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EFFICIENT COPPER EXTRACTION FROM CHALCOPYRITE USING THE «GLYCOLIC ACID – ETHYLENE GLYCOL – SODIUM LAURYL SULFATE» SYSTEM

Abstract: *This research explores a sustainable and efficient method for extracting copper from chalcopyrite, utilizing an innovative leaching system composed of glycolic acid, ethylene glycol, and sodium lauryl sulfate (SLS). The optimal conditions identified were 1,0 M glycolic acid, 20% (v/v) ethylene glycol, 0,8% (w/v) SLS, and a temperature of 75°C, achieving up to 85% copper recovery. Glycolic acid plays a dual role, promoting the breakdown of the chalcopyrite structure and stabilizing copper ions in the solution. SLS improves the leaching efficiency by disrupting the passivating sulfur layer, allowing for better solution penetration. Additionally, ethylene glycol prevents the precipitation of sulfur, further enhancing the process. The*

combination of these components creates a synergistic effect that improves copper recovery while minimizing environmental impact. The findings suggest that this leaching system could serve as a sustainable and efficient alternative to the traditional pyrometallurgical methods, offering potential applications in industrial copper recovery processes.
Key words: *chalcopyrite; copper recovery; leaching; glycolic acid; ethylene glycol; sodium lauryl sulfate.*

Introduction

Copper is an important metallic substance required in various fields such as electronics, building and transportation. Wrought metal also embodies various beneficial properties like high electrical and thermal conductance, or prevention from being corroded and so on, hence it is widely used in the manufacture of electric wirings, plumbing's and many more. The recovery of copper from its primary ores, especially copper grades of chalcopyrite ($CuFeS_2$), thus needs to be carried out for all countries. But together with the common mass concentration of copper ores operationally used today, the pyrometallurgical procedure of copper recovery involves some significant drawbacks regarding energy and environmental aspects [1-4].

Pyrometallurgy techniques inherently produce greenhouse gas emissions which is unacceptable in hydrometallurgical processes. In addition to this, the way it is directed now pyrometallurgy is not effective in the treatment of waste materials because of high energy consumption particularly now that fossil fuels are being done away with. These disadvantages have aroused the new technologies which do not use toxic and wastes to be disposed of for copper metal, thus the rise of hydrometallurgy [5-9].

Hydrometallurgy, which involves the use of aqueous chemistry for metal extraction, offers several advantages over pyrometallurgy, including lower energy requirements, the ability to operate at ambient pressure and temperature, and a reduced environmental footprint [10-12]. However, the hydrometallurgical recovery of copper from chalcopyrite is notoriously challenging. Chalcopyrite, the most common copper-bearing mineral, exhibits a high resistance to leaching, primarily due to its complex crystal structure and the formation of a passivating layer of elemental sulfur throughout the leaching. This sulfur layer acts as a barrier, preventing the leaching solution from effectively penetrating and dissolving the copper within the mineral matrix.

Over the years, various strategies have been explored to overcome the leaching resistance of chalcopyrite [15-18]. High-temperature pressure leaching, bioleaching using microorganisms, and the use of potent oxidizing agents like hydrogen peroxide have shown some success. However, these methods often involve high costs, complex operational requirements, or extended processing times, limiting their practical application on an industrial scale.

In recent developments, the use of non-polar organic solvents has garnered attention as a means to enhance chalcopyrite leaching [17-19]. These solvents, particularly ethylene glycol, have demonstrated the ability to disrupt the formation of passivating sulfur layers, thereby improving copper recovery rates. Ethylene glycol, a widely available and cost-effective solvent, has been shown to interact with the mineral surface, preventing the formation of a continuous sulfur layer and facilitating the extraction process.

In addition to solvent selection, the use of surfactants has been identified as a key factor in improving leaching efficiency. Surfactants such as sodium lauryl sulfate (SLS) can reduce the surface tension of the leaching solution, enhancing the wetting of the mineral surface and promoting better interaction between the leaching agents and the mineral. SLS has also been reported to alter the adsorption behavior of sulfur species on the mineral surface, further aiding in the leaching process.

Given these promising findings, this study aims to investigate the potential of a novel leaching system that combines glycolic acid, ethylene glycol, and sodium lauryl sulfate (SLS) for the efficient recovery of copper from chalcopyrite. Glycolic acid is selected for its strong chelating properties and its ability to dissolve metal ions, while ethylene glycol and SLS are incorporated to enhance the overall leaching efficiency. The study will focus on optimizing key process parameters, including acid concentration, temperature, and leaching duration, to achieve maximum copper recovery.

By exploring the synergistic effects of glycolic acid, ethylene glycol, and SLS, this research seeks to develop a more sustainable and economically viable hydrometallurgical process for copper recovery. The findings from this study could provide valuable insights into improving the efficiency of copper extraction from chalcopyrite and potentially pave the way for the broader adoption of environmentally friendly leaching technologies in the metallurgical industry.

Materials and Methods

Materials

The chalcopyrite sample used in this study was ground to a particle size of less than 74 μm to increase the surface area available for leaching. The glycolic acid (≥ 99% purity) was used as the primary leaching agent. Ethylene glycol (≥ 99% purity) was and served as the solvent to enhance the leaching process. Sodium lauryl sulfate (SLS) (≥ 99% purity) was used as a surfactant to improve the wetting of the mineral surface. Distilled water was used for all solution preparations and washings.

Leaching Procedure

The leaching of chalcopyrite sample were performed out in batch reactors, utilizing 200 mL round-bottom glass vessels fitted with magnetic stirrers to ensure uniform mixing. The reactor temperature was controlled using a thermostatic water bath. Leaching solutions were prepared by dissolving the required amount of glycolic acid in distilled water, followed by the addition of ethylene glycol and SLS in specified ratios. The concentrations of glycolic acid ranged from 0,5 M to 1,5 M, ethylene glycol was used in concentrations ranging from 10% to 30% (v/v), and SLS concentrations was maintained at 0,8% (w/v).

For each experiment, 5 grams of chalcopyrite was added to 100 mL of the leaching solution in the reactor, maintaining a solid-to-liquid ratio of approximately 5%. The temperature was varied from 25 to 75 °C. Samples were taken every 30 minutes, to monitor the leaching progress. Each sample was filtered to separate the solid residue from the leachate.

Analytical techniques

The elemental composition of both the solid and liquid phases was determined using a Savant AA spectrometer (GBC, Malaysia). Before analysis, the solid samples underwent a preliminary digestion process with concentrated nitric acid (HNO_3) at a temperature of 90-95°C and a pressure of 9-10 atm. This digestion was performed using the Tank-Eco microwave decomposition system (Sineo, China), ensuring complete breakdown of the solid matrix for accurate elemental analysis [18].

X-ray diffraction (XRD) patterns of the initial chalcopyrite and the leaching residues were collected using a D8 Advance diffractometer (Bruker, Germany). The instrument operated with CuKα radiation at 40 kV and 40 mA, providing detailed phase identification and structural analysis. The scanning was performed over a wide 20 range to ensure accurate detection of crystalline phases, and the resulting patterns were analyzed to compare the mineralogical composition before and after the leaching process[18].

All measurements of copper content in solid and liquid samples were carried out in three replicates. In all cases, the variation did not exceed 3%. The graphs showing the dependence of copper extraction into solution on experimental conditions were constructed using the average values of copper concentration in the solution.

Results and Discussion

Characterization of initial copper concentrate

The chemical composition (wt. %) of the concentrate was: Cu 25,7, Fe 24,1, Si 10,9.

Chalcopyrite ($CuFeS_2$) and quartz (SiO_2) have been identified as crystalline phases in the starting concentrate according to XRD analysis (Fig.1).

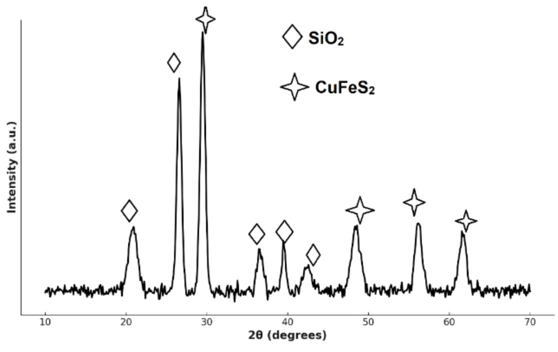

Figure 1 – XRD pattern of chalcopyrite sample

Visually, the concentrate appeared as a finely dispersed powder with a grayish-golden hue and a characteristic metallic luster, indicating a high content of copper sulfides. Light, matte inclusions were observed within the powder, corresponding to quartz impurities. The visual homogeneity of the concentrate suggested a uniform phase distribution, which could facilitate a consistent and efficient leaching process.

Leaching experiments

Effect leaching conditions on copper recovery

Within this period, ranging from 0 to 60 minutes, all three acid concentrations (0,5 M, 1,0 M, 1,5 M) showed an increase in copper recovery. For the 30th minute, copper recovery is 34% for 0,5 M, 41% for 1,0 M, and 47% for 1,5 M. Indeed, the result has shown that with the increment in acid concentration, copper leaching had been performed more efficiently in the first stage. At 60 minutes, copper recoveries further increased to 49% for 0,5 M, 54% for 1,0 M, and 57% for 1,5 M, which stipulates that the leaching process continued accelerating. During the intermediate period, between 60 to 120 minutes, copper recovery further increases at a slow rate. During the end of the 90th minute, the recovery rates were 64% for 0,5 M, 67% for 1,0 M, and 68% for 1,5 M. The uptrend follows through to the 120-minute mark and attains the percentages of recovery: 69% for 0,5 M, 79% for 1,0 M, and 81% for 1,5 M. Conspicuously, the deviation between the 1,0 M and 1,5 M copper recoveries is starting to widen at this moment, where 1,5 M has the better performance. The last stage is the recovery, which, after 120-210 minutes, slowly approaches a plateau. Within the 150th minute, recoveries reach 70%, 81%, and 84% for 0,5 M, 1,0 M, and 1,5 M, respectively. Additional slight increments up to the 210th minute result in the stabilization of copper recovery at 72%, 84%, and 86% recovery for 0,5, 1,0, and 1,5 M, respectively. Increasing the concentration of glycolic acid favored the increase of copper recovery, with the highest gains at higher concentrations. However, at 120 minutes, the rate of increase becomes minimal since complete leaching has taken place, and any further increase in the acid concentration becomes almost negligible.

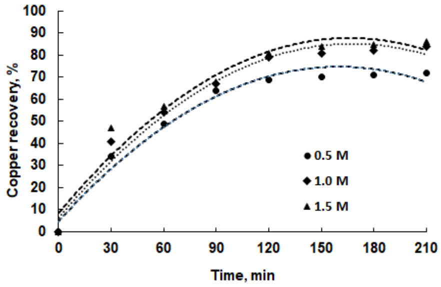

Figure 2 – Effect of glycolic acid concentration on copper recovery into solution at 75ºC in the presence of 30% (v/v) ethylene glycol and 0,8% (w/v) SLS

Since raising the acid concentration beyond 1,0 M did not significantly influence copper extraction into the solution, subsequent experiments were conducted using this acid concentration.

Figure 3 illustrates the impact of ethylene glycol content in the solution on copper extraction, while the other experimental parameters were kept constant: temperature at 75ºC, glycolic acid concentration at 1,0 M, and SLS concentration at 0,8% (w/v).

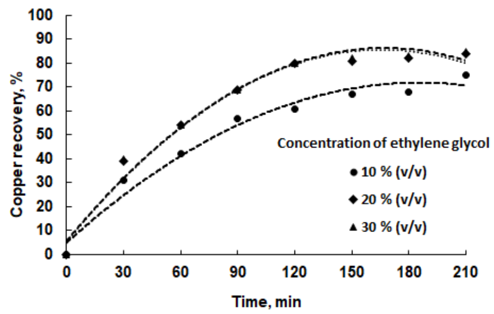

Figure 3 – Effect of ethylene glycol concentration on copper recovery into solution at 75ºC in the presence of 1.0 M of glycolic acid and 0,8% (w/v) SLS

At the beginning of the leaching, copper extraction increases noticeably with higher ethylene glycol concentrations. After 30 minutes, copper recovery reaches 31% with 10% ethylene glycol, 39% with 20%, and 40% with 30%. By the 60 minute, extraction rises to 42% for 10% ethylene glycol and 54% for both 20% and 30%. This trend of increasing copper extraction continues further. By 90 minutes, copper recovery climbs to 57% for 10% ethylene glycol, and 69% for both 20% and 30%. At 120 minutes, extraction reaches 61% for 10% and 80% for both 20% and 30%. After 120 min of leaching, copper recovery begins to level off. At 150 minutes, recovery stands at 67% for 10%, 81% for 20%, and 82% for 30%. By the end of the 210-minute period, extraction reaches 75% for 10% ethylene glycol, 84% for 20%, and 85% for 30%. Subsequent experiments were carried out with 20% (v/v) ethylene glycol in the solution.

It was important to identify the effect of temperature on copper extraction during leaching. Higher temperatures accelerate the dissolution of minerals, and enhance the rate of copper extraction. However, it is also essential to determine the optimal temperature at which the process yields the highest copper recovery without causing unnecessary energy consumption or potential degradation of the leaching agents.

Figure 4 shows the effect of temperature on copper recovery from chalcopyrite in the presence of 1,0 M of glycolic acid, 20% (v/v) ethylene glycol and 0,8% (w/v) SLS.

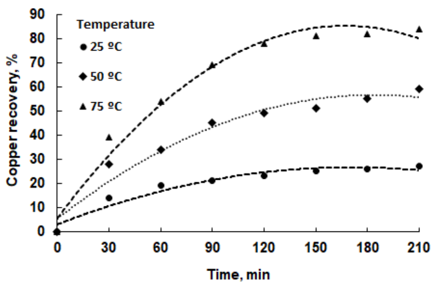

Figure 4 – Effect of leaching temperature on copper recovery into solution in the presence of 1.0 M of glycolic acid, 20% (v/v) ethylene glycol and 0,8% (w/v) SLS

The temperature has a significant effect on the rate of copper extraction. At the lowest temperature of 25ºC, copper recovery reached only 14% after 30 minutes and gradually increased to 27% after 210 minutes. When the temperature is increased to 50ºC, copper recovery improves markedly. After 30 minutes, recovery doubles to 28%, and by 120 minutes, it reaches 49%, more than double the recovery at the same time point for 25ºC. At the highest temperature tested, 75ºC, the copper recovery is even more pronounced. After just 30 minutes, recovery is 39%, which is nearly three times higher than at 25ºC. By 120 minutes, copper recovery reaches 78%, and it continues to increase slightly to 84% by 210 minutes.

Thus, the following optimal conditions for copper leaching from chalcopyrite were found: 1,0 M of glycolic acid, 20% (v/v) ethylene glycol, 0,8% (w/v) SLS, 75ºC. These conditions provide up to 85% copper in solution.

Proposed leaching mechanism

The proposed mechanism for copper recovery from chalcopyrite ($CuFeS_2$) consists of several crucial steps that depend on the synergistic interaction of glycolic acid, sodium lauryl sulfate (SLS), ethylene glycol, and temperature. Glycolic acid serves as the primary leaching agent, breaking the Cu-S bonds in chalcopyrite and facilitating the release of Cu^{2+} ions into the solution:

$$CuFeS_2 + 2H^+ \rightarrow Cu^{2+} + Fe^{2+} + 2HS^-$$

These copper ions are then stabilized by forming complexes with glycolic acid, which prevents their reprecipitation as insoluble compounds and enhances the efficiency of the leaching process.

SLS plays a crucial role as a surfactant, reducing the surface tension of the leaching solution. This reduction in surface tension improves the penetration of the leaching solution into the chalcopyrite matrix and disrupts the formation of passivating sulfur layers that can hinder the leaching process. SLS molecules adsorb onto the surface of the mineral, enhancing the accessibility of the leaching agents to the chalcopyrite, thereby improving copper recovery efficiency:

$$S^{2-} + SLS \rightarrow \text{(surface disruption, aiding } Cu^{2+} \text{release)}$$

Ethylene glycol, employed as a solvent modifier, further improves the leaching process by preventing the formation of continuous sulfur layers, thereby facilitating more effective copper extraction, that might otherwise passivate the mineral surface and impede further leaching. Ethylene glycol also increases the solubility of hydrophobic sulfur species, preventing their accumulation on the mineral surface and facilitating more effective copper extraction:

$$S + C_2H_4(OH)_2 \rightarrow \text{Solubilized Sulfur species (in solution)}$$

The final step involves the recovery of copper as it remains in solution stabilized by glycolic acid and aided by the presence of SLS and ethylene glycol:

$$Cu^{2+}\text{(complexed)} + HOCH_2\,COOH \rightarrow \text{Recovered Copper in Solution } (Cu^{2+}\text{-complex})$$

Conclusions

This work presents the efficiency of the «Glycolic acid – Ethylene glycol – Sodium lauryl sulfate» system for copper recovery from chalcopyrite. The optimal conditions found in this work were 1,0 M glycolic acid, 20% (v/v) ethylene glycol, 0,8% (w/v) SLS, and temperature 75ºC; under these conditions, a copper recovery of up to 85% was achieved. Once the concentration of glycolic acid was > 1,0 M, further increases in the concentration resulted in only a small increase in extraction efficiency, and 20% was sufficient for ethylene glycol. The maximum extent of copper was achieved at 75ºC for the operating temperature. In the leaching process, the combined action of glycolic acid, which dissolved chalcopyrite and complexed copper ions, SLS, which ruptured the sulfur layer, and ethylene glycol inhibited sulfur precipitation.

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ЭФФЕКТИВНОЕ ИЗВЛЕЧЕНИЕ МЕДИ ИЗ ХАЛЬКОПИРИТА С ИСПОЛЬЗОВАНИЕМ СИСТЕМЫ «ГЛИКОЛЕВАЯ КИСЛОТА – ЭТИЛЕНГЛИКОЛЬ – ЛАУРИЛСУЛЬФАТ НАТРИЯ»

В настоящем исследовании рассматривается более эффективный и экологически чистый процесс извлечения меди из халькопирита с использованием недавно разработанной системы выщелачивания, содержащей гликолевую кислоту, этиленгликоль и лаурилсульфат натрия (ЛСН). Соответственно, при оптимальных условиях извлечения меди было достигнуто до 85%: 1,0М гликолевой кислоты, 20% этиленгликоля, 0,8% ЛСН и температуре 75°С. Эта гликолевая кислота действует синергически, способствуя разрушению халькопирита и стабилизируя ионы меди в растворе. ЛСН улучшает проникновение раствора за счет разрушения пассивирующего слоя серы; этиленгликоль предотвращает осаждение серы. Из полученных результатов следует, что данная система выщелачивания может быть альтернативой, более устойчивой и эффективной по сравнению с традиционными пирометаллургическими методами обработки, с возможным применением в промышленном процессе извлечения меди.

Ключевые слова: *халькопирит; извлечение меди; выщелачивание, гликолевая кислота; этиленгликоль; лаурилсульфат натрия.*

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«ГЛИКОЛЬ ҚЫШҚЫЛЫ – ЭТИЛЕНГЛИКОЛЬ – НАТРИЙ ЛАУРИЛ СУЛЬФАТЫ» ЖҮЙЕСІН ПАЙДАЛАНА ОТЫРЫП, ХАЛЬКОПИРИТТЕН МЫСТЫ ТИІМДІ АЛУ

Бұл зерттеу құрамында гликоль қышқылы, этиленгликоль және натрий лаурил сульфаты (НЛС) бар жаңадан әзірленген шаймалау жүйесін пайдалана отырып, халькопириттен мыс алудың тиімдірек және экологиялық таза процесін қарастырады. Тиісінше, мыс алудың оңтайлы жағдайында 85%-ға дейін қол жеткізілді: 1,0 М гликоль қышқылы, 20% этиленгликоль, 0,8% НЛС және 75°C. Бұл гликоль қышқылы синергетикалық әсер етеді, халькопириттің жойылуына ықпал етеді және ерітіндідегі мыс иондарын тұрақтандырады. НЛС күкірттің пассивті қабатын бұзу арқылы ерітіндінің енуін жақсартады; этиленгликоль күкірттің тұнбаға түсуіне жол бермейді. Алынған нәтижелерден, бұл шаймалау жүйесі дәстүрлі пирометаллургиялық өңдеу әдістерімен салыстырғанда неғұрлым тұрақты және тиімді балама бола алады, мыс алудың өнеркәсіптік процесінде қолдануға болады.

Түйін сөздер: *халькопирит; мыс алу; шаймалау, гликоль қышқылы; этиленгликоль; натрий лаурилсульфаты.*

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