Mineral

Pretreatment of copper-bearing refractory gold ores by bio-heap leaching

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Abstract: The refractory gold ores associated with rich copper and trapped in pyrite and quartz were studied. With conventional technique (all-sliming cyanidation), the gold recovery rate is only 51.78%. To eliminate the negative effects of copper and pyrite on cyanidation and increase the gold recovery rate, the investigation on bio-heap leaching pretreatment was made, by which Cu would be dissolved and gold would be liberated from pyrite. The experiment adopted mixed bacteria, mainly *Thiobacillus ferrooxidan* (named T.f1), as the bacterial catalyst for bio-preconditioning and was carried out in a PVC column with a diameter of 20 cm and a height of 1.3 m loaded with gold ores. The temperature was controlled between 28 and 30°C, the pH value was kept between 2.0-2.5, and the flux of sprinkling bacterial liquid was maintained 0.80 L/h. After 45-day's bio-oxidization, among the samples sizing from 0 to 5 mm, the oxidation rates of Cu, Fe and S were respectively 44.62%, 28.16% and 25.46%, and the gold recovery rate by cyaniding increased to 80.35%. The bio-heap leaching pretreatment can therefore effectively dissolve Cu and liberate gold from pyrite and lead to the increase of gold extraction.

Key words: bio-oxidization; pretreatment; pyrite; gold ore; bio-heap leaching

1 Introduction

The resources of free-milling gold ores are diminishing, while many new discovered deposits consist of refractory ores that are characterized by low gold recovery rate and high reagent consumption. The development of efficient reagents and techniques to process these types of ores has become important all over the world due to the increasing demand for minerals and the dwindling supply of high-quality ores. Biological preconditioning comes to be popular because microbes have special interactions with minerals and bio-treatment requires low reagent cost and produces minimal environmental impact.

Dump- and heap-leaching processes on an industrial scale are especially suited for low-grade gold ores because of their low costs and their operational flexibility. Commercial bioleaching began in the 1950s with dump leaching, a process that releases copper from vast quantities of submarginal-grade, primary and secondary copper sulfide materials. Today dump leaching remains a process of great economic significance in copper industry. In the last decade a coupling of dump leaching, copper oxide heap leaching, and industrial microbiology has yielded a successful commercial process for bio-heap leaching of secondary copper ores and the technical demonstration of sulfidic refractory precious metal ore bio-heap leaching [1]. Bio-heap leaching is a simple yet robust process, offering capital and operating cost advantages and environmental benefits.

In this work, the bacterial leaching of the ores associated with copper, gold and silver is studied. The conventional treatment on such materials is ineffective, because high Cu and S contents are strongly unfavorable to cyanidation, which is used conventionally to reclaim the gold from the ores. Bioleaching is an appropriate method for the pretreatment of refractory gold ore, especially the gold encapsuled within sulfides. The commercial application of bioleaching in the oxidation of refractory gold-bearing sulphide concentrates has established /is establishing itself globally a viable alternative to both oxidative roasting and pressure oxidation. A number of large mining companies are now actively investigating the potential of such application on pilot plant scale for an ever increasing demand for the variety of precious and base metal sulphide deposits [2]. As far as the gold ores entrapped in pyrite are concerned, bacteria oxidation can liberate gold particles, thereby is rendered amenable to the cyanidation process [3-4]. So after bio-oxidation the gold recovery rate can be greatly increased.

The optimization of a leaching process thus re-

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quires quantitative information on grain size, as well as the propagation of bacteria inside the mineral grains [5]. In this test, the parameters required in the heap-leaching were examined to provide a practical evidence for the operation of mining companies.

2 Materials and conventional cyanidation

2.1 Characteristics of the samples

The ore used in the study was obtained from Lai-yuan Mine in Hebei Province, China, and identified to be a sulfidic refractory gold ore. The desirable metals in this ore are gold, silver, copper, *etc.* The gold encapsuled in pyrite and quartz is respectively 13.30%

and 15.44%, and a small fraction of gold is trapped in both sulphide and quartz. The chemical analysis is shown in **table 1**.

Mineralogically, the ore consists mainly of sulphide minerals and a few covellines, chalcocites and limonites. The sulphide minerals were composed predominantly of pyrite (which was found mainly in association with gold), galena, chalcopyrite and minor amounts of blende and arsenopyrite. It was noted that gold was associated with silver as ally electrum, and it was disseminated in fine grains. The size distribution of gold grains was: >74 µm, 10.98%; 74-37 µm, 39.83%; 37-1 µm, 46.71%; <1 µm, 2.48 %.

Table 1 Results of chemical analysis   wt%

Au	Ag	Cu	Pb	Zn	As	Fe	S	C	SiO_2	Al_2O_3	MgO	CaO
8.50×10^{-6}	103.00×10^{-6}	0.65	0.77	0.05	0.02	4.90	3.46	0.21	70.48	4.25	2.17	0.76

2.2 Conventional cyanidation

In the conventional cyanidation (all-sliming cyanidation), the grain size was less than 74 µm, the consumptions of CaO and NaCN were 6 and 5 $kg \cdot t^{-1}$, the ore pulp density was 33%, and the pH value was controlled between 10-11. After 48 h's cyaniding, the results presented in **table 2** were obtained. The gold recovery rate was very low.

Table 2 Results of conventional cyanidation

Au content in the ore / $(g \cdot t^{-1})$	Au content in the cyaniding residues / $(g \cdot t^{-1})$	Au recovery rate / %
8.5	4.10	51.78

3 Experimental method

3.1 Medium and bacteria

The most active bacteria in bioleaching belong to the genus *Thiobacillus*. They are Gram-negative, non-spore forming rods which grow under aerobic conditions. Most thiobacilli are chemolithoautotrophic species which use carbon dioxide from the atmosphere as their carbon source for the synthesis of new cell materials. The energy derives from the oxidation of reduced and partially reduced sulphur compounds, including sulfides, elemental sulfur and thiosulfates, and the final oxidation product is sulfates [6].

Now, it is well known that *Thiobacillus ferrooxidan*, *T.thiooxidan* and *Leptospirillum ferrooxidans* are very important species, which can grow well at low pH values, even at the pH values that are much lower than 1. These bacteria can attack mineral sulfides during the oxidation of sulphur compounds and the environmental pH values decrease. The intensive sulfuric acid

production leads to a rapid decomposition of rocks so that acid-soluble metal compounds can pass into solution as sulfates.

However, the most important role in bacterial leaching is played by *T.ferrooxidans*, which was first isolated in 1947 by Colmer and Hinkle [7] from acid coal mine drainage.

In this study, the mixed bacteria consisting mainly of *Thiobacillus ferrooxidan* were isolated from the acidic drainage water of gold mines in China, and adapted to the ore sample by adding small amounts (approximately 1 g) of the ore to glass flash containing 150 mL nutrient medium. 3Leathen medium was used to culture the bacteria during the whole experiment. The constituents of the 3Leathen nutrient medium are: $(NH_4)_2SO_4$, 0.45 g/L; K_2HPO_4, 0.15 g/L; $MgSO_4 \cdot 7H_2O$, 0.5 g/L; KCl, 0.05g/L; $Ca(NO_3)_2$, 0.01 g/L.

The selection of the bacteria used in the test was evaluated by monitoring the Fe^{3+} concentration and the solution potential (E_h) *vs.* time.

3.2 Column leaching test

Three PVC columns with a diameter of 20 cm and a height of 1.3 m were designed for the leaching test and the ores crushed into different particle sizes (less than 5, 10, and 15 mm) were loaded into the three columns, respectively.

The adjustment of correct pH value is a necessary condition for the growth of leaching bacteria and is decisive for the solubilization of metals. Generally, the pH values in the range of 2.0-2.5 are optimum for the bacteria oxidation of ferrous iron and sulfide. In the leaching test, the pH value in the columns was ad-

justed to 2.0 with continuous-flow of diluted H_2SO_4 solution. The pH value of the leaching liquid was monitored with a pH meter. At the beginning of the bioleaching, the ore was leached with 20 L bacterial liquid containing 10^7 cells/mL and then the leaching liquor was circulated in the bioleaching system. Moreover, everyday 5% of newly cultured bacteria liquor, that is 1 L, was added to supplement the loss of water because of the evaporation in the cycling flow and sampling. The air flux compressed into the device for activating the bacteria was maintained at 0.06-0.11 L/min. The flux rate of bacterial liquid which was used to sprinkle the samples in the columns was 0.80 L/h. A flowsheet diagram for bioleaching is shown in **figure 1**.
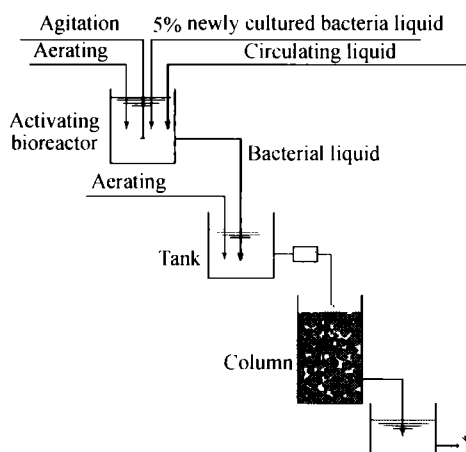

Figure 1   Flowsheet diagram for bio-oxidization.

Temperature was another important parameter in the leaching process. According to the past successful practices [8], the temperature was controlled in 28-30°C. The increase of temperature from 30 to 35°C is deleterious for the extraction process. The data given in the references indicated that the optimum temperature for acidophilic iron-oxidizing bacteria should be in the range of 28-33°C [9-10].

The bio-oxidation time is dependent on mineralogy, the amount of sulfides required oxidation and other factors, such as bio-heap temperature and grain size.

3.3 Cyanidation

The bio-oxidized gold ore is usually rinsed with fresh water to get the constituents that consume lime and cyanides removed. After being rinsed, the bio-oxidized ore is moved from the pad, mixed with lime and re-stacked on a permanent pad for leaching with cyanides or other lixiviant [9].

The residue of bio-oxidation in this test was rinsed with diluted H_2SO_4 till the Fe^{3+} concentration in the solution reduced to 0.2 g/L, and then rinsed with water until the pH value decreased markedly. Finally, NaOH

solution was used for neutralization and the pH value was adjusted to 10-11 and such pH value was kept constant during cyanidation. The contents of gold and silver in the residues after cyanidation were analyzed by fire-assay.

4 Results and discussion

4.1 Selecting microbe

Redox potential, iron concentrations, ferrous/ferric ratios, and arsenic concentrations provide information on the dissolution of pyrite and other iron-bearing minerals and the performance of iron-oxidizing bacteria [1]. In the investigation, the correlation between ferric concentration and redox potential in the solution was measured and shown in **figure 2**.

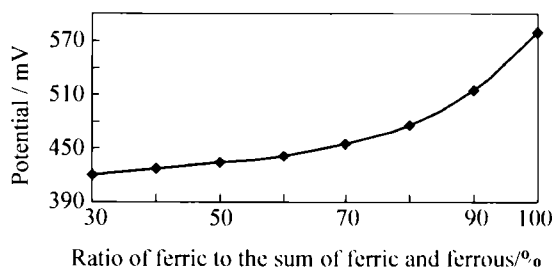Ratio of ferric to the sum of ferric and ferrous/%

Figure 2   Curve of ferric content vs. redox potential.

When the volume of redox potential is more than 530 mV, generally speaking, ferrous iron has almost been oxidized to ferric iron completely. Three mixed bacteria (named T.f1, T.f2, T.f3) that can leach sulphides were cultured and adapted to the ore samples. According to the correlation between the redox potential and the ferric concentration, T.f1 was superior to the other two due to its fast growing speed and excellent ability to oxidize iron. The results were presented in **figures 3** and **4**.
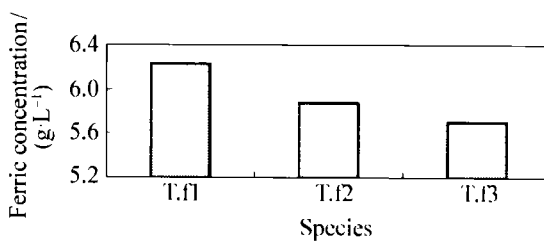

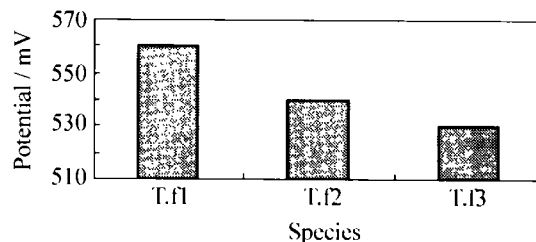**Figure 3 Ferric concentration in different bacterial liquids.**

Figure 4   Redox potential in different bacterial liquids.

After 7-day's adaptation, the ferric concentration and the redox potential in T.f1 solution were higher than those in the other two. Therefore, in the subsequent tests, T.f1 was used to oxidize the samples in the bioleaching process.

4.2 Bio-oxidation

In the bio-oxidization process, the variation of ferric concentration was recorded periodically. The results can be seen in **figure 5**.
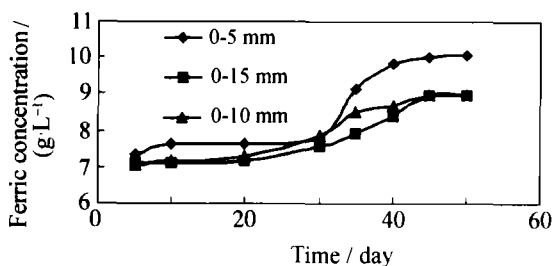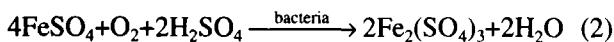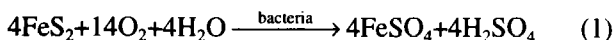

**Figure 5 Variation of ferric concentration vs. time**

Figure 5 shows that after 45-day's bio-oxidation, the ferric concentration tends to remain a constant value without any obvious sign of increase.

The reactions involved in the biological oxidation of pyrite are:

$$4FeS_2 + 14O_2 + 4H_2O \xrightarrow{\text{bacteria}} 4FeSO_4 + 4H_2SO_4 \quad (1)$$

$$4FeSO_4 + O_2 + 2H_2SO_4 \xrightarrow{\text{bacteria}} 2Fe_2(SO_4)_3 + 2H_2O \quad (2)$$

The reactions above are direct ones. In direct bacterial leaching, there is physical contact between the bacterial cell and the sulfide surface, and the oxidation to sulfates takes place via several enzymatically catalyzed steps. In this process, pyrite is oxidized to iron

(III) sulfate [11]. According to the above reactions, the direct bacterial oxidation of pyrite can be summarized by the following reaction:

$$4FeS_2 + 15O_2 + 2H_2O \xrightarrow{\text{bacteria}} 2Fe_2(SO_4)_3 + 2H_2SO_4 \quad (3)$$
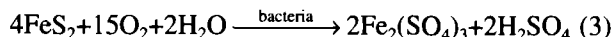
In indirect bioleaching, the bacteria generate a lixiviant which chemically oxidizes the sulfide mineral. In acid solution this lixiviant is ferric iron, and the metal solubilization can be described by the following reaction:

$$MeS + Fe_2(SO_4)_3 \rightarrow MeSO_4 + 2FeSO_4 + S^0 \quad (4)$$
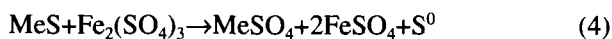
where MeS is a metal sulfide. The ferrous iron arising in this reaction can be re-oxidized to ferric iron by *T.ferrooxidans* or *L.ferrooxidans* and the ferric iron can take part in the oxidation process again. In indirect leaching, the bacteria do not need to make physical contact with the mineral surface. They only have a catalytic function by means of accelerating the re-oxidation of ferrous iron, which takes place very slowly in the absence of bacteria. As expressed by Lacey and Lowson [12], in the range of pH 2-3, the bacterial oxidation of ferrous iron is about 10^5-10^6 times faster than the chemical oxidation of ferrous iron. The direct and indirect reactions in the bioleaching take place simultaneously.

The information from figure 5 indicates that the ferric concentration increases extremely slowly after 45-day's bio-oxidation. Therefore the conclusion that bioleaching has almost finished can be made based on the bioleaching mechanisms above.

The results of the bio-oxidation is listed in **table 3.**

Table 3 Results of bio-oxidation

Particle size / mm	Bio-oxidation time / day	Contents before bio-oxidation / wt%			Contents after bio-oxidation / wt%			Oxidation rates / wt%		
		Fe	S	Cu	Fe	S	Cu	Fe	S	Cu
0-5	45	4.9	3.46	0.65	3.52	2.38	0.36	28.16	25.46	44.62
0-10	45	4.9	3.46	0.65	4.51	2.71	0.42	7.96	21.68	35.38
0-15	45	4.9	3.46	0.65	4.71	2.85	0.44	3.88	17.63	32.31

According to the data in table 3, the bio-oxidization time seems a little long and not very satisfactory. The reasons for such results are: firstly, the smaller surface caused by the coarse particle size leads to less absorption and oxidation opportunities of the bacteria to the ore, and the pyrite is partially entrapped in quartz which can not be oxidized by microorganisms; secondly, the bacteria has the priority to oxidize the copper mineral and the high copper content (0.65wt%) in the ore is unfavorable to bio-oxidation. Also, copper oxidizing was a time-consuming process.

4.3 Cyanidation of the preconditioned ore

The gold ore after bio-oxidation was treated with diluted sulfuric acid and tap water till its pH value was up to neutral. Then, NaOH was used to adjust and remain the pH value in the range of 10-11. During cyanidation, 0.08% of NaCN was kept in the sprinkling solution in the former 15 days, after which, the NaCN concentration in the solution was remained 0.03%-0.05%. The CaO concentration was 0.03% over the whole period of cyanidation. The results of cyanidation are shown in **table 4**.

Table 4   Results of cyanidation

Grain size / mm	CaO consumption / $(kg \cdot t^{-1})$	NaCN consumption / $(kg \cdot t^{-1})$	Contents before pre-conditioning / $(g \cdot t^{-1})$		Contents after cyanidation/ $(g \cdot t^{-1})$		Metal recovery rates / %	
			Au	Ag	Au	Ag	Au	Ag
0-5	4.5	3.76	8.50	103.00	1.67	56.50	80.35	45.15
0-10	4.0	3.52	8.50	103.00	2.47	65.20	70.94	36.70
0-15	4.2	3.47	8.50	103.00	2.67	68.60	68.59	33.40

After bioleaching, the gold recovery rates of the grains with different sizes were respectively 80.35%, 70.94%, 68.59%, which were pretty good contrast with the conventional cyanidation. The detrimental effects of Cu and pyrite on cyanidation were eliminated, and the extraction rate of gold increased from 51.78% to 80.35%. From table 3, it can also be found that among the samples sized from 0 to 5 mm, the oxidation rates of Fe, S and Cu were 28.16%, 25.46% and 44.62%, respectively, which were superior to the other two (the grain sizes were 0-10 mm and 0-15 mm, respectively). Such results can be explained by the solid/liquid contact area. A finer particle provided much a larger surface, which was favorable to bacteria absorption, oxidization and cyanidation.

The principle of biological preconditioning and bioleaching that the higher oxidation rate conduced to the higher gold extraction can be demonstrated by the results given in tables 3 and 4.

5 Conclusions

(1) Bioleaching for the recovery of gold from the recalcitrant cyanidation is considered as a practical technique. In this bio-heap leaching investigation, some important parameters, such as the bio-oxidizing time, grain size, ferric concentration, *etc.*, were examined. After 45-day's bio-oxidation, the removal rates of Fe, S and Cu in the 0-5 mm samples were respectively 28.16%, 25.46% and 44.62%, and the negative effects of copper and pyrite were effectively eliminated.

(2) The gold recovery rate increased from 51.78% without any pre-conditionings to 80.35% after bio-treatment. Therefore, the bio-heap leaching is successful.

(3) The oxidizing rates of Cu, Fe and S in the finer grain size (0-5 mm) were better than those in the other two (0-10 and 0-15 mm). The extraction rates of gold in the 0-5 mm samples were higher correspondingly.

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