

RECOVERY OF IRON-MOLYBDENUM ALLOY FROM COPPER SLAGS

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ABSTRACT

Typical copper smelting slag contains molybdenum in the range 0.01- 0.50% which is the grade for primary mine production of molybdenite. Therefore, recycling copper slags containing molybdenum includes direct reduction of the slag process, which is based on the smelting reduction to produce two phases; a carbon saturated iron-molybdenum-copper alloy and a second slag. The iron rich alloy could be used in the special steel industry, which is the most important market for molybdenum. However, the copper content has to be decreased in order to be used in metallurgical refinery. Therefore, this work studies the feasibility of removing copper from the iron-molybdenum alloy.

Key Words: *Reduction; Copper slag; by-product; molybdenum recovery; direct reduction.*

INTRODUCTION

Currently, economical and environmental issues along with high metals consumptions, have imposed the development of effective and inexpensive methods for the recovery of valuable metals from secondary sources. Chile produces more than 3.5 million ton/year of copper slag containing copper ranging from 0.77% to 1.32%, molybdenum in a range up to 0.4% and large amounts of iron and silica [1]. Therefore, copper slags show an economical potential for recycling by using metals extraction processes.

The presence of molybdenum in some copper slags is due to inefficiencies in the flotation step for separating molybdenite from copper sulfide minerals prior to smelting. Typical copper slags show that the molybdenum is dispersed throughout the iron oxides phase and, at the copper-making step the molybdenum is highly oxidized and associated to the magnetite structure [2].

Therefore, direct reduction for treating copper slag has been reported to recover an iron molybdenum alloy [3]. The copper fayalite slag is reduced with granulated coke at 1460°C, and residence time varying between 30 and 90 minutes under open air conditions. The thermodynamic behavior of reduction process is shown in Figure 1.

In this figure, it can be observed that copper oxide is reduced with a lower energy requirement than iron oxides so that iron is expected to be saturated with copper, and at the reducing conditions, indicated in Figure 1, molybdenum is also reduced and dissolved in the iron-rich alloy. The solubility of carbon in pig iron varies with temperature and at 1400°C is 5%wt approximately according to the of the Fe-C binary system.

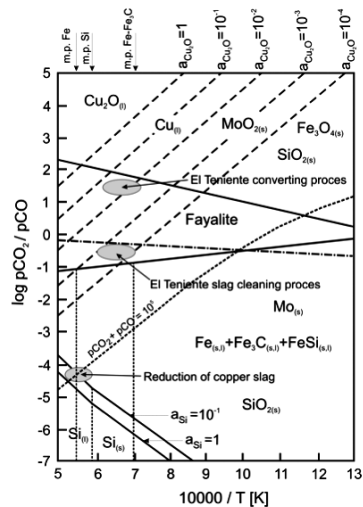


Figure 1: Potential diagram for Cu-O-C, Fe-O-C and Mo-O-C and silica systems [4]

The copper slag from the SCF was mixed with CaO and coke, and it was processed in the temperature range of 1350°C and 1460°C. As result, two phases along with the unreacted coke were obtained [5]. An iron-rich metallic phase and a Portland type slag phase as shown in Figure 2.

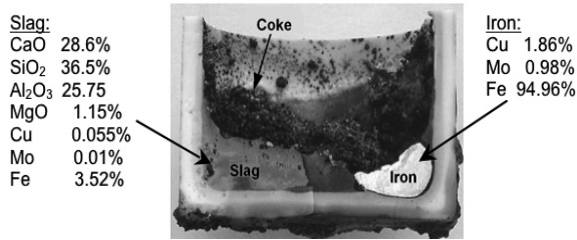


Figure 2: Slag and iron-rich alloy obtained at 1460°C in an alumina crucible [5]

Although, the metallic phase showed three different phases in a very homogeneous dispersion, the matrix is the Fe-Cu alloy with 98,1% of iron and 1,9% of copper with minor inclusions of a copper rich matte of 3%Fe; 25,9%Cu and 32,8%S and an iron rich matte of 97,9%Fe; 1,3%Cu and 0,9%S. However, the copper content is still high for direct application in the steel making industry. Therefore, the obtaining of iron- molybdenum alloy was study by removing copper from the reduced copper slag.

THEORETICAL CONSIDERATIONS

In the molten state, the slag is chemically homogenous with the exception of copper sulfide and copper, which are entrained in the liquid. Also it is well known that sulfur affinity for copper is greater than for iron, and to recover copper oxide dissolved in the slag the following exchange reaction is used:



However, in the presence of carbon the components of the slag are reduced as follow



Where M is Fe, Cu, Mo, among others, and a carbon saturated iron-molybdenum-copper alloy is obtained. Iron also dissolves some sulfur, and its content decreases with the carbon increasing as shown in Figure 3(a) at 1500°C.

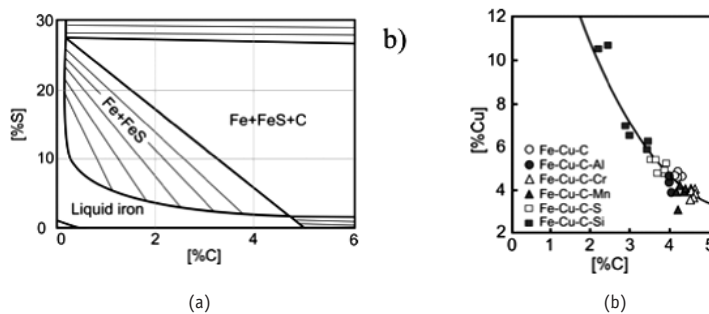


Figure 3: Effect of carbon content on: (a) the dissolution of sulfur in liquid iron at 1500°C and (b) the dissolution of copper in various liquid iron alloys at 1200°C [6]

In this figure, it can also be observed that under carbon saturation condition the sulfur content in liquid iron is the minimum. In Figure 3(b), the effect of carbon on the copper content is shown for various iron-rich alloys at 1200°C. In this figure, it can be observed that copper content decreases in the alloy with the increasing of carbon in liquid iron suggesting that copper could be minimized in the iron-molybdenum alloy by adding a sulfur base flux under carbon saturation condition

The dissolved copper in the iron-rich alloy, in the presence of sulfur based flux is redistributed between the new formed slag, and the iron alloy, and it will be concentrated in the phase containing higher sulfur concentration to form cuprous sulfide according to the following elemental reaction



And the equilibrium constant for Equation 5 can be written as follows

$$K_{(5)} = \frac{a_{\text{CuS}_{0.5}}}{a_{\text{Cu}} a_{\text{S}}^{0.5}} = \frac{\gamma_{\text{CuS}_{0.5}} X_{\text{CuS}_{0.5}}}{\gamma_{\text{Cu}} X_{\text{Cu}} a_{\text{S}}^{0.5}}$$

Therefore, the copper distribution coefficient is expressed as follows

$$L_{\text{Cu}} = \frac{(\text{mass}\% \text{Cu})_{\text{slag}}}{[\text{mass}\% \text{Cu}]_{\text{alloy}}} = CK_{(5)} a_{\text{S}}^{0.5} \frac{\gamma_{\text{Cu}}}{\gamma_{\text{CuS}_{0.5}}}$$

Thus, the copper distribution depends on temperature and sulphur activity therefore in addition to iron sulphide; sodium sulphide is used as flux to increase the copper distribution coefficient as shown in Figure 4.

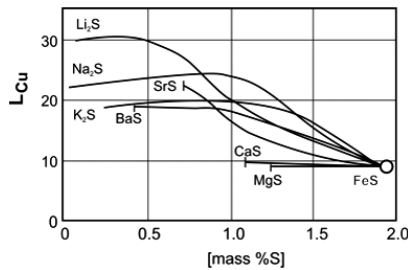


Figure 4: Copper distribution coefficient as function of sulfur content at 1400°C [6]

Figure 4 shows the effect of sulfur on copper removal from carbon saturated liquid iron at 1400°C, and it can be observed that the best results are obtained by adding lithium and sodium sulfide.

EXPERIMENTAL

The typical copper slag composition was synthesized and modified by adding lime and alumina to move the composition from point A to point B shown in Figure 5. After reduction, the metals oxides or sulfides will pass onto the metal phase, and the new slag will be concentrated in silica, alumina and lime causing an increasing in the melting point of the final slag, as shown in Figure 5. In this figure, the point B represents the composition of the slag after reduction. The slag compositions are shown in Table 1.

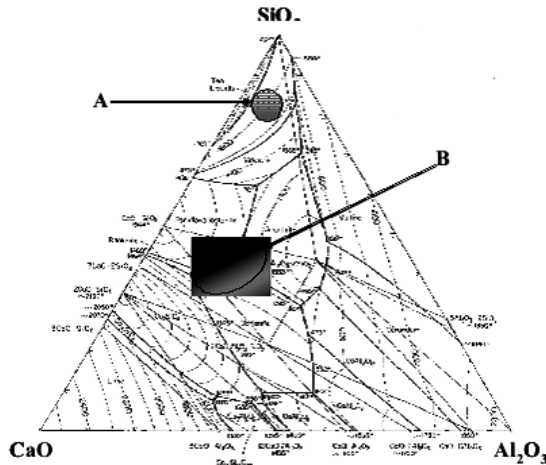


Figure 5: Ternary $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ system

The modified slag is sinterized in a magnesite crucible at 900°C in a vertical furnace during 3 hrs, and after slow cooling in the furnace, it is mixed with carbon and reduced in a graphite crucible at 1400°C under an argon atmosphere.

Table 1: Typical copper slag composition compared with the modified slag

Component	Al_2O_3	CaO	SiO_2	Cu_2O	FeO	Fe_3O_4	MoO_2	FeS
Synthesized (wt %)	3.4	1.1	30.7	1.24	46.89	8.4	0.4	1.37
Modified (wt %)	6.78	27.2	22.67	0.97	34.64	6.26	0.3	1.01

After reduction, the obtained iron alloy was decopperized by using mix of iron sulfide and sodium sulfide as flux in a graphite crucible at 1400°C in a vertical furnace for 3 hrs. The flux was used in different proportions and in a rate alloy:flux = 1:1.

RESULTS AND DISCUSSION

The result of the slag reduction is shown in Figure 6, and in this figure it can be seen the three phases; slag, iron alloy and copper alloy. However, it is also shown that molybdenum concentrates in the iron rich phase and its content remain constant with reduction time. Copper content is reduced in the slag phase with the increasing of reduction time.

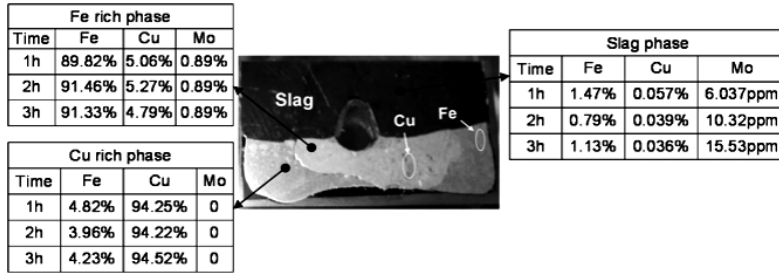


Figure 6: Photograph of the metallic alloys in equilibrium with the slag at 1400°C

However, the metallic alloys are not clean separated therefore in order to obtain a clean separation between the two metallic alloys, different iron-copper ratios were tried, and the results of melting iron and copper are shown in Figure 7.

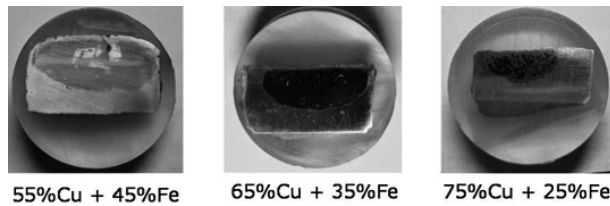


Figure 7: Photograph of the two metallic alloys with different iron-copper proportions

The best phase separation is obtained when copper content is higher than 65%, and the separation results better as the copper content increases suggesting the possibility processing slags with higher copper content, such as converting slags.

In Figure 8 SEM analysis of the obtained alloy shows that iron and copper are fully complementary and sulfur is mainly associated with copper suggesting that this element can be removed by equilibrating the iron-rich alloy with a sulfur based flux. Thus, iron sulfide with different sodium sulfide addition is used to remove copper from the iron alloy obtained by carbon reduction.

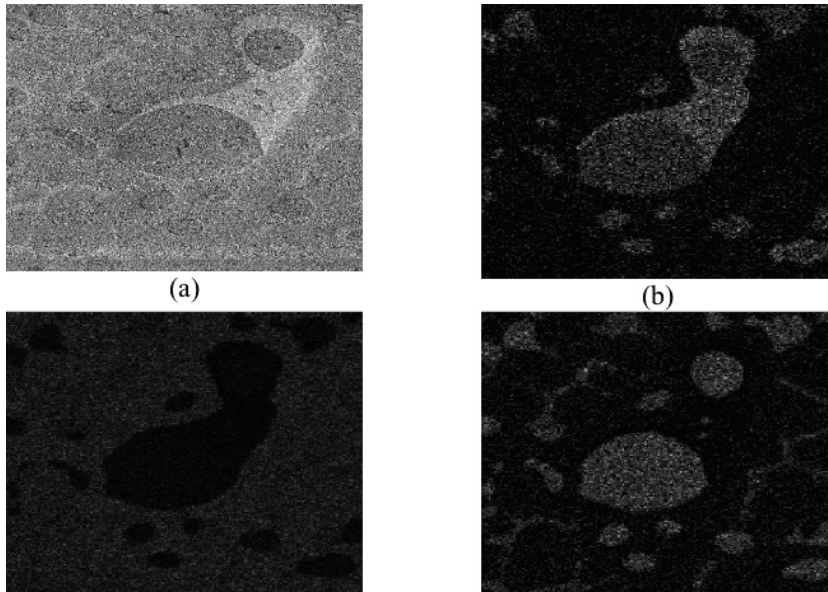


Figure 8: SEM Analysis of iron alloy; (a) image, (b) copper, (c) iron and (d) sulfur

The results of removing copper from the iron alloy by using $\text{FeS-N}_2\text{S}$ flux is shown in Figure 9, and it can be observed that copper content decreases in the iron alloy and its content vary from 0.98 to 1.11% as sodium sulfide in the flux increases. Also, sulfur content in the iron phase decreases drastically with the increasing of sodium sulfide. The maximum copper distribution is obtained with a mix $\text{FeS-Na}_2\text{S}$ of 35% of sodium sulfide.

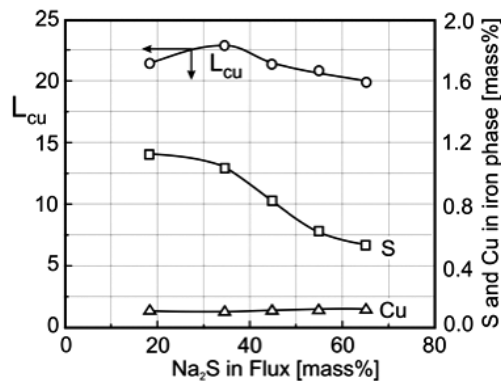


Figure 9: Effect of Na_2S in the flux on de S and Cu content in the iron phase and copper distribution

FINAL REMARKS

Slag recycling by direct reduction with carbon produces a carbon saturated iron alloy which contains copper and molybdenum, and a copper phase. The molybdenum contained in the copper slag is concentrated in the iron phase and sulfur is concentrated in the copper alloy.

Since iron content in the slag is higher than copper content, the amount of iron phase obtained after the slag reduction is larger than the obtained mass of copper, and copper is dispersed in fine particles in the iron phase causing phase separation problems.

Due to the higher affinity of copper for sulfur compared with the other metallic components in the slag, it is possible to remove copper from the iron alloy obtained by direct reduction. Thus, sodium sulfide added to iron sulfide has shown to be an effective flux for decreasing the copper content in the iron alloy from almost 5% to 0.98% using a mix FeS-Na₂S of 35% of sodium sulfide.

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