

Representation of Phosphorus and Vanadium Equilibria between Liquid Iron and Complex Steelmaking Type Slags*

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Synopsis

The relation between phosphate capacity and different scales of optical basicity is examined and discussed.

The coexistence of monomer and dimer phosphate ions is considered and the amount of phosphorus as monomer phosphate ions is related to the slag phosphorus content. Excellent relationship is found between phosphorus capacity, temperature and theoretical optical basicity.

Optical basicities of TiO_2 and VO_y are derived and a linear relationship is found between the vanadate capacity,

$$C_{VO_4^{3-}} = (\%VO_4^{3-})/[\%V][\%O]^{5/2},$$

and the optical basicity of basic steelmaking type slags.

Key words: liquid iron; optical basicity; slag; steelmaking; phosphorus distribution; vanadium distribution.

I. Introduction

Ever since Duffy *et al.*¹⁾ in 1978 first introduced the concept of optical basicity to metallurgists, there has been considerable interest in the possibility of correlating metallurgical data to this single parameter.

The interest arises from the lack of a practical basicity scale applicable to the wide range of complex metallurgical slags.

To summarize shortly, Duffy *et al.*¹⁾ stated that optical basicity of a slag is a measure of the electron donor power of the oxygen present in the slag. Moreover, the optical basicity of a pure oxide was empirically correlated to the Pauling electronegativity of the cation (transition metal oxides excluded). In addition, it was made clear that the theoretical optical basicity of an oxide mixture easily could be calculated and a straight line relationship was displayed between the sulfide capacity and the optical basicity of blast furnace slags.

The concept of optical basicity has later been applied, not only in relation to sulphide capacity²⁻⁶⁾ but also in connection to: phosphorus distribution,⁷⁻¹³⁾ manganese distribution,^{13,14)} carbonate capacities,^{15,16)} and water capacities.^{17,18)}

Gaskell⁷⁾ correlated data of Suito *et al.*¹⁹⁾ On phosphorus distribution to the theoretical optical basicity of the slag. A good relationship was found but limited to a maximum of 0.6 % P_2O_5 in the slag.

Later, Suito and Inoue⁸⁾ examined dephosphorization equilibria in relation to the theoretical optical basicity. Deviation from the straight line relation was found for slags containing 4 % BaO , 7~13 % Na_2O , or 4~5 % P_2O_5 . The reason for this deviation

was, however, not determined. Similar results have also been reported later,^{10,12,13)} and Kunisada and Iwai¹³⁾ claimed that the phosphate capacity might not uniquely be represented by the theoretical optical basicity of all kinds of slag.

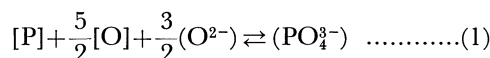
Finally, Masson²⁰⁾ discussed the basicity of slags from the viewpoint of polymer theory and showed a relation between the theoretical optical basicity of an oxide and the value of the dimerization coefficient in two binary systems.

The aim of this contribution will be to examine and discuss phosphorus and vanadium equilibrium between liquid iron and complex steelmaking type slags and perhaps give a better understanding of these relations so as to achieve enhanced control over the important slag-metal reactions in steelmaking.

II. Representation of Dephosphorization Equilibria

The dephosphorization capability of a slag is best described by its phosphate capacity which directly relates the ability of the slag to absorb phosphorus to its composition and temperature.

With phosphorus and oxygen dissolved in the metal and with the assumption that all phosphorus in the slag are present as PO_4^{3-} ions, the phosphate capacity has been defined from the following equilibrium:



Often, it has been convenient to derive the phosphate capacity as:

$$C_{PO_4^{3-}} = \frac{(\%PO_4^{3-})}{[\%P][\%O]^{5/2}} \dots\dots\dots(2)$$

The relation between the phosphate capacity and the equilibrium distribution ratio of phosphorus between slag and steel, L_P , is

$$L_P = \frac{(\%P)}{[\%P]} = \frac{C_{PO_4^{3-}}[\%O]^{5/2}M_P}{M_{PO_4^{3-}}} \dots\dots\dots(3)$$

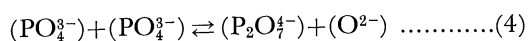
It is to be noted that the derivation of the equations considered above is made with the assumption that the monomer PO_4^{3-} ions being the only structural unit of phosphorus in the slag.

However, this assumption is believed to have a limited validity as the coexistence of ortho-, PO_4^{3-} ,

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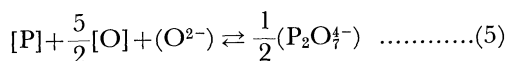
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and pyrophosphate, $P_2O_4^{2-}$, anions has to be considered according to the dimerization equilibria.



From the reaction above it is clear that the amount of the dimer $P_2O_7^{4-}$ ions will increase with increasing slag phosphorus content as well as with decreasing slag basicity.

The equilibrium between phosphorus in metal and dimer phosphate anions can be written



According to the authors knowledge the coexistence of monomer and dimer phosphate anions in connection to dephosphorization equilibria has hitherto only been considered by Selin.^{21,22)}

With the assumption that triphosphate, $P_3O_{10}^{5-}$, anions and those of higher degree of polymerization could be neglected, he expressed the proportion of monomer- to dimer-ions in relation to the phosphorus content:

$$(\%P) = (\%P_M) + (\%P_D) \dots\dots\dots(6)$$

$$(\%P_D) = 1.28 + (\%P) - 1.6\sqrt{0.64 + (\%P)} \dots\dots(7)$$

where, (%P): total phosphorus in the slag
 (%P_M): phosphorus as monomer PO_4^{3-} -ions
 (%P_D): phosphorus as dimer $P_2O_7^{4-}$ -ions in the slag.

The proportion of monomer and dimer phosphate ions as a function of slag phosphorus content is displayed in Fig. 1. In this figure it is observed that the proportion of dimer ions, is a strong function of the slag phosphorus content indeed.

Consequently, the error introduced when assuming PO_4^{3-} as the only phosphate ion present in the slag is,

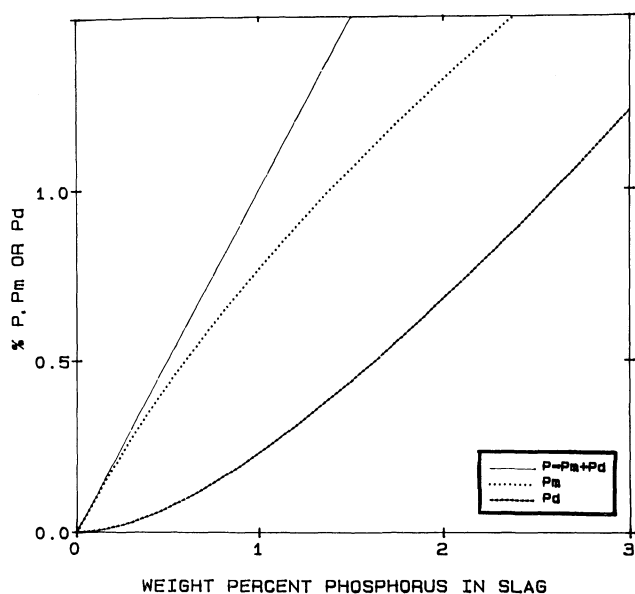


Fig. 1. The proportion of phosphorus as monomer phosphate ions (% P_M) and dimer phosphate ions (% P_D) in the slag as a function of the total amount of phosphorus in the slag.

therefore, a function of the amount of phosphorus in the slag. As a result, from the standpoint of predicting slag metal phosphorus equilibria, it is of importance to pay regards to the slag phosphorus content.

Assuming the validity of the dimerization described above, we may express the slag ability to absorb phosphorus as monomer phosphate ions as

$$C_{P_M} = \frac{(\%P_M)}{[\%P][\%O]^{5/2}} = \frac{L_{P_M}}{[\%O]^{5/2}} \dots\dots\dots(8)$$

where, $(\%P_M) = 1.6\sqrt{0.64 + (\%P)} - 1.28 \dots\dots\dots(9)$

This relation is considered to hold for slags having:
 1) optical basicities ranging from 0.50 to 0.75, and
 2) phosphorus contents less than 2.5 %.

Regarding the last point Selin²²⁾ proposed that best accuracy in his model was to be expected for $(P) \leq 1.5 \%$.

III. Optical Basicity

In metallurgy, the earliest important investigation on optical basicity is that carried out by Duffy *et al.*¹⁾ In their work, the optical basicity of an oxide, A, was related to the Pauling electronegativity, X, of the cation by the basicity moderating parameter γ:

$$A = \frac{1}{\gamma} = \frac{1}{1.36(X - 0.26)} \dots\dots\dots(10)$$

The optical basicity of an oxide computed from Eq. (10) was denoted as the theoretical optical basicity. Furthermore, it was shown that the theoretical optical basicity of an oxide mixture is given by

$$A = X_A A_A + X_B A_B + \dots\dots \dots(11)$$

where, A_A, A_B: the theoretical optical basicity values of the oxides

X_A, X_B: the equivalent cation fractions.¹⁾

Moreover, they stated grave apprehensions about the applicability of the relations above to transition metal oxides. Consequently, these oxides were omitted in their treatment.

Nevertheless, theoretical optical basicities of transition metal oxides have later been computed from Eq. (10), and applied with some success to data on phosphorus distribution.⁷⁻⁹⁾

Sommerville and Sosinsky³⁾ addressed this problem in a different way, and made an attempt to deduce optical basicity values of the transition metal oxides FeO, Fe₂O₃, MnO and TiO₂ by use of sulfide capacity values and a line fitting procedure. The optical basicity of FeO, Fe₂O₃ and MnO thus obtained was considerably greater than could be expected from Pauling electronegativities. In fact, they found FeO and MnO to be more basic than CaO, in apparent disagreement with all other basicity scales. Furthermore, the obtained values were later used to determine the relationship between sulfide capacity, composition and temperature.⁵⁾

A new scale of the theoretical optical basicity based on the average electron density was, proposed by

Nakamura *et al.* in 1986.²³⁾ However it should be noted, that optical basicities calculated in this way differ considerably from the values computed from Pauling electronegativities. Optical basicity values of the three scales described above are compared in Table 1.

Information is obviously needed about the validity of these scales. Therefore, it was decided to assess their applicability by plotting the logarithm of the slag monomer capacity against the optical basicity of the three scales, Fig. 2.

The comparison is based on 130 experiments on phosphorus equilibrium in slags containing 12~79 %

Table 1. A comparison of optical basicity values of different scales.

Oxide	Theoretical from Pauling electro-negativity ^{1,7,9)}	Sommerville <i>et al.</i> from sulfide capacity ³⁾	Nakamura <i>et al.</i> from electron-density ²³⁾
K ₂ O	1.40		1.16
Na ₂ O	1.15		1.11
BaO	1.15		1.08
Li ₂ O	1.0		1.06
CaO	1.0		1.0
MgO	0.78		0.92
TiO ₂	(0.61*)	0.61	0.65
Al ₂ O ₃	0.605		0.66
MnO	0.59	1.21	0.95
FeO	0.51	1.03	0.94
Fe ₂ O ₃	0.48	0.70	0.72
SiO ₂	0.48		0.47
B ₂ O ₃	0.42		0.42
P ₂ O ₅	0.40		0.38
SO ₃	0.33		0.29

* Doubtful value from Ref. 18)

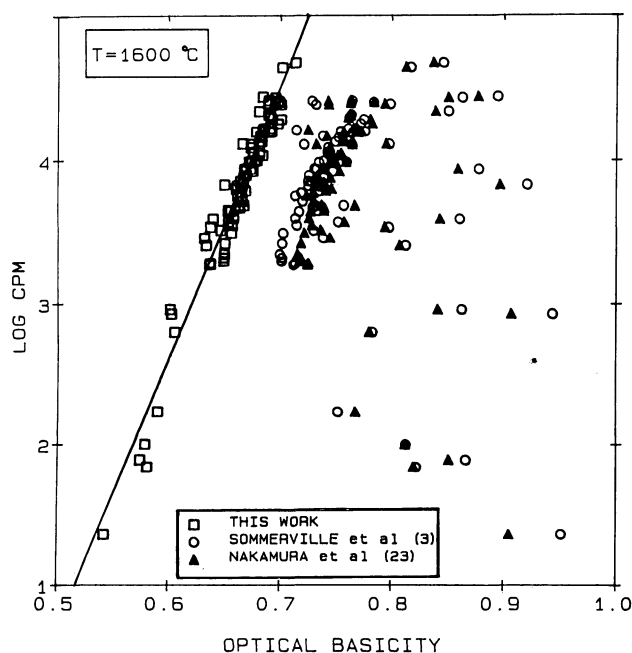


Fig. 2. The relation between the logarithm of the phosphorus capacity $\log C_{P,M}$ and different scales of optical basicity.

FeO, 1~14 % Fe₂O₃, 0~12 % TiO₂ and 0~12 % Al₂O₃.^{19,22,24,25)} The data of Selin²²⁾ used in Fig. 2 are for slags without VO₂. The results in Fig. 2 reveal a most striking difference between the optical basicity after Duffy and the two other scales.

From Fig. 2, it is evident that only the theoretical optical basicity scale based on Pauling electronegativity can be justified.

IV. Relationship between Phosphorus Capacity, Temperature and Theoretical Optical Basicity

As mentioned in the beginning, some anomalies have been reported that claimed some doubts of the universal applicability of the theoretical optical basicity to dephosphorization equilibrium.^{7,8,10,12,13)} It was therefore decided to reexamine this relationship.

Here, the monomer phosphorus capacity represented by Eq. (8) is used to elucidate the relationship with the theoretical optical basicity.

The results at 1 600°C, Fig. 2, show a straight line relationship, Eq. (12), and one can really recognize that the line is well fitted ($R^2=0.94$) to all points. Contrary to earlier results⁸⁾ the slags with 4~5 % P₂O₅ fall within the experimental scatter.

$$\log C_{P,M} = 18.28A - 8.28 \quad (1\ 600^\circ\text{C}) \quad \dots\dots(12)$$

In his excellent piece of experimental work, Selin²²⁾ determined the phosphorus partition between liquid iron and slag. His data is shown in Fig. 3 as compared with similar data of Suito *et al.*¹⁹⁾ The 46 data of Selin²²⁾ show a very good linear relationship, Eq.

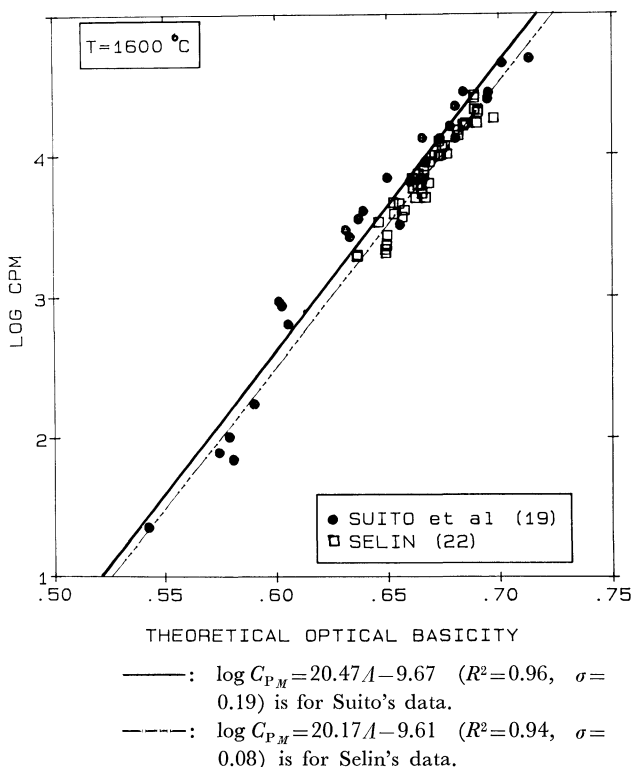


Fig. 3. The variation of $\log C_{P,M}$ with theoretical optical basicity for two sets of experimental data at 1 600 °C.

(13):

$$\log C_{P_M} = 20.17A - 9.61 \quad (1600^\circ\text{C}) \quad \dots\dots(13)$$

The 26 points of Suito *et al.*¹⁹⁾ are more scattered, standard deviations of $\log C_{P_M}$ are 0.08 and 0.19, respectively.

It is also noted that the data of Suito *et al.*¹⁹⁾ result in larger values of phosphorus capacity. The reason may be attributed to the fact that the transfer of phosphorus from slag to metal is not reached to equilibrium from the slag side.

The variation of $\log C_{P_M}$ with theoretical optical basicity at 1550°C, calculated from the data of Suito *et al.*,^{8,19,24)} is shown in Fig. 4. The regression line for all 59 points is given by Eq. (14) below.

$$\log C_{P_M} = 22.22A - 10.27 \quad (1550^\circ\text{C}) \quad \dots\dots(14)$$

Here, also the slags with addition of Na₂O and BaO are well fitted to the line.

From the data of Suito *et al.*^{19,24)} at 1650°C one obtain.

$$\log C_{P_M} = 21.30A - 10.64 \quad (1650^\circ\text{C}) \quad \dots\dots(15)$$

The temperature dependence of the phosphorus capacity derived from the data of Suito *et al.*^{8,19,24)} is

$$\log C_{P_M} = 21.55A + \frac{32912}{T} - 27.90 \quad \dots\dots(16)$$

Bearing the accuracy of the experimental data in mind the optical basicity is taken as a temperature independent term.

The accuracy of Eq. (16) is tested in Fig. 5, by plotting the calculated $\log C_{P_M}$ values against the observed values. The spread of the points in Fig. 5 is believed to be due to the experimental conditions.

V. Optical Basicity of Fe_tO, TiO₂ and VO_y

The routine melt shop analyses are usually done by employing automatic spectroscopic methods. Hence, Fe²⁺ in the slag is seldom determined on a regular basis. Thus, with respect to the practical applicability of any equilibrium model, it is of great interest to examine if all oxidic iron can be expressed as Fe²⁺ by the relation: %Fe_tO = 1.2865 % Fe_{tot} where %Fe_{tot} = wt% total iron in metal free slag.

Even though, the assumption above has already been used by Mori,⁹⁾ it might be appropriate to examine the propriety in doing so.

Therefore, in Fig. 6, optical basicities calculated with his scale; $A_{Fe_2O_3} = 0.51$ and $A_{Al_2O_3} = 0.59$, are plotted against the theoretical optical basicities after Duffy according to Table 1.

The relation is shown in Fig. 6 and given by:

$$A_{Mori^9)} = 1.001A + 0.002 \quad \dots\dots(17)$$

This implies that the assumption can be made without introducing any serious error, as it results in only somewhat higher values of optical basicity.

Actually, only three points in Fig. 6 have a marked deviation from the straight line relationship. The

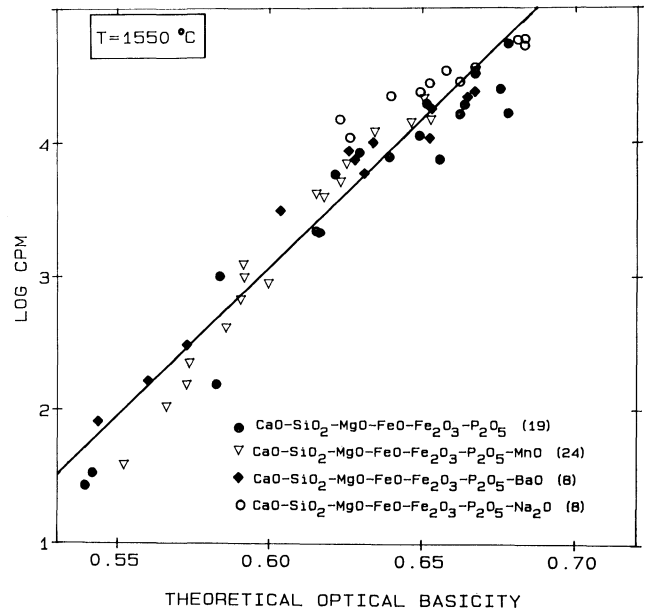


Fig. 4. The variation of $\log C_{P_M}$ with theoretical optical basicity A at 1550°C.

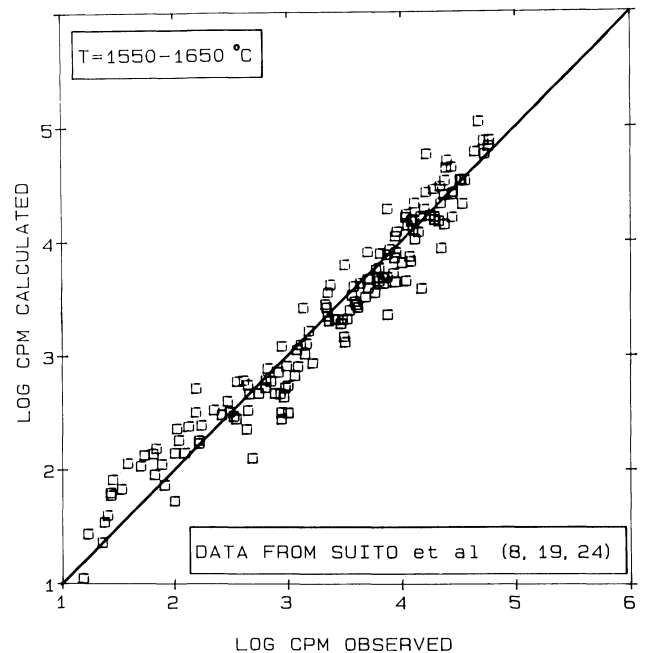


Fig. 5. Comparison of calculated and observed values of $\log C_{P_M}$ in accordance with the present derived equation (16).

points SU 14, SU 25 and SU 31 are identified to Suito *et al.*¹⁹⁾ experimental run Nos. 14, 25 and 31, respectively. The reason for the deviation might be explained by the unexpectedly high Fe³⁺/Fe²⁺ ratios.

In practice, slags in basic oxygen furnace (BOF) and direct reduced iron (DRI) steelmaking may contain considerable amount of the gangue oxides TiO₂ and VO_y. Consequently, for a wider application of the concept of optical basicity, it is highly desirable to establish reliable optical basicities of these oxides.

In the case of TiO₂, the value in Table 1, $A_{TiO_2} = 0.61$, was applied to the data of Selin.²²⁾ The result,

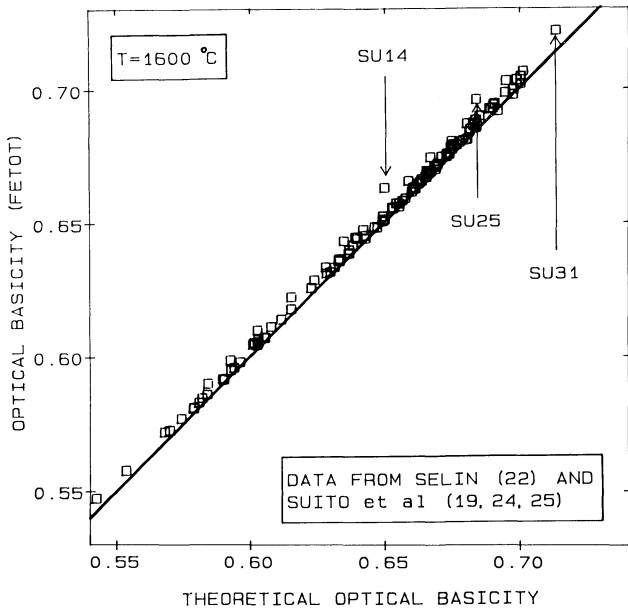


Fig. 6. Comparison of optical basicity of Mori⁹⁾ ($A_{FeO}=0.51$ and $A_{Al_2O_3}=0.59$) with theoretical optical basicity after Duffy (Table 1).

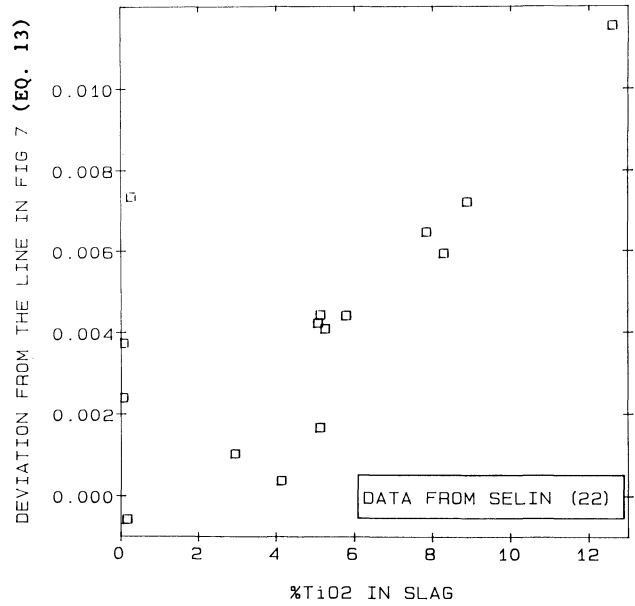


Fig. 8. Deviation of $\log C_{P_M}$ value from the straight line relation, Eq. (13), in Fig. 7 as a function of the TiO_2 content in the slag.

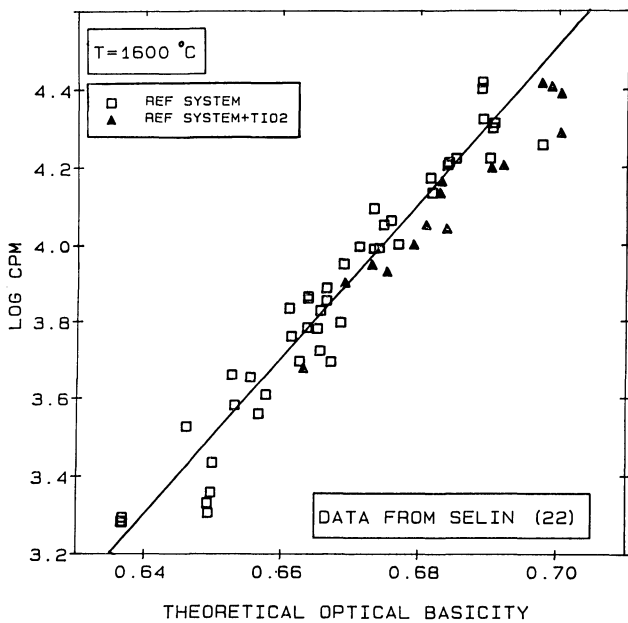


Fig. 7. The variation of $\log C_{P_M}$ with theoretical optical basicity according to Table 1. Plots of open squares is for the system $CaO-SiO_2-MgO_{sat}-FeO-Fe_2O_3-Al_2O_3-P_2O_5$ as compared to TiO_2 containing heats in the same system.²²⁾

in Fig. 7, shows a marked deviation from the line, Eq. (13). This in turn indicated that TiO_2 was assigned quite too high a value in Table 1. Consequently the deviation from Eq. (13) should be a linear function of the TiO_2 content of the slag.

The data plotted in this way is shown in Fig. 8 and the result is taken as a piece of evidence that TiO_2 was assigned too high a value. One way to resolve the optical basicity of TiO_2 is the line-fitting procedure.³⁾ Although, this method can be erroneous, as shown in Fig. 2, it was surmised that it might be

Table 2. Optical basicity values calculated from phosphorus capacity data.

Oxide	λ	Standard deviation	Min.	Max.	Number of heats
TiO_2	0.55	0.024	0.53	0.60	11
VO_2^*	0.57	0.017	0.55	0.60	12

justified when applied to consistent experimental data. The result of this technique when applied to the data of Selin²²⁾ on the heats containing more than 2% TiO_2 is shown in Table 2.

As this result seems to be reasonable, the same method was applied to 12 heats containing 2.85~12.6% VO_2^* from the same experimental work.²²⁾ Here, all vanadium in the slag are taken as V^{4+} as suggested by Selin.²²⁾ Also this result is shown in Table 2.

Slag basicity calculated with the values in Table 2 as hereinafter denoted "optical basicity" in order to distinguish it from theoretical optical basicity after Duffy calculated from the values in Table 1.

The values in Table 2 were applied to the complex slags of Selin²²⁾ and the excellent agreement in Fig. 9 is not only a tribute to an unsurpassed piece of experimental work, but may also without exaggeration be called a triumph for the concept of optical basicity.

VI. Vanadium Distribution Equilibrium between Slag and Metal

Vanadium equilibrium between slag and metal has been measured both at steelmaking temperatures^{21,22,26)} and at ironmaking temperatures.^{27,28)} In order to express the slag ability to hold vanadium, different capacities have been introduced.^{26,27)} However, as pointed out by Werme,²⁷⁾ the capacity of a

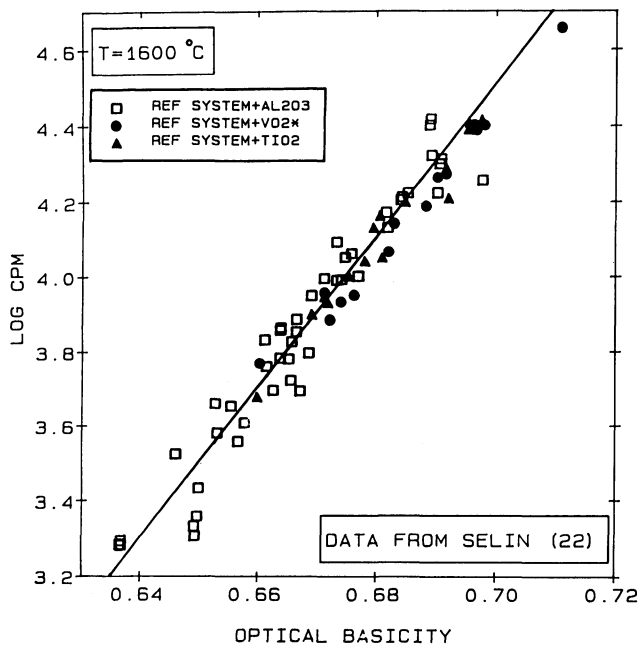
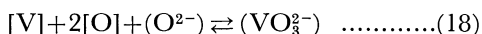


Fig. 9. The relation between $\log C_{PM}$ and optical basicity of complex steelmaking slags. Optical basicity of TiO_2 and VO_2^* according to Table 2.

slag component can only be derived with knowledge of the type of ion formed by the component in the slag. Seeing that, the situation is complex as vanadium may change its valency in metallurgical slag and different oxidation states may coexist.

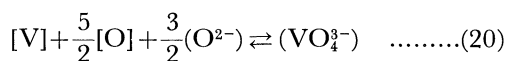
High oxygen potentials and basicities are likely to increase the valency.²⁶⁻²⁸⁾ With vanadium and oxygen dissolved in the metal and with the assumption that vanadium is V^{4+} and all vanadium in the slag are present as VO_3^{2-} ions, the vanadate capacity is derived from the following equilibrium:



here

$$C_{VO_3^{2-}} = \frac{(\%VO_3^{2-})}{[\%V][\%O]^2} \dots\dots\dots(19)$$

Similarly, if the valency is V^{5+} and VO_4^{3-} is the ion formed in the slag:



and

$$C_{VO_4^{3-}} = \frac{(\%VO_4^{3-})}{[\%V][\%O]^{5/2}} \dots\dots\dots(21)$$

Using the data of Selin²²⁾ the logarithms of the capacities above were plotted against optical basicity calculated with the values in Table 2. A regression analysis showed that the latter capacity, Eq. (21), was more significant than the former Eq. (19); regression coefficients (R^2) 0.89 and 0.71, standard deviations 0.066 and 0.091, respectively.

Thus V^{5+} is thought to be the dominating valency in these slags in agreement with results from glass chemistry,²⁹⁾ where it has been found that the upper

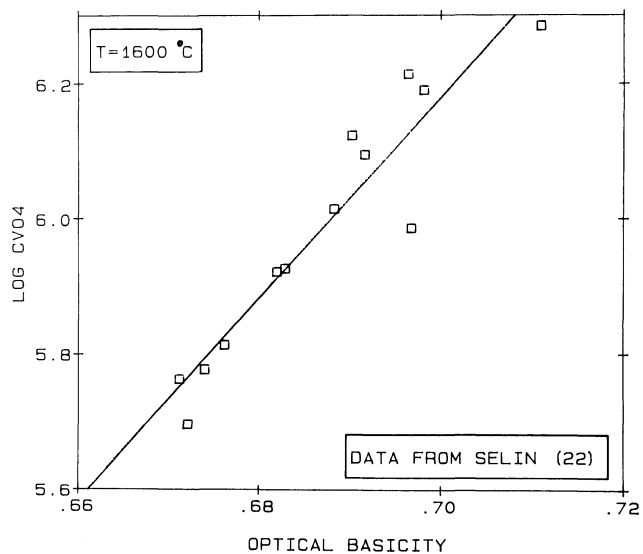


Fig. 10. The variation of $\log C_{VO_4^{3-}}$ with optical basicity at 1600°C.

oxidation states are favored at high basicities.

The relation is given by Eq. (22) and shown in Fig. 10.

$$\log C_{VO_4^{3-}} = 14.92A - 4.26 \text{ (1 600°C)} \dots\dots\dots(22)$$

VII. Conclusions

The principal conclusions emerging from the work described above are summarized briefly as follows:

(1) The coexistence of monomer-, and dimer-phosphate anions in the slag lead to that the phosphorus distribution is a function of the slag phosphorus content itself.

(2) The slag ability to absorb phosphorus as monomer phosphate ions is defined as

$$C_{PM} = \frac{(\%P_M)}{[\%P][\%O]^{5/2}}$$

where, $(\%P_M) = 1.6 \sqrt{0.64 + (\%P)} - 1.28 \dots\dots\dots(9)$

(3) The slag phosphorus capacity can uniquely be related to optical basicity after Duffy. The temperature dependence of the phosphorus capacity is still best expressed as a composition independent term.

(4) The theoretical optical basicity is an excellent measure of slag phosphorus capacity for a wide range of slags and seems not to be restricted to certain components or compositional limits. From a practical point of view, it is also shown that iron as oxides in the slag can be represented by Fe_2O when calculating optical basicity instead of FeO and Fe_2O_3 separately.

(5) Optical basicity values of TiO_2 and VO_2^* were derived by a line fitting procedure to 0.55 and 0.57, respectively.

(6) A linear relationship is found between the logarithm of the vanadate capacity Eq. (21) and the optical basicity of basic steelmaking slags.

(7) Applied correctly, the concept of optical ba-

sicity is of great value and should probably be used more often in the representation of metallurgical data.

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