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**Thermodynamic Behavior of Carbon in CaO-SiO₂
and CaO-Al₂O₃ Slag Systems**

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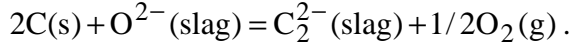
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Abstract

The solubility of carbon in molten CaO-SiO₂ (Al₂O₃) and CaO-SiO₂ (Al₂O₃)-CaF₂ slags was measured at high temperatures to understand the thermodynamic behavior of carbon in molten slags. From the effect of oxygen potential and slag basicity on carbon solubility, the dissolution mechanism of carbon into the slags could be confirmed as



The activity coefficient of carbide in the CaO-SiO₂ slag was affected by the slag composition, while that of the CaO-Al₂O₃ system was not. The addition of CaF₂ greatly increased the carbide capacity of the CaO-SiO₂ slag system, while this effect was not remarkable in the CaO-Al₂O₃ slag.

1. Introduction

Demand for ultra clean steel in various applications will increase as the society develops. The current steelmaking technology has been developed to meet these demands resulting in reaching technological limitation for further development. Understanding of thermodynamic behavior of carbon in the slag for ultra low carbon steelmaking became more important to overcome this barrier. It is believed that certain degrees of carbon solubility exists in the slag, depending on thermodynamic conditions such as temperature, slag composition, and oxygen partial pressure as it is known in phosphorus and sulfur reaction. Previous works indicated that carbon solubility was strongly dependent on oxygen partial pressure and basicity ($a_{\text{O}^{2-}}$) of slags. The dependence of carbon solubility on oxygen partial pressure has been known explicitly, while the effect of basicity on carbon dissolution has not been cleared. For example, the solubility of carbon increased by the increase of SiO₂ content in the CaO-SiO₂-Al₂O₃ slag,^{1,2)} while the solubility increased with increasing content of basic oxides in other basic slags.

In the present study, because CaO-SiO₂ (-CaF₂) and CaO-Al₂O₃ (-CaF₂) systems are the most widely used slags in steelmaking process, the solubility of carbon in both slag systems was measured to understand the reaction mechanism of carbon dissolution into the slags as well as to investigate the effect of fluorspar on carbon dissolution reaction.

2. Experimental procedure

A super kanthal electric furnace was used for equilibration of molten slag and gas phases. 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 CaO, SiO₂, Al₂O₃, and CaF₂. The schematic diagram of the experimental apparatus can be found elsewhere.³⁾

The slag samples of 10g were held in graphite crucibles under CO atmosphere for controlling oxygen partial pressure by C/CO equilibrium⁴⁾. For the effect of oxygen partial pressure on the solubility of carbon, a mixture of CO and Ar was supplied by using mass flow controller (Matheson, Model 8284). The impurities of CO and Ar were removed by passing through CaSO₄, Na₂O • CaO, silica gel, and, especially, Mg turnings at 753K for Ar.

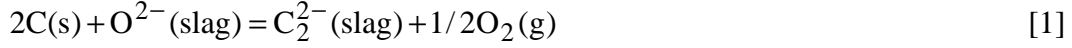
Figure 1 exhibits the carbon content in the CaO-SiO₂-CaF₂ slag system as a function of reaction time at 1873 K under a gas mixture of 60%CO / 40%Ar. The carbon content increases with reaction time and reaches the saturation in about 12 hours. The 16 hours was chosen to ensure thermodynamic equilibrium of the reaction in the present study.

After equilibrating, the samples were quenched by Ar gas and crushed for chemical analysis. The carbon content in slag was determined by a LECO (CS-300). The possibility of carbide precipitation could be evaluated using thermodynamic data available in the literature.⁴⁻⁶⁾ Because the evaluated activities of the carbides for the present experimental conditions are less than 0.05, the discussion in the present study will be limited to the dissolved carbides in molten slags.

3. Results and discussion

3.1. Dissolution Mechanism of Carbon in Slags

Carbon has been known to dissolve into the basic slags by equation [1] and the carbide capacity has been defined as equation [3]⁷⁻⁹⁾.



$$K_{[1]} = \frac{a_{C_2^{2-}} \cdot p_{O_2}^{1/2}}{a_C^2 \cdot a_{O^{2-}}} \quad [2]$$

$$C_{C_2^{2-}} = \frac{K_{[1]} \cdot a_{O^{2-}}}{f_{C_2^{2-}}} = (\text{mass}\% C_2^{2-}) \cdot p_{O_2}^{1/2} \quad [3]$$

Where $K_{[1]}$, a_i , and p_{O_2} are the equilibrium constant of equation [1], the activity of i , and the oxygen partial pressure, respectively. Because graphite crucibles were used to fix the activity of carbon as unity, the following relation could be deduced:

$$\log(\text{mass}\% C_2^{2-}) = -1/2 \log p_{O_2} + \log a_{O^{2-}} - \log f_{C_2^{2-}} + \log K_{[1]} \quad [4]$$

Where $f_{C_2^{2-}}$ is the activity coefficient of C_2^{2-} ion. From equation [4], $\log(\text{mass}\% C_2^{2-})$ and $\log p_{O_2}$ are expected to have a linear relationship with a slope of $-1/2$, under conditions of a fixed composition and temperature. The solubility of carbon in the CaO-SiO₂-CaF₂ system at 1873 K is shown as a function of oxygen partial pressure in Figure 2. The slope of the line, -0.54 is very close to that of the expected value of -0.5 , which confirms the carbon dissolution reaction occurs as equation [1].

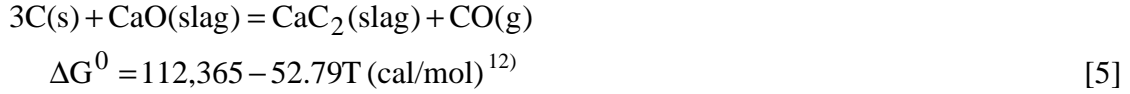
Figure 3 exhibits the dependence of carbon solubility on slag composition at $p_{CO} = 0.6$ atm and 1873 K in the CaO-SiO₂ and CaO-Al₂O₃ systems. The carbon contents in both slag systems increase with increasing slag basicity and exhibit almost the same dependence on basicity.

The dissolution mechanism of carbon can be examined more quantitatively by considering the relationship between the solubility of carbon and the activity of basic oxides as a measure of basicity. In equation [4], $\log(\text{mass}\% C_2^{2-})$ and $\log a_{O^{2-}}$ are expected to have a linear relationship with a slope of unity at a fixed temperature and oxygen partial pressure, assuming that $f_{C_2^{2-}}$ would not be affected by the slag composition.

The carbide capacity is shown as a function of the activity of CaO in Figure 4, assuming that $a_{O^{2-}}$ is directly proportional to a_{CaO} . In the CaO-SiO₂ slag, the slope of the line, 0.5 is smaller than the expected value of unity, while the CaO-Al₂O₃ system shows a linear relationship with the slope of 1.2 , which is close to the expected value. The reason for the discrepancy from the theoretical expectation in the CaO-SiO₂ slag is that the structure of molten slags affects the basicity^{10,11)}, or that the activity coefficient of carbide ion would be varied with slag composition. Based on these results, it is confirmed that the dissolution of carbon into the basic slags can be described by equation [1].

In order to explain the discrepancy from the theoretical expectation in the CaO-SiO₂ slag

system, the activity coefficient of carbide ion is considered based on the following molecular reaction:



$$K_{[5]} = \frac{a_{\text{CaC}_2} \cdot p_{\text{CO}}}{a_{\text{C(gr)}} \cdot a_{\text{CaO}}} \quad [6]$$

Where $K_{[5]}$, a_i , and p_{CO} are the equilibrium constant of equation [5], the activity of i , and the partial pressure of CO, respectively. Because graphite crucibles were used to fix the activity of carbon as unity, the following relation could be obtained:

$$\log a_{\text{CaC}_2} = \log K_{[5]} + \log a_{\text{CaO}} - \log p_{\text{CO}} - \log X_{\text{CaC}_2} \quad [7]$$

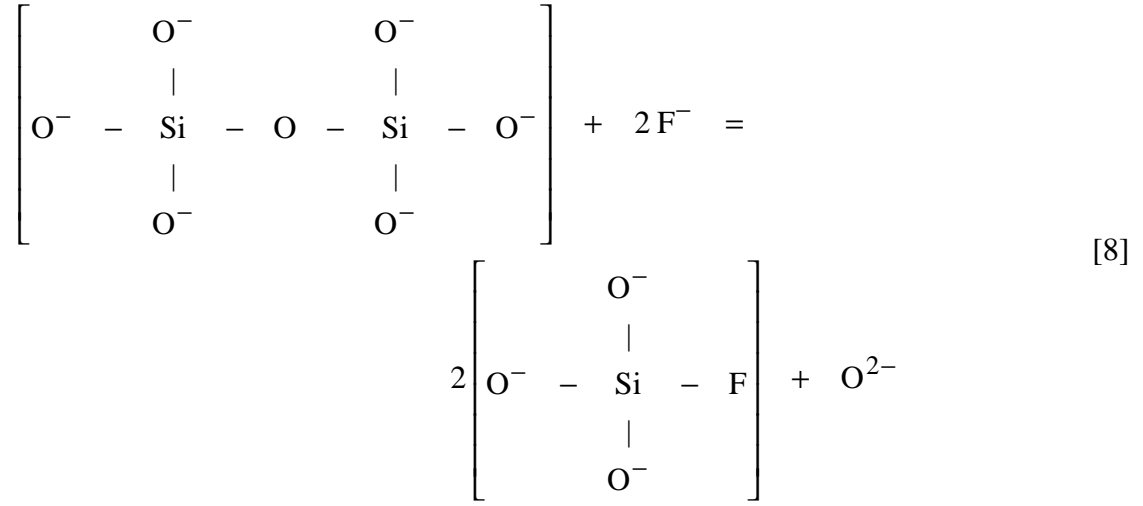
Where a_{CaC_2} and X_{CaC_2} are the activity coefficient and the mole fraction of calcium carbide, respectively.

Figure 5 exhibits the dependence of a_{CaC_2} on the activity of CaO in the CaO-SiO₂ and CaO-Al₂O₃ slag systems. The activity coefficient of carbide in the CaO-SiO₂ system increases with increasing the activity of CaO, however, that of CaO-Al₂O₃ remains constant over the entire composition range. This could be thought that the free oxygen ions are consumed by reacting with silicate polyanions; thus the changes in the network structure continuously occurred in the CaO-SiO₂ system. Therefore, the increase of carbon solubility with CaO activity may be offset by the decrease of solubility with increasing activity coefficient of carbide. On the other hand, the CaO activity of the CaO-Al₂O₃ system exhibits a clear effect of basicity on carbon solubility with constant activity coefficient of carbide, which agrees well with theoretical expectation.

Figure 6 exhibits the effect of temperature on the carbide capacity of the CaO-SiO₂-CaF₂ slag system. The carbide capacity increases with increasing temperature, indicating that the dissolution of carbon is an endothermic reaction. From the slope of the line, the dissociation and dissolution energy of carbon into the slags is evaluated to be about 86 kcal/mol.

3.2. Influence of CaF₂ on Carbon Dissolution

Fluoride has been known to influence the thermodynamic behavior of carbon in molten slags^{3,13}. Figure 7 exhibits the comparison for the solubility of carbon in the CaO-SiO₂ (Al₂O₃) and CaO-SiO₂ (Al₂O₃)-20(mass%)CaF₂ slags as a function of CaO content. The CaF₂ addition increases in both slag systems. The slopes of the lines for with and without CaF₂ slags are not changed remarkably. Also, it can be noticed that the effect of CaF₂ on carbon solubility is more significant in the CaO-SiO₂ system than that of the CaO-Al₂O₃ slag. The increase in carbon solubility by additions of CaF₂ may result from the replacement of oxygen ions needed to break the silicate or aluminate network structure by fluorine ions as shown in equation [8].



This reaction results in an increase of slag basicity or decrease of the activity coefficient of carbide with the additions of CaF_2 .

The optical basicity has widely been used to express the basicity of slag.¹⁴⁻¹⁶⁾ The optical basicity of a slag is simply given by

$$= {}_1X_1 + {}_2X_2 + \cdots \tag{9}$$

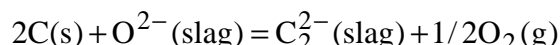
$$\gamma_i = 1.36(\chi_i - 0.26) \tag{10}$$

Where ${}_iX_i (= 1/\gamma_i)$, γ_i being the basicity-moderating parameter), $X_i (= (z_i \cdot r_i)/2)$, z_i and r_i being the oxidation number of cations and the ratio of the cations with respect to the total number of oxides, respectively), and χ_i are the optical basicity of pure oxide i , the equivalent fraction of oxide i , and the Pauling's electro-negativity of the involved metal ions, respectively. In Figure 8, $\log(\text{mass}\% \text{C} \cdot p_{\text{CO}})$ is plotted as a function of the optical basicity calculated by equations [9] and [10] with the previous results^{1, 17-19)}. The relatively similar tendencies for the CaO-SiO_2 and $\text{CaO-Al}_2\text{O}_3$ slags are observed, while the CaO-SiO_2 (Al_2O_3)- CaF_2 slags show some discrepancies from the non- CaF_2 slags. This means that the optical basicity concept should be carefully used in the CaF_2 -containing slags considering the depolymerization reaction of silicate (aluminate) as shown in equation [8].

5. Conclusions

The solubility of carbon in molten CaO-SiO₂ (Al₂O₃) and CaO-SiO₂ (Al₂O₃)-CaF₂ slags was measured at high temperatures to understand the thermodynamic behavior of carbon in molten slags. The results of this study can be summarized as follows:

- 1) From the effect of oxygen potential and slag basicity on carbon solubility, the dissolution mechanism of carbon into the slags could be confirmed by the following reaction:



- 2) The activity coefficient of carbide in the CaO-SiO₂ slag was affected by the slag composition, while that of the CaO-Al₂O₃ system was not.
- 3) The addition of CaF₂ greatly increased the carbide capacity of the CaO-SiO₂ slag system, while this effect was not remarkable in the CaO-Al₂O₃ slag.

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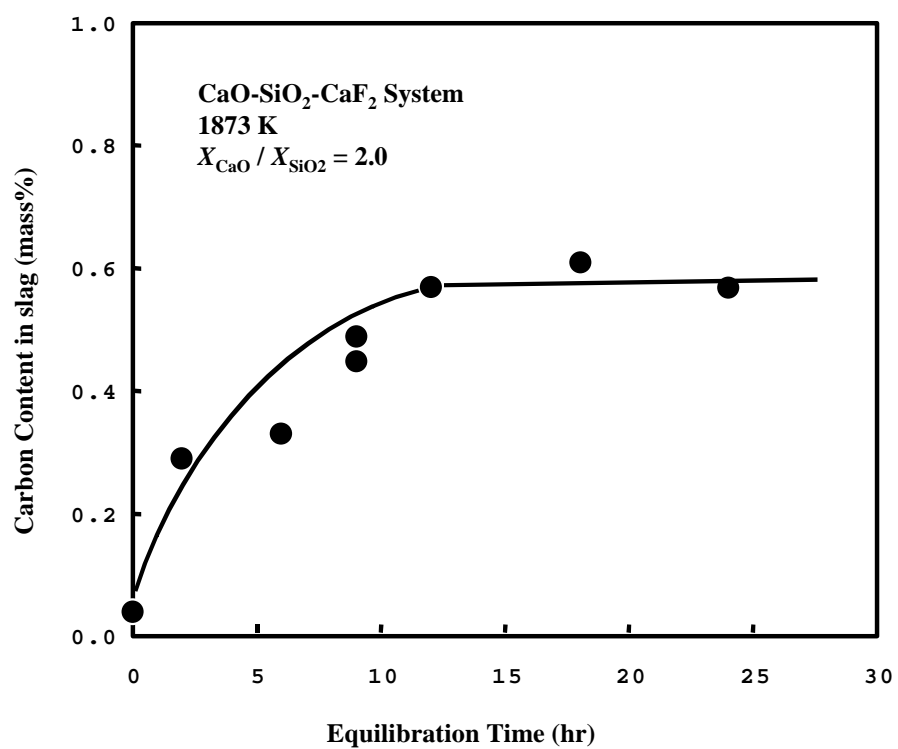


Figure 1. Carbon contents in the CaO-SiO₂-CaF₂ slag with equilibration time.

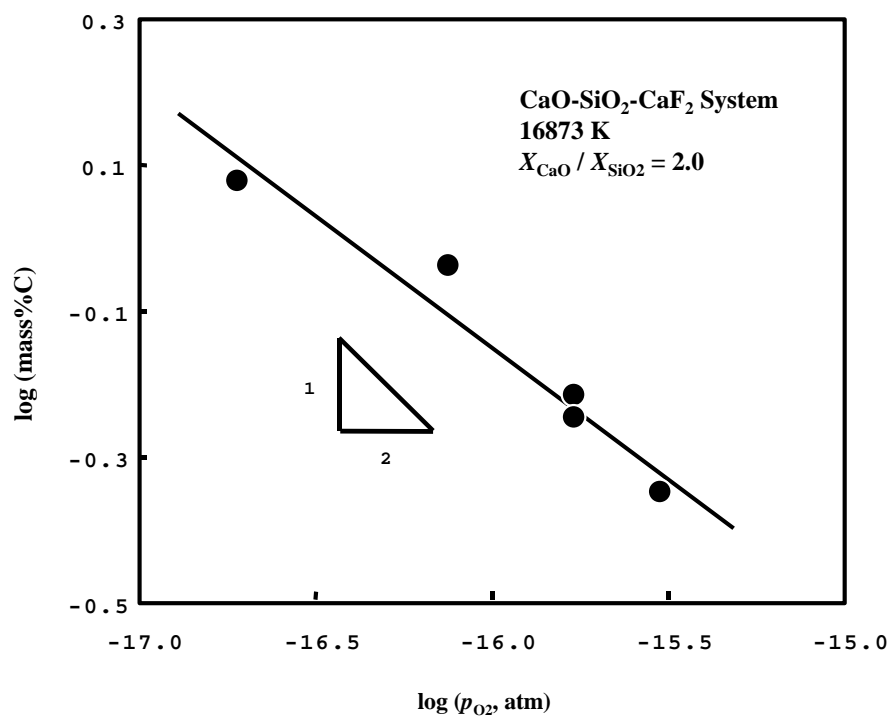


Figure 2. Dependence of carbon solubility on oxygen partial pressure in the CaO-SiO₂-CaF₂ slag.

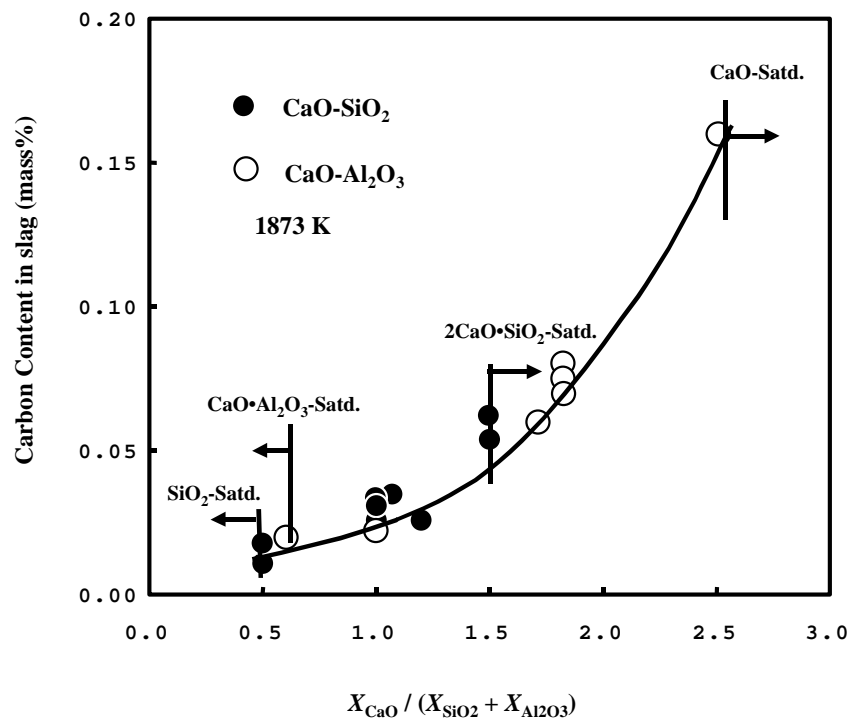


Figure 3. Effects of slag basicity on carbon solubility in the CaO-SiO_2 and $\text{CaO-Al}_2\text{O}_3$ slags at 1873 K.

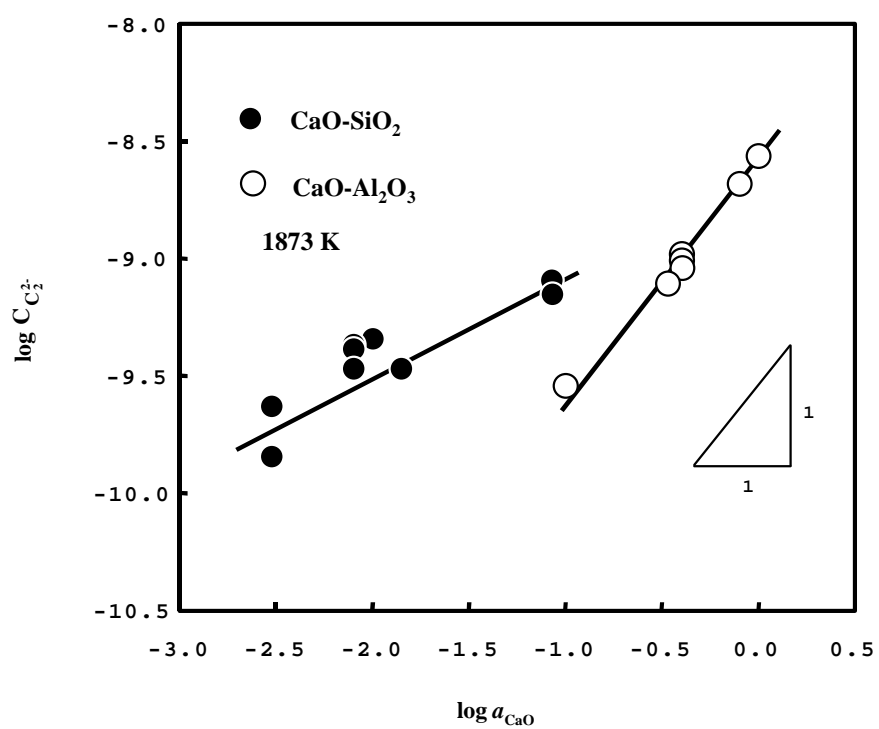


Figure 4. Effects of CaO activity on carbide capacities in the CaO-SiO₂ and CaO-Al₂O₃ slags.

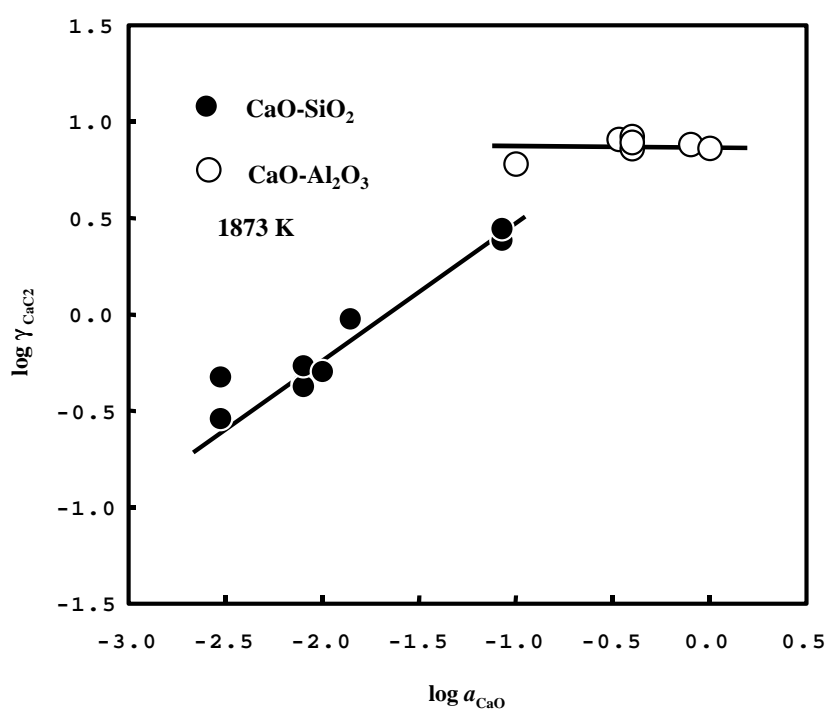


Figure 5. Effects of CaO activity on the activity coefficient of carbide in the CaO-SiO₂ and CaO-Al₂O₃ slags at 1873 K.

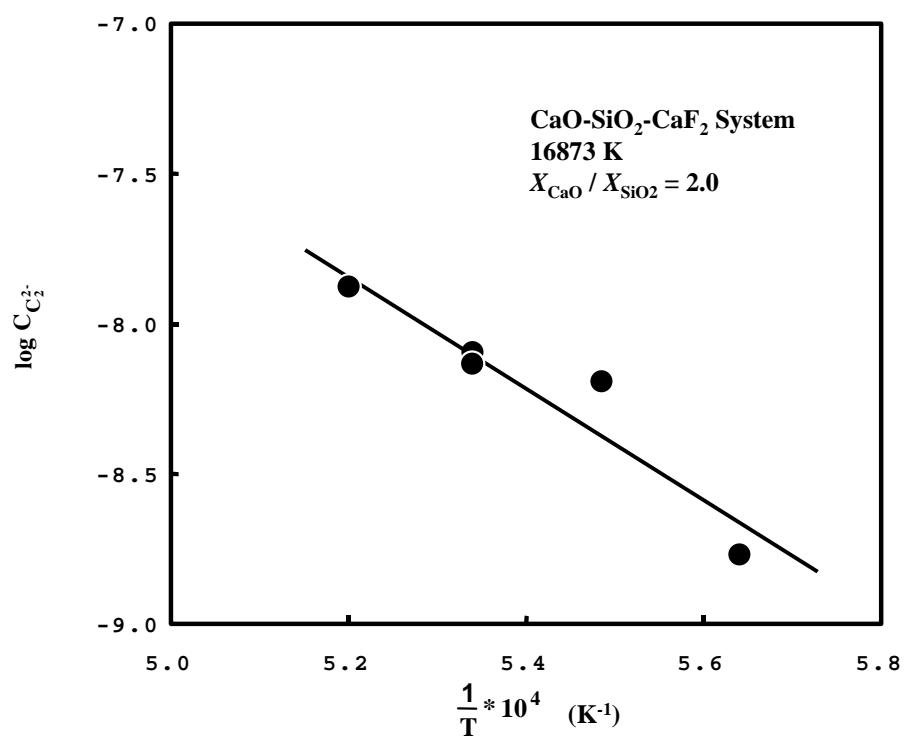


Figure 6. Dependence of carbide capacity on temperature in the CaO-SiO₂-CaF₂ slag.

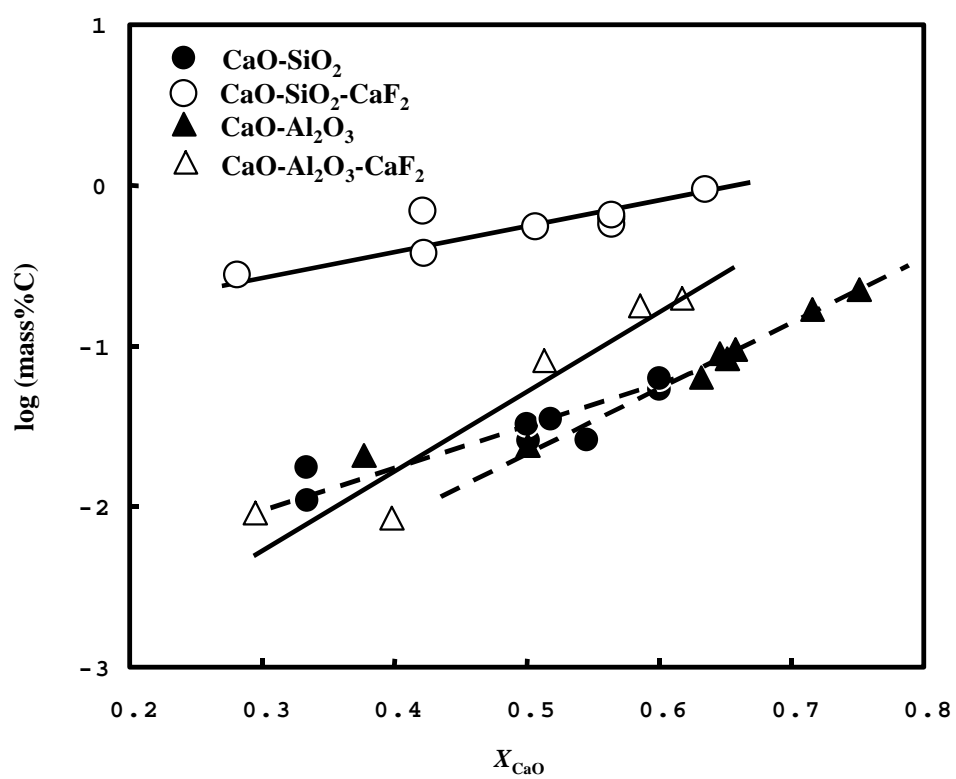


Figure 7. Effect of CaF₂ additions on carbon solubility in the CaO-SiO₂ and CaO-Al₂O₃ systems.

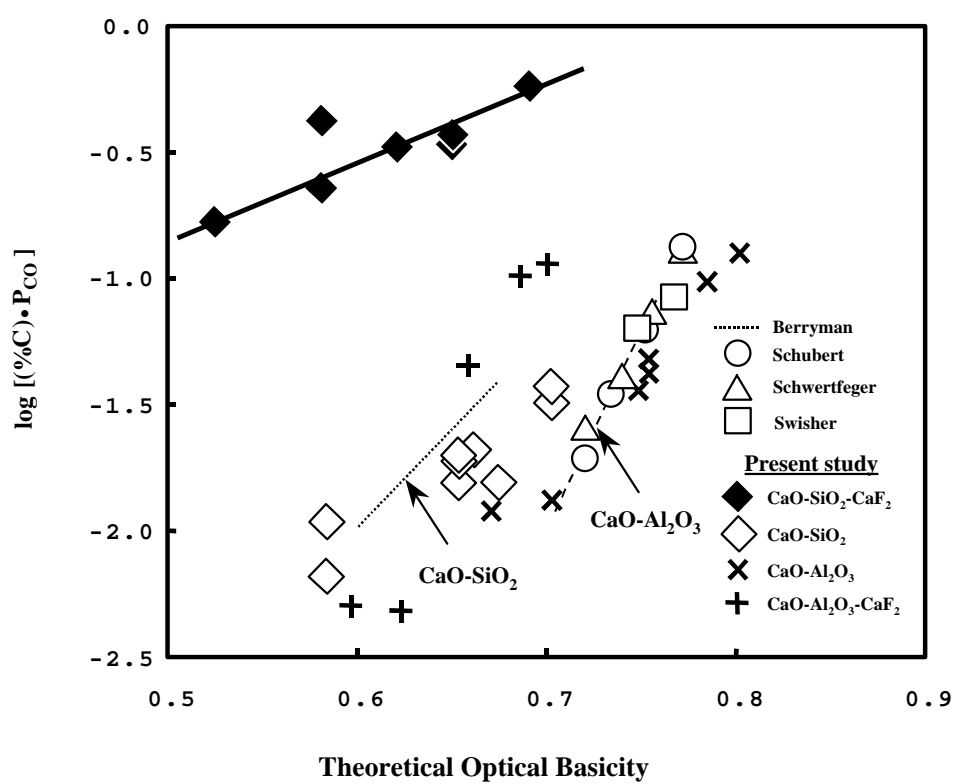


Figure 8. Comparison of carbide capacity for the various slag systems as a function of theoretical optical basicity.

