

## THE USE AND MISUSE OF CAPACITIES IN SLAGS

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### Abstract

With regard to the residual contents of some undesirable solutes in steel, and their minimization through slag-metal reaction, one of the most important and useful approaches has been the use of capacities for these elements in slags. Accordingly, the data available for sulphide, phosphate, water or hydroxyl and carbonate capacities, and their dependence on composition, are reviewed. The first three are reviewed because of their connection with the solutes sulphur, phosphorus and hydrogen, while the last is reviewed because it has been widely accepted as one of the best measures of basicity in slags.

Some sources of concern with regard to the way in which capacities have been either obtained or applied are then discussed. It appears that care is required to ensure that the usefulness and validity of the capacity concept is not compromised.

### 1. Introduction

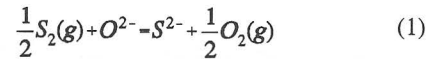
The demand for steels with a high purity requires a strict control of harmful impurities in liquid steel processing. The key operation in the process is making the molten slags with high refining ability in order to absorb the harmful impurities from liquid metal. The concept of capacities of various species in slag has become a popular way of expressing the ability of the slag to hold solutes in solution and has been widely used in the study of metallurgical slags. In this paper the capacity of some important species in steel making processes, such as phosphate, sulphide, carbonate and water capacities, will be reviewed briefly, and the correlation between different capacities are discussed. Some sources of concern and possible misuse of capacities are then highlighted.

## 2 Definitions of Slag Capacities

### 2.1 Sulphide Capacity

The definition of sulphide capacity is commonly derived

from the slag-gas exchange reaction



as

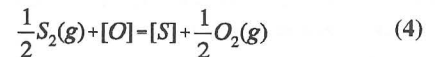
$$C_s = (wt\%S) \left( \frac{P_{O_2}}{P_{S_2}} \right)^{1/2} = \frac{K_1 a_{O^{2-}}}{f_{S^{2-}}} \quad (2)$$

So the  $C_s$  groups together three quantities which are virtually impossible to measure individually. It is thus a very useful quantity since it provides a way of greatly reducing the amount of thermodynamic information required for a satisfactory description of slag-gas and slag-metal equilibria.

Some authors have preferred to define it with reference to the slag-metal reaction, in which case the definition becomes

$$C_{S^{2-}} = (wt\%S) \frac{[a_O]}{[a_S]} \quad (3)$$

The two definitions are, of course, related through the free energy of the gas-metal exchange reaction

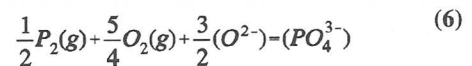


The slag-metal distribution,  $L_S = (\%S)/[\%S]$ , is related to  $C_s$  by the expression:

$$\log L_S = \log C_{S^{2-}} + \log f_S + \frac{1}{2} \log p_{O_2} - \frac{7055}{T} - 1.224 \quad (5)$$

### 2.2 Phosphate Capacity

Dephosphorization reactions between liquid steel and molten slag are often formulated with ionic species as reactants and products. If we assume that all the phosphate ions in the slag are monomeric, the general form of dephosphorization reaction can be written as:



So that the phosphate capacity of the slag is defined as

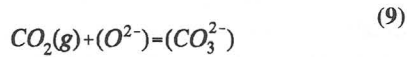
$$C_{PO_4^{3-}} = \frac{(wt\%PO_4^{3-})}{P_{P_2}^{1/2} P_{O_2}^{5/4}} = \frac{K_6 (a_{O^{2-}})^{3/2}}{f_{PO_4^{3-}}} \quad (7)$$

The phosphorus distribution in a refining process can be calculated according to the following equation:

$$\log L_P = \log C_{PO_4^{3-}} + \log f_P + \frac{5}{4} \log p_{O_2} - \frac{6393}{T} - 1.476 \quad (8)$$

### 2.3 Carbonate Capacity

Dissolution of CO<sub>2</sub> in molten slag can be written in the following equation:



$$K_9 = \frac{a_{CO_3^{2-}}}{p_{CO_2} \cdot a_{O^{2-}}} \quad (10)$$

Carbonate capacity of the molten slag is defined as:

$$C_{CO_3^{2-}} = \frac{(wt\% CO_3^{2-})}{p_{CO_2}} = \frac{K_9 a_{O^{2-}}}{f_{CO_3^{2-}}} \quad (11)$$

In the published literature, the carbonate capacity in terms of mole fraction is also used. It is defined by the following equation:

$$C'_{CO_3^{2-}} = \frac{X_{CO_3^{2-}}}{p_{CO_2}} = K_9 \cdot X_{O^{2-}} \cdot \frac{\gamma_{O^{2-}}}{\gamma_{CO_3^{2-}}} \quad (12)$$

The relation between the two forms of slag carbonate capacity is written as follows:

$$\log C_{CO_3^{2-}} = \log C'_{CO_3^{2-}} + \log \Sigma n_i + 1.78 \quad (13)$$

Here  $\Sigma n_i$  is the sum of the number of moles of components in the slag, and changes slightly with the variation of slag composition.

### 2.4 Water Capacity

The water capacity is defined by the expression:

$$C_{H_2O} = \frac{(wt\% H_2O)}{p_{H_2O}^{1/2}} \quad (14)$$

## 3. Correlation of Capacities with Basicity and Temperature

The correlations for oxide system have been discussed previously, so in this paper the emphasis is placed on oxide-halide systems.<sup>(1)</sup>

Fig.1 shows sulphide capacity data for various system at different temperatures. In general, increasing temperature leads to higher C<sub>s</sub> values, and while CaO-based slags and BaO-based slags can be grouped together, it seems to be difficult to include Na<sub>2</sub>O-based slags in this correlation.

A similar plot for phosphate capacities is shown in Figure 2. Here the effect of increasing temperature is clearly to decrease the value of slag phosphate capacity, and again CaO-based and BaO-based slags show rather good agreement.

Data for carbonate capacities are reproduced in Figure 3, showing good correlation at each of the three temperatures and illustrating that the effect of increasing temperature is to reduce the value of slag carbonate capacity.

In the case of water capacity, data on oxide-halides system is very scarce, so Figure 4 is concerned only with oxide systems. Due to the amphoteric nature of water, a markedly curved relationship with basicity is obtained. This figure brings together data for 10 systems and 14 investigations, so that the degree of correlation is impressive. The various

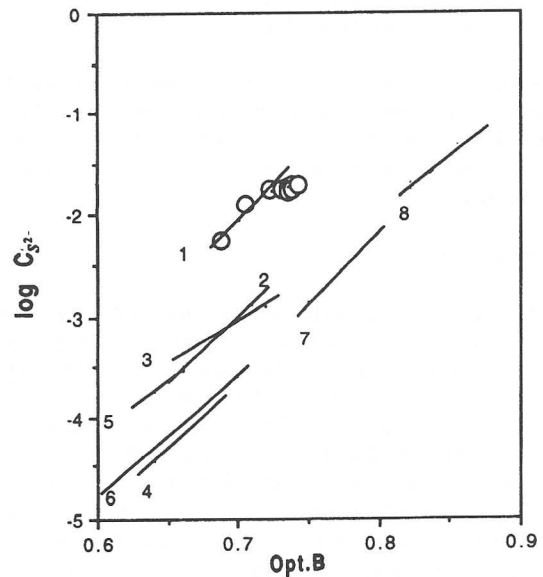


Fig.1 Dependence of  $\log C_{S^{2-}}$  on slag optical basicity.

1. CaO-CaF<sub>2</sub> slag at 1400 °C (this work)
2. CaO-CaCl<sub>2</sub> slag at 1200 °C at 1200 °C<sup>(2)</sup>
3. CaO-CaCl<sub>2</sub>-CaF<sub>2</sub> slag at 1200 °C<sup>(3)</sup>
4. Na<sub>2</sub>O-SiO<sub>2</sub> slag at 1200 °C<sup>(4)</sup>
5. Na<sub>2</sub>O-SiO<sub>2</sub> slag at 1400 °C<sup>(5)</sup>
6. CaO-SiO<sub>2</sub> slag at 1500 °C<sup>(7)</sup>
7. CaO-Al<sub>2</sub>O<sub>3</sub> slag at 1500 °C<sup>(7)</sup>
8. BaO-BaF<sub>2</sub>-SiO<sub>2</sub> slag at 1200 °C<sup>(8)</sup>

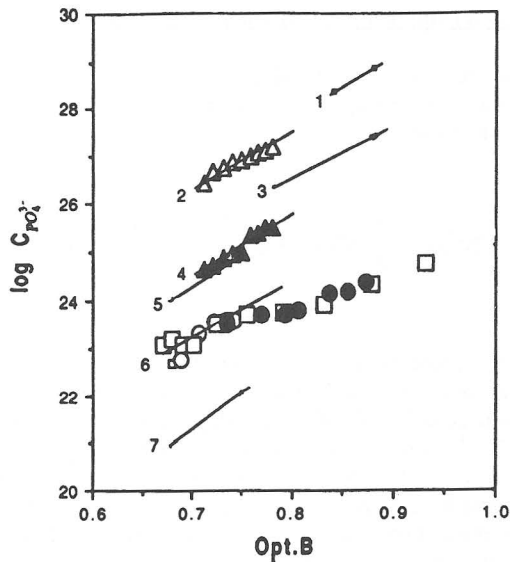


Fig.2 Dependence of  $\log C_{PO_4^{3-}}$  on slag optical basicity.

- CaO-CaF<sub>2</sub> slag at 1400 °C (this work)
- BaO-CaF<sub>2</sub> slag at 1400 °C (this work)
- CaO-BaO-CaF<sub>2</sub> slag at 1400 °C (this work)
- 1. BaO-BaF<sub>2</sub> slag at 1200 °C <sup>(9)</sup>
- 2. BaO-BaF<sub>2</sub> slag at 1300 °C <sup>(9)</sup>
- 3. CaO-CaCl<sub>2</sub> slag at 1200 °C <sup>(10)</sup>
- 4. CaO-CaCl<sub>2</sub> slag at 1300 °C <sup>(10)</sup>
- 5. CaO-CaF<sub>2</sub>-SiO<sub>2</sub> slag at 1300 °C <sup>(11)</sup>
- 6. CaO-CaF<sub>2</sub> slag at 1400 °C <sup>(12)</sup>
- 7. CaO-CaF<sub>2</sub> slag at 1500 °C <sup>(13)</sup>

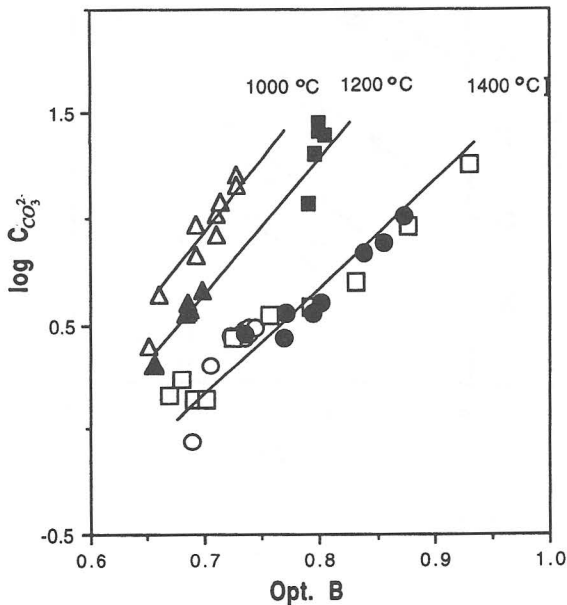


Fig.3 Dependence of  $\log C_{CO_3^{2-}}$  on slag optical basicity.

- CaO-CaF<sub>2</sub> slag at 1400 °C (this work)
- BaO-CaF<sub>2</sub> slag at 1400 °C (this work)
- CaO-BaO-CaF<sub>2</sub> slag at 1400 °C (this work)
- CaO-CaF<sub>2</sub>-NaF slag at 1200 °C (this work)
- ▲ CaO-CaCl<sub>2</sub> slag at 1200 °C <sup>(15)</sup>
- △ CaO-CaF<sub>2</sub>-CaCl<sub>2</sub> slag at 1000 °C <sup>(15)</sup>

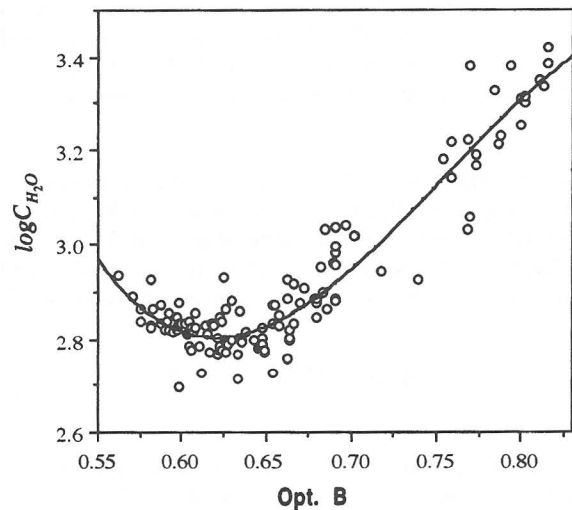


Fig.4 Dependence of  $\log C_{H_2O}$  on slag optical basicity.

studies were unanimous in finding that, within experimental error, temperature variations have no effect on the value of slag water capacity.

It should be mentioned that the values employed for the optical basicities of the various compositions are on the average electron density scale proposed by Nakamura et al. <sup>(16)</sup>

#### 4. Correlation of Capacities with One Another

Since the three capacities display linear correlation with optical basicity, they should similarly show linear correlations with each other, and these correlations can then be used to calculate one from another.

##### 4.1 Correlation between sulphide and carbonate capacities.

In general, from equations (2) and (11), the relation between the sulphide and carbonate capacities is obtained as :

$$\log C_{S^{2-}} = \log C_{CO_3^{2-}} + \log \frac{f_{CO_3^{2-}} \cdot K_1}{K_9 f_{S^{2-}}} \quad (15)$$

For CaO-based slags, this becomes

$$\log C_{S^{2-}} = \log C_{CO_3^{2-}} + \log \frac{f_{CaCO_3}}{f_{CaS}} - \frac{12600}{T} + 7.77 \quad (16)$$

The sulphide and carbonate capacities of CaO-CaCl<sub>2</sub> slags at 1175-1350 °C were studied in author's previous work. <sup>(10,15)</sup> In the previous study the values of sulphide

capacity of the CaO-CaCl<sub>2</sub> slags were calculated from phosphate capacity. Correlation between sulphide and carbonate capacities of CaO-CaCl<sub>2</sub> at 1200 °C is shown in Figure 5. A linear relation is obtained between the two capacities.

Using the experimental data on sulphide capacities of CaO-CaCl<sub>2</sub> slag with X<sub>CaO</sub><0.2 from Sakai and Maeda and carbonate capacity for the same slag from Maeda and McLean, a regression equation related to slag sulphide and carbonate capacities at 1200 °C is obtained as follows:<sup>(2, 15)</sup>

$$\log C_{S^{2-}} = 1.07 \log C_{CO_3^{2-}} - 3.78 \quad (17)$$

The second term on the right hand side of the equation (16) can be calculated, and the obtained value is -3.

The sulphide capacity of CaO-CaF<sub>2</sub>-SiO<sub>2</sub> slags was studied by Susaki, Maeda and Sano and CaO-CaF<sub>2</sub>-CaCl<sub>2</sub> slags by Simeonov, Sakai and Maeda.<sup>(3,18)</sup> The carbonate capacity of CaO-CaF<sub>2</sub>-CaCl<sub>2</sub> and CaO-CaF<sub>2</sub>-SiO<sub>2</sub> slags was studied by Ikeda and Maeda<sup>(14,17)</sup>. Using the data from these studies, a regression equation similar to equation (17) is obtained as follows:

$$\log C_{S^{2-}} = 1.09 \log C_{CO_3^{2-}} - 3.3 \quad (18)$$

The slope of the equation (18) is slightly higher than unity, and the intercept is different than that of equation (17). According to equation (18), the value of second term on the right hand side of equation (16) is calculated as -2.52.

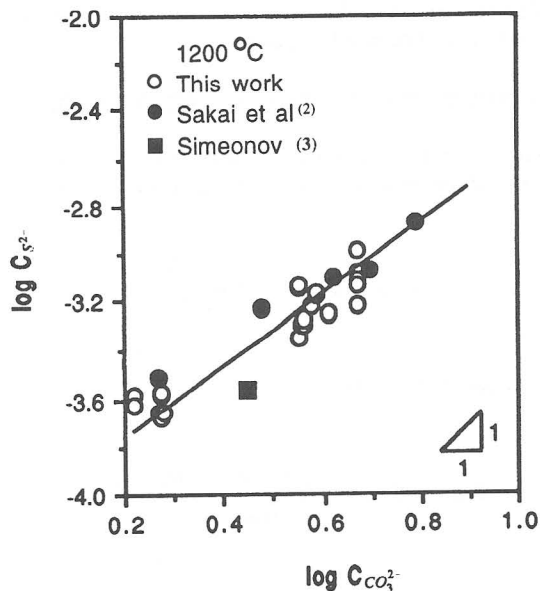


Fig.5 Relation between sulphide capacity and carbonate capacity.

#### 4.2 Correlation between phosphate and sulphide capacities

When using CaO based slags in dephosphorization, the relation between slag phosphate and sulphide capacities is given as follows:

$$\log C_{PO_4^{3-}} = \frac{3}{2} \log C_{S^{2-}} + \log \frac{f_{CaS}^{3/2}}{f_{Ca_{1.5}PO_4}} + \frac{63664}{T} - 13.95 \quad (19)$$

The phosphate capacity of CaO-CaCl<sub>2</sub> slag at 1175 -1350 °C has been studied in author's previous work.<sup>(10)</sup> The sulphide capacity of CaO-CaCl<sub>2</sub> slag was studied at 1000 to 1250 °C.<sup>(2)</sup> Thus the sulphide capacity at the temperature of interest in the present study, from 1175 to 1350 °C, can be estimated by extrapolation of the temperature dependence of the result from Sakai et al.<sup>(2)</sup> A plot of slag phosphate capacity against slag sulphide capacity in the temperature range from 1175 to 1350 °C is given in Figure 6. A linear relation between phosphate and sulphide capacities at different temperatures is found. The slopes of the lines are about 3/2. The value of the second term on the right hand side of equation (19) is between 1.6 and 2.2. This finding is in agreement with the conclusion of Tsukihashi et al.<sup>(19)</sup>

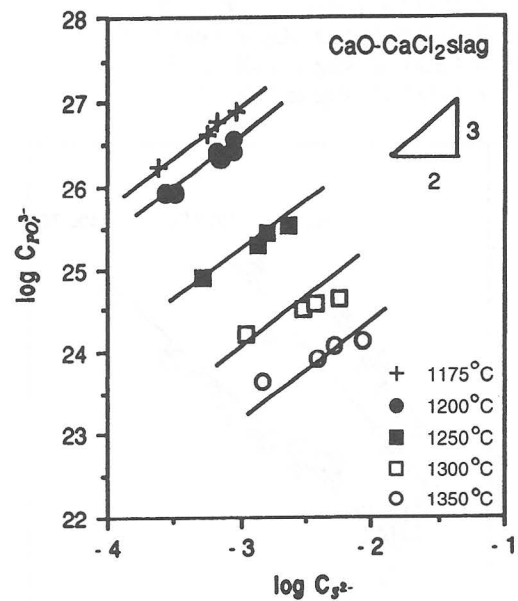


Fig.6 Relation between phosphate capacity and sulphide capacity.

#### 4.3 Correlation between phosphate and carbonate capacities.

Combining equations (7) and (11) gives the expression

$$\log C_{PO_4^{3-}} = \frac{3}{2} \log C_{CO_3^{2-}} + \log \frac{f_{CO_3^{2-}}^{3/2} \cdot K_6}{K_9^{3/2} \cdot f_{PO_4^{3-}}} \quad (20)$$

For CaO-based slags, this becomes

$$\log C_{PO_4^{3-}} = \frac{3}{2} \log C_{CO_3^{2-}} + \log \frac{f_{CaCO_3}^{3/2}}{f_{Ca_1.5PO_4}} + \frac{44764}{T} - 2.29 \quad (21)$$

The carbonate capacity of CaO-CaCl<sub>2</sub> binary slags at 1200 °C was studied by Maeda and McLean.<sup>(15)</sup> The phosphate capacity for the same slags was studied in previous work by using the experimental data from McKague.<sup>(10)</sup> A good linear relation between the two capacities was found, see Figure 7. It can be expressed in the following equation:

$$\log C_{PO_4^{3-}} = \frac{3}{2} \log C_{CO_3^{2-}} + 25.55 \quad (22)$$

Comparing equation (21) with equation (22), the value of second term on the right hand side of equation (21) was obtained to be -2.55.

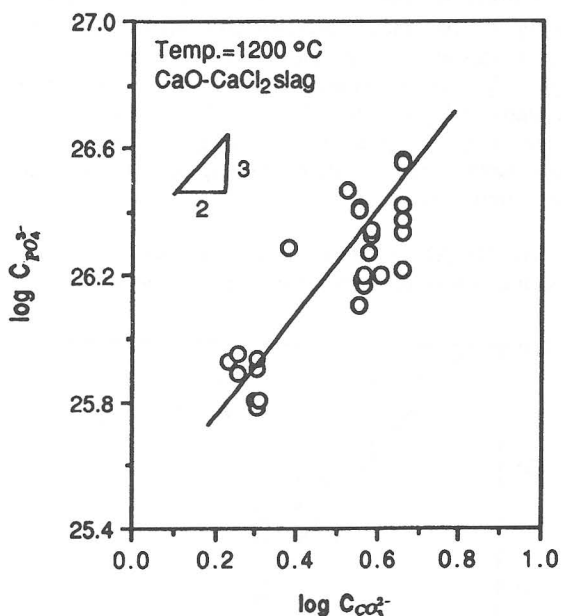


Fig.7 Relation between phosphate capacity and carbonate capacity.

## 5. Sources of Concern regarding Capacities

One source of concern, or at least a cause for caution, with regard to capacities lies in the fact that significantly different values can be obtained depending on the thermodynamic data employed in the calculation. For example, Simeonov et al have shown that P<sub>S2</sub> values varying by a factor of 5 leading to C<sub>S</sub> values varying by a factor of over 2 can be obtained using data from different data bases.<sup>(20)</sup> Thus, there seems to be little point in repeat

determinations to obtain degrees of accuracy greater than that imposed by the inaccuracy of the thermodynamic data available.

Another source of concern and potentially of error is the fact that the various dissolving species may be competing with each other for the available "free" oxygen ions with which to combine or exchange. For example, in the course of sulphide capacity determinations, the oxygen potential is normally controlled by mixtures of either H<sub>2</sub>/H<sub>2</sub>O or CO/CO<sub>2</sub>. Since basic slags have significant capacities for both H<sub>2</sub>O and CO<sub>2</sub>, the dissolution of these species to combine with O<sup>2-</sup> ions to form OH<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> ions respectively, is potentially occurring in parallel with the replacement of O<sup>2-</sup> ions by S<sup>2-</sup> ions, and obviously the more of these O<sup>2-</sup> ions which are consumed by H<sub>2</sub>O or CO<sub>2</sub>, the fewer there are for replacement by S, and the lower the sulphide capacity will be measured to be. Since those C<sub>S</sub> values obtained from slag-metal distribution, where this effect cannot operate, are in general in reasonably good agreement with those obtained from slag-gas studies, it does not seem that this competition for the available oxygen ions introduces serious error. This is presumably due to the fact that the rate of the sulphur-oxygen exchange reaction is faster than those of the combination of oxygen ions with H<sub>2</sub>O and CO<sub>2</sub>, perhaps because of steric factors. If this is the reason, it may not remain true in very basic, highly depolymerized slags where the steric restrictions are less severe, so this concern is worth bearing in mind, particularly in highly basic slags. It may in fact be part of the reason that the plot of log C<sub>S</sub> against optical basicity becomes non-linear at very high basicities.<sup>(21)</sup>

The measurement of very high capacities in highly basic slags leads to another possible cause for concern. This is linked to the fact that implicit in the definition of capacities in terms of the wt% of the solute species is the assumption that the solute is obeying Henry's Law and its activity coefficient is constant. At significant concentrations, this may cease to be true, and if f<sub>solute</sub> increases, then its wt% increases less rapidly with increase in its activity and a non-linear dependence on basicity will result. This may also be part of the explanation for the case noted above, and it would seem wise to restrict the correlation with basicity to the range over which it is linear.<sup>(21)</sup>

## 6. The Misuse of Capacities in Slags

There seem to be three distinct ways in which capacities have been misused, and these will be discussed in turn.

### 6.1 Solutes Dissolved in More than One Form

There appear to be three examples of this. The first is the case of phosphorus, which can be dissolved not only as the monomer PO<sub>4</sub><sup>3-</sup>, but also as the dimer at concentration above about 3%, which caused scatter in correlations with basicity. This highlights the fact that the concept of capacity should be used only when the species in solution is known, and is a single species over the entire

composition range. Where polymerization is possible separate capacities should be defined for the monomer, dimer and so on.

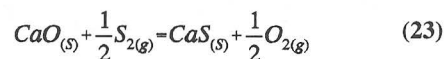
A slightly different situation occurs in the case of nitrogen dissolved in slags. The nitrogen atom or ion is sufficiently small that it can replace oxygen ions in the network (ie. in the polymeric anions), as well as "free" oxygen ions. This was elucidated quantitatively by Martinez and Sano for calcium silicates, and similar considerations would be expected to apply to aluminate, borate and phosphate melts.<sup>(22)</sup> The nitrogen which substitutes for oxygens in the network shows an inverse relationship with basicity, whereas that replacing "free" oxygens is directly related to basicity. Thus, when the two are lumped together, as they are in a nitride capacity defined in terms of the total nitrogen content of the slag, considerable confusion results. In fact, as demonstrated by Ferreira, the nitrogen content in a polymeric melt is governed by structural considerations, and basicity is not the most appropriate parameter for correlation of data.<sup>(23)</sup> It may still be useful to make measurements of the total nitrogen capacities of slags, although using slags for nitrogen removal does not seem to be a very promising procedure, as long as it is appreciated that the plot against composition will tend to have a "V" shape for each binary system, and since the apex of the V will not necessarily occur at the same basicity or molar ratio of basic to acid component, any attempt to rationalize data for different systems on a single curve is unlikely to provide a good correlation.

A third example in this category is the situation where an element can exist in solution in a slag in more than one valency state, possibly including zero (ie. the element). As well as being true for iron, manganese, titanium and vanadium in steelmaking slags, this is also the case for vanadium, niobium, antimony and arsenic in soda-based melts, and for arsenic, antimony and bismuth in calcium ferrite and iron silicate slags, so that the distribution ratios are influenced more by the oxidation state, and therefore by  $P_{O_2}$ , than by differences in basicity (or electronegativity) of the oxides.<sup>(24-29)</sup> This would presumably also apply to capacities at any given  $P_{O_2}$ . The higher the oxidation state, the more acidic the oxide and the greater the distribution ratio and capacity at any value of basicity. This highlights a shortcoming of the optical basicity in being calculated from electronegativity, which does not make a sufficiently clear distinction between valency states.

### 6.2 Solute Concentrations in Excess of the Solubility Limit

Another way in which it appears that capacities may have been misused is in connection with the stability of species in slags. It is suggested that the terms solubility and capacity should be reserved for the situation where the "compound" of the element being dissolved is less stable than its oxide at the temperature concerned. If this criterion is not observed, the compound can be laid down at unit activity even when the oxide activity is less than unity, and this undissolved material will be included in the analyzed value as having been dissolved. For the case where the

oxide activity is one, the relative stabilities can be expressed as the free energy of the exchange reaction, such as for example,



$$\Delta G^0 = 92,470 - 4.60T \quad (J)$$

which is sometimes expressed as  $\Delta(\Delta G^0)$ . The values of  $\Delta(\Delta G^0)$  for oxide-sulphide equilibria are summarized in Figure 8, where they are shown to display a strong dependence on oxide basicity, and almost no temperature dependence. A similar plot for oxide-carbonate equilibria shows considerably more scatter, possibly due to error associated with the free energy of formation of carbonates at these elevated temperatures, but does show a much greater temperature dependence.

Figure 8 indicates that for  $Na_2O$ , for example, the sulphide is more stable than the oxide over a wide range of temperature, including those of interest for desulphurization of iron and steel, which is of course why  $Na_2O$  is such an excellent desulphurizer, and if it were not for its effects on the environment and on refractories, it would almost certainly be the major desulphurizer instead of  $CaO$ . However, this also means that unless rather low values of the gas sulphurizing potential,  $((P_{S_2}/P_{O_2}))^{1/2}$ , are employed, particularly at high values of  $a_{Na_2O}$  in  $Na_2O$ -based slags, the slag can go on apparently absorbing sulphur in excess of the solubility limit, simply by creating  $Na_2S$  as a separate phase at unit activity.

Similarly  $Na_2CO_3$  is more stable than  $Na_2O$  over the temperature range of interest for slags, so that unless very

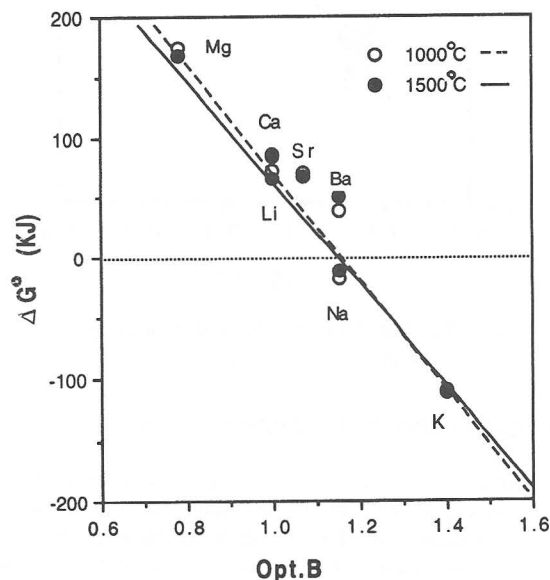


Fig.8 Relation between the free energy for oxide-sulphide equilibria and the optical basicity of the oxide.

low values of  $P_{CO_2}$  are employed, particularly at high  $a_{Na_2O}$  values,  $Na_2CO_3$  can be precipitated as a separate phase and this will be included in the value of the carbonate capacity as if it were truly in solution. By this mechanism, erroneously high values of capacities can be obtained and reported, and a thermodynamic analysis of literature values for various capacities indicates that this has indeed happened.

To illustrate the method of conducting this thermodynamic analysis, the exchange reaction (23) already mentioned will be selected:

for which

$$\log K = \log \frac{a_{CaS}}{a_{CaO}} \left( \frac{P_{O_2}}{P_{S_2}} \right)^{1/2} = -\frac{4808}{T} + 0.24 \quad (24)$$

when  $a_{CaS} = 1$ ,

$$\log a_{CaO} \left( \frac{P_{S_2}}{P_{O_2}} \right)^{1/2} = \frac{4808}{T} - 0.24 \quad (25)$$

and thus at 1600 °C, 1873K,

$$\frac{1}{2} \log \frac{P_{S_2}}{P_{O_2}} = 2.327 - \log a_{CaO} \quad (26)$$

This equation is plotted as the line labelled 1600 °C for CaO in Figure 9, and similar lines for other temperatures and for BaO and  $Na_2O$ , calculated in the same way, are also shown in Figure 9. For CaO and BaO, increase of

temperature decreases the permissible value of  $(P_{S_2}/P_{O_2})$ , whereas for  $Na_2O$  it is the other way around, but the effects are rather small.

Plots for carbonate and water, or hydroxyl, capacities, calculated similarly, are shown in Figures 10 and 11, and the thermodynamic data used in these calculations are listed in Table 1. Obviously, different lines would be obtained depending on the thermodynamic data employed, but superimposition of the experimental conditions used in a number of studies indicates that determinations have been made in the range where creation of a separate phase was occurring and consequently the capacities reported are erroneously high. This appears to be particularly true of some investigations of carbonate capacities, which is very unfortunate since, following the milestone paper of Wagner, carbonate capacities have been widely advocated as the best available measure of basicity.<sup>(30)</sup>

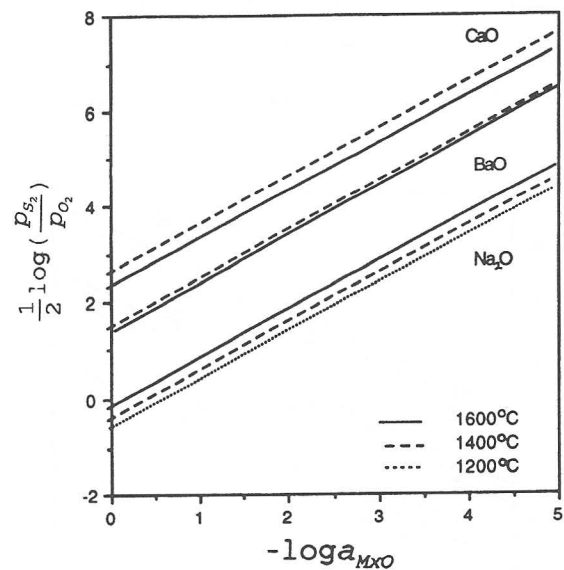


Fig.9 Maximum  $(p_{S_2}/p_{O_2})^{1/2}$  for valid  $C_s$  determination.

Table 1 Summary of Thermodynamic Data Used

Reaction	$\Delta G^0$ (J)
$CaO(s) + 1/2 S_2(g) = CaS(s) + 1/2 O_2(g)$	$92,470 - 4.60T$
$BaO(s) + 1/2 S_2(g) = BaS(s) + 1/2 O_2(g)$	$13,260 + 20.75T$
$Na_2O(l) + 1/2 S_2(g) = Na_2O(l) + 1/2 O_2(g)$	$-39,080 + 15.44T$
$CaO(s) + CO_2(g) = CaCO_3(s)$	$-161,340 + 137.24T$
$BaO(s) + CO_2(g) = BaCO_3(s)$	$-250,750 + 147.07T$
$Na_2O(l) + CO_2(g) = Na_2CO_3(l)$	$-316,350 + 130.33T$
$CaO(s) + H_2O(g) = Ca(OH)_2(s)$	$-102,510 + 130.33T$
$BaO(s) + H_2O(g) = Ba(OH)_2(l)$	$-113,800 + 89.87T$
$Na_2O(l) + H_2O = 2NaOH(l)$	$-206,060 + 94.93T$

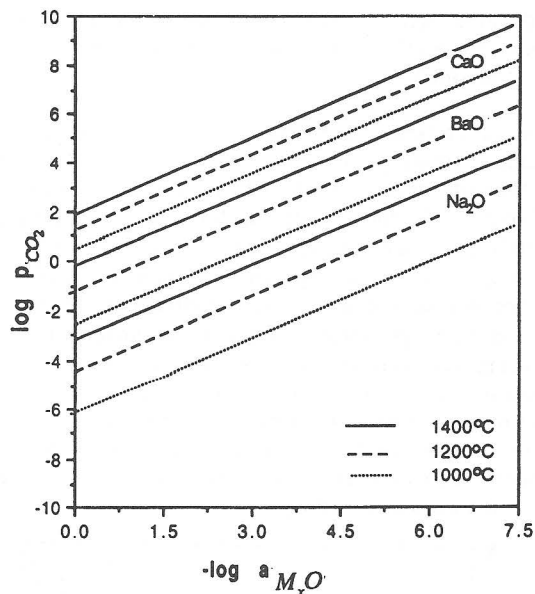


Fig.10 Maximum  $p_{CO_2}$  for valid  $C_{CO_3}$  determination.

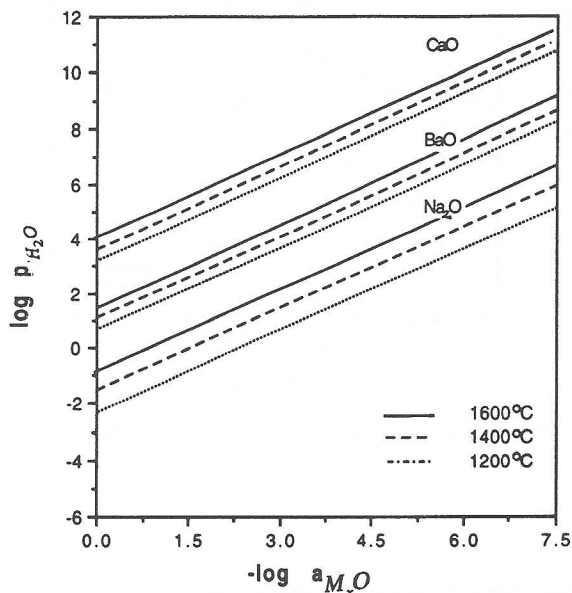


Fig.11 Maximum  $p_{H_2O}$  for valid  $C_{H_2O}$  determination.

It should perhaps be stressed that these calculations, and this possible source of error, apply only to capacities obtained by gas-slag equilibrium. Where capacities have been determined by measuring the slag-metal distribution, the amount of the element being transferred is limited by the experimental conditions employed, and such capacities could well be correct. It is only where the element being dissolved is supplied by the gas phase on a continuous basis that the problem becomes acute. Since phosphate capacities have virtually all been obtained by the slag-metal technique, they are not subject to this source of error, and consequently have not been included in this analysis.

Obviously, this analysis could be extended to the case where there are two or more basic oxides in the slag at comparable concentrations. Ultimately each specific case would need to be examined separately, but for each oxide the likelihood of a problem increases as the activity of the oxide increases, and for each of the solutes considered the severity of the problem increases in the order  $CaO < BaO < Na_2O$ . For  $MgO$ , this problem is less severe than for  $CaO$ , while for  $K_2O$  it is even more severe than for  $Na_2O$ , but these oxides are seldom present in dominant amounts.

### 6.3 Capacity Measurement in Slags which are not Completely Liquid

An extension of the situation discussed previously, where the phase exceeding its solubility limit is one of the oxide components of the slag, also appears to have occurred in a few investigations. In this case, the capacity remains essentially constant from the point of saturation onwards, so that it is underestimated with respect to basicity if the saturating phase is a basic oxide, and overestimated with respect to basicity if the saturating phase is an acid oxide. Since this is normally much easier to detect than the case of supersaturation with the phase whose capacity is being measured, it has not occurred in any large number of cases.

### 7. Summary

Data available for sulphide, phosphate, water or hydroxyl and carbonate capacities have been reviewed with the emphasis on data acquired recently, and on those for oxide-halide systems. Their dependence on composition and temperature, and some of the correlations between capacities have been discussed. In the latter section of the paper, some sources of concern regarding capacities are mentioned, followed by some ways in which capacities could be, and in some cases appears to have been misused. The three problem areas highlighted are solutes dissolved in more than one form, solute concentrations in excess of the solubility limit and capacity measurements in slags which are not completely liquid. Thus, it appears that care must be taken to avoid compromising the usefulness and validity of the capacity concept.

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