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Industrial applications of green circulation and biological extraction of copper from low grade copper ore

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Abstract

In China, the first heap bioleaching plant with annual capacity of 10,000 tons cathode copper was established by Zijinshan copper mine in December 2005. With a long time production of closed cycle, problems like excess acid, iron accumulation and water balance were occurred due to the special characteristics of ore, geographical environment and climate. It was found that the excess dissolution of pyrite was an important factor leading to low productive efficiency. Aiming at this problem, a selective-bioleaching test with 10,000 tons ore was conducted and an annual output of 30,000 tons of cathode copper heap bioleaching-solvent extraction-electrowinning plant was re-established in 2012. During the test, ore particle size was crushed to -40 mm. By using engineering technologies, such as spraying and leisure regulation, free acid neutralization and raffinate COD concentration control, the oxygen concentration of the inside heap was controlled in a lower level, and solution pH, heap temperature and ORP was regulated with 1.5~1.7, ~40 °C and <760 mV (vs. SHE). Therefore, jarosite was self-generated in the heap, and reduced the content of iron in the solution, and sulfur oxidizer dominated microbial community was thus formed. After a leaching period of 227 days, copper leaching rate was reached 82.4%, and iron leaching rate was controlled at 6.2%. The results showed that the selective-bioleaching of Cu from low grade copper ore was succussed. During the application of the new technology in the past five years, a total of 79266.16 tons cathode copper was produced from low grade ore of less than 0.3 % with the production cost of less than 22,000 ￥/t•Cu. The industrial applications of green circulation and biological extraction of copper from low grade copper ore was achieved.

Keywords: industrial application, selective-bioleaching, low-grade, chalcocite, acidophiles

1. INTRODUCTION

Zijinshan gold-copper mine is located in Shanghang county, Fujian province, China. The climate of this area is subtropical monsoon climate, and the average annual temperature and rainfall are 19.8 ℃ and 1537.2 mm, respectively. The mine is one of the largest non-ferrous metal mines discovered and proven in China in the 1980s, and it is a typical gold-copper symbiosis. The gold deposits and copper deposits are all reach large-scale porphyry deposits. The copper mine is a low-grade copper sulfide ore in the primary zone below 600-700 meters, which is the largest low-grade secondary sulfide copper mine in China. The copper and metal industrial reserves approved by National Commission of Mineral Reserves were 1.966 million t, with an average grade of Cu 0.42 %, S 2.58 % and As 0.037 %. The ore contains a high level of sulfur and low copper secondary copper sulfide ore. The main component is copper, mainly existed in the form of its independent mineral output, and the harmful element is arsenic. Due to low copper grade and high arsenic content, it is difficult to treat it by traditional flotation process. Since 1998, General Research Institute for Nonferrous Metals has carried out a series of research, and the results showed that the biological heap leaching of Zijinshan copper mine was feasible (Zhou GY et al, 2008), (Wen JK et al, 2006), (Wu LD, 2003), (Wang GS et al, 2004). Up to now, the mine has built a bio-heap leaching-extraction-electrodeposition copper plant with an annual output of 30,000 tons of cathode copper.

2. RESEARCH COURSE

In the early 1990s, the Zijinshan copper mine built a small flotation plant with a daily processing capacity of 300t to produce copper concentrate for selling. The results of the traditional smelting test showed there are many problems such as high investment, high cost, heavy pollution and no economic benefits need to solve due to the low quality of primary ore. In 1998, General Research Institute for Nonferrous Metals carried out a great deal of research of biological leaching for copper, the results showed that Zijinshan copper mine was suitable for bacterial leaching and the leaching rate of copper reached 88.29%. In 1999, the column leaching experiment was carried out in a period of 167 days with results as follows: the copper leaching rate reached 80.75%, the extraction rate of Cu was 96.00% and the anti-extraction rate was 91.30% (Wen JK, 1999). In December 2000, biological heap leaching-extraction-electrodeposition industrial test research was carried out and cathode copper production was 300 t/a. In 2002, the cathode copper production expanded to 1000 t/a (Wen JK, 2003). From 2003 to 2005, the scale of production was expanded to 10,000 t/a. With a long time production of closed cycle, problems like excess acid, iron accumulation and water balance were occurred due to the special characteristics of ore, geographical environment and climate. Therefore, some research about biological selective leaching was carried out to solve these problems.

3. SELECTIVE BIOLEACHING INDUSTRIAL TEST

The industrial test area was about 50,000 square meters, and the test area was divided into five areas, numbered A1-1, A1-2, A1-3, A1-4 and A1-5, respectively. The test sample was crushed to -40 mm, and then built an 8-meter-high heap. The total amount of ore in the pile is 751,000 tons, the average grade of copper metal and iron were 0.31% and 2.70%, respectively. The selective leaching of copper was achieved by controlling the parameters such as pH value, potential, temperature, bacteria and oxygen content during the test. The process flow diagram is shown in Figure 1.

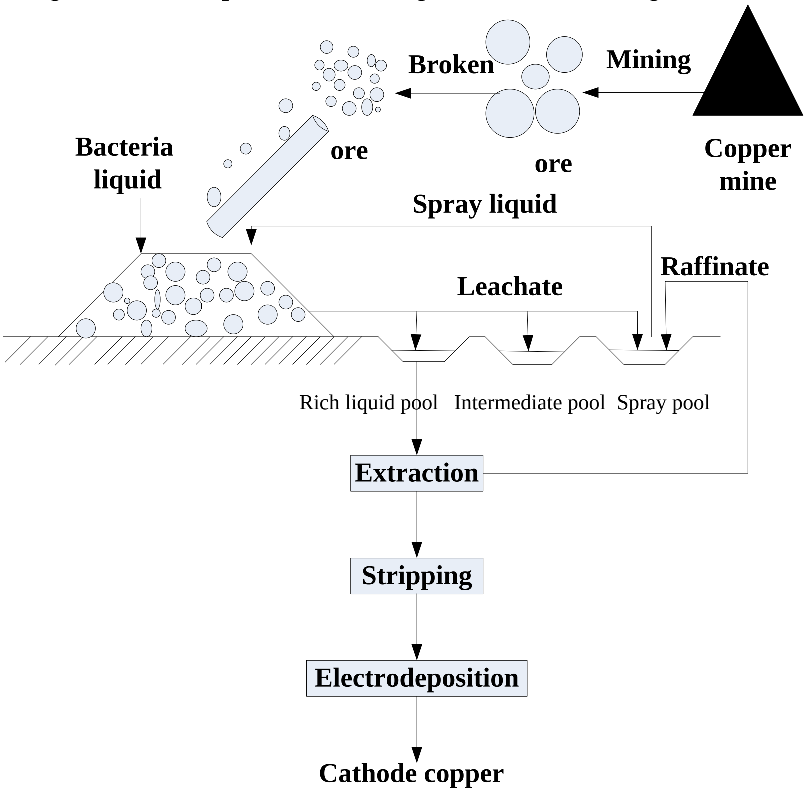

Figure 1. The process flow diagram of bioleaching-solvent and extraction-electrowinning

3.1. Ore samples

The sample chemical multi-element analysis is shown in the table 1. The results shows that the average grade of copper metal and iron are 0.31% and 2.70%, respectively. The MLA analysis indicates that the copper minerals in the samples are mainly existed in the form of chalcopyrite, digenite, covellite and enargite, which accompanied by a small amount of mawsonite, arsenosulvanit and bornite. The existence form of sulfur and ferrous minerals are mainly pyrite, and gangue minerals are mainly silicate ores.

Table 1. The results of multi-element analysis of ore samples

chemical composition	Cu	S	Fe	As	SiO_2	Al_2O_3	CaO	K_2O	Na_2O	MgO
content（%）	0.31	3.51	2.70	0.02	78.77	14.17	0.07	1.48	0.06	0.05

3.2. Industrial amplification and inoculation of bacterial species

The initial bacteria group contained sulfur oxidative bacteria 48.98%, iron oxide bacteria 36.73% and heterotrophic bacteria 14.29%. The flora were first cultured to 500 L through a three-stage culture, and then cultured to 1000 m^3 through the field amplification. Sprinkle the dilute sulfuric acid solution with pH value of 1.3 into the ore heap until the pH of the leachate flowing out of the ore heap reached 1.5, and then inoculate the bacteria into the ore.

3.3. Biological leaching

Copper ore was leached by spraying, and different spray systems were used in different leaching stages. The volume of spray solution was measured by flow meter. In order to meet the pH range needed for the growth of the sulfur oxidizing bacteria, the pH value of the sprayed liquid was kept between 1.5 and 1.7. By limiting the supply of oxygen, controlling leached liquid potential <760 mV (vs. SHE), maintaining temperature of inside pile at about 40 ℃, the community structure leaching system with the advantage of sulfur-oxidizing bacteria as the dominant flora was generated. On the one hand, the dissolution of pyrite was strongly inhibited, and on the other hand, the jarosite was generated in the heap, thereby the content of iron in the solution was declined. The variations of copper and iron leaching rate during the heap leaching process were demonstrated in Figure 2 and 3.

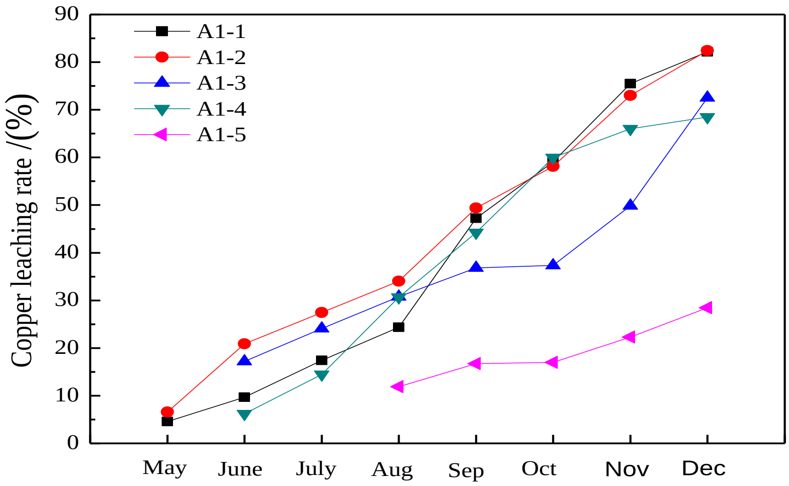

Figure 2. The copper leaching rate of each experimental area

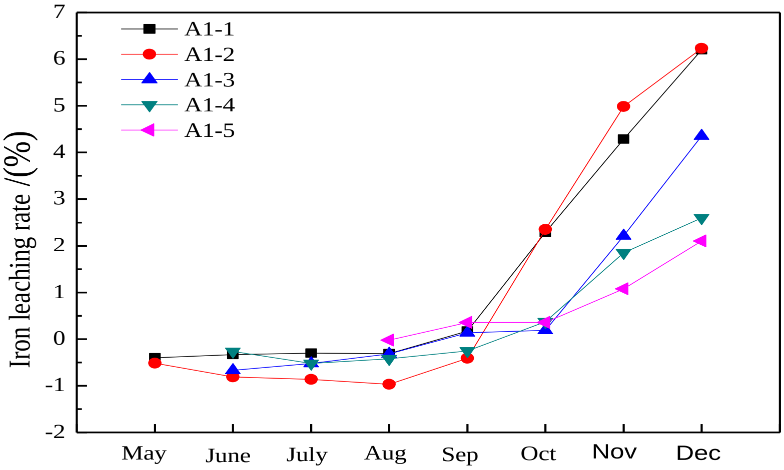

Figure 3. The iron leaching rate of each experimental area

With the inceeased leaching time, the leaching rate of copper was gradually increased. After 3 months, copper leaching rate can be reached to 35%. From 6 to 7 months the copper leaching rate rised from ~70% to ~80%. Finally the copper leaching rate was 82.4% when the industrial test lasted 227 days. The leaching rate of iron in the first 5 months was negative, because some of the iron ions in the leachate were hydrolyzed or precipitated in the heap. The iron leaching rate increased with the oxidation of pyrite in the reactor in the later stage of leaching, but the total iron leaching rate was only 4.1% ~ 6.2%. Thus, the goal of selective bio-leaching of copper was realized, and the problems of excess acid, iron accumulation and water balance wre effectively solved.

3.4. Metal recovery

The extraction of copper in the leachate was recovered by extraction and electrodeposition and the raffinate was returned to circulation.

4. INDUSTRIAL APPLICATION OF SELECTIVE BIOLEACHING

The industrial applications of green circulation and biological extraction of copper from low grade copper ore was achieved, and it was shown in the Figure 4. An annual output of 30,000 tons of cathode copper heap bioleaching plant was built in Shanghang county, Fujian province, China. The solution pool system includes rich liquid pool, intermediate pool and spray pool and the overall storage capacity is 487,000 m^3. The flood control pool adjustment system consists of two pools, with the maximum capacity of 600,000 m^3. The ore was crushed to -40 mm, and the layer height was 8~12 m. The second and the third layer were built after 6 months, respectively. Different spray system was used at different leaching stages, in the first stages of leaching, the pile was sprayed every other day, in the middle stages was sprayed every 4 days, and sprayed every 8 days in the last days. In the whole stages, the raffinate was used as leaching agent and the waste acid mine water was used for spraying. After the stable operation in 2012, the copper leaching rate reached >75% in condition of copper grade of the ore <0.30% and leaching periods < 200 days. The production of cathode copper was 79266.16 tons, and the production cost was lower than 22,000 ￥/t. Compared with the traditional process, there was a significant environmental benefit because of zero release of CO_2, SO_2 and other gas.

Figure 4. Application of bio - heap leaching industry

5. ACKNOWLEDGMENTS

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