

Article

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

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Academic Editor: Hugo F. Lopez

Received: 13 July 2016; Accepted: 25 November 2016; Published: 2 December 2016

Abstract: The dissolution routes of chalcopyrite in acidic sulfate aqueous solution have been discussed by thermodynamic calculation under different aqueous species concentrations, such as Cu^{2+} , Fe^{2+} and H_2S . 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 Cu^{2+} , 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 Cu^{2+} and Fe^{2+} , as well as the preferential release of Fe^{2+} in the chalcopyrite leaching process, have been explained and elucidated.

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

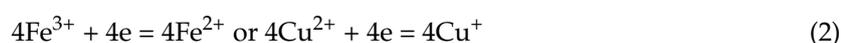
1. Introduction

Chalcopyrite (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 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].

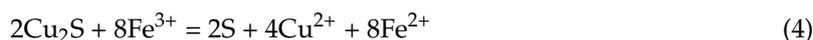
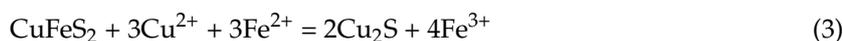
First of all, the oxidative dissolution of chalcopyrite in acidic ferric or cupric solutions can be described by the normal mixed-potential electrochemical model proposed by Nicol et al. [7], and it was also adopted by Jones and Peters [8], Miller et al. [9] and others, where the following anodic reaction



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 Cu_2S in the presence of cupric ions according to Equation (3), then the resulting intermediate Cu_2S is oxidized by ferric ions to 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 2.8×10^{-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 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 H_2S .

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 (S^0) [15,16], disulfide (S_2^{2-}) [17–19], polysulfide (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 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 CuFeS_2 in Sulfuric Acid Solution

Although the final dissolution products of chalcopyrite include Cu^{2+} , Fe^{2+} and elemental sulfur, many possible routes may exist for the preliminary oxidative dissolution of CuFeS_2 in sulfuric acid solution. The equilibrium potentials of selected possible oxidative dissolution reaction routes of 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 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 CuFeS_2 can be attributed to four routes. Fe^{2+} and elemental sulfur are the products of the above reactions. In addition to these, CuS , Cu_2S , Cu_5FeS_4 and 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 Fe^{2+} or Cu^{2+} , or both of them. As a result, the potentials associated with the possible reactions should be compared under different Fe^{2+} and 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 Cu^{2+} concentration is assumed to be varied at the same step with the Fe^{2+} concentration in the range of 10^{-6} mol/L to 1 mol/L. The calculated potentials of different reactions under the same 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 CuS , Cu_5FeS_4 , Cu_2S and Cu^{2+} , respectively (see Figure 1). All of the potentials increase with the increase of the Fe^{2+} concentration, and the sequence order does not change. E_{04-1} , the potential for CuFeS_2 to be oxidized directly to Cu^{2+} ,

is always higher than those in which the CuS, Cu₂S and Cu₅FeS₄ are present as intermediates by at least 0.137 V. Apparently, it is not thermodynamically favorable for CuFeS₂ to be oxidized directly to Cu²⁺ among these oxidative reaction routes based on the potentials required. Consequently, the oxidative reactions taking place on the chalcopyrite surface tend to form intermediates.

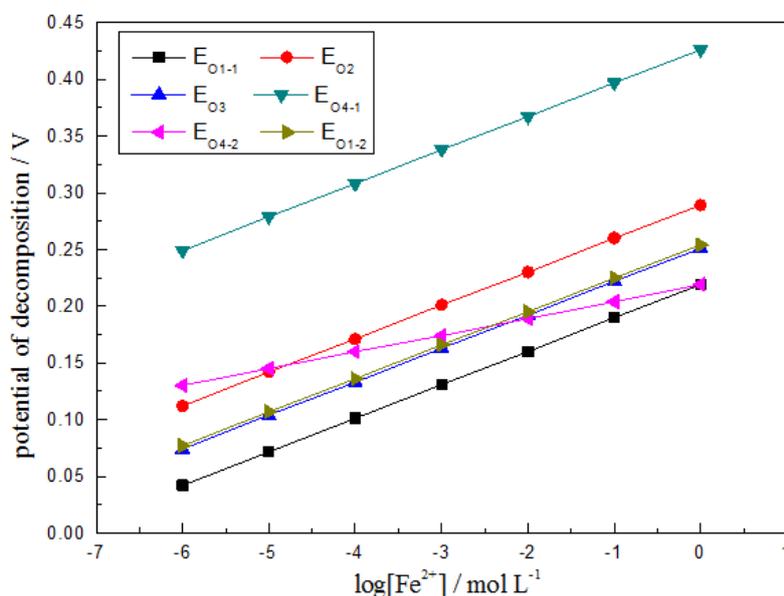


Figure 1. Relation between decomposition potential of chalcopyrite and routes.

Among the other three possible routes, CuS seems to be the most likely intermediate, Cu₅FeS₄ is the second most likely, and Cu₂S 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 Cu₅FeS₄, 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. Cu₂S and CuS can be taken as two of a series of compounds, Cu_{1+x}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_{1+x}S at 25 °C (kJ/mol) [1].

Formula	Cu ₂ S	Cu _{1.96} S	Cu _{1.93} S	Cu _{1.83} S	Cu _{1.75} S	Cu _{1.67} S	Cu _{1.38} S	CuS
ΔG_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 Cu_{1+x}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].

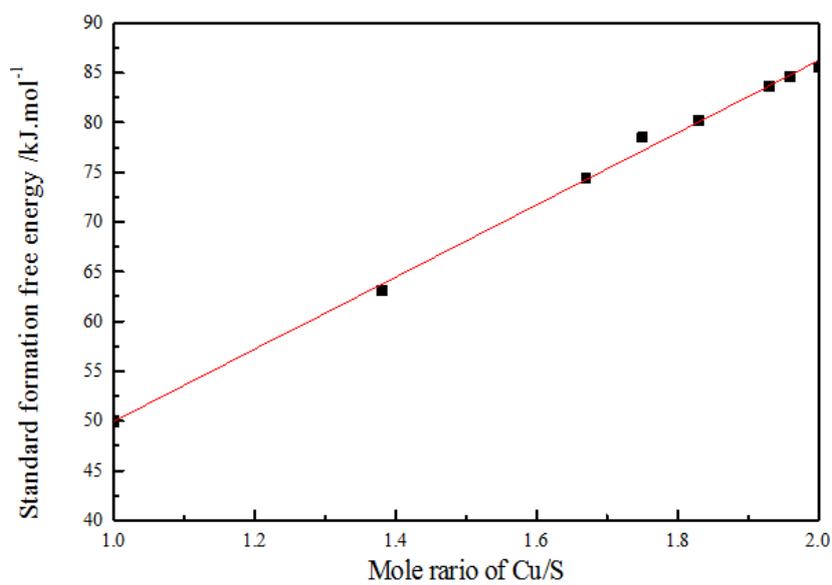


Figure 2. Relation between standard formation free energy and ratio of Cu/S.

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 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, Cu_2S and Cu_5FeS_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, Cu_2S remains unlikely to be the intermediate of chalcopyrite leaching. Then the calculated potential sequence of different reaction routes under the same Fe^{2+} concentration is as follows:



Line E_{01-2} in Figure 1 is almost overlapped with line E_{03} , which means Cu_5FeS_4 and CuS have equal opportunities to present as intermediates on the surface of CuFeS_2 based on the oxidative dissolution mechanism.

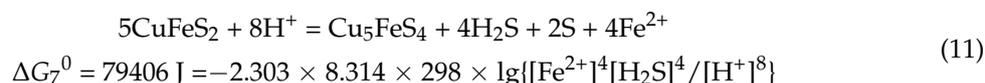
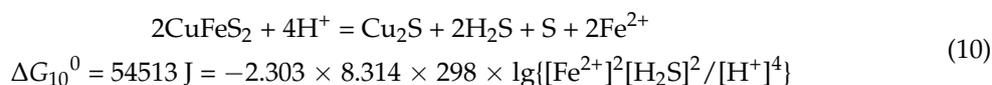
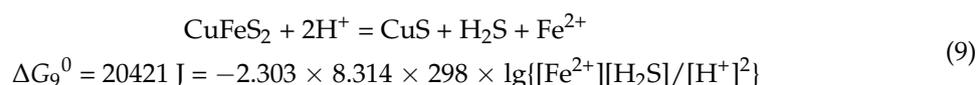
Besides the above analysis, there is a special situation that should be considered. When chalcopyrite leaching takes place along the two reaction paths in which Cu_5FeS_4 and CuS present as intermediates as shown in Equations 3 and 1 in Table 1, the iron in chalcopyrite releases into the solution continuously and the copper remains undissolved. During this period the Fe^{2+} concentration increases continuously, whereas the 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 Cu^{2+} will be released at the initial stage of chalcopyrite leaching. At the same time, the accumulation of the Cu^{2+} concentration lifts line E_{04-1} up higher than E_{01-2} and E_{03} gradually. So there must be a Cu^{2+} concentration above which the direct oxidization reaction of chalcopyrite will be inhibited.

In fact, it can be postulated that the Cu^{2+} concentration equilibrated with CuFeS_2 and CuS is on the scale of 10^{-14} mol/L [34]. Then line Eo_{4-1} , representing the direct oxidizing of chalcopyrite to Cu^{2+} , will turn out to be line Eo_{4-2} . When the Fe^{2+} concentration reaches over $10^{-2.5}$ mol/L, line Eo_{4-2} starts to get lower than Eo_{1-2} and Eo_3 , leading to the termination of the reactions in which Cu_5FeS_4 and CuS generate on the chalcopyrite surface and the dissolution route turns into the direct complete oxidizing mechanism. When the Cu^{2+} concentration increases, line Eo_{4-2} also gets higher. As a result, the addition of Cu^{2+} will be helpful to let chalcopyrite leaching generate a series of intermediates, such as Cu_5FeS_4 and CuS . If the direct complete oxidizing dissolution rate is lower than those reaction routes with Cu_5FeS_4 and CuS intermediates, it will be in accordance with the fact that the addition of 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 Cu_5FeS_4 and CuS are intermediates, must be faster than the direct complete oxidization route in which Cu^{2+} releases in the same step with Fe^{2+} .

As stated above, both Cu_5FeS_4 and CuS can generate as the first batch of intermediates in the oxidative dissolution reaction mechanism of 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 CuFeS_2 in Sulfuric Acid Solution

When CuFeS_2 is attacked by H^+ , the decomposition reaction may take place according to Equations (9)–(11), and then CuS , Cu_2S and Cu_5FeS_4 may generate as intermediates before CuFeS_2 decomposes completely to Cu^{2+} , Fe^{2+} and elemental sulfur.



All three reaction routes are accompanied by the release of H_2S into the solution. The resulting equilibrated H_2S concentrations with different intermediates obey the sequence below:



All the equilibrated H_2S concentrations decline with the increase of the pH and the Fe^{2+} concentration (see Figure 3), and the sequence of the equilibrated H_2S concentrations remains unchanged under the same Fe^{2+} concentration. The H_2S concentration equilibrated with the Cu_2S intermediate is the lowest, and the H_2S concentration equilibrated with the Cu_5FeS_4 intermediate is just slightly higher than that of CuS , which means that both Equations (9) and (11) can give the same highest H_2S concentration on the surface of the chalcopyrite. When Equations (9) and (11) take place, Equation (10) will be inhibited by the high H_2S concentration produced by Equations (9) and (11). It seems that Cu_5FeS_4 and CuS are both the most likely intermediates of chalcopyrite non-oxidative leaching based on the viewpoint of chemical equilibrium. As a result, Cu_5FeS_4 and CuS are both the most likely intermediates of chalcopyrite leaching in a non-oxidative dissolution mechanism. Certainly, the Cu_5FeS_4 intermediate needs to be further decomposed to more simple intermediates, such as CuS , etc. These secondary reactions will take place on the surface of Cu_5FeS_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 Cu_5FeS_4 on the reacted surface of chalcopyrite.

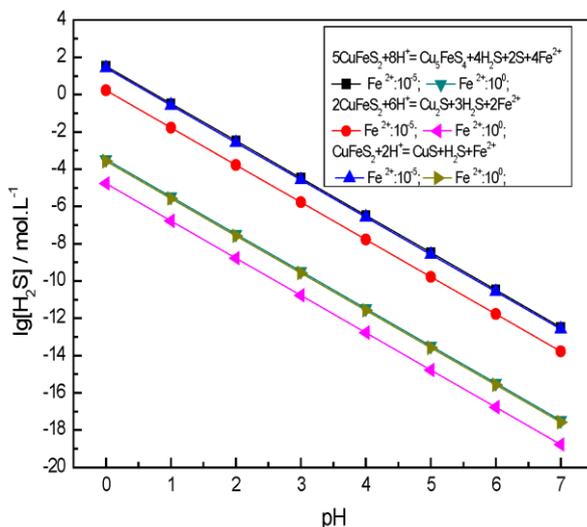


Figure 3. Equilibrated H₂S concentration for acid dissolution of CuFeS₂ in different reactions.

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 CuFeS_2 have been changed in all three reactions. It is worth mentioning that just 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 CuFeS_2 . However, when the redox potential in solution is much lower than the rest potential of CuFeS_2 , as a result, the oxidative dissolution of 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.

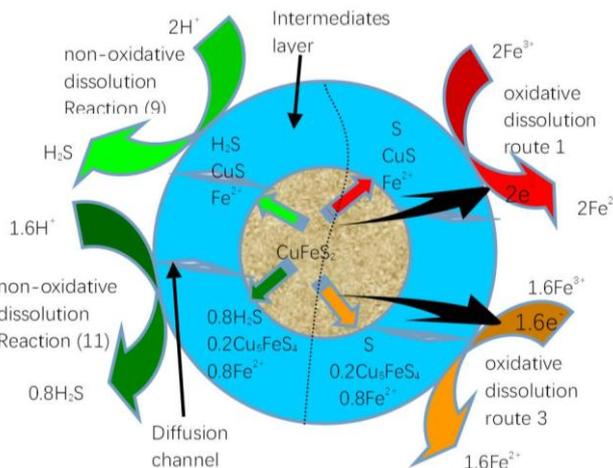


Figure 4. Possible chalcopyrite dissolution reaction routes.

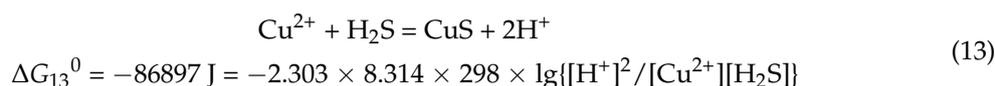
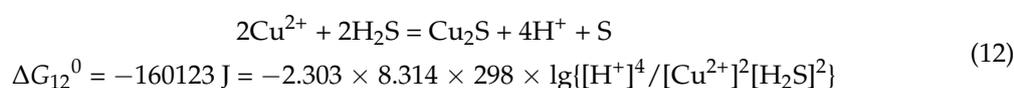
As stated above, in the non-oxidative dissolution of CuFeS_2 , the most likely intermediates should be Cu_5FeS_4 and CuS . The dissolution route of chalcopyrite is in favor of Equations (9) and (11). Based on the discussion above, the most likely starting dissolution routes of chalcopyrite are summarized in the schematic diagram I Figure 4, in which two oxidative routes and non-oxidative routes are involved.

2.3. Balanced Concentrations of Cu^{2+} , H_2S , Fe^{2+} and Fe^{3+} in Aqueous Solution with Simple Sulfides

During chalcopyrite leaching in sulfuric acid solution, many soluble species, such as Cu^{2+} , Fe^{2+} , Fe^{3+} and H_2S 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 Cu^{2+} and H_2S in Aqueous Solution with Copper Sulfides

The possible reactions between Cu^{2+} and H_2S include the formation of Cu_2S and CuS as in Equations (12) and (13).



According to the change of the H_2S concentration with the different given total S^{2-} ion concentration ($\Sigma\text{H}_2\text{S} + \text{HS}^- + \text{S}^{2-}$), almost all of the aqueous S^{2-} ions species exist as H_2S in the acidic range (see Figure 5, calculated based on the database of HSC, except for CuS).

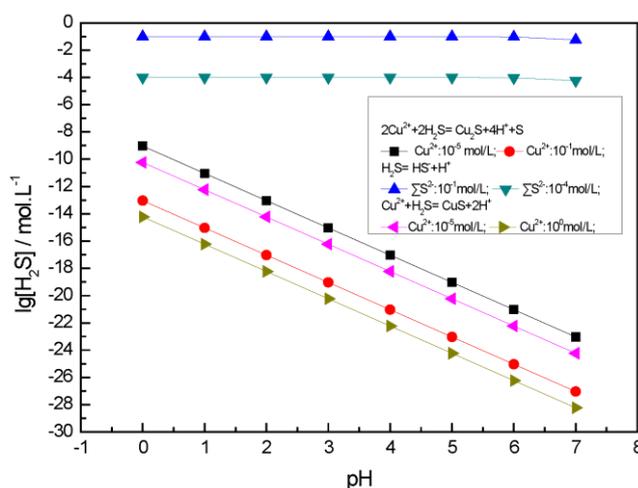


Figure 5. Aqueous H_2S concentration equilibrated with Cu_2S and CuS under different Cu^{2+} concentrations.

It can also be observed from Figure 5 that the H_2S concentrations equilibrated with both Cu_2S and CuS , increased gradually with the decrease of the pH and Cu^{2+} concentration, and the aqueous H_2S concentration can always be kept at a very low level by forming both Cu_2S and CuS . However, the formation of CuS can decrease the aqueous H_2S concentration to about one magnitude lower than that of Cu_2S under the same Cu^{2+} concentration and pH. For example, when the Cu^{2+} concentration is at 10^{-5} mol/L and pH 2, the H_2S concentrations equilibrated with Cu_2S and CuS are $10^{-13.03}$ mol/L and $10^{-14.23}$ mol/L, respectively.

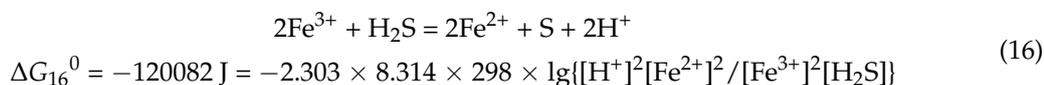
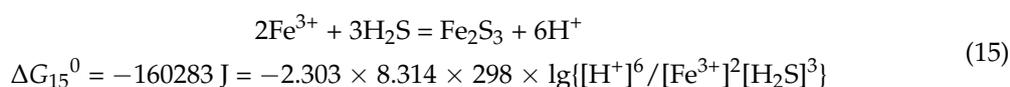
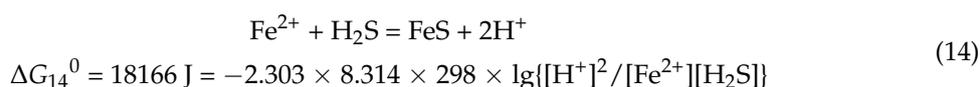
It means that the high aqueous H₂S concentration may exist during the initial stage of chalcopyrite acidic leaching when both the Cu²⁺ concentration and pH are very low. The fact that iron releases into the solution prior to copper might result in such a low Cu²⁺ concentration. Then the non-oxidative dissolution mechanism can play an important role in the initial stage of chalcopyrite leaching. The high H₂S concentration can be reduced to a low level by Cu²⁺ to keep the non-oxidative dissolution reaction going by the addition of Cu²⁺ ions.

For example, when pH = 2 and the Fe²⁺ concentration is 0.1 mol/L, the resulting equilibrated H₂S concentration from the decomposition of CuFeS₂ into Cu₅FeS₄ is 10^{-6.479} mol/L, according to Equation (11). When the Cu²⁺ concentration is 10⁻² mol/L, the balanced H₂S concentration with Cu₂S is 10^{-16.03} mol/L. Apparently, the formation of Cu₂S can reduce the H₂S concentration produced from the decomposition of CuFeS₂ into Cu₅FeS₄. In this case, the secondary Cu₂S may be formed as the intermediate of chalcopyrite leaching. Because Cu₂S dissolves much faster than CuFeS₂, the chalcopyrite leaching rate will be promoted. This hypothesis is in accordance with the fact that the addition of a small amount of Cu²⁺ at the initial leaching stage is helpful to the dissolution of chalcopyrite. Similar to Cu₂S, the formation of CuS can also play the same role in decreasing the H₂S concentration. In particular, CuS can decrease the resulting aqueous H₂S concentration to a lower level than Cu₂S even at very low Cu²⁺ concentrations (see Figure 5). For example, when the equilibrated H₂S concentration from the decomposition of CuFeS₂ into Cu₅FeS₄ is 10^{-6.479} mol/L under the condition that pH = 2 and the Fe²⁺ concentration is 0.1 mol/L, 10⁻² mol/L of Cu²⁺ is enough to reduce the H₂S concentration down to 10^{-17.23} mol/L. It means that Equation (13) takes place more completely than Equation (12) and the formation of CuS takes place prior to Cu₂S. At the same time, CuS, especially newly formed covellite, also dissolves much faster than chalcopyrite in practice. From the thermodynamic viewpoint, 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 Cu₅FeS₄ through the non-oxidative dissolution mechanism, then according to the diffusion rates of Cu²⁺ and H₂S, the released H₂S may react with Cu²⁺ to form CuS either in solution or at the diffusion channel in the Cu₅FeS₄ 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 CuS, Cu₅FeS₄ intermediates were also reported to be detected [31]. Although the dissolution of CuS is faster than that of CuFeS₂, it is slower than the dissolution of Cu₂S. 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, CuS is more likely to be formed than Cu₂S from the reaction between Cu²⁺ and H₂S. The formation of CuS can limit the aqueous H₂S concentration to a very low level by a low concentration of Cu²⁺. On the other hand, the addition of a certain amount of Cu²⁺ is helpful to the non-oxidative dissolution route, in which both Cu₅FeS₄ and CuS become intermediates.

2.3.2. Balanced Aqueous Concentrations of Fe³⁺, Fe²⁺ and H₂S with Iron Sulfides

The reactions that may take place among Fe³⁺, Fe²⁺ and H₂S include the formation of FeS, Fe₂S₃ and elemental sulfur as follows:



It can be expected that the Equations (14)–(16) will set a limit to the aqueous H_2S concentration, respectively. Among them, Equation (16) provides the most effective route to decrease the aqueous H_2S 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 H_2S concentration is as low as about $10^{-15.04}$ mol/L.

From the aspect of controlling the aqueous H_2S concentration, Equation (16) is even more effective than Equation (13). For example, when the resulting equilibrated H_2S concentration from the decomposition of CuFeS_2 into Cu_5FeS_4 is $10^{-6.479}$ mol/L under the condition that $\text{pH} = 2$ and the Fe^{2+} concentration is 0.1 mol/L, 10^{-4} mol/L of Fe^{3+} is enough to reduce the H_2S 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 Cu^{2+} by forming CuS . This indicates that if there is enough Fe^{3+} present during chalcopyrite leaching, the aqueous H_2S product formed through non-oxidative dissolution will be oxidized to elemental sulfur rather than forming CuS .

On the other hand, when the Fe^{3+} concentration is very high, it will diffuse into the cracks of the intermediates. Then H_2S 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 H_2S and H^+ , hindering the further non-oxidative dissolution reactions. It suggests that an excessive 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 Fe^{2+} can decrease the redox potential and the amount of Fe^{3+} diffused into the cracks of intermediates, which will prevent the H_2S 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 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 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.

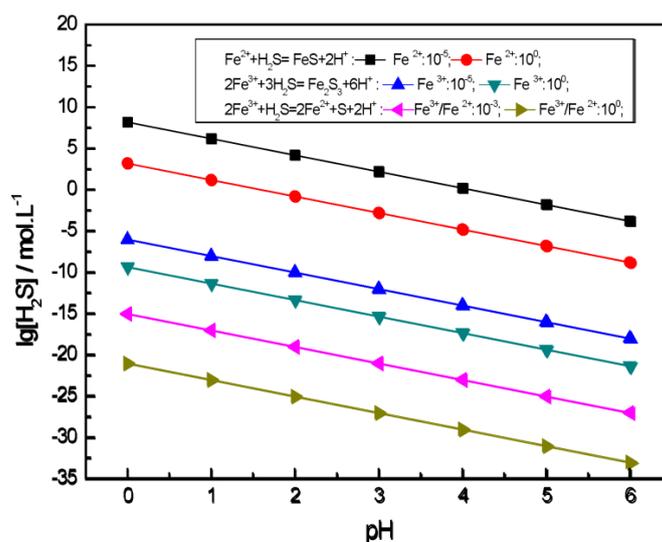


Figure 6. H_2S concentration balanced with Fe^{2+} and Fe^{3+} under different concentrations.

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

reacting with H_2S to form CuS . Meanwhile, the presence of Fe^{2+} can also retard the oxidizing reaction in the cracks by decreasing the potential there. Consequently, the oxidization of CuS will take place on the particle surface and the oxidization of H_2S 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 Cu/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 Cu/Fe on the surface of the leached chalcopyrite particle, which means that the Fe in chalcopyrite takes precedence to release over Cu . At the same time, the existence of oxygen lowers the ratio of Cu/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 Cu/Fe
Ar	Pure water	420	1.04
	pH 2.09	180	1.75
O_2	Pure water	420	1.02
	pH 2.09	180	1.23

As stated above, the H_2S concentration cannot be limited at a low level by the formation of FeS . Fe^{3+} can oxidize H_2S to elemental sulfur. The oxidization reaction can result in the lowest H_2S concentration with a relatively low concentration of Fe^{3+} . There is a proper concentration of Fe^{3+} and solution potential to control the site in which the H_2S is oxidized to elemental sulfur, which can give an explanation for the promotion action of Cu^{2+} and 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, Cu_5FeS_4 and CuS are the most likely intermediates. Cu_5FeS_4 is a little bit more likely to be the intermediate than CuS in both the non-oxidative dissolution mechanism and oxidative dissolution mechanism. When chalcopyrite dissolves by the oxidative dissolution mechanism, the intermediates Cu_5FeS_4 and CuS form together on the chalcopyrite surface. The resulting product of elemental sulfur is mixed equally with the intermediates Cu_5FeS_4 and CuS . The Fe^{2+} product diffuses into the solution through the intermediate layer. Electrons are transferred from the chalcopyrite surface through the semiconductor intermediate layer to Fe^{3+} . On the other hand, in the non-oxidative dissolution mechanism, H^+ transfers from the bulk solution towards the chalcopyrite surface through the intermediate layer and the H_2S and Fe^{2+} products diffuse from the chalcopyrite surface into the solution. The most likely initial intermediates left on the chalcopyrite surface are also Cu_5FeS_4 and CuS . The released H_2S may form CuS with Cu^{2+} or be oxidized by 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 H_2S , the diffusing rate of Fe^{3+} into the intermediate layer and the oxidizing reaction rate of H_2S with 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 Cu_5FeS_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 H_2S product is oxidized to elemental sulfur by Fe^{3+} according to Equation (16). Then, the release of 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 H_2S can lead to another problem. When the oxidation of the H_2S takes place in solution, i.e., the diffusion of H_2S 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 H_2S takes place at the diffusion channel in the Cu_5FeS_4 intermediate phase, i.e., the diffusion of H_2S is very slow, the resulting elemental sulfur will block the diffusion channel in the Cu_5FeS_4 intermediate phase. This will result in the termination of Equation (17) and the direct oxidization of CuS by Fe^{3+} will also be terminated because the elemental sulfur product stops the transmission of both H^+ and Fe^{3+} reactants. Accounting for the H_2S concentration equilibrated with CuS being very low, similar to that controlled by 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.

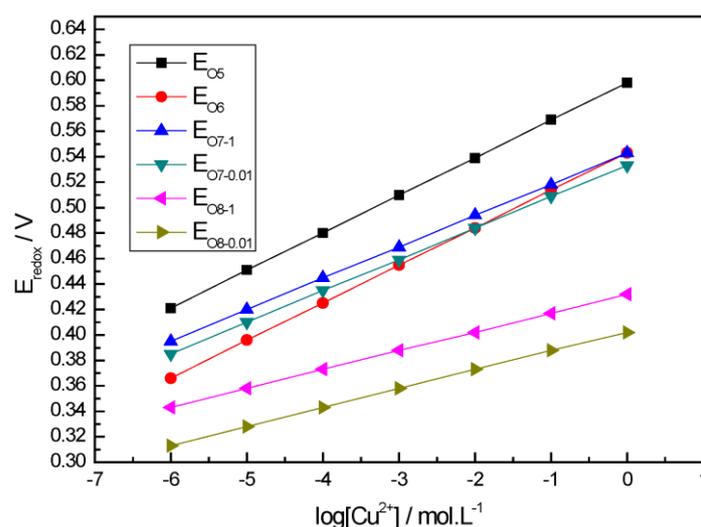


Figure 7. Potentials for bornite oxidization through different routes.

Figure 7 shows that Cu_3FeS_4 is not the likely intermediate during the oxidation process of Cu_5FeS_4 (E_{O6}). It is difficult for Cu_5FeS_4 to be directly oxidized into Cu^{2+} , Fe^{2+} and elemental sulfur ($\text{E}_{\text{O7-1}}$ and $\text{E}_{\text{O7-0.01}}$). The decomposition potential of Cu_5FeS_4 into CuS ($\text{E}_{\text{O8-1}}$ and $\text{E}_{\text{O8-0.01}}$) is lower than that of other reactions under the Fe^{2+} concentration of 1 mol/L or 0.01 mol/L. It means that the oxidizing decomposition of Cu_5FeS_4 seems to include two steps, and CuS and 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 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 CuFeS_2 are all lower than the potential for the decomposition of covellite. The potential of the direct decomposition of CuFeS_2 into Cu^{2+} , 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 Cu^{2+} and it will be increased to 0.569 V with the 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 CuFeS_2 into Cu^{2+} , 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. Cu_5FeS_4 and CuS are the most likely intermediates both in the oxidative dissolution route and in the non-oxidative dissolution route. Cu_5FeS_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 Cu_5FeS_4 intermediate as a secondary intermediate formed by the reaction resulting from H_2S and Cu^{2+} .

The second step involves the decomposition of the intermediates, and the release of Cu^{2+} , Fe^{2+} , and the formation of elemental sulfur. The Cu_5FeS_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 H_2S 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 Cu_5FeS_4 and CuS, while in the non-oxidative dissolution mechanism, the H_2S 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 H_2S , the diffusion rate of Fe^{3+} into the intermediate layer, and the oxidizing reaction rate of H_2S with Fe^{3+} into elemental sulfur. The addition of Cu^{2+} can form CuS, preventing the diffusion channel from being blocked by

elemental sulfur. A similar effect can be accomplished by addition of Fe^{2+} , which maintains a moderate redox potential to prevent H_2S from being oxidized in the diffusion channel by Fe^{3+} .

Acknowledgments: The authors would like to acknowledge the financial support of the National Natural Science Fund of China (Grant No. 51434001 and Grant No. 51574072).

Author Contributions: Dianku Lu wrote the manuscript and performed the thermodynamic analysis; Wei Wang and Yongfeng Chang contributed to some of the data interpretation; Feng Xie and Kaixi Jiang contributed to writing and editing of the manuscript; all co-authors contributed to manuscript proof and submissions.

Conflicts of Interest: The authors declare no conflict of interest.

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