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Effect of Pre-Treatment with Sodium Chloride/Sulfuric Acid on the Bornite Concentrate Leaching in Chloride Medium

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Abstract: In this work, the effect of the pre-treatment of bornite concentrate with a sodium chloride–sulfuric acid mixture prior to leaching with chloride solutions was evaluated. The influence of the dosage of NaCl and the resting time in the copper solution was evaluated. The solid residues of the pre-treatment were characterized by XRD to evaluate the changes that took place in the bornite. The experimental results show that as the sitting time and the amount of sodium chloride added are increased, the dissolution of the sulfide species also increased. The pre-treatment affects Cu preferentially because it has greater mobility than iron in the bornite crystal lattice. The pre-treatment promotes the formation of soluble Cu and Fe species. The efficiency of the pre-treatment depends largely on the formation of hydrochloric acid in the mixture at the particle level, due to the ease with which it diffuses through the bornite particles, achieving greater penetration of the pre-treatment.

Keywords: copper concentrate; bornite; pre-treatment; acid leaching; chloride

1. Introduction

Most of the world's copper reserves are found as sulfide phases, and 80% of the copper from deposits is obtained from Cu-Fe-S ores [1]. Traditionally, froth flotation and pyrometallurgical processes have been used for the treatment of copper concentrates from high-grade copper ores [2,3]. However, the constant decrease in ore grade, presence of toxic elements, and stricter environmental legislations make the hydrometallurgical option way more attractive [4,5]. In the last years, research and development have intensified in the search for hydrometallurgical alternatives to the processing of copper concentrates [6–10]. To improve and optimize the leaching of concentrates, attempts have been made to carry out a previous treatment, and this in turn requires knowing the phenomena that occur during the process.

Pre-treatment with concentrate is the previous step to heap leaching of copper oxide and secondary sulfide ores to improve the leaching process. Acid pre-treatment of ores produces dehydration and inhibits gangue dissolution. The pre-treatment provides an increase in the copper leaching rate by the sulfation of copper species and the acid-consuming gangue's passivation [11].

Recently, there have been ore or concentrate pre-treatment studies, with greater emphasis on chalcopyrite. Different chemical agents have been used for the pre-treatment, to increase the dissolution of copper in the later leaching process. Particularly, the pre-treatment applied to a chalcopyrite ore/concentrate showed excellent results after leaching the ore at 70 °C in a chloride medium, with recoveries close to 100% after 48 h of leaching. The addition of NaCl and sulfuric acid would promote the formation of polysulfides more soluble in aqueous media, and in the presence of chloride ions, the elementary sulfur layer is more porous, facilitating the diffusion of the reagents to its inside. That porosity promotes the formation of HCl and sodium sulfate [12–16]. The resting time of pre-treatment is another variable of interest. For example, the literature reports that chalcopyrite ore's dissolution rate increases as the curing period increases from 15 to 80 days. Researchers conclude that extended periods of pre-treatment can be useful to the hydrometallurgical processing of copper sulfide ores, decreasing the leaching cycle of the irrigation requirement [17].

Bornite, Cu_5FeS_4, is found associated with various sulfur-bearing copper minerals, and it can be found at equilibrium, mainly with chalcopyrite and chalcocite [18,19]. Various studies have been made to determine the leaching kinetics of bornite. Leaching with sulfate/ferric chloride is a complex process, so there is no agreement on the reactions involved. The oxidation of bornite with ferric ion can be divided into two stages. In the first stage, the rapid removal of copper leads to the formation of non-stoichiometric bornite ($Cu_{5-x}FeS_4$), chalcopyrite, and covelline. Non-stoichiometric bornite has cell parameters slightly lower than those of bornite, and it is progressively transformed into Cu_3FeS_4 and covelline. At low temperatures, the reaction ends in the Cu_3FeS_4 phase. In the second stage, the Cu_3FeS_4 product is oxidized to Cu^{2+}, Fe^{2+}, and elemental sulfur, which is a reaction that only occurs by leaching at high temperatures [20–28]. On the other hand, some papers have reported the chloride addition to copper refractory species' hydrometallurgical processing [29,30]. Copper chloride leaching from bornite concentrates and ore demonstrates that bornite was oxidized more readily in saline water (high chloride concentration); mineralogical analyses of the residues showed that the final reaction product was sulfur. However, the kinetic of bornite dissolution in chloride media is more complex. In the initial stages, bornite leaching is fast, and an intermediate "idaite-type" copper mineral is formed. The second stage involves initial sulfur formation. The final step involved the formation of a low-permeable sulfur layer [31–33].

The objective of this research is to study the dissolution of copper by pre-treating a bornite concentrate with a sodium chloride–sulfuric acid mixture and then leaching in a chloride medium. The NaCl dosage and the conditioning time were evaluated, and the formation of hydrochloric acid during the pre-treatment process was also studied.

2. Materials and Methods

2.1. Characterization of the Concentrate

The experimental study involves the use of a bornite concentrate obtained through a flotation process, with a copper content of 54.46% and a granulometry of 80% below 72 µm. The copper content of the concentrate was determined by atomic absorption spectrophotometry (GBC Scientific Equipment Spectrophotometer, SensAA, Dandenong Victoria, Australia). The mineral composition, Table 1, was determined by X-ray diffraction (Siemens® D5000 X-ray diffractometer, The Woodlands TX, USA).

Table 1. Mineralogical composition of the concentrate.

Mineral Species	Chemical Formula	Composition (%)
Bornite	Cu_5FeS_4	66.69
Chalcopyrite	$CuFeS_2$	19.80
Calcium–magnesium silicate	CaMgSi	7.18
Copper hydroxide–silicate	$Cu_5(SiO_3)_4(OH)_2$	5.20

2.2. Experimental Techniques

The pre-treatment consists of the addition of sodium chloride (99.89% pure) to 3-g samples of bornitic concentrate in each dose (Table 2). The mixture was moistened with distilled water to reach

10% moisture concerning the dry concentrate. Sulfuric acid (98% pure) was added in an amount of 30% over the stoichiometric consumption. The stoichiometry is given by reaction (1):

$$Cu_5FeS_4 + 3O_2 + 6H_2SO_4 \rightarrow 5CuSO_4 + FeSO_4 + 6H_2O + 4S^\circ. \quad (1)$$

The material was allowed to rest at 298 K in a controlled temperature reactor, adding distilled water periodically to prevent the drying of the samples.

Table 2. Pre-treatment experimental conditions.

Experimental Variables	Levels
NaCl dose (kg/t)	0, 15, 30, and 60
H_2SO_4 dose (kg/t)	290
Resting time (days)	15 and 30

After the pre-treatment, the samples were subjected to XRD analysis and stirred leaching in chloride medium.

The leaching of the samples was carried out in a stirred 500-mL cylindrical reactor, keeping constant the following experimental parameters: solution volume: 300 mL, chloride ion concentration: 60 g/L, temperature: 298 K, pH: 1.5, leaching time: 48 h. Furthermore, a control sample of concentrate with no pre-treatment was leached for 94 h. The pH was adjusted during the process by adding sulfuric acid. Aliquots of 3 mL were taken at 1, 3, 24, and 48 h, and their iron and copper concentrations were determined by atomic absorption spectrophotometry. The volume of the aliquots was made up of a leaching solution. The residual NaCl content in the leaching solution was determined by titration with silver nitrate (Argentometry).

The solid residues of the leaching selected for XRD analysis were filtered under vacuum and washed with distilled water until constant pH to prevent further reactions due to residual acidity.

3. Results and Discussion

3.1. Leaching without Pre-Treatment

A 3-g sample of the concentrate was leached in a solution with 60 g/L of Cl during 94 h at 298 K, without the initial presence of ferric ion. The dissolutions of copper and iron are shown in Figure 1 (35% Cu and 7.5% Fe dissolved after 94 h). It is seen that copper is extracted preferentially from the bornite, with a minimal dissolution of iron, showing that bornite is not dissolved, which is in agreement with Sullivan's statement [34], when there is ferric ion as the oxidizing agent (Reaction (2)).

$$Cu_5FeS_4 + 6Fe_2(SO_4)_3 \rightarrow 5CuSO_4 + 13FeSO_4 + 4S \quad (2)$$

but rather that its dissolution would lead to the formation of non-stoichiometric bornite according to the following stoichiometry (Reaction (3)).

$$Cu_5FeS_4 \rightarrow Cu_{5-x}FeS_4 + xCu^{2+} + 2x \quad (3)$$

In research on the leaching of bornite done by Pesic and Olson [20], the dissolution of copper from bornite reached 26 to 28% during the first hour of the process in the presence of ferric ion, which are values greater than those obtained in this study in a chloride medium and without the initial presence of ferric ion, as shown in Figure 1. Furthermore, in the studied system, this function can be performed by the Cu^{2+}/Cu^{+} redox pair, which was formed from dissolved soluble copper [35], but it is restricted because the leaching systems require the addition of oxygen for the oxidation of the cuprous products [7,36], according to Reactions (4) and (5).

$$\text{Copper sulfide} + 2\text{Cu}^{2+}(\text{chloride complex}) \rightarrow 4\text{Cu}^{+}(\text{chloride complex}) + \text{S} \quad (4)$$

$$2\text{Cu}^{+}(\text{chloride complex}) + 2\text{H}^{+} + 1/2\text{O}_2 \rightarrow 2\text{Cu}^{2+}(\text{chloride complex}) + \text{H}_2\text{O} \quad (5)$$

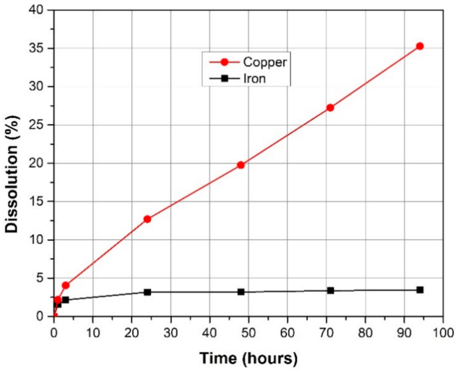

Figure 1. Dissolution kinetics of bornite without pre-treatment. Test conditions: 3-g sample of the concentrate, 60 g/L of Cl, leaching time 94 h, temperature 298 K.

3.2. Pre-Treatment with NaCl-H_2SO_4

3.2.1. Effect of the Dose of NaCl on the Dissolution of Copper

Bornite concentrate samples were treated by adding to them sodium chloride–sulfuric acid and leaving at rest for 15 and 30 days. Once the conditioning had ended, the product was contacted with a solution containing 60 g/L of chloride ion and subjected to stirred leaching.

Figure 2 shows the effect on the dissolution of copper when the concentrate was pre-treated with NaCl-H_2SO_4 mixtures for 30 days, followed by stirred leaching, for sodium chloride dosages of 0, 15, 30, and 60 kg NaCl/t. The results allow stating that the copper dissolved over short times, i.e., up to the first hour of leaching, which corresponds to the soluble copper formed during the applied pre-treatment. The increased amount of copper dissolved in the first hour, compared to the sample of concentrate without pre-treatment, is due exclusively to the dissolution of the soluble species that were formed during the pre-treatment, after which the leaching process continues normally, since the soluble species formed were consumed completely.

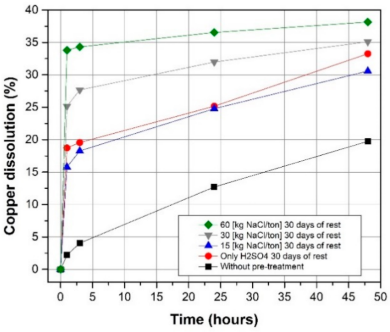

Figure 2. Effect of the NaCl dosage for 30 days of rest. Test condition: 0, 15, 30, and 60 kg NaCl/t.

It is seen that a higher dose of NaCl promotes the formation of soluble copper species. When only sulfuric acid was used, soluble species were also generated, probably sulfates, reaching a copper dissolution of 18.7%. When H_2SO_4 and NaCl were added in doses of 30 and 60 kg NaCl/t, a more aggressive effect was generated, allowing more copper to be solubilized, reaching 25.16% and 33.79%, respectively.

It was found that by increasing the dose of NaCl to values greater than 60 kg/t, there was no further dissolution. For samples pre-treated with 60 and 120 kg NaCl/t, both with 15 days of rest, the dissolved copper reached only 30.6 and 31.03%, respectively. Furthermore, increasing the dose of NaCl to values greater than 60 kg/t of concentrate does not produce any benefit, because, for samples pre-treated with 60 and 120 kg NaCl/t, both with 15 days of rest, the copper solubilized by the conditioning reached values of 30.6 and 31.03% of copper, respectively. The optimal condition for a resting time of 30 days is achieved when 60 kg NaCl/t is added. In this case, a copper dissolution of 38.15% is achieved in 48 h of leaching.

Under the conditions studied, the acid remaining in the pre-treated samples allowed reaching a pH close to 1.5, which had to be adjusted only slightly during the later leaching, and the remaining NaCl in the leaching solution is negligible.

3.2.2. Effect of Resting Time on the Dissolution of Copper and Iron

Figure 3 shows the effect of doubling the resting time for samples pre-treated with 30 and 60 kg NaCl/t of concentrate and later subjected to stirred leaching during 48 h. It is seen that increasing the pre-treatment time from 15 to 30 days causes an increase in the amount of soluble copper formed. When the samples were pre-treated with 30 kg NaCl/t, there was a 9.74% increase in the soluble copper formed on going from 15 to 30 days of rest. When 60 kg of NaCl/t was added, an increase of only 3.13% was achieved, and this is attributed to the fact that there is a limit to the amount of copper that can be solubilized from the bornite during the pre-treatment, which is like what happened in leaching studies in acid medium with ferric ion. Considering this case with more variables, the optimal condition is to work with 60 kg NaCl/t and a rest time of 15 days, with which a copper dissolution of 37.74% is obtained with 48 h of leaching.

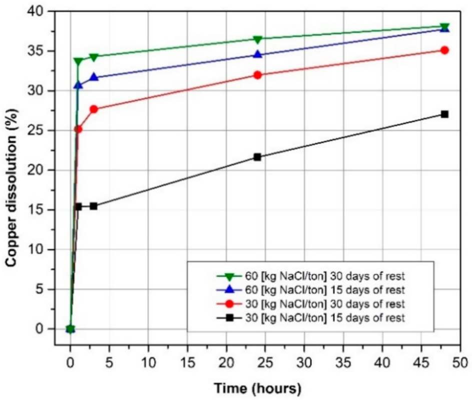

Figure 3. Effect of rest time on the dissolution of copper. Test conditions: 30 and 60 kg NaCl/t and 15 and 30 days of rest.

Figure 4 shows the effect of rest time on the extraction of iron from samples pre-treated with 60 kg NaCl/t. Conditioning of the concentrate with the NaCl-H_2SO_4 mixture promotes the formation of soluble iron species, which are dissolved during the first hour of leaching, after which the process continues normally, with a very low dissolution of Fe.

The amount of soluble iron formed during the pre-treatment with 60 kg NaCl/t of concentrate left to stand for 15 and 30 days is presented in Table 3. It is seen that doubling the resting time increased the amount of soluble iron by 3.25%.

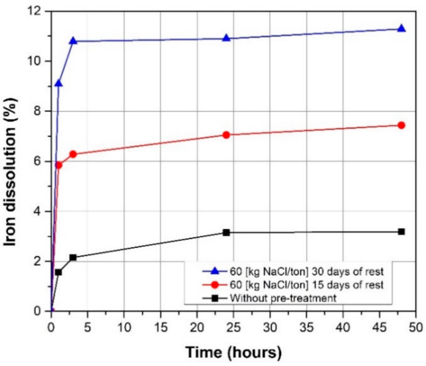

Figure 4. Effect of rest time on the dissolution of iron. Test conditions: without pre-treatment, 60 kg NaCl/t, 15, and 30 days of rest.

The difficulty for extracting the iron from the bornite, despite the aggressive chemical attack, is attributed to the fact that the iron atom is trapped in the crystal lattice of bornite [37], stabilizing the structure, while the copper present in the form of Cu^+ can be diffused more easily, contributing to its faster extraction. This mobility of the cuprous ion was confirmed by Samal and Gilevitch [38], who showed that Cu^+ diffuses at least ten times faster than iron in the crystal lattice of bornite.

Table 3. Iron dissolved under the effect of the pre-treatment applied during 15 and 30 days.

Test	% Fe Resting for 15 Days	% Iron Resting for 30 Days
60 kg NaCl/t of concentrate	5.84	9.09

3.3. Analysis of the Changes Occurring in Bornite during the Pre-Treatment

Samples pre-treated with 60 kg NaCl/t during 15 and 30 days were subjected to XRD analysis, together with their leaching waste. The results are presented in Figure 5. The pre-treated concentrate required a previous wash with distilled water, so it was not possible to determine the soluble Cu and Fe species formed in the pre-treatment, although it was possible to quantify the dissolved percentage by analyzing the solution that resulted from the washing.

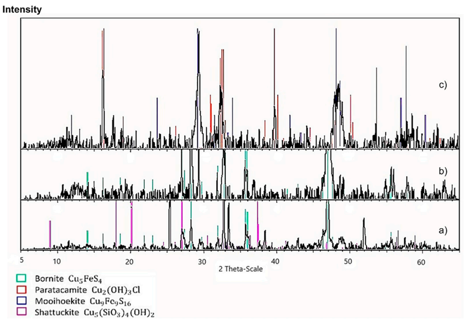

Figure 5. Diffractograms of (**a**) Concentrate without pre-treatment. (**b**) Concentrate pre-treated with 60 kg NaCl/t and allowed to stand for 15 days (**c**) Concentrate pre-treated with 60 kg NaCl/t and allowed to stand for 30 days.

Figure 6 shows the possible evolution of bornite as resting time goes by and it is finally leached. This is based on the results obtained from the XRD and the analysis of the washing solution.

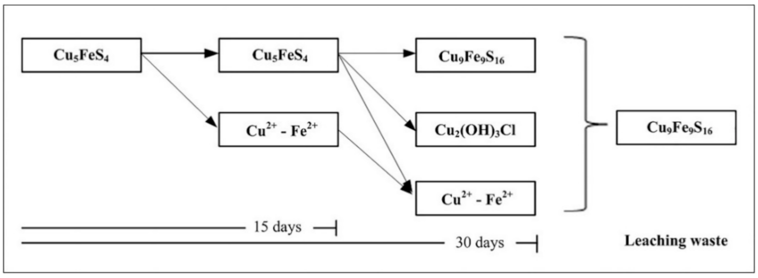

Figure 6. Evolution of bornite during the pre-treatment.

After 15 days of pre-treatment, the sample was identified as bornite, but the previous washing revealed the existence of Cu and Fe in the solution. That is why it is believed that, in addition to bornite, there must be non-stoichiometric bornite, which was not detected because it has cell parameters slightly lower than those of bornite. The soluble Cu and Fe species formed may correspond to sulfates and chloride compounds, as has been found by other researchers in the pre-treatment of the ore and/or the chalcopyrite concentrate [39].

When 30 days of pre-treatment were applied, the bornite was replaced by mooihoekite (Cu_9Fe_9 S_{16}) and a copper chloride compound (paratacamite). It was expected that there should be a transformation of bornite into other non-stoichiometric compounds as reported by Quispe [40]. The washing before the analysis has a high concentration of copper in the water, reaching a dissolution of 20.15%, which means that there was a great formation of soluble sulfate and/or chloride species during the pre-treatment.

Leaching the pre-treated material (15 and/or 30 days) for 48 h, the waste obtained was composed of $Cu_9Fe_9S_{16}$.

The chalcopyrite was not considered in this analysis because it is present in all the samples, and it was not possible to determine whether it corresponds to a reaction product or it was initially found in the concentrate.

3.4. Phenomenological Analysis of the Pre-Treatment with NaCl-H_2SO_4

Studies of pre-treatment with NaCl-H_2SO_4 in chalcopyrite minerals and concentrates denote the formation of gaseous hydrogen chloride in the mixture [41]. This gas has great mobility, allowing a more aggressive chemical attack. Its formation would be given by Reactions (6) and (7):

At temperatures below 323 K:

$$NaCl_{(s)} + H_2SO_{4(l)} \rightarrow NaHSO_{4(s)} + HCl_{(g)}. \tag{6}$$

At temperatures above 323 K:

$$2NaCl_{(s)} + H_2SO_{4(l)} \rightarrow Na_2SO_{4(s)} + 2HCl_{(g)}. \tag{7}$$

In the present work, the bornite concentrate was pre-treated at a constant initial temperature of 298 K and long resting times; the occurrence of Reaction (7) is proposed because it generates an exothermal reaction that raises the temperature above 323 K.

Given the importance of gaseous hydrogen chloride formed locally and its efficacy in the pre-treatment, its formation was confirmed utilizing the arrangement of Figure 7. The following was added to the reactor: concentrated sulfuric acid, distilled water, and a previously determined amount of sodium chloride. Air was injected to drag the generated HCl (gaseous), carrying it to a cylinder that contained a solution of silver nitrate ([$AgNO_3$] = 0.05 M), causing the precipitation of the silver dissolved in the cylinder as silver chloride according to Reaction (8).

$$HCl_{(g)} + AgNO_3 \rightarrow AgCl_{(s)} + HNO_3 \tag{8}$$

Silver chloride precipitates because it has a low solubility product (Reaction (9)).

$$AgCl_{(s)} = Ag^{+} + Cl^{-};\ K_{PS} = 1.56 \times 10^{-10} \quad (9)$$

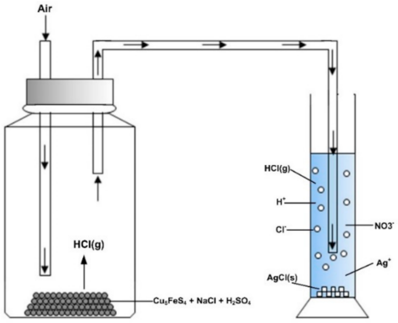

Figure 7. Schematic diagram of the system for the indirect determination of the formation of HCl during the pre-treatment.

Two parallel experiments were carried out with doses of 15 and 60 kg NaCl/t. In both tests, precipitates were formed in the silver nitrate solution, and increased acidity was detected. The precipitates were analyzed by XRD, finding that they corresponded fully to silver chloride, in this way showing that hydrochloric acid was formed during the pre-treatment.

When 60 kg NaCl/t were added, the amount of formed precipitate was considerably higher than when 15 kg NaCl/t was added.

The addition of a greater dose of NaCl causes the formation of a larger amount of hydrochloric acid, leading to increased dissolution of copper. The effectiveness of the pre-treatment is not due exclusively to the hydrochloric acid formed, because sulfuric acid also contributes to solubilizing the copper from the bornite.

Finally, the advantage of producing gaseous hydrogen chloride would be the ease with which it diffuses into the bornite particles, favoring a greater penetration of this gas in the pre-treatment, thereby increasing the number of soluble species formed.

4. Conclusions

The main findings of this research are:

- The pre-treatment with NaCl–H_2SO_4 of base concentrates of bornite generates soluble copper products that can be dissolved in the first hour of the later leaching. Greater resting times and doses of NaCl during the pre-treatment increase the number of soluble compounds formed.
- The formation of hydrochloric acid during the pre-treatment was confirmed, and it would have a direct effect on the increased copper recovery from the concentrate.
- The pre-treatment with NaCl–H_2SO_4 of the bornite concentrate solubilizes part of the iron, but to a lower extent, due to the difficulty of extracting it from the bornite crystal structure.
- Letting stand for 15 days and using 60 kg NaCl/t, the bornite is converted partially into non-stoichiometric bornite, but after standing for 30 days, the whole mineral was converted into compounds with different crystal structures, such as paratacamite and mooihoekite.

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