Integrated Experimental and Thermodynamic Modeling Study of the Effects of Al_2O_3 , CaO , and MgO on Slag–Matte Equilibria in the $\text{Cu-Fe-O-S-Si-(Al, Ca, Mg)}$ System

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Abstract Al_2O_3 , CaO , and MgO are present as impurities in fayalite-based copper smelting systems. A thermodynamic database has been developed to characterize the effects of these impurities on equilibria among the slag, matte, metal and gas phases, using a progressive integrated approach that combines both experimental measurements and thermodynamic modeling. The approach involves the initial assessment of the existing data, planning and undertaking new critical experiments for selected conditions and using the new data to refine the model parameters of the database. The resulting thermodynamic database is capable of predicting, with improved accuracy, the phase equilibria and the distribution of all elements between all of the phases in the $\text{Cu-Fe-O-S-Si-(Al, Ca, Mg)}$ system.

Keywords chemical equilibrium · copper smelting · $\text{Cu-Fe-O-S-Si-(Al, Ca, Mg)}$ system · experimental measurement · matte · metal · slag · thermodynamic modeling

1 Introduction

The Cu-Fe-O-S-Si system describes the principal chemical components present in copper smelting and refining systems. Understanding and accurate quantification of the sensitivity of the system to changes in composition and process variables is of major importance to the optimization of industrial operations. All of these components are distributed among gas, liquid oxide (slag), solid oxide, molten sulfide (matte) and metal phases. Providing accurate phase equilibrium information on this complex, multi-component, multi-phase system is a challenging task.

In a series of articles^[1–12] previous and recent studies of phase equilibria in the Cu-Fe-O-S-Si subsystem have been reported. Importantly, to enable the information to be assessed for accuracy and thermodynamic consistency, and used to develop a comprehensive thermodynamic database, a research methodology involving the integration of experimental studies and thermodynamic database development is used. As a result of this integrated approach, the relationships between key process variables, such as matte grade, Fe/SiO_2 in slag, partial pressure of SO_2 , temperature, copper, sulfur, oxygen concentration in slag, matte and liquid metal phases, have been established.

In industrial practice, fayalite (FeO-SiO_2) based copper smelting slags contain typically 2–5 wt.% Al_2O_3 , 1–4 wt.% CaO and 1–2 wt.% MgO .^[13] The concentrations of these impurity components can be even higher depending on the sources and complexities of the concentrate feeds to the

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smelters. The present paper summarizes the outcomes of the study undertaken to extend the thermodynamic database to describe the effects of Al_2O_3 , CaO and MgO on phase equilibria and elemental distributions between phases.

To illustrate the range of slag compositions and phase associations encountered in these systems, the predicted isothermal sections of phase diagrams in the slag systems are provided in Fig. 1, 2 and 3. The figures show the fully liquid region of fayalite slag at 1250 °C and $P(\text{O}_2) = 10^{-7.8}$ atm in the Al-Fe-O-Si, Ca-Fe-O-Si and Fe-Mg-O-Si systems. In the Al-, Ca- and Mg-free system, the extent of the liquid fayalite slag region is limited by the formation of either tridymite (SiO_2) at low Fe/ SiO_2 ratio or spinel at high Fe/ SiO_2 ratio. The maximum solubility of Al_2O_3 in slag is limited by the formation of mullite. The limits of solubility of CaO are determined by the formation of several calcium silicates. The concentration of MgO is at a maximum in equilibrium with the olivine (Mg_2SiO_4 - Fe_2SiO_4) phase.

In the presence of the matte phase, additional elements Cu and S are introduced into the system, however the primary phase fields bounding the fully liquid slag region are mostly the same as those in the copper- and sulfur-free systems because the concentrations of Cu and S in the slag are relatively small. The liquidus lines for the slag–matte equilibria in the Al-Cu-Fe-O-S-Si, Ca-Cu-Fe-O-S-Si and

Cu-Fe-Mg-O-S-Si systems were calculated using the thermodynamic database developed in the present study and projected onto the pseudo-ternary sections in Fig. 1, 2 and 3. For example, for the Al-Cu-Fe-O-S-Si system, the projection was done by taking the total amounts of Al, Fe and Si in the slag and recalculating them into the amounts of Al_2O_3 , FeO and SiO_2 as if these were the only components of the slag. The projected liquidus lines correspond to 1250 °C, 60 wt.% Cu in matte, equilibrium with a particular solid oxide phase and fixed $P(\text{SO}_2) = 0.5$ atm.

2 Phases and Thermodynamic Models

The list of stable phases in the Al-Ca-Cu-Fe-Mg-O-S-Si system and corresponding references for the thermodynamic models used in the development of the database are given in Table 1. These phases include stoichiometric compounds, solid and liquid solutions. The thermodynamic models for the liquid slag, matte and metal phases used in the database are discussed in further detail in a previous study.^[1]

Fig. 1 Calculated phase diagram of the Al-Fe-O-Si system at 1250 °C and $P(\text{O}_2) = 10^{-7.8}$ atm projected onto the Al_2O_3 -FeO- SiO_2 plane from the oxygen corner. Dashed lines show the liquidus lines for the slag–matte equilibria in the Al-Cu-Fe-O-S-Si system at 1250 °C, 60 wt.% Cu in the matte and $P(\text{SO}_2) = 0.5$ atm, which were calculated using the thermodynamic database developed in the present study and projected onto the Al_2O_3 -FeO- SiO_2 plane as explained in the text

Fig. 2 Calculated phase diagram of the Ca-Fe-O-Si system at 1250 °C and $P(\text{O}_2) = 10^{-7.8}$ atm projected onto the CaO-FeO-SiO₂ plane from the oxygen corner. Dashed lines show the liquidus lines for the slag–matte equilibria in the Ca-Cu-Fe-O-S-Si system at 1250 °C, 60 wt.% Cu in the matte and $P(\text{SO}_2) = 0.5$ atm, which were calculated using the thermodynamic database developed in the present study and projected onto the CaO-FeO-SiO₂ plane as explained in the text

Fig. 3 Calculated phase diagram of the Fe-Mg-O-Si system at 1250 °C and $P(\text{O}_2) = 10^{-7.8}$ atm projected onto the MgO-FeO-SiO₂ plane from the oxygen corner. Dashed lines show the liquidus lines for the slag–matte equilibria in the Cu-Fe-Mg-O-S-Si system at 1250 °C, 60 wt.% Cu in the matte and $P(\text{SO}_2) = 0.5$ atm, which were calculated using the thermodynamic database developed in the present study and projected onto the MgO-FeO-SiO₂ plane as explained in the text

Table 1 List of selected phases in the Al-Ca-Cu-Fe-Mg-O-S-Si system that are most important for the pyrometallurgy of copper

Phase name	Thermodynamic models and references for model parameters
Oxide phases	
Cuprous, cupric oxides	Cu_2O , CuO , stoichiometric compounds ^[14]
Quartz, Tridymite, Cristobalite	SiO_2 , stoichiometric compounds ^[15]
Rankinite	$\text{Ca}_3\text{Si}_2\text{O}_7$, stoichiometric compound ^[16]
Hartrurite	Ca_3SiO_5 , stoichiometric compound ^[16]
Akermanite	$\text{Ca}_2\text{MgSi}_2\text{O}_7$, stoichiometric compound ^[17]
Merwinite	$\text{Ca}_3\text{MgSi}_2\text{O}_8$, stoichiometric compound ^[17]
Andradite	$\text{Ca}_3\text{Fe}_2\text{Si}_3\text{O}_{12}$, stoichiometric compound ^[16]
Delafossite	CuFeO_2 , stoichiometric compound ^[18,19]
Olivine	$[\text{Fe}^{2+}, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Zn}^{2+}]^{\text{M}2}[\text{Fe}^{2+}, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Zn}^{2+}]^{\text{M}1}\text{SiO}_4$ <i>CEF</i> ^[16,17,20,21]
Calcium ferro-aluminates	$\text{Ca}(\text{Al}, \text{Fe})_2\text{O}_4$, $\text{Ca}_2(\text{Al}, \text{Fe})_2\text{O}_5$, $\text{Ca}(\text{Al}, \text{Fe})\text{O}_7$, $\text{Ca}(\text{Al}, \text{Fe})_{12}\text{O}_{19}$, <i>BW</i> ^[15,22]
Pyroxenes	$[\text{Fe}^{2+}, \text{Ca}^{2+}, \text{Mg}^{2+}]^{\text{M}2}[\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mg}^{2+}, \text{Al}^{3+}]^{\text{M}1}[\text{Fe}^{3+}, \text{Al}^{3+}, \text{Si}^{4+}]^{\text{B}}\text{Si}^{\text{A}}\text{O}_6$, <i>CEF</i> ^[16,17,21]
Wollastonites	$(\text{Ca}^{2+}, \text{Fe}^{2+}, \text{Mg}^{2+})\text{SiO}_3$, <i>BW</i> ^[16,17]
Dicalcium silicates	$(\text{Ca}^{2+}, \text{Fe}^{2+}, \text{Mg}^{2+})_2\text{SiO}_4$, <i>BW</i> ^[16,17]
Mullite	$[\text{Al}^{3+}, \text{Fe}^{3+}]_2[\text{Al}^{3+}, \text{Si}^{4+}, \text{Fe}^{3+}][\text{O}^{2-}, \text{Vacancy}]_5$, <i>CEF</i>
Corundum	$(\text{FeO}_{1.5}, \text{AlO}_{1.5})$, <i>BW</i> ^[23,24]
Melilite	$[\text{Ca}^{2+}]_2[\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al}^{3+}][\text{Fe}^{3+}, \text{Al}^{3+}, \text{Si}^{4+}]_2\text{O}_7$, <i>CEF</i> ^[15,16]
Spinel	$[\text{Cu}^{2+}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al}^{3+}, \text{Mg}^{2+}, \text{Zn}^{2+}]^{\text{tet}}[\text{Cu}^{2+}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al}^{3+}, \text{Ca}^{2+}, \text{Mg}^{2+}, \text{Zn}^{2+}, \text{Vacancy}]_2^{\text{oct}}\text{O}_4$, <i>CEF</i> ^[18,23–26]
Monoxide	$(\text{CaO}, \text{MgO}, \text{FeO}, \text{FeO}_{1.5}, \text{AlO}_{1.5}, \text{CuO})$, <i>BW</i> ^[17,18,23,26]
Liquid oxide (Slag)	$(\text{Cu}^{1+}, \text{Fe}^{2+}, \text{Fe}^{3+}, \text{Si}^{4+}, \text{Al}^{3+}, \text{Ca}^{2+}, \text{Mg}^{2+})(\text{O}^{2-}, \text{S}^{2-})$, <i>MQMPA</i> ^[1,15–17,19–21,24–27]
Sulfide phases	
Liquid matte/metal	$(\text{Fe}^{\text{II}}, \text{Fe}^{\text{III}}, \text{Cu}^{\text{I}}, \text{Cu}^{\text{II}}, \text{O}^{\text{II}}, \text{S}^{\text{II}})$, <i>MQMPA</i> ^[14,18,23,28–32]
Pyrrhotite	$(\text{Fe}, \text{Cu}, \text{Vacancy})\text{S}$, <i>BW</i> ^[28,30]
Digenite-bornite	$(\text{Cu}_2, \text{Fe}, \text{Vacancy})\text{S}$, <i>BW</i> ^[29]
Intermediate solid sulfide solution	$(\text{Cu}_2, \text{Fe}, \text{Vacancy})\text{S}$, <i>BW</i> ^[29]
Metallic phases	
fcc–Cu and fcc–Fe	$(\text{Fe}, \text{Cu}, \text{O}, \text{S})$, <i>BW</i> ^[14,18,23]
bcc–Fe	$(\text{Fe}, \text{Cu}, \text{O}, \text{S})$, <i>BW</i> ^[23]
Sulfate phases	
FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CuSO_4 , Cu_2SO_4 , $\text{CuO}\cdot\text{CuSO}_4$	Stoichiometric compounds ^[14,31,32]

BW Bragg–Williams model, *CEF* compound energy formalism, *MQMPA* modified quasichemical model in the quadruplet approximation, *MQMPA* modified quasichemical model in the pair approximation

3 Development of the Thermodynamic Database

3.1 Methodology

The approach used to extend the database has been presented in detail by the authors in previous publications.^[3,33]

In brief, this involves

1. An initial thermodynamic assessment and critical review of the available experimentally determined

data using (if available) or developing a preliminary thermodynamic database.

2. Identification of the critical data that are necessary to improve the database description of the system, to provide missing information or to resolve discrepancies in previous data.
3. Planning and undertaking selected targeted experiments in low order and higher order subsystems under controlled process conditions using an advanced

experimental methodology based on phase composition measurements by microanalysis techniques.

4. Reoptimizing the model parameters of the database using the new data.
5. Testing the predictions, planning and undertaking new experimental measurements to improve the description, if needed, or to further extend the database.

3.2 Initial Thermodynamic Assessment

In the thermodynamic assessment, which sometimes referred to as the thermodynamic optimization, physically realistic mathematical models for the Gibbs energies of all phases are developed. Model parameters are obtained in a procedure of critical evaluation of all relevant thermodynamic and phase equilibrium data. This includes data on low temperature and high temperature heat capacity measurements, enthalpies of mixing, activity measurements by EMF and gas equilibration techniques, liquidus data obtained by equilibration/quenching and other methods, cation occupancies of crystal sublattices for solid phases, distributions of elements between phases, $\text{Fe}^{2+}/\text{Fe}^{3+}$ determined by wet-chemical analysis, etc.

A thermodynamic assessment of a multi-component chemical system involves undertaking thermodynamic optimizations of all subsystems. All subsystems of the 5-component Cu-Fe-O-S-Si system have been assessed and the results have been published for the following subsystems: Fe-O,^[23] Cu-S, Fe-S, Cu-Fe-S,^[28–30] Cu-O and Cu-O-S,^[14] Cu-Fe-O,^[18] Fe-O-S,^[31] Cu-Fe-O-S,^[32] Cu-O-Si,^[27] Fe-O-Si,^[20] Cu-Fe-O-Si,^[19] Fe-O-S-Si and Cu-Fe-O-S-Si.^[1] Furthermore, the Al_2O_3 -, MgO- and CaO-containing subsystems were assessed in the following studies: Al-Fe-O,^[24] Al-O-Si,^[15] Al-Fe-O-Si,^[34,35] Al-Cu-O and Al-Cu-O-Si,^[36] Fe-Mg-O,^[26] Mg-O-Si,^[37] Fe-Mg-O-Si,^[21] Cu-Mg-O and Cu-Mg-O-Si,^[36] Ca-Fe-O,^[22] Ca-Fe-O-Si,^[16] Ca-Cu-O and Ca-Cu-O-Si,^[27] Ca-Cu-Fe-O.^[36] The remaining oxide subsystems were taken from the FactSage FToxid database.^[38–40] As a result, a preliminary thermodynamic database was developed, which is capable of predicting the high-temperature chemical and phase equilibria in the Al-Ca-Cu-Fe-Mg-O-S-Si system of 8 components. The merging of sub-systems into the larger database is possible due to the flexibility and expandable structure of the solution models in the FactSage software.^[38]

In the present study two separate liquid solution models were used, one for the slag and one for the matte/metal phases. The relationship between the copper and sulfur solubility in slag was explained using the ionic slag theory and the concepts of the first-nearest-neighbor (FNN) and second-nearest-neighbor (SNN) short-range ordering.^[1]

The solubilities of Al, Ca and Mg in the liquid matte/metal under conditions of interest for the present study are very small and have not therefore been taken into account in the present assessment. However, the solubilities of these components in the spinel phase have significant impacts on the phase equilibria and were taken into account in the database development.

3.3 Previous Experimental Studies

A review of the literature revealed that only limited data were available on the effects of Al_2O_3 , CaO, and MgO on the equilibria between fayalite-based slags and copper mattes. The results for the Al_2O_3 - and CaO-containing systems were obtained in equilibrium with copper metal, i.e. at very low $P(\text{SO}_2)$.^[41,42] Data are available^[43] for slag-metal equilibria in the S-free system Al-Cu-Fe-O-Si. The concentrations of MgO and the Fe/SiO₂ ratios in slag were not fixed at constant values in the previous studies,^[5,9,12,44,45] making it difficult to establish the trends in behaviour associated with these variables.

All experimental results describing both the experimental data and predicted trends using the database that has been developed in the course of this study are presented in Fig. 4, 5, 6, 7, 8, and 9 on a series of two-dimensional plots as a function of wt.% of Cu in matte, i.e. matte grade. The plots have been used to enable systematic analysis and critical review of previous and new experimental data, and to evaluate the agreement between predictions with the developed database and the experimental data.

3.4 New Experiments Undertaken in the Present Study

Following the critical analysis of the previously existing data, new experiments were designed and undertaken to provide measurements of phase equilibria at selected conditions; both closed and open system techniques have been used. These experiments involve the equilibration of samples at fixed temperature and process conditions, rapid quenching to room temperature and electron probe X-ray microanalysis (EPMA) to measure the compositions of all the condensed phases.^[46] The microanalysis techniques enable the concentrations of chemically dissolved species in each of the phases to be accurately determined, and potential uncertainties and errors associated with the entrainment of second phase droplets eliminated.

According to the Gibbs phase rule, the number of degrees of freedom, F , is given by the equation $F = m + 2 - n$, where m is the number of components in the chemical system and n is the number of phases in thermodynamic equilibrium. For the Cu-Fe-O-S-Si-X (X = Al, Ca or Mg) system, $m = 6$. If all degrees of

Fig. 4 Slag–matte–metal (liquid Cu–Fe alloy or gamma-iron)—tridymite (SiO_2) equilibria in the Al–Cu–Fe–O–S–Si system at 1200 °C, total pressure of 1 atm and fixed wt.% Al_2O_3 in the slag.

Symbols are experimental data^[41,54,55]; lines are calculated using the database developed in the present study

Fig. 5 Slag-matte-tridymite (SiO_2) and slag-matte-spinel equilibria in the Al-Cu-Fe-O-S-Si system at 1200 °C, total pressure of 1 atm, $P(\text{SO}_2) = 0.25$ atm and fixed wt.% Al_2O_3 in the slag. Symbols are

experimental data^[5,9,47,49]: squares represent equilibrium with spinel and circles equilibrium with tridymite. Lines are calculated using the database developed in the present study

Fig. 6 Slag–matte–metal (liquid Cu–Fe alloy or gamma-iron)—tridymite (SiO_2) equilibria in the Ca–Cu–Fe–O–S–Si system at 1200 °C, total pressure of 1 atm and fixed wt.% CaO in the slag.

Symbols are experimental data^[41,54–56]; lines are calculated using the database developed in the present study

Fig. 7 Slag–matte–tridymite (SiO₂) and slag–matte–spinel equilibria in the Ca–Cu–Fe–O–S–Si system at 1200 °C, total pressure of 1 atm, $P(\text{SO}_2) = 0.25$ atm and fixed wt.% CaO in the slag. Symbols are

experimental data^[5,9,47,48]: squares represent equilibrium with spinel and circles equilibrium with tridymite. Lines are calculated using the database developed in the present study

Fig. 8 Slag–matte–tridymite (SiO_2) and slag–matte–spinel equilibria in the Cu–Fe–Mg–O–S–Si system at 1200 °C, total pressure of 1 atm, $P(\text{SO}_2) = 0.25$ atm and fixed wt.% MgO in the slag. Symbols are experimental data^[5,9,12,44,45]; squares represent equilibrium with

spinell and circles equilibrium with tridymite. Lines are calculated using the database developed in the present study. Dashed lines and crosses correspond to the results of Takeda^[44,45] on slag–matte equilibria in MgO crucibles at 1300 °C and $P(\text{SO}_2) = 0.1$ atm

Fig. 9 Slag-matte-tridymite (SiO₂) and slag-matte-spinel equilibria in the Al-Ca-Cu-Fe-Mg-O-S-Si system at 1200 °C, total pressure of 1 atm, $P(SO_2) = 0.25$ atm and 4.5 wt.% Al₂O₃, 2.5 wt.% CaO and

0.9 wt.% MgO in the slag. Circles are experimental data^[50] for equilibrium with tridymite. Lines are calculated using the database developed in the present study

freedom are fixed and $F = 0$, each phase in equilibrium has a fixed composition. The following degrees of freedom are normally fixed when this system is studied experimentally.^[1] (1) Temperature, which is usually selected in the range from 1200 to 1300 °C and kept constant. (2) Total pressure of 1 atm. (3) Presence of the slag phase. (4) Presence of the matte phase. (5) Presence of a solid oxide phase, e.g. tridymite or spinel, which indirectly determines the Fe/SiO₂ ratio in the slag; alternatively, the Fe/SiO₂ ratio itself can be fixed to eliminate one degree of freedom. (6) Fixed partial pressure of SO₂, which is normally done by equilibration of condensed phases with a flow of gas, or by presence of the metal phase, which corresponds to the lowest possible value of $P(\text{SO}_2)$. (7) Fixed wt.% of Al₂O₃, CaO or MgO in the slag; the concentrations of the Al₂O₃, CaO and MgO in the slag are normally measured after the experiment, because the slag composition changes during the equilibration, hence, target concentrations are set approximately in the initial mixture. (8) If the last degree of freedom is varied in a series of experiments, all other measurable variables such as compositions of phases or equilibrium chemical potentials can be presented as lines on two-dimensional plots. For example, the Cu₂S/FeS ratio in the initial mixture is often varied in experiments, resulting in the variation of the measured wt.% of Cu in the matte phase, which is often called the matte grade; all other equilibrium quantities can then be plotted as functions of matte grade. Alternatively, equilibrium oxygen partial pressure can be the last variable degree of freedom, which is controlled in experiments by equilibrating condensed phases with a gas flow of certain composition. All other variables can then be plotted as functions of $P(\text{O}_2)$, or still as functions of matte grade if it was measured. It should be noted that when calculating the number of degrees of freedom, the gas phase should not be normally counted as an equilibrium phase even if $P(\text{SO}_2)$ or $P(\text{O}_2)$ are fixed in the experiments by equilibration with a gas flow. This is because the gas phase in the Cu-Fe-O-S-Si-X system cannot be stable if the sum of partial pressures of all gaseous species formed by these components is less than the total pressure of 1 atm. For the gas phase to be stable, an additional component such as Ar has to be added to the system, so an additional component and an additional phase cancel out, leaving the value of F unchanged.

The results of the new experiments identified and undertaken in the course of the present study.^[12,47–50] are discussed in the following sections and plotted in Fig. 4, 5, 6, 7, 8, and 9 using matte grade as an X-axis.

3.5 Optimization of Model Parameters and Agreement

Having used the preliminary database to select the conditions for the new experimental studies, the results of the previous and new experimental measurements were then used together to improve the thermodynamic description of the system; this involved introducing new model parameters to take into account the presence of the Al₂O₃, CaO and MgO in slag and their interaction with sulfur. The improved database utilizes all existing model parameters for the slag, matte and solid phases shown in Table 1, which were taken from the previous studies. To obtain an improved description of the system, only a limited number of additional sulfur-related model parameters for the slag phase were introduced in the present study, which are shown in Table 2. The selected Gibbs energies of the sulfide end-members of the slag solution, $g_{\text{Al}_2\text{S}_3}^{\circ}$, g_{CaS}° , g_{MgS}° , are consistent with the model by Kang and Pelton.^[51] In the present slag model, default values of the second-nearest-neighbor coordination numbers,^[52] Z , were used for sulfide and oxysulfide systems, which are consistent with the ones for oxide systems. In particular, this means that the SNN coordination numbers of O²⁻ and S²⁻ anions are the same, and the SNN coordination numbers of cations are independent of composition in all oxide, sulfide and oxysulfide binary subsystems, except for the Cu₂O-FeO, Cu₂O-SiO₂ and Fe₂O₃-SiO₂ binaries (see Table 2). The resulting database correctly predicted all the trends discussed in the following subsections. Three new parameters, $g_{\text{Si}^{4+}\text{Al}^{3+}/\text{O}^{2-}\text{O}^{2-}(\text{S}^{2-})}^{001}$, $g_{\text{Si}^{4+}\text{Ca}^{2+}/\text{O}^{2-}\text{O}^{2-}(\text{S}^{2-})}^{101}$ and $g_{\text{Si}^{4+}\text{Mg}^{2+}/\text{O}^{2-}\text{O}^{2-}(\text{S}^{2-})}^{001}$, were introduced into the model of the slag phase to provide good quantitative descriptions of the previous and the new experimental data^[12,47–50] reported here. The target experimental values to optimize the model parameters were concentrations of sulfur and copper in the slag as functions of Al₂O₃, CaO or MgO concentrations.

Figure 4, 5, 6, 7, 8, and 9 show that, in general, good agreement has been achieved between the experimental data and the lines calculated using the model parameters from Table 2.

Small systematic deviations in $P(\text{O}_2)$ are observed between the calculated lines and the experimental results (Fig. 5a, 7a, 8a). The origin of the differences lies in the description of the Cu-Fe-O-S-Si system and the reasons for these differences were discussed earlier.^[1] In the Cu-Fe-O-S-Si system, the sulfur and copper concentrations of slag (Fig. 5i and j) in equilibrium with spinel are slightly underestimated by the model; the sulfur concentration in

Table 2 Model parameters for the slag phase optimized in the present study ^(*)

Parameter	Temperature range (K)	Molar Gibbs energy $g(T)$, J mol ⁻¹	Coordination numbers
$g_{\text{Al}_2\text{Si}_3}^0$ [51]	298.15–1369	$-468,294.5 + 974.3860T - 158.26567\ln T$ $-4,492,584.0T^{-1} + 207526926T^{-2}$ $-32,000.066\ln T$	$Z_{\text{Al}^{3+}\text{Al}^{3+}/\text{O}^{2-}\text{O}^{2-}} = Z_{\text{Al}^{3+}\text{Al}^{3+}/\text{S}^{2-}\text{S}^{2-}} = 2.06617$ $Z_{\text{Ca}^{2+}\text{Ca}^{2+}/\text{O}^{2-}\text{O}^{2-}} = Z_{\text{Ca}^{2+}\text{Ca}^{2+}/\text{S}^{2-}\text{S}^{2-}} = 1.37744$
g_{CaS}^0 [51]	1369–3000	$-671,755.2 + 942.0188T - 156.9007\ln T$	$Z_{\text{Mg}^{2+}\text{Mg}^{2+}/\text{O}^{2-}\text{O}^{2-}} = Z_{\text{Mg}^{2+}\text{Mg}^{2+}/\text{S}^{2-}\text{S}^{2-}} = 1.37744$
g_{MgS}^0 [51]	298.15–3000	$-483,802.2 + 407.5469T - 66.94407\ln T$	$Z_{\text{O}^{2-}} = Z_{\text{AB/XY}} = 1.37744$
$g_{\text{Si}^{4+}\text{Al}^{3+}/\text{O}^{2-}\text{O}^{2-}}^{001}$	298.15–3000	$-361,193.0 + 417.6288T - 66.94407\ln T$	where A and B are Fe^{2+} , Fe^{3+} , Si^{4+} , Cu^{1+} , Al^{3+} , Ca^{2+} , Mg^{2+}
$g_{\text{Si}^{4+}\text{Ca}^{2+}/\text{O}^{2-}\text{O}^{2-}}^{101}$		104,600	X and Y are O^{2-} , S^{2-}
$g_{\text{Si}^{4+}\text{Mg}^{2+}/\text{O}^{2-}\text{O}^{2-}}^{001}$		188,280	Default values are used for $Z_{\text{AB/XX}}^A$ and $Z_{\text{AB/XY}}^A$ [52]
		125,520	except $Z_{\text{Fe}^{3+}\text{Si}^{4+}/\text{O}^{2-}\text{O}^{2-}}^{\text{Fe}^{3+}} = Z_{\text{Cu}^{1+}\text{Fe}^{2+}/\text{O}^{2-}\text{O}^{2-}}^{\text{Cu}^{1+}} = Z_{\text{Cu}^{1+}\text{Si}^{4+}/\text{O}^{2-}\text{O}^{2-}}^{\text{Cu}^{1+}} = 1.37744$
			$\zeta_{\text{Al}^{3+}\text{S}^{2-}} = \zeta_{\text{Al}^{3+}\text{O}^{2-}} = 1.653$
			$\zeta_{\text{Ca}^{2+}\text{S}^{2-}} = \zeta_{\text{Ca}^{2+}\text{O}^{2-}} = 1.377$
			$\zeta_{\text{Mg}^{2+}\text{S}^{2-}} = \zeta_{\text{Mg}^{2+}\text{O}^{2-}} = 1.377$

Parameter notations are available in Ref 52, Eq. (45). ζ_{AX} , the ratio of first-nearest-neighbor to second-nearest-neighbor coordination numbers, is defined by Eq. (2.22) in Ref 53

matte is also lower by 1–2 wt.% (Fig. 5e). These small discrepancies may originate from the description of slag and matte by two separate solution models. The need for this is discussed in more detail in the previous article.^[1] In reality, the mutual solubility between matte and slag drastically increases at high Fe/SiO₂ ratios and low matte grade. Eventually, these two phases form one oxysulfide liquid, which cannot be described by the models used in the present study.

Brief discussions of the trends and agreement of the developed database with previous and new experimental results for each system are given below in the corresponding subsections.

3.5.1 Effects of Al₂O₃

The experimental data available on the slag–matte–metal (liquid Cu–Fe alloy or gamma-iron)—tridymite (SiO₂) equilibria in the Al–Cu–Fe–O–S–Si system at 1200 °C with no alumina present^[41,54,55] or at 8 wt.% Al₂O₃ in the slag^[41] are shown in Fig. 4(g–j). As can be seen from Fig. 4(a) and (b), the addition of Al₂O₃ to the slag causes only minor changes in equilibrium $P(\text{O}_2)$ and $P(\text{S}_2)$. As to be expected, the dissolution of Al₂O₃ in the slag decreases the Fe/SiO₂ ratio (Fig. 4g). Hence, the solubility of sulfur (Fig. 4i) and copper (Fig. 4j) in the slag also decreases.

The experimental data^[47,49] showing the effect of the alumina concentration in the slag on the slag–matte–tridymite or slag–matte–spinel equilibria at $P(\text{SO}_2) = 0.25$ atm and 1200 °C are plotted in Fig. 5. Again, the most significant effect of the alumina additions to the slag is the decrease of the Fe, S and Cu contents of the slag.

3.5.2 Effects of CaO

The experimental data^[41,54–56] on the slag–matte–metal (liquid Cu–Fe alloy or gamma-iron)—tridymite (SiO₂) equilibria in the Ca–Cu–Fe–O–S–Si system at 1200 °C with no CaO present and at several fixed concentrations of CaO in the slag are shown in Fig. 6(g–j). Some scatter of the experimental data is evident from the figures. Similarly to alumina, the most significant effect of CaO dissolution in the slag is the decrease of the Fe, S and Cu contents of the slag, which is well reproduced by the developed database.

The same effect of CaO additions to the slag can be seen in Fig. 7, which shows the experimental data for the slag–matte–tridymite and slag–matte–spinel equilibria at $P(\text{SO}_2) = 0.25$ atm and 1200 °C.^[5,9,47,48]

Fig. 10 The boundaries of the liquid slag region for the slag–matte equilibria in the X–Cu–Fe–O–S–Si system at 1250 °C, 1 atm total pressure, $P(\text{SO}_2) = 0.5$ atm, and at 60 wt.% Cu in the matte, where X is Al, Ca or Mg. The calculated lines correspond to the matte in equilibrium with the slag and one more solid phase as indicated in the figures

3.5.3 Effects of MgO

The effects of MgO on the phase equilibria and distribution of elements between slag and matte are shown in Fig. 8, including the experimental data obtained in recent studies^[12,47] for equilibria with tridymite and spinel at 1200 °C, 1 atm total pressure, $P(\text{SO}_2) = 0.25$ atm and fixed wt.% MgO in the slag. The addition of MgO to the slag has a minor effect on $P(\text{O}_2)$ (Fig. 8a) and Fe, O and S in the matte (Fig. 8c–e). Similar to CaO, the addition of MgO decreases Fe/SiO_2 (Fig. 8g), FeO (Fig. 8h), S (Fig. 8i) and Cu (Fig. 8j) in the slag, but the magnitude of this effect is limited by the low maximum solubility of MgO in these slags (Fig. 8k) due to the formation of the olivine phase (Mg_2SiO_4 – Fe_2SiO_4 solid solution).

Figure 8 also contains the data of Takeda^[44,45] obtained at 1300 °C and $P(\text{SO}_2) = 0.1$ atm in MgO crucibles; the reported amounts of MgO in the slag at this temperature, 6–9 wt.% MgO (Fig. 8k), are significantly greater than at 1200 °C. The slag could not be in equilibrium with MgO in the experiments of Takeda and it is not certain that equilibrium with silica was achieved. In the present study, the lines corresponding to Takeda’s data were calculated to reproduce the reported values of the Fe/SiO_2 ratio and MgO content in the slag by fitting the data in Fig. 8(g) and (k). Clearly, the dissolution of MgO in the slag suppresses the solubility of Fe, S and Cu in the slag both at 1300 °C and 1200 °C. Takeda employed in situ measurements of $P(\text{O}_2)$, using immersed oxygen sensors. As can be seen

from Fig. 8(a), the $P(\text{O}_2)$ calculated in the present study is in good agreement with these data.

3.5.4 Combined Effects of Al_2O_3 , CaO , and MgO

The combined effects of Al_2O_3 , CaO and MgO on phase equilibria were measured by Fallah Mehrjardi et al.^[50] In the present study, one slag model parameter was optimized for each of these oxides to reproduce its effects separately. As can be seen from Fig. 9, the resulting database predicts the combined effects of Al_2O_3 , CaO and MgO without the need to introduce any additional model parameters.

4 Model Predictions

4.1 Effects of Al_2O_3 , CaO , and MgO on the Boundaries of the Liquid Slag Region for Slag–Matte Equilibria at Fixed Matte Grade

To compare the relative effects of Al_2O_3 , CaO and MgO on the slag–matte equilibria, and to demonstrate how the database developed in the present study can be used to interpolate and predict the outcomes in process conditions not previously examined experimentally, a series of calculations was undertaken along the boundaries of the liquid slag fields shown by the dashed lines in Fig. 1, 2 and 3; i.e. the calculations were made for matte in equilibrium with slag and one more solid phase, such as tridymite, spinel, mullite, α' - Ca_2SiO_4 or olivine, at 1250 °C, 1 atm total pressure, $P(\text{SO}_2) = 0.5$ atm, and at fixed matte grade of 60 wt.%. The results are shown in Fig. 10.

The additions of Al_2O_3 , CaO and MgO have very similar effects on both slag–matte–tridymite and slag–matte–spinel equilibria up to approximately 5 wt.% of each component. The most significant effect is the decrease of the Fe, S and Cu concentrations in the slag. The maximum solubilities of Al_2O_3 , CaO and MgO in the slag are limited by precipitation of the other solid phases. In particular, precipitation of olivine limits the solubility of MgO , making it substantially smaller than the solubility of CaO or Al_2O_3 .

4.2 Temperature Versus Fe/SiO₂ Fluxing Diagrams

As can be seen from the experimental data and calculated phase equilibria discussed above, minor additions of Al_2O_3 , CaO and MgO decrease the Fe/SiO₂ ratio in the slags both in equilibrium with tridymite and with spinel. The calculated temperature versus Fe/SiO₂ fluxing diagram at $P(\text{SO}_2) = 0.5$ atm, 60 wt.% Cu in the matte and various fixed levels of Al_2O_3 , CaO and MgO in the slag is shown in Fig. 11. Clearly, the database developed in the present

Fig. 11 Slag liquidus for the slag in equilibrium with matte in the Al–Ca–Cu–Fe–Mg–O–S–Si system at 1 atm total pressure, $P(\text{SO}_2) = 0.5$ atm, 60 wt.% Cu in the matte and at various fixed levels of Al_2O_3 , CaO and MgO in the slag. For each Fe/SiO₂ ratio in the slag, the slag is fully liquid at temperatures above the liquidus lines, which were calculated using the database developed in the present study

study can be used to calculate similar diagrams for other particular conditions. Such diagrams may be useful for selecting optimal fluxing strategies during copper smelting, depending on the operating conditions and specific concentrate feeds to the smelters.

5 Summary

A systematic study has been carried out to measure and describe the effects of Al_2O_3 , CaO and MgO on the phase equilibria in the Cu–Fe–O–S–Si–(Al, Ca, Mg) system. The study has involved

1. An initial thermodynamic assessment and critical review of the available experimentally determined data using a preliminary thermodynamic database.
2. Identification of the critical data that are necessary to improve the description of the system, to provide missing information or to resolve discrepancies in previous data.
3. Planning and undertaking selected targeted experiments in low order and higher order subsystems under controlled process conditions using an advanced experimental methodology based on phase composition measurements by microanalysis techniques.
4. Reoptimizing the model parameters of the database using the new data.

The result of the integrated experimental and modeling program has been the development of a new thermodynamic database capable of accurately describing and

predicting phase equilibria among the gas, slag, matte, metal and solid phases in the Cu-Fe-O-S-Si-(Al, Ca, Mg) system.

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