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A review of phosphorus partition relations for use in basic oxygen steelmaking

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A Review of Phosphorus Partition Relations for Use in Basic Oxygen Steelmaking

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Abstract

Phosphorus removal in basic oxygen steelmaking (BOS) is a significant problem for integrated steelmakers. Phosphorus removal is required due to its deleterious effect on the mechanical properties of steel. However, this is progressively becoming more difficult due to the increasing phosphorus content of many iron ores.

Many studies have investigated dephosphorisation and published empirical phosphorus partition (LP) equations for a range of conditions. The structure of these equations have been used to develop a new partition relation that allows the effect of minor slag constituents such as TiO₂, Al₂O₃ and V₂O₅ on steel dephosphorisation to be tested.

Al₂O₃ was found to have a weak negative effect on the measured LP, except at the lower oxygen potential range tested, where a positive correlation was observed. Increasing TiO₂ and V₂O₅ contents were found to decrease the measured LP, however these correlations became less prevalent at the higher oxygen potential ranges tested.

Keywords: basic oxygen steelmaking (BOS), dephosphorisation, phosphorus partition, slags.
Definitions and Nomenclature

( ) = in slag solution

[ ] = in liquid iron solution

%\(i\) = mass % of \(i\)

(%\(\text{Fe}\)) = mass% of total Fe in slag phase

(%\(\text{Fe}_2\text{O}\)) = mass% of total Fe in slag phase as \(\text{Fe}_2\text{O}\)

\(M_i\) = molecular weight of oxide \(i\)

\(R\) = universal gas constant, 8.314 JK\(^{-1}\)mol\(^{-1}\)

\(N\) = mole fraction of oxide or ion

\(\gamma_i\) = \(L_P\) calculated by model

\(\hat{\gamma}_i\) = \(L_P\) calculated by linear regression line through results to the origin

\(\Lambda\) = optical basicity of slag

\(\Lambda_i\) = optical basicity of single oxide of species \(i\)

\(T\) = Temperature in K
1. Introduction

The deleterious effect of phosphorus on steel properties and the increasing content of phosphorus in iron ores are key drivers in the ongoing research in steel dephosphorisation. Phosphorus removal in the steelmaking process can be represented by the ionic or molecular reactions given in equations (1) and (2), respectively. These equations show phosphorus activity in the metal, oxygen potential and slag basicity play a critical role in phosphorus removal from steel.

\[
\begin{align*}
&[P]+\frac{5}{2}[O]+\frac{3}{2}O^{2-}= PO_{4}^{3-} & (1) \\
&2[P] + 5[O] = (P_{2}O_{5}) & (2)
\end{align*}
\]

Temperature also has a significant effect on phosphorus removal as shown by the Gibbs free energy of reaction (2) as given in equation (3).

\[
\Delta G^{o} = -832384 + 632.65T \text{ Jmol}^{-1} & (3)
\]

Considering equations (1) and (2), phosphorus removal from iron and steel is promoted by high \([P]\) activity, high oxygen potential \([O]\) and high basicity \((O^{2-})\). From equation (3) it can be seen that lowering temperature increases the thermodynamic driving force for phosphorus removal by decreasing \(\Delta G^{o}\).

Unfortunately, for integrated steelmakers, there is no step in the process where all of these conditions are met. Dephosphorisation is typically carried out in either hot metal pretreatment (low temperature, high \(O^{2-}\) but low \(pO_{2}\)) or in the basic oxygen steelmaking (BOS) converter (high temperature, high \(O^{2-}\) and high \(pO_{2}\)). The temperature of the BOS process is dictated by other factors than phosphorus control or partition. If ultra-low phosphorus steel is required, it is also possible to remove phosphorus from the steel through secondary refining processes.

For dephosphorisation it is known that the controlling oxygen potential represents a dynamic relation between the iron oxide in the slag and the carbon in the hot metal/steel. Operational BOS models predicting phosphorus removal often approximate this to a factor that represents the slag iron oxide content such as \(Fe_{O}\), or \(Fe_{r}\).
There are many approaches for evaluating slag basicity that range from empirical plant relations to those founded on thermodynamic and slag structure fundamentals. A full review of these is beyond the scope of this study. The use of the simple V-ratio relation (equation 4) or similar composition acid-base approaches (e.g. equation (5)) is well established by steelmakers. Optical basicity (Λ), as given in equation (6), offers a relatively simple and convenient approach to calculating a single number that represents slag basicity. Optical basicity takes into account the effect of minor slag constituents (such as TiO₂ or V₂O₅) on the basicity.

\[
V = \frac{\% \text{CaO}}{\% \text{SiO}_2} \quad \text{(4)}
\]

\[
B = \frac{N_{\text{CaO}} + N_{\text{MgO}}}{N_{\text{SiO}_2} + 1.05N_{\text{AlO}_1.5}} \quad \text{(5)}
\]

\[
\Lambda = N_i \Lambda_i + N_j \Lambda_j + \ldots \quad \text{(6)}
\]

Dephosphorisation has been studied extensively, with over 90 different empirical correlations of dephosphorisation equilibria or effective equilibria²,³,¹⁹-⁹⁴. These empirical relations are often useful for optimising dephosphorisation in the BOS. However, they are often limited to specific temperature and compositional ranges, or kinetic conditions for which they were developed. Relations developed using industrial data are further limited by being only estimates of the effective equilibria reached under the specific kinetic regime and furnace type for which they were developed. The kinetics of phosphorus removal in BOS process can be affected by, amongst other factors, bath stirring, lance height and design, blow time, and physical properties of slag.

The aim of this study is to develop a phosphorus removal relation that can be used to isolate the effect of minor slag constituents (e.g. TiO₂, Al₂O₃ and V₂O₅). Although published empirical phosphorus partition models are often limited to the conditions for which they were developed, their structure and component coefficients can be used to inform the basicity and oxygen potential representations for a new model. Thus, a two stage approach to model development has been used. In the first stage, published phosphorus partition relations will be assessed using a large industrial dataset to determine which equation best represents the data. In the second stage the focus is to develop a new equation,
determining which representations of temperature, oxygen potential and slag basicity are most appropriate by regression against the large industrial dataset. While this new $L_p$ relation will suffer similar limitations to other plant data derived relations, it will be optimised for the industrial dataset used in this study, thus it may enable testing of the thermodynamic and kinetic effects of minor slag constituents on dephosphorisation.

2. Selection and Filtering of Industrial Data
A filtered dataset of steel and slag compositions, and processing conditions was collated for 11340 heats (dataset 1) from the BlueScope Port Kembla BOS plant. Arc optical emission spectroscopy, sub-lance EMF [O] and X-ray fluorescence were used to obtain compositional data for steel and slag samples, respectively. Samples were obtained routinely via a sub-lance (metal) and from a chill/dip sample (slag). The dataset does not include any heats with incomplete records or unusual processing conditions, including:

- Incomplete data for heat duration, temperature, slag or metal compositions.
- Unknown slag mass due to either de-siliconisation or high quantities of slag remaining in the converter from the previous blow.
- Heats with high pO$_2$ due to re-processing of steel from secondary refining.

A model cannot be accurately assessed against the dataset it was fitted to, as it is likely to outperform models not fitted to the data. Thus, a calibration/fitting dataset and an independent test were required. Consequently, dataset 1 was split arbitrarily into dataset 2 (11274 heats for tuning/fitting the models) and 3 (66 heats for assessing the performance of the model). The larger dataset was used for fitting the models to maximise their fit across a wide range of operating conditions.

3. Methodology and Results
3.1 Evaluation of Published Phosphorus Partition ($L_p$) Equations
The limits of phosphorus removal are given by the dephosphorisation equilibria or effective equilibria. These may be represented in several ways, such as equilibrium constants, phosphate capacities or different forms of the phosphorus partition ($L_p$). In this study the effective equilibria is defined by the $L_p$, as defined in equation (7). Where equations from
other studies are presented, any (effective) dephosphorisation equilibrium term has been converted to \( L_p \) as given in equation (7).

\[
L_p = \frac{\%P}{\%P} \quad (7)
\]

Thirty six published \( L_p \) equations (Table 1) were selected for testing from over 90 published \( L_p \) equations collated for this study\(^2\),\(^3\),\(^{19-94,96}\). Equations chosen for further evaluation were selected if they satisfied one or more of the following criteria:

- Recently published (2000 onwards) using either laboratory or industrial data.
- The \( L_p \) equation was derived using industrial data.
- The \( L_p \) equation included minor BOS slag constituents (e.g. TiO\(_2\), Al\(_2\)O\(_3\), and V\(_2\)O\(_3\)).
- The \( L_p \) equation included optical basicity as an input, allowing the effect of minor slag constituents to be easily incorporated.

Equations were disregarded using the following criteria:

- The \( L_p \) equation included slag additions no longer used for environmental reasons (CaF\(_2\), Na\(_2\)O).
- The \( L_p \) equation had no temperature adjustment term.
- The \( L_p \) equation has since been reviewed and updated.

The thirty six models selected (equations 10-46 in Table 1) all used common representations of basicity and oxygen potential to predict the final \( L_p \). The \( L_p \) equations were evaluated against dataset 3. Performance of the \( L_p \) equations was evaluated by comparing the coefficient of determination \( (R^2) \) for the predicted against measured \( L_p \) values when the line of best fit was constrained to pass through the origin, as calculated by equation (8).

\[
R^2 = \frac{\sum(y_i)^2 - \sum(y_1 - y_i)^2}{\sum(y_i)^2} \quad (8)
\]

The ten models with the highest \( R^2 \) are shown in Figure 1 and Table 2. From Figure 1 and Table 2, it was found that of the selected published models in Table 1 (equations 10-46), models (32 and 18), and were found to have the highest \( R^2 \) value when evaluated against dataset 3. These ten models use (%Fe\(_{\text{O}}\), (%FeO), [%C] or combination of to represent oxygen potential. None of the models utilising the EMF [%O] (23, 24, 27, 29, 34, 36, 38) were ranked in the top 10.
3.2 Development and Testing of a New Phosphorus Partition Model

Numerous methods of representing the oxygen potential ([O], [C], total slag Fe or a combination) and basicity (optical basicity, basicity ratios or various lime equivalents) exist as shown by the published \( L_p \) equations in Table 1. In order to test the best representation for each of the key variables, a series of new \( L_p \) models were developed, as shown in Table 3 and Figure 2. The first set of models was used to find the best representation of oxygen potential (equations 47-49 in Table 3). This was followed by a series of equations (50-55) used to examine the different representations of basicity. Each equation in Table 3 was of the general form:

\[
\log L_p = \sum A_i(basicity \ term \ i) + \frac{B}{T} + \sum C_i(oxygen \ potential \ term \ i) + D
\]

(9)

where the coefficients \( A_i \), \( B \), \( C_i \) and \( D \) used in each model were determined using a root mean square minimisation approach on dataset 2. The new models were tested on dataset 3 and the \( R^2 \) values (Table 3) were calculated and compared to the published models.

All of the \( L_p \) models were developed assuming the measured \( L_p \) had an inverse relationship with temperature as shown by the majority of models in Table 1. In order to examine the best representation of oxygen potential (slag \( \text{Fe}_\text{t} \), \( \log[O] \) and \( [C] \)), the basicity was assumed to be defined by the V-ratio aim (equation (4)) in models (47-49). Model (49), which used a combination of \( \log(\text{Slag \%Fe}_\text{t}) \) and the final \( [\%C] \) was found to have the highest \( R^2 \) value for dataset 3. Thus, the oxygen potential representation from model (49) was used in subsequent models.

Various basicity representations (V-ratio aim, V-ratio measured, \( (\%\text{CaO}) \), \( \log(\%\text{CaO}) \), \( (\%\text{CaO})_{\text{equivalent}} \), and \( \Lambda \) were tested used in the \( L_p \) models given by equations (50-55, Table 3). A comparison of these different \( L_p \) models (50-55) found model (53) had the highest \( R^2 \) for dataset 3 using \( \log(\text{V ratio} - 0.165(\%\text{MgO})) \) to represent slag basicity.
3.3 Assessing the Effect of Minor Slag Constituents on the Measured $L_P$

To help assess the effects of minor slag constituents, dataset 1 was split into narrow ranges of temperature, basicity and oxygen potential, producing 27 small datasets. The basicity and oxygen potential terms from $L_P$ model (53) were used due to the model’s degree of fit to the industrial data. The three largest datasets (292, 1774 and 3253 heats respectively) were selected for further testing, where these datasets are defined in Table 4. Constraining the data to these narrow ranges of temperature, basicity and oxygen potential allowed evaluation of correlations between the measured $L_P$ and minor slag constituents (TiO$_2$, Al$_2$O$_3$ and V$_2$O$_5$). The effects of (TiO$_2$), (Al$_2$O$_3$) and (V$_2$O$_5$) on the measured $L_P$ were plotted in Figure 3.

The slag Al$_2$O$_3$ content was found to have a negative effect on the measured $L_P$ at higher oxygen potentials in the range 0.81-0.93 (datasets 5 and 6, Table 4). At the lower oxygen potential range of 0.75-0.81 (dataset 4, Table 4) Al$_2$O$_3$ was found to correlate with increasing $L_P$ (Figure 3b). The TiO$_2$ and V$_2$O$_5$ content were both found to have negative effects on the $L_P$ (see Figure 3 a) and c)).

4. Discussion

4.1 Evaluation of Published Phosphorus Partition Relations

The published models all gave a low $R^2$ value when compared against dataset 3 (Figure 1 and Table 2). This may be expected for a variety of reasons, including:

- Laboratory equilibrium $L_P$ models often have poor performance when applied to industrial datasets due to the non-equilibrium nature found in many studies, including a recent work by Assis and Fruehan$^{24}$. This is unsurprising and is due to varying kinetic conditions (e.g. changing slag mass due to hot metal [Si], differences in blowing practice between plant operators, changing stirring conditions with lining and lance wear). As industrial phosphorus removal is often kinetically limited, laboratory models developed using equilibrium data (models 11, 22 and 31), may over-predict the actual $L_P$ achieved.
- $L_P$ models developed using kinetically limited, non-equilibrium industrial data will likely be plant specific due to the significant variation in the effective equilibria achieved under different kinetic conditions and operating practices. Thus, industrial $L_P$ models are likely to have a limited fit to other industrial datasets.
• Limitations of empirical models constraining their applicability to the slag and metal composition range from which they were developed. Many heats in dataset 3 may fall outside the suitable composition ranges for some of the published models.

• Different sampling methods may have increased variation in industrially measured \( L_P \). Slag and metal sampling can either be done simultaneously via a sub-lance, or a chill/dip sample of slag may be taken up to 10 minutes later during tapping. Irregular sampling patterns will introduce more variability into the measured \( L_P \) as the dephosphorisation reaction can continue to occur during the interval between sampling of the metal and slag. The other issue is how representative slag sampling via the sub-lance is vs. chill/ dip sampling.

Dephosphorisation is a heterogeneous reaction and it is generally considered that it is the oxygen potential at the metal-slag interface that is important for the reaction. For the current study, this can be considered to be a function of the (%Fe\(_{l}\)), [\%C] or a combination of both. The interfacial oxygen potential has been extensively studied\(^4, 5, 10-13, 97-100\). It is generally accepted it is controlled by a combination of both the metal and slag phases in highly stirred conditions. This oxygen potential can be represented as a balance between reactions (or equivalent slag metal reactions with oxygen in the gas phase) in equations (56) and (57).

\[
(\text{Fe}_x\text{O}_y) = x\text{Fe}_{(l)} + y[O] \quad (56) \\
[C] + [O] = \text{CO}_{(g)} \quad (57)
\]

Recent work by Gu et. al.\(^98\) focussed on iron droplet reactivity in a steel-slag-gas emulsion found dephosphorisation of the droplets was limited by mass transport in the metal phase. This is a relatively new and interesting finding and is the subject of much ongoing research.

Given the current understanding of dephosphorisation and the weight of literature suggesting the optimum representation of oxygen potential in the \( L_P \) models would be a combination of [\%C] and (%Fe\(_{l}\)), this approach was utilised for developing the new \( L_P \) models in Table 3. Further, on review of the published models (10-46), models (32) and (18), utilising this approach, were found to have the highest \( R^2 \) for dataset 3.
In the future inclusion of kinetic terms that represent the degree of mixing or droplet generation in response to blowing regimes or other may improve the fit ($R^2$) of the $L_p$ models, however this is beyond the scope this study.

The majority of the 10 models with the highest $R^2$ values only considered the slag compositional effects of CaO, MgO, Fe$_3$O and P$_2$O$_5$ on $L_p$. However, the high $R^2$ values of models (22, 11 and 31) also incorporated MnO, Al$_2$O$_3$, TiO$_2$, V$_2$O$_5$ and SiO$_2$, suggesting these oxides may also have a significant effect on the $L_p$. Hence, further investigation into the effect of these oxides and minor slag constituents on the $L_p$ may be required.

4.2 Evaluation of New Phosphorus Partition Relations

A series of new models (47-55) were developed and fitted to dataset 2 to test the effect of different representations of oxygen potential and basicity on the comparison between calculated and measured phosphorus removal. The performance of the models was assessed using the $R^2$ value when tested on dataset 3. The highest $R^2$ value achieved by both the published and new models was 0.975, using models (32) and (53). Unsurprisingly both of these models have very similar representations for basicity and oxygen potential. Model (53) has the advantage of incorporating the effect of MgO. Steelmakers routinely add MgO as dolomite to protect the BOS refractories. Incorporating MgO in the model allows for any effect of this addition on phosphorus removal to be determined.

The effects of MnO, P$_2$O$_5$, Al$_2$O$_3$, V$_2$O$_5$ and TiO$_2$ were not included in any of the new $L_p$ models developed, with the exception of the models using an optical basicity term. However, the high $R^2$ values of the published models incorporating these oxides, models (22, 11 and 31), suggest further investigation may allow the new $L_p$ model (53) to be improved.

4.3 Assessing the Effect of Minor Slag Constituents on the Measured $L_p$

As previously discussed, industrial phosphorus partitioning does not reach equilibrium due to kinetic limitations$^{26}$. Consequently, there was significant scatter present in the data
shown in Figure 3. However, the weak correlations with slag composition (TiO$_2$, Al$_2$O$_3$, V$_2$O$_5$) may warrant further investigation under controlled laboratory conditions.

At higher oxygen potentials, the slag Al$_2$O$_3$ content was found to have a negative effect on the measured L$_P$. In contrast, at low oxygen potentials, Al$_2$O$_3$ was found to correlate with increasing L$_P$ (Figure 3b). Al$_2$O$_3$ has little effect on the oxygen potential for dephosphorisation as it typically enters the BOS as carryover slag from the blast furnace or desulphurisation pre-treatment. Al$_2$O$_3$ is amphoteric, thus adding Al$_2$O$_3$ to a basic slag will result in it forming a complex anion therefore it will have an acid oxide character$^{101,102}$. Therefore Al$_2$O$_3$ has a negative effect on the slag basicity and subsequently is expected to decrease the measured L$_P$. CaO dissolution in basic slags increases with Fe$^{2+}$, Mn$^{2+}$ and Mg$^{2+}$ content$^{103}$. At low oxygen potentials there is less Fe$_2$O and MnO available to aid in CaO dissolution. Al$_2$O$_3$ also increases CaO dissolution, thus it is speculated that the correlation between Al$_2$O$_3$ and L$_P$ at low oxygen potentials is due to increased CaO dissolution and subsequently higher basicity.

The TiO$_2$ and V$_2$O$_5$ content of slag are highly correlated, thus it was expected that both oxides would display similar correlations with the measured L$_P$, as shown in Figure 3 a) and c). These oxides were found to decrease the measured L$_P$ with the correlation becoming more pronounced at lower oxygen potentials. This negative correlation is in good agreement with some literature as both [V] and [Ti] reduce the oxygen potential and [P] activity$^{104}$, thereby potentially inhibiting the dephosphorisation reaction, given in equation (1).

Selin$^{41,42,48}$ investigated the effect of Al$_2$O$_3$, TiO$_2$ and V$_2$O$_5$ additions on dephosphorisation in EAF steelmaking slags. Although EAF slags generally have a lower basicity, these slags overlap with the lower basicity ranges of industrial BOS slags. Selin$^{43,44,49}$ found Al$_2$O$_3$, TiO$_2$ and V$_2$O$_5$ all increased the slag phosphate capacity. However, their effects were at least partly counteracted by a significant decrease in the oxygen potential. This resulted in a moderate increase in L$_P$ when SiO$_2$ was replaced with TiO$_2$ and V$_2$O$_5$. The results with Al$_2$O$_3$ varied. This increase in phosphate capacity may help offset the effect of vanadium and
titanium on oxygen potential and may explain the smaller negative correlation of TiO$_2$ and V$_2$O$_5$ on $L_P$ at higher oxygen potentials seen in Figure 3a) and c).

While the thermodynamic effects of TiO$_2$, V$_2$O$_5$ and Al$_2$O$_3$ on $L_P$ may be explained by the results of Selin$^{41, 42, 48}$, the effect of TiO$_2$ on the kinetics of dephosphorisation remains unclear. Assuming the reaction is under a mass transfer control regime, the effect of these oxides on the slag viscosity should be considered. The effect of TiO$_2$ on slag viscosity has been studied primarily in blast furnace slags with the data showing a decrease in viscosity of CaO-SiO$_2$-TiO$_2$ slags under argon atmospheres$^{105-115}$. However, many of these studies also observed the effect of TiO$_2$ on the viscosity to become less pronounced with increasing temperature, basicity (i.e. becoming more like BOS process conditions) and TiO$_2$ content$^{114}$.

Conversely, TiO$_2$ additions may increase the apparent viscosity in high basicity steelmaking slags close to CaO and/or MgO saturation due to the formation of solid calcium and/or magnesium titanates in the liquid slag. Other authors have speculated this is the reason for increased slag foaming with TiO$_2$ content$^{116}$. Ohno and Ross$^{117}$ also found TiO$_2$ additions increased the slag viscosity in CaO-SiO$_2$-Al$_2$O$_3$-TiO$_2$ slags under reducing atmospheres and in the presence of solid carbon due to either the reduction of (TiO$_2$) to [Ti] or Ti(C, N) formation. These conditions may exist in the BOS process early in the heat, before significant decarburisation of the metal has occurred, or close to the MgO-C refractory walls$^{118-121}$.

Ilmenite (FeTiO$_3$) additions to BOS slags have been found to increase slag fluidity and dephosphorisation in industrial trials. However, the exception was high carbon heats (0.4wt% C aim) which were found to have low fluidity slags and higher final [P]$^{122}$. Hence, TiO$_2$ is expected to increase the rate of dephosphorisation in high oxygen potential slags below CaO and MgO saturation. TiO$_2$ is expected to have a negative effect on the rate of dephosphorisation at low oxygen potentials and with high basicity slags due to an increase in apparent slag viscosity. This effect of TiO$_2$ on mass transfer may also partly explain the weaker negative correlation with $L_P$ at higher oxygen potentials, shown in Figure 3a).
4.4 Industrial Significance

Whilst significant scatter is observed in the industrial dataset, laboratory studies\textsuperscript{30, 37, 63, 75, 76, 82} have shown that empirical $L_p$ models of this structure (i.e. $\text{Log}_p$, $1/T$, basicity as a V ratio or CaO equivalence, oxygen potential using slag Fe\textsubscript{tot} and/or [C]) can accurately predict the $L_p$ under equilibrium conditions. The scatter in the industrial data is at least in part a result of kinetic effects that are not readily accounted for in the model.

While many of the process conditions in the BOS are optimised for factors other than phosphorus removal, $L_p$ models can be used to predict slag composition effects on the $L_p$. Thus the $L_p$ model can be used to help determine the required flux additions and aid development of new fluxing/blowing practices.

In practice, steelmakers start each BOF heat with aims for $L_p$, end point temperature, steel and slag compositions. These aims are determined by a heat and mass balance of the BOF using the mass and compositions of all charged materials (hot metal, scrap, fluxes, iron ore etc.) and the required tap specifications for the grade. Thus, steelmakers can use $L_p$ models and the predicted end point temperature, steel and slag compositions to determine if further flux additions are required achieve the aim $L_p$. This would be an iterative process, as any flux additions effect the heat and mass balance, repeated until the aim $L_p$ was achieved.

The $L_p$ model developed in this study is fitted to the Port Kembla steelworks dataset. Thus, this model may or may not work well for other plants due to variations in the effective equilibria achieved, as discussed previously. However, the approach used and the structure of the different representations of basicity, oxygen potential and temperature would be equally applicable. Hence, this study may inform industry on the development of an empirical $L_p$ model fitted their own plant data.

5. Conclusions

Published phosphorus partition equations were compared against a large industrial dataset. A new phosphorus partition model (Model (53)) has been developed for use with industrial data. Terms correlating with the key factors controlling dephosphorisation (temperature, basicity and oxygen potential) were evaluated by regression against the large industrial
dataset. These were found to be $1/T$ for temperature, $\log(V\text{-ratio } -0.165(\%\text{MgO}))$ for basicity, and slag Fe$_t$ and metal [C] for oxygen potential.

The key factors controlling dephosphorisation (temperature, basicity and oxygen potential) were isolated using the new $L_p$ model in order to review the effect of minor slag constituents on the measured $L_p$. The Al$_2$O$_3$ content was found to have a negative effect on the measured $L_p$, except at the low oxygen potential condition tested (dataset 4). It was speculated this is due to the effect of Al$_2$O$_3$ on CaO dissolution at low Fe$_t$O content.

Increasing TiO$_2$ and V$_2$O$_5$ content were found to decrease the measured $L_p$, however these correlations became less prevalent at the higher oxygen potentials tested. This may be due to the increase in the slag phosphate capacity partly offsetting the reduction in oxygen potential$^{41,42,48}$. This observation may also be partly explained by lower slag viscosity increasing the rate of mass transfer. TiO$_2$ is known to decrease slag viscosity when the slag is not saturated in CaO or MgO.

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Figure 1: $L_p$ calculated vs. $L_p$ measured for top 10 models by $R^2$ over dataset 3.
Figure 2: $L_p$ calculated vs. $L_p$ measured for new $L_p$ models developed
Figure 3: $L_P$ measured vs. a) slag (TiO$_x$) mass% b) (Al$_2$O$_3$) mass% c) (V$_2$O$_5$) mass% for datasets 4-6

Tables & Captions
Table 1: A selection of $L_P$ equations developed for slags in CaO-SiO$_2$-Fe$_{1}$O-P$_2$O$_5$-(MgO, MnO, Al$_2$O$_3$, TiO$_2$, and VO$_2$) systems.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Conditions</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log L_P = 0.06(%CaO) + 0.37(%MgO) + 4.65(%P_2O_5) - 0.05(%Al_2O_3) - 0.2(%SiO_2) + \frac{11570}{T} - 10.52 + 2.5\log(%Fe_t)$</td>
<td>MgO-Al$_2$O$_3$, 1600°C</td>
<td>(10)$^{20, 21}$</td>
</tr>
<tr>
<td>$\log L_P = 0.0680(%CaO) + 0.42(%MgO) + 1.16(%P_2O_5) + 0.2(%MnO) + \frac{11570}{T} - 10.52 + 2.5\log(%Fe_t)$</td>
<td>MgO-MnO, 1600-1655°C</td>
<td>(11)$^{24, 25}$</td>
</tr>
<tr>
<td>$\log L_P = 0.07(%CaO) + 0.031(%MgO) + 0.02(%MnO) + 0.31(%Al_2O_3) + \frac{10911}{T} - 11.4 + 2.84\log(%Fe_t)$</td>
<td>MgO-Al$_2$O$_3$-TiO$_2$-V$_2$O$_5$, 1550-1667°C</td>
<td>(12)$^{23}$</td>
</tr>
<tr>
<td>$\log L_P = 0.026(%CaO) + 0.092(%MgO) + 0.04(%MnO) + 0.08(%Al_2O_3) + \frac{12217}{T} - 6.29 + 0.35\log(%Fe_t)$</td>
<td>MgO-Al$_2$O$_3$-TiO$_2$-V$_2$O$_5$, 1650-1727°C</td>
<td>(13)$^{23}$</td>
</tr>
<tr>
<td>$\log L_P = 0.075(%CaO) + 0.025(%MgO) + 0.14(%MnO) + 0.3(%Al_2O_3) + \frac{6042}{T} - 10.27 + 3.5\log(%Fe_t)$</td>
<td>MgO-Al$_2$O$_3$-TiO$_2$-V$_2$O$_5$, 1550-1727°C</td>
<td>(14)$^{23}$</td>
</tr>
<tr>
<td>$\log L_P = 0.431((%CaO)/(%SiO_2))-0.361\log(%MgO)+\frac{13590}{T} - 5.71 + 0.384\log(%Fe_t)$</td>
<td>MgO</td>
<td>(15)$^4$</td>
</tr>
<tr>
<td>$\log L_P = 0.346((%CaO)/(%SiO_2))-0.44\log(%MgO)+\frac{10173}{T} - 5.41 + 0.855\log(%Fe_t)+0.0088*\log[%C]$</td>
<td>MgO</td>
<td>(16)$^4$</td>
</tr>
<tr>
<td>$\log L_P = \frac{9736}{T} + 0.0023(%CaO) - 0.0094(%MgO) - 0.1910[%C] + 0.00053(%Fe_t) - 3.297$</td>
<td>MgO-Al$_2$O$_3$-TiO$_2$-V$_2$O$_5$, ~1650°C</td>
<td>(17)$^{26}$</td>
</tr>
<tr>
<td>$\log L_P = \frac{11913}{T} + 0.0066(%CaO) - 0.0123(%MgO) - 1.2270[%C] + 0.00426(%Fe_t) - 4.384$</td>
<td>MgO-Al$_2$O$_3$-TiO$_2$-V$_2$O$_5$, ~1650°C</td>
<td>(18)$^{26}$</td>
</tr>
<tr>
<td>$\ln L_P = \frac{20.254}{T} + 0.3638\ln(%Fe_t) - 0.0499(%MgO) - 6.299 - 0.82915$</td>
<td>MgO</td>
<td>(19)$^4$</td>
</tr>
<tr>
<td>$\log L_P = -12.24 + \frac{20000}{T} + 2.5\log(%Fe_t) + 6.65\log\left(\frac{(%CaO) + 0.8(%MgO)}{(%SiO_2) + (%Al_2O_3) + 0.8(%P_2O_5)}\right) + 0.13[%C]$</td>
<td>MgO, 1550-1580°C</td>
<td>(20)$^{40}$</td>
</tr>
<tr>
<td>$\log L_P = 2.5\log(%Fe_t) + 0.0715((%CaO) + 0.25(%MgO)) + \frac{7710.2}{T} - 8.55 + (\frac{105.1}{T} + 0.0723)[%C]$</td>
<td>MgO-MnO, 1000-1680°C</td>
<td>(21)$^{34, 32}$</td>
</tr>
<tr>
<td>$\log L_P = 0.0720((%CaO) + 0.15(%MgO) + 0.6(%P_2O_5) + 0.6(%MnO)) + 2.5\log(%Fe_t) + \frac{13570}{T} - 10.50$</td>
<td>MgO, 1600°C</td>
<td>(22)$^{35}$</td>
</tr>
<tr>
<td>$\log L_P = 19.05A - 0.148 + 0.5[\log\sum\left(\frac{[%]}{[%]}\right) + \log(%P_2O_5)] + 2.5\log[%O] - 2.5\left(\frac{115750 - 4.63T}{RT}\right) - 10.50$</td>
<td>MgO-Al$_2$O$_3$, 1570-1600°C</td>
<td>(23)$^{36}$</td>
</tr>
<tr>
<td>$\log L_P = \frac{21740}{T} - 9.87 + 0.071((%CaO) + 0.3(%MgO)) + 2.5\log[%O]$</td>
<td>MgO-MnO, 1600°C</td>
<td>(24)$^{3, 33, 96}$</td>
</tr>
</tbody>
</table>
\[
\log(L_P) = \frac{13958}{T} - 7.9517 + 2.5 \log(\%FeO) - (\%FeO)(1.43 \times 10^{-2} + 1.032 \times 10^{-4}(\%FeO)) - 0.36 \quad (25)\]

\[
\log(L_P) = 5.60 \log[(\%CaO) + 0.3(\%MgO) + 0.05(\%FeO)] + \frac{14800}{T} - 18.038 + 0.5 \log(\%P_2O_5) + 2.5 \log(\%Fe) \quad (26)\]

\[
\log(L_P) = 2.016B' - 0.34(B')^2 + \frac{52600}{T} - 11.993 + 2.5 \log(\%O) \quad (27)\]

\[
\log(L_P) = \frac{5.60 \log[(\%CaO) + 0.3(\%MgO) + 0.05(\%FeO)] + 14800}{T} - 18.038 + 0.5 \log(\%P_2O_5) + 2.5 \log(\%Fe) \quad (28)\]

\[
\log(L_P) = \log \left( \frac{MgO-Al_2O_3-TiO_2-V_2O_5}{1600-1700\degree C} \right) \quad (29)\]

\[
\log(L_P) = 2.016B' - 0.34(B')^2 + \frac{52600}{T} - 11.993 + 2.5 \log(\%O) \quad (30)\]

\[
\log(L_P) = \frac{1.53126 \log(\%FeO) + 3.23369 \log(\%CaO) - 5.3505 + \log[\%O]}{\frac{12940}{T}} - 6.909 + 0.5 \log(\%O) \quad (31)\]

\[
\log(L_P) = \frac{0.6639 \log(\%CaO)/(\%SiO_2) + 8198.1}{T} - 3.113 + 0.3956 \log(\%Fe) - 0.2075 \log(\%C) \quad (32)\]

\[
\log(L_P) = N_{Ca^{2+}} \left( \frac{144270}{T} - 36.70 \right) + N_{Mg^{2+}} \left( \frac{132900}{T} - 36.25 \right) + N_{Mn} \left( \frac{124040}{T} - 36.50 \right) + N_{Fe^{2+}} \left( \frac{118190}{T} - 25.65 \right) - \frac{29542}{RT} - \frac{6.909 + 0.5 \log(\%O)}{RT} \quad (33)\]

\[
\log(L_P) = \frac{1087.2}{T} - 8.566 + 0.0667[(\%CaO)] + 2.5 \log(\%O) \quad (34)\]

\[
\log(L_P) = \frac{11000}{T} + 2.5 \log(\%FeO) + \frac{1}{162(\%CaO) + 127.5(\%MgO) + 28.5(\%MnO)} \cdot 6.28 \times 10^{-4} (\%SiO_2)^2 - 10.76 \quad (35)\]

\[
\log(L_P) = 17.55A + 5.72 - \frac{21680}{T} - 1.87 + \log(\%P) + 2.5 \log(\%O) \quad (36)\]

\[
\log(L_P) = 5.89 \log(\%CaO) + 2.5 \log(\%FeO) + 0.5 \log(\%P_2O_5) + \frac{15340}{T} - 18.542 \quad (37)\]

\[
\ln(L_P) = -558.874 + \frac{2175100}{T} - \frac{1930041500}{T^2} - 24.3 + 2.5 \log(\%O) + 0.36 \quad (38)\]

\[
\log(L_P) = 0.056(\%CaO) + 2.5 \log(\%FeO) + 0.5 \log(\%P_2O_5) + \frac{12000}{T} - 10.42 \quad (39)\]
<table>
<thead>
<tr>
<th>logLP</th>
<th>Equation</th>
<th>Temperature</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>logLP = 5.6 log(%CaO) + 2.5 log(%Fe) + ( \frac{22350}{T} ) - 21.876</td>
<td>~1600°C</td>
<td>(40)</td>
<td></td>
</tr>
<tr>
<td>logLP = ( \frac{22350}{T} ) + 0.08(%CaO) + 2.5log(%FeO) - 16.0</td>
<td>1580-1669°C</td>
<td>(41)</td>
<td></td>
</tr>
<tr>
<td>logLP = ( \frac{22350}{T} ) + 7log(%CaO) + 2.5log(%FeO) - 24.0</td>
<td>1580-1669°C</td>
<td>(42)</td>
<td></td>
</tr>
<tr>
<td>logLP = ( \frac{2625}{T} ) - 7.787 + ( \frac{1}{2} ) log(%P(_2)O(_5)) + 2.5 log(%Fe)</td>
<td>MgO-MnO, 1550-1660°C</td>
<td>(43)</td>
<td></td>
</tr>
<tr>
<td>logLP = -0.56[22N(<em>{\text{CaO}}) + 15N(</em>{\text{MgO}}) + 13N(<em>{\text{MnO}}) + 12N(</em>{\text{FeO}}) - 2N(<em>{\text{SiO}})] - ( \frac{21000}{T} ) + 0.5logN(</em>{\text{P}})(_2)O(_5) - log[%P] +0.5log(%P(_2)O(_5)) +12.15</td>
<td>MgO-MnO, 1550-1660°C</td>
<td>(44)</td>
<td></td>
</tr>
<tr>
<td>logLP = 5.9log(%CaO) +0.5log(%P(_2)O(_5)) + 2.5log(%Fe) -0.00461T+2.0845</td>
<td>MgO-MnO-Al(_2)O(_3), 1650-1735°C</td>
<td>(45)</td>
<td></td>
</tr>
<tr>
<td>logLP = 5.39log(%CaO) +0.5log(%P(_2)O(_5)) + 2.5log(%Fe) -0.00447T-3.0355</td>
<td>MgO-MnO-Al(_2)O(_3), 1650-1735°C</td>
<td>(46)</td>
<td></td>
</tr>
</tbody>
</table>
Table 2: $R^2$ values for top 10 fitting models on dataset 3

<table>
<thead>
<tr>
<th>$R^2$</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.975</td>
<td>32</td>
</tr>
<tr>
<td>0.973</td>
<td>18</td>
</tr>
<tr>
<td>0.972</td>
<td>19</td>
</tr>
<tr>
<td>0.969</td>
<td>17</td>
</tr>
<tr>
<td>0.963</td>
<td>31</td>
</tr>
<tr>
<td>0.942</td>
<td>30</td>
</tr>
<tr>
<td>0.928</td>
<td>22</td>
</tr>
<tr>
<td>0.927</td>
<td>39</td>
</tr>
<tr>
<td>0.926</td>
<td>26</td>
</tr>
<tr>
<td>0.926</td>
<td>11</td>
</tr>
</tbody>
</table>

Table 3: New $L_p$ models with $R^2$ values from testing on dataset 3

<table>
<thead>
<tr>
<th>Equation</th>
<th>Testing Data set 3 $R^2$</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log L_p = 0.0367(V \text{ ratio aim}) + \frac{13782.4}{T} - 5.656 + 0.194\log(%\text{Fe})$</td>
<td>0.968</td>
<td>(47)</td>
</tr>
<tr>
<td>$\log L_p = 0.0380(V \text{ ratio aim}) + \frac{14304}{T} - 5.616 - 0.0594\log[O]$</td>
<td>0.965</td>
<td>(48)</td>
</tr>
<tr>
<td>$\log L_p = 0.0414(V \text{ ratio aim}) + \frac{13781.5}{T} - 5.577 + 0.147\log(%\text{Fe}) - 0.816[C]$</td>
<td>0.970</td>
<td>(49)</td>
</tr>
<tr>
<td>$\log L_p = 0.0623(V \text{ ratio}) + \frac{13019.2}{T} - 5.1795 + 0.109\log(%\text{Fe}) - 0.780[C]$</td>
<td>0.960</td>
<td>(50)</td>
</tr>
<tr>
<td>$\log L_p = 0.0157(%\text{CaO}) + \frac{11572.2}{T} - 5.660 + 0.724\log(%\text{Fe}) - 0.714[C]$</td>
<td>0.951</td>
<td>(51)</td>
</tr>
<tr>
<td>$\log L_p = 0.429(V \text{ ratio}) + \frac{13536.1}{T} - 5.329 + 0.0432\log(%\text{Fe}) - 1.009[C]$</td>
<td>0.971</td>
<td>(52)</td>
</tr>
<tr>
<td>$\log L_p = 0.242\log(V \text{ ratio} - 0.165(\text{MgO})) + \frac{13536.1}{T} - 5.235 - 0.009\log(%\text{Fe}) - 1.010[C]$</td>
<td>0.975</td>
<td>(53)</td>
</tr>
<tr>
<td>$\log L_p = 3.306\log(\Lambda) + \frac{13535.1}{T} - 4.7717 + 0.00017\log(%\text{Fe}) - 0.722[C]$</td>
<td>0.969</td>
<td>(54)</td>
</tr>
<tr>
<td>$\log L_p = 1.782(\Lambda) + \frac{13528.4}{T} - 6.521 + 0.005\log(%\text{Fe}) - 0.703[C]$</td>
<td>0.968</td>
<td>(55)</td>
</tr>
</tbody>
</table>
Table 4: Filters applied to data set 1 to obtain datasets 4-6 for testing secondary factors

<table>
<thead>
<tr>
<th>Data set</th>
<th>Temperature Range</th>
<th>Basicity Range</th>
<th>Oxygen Potential Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1640 – 1680°C</td>
<td>1.08– 1.22</td>
<td>0.75-0.81</td>
</tr>
<tr>
<td>5</td>
<td>1640 – 1680°C</td>
<td>1.08– 1.22</td>
<td>0.81-0.87</td>
</tr>
<tr>
<td>6</td>
<td>1640 – 1680°C</td>
<td>1.08– 1.22</td>
<td>0.87-0.93</td>
</tr>
</tbody>
</table>