Effect of FeSO$_4$ Addition on the Dissolution of Cu from Carbonatite CuFeS$_2$

Stephen Molekoa, Antoine F Mulaba-Bafubiandi and Elvis Fosso-Kankeu

Abstract— Chalcopyrite is the most abundant copper bearing mineral and it compromise about 70% of the world copper. But due to passivation layer formed by insoluble species its disslotion rate is low. This study aims to investigate the influence of FeSO$_4$ concentration on the leaching behavior of CuFeS$_2$, mainly focusing on cincentration and temperature influence. Experiments were conducted on four different treatment conditions: chalcopyrite alone, chalcopyrite with FeSO$_4$, chalcopyrite with Fe$_3$O$_4$, and chalcopyrite with FeSO$_4$ and Fe$_3$O$_4$ and the leaching was performed at temperatures of 25,35,45 and 55°C with leaching time interval from 10-240 minutes. Results showed that FeSO$_4$ concentration influence the dissolution of copper as it increased from 15.54% to 21.08% at 25°C and reached the highest dissolution of 42.41% at 55°C. The rate limiting step was determined using various shrinking core models and was determined to be diffusion through product layer as it had highest R^2 value of 0.9891. lastly activation energy for Cu dissolution was found to be 62.57KJ/mol indicating that the process endothermic.

Keywords— Chalcopyrite, Copper, Leaching, Passivation, Kinetics, Thermodynamics, FeSO$_4$.

I. INTRODUCTION

Chalcopyrite (CuFeS$_2$), the Earth's most abundant Cu bearing mineral, accounts for approximately 70% of the world's copper reserves [1]. Copper is an essential metal used extensively in a variety of sectors, including electronics, construction, and transportation. The poor dissolving rate of chalcopyrite Leaching, primarily due to the passivation layer covering the chalcopyrite surface, causes industrial applications of this process to progress slowly [2-6]. The majority of the identified potential passivating species are composed of insoluble sulfate (SO$_4^{2-}$), elemental sulfur (S$_0$), and polysulfide (S$_n^{2-}$) [7].

FeSO$_4$ can act as a catalyst in the leaching process, promoting the dissolution of copper from the mineral CuFeS$_2$ [8-9]. This is due to the formation of a complex between Fe(II) and Cu(II) ions, which enhances the overall leaching efficiency [10]. The addition of iron salts, such as FeSO$_4$, has been shown to enhance the dissolution of copper from chalcopyrite by increasing the rate of oxidation of sulfide minerals [11]. However, the exact mechanisms by which FeSO$_4$ enhances the dissolution of copper from chalcopyrite are not well understood.

Understanding the effect of FeSO$_4$ addition on the dissolution of copper from chalcopyrite could lead to the development of more efficient processes for the extraction of copper from sulfide minerals. When there were ferrous ions present in the abiotic systems, almost 99% of the copper was recovered during the chalcopyrite dissolving process, High dissolving rates in chalcopyrite leaching have been linked to ferrous ions in solution and the preservation of a low redox potential; both effects must be considered jointly [12].

The effect of adding FeSO$_4$ to chalcopyrite (CuFeS$_2$) to dissolve copper is still a topic of interest in hydrometallurgical processes [13]. Copper extraction efficiency can be greatly impacted by the way FeSO$_4$ and CuFeS$_2$ interact during leaching processes [10], In order to understand how the addition of ferrous sulfate solution to a chalcopyrite particle bed may affect the dissolution of copper from chalcopyrite, it is necessary to review its surface passivation characteristic [14]. The concept of selective chalcopyrite leaching will also be reviewed.

Chalcopyrite is known to exhibit a tendency to dissolve in a leaching oxidant like sulfuric acid and then re-precipitate the dissolved species as a copper (I) sulfide layer on the chalcopyrite surface [15]. This research seeks to better understand the molecular pathways involved in the FeSO$_4$-assisted leaching of CuFeS$_2$ and offer useful insights for improving the effectiveness of copper extraction operations in the mining industry through accurate experimental analysis and data interpretation.

This study aims to investigate the influence of FeSO$_4$ concentration on the leaching behavior of CuFeS$_2$.

The objectives for this experiment are:
• To determine the rate at which copper dissolves from CuFeS$_2$ when FeSO$_4$ is present or absent.
• To determine the rate limiting factor to dissolution of copper from chalcopyrite.

II. METHODOLOGYCHAL COPYRITE SAMPLE CHARACTERIZATION

The CuFeS$_2$ sample was obtained as a concentrate from the Phalaborwa Copper Mining Company (Phalaborwa, South

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Africa). For a dissolution feed, grains smaller than 200 microns (<200 μm) was used. Using X-ray fluorescence (XRF), the samples was analysed for mineral composition. XRF was used to determine elemental composition.Solution preparation

Leaching solutions was sulfuric acid containing various concentrations of ferrous sulphate and with the absent of $FeSO_4$ ($FeSO_4 \cdot 7H_2O$, H_2SO_4, nH_2O). Leaching tests

All experiments was performed on a Stirrer at 400rmp using Erlenmeyer flasks containing 5g chalcopyrite sample and 500 ml solution ($FeSO_4 \cdot 7H_2O$, H_2SO_4, nH_2O) at pH of 1.5. For treatments involving additives, 0.5M $FeSO_4$ and/or 20g Fe_3O_4 was added to the leaching solution using 1:4 ratio of $CuFeS_2$ and Fe_3O_4.

Four different treatment conditions were utilized in the experiment: chalcopyrite alone, chalcopyrite with $FeSO_4$, chalcopyrite with Fe_3O_4, and chalcopyrite with $FeSO_4$ and Fe_3O_4. The leaching solution was heated to one of the following temperatures: 25°C, 35°C, 45°C, or 55°C. the system was allowed to reach equilibrium temperature before the leaching process. Different amounts of time were spent leaching: 10, 30, 60, 120, 180, 210, and 230 minutes. An approximate 15 mL sample of the leachate was taken out at each period, then was filtered to remove solid particles, and then placed in a labelled container for analysis. Analysis

After the completion of the leaching experiments, the concentrations of dissolved Cu in the leaching solutions was analysed using Atomic Absorption Spectrophotometer (AAS).

III. RESULTS AND DISCUSSION

CHARACTERIZATION

According to the XRF data, the major elements in the chalcopyrite ore sample are Cu (21.59%), Fe (20.43%), and Ca (14%), the moderate elements are S (4,76%), Si (2.17%), and Mg (1.64%) and the minor elements are Al (0.52%), Na (0.06%) and Zn (0.06%).

Table 1: XRF results for chalcopyrite ore

XRF analysis(%)				
Cu	Fe	Na	Mg	S
21,59	20,43	0,06	1,64	4,76
Si	Zn	p	Ca	Al
2,17	0,06	0,98	14,02	0,52

A. Dissolution

B. Effect of temperature

Figure 1 below show the effect of 0.5M $FeSO_4$ on the rate of Cu dissolution from $CuFeS_2$ with varying temperatures of 25°C, 35°C, 45°C, and 55°C. The graph provides a comparative analysis of how the dissolution rates change with temperature under a consistent concentration of ferrous sulphate.
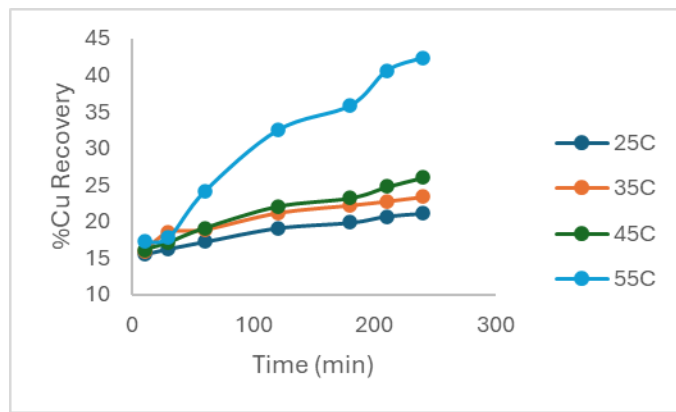

Fig. 1: Copper Dissolution of Chalcopyrite in 0.5M Ferrous Sulphate Solution at Various Temperatures

The amount of copper dissolved increases during the period of time as the temperature increases from 25°C to 55°C, as Figure 2 illustrates the maximum Cu dissolution after 240 minutes at 25°C was 21.08%, whereas the maximum at 55°C was 42.41%. This rapid increase in Cu dissolution shows how important temperature is.

The graphs show an increase in copper dissolution at all temperatures, with higher dissolution observed at higher temperatures. At 25°C, the dissolution increased from 15.54% to 21.08% from 10-240 minutes, indicating that as time increases the dissolution also increases. The dissolution of Cu at 55°C it is more rapid and efficient, as it increased from 17.23% at 10 minutes to 42.41% at 240 minutes, showing that it is more effective. Cu dissolution also improved at 35°C and 45°C, with a maximum recovery of 23.42% at 35°C and 26.05% at 45°C after 240 minutes compared to 25°C.Leaching kinetics

Experimental data were used to investigate the mechanism of chalcopyrite leaching using ferrous sulphate. Various shrinking core models, surface chemical reaction model and the product layer diffusion model, were used for this analysis. The study aimed to understand the kinetic behavior of the leaching process and identify the dominant factors affecting the rate of dissolution

A comprehensive analysis of the data indicated that diffusion through the product layer is the rate-limiting step in the dissolution reaction. As a result, the values from the temperature-related experiments were linearized using the model equation $1-(3/2)*X-(1-X)2/3=kt$. The plot for temperature is illustrated in Figure 2.
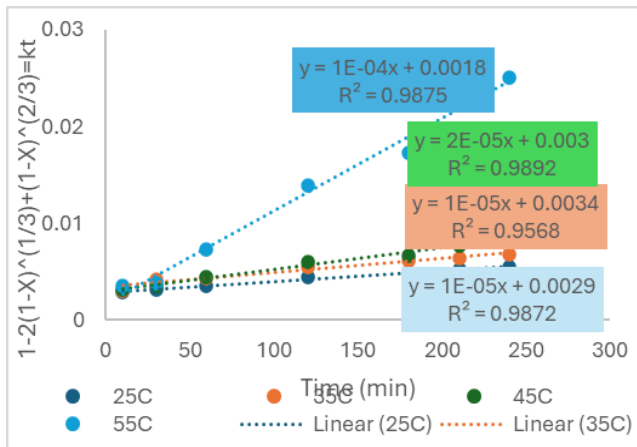
Fig. 2: Graph illustrating the shrinking core model showing the influence of temperature on the reaction rate

Figure 3 displays a plot of lnK against 1000/T, where the slope of the graph is equal to −Ea/R. The activation energy (Ea) for this reaction was determined to be -62.567 kJ/mol over the temperature range of 25 to 55ºC, indicating that the reaction is endothermic.

The increasing slope observed in the graph suggests that the dissolution rate of chalcopyrite is progressively rising with temperature. This trend implies that as the temperature increases, the dissolution process becomes more favourable, enhancing the solubility of copper. In the context of copper dissolution, higher temperatures can lead to a more significant release of copper ions into the solution.
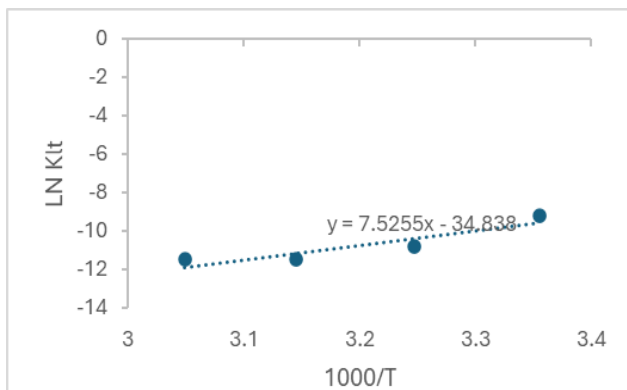

Fig 3: Graph of lnK against the inverse of temperature (Arrhenius plot)

IV. CONCLUSION

This study showed that the concentration of FeSO4 significantly influenced the leaching behavior of CuFeS2, by enhancing copper dissolution rates. as the addition of FeSO4 increased copper dissolution rates from 15.54% to 21.08%, showing its role as a possible catalyst in the dissolution of copper. The temperature also indicated that, as at 55°C, copper dissolution rates increased to 42.41% when $FeSO_4$ was present, compared to 26.76% with chalcopyrite alone.

The analysis of rate-limiting factor indicated that diffusion through the product layer is the primary constraint in the dissolution reaction, this was supported by the R² value of 0.9801 obtained from the shrinking core model, which confirms that this mechanism governs the leaching process. The activation energy (Ea) for this reaction was determined to be 62.567 kJ/mol, indicating that the process is endothermic.

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