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A REVIEW OF CHALCOPYRITE LEACHING IN VARIOUS ACIDIC HYDROMETALLURGICAL SYSTEMS: MECHANISTIC AND TECHNOLOGICAL PERSPECTIVES

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ABSTRACT:

Chalcopyrite hydrometallurgy has been extensively examined, with particular focus on improving dissolution kinetics across a range of acidic environments, including chloride, aqueous sulphate and ammonia systems. In current copper-production practices, increasing priority is on establishing procedures that of treating low-grade sulphide ores that fall outside the applicability of conventional beneficiation routes such as crushing, grinding, and flotation. Furthermore, increasing research efforts are directed toward recuperation of copper from complex sulphide concentrates that are not amenable to pyrometallurgical routes. In most cases, extraction of copper from these materials is accomplished through leaching processes. As chalcopyrite ($CuFeS_2$) represents the most abundant copper sulphide mineral, substantial attention has been devoted to elucidating its leaching characteristics, as such insights are necessary for developing efficient extraction strategies for progressively lower-grade and more complex raw material. Moreover, overarching objective of these investigations is to elucidate kinetic parameters and underlying oxidation mechanisms of chalcopyrite when there are diverse oxidants (O_2, Fe^{3+}, H_2O_2, chloride ions, silver ions, pyrite, and others), while concurrently generating the fundamental data required for advancing copper extraction technologies that comply with increasingly rigorous technological, economic, and environmental constraints. This paper provides a comprehensive synthesis of the current state of knowledge on chalcopyrite leaching, with particular emphasis on the oxidation processes occurring in acidic sulphate and chloride systems.

KEYWORDS: Hydrometallurgy; chalcopyrite; leaching; dissolution; oxidation mechanism.

INTRODUCTION

Chalcopyrite ($CuFeS_2$), comprising approximately 34.5% Cu, 30.5% Fe, and 35.0% S, is a copper iron sulfide mineral characteristically formed through hypogene processes. Its genesis in deep, high-temperature and high-pressure magma derived or geothermal settings underlies its designation as main sulfide constituent (Yuan Li et al., 2019). As near-surface copper oxide reserves become progressively exhausted, chalcopyrite is projected to constitute an increasingly indispensable source within the future global copper supply chain. Strongly bonded Iron-sulphur and copper-sulphur linkages in chalcopyrite impart significant structural stability across diverse geochemical environments, accounting for both its widespread occurrence and its role as the primary global source of copper further to an important source of sulphur (Isabel and Hertel, 2022; Adeline et al,2025). An estimated 70% of global copper resources are hosted in chalcopyrite deposits. Their processing and copper recoveries are predominantly achieved through concentration followed by pyro metallurgical routes, comprising of a sequence of fragmentation, size reduction, froth flotation, metallurgical melting, smelting, and electrolytic metal recovery.

Hydrometallurgical techniques such as metal dissolution, liquid-liquid extraction, and electro winning have been systematically explored for their potential in copper extraction from ores. (Baba et al., 2012). Extended investigation of behaviour of chalcopyrite leaching emerges from rising pyro metallurgical costs, occurrence of deleterious elements, including bismuth and arsenic, in conjunction with the widespread distribution of low-quality ores (Hazen et al., 2019). Heap-based leaching of chalcopyrite is widely recognized as a technically feasible and efficient approach, enabling economically viable and sustainable processing of significant quantities of low-quality mineral resources (Hazen et al., 2019). This approach constitutes a strategically significant alternative, especially in regard to contemporary global copper mining, which increasingly targets deeper primary sulphide deposits, thereby augmenting accessibility of low-grade chalcopyrite amenable to leaching (Carmen et al.2017; Cheloni et al.,2024).

Chalcopyrite ($CuFeS_2$), the primary source of copper (Sandeep et al., 2015), is conventionally processed pyro metallurgical, resulting in substantial release of flue gases accompanied by hazardous sulphur species and heavy metal-laden emissions that threaten aquatic ecosystems (Huseyin et al., 2017; Bryn. 2013). Hydrometallurgical leaching has gained prominence as a more sustainable and cost-effective alternative, particularly for low-grade ores, and has been the subject of extensive research aimed at efficient copper recovery (Kulzira et al., 2025; Huseyin et al., 2017).

Chalcopyrite extraction via leaching is substantially impeded as an outcome of precipitation of an insoluble compound passivation layer on its surface (Sandpeed et al 2015; Victor et al., 2024). Although numerous approaches like increasing chloride concentration, elevating leaching temperatures, and employing strong oxidizing agents have been reviewed to enhance copper recovery (Moisés et al., 2023; Moazzami et al.,2024), the process continues to exhibit low efficiency, necessitating prolonged reaction times, high acid consumption, and elevated thermal conditions (Nyembwe et al., 2024; Veloso et al., 2016).Where there is no external oxidant, chalcopyrite subjected to hydrometallurgical extraction via sulphuric acid undergoes both non-oxidative and reductive pathways, yielding intermediate compounds including chalcocite which are thermodynamically more favourable for subsequent dissolution. The procedure of leaching concluded by utilizing hydrogen peroxide as an oxidizer , enabling transformation of cuprous ions within the mineral lattice into soluble cupric species and thereby enhancing overall copper recovery (Rasouli and Abtin, 2023)

Mechanical activation, when applied as a pre-treatment prior to leaching, has been widely recognized for its capacity to enhance mineral processing efficiency while concurrently minimizing energy usage and waste generation (Bryn. 2013; Hu et al., 2017, Wu et al., 2021; Bai et al., 2021; Tan et al., 2017). This process enables particle size optimization, lowers operational leaching temperature, induces lattice distortions, and promotes configuration of water-soluble compounds, collectively augmenting effectiveness of extraction of target elements. In contrast, conventional leaching approaches, which rely solely on mechanically comminute samples without chemical modification, generally exhibit lower extraction performance. Metal leaching assisted by mechanical pre-treatment from mineral matrices has been recognized as an environmentally advantageous approach, as it mitigates both acid consumption and formation of acidic effluents (Hu et al., 2017). Xu et al. (2017) demonstrated that leaching performance of B_2O_3 was substantially enhanced following mechanical activation, displaying an upward trend from 67.5% to 89.5%. Furthermore, Basturkcu et al. (2017) reported that mechanical activation markedly improved the leaching performance of lateritic nickel-bearing ores, significantly reducing the time required for Ni and Co extraction at 358 K when compared with ores subjected to conventional leaching without prior mechanical treatment. Mohammadabad et al. (2016) demonstrated that mechanical pre-treatment markedly facilitates chalcopyrite leaching and is recognized as a viable approach for optimizing metal recovery, concomitantly reducing energy requirements and processing expenditures.

Li et al. (2019) established that mechanical treatment chalcopyrite with $Fe_2(SO_4)_3 \cdot xH_2O$ produced readily soluble $CuSO_4$, achieving 98% copper recovery within 1.5 h, driven by both particle size reduction and phase transformation. Likewise, mechanically ground $NaClO_2$ decomposes into NaCl and $NaClO_3$ (Alvarado et al., 2025; Itabashi et al.,2015), with $NaClO_3$ serving as an oxidant to enhance chalcopyrite oxidation and subsequent Cu leaching under mild acidic conditions. Unlike $Fe_2(SO_4)_3 \cdot xH_2O$, traditionally employed for mechanical processing, which leads to development of secondary solid residues such as iron oxides during subsequent leaching, $NaClO_2$ offers a cleaner alternative devoid of such by-products. However, mechanistic principles governing co-grinding of $NaClO_2$ with chalcopyrite remain largely unexplored. This study therefore aims to demystify fundamental mechanisms of chalcopyrite leaching facilitated by novel lixiviates, addressing a critical knowledge gap that has not been systematically reviewed in prior research .

1. Chalcopyrite leaching enhanced by ferrous ions

Chalcopyrite dissolution in sulphate media has been evidenced to be significantly enhanced by concurrent presence of Cu^{2+} and Fe^{2+} ions. It's been proposed that chalcopyrite is initially reduced by ferrous ions to yield Cu_2S (Eq. 1). The Cu_2S formed is subsequently oxidized either by dissolved oxygen (Eq. 2) or by ferric ions (Eq. 3), with xxx representing the mole fraction of Cu_2S oxidized by dissolved oxygen relative to the total Cu_2S generated. The overall reaction is described by Eq. (4). It's been demonstrated that reduction of chalcopyrite to chalcocite, which represents rate-limiting step, is favoured under low solution redox potentials, whereas enhanced ferric ion concentrations accelerate oxygenation of the reduction products, thereby facilitating overall leaching process (Flores et al., 2025).

$$CuFeS_2 + 3Cu^{2+} + 3Fe^{2+} \rightarrow 2Cu_2S + 4Fe^{2+} \tag{1}$$

$$2xCu_2S + 8xH^+ + 2xO_2 \rightarrow 4xCu^{2+} + 2xS^O + 4xH_2O \tag{2}$$

$$2(1-x)Cu_2S + 8(1-x)Fe^{3+} \rightarrow 4(1-x)Cu^{2+} + 2(1-x)S^O + 8(1-x)Fe^{2+} \tag{3}$$

$$CuFeS_2 + 4(1-2x)Fe^{3+} + 8xH^+ + 2xO_2 \rightarrow Cu^{2+} + (5-8)Fe^{2+} + 2S^O + 4xH_20 \tag{4}$$

The ferrous-promoted mechanism of chalcopyrite dissolution obviates requirement for external reagents, thereby reducing process costs. Thermodynamically, solution's redox potential is shown (Eq. 5) must remain below a critical threshold (Eq. 6), that acts as an objective of ferrous and cupric ion concentrations, to enable Cu_2S formation, while simultaneously exceeding the Cu_2S oxidation potential (Eq. 7) to permit its subsequent oxidation, satisfying the condition ($E_{ox} < E_S < E_C$). At 298 K and 1 atm, the standard electrode potentials $E_o, E_c^o\ and\ E_{ox}^o$ were evaluated as 0.771 V, 0.681 V, and 0.561 V versus standard hydrogen electrode (SHE), respectively (Flores et al., 2025)

$$E_s = E_o + (RT/F)\ln(a_{Fe}^{3+}/a_{Fe}^{2+}) \qquad (5)$$

$$E_c = E_c^o + (RT/4F)\ln[(a_{Cu}^{3+})3/a_{Fe}^{2+})] \qquad (6)$$

$$E_{ox} = E_{ox}^o + (RT/4F)\ln[(a_{Cu}^{2+})^2 \qquad (7)$$

The validity of the proposed model was rigorously evaluated by examining leaching behaviour during acid-ferric sulphate-mediated chalcopyrite dissolution; with particular emphasize the impact of the preliminary Fe^{2+}/Fe^{3+} ratio and the solution's initial redox potential. In accordance with mechanistic predictions of Flores et al. (2025), copper recovery exhibited a pronounced enhancement approximately threefold when the $[Fe^{2+}]/[Fe^{3+}]$ ratio exceeded 10 (10–100) and the initial redox potential was maintained below 610 mV versus SHE (550 mV < E < 610 mV), underscoring critical role of redox conditions and ferrous ion concentration in governing dissolution kinetics of chalcopyrite.

Yang et al. (2018b) examined results of Cu^{2+}, Fe^{3+}, and Fe^{2+} ions behaviour of chalcopyrite during sulphuric acid leaching at 50 °C. The investigation employed four distinct solution compositions: a control without Cu^{2+}, 0.1 mol/L Cu^{2+} combined with 0.1 mol/L Fe^{3+}, 0.1 mol/L Cu^{2+} with 0.05 mol/L Fe^{3+} and 0.05 mol/L Fe^{2+}, and 0.1 mol/L Cu^{2+} with 0.1 mol/L Fe^{2+}, corresponding to initial redox capabilities of 730, 640, and 520 mV, respectively. The study demonstrated a redox potential shift and/or Fe^{3+}/Fe^{2+} ratio promoted enhanced copper extraction. Additionally, occurrence of iron ions facilitated chalcocite formation, while Raman spectroscopic assessment of leach residues revealed deposition of elemental sulphur on the chalcopyrite surface.

2. Silver-Enhanced Chalcopyrite leaching

Within the conceptual framework of ferrous-ion-assisted chalcopyrite leaching mechanism (Ghahremaninezhad et al., 2015), wherein stringent regulation of Oxidation–reduction potential is acknowledged as pivotal factor for process optimization, silver ions have been suggested to perform a catalytic influence on chalcopyrite dissolution. Conversion of chalcopyrite into Cu_2S through reduction is not exclusively mediated by Eq. (1) but may also proceed via Eq. (8), yielding H_2S. This hydrogen sulphide subsequently reacts with silver ions (Eq. 9) to precipitate as silver sulphide, culminating in the overall transformation described by Eq. (10). Such a mechanism reduces concentration of H_2S within solution and elevates critical potential for Cu_2S formation (Eq. 11), thereby expanding range of redox potentials favourable for accelerated copper extraction (Flores et al., 2025)

$$2CuFeS_2 + 6H^+ + 2e^- \rightarrow Cu_2S + 2Fe^{2+} + 3H_2S \quad (8)$$

$$2Ag^+ + H_2S \rightarrow Ag_2S + 2H^+ \quad (9)$$

$$2CuFeS_2 + 6Ag^+ + 2e^- \rightarrow Cu_2S + 2Fe^{2+} + 3Ag_2S \quad (10)$$

$$E_c(Ag^+) = E_o^c + +(RT/F)ln[(a_{Ag}^+)^3/a_{Fe}^{2+})] \quad (11)$$

E_c^o= 2.365V vs. SHE

This mechanism operates when the solution's redox potential exceeds the oxidation potential of Cu_2S (E_{ox}) but remains below critical potential $E_c(Ag^+)$ (Eq. 11). Presence of silver ions elevates critical potential $E_c(Ag^+)$ above that of E_c (Cu^{2+}) (Eq. 7) observed in their absence, thereby expanding the potential range available for copper recovery. This effect is depicted in figure below, which presents critical potentials with respect to logarithm of corresponding ion under the conditions of 298 K and 1 atm, assuming a ferrous ion activity of 0.1 (Flores et al., 2025).

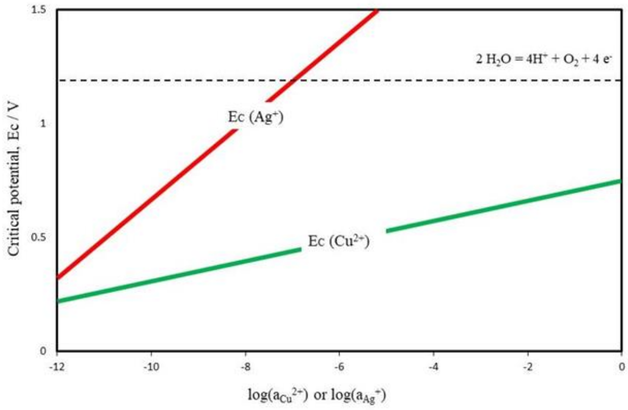

Figure 1; The change in critical potential $E_c(Ag^+)$ in relation to logarithm of silver-ion activity, and that of E_c (Cu^{2+}) in relation to logarithm of cupric-ion activity, is depicted for conditions of 298 K and 1 atm.(Flores et al. 2025).

Alternatively,to the view presented by Flores et al. (2025), Ghahremaninezhad et al. (2015) proposed a distinct mechanism in which silver atoms diffuse into the chalcopyrite lattice after silver cat ions adsorb onto the electrode surface and subsequently form Ag_2S. They contended that configuration of each Ag_2S unit necessitates development of a sulphur vacancy and two electronic holes within the passive film. This process, rather than consumption of hydrogen sulphide by silver ions, proposed to enhance chalcopyrite dissolution by elevating density of sulphur vacancies and whole pairs.

3. Mechanistic analysis of chalcopyrite leaching under chloride containing conditions systems

Building on the silver-catalysed reaction mechanisms governing chalcopyrite leaching described by Ghahremaninezhad et al. (2015), Chloride mediated process influence in governing chalcopyrite dissolution can be rigorously assessed across chloride bearing systems. In such media, both cuprous and cupric species must be embedded in determination of the critical potential, as cuprous ions are stabilized as chlorocuprate(I) complexes (CuCl, $CuCl_2^-$, $CuCl_3^{2-}$, $CuCl_4^{3-}$), unlike in sulphate systems where only cupric ions are typically relevant. Chalcopyrite reduction through cuprous ion interaction follows pathways outlined in Eqs. (12) – (14), and associated critical potentials Chalcopyrite reduction through cuprous ion interaction using Eqs. (15) – (17) (Yoo et al., 2010)

$$CuFeS_2 + 3CuCl^{2-} + e^- \rightarrow 2Cu_2S + FeCl_2 + 4Cl^- \tag{12}$$

$$CuFeS_2 + 3CuCl_3^{2-} + e^- \rightarrow 2Cu_2S + FeCl_2 + 7Cl^- \tag{13}$$

$$CuFeS_2 + 3CuCl_4^{2-} + e^- \rightarrow 2Cu_2S + FeCl_2 + 10Cl^- \tag{14}$$

$$E_c(CuCl_2^-) = E_o^c + (RT/F)\ln[(a_{CuCl3}2-)^3/(a_{FeCl2})(a_{Cl}^-)^4] \tag{15}$$

$$E_c(CuCl_3^{2-}) = E_o^c + (RT/F)\ln[(a_{CuCl3}2-)^3/(a_{FeCl2})(a_{Cl}^-)^7] \tag{16}$$

$$E_c(CuCl_4^{3-}) = E_o^c + (RT/F)\ln[(a_{CuCl4}3-)^3/(a_{FeCl2})(a_{Cl}^-)^{10}] \tag{17}$$

Diagrammatical analysis of Eh–log a_{Cl}^-diagram for $Cu^+/Cu^{2+} - Cl^- - H_20$ system (Zhang et al., 2014) indicates that elevated chloride activities facilitates formation of cupric chloride complexes, notably $CuCl^+$ and $CuCl_2$, which act as additional reductants of chalcopyrite through the pathways outlined in Eqs. (18) and (19). Accordingly critical potentials associated with these species are defined by Eqs. (20) and (21) (Yoo et al., 2010).

$$CuFeS_2 + 3CuCl^+ + 4e^- \rightarrow 2Cu_2S + FeCl_2 + Cl^- \tag{18}$$

$$CuFeS_2 + 3CuCl_2 + 4e^- \rightarrow 2Cu_2S + FeCl_2 + 4Cl^- \tag{19}$$

$$E_c(CuCl^+) = E_o^c + (RT/4F)\ln[(a_{CuCl}+)^3/(a_{FeCl2})(a_{Cl}^-] \tag{20}$$

$$E_c(CuCl_2) = E_o^c + (RT/4F)\ln[(a_{CuCl2}+)^3/(a_{FeCl2})(a_{Cl}^-)^4] \tag{21}$$

Chalcopyrite leaching increases molar concentration of ferrous ions (Fe^{2+}) in solution, leading to progressive decline in oxidation-reduction potential (ORP) with chloride containing media demonstrating the steepest reduction relative to sulphate or combined systems. Yoo et al. (2010) reported that chloride addition facilitates development of chlorocuprate (I) complexes, enhancing critical potential threshold and enhancing leaching kinetics. These results align with ferrous-promoted mechanism (Santos et al., 2017). Evidence from this study highlights effect of ferrous ions as key facilitators in enhancing chalcopyrite dissolution rates.

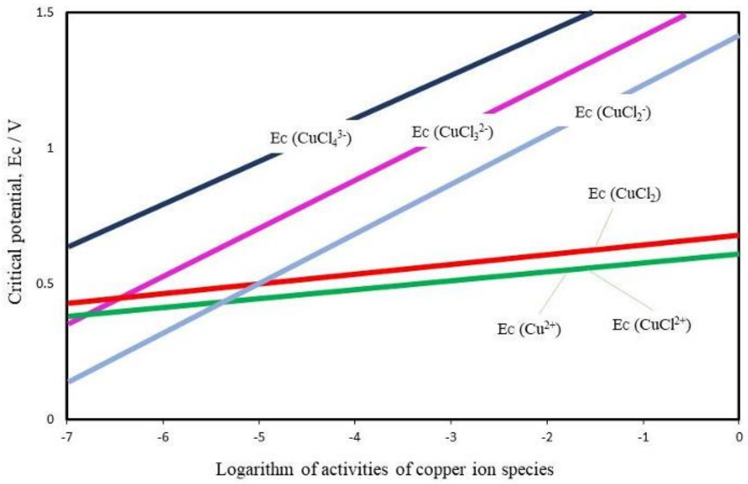

Figure 2: Critical potentials plotted against copper ion activity expressed on a logarithmic scale at 298 K and 1 atm. (Flores et al. 2025).

4. Synergistic oxidative dissolution of chalcopyrite facilitated by pyrite

Studies indicate that pyrite (FeS_2) enhances the rate of chalcopyrite dissolution in sulphate media through Galvanox mechanism (Zhao et al., 2016, Zhao et al.2021), where chalcopyrite acts as anodic site and pyrite as cathodic site, promoting chalcopyrite oxidation (Eqs. 22–24). Effective operation of this mechanism requires pyrite in a mass two to four times that of chalcopyrite

$$4Fe^{3+} + 4e^- \rightarrow 4Fe^{2+} \quad (22)$$

$$CuFeS_2 \rightarrow Cu^{2+} + Fe^{2+} + 2S^o + 4e^- \quad (23)$$

$$CuFeS_2 + 2Fe_2(SO_4)_3 \rightarrow CuSO_4 + 5FeSO_4 + 2S^o \quad (24)$$

Conversely, some researchers contend that catalytic influences of pyrite on galvanic interactions are insufficient to solely explain leaching characteristics of chalcopyrite. While galvanic coupling between pyrite and chalcopyrite may facilitate chalcopyrite oxidation via direct leaching pathways, contemporaneous rapid emergence of a oxide layer prevents this oxidation from improving chalcopyrite disintegrating. Moreover, direct oxidative dissolution of chalcopyrite occurs at approximately 0.5–0.7 V versus Ag/AgCl, which lies outside the optimal span of oxidation-reduction potentials for dissolution of chalcopyrite (0.36–0.5 V versus Ag/AgCl) identified in several studies, where chalcopyrite dissolution by reduction to chalcocite is favoured (Zhao et al., 2016)

Pyrite's catalyst impact on chalcopyrite sulphuric acid facilitates extraction by inhibiting oxidative potential; pyrite addition elevates Fe^{2+} concentrations, which are oxidized by O_2 to Fe^{3+}, raising oxidation-reduction potential to a spectrum ($E_L - E_H$) that enables reactions described in Eqs. (25) and (26) (Zhao et al., 2015). Keeping redox potential constant within optimal range of 360–480 mV versus Ag/AgCl effectively suppresses creation of metal-deficient polysulfide layers (Eq. 29), which are recognized as primary constituents of passivation (Ghahremaninezhad et al., 2016). XPS analysis confirmed this behaviour, showing that elemental sulphur displayed higher concentration at mineral surface from 5% to 10%, while polysulfide (Sn^{2-}) formation was almost entirely inhibited (Zhao et al., 2016)

$$\mathrm{CuFe}S_2 + 3Cu^{2+} + 4e^- \rightarrow 2Cu_2S + Fe^{2+} \tag{25}$$

$$2Cu_2S \rightarrow 4Cu^{2+} + 2S^{\circ} + 8e^- \tag{26}$$

$$E_H = 482 + 47.3\log(a_{Cu^{2+}}) - 15.77\log(a_{Fe^{2+}})/mV \tag{27}$$

$$E_L = 401 + 29.5\log(a_{Cu^{2+}})\,/mV \tag{28}$$

$$CuFeS_2 \rightarrow Cu_{1-x}Fe_{1-y}S_2 + xCu^{2+} + yFe^{2+} + 2(x+y)^{e^-}(x > y) \tag{29}$$

5. Bioleaching

Modulation pertaining to redox potential through pyrite addition is demonstrated to optimize chalcopyrite dissolution during bioleaching with *Leptospirillum ferriphilum* (Zhao et al., 2015b). When exposed to elevated redox potential (>480 mV vs. Ag/AgCl), copper was recovered at a maximum efficiency of approximately 30%. In contrast, ensuring redox potential is sustained within 380–480 mV by incorporating pyrite at a chalcopyrite-to-pyrite ratio of 1:4 led to copper recoveries exceeding 80%. Similar observations were reported by Hong et al. (2021), who noted that pyrite addition did not modify electrochemically induced dissolution pathway of chalcopyrite. These findings indicate that pyrite functions as a reactive potential inhibitor, facilitating degradation of chalcopyrite into intermediate copper-iron phases like chalcocite (Cu_2S). Specifically, pyrite dissolution increases Fe^{2+} concentration in solution, thereby lowering the Fe^{3+}/Fe^{2+} ratio and stabilizing oxidation–reduction redox potential within optimal range ($E_L < E < E_H$) over extended periods (Hong et al., 2021). Hong et al. (2021) demonstrated that maintaining a oxidation–reduction electrochemical potential of 350–370 mV versus Ag/AgCl, using a chalcopyrite-to-pyrite ratio of 1:3, enhanced copper recovery via *Leptospirillum ferriphilum* bioleaching to ~70%

within 25 days. Lower pyrite additions were insufficient to sustain this potential, slowing chalcopyrite disintegration and promoting passivation. Comparable results were reported by Keke et al. (2023), albeit with slightly different optimal redox potentials and mass ratios.

6. Mechanochemical Enhancement of Hydrogen Peroxide-Based Chalcopyrite Leaching

Mechanochemical disintegration of chalcopyrite represents an advanced approach for improving extraction efficiency. Grinding media induces structural defects and lattice distortions, diminishes fragmentation, and promotes removal of passivizing sulphur layers and other inert surface species, thereby enhancing material's reactivity and comprehensive kinetics of leaching process. H_2O_2-assisted investigation was conducted on chalcopyrite dissolution using millimetre-sized glass beads (Laskar et al., 2024) in a 6 L mechanically stirred reactor maintained at 556 rpm with 3 wt. % chalcopyrite and 1 mm beads. At 42 °C, pH 3, Eh 700 mV, and bead-to-solid ratio of 12:1 was employed, copper recovery following 120 h of leaching was 8 % without beads, 27 % with pre-grinding, and 70 % when leaching occurred in the presence of beads, reaching 80 % after 200 h, highlighting substantial enhancement induced by glass beads.

Dakkoune et al. (2023) investigated dissolution of chalcopyrite employing millimetre-scale glass beads, which promoted particle fragmentation, mechanochemical activation, and the elimination of surface reaction products. The study systematically examines impact of attrition-assisted leaching on kinetic dissolution characteristics of chalcopyrite and provides fundamental insights into associated mechanistic pathways. Copper dissolution was systematically evaluated under controlled experimental conditions employing a sample of chalcopyrite concentrate weighing 84 g in conjunction with 1 kg of 2.5 capacity charge of glass beads of H_2SO_4–H_2O, pH 1.3, H_2O_2 up to Eh equals 700 mV across different operational configurations. Dakkoune et al. (2023) reported that incorporation of glass spheres significantly accelerated dissolution kinetics, even in regions occupied by particles pre-passivized via preliminary leaching or in presence of substantial solid by-products, encompassing elemental jarosite and sulphur. This pronounced effect was most notable within initial 40–50 hours through the process of dissolving is attributable not only to layer delamination of passivizing friction-induced surface layers but also associated increase in particle specific surface area due to crushing. Indeed, it has long been established that comminution of particles corresponds to an accelerated dissolution rate. Industrial implementation of glass beads in leaching processes requires further investigation. Although bead reuse appears viable, with over 99% recovery per trial, critical factors including bead temperature, quantity, concentrate hardness and grade must be systematically optimized.

Additionally, energy demand associated with bead agitation needs quantification. Addressing these factors is essential for socioeconomic and ecological of friction-assisted leaching relative to established methods, including chloride leaching and bioleaching (Dakkoune et al., 2023)

6.1 Hydrogen Peroxide-Induced Reductive and Oxidative Leaching

A progressive leaching technique, which merges non-oxidative and reductive steps with subsequent hydrogen peroxide-driven oxidative dissolution, has proven to be highly beneficial. The process systematically optimizes key operational parameters, such as optimizing agitation, particle size, temperature, acid concentration, pulp density, leaching time, copper dissolution yields increased to 82% via non-oxidative/oxidative route and 93% through sequential two-stage dissolution process. These results highlight potential of combining reduction-based, non-oxidative leaching strategies with H_2O_2-assisted oxidation, offering a promising pathway for enhancing metals extraction through increased dissolution efficiency (Nnanwube et al., 2022; Nnanwube et al., 2024). Optimizing these processes could enhance efficiency and sustainability of industrial copper extraction (Kenzhaliyev et al., 2023). Figure 3 depicts Iron and copper over time during two leaching stages: initial non-oxidative/reductive phase (within 240 minutes, green arrow) and subsequent H_2O_2-driven oxidative phase (after 240 minutes, red arrow).

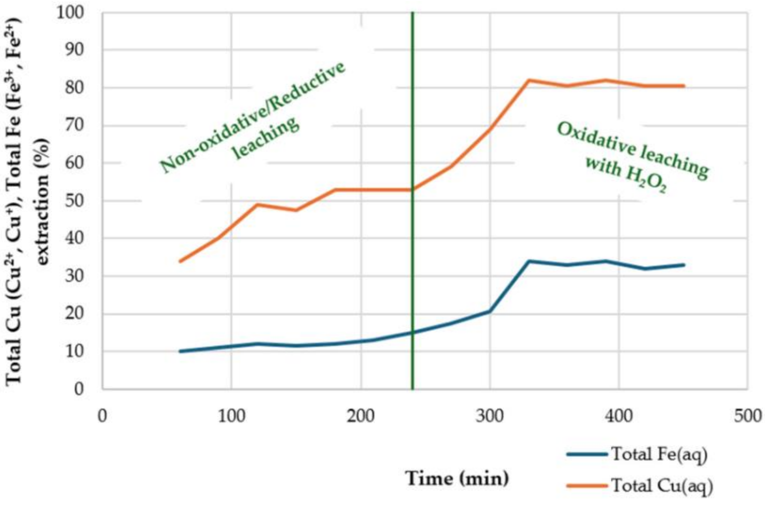

Figure 3. Hydrometallurgical recovery of copper and Iron from chalcopyrite in 300 g/L H_2SO_4 at 80 °C, 2.5% pulp, 600 rpm, followed by 40 °C H_2O_2 leaching (Rasouli et al., 2025).

6.2 Leaching dynamics in H_2O_2 based systems with emerging leachates

Chalcopyrite dissolution represents a typical heterogeneous reaction which is inherently complex and proceeds through multiple sequential stages. Table 1 summarizes activation barrier and rate-limiting steps for chalcopyrite dissolution with H_2O_2 across various media.

Table 1. Hydrogen Peroxide Optimized chalcopyrite dissolution in acidic solution.

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	Chemical reaction	[Wu, et al.,2020]
25-50	2 M $[H_2O_2]$ + 2 M $[H_2SO_4]$	3	60	Chemical reaction	[Miao et al., 2023]
30-60	2 M $[H_2O_2]$ + 0.5 M $[HCl]$	3	19.6	Diffusion	[Petrović et al., 2018]
25-45	1 M $[H_2O_2]$ + 1.5 M $[H_2SO_4]$	4	80	Diffusion	[Sokić et al.,2019]
15-40	3 M $[H_2O_2]$ + 0.6 M $[H_2SO_4]$ + 5.7 M $[CH_3OH]$	5	24.3	Chemical reaction	[Zhong, S., and Li, 2019]
30-60	3 M $[H_2O_2]$ + 3 M $[H_2SO_4]$	2	38.9	Diffusion	[Petrović et al., 2023]
20-50	1 M $[H_2O_2]$+ 2 M $[H_2SO_4]$ + 0.5 M $[C_3H_8O]$	3	60.8	Diffusion	[Michałek, et al., 2024]
30-40	30% (*v/v*) $[H_2O_2]$ + 40%(*w/v*) $[HSO_4]$	3	49.6	Chemical reaction	[Moazzami, Y, et al., 2024]

6.3 Study on chalcopyrite dissolution in alkaline hydrogen peroxide media enhanced by amino acid additives

In hydrophilic degradation pertaining to chalcopyrite at 25–65 °C below atmospheric pressure, Nurtazina et al. (2022) established that lysine, betaine and glycine function as particular copper leach reagents. Environmentally friendly process attains increased copper recovery at elevated thermal conditions using H_2O_2 further enhancing performance through formation of copper amino acid complexes such as copper glycinate(II), copper betainate(II), and copper lysinate(II). Elevated temperatures and diminished H_2O_2 concentrations were observed to substantially accelerate its decomposition into oxygen and water, highlighting sensitivity of reaction kinetics to these parameters, whereas alkaline conditions and lower temperatures significantly retard the process. Table 2 compiles case studies assessing efficacy of H_2O_2-based leaching systems, alongside amino acids and alkaline media to enable selective copper extraction from chalcopyrite.

Table 2. An examination of the H_2O_2–alkaline–amino acid system through case studies (Nurtazina et al., 2022)

Charged material	Ore dissolution	Recovery
Chalcopyrite:90% Cu:35.57% Fe:31.68% P80:58µm 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: 5.57%

7. Overview of Chalcopyrite's dissolution kinetics in alkaline glycine and glycinate media.

Alkaline leaching provides a strategic alternative to acidic systems, with aqueous ammonia and its derivatives extensively applied for base metal, particularly copper, extraction (Ahn et al., 2022; Omoniyi et al., 2024). In chalcopyrite, ammonia coordinates cupric ions, enhancing their stability under alkaline conditions, while sulphide component undergoes oxidation to sulphate or elemental sulphur (Ma et al., 2021; Deng et al., 2022). Simultaneously, iron undergoes hydrolysis and precipitates as oxides, hydroxides, or oxy-hydroxides in neutral to basic media, as highlighted by XPS analyses (Yang et al., 2023; Guoa and Amanda, 2013).

These interactions collectively facilitate selective metal recovery while mitigating common difficulties encountered in with acidic leaching. Yang et al. (2015) investigated chalcopyrite electrochemical oxidation and found via XPS that passivation layers formed with composition dependent on solution pH and applied potential; in alkaline solution (pH 9.2), potentials below 540 mV (vs. SHE) yielded metastable CuS_2 and Fe_2O_3, while potentials above 740 mV produced elemental sulphur, CuO and Fe_2O_3, although passivation was comparatively negligible under mildly acidic (pH 6.8) or strongly alkaline (pH 13) conditions.

Although ammoniacal leaching offers the benefit of copper-selective recovery, it presents several issues related to technology and ecological. The process generates a pungent odor at negligible concentrations, exhibits toxicity to aquatic life, and poses health risks, including respiratory tract irritation and skin burns. Furthermore, reagent loss and high operational costs, driven by volatility and substantial lixiviate-to-metal stoichiometric requirements, hinder its commercial viability (Karimov et al., 2025).

Glycine represents a non-toxic, non-volatile alternative to ammonia as a complexing agent. Similar to ammonia, It is evidenced that selectively extracting copper from oxide and secondary sulphide minerals while suppressing leaching of gangue constituents (Eksteen et al., 2015; Oraby and Eksteen, 2014a, 2015b; Tanda et al., 2017a, 2017b). In alkaline glycine media, chalcopyrite undergoes oxidative dissolution as represented by the following reaction.

$$CuFeS_2 + 2Gly + 19OH^- \rightleftharpoons Cu(Gly)_2 + Fe(OH)_3 + 2SO_4 + 8H_2O + 17e^- \qquad (30)$$

Research on glycine chalcopyrite system is still relatively limited. Eksteen et al. (2017) demonstrated that alkaline glycine solutions, amid of oxygen promote chalcopyrite oxidation, suggesting glycine's potential employed as leachate to enable direct leaching of chalcopyrite or its products from alkaline peroxidation. In ultrafine flotation concentrates subjected to partial alkaline peroxidation, extraction process resulted in a copper recovery of 90%, at 60 °C under atmospheric pressure for 17 h. The study additionally presented conceptual flow sheets for metal leachate recovery with reagent recycling, enabling sustainable process integration. . Oraby and Eksteen (2014b) demonstrated that alkaline glycine–hydrogen peroxide solutions efficient extraction of chalcopyrite, mixed oxide and supergene sulfide copper-gold concentrates. Electrochemical studies indicate that chalcopyrite is not influenced by passivation but instead behaves as a non-ideal semiconductor alternative to passivized metallic copper (O'Connor et al., 2018a, 2018b).While alkaline glycine systems are recognized as effective lixiviates for copper extraction from ores, leaching rates remain insufficiently unexplored. Elucidating dependence of reaction rates on operational parameters not only enables accurate prediction of metal dissolution but also allows for analytical modelling, supporting reactor design, optimization of hydrometallurgical operations and substantial time savings in pilot-scale studies (Ojong et al., 2024).

CONCLUSIONS

This review highlights the necessity for further investigation into chalcopyrite leaching mechanisms, as current understanding remains limited. While trends such as oxidant temperature and concentration are acknowledged to have effect, these largely reaffirm existing investigations. Crucially, composition and role of gases generated during leaching remain uncharacterized, and chalcopyrite reduction is considered to be crucial factor in enhancing copper extraction. Chalcopyrite is amongst the finest refractory copper sulphides, as highlighted by thermodynamic and stability analyses. Reductive leaching converts chalcopyrite primarily to chalcocite, enhancing subsequent copper extraction. Additionally, reductive decomposition is shown to repress and delay creation of passivation products, including jarosite, thereby improving dissolution effectiveness in bioleaching systems. Maintaining an optimal redox potential is pivotal for enhancing chalcopyrite dissolution in models and mechanisms that involve chalcopyrite reduction. Industrial-scale implementation, however, faces challenges including reagent stability, necessity for customized reactor setups and rigorous management of operational parameters. Prospects for further study should explore incorporation of these strategies with emerging strategies such as microwave-induced or photoleaching processes, which, in synergy with H_2O_2, may further optimize leaching effectiveness and significantly reduce processing time. Moreover, additional studies are necessary to assess potential of leaching via reductive mechanisms as viable pre-treatment in metal extraction through hydrometallurgical methods of sulphide minerals.

Declaration of Competing Interest

The authors report no conflicts of interest, financial or personal, that might have influenced findings of this work.

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