

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

**jmr&t**  
Journal of Materials Research and Technology  
[www.jmrt.com.br](http://www.jmrt.com.br)



## Original Article

# An improved understanding of chalcopyrite leaching kinetics and mechanisms in the presence of NaCl

Shan Zhong<sup>a,b</sup>, Yubiao Li<sup>b,c,\*</sup><sup>a</sup> Office of Academic Affairs, Wuhan University of Technology, Wuhan, 430070, China<sup>b</sup> School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan, 430070, China<sup>c</sup> State Key Laboratory of Mineral Processing, BGRIMM Technology Group, Beijing, 100160, China

## ARTICLE INFO

## Article history:

Received 12 February 2019

Accepted 12 June 2019

Available online 28 June 2019

## Keywords:

Chalcopyrite

Leaching

Passivation

NaCl

Mechanism

## ABSTRACT

Copper (Cu) extraction rate from chalcopyrite ( $\text{CuFeS}_2$ ) is normally slowed down by the passivation layers formed on  $\text{CuFeS}_2$  surface. Cost-effective  $\text{CuFeS}_2$  extraction strategies are therefore strongly expected in both academic and industrial worlds. This study investigated  $\text{CuFeS}_2$  leaching in the presence of NaCl and the results showed that NaCl played a significantly positive role on Cu extraction in air-saturated solution. Smaller  $\text{CuFeS}_2$  particle size led to a higher Cu recovery while pH 1.0 was optimum. In addition, the increment of NaCl concentration increased Cu extraction rate and recovery significantly. Moreover, Cu extraction from  $\text{CuFeS}_2$  was increased apparently with increased temperature, with an approximately 100% Cu recovery being achieved at 348 K and 0.1 M NaCl, within 144 h. XRD indicated that the major products formed were crystalline elemental sulfur ( $\text{S}^0$ ) rather than Cu–S like compounds at a NaCl concentration greater than 0.1 M, indicating that crystalline  $\text{S}^0$  did not inhibit Cu extraction. This study therefore provides a promising strategy of applying seawater in hydrometallurgical processing of chalcopyrite.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1. Introduction

Chalcopyrite ( $\text{CuFeS}_2$ ) is the most abundant Cu-bearing mineral, accounting for approximately 70% of the total Cu resources [1,2]. Although 80–85% of the world Cu production is currently pyrometallurgically processed, recent studies have

been focused on hydrometallurgical processing alternatives due to the declining Cu grade and increasingly stringent environmental regulations [3].

Although leaching, as the key step in the hydrometallurgical treatments, has been intensively studied since 1970s [4,5], its application in  $\text{CuFeS}_2$  has not been widely adopted in industry to date, due to its extremely slow leaching kinetics [2,6]. Most previous studies have suggested that Cu extraction from  $\text{CuFeS}_2$  was inhibited by the surface passivation layers (e.g., jarosite, disulfide, polysulfide, elemental sulfur ( $\text{S}^0$ )) formed during leaching process [7], especially under oxidiz-

\* Corresponding author.

E-mail: [Yubiao.Li@whut.edu.cn](mailto:Yubiao.Li@whut.edu.cn) (Y. Li).<https://doi.org/10.1016/j.jmrt.2019.06.020>2238-7854/© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

ing conditions [3,8]. For instance, Olubambi and Potgieter [9] reported that  $S^0$  was the primary surface passivation layer, giving rise to a 7% Cu extraction after 6 h in the sulfuric acid ( $H_2SO_4$ ) system. In addition, numerous methods have been conducted to improve Cu leaching rate and recovery, such as increasing temperature [10], adding catalysts or oxidants [11], grinding [12], adjusting redox potential [13], exerting pressure [14]. Although these methods improve Cu extraction rate and recovery to some extents, high costs hinder their wide application.

To date, seawater has been paid increasing interests in many mineral processing plants (e.g., BHP Nickel in Australia, Grasberg Mine in Indonesian, Las Lucas Mine in Chile) as a promising alternative to freshwater due to water shortage [15,16]. For instance, Torres et al. [17] reported that seawater was beneficial to  $CuFeS_2$  leaching due to chloride ions. Therefore, the investigation of the primary ions containing in seawater (i.e., sodium and chloride) in leaching process has attracted much attention due to catalytic effects and ability to increase metal solubility, etc. [11,18–21].

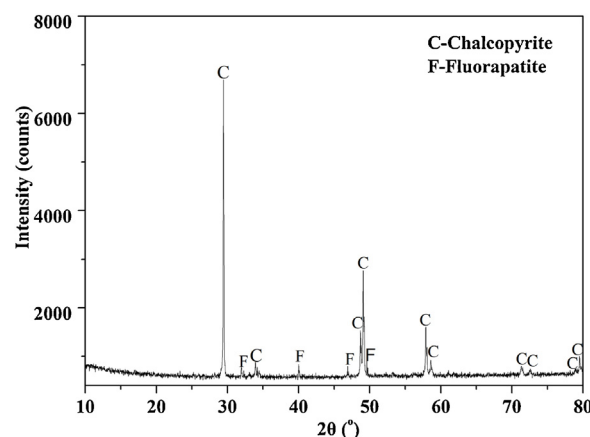
Some studies reported that the formed surface layer was porous  $S^0$  when leaching was carried out in the presence of chloride ions, different from the condensed  $S^0$  layer on  $CuFeS_2$  surface in the absence of chloride ions. Dutrizac [22] reported that the activation energy ( $E_a$ ) of  $CuFeS_2$  leaching was dramatically decreased in chloride solutions, that is, from  $75 \text{ kJ mol}^{-1}$  to  $42 \text{ kJ mol}^{-1}$ . Winand [23] suggested that higher Cu extraction in the presence of  $Cl^-$  ions was due to the formation of  $Cu^+$ ,  $Cu^{2+}$  complexes with  $Cl^-$ . Hernandez et al. [16] reported that the positive role of applying seawater in increasing Cu extraction from  $CuFeS_2$  was ascribed to the formation of Cu chloro-complexes.

The enhanced Cu extraction from  $CuFeS_2$  in the presence of  $Cl^-$  ions is normally ascribed to the following reasons: (1) forming metal chloride complexes; (2) increasing anodic current on  $CuFeS_2$  particles; (3) changing the properties of surface products [8,24]. As stated in Ref. [25], the SEM results indicated a crystalline and porous  $S^0$  layer on  $CuFeS_2$  surface in the presence of NaCl as euhedral sulfur phase was observed. The NaCl concentration in chalcopyrite leaching process was usually within 2 M, with the temperature normally being lower than 373 K [8,18,20], although the pH of the leaching media varied widely, for example, from pH 2 to 0 [6]. In addition,  $H_2SO_4$  was the most frequently used acidic medium for chalcopyrite leaching [6,8,26–28].

However, most of the previous studies with very fast Cu leaching kinetics were completed with the addition of various oxidants (e.g.,  $H_2O_2$ ,  $Fe^{3+}$ ,  $(NH_4)_2S_2O_8$ ), which might hide the real effects of NaCl on  $CuFeS_2$  leaching, due to much stronger oxidative effects from these oxidants. Therefore, the aim of this study is to investigate  $CuFeS_2$  leaching kinetics and mechanisms in NaCl solution under air-saturated conditions, thereby revealing the intrinsic roles of NaCl solutions. As most of our previous studies focused on chalcopyrite leaching at a pH ranging from 1 to 2 [27–29] and temperature lower than 348 K, this study will apply similar leaching conditions. The results obtained will deep the understanding of the possibility to process chalcopyrite using seawater.

**Table 1 – Weight percentage of main elements in  $CuFeS_2$  sample.**

Particle size ( $\mu\text{m}$ )	Cu (%)	S (%)	TFe (%)
–38	29.83	31.89	29.03
+38 to –75	30.20	31.59	29.30
+75 to –150	30.04	30.32	29.37



**Fig. 1 – XRD pattern of  $CuFeS_2$  sample.**

## 2. Methods

### 2.1. Minerals

Chunk  $CuFeS_2$  sample obtained from GEO Discoveries (Australia) was crushed and milled to obtain three size fractions (–38, +38 to –75, +75 to –150  $\mu\text{m}$ ) via wet sieving.  $CuFeS_2$  particles were cleaned through sonication to remove adhering fines and then dried in a vacuum oven at 70 °C for 24 h. Table 1 showed the major elements (i.e., Cu, Fe and S) concerned at three sizes, indicating a relatively homogeneous distribution and high purity of  $CuFeS_2$ .

The XRD (Fig. 1) patterns further indicated a high purity and well crystallized  $CuFeS_2$  with a very small amount of fluorapatite as an impurity phase.

### 2.2. Leaching methods and reagents

1 g of  $CuFeS_2$  powders (–38  $\mu\text{m}$ , +38 to –75  $\mu\text{m}$ , +75 to –150  $\mu\text{m}$ ) was added into 100 mL  $H_2SO_4$  solution (pH 0.5–1.5) in the presence of 0–1.0 M NaCl. The leaching experiments were carried out in shake flasks in an oscillation incubator (BS-S, Changzhou Guohua Electric Appliance CO., LTD, China) at a constant temperature and 150 rpm. 1 mL solution was sampled out by pipette to measure Cu concentration. After that, fresh leaching lixiviant was added to replenish to the original level. All chemicals (NaCl,  $H_2SO_4$ ) used in this study were in analytical grade While the Millipore® (Billerica, MA, USA) ultrapure water with a resistivity of 18.2 M $\Omega$  cm was employed in all tests.

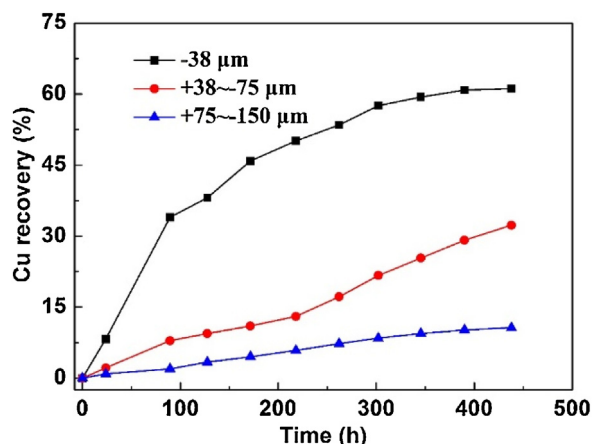


Fig. 2 – Effects of particle size on Cu extraction at 328 K (0.1 M NaCl).

### 2.3. Characterization

The leach residues were filtered, washed, dried and determined by X-ray diffraction (XRD) (Cu  $K\alpha_1$ , D8 Advance, Bruker, Germany). Cu concentration was measured by atomic absorption spectroscopy (AAS, Agilent AA240FS, Agilent Technologies Inc. Santa Clara, CA, USA). The pH meter (pH 2100, Eutech Instruments, America) was used to measure the solution pH.

## 3. Results and discussion

### 3.1. Effects of particle size

The effects of particle size on Cu extraction in pH 1.0 solution controlled at 328 K in the presence of 0.1 M NaCl were investigated at three size fractions (–38, +38 to –75, +75 to –150 μm), to insure the leaching within a reasonable lab time scale. Fig. 2 indicated that Cu extraction was increased with decreased particle size. Specifically, the highest Cu leaching recovery was achieved at –38 μm, for example, a Cu recovery of 61% was observed at 438 h, significantly greater than that of +38 to –75 μm (32%) and +75 to –150 μm (approximately 10%). Apparently, fine particles resulted in greater Cu extraction, similar to that observed in Ref. [18], probably due to greater surface area [30]. Although greatest Cu extraction was obtained at –38 μm, grinding of CuFeS<sub>2</sub> particles to –38 μm would cost much higher energy than other two size fractions. It is widely recognized that the selection of appropriate particle size is essential for industrial implementation as this determines power consumption, plant design and preparation processes for leaching [2]. Therefore, the +38 to –75 μm fraction was selected for further study.

### 3.2. Effects of pH

The influence of pulp pH on Cu extraction was investigated in the solution containing 0.1 M NaCl at 328 K (Fig. 3). In order to avoid the formation of Fe hydroxide precipitation or Na and/or H-jarosite compounds that capable of passivating

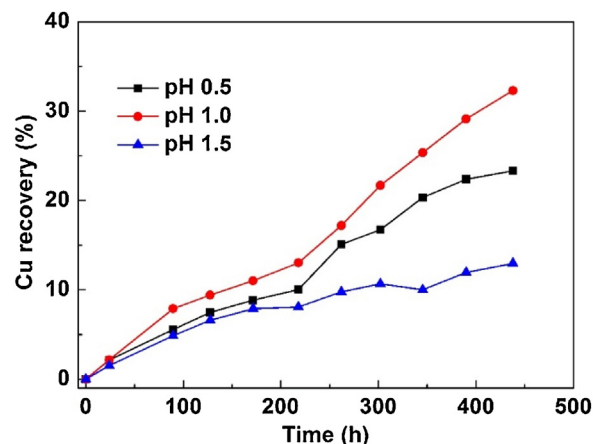


Fig. 3 – Effects of pulp pH on Cu extraction at 328 K (0.1 M NaCl).

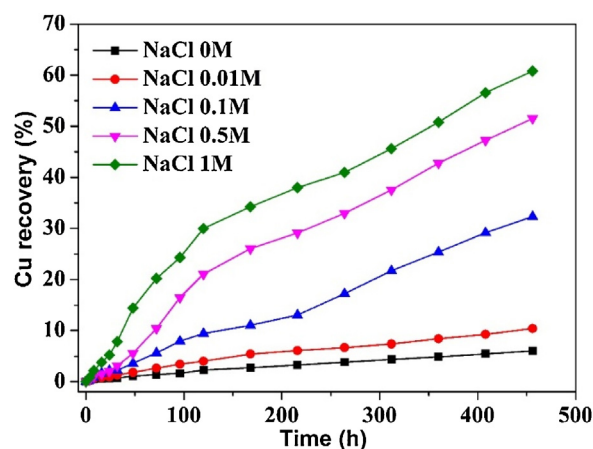


Fig. 4 – Effects of NaCl concentration on Cu extraction.

CuFeS<sub>2</sub> leaching, pH was controlled within the range from 0.5 to 1.5. It is observed that when pH was decreased from 1.5 to 1.0, Cu extraction was increased from 13% to 32% at 438 h. However, when the solution pH was continuous decreased to 0.5, Cu extraction was decreased to 23%. This indicated that pH 1.0 was favorable to CuFeS<sub>2</sub> leaching.

Cu leaching rate is normally increased with increased acid concentration. However, a reasonable H<sup>+</sup> concentration range is recommended for CuFeS<sub>2</sub> leaching. For instance, Antonijevic and Bogdanovic [31] reported that a pH lower than 0.5 (using H<sub>2</sub>SO<sub>4</sub> as leaching medium) reduced Cu leaching rate due to the competition between Fe<sup>3+</sup> and H<sup>+</sup>, especially when acid concentration was increased to 3–5 M. In addition, the increase of acid amount increases the operation costs [1]. Therefore, pH 1.0 was selected for further study.

### 3.3. Effects of NaCl concentration

The effects of NaCl concentration on CuFeS<sub>2</sub> leaching at 328 K and pH 1 were investigated at +38 to –75 μm (Fig. 4). Generally, Cu extraction was increased with increased NaCl concentration. Specifically, only 6% of Cu was extracted at 456 h in the absence of NaCl, consistent with many other studies

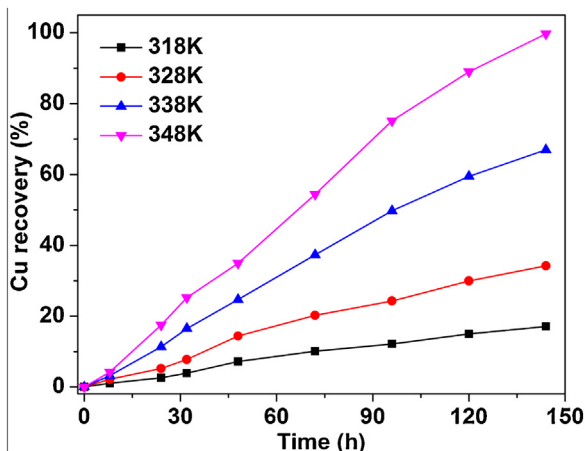


Fig. 5 – Effects of temperature on Cu extraction.

[4,24,31,32]. A slightly increase in Cu extraction was observed when 0.01 M NaCl was applied. A further increase in NaCl concentration to 0.1 M apparently increased Cu extraction to 32%, with much greater Cu extraction being observed at higher NaCl concentration.

The positive roles of NaCl might be because the  $\text{Cl}^-$  ions promoted the formation of porous  $\text{S}^0$  layers on  $\text{CuFeS}_2$  surfaces, favoring Cu extraction. Moreover, the addition of NaCl to the leaching system improved the stability of  $\text{Cu}^{2+}/\text{Cu}^+$  electron pair, thereby forming chlorocuprate (I) ions [8,18]. The presence of chlorocuprate (I) ions increased the critical potential of solution, further resulting in greater Cu extraction due to oxidative dissolution. In order to reveal the possibility to increase Cu extraction at a low concentration of NaCl, 0.1 M was selected for further study.

### 3.4. Effects of temperature

Fig. 5 showed the temperature effects (318 K–348 K) on  $\text{CuFeS}_2$  leaching at 0.1 M NaCl. It is clearly showed that Cu extraction was increased with increasing temperature, for example, Cu recoveries of 17%, 34%, and 67% were observed at 318 K, 328 K, and 338 K at 144 h, respectively, with an almost 100% Cu being extracted when temperature was further increased to 348 K, indicating that  $\text{CuFeS}_2$  leaching was significantly influenced by increased temperature. It should also be noted that Cu extraction followed an almost linear increasing trend with leaching time progressed.

### 3.5. XRD analysis

In order to investigate the phase evolution in the presence of various NaCl concentrations during  $\text{CuFeS}_2$  leaching process, the XRD patterns of the leached residues were collected and analysed. Fig. 6 showed the XRD patterns collected from the leach residues with various NaCl concentrations. Similar XRD results were obtained when NaCl concentrations were at 0 (Fig. 6a) and 0.01 M (Fig. 6b), for example,  $\text{CuFeS}_2$  and Cu-S like phase but no  $\text{S}^0$ . With the increase of NaCl concentration to 0.1 M (Fig. 6c), the characteristic peaks of  $\text{S}^0$  were observed. Further increase in NaCl concentration to 0.5 M (Fig. 6d) and

1.0 M (Fig. 6e) resulted in the formation of more crystalline  $\text{S}^0$ , but Cu-S like phase disappeared. As greater Cu extraction can be obtained at higher NaCl concentration (Fig. 4), the presence of high NaCl concentration might inhibit the formation of Cu-S like passivation layer or the Cu-S like phase can be further oxidised to  $\text{S}^0$  and releasing Cu into solution.

### 3.6. Kinetics analysis

Shrinking core model is the most widely applied one for  $\text{CuFeS}_2$  leaching process [2]. Surface reaction (Eq. 1) and diffusion (Eq. 2) kinetic models can be applied for  $\text{CuFeS}_2$  leaching [10,33], with the slowest one as the rate-determining step.

$$1 - (1 - X)^{\frac{1}{3}} = k_1 t \quad (1)$$

$$1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}} = k_2 t \quad (2)$$

where X is the Cu extraction,  $k_1$  and  $k_2$  correspond to reaction rate constants, t means leaching time. Fig. 7 indicated that the leaching process was controlled by the surface reaction model due to a better linear fitting ( $R^2 > 0.91$  at 348 K,  $> 0.99$  in the other three groups), as compared to the diffusion control model ( $R^2$  were 0.82, 0.95, 0.96 and 0.92 at 348 K, 338 K, 328 K, and 318 K, respectively, Fig. 7b).

As Cu concentrations under differing temperatures were linearly increased with time, Eq. 3 can be used to determine the apparent rate constant k.

$$\frac{dC}{dt} = k \quad (3)$$

where C is Cu concentration (M), t means leaching time (h), k corresponds to the reaction rate constant. Based on the Arrhenius equation (Eq. 4), the  $E_a$  of  $\text{CuFeS}_2$  leaching can be calculated.

$$k = Ae^{-E_a/RT} \quad (4)$$

where A is the pre-exponential factor,  $E_a$  is the activation energy ( $\text{J mol}^{-1}$ ), R is the universal gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ ), T is the absolute temperature in Kelvin (K).

It is widely accepted that  $E_a$  greater than  $20 \text{ kJ mol}^{-1}$  implies a surface reaction while  $E_a$  less than  $20 \text{ kJ mol}^{-1}$  suggests the leaching process is diffusion controlled [2]. Fig. 8a showed a good fitting of Cu concentration against time while Fig. 8b demonstrated a good fitting of  $\ln k$  against  $1/T \cdot 10^{-3}$ . An  $E_a$  of  $55.5 \pm 3.9 \text{ kJ mol}^{-1}$  with a coefficient of determination  $R^2 > 0.98$  suggested that  $\text{CuFeS}_2$  leaching was controlled by surface chemical reaction, consistent with the kinetics analysis shown in Fig. 7.

### 3.7. Mechanisms

According to our previous study [29],  $\text{CuFeS}_2$  leaching can be separated into two steps. In the initial stage, the primary reaction (Eq. 5) is the oxidation of  $\text{CuFeS}_2$  with the cathodic reaction being as the reduction of  $\text{O}_2$  (Eq. 6). With the progress of leaching, soluble Cu and Fe concentrations were increased due to their extraction and release into the solution.  $\text{Fe}^{2+}$



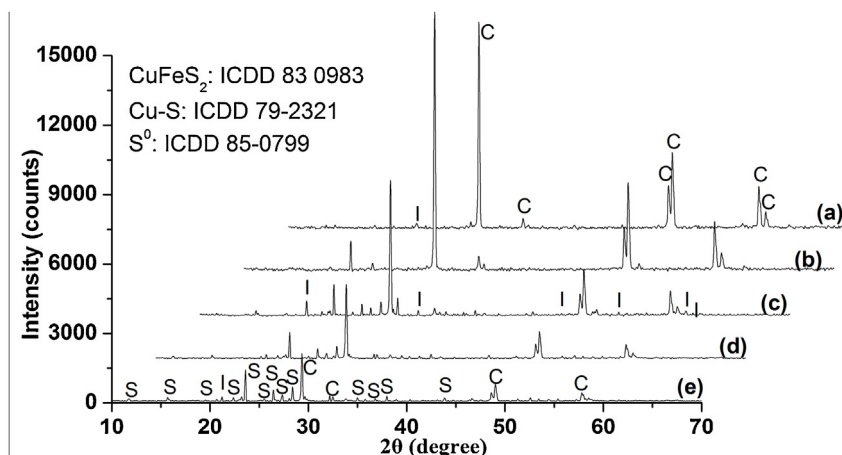


Fig. 6 – XRD patterns of CuFeS<sub>2</sub> leach residues at different NaCl concentrations (a): 0 M, (b) 0.01 M, (c) 0.1 M, (d) 0.5 M and (e) 1.0 M. (C-CuFeS<sub>2</sub>, S-elemental sulfur, I: Cu-S like compounds).

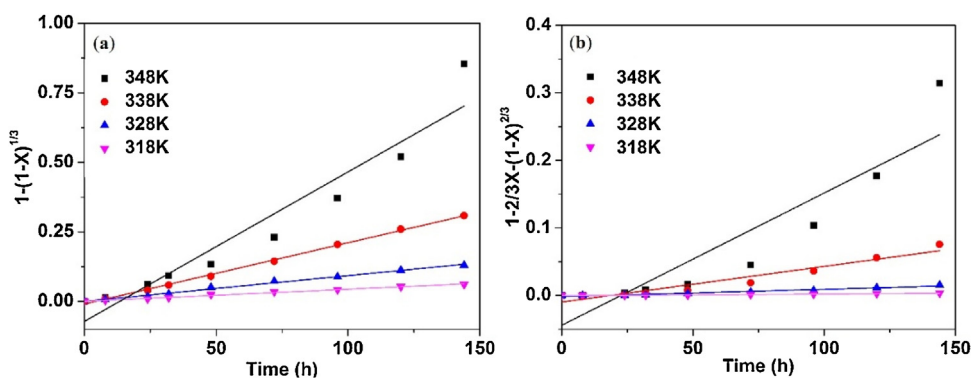


Fig. 7 – Plots of (a)  $1 - (1 - X)^{1/3}$  and (b)  $1 - \frac{2}{3}X - (1 - X)^{2/3}$  vs. time.

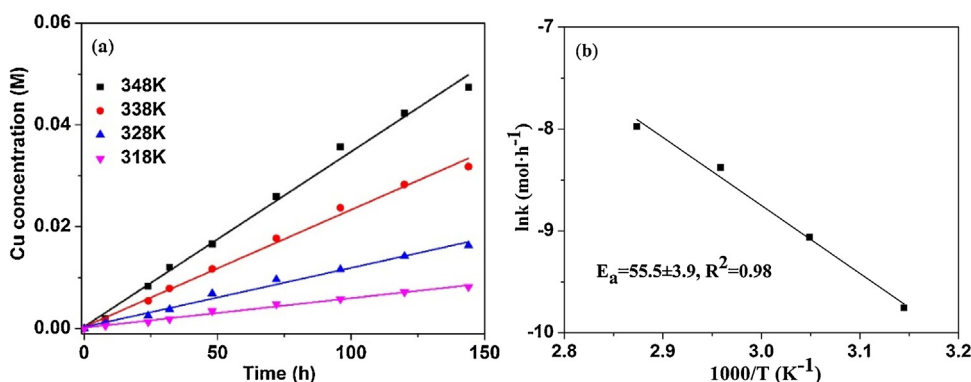
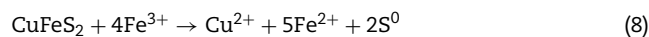
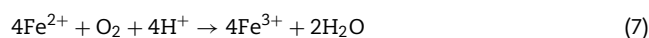
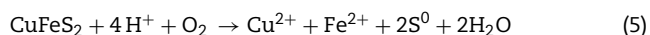


Fig. 8 – (a) Cu concentration vs. time at various temperatures. (b) Arrhenius plot.

formed via Eq. 5 can be oxidized by O<sub>2</sub> (Eq. 7) to generate oxidative Fe<sup>3+</sup> which can further oxidize CuFeS<sub>2</sub> (Eq. 8). As the strong oxidant of Fe<sup>3+</sup> is involved in CuFeS<sub>2</sub> leaching, Cu extraction is increased at the latter stage. However, it is widely recognized that slow kinetics can be found in the latter stage if Eq. 8 occurs [8,21,24,26], as many studies have shown that the limited step for Cu extraction was the transport process via the S<sup>0</sup> layer formed [11,17,20,33].



Eq. 9 represents another possibility if Fe<sup>3+</sup> is present in the solution as oxidant, that is, producing SO<sub>4</sub><sup>2-</sup> rather than S<sup>0</sup>. As both Eqs. 8 and 9 suggest beneficial roles of Fe<sup>3+</sup> in CuFeS<sub>2</sub> leaching, the oxidized S products can be referred to determine

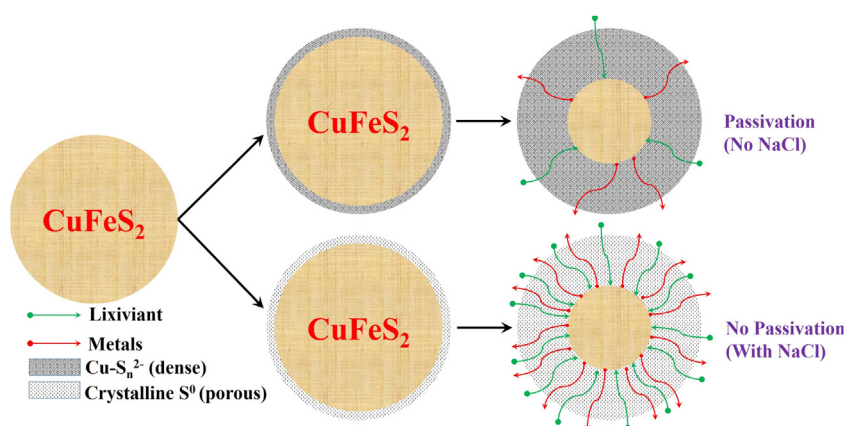
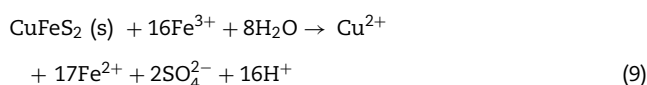


Fig. 9 – Schematics of CuFeS<sub>2</sub> leaching in the absence and presence of NaCl.

which reaction is predominant.



Aromaa and Dutrizac [34] reported that approximately 94% of S was transformed to S<sup>0</sup> while the rest 6% of S from CuFeS<sub>2</sub> was oxidized to SO<sub>4</sub><sup>2-</sup>, similar to that found in Ref. [25]. Our previous studies [29] also showed that the predominant S products upon CuFeS<sub>2</sub> leaching was S<sup>0</sup>. As no extra oxidant was added into the leaching system except O<sub>2</sub> existing in the solution, no strong oxidative conditions were available to produce SO<sub>4</sub><sup>2-</sup> [35]. In other words, the predominant S product was crystalline S<sup>0</sup> rather than SO<sub>4</sub><sup>2-</sup>, consistent with the XRD results shown in Fig. 6. Hence, Eqs. 5 and 8 were the oxidation reactions for the initial and latter leaching stages of CuFeS<sub>2</sub>.

In addition, some studies indicated that the presence of Cl<sup>-</sup> ions increased metal solubility in the leaching system and the porosity of S-containing products formed on CuFeS<sub>2</sub> surface, which improved the diffusion of reagents to CuFeS<sub>2</sub> surface and extracted metals into solution, thereby increasing Cu extraction rate and recovery [8,17,19,25]. Various surface sensitive techniques have been applied to investigate the upmost surface product layer using electrochemistry, XPS, FTIR or even synchrotron, etc. [2,6,36,37]. However, these approaches did not clearly explain that the passivation layer should be focused on the layers from the interface contacting with non-oxidized CuFeS<sub>2</sub> core to the upmost surface contacting with the solution (Fig. 9). Therefore, the whole passivation layer covering on CuFeS<sub>2</sub> surface is key in understanding the passivation mechanisms.

No jarosite or Fe oxy-hydroxide was detected in the leaching residues (Fig. 6), possibly due to the small amounts or no formation of such products. In contrast, only crystalline Cu-S and S<sup>0</sup> were observed in the presence of NaCl (Fig. 6). In addition, with the increase in NaCl concentration, Cu-S disappeared while the intensity of peaks representing S<sup>0</sup> was gradually increased. These suggested that the S<sub>n</sub><sup>2-</sup> layer might be further oxidized to S<sup>0</sup> layer coating on CuFeS<sub>2</sub> surface (Fig. 9). Once NaCl was added into the leaching system, Cu extraction was increased dramatically, especially when NaCl

concentration was greater than 0.01 M (Fig. 4). This result agrees well with the previous published works [11,18–21], suggesting that the crystalline S<sup>0</sup> (detected in XRD, Fig. 6) did not passivate Cu extraction, due to the constant leaching rate observed especially at high temperature (Fig. 5), different from previous published work regarding CuFeS<sub>2</sub> leaching [1,2,26,29,31].

Traditionally, the role of Cl<sup>-</sup> ions in CuFeS<sub>2</sub> leaching process was considered as: (1) a complexing reagent for metal ions; (2) a surfactant assisting in S<sup>0</sup> removal; (3) increase surface area and porosity of insoluble product layer formed on mineral surface. Many research indicated that the presence of Cl<sup>-</sup> ions resulted in a much more crystalline S<sup>0</sup> product. In other words, the S<sup>0</sup> layer coated on CuFeS<sub>2</sub> surface was crystalline and porous in the presence of NaCl while amorphous or cryptocrystalline S<sup>0</sup> film in the absence of NaCl [25].

In addition, when Cl<sup>-</sup> ions are available in the leaching system, a secondary redox couple of Cu<sup>2+</sup>/Cu<sup>+</sup> is operative to generate intermediate product of Cu-Cl complexes [20]. Therefore, Cl<sup>-</sup> ions played positive roles on Cu extraction, especially when crystalline S<sup>0</sup> was formed on CuFeS<sub>2</sub> surface, due possibly to the easier diffusion of leaching reagents and metal ions between CuFeS<sub>2</sub> surface and solution.

Furthermore, the kinetic analysis indicated that CuFeS<sub>2</sub> leaching was controlled by surface chemical reaction, indicating that the diffusion of reagents via surface layer to CuFeS<sub>2</sub> surface did not determine the whole leaching process. In other words, the formed crystalline S<sup>0</sup> (Fig. 6) on CuFeS<sub>2</sub> surface did not passivate Cu extraction in the presence of NaCl, especially with high NaCl concentration up to 1 M. This is different from those traditional CuFeS<sub>2</sub> leaching process controlled by a diffusion mechanisms, especially at latter stage with surface layer being formed [1,2,6,26,37]. These mean that CuFeS<sub>2</sub> leaching in the presence of NaCl is surface chemical reaction controlled, no significant passivation effects was from the crystalline S<sup>0</sup> formed on CuFeS<sub>2</sub> surface.

#### 4. Conclusions

CuFeS<sub>2</sub> leaching under oxidising conditions generally produces passivation layers to slow Cu extraction rate. Many

studies have attempted to relieve the passivation effects, but insignificant improvement was achieved. A common and cheap salt NaCl was applied to increase CuFeS<sub>2</sub> leaching rate and recovery in the absence of extra oxidant except the O<sub>2</sub> available in the leaching solution. Smaller CuFeS<sub>2</sub> particle size gave rise to a higher Cu extraction while an optimum pH 1.0 was observed. In addition, the increase in NaCl concentration within the range of 1 M increased Cu extraction significantly. An almost 100% Cu recovery was obtained in the following leaching condition: particle size of +38 to −75 μm, pulp pH of 1.0, pulp concentration of 10 g/L, NaCl concentration of 0.1 M at 348 K. XRD results indicated that Cu–S passivation layer was an intermediate product prior to the formation of crystalline S<sup>0</sup>. Moreover, the kinetics analyses suggested that the coverage of crystalline S<sup>0</sup> did not passivate Cu extraction in the presence of NaCl. This study therefore brings further insights into the application of seawater in the hydrometallurgical processing of CuFeS<sub>2</sub>.

## Conflicts of interest

The authors declare no conflicts of interest.

## Acknowledgments

The authors acknowledged financial support from National Natural Science Foundation of China under projects of 51604205 and 51774223 and Open Foundation of State Key Laboratory of Mineral Processing (BGRIMM-KJSKL-2019-11).

## REFERENCES

- [1] Córdoba EM, Muñoz JA, Blázquez ML, González F, Ballester A. Leaching of chalcopyrite with ferric ion. Part I: general aspects. *Hydrometallurgy* 2008;93:81–7.
- [2] Li Y, Kawashima N, Li J, Chandra AP, Gerson AR. A review of the structure, and fundamental mechanisms and kinetics of the leaching of chalcopyrite. *Adv Colloid Interface Sci* 2013;197–198:1–32.
- [3] Petrović SJ, Bogdanović GD, Antonijević MM. Leaching of chalcopyrite with hydrogen peroxide in hydrochloric acid solution. *Trans Nonferrous Met Soc China* 2018;28:1444–55.
- [4] Munoz PB, Miller JD, Wadsworth ME. Reaction mechanism for the acid ferric sulfate leaching of chalcopyrite. *Metall Trans B* 1979;10:149–58.
- [5] Haver FP, Wong MM. Recovery of copper, iron, and sulfur from chalcopyrite concentrate using a ferric chloride leach. *JOM* 1971;23:25–9.
- [6] Watling HR. Chalcopyrite hydrometallurgy at atmospheric pressure: 1. Review of acidic sulfate, sulfate–chloride and sulfate–nitrate process options. *Hydrometallurgy* 2013;140:163–80.
- [7] Qian G, Li J, Li Y, Gerson AR. Probing the effect of aqueous impurities on the leaching of chalcopyrite under controlled conditions. *Hydrometallurgy* 2014;149:195–209.
- [8] Carneiro MFC, Leão VA. The role of sodium chloride on surface properties of chalcopyrite leached with ferric sulphate. *Hydrometallurgy* 2007;87:73–82.
- [9] Olubambi PA, Potgieter JH. Investigations on the mechanisms of sulfuric acid leaching of chalcopyrite in the presence of hydrogen peroxide. *Miner Process Extract Metall Rev* 2009;30:327–45.
- [10] Dreisinger D, Abed N. A fundamental study of the reductive leaching of chalcopyrite using metallic iron part I: kinetic analysis. *Hydrometallurgy* 2002;66:37–57.
- [11] Veloso TC, Peixoto JJM, Pereira MS, Leão VA. Kinetics of chalcopyrite leaching in either ferric sulphate or cupric sulphate media in the presence of NaCl. *Int J Miner Process* 2016;148:147–54.
- [12] Baláz P. Mechanical activation in hydrometallurgy. *Int J Miner Process* 2003;72:341–54.
- [13] Hiroyoshi N, Arai M, Miki H, Tsunekawa M, Hirajima T. A new reaction model for the catalytic effect of silver ions on chalcopyrite leaching in sulfuric acid solutions. *Hydrometallurgy* 2002;63:257–67.
- [14] McDonald RG, Muir DM. Pressure oxidation leaching of chalcopyrite: part II: comparison of medium temperature kinetics and products and effect of chloride ion. *Hydrometallurgy* 2007;86:206–20.
- [15] Li YB, Lartey C, Song SX, Li YJ, Gerson AR. The fundamental roles of monovalent and divalent cations with sulfates on molybdenite flotation in the absence of flotation reagents. *RSC Adv* 2018;8:23364–71.
- [16] Hernández PC, Taboada ME, Herreros OO, Torres CM, Ghorbani Y. Chalcopyrite dissolution using seawater-based acidic media in the presence of oxidants. *Hydrometallurgy* 2015;157:325–32.
- [17] Torres CM, Taboada ME, Graber TA, Herreros OO, Ghorbani Y, Watling HR. The effect of seawater based media on copper dissolution from low-grade copper ore. *Miner Eng* 2015;71:139–45.
- [18] Skrobjan M, Havlik T, Ukasik M. Effect of NaCl concentration and particle size on chalcopyrite leaching in cupric chloride solution. *Hydrometallurgy* 2005;77:109–14.
- [19] Deniz Turan M, Boyrazlı M, Soner Altundoğan H. Improving of copper extraction from chalcopyrite by using NaCl. *J Cent South Univ* 2018;25:21–8.
- [20] Ruiz MC, Montes KS, Padilla R. Chalcopyrite leaching in sulfate–chloride media at ambient pressure. *Hydrometallurgy* 2011;109:37–42.
- [21] Liddicoat J, Dreisinger D. Chloride leaching of chalcopyrite. *Hydrometallurgy* 2007;89:323–31.
- [22] Dutrizac JE. The dissolution of chalcopyrite in ferric sulfate and ferric chloride media. *Metall Trans B* 1981;12:371–8.
- [23] Winand R. Chloride hydrometallurgy. *Hydrometallurgy* 1991;27:285–316.
- [24] Jones DL, Peters E. The leaching of chalcopyrite with ferric sulfate and ferric chloride. *Extract Metall Copper* 1976;II:633–53.
- [25] Lu ZY, Jeffrey MI, Lawson F. The effect of chloride ions on the dissolution of chalcopyrite in acidic solutions. *Hydrometallurgy* 2000;56:189–202.
- [26] Hackl RP, Dreisinger DB, Peters E, King JA. Passivation of chalcopyrite during oxidative leaching in sulfate media. *Hydrometallurgy* 1995;39:25–48.
- [27] Li Y, Qian G, Li J, Gerson AR. Kinetics and roles of solution and surface species of chalcopyrite dissolution at 650 mV. *Geochim Cosmochim Acta* 2015;161:188–202.
- [28] Qian G, Li Y, Li J, Gerson AR. Consideration of enthalpic and entropic energy contributions to the relative rates of chalcopyrite dissolution in the presence of aqueous cationic impurities. *Int J Miner Process* 2017;159:42–50.
- [29] Li Y, Wei Z, Qian G, Li J, Gerson A. Kinetics and mechanisms of chalcopyrite dissolution at controlled redox potential of 750 mV in sulfuric acid solution. *Minerals* 2016;6:83.
- [30] Sokić MD, Marković B, Živković D. Kinetics of chalcopyrite leaching by sodium nitrate in sulphuric acid. *Hydrometallurgy* 2009;95:273–9.

- 
- [31] Antonijevic MM, Bogdanovic GD. Investigation of the leaching of chalcopyritic ore in acidic solutions. *Hydrometallurgy* 2004;73:245–56.
- 32 Y. Li, Y. G. Qian, J. Li, A. Gerson, The rate controlling parameters in the hydrometallurgical leaching of chalcopyrite, ALTA 2014, Perth, Australia, 399-410, May 24-31, 2014.
- [33] Aydogan S, Ucar G, Canbazoglu M. Dissolution kinetics of chalcopyrite in acidic potassium dichromate solution. *Hydrometallurgy* 2006;81:45–51.
- [34] Dutrizac JE. Elemental sulphur formation during the ferric sulphate leaching of chalcopyrite. *Can Metall Q* 1989;28:337–44.
- [35] Aromaa J, Pesonen P. Leaching mechanisms and kinetics of complex low-grade sulfidic copper ores. *Physicochem Probl Miner Process* 2007;41:313–22.
- [36] Li Y, Qian G, Brown PL, Gerson AR. Chalcopyrite dissolution: scanning photoelectron microscopy examination of the evolution of sulfur species with and without added iron or pyrite. *Geochim Cosmochim Acta* 2017;212:33–47.
- [37] Ghahremaninezhad A, Dixon DG, Asselin E. Electrochemical and XPS analysis of chalcopyrite ( $\text{CuFeS}_2$ ) dissolution in sulfuric acid solution. *Electrochim Acta* 2013;87:97–112.