SLAG PHASE EQUILIBRIA AND VISCOSITIES IN FERRONICKEL SMELTING SLAGS

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ABSTRACT

The properties of the slag phase are critical to the smooth operation of ferronickel smelting operations. Phase equilibria studies have been carried out on the "FeO"-SiO2-MgO-Al2O3 system in equilibrium with iron in the range of compositions and temperatures directly relevant to the nickel laterite ores. The results of recent studies on liquidus temperatures and primary phase fields in the range 1500 -1650oC have been incorporated in FactSage databases, and the updated databases have been used to develop a fundamentally-based, quasichemical slag viscosity model capable of predicting the effects of changing temperature and slag composition at liquid and sub-liquid conditions over a wide range of compositions. The results of the model predictions of phase equilibria and viscosities are presented in the form of pseudo-binary sections.

The study demonstrates the value of model predictions in identifying trends and the sensitivities of the system to changes in bulk composition and temperature. In particular the influence of the extensive solid solutions in the olivine (Mg,Fe)2SiO4 primary phase field on subliquidus equilibria, and the effects of alumina on phase equilibria and slag viscosities.

1 INTRODUCTION

The "FeO"-SiO2-MgO system forms the basis for the slags produced in the smelting of ferro-alloys from saprolitic nickel laterite deposits [1]. Fig 1 shows the approximate compositions of smelting slags in a number of ferronickel smelting operations projected on to the liquidus surface of the MgO-"FeO"-SiO2 system at metallic iron saturation.

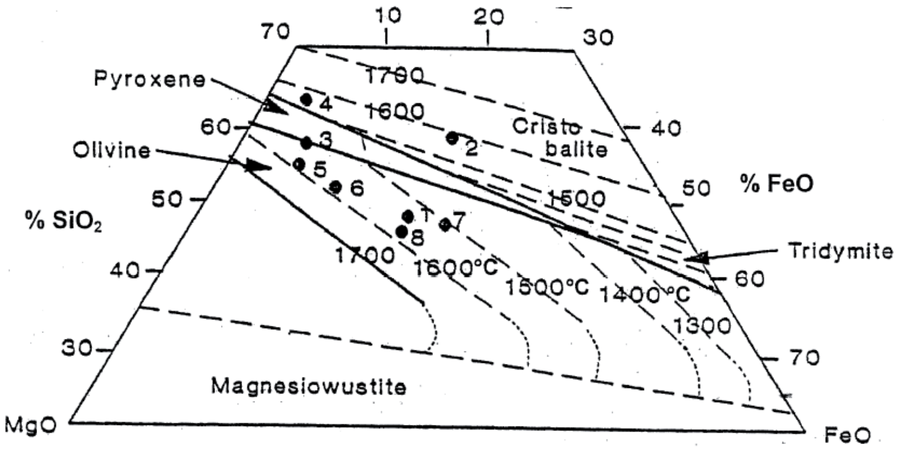

Figure 1: Nominal slag compositions for various ferro-nickel smelting operations[1]

The phase equilibria in this system [2] in the temperature range from 1200 to 1500 °C in equilibrium with iron metal have been well established through careful experimental studies. Recent investigations also at metallic iron saturation have extended the range of compositions and temperatures to 1650^{o}C in the cristobalite, tridymite and pyroxene primary phase fields [3] and in olivine primary phase field [4]. These new data have been incorporated into the Factsage model.

In practice, in addition to the major components, Al_2O_3 and Cr_2O_3 are also present in the ferronickel smelting slags. It has been shown [5-9] that additions of CaO, Al_2O_3 and Cr_2O_3 also decrease the liquidus temperatures in the cristobalite, tridymite and olivine primary phase fields. One of the features of the olivine primary phase is the extensive solid solution between the olivine and fayalite end members. The positions of the tie lines between the solid and liquid phase are functions of temperature and bulk slag composition [2-6]. These data indicate the presence of these extensive solid solutions may make the system particularly sensitive to temperature changes in sub-liquidus conditions. As the proportion of solids increase through the formation of olivine, $2(Mg,Fe)O.SiO_2$, this also leads to increases in silica concentration in the remaining liquid; both increase in % solids and silica concentration in liquid favour increased slag viscosities.

Model predictions [10] of phase equilibria in low MgO relevant to nickel sulphide smelting have been reported and demonstrate the effect of Fe/SiO_2 ratio and CaO addition on liquidus temperatures in the MgO-“FeO”-SiO_2 system at high SiO_2/MgO ratios; these composition ranges are of particular interest to nickel smelting from sulphide ores. Experimental measurements of liquidus and viscosities have been carried out MgO-“FeO”-SiO_2 system with CaO addition [11], again for compositions low in MgO and CaO relevant to nickel sulphide smelting.

In the present study the focus is to provide information on the liquidus and viscosities for studies in MgO-“FeO”-SiO_2 system in composition ranges relevant to ferronickel smelting, with particular focus on saprolitic ores having low SiO_2/MgO ratios and low Fe/ SiO_2 ratios.

2 MODELLING TOOLS

The thermodynamic modelling of oxide systems was carried out using FactSage [12] - the computer package used worldwide for prediction of multi-component multi-phase equilibria and thermodynamic properties. The FactSage databases contain thermodynamic data on over 5000 compounds as well as evaluated databases for complex non-ideal solutions (alloys, slags, salts, mattes, ceramics, etc.). The methodology used for the database development involves a series of related steps. In the thermodynamic "optimisation" of a system, all available thermodynamic and phase equilibrium data for the system are evaluated simultaneously in order to obtain one set of model equations for the Gibbs energies of all phases as functions of temperature and composition. From these equations, all of the thermodynamic properties and the phase diagrams can be back-calculated. In this way, all the data are rendered self-consistent and consistent with thermodynamic principles. Thermodynamic property data, such as activity data, can aid in the evaluation of the phase diagram, and phase diagram measurements can be used to deduce thermodynamic properties. Discrepancies in the available data can be identified. The self-consistent thermodynamic database developed in this way is used within the computer system FactSage. The recent experimental data [2-8] has been incorporated into FactSage database [13].

A structurally based model has been developed that enables the viscosities of slags in the Al_2O_3-CaO-‘FeO’-K_2O-Na_2O-MgO-SiO_2 system to be predicted within experimental uncertainties over a wide range of compositions and temperatures. The Eyring equation is used to express viscosity as a function of temperature and composition. The model links the vaporisation and activation energies in the slag viscosity expression to the slag internal structure through the concentrations of various $Si_{0.5}O$, $Me^{n+}{}_{2/n}O$ and $Me^{n+}{}_{1/n}Si_{0.25}O$ viscous flow structural units. The concentrations of these structural units are derived from a quasi-chemical thermodynamic model of the liquid slag using FactSage computer package and ChemApp software. The model describes a number of slag viscosity features including the charge-compensation effect specific for the Al_2O_3-containing systems. Viscosities of slag slurries (solid/liquid mixtures) obtained at sub-liquidus conditions have been predicted using Roscoe equation. Development of the model is described in a series of publications [14-16].

3 RESULTS

The predictions have been selected to cover a range of compositions and conditions that may be approximate those encountered in smelting of saprolitic ores. All calculations are at pure metallic iron saturation. Iron metal saturation has been selected for convenience of the calculations. The iron activity in practice will depend on alloy composition. It has been shown that the activities iron-nickel alloys are close to ideal [17], under the oxygen partial pressures and temperatures used in ferronickel smelting concentration of Fe^{3+} in the slag is low, all iron can be assumed to be in the form of Fe^{2+}.

To enable the systematic variation of the liquidus, %solids and slag viscosities as a function of composition and temperature a series of sections in the MgO-"FeO"-SiO_2 system and MgO-"FeO"-SiO_2 – Al_2O_3 system have been selected. For comparison of the behaviour of the different slags a temperature of 1500°C has been selected.

3.1 MgO-"FeO"-SiO_2

Fig 2 shows the calculated liquidus temperatures, T_{liq}, for MgO/FeO wt. ratios 0, 1, 2, 3, 4 as a function of SiO_2 concentration in the range 0.4 to 0.6 wt fraction SiO_2. The MgO/FeO wt. ratio of 0 has been included for comparison since this represents the "FeO' - SiO_2 binary; the liquidus shown is for the silica primary phase field, which is seen to increase progressively with increasing silica concentration in this range of compositions. For MgO/FeO wt. ratios 1, 2, 3, 4 in the range investigated, starting at 0.4wt fraction SiO_2 the primary phase field is olivine, transitioning to pyroxene and finally to silica as the silica concentration increases. The liquidus in the primary phase field of pyroxene is seen to almost constant with increasing silica and corresponds to the minimum liquidus temperatures for each of these sections. This minimum moves progressively to higher silica concentrations with increasing MgO/FeO ratio.

The wt % solids present in the slags at 1500°C as a function of SiO_2 concentration MgO/FeO wt. ratios 0, 1, 2, 3, 4 are shown in Fig 3. The liquidus at 1500°C for MgO/FeO = 0 is at 0.45 wt fraction SiO_2, the proportion of solids increasing with increasing silica concentration. For MgO/FeO = 1, the liquidus is at 0.5 wt fraction SiO_2, below this value the wt% solids increase steeply to 58% solids at 0.4 SiO_2; the slag is fully liquid between SiO_2 = 0.5 and 0.56. The behaviour for MgO/FeO = 2 is similar to MgO/FeO = 1 with a displacement of the lines to higher silica concentrations. For MgO/FeO = 3 and 4, the slags are always below the liquidus in the composition range investigated and % solids increases sharply with increasing MgO/FeO ratio.

The changes in the slag viscosities with composition at 1500°C in this range of conditions are given in Fig 4; there are some make interesting comparisons to be drawn from these data. For MgO/FeO = 0 the slag viscosities increase with increasing silica concentration from the liquid only to liquid + solids regions; the slag viscosity at 20vol% solids approximately 0.4 Pa s. For MgO/FeO = 1, when the slag is fully liquid the viscosity increases with increasing silica concentration. Note, however, that the slag viscosity decreases form 0.6 to 0.4 Pas with increasing silica concentration from 0.45 to 0.5. The behaviour for MgO/FeO = 2 is similar to MgO/FeO = 1 with a displacement of the lines to higher silica concentrations. For MgO/FeO = 3, the slags are always below the liquidus in the composition range investigated and viscosities vary sharply with composition as the proportion of olivine and pyroxene solids change with increasing silica concentration. The viscosities for MgO/FeO = 4 have not been included since there is greater than 20vol % solids for all compositions in the range studied.

Selecting a fixed MgO/FeO = 2 the properties of these slags as a function of temperature have also been calculated. Fig 5 shows wt % solids present in the slags at temperatures between 1450 and 1650°C as a function of SiO_2 concentration. Clearly increasing temperature results in the liquidus moving progressively to lower SiO_2 concentrations as the temperatures are increased. Combining this information to demonstrate the effect of temperature on liquid viscosities it can be seen in Fig 6 that the minima in liquid viscosities move to lower SiO_2 concentrations as the temperatures are increased. The minimum viscosity moves from 0.55 to 0.50 SiO_2 as the temperature is raised from 1500 to 1600 °C. At 0.50 SiO_2 the slag viscosity at 1500 °C is 5 times that at 1600 °C.

The phase equilibria and variations in properties with composition and temperature may be viewed from an alternative prospective, by selecting fixed SiO_2/ MgO ratios in the slag. Fig 7 shows the calculated liquidus temperatures, T_{liq}, for SiO_2/MgO wt. ratios 1.5, 2.0, 2.5, 3.0 as a function of FeO concentration in the range 0 to 0.4 wt fraction FeO. For SiO_2/MgO = 1.5 the liquidus appears to be almost independent of the iron oxide concentration in the slag over the range investigated; this is associated with the shape of the olivine liquidus surface. With increasing SiO_2/MgO ratio the liquidus in the olivine primary phase field decreases, however, this is also accompanied by the appearance of the pyroxene and silica primary phase fields, which become increasingly dominant.

At 1500°C the % solids at concentrations less than 0.1 weight fraction are in all cases very high (Fig 8). For For SiO_2/MgO = 1.5 the % solids exceeds 0.20 wt fraction for the whole range of compositions investigated. The viscosities of these slags at 1500°C are shown in Fig 9. Whilst the viscosities of the slags with SiO_2/MgO = 1.5 remain constant with FeO concentration over the limited range in which there is less than 20 volume % solids, the viscosities of all other slags decrease with increasing FeO concentration.

Selecting a fixed SiO_2/MgO = 2 the properties of these slags as a function of temperature have also been calculated. Fig 10 shows wt % solids present in the slags at temperatures between 1400 and 1650°C as a function of FeO concentration. Above 1550 °C and above 0.1 weight fraction FeO the slags are completely liquid. At 1500°C the proportion of solids rises rapidly with decreasing %FeO in the silica primary phase field, the trend is similar at 1400 and 1450 °C with the appearance of silica and pyroxene at low FeO concentrations; at higher concentrations the olivine phase is also present increasing the % solids with increasing FeO.

Fig 11 shows the effect of temperature on liquid viscosities for slags containing fixed SiO_2/MgO = 2. The viscosity of the liquid phase decreases with increasing FeO and increasing temperature in all cases. The sharp increase in slag viscosity at 1450 and 1500 °C is associated with the rapid increase in % solid silica. At 1400 °C there is greater than 20 vol % solids apart from a very narrow range of compositions.

A number of important points to emerge from these calculations;
1) The presence of extensive solid solutions between $2MgO.SiO_2$ and $2FeO.SiO_2$ in the olivine primary phase leads to high liquidus temperatures across a range of MgO/FeO ratios.
2) Slags at sub-liquidus temperatures in the olivine primary phase field contain higher % solids than if there were only stoichiometric $2MgO.SiO_2$ solid formed. These high % solids lead to high sensitivity of slag viscosity to slag composition when operating in the olivine primary phase field.
3) At high silica concentrations even in fully liquid slags the viscosity increases with increasing silica concentration.
4) The slag viscosity and % solids both increase rapidly with decreasing %FeO concentration in the silica primary phase field.

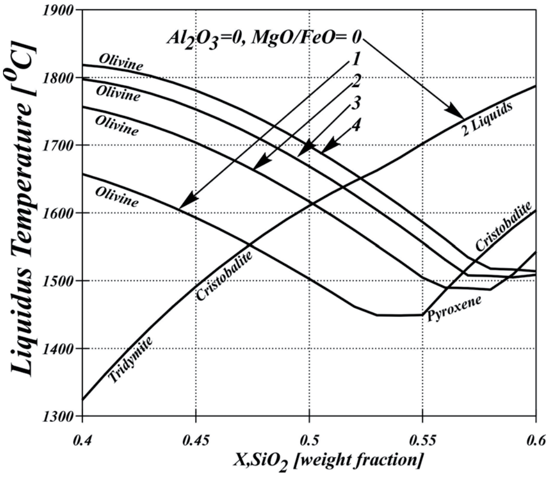

Figure 2: Calculated liquidus temperatures for slags with MgO/FeO wt. ratios 0, 1, 2, 3, 4 as a function of SiO_2 concentration

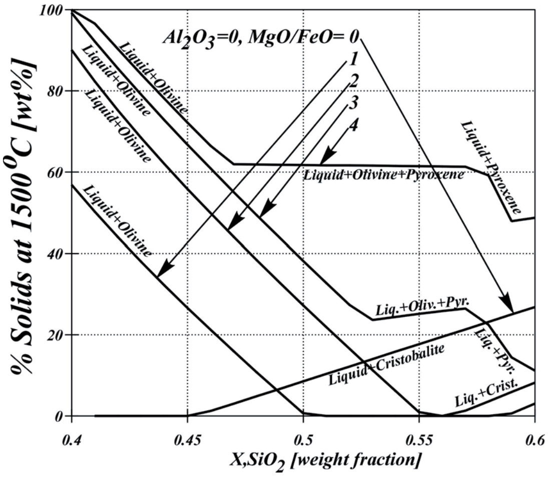

Figure 3: Calculated wt % solids present in slags at 1500°C as a function of SiO_2 concentration for MgO/FeO

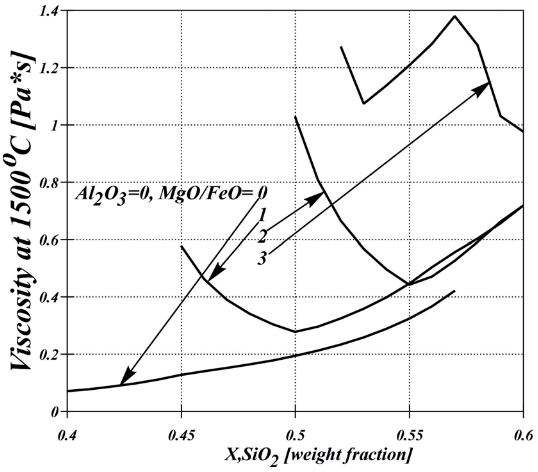

Figure 4: Calculated viscosities in slags at 1500°C as a function of SiO_2 concentration for MgO/FeO wt. ratios 0, 1, 2, 3, 4

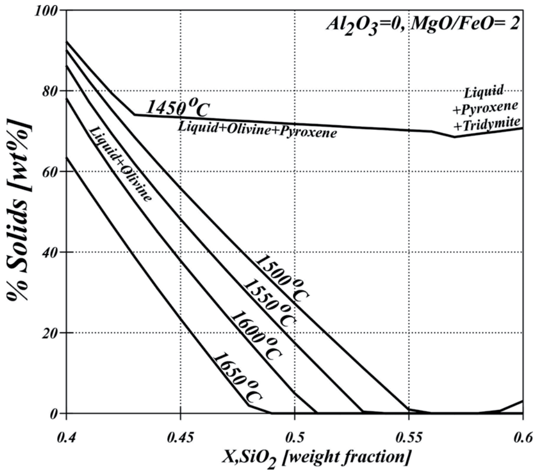

Figure 5: Calculated wt % solids present in slags as a function of temperature and SiO_2 concentration for MgO/FeO wt. ratio = 2

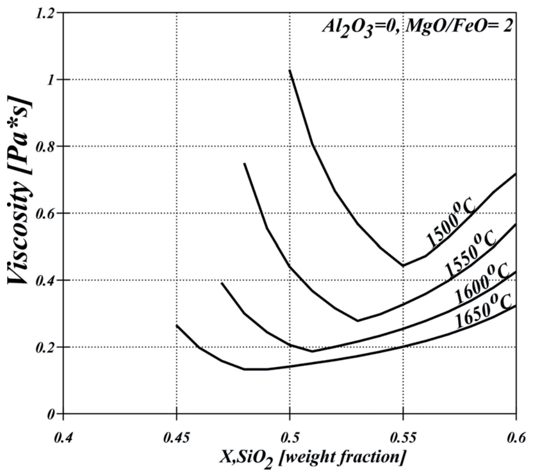

Figure 6: Calculated viscosities in slags as a function of temperature and SiO_2 concentration for MgO/FeO wt. ratio = 2

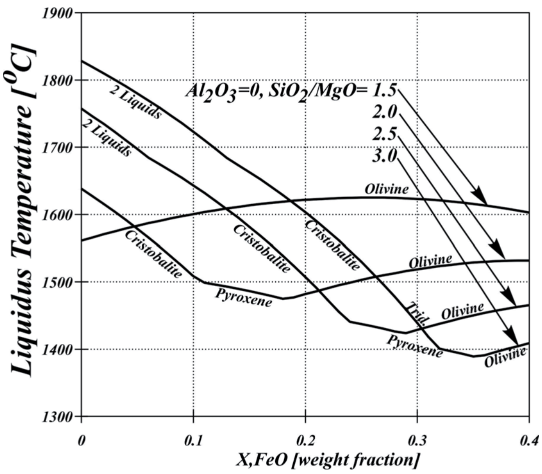

Figure 7: Calculated liquidus temperatures in the slags for SiO_2/MgO wt. ratios 1.5, 2.0, 2.5, 3.0 as a function of FeO concentration

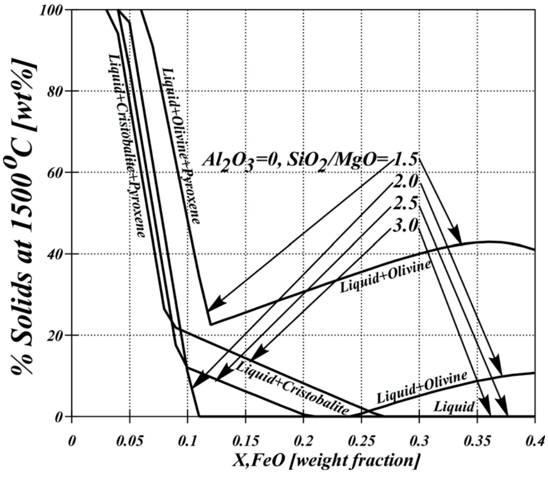

Figure 8: Calculated wt % solids present in the slags at 1500°C for SiO_2/MgO wt. ratios 1.5, 2.0, 2.5, 3.0 as a function of FeO

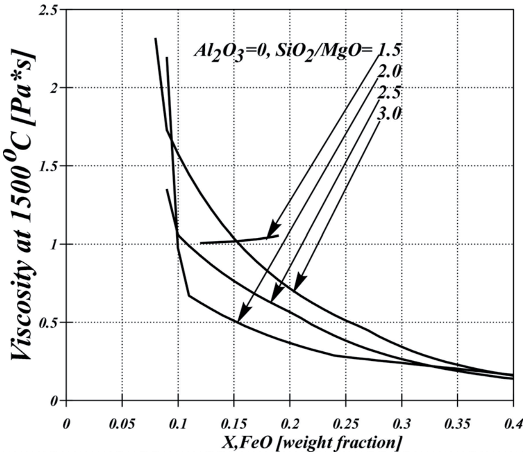

Figure 9: Calculated viscosities in the slags at 1500°C for SiO_2/MgO wt. ratios 1.5, 2.0, 2.5, 3.0 as a function of FeO

concentration at 1500°C.

concentration

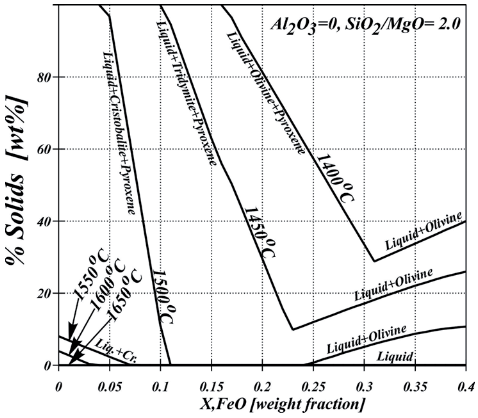

Figure 10: Calculated wt % solids present in the slags for SiO_2/MgO wt. ratio = 2.0 as a function of temperature and FeO concentration

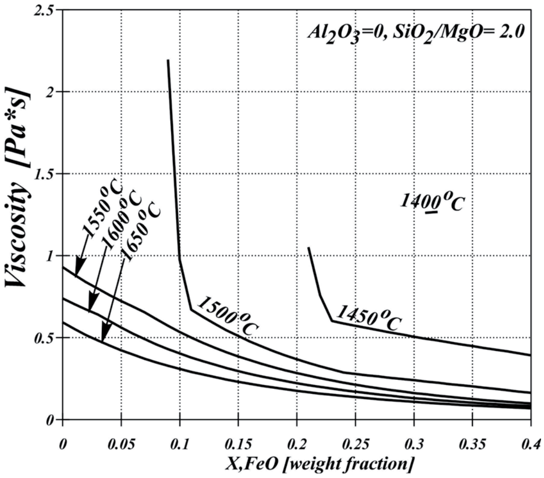

Figure 11: Calculated viscosities in the slags for SiO_2/MgO wt. ratio = 2.0 as a function of temperature and FeO concentration

3.2 MgO-“FeO”-SiO_2 – Al_2O_3

It has been shown that the presence of alumina can significantly reduce liquidus temperatures in the silica, pyroxene and olivine primary phase fields [5, 6]. These effects are now explored in more detail by examining the effect of 3wt% Al_2O_3 in slag and comparing the resulting properties with corresponding alumina-free slags.

Fig 12 shows the calculated liquidus temperatures, T_{liq}, for MgO/FeO wt. ratios 0, 1, 2, 3, 4 as a function of SiO_2 concentration in the range 0.4 to 0.6 wt fraction SiO_2 for 3wt% Al_2O_3 in slag. The liquidus data show identical trends to those in Al_2O_3-free slags (Fig.2) but the liquidus temperatures are lower over silica, pyroxene and olivine primary phase fields.

The wt % solids present in the slags at 1500°C as a function of SiO_2 concentration MgO/FeO wt. ratios 0, 1, 2, 3, 4 for 3wt% Al_2O_3 in slag are shown in Fig 13. The % solids are uniformly lower in these alumina containing slags compared with the Al_2O_3-free slags (Fig.3). The effect of the presence of Al_2O_3 on the slag viscosities is illustrated in Fig 14. Here it can be seen that there are major influences on slags with MgO/FeO wt. ratios 3 and 4; since these slags become fully liquid at the high silica concentrations there are significant decreases in overall slag viscosities with the presence of Al_2O_3. However, whilst the presence of Al_2O_3 has the effect of decreasing the liquidus temperatures and the % solids at any temperature, the presence of Al_2O_3 in the liquid does increase the viscosity of the liquid phase; this can be readily seen by inspecting the viscosities of the fully liquid slags. This trend is also apparent in Fig 15 showing the effect of temperature of viscosities of slags with MgO/FeO =2, and compared to data for alumina-free slags shown in Fig 6.

Fig 16 shows the calculated liquidus temperatures, T_{liq}, for SiO_2/MgO wt. ratios 1.5, 2.0, 2.5, 3.0 as a function of FeO concentration in the range 0 to 0.4 wt fraction FeO for 3wt% Al_2O_3. Comparison with the data shown in Fig 7 shows that the presence of alumina in slag lowers the liquidus temperatures in the silica primary phase field more than in the olivine primary phase field. Again it can be seen in Figs 17 and 18 that the viscosities of fully liquid slags containing alumina are greater than those without alumina (Figs. 9 and 11).

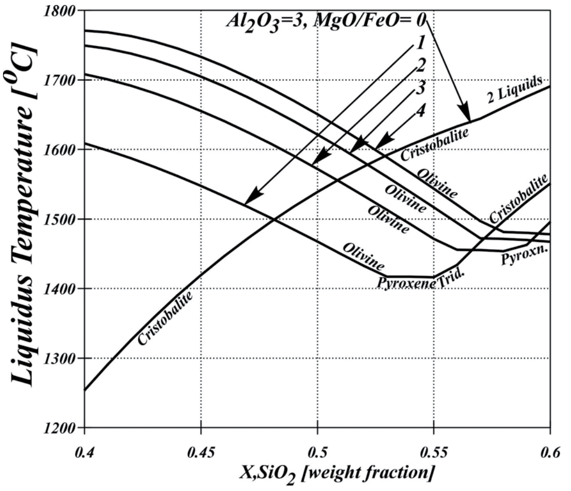

Figure 12: Calculated liquidus temperatures for MgO/FeO wt. ratios 0, 1, 2, 3, 4 as a function of SiO_2 concentration at 3wt%Al_2O_3

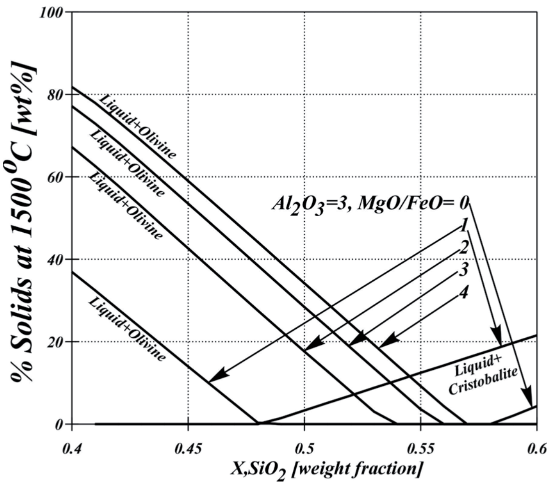

Figure 13: Calculated wt % solids present in slags at 1500°C for MgO/FeO wt. ratios 0, 1, 2, 3, 4 as a function of SiO_2 concentration at 3wt%Al_2O_3

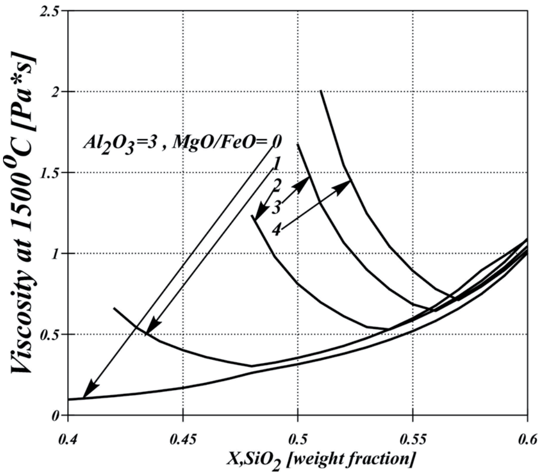

Figure 14: Calculated viscosities in the slags at 1500°C for MgO/FeO wt. ratios 0, 1, 2, 3, 4 as a function of SiO_2 concentration at 3wt%Al_2O_3

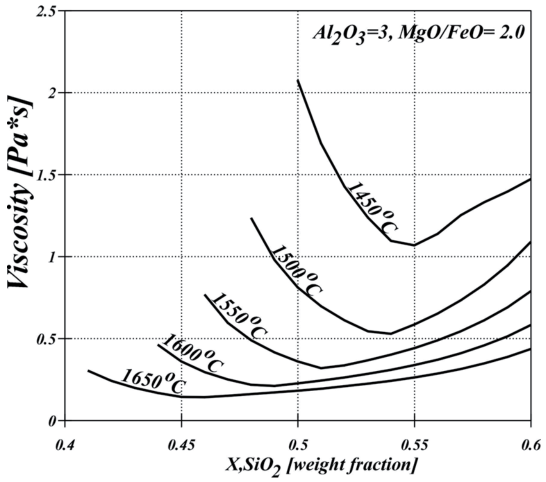

Figure 15: Calculated viscosities in the slags for MgO/FeO wt. ratios = 2 as a function of temperature and SiO_2 concentration at 3wt%Al_2O_3

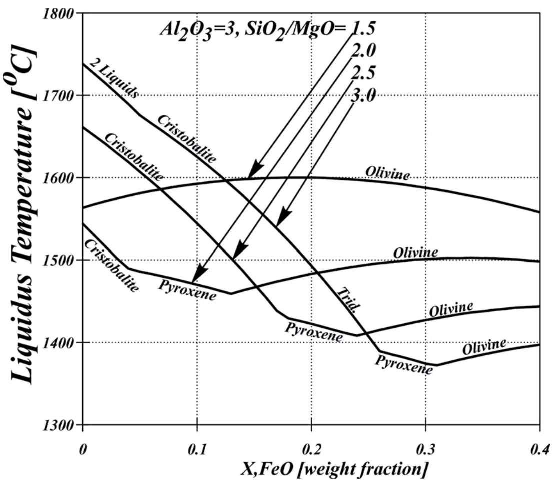

Figure 16: Calculated liquidus temperatures in the slags for SiO_2/MgO wt. ratios 1.5, 2.0, 2.5, 3.0 as a function of FeO concentration at $3wt\%Al_2O_3$

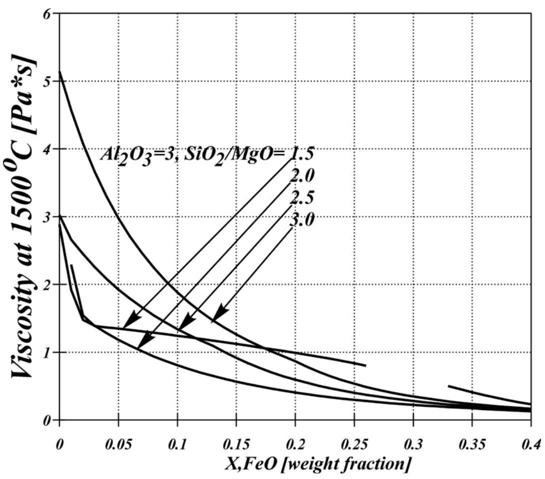

Figure 17: Calculated viscosities in the slags at 1500°C for SiO_2/MgO wt. ratios 1.5, 2.0, 2.5, 3.0 as a function of FeO concentration at $3wt\%Al_2O_3$

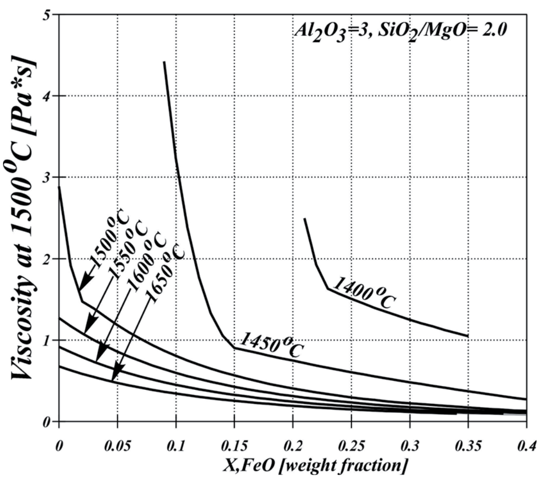

Figure 18: Calculated liquidus temperatures in the slags for SiO_2/MgO wt. ratio = 2.0 as a function of temperature and FeO concentration at $3wt\%Al_2O_3$

4 CONCLUSIONS

Model predictions using FactSage thermodynamic databases and quasichemical viscosity models have been undertaken for the system MgO-“FeO”-SiO_2-Al_2O_3 at metallic iron saturation, examining the range of compositions and temperatures relevant to ferro-nickel smelting of saprolitic nickel-bearing ores. It has been demonstrated that

1) The presence of extensive solid solutions between $2MgO.SiO_2$ and $2FeO.SiO_2$ in the olivine primary phase leads to high liquidus temperatures across a range of MgO/FeO ratios.
2) Slags at sub-liquidus temperatures in the olivine primary phase field contain higher % solids than if there were only stoichiometric $2MgO.SiO_2$ solid formed. These high % solids lead to high sensitivity of slag viscosity to slag composition when operating in the olivine primary phase field.
3) At high silica concentrations even in fully liquid slags the viscosity increases with increasing silica concentration.

4) The slag viscosity and % solids both increase rapidly with decreasing %FeO concentration in the silica primary phase field.
5) The presence of Al_2O_3 in the slags lowers the liquidus in the olivine, pyroxene and silica primary phase fields, but increases the viscosity of the liquid phase.

These trends have implications for the design of metallurgical operations since they indicate the relative sensitivities to changes in operating temperature and bulk composition. Operating below the liquidus in these systems can result in significant changes in % solids and slag viscosity this has implications for accretion build-up and tapping difficulties.

5 REFERENCES

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