

# Viscosity measurements of high “Cu<sub>2</sub>O” containing slags in the “Cu<sub>2</sub>O”-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system in equilibrium with metallic Cu

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**Abstract:** Present study is a part of an overall program on development of the accurate viscosity model of the complex multi-component slag system for Cu production. Viscosity measurements have been carried out in the “Cu<sub>2</sub>O”-rich area of the “Cu<sub>2</sub>O”-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system in equilibrium with metallic copper at temperatures of 1473-1588 K using Al<sub>2</sub>O<sub>3</sub> crucible and spindle aiming to obtain the viscosity data in the “Cu<sub>2</sub>O” and “Cu<sub>2</sub>O”-SiO<sub>2</sub> systems. The custom designed rotating spindle apparatus enables control of the gas atmosphere and rapid quenching of the samples on completion of the experiment. It was found that the solubility of Al<sub>2</sub>O<sub>3</sub> is negligible in the “Cu<sub>2</sub>O” melt and is limited in the “Cu<sub>2</sub>O”-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> melt under experimental conditions. The fact that the samples are quenched directly after the viscosity measurement enables the compositions and phase assemblage of the slag at temperature to be accurately measured and characterized.

The microstructures and phase compositions in the quenched slag samples are determined by Electron Probe X-ray Microanalysis (EPMA). The bulk compositions of the samples are measured with X-ray Fluorescence analysis (XRF).

It is believed that the present data are the first experimental measurements of viscosities in this high “Cu<sub>2</sub>O” slag system in equilibrium with metallic Cu. The self-consistency of the measurements was analysed with Modified Urbain model. The viscosities of “Cu<sub>2</sub>O”-SiO<sub>2</sub> liquid in equilibrium with metallic Cu was derived from the model. A correlation was found between activation energies and against ionic strength ( $z/r$ ). Further development of quasi-chemical viscosity model will be carried out incorporating the Cu<sub>2</sub>O prediction.

**Key words:** Viscosity, “Cu<sub>2</sub>O”-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, Modified Urbain Model, Quasi-chemical viscosity model

## 1. Introduction

The understanding of metallurgical process requires accurate chemical and physical properties of the slag. Viscosity is one of the key physical properties of the slag required for optimum control and improvement of various metallurgical processes. For example, during copper smelting and converting operations, the viscosities of slags can have a strong influence on separation of copper metal from slag and slag tapping rate etc., thus affecting the efficiency of the processes.

The oxides commonly present in the Cu production slags are SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, FeO, CaO, MgO, Al<sub>2</sub>O<sub>3</sub> and Cu<sub>2</sub>O. Many efforts have been made to generate viscosity data for various slags since the early 1930s. Nevertheless, the data available are still too few to meet the high demands of the fast developing technology today. High temperature measurement of the slag systems is a complex, costly- and time- consuming procedure. Viscosity model is an efficient way to predict the behaviour of melts at high temperature. However, comprehensive viscosity models require accurate

experimental data on unary, binary and ternary systems to optimise the parameters for multi-component slags. There are no data found in literature on the viscosities in the “Cu<sub>2</sub>O” and “Cu<sub>2</sub>O”-SiO<sub>2</sub> systems in equilibrium with metallic Cu. The reason is that the aggressive slag reacts with oxide ceramics, and molten metallic copper reacts with noble metals (e.g. Pt, Rh), so that the combination of the slag and molten copper makes it very difficult to select a suitable material for crucible and spindle for viscosity measurements.

An overall program on development of the accurate viscosity model of the complex multi-component slag for Cu production is under way. In the present study, viscosity measurements have been carried out in the “Cu<sub>2</sub>O”-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system in equilibrium with metallic copper using Al<sub>2</sub>O<sub>3</sub> crucible and spindle. The results were analysed using Modified Urbain model [1]. A quasi-chemical viscosity model (QCV) [2, 3] is also revised and, importantly, aimed to be extended to enable the viscosities of Cu smelting, converting and cleaning slags to be predicted within experimental uncertainties over a wide range of compositions and temperatures.

## 2. Experimental

### 2.1 Apparatus

A high-temperature viscosity measurement apparatus has been constructed and commissioned at the Pyrometallurgy Research Centre (PYROSEARCH) at The University of Queensland, Australia [4-6] (see Figure 1 highlighting its key components).

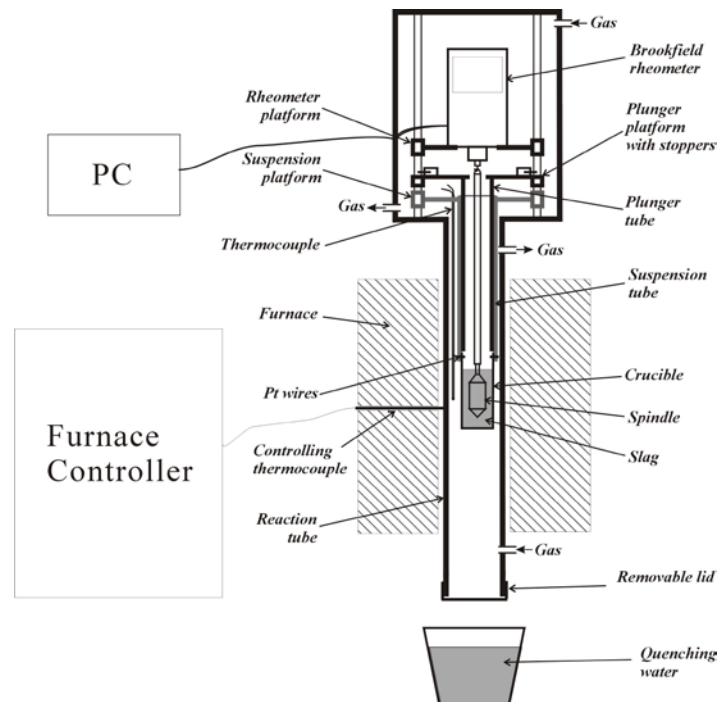


Fig. 1 Schematic of the high temperature viscosity measurement apparatus at PYROSEARCH

A Brookfield digital rotational rheometer (model LV DV III Ultra) controlled by a PC was used in the present work. The full scale torque associated with the rheometer of this model is  $6.73 \times 10^{-5}$  N·m. The acquisition of the torque measured by the rheometer was simultaneously collected by Rheocalc software provided by Brookfield Company.

The rheometer is placed on a movable platform above a furnace and is enclosed in a gas-tight steel chamber. The rheometer rotates co-axially the alumina driving shaft with the cylinder spindle immersed into the slag in the cylinder crucible. The crucible is suspended using an alumina tube and held onto the tube with Pt wires and positioned within the hot zone of the Pyrex tube furnace. The chamber with dense reaction tube enables experiments to be conducted under controlled atmosphere conditions. Constant 0.4 L/min ultra high purity Ar gas (99.999%) was blown into the system from two gas inlets to control gas atmosphere. A Pt/Pt-Rh thermocouple is bound to the suspension tube platform, the tip of which remains adjacent to the crucible at the level where the spindle rotates. This enables accurate temperature of the slag to be measured during the viscosity experiments.

Figure 2 provides dimensional details of the cylindrical crucible and spindle used during the present investigations. The conical spindle, with conical ends and a cylindrical body, has been found to minimise the end-effects that are observed when using plain cylindrical spindles [7]. Each set of spindle and crucible used has been individually calibrated at room temperature using standard calibration liquids (0.0092, 0.0484, 0.0968, 0.51 and 0.96 Pa.s) in water bath at 298.0 K, to minimise uncertainties in the results reported.

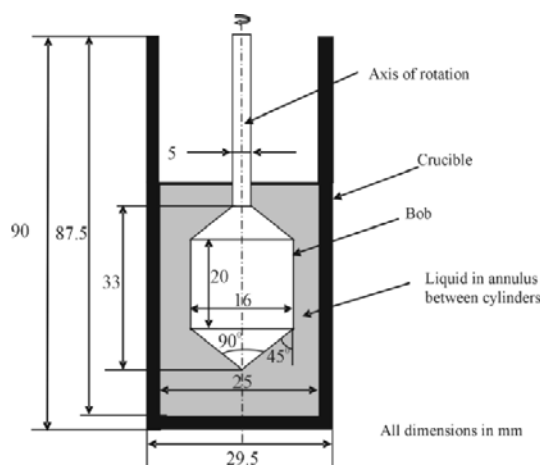


Fig. 2 Dimensional details of crucible and spindle used during present investigations

The main feature of the experimental setup with top suspension is the possibility of quenching a slag sample immediately after viscosity measurement. The ability to quench the slag sample is important since this enables the microstructure of the slag and compositions of the phases present in the slag at the temperature to be characterised directly after the viscosity measurement. In this way the uncertainty associated with the changes of the slag composition during the measurements can be minimised, which is significant to this particular system. The quenching is achieved through using a special “plunger” (the alumina tube held on a separate platform equipped with stoppers). Once activated, the suspension platform holding the crucible moves upward against the fixed plunger, and on doing so, pushes the

crucible out and shears the Pt suspension wires so that the crucible falls down directly into the water bucket beneath the furnace.

## 2.2 Materials and preparation of slags

The materials used in the present work are listed in Table 1.

Approximately 2 grams of Cu metal was placed at the bottom of alumina crucible to maintain the Cu saturation condition. Approximately 80-110 grams of slag sample is required for each viscosity measurements depending on the compositions. Preliminary experiments were carried out to estimate the densities of slags so that the required heights of the liquid slag were obtained. Pure powders of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Cu}_2\text{O}$  were mixed in an agate mortar with desired proportions and then pelletised. The preliminary experiments also showed that the alumina crucibles broke during the cooling period, probably due to the different thermal contraction rate of alumina crucible and slag. No pre-melting procedures were used and the whole required weight of the pelletised sample was placed into the crucible at the same time.

Table 1 Materials used in the present study

Materials	Purity	Supplier	Comment
Silicon oxide ( $\text{SiO}_2$ )	99.90%	Aldrich	
Aluminium oxide ( $\text{Al}_2\text{O}_3$ )	99.99%	Alfa Aesar	
Copper(I) oxide ( $\text{Cu}_2\text{O}$ )	97.00% (Cu+ $\text{Cu}_2\text{O}$ assay)	Alfa Aesar	Used for viscosity
Copper(I) oxide ( $\text{Cu}_2\text{O}$ )	99.90%	Alfa Aesar	Used for phase equilibrium
Cu foil	99.99%	Goodfellow Cambridge Ltd	
Cu powder	99.70%	Aldrich	Used for phase equilibrium
Alumina crucible and spindle	99.9%	Rojan Ceramic	
Argon (Ar)	99.999%	Core Gas	

## 2.3 Viscosity measurement

The alumina crucible containing 80-110 grams pelletised sample was attached to the suspension tube by 0.5 mm diameter Pt wire. The crucible was placed into the hot zone of the furnace. The plunger tube and rheometer were set up to the proper positions. The spindle attached to an alumina shaft was suspended on the rheometer. The furnace was programmed to reach 1273 K so that the required temperature was increased at a linear heating rate of 150 K/h and kept at this temperature. The temperature was then raised to 1373 K and kept for 15 minutes to allow copper metal to be melted. The temperature was then increased to the required one. The spindle attached to the rheometer was then lowered slowly with rotation speed 5 rpm. The position when the spindle touched the surface of the slag was determined from the dramatic increase of the torque reading. From this point the spindle was lowered further 27 mm (note that the height of slag increase with submerging spindle) to enable the whole spindle to be submerged into the slag and reached the target depth in the liquid. Once the spindle is submerged into the slag, the torque readings were taken at a fixed rotation speed. The slag in the crucible and spindle were kept for 20 minutes to reach a steady state rotation and readings.

At a fixed rotation speed, 100 torque readings in 5 seconds interval were taken. Usually several measurements were carried out until the averages of the rest 80 readings in the successive measurements were identical. The constant torque readings in the repetition of measurements show the slag has attained a temporary constant composition at that period. The crucible was quenched immediately so that the measurements could reflect the viscosity at the relative composition.

Inspection of the alumina crucible and spindle shows that their geometries remain the same. The diameters of the spindles before and after viscosity measurement remained almost unaltered. The equipment constant measured from calibration procedure can be used in the slag viscosity calculation.

## 2.4 Sample examination

The quenched samples were sectioned, mounted and polished for the Electron Probe X-ray Microanalysis (EPMA). The polished samples were coated with carbon using JEOL (Japan Electron Optics Ltd) Carbon Coater for electron microscopic examination. A JXA 8200 Electron Probe Micro-analyser with Wavelength Dispersive Detectors was used for microstructure and composition analysis. The analysis was conducted at an accelerating voltage of 15 kV and a probe current of 15 nA. The standards used for analysis were from Charles M. Taylor Co. (Stanford, California):  $\text{Al}_2\text{O}_3$  for Al,  $\text{CuFeS}_2$  for Cu,  $\text{CaSiO}_3$  for Si. The ZAF correction procedure supplied with the electron probe was applied. The average accuracy of the EPMA measurements is within 1 wt pct. Both  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  are present in the samples, however, only the metal cation concentrations can be measured using EPMA. So the phase compositions were recalculated to oxides on the assumption that all copper is presented as  $\text{Cu}^+$  for presentation purpose only.

All quenched samples were also sent to a commercial analytical company for X-ray Fluorescence analysis (XRF).

## 2.5 Dissolution of $\text{Al}_2\text{O}_3$

Preliminary equilibrium experiments were carried out in the " $\text{Cu}_2\text{O}$ "- $\text{Al}_2\text{O}_3$  system in equilibrium with metallic copper. Equilibration/quenching/EPMA technique was used in this study, which was previously described in detail [8]. Pure  $\text{Cu}_2\text{O}$  mixed with 30 wt pct of Cu powder was pelletised and placed on an alumina substrate. Experiments were carried out in Ar gas at the temperature range of 1623-1523 K for 2 hours. The quenched samples were analysed by EPMA. The equilibrium studies showed that very low  $\text{Al}_2\text{O}_3$  concentration ( $< 0.4$  wt%) was dissolved in the  $\text{Cu}_2\text{O}$  melts in equilibrium with Cu metal, which indicated that nearly pure  $\text{Cu}_2\text{O}$  viscosity in equilibrium with metallic Cu could be measured using alumina crucible and spindle. EPMA measurements of quenched samples after viscosity measurements confirmed that less than 0.4 wt%  $\text{Al}_2\text{O}_3$  was present in the slag.

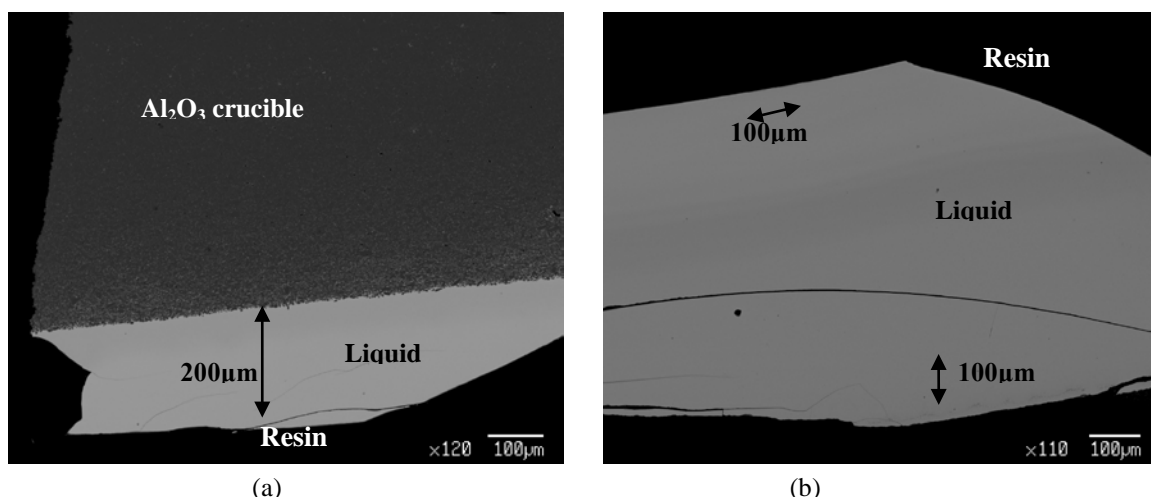


Fig. 3 Backscattered scanning electron micrographs of quenched sample C2 (Composition: 24.4 %  $\text{SiO}_2$ , 12.1 %  $\text{Al}_2\text{O}_3$ , and 63.5 %  $\text{Cu}_2\text{O}$  in weight): (a) at slag/crucible interface (b) at the bulk of quenched sample

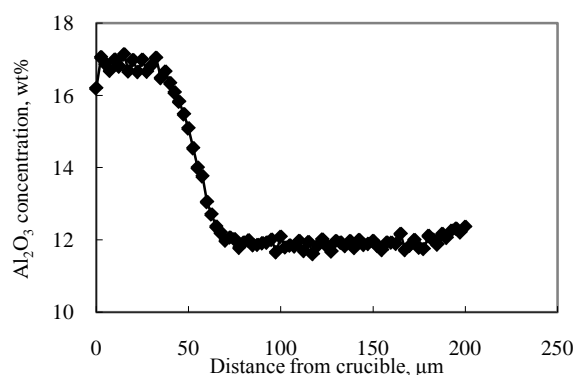


Fig. 4 Composition profile at the crucible/slag interface (Crucible side as the starting point)

Al<sub>2</sub>O<sub>3</sub> dissolves gradually into the melt in the “Cu<sub>2</sub>O”-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system containing SiO<sub>2</sub>. Figure 3 presents the SEM image taken from sample C2 quenched at 1573 K. EPMA analysis was performed across slag at the slag/crucible interface and in the centre of the sample as indicated by the arrows in Figure 3. Figure 4 represents the Al<sub>2</sub>O<sub>3</sub> concentrations in the slag close to the crucible. It can be seen that Al<sub>2</sub>O<sub>3</sub> concentrations are relatively high within 50 μm from the crucible and then reached a constant value. The EPMA measurements indicated that the dissolution of alumina into the slag is limited and slow.

## 2.6 Uncertainty analysis

The measurement of viscosity is a complicated systematic work. Uncertainties from various sources have been analysed and possible measures to increase accuracy were introduced. The thermocouples adjacent to the crucible were calibrated against standard reference thermocouple supplied by the National Measurement Laboratory (CSIRO, Australia). The uncertainty for EPMA analysis was estimated to be within 1 wt %. From the present measurements, the vertical axes of the crucible and spindles were expected to be within 2 mm from each other, which corresponded to a deviation of approximately 0.24% derived from cold experiment simulations. From the trace left on the spindle after viscosity measurement, the depth of bob submerged in the slag liquid could be identified: the deviation for all the experiments carried out is within ± 2 mm.

## 3. Results

Viscosities have been experimentally determined for two different slag systems. The results are summarised in the following sections.

### 3.1 Cu-O system

Two repeated experiments were carried out in the Cu-O system in equilibrium with Cu metal in the temperature range from 1508 to 1588 K. At each temperature, the sample was kept for 20 minutes to ensure the steady state conditions were reached. Two measurements were performed at each temperature at the same rotation speed. The measurements of torque were steady with a good repeatability between two measurements confirming reliability of

results. The torques increased with decreasing temperature in the range of 1588 - 1513 K. At 1508 K the torque increased continuously indicating precipitation of solid phase.

The measured viscosities are shown in Table 2. The viscosities were fairly low and a bit high deviation was found. The standard deviation of two measurements is within 15% and generally agrees with each other.

Table 2 Measured viscosities in “Cu<sub>2</sub>O” melts in equilibrium with Cu

First measurement C8		Second measurement C14	
Temperature/ K	Viscosity/Pa.s	Temperature/ K	Viscosity/Pa.s
1588	0.0109	1588	0.0098
1573	0.0117	1573	0.0101
1548	0.0123	1548	0.0110
1523	0.0141	1523	0.0137
1513	0.0147		

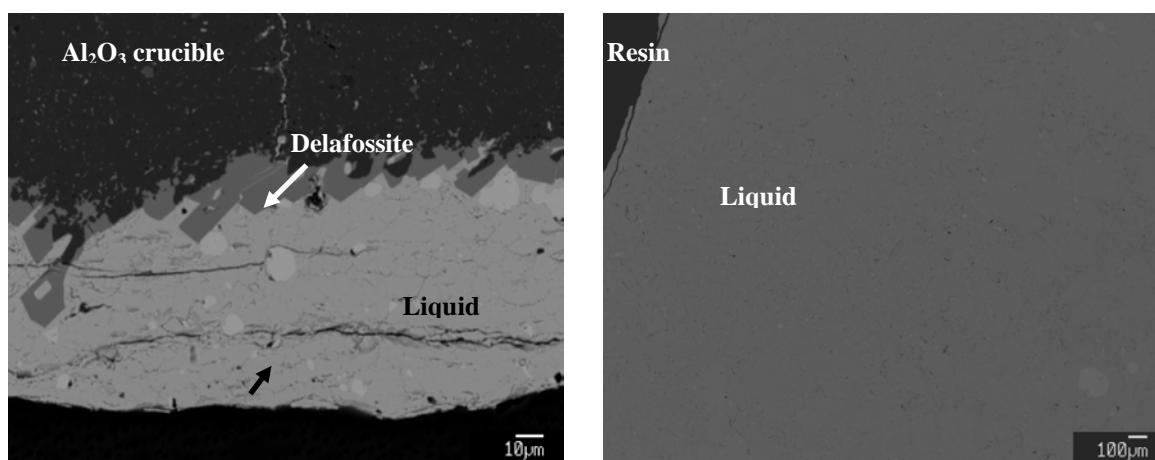


Fig. 5 Backscattered scanning electron micrographs of quenched sample C8 at 1523 K: (a) at slag/crucible interface (b) at the bulk of quenched sample

Figure 5 shows the sample quenched after viscosity measurements at 1523 K. Figure 5a represents the interface between slag and crucible. A layer of delafossite (Cu<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>) was formed next to the crucible, and the thickness of the delafossite layer was estimated to be less than 30 μm. Delafossite crystals were not observed in the bulk slag (Figure 5b). It can be seen from Figure 5 that Cu metal was always present in the slag but not necessarily in the bulk slag. A separate experiment has confirmed that copper metal settled on the bottom of the crucible and far from the slag around the spindle. It is expected that the copper droplets shown in Figure 5a were brought up to the slag during dropping of the sample into water after viscosity measurement.

### 3.2 “Cu<sub>2</sub>O”-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system

Experiments were also carried out in the “Cu<sub>2</sub>O”-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system in equilibrium with Cu metal. The aim of the study is trying to obtain the viscosity measurements close to the “Cu<sub>2</sub>O”-SiO<sub>2</sub> binary system to support model development. Due to the restriction of technique, there are some Al<sub>2</sub>O<sub>3</sub> always dissolves from the crucible and spindle into the slag. In order to determine the exact composition in each measurement, the sample was quenched immediately from each temperature after two identical measurements were taken. In this way, the direct quenched sample minimises

the deviation caused by the change of composition and the most precise viscosities at its relative compositions were represented.

Totally 9 experiments were carried out from 3 starting compositions at 1473, 1523 and 1573 K, respectively. Each quenched sample was analysed with EPMA and XRF. The summary of experimental conditions and results is given in Table 3. The final compositions measured by EPMA were plotted in Figure 6.

In each quenched sample, a Cu plate was found at the bottom of the crucible which ensured that the experiment was carried out in equilibrium with Cu metal. The weights of Cu plates were heavier than the Cu metal put beforehand. The “Cu<sub>2</sub>O” concentrations in the final slag are always lower than in the starting mixture. The phenomenon indicated that copper metal was possibly formed at high temperatures.

During quenching, certain amount of Cu droplets floated upward to the slag. The XRF analysis could only measure the total weight percent of Cu without distinguishing the copper metal and oxide, while the EMPA measured the composition of the liquid slag phase. The analysis of samples by XRF was therefore not listed.

Table 3 Experimental condition of viscosity measurements and their related results

Experiment No.	Temperature/K	Starting composition			Final composition measured by EPMA			Viscosity/Pa.s
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cu <sub>2</sub> O	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Cu <sub>2</sub> O	
C2	1573	20	10	70	24.4	12.1	63.5	0.538
C3	1523	20	10	70	24.9	12.9	62.2	0.776
C4	1473	20	10	70	23.8	12.1	64.1	0.833
C5	1573	20	5	75	23.8	11	65.2	0.323
C6	1523	20	5	75	22.1	10.6	67.3	0.331
C7	1473	20	5	75	23.1	6.2	70.7	0.396
C9	1573	12	0	88	13	8.8	78.2	0.104
C10	1523	12	0	88	15.8	10.6	73.6	0.120
C11	1473	12	0	88	15.7	9.2	75	0.150

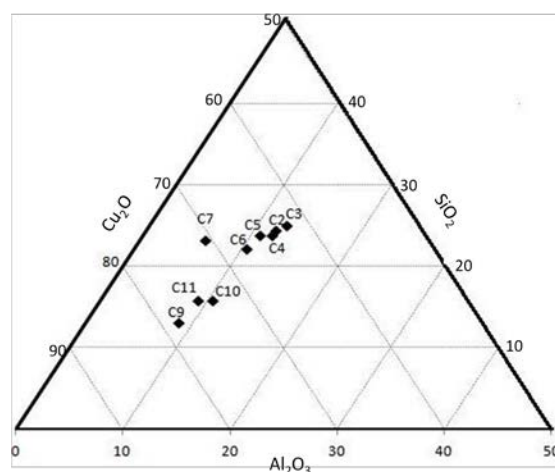


Fig. 6 Ternary diagram of measured compositions in “Cu<sub>2</sub>O”-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system

## 4. Discussion

### 4.1 Analysis of experimental data



Due to the limited number of experiments in the “Cu<sub>2</sub>O”-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> ternary system and lacking the data in the “Cu<sub>2</sub>O”-SiO<sub>2</sub> binary system, as well as the unsystematic values of the compositions, it is difficult to analyse the consistency of the measured values. An empirical model was employed to analyse the whole data set.

The modified-Urbain model [1] was used for the analysis based on the Weymann-Frenkel equation:

$$\eta = AT \exp\left(\frac{1000B}{T}\right) \quad (1)$$

$$-\ln A = mB + n \quad (2)$$

where T is the absolute temperature, B is a function of composition, and m and n are empirical parameters. The expression of B is given as follows:

$$B = \sum_{i=0}^3 b_i^0 X_{Si}^i + \sum_{i=0}^3 \sum_{j=1}^2 b_i^{Cu,j} \times \left(\frac{X_{Cu}}{X_{Cu} + X_{Al}}\right)^j X_{Si}^i \quad (3)$$

where X<sub>GF</sub>, X<sub>A</sub>, X<sub>M1</sub>, X<sub>M2</sub>,... are the molar fractions of the glass formers, amphoteric, and different modifier oxides;  $b_i^0$  and  $b_i^{Cu,j}$  are empirical parameters determined by optimisation.

Parameter m was expressed by assuming the linear function of compositions:

$$m = m_{Si} X_{Si} + m_{Al} X_{Al} + m_{Cu} X_{Cu} \quad (4)$$

where X<sub>Si</sub>, X<sub>Al</sub>, X<sub>Cu</sub> and m<sub>Si</sub>, m<sub>Al</sub>, m<sub>Cu</sub> are the molar fractions and its corresponding parameter of the glass formers, amphoteric, and different modifier oxides.

The parameters optimised from the current experimental data are given in Table 4.

Table 4 Modified Urbain viscosity model parameters

	j/i	0	1	2	3	n	9.322
$b_i^0$	0	13.31	36.981	-177.7	190.03	m <sub>Cu</sub>	0.66
$b_i^{Cu,j}$	1	2.5	91.2	117.94	-215.561	m <sub>Al</sub>	0.37
	2	-7.681	-86.6	-108.8	203.002	m <sub>Si</sub>	0.212

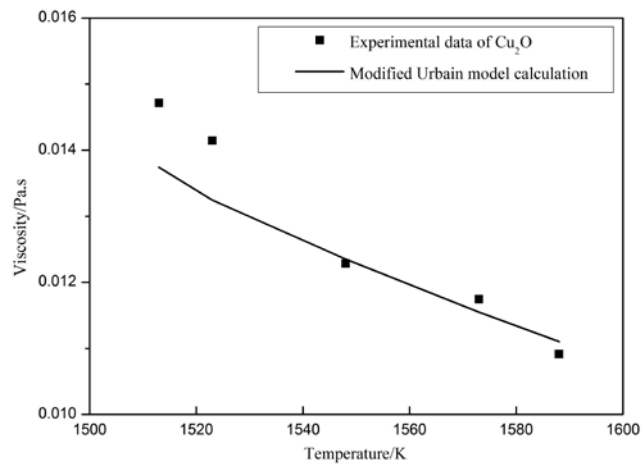


Fig. 7 Experimental data (symbols) and calculated viscosities (line) in the “Cu<sub>2</sub>O” system at 1513 K to 1588 K

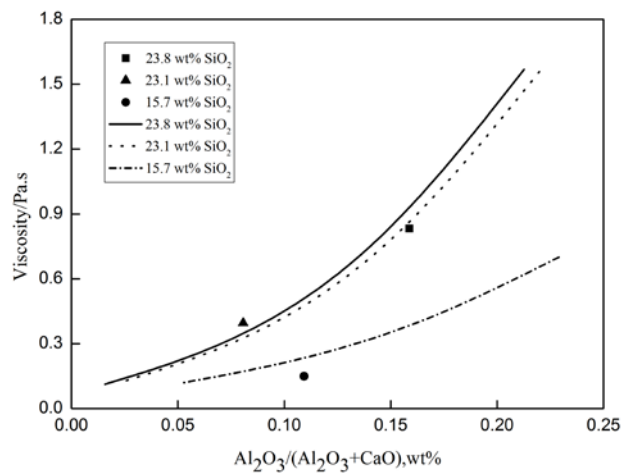


Fig. 8 Experimental data (symbols) and calculated viscosities (line) in the “Cu<sub>2</sub>O”-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system at 1473 K

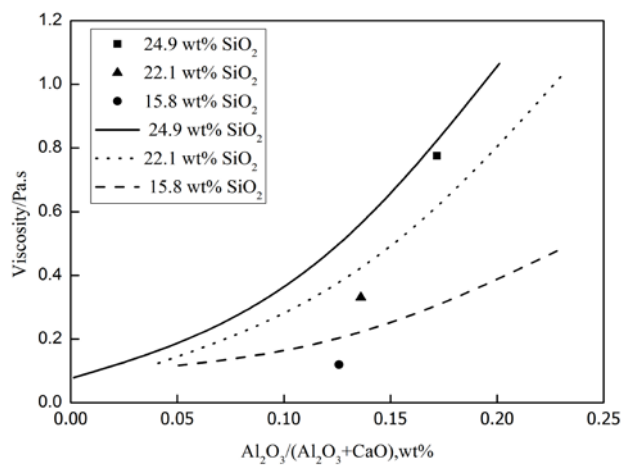


Fig. 9 Experimental data (symbols) and calculated viscosities (line) in the “Cu<sub>2</sub>O”-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system at 1523 K

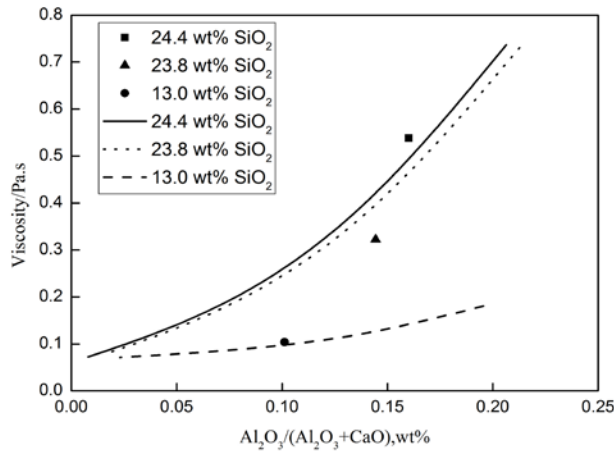


Fig. 10 Experimental data (symbols) and calculated viscosities (line) in the “Cu<sub>2</sub>O”-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> system at 1573 K

Figure 7 to Figure 10 show experimental data and the predictions by the modified Urbain model using the parameters given in Table 4. Larger discrepancy was found at lower temperatures 1513 and 1523 K in Figure 7. One of the possible reasons is that the delafossite layer formed on the crucible and spindle surface and affected the measurements. Further investigations will be carried out to identify the reason. The experimental data are in a good agreement with the model calculations. Based on the optimization in the unary and ternary systems, viscosities in the binary “Cu<sub>2</sub>O”-SiO<sub>2</sub> system were derived (Figure 11).

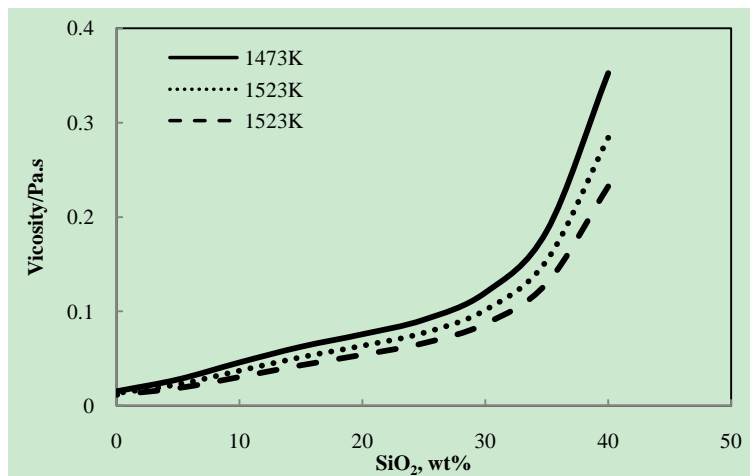


Fig. 11 Prediction of “Cu<sub>2</sub>O”-SiO<sub>2</sub> system from Modified Urbain model

#### 4.2 Comparison of Cu<sub>2</sub>O property with other oxides

A reliable and general model that would enable the viscosities of multi-component slag systems to be predicted over wide ranges of compositions and temperatures is being developed at the Pyrometallurgy Research Centre over a number of years [2, 3]. Further revision of the model has been carried out by Suzuki and Jak [9] in order to improve the accuracy of predictions. The Eyring equation [10] is used to express viscosity as a function of temperature and composition:

$$\eta = \frac{2RT}{\Delta E_v} \frac{(2\pi m_{SU} kT)^{1/2}}{v_{SU}^{2/3}} \exp\left(\frac{E_a}{RT}\right) \quad (6)$$

where R is the gas constant (J/K/mol),  $\pi \approx 3.1416$ , k is the Boltzmann constant (J/K), T is the absolute temperature (K),  $\Delta E_v$  is the energy of vaporization (J/mol),  $E_a$  is the activation energy (J/mol), and  $m_{SU}$  and  $v_{SU}$  are the weight and volume of a structural unit (kg and  $m^3$ , respectively). The model links the vaporisation and activation energies in the slag viscosity expression to the slag internal structure through the concentrations of various  $Si_{0.5}O$ ,  $Me^{n+}_{2/n}O$  and  $Me^{n+}_{1/n}Si_{0.25}O$  viscous flow structural units. The concentrations of these structural units are derived from a quasi-chemical thermodynamic model of the liquid slag using FactSage computer package and ChemApp software. The parameters of this structurally based model in the model are assumed to reflect the behaviour of the structural units.

The procedure of calculation of the average mass and volume of structural unit is describe previously [2]. The mass is calculated from molecular weight and the radii of the ionic cation is taken from Shannon [11]. Therefore,  $m_{SU}$  and  $v_{SU}$  of Cu-O-Cu can be obtained:  $m_{Cu-O-Cu} = 2.375 \times 10^{-26}$  kg and  $v_{Cu-O-Cu} = 4.28 \times 10^{-29}$   $m^3$ . The activation energy ( $E_a$ ) and logarithm of vaporisation energy ( $E_v$ ) of  $Cu_2O$  was calculated from equation (6):  $E_a = 94.65$  kJ/mol and  $\ln E_v = 15.38$ .

An analysis was previously proposed [12] by relating the activation energies of viscous flow of pure oxides and the ionic strength  $z/r$ , where z and r are the formal charge and radius of different cations, respectively. The parameter  $z/r$  was found to be a reasonable estimation of the activation energies of different structural units involving different metal cations and oxygen cations [13]. The ionic radius r was derived from the work by Shannon [11] for a cation with the known coordination number. The activation energies of  $SiO_2$ ,  $Al_2O_3$ , CaO and etc. are calculated from the present model and have a good reproducibility in reproducing the existing experimental viscosity data. The activation energies are plotted in Figure 12 against ionic strength. Most of the oxides have a correlation between the activation energy  $E_a$  and the ionic strength  $z/r$ , while the activation energy of  $Cu_2O$  calculated from the experimental data is higher than the prediction. The difference in  $Cu_2O$  shows the different behaviour compared with other oxides. One of the possible reasons is that presence of CuO was not taken into account.

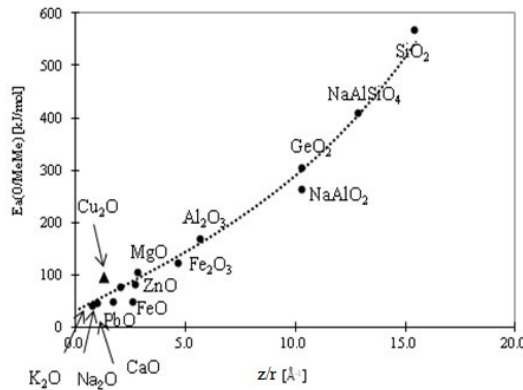


Fig. 12 The activation energies of viscous flow as a function of  $z/r$  parameters

## 5. Conclusion

The viscosities of the Cu-O and “Cu<sub>2</sub>O”-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> systems in equilibrium with metallic copper have been measured using the rotating spindle technique in the temperature range of 1513 to 1588 K. Alumina crucibles and spindles have been employed. The viscosities of pure Cu<sub>2</sub>O at different temperature could be measured due to the very low Al<sub>2</sub>O<sub>3</sub> solubility in the copper oxide melt in equilibrium with metallic Cu. In the “Cu<sub>2</sub>O”-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slags, due to the low dissolution rate of Al<sub>2</sub>O<sub>3</sub> into the liquid, the EPMA analysis showed the liquid slag composition was uniform across the crucible. The viscosities of the “Cu<sub>2</sub>O”-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slags were measured and their corresponding compositions were determined by EPMA.

The analysis using modified Urbain model shows the measured viscosities have systematic trends and are self-consistent. The viscosity of the “Cu<sub>2</sub>O”-SiO<sub>2</sub> system in equilibrium with metallic Cu was derived from the binary and ternary data. The comparison of activation energies in quasi-chemical viscosity model against ionic strength  $z/r$  shows Cu<sub>2</sub>O possibly has a different behaviour compared to other oxides. Further studies will be carried out in this system and more experimental data will be obtained. Present studies are essential foundation for the viscosity model development for the SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Fe<sub>2</sub>O<sub>3</sub>-FeO-CaO-MgO-Cu<sub>2</sub>O multi-component system for the Cu production.

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