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# CARBONATE AND SULFIDE CAPACITIES OF CAO–CAF$_2$ BASED FLUXES

Masafumi Maeda*, Simeon Simeonov** and Takashi Ikeda*

*Institute of Industrial Science, the University of Tokyo, Japan
**Formerly with Institute of Industrial Science, the University of Tokyo, Japan
now with Sofia Technological University, Sofia, Bulgaria

**Synopsis:**

Carbonate capacity and sulfide capacity measured is compared for slags of various compositions and temperatures. Carbonate capacity is not a complete index, however, this exhibits reasonable correlation with sulfide capacity of CaO–CaF$_2$ based flux. Theoretical optical basicity was reviewed and its additivity rule explained. Measured sulfide capacity was plotted against carbonate capacity and theoretical optical basicity.

**Key words:** CaO, CaF$_2$, carbonate capacity, sulfide capacity, optical basicity, Wagner

## Carbonate and Sulfide Capacity

Evaluation of slags in terms of refining power is simplified if the capacity of slags for impurities is considered. For instance if the sulfur is the impurity, it is the sulfide capacity. This parameter depends only on the slag composition and temperature. Comprehensive reviews on this subject is available in the literature[1–4]. However, to measure the sulfide capacity both sulfur and oxygen potentials must be fixed, hence the experimental setup necessary is complicated. If we could correlate capacities, the choice of the flux will be very simple. An suggestion was made by Wagner[5] to choose carbonate capacity as an index. A detailed discussion of the carbonate capacity is in the original literature, however, we will briefly review his comment. The statement below is modified by present authors to understand it clearly.

The dissolution of carbon dioxide into molten fluxes would be formulated as follows:

$$CO_2 + O^{2-} = CO_3^{2-} \tag{1}$$

Because Eq.(1) implies that the content of carbon dioxide would increase with increasing oxygen anion activity, several studies[6,7] have demonstrated the solubility as an index of basicity.

$$\frac{1}{2}S_2 + CO_3^{2-} = S^{2-} + \frac{1}{2}O_2 + CO_2 \tag{2}$$

Assuming a hypothetical reaction between sulfide anion and carbonate anion, we can correlate capacities. The equilibrium constant for the reaction is :

$$K_{(2)} = \frac{a_{S^{2-}} \cdot P_{CO_2} \cdot P_{O_2}^{1/2}}{a_{CO_3^{2-}} \cdot P_{S_2}^{1/2}} = \frac{(wt\%S) \cdot (P_{O_2} / P_{S_2})^{1/2} \cdot P_{CO_2} f_{S^{2-}}}{wt\%CO_3^{2-} \cdot f_{CO_3^{2-}}} \tag{3}$$

For Eq.(1), carbonate capacity is defined as:

$$C_{CO_3^{2-}} = \frac{wt\%CO_3^{2-}}{P_{CO_2}} \tag{4}$$

and sulfide capacity is:

$$C_{S^{2-}} = (wt\%S)\cdot\left(\frac{P_{O_2}}{P_{S_2}}\right)^{\frac{1}{2}} \tag{5}$$

Then Eq.(4) can be rewritten by using sulfide capacity:

$$C_{CO_3^{2-}} = C_{S^{2-}}\cdot K_{(2)}\cdot\frac{f_{S^{2-}}}{f_{CO_3^{2-}}} \tag{6}$$

Suppose we have a reference slag. Its carbonate capacity and sulfide capacity are designated with superscript °. The choice of the reference slag is essentially arbitrary as long as the composition is specified. Hypothetical slag could be used. Then we may obtain an equation similar to Eq.(6) as:

$$C^o_{CO_3^{2-}} = C^o_{S^{2-}}\cdot K_{(2)}\cdot\frac{f^o{}_{S^{2-}}}{f^o{}_{CO_3^{2-}}} \tag{7}$$

where f with superscript ° designates the activity coefficient of a reference slag.
We may take a ratio of Eqs.(6) and (7).

$$\frac{C_{CO_3^{2-}}}{C^o_{CO_3^{2-}}} = \frac{C_{S^{2-}}}{C^o_{S^{2-}}}\cdot\frac{\dfrac{f_{S^{2-}}}{f^o{}_{S^{2-}}}}{\dfrac{f_{CO_3^{2-}}}{f^o{}_{CO_3^{2-}}}} \tag{8}$$

$$C_{CO_3^{2-}} = C_{S^{2-}}\cdot\frac{C^o_{CO_3^{2-}}}{C^o_{S^{2-}}}\cdot\frac{\dfrac{f_{S^{2-}}}{f^o{}_{S^{2-}}}}{\dfrac{f_{CO_3^{2-}}}{f^o{}_{CO_3^{2-}}}} \tag{9}$$

It is reasonable to assume that the compositional dependency of $f_{S^{2-}}$ referred to the reference slag ($f^o{}_{S^{2-}}$) and that of $f_{CO_3^{2-}}$ referred to the reference slag ($f^o{}_{CO_3^{2-}}$) are very similar. Hence, the last term of Eq.(9) can be considered nearly constant. The ratio $C^o{}_{CO_3^{2-}}/C^o{}_{S^{2-}}$ is constant because we have already defined a composition of the reference slag. Therefore, we obtain a linear relation between $C_{CO_3^{2-}}$ and $C_{S^{2-}}$.

The last term in Eq.(9) is constant as discussed above and $f^o{}_{S^{2-}}/f^o{}_{CO_3^{2-}}$ is constant, because the reference slag is fixed. Therefore, $f_{S^{2-}}/f_{CO_3^{2-}}$ is apparently constant. However, we must understand the true implications to avoid mistakes.

### Theoretical Optical Basicity and Sulfide Capacity

Duffy and Ingram[12] defined the basicity index named "optical basicity" in a glass as the ability of oxygen anion to donate negative charge to the solution. Originally this basicity index was defined as the spectroscopic shifts observed in the $^1S_0 \dashrightarrow {}^3P_1$ bands of a prove cation such as $Tl^+$, $Pb^{2+}$ and $Bi^{3+}$ under various environment such as in concentrated acid, fused salts and glasses including sodium borate and sodium silicate[13]. If $Pb^{2+}$ is used as a prove ion, the optical basicity index relative to CaO for a measurable specimen can be calculated as [12]:

$$\Lambda = \frac{(60{,}700-\nu)}{31{,}000} \qquad \textbf{(10)}$$

where $\nu$ is the wave number [$cm^{-1}$] for the ultraviolet absorption observed for the transparent specimens [*1].

They also derived the semi-empirical correlation between Pauling's electronegativity and $\Lambda$ for pure cations by using experimentally obtained absorption which was mentioned earlier by assuming the additivity rule of $\Lambda$ for the components of solution. $\Lambda$ for pure oxide components such as silica, alumina and phosphorus oxide, were back-calculated from their electronegativity values using the above mentioned correlation when it is applied for metallurgical slags. They defined these index as theoretical basicity index $\Lambda_{th}$.

Therefore, the theoretical optical basicity index $\Lambda_{th}$ for an oxide mixture, should be calculated by using $\Lambda_{th\ i}$ for pure oxide components which is estimated by Pauling electronegativity values (12) and the additivity rule for oxide components as Eq.(13).

$$\Lambda_{th\ i} = \frac{1}{1.36\cdot(\chi_i - 0.26)} \qquad \textbf{(11)}$$

$$\Lambda_{th\ mixture} = \Sigma\,\Lambda_{th\ i}\,x_i \qquad \textbf{(12)}$$

where $\chi_i$ is Pauling's electronegativity, $x_i$ is equivalent cation fraction and $\Lambda_{th\ i}$ is theoretical optical basicity index of the pure component i.

Thus, $\Lambda_{th\ mixture}$ is not an experimentally determined index, but it should be regarded as one of the conventional expressions for basicity as a function of slag composition similar to $CaO/SiO_2$ or its modifications. However, we admit that $\Lambda_{th\ i}$ for the pure oxide gives a relative strength of an oxide as a base, since the electronegativity is taken into account.

Sosinsky and Sommerville[15] reported an equation for the relation between the theoretical optical basicity and sulfide capacity for slags without $CaF_2$ based on a large number of experimental data from several authors (Eq. (14)) for temperatures ranging from 1400 to 1700°C. They estimated $\Lambda_{th\ i}$ for opaque oxides such as FeO, $TiO_2$ etc according to Eq.(12) from their $\Lambda_i$ values.

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[*1] The wave number of 31,000 in Eq.(11) was calculated as the difference of ultraviolet absorption of hypothetical free $Pb^{2+}$ (60,700$cm^{-1}$)(*) and that "observed" for $Pb^{2+}$ in solid CaO (29,700$cm^{-1}$)(**). The wave number for CaO was rather uncertain as McClure(**) and, Ingram and Duffy mentioned[14]. However, this is not very important provided the same equation is used for the calculation .

(*)J.A.Duffy and M.D.Ingram: J.of Non-Crystalline Solids, 1976, vol.21, pp373-410

(**)D.S. McClure :Solid State Physics, 1959, vol.60, pp399-525(p518)

$$\log C_{S^{2-}} = 43.6\Lambda_{th} - 25.2 + \frac{(22{,}690 - 54{,}640\cdot\Lambda_{th})}{T} \qquad \textbf{(13)}$$

In order to make comparisons with Eq. (14), the theoretical optical basicity ($\Lambda_{th}$) of present slags was calculated by using Eq.(12) and (13). Optical basicity index of oxide components ($\Lambda_i$) was calculated by their electronegativity according to Eq.(12). $\Lambda_{CaO}$ is unity according to the definition, and for $SiO_2$, 0.48 after Duffy and Ingram[12]. Optical basicity index of $CaF_2$, $\Lambda_{CaF2}$, was determined as 0.67 by Nakamura et al.[16] by means of chemical shift measurement of $Pb^{2+}$ in $CaF_2$.

## Sulfide and Carbonate Capacities of $CaO-CaF_2$ based Slags

Sulfide capacities measured by the author's group are shown in the Figures 1 and 2. Technique used was the equilibrium between molten silver, slag and carbon monoxide, carbon dioxide and argon mixture. Crucibles used are mostly nickel. Detail descriptions of the experiments can be found in the literature[8]. Effect of additives is interesting for the metallurgist. The additions of MgO, $Al_2O_3$, MnO and $Na_2O$ were tried. Results are in Figures 3 and 4.

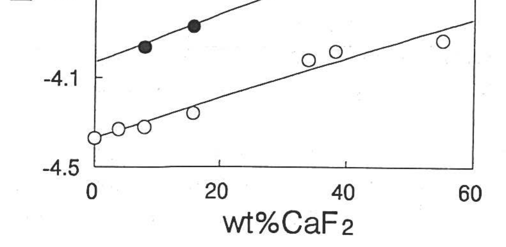

Figure 1 Sulfide capacity of $CaO-CaF_2-CaCl_2$ melts (unpublished work)

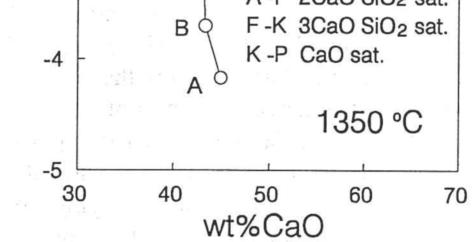

Figure 2 Sulfide capacity versus wt% CaO on the liquidus at 1350°C

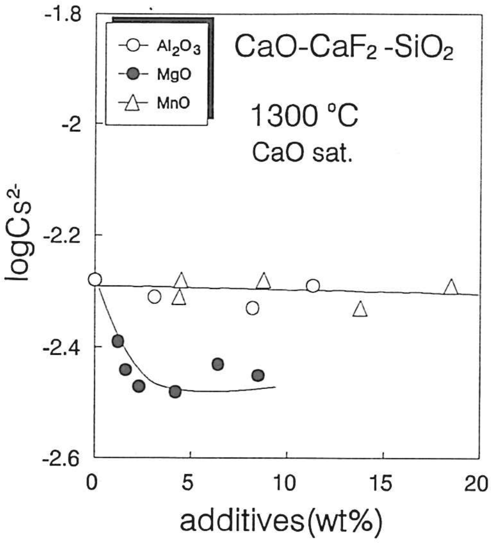

Figure 3 Variation of sulfide capacity with addition of $Al_2O_3$, MgO and MnO

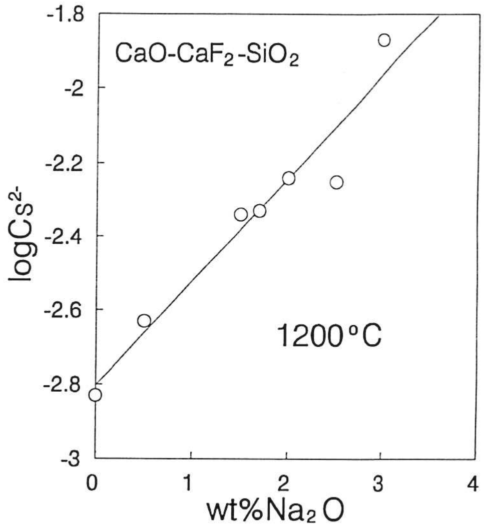

Figure 4 Effect of $Na_2O$ on sulfide capacity

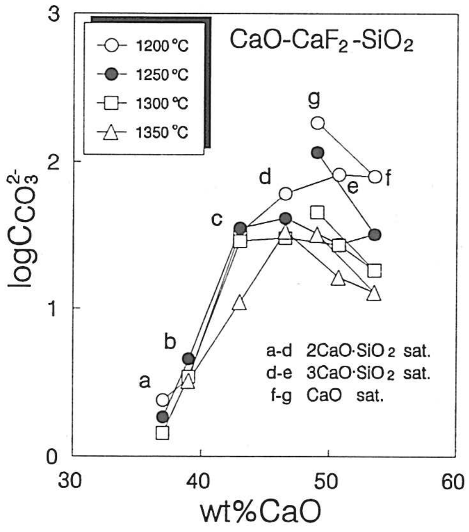

Figure 5 Carbonate capacity of $CaO-CaF_2-SiO_2$ slags at 1300°C

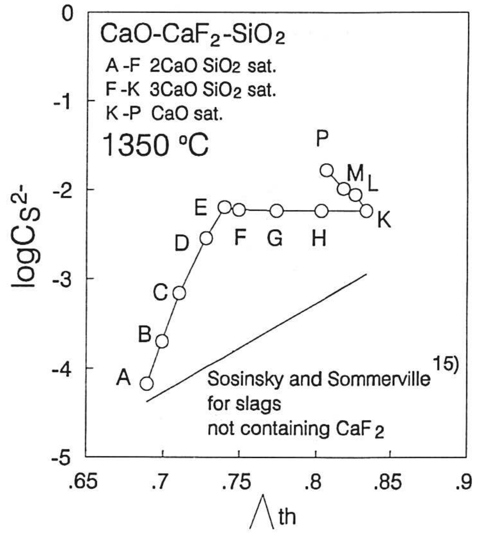

Figure 6 Sulfide capacity as a function of theoretical optical basicity with the Sosinsky and Sommerville equation modified with Nakamura's coefficient for $CaF_2$

Carbonate capacity measured are shown in Figure 5. Thermogravimetric technique and the chemical analysis for quenched samples were used. The experimental aspects are described in previous papers[9–11].

Figure 6 shows the correlation at 1350°C as well as Sosinsky and Sommerville's equation for slags containing no $CaF_2$. It should be noted that, for present slags, no simple relation was obtained. Instead, three lines were obtained individually for $2CaO \cdot SiO_2$, $3CaO \cdot SiO_2$ or CaO saturated slags in order to draw a linear relation between $\Lambda_{th}$ and log ($C_S$2-). Furthermore the present $C_S$2- values are higher than those estimated by the equation for slags without $CaF_2$. Similar behavior was also observed at temperatures investigated other than 1350°C. These results indicate that for highly basic slags such as CaO saturated slags containing $CaF_2$, the theoretical optical basicity calculated by Eq.(12) and (13) is not suitable to estimate sulfide capacities, or that $\Lambda_{CaF2}$ determined by Nakamura et al. is underestimated. Sulfide capacity for $CaO-CaF_2-CaCl_2$ is shown as a function of carbonate capacity in Figure 7 and those for $CaO-CaF_2$, $CaO-CaF_2-Al_2O_3$ and $CaO-CaF_2-SiO_2$ are in Figure 8.

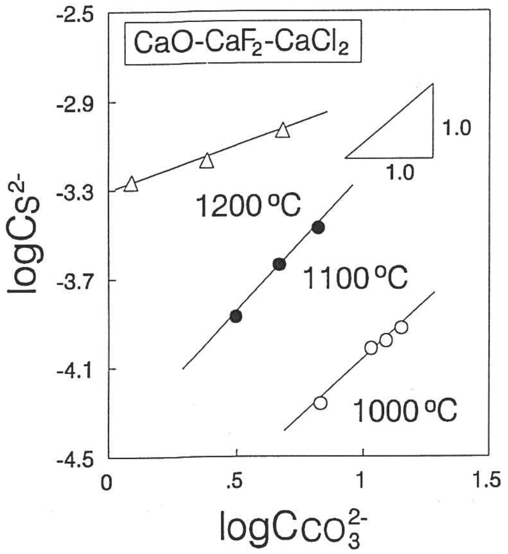

Figure 7 Sulfide capacity for $CaO-CaF_2-CaCl_2$ as a function of carbonate capacity

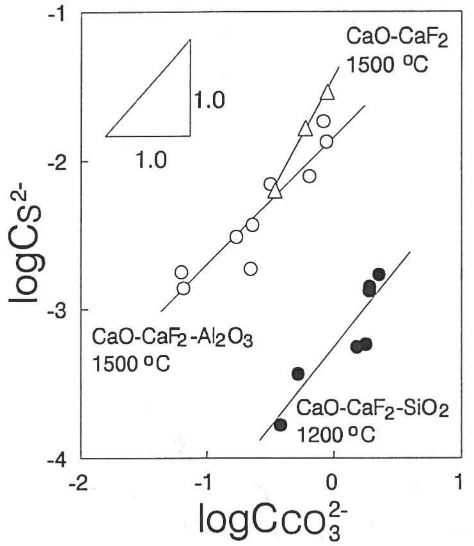

Figure 8 Sulfide capacity for $CaO-CaF_2$, $CaO-CaF_2-Al_2O_3$ and $CaO-CaF_2-SiO_2$ as a function of carbonate capacity

## Conclusion

Carbonate capacity and sulfide capacity measured are compared for slags of various compositions and temperatures. Carbonate capacity is not a complete index, however, this exhibits reasonable correlation with sulfide capacity of $CaO-CaF_2$ based flux. Optical basicity was explained and discussion was made for the theoretical optical basicity.

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