

Review

# Copper Bioleaching in China: Review and Prospect

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**Abstract:** The commercial application of copper bioleaching, an environmentally-friendly approach for low-grade and secondary mineral resources recycling, has increased worldwide since the 2000s. As the world's second-largest economic entity and the largest developing country, China has the largest demand for metal resources, significantly advancing the theory and industrial technology of copper bioleaching. This paper reviews the exploration and application of copper bioleaching in China. Two typical bioleaching applications and technological processes, bioheap leaching at the Zijinshan Copper Mine and bioheap leaching at the Dexing Copper Mine, are introduced. The considerable research completed by researchers is summarized, especially focusing on the isolation and identification of leaching bacteria, the bioleaching mechanism and interface reactions, multistage percolation behavior, bioleaching system reconstruction, the multiphysics coupled model, and enhanced copper bioleaching from waste printed circuit boards (WPCBs). Based on this investigation in China, key trends and prospects in copper bioleaching—such as efficiency improvement, environmental protection, and improved technology applications—are proposed.

**Keywords:** copper bioleaching; biotechnology; heap leaching; dump leaching; review

## 1. Introduction

Due to its excellent ductility and electric and thermal conductivity, copper has been widely applied in the construction, electricity, transportation, and manufacturing industries [1,2]. Since the 1970s, China has experienced rapid economic growth and a related sharp increase in its rate of urbanization. This has resulted in China increasingly significant driving global growth and improving mineral resource demand since the late 2000s, becoming the world's second-largest emerging economic giant [3–7].

Lower-grade extractions and increasing global demand are noticeable barriers to valuable metal extraction [8]. As an efficient recycling approach used for low-grade minerals, complex polymetallic resource, and solid ore waste [9,10], bioheap leaching and biodump leaching have been broadly applied, having potential given the exhaustion of high-quality copper mines. These approaches have been extensively researched and utilized in China, Chile, Spain, and South Africa [11–15]. Bioleaching drives conventional mining revolution to extract minerals from mineral wastes and ore

deposits buried deep in the ground [16–18]. The basic and simplified process of bioheap leaching is shown in Figure 1.

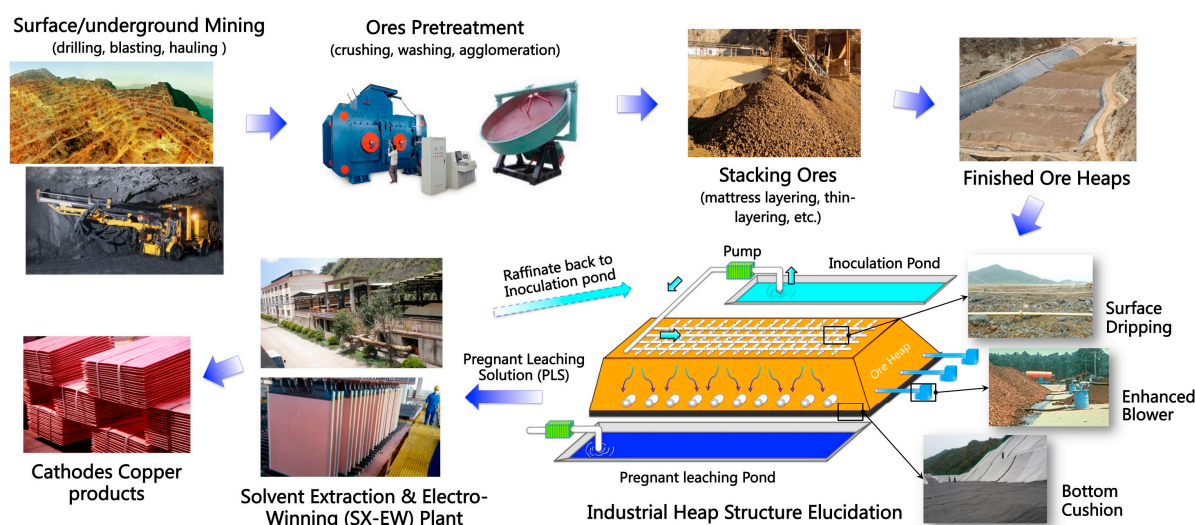


Figure 1. Typical industrial schematic of copper bioheap leaching.

Although copper bioleaching faces many challenges and limitations, progress has been made which mainly focuses on the bioleaching mechanism, pore network, microorganisms cultivation, fluid flow, process catalysis, and so on. Lower-grade copper ore in complex sulfide deposits is extremely difficult to extract [19]. By incorporating the catalytic function of bacteria, the dissolution and copper extraction is increased [20]. Genomic engineering has been implemented to obtain targeted bacteria [21,22]. Additionally, the intervention of precise scanning and observatory technologies—such as computed tomography (CT), magnetic resonance imaging (MRI), particle image velocimetry (PIV), and others [23–26]—have improved on research. Some characterized models have been improved, like the lattice Boltzmann model (LBM) and so on [27–29]. To increase permeability, leaching, and optimal metal extraction rate, some reformative methods like agglomeration of oxide copper minerals [30,31]; enhanced aeration [32,33]; dripping irrigation regulation [34,35]; surfactants like polyethylene glycol, sodium lauryl sulfate, and silver [36–38]; and ultrasonic intensification [39] were proposed. Advanced aerial image analysis has been applied to assess particle size segregation in copper heap leaching [40]. Except for Australia, the United States, and other developed mining countries, the factors controlling commercial application are complex, and China plays an essential role in the technological innovation of copper bioleaching. For copper bioleaching in China, we want to compare the fundamental conditions, developed process and status, outstanding breakthroughs, and exemplary industrial cases with similar studies around the world. However, a systematic and summative research of copper bioleaching is still lacking.

In this paper, the biotechnology progress and current status of copper bioleaching in China is considered. To review the copper biotechnology application and status in China, two industrial case studies of copper bioleaching at the Zijinshan Copper Mine (ZCM, bioheap leaching) and the Dexing Copper Mine (DCM, biodump leaching) are presented. Challenges for copper bioleaching are identified, advanced technologies and improved methods to overcome these issues are discussed. Furthermore, the future prospects for copper bioleaching are presented.

## 2. Copper Bioleaching Development Process in China

### 2.1. Development and Status of Bioleaching around World

Over the years, bioleaching technology, which has been applied to copper, uranium, coal, nickel, and manganese mining [41–43], has progressed considerably, especially in Chile, South Africa, the United States, Australia, India, Mexico, Iran, and China. In 1762, in the Rio Tinto Mine of Spain, Copper (Cu) was leached from pyrite mixed with copper by acid mine drainage (AMD). The appearance of *Acidithiobacillus ferrooxidans* (*A.f*) subtly influenced recycling methods used for copper resources. Temple and Hinkle [44] found bacteria associated with AMD in 1947 and naming of *Thiobacillus ferrooxidans* (*T.f*) from AMD of coalmine in 1951. Three years later, Bryer and Beck [45] found *A.f* leached from a wide range of copper sulfide mines using AMD in copper mines. In 1958, copper extraction significantly progressed when biotechnology was first applied to industrial production in the Bingham mine by the Kennecott copper company [46–48].

Since the 1970s, bioleaching technology has been researched and applied widely around the world, enabling the industrial production of copper, uranium, and gold [49,50]. To date, the bioheap leaching, biodump leaching, and in situ bioleaching processes (uranium mainly) have become the most common bioleaching approaches. Worldwide, about 20% of Cu is extracted using bioleaching [51,52]. Given the gradual exhaustion of mineral resources located in the shallow surface of the earth, copper biotechnology has been playing a more important role in metal extraction [53,54]. For instance, the European Commission applied some innovation methods to in situ leaching without ore stripping and onerous infrastructure operations in 2015. Some in situ copper leaching studies, including heap leaching, were completed at the University of Cape Town, University of Melbourne, Imperial College London, University of Utah, Cornell University, BacTech, Mintek, Rio Tinto, and other authoritative universities and institutions since the 1990s. As relevant reviews have been systemically performed, these are not covered at length in this paper [55,56].

### 2.2. Major Characteristics of Copper Resources in China

China is one of the largest mining countries in the world, with more than 240 mine sites [57]. China's copper deposits are mainly divided into porphyry-type (41%), skarn-type (27%), marine volcanic-type (9.24%), copper-nickel (Cu-Ni) sulfide-type (5.67%) and others (17.09%) [58]. For complex reasons, the majority of the condition of conventional surface and underground mining for copper minerals in China are not very suitable, unlike South Africa and Australia. Chinese copper mines tend to be lower-grade, having an average Cu content of around 0.87%, which is hard to extract using conventional mineral processing. In terms of size, the medium-scale (9%) and small-scale (88%) copper mines dominate, compared to the large-scale mines (3%). Due to the limitations in the metal quantity and quality, the application of conventional mining methods tends to be impossible. Chinese copper mines have complex mineral compositions with associated minerals like nickel, gold, and sulfur, among others. Around 76% associated-gold, 32.5% associated-silver, and 76% sulfur come from copper mines. The mines contain heterogeneous dissemination-type ores. Porphyry copper deposits and skarn copper deposits dominate. China has several copper deposits and production bases (Figure 2). The copper bioleaching bases are concentrated in the central and eastern regions, especially in the southeast, due to the suitable mineral composition. Details of each base are:

- Jiangxi Copper Bases. Jiangxi Province has the richest copper resources and its reserves account for more than 34% of the total copper reserves in China. Some large-scale copper mines, like the Dexing Copper Mine, Yongping Copper Mine, Wushan Copper Mine, Chengmenshan Copper Mine, Dongxiang Copper Mine, and others have been established since 1978.
- Yunnan Copper Bases. Yunnan Province is the second-largest copper bases in China, including the Dongchuan Copper Mine, Yimen Copper Mine, Dayao Copper Mine, and Muding Copper Mine.

- Tongling Copper Bases. This base is located in Anhui Province and is the first copper base that produced about 10,000 t/a of copper in China, and includes the Tongguanshan Copper Mine, Dongguanshan Copper Mine, Shizishan Copper Mine, Xinqiao Copper Mine, and Fenghuangshan Copper Mine.
- Daye Copper Bases. Located in Hubei province can produce about 45,600 t electrolytic copper. The Tonglushan Copper Mine, Tongshankou Copper Mine, Xinye Copper Mine are included in this base.
- Zhongtiaoshan Copper Bases. Established in 1956, the base includes the Tongkuangyu Copper Mine, Bizhigou Copper Mine, and Hujiayu Copper Mine.
- Northeast Copper Bases. This base, located in Northeast region of China in Heilongjiang Province, Jilin Province, and Liaoning Province, has been developed since 1948. Some copper mines, like the Qingyuan Copper-Nickel Mine, Huatong Copper Mine, and Tianbao Copper Mine are established, producing 70,000 t/a electrolytic copper metals.
- Baiyin Copper Bases. This base located in Gansu province and can produce more than 60,000 t/a electrolytic copper metal, including the Zheyaoshan Copper Mine and Tongchanggou Copper Mine.



**Figure 2.** Regional distribution of typical bioleaching industrial plants in China.

### 2.3. History and Evolution of Copper Bioleaching in China

According to Morris' 1984 publication on solution mining for minerals in Australia, China was one of earliest countries to develop solution mining to exploit copper resources. With bronze product smelting and production, copper recycling technology has made considerable progress. As *The Classic of Mountains and Seas* (third century B.C. to second century A.D.) saying goes, "there is abundant copper resources in the shade of Shicui Mountains". During the Western Han Dynasty (206 B.C. to 24 A.D.), the copper was obtained from copper sulfate ( $\text{CuSO}_4$ ) by displacement reaction as written in the *Huainan Encyclopedia* of Liuan Wang. Per Qian Zhang's *Copper Leached Synopsis Records*, the copper was leached from AMD in the earlier Song Dynasty (960–1127). Due to the technology limitations and feudal government blockade policy, the improvement of biotechnology slowed in ancient China.

Since the 1960s, bioleaching research for low-grade copper extraction was applied in underground bioleaching of Tongguanshan Copper Mine which was completed in the 1970s. In 1997, the Dexing Copper Mine constructed the first heap leaching plant and started commercial operation [59]. The Chinese government carried out several key foundation projects—such as the "863 Project",

“973 Project”, and “111 Project”—to effectively promote and develop bioleaching technology. To date, a number of Chinese researchers have contributed, and as a result the bioleaching technology system and application have developed considerably [60]. On the 22th July 2016, the Ministry of Science and Technology of the People’s Republic of China commissioned the “13th Five-Year National Science and Technology Innovation Planning” the largest-scale research project ever, focusing on geological prospecting and in situ fluidized bioleaching of copper, gold and uranium ores. This central government project, costing 10 billion dollars, will run until 2030. This investment is for the improvement of technology and equipment for copper bioleaching.

### 3. Status of Current Copper Bioleaching in China

#### 3.1. Typical Application and Exploration Cases of Copper Bioleaching

Chinese researchers have investigated copper bioleaching in laboratories and industrial applications, in mines such as Dexing Copper Mine and Zijinshan Copper Mine. A review of the application and investigation of copper bioleaching are introduced (Table 1). Figure 2 shows their locations and illustrates the seven copper bases. Bioleaching investigation and application are concentrated in the southeast region, which includes three copper production bases including the Jiangxi Copper Base, Tongling Copper Base, and Daye Copper Base. Among them, the Jiangxi Copper Base—rich in chalcocite and chalcopyrite—is the main base for copper bioleaching due to its mineral richness. Because of lower permeability, in situ copper bioleaching of the deep leachates of primary ores is limited. Some extreme conditions in the area include high attitude, low temperature, and low oxygen content, as found in the Xinjiang Autonomous Region (Sarake Copper Mine, etc.) and Qinghai–Tibet Plateau (Yulong Copper Mine, etc.) potentially have copper resources that may be suitable for bioleaching.

#### 3.2. Typical Commercial Cases of Copper Bioleaching in China

Many bioleaching studies, including laboratory experiments, pilot tests and industrial operations have been conducted on mine sites like the Zijinshan Copper Mine, Dexing Copper Mine, Asele Copper Mine of Xinjiang; Yulong Copper Mine (Table 1). In this section the research conducted on the Zijinshan Copper Mine (ZCM) and Dexing Copper Mine (DCM) mine sites are introduced.



**Table 1.** Exploration and successful industrial cases of copper bioleaching in China.

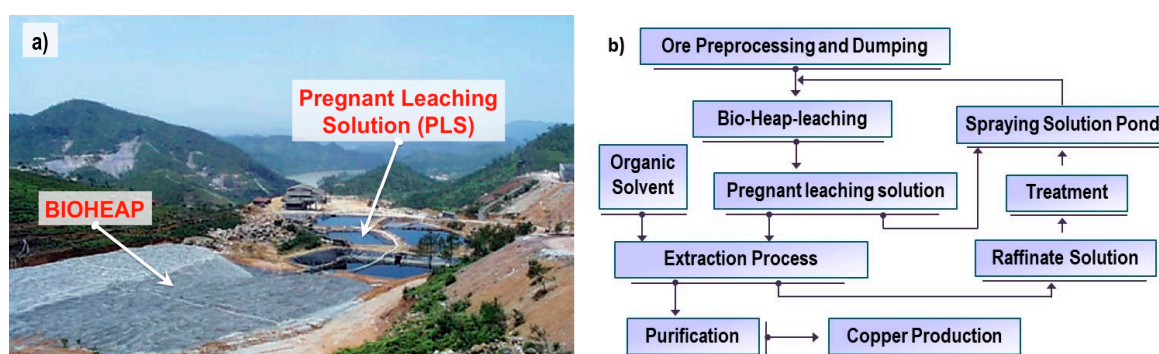
Typical Mine	Location	Features	Minerals	References
Dexing Copper Mine	Dexing, Jiangxi Province	Biodump leaching; extraction rate 30%; >2000 t/a; built in 1965; started to use bioleaching in 1979; built bioleaching factory in 1997	Cu 0.30%; 0.45% primary copper sulfide, 0.028% secondary	[61]
Yangla Copper Mine	Diqing County, Yunnan Province	Alkaline bioleaching of low-grade oxide copper ores by <i>Providencia</i> sp. JAT-1; initial pH 8 and 30 °C; Cu extraction rate is 54.5% after 156 h	Copper oxide ore (Cu 1.01%, malachite 0.36%, chrysocolla 0.29%, chalcopyrite 0.29%)	[62]
Zijinshan Mine	Shanghang City, Fujian Province	bioheap leaching using Solvent extraction/Electro-Winning(SX-EW) technology; Around 20,000 t/a; Bioheap leaching factory was built in 2006	Cu 0.38%; low-grade copper sulfide ore (digenite and covellite)	[63]
Guanfang Copper Mine	Lincang County, Yunnan Province	Bioheap leaching factory of primary copper sulfide and secondary copper sulfide was built in 2003	Cu 0.9% (mainly secondary copper sulfide)	[64]
Zhongtiaoshan Copper Mine	Yuncheng City, Shanxi Province	In situ leaching; underground; bioleaching and acid leaching (extraction electrowinning process); >500 t/a in 2000	Cu 0.65%, SiO <sub>2</sub> 68.44%; secondary copper sulfide 59.1%, free oxide copper 37.4%	[65,66]
Tongguanshan Copper Mine	Tongling City, Anhui Province	Underground bioleaching since 1965; Cu recovery reached 95% in 1980; discontinued production in 2003; Bioleaching tests from 1972 to 1980;	Cu 0.9%	[67]
Dabaoshan Copper Mine	Qujiang County, Guangdong, Province	Biodump leaching by <i>T.f</i> obtained from Dabaoshan mining region	Cu 1.06%, Fe 26.8%; primary and secondary copper sulfide occupied 90% of Cu	[68,69]
Yulong Copper Mine	Jiangda County, Tibet Autonomous Region	Bioheap leaching of oxide and copper sulfide minerals; High altitude (4569–5118 m) of Tibet; Bioleaching SX-EW technology, realizing >80% copper extraction rate of sulfide ores	Cu 2.75%; secondary copper sulfide 28.95%, primary copper sulfides 35%	[70]
Asele Copper Mine	Habahe County, Xinjiang Autonomous Region	Cu recovery reached 80%; Formal operation of bioleaching industrial plant used since July 2004	Cu 2.43%	[71]
Yongping Copper Mine	Shangrao City, Jiangxi Province	Second-largest open copper pit in China; formal operation from October 1984; recycle low grade ores and wastes by bioleaching since the 1990s	Cu 0.32%; primary copper sulfide (65.6%) and secondary copper sulfide (16.3%)	[72]

Table 1. Cont.

Typical Mine	Location	Features	Minerals	References
Saishitang Copper Mine	Hainan Tibetan Autonomous Prefecture, Qinghai Province	High altitude (3450 m); located in Qinghai–Tibet Plateau; bioleaching experiment and plant under extremely high and cold environment	Cu 0.83%; copper sulfide ore and oxide copper ores	[73,74]
Dongchuan Copper Mine	Dongchuan City, Yunnan Province	Built in the 1960s, performed copper bioleaching experiments with the whole plants successfully	Cu 0.9–1.5%; 33% sulfide ore (bornite, chalcocite, chalcopyrite); 41% oxide ores	[75]
Dongguashan Copper Mine	Tongling City, Anhui Province	Bioleaching experiments of low-grade chalcopyrite sample by <i>Acidithiobacillus ferrooxidans</i> and <i>Acidithiobacillus thiooxidans</i>	Cu 0.94–1.06% (chalcopyrite mainly), leaching bacteria is <i>A.f</i> (CUMT-1 & ZJJN-3)	[76]
Jinchuan Copper-Nickel Mine	Jinchang City, Gansu Province	Mainly nickel (Top two in the world); operated from 2006 to 2009; coupled multi-metals included nickel, copper and cobalt; good leachability: copper extraction rate reaches 93.48% after 40 days	Cu 0.44%; primary copper sulfide 69.8%, free oxide copper 20.6% and secondary copper sulfide 8%	[77,78]
Dongxiang Copper Mine	Fuzhou City, Jiangxi Province	In situ bioleaching of low-grade primary chalcopyrite after underground blasting and crushing, high sulfur ores	Cu 1.34% (chalcopyrite 1.01%, chalcocite 0.33%), pyrite 11.48%, Fe 30.05%	[79,80]
Yunfu Ni-Cu sulfide Mine	Meizhou City, Jiangxi Province	Combined bacteria: <i>Betaproteobacteria</i> 47.75%, <i>phylum Nitrospira</i> 0.9%, <i>Gammaproteobacteria</i> 37.84%, <i>Alphaproteobacteria</i> 13.51%	First FeS <sub>2</sub> mine in China	[81]
Sarake Copper Mine	Wuqian, Xinjiang Autonomous Region	Based on experimental plant experiments, extraction rates reached 93.77% after 155 days, applied heaps bioleaching	Cu 1.34%; secondary copper sulfide (chalcocite, digenite and chalcopyrite mainly)	[82]
Zhongwei Copper Mine	Ningxia Hui Autonomous Region	Based on experimental plant experiments, extraction rate reaches 83.03% after 315 days; Existed amount of CaSO <sub>4</sub>	Cu 0.32%; secondary copper sulfide 59.38% and primary copper sulfide 37.5%	
Duobaoshan Copper Mine	Nenjiang County, Heilongjiang Province	Cu extraction rate just 15.5% after 326 days and CaSO <sub>4</sub> passivation disturbed results obviously	Cu 0.51%; primary copper sulfide 0.38% (chalcopyrite mainly)	
Daye Copper Mine	Daye City, Hubei Province	Low-grade, biodump leaching, high-oxide, high-clay; copper extraction rate can reach 83.97% after 80 days	Cu 0.35%; copper sulfide 32.3%, free oxide copper 26.3%, silicate copper 22%	[83–85]
Hami Copper-Nickel Mine	Hami, Xinjiang Autonomous Region	Low grade sulfide ores containing high magnesium; nickel and copper bioleaching; extraction rate: Cu 32.6%, Ni 84.6%	Sulfide ores 3–8% (pyrrhotite, nickel pyrite, chalcopyrite mainly)	

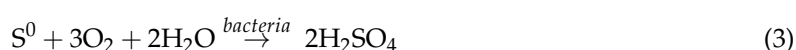
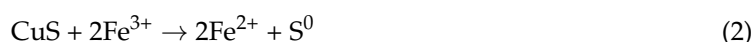
### 3.2.1. Zijinshan Copper Mine (ZCM)

Zijinshan Copper Mine is the largest bio-heap leaching case study, playing a key role in the research and application of copper bioleaching in China. It is located in Shanghang City, Fujian Province. The ZCM has the largest chalcocite deposit, with about 13.9 million tons of low-grade copper sulfide ore (Cu 0.38%). An overview and the flowchart of bioleaching system are shown in Figure 3 [86]. Due to lower recovery and high cost of traditional mining methods, the ZCM has been extracting copper using bioheap leaching since the 1998. A Solvent Extraction/Electro-Winning (SX-EW) commercial bioleaching plant, designed by China ENFI Engineering Corporation was constructed in 2000 and has been operational since the 2005 with a capacity of 20,000 t/a at a copper extraction rate of 80% [87–89].



**Figure 3.** Heaps and technological process of ZCM. (a) Overall view of bioheap plants in Zijinshan Copper mine; (b) Basic flowchart of bioheap leaching system.

The bacteria are mixture strains of *Acidithiobacillus* (>51%), *Leptospirillum* (>48%), and *Ferrimicrobium* (~1%) obtained from AMD, Zijinshan Copper Mine [90,91]. For the bioleaching of ZCM, the core reaction was originally researched and proposed as the dissolution of chalcocite divided into several steps [92–94]



Compared with other large-scale commercial bioheap leaching cases in the world, ZCM's bio-heap leaching has three main characteristics: lower pH value (0.8–1.0), high  $\text{Fe}^{3+}$  concentration (50 g/L), and high temperature (45–60 °C). However, during bioleaching processes, plenty of Fe(III) is precipitated as jarosite, an extracellular polymeric substance (EPS) generated on the ore surface, blocking pores and fractures, causing the copper extraction to reach its peak.

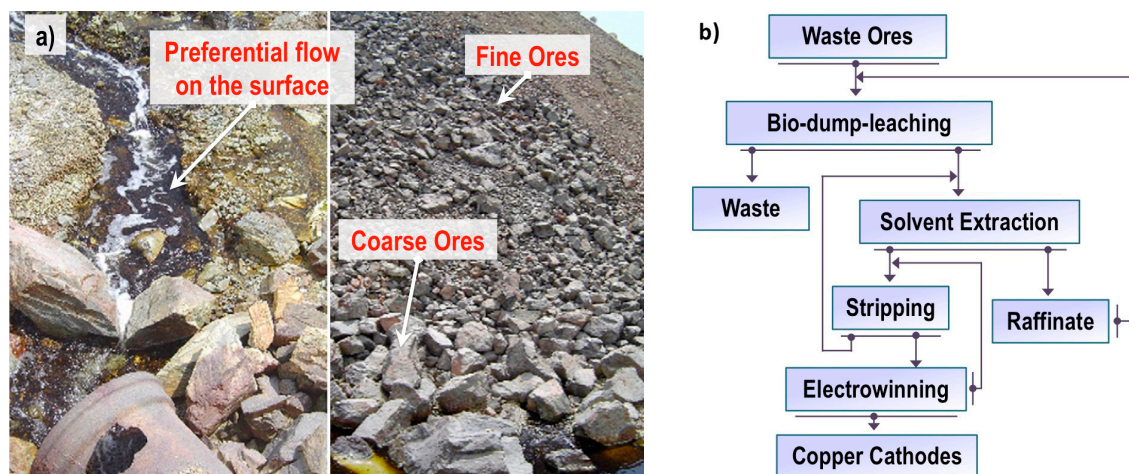
### 3.2.2. Dexing Copper Mine (DCM)

The Dexing copper mine (DCM) is located in Dexing City, Jiangxi Province, which is known as the 'copper homeland of China'. The mine is one of largest porphyry copper deposits around the world. The mine consists of 80% chalcopyrite, 5% pyrite, 5% quartz, and 5% others. Both underground and open-pit extraction have been occurred since the 1965 and 1971 [95–97]. The stripping waste rock dump (WRD) contained 1.2 million tons total copper piled up at a height of 70 m, with an inclination slope angle of 55° and an area of 7,570,000 m<sup>2</sup> with about 600 million tons of waste rocks in total [98]. This negatively affects the environment in terms of occupation of land, dust, and dump sliding.

Recovery of ore from dumps was completed from 1984 to 1996, an industrial scale experiment of 1000 t (1984–1991) resulted in considerable progress, increasing the recovery of copper from 0.121% (1984, average grade of Cu in dumps) to 16.59% (1987) and 30% (1991). Moreover, the feasibility study



(1993) and primary design (1994) was carried out sequentially. In October 1997, the biodump leaching SX-EW plant of DCM was finally finished with 2000 t/a [99,100]. The key technological process is as follows: initial leaching solution (ILS) is sprayed on the top of dump; the concentration of Cu(II) increases when solution percolates through the ores; then the pregnant leaching solution (PLS) is collected at the bottom of dumps. The Figure 4 shows flowchart in DCM.



**Figure 4.** WRD and technological process of DCM. (a) Preferential flow and ore particle segregation; (b) Biodump leaching flowchart.

Compared to bioheap leaching, lacking a pad and higher boulder yield are considered pivotal challenges of biodump leaching. A lower bacteria population and WRD's intrinsic permeability are thought as bottlenecks to better extraction in DCM, as Figure 4 shows [101]. Due to heap's lower permeability in the DCM, seepage phenomenon, like preferential flow, was founded based on CT technology, and its effects on extraction and surface morphology were pinpointed [102]. Mutiphysics interactions were researched. Moreover, the WRD's stability is threatened by certain factors, such as particle size, surface erosion, and bioleaching mechanism, creating a landslide threat. As a notable landmark with great significance, biodump leaching in the DCM confirmed the leachability and potential commercial profits of WRD with lower intrinsic permeability.

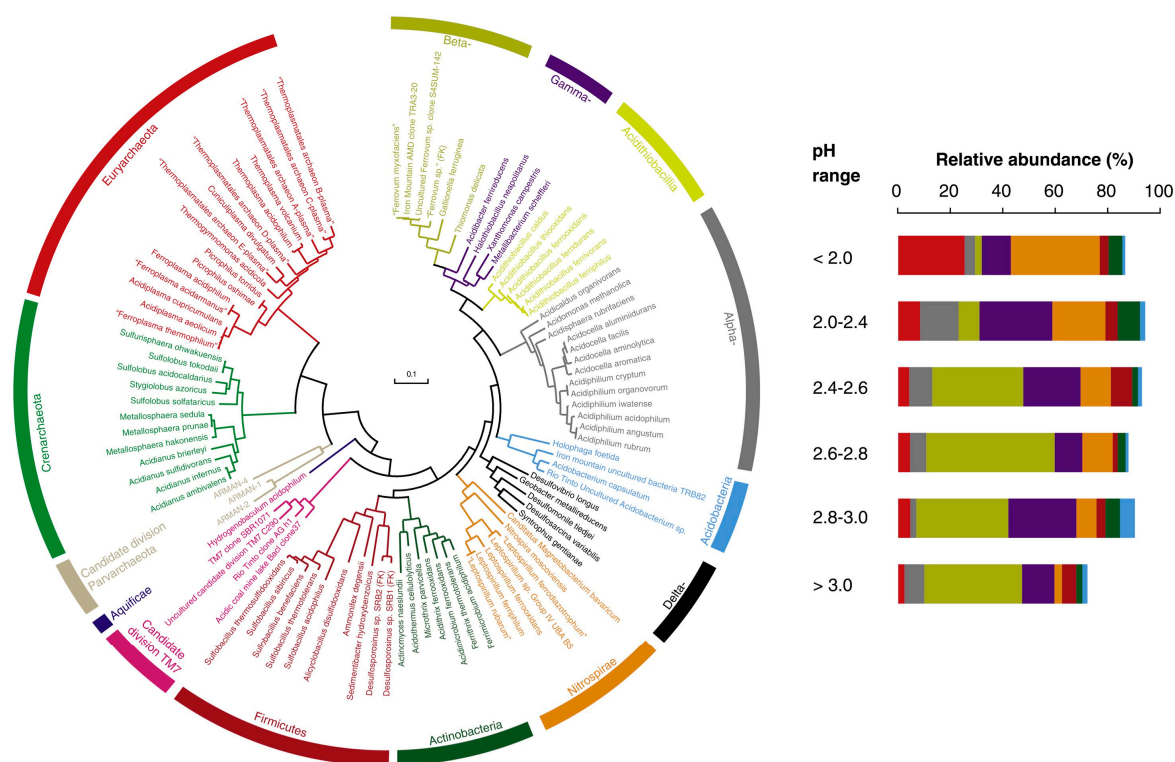
#### 4. Recent Technical Progress of Copper Bioleaching

The successful application of these above-mentioned cases cannot be separated from breakthroughs in key technologies, such as bacteria identification, interface reaction, multistage percolation, a pore structure revolution [103–105]. Given the unique and complex situation of copper minerals in China, researchers have made significant progress, investigating some new typical technologies and innovations. These effective achievements are summarized and enumerated, mainly focusing on Chinese experts and authorities around the world.

##### 4.1. Isolation, Identification, and Enrichment of Bacteria

Bacteria play a crucial role in copper bioleaching [106]. The physiological and phylogenetic biodiversity of acidophilic microorganisms are prominent and less definite [107]. These studies deepened the knowledge of genomics, metagenomics, and proteomics [108]. It is noteworthy that the Chinese research on the isolation, identification, molecular diversity, and inhomogeneous catalysis behavior of leaching bacteria have reached the gene level and have proven efficacious for copper bioleaching [109–112]. For instance, thermophile bacteria are widely distributed in extreme conditions, ranging from 10 °C to 80 °C [113]. The complexity of the microbial community structure differs in different locations of biological heaps [114–118]. Many studies have inferred that mixed bacteria

perform better in copper bioleaching from oxide-copper sulfide and nickel-copper sulfide [119–123]. Some methods of rapid specific detection and quantification like real-time PCR, have been proposed for determining functional genes expressions [124]. Moreover, sulfur and nitrogen, putative efflux transport systems, and sensitivity analysis of the bacteria growth have been researched [125–127]. The heterotrophic strain and bioleaching mechanism of ammonia producing bacteria, whose the optimal growth condition is 30 °C and initial pH value is 8, is not clearly understood. Mineral–bacteria interactions are visualized by Raman and Fourier transform infrared (FTIR) microspectroscopies. Some novel bacteria-obtaining methods, like ultraviolet irradiation, have been proposed [128–130]. The alkaline strain was obtained and its leaching behavior are studied both in China and the world [131,132]. Additionally, a mixed culture of sulfur-oxidizing and iron-oxidizing microorganisms was successfully applied in the bioleaching of arsenopyrite [133]. In 2016, as Figure 5 shows, microbial diversity inside acid solution, biofilms, and sediments of 125 AMD samples with different pH values, were systemically summarized. Anaerobic bioleaching, passivation phenomenon, and removal of surface substances have also been reported.



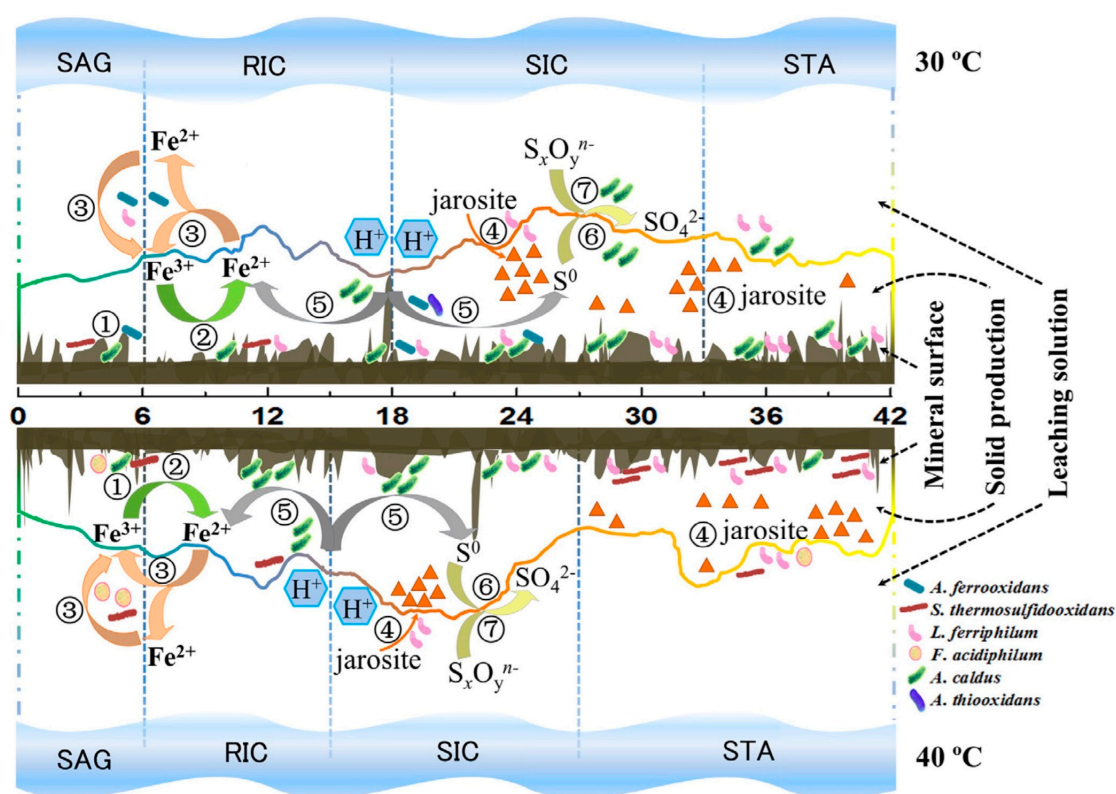
**Figure 5.** Prokaryotic microorganisms in AMD ecosystems inside acid solution, biofilms, and sediments and its distribution with different pH value ranges [134]. Reproduced with permission from Chen, L.X., Current Opinion in Biotechnology, Microbial communities, processes and function in acid mine drainage ecosystems; published by Elsevier, 2012.

#### 4.2. Bioleaching Mechanism and Interface Reaction

One of the challenges in this field has been how to bioleach valuable metal from low-grade ores, this has been the subject of numerous discussions around the world [135]. Due to the complexity of the mineral composition, especially in China, bioleaching mechanisms and interface reactions—such as pH value, ferrous transportation, EPS, quartz addition, and sulfur speciation, etc.—have been extensively studied [136–142]. Microorganism transportation, mechanisms, and reaction pathways of chalcopyrite, carrollite, and djurleite bioleaching [143,144]; synergistic bioleaching processes, like p-type chalcopyrite, n-type chalcopyrite, bornite [145,146]; and other low-grade resources have

been analytically researched. Zhang et al. [147,148] proposed enhancement of copper extraction by the application of bioaugmented treatment and re-inoculation.

In addition, light illumination catalysis [149] was discussed and been demonstrated to accelerate  $\text{Fe}^{2+}/\text{Fe}^{3+}$  cycling. Influence of interfacial interaction on bioleaching behavior was also investigated [150,151], and vital parameters were discussed, including pH value [152], ferric iron enrichment [153], dissolved oxygen concentration, temperature, and bacteria community initial proportion and dynamics [154–156]. Nickel-copper sulfide bioleaching and its community succession were researched (Figure 6) [157–159]. Biosorption processes of physical adsorption, ion exchange, complexation and microprecipitation were discussed by Jing et al. [160]. Additionally, except for biosorption effects, passivations that included EPS, jarosite, and polysulfide are crucial factors limiting copper extraction rate [161,162]. The new integration strategies have been tentatively applied for weakening EPS, jarosite formation [163,164], biofilm formation [165], and other passivation substances [166]. Based on having high-resolution and non-turbulent characteristics, atomic force microscopy (AFM) and epifluorescence microscopy (EFM) were applied to observe the bioleaching interface interaction and organism attachment [167–169].



**Figure 6.** Mechanism model for chalcopyrite bioleaching coupling with the community succession [170]. Reproduced with permission from Ma, L.Y., Hydrometallurgy, Bioleaching of the mixed oxide-copper sulfide ore by artificial indigenous and exogenous microbial community; published by Elsevier, 2012.

#### 4.3. Multistage Percolation Behavior of Leaching Solution

Whether ILS interacts with recyclable minerals is the key link during bioleaching, thus determining the flow behavior and understanding the regulation of leaching solution are important [171]. Aiming at WRD and heaps with high clay content, heap permeability tends to be smaller, the phenomenon and formative mechanism of preferential flow was proposed and researched systematically [172]. This behavior of preferential flow inside heaps has been simulated by CFD model, confirming convective transport through inter-connected pathways [173].



By relying on the difference of particle kinematics and characteristics—such as roughness, particle size, and viscosity—segregation appears during dumping, promoting the formation of straticulate dumps and preferential flow which is thought of as a rapid fluid passing through pores constructed by coarse ores [174,175]. In 2008, to research flow mechanics especially for preferential flow, a field-scale test was conducted in highly heterogeneous industrial ore heaps. Inhomogeneous fluid flow, called moisture liquid dispersion of unsaturated inter-particles, was determined to rely on capillary process driven by van der Waals force and micro forces. Solution flow behavior, like capillary progress among micro pores, was researched [176]. Fluid flow based on three-dimensional dual pore-network models and solute transport models are successfully established [177–179], solute and microbial medium transport, and the response relationship to key operation parameters in heaps [180]. Hydrodynamic dispersion, chaotic advection, and hysteresis phenomenon in liquid holdup and liquid spread mechanisms in unsaturated packed bed and heaps are also described [181]. Furthermore, fine interlayers are resulted to layered structure and obstruct infiltration pathways, influencing the formation of somewhat faint leaching regions [182].

#### 4.4. Reconstruction and Characterization of Multiple Pore Structure

Pore structure insides heaps or dumps are intricate, so Wu et al. searched for a better method to characterize and visualize pore structure [183]. Ore particles with complex shape parameters are accumulated to form ore heaps, configuring unsaturated gas–solid diphase structure especially for ore dumps, creating migration pathways for leaching solution and oxygen. Pore structure is influenced by aperture size, mineral distribution, and connectivity [184]. Compared to ore waste dumps, the permeability of heaps improved remarkably after agglomeration processing, and relevant binders and particle fractions are invented [185,186]. For simple ore particles, the effect of high pressure grinding roll (HPGR) crushing on extraction rate attracted more and more attention [187]. With the introduction of advanced visualization means like uCT, X-ray CT [188], and MRI [189,190], image processing of packed ore particle beds has improved considerably, such as leaching behavior measuring methods [191,192], multi-scale quantification [193], LBM constructions [194], and the three-dimensional characterization, analysis, and reconstructions of ore heap leaching [195–198].

#### 4.5. Multiphysics Coupled Model of Bioleaching Process

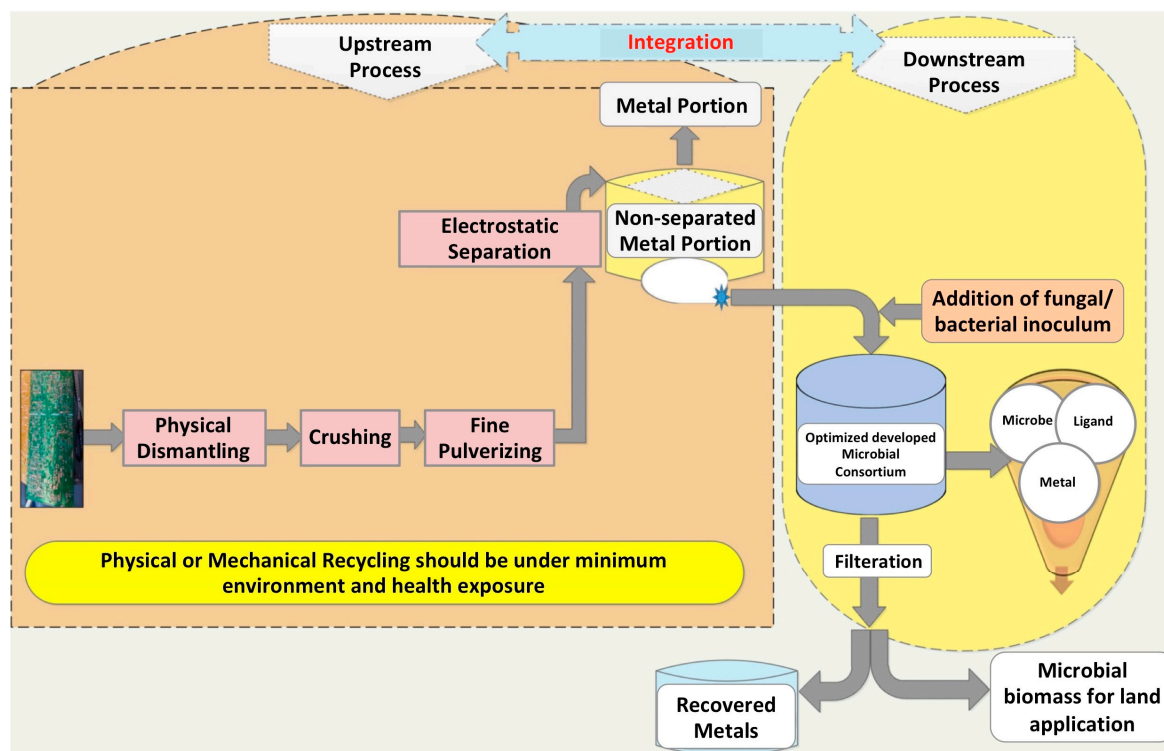
The complexity of bioleaching system has complicated the estimation of extraction rates and effects during leaching processes, as shown by a few specific experiments [199]. Hence, some models were constructed to replace studies where common approaches have not been implemented [200]. For the reaction, fluid flow, and other factors in the complex bioleaching process, model construction and computer simulation have been used as an alternative technology [201]. Besides, some coupled mathematical models and simulations based on Comsol Multiphysics, Fluent, and Simpleware—like solute transportation, seepage, heat transportation and balance, and microbial transport in bioleaching system—were also established [202].

Some comprehensive mathematical models deterministic models of heap leaching have been established for enargite bioleaching [203], grey forecasting model of primary sulfide ore bioleaching, bacterial community monitoring of Ni-Cu sulfide [204], air sparing and distribution inside heaps [205], modeling of copper-sulfide ore in heap and dump, a population balance model of OAs during heap leach operation, kinetics of copper dissolution under pressure oxidative leaching [206], and kinetics modeling of chalcopyrite bioleaching catalyzed by silver ions [207].

#### 4.6. Enhanced Copper Bioleaching from Waste Printed Circuit Boards (WPCBs)

With the promotion and application of electronic products, the impacts of waste electric and electronic equipment (WEEE) on environment are considerable and hard to eliminate [208]. Bioleaching copper is now being sourced from electronic wastes like WPCBs in China [209–211]. Figure 7 shows basic bioprocessing schematic of WPBCs by bacteria. Hence, further exploring

strategies to effectively leach valuable metals is an important field of study [212–215]. Efficiency and electric fields effects of *Acidithiobacillus ferrooxidans* and mixed culture were also proven in copper bioleaching from PCBs [216–219]. Furthermore, to enhance the bioleaching process, new catalyzed materials like biochar, nitrogen-doped carbon nanotubes (NCNTs), and new strategies were applied in hydrometallurgy fields [220–222]. Bioleaching of e-waste will be applied and developed for new applications, introducing more sustainable and practical ways to recover minerals and metals in the future [223,224].



**Figure 7.** Illustration of integrated approach for copper recovery and recycling of WPCBs [225]. Reproduced with permission from Awashi, A.K., Integrated bioleaching of copper metal from waste printed circuit board—a comprehensive review of approaches and challenges; published by Springer, 2016.

## 5. Future Opportunities and Challenges

Sustainable development is a common worldwide theme [226–229]. Biotechnology has an important place in the future, especially for the bioleaching of metal from secondary lower-grade ores [230–233]. Given the conflict between bioleaching and environment protection, issues include environment protection, bio-diversity disturbance, acid pollution, and ore dumping [234–237]. As mines become deeper, costs and security risks inevitably increase. In this case, in situ copper bioleaching is thought to be a niche technology [238]. In this paper, based on previous research and developing trends, some key opportunities and challenges are proposed, based on the foundations in China.

### 5.1. Efficiency Improvement and Guarantee

During the bioleaching process, many key factors are uncontrolled—including fluid flow, bacteria proliferation, temperature distribution, and gas transportation—causing out-of-balance of copper extraction in different areas of heaps. To avoid this lower permeability, bacteria culture and



efficiency limit efficient and high-volume metal recovery. The diversity of microorganisms and their capabilities and function are waiting to be validated and exploited [239].

- Efficiency bacteria obtained via genetic engineering [240] and other induced domestication means, especially for extremophiles [241,242] in severe environments with high temperature, lower oxygen, high osmotic pressure, and so on.
- Enhanced bioleaching methods using external field energy, like enhanced aeration, permeability regulation, geothermal energy, underground pressure, etc.
- Target minerals activation pre-treatment inside ore and other enhanced minerals exposing technology.
- Bioleaching process control, like weakened passivation methods, especially for copper sulfide bioleaching.

### 5.2. Environmental Protection and Security

With the exposition of environmental contamination, increased focus has been placed on leakages and insecurity during the bioleaching progress [243]. Hazardous pollution migrations and their effect of acidophiles inside bioheaps of the ZCM on nearby rivers have negative impacts [244]. In 2014, the greenhouse gas of in situ leaching of copper, uranium, and gold resources were researched [245]. Conversely, as far back in 1993, the microbes had been proposed as a treatment for metal pollution like groundwater bioremediation [246–248]. Thus, to some extent, balancing application and control of bioleaching is a key factor which has limited the layout space.

- Acid leaching solution is a serious hazard to surface runoff and groundwater, presenting risks such as depositing crop pollution, high cancer rates, and animal deformity.
- Exotic bacterium escaping from bioleaching industrial plants could be a momentous threat to native bio-diversity, even leading to crowning calamity of rare species.
- Ore dump and heap collapse threats under internal bioleaching mechanism and external environmental factors such as rainstorms.
- Consummation of relevant environmental assessment (EIA) methods and regulations.

### 5.3. Application of Novel Technology and Methods

Application of advanced technologies and new concepts in copper bioleaching are essential for biotechnology development. For instance, to enhance temperature inside heaps, the solar thermal energy was applied in a Chilean copper mine by setting up flat plate collectors and other integration equipment, improving the copper extraction rates from 67% to 85% [249,250].

- New field energy, like solar thermal energy, wind energy, microwave treatment [251] is used to enhance bioleaching strength, obtaining a better extraction and decreasing environmental pollution.
- New visualization, intellectualization, and fluidization mining methods such as super-precise unperturbed scanning even deeper into the reaction interface, real-time 3D printing during bioleaching, unmanned in situ bioleaching.
- Metal recovery from solid waste like ore dumps WPCBs with surfactant based on bioleaching.
- New leach pad types to increase permeability and decrease OAs of heaps, for instance, standard heap [252], valley fill heap [253], and bacterial thin leaching (BTL) methods [254].
- New in situ copper bioleaching methods to explore mineral resources located in the deep earth.

Last but not least, biotechnology has been proven to be promising for metal recovery from lower-grade ores and wastes [255,256]. In addition to the copper resources discussed in this paper, some critical and scarce metals, even biomining from asteroids in the deep universe and stratum in the deep sea are thought as important directions [257,258].

## 6. Conclusions

China's improvements in science and technology are of concern. Thus, this paper provides an in-depth review of the historical investigation and current scientific research processes on copper bioleaching in China over the course of 5000 years, with research spanning macroscopic industrial cases to molecular and genetic understanding. With prominent advances in leaching bacteria isolation, interface reaction, percolation behavior, heap reconstruction, and other technology applications, copper bioleaching has quickly developed, gaining a considerable market share. The Zijinshan Copper Mine (bioheap leaching) and Dexing Copper Mine (biodump leaching) have advanced the bioleaching of low grade and dumps. In conclusion, even though there are plenty of unknown obstacles and challenges, the potential for cross-disciplinary and technological development in copper bioleaching is remarkable, this brief review lays a good foundation for future research.

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## Abbreviations

AMD	Acid Mine Drainage
<i>A.f</i>	<i>Acidithiobacillus ferrooxidans</i>
AFM	Atomic Force Microscopy
CT	Computed Tomography
DCM	Dexing Copper Mine
EFM	Epifluorescence Microscope
EPS	Extracellular Polymeric Substances
FTIR	Fourier Transform Infrared
HPGR	High Pressure Grinding Rolls
ILS	Initial Leaching Solution
LBM	Lattice Boltzmann Model
MRI	Magnetic Resonance Imaging
NCNTs	Nitrogen-Doped Carbon Nanotubes
PIV	Particle Image Velocimetry
PLS	Pregnant Leaching Solution
<i>T.f</i>	<i>Thiobacillus ferrooxidans</i>
WEEE	Waste Electric and Electronic Equipment
WPCBs	Waste Printed Circuit Boards
WRD	Waste Rock Dump
ZCM	Zijinshan Copper Mine

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