Original Article

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

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\textbf{A B S T R A C T}

Copper (Cu) extraction rate from chalcopyrite (CuFeS\textsubscript{2}) is normally slowed down by the passivation layers formed on CuFeS\textsubscript{2} surface. Cost-effective CuFeS\textsubscript{2} extraction strategies are therefore strongly expected in both academic and industrial worlds. This study investigated CuFeS\textsubscript{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 CuFeS\textsubscript{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 CuFeS\textsubscript{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 (S\textsuperscript{0}) rather than Cu–S like compounds at a NaCl concentration greater than 0.1 M, indicating that crystalline S\textsuperscript{0} did not inhibit Cu extraction. This study therefore provides a promising strategy of applying seawater in hydrometallurgical processing of chalcopyrite.

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1. Introduction

Chalcopyrite (CuFeS\textsubscript{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 CuFeS\textsubscript{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 CuFeS\textsubscript{2} was inhibited by the surface passivation layers (e.g., jarosite, disulfide, polysulfide, elemental sulfur (S\textsuperscript{0}) ) formed during leaching process [7], especially under oxidiz-
ing conditions [3,8]. For instance, Olubambi and Potgieter [9] reported that S0 was the primary surface passivation layer, giving rise to a 7% Cu extraction after 6 h in the sulfuric acid (H2SO4) 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 Luces 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 CuFeS2 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 S0 when leaching was carried out in the presence of chloride ions, different from the condense S0 layer on CuFeS2 surface in the absence of chloride ions. Dutrizac [22] reported that the activation energy (Ea) of CuFeS2 leaching was dramatically decreased in chloride solutions, that is, from 75 kJ mol−1 to 42 kJ mol−1. Winand [23] suggested that higher Cu extraction in the presence of Cl− ions was due to the formation of Cu+, Cu2+ complexes with Cl−. Hernandez et al. [16] reported that the positive role of applying seawater in increasing Cu extraction from CuFeS2 was ascribed to the formation of Cu chloro-complexes.

The enhanced Cu extraction from CuFeS2 in the presence of Cl− ions is normally ascribed to the following reasons: (1) forming metal chloride complexes; (2) increasing anodic current on CuFeS2 particles; (3) changing the properties of surface products [8,24]. As stated in Ref. [25], the SEM results indicated a crystalline and porous S0 layer on CuFeS2 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, H2SO4 was the most frequently used acid 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., H2O2, Fe3+, (NH4)2S2O8), which might hide the real effects of NaCl on CuFeS2 leaching, due to much stronger oxidative effects from these oxidants. Therefore, the aim of this study is to investigate CuFeS2 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 CuFeS2 sample. |
|------------------|----------|----------|----------|
| Particle size (μm) | 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 CuFeS2 sample.

2. Methods
2.1 Minerals

Chunk CuFeS2 sample obtained from GEO Discoveries (Australia) was crushed and milled to obtain three size fractions (−38, +38 to −75, +75 to −150 μm) via wet sieving. CuFeS2 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 CuFeS2.

The XRD (Fig. 1) patterns further indicated a high purity and well crystallized CuFeS2 with a very small amount of fluorapatite as an impurity phase.

2.2 Leaching methods and reagents

1 g of CuFeS2 powder (−38 μm, +38 to −75 μm, +75 to −150 μm) was added into 100 mL H2SO4 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 by pipette to measure Cu concentration. After that, fresh leaching lixiviant was added to replenish to the original level. All chemicals (NaCl, H2SO4) used in this study were in analytical grade While the Millipore® (Billerica, MA, USA) ultrapure water with a resistivity of 18.2 MΩ cm was employed in all tests.
2.3. Characterization

The leach residues were filtered, washed, dried and determined by X-ray diffraction (XRD) (Cu Kα1, 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 CuFeS₂ 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 CuFeS₂ 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 CuFeS₂ leaching.

Cu leaching rate is normally increased with increased acid concentration. However, a reasonable H⁺ concentration range is recommended for CuFeS₂ leaching. For instance, Antonijevic and Bogdanovic [31] reported that a pH lower than 0.5 (using H₂SO₄ as leaching medium) reduced Cu leaching rate due to the competition between Fe³⁺ and H⁺, 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 CuFeS₂ 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.
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 Cl\(^-\) ions promoted the formation of porous S\(^0\) layers on CuFeS\(_2\) surfaces, favoring Cu extraction. Moreover, the addition of NaCl to the leaching system improved the stability of Cu\(^2+\)/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 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 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 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, CuFeS\(_2\) and Cu–S like phase but no S\(^0\). With the increase of NaCl concentration to 0.1 M (Fig. 6c), the characteristic peaks of 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 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 S\(^0\) and releasing Cu into solution.

### 3.6. Kinetics analysis

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

\[
1 - \left(1 - X\right)^{\frac{1}{2}} = k_1 t
\]

\[
1 - \frac{2}{3}X - \left(1 - X\right)^{\frac{2}{3}} = k_2 t
\]

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 liner 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.

\[
\frac{dC}{dt} = k
\]

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 Ea of CuFeS\(_2\) leaching can be calculated.

\[
k = Ae^{-\frac{Ea}{RT}}
\]

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

It is widely accepted that Ea greater than 20 kJ mol\(^{-1}\) implies a surface reaction while Ea less than 20 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 10\(^{-3}\). An Ea of 55.5 ± 3.9 kJ mol\(^{-1}\) with a coefficient of determination R\(^2\) > 0.98 suggested that 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], CuFeS\(_2\) leaching can be separated into two steps. In the initial stage, the primary reaction (Eq. 5) is the oxidation of CuFeS\(_2\) with the cathodic reaction being as the reduction of 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. Fe\(^{2+}\)
CuFeS$_2$ $+$ 4H$^+$ $+$ O$_2$ $+$ 4e$^-$ $\rightarrow$ Cu$^{2+}$ $+$ Fe$^{2+}$ $+$ 2S$^0$ $+$ 2H$_2$O  \hspace{1cm} (5) 

formed via Eq. 5 can be oxidized by O$_2$ (Eq. 7) to generate oxidative Fe$^{3+}$ which can further oxidize CuFeS$_2$ (Eq. 8). As the strong oxidant of Fe$^{3+}$ is involved in CuFeS$_2$ 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$^0$ layer formed [11,17,20,33].

Eq. 9 represents another possibility if Fe$^{3+}$ is present in the solution as oxidant, that is, producing SO$_4^{2-}$ rather than S$^0$. As both Eqs. 8 and 9 suggest beneficial roles of Fe$^{3+}$ in CuFeS$_2$ leaching, the oxidized S products can be referred to determine

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O$$ \hspace{1cm} (6) 

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$$ \hspace{1cm} (7) 

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0$$ \hspace{1cm} (8)
which reaction is predominant.

\[
\text{CuFeS}_2 (s) + 16\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow \text{Cu}^{2+} + 17\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \tag{9}
\]

Aromaa and Dutrizac [34] reported that approximately 94% of S was transformed to \( S^0 \) while the rest 6% of S from CuFeS\(_2\) was oxidized to \( \text{SO}_4^{2-} \), similar to that found in Ref. [25]. Our previous studies [29] also showed that the predominant S products upon CuFeS\(_2\) leaching was \( S^0 \). As no extra oxidant was added into the leaching system except \( O_2 \) existing in the solution, no strong oxidative conditions were available to produce \( \text{SO}_4^{2-} \) [35]. In other words, the predominant S product was crystalline \( S^0 \) rather than \( \text{SO}_4^{2-} \), consistent with the XRD results shown in Fig. 6. Hence, Eqs. 5 and 8 were the oxidation reactions for the initial and later leaching stages of CuFeS\(_2\).

In addition, some studies indicated that the presence of Cl\(^-\) ions increased metal solubility in the leaching system and the porosity of S-containing products formed on CuFeS\(_2\) surface, which improved the diffusion of reagents to CuFeS\(_2\) 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\(_2\) core to the upmost surface contacting with the solution (Fig. 9). Therefore, the whole passivation layer covering on CuFeS\(_2\) 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 \( S^0 \) 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 \( S^0 \) was gradually increased. These suggested that the \( S_n^2^- \) layer might be further oxidized to \( S^0 \) layer coating on CuFeS\(_2\) 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 \( S^0 \) (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\(_2\) leaching [1,2,26,29,31].

Traditionally, the role of Cl\(^-\) ions in CuFeS\(_2\) leaching process was considered as: (1) a complexing reagent for metal ions; (2) a surfactant assisting in \( S^0 \) removal; (3) increase surface area and porosity of insoluble product layer formed on mineral surface. Many research indicated that the presence of Cl\(^-\) ions resulted in a much more crystalline \( S^0 \) product. In other words, the \( S^0 \) layer coated on CuFeS\(_2\) surface was crystalline and porous in the presence of NaCl while amorphous or cryptocrystalline \( S^0 \) film in the absence of NaCl [25].

In addition, when Cl\(^-\) ions are available in the leaching system, a secondary redox couple of Cu\(^{2+}/Cu^+\) is operative to generate intermediate product of Cu–Cl complexes [20]. Therefore, Cl\(^-\) ions played positive roles on Cu extraction, especially when crystalline \( S^0 \) was formed on CuFeS\(_2\) surface, due possibly to the easier diffusion of leaching reagents and metal ions between CuFeS\(_2\) surface and solution.

Furthermore, the kinetic analysis indicated that CuFeS\(_2\) leaching was controlled by surface chemical reaction, indicating that the diffusion of reagents via surface layer to CuFeS\(_2\) surface did not determine the whole leaching process. In other words, the formed crystalline \( S^0 \) (Fig. 6) on CuFeS\(_2\) 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\(_2\) 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\(_2\) leaching in the presence of NaCl is surface chemical reaction controlled, no significant passivation effects was from the crystalline \( S^0 \) formed on CuFeS\(_2\) surface.

### 4. Conclusions

CuFeS\(_2\) 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 CuFeS₂ leaching rate and recovery in the absence of extra oxidant except the O₂ available in the leaching solution. Smaller CuFeS₂ 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 S⁰. Moreover, the kinetics analyses suggested that the coverage of crystalline S⁰ 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 CuFeS₂.

**Conflicts of interest**

The authors declare no conflicts of interest.

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