

Comparative Studies of the Effects of Magnetite and Ferric Chloride in the Leaching of Chalcopyrite

WSC Chauke, W Nheta and E Fosso-Kankeu

Abstract— Chalcopyrite is the most abundant copper mineral, accounting for nearly 70% of global reserves, but its industrial exploitation faces challenges due to its refractory nature and surface passivation during leaching. Conventional ferric chloride systems offer strong oxidative conditions and enhanced copper solubility, while recent studies highlight the role of magnetite as a catalytic additive that enhances dissolution through galvanic interactions. Understanding these comparative effects is vital for optimizing copper recovery and reducing process inefficiencies. In this study, chalcopyrite samples were subjected to controlled leaching experiments using ferric chloride and magnetite enhanced systems under acidic conditions. The methodology involved monitoring leaching kinetics and ion release while varying temperature from 25°C to 65°C at a pH of 1.5, and reagent concentrations varying from a ratio of 1:1 to 1:5. Magnetite's role in galvanic coupling, passivation prevention, and activation energy reduction was particularly evaluated against the baseline ferric chloride system. The obtained results suggest that magnetite-enhanced leaching achieves sustained dissolution rates, reduced activation energy, and minimized passivation effects compared to ferric chloride. Copper recovery of 86% with fewer impurities is anticipated using ferric chloride, also indicating that magnetite provides a cost-effective and environmentally favourable alternative. These findings may guide future hybrid system development for efficient chalcopyrite processing.

Keywords— Chalcopyrite Leaching, Ferric Chloride, Magnetite, Galvanic Interaction, and Copper Recovery.

I. INTRODUCTION

Chalcopyrite (CuFeS_2) is the most abundant copper-bearing mineral and serves as the main source of global copper production, contributing roughly 70% of the world's copper supply [1]. This copper iron sulphide mineral contains about 34.5% copper, 30.5% iron, and 35% sulphur by weight, making it a highly valuable material in the mining industry [2]. With the rising global demand for copper in sectors such as electronics, construction, and renewable energy, understanding the dissolution behaviour of chalcopyrite is essential for improving extraction methods and enhancing the

efficiency of copper recovery operations.

Under different leaching conditions, chalcopyrite outlines different setbacks which appear to be very significant in the hydrometallurgical processing because for its characteristic's attributes in poor dissolution kinetics [3]. Minimal rate of reaction is due to formation of passive layer that acts as an obstacle, sufficiently blocking the leaching process and lowering the recovery of copper [4]. The passive film formed if mainly made up of sulphide phases, elemental sulphur and precipitated iron compounds [5].

In the beginning of the leaching process iron dissolution is mainly favoured rather than copper and this process led to the formations of passive layer. A metal-deficient sulphide layer will then form with a chemical formula, $\text{Cu}_{1-x}\text{Fe}_x\text{S}_2$ [6]. These changes in terms of composition change the chemistry of the surface of the mineral, leading to the development of the protective layer that slowly reduce the leaching rate. With these attributes of the film not fully understood, the impacts on the leaching kinetics are substantial and is a major barrier.

Ferric chloride and magnetite are leaching agents being implemented to help minimize these leaching challenges faced in the leaching of chalcopyrite [7, 8]. Ferric chloride is more favourable because of its oxidizing capabilities and its formation of stable chloride complexes with copper which has the potential to minimize the formation of the film that passivates. Magnetite plays a role of a catalyst as well as encouraging mechanical disturbances of films on the surface while increasing electron transfer reactions [9]. This research compares the action of the two leaching agents in a leaching vessel to increase the efficiency of the leaching of chalcopyrite while minimizing the formation of the passive film.

II. METHODOLOGY

A. Sample Preparation

Chalcopyrite concentrate was pulverized to meet the targeted particles size. Pulverizing was essential for the purpose of acquiring the fines for analysis and liberating the minerals in the concentrate and increase the surface area so that there is an increased chemical reaction.

B. Sample Characterization

The pulverized chalcopyrite concentrate was then taken for

WSC Chauke¹, Department of Metallurgy at the University of Johannesburg in South Africa.

W Nheta², Department of Metallurgy at the University of Johannesburg in South Africa.

Elvis Fosso-Kankeu², Department of Metallurgy at the University of Johannesburg in South Africa

analysis, where the samples different characteristic were identified. Some of the characteristics identified include elemental composition, interlocked minerals, passive films and this analysis helped come up with better ways of acquiring the element of interest withing the concentrate. The techniques used included X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Atomic Absorption Spectroscopy (AAS).

XRF helped in identifying the elemental composition of chalcopyrite. The purpose of XRD was to identify and characterize the crystalline structure of the sample material. SEM provided high-resolution visualization of the surface morphology and microstructure. With SEM, it was possible to identify the passive films responsible for reducing the leaching kinetics of chalcopyrite. Lastly, AAS measured metal concentrations in solution. In each of these techniques, a 10 g sample was analysed.

C. Leaching Agent Preparation

To leaching ferric chloride was crushed into power to allow it to dilute with the solution in the process of leaching. The ferric chloride was then taken for the leaching of chalcopyrite. For Magnetite, the sample was pulverized to very fine particles to increase the surface area to maximize the working reaction of the leaching process.

D. Leaching Process

The experiment was performed in a conical flask with a volume of 250 mL. For each run that was conducted, a 5 g chalcopyrite sample was used. The top was closed with a wash glass so that oxygen was allowed to enter the system while reducing the loss of water. To block significant fluctuations in the redox potential of the solution at the start of the leaching process, the suspension was maintained between 10% to 30% pulp density (w/v). Before the beginning of each test, ferric chloride was added.

The kinetic studies of chalcopyrite leaching with ferric chloride were carried out at different ratios of chalcopyrite to ferric chloride: 1:1, 1:2, 1:3, 1:4, and 1:5. The pH was set at 1.5 using sulfuric acid with a purity of about 98%. The process temperature was varied at 25°C, 35°C, 45°C, 55°C, and 65°C.

The sample solution was then placed in the conical flask and stirred at a speed of 300 rpm. At the end of each time interval of 2, 4, 6, 8, and 10 hours, 10 mL of solution was drawn and filtered. The pregnant leach solution was analysed using Atomic Absorption Spectroscopy (AAS). The process was repeated using magnetite as a leaching agent to allow for a fair comparison between the two leaching agents.

III. RESULTS AND DISCUSSION

A. Characterization Results

XRF

Table 1, shows XRF results obtained from the analysis of Chalcopyrite concentrate. And figure 1 shows calculations of

%Cu as per XRF analysis and the mass of the copper in a 5g chalcopyrite concentrate.

TABLE 1:
XRF RESULTS

COMPONENTS	PERCENTAGE COMPOSITION
SO ₃	20,195 %
CaO	10,1184 %
Fe ₂ O ₃	27,455 %
CuO	32,785 %

The composition presented on table 1 from XRF aligns with typical chalcopyrite mineralogy, which contains substantial amounts of copper and iron sulfides [1, 3]. The high CuO content confirms that the ore was rich in copper, suitable for comparative leaching tests. According to [2], Fe₂O₃ contains about 27,455% plays a role in redox cycling that sustains the oxidative leaching of chalcopyrite.

Therefore, the sample quality was appropriate for both ferric chloride and magnetite leaching comparisons.

XRD

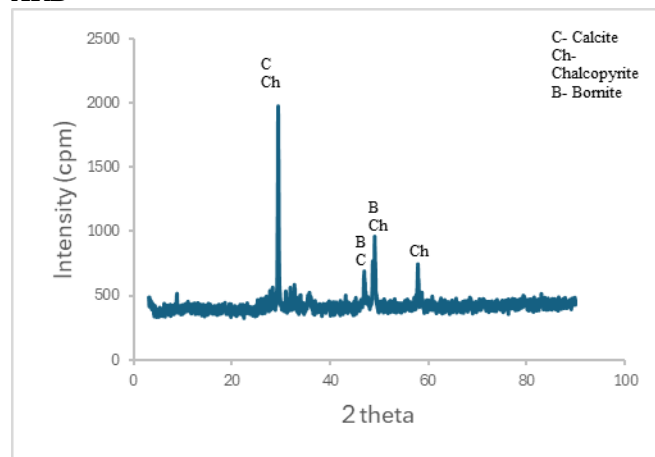


Fig. 2: XRD results of Chalcopyrite

The detection of chalcopyrite confirms the main cause of the leaching difficulty, as this mineral is known for its resistance to dissolution. The presence of bornite (Cu₅ FeS₄), a more reactive secondary copper sulphide, can enhance leaching performance by contributing to higher copper recovery during the initial stages. Meanwhile, calcite (CaCO₃) tends to react with acid, thereby consuming part of the leaching reagent and buffering the solution's pH, which in turn lowers the effective acidity and influences both reagent usage and reaction kinetics.

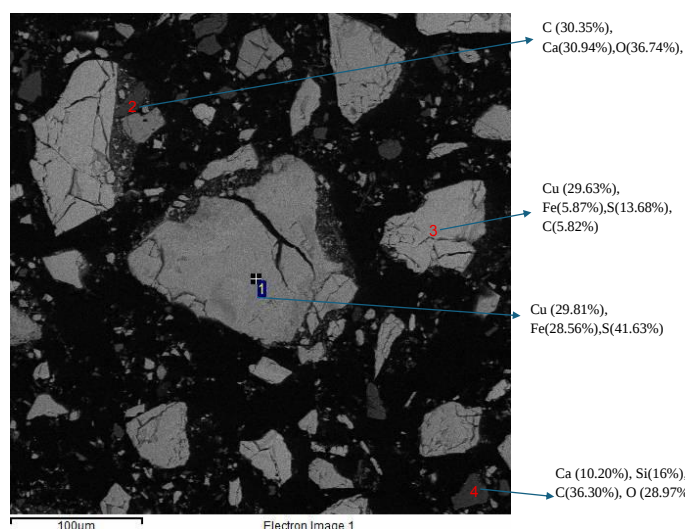


Fig.1: SEM results of Chalcopyrite

The SEM images showed that the chalcopyrite particles possessed irregular shapes with coarse and uneven surfaces, characteristic of natural sulphide minerals. The particles were seen as dense clusters with fine intergrowths and small surface fractures, reflecting mineral heterogeneity and potential reactive sites. Such morphological features indicate that the sample has an adequate surface area to facilitate leaching once in contact with the leaching solution. The observed texture also aligns with the XRD findings, confirming chalcopyrite as the main mineral phase accompanied by minor associated minerals.

RECOVERIES

A. Leaching of Chalcopyrite using Ferric chloride at different ratios

Figure 4 below shows the recoveries in the leachate obtained from the leaching of chalcopyrite using ferric chloride, varying the ratio to get an optimum ratio from the difference ratios used.

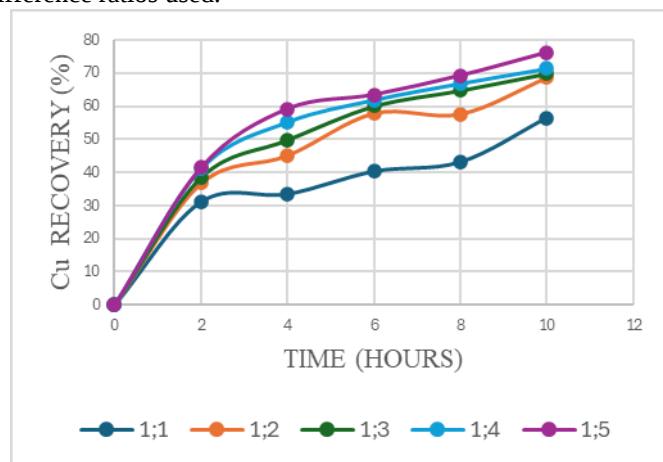


Fig. 4: Recovery of copper using ferric chloride at different ratios

Figure 4 illustrates how different chalcopyrite to FeCl_3

ratios (1:1–1:5) influence copper recovery. The results indicate that copper recovery improved with increasing ferric chloride concentration, achieving an optimum of approximately 78% at a 1:5 ratio. This pattern aligns with the observations of Dutrizac [7] and Carneiro & Leão [10], who reported that higher Fe^{3+} levels promote chalcopyrite dissolution by sustaining a strong oxidation potential. With more ferric ions present, greater Fe^{3+} availability enhances the oxidation of Cu^+ and Fe^{2+} species, leading to breakdown of the sulphide lattice and improved copper dissolution. However, excessive FeCl_3 may cause higher chloride complexation and viscosity, which could restrict mass transfer at very high concentrations [11]. Thus, the plateau beyond the 1:5 ratio suggests that the system attained nearly maximum reaction efficiency under the existing stirring and temperature conditions.

B. Leaching of Chalcopyrite using Ferric chloride at different temperatures

Figure 5 Below shows the recoveries in the leachate obtained from the leaching of chalcopyrite using ferric chloride at different temperature to get the best recovery for the leaching process.

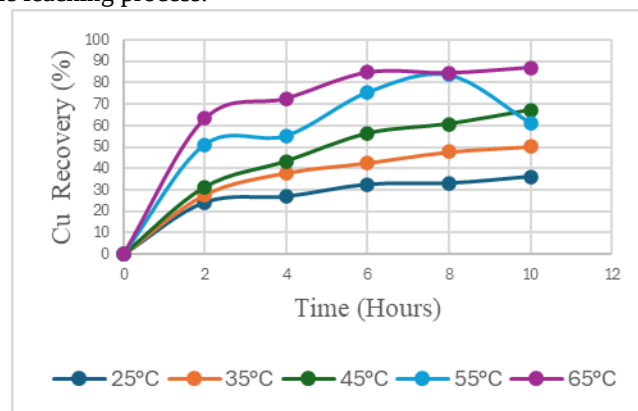


Fig. 5: Recovery of copper using ferric chloride at different temperatures

Figure 5 shows the effect of temperature (25°C–65°C) on chalcopyrite dissolution. The results showed a consistent rise in copper recovery as temperature increased, peaking at around 65°C with approximately 85% recovery. This trend demonstrates the temperature dependence of the leaching kinetics, where higher temperatures enhance both the oxidation of CuFeS_2 and the regeneration of Fe^{3+} ions. The steeper slope at elevated temperatures suggests improved electron transfer and disruption of the passive film. Higher temperatures also promote the dissolution of elemental sulphur, reducing surface passivation. These findings align with literature reports indicating that optimal FeCl_3 leaching occurs between 80–90°C; however, even at 65°C, this study achieved significant recovery, confirming the strong oxidizing capability of the system.

C. Leaching of Chalcopyrite using magnetite at different ratios

Figure 6 below shows the recoveries in the leachate obtained from the leaching of chalcopyrite using magnetite, varying the ratio to get an optimum ratio from the different ratios used.

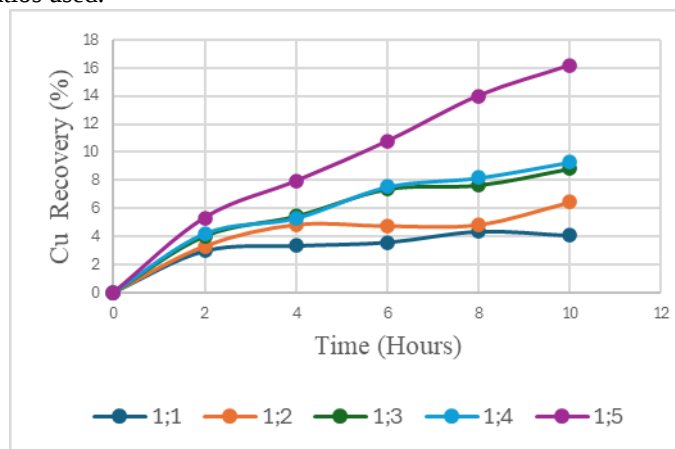


Fig. 6: Recovery of copper using magnetite at different ratios

In this study, magnetite was added at different chalcopyrite-to-magnetite ratios (1:1 to 1:5) to evaluate its catalytic influence. The findings showed a moderate rise in copper recovery, reaching a maximum of about 16% at the 1:5 ratio, though with a gentler slope compared to ferric chloride. Magnetite promotes chalcopyrite leaching primarily through catalytic electron transfer and mechanical activation rather than direct oxidation. The slower reaction rate relative to FeCl_3 leaching occurs because magnetite functions indirectly, depending on surface contact and dissolved oxygen. Hence, increasing magnetite concentration enhances the process by supplying more catalytic sites and surface area, beyond a certain point, further addition yields little improvement, likely due to particle agglomeration or magnetite surface

D. Leaching of Chalcopyrite using magnetite at different temperatures

Figure 7 illustrates the recoveries of Cu obtained from the leaching of chalcopyrite using Magnetite at different temperatures.

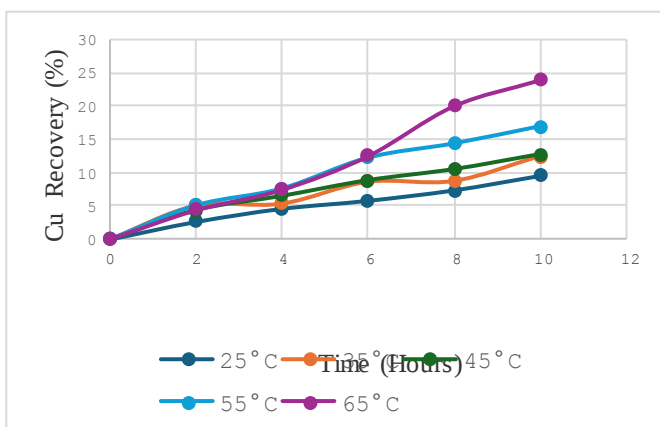


Fig. 7: Recovery of Copper using Magnetite at different temperatures

Figure 7 presents the impact of temperature variation (25°C–65°C) on copper recovery during chalcopyrite leaching in the presence of magnetite as a catalyst. The results showed a steady rise in copper recovery with increasing temperature, reaching about 24% at approximately 65°C. This trend demonstrates that temperature significantly influences the kinetics of chalcopyrite dissolution when magnetite is involved. Higher temperatures accelerate redox reactions and ion diffusion, promoting faster electron transfer between chalcopyrite and magnetite surfaces. Compared with ferric chloride leaching (Figure 3), magnetite-assisted leaching yielded lower overall copper recoveries at similar temperatures. This agrees with reports that magnetite acts primarily as a catalyst rather than a direct oxidant, facilitating galvanic and catalytic effects instead of direct chemical oxidation [12, 13]. Therefore, although increasing temperature enhances reaction kinetics, the overall copper dissolution remains constrained by the limited availability of oxidizing agents in the system.

SHRINKING CORE MODEL

Figure 8 and 9 below shows the Arrhenius plot which helps with the analysis of the activation energy on the effect of leaching time and temperature of ferric chloride and magnetite respectively.

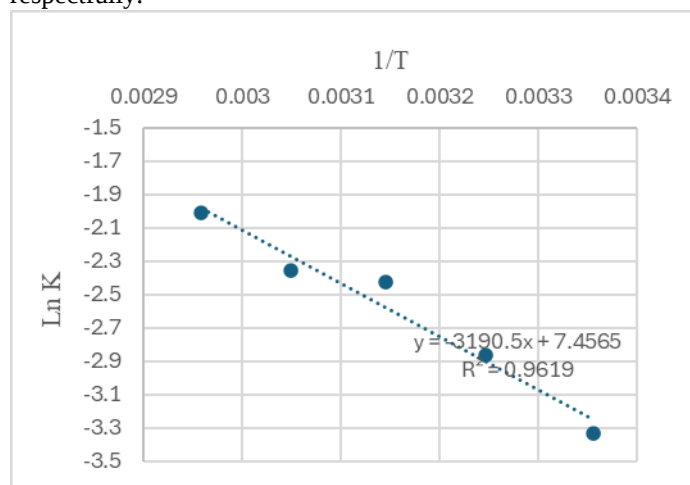


Fig. 8: Arrhenius Plot for the determination of Ea on the effect of leaching time of Ferric

Figure 8 shows a negative slope that the activation energy of the leaching of chalcopyrite using ferric chloride is positive. The activation energy of this reaction is 26,53 kJ/mol. According to Bogdanović et al. [14] and Carneiro & Leão [10], the ferric chloride leaching system usually have an activation energy lying between 40 kJ/mol and 80 kJ/mol, often suggesting that the leaching kinetics is chemically controlled depending on the conditions applied. However, with the Ea of the experimental system being lower than the range it could potentially mean that the system is diffusion controlled.

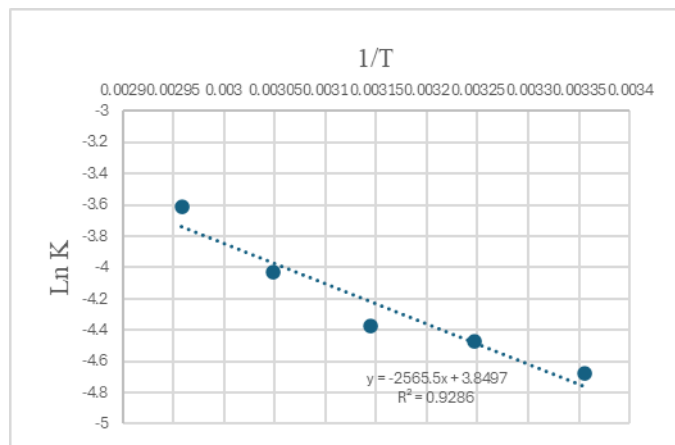


Fig. 9: Arrhenius Plot for the determination of Ea on the effect of leaching time of Magnetite

Figure 9 shows a negative slope that the activation energy of the leaching of chalcopryrite using magnetite is positive. In calculation the activation energy of this reaction is 21,33 kJ/mol. These findings agree with findings by Nyembwe et al. [15] and Nyembwe et al. [9] which indicated that adding magnetite in the leaching system of chalcopryrite reduces the activation energy to 15 kJ/mol to 25 kJ/mol. Therefore, the Ea of 21.3 kJ/mol could potentially mean that the catalyst assists the reaction with lower energy barriers.

IV. CONCLUSION

Therefore, with the aim of the experiment being comparing the studies of the effects of leaching of chalcopryrite using magnetite and ferric chloride, the research has successfully concluded this aim. The research revealed that ferric chloride (FeCl_3) proved to be a more efficient oxidant than magnetite (Fe_3O_4) in chalcopryrite leaching, yielding greater copper recovery and faster reaction rates due to its strong oxidizing ability and chloride complex formation. Although magnetite showed lower reactivity, it enhanced dissolution through catalytic and galvanic interactions, presenting a more sustainable alternative. Both temperature and reagent ratio strongly affected leaching kinetics, with positive activation energies confirming chemical reaction control. In conclusion, ferric chloride exhibited superior leaching efficiency, while magnetite offers potential as an environmentally friendly catalyst for future process improvement and industrial applications.

ACKNOWLEDGMENT

The authors acknowledge the financial support from the Faculty of Engineering and the Built Environment at the University of Johannesburg in South Africa.

REFERENCES

- [1] Kolela J Nyembwe, Elvis Fosso-Kankeu, Frans Waanders, Kasongo D Nyembwe. 2019. Structural, compositional and mineralogical characterisation of carbonatitic copper sulfide concentrator plant streams: Run of mine, concentrate and tailings. *International Journal of Minerals, Metallurgy and Materials*. 26(2): 143-151. <https://doi.org/10.1007/s12613-019-1718-8>
- [2] Kolela J Nyembwe, Elvis Fosso-Kankeu, Frans Waanders and Martin Mkandawire. 2021. pH-Dependent leaching mechanism of carbonatitic chalcopryrite in ferric sulfate. *Transactions of Non Ferrous Metals Society of China*. 31: 2139- 2152. [https://doi.org/10.1016/S1003-6326\(21\)65644-3](https://doi.org/10.1016/S1003-6326(21)65644-3).
- [3] Córdoba, E.M., Muñoz, J.A., Blázquez, M.L., González, F. and Ballester, A., 2009. Comparative kinetic study of the silver-catalyzed chalcopryrite leaching at 35 and 68 C. *International Journal of Mineral Processing*, 92(3-4), pp.137-143. <https://doi.org/10.1016/j.minpro.2009.03.007>.
- [4] Kolela J Nyembwe, Elvis Fosso-Kankeu, Frans Wangers and Edward Ntumba Malenga. 2018. Mineralogical Observation Made During the Kinetic Dissolution Study of Chalcopryrite Mineral in Sulphate Media under Free pH at Room Temperature. Editors: Elvis Fosso-Kankeu, Frans Waanders, Michel Plaisent. 10th Int'l Conference on Advances in Science, Engineering, Technology & Healthcare (ASETH-18) Nov. 19-20, 2018 Cape Town (South Africa). ISBN: 978-81-938365-2-1. Vol II. Pp 144-148.
- [5] Brad Barlow, Elvis Fosso-Kankeu, Kolela J Nyembwe, Frans Waanders and Edward Ntumba Malenga. 2018. Prediction of Dissolution of Copper from a Chalcopryrite Carbonatite Ore of South Africa. Editors: Elvis Fosso-Kankeu, Frans Waanders, Michel Plaisent. 10th Int'l Conference on Advances in Science, Engineering, Technology & Healthcare (ASETH-18) Nov. 19-20, 2018 Cape Town (South Africa). ISBN: 978-81-938365-2-1. Vol I. Pp 96-100.
- [6] Kolela J. Nyembwe, Elvis Fosso-Kankeu, Frans Waanders, Bhekile B. Mamba and Martin Mkandawire. 2024. Chalcopryrite Leaching in Ferric Sulphate: The Effect of Fe_3O_4 - CuFeS_2 Galvanic Couple on the Cu Dissolution. *Minerals*. 14: 162. <https://doi.org/10.3390/min14020162>
- [7] Dutrizac, J.E., 1981. The dissolution of chalcopryrite in ferric sulfate and ferric chloride media. *Metallurgical Transactions B*, 12(2), pp.371-378.
- [8] Deng, S., Yang, J., Wang, Y., Long, T. and Yang, W., 2023. Influence of magnetite on the leaching of chalcopryrite in sulfuric acid. *Arabian Journal of Chemistry*, 16(8), p.104905. <https://doi.org/10.1016/j.arabjc.2023.104905>.
- [9] Kolela J Nyembwe, Elvis Fosso-Kankeu, Frans Waanders, Martin Mkandawire, Didier K Nyembwe, Bhekile B Mamba. 2024. Influence of Fe_3O_4 on redox changes during Cu dissolution from CuFeS_2 in acidified ferric sulfate. *Trans. Nonferrous Met. Soc. China* 34(2024) 1965–1975. [https://doi.org/10.1016/S1003-6326\(24\)66519-2](https://doi.org/10.1016/S1003-6326(24)66519-2)
- [10] Carneiro, M.F.C. and Leão, V.A., 2007. The role of sodium chloride on surface properties of chalcopryrite leached with ferric sulphate. *Hydrometallurgy*, 87(3-4), pp.73-82. <https://doi.org/10.1016/j.hydromet.2007.01.005>.
- [11] Ahmadi, A., Schaffie, M., Petersen, J., Schippers, A. and Ranjbar, M., 2011. Conventional and electrochemical bioleaching of chalcopryrite concentrates by moderately thermophilic bacteria at high pulp density. *Hydrometallurgy*, 106(1-2), pp.84-92. <https://doi.org/10.1016/j.hydromet.2010.12.007>.
- [12] Saavedra, A., García-Meza, J.V., Cortón, E. and González, I., 2018. Understanding galvanic interactions between chalcopryrite and magnetite in acid medium to improve copper (Bio) Leaching. *Electrochimica Acta*, 265, pp.569-576. <https://doi.org/10.1016/j.electacta.2018.01.169>.
- [13] Chehreghani, S., Yari, M., Zeynali, A., Akhgar, B.N., Gharegheshlagh, H.H. and Pishravian, M., 2021. Optimization of chalcopryrite galvanic leaching in the presence of pyrite and silver as catalysts by using Response Surface Methodology (RSM). *Rudarsko-geološko-naftni zbornik*, 36(1). <https://doi.org/10.17794/rgn.2021.1.4>.
- [14] Bogdanović, G., Petrović, S., Sokić, M. and Antonijević, M.M., 2020. Chalcopryrite leaching in acid media: a review. *Metallurgical & Materials Engineering*, 26(2), pp.177-198.

- [15] Kolela Nyembwe, Frans Waanders, Martin Mkandawire, Bhekie Mamba. 2024. Complexity of chalcopyrite mineral affecting copper recovery during leaching. Eds. Elvis Fosso-Kankeu, Bhekie Mamba, Antoine F Mulaba-Bafubandi. 2024. Recovery of Values from Low-Grade and Complex Minerals: Development of Sustainable Processes. Wiley. ISBN: 9781119896418.
<https://doi.org/10.1002/9781119896890.ch6>