = activity coefficient of P in 1 wt % standard state

The \( C_{PO_{4}^{3-}} \) can be related to the \( L_{P} \) at 1600°C as given by equation (2.87) below:

\[
(C_{PO_{4}^{3-}}) = 7.92 \times 10^{4} \left\{ L_{p}/P_{O_{2}}^{5/4} \right\} \tag{2.87}
\]

The partial pressure of oxygen (\( Po_{2} \)) can be calculated from the free energy of formation of \( FeO \) and the activity of \( FeO \) in the slag:

\[
Fe_{(l)} + 1/2O_{2} \leftrightarrow FeO_{n(l)} \tag{2.88}
\]

\[
\Delta G^{0} = -234\ 620 + 46.9T \text{ J/mole}^{(25, 26)} \tag{2.89}
\]
\[ K_{2.88} = a_{FeO_n}/P^{1/2}_{O_2} \]  \hspace{1cm} (2.90)

Where:

i. \( a_{FeO_n} \) = activity of FeO\(_n\) in the slag

ii. \( n = \) value between 1.0 and 1.5

The activity of FeO\(_n\) in the slag is derived from experimental data for oxygen dissolved in iron [%O] using the relation given by Taylor and Chipman \((27)\):

\[ a_{FeO_n} = a_O/a_{O_{sat}} = f_O[\%O]/f_{O_{sat}}[\%O]_{sat} \]  \hspace{1cm} (2.91)

Where:

i. \( \log f_o = (-1,750/T + 0.76)[\%O] + 0.006[\%P] \)  \hspace{1cm} (2.92)

ii. \( \log f_{o(sat)} = (-1,750/T + 0.76)[\%O]_{sat} \)  \hspace{1cm} (2.93)

iii. \( \log [\%O]_{(sat)} = 6,320/T + 2.734 \)  \hspace{1cm} (2.94)

Where, \( a_o, f_o\) and \( [\%O] \) are the activity, activity coefficient and wt. % of the oxygen in the liquid iron, respectively.

Ishii and Fruehan \((25)\) established that, highly basic CaO-MgO\(_{sat}\)-SiO\(_2\)-Al\(_2\)O\(_3\)-FeO\(_n\) slags saturated with MgO are excellent dephosphorizers as shown in Figure 2.8. The \( L_p \) ratio increased with increasing FeO\(_n\) content, following the liquidus line. For slags expected for ladle dephosphorisation, values of \( L_p > 500 \) are possible. Maximum ratios were observed at about 45 wt. % FeO\(_n\) (X\(_{FeO_n} = 0.37\)) and with Al\(_2\)O\(_3\) contents tending to zero. The oxygen content increases with FeO\(_n\) content and decreases with
decreasing temperature. For CaO-MgO<sub>sat</sub>-SiO<sub>2</sub>-FeO<sub>n</sub>, slags average values of log <i>C<sub>PO<sub>n</sub></sub></i> were 19.7 at 1570°C and 19.3 at 1600°C.

The activity of FeO<sub>n</sub> in these systems is close to ideal and a high FeO<sub>n</sub> activity favours dephosphorisation of steel. Figure 2.9 shows the relationship between the logarithm of phosphate capacity (log <i>C<sub>PO<sub>n</sub></sub></i>) and <i>X<sub>FeO</sub></i>. It is clear that <i>C<sub>PO<sub>n</sub></sub></i> for CaO-MgO<sub>sat</sub>-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>n</sub> slags is relatively high, the magnitude of which is almost the same as that of CaO saturated CaO-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>n</sub> slags obtained by Wrampelmeyer et al.\textsuperscript{(28)} <i>C<sub>PO<sub>n</sub></sub></i> also increases with decreasing temperature at the same <i>X<sub>FeO</sub></i>. For CaO-MgO<sub>sat</sub>-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-FeO<sub>n</sub> slags, the average values of log <i>C<sub>PO<sub>n</sub></sub></i> are 19.4 at 1570°C and 19.0 at 1600°C.

In Figure 2.10 Mori’s\textsuperscript{(29)} correlation as given by equations (2.95) and (2.96) for CaO-based slag saturated with MgO is shown by the lines along with the data of Ishii and Fruehan\textsuperscript{(25)}, Wrampelmeyer et al\textsuperscript{(28)} (<i>C</i> = 5.00) and Bany et al\textsuperscript{(30)} (<i>C</i> = 4.62):

\[
\log C_{PO_n} = 19.05 \Lambda + C 
\]  
\text{(2.95)}

\[
C = 4.75 + (1/2) \{ \log \sum (\% i/\mu_i) + \log(\% P_2O_5) \} 
\]  
\text{(2.96)}

Where, (%<i>i</i>) and \mu<sub>i</sub> are the wt. % of component <i>i</i> in the slag and molecular wt. of component <i>i</i>, respectively and \Lambda is the optical basicity.

The correlation of the phosphate capacity with the theoretical optical basicity indicates that Al<sub>2</sub>O<sub>3</sub> decreases the phosphate capacity more than expected for <i>X<sub>Al,O</sub></i> greater than 0.05. Therefore, Al<sub>2</sub>O<sub>3</sub> acts more as an acidic component than expected in the case of dephosphorisation of liquid iron when using these highly basic slags.
Calcium fluoride is added to steelmaking slags to increase the solubility of CaO and to improve the kinetics of desulphurisation and dephosphorisation. For CaO-MgO\textsubscript{sat}-SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}-FeO\textsubscript{n} slags with constant CaO, replacing Al\textsubscript{2}O\textsubscript{3} with 3 wt. % CaF\textsubscript{2}, Lp increases and $\log C_{PO_4^{3-}}$ increases from 19.0 to 19.3, whereas replacing CaO with 3 wt. % CaF\textsubscript{2} for constant Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} content decreases $\log C_{PO_4^{3-}}$ to 18.7 at 1600$^\circ$C. For CaO-MgO\textsubscript{sat}-SiO\textsubscript{2}-FeO\textsubscript{n} slags, Lp slightly decreases when replacing CaO with CaF\textsubscript{2}. The correlation between the theoretical optical basicity and the phosphate capacity shows that CaF\textsubscript{2} acts as a chemically non-participating diluent in these highly basic slags.\textsuperscript{(31)} Using these fluxes for ladle dephosphorisation can produce steels with less than 30 ppm of phosphorus.
Figure 2.8 Phosphorus distribution ratios as a function of wt. % (FeO<sub>n</sub>)<sup>(25)</sup>
Figure 2.9  The relationship between $(\log C_{\text{Fe}^3+})$ and mole fraction of FeO$_n$ $(X_{\text{FeO}_n})^{(25)}$
Figure 2.10  Relation between the optical basicity, $A$ and $\log C_{Po'}$ for highly basic slags at 1600°C$^{(25)}$
2.6.4 Fluospar Slags used in ferrous ladle metallurgy

Fluoride addition to slags is made primarily to lower the liquidus temperature and the viscosity of the slag. The fluoride ions in the slag react with silica and alumina in the slag and water vapour in the furnace atmosphere to form volatile fluorides SiF₄, AlF₃, HF, including the vapour species CaF₂. Turkdogan(32) showed that CaF₂ has only a small effect on the sulphide capacity (Cₛ) of the aluminate slag. However, CaF₂ fluxes both CaS and CaO, therefore, an addition of 5-10% CaF₂ to the injected burnt lime would curtail the coating of lime particles with a layer of CaS, and hence improves the efficiency of lime usage in the ladle desulphurisation. The major role of CaF₂, in the slag is to lower the liquidus temperature and lower the viscosity of the slag for use at hot metal temperatures. The highest distribution ratio of (%P)/[%P] attainable was with lime-saturated slags containing 15-25% FeOₙ and low concentrations of SiO₂ and Al₂O₃. At sufficiently low Po₂, phosphorus dissolves in molten slags and fluxes as a phosphide ion given by reaction (2.97):

\[
[P] + 3/2(O^{2-}) \leftrightarrow 3/2[O] + (P^{3-})
\]  

for which the phosphide capacity Cₚ⁻, of the slag is represented by:

\[
C_{p^-} = \frac{(%P)[a_O]^{1.5}}{[%P]}
\]

Tabuchi and Sano(13) have shown that the transition from the phosphide to phosphate reaction at 1550°C occurs at about 10⁻¹⁸ atm Po₂ for the calcium aluminate based slag and at about 10⁻¹⁶ atm Po₂ for the lime-saturated CaO-CaF₂ based slag. For the lime saturated CaO-CaF₂ based slag, a value of Cₚ⁻ = 3.76x10⁻¹¹ was obtained from the data of Tabuchi and Sano at 1500°C. These data give for the sulphide-phosphide coupled reaction:
\[ [P] + \frac{3}{2}(S^{2-}) \leftrightarrow \frac{3}{2}[S] + (P^{3-}) \quad (2.99) \]

The equilibrium relation is:

\[
\frac{(%P)/[\%P]}{(%S)/[\%S]} = 3 \times 10^{-10} \left\{ \frac{(%S)/[\%S]}{3/2} \right\}^{3/2} \quad (2.100)
\]

Equation (2.100) indicates that the oxide slags have a negligibly small capacity for the phosphide ion in relation to the sulphide ion.

An assessment of the gas-slag-metal equilibrium data shows that CaF$_2$ has little or no effect on the sulphide and phosphate capacities of slags. The primary role of CaF$_2$ is to lower the fusion temperature of lime-based slags suitable for hot-metal refining at relatively low temperature necessary for dephosphorisation.

### 2.7 Determination of Phosphide Capacities in Smelting Slags

In processes such as the electric arc and LD converters the atmosphere above the melt is free from phosphorus bearing combustion gases. This should encourage a continuous transfer of phosphorus from liquid slag to the atmosphere. However, indications are that, the overall rate of phosphorus loss to the atmosphere is low and the phosphorus content of the metal phase is determined primarily by partitioning between the slag and metal phases. The rate of transfer of phosphorus between the slag and metal phases is directly proportional to the area of the slag-metal interface.

The control of phosphorus content in the metal phase is considered in terms of:

i) Partitioning between the gaseous compounds containing phosphorus and phosphorus in solution at the gas-slag interface and

ii) Partitioning of phosphorus between the slag and metal phases at the slag-metal interface.
Phosphorus may be present in a slag as either $\text{P}^{3-}$ or $\text{PO}_4^{3-}$ ions. The phosphide form is only stable at very low oxygen partial pressures ($\text{Po}_2$) of less than $10^{-15}$ atm depending on the composition of the slag. Different authors ascribe different values for the transition point of phosphate ions ($\text{PO}_4^{3-}$) to phosphide ions ($\text{P}^{3-}$), ranging from $10^{-18}$ to $10^{-15}$ atm depending on the slag composition they worked with. When $\text{Po}_2$ is greater than $10^{-15}$ atm, $\text{PO}_4^{3-}$ ions become stable.$^{(10)}$

Figure 2.11$^{(12)}$ shows results from a study by Tabuchi and Momokawa$^{(12)}$, which showed that the partial pressure of oxygen for the transition from the phosphide to the phosphate ion is about $2.5 \times 10^{-18}$ atm for calcium aluminate slag at $1550^\circ \text{C}$ and \text{Pp} = $2.4 \times 10^{-3}$ atm.
Figure 2.11  Phosphide-phosphate solubilities in a calcium aluminate slag$^{(12)}$
2.7.1 Equilibrium considerations

The partitioning of phosphorus between the slag and metal phases can be considered in terms of three simultaneous reactions:

\[
M_3P_2[^{\text{metal}}] \leftrightarrow M_3P_2[^{\text{slag}}] \tag{2.101}
\]

\[
M_3P_2[^{\text{slag}}] + 3\text{CaO}[^{\text{slag}}] \leftrightarrow \text{Ca}_3\text{P}_2[^{\text{slag}}] + 3\text{MO}[^{\text{slag}}] \tag{2.102}
\]

\[
\text{MO}[^{\text{slag}}] + X[^{\text{metal}}] \leftrightarrow M[^{\text{metal}}] + XO[^{\text{slag or gas}}] \tag{2.103}
\]

Where M can be Fe, Mn or Si and X can be Al, C, Mn or Si which combines with the oxygen dissolved in the metal phase. Treatment of partitioning in this way suffers from the disadvantage that only lime is considered to take part in stabilizing the phosphorus in the slag and the process is not clear.

A more satisfactory interpretation is obtained when reactions are expressed in the ionic form that is:

\[
P[^{\text{metal}}] + 3e^- \leftrightarrow P^{3^-}[^{\text{slag}}] \tag{2.104}
\]

To maintain electro-neutrality, a simultaneous transfer is required across the interface of an element that releases electron charges as it enters the slag phase such as:

\[
3/2\text{Fe}[^{\text{metal}}] \leftrightarrow 3/2\text{Fe}^{2+}[^{\text{slag}}] + 3e^- \tag{2.105}
\]

Similarly Si and Al release electron charges when crossing into the slag phase. Alternatively the electrons absorbed by the P cation can be regarded as transferred...
from $O^{2-}$ ions which cross the interface into the metal to take part in the normal oxidation reactions given by equation (2.103) above such that:

$$P\text{(metal)} + 3/2O^{2-}\text{(slag)} \leftrightarrow 3/2O\text{(metal)} + P^{3-}\text{(slag)}$$  \hspace{1cm} (2.106)

$$K_p = \frac{(a_{p^{3-}})[a_{O^{2-}}]^{3/2}}{(a_{O^{2-}})^{3/2}[a_p]}$$  \hspace{1cm} (2.107)

Partitioning between the slag and metal phases at a given temperature is raised by increasing either basicity of the slag or the activity of phosphorus in the metal or by lowering the activity of oxygen in the metal. Equilibrium phosphorus partitioning between the slag and metal phases is given by:

$$L_p = \frac{(\% P)}{[\% P]}$$  \hspace{1cm} (2.108)

Where, $L_p$ is the equilibrium phosphorus distribution ratio.

The partitioning of P between the slag and the furnace gases (atmosphere) can be considered in terms of the following equilibrium reaction:

$$1/2P_2\text{(gas)} + 3/2O^{2-}\text{(slag)} \leftrightarrow P^{3-}\text{(slag)} + 3/4O_2\text{(gas)}$$  \hspace{1cm} (2.109)

The equilibrium constant of reaction (2.109) is given by:

$$K_{2.109} = \frac{(a_{p^{3-}})P_{O_2}^{3/4}}{P_{P_2}^{1/2}(a_{O^{2-}})^{3/2}}$$  \hspace{1cm} (2.110)
Where, \( C_{P^{3-}} \) is the slag phosphide capacity.

The slag phosphide capacity \( (C_{P^{3-}}) \), as the terminology implies, is a measure of the extent to which a slag can hold phosphorus in solution. It is tempting to assume that phosphorus partitioning between the slag and metal phases will also increase with an increase in \( C_{P^{3-}} \) but equation (2.107) shows that other terms are involved in determining the partitioning. The \( C_{P^{3-}} \) does not take into account the effect of various components of the slag on the activities of P and O ions. Stated differently equation (2.111) shows the reactivity of the slag to phosphorus in the atmosphere above the slag. The exchange of P between the charge and furnace gases can give rise to considerable error in the P mass balance calculation.

The significance of the slag phosphide capacity \( (C_{P^{3-}}) \) with respect to P partitioning between the slag and metal is seen by combining reaction (2.109) with P distribution reaction (2.112) to give reaction (2.113).

\[
\begin{align*}
P_{\text{metal}} + 3e^- & \leftrightarrow P^{3-}_{\text{slag}} \quad (2.112) \\
\frac{K_{2.109}(a_{O^{2-}})^{3/2}}{(f_{P^{3-}})} &= \frac{(\%P^{3-})P^{3/4}_{O_2}}{P^{1/2}_{P_2}} = C_{P^{3-}}
\end{align*}
\]

The exchange of P between the charge and furnace gases can give rise to considerable error in the P mass balance calculation.
Equation (2.115) predicts that phosphorus partitioning from the metal to the slag should increase with an increase in the slag phosphide capacity \( C_{P^{3-}} \) for a slag in which the activities of \( O^{2-} \) and \( P^{3-} \) ions are constant.

### 2.7.2 Determination of phosphide capacities of ferromanganese slags

According to J. F. Elliot\(^{(10)} \), reaction (2.109) can be expressed in a slightly variant form to represent the equilibrium distribution of phosphorus between the metal and slag phases as given by reaction (2.116):

\[
\%P_{\text{metal}} + \frac{3}{2}O^{2-}_{\text{slag}} \leftrightarrow P^{3-}_{\text{slag}} + \frac{3}{4}O_2 \text{(gas)}
\]  

(2.116)

Therefore:

\[
K_{2.116} = \frac{(a_{P^{3-}})P^{3/4}_{O_2}}{[a_P](O^{2-})^{3/2}} = \frac{(f_{P^{3-}})(%P^{3-})P^{3/4}_{O_2}}{[f_P][%P](O^{2-})^{3/2}}
\]

(2.117)

Therefore:

\[
C_{P^{3-}} = \frac{(%P^{3-})P^{3/4}_{O_2}}{[f_P][%P]} = \frac{K_{2.116}(O^{2-})^{3/2}}{(f_{P^{3-}})}
\]

(2.118)

Where:

i. \( C_{P^{3-}} \) is the slag phosphide capacity of a smelting slag for example the ferroalloy smelting slag.
ii. $(\%P^{3-})$ is equivalent to the wt. $\%$ of $P$ in the slag phase and is determined by chemical analysis.

iii. $P_{O_2}$ is the partial pressure of $O_2$ to be calculated from the partial oxidation of carbon, reaction (2.119):

$$C_{(s)} + \frac{1}{2}O_{2(g)} \leftrightarrow CO_{(g)}^{(13)} \quad (2.119)$$

Given that:

$$\Delta G^\circ = -112\ 000 - 87.6T \text{ J/mol}^{(13)} \quad (2.120)$$

iv. $[\%P]$ is equivalent to the wt. $\%$ of $P$ in the metal phase and is determined by chemical analysis.

v. $[f_P]$ is the activity coefficient of $P$ in the metal phase to be calculated using the infinity dilute solution treatment.

Therefore from equation (2.118) the phosphide capacity $(C_{P_{3-}})$ of a particular slag in equilibrium with a ferromanganese metal phase during smelting can be calculated. It is to be noted that none of the terms in the relationship on the right of second equal sign can be defined individually. The value of the phosphide capacity of the slag is a function of the composition of the slag and temperature.

It may be difficult to get good agreement between the capacity of a slag for a species based on the reaction with the gas phase. In some cases this is due to inherent uncertainties in the experimental measurements, but also because of the secondary effects of components from the metal phase being present in the slag phase.

The concept of capacity is most appropriately applied to those species which are sparingly soluble in liquid slags for conditions prevailing in typical metallurgical
operations, in particular for total pressures not much greater than the atmospheric pressure.\textsuperscript{(10)}

\section*{2.8 Physico – Chemical Properties of Slags Associated with the Production of High Carbon Ferromanganese\textsuperscript{(44)}}

The slag formed when manganese ores are smelted exerts a direct influence on the operation of the furnace. Figure 2.12 illustrates schematically the zones thought to exist in an electric smelting furnace. The preheating zone is very large in relation to the total volume of the charge due to the low thermal conductivity of the charge at temperatures up to $1000^\circ\text{C}$. As a result, endothermic smelting reactions are localized in a small region beneath the electrodes. The exothermic reduction of $\text{MnO}_2$ contained in the ore through the various lower oxidation states to the monoxide is not sufficient to upset this heat distribution within the furnace. The alloy forms as isolated spheroids within the slag matrix and settles to accumulate on the furnace hearth. The alloy temperature is a direct result of the heat transferred from the slag. Practically the liquidus temperature of the slag should be about $100^\circ\text{C}$ greater than the liquidus temperature of the alloy to facilitate tapping. It is also necessary to maintain a relatively low temperature so that manganese fume losses through volatilization are minimized and an undesirable amount of silicon reduction from the slag is prevented. The viscosity of the continuous slag phase affects the rate at which reactants and products drain through the reaction zone in the electric furnace. Slag of low viscosity will exhibit high rates of bulk diffusion resulting in high rates of reduction of $\text{MnO}$ from the slag. The electrical conductivity of the continuous slag medium affects directly the power that can be dissipated by the process.
Figure 2.12  Schematic diagram of electric furnace showing zone of incipient fusion\(^{(44)}\)
2.8.1 Slag composition and properties

High carbon ferromanganese is produced with low silicon content of less than 1%. In order to obtain this alloy analysis a basic slag must be used. The molar basicity ratio \((MnO + MgO + CaO)/SiO_2\) is usually about 1.5 to 2.\(^{(44)}\)

Manganese II Oxide

The manganese oxide that occurs in the final slags during the production of HC-FeMn is stoichiometric MnO. The addition of MnO lowers the liquidus temperature of these slags. Warren et al.\(^{(45)}\) measured the effect of MnO on the liquidus temperature in the system CaO-MgO-Al\(_2\)O\(_3\)-SiO\(_2\). At 13% MnO content of these slags, the liquidus temperature is decreased except for very basic slags. MnO also decreases the viscosity and increases the electrical conductivity of these slags. Chubinidze and Kekelidze\(^{(46)}\) obtained variations of viscosity of 1.58 to 0.69 N sec m\(^{-2}\) at 1400\(^\circ\)C for slags containing 5-20% MnO. The electrical conductivity varied from 6.6 to 26.7 S m\(^{-1}\) at 1400\(^\circ\)C.

R. H. Eric, et al.\(^{(49)}\) measured liquidus temperature and electrical conductivities of synthetic ferromanganese slags. The slags represented a wide range of compositions likely to be encountered in the operation of ferromanganese electric furnaces. The slag constituents were in the following ranges: MnO; 5 – 30%, CaO; 20 – 35%, MgO; 5 – 15%, SiO\(_2\); 27 – 58%, Al\(_2\)O\(_3\); 5%. R. H. Eric et al found that the liquidus temperatures varied from 1300\(^\circ\)C to 1380\(^\circ\)C and increased with increasing basicity ratio, which varied from 0.55 to 1.4. The temperature increase became more evident above basicity ratio of 1.1. Eric et al also found that increasing the basicity from 0.55 to 1.1 decreased the resistivity of slags substantially. At basicity ratios higher than 1.1 the resistivities tended to increase depending on the MnO content. A peak in resistivities was reached at 10% MnO for basicity ratios of 0.55, 0.8, and 1.1. When the MnO content increased to 25% a sharp drop in resistivities was observed.
Silicon Dioxide
In general the liquidus temperature decreases with increasing SiO$_2$ content. The major influence on viscosity is exerted by SiO$_2$, with viscosity increasing with less basic slags. An increase in SiO$_2$ leads to a decrease in electrical conductivity.

Calcium Oxide
In basic slags increasing CaO results in higher liquidus temperature. The effect on viscosity is small with a slight increasing tendency at 1400°C. Electrical conductivity is slightly increased except at low MnO contents where the effects of higher liquidus temperature is more pronounced.

Magnesium Oxide
When substituted for CaO in small amounts, MgO causes a decrease in the liquidus temperature and a decrease in viscosity with increased electrical conductivity.

Aluminum Oxide
An increase in Al$_2$O$_3$ content increases the liquidus temperature. Viscosities of basic slags tended towards a minimum at 15% Al$_2$O$_3$ and electrical conductivity was maximum between 6 – 10% Al$_2$O$_3$ for slags containing 1.5 to 15% Al$_2$O$_3$

2.8.2 Furnace operation

In the operation of the electric furnace the final slag should have a liquidus temperature of at least 1350°C to ensure that the alloy temperature is sufficiently high but less than 1500°C to minimize fume losses. Electrical conductivity should be as low as possible to encourage a high operating resistance. The viscosity should be as low as possible to promote swift slag – metal separation and easy tapping. A compromise is necessary between low viscosity and low electrical conductivity. The impurity content of manganese ores affects the composition of the final slags. Ores
can be rated based on the slag to metal ratio and physico-chemical slag properties of liquidus temperature, viscosity and electrical conductivity. A low slag to metal ratio means less energy would be expended in melting excess slag. A high temperature operation will lead to higher fume losses than assumed in the blend calculation.

In general slag basicity exerts the most important effect on viscosity and electrical conductivity. MnO displays the greatest influence of the basic oxides. MgO at small additions reduces the liquidus temperature and viscosity and increases electrical conductivity, but large additions have a reverse effect. The optimum slag composition is one that is the best compromise between low liquidus temperature, low viscosity and low electrical conductivity resulting from the minimum of flux additions. Therefore, giving a minimum slag-to-metal ratio.

2.9 Optimum Slag – Alloy Relationships for the Production of Medium to Low Carbon Ferromanganese\(^{(2,3)}\)

Medium to low–carbon FeMn is produced successfully by two different techniques. At Union Carbide, HC-FeMn is decarburized successfully by blowing with oxygen in a converter. Losses of Mn are moderately high. The more popular method involves the contacting of a high grade slag or melt of manganese ore and lime that is rich in oxides of manganese with a silico-manganese reducing agent containing 16 to 30% silicon. The contacting of manganese melt and the alloy phase can be achieved in an electric smelting furnace or in mixing ladles.

From studies conducted by N. A. Barcza, addition of <3.28g of plant alloy to 25g of standard slag, a net overall mass loss occurred because insufficient silicon was provided from the alloy for the complete reduction of the Mn\(^{3+}\) to Mn\(^{2+}\). The observed mass change was thus a loss from the alloy due to silicon being consumed while no Mn was recovered. Only when sufficient alloy had been added to provide enough silicon for complete reduction of Mn\(^{3+}\) to Mn\(^{2+}\) and also to recover enough
Mn to make up for the silicon used for both the reduction of the higher oxide and the recovery of Mn, was a net gain in mass of the alloy achieved. The point of mass balance, where Mn gain compensated for the Si loss from the alloy was termed the “Break – Even Point”. The lowest manganese distribution ratio was obtained when the slag/ alloy ratio was 1:1 giving maximum recovery of manganese. The slag had a low MnO content but the alloy had a 10.8% Si which was too high to meet required alloy specification of < 2%.

To obtain a good Mn recovery, a fairly high initial concentration of Si was needed. Increasing the CaO/SiO$_2$ ratio in the initial slag resulted in a marked decrease in the Mn distribution ratio and an increase in the recovery of Mn. The optimum basicity ratio for recovery of manganese was found to be (CaO + MgO)/SiO$_2$ = 4/3.

A steady increase in the recovery of Mn was observed with the addition of MgO up to an optimum level of CaO/MgO = 3. The recovery increased because as MgO replaced CaO on a mass % basis the number of moles of basic oxides increased. A further reason for the noted increase in recovery with an increase in the activity of MnO in the slag, could be that the free energy of formation of 2CaO.SiO$_2$ is not as negative as is the case for the combined orthosilicate of CaMgSiO$_4$ in the temperature range 1700°K to 1900°K.

Further addition of MgO caused a decrease in recovery because the resultant liquidus temperature of a high MgO containing slag phase was considerably higher than the system temperature of 1500°C which was shown to be the most suitable temperature at which equilibrium should be reached. Also the free energy of formation of slag systems, containing higher MgO contents than can be represented by CaMgSiO$_4$ are less negative and thus the activity coefficient of MnO will also be lower.

For basicity ratios of less than 4/3 the activity coefficient of the MnO is decreased because of the insufficient quantity of basic oxides. The Mn$^{2+}$ ions are thus tied up
partly with the SiO₂ present in these more acid slags. The recovery of Mn is lowered as the (CaO + MgO)/SiO₂ ratio decreases. Silica lowers the activity coefficient of MnO, thereby reducing the recovery of manganese from the slag. This helps to qualify why the addition of CaO and MgO can improve recovery of manganese from such slags.

The increase in the activity coefficient of MnO and hence the increased recovery of Mn as the content of the basic oxides of CaO and to some extent MgO are raised as already discussed in section 2.4.2 can be explained as follows. At low concentrations the basic oxides Ca²⁺, Mg²⁺, and Mn²⁺ cations are associated with larger ionic groups of silica and thus very few free O²⁻ ions exist. This means that MnO will have a low activity coefficient. As the basic oxides contents are increased, the silica network is broken down into smaller anionic groups and more O²⁻ ions become free. There is also an equal increase in the divalent cations of Ca²⁺, and Mg²⁺, which are not associated with the silica ions but with the free O²⁻ ions. The interaction of the more basic cations of Ca²⁺ and Mg²⁺, with silica is stronger than that of Mn²⁺ ions. This results in the Mn²⁺ ions being left out of the association with silica cations to a large extent and hence the higher activity coefficient.

The role of basic oxides is to tie up the existing silica and any secondary silica which results from the reactions. The activity of MnO was shown to be one of the limiting factors governing the equilibrium state attained, and the Si content in the metal at equilibrium also played an important role, sufficient silicon has to be present at equilibrium. If silicon had been denuded prior to complete reduction of MnO, then the limiting factor would be Si activity.

For an alloy with the required Si content in a single-stage contact, use has to be made of a melt that is well in excess of the amount of melt that would give maximum Mn recovery. This is the major limitation of a single-stage contact. In principle, a two-stage contact allows much greater flexibility because an excess alloy can be used in
first contact to strip the slag to a low MnO that is a slag-alloy ratio of 1 instead of 2.5 and a high recovery is achieved (Si: 9 – 12%). In the second stage alloy produced in the first stage can be contacted with fresh melt in such a ratio as to refine the silicon in the alloy to meet the required specification of (<1.5% Si). The resulting slag, still rich in MnO, can be used in the first stage with higher intermediate ratio of slag to alloy, or to produce silicon-manganese (FeMnSi).

2.10 The Equilibrium Distribution of Elements Between the Metal and Slag Phases with Temperature at Carbon Saturation Condition

Y. E. Lee and J. H. Downing developed models to calculate activities of components in the smelting reaction under equilibrium condition and used the results to predict the equilibrium distribution of these components in the slag and metal phases. The calculated distribution of elements between the metal and slag was compared with equilibrium experimental results and the compositions agree fairly well as shown in Figure 2.13 below.

The content of Fe and C decreases gradually with the increase of temperature, and Si increases with temperature. The MnO content in the slag decreases with the temperature, and SiO₂ content begins to decrease with temperature only at a higher temperature than 1773°K (1500°C). The content of Al₂O₃ and CaO increases with temperature, this is due to depletion of MnO and SiO₂. The content of FeO is too small to appear on the same scale.
Fig. 2.13 Variation of slag and metal composition with temperature at carbon saturation condition\(^{(47)}\)