

Article

Pretreatment to Leaching for a Primary Copper Sulphide Ore in Chloride Media

Víctor Quezada ^{1,2,*} , Antoni Roca ¹ , Oscar Benavente ², Montserrat Cruells ¹, Evelyn Melo ² and María Hernández ² 

¹ Departamento de Ciencia de los Materiales y Química Física, Universitat de Barcelona, 08028 Barcelona, Spain; roca@ub.edu (A.R.); mcruells@ub.edu (M.C.)

² Departamento de Ingeniería Metalúrgica y Minas, Universidad Católica del Norte, Antofagasta 1270709, Chile; obenaven@ucn.cl (O.B.); emelo@ucn.cl (E.M.); mhernan@ucn.cl (M.H.)

* Correspondence: vquezada@ucn.cl; Tel.: +56-552651024

Abstract: The dissolution of copper sulphide ores continues to be a challenge for the copper industry. Several media and leaching alternatives have been proposed to improve the dissolution of these minerals, especially for the leaching of chalcopyrite. Among the alternatives, pretreatment prior to leaching was proposed as an option that increases the dissolution of copper from sulphide ores. In this study, a mineral sample from a copper mining company was used. The copper grade of the sample was 0.79%, and its main contributor was chalcopyrite (84%). The effect of curing time (as pretreatment) in a chloride media on copper sulphide ore was evaluated at various temperatures: 25, 50, 70 and 90 °C. The pretreated sample and leaching residues were characterized by X-ray diffraction, scanning electron microscopy, and reflected light microscopy. Pretreatment products such as CuSO₄, NaFe₃(SO₄)₂(OH)₆, and S⁰ were identified although with difficulty, due to the low presence of chalcopyrite in the initial sample (1.99%). Under the conditions of 15 kg/t of H₂SO₄, 25 kg/t of NaCl, and 15 days of curing time, a copper extraction of 93.1% was obtained at 90 °C with 50 g/L of Cl[−] and 0.2 M of H₂SO₄.

Keywords: pretreatment; curing time; leaching; primary copper; sulphides; chloride



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1. Introduction

During the few last decades, hydrometallurgy has played a key role in the development of the copper industry in Chile, supporting the mining industry in being the largest copper producer worldwide [1]. Leaching is a process used to achieve the recovery of copper from oxidized minerals and secondary sulphides [2,3]. There are numerous challenges in maintaining copper production in Chile due to the location of the deposits and their natural conditions, including energy costs, environmental impacts, and water scarcity [4–6]. However, Chile's copper production from hydrometallurgy will suffer a sharp decrease, from 28.8% in 2017 to 11.6%, by 2029 [7] due to the depletion of oxide and secondary sulphides ores, leaving copper extraction from primary sulphides as the almost only alternative [8].

Worldwide, the main source of copper is from sulphide minerals, from which 80% of copper is extracted. The main treatment of oxidized minerals is through hydrometallurgy, and for sulphide minerals, it is through flotation followed by a pyrometallurgical process [9]. Flotation processes have a series of challenges related to the environment, such as the generation of tailings in obtaining copper concentrate, the formation of pollutants such as SO₂ and As₂O₃, high energy consumption, and the complex management of the by-products obtained, among others [10,11].

An alternative for the treatment of copper sulphides is through leaching; however, due to the mineralogical characteristics of these minerals, the corresponding processes are difficult to develop. This is due to the slow dissolution kinetics of these minerals, so

it is necessary to find the adequate conditions to obtain an optimal process [12–15]. The slow dissolution kinetics are due the formation of a passivating layer, which prevents the access of the leaching agent to the mineral surface, inhibiting the reaction [16,17]. The main copper sulphide minerals are bornite (Cu_5FeS_4), enargite (Cu_3AsS_4), covellite (CuS), chalcocite (Cu_2S), and chalcopyrite (CuFeS_2), the latter being the most important and abundant copper sulphide mineral, which is associated with pyrite (FeS_2), galena (PbS) and sphalerite (ZnS), among others [18,19].

In the last 5 years, several studies have proposed the use of a pretreatment prior to the leaching process for copper recovery [20–23]. This pretreatment consists of the agglomeration and curing processes, which lead an increase in the dissolution of copper from sulphide minerals that can be obtained. According to Kodali [24], these stages are the best opportunity to improve the dissolution of copper prior to the construction of the heap. Most of the studies evaluating pretreatment (mainly curing) were developed on chalcopyrite ores.

The benefits of applying the curing process, mainly the resting time or curing time, were evaluated by Hernández et al. [20], Cerda et al. [23], and Velásquez-Yévenes et al. [25]. The study performed by Velásquez-Yévenes [25] evaluated the effect of four curing times: 30, 50, 80, and 100 days for a mineral agglomerated with 5 kg/t H_2SO_4 and using discard brine (32 g/L Cl^-), studying the pretreatment effect on leaching efficiency (copper recovery). The maximum copper dissolution (43%) was achieved for a pretreatment with 100 days of curing and subsequent column leaching at room temperature with intermittent irrigation. The temperature evaluation as part of the pretreatment was investigated by Cerda et al. [23]. The authors demonstrated that a maximum of 93% copper extraction was obtained when the ore (mainly chalcopyrite) was treated with 90 kg Cl^- /t ore, 40 days of curing time, and 50 °C in flask leaching.

The study of Hernández et al. [20] evaluated the effect of NaCl and NaNO_3 on the pretreatment of a mine ore, in which the main copper mineral was chalcopyrite. The authors obtained an optimum copper extraction of 58.6% with the addition of 23.3 kg of NaNO_3 /t, 19.8 kg of NaCl/t, and after 30 days of curing time at 45 °C. In addition, the effect of pretreatment was evaluated by leaching efficiency using mini columns. The optimum copper extraction of 63.9% was obtained in a leaching test conducted at 25 °C with the use of 20 g/L of chloride. Furthermore, these authors proposed a pretreatment mechanism for chalcopyrite (See Reaction 1). According to them, the reaction is thermodynamically possible under atmospheric pressure and between 25 and 45 °C.



On the other hand, a recent study published by Quezada et al. [26] proposed a pretreatment reaction on a chalcopyrite mineral in a sulphuric acid–chloride media. In this work, a sample especially rich in copper (28.5% Cu) was used for the characterization of products formed during the curing step prior the leaching step. The authors developed a mineralogical characterization of the agglomerates obtained after 15 days of curing, 15 kg/t H_2SO_4 , and 25 kg/t NaCl using scanning electron microscopy (SEM), X-ray diffraction (XRD), and reflected light microscopy (RLM). The authors indicated that the pretreatment products were copper sulphate (CuSO_4), natrojarosite ($\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$), elemental sulphur (S^0), and copper hydroxychloride $\text{Cu}_2\text{Cl}(\text{OH})$ (See Reaction 2). The passivation during leaching at temperatures between 30 and 70 °C was attributed to the sulphur layer over the chalcopyrite surface.



This research focuses on the effect of acid curing on primary copper sulphide ore (0.79% Cu) in sulphuric acid–chloride media. The products generated in the pretreatment (agglomerates) and leaching residues were characterized using X-ray diffraction, scanning electron microscopy, and reflected light microscopy. The effect of the pretreatment on leaching efficiency was evaluated at different temperatures, considering the effect of the presence of elevated amounts of gangue in acid consumption. The obtained results are

compared with those obtained over a sample with 28.5% Cu [26]. In general, it is shown that pretreatment increases copper extraction and decreases the leaching time. Furthermore, pretreatment is inexpensive, and leaching presents the higher cost the longer it lasts.

2. Materials and Methods

2.1. Copper Sulphide ore Sample

The sample was obtained from an operating mine in Antofagasta, Chile. This sample was initially crushed by a jaw crusher followed by a secondary and tertiary cone crusher, and it was finally dry milled in a ball mill. The size fraction used was $-38 + 25\ \mu\text{m}$. The mineral particles were reduced in size with a closed crushing and grinding circuit.

The chemical composition of the sample was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Optima 8300, Perkin Elmer, Waltham, MA, USA). Before ICP-OES analysis, the solid sample was digested using 1 g of sample in 20% aqua regia solution and heated reaching the boiling point.

Mineralogical data were obtained by X-ray diffraction (XRD) analysis using a diffractometer (PANalytical, X'Pert PRO MPD Alpha1, Malvern, UK) operating from 4° to 100° 2θ , 45 kV, 40 mA, and $K\alpha$ $1.54\ \text{\AA}$, with a step size 0.017° and a time per step of 150 s. X-ray diffractograms were interpreted using the software X'pert HighScore Plus v.3.0e (PANalytical, Almelo, The Netherlands).

Qemscan analysis was performed using a Model Zeiss EVO 50 (Zeiss, Oberkochen, Germany) with Bruker AXS XFlash 4010 detectors (Bruker, Billerica, MA, USA) and Software iDiscover 5.3.2.501 (FEI Company, Brisbane, Australia). Additionally, a reflected light microscope (Zeiss, Axiovert 100, Milan, Italy) was used. Finally, morphological characterization was conducted using a scanning electron microscope (SEM) (JEOL J-7100F, Tokyo, Japan) operating at 20 kV under high vacuum conditions (Emitech K-950X, Lohmar, Germany) coupled with an energy-dispersive X-ray spectroscopy (EDS) microanalysis system (Oxford Instruments INCA, Oxfordshire, UK). Mineral samples were coated with a thin layer of carbon to improve their conductivity. A carbon source in the form of a rod was mounted in a vacuum system between two high-current electrical terminals. When the carbon source was heated to its evaporation temperature, a fine stream of carbon was deposited onto the specimens before SEM characterization.

2.2. Curing Experiments

A total of two grams of the copper sulphide sample was used in each curing test. The samples were agglomerated on an impermeable plastic surface by manually mixing the ore with the solution. The samples were agglomerated with a solution of 15 kg/t H_2SO_4 and 25 kg/t NaCl using a solid/liquid ratio of 10/2.2 (mass/volume), namely using 0.22 mL of solution per 1 g of ore. A detailed description of this technique was included in a previous paper [26]. Sulfuric acid and NaCl concentrations were reported as favorable in a previous study published by the authors on the pretreatment of a chalcopyrite mineral [22]. After agglomeration, the samples were placed on watch glasses, covered with a protective film (thermoplastic), and cured in a dark at room temperature for 15 days. The cured samples were used for the mineralogical characterization and leaching tests. After the curing time, briquettes were formed for the mineralogical characterization using a reflected light microscope, XRD, and SEM-EDS analysis. The briquettes were prepared and polished without contact with water to avoid the dissolution of the soluble phases. Finally, the cured samples were used to evaluate the effect of the pretreatment on the copper sulphide ore dissolution.

2.3. Leaching Test

The pre-treated and untreated samples were leached using a mechanical stirrer in a 200 mL vessel with a four-neck using 100 mL of leaching solution containing $0.2\ \text{mol}\cdot\text{L}^{-1}$ of H_2SO_4 (19.6 g/L) and 50 g/L of Cl ion (Figure 1). Agitation was applied using a RW 20 digital overhead stirrer (IKA, Staufen im Breisgau, Germany) at $300\ \text{min}^{-1}$ and heated by a

thermostatically controlled water bath (Lauda, Alpha A24, Lauda-Königshofen, Germany) to the required temperature: 25, 50, 70, and 90 °C (± 1 °C). When the solution reached the desired temperature, a 2 g of sample of cured or noncured ore was added to the solution, and leaching was conducted for a period of 48 h. During the leaching process, the holes in the vessel lid were not covered. Evaporation losses were compensated by adding deionised water. All experiments were performed by duplicate, and the results presented here are the averages of the obtained data ($\pm 1.50\%$ in copper extraction).

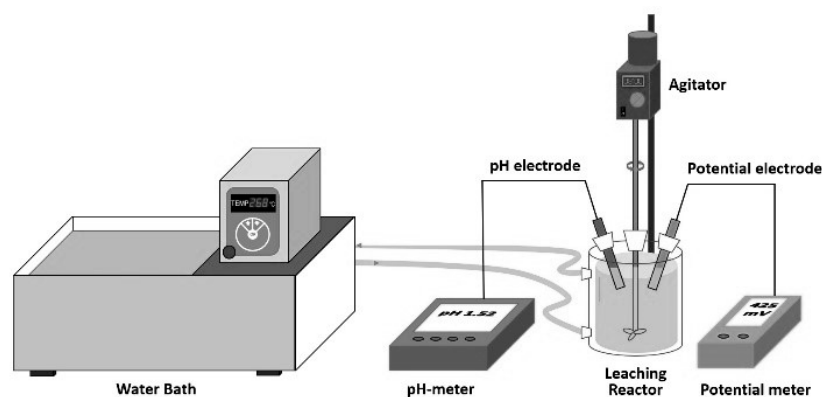


Figure 1. Scheme of the magnetic stirrer leaching system.

Sample solutions (3 mL aliquots) were periodically withdrawn for chemical analysis. The samples were filtered (0.2 μm), and the metal concentrations in the filtrate were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). The pH and redox solution potential were regularly measured using a pH-ORP meter (HANNA Instruments, HI-4222, St. Louis, MO, USA). All solution potentials were converted to values against the standard hydrogen electrode (SHE). The solid residues from the leaching experiments were analysed using XRD analysis.

3. Results and Discussion

3.1. Initial Sample Characterization

The chemical composition of the sample was 0.79% Cu, 2.52% Fe, 2.49% S, and 9.70% Al. Chemical characterization showed that insoluble residue represented 80% of total mass, which suggests the presence of quartz and silicates as insoluble phases.

Figure 2 (X-ray diffractogram) shows that the most abundant species was quartz. In addition, other species such as muscovite, pyrite, and orthoclase were detected. The only copper mineral detected was chalcopyrite. Table 1 shows the mineralogical composition obtained by Qemscan analysis. The main species were muscovite (54.2%) and quartz (29.7%). Other species such as pyrite (3.73%), orthoclase (3.08), and kaolinite (2.51%), were also detected. Chalcopyrite is the most abundant copper mineral (1.99%), representing 84% of the total copper present in the sample. The second largest contributor of the copper was chalcocite (0.150%), representing 10% of the total copper in the sample. Finally, covellite (0.06%) was identified, representing 5.3% of the total copper in the sample.

The high presence of Muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$) coincides with the high presence of aluminum in the sample (9.70%). Furthermore, muscovite and quartz represented 84% of the total sample, which coincides with the insoluble residue of the chemical characterization (80%). These analyses show a high presence of gangue minerals.

According to the images obtained using a reflected optical microscope, chalcopyrite and pyrite were recognized according to the characteristic brightness of each species (Figure 3). SEM-EDS analysis showed the majority of the initial sample was composed of muscovite and quartz. Figure 4a shows an analyzed area of the sample, and Figure 4b shows the enlargement of the lower left area of Figure 4a. Finally, chalcopyrite, pyrite, and muscovite were identified in Figure 4b. Through the semi-quantitative reporting of

elements, Figure 4c shows an atomic Cu:Fe:S ratio of 1:1:2, which indicates the presence of chalcopyrite, while Figure 4d shows an atomic Fe:S ratio of 1:2, which denotes the presence of pyrite. Figure 4e shows an atomic K:Al:Si:O of 1:3:3:14, which was associated with muscovite.

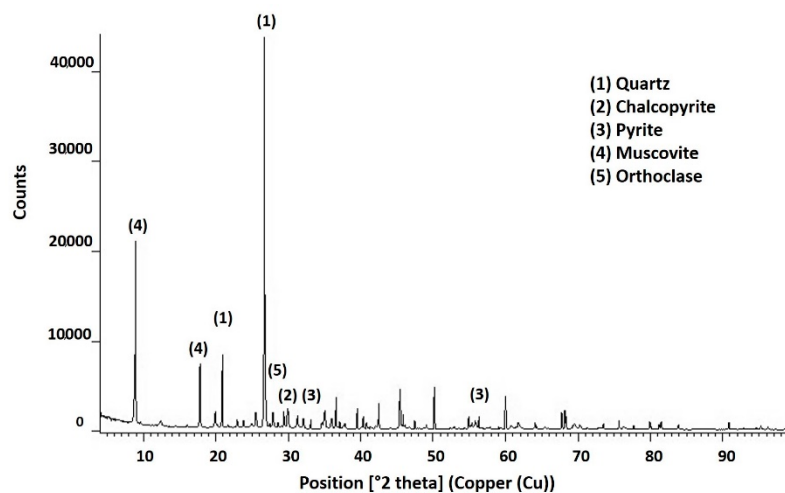


Figure 2. X-ray diffraction pattern of the initial sample.

Table 1. Minerals in the copper sulphide ore sample (mass in %) based on Qemscan analysis.

Mineral	Mass, %
Muscovite	54.2
Quartz	29.7
Pyrite	3.73
Orthoclase	3.08
Kaolinite	2.51
Chalcopyrite	1.99
Smectite	1.32
Alunite	1.18
Chalcocite	0.150
Covellite	0.060

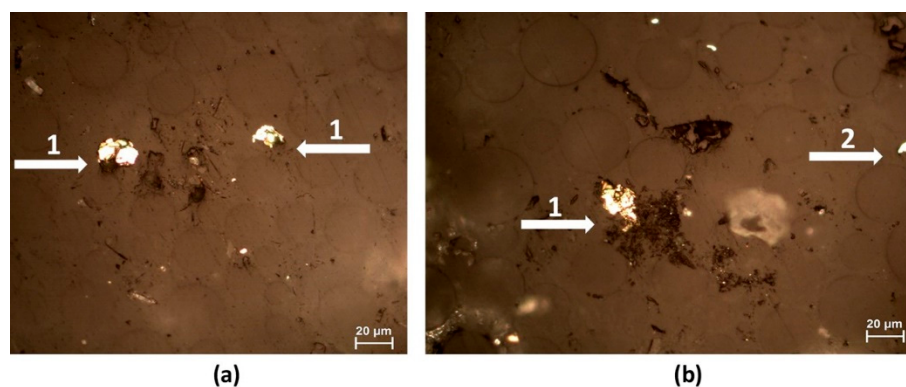


Figure 3. Reflected optical microscope images of the initial sample (a,b). Chalcopyrite identified in (a) as (1) and pyrite (b) as 2.

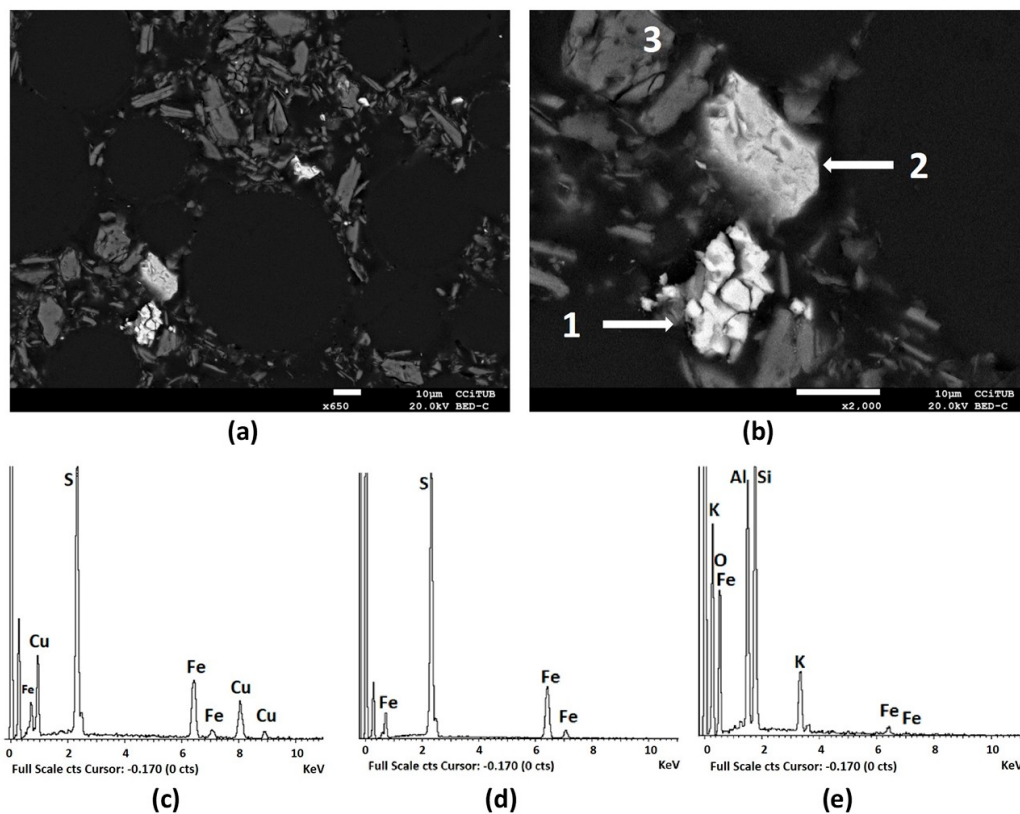


Figure 4. SEM image of the initial sample at various magnifications: (a) $\times 650$, (b) $\times 2000$. In (b), 1: chalcopyrite, 2: pyrite, and 3: muscovite. EDS analysis in (c) of chalcopyrite, in (d) of pyrite, and in (e) of muscovite.

The copper species were in minority content, which coincides with the nature of the sample. According to By et al. [27], species such as quartz and biotite are not reactive against the presence of sulphuric acid. Muscovite was also declared to be of low reactivity in acid media [28]. Furthermore, pyrite is an inert sulphide, strong oxidants have to be employed for its efficient dissolution, and no such conditions exist in the proposed treatment [29].

3.2. Characterization of Cured Ore Samples

The pretreatment products that were obtained (agglomerated solids) were characterized to identify the newly formed products.

Figure 5 shows the characterization performed by optical microscope conducted over a sample with a pretreatment using 15 kg/t H_2SO_4 , 25 kg/t NaCl, and 15 days as curing time. A chalcopyrite particle with green edges was observed, showing the formation of new products. These products were associated with copper sulphate or chloride–copper complexes, as evidenced by Quezada et al. [26]. In Figure 5b, a similar behavior was evidenced but with a greater intensity in the formation of the reaction products around the particle.

The identification of new species by X-ray diffraction analysis is presented in Figure 6. Species such as quartz and muscovite are still the most abundant, compared to the initial sample. Other species such as pyrite and orthoclase were identified as minority species. Chalcopyrite is still present, and other species resulting from the pre-treatment, such as copper sulfate, iron sulfate, or elemental sulphur, were not identified. However, the presence of these species should not be ruled out, according to Hernández et al. [20] and Quezada et al. [26]. Finally, sodium chloride (NaCl) was identified as a product of this pretreatment. This is due to the high presence of NaCl used in the formation of the solution that agglomerates the sample. It is possible to associate the presence of NaCl at angles

31.69° and 45.43° (in 2 theta), the main angles of this species. According to Zhang et al. [30], the presence of this salt is both stable and possible under ambient conditions.

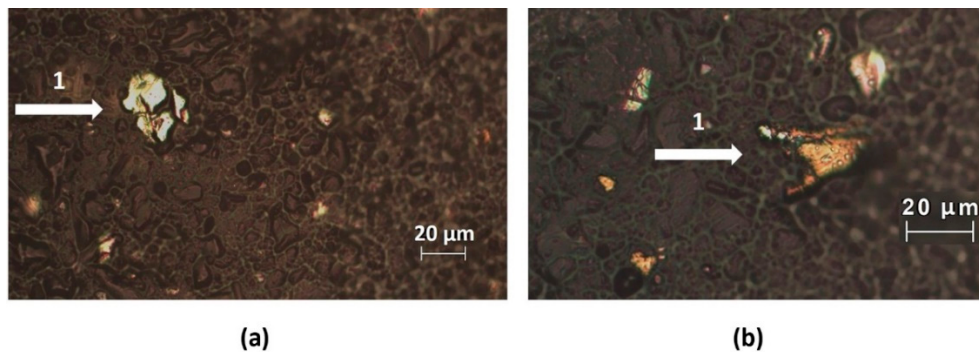


Figure 5. Reflected optical microscope images of the pretreatment products at a magnification of $\times 50$ (a,b). Chalcopyrite identified in (a,b) as (1).

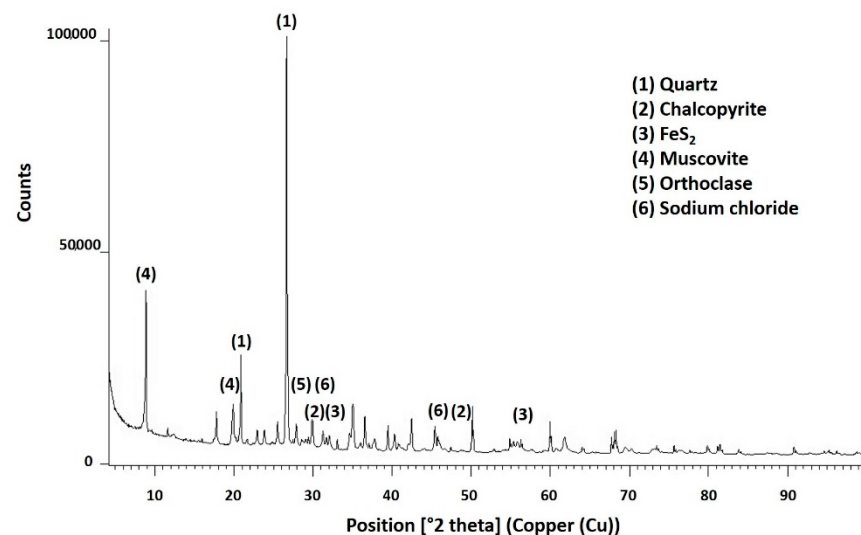


Figure 6. X-ray diffractogram for copper sulphide ore agglomerated with 15 kg/t of H_2SO_4 , 25 kg/t of NaCl, and 15 days of curing time at room temperature.

The initial diffractogram was compared to the diffractogram of the sample that had been pretreated. Following Reaction 2 proposed by the authors in a previous work, Quezada et al. [26], the products formed during the pretreatment of a chalcopyrite mineral were $CuSO_4$, $NaFe_3(SO_4)_2(OH)_6$, and elemental sulphur.

Comparing the initial diffractogram versus the pretreatment diffractogram, the principal angles of natrojarosite appeared. Some hints of its presence were observed. Figure 7 shows the variation in the presence of natrojarosite before and after pretreatment. For high presence, dissolved iron is required, which is mainly associated with chalcopyrite and pyrite. If chalcopyrite reacts, iron will be available. It is important to consider that the presence of chalcopyrite in this sample was 1.99% instead of 74% of the sample used in a previous paper [26].

Regarding the $CuSO_4$, it was difficult to confirm its presence due to the low content of chalcopyrite in the initial sample. Figure 8 shows one of its secondary peaks but not the peak corresponding to the main angle. However, the intensity associated with this angle is very low. Finally, the eventual presence of elemental sulphur is shown in Figure 9, which is associated with secondary but not main angles. In the case of $Cu_2Cl(OH)$, no main or secondary angles were observed. As such, its presence, at least through X-ray diffraction analysis, was not confirmed.

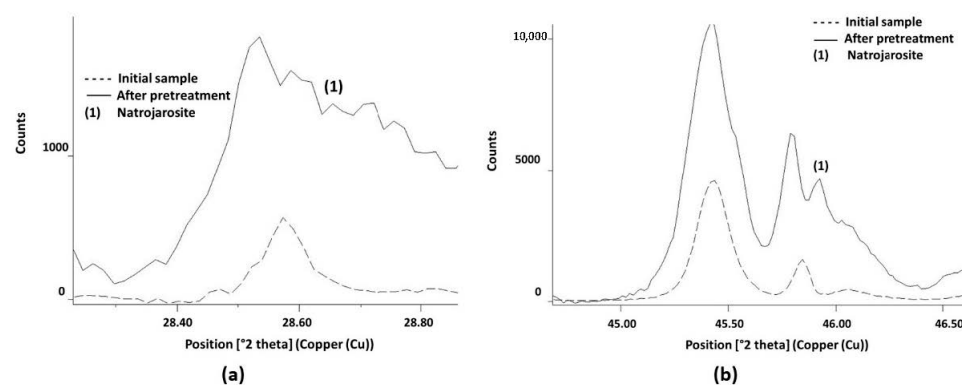


Figure 7. $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$, a product of the pretreatment of copper sulphide ores with 15 kg/t of H_2SO_4 , 25 kg/t of NaCl, and 15 days of curing at room temperature as identified by X-ray diffraction. In (a,b), the new presence of $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ was identified as (1), compared to the initial diffractogram of the sample.

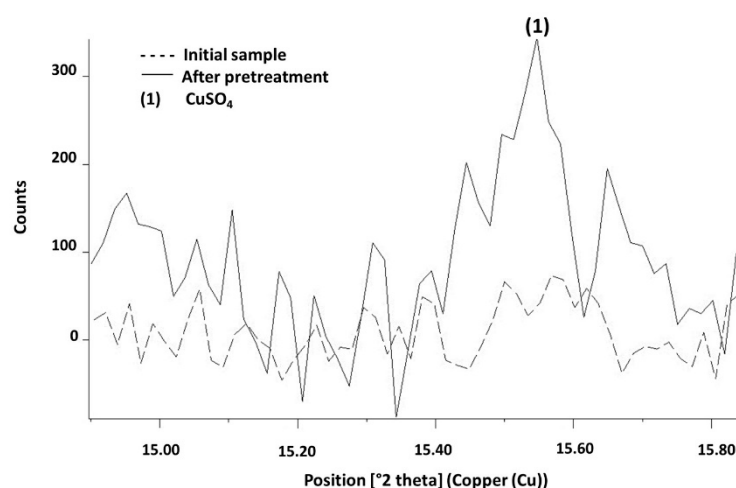


Figure 8. CuSO_4 identification by X-ray diffraction analysis in copper sulphide ore pretreated with 15kg/t of H_2SO_4 , 25 kg/t of NaCl, and 15 days of curing at room temperature.

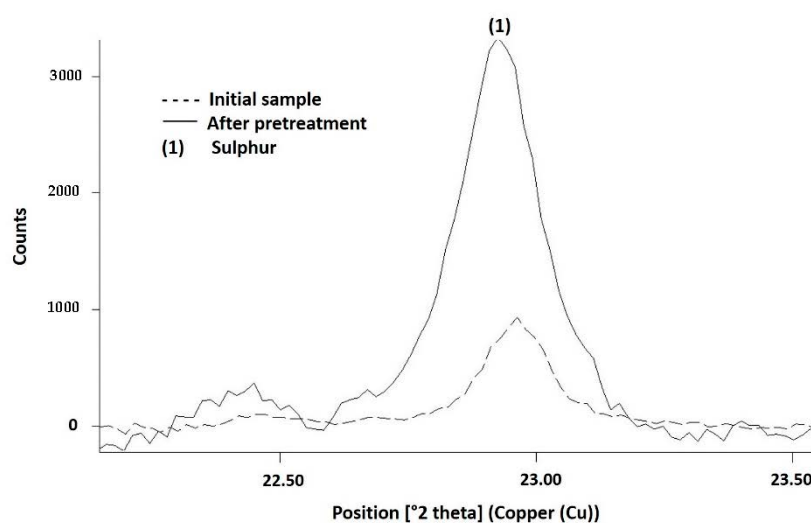


Figure 9. Elemental sulphur identification by X-ray diffraction analysis in copper sulphide ore pretreated with 15 kg/t of H_2SO_4 , 25 kg/t of NaCl, and 15 days of curing at room temperature.

SEM analysis was used to identify species formed during the pretreatment. As in X-ray diffraction analysis, due to the low presence of chalcopyrite, the identification for species

using SEM was limited. The quartz, muscovite, and pyrite species were easy to detect because of their abundance. Furthermore, unreacted chalcopyrite was identified (Figure 10). Figure 10b shows an atomic Cu:Fe:S ratio of 1:1:2, which indicated unreacted chalcopyrite.

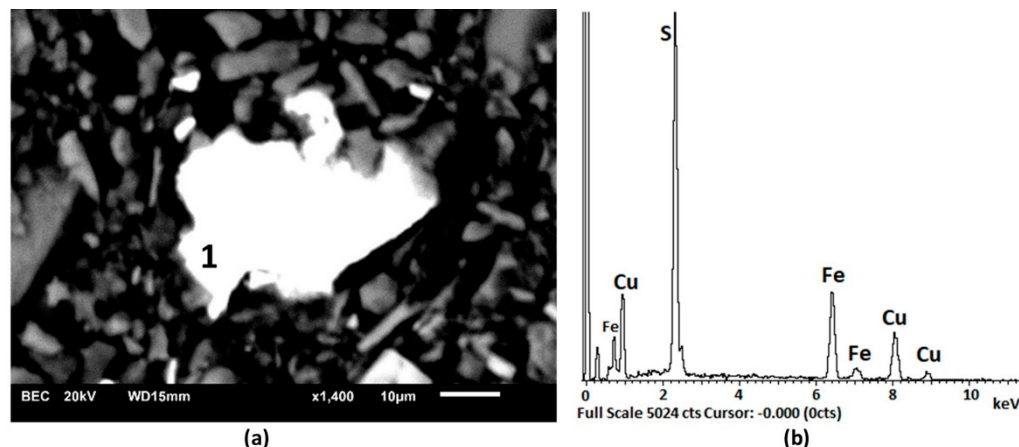


Figure 10. SEM image (a) and EDS analysis (b) of Zone 1. Unreacted chalcopyrite (1) in the products of the pretreatment of copper sulphide ore with 15 kg/t of H_2SO_4 , 25 kg/t NaCl, and 15 days of curing at room temperature. In (a), the image is at a magnification of $\times 1400$.

As postulated in Reaction 2, the pretreatment of chalcopyrite in chloride media prior to leaching proposed the formation of products such as CuSO_4 , $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$, elemental sulphur, and $\text{Cu}_2\text{Cl}(\text{OH})$, which was also considered in studies developed by Hernández et al. [20] and Cerda et al. [23]. Therefore, according to the conditions used in this study, CuSO_4 , $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$, and elemental sulphur were identified. Species such as $\text{Cu}_2\text{Cl}(\text{OH})$ or similar ones were not identified, probably due to the low presence of chalcopyrite in the initial sample (1.99%). Performing this type of test with a pure mineral as conducted in a previous paper becomes highly recommended because it reduces noise in the interpretation [26].

3.3. Leaching with and without Pretreatment

To evaluate the effect of the curing time, copper sulphide ore samples with pretreatment (agglomerated and cured with 15 kg/t of H_2SO_4 , 25 kg/t of NaCl for a period of 15 days) and without pretreatment were leached at 25, 50, 70, and 90 °C.

3.3.1. Leaching Test without Pretreatment

Figure 11 shows the results of the leaching tests without pretreatment. It can be observed that as the temperature increased, the leaching efficiency increased. The test conducted at 25 °C shows a very classic behavior of a mineral whose main contribution is chalcopyrite [31] in that it reached 16.7% copper extraction and had clear passivation. Considering that chalcopyrite represents 84% of total copper, it can be inferred that the extracted copper would be associated with other more soluble phases such as chalcocite (10% of total copper) and covellite (5% of total copper). According to Dutrizac [32], it is always important to consider these contributions, no matter how small, as this presence can undermine the extraction of copper, especially at low temperatures. By increasing the temperature to 50 °C, a copper dissolution of 44.3% was reached. When the temperature increased to 70 °C, the final copper extraction was 64.4%, showing no clear passivation after 48 h of leaching. Finally, the test conducted at 90 °C reached a copper extraction rate of 88.6%.

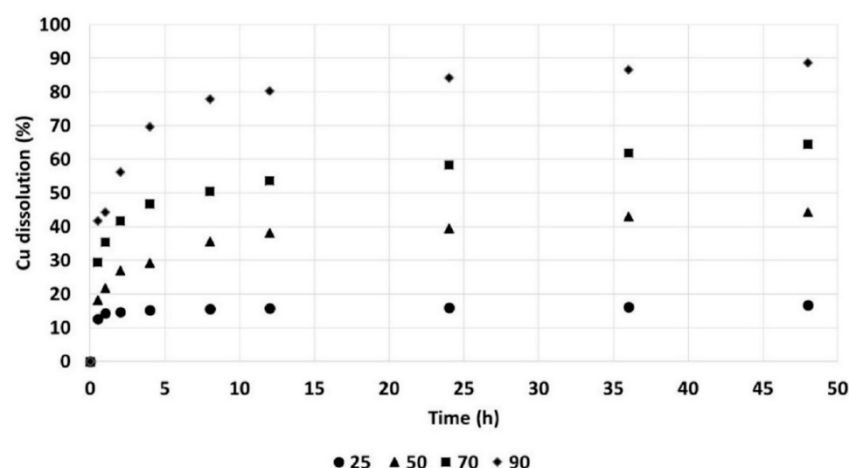


Figure 11. The dissolution of copper from copper sulphide ores without pretreatment in 0.2 M of H_2SO_4 and 50 g/L of Cl^- in deionized water at 25 °C (●25), 50 °C (▲50), 70 °C (■70), and 90 °C (◆90).

3.3.2. Leaching Test with Pretreatment

For the leaching tests performed with pretreatment, the results are shown in Figure 12. A trend very similar to tests without pretreatment was observed but with a higher percentage of copper dissolution. The test performed at 25 °C (with pretreatment) reached a copper extraction rate of 25.9%. This value is almost 10 points higher, compared to the tests without pretreatment. In Figure 12, the passivation of the mineral was evidenced at 25 °C, and the copper extraction was similar to the curing test (27.4%). When the leaching temperature was 50 °C, the copper extraction reached 48.9%, and at 70 °C, 70.2% of copper dissolution was achieved. Finally, at 90 °C, a 93% of copper extraction rate was achieved. There was greater extraction of copper in all tests with pretreatment, resulting in an average of 5% more copper extracted, except at 25 °C, where difference was almost 10% higher.

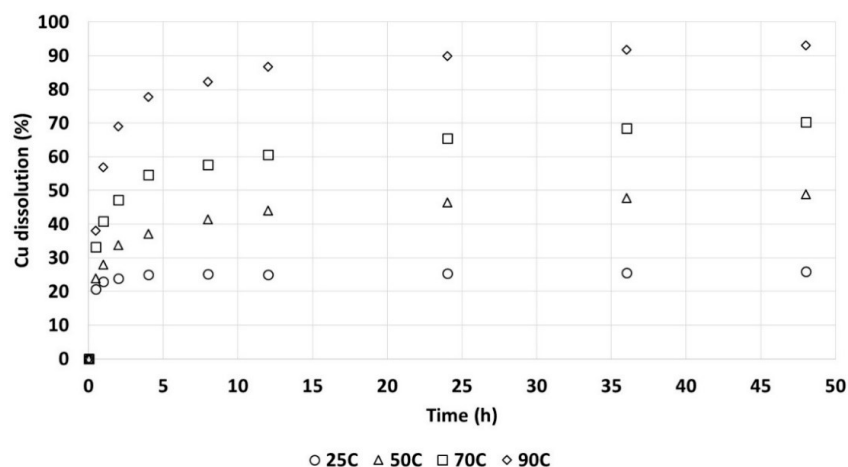


Figure 12. The dissolution of copper from copper sulphide ores with pretreatment in 0.2 M of H_2SO_4 and 50 g/L of Cl^- in deionized water at 25 °C (○25), 50 °C (△50), 70 °C (□70), and 90 °C (◇90).

For tests with pretreatment, the stability of the copper extraction was reached before the tests without pretreatment. This is because the sulfation that was generated becomes a soluble copper product. It was observed that all tests with pretreatment achieved higher copper extraction. In addition, pretreatment tests show greater reactivity in the first two hours of the process. However, as time and temperature increase, the difference in copper extraction decreases. Furthermore, with the pretreatment at 90 °C, a copper extraction of 90% was achieved in 24 h, while without pretreatment, it took 48 h.

According to Hernández et al. [20], the curing time also solubilizes iron, contributing the ferric ions to in the dissolution of the sulphides. This would occur in all of those tests since dissolving more than 20% of copper guarantees iron dissolution as well. This occurs in all tests leached with pretreatment and within the first hour of leaching. Furthermore, a chloride–acid media promotes the formation of copper–chloride complexes due to the rapid incorporation of Cu^{2+} into the system by pretreatment samples [33].

3.3.3. Characterization of Leaching Residues

The characterization of leaching residues was performed in all leaching tests using X-ray diffraction analysis. Table 2 presents a summary of the main species identified by using this technique, with quartz, muscovite, and pyrite being the most abundant in the leaching residue. These results are similar to those obtained in a previous work [26], in which a rich sample of chalcopyrite was used (with small amount of gangue). It can be concluded that there was low acid consumption to dissolve the gangue phases in the sample. These results are in accordance with those obtained by Chetty [28], in which species such as quartz and muscovite were considered of low solubility in an acid media.

Table 2. Summary of the species identified using X-ray diffraction analysis. Tests with pretreatment samples are indicated by (P).

Test	More Abundant Species	Less Abundant Species
25 °C (P)	SiO_2 , $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ and FeS_2	CuFeS_2
25 °C	SiO_2 , $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ and FeS_2	CuFeS_2
50 °C (P)	SiO_2 , $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ and FeS_2	CuFeS_2 and Cu_2S
50 °C	SiO_2 , $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ and FeS_2	CuFeS_2 and Cu_2S
70 °C (P)	SiO_2 , $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ and FeS_2	CuFeS_2 and S
70 °C	SiO_2 , $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ and FeS_2	CuFeS_2 and S
90 °C (P)	SiO_2 , $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ and FeS_2	CuFeS_2 and S
90 °C	SiO_2 , $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ and FeS_2	CuFeS_2 and S

For the tests at 25 °C, the presence of unreacted chalcopyrite was determined. In tests performed at 50 °C, the presence of Cu_2S was confirmed. This Cu_2S could be undissolved mineral from the initial sample or a product of the leaching of the chalcopyrite. Since the presence of Cu_2S is not evident at 25 °C, it is likely to be the product of chalcopyrite leaching [34]. Regarding the tests performed at 70 °C, the presence of chalcocite is no longer evident. The presence of elemental sulphur in the system was observed for the first time due to the dissolution of copper from chalcopyrite (70.2% Cu in test with pretreatment). This does not rule out that at 25 and 50 °C, the presence of elemental sulphur cannot exist; the presence would be so low that it would be difficult to detect. The presence of elemental sulphur is normal in leaching residues, mainly due to the chalcopyrite dissolution, even for processes such as bioleaching [35,36]. Leaching tests at 90 °C reported a composition identical to the tests at 70 °C. The presence of other species that are responsible for the passivation of chalcopyrite, such as natrojarosite or copper polysulfides, were not identified. Furthermore, in systems with the presence of PbSO_4 , a lack of sulphuric acid could result in the precipitation of iron as plumbojarosite and could therefore create difficulties in the recovery of valuable metals [37]. According to the behavior of the pH in all of the tests, the formation of natrojarosite is unlikely. However, according to Lu et al. [38], it is possible to find this species at pH 0.9; the above would only be possible in tests at 90 °C.

4. Conclusions

The chemical composition of the mine ore sample is 0.790% Cu, 2.52% Fe, 2.49% S, and 9.70% Al. The mineralogical composition indicates the presence of 54.2% muscovite, 29.7% quartz, 3.73% pyrite, 3.08% orthoclase, 2.51% kaolinite, 1.99% chalcopyrite, and other elements in minor amounts.

The pretreatment with 15 kg/t H₂SO₄, 25 kg/t NaCl, and 15 days of curing leads to 27% copper extraction prior to the leaching step. This is mainly produced by the generation of copper sulfate identified by comparing the diffractograms of the initial sample versus the generated samples in the pretreatment.

The curing time benefits the kinetics of copper dissolution from copper sulphide ores. In addition, in synergy with the temperature (50 °C and 90 °C), it was possible to generate a difference of 5% in the extraction of copper compared to a mineral without pretreatment. A 93.1% copper extraction was obtained at 90 °C with a pretreatment using 15 kg/t H₂SO₄, 25 kg/t NaCl, and 15 days of curing time.

The leaching test, performed at 25 °C, generated the greatest difference in copper extraction. Extraction values of 16.7% and 25.9% were obtained without and with pretreatment, respectively. Chalcopyrite passivation was quickly achieved as evidenced by the behavior of the copper extraction curve over time (around 4 h of leaching).

For leaching at 70 °C, a copper extraction of 65% in 24 h with pretreatment and in 48 h without pretreatment was obtained. During leaching at 90 °C, a copper extraction of 90% in 24 h with pretreatment and in 48 h without pretreatment was also obtained. Thus, the curing treatment significantly reduced the leaching time needed for copper extraction.

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