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The influence of Fe^{3+}/Fe^{2+} ratio on the viscosity of iron silicate slags

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Viscosity measurement was carried out over a narrow range of silica content around the fayalite composition. A wide range of temperature and oxygen potential was covered where the slag was completely liquid. In order to keep the slag composition and the Fe^{3+}/Fe^{2+} ratio constant, the CO_2/CO ratio was kept constant as the temperature was varied. Increasing the Fe^{3+} content has little effect on viscosity for slags with a silica mole fraction of 0.31. At higher silica contents, increasing the Fe^{3+} content brings about a small decrease in the viscosity.

Introduction

Most of the viscosity measurements on iron silicate slags have been performed under iron saturation conditions, where iron components were used for the crucible and viscometer bob[1–8]. Measurements at higher oxygen potential (p_{O_2}) are limited and show conflicting results on the effect of Fe^{3+}/Fe^{2+} ratio on the viscosity[9–12]. Some of the differing results may be attributed to performing the measurements at constant oxygen potential over a range of temperature.

It is well known that the Fe^{3+}/Fe^{2+} redox couple in iron containing slags follow 'O-type' behaviour and that at a constant oxygen partial pressure, the Fe^{3+}/Fe^{2+} ratio increases as the basicity increases or the melt temperature decreases[13.14]. Therefore during viscosity measurements at a constant p_{O_2}, the equilibrium melt composition changes as the temperature changes. The main reason for this study was to support the development of the viscosity model for iron oxide containing slags[15] and to confirm if there was a local viscosity maximum at the fayalite composition at higher oxygen partial pressures than iron saturation and determine the effect that the Fe^{3+}/Fe^{2+} ratio has on the viscosity of iron silicate slags, iron oxide.

The measurements were performed using a platinum-rhodium alloy crucible and viscometer bob. The approach adopted in this work was to keep the Fe^{3+}/Fe^{2+} ratio constant by keeping the CO_2/CO ratio in the gas phase constant as the temperature was varied. The slags were equilibrated with CO_2-CO gas mixtures with CO_2/CO ratios between 4 and 100. After initial equilibration between the slag and gas, only thermal equilibration was required between viscosity measurements. This paper documents the results of the study.

Experimental

The experimental apparatus used to measure the viscosity of liquids at high temperature is shown in Figure 1. The slag was heated in an $MoSi_2$ element vertical tube furnace with a programmable temperature controller and temperatures were maintained to ± 1°C. A Pythagorus work tube of 95 mm ID with water-cooled brass end caps was used to isolate the crucible within the furnace hot zone. A Pt-13%Rh crucible (67 mm diameter, 70 mm high) containing about 250 g of melt was supported in the hot zone on a ceramic platform cast onto an inverted 8 mm diameter alumina tube closed at one end. The melts were prepared from laboratory reagent grade ferric oxide and silica. Temperature measurements were made with a Pt-13%Rh/Pt thermocouple located in the support tube with the tip in thermal contact with the crucible bottom. The thermal gradient in the stagnant melt had been previously determined by immersion of an alumina sheathed Pt-13%Rh/Pt thermocouple into a test slag. The temperature variation was determined as ± 3°C.

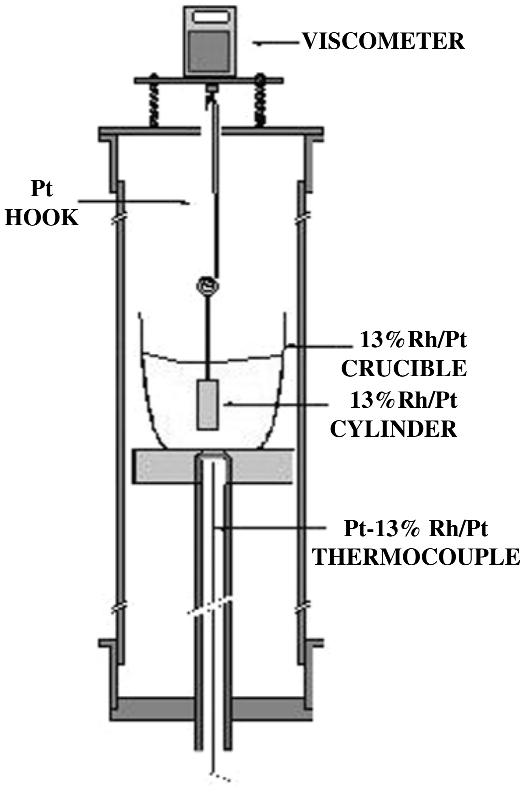

Figure 1. Schematic of furnace work tube and viscosity apparatus

The gas atmosphere in the furnace was maintained by calibrated gas mass flow controllers, where dried and deoxygenated CO_2 and CO were mixed and delivered into the furnace. Gases exiting the furnace passed through bubblers to maintain a slight positive pressure in the furnace.

The melt was prepared by milling the required quantities of silica and iron oxide together, and then the mixture was charged into the crucible and loaded into the cold furnace. The viscometer was then positioned on the end cap and the viscometer bob suspended above the solid slag. The viscometer assembly was then sealed to be gas tight and to prevent oxygen ingress. The furnace was then slowly heated up to temperature while a flowing CO_2-CO atmosphere was maintained in the work tube. When the slag was molten, the bob was lowered into the melt, the viscometer turned on with the bob rotating slowly in the slag to stir the melt, and allowed to equilibrate overnight.

The immersion depth in the melt was established by lowering the spindle into the melt until the top surface was just submerged. The spindle was then lowered a further 10 mm to the desired depth. The torque was then measured at several rotation speeds with either 100 or 200 readings collected at each speed over a period of 5 minutes.

The temperature range studied depended on the CO_2/CO ratio and the temperature at which solids nucleated on the bob. For a series of measurements at a constant CO_2/CO ratio, twenty minutes was allowed between temperature changes for the system to regain thermal/chemical equilibrium, as the Fe^{3+}/Fe^{2+} ratio was not expected to change with temperature. At suitable temperature intervals, a few grams of the slag were collected by quenching slag on a cold steel dip rod for chemical analysis. After measurement at the maximum temperature, the viscosity was again measured at lower temperatures to confirm there were no significant differences.

After completion of a series of measurements at a constant CO_2/CO mixture, the gas composition was changed and the slag was left to re-equilibrate overnight while the rotating bob stirred the melt. After completion of a series of measurements at different CO_2/CO ratios and while the melt was at a high temperature, SiO_2 or Fe_2O_3 was added to the melt, depending on which composition was to be studied. The silica or magnetite was mixed into the melt using the viscometer bob, and the desired CO_2/CO gas mixture set. The melt was then stirred for 20 minutes by the viscometer bob and then the melt was cooled to just above the expected liquidus and stirred overnight. The next series of measurements then commenced. At the end of the experiments, the bob was lifted from the melt and the crucible was allowed to slowly cool to room temperature.

Viscometer calibration and measurement uncertainties

The viscometer bob was calibrated against liquids (silicone oils) of known viscosity at 25°C (0.05–30.8 Pa•s). A 250 cm^3 beaker containing the known standard was placed in a water bath at a constant temperature of 25°C. The equation for determining the spindle constant is given in Equation [1], where η is the viscosity of the standard oil, τ is the measured torque, and *S* is the spindle constant and *K* is an instrument spring constant and *rpm* is the rotation speed of the bob.

$$\eta(Pa \bullet s) = \frac{K \times S \times \tau}{rpm} \qquad [1]$$

Fully immersing the cylinder to a depth of 5 mm in the standard and then measuring the torque at several rotation speeds allowed determination of the spindle constant. The effect of thermal expansion of the Pt at 800–1400°C on the spindle constant was considered negligible. The contribution of the shaft to the spindle constant is also small and a 5 mm displacement from the calibrated depth contributes only a 0.3% error.

The viscometer was also calibrated at high temperature with the SRM slag supplied by Hoogovens RL. The measurement protocol outlined by the authors of the SRM study was adopted[16]. The agreement between the measured viscosities and the recommended values were well within the quoted experimental uncertainties[17].

It was estimated that the uncertainties of temperature measurement in this work were ±10°C, the uncertainties of the viscosity standards were ±1%, and the uncertainty of the bob/viscometer was ±5%. When combined with the uncertainty due to averaging and linear regressions, the overall uncertainty is around ±10%, which is typical of most viscosity measurement.

Chemical analysis

The slag samples collected from this work were pulverized in a ring mill and analyses of the slag were completed by sodium peroxide fusion followed by ICP-OES analysis (Varian Vista) of resultant solutions. The proportion of the total iron as ferrous was determined using the standard titration technique.

Results

The oxidation state of the slag

The measured Fe^{3+}/Fe^{2+} ratios of slag dip samples collected in between different viscosity measurements, over a temperature range of 1200 to 1400°C, are shown in Figure 2. Although there is scatter in the Fe^{3+}/Fe^{2+} ratios, the results show the same trends as observed in equilibrium

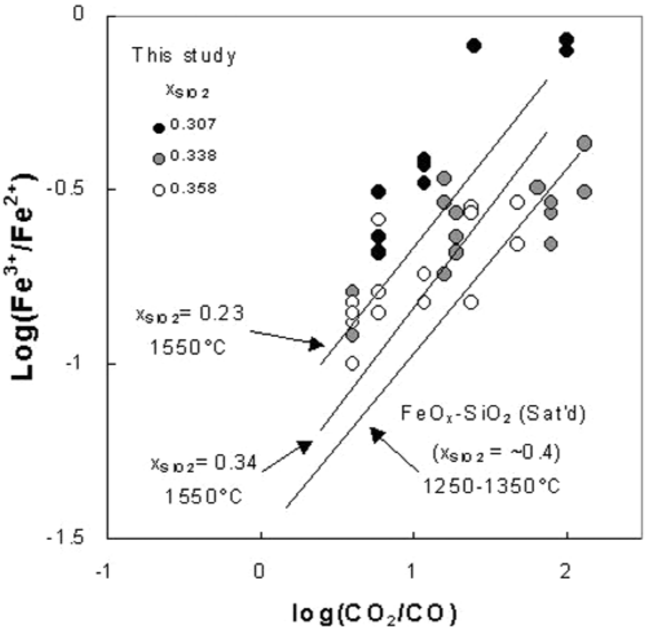

Figure 2. Measured Fe^{3+}/Fe^{2+} ratio as a functiono of the equilibrium gas CO_2/CO ratio for the three slag compositions studied. Symbols—measured Fe^{3+}/Fe^{2+} from this study, lines—equilibrium studies[18,19]

measurements on silica saturated iron silicate slags at 1250–1350°C[18] and iron silicate slags contained in Pt crucibles at 1550°C[19]:

- At a constant silica mole fraction and over the temperature range measured, $\log(Fe^{3+}/Fe^{2+})$ is proportional to $\log(p_{CO_2}/p_{CO})$ and independent of temperature. The results of this study show a slightly weaker dependence on $\log(p_{CO_2}/p_{CO})$ than the equilibrium experiments
- At a constant CO_2/CO ratio, the Fe^{3+}/Fe^{2+} ratio decreases as the silica content increases.

The observed Fe^{3+}/Fe^{2+} ratios of this study at silica mole fractions of 0.31 and 0.33 are higher than that observed for silica mole fractions of 0.24 and 0.34 in the study by Turkdogen and Bills[19] at 1550°C shown in Figure 2. Lower temperature data at the silica contents of this study do not appear to be available for comparison.

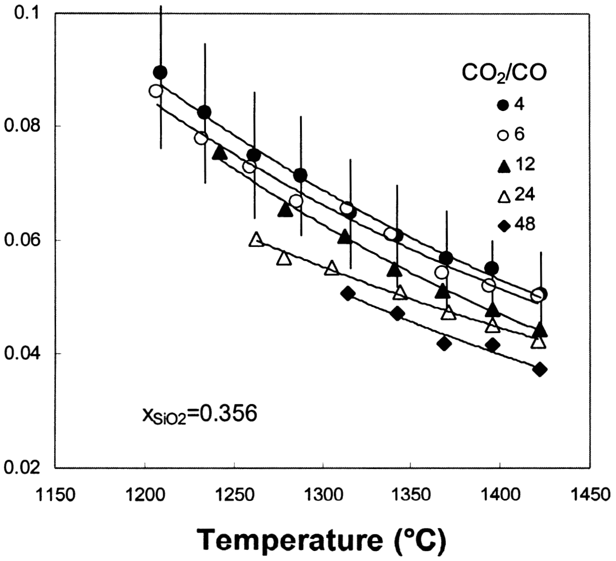

Figure 3. Variation of viscosity with temperature and gas composition of iron silicate slag with a silica mole fraction of 0.356. Uncertainty bars of 15% marked for the measurements where the CO_2/CO ratio was 4

Variation of viscosity with equilibrating atmosphere and slag chemistry

The variation of the viscosity of the three silica contents studied with temperature and CO_2/CO ratio are shown in Figures 3 to Figure 5. The results at the highest silica content studied in this work are shown in Figure 3. At a constant temperature, the viscosity decreased as the CO_2/CO ratio increased. At the fayalite composition shown in Figure 4, the CO_2/CO ratio would appear to have little effect on the viscosity. On the iron rich side of the fayalite composition, as shown in Figure 5, the results are scattered. The viscosity of the low silica melt equilibrated at 1300°C with a 80%CO_2-20%CO gas atmosphere is 40% lower than the melt with the higher silica content studied under the same conditions.

Discussion

A significant proportion of viscosity measurements on iron silicate slags have been under conditions where the slag was iron saturated and the variation in viscosity with silica content was studied[3–7]. Such reducing conditions were not studied in this work and the lowest CO_2/CO ratio studied was 4, corresponding to a 80%CO_2–20%CO atmosphere. The dependence of the viscosity on the silica contents studied in this work at 1300°C are shown in Figure 6. The fayalite composition did not produce a local viscosity maximum as observed by Urbain *et al.*[4] or Shirashi *et al.*[3]. Kaiura *et al.*[9] earlier reported that the local maximum did not exit at oxygen partial pressures higher than iron saturation. Also shown are other measurements under conditions of iron saturation by Ji *et al.*[5–6] and Ducret and Rankin[7]. Other measurements with Mo components by Kucharski *et al.*[8], Kaiura *et al.*[9] and Vartiainen[12], where the gas atmosphere was controlled, are also shown in Figure 6. Together the data suggest a smooth monotonic increase in viscosity as the silica content increases.

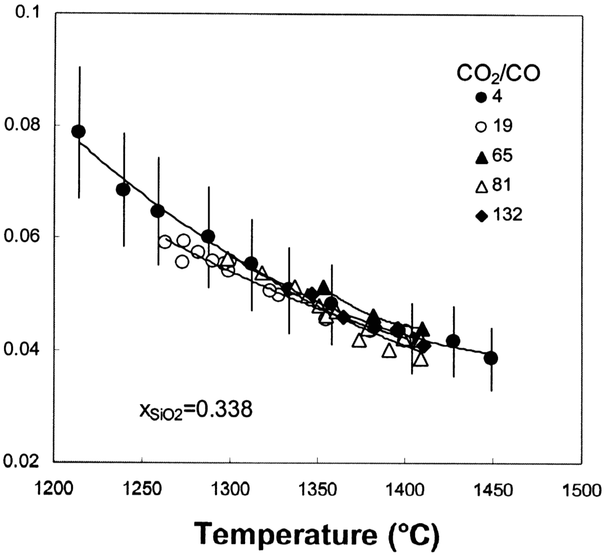

Figure 4. Variation of viscosity with temperature and gas composition of iron silicate slag with a silica mole fraction of 0.338. Uncertainty bars of 15% marked for the measurements where the CO_2/CO ratio was 4

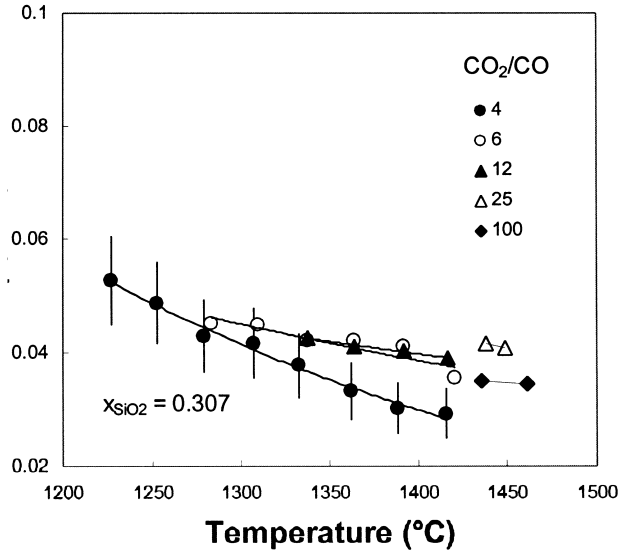

Figure 5. Variation of viscosity with temperature and gas composition of iron silicate slag with a silica mole fraction of 0.307. Uncertainty bars of 15% marked for the measurements where the CO_2/CO ratio was 4

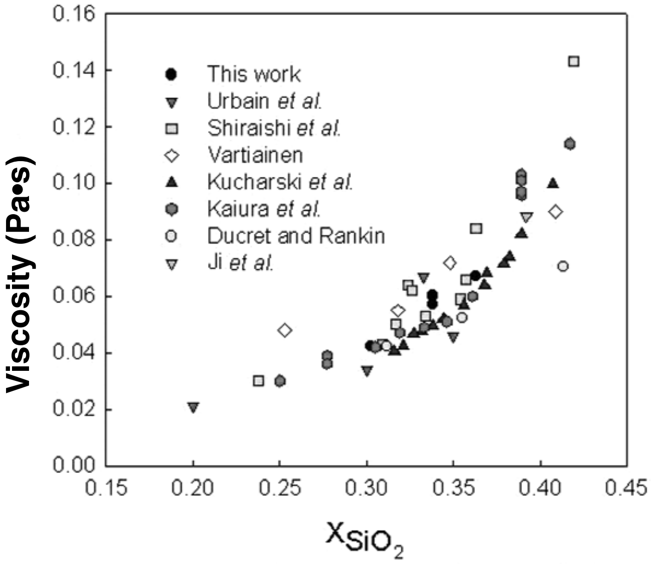

Figure 6. Comparison of the measured viscosity of iron silicate melts at 1300°C from this study, with literature measurements

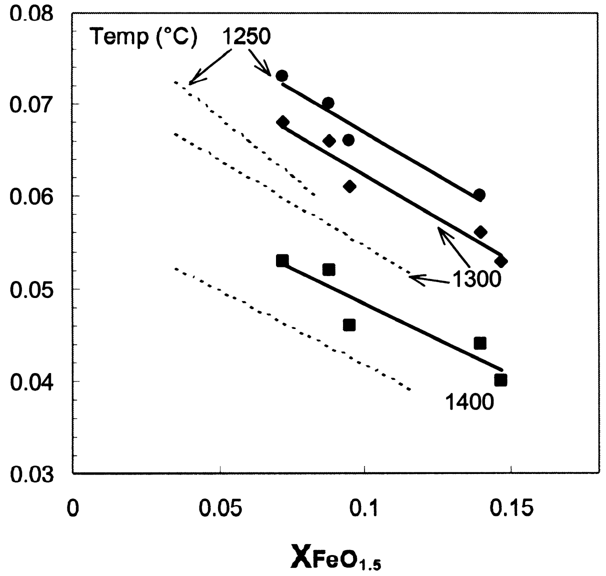

Figure 7. Variation of viscosity with Fe^{3+} content for the slag on the silica rich side of fayalite, x_{SiO_2} = 0.356. Filled symbols—experimental measurement, dashed lines calculated from MPE[20]

The effect of ferric content on the viscosity from this study is shown in Figure 7 to Figure 9, using the analysed Fe^{3+} used in Figure 2. The isothermal viscosity data are also plotted against the equilibrium Fe^{3+} content of the slags, which were calculated for each Fe/SiO$_2$ ratio and CO$_2$/CO ratio used with CSIRO's Multiphase equilibrium (MPE) model[20] for the Fe-O-SiO$_2$ system assuming the slag was in equilibrium with the gas phase. Irrespective of whether the measured Fe^{3+} or the equilibrium Fe^{3+} content were used, the trends with respect to how the Fe^{3+} content changes the viscosity were the same.

The magnitude of the effect that the Fe^{3+} content has on the viscosity is relatively small compared with the effect of the silica content. For example, Figure 7 shows that the viscosity decreased by about 10% as the Fe^{3+} mole fraction increased from 0.05 to 0.18. Comparison of Figure 7 and Figure 9 shows that the viscosity decreased by about 40% as the SiO$_2$ mole fraction decreased from 0.356 to 0.307. As the viscosity decreases, the relative uncertainty of the viscosity measurement increases. In Figure 9, where the silica mole fraction was 0.307, less weight should be placed on the low viscosity measured at 1450°C for the melt where the mole fraction of FeO1.5 was ~ 0.09, and when the uncertainties are considered, the viscosity is independent of the Fe^{3+}/Fe^{2+} ratio. In summarizing the trends observed in this study:

- When x_{SiO_2} = 0.358, or Fe/SiO$_2$ < 2, viscosity decreased as the Fe^{3+} content increased
- At the fayalite composition, x_{SiO_2} = 0.338, viscosity decreased by < 10% as the Fe^{3+} content increased
- When x_{SiO_2} = 0.307 or Fe/SiO$_2$ > 2, the Fe^{3+} content had little effect on the viscosity.

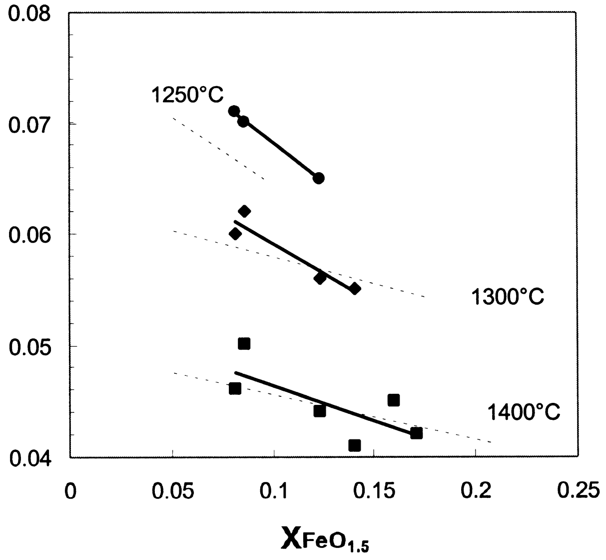

Figure 8. Variation of viscosity with ferric content for the fayalite type slag x_{SiO_2} = 0.338. Filled symbols-experimental measurement, dashed lines calculated from MPE[20]

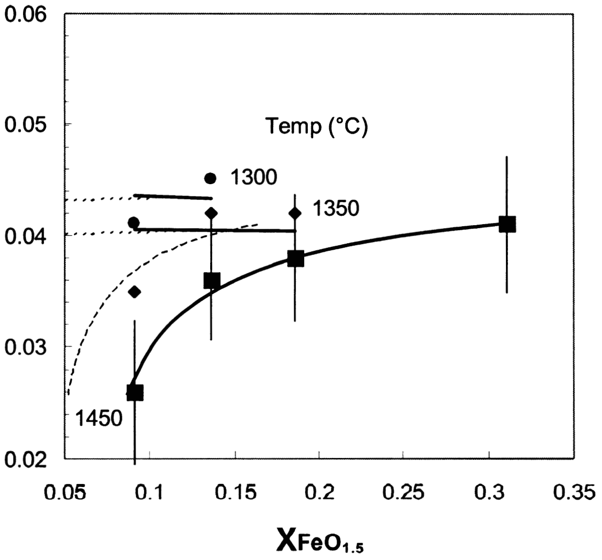

Figure 9. Variation of viscosity with ferric content for the slag on the iron rich side of fayalite, x_{SiO_2} = 0.307. Filled symbols—experimental measurement, dashed lines calculated from MPE[20]. Uncertainty bars of 15% marked for the measurements where temperature was 1450°C

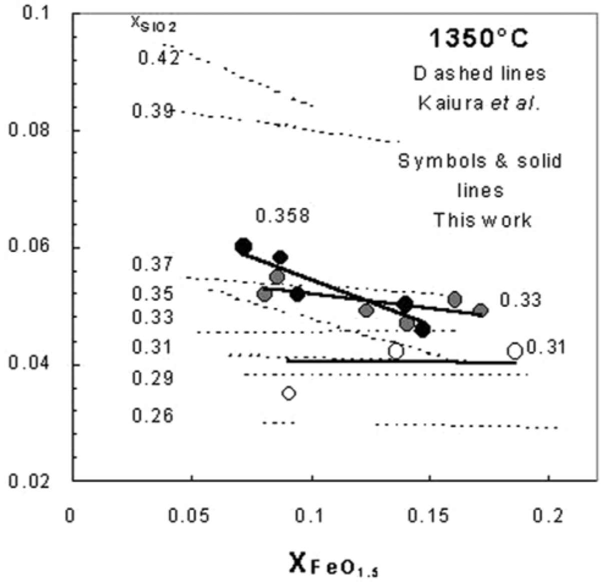

Figure 10. Comparison of the effect of Fe^{3+} content on the viscosity of slag at 1350°C from this study and the measurements of Kaiura *et al.*[9]

The trends observed in this study are consistent with other measurements on the FeO-Fe_2O_3-SiO_2 system[9,12]. This is shown in Figure 10 where the viscosity measurements at 1350°C of Kaiura *et al.*[9] at various silica contents are compared with the results of this study using the measured Fe^{3+} concentration. Kaiura *et al.*[9] measured the viscosity at constant oxygen partial pressure and the Fe^{3+} content in the slag was inferred from the liquidus study of Muan[21]. The agreement between the two studies is good, and they show the same trends as discussed above.

In terms of industrial practice, the ferric content of the slag will have little real effect on the melt viscosity. Most iron silicate based slags will contain varying percentages of Al_2O_3, CaO or MgO, depending upon concentrate quality and the fluxing strategy, as well as Cu_2O, NiO, PbO and ZnO depending upon the product metal. For slags with a fixed silica content, substitution of iron oxide in the slag with Al_2O_3, CaO or MgO will increase the Fe^{3+} content in the melt and the viscosity will increase primarily due to the influence of adding high melting point oxides[15]. The viscosity of copper smelting and converting slags should be slightly lower than iron silicate slags of the same silica content and temperature due to the ability of Cu_2O to break up the silicate network[22]. Similarly for lead oxide containing iron silicate slags[17]. For iron silicate based metallurgical slags, the major influences on the viscosity of homogeneous *liquid slags* in decreasing order of importance is Fe/SiO_2 ratio > temperature > proportions of 'substituting oxides' e.g. Al_2O_3, CaO, MgO, Cu_2O etc, > Fe^{3+}/Fe^{2+} ratio[15].

The substituting oxides do affect the equilibrium Fe^{3+}/Fe^{2+} ratio and the stability of the spinel phase. If the oxygen potential is high enough, the spinel phase may form and the viscosity on the two phase mixture would be significantly higher, depending upon the proportion of spinel crystals formed. Then the volume fraction of 'dispersed' crystals may have a much larger effect on the viscosity than either the Fe/SiO_2 ratio or temperature.

Conclusions

The effect of Fe^{3+}/Fe^{2+} ratio on the viscosity of iron silicate melts was examined. The experiments were performed on melts of fixed silica content in equilibrium with a gas of known CO_2/CO ratio and over a range of temperature. It was found that:

- The Fe^{3+}/Fe^{2+} ratios in the slags show the same trends as observed in equilibrium measurements on iron silicate slags, both silica saturated and unsaturated.
  - At a constant silica mole fraction and over the temperature range measured, $\log(Fe^{3+}/Fe^{2+})$ was proportional to $\log(p_{CO_2}/pCO)$ and independent of temperature but had slightly weaker dependence on $\log(p_{CO_2}/pCO)$ than the equilibrium experiments in the literature.
  - At a constant CO_2/CO ratio, the Fe^{3+}/Fe^{2+} ratio decreases as the silica content increases.
- No local viscosity maximum was observed at the fayalite composition, and over the narrow range of compositions studied, the viscosity increased smoothly as the silica content increased.
- The effect of varying Fe^{3+} content of homogeneous melts on viscosity was small compared with the effect of varying the silica content. For a melt with an SiO_2 ratio mole fraction of 0.356, the viscosity decreased by about 10% as the $FeO_{1.5}$ mole fraction increased from 0.05 to 0.15. Decreasing the silica mole fraction to 0.307 brought about a 40% decrease in the viscosity at 1300°C with an 80%CO_2-20%CO gas atmosphere.
- The changes in viscosity due to the Fe^{3+} content decreased as the silica content decreased, and at a silica mole fraction of 0.307, the Fe^{3+}/Fe^{2+} ratio appeared to have no major influence on the viscosity.

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