

# The Nitrogen Reaction between Carbon Saturated Iron and Na<sub>2</sub>O-SiO<sub>2</sub> Slag: Part I. Thermodynamics

F. TSUKIHASHI and R. J. FRUEHAN

The nitrogen partition ratio between Na<sub>2</sub>O-SiO<sub>2</sub> slags and carbon saturated iron was measured for slags containing from 0.4 to 0.55 mole fraction of Na<sub>2</sub>O and the temperature range 1200° to 1350 °C. The nitrogen is dissolved in the slag as the cyanide ion (CN<sup>-</sup>) and the partition ratio is proportional to the oxygen pressure to the -¼ power as predicted for CN<sup>-</sup> dissolution. The oxygen pressure for carbon saturated iron silicon alloys is controlled by the Si (metal)-SiO<sub>2</sub> (slag) equilibrium. The nitrogen partition ratio and the cyanide capacity increase with Na<sub>2</sub>O content and temperature. Calculations indicate that Na<sub>2</sub>O-SiO<sub>2</sub> slags will absorb three times more nitrogen than CaO-Al<sub>2</sub>O<sub>3</sub> slags at the same basicity and temperature. Based on thermodynamic calculations it is estimated that for a typical Na<sub>2</sub>CO<sub>3</sub> hot metal treatment, half of the nitrogen in the metal could possibly be removed.

## I. INTRODUCTION

THERE has been a growing emphasis on the production of clean steels low in residual elements. Processes have been developed to remove sulfur, phosphorus, carbon, and total oxygen to extremely low levels. Hydrogen can be reduced to less than 1.5 ppm by vacuum degassing. Some nitrogen will be removed during BOF steelmaking by the flushing action of the CO and 10 pct to 20 pct can be removed by vacuum degassing. However, a commercial chemical process for reducing the nitrogen content to low levels does not exist.

Hot metal treatments have been developed in order to optimize the steelmaking process and to remove sulfur and phosphorus. The most common reactants used are CaO, CaO-Mg, Mg, CaC<sub>2</sub>, and Na<sub>2</sub>CO<sub>3</sub>. Soda ash (Na<sub>2</sub>CO<sub>3</sub>) is capable of simultaneously removing sulfur and phosphorus at the low oxygen potentials associated with carbon saturated iron. The Na<sub>2</sub>CO<sub>3</sub> treatment has become more attractive since a refractory material for the process as well as a process for recycling the soda ash have been developed.

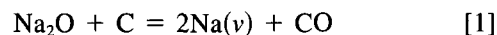
When Na<sub>2</sub>CO<sub>3</sub> is added to hot metal the resulting slag is Na<sub>2</sub>O-SiO<sub>2</sub>. In recent work the solubility of nitrogen in Na<sub>2</sub>O-SiO<sub>2</sub> slags in equilibrium with carbon and CO-N<sub>2</sub> gas mixtures has been measured,<sup>1,2</sup> and the results indicate that the slags can absorb significant quantities of nitrogen. However, the equilibrium distribution partition ratio for nitrogen between carbon saturated iron and Na<sub>2</sub>O-SiO<sub>2</sub>, (pct N)<sub>slag</sub> / [pct N]<sub>metal</sub>, has not been measured. In addition, there is no information on the kinetics of the nitrogen reaction for this system. Exploratory plant studies indicated that Na<sub>2</sub>CO<sub>3</sub> treatment can remove nitrogen from hot metal, but the mechanism and physical chemistry are not known.

It is the purpose of the present work to determine the thermodynamics and kinetics of the nitrogen reaction between Fe-C<sub>SAT</sub>-Si-N alloys and Na<sub>2</sub>O-SiO<sub>2</sub> slags. In Part I the results of the investigation of the thermodynamics of the

reaction as a function of slag composition, oxygen potential, and temperature are given.

## II. EXPERIMENTAL

A schematic of the experimental arrangements used is shown in Figure 1. In one set of experiments, five grams of a Na<sub>2</sub>O-SiO<sub>2</sub>-NaCN slag was equilibrated with five grams of a carbon saturated Fe-Si-N alloy in a graphite crucible as shown in Figure 1(a). With this experimental setup there is a possibility of Na<sub>2</sub>O loss for Na<sub>2</sub>O-rich slag by the reaction



In order to maintain a constant sodium potential, a second experimental arrangement was used in which ten grams of a lead-sodium alloy containing 0.08 pct to 0.2 pct Na was equilibrated with five grams each of the slag and iron alloy. The iron alloy floats between the two melts as shown in Figure 1(b) because of the difference in densities. The solubility of Pb in the iron alloy is negligible. The lead-sodium alloy insures a constant Na potential in the system.

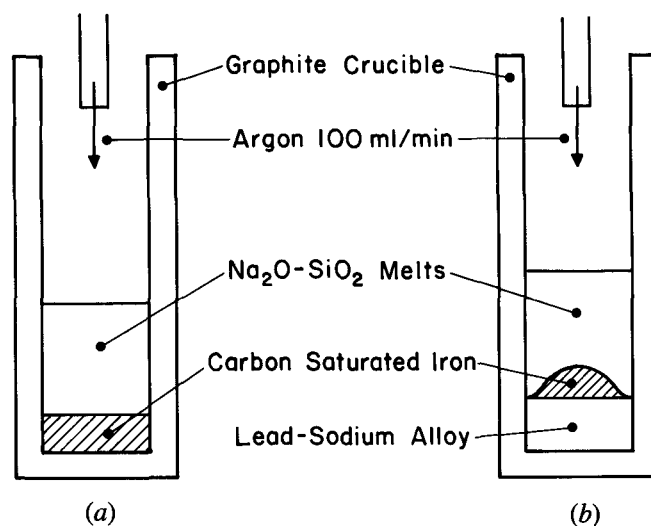


Fig. 1—Schematic of experimental arrangements.

F. TSUKIHASHI, Research Associate, is with Department of Metallurgical Engineering and Materials Science, Carnegie-Mellon University, Pittsburgh, PA 15213 and is on leave of absence from Department of Metallurgical Engineering and Materials Science, Faculty of Engineering, The University of Tokyo, Bunkyo, Tokyo 113, Japan. R. J. FRUEHAN, Professor, is with Department of Metallurgical Engineering and Materials Science, Carnegie-Mellon University, Pittsburgh, PA 15213.

Manuscript submitted November 13, 1985.

The carbon crucible with its contents was heated in a SiC resistance furnace equipped with a mullite reaction tube. The reaction temperature was primarily 1200 °C; however, the temperature dependence of the reaction was measured from 1200° to 1350 °C. The hot zone of the furnace was 100 mm. After equilibration, the graphite crucible was taken out, the melt was quenched under argon flow, and samples taken for chemical analysis. Silicon in the iron alloy was analyzed by molybdenum blue photometric method, silica in the slag by gravimetric method, nitrogen in iron alloy and slag by water vapor distillation-titration method (Kjeldahl method), cyanide by selective cyanide ion electrode, sodium in lead alloy and slag melts by atomic absorption method, and FeO and FeO<sub>1.5</sub> in slag by photometric orthophenanthroline method. In several cases the slags were analyzed for nitride (N<sup>-3</sup>) and the concentration of the nitride was less than 0.001 pct. In the experiment, the measurement of nitrogen solubility in Na<sub>2</sub>O-SiO<sub>2</sub> slag at 1100 to 1300 °C,<sup>1,2</sup> the content of nitride ion, was also found to be negligible compared to the content of cyanide ion. Each iron alloy was melted at the experimental temperature, and it was confirmed by nitrogen analysis that carbon saturated iron was saturated with nitrogen. In each experiment, iron alloys were mixed to obtain a prescribed silicon and nitrogen content in carbon saturated iron. Reagent grade sodium carbonate, silica, and sodium cyanide powders were mixed to get a desirable content for Na<sub>2</sub>O-SiO<sub>2</sub>-NaCN melts and charged into graphite crucible. Initial contents of nitrogen in slag and iron alloy were selected to be close to the expected equilibrium partition of nitrogen estimated from the results of solubility of nitrogen in Na<sub>2</sub>O-SiO<sub>2</sub> melts.<sup>1,2</sup>

Preliminary experiments were conducted to determine the time necessary to establish equilibrium. In one series of experiments there was a high concentration of nitrogen in the slag and nitrogen was transferred from slag to metal; in another series the opposite conditions were used. The nitrogen partition ratio was measured as a function of time. The change in the nitrogen partition ratio with time is shown in Figure 2. The nitrogen partition ratio was the same after 2

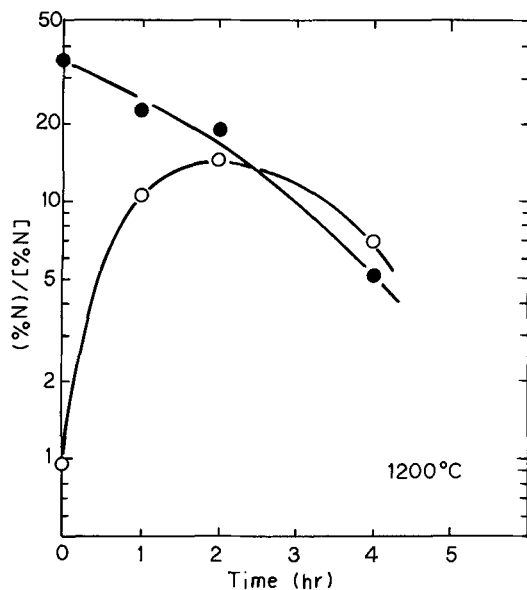


Fig. 2—Change of nitrogen partition ratio with time at 1200 °C.

hours for nitrogen transfer from slag to metal and metal to slag, indicating equilibrium was achieved. The decrease in the nitrogen partition ratio after 2 hours is due to the change of silicon content in the metal which lowered the oxygen potential. Schwerdtfeger *et al.*<sup>12</sup> found that larger equilibration times were necessary in their study of the solubility of nitrogen in CaO-Al<sub>2</sub>O<sub>3</sub> slags. However, they used much larger samples (100 g), and equilibrium was between the slag and the gas phase, while in these experiments, the slag-metal equilibrium was investigated. Tsukihashi *et al.*<sup>1,2</sup> conducted similar experiments for the measurement of phosphorus, manganese, vanadium, niobium, and antimony distribution between Na<sub>2</sub>O-SiO<sub>2</sub> slag and carbon saturated iron and of the nitrogen solubility in Na<sub>2</sub>O-SiO<sub>2</sub> slag and reported that the system is in equilibrium in 0.5 to 2 hours, depending on the slag basicity. In the normal experiments, nitrogen was present in both slag and metal and the starting ratio was close to equilibrium. Also, the necessary equilibration time would be less for higher temperatures and Na<sub>2</sub>O contents since the slags are less viscous under those conditions. The equilibration time varied from 0.5 hour to 2 hours depending on conditions; the short times were used for high Na<sub>2</sub>O slags and high temperatures to minimize Na loss by vaporization. For most conditions, equilibrium was approached from both sides to insure the equilibrium partition ratio was obtained. That is, in separate experiments the initial partition ratio was above and below the anticipated equilibrium value; only if the final ratios for the two experiments were in reasonable agreement were the values taken as representing equilibrium.

### III. RESULTS AND DISCUSSION

#### A. Effect of Oxygen Potential

In order to measure the effect of oxygen potential on the nitrogen partition ratio, the silicon content of the metal was changed anticipating that the partial pressure of oxygen would be set by the silicon-silica equilibrium



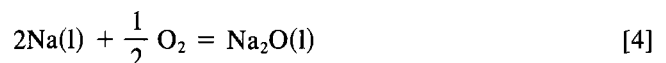
$$\Delta G^\circ = -948,000 + 200T \text{ J/mole}^4$$

The partial pressure of oxygen ( $P_{\text{O}_2}$ ) is given by

$$P_{\text{O}_2} = \frac{a_{\text{SiO}_2}}{\gamma_{\text{Si}} X_{\text{Si}} K_2} \quad [3]$$

where  $K_2$  is the equilibrium constant for reaction [2],  $\gamma_{\text{Si}}$  is the activity coefficient of Si relative to pure Si,  $X_{\text{Si}}$  is the mole fraction of silicon, and  $a_{\text{SiO}_2}$  is the activity of SiO<sub>2</sub> in the slag relative to pure liquid SiO<sub>2</sub>.

In the experiments with the Pb-Na alloy it was found that reaction [4] was controlling the  $P_{\text{O}_2}$ .



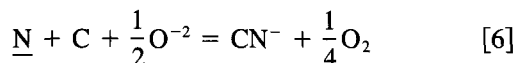
$$\Delta G^\circ = -373,500 + 107.3T \text{ J/mole}^4$$

The partial pressure of oxygen is given by Eq. [5], where the terms are defined as in Eq. [3]:

$$P_{\text{O}_2} = \left( \frac{a_{\text{Na}_2\text{O}}}{(\gamma_{\text{Na}} X_{\text{Na}})^2 K_4} \right)^2 \quad [5]$$

The values for the activities of Na<sub>2</sub>O and SiO<sub>2</sub> in the Na<sub>2</sub>O-SiO<sub>2</sub> slag were taken from the work of Tsukihashi, *et al.*,<sup>5</sup> which was in good agreement with other work.<sup>6,7</sup> The activity of silicon in carbon saturated iron is also known.<sup>2,8</sup> The values for the activity coefficient of Si in carbon saturated iron and of Na in Pb-Na alloys at low concentration are  $1.67 \times 10^{-3}$  and 0.315, respectively, at 1200 °C; the concentrations are low enough to assume Henry's Law.

The nitrogen partition ratio at 1200 °C is plotted vs oxygen partial pressure in Figure 3. Since the nitride concentration is negligible, nitrogen exists primarily in the slag as the cyanide ion. The equilibria between slag and metal can be written as

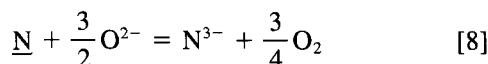


and the equilibrium constant is given by

$$K_6 = \frac{f_{\text{CN}^{-}}(\text{pct CN}^{-})P_{\text{O}_2}^{1/4}}{f_{\text{N}}[\text{pct N}]a_{\text{C}}a_{\text{O}^{-2}}^{1/2}} \quad [7]$$

where  $a_{\text{C}}$  and  $a_{\text{O}^{-2}}$  are the activities of carbon in the metal and oxygen ions in the slag, respectively,  $f_{\text{N}}$  is the activity coefficient of nitrogen in the metal relative to 1 wt pct, and  $f_{\text{CN}^{-}}$  is the activity coefficient of CN<sup>-</sup> in the slag relative to 1 wt pct.

The activity of carbon is unity because a graphite crucible was used in the experiments. The slag composition for each point in Figure 3 is nearly constant; therefore, it is assumed that the activity of O<sup>-2</sup> is constant. Since it is reasonable to consider that the activity coefficient of CN<sup>-</sup> and N are constant with changing the partial pressure of oxygen, it is expected that the nitrogen partition ratio should be proportional to the partial pressure of oxygen to the -1/4 power and the slope of the line in Figure 3 should be -1/4. On the other hand, if nitrogen dissolves as nitride in slag, the reaction is given by



Equilibrium constant is given by

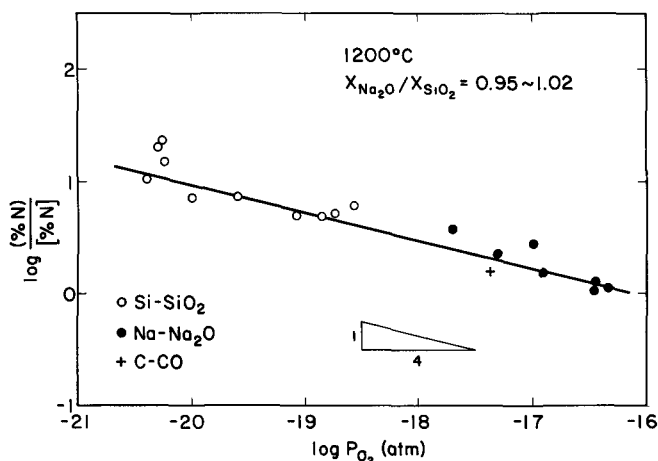


Fig. 3—Effect of oxygen partial pressure on nitrogen partition ratio at 1200 °C.

$$K_8 = \frac{[f_{\text{N}^{3-}}(\text{pct N}^{3-})]P_{\text{O}_2}^{3/4}}{[f_{\text{N}}(\text{pct N})]a_{\text{O}^{2-}}^{3/2}} \quad [9]$$

Assuming that the activity of O<sup>2-</sup> and the activity coefficient of N<sup>3-</sup> and N are independent of the oxygen partial pressure, the nitrogen partition ratio should be proportional to the partial pressure of oxygen to the -3/4 power. The actual slope of the line calculated from the experimental results determined by using the least squares method is -0.26, which is in excellent agreement with the prediction that nitrogen dissolves as cyanide in Na<sub>2</sub>O-SiO<sub>2</sub> slag. Therefore, it is concluded that the reaction of nitrogen between Na<sub>2</sub>O-SiO<sub>2</sub>-NaCN melts and carbon saturated iron is represented by reaction [6] and the partition ratio is proportional to the partial pressure of oxygen to the -1/4 power. Furthermore, the partial pressure of oxygen in the Na<sub>2</sub>O-SiO<sub>2</sub>-NaCN slag-carbon saturated iron system under an argon atmosphere is controlled by the Si-SiO<sub>2</sub> equilibrium at the slag-metal interface.

Tsukihashi *et al.*<sup>1,2</sup> measured the solubility of nitrogen in Na<sub>2</sub>O-SiO<sub>2</sub> melt at 1200 °C under constant oxygen partial pressure of  $2.10 \times 10^{-18}$  atm which was controlled by C-CO equilibrium. The nitrogen content of carbon saturated iron that would be in equilibrium with their gas mixtures can be calculated. The reaction is given by [10] and the equilibrium constant by [11]



$$\Delta G^\circ = 3595 + 23.87T \text{ J/mole}^9$$

$$K_{10} = \frac{f_{\text{N}}[\text{pct N}]}{P_{\text{N}_2}^{1/2}} \quad [11]$$

The activity coefficient of nitrogen in carbon saturated iron for the infinitely dilute reference state is 4.0.<sup>10,11</sup> Using the calculated nitrogen content of the metal, the partition ratio is calculated at the oxygen partial pressure in equilibrium with carbon and carbon monoxide; this point is shown in Figure 3 and is in agreement with the present results.

### B. Effect of Basicity

The basicity of a Na<sub>2</sub>O-SiO<sub>2</sub> slag can be defined by Eq. [12]<sup>3</sup>

$$B = \frac{X_{\text{Na}_2\text{O}}}{X_{\text{SiO}_2}} \quad [12]$$

where X represents the mole fraction.

The effect of basicity on the nitrogen partition ratio at a partial pressure of oxygen of  $1 \times 10^{-20}$  atm is shown in Figure 4. Since the actual Si levels in the metal were not exactly the same in each experiment shown in Figure 4, the partition ratio was calculated for  $1 \times 10^{-20}$  atmospheres assuming the ratio was proportional to  $P_{\text{O}_2}^{-1/4}$ ; the correction was less than 15 pct. The broken line in Figure 4 shows the partition ratio calculated from the solubility of nitrogen at an oxygen potential of  $2.1 \times 10^{-18}$  atm. The partition ratio increases significantly with Na<sub>2</sub>O concentration in the slag.

### C. Temperature Dependence

The temperature dependence of the nitrogen partition ratio for the equimolar composition ( $B = 1$ ) from 1200 °C

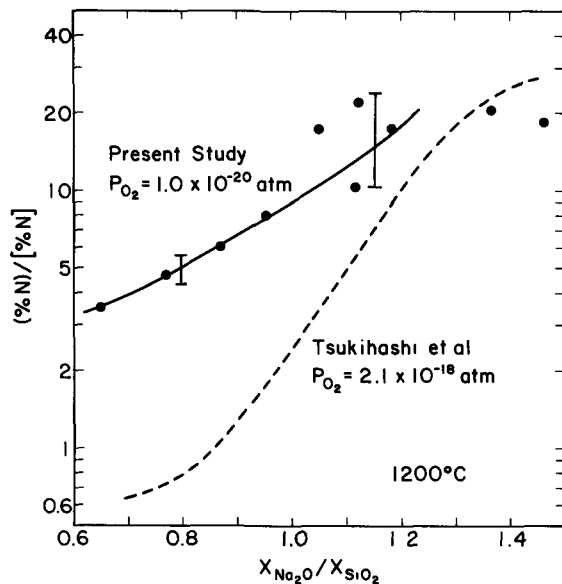


Fig. 4—Effect of basicity on nitrogen partition ratio at 1200 °C.

to 1350 °C is shown in Figure 5 for an oxygen pressure of  $1.0 \times 10^{-18}$  atm. As described previously, the measured partition ratios were corrected slightly for the different oxygen pressures; the correction was less than 15 pct. The solubility results of Tsukihashi *et al.*<sup>1,2</sup> were converted to partition ratios are shown in Figure 5 to be in good agreement with the present study. The temperature dependence of the partition ratio for  $B$  equal to one is given by

$$\log \frac{(\text{pct N})}{[\text{pct N}]} = 7.94 - \frac{1.11 \times 10^4}{T} \quad [13]$$

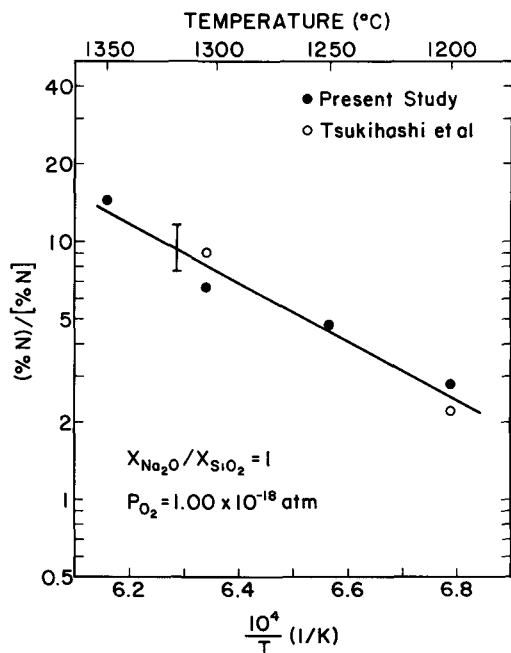
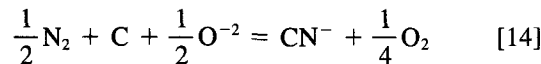


Fig. 5—Temperature dependence of nitrogen partition ratio for  $X_{\text{Na}_2\text{O}}/X_{\text{SiO}_2} = 1$  from 1200 °C to 1350 °C.

#### D. Cyanide Capacity

In order to compare the ability of a slag to absorb nitrogen as  $\text{CN}^-$ , it is convenient to use the concept of the cyanide capacity. The reaction for the absorption as cyanide can be written as



$$K_{14} = \frac{f_{\text{CN}^-}(\text{pct CN}^-)P_{\text{O}_2}^{1/4}}{P_{\text{N}_2}^{1/2}a_{\text{C}}a_{\text{O}^{-2}}^{1/2}} \quad [15]$$

The cyanide capacity  $C_{\text{CN}^-}$  is defined similarly to the sulfite capacity and is given by

$$C_{\text{CN}^-} = \frac{(\text{pct CN}^-)P_{\text{O}_2}^{1/4}}{a_{\text{C}}P_{\text{N}_2}^{1/2}} \quad [16]$$

and is related to the equilibrium constant  $K_{14}$  by

$$C_{\text{CN}^-} = \frac{K_{14}a_{\text{O}^{-2}}^{1/2}}{f_{\text{CN}^-}} \quad [17]$$

Substituting the equilibrium partial pressure of oxygen and nitrogen and the concentration of  $\text{CN}^-$  in the slags, the cyanide capacity was calculated. The cyanide capacity at 1200 °C is given as a function of basicity in Figure 6, along with that previously reported by Tsukihashi *et al.*<sup>1,2</sup> There is good agreement with the values at low basicity but not at high basicities. The present results at high basicities are subject to large uncertainties for the following reasons. The reaction time was short, 30 minutes, in order to avoid  $\text{Na}_2\text{O}$  loss, and equilibrium may not have been achieved. Uncertainties also arise in the calculation of  $P_{\text{O}_2}$  because of possible errors in the values used for the activity of  $\text{SiO}_2$ .

The temperature dependence of the cyanide capacity is given by

$$\log C_{\text{CN}^-} = 2.74 - \frac{1.24 \times 10^4}{T} \quad [18]$$

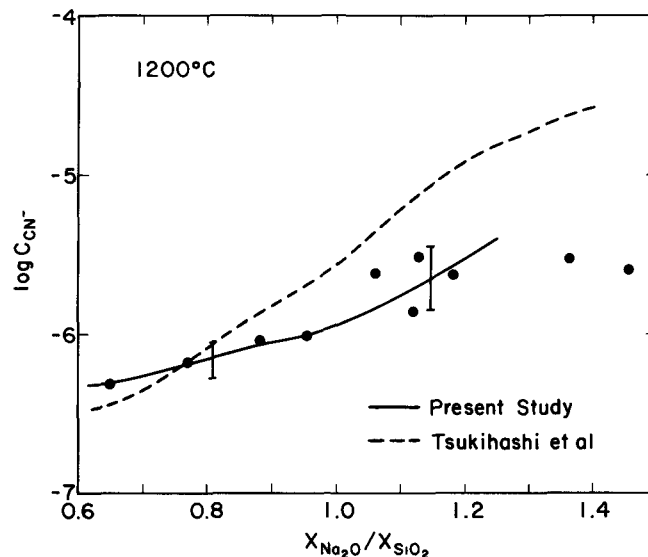
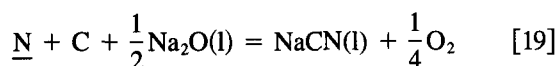


Fig. 6—Relation between cyanide capacity and basicity at 1200 °C.

There have been previous measurements of the solubility of nitrogen in CaO-Al<sub>2</sub>O<sub>3</sub> and CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> slags.<sup>12, 13, 14</sup> In these slags the nitrogen dissolves as CN<sup>-</sup> and N<sup>-3</sup> ions. In general the cyanide capacity increases with basicity and temperature. At the oxygen pressures of interest the concentration of CN<sup>-</sup> is significantly higher than that of N<sup>-3</sup>. In order to compare the cyanide capacity of Na<sub>2</sub>O-SiO<sub>2</sub> slags to CaO-Al<sub>2</sub>O<sub>3</sub> slags, the present results were extrapolated to 1600 °C (assuming Eq. [18] is valid to 1600 °C). The cyanide capacities are compared in Figure 7. The cyanide capacity of Na<sub>2</sub>O-SiO<sub>2</sub> slags is about three times higher than CaO-Al<sub>2</sub>O<sub>3</sub> slags.

### E. Activity Coefficient of NaCN

Since the free energy change of reaction [19] is known, the activity coefficient of NaCN (l) can be calculated from results of measurements.



$$\Delta G^\circ = 101,500 - 53.88T \text{ J/mole}^4$$

The equilibrium constant is given by

$$K_{19} = \frac{a_{\text{NaCN}} P_{\text{O}_2}^{1/4}}{a_{\text{N}} a_{\text{C}} a_{\text{Na}_2\text{O}}^{1/2}} \quad [20]$$

$$\gamma_{\text{NaCN}} = \frac{K_{19}(f_{\text{N}}[\text{pct N}]) a_{\text{C}} a_{\text{Na}_2\text{O}}^{1/2}}{X_{\text{NaCN}} P_{\text{O}_2}^{1/4}} \quad [21]$$

The activity coefficient of NaCN is given by Eq. [21], where  $\gamma_{\text{NaCN}}$  is the activity coefficient of NaCN in slag relative to pure liquid NaCN. The activity coefficient of NaCN calculated from Eq. [21] is shown in Figure 8. Activity coefficient is increasing with increasing the basicity of slag.

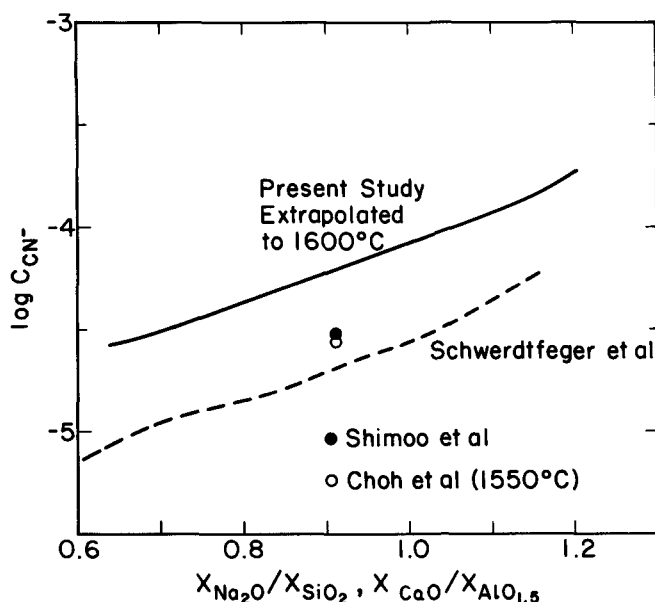


Fig. 7—Comparison of cyanide capacity for the Na<sub>2</sub>O-SiO<sub>2</sub> system with that for the CaO-AlO<sub>1.5</sub> system.

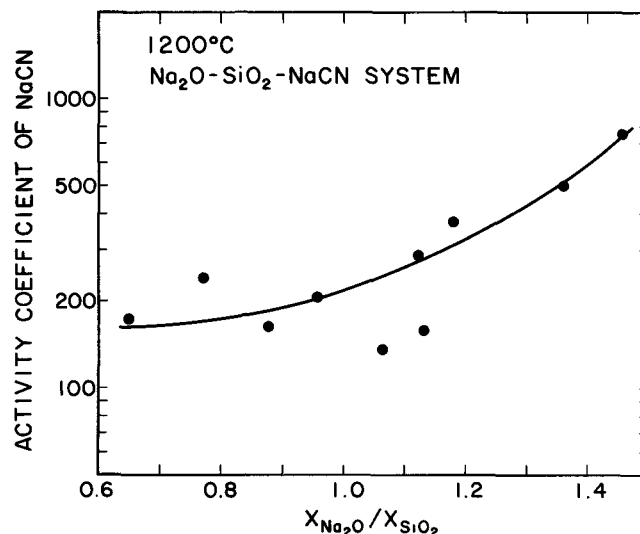
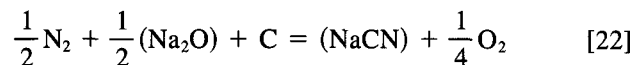


Fig. 8—Activity coefficient of NaCN for the Na<sub>2</sub>O-SiO<sub>2</sub>-NaCN system at 1200 °C.

### F. Heat of Solution of NaCN

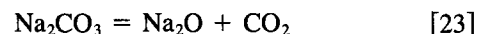
Since the cyanide capacity is based on reaction [14], which is the equivalent of reaction [22], the heat of reaction [22] can be calculated from the slope of the line in Figure 5 and is 56.6 kcal (237 kJ)



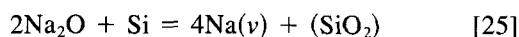
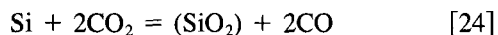
The Na<sub>2</sub>O and NaCN are dissolved in the slag. The heat of reaction [22] if all compounds are in their standard state (pure) is 25.1 kcal (105 kJ). The differences in these heats of reaction,  $(\frac{1}{2}\Delta\bar{H}_{\text{Na}_2\text{O}} - \Delta\bar{H}_{\text{NaCN}})$  is equal to 31.5 kcal (132 kJ) where  $\Delta\bar{H}_{\text{Na}_2\text{O}}$  and  $\Delta\bar{H}_{\text{NaCN}}$  are the partial molar heats of solution of Na<sub>2</sub>O and NaCN in the slag, respectively. Yamaguchi *et al.*<sup>6</sup> and Rego *et al.*<sup>7</sup> measured the value of  $\Delta\bar{H}_{\text{Na}_2\text{O}}$  for the Na<sub>2</sub>O-SiO<sub>2</sub> system; for  $X_{\text{Na}_2\text{O}} = 0.58$  the value is -30 kcal/mole (-125 kJ/mole) in the temperature range of interest. Therefore, the heat of solution of NaCN in Na<sub>2</sub>O-SiO<sub>2</sub>-NaCN slags at  $X_{\text{Na}_2\text{O}} = 0.5$  is estimated to be -46 kcal/mole (-192 kJ/mole).

### G. Predicted Nitrogen Removal in Practice

Based on the thermodynamics developed in the present study, it is possible to calculate the possible nitrogen removal by a Na<sub>2</sub>CO<sub>3</sub> treatment. When Na<sub>2</sub>CO<sub>3</sub> is added to hot metal it reacts with the silicon in the metal to form a Na<sub>2</sub>O-SiO<sub>2</sub> slag. The composition of the slag depends on the amount of Na<sub>2</sub>CO<sub>3</sub> added, the silicon in the hot metal, and the amount of Na<sub>2</sub>O reacting with carbon and vaporizing. For the present example let us assume 12 kg of Na<sub>2</sub>CO<sub>3</sub> is added to hot metal containing 0.3 pct Si which will be lowered to 0.1 pct by the reaction with the Na<sub>2</sub>CO<sub>3</sub>. Furthermore, when Na<sub>2</sub>CO<sub>3</sub> is added it dissociates by the reaction



It is assumed that Na<sub>2</sub>O loss by reaction [1] is negligible. The Si is removed from the hot metal by oxidation by CO<sub>2</sub> and Na<sub>2</sub>O:



Reasonable assumptions indicate that the final slag will be 10 kg per 1000 kg of metal of a Na<sub>2</sub>O-SiO<sub>2</sub> slag with a basicity of 1.3 to 1.4.

The work of Koros *et al.*<sup>15</sup> and Kaell and Mayer<sup>3</sup> indicate that there is typically 50 to 65 ppm nitrogen in blast furnace hot metal, with 58 ppm being a reasonable average. The value of the nitrogen partition ratio at 1350 °C for a basicity of 1.3 to 1.4 extrapolated from the present work is about 50. Using a simple mass balance, the calculated final nitrogen content of the metal for the above conditions would be about 30 ppm or about half of the nitrogen removed. In the pilot plant work by Kaell and Mayer, they decreased the nitrogen content of the hot metal from 65 ppm to 25 ppm using 12 kg/t of Na<sub>2</sub>CO<sub>3</sub>, which is in reasonable agreement with our prediction.

It should be emphasized that the above calculation is only a rough estimation because it is difficult to predict the final slag composition and amount. Furthermore, it was assumed that the kinetics are fast and equilibrium is achieved. However, the results do indicate a considerable amount of the nitrogen may be removed by Na<sub>2</sub>CO<sub>3</sub> treatment.

#### IV. SUMMARY AND CONCLUSIONS

Na<sub>2</sub>O-SiO<sub>2</sub> slags can absorb significant quantities of nitrogen from carbon saturated iron. The nitrogen in the slag is primarily present as the cyanide ion CN<sup>-</sup>. The nitrogen partition ratio increases with Na<sub>2</sub>O concentration and temperature. The value of the partition ratio is proportional to the oxygen pressure to the -1/4 power which confirms that the nitrogen is present as CN<sup>-</sup> in the slag. For carbon saturated iron-silicon alloys the oxygen pressure governing the cyanide concentration of the slag is determined by the Si (metal)-SiO<sub>2</sub>(slag) equilibrium. The partition ratio increases with Na<sub>2</sub>O content in the slag. The cyanide capacity was calculated from the results and increases with basicity and temperature. The cyanide capacity of Na<sub>2</sub>O-SiO<sub>2</sub> slags is estimated to be about three times higher than for CaO-Al<sub>2</sub>O<sub>3</sub> slags of the same basicity. The present results are in agreement with previous work on the solubility of nitrogen in

Na<sub>2</sub>O-SiO<sub>2</sub> slags. Based on the thermodynamics developed in the present study, it is predicted that Na<sub>2</sub>CO<sub>3</sub> will remove nitrogen from hot metal. For example, it is predicted for a typical hot metal that 12 kg of Na<sub>2</sub>CO<sub>3</sub> will remove about half of the nitrogen in the metal.

#### ACKNOWLEDGMENTS

The authors wish to thank Professor N. Sano (The University of Tokyo) for his helpful discussions, as well as Dr. B. Ozturk, Dr. P. Glaws, Dr. J. Niedringhaus, A. Chan, and J. Pak for their helpful discussions and assistance in the experiments. Support of National Science Foundation through Grant CPE-8403593 is gratefully acknowledged.

#### REFERENCES

1. Fumitaka Tsukihashi, Fumiaki Matsumoto, Tatsuya Hyodo, Masaya Yukinobu, and Nobuo Sano: *Tetsu-to-Hagané*, 1985, vol. 71 (7), pp. 823-30.
2. F. Tsukihashi, A. Werme, F. Matsumoto, A. Kasahara, M. Yukinobu, T. Hyodo, S. Shiomi, and N. Sano: *Second International Symposium on Metallurgical Slags and Fluxes*, TMS-AIME, 1984, p. 89.
3. N. Kaell and F. Mayer: *Met. Reports CRM*, 1974, vol. 40, p. 11.
4. E. T. Turkdogan: *Physical Chemistry of High Temperature Technology*, Academic Press, 1980, pp. 5-24.
5. Fumitaka Tsukihashi and Nobuo Sano: *Tetsu-to-Hagané*, 1985, vol. 71, pp. 815-22.
6. Shu Yamaguchi, Atsuo Imai, and Kazuhiro S. Goto: *J. Japan Institute of Metals*, 1983, vol. 47, pp. 736-42.
7. D. N. Rego, G. K. Sigworth, and W. O. Philbrook: *Metall. Trans. B*, 1985, vol. 16B, pp. 313-23.
8. J. Chipman and R. B. Baschwitz: *Trans. Metall. Society AIME*, 1963, vol. 227, p. 473.
9. J. F. Elliott, M. Gleiser, and V. Ramakrishna: *Thermochemistry for Steelmaking*, Addison-Wesley Publishing Co., Reading, MA, 1963, vol. 11, p. 514.
10. Fujio Ishii, Shiro Ban-ya, and Tasuku Fuwa: *Tetsu-to-Hagané*, 1982, vol. 68, pp. 1551-59.
11. H. Schenk, M. G. Froberg, and H. Graf: *Arch. Eisenhüttenwes.*, 1958, vol. 29, p. 673.
12. Klaus Schwerdtfeger and Hans Georg Schubert: *Metall. Trans. B*, 1977, vol. 8B, pp. 535-40.
13. Toshio Shimoo, Hiroshi Kimura, and Masao Kawai: *J. Japan Institute of Metals*, 1972, vol. 36 (8), pp. 723-27.
14. Takao Choh, Yukio Hanaki, Takehiko Kato, and Michio Inouye: *Trans. Iron Steel Institute of Japan*, 1973, vol. 13, pp. 218-25.
15. P. J. Koros, S. S. Lewis, S. G. Shawgo, and J. Scher: *National Open Hearth Conference Proceedings*, Iron and Steel Society of AIME, 1970, vol. 53, p. 97.