

LIQUIDUS TEMPERATURES IN CALCIUM FERRITE SLAGS EQUILIBRATED WITH MOLTEN COPPER

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ABSTRACT

Calcium ferrite slags are currently used in a number of copper-converting processes. The present study was initiated to further investigate and characterize the phase equilibria of this important industrial slag system. Recently, a modified experimental method has been developed; this involves rapid quenching of slag samples equilibrated at high temperatures, with the resulting phase compositions analyzed using electron probe X-ray microanalysis (EPMA). In the present study, experimental samples were equilibrated in either a gas with a fixed oxygen partial pressure or argon gas atmosphere in the temperature range of 1100 °C-1250 °C. The investigated slags were supported during equilibration by a substrate of the primary phase. This technique removes the limitations arising from the use of crucibles and facilitates rapid quenching of the melt. Liquidus data are reported for the primary phase field of spinel, dicalcium ferrite, $\text{Ca}_4\text{Fe}_9\text{O}_{17}$, cuprite and lime. The analyzed compositions of liquid phases were used to construct projections of the liquidus surface in the $\text{Cu}_2\text{O}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{CaO}$ system in equilibrium with metallic copper.

INTRODUCTION

Copper converting, as currently practised using Peirce-Smith converter technology, involves the use of iron-silicate slags. Due to a number of issues associated with Peirce-Smith converters, including difficulties in fugitive gas capture [1], continuous copper converting processes, such as the Mitsubishi continuous copper production process [2] and the Kennecott-Outokumpu flash copper-converting furnace [3], have been developed that utilize calcium ferrite slags. In addition, new processes, such as the ISACONVERT™ process [4, 5], are under active development for the continuous converting of copper matte. Calcium ferrite slags have been selected for use in these continuous converting processes due to the prevalent stability of the liquid phase over solid magnetite at blister copper saturation [1]. Additional benefits of this system are a lower slag volume, lower copper losses, greater fluidity, and more efficient impurity removal from the molten copper when compared to iron silicate slags [1].

These beneficial properties of calcium ferrite slags were first established by the research of Yazawa [6, 7] and Takeda [8]. This research facilitated the commercialization of these slags in the existing continuous converting processes [1]. Research into the liquidus phase equilibria of calcium ferrite slags saturated with metallic copper has been reported by four studies: Hino [9], Takeda [10], Ilyushechkin *et al.* [11] and most recently Nikolic *et al.* [12]. In the most recent study [12] modifications and refinements to the rapid quenching primary phase substrate experimental technique with EPMA analysis, employed by previous authors [11, 13, 14, 15, 16, 17] were reported. The modified technique was implemented in order to determine the phase equilibria in the $\text{Cu}_2\text{O-FeO-Fe}_2\text{O}_3\text{-CaO}$ system at copper saturation on the spinel liquidus at 1200°C and 1250°C at fixed oxygen partial pressures in the range from $10^{-5.0}$ atm to $10^{-6.5}$ atm. This work described the production and application of the spinel substrate, which enabled the experimental determination of the phase equilibria of this system.

Further investigation of this system is required to allow for characterization of this slag system in the region of direct importance to continuous copper converting. The aims of the present study are:

- Investigate the dicalcium ferrite and spinel liquidus isotherms at fixed oxygen partial pressures.
- Experimentally determine the phase equilibria of this system at metallic copper saturation from 1100°C to 1250°C.

METHODOLOGY

In order to obtain accurate phase equilibrium data in the present study on the $\text{Cu}_2\text{O-FeO-Fe}_2\text{O}_3\text{-CaO}$ system at copper saturation, the rapid quenching primary phase substrate technique with EPMA analysis, defined in the previous paper [12], was selected and then further refined. The rapid quenching technique allows for the phase assemblages present at equilibration to be retained at room temperature. The use of support substrate materials, made from the solid of the primary phase field being investigated, eliminates possible contamination from ceramic crucible materials and avoids dissolution of metallic crucibles by copper metal. Compared with normal crucible experiments, higher cooling rates can be achieved as the relatively smaller mass of liquid slag directly contacts the quenching media.

Experimental Apparatus and Procedure

An explanation and justification of the vertical tube furnace and glass capillary gas flow meter setup used for the experiments conducted in the present study are contained in the preceding papers [12, 16, 17]. A summary of this procedure is presented below:

- Experimental samples were first suspended, with platinum wire, in the reaction tube in the cold zone at the base of the furnace.
- After sealing the furnace, ultra high purity (UHP) argon gas (99.999% pure) was flushed through the furnace tube at a rate of 0.5L/min for a period of thirty minutes, to remove all air.
- The relevant gas flow rates, using CO/CO₂ and H₂/CO₂ gases, required to fix the oxygen partial pressure, if applicable, were established before the samples were pre-melted.
- Pre-melting of the samples was undertaken for a period of 30mins, at a temperature 10°C above the equilibration temperature and, if applicable, at the same oxygen partial pressure as the final equilibration.
- After equilibration the end of furnace tube was immersed in a sodium chloride (NaCl) saturated water solution, which suppresses vaporization during quenching, and the samples were quenched by being dropped directly into this solution from the hot-zone of the furnace.
- The samples were then thoroughly washed in water before being dried, mounted in epoxy resin, and polished for metallographic examination and microanalysis.

Substrate Design

There were three primary phase substrates used in the present study: spinel (Figure 1a), dicalcium ferrite (Figure 1b) and cuprite (Figure 1c). These three substrate shapes maximized the available surface area used for suspending slag whilst minimizing the mass of the substrate and thereby maximizing the cooling rate of the slag on quenching.

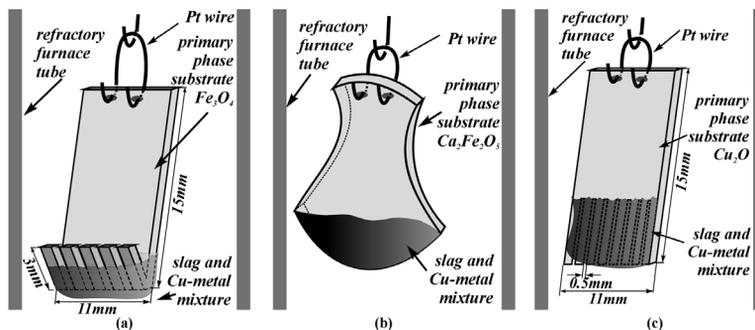


Figure 1: Primary phase substrates used in the present study – (a) Spinel (Fe₃O₄), (b) Dicalcium ferrite (Ca₂Fe₂O₅) and (c) Cuprite (Cu₂O)

Details regarding the manufacture of these substrates are provided below:

- Spinel (Fe₃O₄) - defined in the preceding paper [12]
- Dicalcium ferrite (Ca₂Fe₂O₅) - prepared from a stoichiometric mixture of Fe₂O₃ powder and calcined CaO powder pelletized (at a pressure of 30 MPa) to a 15 mm diameter,

2 mm thick pellet. Pressed pellets had 4 mm cut from the upper section of both sides, minimizing the mass of substrate used for slag suspension. Two holes were drilled in the substrate to allow for the insertion of platinum wire holding hooks. This created the desired shape (refer to Figure 1b) which was then calcined at 1250°C in air for 6-24 hrs

- Cuprite (Cu_2O) - prepared from 99.9 wt% pure copper foil (0.1mm thick) that had been cut to the flat substrate design (refer to Figure 1c) and oxidized to Cu_2O in a stream of air at 1075°C for 30 minutes followed by another 30 minutes at 1125°C. The complete oxidation of the samples to Cu_2O was confirmed gravimetrically.

Mixture Preparation

Synthetic starting mixtures, pre-saturated with metallic copper, were bound to the designed substrates with approximately 3 mg of 0.065 mm diameter Fe wire (99.5% pure) and approximately 30 mg of 0.125 mm diameter Cu wire (99.9% pure). These mixtures were made from CaO powder (calcined from 99.9+ wt% pure CaCO_3 powder), Fe_2O_3 powder (99+ wt% pure), Cu_2O powder (made from 0.1mm thick 99.9% pure Cu-foil that had been oxidized in air at 1075°C for 30 minutes then at 1125°C for 30 minutes and then ground in an agate mortar and pestle) and metallic copper powder (99.7% pure). The copper powder was 30% by weight in excess of the mass of the oxide components of the mixture. Appropriate proportions of these powders were first mixed in an agate mortar with pestle for thirty minutes and then pelletized using a pressure of 40 MPa to produce a 15 mm diameter, 1mm thick pellet.

Equilibration Time for Argon Experiments

Equilibration trials were conducted for the investigation of the phase equilibria of the Cu_2O -FeO- Fe_2O_3 -CaO system at metallic copper saturation in a stream of argon gas with two mixtures that targeted copper oxide in liquid concentrations of approximately 50wt% and 10 wt%. These high and low copper concentrations were selected so that any possible oxidizing or reducing effect of the streaming UHP argon gas could be eliminated. Experiments were conducted using spinel substrates at 1150°C and 1200°C with equilibration times of 1 and 4 hours, the results of these experiments are given in Table 1. The results for the liquidus measurements are within 0.4 wt% and the solidus measurements within 0.2 wt% of each other at the two investigated time intervals. Therefore the equilibration time of 1 hour was found to be adequate to investigate the pseudo-ternary phase equilibria of this system.

Table 1: Phase compositions in Cu_2O -FeO- Fe_2O_3 -CaO system at metallic Cu saturation investigating achievement of equilibrium under a flow of Argon gas

No.	Temperature	Equilibration	Phase	CaO (wt%)	Cu_2O wt%)	Fe_2O_3 (wt%)*
A	1150°C	1hr	Liquid	6.8	53.3	39.9
			Spinel*	1.5	5.0	93.5
B	1150°C	4hrs	Liquid	6.4	53.4	40.2
			Spinel*	1.6	5.1	93.3
C	1200°C	1hr	Liquid	20.1	10.5	69.4
			Spinel*	3.5	0.7	95.8
D	1200°C	4hrs	Liquid	19.9	10.5	69.6
			Spinel*	3.4	0.9	95.7

* EPMA measured Fe recalculated to Fe_2O_3 to ensure unambiguous representation of data – actual composition will contain variable $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio

Equilibration Time for Fixed Oxygen Partial Pressure Experiments

Two methods were used to determine the achievement of equilibrium in the $\text{Cu}_2\text{O-FeO-Fe}_2\text{O}_3\text{-CaO}$ system at metallic copper saturation at fixed oxygen partial pressures:

Achievement of Equilibrium – Time

Equilibration time experiments were performed using both spinel and dicalcium ferrite substrates at 1250°C and a fixed oxygen partial pressure of 10^{-6} atm using the same starting mixture batch. The spinel substrate experiments were equilibrated for 1, 8, 16 and 24 hours and the dicalcium ferrite substrate experiments were equilibrated for 1 and 19 hours. The results of the EPMA measurements on the quenched slags are given in Table 2. In all cases the compositions of the liquid and solid phases, for the relevant substrate phase, were found to be reproducible to within 1wt% without any particular trend in the results with time.

Table 2: Equilibration time test for $\text{Cu}_2\text{O-Fe}_2\text{O}_3\text{-CaO}$ system at metallic Cu saturation equilibrated at a fixed oxygen partial pressures (P_{O_2}) of 10^{-6} atm

No.	Temperature	Equilibration	Phase	CaO (wt%)	Cu_2O (wt%)	** Fe_2O_3 (wt%)
1	1250°C	1hr	Liquid	19.5	8.1	72.4
			Spinel**	2.0	0.6	97.3
2	1250°C	8hrs	Liquid	18.6	7.8	73.5
			Spinel**	2.4	0.4	97.2
3	1250°C	16hrs	Liquid	19.4	8.2	72.4
			Spinel**	2.6	0.6	96.7
4	1250°C	16hrs	Liquid*	19.3	8.6	71.9
			Spinel**	2.4	0.4	97.2
5	1250°C	24hrs	Liquid*	19.5	7.7	72.6
			Spinel**	2.4	0.5	72.6
6	1250°C	1hr	Liquid*	23.1	8.6	68.3
			Dicalcium ferrite	42.1	0.2	57.7
7	1250°C	19hrs	Liquid	22.7	8.6	68.7
			Dicalcium ferrite	41.7	0.2	58.1

* Standard deviations of the compositions of these liquid phases were within 2.0 wt% but they are included for the purpose of comparison

** EPMA measured Fe recalculated to Fe_2O_3 to ensure unambiguous representation of data – actual composition will contain variable $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio

Achievement of Equilibrium – Direction

Equilibration tests were also undertaken to determine if equilibrium could be reached from both high and low copper oxide concentrations at a fixed oxygen partial pressure. Experiments were undertaken using the dicalcium ferrite substrate at 1200°C targeting a fixed oxygen partial pressure of $10^{-5.5}$ atm. Copper oxide concentrations of the starting mixtures were 26.3% and 10.3% with equilibration tests run for 1, 2 and 4 hours. These experiments were difficult to undertake due to substrate precipitation and dissolution problems and therefore the results reported in Table 3 have a standard deviation within $\pm 2\text{wt}\%$ for all compositional components. Irrespective of the higher standard deviations of the measurements given in Table 3, these results showed no particular compositional trend as a function of starting composition.

The two methods used to determine achievement of equilibrium, combining the information given in Table 2 and Table 3, indicated that a one hour equilibration time was sufficient for gas/liquid-slag/solid/Cu-metal equilibrium to be reached in these metallic copper saturated calcium ferrite slags at fixed oxygen partial pressures.

Table 3: Equilibration direction test for $\text{Cu}_2\text{O-Fe}_2\text{O}_3\text{-CaO}$ system at metallic Cu saturation equilibrated at a fixed oxygen partial pressures (P_{O_2}) of $10^{-5.5}$ atm

No.	Temperature	Equilibration	Starting Cu_2O wt%	Phase	CaO (wt%)	Cu_2O (wt%)	** Fe_2O_3 (wt%)
8	1200°C	1 hr	26.3	Liquid*	19.9	19.4	60.7
				Dicalcium ferrite	41.6	0.1	58.2
9	1200°C	1 hr	10.3	Liquid*	20.9	21.0	58.1
				Dicalcium ferrite	41.4	0.6	58.1
10	1200°C	2 hrs	10.3	Liquid*	19.9	19.2	60.9
				Dicalcium ferrite	41.7	0.5	57.8
11	1200°C	4 hrs	26.3	Liquid*	20.7	21.3	58.0
				Dicalcium ferrite	41.5	0.3	58.2

* Standard deviations of the compositions of these liquid phases were within 2.0 wt%

** EPMA measured Fe recalculated to Fe_2O_3 to ensure unambiguous representation of data – actual composition will contain variable $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio

Sample Analysis

Analysis of the compositions of the various phases within the quenched samples was undertaken using a JEOL 8200L (JEOL is a trade mark of Japan Electron Optics Limited of Tokyo, Japan) electron microprobe analyzer (EPMA) with wavelength dispersive detectors (WDD). An accelerating voltage of 15kV and a probe current of 15nA were used. The Duncumb-Philibert ZAF correction procedure supplied with the JEOL 8200L probe was applied. The standards (Charles M. Taylor, Stanford, CA) that were used in the EPMA measurements were: wollastonite (CaSiO_3) for Si and Ca, chalcopyrite (CuFeS_2) for Cu and hematite (Fe_2O_3) for Fe. The compositions were measured to an accuracy of ± 1 wt% [10].

Measurement of phases by EPMA provides information only on the total concentration of a particular element; this technique does not provide information on the proportion of cations of the same element having different valencies. In the slags investigated in the present study iron is present as both Fe^{2+} and Fe^{3+} , whilst copper is present as both Cu^{2+} and Cu^+ . Since the concentrations of the various cations were not measured in the present study, for representation purposes, all of the copper was recalculated to the cuprous state Cu^+ and all of the iron was recalculated to the ferric state Fe^{3+} . In effect the composition is represented as a projection onto the $\text{Cu}_2\text{O-Fe}_2\text{O}_3\text{-CaO}$ plane. Figure 2 illustrates how the actual slag compositions, marked in grey, are projected onto the $\text{Cu}_2\text{O-Fe}_2\text{O}_3\text{-CaO}$ plane, by maintaining the Ca/Fe/Cu ratio.

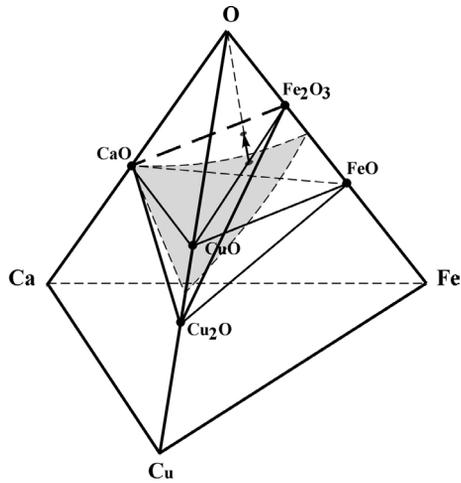


Figure 2: Projection of the Cu-Fe-Ca-O system onto the Cu_2O - Fe_2O_3 -CaO plane

RESULTS AND DISCUSSION

Microstructures in the Cu_2O -FeO- Fe_2O_3 -CaO System at Copper Saturation

Experiments within the Cu_2O -FeO- Fe_2O_3 -CaO system at metallic copper saturation were conducted at temperatures between 1100°C and 1250°C at 50°C steps, in a flow of UHP argon gas, and at 1200°C and 1250°C at fixed oxygen partial pressures in the range of $10^{-5.0}$ to $10^{-6.5}$ atm. SEM micrographs of equilibrated experimental samples illustrating all the phase assemblages identified in the present study are presented in Figure 3. These show, in each case, well-quenched liquid slag (marked as glassy slag in high magnification inserts) and metallic copper in equilibrium with the relevant solid phases. Analysis of the liquid phases, with EPMA, was undertaken on the well-quenched glassy slags, shown in the inserts in Figure 3(a)-(f), which are found at the liquid/quenching medium interface.

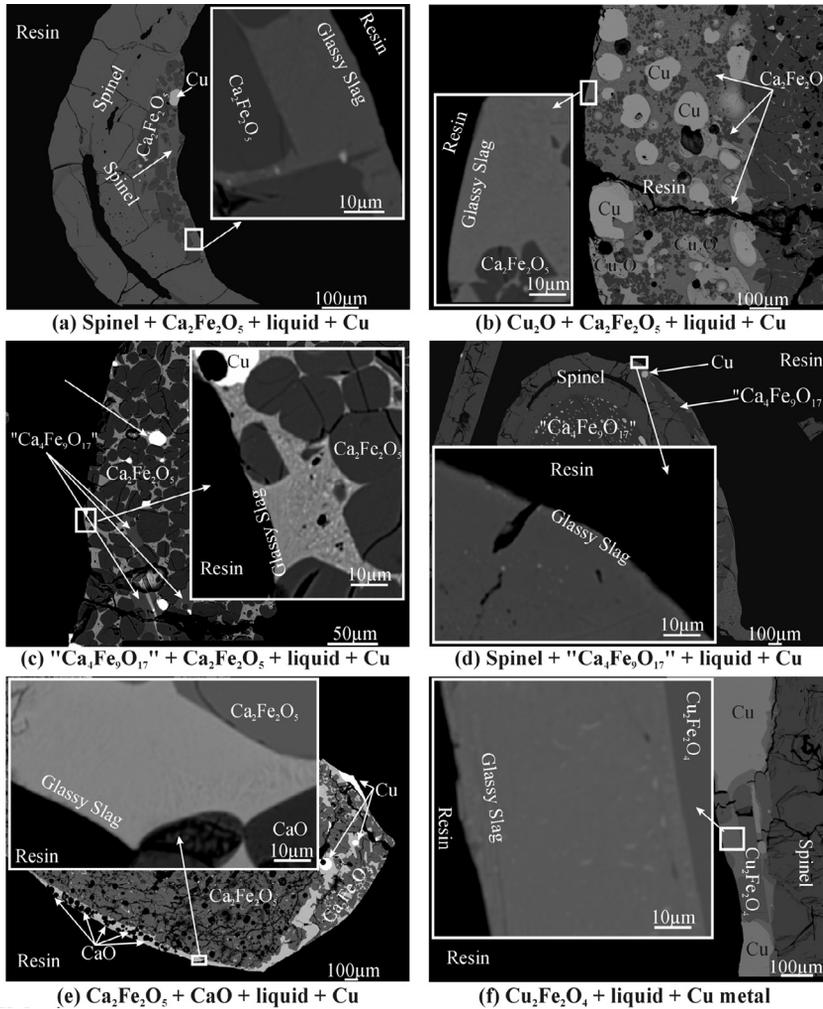


Figure 3: SEM micrographs of typical well-quenched slag samples showing all phase assemblages identified in the present study with solid crystal(s) in equilibrium with liquid slag and metallic copper obtained using the primary phase substrate technique.

The $\text{Cu}_2\text{O}-\text{Fe}_2\text{O}_3-\text{CaO}$ System at Cu Saturation and Fixed Oxygen Partial Pressures

Experiments within the $\text{Cu}_2\text{O}-\text{Fe}_2\text{O}_3-\text{CaO}$ system at copper saturation, at fixed oxygen partial pressures in the range of $10^{-5.0}$ to $10^{-6.5}$ atm, were conducted in the spinel and dicalcium ferrite primary phase fields at 1200°C and 1250°C . The spinel primary phase field experiments, conducted in the previous work [12], were repeated in the present study due to the implementation of additional refinements in the experimental technique, which were developed after the publishing of the previous results [12]. These additional refinements ensured that all liquid phases were analyzed only on the well surface, which had direct contact with the quenching medium. This allowed for the definition of the liquidus compositional results contained in Figure 4. Oxygen isobars that connect the relevant measured compositions, at a particular oxygen partial pressure and temperature, on the spinel liquidus to the dicalcium ferrite liquidus at 1250°C and 1200°C are represented by dashed and dotted lines respectively.

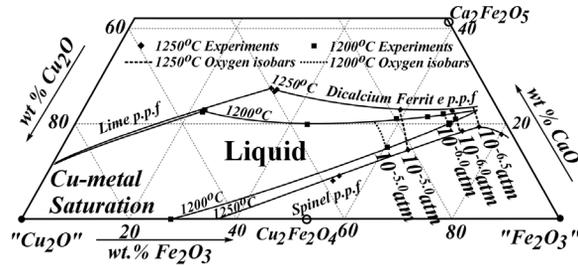


Figure 4: Isothermal sections of the $\text{Cu}_2\text{O}-\text{Fe}_2\text{O}_3-\text{CaO}-\text{SiO}_2$ system at metallic copper saturation and fixed oxygen partial pressures at 1250°C and 1200°C

Figure 4 indicates that a decrease in temperature from 1250°C to 1200°C, at a fixed oxygen partial pressure of $10^{-6.0}$ atm, results in an increase of approximately 2.5 wt% copper oxide in the slag phase. For a fixed oxygen partial pressures of $10^{-5.0}$ atm this same decrease in temperature results in an increase of copper oxide concentration in the slag of approximately 5 wt%. Alternatively, if the oxygen input into a process was held constant, and the temperature decreased, the oxygen partial pressure of the system would be lowered and therefore target sulfur in blister concentrations may not be reached. This information highlights the sensitivity of this system to changing temperature / gas atmosphere conditions and the importance of adequate control of both temperature and oxygen partial pressure during the copper converting process.

Liquidus Temperatures defined by Cu_2O Concentration and Fe/CaO Wt Ratio

In industrial practice selection of operating conditions in copper converting furnaces typically involves fixing the Fe/CaO ratio and targeting a fixed copper oxide concentration in the slag phase at a selected temperature. The Fe/CaO ratio and the copper oxide concentration in the slag can be controlled through effective mass balancing of the system by accurately measuring and controlling oxygen inputs, and feed flow rates and compositions. The temperature of the system is the other key process variable, therefore it is important to consider how the copper oxide concentration and Fe/CaO ratio affect the liquidus of the system as detailed in Figure 5 and 6.

The phase equilibria data for the $\text{Cu}_2\text{O}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{CaO}$ system have been represented in Figure 5 as a function of copper oxide concentration in the slag phase and fluxing Fe/CaO wt ratio. This indicates that the liquidus is very sensitive to both Fe/CaO ratio and dissolved copper oxide in the slag.

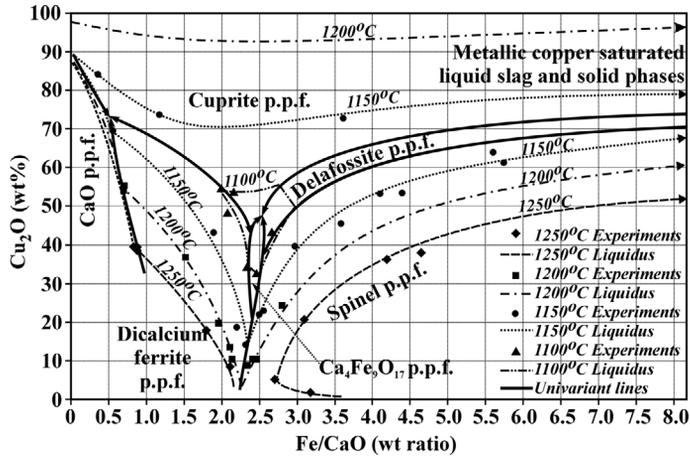


Figure 5: Liquids temperatures in the $\text{Cu}_2\text{O}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{CaO}$ system at copper saturation as a function of Cu_2O concentration and Fe/CaO ratio in the slag

The minimum liquidus temperatures, at each fixed copper oxide concentration, in Figure 6, are based on extrapolations of the experimental liquidus data and the positions of the univariant lines in the system (refer to Figure 5). The information in Figure 6 indicates that the minimum liquidus temperatures of the slags will decrease as the copper oxide concentrations increase from 10 to 40 wt% and will continue to decrease until the ternary eutectic of the system is reached.

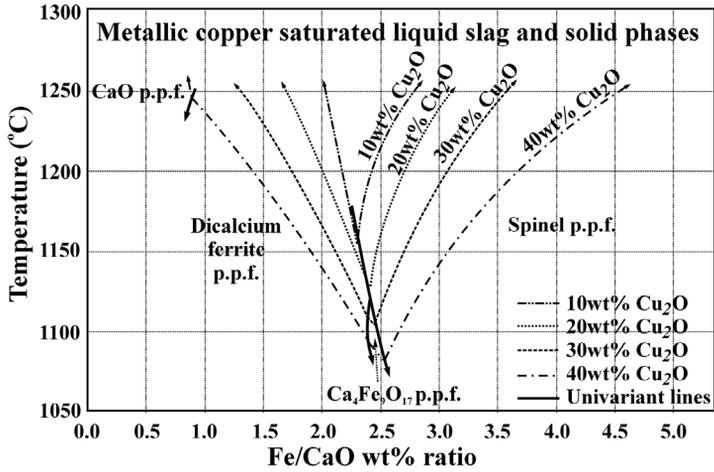


Figure 6: Liquidus in the $\text{Cu}_2\text{O}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{CaO}$ system represented as Fe/CaO wt% ratio at different Cu_2O concentrations in liquid

CONCLUSIONS

The equilibration/rapid-quenching/EPMA substrate suspension experimental approach has been applied in the present study to the investigation of the phase equilibria of calcium ferrite slags at metallic copper saturation described by the Cu_2O -FeO- Fe_2O_3 -CaO system. Synthetic slag samples were equilibrated in both fixed oxygen partial pressure and argon gas atmospheres in the temperature range of 1100°C -1250°C. Liquidus data were reported for the primary phase fields of spinel, delafossite, dicalcium ferrite, $Ca_4Fe_9O_{17}$, cuprite and lime; the resulting data were used to construct liquidus isotherms in the system at copper saturation. This allowed for the construction of two projections of the liquidus surface inter-relating the copper oxide concentration, Fe/CaO ratio and liquidus temperature of the slag phase. These projections highlighted the sensitivity of this system and the importance of adequate control of the copper converting process.

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