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Review

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Hydrometallurgical processing of chalcopyrite: A review of leaching techniques

Darwin Michell Cheje Machaca✉, *Amilton Barbosa Botelho Junior*, *Thamyres Cardoso de Carvalho*, *Jorge Alberto Soares Tenório*, *and Denise Crocce Romano Espinosa*

Department of Chemical Engineering, University of Sao Paulo, São Paulo, Brazil
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Abstract: Copper, an essential metal for the energy transition, is primarily obtained from chalcopyrite through hydrometallurgical and pyrometallurgical methods. The risks and harmful impacts of these processes pose significant concerns for environmental and human safety, highlighting the need for more efficient and eco-friendly hydrometallurgical methods. This review article emphasizes current processes such as oxidative leaching, bioleaching, and pressure leaching that have demonstrated efficiency in overcoming the complicated chalcopyrite network. Oxidative leaching operates under benign conditions within the leaching media; nevertheless, the introduction of oxidizing agents provides benefits and advantages. Bioleaching, a non-aggressive method, has shown a gradual increase in copper extraction efficiency and has been explored using both primary and secondary sources. Pressure leaching, known for its effectiveness and selectivity in copper extraction, is becoming commercially more viable with increased research investments. This research also provides important data for advancing future research in the field.

Keywords: chalcopyrite leaching; bioleaching; ionic liquids; chloride; hydrogen peroxide

1. Introduction

The global demand for copper has surged rapidly owing to population growth and advances in industry and technology aimed at achieving a more sustainable society. Copper is extensively utilized across various sectors, such as electrical, electronic, mechanical, architectural, and military industries [1–2]. Its most important application lies in its vital role in the energy transition and industrial decarbonization, which enhances sustainability and reduces carbon emissions. Copper is integral to more than ten energy technologies, earning it the label of a "cross-cutting" metal for these fields [3]. By 2050, the demand for copper is expected to surpass 800000 Mt, marking a growth between 60% and 300% compared to previous years, driven by the global shift toward clean energy and environmental sustainability to mitigate temperature rise by 1.5°C [4–6].

Over the last few decades, copper has emerged as a crucial metal essential in various technological fields. According to a recent report from the European Commission [7], copper is classified as a strategic material for advancements in military and scientific technologies. Beyond Europe, Canada recognizes copper, along with 30 other critical minerals, as vital for its development [8]. In the USA, copper is considered a critical material, especially owing to the potential supply disruptions anticipated between 2025 and 2035 [9]. Latin America is a leading copper producer, representing 40% of world production and 35% of world lithium production, with large volumes of usable resources [10].

The rapid increase in demand for copper resources has led to the exploration of more than 200 copper-containing minerals, notably cuprite (89% of copper), malachite (58% of copper), and azurite (56% of copper) [11]. Low-grade refractory minerals like chalcopyrite (34.6% of copper), bornite (63% of copper), and enargite (48% of copper) are being studied for their potential profitability as sources of copper [12–13]. Sulfide minerals are economically attractive owing to their abundance and contribution to 80% of mineralogical copper [14–15]. Chalcopyrite ($CuFeS_2$) is the most common and abundant copper mineral, representing more than half of the world's copper mineral reserves [16]. Approximately 20% of copper has been supplied by oxidized ores obtained through hydrometallurgical processes; however, this may decrease to 12% owing to the depletion of this mineral by 2027 [17].

2. Copper production and mining

2.1. Global production

In 2022, the estimated global copper reserves stood at approximately 890000 Mt, with five countries holding significant shares: Chile (21.3%), Australia (10.9%), Peru (9.1%), Russia (7%), and Mexico (5.9%) [18–19]. World copper production in 2022 reached 22000 Mt, reflecting a 3.7% growth compared to the previous year, with a higher growth rate of 5.1% projected for the coming years [5,20]. Chile, Peru, and the Democratic Republic of the Congo (DRC) accounted for

✉ Corresponding author: Darwin Michell Cheje Machaca E-mail: dcheje12@usp.br
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43.6% of global production in 2022 [18–19].

As shown in Fig. 1, the price of copper has been rising since the last decade. Oscillations were observed but significant increases were observed from 2016 onward (Fig. 1(b)). In 2011, the annual price of copper was US$8828 per metric ton, one of its highest historical prices [21]. However, in 2019, owing to the pandemic, copper prices decreased, settling at US$8375 per metric ton in 2022 [22–30].

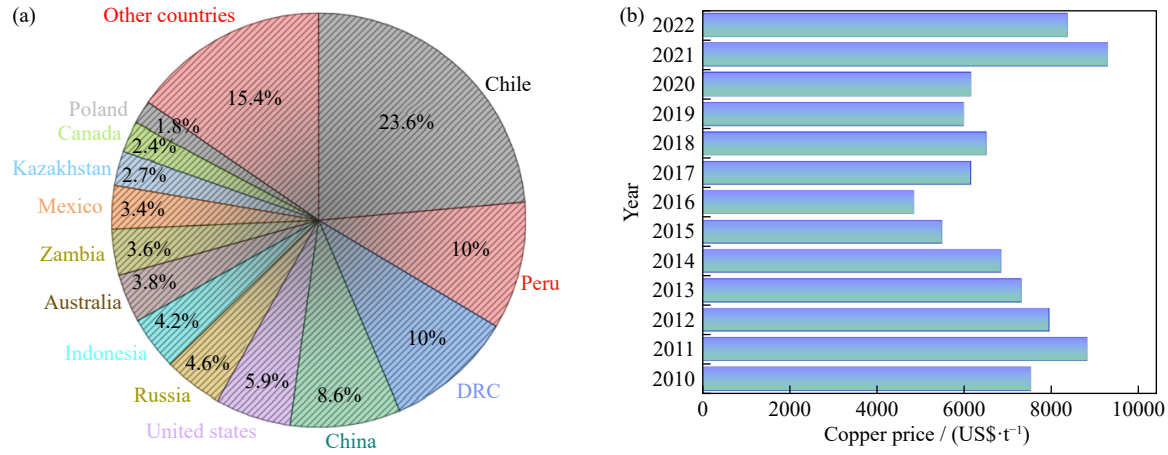


Fig. 1. (a) Main copper-producing countries worldwide in 2022 [18]. (b) Copper prices per metric ton worldwide from 2010 to 2022 [22–23].

Projections indicate a 2.7% deceleration in global copper growth in the ensuing years. This forecast considers various factors, including the enduring effects of COVID-19, the protracted Russia–Ukraine conflict, elevated living costs, and constrictive financial conditions [29].

2.2. Copper mining

Open pit mining typically yields copper grades of 0.3% copper, whereas underground mining results in higher grades of 1.7% copper [12]. Different procedures are required for processing oxidized and sulfide minerals. Oxidized minerals that are usually found on the surface of the Earth's crust are processed by hydrometallurgical techniques. Hydrometallurgy consists of 3 main stages, as shown in Fig. 2 [25]. (1) Heap leaching consists of leaching Cu^{+} or Cu^{2+} from oxidized minerals using a sulfuric acid (H_2SO_4) solution. This solution contains impurities such as Fe, Al, Co, Mn, Zn, Mg, and Ca. The solid phase (leach residue) contains alumina, silica, and insoluble iron oxides/hydroxides/sulfates. (2) Solvent extraction (SX). The leach solution reacts with a specific organic solvent for the selective separation of copper over impurities. An acid solution is further required for copper stripping. (3) Electrowinning. The purified solution is fed into reactors for electrowinning reactions, obtaining 99.99% pure copper in the cathode. The anode, containing H_2SO_4 solution, is reused in the leaching or solvent extraction steps [6,24–25].

The pyrometallurgy process for sulfide minerals is defined by four main stages (Fig. 2 [25]) [31–34]. (1) Foam flotation: Sulfide minerals are inserted into a flotation tank with chemical reagents or specific foams, allowing them to join with the copper and form hydrophobic solutions. This stage separates gangue material from copper. O_2 bubbles supplied at the bottom of the flotation tank drag enriched copper sulfide particles to the surface while the gangue is removed as tailings. (2) Thickening: The foams are passed to the thickeners, where the copper-enriched bubbles permeate, and the solid part settles at the bottom of the tank. A filtration stage eliminates excess water, which is recirculated for other production stages. The copper content after this process is 25%–30%. (3) Smelting: The copper concentrate is sent to smelting furnaces at 1250°C to oxidize the sulfur and iron, producing a copper matte enriched with oxygen from the air. The smelting products include a sulfide matte with (50%–70%) and an oxide matte with low copper content. The sulfide matte is then melted again and enriched with oxygen to form impure molten copper of 98% purity. Approximately 60% of the SO_2 released during this process is used to manufacture H_2SO_4. (4) Electrolysis: The impure molten copper is immersed in pools of copper sulfate and sulfuric acid with thin copper sheets and hung between the anodes. The applied electric current allows ion migration toward the cathodes, achieving 99.99% purity [6,31,34].

Fig. 3 illustrates the traditional scheme for producing metallic copper. Pyrometallurgical processes are best suited for treating sulfide minerals such as chalcopyrite owing to their composition and stable structure. However, pyrometallurgical processes have not yet achieved the necessary expansion because they lack optimal features for adequate sustainability. High energy consumption and the emission of sulfur gases into the environment are the main disadvantages that hinder the process. According to the Cochilco report (2022), energy consumption is substantial, with the pyrometallurgical process in the concentrated area consuming 50000 TJ annually. This is followed by the three main hydrometallurgy processes (LX/SX/EX) with 10000–20000 TJ [26]. Additionally, the Cochilco (2023) report projects energy consumption until 2033 for the copper industry [27]. The study estimates that electricity consumption will grow from 23.5 TWh in 2022 to 32.8 TWh in 2033, representing an increase

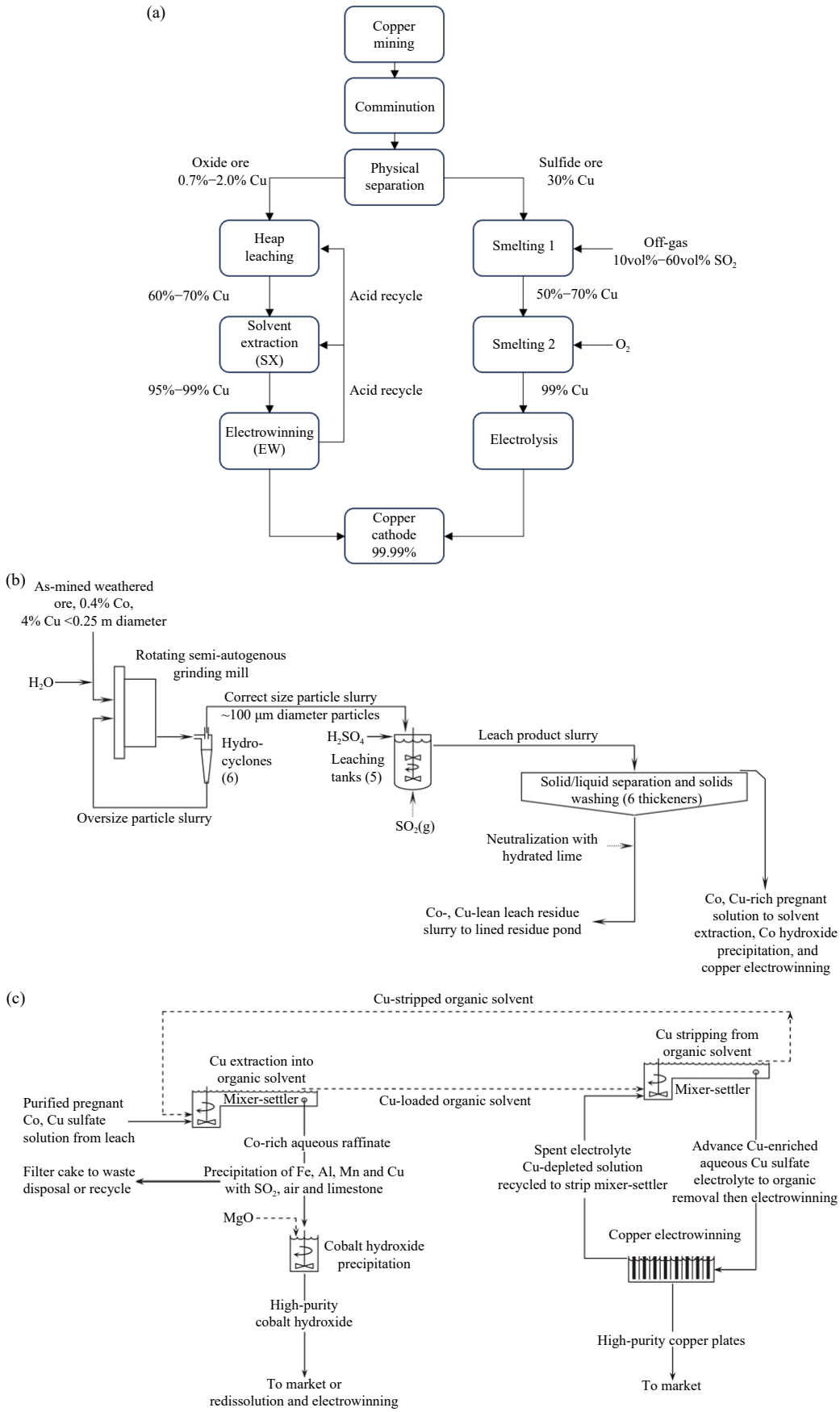


Fig. 2. (a) Processing diagram of copper ores by hydrometallurgical and pyrometallurgical processes; (b) flowchart for grinding and leaching of weathered cobalt–copper ore; (c) production of high-purity cobalt and copper from the purified pregnant solution containing copper and cobalt sulfate [25]. Reprinted from *Extractive Metallurgy of Nickel, Cobalt and Platinum-Group Metals*, F.K. Crundwell, M.S. Moats, V. Ramachandran, *et al.*, Copyright (2011), with permission from Elsevier.

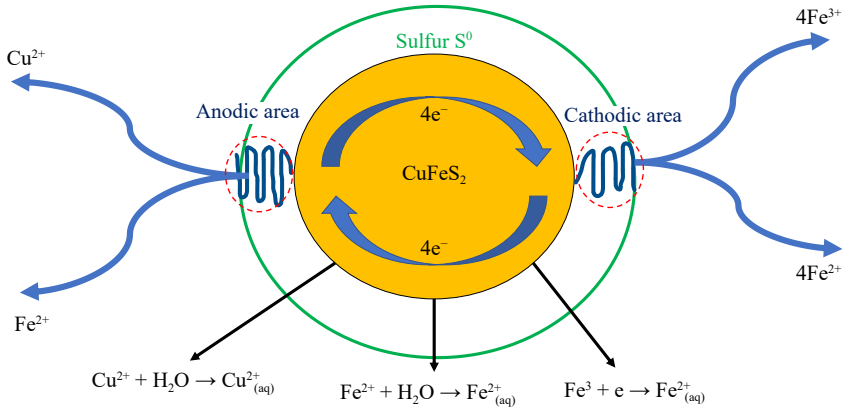


Fig. 3. Elemental sulfur formation during chalcopyrite leaching in the Fe^{3+} medium.

of 39.5%. The highest energy consumption is contained in the concentration stage of the pyrometallurgical process, which is forecasted to consume 21.7 TWh by 2033, 66.1% of total electricity consumption.

Hydrometallurgy has proven to be more efficient than pyrometallurgy, offering advantages such as reduced cost and lower energy consumption, making it more environmentally sustainable. Therefore, this work aims to evaluate chemical systems that could be applied in the future, identifying the challenges in leaching chalcopyrite by assessing the main factors that affect copper recovery rates, reaction mechanisms, and commercial-scale applications. The goal is to achieve higher copper production rates to meet future demand. Furthermore, state-of-the-art chalcopyrite hydrometallurgy was developed based on the sustainable development goals (SDGs), intending to mitigate the negative impacts of mining while pursuing an environmentally sustainable future, economic growth, and social participation. Therefore, this review aligns with the following SDGs: SDG 7 (clean and affordable energy), SDG 8 (economic growth and decent work), SDG 9 (resilient infrastructure and sustainable industrialization), and SDG 12 (responsible production and consumption) [28–31].

3. Review of hydrometallurgical processing of chalcopyrite

Within hydrometallurgy, leaching processes are solid/liquid techniques that enable metal extraction and have seen increasing utilization in recent years. Chalcopyrite is one of the refractory minerals with economic interest owing to its composition (Cu 34.6%, Fe 30.4%, and S 34.9%) and its abundance in the Earth's crust [32–33].

Leaching of chalcopyrite occurs at a redox potential higher than 0.4 V and at a pH lower than 5, with copper being found as an ionic species [34]. Beyond these conditions, various metallic, oxidized, intermediate, and passivating species can form, depending on the water limits. Chalcopyrite in an aqueous medium tends to form passivating substances such as elemental sulfur (S^0), jarosites (Fe–O–OH), disulfide (S^{2-}), or polysulfide (S_n^{2-}) [35]. Research shows that copper extraction can be carried out through an oxidative process that releases copper and iron into the solution and polymerizes monosulfide (S^{2-}) to polysulfide (S_n^{2-}), followed by a reductive process that releases cations into the solution [36]. To prevent the reductive process from reverting to form S^{2-}, an additional oxidation process can be applied to form elemental sulfur. Currently, the diversification of methods proposed for the correct oxidation of chalcopyrite and copper extraction has led to the evaluation of leaching systems in three ways: oxidative leaching at atmospheric pressure, bioleaching, and pressure leaching. Mechanical activation is often evaluated as a process before leaching.

3.1. Oxidative leaching at atmospheric pressure

Over the last decade, different authors have studied leaching processes in sulfuric acid media to oxidize sulfides and convert them into sulfates using oxidizing agents with a higher oxidation potential than chalcopyrite. The dissolution rate of chalcopyrite in sulfated media at atmospheric pressure is slow (Eq. (1)). This may occur because the ferrous ions formed during the process can be oxidized to ferric ions in the presence of oxygen or as the process progresses (Eq. (2)). However, the formation of ferric ions is limited because it requires extreme conditions for their consistent production throughout the process.

$$CuFeS_2 + O_2 + 4H^+ \rightarrow Cu^{2+} + Fe^{2+} + 2S^0 + 2H_2O \quad (1)$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (2)$$

Current technologies suggest the use of oxidizing agents to enhance extraction while evaluating alternative leaching agents, such as ionic liquids, methanesulfonic acid, organic acids, and chlorides of alkali and alkaline earth metals. These alternatives accelerate and improve reaction speed by reducing sulfuric acid consumption. The diversification of current processes and ongoing research continues to open new paths for copper extraction through hydrometallurgical processes [37].

3.1.1. Ferric sulfate

Reagents based on ferric/ferrous ions continue to be highly discussed in the literature owing to the slow oxidation of chalcopyrite and the resulting minor copper extractions [38]. This may be because the iron present in chalcopyrite samples, such as $FeSO_4$, can be used catalytically in the process. As oxidative leaching progresses, dissolved $FeSO_4$ can be oxidized to $Fe_2(SO_4)_3$ under very acidic pH conditions. A

decrease in the solution's acidity can cause the precipitation of the Fe^{3+} ions [39] or the formation of insoluble compounds, favoring surface passivation [40]. The proposed mechanism is shown in Fig. 3. Chalcopyrite leaching by Fe^{3+} ions generates elemental sulfur S^0 as a byproduct of the oxidation of sulfide (S^{2-}). This elemental sulfur can be further oxidized into sulfate (SO_4^{2-}); however, excessive oxidation allows SO_4^{2-} to be converted into H_2SO_4 in the presence of oxygen. Literature suggests that the mechanism may be based on the dielectric breakdown potential of chalcopyrite, where a chemically stable surface layer prevents further copper dissolution, or the rapid formation of a p–n junction on the leached chalcopyrite surface hinders the electrochemical process [41]. Furthermore, the formation of elemental sulfur is stable under atmospheric conditions, forming layers on the chalcopyrite surface.

A way to represent the leaching of chalcopyrite by ferric ions (Fe^{3+}) is shown in Eqs. (3) and (4), proposed by Córdoba *et al.* [41].

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0 \quad (3)$$

$$CuFeS_2 + 16Fe^{3+} + 8H_2O \rightarrow Cu^{2+} + 17Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

Various low-extraction results can be attributed to the fact that these ferrous systems are affected by leaching parameters if not adequately controlled. For instance, Nyembwe *et al.* [42] demonstrated that leaching with ferric ions is efficient under varying pH conditions owing to the formation of transient phases in the waste after chalcopyrite leaching in an H_2SO_4–$FeSO_4$–$Fe_2(SO_4)_3$–H_2O system. In the carbonatitic chalcopyrite sample, soluble intermediate compounds (Cu_5FeS_4 and Cu_2S) were identified at a pH of 1.0–1.8, resulting in low recoveries <15% owing to the formation of insoluble intermediates or refractory compounds (CuS and $Cu_{3.39}Fe_{0.61}S_4$) at a pH of 0.5–1, contributing to surface passivation.

Al-Harahsheh *et al.* [43] reported that agitation inhibits copper recovery in open systems owing to the elimination of cupric complexes formed at the reaction interface between chalcopyrite particles and ferric ions when analyzed at agitation speeds >400 r/min. In closed systems, the authors observe a 42% copper recovery in a chalcopyrite concentrate sample with a particle size of <25 μm at room temperature. Tkácová and Baláz [44] evaluated the effect of temperature in the range of 60–105°C on the kinetics of mechanically activated chalcopyrite samples. Córdoba *et al.* [35] evaluated the influence of redox potential on chalcopyrite leaching, highlighting that an initial potential >450 mV leads to the formation of iron precipitates. Conversely, potentials of <450 mV, combined with an increased iron concentration of up to 10 times, help achieve the balance of the Fe^{3+}/Fe^{2+} pair, favoring the control of ferric ion hydrolysis. Without proper control, these conditions in the copper industry often lead to lower-than-expected results, causing economic losses and generating acid waste.

Over the last decade, some studies have focused on improving surface oxidation in ferrous media using iodine/iodide electrochemical pairs, demonstrating excellent viability in chalcopyrite oxidation. The literature suggests better dissolution when the system is assisted by iodine, produced through the oxidation of iodide by iron (III) [45–46]. Furthermore, the addition of iodide ions (I^-) to ferric systems improves solubility by creating pairs (Fe^{3+}/I^-) that can act as powerful oxidants of iron ions [47]. This synergistic effect, from a thermodynamic perspective, indicates that iron has a higher oxidation potential than iodine. Therefore, a possible explanation for the increased leaching rates is the faster kinetics associated with chalcopyrite oxidation by iodine [45,48–50]. This is because the ferric ion is the final electron acceptor in chalcopyrite leaching, as shown in Eqs. (5) and (6) [48]:

$$2I^- + 2Fe^{3+} \rightarrow I_2 + 2Fe^{2+}, \Delta G^{\ominus} = -12.7\ \text{kJ/mol} \quad (5)$$

$$CuFeS_2 + 2H_2SO_4 + 2I_2 \rightarrow CuSO_4 + FeSO_4 + 4HI + 2S^0 \quad (6)$$

The commercial-scale application is being evaluated as a promising innovation in chalcopyrite processing. The JX Group (Japan) has developed iodine-catalyzed heap leaching of chalcopyrite, and ongoing projects, such as the SQM S.A. project in Chile, are expected to begin implementation in 2025 [51].

3.1.2. Hydrogen peroxide

Hydrogen peroxide (H_2O_2), with its potential of 1.77 V versus the standard hydrogen electrode (SHE), is a strong and commonly used oxidant in chalcopyrite dissolution, surpassing the ferric ion, which has a potential of 0.77 V vs. SHE [52]. Its oxidative action in acidic media is demonstrated in Eq. (7). Additionally, it can act as a reducing agent, decomposing into oxygen and releasing electrons, as shown in Eq. (8) [53–54].

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (7)$$

$$H_2O_2 \leftrightarrow O_2 + 2H^+ + 2e^- \quad (8)$$

Arslanoğlu and Yaraş [55] and Sokić *et al.* [56] propose the development of hydrogen peroxide in the leaching processes of chalcopyrite; Eqs. (9) and (10) represent the action of hydrogen peroxide with chalcopyrite in an acidic medium, where the synergistic effect between hydrogen peroxide and sulfuric acid allows the oxidation of S^{2-} to SO_4^{2-}. As the process progresses, sulfate is gradually converted into elemental sulfur (S^0).

$$2CuFeS_2 + 17H_2O_2 + 2H^+ \rightarrow 2Cu^{2+} + 2Fe^{3+} + 4SO_4^{2-} + 18H_2O \quad (9)$$

$$2CuFeS_2 + 5H_2O_2 + 10H^+ \rightarrow 2Cu^{2+} + 2Fe^{3+} + 4S^0 + 10H_2O \quad (10)$$

Most research focuses on the sulfuric medium, and the addition of hydrogen peroxide has shown high leaching rates (>80%), as reflected in the literature [54,57–61]. A drawback of using hydrogen peroxide is its stability throughout oxidative leaching processes. Agacayak *et al.* [62] evaluated the leaching temperature of chalcopyrite with hydrogen peroxide up to 60°C, achieving leaching rates of 80% in 90 min at

40°C. However, they observed slight decreases in copper extraction within the range of 50–70°C over 90–240 min, with leaching rates gradually decreasing as the process progresses. Adebayo *et al.* [60] studied the dissolution kinetics of a chalcopyrite concentrate, identifying two essential factors affecting the leaching rate: First, the agitation rate, evaluated at 400 r/min, showed optimal conditions, but higher agitation rates led to the inevitable decomposition of H_2O_2, hindering the contact between chalcopyrite particles and O_2. They found that the best copper extraction occurred without agitation. Second, the presence of metal ions contributes to the decomposition of hydrogen peroxide, as confirmed by other studies [59–60,62].

To avoid the rapid decomposition of hydrogen peroxide, some stabilizers have recently been proposed in leaching processes as emerging alternatives to improve leaching rates. Organic acids are potential ecological reagents with projections to enhance chalcopyrite leaching [63–64]. Therefore, the addition of organic acids (such as acetone, ethylene glycol, methanol, and 2-propanol) in H_2SO_4–H_2O_2 has been evaluated [63]. The best stabilization over a 6-h leaching period was achieved with acetone, resulting in a 35% extraction rate. However, beyond this time, leaching with acetone drastically reduces copper extraction, while the test with ethylene glycol demonstrated a linear growth slope over 12 h. These results are corroborated by the literature [65–66], which observed improved reaction kinetics with the addition of ethylene glycol to the leaching process of chalcopyrite in a sulfuric medium with H_2O_2, comparing it with a conventional H_2SO_4–H_2O_2 system, resulting in increased leaching rates from 30% to 40%. Ruiz-Sánchez and Lapidus [67] evaluated the addition of ethylene glycol in the dissolution of chalcopyrite using the shrinking particle model controlled by chemical reactions. He found that the crucial parameter is temperature, with optimal results observed within the range of 10–30°C, where peroxide decomposition is avoided, as opposed to decreases seen in the 40–50°C range. Bai *et al.* [68] investigated the stabilization of hydrogen peroxide by ethylene glycol in a molybdenite sample. Electrochemical studies suggest that ethylene glycol improves peroxide stability, increasing extraction rates from 73% to 94.5%. The Oximetal Process™ is based on increasing the oxygen concentration from 6.7 to 30–40 ppm, positioning itself as an alternative to conventional heap leach aeration systems [69].

3.1.3. Ionic liquids (ILs)

Leaching chalcopyrite with ionic liquids is an emerging alternative for copper extraction compared to traditional methods that use more aggressive chemical reagents. Ionic liquids are molten salts with melting points <100°C and are considered conventional organic solvents owing to their wide working range and environmental sustainability characteristics. They are composed of a cationic part (organic) and an anionic part (organic or inorganic) [70–74], as shown in Fig. 4 [75]. Owing to their physical and chemical properties, understanding the interaction of ionic liquids in the leaching of chalcopyrite is fundamental. These compounds interact with the mineral surface, facilitating the leaching process. The ability of ionic liquids to release H^+ ions in an aqueous medium is attributed to their role as Brønsted acids. The ions in ionic liquid gradually replace the ions in the crystalline structure of chalcopyrite [71]. This ion exchange may be attributed to differences in Gibbs free energy between the ions in the mineral and those in the ionic liquid, resulting in the release of chalcopyrite ions into the solution. The dissociation of [bmim][HSO_4], commonly used in chalcopyrite leaching, is described in Eq. (11) [71–73]:

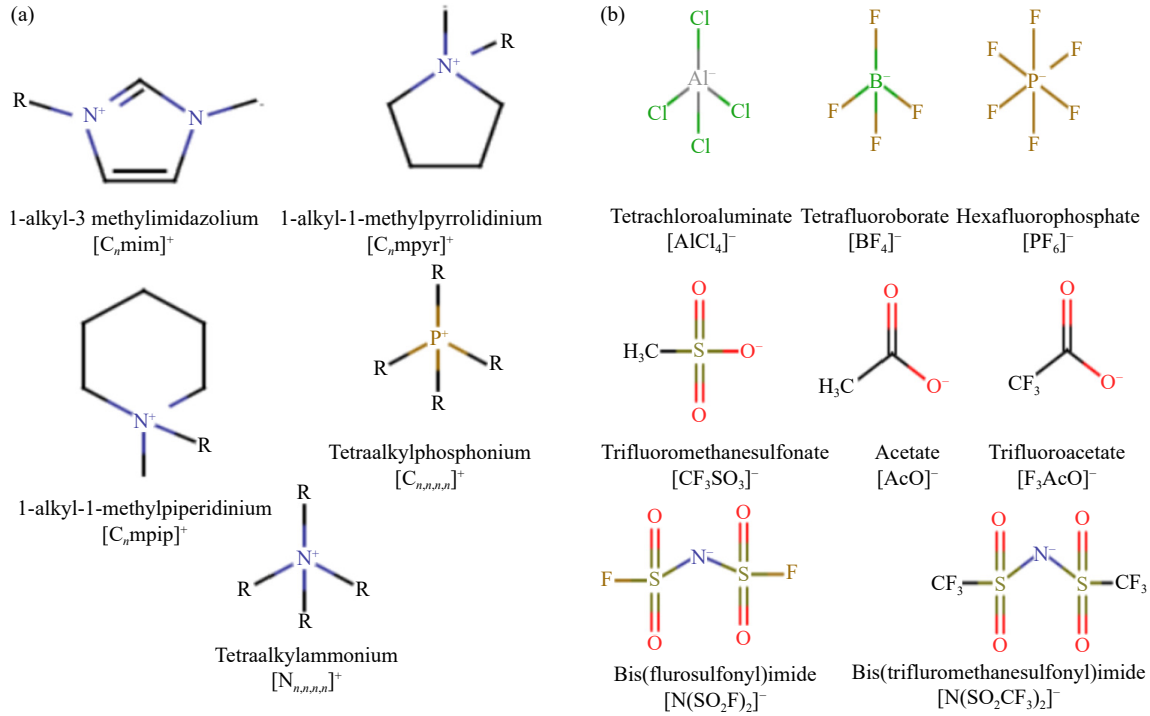


Fig. 4. Ionic liquid composition: (a) organic cationic part; (b) anionic part [75].

$$[bmim][HSO_4]_{(aq)} \leftrightarrow [bmim]^+_{(aq)} + H^+_{(aq)} + SO^{2-}_{4(aq)} \quad (11)$$

The acceptability of ionic liquids in oxidative leaching processes in extractive metallurgy has been increasingly reported, generating growing interest in their use and the necessary conditions for developing these liquids. For example, research has highlighted process improvements by increasing or controlling leaching parameters. Whitehead *et al.* [74] demonstrated that increasing both the concentration (10%–100%) of the ionic liquid and the temperature (60–70°C) yielded promising results. By increasing the concentration of 1-butyl-3-methyl-imidazolium [bmim][HSO_4] to almost 90%, they achieved leaching rates of 87%. Furthermore, the increase in the leaching rate was attributed to several factors, such as the presence of Fe^{3+} as an oxidant, oxygen solubility, and an increase in ionic strength and acidity. Subsequent studies confirmed these findings, showing that using [bmim][HSO_4] in the presence of O_2 reacting with chalcopyrite can achieve up to 88% recovery. Important parameters for this reaction include the ionic liquid concentration (10vol%–60vol%) and temperature (60–70°C), with redox potential and pH being critical at 0.56 V and −0.61, respectively [75].

Research suggests that improvements in leaching systems using ionic liquids can be achieved through the addition of agents that facilitate chalcopyrite leaching. For instance, the synergistic effect of the ionic-liquid–H_2SO_4 system decreases the hydrophobic resistance of the solid solution, allowing continuous acid leaching on the mineral surface [72]. Under conditions of 50vol% ionic-liquid–H_2SO_4, 60°C, and a duration of 20 h, a recovery rate of up to 70% was achieved. The addition of oxidants to improve leaching systems has garnered significant interest. Aguirre *et al.* [73] evaluated chalcopyrite dissolution using surface optimization methodology. They proposed that [bmim][HSO_4] as a lixiviant can reach optimal conditions by varying the temperature (30–90°C) and Cl^- concentration (0–100 g/L). Chloride addition results in a synergistic ionic-liquid–Cl^- effect that improves the proton activity of the anion [HSO_4]; in addition, chloride ions favor the formation of cupric complexes, obtaining copper extraction rates of 91.5% compared to the ionic-liquid–H_2SO_4 system. In addition, Hu *et al.* [76] evaluated the addition of H_2O_2 as an oxidizing agent with ionic-liquid–[Hmim][HSO_4]. Under optimal conditions, namely 10vol% ionic liquid, solid-to-liquid ratio of 10 g/L, particle size 45 μm, 45°C, 200 r/min, and 25% H_2O_2, they achieved extraction rates of 98.3%. It is worth noting that peroxide requires special conditions to achieve to be effective. Kuzmina *et al.* [77] evaluated chalcopyrite leaching with 7 ionic liquids by analyzing the nature of the cations (imidazolium and ethylammonium) and anions (hydrogen sulfate, nitrate, acetate, or dicyanamide) in liquid–solid–gas systems. They demonstrated that solutions based on [HSO_4] exhibited 1.8% greater efficiency; likewise, the CS_2 produced during the leaching stage reduces the sulfur layer, thus favoring chalcopyrite leaching.

The literature has demonstrated significant advances in copper extraction processes, achieving recoveries >90% [33,78–81]. This success may be attributed to the synthesis of new ionic liquids used in the chalcopyrite leaching, such as 1,2-ethane diammonium hydrogen sulfate [EDA][HSO_4] [33] and 1-ethyl-3-methyl-imidazolium [EMIm][HSO_4] [81], which increase the redox potential and decrease resistance to charge transfer for chalcopyrite oxidation. Other studies focus on using agents such as Br^- ions [80] and $K_2Cr_2O_7$ [81] and their application in solvent extraction (SX) [82–84], generating additional interest in these types of reagents.

3.1.4. Methanesulfonic acid

Methanesulfonic acid (MSA) is a highly stable chemical compound that has emerged as a solution to leaching problems owing to its electrochemical potential (>3.8 V) and acid strength comparable to that of mineral acids. Its interaction in extractive metallurgy processes to dissolve copper from chalcopyrite has been evaluated, focusing on the reaction between the two compounds. Eq. (12) refers to the formation of a soluble complex in the presence of methanesulfonic acid, generating byproducts similar to those produced during sulfuric acid leaching.

$$CuFeS_{2(s)} + 2CH_3SO_3H_{(l)} \rightarrow Cu(CH_3SO_3)_{2(aq)} + FeS_{2(s)} + H_2SO_{4(l)} \quad (12)$$

The efficiency and feasibility of this process depend on various conditions, such as acid concentration, temperature, mineral particle size, and other design factors. Furthermore, MSA alone is a poor lixiviant for chalcopyrite owing to its non-oxidizing nature. However, combining MSA with oxidizing agents can enhance its leaching effect. This has been corroborated by literature [16,85–88], suggesting an enhancement effect by using Fe^{3+} ions and hydrogen peroxide (H_2O_2). As mentioned above, peroxide has drawbacks in the leaching process. Wu *et al.* [85] proposed in one of their tests of the MSA–H_2O_2 system that avoiding the periodic addition of excess peroxide limits the system's effectiveness owing to the influence of temperature. They observed that at temperatures >75°C, peroxide decomposition occurs, resulting in a 60% recovery rate in 96 h of leaching compared to periodic peroxide addition. Furthermore, the presence of foreign agents can destabilize the system. Concurrently, Ahn *et al.* [86] achieved their best results by adding peroxide while controlling temperature (75°C) and the oxidant concentration. Excessive oxidant causes ion diffusion on the surface, creating an oxide barrier. Fe^{3+} ions have been shown to favor chalcopyrite dissolution. Hidalgo *et al.* [16] evaluated the MSA–Fe^{3+} system, finding that acid decreases iron precipitate formation, forming highly soluble iron methasulfonates. They determined that particle size (−45 to +38 μm) and temperature (90°C) were crucial to achieving 100% recoveries in 24 h at pH −0.5, ideal for developing the acid effect.

Other studies have also proposed using oxidizing agents such as $Cr_2O_7^{2-}$ and NO_3^- ions. Possible interaction mechanisms of these oxidants with chalcopyrite, as shown in Eqs. (13) and (14), highlight the influence of oxidant concentration. As the concentration increases to 10 g/L, recoveries ≥ 90% are observed [87–88].

$$6CuFeS_2 + 5K_2Cr_2O_7 + 70CH_4SO_3 \rightarrow 6Cu^{2+} + 6Fe^{3+} + 12S^0 + 10K^+ + 10Cr^{3+} + 70CH_3SO_3 + 35H_2O \quad (13)$$

$$3CuFeS_2 + 4NaNO_3 + 16CH_4SO_3 \rightarrow 3Cu^{2+} + 3Fe^{2+} + 6S^0 + 4Na^+ + 4NO + 16CH_3SO_3 + 8H_2O \quad (14)$$

In comparison with oxidizing agents such as H_2O_2 (1.17 M), which achieved an extraction efficiency of 99%, the MSA–NO_3^- system is highlighted as the most sustainable, with an activation energy of 43 kJ/mol. Although the MSA–$Cr_2O_7^{2-}$ system generates a jarosite residue, it allows the activation of surface passivation with a lower activation energy of 23 kJ/mol.

MSA is a very novel and attractive leaching alternative for chalcopyrite hydrometallurgy. However, its application on an industrial scale remains highly debated because achieving higher extractions requires special conditions [89].

3.1.5. Organic acids

Among organic acids, glycine (Gly) is a promising leaching alternative owing to its high affinity for copper, forming (Gly–Cu) complexes. Eq. (15) illustrates the global interaction reaction when chalcopyrite is dissolved in an alkaline glycine medium with oxygen as an oxidant. Here, the glycine anion chelates with copper and remains in the aqueous phase. The extracted iron precipitates as iron oxide, and the sulfide is oxidized into sulfate [90–91].

$$2CuFeS_2 + 4NH_2CH_2COO^- + 7O_2 + 2OH^- \rightarrow 2Cu(NH_2CH_2COO)_2 + 2FeOOH + 3SO_4^{2-} + S^0 \quad (15)$$

Existing literature has inspired research into incorporating glycine in leaching processes [90–95]. However, it is essential to note that glycine leaching is a complex process, and its efficiency depends on several factors, such as particle size and specific operating conditions. O'Connor *et al.* [95] evaluated the complexing conditions of glycine and found that at pH < 10, dissolution is limited by the low molar fraction of the glycinate ion, while at pH > 10.5, recovery is reduced owing to the formation of oxide species on the mineral surface, making chalcopyrite dissolution difficult.

The conditions necessary for chalcopyrite dissolution, particularly avoiding surface passivation, has been reported by Eksteen *et al.* [90] and Tanda *et al.* [93]. They demonstrated that using an ultrafine particle size (−10 μm) of the concentrates allows reaching extractions ≥90% [90]. As depicted in Fig. 5 [93], copper leaching reaches 80% in 60 min with a particle size of −10 μm, while for particles >20 μm, the extraction rate is only 20%.

Concurrently, Shin *et al.* [91] used a particle size P_{80} of 40 μm, resulting in a 21% extraction rate when they increased the temperature to 45°C. Additionally, Khezri *et al.* [92] investigated the effect of finely comminuted particle size as pretreatment in mechanically activated chalcopyrite with a pulp density of 2%, achieving 95% copper leaching in the first 12 h. Literature reports [90,92–93] asserted that increasing the temperature up to 60°C can double or maximize extraction rates. Shin *et al.* [91] evaluated the effect of temperatures up to 45°C, resulting in partial decreases in copper extraction owing to copper precipitation in the form of sulfates and sulfides, which also increased the iron content in the solution. They found that adding peroxide in a glycinate medium at pH 10.5 can significantly enhance the leaching rate [91] or that controlling dissolved oxygen as a powerful oxidant can be effective [90,92–93].

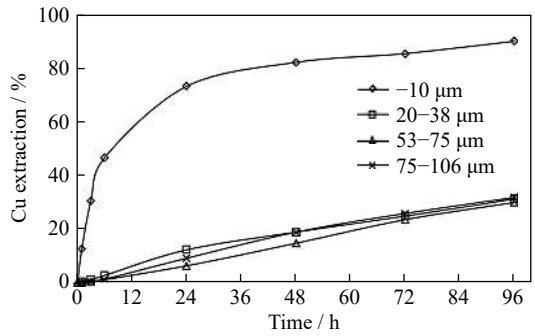


Fig. 5. Effect of particle size on the leaching kinetics of chalcopyrite: [glycine] 0.5 M, 50°C, pH 11.5, [O_2] 15 ppm, SS 400 r/min, and 0.75% solids [93]. Reprinted from *Miner. Eng.*, 135, B.C. Tanda, J.J. Eksteen, E.A. Oraby, *et al.*, The kinetics of chalcopyrite leaching in alkaline glycine/glycinate solutions, 118–128, Copyright 2019, with permission from Elsevier.

Studies based on glycine have explored various aspects, including the investigation of electrochemistry and the possible use of ammonium chloride or glycine in copper heap leaching. However, at pH 10, glycine (0.1 M) shows less favorable results than ammonium chloride, which is inconsistent with the optimal pH of glycine (10.5) [96]. Attia and Awny [97] evaluated copper leaching with glycine from a sandy dolomite mineral under the following conditions: 0.2 M glycine, pH 7.5, solid-to-liquid ratio of 1:7, for 3 h of contact, and 2% H_2O_2 at room temperature (25°C), achieving copper leaching efficiencies of 98.2%. Hidalgo *et al.* [98] studied thermal stability in 11 leaching systems, including glycine, varying temperatures between 100 and 170°C, resulting in 6% of copper extracted after 98 h with the Gly–O_2 system.

Oxalic acid. Leaching chalcopyrite with oxalic acid is a selective and relatively gentle process compared to using strong mineral acids such as sulfuric acid. This means that oxalic acid is less likely to damage other mineral components or cause environmental problems, but it may also be less efficient in copper extraction. Sarı *et al.* [99] and Turan *et al.* [100] demonstrated that oxalic acid not only has an affinity for copper ions, forming copper oxalates (Eq. (16)) but can also form complexes with ferrous and ferric oxalates depending on the concentration and pH in leaching processes [99], as shown in Eqs. (17) and (18) [101] (K_{sp} is the solubility product constant).

$$Cu^{2+} + C_2O_4^{2-} \rightarrow CuC_2O_4 \downarrow, K_{sp} = 4.43 \times 10^{-10} \quad (16)$$

$$Fe^{2+} + 2C_2O_4^{2-} \rightarrow Fe(C_2O_4)_2^{2-} \quad (17)$$

$$Fe^{3+} + 3C_2O_4^{2-} \rightarrow Fe(C_2O_4)_3^{3-} \quad (18)$$

The results depicted in the literature have shown comparable efficiencies with glycine when combined with oxidizing agents [64,100–101]. However, its application may depend

on factors such as the availability of oxalic acid, the mineralogical composition of the mineral, and the economic and environmental conditions of the mining operation. Ruiz-Sánchez *et al.* [101] presented a two-stage extraction process under conditions of 26°C and 1.01 bar for iron and copper dissolution. The speciation diagram varying the pH is shown in Fig. 6. In the first stage, leaching with oxalic acid achieved an extraction of 49% Cu and 29.5% Fe in the first 6 h under conditions of 1 M H_2O_2, 0.4 M oxalic acid, and 50 g/L pulp density. In the second stage, using an H_2SO_4–H_2O_2–ethylene glycol system, they obtained a solution with 90% Cu and 35% Fe under conditions of 0.1 M ethylene glycol, 0.007 M H_2SO_4, 2 M H_2O_2, 0.4 M EDTA, and 50 g/L pulp density.

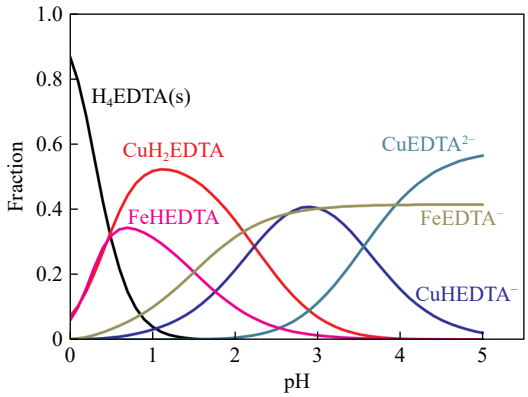


Fig. 6. Species distribution diagram for EDTA elaborated with the Medusa© software suite at 25°C, considering the concentration of copper and iron expected if the chalcopyrite (22.5 g/L) was completely leached [101]. [EDTA] = 0.192 M, [Fe^{3+}] = 0.113 M, and [Cu^{2+}] = 0.080 M. Reprinted from *Hydrometallurgy*, 193, A. Ruiz-Sánchez, I. Lázaro, and G.T. Lapidus, Improvement effect of organic ligands on chalcopyrite leaching in the aqueous medium of sulfuric acid-hydrogen peroxide-ethylene glycol, 105293, Copyright 2020, with permission from Elsevier.

Turan *et al.* [100] presented a methodology for dissolving iron in the $H_2C_2O_4$–H_2O_2 system, leveraging the solubility in acidic media to form iron oxalate (0.008 g/100 g H_2O at 20°C) compared to copper (2.16×10^{-10} g/100 g H_2O at 20°C). This method resulted in the recovery of 1.5% Cu and 70% Fe, leaving copper in the residue along with elemental sulfur. Turan *et al.* [101] proposed a two-stage leaching process: the first stage uses leaching with oxalic acid and peroxide to eliminate iron and maintain copper in the residue, which is then leached with HCl.

Sarı *et al.* [99] followed a similar methodology for iron removal with oxalate, achieving 77% Cu and 3% Fe in solution with HCl under the following conditions: 5 M HCl, 45°C, solid-to-liquid ration of 1:25, and 400 r/min in 2 h. Turan *et al.* [100] proposed improving this methodology by applying pressure. They determined that under conditions of 5 M H_2O_2, 45°C, 100 g/L $H_2C_2O_4$ in 3 h, extractions of 90.6% Fe and 1.73% Cu were achieved. However, increasing the temperature to 170°C and applying a pressure of 54.6 bar reversed the dissolution behaviors, resulting in 88% Cu and 2% Fe extracted in 3 h of leaching.

3.2. Chalcopyrite leaching in chloride medium

An alternative to improve traditional leaching systems is the addition of chloride ions (Cl^-), which significantly increase leaching rates, enhance kinetics, and modify redox potentials. This allows for obtaining lower oxidation potentials in chalcopyrite leaching (540 mV) compared to the potential typically required in a sulfated medium (>750 mV) [102]. The waste generated attributes morphological changes owing to the formation of elemental sulfur or the generation of iron precipitates in the form of natrojarosite ($Na[Fe(OH)_2]_3(SO_4)_2$) owing to the presence of Na^+ ions [69]. Furthermore, chloride ions can generate secondary redox couples, allowing Cu^+ ions to be thermodynamically stabilized and making Cu^{2+} ions available for dissolution reactions at high concentrations [32]. This method has emerged as an attractive technique owing to its ability to overcome surface passivation, making it a promising alternative for treating chalcopyrite.

3.2.1. Oxidative leaching by ferric ions in chloride medium

The focus on chloride systems is based on the high solubility and ease of regeneration of copper and iron ions, which demonstrate faster kinetics than ferric sulfate solutions. Economically, the use of ferric chlorides has shown feasibility in copper extraction, although its kinetics can be similar to sulfate systems if conditions are not adequately controlled. The literature describes some drawbacks in leaching processes with ferric chloride. For instance, Al-Harahsheh *et al.* [43] observed an inhibition in recovery rates with an increase in the agitation rate (>400 r/min) in a 0.5 M $FeCl_3$–0.5 M HCl system. This resulted in the elimination of stronger cupric complexes towing to the lower availability of chalcopyrite crystals, achieving 24% recovery. Systems without agitation showed better copper recovery, reaching 41%.

Dutrizac [103] evaluated the leaching temperature in a range of 50–100°C, showing linear kinetics compared to the parabolic trends of sulfate systems. Moreover, the activation energy of the chloride system was 47 kJ·mol^{-1}, higher than the activation energy of the sulfate system (37 kJ·mol^{-1}), consistent with later studies [104]. Maurice and Hawk [105] studied the effect of particle size through the mechanical activation of a copper concentrate, achieving 95% after 3 h of leaching with 5 M chloride owing to increased surface area and density of defects. In chalcopyrite leaching in a chloride medium, it is crucial to maintain the oxidation potential at high values and sustain a high Cu^{2+}/Cu^+ ion ratio using high chloride concentration, high temperature, and low pH [104]. Phuong Thao *et al.* [106] corroborated this by investigating the influence of redox potential on chalcopyrite leaching, finding favorable results at a potential of 442 mV. At higher potentials, the rate diffusion rates of reactants began to slow down.

The literature promotes industrial application, instrumentation control, and lower operating and capital costs. One of the first leaching processes for chalcopyrite with ferric chloride was developed by the Reno Metallurgical Research Center of the Bureau of Mines in 1971 (USA). This process in-

volved dry grinding of the concentrate (−375 mesh) and feeding it into a tank at a temperature of 104°C with a solution of 36% $FeCl_3$ and 1% HCl, dissolving 99% Cu and 84% Fe [107]. Later, the Duval Corporation's Clear process [108] used counterflow leaching in two stages to obtain a high copper yield. The first stage operated at 105°C with a solution composed of 20 g/L of $CuCl_2$, 4 g/L of $FeCl_2$, 80 g/L of NaCl, and 44 g/L of KCl. The second stage involved the precipitation of jarosite and β-FeOOH, controlling sulfate and iron presence. Despite its initial success, the process operated commercially for only six years owing to technical and economic reasons. Improvements have been suggested, such as combining chalcopyrite leaching with chloride with solvent extraction and conventional sulfate electrowinning to recover a pure product. This approach focuses on the hematite stage, where no air is introduced into the leaching, allowing the separate production of sulfur and iron waste. In the goethite stage, air/oxygen is sprayed into the leach to precipitate iron as goethite (FeOOH), which is removed along with the leach residue [109].

3.2.2. Oxidative leaching by cupric ions in chloride medium

Leaching with cupric chloride relies on the thermodynamic formation of stronger complexes, which increases the activity of Cu^{2+} ions compared to the weaker complexes formed by $FeCl_3$. This is attributed to the higher redox potential of the Cu^{2+}/Cu^{+} pair compared to the Fe^{3+}/Fe^{2+} redox couple in concentrated chloride solutions [110]. Eq. (19) describes a direct leaching process that forms chlorinated complexes [111].

$$CuFeS_2 + 3CuCl_2 \rightarrow 4CuCl + FeCl_2 + 2S^0 \quad (19)$$

Some authors have proposed that the formation of these complexes is not direct and depends on various factors. Torres *et al.* [110] studied chalcopyrite dissolution with the addition of Cl^- ions, finding that the inclusion of cupric ions significantly improves reaction kinetics by increasing the oxidation potential of the Cu^{2+}/Cl^- pair, resulting in maximum extraction of 49.7% under the following conditions: $[Cl^-]$ = 10 $g \cdot L^{-1}$, $[Cu^{2+}]$ = 2.5 $g \cdot L^{-1}$, pH = 1, 60°C, 450 r/min, d_{80} = 100 μm, solid-to-liquid ratio of 1:200, and over a period of 120 h. Rasouli *et al.* [112] studied a chalcopyrite concentrate with cupric ions in a chlorinated medium using 3 M HCl. They achieved a 62.64% copper extraction under the following conditions: 85°C, 7 h, and $[CuCl_2]$ = 0.7 M, solid-to-liquid ratio of 1:10, and 550 r/min. Furthermore, thermodynamic simulations demonstrated that the copper complex is formed at an optimal pH in the range of 0.5–2. However, at pH below 0.5, iron dissolution is facilitated. Furthermore, Wang *et al.* [111] first showed the decomposition of chalcopyrite to cupric sulfide (Eq. (20)), followed by the reaction with cuprous chloride to generate a stable complex of cupric chloride and elemental sulfur (Eq. (21)).

$$CuFeS_2 \rightarrow CuS + FeS \quad (20)$$

$$CuS + CuCl_2 \rightarrow 2CuCl + S^0 \quad (21)$$

This acid leaching method with cupric chloride is being implemented in current technological processes such as HydroCopper™ [113], which involves leaching in a strong solution (250–300 g/dm^3) of NaCl that contains $CuCl_2$. The process is oxidized by cupric ions in stirred reactors at temperatures of 85–95°C, generating residues of iron oxides or hydroxides.

3.2.3. Sodium chloride

An approach that has attracted attention is using sodium chloride in chalcopyrite leaching, which stands out for its improvements in dissolution kinetics at ambient pressures and temperatures. Furthermore, this processing method allows for the direct use of seawater, reducing the demand on freshwater reserves and enabling the generation of leaching agents [27]. Since 2019, the use of seawater in copper mining reached 4.06 m^3/s, representing 25% of the water used in mining. Since then, 14 companies in Chile have adopted seawater in their processes [114]. Cochilco [27] projects an average annual rate of 6% in seawater consumption, reaching 10.9 m^3/s by 2031.

Recent studies have examined the effect of chloride ions on the leaching of different sulfide minerals, proposing that a porous sulfur layer (a reaction product) forms in the presence of NaCl, facilitating reagent diffusion to the mineral surface [115–119]. Increasing the concentration of NaCl greatly favors reagent diffusion. For instance, Chen *et al.* [120] found that increasing NaCl concentration from 0 to 0.8 M improved copper recovery to 84.98% and iron recovery to 73.36%. Abdelraheem and Agacayak [115] investigated the addition of NaCl (0.1 M and 0.5 M) in an HCl–H_2O_2 system, achieving up to 58.11% copper extraction under the following conditions: 0.5 M HCl, 2 M H_2O_2, 600 r/min, 50°C, particle size −106+75 μm, and solid-to-liquid ratio of 2 g/L.

Chalcopyrite leaching in H_2SO_4–NaCl systems exhibits synergy, allowing greater extraction of chlorocuprous complexes. Ruiz *et al.* [121] evaluated the leaching of a chalcopyrite concentrate with oxygen at ambient pressure in an H_2SO_4–NaCl system, setting the temperature at 80°C and achieving 20% extraction in 3 h. Increasing the temperature to 100°C dissolved more than 90% of the copper owing to a significant increase in NaCl concentration from 0 to 0.5 M. Zhong and Li [118] demonstrated that 1 M NaCl in sulfuric acid systems (pH 0.5–1.5, 55°C, and 150 r/min) allowed 61% copper extraction, compared to only 6% without NaCl over 456 h.

Curing processes have increased chalcopyrite dissolution by agglomerating in the presence of the chloride ions, facilitating solubilization. A study showed that pretreating chalcopyrite with NaCl before leaching using 15 kg/t H_2SO_4 and 15 kg/t NaCl and curing for 15 d resulted in 19.56% solubilization [116], which increased to 93.1% at 90°C [117].

The use of sodium chloride salts has been demonstrated in pilot-scale processes, such as the HydroCopper™ process that utilizes NaCl. The PLATSOL® process [122] involves adding chloride ions to the autoclave feed, finding that concentrations as low as 3 g/L (5 g/L NaCl) dissolved most PGM and copper (>95%) in the autoclave. The Intec Copper pro-

cess [123] employs multi-stage countercurrent leaching (NaCl–NaBr) at 80–85°C with air addition at atmospheric pressure to precipitate iron as a goethite-type compound, followed by a two-stage purification process to separate impurities into metallic and other forms.

3.3. Chalcopyrite bioleaching

The high demand for profitability and ecologically processing low-grade chalcopyrite, along with the need for more efficient resource use in mining processes, has driven the mining industry to incorporate new technologies to maintain competitiveness and promote sustainable development. Leaching by microorganisms, often characterized by community succession during the bioleaching process, is one such technology gaining traction. Currently, bioleaching accounts for 10%–20% of global copper production [124], with heap bioleaching contributing around 7% and landfill bioleaching contributing between 6% and 11% [125]. Bioleaching typically uses chemolithoautotrophic microorganisms such as *Acidithiobacillus ferroxidans, Acidithiobacillus thiooxidans*, and *Leptobacillus ferroxidans*, which thrive in highly acidic environments (pH <5) and temperatures below 40°C, to extract copper and other metals from minerals [126]. This technology relies on microorganisms that act as oxidizers of sulfur (Eq. (22)) and iron (Eq. (23)), regenerating key oxidants (SO_4^{2-} and Fe^{3+}) for dissolving sulfide minerals, as shown in Eq. (24) [127].

$$2S^0 + 3O_2 + 2H_2O + (\text{sulfur oxidizing bacteria}) \rightarrow 2SO_4^{2-} + 4H^+ \quad (22)$$

$$4Fe^{2+} + 4H^+ + O_2 + (\text{iron oxidizing bacteria}) \rightarrow 4Fe^{3+} + 2H_2O \quad (23)$$

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 2S^0 + 5Fe^{2+} \quad (24)$$

This technology has slow kinetics and low copper extractions owing to the use of weak oxidants such as ferric ions in sulfate media [128–130]. To improve bioleaching processes, studies have shown that incorporating chlorinated media at high concentrations can favor copper extraction. Martins *et al.* [131] investigated bioleaching using the microorganism *Sulfolobus acidocaldarius* in a chloride medium at high concentrations (1 M) at 67.5°C, reaching 100% copper dissolution after 14 d. These high extractions are attributed to the presence of NaCl that accelerates the formation of elemental sulfur and jarosites, as detected by Raman spectroscopy.

Galvanic interactions have considerably improved chalcopyrite dissolution. Hong *et al.* [132] investigated the addition of pyrite in the presence of *Leptospirillum ferriphilum*, finding that it greatly enhances chalcopyrite dissolution, especially when the mass ratio of pyrite and chalcopyrite is 3:1 with an ORP of 350–370 mV vs. Ag/AgCl. In addition, pyrite helps control the redox potential and reduces chalcopyrite to secondary copper–iron species such as chalcocite (Cu_2S), allowing for up to 70% copper recovery. Liang *et al.* [133] evaluated the galvanic effect of carbon on chalcopyrite leaching using the microorganism *Acidianus manzaensis* YN25, increasing recovery from 64% to 95% and generating residues of jarosite, elemental sulfur, and chalcocite. Different types of microorganisms yield varying copper extraction rates: mesophilic microorganisms achieve less than 50%, moderate thermophilic microorganisms can reach up to 70%, and extreme thermophiles can exceed 80% [131].

Bioleaching has become prominent in mining owing to its lower economic investments compared to traditional metal extraction methods. Several commercial-scale companies now utilize chalcopyrite bioleaching and other sulfide minerals for copper extraction. Notable companies include BHP Billiton, Codelco, and Mintek, which have implemented bioleaching in operations like the Escondida mine in Chile. Additionally, other companies, such as Freeport McMoran, have implemented bioleaching at the Morenci mine in Arizona, USA. Anglo American uses bioleaching at the Skouriotissa copper mine in Cyprus. Rio Tinto has experimented with bioleaching technologies at different copper mines, including the Bingham Canyon mine in Utah, USA. Antofagasta Minerals employs bioleaching in some of its operations, such as the Los Pelambres mine in Chile. Grupo México also operates several copper mines and has implemented bioleaching in some of them.

3.4. Oxidative leaching of chalcopyrite under pressure

Currently, pressure leaching of chalcopyrite is a technique that has evolved over the years. This process employs pressure as its main component to favor chalcopyrite dissolution in sulfuric acid liquors (H_2SO_4) and uses oxidants such as oxygen (O_2) to promote sulfide oxidation [134]. The growing interest in using pressure leaching to treat chalcopyrite has been reported in the literature (Table 1), showing copper recovery rates exceeding 90%. However, the dissolution of other interferent elements, such as iron, depends on the precise control of temperature and pressure [135]. Different authors have classified pressure leaching based on the temperature regime to achieve selective copper liquors [136–138].

Pressure leaching (<100°C). This process requires mechanical activation, ultrafine grinding or the addition of powerful oxidizing agents to accelerate the reaction rate and convert S^{2-} to S^0, as shown in Eq. (25):

$$CuFeS_2 + O_2 + 2H_2SO_4 \rightarrow CuSO_4 + FeSO_4 + 2S^0 + 2H_2O \quad (25)$$

Pressure leaching (100–180°C). This type of leaching requires fine grinding and the addition of agents (chloride, carbon) that prevent contact between molten sulfur and the chalcopyrite surface, which slows down the reaction rate. This process generates conversion residues from S^{2-} to S^0 with smaller amounts converting to SO_4^{2-}, as shown in Eq. (26):

$$2CuFeS_2 + 2.5O_2 + 2H_2SO_4 \rightarrow 2CuSO_4 + Fe_2O_3 + 4S^0 + 2H_2C \quad (26)$$

Pressure leaching (>200°C). In this regime, the addition of agents or fine grinding is not required because the reaction speed is fast owing to the formation of acid (H^+) and the corresponding sulfates, shown in Eqs. (27)–(29):

Table 1. Summary of the most important aspects of pressure leaching of chalcopyrite [134,136,139–150]

Leaching medium	Oxidant agent	Leaching conditions				Leaching / %	
		Pressure / MPa	Temperature / °C	Time / min	Solid-to-liquid ratio (g·mL^{-1})	Cu	Fe
H_2SO_4, 1 M	O_2	2	180	90	1:10	94.5	4.2
H_2SO_4, 100 g/L	O_2	1	140	240	1:6	96	62
H_2SO_4, 130 g/L	O_2	0.098	100	180	1:10	98	94.69
H_2SO_4, 5 g/L	O_2	2.53	220	60	1:10	97.2	2
H_2SO_4, 2 M	O_2	1.136	207.2	287.7	1:10	93.1	92.2
H_2SO_4, 1 M	O_2	1	160	60	1:10	97.6	95.37
H_2SO_4, 1 M	O_2	0.7	150	180	1:100	79	81
H_2SO_4, 0.5 M	O_2	1.2	200	120	1:8	98.2	30.05
$H_2C_2O_4$, 100 g/L	H_2O_2	3	170	180	1:25	88.5	2.11
H_2O	O_2	1.2	200	120	1:10	99.9	
H_2O	O_2	1.2	200	120	1:10	99.9	11.17
H_2O	O_2	1.5	180	90	1:37.5	96.4	<5
H_2O	O_2	1.5	180	90	1:37.5	96.4	<13
H_2O	O_2	0.607	190	120	1:5	99	2.5

$$2CuFeS_2 + 8.5O_2 + H_2SO_4 \rightarrow 2CuSO_4 + Fe_2(SO_4)_3 + H_2O \quad (27)$$

$$CuFeS_2 + 8Fe_2(SO_4)_3 + 8H_2O \rightarrow CuSO_4 + 17FeSO_4 + 8H_2SO_4 \quad (28)$$

$$2FeSO_4 + 0.5O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O \quad (29)$$

Table 1 shows traditional pressure leaching processes that use dilute sulfuric acid to improve sulfide conversion to sulfates [134,136,139–150]. While pressure and temperature are the most influential parameters, other factors also affect the copper recovery rate. For instance, Jiang *et al.* [141] found that stirring speed is crucial for the leaching rate, with speeds lower than 700 r/min having no significant effect. Adjusting the agitation to 900 r/min yielded greater benefits. Bai *et al.* [142] studied the impact of mechanical activation, which promotes copper extraction by increasing lattice deformation and crystalline defects, thereby increasing chalcopyrite instability and boosting extraction rates up to 77.7%.

Currently, hydrometallurgy is enhancing leaching processes by assessing the presence of specific components. Some studies [141,147–150] have presented novel alternatives to chalcopyrite leaching, omitting the use of H_2SO_4 while maintaining selectivity in copper recovery over iron dissolution under similar research conditions.

Commercial-scale practice using pressure leaching is desirable for obtaining high-quality copper cost-effectively and efficiently. In recent years, the pressure method has shown potential for commercialization as a treatment for sulfide minerals. Currently, companies such as GRINM Group, JX Nippon Mining & Metals, Freeport McMoran, Freeport Minerals, Phelps Dodge, Outotec, and BHP Billiton are investing in research technologies to boost copper extraction [144].

3.5. Mechanical activation

An emerging alternative is a mechanical activation that has demonstrated the ability to enhance the leaching of nonferrous metals from sulfide minerals [151]. Mechanical activation involves high-intensity grinding operations to induce physicochemical modifications in the mineral, resulting from the transfer of large amounts of energy to the minerals [152]. The phenomena occurring owing to the increase in surface area and energy transmitted during mechanical activation can lead to increased metal dissolution and selective extraction of specific metals [153]. Baláž [152] have shown that mechanical activation positively influences leaching kinetics. This is attributed to the breaking of bonds in the crystal lattice of the mineral, which decreases the activation energy (ΔE^*) and increases the leaching rate, as shown in Eqs. (30) and (31).

$$\Delta E^* = E - E^* \quad (30)$$

$$k^* = k\exp\left(\frac{\Delta E^*}{RT}\right) \quad (31)$$

where E represents the apparent activation energy of the non-disordered mineral, E^* is the apparent activation energy of the disordered mineral, k is the leaching rate constant of the non-disordered mineral, and k^* is the leaching rate constant in a specific temperature, R is the gas constant, and T is the temperature. If $E > E^*$, it can be deduced that the leaching rate of a disordered mineral is greater than that of an ordered mineral, as indicated by Eq. (31).

Therefore, mechanical activation has been asserted [154–159] as a favorable pretreatment process for processing sulfides before leaching for copper recovery. Increases in leachability rates may result from a combination of mechanically induced structural defects and chemical reactions involving the mineral and the local environment. Some studies have focused on the oxidative leaching of activated chalcopyrite in sulfate or chloride media. For example, Li *et al.* [159] investigated mechanical activation as a pre-stage of chalcopyrite leaching. They demonstrated that comminuting the concentrate with an oxidant ($Fe_2(SO_4)_3 \cdot xH_2O$) allows the formation of new phases such as S^0, $FeSO_4$, and $CuSO_4$. This occurred owing to the structural disorder produced by mechanical activation and solid-state reactions forming soluble

compounds, achieving 98% copper in 2 h. Without ferric hydrate during grinding, only 8% copper was recovered.

Li *et al.* [155] applied mechanical activation to a chalcopyrite concentrate before leaching. Their study using X-ray diffraction analysis indicated that increasing lattice tension in chalcopyrite favored copper recovery (86%). In addition, grinding caused structural modification and phase transformation into a solid state, forming water-soluble CuCl compounds through comminution with $NaClO_2$. Other studies have focused on improving chalcopyrite leaching without oxidants. Yang *et al.* [157] studied the effect of mechanical activation on a chalcopyrite concentrate using three modes: dry grinding, wet grinding (solid-to-liquid ratio of 5 g/mL), and wet grinding (solid-to-liquid ratio of 1 g/mL). They found that dry ground samples exhibited a higher degree of amorphization and decreased surface passivation owing to oxidation and selective rupture of the network, achieving 81.5 times greater copper extraction.

Most commercial-scale projects have referenced the evidence of mechanical activation in industrial practice as pretreatment in chalcopyrite leaching (Table 2 [113,144]). Notable processes include the Albion process [160], Activox [152], Nenatech [161], and Bactech/Mintek [162]. These processes utilize ultrafine grinding to achieve particle sizes <15 μm and subsequent pressure oxidative leaching process. The Bactech/Mintek process, however, subjects the concentrate to bacterial leaching in aerated/agitated tanks after grinding. In these ultrafine grinding processes, a high degree of stress is introduced into the sulfide mineral framework, generating several grain boundary fractures and defects in the mineral network. This reduces the activation energy required for sulfide oxidation, allowing leaching under atmospheric conditions and increasing the dissolution rate owing to the expanded mineral surface [162].

Table 2. Commercial industrial process for chalcopyrite leaching processes [113,144]

Industrial process	State	Leaching conditions				
		Acid	Oxidizer	Size D_{80} / μm	Temperature / °C	Pressure / atm
Mount Gordon	C	H_2SO_4 diluted	O_2, Fe^{3+}	100	80–90	8
Activox	P	H_2SO_4 diluted	O_2, Fe^{3+}	5–10	90–110	10–12
Las Cruces	C	H_2SO_4 diluted	H^+, O_2, Fe^{3+}	10–15	90	1
Galvanox	P	H_2SO_4 diluted	O_2, pyrite or silver	75	80	1
Anglo American Corporation/University of British Columbia (AAC/UBC)	P	H_2SO_4 diluted	O_2, surfactants	10–15	150	10–12
Freeport McMoran (MT-DEW-SX)	C	H_2SO_4 diluted	O_2, surfactants	15	140–180	14
Freeport McMoran (TPOX)	S	H_2SO_4 diluted	O_2	53	200–230	30–40
CESL	P	H_2SO_4 diluted	O_2, Cl^-	37	150	10–12
PLATSOL	P	H_2SO_4 diluted	O_2, NaCl	15	220–230	30–40
Albion	P	H_2SO_4 diluted	O_2, Fe^{3+}	50–10	85	1
Cuprochlor	C	H_2SO_4 diluted	$CaCl_2$	0.5 in	25	1
Intec Ltd	P	H_2SO_4 diluted	Halide	40	85	1
HydroCopper™	P	H_2SO_4 diluted	Cu^{2+}, NaCl	53	90	1
Sepon Copper	C	H_2SO_4 diluted	Fe^{3+} O_2	100 50	80 230	1 30–32
BioCop	C	Thermophile extreme bacteria	O_2, Fe^{3+}	37	65–80	1
Biosigma	P	Bacteria	O_2, Fe^{3+}	1.5 in	25	1
BacTech-Mintek	D	Moderate thermophile bacteria	O_2, Fe^{3+}	5–10	35–40	1

Note: P—Pilot plant; C—Commercial plant; S—Semi-commercial plant; D—Demonstration plant.

4. Discussion and analysis

4.1. Adaptation of leaching processes on an industrial scale

Table 2 demonstrates the traditional and current processes in which various factors studied have significantly impacted copper extraction. The application of atmospheric pressure leaching, bioleaching, mechanical activation, and pressure oxidative leaching processes on an industrial scale is booming. These methods are emerging as viable options for widespread adoption.

In the past decade, significant efforts have been made to mitigate the negative impacts of copper mining. Notable processes in biohydrometallurgy, such as BioCop, Biosigma, and BacTech-Mintek, have demonstrated acceptability in copper recovery. However, these methods face challenges, such as the slow dissolution kinetics of chalcopyrite and the high time and costs to maintain optimal conditions for bacterial growth. These drawbacks can be mitigated by using bacteria that are more resistant to harsh leaching conditions.

However, this could result in greater oxygen consumption by the bacteria, resulting in premature death and a potential decrease in the leaching process efficiency. Leaching technology using organic acids is an emerging field expanding its commercial applications. For example, glycine-based solutions have proven effective in copper recovery. Reusing alkaline solutions with glycine can achieve similar effects to new glycine solutions [90]. Studies have shown that around 24.5% copper can be recovered in 100 h of leaching with reused glycine solutions compared to 26% with new solutions.

Hydrogen sulfide has been explored for copper precipitation after glycine leaching, achieving recoveries greater than 99% through solvent extraction using LIX 84I at 10vol% [96]. Mextral 84H (2-hydroxy-5-nonylacetophenone oxime) and Mextral 54–100 (1-benzoyl-2-nonyl ketone) were evaluated for copper separation in solvent extraction reactions [94]. Oxalic acid, commonly used in acidic solutions, allows greater selectivity for iron to form oxalates [101].

Traditional commercial-scale processes have achieved recoveries greater than 90% of copper under severe leaching conditions. By contrast, bioleaching typically results in less than 50% copper recovery under labile conditions. The high leaching rates of conventional processes are influenced by factors such as fine grinding, temperature, reagent concentration, and pressure. These factors, however, generate additional costs in energy consumption and require large quantities of freshwater, posing challenges for sustainable resource management. Seawater's richness in ions presents an emerging alternative to leaching [69]. However, its excessive ion content can cause scale and corrosion throughout the processing system.

4.2. Economic appraisal of leaching reagents

Table 3 refers to the quotation of the reagents evaluated in this article that have shown the ability to improve chalcopyrite leaching. Some alternatives, such as ferric chloride and hydrogen peroxide, cost less than $50/kg, while ferric sulfate costs more than $150/kg. Recycling ferrous solutions through catalytic oxidation with carbon can regenerate 90.7% of Fe^{3+} and recover 75.6% of copper [69].

Other alternatives include ionic liquids priced above $1000/kg. Their recyclability remains under discussion owing to the toxicity of the imidazolium ion in their structure and the lack of defined recycling methods. The ionic liquid market was estimated at $43.0 million in 2021, with projections reaching $55.8 million by 2026 [163]. MSA, although similar to sulfuric acid, has a high price owing to its strong acidity and high leaching rates. This makes its use very expensive, and discussions are ongoing regarding its recyclability, consumption, and degradation. The most promising alternatives are glycine and oxalic acid because they are less benign reagents. However, their significant costs make them less attractive despite articles referencing the recyclability of glycine, which mitigates its high price [90].

Table 3. Reagent quotation (lab purity)

Reagent	Purity / %	Amount	Price / US$
H_2SO_4	95–98	A	57.55
$Fe_2(SO_4)_3 \cdot xH_2O$	97	B	192.65
$FeCl_3$	97	B	41.02
H_2O_2	>35	A	38.57
bmim[HSO_4]	95	B	1104.9
MSA	≥99	A	314.28
NH_2CH_2COOH	≥99	B	124.69
$H_2C_2O_4$	98	B	245.91
NaCl	≥99	B	92.45

Note: A—1 L; B—1 kg.

4.3. Environmental prospects for copper

The growth trends of raw materials, especially critical metals, imply greater water consumption and excessive waste generation (around 5 Gt), along with an increase in greenhouse gas emissions [164]. This is reflected in the excessive demand for copper to achieve the energy transition. For instance, copper estimates include up to 11.9% for solar panel units, 23.3% for wind turbine units, and 14% for automobile batteries, with projections extending to 2035. Therefore, the rising demand for copper implies significant environmental, social, and governance risks in meeting energy transition goals in the coming years. The impacts of copper mining have been evaluated [165], showing that the copper industry uses 32 m^3/t of copper produced, generates 67 t of acid waste, contributes 20% to biodiversity risk, and generates 110 t of sludge and 200 t of waste dump waste [166]. Lallana and Evans [166] reported that the production of 7 metals, including copper, accounts for 7% of greenhouse gas emissions; therefore, producing 1 t of smelted copper generates 3 t of CO_2, with the carbon footprint per ton being higher for the extraction of critical metals.

Copper recycling offers significant benefits such as lower energy consumption, between 60% and 95% less and 0.1 tons of CO_2 emitted in the smelting of recovered copper. Based on this information, the study suggests that recovering uneconomic metals poses substantial challenges and economic trends with future visions of copper mining.

4.4. Economic alternatives for the recovery of copper

Over the years, potential sources of copper with contents of 5% have decreased to less than 1% in their minerals [167–168], generating uncertainty about possible future economic alternatives. Urban mining has emerged as an important source of copper supply that was previously considered economically unviable. Within urban mining, electronic waste is a potential source for obtaining copper. In 2021 alone, more than 50 Mt of electronic waste were generated, of which 17.4% are recycled annually, and 4% are used [167]. By 2030, electronic waste may exceed 74 Mt, potentially generating recoveries of more than US$ 50 billion [167]. Consistent with these findings, a study conducted in Ref. [23] projected the e-waste market to reach values greater than US$ 137 billion by 2029, registering a compound annual growth rate of 12.9% from 2023 to 2029. In a study on the global perspective on electronic waste recycling, Liu

et al. [169] evaluated that as of 2017, the price of copper per 1900 kt was quoted at 10.6 billion euros, with growth prospects in the coming years.

5. Conclusions and prospects

The goal of this work was to review the literature on the hydrometallurgical processing of chalcopyrite. We analyzed the use of various methods, including atmospheric pressure leaching (using ferric sulfate, hydrogen peroxide, ionic liquids, MSA, and organic acids), chloride media leaching, pressure leaching, and bioleaching. Our technoeconomic analysis demonstrated that such processes are associated with low environmental impacts. Organic acids have shown feasibility with the lowest environmental impact, particularly if produced through biotechnological routes. Mechanical activation has proven to be an efficient pretreatment for sulfides before leaching. The high refractoriness of chalcopyrite in hydrometallurgical processes remains a challenge when defining appropriate leaching processes. Bioleaching offers significant economic and environmental benefits. In conclusion, this research provides a solid foundation for future studies on chalcopyrite leaching. The findings presented here may be of great importance to the mining industry and copper recovery, offering opportunities to optimize processes and improve sustainability in this area. Future projects can focus on upscaling these technologies, such as organic acids, ionic liquids and bioleaching for copper extraction from chalcopyrite. Another point not explored in this study is the improvement and development of new technologies and materials in chalcopyrite processing.

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Conflict of Interest

The authors declare no conflict of interest.

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