

Chalcopyrite Dissolution in Acidified Ferric sulfate: a Thermodynamic Study of Intermediate Phases

Kolela J Nyembwe, Elvis Fosso-Kankeu*, Frans Waanders and Martin Mkandawire

Abstract—The leaching of chalcopyrite (CuFeS_2) is characterized by slow Cu dissolution rate and poor recoveries, mainly at atmospheric pressure and low temperature. It is believed that, the parabolic rate is caused by the solid-state transformation that takes place during mineral dissolution which leads to the formation of a dissolution barrier that prevents further Cu removal from CuFeS_2 . In this study, the dissolution of copper from CuFeS_2 mineral was investigated in acidified ferric sulfate at atmospheric pressure. The results revealed that only 22% Cu were recovered after 5 hours at 50°C at a solution pH of 1.8. It was observed that, the dissolution of Cu was accompanied by intermediate phases formation which seem to have a retarding effect on the direct oxidation of CuFeS_2 . The transient metastable phases were Copper sulphides rich minerals including bornite (Cu_5FeS_4), chalcocite (Cu_2S) and covellite (CuS). Thermodynamic predictions revealed that Cu_5FeS_4 and Cu_2S were the soluble intermediates and were characterized by a slow dissolution rate. Whereas, CuS has been identified as a refractory intermediate inhibiting Cu dissolution. The dissolution phase diagram was obtained and further discussed with regard to the intermediate phase formation, evolution, transformation and dissolution.

Key words—chalcopyrite, dissolution, ferric sulfate, solid state diagram

I. INTRODUCTION

Efficient leaching of chalcopyrite concentrates at ambient pressure remains a challenge because of the slow dissolution kinetics of this mineral in most leaching media [1,2]. The slow and incomplete dissolution is attributed to the formation of a passive layer on the mineral surface regardless of the method used whether chemical or bioleaching [3-7]. The nature and composition of this barrier, remain subject to controversy up-to-date [8-10]. The most often suggested candidates to form

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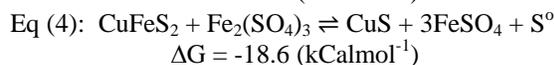
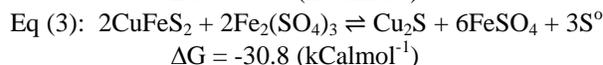
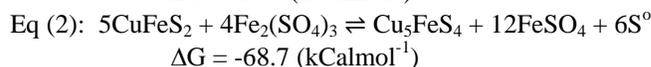
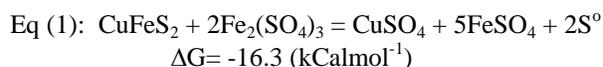
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the passivating layers are metal-deficient phases, elemental sulphur and jarosite [11]. In order to enhance the Cu dissolution from the CuFeS_2 mineral, different methods and techniques have been proposed from various laboratory studies. These methods include the use of sulfate-chloride solutions, microorganisms, fine/ ultra-grinding and silver ions addition [12].

During mineral dissolution, both the pH and potential (Eh) are the major chemical factors that control the leaching mechanism (kinetic or equilibrium), availability for leaching, complexation, and sorption processes. However, it was reported that the media pH has a minimal response on the CuFeS_2 dissolution rate in acidified ferric sulfate and had to be maintained low in order to avoid iron (Fe) hydrolysis and/ or hydroxy precipitates formation [13-16]. It was Cordoba et al., [17] who identified that high Cu recoveries were achieved at acidic pH values in the range of 1.5 - 2. The existence of narrow potential Eh zone in which the dissolution rate and recovery are optimal was identified to lie between 400–450 mV/ Ag/AgCl [18-21].

Both pH and Eh are well summarized on the pourbaix (Eh-pH) diagram, it serves as initial identification for eventual dissolution reactions under both oxidizing and reducing environment at different pH values. From the diagram, the increase in potential value on the surface of the dissolving mineral leads to the occurrence of different oxidation reactions which favor the formation of intermediates phases. These transitory phases include the formation of bornite (Cu_5FeS_4 Eq(2)), chalcocite (Cu_2S Eq(3)) and covellite (CuS Eq(4)) all of which are successfully dissolved at potential above 0.5 V at pH values ranging from 0 to 2.



The issue rising with the direct application of the Eh-pH diagram to sulfide leaching is the formation of various intermediate. These phases may to some extent slow the chemical kinetics associated with the Cu dissolution from

CuFeS_2 and it is difficult to predict the presence of intermediates from thermodynamics only. It is, therefore, appropriate to review the kinetic aspect of the dissolution in order to obtain a better understanding. To that, the formation and evolution of the transition phases could help explain the leaching process.

The aim of the present investigation is to (1) study Cu dissolution from CuFeS_2 in $\text{H}_2\text{SO}_4\text{-Fe}_2(\text{SO}_4)_3\text{-FeSO}_4\text{-H}_2\text{O}$ system (2) to observe the formation and evolution of intermediates phases during CuFeS_2 leaching (3) to carry out a brief thermodynamic and kinetic investigation on the intermediate phase (4) identify the refractory transient phase at 50°C and media pH of 1.8.

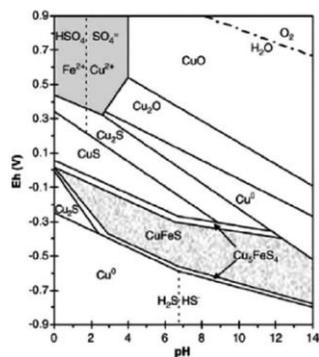


Fig. 1: potential-pH diagram Cu-Fe-S-H₂O at 250°C

II. MATERIALS AND METHODS

A. Materials

Solutions of the desired pH were prepared using analytical reagent-grade sulphuric acid (H_2SO_4 98% ACE), ferric sulphate ($\text{Fe}_3(\text{SO}_4) \cdot \text{H}_2\text{O}$ ACE), and deionized water ($<5.0 \mu\text{s}/\text{cm}$). The measured redox potential (Ag/AgCl) measurements were referenced to the Standard Hydrogen Electrode (SHE).

B. Chalcopyrite sample

CuFeS_2 sample originated from a Limpopo province, (Phalaborwa South Africa). The received samples were dried in an oven at 50 degrees Celsius ($^\circ\text{C}$) for seven days. Laboratory sub-sampling and homogenization were conducted according to the soil sampling protocol published by the US Environmental Protection Agency [22].

Figures 2 summarizes the sample mineral, the XRD patterns further indicated a high purity and well crystallized CuFeS_2 (70%) accompanied by $\text{Mg}(\text{CaCO}_3)$ (24.3%) and with a very small amount of SiO_2 (4.09%) and Fe_2O_3 (1.58%). A grain size of $-38+20 \mu\text{m}$ was used as a dissolution feed.

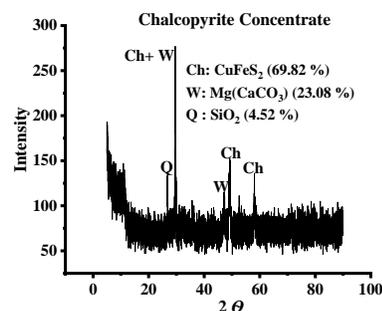


Fig. 2: CuFeS₂ sample mineral characterization

C. Leaching test

CuFeS_2 dissolution was conducted in acidified ferric sulphate solution ($\text{H}_2\text{SO}_4\text{-Fe}_2(\text{SO}_4)_3$), obtained by mixing $\text{Fe}_2(\text{SO}_4)_3$ with H_2O water and H_2SO_4 . An initial Fe content ($\text{Fe}^{3+} = 0.05 \text{ MFe}$) was used for all tests. The media was agitated for 12 hours prior to use. Dissolution tests were performed in at atmospheric conditions at 50°C the media pH was measured and maintained at 1.8 with periodic addition of H_2SO_4 (98%) while the solution ORP was allowed to evolve throughout the dissolution test and was periodically (10 minutes) recorded.

The redox potential of the leaching solution was measured with a platinum electrode using a saturated Ag/AgCl (3 M KCl) electrode as the reference.

Solid leached residues were analyzed for mineral composition using XRD analysis (Rigaku Ultima IV) operating at 40 kV and 30 mA and PDXL analysis software was used; the instrument's detection limit was 2%. Data were recorded over the range $5^\circ \leq 2\theta \leq 95^\circ$ at scan rate of $0.5^\circ/\text{min}$ and a step width of 0.01° .

III. RESULTS AND DISCUSSION

A. Dissolution curve and recovery

Fig 4. shows the Cu dissolution recovery curve (a) and potential (ORP) evolution (b). Only 21% Cu were dissolved for the pure concentrate (CuFeS_2). The dissolution curve was asymptotic and characterized by three stages: the first rapid (from 0~60 min) than second (40~360 min) and the third was the plateau with no Cu dissolution (360~720 min). It could suggest that the first rapid stage could be related to the Cu dissolution on the fresh surface while the second may be attributed to the leaching of intermediate phases if they are existent and the plateau stage could represent the passivation phenomenon whereby the undissolved CuFeS_2 is completely enveloped by refractory material.

A sharp drop (Fig.3 (b)) in the solution potential (from 336.7 to 325.4 mV) was observed and could be due to the rapid consumption of ferric (Fe^{3+}) leading to Cu withdrawal and favoring the increase in Fe^{2+} .

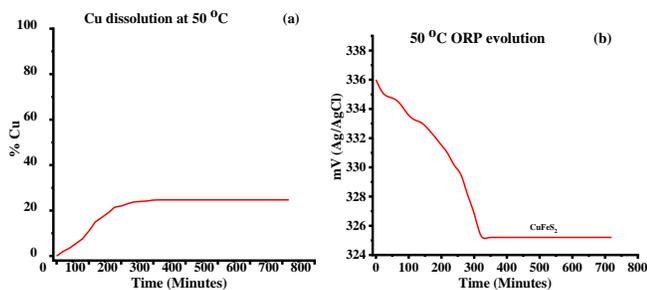


Fig. 3: Cu dissolution recovery and Eh (Ag/AgCl) evolution

B. Solid residue characterization

Fig. 4 shows the solid residue characterization. The CuFeS_2 main peaks ($2\theta = 29.46, 48.93$ and 57.95), appeared to have decreased in their intensity compared to the feed sample, suggesting a progressive Cu dissolution. In addition to that, Cu rich phase (bornite (Bo), chalcocite (Cx), and covellite (Co)) were observed. The presence of these Cu-rich intermediates appeared to support earlier investigation by Acero, et al.,[23] which underlined the preferential dissolution of Fe over Cu leading to the formation of an Fe deficient chalcopyrite mineral (defect chalcopyrite structure $\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_{2-z}$) to which our identified species could be part of.

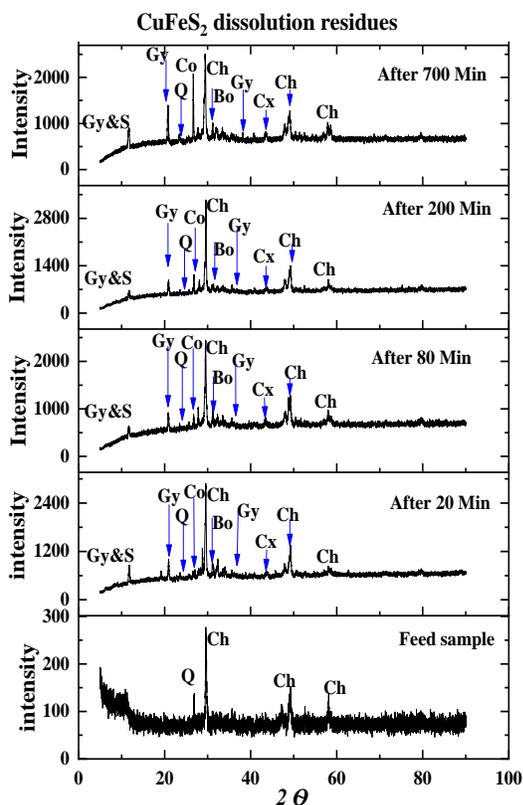
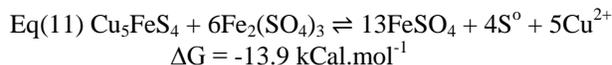
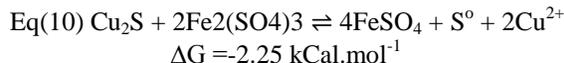
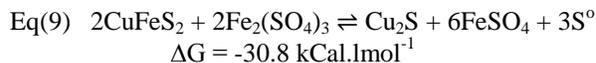
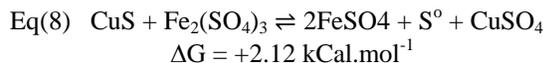
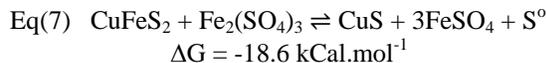
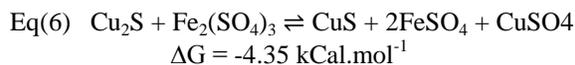
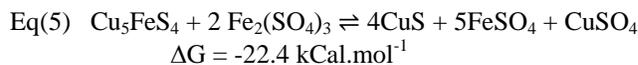


Fig. 4: mineral phase of solid leached residue

Sulphur (S), gypsum (Gy) and goethite (Go) and jarosite (Ja) were also identified in the leached residue. Sulphur must be a reaction product according to Equation 1 (Eq(1)). Gypsum could be related to the carbonatite host rock. Goethite (Go) and jarosite would be formed through the hydrolysis of Fe during leaching.

Thermodynamically bornite is the most favorable phase to be formed (Eq(2)), followed by chalcocite (Eq3) and, lastly, covellite (Eq4). These Cu-S phases could further evolve into other phases (Eq(5) to (9)), or dissolve to promote Cu recovery (Eq(10) to (13)). CuS is likely to form from Cu_5FeS_4 (Eq7) than Cu_2S (Eq8). Similarly, Dutrizac et al. [24] and Zhao et al.[25] also ascribed the presence of CuS to a transient specie during the ferric leaching of Cu_5FeS_4 . The intersection points between the various intermediates phases could suggest on one hand the dissolution competition between phases. While on the other hand, could also suggest the transformation from one phase into the other. In that sense, **I₁**, **I₂** and **I₃** observed between $\text{CuS}/\text{Cu}_5\text{FeS}_4$, $\text{CuS}/\text{Cu}_2\text{S}$ and $\text{CuS}/\text{CuFeS}_2$ suggest the competition between the respective dissolution reactions and since CuS is refractory (Eq8), Cu_5FeS_4 , Cu_2S and CuFeS_2 dissolve by transformation into CuS according to Eq7, Eq 8 and Eq9. This explains the increase in the CuS content and its cumulative behavior (Eq9) as observed in the XRD analysis. While I4 strictly represents the direct conversion of CuFeS_2 to Cu_2S without any Cu^{2+} withdrawal according to Eq9.



IV. CONCLUSION

This work investigated the dissolution of CuFeS_2 in acidic $\text{Fe}_2(\text{SO}_4)_3$ at atmospheric conditions, 50°C and pH value of 1.8. The results revealed a low copper dissolution due to the decrease in solution potential. However, it was observed that copper dissolution from chalcopyrite took place through solid state transformation by the formation of intermediate phases including Cu_5FeS_4 , Cu_2S and CuS . These intermediate phases were found to cause a retarding effect during Cu dissolution and hindered direct CuFeS_2 oxidation. Thermodynamic predictions revealed that Cu_5FeS_4 and Cu_2S were the soluble intermediates and were characterized by a slow dissolution rate. Whereas, CuS has been identified as a refractory intermediate. The

dissolution barrier could be a combination of Fe precipitates, covellite, and gypsum. Further investigation focusing on the control of redox potential should be considered to improve the Cu dissolution rate.

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