RECOVERY OF MOLYBDENUM FROM ROASTED COPPER SLAGS

Dusan Busolic, Fernando Parada, Roberto Parra,
Arcadio Ulloa & Juan Carlos Carrasco
University of Concepcion, Chile

José Palacios
University of Atacama, Chile

Andrés Reghezza, Carlos Caballero & Jorge Zuñiga
Division Codelco-Norte, Chile

Mario Sanchez
Hatch, Chile

ABSTRACT

Recycling copper slag to recover metals has been focused on copper, which is contained in the range of 0.77 to 1.32% however some slags also contains molybdenum in amounts up to 0.4% transforming the copper smelting slags into a potential raw material for the development of new processes to obtain new products. In this regard, copper slags were treated by using roasting-leaching process in order to recover the molybdenum content in the slag. Oxidative roasting is used to convert the iron oxide into insoluble hematite, and copper and molybdenum into the soluble form in acidic solution. Since molybdenum is associated to iron oxide spinel type phase, its recovery was influenced by the magnetite content in the slag during the leaching process. Sulphuric acid was used for leaching the slag, and molybdenum shows recovery higher than 80%. Thus, the obtained results show the feasibility for recovering molybdenum by using two step processes, oxidative roasting followed by an acidic leaching.

Key Words: *Reduction; Copper slag; by-product; molybdenum recovery; roasting; zero waste.*

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.

Various hydrometallurgical methods have been proposed for extracting metals from the copper slags, including direct leaching in sulfuric acid or ferric chloride [2, 3]. Roasting of the slag with sulfuric acid, ammonium sulfate, ferric sulfate or in reduction conditions followed by acidic leaching have also been reported [4, 5, 6, 7, 8]. However, all these applications were proposed to recover copper and cobalt or nickel and very limited data have been reported on recovery of molybdenum from copper slags via hydrometallurgical processes.

However, roasting of low grade molybdenum concentrate with lime or soda ash has been proposed to convert molybdenum to molybdate [9, 10, 11], and roasting of spent catalysts with soda ash has also been investigated for recovering soluble molybdate [12]. Thus, the most efficient route to produce molybdenum is the roasting of molybdenum concentrates to obtain molybdenum trioxide and the subsequent reduction of the MoO_3 to get the metal. Therefore, the main objective of this work is to study the feasibility of recovering molybdenum from copper slag by using oxidative roasting followed by an acid leaching.

THEORETICAL CONSIDERATIONS

The mineralogical composition and phases present in copper slags depend on several factors such as; type of ores processed, type of furnaces and cooling methods [13]. Slow cooling result in a significant crystallization of slag components, forming a large number of different mineral phases. The lower the cooling rate, the larger the mineral phases grow [14], and the fast cooling may produce an amorphous slag and hence the slag is more homogeneous in metal distribution. When copper slag is crystalline, the major phases are usually fayalite along with other silicates and metals oxides. Copper is in the form of oxides or sulfides or a mixture of them.

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 as shown in Figure 1.

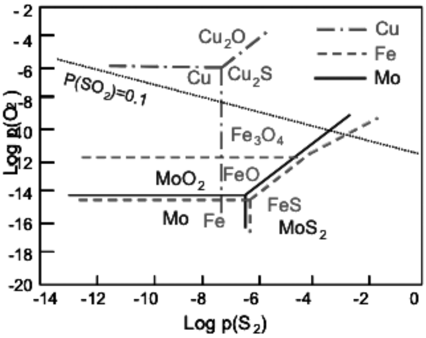

Figure 1 Stability diagram of Cu-O-S, Fe-O-S and Mo-O-S systems at 1300°C

The molybdenum present in the slag is due to inefficiencies in the flotation step for separating molybdenite from copper sulfide minerals prior to the smelting step. Also, it was reported that molybdenum is bound in a spinel which belong to the $2FeO{\cdot}MoO_2$-Fe_3O_4 series, in which it presents a low degree of leaching [15].

In the molten state, the slag is chemically homogenous with the exception of some copper and copper sulfide which are entrained in the liquid, and it retains a homogeneous state when is rapidly cooled. When the slag is cooled slowly, at least two solid phases may form; a ferrous silicate and oxides phases. Thus, copper, copper sulfide and copper oxide in highly oxidative conditions are oxidized according to the following reactions

$$Cu_2O + \tfrac{1}{2}O_2 = 2CuO \tag{1}$$

$$Cu_2S + 2O_2 = 2CuO + SO_2 \tag{2}$$

$$Cu + \tfrac{1}{2}O_2 = CuO \tag{3}$$

Also, iron silicates decompose when heated at temperatures between 800 and 1100°C in an oxygen atmosphere as follows [16].

$$2FeO{\bullet}SiO_2 + 1/2O_2 = Fe_2O_3 + SiO_2 \tag{4}$$

$$2FeO{\cdot}SiO_2 + 1/3O_2 = 2/3Fe_3O_4 + SiO_2 \tag{5}$$

The molybdenum bound in the iron oxide spinel is liberated from this complex compound according to te following reaction

$$Fe_xO_y{\cdot}MoO_2 + (0.75x\text{-}0.5y\text{+}0.25)O_2 = 0.5xFe_2O_3 + MoO_3 \tag{6}$$

Therefore, oxidizing roasting will produce the decomposition of iron silicates forming hematite and silica, both insoluble in the acidic solutions. Thus, the product of roasting process is easily treated by acid leaching at room temperature with an efficient recovery of molybdenum and remaining copper contained in the slag.

EXPERIMENTAL

A series of copper smelter slag, including slow cooled and rapidly cooled slags, was chemically characterized, and the results are shown in Table 1.

Table 1: Chemical characterization of the series of copper smelter slags

Slag	Fe_3O_4 (%)	Cu (%)	Fe (%)	Mo (%)
Slag I-S	23.4	1.21	42.2	0.27
Slag I-R	1.4	0.85	48.4	0.30
Slag II-S	14.1	1.32	50.7	0.20
Slag III-S	7.9	1.19	45.7	0.40
Slag III-R	13.6	0.77	43.0	0.40

Slag S series correspond to the slow cooled slags and Slag R series correspond to the rapidly cooled slags.

The solubility of the slags was studied by using leaching tests were the extraction of iron and molybdenum were determined. The leaching tests were run under the following conditions:

Temperature	H_2SO_4	L/S ratio	Grain size	Time
18 – 20°C	150 g/l	10/1	100% -200 #	2 h

The roasting and leaching tests of the slag series were run in a fluid bed and fix bed laboratory roaster under the following conditions

Roasting:	**Temperature**	**% O_2**	**% SO_2**	**Grain size**
	700°C	18	10	100% - 400#
Leaching:	**Temperature**	**H_2SO_4**	**L/S ratio**	**Time**
	18 – 20°C	25 g/l	10/1	2 h

RESULTS AND DISCUSSION

Slag characterization by using SEM technique is shown in Figure 2, and the microprobe analysis shows complex precipitated oxides and silicates, where the molybdenum form a separate phase of Fe-Mo-O type, with iron content between 52.03 and 63.57%, and a Mo content in the range of 1.25 and 6.35% as shown in phases 1, 2 and 4. Also, these phases have low silica content suggesting that iron could be present in a spinel structure of magnetite type, such as $FeO·MoO_2$-Fe_3O_4. Phase 3 shows a glassy iron silicate type silica rich solution with low content of molybdenum.

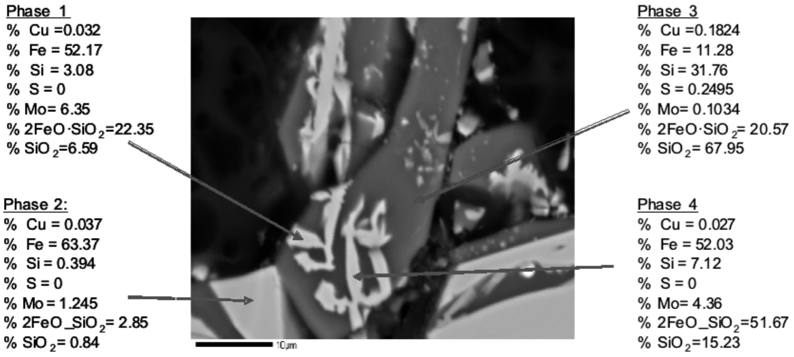

Figure 2: Slag characterization by using SEM technique

Figure 3 shows the electronic microprobe analysis of the slag, and it can be observed the distribution of Fe (a) and Mo (b).

In Figure 3(a), it is shown the iron distributed throughout the glassy iron silicate phase and the molybdenum is dispersed along this silicate phase as shown in Figure 3(b) and, it can be observed that molybdenum distribution is closely associated to the iron distribution path in the slag.

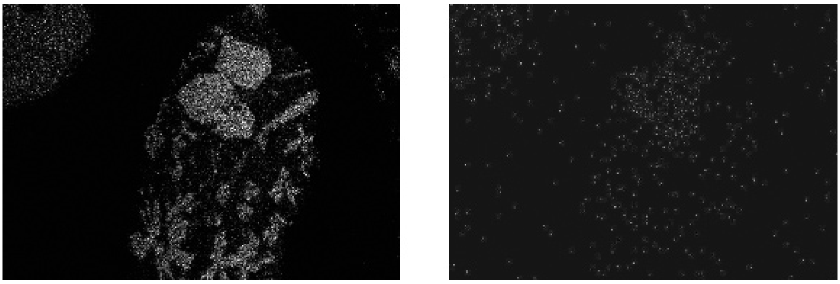
(a) (b)

Figure 3. SEM analysis of the slag: (a) iron distribution and (b) molybdenum distribution

The results of the solubility tests of the slags are shown in Table 2, and it can be observe that the molybdenum extraction increases as the magnetite content in the slag decreases however the iron extraction is also elevated.

Table 2: Extraction of iron and molybdenum after slag acid leaching

Slag	Fe_3O_4 (%)	Extraction of Fe (%)	Extraction of Mo (%)
Slag I-S	23.4	82.0	22.0
Slag I-R	1.4	65.0	95.0
Slag II-S	14.1	57.0	30
Slag III-S	7.9	77.0	18
Slag III-R	13.6	47.0	30

Slag S series correspond to the slow cooled slags and Slag R series correspond to the rapidly cooled slags.

Thus, high iron extraction indicates the dissolution of great part of iron silicates causing elevated acid consumption, and elevated silica presence in the solution with the further difficulties in the later molybdenum separation by ionic exchange. The sulphuric acid consumption was in the range of 800 and 1000 kg/ton of slag, and the silica concentration in the solution varies between 10 and 15 g/lt.

The results of the slags containing different magnetite content treated by roasting-leaching process are presented in Figure 4, and it can be seen that molybdenum recovery increases with the decreasing of magnetite content in the slag.

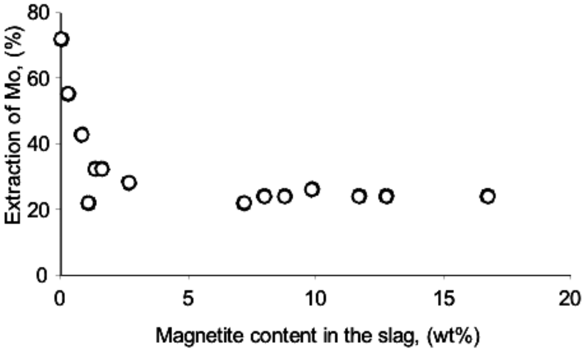

Figure 4: Effect of the magnetite content in the slag on the molybdenum recovery

Since molybdenum is associated to iron oxide spinel type, which is stable to the acid leaching, it needs to be oxidized to the soluble form of MoO_3 for being dissolved during the leaching process and iron is oxidized to hematite to permit selective leaching of the molybdenum values.

During oxidation, the iron silicate is converted to ferric oxide, ferrous oxide and cristobolite. Thus, the molybdenum is released from the iron spinel phase type and also is oxidized to its highest oxidation state and reacts to form thermally stable compounds that are not limited to be selectively leached from the iron oxides and the silica.

It should be noted that above the melting point of the slag, these compounds are soluble in one another, and due to the oxidation state of the copper slag, determined by the FeO and Fe_3O_4, it can be conclude that molybdenum is present in the reduced state Mo^{+4} in the presence of magnetite. This conclusion can be drawn on the basis of the following reaction:

$$3FeO + MoO_3 = Fe_3O_4 + MoO_2$$

The presence of MoO_2 is hard to be proven analytically because of the very low concentrations of molybdenum in the slag, compared with the much higher concentrations of iron oxides in the oxidation states Fe^{+2} and Fe^{+3}, also present. However, it is clear that the slag that crystallizes with the spinel magnetite, in which a solid solution of MoO_2 is present, exhibits a very low leaching value for molybdenum.

FINAL REMARKS

The iron is distributed throughout the glassy iron silicate phase as well as molybdenum, and molybdenum distribution is closely associated to the iron distribution path in the slag. Thus, molybdenum is associated to iron silicate and iron oxide spinel type phases.

Since iron oxide and silica are the major constituents of the slag, oxidation destroys the slag structure to produce hematite and cristobolite. The other minor oxides components should appear with the silica phase. Thus, silicates and iron oxide are the two basic phases expected in the completely oxidized slag

As a result of the slag oxidation, it is understood that the molybdenum and iron are oxidized to their highest state, so that, molybdenum is selectively leached from the oxidized particulate slag by using an acid leaching process.

The presence of magnetite in the slag suggests that molybdenum is fixed in the spinel solid phase, which shows a very low solubility in acidic solutions. However, the results of the solubility tests of the slags show that the molybdenum extraction increases as the magnetite content in the slag decreases.

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