

Phase Equilibria of “Cu₂O”-“FeO”-SiO₂-CaO Slags at PO₂ at 10⁻⁸ atm in Equilibrium with Metallic Copper

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ABSTRACT: Limited data are available on phase equilibria of the “Cu₂O”-“FeO”-SiO₂-CaO slag system at the oxygen partial pressures used in the copper smelting, converting and slag cleaning processes. Recently experimental procedures have been developed and have been successfully applied to characterise a number of complex industrial slags. The experimental procedures involve high temperature equilibration on a primary phase substrate and rapid quenching of the sample followed by the electron probe X-ray microanalysis. This technique has been used to construct the liquidus isotherms in the “Cu₂O”-“FeO”-SiO₂-CaO slag system in equilibrium with copper. The liquidus isotherms and solubilities of copper oxide in liquid slags at the controlled oxygen partial pressure of 10⁻⁸ atm and temperatures between 1150 and 1350 °C have been determined in equilibrium with metallic copper and the tridymite, olivine, wustite, wollastonite or pseudo-wollastonite solid phases. The new experimental data on copper solubility in slag at different temperatures have been analysed using a regular solution model to describe the activity coefficients of copper oxide as a function of temperature and liquid slag composition. The new experimental equilibrium results are presented in the form of ternary sections and the effects of slag composition on the calculated activity coefficients of liquid CuO_{0.5} in slag are reported. The activity coefficient $\gamma_{\text{CuO}_{0.5}}$ is shown to significantly increase with increasing CaO/SiO₂ and Fe/SiO₂ weight ratios.

1. INTRODUCTION

Optimal control of the slag chemistry in copper smelting, converting and slag cleaning is one of the important issues influencing the efficient and stable operation of these processes. Further improvements to industrial copper production processes require detailed knowledge of the slag properties and the effects of the fluxes, such as, SiO₂ and CaO.

Extensive experimental data on the equilibria between the Fe-O-S-Si-(Ca-Mg-Al) slags and copper metal or matte have been reported in a number of papers [1-16]. Those previous experimental studies used the equilibration and quenching technique, with the samples contained in quartz, magnesium oxide or alumina crucibles. Following quenching, the slag and matte (and/or metallic copper) phases were physically separated, and the bulk compositions of the separated phases were measured and reported. Those techniques have the following limitations. The results obtained from the bulk phase analysis have uncertainties depending on the proportions and compositions of the solid and matte or copper phases suspended in the liquid oxide phase. Crystalline oxide phases formed due to the crucible-slag interaction are commonly found to be suspended inside the liquid oxide solution phase in different proportions. In addition, it is possible that the matte or copper metal is also entrapped as droplets inside the liquid oxide solution. It is practically impossible to guarantee a complete physical separation of liquid oxide phase from the crystalline oxide and the entrapped matte or copper metal phases when attempting to analyse the liquid oxide phase by bulk chemical

methods. As a consequence of the limitation imposed by the crucible, experimental data for the equilibria between liquid and matte or copper metal at conditions relevant to copper smelting are not reported in the literature.

The experimental procedures used in the present study have been developed by the Pyrometallurgy Research Centre (PYROSEARCH) at the University of Queensland [17-19] that have resolved a number of experimental difficulties and have been successfully applied to a number of complex industrial slag systems. The experimental procedures involve a high temperature equilibration using primary phase suspension approach and quenching followed up by the electron probe X-ray microanalysis (EPMA) of the compositions of phases observed in the sample. This technique has been used recently by the authors to construct the phase equilibrium diagram for the “Cu₂O”-“FeO”-SiO₂-CaO slag system at controlled oxygen partial pressure and to evaluate the effects of Al₂O₃ and MgO additions at the conditions relevant to the particular copper smelting, converting and slag cleaning systems [20-27]. Further extension and application of this experimental technique to systematically characterize the “Cu₂O”-“FeO”-SiO₂-CaO system at a fixed oxygen partial pressure of 10⁻⁸ atm and temperatures from 1150 °C to 1350 °C is outlined in this manuscript.

2. EXPERIMENTAL TECHNIQUE AND PROCEDURE

The synthetic slag starting mixtures were made of high purity (>99.9 wt%) Cu, Cu₂O, CaO, SiO₂, Fe₂O₃ and Fe powders. The powders for each sample were weighed and mixed with an agate mortar and pestle. The sample compositions were selected to obtain a liquid slag phase in equilibrium with solids so that the liquidus and solidus compositions “a” and “c” respectively can be measured (see Figure 1). The spinel (Fe₃O₄) substrate was prepared from 99.85 wt% pure iron foil folded into the shape indicated in Figure 2 and then oxidised at PO₂ of 10⁻⁸ atm and the selected experimental temperature. The silica (SiO₂) substrate (see Figure 2) was prepared from a slice of high purity silica rod. The mixtures, selected for each sample were pelletized and 0.2 g placed on the substrate. The substrates were supported by platinum wire within the vertical reaction tube. Special care was taken to avoid the contact of the slag mixture with the platinum wire, and to ensure that the final compositions of slag and metal are free from contamination. The open substrate shape ensured that the liquid oxide solution is a) directly exposed to the gas atmosphere, and b) the first material to contact the quenching medium thereby achieving the faster quenching rate.

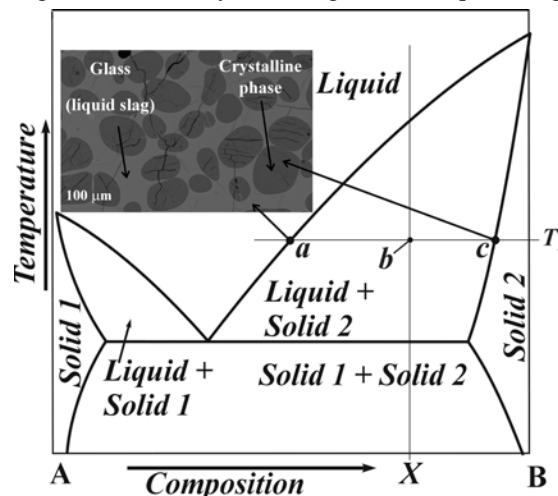


Figure 1: Experimental approach to phase equilibrium determination using sub-liquidus equilibration, quenching and EPMA

All the equilibration experiments in the present study were conducted in a vertical reaction tube (impervious recrystallised alumina, 30-mm i.d.) using electrical resistance silicon carbide (SiC) heated furnaces. The furnace temperature was controlled within ± 1 K by an alumina shielded Pt/Pt-13wt%Rh thermocouple placed immediately adjacent to the sample. The thermocouple was periodically calibrated against a standard thermocouple (supplied by “National Measurement Institute of Australia”, West Lindfield, NSW, Australia). The overall temperature accuracy is estimated to be within 5 K. The atmosphere within the reaction tube was maintained at a fixed oxygen partial pressure of $10^{-8.0}$ atm. using CO-99.5 wt% pure, CO₂-99.99 wt% pure gas mixtures. The flow rates of gases to the furnace were controlled using glass capillary flow meters with the gas flowing from the bottom to the top of the furnace. The volumetric ratio of the gases used to achieve the selected oxygen partial pressure at a set temperature was calculated using the FactSage thermodynamic package 6.2 [28, 33]. The oxygen partial pressures were periodically checked with a partially stabilised zirconium oxygen probe (SIRO₂®, DS-type oxygen probe supplied by Australian Oxygen Fabricators (AOF), Melbourne, Australia). It was confirmed that the results of the measurements in the present study are at least within the accuracy of the DS-type oxygen probe, i.e. within log PO₂ of ± 0.1 units (PO₂ in atm)[34]. Later experiments indicated that the actual accuracy of the oxygen partial pressure control during experiments is even better.

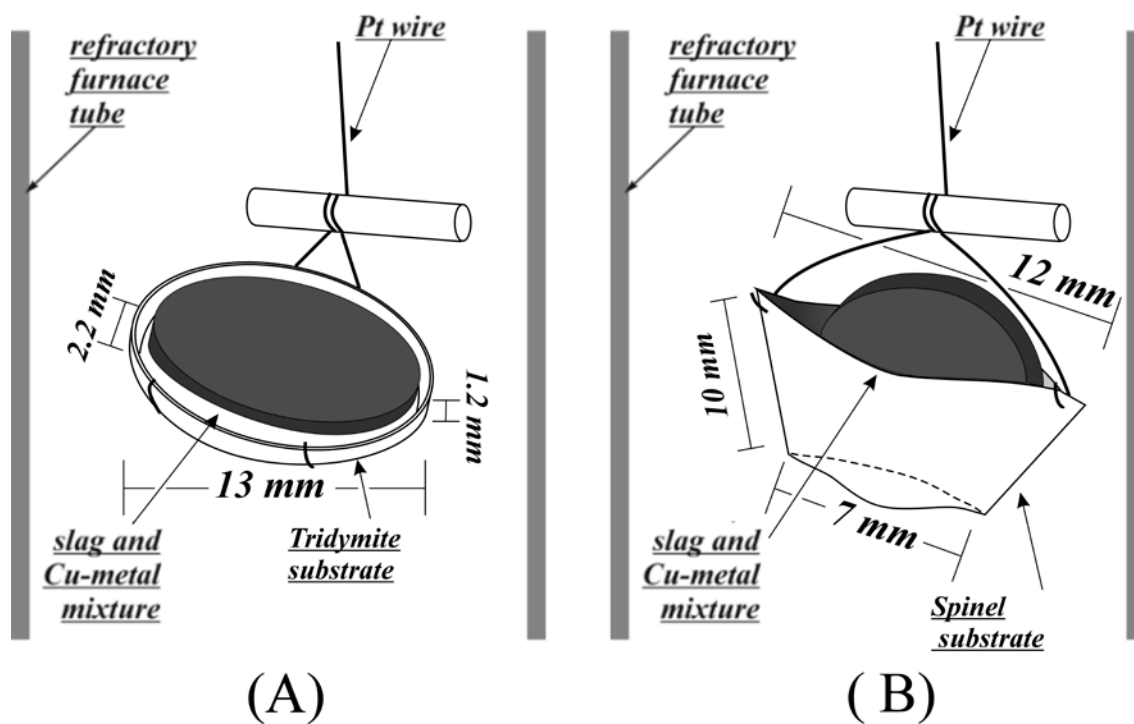


Figure 2: Schematic of the sample holders used in the experiments with substrates of (a) tridymite and (b) spinel.

Particular attention was paid and focused efforts were made to ensure the achievement of equilibrium. First, in order to approach the equilibrium from two different directions, metallic Fe and metallic Cu powders were used to make the starting mixtures on different sides from the final equilibrium point. The achievement of equilibria was also ensured by checking the chemical homogeneity of the phases using EPMA and by carrying out experiments for different equilibration times: one experiment was carried out for 12 hours, while another for a prolonged time. The result indicated that even 12 hours holding time was sufficient to achieve equilibrium. A holding time of 24 hours was used

for experiments. Premelt at higher temperature for short time (5-30 min) was always used before the temperature was lowered to the final equilibration temperature to ensure homogenization of the liquid oxide solution, precipitation of “fresh” crystals from the liquid oxide phase and elimination of the uncertainty that some of the initial solids remained un-dissolved. The reactions taking place during the achievement of equilibria were considered, and traces of possible incomplete processes, such as inhomogeneous spinel crystals or noticeable differences of copper concentrations on different sample locations, were searched for in all samples.

After the holding time, the base of the reaction tube was immersed in water and ice, the lower rubber stopper sealing the tube was removed, the sample was dropped directly into the iced-water, dried, mounted in epoxy resin, and polished for metallographic observation and micro-analysis.

The liquid oxide solution phase is converted on quenching into glass, and the crystalline solids present at high temperature remain unaltered. Measurement of the compositions of the various phases within the sample was undertaken using a JEOL JXA 8200L (trademark of Japan Electron Optics Ltd., Tokyo) electron X-Ray probe microanalyzer (EPMA) with wavelength dispersive detectors (WDD). An accelerating voltage of 15 kV and a probe current of 15 nA were used. The Duncumb-Philibert ZAF correction procedure supplied with the JEOL JXA 8200L probe was applied. The standards (Charles M. Taylor, Stanford, CA) that were used in the EPMA measurements were Cu_2O for Cu, wollastonite (CaSiO_3) for Si and Ca, and hematite (Fe_2O_3) for Fe. The compositions were measured to the accuracy better than 1 wt %.

Iron oxide is present in the sample in 2+ and 3+, and copper oxide in 1+ and 2+ oxidation states. Only the Fe and Cu cation concentrations were measured with EPMA. All the iron and copper were recalculated to the ferrous state 2+ (FeO) and cuprous state 1+ (Cu_2O) respectively for presentation purposes and to ensure that the projected points are unambiguously defined.

In addition, the experiments were planned and conducted with the aim of representing the information in the form of pseudo-ternary sections, thus, all compositions were projected onto the “FeO-SiO₂-CaO section.

3. EXPERIMENTAL RESULTS

The series of experiments carried out to obtain the liquidus in the “Cu₂O”-“FeO”-SiO₂-CaO system was completed to evaluate the liquid/tridymite/copper, liquid/spinel(or wustite)/copper and liquid/wollastonite (or pseudowollastonite) / copper equilibria. Typical microstructures observed using scanning electron microscopy (SEM) in the quenched samples are presented in Figure 3.

The projections of the liquidus isotherms at the experimental temperatures between 1150 °C and 1350 °C are given in Figure 4; the ratios of only “FeO”, SiO₂ and CaO concentrations in a phase normalised to 1 are plotted; the concentrations of copper in the liquid at every experimental point are also given in the figure.

As a general tendency, it is observed that the concentration of copper in the liquid slag decreases with increasing CaO/SiO₂ and Fe/SiO₂ weight ratio at a given temperature. The concentration of copper in the liquid slag at fixed proportions of major elements increases with decreasing temperature.

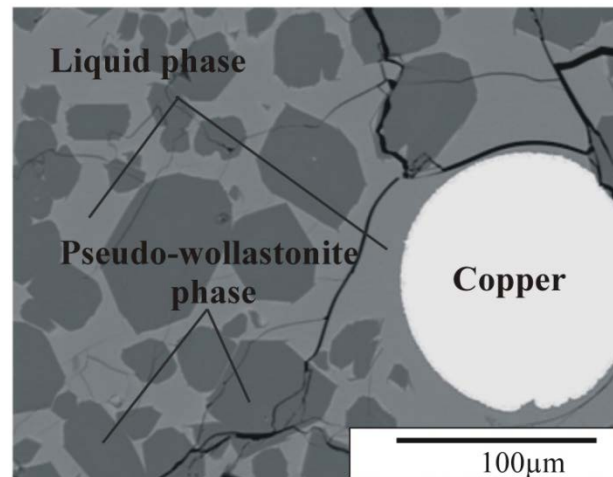
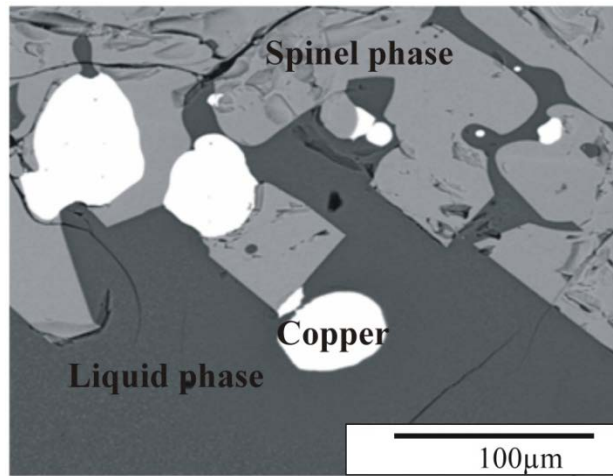
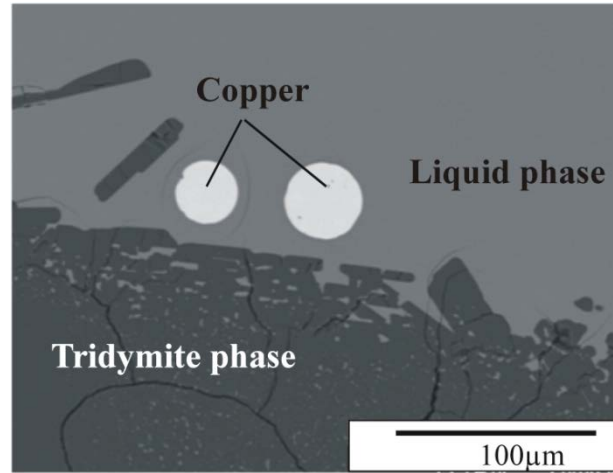


Figure 3: SEM backscattered images of slag in equilibrium with copper and tridymite, spinel and pseudo-wollastonite

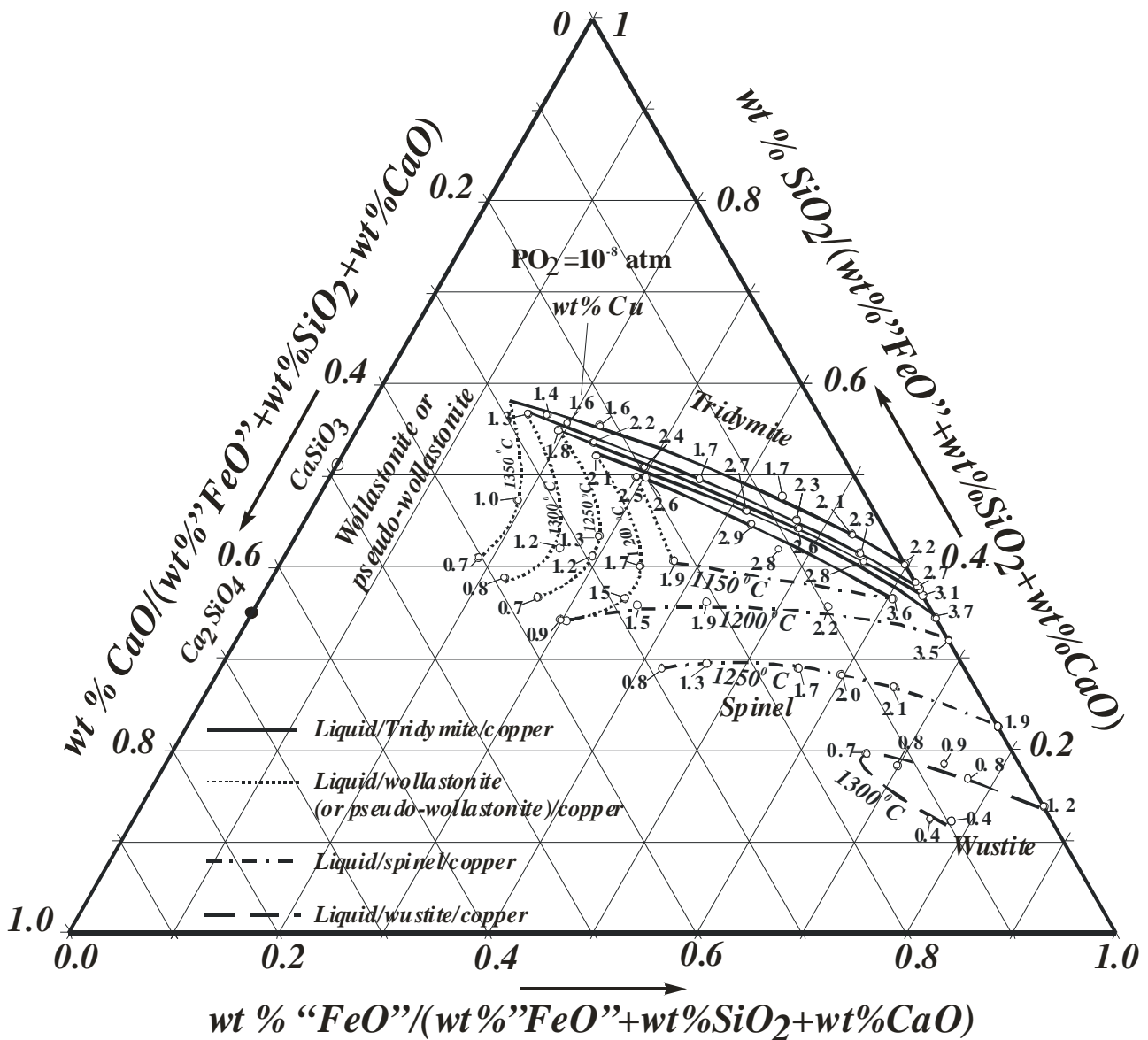


Figure 4 Liquidus surface and concentrations of dissolved copper in slags “Cu₂O”-“FeO”-SiO₂-CaO at PO₂=10⁻⁸ atm., 1150 to 1350 °C at copper metal saturation.

3.1 Activity coefficient of copper oxide (CuO_{0.5})

The dissolution of Cu in the slag can be analysed on the basis of the following reaction and corresponding equation:



where $\gamma_{\text{CuO}_{0.5}}$ is the activity coefficient of CuO_{0.5} (relative to the pure liquid CuO_{0.5} standard state), $N_{\text{CuO}_{0.5}}$ is the molar fraction of CuO_{0.5} in the slag phase and a_{Cu} is the activity of copper (pure liquid Cu standard state). The concentration of iron in copper at the experimental conditions of the present work is less than 1wt%, thus, $a_{\text{Cu}} \approx 1$. The CuO_{0.5} activity coefficient in slag can therefore be calculated from the present experimental slag composition using the equilibrium constants taken from the FactSage database 6.2 ($K_{\text{eq}}=12.09$ at 1423 K (1150°C), $K_{\text{eq}}=10.7$ at 1473 K (1200°C), $K_{\text{eq}}=9.04$ at 1523 K (1250°C), $K_{\text{eq}}=7.73$ at 1573 K (1300°C), $K_{\text{eq}}=6.68$ at 1623 K (1350°C)).

The present experimental technique allows only the equilibrium with a given solid phase (substrate) to be investigated. Information in the fully liquid phase would require container-less experiments. The data in the present study have been obtained from large number of experiments over a wide range of temperatures and compositions; this provides the opportunity to evaluate the behaviour of the dissolution of copper in liquid slag over the wide range of temperatures and compositions.

It has been reported in a previous experimental study [1] that the activity coefficient of Cu_2O in the “ Cu_2O ”-“ FeO ”- SiO_2 - CaO system does not change significantly with the Cu_2O concentration in slag up to 10 wt% (oxygen partial pressures of approximately 10^{-6} atm). In order to analyse the behaviour of the system in the present study, it has been assumed that the temperature dependence of the copper activity can be approximately reasonably described by a regular solution model (even though the behaviour of the system does not exactly correspond to that behaviour). Using this assumption it can be shown that

$$\ln \gamma_{\text{CuO}_{0.5}}(T_2) / \ln \gamma_{\text{CuO}_{0.5}}(T_1) = T_1/T_2 \dots \dots \dots (3)$$

where T is the absolute temperature (K). The experimentally determined $\text{CuO}_{0.5}$ values obtained at various temperatures were adjusted to the corresponding values at 1250 °C for each given slag composition using equation (3). The activity coefficients $\gamma_{\text{CuO}_{0.5}}$ recalculated to 1250 °C were then expressed in terms of the CaO/SiO_2 and Fe/SiO_2 weight ratios using the following relationship:

$$\gamma_{\text{CuO}_{0.5}}(1523\text{K}) = 0.808 + 1.511(\text{Fe}/\text{SiO}_2) + 2.734(\text{CaO}/\text{SiO}_2) + 6.14(\text{CaO}/\text{SiO}_2)^2 \quad (R^2=0.91) \quad (4)$$

or

$$\gamma_{\text{CuO}_{0.5}}(T) = [0.808 + 1.511(\text{Fe}/\text{SiO}_2) + 2.734(\text{CaO}/\text{SiO}_2) + 6.14(\text{CaO}/\text{SiO}_2)^2]^{(1523/T)} \quad (4')$$

Ranges of application: a) within liquidus constraints – only for fully liquid slag,
 b) $1423\text{K} (1150^\circ\text{C}) < T < 1623\text{K} (1350^\circ\text{C})$, and c) $0.2 < \text{Fe}/\text{SiO}_2(\text{wt ratio}) < 7$, $0 < \text{CaO}/\text{SiO}_2(\text{wt ratio}) < 1.0$

The parameters in equation (4) were obtained by minimising the sum of squared differences between calculated and experimental values to obtain the best fit. The agreement between experimental and calculated values of activity coefficients is illustrated in Figure 5. The use of these simplified mathematical expressions is justified by the relatively small range of compositions investigated.

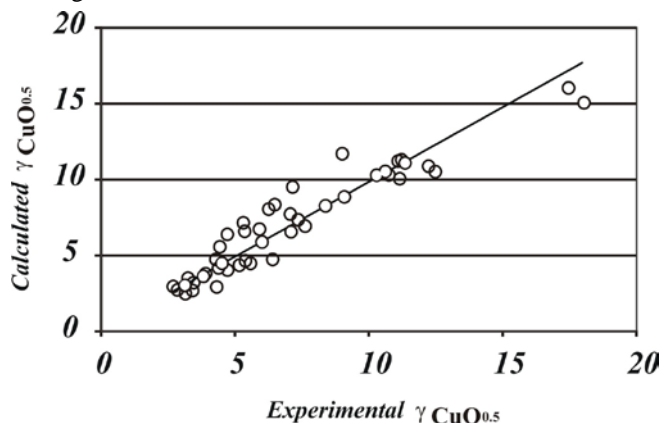


Figure 5. Experimental and calculated (using equation (4)) activity coefficients of $\text{CuO}_{0.5}$ in “ Cu_2O ”-“ FeO ”- SiO_2 - CaO at metallic copper saturation, $P_{\text{O}_2}=10^{-8}$ atm., at 1250 °C

The parameters in equation (4) are an indication of the separate effects of CaO/SiO₂ and Fe/SiO₂ weight ratios on the activity coefficient. Figure 6 shows the experimental and the corresponding calculated activity coefficients at 1250 °C and the iso-activities lines.

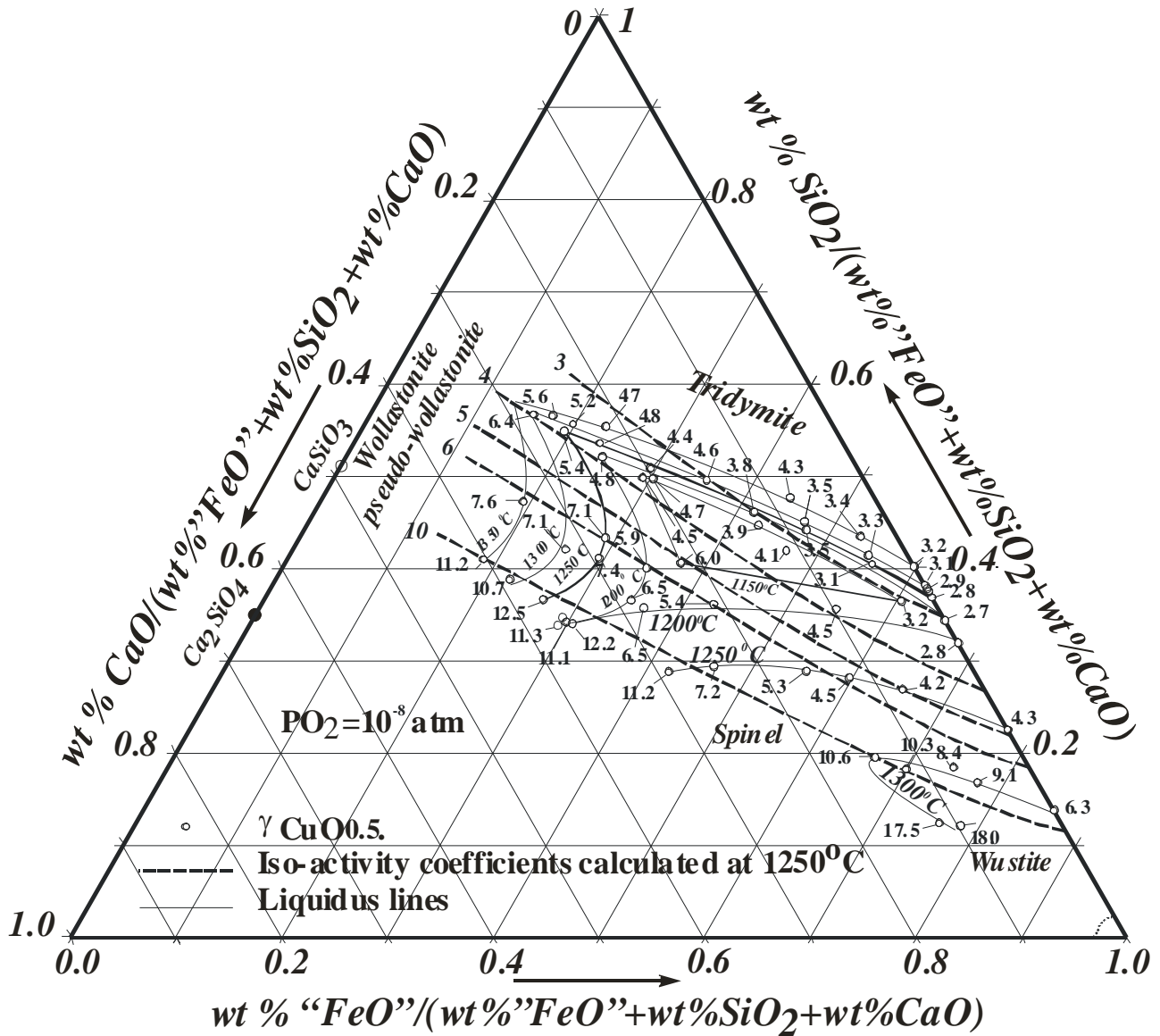


Figure 6. Recalculated activity coefficients at 1250 °C (using equation (3)) and calculated (using equation (4)) iso-activity coefficient lines for “Cu₂O”-“FeO”-SiO₂-CaO at PO₂=10⁻⁸ atm in equilibrium with copper metal.

Figure 7 shows a comparison between the present experimental results in the system “Cu₂O”-“FeO”-SiO₂ with those reported in the literature for the equilibrium with tridymite (no data on equilibrium with spinel or wustite have been found for the “Cu₂O”-“FeO”-SiO₂ system). Significant disagreements between the experimental results reported by different authors are observed, with the reported values of the CuO_{0.5} activity coefficients ranging between 1.4 [5] and 4.4 [11]. The figure includes the calculated activity coefficients using equation (4) for CaO = 0 wt % and for the weight ratio CaO/SiO₂ = 0.43.

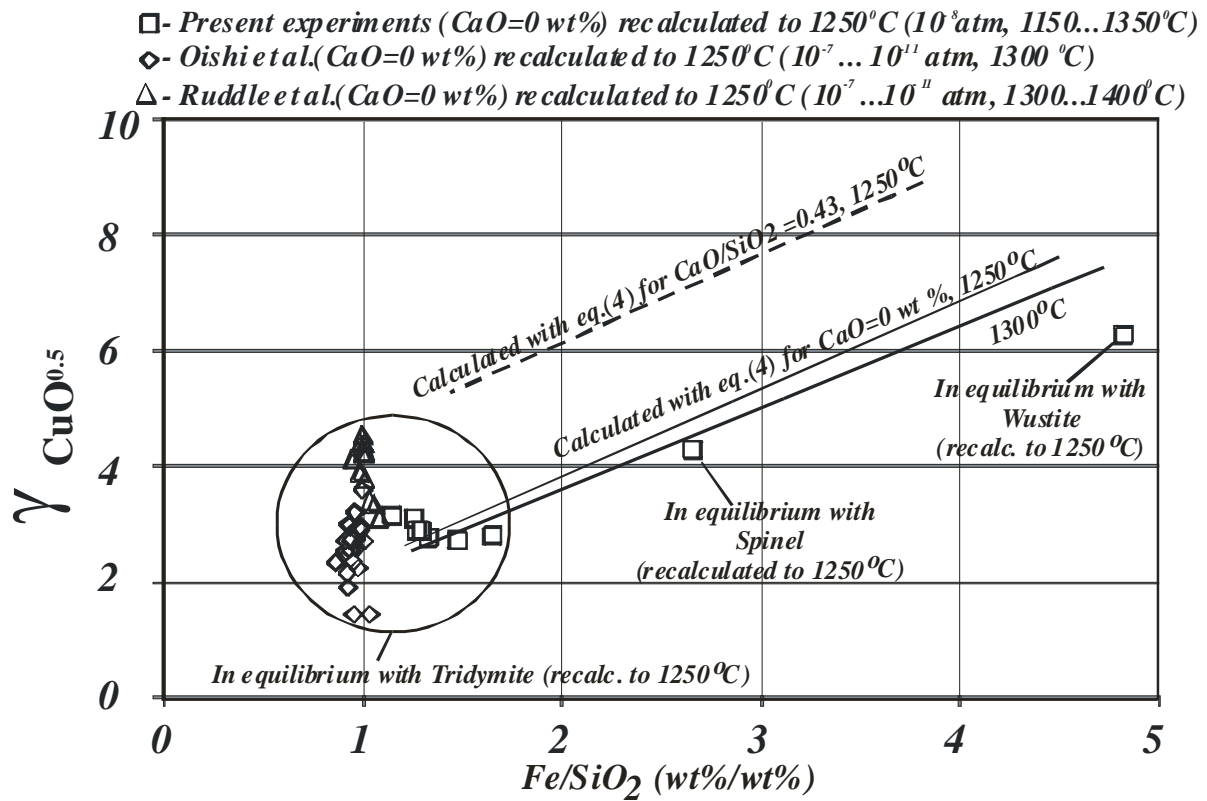


Figure 7. Comparison of the recalculated $\text{CuO}_{0.5}$ activity coefficients at 1250°C for the “ Cu_2O ”-“ FeO ”- SiO_2 system (wt% $\text{CaO}=0$) obtained in the present study in equilibrium with copper metal, tridymite, wustite or spinel with those reported in the literature.

Figure 8 shows comparisons of the present experimental results for the system “ Cu_2O ”-“ FeO ”- SiO_2 - CaO with obtained from other sources [1, 22]. Takeda [1] used MgO crucibles; but did not undertake experiments in equilibrium with spinel. The results [1] indicate the same tendency as is observed in the present study only for the concentration of SiO_2 between 30 and 45wt%. It is important to point out that the technique used in the present work enables results to be obtained in equilibrium with spinel, thus, the present trends in the high- FeO composition area are the interpolations supported by the actual experimental data. The experimental data by Nikolic *et al* [22] for the concentration of copper in slag up to 5 wt % at temperatures of 1250 °C and 1300 °C and PO_2 of 10^{-6} atm agree with the present work in the same compositional areas.

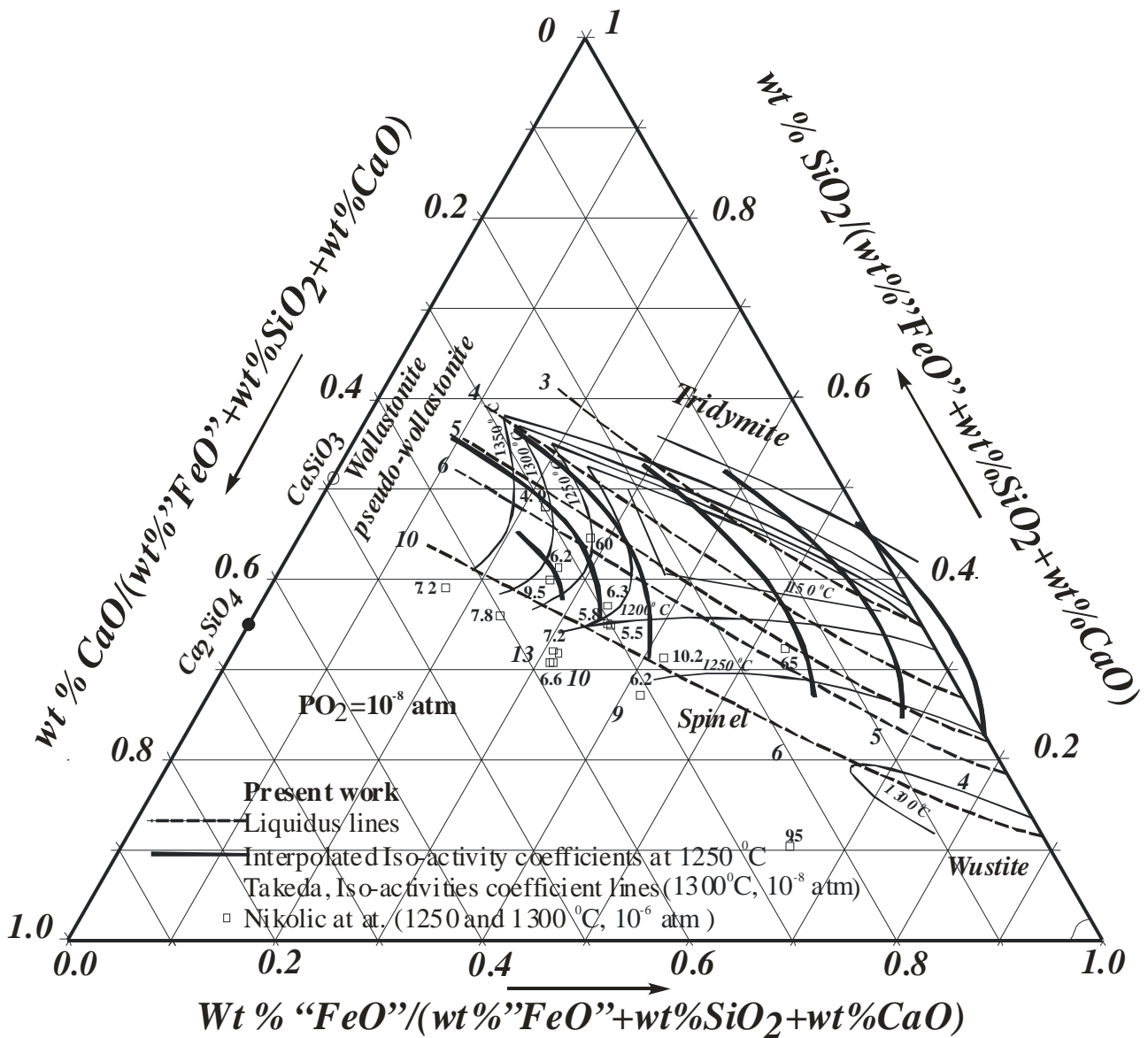


Figure 8. Comparison of present results of activity coefficients of $\text{Cu}_{0.5}$ with those reported by Takeda [1] and Nikolic et al [22].

4. CONCLUSIONS

Using experimental data obtained in the present study the liquidus isotherms in the “ Cu_2O ”-“ FeO ”- SiO_2 - CaO system at the oxygen partial pressure of 10^{-8} atm between 1150 and 1350°C in equilibrium with metallic copper have been constructed.

The liquidus surfaces for the tridymite, wollastonite (or pseudowollastonite) and spinel (or wustite) have been investigated.

From the measured concentrations of dissolved copper in liquid slag, a set of data of activity coefficients were obtained by recalculation to 1250⁰C using a regular solution model. The resulting values were used to describe the activity coefficients of CuO_{0.5} as a function of the CaO/SiO₂ and Fe/SiO₂ (weight ratios).

It is observed that the values of activity coefficients are strongly dependent on the CaO/SiO₂ and Fe/SiO₂ weight ratios.

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