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OCCURRENCE AND SPECIATION OF COPPER IN SLAGS OBTAINED DURING THE PYROMETALLURGICAL PROCESSING OF CHALCOPYRITE CONCENTRATES AT THE HUELVA SMELTER (SPAIN)

J.C. Fernández-Caliani[*,#], **G. Ríos**[**], **J. Martínez**[**], **F. Jiménez**[**]

[*]Department of Geology, University of Huelva, 21071-Huelva, Spain
[**]Atlantic Copper S.A., Avda. Francisco Montenegro s/n, 21001-Huelva, Spain

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Abstract

Slags involved in smelting-converting-refining operations to produce blister copper at the Atlantic Copper smelter, in Huelva (Spain), have been investigated by quantitative electron microprobe analysis, X-ray diffraction and digital imaging techniques. The results showed that mechanically entrapped matte particles are the dominant copper losses in the slags. The largest proportion of Cu-bearing particles (2.0-3.5 vol %) is present in the magnetite-rich converter slags, due to the negative effect of viscosity on coalescence and precipitation of copper matte during conversion. They consist of high-grade matte particles with a core of copper metal rimmed by a copper sulfide phase (Cu_2S). The mechanical entrainment of copper matte by slags from both the flash and electric furnaces resulted in copper losses accounting for less than 1.5 vol %, mostly occurring as tiny particles with a stoichiometric composition close to that of bornite (Cu_5FeS_4). Copper was not found to be enriched in fayalite and magnetite as solid solution.

Keywords: Smelting; Matte conversion; Slag; Copper; Chalcopyrite

1. Introduction

Copper losses in slag become a global problem in copper pyrometallurgy that is strongly influencing the economy of the extraction process [1]. Silicate slags

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[#] *Corresponding author: caliani@uhu.es*

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produced from smelting copper ores and matte conversion to blister copper contain an appreciable amount of copper arising mainly from partially dissolved copper and mechanically entrained particles of matte. The value of the copper in these slags is too high to justify the common practice of discarding them and, accordingly, a variety of strategies have been proposed for minimizing the amount of copper lost, such as reducing the mass of slag generated, minimizing the percentage of copper in slag, and processing the slags for metal recovery. In detail, the concentration of copper in slag can be minimized by the following measures [2]: a) maximizing slag fluidity by avoiding excessive magnetite in the slag; (b) providing enough silica to form distinct matte and slag phases; (c) providing a large quiet zone in the smelting furnace; (d) avoiding an excessively thick layer of slag; and (e) avoiding tapping of matte with slag.

Knowledge of the mineralogy and texture of solidified slag as well as chemical composition of copper-bearing phases are of particular industrial interest, as depending on the occurrence and speciation of copper in the slag the reduction of copper losses in the slag or the slag cleaning process could be suggested [3, 4].

In that context, this paper investigates the abundance and distribution of species of copper in various types of slags (flash smelting furnace slag, electric furnace slag and converter slag) resulting from smelting-converting operations, with the goal to provide valuable information for the copper smelter management and for developing new methods to reduce copper losses.

2. Materials and methods

The study was carried out using copper slag samples from the Huelva smelting plant, in southwestern Spain. This smelter is operated by Atlantic Copper S.A., one of the world's most important producers of copper, with an annual production capacity of about 310,000 tons of copper anodes, 260,000 of which are refined into high-purity copper cathodes. The main by-products are sulfuric acid and electrolytic slimes rich in precious metals. The principal raw material is copper sulfide concentrate, mainly chalcopyrite, which Atlantic Copper receives from the world-class Grasberg mine in Indonesia [5], smelting approximately one million tons of concentrate per year.

The Huelva smelter has been operated with Outokumpu flash smelting technology [6] since the 1970's. In the mid 1990's the plant was expanded to take full advantage of the flash furnace potential. The sulfide ore concentrate (*ca.* 30 wt % Cu) is treated for copper extraction using a two-stage pyrometallurgical process: 1) smelting concentrates in flash furnace to matte, in which the average copper content is raised from 30 to 62 wt %; and 2) converting matte to blister copper with an average content of 99.5 wt % Cu). The silicate slags produced from both the flash furnace and the converters are treated in an electric furnace to reduce the contained copper from 2 and 6 wt % respectively to less than 1 wt %. After thermal refining, the copper is cast into anodes and further refined by electrolysis to cathodes with a copper content greater than 99.9 wt %.

A total of eleven slag samples were

collected manually by means of a small ingot mold which was dipped in the slag stream (Fig. 1). Regarding the flash furnace and electric furnace, the samples were drawn after 10-15 min the slag tapping was initiated. The slag samples from the flash furnace were drawn from three different launders located at 15, 35 and 45 cm above the matte level (namely samples HF15, HF30 and HF45 respectively). In addition, four samples were taken from the converter (samples C1, C2, C3 and C4), and two from the electric furnace with and without addition of slag from the converter (samples HE1 and HE2, respectively), as well as one sample of water-granulated slag (EG sample).

Each slag sample was crushed to fragments of about 5 mm in diameter. Selected fragments were embedded in epoxy resin, polished to obtain a smooth surface, and coated with carbon for electronic conductivity. Electron microscope examination and electron probe microanalysis (EPMA) were performed by using a JEOL JXA-8200 SuperProbe equipped with four wavelength dispersive X-ray spectrometers (WDS), an energy dispersive X-ray spectrometer (EDS), and back-scattered and secondary electron detectors. Quantitative chemical analyses were carried out by WDS at very small spot sizes (1-5 µm), using an accelerating voltage of 15 kV and a beam current of 20 nA. A combination of well-characterized minerals and synthetic materials were used as standards for calibration, and the conventional ZAF correction procedure was applied to the data.

Representative back-scattered electron (BSE) images of the slag samples were analyzed using *ImageJ* software, a Java-based image processing program developed by Rasband [7], in order to determine the modal abundance of the main metallurgical phases, and the size distribution and basic

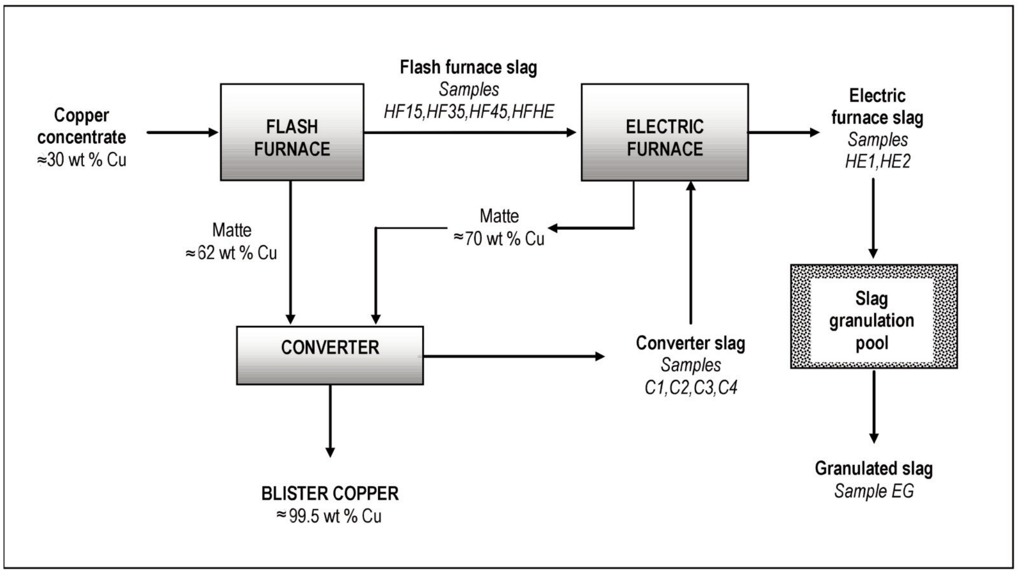

Figure 1. Simplified flowsheet of the current pyrometallurgical process at Huelva smelter plant showing the location of the slag samples taken for this study.

shape parameters (area, perimeter, circularity and roundness) of more than 16,000 individual Cu-bearing particles. An automatic variable threshold (binary contrast enhancement) tool was used for segmentation. Copper-bearing particles and background (voids and matrix) discrimination was done by thresholding. Circularity (C) and roundness (R) are dimensionless numbers calculated as follows: $C = 4\pi \times [\text{Area}] / [\text{Perimeter}]^2$, and $R = 4 \times [\text{Area}] / \pi \times [\text{Major axis}]^2$.

The rest of the slag fragments were ground in an agate mortar and sieved to obtain a fine powder (<63 μm) for X-ray diffraction (XRD) analysis. The major crystalline phases were identified with a BRUKER-AXS D8-Advance diffractometer, using monochromatic CuKα radiation operated at 40 kV and 30 mA. Randomly oriented powders were scanned from 3 to 65º 2Θ, with a step size of 0.02º and a counting time of 0.6 s per step.

3. Results and discussion

3.1. Slags characterization

Fayalite ($Fe^{2+}SiO_4$) and magnetite ($Fe^{2+}Fe^{3+}{}_2O_4$) were the major crystalline phases identified by XRD analysis in the slag samples (Fig. 2), but it does not rule out the occurrence of undetectable amounts of minor phases, including copper matte particles and amorphous or short-range order phases, which were identified by EPMA as presented later in this paper. The relative abundance of fayalite and magnetite varied greatly between slag types, as it can be deduced by comparing the ratio of the integrated areas of the most intense diffraction peaks, whose *d*-spacing values correspond to 2.83 and 2.53 Å, respectively.

Microscopic examination and image analysis of BSE images (Fig. 3) showed that the converter slag samples are characterized by a hypocrystalline texture made almost entirely of fayalite (50-56 vol %) and

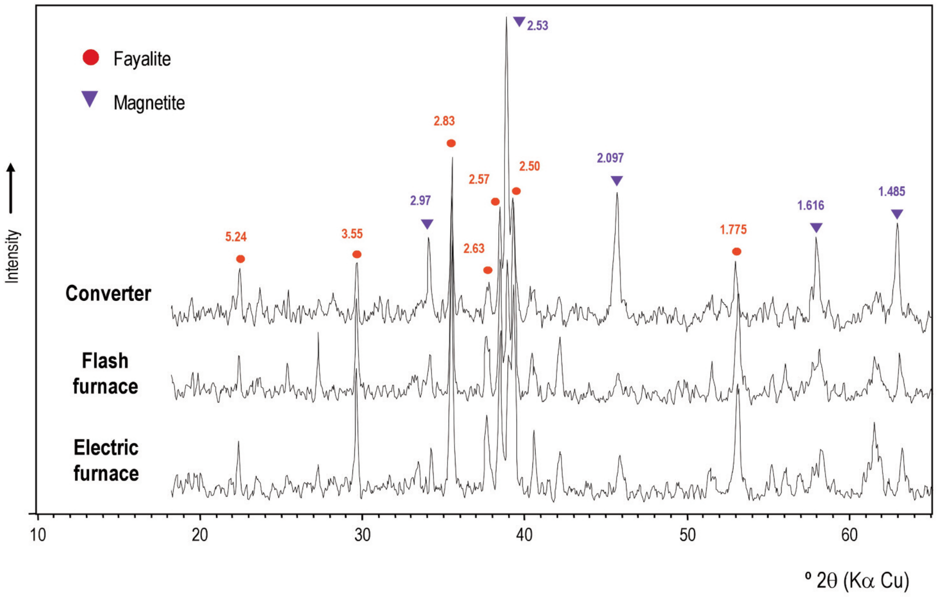

Figure 2. XRD patterns of representative samples of the copper slags.

magnetite (27-34 vol %), with lesser amounts of ferrosilite and glass (<15 vol %). Feathery elongated crystals of fayalite (up to several hundreds of micrometers in length) display a subparallel arrangement, the interstices of which are filled with amorphous glassy material, whereas magnetite occurs as smaller euhedral to subheudral crystals up to 100 µm on edge. This textural pattern suggests that magnetite formed earlier than fayalite after being slowly crystallized from the iron oxide that remained insoluble in the melt, although incipient dendritic branching is also evident in some magnetite crystals. Ferrosilite ($FeSiO_3$) is a late-crystallized phase occurring as rims on magnetite crystals or filling the interstitial space between the columnar phenocrysts of fayalite.

The flash smelting furnace slags showed a typical spinifex texture, defined by large, lath-shaped, skeletal crystals of fayalite up to a few mm in length, and a lattice-like network of magnetite crystals. Smaller delicate dendritic crystals of fayalite and magnetite were also present in the slag. The crystal growth morphologies observed in both metallurgical phases are indicative of extreme undercooling and rapid crystallization from a supersaturated melt. In this slag type, the proportion of magnetite (7-11 vol %) is much lower than in the converter slags, as previously reported in the literature [8].

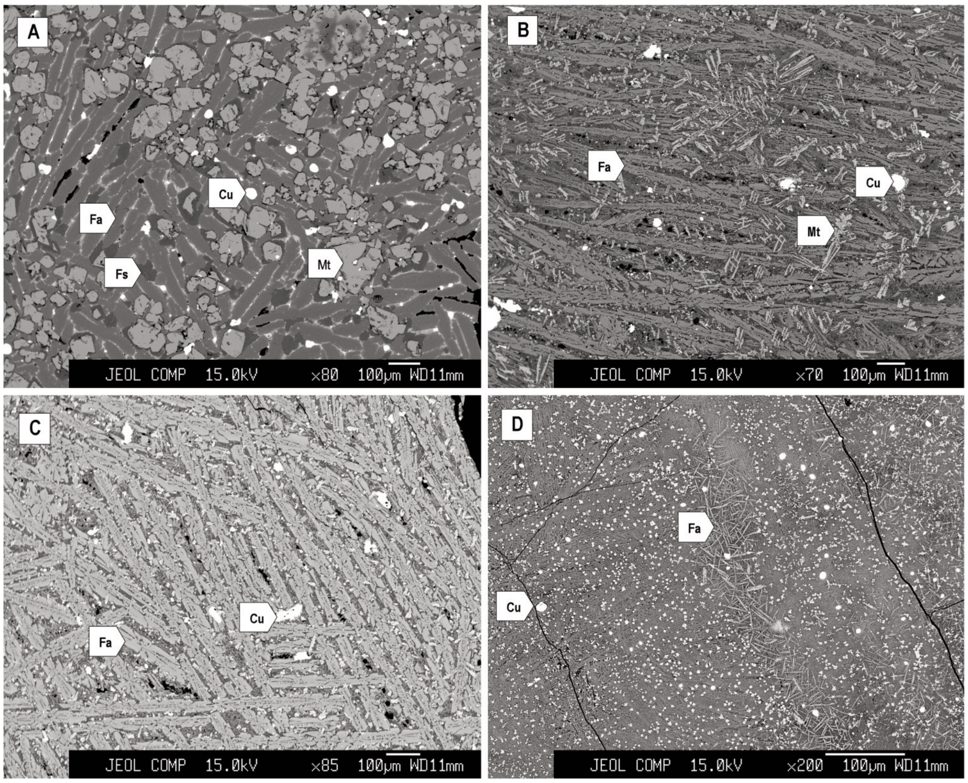

Figure 3. BSE images showing textural and compositional features of the copper slag samples from (A) converter, (B) flash smelting furnace, (C) electric furnace, and (D) granulate slag. Phase abbreviations: Cu (copper-bearing particles); Fa (fayalite); Fs (ferrosilite); Mt (magnetite).

The slags produced from the electric furnace are similar in composition and textural pattern, regardless of whether the converter slag is added or not to the furnace. They are spinifex-textured slags, with highly elongated, skeletal crystals of fayalite showing subparallel, radiating and branching growths of millimeter-scale. Magnetite occurs as tiny crystals (< 10 μm in size), often adopting a cruciform morphology, and infilling the hollows and gaps of the skeletal crystals of fayalite. The electric furnace slag samples contain larger proportion of fayalite (72-73 vol %) and lower contents of magnetite (6-8 vol %), when compared with the rest of the slag types.

After water quenching and granulation, the slag is composed basically of vitreous material and dendritic fayalite. Magnetite is an accessory phase (<5 vol %) that occurs as disseminated subeuhedral crystals, with an edge length up to 5 μm, accompanied by needle-like crystals of fayalite in some slower cooling crystalline domains of the slag.

3.2 Copper losses in slags

Quantitative analysis of BSE images, based on atomic number contrast images, showed that the proportion of Cu-bearing particles present in the samples is variable depending on the slag type. The highest content was recorded in the converter slag samples (2.0-3.5 vol %), whereas the lowest proportion was observed in the flash smelting furnace slag samples (<1.0 vol %). The volume percent of copper-enriched phases slagged in the electric furnace slag samples ranged from 1.0 to 1.5%.

A number of papers have revealed that slag composition has strong influence on copper losses to slag [9-11]. In addition, the distribution of Cu (and other non-ferrous metals) between the slag and the matte during the smelting process also depends on the content of copper in the matte [12]. An increase of the iron concentration in the slag leads to separation of magnetite crystals, which causes heterogenisation of the silicate melt and sudden increase of its viscosity [1], thus inhibiting the slag-matte separation and so increasing the mechanical losses of copper to the slag. This fact could explain the higher abundance of copper-bearing particles found in the magnetite-rich slag samples from the converter.

The copper losses in the converter slag samples were mainly in the form of mechanically entrained matte prills due to the effect of slag viscosity. The matte particles can be seen scattered throughout the slag matrix, mostly occupying the gaps between the large elongated skeletal crystals of fayalite (Fig. 4A) although, more rarely, they were also observed as inclusions within the magnetite crystals. The copper matte particles often exhibit a distinct compositional zoning (Fig. 4B), and vary widely in size and shape, even within the same slag sample, because of the occurrence of sporadic large matte granules (up to about 300 μm in length). In general, the copper matte particles from the converter slag samples are the largest in mean area (Fig. 5A), and they have the lowest mean values of circularity and roundness (Fig. 5B).

The Cu-bearing particles examined in the slag samples from the flash smelting furnace are mostly under 25 μm^2 in area, and have high mean values of roundness (0.75-0.80) and circularity (≈ 0.95). A large matte granule (*ca.* 400 μm in size) was found in the sample HF45, which tended to skew the size distribution. The tiny matte particles most commonly occurred in the interstitial voids of the skeletal and dendritic crystals of fayalite (Fig. 4C). It must be noted that some copper particles appear to be wrapped by rim overgrowths of fayalite or magnetite (Fig. 4D) suggesting that they acted as a substrate for heterogeneous nucleation of both phases in the molten slag.

The slag samples from the electric furnace had a matte size distribution similar to that of the flash furnace slag samples, but the copper particles displayed a greater diversity in morphology, including spherical, elongate, ovoidal and tear-drop shapes. A number of matte particles showed dendritic overgrowths of fayalite and magnetite (Fig. 4E).

The copper matte particles found in the granulated slag sample were by far the smallest in size (Fig. 5A). They are usually highly spherical and well-rounded particles (R≈ 0.85), with a mean surface of approximately 2 μm^2, occurring as disseminations in the slag. Veins of copper metal were detected in some matte particles (Fig. 4F). Magnetite crystals with occasional matte inclusions were also found.

3.3 Copper speciation

The vast majority of the copper particles was entrapped in the converter slags as high-grade matte. The results of the EPMA

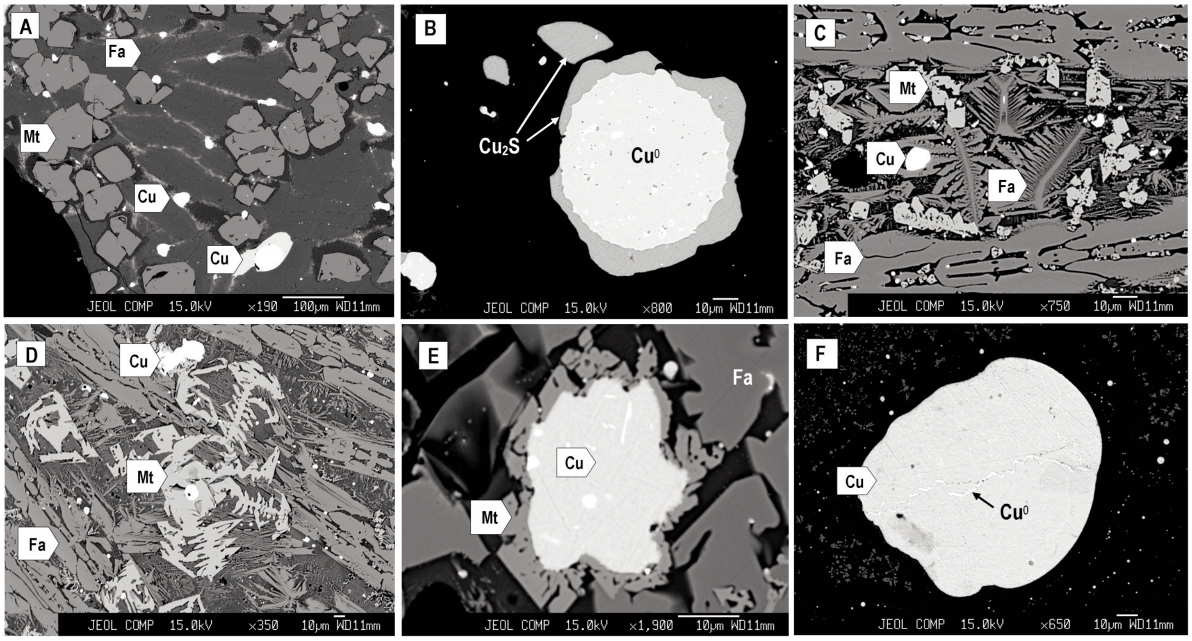

Figure 4. BSE images showing detailed textural relationships of the Cu-bearing particles with other metallurgical phases in the slag samples from converter (A,B), flash furnace (C,D), electric furnace (E) and granulated slag (F). Phase abbreviations: Cu (copper-bearing particles); Cu^0 (metal copper), Cu_2S (chalcocite); Fa (fayalite); Fs (ferrosilite); Mt (magnetite).

analysis (Table 1, Fig. 6A) revealed a compositional zoning pattern (see Fig. 4B), in which a nearly spherical core of copper metal (mean of 96.85 Cu wt %) appears rimmed by an irregular border of copper sulfide having a stoichiometric composition (77.90 wt % Cu and 20.46 wt % S, on average) close to that of chalcocite (Cu_2S). A similar partitioning of copper has been reported [9] for converter slags from the Zhongtiaoshan Non-ferrous Complex (China). Clusters of submicron-sized inclusions of chalcocite and an undefined Pb-rich phase are usually present as impurities in the metallic core of the matte particles. The mean concentrations of CuO in selected crystals of fayalite and magnetite (Table 2) were as low as 0.19 and 0.08 wt %, respectively, as a result of very limited ionic substitution in the crystal lattice of such metallurgical phases.

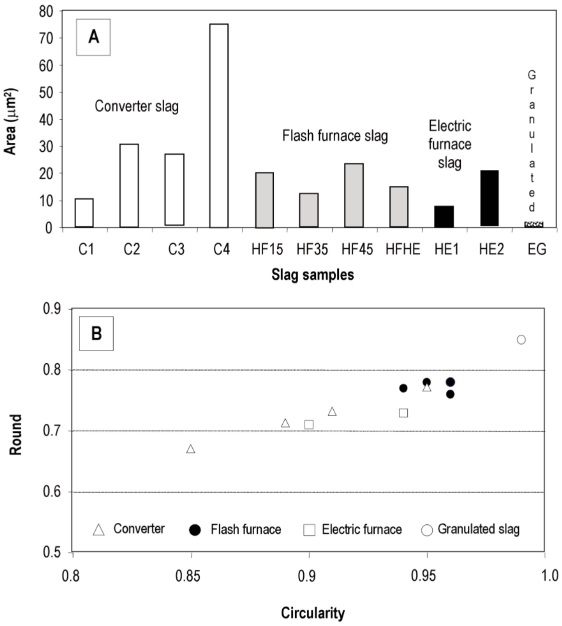

Figure 5. Size and basic shape parameters of the Cu-bearing particles. (A) mean area; and (B) average values of circularity (4π area/perimeter^2) and roundness (4 · area/(π major axis^2).

The compositional variation of entrained matte phases is by far greater in the slag samples from the flash smelting furnace than in the converted slag samples. They can be described as iron-copper sulfides with a wide range of compositions, ranging from chalcocite to cubanite (Fig. 6B), and containing fine lamellar intergrowths due to exsolution upon cooling. The EPMA results (Table 1) showed that most particles have concentrations around 65 wt % Cu, 24 wt % S and 10 wt % Fe, with a stoichiometric relationship that approximates to bornite

Table 1. Mineral speciation and mean concentrations (values in wt %) of Cu, Fe and S of the Cu-bearing particles analyzed by EPMA in the slag samples (n: number of analysis)

Slag type	Converter slag		Flash furnace slag			Electric furnace slag		Granulated slag
Phase	Copper metal (core)	Chalcocite (border)	Bornite	Bornite / Chalcopyrite	Cubanite	Bornite	Bornite / Chalcopyrite	Bornite / Chalcocite
n	11	13	10	5	4	5	3	5
Cu	96.85±1.29	77.90±1.41	65.65±2.14	51.25±1.61	23.57±2.27	65.86±3.03	53.94±1.45	68.82±3.00
Fe	2.05±1.96	1.96±2.05	9.35±1.50	19.83±1.40	39.65±1.73	8.73±2.71	17.51±1.40	7.12±2.17
S	0.06±0.10	20.46±0.40	23.77±0.85	28.15±0.53	32.71±1.22	23.14±1.20	27.07±0.80	21.54±0.57

(Cu_5FeS_4), a sulfur deficient phase in which chalcopyrite tend to be transformed when loses its labile sulfur [13]. The concentration of copper in fayalite crystals was almost negligible (mean 0.05 wt % CuO), however the rims of skeletal magnetite surrounding the matte particles housed appreciable amounts of copper (up to 0.43 wt % CuO).

Likewise, the copper matte particles analyzed in the slag samples from the electric furnace were compositionally complex. The majority of particles had a chemical composition similar to the theoretical composition of bornite (Fig. 6C), with concentrations in the range of 61.5-69.3 wt % Cu. The EPMA results (Table 2) also showed low contents of CuO (mean 0.10 wt %) in the crystal structure of both fayalite and magnetite.

Finally, the copper losses in the granulated slag sample are consistent with high-grade matte particles (64-72 wt % Cu, and 68.82 wt % Cu on average), showing intermediate compositions along the chalcocite-bornite join (Fig. 6D). In this slag, copper was also not found to be enriched in fayalite (mean 0.14 wt % CuO) and magnetite (mean 0.04 wt % CuO) as solid solution.

Table 2. Chemical composition of fayalite and magnetite crystals analized by EPMA in the slag samples (n: number of analysis)

(wt. %)	Fayalite				Magnetite*			
	Converter	Flash furnace	Electric furnace	Granulated	Converter	Flash furnace	Electric furnace	Granulated
	slag (n= 13)	slag (n= 10)	slag (n=8)	slag (n=2)	slag (n=12)	slag (n=9)	slag (n= 6)	slag (n=3)
SiO_2	38.13±1.12	30.14±0.25	30.20±0.40	24.46±10.10	0.57±0.20	1.01±0.32	0.79±0.23	0.77±0.17
Al_2O_3	0.61±0.10	0.14±0.05	0.22±0.06	2.86±0.03	0.79±0.50	3.09±0.31	5.45±1.42	4.65±0.31
FeO(t)	57.12±1.02	64.01±0.81	64.46±1.32	65.22±10.91	89.61±0.78	85.67±1.01	83.33±2.28	83.19±0.48
CaO	0.06±0.03	0.31±0.03	0.40±0.07	1.16±0.33	-	0.06±0.02	0.06±0.03	0.06±0.03
MgO	0.28±0.04	4.02±0.52	3.72±1.09	1.71±0.73	0.05±0.03	0.47±0.07	0.47±0.24	0.51±0.07
Na_2O	0.13±0.05	0.03±0.02	0.03±0.01	0.22±0.15	-	0.03±0.02	-	0.04±0.03
K_2O	0.06±0.02	0.02±0.01	0.03±0.02	0.59±0.31	-	0.02±0.01	0.03±0.02	0.02±0.02
TiO_2	-	0.06±0.03	0.06±0.04	0.34±0.32	0.06±0.03	1.21±0.29	1.66±0.38	1.27±0.13
MnO	0.06±0.02	0.10±0.04	-	0.08±0.02	-	0.02±0.01	0.03±0.01	0.01±0.01
CuO	0.19±0.23	0.05±0.03	0.10±0.11	0.14±0.04	0.08±0.08	0.13±0.13	0.10±0.11	0.04±0.02
ZnO	2.22±0.35	1.27±0.12	1.05±0.09	1.10±0.07	1.04±0.07	0.85±0.05	0.90±0.26	0.65±0.06
SO_3	-	-	0.02±0.01	0.61±0.24	-	0.04±0.01	0.03±0.02	0.02±0.01
Total	98.49±1.08	100.11±0.65	100.33±0.45	98.50±0.27	91.89±0.56	92.56±0.30	92.81±0.81	91.22±0.72

** Magnetite totals are below 93% because most of the Fe is present as Fe_2O_3*

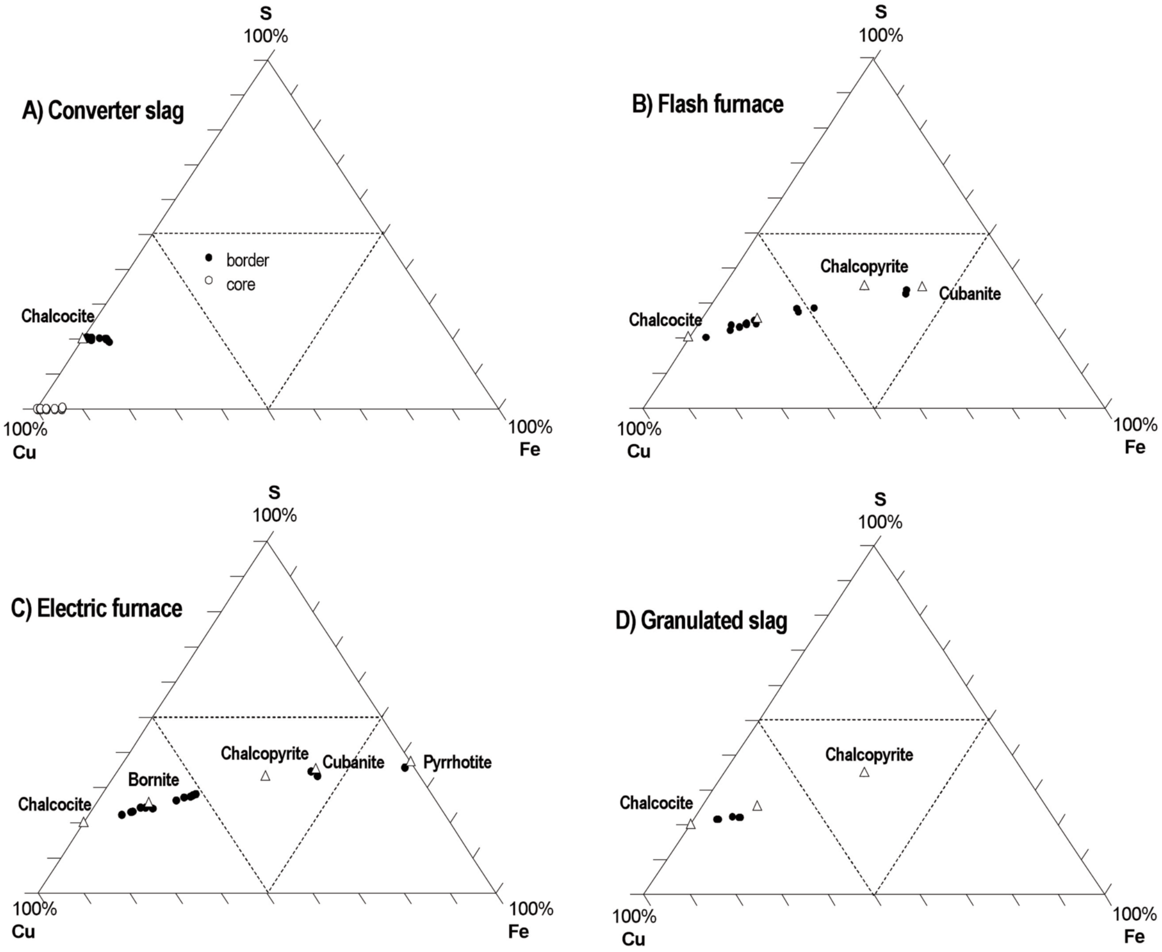

Figure 6. Ternary diagrams showing the composition of the copper-bearing particles, in atomic proportions of Cu, Fe and S, as analyzed by EPMA. Theoretical compositions of the main copper-iron sulfides are projected for reference purposes.

4. Conclusions

The copper slags resulting from the pyrometallurgical processing of chalcopyrite concentrates by Atlantic Copper at the Huelva smelter are spinifex-textured materials composed basically of fayalite and magnetite, with minor amounts of copper matte particles and amorphous or short-range phases. The converter slags contain the largest proportions of magnetite and high-grade copper matte particles, suggesting that slag composition and copper grade of the matte play an important role in the copper losses.

The copper losses in the slags are mainly as mechanically entrapped matte particles varying in size from a few to several hundreds of microns, and occupying the gaps between the skeletal and dendritic crystals of fayalite. However, copper sequestration by the crystal lattices of fayalite and magnetite was negligible, as indicated by the very low concentration of CuO detected in such metallurgical phases. These data support the suggestion that a considerable amount of entrained matte could be efficiently recovered from the solidified slag by fine grinding and froth flotation.

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