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**Efecto del pH en la lixiviación
de calcopirita con fosfato para
la recuperación de cobre**

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Effect of pH on chalcopyrite leaching with phosphate for copper recovery

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Abstract

Chalcopyrite is one of the most abundant copper minerals found in the Earth's crust. It typically undergoes a series of concentration stages to produce a copper concentrate, which is then processed through pyrometallurgical methods. Although a hydrometallurgical method presents an interesting alternative, it faces significant challenges owing to the high chemical stability of chalcopyrite, which imparts refractory properties and hinders copper leaching. This study investigates the effect of pH on copper leaching in a PO_4^{3-} – H_2O_2 system. The copper recovery was found to be strongly dependent on both pH and H_2O_2 concentration. At a pH of 3, increasing the H_2O_2 concentration to 0.5 M enhanced the kinetics of chalcopyrite oxidation at low solid-to-liquid (S/L) ratios (20–50 g/L), resulting in rapid and efficient copper recovery (> 90%). In contrast, at higher ratios (100–200 g/L), the kinetics and overall efficiency were reduced. Iron dissolution remained below 3%, with phosphate enhancing copper recovery and reducing iron solubility.

Introduction

Copper is one of the few metals that can be found in its native (metallic) form in nature. It was among the first metals used by humans for various purposes, including domestic use, ceremonial activities, and production, with usage dating back to around 8500 BC [1]. In nature, copper exists primarily as oxides, hydroxides, and sulfides [2]. Recently, researchers have been focusing on recovering copper from ores and concentrates using hydrometallurgical methods [3]. Approximately 20% of copper is sourced from oxidized minerals obtained through these hydrometallurgical processes [4].

Among sulfide minerals, chalcopyrite (CuFeS_2) is the most commercially important copper sulfide and the primary source of copper production [5]. However, extracting copper from chalcopyrite using hydrometallurgical methods is challenging owing to its refractory nature [6]. Several factors hinder the leaching process, including the formation of a passive layer on the surface of chalcopyrite, caused by byproducts such as elemental sulfur, metal sulfides, or jarosite [7]. To address these challenges, various

alternatives have been proposed, including bioleaching, the use of organic agents, chlorides, and pressure leaching under controlled conditions. High copper extractions of over 90% can be achieved through pressure oxidation at approximately 200 °C and 0.7 MPa of oxygen, or by adding pyrite as a catalyst, which enhances oxidation and minimizes surface passivation [8, 9].

In chalcopyrite leaching, oxidizing agents such as hydrogen peroxide [10, 11], dichromate ions [12], chlorate ions [13], ozone [14], and nitrate ions [15] are essential. Among these, hydrogen peroxide (H_2O_2) is regarded as one of the cleanest and most versatile oxidants, widely utilized in both industrial and environmental applications. Its high oxidation–reduction potential of 1.77 V versus SHE (Standard Hydrogen Electrode) makes it a promising reagent for the oxidative leaching of metal sulfides, which is why it has been the focus of numerous studies [16]. However, despite considerable experimental evidence, its large-scale application in mining remains limited [10]. This limitation arises because the oxidation of sulfide minerals, such as chalcopyrite, generates surface species including elemental sulfur and polysulfides that form passive layers, thereby reducing leaching efficiency [17].

This behavior indicates that the medium in which leaching occurs directly impacts the oxidation kinetics and the solubility of metals. It highlights the necessity of introducing additional agents that can stabilize copper in solution

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while simultaneously restricting iron dissolution [18, 19]. Research indicates that in acidic environments, the presence of H^+ protons can promote reductive reactions that transform copper into stable sulfides, which limits its recovery [17, 20]. In this context, the use of phosphates proves advantageous, as they stabilize copper in solution as Cu^{2+} and forming soluble complexes such as $CuHPO_4^+$ [21], furthermore, they promote the precipitation of iron as hydrated ferric phosphate ($FePO_4 \cdot 2H_2O$), which enhances the selectivity of the leaching process [22]. However, the use of phosphates for copper recovery from chalcopyrite has not been previously reported. Therefore, this study aims to provide new evidence regarding the role of phosphate as a copper-complexing agent in chalcopyrite leaching, evaluating its effect on copper stabilization, and its potential to limit iron solubility. Phosphate facilitates the formation of stable complexes with copper while encouraging the precipitation of iron as $FePO_4$, thereby improving copper selectivity during the leaching process.

Materials and methodology

All the reagents used were of analytical grade, including dipotassium phosphate (K_2HPO_4), hydrogen peroxide (H_2O_2), dilute nitric acid, and deionized water, which were employed for all leaching tests. The mineral sample was obtained from the state of Sonora, Mexico, and was manually crushed and sieved to achieve a homogeneous particle size ranging from -200 to -325 mesh ($74 \mu m$ to $52 \mu m$, respectively).

To determine the metallic content, 0.1 g of sample (triplicate) was digested with aqua regia, at its boiling temperature and constant magnetic agitation. The solutions were allowed to cool and then were filtered and diluted with deionized water. All samples were analyzed by atomic absorption spectrometry (AAS; Varian SpectraAA 220FS) to quantify the metals copper (Cu) and iron (Fe). Mineralogical characterization was performed using X-ray diffraction (XRD) with an EMPYREAN diffractometer, which was equipped with a Ni filter, a fine-focus Cu tube, and a PIXcel3D detector. The powdered sample was homogenized with an agate mortar and mounted on a double-loaded stainless-steel sample holder, which was used for nonoriented fractions. Measurements were taken in the 2 theta range of $4-80^\circ$, with a step size of 0.003° and an integration time of 40 s per step. Phase identification was carried out using the RIR method in HighScore v4.5 software, referencing both the ICDD (International Center for Diffraction DATA) and ICSD (Inorganic Crystal Structure Database).

Leaching experiments were conducted in a 250-mL glass reactor equipped with a mechanical stirrer (Cafra-BDC250) set at 400 rpm to ensure the suspension of solids

and maintain homogeneity. The pH of the solution was continuously monitored using a calibrated pH meter (Hanna HI 99100). The leaching solution was prepared by dissolving K_2HPO_4 in deionized water to achieve a concentration of $0.05 M PO_4^{3-}$. The pH was adjusted to constant values of 3, 4, and 5 for each test by adding aliquots of diluted HNO_3 .

To evaluate the effect of oxidant concentration, 2 g of sample was added to 100 mL of solution (20 g/L) with hydrogen peroxide (H_2O_2) at three different concentrations, 0.1 M, 0.3 M, and 0.5 M. The influence of the solid-to-liquid (S/L) ratio was also investigated at concentrations of 20 g/L, 50 g/L, 100 g/L, and 200 g/L, while maintaining a pH of 3, a phosphate concentration of $0.05 M (PO_4^{3-})$, and a hydrogen peroxide concentration of 0.5 M.

Results and discussion

The sample was analyzed by chemical analysis and showed a composition of 0.40% copper and 0.52% iron.

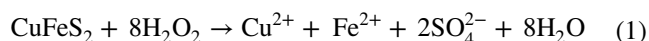
X-ray diffraction analysis (Fig. 1) suggested that copper was present in the form of chalcopyrite ($CuFeS_2$). In addition, several gangue minerals were identified, including quartz (SiO_2), augite ($Na_{0.01}Ca_{0.85}Mg_{0.852}Ti_{0.01}Cr_{0.001}Mn_{0.008}Fe_{0.238}Al_{0.13}Si_{1.928}O_6$), diopside ($(Mg_{0.91}Fe_{0.09})Ca(SiO_3)_2$), orthoclase ($KAlSi_3O_8$), and muscovite ($K_{0.74}Na_{0.17}Ca_{0.01}Mg_{0.02}Ti_{0.02}Fe_{0.03}Al_{2.83}Si_{3.10}O_{10}(OH)_2$). This mineralogical profile aligns with the typical chalcopyrite ores reported in previous studies [5, 6], confirming the prevalence of silicate phases alongside copper sulfides in natural deposits.

Effect of pH

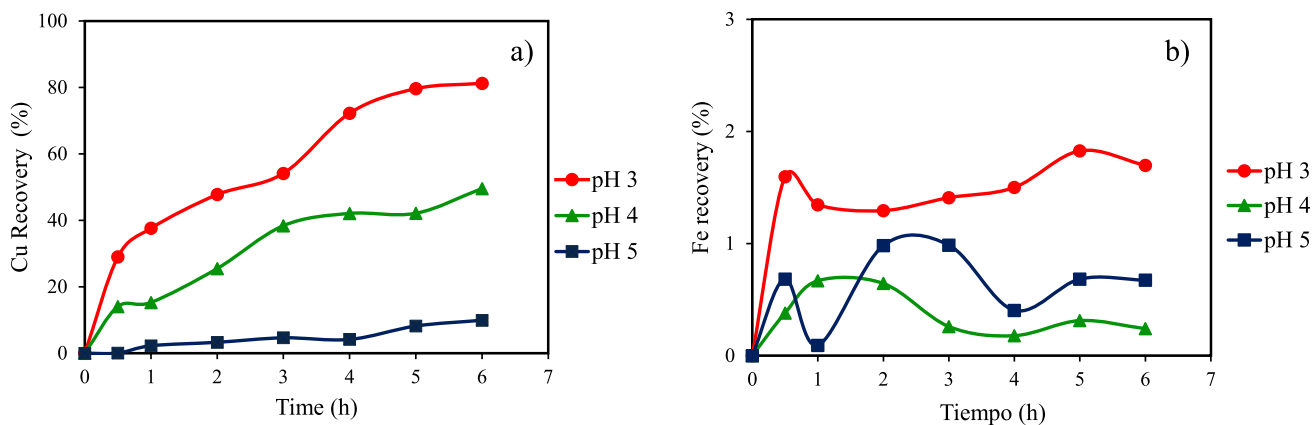
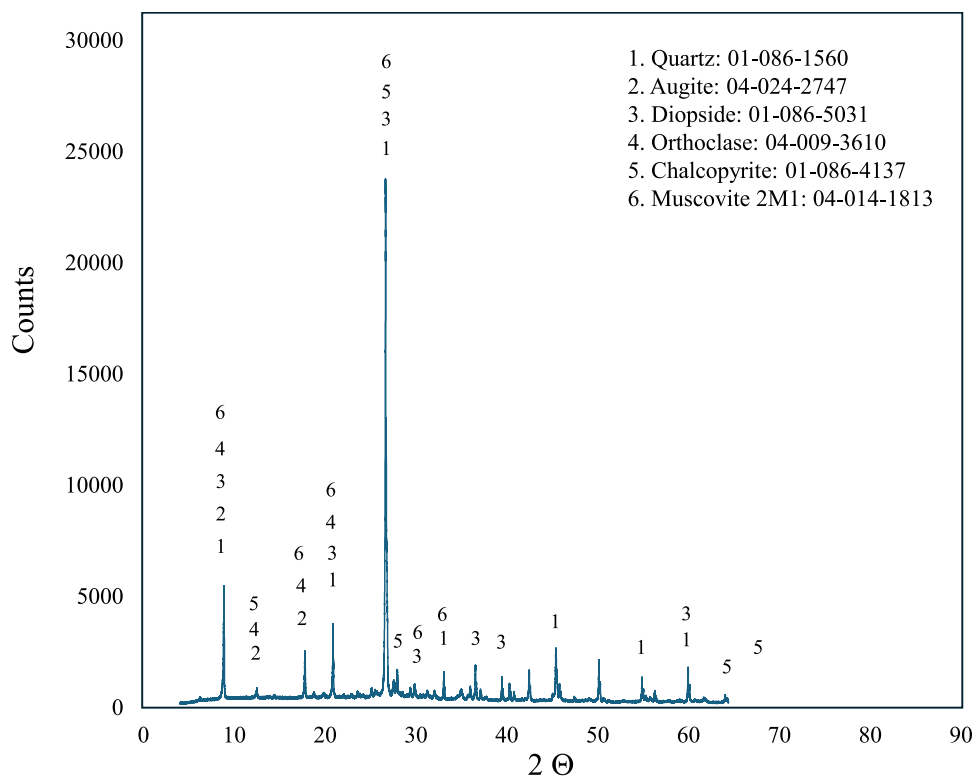
Figure 2 demonstrates that pH significantly influences chalcopyrite leaching in the $PO_4^{3-}-H_2O_2$ system.

The highest copper recovery (80%) was obtained at pH 3 (Fig. 2a), which may be attributed to the high reactivity and stability of hydrogen peroxide under acidic conditions, favoring chalcopyrite oxidation (Eq. 1) and the formation of soluble Cu^{2+} -phosphate complexes.

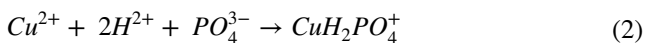
The highest recovery of copper, which reached 80%, occurred at a pH of 3 (Fig. 2a). This result can be explained by the increased reactivity and stability of hydrogen peroxide in acidic conditions. These factors enhance the oxidation of chalcopyrite (Eq. 1), leading to the release of copper and the formation of soluble Cu^{2+} -phosphate complexes.



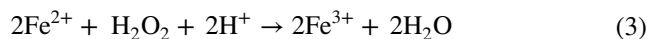
In an acidic medium (pH 3), the formation of the $CuH_2PO_4^+$ species is promoted by the interaction of Cu^{2+}

Fig. 1 X-ray diffraction pattern of the industrial sample**Fig. 2** Effect of pH on the Cu (a) and Fe (b) recovery with 0.05 M PO_4^{3-} , 0.3 M H_2O_2 , and 20 g/L

ions released from chalcopyrite with phosphate anions, as shown in Eq. 2.

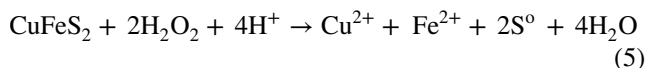


Hydrogen peroxide at pH 3 decomposed slowly and maintained a high redox potential, allowing oxidation of sulfur in chalcopyrite to sulfate [2]. Subsequently, Fe^{2+} ions released were oxidized to Fe^{3+} in the presence of peroxide (Eq. 3) and removed from solution through precipitation as ferric phosphate (Eq. 4).



At a pH of 4, the recovery rate of copper drops to approximately 50%. This reduction is due to the decreased oxidizing capacity of hydrogen peroxide (H_2O_2) and the potential formation of elemental sulfur on the mineral surface through oxidation reactions, which could be attributed to the likely creation of a passivating layer (Eq. 5). As the pH increases,

the concentration of protons (H^+) available for the leaching of chalcopyrite decreases, thereby limiting both oxidation and metal dissolution. For iron, the concentration in solution was around 1.5 ppm, indicating its oxidation and subsequent precipitation as ferric phosphate.



At pH 5, copper recovery was minimal, below 15%. This low recovery was primarily due to accelerated decomposition of peroxide, and suggests a significant surface passivation by elemental sulfur. As a result, the stability of $Cu_3(PO_4)_2$ and $CuHPO_4$ solids was enhanced, which reduced the concentration of soluble copper species. In contrast, iron remained well-controlled in solution, with a low recovery rate of only 2% (1.7 ppm).

These findings highlight the strong influence of pH on both oxidation kinetics and metal selectivity during chalcopyrite leaching. At pH 3, the PO_4^{3-} – H_2O_2 system exhibited optimal performance, achieving a copper recovery rate of 80% and very low iron solubility, less than 2 ppm. This behavior is consistent with previous studies that indicate phosphate stabilizes copper species in solution and facilitates the precipitation of ferric phosphate ($FePO_4 \cdot 2H_2O$), thereby improving leaching selectivity [21, 22].

Effect of H_2O_2

Figure 3a shows that copper recovery progressively increased with the concentration of H_2O_2 at pH 3, from 0.1, 0.3, and 0.5 M, achieving recoveries of 54%, 81%, and 94% respectively. Throughout these cases, iron dissolution remained below 2%, as shown in Fig. 3b.

This trend can be attributed to the increased availability of certain factors, which enhances the oxidative capacity of

the system and promotes the dissolution of chalcopyrite, as described in Eq. 1. Under these conditions, some Cu^{2+} ions are likely to be stabilized as $CuH_2PO_4^+$. Meanwhile, Fe^{2+} generated from chalcopyrite oxidation is further oxidized to Fe^{3+} and subsequently precipitates as $FePO_4 \cdot 2H_2O$ in the presence of phosphate, as shown in Eq. 4.

These results align with previous studies that report hydrogen peroxide improves the oxidation kinetics of chalcopyrite under acidic conditions by providing a high redox potential. However, excessive decomposition of peroxide can reduce efficiency at higher concentrations. Furthermore, the precipitation of Fe^{3+} as ferric phosphate limits its solubility and enhances the selectivity of copper [21, 22].

Therefore, the PO_4^{3-} – H_2O_2 system demonstrates a strong selectivity for copper, keeping iron dissolution below 2%. Unlike other oxidizing systems, in which Fe^{3+} may reprecipitate as jarosite or ferric hydroxide [6, 7], phosphate appears to immobilize iron as a stable ferric phosphate phase, thus preventing contamination of the copper-rich leachate.

Effect of solid/liquid ratio (S/L)

Figure 4 shows that at a pH of 3 and a concentration of 0.5 M H_2O_2 , copper recovery exceeded 90% at low solid-to-liquid (S/L) ratios ranging from 20 to 50 g/L. However, as the S/L ratio increased to 100 and then 200 g/L, copper recovery decreased to 80% and 60%, respectively.

This trend can be attributed to improved contact between the mineral and the reactant, as well as greater availability of the oxidant per unit mass of mineral at low S/L ratios. These factors enhance mass transfer and facilitate the surface oxidation of chalcopyrite. Conversely, at higher S/L ratios, the limited availability of the oxidant and phosphate likely reduces the efficiency of the reactions and restricts copper dissolution. This behavior is consistent with previous

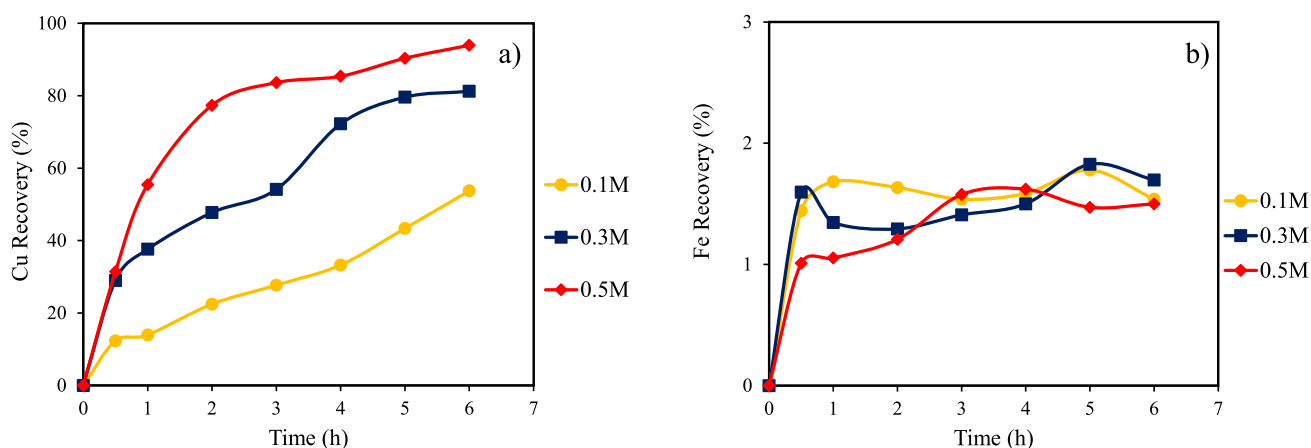


Fig. 3 Effect of H_2O_2 concentration on recovery of Cu (a) and Fe (b) at 0.05 M PO_4^{3-} , pH 3, with 20 g/L, at room temperature

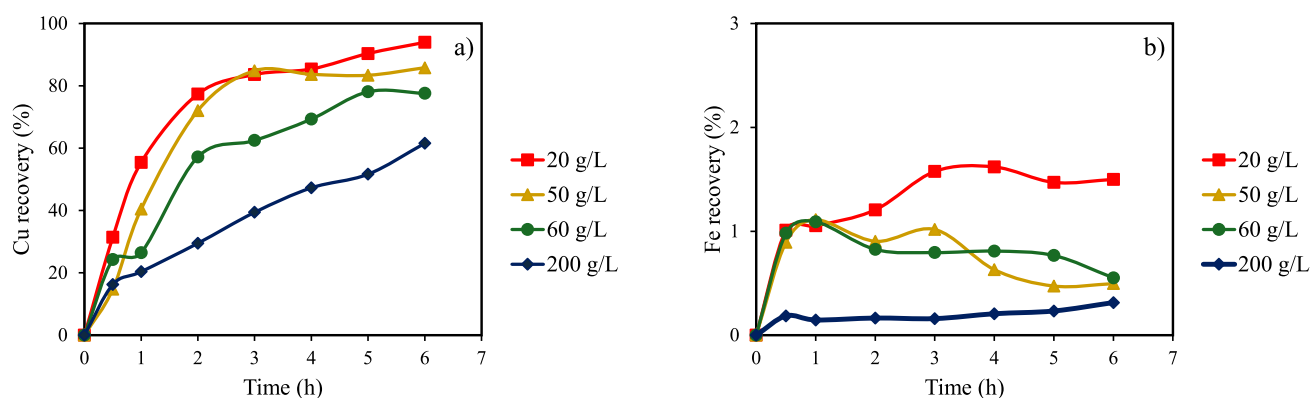


Fig. 4 Effect of S/L ratio on Cu (a) and Fe (b) recovery at pH 3, 0.05 M PO_4^{3-} , and 0.5 M H_2O_2 at room temperature

findings that highlight diffusion-controlled processes in other sulfide systems [6, 10].

Although the dissolution of iron remained below 2% in all tests, its concentration in solution varied with the solid load. Specifically, at a solid load of 20 g/L, the iron recovery was 1.5% (1.5 ppm). At 50 g/L, this decreased to 0.1% (0.3 ppm); at 60 g/L, it increased to 0.5% (1.7 ppm); and at both 100 g/L and 200 g/L, the recovery stabilized at 0.3%, with dissolved iron concentrations increasing to 2.04 ppm and 3.25 ppm, respectively. These results suggest that, even when the fraction of leached iron is minimal, its absolute concentration in solution scales with the amount of solids present.

Phosphate plays a critical role in immobilizing iron as $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ across the tested solid-to-liquid (S/L) ratios, preventing iron from accumulating in the leachate and sustaining selectivity. As a result, the PO_4^{3-} – H_2O_2 system not only facilitates high copper recoveries under mild conditions but also maintains low iron solubility. This aligns with previous observations regarding phosphate-mediated copper stabilization and selective iron precipitation [21, 22].

In this study, the leaching of chalcopyrite in a system containing phosphate and hydrogen peroxide was studied, assessing the effects of pH, H_2O_2 concentration, and S/L ratio. Phosphate helps keep copper in solution as Cu^{2+} and $\text{CuH}_2\text{PO}_4^+$, at pH 3, which prevents copper precipitation. Concurrently, it limits iron solubility by promoting its precipitation as $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$, thereby improving the selectivity toward copper.

The process is pH-dependent; at pH 3, with 0.5 M H_2O_2 , the oxidation rate of chalcopyrite is high (94%). Lower solid-to-liquid ratios (20–50 g/L) favored faster and more efficient dissolution, while higher ratios (100–200 g/L) slowed the reaction owing to reduced oxidant availability per unit mass of mineral and the formation of passive layers of elemental sulfur (S^0), which decreased the efficiency of the process. In all tests, the iron concentration in solution remained below

3%, confirming the role of phosphate as a limiting agent for its dissolution in the liquid phase.

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Data availability The data that support the above-presented results are available from the corresponding author upon reasonable request.

Declarations

Conflicts of interest The authors declare no conflicts of interest.

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