Effectiveness of bacterial sulfidation flotation for the separation of malachite: Impact of pH, sulfide concentration and sulfidation time

Xu Wang¹, Yaozong Chen¹, Zibo Song¹, Mengfei Liu¹, Min Gan¹,*, Jianyu Zhu¹,² and Daixiong Chen², c

¹ School of Minerals Processing and Bioengineering, Central South University, Changsha, Hunan Province, 410083, China
² Hunan Provincial Key Laboratory of Complex Copper Lead Zinc Associated Metal Resources Comprehensive Utilization, Hunan Research Institute for Nonferrous Metals, Hunan Province, 410199, China
*email: ganmin0803@sina.com; cemail: chendaixiong888@163.com
b*Corresponding author’s e-mail: zhujy@csu.edu.cn;

Abstract. Previous research paid less attention on the mechanism and application of bacterial sulfidation in mineral flotation. In this study, sulfate reducing bacteria strains reduce sulfate to produce sulfides, which are used as sulfidizing reagents for malachite. Then, the system influence factors such as pH, sulfides concentration and sulfidation time are controlled. The results showed that the most suitable conditions of malachite bacterial sulfidation system were pH of 9.0, sulfide concentration of 140mg/L and sulfidation time of 15mins. For further study, SEM and FTIR were used to perform of sulfide film formed on the surface of malachite. The result of sulfide film on the malachite surface is compact, and the malachite flotation properties are greatly improved after bacterial sulfidation.

1. Introduction

Copper resources is abundant all over the world, but with less rich ore, ore, ore and more dispersed, and there are a variety of metal deposits associated with low-grade ore, refractory copper oxide ore with a large proportion of the development and utilization of the bottleneck problem is more prominent. In order to improve the supply of copper metal in China and develop green, efficient and low-cost low-grade and refractory copper resources, the key technology problems need to be solved urgently.

Copper oxide ore is a typical copper mineral resource with low grade, high oxidation rate[1]and high bonding rate[2]. According to its different properties, there are many corresponding processing and processing schemes at present. Flotation and chemical beneficiation are mainly two processes for copper oxide ore processing. Under the assistance of collectors, flotation method can direct deal with copper oxide ore without prior sulfidation in the early stage. However, it was gradually replaced by sulfide flotation due to limited applicability and poor flotation index[3]. Sulfide flotation method makes the mineral surface form a copper sulfide film under the action of sulfiding agents, and then use xanthate as a collector for flotation[4, 5].

Sulphidation is the key step of sulphide flotation because its quality determines the effect of
sulphidation flotation. Traditional sulfidation technology hold extensive application range, but selectivity generally poor, sodium sulfide dosage control not easy, and process complex. The calcination and hydrothermal sulfidation process requires high-temperature high-pressure apparatus, which is costly and can cause air pollution. Therefore, it is very important to develop a low cost, green and environmentally friendly mineral sulfidation treatment technology for low grade copper oxide ore. The biological sulfidation is a promising alternative method owing to cost-effect, simple operation process, and environmental friendliness.

In this study, the reduction effect of sulfate-reducing bacteria was used to sulfide the copper oxide ore-malachite. By analyzing the surface morphology, the changes of elements and the structure of the group molecules, the effects of sulfate-reducing bacteria and mineral sulfates were clarified, and preliminary explorations were made for the practical application of biological sulfidation flotation.

2. Materials and methods

2.1. Minerals and reagents

The malachite used in this experiment form Libya. Butyl xanthate, 2#oil, BX and BP-1# were all industrial products and obtained from Zhuzhou mineral processing pharmaceutical factory, Hunan province, China; sulphuric acid and sodium hydroxide are all analytically grade.

2.2. Enrichment and culture of sulfate reducing bacteria
The sulphate-reducing bacteria used in the experiments were enriched in an anaerobic environment from the Xiangjiang River substrate. After each inoculation, the medium was filled into 100mL anaerobic bottles, sealed with liquid paraffin solution and rubber stoppers. The anaerobic flasks were incubated at 30°C and counted regularly during the incubation.

2.3. Characterization
The formation and distribution of sulphide films on ore surface before and after reaction were observed and analyzed using a scanning electron microscope (SEM) (JV-82C). The NEXUS-670 FTIR spectroscopy was used to determine the infrared spectra of mineral samples, drug samples, minerals after the action of pharmaceuticals and minerals.

2.4. Batch experiment
The effects of the initial pH, sulphide concentration and sulphation time on bio-sulphidation were investigated. The pH was adjusted with 0.1M H₂SO₄ and 0.1M NaOH. After the sulfidation was completed, the liquid was poured, and the mineral was washed into the flotation machine with distilled water. After filling the distilled water into the slot, the flotation experiment was carried out. The fixed collector was 80mg/L butyl xanthate, the foaming agent was 50 mg/L 2# oil, the collecting time set as 1min.

2.5. Analytical method
The concentration of sulphide in the solution was determined using methylene blue spectrophotometry at 665nm.

3. Results and discussion

3.1. Characterizations
As shown in Figure 1 (a), the surface of the raw ore is smooth and there is no sediment. After 1min, 5min, and 30min of biological sulfidation (Figure 1(b-d)), it can be seen that the mineral surface has the formation of vulcanized layer, and the sulfide deposits on the mineral surface keep increasing with sulfidation time. After 24 h of bio-sulfidation (Figure 1 (e)), the sulphide deposits on mineral surfaces become thicker than short-time treatment.
Figure 1 SEM image of raw mineral (a), 1min (b), 5min (c), 30min (d) and 24h (e) of bio-sulfuration treatment.

Figure 2 shows the FTIR spectra of malachite before and after butyl xanthate treatment. The vibration absorption of -OH of Malachite at 3415.11cm⁻¹ is still clear after butyl xanthate treated, and the C-H of used dibutyl Xanthate (2963.89cm⁻¹ and 2873.09cm⁻¹) is obviously weakened. At the peaks of 1203.63cm⁻¹ and 1110.08cm⁻¹, the C-O-C shifted considerably in xanthate.

The chemical adsorption of butyl xanthate in the action of Malachite was compared before and after reaction, but by calculating the ester water separation coefficient (LogP) of butyl xanthate, the LogP value of butyl xanthate was only 2.48. The hydrophobicity of Malachite was slightly improved by the simple xanthate adsorption. The xanthate of butyl xanthate was found in the flotation experiment, which attributed to the huge consumption of unactivated Malachite minerals. From Malachite ore (Figure 2 (b)), the peaks at 3405cm⁻¹ and 3317cm⁻¹ corresponded to the hydroxyl groups; the 1099cm⁻¹ is the symmetrical telescopic vibration absorption peak of CO₃²⁻, the peaks at 875cm⁻¹, 748cm⁻¹ and 519cm⁻¹ attributed to the special CO₃²⁻. After biological sulfidation, the absorption peak of the hydroxy expansion vibration of malachite and the absorption peak of the flexural vibration are still clearly visible, while the carbonate roots at 519cm⁻¹ is weakened, and the new absorption peak is not formed at 502cm⁻¹, indicating the formation of copper sulfide loaded on mineral surface.

Figure 2 FTIR of butyl xanthate and Malachite before and after action (a) and malachite at different sulfidation times (b)

3.2. Growth curve of bacteria and changes in system sulfides
The growth curve of sulfate reducing bacteria is as shown in Figure 1. It can be seen from the map that the sulfate reducing bacteria entered the logarithmic growth period after one day of inoculation and entered the stable period on the third day, and still did not enter the decline period after two days of smooth growth. As shown in Figure 2, by measuring the content of sulphides dried in the process of
bacterial culture and comparing Figure 1, it can be found that the content of sulphide in the system is approximate to the growth curve of bacteria. It enters logarithmic growth period after a day of inoculation, and reaches the peak in third days, and the peak of sulphide concentration can reach more than 180mg/L. After third days of culture, the high sulphide concentration of the curing system can meet the needs of the biological sulfidation malachite.

![Figure 3 Growth curve of sulfate reducing bacteria (a) and variation of sulfide within bacterial culture](image)

**3.3. Effect of sulfidation system conditions on bio sulfidation flotation**

**3.3.1. The effect of pH**

Figure 4 (a) shows that the pure minerals of peacock stone are under biological sulfidation. The recovery rate in the range of pH from 4 to 9 increased with the increase of sulfidation pH, reaching the maximum at pH=9, and the recovery rate decreases when pH continues to rise, and the decline trend is more intense when it exceeds 10. It can be seen that the optimum pH for the biological sulfidation of the peacock stone is about 9. When the sulfide environment pH is strongly alkaline, it has a greater negative effect on flotation.
3.3.2. The effect of sulfide concentration

Figure 4 (b) shows that the recovery rate of Malachite increased with the increase of sulfide concentration in the biological sulfidation system. The recovery of pure minerals of peacock stone reached the highest when the concentration of sulfide reached 140 mg/L. With the further increase of sulfide content, the excess of sulfide in the system has no obvious inhibitory effect on the flotation of malachite. It shows that the inhibition of the flotation of Malachite by excessive use of vulcanizing agent is mainly caused by the effect of the remaining HS\(^-\) and S\(^2-\) on the mineral and the collector and the floatation of the collector. In the process of biological sulfidation, excessive sulphide only exists in the sulfidation system and does not enter the flotation system. Excessive HS\(^-\) and S\(^2-\) have no obvious adverse effects on the formation of mineral surface sulfidation film.

3.3.3. The effect of sulfidation time

Figure 4 (c) shows the rule of the recovery rate of pure mineral from peacock stone with the curing time. It can be seen from the diagram that the recovery rate of Malachite increases with the increase of curing time when the sulfidation time is 1 min to 10 min, and the recovery rate of malachite is above 55% when the sulfidation time is 10 min to 30 min, and the recovery rate of Malachite has a tendency to decrease obviously. It shows that the best curing time of biological sulfidation should be limited to 10 min to 30 min, and the longer curing time will lead to worse curing effect.

3.4. Dynamic potential analysis of before and after sulfidation

Figure 5 (a) shows the relationship between the dynamic potential, pH of Malachite raw ore and the ore samples bio-sulfidation treatment and chemical sulfidation is placed in Zeta 8. Under higher pH conditions, the malachite surface is negatively charged, while the malachite surface is positive with low and neutral pH, and the potential from positive to negative is pH=9.8, which is the isoelectric point of the original ore. Figure 5 (b) shows that the kinetic potential and the isoelectric point of the malachite surface changed obviously after biochemical sulfidation. The sulfidation treatment makes the mineral surface dynamic potential keep negative in a wide pH range, while the IEP in chemical sulfidation is shifted left, and IEP was disappeared in the biological sulfidation. The Zeta potential value of the mineral surface is negatively shifted and the IEP value of the mineral is reduced by sulfidation, indicating that the reaction of HS\(^-\) in the sulfide solution to Cu\(^2+\) ions on the malachite surface produces CuS film and is adsorbed on the surface of the mineral. Compared with chemical sulfidation, the adsorption in biological sulfidation is more thorough, and the chemisorption of sulfidation agent and mineral surface is more intense.
4. Conclusions
In this work, malachite was sulphated using sulphate-reducing bacteria and the effect of each single factor condition on the bio-sulphidation was investigated. Results shows that the mineral surface formed dense sulfidation film after biological sulfidation, which significantly improved the flotation performance of malachite. The pH value, sulphide concentration and sulfidation time in the biological sulfidation system have great influence on the flotation effect of malachite. The most suitable conditions for the malachite biological sulfidation flotation are the sulfidation system pH=9.0, the sulphide concentration 140mg/L, and the sulfidation time 15min. All of our results demonstrated that the bio-sulphidation shows great potential to be a new strategy for sulphiding copper oxide ores.

Acknowledgements
This work was supported by the National Natural Science Foundation of China NO.41773089.

References
[1] P. Ding, Q.J. Liu, W.H. Pang, Study on Beneficiation of a Low-Grade Refractory Copper Oxide Ore in Tajikistan, Advanced Materials Research, 676 (2013) 85-88.
[2] G. Zou, Z.L. Wu, X.K. Lai, L.C. Zou, R.M. Ruan, S. Papirio, J. Puhakka, Column Bioleaching of Low Grade Copper Sulfide Ore at Extreme Conditions for Most Mineral Processing Bacteria, Advanced Materials Research, 825 (2013) 318-321.
[3] P. Abhyarthana, R. Venugopal, Investigation of Adsorption Mechanism of Reagents (Surfactants) System and its Applicability in Iron Ore Flotation – An Overview, Colloids and Interface Science Communications, 25 (2018) 41-65.
[4] H. Matsuoka, K. Mitsuhashi, M. Kawata, T. Kato, A. Shibayama, Surface properties of copper-sulfide minerals with sodium-hydrosulfide activation, Minerals Engineering, 156 (2020) 106530.
[5] I. Ancutiene, V. Janickis, R. Ivanauskas, R. Stokiene, N. Kreiveniene, Preparation and some properties of conductive copper sulfide, Cu xS, films formed on the polymers surface by the use of polythionic acids, Polish journal of chemistry, 81 (2007) 381-391.