

# THE INTERACTION BETWEEN CUPRIC FERRITE AND COPPER MATTE/ SLAG AT 1300°C

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## ABSTRACT:

Cupric ferrite, a common compound formed during dead roasting of copper concentrate, can be recovered in the copper flash smelting process. The principal interaction between cupric ferrite, slag and matte can be represented by the following overall reaction:



The effect of the slag/matte ratio, reaction time and silica content has been studied in an experimental set similar to industrial conditions. Experimental results show that reaction is possible and most of the copper from cupric ferrite can be obtained in the matte phase.

## Introduction

A new alternative<sup>[1]</sup> to process copper matte and white metal is being developed. This new process could replace the conventional Peirce-Smith converting and produce electrolytic copper.

The process consist of a dead roast at 780-820°C of the ground matte or white metal to remove all of the sulfur as SO<sub>2</sub>, and a calcine formed mostly of CuO and cupric ferrite followed by a leaching of the calcine with spent electrolyte from the EW cells. The copper can be obtained from the pregnant electrolyte, which is of high purity.

The solid residue after solid - liquid separation is cyanidated to recover the precious metals contained, The residue, which consist essentially of cupric ferrite formed in the roasting steps<sup>[2,3]</sup>, is used back into the smelting furnace to recover the copper contained, by exchanging the oxygen from the copper in the ferrite by the sulfur associated to the iron in the matte.

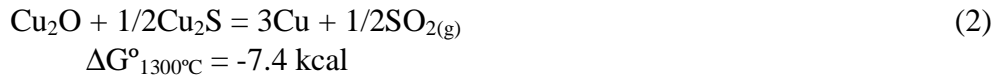
## Thermodynamic feasibility

The matte is formed mainly of Cu<sub>2</sub>S and FeS, Some oxides are also dissolved in matte, such as wüstite FeO and magnetite Fe<sub>3</sub>O<sub>4</sub><sup>[4,5,6]</sup>. Since the cupric oxide CuO is unstable at temperature above 1060°C, only the cuprous oxide Cu<sub>2</sub>O is present under smelting conditions.

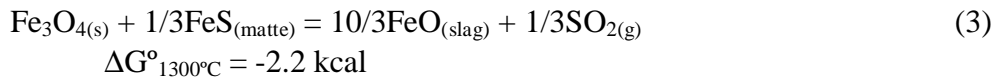
Cu<sub>2</sub>O can exist only in high-grade mattes. In low grade mattes (Cu<65%) where exists enough FeS, the following reaction takes place:



The dissolution of Cu<sub>2</sub>O in mattes is limited even in high grade-mattes due to following reaction that occurs<sup>[7]</sup>:



The Fe<sub>3</sub>O<sub>4</sub> is formed only under relatively oxidizing conditions such as in flash. Since mattes have very limit capacity to dissolve magnetite, this exists in solid as a separate phase. Moreover, in low-grade mattes the presence of magnetite is less possible due to the reaction with iron sulfide<sup>[8]</sup>:



Since magnetite is found in solid mattes, the following reaction appears to take place during the cooling process:



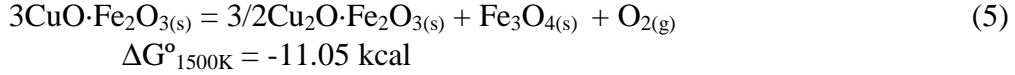
The solubility of FeO in matte depends on temperature, oxygen partial pressure of the system and matte grade. The lowest temperature eutectic exists at 840°C for the system of FeS-Cu<sub>2</sub>S-FeO, with an increasing fusion temperature with the increase Cu<sub>2</sub>S content. On the other hand, FeO and FeS form an ideal solution. The FeO dissolution in FeS-Cu<sub>2</sub>S mattes decreases with increasing the matte grade, until the composition pure Cu<sub>2</sub>S which can not dissolved FeO<sup>[4,9]</sup>.

The oxidation roasting of matte is similar to that of copper sulfide concentrates with the formation of CuO, Fe<sub>2</sub>O<sub>3</sub>, CuFeO<sub>2</sub> (delafossite) and CuFe<sub>2</sub>O<sub>4</sub> (cupric ferrite). The solubility between the last product and magnetite is quite limit, and they only can dissolve each other when the temperature is over 1000°C<sup>(2,3)</sup> to form a solid solution called spinel.

Copper ferrite formed from matte or white metal should be rather high purity. This ferrite should not present a problems its return into the smelting process, except that it will generates more slag. The reaction mechanisms of copper ferrite during the smelting can be studied thermodynamically and experimentally, particularly the copper losses in the slag and the formation of magnetite.

Cupric ferrite shows two thermal anomalies, at 675K and 795K. The low temperature anomaly had a minor change in the crystal structure and the higher temperature anomaly a magnetic transition. The highest temperature reached with ferrite was 1102.3K. At a somewhat higher

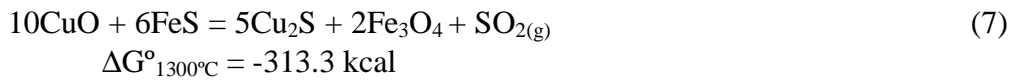
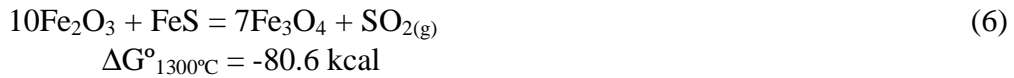
temperature, the oxygen pressure caused by decomposition of the ferrite becomes significant. Although several decomposition reactions are possible and could occur simultaneously, it is believed that the main one is the following<sup>[9]</sup>:



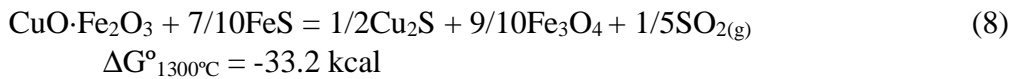
X-ray diffraction of samples decomposed at a temperature close to 1100K gave strong evidence of magnetite and a slight evidence of hematite. Small amounts of cuprous oxide also appeared in the decomposition product.

The ternary diagram Cu-Fe-O at 1300°C estimated by Luraschi<sup>[10,11,12]</sup>, shows that the spinel is stable at 1300°C under an oxygen partial pressure between  $10^{-8}$  to 1 atm. The spinel decomposes into copper liquid ( $l_1$ ) and FeO decreasing the oxygen partial pressure due to the eutectic reaction. The stability zone of the spinel exists near the Fe-O binary, a narrow band from  $\text{Fe}_3\text{O}_4$  to  $\text{CuFe}_2\text{O}_4$ . At oxygen partial pressure near to  $10^{-4}$  atm, a liquid oxide slag ( $l_2$ ) can exist in equilibrium with liquid copper ( $l_1$ ). It also can be observed in this diagram that FeO and copper liquid ( $l_1$ ) are immiscible while  $\text{Fe}_3\text{O}_4$  can dissolve copper to form spinel solid solution. Therefore in order to decompose copper ferrite in the smelting process, it is required to maintain the oxygen potential of the system in a low value to avoid the formation of magnetite.

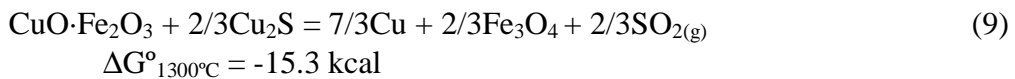
However, when cupric ferrite is in equilibrium with matte, the sulfur or more correctly the  $\text{SO}_2$  partial pressure will influence the decomposition of ferrite. The interaction between ferrite and matte can be explained using the Cu-Fe-S-O quaternary system. It is believed that cupric ferrite will decompose in presence of matte, according to the following reactions that can take place<sup>(\*)</sup>



In terms of the overall reaction, it will be:



If the matte grade is high, the  $\text{Cu}_2\text{S}$  also can react with the ferrite. In this case, metallic copper would be produced according to reaction (4):

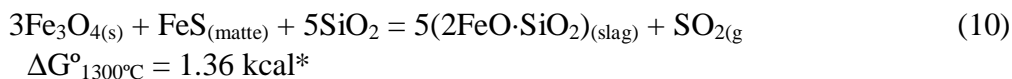



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(\*) All values used to calculate  $\Delta G^\circ$  are from the HSC Database of Outokumpu, except for equation (5).

The magnetite generated it is an undesirable product due to the high melting point and high viscosity of the slag, as well as the high losses of copper in the slag<sup>[13,14,15,16,17,18,19,20,21]</sup>.

If the oxygen potential of the system is low enough, or the sulfide content in the matte is high enough to take place reaction (3), the magnetite can be reduced to wüstite, which can be slagged with silica as fayalite if the slag is saturated in silica<sup>[22]</sup>:



The thermodynamic analysis indicates that the reactions that take place between copper ferrite and matte/slag are very complex. The addition of ferrite into the matte/slag melt will cause a new equilibrium and a change of the composition of the system. Normally in copper smelting system there are five elements: Cu-Fe-S-O-SiO<sub>2</sub>, and at least three phases: matte, slag and gas. The degrees of freedom of the system therefore can be four. If there are two more phases, for example, liquid copper, solid magnetite or silica saturation, it is possible therefore define the concentration of each composition when the system is in equilibrium at a constant temperature and oxygen potential.

## Material and experimental procedure

Cupric ferrite used in this studying was prepared with pure CuO (>99) and Fe<sub>2</sub>O<sub>3</sub> (>99%) from MERCK®. After drying and mixing the oxides according to the weight ratio of CuO and Fe<sub>2</sub>O<sub>3</sub>, the mixed material was used to make pellets of 2.45 mm diameter by 15 mm thick under a pressure of 6000kg/cm<sup>2</sup>. The pellets were headed in a muffle furnace at 800 - 850°C for 4 days in air. The RXD analysis of the ferrite produced indicate that the ferrite contain 100% of CuO·Fe<sub>2</sub>O<sub>3</sub> with no detectable CuO or Fe<sub>2</sub>O<sub>3</sub>. Chemical analysis of the cupric ferrite used in this experiment is shown in Table 1.

The copper matte used was from the Chalgre flash smelting of Empresa Minera Disputada de Las Condes S. A., Chile. Chemical analysis result of this matte is shown in Table 1. The sum of copper, iron and sulfur is 97.92%. The slag used was from the flash smelting of Chuquicamata, Chile. Its composition can be seen also in Table 1. The silica flux used was national quarts with purity near 98%.

In all tests, the materials were dried and ground –100/+140 mesh Tyler.

Tests were performed in a crucible furnace under nitrogen protection. Reagents were mixed before to add them into an alumina crucible. The crucible was introduced into the furnace at 800°C, and then the furnace was heated to 1300°C. After the test, the melt was cooled inside the furnace until 800°C before removing it from the furnace. The flow rate of deoxygenated nitrogen was maintained constant at 1l/min, during all tests.

**Table 1 Chemical analysis of the materials used in the study**

Material name	Cu%	Cu <sub>(ox.)</sub> %	Fe%	S%	SiO <sub>2</sub>
Cupric ferrite	26.46	-	44.14	-	-
Matte	61.08	2.15	14.45	22.39	0.25
Slag	1.57	0.28	43.56	0.41	31.88

The crucible was cut in two parts, one of them was used for microscopy analysis and the other for chemical analysis of both the matte and the slag, if two phases have been formed.

## **Results and Discussion**

Three types test were performed in order to understanding the interaction between copper ferrite and copper matte/slag:

I-.Qualitative tests to obtain basic knowledge on how the cooper from the ferrite is distributed into the matte and the slag during the smelting process;

II-. Batch tests to study the controlled addition of ferrite in a molten bath of matte/slag, as a function of reaction time, slag/matte ratio and ferrite/matte/slag ratio.

III-. Kinetic studies to measure the reaction rate of copper ferrite in a molten bath of matte/slag.

### I-.Qualitative tests:

The qualitative tests with copper ferrite, matte, slag and silica were performed at a constant temperature of 1300°C for 2 hrs under nitrogen atmosphere. The chemical analysis results are shown in Table 2. In this Table it can be observed that concentration of each phase has changed with respect to the initial composition.

Some conclusions can be drown from this results:

-. Melting matte and slag together as in test ES-1, forms two separated phases well defined. In the slag phase it can identified two main compounds, one of Fe-Al-O and other the Fe-Si-O, indicated with the letter “a” and “b” in Figure 1, respectively. The compositions of these two compounds are shown in Table 3.

**Table 2 Qualitative tests for the interaction between ferrite and matte/slag**

Test N°	Ratio of reagents	Matte phase					Slag phase				
		Fe	Cu	Cu <sub>ox</sub>	S	SiO <sub>2</sub>	Fe	Cu	Cu <sub>ox</sub>	S	SiO <sub>2</sub>
ES-1	Matte : slag = 7 : 3	12.21	60.79	3.55	21.35	1.48	47.43	4.10	0.53	1.62	27.64
CE-1	Ferrite : matte = 3 : 10	9.99	70.89	3.03	18.80	1.84					
CE-2s	Ferrite:matte:SiO <sub>2</sub> = 8:5:1	-	69.28	1.92	18.20	-	46.93	12.82	1.53	1.02	11.92
CES-2	Ferrite:matte:slag = 3:10:3	6.70	71.83	0.85	19.59	-	50.41	3.54	0.79	1.22	18.45
CES-4	Ferrite:matte:slag = 2:10:4	7.90	67.85	2.98	20.15	2.27	45.69	2.63	0.72	1.09	20.45
CES-5	Ferrite : matte : slag : SiO <sub>2</sub> = 3 : 9 : 3 : 1	4.98	69.14	2.55	19.47	3.43	40.01	1.71	0.51	0.41	27.81

-. Melting copper ferrite with matte as in test CE-1, the slag phase does not form over the matte phase. However, a film with a different color from the matte was found between the melt and the crucible. This compound can creep along the crucible up to a position higher than the melt. This substance appears to be magnetite, since the sulfur in matte is lower than the required to form iron sulfide. This result could be explicated according to the following reaction:



Microscopic analyses shows that this film consists mainly of matte and magnetite, which are indicated with the letter “a” and “b” in Figure 2, respectively. The compositions of these two compounds are shown also in Table 3. In the matte phase of this test, the main compound was white metal and some metallic copper. Chalcocite and iron oxides can also be found. (Table 3)

-. In the case of ferrite/matte melt with silica addition (Test CE-2s), three phases are clearly formed: copper metal, matte and slag. This result indicates that silica can avoid the formation of magnetite by forming fayalite slag, although thus the slag could contain copper. Therefore, reactions (8) to (10) can take place simultaneity.

In these tests phase separation was near perfect, and the matte was internally pure white metal, however, some matte inclusion were found in metallic copper phase, as well as some copper in the matte phase. Table 3 shows the microscopic analyses results. The slag phase is rather complex since there are present a Fe-Si-O compound, a Fe-Al-O compound, iron oxide and metallic copper particles. (Figure 3)

-. By comparing the results of Test CES-2, CES-4 and CES-5 with ES-1 in which no copper ferrite was added, the matte composition of those tests has changed significantly. It can be observed that the copper concentration increased while the iron concentration decreased. This appears as a clear indication that some interaction between copper ferrite and matte/slag occurred at 1300°C, with the copper from the ferrite was transferred into the matte while the iron from the matte was transferred into slag, since there is a clear increase of the matte grade.

Result of Test CES-5 shows that silica has a positive effect in decreasing the copper content in the slag. In this test the ratio of Fe/SiO<sub>2</sub> in slag is lower than 1.86, which is the stoichiometric ratio of fayalite.

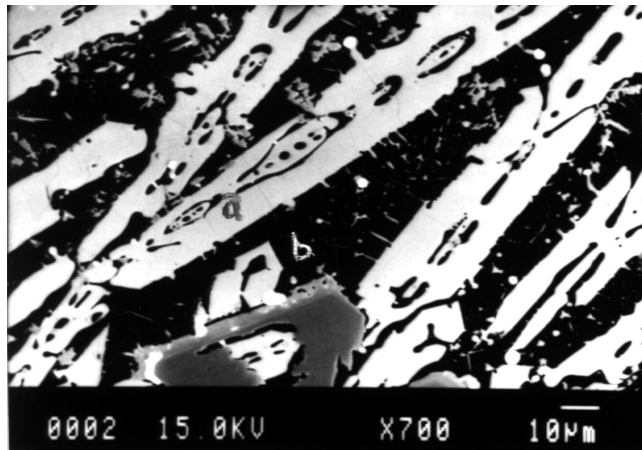


Fig 1: Micrograph of the sample of Test ES-1. (slag phase)

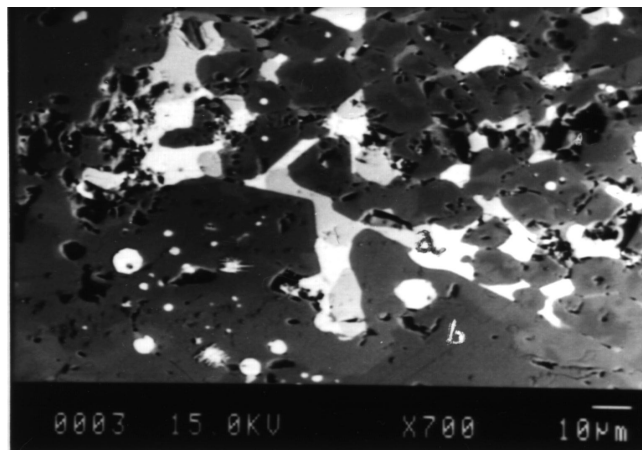


Fig 2: Micrograph of the sample of Test CE-1. (slag phase)

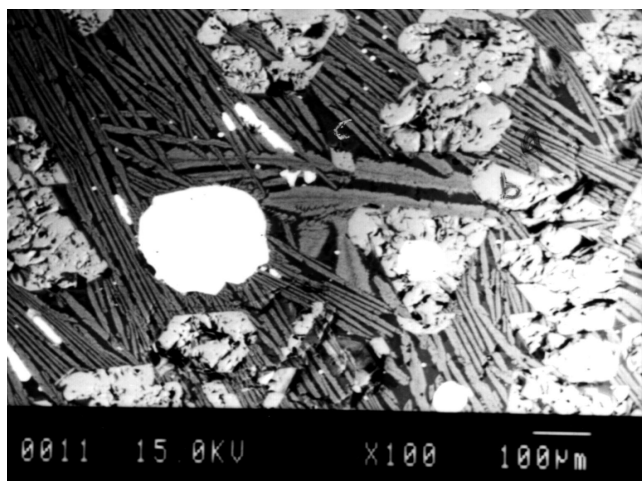
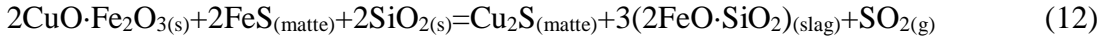


Fig 3: Micrograph of the sample of Test CE-2s. (slag phase)

The overall reaction can be written as follow:



**Table 3 Results of microscopic analysis**

Sample	Phase	Microscopic Analyses	Cu%	Fe%	Al%	Si%	S%	Total	Point	in Fig
ES-1	Slag	Clear phase, clear in slag	-	33.77	26.62	0.08	0.02	60.48	"a"	1
ES-1	Slag	Clear phase, dark in slag	-	48.94	0.12	13.99	-	63.05	"b"	1
CE-1	Matte	Clear phase	77.89	1.25	-	0.01	20.68	99.83		
CE-1	Matte	Round particle in matte	99.41	0.32	0.06	0.03	0.09	99.90		
CE-1	Matte	Dark particle in clear phase	34.09	34.63	0.02	0.02	11.17	79.92		
CE-1	Slag	Clear phase, clear in slag	0.18	39.10	23.49	0.04	-	62.81	"a"	2
CE-1	Slag	Clear phase, dark in slag	0.20	69.01	0.47	0.25	0.02	69.95	"b"	2
CE-2s	Metal	Metal	99.38	0.06	-	-	0.02	99.47		
CE-2s	Metal	Dark phase in metal	79.66	-	-	0.01	20.23	99.91		
CE-2s	Matte	Matte	79.27	0.02	-	-	20.36	99.66		
CE-2s	Matte	Metal in matte	99.75	0.02	-	-	0.054	99.83		
CE-2s	Slag	Acicular phase in slag	0.06	47.22	0.34	15.73	-	63.36	"a"	3
CE-2s	Slag	Magnetite in slag	-	58.67	7.05	0.09	-	65.81	"b"	3
CE-2s	Slag	Dark phase interstitial	0.07	18.31	9.47	27.10	-	54.95	"c"	3
CES-5	Matte	Clear phase	75.69	0.89	-	0.02	20.66	97.27		
CES-5	Matte	Round particle in matte	99.38	0.18	0.01	0.01	0.05	99.63		
CES-5	Slag	Clear acicular, slag	0.08	49.84	0.10	14.23	-	64.25		
CES-5	Slag	Dark phase	-	38.71	23.78	0.14	-	62.63		
CES-5	Slag	Matte in slag	82.62	0.61	0.05	0.05	8.88	92.51		

## II- Batch tests:

In the batch tests the following variables were studied:

a). Copper ferrite addition of a constant matte/slag ratio for different silica ratios. In all tests, it was kept constant the temperature (1300°C), and the time (1 hr).

Silica addition was equivalent to 0, 12.5 and 25 wt-%, with respect to the mass of matte + slag. Copper ferrite addition was 0, 8.3, 16.7, 25.0 and 33.3 wt-%; in each test.

All of the melt had good separation of two phases (matte and slag), except that the test with 0.0 ferrite and 25 wt-% of silica addition due to higher melting point of the melt. The copper content in the resulting matte and slag phases is shown in Figures 4 and 5.



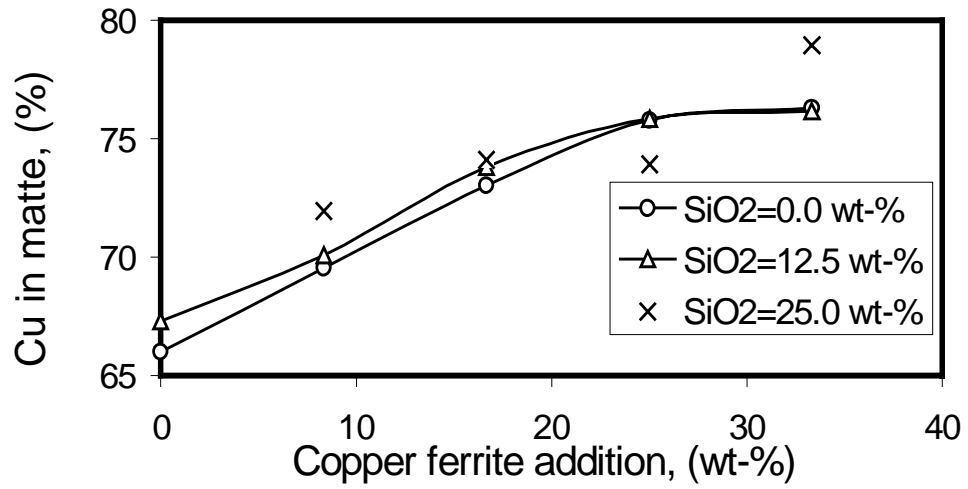


Fig. 4: Copper content in the matte phase as a function of the ferrite addition for difference silica ratios (slag ratio of 30 wt-%, 1300°C, 1 hr and nitrogen atmosphere).

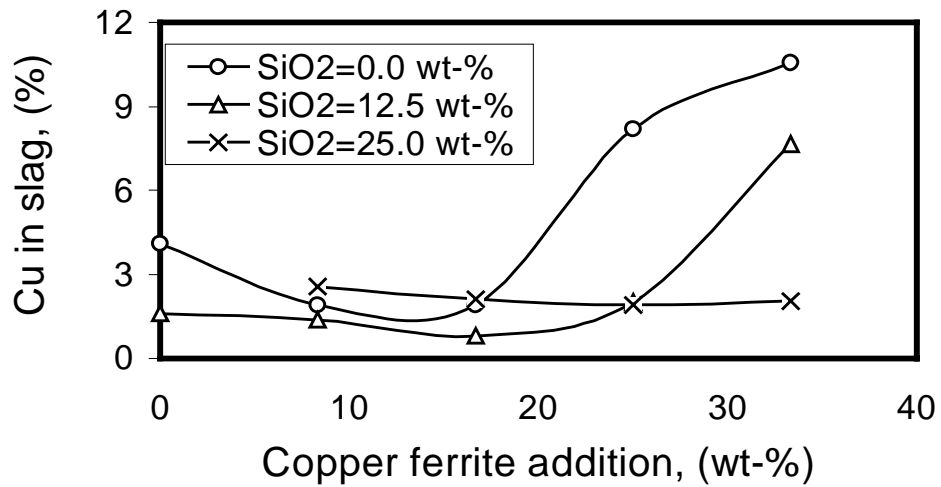


Fig. 5: Copper content in the slag phase as a function of the ferrite addition for difference silica ratios (slag ratio of 30 wt-%, 1300°C, 1 hr and nitrogen atmosphere).

The chemical analysis indicates that the copper grade in the matte increases as the copper ferrite addition increasing. The silica does not have much influence in the copper grade in matte, since the matte can dissolve all copper ferrite, that is, there is enough FeS in the matte for the exchange of oxygen and sulfur between the ferrite and the matte.

Nevertheless, it is evident that silica has a strong effect on the copper content in the slag. When no silica or only 12.5 wt-% was added to the system, the copper in the slag increases with the

increase of the copper ferrite addition, since the more copper ferrite is dissolved in matte, the more magnetite is produced. For the condition of low of silica in the slag, magnetite does not get converted to fayalite, therefore a high copper content is found in the slag. For the same reason, for high silica addition (above 25 wt-%), the slag becomes saturated in silica even for the maximum copper ferrite addition of 33.3 wt-%. In these cases the copper content in the slag is near constant.

b). Tests with different slag/matte ratios were performed under constant conditions of temperature of 1300°C, 1 hr, silica addition of 12.5 wt-% with total weight of matte and slag, and nitrogen atmosphere. The ratio of slag which defines as slag/(slag + matte) was 20, 25, 30, 35 and 40 wt-% with total weight of matte and slag, respectively. The ferrite additions were 16.7 and 33.3 wt-%. The copper content in the matte is shown in Figure 6. It can be observed that increasing the amount of slag increases lightly the copper grade in the matte.

c). The influence of reaction time on the copper in the matte was studied under constant conditions of temperature of 1300°C, slag/(slag + matte) ratio of 30 wt-% and silica addition of 12.5 wt-%. The reaction time was 0.5 to 4.0 hrs and the ferrite addition was 16.7 and 33.3 wt-%, respectively. The copper content in the matte is shown in Figure 7. It can be seen that the reaction time has not much effect on the interaction between copper ferrite and matte/slag for a reaction time above about 0.5 hrs, which indicates that the oxygen – sulfur exchange reaction proceed with high velocity.

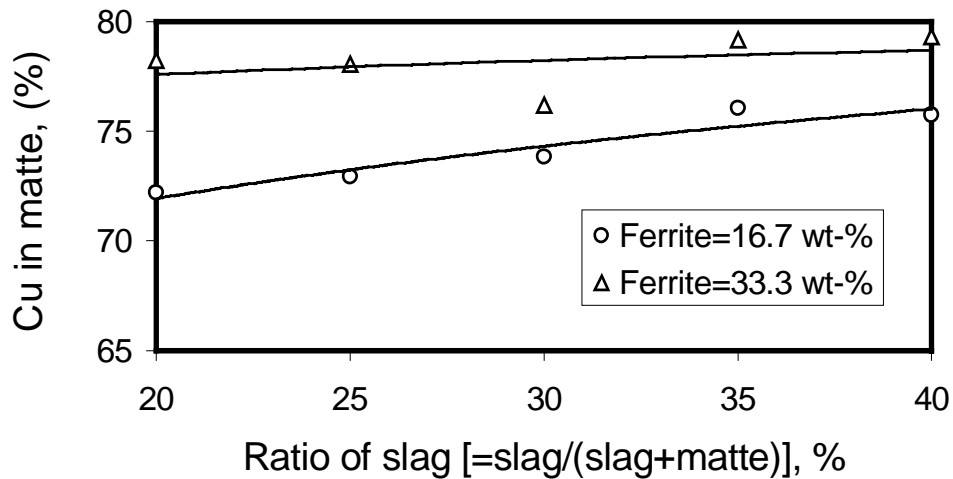


Fig. 6: Copper content in the matte as a function of the slag/(slag + matte) ratio for different ferrite addition, (silica addition of 12.5 wt-%, 1300°C, 1 hr and nitrogen atmosphere).

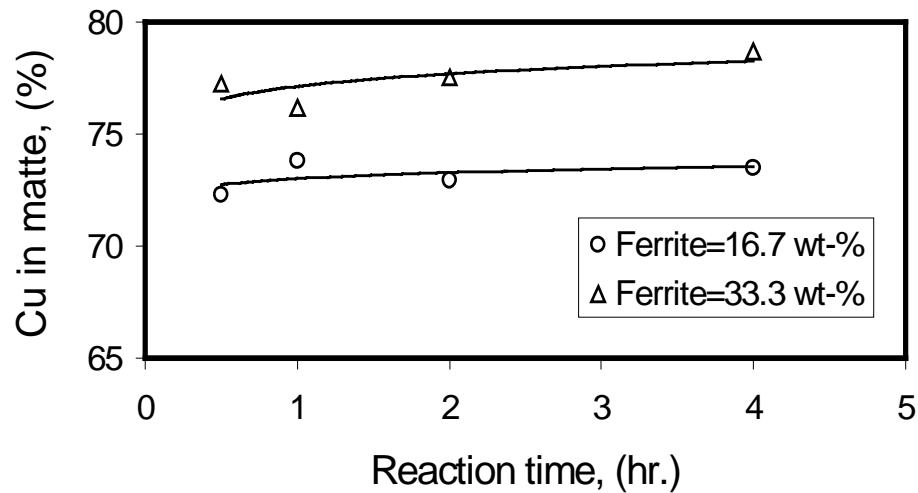


Fig. 7: Copper content in the matte as a function of the reaction time, for different ferrite addition, (slag ratio of 30 wt-%, silica addition of 12.5 wt-%, 1300°C, 1 hr and nitrogen atmosphere).

### III-. Kinetic tests:

This type test were performed according to the following procedure:

- Melt a blend of matte and slag with a slag ratio of 30 wt-%, 12.5 wt-%  $\text{SiO}_2$  addition at 1300°C and under nitrogen atmosphere,
- Samples were taken with a stainless steel rod after an half hour, when the temperature has reached 1300°C. The ferrite addition with a weight ratio of 16.7 wt-% was injected into the surface of the melt,
- Slag samples were taken every 3 to 5 min, without stirring the melts. The copper in the slag sample represents the dissolution rate of copper ferrite in the bath. The results obtained are shown in Figure 8.

Results indicate that the dissolution of ferrite in the matte/slag bath is quite fast. The copper content in the slag shows a large increasing after adding the ferrite, following by a rapid decreased. It is evident that the interaction of the ferrite with the melt becomes complete in 5 min. However, the copper content in the slag as a function of time shows considerable scatter, probable associated to the stirring the melt when the samples were taken.

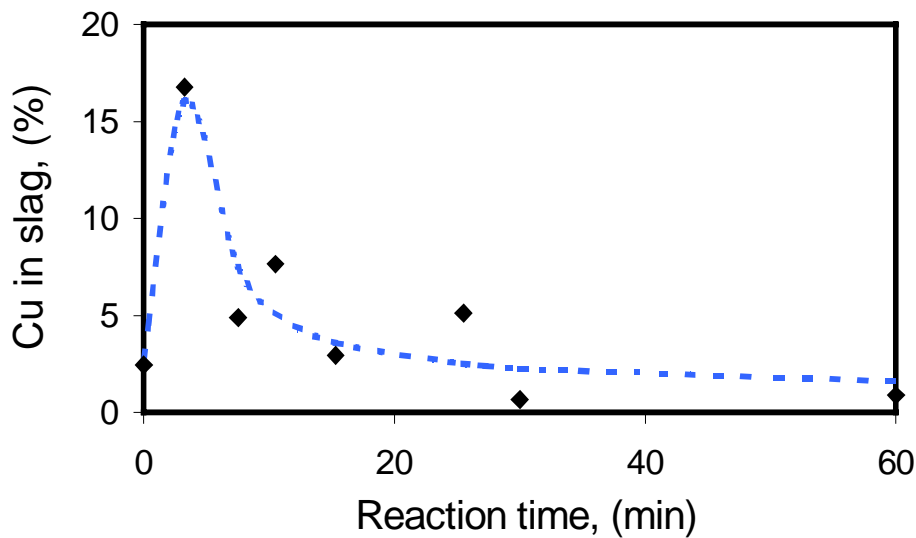


Fig. 8: Copper content in the slag as a function of the reaction time, for ferrite addition 16.7%, (slag ratio of 30 wt-%, silica addition of 12.5 wt-%, 1300°C, 1 hr and nitrogen atmosphere).

## Conclusions

The following conclusions can be drawn from this study:

- Copper ferrite dissolves easily in baths of matte/slag at 1300°C under neutral atmosphere. Copper contained in the copper ferrite is transferred into the matte phase increasing its grade as well replacing the iron of the matte, while the iron from copper ferrite is transferred into the slag phase to form fayalite by reacting with silica, or form magnetite.
- The dissolution rate of copper ferrite in the smelt is relatively fast.
- The slag composition is important in decreasing the copper content in the slag phase. Results show that silica addition decreases the copper losses in the slag, since it reacts with the iron oxide of the copper ferrite to form fayalite. This can decrease the magnetite content that results in decreasing the copper losses in the slag.
- Since there are many variables in the system ferrite/matte/slag/gas, in order to obtain a good understanding some additional studies are required, particularly the structure, composition as well as the distribution of the main elements in each phase under different conditions.

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