

## Research progress in intensified bioleaching of chalcopyrite: A review

Xuemin Zou<sup>1, \*</sup>, Yisheng Zhang<sup>2</sup>, Shuang Zhou<sup>2, \*</sup>, Zimeng Wang<sup>2</sup>, Bibi Wei<sup>2</sup>, Lemei Zhu<sup>1</sup>

<sup>1</sup> School of Public health, Changsha Medical University, Changsha, China;

<sup>2</sup> School of Minerals Processing and Bioengineering, Key Laboratory of Biohydrometallurgy of Ministry of Education, Central South University, Changsha, China

\* Corresponding Author Email: zouxuemin2022@163.com

zhoushuang@csu.edu.cn

**Abstract.** Chalcopyrite ( $\text{CuFeS}_2$ ) as one of the most abundant copper sulfide minerals, is refractory to conventional hydrometallurgical and pyrometallurgical processes. Bioleaching is a practice of extracting valuable metals by using acidophilic bacteria to catalyse the dissolution of sulfide/iron-containing ores. It has been widely adopted in copper ores processing due to environmental and economic performance over the conventional methods, especially its use in low-grade sulfide minerals. To date, low copper extraction is a common problem during chalcopyrite bioleaching, which limits its industrial application. Hence, it is of particular importance to find methods to enhance the leaching rate. Chalcopyrite dissolution is a complex process with the participation of microorganisms, minerals and gas and liquid phases. All these physicochemical, microbiological, mineralogical and processing parameters have influences on the rate and efficiency at which bioleaching proceeds. High copper yield can be achieved by optimizing leaching conditions in an optimum range. A number of researches has been conducted to explore the influence of leaching parameters on bioleaching rate. This review intends to briefly describe the effect of some parameters on the bioleaching of chalcopyrite. And it lays the emphasis on the presentation of methods to promote the efficiency of bioleaching and the strengthening mechanisms.

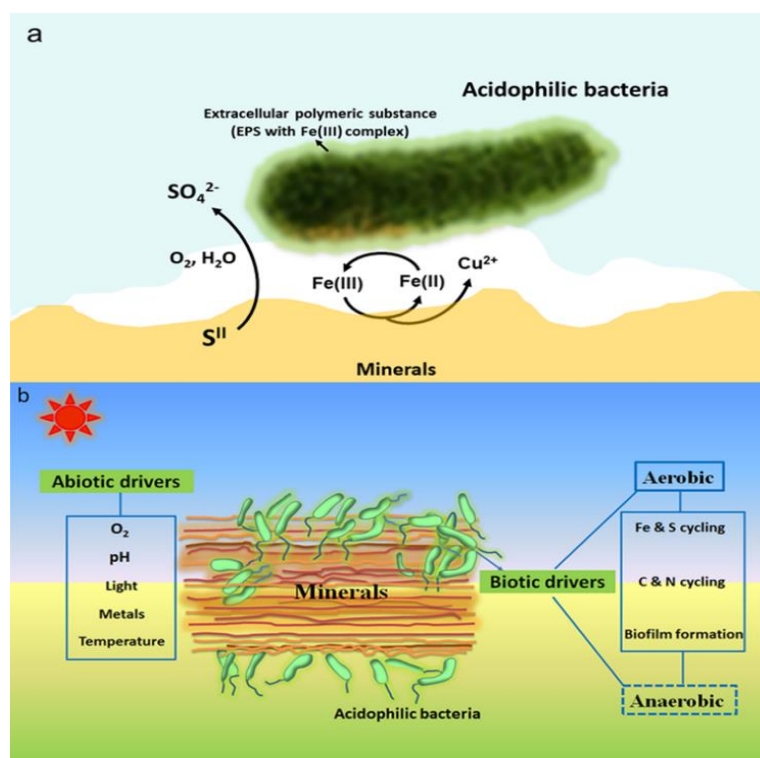
**Keywords:** Chalcopyrite; intensified bioleaching; mechanisms; acidophiles.

### 1. Introduction

Chalcopyrite ( $\text{CuFeS}_2$ ) accounting for approximately 70% of the total copper resources, is a refractory copper-bearing ores [1]. Hydrometallurgical and pyrometallurgical techniques are routine processing methods to extract copper from chalcopyrite. However, these techniques are considered to be more beneficial for high-grade copper ores than low-grade copper ores. Additionally, they are costly and always provide low metal extraction. These mining techniques also cause severe water, air, and land pollution [2]. In the course of the last decades, bioleaching metallurgy is attracting ever more attention in the copper extraction from chalcopyrite or low-grade copper ores due to its environmental and economic advantages over the conventional process [3].

Bioleaching is the metal-extracting process from sulfide and/or iron-containing minerals by using acidophilic microorganisms [4]. Most of the bioleaching microorganisms are iron and/or sulfur oxidizers. They can sustain growth by oxidizing sulfur ( $\text{S}^0$ ) and ferrous iron ( $\text{Fe}^{2+}$ ) originated from ores (Figure 1a). Their metabolic activities or metabolites are capable of converting insoluble metallic minerals into soluble forms. Then the dissolved metals can be recovered [5]. The bioleaching of chalcopyrite by iron- and sulfur-oxidizing acidophiles has been widely adopted. But the formation of compact passivation layer on mineral surface as a result of jarosite and sulfur accumulation hampered the dissolution of minerals. To date, the low copper extraction during bioleaching of chalcopyrite is the common problem, which limits the industrial application of chalcopyrite bioleaching [6]. Hence, for the practical application of chalcopyrite bioleaching, a better understanding of the kinetics and mechanism of chalcopyrite bioleaching is of particular importance. The bioleaching efficiency is largely dependent on the microbial activity, mineralogical composition of ores, and other processing

parameters (Figure 1b). High copper yield can be achieved by optimizing the leaching conditions in an optimum range for bacterial growth. It has been demonstrated that several strategies are beneficial for enhancing chalcopyrite bioleaching, including the addition of catalysts (surfactants, cysteine, activated carbon, pyrites, silver and chlorine) and controlling acidity (pH) and redox potential (ORP). The photocatalysis process is also proved to accelerate chalcopyrite bioleaching. The study on bioleaching is of great academic and practical value, especially in the mining industry. Researchers continue to progress in methods studies for improving bioleaching. The goals of this review are 1) to describe the fundamental process of chalcopyrite bioleaching; 2) to present some factors affecting the kinetics and rate of chalcopyrite bio-dissolution; 3) to introduce some methods that have been tested to promote the efficiency of chalcopyrite bioleaching in succinct and their mechanisms; and 4) to describe some challenges confronted with bioleaching and its perspectives.



**Figure 1.** Schematic representation of mutual effect between minerals, abiotic drivers and biotic drivers in bioleaching system.

## 2. Methods of enhancing chalcopyrite bioleaching

### 2.1. pH adjustment

Among some parameters, pH plays a vital role in the minerals bioleaching. It affects the growth, activity of microorganisms and microbial community. The pH constantly changes as the bioleaching proceeds, sometimes below 0.8, sometimes up to 3.0. The pH changes significantly, especially when a sudden rainfall or sustained drought appears in bio-heap. However, high pH environment has pernicious effects on the oxidization ability of microbe and could decrease permeability of leaching due to ferric precipitation in the heap bed [7]. Besides, the extreme low pH environment would inhibit the activity of microbe, resulting in lower bioleaching efficiency [8]. It has been demonstrated that bioleaching microorganism can produce extracellular polymeric substances (EPSs), which can mediate the bacteria attachment to sulphide minerals during bioleaching with then forming a biofilm on the surfaces of ore grain. The EPS involved in the dissolution of minerals via an “EPS contact-leaching mechanism” [9]. An investigation of the effect of pH on the formation of EPSs by *Acidithiobacillus ferrooxidans* (*A. ferrooxidans*) during chalcopyrite bioleaching at different stages was conducted [10]. It was revealed that the pH of the bacteriological culture was a factor mainly

affecting EPSs production in the adherent cells, which may have influence on the ability of bacteria to resist harsh environment and exercise oxidation-reduction. It implied that leaching rate can be achieved by controlling the pH.

## 2.2. Redox potential adjustment

There is a positive correlation between ORP value and the presence of oxidizing agents ( $\text{Fe}^{3+}$  and oxygen) and a negative correlation between ORP and the presence of reductants in the medium ( $\text{Fe}^{2+}$  and carbon) [11]. In both chemical leaching (ferric leaching) and bioleaching,  $\text{Fe}^{3+}$  as the main oxidant drives the bioleaching process. Some complex oxidation and reduction reactions are involved in the process of chalcopyrite bioleaching, where the solution compositions, namely  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  species vary all the time, which determine the operating potential in terms of the ratio of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . Generally, the transfer of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  by microbe changes the ORP value and affects bioleaching process.

Some studies have revealed that chalcopyrite dissolution is accelerated at low ORP because extremely high ORP ( $> 600$  mV) can result in jarosite accumulation and precipitation on the surface of chalcopyrite [12], and the passive layer increases as the potential increases [13]. All can hinder the dissolution of chalcopyrite. Ahmadi et al. [14] found that chalcopyrite was effectively extracted by the control of redox potential in the range of 400–425 mV by utilizing an electro-bioreactor. Additionally, it has been proposed that at low redox potential chalcopyrite is more prone to be leached due to that the passive layer was not easily formed as the result of the reduction of chalcopyrite to chalcocite ( $\text{Cu}_2\text{S}$ ) and its subsequently fast oxidization. Zhao et al. [15] used a proposed mathematic model to predict the optimal redox potential in chemical leaching and chalcopyrite bioleaching. They concluded that ORP should be regulated at an optimum range to get high bioleaching efficiency.

## 2.3. Energy source addition

Bioleaching involves the use of acidophilic bacterium to catalyse the dissolution of the valuable metals-bearing minerals. The most of acidophiles are chemolithotrophic and inorganic compounds are required for their cellular metabolism, new cells and metabolites biosynthesis. Most of them are iron- and/or sulfur-oxidizers.  $\text{Fe}^{2+}$  and  $\text{S}^0$  can serve as the energy source for them to sustain growth. Whereas, during bioleaching, iron and sulfur species are just derived from minerals and are oxidized to  $\text{SO}_4^{2-}$  and  $\text{Fe}^{3+}$ , respectively. In the early stage, there is not enough  $\text{Fe}^{2+}$  and  $\text{S}^0$  for acidophile microbes to oxidize and gain energy, which to some extent slows the leaching kinetic. Liu et al. [16] investigated the effects of  $\text{Fe}^{2+}$  addition on the chalcopyrite bioleaching by *A. ferrooxidans*. They found external supply of  $\text{Fe}^{2+}$  provided the initial energy source for bacteria, and the produced  $\text{Fe}^{3+}$  can enhance the oxidation of sulfide ores. Meanwhile, released  $\text{Fe}^{2+}$  from the mineral was then oxidized to  $\text{Fe}^{3+}$ , further facilitating bioleaching. At the starting of the bioleaching,  $\text{S}^0$  plays an important role in supplying source energy for sulfur-oxidizing bacteria. Sulfuric acid as the production of sulfur oxidation is beneficial for the dissolution of chalcopyrite on account of mineral leaching defined as acid consumption. From the studies of Xia et al. [17]  $\text{S}^0$  was provide to promote the growth of *Acidithiobacillus thiooxidans* (*A. thiooxidans*) and thus enhanced the dissolution of minerals. But extremely low pH inhibits the activity of microorganisms and has adverse effect on bacterial leaching. In addition, a layer of  $\text{S}^0$  accumulation may be formed on the chalcopyrite surface due to excess addition, which acted as a barrier against the diffusion of  $\text{O}_2$  or  $\text{Fe}^{2+}$  with preventing the oxidation of chalcopyrite [18].

## 2.4. Metal ion (ferric, copper and silver) addition

$\text{Fe}^{3+}$ , the commonly used oxidant, has been found to have effect on the leaching rate of chalcopyrite. A work focusing on the influence of  $\text{Fe}^{3+}$  on bioleaching was carried out [19]. They found in the initial stage of bioleaching the increasing concentration of  $\text{Fe}^{3+}$  enhanced the extraction rate while above this range increasing the concentration had little or negative influence on dissolution rates.  $\text{Fe}^{3+}$  can directly attack the mineral to enhance the dissolution of chalcopyrite. And the dissolved

$\text{Fe}^{2+}$  can provide the energy for iron oxidizers to sustain their growth, resulting in more frequent bacteria-mineral interaction and copper release. But too high concentration of  $\text{Fe}^{3+}$  leads to jarosite precipitation, which limits bioleaching.

As referred above, EPS secreted by microorganisms facilitates the attachment of microorganisms to mineral surface, which plays a vital role in the bioleaching. Yu et al. [20] studied the interaction mechanism of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$  and EPS during chalcopyrite bioleaching by *A. ferrooxidans*. An interesting phenomenon was found that more EPS was produced by  $\text{Cu}^{2+}$  stimulation instead of  $\text{Fe}^{3+}$ . More produced EPS facilitated the interaction between bacteria and ores. In addition, a newly proposed mathematic model to predict the optimum ORP during chalcopyrite bioleaching was used. The concentrations of soluble  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  were the main factor affecting ORP. The oxidation of chalcopyrite can be enhanced by  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  additions at the starting stage of bioleaching and it was further depressed by the produced jarosite.

Recently years,  $\text{Ag}^+$  has received attention due to its recoverability and efficient catalysis in mineral bioleaching [21]. The role of  $\text{Ag}^+$  in the chalcopyrite bioleaching still remains controversial because the reaction on mineral surface with the participation of  $\text{Ag}^+$  is complex. The mostly accepted  $\text{Ag}^+$  catalytic mechanism during bioleaching of chalcopyrite is that a silver sulfide ( $\text{Ag}_2\text{S}$ ) intermediate formed on the mineral surface is easily oxidized by  $\text{Fe}^{3+}$ , alleviating surface passivation through forming a less stable and more porous sulfur layer. Therefore, the electron transfer from minerals to oxidizers is enhanced, and the leaching rate increases.

## 2.5. Chloride addition

Chloride is well known to facilitate chalcopyrite bioleaching. The presence of chloride results in the formation of a more porous crystalline sulfur layer rather than crypto-crystalline or amorphous sulfur, which disrupts the passivating sulfur layer and provides larger areas for the diffusion of reactant to the chalcopyrite surface [22, 23]. Carneiro et al. [24] examined the surface area and porosity of leaching residues with the NaCl addition or not at 95 °C. NaCl of certain concentration (ranging from 0.5 to 2.0 M) can increase the surface area and porosity of secondary solid phases. Liang et al. [25] also found that sodium NaCl (11 mM) significantly decreased the formation of passivation layer in the chalcopyrite bioleaching with thermophilic. The effect of NaCl on the bioleaching of chalcopyrite in shake flasks and stirred tank bioreactors was also investigated by Bevilaqua et al. [26]. For their work, chalcopyrite leaching was enhanced with adding NaCl to solution containing bioleaching bacteria and ferrous iron under low redox potential conditions. The presence of Na-chloride decreased the formation of secondary phases and the Fe(III) precipitation. Cu-chloride complexes may be also the cause for higher dissolution rates. The produced soluble  $\text{Cu}^+-\text{Cl}^-$  complexes can enhance chalcopyrite dissolution in comparison with  $\text{Cu}_2\text{S}$  and covellite coating on mineral surface as block for the leaching.

## 2.6. Galvanic interaction

### 2.6.1 Activated carbon addition

Zhang et al. [27] used the mixture of *A. ferrooxidans* and *A. thiooxidans* to leach the low-grade primary copper sulfides, and found that 3.0 g/L activated carbon was the most beneficial for accelerating the efficiency of mineral dissolution. Liu et al. [28] studied the correlation between the acceleration effect of activated carbon and passivation formation during chalcopyrite bioleaching with mixed thermophilic archaea, and found the presence of 2 g/L activated carbon could obviously enhance the bioleaching of chalcopyrite. Results of XRD and XANES spectra analysis of the leach residues suggested that activated carbon could change the transfer path of electrons via galvanic interaction at low redox potential (400 mV) to form more vulnerable dissolved secondary mineral chalcocite and consequently improved extraction of copper. Carbon materials were found to lower the solution pH, sustain suitable ORP and enhance the attachment of bacteria, leading to high bio-dissolution rate of chalcopyrite. Generally, activated carbon performs the significant catalytic effect of on chalcopyrite bioleaching.

### 2.6.2 Pyrite addition

In the leaching process, the present semiconducting minerals are in contact, facilitating the charge transfer and resulted in the enhancement of leaching. In the galvanically coupling, sulphide minerals with greater rest potentials act as cathodes while minerals with smaller rest potentials act as anodes. The anodic mineral with the smaller rest potential can be oxidized to release metals and the cathodic mineral with the greater rest potential is protected [29]. It has been revealed that the oxidation of chalcopyrite can be enhanced when pyrite was added. Chalcopyrite with the lower rest potential is anodically oxidized while pyrite with the higher rest potential acting as a cathodic site for oxygen reduction is protected (Figure 2). Mehta et al. [30] studied galvanic interactions of pyrite-chalcopyrite and pyrite-sphalerite couples. The results showed increasing the amount of pyrite could enhance the dissolution of chalcopyrite and sphalerite, and the galvanic effect was the critical factor which governs the dissolution rate. Ahmadi et al. [31] investigated the effect of pyrite on chalcopyrite dissolution in chemical, biological and electro-biochemical systems. They found that the efficiency of copper extraction was significantly improved with the addition of pyrite to chalcopyrite

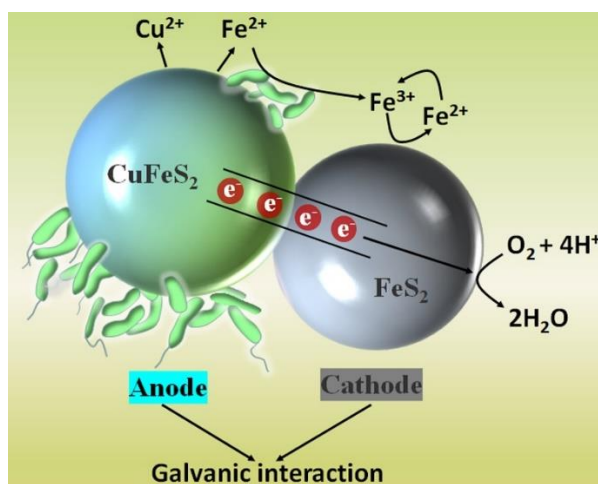


Figure 2. Galvanic reaction between chalcopyrite and pyrite.

### 2.7. Surfactants

Among the chemical surfactants, non-ionic surfactants, namely polysorbate (Tween), t-octyl phenoxy polyethoxy ethanol (Triton X-100), polyethylene glycol (PEG), fatty alcohol alkoxytype wetting agents (Plurafac) and fatty alcohol polyoxyethylene ether wetting agents (Lutensol), have been investigated with chalcopyrite bioleaching. Su et al. [32] found that appropriate concentration of Tween 20 facilitated chalcopyrite bioleaching in the presence of *Acidianus manzaensis*. They concluded that indirect reaction was mainly involved in the bioleaching, and the improved leaching rate was due to the decrease of attached cells on mineral surface. Tween 80 was also reported to increase copper extraction from chalcopyrite [33]. It was found that addition of surfactant reduced the hydrophobicity of mineral grains and lead to the increasement of copper extraction. It was found that the bioleaching yield of copper was increased with the addition of Triton X-100, which was attributed to more bacteria and reduction of inhibitory jarosite and  $S^0$  induced by Triton X-100. Three other fatty alcohol alkoxytype wetting agents, identified as EVD 61549, EVD 65062 and EVD 57476, were moderately added to the sulphide mineral leaching solution and the copper yield indeed increased [34].

Biosurfactants produced by bacteria are mostly composed of sugar and fatty acid moieties, which make them single amphiphilic organic molecules with both hydrophilic groups and hydrophobic groups [35]. These amphiphilic substances can change the surface properties of minerals. Besides, lower toxicity and excellent biological activities are the characteristics of biosurfactants. Hence, biosurfactants of microbial origin are gaining attention. Previous studies have shown that amino acids can enhance the bio-dissolution of chalcopyrite with *T. ferrooxidans* [36]. The influence of L-aspartic

acid, L-glutamic acid, L-histidine and L-serine was investigated. Increased copper extraction with the addition of these amino acids in different concentrations achieved. The improved leaching efficiency may be attributed to increased bacterial metabolic rate by the action of these amino acids to decreasing the  $\text{Cu}^{2+}$  toxicity.

## 2.8. Photocatalysis

Chalcopyrite is a semiconducting mineral, which possesses an electron structure constituted of a valence band (VB) and a conduction band (CB). When it is attacked by photons with energy equal to or greater than the band-gap energy, the excitation of valence band electrons ( $e^-$ ) to the conduction band could occur. In the study of Zhou et al. [37], the photocatalytic effects of light on chalcopyrite bioleaching in aeration reactors and shake flasks were evaluated by applying photocatalysis systems with the participation of chalcopyrite, light and *A. ferrooxidans*. It was found that light promoted the bio-dissolution of chalcopyrite and thus more copper was released. By exposing to light, electrons were excited and migrated to the chalcopyrite surface, which accelerated the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . The regeneration of  $\text{Fe}^{2+}$  facilitated the growth of *A. ferrooxidans*, lower pH and redox potential, which enhanced the bioleaching of chalcopyrite.

## 3. Conclusions

With the purpose of improving the bioleaching rate, understanding the (bio) chemical aspects to optimize the bioleaching process is always of concern. Extensive work has been carried out to explore what factors influence the mineral bioleaching. It has been demonstrated that some parameters including pH, redox potential, energy substrates, additives, galvanic interactions, surfactants and visible light, can affect the microbial activity and leaching rate. Thus, this paper provides a review of the process of chalcopyrite bioleaching, particularly focusing on the ways to improve the bioleaching rate. This review mainly presents intensified methods including the controls of pH, Eh and addition of ferrous iron, sulfur,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ , activator, pyrite, surfactants and light induction. Except for the factors referred above, there are many physicochemical, microbiological, mineralogical and processing parameters capable of influencing the bioleaching rate and efficiency. Hence, exploring the influencing factors and find a more progressive, environment-friendly and economical bioleaching technology for chalcopyrite processing is the goal in the future work.

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