



Article Influence of Slag Composition on the Distribution Behavior of Cu between Liquid Sulfide and Cu-Containing Multicomponent Slag via Thermodynamic and Kinetic Assessment

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Abstract: At present, copper smelting slag is not effectively recycled and is wasted. Copper smelting slag contains Fe_xO at more than 40 mass%. For the utilization of copper slag as a Fe resource, it is necessary to separate the Cu in the slag. For copper recycling from slag, FeS-based matte can be introduced to use sulfurization to concentrate Cu from the slag into the sulfide and finally recover the copper. In a previous paper, a kinetic model was developed to simulate the coupled reactions between the multicomponent slag and FeS-based matte by using previously reported thermodynamic data. Building on this work, we carried out equilibrium experiments to supplement the thermodynamic data used in the previously developed model. An empirical formula for the Cu₂O activity coefficient of Cu₂O-FeO_X-CaO-MgO-SiO₂-Al₂O₃ system slag was obtained. In addition, the effect of alumina content in the slag on the Cu₂O activity coefficient in the slag was investigated. The model was also supplemented to account for MgO solubility. By the developed model and the industrial conditions, we investigated the effect of slag composition on the behavior of Cu between matte and Cu₂O-FeO_X-CaO-MgO-SiO₂-Al₂O₃ system slag for the copper loss.

Keywords: copper smelting slag; Cu removal; matte; kinetics; coupled reaction model

1. Introduction

Copper is one of the most important basic metals and is used mostly for electrical wire, electric motors, roofing, and plumbing due to its superior electrical and physical properties. As an important energy source, copper can play an important role in human development and sustainable development [1]. Typically, copper is produced by smelting Cu-based sulfide ores and electrical refining processes. In general, approximately two tons of copper smelting slag, which includes approximately 2 mass% Cu oxide, is generated for every one ton of copper produced [2,3]. Moreover, the amount of generated slag increases every year because of the lack of copper ore with high Cu content [4]. However, no efficient strategy for the extraction of Cu from copper smelting slag has been established yet, and most of the slag is landfilled or used as raw material for cement and sandblasting materials [5].

Several possible methods of extracting Cu from copper smelting slag have previously been proposed, such as carbon reduction, magnetic separation, and sulfurization using FeS-based sulfides [5–7]. Since copper oxide can be reduced by reacting with the iron in the slag [8], the Cu-containing Fe resources combined with carbon resources are not appropriate for steelmaking processes. Magnetic separation of Cu and Fe is difficult because of the large amounts of fayalite (Fe₂SiO₄) present in copper slag [5]. By the sulfurization of FeS-based matte [5,7], Cu in slag can be extracted as sulfide, and the final sulfurized materials can be used as copper resources. Moreover, iron compounds in slag with very low Cu remaining can be recovered as iron resources for steel production.



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/). To investigate the distribution behavior of Cu between matte and slag, we previously developed a simulation model for the reaction between Cu-containing multicomponent slag and FeS-based matte using double-film theory [8,9]. This model is well-known as a coupled reaction model and can be used to simulate the reaction kinetics for ferrous metallurgy processes such as steelmaking, high-temperature metal pretreatment [10,11], basic oxygen furnace operation [12], secondary refining [13,14], and the recovery of Mn from steelmaking slag using the reaction between Mn-containing multicomponent slag and FeS-based matte [8].

In addition, in the case of a copper flash smelter, a model of the copper converter was developed based on the thermodynamic equilibrium by Goto [15]. Activity coefficients for the main components of FeO-SiO₂ slag and the activity coefficient equations for FeS, FeO, and Fe₃O₄ have also been reported [14,15]. Furthermore, Goto et al. provided a quantitative description of the copper smelting processes by calculating components for the Cu-Fe-Pb-Zn-O-S-N-C-H system, and a heat balance was added to predict the temperature variation of the model [16]. Then, a kinetic model was developed to cover the copper flash furnace [17] and the addition of a calculation of oxygen consumption [18,19]. Noranda's continuous-converter model was further developed by Nagamori et al. to calculate the distribution behaviors of the components between matte and slag [20–23].

Briefly, the thermodynamic data used in the developed model are as follows: the activity coefficients of FeS, CaS, and Cu₂S in the matte were used with the reported activity coefficient data [24–26]. In the case of the slag, the activity coefficients of CaO, SiO_2 , and FeO_X were calculated using the regular solution [27] and interaction parameters [8], although the activity coefficient of Cu₂O was assumed to be unity due to its low concentration in the slag. In the present study, to simulate the precise distribution of Cu between matte and multicomponent slag, the activity coefficients of Cu_2O were measured by the equilibrium relationship between molten Ag and slag with varying Al₂O₃ concentrations and high slag basicity. An empirical formula for the activity coefficient of CuO_{0.5} was derived based on regression analysis using the measured compositions of Cu₂O-FeO_X-CaO-MgO-SiO₂-Al₂O₃ slag. The activity coefficients of Cu₂O in slag without Al₂O₃, reported by Takeda and Henao [26,28,29], were also compared with the empirical formula obtained in this study. In addition, copper smelting slag generally contains alumina, and previous reports have not discussed the effect of alumina. Therefore, in this study, the relationship between the Cu oxide activity coefficient and alumina content was investigated. Furthermore, changes in the concentration of MgO dissolved in the slag were simulated by modifying the apparent mass transfer coefficient between the slag and matte during kinetic experiments because the changes in slag composition are able to affect the activity coefficients of Cu_2O . It can play an important role in exploring the specifics of e-learning [30].

As a result, the obtained thermodynamic data were applied to the model developed in this study, and the copper solubility in the slag was calculated at the equilibrium state of the reaction between slag and matte based on the developed model and the results were compared with reported experimental data. The developed model was expanded to the scale used in actual industrial processes and used to propose ways to reduce the Cu content of the slag. Based on one ton of slag, the effect of slag composition on the behavior of Cu between matte and slag was investigated to determine the overall trends.

2. Materials and Methods

Figure 1 shows the experimental setup used to measure the Cu₂O activity coefficient in multicomponent slag equilibrated with molten pure Ag. Table 1 lists the initial compositions of the slag with various ratios of FeO_X/SiO₂ at 1573 K. CaO was calcined at 1273 K for 2 h. The powders of FeO, Fe₂O₃, Cu₂O, SiO₂, Al₂O₃, CaO, and MgO were mixed to prepare the slag samples. Then, 4 g of slag and silver was charged into the MgO crucible (13.67 mm in inner diameter, 40 mm in height). The holding temperature was kept constant at 1573 K, and the atmosphere was controlled by flowing 100 mL/min of mixing gas consisting of CO (12 mL/min) and CO₂ (88 mL/min) after charging the crucible. The oxygen partial pressure was controlled to be 10^{-8} by mixing CO gas and CO₂ gas using Equations (1) and (2). After 24 h, the sample was taken out from the furnace and was water quenched simultaneously with Ar gas injection.

$$CO(g) + 1/2O_2(g) = CO_2(g), \ \Delta G^\circ = -282580 + 86.015T$$
 (1)

$$P_{O_2}^{0.5} = \left(\frac{P_{CO_2}}{P_{CO}}\right) \cdot \frac{1}{K_{(10)}}$$
(2)



Figure 1. Experimental setup.

Table 1. Initial compositions of the slag before the equilibrium experiment.

Experiment	Tomn (K)	Composition (mass%)								
Experiment	Temp (K)	FeO	Fe ₂ O ₃	Cu_2O	SiO ₂	Al_2O_3	CaO	MgO		
А	1573	42	7	2	33	5	6	5		
В		37	6	2	30	5	15	5		
С		33	5	2	25	5	25	5		
D		38	6	1	30	5	15	5		
E		38.5	6	0.5	30	5	15	5		
F		28	5	2	37	5	18	5		
G		35	6	2	28	7	17	5		
Н		35	6	2	28	13	11	5		

The slag and silver were carefully collected and separated from the quenched sample with the MgO crucible. The obtained samples were finally crushed using a ball mill. The samples of slag and silver were carefully collected. The amounts of Fe, Cu, Ca, Mg, and Al in the slag were determined by chemical analysis using ICP-AES. The concentration of SiO₂ in the slag was calculated as the remainder of the sum of the measured concentrations of oxides. The Cu and Fe content in the silver was also analyzed using the ICP-AES.

3. Results

3.1. Kinetics of MgO Solubility in Multicomponent Slag

In our previous study, the kinetic reaction between Cu-containing multicomponent slag and FeS-based matte was investigated at 1573 K. We also compared the experimental data with calculated data by using the model developed under the same conditions. The simulation results for the slag and matte were similar to the experimental results, but in the case of MgO content, there was no good agreement. The solubility of MgO from the crucible into the slag should be considered because the reaction area between the refractory and the slag is relatively large. Therefore, in the present study, the MgO solubility in the

slag was simulated using measured apparent mass transfer coefficients. The dissolution of MgO in the slag phase can be described by the following equation.

$$\frac{d(\%MgO)}{dt} = \frac{Ak}{V} \{(\%MgO)_{Sat.} - (\%MgO)\}$$
(3)

$$\alpha = \ln \frac{\left\{ (\%MgO)_{\text{Sat.}} - (\%MgO)_{\text{Init.}} \right\}}{\left\{ (\%MgO)_{\text{Sat.}} - (\%MgO) \right\}} = \frac{Ak_{\text{MgO}}}{V}t$$
(4)

In Equation (3), *A* is the interfacial area between the slag and the refractory material (m³), k_{MgO} is the mass transfer coefficient of MgO in slag (m/s), and *V* is the volume of slag (m³). In addition, (%MgO)_{Sat} and (%MgO)_{Init} show the saturated and initial MgO concentrations, respectively. A detailed description of the solubility of MgO is given in a previously published paper [8]. In Figure 2, the obtained value of Ak/V from the experiments was 0.00118, and the calculated value of α was plotted with time. The composition changes in MgO were the result obtained from the previous experiment using a kinetic reaction between the slag and FeS-based matte [9]. In Figure 2, Exp. J and K are represented in Table 2.



Figure 2. MgO content of the slag as a function of time and the calculated Ak/V value.

			Composition (mass%)								
No.	Temp (K)		Matte								
		FeO	Fe ₂ O ₃	Cu ₂ O	SiO ₂	Al_2O_3	CaO	MgO	FeS	CaS	
Ι		42	-	1	24	6	19	8	100	0	
J	1573	45	8	1	27	6	5	8	100	0	
Κ		45	8	1	27	6	5	8	90	10	

Table 2. Initial compositions of the slag and matte reported by [8].

3.2. Cu₂O Activity Coefficient Measurement Results

The activity coefficient of Cu_2O in the copper-containing multicomponent slag was calculated as follows:

$$Cu_{inAg} + 1/4O_{2(gas)} = CuO_{0.5(liquid)}$$
(5)

$$K_{(5)} = (\gamma_{CuO_{0.5}} \times X_{CuO_{0.5}}) / (a_{Cu_{inAg}} \times P_{O_2}^{1/4})$$
(6)

$$\gamma_{\rm CuO_{0.5}} = \left(K_{(5)} \times \gamma_{\rm Cu_{inAg}} \times X_{\rm Cu_{inAg}} \times P_{\rm O_2}^{1/4} \right) / X_{\rm CuO_{0.5}}$$
(7)

$$\Delta G^{\circ} = -58,800 + 19.55T \tag{8}$$

In Equation (7), the activity coefficient of Cu in Ag was obtained from previously reported experimental data [31]. The equilibrium constant was obtained from the liter-

ature [32]. The oxygen partial pressure during the experiments was kept at 10^{-8} atm by flowing a mixing gas of CO/CO₂. Table 3 shows the compositions of the slag and silver after equilibrium experiments. The content of Al₂O₃ in slag for Samples A to H was 5 mass%, and the Al₂O₃ content in slag samples G and H was 7 and 13 mass%, respectively. The CuO_{0.5} activity coefficients in the slag were calculated using Equations (5)–(8). As a result, the CuO_{0.5} activity coefficient was calculated, as shown in Table 3.

Table 3. Compositions of the slag and silver after the experiment and the calculated $CuO_{0.5}$ activity coefficients.

		Composition (mass%)									
Experiment	Temp (K)	Temp (K) Slag Silver									
		FeO _x	Cu ₂ O	SiO ₂	Al ₂ O ₃	CaO	MgO	Cu			
А		55.2	0.1	24	4.7	6	10	1.7	5.2		
В	1573	47.8	0.1	22.7	4.9	15	9.7	1.7	7.9		
С		40.7	0.1	20.2	4.8	25	9.6	1.8	10.2		
D		48.9	0.1	21.2	4.9	15	10.1	0.9	6.6		
Е		47.3	0.1	22.6	4.7	15	10.5	0.5	7.6		
F		34.2	0.1	32	4.8	18	11.2	2	8.8		
G		45.9	0.1	20.9	6.7	17	9.8	1.7	7.3		
Н		46.7	0.2	20.6	12.5	11	9.2	1.6	2.9		

Figure 3 shows the effect of the CaO/Al₂O₃ ratio on the activity coefficient of Cu₂O in the slag at 1573 K when the content of MgO, the FeO_X/SiO₂ ratio, and the oxygen partial pressure were almost constant. The Cu₂O activity coefficient in the Cu₂O-FeO_X-CaO-MgO-SiO₂-Al₂O₃ slag increased as the CaO/Al₂O₃ ratio was increased. On the other hand, when the Al₂O₃ in the initial slag reaches 13 mass% and the CaO/Al₂O₃ ratio was lower than 1, the Cu₂O activity coefficient decreased to approximately 3. This means that the copper in the slag can be removed as the content of Al₂O₃ in the slag decreases and the CaO content increases.



Figure 3. Effect of the CaO/Al₂O₃ ratio on the activity coefficient of Cu₂O in the slag at 1573 K. The content of MgO is 9–10 mass%, the ratio of FeO_X/SiO₂ is 2 to 2.3, and the oxygen partial pressure is 10^{-8} atm.

The obtained CuO_{0.5} activity coefficients in each Slag (A~H) are plotted on the reported Takeda's phase diagram [26] as shown in Figure 4. The experimental conditions reported by Takeda include a temperature and oxygen partial pressure of 1573 K and 10^{-8} – 10^{-6} , respectively. The conditions of previously reported experiments are similar to the conditions used in this study. The results of Takeda's experiments showed that most of the (CaO + MgO)/SiO₂ mass ratios were less than one. In the present study, the experimental conditions ensured that the (CaO + MgO)/SiO₂ mass ratio was higher than

one. Although general copper smelting slag has been reported to contain small amounts of alumina, Takeda's slag did not contain Al_2O_3 . However, it was confirmed that the activity coefficients calculated for Samples A–F fall almost exactly on Takeda's $CuO_{0.5}$ activity coefficient line. In the case of Samples G and H, the calculated activity coefficients were different from the reported experimental data. This means that if the content of alumina in the slag is 7 mass% or more, the activity coefficient of the copper oxide is affected. On the other hand, it was confirmed that 5 mass% Al_2O_3 in the slag does not significantly affect the activity coefficient of the copper oxide.



Figure 4. Activity coefficients obtained by the equilibrium experiment results compared with Takeda's experimental data at 1573 K and $P_{O2} = 10^{-8} - 10^{-6}$.

Figure 5 shows the relationship between the measured and empirically calculated values of the activity coefficients of $CuO_{0.5}$ using regression analysis based on the obtained activity coefficients of $CuO_{0.5}$ and slag composition for slag Samples A to H. The content of FeO_X in the slag ranges from 10 to 75 mass%, that of SiO₂ from 17.8 to 51 mass%, (CaO + MgO) from 3.5 to 40 mass%, and Al₂O₃ from 0 to 13 mass%. The empirical formula is as follows:

$$\gamma_{CuO_{0.5}} = 0.006(\% FeO_X) + 0.003(\% SiO_2) + 0.021(\% CaO + \% MgO) - 0.013(\% Al_2O_3)$$
(9)



Figure 5. Empirical formula using regression analysis.

In Figure 5, the horizontal axis is the value of log γ_{Cu2O} calculated from the obtained empirical formula, and the vertical axis is the measured activity coefficient of CuO_{0.5}. In

this figure, the calculated values using the empirical formula showed good agreement with the measured values.

Figure 6 shows the calculated value of the $CuO_{0.5}$ activity coefficient as a function of the (CaO + MgO)/SiO₂ ratio with various ratios of FeO_X/SiO_2 in the slag. The activity coefficients of most copper oxides have been reported when the FeO_X/SiO_2 ratio in the slag is lower than 1.5. Therefore, in this study, it was considered that the FeO_X ratio would rise due to the decrease in the quality of copper ore. Thus, the FeO_X/SiO_2 ratio was set to 1.5 or more. As a result, the empirical formula was separated into two ranges of FeO_X/SiO_2 ratio values, as shown in Figure 6. In the figure, the CuO_{0.5} activity coefficient also increases until the $(CaO + MgO)/SiO_2$ ratio reaches approximately 1.5. Then, the activity coefficient of $CuO_{0.5}$ became almost constant after the ratio of $(CaO + MgO)/SiO_2$ reached 1.5. The data shown in the figure confirm that when the FeO_X/SiO_2 ratio is between 0.5 and 1.5, the reported activity coefficients are similar to the empirical formula line obtained from this study. Additionally, when the ratio of FeO_X/SiO_2 is 1.5–2, the empirical formula line is similar to the values measured in this study. Therefore, by applying the empirical formula obtained in this study, the developed model can calculate reliable results even if the FeO_X/SiO_2 ratio in the initial slag reaches two. The slag systems studied by Takeda [26] and Henao [29] did not contain Al₂O₃, but copper smelting slag generally contains approximately 5 mass% Al₂O₃ [1]. Therefore, in this study, we carried out experiments by adding Al₂O₃. As a result, it was found that even if the amount of alumina contained in the slag is approximately 5 mass%, the activity coefficient of the copper oxide is not significantly affected. However, when the Al₂O₃ content reached 13 mass%, it was confirmed that the activity coefficient of the copper oxide in the slag was considerably influenced.





3.3. Simulation of Cu₂O Contents in the Multicomponent Slag by Reaction with Matte

As a result, the MgO solubility and an empirical formula for Cu_2O activity coefficient were applied to the developed model. In the present study, to increase the reliability at the laboratory scale by applying the empirical formula obtained from regression analysis, we compared the kinetic experiments and the simulation results by using the reaction model. Then, the copper solubility obtained from the developed simulation model and the currently reported copper solubility were compared with each other.

Figure 7 shows the composition changes in Cu₂O and MgO in the slag as a function of time by varying the initial composition of slag and matte at 1573 K. The initial compositions of the slag and matte are shown in Table 2 and reported in our prior works [9]. Since the values of the remaining elements, such as composition changes of Fe, Si, and Ca in matte, hardly differ from the present simulation values, the simulated composition changes in Cu₂O and MgO in the slag were precisely compared with the previously measured values. The composition changes in MgO and Cu₂O in Figure 7A–C were simulated by the conditions of I, J, and K in Table 2, respectively. The measured contents of MgO and Cu₂O

in Figure 7A–C were the previously reported results [8]. In Figure 7A, the MgO content in the slag increased from 8% to approximately 11%, and, in Figure 7B,C, the content of MgO increased to approximately 13 mass%. In Figure 7, the simulated composition changes of MgO using the present model had a good agreement with the measured values than the previous simulation results because of including the dissolution reaction of MgO to the slag phase as mentioned above. Furthermore, the measured behavior of copper in the slag was more similar to the present simulated results than the previously calculated results. Therefore, in this study, by the measurement of Cu₂O activity coefficients and the solubility of MgO in the slag, the simulation results were more precisely obtained even if the initial slag compositions varied.



Figure 7. Comparison of the composition changes in MgO and Cu₂O as a function of time for various slag composition by reacting with matte at 1573 K. The measured contents of MgO and Cu₂O in (**A–C**) were the previously reported results [8]. The composition changes in MgO and Cu₂O in (**A–C**) were simulated by the conditions of I, J, and K in Table 2, respectively.

Figure 8 shows the simulation results plotted on the reported copper solubility line in the CaO-MgO-SiO₂-FeO_X slag [26]. This copper solubility value of the equilibrium state is classified as a function of the content of Cu and Fe in the initial matte. As shown in Figure 8A, the value of the copper solubility is 50 mass% Cu and 24 mass% Fe in the initial matte. The simulated results are plotted as dots, and the simulation conditions are presented in Table 4. The furnace diameter was assumed to be approximately 800 mm, and the reaction time was set at about 3600 s to ensure that equilibrium was reached. Each simulation condition A (1–5) is plotted on the solubility value line of 0.3–1 mass% Cu content in the slag. The calculated data were in good agreement with the reported experimental data. Figure 8B shows the calculated copper value for reported experimental data when the Cu content in the initial matte was 79 mass% and that of Fe was 0.3 mass%. The results for simulation condition B (1–5) were plotted on a 2–5 mass% line of copper solubility in the slag. The figure shows that the obtained simulation results are almost identical to the reported experimental data lines. It is thus confirmed that this model can simulate Cu behavior between slag and matte at 1573 K even if the copper content in the initial matte reaches 79 mass% Cu.



Figure 8. Comparison of the CaO-MgO-SiO₂-FeO_X phase diagram with previously reported data [25] and simulation results for Cu solubility as a function of initial Cu content in the matte at 1573 K. The matte compositions in (A,B) and are 50 mass% Cu-24 mass% Fe and 79 mass% Cu-0.3 mass% Fe, respectively.

Table 4. Simulation conditions of the slag and matte as a function of the change in Fe and Cu content in the matte and slag compositions.

	Temp (K)	Composition (mass%)							
Calculation			Sla	Μ	Matte				
		FeO _X	SiO ₂	CaO	MgO	Fe	Cu		
A-1		29	31	35	5	24	50		
A-2		39	34	22	5	24	50		
A-3		50	35	10	5	24	50		
A-4		48	24	23	5	24	50		
A-5	1 5 5 0	60	25	10	5	24	50		
B-1	1573	25	36	34	5	0.3	79		
B-2		36	31	28	6	0.3	79		
B-3		40	35	20	5	0.3	79		
B-4		59	29	7	5	0.3	79		
B-5		67	30	2	1	0.3	79		

Figure 9 shows the copper content in the slag obtained by the prior and present simulations and the reported experimental data as a function of the mass ratio of matte and slag [33]. The present simulation was conducted with the addition of γ_{Cu2O} and MgO solubility using the empirical formulas in Equations (3) and (9). As shown in Table 5, the slag composition used in the simulation calculations was assumed to be the composition of a typical copper smelting slag. When the mass ratio of the matte/slag was larger than 0.2, both simulation results were similar to the reported experimental data. The results were slightly different for a matte/slag ratio of 0.1, but when the matte/slag ratio was between 0.2 and 0.3, the simulation results were consistent with the reported experimental data. As a result, it was confirmed that the Cu content of the slag decreased as the input amount of FeS was increased.



Figure 9. Simulation results and experimental data comparing the copper content of slag with a FeS input to matte at 1573 K.

Table 5. Simulation conditions of slag and matte for comparison with reported experimental data.

Calc. No. To					Slag				Matte	
	Temp (K)	Mass (g)		C	Compositi		Comp. (mass%)	Mass (a)		
		Ivias	W1855 (g)	FeO _X	Cu ₂ O	SiO ₂	Al_2O_3	CaO	MgO	FeS
С	1573	100	50	1	33	5	6	5	100	5–30

4. Discussion

Based on the developed model, the effects of the slag composition on the behavior of Cu between slag and matte were investigated via the sulfurization of 1000 kg of copper smelting slag. Figure 10A,B show the Cu content of the slag as a function of the change in the CaO/SiO₂ mass ratio in the slag at 1573 K as a function of the FeO_X/SiO₂ ratio. Table 6 shows the slag and matte compositions used for the simulations. In the graph, A, B, and C indicate the changes in the FeO_X/SiO_2 ($R_{F/S}$) ratio in the slag, respectively. The matte/slag ratio was set at 2, and the FeO_X/SiO_2 ratio was set at 1–2. The furnace diameter was assumed to be approximately 800 mm, and the reaction time was 3600 s. The mass transfer coefficient of the slag and matte in the reaction model was assumed to be 0.003 m/s. This value was calculated using the same formula previously used to calculate the mass transfer coefficient of the slag-metal system [32]. The simulation results in Figure 10A show that the Cu content decreased as the initial slag CaO/SiO_2 ratio was increased. Furthermore, Figure 10B shows that as the CaO/SiO₂ ratio and the FeO_X/SiO_2 ratio in the slag were increased, the copper content in the matte increased. The reason for this is shown in Figure 6. Figure 6 shows the $CuO_{0.5}$ activity coefficient applied to the model. This figure shows that the $CuO_{0.5}$ activity coefficient increases in the slag as the CaO/SiO₂ ratio increases. In other words, the $CuO_{0.5}$ activity coefficient was increased on the basis of Equation (10), indicating that the sulfurization reaction of Cu occurred actively at the interface. This is because, in Equation (11), as the activity coefficient of Cu oxide increases, the Cu content in the slag decreases. In addition, the copper content from the initial slag CaO/SiO_2 ratio of 1.5 to 2 is almost constant. In the empirical formula in Figure 6, the activity coefficient of $CuO_{0.5}$ is almost constant for CaO/SiO₂ ratios above 1.5. Therefore, even if the CaO/SiO_2 ratio is increased, there is no change in the copper content.

$$Cu_2O + 1/2S_2 = Cu_2S + 1/2O_2$$
(10)

$$K_{(10)} = \left(a_{Cu_2S} \times P_{O_2}^{1/2}\right) / \left(\gamma_{Cu_2O} \times X_{Cu_2O} \times P_{S_2}^{1/2}\right)$$
(11)



Figure 10. Simulation results of the copper content of the slag at 1573 K as a function of CaO/SiO₂ and FeO_X/SiO₂ ratios at 1573 K. Figures (**A**) and (**B**) show Cu content in the slag and that in the matte, respectively.

Table 6. Simulation conditions of the slag and matte as a function of the changes in the CaO/SiO₂ ratio and changes in the CaS/FeS ratio.

	Temp (K)	Slag							Matte			
Calc. No. Te		Waight (kg)		Co	mpositi		Comp. (mass%)	Waight (1.g)				
		weight (kg)	FeO _X	Cu ₂ O	SiO ₂	Al ₂ O ₃	CaO	MgO	FeS	weight (kg)		
D-1					53	1	24	5	12	5		
D-2			49	1	20	5	20	5	100	2000		
D-3			43	1	18	5	28	5				
D-4	1550	1000	40	1	16	5	33	5				
E-1	1573 1000	1000	44	1	30	5	15	5	100	2000		
E-2			38	1	25	5	26	5				
E-3			34	1	22	5	33	5				
E-4			29	1	20	5	40	5				

Our previous study focused on the possibility of removing copper from slag and the changes in the Cu concentration using a kinetic model and thermodynamic data. It was reported in that paper that of the matte the copper in the slag could be removed and concentrated to the matte through sulfurization, and a Cu₂S-enriched matte could be formed through continuous sulfurization by adding new molten copper slag. This study focused on the changes in the Cu concentration in slag as a function of changes in slag composition by combining thermodynamic data with a previously developed model. The empirical formula for the Cu₂O activity coefficients obtained from the experiments in this study was compared with the reported experimental data. This comparison showed that the empirical formula produced results almost identical to the reported data. Validated empirical formulas for Cu₂O activity coefficients and empirical formulas for previously reported MgO solubility were also applied to the model. It was found from comparisons with experimental data that the model developed in this study is more reliable than the previously developed model.

5. Conclusions

In order to simulate the behavior of Cu between FeS-CaS-based matte and multicomponent slag, the activity coefficients of Cu₂O in Cu₂O-FeO_X-CaO-MgO-SiO₂-Al₂O₃ slag were investigated by equilibrated with a molten Ag phase at 1573 K. Using the developed kinetic model and the obtained empirical equation for the activity coefficients of Cu₂O in Cu₂O-FeO_X-CaO-MgO-SiO₂-Al₂O₃ slag, the influence of slag composition on the Cu behavior between matte and multicomponent slag was investigated and the obtained results can be summarized as follows.

- A. To simulate a change in the MgO content of the slag, the apparent dissolution rate of MgO in the Cu₂O-FeO_X-CaO-MgO-SiO₂-Al₂O₃ slag under MgO saturation conditions was obtained at 1573 K. By assuming equilibrium with Ag at 1573 K, the activity coefficient of Cu₂O in the slag was obtained as a function of slag composition. The activity coefficient of Cu₂O in the slag was found to increase with the increasing CaO/Al₂O₃ ratio when the FeO_X/SiO₂ ratio in the slag was between 2.0 and 2.3. However, when the content of Al₂O₃ in the slag was less than approximately 5 mass%, the activity coefficients of Cu₂O were almost the same as those in the Cu₂O-FeO_X-CaO-MgO-SiO₂ slag. The empirical formula for the activity coefficients of Cu₂O in the Cu₂O-FeO_X-CaO-MgO-SiO₂-Al₂O₃ slag was also obtained using regression analysis and the equilibrated slag composition. Furthermore, the activity coefficients of Cu₂O in FeO_X-CaO-SiO₂ slag with/without MgO and Al₂O₃ were accurately calculated by the empirical formula for various slag compositions.
- B. By the simulation model using the apparent dissolution rate of MgO and the empirical formula for Cu₂O activity coefficients, the composition changes in Cu₂O and MgO in the Cu₂O-FeO_X-CaO-MgO-SiO₂-Al₂O₃ slag were obtained with the reaction of FeS-based matte at 1573 K. The simulated composition changes in Cu₂O and MgO in the slag was in good agreement with the measured values. In addition, the copper solubility in the FeO_X-CaO-SiO₂-MgO slag calculated by the present model with varying Cu content in the matte showed good agreement with previous experimental results. By varying the mass ratio of the slag and the matte, the simulated Cu content in the typical copper smelting slag agreed more with the measured value than with the prior simulation results. It was found that the copper content in the slag decreased as the initial mass of the liquid iron sulfide was increased.
- C. The effect of slag composition on the behavior of Cu between 1 ton of coppercontaining slag and liquid iron sulfide was investigated using the present simulation model. The Cu content in the slag decreased as the ratios of CaO/SiO₂ and FeO_X/SiO₂ in the slag were increased due to the increase in the activity coefficient of Cu₂O. On the other hand, the Cu content in the matte increased at least four times more than it decreased in the slag. To improve the sulfurization of copper in the slag, it is important to control the CaO content of the Cu-containing slag.

The simulation results produced by the present kinetic model were verified with previous experimental data obtained with various compositions of slag and matte. However, the behaviors of the nonmetallic and minor elements, such as S, O, Pb, and As, were not verified because the kinetics of those elements have not been investigated thoroughly enough yet. We will conduct further research to simulate the distribution behavior of those elements between the matte and the slag for industrial-scale processes.

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