

DETERMINATION OF THE BEHAVIOUR OF VALUABLE METALS DURING THE CONTROLLED COOLING OF COPPER SMELTING SLAGS TO CLARIFY THEIR RECOVERY BY GRINDING AND FLOTATION

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Introduction

During the first stage of the pyrometallurgical production of metallic copper from copper sulphide concentrate, large amounts of slag are generated and subsequently treated in electric furnace in order to recover the entrained copper, which consists of suspended matte/metal droplets due to turbulence and the presence of solid magnetite. The treatment results in the production of two immiscible phases, a copper matte which is sent to the converting stage, and a reduced slag that is usually discarded although it still contains large amounts of iron and silica, and minor valuables elements such as copper (0.6 to 1.3 wt%), molybdenum (up to 0.5 wt%), and silver (2 to 20 ppm), between others¹⁻⁴.

In the smelting stage of copper sulphide concentrate, molybdenum sulphides are easily oxidised and most of this element goes to smelting slag⁵ especially at higher copper matte grade⁶. Molybdenum is preferentially present in high iron and low silica copper slags, which suggests that it forms part of a spinel structure type magnetite⁷. In the case of silver, its distribution coefficient between matte and slag varied between 100 and 200 in the matte grade range of 50 to 70 wt% of copper¹.

The relevant content of valuables into the discarded slag³ and the increase in the cost of electricity have promoted the alternative process to treat smelting slags involving controlled cooling, grinding and froth flotation, where the cooling rate is an important variable of control because it has effects on sedimentation and coalescence of the entrained valuables, and crystallinity of the slag matrix, as well. As a result of the controlled cooling stage, a sulphur phase of copper matte precipitates and solidifies, and then it is sent to the converting stage; also a remaining slag is formed, solidified and sent to grinding and froth flotation. Thus, the cooling rate determines the generation of different products, in terms of mass and composition.

Slow cooling may result in a significant crystallisation of slag components, forming a large number of different mineral phases due to diffusion and coalescence of the small particles, forming a sulphide phase. Fast cooling may produce an amorphous slag

where a more homogeneous metal distribution occurs⁸⁻¹⁰, encapsulating the valuable particles in a glassy phase making difficult their subsequent recovery¹⁰. In this case, the copper content in the slag is higher, but energy consumption during grinding will increase due to ductility of copper. The objective of this research was to determine the behaviour of molybdenum and silver contained into copper smelting slag during its controlled cooling process at two different rates to clarify their later recovery by grinding and froth flotation.

Experimental

In this work, experiments considering 70 g of industrial copper smelting slag doped with 0.3, 1.4 and 2.4 and 10, 100, 200 ppm of high purity molybdenum and silver, respectively, were charged in a high alumina crucible and melted at 1300 °C under controlled partial pressure of oxygen of 10⁻⁸ atm. according to industrial conditions of Teniente Converter technology. The molten slags were kept inside the furnace for 8 hours to reach the equilibrium and then taken outside and cooled at two different rates of, instant quenching into water (fast cooling), and N₂ natural convection (slow cooling). Finally, after solidification, representative samples of formed matte and remaining slag were taken and characterised by using optical microscopy, SEM, XRD, XRF and ICP.

Results and Discussion

The main phases and their corresponding composition normalised to 100 wt% for the slags doped with 2.4 wt% of Mo and 200 ppm of Ag quenched into water and natural convection were obtained by crossing results from XRD and XRF/ICP analyses, they are shown in Table 1. In addition, in some cases SEM was used to clarify some phases and the distribution of valuable minor elements between them, Figure 1 is shown a SEM photo of a remaining slag.

Table 1: Quantitative XRD analyses of remaining slag obtained after cooling smelting slag doped with 2.4 wt% Mo and 200 ppm of Ag in the charge

Type of cooling rate	Main phases (wt%)	
	Fayalite (Fe ₂ SiO ₄)	Magnetite (Fe ₃ O ₄)
Quenching	94.2	5.8
Natural Convection	59	41

From the results, it was noted that at slower natural convection cooling rate increased the content and size of the magnetite crystals in the remained matrix slag, and also copper appears more widespread on it, this can be attributed to the greater sedimentation and coalescence of copper entrained species, metallic and sulphide, towards the formed matte phase on the bottom of the crucible.

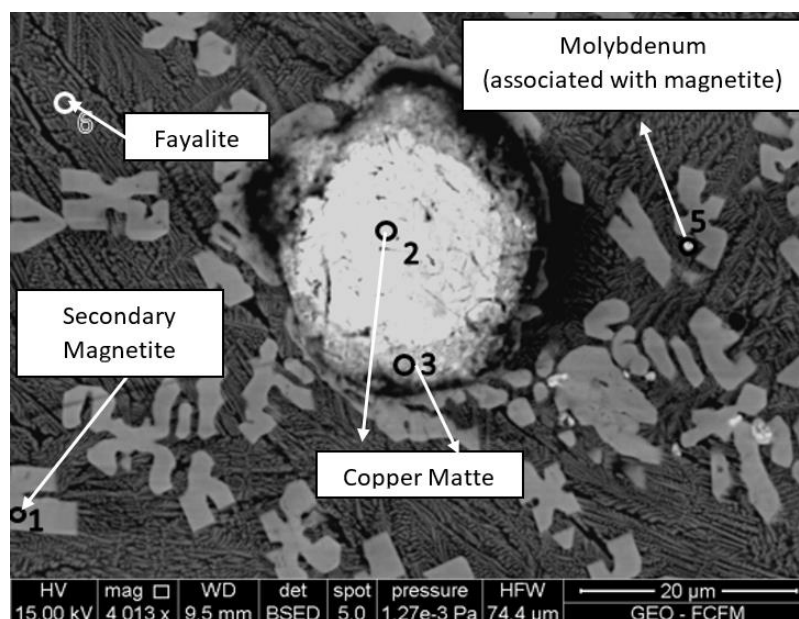


Figure 1: SEM of remaining slag obtained after cooling at natural convection rate a smelting slag doped with 2.4 wt% of Mo and 200 ppm of Ag in the charge

Distribution coefficient of Silver and Molybdenum

Regarding, the distribution of valuable element “x” between remaining slag “s” and formed matte “m”, defined as $D_x^{s/m}$, where x could be silver or molybdenum, slower cooling rate of smelting slag increases metallurgical recovery of silver towards the formed matte phase on the bottom of the crucible due to the increase of sedimentation and coalescence time of drops associated with copper species and the affinity of silver for this element, nevertheless, the recovery of molybdenum into the matte is slightly negative affected because most of this element tends to be oxidised forming an spinel phase together with magnetite in the remaining slag. Both previously mentioned effects for silver and molybdenum increase with increasing the amount of them, as valuable minor elements, into the initial copper smelting slag.

According to the obtained results, it can be expected that an slow cooling of smelting slag may enhanced the recovery of copper and silver into the produced button matte that is sent to converting stage, nevertheless it would leave few copper species dispersed on the remaining slag that has to be later treated by grinding and froth flotation, since most contained molybdenum tends to quickly be oxidised, it will be caught by magnetite into that remaining slag as well, making difficult its recovery during froth flotation and therefore will go into the tailing. A super slowly cooling could be the solution to treat smelting copper slag in order to recover copper and silver into the produce matte and generate a remaining slag with large crystal size of magnetite that allow to release molybdenum, in an easy way under low cost during grinding stage and recover it on froth flotation by dragging considering a fine size feed. The treatment of smelting slag by controlled cooling, grinding and froth flotation is a process that has to be evaluated in a particular and integrated way with its corresponding copper smelter.

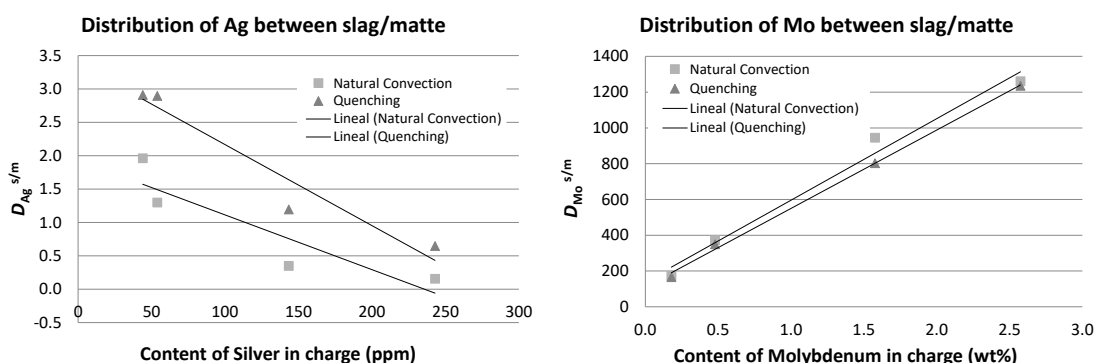


Figure 2: Distribution coefficients of silver (left) and molybdenum (right) between remaining slag and matte after cooling against their content in the smelting slag

References

1. H. Shen and E. Forssberg, "An Overview of Recovery of Metals from Slags", *Waste Manage*, **23** 933–949 (2003).
2. K. Avarmaa, H. O'Brein, H. Johto and P. Taskinen, "Equilibrium Distribution of Precious Metals Between Slag and Copper Matte at 1250 - 1350°C", *J Sust Metall*, **1** (3) 216-228 (2015).
3. H. Kucha and R. Cichowska, "Precious Metals in Copper Smelting Products", *Physicochem Probl Mi*, **35** 91-101 (2201).
4. J. Palacios and M. Sanchez, "Wastes as Resources: Update on Recovery of Valuable Metals from Copper Slags", *Miner Process Extr M*, **120** (4) (2011).
5. F. Parada, M. Sanchez, A. Ullua, J. C. Carrasco, J. Palacios and A. Reghezza, "Recovery of Molybdenum from Roasted Copper Slags", *Miner Process Extr M*, **119** (3) 2010.
6. J. Lotens and A. Van Del Giesen, "Method for the non leachable immobilisation of molybdenum compounds in a slag", in *International Patent WO 00/29071*, 2000.
7. M. Sánchez and M. Sudbury, "Reutilisation of Primary Metallurgical Wastes: Copper Slag as a Source of Copper, Molybdenum and Iron - Brief Review of Test Work and the Proposed Way Forward", In *Proceeding of the 3rd Int. Slag Valorisation Symposium*, Leuven, Belgium, 2013.
8. A. D. Westland and A. H. Webster, "Distribution of Molybdenum Between Slag, Copper Matte and Copper Metal at 1300°C", *Can Metall Q*, **29** (3) 217-225 (1990).
9. A. Sarrafi, B. Rahmati, H. Hassani and H. Shirazi, "Recovery of Copper from Reverberatory Furnace Slag by Flotation", *Miner Eng*, **17** 457-459 (2004).
10. N. Tshiongo, R. K. K. Mbaya, K Maweja and L. C. Tshabalala, "Effect of Cooling Rate on Base Metals Recovery from Copper Matte Smelting Slags", *World Academy of Science, Engineering and Technology, Int. J of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering*, **10** (4) 649-653 (2010).