Comparative Effects of $CuFeS_2/MnO_2$ and $CuFeS_2/Fe_3O_4$ Galvanic Couples during the Kinetic Dissolution of Cu

Michelle Moganedi, Edward Malenga and Elvis Fosso-Kankeu

***Abstract*—** Due to a decrease in high grade ores of Chalcopyrite (CuFeS2) and the attempt to contribute to a low carbon economy, hydrometallurgical methods have become more attractive when it comes to copper extraction from chalcopyrite ore. Theres different hydrometallurgical methods that can be used to extract copper from chalcopyrite, which include metal ion catalysis, adding surfactants, bioleaching and galvanic interactions. In this study we will be looking at galvanic interactions, they are electrochemical processes where two different metals (conductors or semiconductors) come into contact in an electrolytic cell. Galvanic interactions that result in copper (Cu) dissolution from chalcopyrite are hindered by the effect of passivation, which can be formed by factors like elemental sulphur. It is found through literature that passivation can be overcome by the formation of galvanic couples,hence in this study we will be comparing different galvanic couple to investigate which galvanic couple between that of Chalcopyrite and magnetite(Fe_3O_4) and that of chalcopyrite and pyrolusite(MnO_2) will result in a higher copper dissolution .Chalcopyrite ore from a mine in Mpumalanga was characterized using X-ray fluorescence (XRF) and scanning electron microscopy (SEM).During the experiment different parameters were varied, which were time(10, 30, 60, 90, 120, 150, 180, 210, 240) in minutes and temperature(25, 35, 45, 55). The galvanic couples of 400 ml contained H_2SO_4 of 6 mol , had a ratio of 1:1 ,a rpm of 460 and a pH of 1.5 which was kept constant throughout the entire experiment, after filtering and leaching the sample was analysed with AAS. The results showed that the galvanic couple of chalcopyrite and pyrolusite resulted in a higher copper recovery(76%) compared to the couple of chalcopyrite and magnetite that had a recovery of 21%.$MnO_2/CuFeS_2$ couple had a lower activation energy of 45 compared to the couple of $Fe_3O_4/CuFeS_2$ that had an activation energy of 46.To get higher copper dissolution a lot of things could be done like using the ratio of 4:1 or using the solvometallurgical process, which is the use of organic solvents like ethylene glycol with ferric chloride instead of traditional aqueous solutions.

***Keywords*—** Chalcopyrite, galvanic interactions, copper, manganese dioxide, magnetite, passivation, kinetics, thermodynamics.

I. Introduction

When two different metals come into contact in an electrolyte cell, an electrochemical process known as galvanic interactions occurs. This process allows electrons to move between the metals and has the potential to cause galvanic corrosion. Between two distinct conducting materials, there are galvanic interactions, which play an important part in the sulphide ore leaching process. Known as semiconductors, sulphide minerals are difficult to extract or leach because of their resistance to dissolution. Chalcopyrite is the sulphide under investigation in this study, and it is thought to be the most prevalent and important commercial primary source of copper. A significant portion of the minerals being treated aren't solubilized when the hydrometallurgical treatment of chalcopyrite passivation takes place [1]. The benefit of recovering copper by electrolysis is that it's a straightforward procedure with minimal use of energy. To dissolve copper, chalcopyrite will interact galvanically with magnetite and pyrolusite, in that order. According to Nyembwe et al. [2] copper has been identified as a vital element that can help create a low-carbon and more sustainable economy.

Pyrolusite's chemical formula, MnO_2, indicates that it is a metal oxide. While MnO_2 is a semiconductor, its rest potential is larger than chalcopyrite's. A galvanic pair is created when manganese oxide and base-metal sulphide (chalcopyrite) interact galvanically [3]. $CuFeS_2/MnO_2$ is a galvanic pair in which MnO_2 forms a cathode and $CuFeS_2$ an anode. The driving factor behind the accelerated rate of dissolution of the metal oxide and sulphide is the potential difference between the electrodes [4]. Without a reducing agent, MnO_2 is difficult to dissolve in diluted mineral acids, and chalcopyrite is similarly difficult to dissolve in the absence of an oxidizing agent.

The galvanic current between the $MnO_2/CuFeS_2$ pair was shown to be significantly influenced by hydrogen ions [5]. Additionally, it is stated that MnO_2 and $CuFeS_2$ corrode when Cu dissolves. The chemical formula of magnetite is Fe_3O_2, which is a magnetic oxide. Chalcopyrite functions as the anode and magnetite as the cathode in a galvanic interaction between the two minerals.

In order to successfully dissolve Cu using the galvanic method and to get a notable difference in the galvanic reaction, the appropriate amount of magnetite should be introduced to a couple of $CuFeS_2/Fe_3O_2$ [6]. According to Saavedra et al. [1], Fe_3O_2 inhibits the creation of a passive layer and releases twice as many Cu ions during mineral electrooxidation as pure $CuFeS_2$. During the hydrometallurgical treatment of $CuFeS_2$,

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the galvanic interaction of chalcopyrite and minerals in a crude phase such as magnetite is the approach used to overcome passivation and improve metal recovery. In 2024, Nyembwe et al. [2] The efficiency of the kinetic dissolution of copper is influenced by a number of factors, including temperature, catalyst presence or absence, type and concentration of the dissolving agent, copper surface area, pH of the solution, pressure, cathode to anode ratio, and potential. The rate at which chalcopyrite oxidizes depends on these variables being at their ideal levels, but if they are not, inefficiency or the creation of complex reactions and byproducts could occur, creating difficulties in
regulating the entire response.

The aim of this project is to systematically compare and analyse the impact of the galvanic interactions occurring in the $CuFeS_2/MnO_2$ and $CuFeS_2/Fe_3O_4$ systems during the kinetic dissolution of Cu.

II. METHODOLOGY

A. Solution preparation

6 M diluted H_2SO_4 was prepared using analytical reagent-grade of H_2SO_4 (98% A.C.E). A pulp of the galvanic couple solutions' ($CuFeS_2/MnO_2$, $CuFeS_2/Fe_3O_4$) and $CuFeS_2$ was made respectively, through the dissolution of salt in deionised water.

B. Chalcopyrite, Manganese oxide and magnetite sample characterization

The chalcopyrite ($CuFeS_2$) ore sample from Mpumalanga mine was dried in a furnace at 50°C for two days before characterization. Homogenization was performed. The samples chalcopyrite ($CuFeS_2$), manganese oxide (MnO_2), and magnetite (Fe_3O_4) were analysed for mineral composition and bulk chemistry using X-ray diffraction (XRD), X-ray fluorescence (XRF), and scanning electron microscopy (SEM), respectively. XRD was utilized to primarily characterize material properties such as crystal structure, crystallite size, and strain of the ore. XRF was employed to determine the elemental composition of the ore and the SEM was used 12 for morphology analysis. The XRD was operated at 40kV and 30mA, with integrated X-ray powder diffraction software used for identifying mineral phases and an instrument detection limit of 2%. Data were recorded over the range of $5° \leq 2\theta \leq 95°$ at a scan rate of 0.5 degrees/min and a step width of 0.01°. The XRF elemental composition analysis was conducted at 4kW, 40kV, and 150mA. Additionally, SEM was performed for chalcopyrite ($CuFeS_2$), manganese oxide (MnO_2), and magnetite (Fe_3O_4).

C. Leaching process

A pulp that had 400 ml solution of deionised water was made where $CuFeS_2$ was dissolved in diluted sulphuric acid of 6 M with MnO_2, Fe_3O_4 respectively and without either Oxidants. A ratio of $CuFeS_2/Fe_3O_4$ and of $CuFeS_2/MnO_2$ of 1:1 was used to evaluate the effect of Fe_3O_4 and MnO_2 addition on Cu dissolution respectively. Dissolution tests were conducted at temperature varying from 25˚C, 35˚C, 45˚C, and 55˚C respectively. An electrochemical potential meter was used to check the potential of the galvanic couples, and the mixing speed was kept at 460 rpm. The pH was kept constant at 1.5 throughout the entire experiment by adding drops of diluted Sulphuric acid. If the pH increased during the dissolution of Cu, going lower than 1.5, drops of ammonia would be added to restabilize the pH. Time varied from 10, 30, 60, 90, 120, 150, 180, 210 and 240 mins respectively to investigate the effect of time on dissolution of Cu. A solid liquid ratio of 10% was used for the entire experiment. After leaching was achieved filtering of the solutions was conducted using a filter paper to remove the solids and the solution was taken for further analysis using atomic adsorption spectroscopy (AAS). This was done to evaluate and compare the copper concentrations of the galvanic interaction between $CuFeS_2/MnO_2$, $CuFeS_2/Fe_3O_4$ on the dissolutions of Cu.

III. RESULTS AND DISCUSSION

4.1 Ore characterization (SEM and XRF)

4.1.1 XRF

XRF results for Chalcopyrite ore showed the presence of copper and iron in the form of CuO (27,6728%), which was the highest and Fe_2O_3 (24,133%) respectively. The elemental composition of Cu in CuO was found to be 22.10693% and the elemental composition of Fe in Fe_2O_3 was found to be 15.46198%.

4.1.2 SEM

The figure below shows micrograph one of the SEM results for the chalcopyrite ore. In spectrum one its seen that there's a weight percent of 34.79% of Cu in the form of CuO and there's a weight percent of 0.78% of Fe in the form of Fe_2O_3 in the ore.

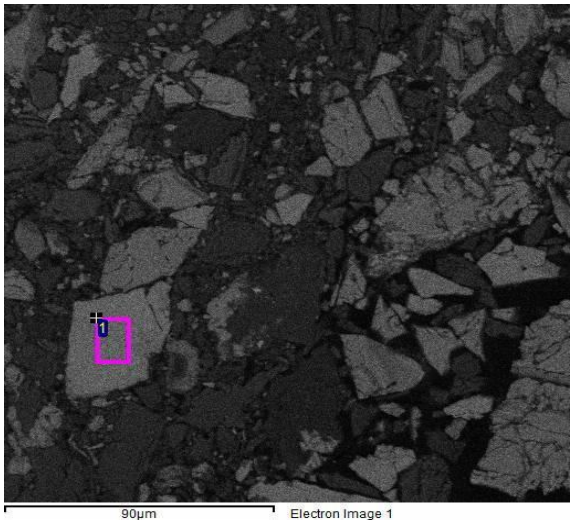

Fig. 1: Chalcopyrite SEM Spectrum 1

4.2 Copper recovery curve

The recovery of copper (Cu) during the galvanic reaction of chalcopyrite, with and without an oxidant, shows significant

differences consistent with existing literature. Increased time and temperature led to higher Cu dissolution, regardless of the presence of an oxidant. The two oxidants exhibit different rest potentials, influencing Cu dissolution from chalcopyrite. Notably, at 240 minutes and a high temperature of 55°C, a recovery of 79% Cu occurs using pyrolusite as an oxidant. This difference in recovery dynamics is attributed to the varying rest potentials of chalcopyrite and pyrolusite. Between 30 to 180 minutes, Cu recovery remains static hence the linear nature of the graphs especially at 25°C, 35°C and 45°C, likely due to passivation. While there’s a dramatic increase in recovery from 180 to 240 minutes at 55°C, this could be because passivation was overcome.

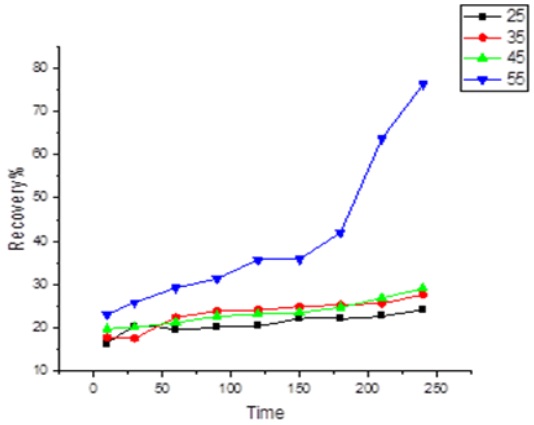

Fig. 2: Recovery of Cu with Pyrolusite as oxidant

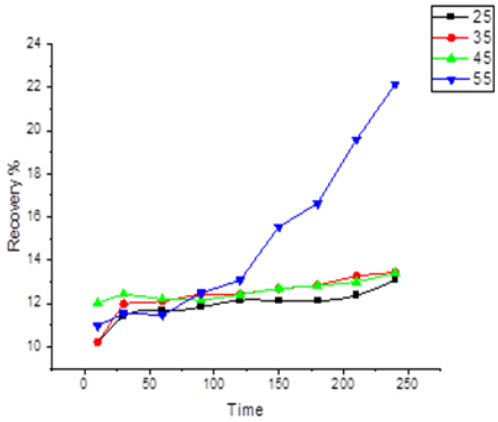

Fig. 3: Recovery of Cu with magnetite as oxidant

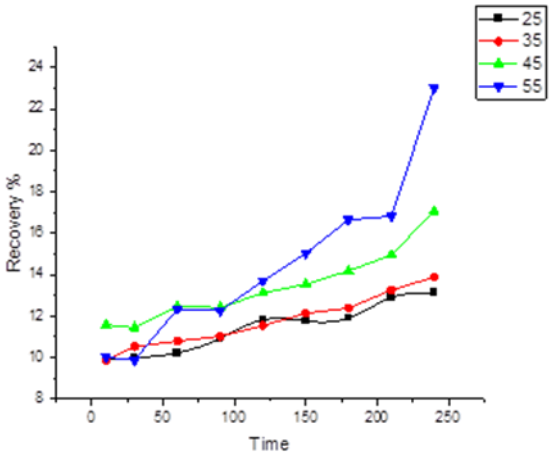

Fig. 4: Recovery of Cu without an Oxidant

4.3 Effect of temperature

Temperature had a positive effect on Cu recovery. The effect of temperature on Cu dissolution was further investigated using the shrinking core model. According to the shrinking core model, the reaction is thought to take place on the outer surface of the solid, and the surface shrinks towards the centre of the solid as the reaction proceeds, leaving an inert solid layer called ash layer, around the core of the reacted ore [7]. Different models of the shrinking core models were used as shown below [8], where x is the copper ion concentration, K′ corresponds to the reaction rate constant and t means the leaching time.

$$K't = 1 - (1 - x)^{1/3}$$

Equation 1: Surface chemical reaction control mechanism

$$K't = 1 - 3(1 - x)^{2/3} + 2(1 - x)$$

Equation 2: Solid product layer diffusion control mechanism

$$K't = x$$

Equation 3: Liquid film diffusion control mechanism

The Arrhenius equation below was used to calculate the activation energy of chalcopyrite leaching. A is the pre-exponential factor, Ea is the activation energy (KJ·mol^{-1}), R is the universal gas constant (J·mol^{-1}·K^{-1}) and T is the absolute temperature in Kelvin (K).

$$K' = Ae^{-(Ea/RT)}$$

Equation 4: Arrhenius equation

Fig 4a shows the fitting of the lnk′ against 1/T (Arrhenius plot) according to the Cu extraction data, showing the fitting of the lnk′ against 1/T. The shrinking core model has established a few things about galvanic couples. It has been established that during the galvanic interaction of chalcopyrite and pyrolusite, the rate limiting step was the liquid film diffusion control mechanism due to the mean of the coefficient of determination being the highest during these conditions. Liquid film diffusion control mechanism was the rate limiting step for chalcopyrite

(standard). For the galvanic interaction of magnetite and chalcopyrite, it was seen that the rate limiting factor was the surface chemical reaction control mechanism as this condition had the highest mean of the coefficient of determination.

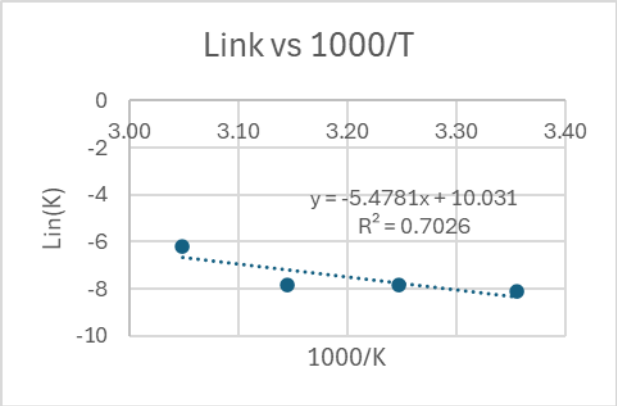

Fig. 5: Pyrolusite Arrhenius plot

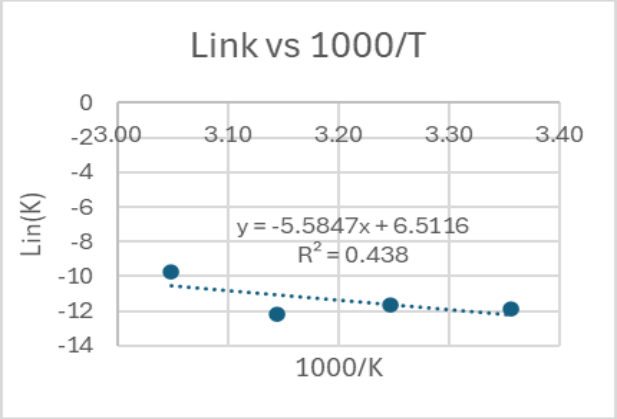

Fig. 6: Magnetite Arrhenius plot

The activation energy for the galvanic couple of chalcopyrite/magnetite and chalcopyrite/pyrolusite is 46.4312 KJ·mol^{-1} and 45.54492 KJ·mol^{-1} respectively. According to Dreisinger [9], its generally recognized that systems with an activation energy exceeding 40KJ/mol are governed by chemical reaction, characterized as linear leaching. In contrast, systems with an activation energy below 40 KJ·mol−1 are governed by a transport process, which can manifest as parabolic leaching, either within the product layer or in the boundary fluid film. Chemically controlled processes that experience a small increment in temperature usually lead to tremendous enhancement in reaction kinetics, hence the high recovery in copper for galvanic couple of pyrolusite and chalcopyrite [10-14]. According to Hiskey and Wadssworth [15] a reductive leaching of chalcopyrite for the dissolution of copper in a H_2SO_4 solution tends to have a chemical control system with an activation energy of around 48,12 KJ·mol^{-1}.

IV. Conclusion

This study investigated two different galvanic couples to compare as to which galvanic couple will result in more copper dissolution in an acidic medium of 6 M H_2SO_4. The results show that both oxidants had a positive impact on copper dissolution which correlated with temperature and time. The results showed that the galvanic couple of pyrolusite and chalcopyrite had a high copper recovery of 76% at high temperature (55˚C) and time (240 minutes), at a ratio of 1:1. It was seen that the activation energy for $CuFeS_2/MnO_2$ was 45.54492 KJ·mol^{-1} compared to that of $CuFeS_2/Fe_3O_4$ which was around 46.4312 KJ·mol^{-1}, therefore meaning they are both governed by chemical control and it also means that the galvanic couple of $CuFeS_2/MnO_2$ will result in a higher reaction rate.

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