Effect of pH during the Reductive Leaching of Chalcopyrite with Activated Carbon

TP Mnguni, O Botlhoko and E Fosso-Kankeu

Abstract— The aim of this study was to determine the effect of pH during the reductive leaching of chalcopyrite with activated carbon. Leaching chalcopyrite is generally slow when using sulphuric acid as a leaching reagent, limiting its potential as an alternative to pyrometallurgical methods. Reductive leaching is used to improve copper extraction by breaking down passivation layers of the mineral using reducing agents like AC, making it easier to dissolve copper. Additionally, AC helps to improve the rate of leaching, especially working in sulphate solutions. The experiment had two leaching stages, first stage being the effect of pH (1.5, 2, 2.5 and 3) at constant temperature of 50ºC. Optimum pH of 1.5 was found in first stage and used in the second leaching stage as a constant where the temperature was varied (25, 35, 45, 55, 65ºC). For both stages time was varied from 2,3,4,5,6,7, to 8 hours and sulphuric acid was the leaching reagent. It was observed that using activated carbon as a catalyst minimized the effect of passivation during leaching, as the highest recovery without the use of AC yielded 2.3% at 1.5 pH and with activated carbon yielded 7.4% at 2pH after 2 hour. Optimal condition at 45ºC for 8hours at the pH of 1.5 yielded 35.26%. Kinetics studies showed the rate limiting factor attributed to the dissolution of Cu to CuFeS2 to be the chemical reaction mechanism. This experimental model was mathematically validated with the near correlation of 0.817. Additionally, activation energy was found to be 25.42 KJ/mol which means that diffusion controlled is the rate limiting step.

Keywords— Chalcopyrite, Activated Carbon, Reductive Leaching, Chemical Reactions.

I. INTRODUCTION

Reductive leaching is a hydrometallurgical method that extracts copper from chalcopyrite by using reducing agents like chromium (II) chloride or vanadium (II) sulphate, resulting in faster reaction rates and better copper recovery compared to traditional oxidative leaching [1]. Activated carbon plays a role in this process as it acts as a catalyst and reducing agent to facilitate electron transfer and breaking the passivation sulphur layer by through galvanic interactions between chalcopyrite(anode) and carbon (cathode). Advantages of this method are higher copper recovery rates, reduced reagent consumption, and lower environmental impact compared to traditional leaching processes, as it minimizes waste generation and energy-intensive oxidation steps. Sulphuric acid is the leaching reagent that will be used to remove cupper from the chalcopyrite concentrate. During leaching, parameters like concentration of leaching reagent, particle size distribution, agitation rate, time, temperature, and pH will be looked at since they affect the rate of leaching. Concentration, time, and leaching temperature will be varied while the other conditions are kept constant at optimum conditions [2].

Chalcopyrite ($CuFeS_2$) holds a significant portion, roughly 70%, of the Earth's copper. While most copper is currently obtained through pyrometallurgy processes, there is growing interest in using hydrometallurgical processing routes. Hydrometallurgical extraction of copper from chalcopyrite is thought to offer potential advantages in cost and environmental impact when compared to pyrometallurgical extraction, particularly for ores with lower copper concentrations [3].

Pyrometallurgical processes for treating copper concentrates have been favoured for their simplicity and cost-effectiveness. However, the presence of unwanted byproducts and the current environmental regulations that limit the emission of toxic gases into the atmosphere make their treatment in smelters more complicated and expensive because it requires additional steps for the removal and safe disposal of the waste materials generated during pyrometallurgical processes. Therefore, hydrometallurgical possessing is used as an alternative for extracting copper from chalcopyrite [4].

Hydrometallurgical processes have benefits compared to pyrometallurgical processes, as impurities stay in the leach solution, allowing them to form harmless solids instead of harmful gases like SO_2, making the process to be more environmentally friendly. Additionally, it offers cheap operating costs. However, lower metal recoveries usually make hydrometallurgical options less practical for business, so improving recovery rates is important to make the competitive alternatives [5].

Chalcopyrite is difficult to extract using hydrometallurgical method because it forms thin layers on its surfaces during leaching. The passivation layers are made of sulphur and iron hydroxides, which further block the reaction and reduce leaching efficiency. Reductive leaching helps by using reducing agents to change the mineral’s oxidation state, breaking down these blocking layers. This process improves copper extraction effectively [6].

TP Mnguni[1] is with the Department of Metallurgy at the University of Johannesburg in South Africa.

O Botlhoko[2] is with the Department of Metallurgy at the University of Johannesburg in South Africa

Elvis Fosso-Kankeu[3] is with the Department of Metallurgy at the University of Johannesburg in South Africa

https://doi.org/10.17758/EARES23.EAP1225219

Activated carbon is used as a catalyst in leaching because of its very porous structure and large surface area, which make it very effective, especially for sulphide minerals like chalcopyrite. Activated carbon acts as a reducing agent by donating electrons, which helps dissolve metal ions and improve the recovery during the leaching process [7].
Chalcopyrite leaching involves dissolving copper into solution under controlled pH and redox conditions. Pourbaix diagram of copper at various pH and potentials, helps to identify optimal leaching conditions, at what pH will copper dissolve in sulphate medium. Copper ions dissolve in acidic solutions with pH typically below 3 and at potentials above 0.5 V at room temperature. Choosing a leaching reagent that maintains these conditions will make efficient copper dissolution and prevent precipitation of insoluble copper compounds [7].

II. METHODOLOGY

A. Characterization

The experiment was conducted using prepared 150g unroasted chalcopyrite concentrate, where 30g was taken for XRF (10g) to determine the elemental composition of the initial concentrate sample, 10g for XRD to identify the mineral phases present, and another 10g for SEM-EDS to examine the morphology and elemental composition of individual particles. The remaining mass was used for the leaching process. After leaching, the next process was solid liquid separation where filtration was used to separate the solid residue from the liquid filtrate (pregnant solution). The liquid filtrate contained the dissolved copper ions and other metals. The pregnant solution was analysed using atomic adsorption spectroscopy (AAS) to determine the concentration of copper.

EXPERIMENTAL PROCEDURE

B. Sample preparation

The activated carbon was pulverized into the pulveriser for 5 minutes to increase its surface area which was further used in the leaching process.

LEACHING PROCESS

The experiment was conducted using unroasted chalcopyrite concentrate. 100g of chalcopyrite concentrate was used for acid leaching process whereby sulphuric acid was used as a leaching reagent and activated carbon was used as a catalyst. The leaching process was conducted at different conditions of pH, time and temperature. In this experiment two leaching stages were used, first stage being the effect of pH and second stage being the effect of temperature. In each stage, 5g of chalcopyrite concentrate was weighed using a glass watch on the top balance then placed into separate beakers of 400ml. After preparing the acid, the 5g of chalcopyrite sample and 10 grams of activated carbon were added at the solution of 150ml of sulphuric acid and the solution was stirred without forming a vortex using a magnetic stirrer at 300rpm whilst maintaining the pH and temperature. The beakers were closed to avoid evaporation. The first stage of leaching process was carried out at four different pH of 1.5, 2, 2.5, and 3 at the constant temperature of 50 ºC and time varied from 2, 3, 4, 5, 6,7, and 8 hours. The optimum pH was found to be 1.5 which was used on the second stage leaching process as a constant were five different temperatures from 25, 35, 45, 55, and 65ºC were used, time varied from 2, 3, 4, 5, 6, 7 and 8 hours. Collecting 15ml every 1-hour interval of the varied time from 2 to 8 hours using a syringe. After the leaching process, the slurry was filtered to separate the filtrate and the residual, and the residue was washed several times with distilled water and then dried in an oven. The pregnant leach solutions were analysed by AAS chemical analysis to determine the concentration of copper. Finally, the copper concentration was used to calculate the percentage yield of copper extracted from the concentrate.

III. RESULTS AND DISCUSSION

A. Characterization

XRF

Before leaching, the X-Ray Fluorescence (XRF) was used to provide the elemental composition of Chalcopyrite concentrate and activated carbon. Table 1 showing the major compounds of chalcopyrite concentrate showing CuO of 29.88% and Fe_2O_3 of 27.82%. The head grades were also calculated obtained to be 26.27% Cu and 19.47% Fe. Table 2 are the major compounds obtained on the XRF results of activated carbon showing Fe_2O_3 of 76.25% and SiO_2 17.68%

TABLE I:
CHALCOPYRITE XRF RESULTS OF MAJOR COMPOUNDS

Oxides	**CuO**	**Fe_2O_3**
Oxides mass%	**32.8751**	**27.8164**
Metal	**Cu**	**Fe**
Metal mass%	**26.27**	**19.47**

TABLE II:
XRF RESULTS FOR ACTIVATED CARBON SHOWING THE MAJOR COMPOUNDS

Oxides	**Mass%**
Fe_2O_3	**76.25**
Fe_2O_3	**17.68**

XRD

Before leaching, X-Ray Diffraction was used to identify and quantify the crystalline phases present in the concentrate, determine relative abundances of minerals, and help in characterizing the physical and chemical properties of the sample. Figure 1 shows the peaks of the minerals that are present in the chalcopyrite concentrate.

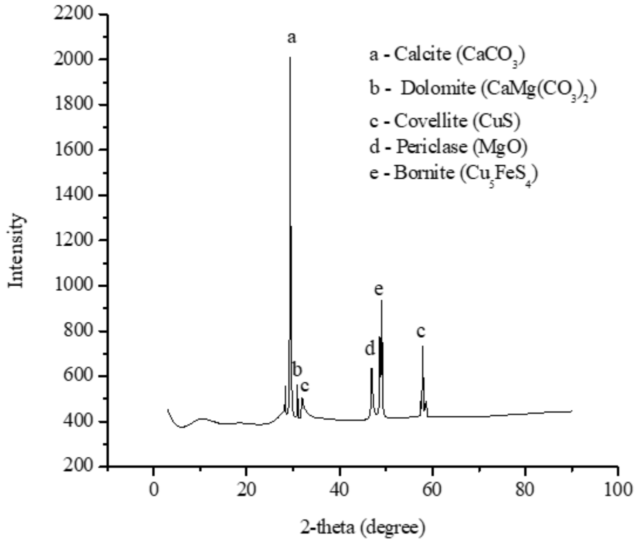

Fig. 1: Chalcopyrite XRD results

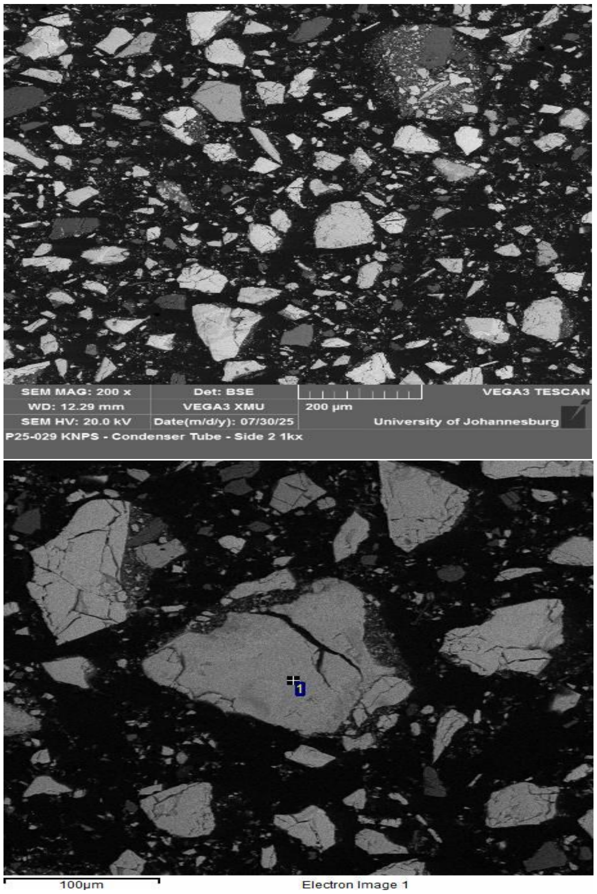

Fig. 2: Chalcopyrite SEM Results before leaching

TABLE III
EDS ANALYSIS SHOWING % COMPOSITION OF THE METALS IN THE AGGREGATE OF CHALCOPYRITE CONCENTRATE

	S%	Cu%	Fe%
Spectrum 1	39.21	59.78	1.01
Spectrum 2	37.47	41.67	20,91

The SEM (Scanning Electron Microscopy) analysis of chalcopyrite reveals both morphological and compositional characteristics typical of this mineral phase. Quantitative EDS analysis, as given in Table 3, demonstrates that the chalcopyrite grains consist of Sulphur (S), iron (Fe) and copper (Cu) of spectrum 1 and 2, having the % composition as shown in Table 3, which is also shown in Figure 2.

B. Effect of pH on Cu recovery without the use of activated carbon

This was the trial leaching process whereby the pH was varied from 1.5, 2, 2.5 and 3 while the temperature was kept constant at 50°C for 2 hours using sulphuric acid as a leaching reagent only. The recoveries were obtained as shown in table 5 and highest recovery at the pH of 1.5 yielded 2,3443%.

TABLE IV:
EFFECT OF PH ON CU RECOVERY WITHOUT ACTIVATED CARBON

	pH	**%Recovery**
2hour leaching	**1.5**	2,3443
	2	1.5433
	2.5	1.0344
	3	0.9384

C. Effect of pH on copper recovery

Figure 6 shows the effect of pH during leaching of chalcopyrite for 2 hours where the temperature was kept constant at 50°C, using sulphuric acid as a reagent and activated carbon as a catalyst and reducing agent. It is observed that the recovery was highest at the pH of 2 at 7.4% followed by pH of 1.5 at 5.4% as shown in table 6. The Cu %recovery decreased as the pH increases to 2.5 and 3 and this shows that the highest recoveries are obtained at low pH values and these results align with the theory in the literature by Alvial Hein, 2017.

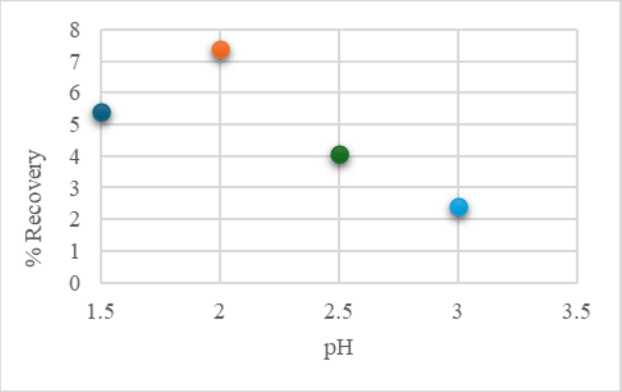

Fig. 3: Graph of Cu %recovery vs pH at 2hour

TABLE V:
TABLE SHOWING DIFFERENT PH AND CU %RECOVERIES AT 2HOUR

	pH	**%Recovery**
2hour leaching	**1.5**	5,4053
	2	7,3974
	2.5	4,0632
	3	2,3900

D. Effect of pH and time on copper recovery

These are the results of stage 1 of leaching, where the pH and time was varied while the temperature was kept constant at 50°C. Sulphuric acid and activated carbon was used.

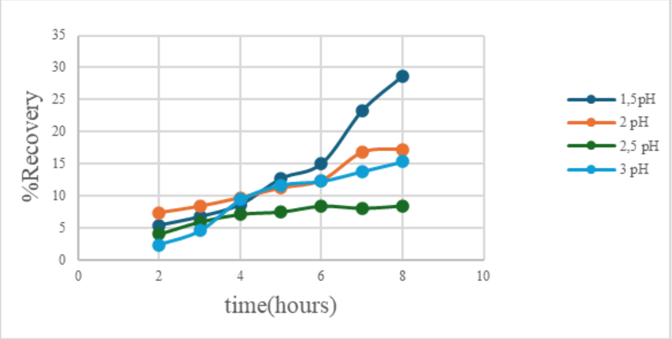

Fig. 4: Effect of pH of the recovery of copper

Figure 4 shows an increasing recovery of copper as the time and pH increases from 2 to 8 hours and 1.5 to 3 respectively. The highest recovery of copper obtained at 2 hours was at the pH of 2 and the lowest at the pH of 3 with 7.4% and 2.4% respectively shown in table 9 in the appendix. The highest recovery of copper obtained at 8 hours was at the pH 1.5 and the lowest at the pH of 2.5 with 28.7% and 8.4% respectively shown in table 9 in the appendix. The pH of 1.5 ended up having higher recovery than pH 2 and this shows that time is also a factor during the leaching process [. Results show that the ideal leaching pH would be 1.5 and the time of leaching would be 8hour (28,719% Cu recovery).

E. Effect of temperature on Cu recovery

These are the results for the second stage of leaching where the optimal pH of 1.5 found the stage 1 of leaching is used as a constant. The temperature and time were varied, using sulphuric acid as a reagent and activated carbon as a catalyst.

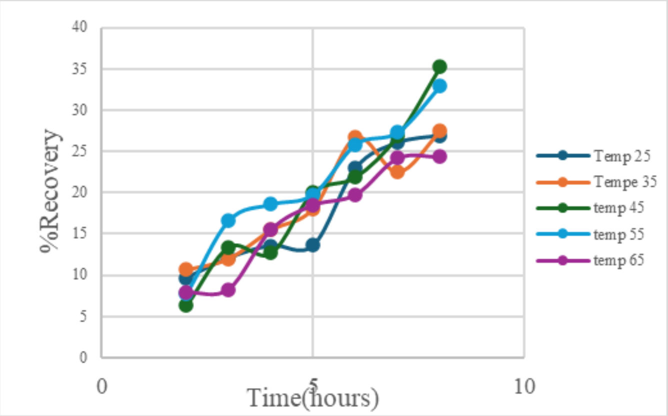

Fig. 5: Effect of temperature on the recovery of copper

The graph on Figure 5 shows the recoveries of copper with change in temperature and time from 25 to 65˚C and 2 to 8 hours at the constant pH of 1.5 respectively. The graph shows an increasing trend as time increases the % recovery of copper also increases. The highest recovery of copper obtained at 2 hours was at the temperature of 35˚C and the lowest at the temperature of 45˚C with 10.7% and 6.3% respectively shown in table 10 in the appendix. The highest recovery of copper obtained at 8 hours was at the moderate temperature of 45˚C and the lowest at the temperature of 65˚C with 35.3% and 24.4% respectively shown in Table 5 in the appendix.

F. Thermodynamic results of leaching

The reductive leaching of chalcopyrite with activated carbon in sulfuric acid follows a unique combination of thermodynamic principles and reaction mechanisms. In this process, activated carbon acts as a reducing agent and catalyst, facilitating galvanic interactions and electron transfer that enhance copper extraction. During the dissolution of chalcopyrite ($CuFeS_2$), copper and iron ions are the main species released into solution, with elemental sulphur as a common byproduct.

Chalcopyrite Dissolution by Sulfuric Acid

$CuFeS_2$ (s) + $4H_2SO_4$ (aq) → $CuSO_4$ (aq) + $FeSO_4$ (aq) + 2S0 (s) + $4H_2O$ (l)

Oxidative Leaching with Fe (III) or Oxygen

$CuFeS_2$ (s) + $4Fe_2(SO_4)_3$ (aq) → $CuSO_4$ (aq) + $5FeSO_4$ (aq) +2 S_0 (s) (2)

The standard free energy, enthalpy and entropies of formations from the table were used to calculate the Gibbs free energy, ΔG°. The large negative Gibbs free energy values for all reactions indicate that they are thermodynamically favourable.

TABLE VI:
THERMODYNAMICS DATA

	kJ/mol	kJ/mol	J/mol. K
	dG	dH	dS
$CuFeS_2$	-324	-324	124.98
H_2SO_4	-690.1	-813.99	156.9
$CuSO_4$	-661.9	-771.4	108.8
$FeSO_4$	-825.1	-928.4	120.9
S^0	0	0	31.9
H_2O	-237.2	-285.8	69.9
$Fe_2(SO_4)_3$	-2263.1	-2581.5	307.2
Overall dG	Reaction 1 = - 241.0kJ/mol	Reaction 2 = - 523.6kJ/mol	

Leaching kinetics

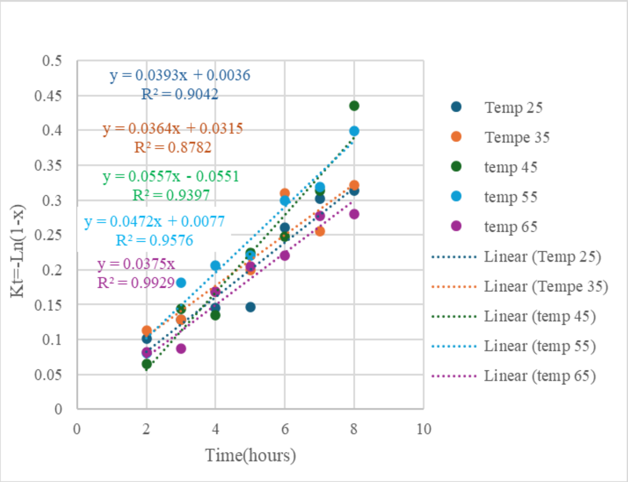

Fig. 6: Diffusion controlled reaction

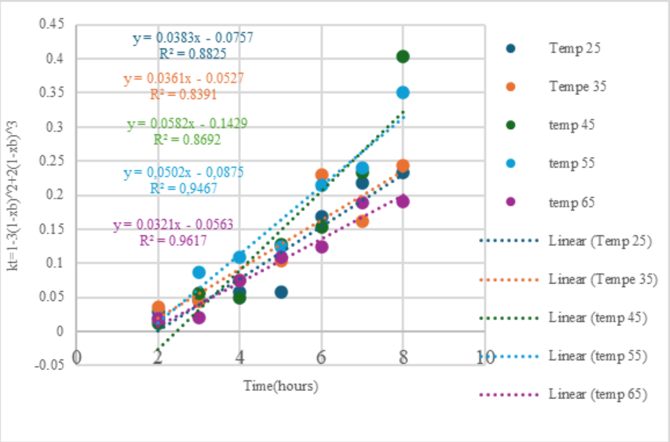

Fig. 7: Ash diffusion-controlled reaction

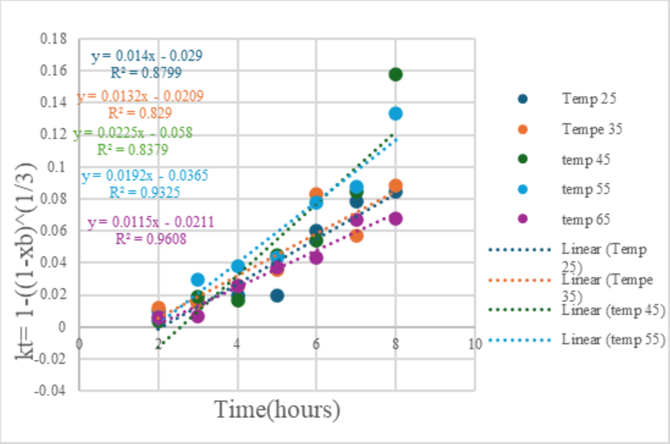

Fig.*8*: Chemical reaction at interface

TABLE VII: AVERAGE R-SQUARE VALUES OF DIFFERENT KINETIC MECHANISMS UTILIZED

R^2 values		
0,9042	0,8825	0,8799
0,8782	0,8391	0,829
0,9397	0,8692	0,8379
0,9576	0,9467	0,9325
0,9929	0,9617	0,9608
0,93452	0,89984	0,88802

Kinetic studies done using the 3 models were done on the (X) fractions of Cu recoveries after leaching. Graphs were plotted in Figure 6, 7 and 8 above. To highlight the mechanism that best fit and controlled the rate of reaction, R^2 values from each model which are tabulated in table8 were used to determine the total average. Based on the average R^2 highest and closest to 1, the rate limiting factor during the dissolution of Cu from $CuFeS_2$ after leaching follows the solid product layer diffusion kinetic mechanism R^2 value being 0.93452. This means, rising the temperature makes the chemical reaction to increase faster than diffusion, and the overall Cu recoveries are limited by how quicky reactants can diffuse through the product layer.

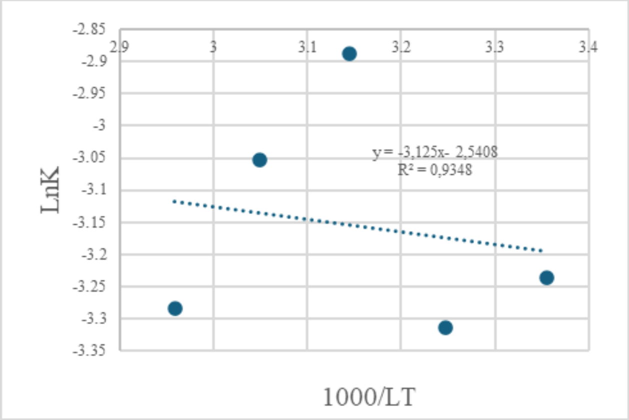

Fig.9: ln(k) vs. 1000/T Graph for the determination of activation Energy

The temperature dependence on the rate constant (k) for most chemical reactions is defined by the Arrhenius equation:

$\boldsymbol{k}=\boldsymbol{k0exp}\ (-\boldsymbol{Ea}/\boldsymbol{RT})$

Ln(k) = In (k) ($-Ea$/RT)

Slopes of the fitted straight lines were considered as the rate constants. Using the apparent rate constants along with the Arrhenius plots of ln(k) vs. 1000/T the activation energy was calculated.

EaCu = -k × R

EaCu =-(-3,125) *8,214

EaCu = 25,4188 KJ/mol

Activation energy is regarded as the minimum energy required for a reaction to occur, smaller activation energy values (<40 KJ/mol) are related to the case where diffusion is rate-limiting step. This implies that the dissolution rate is dependent on diffusion controlled whereby the reactions generally have relatively low activation energies since they mainly depend on the energy needed for molecules to move through the medium. This can be seen by more copper going to the solution as leaching temperature is increasing.

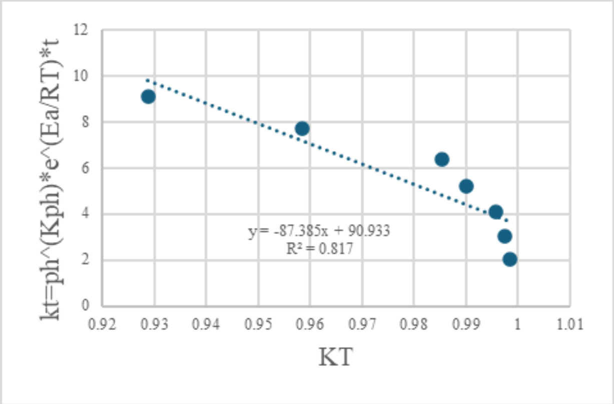

Fig. 10: Mathematical Validation of the Diffusion controlled mechanism

To validate the controlling mechanism identified for further certainty, diffusion control mechanism kinetic was mathematically plotted where, the R^2 value of 0,817 shows the mathematical validity and the near correlation of the calculated model to the experimental model utilized.

IV. CONCLUSION

The aim of this study was to determine the effect of pH during the reductive leaching of chalcopyrite with activated carbon. It was observed that using activated carbon as a catalyst minimized the effect of passivation during leaching, as the highest recovery without the use of AC yielded 2.3% at 1.5pH and with activated carbon yielded 7.4% at 2pH after 2 hour. Ideal leaching condition at 45ºC for 8hours in a pH of 1.5 yielded 35.26% Copper. Kinetic studies revealed the rate limiting factor attributed to the dissolution of Cu from $CuFeS_2$ when in contact with sulphuric acid at the ideal leaching conditions to be the chemical reaction mechanism. This experimental model was mathematically validated and achieved a near correlation of 0.817. Additionally, the activation of 25,4188 KJ/mol was obtained which is emphasis the case where diffusion controlled is the rate limiting step.

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] Dreisinger, D. (2016). A fundamental study of the reductive leaching of chalcopyrite using metallic iron part I: kinetic analysis. Hydrometallurgy,, 37-57. https://doi.org/10.1016/S0304-386X(02)00079-8
[2] Mostoufi, N. (2022). Kinetics of leaching: a review. Reviews in Chemical Engineering,, 113-148.
[3] Rasouli, A. (2023). Copper Extraction from Chalcopyrite Through a Two-Step Nonoxidative/Oxidative Leaching Process. 1-5.
[4] Jacob, J. (2020). A hydrometallurgical technology for sulphides. In HydroProcess., 1-12.
[5] Zhang, Y. (2023). Life cycle assessment of valuable metal extraction from copper pyrometallurgical solid waste. Resources, Conservation and Recycling., 91-97. https://doi.org/10.1016/j.resconrec.2023.106875
[6] Togtokhbaatar, P. (2022). Leaching of copper and gold concentrate in the presence of halides. 16-20.
[7] Rivera-vasquez, B. (2017). Leaching process for copper concentrates with a carbon catalyst. 16-17.
[8] Alvial Hein, G. (2017). Catalytic effect of activated carbon on chalcopyrite and enargite leaching in chloride media . Department of metallurgy, 12-15.
[9] 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
[10] Kolela J Nyembwe, Elvis Fosso-Kankeu, Frans Waanders and Martin Mkandawire. 2021. pH-Dependent leaching mechanism of carbonatitic chalcopyrite in ferric sulfate. Transactions of Non Ferrous Metals Society of China. 31: 2139- 2152. https://doi.org/10.1016/S1003-6326(21)65644-3.
[11] Kolela J Nyembwe, Elvis Fosso-Kankeu, Frans Wanders and Edward Ntumba Malenga. 2018. Mineralogical Observation Made During the Kinetic Dissolution Study of Chalcopyrite Mineral in Sulphate Media under Free pH at Room Temperature. Editors: Elvis Fosso-Kankeu, Frans Waansders, 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.

[12] Brad Barlow, Elvis Fosso-Kankeu, Kolela J Nyembwe, Frans Waanders and Edward Ntumba Malenga. 2018. Prediction of Dissolution of Copper from a Chalcopyrite Carbonatite Ore of South Africa. Editors: Elvis Fosso-Kankeu, Frans Waansders, 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.

[13] Kolela J. Nyembwe, Elvis Fosso-Kankeu, Frans Waanders, Bhekie B. Mamba and Martin Mkandawire. 2024. Chalcopyrite Leaching in Ferric Sulphate: The Effect of Fe3O4-CuFeS2 Galvanic Couple on the Cu Dissolution. Minerals. 14: 162. https://doi.org/10.3390/min14020162

[14] Kolela J Nyembwe, Elvis Fosso-Kankeu, Frans Waanders, Martin Mkandawire, Didier K Nyembwe, Bhekie B Mamba. 2024. Influence of Fe3O4 on redox changes during Cu dissolution from CuFeS2 in acidified ferric sulfate. Trans. Nonferrous Met. Soc. China 34(2024) 1965−1975. https://doi.org/10.1016/S1003-6326(24)66519-2

[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-Bafubiandi. 2024. Recovery of Values from Low-Grade and Complex Minerals: Development of Sustainable Processes. Wiley. ISBN: 9781119896418 https://doi.org/10.1002/9781119896890.ch6