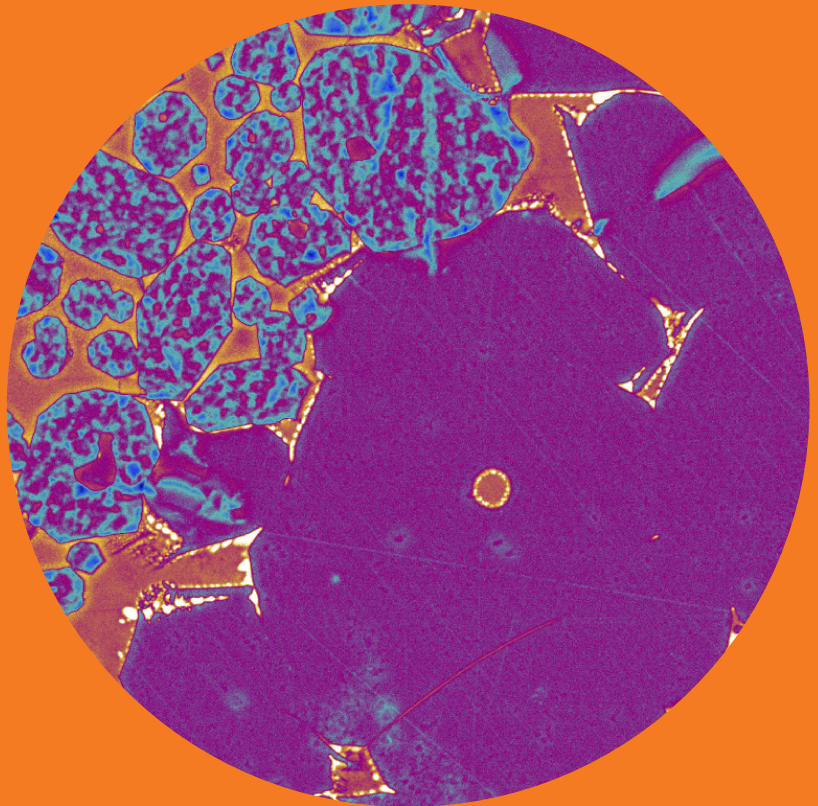


Solubility of high melting temperature oxides (CaO , Al_2O_3 , Cr_2O_3) in copper oxide liquid

Joseph Hamuyuni



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Aalto University
School of Chemical Technology
Department of Materials Science and Engineering
Metallurgical Thermodynamics and Modelling

Supervising professor

Professor Pekka Taskinen

Thesis advisor

Professor Pekka Taskinen

Preliminary examiners

Professor Caisa Samuelsson, Luleå University of Technology, Sweden

Dr. Johan Zietsman, University of Pretoria, South Africa

Opponent

Professor Anders Tilliander, Royal Institute of Technology (KTH), Sweden

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Abstract

Thermodynamic databases consisting of carefully acquired phase equilibrium and thermochemical data for oxide systems are an invaluable tool towards optimization and improved control of current copper making processes. Fluxing, which is the main control procedure in copper smelting processes can be fully optimized by employing an accurate thermodynamic database. The result of optimization is a controlled process, which is both efficient in utilization of input materials and versatile to continually changing raw materials. Because a thermodynamic database for metal making processes cannot be modelled solely from first principle calculations, experimental phase equilibrium data is critical in obtaining a consistent database relevant for industrial applications. In this study, an equilibration and quenching technique was adapted to acquire experimental phase equilibria data for selected systems in temperature and composition ranges either poorly known or not previously investigated.

For the system Cu-O-CaO in oxidizing conditions, new experimental liquidus data between 1300 and 1500 °C are presented in this study. In the system Cu-O-CaO-Al₂O₃, experimental phase equilibria of the triple points of the system by the quenching technique are presented for the first time. Prior to this study, phase equilibria of the system Cu-O-CaO-Al₂O₃ has not been experimentally studied, otherwise equilibria of the system was estimated by extrapolations. The liquidus of the system Cu-O-Cr₂O₃ has also been investigated by the equilibration technique for the first time.

Experimental results of this thesis reveal that liquidus data for simple oxide systems of copper are poorly known and currently insufficient to accurately predict higher order systems. The experimental phase equilibria data acquired in this dissertation will improve prediction of high order oxide systems for process metallurgy.

Keywords Phase equilibria, liquidus, quenching, EPMA, thermodynamic database, MTOX

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Tiivistelmä

Termodynaamiset tietokannat, jotka sisältävät huolellisesti mitattua faasitasapainodataa ja termodynaamisia ainearvoja oksidisysteemeille, ovat korvaamattomia työkaluja kuparin valmistusmenetelmien optimoinnissa ja prosessin parantamisessa. Fluksaus, joka on kuparin sulatuksen pääasiallinen hallintamenetelmä, voidaan optimoida käyttämällä näitä tarkkoja termodynaamisia tietokantoja. Optimoinnin tuloksena saavutetaan hallittu valmistusmenetelmä joka on sekä tehokas syötemateriaalin käytössä, että joustava pystyen vastaamaan jatkuvasti vaihtuviin raaka-aineisiin.

Koska termodynaamista tietokantaa metallinvalmistusmenetelmiä varten ei voida mallintaa puhtaasti laskennallisesti, kokeellinen faasitasapainodata on kriittistä yhtenäisen, teollisille sovelluksille merkityksellisen tietokannan kehittämiseksi. Tässä työssä sovellettiin tasapainotus- ja sammutusmenetelmää faasitasapainodatan mittaamiseksi valituille systeemeille ennestään tuntemattomilla lämpötila- ja koostumusalueilla.

Tässä työssä on mitattu uusia tasapainoarvoja Cu-O-CaO-systeemissä hapettavissa olosuhteissa lämpötilavälillä 1300 °C-1500 °C. Cu-O- Al_2O_3 -CaO-systeemin faasitasapainoa kolmoispisteissä mitattiin tässä työssä ensimmäistä kertaa sammutusmenetelmällä.

Aikaisemmissa malleissa systeemin faasitasapainot on arvioitu ekstrapoloimalla kokeellisen tiedon puutteen takia. Myös Cu-O- Cr_2O_3 -systeemin likvidusta on tutkittu sammutus- ja tasapainotusmenetelmällä ensimmäistä kertaa.

Väitöstyön kokeelliset tulokset paljastavat, että yksinkertaisten kuparioksidisysteemien likvidus on huonosti tunnettu ja tällä hetkellä riittämätön mahdollistaakseen monikomponenttisten systeemien tarkan ennustamisen. Tässä väitöstyössä saadut tulokset parantavat monikomponenttisten oksidisysteemien ennustuksen luotettavuutta prosessimetallurgiassa.

Avainsanat Faasitasapaino, likvidus, EPMA, sammutus, Termodynaamiset tietokannat, MTOX

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Preface

The research presented in this doctoral thesis was carried out at Aalto University School of Chemical Technology, in the research group of Metallurgical Thermodynamics and Modelling (TDM), between 2013 and April 2016.

I would like to thank my supervisor and advisor, Professor Pekka Taskinen, firstly, for the freedom and opportunity he gave me to conduct research in his laboratory. His extensive knowledge of thermodynamics is exceptional. I am grateful also that his door was ever open for me to discuss thermodynamics. It has been such a joy working under his instruction.

This Ph.D project was carried out with support from Systems Integrated Metal Processing (SIMP) Show Case 1 (SC1) – a project of the FIMECC- programme and Tekes – the Finnish Funding Agency for Technology and Innovation. All the partners of the SIMP project are acknowledged. The financial support from Fund for the Association of Finnish Steel and Metal Producers is also acknowledged.

Heartfelt thanks also go to Dr. Annukka Santasalo-Arnio and Dr. Fiseha Tesfaye, for proofreading this compendium. I thank Petteri Piskunen and Lassi Klemettinen for helping me with SEM-EDS analysis. I also thank Professor Guven Akdogan, Iina Vaajamo for their encouragements at the beginning of my research.

Naturally, the TDM research group members are acknowledged for their positive influence on my research work. Especially a colleague and office mate Niko Héllsten for most of the abrupt discussions about thermodynamics, and the “Finnish jokes,” I certainly enjoyed the combination.

Last but not the least, I must thank my family for their encouragement and support.

Espoo, 14 April 2016
Joseph Hamuyuni

List of Publications

This doctoral dissertation consists of a summary of the following publications which are referred to in the text by their corresponding Roman numerals. Articles are appended to this compendium in the same sequence.

- [I] **J. Hamuyuni**, N. Hellstén, G. Akdogan, P. Taskinen, “Experimental determination of the liquidus of the binary system Cu_2O - CaO in air from 1050 to 1500 °C,” *Journal of Chemical Thermodynamics*, 77 (2014). 112-115, ISSN: 0021-9614. doi:10.1016/j.jct.2014.05.012.

- [II] **J. Hamuyuni**, N. Hellstén, G. Akdogan, P. Taskinen, “The liquidus in Cu - O - CaO system at metallic copper saturation up to 1698 K,” *Journal of the American Ceramic Society* 98 (2015) 320–323, ISSN: 1551-2916. DOI: 10.1111/jace.13282.

- [III] **J. Hamuyuni**, P. Taskinen, “Experimental phase equilibria of the system Cu-O- CaO - Al_2O_3 in air,” *Journal of the European Ceramic Society*, 36 (2016), 847–855, ISSN: 0955-2219. doi:10.1016/j.jeurceram-soc.2015.10.047

- [IV] **J. Hamuyuni**, P. Taskinen, “Liquidus experimental data for the system Cu-O- Cr_2O_3 in air,” *Thermochimica Acta* 638 (2016), 96 - 102 ISSN: 0040-6031. doi:10.1016/j.tca.2016.06.020

Author's Contribution

In all publications included in this compendium [I-IV], the author defined the research plan. He then conducted all equilibration experiments, analysed the data and wrote the first version of the manuscripts. The author prepared the final version of manuscripts with input from co-authors.

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List of Abbreviations and Symbols

Abbreviations

CALPHAD	CALculation of PHase Diagrams
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
EDS	Energy Dispersive Spectrometry
EMF	Electromotive Force
EPMA	Electron Probe Micro-Analyzer
EQ	Equilibration and Quenching method
FCC	Face-centred cubic
GTK	Geological Survey of Finland
HSM	Hot Stage Microscopy
MIRO	Mineral Industry Research Organization, UK
MTDATA	Thermochemical software, NPL, UK
MTOX	Metal-oxide-sulfide-fluoride thermodynamic database
NPL	National Physical Laboratory, UK
SEM	Scanning Electron Microscope
TGA	Thermal Gravimetric Analysis
WDS	Wavelength Dispersive Spectrometry

Symbols

ΔG_f	free energy of formation
ΔS_r	entropy of reaction
a	activity
c	number of components in a system

F	number of degrees of freedom
L_1	liquid copper
L_2	liquid oxide
p	number of phases in a system
P	Pressure [Pascal, atm)]
S	solid phase (s)
T	Temperature [K, °C]

Subscripts and superscripts

μ	chemical potential
i	species
α, β	a phase with defined crystal structure
g	gas
$^\circ$	standard state

1. Introduction

The increase in global demand for copper has triggered growth on global copper production capacity. As a result, high-grade sulfide ores, which for centuries have been the primary source of copper are depleting at a fast rate. Consequently, smelting processes have to adapt to low-grade feed materials. Low-grade feed materials, however, are increasingly becoming complex for conventional processing routes from ore to pure metal. From both economic and process perspectives, optimization of current processing strategies is mandatory to meet the demand. Thermodynamic databases containing carefully acquired experimental phase equilibrium and thermochemical data are an invaluable tool towards achieving this goal [1,2]. Using this data, process conditions that can result from known input materials can be predicted and controlled with high accuracy [2,3].

Fluxing is a fundamental process control procedure in all industrial copper smelting operations [5,6]. It is applied for slagging iron oxides (solids) that are formed during the oxidation of sulfide concentrates to molten form. Slag is thus primarily a mixture of oxides in molten state. The procedure also controls the dissolution of high melting gangue minerals and their reaction products with slag. Fluxing therefore controls slagging process. The success of this procedure depends on the knowledge of the slag chemistry [3]. Phase equilibrium data for copper smelting slag is therefore important.

During copper smelting processes, silica is the main fluxing material [5]. The silica used in fluxing always contains CaO, Al₂O₃, and MgO in smaller proportions. In calcium ferrite slag based processes, the CaO content in slag is significant (resulting in up to 20 %). A typical copper smelting slag therefore consists of molten oxides including silica, Al₂O₃, and CaO. Copper smelting slag is always in contact with the copper rich matte as well as with the refractory, which contains Cr₂O₃. Due to the extremely high oxidizing nature of the process, copper also dissolves into the slag phase mainly as Cu₂O [7]. The chemical dissolution of copper in slag is based on reaction between matte (blister copper) and slag according to equation 1:



In equation (1), the square brackets [] and parentheses () represents sulfide matte and slag, respectively. Equation (1) also indicates that increasing oxygen

pressure increases the amount of copper loss to slag. The fundamental role of slag in copper smelting processes is thus evident.

For slag to carry out its process functions effectively, it must stay liquid for the entire duration of the smelting process [7,8]. Too high slag temperature is undesirable because it causes high refractory wear [7,9]. Optimal temperature must therefore be high enough to keep the slag liquid, yet low enough to minimize its reaction with the refractory components. Liquidus temperature of the molten slag is thus important to copper smelting. Above the slag liquidus temperature, slag is completely liquid while below it, the liquid coexists with undesired solid precipitates.

In phase diagram sense, liquidus represents the locus of temperature-composition at maximum solubility of solid into liquid phase [10-12]. In binary and ternary phase diagrams, the liquidus is represented as a line and surface (often curved), respectively [10-12].

The CALPHAD (CALculation of PHase Diagrams) method is a powerful tool in performing thermodynamic assessments in order to establish a consistent thermodynamic database [13-15]. This, however, requires accurate experimental phase equilibrium and thermochemical data for simple systems such as binaries and ternaries [15]. In simple oxide systems of Cu-O (CaO , Al_2O_3 , Cr_2O_3), experimental phase equilibrium data in certain temperature and composition ranges is either nonexistent or poorly known. For instance, the liquidus in the ternary system Cu-O-CaO in equilibrium with air was previously only measured up to 1300 °C [16]. Above this temperature no experimental data is available. The system Cu-O-CaO in equilibrium with copper is based on the works of Kuxmann and Kurre [17] as well as Takeda [18], using quartz and magnesium oxide crucible material, respectively, which may have introduced impurities to the system. No experimental liquidus data for the systems Cu-O-CaO- Al_2O_3 or Cu-O- Cr_2O_3 was found in the literature. The methods employed by Gadalla and White [19] as well as Jacob et al [20] are not suitable for acquiring liquidus data.

1.1 Objective of the thesis

To develop an accurate thermodynamic database for oxide systems relevant for industrial copper smelting, missing phase equilibrium data of simple systems must be acquired by experimentation. The objective of this thesis is therefore:

1. to study the phase equilibria of selected Cu-O containing systems experimentally, at various conditions of temperature, oxygen pressure and composition,
2. to provide knowledge and new experimental phase equilibrium data in previously unexplored temperature and composition ranges.

Despite many centuries of scientific research on copper making processes and process technologies, there are still numerous unknowns in phase equilibria of copper containing oxide systems. Phase equilibria at lower (sub solidus) temperatures for both simple and multicomponent oxide systems are well known. However, this data is not on its own adequate for smelting operations where input materials need to be brought to molten state to facilitate separation. Liquidus data, therefore, is the most critical type of reaction data needed.

To acquire accurate experimental phase equilibrium data, the equilibration and quenching (EQ) technique has been chosen in this study. The Electron Probe Micro Analyzer (EPMA) was employed as the analytical tool for quantifying chemical composition. This is the most suitable method for studying liquidus of oxide systems [21-23]. Experimental phase equilibrium data for these simple systems studied will be used together with other carefully selected data in literature to obtain optimized thermodynamic parameters for the oxide database (MTOX) [24,25] for industrial application.

1.2 New scientific contribution

This study contributes new scientific knowledge of liquidus and solubility for the selected copper containing oxide systems. Prior to this study, the liquidus in the Cu-O-CaO system in equilibrium with air was only experimentally measured up to 1300 °C. Experimental liquidus data in the Cu-O-CaO system in equilibrium with air between 1300 and 1500 °C are presented in this study for the first time. In copper saturation conditions, the liquidus results are given for the first time when this system is studied without impurities. All preceding experimental studies have employed ‘foreign’ soluble containment materials, which resulted in contamination. The utilization of self-made CaO “crucibles” (which is part of the system) as containment material for this study ensured the system was kept pure.

In the system Cu-O-CaO-Al₂O₃, experimental phase equilibria of the triple points of quaternary system by the equilibration and quenching technique (or simply quenching technique) is presented for the first time. Prior to this experimental study, the system Cu-O-CaO-Al₂O₃ has not been studied solely, otherwise estimations of its phase equilibria were made by extrapolations.

The liquidus of the system Cu-O-Cr₂O₃ has been investigated by the equilibration technique for the first time. Before this study, Cr₂O₃ solubility in copper molten phase was estimated higher than it actually is.

1.3 Practical application

Metal producing industries face two major challenges related to raw materials. These are scarcity and complexity of raw materials, to which there is no control parameter. Additionally, for these industrial processes to be sustainable, they must use fewer raw materials, less energy to process these raw materials, minimize emission of toxic substances to the environment and generate easily recyclable products. Without appropriate tools, this is a daunting task.

Copper producing industries currently use fluxing as a basic tool for controlling most smelting operating parameters. This in turn helps eradicate or lessen the effects of most of these challenges. In other ways, the optimal operating conditions of the smelting furnace are only attained by good fluxing philosophy. One of the most challenging but critical materials to control in copper smelting is molten slag. However, slag is almost fully controlled by fluxing. Knowledge of slag chemistry therefore plays a key role in developing good fluxing practices, which results in good smelting practices. Experimental data from this study will improve understanding of slag's phase chemistry.

Experimental phase equilibrium data obtained in this study will be used to perform critical thermodynamic assessment to achieve consistent parameters that offer the best possible way of predicting reaction phenomena. Industries can use these data for prediction and control purposes.

Additionally, since the information obtained can be stored once thermodynamic parameters have been optimized, the database is not limited to one process and as such can be coupled with other information and utilized for other applications such as in recycling.

The work of generating experimental data for oxide systems is one of National Physical Laboratory's (NPL) projects to develop a thermodynamic database for oxide systems, MTOX [24,25]. The Mineral Industry Research Organization (MIRO) is involved in updating the current MTOX database through industrial partners and research groups.

1.4 Thesis outline

This compendium comprises four publications in peer reviewed scientific journals [I-IV]. These publications are appended to the compendium. The quenching technique for studying equilibria of oxide systems, its thermodynamic basis and some important aspects of the technique are presented in Chapter 2. Chapter 3 follows up with a detailed explanation of how the equilibration and quenching technique has been adapted to conduct experiments in this study. In Chapter 4, the results and their discussion is given. Chapter 5 outlines the conclusions from this research.

2. The quenching technique for phase diagram determination

When materials are subjected to thermodynamic constraints of temperature and pressure, they undergo transformation i.e. chemical reaction [10]. These reactions are therefore a function of the magnitude of constraints applied. An environment, also known as a system can be carefully chosen for study whereby the constraints may either be fixed at some known value or varied. Material transformations usually form physically distinct, homogenous parts of a system known as phases [11]. When studying reactions in a chosen environment, temperature pressure and composition are the only available control parameters [10]. Stability of phases in a system are thus governed by these three variables. The relationship among these variables is best depicted graphically using phase diagrams. Because of the large amount of materials as well as interactions, acquiring phase diagram information for all materials has been a challenging task. In the past centuries however, methods have been developed to accurately acquire phase equilibrium information for many systems [22]. It has been previously observed that to acquire accurate phase equilibrium information, experimental studies are critical [15]. The reliability of experimental data is to a great extent dependent on the experimental method chosen for phase equilibria study.

2.1 The quenching technique and other experimental methods

Experimental techniques to study phase equilibria fall into two broad categories, namely dynamic and static [21-23], see Figure 1.

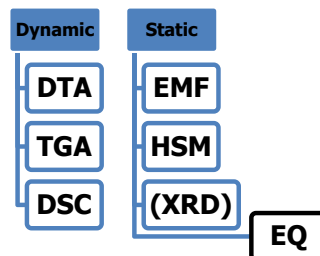


Figure 1. Major phase equilibria experimental methods.

Dynamic equilibration techniques are employed to measure the property data while phase transformation in the system is still ongoing [22]. Differential Thermal Analysis (DTA) [26], Thermal Gravimetric Analysis (TGA) [27,28], and Differential Scanning Calorimetry (DSC) [29-31] are by far the most widely applied dynamic techniques for acquiring thermodynamic data for oxide systems. DTA is a popular option when studying transition points in exothermic and endothermic reactions as a function of temperature. Decomposition reactions that are accompanied by a loss in mass of material can be studied by TGA. DSC is applied when measuring specific heat and heat of transition. Dynamic techniques are most suitable when acquiring experimental data of systems with rapid kinetics. The main drawback from all dynamic techniques is the measurement of property data when the system is not in thermodynamic equilibrium. When studying phase equilibria, this results in metastability related inaccuracies in measurements for systems whose phase transformation is slow, such as high viscosity oxide melts [21,23].

For static techniques, property data is acquired only after the system under investigation has reached equilibrium, such that no more phase transformations will occur when equilibrium time is extended [21-23]. The Hot Stage Microscopy (HSM) [32], Electromotive Force (EMF) [33-38] and X-ray diffraction [36,38] techniques are some of the popular options for this purpose. HSM finds applications in measuring the liquidus of transparent low vapour pressure systems [32]. Thermochemical properties that include free energy of formation (ΔG), entropy of reaction (ΔS), and activity (a_i), can be obtained by the EMF method. XRD (which is not a stand alone method) has found applications in phase identification, as well as establishing lattice parameters for different materials. Static experimental methods are useful in studying systems with sluggish (slow) kinetics [22].

Acquiring experimental data to construct a complete phase diagram usually demands application of several methods from these two categories [22]. A technique suitable for one part of the phase diagram might not be the best option on the other. As such, success in acquiring accurate phase equilibrium data is also a result of careful attention in selecting the best-suited method or combinations [22].

The best option for investigating liquidus of oxide systems with sluggish kinetics is the equilibration and quenching technique (EQ) [21-23]. The equilibration and quenching technique is a variation of static techniques. The technique allows experimenting at high temperature but with a convenient option of analyzing the specimen's phase compositions at room temperature. This is because the molten phase equilibrated at elevated temperatures can in many cases be "frozen" (by quenching) to a "glassy" or microcrystalline phase [21-23]. High accuracy tools such as Electron Probe Micro Analyzer (EPMA) [39] can then be employed to quantify the chemical composition of the liquid and solid phases in equilibrium. Typical routines during experimentation by this technique are summarized in Figure 2.

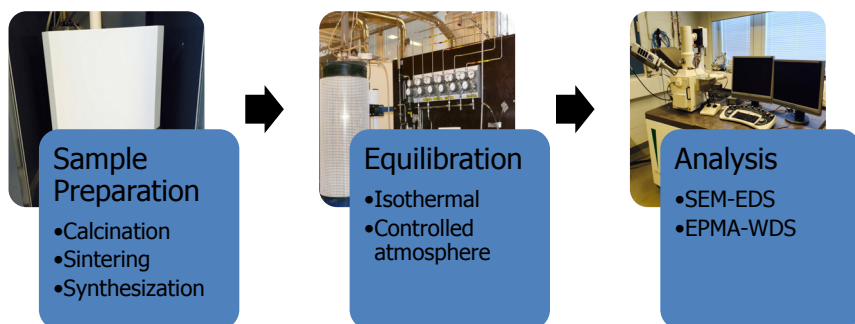


Figure 2. Selected sub-routines of the equilibration and quenching method.

From Figure 2, sample preparation will vary depending on the needs of an experiment, as such the routines listed here are representative. High purity starting materials must always be employed if accurate results are to be realized. Accurate results will require exact temperature measurement and controlled atmosphere. EDS and WDS are tools for quantifying composition of the microcrystalline quenched phases.

2.2 Thermodynamic basis of the quenching technique

The interpretation of experimental results obtained by the quenching technique is based on a fundamental thermodynamic relation known as the Gibbs phase rule [10,40,41]:

$$F = c - p + 2 \quad (2)$$

Where F is the number of degrees of freedom (pressure, temperature, composition) that can be altered independently and arbitrarily without bringing about disappearance of a phase or formation of a new one [10]; c is the number of components in a system, and p is the number of physically distinct homogenous phases. The number two (2) denotes the intensive variables. In a condensed system, this number is reduced to one (1) because the vapour pressure of liquid and solid phases is too small when compared to atmospheric pressure [10-12].

This rule is derived from the works of J. Willard Gibbs dating back to the years 1876 and 1878, published in Transactions of Connecticut academy of sciences [42]. The thermodynamic constraints on an equilibrium imposed by Gibbs have been instrumental in developing and interpreting phase diagrams.

The Gibbs phase rule assumes that the system being investigated using the quenching technique must be in thermodynamic equilibrium. Under these conditions, the gradient of the chemical potential (the driving force for a reaction), in the system equals zero, or minimum Gibbs energy, see equation 3:

$$\mu_i^\alpha = \mu_i^\beta \quad (3)$$

In equation 3, μ is the chemical potential of species, α and β are the different phases in which the species exist [10]. Therefore, at equilibrium, the chemical potential of species i is constant both in α and β phases.

2.3 Experimental aspects of the quenching technique

There are several factors that need consideration before and when using the equilibration and quenching method for experimental measurements. These include choice of primary phase [21,23], equilibrium time, specimen's quenchability, and characterization of specimen [21-23].

2.3.1 Selection and preparation of primary phase

The choice of primary phase plays a major role when using the equilibration method for carrying out experiments [23]. Firstly, it affects equilibration experiment time. Depending on the choice of primary phase material or composition, the path to equilibrium is primarily fixed. In cases where two phase transformation stages occur, experimentation might not be feasible especially at higher temperatures [43]. Secondly, the choice of primary phase dictates the options available for keeping the system pure. Handling of reactive liquid copper oxide for example is a challenging task. The only available options to contain the liquid without introducing impurities to the system are either using the solid phases in equilibrium with liquid oxide or using an inert containment material.

To achieve the above tasks, available databases, such as MTOX [24,25] through MTDATA are used to estimate the possible outcome by computation thermodynamics. These projected outcomes are validated and then implemented stepwise experimentally.

2.3.2 Equilibrium time and criteria

As highlighted in section 2.3.1, one of the factors that affect equilibration time is the choice of primary phase or choice of the path to equilibrium. Time is a critical parameter in rendering the method more viable compared to others. If energy consumption is neglected, extended equilibrium time exerts pressure on both containment material and equipment, and that should be avoided. This also demands that for every system investigated, the shortest possible equilibrium time must be chosen. Trial experiments are usually conducted to optimize the equilibration time.

One other critical step in conducting experiments by the equilibration technique is to know when equilibrium for a particular system has been attained. A systematic approach is applied combining thermodynamic theories and phase characterization procedures [21,23]. Firstly, using the Gibbs phase rule [10,40,41], the possible number of phases can be estimated using the known number of components as well as the number of fixed intensive variables. Once

the correct number of phases has been established, the second step, which involves characterization of phases, is employed. Using SEM-EDS and EPMA [39], each phase's composition is measured to establish if each phase is homogenous within itself. Several points in each phase are selected and compared and composition of each point must be the same for a homogenous phase. Thirdly, this established equilibrium is given different equilibration times incrementally after which phase composition established in second stage is checked again. Equilibrium should have been attained, when there is no more change in composition of the phases and phases stay distinct [21,22,23]. This is usually tried by approaching this equilibrium from different paths as in section 2.3.1.

2.3.3 Quenching ability of specimen

Quenching is one of the fundamental aspects of the equilibration and quenching technique. In fact, specimen's ability to quench determines whether or not the equilibration and quenching method is the most suitable option for studying phase equilibria of a material [22]. Good quenching entails sufficiently high cooling rates, so that high temperature phases are retained as a "glassy" or microcrystalline phase without segregation [23]. In certain cases minor localised segregations are tolerated. Factors that greatly affect quenching are specimen's properties, specimen size, and type of quenchants.

Oxides of high viscosity such as silica tend to quench well due to their glass forming properties [23]. Some neutral oxides have also been observed to have this feature. Such oxides have a sluggish phase change when temperature is dropped fast enough, which helps to retain the high temperature phases [21-23].

Because heat transfer is a function of specimen thickness [44,45], samples employed when using the equilibration and quenching method must be very small, i.e. ≤ 1 g. This way, cooling rates of up to 1000Ks^{-1} can be achieved with the drop quenching method [23].

The quenching media must cool the sample rapidly enough without reaction. Water and brine in increasing order of quenching ability, are the best quenching media for most oxide systems. Brine solution's superiority as a quenching media is based on the reduced atmospheric gas absorption ability [45]. Absorption of atmospheric gases during quenching causes formation of gas envelopes around the sample, which inhibit cooling rates of samples.

2.3.4 Characterization of quenched samples

The ability to analyze and quantify the chemical composition of individual phases equilibrated at elevated temperatures, as high as 1500°C , makes the equilibration technique superior among static methods for systems whose equilibrium phases can be effectively quenched [21-23]. This is largely because quenching brings samples to room temperature, where their glassy or microcrystalline phases can be conveniently analyzed by tools such as SEM and EPMA.

SEM is often coupled to an Energy Dispersive Spectrometer (EDS) and thus mostly referred to as SEM-EDS. SEM employs a beam of high energy-electrons to generate a variety of signals at specimen surfaces. The signals generated from electron-specimen interactions contain valuable information about crystal structure and chemical composition of sample. The major advantage of SEM-EDS is the speed of analysis. By this method, a full spectrum can be acquired in seconds, which makes it a better tool for preliminary identification of phases. However, SEM-EDS has relatively poor energy resolution and can not be relied upon to quantify elements that exist in smaller concentrations. [39]

Electron probe Micro-Analysis EPMA, is a combined qualitative and quantitative analytical tool applied in determination of chemical compositions. Unlike SEM-EDS, which is based on EDS detectors, EPMA employs Wavelength Dispersive Spectrometers (WDS) for analyzing samples. WDS has higher peak resolution whereby elements present in trace amounts can be detected more accurately. WDS have up to 100 times more sensitivity than EDS in detection of trace elements. EPMA's is therefore superior in quantifying the composition of the liquid. Its compatibility with other routine analysis methods allows easy interpretation of results [39]. Better spectral resolution is one of the other advantage of this technique. EPMA has capability to analyze up to ± 1 wt % accuracy. Detection limits are in the order of 100 ppm. [39]

3. Experimental section

This section provides a summary of information on the materials, apparatuses, and procedures employed in the study. The equilibration technique followed by fast quenching and microanalysis of samples has been applied. The equilibration technique as applied in this study, has been adapted so that handling of the molten phase without introducing impurities to the system investigated, was possible. A detailed approach to each experiment is given in appendices [I-IV].

All equilibration experiments were conducted using high purity substances. Primary phases for the Cu-O-CaO system in oxidizing conditions were calcium oxide and copper (I) oxide (cuprite). In reducing conditions, metallic copper was added. For the quaternary system Cu-O-CaO-Al₂O₃ under oxidizing conditions, calcium aluminates employed as primary phase, were synthesized from calcined high purity powders of alumina and calcium oxide. For the system Cu-O-Cr₂O₃ in oxidizing conditions, copper (I) oxide and Cr₂O₃ powders were employed as starting materials

3.1 Materials preparation and characterization

For experiments on the system Cu-O-CaO in both oxidizing and reducing conditions, calcium oxide powders were employed as a source of CaO. Calcium oxide for this purpose was obtained by thermal decomposition of calcium oxalate monohydrate powders at temperature of 800-850 °C in a Lenton muffle furnace (Type; UAF 16/10) [46]. Calcium oxide was then pressed into pellets and sintered at 1450 °C for 3 hours in the same furnace. Pressing and sintering was performed to reduce porosity of the pellets to contain the reactive oxide liquid phase [47, 48].

The Cu₂O employed in the study was self-made by oxidizing A-grade cathode copper. Pure cathode copper pellets or buttons were oxidized at 1050 °C in air for 120 hours in a Lenton muffle furnace (Type; UAF 16/10). Extended oxidizing time was provided to ensure complete oxidation. After confirming purity, Cu₂O was pulverized in an agate mortar to fine powders to enhance mixing with other powders and increase the surface area for reactions. When preparing crucibles out of Cu₂O, shaped copper foils (A grade cathode copper) were oxidized using the same procedure. In this case pulverization was not necessary.

The calcium aluminates: tricalcium aluminate, 3CaO·Al₂O₃ (C₃A); dodeca-calcium hepta-aluminate, 12CaO·7Al₂O₃ (C₁₂A₇); monocalcium aluminate,

$\text{CaO} \cdot \text{Al}_2\text{O}_3$ (CA); monocalcium dialuminate, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ (CA_2); and monocalcium hexa-aluminate, $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ (CA_6) employed in the study were synthesized from pure calcium oxide and alumina powders. Calcium oxide, and alumina powders were calcined as part of each experimental preparatory stage to remove moisture. Calcined powders were mixed in correct proportions and pressed into 1 g pellets. Pressed-powders result in more intimate contact of the components [49]. Pellets were then fired at suitable temperatures in a Lenton muffle furnace (Type; UAF 16/10) between 1365 and 1600 °C, depending on phases being synthesized [III]. Synthesized phases were pulverized in an agate mortar to fine powders for easy mixing with self-made cuprite powders. The source and purity of materials are depicted in Table 1.

Table 1. Source and purity of materials used in this study.

Chemical	Form	Mass fraction purity	Source
Aluminium (III) oxide	Powder	0.999	Sigma-Aldrich (Germany)
Argon	Gas (compressed)	0.99999	AGA (Finland)
Calcium oxalate mono hydrate	Powder	0.99	Johnson-Matthey Noble Metals (England)
Calcium oxide	Powder	0.99	Alfa Aesar (Germany)
Calcium oxide	Powder	0.999	Sigma-Aldrich (Germany)
Copper	Lump & pellet	0.99996	Boliden Harjavalta Oy (Finland)
Copper (II) oxide	Powder	0.99995	Alfa Aesar (Germany)
Chromium (III) oxide	Powder	0.9997	Sigma-Aldrich (Germany)
Platinum	Wire	0.9999	Johnson-Matthey Noble Metals (England)

Table 1 shows that high purity materials have been used in the study. SEM-EDS and XRD methods were primarily employed in confirming the purity of the synthesized primary phases. In certain cases, a single method was sufficient while other cases required both methods to confirm purity of the phases or phase assemblage. The Scanning Electron Microscope (SEM) employed was a LEO 1450 coupled to an Inca X-sight 7366 EDS analyzer. A PANalytical X'Pert Pro Powder (Almelo, Netherlands) was employed for XRD analysis of the solid phases.

3.2 Experimental apparatus and procedure

All equilibration experiments in this thesis were carefully carried out in a Lenton vertical electrical resistance tube furnace (Type; LTF- 16/450) with a 35-mm inner diameter alumina work tube as depicted in Figures 3 and 4. The furnace is fitted with four heating elements and provides a sufficient constant temperature hot zone length within which samples are introduced and kept for the duration of the experiment [I - IV]. In all the experiments, temperature measurement was achieved with a calibrated S-type thermocouple (Johnson-Matthey Noble Metals, UK). The thermocouple was connected to a Keithley 2010 DMM multimeter (Figure 3C), and cold junction compensation was performed

with a PT100 resistance thermometer (SKS-Group, Finland, tolerance class B 1/10), connected to a Keithley 2000 DMM multimeter Figure 3C.

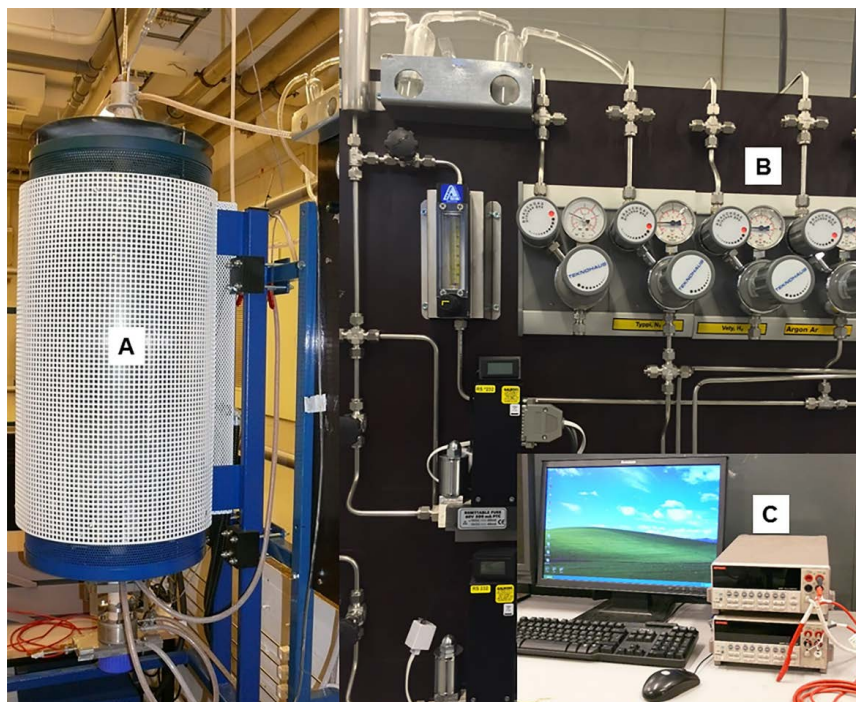


Figure 3. Equilibration experimental apparatus. A- Lenton vertical electrical resistance tube furnace (Type; LTF- 16/450), B- Gas flow control mechanism, C-Temperature measurement devices.

Experiments by the equilibration and quenching technique are performed at a fixed temperature [23]. In this study, the exact temperature was established by means of the calibrated thermocouple. This procedure involved mapping temperature profiles of the furnace hot zone (uniform temperature zone). By this procedure, a region with constant temperature ‘hot zone’ was established (from 4 to 5 cm at $\pm 2^\circ\text{C}$).

The Lenton vertical electrical resistance tube furnace (Type; LTF- 16/450) was fitted with a gas control system to achieve the desired equilibration oxygen pressure. For experiments in copper saturation, passing a constant flow of purified argon gas provided an inert atmosphere. 1 % oxygen in 99 % nitrogen gas mixture was employed at the same flowrate for experiments above the critical point in the Cu-O system under low oxygen pressure conditions [II]. When conducting experiments in air, an open work tube from both ends allowed the passage of air through the furnace during experiments.

All samples were introduced into the furnace’s hot zone supported by platinum wire. Samples were pulled from the bottom of the furnace’s work tube with the help of this platinum wire. For experiments in reducing conditions and which required passing of a constant flow of gas, samples were held away from

hot zone for 30 minutes during which residual gas was flushed out. Argon gas and 1% oxygen in 99% Nitrogen gas mixture (for experiments above the critical point) were employed for this purpose. After 30 minutes the samples were brought into the hot zone of the equilibration furnace. Depending on the system, direction from which equilibrium was approached and the target equilibrium temperature, the optimal equilibration time varied from 1 to 24 hours. To determine sufficient equilibration time, a time series set of equilibration experiments for optimizing the equilibration time preceded all the experiments [I - IV].

Generally, equilibration experiments in air took much longer time at lower temperature while experiments in reducing conditions were faster for the entire temperature range. This may be attributed to the variations in the kinetics of the system in these two different conditions. Oxygen diffuses as ions in oxidizing conditions while it is atomic in metal rich reducing conditions. To reduce the time required, it was necessary to premelt the sample in selected experiments in air, by raising the temperature higher than the target temperature for up to 30 minutes before bringing to target equilibration temperature [I, III, IV]. This greatly reduced the equilibration time in certain cases.

Platinum wire and envelopes were employed in holding the samples during equilibration experiments. An example of the sample holder is depicted in the schematic of Figure 4. Platinum was chosen because it is unreactive (inert) to the systems investigated under these chosen equilibration conditions. This ensured that all the systems were equilibrated without impurities. This was also supported by the design of substrates in this study. Whenever substrate material was required in this study, they were containing materials only from the system being equilibrated. For example when studying the Cu-O-CaO system, CaO substrates were employed.

Because of the different needs of each experimental study, the quenching method in this dissertation has been adapted continuously to meet the requirements while keeping in mind the thermodynamic constraints. This also resulted in a large number of experiments when testing the reproducibility at each of the adopted conditions.

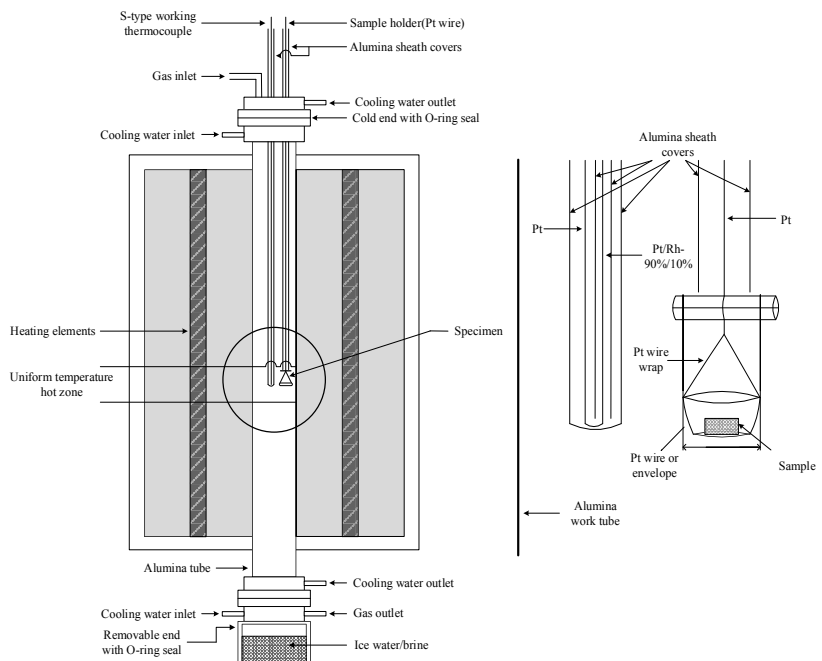


Figure 4. A schematic vertical section of the furnace and its auxiliaries, and the suspension technique.

At the end of each equilibration experiment, a flask of either cold water or NaCl (20 wt %) solution (depending on the demands of an experiment) was placed at the bottom of the work tube. The specimen was then released so that it dropped and quenched into the quenching media. Samples were washed in clean water, dried and embedded in epoxy resin. All quenched specimens in this study were prepared using established metallographic techniques. Careful attention was paid to the positioning of specimens so that sections of interest were exposed to the surface for characterization. Because of the hygroscopic nature of CaO and some of its compounds with alumina, all specimens were prepared with non-water-based lubricants. Therefore, Propylene glycol (Sigma Aldrich, Germany) and DP brown (Struers, Denmark) were employed for polishing of specimens. The samples were also stored in a desiccator when awaiting analysis. A Leica EM SCD050 Coater (supplied by Leica Mikrosysteme GmbH, Wien, Austria.), was employed to carbon coat the specimens before SEM-EDS and EPMA analyses. Carbon coating creates a conductive layer on the sample. This inhibits charging of samples during imaging, reduces thermal damage of samples and improves secondary electron signal thereby enhancing imaging [39].

3.3 Analysis of samples

In all the experiments, the composition of homogenous phases from polished sections of quenched samples, were quantified using Scanning Electron Microscopy (SEM-EDS) and Electron Probe Micro-Analyzer (EPMA). Because EPMA provides more accurate results (see section 2.3.4) SEM-EDS was only employed

for preliminary examination of phase compositions. Verification by EPMA was mandatory for all samples and as such, only results acquired by EPMA have been included both in this compendium and appendices [I-IV].

For SEM-EDS analysis, a LEO 1450 (Carl Zeiss Microscopy GmbH, Jena, Germany) scanning electron microscope coupled to an Inca X-Sight 7366 EDS analyzer (Oxford Instruments plc, Abingdon, Oxfordshire, UK) operated with a 15 kV acceleration voltage was applied.

For EPMA analysis, a CAMECA SX100 (Cameca SAS, France), equipped with five wavelength dispersive spectrometers (WDS) and a probe current ranging from 20 - 40 nA (based on the sample) was applied. Depending on the phases of the system being investigated, the beam diameter was kept between 1-20 μm for all experiments. The accelerating voltage varied between 15 - 20 kV.

Standards and lines employed for EPMA analysis were Al K α (almandine), Cu K α (chalcopyrite), or K α (Cu metal) O K α (hematite) and Ca K α (Diopside), all of which are natural minerals. All standards applied in the study were acquired from Astimex Scientific ltd. The PAP matrix correction procedure [50] was applied for raw data correction. Elemental detection limits for EPMA results were: Cu; 0.03 - 0.1, Ca; 0.01 - 0.04, Al; 0.01 - 0.02, O; 0.09 - 0.3, Cr; 0.02 wt %.

For all the phase compositions provided in appendices [I-IV], each point represents at least 10 independent measured values from different locations of the same phase with a standard deviation not exceeding 1 wt%. The uncertainties of the measurements are provided in appendices [I-IV].

4. Results and discussion

The main objective of this research was to acquire accurate experimental phase equilibria data for the selected systems Cu-O-CaO, Cu-O-CaO-Al₂O₃, Cu-O-Cr₂O₃, in temperature and compositions ranges either poorly known or not previously experimented on. Phase equilibrium data, and particularly liquidus data for the systems in question have been acquired. This data will be added to the available literature data to perform thermodynamic assesement that will result in more consistent and accurate thermodynamic database of oxide systems relevant to copper smelting processes. Main findings from this research are discussed in this section while a more detailed account can be found in the appended published articles [I-IV].

4.1 The Cu-O system

Phase equilibria of the Cu-O system have a decisive role to the copper making process. As such, it forms the main link to this experimental study. This could also be the main reason why phase equilibria and thermochemical data of the Cu-O system have been an area of intense study in the past decades [51-58]. This study focuses on the copper rich side of the Cu-O phase diagram. As such, equilibria of the oxygen rich side of the diagram is excluded.

At temperatures above 1026 ± 2 °C, cuprite (Cu₂O) is the stable phase of copper oxide instead of tenorite (CuO) in air [51-56]. Cuprite melts at 1123 ± 2 °C in air. The melting point of cuprite rises to 1223 ± 2 °C when it is equilibrated with metallic copper. Tenorite (CuO) is the stable phase of copper oxide in air at temperatures below 1026 ± 2 °C. Figures 5-6 show stability ranges of phases present in the copper oxygen system. The diagrams have been calculated using Factsage.

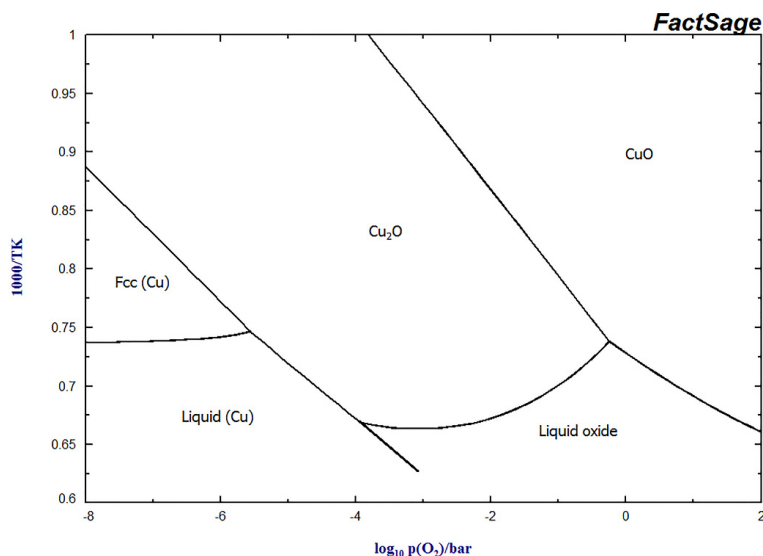


Figure 5. The oxygen potential phase diagram of the Cu-O system [52].

The miscibility gap in Cu-O system has previously been extensively studied [51-58]. This gap terminates at the critical temperature 1350 °C (or convolution point), above which, the liquid is continuous from metallic copper to copper oxide, see Figure 6.

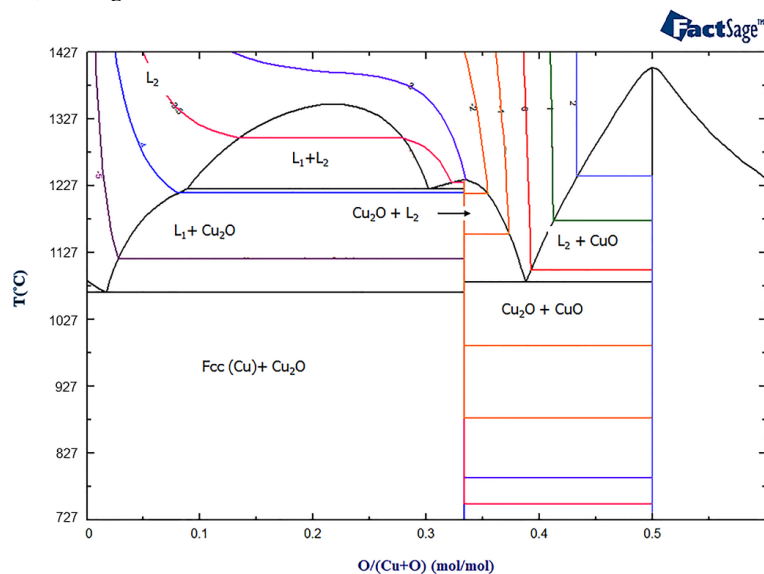


Figure 6. The calculated copper-oxygen phase diagram. L₁ is liquid copper, L₂ is liquid oxide [52].

4.2 The Cu-O-CaO system

The liquidus of the system Cu-O-CaO has been experimentally investigated over a wide temperature range and at different oxygen pressures. In this section the results obtained in the study, and also published in [I, II] are discussed. In the first part, the experimental results for the system Cu-O-CaO in equilibrium with air are briefly discussed. This is followed by the summary of results in copper saturation conditions.

Figure 7 shows a calculated isothermal ternary section of the system Cu-O-CaO at 1100 °C. In the diagram it can be observed that halite (CaO) and cuprite (Cu_2O) are the stable solid phases in equilibrium with the liquid oxide. These were the only choices for substrate materials.

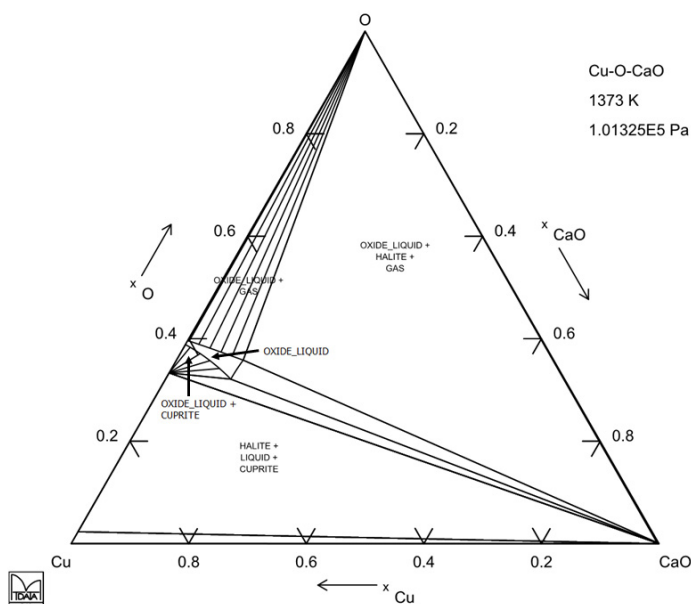


Figure 7. A calculated isothermal ternary section in the Cu-O-CaO system at 1100 C.

4.2.1 The system in equilibrium with air

The composition of the liquidus of Cu-O-CaO system in air at 0.21 atm is presented in appendix [I]. In the study, the liquidus was investigated in the temperature range from 1300 to 1500 °C. The liquidus is of the pseudo binary Cu_2O -CaO which is of great importance to the copper smelting. The amount of CaO contained in the liquid oxide is depicted in Figure 8. In the figure, the results are compared with literature.

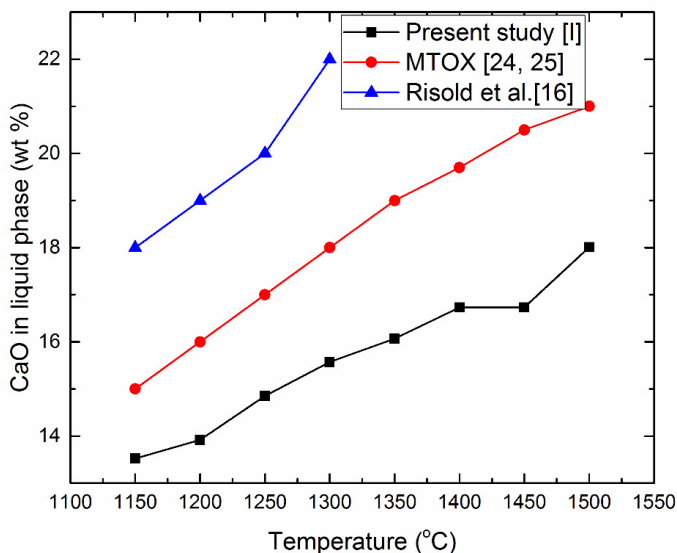


Figure 8. Solubility of CaO in liquid oxide phase for the system Cu-O-CaO in air.

Prior to this study, there were no experimental data at temperatures above 1300 °C for the liquidus of the system investigated. The liquidus of the phase diagrams from MTOX database [24,25] and Risold et al., [16] employed for comparisons are based on extrapolated values for temperatures above 1300 °C.

At the beginning of the study, it was realised that CaO and Cu₂O to be used as proposed substrate or crucible materials were not commercially available. Therefore crucibles of CaO and Cu₂O were self-made from CaO powders and A-grade copper cathode, respectively, which were commercially available.

From the study, it was observed that the CaO solubility in liquid phase falls within a narrow range of composition for the entire temperature range under consideration. The composition of CaO in the liquid phase was found to be between 13 and 19 wt %. This range is fairly consistent with previous study estimations. In the study, it was also observed that the Cu₂O solubility in CaO was small, i.e. ≤ 1 wt % Cu₂O.

Despite the lack of experimental data in literature, experimental results of the liquidus in this study were in good agreement with literature values for the greatest part of temperature range studied. It was however observed that at temperatures above 1300 °C the experimentally measured compositions deviate from the literature data. Using Kytö's unpublished data [59], and Oishi et al., [60] Rannikko [61] had earlier conducted a thermodynamic assessment of the system Cu-O-CaO as part of the system Cu-O-CaO-SiO₂. Experimental results of this study for the system when compared to Rannikkos' are also consistent except at temperatures above 1300 °C. The experimental errors of the data used and alluded to by Rannikko are assumed to be the main source of this deviation. The two experimental points of the hypoeutectic of the binary are consistent

with literature. This is supported by the large number of experimental and theoretical studies of this phase area of the diagram [51-58].

4.2.2 The system in equilibrium with copper

The liquidus of the system Cu-O-CaO in equilibrium with metallic copper was investigated by equilibration technique. Prior to the study, it was observed that all previous experimental studies, which have been the basis of assessed phase diagram for the system, employed foreign containment materials because of the reactive liquid oxide phase [II]. The use of quartz [17] and magnesium oxide [18] crucibles may have introduced impurities of silica and magnesium oxide, respectively. Re-examination of the liquidus experimentally was therefore necessary. Using CaO as containment material, the system was kept without impurities since CaO is part of the system. The results of this study are compared to MTOX [24,25] and Kuxmann and Kurre [17] in Appendix [II] and Figure 9.

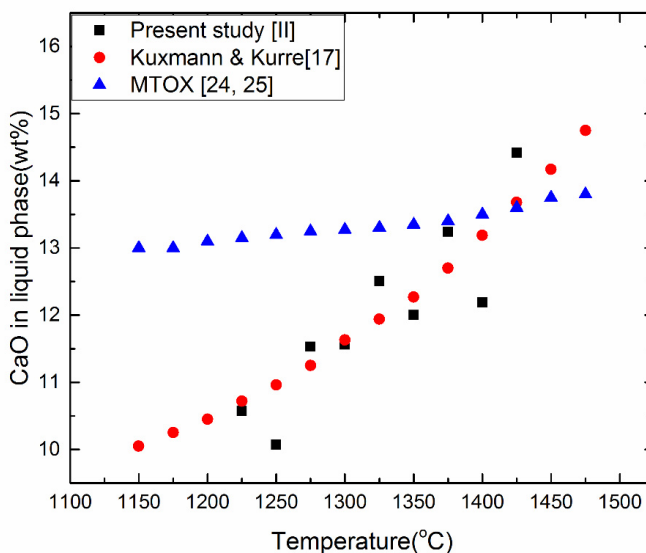


Figure 9. Solubility of CaO in liquid oxide phase for the system Cu-O-CaO in equilibrium with copper.

The solubility of CaO in the liquid oxide phase falls within a narrow composition range which was found to be 4.35 wt % CaO. Only a small solubility of CaO in Cu_2O was observed i.e. ≤ 1 wt %.

In comparison with two main experimental studies, the results of this study are fairly consistent with literature above 1350 °C, which is the critical point in the Cu-O system. Below this temperature, it was found that CaO solubilities in liquid phase are overestimated in the MTOX database [24,25].

Quenching samples in equilibrium with copper resulted in better quenching of the liquid oxide phase when compared to the experiments conducted in oxidizing atmosphere in air [II]. The presence of metallic copper phase was assumed to be the main contributing factor.

When the two cases in 4.2.1 and 4.2.2 are compared, it is observed that the copper oxide liquid phase for the system in air is richer in CaO than the system in equilibrium with metallic copper. This can be explained by higher oxygen activity. In copper saturation conditions, oxygen activity is much lower than in air at 0.21 atm. This translates into low chemical potential, the driving force for a reaction.

4.3 The system Cu-O-CaO-Al₂O₃ in air

Phase equilibria in the quaternary system Cu-O-CaO-Al₂O₃ in air was experimentally investigated for the first time using equilibration technique. The focus of the experimental measurements was the liquidus surface of the system in the temperature range 1150-1400 °C, in steps of 50 °C. The liquidus results obtained are discussed in this section. The pseudo binary CaO-Al₂O₃ in the ternary system Cu₂O-CaO-Al₂O₃ has been intensely studied [62-72] and is thus outside the scope of this study.

Furthermore, using the triple points of the isothermal ternary sections for the system Cu₂O-CaO-Al₂O₃, the liquidus surface for the system was estimated and presented for the temperature range of interest. For discussion purposes, these triple points were numbered 1 – 5, to represent the phases in equilibrium at a particular temperature, see Table 2

Table 2. Three-phase equilibria for the five triple points.

Triple point	Corresponding three phase equilibria
1	Liquid + Halite + C ₃ A
2	Liquid + C ₃ A + C ₁₂ A ₇
3	Liquid + C ₁₂ A ₇ + CA
4	Liquid + CA + CA ₂
5	Liquid + CA ₂ + CA ₆ (CuAlO ₂ at 1150 °C)

Isothermal ternary sections of Figures 10 and 11, also in appendix [III] were calculated utilizing MTDATA's multiphase module, and MTOX database. By defining the system as Cu-O-CaO-Al₂O₃, potential computation errors associated with the Cu-O system were avoided. Temperature and oxygen partial pressure were fixed according to experimental parameters. Once the calculations were performed, they were plotted on the isothermal section Cu₂O-CaO-Al₂O₃.

Within the boundaries of this study, the liquid phase domain of the ternary system under isobaric conditions was observed to vary to great extent as a function of temperature, expanding largely from the cuprite (Cu₂O) corner and towards the Al₂O₃-CaO joint. This is largely due to the low melting temperature of Cu₂O (1123 °C) in air. When Cu₂O melts, it generates a copper liquid oxide which dissolves the high melting oxides, CaO (2572 °C) and Al₂O₃ (2045 °C).

4.3.1 Stability range of CuAlO_2 and C_{12}A_7

In this study, the stability of the cuprous aluminate delafossite (CuAlO_2) was confirmed at 1150 °C, which is consistent with literature data [73-78]. This is depicted by triple point 5 of the isothermal section at this temperature in Figure 10. This phase is however stable only in a narrow temperature range and disappears at a temperature below 1200 °C as confirmed by the study [III].

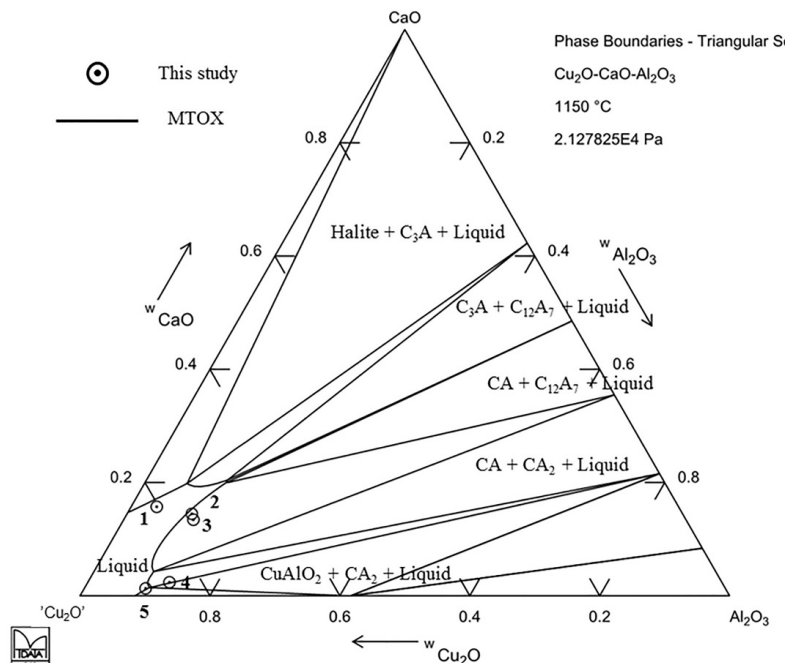


Figure 10. Calculated isothermal ternary section of the system 'Cu₂O'-CaO-Al₂O₃ at 1150 °C and experimental points superimposed; numbers refer to phase equilibria of Table 2.

In the study, the stability range of dodeca-calcium hepta-aluminate, $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (C_{12}A_7) phase was investigated. For the temperature range of interest in this system, it was observed that this phase is only stable between 1150 and 1350 °C, and that it melts below 1400 °C. This is in agreement with MTOX database, where it is proposed that the melting point of the phase is ~ 1374 °C [24]. In this study this was validated by the degradation of the three phase equilibria to only two phases at 1400 °C, see Figure 11

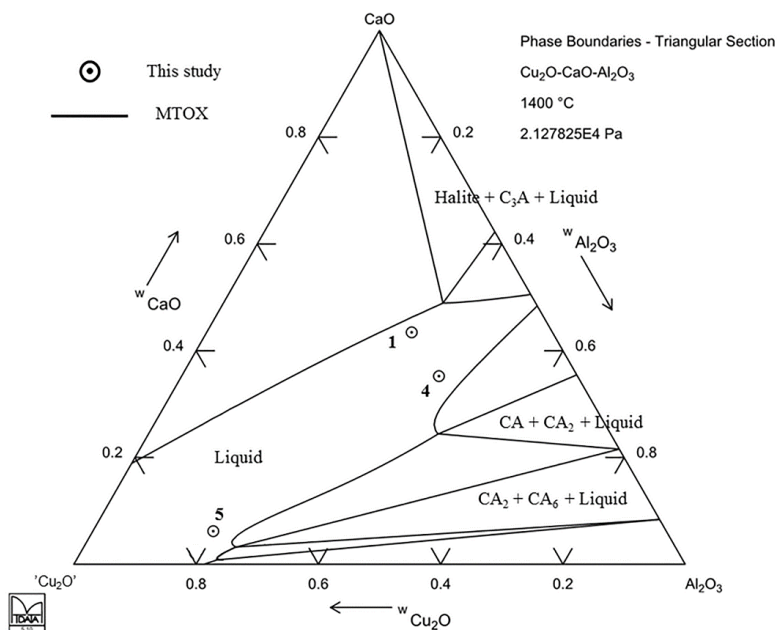


Figure 11. Calculated isothermal ternary section of the system 'Cu₂O'-CaO-Al₂O₃ at 1400 °C and experimental points superimposed; numbers refer to phase equilibria of Table 2.

4.3.2 Solubility of cuprite in solid phases

The solubility of Cu₂O in calcium aluminates as well as halite (CaO) phase was quantified in this study. It was observed that there is a significant amount of Cu₂O in solid phases ranging from 0.5 to 2.23 wt %, refer to Figure 12.

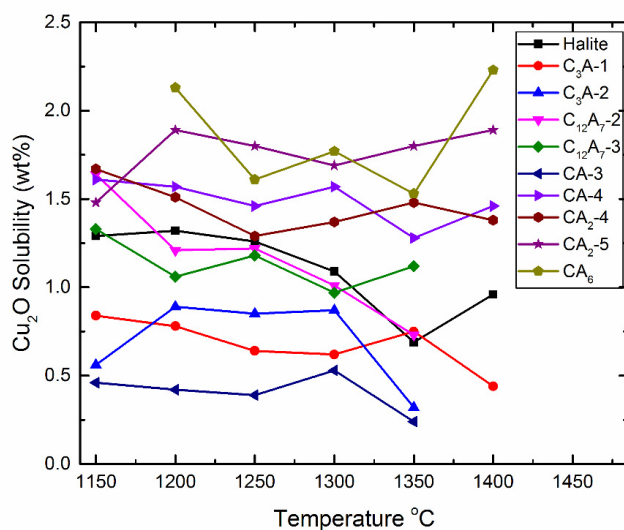


Figure 12. The solubility of cuprite in halite and calcium aluminate. The number at the end of each label denotes a three phase equilibrium of Table 2.

Tricalcium aluminate (C_3A -2) and monocalcium aluminate (CA-3) were observed to have the least amount of Cu_2O . Dodeca-calcium hepta-aluminate ($C_{12}A_7$), monocalcium dialuminate (CA_2), monocalcium hexa-aluminate (CA_6), had comparatively higher amounts of Cu_2O ranging from 1.0 to 2.5 wt%.

It was observed that the Cu_2O solubility in individual solid phases varied depending on which phase region (of Table 2) it belongs. For example, CA-3 has the least amount of Cu_2O at nearly ≥ 0.5 for the entire temperature range, while CA-4 has much higher Cu_2O content at ≥ 1.25 wt %.

Furthermore, it was observed that except for two phases: Halite and $C_{12}A_7$, there was only a negligible effect of temperature on the Cu_2O solubility in all the solid phases. On the contrary, Cu_2O solubility in halite and $C_{12}A_7$ exhibited a phenomenon analogous to retrograde (inverse) solubility whereby the amount of Cu_2O decreased with an increase in equilibration temperature. This phenomenon is depicted in Figure 13.

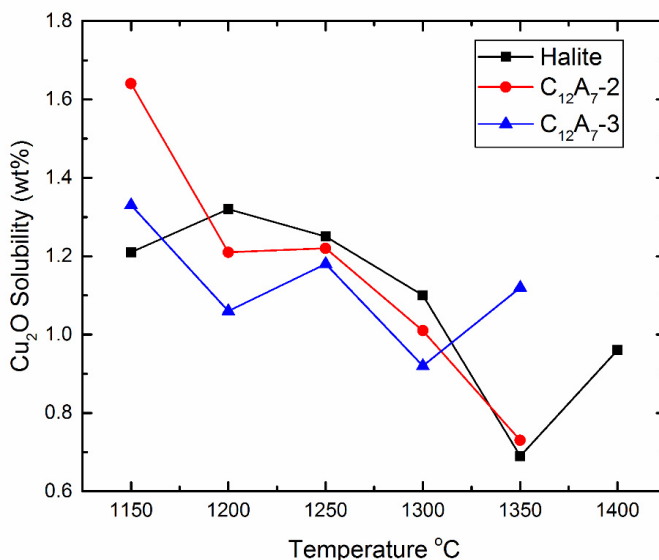


Figure 13. The solubility of cuprite in halite and dodeca-calcium hepta-aluminate.

During the study, minor precipitation of Cu_2O was observed in some of the samples' polished sections. This was observed using micrographs of polished sections obtained by SEM as seen in Figure 14 for triple point 2 equilibria of Table 2.

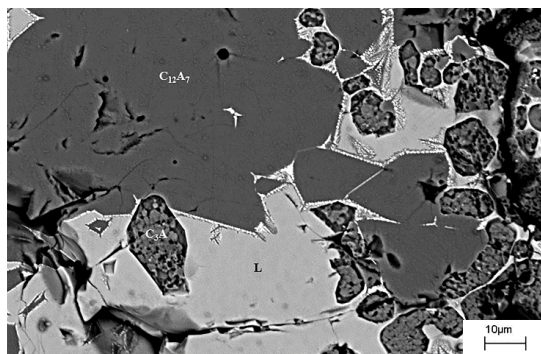


Figure 14. A backscattered SEM image of a polished section from a quenched sample equilibrated at 1200 °C. Cu_2O precipitates can be observed at the liquid oxide–solid boundary

The precipitates are the result of quenching a molten phase, which has rapid phase change [21-23]. This tends to form a eutectic composition expressed in equation (4):



In equation (4) L is the liquid oxide phase while S represents the solid(s) in equilibrium with the liquid oxide phase. Varying the beam diameter during EPMA analysis helps avoiding the uncertainties associated with this phenomenon [79]. This did not affect the results since precipitation was confined to the liquid-solid phase boundaries and as such, large enough areas with homogenous liquid phase were still available for quantifying the chemical composition of the liquid phase.

The CaO rich solid phases were found to be hygroscopic, especially C_3A as in Figure 14 where it is seen to break down. This is consistent with literature [78,80].

4.3.3 Composition of liquid phase

The measured liquid oxide composition for triple point one was found to be stable between 1150 and 1350 °C. Above that it sharply shifts towards the CaO- Al_2O_3 binary joint. A comparison with literature data calculated from MTOX database [21,22] showed large deviation at 1300 and 1350 °C, i.e., up to 40 %wt in Cu_2O , 20 %wt in CaO, 30 %wt in Al_2O_3 . Triple point 4 measured compositions are inconsistent with MTOX database at temperatures between 1350 and 1400 °C. The measured liquid oxide compositions of triple points 2, 3 and 5 are fairly consistent with MTOX database for the entire temperature range with those of 2 and 3 staying within 10 wt% in Cu_2O , Al_2O_3 and CaO.

It was assumed that some estimations errors in the MTOX database were possibly due to the derivation criteria, for example, higher order systems' data were obtained by extrapolations, i.e., from unaries and parameters for these unaries were obtained by substituting the Gibbs energy change associated with a vacancy regardless of the occupancy of tetrahedral or octahedral sites [22].

4.4 The system Cu-O-Cr₂O₃

The liquidus of the system Cu-O-Cr₂O₃ in air was experimentally investigated for the first time using equilibration technique. The liquidus of the system Cu-O-Cr₂O₃ in air below the peritectic temperature is presented in this section as well as in appendix [IV]. In Figure 15, liquidus experimental results of Appendix [IV] are compared with MTOX database.

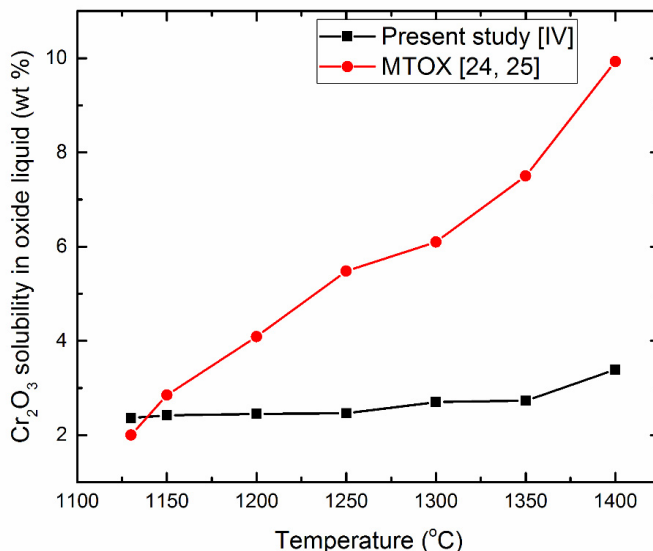


Figure 15. Solubility of Cr₂O₃ in liquid liquid phase in the system Cu-O-Cr₂O₃ in air.

The results of figure 15 show that the Cr₂O₃ content of the liquid oxide phase for the temperature range of interest is very small between 2.36 and 3.39 wt % Cr₂O₃. This is in contrast with literature data.

Gadalla and White [10] as well as Jacob et al. [9], had earlier experimentally studied the phase equilibria of the system with their results included in MTOX database. From figure 15, all previous studies had overestimated the Cr₂O₃ content of the liquid oxide phase at temperatures above 1300 °C. This may be attributed to the lack of experimental data to obtain accurate assessments.

In this study, the eutectic temperature and compositions were found to be at 1112±2 °C and at composition of 2.06 wt. % Cr₂O₃. Large discrepancies in eutectic temperature and composition of this study and previous authors have also been observed.

Based on these experimental results, it was also proposed that the peritectic temperature and composition of the system in literature could be far from experimental values. This however demands more experimental work at higher temperatures than investigated in this study. See Figure 16 which illustrates the solubility of Cr₂O₃ in liquid phase depicted as a Cr₂O₃/Cu mole ratio.

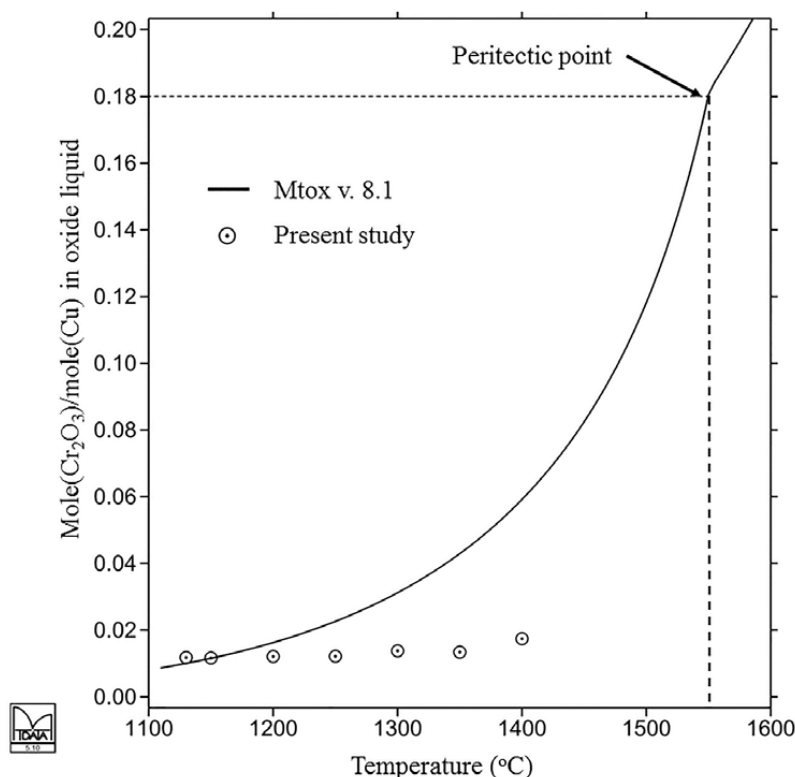


Figure 16. A comparison of calculated (MTOX) and experimental results for the system Cu-O-Cr₂O₃ in air at solid oxide saturation.

4.5 Future work

Experimental phase equilibrium data have a two-fold function in understanding thermodynamics of processes. On one hand they can be used as a stand alone source of information to predict industrial processes phenomena. On the other hand, they can be applied to validate modelling from first principles. Experimental results from this dissertation reveal the inconsistencies in simple copper-oxygen-oxide(s) systems leading to errors in predicting higher order systems. There is thus need to further examine experimentally other simple copper-oxygen-oxide(s) systems experimentally to realise a consistent thermodynamic oxide database. Together with carefully selected data in literature, results of this work will be used to perform thermodynamic reassessment using MTDATA to achieve a more consistent database.

5. Conclusions

Developing an accurate thermodynamic database of oxide systems for industrial applications in copper smelting depends on both phase equilibria and thermochemical data. Since phase equilibrium data of oxide systems cannot be solely acquired by modelling from first principles, acquiring accurate experimental data is mandatory. Especially phase equilibria of simple systems is important in understanding complex systems. The equilibration and quenching method is one of the most suitable type of static equilibria technique available for acquiring accurate phase equilibrium data of liquidus. By this method the chemical composition of liquid oxide and its associated solid phases equilibrated at high temperature can be analysed at room temperature as a “glassy” or microcrystalline phase by EPMA, a high accuracy tool for quantifying chemical composition.

In this research, liquidus data for the systems Cu-O-CaO, Cu-O-Cr₂O₃, Cu-O-CaO-Al₂O₃, have been experimentally investigated by the equilibration and quenching method, in previously unexplored temperature and composition ranges. Purity of systems have been maintained by employing self-made substrates, which incorporate the solid phases in equilibrium with the liquid oxide phase.

For the system Cu-O-CaO in equilibrium with air [I], results from this study reveal that the CaO solubility in the liquid oxide phase for the binary (Cu₂O-CaO) is only consistent with literature at lower temperatures. Above 1300 °C, where experimental data was obtained for the first time in this study, there is a systematic deviation in CaO solubility in the liquid oxide phase, which increases with temperature. The hypoeutectic liquidus compositions of the system are however consistent with the available literature data.

In the system Cu-O-CaO in equilibrium with metallic copper, the liquidus data of the (Cu₂O-CaO) pseudo-binary was obtained by equilibration method, and without impurities for the first time. In the study, the hypereutectic liquidus data of the system Cu-O-CaO in equilibrium with copper from this study [II], are only consistent with data obtained in literature above the critical point in the Cu-O system. The solubility of CaO in liquid oxide phase below the critical temperature in literature has previously been overestimated.

Phase equilibrium data for the system Cu-O-CaO-Al₂O₃ in air were experimentally investigated for the first time using equilibration techniques. In the system Cu-O-CaO-Al₂O₃ in equilibrium with air, the liquid oxide compositions for triple points 2, 3, and 5 (as assigned in this study) were consistent with literature data in the temperature range of interest.

To the contrary, large deviations were observed in the liquidus data of triple points 1 and 4 with the largest deviations observed at temperatures between 1350 and 1400 °C, where the composition of liquid oxide phase deviates up to 40 wt%.

In the system Cu-O-CaO-Al₂O₃ in equilibrium with air, tricalcium aluminate (C₃A-2) and monocalcium aluminate (CA-3) dissolves copper the least. Dodecacalcium hepta-aluminate (C₁₂A₇), monocalcium dialuminate (CA₂), and monocalcium hexa-aluminate (CA₆), dissolves the largest amount of Cu₂O.

The liquidus compositions of the system Cu-O-Cr₂O₃ in equilibrium with air were experimentally investigated for the first time using equilibration technique. Experimental findings from this study do not agree with the available literature data. All previous studies have over estimated the amount of soluble Cr₂O₃ in the liquid oxide phase. The inability to quantify the composition of liquid phase by both experimental techniques previously applied partially justifies this finding.

By the equilibration and quenching technique, the eutectic of the quasi-binary Cu₂O-Cr₂O₃ was found to be at 1112±2 °C and at composition of 2.06 wt. % Cr₂O₃.

Results from this research reveal that liquidus data of simple copper-oxygen-oxide(s) systems are still poorly known and currently insufficient for prediction of multicomponent oxide systems that constitute slag. Liquidus data from this study will contribute to understanding of these simple systems and improve prediction of multicomponent systems.

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Thermodynamic databases are a valuable tool in predicting behavior of high temperature chemical processes. Predictive tools enable easy process control. Databases are obtained from experimental phase equilibrium and thermochemical data.

This study provides knowledge and new experimental phase equilibrium data of selected copper-oxygen-oxide(s) systems in previously unexplored temperature and composition ranges. Experiments were conducted using the equilibration and quenching method. Electron Probe Micro-Analysis (EPMA) was employed as the analytical tool for quantifying chemical composition of phases.

The experimental phase equilibrium data acquired in this research will improve thermodynamic prediction of high order oxide systems of the copper smelting process.



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