

# BEHAVIOUR OF ELEMENTAL SULPHUR IN BIOOXIDATION OF GOLD-BEARING SULPHIDE ORES<sup>①</sup>

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## ABSTRACT

The behaviour of elemental sulphur in the biooxidation process of arsenopyrite and pyrite has been investigated it was found that the  $\alpha$ -S<sup>0</sup> produced in the bioleaching residue of arsenopyrite was formed by the process of chemical oxidation, while little sulphur was detected in the bioleaching residue of pyrite. The reason of the high consumption of cyanide for the bioleaching residue of Banbishan gold concentrate has been studied and a pretreatment method has been suggested to improve the cyanidation process.

**Key words:** removing of arsenic by bacteria sulphur cyanidation of gold

## 1 INTRODUCTION

Gold is widely distributed in the earth's crust with an average terrestrial concentration of about  $5 \times 10^{-9}$  g/t. The yield and reserve of gold in a country represent its economic position in the world because of the important financial value of gold, so that the extraction of gold has gained great attention<sup>[1]</sup>.

The extraction of gold from the refractory gold-bearing ores has been studied extensively in recent years. The term "refractory" is used to describe those gold ores that do not yield satisfactory recovery of gold by conventional cyanidation methods. Some of the refractory gold ores were arsenic-bearing gold sulphide ores and were not used effectively because of the limitation of extraction technology. But in recent years it was reported that the biooxidation technology can be used to treat the arsenic-bearing gold ores and has been practised at laboratory and pilot scales in many countries<sup>[2-4]</sup>. There are nine biooxidation plants in the world specialized in pretreatment of the arsenic-bearing gold

sulphide ores and the details of them were shown in Table 1<sup>[5]</sup>. Meanwhile, some of the semi-commercial plants have also been built in Spanish and Franch etc, and before long this technology would be applied in the mining industry in these countries.

The experimental results showed that for the Banbishan arsenic-bearing gold sulphide concentrate, both of the extraction of gold and the consumption of cyanide increased after bioleaching compared with direct cyaidation without bioleaching<sup>[6]</sup>. By investigating the relationship between the behaviour of sulphur in the bioleaching process and the consumption of cyanide, a method for reducing the consumption of cyanide was proposed.

## 2 MATERIALS AND METHODS

### 2.1 Culture

The strain 8<sup>#</sup> of *Thiobacillus ferrooxidans* used in this study was isolated from the acidic water of a arsenopyrite mine in Yunfu county,

① Received Mar. 28, 1994

**Table 1 The plants specialized in biooxidation and cyanidation of refractory gold ores**

Country	Mine or Company	Grade	Scale t /day	Recovery of gold, %	Date of Production
South Africa	Fairview	Concentrate; Au 145 g/t	12	>95	1986, 9
		S 29.3 g/t As <sub>2</sub> O <sub>3</sub> 8 wt.-%			
	Vaal Reef		20		1989
Canada	Giant Bay	Concentrate	10	96.5	1987
		Au 24 g/t	1 000		1989
	Congress	Concentrate;	300		1989
	Equity	Residue	10		
		Au 5.5 g/t Ag 75—100 g/t			
American	Tomkin Springs	Raw Ore Au 3 g/t	1 300	90	1989
Brazil	Sao Bento		240		
Australia	Harbour Lights		10		1987
Zimbabwe	Broomstock		100		being built

Guangdong Province.

## 2.2 Ore

The sample of arsenopyrite and pyrite were comparatively purified minerals. The Banbishan gold concentrate was mainly composed of hurinite, quartz and arsenopyrite etc. Table 2 shows the main chemical analysis of these samples.

## 2.3 Experimental Procedures

### 2.3.1 Bioleaching Experiments

All experiments were carried out in 250 mL shake flasks containing 90 mL of improved Leathen medium with 7.2 g/L of Fe<sup>2+</sup>, inoculated with 10 mL of activated culture of *Thiobacillus ferrooxidans*. The pH was adjusted to 1.8 with 10 mol/L H<sub>2</sub>SO<sub>4</sub> and the flasks were incubated on a gyratory shaker (120 min<sup>-1</sup> at 28 °C in a dark room). Certain amount of samples were added to the media after 48 h of incubation. The particle size of the samples was 320 mesh.

### 2.3.2 Extraction of Gold From Bioleaching

### Residue

After bioleaching the residue was treated by conventional cyanidation for gold extraction. In the cyanidation tests, plups containing 33.3 wt.-% solid content were treated for 24 h at pH=10~11 with cyanide. At the end of the tests, the pulps were filtered and the filtrate was used for determination of gold and sulphur.

**Table 2 Chemical analysis of samples**

Sample	Source	Composition				
		As %	Fe %	S %	Au g/t	Ag g/t
Arsenopyrite	Huanan	41.2	32.7	14.5		
Pyrite	Shandong		46.7	50.9		
Banbishan gold conc.	Hebei	4.6	12.8	7.5	23.5	35.7

### 2.3.3 Analysis Method

Arsenic; Heterpoly molybdenum blue method  
Total sulphur; Peacock colorimetric method  
Elemental sulphur; Carbon tetrachloride gravimetric method

Gold; Atomic absorption spectrophotometry method

Sodium cyanide; Silver nitrate titration method

pH; Measured by pH meter SA 520

Number of cells; Calculated by Petroff-Hauser counting chamber

### 3 RESULTS AND DISCUSSION

#### 3.1 The Oxidation of Sulphur in the Bioleaching Process of Arsenopyrite and Pyrite

Table 3 shows the oxidation rate of sulphur in the bioleaching process of arsenopyrite and pyrite. It can be seen that the decomposed sulphur in pyrite was dissolved into the solution in the oxidized form such as  $\text{SO}_4^{2-}$  etc, while some of the decomposed sulphur of arsenopyrite existed as  $\text{S}^0$ . The pH value in the leaching solution of arsenopyrite increased gradually with time, while that of pyrite decreased with time.

Table 4 shows the numbers of cells in the bioleaching period. In the initial period of time, the decomposition rates of iron and sulphur from the arsenopyrite were faster than those from the pyrite<sup>[3]</sup>, which led to more bacteria existing in the bioleaching solution of the arsenopyrite. With the proceeding of the biooxidation, the extraction of sulphur from pyrite became gradually higher than that of arsenopyrite in spite of that the extraction of iron from pyrite was still lower. Because the energy released from the oxidation process of  $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$  was much less than that of  $\text{S}^{2-} \rightarrow \text{SO}_4^{2-}$ , the bioleaching system of pyrite can provide more energy for the growth of bacteria, which led to more bacteria existing in the bioleaching solution of pyrite.

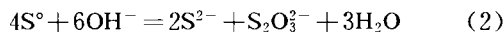
#### 3.2 The Method to Reduce the High Consumption of Sodium Cyanide

A key step in the extraction of gold is the conversion of the solid metal into a soluble cyanide complex. Using cyanidation to extract refractory gold is both difficult and uneconomical principally, because the gold is embedded in arsenopyrite or pyrite which is difficult to break down. The purpose of biohydrometallurgy is to break down the sulphide crystals to liberate the precious metals so as to achieve a satisfactory recovery of gold.

The experimental results of Banbishan arsenic-bearing gold sulphide concentrate shows that the extraction of gold increased with the extent of biooxidation. The extraction of gold was only 52.4% and the consumption of cyanide was 6.6 kg/t if the concentrate was not pretreated by bacteria, whereas when arsenic extraction  $\geq 85\%$ , more than 90% of gold can be extracted and the consumption of cyanide was 13.9% kg/t. The X-ray powder photographs of concentrates in Fig. 1 shows that the amount of  $\alpha\text{-S}^0$  existing in the residue increased with the biooxidation time. In the experiments it was found that part of sodium cyanide added was consumed by the reaction between  $\text{S}^0$  and  $\text{CN}^-$ :



In order to reduce the amount of sodium cyanide, 300 mL of 1 mol/L NaOH solution was added to 100 g of bioleaching residue and treated for 1 h at 80–90 °C. At this time, the  $\text{S}^0$  dissolved into the leaching solution in the soluble form of  $\text{S}^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  etc.:



The experimental results in Table 5 and Fig. 2 indicate that nearly half of the sodium cyanide can be reduced after pretreatment of NaOH solution. Taking the profit into consideration, the lime instead of NaOH was adapted to reduce the consumption of sodium cyanide and at this time the extraction of gold was affected only slightly.

Table 3 The oxidation of sulphur and the change of pH during the bioleaching period of arsenopyrite and pyrite

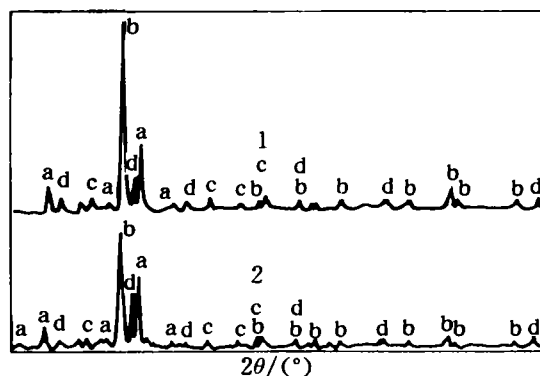
Time/h	Oxidation of sulphur(%)		Production of $\text{S}^0$ (%)		pH	
	Arsenopyrite	Pyrite	Arsenopyrite	Pyrite	Arsenopyrite	Pyrite
48	7.3	5.6	1.6	/	1.82	1.78
96	14.2	10.3	2.8	/	1.84	1.73
192	18.4	24.6	4.5	/	1.89	1.72
288	24.1	46.5	6.2	/	1.97	1.68

\* Initial concentration of  $\text{Fe}^{3+}$  8.0 g/L; initial pH 1.80; initial number of cells  $3.8 \times 10^6 \text{ mL}^{-1}$

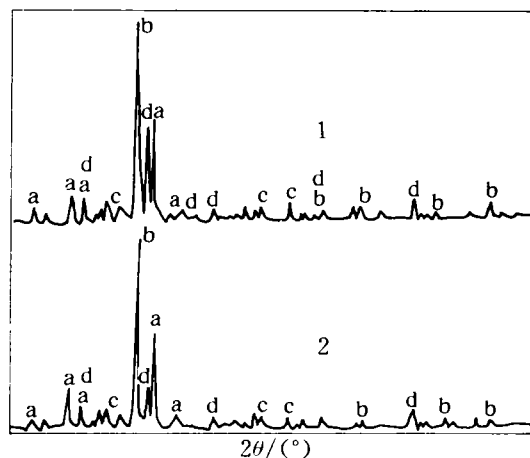
**Table 4** The numbers of cells in the bioleaching solution of arsenopyrite and pyrite

Time/h	Numbers of cells, $\times 10^6 \text{ mL}^{-1}$	
	Arsenopyrite	Pyrite
48	6.0	5.4
96	12.3	9.0
144	13.5	20.2
192	14.9	25.2
288	20.1	47.2

\* Experimental condition are the same as Table 3

**Fig. 1** X-ray powder photography of the bioleaching residue of Banbishan arsenic-bearing gold sulphide concentrate

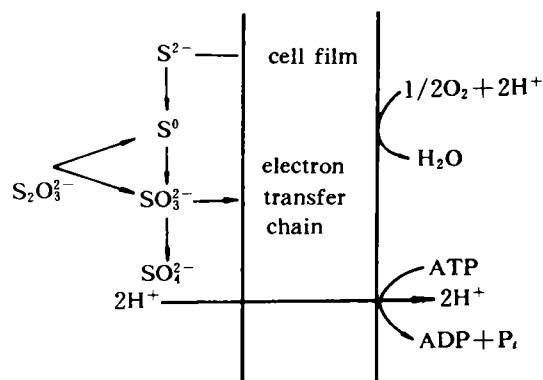
1—72 h, treated by dilute HCl solution;  
 2—96 h, treated by dilute HCl solution;  
 a— $\text{CaAl}_2\text{Si}_2\text{O}_8$ ; b— $\text{SiO}_2$ ; c— $\text{FeAsS}$ ; d— $\text{S}^0$

**Fig. 2** X-ray powder photographs of the bioleaching residue of Banbishan arsenic-bearing gold sulphide concentrate after alkaline pretreatment

1—120 h, treated by dilute HCl solution;  
 2—120 h, treated by dilute HCl solution and alkali;  
 a— $\text{CuAl}_2\text{Si}_2\text{O}_8$ ; b— $\text{SiO}_2$ ; c— $\text{FeAsS}$ ; d— $\alpha\text{-S}^0$

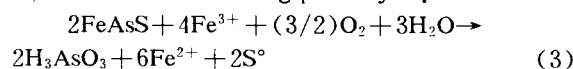
**Table 5** Effect of alkaline pretreatment on the composition of the bioleaching residue of Banbishan arsenic-bearing gold sulphide concentrate

Biooxidation time/h	Prior to treatment (wt.-%)			after treatment (wt.-%)		
	As	Fe	S	As	Fe	S
72	1.6	8.3	5.7	1.5	8.3	0.4
120	0.7	7.2	4.0	0.5	7.1	0.2

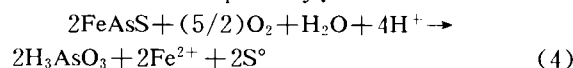
**Fig. 3** Schematic representation of oxidation of inorganic sulphide by thiobacilli

### 3.3 The Producing of $\text{S}^0$ in the Biooxidation Process of Sulphide Ores

The  $\text{S}^0$  existing in the bioleaching residue of arsenopyrite is produced probably by two ways, that is, the chemical oxidizing pathway<sup>[8]</sup>:



or the biooxidation pathway:



The general course of the oxidation of sulphur compound is presented in Fig. 3<sup>[7]</sup>. It can be seen that the sulphide was oxidized gradually.  $\text{S}^0$  was formed when the producing rate is greater than the oxidizing rate. X-ray powder photographs of arsenopyrite leached by bacteria and ferric sulphate were presented in Fig. 4 and Fig. 5, respectively. It was found that  $\alpha\text{-S}^0$  existing in the leaching residue of arsenopyrite was generated via chemical oxidizing pathway, Whereas no  $\text{S}^0$  was detected in the leaching residue of pyrite.

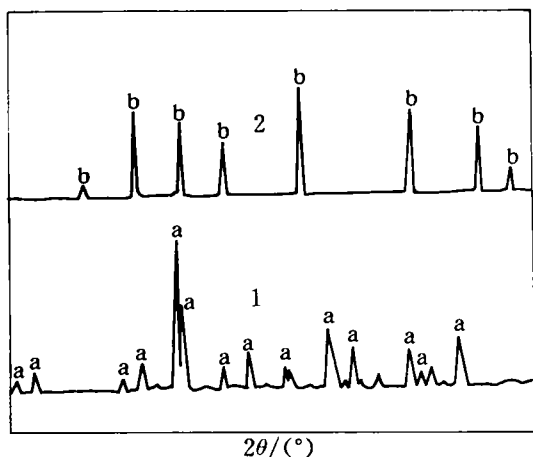


Fig. 4 X-ray powder photographs of arsenopyrite and pyrite leached by cell suspended solution

1—leaching residue of arsenopyrite treated with dilute HCl solution; 2—leaching residue of pyrite treated with dilute HCl solution;  
a—FeAsS; b—FeS<sub>2</sub>; bioleaching time 192 h

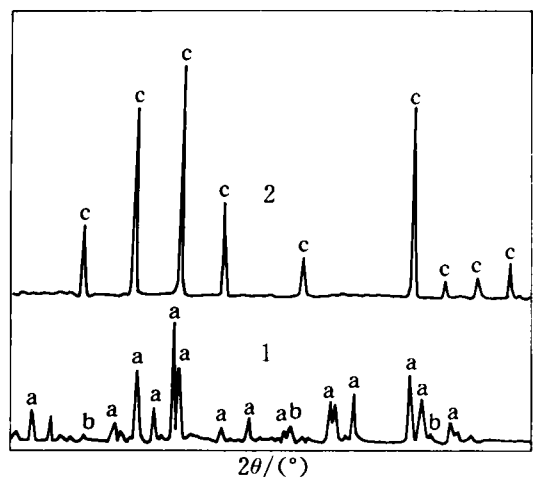


Fig. 5 X-ray powder photographs of arsenopyrite and pyrite leached by ferric sulphate

1—leaching residue of arsenopyrite treated with dilute HCl solution; 2—leaching residue of pyrite treated with dilute HCl solution;  
a—FeAsS; b— $\alpha$ -S°; c—FeS<sub>2</sub>; bioleaching time 192 h

#### 4 CONCLUSIONS

(1) The sulphur existing in pyrite is easier to be decomposed than that in arsenopyrite during the bioleaching process. The numbers of cells in the leaching solution is determined mainly by the biooxidation extent of sulphur

(2) The high consumption of sodium cyanide in the cyanidation process of the bioleaching residue of Banbishan arsenic-bearing gold sulphide concentrate could be reduced by addition of NaOH solution or lime water due to the generation of  $\alpha$ -S°.

(3)  $\alpha$ -S° existing in the bioleaching residue of arsenopyrite was produced via chemical reaction between ferric iron and arsenopyrite. No S° was detected in the bioleaching residue of pyrite, under the same conditions.

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