

Solubility of Silver in Molten Slags as a Measure of Basicity

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Abstract

The solubility of silver in molten MO-B₂O₃ (MO = CaO, BaO, and Na₂O), CaO-RO (RO = B₂O₃, SiO₂, and Al₂O₃), and CaO-Al₂O₃-CaF₂ slags was measured at high temperatures to modify a measure of basicity (B_S). The relative basicity of pure BaO and Na₂O was obtained as 1.3 and 2.4 with reference to CaO (1.0), respectively, based on Ag solubility in MO-B₂O₃ slags; and that for the acidic oxides such as SiO₂ and Al₂O₃ was estimated to be 2.6 and 3.8 with reference to B₂O₃ (1.0), respectively. The relative basicity of CaF₂ was also obtained to be 1.3 with reference to CaO. The relationship between the viscosity of various slags and B_S indicated the compensation for the effect of Al₂O₃ in silicate melts and the effect of CaF₂ on slag viscosity. The nitride and sulfide capacities in various slags could be also expressed as a good linear equation by using the present measure of basicity.

INTRODUCTION

Basicity ($a_{O^{2-}}$) is one of the most important thermodynamic concepts affecting the physicochemical properties of molten slags. However, because of the impossibility of direct measurement of single-ion activity,^[1] an empirical Vee ratio has widely been used in iron and steelmaking processes, although there is very little theoretical meaning to this expression.^[2] Since the ionic characteristic of slag was reported, various indirect

measures such as capacity,^[3] redox equilibrium of transition metal ions,^[4] activity of basic oxides,^[5] and (theoretical) optical basicity^[6] have been proposed; but these basicity measures have been restricted within slag systems.

Recently, it has been reported that solubility of noble metals such as platinum^[7] and silver^[8,9] in molten slags could be an indirect measure of basicity. Previous studies showed the dissolution mechanism of silver into the slags and indicated that Na₂O was considered to be more basic than BaO was, followed by CaO in the B₂O₃-bearing slags.^[9]

In the present study, the slag system was extended to the CaO-RO (RO = B₂O₃, SiO₂, and Al₂O₃) and CaO-Al₂O₃-CaF₂ to understand the relative basicity of pure acidic oxides and the effect of CaF₂ on slag basicity; thereafter the basicity scale of slags containing CaO, BaO, Na₂O, B₂O₃, SiO₂, Al₂O₃, and CaF₂ in the form of modified Vee ratio considering the ionic character of slag was suggested and was compared to the viscosity data, nitride and sulfide capacities reported in the current research literature.

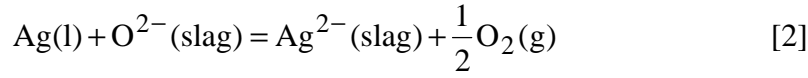
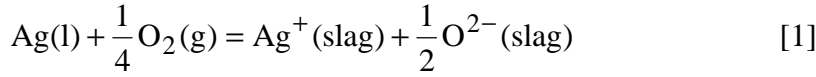
EXPERIMENTAL

A super kanthal electric furnace was used for an equilibration of silver and slag melts. The temperature was controlled within ± 2 K using an R-type (Pt-13Rh/Pt) thermocouple and a proportional-integral-differential (PID) controller. The slag samples were prepared using reagent-grade pure oxides and CaF_2 . A schematic diagram of the experimental apparatus is available in previous articles.^[8,9]

The slag samples and silver were maintained in graphite crucibles under a CO atmosphere to control the oxygen partial pressure by C/CO equilibrium reaction. The impurities in the gases were removed by passing the gases through CaSO_4 , $\text{Na}_2\text{O} \cdot \text{CaO}$, and silica gel. The equilibration time was predetermined as 12 to 18 hours for each slag system. After equilibrating, the samples were quenched by Ar gas and crushed for chemical analysis. The content of silver and that of each component in the slag was determined by atomic absorption spectrometry (Shimadzu, AA-6601 F/G) and titration methods, respectively.

THEORETICAL CONSIDERATION

The dissolution of silver into the slags, which is dependent of slag basicity, under reducing condition has been known to occur by equations [1] and [2] in an arbitrarily acidic and basic slags, respectively:^[8,9]



By using the equilibrium constant of equation [1], the following relation can be deduced.

$$\begin{aligned} \log (\text{mass\% Ag}^+) &= -\frac{1}{2} \log a_{\text{O}^{2-}} + \frac{1}{4} \log p_{\text{O}_2} - \log f_{\text{Ag}^+} + \log K_{[1]} \\ &= -\frac{1}{2} \log a_{\text{O}^{2-}} + C \end{aligned} \quad [3]$$

where $a_{\text{O}^{2-}}$, p_{O_2} , f_{Ag^+} , $K_{[1]}$, and C are respectively the activity of the O^{2-} ion, the oxygen partial pressure, the activity coefficient of the Ag^+ ion, the equilibrium constant of equation [1], and a constant at a fixed p_{O_2} , f_{Ag^+} , and $K_{[1]}$. The solubility of silver ($\log (\text{mass\% Ag}^+)$) is expected to be inversely proportional to the activity of the O^{2-} ion ($\log a_{\text{O}^{2-}}$), with the slope of 1/2 at a fixed temperature and oxygen partial pressure, assuming that f_{Ag^+} is independent of slag composition. This could be qualitatively confirmed from the experimental results that the activity coefficient of Ag_2O was independent of composition in each slag system with approximately the same value. Then, the following general expression can be deduced:

$$\begin{aligned}
\log (\text{mass\% Ag}^+)_{\text{slag I}} - \log (\text{mass\% Ag}^+)_{\text{slag II}} = \\
-\frac{1}{2} [\log (a_{\text{O}^{2-}})^{\text{MO}^{\text{I}}} - \log (a_{\text{O}^{2-}})^{\text{MO}^{\text{II}}}] + (C_{\text{I}} - C_{\text{II}}) \quad [4] \\
\propto [\log (a_{\text{O}^{2-}})^{\text{MO}^{\text{I}}} - \log (a_{\text{O}^{2-}})^{\text{MO}^{\text{II}}}]
\end{aligned}$$

where $(a_{\text{O}^{2-}})^{\text{MO}^i}$ and C_i are respectively the activity of the O^{2-} ion dissociated from the basic oxide MO^i in the same activity of MO^i and a constant defined in equation [3]. If $(C_{\text{I}} - C_{\text{II}})$ term is constant within experimental uncertainty ($\pm 5.3\%$), the difference in Ag solubility in different slags will be directly proportional to the difference of basicity between each oxide MO^i . This means that the relative basicity of basic oxides can be estimated in the simple binary slag system with the same acidic oxide.

In the same way, the relative basicity of acidic oxides can also be expected. In this case, because the activity of the O^{2-} ions dissociated from CaO in the CaO- B_2O_3 , CaO- SiO_2 , and CaO- Al_2O_3 systems is not identical, $(a_{\text{O}^{2-}})^{\text{MO}^i}$ is replaced by $(a_{\text{O}^{2-}})^{\text{CaO}^i}$ in equation [4], here i means different slag system.

RESULTS AND DISCUSSION

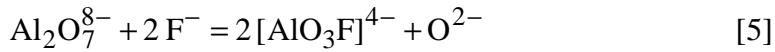
Silver Solubility in Borate, Silicate, and Aluminate Melts

Figure 1 exhibits the solubility of silver in the MO- B_2O_3 (MO = CaO, BaO, and Na_2O),^[8,9] CaO-RO (RO = SiO_2 and Al_2O_3), and CaO- Al_2O_3 -CaF₂ slags as a function of the content of basic oxides. In the B_2O_3 -bearing slags, the compositions of 65 (mol%) CaO, 45 (mol%) BaO, and 35 (mol%) Na_2O exhibits a minimum Ag solubility, in each slag system. The order of Ag solubility in the left hand side of the minimum point is “CaO- $\text{B}_2\text{O}_3 > \text{BaO-B}_2\text{O}_3 > \text{Na}_2\text{O-B}_2\text{O}_3$ ”; thus it was indicated that Na_2O would be more

basic than BaO would be, followed by CaO.^[9]

In the CaO-bearing binary slags, the order of Ag solubility is “CaO-Al₂O₃ > CaO-SiO₂ > CaO-B₂O₃”. Since it has been generally accepted that the interaction between Ca²⁺ ions and borate polyanions (B_xO_yⁿ⁻) is larger than that of Ca²⁺ and Si_xO_yⁿ⁻, followed by that of Ca²⁺ and Al_xO_yⁿ⁻ at the same composition,^[10] it is suggested that B₂O₃ exhibits a more acidic characteristic than SiO₂ exhibits, followed by Al₂O₃.

The solubility of silver in the CaO-Al₂O₃-CaF₂ (X_{CaF₂} = 0.25) system also exhibits a minimum Ag solubility at about 45 (mol%) CaO, which is shifted to the more acidic composition than that of CaO-Al₂O₃ system (65 (mol%) CaO); thus it is suggested that 25 (mol%) CaF₂ addition qualitatively enhances the basicity of slag by the following equation:



Equation [5] is not an overall reaction for the depolymerization of aluminate, because the slag is constituted by many other polymeric groups.

The relationship between log (mass%Ag⁺) and log *a*_{MO} (MO = basic oxide) is shown in Figure 2.^[11-14] The slopes of the lines for the acidic B₂O₃-bearing and silicate melts are close to the expected value of -1/2, while the slopes are larger than -1/2 in the acidic CaO-Al₂O₃ (-CaF₂) systems. The origin of the discrepancy in these systems may be on the interactions between O²⁻ ions and aluminate polyanions. However, the exact reason why occurred these phenomena is not manifested yet.

In the acidic B₂O₃-bearing slags, the relative basicity of CaO, BaO, and Na₂O can be estimated as about 1.0, 1.3, and 2.4, respectively, from the difference in Ag solubility at the same activity of MO in each slag system. In the CaO-bearing slags, the order of relative basicity of B₂O₃, SiO₂, and Al₂O₃ is found to be about 1.0, 2.6, and 3.8. In addition, it can be estimated that the effect of CaF₂ on Ag solubility is about 1.3 times larger than CaO. Based on the present results for Ag solubility in various slags, a new

basicity scale (B_S) in the slags containing CaO, BaO, Na₂O, B₂O₃, SiO₂, Al₂O₃, and CaF₂ established as a form of modified Vee ratio is as follows:

$$B_S = \frac{(X_{\text{CaO}} + 1.3X_{\text{BaO}} + 2.4X_{\text{Na}_2\text{O}} + 1.3X_{\text{CaF}_2})}{(X_{\text{B}_2\text{O}_3} + 2.6X_{\text{SiO}_2} + 3.8X_{\text{Al}_2\text{O}_3})} \quad [6]$$

The solubility of silver in each slag system is shown as a function of B_S in Figure 3. The solubility data and B_S show a linear correlation on either side of the minimum solubility region with some experimental scatters. The solubility is also shown as a function of theoretical optical basicity (Λ_{th}) in Figure 4. There are distinct discrepancies between data points; this reveals that the relative basicity of BaO and Na₂O would be underestimated in the calculation of Λ_{th} . In addition, the effect of CaF₂ on slag basicity was also underestimated, although the equation for CaF₂-containing melts suggested by J.A. Duffy was employed to calculate Λ_{th} in the CaO-Al₂O₃-CaF₂ slag.^[15]

Relationship between Slag Viscosity and B_S

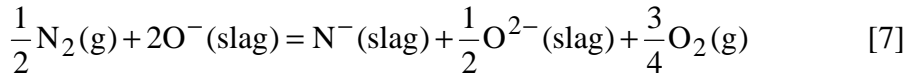
There have been many investigations to correlate viscosity data and slag composition by using NBO/T ratio (*i.e.*, the number of non-bridging oxygen per tetrahedrally-coordinated atoms) and corrected optical basicity (Λ^{corr}), because the viscosity has been known to be affected by the degree of polymerization of the melt and by the nature of the network-breaking cations (*e.g.* Ca²⁺ and Mg²⁺, *etc.*).^[16,17]

Figure 5 exhibits the viscosity in the borate, silicate, aluminate, and alumino-silicate melts with and without CaF₂ as a function of B_S .^[18-20] The viscosity drastically

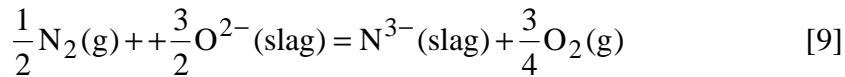
decreases with increasing B_S up to $B_S \cong 0.5$, followed by nearly constant value. The remarkably high correlation is shown in 17 slag systems with CaF_2 -containing slags in the temperature range within ± 55 K, approximately. As shown in Figure 5, B_S compensates the effect of different melts such as borate, silicate, aluminate, and alumino-silicate melts. However, a more detailed investigation is required to understand the effect of FeO on slag viscosity, the slag used in steelmaking processes.

Relationship between Nitride Capacity and B_S

The dissolution reaction of nitrogen into the acidic and basic slags is respectively suggested by equations [7] and [9] with the capacities in each case (equations [8] and [10]).^[11]



$$C_{\text{N}^-} = \frac{(\text{mass\% N}) \cdot p_{\text{O}_2}^{3/4}}{p_{\text{N}_2}^{1/2}} = \frac{K_{[7]} \cdot a_{\text{O}^-}^2}{a_{\text{O}^{2-}}^{1/2} \cdot f_{\text{N}^-}} \quad [8]$$



$$C_{\text{N}^{3-}} = \frac{(\text{mass\% N}) \cdot p_{\text{O}_2}^{3/4}}{p_{\text{N}_2}^{1/2}} = \frac{K_{[9]} \cdot a_{\text{O}^{2-}}^{3/2}}{f_{\text{N}^{3-}}} \quad [10]$$

where p_i , $K_{[n]}$, a_i , and f_i are the partial pressure of i , the equilibrium constant of

equation [n], the activity of i , and the activity coefficient of i , respectively.

In Figure 6, the nitride capacity in various slags is shown as a function of B_S' .^[11,21-27] Here, B_S' different from B_S for the effect of Al_2O_3 on nitride capacity is introduced as follows:

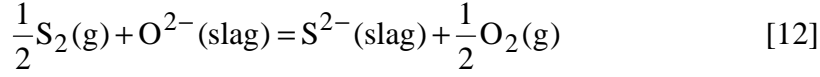
$$B_S' = \frac{(X_{CaO} + 1.3X_{BaO} + 2.4X_{Na_2O} + 1.3X_{CaF_2})}{(X_{B_2O_3} + 2.6X_{SiO_2} + 1.8X_{Al_2O_3})} \quad [11]$$

The coefficient of Al_2O_3 (1.8) was obtained by a trial and error method. The reason why it was changed the coefficient of Al_2O_3 is mainly due to the difference in the stability of nitride between the silicate and aluminate melts, which is reported by K. Ito and R.J. Fruehan.^[23] This difference in the activity coefficient of AlN and $Si_{0.75}N$ qualitatively indicates the overestimation for the coefficient of Al_2O_3 (3.8) in B_S (equation [6]). The coefficient of Al_2O_3 in B_S' (1.8) is reasonably comparable to the result reported by K. Tomioka and H. Suito ($X_{SiO_2} + 0.5X_{Al_2O_3}$).^[24]

As shown in Figure 6, the incorporated and free nitride capacities in various slags with and without CaF_2 in the temperature range within ± 65 K approximately exhibit good linear correlations as a function of B_S' on either side of the minimum point within scatters of ± 5.8 %.

Relationship between Sulfide Capacity and B_S

The principle desulfurization reaction is known as equation [12] based on gas-slag equilibrium.^[28]



By using the equilibrium constant of equation [12], the sulfide capacity is defined by the following equation:

$$C_{S^{2-}} = (\text{mass}\%S) \cdot \left(\frac{p_{O_2}}{p_{S_2}} \right)^{\frac{1}{2}} = \frac{K_{[12]} \cdot a_{O^{2-}}}{f_{S^{2-}}} \quad [13]$$

where p_i , $K_{[12]}$, $a_{O^{2-}}$, and $f_{S^{2-}}$ are the partial pressure of i , the equilibrium constant of equation [12], the activity of the O^{2-} ion, and the activity coefficient of the S^{2-} ion, respectively. Hence, the sulfide capacity is a function of temperature, slag basicity, and the stability of sulfide ion in the slag.

In Figure 7, the sulfide capacity in various slags is shown as a function of B_S'' .^[28-34] Here, B_S'' different from B_S is introduced as follows:

$$B_S'' = \frac{(X_{CaO} + 1.3X_{BaO} + 2.4X_{Na_2O} + 1.3X_{CaF_2})}{(X_{B_2O_3} + 2.6X_{SiO_2} + 2.8X_{Al_2O_3})} \quad [14]$$

The coefficient of Al_2O_3 (2.8) was obtained by a trial and error method. The reason why it was changed the coefficient of Al_2O_3 is not fully understood; it would probably result from the opposite tendency for the dependence of the activity coefficient of CaS (γ_{CaS}) on slag composition in the silicate and aluminate melts.^[35,36] The value of γ_{CaS}

in the CaO-SiO₂-CaS melt increased with increasing X_{CaO} and *vice versa* in the CaO-Al₂O₃-CaS melt. This difference in the activity coefficient of CaS in the silicate and aluminate melts qualitatively indicates the overestimation for the coefficient of Al₂O₃ (3.8) in B_S (equation [6]). The coefficient of Al₂O₃ in B_S'' (2.8) is close to the result reported by P. Herasymenko and G.E. Speight ($X_{\text{SiO}_2} + 0.9X_{\text{Al}_2\text{O}_3}$)^[37] and that of C.E. Sims ($X_{\text{SiO}_2} + X_{\text{Al}_2\text{O}_3}$).^[38] In addition, the coefficient of Na₂O (2.4) is exactly same to the result reported by A.H. Chan and R.J. Fruehan ($18.6X_{\text{Na}_2\text{O}} + 7.6X_{\text{CaO}}$).^[39] However, some other values were also reported as 1.4^[33] and 3.3.^[40]

The effect of CaF₂ on $C_{S^{2-}}$ has been examined, but there is as yet insufficient thermodynamic data available on desulfurization of CaF₂-containing slags. It has been found that CaF₂ additions did not enhance $C_{S^{2-}}$ of the basic steelmaking slags and that of the Na₂O-CaO-SiO₂ slag.^[40,41] However, A. Bronson and G.R. St. Pierre have shown that $C_{S^{2-}}$ of the CaO-SiO₂-CaF₂ slag increased with CaF₂ additions by the increase of O²⁻ ions, resulting from the reaction between F⁻ and complex silicate anions.^[31] As shown in Figure 7 and equation [14], the coefficient of CaF₂ is about 1.3, indicating that CaF₂ enhances $C_{S^{2-}}$ of the CaO-SiO₂-CaF₂ and CaO-Al₂O₃-CaF₂ slags. Although the coefficient of CaF₂ is equal to that of BaO, there is a difference between a direct contribution of BaO on the refining ability by donating O²⁻ ions into the melt and an indirect effect of CaF₂ by reacting silicate (or aluminate) polyanions. The proposed values for the basic oxides and CaF₂ in B_S'' are very close to that obtained from the dependency of phosphate capacity on slag composition in the Na₂O (BaO)-CaO-MgO-SiO₂-CaF₂ slags ($X_{\text{CaO}} + 1.3X_{\text{BaO}} + 2.1X_{\text{Na}_2\text{O}} + 1.2X_{\text{CaF}_2}$).^[42]

As shown in Figure 7, the sulfide capacity in various slags with and without CaF₂ at 1773 K exhibits a good linear correlation as a function of B_S'' within scatters of ± 5.0 %.

The sulfide capacity data is shown as a function of theoretical optical basicity (Λ_{th})

in Figure 8.^[15] The CaO-bearing slags exhibits a good linear correlation with Λ_{th} , which is in good agreement with the result established by I.D. Sommerville and D.J. Sosinsky:^[43] However, some modifications for the Na₂O-bearing and CaF₂-containing slags have been discussed by other researchers.^[33,44,45]

In summary, the estimated values indicating the effect of each oxide and CaF₂ on the refining indices are listed in Table I. There are large discrepancies for the same oxide, for example 1.1 to 3.3 for Na₂O, according to the different measures. The relative acidity of SiO₂ and Al₂O₃ is not known explicitly, which is mainly due to the amphoteric characteristic of Al₂O₃. The effect of CaF₂ on refining ability is generally similar to that of CaO or slightly larger than CaO. The origin of these discrepancies may be on the interactions between slag components and reaction products in each case. In future works, a more detailed investigation is required to understand the basicity of various oxides including transition metal oxides and fluorides; and to describe quantitatively the basicity of slag.

CONCLUSIONS

The solubility of silver in molten MO-B₂O₃ (MO = CaO, BaO, and Na₂O), CaO-RO (RO = B₂O₃, SiO₂, and Al₂O₃), and CaO-Al₂O₃-CaF₂ slags was measured at high temperatures to modify a measure of basicity. The results of the present study can be summarized as follows:

1. The relative basicity of pure BaO and Na₂O was obtained as 1.3 and 2.4 with reference to CaO (1.0), respectively, based on Ag solubility in MO-B₂O₃ slags; and that for the acidic oxides such as SiO₂ and Al₂O₃ was estimated to be 2.6 and 3.8 with reference to B₂O₃ (1.0), respectively. The relative basicity of CaF₂ was also obtained to be 1.3 with reference to CaO. Hence, a new measure of basicity (B_S) could be defined by the following equation:

$$B_S = \frac{(X_{CaO} + 1.3X_{BaO} + 2.4X_{Na_2O} + 1.3X_{CaF_2})}{(X_{B_2O_3} + 2.6X_{SiO_2} + 3.8X_{Al_2O_3})}$$

2. The relationship between the viscosity of various slags and B_S indicated the compensation for the effect of Al₂O₃ in silicate melts and the effect of CaF₂ on slag viscosity.
3. The nitride and sulfide capacities in various slags could be also expressed as a good linear equation by using the present measure of basicity.

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REFERENCES

1. T. Førland and K. Grjotheim, Metall. Trans. B, vol. 9B, 1978, p. 45.
2. T. Nakamura, T. Yokoyama, and J.M. Toguri, ISIJ Int., vol. 33, 1993, p. 204.
3. C. Wagner, Metall. Trans. B, vol. 6B, 1975, p. 405.
4. S. Nakamura and N. Sano, Metall. Trans. B, vol. 22B, 1991, p. 823.
5. T. Yokokawa, Proc. 4th Int. Conf. Molten Slags & Fluxes '92, Sendai, Japan, June, 1992, p. 121.
6. J.A. Duffy, M.D. Ingram, and I.D. Sommerville, J. Chem. Soc. Faraday Trans. I, vol. 74, 1978, p. 1410.
7. S. Nakamura and N. Sano, Metall. Mater. Trans. B, vol. 28B, 1997, p. 103.
8. J.H. Park and D.J. Min, Metall. Mater. Trans. B, vol. 30B, 1999, p. 689.
9. J.H. Park and D.J. Min, Mater. Trans., JIM, vol. 41, 2000, p. 425.
10. F.D. Richardson, Physical Chemistry of Melts in Metallurgy, Academic Press, London, 1974, vol. 1, pp. 247-270.
11. D.J. Min and R.J. Fruehan, Metall. Trans. B, vol. 21B, 1990, p. 1025.
12. J.H. Park and D.J. Min, Metall. Mater. Trans. B, to be published.
13. R.H. Rein and J. Chipman, Trans. TMS-AIME, vol. 233, 1965, p. 415.
14. M. Hino, S. Kinoshita, Y. Ehara, H. Itoh, and S. Ban-ya, Proc. 5th Int. Conf. Molten Slags, Fluxes & Salts, Sydney, Australia, January, 1997, p. 53.
15. J.A. Duffy, J. Non-Cryst. Solids, vol. 109, 1989, p. 35.
16. K.C. Mills and S. Sridhar, Ironmaking and Steelmaking, vol. 26, 1999, p. 262.
17. K.C. Mills, ISIJ Int., vol. 33, 1993, p. 148.
18. Y. Kawai and Y. Shiraishi (Ed.), Handbook of Physico-chemical Properties at High Temperatures, ISIJ, Japan, 1998, pp. 93-144.
19. N.P. Bansal and R.H. Doremus, Handbook of Glass Properties, Academic Press, Orlando, 1986, pp. 223-305.
20. K.C. Mills, Slag Atlas, 2nd ed., Verlag Stahleisen GmbH, Düsseldorf, 1995, pp. 349-401.
21. S.J. Kong and H.G. Lee, Thesis, Pohang University of Science and Technology,

Pohang, Korea, 1999.

22. K. Tomioka and H. Suito, ISIJ Int., vol. 31, 1991, p. 1316.
23. K. Ito and R.J. Fruehan, Metall. Trans. B, vol. 19B, 1988, p. 419.
24. K. Tomioka and H. Suito, Steel Res., vol. 63, 1992, p. 1.
25. T. Kozono and H. Suito, Ironmaking and Steelmaking, vol. 19, 1992, p. 145.
26. E. Martinez, V. Espejo, and F. Manjarrez, ISIJ Int., vol. 33, 1993, p. 48.
27. E. Martinez and N. Sano, Metall. Trans. B, vol. 21B, 1990, p. 105.
28. C.J.B. Fincham and F.D. Richardson, Proc. R. Soc. London, vol. 223A, 1954, p.40.
29. P.T. Carter and T.G. Macfarlane, J. Iron and Steel Inst., vol. 185, 1957, p. 54.
30. G.J.W. Kor and F.D. Richardson, Trans. TMS-AIME, vol. 245, 1969, p. 319.
31. A. Bronson and G.R. St. Pierre, Metall. Trans. B, vol. 10B, 1979, p. 375.
32. M. Hino, S. Kitagawa, and S. Ban-ya, ISIJ Int., vol. 33, 1993, p. 36.
33. K. Kunisada and H. Iwai, ISIJ Int., vol. 33, 1993, p. 43.
34. E. Drakaliysky, D. Sichen, S. Seetharaman, Can. Metall. Quart., vol. 36, 1997, p. 115.
35. R.A. Sharma and F.D. Richardson, J. Iron and Steel Inst., vol. 198, 1961, p. 386.
36. R.A. Sharma and F.D. Richardson, J. Iron and Steel Inst., vol. 200, 1962, p. 373.
37. P. Herasymenko and G.E. Speight, J. Iron and Steel Inst., vol. 166, 1950, p. 289.
38. C.E. Sims (Ed.), Electric Furnace Steelmaking, Interscience, New York, 1963, vol. 2, p. 208.
39. A.H. Chan and R.J. Fruehan, Metall. Trans. B, vol. 20B, 1989, p. 71.
40. W.H. Van Niekerk and R.J. Dippenaar, ISIJ Int., vol. 33, 1993, p. 59.
41. G.J.W. Kor, Metall. Trans. B, vol. 8B, 1977, p. 107.
42. Z. Zou and L. Holappa, Proc. 6th. Int. Iron and Steel Cong., Nagoya, Japan, October, 1990, p. 53.
43. D.J. Sosinsky and I.D. Sommerville, Metall. Trans. B, vol. 17B, 1986, p. 331.
44. K. Kunisada and H. Iwai, Proc. 6th. Int. Iron and Steel Cong., Nagoya, Japan, October, 1990, p. 248.
45. D.R. Gaskell, Metall. Trans. B, vol. 20B, 1989, p. 113.
46. J.O'M., Bockris, J.A. Kitchener, S. Ignatowicz, and J.W. Tomlinson, Trans. Faraday Soc., vol. 48, 1952, p. 75.

47. E. Ichise and A. Moro-Oka, ISIJ Int., vol. 30, 1990, p. 971.
48. T. Nakamura, Y. Ueda, and J. M. Toguri, Proc. 3rd. Int. Conf. Molten Slags & Fluxes, Glasgow, UK, June, 1988, p. 146.
49. R. Inoue and H. Suito, Trans. ISIJ, vol. 22, 1982, p. 514.
50. R. Inoue and H. Suito, Trans. ISIJ, vol. 25, 1985, p. 118.
51. H. Suito and R. Inoue, Trans. ISIJ, vol. 24, 1984, p. 47.
52. H. Suito and R. Inoue, Trans. ISIJ, vol. 22, 1982, p. 869.
53. T. Usui, K. Yamada, M. Mugita, Y. Miyashita, M. Hanmei, and K. Taguchi, Tetsu-to-Hagane, vol. 67, 1981, p. S943.
54. Y. Fukami, Y. Nakajima, T. Moriya, and S. Maruhashi, Tetsu-to-Hagane, vol. 71, 1985, p. S280.
55. K. Marukawa and T. Hirata, The 19th. Steelmaking Comm., The Jpn. Soc. Promotion Sci., Rep. No. 10566, May, 1984.
56. K. Hayashi, M. Ikeda, and H. Katagiri, Trans. ISIJ, vol. 24, 1984, p. B207.
57. K. Kunisada and H. Iwai, Trans. ISIJ, vol. 27, 1987, p. 263.

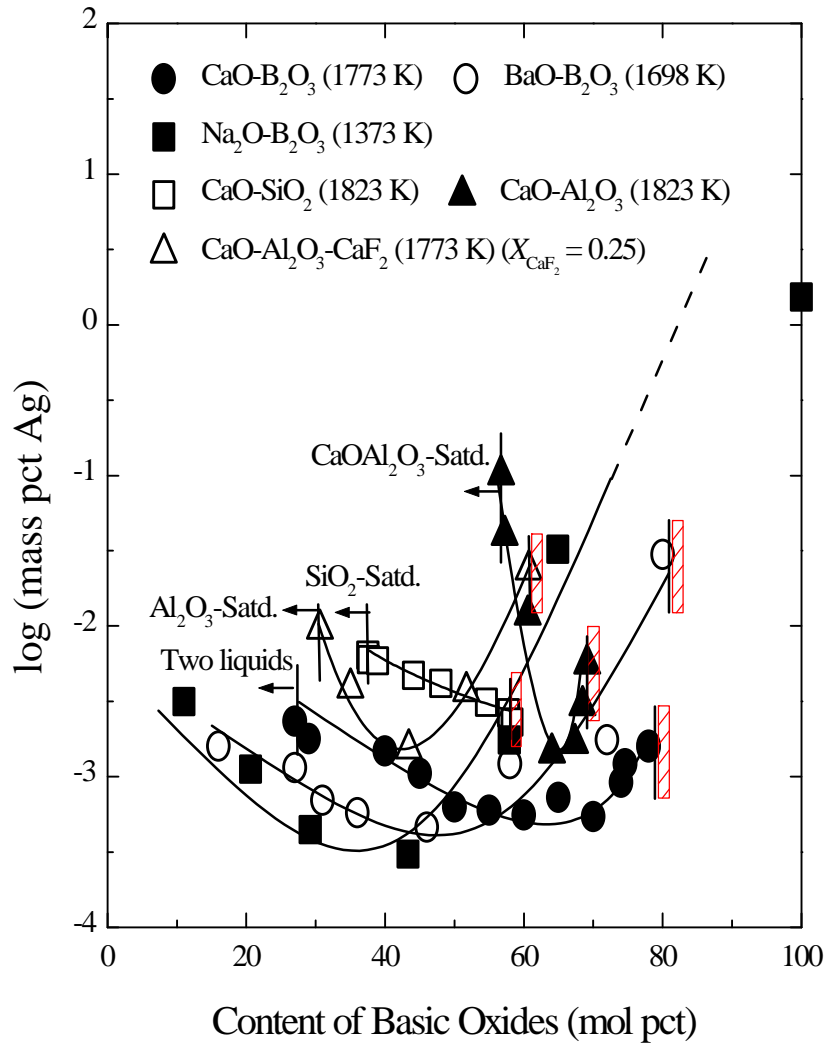


Figure 1: Dependence of Ag solubility on the composition of various slags (Shaded squares mean the CaO (BaO) saturation).

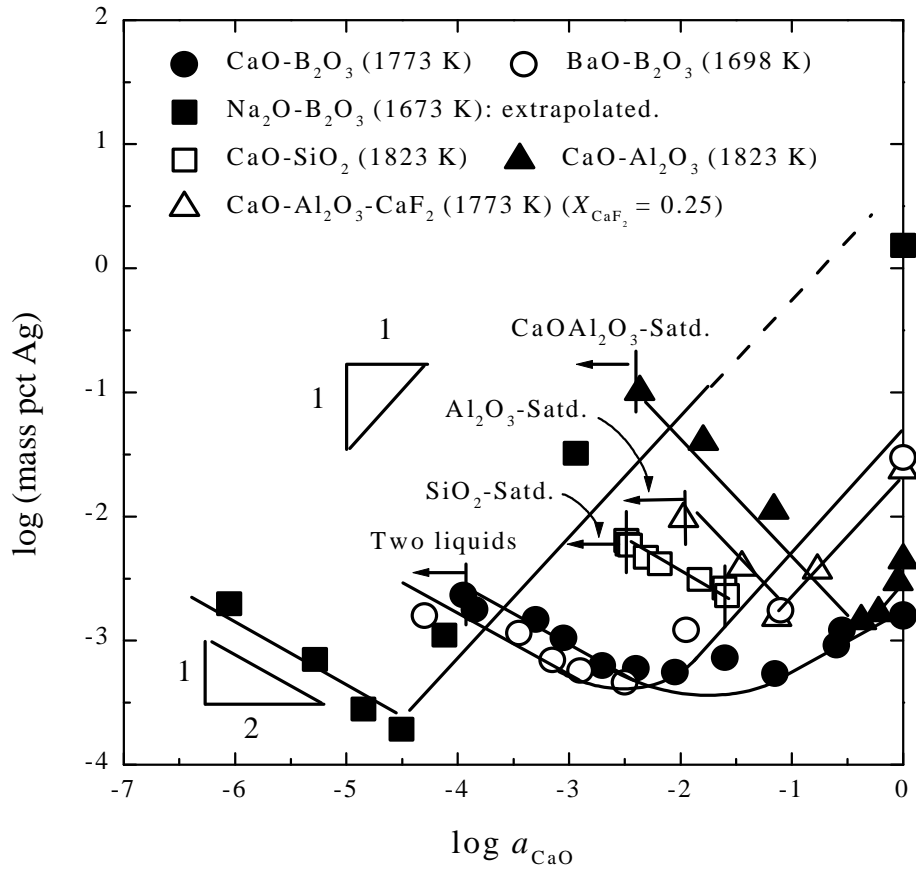


Figure 2: Dependence of Ag solubility on the activity of basic oxides in various slags.

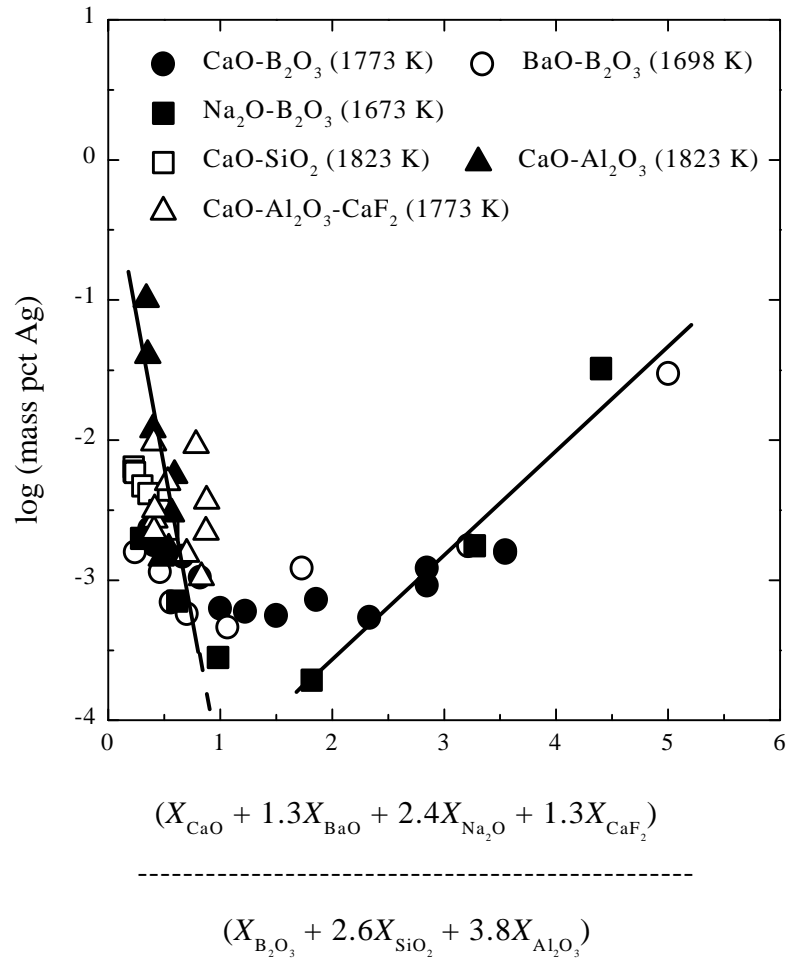


Figure 3: Ag solubility as a function of B_s in various slags.

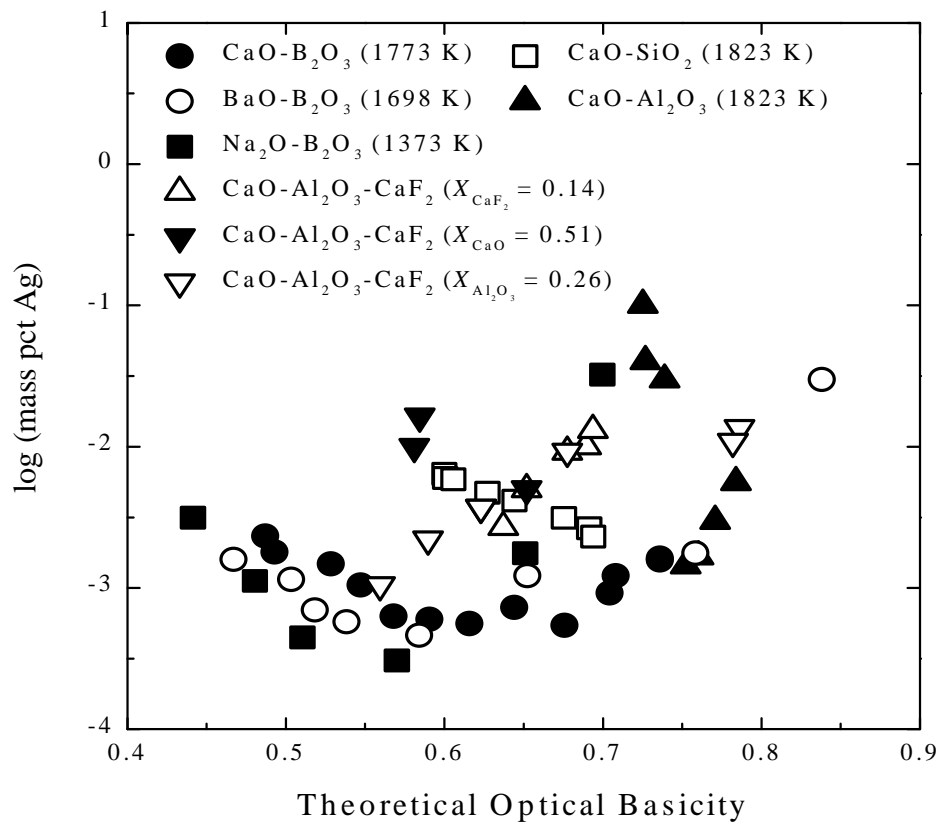


Figure 4: Relationship between Ag solubility and theoretical optical basicity.

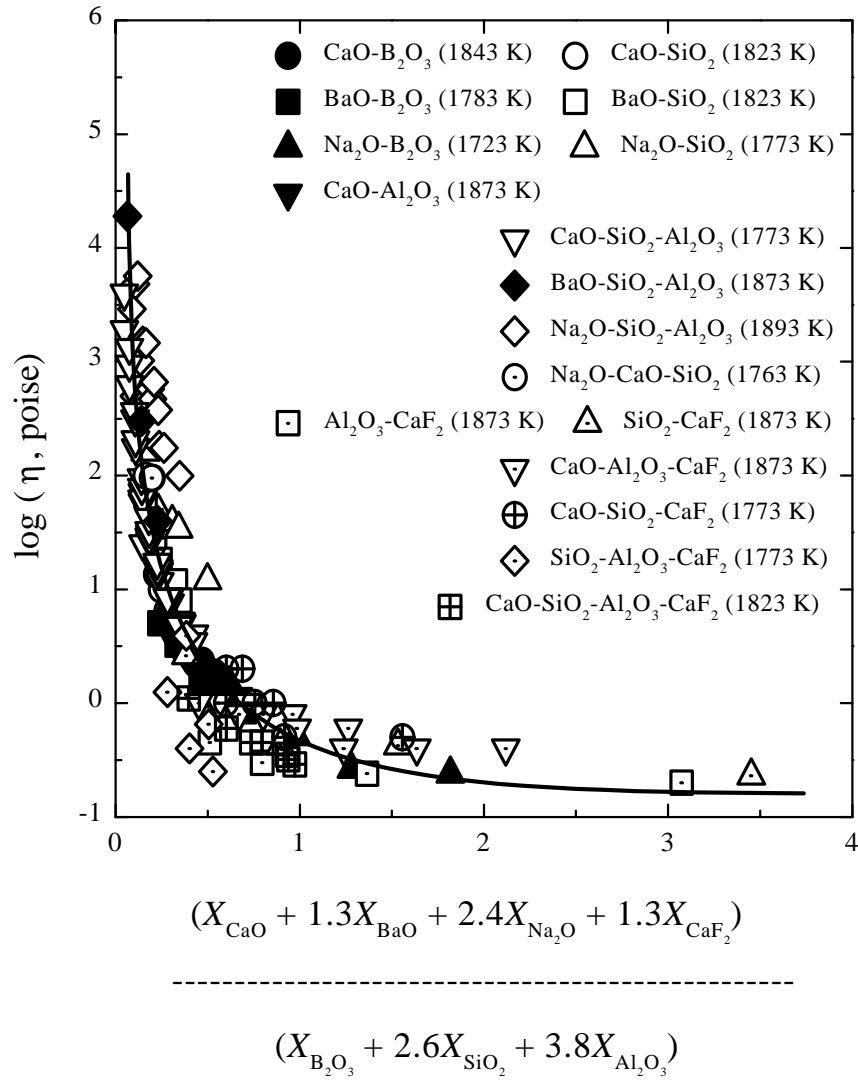


Figure 5: Viscosities of various slags as a function of B_S .

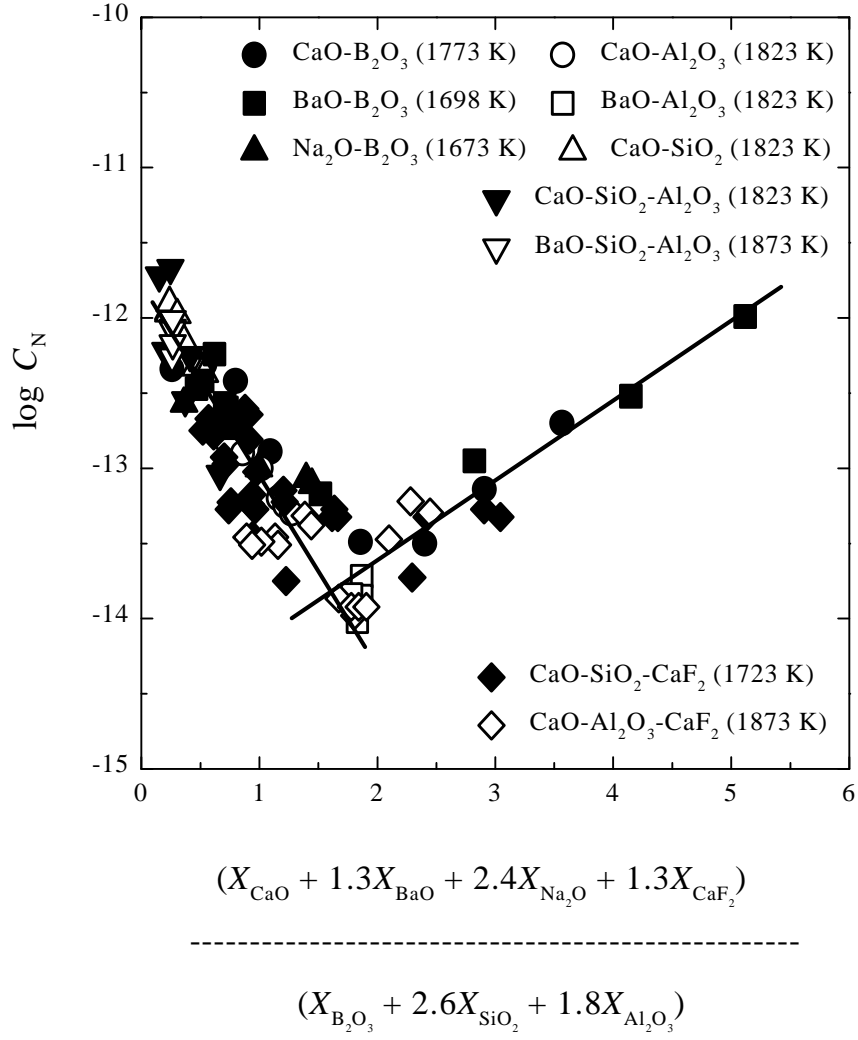


Figure 6: Nitride capacities of various slags as a function of B'_S .

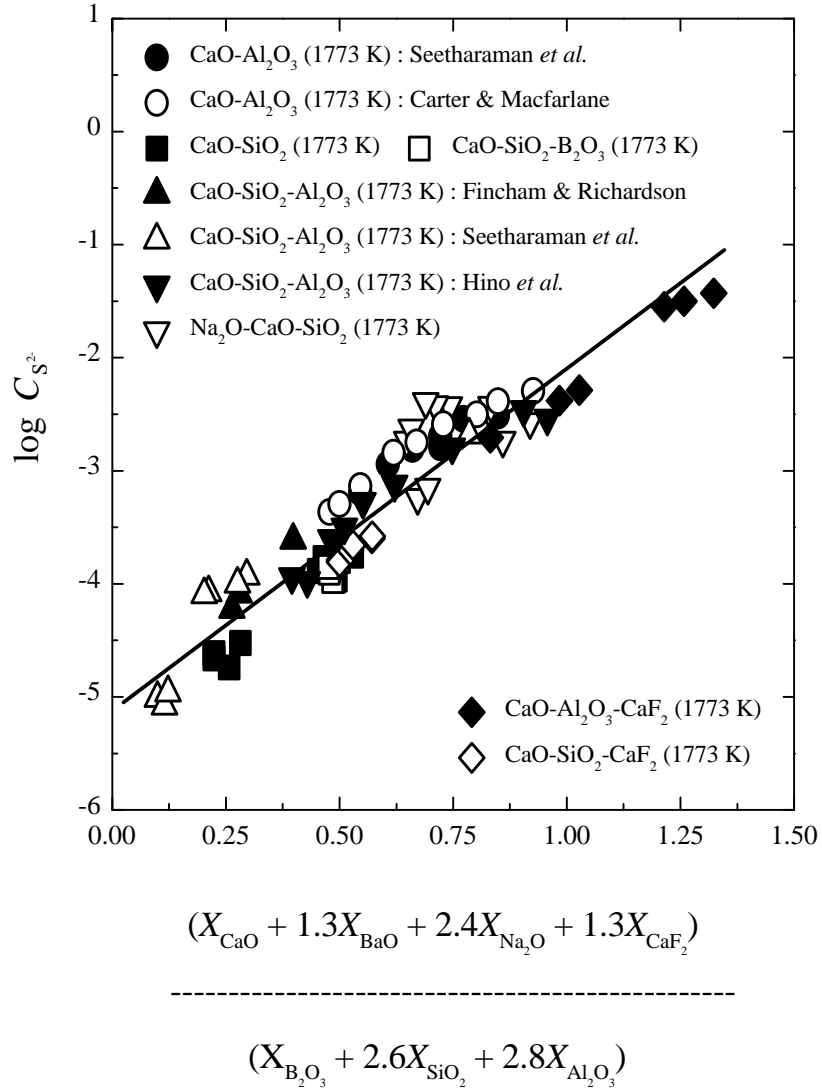


Figure 7: Sulfide capacities of various slags as a function of B_s'' .

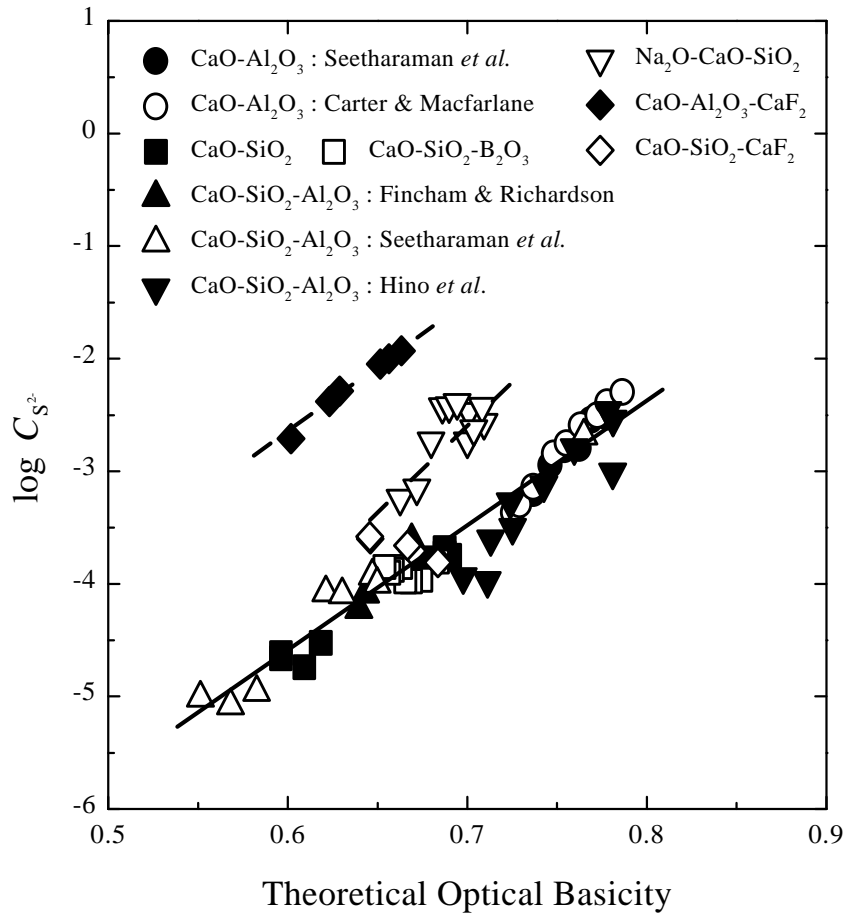


Figure 8: Relationship between sulfide capacities of various slags and theoretical optical basicity.

Table. I: Effects of basic and acidic oxides and CaF₂ on the refining indices.

Measures	CaO	BaO ¹⁾	Na ₂ O ¹⁾	B ₂ O ₃	SiO ₂ ¹⁾	Al ₂ O ₃ ¹⁾	CaF ₂ ²⁾	Authors	Ref.
(% Ag)	1.0	1.3	2.4	1.0	2.6	3.8	1.3	Present Work	
(% Ag) & C _N	1.0	1.3	2.4	1.0	2.6	1.8	1.3	//	
(% Ag) & C _S	1.0	1.3	2.4	1.0	2.6	2.8	1.3	//	
I ³⁾	1.00	1.32	1.94	1.00	0.96	1.41	-	J.O' M. Bockris <i>et al.</i>	46
O ²⁻ Ion F raction	-	-	-	-	1.0	0.9	-	P. Herasymenko <i>et al.</i>	37
E ^o ⁴⁾	1.00	1.11	1.36	1.00	1.44	1.23	-	E. Ichise <i>et al.</i>	47
Λ _{th} ⁵⁾	1.00	1.15	1.15	1.00	1.14	1.43	0.43	J.A. Duffy	6, 15
Λ _{th} ' ⁶⁾	1.00	1.08	1.10	1.00	1.12	1.62	-	T. Nakamura <i>et al.</i>	48
C _N ⁷⁾	-	-	-	-	1.0	0.9	-	K. Tomioka <i>et al.</i>	24
C _S ⁸⁾	1.0	-	1.4	-	1.0	0.5	-	K. Kunisada <i>et al.</i>	33
	1.0	-	3.3	-	-	-	-	W.H.V. Niekerk <i>et al.</i>	40
	1.0	-	2.4	-	-	-	-	A.H. Chan <i>et al.</i>	39
	1.0	-	3.3	-	-	-	-	R. Inoue <i>et al.</i>	49
C _P ⁹⁾	1.0	1.3	2.1	-	-	-	1.2	Z. Zou <i>et al.</i>	42
	1.0	-	1.4	-	-	-	0.6 - 0.9	R. Inoue <i>et al.</i>	50
	1.0	0.9	1.2	-	-	-	1.2	H. Suito <i>et al.</i>	51
	1.0	-	-	-	-	-	1.0	H. Suito <i>et al.</i>	52
	1.00	-	1.58	-	-	-	-	T. Usui <i>et al.</i>	53
	1.00	-	1.42	-	-	-	-	Y. Fukami <i>et al.</i>	54
	1.0	-	1.7	-	-	-	-	K. Marukawa <i>et al.</i>	55
	1.0	-	1.2	-	-	-	1.0	K. Hayashi <i>et al.</i>	56
	1.0	-	1.6	-	-	-	-	K. Kunisada <i>et al.</i>	57

1) Converted values with reference to CaO (B₂O₃). 2) Relative Basicity with reference to CaO.

3) Ion-Oxygen Attraction 4) Lattice Energy 5) Electronegativity 6) Electron Density 7) Nitride Capacity

8) Sulfide Capacity 9) Phosphate Capacity