

## Article

# Thermodynamic Analysis of Possible Chalcopyrite Dissolution Mechanism in Sulfuric Acidic Aqueous Solution

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**Abstract:** The dissolution routes of chalcopyrite in acidic sulfate aqueous solution have been discussed by thermodynamic calculation under different aqueous species concentrations, such as  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{H}_2\text{S}$ . The results show that for both oxidative dissolution and non-oxidative dissolution of chalcopyrite, the dissolution process undergoes several intermediate steps before completely decomposing to  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and elemental sulfur, in which bornite and covellite are the most likely intermediates. The dissolution routes of the secondary intermediates have also been discussed and covellite is the most likely final intermediate. Based on these results, some frequently reported phenomena, such as the existence of an optima redox potential range, the promotive action of the addition of  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$ , as well as the preferential release of  $\text{Fe}^{2+}$  in the chalcopyrite leaching process, have been explained and elucidated.

**Keywords:** chalcopyrite leaching; intermediates; covellite; oxidative dissolution; non-oxidative dissolution

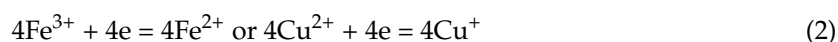
## 1. Introduction

Chalcopyrite ( $\text{CuFeS}_2$ ) is one of the most abundant and wide-spread copper-bearing minerals, accounting for approximately 70% of the earth's copper [1]. Since the current pyrometallurgical methods for copper extraction from chalcopyrite have environmental issues, many studies have considered the leaching and dissolution of  $\text{CuFeS}_2$  in different aqueous media [2,3]. To date, chalcopyrite leaching has not been widely adopted by industry due to its extremely slow leaching kinetics [4]. Hence, there is a need to better understand the kinetics and mechanism of chalcopyrite leaching for successful industrial hydrometallurgical leaching implementation [5]. Several alternative mechanisms have been suggested, involving oxidative, reductive/oxidative, non-oxidative and a combination of non-oxidative/oxidative processes [6].

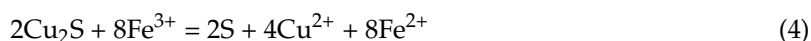
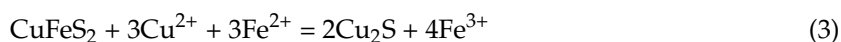
First of all, the oxidative dissolution of chalcopyrite in acidic ferric or cupric solutions can be described by the normal mixed-potential electrochemical model proposed by Nicol et al. [7], and it was also adopted by Jones and Peters [8], Miller et al. [9] and others, where the following anodic reaction



is coupled to the cathodic reactions



For oxidative leaching of chalcopyrite with dissolved oxygen and ferric ions in sulfate media, Kametani and Aoki [10], and subsequently Hiroyoshi et al. [11,12], found that the rate was enhanced in the presence of high concentrations of ferrous ions in sulfuric acid solutions containing cupric ions. In order to elucidate the enhancement of chalcopyrite leaching by ferrous and cupric ions, they proposed a two-step reaction model, i.e., the reductive/oxidative model. In this model, chalcopyrite is firstly reduced by ferrous ions to  $\text{Cu}_2\text{S}$  in the presence of cupric ions according to Equation (3), then the resulting intermediate  $\text{Cu}_2\text{S}$  is oxidized by ferric ions to  $\text{Cu}^{2+}$  and elemental sulfur following Equation (4).



However, this model fails to explain how Equation (3) can be achieved. There is no experimental evidence to support the reduction of chalcopyrite to chalcocite at potentials higher than 0.5 V.

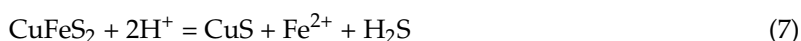
As for the non-oxidative reaction mechanism, the dissolution of chalcopyrite in acidic solutions under non-oxidative conditions can be obtained by a reaction such as:



Equation (5) is not thermodynamically spontaneous;  $K$ , the equilibrium constant, is  $2.8 \times 10^{-19}$  at 35 °C, under normal conditions [13]. Nicol and Lazaro [14] extended the non-oxidative model to include the overall oxidative dissolution process. Thus, Equation (5) can be combined with (6) to give the overall reaction.



This model predicts that the rate of dissolution of chalcopyrite should not increase significantly with the addition of ferric ions higher than 0.1 M because of the formation of  $\text{Fe}^{2+}$  according to Equation (6), which will inhibit the dissolution of chalcopyrite as shown in Equation (5) [6]. However, the deduction that the addition of ferrous ions reduces the dissolution rate is apparently in contradiction to the previously reported results. At the same time, another non-oxidative acidic dissolution reaction of chalcopyrite was proposed as Equation (7):



Equation (7) is also not thermodynamically spontaneous ( $K = 3.4 \times 10^{-4}$  at 35 °C, calculated by the authors) under normal conditions. However, this reaction might be feasible under practical conditions due to the low concentration of  $\text{H}_2\text{S}$ .

On the other hand, many phenomena have been discovered and proved by different experimental studies and have not been well elucidated. One of these is the formation of a surface products layer during chalcopyrite leaching. A number of surface species within the layer have been proposed, e.g., sulfur ( $\text{S}^0$ ) [15,16], disulfide ( $\text{S}_2^{2-}$ ) [17–19], polysulfide ( $\text{S}_n^{2-}$ ) [5,13] and Fe-oxyhydroxide [20,21]. However, no universal agreement has been reached on the composition of the surface layers formed on the  $\text{CuFeS}_2$  surface [19] and the effect of these newly formed surface species on the leaching process. Another phenomenon is that there is an optimum redox potential for the leaching of chalcopyrite, i.e., the leaching rate increases with increasing the redox potential and then reaches a maximum rate at an optimum redox potential, after which it decreases with the increasing of potentials, and the rate becomes less dependent on the potential at very high potentials [6,10,22–24]. Besides the above two phenomena, iron is preferentially dissolved into solutions compared to copper during the initial period of chalcopyrite leaching and a copper-rich layer is formed on the surface of the chalcopyrite particles [24–26]. A contradiction also exists on the composition and the function of the copper-rich layer.

To the authors' knowledge, neither the oxidative dissolution model nor the non-oxidative/oxidative model can give a satisfactory explanation for the above-mentioned phenomena. Both the oxidative dissolution model and the non-oxidative/oxidative model cannot result in the formation of many new surface species as reported above. Reductive/oxidative dissolution can partly lead to the formation of the above surface species, such as elemental sulfur and covellite, and it can also explain the existence of an optimum redox potential and iron being preferentially dissolved, but this model seems to contradict the thermodynamics principal.

It should be apparent from this brief review of the mechanisms of the dissolution of chalcopyrite in sulfate media that there is little agreement on the nature of the rate-determining step and the mechanisms involved in this important process. Thermodynamic analysis can assume specific conditions for the surface chemical reaction, which will be helpful to understand the dissolution process. In the present paper, the possible reaction routes of chalcopyrite leaching in sulfuric acid media under ambient conditions are analyzed based on thermodynamic principals, which aims to further the understanding of the above phenomena.

## 2. Thermodynamic Analysis of the Possible Reactions

### 2.1. Possible Oxidative Dissolution Reactions of $\text{CuFeS}_2$ in Sulfuric Acid Solution

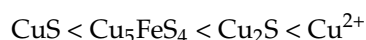
Although the final dissolution products of chalcopyrite include  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and elemental sulfur, many possible routes may exist for the preliminary oxidative dissolution of  $\text{CuFeS}_2$  in sulfuric acid solution. The equilibrium potentials of selected possible oxidative dissolution reaction routes of  $\text{CuFeS}_2$  in sulfuric acid solution are summarized in Table 1, based on the previously reported intermediates.

**Table 1.** The equilibrium potentials of selected possible oxidative dissolution reaction routes of  $\text{CuFeS}_2$  in sulfuric acid solution.

Routes	Reactions	Equilibrium Potentials
1	$\text{CuFeS}_2 = \text{CuS} + \text{S} + \text{Fe}^{2+} + 2\text{e}$	$E_{01} = 0.219 + 0.0295\lg[\text{Fe}^{2+}]$
2	$2\text{CuFeS}_2 = \text{Cu}_2\text{S} + 3\text{S} + 2\text{Fe}^{2+} + 4\text{e}$	$E_{02} = 0.289 + 0.0295\lg[\text{Fe}^{2+}]$
3	$10\text{CuFeS}_2 = 2\text{Cu}_5\text{FeS}_4 + 12\text{S} + 8\text{Fe}^{2+} + 16\text{e}$	$E_{03} = 0.251 + 0.0295\lg[\text{Fe}^{2+}]$
4	$\text{CuFeS}_2 = \text{Cu}^{2+} + 2\text{S} + \text{Fe}^{2+} + 4\text{e}$	$E_{04} = 0.426 + 0.0148\lg[\text{Fe}^{2+}] + 0.0148\lg[\text{Cu}^{2+}]$

The four reactions in Table 1 belong to the starting reactions and the further decomposition reactions of the resulting intermediate will be discussed later. The starting oxidative dissolution reactions of  $\text{CuFeS}_2$  can be attributed to four routes.  $\text{Fe}^{2+}$  and elemental sulfur are the products of the above reactions. In addition to these,  $\text{CuS}$ ,  $\text{Cu}_2\text{S}$ ,  $\text{Cu}_5\text{FeS}_4$  and  $\text{Cu}^{2+}$  are also present as the products or intermediates of the four reaction routes, respectively.

As shown in Table 1, all the potentials associated with the possible reactions are functions of the concentration of  $\text{Fe}^{2+}$  or  $\text{Cu}^{2+}$ , or both of them. As a result, the potentials associated with the possible reactions should be compared under different  $\text{Fe}^{2+}$  and  $\text{Cu}^{2+}$  concentrations. The relationships between the potentials and the concentration of resulting species are demonstrated in Figure 1. The symbols  $E_{01-1}$ ,  $E_{02}$ ,  $E_{03}$  and  $E_{04-1}$  are used to identify the four potentials of reactions 1–4 according to the database from HSC chemistry [27], respectively. The  $\text{Cu}^{2+}$  concentration is assumed to be varied at the same step with the  $\text{Fe}^{2+}$  concentration in the range of  $10^{-6}$  mol/L to 1 mol/L. The calculated potentials of different reactions under the same  $\text{Fe}^{2+}$  concentration based on the database of HSC [28,29] follow the sequence order below:



The potentials  $E_{01-1}$ ,  $E_{02}$ ,  $E_{03}$  and  $E_{04-1}$  are associated with  $\text{CuS}$ ,  $\text{Cu}_5\text{FeS}_4$ ,  $\text{Cu}_2\text{S}$  and  $\text{Cu}^{2+}$ , respectively (see Figure 1). All of the potentials increase with the increase of the  $\text{Fe}^{2+}$  concentration, and the sequence order does not change.  $E_{04-1}$ , the potential for  $\text{CuFeS}_2$  to be oxidized directly to  $\text{Cu}^{2+}$ ,

is always higher than those in which the CuS, Cu<sub>2</sub>S and Cu<sub>5</sub>FeS<sub>4</sub> are present as intermediates by at least 0.137 V. Apparently, it is not thermodynamically favorable for CuFeS<sub>2</sub> to be oxidized directly to Cu<sup>2+</sup> among these oxidative reaction routes based on the potentials required. Consequently, the oxidative reactions taking place on the chalcopyrite surface tend to form intermediates.

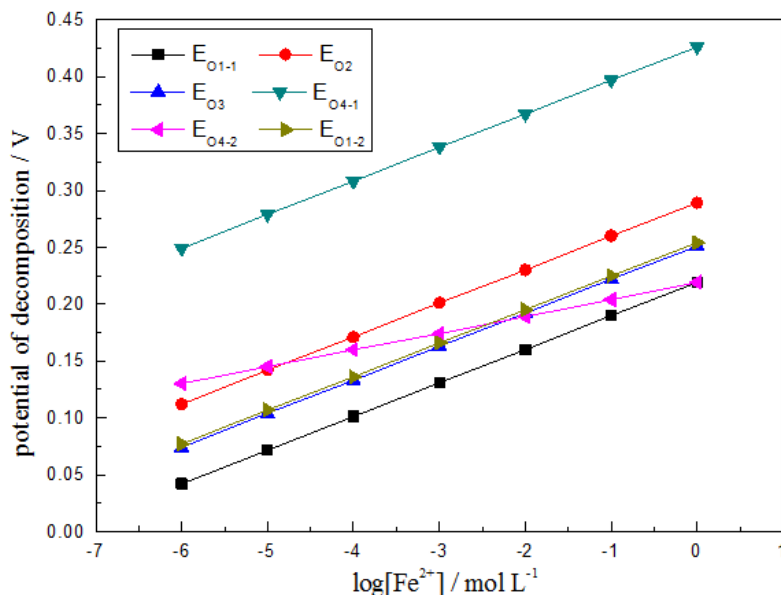


Figure 1. Relation between decomposition potential of chalcopyrite and routes.

Among the other three possible routes, CuS seems to be the most likely intermediate, Cu<sub>5</sub>FeS<sub>4</sub> is the second most likely, and Cu<sub>2</sub>S is the least likely intermediate according to its relatively high potential. However, Warren proposed two intermediate sulfide phases which appeared to be formed based on the current and mass balance measurements [30]. Majuste detected the existence of bornite as an intermediate during an electrochemical dissolution experiment of chalcopyrite by synchrotron small-angle X-ray diffraction [31]. It means that a copper-rich compound, such as Cu<sub>5</sub>FeS<sub>4</sub>, might be also present together with CuS as an intermediate. In order to elucidate this fact based on thermodynamics, the values of the standard free energy of the associated compounds need to be examined further.

Among these compounds, the value of the standard free energy of CuS differs greatly in different references. For example, it is −56.611 kJ/mol in the database of HSC [27]. However, it is reported to be −53.906 kJ/mol [32], −48.929 kJ/mol [32] and −47.007 kJ/mol [33] in other related documents. Apparently, there is a great difference among the reported values of the standard free energy of CuS. In order to calibrate the great difference, we attempt to derive a reasonable value. Cu<sub>2</sub>S and CuS can be taken as two of a series of compounds, Cu<sub>1+x</sub>S ( $x = 0-1$ ). Some compounds in this series and the values of their standard free energy of formation are selected in Table 2. By drawing the values of their standard free energy of formation vs.  $x$ , it can be found that there is an accurate linear relationship between the standard free energy and  $x$  (see Figure 2 and Equation (8)).

Table 2. Selected standard free energy of formation of Cu<sub>1+x</sub>S at 25 °C (kJ/mol) [1].

Formula	Cu <sub>2</sub> S	Cu <sub>1.96</sub> S	Cu <sub>1.93</sub> S	Cu <sub>1.83</sub> S	Cu <sub>1.75</sub> S	Cu <sub>1.67</sub> S	Cu <sub>1.38</sub> S	CuS
$\Delta G_f^0$	−85.52	−84.60	−83.60	−80.25	−78.50	−74.40	−63.11	−48.93

The expression of the standard free energy of formation of  $\text{Cu}_{1+x}\text{S}$  is derived as Equation (8) from the linear relationship.

$$\Delta G_f^0 = -49.947 - 36.30 \times (\text{coefficient of determination is } 0.9962) \quad (8)$$

Then  $-49.947$  kJ/mol is deduced to be the value of the standard free energy of CuS from Equation (8). It is between the values reported in [32,33], corresponding closely to the value  $-48.929$  [32].

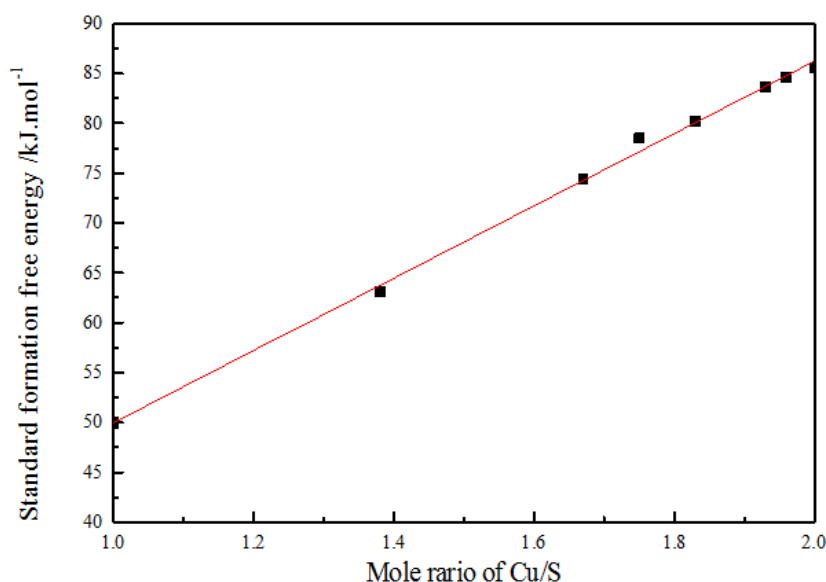
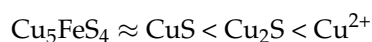


Figure 2. Relation between standard formation free energy and ratio of Cu/S.

When  $-49.947$  kJ/mol is used to replace  $-56.611$  kJ/mol for the calculation of potentials of reaction route 1, the standard potential of reaction route 1 becomes 0.254 V. It is almost the same as that for route 3 (0.251 V). When the  $\text{Fe}^{2+}$  concentration increases from  $10^{-6}$  mol/L to 1 mol/L, the potentials  $E_{01-2}$ ,  $E_{02}$  and  $E_{03}$ , associated with CuS,  $\text{Cu}_2\text{S}$  and  $\text{Cu}_5\text{FeS}_4$ , increase in the range of 0.077–0.254 V, 0.112–0.289 V and 0.074–0.251 V, respectively. Apparently, line  $E_{02}$  is always above  $E_{01-2}$  and  $E_{03}$ . As a result,  $\text{Cu}_2\text{S}$  remains unlikely to be the intermediate of chalcopyrite leaching. Then the calculated potential sequence of different reaction routes under the same  $\text{Fe}^{2+}$  concentration is as follows:



Line  $E_{01-2}$  in Figure 1 is almost overlapped with line  $E_{03}$ , which means  $\text{Cu}_5\text{FeS}_4$  and CuS have equal opportunities to present as intermediates on the surface of  $\text{CuFeS}_2$  based on the oxidative dissolution mechanism.

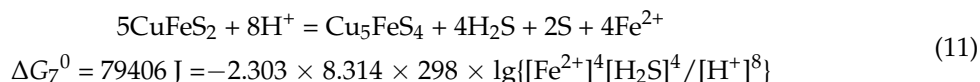
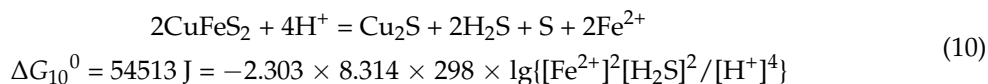
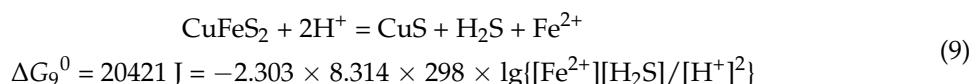
Besides the above analysis, there is a special situation that should be considered. When chalcopyrite leaching takes place along the two reaction paths in which  $\text{Cu}_5\text{FeS}_4$  and CuS present as intermediates as shown in Equations 3 and 1 in Table 1, the iron in chalcopyrite releases into the solution continuously and the copper remains undissolved. During this period the  $\text{Fe}^{2+}$  concentration increases continuously, whereas the  $\text{Cu}^{2+}$  concentration remains at zero. If it is true, line  $E_{04-1}$  will get much lower than the other three lines in Figure 1 according to the potential calculation equation in Table 1. Then it must be in favor of direct oxidization and a certain amount of  $\text{Cu}^{2+}$  will be released at the initial stage of chalcopyrite leaching. At the same time, the accumulation of the  $\text{Cu}^{2+}$  concentration lifts line  $E_{04-1}$  up higher than  $E_{01-2}$  and  $E_{03}$  gradually. So there must be a  $\text{Cu}^{2+}$  concentration above which the direct oxidization reaction of chalcopyrite will be inhibited.

In fact, it can be postulated that the  $\text{Cu}^{2+}$  concentration equilibrated with  $\text{CuFeS}_2$  and  $\text{CuS}$  is on the scale of  $10^{-14}$  mol/L [34]. Then line  $\text{Eo}_{4-1}$ , representing the direct oxidizing of chalcopyrite to  $\text{Cu}^{2+}$ , will turn out to be line  $\text{Eo}_{4-2}$ . When the  $\text{Fe}^{2+}$  concentration reaches over  $10^{-2.5}$  mol/L, line  $\text{Eo}_{4-2}$  starts to get lower than  $\text{Eo}_{1-2}$  and  $\text{Eo}_3$ , leading to the termination of the reactions in which  $\text{Cu}_5\text{FeS}_4$  and  $\text{CuS}$  generate on the chalcopyrite surface and the dissolution route turns into the direct complete oxidizing mechanism. When the  $\text{Cu}^{2+}$  concentration increases, line  $\text{Eo}_{4-2}$  also gets higher. As a result, the addition of  $\text{Cu}^{2+}$  will be helpful to let chalcopyrite leaching generate a series of intermediates, such as  $\text{Cu}_5\text{FeS}_4$  and  $\text{CuS}$ . If the direct complete oxidizing dissolution rate is lower than those reaction routes with  $\text{Cu}_5\text{FeS}_4$  and  $\text{CuS}$  intermediates, it will be in accordance with the fact that the addition of  $\text{Cu}^{2+}$  can promote the leaching rate of chalcopyrite. The iron in chalcopyrite taking precedence to release into the solution can also be explained. As a result, the reaction routes, in which  $\text{Cu}_5\text{FeS}_4$  and  $\text{CuS}$  are intermediates, must be faster than the direct complete oxidization route in which  $\text{Cu}^{2+}$  releases in the same step with  $\text{Fe}^{2+}$ .

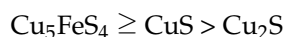
As stated above, both  $\text{Cu}_5\text{FeS}_4$  and  $\text{CuS}$  can generate as the first batch of intermediates in the oxidative dissolution reaction mechanism of  $\text{CuFeS}_2$ . The dissolution path of chalcopyrite is in favor of reaction routes 3 and 1 in Table 1.

## 2.2. Possible Non-Oxidative Dissolution Reactions of $\text{CuFeS}_2$ in Sulfuric Acid Solution

When  $\text{CuFeS}_2$  is attacked by  $\text{H}^+$ , the decomposition reaction may take place according to Equations (9)–(11), and then  $\text{CuS}$ ,  $\text{Cu}_2\text{S}$  and  $\text{Cu}_5\text{FeS}_4$  may generate as intermediates before  $\text{CuFeS}_2$  decomposes completely to  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and elemental sulfur.



All three reaction routes are accompanied by the release of  $\text{H}_2\text{S}$  into the solution. The resulting equilibrated  $\text{H}_2\text{S}$  concentrations with different intermediates obey the sequence below:



All the equilibrated  $\text{H}_2\text{S}$  concentrations decline with the increase of the pH and the  $\text{Fe}^{2+}$  concentration (see Figure 3), and the sequence of the equilibrated  $\text{H}_2\text{S}$  concentrations remains unchanged under the same  $\text{Fe}^{2+}$  concentration. The  $\text{H}_2\text{S}$  concentration equilibrated with the  $\text{Cu}_2\text{S}$  intermediate is the lowest, and the  $\text{H}_2\text{S}$  concentration equilibrated with the  $\text{Cu}_5\text{FeS}_4$  intermediate is just slightly higher than that of  $\text{CuS}$ , which means that both Equations (9) and (11) can give the same highest  $\text{H}_2\text{S}$  concentration on the surface of the chalcopyrite. When Equations (9) and (11) take place, Equation (10) will be inhibited by the high  $\text{H}_2\text{S}$  concentration produced by Equations (9) and (11). It seems that  $\text{Cu}_5\text{FeS}_4$  and  $\text{CuS}$  are both the most likely intermediates of chalcopyrite non-oxidative leaching based on the viewpoint of chemical equilibrium. As a result,  $\text{Cu}_5\text{FeS}_4$  and  $\text{CuS}$  are both the most likely intermediates of chalcopyrite leaching in a non-oxidative dissolution mechanism. Certainly, the  $\text{Cu}_5\text{FeS}_4$  intermediate needs to be further decomposed to more simple intermediates, such as  $\text{CuS}$ , etc. These secondary reactions will take place on the surface of  $\text{Cu}_5\text{FeS}_4$  intermediates but not on chalcopyrite. However, the formation of bornite as an intermediate product of chalcopyrite oxidation was evaluated at 0.50 V (SHE) on the basis of the thermodynamic analysis by Warren and the results suggested the bornite formation was in the anodic prewave region. At higher potentials,



this product would be oxidized to covellite (CuS) and, subsequently, to elemental sulfur (S), through consecutive stages. However, there are some uncertainties regarding the nature of the intermediate products formed at anodic prewave conditions. Hence, except for Majuste having detected bornite by synchrotron small-angle X-ray diffraction on oxidized chalcopyrite electrodes after chronoamperometry at 0.70 and 0.80 V vs. SHE, most studies have not detected the existence of  $\text{Cu}_5\text{FeS}_4$  on the reacted surface of chalcopyrite.

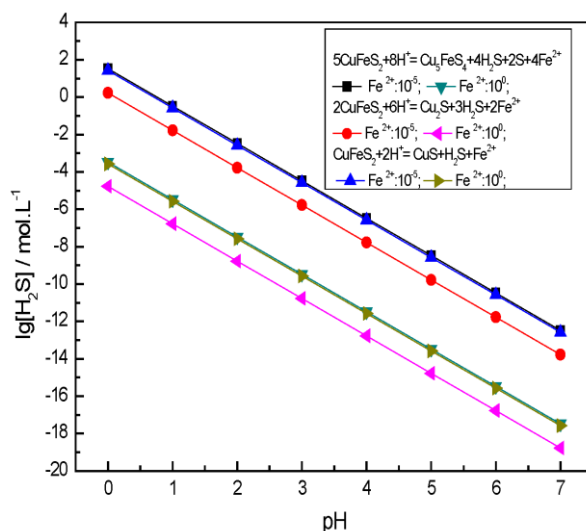


Figure 3. Equilibrated  $\text{H}_2\text{S}$  concentration for acid dissolution of  $\text{CuFeS}_2$  in different reactions.

In fact, the non-oxidative dissolution Equations (9)–(11) can be taken as self-oxidative/reductive reactions. The valence states of copper, iron and elemental sulfur in  $\text{CuFeS}_2$  have been changed in all three reactions. It is worth mentioning that just  $\text{CuFeS}_2$  plays the role of the oxidative agent in these reactions. If so, it means that the non-oxidative dissolution Equations (9)–(11) will be inhibited when the redox potential is higher than the rest potential of  $\text{CuFeS}_2$ . However, when the redox potential in solution is much lower than the rest potential of  $\text{CuFeS}_2$ , as a result, the oxidative dissolution of  $\text{CuFeS}_2$  and the intermediates will also be inhibited, which results in the termination of further dissolution. This conflict leads to the occurrence of an optimal leaching potential.

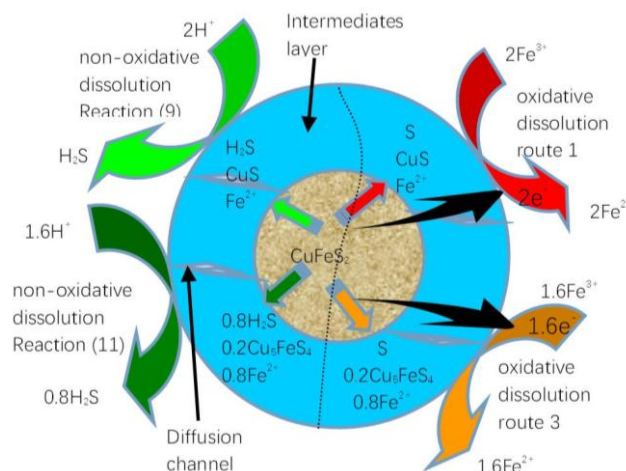


Figure 4. Possible chalcopyrite dissolution reaction routes.

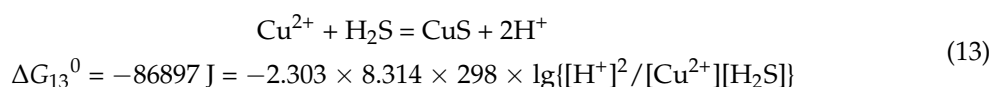
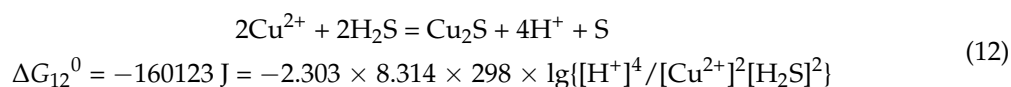
As stated above, in the non-oxidative dissolution of  $\text{CuFeS}_2$ , the most likely intermediates should be  $\text{Cu}_5\text{FeS}_4$  and  $\text{CuS}$ . The dissolution route of chalcopyrite is in favor of Equations (9) and (11). Based on the discussion above, the most likely starting dissolution routes of chalcopyrite are summarized in the schematic diagram I Figure 4, in which two oxidative routes and non-oxidative routes are involved.

### 2.3. Balanced Concentrations of $\text{Cu}^{2+}$ , $\text{H}_2\text{S}$ , $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ in Aqueous Solution with Simple Sulfides

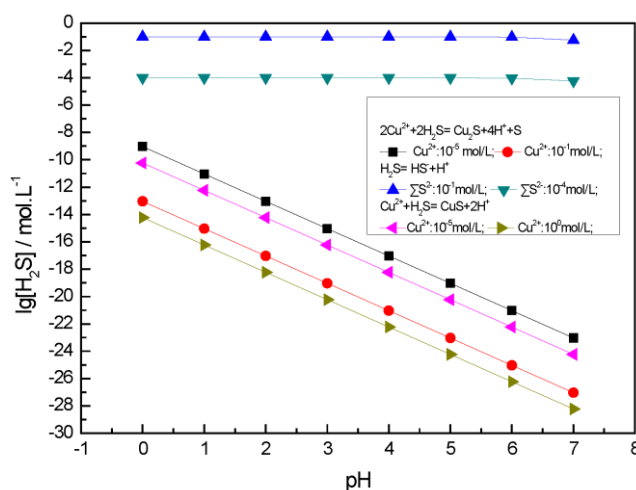
During chalcopyrite leaching in sulfuric acid solution, many soluble species, such as  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{H}_2\text{S}$  in aqueous solution, keep balance with the solid minerals. These balanced species concentrations, or, more accurately, activities, have a great effect on the leaching reactions and reaction routes. As a result, the relationship among them should be determined in order to understand the leaching process in detail.

#### 2.3.1. Balanced Concentrations of $\text{Cu}^{2+}$ and $\text{H}_2\text{S}$ in Aqueous Solution with Copper Sulfides

The possible reactions between  $\text{Cu}^{2+}$  and  $\text{H}_2\text{S}$  include the formation of  $\text{Cu}_2\text{S}$  and  $\text{CuS}$  as in Equations (12) and (13).



According to the change of the  $\text{H}_2\text{S}$  concentration with the different given total  $\text{S}^{2-}$  ion concentration ( $\Sigma\text{H}_2\text{S} + \text{HS}^- + \text{S}^{2-}$ ), almost all of the aqueous  $\text{S}^{2-}$  ions species exist as  $\text{H}_2\text{S}$  in the acidic range (see Figure 5, calculated based on the database of HSC, except for  $\text{CuS}$ ).



**Figure 5.** Aqueous  $\text{H}_2\text{S}$  concentration equilibrated with  $\text{Cu}_2\text{S}$  and  $\text{CuS}$  under different  $\text{Cu}^{2+}$  concentrations.

It can also be observed from Figure 5 that the  $\text{H}_2\text{S}$  concentrations equilibrated with both  $\text{Cu}_2\text{S}$  and  $\text{CuS}$ , increased gradually with the decrease of the pH and  $\text{Cu}^{2+}$  concentration, and the aqueous  $\text{H}_2\text{S}$  concentration can always be kept at a very low level by forming both  $\text{Cu}_2\text{S}$  and  $\text{CuS}$ . However, the formation of  $\text{CuS}$  can decrease the aqueous  $\text{H}_2\text{S}$  concentration to about one magnitude lower than that of  $\text{Cu}_2\text{S}$  under the same  $\text{Cu}^{2+}$  concentration and pH. For example, when the  $\text{Cu}^{2+}$  concentration is at  $10^{-5} \text{ mol/L}$  and pH 2, the  $\text{H}_2\text{S}$  concentrations equilibrated with  $\text{Cu}_2\text{S}$  and  $\text{CuS}$  are  $10^{-13.03} \text{ mol/L}$  and  $10^{-14.23} \text{ mol/L}$ , respectively.



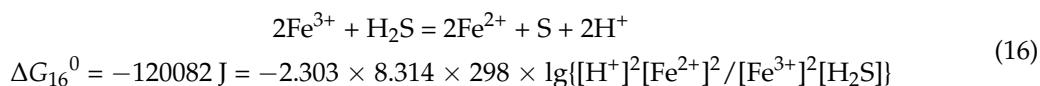
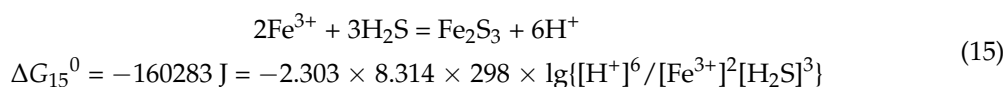
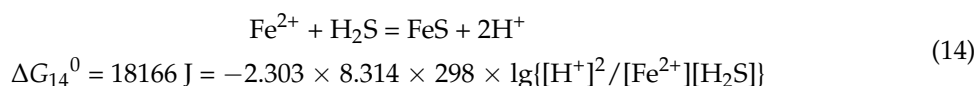
It means that the high aqueous  $\text{H}_2\text{S}$  concentration may exist during the initial stage of chalcopyrite acidic leaching when both the  $\text{Cu}^{2+}$  concentration and pH are very low. The fact that iron releases into the solution prior to copper might result in such a low  $\text{Cu}^{2+}$  concentration. Then the non-oxidative dissolution mechanism can play an important role in the initial stage of chalcopyrite leaching. The high  $\text{H}_2\text{S}$  concentration can be reduced to a low level by  $\text{Cu}^{2+}$  to keep the non-oxidative dissolution reaction going by the addition of  $\text{Cu}^{2+}$  ions.

For example, when  $\text{pH} = 2$  and the  $\text{Fe}^{2+}$  concentration is  $0.1 \text{ mol/L}$ , the resulting equilibrated  $\text{H}_2\text{S}$  concentration from the decomposition of  $\text{CuFeS}_2$  into  $\text{Cu}_5\text{FeS}_4$  is  $10^{-6.479} \text{ mol/L}$ , according to Equation (11). When the  $\text{Cu}^{2+}$  concentration is  $10^{-2} \text{ mol/L}$ , the balanced  $\text{H}_2\text{S}$  concentration with  $\text{Cu}_2\text{S}$  is  $10^{-16.03} \text{ mol/L}$ . Apparently, the formation of  $\text{Cu}_2\text{S}$  can reduce the  $\text{H}_2\text{S}$  concentration produced from the decomposition of  $\text{CuFeS}_2$  into  $\text{Cu}_5\text{FeS}_4$ . In this case, the secondary  $\text{Cu}_2\text{S}$  may be formed as the intermediate of chalcopyrite leaching. Because  $\text{Cu}_2\text{S}$  dissolves much faster than  $\text{CuFeS}_2$ , the chalcopyrite leaching rate will be promoted. This hypothesis is in accordance with the fact that the addition of a small amount of  $\text{Cu}^{2+}$  at the initial leaching stage is helpful to the dissolution of chalcopyrite. Similar to  $\text{Cu}_2\text{S}$ , the formation of  $\text{CuS}$  can also play the same role in decreasing the  $\text{H}_2\text{S}$  concentration. In particular,  $\text{CuS}$  can decrease the resulting aqueous  $\text{H}_2\text{S}$  concentration to a lower level than  $\text{Cu}_2\text{S}$  even at very low  $\text{Cu}^{2+}$  concentrations (see Figure 5). For example, when the equilibrated  $\text{H}_2\text{S}$  concentration from the decomposition of  $\text{CuFeS}_2$  into  $\text{Cu}_5\text{FeS}_4$  is  $10^{-6.479} \text{ mol/L}$  under the condition that  $\text{pH} = 2$  and the  $\text{Fe}^{2+}$  concentration is  $0.1 \text{ mol/L}$ ,  $10^{-2} \text{ mol/L}$  of  $\text{Cu}^{2+}$  is enough to reduce the  $\text{H}_2\text{S}$  concentration down to  $10^{-17.23} \text{ mol/L}$ . It means that Equation (13) takes place more completely than Equation (12) and the formation of  $\text{CuS}$  takes place prior to  $\text{Cu}_2\text{S}$ . At the same time,  $\text{CuS}$ , especially newly formed covellite, also dissolves much faster than chalcopyrite in practice. From the thermodynamic viewpoint,  $\text{CuS}$  is more suitable to being another secondary intermediate of chalcopyrite leaching through the non-oxidative dissolution route. That is, chalcopyrite can be transformed to  $\text{Cu}_5\text{FeS}_4$  through the non-oxidative dissolution mechanism, then according to the diffusion rates of  $\text{Cu}^{2+}$  and  $\text{H}_2\text{S}$ , the released  $\text{H}_2\text{S}$  may react with  $\text{Cu}^{2+}$  to form  $\text{CuS}$  either in solution or at the diffusion channel in the  $\text{Cu}_5\text{FeS}_4$  intermediate phase, as shown in Figure 4. This assumption is in accordance with the report of Warren [30], in which two intermediate products formed during the anodic dissolution of chalcopyrite. In the low potential region these intermediates form passive layers, and the rate of transport is well correlated by the SatoCohen passivation model. Besides  $\text{CuS}$ ,  $\text{Cu}_5\text{FeS}_4$  intermediates were also reported to be detected [31]. Although the dissolution of  $\text{CuS}$  is faster than that of  $\text{CuFeS}_2$ , it is slower than the dissolution of  $\text{Cu}_2\text{S}$ . That may be the reason that the leaching rate of chalcopyrite is often slow, even milled to very fine particles.

As stated above in this section,  $\text{CuS}$  is more likely to be formed than  $\text{Cu}_2\text{S}$  from the reaction between  $\text{Cu}^{2+}$  and  $\text{H}_2\text{S}$ . The formation of  $\text{CuS}$  can limit the aqueous  $\text{H}_2\text{S}$  concentration to a very low level by a low concentration of  $\text{Cu}^{2+}$ . On the other hand, the addition of a certain amount of  $\text{Cu}^{2+}$  is helpful to the non-oxidative dissolution route, in which both  $\text{Cu}_5\text{FeS}_4$  and  $\text{CuS}$  become intermediates.

### 2.3.2. Balanced Aqueous Concentrations of $\text{Fe}^{3+}$ , $\text{Fe}^{2+}$ and $\text{H}_2\text{S}$ with Iron Sulfides

The reactions that may take place among  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{H}_2\text{S}$  include the formation of  $\text{FeS}$ ,  $\text{Fe}_2\text{S}_3$  and elemental sulfur as follows:



It can be expected that the Equations (14)–(16) will set a limit to the aqueous  $\text{H}_2\text{S}$  concentration, respectively. Among them, Equation (16) provides the most effective route to decrease the aqueous  $\text{H}_2\text{S}$  concentration and this trend increases with the increase of the pH and the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio (see Figure 6). Even at the most disadvantageous situation, such as when  $\text{pH} = 0$  and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  is equal to  $10^{-3}$  mol/L, the equilibrated aqueous  $\text{H}_2\text{S}$  concentration is as low as about  $10^{-15.04}$  mol/L.

From the aspect of controlling the aqueous  $\text{H}_2\text{S}$  concentration, Equation (16) is even more effective than Equation (13). For example, when the resulting equilibrated  $\text{H}_2\text{S}$  concentration from the decomposition of  $\text{CuFeS}_2$  into  $\text{Cu}_5\text{FeS}_4$  is  $10^{-6.479}$  mol/L under the condition that  $\text{pH} = 2$  and the  $\text{Fe}^{2+}$  concentration is 0.1 mol/L,  $10^{-4}$  mol/L of  $\text{Fe}^{3+}$  is enough to reduce the  $\text{H}_2\text{S}$  concentration down to  $10^{-19.04}$  mol/L. It is much lower than  $10^{-17.23}$  mol/L, which is obtained with  $10^{-2}$  mol/L of  $\text{Cu}^{2+}$  by forming  $\text{CuS}$ . This indicates that if there is enough  $\text{Fe}^{3+}$  present during chalcopyrite leaching, the aqueous  $\text{H}_2\text{S}$  product formed through non-oxidative dissolution will be oxidized to elemental sulfur rather than forming  $\text{CuS}$ .

On the other hand, when the  $\text{Fe}^{3+}$  concentration is very high, it will diffuse into the cracks of the intermediates. Then  $\text{H}_2\text{S}$  can also be oxidized to elemental sulfur not only in bulk solution but also in the cracks of the intermediates. The resulting elemental sulfur fills up the diffusion channel of both  $\text{H}_2\text{S}$  and  $\text{H}^+$ , hindering the further non-oxidative dissolution reactions. It suggests that an excessive  $\text{Fe}^{3+}$  concentration will also retard the dissolution of chalcopyrite. This inference is in good agreement with the fact that there is an optimum redox potential for the leaching of chalcopyrite. The solution potential is proportional to the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio, and as a result, the addition of a certain amount of  $\text{Fe}^{2+}$  can decrease the redox potential and the amount of  $\text{Fe}^{3+}$  diffused into the cracks of intermediates, which will prevent the  $\text{H}_2\text{S}$  product from being oxidized at the diffusion channel. This phenomenon is in accordance with Silvester's work [34]. Copper sulfide sols, when first precipitated from solution, are "golden-brown" in color. Electron diffraction studies indicate that the particles are a poorly crystalline form of covellite while XPS analysis shows that copper is exclusively in the form of  $\text{Cu}^+$ . With time, and at an enhanced rate at a higher temperature, these sols change to a green color and concomitantly become more crystalline. In addition to this, a higher  $\text{Fe}^{3+}$  concentration and aqueous redox potential can also inhibit the non-oxidative dissolution route by lifting the potential above the rest potential of chalcopyrite. This also supports the existence of an optimal potential range in the dissolution of chalcopyrite.

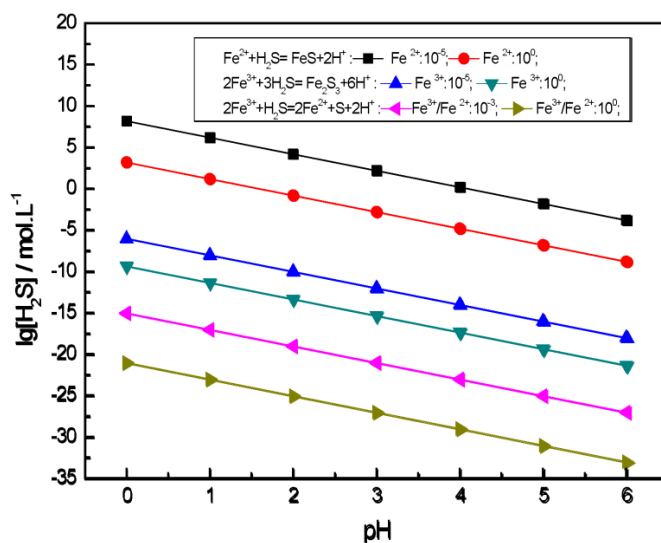


Figure 6.  $\text{H}_2\text{S}$  concentration balanced with  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  under different concentrations.

It can also explain the phenomenon of iron dissolving prior to copper. When there is a certain amount of  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  at the initial stage of leaching, there would be enough  $\text{Cu}^{2+}$  in the cracks

reacting with  $\text{H}_2\text{S}$  to form  $\text{CuS}$ . Meanwhile, the presence of  $\text{Fe}^{2+}$  can also retard the oxidizing reaction in the cracks by decreasing the potential there. Consequently, the oxidization of  $\text{CuS}$  will take place on the particle surface and the oxidization of  $\text{H}_2\text{S}$  will take place in solution. If so, the non-oxidative dissolution route can occur in the process of chalcopyrite dissolution, even under oxidative atmosphere. It is in accordance with the research result reported by Liu [35]. In that work, a pure chalcopyrite powder sample is leached under an oxygen and argon atmosphere, respectively. The ratio of  $\text{Cu}/\text{Fe}$  on the surface of a leached chalcopyrite particle is shown in Table 3. It can be seen that the solution acidity has a great effect on the rate of the non-oxidative dissolution reactions under both argon and oxygen atmosphere. Low pH results in a high ratio of  $\text{Cu}/\text{Fe}$  on the surface of the leached chalcopyrite particle, which means that the  $\text{Fe}$  in chalcopyrite takes precedence to release over  $\text{Cu}$ . At the same time, the existence of oxygen lowers the ratio of  $\text{Cu}/\text{Fe}$  on the surface of the leached chalcopyrite particle, which means that the release of copper is attributed to the function of the oxidation of oxygen.

**Table 3.** Chalcopyrite's surface atomic ratio (XPS) [32].

Atmosphere	Solution Acidity	Leaching Time (min)	Ratio of $\text{Cu}/\text{Fe}$
Ar	Pure water	420	1.04
	pH 2.09	180	1.75
$\text{O}_2$	Pure water	420	1.02
	pH 2.09	180	1.23

As stated above, the  $\text{H}_2\text{S}$  concentration cannot be limited at a low level by the formation of  $\text{FeS}$ .  $\text{Fe}^{3+}$  can oxidize  $\text{H}_2\text{S}$  to elemental sulfur. The oxidization reaction can result in the lowest  $\text{H}_2\text{S}$  concentration with a relatively low concentration of  $\text{Fe}^{3+}$ . There is a proper concentration of  $\text{Fe}^{3+}$  and solution potential to control the site in which the  $\text{H}_2\text{S}$  is oxidized to elemental sulfur, which can give an explanation for the promotion action of  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  at the initial leaching of chalcopyrite. In addition, the non-oxidative dissolution route may take part in the process of chalcopyrite dissolution even under oxidative atmosphere.

#### 2.4. Dissolution of Secondary Copper Sulfides in Sulfuric Acid Solution

The whole chalcopyrite leaching process includes the generation of secondary copper sulfides and further dissolution of these intermediates. Either in the non-oxidative dissolution mechanism or in the oxidative dissolution mechanism,  $\text{Cu}_5\text{FeS}_4$  and  $\text{CuS}$  are the most likely intermediates.  $\text{Cu}_5\text{FeS}_4$  is a little bit more likely to be the intermediate than  $\text{CuS}$  in both the non-oxidative dissolution mechanism and oxidative dissolution mechanism. When chalcopyrite dissolves by the oxidative dissolution mechanism, the intermediates  $\text{Cu}_5\text{FeS}_4$  and  $\text{CuS}$  form together on the chalcopyrite surface. The resulting product of elemental sulfur is mixed equally with the intermediates  $\text{Cu}_5\text{FeS}_4$  and  $\text{CuS}$ . The  $\text{Fe}^{2+}$  product diffuses into the solution through the intermediate layer. Electrons are transferred from the chalcopyrite surface through the semiconductor intermediate layer to  $\text{Fe}^{3+}$ . On the other hand, in the non-oxidative dissolution mechanism,  $\text{H}^+$  transfers from the bulk solution towards the chalcopyrite surface through the intermediate layer and the  $\text{H}_2\text{S}$  and  $\text{Fe}^{2+}$  products diffuse from the chalcopyrite surface into the solution. The most likely initial intermediates left on the chalcopyrite surface are also  $\text{Cu}_5\text{FeS}_4$  and  $\text{CuS}$ . The released  $\text{H}_2\text{S}$  may form  $\text{CuS}$  with  $\text{Cu}^{2+}$  or be oxidized by  $\text{Fe}^{3+}$  to elemental sulfur along the diffusing path and in solution. The site for the formation of elemental sulfur is determined by the diffusing rate of  $\text{H}_2\text{S}$ , the diffusing rate of  $\text{Fe}^{3+}$  into the intermediate layer and the oxidizing reaction rate of  $\text{H}_2\text{S}$  with  $\text{Fe}^{3+}$  to elemental sulfur.

#### 2.4.1. Non-Oxidative Dissolution of Secondary Copper Sulfides in Sulfuric Acid Solution

Cuprous ions are not stable in sulfate solution, so the dissolution routes of the  $\text{Cu}_5\text{FeS}_4$  intermediate are often accompanied by the transfer of electrons. The non-oxidative dissolution of secondary copper sulfides is limited to covellite.

The already formed CuS intermediate maybe consumed by non-oxidative dissolution as in Equation (17), and the  $\text{H}_2\text{S}$  product is oxidized to elemental sulfur by  $\text{Fe}^{3+}$  according to Equation (16). Then, the release of  $\text{Cu}^{2+}$  from CuS by Equation (17) can occur. This provides the CuS intermediate with a non-oxidative dissolution route.



The dissolution of the CuS intermediate in this way and the oxidization of the  $\text{H}_2\text{S}$  can lead to another problem. When the oxidation of the  $\text{H}_2\text{S}$  takes place in solution, i.e., the diffusion of  $\text{H}_2\text{S}$  is very fast, the resulting elemental sulfur will suspend in the solution and has little effect on the further dissolution of chalcopyrite. However, when the oxidation reaction of the resulting  $\text{H}_2\text{S}$  takes place at the diffusion channel in the  $\text{Cu}_5\text{FeS}_4$  intermediate phase, i.e., the diffusion of  $\text{H}_2\text{S}$  is very slow, the resulting elemental sulfur will block the diffusion channel in the  $\text{Cu}_5\text{FeS}_4$  intermediate phase. This will result in the termination of Equation (17) and the direct oxidization of CuS by  $\text{Fe}^{3+}$  will also be terminated because the elemental sulfur product stops the transmission of both  $\text{H}^+$  and  $\text{Fe}^{3+}$  reactants. Accounting for the  $\text{H}_2\text{S}$  concentration equilibrated with CuS being very low, similar to that controlled by  $\text{Fe}^{3+}$ , the non-oxidative dissolution route may have little effect on the dissolution of CuS.

#### 2.4.2. Oxidative Dissolution of Secondary Copper Sulfides in Sulfuric Acid Solution

The further dissolution of the intermediates can also occur according to the oxidative reaction mechanism. The possible oxidative reactions are shown in Table 4. The relationship between their potentials and the resulting metal ion concentration are shown in Figure 7.

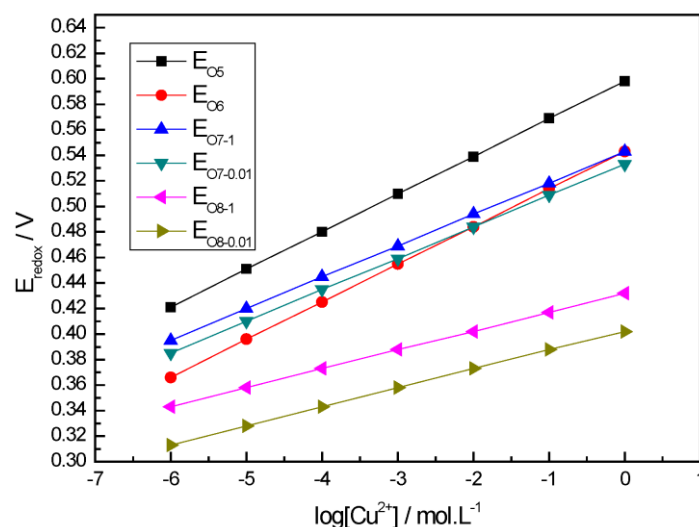


Figure 7. Potentials for bornite oxidization through different routes.

Figure 7 shows that  $\text{Cu}_3\text{FeS}_4$  is not the likely intermediate during the oxidation process of  $\text{Cu}_5\text{FeS}_4$  ( $\text{E}_{\text{O6}}$ ). It is difficult for  $\text{Cu}_5\text{FeS}_4$  to be directly oxidized into  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and elemental sulfur ( $\text{E}_{\text{O7-1}}$  and  $\text{E}_{\text{O7-0.01}}$ ). The decomposition potential of  $\text{Cu}_5\text{FeS}_4$  into CuS ( $\text{E}_{\text{O8-1}}$  and  $\text{E}_{\text{O8-0.01}}$ ) is lower than that of other reactions under the  $\text{Fe}^{2+}$  concentration of 1 mol/L or 0.01 mol/L. It means that the oxidizing decomposition of  $\text{Cu}_5\text{FeS}_4$  seems to include two steps, and CuS and  $\text{Cu}^{2+}$  are the products in sequence,

respectively. Among the two steps, the decomposition potential of CuS is relatively high ( $E_{05}$ ), which means that the most difficult oxidative step is the dissolution of CuS.

**Table 4.** Selected oxidative dissolution of secondary copper sulfides in sulfuric acid solution.

Equation Number	Reactions	Potentials
5	$\text{CuS} = \text{S} + \text{Cu}^{2+} + 2\text{e}$	$E_{05} = 0.598 + 0.0295\lg[\text{Cu}^{2+}]$
6	$\text{Cu}_5\text{FeS}_4 = \text{Cu}_3\text{FeS}_4 + 2\text{Cu}^{2+} + 4\text{e}$	$E_{06} = 0.543 + 0.0295\lg[\text{Cu}^{2+}]$
7	$\text{Cu}_5\text{FeS}_4 = 5\text{Cu}^{2+} + \text{Fe}^{2+} + 4\text{S} + 12\text{e}$	$E_{07} = 0.543 + 0.0246\lg[\text{Cu}^{2+}] + 0.00492\lg[\text{Fe}^{2+}]$
8	$\text{Cu}_5\text{FeS}_4 = 4\text{CuS} + \text{Fe}^{2+} + \text{Cu}^{2+} + 4\text{e}$	$E_{08} = 0.432 + 0.0148\lg[\text{Cu}^{2+}] + 0.0148\lg[\text{Fe}^{2+}]$

From this point of view, whether the chalcopyrite leaching is through the non-oxidative dissolution mechanism or the oxidative dissolution mechanism, it is just the decomposition reaction of CuS which needs the highest potential. If the dissolution rate of chalcopyrite is slower than the decomposition rate of covellite, it must be some other processes, such as the mass transfer process and the original decomposition process of  $\text{CuFeS}_2$  into intermediates, which slow down the dissolution rate of chalcopyrite.

By comparison with Figure 1, the potentials of the four original decomposition routes of  $\text{CuFeS}_2$  are all lower than the potential for the decomposition of covellite. The potential of the direct decomposition of  $\text{CuFeS}_2$  into  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and elemental sulfur is lower than 0.426 V. However, the potential for CuS decomposition is 0.421 V even under  $10^{-6}$  mol/L of  $\text{Cu}^{2+}$  and it will be increased to 0.569 V with the  $\text{Cu}^{2+}$  concentration of  $10^{-1}$  mol/L. It means that when the formed CuS begins to decompose, all four original reaction routes of chalcopyrite leaching have a chance to take place. However, the solution redox potential, which is closer to the potential on the intermediate surface, may be higher than that on the surface of chalcopyrite. That is, there is a potential gradient across the intermediate layer. Direct oxidization of  $\text{CuFeS}_2$  into  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and elemental sulfur is unlikely to occur on a large scale. On the other hand, the likely intermediate bornite is easily oxidized to CuS due to the low potential required and exposed to the solution. For this reason, most research works have detected the CuS intermediate on the surface of leached chalcopyrite particles, but not bornite.

### 3. Conclusions

The chalcopyrite dissolution process can be divided into two steps. The first dissolution step can take place either through the non-oxidative dissolution route or through the oxidative dissolution route.  $\text{Cu}_5\text{FeS}_4$  and CuS are the most likely intermediates both in the oxidative dissolution route and in the non-oxidative dissolution route.  $\text{Cu}_5\text{FeS}_4$  is more likely to be the intermediate than CuS during the preliminary dissolution step. CuS can also be present in the cracks of the  $\text{Cu}_5\text{FeS}_4$  intermediate as a secondary intermediate formed by the reaction resulting from  $\text{H}_2\text{S}$  and  $\text{Cu}^{2+}$ .

The second step involves the decomposition of the intermediates, and the release of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ , and the formation of elemental sulfur. The  $\text{Cu}_5\text{FeS}_4$  intermediate will be turned into CuS through an oxidative route firstly. CuS is the only final intermediate, which can be dissolved either by the oxidative dissolution route or by the non-oxidative dissolution route. However, the non-oxidative dissolution route may play a less important role than the oxidative route in the decomposition of CuS due to the very low aqueous  $\text{H}_2\text{S}$  concentration equilibrated with CuS.

When chalcopyrite dissolves in the oxidative dissolution mechanism, the elemental sulfur formed in the preliminary dissolution step of chalcopyrite is mixed equally with the intermediates  $\text{Cu}_5\text{FeS}_4$  and CuS, while in the non-oxidative dissolution mechanism, the  $\text{H}_2\text{S}$  product may be oxidized into elemental sulfur both along the diffusing path and in the solution.

The site where elemental sulfur forms is determined by the diffusion rate of  $\text{H}_2\text{S}$ , the diffusion rate of  $\text{Fe}^{3+}$  into the intermediate layer, and the oxidizing reaction rate of  $\text{H}_2\text{S}$  with  $\text{Fe}^{3+}$  into elemental sulfur. The addition of  $\text{Cu}^{2+}$  can form CuS, preventing the diffusion channel from being blocked by

elemental sulfur. A similar effect can be accomplished by addition of  $\text{Fe}^{2+}$ , which maintains a moderate redox potential to prevent  $\text{H}_2\text{S}$  from being oxidized in the diffusion channel by  $\text{Fe}^{3+}$ .

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