



Nitrogen solubility in molten CaO-SiO₂ slags

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Synopsis

The equilibrium nitrogen solubility in the CaO-SiO₂ system was studied by a slag-gas equilibration technique, in graphite crucibles at 1823K under a CO-N₂ atmosphere. The nitrogen content of the slags was determined by the Kjeldahl method. A reliable technique was used to obtain an initial nitrogen content in the master slags, from the addition and pre-melting of silicon nitride. Reduction of silica by graphite was found to occur during the equilibration experiments, resulting in compositional changes of the slags. The results were extrapolated to equilibrium by kinetic evaluation of the data. The nitrogen solubility showed good agreement with the result of Suito and Sano, while Fruehan's results were lower. However, the results of the present study do not support the maximum nitrogen solubility values found by Sano.

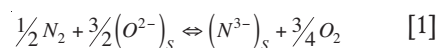
Introduction

During treatment and casting of deoxidized steel, nitrogen is readily absorbed from the atmosphere by the steel bath. No effective means exists to control the nitrogen content of steel, more specifically to remove nitrogen from the steel. The removal of nitrogen by vacuum degassing or inert gas bubbling is only partially effective, even though it is thermodynamically feasible. Surface active elements like oxygen and sulphur significantly retard the transfer of nitrogen across the interface during degassing. The interest in the possibility of the removal of nitrogen by a slag treatment prompted research into the behaviour of nitrogen in metallurgical slags. However, the nitrogen distribution ratios between slag and metal achievable under industrial conditions are too low to enable efficient removal of nitrogen from steel. Although some special fluxes (e.g. BaO-TiO₂ slags) achieve higher ratios, their cost precludes economical use.

Thermodynamic considerations

The transfer of nitrogen to or from the slag phase has been shown to occur by an exchange with oxygen,¹⁻⁴ as shown in

Equation [1] for the reaction between a slag and gas phase. The nitride capacity has been defined analogous to the sulphide and phosphorus capacities as in Equation [2]²⁻⁴. Similar equations can be written for the reaction of nitrogen between metal and slag, with the elements in solution in the metal replacing the molecular gaseous species.



$$C_{N^{3-}} = (\%N^{3-})_s \frac{p_{O_2}^{0.75}}{p_{N_2}^{0.5}} = K_{[1]} \frac{a_{O^{2-}}^{1.5}}{f_{N^{3-}}} \quad [2]$$

where $C_{N^{3-}}$ is the nitride capacity, $(\%N^{3-})$ the nitrogen content of the slag, p_{O_2} and p_{N_2} the partial pressures of oxygen and nitrogen respectively, $K_{[1]}$ the equilibrium constant of reaction [1], $a_{O^{2-}}$ the oxygen anion activity in the slag, and $f_{N^{3-}}$ the activity coefficient of nitrogen in the slag. The nitride capacity is a function of slag composition and temperature only and this allows the direct comparison of the values obtained (at specific temperatures), even though different experimental techniques were used.

Extensive studies of various slag systems²⁻⁷ indicated that the behaviour of nitrogen in metallurgical slags is more complicated than the behaviour of, for example, sulphur or phosphorus. It appears that the nitrogen solubility depends on the slag structure, especially with respect to the concentration of free oxygen ions (or the extent of polymerization of the slag). A dual mechanism of nitrogen dissolution^{4,6} into slags was proposed in which the nitrogen can dissolve as a free

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Nitrogen solubility in molten CaO-SiO₂ slags

nitride ion or nitride incorporated into the network of the slag. The nitrogen would be dissolved mainly as a free nitride ion in basic slags, and as incorporated nitrogen in acid slag compositions. The variation of nitrogen solubility with basicity is then predicted to exhibit a minimum at intermediate basicity; this was indeed found to be the case in most slag systems studied. A notable exception was the study by Sano *et al.*⁴, which showed a maximum nitrogen content at intermediate basicities in the CaO-SiO₂ system. This contradiction warranted further study.

Experimental techniques

Master slags were prepared by mixing reagent grade SiO₂ and CaCO₃ in the correct ratio to yield the desired compositions as indicated in Table I after subsequent calcination at 1573K. The slag compositions were chosen to span the liquid composition range in the SiO₂-CaO system at 1823K. Silicon nitride was added to the calcined mixture, which was then thoroughly mixed, pressed into a pellet and pre-melted for 10 minutes in a molybdenum crucible under nitrogen atmosphere. The resulting slag melt was cooled under a nitrogen atmosphere, crushed and part of it analysed for the nitrogen content. The rest was used as starting material for the equilibration experiments. This procedure ensured a homogeneous slag with known initial nitrogen content.

Experiments were performed in a lanthanum chromite resistance heated vertical tube furnace, with PID temperature control. Up to seven slag samples, each in its own graphite crucible, were contained in a larger graphite crucible for simultaneous reaction with the gas atmosphere. Each slag sample had a mass of 2 g and was contained in a graphite crucible of 12 mm inside diameter and 40 mm height. The larger graphite crucible—which held up to seven of the smaller slag-containing crucibles—was suspended from an alumina tube by molybdenum wire. Thus, seven slag samples could be exposed to identical experimental conditions simultaneously. The reaction gas mixture was blown onto the crucibles through the alumina tube from which the larger crucible was suspended. The gas flow rate was set at between 5 and 10 cm³.s⁻¹ (at standard temperature and pressure). The crucible assembly was inserted into the furnace muffle tube pre-flushed with argon and after a further period of flushing, the CO-N₂ gas mixture was admitted to the furnace. The crucibles were then slowly lowered into the hot zone of the furnace, controlled at 1823K. After the required equilibration time, the crucibles were drawn out of the furnace and cooled under a stream of argon gas. The crucibles were then broken to remove the reacted slag sample. Crushed samples were submitted for Kjeldahl analysis and solid pieces of the slag were set in resin and polished for chemical composition

determination by microprobe analysis.

Capillary flow meters⁸ were used to control the flow rate of the gases, by which the desired flow rate is set by maintaining a specific pressure drop through a capillary tube. The pronounced effect of temperature on the flow rate at a given pressure (the result of the effect of temperature on the viscosity of the gases) was counteracted by immersing the capillary tubes in temperature controlled water baths. The flow rates of purified CO and N₂ were individually controlled by the capillary flow meters. The gases were mixed beyond the flow meters to yield the desired gas composition of 95%CO and 5%N₂ (volume per cent).

Kjeldahl analysis

Slags were prepared for Kjeldahl analysis^{3,4} by grinding to fine powder in a tungsten carbide grinding vessel. The sample was dried and a known mass (of approximately 0.3 g, weighed to 0.001 g precision) was transferred to a plastic beaker in which it was digested with a mixture of 20 cm³ hydrochloric acid (diluted 1+1 with water) and 5 cm³ hydrofluoric acid (diluted 1+1 with water). Digestion was carried out at 353K (80°C) for 4 hours. Hydrofluoric acid was necessary to break down the network formers of the slag and to liberate the nitrogen associated with it. In the digestion step the nitrogen in the sample is converted to an ammonium ion (NH₄⁺) which is stable in an acid medium.

The digested sample solution was then transferred to the distillation flask of the Kjeldahl distillation still, connected to a double walled condenser. A concentrated alkali solution was added to the digested solution, after the receiving solution consisting of a 4% boric acid solution, was placed under the outlet of the condenser. In an alkaline medium, the ammonium ion is converted into ammonia (NH₃), which escapes from the solution with the steam generated and is distilled into the receiving solution. In the receiving solution the ammonia is effectively captured by reaction with the boric acid to form H₂BO₃⁻ and NH₄⁺ ions. The receiving solution, containing a mixed bromocresol green and methyl red indicator, was titrated to the endpoint of the indicator with 0.01 mol/dm³ hydrochloric acid. A blank distillation was also carried out with every set of analyses and the difference between the quantity titrated for the sample and the blank corresponds to the quantity of nitrogen in the sample.

A critical area of the analysis is the possibility of carry-over of highly alkaline solution from the solution being distilled into the condenser to the receiving solution; such carry-over would render the titration meaningless. Gentle steam distillation was found to be most effective in preventing this. The accuracy of the titration has a pronounced effect on the accuracy of the analysis and the burette used was graduated in 0.01 cm³ intervals and the indicator endpoint could be determined within 0.02 cm³, corresponding theoretically to 10ppm nitrogen on a 0.3 g sample. The purity of the water used throughout was also found to be important. Suitable nitrogen standards were not available, and it was found that pure Si₃N₄ was not digested and thus was not detected by the analytical technique. For these reasons, a standard solution of ammonium chloride (NH₄Cl) was used for calibration. The calibration was performed with 6 cm³ of the standard solution corresponding to 1 mg of nitrogen; for which the titrated volume was 7.0

Table I

Starting compositions (mass per cent) of slag samples for equilibration runs, with corresponding slag composition codes

Slag code	C1	C2	C3	C4	C5	C6
% CaO	54.3	48.3	46.3	43.3	41.3	38.4
% SiO ₂	45.7	51.7	53.7	56.7	58.7	61.6

Nitrogen solubility in molten CaO-SiO₂ slags

cm³ of 0.01 mol/dm³ HCl. It was found that the overall analytical technique as used for the present study could repeatedly analyse the nitrogen content of the slag sample to within 50ppm.

Results and discussion

Preparation of master slags

The technique of pre-melting the slags resulted in repeatable nitrogen contents, although a slight loss of nitrogen was found compared to the calculated nitrogen content based on the quantity of silicon nitride added. The quantity of nitrogen dissolving into the slag—expressed as a percentage of the nitrogen in the nitride added—varied between 65 to 85 per cent. The yields are graphically presented in Figure 1. Thermodynamically feasible causes of the nitrogen loss during pre-melting include oxidation of Si₃N₄ by the prevailing partial oxygen pressure (of the gas atmosphere) or by the silica in the slag, forming nitrogen gas (and SiO in vapour form) which are lost from the slag. Trials with pre-melting in graphite crucibles under pure nitrogen, and under a mixture of 5% N₂ and 95% CO, indicated that higher and more reproducible recoveries of nitrogen were achieved with a pure nitrogen atmosphere—for which a lower partial oxygen pressure and higher nitrogen partial pressure is expected than for a N₂-CO mixture.

Establishment of a known nitrogen content at the start of reaction of the slag sample with the gas was essential to the analysis of the reaction kinetics. Obtaining a known initial nitrogen content in the slags requires both a reproducible yield during pre-melting, and retention of the nitrogen during subsequent melting of the slag at the start of the equilibration experiment. Trials showed that the pre-melted slags did indeed retain their nitrogen content after subsequent melting (at the start of equilibration), whereas physical mixtures of ground slag and nitride (which were not pre-molten), suffered significant losses of nitrogen.

Slag composition analysis

The analysed composition of slags before and after equilibration runs indicated that the silica fraction had decreased (and hence the CaO fraction had increased)—due to loss of silica from the slag samples. The extent of compositional change increased with increasing reaction time (as would be expected) and was in the range of a 1.5 to 3.0% reduction in silica content. The available data were used as a general guideline to predict the compositional change during other equilibration experiments, for which complete analyses were not available. No evidence of silicon carbide formation could be found in polished thin sections of equilibrated slag; the reduction of silica content was presumably due to formation of SiO gas through reduction of SiO₂ by the graphite crucible (this reaction is thermodynamically feasible under the experimental conditions).

Kinetics

The kinetics of the reactions was considered as basis to extrapolate the available experimental data to the estimated equilibrium nitrogen content. In a particular equilibration run

(E5 to E10 in Table II), two samples of each slag composition (C1 to C5 in Table II) were typically used; one of these samples was given an initial nitrogen content higher than the expected equilibrium nitrogen content, and one a lower initial nitrogen content. Full equilibrium would be achieved if these samples converged on the same nitrogen content during the experimental run. While the final nitrogen contents of such slag pairs were generally close to one another (see Table II), they did differ, showing that equilibrium had not been fully achieved. It was not feasible to extend the time of the equilibration runs (to try to approach equilibrium more closely), because loss of silica (through reduction to SiO) caused a slow but steady change in the slag composition.

For this reason, the expected reaction kinetics were used to extrapolate the experimental data to the estimated equilibrium nitrogen content. The reaction kinetics were evaluated according to Equation [3] for first-order behaviour (which would be the case under diffusion mass transfer in the slag) and according to Equation [4] for second-order behaviour (for gas phase mass transfer control or chemical reaction control).

$$\frac{d(\%N)}{dt} = k_1 [(\%N)(t) - (\%N)_{eq}] \quad [3]$$

$$\frac{d(\%N)}{dt} = k_2 [(\%N)^2(t) - (\%N)_{eq}^2] \quad [4]$$

In these equations (%N)(t) is the average nitrogen content of the slag at time t, (%N)_{eq} the equilibrium nitrogen content, and k₁ and k₂ the first and second order rate constants respectively. Solving for the two limiting kinetic relationships (Equations [3] and [4]) yields values of the equilibrium nitrogen content—(%N)_{eq}—and the rate constant—k₁ or k₂. Finding these two values requires two sets of data—and, as Table II shows, two such sets were generally available for specific slag compositions during a particular experimental run. The assumptions in the calculation were that a pair of slag samples with the same (SiO₂-CaO) composition (but with different initial nitrogen contents) would yield the same equilibrium nitrogen content during a particular run, and that the rate constants for the

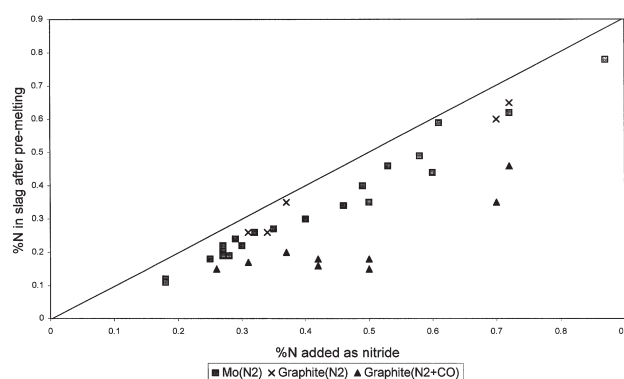


Figure 1—Recovery of nitrogen from nitride addition during pre-melting under different experimental conditions. In the legend, Mo (N₂) refers to samples molten in a molybdenum crucible under a nitrogen atmosphere, Graphite (N₂) to samples molten in a graphite crucible under a nitrogen atmosphere, and Graphite (N₂+CO) to samples molten in a graphite crucible under a 95%CO-5%N₂ atmosphere

Nitrogen solubility in molten CaO-SiO₂ slags

Table II

Summary of experimental conditions and results for the experimental runs. E5 to E10 refer to different experimental runs (at 1823K) in which slags with the compositions indicated in the second column were exposed simultaneously. The exposure time and gas flow rates are indicated in the first column. ‘%N time’ gives the analysed nitrogen content after the exposure period, and ‘%N equilibrium’ the calculated equilibrium content according to extrapolations based on first-order and second-order kinetics respectively

Run	Slag code	%N initial	%N time	%N equilibrium	
				1st Order	2nd Order
E5 22 hours 10 cm ³ .s ⁻¹	C2	0.219	0.186	0.167	0.153
	C2	0.397	0.251	0.167	0.153
	C5	0.238	0.244	0.250	0.254
	C5	0.518	0.388	0.250	0.254
E6 9 hours 8 cm ³ .s ⁻¹	C2	0.219	0.164	0.145	0.127
	C2	0.397	0.210	0.145	0.127
	C4	0.000	0.134	-	-
	C5	0.000	0.127	0.159	0.167
	C5	0.238	0.175	0.144	0.096
	C5	0.518	0.267	0.174	0.216
E7 24 hours 5 cm ³ .s ⁻¹	C1	0.000	0.118	0.129	0.133
	C1	0.215	0.137	0.129	0.133
	C2	0.000	0.110	0.152	0.159
	C2	0.206	0.167	0.152	0.159
	C3	0.000	0.153	0.184	0.194
	C3	0.302	0.204	0.184	0.194
	C4	0.342	0.206	-	-
E8 24 hours 5 cm ³ .s ⁻¹	C3	0.302	0.233	-	-
	C4	0.000	0.145	0.224	0.244
	C4	0.342	0.266	0.224	0.244
	C5	0.000	0.150	0.243	0.242
	C5	0.238	0.241	0.243	0.242
	C6	0.000	0.160	0.240	0.241
	C6	0.250	0.243	0.240	0.241
E9 24 hours 5 cm ³ .s ⁻¹	C3	0.122	0.206	0.222	0.221
	C3	0.192	0.217	0.222	0.221
	C4	0.108	0.212	0.261	0.254
	C4	0.189	0.238	0.261	0.254
	C5	0.181	0.246	0.261	0.261
	C5	0.265	0.262	0.261	0.261
E10 10 hours 10 cm ³ .s ⁻¹	C3	0.122	0.167	0.197	0.197
	C3	0.192	0.195	0.197	0.197
	C4	0.108	0.163	0.192	0.192
	C4	0.189	0.191	0.195	0.206
	C4	0.342	0.249	0.192	0.193
	C5	0.181	0.202	0.207	0.208
	C5	0.265	0.218	0.207	0.208

increase and decrease in nitrogen content (for that experimental run and slag composition) were identical.

The resulting calculated equilibrium nitrogen contents are given in Table II, and the different values for the first and second order rate constants are shown graphically in Figure 2 for each equilibration run. This figure shows that the values of the calculated rate constants varied somewhat between experiments—which is not unexpected, since the gas flow rates differed slightly for the different runs (see Table II). However, a more serious concern is which estimate of the equilibrium nitrogen content is more accurate—that obtained from assumed first-order or from second-order kinetics. As Table II indicates, the estimated equilibrium content was slightly different for the two kinetic models. It is shown

elsewhere that evaluation of the expected rate constants from literature data on gas-phase mass transfer, gas-slag reaction kinetics and diffusion in the slag does not yield a clear verdict on whether first-order or second-order kinetics should prevail under the experimental conditions⁹. However, analysis of data from those runs (E6 and E10) during which three samples of the same slag composition (compositions C5 and C4 respectively) were reacted, can also be used to compare the applicability of the two kinetic models, as discussed below.

For the two cases (run E6/slag C5 and run E10/slag C4) which yielded three sets of data for a single run and slag composition, three estimates of k and $(\%N)_{eq}$ can be calculated for assumed first-order and second-order behaviour respectively. The results are shown in Figure 3 and Figure 4. Based on a much smaller difference between the three estimates for first-order kinetics (for both the rate constant—Figure 3—and the equilibrium nitrogen content—Figure 4) it appears that the first-order model is more appropriate (implying that, that diffusion in the slag phase is the rate-determining step in the overall reaction for these two cases). For these reasons, the equilibrium nitrogen contents estimated from assumed first-order kinetics were used in the comparisons presented below.

Equilibration experiments

As an example, Figure 5 depicts the calculated change of nitrogen content with time (full lines) for slag composition C3 during equilibration experiments E7 to E10, based on the calculated first-order rate constant. (Complete results for other slag compositions are shown in Table II). As indicated by Figure 5, samples of the same slag (C3 in this case) appeared to converge to slightly different equilibrium nitrogen contents in different experimental runs. This was also found for other slag compositions (see Table II). The difference in equilibrium nitrogen contents found in different equilibration runs for the same slag composition (following the consistent relationship E9 > E10 > E7) could only be attributed to slight differences in gas mixture composition between different runs. A higher nitrogen content in the gas mixture would have resulted in a higher equilibrium nitrogen content, according to Equation [2]—and it appears that it was possible that the gas composition could have drifted slightly during the equilibration runs. Equation [2] was used to recalculate the equilibrium nitrogen content for the target gas composition of $p_{N_2} = 0.05$ atm, based on the nitrogen content achieved with the (assumed) slightly different gas composition during equilibration. Correction was limited to 0.01 atm either side of the target composition ($p_{N_2} = 0.04$ to 0.06 atm) and was applied consistently to all the data from a specific run. The compositional changes in the slag were also taken into account and the final equilibrium nitrogen content results are plotted in Figure 6 versus the slag composition. The average values on the trend line in Figure 6 are further used in the comparison with results of other researchers.

As the aim of the study was to investigate the unusual maximum in nitrogen content found by Sano *et al.*⁴, the results of the present study are compared to those of Sano. In order to compare the results of the present study to additional results (all at 1823K) of Fruehan² and Suito³ the nitrogen contents ($\%N$) were converted to the nitride capacity

Nitrogen solubility in molten CaO-SiO₂ slags

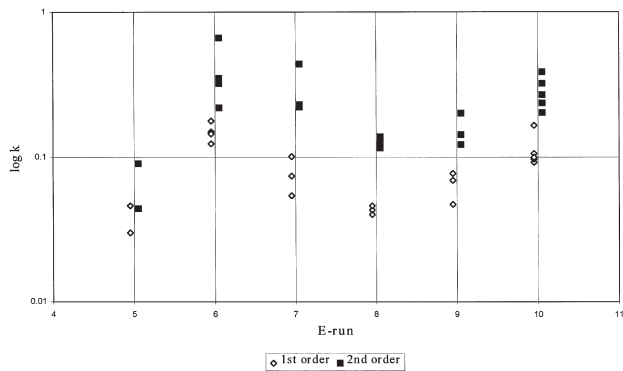


Figure 2—Apparent first and second order rate constants for different experimental runs (units of first order constant are h⁻¹, and %⁻¹h⁻¹ for the second order constant)

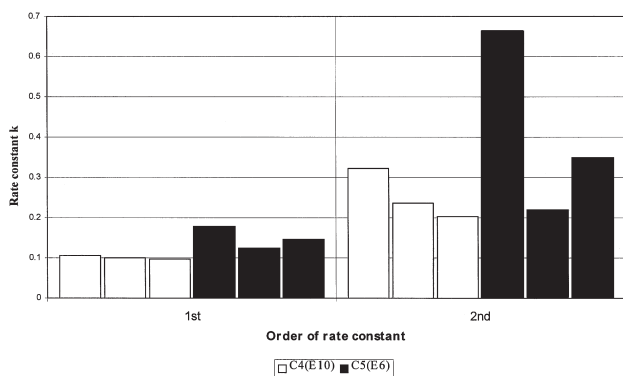


Figure 3—Apparent first and second order rate constants calculated for the two cases of three identical slag basicities reacted during a specific run (slag C4 during run E10, and slag C5 during run E6 respectively). The units of the first order constant are h⁻¹, and %⁻¹h⁻¹ for the second order constant

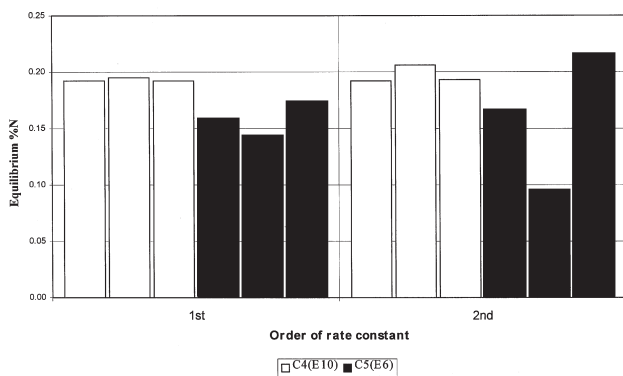


Figure 4—Estimated equilibrium nitrogen content calculated for the two cases of three identical slag basicities reacted during a specific run (slag C4 during run E10, and slag C5 during run E6 respectively). The estimates for the equilibrium nitrogen content are shown for extrapolations based on first-order and second-order kinetics respectively

according to Equation [2], as different experimental conditions were employed. Fruehan's experiments² were also conducted in graphite crucibles, but with varying mixtures of N₂ and CO gas (p_{N_2} between 0.2 and 0.6) at a flow rate of 2-3 cm³/s. Suito³ performed the experiments in CaO and

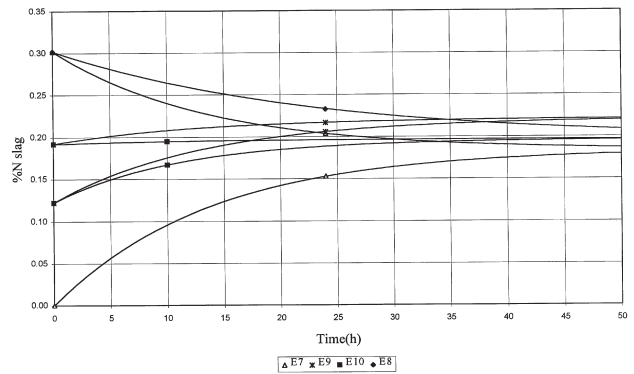


Figure 5—Change of nitrogen content with time for slag composition C3. Symbols give the analysed nitrogen contents (as given in Table II) and lines give the calculated time dependence of the nitrogen content (using the calculated first-order rate constant)

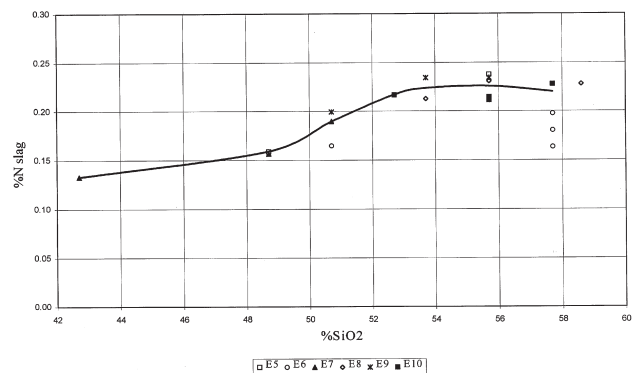


Figure 6—Equilibrium nitrogen content versus %SiO₂, corrected for compositional change during equilibration and gas composition

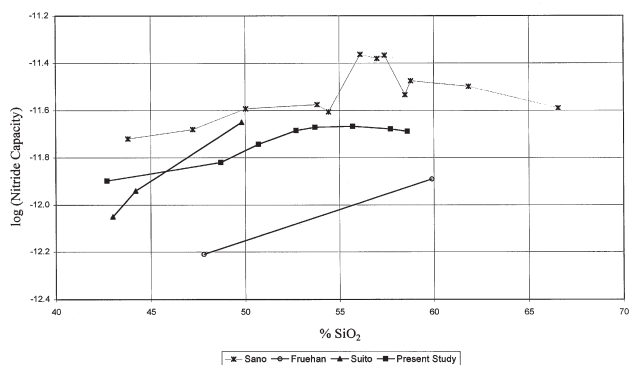


Figure 7—Comparison of nitride capacity values for the CaO-SiO₂-system at 1823K, showing results from the present study, and those reported by Martinez and Sano⁴, Ito and Fruehan², and Tomioka and Suito³

molybdenum crucibles and set the p_{O_2} by the H₂-H₂O equilibrium in 90%N₂-10%H₂+H₂O (by volume) gas mixture at 13 cm³/s. The experimental conditions of the present study agreed with those of Sano⁴. In Figure 7 it is shown that the results of Sano, Suito and the present study agree well at low silica content, although the increase with increasing %SiO₂ is steeper for Suito's results. Fruehan's results² include only two points in the system of interest, which do not cover the

Nitrogen solubility in molten CaO-SiO₂ slags

composition where a maximum is found by Sano⁴; these two data points also indicate significantly lower nitride capacities than the other data sets. However, the main conclusion apparent from Figure 7 is that the results of the present study do not support the maximum nitrogen solubility values found by Sano at intermediate basicity values.

Conclusions

The equilibrium nitrogen solubility in molten CaO-SiO₂ slags was studied by a slag-gas equilibration technique, in order to investigate the maximum solubility at intermediate basicities found by Sano *et al.* It was found that reduction of silica did occur during the equilibration, resulting in compositional changes. A reliable technique was used to achieve an initial nitrogen content of the master slags, by pre-melting the slag with nitride additions. This was necessary as it was found that significant losses of nitrogen occurred during melting of the slag and nitride mixture at the start of the equilibration experiment, which was eliminated by the pre-melting procedure. By kinetic evaluation of the results, the equilibrium nitrogen contents and rate constants were calculated and first order behaviour (diffusion in slag phase) was inferred. The determined equilibrium nitrogen contents show fair agreement with studies by Suito and Sano. However, the results do not support the maximum found by Sano at intermediate basicities.

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References

1. MULFINGER, H. Physical and Chemical solubility of nitrogen in glass melts *J. Am. Cer. Soc.*, 1966, vol.49, pp. 462-467.
2. ITO, K. and FRUEHAN, R.J. Thermodynamics of nitrogen in CaO-SiO₂-Al₂O₃ slags and its reaction with Fe-C_{sat.} melts. *Metall. Trans. B*, 1988, vol.19B, pp. 419-425.
3. TOMIOKA, K. and SUIITO, H. Nitride capacities in CaO-SiO₂ and CaO-SiO₂-Al₂O₃ melts. *Steel Research*, 1992, vol. 63, pp. 1-6.
4. MARTINEZ, E. and SANO, N. Nitrogen solubility in CaO-SiO₂, CaO-MgO-SiO₂ and BaO-MgO-SiO₂ melts. *Metall. Trans. B*, 1990, vol 21B, pp. 97-104.
5. MARTINEZ, E. and SANO, N. Nitrogen solubility in CaO-CaF₂-SiO₂ melts. *Metall. Trans. B*, 1990, vol 21B, pp. 105-109.
6. MIN, D.J. and FRUEHAN, R.J. Nitrogen solution in BaO-B₂O₃ and CaO-B₂O₃ slags. *Metall. Trans. B*, 1990, vol. 21B, pp. 1025-1032.
7. FERREIRA, J.P., SOMMERVILLE, I.D., and McLEAN, A. Synthetic slags for nitrogen removal. *1991 Electric Furnace Conference Proceedings*, pp. 225-231.
8. NAFZIGER, R.H., ULMER, G.C., and WOERMANN, E. Research techniques for high pressure and high temperature, G.C. Ulmer (ed.), 1971, *Springer Verlag*, New York, pp. 9-41.
9. OLTMANN, H.G. Nitrogen solubility in molten CaO-SiO₂ slags., M.Eng thesis, University of Pretoria, 1998. ◆



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