

Bacterial leaching of discarded copper ores from Yongping, China

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Abstract: The elementary and phase analysis of discarded copper ores from Yongping of China has been performed. The experiments of extracting copper from the discarded copper ores were done with the mixed bacteria obtained through a series of enrichment, separation, domestication and combination tests. The results show that in the process of bioleaching, the pH value rises at first and drops gradually. The E_h value keeps rising along with the time and the appropriate E_h value varying between 750 and 800 mV will benefit the bioleaching copper. The high concentration of ferric ions is detrimental to the bioleaching copper. The results of bioleaching copper are good. That is, the copper recovery is 31.8% after 27 days.

Key words: bioleaching; discarded copper ores; mixed bacteria

1 Introduction

At present, mineral resources are going to be short-age bit by bit. However, the consumption of them is being increased and the consciousness of environmental protection is being strengthened. Therefore, recycling useful metals from discarded ores has been urgent affairs. In all kinds of technologies applied on dealing with discarded ores, bioleaching [1-3] is given more attention. Bioleaching has a potential usefulness and capacious exploited foreground because of lower cost, simpler manipulation, shorter industrial flow and lower pollution. Bioleaching begins to challenge with traditional technologies and offers a new approach on recycling useful metals from low-grade mineral ores or discarded ores. The copper mine from Yongping of China brings a mass of discarded ores in the process of exploitation. The successful application of bioleaching technology to the copper mine not only can recycle copper, but also can deal with environmental pollution. In this paper, the experiments of bioleaching copper ores are proceeded with mixed bacteria (*Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*) in order to discuss about a series of bioleaching parameters and provide technical foundation for the half-industrial trial and the industrial production on the based of those analysis.

2 Experiment

2.1 Microorganisms

The mixed bacteria (*Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*), gained from an acidic water

at Yongping's copper mine through a series of enrichment, separation, domestication and combination tests, was maintained at pH=1.80, $4 \text{ g}\cdot\text{L}^{-1} \text{ Fe}^{2+}$ and 30°C through numerous serial cultures with the discarded copper ores (10wt%) as the sole substrate. It was adapted to copper ores as the sole energy source. The aqueous growth medium [4] is a 9K+S culture containing 3 g $(\text{NH}_4)_2\text{SO}_4$, 0.1 g KCl, 0.5 g K_2HPO_4 , 0.5 g $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$, 0.01 g $\text{Ca}(\text{NO}_3)_2$ and 1 g S per litre, adjusted to pH=1.80 with sulphuric acid.

2.2 Discarded copper ores from Yongping

The discarded copper ores from Yongping were pulverized in a ring earthen bowl. The fine copper ores, with a particle size of about less than 5 mm, were used for all bioleaching experiments. The analytical composition of the copper ores and the copper phase were determined by quantitative X-ray diffraction (tables 1 and 2).

2.3 Procedures of bioleaching experiments

All bioleaching experiments were performed in 250 mL Erlenmeyer shake flasks, containing 100 mL of leach solution. Flasks were placed on an orbital shaker (130 r/min) and incubated at 30°C . The growth medium was a 9K+S culture. The pH value was adjusted to 1.20-1.50 (at the beginning, pH=1.20) with sulphuric acid. The pulp density was 25wt%, Fe^{2+} was $1 \text{ g}\cdot\text{L}^{-1}$ and the inoculation concentration was 10vol%.

2.4 Analytical methods

The soluble copper was determined by atomic absorption spectrophotometry (AAS). Ferrous ions and

ferric ions were determined by titration with EDTA. The pH value was measured at each sampling interval by a pH probe calibrated with a low pH buffer. The E_h value was measured with an Ag/AgCl chloride double reference oxidation-reduction probe. Redox electrodes

were tested periodically by placing in a solution of pH buffer saturated with quinhydrone at 25°C. The Ag/AgCl reference probes gave a reading of 263 mV in this solution [5].

Table 1 Chemical composition of the copper ores

									wt%
SiO ₂	Al ₂ O ₃	Fe	P ₂ O ₅	MgO	CaO	Na ₂ O	K ₂ O	Cu	S
45.00	6.74	15.58	0.050	1.80	8.38	0.26	1.76	0.40	13.36

Table 2 Phase of copper in the discard copper ores

					wt%
Phase	Dissociative oxidated copper	Associative oxidated copper	Subproterozoic sulfureted copper	Proterozoic sulfureted copper	Total of copper
content	0.0053	0.0026	0.0074	0.38	0.40

3 Results and discussion

3.1 Analysis of pH

The pH values varying with bioleaching time in the bioleaching solution are shown in **table 3**. At the beginning of bioleaching, the pH value rises rapidly. During this period, the pH value is mainly adjusted to

1.20-1.50 with sulphuric acid. After about 10 days, the pH value in the bioleaching solution begins to drop slowly. It indicates that after about 10 days, *Thiobacillus thiooxidans* begins to develop, comes into action, counteracts the alkaline substance and makes the pH value in the bioleaching solution drop slowly.

Table 3 Values of pH varying with bioleaching time

Time/day	0	0.34	1	2	3	4	5	6	7
pH	1.18	1.30	1.48→1.20	1.51→1.20	1.59→1.20	1.44→1.20	1.49→1.20	1.40	1.48
Time/day	8	9	10	11	12	13	17	18	20
pH	1.62→1.20	1.37	1.46→1.20	1.31	1.35	1.32	1.20	1.19	1.21
Time/day	22	24	27	30	33	37	41		
pH	1.20	1.25	1.37	1.25	1.28	1.22	1.33		

3.2 Analysis of iron

From **figure 1** it can be seen that *Thiobacillus ferrooxidans* in the bioleaching solution can be quickly adapted to ores and begins to develop after 4 days. The transformation rate of ferrous ions is about 85%. But with the bioleaching time increasing, the transformation rate of ferrous ions fluctuates around 85%, the total iron concentration still keeps to increase. It

shows that the development of *Thiobacillus ferrooxidans* is restrained. When the leaching time is 17 days, Fe²⁺ in the bioleaching solution is transformed completely. It indicates that *Thiobacillus ferrooxidans* can be adapted to ores again. At the same time, the increased rate of iron keeps to enlarge constantly. Moreover, the increased rate of iron is very high and reaches 289.30% (**figure 2**).

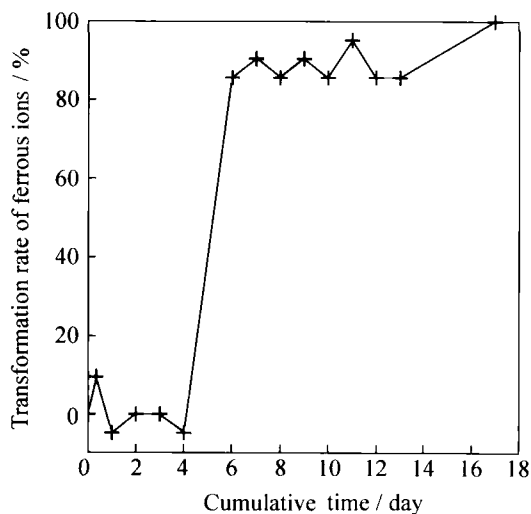


Figure 1 Relationship between the transformation rate of ferrous ions and bioleaching time.

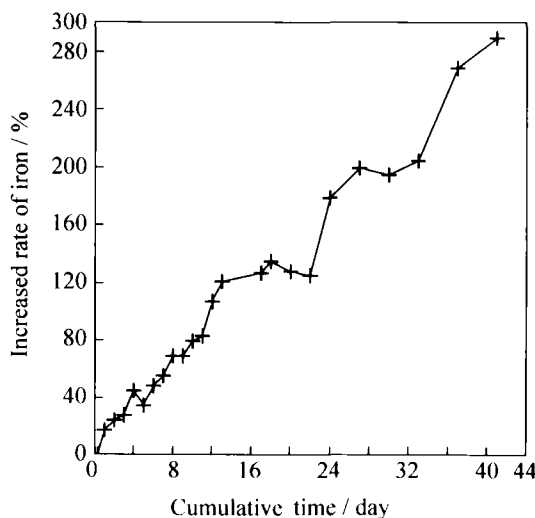


Figure 2 Relationship between the increased rate of iron and bioleaching time.

3.3 Analysis of E_h

After 4 days, the E_h value begins to rise quickly (figure 3). It indicates that *Thiobacillus thiooxidans* can be adapted to ores quickly and come into action. While, the E_h value begins to drop a little when the leaching time is 13 days, then it continues to rise slowly. After 13 days, the E_h value increases very slowly. In a word, the E_h value changes from 725 to 760 mV during the following 14 days. It shows that *Thiobacillus thiooxidans* has been restrained during this time. After 27 days, it begins to increase quickly and then reaches about 800 mV. At this time, it can indicate again that *Thiobacillus thiooxidans* can be adapted to bioleaching ores and develop very well.

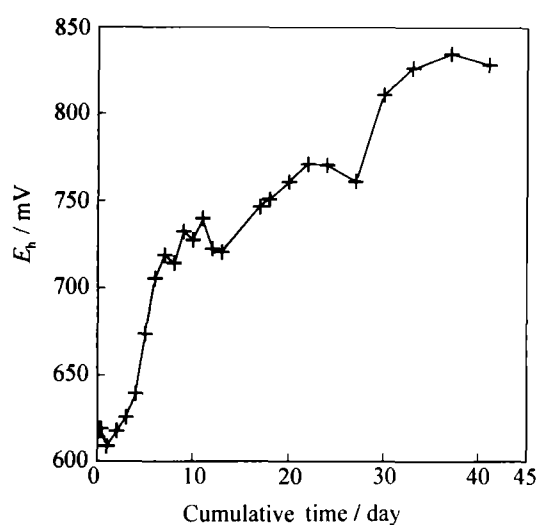


Figure 3 Relationship between the E_h value and bioleaching time.

3.4 Analysis of copper recovery

Along with the bioleaching time increasing, the mixed bacteria begin to be adapted to copper ores and play an important role. At the same time, ferrous iron

is transformed completely when the leaching time is 17 days, the copper recovery is also increasing (figure 4). At the same time, the copper recovery begins to increase quickly and reaches 14.8%. When the bioleaching time is 27 days, the copper recovery is 31.8%. From the former analysis of E_h and iron, it shows that the E_h value fluctuates between 750 and 800 mV and the increased rate of iron varies from about 120% to about 200% during this time. After 27 days, the copper recovery begins to increase slowly. At this time, the E_h value keeps increasing and reaches about 800 mV. Furthermore, the increased rate of iron is above 200%. It shows that the E_h value (750-800 mV) and the appropriate Fe^{3+} will benefit the bioleaching copper. This result is also similar to the correlative report [6].

Lastly, compared with the correlative report [7] (table 4), the results of this study are better.

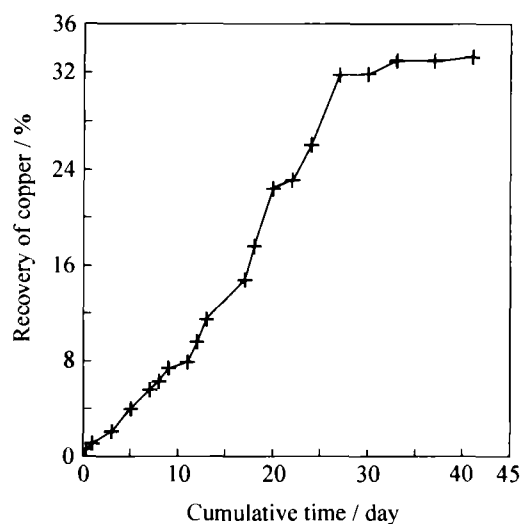


Figure 4 Relationship between the recovery of copper and bioleaching time.

Table 4 Contrast of bioleaching copper

Sample	Proterozoic sulfured ore / %	Inoculation concentration / %	Pulp density / %	pH	Ore grain size / mm	Recovery of copper (10 days)	Recovery of copper (27 days)
A	72.4	10	10	2.0	<0.076	10.0%	25.0%
B	90.0	10	25	1.2-1.5	<5.000	7.7%	31.8%

Note: A denotes the sample in this study and B denotes the sample in the correlative report.

4 Conclusions

(1) In the process of bioleaching, the pH value in the bioleaching solution rises at first, then drops gradually. While, the E_h value keeps rising slowly, increases quickly after 4 days, fluctuate from 725 to 760 mV and rises slowly when the leaching time is 27 days.

(2) The appropriate E_h value (750-800 mV) will benefit the bioleaching copper, while the high concentration of ferric ions is detrimental to the bioleaching copper.

(3) How to control the E_h value and the concentration of ferric ions in the process of bioleaching tests is important to increase the copper recovery.

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