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Review

Use of Hydrogen Peroxide as Oxidizing Agent in Chalcopyrite Leaching: A Review

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Abstract: Leaching represents a significant challenge for the mining industry due to its slow and incomplete kinetics under ambient conditions (20 °C, 1 atm) and its increased prevalence in global ore deposits. In this context, the use of hydrogen peroxide (H_2O_2) has proved to be a promising oxidizing agent for improving process efficiency. This article reviews the most recent breakthroughs in the use of H_2O_2 for chalcopyrite leaching, analyzing the experimental conditions that maximize copper extraction, including combinations with novel leachants such as organic systems, inorganic salts, and amino acids. In addition, the main challenges associated with the use of H_2O_2, such as its catalytic decomposition and thermal stability, are highlighted, along with strategies to overcome these limitations. Perspectives and challenges for its application are presented, emphasizing the need for hybrid and optimized approaches to integrate this oxidizing agent in sustainable hydrometallurgical processes. The objective of this paper is to make an exhaustive review of what has been published on chalcopyrite leaching in order to find ways to leach it in large quantities and in a simple way.

Keywords: chalcopyrite; leaching; copper; oxidant; hydrogen peroxide; sulfide ore

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1. Introduction

Chalcopyrite ($CuFeS_2$), a copper iron sulfide containing 34.5% Cu, 30.5% Fe, and 35.0% S, is a mineral typically of hypogene origin. It forms in deep environments under high temperature and pressure conditions, such as in magmatic or hydrothermal processes. This deep-seated genesis explains its classification as a primary sulfide [1,2]. The Cu–S and Fe–S covalent bonding of chalcopyrite contributes to its stability in a wide range of geochemical conditions, which explains its abundance [3], currently being the main source for copper extraction and production and one of the main sources of sulfur [4]. Approximately 70% of the world's copper reserves are contained in chalcopyrite ore. Concentration and pyrometallurgical processes are currently used to process it and extract the copper, which involves a series of processes such as crushing, grinding, flotation, smelting, refining, and electrorefining. However, and for a long time, different hydrometallurgical processes have been explored for the extraction of copper from copper ore, including leaching, solvent extraction, and electrowinning [5].

The growing interest in chalcopyrite leaching comes in response to term aspects such as the increasing costs of pyrometallurgy, the presence of penalizing elements (arsenic and bismuth), and the vast availability of low-grade ores [6].

Heap leaching of chalcopyrite is seen as a practical and efficient option as it effectively treats large volumes of low-grade ores in an economical and sustainable manner [7].

It represents an attractive alternative since, as copper mines around the world deepen their operations in primary sulfide deposits, more and more low-grade chalcopyrite will be available for leaching, as indicated by Watling [8]; Ji et al. [4]; and de Melo Silva Cheloni et al. [9].

The leaching of chalcopyrite from flotation concentrates is considered a more convenient alternative to pyrometallurgy, which requires high temperatures (greater than 1000 °C) and generates SO_2 emissions, a gas that requires capture systems to mitigate pollution and acid rain [1]. Unlike smelting, which faces difficulties caused by impurities such as arsenic, leaching allows managing these contaminants more efficiently and improves the quality of the copper obtained [8].

However, Nyembwe et al. [10], Hiskey et al. [11], and Kuhn et al. [12] indicate that chalcopyrite is considered one of the most difficult minerals to leach due to its slow and incomplete kinetics resulting from the formation of a diffusion barrier that prevents further attack of the leaching solution on the unreacted mineral surface. Nyembwe et al. [10] indicate that this barrier occurs as a consequence of the formation of elemental sulfur (S^0), the generation of copper polysulfides coming from the preferential dissolution of iron, or the precipitation of iron compounds such as jarosite, which clog the ore surface, thus creating a passivating layer that wraps the ore surface and blocks access of the leachant.

Therefore, advanced techniques are required to leach chalcopyrite, such as pressure and high-temperature leaching [13], ultrasonic-assisted leaching [14], the use of novel leaching agents such as ammonia solutions, hypochlorites, ionic liquids, glycine, metasulfonic acid, ferric chloride and sulfate [3], or bioleaching methods [15].

According to studies by Barton and Hiskey [3], oxidants are more important than leachants in leaching kinetics and leaching performance. Hydrogen peroxide is another oxidant studied by these authors, suggesting that the role of this oxidizing agent is more significant than leachates in terms of the rate at which the reaction occurs and the amount of copper extracted. Therefore, paying attention to the use of hydrogen peroxide as an oxidizing agent is crucial to optimize the leaching process.

Different oxidants have been investigated to be used in chalcopyrite leaching, such as cupric ion [16–18], ferric ion [19–22], dichromate ion [23–25], nitrate ion [26], hypochlorite [27], and oxygen [28,29], among others. Al-Harahsheh et al. [30] investigated the leaching of chalcopyrite using ferric chloride ($FeCl_3$) and examined the synergistic effect of cupric chloride ($CuCl_2$). The results showed that the presence of $CuCl_2$ significantly enhanced chalcopyrite dissolution, suggesting that Cu^{2+} acts as an effective oxidizing agent in chloride media. Liddicoat and Dreisinger [16] developed new flowsheets combining chalcopyrite leaching in chloride-containing media with solvent extraction. The study highlighted the advantages of using chloride media to improve metal solubility and increase leaching rates. Lundström et al. [17] analyzed chalcopyrite leaching in cupric chloride solutions, focusing on the influence of Cu^{2+} concentration, temperature, and pH on the dissolution rate. They found that Cu^{2+} concentrations above 9 g/L are necessary for effective operation and that chloride solutions provide stability to monovalent copper complexes, thereby facilitating leaching. Skrobian et al. [31] studied the effect of NaCl concentration and particle size on the leaching rate of chalcopyrite in acidified cupric chloride solutions. The results indicated that the addition of NaCl had a positive effect on the leaching rate, while particle size was found to be almost irrelevant under stirred reactor conditions. Tchoumou and Roynette [32] explored the leaching of complex sulfide concentrates in acidic cupric chloride solutions. They observed that the presence of chlorine-containing compounds, such as liquid chlorine, can regulate the redox potential and enhance chalcopyrite dissolution. Yévenes et al. [18] analyzed chalcopyrite leaching in chloride solutions without the presence of sulfates. They found that the addition of

chloride ions improved the leaching rate and that the Cl^- concentration was positively correlated with copper extraction efficiency. These studies underscore the importance of copper and chloride ions in enhancing chalcopyrite leaching, providing valuable insights for the development of more efficient hydrometallurgical processes. Anh et al. [33] explored the use of dichromate and nitrate as alternative oxidants in the leaching of chalcopyrite with methanesulfonic acid. Both oxidants achieved copper extraction greater than 90% at 75 °C. Kinetic analysis suggested that the nitrate system is more efficient and sustainable for chalcopyrite leaching. Vardner et al. [34] developed a hydrometallurgical process using chromium(II) chloride for the reductive leaching of chalcopyrite. This approach, unlike traditional oxidative treatments, achieved a complete reaction within minutes at ambient temperature and pressure, resulting in the formation of copper(I) chloride (CuCl). Ji et al. [35] proposed a novel acid-free leaching process for complex chalcopyrite under oxygen pressure. A copper leaching efficiency of 99.86% was achieved after 120 min at 200 °C and 1.2 MPa, indicating that the process is controlled by a chemical reaction with an apparent activation energy of 50.646 kJ/mol. Miao et al. [36] examined the leaching behavior and kinetics of chalcopyrite under pressure oxidation conditions in water, without the addition of acid. Copper was efficiently dissolved, achieving a leaching rate of 96.4% under optimal conditions, with an apparent activation energy of 62.34 kJ/mol. Recently, Karimov et al. [37] studied low-temperature (100 °C, 0.2–0.8 MPa) pressure leaching of pyrite, chalcopyrite, and their mixture. Oxygen pressure had a slight effect on chalcopyrite dissolution but significantly enhanced pyrite oxidation. The surfaces of both minerals showed passivation by elemental sulfur. This methodology can be used to process pyrite-rich copper ores and to pretreat copper concentrates with gold-bearing pyrite, improving gold and silver recoveries.

Hydrogen peroxide presents a standard potential of +1.77 V, similar to potassium permanganate (+1.51 V) and higher than chlorine (+1.36 V). It is a strong oxidant capable of directly oxidizing copper sulfides, while other oxidants such as $FeCl_3$ (+0.77 V) have lower oxidation capacity, which may result in slower kinetics when compared to H_2O_2.

Hydrogen peroxide is particularly efficient in acidic media due to the participation of H^+, while it adds an environmental advantage, as it decomposes to water and oxygen. However, careful control is required, as the catalytic decomposition of hydrogen peroxide may cause its leaching efficiency to be reduced [38–40].

According to the results shown by Zandevakili and Akhondi [41], ferric sulfate and ferric chloride have a lesser effect on copper extraction than H_2O_2. Despite all the benefits of ferric sulfate leaching, its slower reaction rate compared to H_2O_2 leaching stands as its main disadvantage.

By using hydrogen peroxide instead of ferric iron, some of the potential problems associated with excessive iron concentration can be avoided. A high iron content in solution can lead to the precipitation of jarosite or other ferric compounds, forming a passivating layer on chalcopyrite. It also increases sulfuric acid consumption by promoting the formation of iron sulfates and may even induce copper precipitation as secondary sulfides or copper jarosite. Additionally, excessive iron can interfere with downstream processes, such as solvent extraction, thereby reducing the quality of the pregnant leach solution (PLS) and complicating the electrowinning process. If arsenic is present, Fe^{3+} further promotes the formation of scorodite and other arsenical compounds, potentially leading to environmental concerns. The activity of hydrogen peroxide persists at a higher molarity than that achieved with ferric oxidant.

As to the use of hydrogen peroxide in the leaching of chalcopyrite, Olubambi and Potgieter [42] established a solid foundation after investigating the leaching mechanisms with sulfuric acid and hydrogen peroxide. Hu et al. [43] demonstrated how hydrogen peroxide

enhances dissolution in ethylene glycol medium. Ahn et al. [44] revealed the synergy between methanesulfonic acid and hydrogen peroxide. Nicol [45] provided an in-depth understanding of the use of hydrogen peroxide in acidic solutions. Petrović et al. [46] confirmed its effectiveness in the extraction of copper in sulfuric acid solution. Karppinen et al. [47] expanded its application to include the leaching of Ni, Co, Cu, and Zn from sulfide tailings, demonstrating the versatility of hydrogen peroxide in various leaching contexts. The authors investigated the effect of using hydrogen peroxide at different temperatures. They note that hydrogen peroxide can act as both a reducer and an oxidant in leaching; this is because the oxidation state of O_2 is −1. Sulfide ores react with sulfuric acid and hydrogen peroxide. Sulfur sulfide is oxidized to sulfate in a reaction with hydrogen peroxide. Pyrite is oxidized in acid media at high concentration. The results show that the dissolution of nickel, cobalt, iron, zinc, and copper was favored with the addition of H_2O_2. However, the authors indicate that the use of H_2O_2 can be problematic due to its high environmental impact. The production of H_2O_2 has a global warming potential that varies between 442 and 687 kg of CO_2 equivalent per ton produced. Furthermore, its partial decomposition by ferric ions can increase its consumption, issues that must be considered when scaling up to industrial scale.

It is for the above reason that this article intends to review the scientific literature regarding the use of hydrogen peroxide (H_2O_2) in the leaching of chalcopyrite ($CuFeS_2$) in recent years, pointing out the prospects and challenges posed by its future use in the copper mining industry, especially in the hydrometallurgy of primary sulfides such as chalcopyrite.

The literature review was conducted using the following criteria: (1) Topical relevance: includes studies on chalcopyrite leaching in an acidic medium using H_2O_2; (2) publication period: with an emphasis on the 2020–2024 period to ensure scientific relevance, although older key articles are included; (3) type of study: prioritizes experimental studies (laboratory or pilot) and systematic reviews; (4) source quality: publications in indexed scientific journals: WoS, Scopus, SciELO, etc. Avoid non-peer-reviewed publications or publications from conferences with low scientific rigor; (5) key variables and indicators for study selection: Cu or Fe dissolution kinetics. Effect of H_2O_2 concentration and acidity. Temperature, agitation, and leaching time. Pre- and post-leaching mineralogical characterization. (6) Keywords: chalcopyrite; leaching; copper; oxidant; hydrogen peroxide; sulfide ore, and (7) geological or mineralogical context: chalcopyrite in ores, concentrates, and pure form.

2. Use of Hydrogen Peroxide in Chalcopyrite Leaching

Hydrogen peroxide has emerged as a widely used oxidizing agent in the leaching field, particularly in acidic environments. All physical, chemical, thermodynamic, and kinetic aspects are of key importance to understanding the use of hydrogen peroxide as an oxidizing agent in chalcopyrite leaching.

2.1. Physical Aspects

Hydrogen peroxide is a clear, colorless liquid that is miscible with water in all proportions and stable at room temperature when 100 wt.%. It presents a melting point of −0.43 °C and a boiling point of 150.2 °C at 101.3 kPa. Its heat of fusion is 368 J/g, while its heat of vaporization at 25 °C is 1519 J/g K and at boiling point is 1387 J/g K. The specific heat of hydrogen peroxide in the liquid state at 25 °C is 2629 J/g K, and in the gaseous state at 25 °C it is 1269 J/g K. Its relative density is 1.4700 g/cm^3 at 0 °C, decreasing to 1.4425 g/cm^3 at 25 °C. The viscosity of hydrogen peroxide is 1.819 mPa-s at 0 °C and 1.249 mPa-s at 20 °C. Its critical temperature is 457 °C, and its critical pressure is 20.99 MPa. The refractive index of hydrogen peroxide is 1.4084 at 20 °C [48].

Depending on the concentration, aqueous solutions of hydrogen peroxide show variations in their physical properties. That is, by varying the concentration of hydrogen peroxide (H_2O_2) in aqueous solutions, its density is observed to increase as the concentration and temperature also increase. For example, at 0 °C, the relative density goes from 1.1441 g/cm^3 for a 35% solution to 1.4136 g/cm^3 for a 90% solution. At 20 °C, these densities are 1.1312 g/cm^3 and 1.3920 g/cm^3, respectively, while at 25 °C they are 1.1282 g/cm^3 and 1.3867 g/cm^3. In addition, the viscosity, refractive index, and boiling point also increase with higher concentrations, while the melting point decreases. At 30 °C, the partial pressure of H_2O_2 varies from 0.05 kPa for 35% to 0.2 kPa for 90% [48].

2.2. Chemical Aspects

Yepsen et al. [49] indicate that the leaching of chalcopyrite can be distinguished by its low solubility in water, especially at acidic pH, according to reaction (1):

$$CuFeS_2 + 2H^+ \rightarrow Cu^{2+} + Fe^{2+} + 2HS^- \ (pK_{ps}) = -35.27, \quad (1)$$

Cu^{2+} is initially released from the chalcopyrite surface, followed by Fe^{2+}, leading to the formation of a nonstoichiometric sulfur-rich polysulfide layer, which effectively passivates the mineral surface. Reaction (2) occurs during the formation of such a layer:

$$CuFeS_2 + 4z\ H_2O \rightarrow Cu_{1-x}Fe_{1-y}S_{2-z} + y\ Fe^{3+} + z\ {SO_4}^{2-} + 8z\ H^+ + (2x + 3y + 6z)e^-, \quad (2)$$

In reaction (2), coefficient "y" represents the stoichiometric coefficient for the generation of Fe^{3+}, and "z" represents the stoichiometric coefficient for the generation of ${SO_4}^{2-}$.

Chalcopyrite solubility improves with increasing electrochemical potential during the dissolution process. H_2O_2 is used as an electrochemical potential modifier of the slurry and acts mainly as an oxidizing agent (E^0 = +1.76 V *v/s* SHE). Equations (3)–(5) illustrate this redox mechanism:

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

$$S^{2-} \rightarrow 2e^- + S^0 \quad (4)$$

$$2H_2O_2 + 4H^+ + 4e^- \rightarrow 4H_2O \quad (5)$$

H_2O_2 molecules can react with ferrous ions contained in the ore to produce ferric ions, as these are more reactive and can aid in the dissolution of chalcopyrite. The effectiveness of H_2O_2 has been attributed to its ability to promote the formation of elemental sulfur and sulfate ions, which can help dissolve chalcopyrite, as seen in reactions (6) and (7):

$$CuFeS_2 + 2H_2SO_4 + \frac{5}{4}O_2 + \frac{1}{2}H_2O \rightarrow CuSO_4 + Fe(OH)_3 + 2S^0 \quad (6)$$

$$S^0 + \frac{3}{2}O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-} \quad (7)$$

In turn, Klauber [50] sustains that the oxidative activity of peroxide in acidic media is given by reaction (8):

$$2CuFeS_2 + 17H_2O_2 + 2H^+ \rightarrow 2Cu^{2+} + 2Fe^{3+} + 4{SO_4}^{2-} + 18H_2O, \quad (8)$$

At the same time, a small part of the sulfide is oxidized to its elemental form. This is confirmed when the leaching residue and a leaching degree of 55% are subjected to X-ray diffraction analysis. The reaction is presented by reaction (9):

$$2CuFeS_2 + 5H_2O_2 + 10H^+ \rightarrow 2Cu^{2+} + 2Fe^{3+} + 4S^0 + 10H_2O, \quad (9)$$

Increasing the H_2O_2 concentrations increases the degree of copper extraction in chalcopyrite leaching [46]. According to Moazzami et al. [51], the increase in copper extraction from $CuFeS_2$ with higher concentrations of hydrogen peroxide could respond to the increased solubility of oxygen or the elevated oxidation potential of hydrogen peroxide. According to Agacayak et al. [52], copper extraction is directly proportional to hydrogen peroxide concentrations but decreases at temperatures above 60 °C due to the decomposition of hydrogen peroxide.

In addition, the increase perceived in chalcopyrite dissolution in the presence of hydrogen peroxide can be attributed to the reaction between hydrogen peroxide and mineral substances, as depicted in reaction (10):

$$H_2O_2 \rightarrow 2OH, \quad (10)$$

This reaction leads to the decomposition of hydrogen peroxide into hydroxide ions (OH^-) and hydroxyl radicals (OH·). Hydroxyl radicals (OH·) react with chalcopyrite by reaction (11), creating elemental sulfur:

$$2OH + 2S^{2-} \rightarrow 2S^0 + H_2O + 0.5O_2, \quad (11)$$

Elemental sulfur is also transformed into sulfate ions by reaction (12):

$$2S^0 + 2H_2O + 3O_2 \rightarrow 2{SO_4}^{2-} + 4H^+, \quad (12)$$

Finally, after reaction (12), copper ions react with sulfate ions, resulting in the formation of an aqueous copper sulfate solution according to reaction (13):

$${Cu^{2+}}_{(aq)} + {SO_4}^{2-}{}_{(aq)} \rightarrow CuSO_{4(aq)}, \quad (13)$$

The decomposition of hydrogen peroxide occurs because of the Fenton reaction between leached iron and hydrogen peroxide, catalyzed by dissolved copper [53]. Thus, its consumption during the leaching process is produced by reactions other than those of chalcopyrite and the elemental sulfur oxidation [54].

Agacayak et al. [52] identified that higher concentrations of H_2O_2 increase copper extraction, but only up to 60 °C; from then on, the extraction level drops owing to the decomposition of H_2O_2. If, instead of 3 M, 1 M H_2O_2 is used, copper extraction drops from 99% to 48%.

The results obtained by Petrović et al. [46] demonstrate that copper extraction undergoes a substantial increase within the initial 60 min of the reaction. However, as a consequence of the catalytic decomposition of hydrogen peroxide, the dissolution of chalcopyrite ceased thereafter.

In acid solutions, pyrite (accompanying chalcopyrite) must also be considered when leaching chalcopyrite, as it can be dissolved by hydrogen peroxide according to Equations (14)–(16) [55]:

$$2FeS_2 + 15H_2O_2 \rightarrow 2Fe^{3+} + 4{SO_4}^{2-} + 2H^+ + 14H_2O, \quad (14)$$

$$2FeS_2 + 15H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 4{HSO_4}^- + 14H_2O, \quad (15)$$

$$2FeS_2 + 3H_2O_2 + 6H^+ \rightarrow 2Fe^{3+} + 4S^0 + 6H_2O, \quad (16)$$

2.3. Thermodynamic Aspects

According to the Pourbaix diagram of the Cu-Fe-O-S-H_2O system (or Cu-Fe-S-H_2O system) at 25 °C, reported by Schlesinger and Biswas [56], chalcopyrite dissolves in acid media and undergoes solid transformation into other copper-rich intermediate sulfides

(Cu_5FeS_4, CuS, Cu_2S). To dissolve copper from chalcopyrite, a pH below 4 and an oxidizing redox potential above +400 mV are required.

The potential for chalcopyrite leaching can be adjusted by the presence of H_2O_2. For example, according to Taboada et al. [57], this oxidant caused a greater effect on the redox potential of the leachate solution, increasing the potential from 530 mV to 600 mV v/s SHE. However, low concentrations of hydrogen peroxide obtain low concentrations of copper in the leachate solution. This was also reported by Velásquez-Yévenes [58], whose study revealed that copper extraction was increased in the redox potential range of 550 to 620 mV.

Dong et al. [59] and Dakkoune et al. [60] reported low copper extractions (around 10%) under working conditions of 170 h, pH of 1 in leaching medium with H_2SO_4, T = 42 °C, and Eh = 750 mV v/s SHE adjusted and controlled with H_2O_2 solution, although Dong et al. [59] worked at a 0.3 wt.% ratio in contrast to Dakkoune et al. [60], who worked at 3.2 wt.%. These authors also showed that, under these conditions, copper yield reached 80% after approximately 300 h and that leaching was significantly activated at higher temperatures (65–75 °C). Khoshkhoo et al. [61] obtained a copper recovery of 50% after only 144 h (pH = 1.4 and Eh = 710 mV v/s SHE), though the temperature was much higher (T = 80 °C).

Hydrogen peroxide can behave as an oxidizing and reducing agent. Systems with a redox potential $E_0 < -1.80$ V at pH 0 cannot be oxidized by hydrogen peroxide; systems with a redox potential $E_0 > -0.66$ V at this pH cannot be reduced by hydrogen peroxide [48].

For Bockris and Oldfield [62], the measured potential is not a function of the hydrogen peroxide activity (αH_2O_2), as suggested by Nernst Equation (17):

$$E\ (V) = 1.763 + 0.0295 \times \log(\alpha H_2O_2) - 0.059 \times pH, \quad (17)$$

but, as shown in Equation (18), it depends on pH:

$$E\ (V) = 0.835 - 0.059 \times pH, \quad (18)$$

And it is valid in the pH range of 0 to 13.5, determined in the absence of dissolved copper and iron ions as well as organic ligands.

The decomposition of hydrogen peroxide is highly exothermic and takes place in the presence of small amounts of catalyst, even in aqueous solutions. The decomposition can be both homogeneously catalyzed by dissolved ions (especially iron, copper, manganese, and chromium) and heterogeneously by suspended oxides and hydroxides (e.g., from manganese, iron, copper, palladium, or mercury) and by metals such as platinum, osmium, and silver [48]. The heat of formation and decomposition of hydrogen peroxide is represented by Equations (19)–(22):

$$H_{2(g)} + O_{2(g)} \rightarrow H_2O_{2(g)},\ \Delta G = -136.2\ kJ/mol, \quad (19)$$

$$H_{2(g)} + O_{2(g)} \rightarrow H_2O_{2(l)},\ \Delta G = -187.9\ kJ/mol, \quad (20)$$

$$H_2O_{2(g)} \rightarrow H_2O_{(g)} + \frac{1}{2}O_{2(g)},\ \Delta G = -105.8\ kJ/mol, \quad (21)$$

$$H_2O_{2(l)} \rightarrow H_2O_{(l)} + \frac{1}{2}O_{2(g)},\ \Delta G = -98.3\ kJ/mol, \quad (22)$$

The temperature of the hydrogen peroxide solution is an important variable, as the rate of decomposition is doubled roughly every 10 °C increase [63].

The catalytic decomposition of hydrogen peroxide was observed in the H_2SO_4-H_2O_2 system but with less intensity than in an HCl-H_2O_2 system. The hydrogen peroxide decomposed spontaneously with the evolution of oxygen gas, a process more evident in the

presence of Fe(III) ions generated by the same dissolution process, and acted as a catalyst for peroxide decomposition.

2.4. Kinetic Aspects

The higher the stirring rate, the faster the acceleration of the H_2O_2, which makes more of the O_2 molecules generated on the surface of $CuFeS_2$ be absorbed and prevents their absorption on the surface of chalcopyrite. As a result, the dissolution rate decreases significantly [51]. On the other hand, the chalcopyrite dissolution reaction rate, using H_2O_2 as an oxidant, is highly dependent on temperature [26,41]. Thus, increasing the temperature leads to an increase in the reaction rate. In general, a twofold increase in reaction rates is reported to occur for every 10 °C increase in temperature [41]. In another investigation, increasing the temperature from 70 °C to 90 °C boosted the leaching efficiency from 28% to 70% after 2 h in sulfate medium [26]. The effect of temperature can be quantified by measuring the activation energies at high and low temperatures, respectively. Based on published data, the activation energy during the initial stages of the reaction was calculated to be 48 kJ/mol at low temperature and 20 kJ/mol at high temperature [64].

Activation energy values obtained from kinetic studies conducted on the leaching of chalcopyrite with hydrogen peroxide in acidic media cover a wide range. For example, Antonijević and Bogdanović [38] showed that the oxidation kinetics of chalcopyrite follows a shrinking core model with the surface chemical reaction as a rate-controlling step; also, an activation energy of 60 kJ/mol was determined. Mahajan et al. [39] reported that the activation energy of the chalcopyrite leaching process was 30 kJ/mol while the leaching reaction follows the surface reaction controlled model. According to Adebayo et al. [65], the dissolution kinetics follow a retractable core model controlled by the surface chemical reaction as a rate-determining step, while an activation energy value of 39 kJ/mol was calculated. Sokić et al. [66] reported that the kinetic data for copper leaching are in strong agreement with the diffusion-controlled model, while the calculated activation energy value was 80 kJ/mol. Hu et al. [43] examined the kinetics of the copper extraction process in an aqueous solution of $[Hmim]HSO_4$ with H_2O_2 as the oxidizing agent and found out that the copper leaching process was controlled by a chemical reaction with an activation energy of 52.06 kJ/mol and sulfur formation as the main leaching product located near the unleached chalcopyrite. Ahn et al. [44] calculated the activation energy to be 39.9 kJ/mol and indicated that the rate-determining step was the surface chemical reaction.

Table 1 presents the limiting stage of chalcopyrite leaching with H_2O_2 according to different experimental conditions. Factors such as the temperature, reagent concentration, and leaching time affect the activation energy (E_a) and limiting stage, which can occur by chemical reaction or diffusion.

Table 1. Chalcopyrite leaching mechanism with H_2O_2 in different media.

Sample Type	Temperature (°C)	System H_2O_2-H_2SO_4	Leaching Time (h)	E_a (kJ/mol)	Limiting Stage	References
Concentrate 32% Cu, 100–300 µm	30−50	5.9 M [H_2O_2] + 0.1 M [H_2SO_4].	2	39	Chemical reaction	[65]
Low grade ore 0.58% Cu 0–5 mm	25−50	2 M [H_2O_2] + 2 M [H_2SO_4].	3	60	Chemical reaction	[38]
Concentrate 27% Cu +75–37 µm	25−45	1 M [H_2O_2] + 1.5 M [H_2SO_4].	4	80	Diffusion	[66]
Concentrate 25% Cu +0–75 µm	30−60	3 M [H_2O_2] + 3 M [H_2SO_4].	2	38.9	Diffusion	[46]

An increase in the concentration of H_2O_2 in the leaching medium can decrease the activation energy value since the hydrogen peroxide acts as a powerful oxidizing agent, facilitating chemical reactions that dissolve the compounds contained in the ore. This action improves the kinetics of leaching by reducing the energy barrier necessary for the reaction to occur. However, the dynamic decomposition of hydrogen peroxide is observed to take place when its concentration is relatively elevated and the temperature is high (>50 °C). In practice, both facts tend to exclude leaching conditions with high H_2O_2 concentrations and temperature.

Petrović et al. [46] discuss the effect of adding leachant (H_2O_2-H_2SO_4) in time periods versus a single addition at the beginning of the process, indicating that the addition of leachant (H_2O_2-H_2SO_4) in portions does not necessarily mean that more metal will be extracted, as the copper extraction was 10% lower (30% Cu) when the leachant was added in portions, as compared to the single addition at the start (41% Cu). On the other hand, Wu et al. [67] revealed that periodic addition of H_2O_2 provided sufficient oxidant for oxidative leaching of chalcopyrite in methanesulfonic acid solution, which contributed to the consumption of the reducing reagent. Another study on copper slag leaching [68] showed that the leachant should be continuously added to the leaching suspension instead of only once at the beginning of the leaching experiment. The inconsistency among the authors might be explained by the different experimental conditions, types of ores, reagent concentrations, or even the specific nature of the leaching systems studied.

2.5. Safety Aspects for Hydrogen Peroxide

The explosion hazard of pure solutions of highly concentrated hydrogen peroxide has been examined through different methods, but the sometimes contradictory results are hard to interpret in a consistent manner. The results are mainly influenced by the assay conditions rather than by the hydrogen peroxide concentrations. For example, 90.7 wt.% of hydrogen peroxide in a tube with an internal diameter of 2.67 cm (1.05 in.) failed to explode after the detonation impact of a tetryl booster, whereas the explosion did occur in a tube with an internal diameter of 4.09 cm (1.61 in.). Similarly, 86 wt.% hydrogen peroxide in a 4.09 cm—internal diameter tube exploded by raising the temperature above 50 °C (122 °F). The decisive factors for the explosion of pure aqueous hydrogen peroxide seem to be the level of occlusion, insulation, and detonation energy [48].

2.6. General Aspects of the Effect of Hydrogen Peroxide on Chalcopyrite Leaching

Chalcopyrite leaching is influenced by multiple factors, including operating conditions such as temperature, pH, agitation, and solid/liquid ratio (summarized in Table 2). Other important factors also play a role, such as the galvanic effect of pyrite, the presence of additives, chelating agents, oxygen availability, chlorides, etc.

The efficiency of oxidative leaching using H_2O_2 is influenced by the solid-liquid ratio. For better results, it is recommended to use a diluted concentration, such as a 1:100 ratio, since more concentrated ratios like 1:50 or 1:19 can decrease the leaching efficiency.

Agitation also plays an important role, as it accelerates the decomposition of H_2O_2, reducing concentration and, consequently, the leaching efficiency.

Finally, temperature and pH affect the stability of H_2O_2. Higher temperatures can improve copper extraction but also increase hydrogen peroxide decomposition. Additionally, in acidic environments with high concentrations of H_2SO_4, hydrogen peroxide decomposes more rapidly, but these conditions also favor greater copper recovery. The presence of iron and copper in solution and mineral particles can catalyze hydrogen peroxide decomposition, but this can be countered by adding organic solvents that reduce this effect.

Table 2. Summary of factors affecting oxidative leaching.

Variables	Effect on H_2O_2	Alternatives to Counteract the Negative Effect	Reference
Solid/ liquid ratio	Sufficient/insufficient hydrogen peroxide concentration.	Better extractions are obtained at diluted solid/liquid concentrations of 1:100. Unfavorable effects are seen at ratios of 1:50 or 1:10.	[46,52,67,69]
Stirring	Accelerates hydrogen peroxide degradation. Then, the concentration of hydrogen peroxide decreases due to its decomposition.	Work in the range of 0–600 rpm.	[46,65,69]
Temperature	It affects the stability of H_2O_2 which is consumed in the reaction and decomposes and influences the oxidation rate of chalcopyrite mainly in the initial leaching stage.	Higher temperatures result in higher copper extraction; however, this is a very relative concept.	[44,46]
pH	Higher concentrations of H_2SO_4 promotes the intensive decomposition of H_2O_2 in acidic pH ranges.	Higher concentrations of H_2SO_4, allow for higher copper extractions.	[46]
Iron or copper in solution and solid mineral particles	Catalytic decomposition	Lower kinetics caused by decomposition; could be counteracted by the addition of organic solvents.	[46]

3. Use of Hydrogen Peroxide with Novel Leachants

3.1. Chalcopyrite Leaching in the H_2O_2 System-Organic

3.1.1. Effect of Organic Liquids-H_2O_2 on Chalcopyrite Leaching

The combination of non-polar organic solvents with hydrogen peroxide has been proved to be effective for the leaching of chalcopyrite [39,70,71]. On the other hand, the addition of organic ligands such as ethylenediaminetetraacetic acid (EDTA) or oxalic acid delays, but does not prevent, the breaking down of H_2O_2 [54].

In the mixed potential range of 0.55–0.75 V, the presence of ethylene glycol is not observed to increase the oxidation of chalcopyrite. However, the adsorption of ethylene glycol (EG) on the sulfide surface is a sufficient obstacle to hinder the dismutation of hydrogen peroxide, this being the main cause of its decomposition in EG-free acidic solutions. At the same time, the decrease in interfacial tension favors the contact of chalcopyrite with the solution. Finally, the formation of similar products on the chalcopyrite surface suggests that organic additives do not alter the dissolution mechanism [52].

Analyses by electrochemical impedance spectroscopy reported in Liu et al. [72] show that acid leaching of chalcopyrite in the presence of H_2O_2 generates a passivating layer thickness that increases over time. Petrović et al. [46] confirmed this by XRD (X-ray diffraction) and SEM-EDS (scanning electron microscopy with energy-dispersive detector) analysis. However, in an H_2O_2-ethylene glycol system, the thickness of the passivating layer is reduced. In an H_2O_2-Tween80 (polysorbate) system, the growth of the layer is localized and controlled, which could improve the leaching efficiency under certain conditions [72].

3.1.2. Kinetic Aspects in Systems H_2O_2-Organic

Table 3 compares the mechanisms of chalcopyrite leaching with hydrogen peroxide in different organic systems, highlighting the influence of experimental conditions, such as

temperature, reagents involved, and leaching time, on the limiting stages of the process and activation energies (E_a).

Table 3. Chalcopyrite leaching mechanism with H_2O_2 and novel leachants.

Temperature (°C)	System H_2O_2-Leachant	Leaching Time (h)	E_a (kJ/mol)	Limiting Stage	References
15−40	3 M [H_2O_2] + 0.6 M [H_2SO_4] + 5.7 M [CH_3OH]	5	24.27	Chemical reaction	[71]
20−50	1 M [H_2O_2] + 2 M [H_2SO_4] + 0.5 M [C_3H_8O] + 0.5 M [C_3H_8O]	3	60.68	Diffusion	[73]
30−40	30% (*v*/*v*) [H_2O_2] + 40% (*w*/*v*) [Bmim][HSO_4]*.	3	49.61	Chemical reaction	[51]

[Bmim][HSO_4]* is an ionic liquid 1-butyl-3-methyl-imidazolium hydrogen sulfate.

Systems where the limiting step is a chemical reaction tend to require lower activation energy. In contrast, when the limiting step is diffusion, as in propanol systems, the activation energy is higher, suggesting greater resistance to mass transport.

As described in point 2 above, it is established that chalcopyrite leaching can be affected by the formation of passivating layers, such as intermediate oxides or sulfides. The systems involving ionic liquids or adjuvants described in Table 3 would help reduce this effect, improving the exposure of the reactive mineral.

3.1.3. Case Studies H_2O_2 System-Organic

Mahajan et al. [39] studied the leaching of chalcopyrite in organic-oxidizing media in a peroxide–glycol system by leaching previously crushed copper ore using a leaching solution consisting of sulfuric acid, ethylene glycol, and hydrogen peroxide, all at room temperature. The objective is to analyze the effect of H_2O_2 and ethylene glycol on copper extraction and the effect of organic compounds on peroxide decomposition.

In the first series of leaching experiments, the impact of ethylene glycol on the dissolution of chalcopyrite was investigated. Copper extraction was approximately 15% without glycol, in whose presence copper extraction is significantly increased. The effect of hydrogen peroxide concentration on chalcopyrite dissolution was also analyzed, observing an increase from 15% to 70% after 4 h of leaching with additions of H_2O_2 from 0.048 M to 0.4 M. Besides the increase in copper extraction, the presence of ethylene glycol proved to be positive in the hydrogen peroxide decomposition process. The decomposition of hydrogen peroxide was observed to accelerate with temperature and the presence of ferric and cupric ions. Furthermore, the same study determined that in the absence of ethylene glycol, an essentially complete decomposition of hydrogen peroxide was achieved after 2 h of leaching. However, the presence of ethylene glycol significantly inhibited the process, achieving only about 25% decomposition of the initial peroxide after 4 h of leaching with 8 mL/L glycol.

The study carried out by Ruiz-Sánchez and Lapidus [70] discovered that the kinetics is a first-order function of H_2O_2 concentration and does not depend on H^+ concentration, though the decomposition of H_2O_2 increases slightly at high pH. Likewise, it was observed that at lower H_2O_2 concentrations, copper extraction decreases. A first test without ethylene glycol revealed a 99% consumption of H_2O_2 in 24 h in response to the catalytic effect of Fe^{2+}, Fe^{3+}, and Cu^{2+} ions (Fenton reagents). The redox potential increases for a short while, then it decreases, and finally stabilizes, which correlates directly with the H_2O_2

decrease, thus limiting copper extraction. A second leaching with ethylene glycol shows a consumption of only 16% of H_2O_2 in 24 h, indicating that in EG-bearing solutions, no hydroxyl radicals are detected, which suggests that ethylene glycol inhibits the Fenton-type reactions that decompose the peroxide. In turn, the low H_2O_2 consumption allows for continuous dissolution of chalcopyrite and a steady increase in redox potential, suggesting that the solution is becoming more oxidizing as copper and iron are extracted.

Based on these studies, Ruiz-Sánchez and Lapidus [74] studied the effect of different organic additives on chalcopyrite leaching in an oxidizing medium with H_2O_2. They also analyzed the effect of organic additives on the decomposition of hydrogen peroxide. To that end, they performed leaching tests using copper concentrates (23.68% Cu and 29.45% Fe) with a chalcopyrite concentration of 69%. The leaching experiments were carried out in 500 mL jacketed reactors at 25 °C and a stirring speed of 400 rpm. The leaching solution consisted of 0.007 M H_2SO_4, 1 M H_2O_2 and 0.1 M of the organic additive, of which methanol, ethanol, ethylene glycol, isopropanol, cyclohexanol, and acetone were studied.

The results obtained show that, except for ethanol and acetone, the copper dissolution kinetics behave in the same way during the first 60 min, in the presence or absence of the organic additives. Although the H_2O_2 concentration decreases with time, no dependence on copper dissolution kinetics is shown, suggesting that, despite the first-order kinetics with respect to hydrogen peroxide, copper extraction does not vary significantly with the different additives.

Ahn et al. [44] found out that H_2O_2 is consumed in the reaction and decomposes at high temperatures. If periodically added, H_2O_2 can improve extraction and maintain the optimal oxidant. An addition of 1.5% H_2O_2 achieved higher copper extraction (75%) than an addition of 0.6% H_2O_2, copper extraction of 69%. When H_2O_2 was not added, the extraction of copper in 96 h amounted to 60%, close to the result with the 0.6% addition of H_2O_2. However, the kinetics is faster with the addition of hydrogen peroxide. Periodic addition of H_2O_2 increases the extraction by direct oxidation of the ore and oxidation of the ferrous iron leached into ferric iron. H_2O_2 lower than 0.9% extracts less copper due to insufficient oxidant needed by chalcopyrite leaching. H_2O_2 above 0.9% extracts less copper, which might be caused by the ferric passivation mechanism (ferric is hydrolyzed under highly oxidizing, thermally acidic conditions, which produces iron hydroxide, oxyhydroxides, and jarosites, so the redox potential of solutions above 700 mV vs. Ag/AgCl with hydrogen peroxide at >0.9% is a suitable condition for ferric hydrolysis and passivation of chalcopyrite); another reason may be passivation on the surface (due to excessive use of oxygen-containing H_2O_2, which may be adsorbed on the surface and function as a reaction barrier, hindering mass transport; thus, to avoid passivation, an addition of $H_2O_2 < 1.5\%$ is used).

In their study, Ruiz-Sánchez et al. [54] used organic ligands such as oxalic acid and EDTA, which promoted the formation of metal complexes that help avoid the decomposition of hydrogen peroxide resulting from Fenton reactions. Thus, the extraction percentages of copper and iron are increased, and a PLS resulting from the second stage with a high concentration of copper and iron is obtained, which makes it suitable for direct electrodeposition without the need to apply solvent extraction. In the first stage, the H_2O_2 concentration decreases, while the redox potential of the solution reaches a stability of 0.75 V *v/s* SHE, indicating that H_2O_2 is consumed in the oxidation reactions of the ore and contributes significantly to maintaining the redox potential. Thus, copper and iron extraction of 49 and 29.5%, respectively, are obtained. In the second stage, the addition of hydrogen peroxide is justified by the need to oxidize the unreacted chalcopyrite still present in the first-stage solid residue.

Price [75] indicates that H_2O_2 helps maintain an oxidizing environment that facilitates copper leaching, avoiding problems associated with excessive ferric iron concentrations that may lead to chalcopyrite passivation.

In their study, Michałek et al. [73] found out that the absence of H_2O_2 means very slow kinetics and copper extractions of 2.3%. Increasing H_2O_2 concentrations from 0.5 to 2 M yields significant increases in both kinetic coefficients k (from 5×10^{-4} to 12×10^{-4} min^{-1}, respectively) as well as in maximum extractions (from 37% to 54%, respectively). However, the use of a concentration of CH_2O_2 = 2.0 M in the leaching medium causes foam to be formed in the reactant solution due to exothermic decomposition of H_2O_2 with subsequent release of O_2. The positive influence of isopropanol (IPA) is attributed to its ability to protect H_2O_2 from decomposition by free radical reactions. The iron compounds (Fe_2O_3, Fe_3O_4, and FeS_2) present in chalcopyrite are more stable (less leachable) during the leaching process when isopropanol is added to the solution, probably due to the stabilizing role of isopropanol for H_2O_2.

Moazzami et al. [51] observed that the leaching efficiency of $CuFeS_2$ increases as the concentration of H_2O_2 increases. However, after reaching its peak, the efficiency decreases at higher H_2O_2 concentrations. The reason may be that the decomposition of H_2O_2 is directly related to its concentration. At higher H_2O_2 concentrations, its decomposition rate also increases. H_2O_2 decomposition is accelerated by increasing the stirring speed and temperature. Chalcopyrite dissolution rate slows down as a result of lower H_2O_2 concentration in the solution at higher temperatures. The dissolution of $CuFeS_2$ increased when the concentration of [Bmim][HSO_4] increased, which may be associated with higher dissolved oxygen concentrations and the higher solution acidity in the presence of [Bmim][HSO_4].

Table 4 presents a detailed summary of the optimum conditions for the extraction of copper from chalcopyrite using hydrogen peroxide as the oxidizing agent in different leaching systems. These systems vary according to the reagents used, concentrations, temperatures, and other experimental parameters.

Table 4. Optimal conditions for copper extraction from chalcopyrite using H_2O_2 in different organic media.

N°	Feeding Conditions	Optimal Leaching Conditions	Copper Extraction	Reference
1	Chalcopyrite: 65%. Cu: 25%. Fe: 32% Fe: 32% P80: 37–49 µm Concentration: 3.75 g/L	[H_2O_2]: 1 M [H_2SO_4]: 0.7 M [Ethylene glycol]: 3.5 M T: 20 °C Stirring: 600 rpm time: 24 h	Cu: 90%	[70]
2	Chalcopyrite: 89.5%. Cu: 28.8% Cu: 28.8% Fe: 26.4% Fe: 26.4% Fe: P80: 40 µm Concentration: 10 g/L	[H_2O_2]: 0.3 M [Metasulfonic acid]: 30 g/L T: 75 °C time: 96 h	Cu: 99%	[44]
3	Chalcopyrite: 60.1%. Cu: 22.4%. Fe: 28.2% P80: 63 µm Concentration: 50 g/L	First Stage: [H_2O_2] = 1 M [H_2SO_4] = 0.007 M [Ethylene glycol] = 0.1 M [Oxalic acid] = 0.4 M Second Stage: [H_2O_2] = 2 M [H_2SO_4] = 0.007 M [Ethylene glycol] = 0.1 M [EDTA] = 0.4 M T: 26 °C Stirring: 400 rpm time 24 h.	Cu: 90%	[54]

Table 4. *Cont.*

N°	Feeding Conditions	Optimal Leaching Conditions	Copper Extraction	Reference
4	Chalcopyrite: 84.6%. Cu: 28.8% Fe: 26.4% P80: 40 µm Concentration: 10 g/L	$[H_2O_2]$: 0.9 M [Metasulfonic acid]: 75 g/L T: 65 °C time: 96 h	Cu: 94%	[75]
5	Chalcopyrite: 94.5%. Cu: 31.35% Cu: 31.35% Fe: 30.01% P80: 3.55 µm Concentration: 6 g/L	$[H_2O_2]$: 1 M $[H_2SO_4]$: 1.75 M [2-propanol]: 30% *v*/*v* T: 40 °C Stirring: 100 rpm time: 5 h	Cu: 75%	[76]
6	Chalcopyrite: 94.5%. Cu: 31.35% Fe: 30.01% P80: 3.55 µm Concentration: 6 g/L	$[H_2O_2]$: 1 M $[H_2SO_4]$: 1.75 M [Ethanol]: 30% *v*/*v* T: 40 °C Stirring: 100 rpm time: 5 h	Cu: 53%	[76]
7	Cu: 31.67% Fe: 34.55%. P80: 5–100 µm Concentration: 10 g/L	$[H_2O_2]$: 1 M $[H_2SO_4]$: 0.5 M [Isopropanol]: 2 M T: 50 °C Stirring: 400 rpm time: 3 h	Cu: 70%	[73]
8	Chalcopyrite Cu: 29% Fe: 28% P80: 37–100 µm Concentration: 10 g/L	$[H_2O_2]$: 30% (*v*/*v*) [Bmim][HSO_4]: 40% (*w*/*v*) T: 40 °C Stirring: 300 rpm time: 3 h	Cu: 90.32%	[51]

3.2. Chalcopyrite Leaching in H_2O_2 System-Inorganic Salts

The chemical mechanism leading to leaching in this system can be described from reactions (23)–(29) [57]:

$$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O, \quad (23)$$

$$2CuFeS_2 + 10H^+ + 5H_2O_2 \rightarrow 2Cu^{2+} + 2Fe^{3+} + 4S + 10H_2O, \quad (24)$$

$$2CuFeS_2 + 2H^+ + 17H_2O_2 \rightarrow 2Cu^{2+} + 2Fe^{3+} + 2S + 18H_2O, \quad (25)$$

$$CuFeS_2 + 3CuCl^+ + Cl^- \rightarrow 4CuCl + Fe^{2+} + 2S^0, \quad (26)$$

$$I_2 + I^- = I_3^-, \quad (27)$$

$$CuFeS_2 + 2I_3^- = Cu^{2+} + Fe^{2+} + 2S^0 + 6I^-, \quad (28)$$

$$CuFeS_2 + 2I_2 = Cu^{2+} + Fe^{2+} + 2S^0 + 4I^-, \quad (29)$$

Upon reaction of hydrogen peroxide with iodide ion (I^-) in acidic media, three mechanisms occur that describe the formation of different iodine species. The reaction of hydrogen peroxide with iodide triggers a series of reactions that generate new species such as I_2 and I_3, as well as the generation of intermediates such as HIO, OH, and OOH. The

general equations for the decomposition of peroxide with iodide or iodate are given by Equations (30) and (31):

$$H_2O_2 + 2I^- + 2H^+ \rightarrow I_2 + 2H_2O,\ E^0 = 1.141\ V, \quad (30)$$

$$5H_2O_2 + 2IO_2{}^- + 2H^+ \rightarrow I_2 + 2H_2O,\ E^0 = 2.083\ V, \quad (31)$$

Total transformation of iodide into iodine is achieved with high acid concentrations; however, the concentration of iodide ions will always remain subject to the equilibrium of Reaction (32):

$$I_2 + I^- \rightarrow I_3{}^-,\ E^0 = 0.082\ V, \quad (32)$$

Granata et al. [77] describes the chalcopyrite leaching mechanism in iodide-peroxide medium as a two-step cyclic process, where ferric ions oxidize iodide into iodine, while iodine generates the oxidation of chalcopyrite, according to reactions (33) and (34):

$$2I^- + 2Fe^{3+} \rightarrow I_2 + 2Fe^{2+},\ E^0 = 0.074\ V, \quad (33)$$

$$CuFeS_2 + 2H_2SO_4 + 2I_2 \rightarrow CuSO_4 + FeSO_4 + 4HI + 2S^0,\ E^0 = 0.164\ V, \quad (34)$$

Case Studies H_2O_2 System-Inorganic Salts

Moraga et al. [78] studied chalcopyrite leaching in saline media, using inorganic iodide species in combination with hydrogen peroxide. Leaching tests of copper concentrates were conducted in stirred reactors at room temperature, using leaching solutions composed of sodium chloride (NaCl), sodium iodate ($NaIO_3$), potassium iodide (KI), sulfuric acid, and hydrogen peroxide, as shown in Table 5.

Table 5. Experiment design [78].

	Low Level (M)	Low Level (g/L)	High Level (M)	High Level (g/L)
NaCl	0.00	0.00	1.54	90.00
$NaIO_3$	0.00	0.00	0.01	2.00
KI	0.00	0.00	0.01	2.30
H_2O_2	0.09	3.00	0.44	15.00
H_2SO_4	0.05	5.30	0.27	26.30

The results exhibit that, in leaching experiments without hydrogen peroxide, low extraction percentages were obtained, lower than 10% after six hours, as shown in Figure 1. The use of reagents such as NaCl, KI, and $NaIO_3$, together with a higher acid concentration, slightly increased copper extraction, going from 4.2% to 9% after six hours of leaching. However, in tests with leaching solutions without peroxide, a steady state was not achieved even after treatment for 96 h.

After adding hydrogen peroxide to the leaching solution, a significant increase in copper extraction was perceived, going from 9.3% to 17.3% in solutions A and C, respectively. In a solution containing iodine and chlorine species, in addition to a high acid concentration, the impact of peroxide was significant, increasing the extraction from 19.4% (solution B) to 60.2% (solution D) after 96 h of leaching.

Taboada et al. [57] state that, in order of importance, the most favorable species for chalcopyrite leaching are H_2O_2, H_2SO_4, NaCl, and KI. Low concentrations of H_2O_2 are seen to have a negligible effect on Cu concentration. On the other hand, the authors found that tests with high peroxide contents in the leaching solution help obtain adequate PLS levels. On average, the KI—selected to avoid direct losses to the environment—had less effect on the process due to its low concentration.

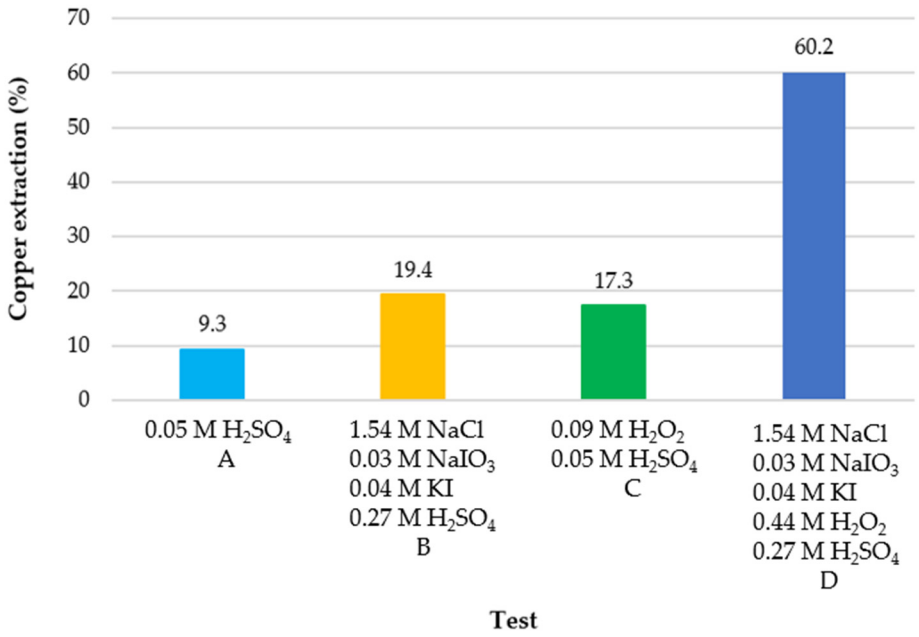

Figure 1. Effect of hydrogen peroxide on copper extraction. Leaching solutions: Test A, 0.05 M H_2SO_4, Test B, 1.54 M NaCl, 0.03 M $NaIO_3$, 0.04 M KI, 0.27 M H_2SO_4, Test C, 0.09 M H_2O_2, 0.05 M H_2SO_4, Test D, 1.54 M NaCl, 0.03 M $NaIO_3$, 0.04 M KI, 0.44 M H_2O_2, 0.27 M H_2SO_4. Modified from Moraga et al. [78].

According to Zandevakili and Akhondi [41], copper recovery under microwave conditions (75.43%) is higher than with conventional leaching (42.5%) in the same temperature range. The improvement appears to occur as a result of a temperature gradient and overheating at the solid/liquid interface. Table 6 presents case studies analyzing the effectiveness of the leaching system based on H_2O_2 and inorganic salts for copper extraction from chalcopyrite under different experimental conditions.

Table 6. Case studies H_2O_2 system-inorganic salts.

Feeding Material Conditions	Leaching	Extraction	Reference
Chalcopyrite: 63.7%. Pyrite: 16.4%. Cu: 29.79% P80: 61 µm Concentration: 100 g/L	[H_2O_2]: 0.44 M [H_2SO_4]: 0.268 M [NaCl]: 1.54 M [KI]: 3.13 mM T: 20 °C Stirring: 600 rpm time: 45 min	Cu: 27%	[57]
Chalcopyrite: 60% Cu: 20.93% Fe: 31.22% P80: 75 µm Concentration: 12.5 g/L	[H_2O_2]: 0.25 M [H_2SO_4]: 0.5 M [NaCl]: 2 M T: 90 °C Stirring: 300 rpm time: 3 h	Cu: 39.7%	[41]
Chalcopyrite: 60% Cu: 20.93% Fe: 31.22% P80: 75 µm Concentration: 12.5 g/L	[H_2O_2]: 0.25 M [H_2SO_4]: 0.5 M [NaCl]: 2 M T: 90 °C Stirring: 300 rpm time: 3 h Applies microwave-assisted leaching.	Cu: 75.3%	[41]

3.3. Chalcopyrite Leaching in H_2O_2 System-Alkaline-Amino Acids

Case Studies H_2O_2 System-Alkaline-Amino Acid

Nurtazina et al. [79] demonstrated that amino acids such as glycine, betaine, and lysine can be applied as selective copper leaching agents in the process of hydrochemical oxidation of chalcopyrite at atmospheric pressure and under temperature ranges of 25–65 °C. The advantage offered by this method is its relative environmental friendliness and the increase in copper extraction efficiency as the experiment continues to be developed and the process temperature is higher. These authors indicate that, due mainly to the complexation of copper glycinates(II), copper betainates(II), and copper lysinates(II), the leaching of chalcopyrite with amino acids can be improved by adding hydrogen peroxide to the system as an oxidant. They observed also that the decomposition of hydrogen peroxide (in oxygen and water) occurs faster at high temperatures and low concentrations, while in alkaline solutions and low temperatures the decomposition is delayed. Table 7 presents case studies evaluating the use of the H_2O_2-based leaching system combined with alkaline media and amino acids for the extraction of copper from chalcopyrite.

Table 7. Case studies H_2O_2-alkaline-amino acid system [79].

Feeding Material	Leaching	Extraction
Chalcopyrite: 90% Cu: 35.57% Fe: 31.68% P80: 58 µm Concentration: 2 g/L	[H_2O_2]: 0.1 M [NaOH]: 0.1 M [Glycine]: 0.1 M T: 65 °C pH: 10 Stirring: 160 rpm time: 30 min	Cu: 7.76%
Chalcopyrite: 90% Cu: 35.57% Fe: 31.68 P80: 58 µm Concentration: 2 g/L	[H_2O_2]: 0.1 M [NaOH]: 0.1 M [Betaine]: 0.1 M T: 65 °C pH: 10 Stirring: 160 rpm time: 30 min	Cu: 6.26%
Chalcopyrite: 90% Cu: 35.57% Fe: 31.68 P80: 58 µm Concentration: 2 g/L	[H_2O_2]: 0.1 M [NaOH]: 0.1 M [Lysine]: 0.1 M T: 65 °C pH: 10 Stirring: 160 rpm time: 30 min	Cu: 2.40%

Low efficiency can be observed in copper extraction, reaching values below 10% under the conditions studied.

3.4. Leaching Kinetics in Systems with H_2O_2 and Novel Leachants

The main characteristic of heterogeneous reactions, such as chalcopyrite leaching, is their complexity and their occurrence in multiple stages. Table 8 shows the activation energy and limiting stage in the leaching of chalcopyrite with H_2O_2 in different media.

Table 8. Operational chalcopyrite leaching conditions using H_2O_2 in acid media.

Temperature (°C)	System H_2O_2-X	Leaching Time (h)	E_a (kJ/mol)	Limiting Stage	References
30–50	5.9 M [H_2O_2] + 0.1 M [H_2SO_4].	2	39.0	Chemical reaction	[65]
25–50	2 M [H_2O_2] + 2 M [H_2SO_4]	3	60.0	Chemical reaction	[38]
30–60	2 M [H_2O_2] + 0.5 M [HCl]	3	19.6	Diffusion	[80]
25–45	1 M [H_2O_2] + 1.5 M [H_2SO_4].	4	80.0	Diffusion	[66]
15–40	3 M [H_2O_2] + 0.6 M [H_2SO_4] + 5.7 M [CH_3OH]	5	24.3	Chemical reaction	[71]
30–60	3 M [H_2O_2] + 3 M [H_2SO_4]	2	38.9	Diffusion	[46]
20–50	1 M [H_2O_2]+ 2 M [H_2SO_4] + 0.5 M [C_3H_8O]	3	60.8	Diffusion	[73]
30–40	30% (v/v) [H_2O_2] + 40% (w/v) [Bmim][HSO_4]	3	49.6	Chemical reaction	[51]

4. Prospects and Challenges in the Use of Hydrogen Peroxide

Hydrogen peroxide has proved to be an efficient oxidant in copper extraction; however, its implementation at an industrial scale must overcome several challenges that require innovative solutions. The main technical obstacle is its thermal instability and catalytic decomposition in the presence of ferric ions, translated into excessive reagent consumption. This situation is reflected in high operating costs, amplified by the need for specialized infrastructure, including oxidation-resistant equipment, accurate dosing systems, and rigorous safety protocols. Although only water and oxygen are produced by their final decomposition, their environmental footprint is mainly linked to the industrial production process, which involves high energy consumption. Technical challenges span even to the chemical complexity of the process, made evident by side reactions and difficulties in controlling concentrations, along with limitations in mineral selectivity and scale-up. Faced with these challenges, several optimization strategies have been developed and will be explored in the following sections, including methods to delay the decomposition of H_2O_2, alternative activation techniques, and hybrid approaches that seek to maximize their efficiency while minimizing their limitations.

4.1. H_2O_2 Decomposition Delay

Some alternatives to counteract the challenges of chalcopyrite leaching in the presence of H_2O_2 lie in the use of non-polar organic solvents contained in the leaching solution, which would act as stabilizing factors for the cuprous ions (the product from chalcopyrite leaching) or have a stabilizing effect for the oxidant (H_2O_2), respectively, resulting in higher process efficiency and a positive impact on the reaction rate [73]. The positive effect of polar organic additives has been attributed to cuprous ion or hydrogen peroxide stabilization [81].

Adding organic polar solvents [82] or organic ligands such as oxalate ion in the form of oxalic acid, citrate ion in the form of citric acid, or ethylenediaminetetraacetic acid [53,54] in the aqueous solution of hydrogen peroxide and sulfuric acid promotes the formation of copper and iron complexes that help delay, but not prevent, the decomposition of hydrogen peroxide.

4.2. Microwave Leaching in the Presence of H_2O_2

Microwave-assisted heating is a new processing technology normally used to recover copper from chalcopyrite by leaching. Copper recovery under microwave irradiation was far superior to the recovery by conventional leaching [41]. The effects of microwave heating on attaining better results from the leaching of complex copper sulfide concentrates probably refer to the creation of large thermal convection currents, which stirred the particle surface and swept off the formed sulfur layer. Ma et al. [83] demonstrated that microwave technology has great potential to improve leaching efficiency and reduce leaching time, while Zandevakili and Akhondi [41] showed higher copper recovery under microwave conditions (75.43%) than that of conventional leaching (42.5%) in the same temperature range. Behera et al. [84] investigated microwave-assisted leaching of Cu and Cr from a spent Cu–Cr catalyst. The optimum state was 900 W power, 2 min treatment time, 10% H_2O_2 (v/v), and 1 M sulfuric acid during microwave irradiation followed by leaching with a very low concentration of H_2SO_4 (1 wt.%), which was adequate for quantitative extraction of both metals from the spent catalyst phase. The XRD (X-ray diffraction) and EDAX (energy-dispersive X-ray spectroscopy) feature pattern of the residue samples resulted in optimum leaching conditions, which were further determined in the substantial extraction of copper (99.99%) and chromium (98.56%) during the spent catalyst phase.

Likewise, the elemental sulfur formed during the first stage of chalcopyrite leaching was observed to dissolve after being subjected to microwave treatment for 8 min, probably because of reaction (35) [85]:

$$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O, \quad (35)$$

The above observation could be attributed to the presence of a superheated layer near the periphery of the reactor and selective heating of the mineral particles [86]. In conventional leaching, the reaction product could cover the mineral surface. On the contrary, in microwave-assisted leaching, thermal currents created by the temperature gradient between liquid and solid could sweep the reaction product layer off the particle surface, reducing the diffusion-limiting effect [41,85].

The leaching efficiency, in turn, is maximized in the presence of H_2O_2; e.g., an H_2O_2 concentration of 0.25 M [41]. This could be explained by the fact that active hydroxyl radical (OH·) species could be generated from H_2O_2 under microwave-H_2O_2 conditions, as shown in Equation (10).

The reduction potential of OH· oxidation (2.8 eV) was higher than that of H_2O_2 (1.8 eV), which could benefit the destruction of metal-binding structures [87]. H_2O_2 had a negative effect on copper leaching efficiency at concentrations higher than 0.25 M. This fact could be associated with the consumption of OH· radicals, resulting in the production of the less reactive OH_2· radicals, as shown in Equations (36) and (37) [41]:

$$OH\cdot + H_2O_2 \rightarrow 2HO_2\cdot + H_2O, \quad (36)$$

$$2HO_2\cdot \rightarrow H_2O_2 + O_2, \quad (37)$$

This meant that excess H_2O_2 could inhibit the formation of OH· radicals, suppressing the oxidizing capacity of H_2O_2.

4.3. Photoleaching in the Presence of H_2O_2

Photoleaching has sparkled great interest in the extraction of copper from low grade ores such as chalcopyrite where the presence of H_2O_2 is essential as it contributes as (1) Precursor of reactive oxygen species acting as the main source of hydroxyl radicals

(HO^-) through the Fenton and photo-Fenton mechanisms, creating a highly oxidizing environment that favors the dissolution of the mineral; (2) indirect catalyst by interacting with Fe^{2+} released during ore dissolution, H_2O_2 catalyzes the Fenton reactions, accelerating the leaching process; (3) autocatalytic generation of the process due to the photogenerated electrons in the mineral conduction band that can catalyze additional H_2O_2 production; (4) modifier of the electrochemical potential of mineral slurry, optimizing the conditions for oxidative dissolution [49].

Advanced oxidation processes (AOP) are efficient methods to remove persistent organic pollutants in water through the actions of strongly oxidizing reactive oxygen species (ROS), such as sulfate (SO_4^{2-}) and hydroxyl radicals (OH). Oxidant is an important factor affecting functional ROS, and one of the most commonly used oxidants is H_2O_2 [88,89].

Chalcopyrite has a huge potential for advanced oxidation processes (AOP) driven by chemical energy; e.g., hydrogen peroxide as an oxidant at different positions on the surface of chalcopyrite shows that the original oxygen–oxygen (O–O) bond length in the H_2O_2 molecule is 1.471 Å. Upon adsorption at different points on the $CuFeS_2$ surface, this bond length undergoes slight variations: 1.482 Å at the Fe location, 1.478 Å at the Cu location, and 1.476 Å at the S location. The adsorption energies of H_2O_2 at these spots are −0.666 eV, −0.297 eV, and −0.324 eV, respectively. This suggests a moderate interaction between H_2O_2 and the $CuFeS_2$ surface, with a slight preference for the Fe site due to its more negative adsorption energy [90].

4.4. Mechanically Assisted Leaching

Mechanical leaching of chalcopyrite has emerged as an innovative approach to enhance leaching performance. Grinding media are incorporated into the leaching process to induce structural defects, reduce particle size, and facilitate the removal of passivating layers of sulfur and other unreactive compounds.

Recent studies have explored H_2O_2-assisted chalcopyrite leaching with millimeter-sized glass beads [91]. The researchers conducted experiments in a 6 L stirred reactor (556 rpm) using chalcopyrite concentrate (3% by mass relative to the suspension) and 1 mm glass beads. The operating conditions included a temperature of 42 °C, atmospheric pressure (1 atm), pH 3, an oxidation–reduction potential (Eh) of 700 mV, a glass bead-to-solid mass ratio of 12, and the addition of 1.5 moles of H_2O_2. After 120 h, the leached copper yield was 8% without glass beads, 27% when pre-grinding with glass beads was applied before leaching, and 70% when leaching was performed in the presence of glass beads. In the latter case, the yield increased to 80% after 200 h of leaching.

Dakkoune et al. [60] reported the investigation of a chalcopyrite leaching process where millimeter-sized glass beads were implemented and agitated in the leaching reactor to combine particle grinding, mechanical activation, and surface removal of reaction products. This research focuses on demonstrating the impact of the so-called attrition-leaching phenomenon on the leaching rate of a chalcopyrite concentrate and provides a first insight into the underlying mechanisms. To that effect, the copper leaching yield was compared for different configurations and under controlled chemical conditions (1 kg of glass beads and 84 g of chalcopyrite concentrate in 2.5 L of H_2SO_4-H_2O solution, pH = 1.3, H_2O_2 up to E_h = 700 mV vs. SHE, and T = 42 °C). Thus, they demonstrated that glass beads led to a remarkable improvement of the leaching rate under conditions where the particles were already passivated by simple leaching and even when large amounts of solid products (elemental sulfur and jarosite) were present. Dakkoune et al. [60] observed the remarkable positive effect that glass beads generate on chalcopyrite leaching, occurring mainly during the first 40–50 h, which could be attributed not only to the exfoliation of the passivating layers formed on the particles (the so-called friction effect) but also to the increase in the

specific surface area of the particles after grinding. In fact, it was long ago established that the smaller the particle size, the faster the leaching rate.

As to the likely use of glass beads in an industrial process, many questions remain to be answered. Although reuse of the beads does not seem to be a problem (more than 99% of the beads are recovered after each test), many parameters (e.g., the bead temperature, amount, and hardness, and the amount of concentrate) need to be studied and optimized. In addition, the additional energy cost required for bead agitation must be quantified. All these elements will help compare the economic and environmental aspects of a friction-assisted leaching process with other more developed options, such as chloride leaching or bioleaching [60].

4.5. Non-Oxidative/Reductive and Oxidative Leaching with H_2O_2

An innovative approach combining non-oxidizing and reductive mechanisms followed by oxidative leaching, using hydrogen peroxide as the oxidizing agent, has shown promising results. This process optimizes key factors such as temperature, pulp density, agitation speed, leaching time, acid concentration, and particle size, achieving copper recoveries of 82% through non-oxidative/oxidative leaching and 93% through a consecutive two-stage leaching process. These advances open new windows into improving chalcopyrite leaching efficiency and highlighting the potential of using H_2O_2 as an oxidizing agent in combination with reductive and non-oxidative approaches. Optimization of these processes may offer more efficient and sustainable solutions for copper extraction in the industry [55]. Figure 2 shows the extraction of metals (Cu and Fe) as a function of time (in minutes) during two different stages of a leaching process: (1) non-oxidative/reductive leaching (initial stage, before 240 min, as indicated by the green arrow); (2) oxidative leaching with H_2O_2 (subsequent stage, after 240 min, as indicated by the red arrow).

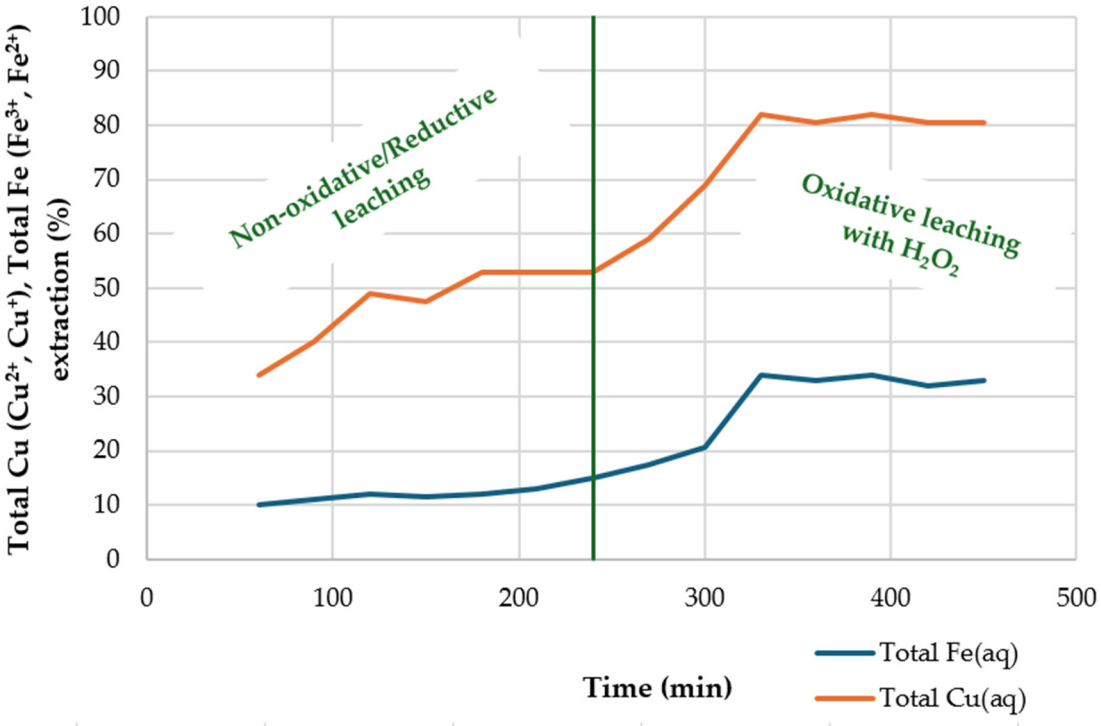

Figure 2. Behavior of copper and iron dissolution during chalcopyrite leaching with sulfuric acid at an initial acid concentration of 300 g/L, temperature of 80 °C, agitation speed of 600 rpm, pulp density of 2.5%, P80 of 82.5 µm, during four hours of leaching with sulfuric acid and then leaching with hydrogen peroxide at a temperature of 40 °C. Modified from Rasouli [55].

Ghomi et al. [81] applied novel leachants in the presence of H_2O_2 and noted that 2-propanol was the most efficient additive in terms of copper extraction when compared to ethanol, methanol, acetone, and ethylene glycol with a leaching liquor composed of H_2O_2 (2 M), H_2SO_4 (0.5 M), and the organic additive (4 M).

5. Conclusions

H_2O_2 stands out as an effective and environmentally friendly oxidizer due to the formation of non-toxic water and oxygen by-products. This characteristic makes it an attractive option over other more polluting oxidizing agents.

The use of H_2O_2 can improve chalcopyrite dissolution rates, particularly under low copper grade conditions, making this process suitable for deposits with lower ore concentrations.

Despite the number of studies reporting on the use of H_2O_2 as an oxidant in the leaching of chalcopyrite, experimental results may show differences in leaching rates and copper extraction efficiency. This variability can be attributed to several factors, such as the presence of accompanying minerals in the chalcopyrite, which can affect the process behavior. In addition, operating conditions, such as ore particle size, pH of the medium, agitation speed, temperature, H_2O_2 concentration, characteristics of the leaching medium, and leaching time, have a direct influence on results.

The chalcopyrite leaching process with hydrogen peroxide is typically carried out at moderate temperatures, between 40 °C and 80 °C. At higher temperatures, the leaching process may be more efficient, but there is also the risk of hydrogen peroxide decomposition and oxygen generation, which could decrease efficiency. At lower temperatures, the reaction may be slower. Therefore, the range of 60 °C to 70 °C is often considered optimal to achieve a good balance between reaction speed and hydrogen peroxide stability during chalcopyrite leaching.

The main technical limitation of H_2O_2 lies in its catalytic decomposition in the presence of metal ions, which raises operating costs. The stability of hydrogen peroxide can be improved by the use of stabilizers or by controlled addition strategies to prevent losses during the leaching process. Strategies such as the use of organic additives (e.g., ethylene glycol) have been shown to significantly reduce this decomposition and improve process efficiency.

The H_2O_2-organic, H_2O_2-organic salts, and H_2O_2-amino acid systems combining H_2O_2 with organic solvents, inorganic salts, or amino acids present a significant potential by optimizing leaching when reducing the formation of passivating layers on the chalcopyrite surface. However, more research is needed on the synergistic effects and optimization of these systems in terms of kinetics and thermodynamics.

Industrial-scale implementation demands the overcoming of barriers such as reagent stability, specialized reactor designs, and precise control of operating conditions. Future research should focus on the integration of these processes with emerging technologies such as microwave-assisted leaching or photoleaching that, in combination with H_2O_2, could further boost process efficiency and reduce leaching time.

From an environmental perspective, the use of H_2O_2 is favorable, since its decomposition produces oxygen and water, reducing the ecological impact compared to other oxidizing agents.

6. Recommendations

1. Detailed ore characterization: Thoroughly analyze the ore samples, considering their mineralogical composition, copper content, and presence of trace elements or impurities that may act as catalysts or inhibitors. This characterization will allow for a

better understanding of the chalcopyrite dissolution mechanisms and a more efficient optimization of the leaching process parameters.

2. Exploration of chemical combinations: Investigate combinations of H_2O_2 with stabilizing agents and other leaching agents to improve copper extraction efficiency and reduce operating costs. In particular, it is suggested to evaluate the interaction of H_2O_2 with organic solvents, amino acids, and complexing agents that can improve leaching rates, especially under low-grade copper conditions.
3. Pilot-scale trials: Conduct pilot-scale trials to determine the technical, economic, and environmental feasibility of using H_2O_2 in large-scale chalcopyrite leaching. These trials should consider process efficiency and performance, costs associated with the safe use and handling of H_2O_2, and environmental risks, such as by-product or waste generation.
4. Development of advanced kinetic models: Models capable of integrating the chemical complexity of the leaching system, including the reactions of H_2O_2 with the components of the mineral and the medium. These models must be able to accurately predict the leaching rates under different operating conditions and be useful on an industrial scale.
5. Evaluation of emerging technologies: Consider innovative technologies that can complement the leaching process with H_2O_2, such as microwave-assisted leaching to accelerate the breakdown of the crystalline structure of chalcopyrite; photoleaching, using light to enhance the reactivity of H_2O_2; and mechanical leaching, increasing the surface exposure of the mineral to the leaching agents. These technologies should be evaluated in combination with H_2O_2 to determine their potential, increase efficiency, and reduce leaching times.
6. Sustainability and H_2O_2 production: Investigate sustainable methods for the production of H_2O_2, using renewable energy sources such as solar or wind. This would help reduce the carbon footprint of the process and could make the use of H_2O_2 more cost-effective and environmentally friendly in the long term.
7. Environmental impact and waste management: Develop strategies to minimize the environmental impact of the process, including efficient management of by-products generated during H_2O_2 leaching. This should include recovery and reuse of chemical components whenever possible.

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