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Development of a new phosphorus partition relation for Australian steelmakers

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Development of a new phosphorus partition relation for Australian steelmakers

Abstract

Phosphorus is generally undesirable in steel. Decreasing availability of low phosphorus iron ores and the desire to recycle waste materials like basic oxygen steelmaking (BOS) slags is driving renewed interest in phosphorus removal. A number of phosphorus partition (LP) equations have been proposed in the literature for specific slag compositions and temperature ranges at equilibrium. These LP equations have been evaluated against the historic data on the phosphorus removal from an industrial top blown bottom stirred basic oxygen convertor. Further, the performance of these partition equations has been used to inform the development of a new LP model more suitable to the prevailing conditions in the Australian steelmaking industry. The new model has been used to isolate the key factors controlling dephosphorisation, namely lower temperature, higher basicity and higher oxygen potential. This LP model has allowed secondary factors influencing dephosphorisation to be assessed, including TiO_x load, heat duration and stirring rate.

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Development of a New Phosphorus Partition Relation for Australian Steelmakers

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Phosphorus is generally undesirable in steel. Decreasing availability of low phosphorus iron ores and the desire to recycle waste materials like basic oxygen steelmaking (BOS) slags is driving renewed interest in phosphorus removal. A number of phosphorus partition (L_P) equations have been proposed in the literature for specific slag compositions and temperature ranges at equilibrium. These L_P equations have been evaluated against the historic data on the phosphorus removal from an industrial top blown bottom stirred basic oxygen convertor. Further, the performance of these partition equations has been used to inform the development of a new L_P model more suitable to the prevailing conditions in the Australian steelmaking industry. The new model has been used to isolate the key factors controlling dephosphorisation, namely lower temperature, higher basicity and higher oxygen potential. This L_P model has allowed secondary factors influencing dephosphorisation to be assessed, including TiO_x load, heat duration and stirring rate.

Keywords: basic oxygen steelmaking, BOF, BOS, dephosphorisation, empirical process models, industrial data, phosphorus partition, slags.

1 Introduction

Phosphorus (P) is generally undesirable in steel lowering ductility and causing embrittlement [1, 2]. Historically P in steel has been controlled primarily by the selection of low P iron ores. However, the P content of iron ores is generally increasing as low P ores are exhausted. Steelmakers have also sought to recycle basic oxygen steelmaking (BOS) slag to recover iron and lime at the expense of increasing the P load entering steelmaking furnace. Given this increasing P load in a BOS vessel, a better understanding of dephosphorisation fundamentals (thermodynamics and kinetics) is required if this increasing load is to be managed.

P removal in BOS steelmaking is generally described by the ionic reaction shown in (1). From (1) it can be seen that a high [P] activity, high oxygen potential [O] and high basicity O^{2-} all promote phosphorus removal. P removal may also be represented by the simple molecular reaction, given in (2), allowing a Gibbs free energy to be calculated using (3).



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

In this paper basicity has been evaluated by considering V ratio as defined in (4) and optical basicity Λ in (5).

$$V = \frac{\%CaO}{\%SiO_2} \quad (4) \quad [4, 5]$$

$$\Lambda = N_i \Lambda_i + N_j \Lambda_j + \dots \quad (5) \quad [6]$$

There are a number of ways to represent dephosphorisation equilibria or effective equilibria in the case of industrial data including phosphate capacities of the slag, equilibrium constants and different forms of the P partition. The removal of P in steelmaking has been extensively researched producing over 80 different empirical correlations of dephosphorisation equilibria [2, 3, 7-80]. For this study the common form of the P partition (L_P), as defined in (6) is used. Where equations from other studies are presented they have been converted to this form to aid comparison.

$$L_P = \frac{(\%P)}{[\%P]} \quad (6)$$

While these empirical relations are useful and aid optimisation of BOS dephosphorisation, they are often limited to the narrow range of slag/metal compositions for which they were developed. Hence, these models may over or under predict the L_P outside the composition range used for the model derivation. A number of these relations were developed using industrial data which only approaches equilibrium under high stirring conditions and longer heat durations and are therefore limited to the specific kinetic regime and furnace type for which they were developed (bath stirring, lance height and design, blow time, physical properties of slag, etc.).

To aid optimisation of BOS dephosphorisation for Australian steelmakers, a new L_P equation specific to the composition ranges, kinetic conditions and configuration of their furnaces has been developed. Further, this L_P has been used to isolate secondary factors influencing on plant dephosphorisation.

3 Methodology and Results

3.1 Industrial Data Selection

A 10 year data set of the BOS operation at BlueScope Port Kembla, NSW, was used in the development and testing of a L_P equation. The composition data within the database were obtained from arc optical spectroscopy of steel sampled with a sub-lance and X-ray fluorescence of the slag from a chill/dip sample. The following data were excluded from the data set used to develop the partition equation:

- Heats with incomplete data sets for heat duration, temperature, slag or metal compositions.
- Heats that were subjected to a de-siliconisation process prior to full decarburization blow.
- Heats with significant quantities of retained slag from previous blow.
- Heats containing returned steel from the secondary refining processes.

After these exclusions were applied a data set of 11340 heats was obtained, referred to as data set 1. Data set 1 was split by date into data sets 2 and 3 containing 9 years (11274 heats) and 1 year (66 heats) of data, respectively. Data set 2 was used for derivation and fitting of the new L_P equations, while data set 3 was used for evaluation of both published and new partition models developed. Note that the data used for evaluating the new models were not used in the derivation. Use of data set 3 for evaluation of both the new and published models allows a direct comparison of model performance.

3.2 Testing of Published Phosphorus Partition Models

Of the P equilibria models found in the literature, 35 were identified for further investigation and are given in Table 1. The criteria used to select these models were:

- The model had an input for titanium oxides i.e. the model had been derived for slag compositions containing titanium oxides.
- Recently published (2000 onwards) or reviewed L_P models using either laboratory or industrial data.
- The model was derived using industrial data.
- Models developed using optical basicity as an input, as these have the potential to incorporate titanium oxides regardless of whether these oxides were used in the model development.

The performance of published models was assessed using (7) to calculate the R^2 for the degree of fit of the calculated L_P to the measured L_P for an equation constrained to pass through the origin using data set 3. The 10 models with the highest R^2 values are shown in Figure 1 and Table 2.

$$R^2 = \frac{\sum(y_i)^2 - \sum(\hat{y}_i - y_i)^2}{\sum(y_i)^2} \quad (7)$$

Table 1: A selection of L_P Equations developed for slags in CaO-SiO₂-Fe_tO-P₂O₅-(MgO, MnO, Al₂O₃, TiO₂, and VO₂) systems.

Equation	Conditions	Ref.	No.
$\log L_P = 5.39 \log(\%CaO) + 0.5 \log(\%P_2O_5) + 2.5 \log(\%Fe_t) - 0.00447T - 3.0355$	MgO-MnO-Al ₂ O ₃ , 1650-1735°C	[8-10, 12]	(8)
$\log L_P = 5.9 \log(\%CaO) + 0.5 \log(\%P_2O_5) + 2.5 \log(\%Fe_t) - 0.00461T + 2.0845$	MgO-MnO-Al ₂ O ₃ , 1650-1735°C	[8-10, 12]	(9)
$\log L_P = -0.56[22N_{CaO} + 15N_{MgO} + 13N_{MnO} + 12N_{FeO} - 2N_{SiO_2}] - \frac{21000}{T} + 0.5 \log N_{P_2O_5} - \log[\%P] + 0.5 \log(\%P_2O_5) + 12.15$	MgO- MnO, 1550- 1660°C	[16, 17]	(10)
$\log L_P = \frac{2625}{T} - 7.787 + \frac{1}{2} \log(\%P_2O_5) + 2.5 \log(\%Fe_t)$	MgO- MnO, 1550- 1660°C	[17, 18]	(11)
$\log L_P = \frac{22350}{T} + 7 \log(\%CaO) + 2.5 \log(\%Fe_tO) - 24.0$	1580-1669°C	[19]	(12)
$\log L_P = \frac{22350}{T} + 0.08(\%CaO) + 2.5 \log(\%Fe_tO) - 16.0$	1580-1669°C	[19]	(13)
$\log L_P = 5.6 \log(\%CaO) + 2.5 \log(\%Fe_t) + \frac{22350}{T} - 21.876$	~1600°C	[22]	(14)
$\log L_P = 5.49 \log(\%CaO) - 10.093 + \frac{1}{2} \log(\%P_2O_5) + 2.5 \log(\%Fe_t)$	MgO-MnO-TiO ₂ - Al ₂ O ₃ , 1550°C	[23]	(15)
$\log L_P = 0.056(\%CaO) + 2.5 \log(\%Fe_t) + 0.5 \log(\%P_2O_5) + \frac{12000}{T} - 10.42$	~1600°C	[24]	(16)
$\log L_P = 5.645 \log[1.58(\%Na_2O) + (\%CaO) + 0.3(MgO) - 0.05(\%Fe_tO)] + 2.5 \log(\%Fe_tO) + 0.5 \log(\%P_2O_5) - 9.8799$	1600°C	[28]	(17)
$\ln L_P = \Lambda \left(-558.874 + \frac{2175100}{T} - \frac{1930041500}{T^2} \right) - 24.3 + 2.5 \ln[\%O] + 0.36$	MgO, 1550-1650°C	[29]	(18)
$\log L_P = 5.89 \log(\%CaO) + 2.5 \log(\%Fe_t) + 0.5 \log(\%P_2O_5) + \frac{15340}{T} - 18.542$	MgO-Al ₂ O ₃ -TiO ₂ , 1300-1400°C	[30]	(19)
$\log L_P = 17.55\Lambda + 5.72 - \frac{21680}{T} - 1.87 + \log[\%P] + 2.5 \log[\%O]$	MgO-MnO, 1550- 1650°C	[25]	(20)
$\log L_P = \log(22.4\Lambda + 3.14) + \log 0.326 + 2.5 \log[\%O]$	MgO-Na ₂ O, 1600°C	[41]	(21)
$\log L_P = \frac{11000}{T} + 2.5 \log(\%FeO) + \frac{1}{T} [162(\%CaO) + 127.5(\%MgO) + 28.5(\%MnO)] - 6.28 \times 10^{-4} (\%SiO_2)^2 - 10.76$	MgO-MnO, 1550- 1650°C	[45]	(22)
$\log L_P = \frac{19872}{T} - 8.566 + 0.0667[(\%CaO) + (\%CaF_2)] + 2.5 \log[\%O]$	MgO- MnO, 1520- 1723°C	[46]	(23)
$\log L_P = N_{Ca^{2+}} \left(\frac{144270}{T} - 36.70 \right) + N_{Mg^{2+}} \left(\frac{132900}{T} - 36.25 \right) + N_{Mn} \left(\frac{124040}{T} - 36.450 \right) + N_{Fe^{2+}} \left(\frac{118190}{T} - 25.65 \right) - \frac{29542}{T} - \frac{(-122173 - 19.25T)}{RT} - 2.5 \frac{(-115750 - 4.63T)}{RT} + 0.5 \log(\sum N_i M_i) + \log(\%O^2) - 14.12$	MgO-MnO, 1600- 1680°C	[47]	(24)
$\log L_P = 1.53126 \log(\%FeO) + 3.23369 \log(\%CaO) - 5.3505 + \log \left(\frac{1.6 + \sqrt{(\%P_D)}}{1.820} \right) - 0.00129 \left(\frac{(\%Al_2O_3)}{(\%Al_2O_3) + (\%SiO_2) + (\%TiO_2) + (\%VO_2)} \right) - 0.00098 \left(\frac{(\%TiO_2)}{(\%Al_2O_3) + (\%SiO_2) + (\%TiO_2) + (\%VO_2)} \right) - 0.00026 \left(\frac{(\%VO_2)}{(\%Al_2O_3) + (\%SiO_2) + (\%TiO_2) + (\%VO_2)} \right) - 6.909 + \frac{12940}{T}$	MgO 1600°C	[53-55]	(25)
$\log L_P = 3.52 \log(\%CaO) + \frac{4977}{T+17.8} + 2.5 \log(\%FeO) + 0.5 \log(\%P_2O_5) - 10.46$	1550-1650°C	[2]	(26)

Table 1: A selection of L_P Equations developed for slags in CaO-SiO₂-Fe_tO-P₂O₅-(MgO, MnO, Al₂O₃, TiO₂, and VO₂) systems. (Continued)

Equation	Conditions	Ref.	No.
$\log L_P = 21.55\Lambda + \frac{32912}{T} - 27.90 + 2.5 \log[\%O]$	MgO-Al ₂ O ₃ -TiO ₂ -VO ₂ 1550-1650°C	[56, 57]	(27)
$\log L_P = 21.55\Lambda + \frac{32912}{T} + 2.5\log(\% Fe_t) - 34.678$	MgO-Al ₂ O ₃ -TiO ₂ -VO ₂ 1600°C	[56, 57]	(28)
$\log L_P = 2.016B' - 0.34(B')^2 + \frac{52600}{T} - 11.993 + 2.5 \log[\%O]$	MgO, 1600°C	[58]	(29)
$\log L_P = 5.60 \log[(\%CaO) + 0.3(\%MgO) + 0.05(\%Fe_tO)] + \frac{14800}{T} - 18.038 + 0.5\log(\%P_2O_5) + 2.5 \log(\%Fe_t)$	MgO-Al ₂ O ₃ -TiO ₂ 1600-1700°C	[61]	(30)
$\log L_P = -18.671 + 35.84\Lambda - 22.35\Lambda^2 + \left(\frac{22930\Lambda}{T}\right) - 0.06257(\%FeO) - 0.04256(\%MnO) + 0.359(\%P_2O_5)^{0.3} + 2.5\log[\%O]$	MgO-MnO-Al ₂ O ₃ , 1600-1650°C	[62, 63]	(31)
$\log L_P = \frac{21740}{T} - 9.87 + 0.071[(\%CaO) + (\%CaF_2) + 0.3(\%MgO)] + 2.5\log[\%O]$	MgO-MnO, 1600°C	[3, 65, 66]	(32)
$\log L_P = 19.05\Lambda - 0.148 + 0.5[\log \sum \left(\frac{\%i}{M_i}\right) + \log(\%P_2O_5)] + 2.5\log[\%O] - 2.5 \frac{(-115750 - 4.63T)}{RT}$	MgO-Al ₂ O ₃ , 1570-1600°C	[67]	(33)
$\log L_P = 0.0720[(\%CaO) + 0.15(\%MgO) + 0.6(\%P_2O_5) + 0.6(\%MnO)] + 2.5 \log(\%Fe_t) + \frac{11570}{T} - 10.50$	MgO, 1600°C	[68]	(34)
$\log L_P = 1.987 \left(\frac{(\%CaO) + (\%MgO)}{(\%SiO_2) + (\%Al_2O_3) + (\%P_2O_5)} \right) + 0.089[(\%Fe_tO) + (\%MnO)] - 1.708$	MgO-MnO-Al ₂ O ₃ , 1600°C	[69]	(35)
$\log L_P = 2.5\log(\%Fe_t) + 0.0715[(\%CaO) + 0.25(\%MgO)] + \frac{7710.2}{T} - 8.55 + \left(\frac{105.1}{T} + 0.0723 \right) [\%C]$	MgO-MnO, 1000-1680°C	[70, 71]	(36)
$\log L_P = 2.5\log(\%Fe_t) + 0.0715 \left(\frac{(\%CaO)/(\%SiO_2)}{1 + (\%CaO)/(\%SiO_2)} \right) \left(80 - \frac{71.85}{55.85} (\%Fe_t) \right) - 3.23$	MgO-MnO, 1000-1680°C	[70, 71]	(37)
$\log L_P = -12.24 + \frac{20000}{T} + 2.5\log(Fe_tO) + 6.65 \log \left(\frac{(\%CaO) + 0.8(\%MgO)}{(\%SiO_2) + (Al_2O_3) + 0.8(\%P_2O_5)} \right) + 0.13[\%C]$	MgO, 1550-1580°C	[72]	(38)
$\log L_P = \frac{11913}{T} + 0.0066(\%CaO) - 0.0123(\%MgO) - 1.2270[\%C] + 0.00426(\%Fe_tO) - 4.384$	MgO-Al ₂ O ₃ -TiO ₂ -V ₂ O ₅ ~1650°C	[76]	(39)
$\log L_P = \frac{9736}{T} + 0.0023(\%CaO) - 0.0094(\%MgO) - 0.1910[\%C] + 0.00053(\%Fe_tO) - 3.297$	MgO-Al ₂ O ₃ -TiO ₂ -V ₂ O ₅ ~1650°C	[76]	(40)
$\log L_P = 0.0680[(\%CaO) + 0.42(\%MgO) + 1.16(\%P_2O_5) + 0.2(\%MnO)] + \frac{11570}{T} - 10.520 + 2.5 \log(\%Fe_t)$	MgO-MnO, 1600-1655°C	[77, 78]	(41)
$\log L_P = 0.06[(\%CaO) + 0.37(\%MgO) + 4.65(\%P_2O_5) - 0.05(Al_2O_3) - 0.2(\%SiO_2)] + \frac{11570}{T} - 10.52 + 2.5\log(\%Fe_t)$	MgO-Al ₂ O ₃ , 1600°C	[79, 80]	(42)

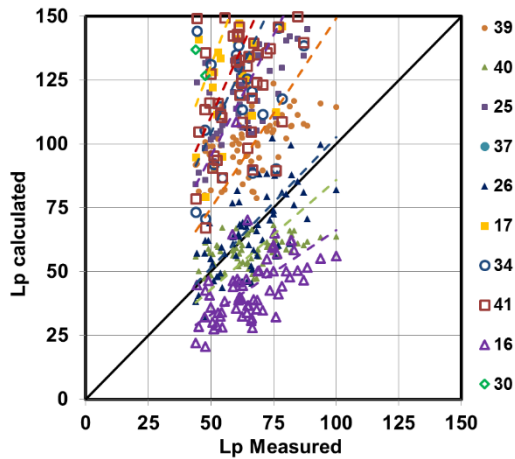


Figure 1: L_P calculated vs. L_P measured for top 10 models by R² over data set 3.

Table 2: R² values for top 10 fitting models

R ²	Equation
0.9732	39
0.9694	40
0.9630	25
0.9423	26
0.9404	37
0.9365	17
0.9279	34
0.9257	41
0.9266	16
0.9263	30

3.3 Development and Testing of a New Partition Phosphorus Model

The published models given Table 1 use different terms to represent the basicity (optical basicity, basicity ratios or various lime equivalents) and oxygen potential ([O], [C], total slag Fe or [C]). Hence, a series of new models were developed to evaluate different combinations of these basicity and oxygen potential representations, as shown in Table 3. The models were developed and the fitting parameters (model coefficients) established using data set 2 and a root mean square approach. Subsequently, the new models were then tested on data set 3 allowing the R² values to be calculated and compared to the published models.

The initial models developed (Table 3, model number (43)-(45)) assumed the temperature was represented by an inverse temperature term and the basicity term was represented by the aim V ratio. Thereby allowing the various representations of oxygen potential (Slag Fe_t, log[O] & slag Fe_t + [C]) to be evaluated. The highest R² value was achieved when the oxygen potential was represented by a combination of Log(Slag %Fe_t) and the final [%C], as shown by the R² value for model (45) evaluated for data set 3 in Table 3. This corresponds to the oxygen potential representation used in the two best fitting published models, (39) and (40). Subsequently, the various basicity representations were tested (V ratio aim, V ratio measured, (%CaO), log(%CaO), (%CaO) equivalent, and Λ), as shown in (45) to (51). The model with the best fit (highest R²) was model (49) where the basicity was represented by log(V ratio - 0.165(%MgO)).

Table 3: New L_P models with R² values when fitted to Data set 2 and tested on Data set 3

Equation	Fitting Data set 2 R ²	Testing Data set 3 R ²	No.
$\log L_p = 0.0367(\text{V ratio aim}) + \frac{13782.4}{T} - 5.656 + 0.194\log(\%Fe_t)$	0.920	0.968	(43)
$\log L_p = 0.0380(\text{V ratio aim}) + \frac{14304}{T} - 5.616 - 0.0594\log[O]$	0.920	0.965	(44)
$\log L_p = 0.0414(\text{V ratio aim}) + \frac{13781.5}{T} - 5.577 + 0.147\log(\%Fe_t) - 0.816[C]$	0.922	0.970	(45)
$\log L_p = 0.0623(\text{V ratio}) + \frac{13019.2}{T} - 5.1795 + 0.109\log(\%Fe_t) - 0.780[C]$	0.922	0.960	(46)
$\log L_p = 0.0157(\%CaO) + \frac{11572.2}{T} - 5.660 + 0.724\log(\%Fe_t) - 0.714[C]$	0.922	0.951	(47)
$\log L_p = 0.429(\text{V ratio}) + \frac{13536.1}{T} - 5.329 + 0.0432\log(\%Fe_t) - 1.009[C]$	0.922	0.971	(48)
$\log L_p = 0.242\log(\text{V ratio} - 0.165(\%MgO)) + \frac{13536.1}{T} - 5.235 - 0.009\log(\%Fe_t) - 1.010[C]$	0.923	0.975	(49)
$\log L_p = 3.306\log(\Lambda) + \frac{13535.1}{T} - 4.7717 + 0.00017\log(\%Fe_t) - 0.722[C]$	0.920	0.969	(50)
$\log L_p = 1.782(\Lambda) + \frac{13528.4}{T} - 6.521 + 0.005\log(\%Fe_t) - 0.703[C]$	0.920	0.968	(51)

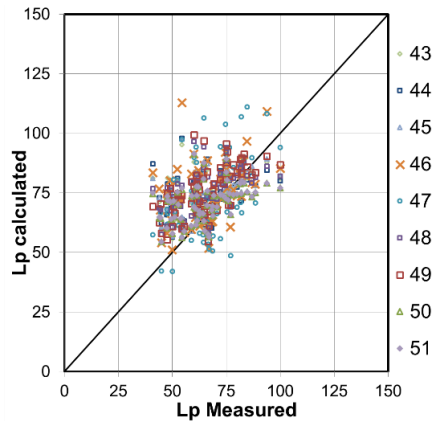


Figure 2: L_P calculated vs. L_P measured for new L_P models developed

3.4 Assessing the Effect of Secondary Factors on the L_P

Based on the high R^2 value of model (49) defined in Table 3, the basicity, oxygen potential and temperature representations used in this model were selected to evaluate the key variables controlling dephosphorisation. The basicity, oxygen potential and temperature representations used in model (49) were each divided into 3 equal ranges and used to filter data set 1 to obtain 27 subsets of data. For brevity the 3 data sets (data sets 4-6) containing the largest number of heats for a fixed temperature and basicity range were selected for demonstrating the correlations observed. Data sets 4-6 are defined in Table 4 and contain 292, 1774, 3253 heats of data, respectively. Since the data are constrained for the key variables of dephosphorisation (temperature, basicity and oxygen potential) then correlations between the measured L_P and secondary factors possibly affecting the L_P such as TiO_x load, heat duration and stirring rate can be evaluated. Plots of the measured L_P vs. the stirring rate and TiO_x load were produced as shown in Figure 3.

Table 4: Filters applied to data set 1 to obtain data sets 4-6 for testing secondary factors

Data set	Temperature Range	Basicity Range ($10^{0.243 \log((CaO)/(SiO_2) - 0.165(MgO))}$)	Oxygen Potential Range ($10^{-0.0092 \log(\%Fe_t) - 1.0098[C]}$)
4	1640 – 1680°C	1.08– 1.22	0.75-0.81
5	1640 – 1680°C	1.08– 1.22	0.81-0.87
6	1640 – 1680°C	1.08– 1.22	0.87-0.93

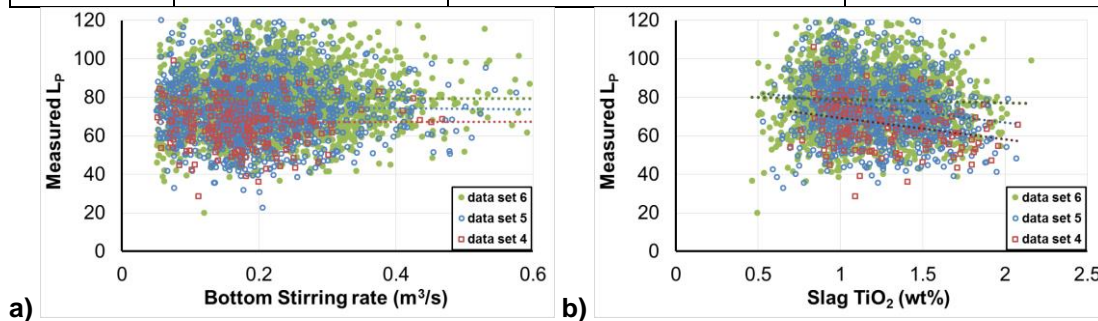


Figure 3: L_P measured vs. a) stirring rate b) slag TiO_x mass% for data sets 4-6

4 Discussion

4.1 Testing of Published Phosphorus Partition Models

The published models in Table 1 were found to have a poor fit when tested on data set 3, as shown in Figure 1 and Table 2. There are a number of reasons for the poor fit of these models including:

- Plant specific nature of non-equilibrium industrial data caused by different oxygen blowing practices, slag and metal compositions, furnace geometry and lance design. Hence, models developed from industrial data (39, 40, 37, 26, 17, 34, 41, 16, 30) with different operating conditions may have a lower fit to the data set 3. Models developed from equilibrium data ((25), (34) and (41)) may also have a poor fit the effective equilibrium L_P measured in the industrial data

- Empirical models are limited to the slag and metal composition range for which they were developed. Thus, any heats in data set 3 outside a model's composition range may result in a poor fit.
- Different slag and metal sampling methods can cause significant variation in the measured L_P . Slag and metal samples may be taken simultaneously via the sub-lance or the slag sample may be taken up to 10 minutes later via a chill/dip sample when the furnace is tapping. Non-simultaneous sampling results in a higher measured L_P as the dephosphorisation reaction (1) continues during the delay in obtaining the slag sample. Chill/ dip sampling of slags may not include solid phases present in the slag, thus slag the sample may not be representative of the slag composition.

Models (39) and (40) had the highest R^2 values when tested on data set 3. These two models were developed from industrial data and both used an oxygen potential term that combines both the slag Fe_tO content and the metal [C] content. This is consistent with the findings of Wei *et al.* [81, 82] who found that the oxygen potential control is a mix between both the metal and slag phases in a highly stirred system. This approach was utilised for developing the new L_P model.

The majority of the published models only consider the effect of CaO, MgO, Fe_tO and P_2O_5 on the L_P . However, the high R^2 values of models (34), (41) and (25) that incorporate MnO, P_2O_5 , Al_2O_3 , VO_2 and TiO_2 , suggest these oxides may have a significant effect on the L_P . Hence, further investigation into the effect of these oxides on the L_P is required.

4.2 Development and Testing of a New Phosphorus Partition Model

A series of new models using different oxygen potential and basicity representations were developed and fitted to data set 2. Subsequently, the new models were tested on data set 3 and the R^2 value was calculated. Model (49) was the only new model found to produce a higher R^2 value (0.975) than all the published models (Table 2) for data set 3. However, all the new models developed performed better than 32 of the 35 published models tested on data set 3. The effect of MnO, P_2O_5 , Al_2O_3 , VO_2 and TiO_2 were not included in the new L_P models developed. However, the high R^2 values of the models incorporating these oxides ((34), (41), and (25)) suggest further investigation may allow the new L_P model to be improved.

4.3 Assessing the Effect of Secondary Factors on the Phosphorus Partition

Constraining the key variables controlling dephosphorisation in data sets 4, 5 and 6 allows these data sets to be used to evaluate any correlations with secondary factors influencing dephosphorisation. Dephosphorisation is reported to be a 1st order mass transfer controlled reaction [20, 36, 81, 83-94]. Subsequently, the secondary factors of interest all related to improved rates of mass transfer, including:

- Stirring rate & heat duration – allows data to be assessed for approaching an effective equilibrium.
- Slag composition – specifically the effect of TiO_x load due to the large variations caused by iron ore availability and selection.

Many researchers, including a recent study by Assis and Fruehan [77] have shown industrial phosphorus partitioning data does not achieve equilibrium. Hence, the data sets 4-6 contain non-equilibrium data, and secondary factors influencing dephosphorisation kinetics may be observed. Subsequently, the measured L_P was plotted against the stirring rate and heat duration to determine any correlation. No correlation between the measured L_P and stirring rate was observed, as shown in Figure 3a). A weak negative correlation between the measured L_P and the heat duration was observed whereby the L_P appears to be lower (phosphorus reversion) at longer heat durations.

[Ti] is known to significantly reduce the oxygen potential and [P] activity [95], thereby inhibiting the dephosphorisation reaction, given in (1). However, Selin [53-55] found the addition of TiO_2 (up to 12.60 mass%) to steelmaking slags independent of [Ti] caused a minor increase in the L_P , given in (25). This effect may be due to the reduction of TiO_2 (amphoteric) to form basic titanium oxides (Ti_2O_3 , TiO). However, TiO_2 is reported to be the dominant oxide at the oxygen potentials found in the BOS (10^{-10} to 10^{-8} atm), with Ti_2O_3 representing less than 4% of total slag titanium content [96, 97]. Thus, the negative effect of increasing [Ti] on the oxygen potential is only weakly offset by the effect of titanium oxides on the basicity. Subsequently, steelmakers have generally considered increasing [Ti] to have a detrimental effect on dephosphorisation.

While the effect of TiO_2 on L_P has been established by Selin [53-55], the effect of TiO_x on mass transfer and subsequently the kinetics of dephosphorisation remains unclear. Mass transfer in steelmaking slags

is promoted via high rates of stirring and low slag viscosity, hence the effect of TiO_x on slag viscosity of particular interest to this study. A number of viscosity studies have found increasing TiO_2 contents (using high purity TiO_2) to decrease the viscosity of $CaO-SiO_2-TiO_2$ slags under argon atmospheres [98-108]. However, many of these studies also observed the effect of TiO_2 on the viscosity to become less pronounced with increasing temperature, basicity and TiO_2 content [107]. Conversely, Ohno and Ross [109] found TiO_2 additions increased the slag viscosity in $CaO-SiO_2-Al_2O_3-TiO_2$ slags under reducing atmospheres and in the presence of carbon due to the reduction of TiO_2 . Furthermore, published plant trials using Ilmenite ($FeTiO_3$) fluxes found the slag fluidity and subsequently mass transfer and dephosphorisation improved generally with increasing $FeTiO_3$ addition. The exception was high carbon heats (0.4wt% C aim) which were found to have low fluidity slags and higher final [P] [110]. Hence, TiO_2 is expected to increase the rate of dephosphorisation by lowering the viscosity of basic oxygen steelmaking slags for high oxygen potential heats. Conversely, TiO_2 is expected to have a negative effect on the rate of dephosphorisation in low oxygen potential heats due to higher slag viscosity.

The effect of TiO_2 was tested against data sets 4-6 as shown in Figure 3b). The measured L_P was found to be independent of the slag TiO_2 at high oxygen potentials (data set 6). A negative correlation was expected given the effect of [Ti] on the oxygen potential and [P] activity. This suggests that improved rates of mass transfer caused by lower slag viscosity may offset the negative effect on the L_P in high oxygen potential heats. However, increasing TiO_2 load was found to have a weak correlation with decreasing L_P at lower oxygen potentials (Data set 4 and 5). This is in good agreement with the plant trial findings of Sharma and Miller [110]. Hence, increasing TiO_2 load appears to have a negative effect on the L_P in low oxygen potential heats. In addition, higher TiO_2 contents than the low levels observed in the industrial data (0.5-2 mass%) may have a more significant effect on the dephosphorisation rate.

5 Conclusions and Recommendations

A phosphorus partition model has been produced to deal with the prevailing conditions experienced by Australian BOS steelmakers. The new model has a higher fit to the industrial data than any published model. The new L_P model has been used to isolate the key factors controlling dephosphorisation (temperature, basicity and oxygen potential) in order to determine trends in secondary dephosphorisation factors (stirring rate, heat duration and TiO_2 load). The L_P was found to decrease with longer heat duration, thus it was concluded the industrial data was not at equilibrium.

The phosphorus partition was found to be independent of the TiO_2 load at high oxygen potentials. However, increasing TiO_2 load was found to have a negative effect on the L_P in the lower oxygen potential heats (i.e. high [C] aim). This is in agreement with the plant trials published by Sharma and Miller [110]. The absence of a negative correlation between L_P and TiO_2 at high oxygen potentials may be due to changes in the physical properties of the slag, thereby improving the kinetics of dephosphorisation. The effect of titanium on the kinetics of phosphorus removal in basic oxygen steelmaking requires further investigation.

6 Definitions and Nomenclature

The terms used in (1) to (51) are defined as follows:

() = in solution in slag	[] = in solution in liquid iron
%i = oxide mass %	T = temperature at end of heat (K)
(%Fe _t) = total Fe in slag phase in wt%	(%Fe _t O) = total Fe as FeO in slag phase in mass%
M _i = molecular weight of oxide	R = gas constant = 8.314 JK ⁻¹ mol ⁻¹
(%P _D) = $1.28 + (\%P) - 1.6\sqrt{0.64 + (\%P)}$	N = mole fraction of oxide or ion
y_i = the L_P calculated by model	\hat{y}_i = L_P calculated by linear regression line through results to the origin
$B = \frac{N_{CaO} + N_{MgO}}{N_{SiO_2} + 1.05N_{AlO_{1.5}}}$	Δ = optical basicity of slag
Δ_i = optical basicity of slag species <i>i</i> . Values for various oxides have been reviewed by Sommerville & Yang [6]	

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