Industrial practice of a distinct bioleaching system operated at low pH, high ferric concentration, elevated temperature and low redox potential for secondary copper sulfide

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1. Introduction

Zijinshan copper mine is the largest secondary copper sulfide mine in China. It has an ore reserve over 400 million tones with average copper grade of 0.43% and geological reserve of metal copper of 1.72 million tones. A pilot bioheapleaching plant with a production capacity of 300 t/year copper cathode was built at the Zijinshan copper mine by the end of 2000, then the plant was scaled up to a capacity of 1000 t/year copper cathode by June 2002 (Ruan et al., 2006). In December 2005, a commercial underground mining — bioheapleaching—SX–EW plant was commissioned with a capacity of 10,000 t/year copper cathode. From year 2006 to 2009, total copper cathode production was 37,633.6 t, the average operation cost for copper cathodes was 1.10 USD/lb, and total profit and tax exceeded 149 million USD (Huang, 2010). This plant is the first commercial application of bioheapleaching in China. By using bacterial assisted heapleaching, low production cost was achieved in Zijinshan. Furthermore, life cycle assessment of the process showed that this technology has advantages of energy saving and less environmental impact when compared with traditional flotation–flash smelter process (Ruan et al., 2010a, 2010b). In 2010, the plant was scaled up to a design capacity of 20,000 t/year of copper cathode. The new plant is capable of treating even lower grade of the ROM (run of mine) that enables a lower copper cut-off grade that subsequently increases copper geological reserve of the mine.

During the past few decades, bioheapleaching has been well established all over the world. The operating leaching temperature was usually at ambient or moderate temperatures up to 50 °C (Brierley and Brierley, 2001, Rawlings and Johnson, 2007). The total iron concentration was usually around 20–900 mg/L (Demergasso, 2009; Ibacetea et al., 2005). The Eh is usually around 800–900 mV vs. SHE (Demergasso, 2009) and the operating pH was around 1.5–2.0 (Demergasso, 2009). Comparing with other bioheapleaching plants worldwide (Brierley and Brierley, 2001; Domic, 2007), bioheapleaching at Zijinshan was facing special engineering challenges such as acid and iron accumulation in the solution system from the high content of pyrite and, high mean annual rainfall (1676.6 mm) concentrated from March to August. According to the distinct mineralogy of the ore, by using proper engineering design and operation parameter, a distinct low redox potential bioheapleaching system was established at Zijinshan plant. The unique characteristics of
the system include: a) low operating pH (0.8–1.0), high concentration of total iron (exceeded 50 g/L) and high temperature (up to 60 °C) in the Pregnant Leach Solution (PLS); and b) sulfur oxidizers were dominant in the heap. In this system, copper was recovered in high efficiency, excessive iron in the solution phase was removed by the formation of jarosite in the heap and free acid in the rafinate was neutralized by limestone. Thus iron was balanced at low cost. For water balance, solution was recycled in leach–SX system and copper-rich acid mine drainage was treated by membrane technology in dry season. In wet season, rafinates from leaching–SX process and acid mine drainage were neutralized with lime so as to meet national effluent discharge standards.

2. Mineralogy

According to previous mineralogical investigation (Dong and Ma, 1995; Ge, 2005) and recent MLA (Mineral Liberation Analysis, JKtech) analysis (Liang, 2010), pyrite predominates the sulfides in the ore. Part of the pyrite associates intimately with copper sulfides, rimed and cross-cut by copper sulfides (Figs. 1 and 2A). The main copper sulfides are digenite, covellite and enargite, accompanied by rare chalcocite, chalcopyrite and bornite. Most of the copper sulfides occur in form of sulfide aggregates, and coarse grains of sulfide aggregates are the most common form of copper minerals (Fig. 2).

The gangue minerals include quartz, dickite, alunite mainly, and minor amounts of sericite and feldspar. The matrix of gangue minerals in the ore body is dominantly quartz (about 70%) because almost all the feldspar grains in the granite host rock were replaced by clay minerals and secondary quartz during hydrothermal alteration process (Fig. 3). The collapse of the granite structure together with the intergrowth of the copper sulfides and clay minerals benefits the liberation of the copper sulfide from gangue minerals during crushing and leaching.

Table 1 shows the chemical composition in ROM of the commercial plant, indicating a high sulfur content. Table 2 reflects the mineral composition in ROM of Zijinshan copper ore. A high content of pyrite (5.8 wt.%) within the ROM would be responsible for large amount of acid and iron generated during the bioleaching process. Meanwhile, there is 11.67% of alunite inside the ROM, a sign of dissolved potassium ion for jarosite precipitation.

The leached residue was investigated by optical microscope. In the bioleach residue from industrial heap, leached digenite or covellite voids were readily observed. Fig. 4 shows the voids from leached copper sulfide.

3. Process description

3.1. Mining, comminution and ore stacking

Before year 2008, underground mining produced ROM ore that was transported to the crushing system with 20 t trolley locomotive. From year 2009, 60% of the ROM was from open-pit. The ROM ore smaller than 1 m was crushed by two stage crushing to a size of 80%
passing 40 mm. The dump truck was used to load ores to the heap area and the bulldozer was used to assist in the ore stacking. Average copper grade of the stacked ores was decreased from 0.42% in 2006 to 0.34% in 2009 with an average grade of 0.38%. The overall heap area was 0.2 million square meters. After leveling the bottom of the heap area, a prepared base was covered with 1 m of soil and sand. On top of the base, an impermeable liner comprising a 2 mm HDPE liner and plastic grid liner was used. Multi-lift permanent stacking was used. After the first lift was launched, raffinate was irrigated for 30–60 days, then on top of the first lift, the second lift was begun to stack, and so on. Currently, the heap consists of three lifts, each with a height of 8–10 m. The ROM was crushed to coarse particle sizes, which prevented fine particles from agglomerating to ensure permeability. Though the dump truck was used for ore stacking, good permeability inside the heap was achieved.

3.2. Bioheapleaching

In Oct. 2005, the heap was launched. Acid mine water was adjusted to a pH of 1.7 by dilute sulfuric acid (2%) before irrigated into the heap. Irrigation pipe system was arranged in 3 m × 3 m grid and sprinkler leaching was used with a solution irrigation rate around 12–16 L/m² h.

The heap was not aerated. The bioleaching system has five solution ponds for PLS (51,000 m³), irrigation (55,000 m³), raffinate (63,000 m³), flood collection (88,000 m³) and standby (41,000 m³), respectively. From March 2006 to Sept 2006, 131,964 m³ of solutions with high concentration of ferric from the pilot plant were continually applied to the commercial leach circuit. After the ferric-rich solution from the pilot plant was applied, the copper production increased significantly (Table 3), indicating the fact that a high ferric concentration facilitates copper dissolution.

Since the ore in Zijinshan copper bioheapleaching process contains high content of pyrite, acid and iron were produced from pyrite dissolution. Furthermore, the oxidation of reduced inorganic sulfur compound (RISC) generated heat which increased the temperature inside the heap. As a result, copper sulfide and pyrite dissolution was promoted. By using multi-lift permanent stacking and non-aeration, the heat loss was reduced and the temperature of PLS was maintained around 45–60 °C for the whole year (Fig. 5), thus we estimated that the temperature inside the heap may exceed 70 °C. Fig. 6 showed the variation in pH of PLS and iron concentration. It is clear that due to the high content of pyrite, the acidity and iron concentration were significantly increased during the operation. In Dec. 2007, the pH of PLS decreased to 0.85, at the same time, the acidity reached 30 g/L and the total iron concentration reached 50 g/L. The unusual low pH has negative effect on the subsequent solvent extraction process. Thus in 2008, a system was built for neutralization of the free acid within the raffinate, and the capacity was 200 m³/h. In this system, limestone was used and the pH of raffinate was elevated to 1.2. Since Oct. 2008, the pH and the Eh of PLS is maintained around 0.9–1.0 and 700–740 mV vs. SHE, respectively (Table 4). Due to the high temperature and high iron concentration, jarosite was formed inside the heap. SEM image showed that the formed jarosite crystal is crystallized with good integrality (Fig. 7) which is unable to block the mineral dissolution. As excessive iron could form jarosite in the heap, the iron concentration in the solution phase was stabilized. In the steady stage, the leaching system was maintained at high acid and iron concentrations, high salinity, and low pH which achieved high copper recovery (Table 5).

3.3. Solvent extraction (SX) and electrowinning (EW)

The SX unit was designed as a conventional 2E, 1W and 1S circuit (two-stage extraction, one-stage wash and one-stage stripping). Zijin 988 (produced by Zijin reagent plant) was selected as the copper extractant. 260# kerosene was used as diluent. The extractant volume percent is around 15–20%. Electrowinning is operating at a current density of 180 A/m² in 98 electrolytic cells. Copper and iron concentration in the tank house were 48 g/L and lower than 3 g/L respectively. Each electrolytic cell contains 54 cathodes and 55 anodes with a current efficiency around 85–90%. Standard cathodes copper
(Cu-CATH-2) is being stripped from stainless steel blanks, at a cathode weight around 40 kg each.

3.4. Water treatment

The mean annual rainfall and evaporation in Zijinshan are 1676.6 mm and 1300 mm respectively. As the rainfall is concentrated from March to August, the water balance in the leaching system is a challenge. There are three systems for water treatment which include one membrane system and two lime neutralization systems. The acid mine water produced by mining activity at Zijinshan plant contains Cu\(^{2+}\) of 273 mg/L, total Fe of 209 mg/L and pH of 2–3. Membrane technology was used to treat this acid mine water with a capacity of 3,300–3,600 m\(^3\)/d. The copper rich water (2 g/L Cu\(^{2+}\)) retained by the membrane treatment plant was directly pumped into the SX system. In the rainfall season, large amount of rain water would enter the leaching system, thus a flood collection and a standby pond was in use. Excessive water from the leaching system was reserved in flood collection pond. This water was treated by lime neutralization or solvent extraction depending on the copper concentration of the solution. Furthermore, excessive acid mine water in rainfall season was treated by another lime neutralization system. The solid waste residues from two lime neutralization system were proper stored in tailing storehouse. To improve water balance, there is a plan to expand the volume of the flood collection ponds and increase the capacity of the membrane system next year. Thus in the wet season, excessive water from the leaching system will be reserved and recycled, and all of the acid mine water will be treated by membrane system.

4. Microbial community structure succession

Microbial community succession was studied previously using 16S rRNA gene clone library and real-time quantitative PCR (polymerase chain reaction) (Chen et al., 2009; Liu et al., 2010). The dominant group in the acid mine water inoculated into the system was mainly Acidithiobacillus (unpublished data). After inoculation, the microbial community changed evidently. Fig. 8 showed the dramatic time-dependent community structure change in the system. In the start-up stage (June 2006), *Leptospirillum* is dominant which accounts for 74% of the community, and *Ferroplasma* is the only detected archaea which accounts for 6% of the whole prokaryotes. Pyrite dissolution might be accelerated by these prevailing iron oxidizers. While at steady operation stage (May 2008), the proportion of genus *Leptospirillum* was sharply reduced (from 48.5% to 5%) from higher depth to lower depth and reverse correlation of increased *A. ferrooxidans* (from 0.95% to 15.00%) and *S. thermotolerans* (from undetectable to 7.00%) were found in the system.
heap. Sulfur oxidizers including moderate thermophilic *A. albertensis* and *A. caldus* vertically increased from higher depth to lower depth (from 50.47% to 70.00%). Real-time PCR results were consistent with clone libraries, indicating that the growth of iron oxidizers was inhibited and the growth of sulfur oxidizers was achieved in this heap. Furthermore, cell number in the leaching solution was significantly decreased from 10⁶/mL (start-up stage) to 10⁴/mL (steady stage) (Chen et al., 2009; Liu et al., 2010).

### 5. Discussion

Commercial operation of Zijinshan bioheapleaching plant has overcome the difficulties caused by a high content of pyrite in the feed and a high average annual rainfall. Technical measures were effectively implemented to achieve high copper recovery and low cost of acid and iron removal. A successful operation of Zijinshan bioheapleaching system has demonstrated the adaptability of the system for broad applications according to mineralogy and external environment.

Compared with many other copper mines, the copper grade of ROM at the Zijinshan copper mine is relatively low (0.4%), with a high content of pyrite. Besides, low content of acid consuming gangues was presented in the ROM. As a result, acid and iron might be accumulated in the leaching solution system during the bioleaching process, (Tables 3 and 4) and leaching temperature may increase. With regard to the secondary copper sulfide (digenite and chalcocite), the leaching process in acid and iron solutions could be divided into two stages. In the first stage, copper was removed from secondary copper sulfide and covellite-like product was produced. Previous research revealed that the first stage leaching of chalcocite is very fast compared with the second stage, and the second dissolution stage is slow (Dutrizac and MacDonald, 1974), which makes the second stage the rate-determine step. Investigation for the second stage leaching kinetics of chalcocite showed that high iron concentration and high temperature could speed up the oxidation rate of second leaching stage (Marcantonio, 1976; Bolorunduro, 1999). Previous research also noted that elevated temperature could improve the leaching kinetics of covellite and engargite more effectively than chalcocite (Lee, et al., 2011; Dew, et al., 1999). Thus relative high copper recovery (more than 80 wt%.) was achieved in Zijinshan bioheapleaching system as a result of high ferric concentration maintained in the leaching solution and high temperature inside the heap (Table 5).

In bioheapleaching system, dominance of iron oxidizers, especially genus *Leptospirillum*, could effectively oxidize Fe²⁺ to Fe³⁺. As a result, ferric supply by microbial oxidation may be higher than ferric demand for mineral oxidation and the redox potential may increase. This observation was verified by previous research that dominance of *Leptospirillum* in copper sulfide bioheapleaching system was correlated with fast ferrous oxidation and the increase of Eh to 800 mV vs. SHE in the initial leaching stage (Demergasso, 2005; Demergasso et al., 2005). But for an Eh that is lower between 700 and 760 mV vs. SHE, pyrite dissolution was limited while secondary copper sulfide still has good leaching kinetics. However, pyrite dissolution could be accelerated when Eh is higher than 800 mV vs. SHE as observed by Wu (Wu et al., 2009). High acidity, high iron concentration and high salinity were maintained in the Zijinshan bioheapleaching system by recycling the leaching solution system continuously. Multi-lift permanent stacking was used to keep the heap in high temperature. Under such environment, the growth and ferrous oxidation of genus *Leptospirillum* was inhibited, which was consistent with previous research outcomes (Bestamin et al., 2007; Jochen and Ojumub, 2007; Penev and Karamaneva, 2009). Thus the Eh of Zijinshan leaching system was kept in low level (710–740 mV vs. SHE), and the dissolution of pyrite was restricted.

Previous research noted that jarosite could be formed under conditions of high ferric concentration, low pH value and elevated temperature (Rabald, 1961). Such environment was created in the
Zijinshan heap due to the distinct mineralogy and technical measure listed above. As a result, jarosite was easily formed in the Zijinshan heap, and neutralization was against free acid but not iron. The expense for iron and acid removal was decreased.

A number of cost cutting measures were implemented such as multi-lift permanent stacking, large particle size (80% passing 40 mm), ore stacking by dump truck, non-aeration and non-agglomeration to achieve a low operating cost of 1.10 USD/lb, even though the average copper grade of ROM was continually decreased to as low as 0.38%.

Bioleaching practice in Zijinshan plant showed that high concentration of ferric ion and elevated temperature could facilitate copper leaching with low bacteria activity. This is consistent with Marcantonio and Samuel’s observation (Marcantonio, 1976; Borolunduro, 2009), two technical measures might improve kinetics of copper dissolution, namely, a) increase of heap height or heap temperature and; b) direct addition of $\text{Fe}_2(\text{SO}_4)_3$ into the leaching system or fast dissolution of pyrite during the start-up stage to increase the ferric concentration of the solution.

To further optimize iron balance in the Zijinshan plant, research projects are being conducted on the kinetics of pyrite dissolution and jarosite formation under conditions of high ferric concentration and elevated temperature as well as on optimum heap height and irrigation rate to better control heap temperature.

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References


Dong, L., Ma, X., 1995. Mineralogical Investigation for Zijinshan Copper Ore by Optical Microscope. Zijin Research Institute, (Fujian), Shanghang.

Huang, X., 2010. Special Audit for Zijin Mining Group Co., Ltd., Chengxing Public Accounting Firm (Fujian), Fuzhou.


