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Bioleaching of refractory gold ore (Ⅲ)①

——Fluid leaching Jinya refractory gold concentrate by *Thiobacillus ferrooxidans*

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[Abstract] A novel fluidized-bed reactor was designed and installed for bioleaching in a semi-continuous way, by which a process for bioleaching-cyanidation of Jinya refractory gold arsenical concentrate was studied. The arsenic extraction rate reaches 82.5% after 4-day batch biooxidation of the concentrate under the optimized condition of pH 2.0, ferric ion concentration 6.5 g/L and pulp concentration 10%. And leached rate of gold in the following cyanidation is over 90%. The parameters of three series fluidized-bed reactors exhibit stability during the semi-continuous bioleaching of the concentrate. Arsenic in the concentrate can be got rid of 91% after 6-day leaching. Even after 4 days, 82% of arsenic extraction rate was still obtained. The recovery rates of gold are 92% and 87.5% respectively in cyaniding the above bioleached residues. The results will provide a base for further commercial production of gold development.

[Key words] refractory arsenical gold concentrate; fluid-bed reactor; semi-continuous bioleaching
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1 INTRODUCTION

Gold ores those yield low recoveries of gold when treated by the conventional grinding and cyanidation process are called refractory gold ore. A common cause of producing refractoriness is encapsulation of fine gold within the matrix of sulfide minerals, particularly arsenopyrite (FeAsS) and pyrite (FeS_2)[1,2]. The size and location of the gold within the sulfide matrix determine to a great degree the nature of the process required for its liberation and recovery. Submicroscopic gold is liberated by destruction of the sulfide with process based on the use of thermal, chemical or biological oxidation[3~5].

Several methods have been proposed and applied for the oxidation of refractory gold bearing iron sulfide including roasting, pressure oxidation, chemical leaching and bacterial oxidation. Bacterial oxidation offers great advantages in contrast with other pyro or hydrometallurgical pre-treatments, reagent costs are low and it is carried out under atmospheric pressure and moderate temperature conditions, which reduces both operation costs and its environmental impact[6,7].

The Jinya gold deposit, located at Fengshan County Guangxi, P. R. China, which is a typical Carlin-type gold deposit. Spot technological flow was used as following: the flotation gold concentrates were pretreated by roasting oxidation to get rid of arsenic and white arsenic was recycled from the dust. The waste gases entered into the atmosphere and the calcine were delivered to copper smelting plant for recovery of gold. Roasting is expensive and has negative environmental implications. With the saturation of the white arsenic market problem, the effective or expensive ways have to be taken for managing the white arsenic[8].

This study is aimed at finding out an effective technique to biooxidation of Jinya refractory gold ores. According to the features of the biological oxidation, fluid-leaching technique is used. For this purpose, a novel fluidized-bed reactor is designed and installed for bioleaching in batch and semi-continuous ways.

2 MATERIALS AND METHODS

2.1 Jinya gold ore

Direct cyanidation experiment with the ore showed that 0.2% NaCN, pH 10~11 and an agitation leaching time of 48 h resulted in a gold recovery of only 10%. Further, considering the low content of gold in the ore and the clay mineral content is high, the ore is not suitable for direct bioleaching and, thus, the sulfide mineral must be concentrated by flotation.

A sulfide flotation concentrate containing 43.5 g/t Au, 27.92% sulfur, 31.18% total Fe, and 12.35% arsenic as seen in Table 1 was used. Without biooxidation pretreatment, a maximum gold re-

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covery of 12.5% was obtained by direct cyanidation. Even after roasting (temperature 750 ℃, 3 h), gold recovery was still only 47.4%, because of existing quadric sinter cake. Table 2 and Table 3 give the arsenic phase analysis results and gold distribution state in concentrate respectively. Most of arsenic is in arsenopyrite, and gold is mainly encapsulated in sulfide. Size distribution of the concentrate is given in Table 4.

2.2 Setup for batch and semi-continuous bioleaching

Bacterial oxidation of a sulfide mineral concentrate is a complex exothermic reaction involving gaseous, liquid and solid phases. The conditions within the bacterial oxidation reactor must be maintained in a range where the maximum oxidation rate occurs and the bacterial culture can thrive[9]. According to the biooxidation feature, gas-liquid-solid three-phase fluid leaching technology was used in this study as shown in Fig. 1.

The whole setup consists of several reactors. It can be used for batch and semi-continuous bioleaching with different experimental requirement. The bioleaching reactor divides into two parts: temperature control part and aerating part. Bioleaching temperature is controlled by the cycling water jacket outside of reactor. Air is provided by model HG-780 increased-oxygen motor. The columnar reactor is made of organic glass whose height-diameter ratio was 5∶1. The bubbler is installed on the conical bottom of the reactor. With the range of 0.8~1.5 L/min gas flow rate, effective suspension was obtained for 1 liter pulp with solid concentration of 5%~20%. In comparison of fluidized-bed leaching with the shaking test and mechanical agitation test, the effectiveness of arsenic leaching is the best in fluidized-bed as illustrated in Fig. 2.

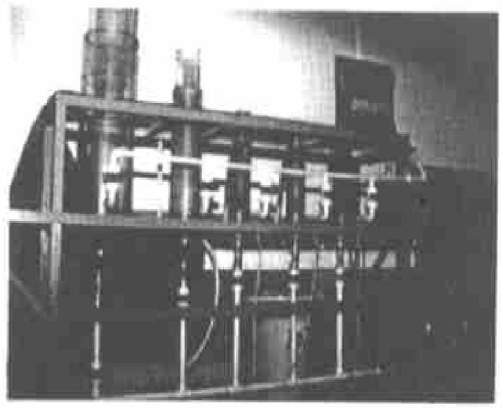

Fig. 1 Setup for bioleaching

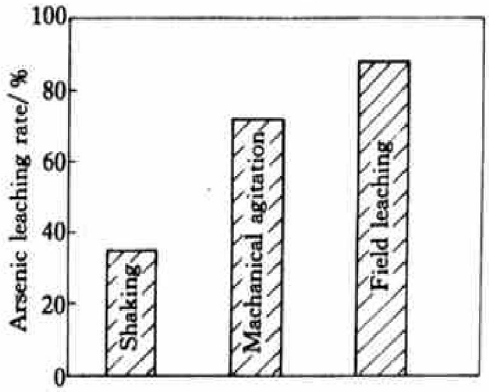

Fig. 2 Effectiveness of arsenic leaching in different reactor

Table 1 Chemical analysis results of Jinya gold concentrate

Composition	As	S	Fe	Sb	Cu	SiO_2	Al_2O_3	Zn	Pb	Au(g/t)
Content/%	12.35	27.92	31.18	0.66	0.04	24.23	1.27	0.12	0.10	43.5

Table 2 Arsenic phase analysis results

Phase	Arsenic in arsenopyrie	Arsenic in arsenate	Arsenic in oxidation state	Total
Content/%	10.56	1.33	0.85	12.76
Occupancy/%	82.8	10.5	6.7	100.0

Table 3 Gold distribution state in gold concentrate

Gold distribution	Free and intergrowth gold	Gold encapsulated in sulfide	Gold in gangue	Gold in oxide	Total
Content/($g\cdot t^{-1}$)	4.65	39.73	0.56	0.26	45.20
Occupancy/%	10.28	87.90	1.24	0.58	100.0

Table 4 Size distribution of gold concentrate

Grade/μm	+450	−450~−150	−150~+75	−75~+45	−45
Distribution/%	0.70	4.90	10.50	16.70	67.20

2.3 Ferrooxidans culture

The bacterium Thiobacillus ferrooxidans was provided by the Chinese Academy of Science. The medium for the bacterial culture and the reactor experiment consisted of 0.45 g $(NH_4)_2SO_4$, 0.15 g K_2HPO_4, 0.5 g $MgSO_4 \cdot 7H_2O$, 0.05 g KCl, 0.01 g $Ca(NO_3)_2$ per liter adjusted to pH 2.0 with sulfuric acid.

The acclimatization of bacteria was carried on firstly using the incubation media containing the concentrate and Fe^{2+} ions to culture the bacterial, with adjusting the ore pulps concentration from 0 to 10%. When complete oxidation time of Fe^{2+} ions was same as that in media without the concentrate, it could be considered that the bacterial had adapted the concentrate. Because of high content of arsenic in the concentrate, it is necessary for adding arsenic ions to the media to obtain the bacteria with a powerful ability of arsenic toleration (10 g/L arsenic ion).

3 FLUID BATCH BIOLEACHING-CYANIDATION

3.1 Batch experiment process

Batch bioleaching experiment was done in fluidized-bed reactor of 1.5-liter useful volume, containing 1-liter pulp. A 0.5-liter culture media was added into the reactor containing gold concentrate, and after pulp pH value was adjusted with 6 mol/L sulfuric acid, 0.5-liter active bacterial solution containing ferric iron was put in the reactor. After bioleaching, the residue was washed by dilute hydrochloric acid repeatedly. With drying and weighing the residue and assaying the arsenic content in the residue, the leached rate of arsenic was calculated. Cyanidation experiment, furthermore, was conducted in the mechanical agitation reactor.

3.2 Influence factors

3.2.1 Initial pH value

The influences of initial pH on bioleaching are listed in Table 5. When pH value was 2.0, the best result of leaching arsenic was obtained as 89.3%, and corresponding gold recovery got 94.7%. With respect to bioleaching of this concentrate, the optimum pH of is 2.0.

3.2.2 Pulp concentration

Table 6 shows the results with the variation of pulp concentration. With increasing pulp concentration, the bioleaching rate of arsenic decreased. As the pulp concentration increased to 15%, the leaching rate of arsenic could be got to 54.3% and gold recovery decreased to 73.6%. Even if the leaching time was extended to 6 days, arsenic-leaching rate also got only 60.1%. As for 20% pulp concentration, the leached rate of arsenic within 7 days did not exceed

Table 5 Results obtained by variation of pH (pulp concentration 5%, $[Fe]^{3+}$ 6.5 g/L)

Item		Number 1	2	3	4	5
Condition	pH	1.0	1.5	2.0	2.5	3.0
	Time/d	4	3	3	3	3
Mineral weight	Added Mineral weight/g	50	50	50	50	50
	Acidwashing residues weight/g	40.5	37.7	34.8	36.2	38.7
	Residues ratio/%	80.9	75.3	69.6	72.3	77.3
Arsenic leaching results	Arsenic in residues/%	4.85	3.14	1.89	2.32	3.48
	Arsenic leaching rate/%	68.2	80.8	89.3	86.4	78.2
Gold leached	Gold in cyanidation residues/($g \cdot t^{-1}$)	12.26	5.65	3.26	4.44	6.22
	Gold recovery/%	77.2	90.3	94.7	92.6	88.9

Table 6 Results obtained by variation of pulp concentration (pH 2.0, $[Fe]^{3+}$ 6.5 g/L)

Item		Number 1	2	3	4	5	6	7
Condition	Pulp concentration/%	8	10	15	15	15	20	20
	Time/d	4	4	4	5	6	4	7
Mineral weight	Added mineral weight/g	80	100	150	150	150	200	200
	Acidwashing residues/g	55.4	75.2	125.5	124.7	122.9	177.8	179.8
	Residues ratio/%	69.2	75.2	83.7	83.1	82.0	88.9	89.9
Arsenic leaching results	Arsenic in residues/%	2.17	2.87	7.18	6.18	82.0	8.43	6.85
	Arsenic leaching rate/%	87.8	82.5	54.3	58.2	60.1	39.3	50.1
Gold leached	Gold in cyanidation residues/($g \cdot t^{-1}$)	3.92	5.74	13.74	12.74	11.83	22.27	17.40
	Gold recovery/%	93.7	90.0	73.6	75.7	77.7	54.5	64.0

50.1%. Therefore, it is rational for selecting 10% pulp concentration.

3.2.3 Ferric iron concentration

The influence of Fe^{3+} concentration on the bioleaching is shown in Table 7. While Fe^{3+} concentration was low, the leaching rate of arsenic increases quickly with the increasing of Fe^{3+} concentration. From 1.5 g/L to 4.2 g/L of Fe^{3+} concentration, the arsenic leaching rate grows from 50.8% to 75.3%. However, when Fe^{3+} concentration reaches the value of 6.5 g/L, relative micro-variation of the leaching arsenic rate appears. Thereby, it is proper that Fe^{3+} concentration is kept at about 6.5 g/L.

3.2.4 Leaching time

Table 8 lists the results gained by the variation of bioleaching time. With increasing time, the leaching rate of arsenic increases obviously. Under the pulp concentration of 10%, complete bioleaching requires for 5 days.

4 FILUID SEMI-CONTINUOUS BIOLEACHING AND CYANIDATION

4.1 Semi-continuous bioleaching process

Semi-continuous bioleaching experiment was conducted in 4 serial connected fluidized-bed biological reactors. According to priority, these tanks could be entitled regulating tank, leaching tank 1, leaching tank 2 and leaching tank 3 respectively. Regulating tank was used for mixing pulp and concentrates were added to it at a concentration of 10%. Sulfuric acid was added to the pulp in order to lower pH to about 2.0. Leaching tank 1 was used for enrichment, after several days leaching, the feed drawn from tank 1 injected into tank 2 until the following tanks were slowly filled. The feed rate was 150~ 300 mL.

4.2 Results and discussion

Total residence time of condition 1 and condition 2 was 144 h and 96 h respectively. The leaching results under two conditions are shown in Table 9 and Table 10. Under condition 1, the leaching rate of arsenic of tanks 1, 2, 3 is s 59%, 78% and 91% respectively and most of arsenic is rid of in the first tank. With decreasing residence time, i.e. under condition 2, the role of two tanks behind is relatively obvious.

According to arsenic leaching rate and deferrization rate, the oxidation rate of pyrite and arsenopyrite could be calculated theoretically. The results from selective oxidation coefficient show that selective oxidation existed in the process of bioleaching, i.e. arsenopyrite was oxidized preferentially. Because gold in the concentrates is mostly encapsulated in arsenic but little in pyrite, the selective oxidation is significant for bioleaching the Jinya refractory gold concentrates.

Under condition 1, pH decreases from 2.05 in

Table 7 Results obtained by variation of Fe^{3+} concentration(pulp concentration 10%, 4days)

Item		Number 1	2	3	4	5
Condition	Fe^{3+} concentration/ ($g \cdot L^{-1}$)	1.5	4.2	6.5	9.5	11.5
Mineral weight	Added mineral weight/ g	100	100	100	100	100
	Acidwashing residues weight/ g	88.3	78.1	75.2	74.7	74.4
	Residues ratio/ %	88.3	78.1	75.2	74.7	74.4
Arsenic leaching results	Arsenic in residues/ %	6.88	3.91	2.87	2.74	2.45
	Arsenic leaching rate/ %	50.8	75.3	82.5	83.4	85.2
Gold leached	Gold in cyanidation residues/ ($g \cdot t^{-1}$)	16.35	8.52	5.74	6.01	4.70
	Gold recovery/ %	66.8	84.7	90.0	89.6	91.9

Table 8 Results obtained by variation of bioleaching time ($[Fe]^{3+}$ 6.5 g/ L)

Item		Number 1	2	3	4	5	6	7
Condition	Time/ d	3	3	3	4	4	4	5
	Pulp concentration/ %	5	8	10	5	8	10	10
Mineral weight	Added mineral weight/ g	50	80	100	50	80	100	100
	Acidwashing residues/ g	34.8	61.7	81.7	33.8	55.4	75.2	68.5
	Residue ratio/ %	69.6	77.2	81.7	67.6	69.2	75.2	68.5
Arsenic leaching results	Arsenic in residues/ %	1.89	3.85	4.50	1.86	2.17	2.87	2.25
	Arsenic leaching rate/ %	89.3	75.9	70.2	89.8	87.8	82.5	87.5
Gold leached	Gold in cyanidation residues/ ($g \cdot t^{-1}$)	3.26	6.52	9.43	3.02	3.92	5.74	3.82
	Gold recovery/ %	94.7	88.4	82.2	95.3	93.7	90.0	93.9

Table 9 Main indexes of stable operation under the first condition*

	Main indexes	Serial number of reactor 1	2	3
Solvent iron	Residence time/ h	48	96	144
	pH	2.05	1.70	1.65
	E/ mV	508	548	560
	Oxygen content/ ($mg \cdot L^{-1}$)	7.0	7.8	7.6
	Iron in liquid phase/ ($g \cdot L^{-1}$)	8.47	9.72	11.06
	Precipitated iron/ ($g \cdot L^{-1}$)	1.50	4.62	5.77
	Total iron/ ($g \cdot L^{-1}$)	9.97	14.34	16.83
	Deferrization rate/ %	32	44	54
Solvent arsenic	Arsenic in liquid phase/ ($g \cdot L^{-1}$)	6.39	7.18	6.94
	Precipitated arsenic/ ($g \cdot L^{-1}$)	0.87	2.41	4.25
	Total arsenic/ ($g \cdot L^{-1}$)	7.25	9.59	11.19
	Arsenic leaching rate/ %	59	78	91
Theory oxidation rate	Arsenopyrite oxidation/ %	59	78	91
	Pyrite oxidation/ %	20.7	29.8	38.5
	Selective oxidation coefficient	2.85	3.64	2.36

* First operation condition: pulp concentration 10%, dilute rate 0.0069 h^{-1}, total residence time 144 h, transition volume 250 mL per transition, transition time-interval 12 h, concentrate size of 70% of < 44 μm, leaching temperature 30 ±2 ℃

Table 10 Main indexes of stable operation under the second condition

	Main indexes	Serial number of reactor 1	2	3
Solvent iron	Residence time/ h	32	64	96
	pH	2.08	1.78	1.73
	E/ mV	489	517	550
	Oxygen content/ ($mg \cdot L^{-1}$)	8.2	8.0	8.6
	Iron in liquid phase/ ($g \cdot L^{-1}$)	5.18	7.83	8.92
	Precipitated iron/ ($g \cdot L^{-1}$)	1.05	3.08	5.11
	Total iron/ ($g \cdot L^{-1}$)	6.24	10.91	14.03
	Deferrization rate/ %	20	35	45
Solvent arsenic	Arsenic in liquid phase/ ($g \cdot L^{-1}$)	4.82	6.99	7.58
	Precipitated arsenic/ ($g \cdot L^{-1}$)	0.35	1.65	2.50
	Total arsenic/ ($g \cdot L^{-1}$)	5.17	8.64	10.08
	Arsenic leaching rate/ %	42	70	82
Theory oxidation rate	Arsenopyrite oxidation/ %	42	70	82
	Pyrite oxidation/ %	10.8	20.3	29.5
	Selective oxidation coefficient	3.89	3.45	2.78

Second operation condition: Pulp concentration 10%, Dilute rate 0.010 h^{-1}, Total residence time 96 h, Transition volume 250 mL per transition, Transition time-interval 8 h, Concentrate size 70% of < 44 μm, Leaching temperature 30 ±2 ℃

the first tank to 1.65 in the last one and pulp potential increases from 508 mV to 560 mV (SCE). Iron in the liquid phase is varying from 8.47 g/L to 11.06 g/L. Under condition 2, pH decreases from 2.08 to 1.69, and pulp potential increases from 489 mV to 550 mV. Iron in the liquid phase is varying from 5.18 g/L to 8.92 g/L. Under both conditions, the oxygen content of pulp is about 8.0 g/L basically.

4.3 Cyanidation of residues

Triple bioleaching residues were selected stochastically from the last tank of both operation conditions for cyanidation and the cyanidation results are shown in Table 11. From table 11, it can be seen that the gold cyanidation rate all exceeds 80% and maximum value can reach 93%.

5 CONCLUSIONS

The fluid bioleaching shows good results. For the Jinya refractory gold concentrate containing 12.35% arsenic and 43.5 g/t gold, an arsenic extraction rate reaches 82.5% after 4-day of batch fluid bioleaching under the optimized condition of pH 2.0, ferric ion concentration 6.5 g/L and pulp concentra-

Table 11 Cyanidation results of semi-continuous bioleaching residues

Operation condition	Number	Gold in bioleaching residue/ ($g\cdot t^{-1}$)	Gold in cyanidation residue/ ($g\cdot t^{-1}$)	Gold recovery/ %
First condition	1-1	48.2	3.8	92.1
	1-2	46.5	2.9	93.7
	1-3	47.8	4.7	90.1
	Average value	47.5	3.8	92.0
Second condition	2-1	45.2	5.8	87.2
	2-2	46.8	6.5	86.1
	2-3	44.7	4.9	89.0
	Average value	45.6	5.7	87.5

tion 10%. And leaching rate of gold in the following gold cyanidation is over 90%. The semi-continuous fluid bioleaching shows that arsenic in the concentrate can be rid of 91% after 6-day leaching, even after 4 days 82% of arsenic extraction rate is still obtained. The recovery rates of gold are 92% and 87.5% respectively in cyaniding the above bioleached residues.

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