

EXPERIMENTAL DETERMINATION OF THE INFLUENCE OF SiO_2 IN THE PHASE DIAGRAM OF THE Cu-Fe-O SYSTEM AS AN APPROXIMATION TO THE $\text{Cu}_2\text{O-FeO}_x\text{-SiO}_2$ SYSTEM BETWEEN 1250°C AND 1300°C .

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ABSTRACT: The knowledge of Cu-Fe-O diagram and its relationship with the SiO_2 is important in many copper industrial slags. In this paper are presented part of the phase equilibrium of the $\text{Cu}_2\text{O-FeO}_x\text{-SiO}_2$ system at 1250°C and 1300°C , starting from the modifications on the Cu-Fe-O ternary by the presence of SiO_2 . Several equilibrium studies were realised for the slag/copper system under neutral atmosphere for different Cu/Fe ratios and a constant SiO_2 content. The representation of this equilibrium line was done showing the oxygen content versus $\alpha = \% \text{Fe} / (\% \text{Fe} + \% \text{Cu})$ in the slag, for each SiO_2 content. From the experimental data the calculation of the activities of Cu_2O in the melt was done.

Introduction

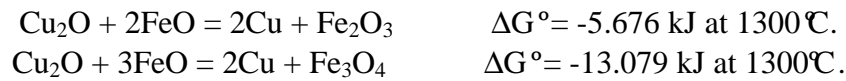
In the pyrometallurgical processes, the knowledge of the physico chemical properties of the phases (metals, mattes and slags) are critical to operate and optimise a particular process or reactor. In spite of many decades of development of new or improved metallurgical processes, still exists many gaps on the knowledge of several important metallurgical systems, both on the transport properties and in the phases diagram. In this paper are presented some experimental results obtained for the ternary phases diagram $\text{Cu}_2\text{O-FeO}_x\text{-SiO}_2$ between $1250\text{-}1300^\circ\text{C}$.

The system $\text{Cu}_2\text{O-FeO}_x\text{-SiO}_2$ is located in the base of the quinary system $\text{Cu-Fe-O-S-Si(SiO}_2\text{)}$, system that defines in a broad sense the different process used in the smelting-converting-fire refining ore sulphides copper metallurgy. The ternary system that best represents the slag produced in the steps of smelting-converting is the $\text{Cu}_2\text{O-FeO}_x\text{-SiO}_2$ one. This system also represents the conditions prevailing in some of the slag cleaning processes, continuous smelting-converting and oxidising roasting - smelting reduction of calcines. The system can be defined as a simple quaternary system: Cu-Fe-O-Si . In this paper are given the results obtained on the influence of the silica in the ternary Cu-Fe-O at $1250\text{-}1300^\circ\text{C}$, as an approximation to the ternary $\text{Cu}_2\text{O-FeO}_x\text{-SiO}_2$. This representation has the advantage to show the equilibrium metal (ℓ_1) / slag (ℓ_2) which is not possible to obtain in the $\text{Cu}_2\text{O-FeO}_x\text{-SiO}_2$ diagram.

$\text{Cu}_2\text{O-FeO}_x\text{-SiO}_2$ system

There is not much information on the literature on the system $\text{Cu}_2\text{O-FeO}_x\text{-SiO}_2$. The binary $\text{Cu}_2\text{O-SiO}_2$ presents an eutectic at the Cu_2O corner with a considerable dispersion regarding the eutectic temperature measured that ranges from $1050^\circ\text{C}^{[3]}$ to $1152^\circ\text{C}^{[1]}$. The eutectic

composition is not well defined either, with values from 6.9%^[3], 7.7%^[11] y 8%^[2] as wt% of SiO₂. The binary FeO-SiO₂^[4] is well defined due to his relation with the iron and steel industry. With respect to the binary Cu₂O-FeO, it does not exists due to the "autor reduction" reaction that occurs at temperature above the melting points of Cu₂O and FeO:



This reaction has been not study and there is only one paper^[5] that mentions the possible production of metals by reduction with FeO.

With respect to the metal phase of interest, the Cu-Fe system is well defined and permit a precise quantitative description of the thermodynamics properties of both the solid and liquid solutions. For the liquid, there is agreement between several authors for the activity coefficient and the heat of mixing. The value of ΔG^{xs} at infinite dilution of 36 215 J/mol at 1300°C was determined by Hultgren et al.^[7] and is widely used in the literature as by Kubachewsky & Alcock^[8]. This value is in agreement with others determined by several researchers, which gives a value for γ^∞ for the iron in copper at 1300°C of 16. The dissolution of iron in copper can reaches up to 4wt% at the melting point and 10wt% at 1300°C^[9]. For the binary Cu-O, the work of Schmid^[9] is useful for the determination of the equilibrium conditions for the metal phase, starting from the oxygen potential isobars. Finally, the binary Fe-O is very well known, for example, in the work of Muan & Osborn^[11].

The ternary Cu-Fe-O is the base for this study. Although this system is of relevance in the copper metallurgy, there is not much studies done on it. Probable the best study due to the broad scope of it is the one done by A. Luraschi y F. Elliot^[13] who made a complete review of the Cu-Fe-S-O-Si(O₂) system. Their analysis of the Cu-Fe-O was the basis for several studies done by Acu ñ^[14] y Espinel^[15] who studied the system for different oxygen potentials and temperatures, particularly those regarding the fire refining conditions. Their studies permitted to validate some areas of this ternary proposed by Luraschi and Elliot, particularly the precise definition of the limits of the Cu(ℓ_1)-slag(ℓ_2) system. Their studies also permitted to calculate the activities in the ternary for both the metal phase (ℓ_1) and the slag phase (ℓ_2). The experimental determination at 1300°C is shown in Figure 1.

Other study by Oishi et al^[16] determined this system at 1500°C (Figure 2.). It can be observed the influence of temperature on the evolution of the liquidus line in biphasic area ℓ_1/ℓ_2 in Figure 2 respect to Figure 1 at 1300°C. A temperature increase translate the liquidus line over the Cu_xFe_{3-x}O₄ spinel phase, reaching a composition close to FeO. Preliminary analysis using the data obtained in the smelting reduction of Cu₂O at 1260°1300°C done by Parra et al.^[6] permits to assume a similar effect regarding the increase of this bifasic area by the silica addition. This assumption also can be drawn from the analysis of the Cu₂O-SiO₂ and FeO-SiO₂ binaries since the silica forms eutectics in both systems.

Basis for the study.

As it was mentioned, the system Cu₂O-FeO_x-SiO₂ can be studied by adding silica to the ternary Cu-Fe-O to study the evolution of the liquidus at equilibrium conditions, which permits to know the slag phase (ℓ_2) and the metal phase (ℓ_1). The modification of other equilibrium areas proposed by Luraschi and Elliot^[11], Acu ñ^[12] y Espinel^[13] for the trifasic

equilibrium ℓ_1 - ℓ_2 -spinel, ℓ_1 -spinel-FeO, ℓ_1 -FeO-Fe(γ) and the bifasic equilibrium can be evaluated by using these proposed diagram and considering that the addition of silica modifies the activities of the different compounds presents. To quantify this effect it was traced the liquidus of the ℓ_2/ℓ_1 equilibrium for the Cu-Fe-O system adding SiO₂ as an external additional parameter.

The basis for this representation is the Gibbs Phase Rule that states that the degrees of freedom (F) of a system is given by:

$$F = C - P + 2$$

Where C is the number of components and P the number of phases.

By fixing the temperature and the total pressure, the number of phases required is three to have an invariant condition. The addition of a new component then can represent the formation of a new phase, according to:

$$F = C - P + 2(T,P) + 1(\% \text{SiO}_2)$$

If the experimental conditions are chosen in a form to avoid the formation of a new phase, the additional degree of freedom obtained can be associated to an external variable, therefore, it is possible to study the ternary system Cu₂O-FeO_x-SiO₂ starting from the ternary Cu-Fe-O under a constant content of silica. This assumption is based on the hypothesis that the silica does not interact with the melt forming other compounds that can precipitate.

The selection of the required composition was done in order to avoid the saturation conditions for SiO₂. Since there is not previous experimental evidence for this conditions, to verify this aspects after each test, the samples were studied by means of micrographic analysis and by microprobe.

Experimental Study

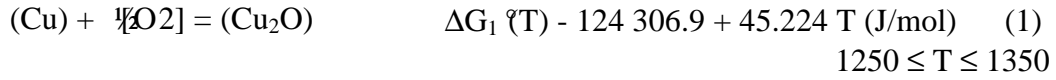
The experimental study was done by establishing the ℓ_1/ℓ_2 equilibrium in alumina crucibles at 1250 and 1300 °C. The samples were prepared with a fixed ratio Cu/Fe using Pro Analysis products (Fe₂O₃, CuO, Cu₂O y Fe). As initial composition they were used conditions similar to those of the ℓ_1/ℓ_2 equilibrium used by Espinel^[15] adding silica up 5, 10 and 15 wt% in the liquid phase ℓ_2 . Since no clear evidence of the liquidus exists, the SiO₂ content at the equilibrium condition was determined by means of an experimental iterative approach. The average values measured with an uncertainty of 1.4 were 5.84%, 8.48% y 10.9% of SiO₂. In addition to this, it was verified the equilibrium conditions in the system Cu-Fe-O with no silica in it, according to those used by Espinel^[15] and Acuñá^[14].

The experimental apparatus is shown in Figure 3. The procedure consists in preparing the sample and introducing them in the furnace at 650 °C under neutral atmosphere (nitrogen), and controlled heating the system. The nitrogen was deoxygenated previously in a furnace fitted with copper mesh.

Exploratory tests were performed previously in order to determine the required time to reach equilibrium conditions. It was found that it was enough to kept the samples for 5 hours at the desired temperature. This time is slightly lower that the required for the equilibrium in the system Cu-Fe-O in absence of SiO₂^[14]. The chemical analysis were performed on the ℓ_2 by analysing Cu, Fe, Al and SiO₂. The oxygen was calculated by difference. The aluminium was analysed due to the dissolution shown by the alumina crucible. The chemical composition was normalised between Cu-Fe-O assuming the aluminium was present as Al₂O₃.

Calculation of the cuprous oxide activity in the slag.

The calculation of the CuO_{0.5} activity can be done knowing the Cu and Fe content in the metallic phase. The Cu/Cu₂O equilibrium between metal and slag can be represented according to the following reaction:



Starting from equation (1) the expression of $a(\text{Cu}_2\text{O})$ is:

$$\ln a(\text{Cu}_2\text{O}) = \frac{\Delta G_1^\circ(T)}{-RT} + 2 \ln a(\text{Cu}) + \ln a(\text{O}) \quad (4)$$

Note that the oxygen activity is equivalent to $P_{\text{O}_2}^{1/2}$ for the choice of standard state made for oxygen.

Considering a diluted solution for the O in the Cu:

$$\ln a(\text{O})_{\text{Cu}} = \left(\ln g_{(\text{O})_{\text{Cu}}}^\infty + e_{\text{O}}^{\text{O}} X(\text{O})_{\text{Cu}} + e_{\text{Fe}}^{\text{O}} X(\text{Fe})_{\text{Cu}} \right) + \ln [X(\text{O})_{\text{Cu}}] \quad (5)$$

The values of e_{O}^{Fe} , e_{O}^{O} and $g_{(\text{O})_{\text{Cu}}}^\infty$ taken from the critical review of Luraschi^[17] are:

$$\ln g_{(\text{O})_{\text{Cu}}}^\infty = 4.53 - \frac{8978}{T} \quad (6)$$

$$e_{\text{O}}^{\text{O}} = 9.738 - \frac{25253}{T} \quad (7)$$

$$e_{\text{O}}^{\text{Fe}} = -565 \quad (8)$$

Since the content of Fe in the Cu is very low the effect of $e_{\text{O}}^{\text{Fe}} X(\text{Fe})$ on $\ln g_{(\text{O})_{\text{Cu}}}$ is quite negligible. In this way, it can be considered the value of $a(\text{Cu})$ by means of the integration of the Gibbs-Duhem equation which is applied for the simplification of the equation (5) to express $g_{(\text{O})_{\text{Cu}}}$:

$$\ln g_{(\text{O})_{\text{Cu}}} = \ln g_{(\text{O})_{\text{Cu}}}^\infty + e_{\text{O}}^{\text{O}} X(\text{O})_{\text{Cu}} \quad (9)$$

$$\Rightarrow \ln g_{\text{Cu}} = e_{\text{O}}^{\text{O}} \times [X(\text{O})_{\text{Cu}} + \ln(1 - X(\text{O})_{\text{Cu}})] \quad (10)$$

Replacing the expressions 6,7 and 8 into the equation (5) and introducing the resultant as well as the equation (10) into the expression 4, it can obtain that the $a(\text{Cu}_2\text{O})$ as a function of the O content in copper at a given temperature.

Finally the relation between $a(\text{CuO}_{0.5})$ and $a(\text{Cu}_2\text{O})$ is:

$$a(\text{CuO}_{0.5}) = \sqrt{a(\text{Cu}_2\text{O})} \quad (11)$$

Results

The results are shown in the Figure 4, Figure 5 and Figure 6. The chemical compositions reached in the slag phase (ℓ_2) under equilibrium conditions are summarised in Table 1.

A good agreement is observed between the results published previously by Espinel^[15] and those in this work for the slag without SiO_2 (Run A). The effects of the addition of SiO_2 and the increase of temperature are shown in Figures 4 and 5. It is clear that at a fixed temperature, the increasing content of SiO_2 in the melt can expand the two-phase zone ℓ_2/ℓ_1 . In the same way, for a fixed content of SiO_2 the increasing of temperature can displace the line that limits this two-phase zone. These results confirm the hypothesis that is equivalent to increase the temperature or the SiO_2 content to expand the two phases (ℓ_2/ℓ_1) boundaries.

The presence of SiO_2 in the melt modifies the activity of the cuprous oxide as it is shown in the figure 7. This effect increases strongly from 8%. The decrease of the value of $a(\text{CuO}_{0.5})$ between 8 and 10% is at least twice the one taken place between 0% and 8% SiO_2 .

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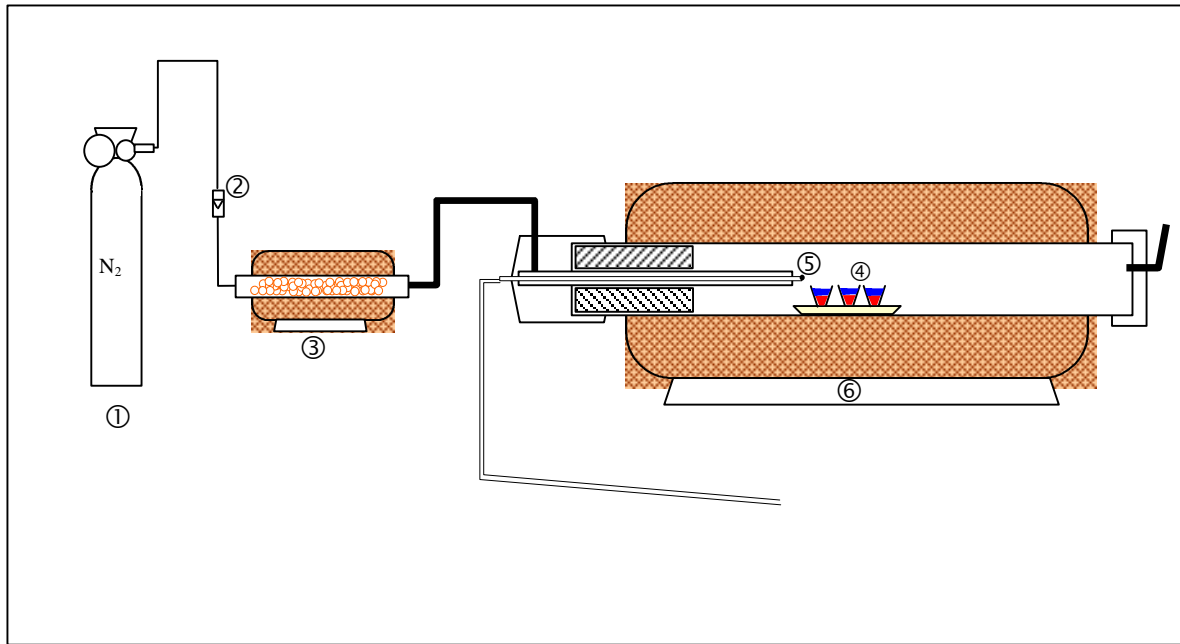


Figure 3: Experimental apparatus for the equilibrium study under neutral atmosphere.

- | | |
|---------------------------|---------------------------------------|
| ① : Nitrogen bottle. | ④ : Samples crucibles. |
| ② : Flowmeter. | ⑤ : Thermocouple. |
| ③ : Deoxidization furnace | ⑥ : High Temperature tubular furnace. |

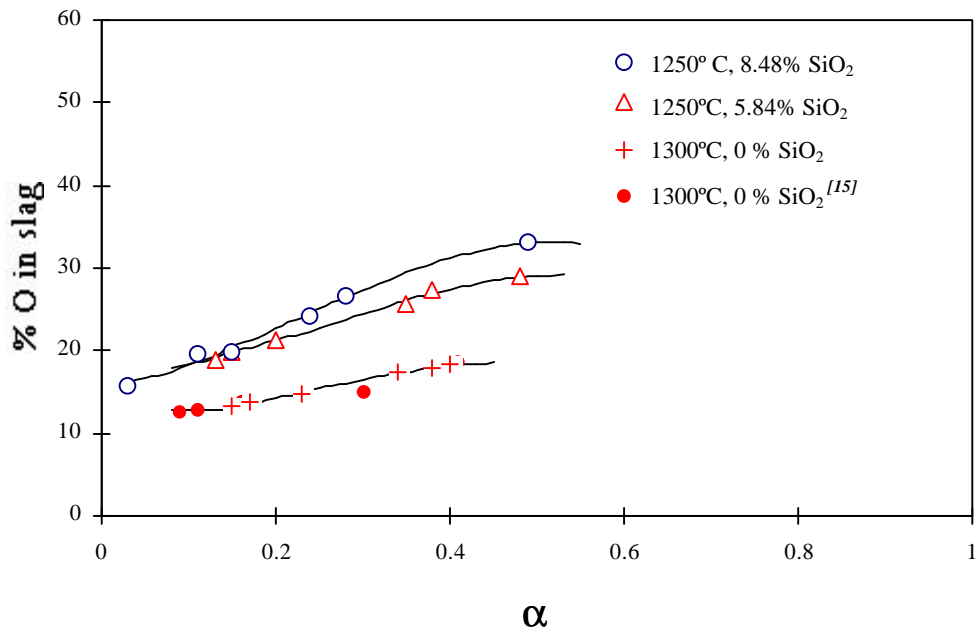


Figure 4: SiO_2 effect on the oxygen content in the slag as a function of $\alpha = \% \text{Fe} / (\% \text{Fe} + \% \text{Cu})$ at 1250°C. Results for 0% SiO_2 at 1300°C by Espinel (●)^[15] and this work (+).

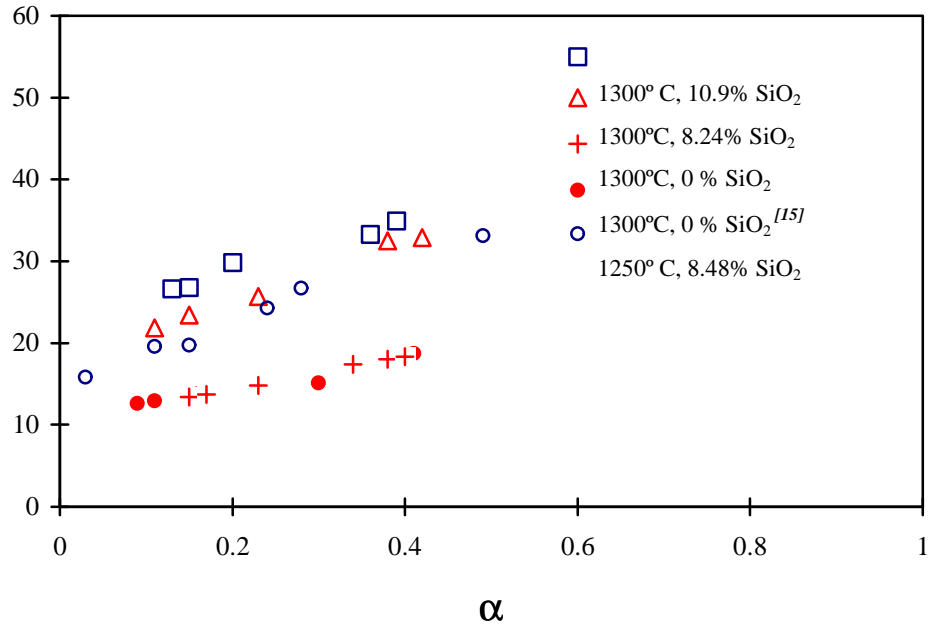


Figure 5: SiO_2 effect on the oxygen content in the slag as a function of α at 1300°C. Comparison for SiO_2 content around 8% between 1250 and 1300°C.

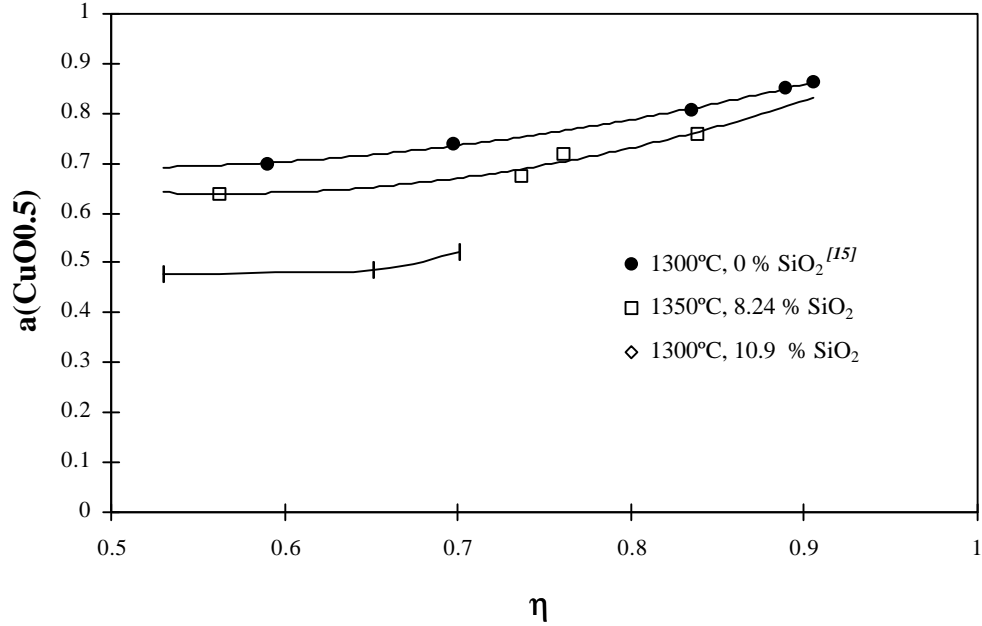


Figure 6: Activity of cuprous oxide at 1300°C as a function of $\eta=(1-\alpha)$ for 0%, 8% and 10% SiO_2 .

Tables

Tabla 1: Análisis químico en la escoria y metal.

Run	Temperature	%SiO ₂	%Cu	%Fe	%O	(<u>O</u>) _{Cu}
A	1300	0	73.62	12.99	13.39	
			71.62	14.67	13.71	
			65.58	19.59	14.83	
			50.85	31.16	17.99	
			49.02	32.68	18.30	
I	1250	5.84	44.80	27.83	27.37	
			44.80	27.83	27.37	
			48.77	25.69	25.55	
			36.87	34.03	29.10	
			63.22	15.57	21.21	
III	1250	8.48	68.17	12.03	19.80	
			70.60	10.41	18.99	
			33.85	33.05	33.10	
			52.78	20.52	26.70	
			57.65	18.05	24.30	
II	1300	8.24	68.16	12.07	19.77	
			71.62	8.79	19.59	
			81.67	2.53	15.80	
			41.85	25.65	32.50	0.0324
			38.99	28.11	32.90	
IV	1300	10.90	57.01	17.29	25.70	0.0376
			65.30	11.30	23.40	
			69.58	8.60	21.82	0.0451
			81.48	2.83	15.68	0.0553
			42.46	24.29	33.26	
			39.41	25.69	34.90	0.0156
			55.86	14.28	29.86	0.0162
			62.53	10.72	26.75	0.0194
			63.82	9.55	26.63	