Studies on dephosphorisation during steelmaking

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Doctoral Thesis

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ABSTRACT

This work is aimed at understanding the thermodynamic principles influencing the phosphorus partition between slag and steel during steelmaking, particularly during refining of high-phosphorus hot metal using the basic oxygen steelmaking (BOS) process. Mapping of the slag path has been carried out using a mass balance model based on input conditions and off-gas analysis, which has been validated by intermediate measurements of slag and metal composition in an industrial basic oxygen furnace (BOF). The slag composition is found to vary over a wide range of basicity (%CaO/%SiO₂) and iron oxide content. The partition of phosphorus increases with progress of refining but reduces during the intermediate period, corresponding to a decrease in iron oxide concentration and formation of “dry slag”. The phosphorus partition ratio increases again towards the end of the process. The equilibrium partition ratios for such conditions have been theoretically estimated using slag “model(s)”, based on the estimated slag compositions. It is seen that the partition ratio of phosphorus remains within 45% – 60% of the equilibrium value, showing a gradual decrease with progress of the refining process.

Equilibrium phosphorus partition ratios for slags containing low concentrations of MnO and Al₂O₃ have been experimentally determined, over the ranges of basicity and iron oxide concentration approximately corresponding to that observed in the typical BOS process. It is seen that the equilibrium phosphorus partition ratio is practically independent of basicity greater than 2.5 – 2.6, over the entire range of temperature and FeO₆ concentration studied.

Variation of the activity of P₂O₅ with basicity and FeOₓ concentration has been investigated to explain the trends observed in the variation of phosphorus partition ratio. It is seen that the activity coefficient of P₂O₅ is lowest, and hence most conducive for removal of phosphorus from steel, over certain finite ranges of basicity and iron oxide concentration. It follows that the efficiency of
dephosphorisation is likely to be maximum if the basic oxygen steelmaking process is operated within these ranges.

Simultaneous with this work, mathematical correlations have been developed for estimation of $P_2O_5$ activity coefficient and phosphorus partition ratio as functions of slag composition. The correlations are compared with those proposed by earlier workers and are found to result in better predictions over certain composition ranges.
ACKNOWLEDGEMENTS

…… how do you thank someone
Who has taken you from crayons to perfume?
It isn't easy, but I'll try ……

I can’t help borrowing from these 1967 lyrics since I fail to find words to thank my supervisor Prof. Seshadri Seetharaman, who showed me the way forward. Thank you professor for the confidence you instilled in me, particularly at times when the going was not smooth.

This thesis would not have seen the light of the day without the advice and guidance of Prof. Ashok Kumar Lahiri. I do not have words to thank you either.

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I can never fully emphasize the role played by my parents in bringing me up to whatever I am today.

Somnath Basu

Stockholm, June 2007
Gravitation is not responsible for people falling in love …

\textit{Isaac Newton}

Anyone who has never made a mistake has never tried anything new…

\textit{Albert Einstein}
SUPPLEMENTS

This thesis is based on the following publications.

Supplement 1  “Change in phosphorus partition during blowing in a commercial BOF”
Somnath Basu, Ashok Kumar Lahiri, Seshadri Seetharaman and Jayanta Halder

Supplement 2  “Phosphorus partition between liquid steel and CaO-SiO₂-P₂O₅-MgO slag containing low FeO”
Somnath Basu, Ashok Kumar Lahiri and Seshadri Seetharaman

Supplement 3  “Phosphorus partition between liquid steel and CaO-SiO₂-FeOₓ-P₂O₅-MgO slag containing 15 – 25% FeO”
Somnath Basu, Ashok Kumar Lahiri and Seshadri Seetharaman

Supplement 4  “A model for activity coefficient of P₂O₅ in BOF slag and phosphorus distribution between liquid steel and slag”
Somnath Basu, Ashok Kumar Lahiri and Seshadri Seetharaman
Accepted for publication in ISIJ International, 2007

Parts of this work have also been presented at the following conference

1.  “Property measurements of slags and fluxes towards slag design in blast furnace, BOF and continuous casting”
A. Shankar, S. Basu, A. K. Lahiri and S. Seetharaman
The author’s contribution of the supplements in this thesis

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# ABBREVIATIONS AND SYMBOLS

The following abbreviations and symbols have been used throughout the thesis, as well as the supplements. Other symbols, which may have been used occasionally, have been explained at the respective places.

**List of abbreviations and symbols used in the thesis**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>BOS</td>
<td>Basic oxygen steelmaking</td>
</tr>
<tr>
<td>BOF</td>
<td>Basic oxygen furnace</td>
</tr>
<tr>
<td>EAF</td>
<td>Electric arc furnace</td>
</tr>
<tr>
<td>$a_i$</td>
<td>Raoultian activity of species “i” in slag (assuming standard state of pure “i”)</td>
</tr>
<tr>
<td>$h_i$</td>
<td>Henrian activity of species “j” in metallic solution (assuming standard state of unit activity coefficient at infinite dilution, i.e. $\lim_{[%]} f_j = 1$)</td>
</tr>
<tr>
<td>$\gamma_i$</td>
<td>Activity coefficient of species “i” in slag</td>
</tr>
<tr>
<td>$f_j$</td>
<td>Henrian activity coefficient of species “j” in metallic solution</td>
</tr>
<tr>
<td>(%)</td>
<td>Concentration, in mass pct., of species “i” in slag</td>
</tr>
<tr>
<td>[%]</td>
<td>Concentration, in mass pct., of species “j” in metallic solution</td>
</tr>
<tr>
<td>$K$</td>
<td>Equilibrium constant of a chemical reaction</td>
</tr>
<tr>
<td>$K'$</td>
<td>Equilibrium constant of a reaction involving ionic species</td>
</tr>
<tr>
<td>$N(i)$</td>
<td>Molar fraction of species “i”</td>
</tr>
<tr>
<td>$X(j)$</td>
<td>Ionic fraction of species “j”</td>
</tr>
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1. INTRODUCTION

Close control on the impurity levels is essential for production of quality steel. Phosphorus’ tendency to impart cold shortness in steels has been known for a long time. In the more recent times, lowering of phosphorus content has become a critical requirement for steels used in thin sheets for deep drawn applications, automobile exteriors and pipelines for transportation of natural gas and petroleum products. \(^{[1]}\)\(^{[2]}\) Table 1 shows a summary of the effect of phosphorus on steel properties.

<table>
<thead>
<tr>
<th>Property</th>
<th>Effect of phosphorus</th>
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<tr>
<td>Strength</td>
<td>++ (ferrite strengthener)</td>
</tr>
<tr>
<td>Bake hardenability</td>
<td>+</td>
</tr>
<tr>
<td>Ductility</td>
<td>– –</td>
</tr>
<tr>
<td>Fe-Zn galvanneal</td>
<td>may improve resistance to powdering</td>
</tr>
<tr>
<td>Phosphatability</td>
<td>+</td>
</tr>
<tr>
<td>Enamelling steels</td>
<td></td>
</tr>
<tr>
<td>Fish-scaling</td>
<td>–</td>
</tr>
<tr>
<td>Pickling</td>
<td>+</td>
</tr>
<tr>
<td>Weldability</td>
<td>Not harmful for &lt; 0.1 mass%</td>
</tr>
<tr>
<td>Core loss in motor laminations</td>
<td>– –</td>
</tr>
<tr>
<td>Fracture toughness</td>
<td>– –</td>
</tr>
</tbody>
</table>

+ increase       ++ strong increase       – decrease       – – strong decrease

Therefore, it is of no surprise that the removal of phosphorus during steelmaking has bothered metallurgists for several decades. \(^{[3]}\) The products of oxidation of the dissolved solutes and impurities, during steelmaking, either join the slag (e.g. SiO\(_2\)) or escape as gas (e.g. CO). Unfortunately, neither does the product of oxidation of phosphorus escape as gas nor does it have adequate
stability in the slag phase. This leads to the risk of phosphorus reversal from the slag to liquid steel.

Over the past couple of decades, there have been reports of increasing levels of phosphorus in the raw materials used in steelmaking, \[^{[4]}\] \[^{[5]}\] due to a gradual shortage of low-phosphorus iron ores and coking coals. Thus, the steel makers are facing stiffer challenge in achieving the desired phosphorus levels in the finished products. Several steel plants have adopted the practice of external dephosphorisation, where a part of the phosphorus is removed either before or after the main steelmaking process. However, the commercial viability of such a technique depends on the circumstances particular to an individual steelmaker.

1.1 Background of the present work

The present investigations were initiated at the instance of Tata Steel Ltd., who use the blast furnace – basic oxygen steelmaking (BF-BOF) route for production of liquid steel. The iron ore and coal, obtained from the mines available with Tata Steel, typically contain high levels of phosphorus. As a result, the phosphorus content in the hot metal reaches as high as 0.2 – 0.25 mass%; a condition highly unfavourable for production of low-phosphorus steel. External dephosphorisation through hot metal pre-treatment has worked successfully in several steel plants. However, such technique was not technocommercially feasible due to the conditions prevailing in that particular steelmaking shop. As a consequence, the target for production of low-phosphorus steel has to be achieved by single-stage blowing of high-phosphorus hot metal in the BOF. Therefore, it is very important to maximise the extent of dephosphorisation during steelmaking, within the constraints of the process adopted.
This prompted the present work to be taken up, with the aim of establishing the maximum extent of phosphorus partition achievable in basic oxygen steelmaking, and identifying means to attain the same.
2. AN OVERVIEW OF THE BASIC OXYGEN STEELMAKING (BOS) PROCESS

Modern steelmaking is often viewed as the brainchild of Sir Henry Bessemer, the Leonardo da Vinci of metallurgy, who first produced steel by blowing air through a bath of molten pig iron using a submerged fireclay blow-pipe. The process was described in Bessemer’s patent application of 1855 as “… a current of air … is then to be forced into the fluid metal and allowed to bubble up through it”. Scientific understanding of the associated metallurgical reactions has evolved over the subsequent years. The oxygen supplied to the molten metal bath causes oxidation of carbon, silicon, manganese, phosphorus and other oxidisable impurities, along with some amount of iron. This has remained the fundamental principle of steelmaking and the various industrial processes, developed over the years, differ mainly in the way oxygen is supplied to the metal bath. Oxygen can be made available in the form of air (e.g. Bessemer and Thomas process), solid iron ore (e.g. open hearth furnace) or as pure oxygen gas (basic oxygen furnace). In all cases, the products of oxidation can either join the slag (e.g. SiO₂) or escape as gas (e.g. CO).

The basic oxygen steelmaking process took birth in the years following the Second World War, when rapidly increasing demand for quality steel prompted a search for steelmaking techniques that could significantly exceed the productivity and energy efficiency of the open hearth process. The first successful BOS heat was produced on 27th November, 1952, at the Linz steelworks of Vereinigte Österreichische Eisen- und Stahlwerke (VÖEST) in Austria and the feat was subsequently replicated at the Donawitz steelworks of Österreichisch-Alpine Montangesellschaft (ÖAMG) within a few months. Owing to the geography of its early success, the technique was given the name Linz-Donawitz (LD) process. However, there have been claims of earlier success where a bath of molten pig iron was top-blown with pure oxygen in April 1936 in the erstwhile USSR.
The process involves blowing of oxygen through a top lance into a bath of molten pig iron or hot metal. The liquid metal containing carbon, silicon, manganese, phosphorus and other dissolved solutes is contained in a refractory-lined vessel.\textsuperscript{[12]} The flue gases escape through the open top of the vessel, and are directed through the waste gas cleaning devices. The liquid steel is removed by tilting the vessel. The slag floats to the top due to difference in density, and is separated from steel by controlling the angle of tilting. The refractory used for lining the steelmaking vessel is basic in nature and hence this process has been designated “basic oxygen steelmaking (BOS)”. The vessel where the refining reactions take place is given the term “basic oxygen furnace (BOF)".
3. DEPHOSPHORISATION DURING STEELMAKING

Herty remarked in 1940 “…elimination of undesirable elements such as phosphorus and sulphur is entirely a matter of slag composition and physical nature …”. [13] This observation holds good till date. Removal of phosphorus from liquid steel is thermodynamically favoured at lower temperatures. [14] [15] This was demonstrated by the fact that as much as 70 – 80% of input phosphorus in the metallic charge in a basic open hearth furnace could be oxidised during the lime boil period, when the metal bath temperature typically stayed below 1750 – 1800 K. [16] However, the lime boil duration in a conventional open hearth furnace would exceed the total tap-to-tap time in a modern BOF. Consequently, phosphorus removal now has to be achieved in the BOF under higher temperatures and thermodynamically less favourable conditions.

Research on the removal of phosphorus during steelmaking started with the Bessemer and open hearth processes, during the late years of the 19th century. Snelus [17] was among the earliest workers, starting in 1872, to study the reaction of phosphorus during the Bessemer process of steelmaking. He patented the use of a basic lining, based on lime and magnesia, for the removal of phosphorus from high-phosphorus pig irons. Thomas and Gilchrist [18] independently investigated the influence of the lining materials and fluxes on the elimination of phosphorus during blowing of a high-phosphorus pig iron using the Bessemer process. Following experiments and trials spanning close to three years, they concluded that the presence of a basic lining and addition of basic fluxes were essential for production of low phosphorus steel from phosphorus-bearing hot metal. Snelus, as well as Thomas and Gilchrist, successfully demonstrated the benefits of using a basic lining and basic slag on an industrial scale and their findings led to the adoption of basic linings in Bessemer-type pneumatic steelmaking converters. This technique was gradually
adopted in several countries and gained fame as the “Thomas process”. Around the same time, Harmet proposed the idea of “repouring” to produce low phosphorus steel using a Bessemer converter. \[19\] He suggested a two-stage blowing, where silicon was first oxidised in a vessel with acidic lining and the desiliconised metal was then transferred to a second vessel with a basic lining for oxidation of phosphorus and carbon. Adoption of the two-stage process sharply reduced the consumption of basic fluxes since no basic flux was necessary during the first part of the blow. This concept became popular with several steelmakers, particularly those using pig iron and/or hot metal with high [P]/[Si] ratio, and has been adopted in some of the recent steelmaking techniques as well. \[20\] \[21\] Pourcel carried out similar investigations, independent of other workers, and compared the efficiency of phosphorus removal achievable in Bessemer-type converters with other processes for manufacture of steel and wrought iron. \[22\] His work led to the following inferences:

a) A basic lining and addition of basic fluxes were essential for the removal of phosphorus

b) The slag, after oxidation of silicon during the early part of the blow, contained considerable amount of P₂O₅ as well

c) Low phosphorus steel could be consistently produced if the initial slag was removed and blowing was resumed after addition of fresh basic fluxes.

d) Hard-burnt magnesio-lime refractory bricks were most suitable for such operation

e) The degree of dephosphorisation was inversely dependent on temperature

These findings were applied to the open-hearth steelmaking furnaces as well and culminated in the development of the basic open-hearth process.

Several obstacles plagued early work on the thermodynamics of phosphorus transfer between liquid steel and slag. The most formidable among those was
the limited availability of a material suitable for holding liquid steel and slag for
the requisite durations, at the steelmaking temperatures. These predicaments
were summarised by Larsen in 1940. [23]

i) Temperatures of 1600° and above limit the choice of materials available
for making crucibles and mechanical stability of the equipment suffers due
to extreme temperature gradients

ii) Slag containing iron oxide is corrosive to most materials that are capable
of holding liquid metal

iii) Extremely low partial pressure of oxygen in equilibrium with liquid iron
makes the system prone to oxidation

Barrett and co-workers attempted to overcome some of these problems by
developing a technique of “liquid metal crucible”, which prevented direct
contact of molten slag with the crucible refractory. [24] A refractory crucible,
containing the liquid metal, was rotated about the vertical axis. The rotating
metal formed a paraboloid depression that acted as the crucible for holding the
slag. Using this technique, it was possible to study slag-metal equilibrium
without corrosion of the crucible refractory.

Colclough [26] [27] carried out a series of experiments on the oxidation of
phosphorus, carbon and manganese from the hot metal bath in a basic open-
hearth furnace and concluded that P₂O₅ in the slag existed in the form of tetra-
calcium phosphate (4CaO.P₂O₅). He further inferred that iron oxide acted only
as a source of oxygen, with no contribution as basic oxide. However, Colclough
collected all the samples from furnaces in commercial operation, where the
conditions might not have attained equilibrium. A few years later, Herty carried
out experiments using a laboratory-scale furnace as well as 100T and 200T basic
open-hearth furnaces in industrial operation [28]. He was perhaps the first to
suggest the use of phosphorus partition ratio as an index of the
dephosphorising capacity of steelmaking slags and observed that partition of phosphorus followed the Nernst distribution law. The theoretical treatment proposed by Herty was based on the assumption that phosphorus from the metal was oxidised by FeO in the slag and the product joined the slag phase in the form of a phosphate of calcium. He differed with Colclough by assuming that phosphorus in the slag formed tri-calcium phosphate, and not tetracalcium phosphate.

\[ 2[P] + 8(\text{FeO}) = (3\text{FeO}.P_2\text{O}_3) + 5[\text{Fe}] \]  \hspace{1cm} (1)

\[ (3\text{FeO}.P_2\text{O}_3) + 3(\text{CaO}) = (3\text{CaO}.P_2\text{O}_3) + 3(\text{FeO}) \]  \hspace{1cm} (2)

In summary, \[ 2[P] + 5(\text{FeO}) + 3(\text{CaO}) = (3\text{CaO}.P_2\text{O}_3) + 5[\text{Fe}] \]  \hspace{1cm} (3)

\[ \log \left\{ K_p \times 10^{-5} \right\} = \frac{(\%P_2O_5)}{(\%P)^2 (\%\text{FeO})^5 (\%\text{CaO})^3} = \left( \frac{1}{1.322} \right) \left( \frac{1}{T^2} \times 10^5 \right) - 28.52 \]  \hspace{1cm} (4)

Herty reported a negative correlation between the equilibrium constant for reaction (4) and temperature, as illustrated in Fig. 1, which implied that decrease of temperature was beneficial for dephosphorisation and supported the observations of Pourcel. \[^{[22]}\]
Fig. 1: Effect of temperature on equilibrium constant for phosphorus oxidation

Several researchers raised concerns about the presence of undissolved lime in otherwise fluid slag in basic open hearth furnaces. Investigations using petrographic microscopy showed that such undissolved lime particles were coated with a layer of dicalcium silicate, having melting temperature greater than 2200K. This layer, which retarded the dissolution of lime particles in the slag, could be removed by the action of iron oxide in high concentrations and by the addition of fluorspar.\textsuperscript{[13]} Based on analysis of data from eight different steel plants, all using basic open hearth furnaces, Fetters and Chipman observed that the affinity $P_2O_5$ towards CaO in slag was approximately half of that of SiO$_2$ and proposed to define basicity as the ratio\textsuperscript{[29]}

$$R = \frac{(CaO)}{(SiO_2) + 0.634(P_2O_5)}$$

However, Fetters and Chipman paid more attention to the removal of carbon, manganese and sulphur from the steel bath, vis-à-vis the variations of MnO, SiO$_2$ and iron oxide concentrations in slag. Consequently, no detail on the oxidation of phosphorus was reported by them.
Taylor and Chipman carried out several studies on the equilibrium between liquid steel and slag using the rotating crucible technique, initially designed by Barrett and coworkers.\textsuperscript{[30]} Their work led to publication of fairly reliable values for the solubility of oxygen in liquid iron and the corresponding activities of FeO in slag, in addition to a critical comparison of the oxygen activity values published earlier.

Trömel\textsuperscript{[31]} equilibrated phosphorus-rich Thomas slags, saturated with lime, and observed the presence of solid calcium silico-phosphate in slag samples quenched from above 1873K. This phase had no definite stoichiometry but the composition varied between $5\text{CaO.P}_2\text{O}_5.\text{SiO}_2$ and $9\text{CaO.P}_2\text{O}_5.3\text{SiO}_2$. Trömel described the same as “mixed crystal” and advised against using any specific chemical formula. He further observed that FeO and MnO had practically no role in the formation of this silico-phosphate, provided the concentration of CaO in the slag was stoichiometrically sufficient to stabilise both P$_2$O$_5$ and SiO$_2$ as $3\text{CaO.P}_2\text{O}_5$ and $2\text{CaO.SiO}_2$, respectively. The remaining liquid consisted of a solution of CaO, FeO and MnO. Presence of SiO$_2$ reduced the miscibility gap in the CaO-FeO-P$_2$O$_5$ system and no liquid-state segregation usually occurred in commercial Thomas slags.

Balajiva and coworkers, during the 1940’s, carried out a series of experiments using a miniature EAF and proposed a correlation of equilibrium phosphorus partition ratio with a wide range of slag compositions and temperatures.\textsuperscript{[32]}\textsuperscript{[33]}

\[
\log \left( \frac{\% P}{\% P} \right) = 5.9 \log (\% \text{CaO}) + 2.5 \log (\% \text{FeO}) + 0.5 \log (\% \text{P}_2\text{O}_5) \\
- 0.5\times C - 0.36
\]  

(5)

where $C$ is constant for a particular temperature.

The values of $C$ at 1823 K, 1858 K and 1908 K were reported as 21.13, 21.51 and 21.92 respectively. However, attainment of equilibrium in the experiments performed by Balajiva and coworkers, has been questioned in recent times by Ide and Fruehan, who suggested that the values obtained by the use of Eq. (5)
are lower than the actual equilibrium phosphorus partition ratio.\[^{34}\] Notwithstanding these limitations, the work of Balajiva \textit{et al.} clearly showed that the partition of phosphorus between slag and steel was enhanced by the presence of CaO and FeO in the slag and decreased with increasing temperature.

### 3.1 Thermodynamics of P\(_2\)O\(_5\) in steelmaking slag

Attempts to predict the behaviour of P\(_2\)O\(_5\) in steelmaking slag have a long history. The work of Colclough \[^{26,27}\] and Schenk \[^{35}\] represent the early efforts where the researchers used the molecular theory to describe the structure of steelmaking slags. The prolonged refining time in the open-hearth process allowed the scientists to study the interactions between different constituents in detail, and hence, most of those investigations were based on the partition of phosphorus between liquid steel and basic open-hearth slags. Darken & Larsen, after meticulous study of FeO-MnO-CaO-SiO\(_2\)-P\(_2\)O\(_5\) system, arrived at the following conclusions.\[^{36}\]

i) Iron in slag was present in equilibrium proportion of FeO and Fe\(_2\)O\(_3\)

ii) Fe\(_2\)O\(_3\) at the slag-metal interface was reduced to FeO by metallic iron or carbon dissolved in iron

iii) Entire amount of P\(_2\)O\(_5\) in slag existed in the form of 4CaO.P\(_2\)O\(_5\)

iv) SiO\(_2\) was present in the form of 2MO.SiO\(_2\) or 3MO.SiO\(_2\) (MO = basic oxide); free SiO\(_2\) concentration in the slag was negligible

Flood and Grjotheim \[^{37}\] proposed a modified ionic model for the non-ideal mixing of constituent oxides in slag and observed that the logarithmic value of the equilibrium constant of phosphorus oxidation in the case of a multi-component slag could be expressed as the algebraic summation of the cation
fractions multiplied by the logarithmic equilibrium constants of the respective oxides.

\[ \log K' = N_{Ca^{2+}} \log K'_{Ca} + N_{Fe^{2+}} \log K'_{Fe} + N_{Mg^{2+}} \log K'_{Mg} + \ldots \]  

(6)

where \( N_{i}^{n+} \) = cation fraction of the respective species

\( K'_{i} \) = ionic equilibrium constant assuming only oxide of “i”

When applied to oxidation of phosphorus, \( 2[P] + 5[O] + 3O^{2-} = 2PO_{4}^{3-} \), the treatment proposed by Flood and Grjotheim led to fairly satisfactory results for temperature of 1873±10 K.

However, the reports of Darken and Larsen, and Trömel, could not put to rest the debate in the metallurgical community over the form in which phosphorus existed in slag. It was proposed by some workers that \( P_{2}O_{5} \) formed a solid solution with \( 2CaO.SiO_{2} \) and co-precipitated around the undissolved lime particles \(^{38}[^{39}] \). Variation of this mechanism was, however, proposed as early as 1943 when Trömel reported the presence of calcium silico-phosphate “mixed crystals” in phosphorus-rich Thomas slags containing excess CaO. Similar views were presented by van der Knoop et al. \(^{40} \), and also by Deo \(^{41} \) who inferred that \( P_{2}O_{5} \) reacted with free CaO to form \( nCaO.P_{2}O_{5} \) \((n = 3, 4)\), followed by co-precipitation of \( 2CaO.SiO_{2} \) and \( nCaO.P_{2}O_{5} \). However, researchers like Ghosh \(^{42} \) have disputed the solid-solution hypothesis on the ground that the kinetics of phosphorus transfer in the solid solution would be significantly slower than that in liquid slag. Consequently, the formation of phosphorus-bearing solid solution, while possible in the basic open hearth slags, would be of lesser significance in basic oxygen steelmaking, particularly due to the short refining durations.

It is interesting to note that simple treatments based on the molecular concept often leads to results that are comparable to those provided by the more
sophisticated models. Turkdogan and Pearson, in 1953, estimated the
equilibrium constant for the reaction \(2[P] + 5[O] = (P_2O_5)_p\)\(^{[43]}\)

\[
\log K_p = \frac{37160}{T} - 29.67
\]  

(7)

They combined the value of \(K_p\) calculated using equation (6) with the data of
Balajiva et al.\(^{[32]}\)\(^{[33]}\) and Fisher and vom Ende,\(^{[44]}\) and with the activity of FeO
compiled in an earlier work of Turkdogan and Pearson,\(^{[45]}\) for calculating the
activity coefficient of \(P_2O_5\).\(^{[43]}\) It was seen that \(\log (\gamma_{P_2O_5})\) could be expressed
as a linear function of the molar fractions of the constituent oxides in slag.

\[
\log (\gamma_{P_2O_5}) = -1.12\left(22N_{CaO} + 15N_{MgO} + 13N_{MnO} + 12N_{FeO} - 2N_{SiO_2}\right)
- \frac{42000}{T} + 23.58
\]  

(8)

It is worth mentioning here that Turkdogan and Pearson assumed ideal Henrian
behaviour of the solutes in liquid iron. The reason for this was not explicitly
mentioned. However, non-availability of reliable values of the interaction
parameters, at the time this work was carried out, was most probably the factor
responsible for this simplification.

Almost 30 years later, Suito et al. experimentally measured the phosphorus
distribution between liquid iron and MgO-saturated CaO–MgO–FeO–SiO\(_2\)
slags, containing 30 – 40 mass\% CaO, over the temperature range 1823 – 1923
K.\(^{[46]}\) Based on the experimental results, they derived the activity coefficient of
\(P_2O_5\) and observed that their findings could be expressed by a mathematical
correlation that was similar in form to that proposed by Turkdogan and
Pearson.\(^{[43]}\)

\[
\log (\gamma_{P_2O_5}) = -1.01\left(23N_{CaO} + 17N_{MgO} + 8N_{FeO}\right) - \frac{26300}{T} + 11.2
\]  

(9)
The correlation proposed by Suito et al. indicates significantly lower temperature dependence of $\gamma_{P_2O_5}$, compared to that suggested by Turkdogan and Pearson. They further suggested that the variation of log $K_p$ vs. mass% CaO became non-linear for CaO concentrations exceeding approximately 35 mass%.

Sobandi and co-workers carried out extensive studies on the activity coefficient of $P_2O_5$ in CaO-MnO-SiO$_2-P_2O_5$ slags containing FeO and MgO, as a function of the chemical composition and temperature of the slag, and proposed the following correlation.

$$\log \gamma_{PO_{2.5}} = \frac{1400}{T} - 5.75 - \frac{2.59}{(\% SiO_2)} \{(% CaO) + 0.33(% MnO) + 0.55 (\% MgO) - 0.9(\% Fe_2O) - 0.77(\% PO_{2.5})\}$$

(10)

However, correlation (10) was developed primarily for high-MnO, low-FeO slags, over the temperature interval of 1623 – 1673 K. Therefore, it has limited relevance to dephosphorisation in the BOF and is probably more relevant to dephosphorisation of manganese-bearing hot metal.

Ohara and co-workers estimated the activity coefficient of $P_2O_5$ in iron oxide bearing slags and experimentally determined the interaction parameters of $P_2O_5$ with slag constituents like CaO, SiO$_2$ and MgO. Similar experiments were carried out by several researchers, each of whom proposed a different correlation to express phosphorus partition ratio between liquid steel and slag.

[49] [50] [51] [34]

In 2000, Turkdogan published an exhaustive assessment of $\gamma_{P_2O_5}$ for slags with a wide range of CaO, FeO and $P_2O_5$ concentrations. Combining the data of Suito et al., Selin, Wrampeymeyer et al. and Knüppel and Oeters, the following correlation for CaO-based slags containing 0.2 – 10.0 mass% $P_2O_5$ was proposed.
\[
\log (\gamma_{P_2O_5}) = -9.84 - 0.142 \ (%\text{CaO} + 0.3 \ %\text{MgO})
\] (11)

It is interesting to note that, in this correlation, \(\gamma_{P_2O_5}\) is independent of temperature. Unfortunately, the works of Suito et al.\textsuperscript{[46]} as well as Turdogan\textsuperscript{[52]} persisted with the assumption of ideal Henrian behaviour of phosphorus and oxygen in liquid iron, as has been mentioned in supplement #4.

Suito and Inoue\textsuperscript{[56]} equilibrated liquid iron with MnO-containing CaO-SiO\textsubscript{2}-Fe\textsubscript{2}O\textsubscript{3} slag, in MgO crucible at 1873 K, and proposed a correlation for estimation of phosphorus distribution between liquid steel and MnO-bearing slags, using the chemical composition of slag.

\[
\log \left( \frac{\%P}{\%P} \left(\frac{\%\text{Fe}_2O_3}{2.5}\right) \right) = 0.072 \left\{ \%\text{CaO} + 0.3 \%\text{MgO} + 0.6 \%\text{P}_2\text{O}_5 \right\}
+ 0.2 \%\text{MnO} + 1.2 \%\text{CaF}_2 - 0.5 \%\text{Al}_2\text{O}_3 \right\} + \frac{11570}{T} - 10.52
\] (12)

This correlation was based on experiments carried out at 1873 K as well as results reported by other researchers.\textsuperscript{[32]} Fig. 2 shows the phosphorus partition ratio calculated using the correlation (Eq. 12) proposed by Suito and Inoue, as a function of total iron content of the slag. The equilibrium phosphorus partition ratios achievable at 1923 K with typical basic oxygen steelmaking slags, free of MnO and CaF\textsubscript{2}, at 1923K, were recalculated using Eq. 12 and were found to be in the range of 250 – 350.

Based on the experimental results on MnO-bearing slags, Nakashima\textsuperscript{[57]} concluded the following.

- the activity coefficient of iron oxide, \(\gamma(\text{FeO})\), decreased with increasing \%\text{MnO} 
- dilution of CaO in the slag causes some reduction in \(\gamma(\text{CaO})\)
- presence of MnO caused marginal increase in \(\gamma(\text{P}_2\text{O}_3)\)
Fig. 2: Effect of MnO concentration of the variation of phosphorus partition ratio with %Fe<sub>i</sub><sup>[56]</sup>

Thus, the overall effect of the presence of MnO in steelmaking slag is a reduction in the equilibrium phosphorus partition ratio. This was realised by the previous workers, all of who advised against addition of manganese oxide to the BOF slag.

In 1970, Healy<sup>[58]</sup> combined the results of Scimar<sup>[59]</sup>, Schwerdtfeger and Engell<sup>[60]</sup>, Trömel and Schwerdtfeger<sup>[61]</sup> and Bookey <i>et al</i><sup>[62]</sup><sup>[63]</sup> to obtain a correlation that bears his name. Healy used a modified Flood-Grjotheim ionic treatment to obtain an estimate of the equilibrium phosphorus partition ratio as a function of composition and temperature of steelmaking slags.

\[
\log \left( \frac{\%P_2O_5}{\%P} \right) = \frac{22350}{T} - 21.0 + 7\log(\%CaO) + 2.5\log(\%FeO) \\
+ \{11\log N + 7\log K'_{CaO,sat} + 2.5\log K'_{FeO} - 8.5\log \Sigma \pm \} \quad (13)
\]

where, \( N^\circ \) = electrically equivalent ionic fraction
\[ K' = \text{apparent equilibrium constant for ionic reaction} \]
\[ \Sigma \pm = \text{total sum of charges per 100 gm of slag} \]

Eq. (12) was further simplified to –
\[
\log \left( \frac{\%P}{\%P} \right) = \frac{22350}{T} + 0.08 (\%\text{CaO}) + 2.5 \log (\text{Fe}_{\text{total}}) - 16 \pm 0.4 \quad (14)
\]

Eq. 14 has become extremely popular with steelmakers due to its simplicity and ease of calculation using parameters that are regularly measured in a steel plant.

However, it is seen in Fig. 3 that the phosphorus partition levels estimated using Healy’s correlation are higher than the that typically attained in industrial basic oxygen steelmaking of similar slag composition by a factor of 2 – 4. This indicates that the phosphorus distribution in industrial steelmaking processes remains far short of equilibrium.

![Graph comparing phosphorus partition ratio](image)

**Fig. 3:** Comparison of phosphorus partition ratio predicted by Healy’s correlation with that practically attained during steelmaking
4. **EXPERIMENTAL METHODS**

The present work included experiments of two types –

i) Intermediate sampling in a commercially running BOF

ii) Laboratory-scale experiments to determine equilibrium values

4.1 **Experiments in running BOF**

Intermediate sampling was necessary to establish the slag path and the variation of phosphorus partition ratio with refining time in commercial BOF operation. Owing to the absence of a sub-lance facility at the BOF shop where these experiments were carried out, the oxygen blow in the BOF was interrupted at pre-determined intervals for collection of samples. A cold, but dry, steel rod was immersed into the slag and rapidly withdrawn. This resulted in a chilled layer of solidified slag on the surface of the rod. Samples of steel were collected using the usual “lollypop” sampler. The volumetric flow rate of exhaust gas, and the concentrations of CO, CO₂, N₂ and O₂ therein, were continuously measured using on-line gas analysers.

Details of the sampling procedure have been described in Supplement #1. The particles of entrapped steel were removed by magnetic separation after the solidified slag was removed from the steel rod and crushed to fine powder using agate mortar. The steel and slag samples were then despatched for chemical analysis.

4.2 **Laboratory-scale experiments**

Experimental determination of equilibrium phosphorus partition ratio was carried out using an electrically heated horizontal tube furnace. The details of the furnace have been given in Supplement #2. Fig. 4 shows a schematic view of this furnace, including the gas supply connections.
Measured quantities of electrolytic iron and synthetic slag, both in powdered form, were placed in a refractory crucible and heated to the desired temperature. An inert atmosphere was maintained inside the furnace tube by a constant flow of purified argon. Once the desired temperature was attained, the sample was left for the planned equilibration time and then cooled fast by rapid withdrawal from the furnace hot zone. The layout of the gas cleaning arrangement and the selection of optimum equilibration time has been discussed in Supplement #2. It was important to restrict the rate of heating and cooling of the furnace tube to less than 3 K min$^{-1}$ in order to avoid the risk of tube fracture from thermal stress. The samples of steel and slag were subsequently separated from the crucible and subjected to detailed chemical analysis.

![Diagram of furnace setup](image)

**Fig. 4:** Schematic diagram of the high temperature furnace used for measuring the equilibrium phosphorus partition ratios

The detailed specifications of the high temperature furnace are listed in Table 2.
Experimental methods

Table 2: Details of the high temperature furnace

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum working temperature</td>
<td>1973 K (for continuous working)</td>
</tr>
<tr>
<td>Furnace tube material</td>
<td>Recrystallised alumina, dense-sintered</td>
</tr>
<tr>
<td>Diameter of furnace tube</td>
<td>( \phi 54 \text{ mm (I.D.)} ) / ( \phi 62 \text{ mm (O.D.)} )</td>
</tr>
<tr>
<td>Length of furnace tube</td>
<td>1200 mm</td>
</tr>
<tr>
<td>Uniform temperature zone</td>
<td>150 mm</td>
</tr>
<tr>
<td>End-cooling</td>
<td>Copper spiral for water circulation</td>
</tr>
<tr>
<td>Closing arrangement at the ends</td>
<td>Silicone rubber stopper</td>
</tr>
<tr>
<td>Type of thermocouple</td>
<td>B-type (Pt-6%Rh / Pt-30%Rh)</td>
</tr>
<tr>
<td>Thermocouple sheath</td>
<td>Recrystallized alumina</td>
</tr>
<tr>
<td>Heating element</td>
<td>Molybdenum disilicide</td>
</tr>
<tr>
<td>Crucible dimensions</td>
<td>( \phi 30 \times 35 \text{ mm} )</td>
</tr>
<tr>
<td>Crucible holder</td>
<td>94% MgO castable</td>
</tr>
</tbody>
</table>

The chemical compositions during the laboratory scale experiments were chosen to simulate the variation of slag chemistry during the blow in a BOF. The chemical compositions identified, sourcing and preparation of raw materials have been described in Supplement #2. The wustite used for preparation of the synthetic slags was synthesised in-house by reduction of hematite \( \text{(Fe}_2\text{O}_3 \) with electrolytic pure iron. A marginally excess quantity of iron powder was used to ensure that no hematite remained unreacted. Unreacted iron in the final product was removed by magnetic separation. Conversion of hematite to wustite was verified through X-ray diffraction of the product. Fig. 5 shows a typical XRD plot of the synthetic wustite used in this study. The positions corresponding to the peaks of wustite have been marked on the figure. The small peak at around 2.027 Å corresponds to elemental iron and represents a trace of unreacted metallic iron. Proportion of hematite or magnetite in the specimens tested was negligible.
4.2a Choice of crucible material

Several possibilities were explored for selecting the appropriate crucible material that could safely hold liquid steel and slag over the required duration. Table 3 shows the relative suitability of different materials for this purpose. In addition to the materials listed in Table 3, trials were also carried out using boron nitride (BN). Unfortunately, the BN crucibles were excessively reactive to molten slag containing CaO and iron oxide, and hence this material had to be rejected in spite of excellent mechanical stability up to 1923K. Trömel [33] had reported the use of rhodium crucibles under oxidising conditions, but also reported about partial dissolution of iron in rhodium, and vice versa. After considering all the factors, dense-sintered magnesia crucibles were finally selected for carrying out slag-metal equilibration.
### Table 3: Suitability of crucible materials

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Calcia (CaO)</th>
<th>Magnesia (MgO)</th>
<th>Spinel (MgO.Al₂O₃)</th>
<th>Platinum (Pt)</th>
<th>Alumina (Al₂O₃)</th>
<th>Molybdenum (Mo)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical strength</td>
<td>--</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>High temperature stability</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>Inertness towards molten slag</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>• High basicity</td>
<td>++</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>--</td>
<td>+</td>
</tr>
<tr>
<td>• High FeOₓ</td>
<td>+</td>
<td>–</td>
<td>–</td>
<td>++</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>• Low basicity</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>++</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Corrosion by liquid iron</td>
<td>++</td>
<td>++</td>
<td>+</td>
<td>--</td>
<td>++</td>
<td>--</td>
</tr>
<tr>
<td>Resistance to thermal shock</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>++</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Cost</td>
<td>–</td>
<td>++</td>
<td>–</td>
<td>--</td>
<td>++</td>
<td>–</td>
</tr>
<tr>
<td>Ease of availability</td>
<td>--</td>
<td>++</td>
<td>--</td>
<td>+</td>
<td>++</td>
<td>+</td>
</tr>
</tbody>
</table>

++ Strongly favourable  + Favourable  -- Strongly unfavourable  – Unfavourable

1 Resistance to thermal shock decreases with increased cyclic exposure to high temperature

### 4.3 Development of mathematical model

The activity of P₂O₅ in the slag samples, covered in the present work, were calculated using the correlations published earlier.⁴³ [⁴⁶] [⁵²] It was observed that the results differed widely from the measured values. Therefore it became necessary to develop a correlation that would successfully estimate the activity coefficient of P₂O₅ over the entire range of chemical composition investigated. The method of calculation and the mathematical treatment, adopted for this purpose, is discussed in Supplement #4.
5. RESULTS

5.1 Experiments in running BOF

The objectives of the experiments involving intermediate sampling in the BOF were two-fold:

i) Mapping of slag path in the BOF

ii) Determining the variation of phosphorus partition ratio along the blow

5.1a Mapping of slag path

The term “slag path” usually refers to the variation of slag composition with progress of reaction time in a metallurgical refining process. Knowledge of the BOF slag path assumes importance since the refining capability of the BOF slag, removal of phosphorus and sulphur in particular, depends strongly on its chemical composition. The slag path, observed through collection and analysis of the intermediate samples from BOF, has been described in supplement #1.

BOF slag consists primarily of CaO, SiO₂ and iron oxides. Therefore, in the absence of external additions of MgO, MnO, Al₂O₃, etc., the slag composition can be approximated by the CaO-FeO-SiO₂ ternary system. Fig. 6 shows the typical variations in FeO concentration and basicity (%CaO/%SiO₂) from the beginning of the refining process. It is seen clearly in the figure that, excepting the initial period, the basicity of the slag increases monotonically during the refining process. It should be noted here that the basicity shown in Fig. 6 has been derived from the overall chemical composition of the slag. Some of the samples at higher basicity may have contained some proportion of undissolved CaO. The actual CaO concentration in the liquid slag would, in such cases, be somewhat lower than that indicated in Fig. 6.
Fig. 6: Variation of FeO concentration and basicity of BOF slag during refining

The concentration of iron oxide increases during the initial part of the process and then starts to decrease. It reaches a minimum value at approximately 75% – 80% of the process and increases again towards the end. The high FeO concentration during the initial period corresponds to the ”soft blow” in the BOF when the rate of decarburisation remains low and iron is preferentially oxidised along with silicon. This is followed by a decrease in the FeO concentration that corresponds to an acceleration in the rate of carbon oxidation, typically after the liquid metal has been depleted of the dissolved silicon. Oxidation of carbon, during this period, attains a rate where the supply of oxygen through external injection becomes insufficient and oxidation proceeds by reduction of FeO.

Evidence in support of this reasoning is provided by Fig. 7, which shows the variations in silicon and carbon concentrations in the liquid metal phase. The continuous lines represent the concentrations calculated from mass balance
while the discrete markers show the measured values. It is seen from Fig. 7 that
the rate of oxidation of carbon reaches maximum after around 35% of the
refining process, and continues to remain so till around 80%. The rate of
oxygen consumption for decarburisation during this period exceeds the rate of
external oxygen supply, and this leads to a reduction in the FeO concentration
in slag.

![Graph showing metal composition vs refining time]

Fig. 7: Variation of silicon and carbon concentrations during refining

The relative proportion of supplied oxygen utilised for oxidation of carbon is
denoted as $\dot{O}_C$, which is defined numerically as

$$\dot{O}_C = \frac{\text{rate of oxygen consumption for decarburisation}}{\text{rate of oxygen supply from external sources}}$$  \hspace{1cm} (15)

A value of $\dot{O}_C$ greater than 100% indicates a situation where the rate of supply
of oxygen falls short of the rate of its consumption for decarburisation. In such
a situation, FeO in the slag acts as an auxiliary source of oxygen and hence its
concentration in the slag decreases.
Fig. 8 shows the variation in the utilisation of oxygen for decarburisation with progress of refining. It is seen from the figure that the demand of oxygen for decarburisation starts to increase sharply after approximately 40% of the refining is completed, and exceeds the rate of external supply at around 45%. This phenomenon roughly corresponds to a decrease in the FeO concentration in the slag. The rate of decarburisation starts to decrease after about 80% of the blow and a corresponding increase in the FeO concentration is evident from Fig. 6.

![Graph showing variation of oxygen utilisation for decarburisation during refining](image)

**Fig. 8: Variation of oxygen utilisation for decarburisation during refining**

### 5.1b Variation of phosphorus partition ratio

Fig. 9 shows the variation of phosphorus partition ratio with progress of refining in the BOF. The equilibrium partition ratios were calculated using the slag composition derived from mass balance and the Regular Solution model of Ban-ya. These results have been presented in Supplement #1. The period spanning from 35% to 60% of the refining time in a BOF is typically
characterised by low FeO concentration and increasing basicity of the slag. The phosphorus partition ratio, shown in Fig. 9, undergoes very small variation during that period. The equilibrium phosphorus partition ratio shows a similar behaviour. It appears that the compositional changes occurring in the BOF slag during this period exert opposing influences on the partition of phosphorus. The influence of basicity and FeO concentration, discussed in the subsequent sections, will explain this phenomenon further.

![Graph showing variation of phosphorus partition ratio during refining](image)

Fig. 9: Variation of phosphorus partition ratio during refining

5.2 Laboratory scale experiments

These experiments were carried out with the objective of determining the equilibrium phosphorus partition ratio achievable for different levels of basicity and FeO concentration in the slag. Results were obtained at two different temperatures, 1873 K and 1923 K. The chemical analyses of the slag and steel samples have been presented in Supplements #2 and #3.
5.2a Effect of basicity on phosphorus partition ratio

Fig. 10 shows the effect of basicity on the equilibrium phosphorus partition ratio, at 1873 K and 1923 K.

Fig. 10: Influence of basicity on equilibrium phosphorus partition ratio  
(a) at 1873 K  
(b) at 1923 K
These results have been partly presented in supplements #2 and #3, which cover the results corresponding to less than 15 mass% FeO and 15 – 25 mass% FeO, respectively. A more comprehensive treatment has been attempted in this section, covering the entire range of 5 – 35 mass% FeO investigated during the present work.

The apparent scatter in the figures is primarily the result of variation in FeO concentration, at any given basicity. Fig. 10 shows that increase of basicity up to around 2.5 causes an increase in the equilibrium phosphorus partition ratio. Thereafter, the rate of increase becomes less pronounced and the partition ratio remains practically unchanged at basicities exceeding 2.6 – 2.7. The trends at 1873 K and 1923 K are very similar in this respect. In other words, increase of basicity beyond 2.6 – 2.7 has no effect on the equilibrium phosphorus partition ratio.

5.2b  Effect of iron oxide concentration on phosphorus partition ratio

It is already seen in section 5.1 that FeO concentration, together with basicity, are the most significant variables characterising the chemical composition of BOF slag. The influence of FeO concentration on the equilibrium phosphorus partition ratio, at 1873 K and 1923 K, has been shown in Fig. 11. Similar to the sub-section 5.2a, the results presented here cover the entire range of chemical composition studied, incorporating the results contained in the supplements #2 and #3. Even though the results have been classified in terms of basicity, for either temperature, variations of basicity within the individual ranges have led to some scatter in the results.

Fig. 11(a) shows that increase of FeO concentration initially enhances the equilibrium phosphorus partition ratio but the trend is reversed beyond a certain level. Similar behaviour is seen in Fig. 11(b). The FeO concentration
corresponding to this transition varies with basicity and temperature but remains within the overall range of 15 – 20 mass%.

Fig. 11: Variation of equilibrium phosphorus partition ratio with FeO concentration in slag; (a) at 1873 K  (b) at 1923 K
5.2c Dissolution of MgO in steelmaking slag

The slag sample, at the end of each experiment, was saturated with MgO due to dissolution from the magnesia refractory crucible. Since all the experiments were carried over equilibration time of at least 8 hours and, as discussed in supplement #2, exposure for 6 hours was sufficient to saturate the slags with MgO, the concentrations measured in the slag samples are taken as the saturation solubility of MgO in the corresponding slags in equilibrium with solid MgO. Fig. 12 shows the effect of basicity on the dissolution of MgO into CaO-FeO-SiO$_2$ slag containing P$_2$O$_5$, as well as MgO.

![Graph showing MgO solubility vs. basicity](image)

**Fig. 12: Influence of basicity on the solubility of MgO in slag**

The results shown in Fig. 12 have been classified on the basis of FeO concentration. In spite that, multiple values are seen corresponding to any particular basicity. Variation of FeO concentration within the individual bands is the primary reason behind this scatter.
At basicities less than 2.0, the solubility of MgO decreases with increasing basicity. At higher values of basicity, however, dissolution of MgO is less affected and attains constant value beyond basicity of 2.6 – 2.7. This behaviour is seen at 1873 K as well as at 1923 K. However, the exact value of basicity corresponding to this transition, and the saturation solubility of MgO at higher basicities, depends upon temperature and the concentration of FeO. The solubility of MgO at lower concentrations of FeO (less than 20 mass%) is approximately 4 mass% at 1873 K and 6 mass% at 1923 K. Increase in the average FeO concentration from 15 – 20 mass% to 25 – 30 mass% increases the solubility of MgO by 2.5 – 3.0 mass%.

5.2d Variation of phosphorus partition ratio with MgO concentration

Fig. 13 shows the variation of equilibrium phosphorus partition ratio with MgO concentration in the slag. The figure, at first glance, appears to indicate a strong negative effect of MgO on phosphorus partition. However, it is important to mention here that the MgO concentration of each sample shown in Fig. 13 corresponds to the saturation solubility value, which in itself is strongly influenced by basicity. Therefore, the trend shown in Fig. 13 should not be taken as the true influence of MgO concentration on equilibrium phosphorus partition ratio.
Fig. 13: Variation of phosphorus partition ratio with MgO concentration

5.3 Estimation of $\gamma(P_2O_5)$

Fig. 14 shows a comparison of the values of $\gamma(P_2O_5)$, obtained in the present work, with the values estimated through the use of equations (8), (9) and (11). The two broken lines represent deviation from the measured values by two orders of magnitude, on either side. The activity coefficients were obtained in the present work from the measured chemical compositions of slag and steel, through the use of Eq. 16.

$$\gamma(P_2O_5) = \frac{K_{P}\cdot[^{\%}P]^2\cdot[^{\%}O]^5\cdot f_{P}^5}{X_{P_2O_5}} \quad (16)$$

The interaction parameters, used for calculation of the activity coefficients of phosphorus and oxygen, were obtained from standard sources.\textsuperscript{65}

$$\log f_{P} = \sum e_{P}^i \cdot [\%] \quad (17a)$$

$$\log f_{O} = \sum e_{O}^i \cdot [\%] \quad (17b)$$
The values of $f_p$ and $f_o$ were obtained within the range of $1.01 - 1.05$ and $0.912 - 0.996$, respectively.

It is seen in Fig. 14 that the differences between the calculated and measured values are largest in the case of the correlation proposed by Turkdogan and Pearson. The correlation of Suito et al. provides the closest agreement but still deviates from the measured values by more than one order of magnitude. Derivation of a new correlation for estimation of $\gamma(P_2O_5)$ was attempted with the slag chemistry expressed in terms of mass pct., mole fraction, ion fraction and optical basicity. The correlation in terms of ionic fractions led to the best agreement with experimental measurements and the results are shown in Fig. 15.

$$\log \gamma(P_2O_5) = -8.172X_{Ca^{2+}} - 7.169X_{Fe^{2+}} - 1.323X_{Mg^{2+}} + 1.858X_{SiO_4^{4-}} + \frac{340}{T} - 11.66$$  \hspace{1cm} (18)
Fig. 15: Comparison of measured $\gamma(P_2O_3)$ values with the correlation developed in the present work
6. DISCUSSIONS

6.1 Phosphorus partition in commercially running BOF

Fig. 9 has clearly shown that the phosphorus partition ratio practically attained during steelmaking in a commercial BOF remains significantly lower than the equilibrium values. The deviation from equilibrium, at any stage of the refining process, can be expressed in terms of the “approach to equilibrium” which is defined as the ratio –

\[
\text{Approach to equilibrium} = \frac{\text{phosphorus partition ratio attained}}{\text{equilibrium phosphorus partition ratio}}
\] (19)

The variation of this parameter during the refining process has been illustrated in Fig. 16. It is seen that the partition of phosphorus varies within the range of 35 – 60%, but continuously decreases with the progress of refining. The rate of decrease becomes particularly significant during the last quarter of the process.

![Graph showing the approach to equilibrium over refining time.](image)

Fig. 16: Deviation of phosphorus partition ratio during basic oxygen steelmaking from the equilibrium values
This behaviour is most likely the result of a number of factors.

(a) The basicity of the slag (Fig. 6) maintains a continuously increasing trend onward from 20 – 25% of refining time. The thermodynamic software ThermoCalc™ was used to estimate the phases present in the slag, and their relative proportions. The results have shown that the slag is likely to contain some solid phases at basicity of 2.5 and higher. The presence of the second phase has been reported to reduce the overall fluidity of the BOF slag. [66]

(b) It is further seen in Fig. 6 that the FeO concentration in the slag decreases during 40 – 80% of the process, leading to a situation that is commonly known as “dry slag”. Such a slag is characterised by poor fluidity. It follows naturally that the reduced fluidity would retard the kinetics of dephosphorisation, which manifests in decreasing values of the “approach to equilibrium”. The FeO concentration in the slag does increase during the last 20% of the refining process but it appears that the resulting change in viscosity is not sufficient to increase the “approach to equilibrium” substantially.

(c) In addition, Fig. 7 shows that the carbon concentration in the liquid metal decreases to less than 1 mass%, compared to the initial level of more than 4 mass%, during the last 20% of the refining time. The rate of decarburisation is also reduced during this period, as suggested by Fig. 8. This reduces the extent stirring in the BOF, thereby exerting a negative effect on the kinetics of the refining reactions. As a result, the “approach to equilibrium” suffers.

(d) The overall slag composition shows a very high level of basicity towards the end of the refining process (Fig. 6). The mathematical model used for estimation of the equilibrium phosphorus partition ratio, discussed in subsection 5.1b, assumes the entire quantity of CaO to be in solution.
However, thermodynamic calculations, as well as reports from other workers \([13][67][68][69][70][71]\) indicate that some amount of CaO is likely to remain undissolved in steelmaking slags, particularly at high basicities. Also, the short refining duration in a commercial BOF may not allow sufficient time for complete dissolution of lime. Therefore, the actual liquid slag probably contains lower concentration of CaO than what is indicated by the gross chemical composition. The phosphorus partition ratio would naturally be lower in such a situation.

It follows from these discussions that phosphorus partition in a commercial BOF remains low primarily because of kinetic constraints, particularly towards the end of the refining process. Significant improvement in the extent of dephosphorisation appears possible if the “approach to equilibrium” can be enhanced, even without any further change in the thermodynamic limits.

### 6.2 Equilibrium phosphorus partition ratio

It is widely reported in literature that the phosphorus partition ratio increases with increasing basicity of slag. \([14][15][12][72]\) However, in course of the present study, it was seen that this is only partially true. Phosphorus partition ratio does increase with basicity, but only when the basicity is low. At higher basicities, phosphorus partition ratio remains practically constant. The level of basicity corresponding to this transition and the value of the partition ratio at high basicities are functions of temperature and iron oxide content.

Fig. 17 and Fig. 18 show the effect of basicity on the activity and activity coefficient, respectively, of \(P_2O_5\). The details of the calculation have been reported in supplements #2 and #3. It is clearly seen that the activity of \(P_2O_5\) remains practically constant at basicities of 2.5 and above. Similar trend is seen for the activity coefficient of \(P_2O_5\) as well. This indicates that the slag probably becomes heterogeneous at such high basicities. If two phases exist in
equilibrium, it follows from the principles of thermodynamics that the chemical potential of any constituent must remain constant across the two-phase region.

It has been reported that steelmaking slag, at such high levels of basicity, contains solid phosphate or silico-phosphate of calcium. \cite{31} \cite{55} \cite{67} \cite{73} Knuppel and Oeters \cite{55}, as well as Hasegawa et al. \cite{73} had observed the activity of $P_2O_5$ in CaO-$P_2O_5$-$Fe_2O$ slags to remain constant across the multi-phase region, in spite variations in the overall chemical composition. Therefore, it can be safely concluded that the slag, in samples with basicities exceeding 2.5, is heterogeneous in nature and hence the activity of $P_2O_5$ is unaffected by change in basicity.

It is seen in Fig. 19 that the activity of oxygen too follows a trend similar to that of $P_2O_5$, and remains unchanged at basicity greater than 2.5. Taking these into consideration, it follows that the phosphorus partition ratio would obviously remain constant at the higher levels of basicity.

![Graph](image)

**Fig. 17:** Variation of activity of $P_2O_5$ with basicity
Fig. 18: Variation of the activity coefficient of $\text{P}_2\text{O}_5$ with basicity

Fig. 19: Variation of oxygen activity with basicity
The effect of FeO concentration on the equilibrium phosphorus partition ratio, as observed in course of the present study, is largely similar to that reported by others. The partition ratio initially increases with rise in FeO concentration, then reaches a crest and finally shows a decreasing behaviour. The variations at 1873 K and 1923 K are similar in nature. However, the exact level of FeO concentration, corresponding to this transition, shows subtle variations depending on the basicity of slag and temperature.

Fig. 20 shows the effect of FeO concentration on the activity of $P_2O_5$. The apparent scatter in the results is due to variations in basicity, for any particular level of FeO concentration. The trends are similar at both 1873 K and 1923 K, even though the numerical values differ. Increase of FeO concentration upto 15 mass% causes a decrease in the activity of $P_2O_5$. Within the range of 15 – 20 mass% FeO, the behaviour of $a(P_2O_5)$ changes and it starts to increase as the FeO concentration increases beyond 20 mass%.

![Fig. 20: Variation of activity of $P_2O_5$ with FeO concentration](image)
The trend shown in Fig. 20 corresponds to an inverse image of the variation of equilibrium phosphorus partition ratio with FeO concentration, at either temperature. Increase in \( a(P_2O_5) \) beyond 20 mass\% FeO is reflected in a lowering of the phosphorus partition ratio, as illustrated in Fig. 11.

6.3 Solubility of MgO

It has been explained in sub-section 5.2c that saturation of the slag with MgO was inevitable, even though the presence of MgO not initially planned. It is seen from Fig. 12 that the solubility of MgO decreases with increasing basicity and then attains a nearly constant value, irrespective of temperature and FeO concentration. This behaviour can be explained, at least to some extent, by the fact that CaO and MgO are both basic oxides. But CaO is a stronger base and tends to replace MgO in liquid slag. Increase of basicity, therefore, reduces the solubility of MgO.

It is also known that the slag ceases to remain homogenous if the basicity exceeds a level of 2.5 – 2.6. The excess CaO forms solid precipitates of phosphates and/or silico-phosphates of calcium, and the true basicity of the liquid fraction of the slag undergoes very little variation. This may be the reason behind the apparently constant solubility of MgO at higher basicities.

The equilibrium solubility of MgO in CaO-SiO\(_2\)-FeO-P\(_2\)O\(_5\)-MgO slag was calculated at 1873K and 1923K using the thermodynamic software packages ThermoCalc\textsuperscript{TM} and FACTSage\textsuperscript{TM}. Fig. 21 shows the results, along with the experimentally measured values of MgO solubility. The results from the thermodynamic packages have been computed for a typical CaO-SiO\(_2\)-FeO-P\(_2\)O\(_5\)-MgO slag containing 4 – 5 mass\% P\(_2\)O\(_5\), and FeO concentrations of 15 and 20 mass\%, at temperature of 1873 K. It is seen very clearly from Fig. 21 that the calculations from both these packages indicate a nearly constant value
of the solubility of MgO, at higher levels of basicity, and are in agreement with the measured values.

![Graph](image)

**Fig. 21:** Effect of basicity on solubility of MgO

Calculated using ThermoCalc™ and FACTSage™

(The two lines for each package correspond to FeO concentrations of 15 mass% and 20 mass%)

### 6.4 Correlation for estimation of P₂O₅ activity coefficient

It is seen from Fig. 14 that the correlations proposed earlier by Turkdogan and Pearson, [43] Suito *et al.* [46] and Turkdogan [52] are only partially successful in predicting the activity coefficient of P₂O₅ in steelmaking slags. In comparison, the correlation developed during the present work allows better estimation of \( \gamma(\text{P}_2\text{O}_5) \). Fig. 15 clearly shows that Eq. 18 predicts the activity coefficient of P₂O₅ within one order or magnitude of the measured values.

The correlation of Turkdogan and Pearson was published in 1953, at a time when the interaction coefficients of most solutes in liquid iron were not
published. This was probably the reason that prompted these authors to assume ideal Henririan behaviour of the solutes in liquid iron. Unfortunately, the same assumption persisted in the subsequent work of Suito et al. and Turkdogan. Thus their results suffer from the risk of error since the calculation of $\gamma(P_2O_3)$ involves the activity coefficients of phosphorus and oxygen raised to the second and fifth powers, respectively. This is one of the likely factors causing the large deviation of calculated values from experimental measurements.

In addition, the correlation developed in the present work is based on a wider range of chemical composition than Eq. 8 and 9. The ranges of CaO concentration (in molar fraction) for Eq. 8, 9 and 18 are 0.5 – 0.61, 0.32 – 0.47 and 0.19 – 0.6, respectively. The corresponding ranges of FeO concentration (in molar fraction) are 0.11 – 0.22, 0.2 – 0.29 and 0.05 – 0.36. The investigations of Turkdogan and Pearson as well as of Suito et al. considered the variation of SiO$_2$ concentration over a narrow range. However, the present work took into consideration SiO$_2$ concentration over the range of 0.09 – 0.3. This may also explain the better agreement between the measured values of $\gamma(P_2O_3)$ and those calculated through the use of Eq. 18. A detailed discussion on this has been included in supplement #4.
7. CONCLUSIONS

The present work was aimed at establishing the thermodynamic limit of phosphorus partition ratio achievable during basic oxygen steelmaking. The results obtained during the investigations lead to the following conclusions.

1) The phosphorus partition ratio attained in commercial basic oxygen steelmaking varies from 35 – 60% of the equilibrium value. The deviation from equilibrium, excluding the initial period of slag formation and the dry slag period, usually increases with progress of the refining process.

2) Enhancement of the phosphorus partition ratio, particularly towards the end of the refining time, is hindered primarily by kinetic constraints. Reduction in the rate of dephosphorisation, due to changes in the physico-chemical conditions in the liquid metal and slag, lead to increase in the deviation from equilibrium towards the end of the process. The thermodynamic limit is fairly high and it is possible to significantly improve the extent of dephosphorisation by enhancing the kinetics, even without any change in the equilibrium phosphorus partition ratio.

3) Increase of basicity of the slag improves phosphorus partition ratio only upto a level of %CaO/%SiO₂ = 2.6 – 2.7. Equilibrium phosphorus partition ratio is practically constant at higher levels of basicity. The apparent lack of variation results from the fact that the activities of both P₂O₅ and oxygen are nearly independent of basicity for %CaO/%SiO₂ = 2.5 and higher.

4) The equilibrium phosphorus partition ratio initially increases with rise in FeO concentration in the slag but changes to a negative trend at higher levels. The FeO concentration corresponding this transition is a function of temperature and basicity.
REFERENCE


41. B. Deo: Indian Institute of Technology Kanpur (India), private communication, 2002.

42. A. Ghosh: Independant consultant, formerly at Indian Institute of Technology Kanpur (India), private communication, 2003.


64. S. Ban-ya: *ISIJ International*, vol. 33(1), 1993, pp. 2-10.


