Thermodynamic Calculation of Liquidus Surface of FeO$_x$–CaO–SiO$_2$ System

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As world's reserve of high grade iron ores decline, the gangue minerals, such as Al$_2$O$_3$, of iron ore have been increasing. To counter the adverse impact of alumina on sinter quality, MgO fluxes are often added to increase sinter MgO. The liquidus surface of Al$_2$O$_3$ and MgO containing FeO$_x$–CaO–SiO$_2$ system is therefore of fundamental importance to understanding of the melting mechanism in the sintering process. In this study, the literature data on the liquidus surface of the FeO$_x$–CaO–SiO$_2$ system containing Al$_2$O$_3$ and MgO under various temperatures and oxygen partial pressures, which are relevant to the iron ore sintering, were carefully reviewed, and the differences between various data sources were analysed. A modified version of the thermodynamic package: Multi-Phase Equilibrium (MPE) software developed by CSIRO was compiled, including refinement of its slag database, to cover the compositional and atmospheric conditions encountered in the sintering process. The effects of oxygen partial pressure and additions of Al$_2$O$_3$ and MgO on the liquidus of the FeO$_x$–CaO–SiO$_2$ system were modelled. The model predictions represent experimental results well, and show that the liquid field at 1 573 K shrinks with the oxygen partial pressure decreasing from 10$^{-3}$ to 10$^{-8}$ atm and separates into two distinct liquid fields. As the oxygen partial pressure decreases further from 10$^{-8}$ to 10$^{-10}$ atm, both liquid fields expand and merge to form a continuum. Addition of Al$_2$O$_3$ and MgO is found to increase the stability of the magnetite (spinel) phase, shift the liquidus away from the FeO$_x$ corner, and therefore suppress the formation of the melt during sintering.

KEY WORDS: thermodynamic modelling; liquidus; CaO–SiO$_2$–FeO$_x$ system; iron ore sintering; oxygen partial pressure; melting behaviour.

1. Introduction

Sintering is an important process used to convert iron ore fines into a suitable lumpy product through a series of physical and chemical reactions for blast furnace ironmaking use. During the sintering process, combustion of coke particles in the sinter mixture continues to raise the temperature of the mixture to achieve partial fusion and generate a melt phase, which assimilates surrounding coarse particles and adhering fines and on cooling solidifies into the sinter matrix that bonds the sinter structure together. Hence the volume and properties of the sinter melt formed become extremely important and determine the quantity and quality of the sinter matrix and, therefore, sinter quality and yield.

Due to the limited reserves and increasing depletion of high-grade iron ore resources, the alumina and phosphorus contents and the loss on ignition (LOI) of iron ores are expected to gradually increase. A small increase in the alumina content of sinter blends can have a significant adverse impact on the strength of final sinter, particularly, the sinter strength after low temperature reduction (RDI). To counter the adverse impact of alumina on sinter RDI, additional MgO fluxes are often added to increase sinter MgO.

The chemical composition of the primary melt formed during iron ore sintering can be considered to fall within the range of the FeO$_x$–CaO–SiO$_2$ system.$^{11}$ Though the oxygen partial pressure corresponding to the iron ore sintering process is not well defined, it is expected to be in the range of 10$^{-8}$ to 10$^{-3}$ atm.$^{11}$ The liquidus surface of the FeO$_x$–CaO–SiO$_2$ (FCS) system containing MgO and Al$_2$O$_3$ under different oxygen partial pressures is therefore of fundamental importance to understanding of the formation mechanism of sinter melt in the sintering process.

The literature data available up to Year 2000 on the effect of oxygen partial pressure and additions of Al$_2$O$_3$ and MgO on the liquid region of the FeO$_x$–CaO–SiO$_2$ and its sub-systems are critically reviewed by Yazawa.$^{21}$ More experimental$^{1–8}$ and modelling efforts$^{9,10}$ have since been made on the FeO$_x$–CaO–SiO$_2$ system under the compositional conditions and oxygen partial pressures more relevant to the iron ore sintering process. However, the model prediction$^{9,10}$ does not agree with the experimental data by Shigaki et al.$^{11}$ particularly in magnetite saturation region.

The experimental and modelling studies in the literature have provided valuable information for improved understanding of the liquidus region of the system at intermediate oxygen partial pressures, particularly when the experimental data are limited. However, there were considerable discrepancies in the position of the liquidus surface at 1 573 K under various oxygen partial pressures in the litera-
ture$^{3–8,11–13}$) and between the experimental data$^{3–8,11}$) and modelling results.$^{9,10}$

In this paper, a modified version of the computational package: Multi-Phase Equilibrium (MPE) software developed by CSIRO$^{14,15}$ was used to quantify the liquidus surface of the FeO$_n$–CaO–SiO$_2$ system containing Al$_2$O$_3$ and MgO at various intermediate oxygen partial pressures.

2. Method of Thermodynamic Calculation for FCS System

The cell model based on binary parameters only was proposed by Kapoor and Frohberg$^{16}$) and later extended by Gaye and Welfringer$^{17}$ for describing the slag phase. The CSIRO group adopted the cell model and developed a comprehensive database to include a substantial list of oxide species commonly found in both ferrous and non-ferrous metal smelting. The model was incorporated in a computational package: Multi-Phase Equilibrium (MPE).$^{14,15}$ For the better description of Al$_2$O$_3$-containing slags, the cell model was further extended by introducing ternary parameters by Zhang$^{18}$) MPE has been validated and successfully applied for process design and optimization of ironmaking and non-ferrous smelting processes.$^{19,20}$ Compared with the ironmaking and non-ferrous smelting processes, the oxygen partial pressure encountered in the sintering process is much higher, likely varying from $10^{-6}$ to $10^{-3}$ atm at the end of melt formation, and therefore the sinter melt formed during sintering are expected to be rich in Fe$^{3+}$.

MPE is capable of calculating the liquidus of the slag under varied oxygen partial pressure and temperature. It was found that the liquidus of the FeO$_n$–CaO–SiO$_2$ system under iron saturation can be represented very well by MPE. However, the MPE fit to the liquidus of the FeO$_n$–CaO–SiO$_2$ system in the air is not accurate. In the present study, two Fe$_2$O$_3$–CaO–SiO$_2$ ternary parameters were introduced and the SiO$_2$–FeO$_2$ binary parameters were re-optimized to fit the liquidus data of FeO$_n$–CaO–SiO$_2$ system in the air at 1 573 K.$^{5,7,12,13}$

Figure 1 compares the liquidus surface of the FeO$_n$–CaO–SiO$_2$ system in air at 1 573 K and 1 513 K measured by Henao$^{19}$ et al., by Nikolic$^{19}$ et al., by Phillips and Muan,$^{12}$) by Pownceby$^{13}$ et al., and the model calculation. There is general agreement between these sets of data except for the region of SiO$_2$ content ranging from 10 to 20 mass%. As shown in Fig 1(a), two separate liquid fields were reported for this region at 1 573 K by Phillips and Muan.$^{12}$ However, the liquid field measured by Pownceby$^{13}$ et al. extends across the entire compositional range at 1 573 K, and shrinks with decreasing temperature and splits into two distinct fields only at the temperature below 1 528 K. Compared with 64 compositions covered in Pownceby’s study,$^{13}$) only 16 mixtures from Phillips and Muan$^{12}$ were within the compositional range covered by Pownceby et al.$^{13}$ Therefore, the liquid surface data reported by Pownceby et al. for the region from 10 to 20 mass% SiO$_2$ is considered to be better defined, and used for optimising the SiO$_2$–FeO$_2$ binary and FeO$_n$–CaO–SiO$_2$ ternary parameters, which are listed in Table 1.

The agreement between the model calculation and the experimental measurements confirms the model parameters have been set properly.

The refined model was ready to be used for predicting the liquidus surface of the system under various oxygen partial pressures, temperature, and slag chemistry which are of interest to iron ore sintering process.

3. Results

3.1. Effect of Oxygen Partial Pressure

In Fig. 2(a), the liquidus surface of the FeO$_n$–CaO–SiO$_2$ system at $P_{O_2}$ of $5 \times 10^{-3}$ atm and 1 573 K predicted by model is compared with the liquidus surface of the system...
measured by Pownceby and Clout\textsuperscript{3}) and by Kimura et al.\textsuperscript{4}) As shown in Fig. 2(a), model prediction agrees with the Pownceby’s measurement\textsuperscript{3}) well, in particular, in FeO, rich region. Figure 2(a) also shows that the liquidus surface measured by Kimura et al.\textsuperscript{4}) is much broader than that from Pownceby and Clout.\textsuperscript{3}) The reason for the discrepancy observed between the two studies is not clear. The liquidus surface of the FeO–Fe\textsubscript{3}O\textsubscript{4}–CaO system was also measured at the oxygen partial pressure of 10\textsuperscript{1}/H\textsubscript{2} 3 atm and the temperature of 1 473 and 1 573 K by Takeda et al.\textsuperscript{21}) It was found that at 1 573 K and oxygen partial pressure of 10\textsuperscript{3} atm, the liquid boundary is within the CaO content from 18 to 27 mass\%. This is in close agreement with the model calculation. It is worthwhile pointing out that the predicted liquidus surface at the oxygen partial pressure of 5\textsuperscript{1}/H\textsubscript{2} 10\textsuperscript{3} atm is slightly narrower than the prediction of the system in the air. While this is opposite to the experimental results,\textsuperscript{3}) the model prediction is supported by Takeda’s measurement\textsuperscript{21}) showing that the stability of magnetite improves, hence the liquid field contracts, with oxygen partial pressure decreasing from 0.21 to 10\textsuperscript{1}/H\textsubscript{2} atm. Figure 2(b) shows the comparison of the liquidus surface at \(P_{O_2}\) of 5\times10\textsuperscript{3} atm and 1 513 K between model calculation and experimental data by Pownceby and Clout.\textsuperscript{3})

The comparison of calculated liquidus in the SiO\textsubscript{2} and magnetite saturation region at the oxygen partial pressure of 4\times10\textsuperscript{1}/H\textsubscript{2} atm and 1 573 K with the experimental data by Henao et al.\textsuperscript{5}) and Nikolic et al.\textsuperscript{7}) is plotted in Fig. 3. It is clear that model prediction agrees very well with the data from the experimental study.\textsuperscript{5,7} Figure 3 also shows that there exists considerable difference in the literature data.\textsuperscript{5,7} As analysed by the authors of both studies,\textsuperscript{5,7} the results by Nikolic et al.\textsuperscript{7}) is more reliable. As shown in Figs. 1(a) and 3, both model calculation and experimental data by Nikolic et al.\textsuperscript{7}) show that the liquid surface shrinks at high SiO\textsubscript{2} area, and the magnetite saturation boundary moves away from the FeO\textsubscript{3} corner as the oxygen partial pressure decreases from 0.21 to 4\times10\textsuperscript{1}/H\textsubscript{2} atm. This is opposite to the findings by Pownceby and coworkers\textsuperscript{3,13)} in Figs. 1(a) and 2(a). The opposite trend observed by different researchers is probably due to the fact that the change of the liquidus surface with oxygen partial pressure is so small that it could be easily masked by experimental uncertainties. This explanation is at least partially supported by the experimental results from Henao et al.\textsuperscript{5}) and Nikolic et al.\textsuperscript{7}) As shown in Fig. 1(a), the hematite saturated liquid boundary reported by Pownceby and Clout\textsuperscript{3}) shifted slightly but consistently away from the FeO\textsubscript{3} corner compared with the results by Henao et al.\textsuperscript{5}) and Nikolic et al.\textsuperscript{7}), which are in good agreement with each other.

Figure 4 shows the liquidus surface of the FCS system at 1 573 K and oxygen partial pressure of 10\textsuperscript{1}/H\textsubscript{2} atm measured by Kimura et al.,\textsuperscript{4}) Henao et al.,\textsuperscript{5}) Nikolic et al.,\textsuperscript{6}) Matsuura et al.\textsuperscript{8}) and model prediction. As shown in Fig. 4, the model calculated liquid surface of the system agrees with the measurement by Henao et al.,\textsuperscript{5}) Nikolic et al.,\textsuperscript{6}) and Matsuura et al.\textsuperscript{8}) However, the liquidus reported by Kimura et al.\textsuperscript{4}) is much broader than the model calculation and other experimental data. As confirmed by the same group of investigators,\textsuperscript{8}) the contamination of the liquid sample with solid phases by Kimura et al.\textsuperscript{4}) is responsible for the discrepancy observed. Figure 4 also shows that the liquidus of the Ca\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5} saturated region, the liquid area predicted by model is broader than that measured by Henao et al.\textsuperscript{5}) This is probably due to the experimental error introduced by the chemical analysis of the samples. It was found to be difficult in some cases to distinguish the quenched Ca\textsubscript{2}Fe\textsubscript{2}O\textsubscript{5} crystals from the primary crystals, which were in equilibrium with the melt.\textsuperscript{3})

The calculated liquidus of the magnetite saturation re-
region at oxygen partial pressure of 10^{-6} atm and various temperatures are compared with the experimental data by Henao et al.\(^5\) and by Nikolic et al.\(^6\) in Fig. 5(a). The comparison of the calculated liquidus surface of high SiO\(_2\) region at 1523 K and oxygen partial pressures of 10^{-5} and 10^{-6} atm with the experimental data by Nikolic et al.\(^6\) are plotted in Fig. 5(b). As shown in Figs. 5(a) and 5(b), the stability of magnetite decreases drastically with increasing temperature and decreasing oxygen partial pressure, which can be represented very well by model calculation. It can also be seen in Fig. 5(b) that the liquid boundary saturated with SiO\(_2\) and CaSiO\(_3\) solid phases was not affected by the oxygen partial pressure. The reason for this is that the effect of the oxygen partial pressure on the stability of SiO\(_2\) and CaSiO\(_3\) phases is insignificant.

Figure 6 shows the calculated liquidus surface of the system at the oxygen partial pressure of 10^{-7} atm along with the experimental data by Henao et al.,\(^5\) Matsuura et al.\(^8\) and by Shigaki et al.\(^11\). It can be seen that the model calculation agrees with the magnetite saturated liquid boundary by Henao et al.\(^5\) and Matsuura et al.\(^8\). The position of the magnetite saturated liquidus by Shigaki et al.\(^11\) is much higher. It is probably because the equilibrium time in Shigaki’s experiment was only 3 h, which is unlikely sufficient to allow the samples to reach equilibrium.

The experimental measurement of the liquidus of FCS system at 1573 K and oxygen partial pressure of 10^{-8} atm by Kimura et al.\(^4\) and by Henao et al.\(^5\) are plotted in comparison with model prediction in Fig. 7(a). There is general agreement between the model calculations and experimental studies,\(^4,5\) except that at the FeO-rich corner. The wustite saturation region measured by Kimura et al.\(^4\) is much smaller than that by Henao et al.\(^5\) and model calculation. The liquidus of the system saturated with metallic iron at the FeO corner was also plotted in Fig. 7(a). Taking into account of the fact that increase in oxygen partial pressure from iron saturation to 10^{-8} atm stabilizes wustite, therefore, enlarges the solid saturation area in FeO corner, the published liquidus at the FeO corner under iron saturation tends to support the Henao’s measurements and the model calculation. As shown in Fig. 7(b), the model calculation generally agrees with the experimental measurements by Matsuura et al.\(^8\) that the liquid filed is separated into two regions at 1523 K.

The calculated liquid region of the FCS system at 1573 K and varied oxygen partial pressure are summarized
in Figs. 8(a) and 8(b). As shown in Fig. 8(a), the liquid region shrinks and separates into two distinct liquid fields as the oxygen partial pressure decreases from $10^{-3}$ to $10^{-5}$ atm. This is because more Fe$^{2+}$ is generated as the oxygen partial pressure decreases, which promotes transition of hematite to magnetite at the FeO corner, and therefore shrinks the liquid field. As the oxygen partial pressure decreases further from $10^{-6}$ to $10^{-8}$ atm (Fig. 8(b)), the excess Fe$^{2+}$ combines with SiO$_2$ to form low melting point silicate slags, so that both liquid fields are expanded and rejoined to form a continuum. The effect of oxygen partial pressure on the phase constitution of a typical sinter mixture (5 mass% SiO$_2$, 12 mass% CaO, 83 mass% FeO$_x$) at 1573 K was quantified by model calculation. As shown in Fig. 9, the amount of liquid phase varies with oxygen partial pressure in a “dumpbell” shape. The liquid phase reaches about 46 mass% at the oxygen partial pressures of $10^{-3}$ and $10^{-7}$ atm. However, in the $P_{O_2}$ range of $10^{-5}$ to $10^{-6.5}$ atm, the stability of magnetite reaches a maximum where the liquid phase contracts to 10 mass% and about 15 mass% dicalcium silicate precipitates from the melt.

### 3.2. Effect of Temperature

Figure 10 shows the effect of temperature on the liquidus surface of FeO$_x$–CaO–SiO$_2$ system at the oxygen partial pressure of 10$^{-7}$ atm. It’s not surprising that two liquid fields at 1523 K are expanded with increasing temperature, and jointed to form a continuum at 1573 K. The liquid field is further broadened with increasing temperature to 1623 K. It is clear from the Fig. 5(a) and Fig. 10 that the temperature has a significant effect on the stability of wustite/magnetite, hence the liquidus of the wustite/mag-
netite saturation region, where the composition of the sinter mixture falls in.

3.3. Effect of Al$_2$O$_3$

Figure 11(a) presents the liquidus surface of FeO$_x$–CaO–SiO$_2$ system with 2 mass% Al$_2$O$_3$ at 1573 K in the air reported by Yan et al.\textsuperscript{23} and model prediction. Both results suggest that addition of Al$_2$O$_3$ up to 2 mass% has no significant impact on the liquidus.

The model calculated liquid region of the FeO$_x$–CaO–SiO$_2$ system containing 5 mass% Al$_2$O$_3$, at 1573 K and oxygen partial pressures of $10^{-3}$, $10^{-6}$ and $10^{-8}$ atm, is presented in Figs. 11(b) to 11(d) along with the experimental data of Shigaki et al.\textsuperscript{11} and Kimura et al.\textsuperscript{24} As can be seen, there is significant difference between the model prediction and the experimental data by Kimura et al.\textsuperscript{24} particular at the oxygen partial pressure of $10^{-3}$ and $10^{-6}$ atm. As pointed out by Matsuura et al.\textsuperscript{4}, the solid phases which coexist with the melt prior to quench were not accounted by Kimura et al.\textsuperscript{4,24} As Al$_2$O$_3$ is introduced into the system, solid phase such as melilite is likely to precipitate from the melt.

The effect of Al$_2$O$_3$ on the liquidus of FCS system in FeO$_x$ corner at the temperatures of 1523 and 1573 K and oxygen partial pressures of $10^{-6}$ and $10^{-8}$ atm was investigated by Henao et al.\textsuperscript{25} It was found that magnetite (spinel) stability improves with increasing Al$_2$O$_3$ addition. That is simply because FeAl$_2$O$_4$ is thermodynamically much more stable than Fe$_3$O$_4$.\textsuperscript{26} Shigaki et al.\textsuperscript{11} measured the liquid region of the FeO$_x$–CaO–SiO$_2$ system containing 5 mass% Al$_2$O$_3$ at 1573 K and oxygen partial pressure of $10^{-7}$ atm. As shown in Fig. 11(d), similar to the Al$_2$O$_3$ free FCS system, the liquid boundary saturated with magnetite by Shigaki et al.\textsuperscript{11} does not agree with the model prediction and

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig10}
\caption{Effect of temperature on the liquid region of the FeO$_x$–CaO–SiO$_2$ system at oxygen partial pressure of $10^{-7}$ atm.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig11}
\caption{Effect of Al$_2$O$_3$ on the liquid region of the FeO$_x$–CaO–SiO$_2$ system at 1573 K and various oxygen partial pressures.}
\end{figure}
the data of Nikolic et al.6) As explained in the preceding section, the difference is probably caused by the insufficient reaction time adopted in Shigaki’s experiment, which did not allow the sample to reach equilibrium. Nevertheless, the data of Shigaki et al.11) qualitatively confirmed the findings of the present model (Figs. 11(a) to 11(d)), early modelling study by Jak et al.9) and Kongoli et al.10) and experimental study by Henao et al.25) that addition of Al2O3 stabilizes magnetite and shifts the liquid region towards SiO2 and CaO corner.

Figure 11(d) also shows that addition of Al2O3 results in transition of the wustite primary phase region to magnetite (spinel) primary phase region at the oxygen partial pressure of 10^{-8} atm, which agrees with the modelling study by Kongoli and Yazawa.10)

3.4. Effect of MgO

The model predicted liquid region of the FCS system containing 5 mass% MgO at 1 573 K and oxygen partial pressures of 10^{-7}, 10^{-6} and 10^{-5} atm is presented in Fig. 12 along with the experimental data of Kimura et al.24) As discussed earlier, the difference observed on the magnetite saturation boundary between the modelling results and experimental data was probably due to the sample contamination.

From Figs. 12(a) and 12(b), the modelling results suggest that addition of MgO also stabilizes the magnetite (spinel) phase at oxygen partial pressure of 10^{-5} and 10^{-6} atm, which agrees with the experimental finding of Henao et al.25) and the modelling study by Kongoli et al.10) That is due to the fact that similar to FeAl2O4, the spinel MgFe2O4 phase is thermodynamically more stable than Fe3O4.26) Figure 12(c) shows that at oxygen partial pressure of 10^{-8} atm, addition of MgO stabilizes wustite, and enlarges wustite saturation region in FeO corner, which was supported by the modelling results by Kongoli et al.10) Kongoli’s results show that at oxygen partial pressure of 10^{-8} atm and with 3 mass% MgO addition, the primary solid phase at the FeO corner of the FCS system is wustite when the temperature is above 1 548 K. Below 1 548 K, the primary solid phase is magnetite.10) However, it was reported by Henao et al.25) that addition of MgO results in transition of the wustite primary phase region to magnetite primary phase region at 1 573 K and oxygen partial pressure of 10^{-8} atm. There are no other experimental liquidus data on the MgO containing FCS system at the temperature and oxygen partial pressure relevant to the sintering process. Due to scarce experimental data and obvious disagreement in the literature, more experimental work is required to verify the model prediction.

3.5. Effect of Combined Addition of MgO and Al2O3

The combined effect of Al2O3 and MgO on the liquidus surface of the system at 1 573 K and oxygen partial pressure of 10^{-6} atm was calculated and illustrated in Fig. 13.

Fig. 12. Effect of MgO on the liquid region of the FeO_x–CaO–SiO2 system at 1 573 K and various oxygen partial pressures.
The phase relations in Fig. 13 is believed to be more representative of the industrial sintering conditions since industrial sinter often contains both Al₂O₃ and MgO. Similar to the individual effect of Al₂O₃ or MgO, addition of 2 mass% Al₂O₃ and 2 mass% MgO in the system stabilizes the magnetite (spinel), moves the liquidus surface away from the FeO₃ corner, and suppress the formation of the melt during sintering.

4. Implications of Model Prediction for the Iron Ore Sintering

The volume and properties of the sinter melt formed determine the quantity and quality of the sinter matrix and, therefore, sinter quality and yield. As shown in Fig. 5(a) and Fig. 10, the liquidus of the magnetite/wustite saturation region of FCS system, where the composition of the sinter mixture falls in changes significantly with the temperature. Therefore, both the volume and properties of the melt formed during sintering depend heavily on temperature, which determines the fuel requirement for sintering. However excess melt formation should also be avoided as it leads to poor sintering productivity. This can be achieved by optimising fuel addition.

It is generally appreciated that melt formation during sintering is accompanied with a declining oxygen partial pressure from 10⁻⁸ atm in the beginning of melt formation to 10⁻³ atm at the end of melt formation. Based on the model prediction, the liquid field of the FeO₃-CaO–SiO₂ system at 1 573 K shrinks slightly with the oxygen partial pressure decreasing from 10⁻³ to 10⁻⁸ atm, and then expands as the oxygen partial pressure decreases further from 10⁻⁸ to 10⁻⁴ atm. The predicted expansion of liquidus surface under more reducing conditions, particularly in the FeO₃ rich region, is expected to promote the melt formation. As shown in Fig. 9, the amount of liquid phase increases remarkably from 0 to 46 mass% at 1 573 K as the oxygen partial pressures decrease from 10⁻⁵ and 10⁻³ atm. It is therefore expected that careful control of the oxygen partial pressure will have considerable impact on the formation temperature of the initial melt, hence the fuel rate and quality of sinter.

As shown in Fig. 11, addition of Al₂O₃ improves the stability of the magnetite phase and shrinks the liquidus surface. The viscosity of the melt may also increase with addition of Al₂O₃. A higher fuel rate is therefore required to achieve a higher sintering temperature to ensure a sufficient liquidus surface. Modification of sinter chemistry is considered to be very effective to reduce the liquidus and viscosity of the melt and therefore improve the sinter quality. From model prediction, MgO stabilizes the magnetite, and suppresses the formation of sinter melt even though it was reported to improve the sinter RDI. The modelling results by Chen et al. show that addition of MnO to the blast furnace slag would extend the solubility limit of Al₂O₃ while decreasing the liquidus temperature and viscosity. The addition of MnO may also improve the formation of the melt during iron ore sintering. Since the thermodynamic stability of the MnFe₂O₄ is lower than that of magnetite, it is therefore expected that the addition of MnO would destabilize the magnetite solid phase and extend the liquidus surface.

It is believed that the initial melt forms in the layer of adhering fines through Fe₂O₃–CaO interactions. The initial melt then assimilates surrounding flux and ore particles, resulting in dissolution of the solid particles. As shown in Fig. 14(a), the dissolution of SiO₂ into the calcium ferrite initial melt formed during the heating stage (10⁻⁸ atm<Pₒ₂<10⁻⁴ atm) increases the liquidus. The max-

![Fig. 13. Combined effect of Al₂O₃ and MgO on the liquid region of the FeO₃-CaO-SiO₂ system at 1 573 K and oxygen partial pressure of 10⁻⁶ atm.](image)

![Fig. 14. Effect of the oxygen partial pressure and melt chemistry on the liquidus of the initial melt formed during sintering.](image)
minimum point of the liquidus shifts towards higher oxygen partial pressure region with increasing SiO$_2$ content in the melt. Figure 14(b) shows the effect of the oxygen partial pressure on the liquidus of the low melting point with high SiO$_2$ content. It is clear that increasing CaO content leads to a decrease in melt liquidus in the SiO$_2$ primary phase field. However, the liquidus increases with the CaO content in the magnetite primary phase field. All this suggests that reactivity of flux and ore particles plays an important role in determining the composition and therefore liquidus surface of final sinter melt.

5. Conclusions

CSIRO thermodynamic package, MPE, was modified, including refinement of its slag database, to cover the compositional and atmospheric conditions encountered in the sintering process. Satisfactory agreement was confirmed between the experimental data and model calculation. The model was used for predicting the liquidus surface of the system under various oxygen partial pressures, temperature, and slag chemistry which are of interest to iron ore sintering process.

The liquid field of the FeO$_2$–CaO–SiO$_2$ system at 1 573 K shrinks and separates into two distinct liquid fields with the oxygen partial pressure decreasing from 10$^{-3}$ to 10$^{-5}$ atm. As the oxygen partial pressure decreases further from 10$^{-3}$ to 10$^{-8}$ atm, both liquid fields expand and merge to form a continuum. The quantity of the melt formed during sintering at 1 573 K and various oxygen partial pressures was also calculated for equilibrium.

The modelling results show that addition of Al$_2$O$_3$ and MgO is found to increase the stability of the magnetite (spinel) phase in the iron corner, hence increase the liquidus temperature in magnetite saturation region, and suppress the formation of the melt.

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