A thermodynamic optimization of "Cu$_2$O"-containing slags systems

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Abstract: Prediction of phase equilibria and thermodynamics of complex copper smelting, converting and cleaning slag system is essential for further improvements in industrial operations. The previously existing chemical thermodynamic database for the system is being improved as part of the overall integrated research program on complex copper slag-matte-metal-solids systems combining experimental and thermodynamic modeling studies.

Computerized thermodynamic database for the liquid slag and solid oxide phases for the "Cu$_2$O"-Al$_2$O$_3$-CaO-FeO-Fe$_2$O$_3$-MgO-SiO$_2$-S system at conditions of equilibrium with metallic copper is further improved by critical evaluation/optimization of all previous available phase diagram-thermodynamic data and new experimental data that have been deliberately characterized in PYROSEARCH-UQ to support the present thermodynamic optimization work. The database contains parameters of models for the molten slag and solid oxide solutions such as olivine, melilite, pyroxene, monoxide, spinel, etc. The Bragg-Williams and Modified Quasi-chemical models are used to describe the Gibbs free energy of the molten slag solution. Model parameters are derived by the optimization process to reproduce all thermodynamic and phase diagram data within experimental error limits. All binary, ternary and higher order Cu-oxide-containing sub-systems are optimized simultaneously to obtain a self-consistent set of model parameters. This results in a significant improvement in the predictive ability of the computer model. The models permit extrapolation into regions of temperature and composition where experimental data are not available. Details of the recent thermodynamic optimization of the investigated system are presented.

The thermodynamic database is automatically accessed by FactSage software that calculates complex multi-component, multi-phase equilibria involving simultaneously slag, metal, solid and gas phases over wide ranges of temperatures and oxygen partial pressures.

The ability to calculate and predict the phase equilibria, partitioning of major and minor elements between phases, activities, vapor pressure, and other thermodynamic properties over a wide range of process conditions in copper production can enable informed decision to be made in relation to the optimum slag compositions, fluxing strategies, and operating conditions in copper smelting, converting, and slag cleaning processes for given feed and product requirement.

Industrial application of the database for the copper metallurgical process is discussed.

Keywords: Copper smelting, thermodynamics database, phase diagrams, pyrometallurgy, slag chemistry.

1. Introduction

Improvement of the industrial copper productions can be made through an informed decision on the selections of slag compositions, fluxing strategies, and operating conditions (temperature and oxygen blow) for given feed and product requirement. This can be facilitated through thermodynamic modeling in which phase equilibria, partitioning of major

and minor elements between phases, activities, vapor pressure, and other thermodynamic properties of the relevant systems can be predicted/calculated rapidly and accurately over a wide range of process conditions in copper smelting, converting, and slag cleaning processes.

The "Cu_2O"-Al_2O_3-CaO-FeO-Fe_2O_3-MgO-SiO_2-S system is important for copper smelting, converting, and slag cleaning processes. An accurate evaluation and optimization of the system has been hindered by previously lack of reliable data, especially in the conditions of equilibrium with metallic copper. New experimental data of the systems for various compositions and conditions relevant to copper production process have been generated as part of the overall research program on complex copper system in PYROSEARCH-UQ combining experimental and thermodynamic modeling studies.

In this article, further improvement of the previously existing chemical thermodynamic FactSage database for the system is outlined. The previously available data and new experimental data of the system are critically evaluated and then used to obtain a set of model parameters for Gibbs free energies of molten slag phase as functions of temperature and composition. Industrial application of the database for the copper metallurgical process is discussed.

2.   Previous assessments

The thermodynamic properties and phase diagrams of copper-containing slags system have been assessed and optimized previously [1, 2]. Cu^{1+} was considered to be the only copper species present in the slag, since over the range of copper-smelting/converting/cleaning the conditions were assumed to be reducing to have negligible Cu^{2+} in the system.

Binary systems of Cu_2O with CaO, FeO, Fe_2O_3, Al_2O_3, and SiO_2 were critically evaluated and optimized by Dessureault [1]. There were difficulties in optimizing Cu_2O-SiO_2 and Cu_2O-FeO-Fe_2O_3 systems; the later was mainly due to limited reliable data present in the system at the time when the optimization was carried out. Dessureault [1] continued with the evaluation of complex "Cu_2O"-Al_2O_3-CaO-FeO-Fe_2O_3-MgO-SiO_2-S system, which was later revised by Degterov and Pelton [2]. The solubilities of copper in S-free and S-containing slags were calculated and compared with the available experimental data at tridymite saturation, in equilibrium with iron, copper, or copper-gold alloys at fixed O_2 or SO_2 partial pressures and at different concentrations of CaO, MgO, or Al_2O_3 in the slag.

3.   Phases and thermodynamic models

Thermodynamic databases are developed through thermodynamic optimization that involves selection of proper thermodynamic models for all phases in a system, critical simultaneous evaluation of all available thermodynamic and phase equilibrium data and optimization of thermodynamic model parameters to obtain one self-consistent set of model equations for the Gibbs energies of all phases best reproducing the experimental data as functions of temperature and composition. From these equations, the thermodynamic properties and the phase diagrams can be back-calculated. Thermodynamic property data, such as activity data, can aid in the evaluation of the phase diagrams, and phase diagram measurements can be used to deduce thermodynamic properties. Discrepancies in the available data can be identified during the development of the model. These discrepancies can then be resolved through new experimental studies that, if

possible, are undertaken in areas essential for further thermodynamic optimizations. Multi-component data, if available, are used to derive low-order (binary and ternary) model parameters, and if multi-component data for a system are lacking, the low-order parameters are extrapolated. In this way, the thermodynamic databases are developed and all the data are rendered self consistent and in concordance with thermodynamic principles. The FactSage thermodynamic software package [3] was used to perform the thermodynamic optimization in the present study.

The liquid copper phase [2] and liquid Cu-Fe-S matte phase [9] were modeled previously as two separate solutions. No significant concentration of Al, Ca, Mg or Si was found in the liquid copper alloy and matte; as a result their presence in the solutions was neglected. The recently improved modified quasi-chemical model was found to be adequate to reproduce available experimental data in the Cu-Fe-S system over the entire metal-rich and sulfur-rich composition ranges in one solution model [3, 10].

Quartz, tridymite, and cristobalite (SiO_2) were treated as stoichiometric compounds; their non-stoichiometry was assumed to be negligibly small. The solubilities of Al_2O_3 in hematite and Fe_2O_3 in corundum were described in the corundum solution [3]. The olivine solution was described by considering two octahedral sites and the mixing of cations on three sublatices was taken into account for melilite and pyroxenes [8]. The monoxide (wustite, lime and magnesia) and spinel solutions were modeled previously [11] using a polynomial solution and a compound-energy formalism [12] models, respectively. The later takes into account the crystal structure and physical nature of the spinel solution which comprises of cations and vacancies distributed over tetrahedral (T) and octahedral (O) sites: $(Al^{3+}, Fe^{2+}, Fe^{3+}, Mg^{2+})^T[Al^{3+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Va]_2^O O_4$.

The modified quasi-chemical model [4-7], which takes into account short-range ordering of second-nearest-neighbor cations in the ionic melt, has been used to model the interactions between most of the oxides in the molten slag phase. The Al_2O_3-CaO-FeO-Fe_2O_3-MgO-SiO_2-S system has already been critically evaluated and optimized [8], and the optimized model parameters of this system have been used as a framework for the present optimization work. The Bragg-Williams [4] model has been used in the present study to model the interactions between several oxides in the slag. The use of Bragg-Williams model results in a greater flexibility in fitting the experimental data of the slag solutions with strongly positive excess properties.

4.   Evaluation/Optimization of experimental data

Preliminary thermodynamic optimizations have been performed in the "Cu_2O"-Al_2O_3-CaO-FeO-Fe_2O_3-MgO-SiO_2-S system for all binary, ternary, and higher-order subsystems. Most of the interactions between oxides are described by the modified quasi-chemical model [4-7]. The "Cu_2O"-SiO_2 and "Cu_2O"-FeO-Fe_2O_3 systems, with positive deviations from ideal solution behavior, are described by the Bragg-Williams [4] model.

Some of the details of thermodynamic optimizations are briefly presented in the following section. Fig. 1 shows experimental data [13-15] and calculated phase diagram of the "Cu_2O"-SiO_2 system in equilibrium with metallic copper. The most recent data by the authors [13] were obtained in parallel with the thermodynamic optimization work using an equilibration and quenching technique followed by electron probe X-ray microanalysis (EPMA), and were given

preference. Fig. 2 presents the predicted pseudo-binary phase diagram of "Cu_2O"-CaO system in equilibrium with metallic copper. All experimental phase equilibria data by Kuxmann & Kurre [14], Takeda [16], Coursol [17], and Nikolic et al [18] were described within the experimental uncertainties. Three pseudo-ternary "Cu_2O"-CaO-SiO_2, "Cu_2O"-MgO-SiO_2, and "Cu_2O"-Al_2O_3-SiO_2 subsystems in equilibrium with metallic copper [13], which were previously unavailable, have been characterized experimentally in PYROSEARCH-UQ to support the present thermodynamic optimization work. These data were reproduced by the model within the experimental errors (Fig. 3).
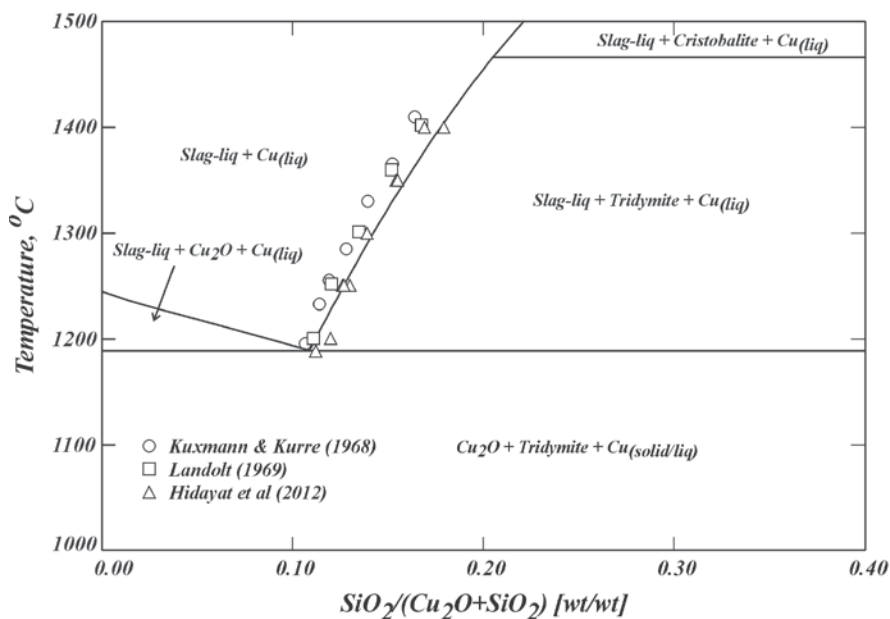
Fig. 1 Calculated phase diagram of the "Cu_2O"-SiO_2 system in equilibrium with metallic copper.
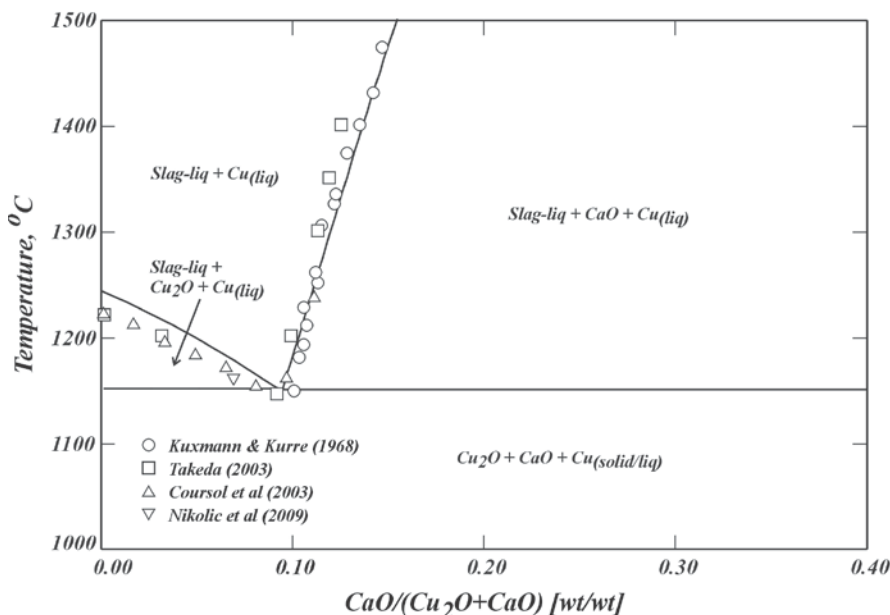
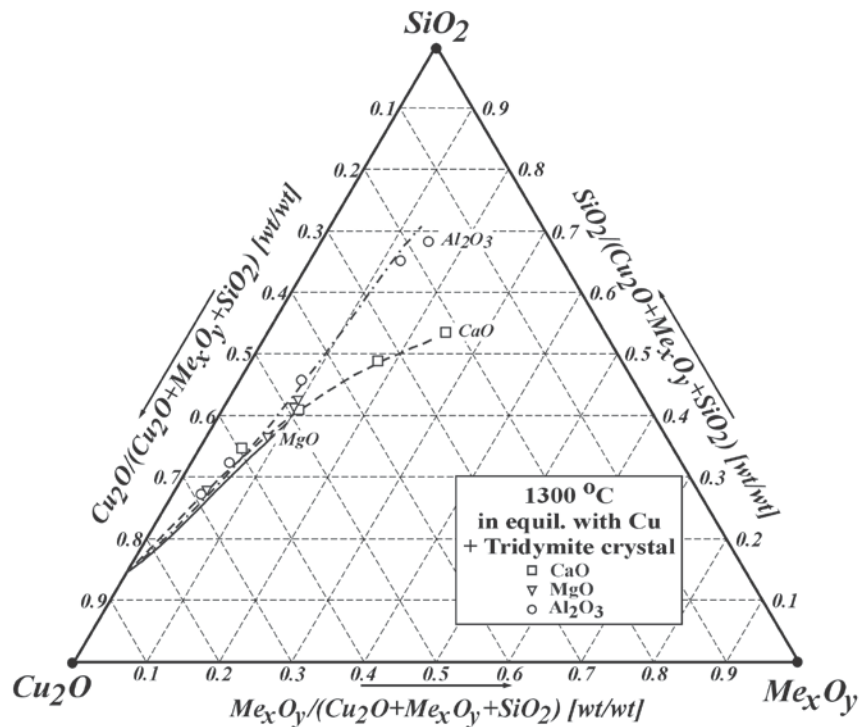Fig. 2 Calculated phase diagram of the "Cu_2O"-CaO system in equilibrium with metallic copper.

Fig. 3 Calculated phase diagram of the "Cu_2O"-Me_xO_y-SiO_2 systems (Me_xO_y =CaO, MgO, and Al_2O_3) in equilibrium with metallic copper.

The optimization was also carried for the fundamental system of "Cu_2O"-FeO-Fe_2O_3. Fig. 4 shows the calculated pseudo-binary diagram of the "Cu_2O"-"Fe_2O_3" system in equilibrium with metallic copper (Cu-Fe alloy). For the assessment of this system, preference were set on the data by Ilyushechkin et al [19] and Nikolic et al [18]. Both the data were generated by using synthetic primary phase materials as substrates to support the liquid slags; therefore the slags only contained chemical elements of interest. The data of Takeda [16] were not considered in this optimization due to the possibility of contamination by the MgO crucible used to contain the liquid slag.
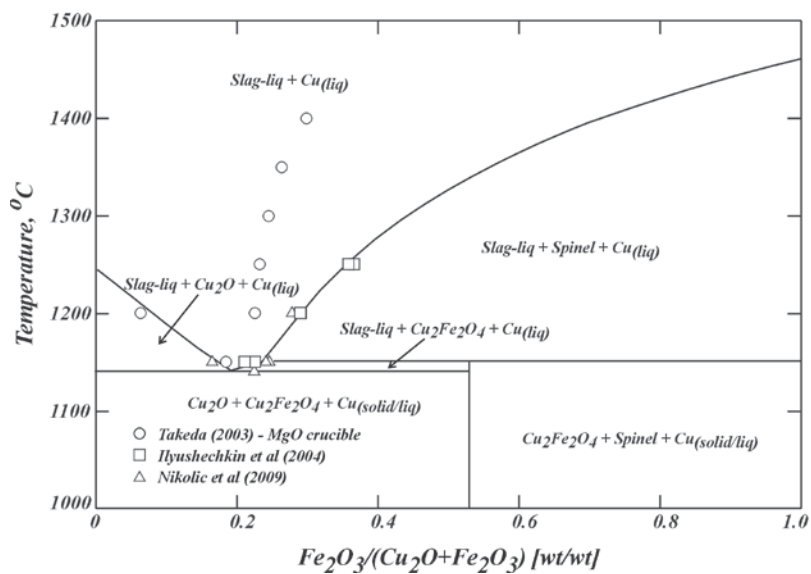

Fig. 4 Calculated phase diagram of the "Cu_2O"-"Fe_2O_3" system in equilibrium with metallic copper.

Two important multi-component systems of "Cu_2O"-CaO-FeO-Fe_2O_3 and "Cu_2O"-FeO-Fe_2O_3-SiO_2 in equilibrium with metallic copper (Cu-Fe alloy), which form basis for copper production slag, have been optimized. Information in the "Cu_2O"-CaO-FeO-Fe_2O_3 system in equilibrium with metallic copper is particularly important for some copper converting process. There are several measurements available in this system [16, 19, 20], however differences are found in relation to the liquidus compositions of spinel and dicalcium ferrite primary phase fields. The data by Ilyushechkin et al [19] and Nikolic et al [20] were given preference since they were obtained by equilibration technique on substrates made of primary phase materials, hence avoiding contamination that maybe introduced in previous studies [16] by common crucible materials such as MgO. The two data sets [19, 20] were reproduced within the experimental uncertainty as shown in Fig. 5.
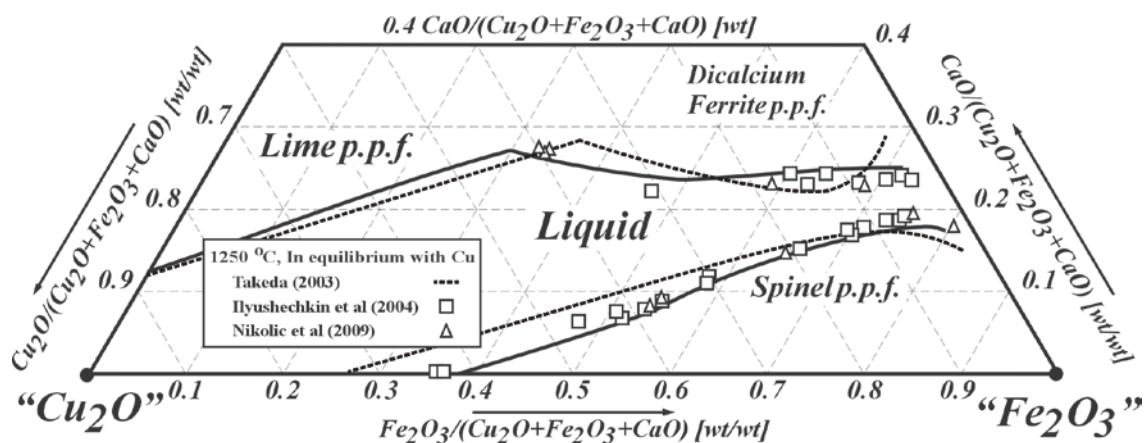

Fig. 5 Calculated phase diagram of the "Cu_2O"-CaO-"Fe_2O_3" system in equilibrium with metallic copper at 1250 ^{o}C.

Previously, there was no complete phase diagram information available in the "Cu_2O"-FeO-Fe_2O_3-SiO_2 system in equilibrium with metallic copper. New experimental data [21] were deliberately generated to support present modeling work. Agreement between the predictions and the new experimental liquidus is demonstrated in Fig. 6. The activities of $CuO_{0.5}$ (pure $CuO_{0.5(l)}$ standard state) in the "$CuO_{0.5}$"-"FeO"-SiO_2 system at 1300 ^{o}C by the current model and from the experimental data are provided in Fig. 7. The experiments were conducted by equilibrating the Cu-Fe-O-Si slag either with liquid copper [21-23] or copper alloy [24-26] at fixed oxygen potential. It can be clearly seen that the $CuO_{0.5}$ in this slag has a tendency of positive deviation from the ideal solution behavior.
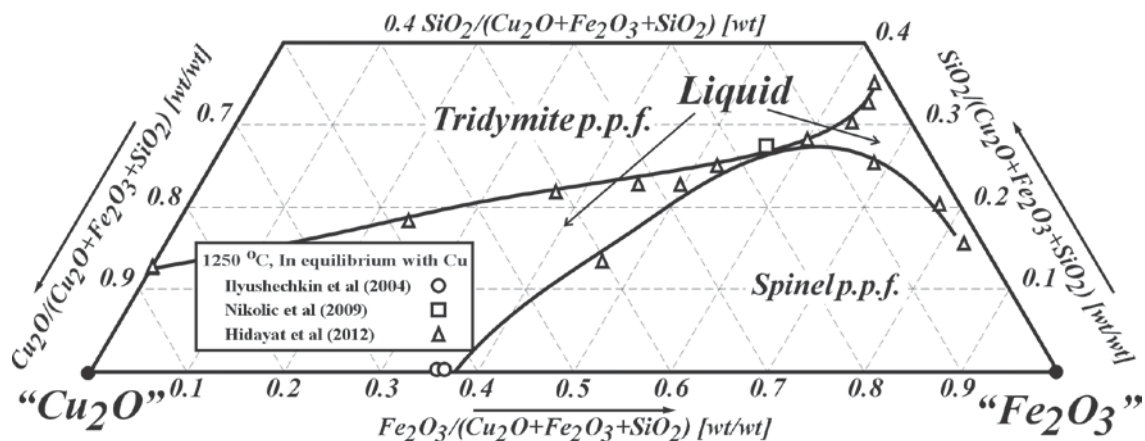
Fig. 6 Calculated phase diagram of the "Cu_2O"-"Fe_2O_3"-SiO_2 system in equilibrium with metallic copper at 1250 ^{o}C.
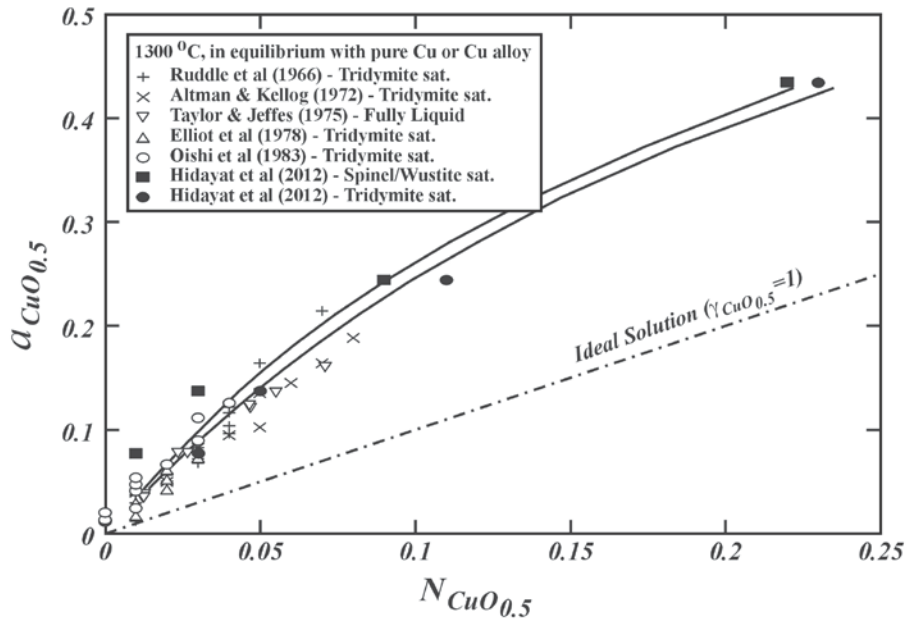

Fig. 7 Activity of liquid $CuO_{0.5}$ (pure $CuO_{0.5(l)}$ standard state) in the Cu-Fe-O-Si slag equilibrated with metallic copper or copper alloy at 1300 ^{o}C as a function of molar fraction of $CuO_{0.5}$.
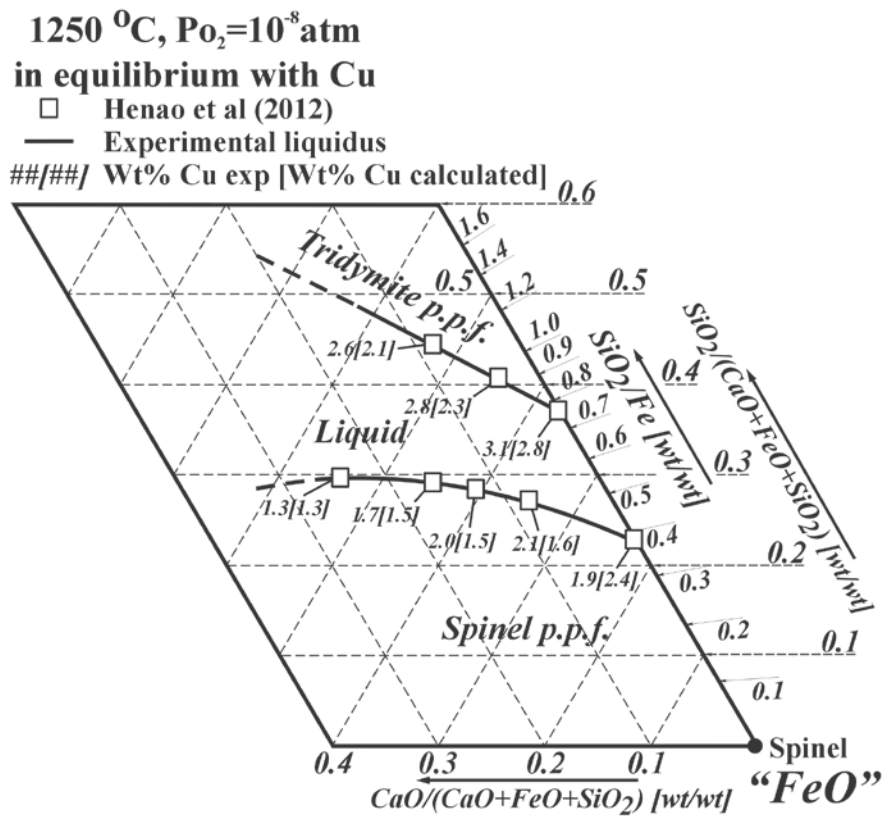

Fig. 8 Solubility of Cu in the "Cu_2O"-CaO-"FeO"-SiO_2 slag in equilibrium with metallic copper at 1250 ^{o}C at $p_{O_2} = 10^{-8}$ atm (experiments [27] were carried out in spinel and tridymite primary phase fields).

Recent experimental data on the solubility of copper in the $CaO\text{-}FeO\text{-}Fe_2O_3\text{-}SiO_2$ slag system in equilibrium with metallic copper at oxygen partial pressure of 10^{-8} atm along the spinel and tridymite liquidus have been provided by Henao et al [27]. The experimental and calculated copper concentrations at the given $CaO\text{-}\text{"}FeO\text{"}\text{-}SiO_2$ fractions are provided in Fig. 8. The experimental data and calculation results show the same trend; copper solubility in the spinel- and tridymite-saturated slag decreases with increasing CaO concentration. The copper solubility in the $CaO\text{-}\text{"}FeO\text{"}\text{-}SiO_2$ slag at $1250\ ^oC$ at $p_{0_2}=10^{-8}$ atm is reproduced by the model within $\pm\ 0.5$ wt pct from the experiments.

Data on the multi-component system $\text{"}Cu_2O\text{"}\text{-}Al_2O_3\text{-}CaO\text{-}FeO\text{-}Fe_2O_3\text{-}MgO\text{-}SiO_2$, important for the copper production process, can be used to verify the consistency of the current database. The experimental data reported by Henao et al [28] in the $\text{"}Cu_2O\text{"}\text{-}Al_2O_3\text{-}CaO\text{-}\text{"}FeO\text{"}\text{-}MgO\text{-}SiO_2$ system in equilibrium with metallic copper at fixed oxygen partial pressure of $10^{-8.5}$ atm have been used for this purpose. It can be seen in Fig. 9 and Fig. 10 that the trends of the copper solubility as a function of temperature at given compositions of $Al_2O_3\text{-}CaO\text{-}\text{"}FeO\text{"}\text{-}MgO\text{-}SiO_2$ can be reproduced reasonably.

All predictions are consistent with all available experimental information. The typical scatter of experimental data and the accuracy of model calculations are within experimental error limits for most of the data points. The thermodynamic database that has been developed makes it possible to calculate any other phase diagram sections including regions of composition and temperature where no experimental data are available. All of these sub-systems are currently being further revised to produce the final self-consistent set of thermodynamic parameters.
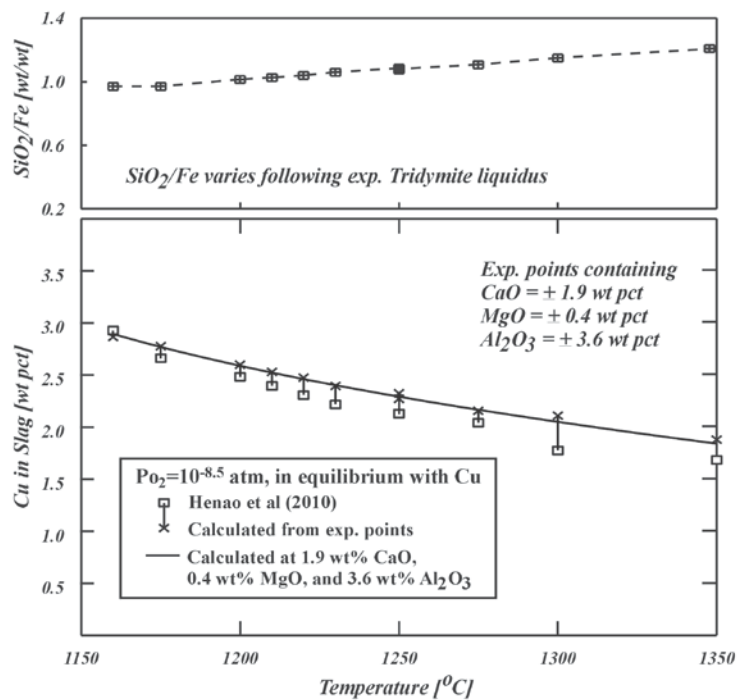

Fig. 9 Solubility of Cu in the $\text{"}Cu_2O\text{"}\text{-}Al_2O_3\text{-}CaO\text{-}\text{"}FeO\text{"}\text{-}MgO\text{-}SiO_2$ slag in equilibrium with metallic copper at $p_{0_2} = 10^{-8.5}$ atm (experiments [28] were carried out in tridymite primary phase field at $\pm\ 1.9$ wt pct CaO, $\pm\ 0.4$ wt pct MgO, and $\pm$
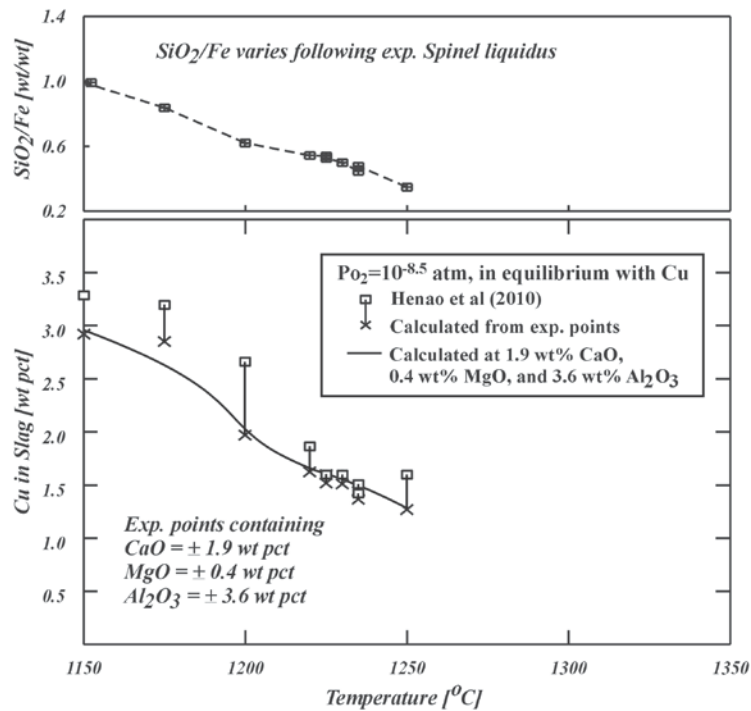
3.6 wt pct Al_2O_3).

Fig. 10 Solubility of Cu in the "Cu_2O"-Al_2O_3-CaO-"FeO"-MgO-SiO_2 slag in equilibrium with metallic copper at p_{O_2} = $10^{-8.5}$ atm (experiments [28] were carried out in spinel primary phase field at $\pm$ 1.9 wt pct CaO, $\pm$ 0.4 wt pct MgO, and $\pm$ 3.6 wt pct Al_2O_3).

5. Industrial Application

With the depleting availability of clean concentrate resources, operations are moving generally to slag systems containing more impurities, such as MgO, CaO and Al_2O_3. The effects of these elements on slag phase equilibria are complex, hence their potential problems toward increasing operational costs associated with the amount of flux required and copper loss into the slag are not well characterized. By having a thermodynamic database of the relevant slag system it is now possible to have a good estimation on the effects of impurities toward the consumption of flux and copper loss during the process. An example of such analysis is given below.

The spinel/wustite and tridymite liquidus, and the O_2 isobars are predicted in the "Cu_2O"-FeO-Fe_2O_3- SiO_2 system at 1275 ^oC over a range of compositions as shown in Fig. 11. The effects of addition of 0.4 wt pct MgO, 1.9 wt pct CaO, and 3.6 wt pct Al_2O_3 on the liquidus and O_2 isobars are also provided in the figure. According to the predictions, the addition of the MgO, CaO and Al_2O_3 into the Cu-Fe-O-Si slag system results in the shift of the fully liquid area towards higher SiO_2 concentration. This means that if the operation was carried out in the spinel primary phase field appropriate adjustments to the SiO_2/Fe ratio in the slag and corresponding SiO_2 flux additions have to be introduced to avoid excessive solids formation and buildups. Fig. 11 also indicates differences in the positions of O_2 isobars between

impurities-free and impurities-containing slag system. With the presence of 0.4 wt pct MgO, 1.9 wt pct CaO, and 3.6 wt pct Al_2O_3 in the slag, the O_2 isobars slightly shift toward higher Cu_2O concentration.
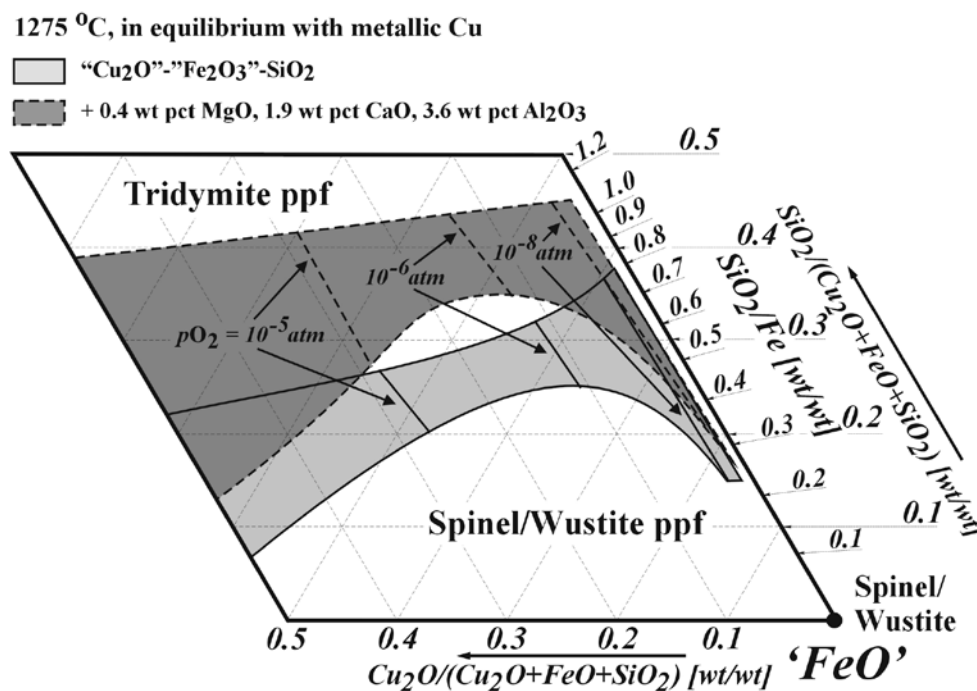

Fig. 11 The effect of impurities on the Cu-Fe-O-Si slag in equilibrium with metallic copper at 1275 ^oC.

These results provide an important basis for trend analysis of slag behavior for a copper smelting/converting slag to assist with the selection of fluxing and prediction of copper loss in the slag. Later, the new thermodynamic database can also be used to predict partitioning of major and minor elements between phases, activities, vapor pressure, and other thermodynamic properties over a wide range of process conditions in copper production.

There is a general tendency to simplify the representation of the phase equilibria data, such as into rectangular compositional coordinates for both axes with different basis such as Fe/SiO_2 ratio, CaO/SiO_2 ratio, etc. Although the simplified representation is a convenient way to indicate fluxing or other industrial parameters, it results in a loss of scientific information that would be present if the data were presented in the Gibbs triangle diagrams. For example, in the graph with the rectangular compositional coordinates the "lever rule" cannot be applied and the solidification/crystallization path of a given slag composition cannot be tracked.

6.   Conclusions

Preliminary thermodynamic optimizations of liquid slag "Cu_2O"-Al_2O_3-CaO-FeO-Fe_2O_3-MgO-SiO_2 at conditions of equilibrium with metallic copper has been carried out. The previously available data and new experimental data on the system were critically evaluated and used to obtain a self-consistent set of model parameters for all binary, ternary and higher order sub-systems. The Modified Quasi-chemical and Bragg-Williams models were used to describe the Gibbs free energy of liquid slag as functions of temperature and composition. The model reproduces all experimental data within experimental error limits and permit good estimations of the thermodynamic properties of multi-component solution to be

made. Industrial application of the database for the copper metallurgical process presented in the paper demonstrates an example of approach to the use of this powerful thermodynamic modeling tool.

Acknowledgements

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