

Mineralogical Observation Made During the Kinetic Dissolution Study of Chalcopyrite Mineral in Sulphate Media under Free pH at Room Temperature

Kolela J Nyembwe, Elvis Fosso-Kankeu*, Frans Wanders and Edward Ntumba Malenga

Abstract- An attempt to determine the various phenomena at play and leaching mechanism of chalcopyrite dissolution, was conducted on a chalcopyrite concentrate. The study was performed at atmospheric conditions (room temperature) in a stirred Erlenmeyer flask with 10% solid at free pH in acidic sulphate system. It appears that, the mineral dissolution is to some extent dependent on the pH. The Cu dissolution curve was characterized at the early stage by a rapid withdrawal of both copper and solid residue. Leachate solid residue characterization results, obtained from the X-ray diffraction revealed the presence of intermediate minerals phases including bornite, covelite and chalcocite. Thermodynamic calculations predict that the dissolution of bornite and chalcocite would be spontaneous while covelite was found to be refractory. In addition to that, sulfur and gangue related mineral were identified as the dissolution reaction products.

Keywords: Chalcopyrite, dissolution, mechanism, mineral phases

I. INTRODUCTION

Approximately 70-80% of metallic copper (Cu) is produced from the chalcopyrite mineral, the major copper sulfide mineral in nature used for copper production [1, 2] and the most refractory copper sulfide towards hydrometallurgy [3]. An

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Kolela J Nyembwe is with the Water Pollution Monitoring and Remediation Initiatives Research Group, School of Chemical and Minerals Engineering, Faculty of Engineering, North-West University, South Africa.

Elvis Fosso-Kankeu is with the Water Pollution Monitoring and Remediation Initiatives Research Group, School of Chemical and Minerals Engineering, Faculty of Engineering, North-West University, South Africa.

Frans Wanders is with the Water Pollution Monitoring and Remediation Initiatives Research Group, School of Chemical and Minerals Engineering, Faculty of Engineering, North-West University, South Africa.

Edward Ntumba Malenga is with the Mineral Processing and Technology Research Centre, Department of Metallurgy, School of Mining, Metallurgy and Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg.

estimation of 85 % of the copper production worldwide is obtained via the pyrometallurgical route [4]. Efforts made over the past three decades in order to promote copper extraction through the hydrometallurgical method continue to be vain due to the controversy surrounding the mechanism of the dissolution and the incomplete copper recovery [5]. This, has resulted in several leaching processes in which the ferric sulphate system possess many advantages including a simple chemistry, low capital and operation cost, environment [6-15] and it is convenient for the recovery of copper by solvent extraction and electrowinning [16, 17].

The hindered dissolution and slow dissolution kinetic is believed to be caused by the formation of a passive layer, building up on the mineral surface. The nature, characters (composition) and its formation mechanism are subject to controversy [18, 19]. There are four main hypotheses explaining the structure of the impermeable passive layer. According to the first hypothesis, the elemental sulphur formed as the reaction product to prevent further diffusion of reactant to unleached chalcopyrite [20, 21]. The second theory and the commonly cited [22] suggests the formation of the copper rich polysulfide which takes place as a result of solid state transformation through the preferential iron dissolution. This theory is referred to as the metal-deficient sulfide. The third theory holds responsible iron precipitates compounds, which act as a barrier hindering the dissolution. The candidates for this last theory include jarosite, jarosite like and goethite. These phases are usually formed due to the hydrolysis of iron [23].

To the authors knowledge most of the dissolution studies conducted on the chalcopyrite mineral focus mainly on the mechanistic, electrochemical, morphological. In these investigation the kinetic information with regards to the Cu dissolution were obtain from the leachate characterization after periodic withdrawal of a small solution portion. While, the residue characterization are usually assessed at the study time resolved. The purpose of this work is to present the kinetics in regards to Cu dissolution and simultaneously using the diffraction analysis to present the mineralogical changes taking place during the leaching of chalcopyrite. Lastly, to use thermodynamic prediction, in order to explain the dissolution and mineralogical observations.

II. MATERIAL AND METHOD

A. Material

Similar concentrate sample as earlier characterized by Nyembwe et al [24] was used in this study. The sample was obtained from a local South African mining company. The chemical analysis (XRF) exposed the presence of Cu, Fe and S respectively, at 36.4, 26 and 10 %. Calcium associated to carbonate at 15% followed by silicon at 2% were found as the major impurities. The tables below (Tables 1 and 2) present the chemical composition of the sample used in this study while Fig 1 shows the mineralogical composition of the sample.

TABLE I: CHEMISTRY MAIN ELEMENTS

Bulk Chemistry Main elements (XRF results)				
Elements	Ca	Fe	Cu	S
Composition (%)	15.21	26.23	36.39	10.61

TABLE II: TRACE ELEMENTS

Bulk Chemistry trace elements (XRF results)				
Elements	Mg	Al	Si	Sr
Composition (%)	4.04	1.01	4.67	0.23

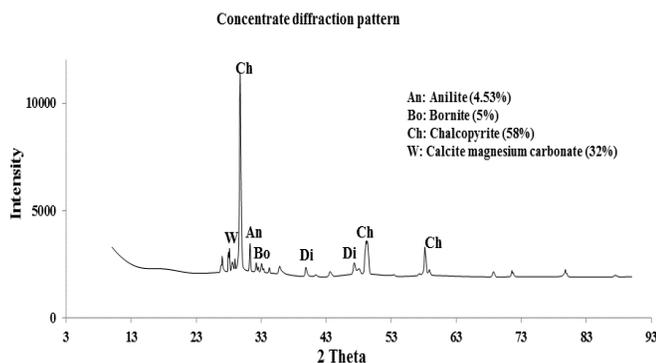


Fig 1: Sample mineralogy

B. Method

The dissolution test was performed at atmospheric pressure in a glass (600 cm³) reactor on continuous basis for twelve hours at room temperature. The leach slurry was magnetically stirred (6 cm) at a constant speed of 200 rpm (adjusted in order to avoid vortex creation). The experiment was conducted in sulphate system (H₂SO₄-Fe₂(SO₄)₃). The media was prepared by mixing distilled water, sulfuric acid and ferric sulphates (0.05 moles) at an initial pH of 0.5. A 10 % solid-liquid ratio was used for the experiment.

The pH was free (not maintained constant), this intended to establish the nature of the dissolution reaction in regard to acid consumption. Kinetics information was obtained after collecting 10 milliliters from the dissolution vessel each 20 minutes. The leachate was filtered and analyzed for its metallic content (Cu and Fe) under atomic absorption flame spectrometer (AAFS –thermo fisher). The solid residue was characterized using X-ray diffraction (XRD) for its mineralogical content.

Mineral content: The diffraction pattern associated to the mineral composition of the various samples was obtained after subjecting the sample under X-ray diffraction analysis (XRD)

using the Rigaku Ultima IV with PDXL analysis software, set at 40 kV and 30 mA, with a detection limit of 2%. This technique enables the identification of the various mineral phases and their quantification [21]. The operating condition of the diffractometer was Cu radiation 30 kV and 25 mA recorded at 2 theta, varying from 5-95. The powered samples were scanned at a speed of 0.5 degrees per minute, with a width step of 0.01 degrees.

The leachate metallic content was quantified by means of Atomic Absorption Flame Spectrometer (AAFS-Thermo Scientific ICE 3000 series & Varian 220). The equipment was alimented by air/ acetylene burning at high temperatures. The leachate samples were aspirated into the flame alimented by air/ acetylene, burning at high temperature in order to favor atomization of metallic traces.

III. RESULTS AND DISCUSSION

A. Leachate characterization

Figure 3 displays the dissolution curve of Cu from and Fe the chalcopyrite concentrate in acidified sulphate solution at free pH (0,5 initial pH). It also shows the evolution or behavior of pH. Iron content (Fe) as presented in the figure summarizes the dissolved Fe originating from the mineral, obtained after subtracting the initial Fe content (virgin leaching) solution used to prepare the leaching solution from the collected leachate Fe content. (Fe (mineral) = Fe (AAFS)-Fe (in leaching liquor).

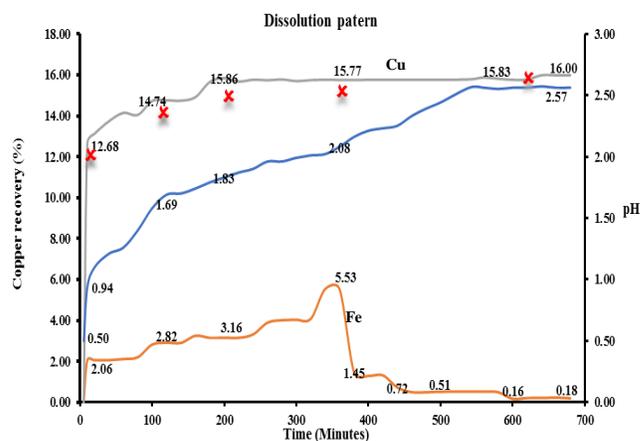


Fig 2: leachate metallic content and pH evolution

It was observed that the Cu dissolution curve obeyed to the parabolic like behavior as in previous studies [25]. Only 16% of Cu from the mineral was recovered in the leachate after 12 hours dissolution. The curve shows a rapid Cu withdrawal at the early stage of the dissolution (the first 20 minutes). This rapid stage was associated to a low pH value. Based on this fact, it could be said that the acid content or pH plays a vital role in the recovery (dissolution) of copper. Similarly, the earlier study, conducted by Aydogan et al [26], reported that the Cu dissolution rate increased with increasing the sulfuric acid concentration. This could probably explain the sharp Cu withdrawal as observed at the earlier stage of the dissolution.

The dissolution appears to be hindered at relatively high pH values which are accompanied with Fe precipitation. The

obtained results support the earlier study suggesting that the dissolution of chalcopyrite appears to be an acidic consuming reaction [27]

B. Leaching solid residue XRD characterization

Figure 3, Tables 3 and 4 show the mineral content of the various solid residues collected according to the red dots as shown on the Cu dissolution curve. The progressive chalcopyrite dissolution was observed; a decrease in its major peak intensity was noticed suggesting an effective mineral dissolution [28]. In addition to that, the Cu dissolution appeared to be accompanied with new mineral phases formation. These new phases include bornite chalcocite and covelite. They are regarded as intermediate phase step before the complete decomposition to Cu²⁺ and Fe²⁺ [29].

Apart from the intermediate phases formed, precipitates minerals associated to the mineral matrix nature and the leaching media system was also observed to evolve. These precipitates were gypsum related to the carbonatite calcite while the iron products (hydroxide and/ or oxides) and elemental sulphur were linked to the dissolution media system. The precipitates also displayed an increase in their respective content through increasing peak intensity, and were found to progressively cumulate.

The presence of gypsum could be attributed to the carbonatite hosting ore. Calcium (Ca) is susceptible to form sulphate compound in the presence of sulfuric acid [30].

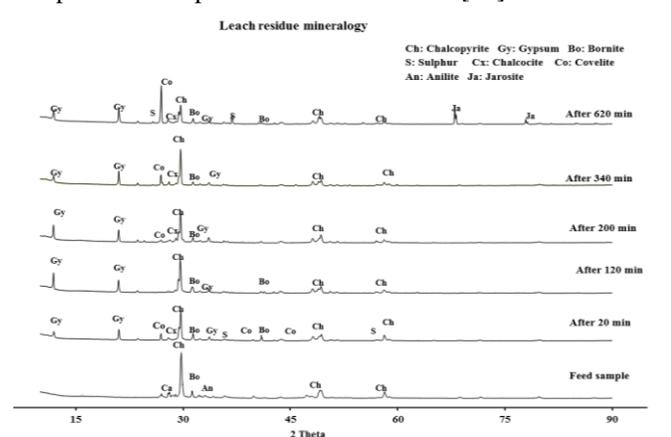


Fig 3: XRD results

TABLE III: MINERAL PHASE'S QUANTIFICATION (CU AND FE PHASES RIR RESULTS)

Bulk Chemistry Main elements (XRF results)							
Copper phase (%)				Iron phases (%)			
	Ch	Cx	Co	Bo	Wu	Mag	Hem
Feed	58.01	***	***	5.00	32.0	***	***
20	47.2	9.7	4.8	5.6	2.1	0.8	***
200	28.8	13.0	6.8	7.0	3.2	1.5	0.7
200	22.7	12.0	5.8	5.3	3.5	2.1	1.9
400	22.9	6.8	5.7	1.3	2.8	3.5	2.9
620	20.5	7.8	4.7	1.5	3.0	4.6	3.0

Ch: Chalcopyrite, Cx: chalcocite, Co: covelite, Bo: bornite, Wu: Wustite, Mag: magnetite and Hem: hematite

TABLE IV: MINERAL PHASE'S QUANTIFICATION (JAROSITE, SULPHUR AND GYPSUM RIR RESULTS)

Bulk Chemistry Main elements (XRF results)			
	System phases (%)		Mineral gangue
	Ja	S	Gy
Feed	***	***	***
20	9.7	2.0	25.7
200	13.1	3.4	29.1
200	12.6	7.1	34.0
400	14.0	10.6	30.0
620	10.7	2.5	16.2

Ja: jarosite, S: sulphur and Gy: gypsum

C. Thermodynamic consideration

Theoretically the dissolution of chalcopyrite can be discussed on the basis of the thermodynamic stability zone as summarized on the Eh-pH (pourbaix) diagram. The Eh-pH (Pourbaix) diagram favors the oxidative dissolution of sulfide minerals [31]. The diagram predicts the predominance area of the various susceptible pieces or phase in regards to their equilibrium condition for all possible redox reactions [32].

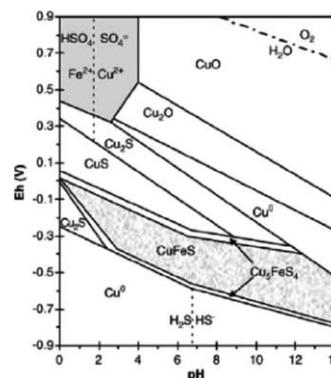


Fig 4: potential -pH diagram Cu-Fe-S-H₂O at 25^oC

It could be seen that as the potential increase on the mineral surface during the dissolution, various oxidation reaction reactions could take place in acidic pH. These reactions promote the formation of intermediates phases including: bornite, covelite, and chalcocite. The diagram also shows that, successful copper dissolution from the mineral could be achieved after increasing the redox potential above 0.44V [33]. In addition to that, all intermediate formed phases are susceptible to dissolve in acidic media at potential above 0.5V (SHE).

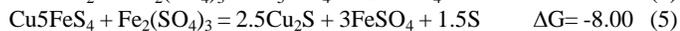
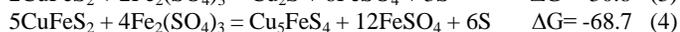
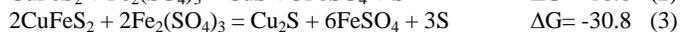
The residue XRD analysis showed the possibility to obtain chalcocite, covelite and bornite as products of the dissolution in sulphate media. Equations 1 to 3, respectively show the Gibbs energy (spontaneity) calculation for the intermediates phases' mineral formation was obtained using the HSC chemistry 5.

3.1.1 Direct chalcopyrite mineral dissolution

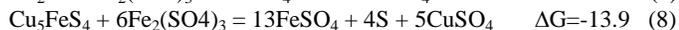
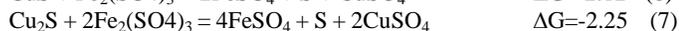


3.1.2 Chalcopyrite dissolution through mineral intermediate phase's formation (covellite, chalcocite and bornite)

3.1.2.1 Formation of copper intermediates phases



3.1.2.2 Dissolution of intermediate phases for complete copper dissolution



3.1.2.3 Phases formation related to gangue mineral



The thermodynamic prediction show that, even though direct mineral dissolution is possible as shown in Equation (1), mineral phases intermediate are more likely to form during the dissolution of the mineral. Spontaneous reactions were those involving mineral phases' mutations or intermediates (2 to 5). The dissolution of the intermediates phase was also feasible mainly for chalcocite and bornite (7 and 8). However, covellite (6) indicates that the reaction is not spontaneous at room temperature and could contribute to the passivation layer, hindering further copper dissolution. In addition, the formation of gypsum, as identified in the XRD and demonstrated in (9), could also contribute to the hindered dissolution. Moreover, the existence of elemental sulphur and iron precipitate (Jarosite) contribute to the passivation phenomenon.

IV. CONCLUSION

During the dissolution of copper from chalcopyrite at room temperature in ferric sulphate, intermediates mineral phases are likely to occur. These intermediate phases include covellite, chalcocite and bornite. The thermodynamic predictions have shown that bornite was more likely to form followed by chalcocite and lastly covellite. The dissolution of the later phase was found to not be spontaneous unlike the other observed phases: bornite and chalcocite. The covellite phase was therefore likely to contribute to the passivation phenomenon. In addition to that the XRD leach residue demonstrated the presence various precipitates including elemental sulphur, iron products (goethite, jarosite) and gangue related mineral (gypsum) which could contribute to the hindered dissolution.

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