

# SOLUBILITY OF NITROGEN IN CaO-SiO<sub>2</sub>-CaF<sub>2</sub> SLAG SYSTEM

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## ABSTRACT

The solubility of nitrogen in CaO-SiO<sub>2</sub>-CaF<sub>2</sub> slag at high temperature was measured to understand the dissolving mechanism of nitrogen by using chemical equilibrating technique. The effects of oxygen potential and temperature on nitride capacity were shown good agreement with theoretical expectations. A minimum value of the nitride capacity was found at about 2.0 slag basicity and the nitride capacity increased in both more acidic and basic regions. This may be explained by two mechanisms for nitrogen dissolution; incorporated nitride ion and free nitride ion state. The effects of BaO and MgO to substitute CaO on nitride capacity showed similar behaviors. Both components were not effective for increasing nitride capacity of the slag. It was found that nitride capacity and optical basicity had a close relationship even in the different basic oxide systems.

## 1. Introduction

Nitrogen is one of the most important elements in steel due to its beneficial or detrimental effects on the mechanical properties of steel. In spite of many studies and efforts tried in plant and laboratory, nitrogen has always been a very difficult element to remove from liquid steel. For instance, different degassing processes that usually work well for hydrogen are not effective for nitrogen removal to the desired levels because of the smaller diffusivity and its tendency to form nitride in steel<sup>1</sup>. The nitrogen pick up from air during tapping operation of the converter as well as secondary ladle refining provides another problem to control the nitrogen level<sup>2</sup>.

Recently there is a growing interest for nitrogen control by using steelmaking slag. The solubility of nitrogen in various slag systems has been studied by several investigators to obtain reliable data which can be used for nitrogen removal from molten steel as well as protection of steel from nitrogen absorption<sup>2-6</sup>. The recent work<sup>2</sup> with CaO-CaF<sub>2</sub> system indicated that nitrogen

dissolution in the melts strongly depends on the activity of the basic component of the melt. On the other hand, it is also reported that the role of SiO<sub>2</sub> in the nitrogen dissolution is significant. It is not quite clear whether nitrogen dissolution is enhanced by the presence of basic or acidic components.

In this study, the solubility of nitrogen in molten CaO-SiO<sub>2</sub>-CaF<sub>2</sub> and CaO(MgO, BaO)-SiO<sub>2</sub>-CaF<sub>2</sub> systems has been measured. The effects of oxygen partial pressure, temperature and slag basicities on nitrogen dissolution in slag are also discussed.

## 2. Experimental procedures

The experiments carried out by equilibrating the slag in a graphite crucible with CO, N<sub>2</sub> and Ar gas mixtures. Figure 1 shows the schematics of the experimental apparatus. The master slags were prepared by melting CaO, SiO<sub>2</sub> and CaF<sub>2</sub> of reagent grade in a graphite crucible under Ar atmosphere. The graphite crucible with 12g of slag was put into the furnace after reaching the reaction temperature. The 500cc/min of mixed gas was blown onto the surface of the melts through the alumina tube which was placed 1cm above the sample in order to ensure that oxygen potential was given by C-CO equilibrium reaction<sup>7</sup>. Partial pressures of oxygen and nitrogen were changed to investigate their effects on nitrogen solubility of slags.

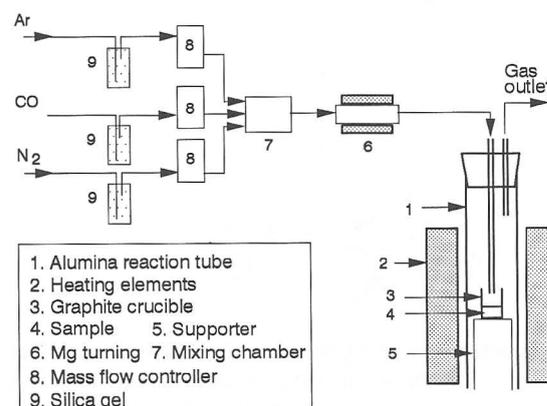


Figure 1. Schematic diagram of experimental apparatus

In order to determine the time to reach equilibrium, preliminary tests were carried out. The results in figure 2 show the changes of nitrogen contents in slag with reaction time at 1600°C, 0.6atm of CO and 0.4atm of N<sub>2</sub> partial pressure in CaO-SiO<sub>2</sub>-CaF<sub>2</sub> slag system. It can be seen that the system reaches equilibrium after about 20 hours. After 24 hours of holding, the slag samples were taken out of the furnace, quenched by argon and then prepared for chemical analysis. Nitride in slag was analyzed by the "Kjeldahl method"<sup>8</sup>.

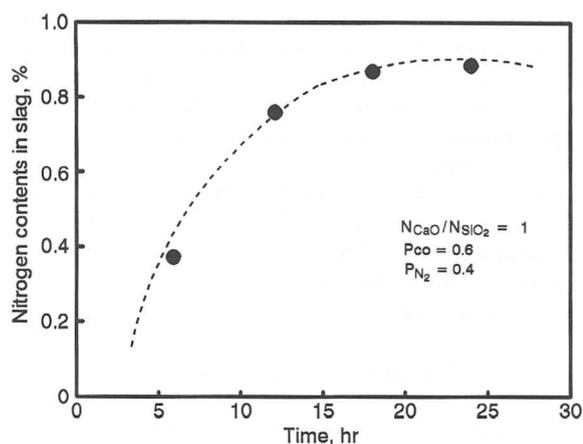


Figure 2. Changes of nitrogen contents in CaO-SiO<sub>2</sub>-CaF<sub>2</sub> system with time at 1600°C

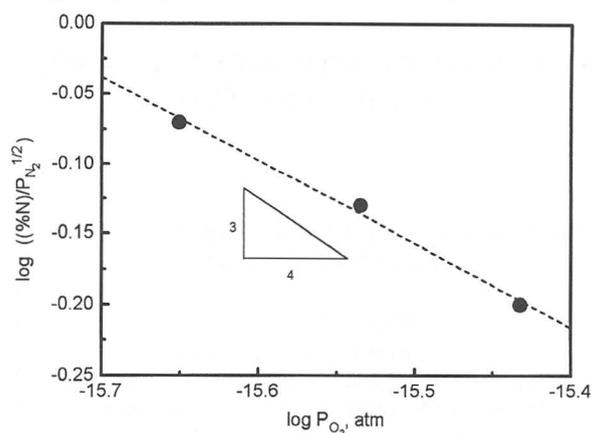
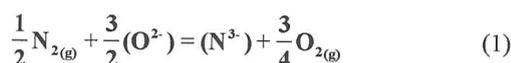


Figure 3. Nitrogen distribution in slag as a function of oxygen partial pressure at 1600°C

### 3. Results and discussion

#### 3.1 Effects of oxygen partial pressure and temperature

Nitrogen dissolution reaction between gas and slag, in general, may be expressed as follows<sup>10</sup>.



$$K_1 = \frac{P_{O_2}^{\frac{3}{4}} f_{N^{3-}} (\%N^{3-})}{P_{N_2}^{\frac{1}{2}} a_{O^{2-}}^{\frac{3}{2}}} \quad (2)$$

$$C_{N^{3-}} = \frac{P_{O_2}^{\frac{3}{4}} (\%N^{3-})}{P_{N_2}^{\frac{1}{2}}} = \frac{K_1 a_{O^{2-}}^{\frac{3}{2}}}{f_{N^{3-}}} \quad (3)$$

It is expected that nitrogen distribution ratio between gas and slag is dependent on oxygen partial pressure and its coefficient is  $-3/4$  from equation (3) theoretically. Figure 3 shows the relationship between nitrogen distribution ratio and oxygen partial pressure and the slope of line agrees reasonably to the theoretical value. The temperature dependency of nitride capacity in slag is shown in figure 4. It increased with temperature. The activation energy calculated from the slope of the data line for nitrogen dissolution reaction is about 36 kcal/mole. It can be inferred that this temperature dependency is mainly due to the chemical reactions including absorption and desorption of nitrogen ions.

#### 3.2 Effect of CaF<sub>2</sub>

Spar is used as a fluxing component to industrial slags in metallurgical processes. Nitrogen in slag which

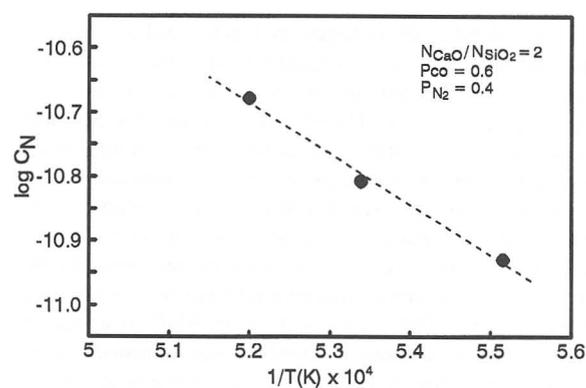


Figure 4. Nitride capacity of CaO-SiO<sub>2</sub>-CaF<sub>2</sub> system as a function of temperature

contained network former has shown to behave both as free nitride and as incorporated nitride<sup>6</sup>. Figure 5 shows the changes of nitrogen contents with CaF<sub>2</sub> concentration at the slag basicity,  $N_{(CaO)} / N_{(SiO_2)}$ , of 2. Nitrogen increased with CaF<sub>2</sub> to reach a maximum value at about 20wt%CaF<sub>2</sub> and then decreased with further CaF<sub>2</sub> addition. In case of low CaF<sub>2</sub> region, CaF<sub>2</sub> and silicate reaction lead to the formation of fluorosilicates to increase the number of reaction site of silicate resulting in a higher nitrogen content. However, due to dilution of silicate with still higher CaF<sub>2</sub>, the nitrogen content will decrease.

#### 3.3 Effect of slag basicity

As shown in figure 6, nitride capacity decreases with increasing CaO contents, to reach a minimum value and then increases with further increase in CaO mole fraction. It can be speculated from these results that dissolution of nitrogen in a slag is characterized by two simultaneous reactions, one with a acidic component and the other with a basic component. Nitrogen may dissolve in slag as a

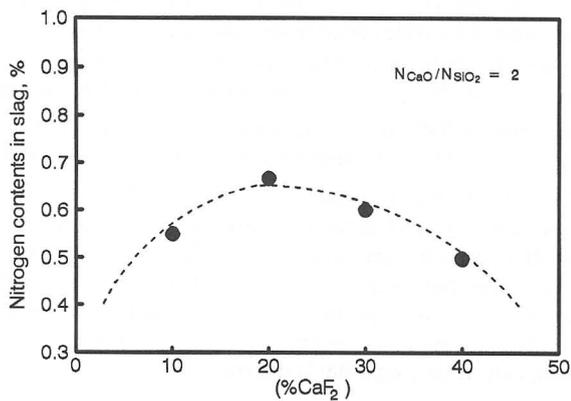


Figure 5. Effects of  $\text{CaF}_2$  contents in slags on nitrogen solubility of  $\text{CaO-SiO}_2\text{-CaF}_2$  system at  $1600^\circ\text{C}$

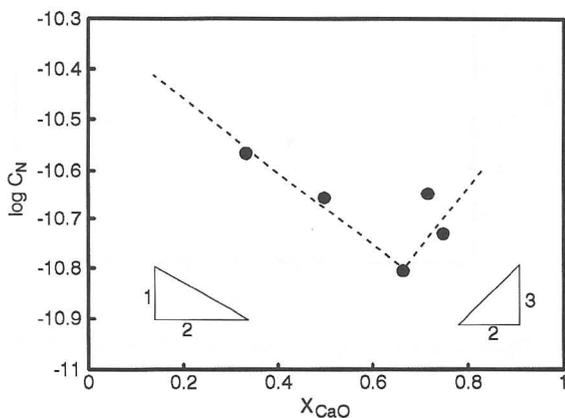
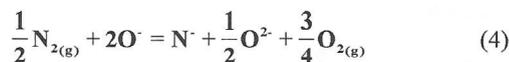


Figure 6. Effects of  $X_{\text{CaO}}$  in slag on nitride capacity of  $\text{CaO-SiO}_2\text{-CaF}_2$  system at  $1600^\circ\text{C}$

incorporated nitride which is related to silica ions in slag and stable form in a acidic region because nitrogen solubility is decreased with  $\text{CaO}$  contents increasing. In less basic slags, the nitrogen capacity decreases with  $\text{CaO}$  addition because it reduces the silica activity and the reaction site. The reaction of nitrogen dissolution in this region can be expressed by equation (4).



$$C_{\text{N}^-} = \frac{P_{\text{O}_2}^{\frac{3}{4}} (\text{wt}\% \text{N})}{P_{\text{N}_2}^{\frac{1}{2}}} = \frac{K_5 a_{\text{O}^-}^2}{a_{\text{O}^{2-}}^{\frac{1}{2}} f_{\text{N}^-}} \quad (5)$$

Where  $\text{O}^-$  and  $\text{N}^-$  are nonbridging oxygen and nonbridging nitride incorporated with silica which is a network former in slag, respectively. Nitrogen dissolution following equation (1) may be referred to as "free nitride" and that following equation (4) as "incorporated nitride". The experimental results for nitrogen dissolution behavior in a

acidic region in this study are in good agreement with other studies<sup>5,9,10</sup>. It is thought that nitrogen may exist as a free nitride as in equation (1) in case of further increase of  $\text{CaO}$  concentration from this consideration. The free nitride is more stable than incorporated ion as the activity of oxygen ion is increased in basic region and it shows high free nitride capacity. These facts indicate that nitrogen dissolution behavior may be related to the stability of nitride ions which is dependent very much on the oxygen ions, slag basicity. The reaction mechanism can be changed according to the changes of stability for nitride ion with the basicity of slag.

Nitride capacities were plotted over  $N_{(\text{CaO})} / N_{(\text{SiO}_2)}$  which is often used to define basicity. As shown in Figure 7, the tendency of forming V-shape with minimum value around 2 of basicity is more pronounced. Nitride capacities of the system investigated in the present study are compared to those of several other slag systems<sup>2,6,9,11-13</sup> in figure 8. Nitride capacities in this study are relatively high,  $1.0 \times 10^{-11}$ . Difference in nitride capacities from those of Martinez et al.<sup>11</sup> may have been caused by the temperature difference of two studies on same slag system. Other results<sup>9,13</sup> show steady decrease of nitride capacities with increasing basic oxide(MO) content in high basic region as shown in figure 8.

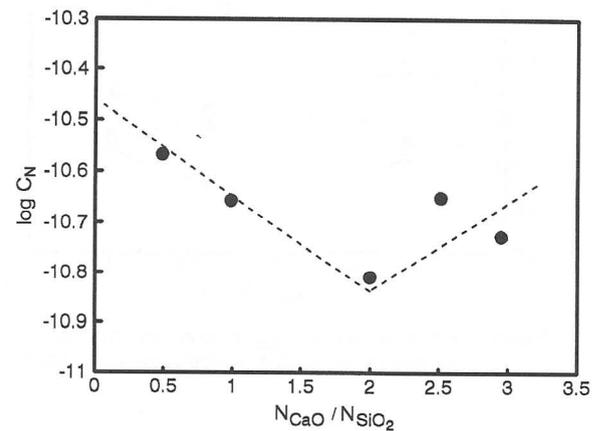


Figure 7. Effects of slag basicity on nitride capacity of  $\text{CaO-SiO}_2\text{-CaF}_2$  system at  $1600^\circ\text{C}$

### 3.4 Effects of other basic oxide on nitride capacities

Effects of substituting other basic components ( $\text{MgO}$  and  $\text{BaO}$ ) for  $\text{CaO}$  were investigated to examine the dependence of nitride capacity on basic oxides of the melt. One is weaker and the other is stronger basic component than  $\text{CaO}$ . The effects of substitution  $\text{CaO}$  by  $\text{MgO}$  on nitrogen dissolution are shown for each slag basicity in figure 9. For slag basicities, 1 and 2, there are small increase in nitride capacities with increasing the substitution ratio up to 0.5 of  $N_{(\text{MgO})} / N_{(\text{CaO})}$ , and then decrease with further increasing of substitution ratio.

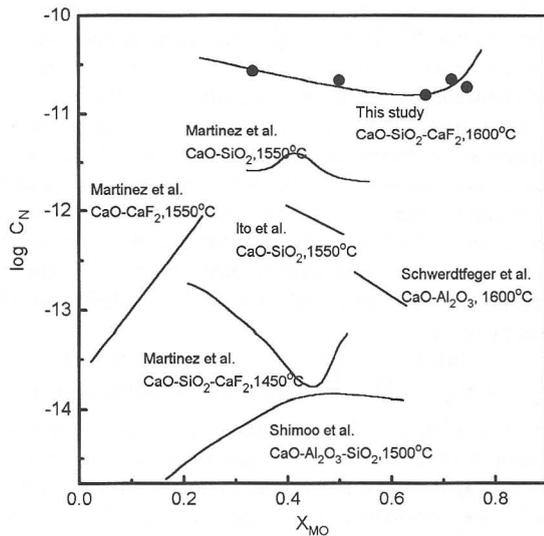


Figure 8. Nitride capacities of various slag systems as a function of mole fraction of basic components

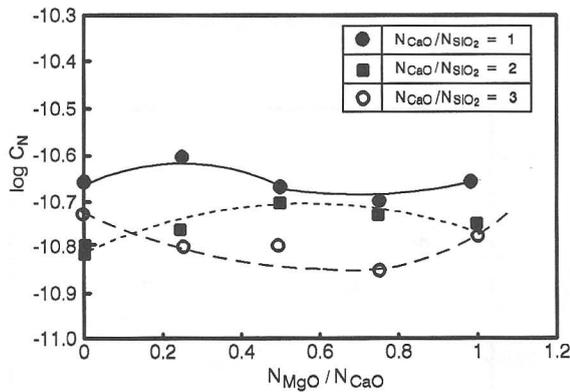


Figure 9. Effects of  $N_{MgO} / N_{CaO}$  ratio in slag on nitride capacity of CaO-SiO<sub>2</sub>-MgO-CaF<sub>2</sub> system at 1600°C

However, there is more or less a steady decrease with increasing it in a higher basicity region of 3. The possible explanations for different behavior with slag basicities in the low basic region would be due to presence of incorporated nitride as shown in figure 6. Nitride solubility increased as the activity of SiO<sub>2</sub> increased because nitrogen was thought to be bound with silicate network. In general, in terms of oxygen ion supply capacity, MgO is less than that of CaO and activity of silicate network in melt would increase with increasing MgO. For higher slag basicity region, nitride solubility decrease initially and then increased again as the substitution ratio of CaO by MgO increased. Slag is almost saturated with CaO at slag basicity of 3 and 1600°C. Dilution of CaO by MgO in this region decreases the activity of oxygen ion and resulting in lower nitride capacity.

The effects of BaO on nitride capacity was reported to increase the nitride capacity for basic slags<sup>10</sup>. The results in figure 10 shows that nitride capacity decreased slightly up to 0.05 of  $N_{(BaO)} / N_{(CaO)}$  and then increased for further increase of BaO. But nitride capacity even in case of 0.2 of  $N_{(BaO)} / N_{(CaO)}$  is almost the same as slag without BaO. In case of small BaO addition, dilution effect of CaO by BaO and effect of capacity increase of oxygen ion supply by BaO in melt were nearly offset. Therefore this complex effect does not increase the activity of oxygen ions in melt. However, it is expected that BaO would increase the activity of oxygen ion and nitride capacity in higher basicity slag only at very high BaO concentration.

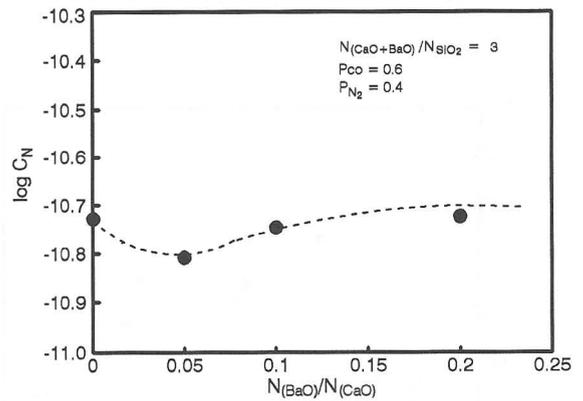


Figure 10. Effects of  $N_{(BaO)} / N_{(CaO)}$  in slags on nitride capacity of CaO-BaO-SiO<sub>2</sub>-CaF<sub>2</sub> system at 1600°C

The effects of substitution BaO for CaO on nitride capacity showed similar behaviors as MgO in this study. Those phenomena for substitution effects of MgO and BaO could be explained by complex effects of ionic strength and dilution between CaO and these basic oxides. The concept of optical basicity was used as a measure of slag basicities<sup>14</sup>. Figure 11 shows nitride capacities as a function of optical basicities. The nitride capacities of all slag systems

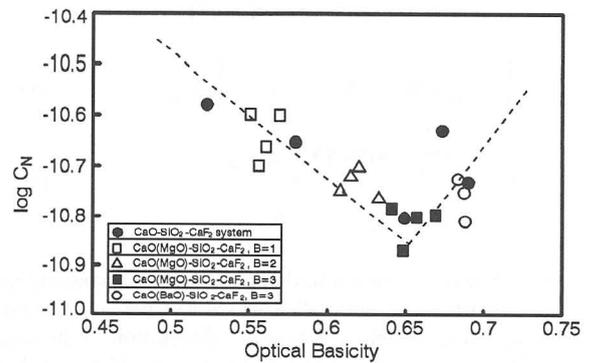


Figure 11. Relationship between optical slag basicity and nitride capacities of various slag compositions at 1600°C

regardless of its constituents can be correlated with linear relationship. It shows an adverse basicity dependence at 0.65 as boundary. As seen in the figure, the effects of MgO for basicities between 1 and 2 and 3 are different because transition range which the reaction mechanism changed might be included for basicity 3. However, in the case of BaO addition, equation (1) is valid for highly basic region. As discussed previously, the dilution effect of CaO by BaO and effect of capacity increase of oxygen ion supply by BaO in melt were almost balanced, this complex effect does not increase the activity of oxygen ions in melt.

#### **4. Conclusion**

The solubility of nitrogen in molten CaO-SiO<sub>2</sub>-CaF<sub>2</sub> slag system in equilibrium with carbon and gas mixtures of CO, N<sub>2</sub> and Ar at 1600°C was measured. The solubility of nitrogen increased with decreasing the oxygen potential and increasing the reaction temperature. Nitrogen dissolution was found to be endothermic reaction and the activation energy was calculated to be 36kcal/mol. A minimum value of the nitride capacity was found at about 2.0 slag basicity and the nitride capacity increased in both more acidic and basic regions. This may be explained by two mechanisms for nitrogen dissolution; incorporated nitride ion and free nitride ion state. MgO increases the nitride capacity in case of slag basicity less than 2.0. However, it decreases nitride capacity slightly with MgO contents at higher slag basicity. The effects of substituting BaO for CaO on nitride capacity showed similar behaviors as MgO. Those phenomena for substitution effect of MgO and BaO could be explained complex effects of ionic strength and dilution of CaO by other basic oxides. Nitride capacity has a clear relationship with optical basicity in spite of the different basic oxide system.

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