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Recovery of Gold from Refractory Arsenic Gold Concentrate by a Process of Thiobacillus Ferrooxidans Oxidation - Cyanidation

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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 Guangxi Jinya refractory gold arsenical concentrate was studied. An 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 6.5g/L and pulp concentration 10%. And leaching rate of gold in the following gold cyanidation is over 90%. The parameters of three series fluid-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.

Keywords: refractory arsenical gold concentrate, fluidized-bed reactor, semi-continuous bioleaching

1. Introduction

Ores those that yield low recoveries of gold when treated by the conventional grinding and cyanidation process are called refractory gold ores. A common cause of 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 gold within the sulfide matrix determine to a very large 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 [3,4,5,].

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 Guangxi Jinya gold deposit, which is a typical Carlin-type gold deposit, located at Fengshan County, the northwest part of Guangxi, China, lies to southeast of Yunnan, Guizhou and Guangxi Gold Triangle area. Spot technological flow was used as following: 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 smelting plant for recovery of gold. Roasting is an expensive pretreatment and has negative environmental implications. With the saturation of white arsenic market problem, the effective or expensive ways have to be taken for managing white arsenic [8,9]. Therefore, it is of great importance to develop biooxidation technique for leaching gold from Guangxi Jinya gold concentrates.

On the basis of our previous fundamental studies on bioleaching mechanism of sulfide minerals, martrix of gold, including arsenopyrite[2] and pyrite[1], a novel fluidized-bed reactor is designed and installed for bioleaching in batch and semi-continuous ways, which is aimed at bioleaching Jinya refractory gold concentrates.

2. Materials and Methods

2.1 JINYA Gold Concentrate

Direct cyanidation experiment with the ore showed that 0.2% NaCN, pH 10~11 and an agitation leaching time of 48 hours 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 and clay mineral must be concentrated by flotation.

A sulfide flotation concentrate contains 43.5g/t Au, 27.92%

sulfur, 31.18% total Fe, and 12.35% arsenic as seen table 1. Without biooxidation pretreatment, a maximum gold recovery of 12.5% was obtained by direct cyanidation. Even after roasting (temperature 750℃,3 hours), gold recovery from the calcine was still only 47.4%, because of existing quadric sinter cake. Table 2 and table 3 give the arsenic phase analysis 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 listed in table 4.

Table 1. Chemical analysis of Jinya gold concentrate

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

Table 2. Arsenic phase analysis

Phase	Arsenic in arsenopyrie	Arsenic in arsenate	Arsenic in oxidation state	Total
Content (%)	10.56	1.33	0.85	12.76

Table 3. Gold distribution state in gold concentrate

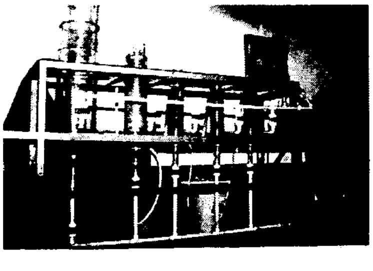
Gold distribution	Free and intergrowth gold	Gold encapsulated in sulfide	Gold in gangue	Gold in oxide	Total
Content (g/t)	4.65	39.73	0.56	0.26	45.20
Occupancy (%)	10.28	87.90	1.24	0.58	100.0

Table 4. Size distribution of gold concentrate

Grade (mesh)	+45	-45 ~ +110	-110 ~ +200	-200 ~ +320	-320
Distribution (%)	0.70	4.90	10.50	16.70	67.20

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 [10]. According to the biooxidation feature, a gas-liquid-solid three-phase fluid leaching technology was used in this study as shown in Fig.1.



Figur 1 Setup for bioleaching

The whole setup consists of several reactors. It can be used for batch and semi-continuous bioleaching with different experimental requirement. The bioleaching reactor divided into two parts, temperature control part and aerating part. Bioleaching temperature is controlled by the cycling water jacket outside reactor. Air is provided by model HG-780 increased-oxygen motor. The columnar reactor is made of organic glass with the ratio of height and diameter ratio being 5:1. The bubbler is installed on the conical bottom of the reactor. With the range of 0.8-1.5L/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 leaching as illustrated in fig.2.

2.3 T. Ferrooxidans Culture

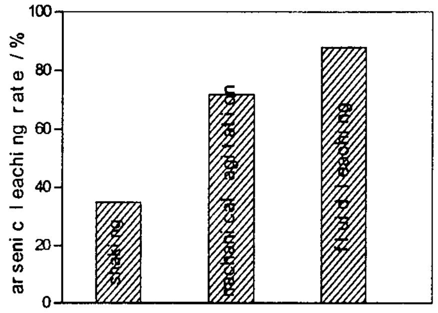


Figure 2. effectiveness of arsenic leaching in different reactor

The bacterium Thiobacillus ferrooxidans was provided by the Chinese Academy of Science. The medium for the bacterial culture and bioleaching experiment consists of 0.45g $(NH_4)_2SO_4$, 0.15g K_2HPO_4, 0.5g $MgSO_4 \cdot 7H_2O$, 0.05g KCl, 0.01g $Ca(NO_3)_2$ per liter, with adjusting pH to 2.0 by 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 bacteria 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 (10g/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 l-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 residue, the leaching 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 were listed in table 5. When pH value was 2.0, the best result of leaching arsenic was obtained for 89.3%, and the corresponding gold recovery got 94.7%. With respect to bioleaching of this concentrate, the optimum pH of was 2.0.

Table 5 Experimental conditions and results with the variation of pH (pulp concentration 5%、[Fe]$^{3+}$ 6.5g/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 leaching results	Gold in cyanidation residues (g/t)	12.26	5.65	3.26	4.44	6.22
	Gold recovery (%)	77.2	90.3	94.7	92.6	88.9

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 could be was 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 leaching rate of arsenic within 7 days did not exceed 50.1%. Therefore, it was rational for selecting 10% pulp concentration.

Table 6 Experimental conditions and results with the variation of pulp concentration (pH2.0、[Fe]$^{3+}$ 6.5g/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 leaching results	Gold in cyanidation residues (g/t)	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

3.2.3 Ferric iron concentration

The influence of Fe^{3+} concentration on the bioleaching was shown in table 7. While Fe^{3+} concentration was low, the leaching rate of arsenic increased quickly with the increase in Fe^{3+} concentration. From 1.5g/L to 4.2g/L of Fe^{3+} concentration, the leaching arsenic rate grew from 50.8% to

75.3%. However, when Fe^{3+} concentration reached the value of 6.5g/L, relative micro-variation of the leaching rate appeared. Thereby, it is proper that Fe^{3+} concentration was kept in about 6.5g/L.

Table 7 Experimental conditions and results obtained with the variation of Fe^{3+} concentration (pulp concentration10%、4days)

Item	Number	1	2	3	4	5
Condition	Fe^{3+} concentration (g/L)	1.5	4.2	6.5	9.5	11.5
Mineral weight	Added mineral weight(g)	100	100	100	100	100
	Acidwashi-ng 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 leaching results	Gold in cyanidatio-n residues (g/t)	16.35	8.52	5.74	6.01	4.70
	Gold recovery (%)	66.8	84.7	90.0	89.6	91.9

3.2.4 Leaching time

Table 8 Experimental conditions and results obtained with the variation of bioleaching time ($[Fe]^{3+}$ 6.5g/L)

Item	Number	1	2	3	4	5	6	7
Condition	Time (d)	3	3	3	4	4	4	5
	Pulp concentrati-on(%)	5	8	10	5	8	10	10
Mineral weight	Added mineral weight (g)	50	80	100	50	80	100	100
	Acidwashi-ng 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 leaching results	Gold in cyanidation residues (g/t)	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 8 lists the results with the variation of bioleaching time. With increasing time, the leaching rate of arsenic increased obviously. Under the pulp concentration of 10%, complete bioleaching required for about 5 days.

4. Fluid 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 150-300mL, introduced in 2 or 3 increments per day.

4.2 Results and Discussion

Table 9 main indexes of stable operation under the first condition

1	Pulp concentration (w/v) %	10
2	Dilute rate (h^{-1})	0.0069
3	Total residence time (h)	144
4	Transition volume (ml)	250 per transition
5	Transition time-interval (h)	12
6	Concentrate size	70% of -320 mesh
7	Leaching temperature (℃)	30℃±2

Main indexes		Serial number of reactor 1	2	3
Residence time (h)		48	96	144
pH		2.05	1.70	1.65
E (mV)		508	548	560
Oxygen content (mg/L)		7.0	7.8	7.6
Solvent iron (g/L)	Iron in liquid phase	8.47	9.72	11.06
	Precipitated iron	1.50	4.62	5.77
	Total iron	9.97	14.34	16.83
Deferrization rate (%)		32	44	54
Solvent arsenic (g/L)	Arsenic in liquid phase	6.39	7.18	6.94
	Precipitated arsenic	0.87	2.41	4.25
	Total arsenic	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	2.64	2.36

Total residence time of condition1 and condition 2 was 144 hours and 96 hours respectively. The leaching results under two conditions were shown in table 9 and table 10. Under condition 1, the leaching rate of arsenic of tanks was 59%, 78% and 91% respectively and most of arsenic was got rid of in the first tank. With decreasing residence time, i.e. under condition 2, the role of two tanks behind was relatively obvious.

Table 10 main indexes of stable operation under the second condition

1	Pulp concentration (w/v) %	10
2	Dilute rate (h^{-1})	0.010
3	Total residence time (h)	96
4	Transition volume (ml)	250 per transition
5	Transition time-interval (h)	8
6	Concentrate size	70% of -320 mesh
7	Leaching temperature (℃)	30℃±2

Main indexes		Serial number of reactor		
		1	2	3
Residence time(h)		32	64	96
pH		2.08	1.78	1.73
E(mV)		489	517	550
Oxygen content (mg/L)		8.2	8.0	8.6
Solvent iron(g/L)	Iron in liquid phase	5.18	7.83	8.92
	Precipitated iron	1.05	3.08	5.11
	Total iron	6.24	10.91	14.03
Deferrization rate (%)		20	35	45
Solvent arsenic (g/L)	Arsenic in liquid phase	4.82	6.99	7.58
	Precipitated arsenic	0.35	1.65	2.50
	Total arsenic	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

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 showed that selective oxidation existed in the process of bioleaching, i.e. arsenopyrite was oxidized preferentially. Because gold in the concentrates was mostly encapsulated in arsenic but little in pyrite, the selective oxidation was significant for bioleaching the Jinya refractory gold concentrates.

Under condition 1, pH decreased from 2.05 in the first tank to 1.65 in the last one and pulp potential increased from 508 mV to 560 mV (SCE). Iron in the liquid phase was varying from 8.47g/L to 11.06g/L. Under condition 2, pH decreased from 2.08 to 1.69, and pulp potential increased from 489mV to 550 mV. Iron in the liquid phase was varying from 5.18g/L to 8.92g/L. Under both conditions, the oxygen content of pulp was about 8.0g/L basically.

Residues Cyanidation

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

Table 11 Cyanidation results of semi-continuous bioleaching residues

Operation condition	Number	Gold in bioleaching residues g/t	Gold in cyanidation residues g/t	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

Conclusion

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 6.5g/L and pulp concentration 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 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.

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