

# Liquidus Temperatures and Viscosities of FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CaO-MgO Slags at Compositions Relevant to Nickel Matte Smelting

by

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## ABSTRACT

Although the liquidus temperatures and viscosities of iron silicate slags are critical in the operation of many pyrometallurgical processes there is relatively little published data relating to complex, multi-component systems. In this study, liquidus temperatures and viscosities in the FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CaO-MgO slag system were determined at conditions relevant to base metal smelting processes. The classical quench technique was used to measure liquidus temperatures to an accuracy of  $\pm 5$  °C at Fe/SiO<sub>2</sub> ratios of 1.3 to 1.8, CaO contents up to 9 wt%, MgO contents up to 12 wt% and at oxygen partial pressures of  $10^{-11}$  and  $10^{-8}$  atm. The addition of MgO was found to lead to large increases in liquidus temperature. The addition of CaO generally led to a moderate fall in liquidus temperature but the magnitude and direction of the change depended on the Fe/SiO<sub>2</sub> ratio and MgO content. At CaO contents greater than about 3%, increasing the oxygen partial pressure of the system raised the liquidus temperature moderately and lowered the ability of CaO to depress the liquidus temperature.

The viscosity of the slags was measured over similar composition ranges at iron saturation by means of a coaxial, cylindrical cup and bob arrangement. The results obtained are believed to be accurate to  $\pm 5$  mPa.s and are the most comprehensive to date for the composition range. The slags were found to be Newtonian in behaviour above their liquidus temperatures. Viscosity decreased significantly as the Fe/SiO<sub>2</sub> ratio was increased in the range 1.3 to 2.00. The addition of low levels of CaO or MgO lowered the viscosity but the addition of further MgO increased the viscosity. The MgO content at which the viscosity began to increase decreased with increased CaO content. The results may be used to optimise slag composition in smelting processes particularly for concentrates which contain higher than desirable levels of magnesia.

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## INTRODUCTION

Many base metal smelting slags contain moderate levels of magnesia introduced from the concentrate. It is well known that magnesia increases the liquidus temperature of slags and, beyond certain low levels, raises the viscosity of slags. Smelting processes generally operate above the liquidus temperature of the slag since the presence of solid primary crystallisation phases can cause accretion build-up on refractories and tuyeres and, if the solids are well dispersed, raise the ‘apparent’ viscosity of the slag resulting in tapping difficulties and entrainment of matte and/or metal in the slag. Operating above the liquidus temperature overcomes the former of these problems but the latter problems can still occur unless the viscosity is sufficiently low. This investigation was performed to determine the liquidus temperatures and viscosities of slags relevant to nickel matte smelting; however, the results are of relevance to other base metal smelting processes.

Nickel matte smelting slags belong to the FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CaO-MgO system. Additionally, the slags contain a small amount of NiO and, usually, Al<sub>2</sub>O<sub>3</sub>. Matte smelting operates over an oxygen partial pressure range of around 10<sup>-8</sup> to 10<sup>-10</sup> atm at 1300 °C<sup>1</sup>. In this investigation the range of compositions was selected to cover iron silicate slags of iron saturation for Fe/SiO<sub>2</sub> ratios of 1.3 to 1.8, and at an oxygen partial pressure of 10<sup>-8</sup> atm (at 1300 °C) for an Fe/SiO<sub>2</sub> ratio of 1.5. The objective was to examine the effect of additions of up to 9 wt% lime and 12 wt% magnesia on liquidus temperatures and viscosities. Iron saturated slags are about an order of magnitude more reduced than the most reduced matte smelting slags but were chosen because the use of iron crucibles enabled the slag composition to be accurately controlled. The tests at higher oxygen partial pressure were performed in order to determine the magnitude of the effect of oxygen potential.

While liquidus temperature in the FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CaO and FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-MgO systems are well established<sup>2-6</sup>, particularly at iron saturation, there are virtually no experimental data for the effect of magnesia on the liquidus temperatures of FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CaO slags in the composition range of relevance to nickel matte smelting. Relevant viscosity data is also scarce. While viscosity in the FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system has been investigated extensively<sup>7-11</sup> there are large variations between the studies and there are, again, virtually no systematic studies of the effect of magnesia on the viscosity of FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CaO slags.

The classic quench technique was used for liquidus determinations. In this technique, a sample is held at a test temperature until it has reached equilibrium, then quenched and the phases present observed. If primary crystals are present, the sample had not been fully molten at the test temperature and the test is repeated at a higher temperature. If the sample consists wholly of glass or very fine “quench” crystals, the sample had been fully molten and the test is repeated at a lower temperature. By an iterative process the liquidus temperature is determined as accurately as time and equipment permit. The coaxial, rotating bob and cup technique was used for measuring viscosities. In this technique a bob is lowered into a cup containing the molten slag and the torque required to rotate the bob at set speeds is measured. These torques are converted to viscosity by calibration of the equipment with known fluids. The most accurate viscosity measurements are obtained with a very small cup – bob fluid space, which is impractical for slags due to their high temperature and corrosive nature or in infinite fluids, which can never be achieved but which was approached with the relatively large melt volumes used in the present study.

## EXPERIMENTAL

### *Liquidus measurements*

Crucibles of 6 mm internal diameter and 18 mm length were machined from mild steel or nickel rod. The slags were prepared from reagent grade  $\text{SiO}_2$ , Fe,  $\text{Fe}_2\text{O}_3$ , CaO and MgO powders. Iron saturated master slags were prepared for each of the Fe/ $\text{SiO}_2$  ratios of 1.3, 1.6 and 1.8 from  $\text{SiO}_2$ , Fe and  $\text{Fe}_2\text{O}_3$  by mixing the ingredients and melting them in a large iron crucible at 1300 °C under dry, de-oxidised nitrogen then quenching into water. The high oxygen potential slag was prepared by melting iron-saturated slag in a large nickel crucible suspended in a flowing atmosphere of  $\text{CO}_2$  and CO of volumetric ratio 7.4 at 1300 °C for 48 hours then quenching into water. The compositions of the four master slags are shown in Table I. The pulverised slags were weighed into small parcels and to each was added the appropriate mass of CaO and/or MgO to make about 20 g of the desired slag composition. To ensure each parcel was well mixed, it was ground in a ring mill for about 30 seconds. The parcels were stored in air tight containers until required.

A vertical tube furnace was used for the liquidus measurement. Dry, de-oxidised argon and CO and  $\text{CO}_2$  were introduced through a water-cooled bottom jacket and exited through a top jacket. The crucible support assembly is illustrated in Figure 1. This arrangement enabled four slag compositions to be tested at one time. For iron saturation experiments, the disc was of mild steel with 5 equally spaced holes. One hole was used to locate a Pt - Pt/13% Rh thermocouple to monitor the temperature and the others to hold the crucibles. The disc was supported on a 5 mm diameter steel rod. The same arrangement was used for the high oxygen potential experiments, except that a nickel disc and rod were used.

The furnace was set to 50 °C above the desired test temperature and the appropriate atmosphere was introduced. About 0.5 g of slag mixture was added to each crucible and the crucibles placed in the support, with a thermocouple, then the whole assembly was lowered into the hot zone of the furnace in four or five steps of about 300 °C. After at least 20 minutes to ensure the slag had melted, the set point temperature was lowered 50 °C and the crucibles were held at the new temperature for at least an hour. For experiments near the maximum furnace temperature (1450 °C) the initial 50 °C elevation was not possible and in these cases the sample was heated to the test temperature and held for a minimum of 2 hours. Following equilibration at the test temperature the samples were quenched by releasing the support rod and allowing the assembly to fall into a container of water.

The quenched samples were sectioned, mounted and examined by optical and scanning electron microscopy. The optical microscope was used to determine if the sample had been above or below its liquidus temperature while the SEM, which was fitted with an energy dispersive system, was used to estimate the Fe, O, Si, Ca, Mg and Ni contents of the primary crystallisation phases of those samples which were just below the liquidus temperature.

### *Viscosity measurements*

The viscosity measurements were performed in a muffle furnace, with molybdenum disilicide heating elements, which had a maximum operating temperature of 1700 °C. The furnace had a front opening door with two access ports and a third port through the top of the furnace. The control thermocouple was located in the middle of the rear wall of the furnace. The working volume of the furnace was cubic of side 250 mm. The overall arrangement of the cup and bob

within the furnace is shown in Figure 2. The shaft was connected to a Brookfield<sup>TM</sup> LVT viscometer by a wire loop to reduce heat conduction to the viscometer. Rotation of the bob was possible at several speeds up to 60 rpm. The lower section of the shaft was protected from oxidation by an alumino-silicate sheath cemented in place just above the neck of the bob. The cup and bob were machined from mild steel. Master slags were prepared in the same manner as for the liquidus measurements. Table II gives the composition of the master slags determined on a sample taken just prior to quenching.

The furnace temperature was uniform within the working volume and close to the control temperature. Several runs were performed with a thermocouple placed in slag in the cup while the furnace was heated and cooled. From these, thermal calibration curves were generated for predicting the slag temperature from the set point temperature. The viscometer was calibrated using six standard oils. The oils were high quality lubrication oils and their viscosities had been accurately determined using cone and plate viscometers. Repeat calibration runs on a bob before and after its use in slag experiments showed that the changes were well within the manufacturers quoted tolerance of  $\pm 1\%$ .

To carry out a viscosity measurement, a cup was placed in an alumino-silicate crucible and pressed into a layer of alumina powder. Then the lid of the crucible, with a 25 mm hole, was cemented in place. Approximately 500 g of master slag, CaO and MgO were weighed, mixed and placed in the cup and the crucible assembly was then placed in the furnace. Alternatively, the composition of a slag that had already been used in a previous experiment was adjusted by removing the crucible assembly from the furnace and adding appropriate amounts of CaO and MgO on top of the solidified melt. The assembly was then replaced in the furnace. Cups were generally re-used three or four times before being discarded. The crucible was aligned within the furnace and the gas lances placed in position. Gas flows were commenced and the furnace heated to at least 100 °C above the expected liquidus temperature. The ratio of CO and CO<sub>2</sub> was varied using mass flow controllers during heating and cooling to maintain the appropriate oxygen potential. Argon was added to ensure the total flow rate was high enough to flood the system and prevent ingress of air. After at least 30 minutes at temperature, the melt was manually stirred, then the bob was lowered to 10 mm from the bottom of the cup and rotated at about 12 rpm for 20 minutes to allow it to reach thermal equilibrium with the melt. The bob depth was then checked and readjusted as thermal expansion over the length of the iron shaft was significant. The location of the bob was also visually checked to ensure it was central to the cup.

Readings were taken at 30 and 60 rpm. The furnace was then adjusted to the next temperature and held for 20 minutes before taking further readings. This process was repeated until the entire temperature cycle was completed. The cycle involved cooling the slag in 50 °C intervals until the expected liquidus temperature was approached, then cooling in 25 °C steps. Once the slag began solidifying, the furnace was heated in 50 °C intervals to 1400 °C then in 25 °C intervals to 1450 °C. After the last reading was taken, the shaft and bob were removed and the furnace turned off. The CO<sub>2</sub>, CO and Ar gas flows were maintained until the furnace had cooled to at least 500 °C then argon alone was used. The master slag of Fe/SiO<sub>2</sub> = 1.32 was analysed after preparation and after being used twice at iron saturation. The analyses showed that there were no significant changes in composition.

## RESULTS

### *Liquidus Temperatures*

Optical examination of the quenched samples revealed three distinct types of microstructure:

- glass;
- quench crystals, consisting of fine dendrites, streaks or angular inclusions generally no larger than 5 to 10  $\mu\text{m}$ ; and
- primary crystals consisting of large dendrites or angular inclusions; these could be very large but were at least 50  $\mu\text{m}$ .

The slag adjacent to the walls solidified more rapidly than the centre of the samples and, therefore, microscopic examination was restricted to these areas. Three main types of primary crystals were observed: dark grey grains of olivine; light grey grains of wustite; and grey grains which were usually fayalite but were occasionally, olivine. The light grey grains occasionally formed large dendrites. In MgO-containing slags, the wustite contained magnesium (generally less than 6 mole % but occasionally up to 15 mole %). The primary crystals were generally easy to differentiate from quench crystals, the exception being iron-saturated iron silicate slags which had bulk compositions close to fayalite. As fayalite was the primary crystallisation phase, these crystals were difficult to differentiate from the background glass.

At the completion of the measurements, slags from four tests on FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> slags at high oxygen partial pressure (Slag D, Table 1) equilibrated in the range 1180 to 1220 °C were aggregated and analysed to determine if any change in bulk composition had occurred. The aggregate composition was 48.1% FeO, 15.0% Fe<sub>2</sub>O<sub>3</sub>, 4.0% NiO and 32.9% SiO<sub>2</sub>, indicating that the Fe/SiO<sub>2</sub> ratio had decreased from 1.59 to 1.46, due to iron absorption by the nickel crucible, but that the nickel content had remained unchanged.

The results for the iron saturation experiments are presented in Figures 3 to 5 while the results for the higher oxygen pressure experiments are shown in Figure 6. The tabulated experimental data are provided elsewhere<sup>15</sup>. The regions of primary crystallisation were determined by interpolation between experimental points. Taking into account the furnace temperature profile ( $\pm 1$  °C in the hot zone), thermocouple calibration ( $\pm 0.9$  °C) and the temperature range between samples straddling the liquidus point ( $\pm 2.5$  °C), the overall uncertainty in the liquidus temperature measurements is no more than  $\pm 5$  °C.

For the composition range investigated in the present work within the FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system at iron saturation, Bowen and Schairer<sup>2</sup> have performed the seminal work on liquidus temperatures. Figure 7 compares the results of interest and shows that the present liquidus temperatures for FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> slags are in good agreement. The results of previous investigations in the FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CaO and FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-MgO systems at iron saturation are summarised in Table III<sup>3-5</sup>. Comparison of these with the present results indicates excellent agreement except at Fe/SiO<sub>2</sub> = 1.6 and 9 wt% CaO. The present work indicates a liquidus temperature of 1178 °C while Allen and Snow<sup>5</sup> (for Fe/SiO<sub>2</sub> = 1.67 and 8.81% CaO) found a liquidus temperature of approximately 1136 °C.

FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> slags have been investigated at higher oxygen pressures by Muan<sup>6</sup> but it is difficult to compare the present high oxygen partial pressure results to these because of the presence of approximately 4 wt% NiO in the melt. From an examination of the FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> phase diagram<sup>16</sup> it is apparent that this level of NiO depressed the liquidus temperature by about

40 °C. However, if the NiO is treated as FeO (i.e., the Fe/SiO<sub>2</sub> ratio is increased from 1.46 to 1.54) the liquidus temperature from the phase diagram (1215 °C) is similar to that measured (1208 °C). Therefore, it seems reasonable to treat NiO as FeO at low levels of NiO. There are few data at high oxygen partial pressures for slags containing CaO and MgO. Muan and Osborn<sup>17</sup> obtained one, inconclusive, result at an oxygen pressure of 10<sup>-8.9</sup> atm at a composition within the range of the present study:

	%MgO	%SiO <sub>2</sub>	%FeO	%Fe <sub>2</sub> O <sub>3</sub>	T <sub>L</sub> (°C)
Muan and Osborn <sup>17</sup>	6.5	36.9	46.1	9.1	>1275
Present investigation	6.0	30.8	49.1*	14.0	1338

\*includes NiO

### Viscosity

The results for a typical viscosity experiment at 60 rpm are shown in Figure 8. If the slag had not reached thermal equilibrium during each measurement, a hysteresis effect would have been observed between measurements taken when cooling and when heating the slag. The 30 rpm data had significantly larger uncertainties (about ±10 mPa.s) than the 60 rpm data; however, within experimental uncertainty there was no difference in the viscosities measured at the two speeds, confirming the Newtonian nature of the slags above the liquidus temperature. Readings obtained below the liquidus temperature were high and extremely variable due to the presence of primary crystallisation phase. The temperature of onset of these high readings corresponded well with the independently measured liquidus temperatures.

The results are shown in Figures 9 to 12. The tabulated experimental data are provided elsewhere<sup>15</sup>. With the slag unstirred, the temperature profile throughout the slag in the cup was found to vary by no more than ±3 °C. This profile would be expected to be less variable when the slag was stirred by the bob. The thermocouple used in calibrating the furnace had an error of ±0.9 °C. The lack of hysteresis in readings obtained while heating and cooling (Figure 8) shows that the slags were close to thermal equilibrium when readings were taken. The correction factors used to estimate the melt temperature from the control thermocouple temperature introduced the largest uncertainty; tests demonstrated that this was less than ±11 °C. Therefore the total error in temperature is estimated to be ±15 °C. The accuracy of the viscosity readings were limited by the inherent accuracy of the viscometer and the repeatability of the experiments. At 60 rpm, these factors result in an uncertainty of ±5 mPa.s or on average about ±10% .

There is a large spread of viscosity data in the literature for the iron silicate system. For the FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system at conditions there have been numerous investigations<sup>7-14</sup>. The measurements in this study are in broad accord with the literature values, except at the higher silica content (Fe/SiO<sub>2</sub> = 1.6) where the data are lower than previously reported values. For comparison, the present data for FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> slags at 1300 °C are compared with published data in Figure 13. The variation between studies is indicative of the state of the art of viscosity measurements as demonstrated by the study of Broadbent *et al.*<sup>18</sup> in which 13 reputable laboratories measured viscosities of the same synthetic slag. The values obtained varied around the mean by as much as 50%. A comparison of measured viscous activation energies is shown in Figure 14. There is a large variation in the literature data of activation energies, and the current results fall well within this variation.

There has been some debate in the literature about the viscosity bump measured around the fayalite composition by Shiraishi<sup>9</sup> and Urbain<sup>12</sup>. The behaviour is not really

consistent with other binary silicates which show a smooth decrease in viscosity as the silica content decreased. Viscosity models of the iron silicate system have tended to ignore the fayalite bump or place greater weight on other data<sup>11,19,20</sup>. The three compositions of this study straddle the contentious region and show only a smooth decrease in viscosity. Previous measurements on the CaO-FeO<sub>x</sub>-MgO-SiO<sub>2</sub> system have been generally related to steelmaking type slags with greater lime and MgO contents than this study. Of the systems that are relevant to this study, Johannsen and Wiese<sup>21</sup> studied CaO-FeO<sub>x</sub>-SiO<sub>2</sub> melts. The measured viscosities are about 30% higher than this study, and at a constant silica content, lime had only a small effect on viscosity. Williams *et al.*<sup>22</sup> also studied CaO-FeO<sub>x</sub>-MgO-SiO<sub>2</sub> melts containing up to 8% MgO and 15% CaO at a silica content comparable to this study, but some of the slags were contaminated with zirconia and some of the measurements were in the two phase region.

## DISCUSSION

The effects of Fe/SiO<sub>2</sub>, %CaO and %MgO on liquidus temperature and viscosity are complex but, nevertheless, some clear trends are apparent.

At each Fe/SiO<sub>2</sub> ratio and at all concentrations of CaO, the addition of MgO raised the liquidus temperature. MgO had the strongest effect on liquidus temperature of the three parameters. In both the iron-saturated and higher oxygen potential slags, the effect of CaO was complex and dependent on the MgO concentration. The general trend at constant MgO concentration is for the liquidus temperature to pass through a maximum (for Fe/SiO<sub>2</sub> = 1.3) or a minimum (Fe/SiO<sub>2</sub> = 1.6 and 1.8) as the CaO concentration is increased. The effect of an increase in CaO concentration on liquidus temperature was less than the effect of a similar increase in MgO concentration:

- *Fe/SiO<sub>2</sub> = 1.3 (Fe-sat)*: the addition of multiples of 3 wt% MgO results in liquidus temperature increases of 50 to 100 °C; the addition of multiples of 3 wt% CaO results in small liquidus temperature increases or decreases (usually much less than 50 °C);
- *Fe/SiO<sub>2</sub> = 1.6 (Fe sat)*: the addition of multiples of 3 wt% MgO results in liquidus temperature increases of up to 110 °C; the addition of multiples of 3 wt% CaO results in moderate decreases (around 40 °C) of liquidus temperature at low CaO levels, slight decreases in liquidus temperature at high CaO and high MgO concentrations, and slight increases of liquidus temperature at high CaO and low MgO concentrations;
- *Fe/SiO<sub>2</sub> = 1.8 (Fe sat)*: similar trends to Fe/SiO<sub>2</sub> = 1.6.

MgO had a similar effect on the higher oxygen potential slag of Fe/SiO<sub>2</sub> = 1.54 (treating NiO as FeO); the liquidus temperature increased by 50 to 100 °C for every 3% increase in MgO concentration. The increased oxygen pressure had little effect on liquidus temperatures, relative to the iron saturated slags at comparable CaO and MgO contents, at CaO levels up to about 3% but increased the liquidus temperature at higher levels of CaO, the effect becoming greater the higher the CaO concentration.

As expected, temperature had the greatest effects on viscosity and viscosity decreased several fold over the range 1150 to 1450 °C. Silica content (Fe/SiO<sub>2</sub> ratio) had the next largest effect and, at all temperatures, there was a drop in viscosity as the Fe/SiO<sub>2</sub> ratio increased from 1.32 to 2.00; however, this effect was small relative to the effect of temperature. The effects of CaO and MgO were, as with liquidus temperatures, complex. The addition of low

concentrations of CaO or MgO lowered the viscosity and, generally, CaO had the slightly greater effect on viscosity on a mass percent basis. However, above a certain concentration of MgO, further addition of MgO resulted in an increase in the viscosity. The addition of equal proportions of CaO and MgO led to lower viscosities than either component alone; e.g., the addition of 3% CaO and 3% MgO resulted in a lower viscosity than the addition of either 6% CaO or 6% MgO.

An effective strategy for handling high MgO-containing slags is suggested by the present results. At high MgO concentrations in slag, the liquidus temperature decreases with addition of CaO above certain concentrations of MgO and CaO depending on the Fe/SiO<sub>2</sub> ratio. The widest range and greatest effect occurs at Fe/SiO<sub>2</sub> = 1.3 and is evident at Fe/SiO<sub>2</sub> = 1.6 but applies only at the highest MgO concentration (12%) at Fe/SiO<sub>2</sub> = 1.8. Hence the best operating range for MgO-containing slags is the lowest practical Fe/SiO<sub>2</sub> ratio and CaO concentrations greater than 4-5%. Given the relative effects on temperature and Fe/SiO<sub>2</sub> ratio on viscosity, it is unlikely that slag viscosity would be a consideration in choosing the Fe/SiO<sub>2</sub> ratio.

## SUMMARY

The quench technique has been used to measure the liquidus temperature of slags in the FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CaO-MgO system. Primary crystallisation phases were determined using scanning electron microscopy. The liquidus temperature results obtained are the most comprehensive to date for the composition range in the quinary system of interest. It has been found that the addition of MgO led to large increases in liquidus temperature while the addition of CaO led to smaller increases or decreases depending on the composition. At concentration of CaO above about 3%, increasing the oxygen pressure in the system raised the liquidus temperature moderately and lowered the ability of CaO to depress the liquidus temperature.

A coaxial, cylindrical cup and bob arrangement was used to measure the viscosity of fayalite slags at iron saturation. The reliability of the results was established by comparison with published data although viscosity data are sparse in the composition range of interest and are highly variable. The current data fits into the historical trend of increasingly lower measured viscosities for a given composition. All results were obtained to an accuracy of  $\pm 5$  mPa.s and are the most comprehensive to date for the composition range of interest. The slags were determined to be Newtonian in behaviour above their liquidus temperatures. There is a significant drop in viscosity as the Fe/SiO<sub>2</sub> ratio increases from 1.32 to 2.00. Addition of low levels of CaO or MgO lowered viscosity. Addition of more MgO increased viscosity. The MgO content at which this inflection from falling to rising viscosity occurred decreased with increased CaO content.

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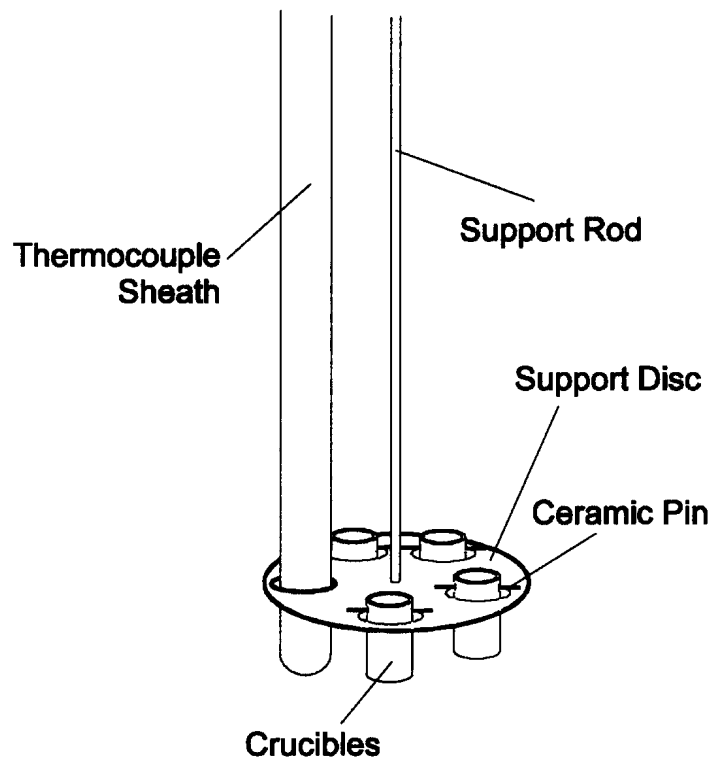


Figure 1. Schematic of crucible supports for liquidus determinations.

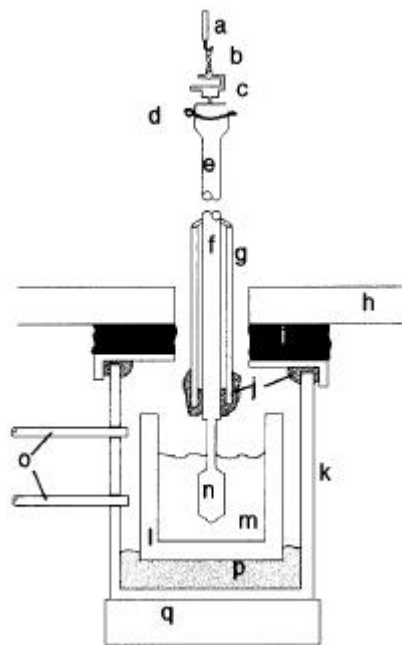


Figure 2. Schematic of arrangement used for viscosity determinations - *a*: hook connection to viscometer, *b*: wire loop, *c*: shaft connector, *d*: pin, *e*: upper shaft, *f*: lower shaft, *g*: ceramic sheath, *h*: furnace ceiling, *i*: insulating material, *j*: ceramic cement, *k*: alumino-silicate crucible and lid, *l*: iron cup, *m*: molten slag, *n*: iron bob, *o*: gas delivery lances, *p*:  $\text{Al}_2\text{O}_3$  powder and *q*: firebrick support.

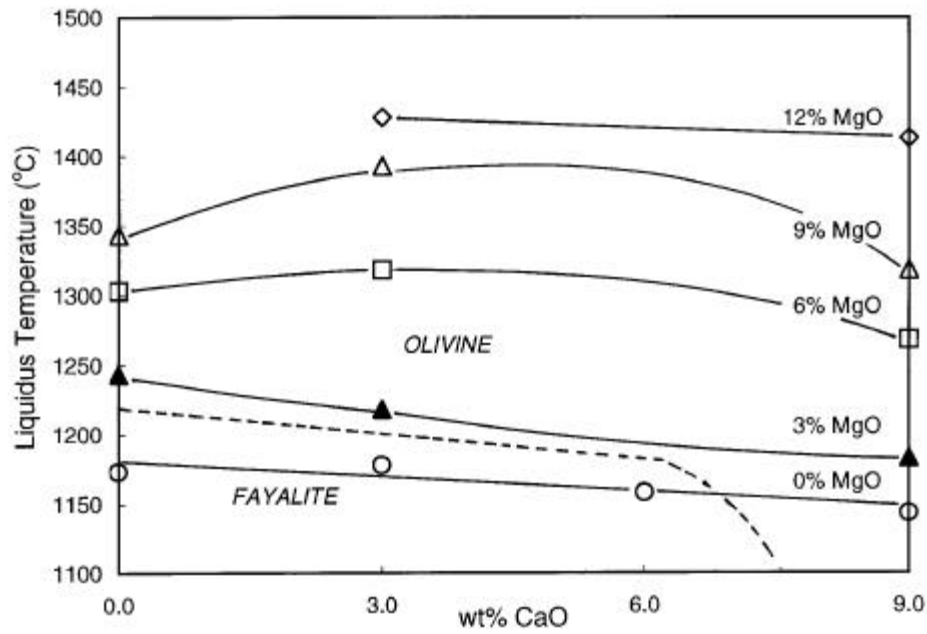


Figure 3. Liquidus temperature results for iron-saturated FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CaO-MgO slags of Fe/SiO<sub>2</sub> = 1.3. Dashed line indicates boundary between primary phases.

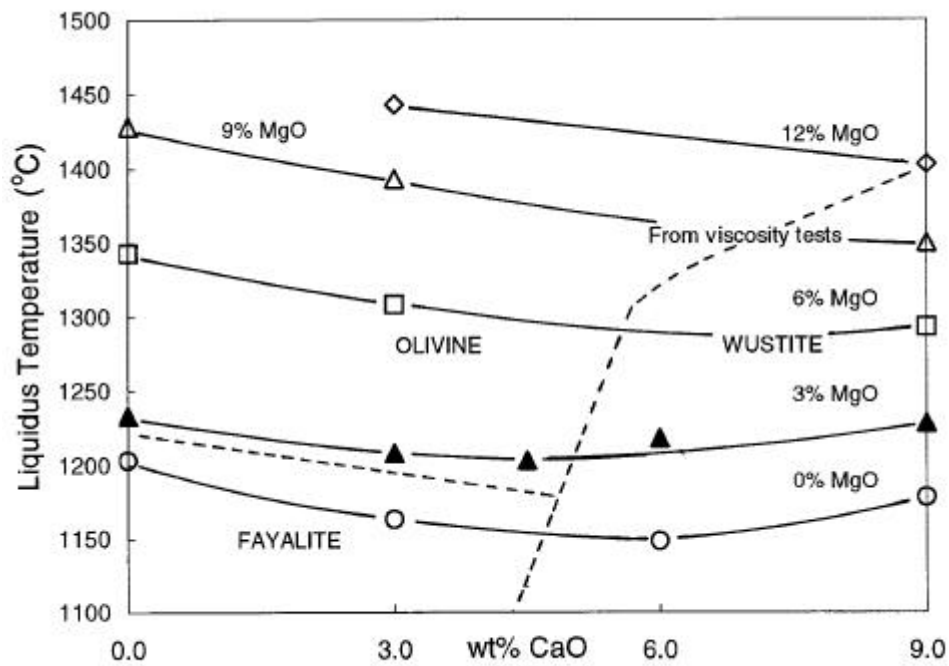


Figure 4. Liquidus temperature results for iron-saturated FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CaO-MgO slags of Fe/SiO<sub>2</sub> = 1.6. Dashed line indicates boundary between primary phases.

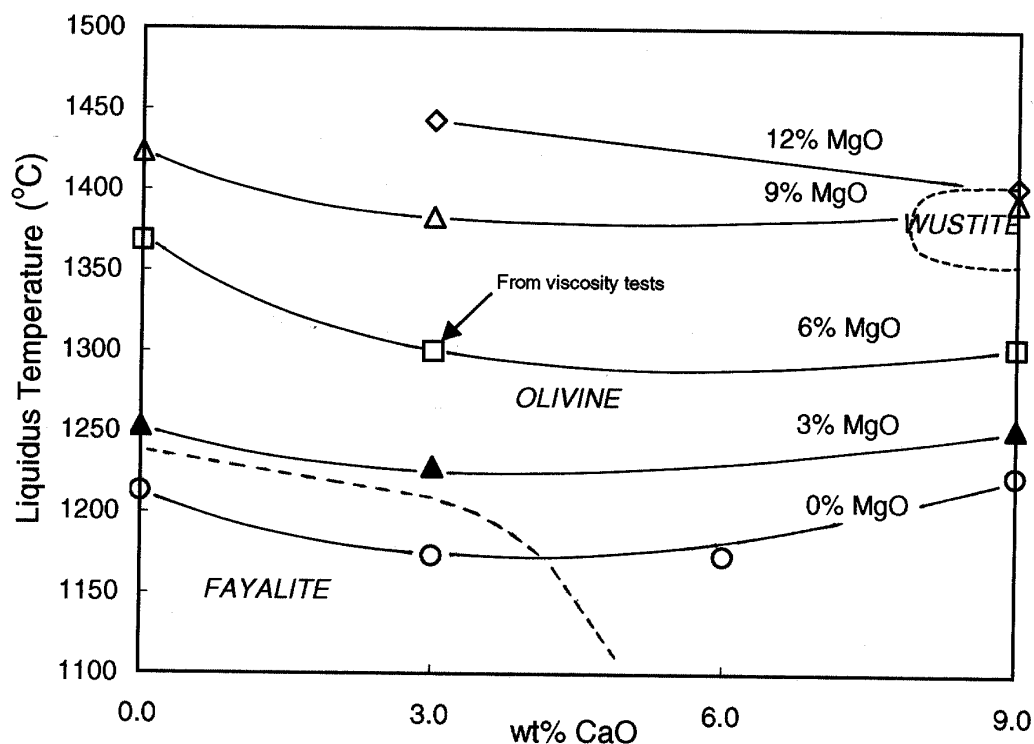


Figure 5. Liquidus temperature results for iron-saturated FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CaO-MgO slags of Fe/SiO<sub>2</sub> = 1.8. Dashed line indicates boundary between primary phases.

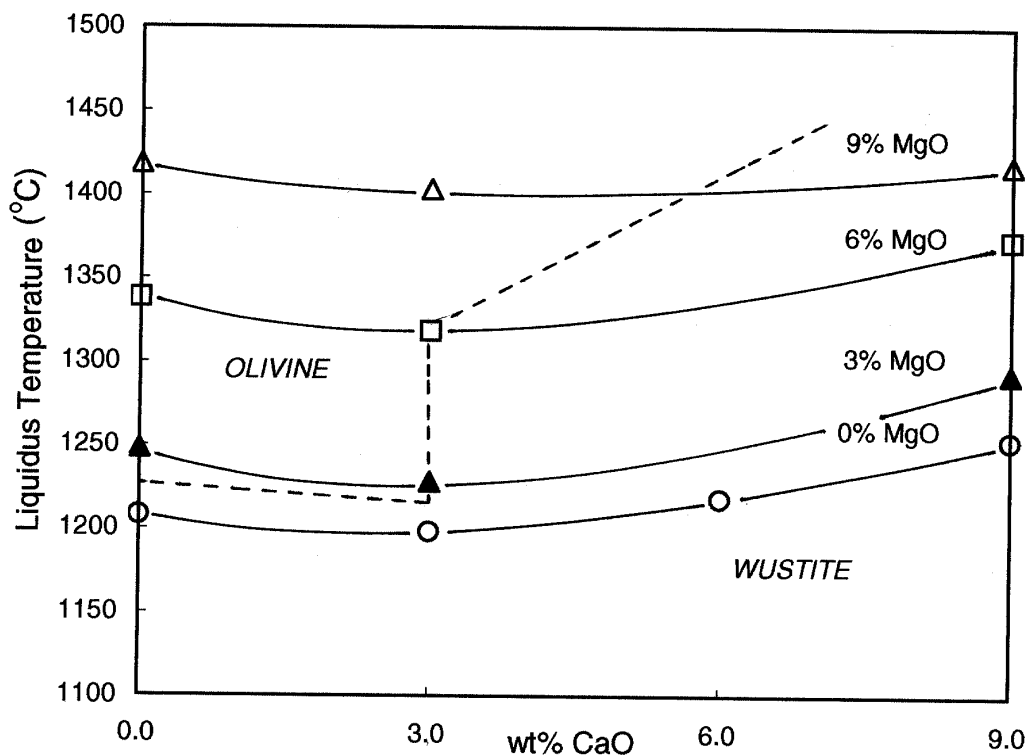


Figure 6. Liquidus temperature results for FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CaO-MgO slags of Fe/SiO<sub>2</sub> = 1.59 at oxygen partial pressure of 10<sup>-8</sup> atm (at 1300 °C). Dashed line indicates boundary between primary phases.

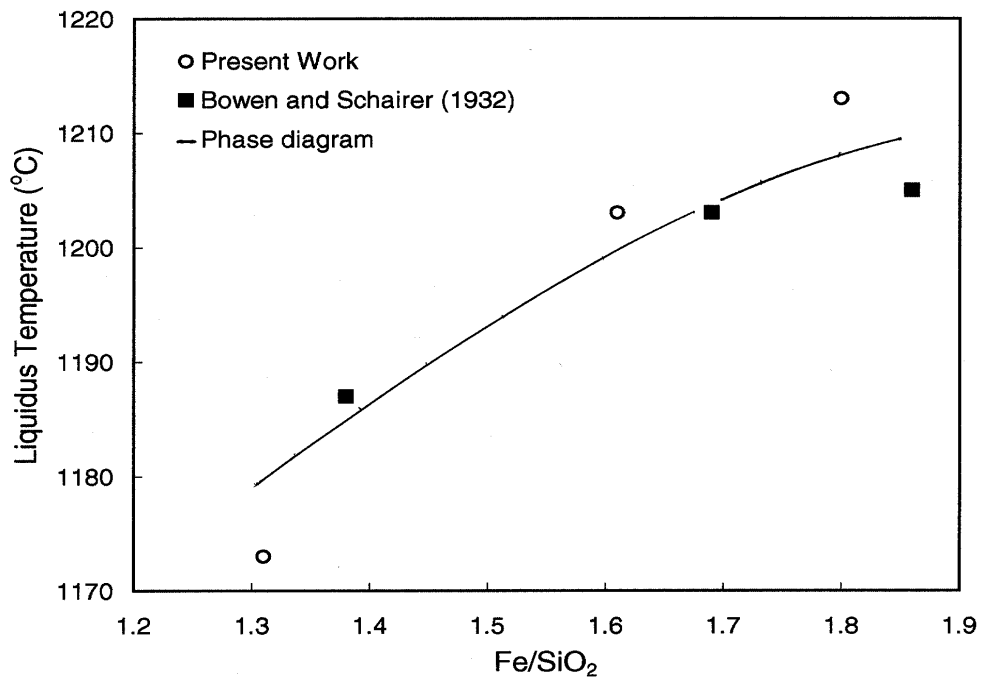


Figure 7. Comparison of the liquidus temperatures in the literature with those determined in the present investigation for FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> slags at iron-saturation.

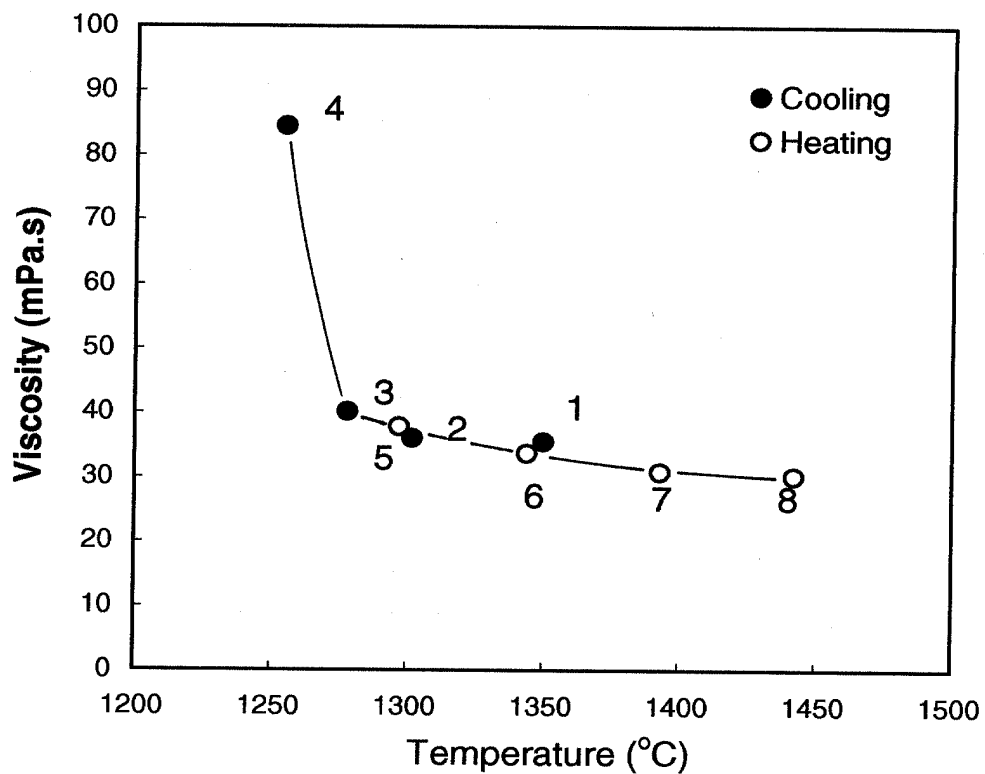


Figure 8: Viscosity results for iron saturated slags of Fe/SiO<sub>2</sub> = 1.66 containing 0% CaO, 3% MgO obtained over one complete cooling and heating cycle. Data points are numbered in the order they were obtained.

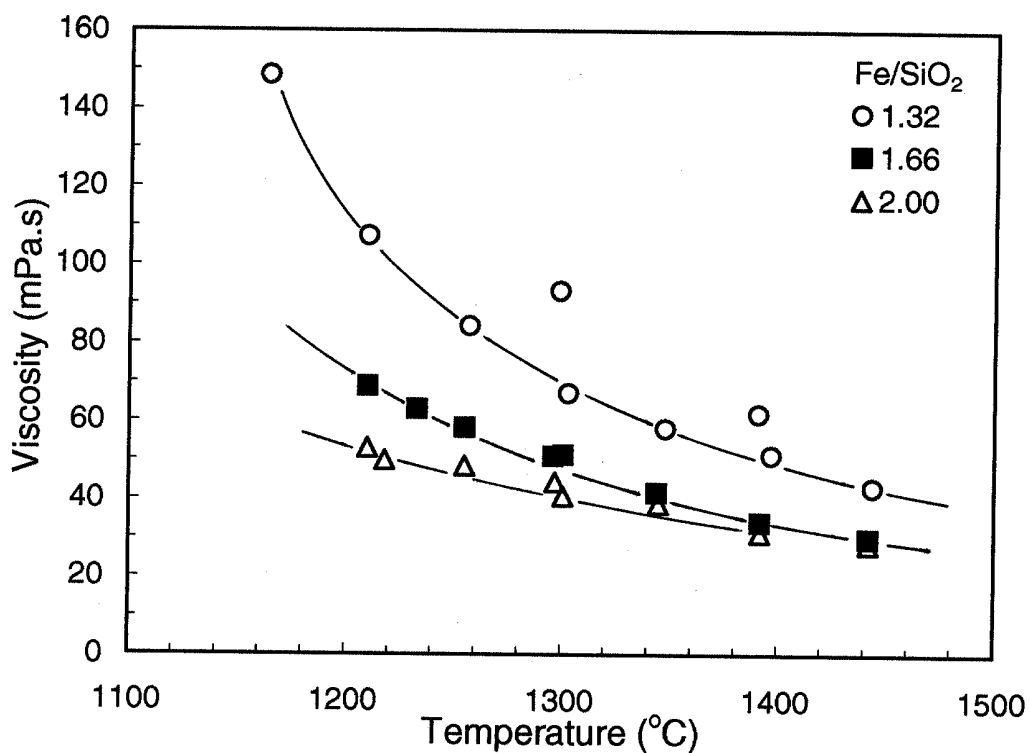


Figure 9: Viscosity results for FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> slags.

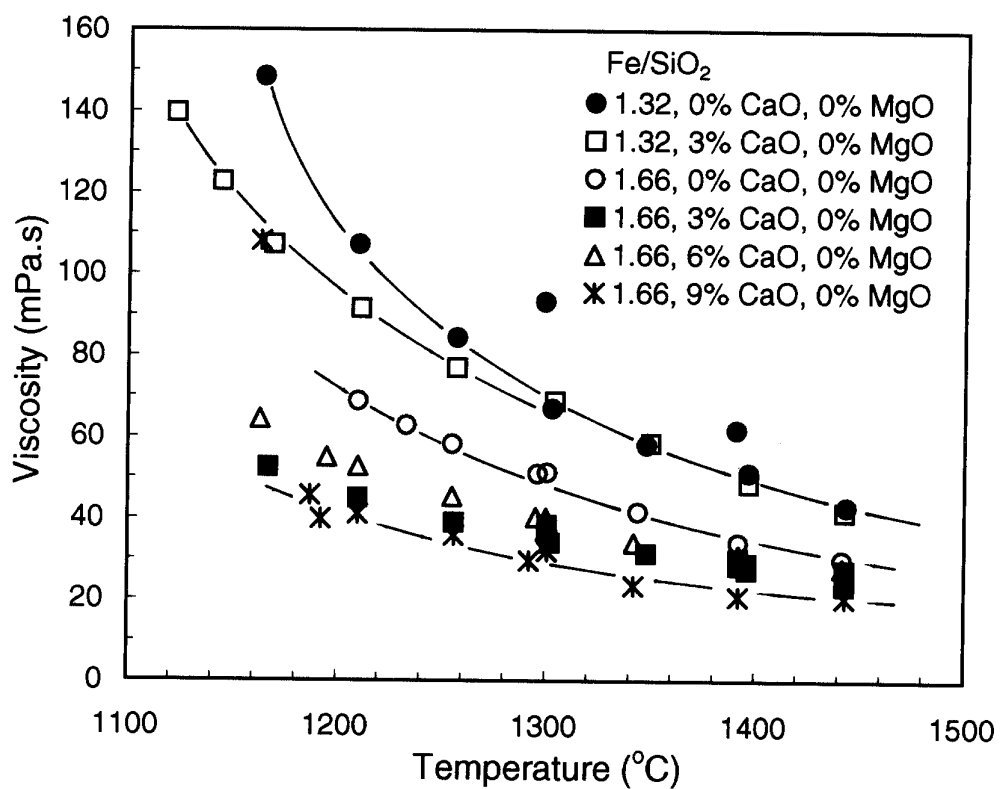


Figure 10: Viscosity results for FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CaO slags.

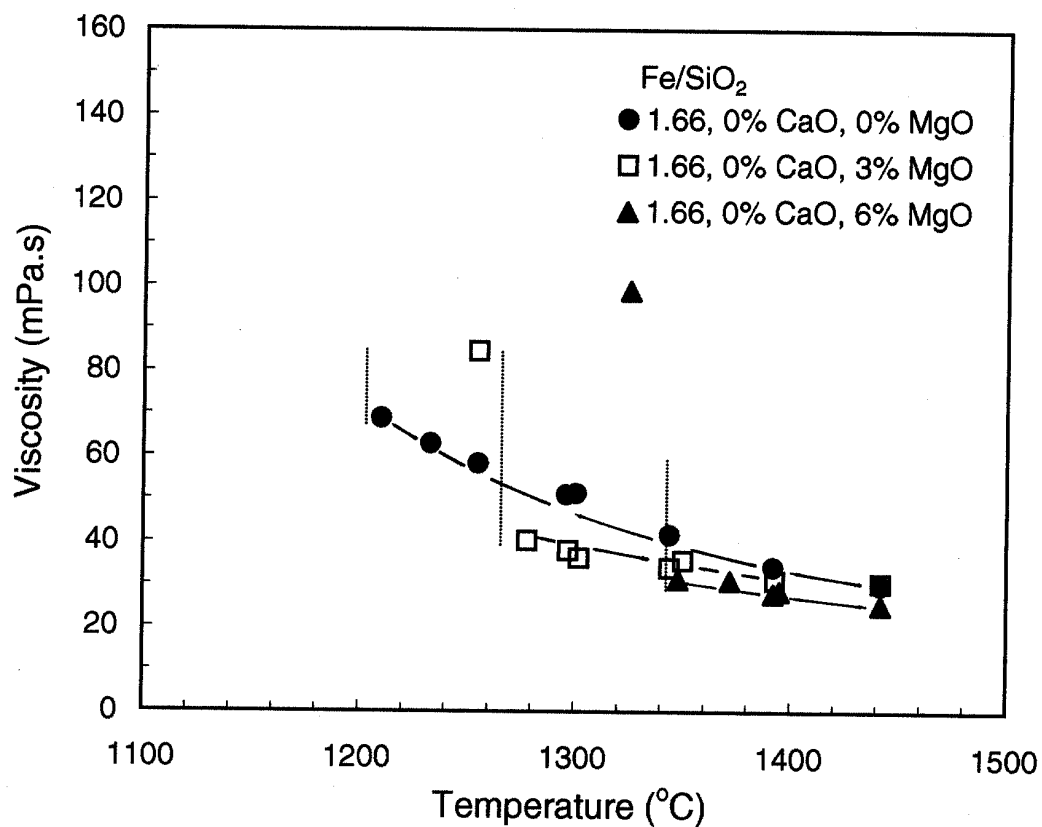


Figure 11: Viscosity results for FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-MgO slags.

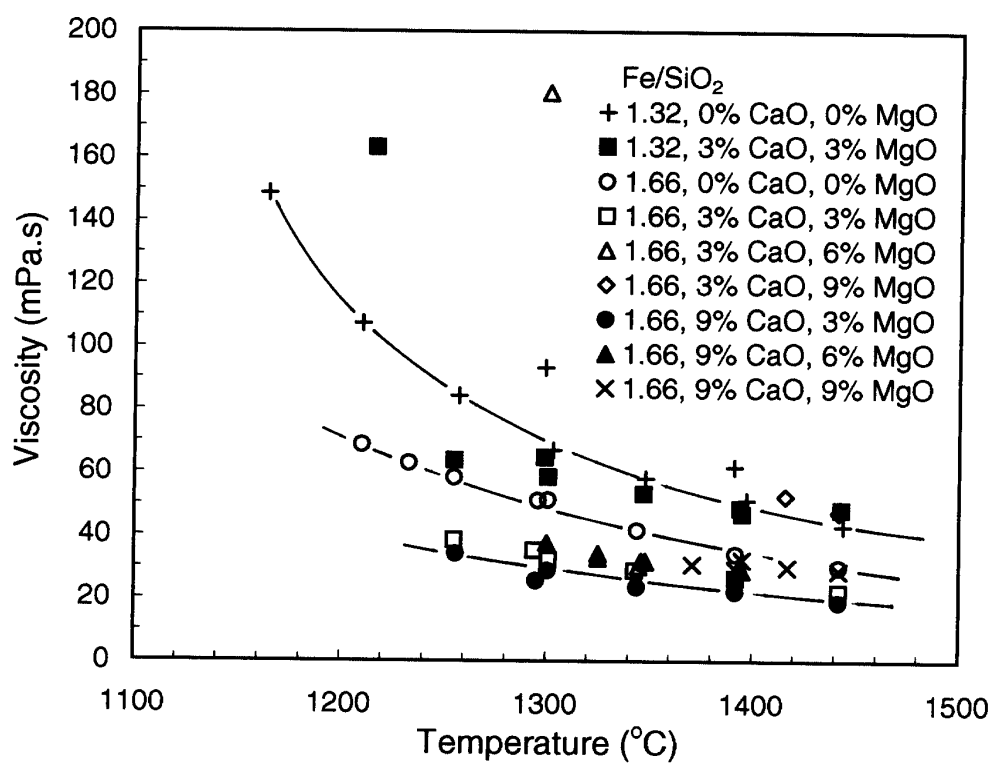


Figure 12: Viscosity results for FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CaO-MgO slags.

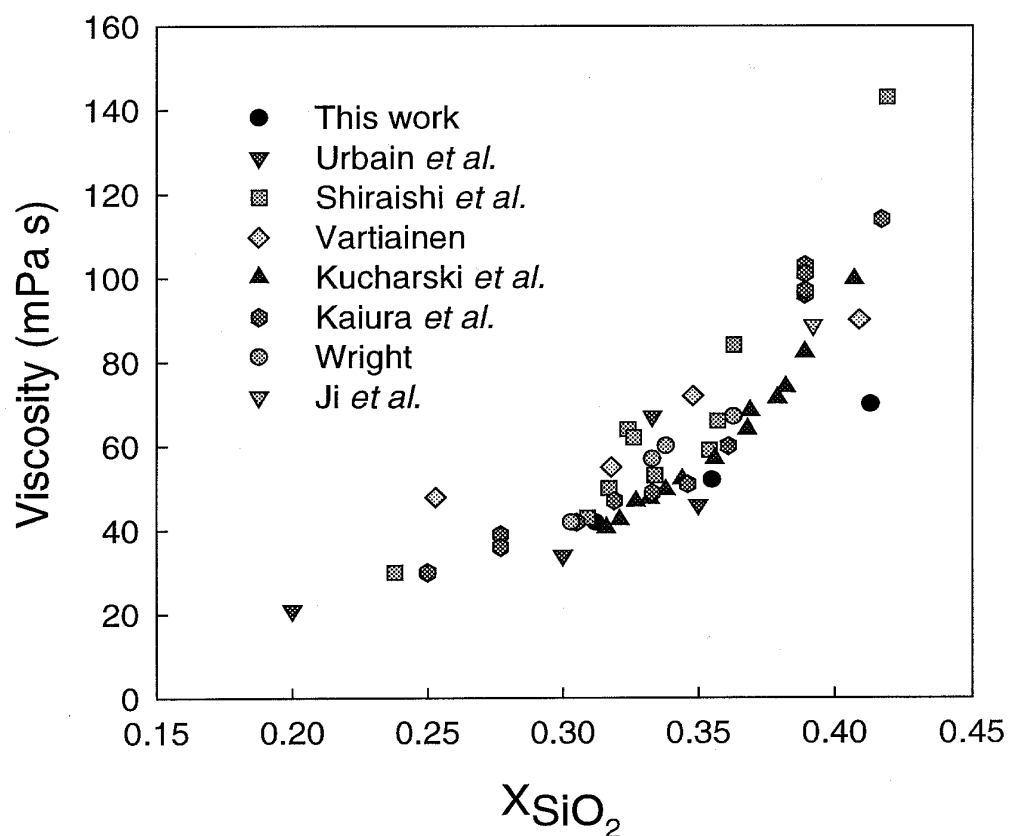


Figure 13. Comparison of present results for iron-saturated  $FeO-Fe_2O_3-SiO_2$  slags at  $1300\text{ }^{\circ}C$  with results of previous investigations.

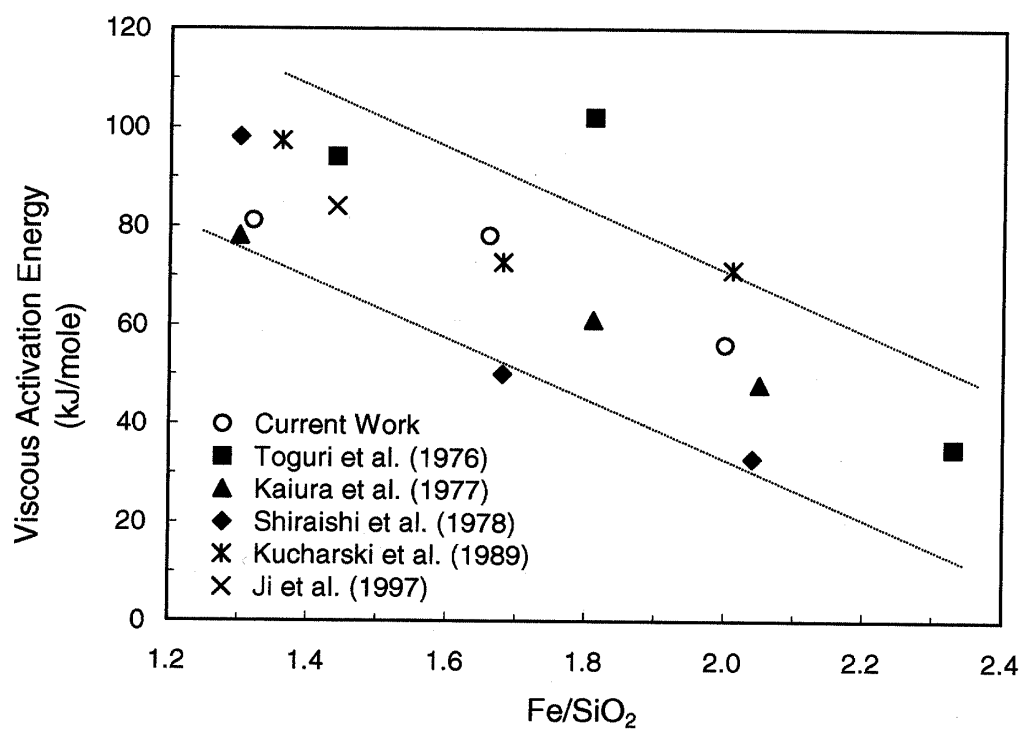


Figure 14. Comparison of the present viscous activation energies to the range in the literature<sup>7-14</sup> for  $FeO-Fe_2O_3-SiO_2$  slags.



Table I. Master Slag Compositions for Liquidus Temperature Determination

	Composition (wt%)				
	FeO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	NiO	Fe/SiO <sub>2</sub>
Slag A (iron saturated)	58.7	4.2	37.1	-	1.31
Slag B (iron saturated)	63.7	3.8	32.5	-	1.61
Slag C (iron saturated)	64.9	5.1	30.0	-	1.80
Slag D (CO <sub>2</sub> /CO=7.4)	56.9	7.8	31.3	4.0	1.59

Table II. Composition of Master Slags used in the Viscosity Measurements

	Composition (wt%)			
	FeO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe/SiO <sub>2</sub>
Slag E (iron saturated)	61.07	2.03	36.90	1.32
Slag F (iron saturated)	62.89	5.42	31.69	1.66
Slag G (iron saturated)	67.50	4.65	27.85	2.00

Table III. Liquidus Temperatures and Primary Crystallisation Phases in the Systems FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-CaO-MgO at Iron Saturation.

Investigators	Fe/SiO <sub>2</sub>	Composition (wt%)					T <sub>L</sub> (°C)
		FeO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MgO	
Bowen <i>et al.</i> (1933) <sup>3</sup>	1.27	54.42	1.73	34.13	9.72	0.00	1140
	1.33	57.37	1.65	34.35	6.63	0.00	1160
Bowen and Schairer, (1935) <sup>4</sup>	1.21	57.73	1.38	37.82	0.00	3.07	1242
	1.35	58.64	1.77	34.64	0.00	4.95	1305
	1.42	56.10	1.46	31.36	0.00	11.08	1450
	1.60	61.89	1.65	30.74	0.00	5.72	1340
Allen and	1.67	56.90	5.31	28.78	8.81	0.00	1136
Snow (1955) <sup>5</sup>	1.74	56.72	5.63	27.58	9.93	0.00	1124-54