

Article

Experimental Determination of the Effect of CaO and Al₂O₃ in Slag Systems Related to the Conversion Process of High Copper Matte Grade

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Abstract: The slags generated in the conventional copper conversion process are mainly composed of Cu₂O–Fe₂O₃–SiO₂ with CaO, Al₂O₃, and MgO compounds—in concentrations up to 10 wt %. The present work contributes to the knowledge of the conversion process, generating experimental data for the phase diagrams of the Cu₂O–Fe₂O₃–SiO₂–Al₂O₃ and Cu₂O–Fe₂O₃–SiO₂–CaO systems. The experiments were carried out in a tubular furnace at temperatures of 1150 °C and 1200 °C, under a condition of saturation with tridymite and spinel. Once the equilibrium was reached, the samples were immediately quenched in water. The phases in the samples were observed through a scanning electron microscope (SEM) and the elemental composition of the phases were analyzed by means of energy-dispersive X-ray spectroscopy (EDS) detectors. The addition of Al₂O₃ and CaO into the Cu₂O–Fe₂O₃–SiO₂ system resulted in an appreciable displacement of the liquidus lines, corresponding to an expansion of the liquid in the tridymite primary phase field. The addition of CaO and Al₂O₃ combined was evaluated on industrial slags and from samples obtained in a Peirce–Smith furnace, with increasing amounts of CaO in the flux.

Keywords: liquidus temperatures; copper converting; slag

1. Introduction

In most Chilean smelters, conversion Peirce–Smith Furnaces are loaded with high copper matte (70–75 wt % Cu) [1]. Due to the low concentration of iron in these mattes (up to 5 wt %), it is considered that separating the conversion process into two stages is neither operational nor environmentally convenient. Therefore, the process is carried out in a single stage and the generated slag is reported to contain a large proportion of solid phases and relatively high concentrations of copper (wt % Cu > 40) [2]. A high proportion of solid phases increases the apparent viscosity and creates a number of difficulties during the smelting operation.

The basic thermodynamic system to represent these slags is Cu₂O–Fe₂O₃–SiO₂. The phase diagram of this system, at the temperatures of interest (between 1150 °C and 1400 °C), was recently reported in the literature [3]. The reported phase diagram indicates an appreciable reduction of the liquid area at temperatures below 1250 °C and Cu₂O concentrations between 15 and 20 wt %. This fact explains the observed formation of solid phases during the conversion process and consequently, the reported ejection of materials from the furnace, the generation of slags with high viscosity that are difficult to remove from the furnace, and the buildup of accretions in the furnace [1].

The addition of CaO and Al₂O₃ has the potential to expand the liquid area of FeO_x–SiO₂ slag systems, as demonstrated in a number of publications [4–9]. Technical works related to industrial

operations with added CaO and Al₂O₃ are also available in the literature [10–13]. While there are indications of improvements in slag viscosity properties [14–16], systematic thermodynamic information related to the effect of CaO and Al₂O₃ in the Cu₂O–FeO_x–SiO₂ system is at the moment not reported in the literature.

In the present work, the effect of Al₂O₃ and CaO on the Cu₂O–Fe₂O₃–SiO₂ system has been systematically studied via laboratory smelting conversion conditions. The experimental results were the base for industrial tests in a Peirce–Smith converter.

The analysis of the obtained laboratory experiments and industrial tests is the topic of the present publication.

2. Materials and Methods

2.1. Experimental Method

The experimental work was carried out at three different levels:

1. Equilibrium of synthetic slag/copper with CaO or Al₂O₃ addition
2. Equilibrium of industrial slag/blister copper with addition of CaO
3. Industrial smelting tests with addition of CaO and Al₂O₃

The experiments of level 1 were carried out according to the experimental procedures described in previous work [3,17]. The starting mixtures for the experiments with synthetic slags were made from Al₂O₃, CaO, and SiO₂ powders with 99.9 wt % purity and Cu₂O, Fe₂O₃, and Cu powders with 99.0 wt % purity. Approximately 1.0 g of sample was weighted, mixed in an agate mortar and pestle, pelletized, and finally placed in a silica or iron oxide substrate, depending on whether the experiments were to be performed in the tridymite or spinel primary phase field, respectively. The experiments were conducted in a vertical reaction alumina tube (30 mm i.d.) with electrically heated furnaces and the sample was placed at the target temperature for six hours, as shown in Figure 1. The furnace temperature was controlled by a type-K thermocouple placed immediately adjacent to the sample. This thermocouple was periodically calibrated against the melting point of metallic copper. The overall absolute temperature accuracy is estimated to be within 3 K. The inert atmosphere for the experiments was maintained by using high purity argon gas.

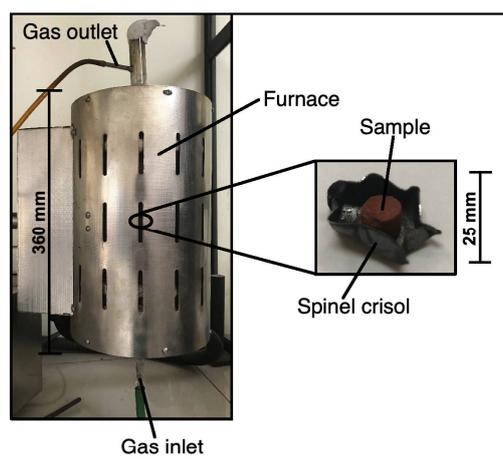


Figure 1. Electrical furnace (Nabertherm RT 30-200) used in experiments and a sample placed within the silica crisol.

The experiments of level 2 were carried out by introducing an industrial slag, blister copper, and incremental additions of CaO in a silica ampoule, similar to the method described in the previous paragraph. The ampoule was fluxed with high purity argon gas and then vacuumed and sealed. The

objective of this procedure was to conserve the partial pressure of oxygen and sulfur in the experiment, to replicate the gas phase of a smelting operation.

Once the time of the experiment had elapsed, in experiments of level 1 and 2, the sample was quenched in water, mounted in an epoxy resin, and a conventional metallographic polishing technique was used for further microanalysis. With the adopted quenching technique, the observed slag did not conform to a glassy material, and an area analysis of $100\ \mu\text{m} \times 100\ \mu\text{m}$ was performed. The available instrument, EPMA/WDS (JEOL JXA 8200L), does not allow a large area analysis of $100\ \mu\text{m} \times 100\ \mu\text{m}$. That analysis was made possible by the EDS (Carl Zeiss, Oberkochen, Germany, EVO MA 10/EDS Oxford Instruments X-Act) technique. It is important to remark that the WDS analysis only has meaning when the probe or volume to be analyzed is completely homogeneous. High purity internal standards of tridymite, Fe_2O_3 , $\text{Cu}_2\text{O}\cdot\text{Fe}_2\text{O}_3$, and Cu were used for the microanalysis.

An analysis of the degrees of freedom was made and the temperature and total pressure were fixed. The number of elements in the system was 5 (Fe, Cu, Si, O, and addition of Al or Ca) and the number of phases was 3 (liquid slag, liquid copper, and tridymite or spinel). The number of degrees of freedom was obtained by using Equation (1). From the initial composition, the amount of Cu_2O and CaO or Al_2O_3 was fixed, thus there are no degrees of freedom.

$$F = C - P + 2 \quad (1)$$

The experiments of level 3 were carried out by adding CaO and Al_2O_3 in an industrial Pierce–Smith furnace. The temperature of the furnace was controlled between $1230\ ^\circ\text{C}$ and $1250\ ^\circ\text{C}$. CaO and Al_2O_3 were added as cold charges. Once the blowing time was reached, samples of slags were taken and analyzed by SEM/EDS (Carl Zeiss, Oberkochen, Germany, EVO MA 10/EDS Oxford Instruments X-Act). The experiments were also monitored to observe the fluidity of the slags during tapping and the formation or dissolution of accretions in the mouth of the furnace.

2.2. Confirmation of Achievement of Equilibrium

To guarantee the achievement of equilibrium, two types of measurements were used. The first being a comparison between the compositions of the phases for two different experimental times: 3 h and 6 h. The second one is the measurement of the compositions in different places of the same phase to ensure their homogeneity. An area analysis by SEM/EDS was used to obtain composition data of the liquid phase as can be observed in Figure 2. As for the tridymite phase, a point analysis was selected for the composition measurement. The average and the standard deviation (σ) of the results are presented in Table 1. The results showed that all the phases studied were homogeneous and that experiments performed for 3 h were enough to reach equilibrium. To make sure and confirm that equilibrium was reached, 6 h of experiment time was selected for this study.

Table 1. Liquid and tridymite average compositions and their standard deviations determined experimentally for the $\text{Cu}_2\text{O}\text{--}\text{Fe}_2\text{O}_3\text{--}\text{SiO}_2$ system in equilibrium with tridymite, saturated with metallic copper, for equilibration times of 3 h and 6 h and temperature of $1200\ ^\circ\text{C}$.

Phase	Equilibration Time	Statistic	Composition (wt %)		
			SiO_2	Fe_2O_3	Cu_2O
Tridymite	3 h	Average	98.4	0.5	1.2
		σ	0.2	0.1	0.0
Liquid	3 h	Average	19.6	25.2	55.2
		σ	0.4	0.8	0.7
Tridymite	6 h	Average	98.2	0.4	1.3
		σ	0.3	0.1	0.2
Liquid	6 h	Average	17.9	23.8	58.3
		σ	0.2	0.4	0.5

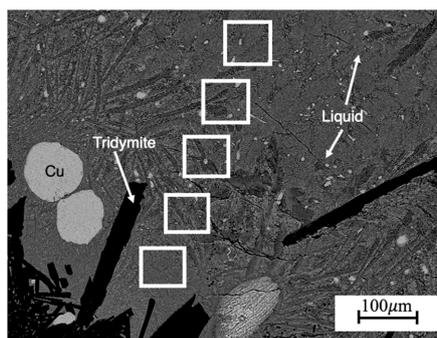


Figure 2. Scanning electron micrograph of a quenched liquid slag equilibrated for 3 h saturated with tridymite and metallic copper. The white squares indicate the analyzed areas.

3. Results

3.1. Equilibrium of Synthetic Slag/Copper with CaO or Al₂O₃ Addition

The SEM/EDS area analysis of the liquid phase showed that the standard deviations were in the range of 0.1–0.4 for Al₂O₃ and CaO, 0.5–1.0 for SiO₂, 0.2–0.4 for Fe₂O₃, and 0.5–1.1 for Cu₂O.

3.1.1. Al₂O₃ Addition

The results of EDS measurements of experiments carried out with the addition of Al₂O₃ at 1150 °C and 1200 °C in equilibrium with metallic copper and tridymite are summarized in Table 2. Liquid compositions of the Cu₂O–Al₂O₃–SiO₂ system are presented for samples 14–18 at 1200 °C.

Table 2. Phase compositions determined experimentally for the Cu₂O–Fe₂O₃–SiO₂–Al₂O₃ system in equilibrium with metallic copper at 1150 °C and 1200 °C.

Sample	Temperature °C	Phase	Composition (wt %)			
			Cu ₂ O	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃
1	1150	Liquid	67.0	12.8	18.5	1.7
		Tridymite	6.7	1.4	91.8	0.1
2	1150	Liquid	60.7	12.8	23.0	3.5
		Tridymite	1.7	0.4	97.8	0.1
3	1150	Liquid	47.1	19.3	29.2	4.4
		Tridymite	2.4	0.8	96.4	0.4
4	1150	Liquid	51.0	16.6	27.1	5.3
		Tridymite	2.0	0.5	96.9	0.6
5	1150	Liquid	57.9	12.1	25.7	4.3
		Tridymite	0.5	2.6	96.5	0.4
6	1150	Liquid	52.0	20.7	25.0	2.3
		Tridymite	1.2	0.5	98.2	0.1
7	1150	Liquid	45.1	26.8	24.1	3.9
		Tridymite	2.0	0.6	97.4	0.0
8	1200	Liquid	55.4	21.4	21.2	2.1
		Tridymite	1.8	0.5	97.7	0.0
9	1200	Liquid	59.3	21.2	17.0	2.5
		Tridymite	1.6	0.2	98.2	0.0
10	1200	Liquid	50.7	25.1	20.6	3.6
		Tridymite	1.6	0.3	98.1	0.0
11	1200	Liquid	58.3	24.0	14.0	3.7
		Tridymite	2.0	0.1	97.9	0.0
12	1200	Liquid	43.5	28.3	23.4	4.8
		Tridymite	1.2	0.8	98.0	0.0
13	1200	Liquid	53.6	26.9	14.9	4.6
		Tridymite	4.9	2.0	93.1	0.0
14	1200	Liquid	58.4	0.0	36.1	5.4
15	1200	Liquid	61.2	0.0	32.5	6.3
16	1200	Liquid	77.0	0.0	21.2	2.0
17	1200	Liquid	70.0	0.0	26.4	4.0
18	1200	Liquid	65.9	0.0	29.2	4.9

3.1.2. CaO Addition

Results of the EDS analysis of experiments that were carried out with the addition of CaO at 1200 °C in the slag/tridymite and slag/spinel equilibrium under conditions of copper saturation are summarized in Table 3. Examples of scanning electron micrographs of samples with slag/tridymite and slag/spinel equilibrium are presented in Figure 3.

Table 3. Phase compositions determined experimentally for the Cu_2O – Fe_2O_3 – SiO_2 – CaO system in equilibrium with metallic copper at 1200 °C.

Sample	Phase	Composition (wt %)			
		SiO_2	Fe_2O_3	Cu_2O	CaO
19	Liquid	17.6	23.8	58.6	0.0
	Tridymite	98.1	0.5	1.4	0.0
20	Liquid	14.4	21.2	64.4	0.0
	Tridymite	98.6	0.3	1.1	0.0
21	Liquid	30.3	0.0	66.1	3.6
	Tridymite	98.8	0.0	1.2	0.0
22	Liquid	35.9	0.0	58.5	5.6
	Tridymite	98.7	0.0	1.3	0.0
23	Liquid	36.0	0.0	56.2	7.8
	Tridymite	98.3	0.0	1.7	0.0
24	Liquid	25.7	10.7	60.7	2.9
	Tridymite	98.9	0.0	1.1	0.0
25	Liquid	36.7	9.2	48.8	5.3
	Tridymite	96.5	0.0	3.2	0.3
26	Liquid	34.0	9.2	49.6	7.2
	Tridymite	94.3	0.4	5.0	0.3
27	Liquid	26.6	23.6	47.1	2.7
	Tridymite	99.3	0.0	0.7	0.0
28	Liquid	36.4	23.7	34.4	5.5
	Tridymite	98.8	0.0	1.2	0.0
29	Liquid	16.8	26.7	49.6	6.9
	Delafossite	0.0	44.8	55.2	0.0
	Spinel	0.0	93.0	7.0	0.0
30	Liquid	15.3	38.2	41.7	4.8
	Delafossite	0.0	49.7	50.3	0.0
	Spinel	0.0	93.9	6.1	0.0

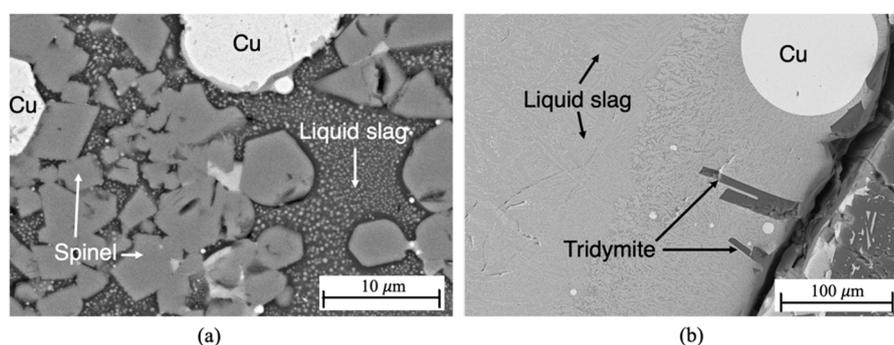


Figure 3. Scanning electron micrographs of quenched liquid slags in equilibrium with spinel (a) and tridymite (b) and saturated with metallic copper.

3.2. Equilibrium of Industrial Slag/Blister Copper with Addition of CaO

The compositions of liquid slags in experiments conducted with industrial slags and blister copper and with the addition of lime at 1150 °C and 1200 °C can be observed in Table 4. The solid phase

wollastonite had an average composition of 52.8 wt % SiO_2 and 44.4 wt % CaO and the composition of the solid phase tridymite was 98 wt % SiO_2 ; and minor oxides make up the rest of these compositions.

Table 4. Liquid compositions (wt %) of industrial slag samples after equilibration at 1150 °C and 1200 °C.

Sample	T °C	Liquid Slag Composition (wt %)					
		Cu_2O	Fe_2O_3	SiO_2	CaO	Al_2O_3	MgO
31	1150	40.8	8.6	40.6	9.2	0.8	0.0
32	1150	45.9	14.1	33.2	5.9	0.9	0.0
33	1150	40.1	8.4	40.5	10.2	0.8	0.0
34	1200	33.8	8.2	44.1	12.7	0.7	0.5
35	1200	44.5	21.7	29.6	3.3	0.9	0.0
36	1200	26.8	13.6	44.5	14.5	0.3	0.3

Examples of scanning electron microscopy images of quenched samples are provided in Figure 4. Slag/tridymite and slag/wollastonite equilibrium can be observed.

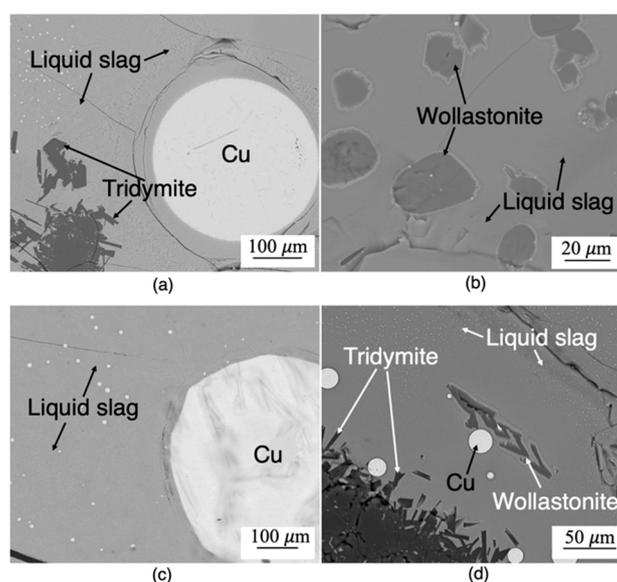


Figure 4. Scanning electron micrographs of quenched industrial liquid slags in equilibrium with solid phases, saturated with metallic copper and with addition of CaO . (a) Tridymite at 1150 °C; (b) wollastonite at 1150 °C; (c) tridymite at 1200 °C; (d) tridymite and wollastonite at 1200 °C.

3.3. Industrial Smelting Tests with Addition of CaO and Al_2O_3

As explained in the procedure, CaO and Al_2O_3 were directly added to the Peirce–Smith converter and the results of the samples taken are summarized in Table 5. The microscopic image shown in Figure 5 indicates the slag in equilibrium with the solid-phase spinel.

Table 5. Liquid slag compositions (wt %) of industrial tests at temperature between 1230 °C and 1250 °C.

Sample	Liquid Slag Composition (wt %)					
	Cu_2O	Fe_2O_3	SiO_2	CaO	Al_2O_3	MgO
37	24.8	34.7	32.0	3.7	4.8	0.0
38	17.1	27.6	43.2	7.7	4.2	0.2

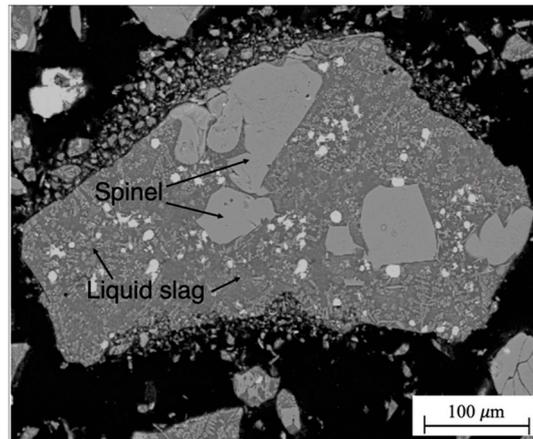


Figure 5. Scanning electron micrograph of liquid slags in equilibrium with spinel in industrial tests carried out with the addition of CaO and Al₂O₃.

4. Discussion

4.1. Cu₂O–Fe₂O₃–SiO₂–Al₂O₃ System

The experimental results of the liquid composition, presented in Table 2, for the Cu₂O–Al₂O₃–SiO₂ system at 1200 °C are shown in Figure 6. The lines indicate the results of the liquidus lines reported in the literature [17]. A reasonable agreement was observed between the present experimental work and that obtained by Hidayat [3].

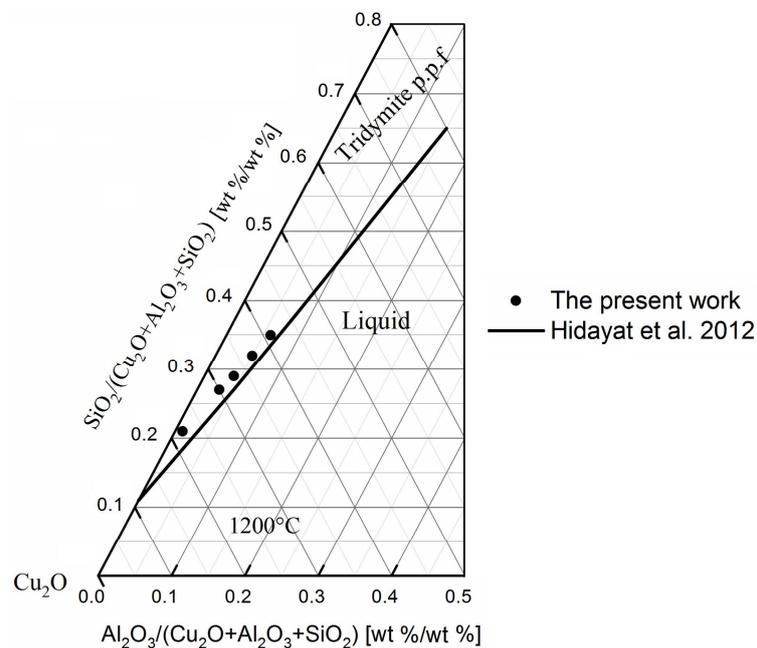


Figure 6. Liquidus lines of the Cu₂O–Al₂O₃–SiO₂ system in equilibrium with tridymite and metallic copper.

Figures 7 and 8 provide the phase diagrams of the Cu₂O–Fe₂O₃–SiO₂ system and the effect of Al₂O₃ that was observed.

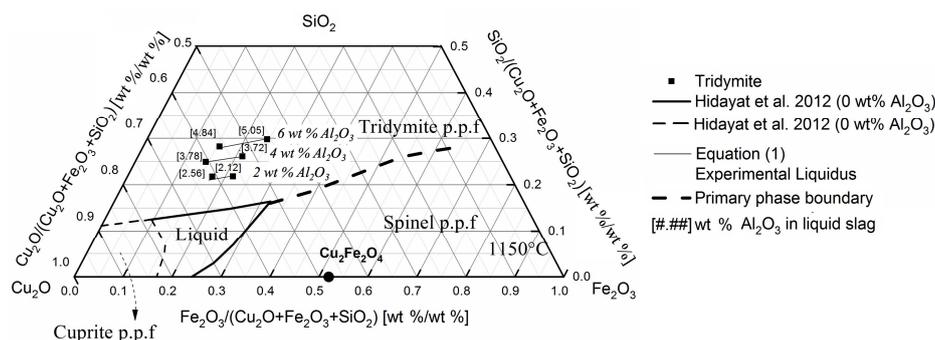


Figure 7. Liquidus for the equilibrium slag/tridymite of the $\text{Cu}_2\text{O}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ system with additions of Al_2O_3 at 1150°C , in equilibrium with metallic copper.

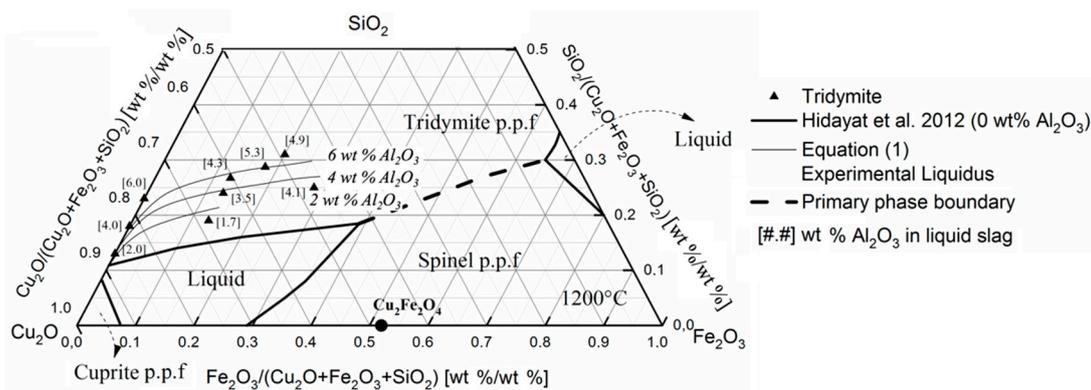


Figure 8. Liquidus for the equilibrium slag/tridymite of the $\text{Cu}_2\text{O}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ system with additions of Al_2O_3 at 1200°C , in equilibrium with metallic copper.

Equation (2) was calculated using an adjustment of the experimental data obtained for 2 wt %, 4 wt %, and 6 wt % Al_2O_3 at 1200°C and the liquidus lines were drawn, as can be seen in the phase diagram of Figure 8. The liquidus lines of the phase diagram of Figure 7 were drawn manually.

$$\text{Wt \% SiO}_2 = 5.3 (\text{wt \% Fe}_2\text{O}_3)^{0.29} + 2.0 (\text{wt \% Cu}_2\text{O})^{0.2} + 3.4 (\text{wt \% Al}_2\text{O}_3)^{0.7}, (T = 1200^\circ\text{C}). \quad (2)$$

The results were compared with the experimental work reported in the literature [3] without addition of Al_2O_3 . It was clear that the addition of alumina resulted in a considerable increase of the liquid region in the primary phase field of tridymite.

4.2. $\text{Cu}_2\text{O}-\text{Fe}_2\text{O}_3-\text{SiO}_2-\text{CaO}$ System

The data of the liquid composition, presented in Table 3, for the " $\text{Cu}_2\text{O}-\text{CaO}-\text{SiO}_2$ " system are shown in the phase diagram of Figure 9 and were compared with experimental results obtained by Hidayat [17]. A reasonable agreement between both experimental results was observed.

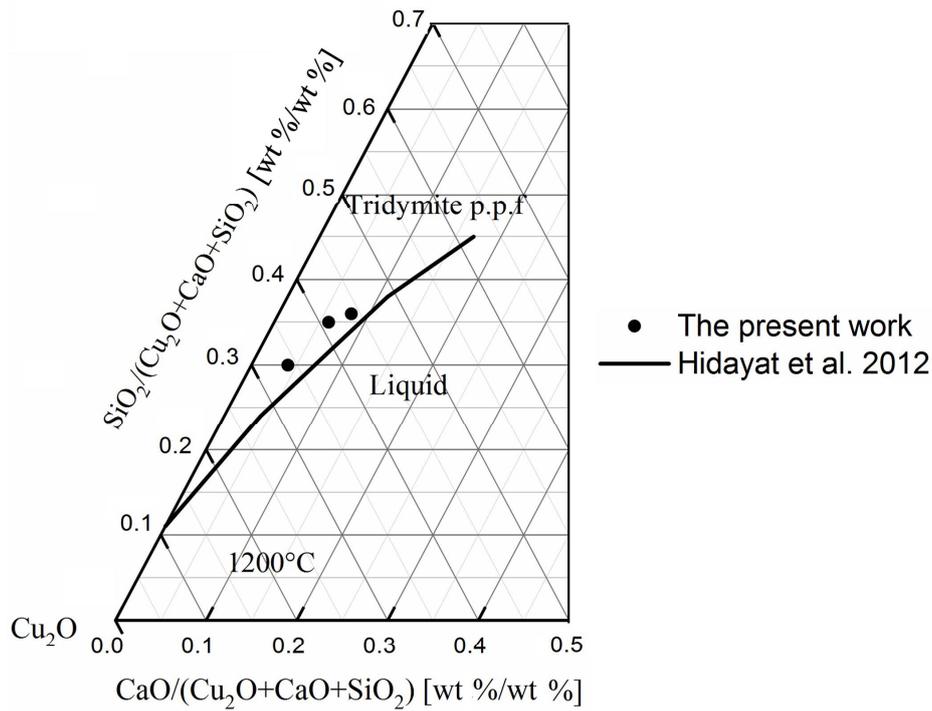


Figure 9. Liquidus lines of the Cu_2O – CaO – SiO_2 system in equilibrium with tridymite and metallic copper at 1200 °C.

Figure 10 represents the data of Table 3 for different additions of CaO projected in the Cu_2O – Fe_2O_3 – SiO_2 system. Three experiments were conducted with no addition of lime and the results of the liquid composition were plotted in the phase diagram of Figure 9. Two of these experiments were performed in 6 h and one in 3 h. It could be seen that the results of the present work were very similar to those reported by Hidayat [3], and that the difference between the compositions of experiments carried out with different experimental times was almost negligible.

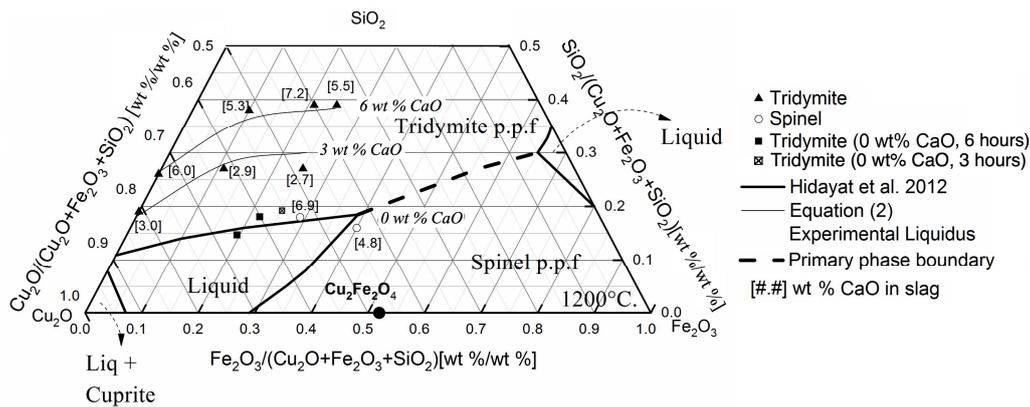


Figure 10. Liquidus for the equilibrium slag/tridymite of the Cu_2O – Fe_2O_3 – SiO_2 system with additions of CaO at 1200 °C, in equilibrium with metallic copper.

From the experimental data, a mathematical expression for the relationship between wt % SiO_2 and the concentration of Cu_2O , Fe_2O_3 , and CaO was obtained and is represented by Equation (3). The correlation coefficient of the equation is $R^2 = 0.94$.

$$\text{wt \% SiO}_2 = 6.0 (\text{wt \% Fe}_2\text{O}_3)^{0.2} + 3.2 (\text{wt \% Cu}_2\text{O})^{0.1} + 6.0 (\text{wt \% CaO})^{0.7}. \quad (3)$$

The liquidus lines at selected levels of CaO were plotted using Equation (2) and are included in Figure 10. The results of the present work were compared with the experimental work reported in the literature [3] without addition of CaO. It was clear that the addition of lime resulted in a large increase of the liquid region in the primary phase field of tridymite.

4.3. Comparison between Al_2O_3 , CaO, and MgO Addition in the $Cu_2O-Fe_2O_3-SiO_2$ System at 1200 °C

A comparison between the effect of CaO, Al_2O_3 , and MgO on the liquid isotherm at 1200 °C is made. The data of a previous study [18] on the influence of MgO over the liquidus lines of the $Cu_2O-Fe_2O_3-SiO_2$ system were used.

The effect on increase in the liquid region of the $Cu_2O-Fe_2O_3-SiO_2$ system was more pronounced with the addition of lime than with the addition of alumina or magnesia. This can be observed in Figure 11, where liquidus lines at 1200 °C, with concentrations of Al_2O_3 and CaO at 2, 4, and 6 wt % and MgO at 2 and 4 wt % are presented. A reduction in the tridymite primary phase field was observed with increasing concentrations of any of these three compounds in the liquid phase.

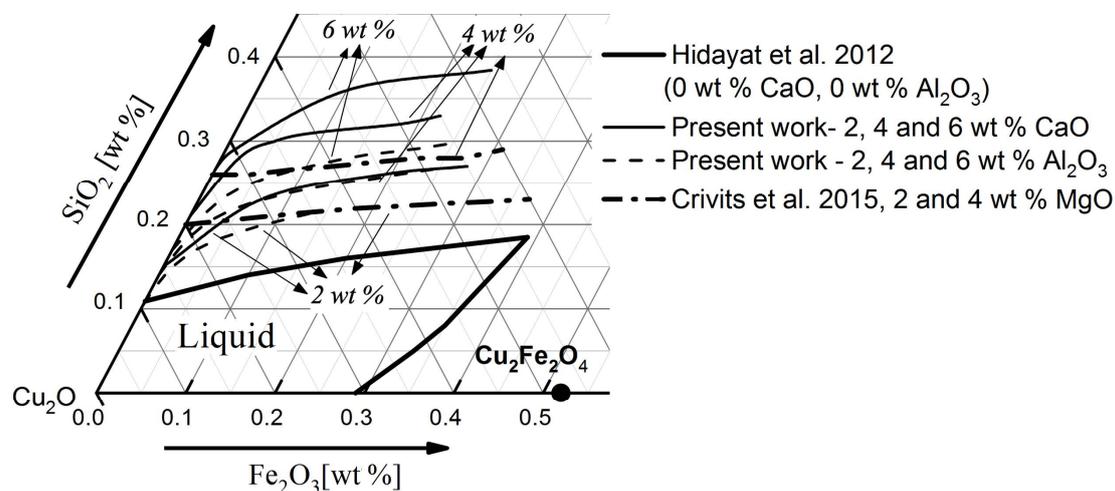


Figure 11. Liquidus for the equilibrium slag/tridymite of the $Cu_2O-Fe_2O_3-SiO_2$ system with different additions of CaO and Al_2O_3 at 1200 °C, in equilibrium with metallic copper.

4.4. Equilibrium of Industrial Slags and Industrial Smelting Tests

The data of Tables 4 and 5 obtained after equilibrium experiments with industrial slags and industrial tests are represented in Figure 12. Liquid compositions in equilibrium with tridymite of experiments carried out with industrial slags, were similar to those obtained with synthetic slags with the addition of CaO. The liquid compositions are represented with the liquidus lines in the phase diagram of Figure 12.

The results of equilibration experiments with industrial slags showed a liquid phase in equilibrium with tridymite and wollastonite (Figure 4b,d). The formation of wollastonite was observed with concentrations of 11.0 wt % CaO + Al_2O_3 at 1150 °C and 14.9 wt % CaO at 1200 °C (Table 4).

The observed micro-photography of Figure 5 shows the slags saturated in spinel with a relatively high concentration of SiO_2 in the liquid phase, with values up to 50 wt % (Figure 12). A similar indication was obtained in the experimental results at saturation with spinel plotted in Figure 10. This indicated that the addition of CaO and Al_2O_3 reduced the liquid phase in the spinel primary phase field. However, supplementary experimental data will be required to define with precision the observed tendency and to determine the slag composition at which both spinel and tridymite precipitation occurs.

From an operational point of view, it will be convenient to generate slags with relatively high concentration of silica, between 30 wt % and 40 wt % in order to reduce the proportion of tridymite and spinel phases.

During the industrial tests, a careful observation was carried out regarding the behavior of the slags. It was apparent that the addition of CaO/Al₂O₃ generated a reduction in the viscosity of the slags and a decrease in the formation of accretions around the mouth of the furnace. Furthermore, the operation problems mentioned in the introduction, were significantly reduced.

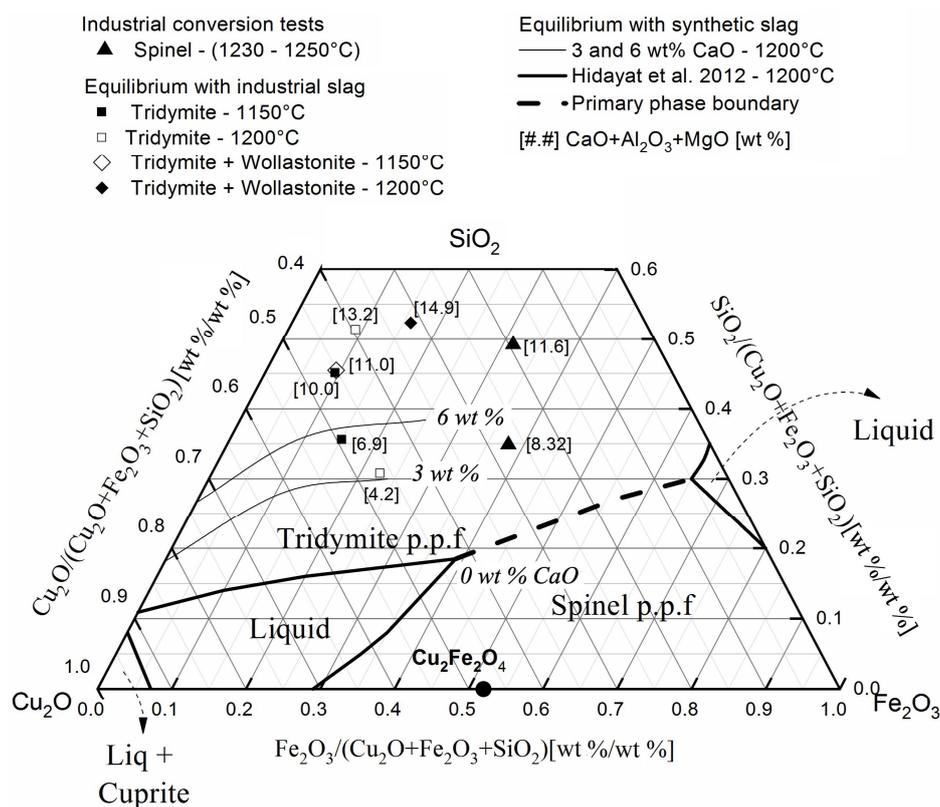


Figure 12. Liquid compositions of equilibrium experiments with industrial slags and industrial tests projected in the phase diagram of the Cu₂O–Fe₂O₃–SiO₂ system compared with equilibrium experiments of synthetic slags with the addition of CaO.

5. Conclusions

The experimental results indicate that increasing the addition of Al₂O₃ or CaO expands the liquid field in the primary phase field of tridymite. No additional phases are observed in experiments with an Al₂O₃ and CaO concentration up to 5 wt % and 8 wt %, respectively. The effect of increasing the liquid region of the Cu₂O–Fe₂O₃–SiO₂ system is larger with the addition of lime than with the addition of alumina. Also, the solid-phase wollastonite appears with additions of CaO larger than 10 wt %.

From an industrial point of view, the operational difficulties associated with slag handling can be overcome with a 6 wt % addition of CaO or Al₂O₃ and a silica amount between 30 wt % and 40 wt %.

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