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Biotech key to unlock mineral resources value

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Abstract: This work aims to describe the history of biometallurgy in China, introduce the development and application of biometallurgy technologies in exploitation of mineral resources, and identify the main challenges and future directions. Although the earliest biometallurgy activities in China were documented in 6th−7th century BC, fundamental research and biometallurgy applications started relatively late in this country. Rapid development, from phenotypic to genotypic characterization of biometallurgy microorganisms, as well as from theoretical to practical applications, has been made in China since the 1950s. The integrated applications of biometallurgy technology in copper, gold, and uranium extraction ensured China's economic reserves of strategic mineral resources. Developing more efficient microorganisms and strengthening the micro-interface reactions will be an effective way to improve the biometallurgy efficiency. Biometallurgy technologies can also be adapted to recovery of valuable metal from marine minerals and e-wastes and environmental protection including carbon sequestration and heavy metal polluted soil/sediment bioremediation.

Key words: biotechnology; biometallurgy; bioleaching; mineral resources; nonferrous metals

1 Introduction

The earliest record of biometallurgy activities in China can be traced back to the 6th–7th century BC in the book titled *Shan-hai Ching*, where it was written that "the Luoshui River flows out and into Weishui River in Songguo Mountain, which contains significant amounts of copper". Later on, An LIU, the Huainan King, wrote a book titled *Huai Nan Wan Bi Shu* in the second century BC and recorded copper extraction from acid mine drainage (AMD): "copper was obtained when iron was put into Baiqing solution". During the Tang Dynasty (600–960 AD), factories producing copper using hydrometallurgy were established, and annual copper production reached more than 1000 t [1]. During the Song Dynasty (960−1279 AD), the pioneering hydrometallurgist Qian ZHANG wrote a book *Synopsis of Copper Leaching* to introduce the copper extraction by hydrometallurgy [2].

As early as 1670, the leaching of copper-bearing ore with acid mine drainage (AMD) was found at the Rio Tinto Mine in Spain. In 1947, the bioleaching bacteria *acidithiobacillus ferrooxidans* was isolated for the first time. In 1958, the first biometallurgy patent was successfully applied [3]. The first laboratory focusing on biometallurgy in China was built by Professor Fu-xu HE in Central South Institute of Mining and Metallurgy (now Central South University (CSU), Changsha, China) in 1958. Characterization of bioleaching micro-organisms and bioleaching of metal ores were started in China at that time. In 1960, industrial applications were conducted at the Tongguanshan Copper Mine (Tongling, Anhui Province, China) by

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the Institute of Microbiology, Chinese Academy of Sciences (CAS). Bioleaching technology was subsequently applied in a demonstration plant to extract uranium from a low-grade uranium ore heap comprising 700 t of ore. In 1995, CSU exploited and tested copper extraction from low-grade copper ore wastes by biometallurgy at the Dexing Copper Mine, Jiangxi Province, China. Two years later, a bioleaching plant with an annual production of 2000 t of cathode copper was successfully established at the mine (Fig. 1). In 1999, the group headed by Prof. Guan-zhou QIU (CSU) started to cooperate with the Oak Ridge National Laboratory (USA) to carry out ecological and genomic research of bioleaching microorganisms, initiating the era of genomic studies in the field of biometallurgy in China. In 2000, the first pilot-scale plant for biooxidative pre-treatment of refractory gold ore with annual treatment of 50 t gold concentrate was officially launched. In 2004, the whole genome of *Acidithiobacillus ferrooxidans* 23270, a model microbe for biometallurgy, was sequenced for the first time in the world. Soon afterwards, the national standards, the methods of testing *Acidithiobacillus ferrooxidans* and its activity by microarray technology (GB/T 20929—2007), was formulated by CSU in 2007, which realized the rapid and accurate screening of high-efficiency

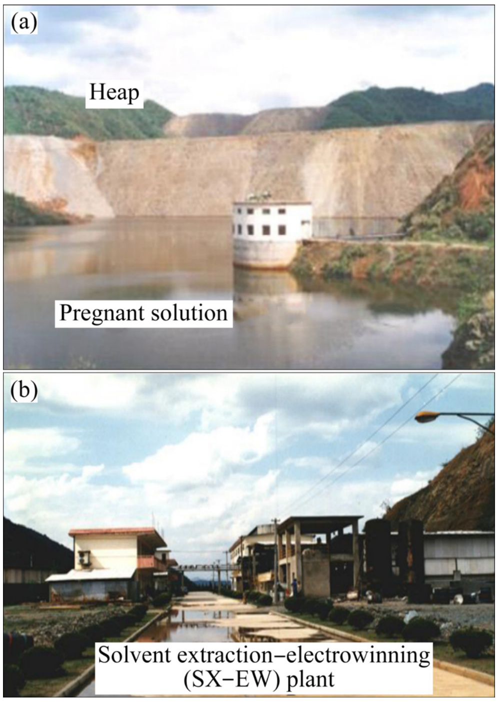

Fig. 1 Biometallurgy plant set in 1997 in Dexing Copper Mine, Jiangxi Province, China

bioleaching bacteria [4]. Besides, a biometallurgy plant with a capacity of 30 kt of cathode copper was built in Zijin Mining Company in 2005, and the cathode copper purity reached LME grade A.

Currently, the main research activities on biometallurgy in China are performed in CSU, General Research Institute for Nonferrous Metals, Institute of Process Engineering and Institute of Microbiology of Chinese Academy of Sciences, Shandong University, Changchun Gold Research Institute, Beijing Research Institute of Chemical Engineering and Metallurgy of China, Northeastern University, University of Science and Technology Beijing, National Nuclear Corporation, Kunming University of Science and Technology, East China University of Technology, etc. The research carried out on bioleaching includes mainly: (1) microbiology of bioleaching [5−9]; (2) microbial–mineral interactions [10−13]; (3) multiple factors that strongly influence the bioleaching efficiency [11,14−18]. The Chinese government has given major financial support for fundamental research and application of biometallurgy, and has established a number of national science and technology plans, including “National Basic Research Program of China (973 Program)”, “National High Technology Research and Development Program (863 Program)”, and “National High Technology Industrialisation Demonstration Project”. The National Natural Science Foundation of China (NSFC) has also provided funding (approximately 1 billion RMB Yuan; approx. $155 million USD). For instance, the number of approved projects in its Engineering and Materials Department increased from 10 in 2000 to 50 in 2010, and the total budget increased tenfold.

2 Significance of biometallurgy to development of nonferrous metal industry in China

With the rapid industrialization in China, the consumption of nonferrous metals such as copper, gold, and uranium has increased sharply. Thus, mineral resources security in China is grim. For example, the guarantee period of copper and gold mineral resources is less than 20 and 15 years, respectively. In addition, 70% of nonferrous metal minerals are low grade polymetallic complex. It is non-feasible to use traditional beneficiation−

metallurgy combination process. This makes the supply of metal mineral resources in a serious shortage and has become one of the main factors restricting economic development in China. Biometallurgy is a novel technology that uses microorganisms (bacteria, fungi, microalgae, etc) to dissolve valuable metals in ores and recover high-purity metals through electrode extraction process. Compared with other metallurgical processes, biometallurgy has the characteristics of low operating cost and environmental friendliness (Fig. 2). This makes it advantageous in effectively recovering low-grade polymetallic mineral resources.

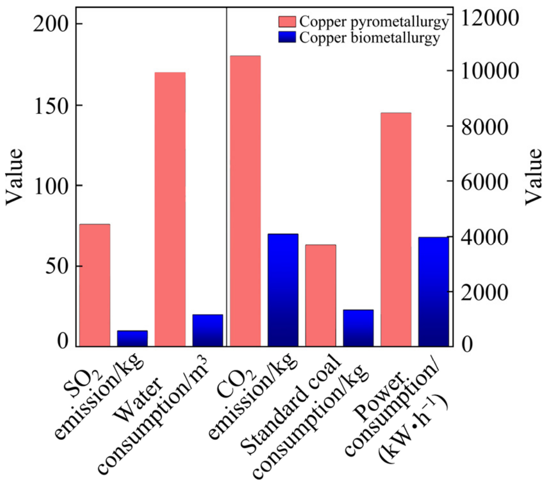

Fig. 2 Comparison of energy consumption and pollutants emission between copper biometallurgy and copper pyrometallurgy

China is the largest copper consumer in the world, while its domestic copper production only accounts for about 20% of consumption. Using biometallurgy technology to exploit low-grade copper resources can decrease economically usable copper grade to 0.1%. Subsequently, the amount of copper resources in China will be increased by more than 20 million tons. Besides, more than 2/3 of gold reserves in China belong to refractory gold ores, leading to difficult development and utilization. However, biometallurgy for the pre-treatment of gold ores can effectively utilize these resources. With the development of this pre-treatment technology, China has become the largest gold producer for four consecutive years in the world. It is of great significance to maintain the world leading level and international competitiveness of China's gold production. In addition, biometallurgy technology can make effective use of a large number of sulfide encapsulated uranium resources in China. It is expected that the exploitation grade of uranium resources will be reduced from the present 1/1000 to 3/10000. Thus, the exploitable uranium reserves are greatly increased.

3 Biometallurgy development in China

3.1 Macroscopic to microscopic views of biometallurgy

In China, the early research in bio-metallurgy focused mainly on the macro level. Metallurgists often used AMD for improving the bioleaching efficiency of metal ores, without knowing how the bioleaching process worked. Since the discovery of bacteria associated with AMD in 1947 by COLMER et al [19,20], microbiologists started to search for, isolate and select strains of microorganisms that were more effective in biometallurgy applications. In 2004, CSU participated in whole genome sequencing of the type strain of *Acidithiobacillus ferrooxidans*, which was the first sequencing of a biometallurgy microorganism. Based on the data, a national standard (GB/T 20929—2007) entitled "Methods for the detection of *At. ferrooxidans* and its oxidation activity by microarray" was established by CSU. The establishment of a national standard enabled rapid and accurate screening of bioleaching microorganisms with high iron- and/or sulfur-oxidizing abilities. The full map and annotation of the genome of *At. ferrooxidans* laid the foundation for studying bioleaching mechanisms at the molecular level and realizing the orientation of microbial leaching research from phenotypic to genotypic level. In Shandong University, extensive activities on genetic modification of biometallurgy microorganisms for understanding iron and sulfur metabolisms in acidophiles, and improvement of biometallurgy efficacy have been ongoing [21−23].

3.2 From qualitative to quantitative analysis

Biometallurgy microorganisms usually comprise acidophiles which perform iron and/or sulfur oxidation activities [24]. It is essential to find a way to quantitatively analyze microbial composition and function for the clarification of multifactors influencing bioleaching efficiency.

With the rapid development of molecular methods, genetic, genomic, and metagenomic technologies are increasingly being applied in biometallurgy applications. In particular, the application of genomics has led to significant progress in quantitative analysis of bioleaching systems, such as community structure and function. The development of microbial functional gene array and community genomic array technologies has led the research level from single function of a single population to whole functions of a single population and whole functions of a microbial community. Based on these technologies, the dynamics of microbial community structures and leaching functions can be detected quantitatively and may be used to analyze the effect of leaching parameters on microbial growth and iron-/sulfur-oxidation ability. The established microbial function gene array developed in CSU was used to study the microbial structure and function, allowing the simultaneous detection of the microbial community structure and function in bioleaching system. Based on results from studying the succession mechanism of bioleaching microbial community structure and function, the microbial consortium was optimized through combining different species and strains of microorganisms. The new optimized consortium was successfully applied for the bioleaching of low-grade copper sulfide at the Yushui Copper Mine, Guangdong Province, China, leading to enhanced levels of copper extraction and recovery.

3.3 From theory to practice

3.3.1 Biometallurgy of copper ores

China is currently the top global consumer of copper, but its present domestic production accounts for only about 20% of its copper demand. Biometallurgy technologies facilitate the exploitation of low-grade copper resources in China as elsewhere and can therefore enhance global copper production. As below, several biometallurgy industry applications for copper production are listed and described.

(1) Dexing Copper Mine

The heap bioleaching plant in Dexing Copper Mine is an example of a successful application of biometallurgy technology. More than 3.5 Gt of waste ores have been produced during the life of the mine. These contain 0.05%−0.25% (in mass fraction) copper, so there are approximately 600 kt of residual copper metal in this material. Since the waste ores are mainly composed of primary copper sulfides such as chalcopyrite, it has been proven difficult to obtain high leaching rate using conventional biometallurgy. In order to improve bioprocessing of the Dexing copper waste ores, two research projects “Studies on bioleaching of low-grade sulfide ore with selected bacterial consortium” and “Studies on the catalytic mechanism and strengthening bioleaching strains isolated from Dexing Copper Mine, and their industrial application” were carried out. Using the quantitative analysis technology developed by CSU, strains of *Acidithiobacillus* spp. and *Leptospirillum* spp. and other biometallurgy prokaryotes, with high growth rate, high oxidation ability, and high resistance to metal ions were obtained by microarray screening and used to improve copper extraction. Copper recovery was further enhanced by upgrading the SX−EW plant at the mine (Fig. 1) [25,26].

(2) Zijinshan Copper Mine

The Zijinshan Copper Mine was the first example of a successful industrial application of biometallurgy in China. This mine is located in Shanghang County (a subtropical region) in Fujian Province, and the copper sulfide deposit contains 240 Mt of ore averaging 0.063 wt.% copper. Chalcocite and covellite are the copper minerals comprising the secondary sulfides. Since the copper grade is very low and the deposit contains significant amounts of arsenic, the traditional flotation and smelting process cannot be applied to extracting copper economically and effectively, and in 1998 the mine operators began extracting copper using heap bioleaching [16]. Due to the relatively warm climate (average atmospheric temperature at the mine is 16−20 °C), heap bioleaching is favorable. Several steps, from shake flask tests to column tests and pilot tests combined with SX−EW, were initially trialed to improve microbial efficacy and copper recovery. Not surprisingly, *Acidithiobacillus* spp. and *Leptospirillum* spp. appeared to be the dominant leaching organisms in the bioleaching process [27,28]. From these early experimental studies (Fig. 3), the Zijinshan Copper Mine established a heap bioleaching factory with an ore processing rate of 60 Mt/a and an annual cathode copper production of 10 Mt. Exploitable copper reserves have increased from 2.7 to 3.1 Mt by using biometallurgy technology. The copper recovery for heap bioleaching reaches 80% in a leaching period of approximately 200 days.

(3) Chambishi Copper Mine (Zambia)

Biometallurgy technology developed in China was used to extract and recover copper in Zambia. In 2010, a strategic framework agreement was signed between the Zambian Ministry of Mines and Minerals Development and CSU. Based on the agreement, the "China Nonferrous Metal Mining (Group) Co., Ltd−CSU−Zambia biohydrometallurgy Technology Industrialisation Demonstration Base" was established. Chambishi Copper Mine contains about seven million tons of copper, with the chief copper minerals in the ore being bornite and chalcocite, and minor amounts of chalcopyrite. In March 2011, the Zambia Chambishi Copper Company cooperated with CSU to exploit the low-grade copper ore in Chambishi by heap bioleaching. Firstly, the indigenous microorganisms were screened, enriched, and adapted to the heap environment. Then, the adapted microorganisms were sub-cultured in 10 L, 70 L, 2 m^3, 28 m^3, and 150 m^3 stirred tank reactors, successively (Fig. 4). The microbial consortium was inoculated into ore heap by irrigation and spraying. The cell numbers were maintained at approximately 10^8 cell/mL in the leachate liquors [29]. In the heap bioleaching of 600 kt of low-grade copper ore, copper extraction reached up to 50% in 2 months. Bioleaching solution was processed using SX−EW, producing cathode copper at a rate greater than 10 kt/a. Biometallurgy technology was estimated to increase copper recovery by 20%, and to reduce

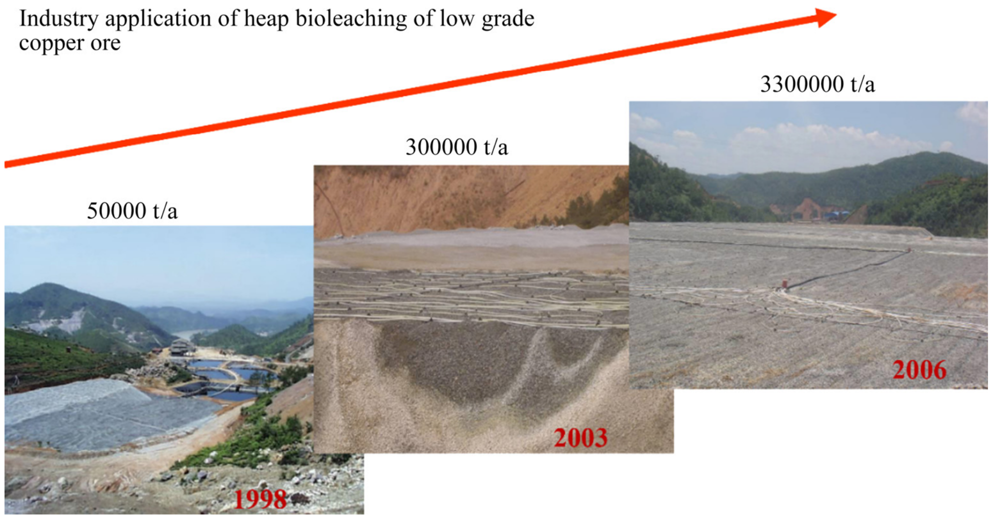

Fig. 3 Heap bioleaching industrial application in Zijinshan Copper Mine, Fujian Province, China

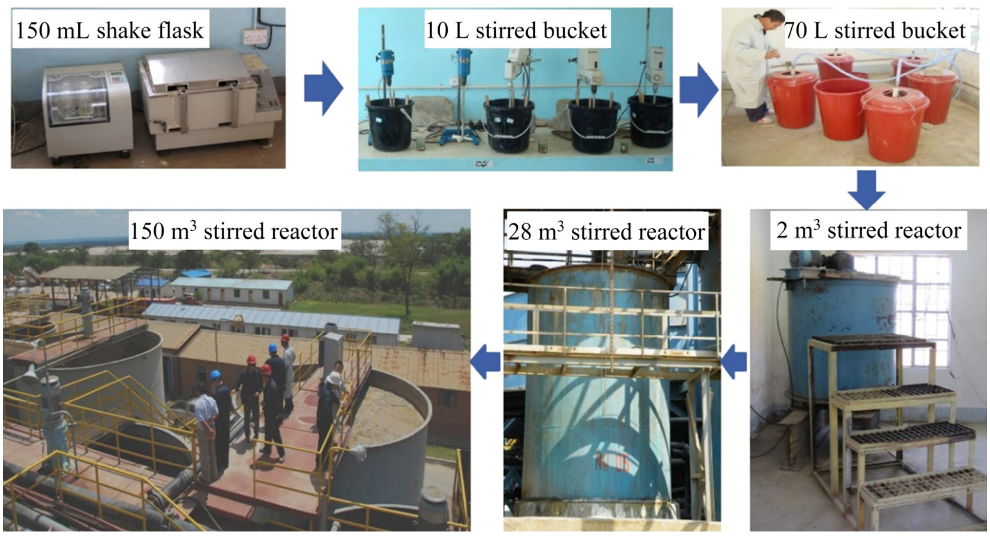

Fig. 4 Scale-up of adaption process of bioleaching microorganisms from shake flasks to 150 m^3 stirred reactors

acid consumption by at least 35%, compared to the acid leaching process using sulfuric acid. This was a clear demonstration of how low-grade copper resources can be exploited by using biometallurgy technology [30].

3.3.2 Biometallurgy of uranium ores

In order to keep pace with the increasing demand of uranium for nuclear power generation, China's uranium production has been orientated to the exploitation of low-grade or refractory uranium ore, and other mineral resources associated with the processing of uranium. During (indirect) bioleaching of uranium ore, U(IV) is oxidized to U(VI) by ferric iron which is regenerated by iron-oxidizing acidophiles, thereby maintaining the leaching reaction [31]. In terms of uranium resources, biometallurgy can enable an efficient use of a large number of idle or abandoned uranium sulfide resources in China and is expected to become increasingly important with projected decline in the grade of uranium resources from 0.1% to 0.03%. Bioprocessing has the potential to significantly lower the cut-off grade of uranium ores and thereby increase the economic mining exploitation of low-grade uranium deposits.

The Institute of Microbiology of CAS started biometallurgy technology for uranium recovery, in the 1970s, with a pilot-scale study of heap leaching conducted in Uranium Mine 711, (Hunan Province, China). A total of 2 t concentrated uranium was enriched from the surface ore containing 0.02%−0.03% of uranium by biometallurgy for 8 years in the Bofang Copper Mine, Hengyang, Hunan Province, China. In the 1980s, heap biometallurgy of uranium gained rapid development and was applied at the Chaotaobei Uranium Mine (Ganzhou, Jiangxi Province, China), a uranium mine in Xinjiang Autonomous Region, China and Xiangshan Uranium Mine (Jiangxi Province, China). Using the optimized mixed culture in heap leaching at Fuzhou 721 Mine in Jiangxi Province, China, up to 96.8% extraction of uranium was achieved in 97 days.

Most of the examples cited are pilot-scale tests. The promotion and application of biohydrometallurgy could make a large number of idle or abandoned uranium sulfide resources available in China. It is anticipated that biometallurgy can improve the exploitable uranium grade from the current limit of 0.1% to 0.03%.

3.3.3 Biometallurgy for pre-treatment of gold ores

Refractory gold deposits are considered to account for about two-thirds of known global gold reserves, but these are not readily processed using conventional technologies. Biooxidation, however, can be used as a pre-treatment of refractory gold ores, allowing the previous metal to be accessed and solubilized by lixiviants such as cyanide [32]. China has become the world's largest producer of gold (Fig. 5) and incorporating biooxidation technology for refractory deposits will help to keep China at the forefront of global gold production.

The Shaanxi Provincial Authority of Land and Mines conducted a pilot-scale study on bioleaching pre-treatment of 2000 t of pyritic gold ore (containing Au 0.54 g/t) in 1994. Following the biooxidation, gold recovery reached 58%. Direct extraction of gold by cyanidation of an arsenic-

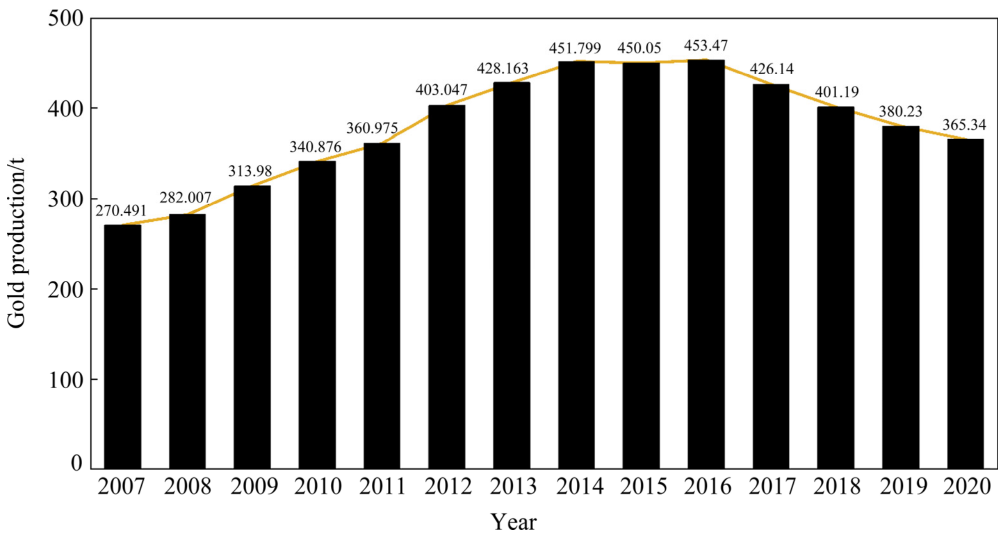

Fig. 5 Gold production in China from 2007 to 2020

containing concentrate achieved only 35% gold recovery, whereas this was increased to 93% after 5-day pre-biooxidation. In Xinjiang Autonomous Region, China, the Baogutu Gold Mine used biooxidation pre-treatment and gold leaching reached 92%−97%.

The first biooxidation plant for processing gold ore in China was built at the Zhenyuan Gold Mine, Yunnan Province, China. In 1998, Shaanxi Zhongkuang Technology Co. Ltd. established a biooxidation plant for pre-treatment of gold ore concentrates with a processing capacity of 10 t/d. In 2001, Tiancheng Gold Co., Ltd. imported the BacTech technology from Australia and built a biooxidation plant with a concentrate processing capacity of 100 t/d, which is no longer operating. In July, 2000, the construction of the first commercial biooxidation plant started at the Yantai Gold Smelter. The plant went into operation at the end of 2000 [33]. The China National Gold Group Corporation works on the exploitation of arsenic-refractory gold concentrates at the Tianli Gold Company, Liaoning Province, China. They have been extensively working on biooxidation/cyanidation technology and developed "CCGRI" biotechnology in 2005. The processing capacity reached 150 t/d. The microorganisms (the "HY series" bacteria) employed in this technology are active at 35−52 °C and tolerate up to 22 g(As)/L. The HY bacteria were shown to grow in the presence of gold concentrate with a pulp density of 25%−27% and 13%−15% arsenic content.

Recently, biooxidation of refractory gold ores has developed rapidly and has reached an internationally advanced level. China has built more than 10 biooxidation–cyanide gold plants and currently has the largest number of biooxidation gold plants worldwide. This biotechnology is estimated to contribute about 8% of gold production in China in the near future.

4 Future perspectives

Biometallurgy technologies have undergone significant development in China, and the application of biometallurgy for metal recovery has been industrialized for copper, uranium, gold, and nickel. However, biometallurgy still needs to overcome some detractions in order to facilitate further expansion. For instance, copper production by biometallurgy accounts for less than 8% of the total copper produced in China. This number is still lower than the estimated global level of 10%−20%. Microbial strains that are more effective in industrial applications (e.g., tolerance to high ore pulp density and/or toxic metals) could lead to improvements, and these may be enriched and selected from both natural and anthropogenic environments. For instance, heap biometallurgy applications in northern China could benefit from using consortia that contain psychrophilic/psychrotolerant strains remaining active at low temperatures. Fresh water is scarce in many places in China (as in many parts of Chile and Australia) and bioleaching using saline and/or brackish waters would help the expansion of biometallurgy, though this requires salt-tolerant, mineral-degrading acidophiles. Designing microbial consortia that can collaborate metabolically to catalyze complex reactions through a synthetic biology approach will be an effective way to improve the biometallurgy efficiency. In addition, microbe−mineral−solution interface is the main reaction site of biometallurgy. In-depth understanding the mechanism of micro-interface reaction and strengthening its reaction process will also be an important research direction to improve the efficiency of biometallurgy.

The vast amount of marine mineral resources, such as polymetallic nodules, marine manganese crusts, and massive sulfide deposits on the seafloor, could help to meet the expanding demand for metals in China and other countries, as could for the recovery of base and precious metals from e-wastes. Biometallurgy technologies can be adapted to process these materials.

Last but not least, biometallurgy technology also has application potential in the field of ecological environment protection. For example, the contribution of biometallurgy autotrophs which fix CO_2 to the carbon sequestration in a global scale has to be discussed, considered and estimated and this may give additional advantages for the expanding of this green technology in China and the rest of the world, though this carbon sequestration is transient and not likely to be a useful means of carbon sequestration like managed forestry. In addition, considering both economic and environmental objectives, biometallurgy technology is also a preferable option for removing the heavy metal from solid materials such as soils and sediments, due to its low cost and environmental safety.

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用生物技术的钥匙开启矿产资源利用的大门

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摘　要：介绍生物冶金在中国的发展历史及其研究进展，指出未来生物冶金在矿产资源开发中的主要挑战和发展方向。中国最早的生物冶金活动出现在公元前 6~7 世纪，但生物冶金的基础研究和应用起步较晚。自 20 世纪 50 年代以来，中国生物冶金取得了从微生物表型到基因型分析，从理论研究到实际应用的快速发展。生物冶金技术在铜、金、铀开采中的综合应用，确保了中国战略矿产资源的安全储备。开发更高效的微生物菌剂及强化微生物−矿物−溶液的微界面反应过程将是提高生物冶金效率的有效途径。生物冶金技术也可用于提取海洋矿产资源和电子废物中的有价值金属，以及环境保护如二氧化碳固存、重金属污染土壤/底泥生物修复。

关键词：生物技术；生物冶金；生物浸出；矿产资源；有色金属

(Edited by Bing YANG)