



Influence of Fe_3O_4 on redox changes during Cu dissolution from CuFeS_2 in acidified ferric sulfate

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Abstract: Chalcopyrite (CuFeS_2) leaching under oxidizing conditions is generally characterized by slow dissolution rates due to the formation of passivation layers. The aim of this study is to develop a method that will allow the minimization of the passivation effect on the leaching of chalcopyrite and enhance copper recovery. To achieve this goal, the effect of parameters such as magnetite (Fe_3O_4) addition to the lixiviant $\text{Fe}_2(\text{SO}_4)_3\text{--H}_2\text{SO}_4$ during the leaching of CuFeS_2 at various pH (1.0, 1.5 and 1.8) and temperatures (25 and 50 °C) on copper dissolution rate overtime, was investigated. The results revealed that the solution pH, potential and temperature played a vital role during the dissolution. The highest recovery rate (70%) of Cu was achieved at pH 1.8, 50 °C and 400 mV from the mixed $\text{Fe}_3\text{O}_4\text{--CuFeS}_2$, whereas the recovery rate of Cu from CuFeS_2 in the absence of Fe_3O_4 was relatively low (48%). It was found that the addition of Fe_3O_4 allowed to maintain higher redox potential values. The addition of Fe_3O_4 also decreased the activation energy from 79.04 to 53.69 kJ/mol, suggesting that CuFeS_2 is easily oxidized in the presence of Fe_3O_4 through the formation of more soluble intermediates (bornite (Cu_5FeS_4) and chalcocite (Cu_2S)). Both dissolution processes were chemically controlled on the surface of the mineral. Furthermore, the mineralogical analysis of leaching residues showed that jarosite which is a candidate for surface passivation appeared in higher concentration in the absence of Fe_3O_4 . Therefore, the addition of Fe_3O_4 reduced the formation of a passivation layer and enhanced the recovery rate of Cu.

Key words: chalcopyrite; dissolution; magnetite; galvanic couple; passivation

1 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 [1–4]. The slow and incomplete dissolution is attributed to the formation of a passive layer on the mineral surface, regardless of the method of chemical or bioleaching [5–7]. The

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nature and composition of this barrier, remain subject to controversy up to date [8–10]. It is often reported that the passivation layers are formed by metal-deficient phases, elemental sulfur and jarosite [10,11]. 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, micro-organisms, fine/ultra-grinding and silver ions addition [11,12].

Galvanic effect is susceptible to occur between minerals in aqueous system such as flotation, and leaching is another approach exploited to accelerate mineral dissolution and takes place when electrically conducting minerals are present and in contact with a medium which facilitates charge transfer [13]. The voltaic interaction results in rates variation of both anodic and cathodic half-reactions that occur on each mineral surface, leading to a prone oxidative dissolution of anode, while the cathode is well protected [14,15]. Particular interests have been placed on the galvanic couple between CuFeS_2 and FeS_2 , and numerous experimental works [14,16,17] have been conducted to understand and provide more insight on this alternative route of CuFeS_2 dissolution. In the galvanic set-up between FeS_2 and CuFeS_2 , the dissolution rate of the FeS_2 (cathode) particle decreases and FeS_2 becomes galvanically protected due to the reduction of the active oxidant in the system, while the dissolution of the CuFeS_2 (anode) is significantly enhanced. DIXON et al [16] reported appreciable results at a Cu recovery of 98% with a FeS_2 -to- CuFeS_2 (Py:Cp) mass ratio being from 2:1 to 4:1, solution potential varying from 440 to 470 mV (vs Ag/AgCl) and media temperature in the range from 70 to 80 °C.

Magnetite (Fe_3O_4) could also be found to be an existing impurity in the CuFeS_2 ore matrix, especially in the case of carbonatite [14,17,18]. Being a spinel, the magnetite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$) in aqueous solutions could represent a substantial source of oxidant in the system. Recently, SAAVEDRA et al [19] reported the existence of galvanic interactions between CuFeS_2 and Fe_3O_4 . These interactions might be a second new alternative for application in the industrial recovery of Cu from CuFeS_2 after the FeS_2 – CuFeS_2 combination. It is therefore worthwhile to study the

CuFeS_2 – Fe_3O_4 galvanic couple considering that any addition to our knowledge on the subject of Fe_3O_4 – CuFeS_2 voltaic couple is worth being recorded. Both the pH and the redox potential are the most important chemical aspects that control the dissolution mechanism. This study therefore investigated the kinetics of Cu dissolution from a carbonatite CuFeS_2 with and without addition of Fe_3O_4 in an acidified ferric sulfate solution (H_2SO_4 – $\text{Fe}_2(\text{SO}_4)_3$) at varying pH values (1.0–1.8) and temperatures of 25 and 50 °C.

2 Experimental

2.1 Materials

2.1.1 Chalcopyrite and magnetite samples

Chalcopyrite and magnetite samples were obtained from South Africa, with the CuFeS_2 and Fe_3O_4 concentrate samples originating from the Limpopo Province (Phalaborwa) and northern KwaZulu Natal (Richards Bay), respectively. The received samples were dried in an oven at 50 °C for 7 d. Laboratory sub-sampling and homogenization were conducted according to the soil sampling protocol published by the US Environmental Protection Agency [20].

Figures 1(a) and (b) summarize the sample

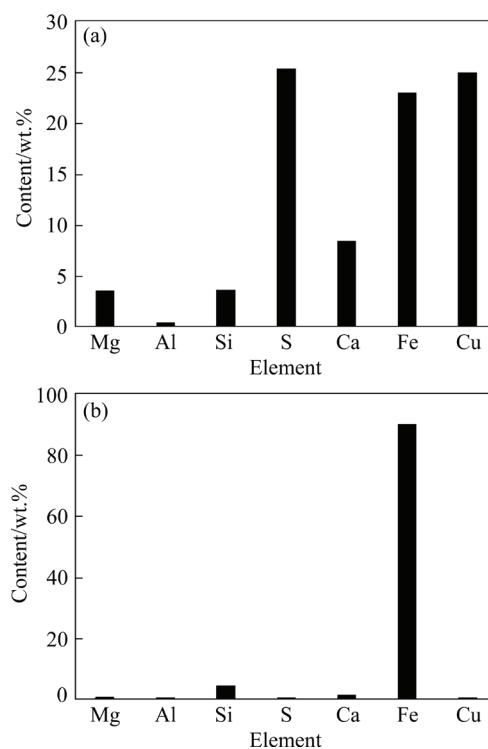


Fig. 1 Chemical compositions of CuFeS_2 (a) and Fe_3O_4 (b) concentrates by XRF

bulk chemistry of CuFeS_2 and Fe_3O_4 , respectively. The XRD patterns (Fig. 2) 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%); while, 96% purity was identified for the Fe_3O_4 with SiO_2 and CaCO_3 at 3.0% and 1.0%, respectively. For the distribution of size fractions, the 53–75 range was used, which was obtained by wet sieving.

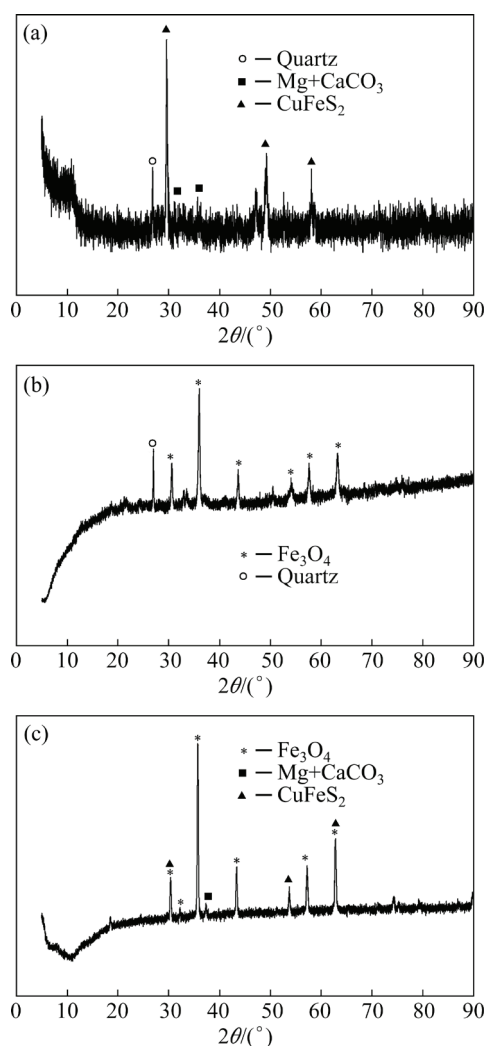


Fig. 2 XRD patterns of CuFeS_2 (a), Fe_3O_4 (b) and Fe_3O_4 – CuFeS_2 (c) samples

2.1.2 Characterization techniques

Solid samples were analyzed for mineral composition and bulk chemistry using X-ray analysis. i.e., XRD and XRF, respectively. An XRD Rigaku Ultima IV was operated at 40 kV and 30 mA. PDXL analysis software was used for mineral phases, and the instrument's detection limit was 2%. Data were recorded over the range of

$5^\circ \leq 2\theta \leq 95^\circ$ at a scan rate of $0.5^\circ/\text{min}$ and a step width of 0.01° . The elemental composition (XRF) powder method was carried out on a Rigaku-ZSX Primus II in conjunction with the SQX analysis software, which was operated at 4 kW, 60 kV, and 150 mA.

2.1.3 Electrolyte preparation

Solutions of the desired pH (1.8) value were prepared at a constant Fe^{3+} amount of 0.05 mol using $\text{Fe}_2(\text{SO}_4)_3$ at 25 and 50 °C, which were referred to as Solutions 1 and 2 (S_1 and S_2) respectively throughout this investigation. An additional solution (S_3) at 400 mV was prepared by mixing $\text{Fe}_2(\text{SO}_4)_3$ and FeSO_4 with a constant total Fe content of 5 g/L at pH 1.8 and 50 °C; this solution could assist in determining the effect of redox potentials on the recovery of copper. All chemical reagents, namely the $\text{Fe}_2(\text{SO}_4)_3$ and FeSO_4 were of analytical grade. The acidified ferric sulfate was used as the leaching system because the acidity prevented precipitation of iron while the ferric ion ensured the leaching of chalcopyrite.

A pH meter with a temperature probe (Hanna pH meter, HI 8314) was used to measure pH, which was regularly calibrated with standard buffer solutions with pH 1, 4 and 7. The effect of the redox potential on the leaching rate has been reported by many authors [21–23] and related to passivation; hence, in this study the initial leaching potential was determined in order to monitor the variation of redox potential and therefore formation of the passivation layer. The redox potential was measured using a HI8314 Ag/AgCl probe allowing to vary within ± 8 mV.

2.2 Dissolution test

The leaching tests of both CuFeS_2 samples (with and without Fe_3O_4 addition) were conducted at room temperature (25 °C) and 50 °C. These temperatures were kept steady using a water bath. The leaching solution had a pH value of 1.8. The comparison between CuFeS_2 and CuFeS_2 – Fe_3O_4 (mass ratio 1:1) dissolution recovery was intended to highlight the effect of Fe_3O_4 on the Cu dissolution under atmospheric pressure.

Another dissolution test was conducted using the Fe_3O_4 – CuFeS_2 sample at pH 1.8, 50 °C and an initial redox potential of 400 mV (vs Ag/AgCl) to observe the dependency of the galvanic couple (Fe_3O_4 – CuFeS_2) on the potential.

The pH of all dissolution tests was kept steady (pH 1.8) by continual addition of H_2SO_4 conducted at a solid/liquid ratio of 10% and for 12 h. Dissolution kinetics investigations were carried out through a periodic withdrawal of 10 mL of the slurry each 20 min, while the ORP was recorded every 10 min. The total dissolved Cu content was analyzed using an atomic absorption flame spectrometry (AAFS, Thermo Scientific ICE 3000series).

3 Results and discussion

Figure 2 and Table 1 present the chemical and mineral contents of the CuFeS_2 and Fe_3O_4 samples used in this study. The figure also specifies the ratio of Fe_3O_4 to CuFeS_2 and presents the new mixed sample characteristics. A mass ratio of 1:1 ($\text{Fe}_3\text{O}_4\text{--CuFeS}_2$) was used to make a mineralogical content ratio ($\text{Fe}_3\text{O}_4\text{--CuFeS}_2$) of 1.4:1.

Table 1 Mineralogical compositions of CuFeS_2 , Fe_3O_4 and $\text{Fe}_3\text{O}_4\text{--CuFeS}_2$ samples

Mineral	Content/wt.%				
	Silica (SiO_2)	CuFeS_2	Fe_3O_4	Fe_2O_3	$\text{Fe}_3\text{O}_4\text{--CuFeS}_2$
CuFeS_2	4.09	70.01	–	1.58	24.3
Fe_3O_4	3	–	96.01	–	1
$\text{Fe}_3\text{O}_4\text{--CuFeS}_2$	3.73	34.45	49.04	0.78	11.62

3.1 Copper dissolution curve

The Cu dissolution curves obtained from the CuFeS_2 and $\text{Fe}_3\text{O}_4\text{--CuFeS}_2$ samples at two different experimental temperatures (25 and 50 °C) and different pH values are presented in Fig. 3. In all cases it was observed that more Cu dissolved at 50 °C than at 25 °C and slightly more at pH 1.8 than pH 1.5 and pH 1.0 (evident at 50 °C, not so at 25 °C). The obtained recoveries agreed with those of ANTONIJEVIĆ and BOGDANOVIĆ [24], and CORDOBA et al [25] who pointed out that chalcopyrite was easily oxidized at higher pH values when oxygen was present in solutions.

All dissolution curves were asymptotic and characterized by three stages: the first rapid stage (0–60 min), the second stage (40–360 min) and the third stage which exhibited a plateau with no further Cu dissolution (360–720 min). Our results supported those of KLAUBER et al [11], SALINAS

et al [26], and TORRES et al [27], but did not support those of JONES and PETERS [28] who observed a linear kinetics probably due to an extended dissolution time over 55 d.

3.2 Effect of Fe_3O_4 addition

A high Cu recovery was obtained from the mixed sample ($\text{Fe}_3\text{O}_4\text{--CuFeS}_2$) in comparison to the pure CuFeS_2 concentrate (Fig. 3). For instance, 30% Cu was recovered from $\text{Fe}_3\text{O}_4\text{--CuFeS}_2$ at pH 1.8 as opposed to the pure CuFeS_2 concentrate which yielded only 23% at room temperature. Furthermore, 53.2% Cu was recovered from the mixed sample ($\text{Fe}_3\text{O}_4\text{--CuFeS}_2$) while the concentrate sample produced 25% of Cu at 50 °C. This increase in Cu recovery in the presence of Fe_3O_4 was observed under all experimental conditions and in some instances, it even doubled when the temperature increased from 25 to 50 °C. The obtained results agreed with SAAVEDRA et al [19] who highlighted that the presence of Fe_3O_4 was beneficial to CuFeS_2 dissolution in an acid microbial culture medium. It was reported that the presence of Fe_3O_4 allowed to leach more Cu and Fe. Suggesting that the Fe_3O_4 strongly accelerates the mineral solubilization due to the galvanic couple formed when mixing Fe_3O_4 and CuFeS_2 , it could be said that the presence of Fe_3O_4 undeniably has a positive effect during Cu dissolution from CuFeS_2 .

3.3 Effect of temperature

The general effect of temperature was studied when the leaching temperature was raised from 25 to 50 °C (Fig. 3). In all cases it was observed that the increase of temperature leads to an increase in content of Cu dissolved. Previous studies reported the positive impact of temperature during the dissolution, and more than tenfold increase in copper extraction has been reported with temperature increase within 30–90 °C [29]. At pH 1.8 for instance, the Cu recovered from the concentrate sample increased from 23% to 30% while in the case of the mixed sample ($\text{Fe}_3\text{O}_4\text{--CuFeS}_2$), Cu recovery increased from 25% to almost 40% with temperature increasing from 25 to 50 °C. It could be said that the effect of temperature was well pronounced in the presence of Fe_3O_4 as opposed to the pure CuFeS_2 concentrate.

The effect of temperature was further evaluated at pH 1.8 under free redox potential. The

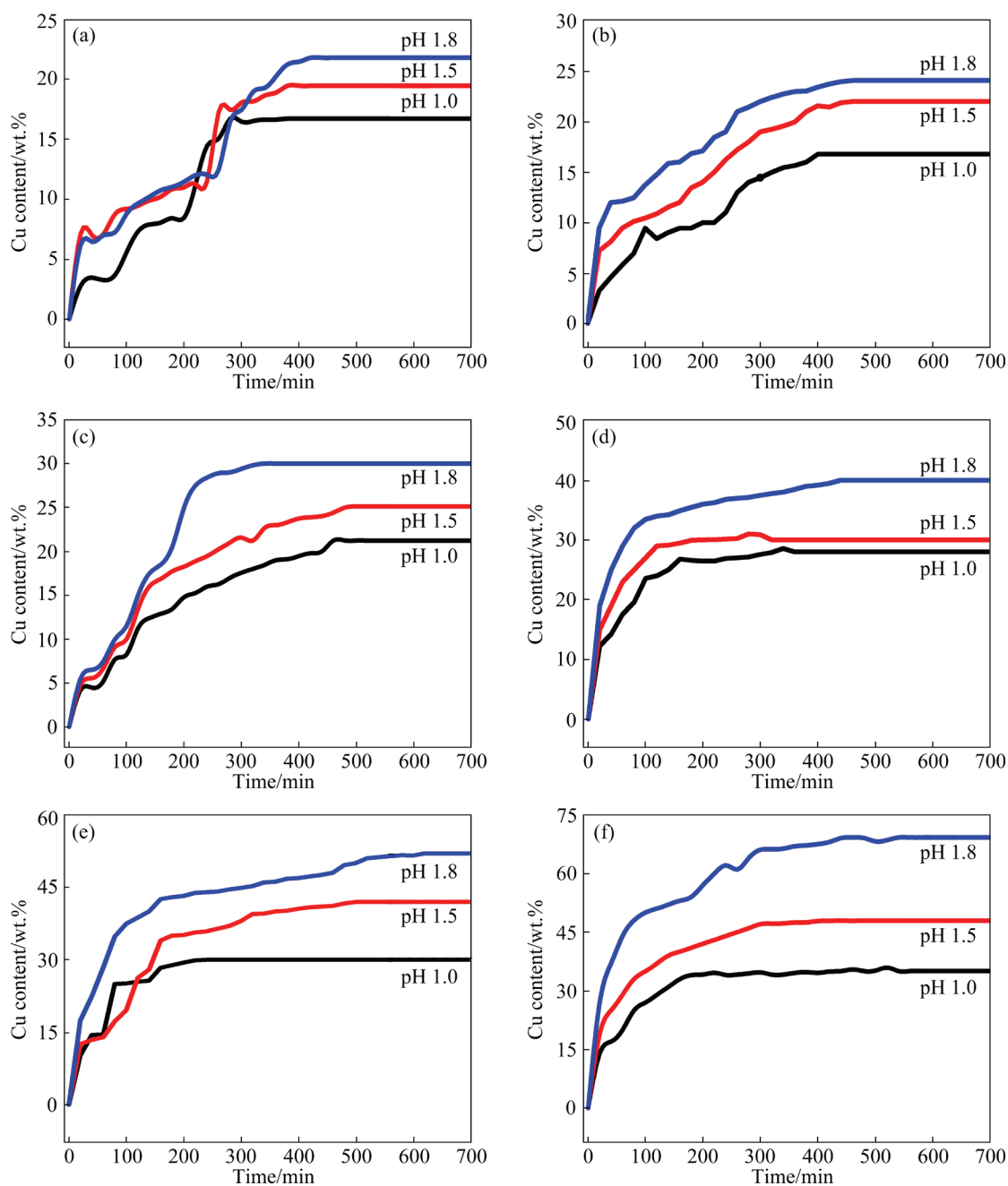


Fig. 3 Cu dissolution curves under different conditions: (a) 25 °C, 348 mV (vs Ag/AgCl), CuFeS₂; (b) 25 °C, 348 mV (vs Ag/AgCl), Fe₃O₄–CuFeS₂ (mass ratio 1:1); (c) 50 °C, 335 mV (vs Ag/AgCl), CuFeS₂; (d) 50 °C, 335 mV (vs Ag/AgCl), Fe₃O₄–CuFeS₂ (mass ratio 1:1); (e) 50 °C, 400 mV (vs Ag/AgCl), CuFeS₂; (f) 50 °C, 400 mV (vs Ag/AgCl), Fe₃O₄–CuFeS₂ (mass ratio 1:1)

simplified shrinking core model (Eq. (1)) was applied on the Cu dissolution curve obtained at each temperature, as shown in Fig. 3. The apparent rate constant and the correlation coefficient were obtained from the straight lines in Fig. 4. The Arrhenius equation (Eq. (2)) was used to estimate the activation energy for the process (Fig. 4). The obtained E_a values for the concentrate and mixed sample (Fe₃O₄–CuFeS₂) were 79.04 and

53.69 kJ/mol, respectively. The obtained E_a value for the CuFeS₂ concentrate (79.04 kJ/mol) appeared to be within the range (71–88 kJ/mol) reported in the literature [19], while in the case of the mixed sample, the E_a value was lower and could be attributed to the impact of Fe₃O₄, suggesting that it is much easier to dissolve Cu from CuFeS₂ under the action of Fe₃O₄. However, both E_a values were found to be above 40 kJ/mol and could imply that

the dissolution is chemically controlled through the particle surface reaction [30].

$$1-(1-x)^{1/3}=k_r t \quad (1)$$

$$\ln(k_1/k_2)=(E_a/R)[(1/T_2)-(1/T_1)] \quad (2)$$

where x is the fraction of CuFeS_2 dissolved at time t ; k_r , k_1 and k_2 are the rate constants, R is the molar gas constant ($8.314 \text{ J}/(\text{mol}\cdot\text{K})$), and T is the thermodynamic temperature.

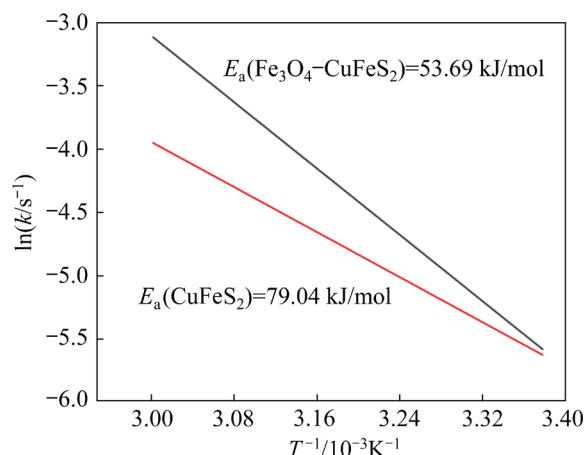


Fig. 4 Arrhenius plot for CuFeS_2 dissolution in presence and absence of Fe_2O_3

3.4 Effect of initial potential

The evolution of the dissolution potential (vs Ag/AgCl) is shown in Fig. 5. Figures 5(a, b) show the solution potential with an initial Fe^{3+} amount of 0.05 mol at 25°C (S_1) and 50°C (S_2), individually, while Fig. 5(c) shows the results under conditions of 400 mV and 50°C (S_3). It could be seen for both samples (with and without Fe_3O_4 addition) that directly after addition of the sample into the solution, the potential begins dropping and could be due to the rapid consumption of ferric (Fe^{3+}) ion, leading to Cu withdrawal and favoring the increase in Fe^{2+} . The CuFeS_2 concentrate without Fe_3O_4 addition revealed a sharp drop in its solution potential as opposed to the mixed sample $\text{Fe}_3\text{O}_4\text{-CuFeS}_2$. A decrease from 348 to 337.9 mV and from 335.1 to 325 mV was recorded for the CuFeS_2 concentrate sample respectively at 25 and 50°C . While for the dissolution of the $\text{Fe}_3\text{O}_4\text{-CuFeS}_2$, the initial potential decreased from 348 to 341 mV and from 337 to 334.2 mV at 25 and 50°C , respectively. A similar trend was also observed when the leaching conditions were 50°C and 400 mV (initial potential), the ORP of the mixed ($\text{Fe}_3\text{O}_4\text{-CuFeS}_2$) sample only dropped from 400 to

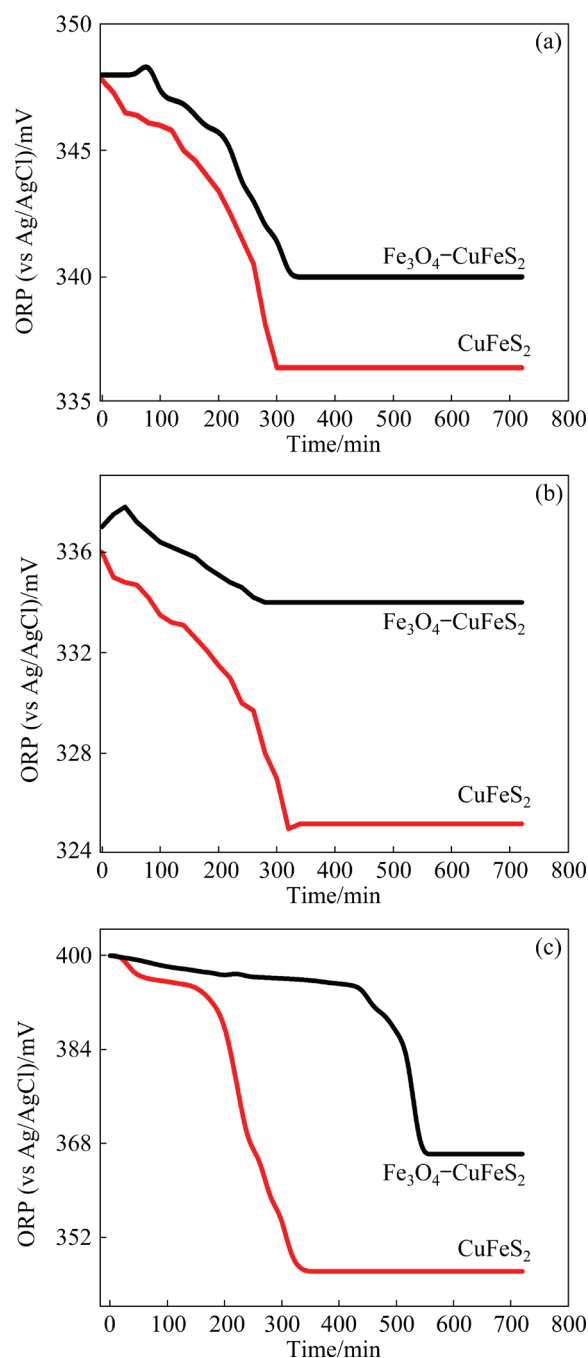


Fig. 5 Oxidation–reduction potential (ORP) evolution of Solutions S_1 (a), S_2 (b) and S_3 (c)

390 mV after 440 min, thereafter, sharply dropped to 367 mV. It could be said that the addition of Fe_3O_4 appears to stabilize the dissolution potential. A stationary region (phase) was observed for the mixed $\text{Fe}_3\text{O}_4\text{-CuFeS}_2$ dissolution. The presence of this stationary phase could be attributed to the galvanic couple existing between Fe_3O_4 and CuFeS_2 ($\text{Fe}^{3+}/\text{Fe}^{2+}$). In fact, the potential of the leach solution is related to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple; for high ratios, the potential will be high while for low ratios

the potential will be low [31]. It can therefore be observed that the leaching curve is inversely related to the potential curve, implying that ferrous iron is co-leached with copper over time, therefore reducing the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. The stationary phase was only observed at the early stage of the dissolution at 0–80 min in S_1 and S_2 while in S_3 this region lasted up to 400 min, confirming that the potential is related to the galvanic couple $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. However, after a period of time there is jarosite precipitation that limits further leaching of iron, therefore leading to stable conditions. In previous work [14,31], the influence of the redox potential on copper leaching rate has already been reported; however, it is important to mention that the initial copper recovery rate is attributed to the leaching of secondary copper minerals; hence the chalcopyrite leaching will only be observed in the decreasing zone of the redox potential curve.

The increase in temperature from 25 to 50 °C appeared to decrease the solution initial potential from 348.7 to 335.1 mV (Figs. 5(a) and (b)). This could be due to the formation of complex species belonging to the $\text{Fe(III)}\text{--Fe(III)}\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ [32].

Earlier studies [33] showed the existence of a potential range interval, referred to as critical (in the vicinity of 0.500 V (vs Ag/AgCl) within the mid-potential range from 0.45 to 0.55 V (vs Ag/AgCl)). All experimental potential values were below the critical range and could explain the relatively low Cu recoveries.

3.5 XRD data of solid residues

Figure 6 shows XRD patterns of the solid residues at pH 1.8, and in the figure a comparison of the mineral phase of the CuFeS_2 samples with and without Fe_3O_4 addition, is shown. Furthermore, in the case of galvanic interaction between CuFeS_2 and Fe_3O_4 , it is assumed that Fe_3O_4 is unaltered, or its content remained virtually unchanged throughout the dissolution. In all cases, the solid residues confirmed the progressive dissolution of the Cu, and the CuFeS_2 peaks ($2\theta=29.46^\circ$, 48.93° and 57.95°) appeared to some extent distorted and decreased in its intensity. In addition, Cu-rich phases (bornite (Bo), chalcocite (Cx), gerite (Ge) and covellite (Co)) were observed. The presence of these Cu-rich intermediates appeared to support earlier investigation by ACERO et al [31], who 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 the present identified species could belong. In addition, NYEMBWE et al [35,36] identified the correlation of these transient phases to the media pH values and thermodynamically highlighted covellite as the main refractory transition phase, hindering further dissolution as opposed to bornite and chalcocite. Similarly, DENG et al [37] reported an enhanced CuFeS_2 dissolution in the presence of Fe_3O_4 through preferential formation of chalcocite (Cu_2S). This could imply that the presence of Fe_3O_4 favors the formation of soluble Cu-rich intermediate and further supports the rapid Cu withdrawal and high dissolution content obtained (Figs. 6(a), (c) and (e)).

The $\text{Fe}_3\text{O}_4\text{--CuFeS}_2$ spectrum remained mostly dominated by the presence Fe_3O_4 , suggesting that little dissolution of Fe_3O_4 took place. Thus, the galvanic couple exists when Fe_3O_4 is combined to CuFeS_2 , since a high content of Cu is dissolved from the mixed $\text{Fe}_3\text{O}_4\text{--CuFeS}_2$ sample, as opposed to the pure CuFeS_2 sample. Overall, the Fe_3O_4 content in the mixed $\text{Fe}_3\text{O}_4\text{--CuFeS}_2$ sample practically decreased by a small margin when compared to its content in the feed sample and appeared to be ORP dependent. The results showed that the Fe_3O_4 content dropped by 9.7%, 12.3% and 6.4% from its respective content in the feed for the solutions with ORP values of 348.7 mV (25 °C), 335.1 mV (50 °C) and 400 mV (vs Ag/AgCl) (50 °C), respectively. This further implies that a complete recovery of Fe_3O_4 could be achievable by a regulation of the solution potential which is subjected to further research.

Elemental sulphur (S^0) and jarosite were also identified in both solid residues. The former could be regarded as a dissolution product while the latter phase occurred due to the hydrolysis of Fe products. S^0 was clearly identified and its content was higher in the case of the mixed $\text{Fe}_3\text{O}_4\text{--CuFeS}_2$ sample, as opposed to the CuFeS_2 concentrate. This observation supports the positive impact of Fe_3O_4 on Cu dissolution from CuFeS_2 and its high content also tends to agree to previous studies that have ruled out S^0 as responsible for the slow dissolution [38,39]. It was observed that S^0 had a porous morphology which allowed transport processes through and from the dissolving mineral, therefore could not be held responsible for passivation [25,34].

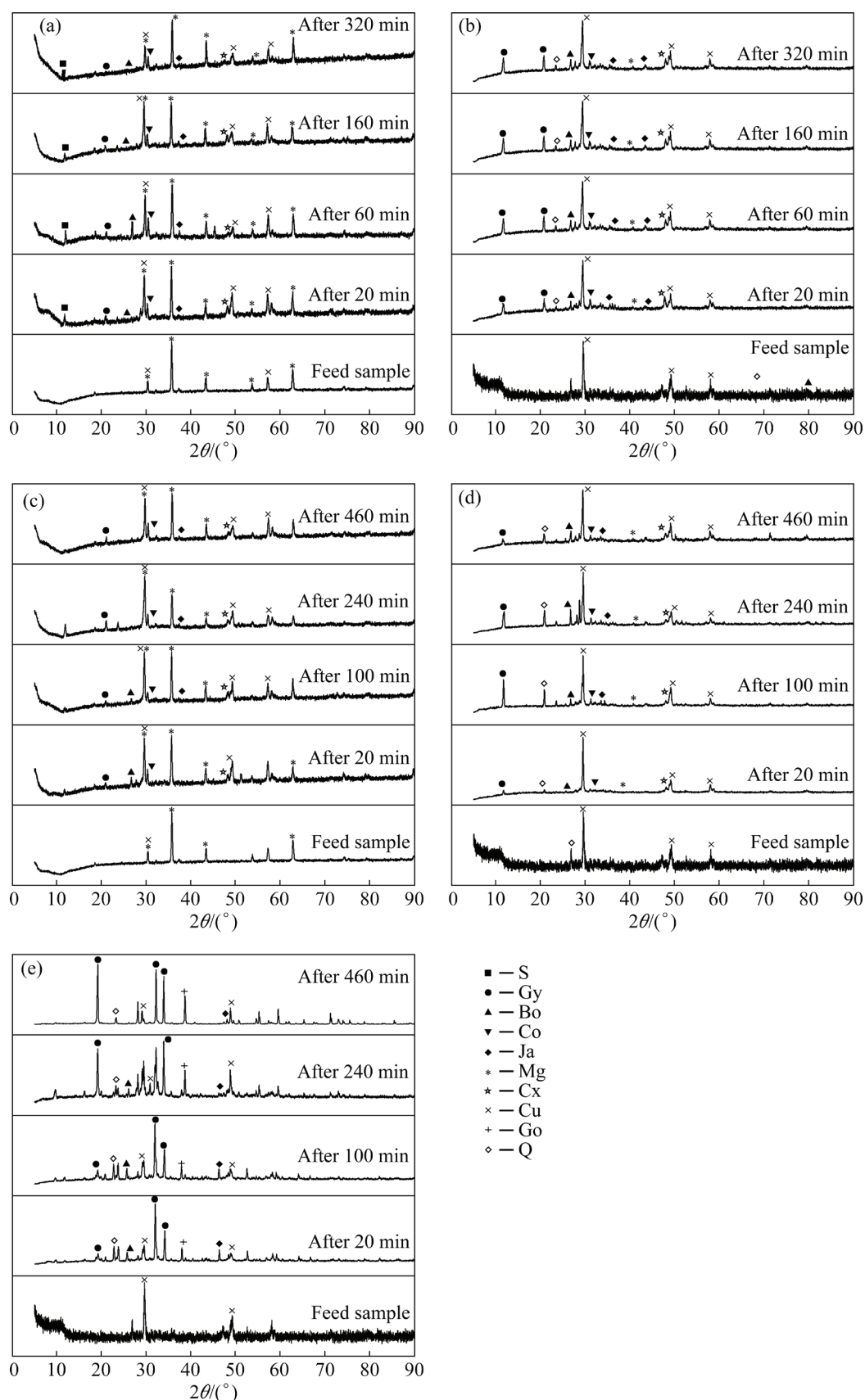


Fig. 6 XRD patterns of solid residues at pH 1.8: (a) $\text{Fe}_3\text{O}_4\text{-CuFeS}_2$ residue at 25 °C; (b) CuFeS_2 concentrate residue at 25 °C; (c) $\text{Fe}_3\text{O}_4\text{-CuFeS}_2$ residue at 50 °C; (d) CuFeS_2 concentrate residue at 50 °C; (e) $\text{Fe}_3\text{O}_4\text{-CuFeS}_2$ residue at 50 °C and 400 mV (Gy—Gypsum; Co—Covellite; Cx—Chalcocite; Bo—Bornite; Go—Goethite; Ja—Jarosite; Q—Quartz)

Jarosite was identified in all solid residues, its content was high in the CuFeS_2 concentrate, as opposed to the mixed sample ($\text{Fe}_3\text{O}_4\text{--CuFeS}_2$), and could be probably due to the Fe_3O_4 addition to CuFeS_2 which has diluted the jarosite content. Furthermore, the jarosite content was observed to be pH dependent. However, the high Cu recovery was obtained at a higher pH (1.8) value than at lower pH values (highly acidic solution, pH 1.5 and 1.0); this could suggest that jarosite has little effect on the Cu dissolution [35,36].

4 Conclusions

(1) Both chemical and physical factors play a vital role during aerobic dissolution of CuFeS_2 in acidic ferric sulfate at different pH (1.0–1.8) and temperature (25 and 50 °C) values. Cu dissolves more easily at higher pH values than at lower pH values ($\text{pH}1.8 > \text{pH}1.5 > \text{pH}1.0$), evidently at 25 and 50 °C.

(2) Elemental sulfur and jarosite had little effect on CuFeS_2 dissolution. The addition of Fe_3O_4 had a positive effect on Cu dissolution. Both dissolution rate and recovery increased after addition of Fe_3O_4 due to the formation of a $\text{Fe}_3\text{O}_4\text{--CuFeS}_2$ galvanic couple. The analysis of the solid residues confirmed the existence of this voltaic couple as the leached residues remained dominated by Fe_3O_4 .

(3) The estimated activation energies of 79.04 and 53.69 kJ/mol were obtained for the concentrate and mixed $\text{Fe}_3\text{O}_4\text{--CuFeS}_2$ sample, respectively. The obtained results present an alternative dissolution route for the CuFeS_2 mineral; however, further research in regard to process optimization should be conducted.

CRedit authorship contribution statement

Kolela J NYEMBWE: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing – Original draft preparation, Visualization; **Elvis FOSSO-KANKEU:** Conceptualization, Methodology, Validation, Investigation, Resources, Supervision, Project administration, Funding acquisition; **Frans WAANDERS:** Validation, Resources, Project administration; **Martin MKANDAWIRE:** Validation, Investigation, Resources, Writing – Review and editing, Supervision, Funding acquisition; **Didier K NYEMBWE:** Software, Validation; **Bhekhe B MAMBA:** Software, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Fe₃O₄ 对黄铜矿在酸性硫酸铁溶液中铜溶解氧化还原反应的影响

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摘 要: 由于钝化层的形成, 黄铜矿(CuFeS₂)在氧化条件下浸出通常具有溶解速率缓慢的特点。为了将黄铜矿浸出过程中的钝化效应降至最低并提高铜的回收率, 研究了 CuFeS₂ 在不同 pH 值(1.0、1.5 和 1.8)和温度(25 和 50 °C)条件下浸出时, 向 Fe₂(SO₄)₃-H₂SO₄ 浸出剂中添加磁铁矿(Fe₃O₄)对铜溶解速率的影响。结果表明, 溶液 pH 值、电位和温度在溶解过程中起着关键作用。在 pH 1.8、50 °C 和 400 mV 的条件下, Fe₃O₄-CuFeS₂ 混合体系中铜的回收率达到最大值(70%), 而未添加 Fe₃O₄ 时, CuFeS₂ 中铜的回收率较低(48%)。添加 Fe₃O₄ 有助于维持较高的氧化还原值。添加 Fe₃O₄ 还使活化能从 79.04 kJ/mol 降低到 53.69 kJ/mol。这表明, 当 Fe₃O₄ 存在时, 由于形成了更易溶解的中间体斑铜矿(Cu₅FeS₄)和辉铜矿(Cu₂S), CuFeS₂ 更易被氧化。两种溶解过程都受到矿物表面的化学控制。此外, 对浸出残渣的矿物学分析表明, 当无 Fe₃O₄ 存在时, 作为表面钝化物的黄钾铁矾浓度较高。因此, 添加 Fe₃O₄ 减少了钝化层的形成, 提升了铜的回收率。

关键词: 黄铜矿; 溶解; 磁铁矿; 电偶; 钝化

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