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# EFFECTS OF CaO, Al<sub>2</sub>O<sub>3</sub> 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 slags relevant to the copper smelting/converting operations have been experimentally studied over a wide range of slag compositions, temperatures and atmospheric conditions. Selected systems are of industrial interest and fill the gaps in fundamental information required to systematically characterise and describe copper slag chemistry. The experimental procedures 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 °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 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 °C and low  $Po_2$ , the spinel (Fe<sup>2+</sup>,Mg<sup>2+</sup>)O.(Al<sup>3+</sup>,Fe<sup>3+</sup>) primary phase field can be replaced by wustite (Fe<sup>2+</sup>,Mg<sup>2+</sup>)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<sub>2</sub>, 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<sub>2</sub>S-FeS melts (mattes) and oxygen–rich FeO-SiO<sub>2</sub> phase (slag) can be produced through the addition of silica to the system. It is now well established that the partitioning of the various 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<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> for a range of oxygen pressures, "FeO"-CaO-SiO<sub>2</sub> at iron metal saturation and FeO-Fe<sub>2</sub>O<sub>3</sub>-CaO-SiO<sub>2</sub> in air [7]. The liquidus temperatures in the system Fe-Ca-O have also been determined at temperatures between 1200 and 1300 °C [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

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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<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> [8] and "FeO"-SiO<sub>2</sub>-CaO-MgO [9] at iron saturation have been investigated in the composition ranges related to smelting slags. However, copper copper smelting/converting processes operates at intermediate oxygen partial pressures between 10<sup>-5</sup> and 10<sup>-9</sup> 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. It 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<sub>2</sub>O<sub>3</sub>-CaO-SiO<sub>2</sub> at the intermediate oxygen partial pressures between 10<sup>-5</sup> and 10<sup>-9</sup> atm have been reported recently [10-11]. However, limited information is available on the effects of MgO and Al<sub>2</sub>O<sub>2</sub> 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

Experimental procedure, including sample preparation, equilibration and examination, applied in this paper is in accordance with already presented details in Ref.[10].

## 2.1 Sample preparation

High purity oxide and metal powders were used as starting materials, i.e. CaO powder (calcined at 1000 °C from 99.0 wt. % pure CaCO<sub>3</sub> powder), SiO<sub>2</sub> (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<sub>2</sub>O<sub>3</sub> (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 solid phases. Each mixture was then pressed with pressure of 40 MPa to produce a pellet weighing less than 0.2 grams [10].

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 no unexpected components are introduced into the slag. It was found that under the experimental conditions a small amount of iron was dissolved in the platinum. Although this would slightly change the bulk composition of the mixture, the compositions of the phases in equilibrium at temperature will be unchanged.

At 1300 °C and  $Po_2 = 10^{-9}$  atm the SiO<sub>2</sub> concentration in liquid in wustite primary phase field is relatively low, which results in high fluidity of the slag. On cooling the crystallisation rates are very high. The liquid phase in this system is therefore 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 wt. % Fe, 0.1 mm thickness) supplied by Goodfellow Ltd. The substrate was first made to the shape required in the final experiment and then treated at required temperature and Po, to form wustite. The slag mixture was placed on the outside of the substrate and raised to the temperature in a Po<sub>2</sub> controlled by  $CO_{\gamma}/CO$  gas mixtures. As the slag melts the mixture was 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 cooling 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 recrystallised alumina thermocouple sheath. The temperature of the experiment was continuously controlled within 1 °C of the target temperature. It is estimated that the overall absolute temperature accuracy of the experiment is within 3 °C [10].

The oxygen partial pressure inside the reaction tube was controlled by introducing gas with a specific  $CO/CO_2$  ratio. The experiments 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 400-600 ml/min and the fluctuation of the gas flow-rate was found less than 1 % of the total flow-rate [10].

A DS-type oxygen probe supplied by Australian Oxygen Fabricators (AOF, Melbourne, Australia) was used to confirm the oxygen partial pressures 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 DS-type oxygen probe. By this arrangement, the oxygen partial pressure during the equilibration was directly measured. The results of the measurements in the present study are within the accuracy of the DS-type oxygen probe, i.e.  $\pm 0.1 \log (Po_2)$  units.

Equilibration experiments were carried out in a vertical tube furnace [10]. 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 sample was carried out at

temperature 20 °C above the target temperature. After 30 minutes of pre-melting, the sample was equilibrated 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. The quenched sample was dried on a hot plate, sectioned 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 (EPMA) 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<sub>2</sub>O<sub>3</sub> for Al, CaSiO<sub>3</sub> for Ca and Si, Fe<sub>2</sub>O<sub>3</sub> for Fe and MgO for Mg. The average accuracy of the EPMA measurements was estimated to be within  $\pm 1$  weight percent of the element concentration. Iron is present in the slag in both Fe<sup>2+</sup> and Fe<sup>3+</sup> forms. EPMA cannot measure Fe<sup>2+</sup> and Fe<sup>3+</sup> separately. All iron is calculated as "FeO" in this article for presentation purpose.

## 3. Results

Iron oxide (spinel or wustite) and tridymite  $(SiO_2)$  are major primary phases in the composition ranges investigated. Typical microstructures of the quenched samples are presented in Figures 1 and 2, showing



Figure 1. Typical microstructures of quenched slags from a) spinel and b) tridymite primary phase fields, 1300 °C,  $Po_2 = 10^{-7}$  atm

well-quenched liquid slag in equilibrium with the 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<sub>2</sub> concentration and is difficult to quench to homogenous glass using conventional approaches. An iron oxide substrate rather than a Pt envelope was used in this experiment; it can be seen that homogenous glass was obtained as a result of this rapid quenching technique.



Figure 2. A typical microstructure of quenched slag from the wustite primary phase field, 1300 °C,  $Po_2 = 10^{-9}$  atm

Phase diagrams in the multi-component systems "FeO"-SiO<sub>2</sub>-CaO-MgO-Al<sub>2</sub>O<sub>3</sub>, for convenience of use, are often presented in a form of pseudo-ternary sections "FeO"-SiO<sub>2</sub>-CaO at fixed Al<sub>2</sub>O<sub>2</sub> 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 introduced to analyse and interpolate all experimental data having a range of concentrations of the minor components Al<sub>2</sub>O<sub>3</sub> or MgO in the liquid at a given primary phase field, temperature and oxygen partial pressure. The basis of the optimisation is that at a given CaO concentration in liquid the "FeO"/SiO, ratio in liquid is function of Al<sub>2</sub>O<sub>3</sub> and MgO concentrations. The experimental measurements can then be described by the following empirical equations:

$$\begin{split} X(F/S) &= F_0 + F_{Ca1}^* (X_{Ca})^2 + F_{Ca2}^* X_{Ca}^+ \\ &+ F_{A1}^* X_{A1}^- + F_{Mg}^* X_{Mg}^- \qquad ...(1) \end{split}$$

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

$$X_{Fe} = 100 - X_{Ca} - X_{Al} - X_{Mg} - X_{Si}$$
 ...(3)

where X(F/S) is the weight ratio of "FeO"/SiO<sub>2</sub>, F<sub>0</sub>, F<sub>Ca1</sub>, F<sub>Ca2</sub>, F<sub>A1</sub> and F<sub>Mg</sub> are the interpolation coefficients obtained for a given temperature and Po<sub>2</sub> by minimising the sum of squared differences of experimental and calculated concentrations, and X<sub>si</sub>, X<sub>Fe</sub>, X<sub>Ca</sub>, X<sub>A1</sub> and X<sub>Mg</sub> are the concentrations of SiO<sub>2</sub>, "FeO", CaO, Al<sub>2</sub>O<sub>3</sub> and MgO respectively in weight percent in the liquid.

The examples of the interpolation results for relationship between "FeO" (or SiO<sub>2</sub>) concentration and Al<sub>2</sub>O<sub>3</sub> in liquid are shown in Figures 3 and 4 for 1300 °C and Po<sub>2</sub> =  $10^{-7}$  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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgO. Isotherms at any required fixed concentration within the investigated composition range can then be constructed using this set of interpolation coefficients.



Figure 3. Correlations between "FeO" and  $Al_2O_3$ concentrations in the liquid in equilibrium with spinel at 1300 °C and Po<sub>2</sub> = 10<sup>-7</sup> atm in the "FeO"-SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> 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



Figure 4. Correlations between SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> concentrations in the liquid in equilibrium with spinel at 1300 °C and Po<sub>2</sub> =  $10^{-7}$  atm in the "FeO"-SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> concentration, the "FeO" concentrations in the liquid decrease with increasing CaO concentration. Similarly, Figure 4 shows that at a given CaO concentration the SiO<sub>2</sub> concentrations in the liquid increase with increasing Al<sub>2</sub>O<sub>3</sub> concentration. At a given Al<sub>2</sub>O<sub>3</sub> concentration, the SiO<sub>2</sub> 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"/SiO2 ratio. Increased CaO and Al<sub>2</sub>O<sub>2</sub> concentrations in the slag require extra SiO<sub>2</sub> flux to remain the same liquidus temperature and to avoid the formation of spinel solid.

Using the above relationships the liquidus isotherms for 1300 °C 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 °C isotherms with 0, 2, 4 and 6 wt%  $Al_2O_3$  or MgO in liquid onto the plane "FeO"-SiO<sub>2</sub>-CaO. It can be seen that the isotherms in both spinel and tridymite primary phase fields move towards SiO<sub>2</sub> 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.



**Figure 5.** Effect of  $Al_2O_3$  on liquidus isotherms at 1300 °C and  $Po_2 = 10^{-7}$  atm in the "FeO"-SiO<sub>2</sub>-CaO- $Al_2O_3$  slags, projected onto the "FeO"-SiO<sub>2</sub>-CaO plane



Figure 6. Effect of MgO on liquidus isotherms at 1300 °C and Po<sub>2</sub> = 10<sup>-7</sup> atm in the "FeO"-SiO<sub>2</sub>-CaO-MgO slags, projected onto the "FeO"-SiO<sub>2</sub>-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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> present in the slag, the primary phase at high-iron region is changed from spinel to wustite at oxygen partial pressure between 10<sup>-8</sup> and 10<sup>-9</sup> 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.



**Figure 7.** Effect of Po, on isotherms at 1300 °C and 4 wt% Al<sub>2</sub>O<sub>3</sub> in the "FeO"-SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> slags, projected on the "FeO"-SiO<sub>2</sub>-CaO plane



Figure 8. Effect of Po, on isotherms of 1300 °C and 4 wt% MgO in the "FeO"-SiO<sub>2</sub>-CaO-MgO slags, projected on the "FeO"-SiO<sub>2</sub>-CaO plane

Al<sub>2</sub>O<sub>2</sub>, 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<sub>2</sub>O<sub>2</sub>/CaO/MgO concentration. The starting "FeO"-ŠiO<sub>2</sub> slag has Fe/SiO<sub>2</sub> ratio of 2.33. It can be seen that the spinel liquidus moves towards low Fe/SiO<sub>2</sub> ratio with increasing Al<sub>2</sub>O<sub>2</sub>/CaO/MgO concentration in the liquid. In the other word, the liquidus temperatures in the spinel primary phase field are increased with increasing Al<sub>2</sub>O<sub>3</sub>/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<sub>2</sub> ratio in the liquid needs to be decreased to balance the increment in Al<sub>2</sub>O<sub>3</sub>/CaO/MgO concentration. For example, at 1300 °C and Po<sub>2</sub> =  $10^{-7}$  atm, the Fe/SiO<sub>2</sub> ratio is 2.33 for a slag without Al<sub>2</sub>O<sub>3</sub>, CaO and MgO. If the CaO concentration in this slag is increased to 10 wt%, the Fe/SiO<sub>2</sub> 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<sub>2</sub> ratio and Al<sub>2</sub>O<sub>3</sub>/CaO/MgO concentrations at 1300 °C and Po<sub>2</sub> =  $10^{-7}$  atm are shown in Figure 10. It can be seen clearly from Figure 10 that Al<sub>2</sub>O<sub>3</sub>, CaO and MgO show slightly different effect on Fe/SiO<sub>2</sub> ratio. CaO seems to have more significant effect.



*Figure 9.* Effect of Al<sub>2</sub>O<sub>3</sub>/CaO/MgO on isotherms of 1300 °C and Po<sub>2</sub> = 10<sup>-7</sup> atm in the spinel primary phase field, projected on the "FeO"-SiO<sub>2</sub>-CaO plane



Figure 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<sub>2</sub> weight ratio at Po<sub>2</sub> =  $10^{-8}$  atm. The lines are calculated results by FactSage 6.2 [14] and

the 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<sub>2</sub>, "FeO"-SiO<sub>2</sub>-CaO and "FeO"-SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> slags. Olivine is also a primary phase in "FeO"-SiO<sub>2</sub>-CaO-MgO slag. Liquidus temperatures always decrease in tridymite primary phase field and increase in spinel and olivine primary phase fields with increasing the Fe/SiO<sub>2</sub> ratio.

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

in "FeO"-SiO<sub>2</sub> system, experimentally determined liquidus in the spinel primary phase field is at a Fe/SiO<sub>2</sub> 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<sub>2</sub> weight ratio less than 1.6 are saturated with silica.

in "FeO"-SiO<sub>2</sub>-CaO and "FeO"-SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub> systems, experimentally determined liquidus temperatures in spinel primary phase field are approximately 15 and 20 °C respectively higher than the predictions.

in "FeO"-SiO<sub>2</sub>-CaO-MgO system, experimentally determined liquidus temperatures in wustite primary phase field (Fe/SiO<sub>2</sub> = 2.5) is approximately 10 °C higher than the predictions. However, at Fe/SiO<sub>2</sub> = 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.



Figure 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<sub>2</sub>O<sub>3</sub>, CaO and MgO on the phase equilibria and liquidus temperatures 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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#### References

- [1] A. Yazawa, M. Kameda, Tech Repts Tohoku Univ., (1953) 50-58; (1954) 1-22; (1955) 239-250, 251-261; (1956) 31-50.
- [2] E. Motonori, A. Yazawa, Trans. J. Inst. Metals, 18 (1977) 353-360.
- [3] K. Masaru, E. Motonori, A. Yazawa, Trans. J. Inst. Metals, 19 (1978) 152-158.
- [4] C. Acuna, A. Yazawa, Trans. J. Inst. Metals, 28 (1987) 498-506.
- [5] A. Yazawa, Can. Met. Quart., 13 (1974) 443-453.
- [6] Y. Takeda, S. Nakazawa, A. Yazawa, Can. Met. Quart., 19 (1980) 297-305.
- [7] VDEh, Slag Atlas, 2nd ed, Verlag Stahleisen, 1995.
- [8] B. Zhao, E. Jak, P.C. Hayes, Metall. Mater. Trans. B, 30B (1999) 597-605.
- [9] B. Zhao, E. Jak, P.C. Hayes, Metall. Mater. Trans. B, 30B (1999) 1017-1026.
- [10] T. Hidayat, P.C. Hayes, E. Jak, Metall. Mater. Trans. B, 43B (2012) 14-26.
- [11] T. Hidayat, P.C. Hayes, E. Jak, Metall. Mater. Trans. B, 43B (2012) 27-38.
- [12] B. Zhao, C. Nexhip, D. P. George-Kennedy, P.C. Hayes, E. Jak, Copper 2010, Hamburg, Germany, 2010, Vol. 3, p. 1297-1312.
- [13] E. Jak, B. Zhao, C. Nexhip, D. P. George-Kennedy, P.C. Hayes, Copper 2010, Hamburg, Germany, 2010, Vol. 2, p. 811-821.
- [14] C.W. Bale, P. Chartrand, S.A. Decterov, G. Eriksson, K. Hack, R.B. Mahfoud, J. Melançon, A.D. Pelton, S. Petersen, 2002. FactSage, Ecole Polytechnique, Montréal. http://www.factsage.com/