*Article*

# Pyrometallurgical Removal of Arsenic from Dusts Collected in Electrostatic Precipitators of Copper, Part I-Dust from a Flash Smelting Furnace

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**Abstract:** This article (the first in a series of two) seeks to describe the experimental results of removing arsenic from the dust collected in the electrostatic copper precipitators within the gas cleaning system of a smelting plant. The first work corresponds to the treatment of the dust contained in the gas generated in the Copper Flash Smelting Furnace process (FS dust). While the second focuses on the treatment of the dust generated by a Fluidized Bed Roasting Furnace (RP dust). The generation of dust in the copper smelting worldwide ranges from 2–15 wt% per ton of a copper concentrate that is processed. In Chile, copper smelters produce 110 kt/y of dust with a concentration of arsenic between 1 and 15 wt%. The dust is a complex of sulfur oxide metals with copper concentrations greater than 10 wt% and relatively high silver concentrations. Since its arsenic concentration is above 5 wt%, it is difficult to recover valuable metals through hydrometallurgical processes or by direct recirculation of the dust in a smelting furnace. Thus, the development of pyrometallurgical processes aimed at reducing the concentration of arsenic in the dust (<0.5 wt%) is the main objective of this study, giving particular attention to the production of a suitable material to be recirculated in operations of copper smelting. The works realized to provide a detailed characterization of the dust including the Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN), Scanning Electron Microscope-Energy Dispersive X-ray Analysis (SEM/EDS), X-Ray Diffraction (XRD), the elemental chemical analysis using Atomic Adsorption (AAS), and X-Ray Fluorescence (X-RF). By considering that arsenic volatilization requires a process of sulfidation-decomposition-oxidation, this paper seeks to explore the roasting of mixtures of copper concentrate/dust, sulfur/dust, and pyrrhotite/dust. By the elemental chemical analysis of the mixture after and before the roasting process, the degree of arsenic volatilization was determined. The results indicated the effects of parameters such as roasting temperature, gas flow, gas composition, and the ratio of mixtures (concentrate/dust, sulfur/dust, or pyrrhotite/dust) on the volatilization of arsenic. According to the findings by the proposed treatment, the concentration of arsenic in the roasted FS dust can be reduced to a relatively low level (<0.5 wt%), which allows its recirculation in the smelting process.

**Keywords:** copper smelter dust; electrostatic precipitators of copper; removal of arsenic; sulfidation; roasting process

## 1. Introduction

In the copper smelting process, an important part of the arsenic contained in the copper concentrate is volatilized and then precipitated as fine particles (FS dust) in the Electrostatic

Precipitator [1,2]. Depending on the smelting technology and the specific condition of the smelter process, the amount of dust produced worldwide corresponds to between 2 and 15 wt% of the feed copper concentrate [3]. In Chile, approximately 15 million tons of copper concentrates are produced annually, of which approximately one third are processed in the existing smelters generating 110 kt/y of flue dusts with arsenic concentrations between 1–15 wt%; 85% of the total is treated by leaching processes and the arsenic is disposed as the scorodite together with Sb and other impurities [4,5]. The literature reports the FS dust as 1–2 μm of a fine oxide-sulfide complex metal, embedded in larger spherical particles of 8 to 10 μm [6], with copper concentrations above 10 wt% and a silver content, which in some cases corresponds to 25% of the total inventories of elements in smelters [7].

Several processes propose recovering Cu and Ag from the dust, such as the leaching of dust with sulfuric acid and the stabilization of arsenic by hydrometallurgical treatments [8–10]. The dust leaching process and the fixation of arsenic as the scorodite are currently carried out at an industrial scale. The published industrial information claims that the produced scorodite is a non-hazardous waste and that the material is classified as non-reactive [11,12]. The downsides of the processes include an expensive pretreatment for the oxidation of As (III) to As (V) and the uncertainty for the long-term stability of the scorodite [13,14]. Furthermore, the leaching of dust with sulfuric acid, requires a comparatively high acid concentration (>0.8 M) and high temperatures (>80 °C). In order to obtain Cu extractions above 60 wt%, it is reported here that the leaching process generates solid residues around 40 wt% with respect to the original material [15].

Pyrometallurgical processes to remove arsenic from FS dust produced in copper smelting are described in registered patents and publications [16,17]. These included reactions of mixtures of the copper concentrate (or sulfur) and FS dust at temperatures between 500 and 900 °C, producing a material with concentrations of 0.3 wt% of arsenic. Other patents and publications claim that the reduction of the FS dust with coal or reducing gases of CO can volatilize arsenic [18,19], obtaining calcines of less than 3 wt% of As (85 wt% arsenic volatilization) and precipitate from the produced gas with a content of $As_2O_3$ above 90 wt%. One of the registered patents describes a process flowsheet where the dust is mixed with the concentrate and processed in a roasting furnace, where the product is then recycled to a smelting furnace [20]. The pyrometallurgical processes described suggest the simultaneous reaction of sulfidation-decomposition-oxidation.

Scorodite and other arsenic content residues generated in the metallurgy industry are considered waste materials. The literature reports different options for the disposal of the generated residues of arsenic trioxide, including encapsulation of arsenic trioxide in the Portland Cement [21], the production of scorodite discussed above [13,14], and the production of glassy material with concentrations of arsenic up to 20 wt% [10–14]. In terms of stability, the fixation of arsenic as a vitreous material can be considered the best option as it keeps the arsenic stable for geological periods [13].

The copper concentrate with high concentrations of arsenic (~5 wt%) was used as the material of study in this work, as indicated in the Materials and Methods Section. The material used was copper ores that came from the northern zone of Chile, which reported high concentrations of enargite/tennantite ($Cu_3AsS_4$/$Cu_{12}As_4S_{13}$). The concentrate obtained from these deposits is treated in a furnace of the fluidized bed to volatilize arsenic and produce a roasted product with less than 0.5 wt% arsenic, which feeds a smelting flash furnace. Thus, an important section of this work was the characterization and the study of the roasting behavior of the copper ores used. Experimental works related to the roasting processes of concentrates with high arsenic concentrations are reported in the literature [22–24]. These studies have proposed mechanisms of reactions and evaluated the kinetics of decomposition and oxidation of Cu-As-S minerals in partial roasting of copper concentrates.

It is important to point out that copper sulphide deposits worldwide exhibit an increasing concentration of arsenic and the treatment and disposal of arsenic remains an unsolved international problem [4,25]. Thus, it is imperative for the development of processes to be aimed at improving the treatment and disposal of arsenic. Although, hydrometallurgical processes are the main technological practice to treat metallurgical arsenic residues, the pyrometallurgical process for the treatment of metallurgical dust has the potential to increase the recovery of valuable metals (Cu, precious metals) and generate a residual with high concentrations of dry arsenic oxide suitable for the production of glassy materials. Furthermore, contrary to the hydrometallurgical process, the material obtained after the volatilization of arsenic (materials with <0.3 wt% As) can be recycled to the smelting furnace without additional solid waste being generated.

Typical results of chemical elemental concentration of a Flush Furnace Dust

Despite the existing information of volatilization of arsenic from metallurgical dust, the literature does not describe in detail the operational parameters. Furthermore, there are no reports of an industrial practice which mixes dust from a Flash Smelting Furnace with high arsenic concentrates. Thus, this work contributes to a better understanding of the suggested reduction-decomposition-oxidation processes by carrying out roasting experiments of a mixture of FS dust with the copper concentrate, sulfur, pyrrhotite, or in reaction with sulfur dioxide. Given the important role of the copper concentrate in the process, a set of experiments were carried out to determine the effect of temperature and time in the removal of arsenic during roasting. The work includes the microscopic and chemical characterization of the copper concentrate, FS dust, and the products of roasting. The results obtained from the experimentation provided valuable information regarding the volatilization of arsenic in differing ranges of temperature, flow, composition of gases, and mixtures of FS dust/concentrate. This information is intended to be a source of reference in the application of industrial processes and the development of roasting furnaces for the exclusive purpose of treating FS dust.

## 2. Materials and Methods

### *2.1. Thermodynamics of Sulfidation-Decomposition-Oxidation Reactions*

The following reactions were proposed for thermal decomposition of enargite ($Cu_3AsS_4$):

$$2Cu_3AsS_4(s) = 3Cu_2S(s) + As_2S_3(g) + S_2(g) \quad (1)$$

$$4Cu_3AsS_4(s) = 6Cu_2S(s) + As_4S_4(g) + 3S_2(g) \quad (2)$$

$$4Cu_3AsS_4(s)=6Cu_2S(s)+As_4(g)+5S_2(g) \quad (3)$$

The analysis of Reactions (1), (2), and (3) indicated spontaneity at temperatures exceeding 470 °C [16].

The oxidation of enargite was described by the following chemical reactions [22,23]:

$$2Cu_3AsS_4(S) + 13/2O_2(g) = As_2O_3(g) + 3Cu_2S(s) + 5SO_2(g)\ \Delta G^0\ (700\ °C) = -141.4\ \text{kJ/mol}\ As_2O_3 \quad (4)$$

The reaction at 700 °C indicates the formation of $As_2O_3(g)$.

The reaction of sulfidation of arsenic oxide was represented by the reaction [23,24].

$$As_2O_3(g) + 3Cu_2O(s) + 11/2S_2(g) = 2Cu_3AsS_4(s) + 3SO_2(g)\ \Delta G°_{700} = -117\ \text{kJ/mol}\ As_2O_3 \quad (5)$$

Thus, it is expected that the arsenic contained in enargite will volatilize by decomposition and simultaneously oxidize at the temperatures of operation of a Fluidized Bed Roaster Furnace of 700 °C.

The equilibrium between arsenic trioxide (1 mol) with $S_2$ (g) (1.5 moles), considering a total pressure of 1 atm, was simulated at temperatures between 500 and 700 °C using the thermodynamic package FactSage 7.1 (databases FactPS and FToxide). There were many reactions involved in this calculation. However, it is possible to consider the following reactions as the main ones:

$$As_2O_3 + S_2 = 2AsS + 3/2O_2 \quad (6)$$

$$As_2O_3 + 3/2S_2 = As_2S_3 + 3/2O_2 \quad (7)$$

$$1/2S_2 + O_2 = SO_2 \quad (8)$$

The results of the simulation for the partial pressure of main gaseous compounds are shown in Figure 1. The results indicated that $As_4S_4$ and $As_4O_6$ gases were the most predominant arsenic species, whose partial pressures were around 0.2 atm.

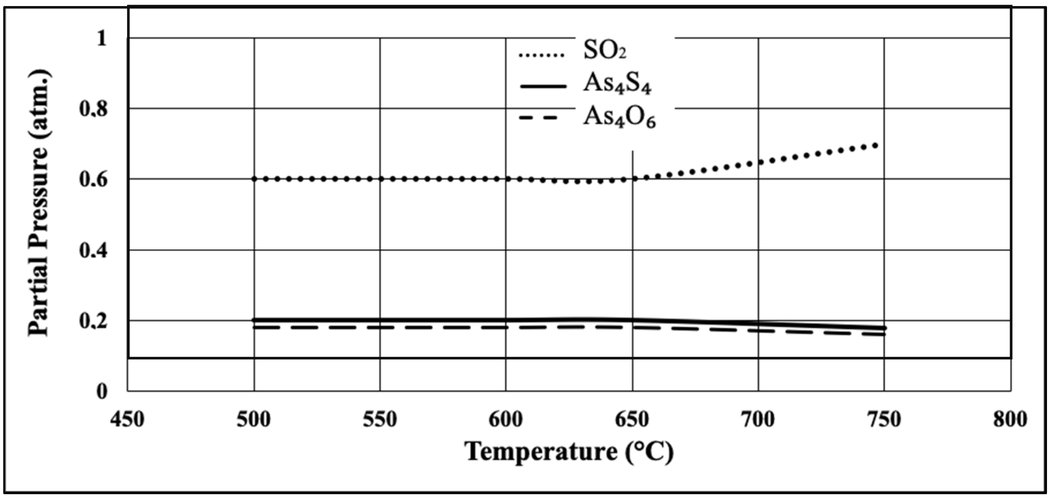

**Figure 1.** Relationship between partial pressure of $As_4O_6$, $As_4S_4$, and $SO_2$ versus temperature for the equilibrium $As_2O_3/S_2$.

According to the thermodynamic analysis of Reactions (1)–(8), a sulfidation-decomposition-oxidation process is possible if a material containing arsenic oxides (FS dust) is mixed and roasted with other material (copper sulfides, pyrrhotite, elemental sulfur, or $SO_2$), which has the potential to generate the partial pressure of $S_2$ required during the sulfidation process.

However, as will be indicated in the section of FS dust characterization, arsenic oxides are only a component of the species reported by the XRD and SEM/EDS analysis. Therefore, experimentation is required to verify that the FS dust reacts according to the thermodynamic calculations. The roasting experiments used a mixture of FS dust produced in a flash smelting furnace and copper concentrate. The characterization of each material is described in the following sections.

### *2.2. Characterization of the Copper Concentrate with High Arsenic Concentration*

The mineralogical and elemental compositions of the copper concentrate analyzed by QEMSCAN (TSCAN, Model: VEGA3 LM) are shown in Table 1, where the arsenic is present mostly as enargite/tennantite.

The XRD (XRD STOE, Model: STADI_MP, Detector DECTRIS MYTHEM 1K, Database Match) and SEM/EDS (SEM: Zeiss Evo Model: MA10, EDS: Oxford X-Act, Detector BS, Software INCA) analysis are shown in Figures 2 and 3, respectively. These analyses corroborated the results obtained by the QEMSCAN analysis. The elemental chemical analysis of the copper concentrate by AAS (AAS Perkin Elmer, Model: PinAAcle 900F Flame) is shown in Table 2. The concentration of arsenic with a value of 5.23 wt% will be the data used in future calculations.

**Table 1.** The Quantitative Evaluation of Minerals by QEMSCAN analysis of the copper concentrate (analysis conditions: Probe current = 4.55 nA, beam intensity: 25 kV).

| Normalized Mineralogical Composition | | Normalized Elemental Composition | |
|---|---|---|---|
| **Phase** | **(wt%)** | **Element** | **(wt%)** |
| Chalcocite/Digenite | 36.1 | Cu | 46.9 |
| Enargite/Tennantite | 30.5 | S | 32.5 |
| Pyrite | 24.4 | Fe | 13.0 |
| Chalcopyrite | 3.2 | As | 5.8 |
| Bornite | 2.5 | O | 0.8 |
| Covellite | 0.7 | Zn | 0.4 |
| Quartz | 0.7 | Si | 0.4 |
| Sphalerite | 0.6 | Al | 0.1 |
| Hematite/Magnetite | 0.4 | Ca | 0.1 |
| Tenorite | 0.2 | K | 0.02 |
| Calcite, clay, alunite, others | 0.65 | Others | 0.05 |

**Table 2.** Atomic absorption analysis of the copper concentrate with high concentration of arsenic.

| Concentration (wt%) | | | | |
|---|---|---|---|---|
| **Cu** | **Fe** | **As** | **S** | **Insoluble** |
| 42.1 | 11.1 | 5.23 | 30.0 | 11.6 |

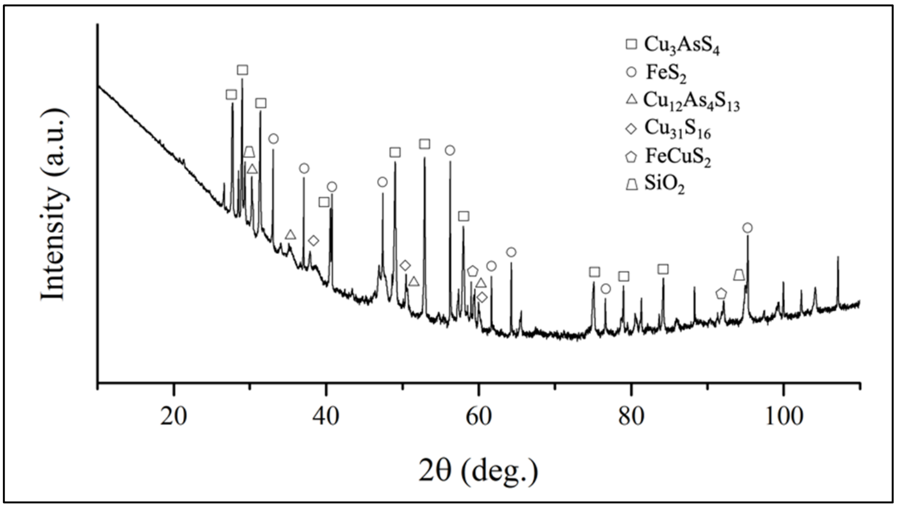

**Figure 2.** XRD analysis of the copper concentrate (analysis conditions: t/step = 17 s, step = 2.1, 2θ = 10–100, time = 15 min).

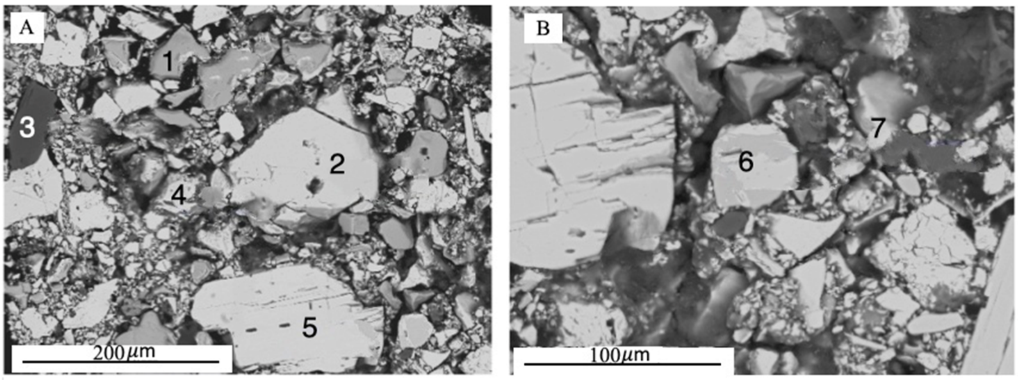

**Figure 3.** Scanning electron micrographs of a copper concentrate. (A) EDS analyzed points of $FeS_2$, ZnS, $SiO_2$, $Cu_2S$ and $Cu_3(As,Sb)S_4$ phases, (B) EDS analyzed points of $CuFeS_2$ and $Cu_3AsS_4$ phases.

The main phases present in the sample are chalcocite, tennantite, and pyrite. The highest arsenic content is present in the tennantite as shown in Table 3.

**Table 3.** Phases of the copper concentrate and their elemental composition analyzed by EDS (analysis condition: Acceleration voltage = 15 kV, beam current = 11 nA).

| **Nº** | **Phase** | **Normalized Composition (wt%)** | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | **O** | **Si** | **S** | **Fe** | **Cu** | **Zn** | **As** | **Sb** |
| 1 | $FeS_2$ | 0.0 | 0.0 | 55.7 | 43.5 | 0.7 | 0.0 | 0.1 | 0.0 |
| 2 | ZnS | 0.0 | 0.0 | 34.4 | 0.3 | 0.3 | 64.9 | 0.0 | 0.1 |
| 3 | $SiO_2$ | 52.6 | 46.4 | 0.0 | 0.1 | 0.7 | 0.0 | 0.2 | 0.0 |
| 4 | $Cu_2S$ | 2.6 | 0.2 | 22.0 | 0.5 | 74.7 | 0.0 | 0.0 | 0.0 |
| 5 | $Cu_3(As,Sb)S_4$ | 0.0 | 0.0 | 34.1 | 0.0 | 46.3 | 0.0 | 15.1 | 4.5 |
| 6 | $CuFeS_2$ | 0.0 | 0.0 | 36.6 | 29.8 | 33.5 | 0.0 | 0.1 | 0.0 |
| 7 | $Cu_3AsS_4$ | 0.0 | 0.0 | 35.4 | 0.5 | 47.2 | 0.0 | 16.9 | 0.0 |

### *2.3. Characterization of the FS Dust*

The phases and elements present in the FS dust collected in the electrostatic precipitators of the Flash Smelting process, as well as the arsenic distribution in these phases, analyzed by QEMSCAN, are summarized in Table 4. This analysis identified main phases of complex oxides, iron oxides (hematite, magnetite, delafosite), copper oxides (CuO) and minerals such as chenevixite and clinoclase. The elemental composition obtained by XRF and AAS is indicated in Table 5. A good agreement is observed between the results of both analyses. Given that the XRF is semi-quantitative, the concentration of arsenic reported by AAS in Table 4 will be the data used in further calculations.

Figure 4 shows the SEM micrographs of FS dust. The elemental chemical composition of selected points analyzed by EDS is summarized in Table 6. The results indicated that the FS dust is mainly composed of particles with sizes between 10 and 100 µm, with a glassy matrix and crystals of iron oxides. Based in the elemental composition indicated, in Table 6 is assigned a phase name to each observed and analized point. Thus, the SEM/EDS indicate the presence of a complex oxide material (glassy), chenevixite, clinoclase and iron oxides. It is important to observe that arsenic is reported in the glassy matrix, in complex Fe-Cu-Zn-As oxide phases and in chenevixite, clinoclase minerals.

**Table 4.** QEMSCAN analysis of the Flash Smelting (FS) dust (analysis conditions: Probe current = 4.55 nA, beam intensity: 25 kV).

| **Phase** | **Normilized mineralogical composition (wt%)** | **Distribution of arsenic in each phase (wt%)** |
|---|---|---|
| Hematite/Magnetite/Delafosite: $Fe_2O_3/Fe_3O_4/CuFe_3O_2$ | 30.1 | -- |
| Cu-Fe-O-S-As-Zn-Al-Si-K-Sb | 46.8 | 50.5 |
| Tenorite: CuO | 8.8 | -- |
| Chenevixite: $Cu_2Fe_2(AsO_4)_2(OH)_3$ | 5.3 | 29.3 |
| Clinoclase: $Cu_3(AsO_4)(OH)_3$ | 4.5 | 19.7 |
| Silicate-Fe | 1.0 | -- |
| Quartz:$SiO_2$ | 0.6 | -- |
| Calcite: $CaCO_3$ | 0.5 | -- |
| Others | 2.4 | 0.5 |

**Table 5.** Elemental chemical analysis of the FS dust with high concentrations of arsenic by Atomic Adsorption.

| | **Elemental composition (wt%), Ag (ppm)** | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Element** | **O** | **Cu** | **Fe** | **S** | **As** | **Zn** | **Si** | **Pb** | **K** | **Na** | **Al** | **Ca** |
| **AAS** | | 24.8 | 12.9 | 9.7 | 5.2 | 3.3 | 2.1 | 0.09 | 1.12 | 0.22 | 0.7 | 0.38 |
| **XRF** | 35.0 | 27.7 | 12.1 | 10.6 | 4.5 | 3.0 | 2.0 | 1.6 | 0.96 | 0.67 | 0.59 | 0.41 |
| **Element** | **Bi** | **Mo** | **Cd** | **Sb** | **Ti** | **Mn** | **Ge** | **Sn** | **Pb** | **P** | **Ag** | |
| **AAS** | | 0.18 | | 0.06 | | 0.02 | | | | 0.04 | 279 | |
| **XRF** | 0.29 | 0.21 | 0.15 | 0.06 | 0.03 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | | |

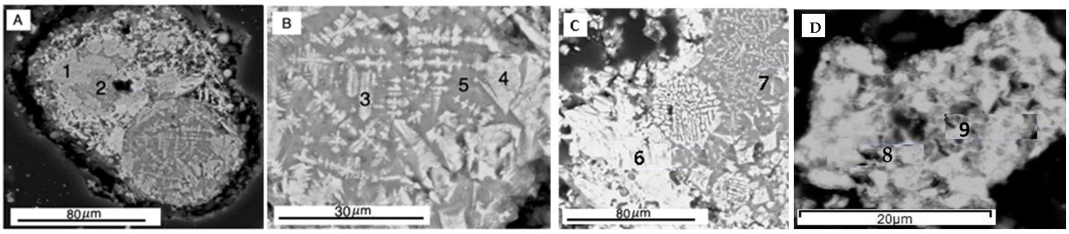

**Figure 4.** Scanning electron micrograph of FS dust. (A) EDS analyzed points of glassy matrix and iron oxides, (B) EDS analyzed points of iron oxides and glassy matrix, (C) EDS analyzed points of complex Fe-Cu-Zn-As oxide phases and glassy matrix, (D) EDS analyzed points of chenexivite and clinoclase.

**Table 6.** The SEM/EDS analysis of FS dust (analysis condition: Acceleration voltage = 15 kV, beam current = 11 nA)

| **Phase** | **Analyzed point** | **Composition (wt%)** | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **O** | **Al** | **Si** | **S** | **K** | **Ca** | **Fe** | **Cu** | **Zn** | **As** | **Sb** |
| Cu-Fe-O-S-As-Zn-Al-Si-K-Sb | 7 | 37.1 | 1.4 | 9.5 | 0.5 | 0.5 | | 42.1 | 4.8 | 1.2 | 1.9 | 1.1 |
| | 2 | 40.7 | 1.8 | 11.7 | | 0.5 | | 27.5 | 9.2 | 6.4 | 2.2 | |
| | 5 | 43.4 | 1.8 | 14.9 | 0.3 | 0.3 | 0.32 | 24.8 | 1.5 | 10.2 | 1.1 | 0.9 |
| Chenexivite | 8 | 35.0 | | | | | | 22.0 | 21.4 | 0.6 | 16.0 | 5.1 |
| | 9 | 34.3 | | | | | | 34.1 | 16.1 | | 10.8 | 4.7 |
| $Fe_3O_4$ | 3 | 39.4 | 2.5 | 5.3 | | | | 46.5 | 4.0 | 2.0 | | |
| | 4 | 35.4 | 2.1 | 3.7 | | | | 44.9 | 2.1 | 11.3 | | |
| | 1 | 32.2 | | | | | | 54.1 | 5.2 | 3.2 | 5.4 | |
| Clinoclase | 6 | 18.1 | | | 1.1 | | | 2.6 | 48.9 | 2.3 | 27.0 | |

XRD analysis of FS dust presented identified peaks of oxides such as hematite ($Fe_2O_3$), delafosite ($CuFe_3O_2$) and paramelaconite ($Cu_4O_3$), The iron, copper arsenic, sulfur compounds was recognized as tetrahedrite-tennantite and complex compounds of Si, Al, K as muscovite.

### *2.4. Experimental Method*

The experiments included the roasting of copper concentrates and the roasting of a mixture of copper concentrate/FS dust, sulfur/FS dust, pyrrhotite/FS dust, and FS dust in an atmosphere of $SO_2$ gas. The experiments were carried out using the equipment shown and described in Figure 6. The arrangement aims to achieve a uniform mixture of gases with the sample, as well as a stable temperature for both of the gases and the sample in such a way that it reproduces the conditions of an industrial Fluidized Bed Roaster.

The reactor was constructed from a boron silicate glass resistant to temperatures of 750 °C, an installed fritted glass disk formed the base for the bed of the reactor. In order to guarantee the uniform

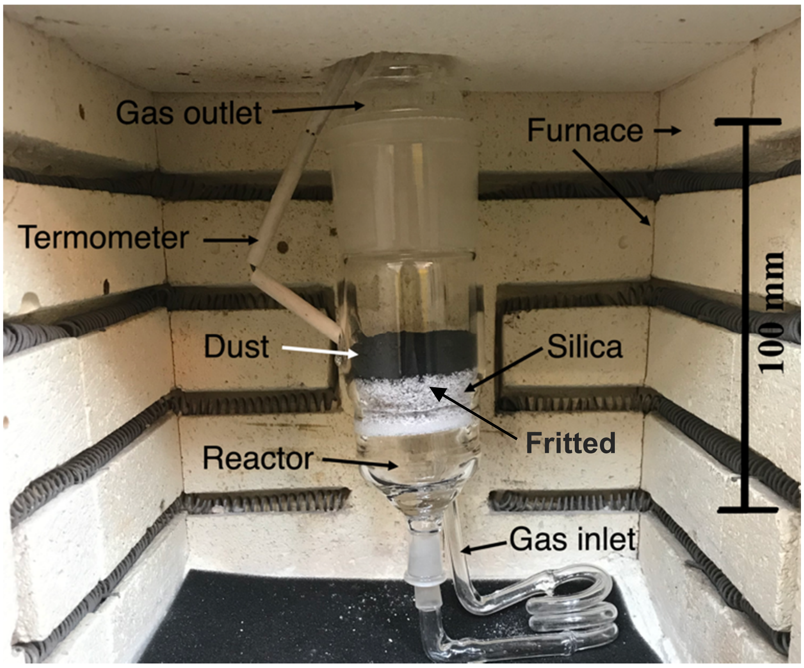

**Figure 6.** Experimental equipment.

distribution of gas and obtain a uniform temperature of the gas and sample, 5 g of silica with a range of sizes between 100 and 200 µm was used as a bed in the reactor.FS dusts were mixed with the concentrate (elemental sulfur or pyrrhotite) depending on the experiment that was being carried out and the 5 g sample was then placed on top of the bed of silica. The muffle placed under a fume hood, was preheated to 200 °C, where the reactor was installed inside. A stream of nitrogen of 20 mL/min was circulated to avoid oxidation of the sample. The muffle temperature was then increased until it reached a working temperature. At this time, the nitrogen current was changed by a determined air or $SO_2$ flow (for example 10 mL/min) and the experiment time measurement began. Once the roasting time had ended, the nitrogen current was switched on again and the temperature of the muffle was reduced to extract the sample from the reactor. The sample, once extracted from the reactor, was separated in a screen of 100 meshes. The oversized material contained the silica and the under size contained the calcined sample. The oversized material containing the silica bed was analyzed, reporting concentrations of iron and copper <0.5 wt% and arsenic <0.05 wt%, this indicated a good separation between the silica material used as the bed and the calcined sample. During the tests, the temperature was controlled with a thermocouple type K in a range of ± 5 °C. The elemental composition of the samples was determined by Atomic Absorption, whilst, the sulfur content was determined using a LECO equipment (analyzed by Australia Laboratory Service-Chile).

The percentage of the volatilization of species (As) was defined as:

$$\%\ \text{Volatilization As} = 100 \times ([\text{wt\% As}]_{\text{initial}} - [\text{wt\% As}]_{\text{final}})/[\text{wt\% As}]_{\text{initial}} \tag{9}$$

where $[\text{wt\% As}]_{\text{initial}}$ was the concentration of arsenic measured in the loaded sample and $[\text{wt\% As}]_{\text{final}}$ was the concentration of arsenic measured for the sample after the roasting process.

The volatilization percentage was defined in terms of the percentage wt% and not by the total mass balance of the element under analysis. The reason for this is that the total weight of the sample does not change appreciably during the roasting process. In addition, it is difficult to quantify the amount of sample lost during its manipulation, loss of sample in the conduct of gases during the process, and the possible contamination of the sample with silica due to the inevitable friction between the grains in the fluidized state.

## 3. Results

### *3.1. Results of Roasting the Concentrate with High Concentration of Arsenic*

The experimental plan was designed based on the study of a mixture of copper concentrate with high contents of arsenic/FS dust. The first set of experiments was carried out using a selected copper concentrate to evaluate which conditions of the roasting process allowed the greatest volatilization of the arsenic. Therefore, this result was used as a base case. Roasting times and temperatures were the variables to consider in this context. Later in this work, based on this information, a set of experiments for the mixtures were developed.

The volatilization of arsenic for the concentrate under different conditions of temperature and time for the roasting process under a constant air flow of 10 (mL/min) are presented in Table 7. As a result of injected gas flow levels above 10 (mL/min), they did not show an appreciable increase in arsenic volatilization. All experiments of this work were carried out for a gas flow of 10 (mL/min).

By analyzing the results in Table 7, it is evident that the arsenic volatilization was greater than 90% with a given temperature of 600 °C and a roasting time of 5 min. However, with a temperature of 650 °C and a time of 15 min the volatilization of arsenic was close to 96%. The mineralogical and elemental normalized compositions obtained by QEMSCAN analysis of the copper concentrate after the roasting for experiment 8 of Table 7 are summarized in Table 8.

The next set of experiments was carried out under these (650 °C, 15 min) conditions and the purpose was to find the ratio of the copper concentrate/FS dust mixture that would allow a high volatilization of the arsenic with the highest amount of FS dust in the mixture. An appreciable volatilization of arsenic was obtained for ratios above 50/50, as indicated in Table 9.

**Table 7.** Volatilization of arsenic for the copper concentrate under different conditions of temperature and time of the roasting process.

| | **Experimental Conditions** | | **Chemical Analysis (wt%)** | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **Temperature** | **Time** | **Cu** | **Fe** | **As** | **S** | **Insoluble** | **As Volatilization** |
| **Experiment** | **(° C)** | **(min.)** | | | | | | |
| 1 | 600 | -- | 46.2 | 10.2 | 5.50 | 27.8 | 10.1 | 0.0 |
| 2 | 600 | 2 | 42.5 | 10.2 | 4.26 | 26.4 | 9.38 | 22.5 |
| 3 | 600 | 5 | 45.0 | 11.6 | 0.44 | 21.0 | 13.1 | 92.0 |
| 4 | 600 | 15 | 45.8 | 11.3 | 0.40 | 17.9 | 12.8 | 92.7 |
| 5 | 600 | 30 | 39.6 | 10.3 | 0.41 | 12.1 | 14.5 | 92.5 |
| 6 | 650 | 2 | 46.3 | 11.0 | 3.64 | 23.8 | 7.94 | 33.8 |
| 7 | 650 | 5 | 46.4 | 10.6 | 0.45 | 24.4 | 12.0 | 91.8 |
| 8 | 650 | 15 | 48.7 | 11.3 | 0.23 | 18.4 | 10.4 | 95.8 |
| 9 | 650 | 30 | 43.7 | 10.6 | 0.25 | 12.6 | 13.3 | 95.5 |
| 10 | 700 | 2 | 45.4 | 10.8 | 2.25 | 24.1 | 8.52 | 59.1 |
| 11 | 700 | 5 | 47.7 | 11.8 | 1.65 | 23.6 | 6.58 | 70.0 |
| 12 | 700 | 15 | 48.8 | 11.7 | 0.85 | 18.6 | 6.96 | 84.5 |
| 13 | 700 | 30 | 45.1 | 11.6 | 0.22 | 7.32 | 13.4 | 96.0 |

The mineralogical and elemental normalized compositions obtained by QEMSCAN analysis of the copper concentrate after the roasting for experiment 8 of Table 7 are summarized in Table 8.

**Table 8.** QEMSCAN analysis of the roasted copper concentrate at 650 °C and 15 min of the roasting process for experiment 8 of Table 7 (analysis conditions: Probe current = 4.55 nA, beam intensity: 25 kV).

| Normalized Mineralogical Composition | | Normalized Elemental Composition | |
|---|---|---|---|
| **Phase** | **(wt%)** | **Element** | **(wt%)** |
| Bornite | 63.5 | Cu | 55.5 |
| Chalcopyrite | 6.6 | S | 20.7 |
| Chalcocite | 6.2 | Fe | 12.6 |
| Tenorite | 5.0 | O | 7.2 |
| Quartz | 4.7 | Si | 2.4 |
| Brochantite/Antlerite | 4.6 | Zn | 0.6 |
| Hematite/Magnetite | 3.9 | As | 0.5 |
| Clinoclase | 1.4 | Cl | 0.2 |
| Cuprite | 1.1 | Al | 0.2 |
| Chenevixite | 0.9 | Others | 0.3 |
| Sphalerite | 0.8 | | |
| Mica | 0.4 | | |
| Enargite/Tennantite | 0.2 | | |
| Others | 0.7 | | |

**Table 9.** Volatilization of arsenic for different ratios of the copper concentrate/FS dust mixture, at 650 °C and 15 min of the roasting process.

| Experiment | Ratio Copper concentrate/FS dust | As Volatilization (%) |
|---|---|---|
| 14 | 0/100 | 0 |
| 15 | 10/90 | 0 |
| 16 | 30/70 | 0 |
| 17 | 50/50 | 51.1 |
| 18 | 75/25 | 84.3 |
| 19 | 80/20 | 91.8 |
| 20 | 90/10 | 93.0 |
| 21 | 100/0 | 95.9 |

### *3.2. Results of the Copper Concentrate/FS Dust Mixture Roasting*

The ratio of the copper concentrate/FS dust mixture of 75/25 has a volatilization of arsenic over 80%. A new set of experiments were carried out keeping this mixture ratio, to evaluate how time and temperature can affect the volatilization of arsenic during of the roasting process. The results are tabulated in Table 10.

**Table 10.** Volatilization of arsenic for a mixture concentrate/FS dust of 75/25, under different temperatures and roasting times.

| Mixture | Experiment | Time minutes | Temperature °C | Final As wt% | As Volatilization wt% |
|---|---|---|---|---|---|
| Copper concentrate/FS dust 75/25 (wt%/wt%) | Initial Dust | | | 5.38 | 0 |
| | 21 | 5 | 650 | 0.49 | 90.9 |
| | 22 | 15 | 650 | 0.37 | 93.1 |
| | 23 | 30 | 650 | 0.30 | 94.4 |
| | 24 | 5 | 700 | 0.26 | 95.2 |
| | 25 | 15 | 700 | 0.31 | 94.2 |
| | 26 | 30 | 700 | 0.26 | 95.2 |

| | | | | | |
|---|---|---|---|---|---|
| | Initial | | | 5.23 | 0.0 |
| Sulfur/FS dust<br>5/95 (wt%/wt%) | 27 | 15 | 600 | 4.5 | 13.9 |
| | 28 | 15 | 650 | 4.6 | 12.0 |
| | 29 | 15 | 700 | 4.7 | 10.1 |

The QEMSCAN analysis of the roasted sample for experiment 25 of Table 10 is presented in Table 11.

**Table 11.** QEMSCAN analysis of roasting of a mixture of a copper concentrate/FS dust for experiment 25 of Table 10 (analysis conditions: Probe current = 4.55 nA, beam intensity: 25 kV).

| **Normalized Phase Composition** | | **Normalized Elemental Composition** | |
|---|---|---|---|
| **Phase** | **(wt%)** | **Phase** | **(wt%)** |
| Tenorite | 32.9 | Cu | 48.5 |
| Brochantite/Antlerite | 20.6 | O | 22.0 |
| Bornite | 17.1 | Fe | 12.6 |
| Quartz | 12.3 | S | 8.2 |
| Hematite/Magnetite | 9.9 | Si | 6.0 |
| Chalcocite | 3.6 | Cl | 1.0 |
| Cuprite | 1.2 | Zn | 0.8 |
| Mica | 0.7 | H | 0.4 |
| Sphalerite | 0.4 | Others | 0.5 |
| Chalcopyrite | 0.3 | | |
| Others | 1.1 | | |

Note: Arsenic was not reported in Table 11 because it was outside the detection limit of the equipment. This indicates that there was an efficient volatilization of arsenic in the sample.

According to the results of Tables 10 and 11, the mixture of the copper concentrate/FS dust of 75/25 volatilized more than 90% of the arsenic present before the roasting, while the mixture of sulfur/FS dust obtained lower volatilization values of arsenic close to 12%.

## 4. Discussion

### *4.1. Copper Concentrate Roasting*

The roasting of concentrates in an air or nitrogen atmosphere indicated a high volatilization of arsenic (>90%) in air, even at 600 °C. Whereas, the low volatilization (<50 wt%) in an atmosphere of nitrogen at temperatures below 650 °C can be seen in Figure 7. The results were in accordance with thermodynamic calculations, where the volatilization by oxidation occurs spontaneously at the low temperature of 600 °C [22]. While, simultaneous decomposition for the reactions (1)–(3) took place at a temperature above 630 °C [23,24]. The results were also in congruence with kinetic results from reported experiments, where at 5 min of roasting, an appreciable thermal decomposition of enargite occurred around 70 wt% at a temperature of 675 °C and less than 25 wt% at a temperature of 625 °C [22].

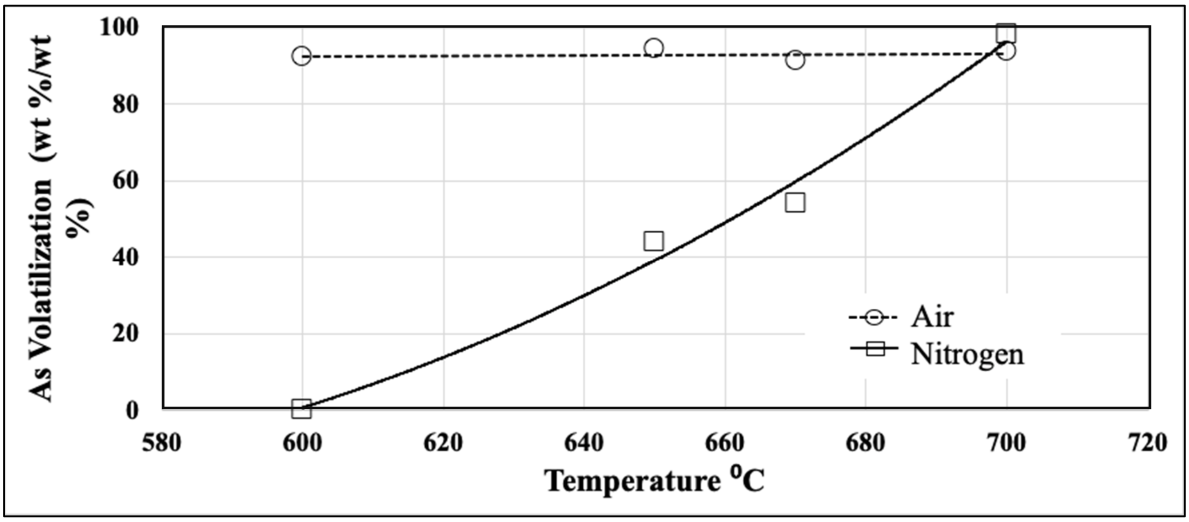

**Figure 7.** Relationship between temperature and arsenic volatilization for roasting of the copper concentrate in an air or nitrogen atmosphere (roasting time: 15 min).

The results summarized in Table 7 were plotted in Figures 8 and 9. It was apparent that the temperatures between 600 and 700 °C had a marginal effect on the volatilization of arsenic and on the concentration of sulfur. It was also observed that the volatilization of arsenic increased at a high rate until it approached a time of 5 min. Then, the volatilization stabilized at a value of around 90 wt%, with a concentration of arsenic in the calcine between 0.2 and 0.5 wt%. The concentration of sulfur in the concentrate also decreased over time, reporting a value around 20 wt% during the period of 5 min.

The results of QEMSCAN for experiment 8 of Table 7 (650 °C, 15 min) were shown in Table 8. The predominant sulfur compound was bornite while enargite was reduced to 0.2 wt%.

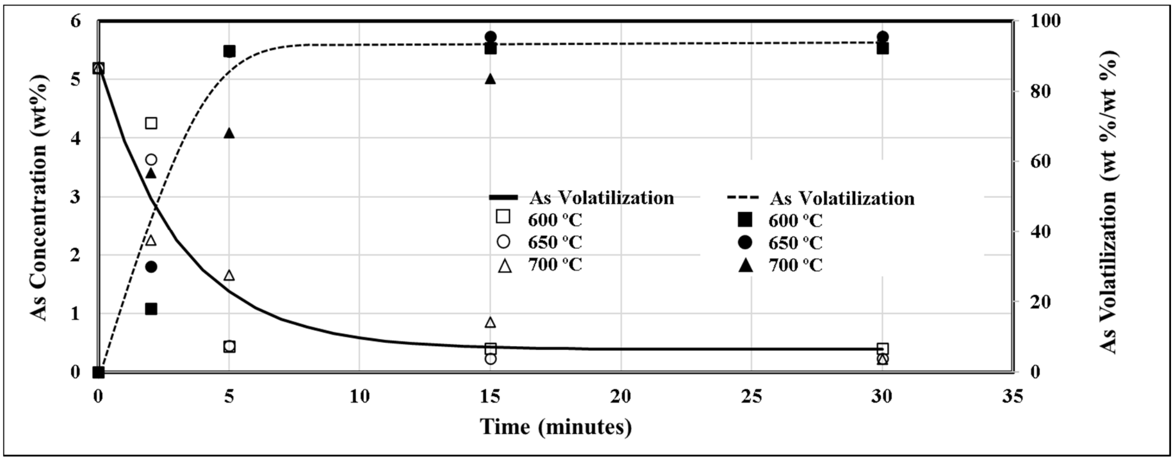

**Figure 8.** Volatilization of arsenic for the copper concentrate under different conditions of temperature and time of the roasting process.

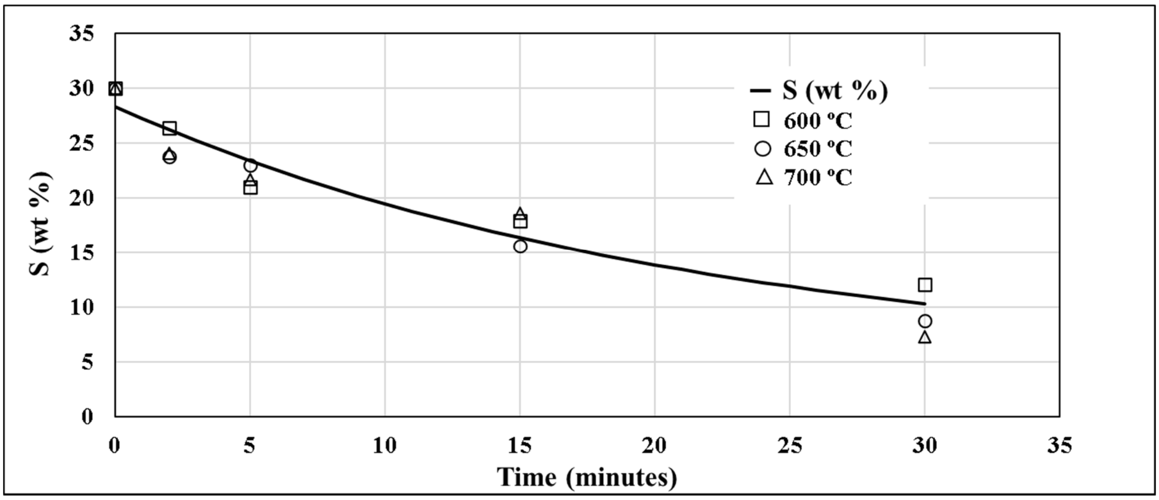

**Figure 9.** Sulfur in the copper concentrate under different times of the roasting process.

### 4.2. Copper Concentrate/FS Dust Mixture Roasting

The results presented in Table 9 are plotted in Figure 10, which include the results of a mass balance calculated considering zero volatilization of arsenic from the dust of the mixture. By comparing the lines of trends, it is possible to state that only for mixtures with ratios of copper concentrate/FS dust above 50/50 had a significant volatilization of arsenic. Therefore, it is important to consider that from an operational point of view, a large amount of concentrate would be required to volatilize the arsenic contained in the FS dust.

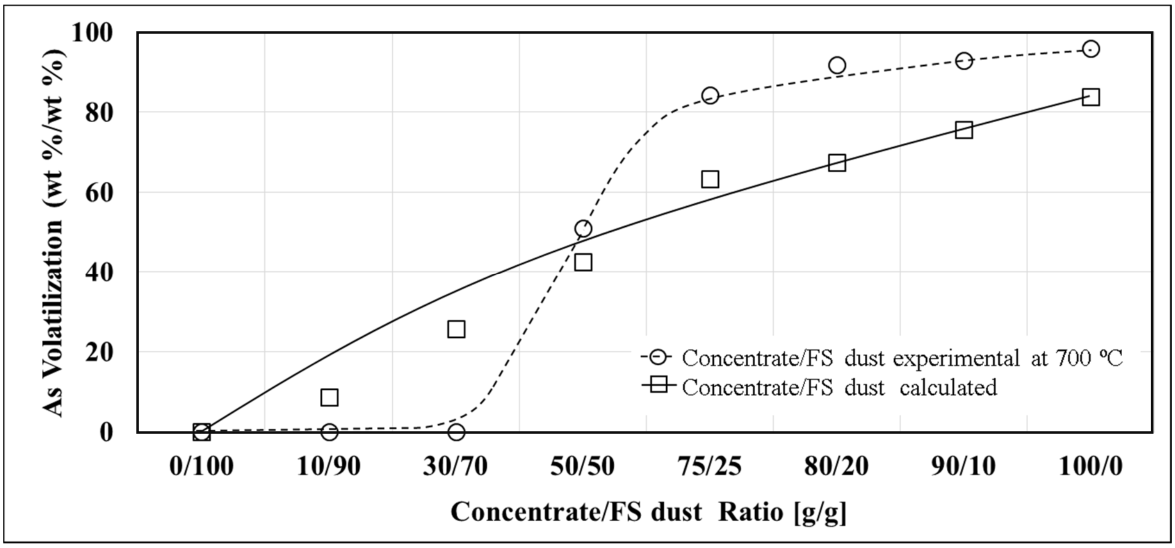

**Figure 10.** Effect of the copper concentrate/FS dust mixture ratio on the volatilization of arsenic and calculated data considering zero volatilization of arsenic from the dust at 700 °C.

A mixture of copper concentrate/FS dust 75/25 was used to determinate the effect of temperature and time of roasting—Table 10 shows that at a temperature of 650 °C and a roasting time of 5 min, the volatilization of arsenic reached a value of 90 wt%. Longer roasting times did not substantially increase the volatilization of arsenic. At the temperature of 700 °C, the volatilization of arsenic reached a value between 94–95 wt%, showing an asymptotic behavior in the range of roasting time tested.

The experiments included roasting of sulfur/FS dust and pyrrhotite/FS dust that are summarized in Table 12 and in Figure 11. It can be concluded that pyrrhotite volatilizes around 50 wt% of arsenic in the sample. However, the copper concentrate/FS dust was the only mixture that obtained low values of arsenic (<0.5 wt%) required for a material to be suitable for recycling in a smelting furnace. The mixture sulfur/FS dust reported a volatilization of the order of 10 wt%.

**Table 12.** Effect of the roasted sample material and flow gas used on the arsenic volatilization.

| Exp. | Roasted sample | Flow Gas Used | Composition (wt%) | | | | | Volatilization (wt%) | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Cu | Fe | S | As | Sb | As | Sb |
| 15 | FS dust | Nitrogen | 31.0 | 12.0 | 3.7 | 3.9 | 0.3 | 25.4 | 70.0 |
| 16 | FS dust | Air | 24.1 | 12.9 | 7.7 | 5.1 | N/A | 2.5 | N/A |
| 17 | FS dust | $SO_2$ | N/A | N/A | N/A | 5.1 | 0.1 | 2.5 | 90.0 |
| 18 | Copper concentrate/FS dust 75/25 (wt%/wt%) | Air | 41.2 | 12.9 | 6.1 | 0.3 | N/A | 94.4 | N/A |
| 19 | Sulfur/FS dust 5/95 (wt%/wt%) | Air | N/A | N/A | N/A | 4.7 | 0.2 | 10.1 | 80.0 |
| 20 | $Fe_7S_8$/FS dust 10/95 (wt%/wt%) | Air | N/A | N/A | N/A | 2.7 | 0.1 | 48.4 | 90.0 |

N/A: No analyzed

The main objective of the work was the study of volatilization of arsenic. However, the chemical analysis of antimony was included in most of the experiments. Thus, Table 12 included the results obtained for the volatilization of antimony. It is observed that this element volatilizes above 70% at all experimental conditions.

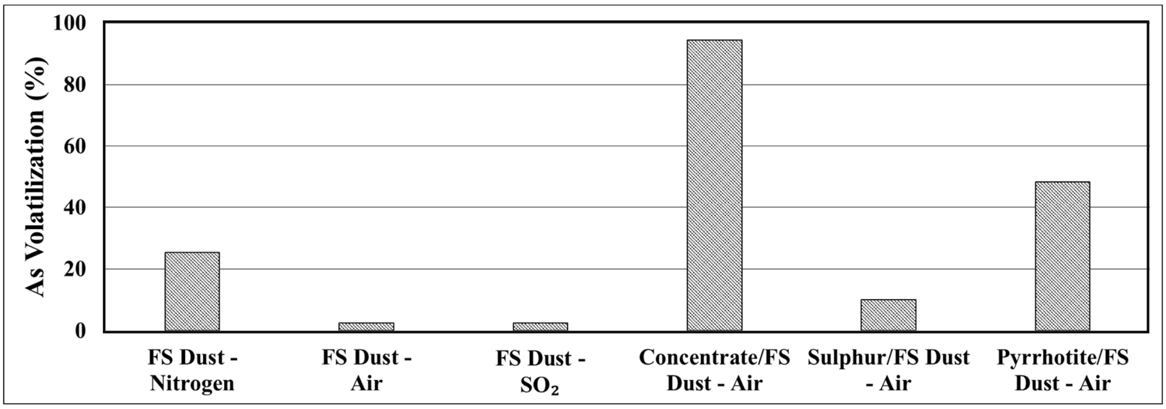

**Figure 11.** Volatilization of arsenic using different sources to the sulfidation process.

## 5. Conclusions

Scanning electron microscope images and SEM/EDS of FS dust indicated that it is mainly composed of particles with sizes between 10 and 100 µm, with a glassy matrix and crystals of iron oxides. The arsenic was found in the glassy matrix, in complex Fe-Cu-Zn-As-O-S-(and other elements) oxide phases such as Chenevixite, Clinoclase, tetrahedrite/tennantite. In the literature, the FS dust is characterized as small amorphous particles of arsenic oxides. Based on the results, it is plausible to propose that the arsenic present in the gases inside the Flash Smelting Furnace interacts with the suspended particles of liquid slag (<100 µm in size). When the exhausted gases cool, a glassy matrix in arsenic appears. The arsenic in the gas also precipitate as complex oxides.

The results of roasting the copper concentrate with high concentrations of arsenic were in accordance with the results reported in the literature for thermal decomposition and oxidation of enargite. The main contribution of the experiments carried out for this material revealed that to obtain a high volatilization of arsenic, the roasting process had better to take place at temperatures of 700 °C.

The data obtained through this work indicated that the arsenic present in the FS dust can be volatilized through roasting a mixture of copper concentrate/FS dust at temperatures above 600 °C and roasting times that are less than 5 min. The mixing to roaster requires a weight ratio of copper concentrate/FS dust greater than 50/50. At an industrial level, it would be effective to take this process in an alternate roasting furnace and then recirculate it in the copper smelting process.

The results obtained for antimony indicated that this element can also volatilize with the mixture of copper concentrate/FS dust. Furthermore, even a direct oxidation of the FS dust would be enough to obtain volatilization of the order of 90%.

There were interesting findings where the arsenic volatilization was not effective for the pyrrhotite/FS dust mixture and sulfur/FS dust mixture. Considering that both materials, sulfur and pyrrhotite, generate a high partial pressure of $SO_2$, an explanation was not found for the fact that the sulfidation-decomposition-oxidation process did not occur with the same success as the mixture between copper concentrate and FS dust. However, a more extensive and detailed experimental research would be required for these materials to confirm what was found.

The removal of arsenic by means of a sulfidation-decomposition-oxidation process from the copper concentrate/FS dust mixtures was analyzed using SEM/EDS, in order to find the formation of "fresh" enargite-tenantite crystals, which were not detected. A more detailed experiment and SEM/EDS, XRD, and QEMSCAN characterization will be required to detect the possible formation of crystals of enargite-tenantite. However, given the successful volatilization of arsenic reported in the experimental results, it is possible to consider that the sulfidation-decomposition-oxidation occurs simultaneously without the formation of these crystals.

Future research may be directed to the design of a roasting dedicated to the roasting of mixtures of copper concentrate/FS dust, with an application of the information found in this research. Simultaneously, a study estimating the correct amount of sulfur would be necessary to have an autogenous roasting process.

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