Effects of CaO, Al_2O_3 and MgO on liquidus temperatures of copper smelting and converting slags under controlled oxygen partial pressures

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Abstract: Phase equilibria of silicate slag systems relevant to the copper smelting/converting operations have been experimentally studied over a wide range of slag compositions, temperatures and atmospheric conditions. The systems selected are of industrial interest and fill the gaps in fundamental information required to systematically characterise and describe copper slag chemistries. The experimental procedures developed at the Pyrometallurgy Research Centre (PYROSEARCH) that have been used, include equilibration of synthetic slag at high temperatures, rapid quenching of resulting phases, and accurate measurement of phase compositions using electron probe X-ray microanalysis (EPMA). The effects of CaO, Al_2O_3 and MgO on the phase equilibria of this slag system have been experimentally investigated in the temperature range 1200 to 1300 ^{o}C and oxygen partial pressures between 10^{-5} and 10^{-9} atm.

It was found that spinel and silica are major primary phases in the composition range related to copper smelting/converting slags. In addition, olivine, diopside and pyroxene may also appear at certain conditions. The presence of CaO, MgO and Al_2O_3 in the slag increases the spinel liquidus and decreases the silica liquidus. Liquidus temperatures in silica primary phase field are not sensitive to Po_2; Liquidus temperatures in spinel primary phase field increase with increasing Po_2. At 1300 ^{o}C and low Po_2, the spinel $(Fe^{2+},Mg^{2+})O.(Al^{3+},Fe^{3+})$ primary phase field can be replaced by wustite $(Fe^{2+},Mg^{2+})O$.

Key words: copper smelting, copper converting, liquidus temperature, slag

1. Introduction

Copper sulphide ores are the major source of the world's primary copper; the copper is present in a number of minerals, common examples being CuS, Cu_2S, $CuFeS_2$, Cu_5FeS_4, $Cu_{12}As_4S_{13}$. Associated with these minerals are typically, FeS, FeS_2, silicate-based and minor minerals from the host rock. The copper must be chemically separated from sulphur, iron and a wide range of impurity elements in order to meet specifications for sale on world markets. The pyrometallurgical processing of these ores involves a series of high temperature oxidation reactions under controlled conditions.

The overall scientific basis for the pyrometallurgical production of copper is now well understood, and work in this field is exemplified by a series of experimental studies carried out by Prof Akira Yazawa, and subsequent co-workers at Tohuku University, Japan [1-6]. These studies essentially demonstrated that the Cu-Fe-O-S liquids generated during partial oxidation of copper concentrates are completely miscible, but that phase separation to sulphur-rich Cu_2S-FeS melts (mattes) and oxygen–rich FeO-SiO_2 phase (slag) can be produced through the addition of silica to the system. It is now well established that the partitioning of the various metallic elements between metal, matte, slag and gas phases are principally functions of bulk composition, oxygen and sulphur partial pressures and temperature.

The liquidus temperatures (conditions when the system is completely liquid) have been determined for the system FeO-Fe_2O_3-SiO_2 for a range of oxygen pressures, “FeO”-CaO-SiO_2 at iron metal saturation and FeO-Fe_2O_3-CaO-SiO_2 in air [7]. The liquidus temperatures in the system Fe-Ca-O have also been determined at temperatures between 1200 and 1300 ^oC [6].

One of the important objectives of copper smelting/converting process is to remove impurities from matte or metal through the formation of the slag phase. The major components of the copper smelting and converting slags are iron oxide and silica. Other components can also present in the slags, such as CaO, Al_2O_3 and MgO. Knowledge of the phase equilibria information of this slag system is required to determine the optimum operating temperature. An optimum operating temperature should enable 1) the slag to be tapped smoothly; 2) freeze lining is formed between the slag and refractory to increase the life of the furnace; 3) matte or metal can be separated from the slag. Phase equilibria of ferrous silicate slags in the systems “FeO”-SiO_2-CaO-Al_2O_3 [8] and “FeO”-SiO_2-CaO-MgO [9] at iron saturation have been investigated in the composition ranges related to copper smelting slags. However, copper smelting/converting processes operates at intermediate oxygen partial pressures between 10^{-5} and 10^{-9} atm. Information of the chemistries and phase equilibria of ferrous silicate slags in air or at iron saturation is not sufficient to accurately describe the commercial copper smelting/converting processes. Ii is important to obtain the information of phase equilibria and liquidus temperatures at the intermediate oxygen partial pressures relevant to copper smelting and converting for the improvement of existing and development of new technologies. Phase equilibria and liquidus temperatures in the system FeO-Fe_2O_3-CaO-SiO_2 at the intermediate oxygen partial pressures between 10^{-5} and 10^{-9} atm have been reported recently by the authors [10-11]. However, limited information is available on the effects of MgO and Al_2O_3 on phase equilibria and liquidus temperatures at the intermediate oxygen partial pressures relevant to copper smelting and converting slags.

The aim of the present study is to demonstrate the methodology that is now being used to provide information on the slag chemistries of MgO- and Al_2O_3-containing silicate slags, and to show that the gaps in fundamental information, encompassing the conditions of industrial interest, in particular copper production operations, can be filled through careful systematic laboratory-based studies. Examples of new phase equilibrium information are provided in this study on important ferrous calcium silicate slag systems.

2. Experimental

2.1 Sample preparation

High purity oxide and metal powders were used as starting materials, i.e. CaO powder (calcined at 1000 ^oC from 99.0 wt. % pure $CaCO_3$ powder), SiO_2 (99.99 wt. % pure 1-3 mm fused lump that had been ground with an agate mortar and pestle), Fe_2O_3 powder (99.99 wt. % pure), MgO powder (99.95 wt. % pure), Al_2O_3 (99.99 wt. % pure) and Fe powder (99.9 wt. % pure). Mixtures of various compositions were prepared by accurately weighing the oxide/metal powders and mixing them thoroughly using an agate mortar and pestle. The initial compositions of the mixtures were selected such that at equilibrium there would be liquid phase in equilibrium with one or more condensed phases. Each mixture was then pressed with pressure of 40 MPa to produce a pellet weighing less than 0.2 grams.

To avoid contamination of the slag by the crucibles, appropriate types of containment materials must be selected. For the slag system investigated in this study, platinum envelopes were used. The size of the platinum envelope was 10 mm x 12 mm, made from 0.025 mm-thick platinum foil. The use of platinum envelope ensures that there will not be any unexpected component introduce into the slag. It was found that under the conditions investigated only a small amount of iron was dissolved in the platinum. Although this would slightly change the bulk composition of the mixture, the compositions of phases at equilibrium in the multiphase equilibrium conditions will be unchanged.

At 1300 ^{o}C and $Po_2 = 10^{-9}$ atm the SiO_2 concentration in liquid in “FeO” primary phase field is relatively low, which results in very high fluidity of the slag. On cooling the crystallisation rates are very high. The liquid phase in this system is therefore very difficult to be quenched. New experimental procedures have been developed to overcome this difficulty [12-13]. The new technique, the primary phase substrate suspension technique used in the present study, involves the preparation of substrate materials that are known, from preliminary experiments, to crystallise first during solidification of the melt. The iron oxide substrate used in this project was prepared from iron foil (99.5 % Fe, 0.1 mm thickness) supplied by Goodfellow Ltd. The subtrate was first made to the shape required in the final experiment and then treated at required temperature and Po_2 to form wustite. The slag mixture is placed on the outside of the substrate and raised to temperature in a controlled gas atmosphere with PO_2 controlled by CO_2/CO gas mixtures. As the slag melts the mixture is held on the surface of the substrate by surface tension forces, forming a thin film approximately 100 μm thickness. Following equilibration the substrate and sample are released and quenched directly into water. The direct contact of the liquid slag with the quenching medium and the thin slag film leads to rapid quenching rates, much greater than can be achieved with the use of larger samples contained in metal foil or in crucibles.

2.2 Equilibration

To monitor the actual temperature surrounding the sample, a calibrated working thermocouple was placed immediately adjacent to the sample in a re-crystallised alumina thermocouple sheath. The temperature of the experiment was continuously controlled within 1 ^{o}C of the target temperature. It is estimated that the overall absolute temperature accuracy of the experiment is within 3 ^{o}C.

The oxygen partial pressure inside the reaction tube was controlled by introducing gas with a specific CO/CO_2 ratio. In this study, equilibrations were carried out at oxygen partial pressures between 10^{-5} and 10^{-8} atm. These oxygen partial pressures required very low CO/CO_2 ratios, thus premixed CO and Ar gases were used to achieve the target CO/CO_2 ratios. 5% and 20% CO diluted in high purity Argon (Beta standards, 0.02 % uncertainty) mixtures were supplied by BOC and high purity CO_2 (99.995 % pure) was supplied by Coregas. The proportion of each gas was controlled using pressure differential type flow-meter. The total flow-rate of the gas inside the furnace was between 400-600 ml/min and the fluctuation of the gas flow-rate was found less than 1 % of the total flow-rate.

A DS-type oxygen probe supplied by Australian Oxygen Fabricators (AOF, Melbourne, Australia) was used to confirm the oxygen partial pressures present during the experiments. This was done by directing the output gas from the equilibration furnace into a separate vertical tube furnace held at the same temperature equipped with the DStype oxygen probe. By this arrangement, direct monitoring of the oxygen partial pressure during the equilibration was possible. The results of the measurements in the present study are within the accuracy of the DS-type oxygen probe, i.e. ± 0.1 Log (Po_2) units.

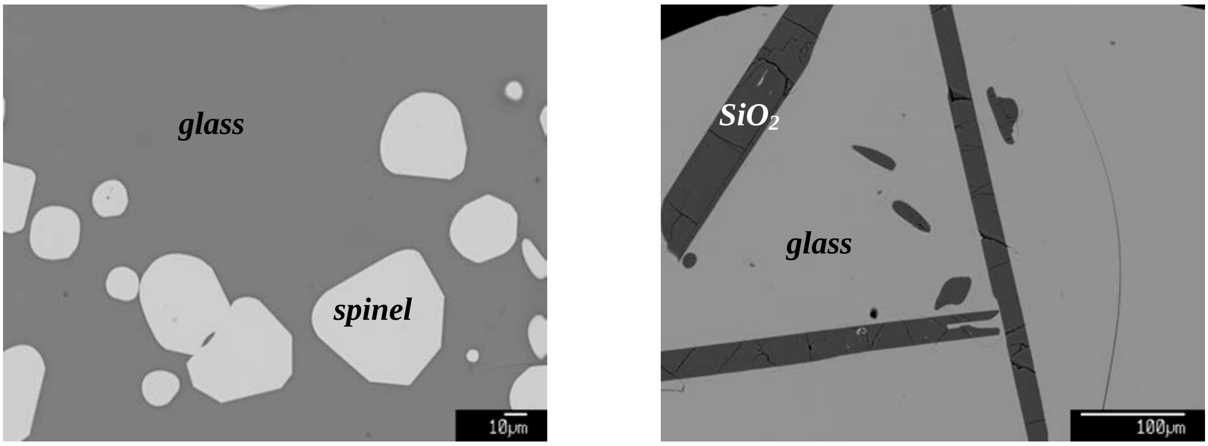
Equilibration experiments were carried out using a vertical tube furnace. The specimen with suitable container material was introduced from the bottom of a vertical tube furnace and suspended on a sample holder made of platinum wire. Before the specimen was raised into the hot zone of the furnace, the reaction tube was preconditioned for 30 minutes to the required temperature and oxygen partial pressure/gas compositions. The specimen was then raised into the hot zone of the furnace and pre-melting of the sample was carried out by increasing the temperature 25 ^{o}C above the target temperature. After 30 minutes of pre-melting, the temperature of the furnace was adjusted back to the target temperature. Equilibration was then carried out for 24 hours at the target temperature and oxygen partial pressure/gas condition. After the equilibration the bottom end of the furnace was released and the base of the furnace was immersed in water. The specimen was rapidly quenched into the water by pulling the sample holder upward until the specimen was released from the sample holder. The quenched sample was dried on a hot plate, crushed into smaller pieces and mounted in epoxy resin. The mounted sample was then polished for metallographic and EPMA examinations.

2.3 Examination

The polished samples were initially examined using an optical microscope to identify the phases present. Then the sample was coated with carbon film using a JEOL (Japan Electron Optics Ltd) Carbon Coater for electron microscopic examination. A JXA 8200 Electron Probe Microanalyser was used for further analysis. Quantitative analysis was performed at an accelerating voltage of 15 kV and a probe current of 15 nA. The Duncumb-Philibert ZAF correction procedure supplied with the EPMA was applied. The standards used for analysis were from Charles M. Taylor Co. (Stanford, California): Al_2O_3 for Al, $CaSiO_3$ for Ca and Si, Fe_2O_3 for Fe and MgO for Mg. The average accuracy of the EPMA measurements was estimated to be within ± 1 weight percent of the element concentration. Iron is present in the slag in both Fe^{2+} and Fe^{3+} forms. EPMA cannot measure Fe^{2+} and Fe^{3+} separately. All iron is calculated as “FeO” in this article for presentation purposes.

3. Results

Iron oxide (spinel or wustite) and silica are major primary phase fields in the composition ranges investigated. Typical microstructures of the quenched samples are presented in Figures 1 and 2, showing well-quenched liquid slag in equilibrium with primary phases. Figure 1a shows a typical microstructure of quenched sample from the spinel primary phase field; Figure 1b shows a typical microstructure of quenched sample from the tridymite primary phase field. Figure 2 shows a typical microstructure of quenched sample from the wustite primary phase field. The liquid phase present in this sample has a low SiO_2 concentration and is difficult to quench to glass using conventional approaches. An iron oxide substrate rather than a Pt envelope was used in this experiment; it can be seen that a uniform glass was obtained as a result of this rapid quenching technique.



(a) (b)

Fig. 1 Typical microstructures of quenched slags from a) spinel and b) tridymite primary phase fields, 1300 ^{o}C, Po$_2$ = 10^{-7} atm

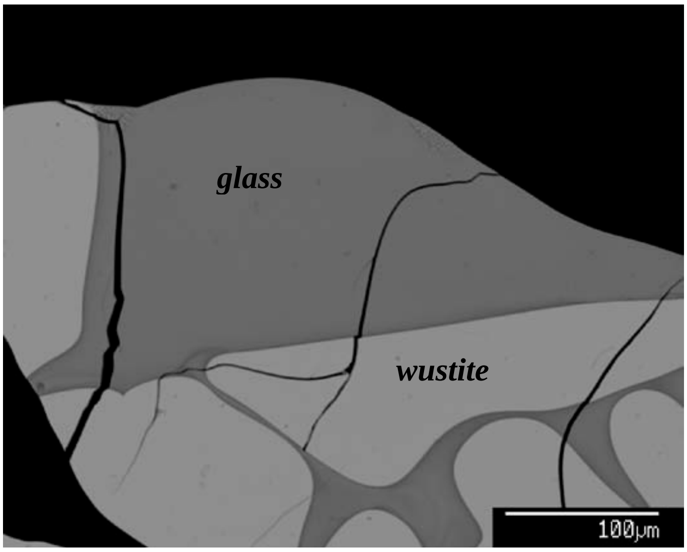


Fig. 2 A typical microstructure of quenched slag from the wustite primary phase field, 1300 ^{o}C, Po$_2$ = 10^{-9} atm

Phase diagrams in the multi-component systems "FeO"-SiO_2-CaO-MgO-Al_2O_3, for convenience of use, are often presented in a form of pseudo-ternary sections "FeO"-SiO_2-CaO at fixed Al_2O_3 or MgO concentrations. For these multi-component systems it is difficult to experimentally obtain the exact target concentrations of all components in the liquid phase (for example, MgO = 4.0 wt %) due to the precipitation of solid phases from the melt and interaction of the liquid with the container/substrate. An optimisation procedure has therefore been used to analyse and interpolate all experimental data having a range of concentrations of the minor components Al_2O_3 or MgO in the liquid at a given primary phase field, temperature and oxygen partial pressure. The basis of the optimization is that at a given CaO concentration in liquid the "FeO"/SiO_2 ratio in liquid is function of Al_2O_3 and MgO concentrations. The experimental measurements can then be described by the following empirical equations:

$$X(F/S) = \quad F_0 + F_{Ca1}*(X_{Ca})^2 + F_{Ca2}*X_{Ca} + F_{Al}*X_{Al} + F_{Mg}*X_{Mg} \qquad (1)$$

$$X_{Si} = (100-X_{Ca} - X_{Al} - X_{Mg})/(1+X(F/S)) \tag{2}$$

$$X_{Fe} = 100-X_{Ca} - X_{Al} - X_{Mg}-X_{Si} \tag{3}$$

where X(F/S) is weight ratio of “FeO”/SiO_2, F_0, F_{Ca1}, F_{Ca2}, F_{Al} and F_{Mg} are interpolation coefficients obtained for a given temperature and Po_2 by minimising the sum of squared differences of experimental and calculated concentrations, and X_{Si}, X_{Fe}, X_{Ca}, X_{Al} and X_{Mg} are concentrations of SiO_2, “FeO”, CaO, Al_2O_3 and MgO respectively in weight percent in the liquid.

The examples of the interpolation results for relationship between “FeO”/SiO_2 ratio and Al_2O_3 in liquid are shown in Figures 3 and 4 for 1300 ^oC and $Po_2 = 10^{-7}$ atm. In these figures solid symbols represent experimental points, straight lines represent the interpolation at a given CaO concentration and open symbols represent calculated points at the same Al_2O_3 concentrations. It can be seen that not only the Al_2O_3 concentration but also CaO concentration has significant effect on the liquidus composition. This interpolation procedure introduces a number of advantages. It enables the consistency of experimental results to be checked during the course and after the investigation. Experiments are planned so that the whole range of concentrations of interest is described with one set of interpolation coefficients rather than focusing on exact fixed compositions. All experiments at a given temperature and oxygen partial pressure are used simultaneously for a given fixed concentration of “FeO”, CaO, SiO_2, Al_2O_3 and MgO. Isotherms at any required fixed concentration within the investigated range can then be constructed using this set of interpolation coefficients.

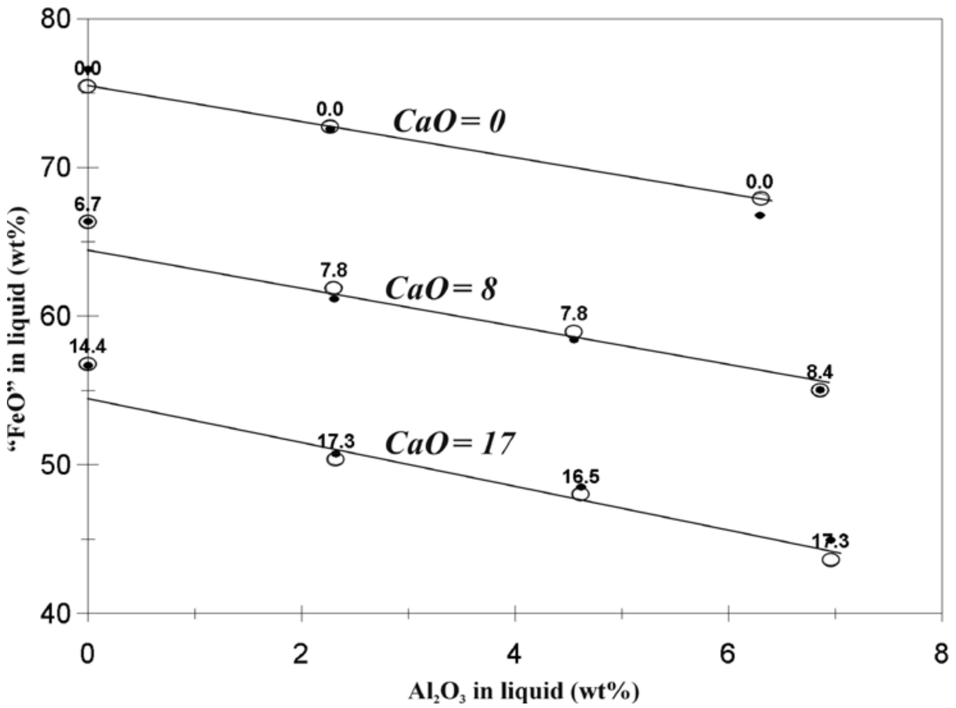


Fig. 3 Correlations between “FeO” and Al_2O_3 concentrations in the liquid in equilibrium with spinel at 1300 ^oC and $Po_2 = 10^{-7}$ atm in the “FeO”-SiO_2-CaO-Al_2O_3 slags, the number above each of the symbol is the actual CaO concentration in liquid; Solid symbols: experimental results; Open symbols: interpolated points Straight line: best fitted line for the given CaO concentration

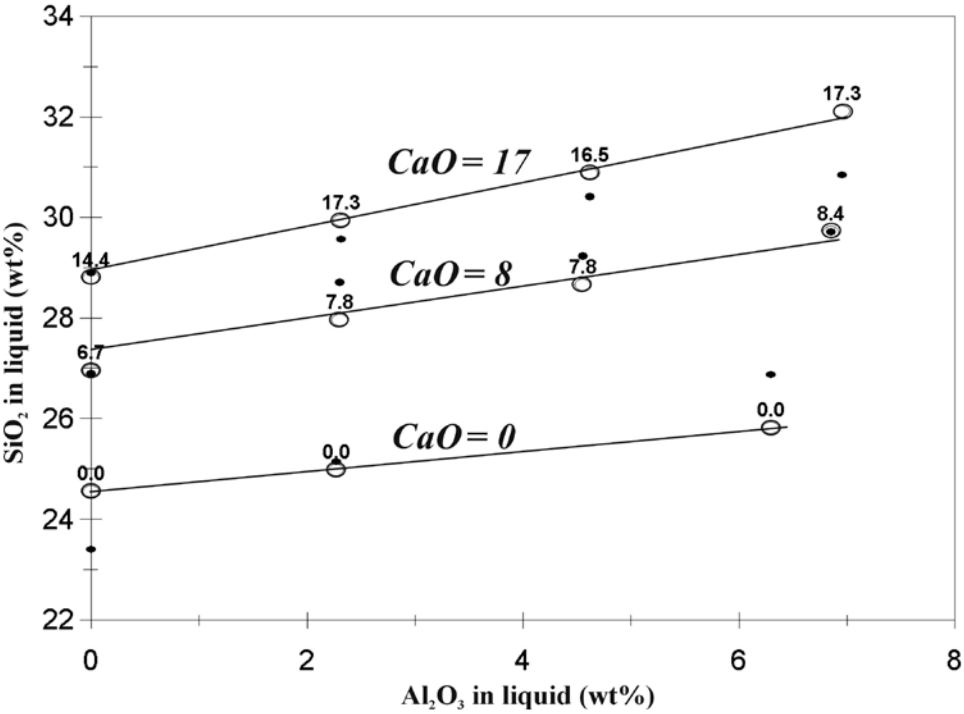


Fig. 4 Correlations between SiO_2 and Al_2O_3 concentrations in the liquid in equilibrium with spinel at 1300 ^oC and $Po_2 = 10^{-7}$ atm in the "FeO"-SiO_2-CaO-Al_2O_3 slags, the number above each of the symbol is the actual CaO concentration in liquid; Solid symbols: experimental results; Open symbols: interpolated points Straight line: best fitted line for the given CaO concentration

It can be seen from Figure 3 that both Al_2O_3 and CaO have significant effects on the "FeO" concentration in the liquid. At a given CaO concentration, the "FeO" concentrations in the liquid decrease with increasing Al_2O_3 concentration. The slopes of the three lines at 0, 8 and 17 wt% CaO in Figure 3 are approximately -1.4 regardless CaO concentrations. At a given Al_2O_3 concentration, the "FeO" concentrations in the liquid decrease with increasing CaO concentration. Similarly, Figure 4 shows that at a given CaO concentration the SiO_2 concentrations in the liquid increase with increasing Al_2O_3 concentration. At a given Al_2O_3 concentration, the SiO_2 concentrations in the liquid increase with increasing CaO concentration. It is well known that liquidus temperatures in spinel primary phase field increase with increasing "FeO"/SiO_2 ratio. Increased CaO and Al_2O_3 concentrations in the slag require extra SiO_2 flux to remain the same liquidus temperature and to avoid the formation of spinel solid.

Using the above relationships the liquidus isotherms for 1300 ^oC at $Po_2 = 10^{-7}$ atm are presented in Figures 5 and 6 for additions of Al_2O_3 and MgO respectively. These are the projection of the 1300 ^oC isotherms with 0, 2, 4 and 6 wt% Al_2O_3 or MgO in liquid onto the plane "FeO"-SiO_2-CaO. It can be seen that the isotherms in both spinel and tridymite primary phase fields move towards SiO_2 direction with increasing Al_2O_3 or MgO concentration in liquid. This indicates that the liquidus temperatures in the spinel primary phase field increase with increasing Al_2O_3 or MgO concentration in liquid. In contrast, the liquidus temperatures in the tridymite primary phase field decrease with increasing Al_2O_3 or MgO concentration in liquid.

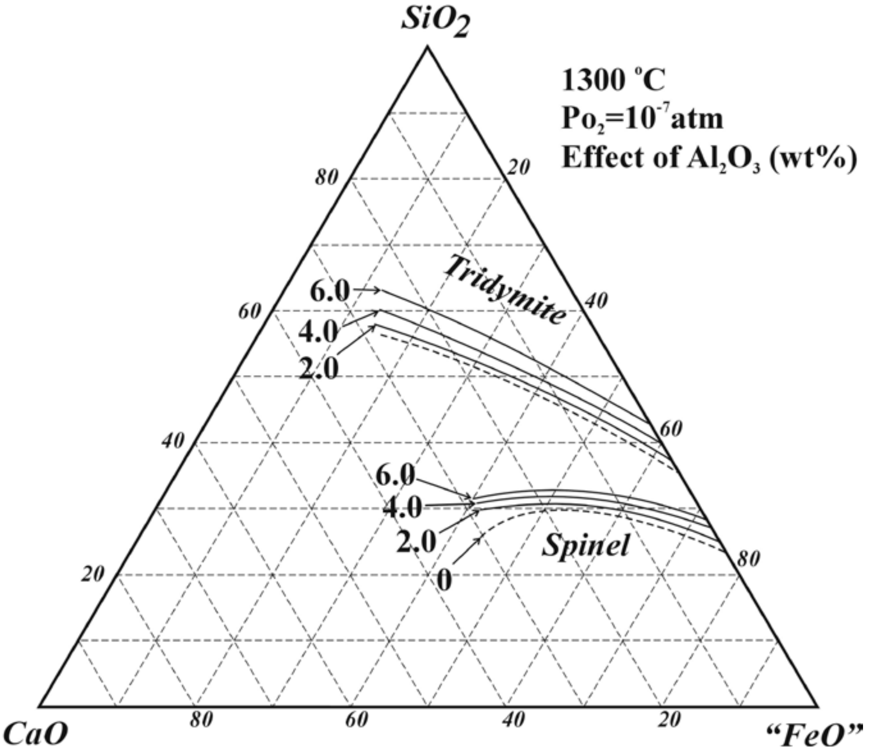


Fig. 5 Effect of Al_2O_3 on liquidus isotherms at1300 °C and $Po_2 = 10^{-7}$ atm in the "FeO"-SiO_2-CaO-Al_2O_3 slags, projected onto the "FeO"-SiO_2-CaO plane

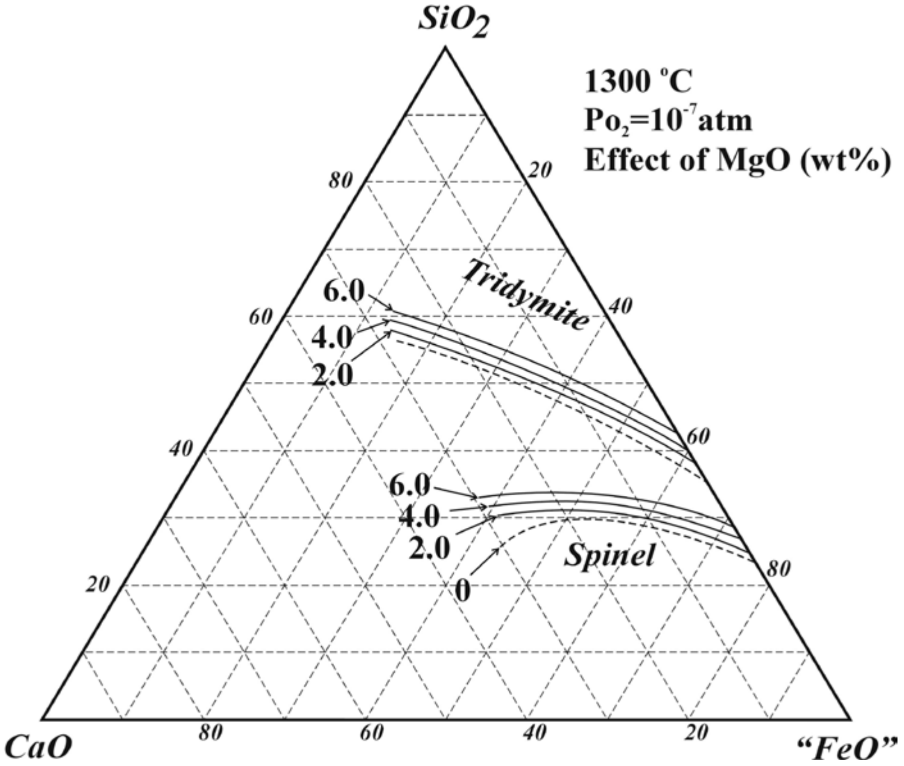


Fig. 6 Effect of MgO on liquidus isotherms at 1300 °C and $Po_2 = 10^{-7}$ atm in the "FeO"-SiO_2-CaO-MgO slags, projected onto the "FeO"-SiO_2-CaO plane

Figures 7 and 8 show experimentally determined isotherms of 1300 °C at $Po_2 = 10^{-5} – 10^{-9}$ atm for additions of 4 wt% Al_2O_3 or 4 wt% MgO respectively. It can be seen that the isotherms in tridymite primary phase field are not sensitive to oxygen partial pressure. The isotherms in spinel primary phase field move towards SiO_2 direction with increasing oxygen partial pressure. This indicates that the liquidus temperatures in the spinel primary phase field increase with increasing oxygen partial pressure. It can be seen from the Figure 7 that with 4 wt% Al_2O_3 present in the slag, the primary phase at high-iron region is changed from spinel to wustite at oxygen partial pressure between 10^{-8} and 10^{-9} atm. The solid thick line indicates the boundary between the spinel and wustite primary phase field. It can be seen from Figure 8 that with 4 wt% MgO present in the slag, the primary phase at high-iron region is changed from spinel to wustite at oxygen partial pressure between 10^{-7} and 10^{-8} atm. The liquidus temperatures in the wustite primary phase field seem not to be sensitive to changes in oxygen partial pressure between 10^{-8} and 10^{-9} atm.

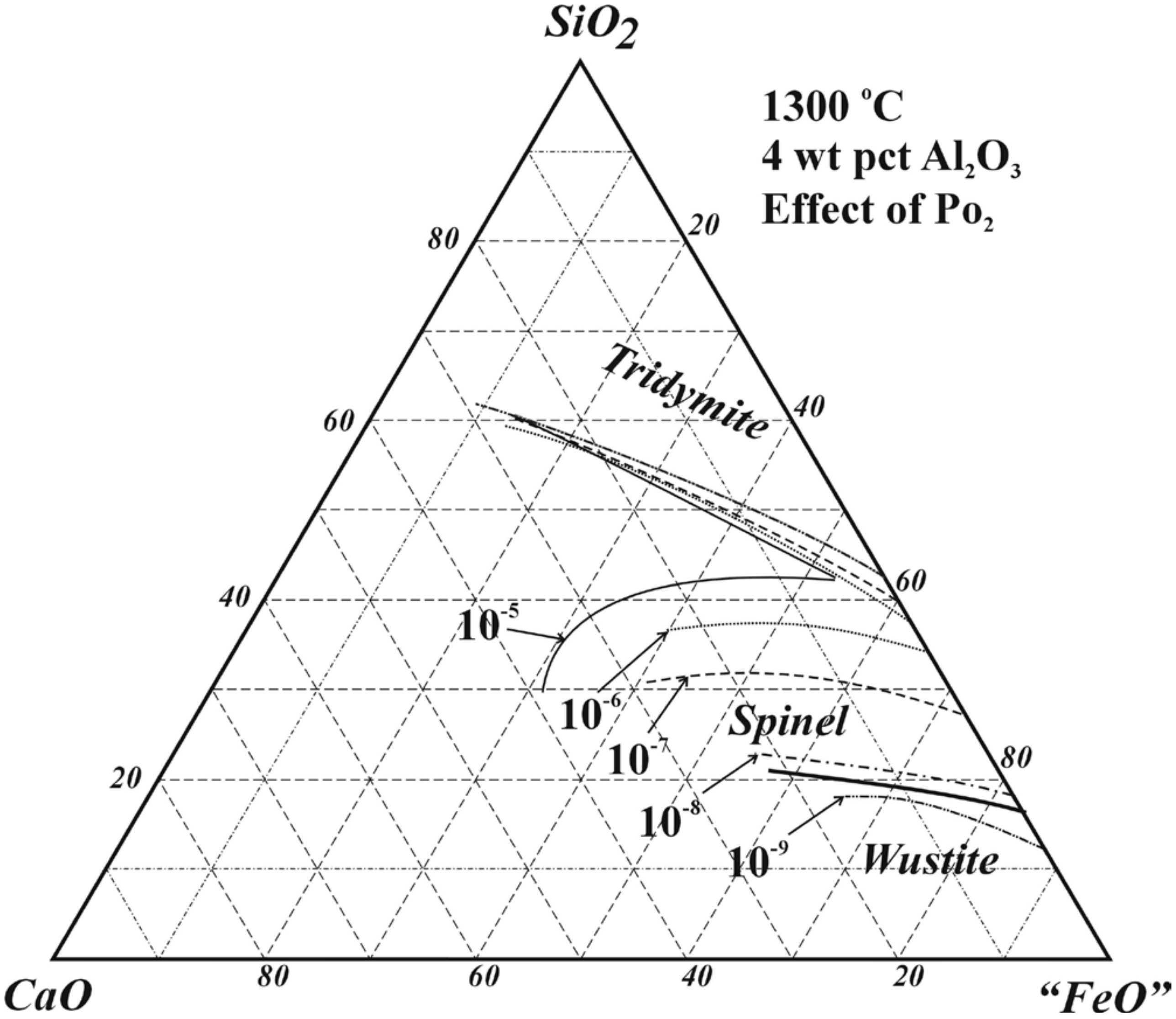


Fig. 7 Effect of Po_2 on isotherms at 1300 °C and 4 wt% Al_2O_3 in the "FeO"-SiO_2-CaO-Al_2O_3 slags, projected on the "FeO"-SiO_2-CaO plane

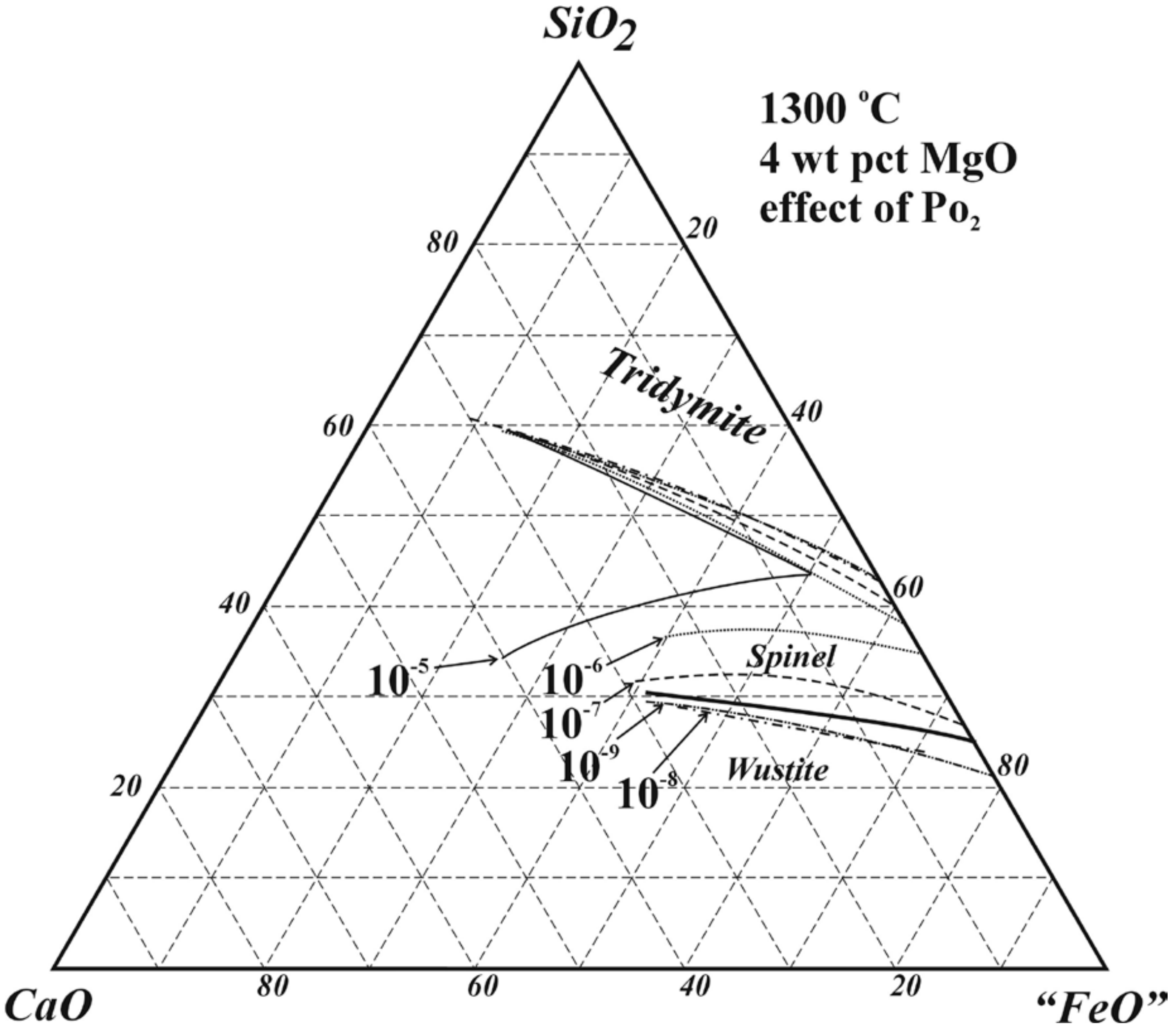


Fig. 8 Effect of Po_2 on isotherms of 1300 °C and 4 wt% MgO in the “FeO”-SiO_2-CaO-MgO slags, projected on the “FeO”-SiO_2-CaO plane

Al_2O_3, CaO and MgO are usually present in copper smelting slag as minor elements. They are introduced through concentrate, flux, coal and refractories. Analysis of experimental data shows that they have similar effect on the liquidus temperature in spinel primary phase field. Figure 9 shows the movement of the spinel liquidus at 1300 °C and $Po_2 = 10^{-7}$ atm with increasing Al_2O_3/CaO/MgO concentration. The starting “FeO”-SiO_2 slag has Fe/SiO_2 ratio of 2.33. It can be seen that the spinel liquidus moves towards low Fe/SiO_2 ratio with increasing Al_2O_3/CaO/MgO concentration in the liquid. In the other word, the liquidus temperatures in the spinel primary phase field are increased with increasing Al_2O_3/CaO/MgO concentration in the liquid. The order of the effect on the liquidus temperature is CaO > MgO > Al_2O_3. To maintain the same liquidus temperature, Fe/SiO_2 ratio in the liquid has to be decreased to balance the increment in Al_2O_3/CaO/MgO concentration. For example, at 1300 °C and $Po_2 = 10^{-7}$ atm, the Fe/SiO_2 ratio is 2.33 for a slag without Al_2O_3, CaO and MgO. If the CaO concentration in this slag is increased to 10 wt%, the Fe/SiO_2 ratio has to be decreased to 1.71 to maintain the same liquidus temperature. This means that more silica flux has to be added.

More detailed correlations between Fe/SiO_2 ratio and Al_2O_3/CaO/MgO concentrations at 1300 °C and $Po_2 = 10^{-7}$ atm are shown in Figure 10. It can be seen clearly from Figure 10 that Al_2O_3, CaO and MgO show slightly different behavior on Fe/SiO_2 ratio. CaO seems to have more significant effect.

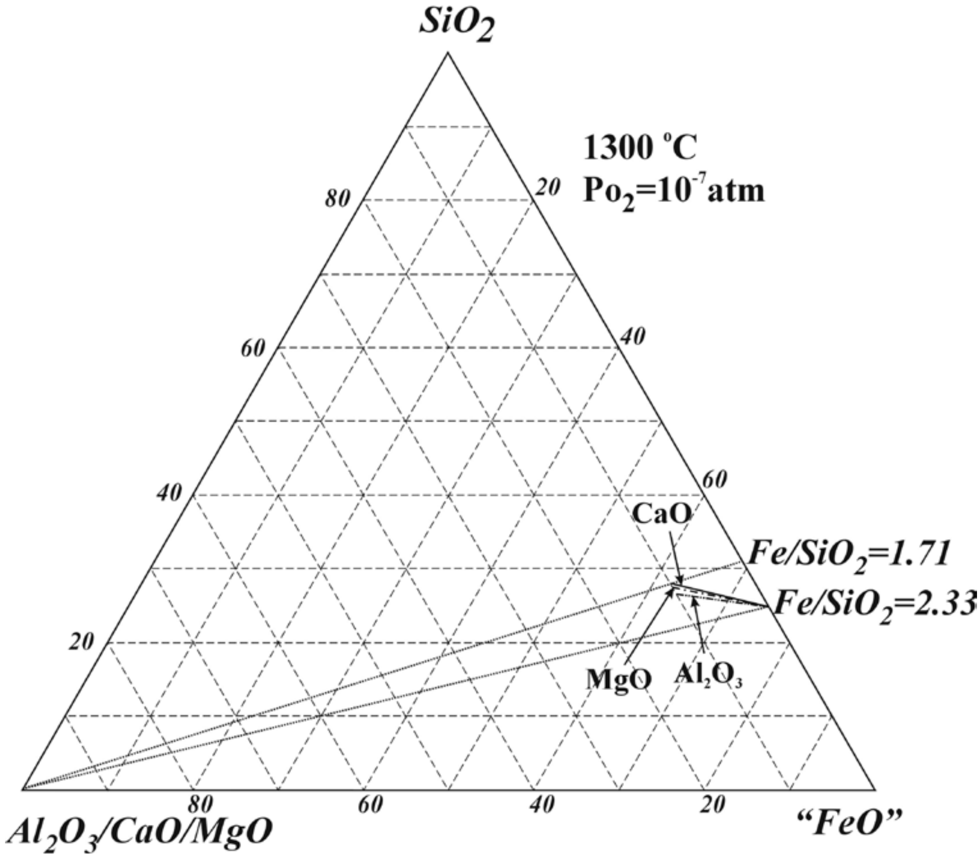


Fig. 9 Effect of Al_2O_3/CaO/MgO on isotherms of 1300 °C and $Po_2 = 10^{-7}$ atm in the spinel primary phase field, projected on the "FeO"-SiO_2-CaO plane

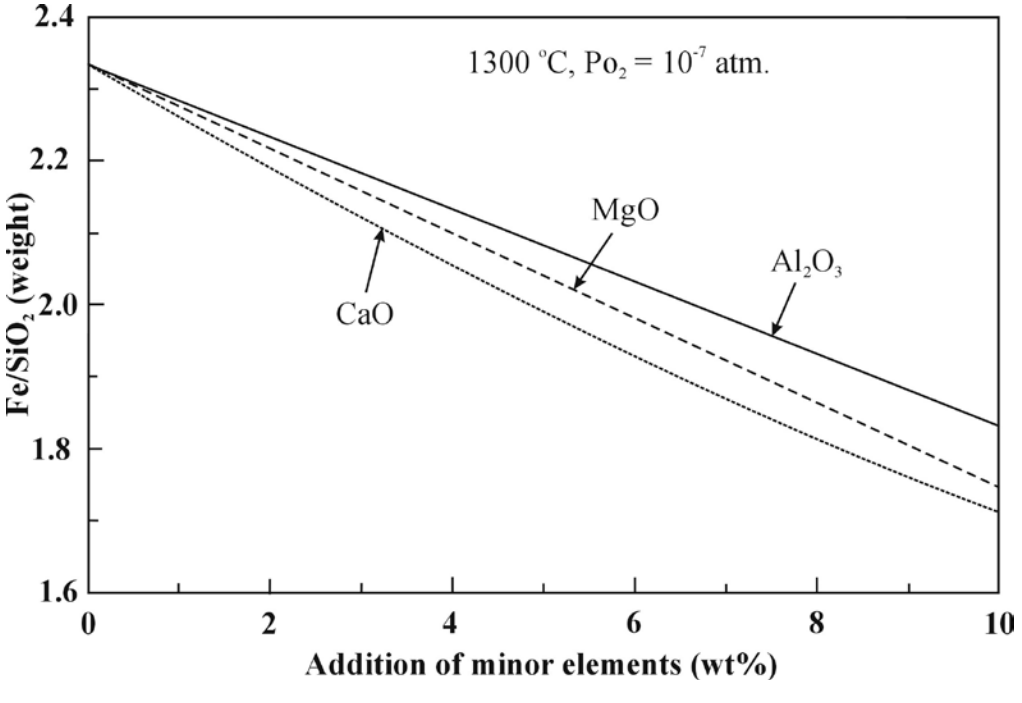


Fig. 10 Correlations between Fe/SiO_2 weight ratio and Al_2O_3/CaO/MgO concentrations at 1300 °C and $Po_2 = 10^{-7}$ atm

Figure 11 shows liquidus temperature as a function of Fe/SiO_2 weight ratio at $Po_2 = 10^{-8}$ atm. The lines are calculated results by FactSage 6.2 [14] and symbols are experimental results interpolated from present experimental data. It can be seen from FactSage calculations that spinel and tridymite are the primary phases present in this composition range for "FeO"-SiO_2, "FeO"-SiO_2-CaO and "FeO"-SiO_2-CaO-Al_2O_3 slags. Olivine is also a primary phase in "FeO"-SiO_2-CaO-MgO slag. Liquidus temperatures always decrease in tridymite primary phase field and increase in spinel and olivine primary phase fields with increasing Fe/SiO_2 ratio.

Four experimentally determined liquidus at 1200 °C and one at 1300 °C are shown in the figure for comparison. The data at 1200 °C are from the spinel primary phase field and the data at 1300 °C is from the wustite primary phase field. It can be seen from the comparison that

1) in "FeO"-SiO_2 system, experimentally determined liquidus in the spinel primary phase field is at a Fe/SiO_2 weight ratio of 1.4 rather than 1.7 predicted by FactSage. The actual liquidus temperatures in spinel primary phase field are higher than the predictions. FactSage indicates the slags with Fe/SiO_2 weight ratio less than 1.6 are saturated with silica.
2) in "FeO"-SiO_2-CaO and "FeO"-SiO_2-CaO-Al_2O_3 systems, experimentally determined liquidus temperatures in spinel primary phase field are approximately 15 and 20 °C respectively higher than the predictions.
3) in "FeO"-SiO_2-CaO-MgO system, experimentally determined liquidus temperatures in wustite primary phase field (Fe/SiO_2 = 2.5) is approximately 10 °C higher than the predictions. However, at Fe/SiO_2 = 1.2, olivine is predicted to be the primary phase and experimentally it has been shown that this is the spinel primary phase. The measured spinel liquidus is approximately 40 °C lower than the predicted olivine liquidus.

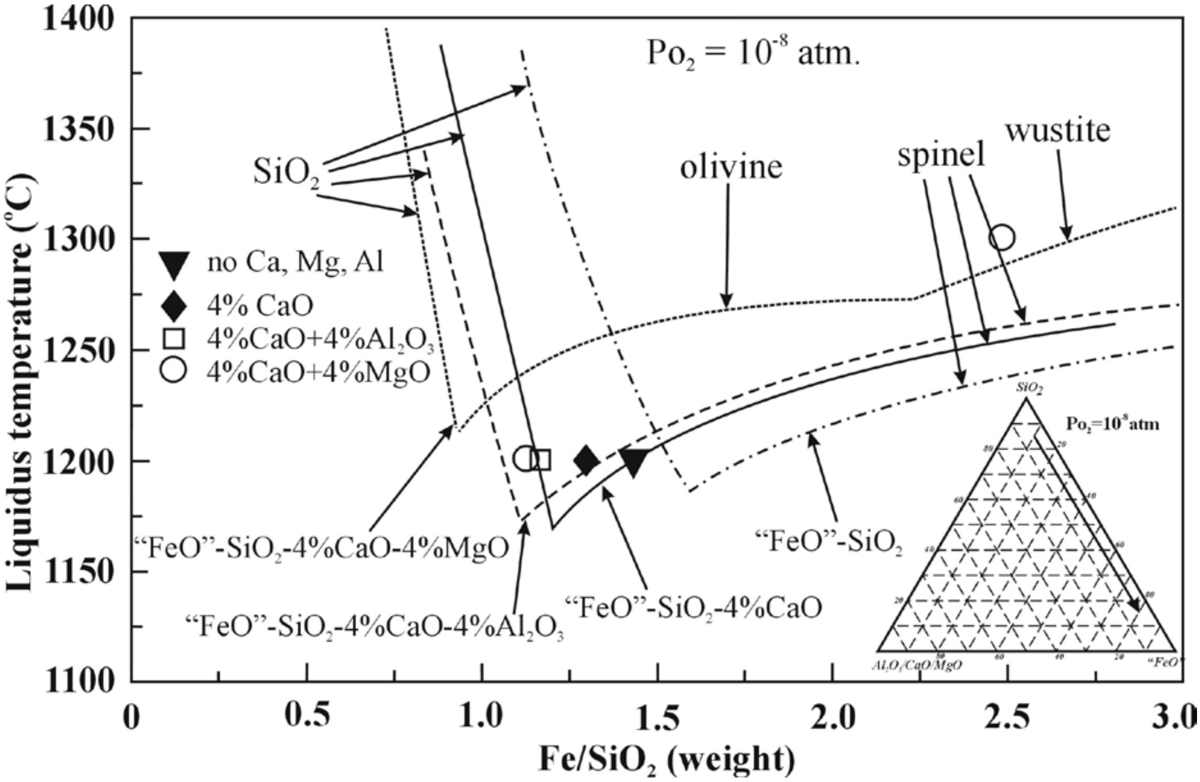


Fig. 11 Liquidus temperature as a function of Fe/SiO_2 weight ratio, $Po_2 = 10^{-8}$ atm, lines are calculated by FactSage 6.2, symbols are experimental results in spinel (1200 °C) and wustite (1300 °C) primary phase fields

4. Conclusions

The liquidus temperatures of copper smelting/converting slags have been determined by equilibration/quenching/EPMA technique. It has been demonstrated that phase equilibria can be determined over a wide range of compositions, temperatures and oxygen partial pressures to provide the essential information required to describe copper slag chemistries. The effects of oxygen partial pressure and additional minor components Al_2O_3, CaO and MgO on the phase equilibria and chemistries of silicate slags have been discussed. The information will be used to improve the industrial operations and for the optimisation of thermodynamic databases.

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