Leaching Chalcocite in Chloride Media

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Chalcocite is the most abundant secondary copper sulfide globally, with the highest copper content, and is easily treated by conventional hydrometallurgical processes, making it a very profitable mineral for extraction. Among the various leaching processes to treat chalcocite, chloride media show better results and have a greater industrial boom. Chalcocite dissolution is a two-stage process, the second being much slower than the first. During the second stage, in the first instance, it is possible to oxidize the covellite in a wide range of chloride concentrations or redox potentials (up to 75% extraction of Cu). Subsequently, CuS2 is formed, which is to be oxidized. It is necessary to work at high concentrations of chloride (>2.5 mol/L) and/or increase the temperature to reach a redox potential of over 650 mV, which in turn decreases the thickness of the elemental sulfur layer on the mineral surface, facilitating chloride ions to generate a better porosity of this.

Keywords: Cu2S ; CuS

1. Effect on Chloride Concentration

Several authors point out that chalcocite leaching in a chloride medium is the best way to dissolve this copper sulfide [1][2][3][4][5][6]. Even if chloride ions are added to a chalcocite leaching with H_2SO_4 or HNO_3, the kinetics increases considerably. As explained by Cheng and Lawson [3], this occurs because in leaching with only sulfate or nitrate ions, a layer of elemental sulfur is formed on the surface of the particles. In this way, an impermeable particle is generated, that is, contact between the particle with the leaching agent is prevented. This implies that the kinetics decrease in the first leaching stage and prevent the reaction in the second stage. However, when chloride ions are found, either alone or associated with sulfate or nitrate, dissolution kinetics increase along with copper extraction, as shown in **Figure 1**.

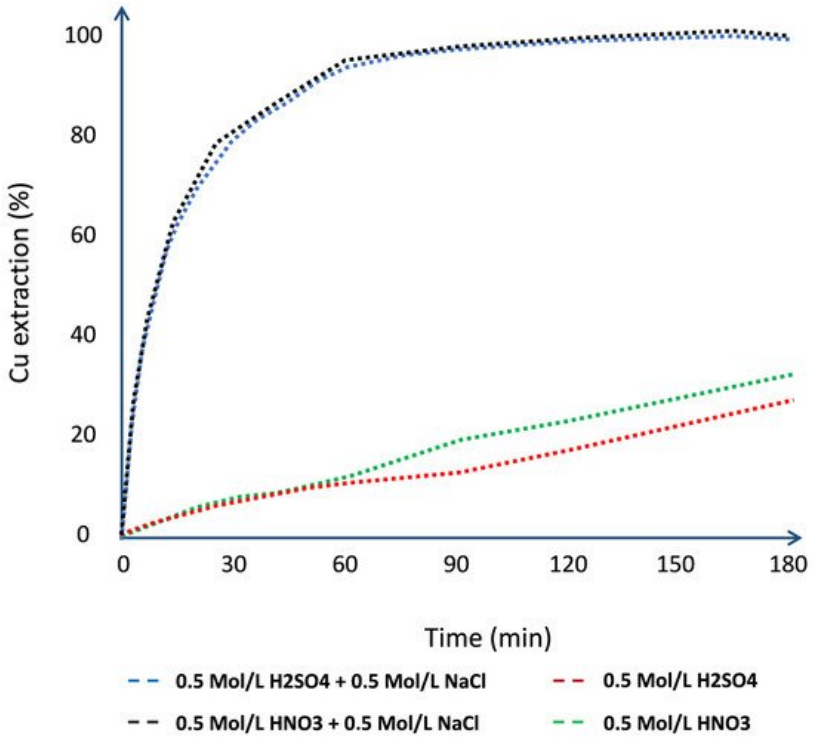

Figure 1. Effect of chloride ions on the acid leaching of chalcocite (T = 85 °C, particle size 31 µm) (Modified from: [3]).

Several studies have shown that working at high chloride concentrations favors the leaching kinetics of secondary sulfides [3][4][7][8]. Chloride ions pass through the sulfur layer and generate a porous layer instead of an amorphous layer formed in the sulfate and nitrate system. The porous layer allows the entry of the leaching solution through said pores, thus allowing

contact with the particle, thus accelerating the leaching kinetics in the first stage and making possible the dissolution reaction in the second stage of leaching [3][9][10]. In the study carried out by Toro et al. [2], leaching tests were carried out in stirred reactors for a pure mineral of chalcocite in an acid medium, comparing different concentrations of chloride in the system (20, 40, and 100 g/L). In their results, the authors indicate that the highest Cu extractions are obtained when working at the highest chloride concentrations (see **Figure 2**). Furthermore, in other studies [11][12] involving the use of seawater (20 g/L Cl^-) and wastewater from desalination plants (~40 g/L Cl^-) for the dissolution of Cu_2S in an acid medium, the researchers point out that better results are obtained when working with wastewater compared to seawater due to its higher concentration of chloride. Additionally, it is highlighted that the waste generated when working with wastewater is stable (such as elemental sulfur) and non-polluting.

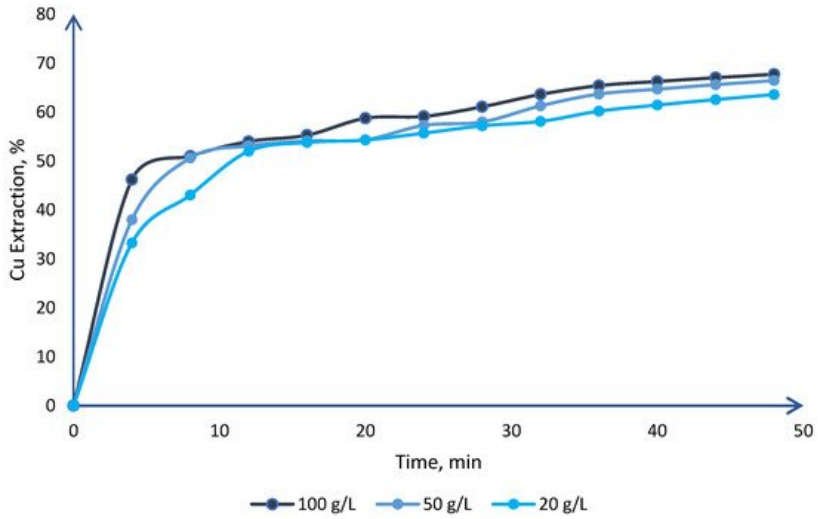

Figure 2. Effect of the chloride concentration in Cu_2S solution (T = 25 °C, H_2SO_4 = 0.5 mol/L) (Modified from: [2]).

The high dissolution rate in the chloride system relative to the sulfated system is attributed to the ability of the chloride ion to stabilize the cuprous ion through the formation of $CuCl_{2-3}$. In the chloride system, copper can be extracted directly from the chalcocite without causing the oxidation of Cu^+ to Cu^{2+}. On the other hand, in the sulfated system, Cu+ must be oxidized to Cu^{2+} on the surface of the particles before copper is released into the solution [1][2][5][8]. The addition of chloride ions allows breaking the passivated sulfur layer since an increase in the concentration of chloride ions implies an increase in the redox potential [13], and a higher redox potential generates a thinner layer that makes it easier for chloride ions to generate porosity [2].

2. Effect on Stirring Speed

The agitation speed in a reactor leaching system decreases the thickness of the boundary layer and maximizes the gas–liquid interface area [14]. This variable is not very significant in copper extraction for tests of the dissolution of Cu_2S in an acid–chloride medium. There is a consensus on the part of different authors in previous research [3][4][15][16][17] where it is stated that it is only necessary to stir at a sufficient speed to keep all the chalcocite particles in suspension within the reactor. Additionally, it is important to note that of the various agitation systems used in these investigations it is advisable to work with mechanical agitation since with other systems anomalous results are obtained, for example, in the study carried out by Herreros and Viñals [16] the authors indicate that in their air agitation tests the results were superior under the same operational conditions compared to mechanical agitation tests. This occurred because the air increased the extraction of copper. After all, the oxygen reacted with the CuCl (solid) formed during the leaching process, favoring the formation of $CuCl^+$. On the other hand, Velásquez-Yévenes [17], in his study, mentions that when working with the use of magnetic agitation the mineral is reduced in size due to the abrasion that is generated when it passes under the rotating magnet, generating an increase in the dissolution of chalcocite.

3. Effect on Acid Concentration

Regarding the acid concentration in a sulfate–chloride system, the findings presented by Dutrizac [18], Cheng and Lawson [3], Senanayake [19], Toro et al. [2], Saldaña et al. [7], and Torres et al. [12] confirm that the concentration of chloride ions in the system is the variable that most influences the kinetics of the dissolution of chalcocite at room temperature, making other operational variables, such as acid concentration, particle size, stirring speed, etc., less relevant. These same results were obtained for other copper sulfides such as covellite [8] and chalcopyrite [20].

Toro et al. [2] performed statistical analysis (ANOVA) for the dissolution of Cu_2S in a chloride medium in stirred reactors. For this, the copper extraction was evaluated through the effect of the independent variables with the response surface optimization method (See **Table 1**). In their results, the researchers indicate that, although sulfuric acid helps to improve the dissolution kinetics of the mineral, the chloride concentration in the system has much more impact on copper extraction, as shown in **Figure 3**. These results are consistent with those presented by Cheng and Lawson [3], where the researchers mention that a low concentration of H_2SO_4 (0.02 mol/L) is sufficient to dissolve chalcocite and later phases of it such as djurleite and digenite. However, it is essential to maintain a high concentration of chloride ions since in its absence the dissolution kinetics considerably decrease (first stage) and later the covellite is not dissolved (second stage). On the other hand, a recent study by Torres et al. [12] worked with wastewater at different concentrations of sulfuric acid to dissolve a pure chalcocite mineral. The authors mention that the same results were obtained in their results, even in short periods of time at H_2SO_4 concentration ranges between 0.1 and 1 mol/L (see **Figure 4**).

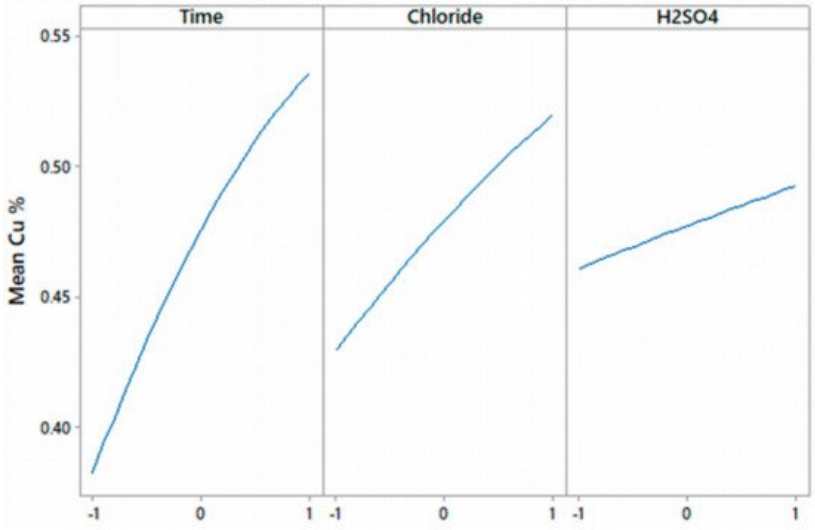

Figure 3. Linear effect graph for the extraction of Cu from chalcocite in a chloride medium [2].

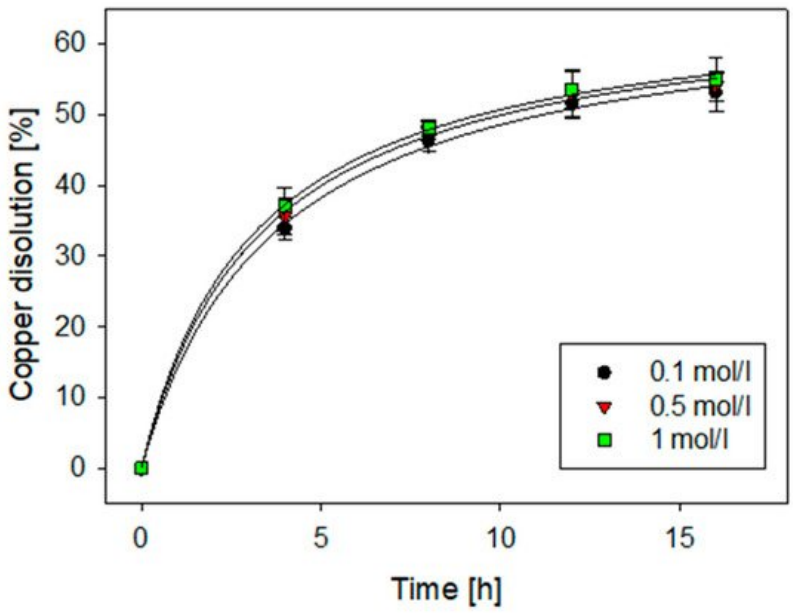

Figure 4. Effect on the H_2SO_4 concentration in the Cu_2S solution with the use of wastewater (~40 g/L Cl^-) [12].

Table 1. Experimental parameters used in statistical analysis [2].

Experimental Parameters	Low	Medium	High
Time (h)	4	8	12
Cl^- concentration (g/L)	20	50	100
H_2SO_4 (mol/L)	0.5	1	2

4. Particle Size Effect

The effect of particle size on chalcocite leaching has been studied by different authors; however, these studies have been carried out with relatively small particle sizes: 25 to 4 mm [21]; 4 mm to 12 µm [16]; 4 to 0.054 mm [22]; 11 to 63 µm [3]; 150 to 75 µm [6]; 150 to 106 µm [23]. These authors agree that a smaller particle size implies an increase in the dissolution kinetics and the extraction rate in the first leaching stage. But the effect decreases significantly in the second stage. Naderi et al. [21] reported that for fine particle sizes the first stage is controlled by diffusion through the liquid film. In the second stage, the accumulation of the elemental sulfur layer in the solid product, accompanied by a jarosite precipitate, transformed the control mechanism into solid diffusion. Phyo et al. [22] studied the effect on the dissolution kinetics of Cu_2S in stirred reactors using an acid medium. In their results, as can be seen in **Figure 5**a, a significant effect of the particle size is observed in the dissolution of copper, especially in the size of −0.074 + 0.054 mm, which in 2.5 h had already reached 45% recovery compared to the almost 17 hours it took to achieve the same recovery with −4 + 2 mm particles. In **Figure 5**b, the researchers observed a turning point of around 75% copper dissolution at different times depending on the granulometry and divided the second stage into two sub-stages, indicating that the first sub-stage has a dissolution speed 20 times faster than the second sub-stage.

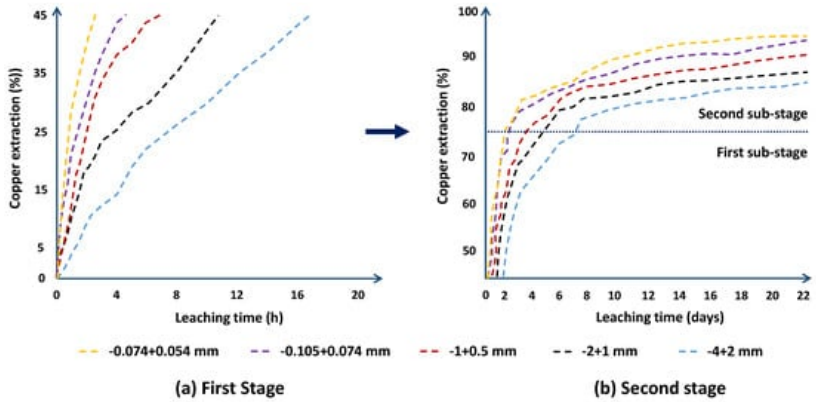

Figure 5. Cu_2S dissolution at different particle sizes in two different stages: (**a**) first stage, (**b**) second stage ($[Fe^{3+}]$ = 10 g/dm^3, pH = 1.00–1.50, Eh = 750 mV, temperature = 45 °C) (Modified from: [22]).

5. Effect of Temperature

It is known that temperature is the operational variable that most influences the dissolution of copper sulfide minerals [11][24][25]. For the specific case of chalcocite, it becomes a critical parameter during the second stage, being much slower, and can be accelerated with temperature, which indicates that the process is controlled by chemical and/or electrochemical reactions [11][26]. Miki et al. [4] pointed out that the dissolution rate of CuS is largely independent of the concentration of chloride and HCl in the ranges of 0.2 to 2.5 mol/L and 0.1 to 1 mol/L, reporting activation energy values of 71.5 kJ/mol. Therefore, it can be concluded that the process is controlled by a chemical or electrochemical reaction on the surface of the mineral.

In the results presented by Pérez et al. [11] for the dissolution of a pure chalcocite mineral in a chloride medium in a stirred reactor at different temperatures, the authors point out that at temperatures above 65 °C extractions of copper were close to 40% in short periods of time (15 min) (see **Figure 5**), which, the researchers concluded, is due to the phase change that governs the first stage of leaching from chalcocite to covellite, which requires low activation energy. More energy is necessary for the second stage to become a copper polysulfide, which requires more demanding conditions to achieve its complete dissolution. In addition, Pérez et al. [11] mentioned that there is good synergy between the chloride concentration in the system and the temperature, since, in their research, they achieved copper extractions of 97% in 3 hours under the conditions operations that are presented in **Figure 6**. The research carried out by Ruiz et al. [27] investigated the dissolution of white metal (chalcocite and djurleite) working under similar operational conditions. Without chloride in the system, 55% extractions were obtained in a time of 5 hours at a temperature of 105 °C.

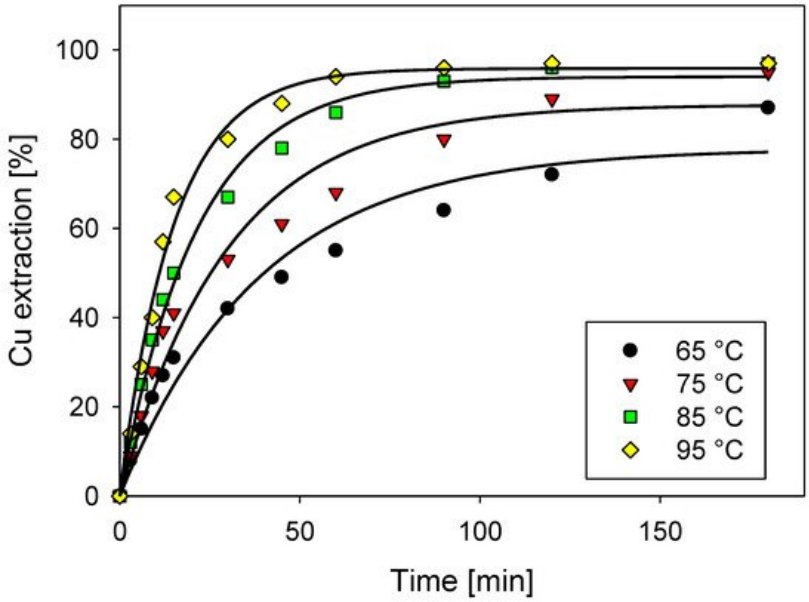

Figure 6. Cu_2S dissolution as a function of temperature (0.5 mol/L H_2SO_4 and 100 g/L of Cl^-) [11].

6. Effect of Redox Potential

Miki et al. [4] studied the effect of the redox potential in a Cu_2S solution (synthetic) with the use of a 0.2 M HCl solution, 0.2 g/L of Cu (II), and 2 g/L of Fe (III)/Fe (II) at a temperature of 35 °C. The researchers, in their findings, reported that the dissolution of Cu_2S occurs rapidly at a potential of 500 mV but then stops when 45% copper is removed (end of the first stage). For potentials of 550 mV, there is then an increase in the dissolution until reaching 50% extraction of copper. Subsequently, the copper mineral present is mainly covering, which requires potentials of at least 600 mV to be able to dissolve. However, Niu et al. [28] point out that these results were not determined in a range of industrial redox potentials. In their experiments for the dissolution of Cu_2S, Niu et al. [28] worked in mini glass columns (30 cm long and 6 cm in diameter), adding $Fe_2(SO_4)_3$ as a leaching agent. In their results, the researchers note that the dissolution rate of the second stage of Cu_2S leaching was insensitive to the redox potential at moderate temperatures (30–40 °C) in the industrial range of 650–800 mV. In the study conducted by Hashemzadeh et al. [6], the researchers modeled the dissolution kinetics of Cu_2S in chloride media using leaching data obtained under fully controlled temperature, pH, and solution potential. In their results, the researchers mentioned that an increase in the chloride concentration and temperature generated an increase in the redox potential, increasing from 680 to 830 mV with the addition of 0.1 chlorides and 3 mol/L of NaCl, respectively, and consequently higher dissolution kinetics, mainly in the second leaching stage.

The results obtained from the aforementioned studies are directly related to the formation of a layer of elemental sulfur on the surface of the covellite in the second stage, which decreases with the increase in the potential of the solution; however, the layer in the solid surface is a mixture of sulfur and polysulfides (CuS_n) [13], where these could be responsible for a slow reaction during this stage.

7. Effect of Oxidizing Agents

7.1. Air

In another study carried out by Cheng and Lawson [3], the effect of aeration on the leaching of chalcocite was seen, but in this case, agitating leaching was carried out, showing that there is no greater contribution. Moreover, by adding a greater flow of air to the system slightly lower recoveries are obtained. This is because the particles adhere to the bubbles generated and are dragged toward the walls of the reactor. On the other hand, in the research carried out by Liu and Granata [29], the effect of aeration was studied by analyzing historical data in two leaching piles of chalcocite as the main mineral present, one with and the other without aeration. In the results, they observed that in leaching in an aerated heap, better results were obtained, but there was only a comparative change after 200 days of leaching with respect to the non-aerated heap. For the aerated pile, from 200 days onward, there was no significant change in copper recovery. This is because aeration is no longer beneficial at this point. After all, we are in the second stage of the dissolution of chalcocite, which is a controlled chemical reaction. Furthermore, the authors mentioned that the total acid consumption per ton of ore processed was higher in the case of the aerated pile, but the net acid consumption per ton of copper produced was the same in both cases.

7.2. Ferric Ions

The effect of the concentration of ferric ions in the leaching of chalcocite has also been studied. For the first reaction stage, there is a positive effect on the leaching kinetics with an increase in the concentration of ferric ions. When the concentration is lowered, the leaching rate of chalcocite is considerably lower. For the second stage, the ferric ions are not as noticeable as in the first stage. Still, better reaction rates are obtained by increasing their concentration because of the increase generated in the redox potential of the leaching solution [3][9][23].

7.3. MnO_2

The use of MnO_2 as an oxidizing agent in chloride media has recently been studied for secondary and primary sulfides [12][20][30][31][32] where positive results have been obtained in the dissolution of copper. For example, for a mineral refractory to conventional processes such as chalcopyrite, in the study carried out by Toro et al. [20] it was possible to extract 77% of copper at room temperature when working at high concentrations of MnO_2 (4/1 and 5/1) and chloride (~40 g/L), which allowed maintaining of the redox potential values between 580 and 650 mV. For the specific case of chalcocite, Torres et al. [12] worked under the same operational conditions as Toro et al. [2]. In their results, Torres et al. (2020a) showed that incorporating MnO_2 at low concentrations significantly improves the dissolution of chalcocite in short periods, which is important in continuous leaching operations.

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