

Intensified alkaline leaching pretreatment of refractory gold concentrates at common temperature and pressure^①

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Abstract: A new process for the hydrometallurgy of refractory gold concentrates was presented. The process comprises grinding-leaching, intensified alkaline leaching (IAL), cyanidation and adsorption. In a stirring-type pulverizing-leaching tower mill, the concentrate is ground to $< 35.6 \mu\text{m}$ of 95.5 % while simultaneously leached by NaOH of 12 kg/t, then carried out intensified alkaline leaching for 48 h by NaOH of 108 kg/t in enhanced agitation tanks with the pulp concentration of 40% solids at the environmental temperature of $9.5 \sim 13.5^\circ\text{C}$ and the environmental pressure of 10^5 Pa . The oxidation rate of As is 94.9%, and 47.6% for S. The total consumption of NaOH is only 20% of that theoretically calculated under the conditions of full oxidation at the same oxidation rates of arsenic to arsenate and sulfur to sulfate. The gold leaching rate by NaCN in 24 h is increased from 9.2% before pretreatment to 94.2%. The consumption of NaCN is 7.5 kg/t, which is one times less than that before pretreatment. The extraction cost of gold is about 422 Yuan/t.

Key words: refractory gold concentrates; grinding-leaching; intensified alkaline leaching (IAL); pretreatment; common temperature and pressure

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1 INTRODUCTION

When a proportion of gold contained in a sulfidic concentrate is in solid solution within arsenopyrite, ultrafine grinding may not result in complete gold liberation, and oxidative destruction of the sulfides may be necessary. The options are roasting, pressure oxidation or bacterial oxidation^[1]. Conventional methods of alkaline leaching of gold arsenosulfide concentrates in an autoclave require expensive equipment as well as high-cost energy and reagents. Rossovsky^[2] reported an alkaline leaching method which contains fine grinding ($< 40 \mu\text{m}$), intensive agitation, flotation and cyanidation. After alkaline leaching, the regulation of the pulp must be done at first, then flotation be carried out. Particles larger than $10 \mu\text{m}$, along with occasional undecomposed ones, were extracted to the froth product. For the flotation of fine particles, it is not easy to be completed. Moreover, the froth product amounted to be about 8%~12% of the total concentrates which needs to be returned to alkaline leaching is subjected to ultrafine grinding to $< 10 \mu\text{m}$. For any type mill available now, it is difficult to reach the milling size of $<$

$10 \mu\text{m}$. The flotation tailings containing practically no sulfides are leached by cyanide, in the meantime meaning that the consumption of NaOH in alkaline leaching is very high.

In this paper, a hydrometallurgical method is described for processing refractory gold concentrates, of which intensified alkaline leaching (IAL) is finished at common temperature and pressure, and then followed by cyanidation and adsorption of the slurry without flotation^[3]. This process was tested under laboratory conditions with 11 sorts of concentrates of typically refractory gold deposits in China, and resulted in consistent gold extractions in the range of 93%~98% from 0~20% before pretreatment.

2 EXPERIMENTAL

2.1 Experimental flowsheet and apparatus

The experimental flowsheet is shown in Fig. 1. The main apparatus used in this experiment include feeder, stirring-type pulverizing-leaching tower mill^[4] with size of $d 159 \text{ mm} \times 840 \text{ mm}$, enhanced agitation tank^[5] of $d 190 \text{ mm} \times 285 \text{ mm}$, laser sizer (Mastersizer Ver. 2.15), temperature gauge, pH

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gauge, air compressor, effusion meter, cyanidation-adsorption tank, filter, baking oven, and XRD, etc.

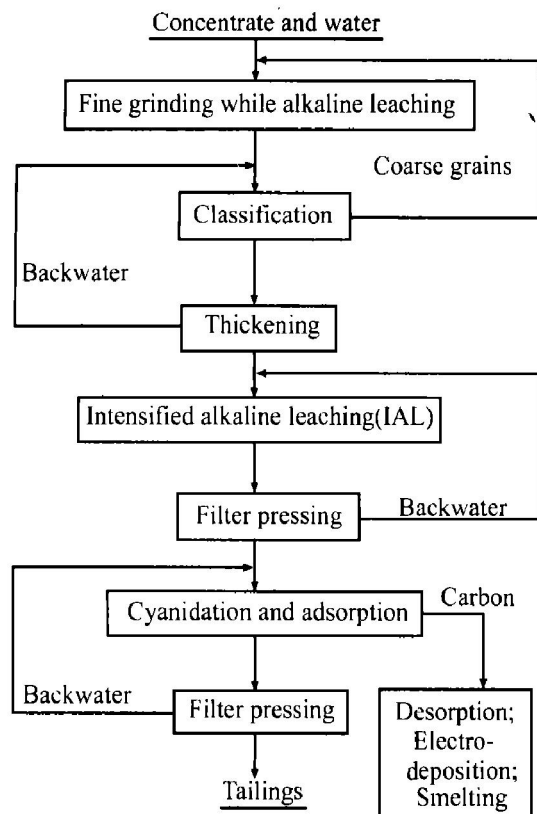


Fig. 1 Flowsheet of gold extraction process

2.2 Raw material and reagents

The concentrate used in this work is produced by Danyin Ltd. in Liaoning Province in China. The concentrate contains Au 62 g/t, Ag 110 g/t, As 4.1%, S 21%, Fe 21.63%, Cu 0.026%, Pb 0.17%, C 2.33%, Zn 1.28%, Al 4.0%, CaO 3.75%, and MgO 2.45%. 80% of the total gold is not visible, and 72.8% of the total gold is distributed in FeAsS, and 4.4% in FeS₂. The size of other visible gold is < 10 μm. By conventional cyanide leaching directly under the grinding size of < 35.6 μm of 95.5%, the gold leaching rate is only 9.2% with the consumption of NaCN 15 kg/t. This is a typical refractory gold concentrate.

The reagents used in this test are NaOH (IR), NaCN (AR), CaO (IR), Ca(ClO)₂ (IR), Fe₂(SO₄)₃ (AR). The water comes from the city water pipe.

2.3 Experimental conditions

Based on the presented concentrate, the optimum conditions for this work are shown in Table 1–3.

3 RESULTS AND DISCUSSION

3.1 Grinding while simultaneously alkaline leaching

When grinding while simultaneously alkaline

Table 1 Conditions for grinding-leaching

Concentrate	Water	Particle size of product	Aerating air
20 kg/d	20 L/d	95.5%, < 35.6 μm	0.1 m ³ /h
NaOH	Temperature	Pressure	Concentration
12 kg/t	9.5–13.5 °C	1 × 10 ⁵ Pa	50% solids

Table 2 Conditions for IAL

Water of regulation	Conc.	Temp.	Pressure	Aerating air
10 L/d	40% solids	9.5–13.5 °C	1 × 10 ⁵ Pa	0.3–0.4 m ³ /h
Speed of agitation	NaOH	pH	Time of leaching	Temperature of pulp*
10–13 m/s	108 kg/t	~ 11	48 h	26 °C (beginning) 63 °C (peak) 43 °C (end)

* Without preheating and incubation

Table 3 Conditions for cyanidation-adsorption

CaO		Concentration of pulp	Concentration of carbon
70 kg/ t		37% - 40% solids	30 g/ L
NaCN	pH	Temperature of pulp	Time
7.5 kg/t	~ 11	11 - 14 °C	24 h

leaching completes in the pulverizing-leaching tower mill, namely, at the beginning of intensified alkaline leaching (IAL), the oxidation rate of As is 22%, and 4.5% for S. The corresponding gold leaching rate by cyanide for 24 h is increased to 14.5% from 9.2% at the same grinding size without adding alkaline while pulverizing. Due to the precipitation reaction, there are almost no As and Fe (< 0.1 mg/L), but 1.6 g/L S in the solution. The contribution to arsenic oxidation in the tower mill is large.

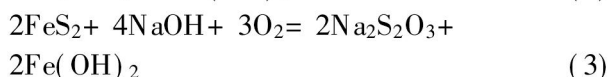
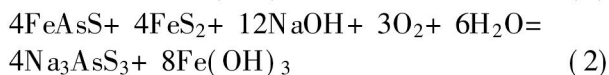
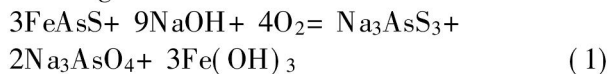
An important feature of the pulverizing-leaching tower mill is that it enables chemical leaching to be run with the size reduction while simultaneously pulverizing^[4,6–9] so that the tower mill can be used as a pre-reactor^[3,9] which contributes to the oxidation of arsenopyrite (FeAsS), due to the intensive and active functions^[4,6,9,10] as follows:

- enhanced mass transfer conditions;
- freshly liberated FeAsS particles are subjected to O₂ and NaOH;
- surface coating and tarnishing are removed from the FeAsS particles;
- passivation due to oxide film is not possible under the high shear conditions;
- coarse FeAsS particles are pulverized fine, their surface area is increased and hence the oxidation

speeds up;

(f) the heat generated by grinding and oxidation reactions increases the oxidation speed.

Thus, the grinding-leaching combined with the enhanced agitation can substantially increase the reaction kinetics of alkaline leaching so that the oxidation of FeAsS can be induced at common temperature and pressure instead of at high ones as follows:



Under certain conditions, the anions $\text{S}_2\text{O}_3^{2-}$ and AsS_3^{3-} can be further oxidized to SO_4^{2-} and AsO_4^{3-} , $\text{Fe}(\text{OH})_2$ oxidized to $\text{Fe}(\text{OH})_3$, and $\text{Fe}(\text{OH})_3$ decomposed to Fe_2O_3 . The extent of reaction (3) depends on the reactivity of FeS_2 (pyrite). Due to the generation of thiosalts, the smaller amounts of NaOH compared to those theoretically calculated under the conditions of full oxidation of arsenic to arsenate and sulfur to sulfate are required.

3.2 Intensified alkaline leaching (IAL)

3.2.1 Selective oxidation kinetics of arsenic and sulfide

As shown in Fig. 2, after grinding-leaching and with the IAL going on in enhanced agitation tanks, arsenic and sulfide are selectively oxidized, and arsenic is oxidized faster than sulfide. When IAL for 6, 12, 24, 36, and 48 h, the oxidation rates of As are 77.9%, 90.4%, 92.4%, 94.4%, and 94.9% respectively; but 28.6%, 32.1%, 38.1%, 43%, and 47.6% for S. The corresponding cyanide leaching rates of gold in 24 h are respectively enhanced to 83.9%, 87.9%, 90%, 93.1%, and 94.2%. There is a linear relationship between the cyanide leaching rate of gold and the oxidation rate of As. Without ultra-fine grinding, the IAL process can meet the requirements of mineralogical liberation characteristics, and then high gold recovery can be reached.

The selective oxidation of arsenic and sulfide combining with the generation of thiosalt means that the very smaller amount of NaOH is required. After IAL for 48 h, the consumption of NaOH accumulated the quantity of 12 kg/t in grinding is 120 kg/t, which is only 20% of that theoretically calculated under the conditions of full oxidation at the same oxidation rates of arsenic to arsenate and sulfur to sulfate.

3.2.2 Property changes of pulp and solution

The color of the IAL solid phase is changing fast. When IAL for 6 h, the yellowed color of the solids is getting obvious, which shows the presence of Fe_2O_3 . But the liquor color is getting brown and

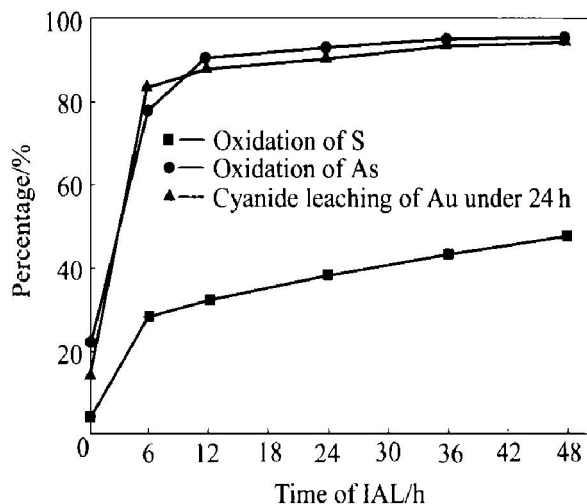


Fig. 2 Selective oxidation kinetics of arsenic and sulfide and correspondingly gold recovery

brown.

Fig. 3 and Fig. 4 describe the property changes of pulp and solution. When IAL 12 h, the φ_h of the pulp, and the contents of As and Fe in the solution, reach their peak values of -27 mV, 7.3 g/L and 4.43 g/L, respectively. Afterwards, they all gradually fall down. At the end of IAL, the solution contains As 4.9 g/L and Fe 1.11 g/L, but the content of S successively increases to 43.8 g/L.

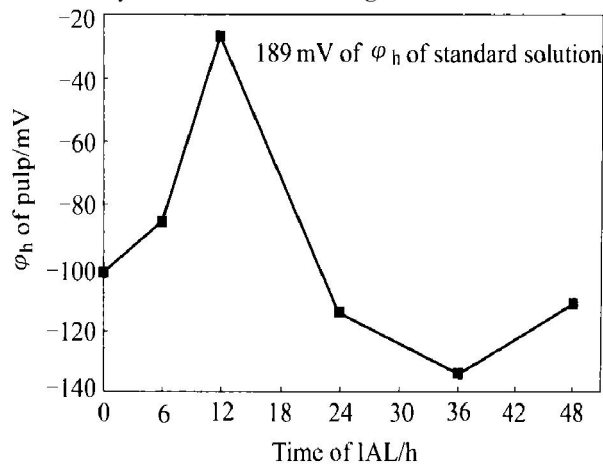


Fig. 3 φ_h change of pulp under pH= 11

Due to the precipitation of Fe^{3+} and AsO_4^{3-} in the solution of IAL, the oxidized As is again turned into the solid phase. At the end of IAL, the solid residue contains As 3.26% and S 11% . After the regulation of the pulp by CaO 70 kg/t, the contents of As and Fe in the solution respectively decrease to 0.82 g/L and 0.0073 g/L. And the filterability of the pulp can be improved so that the slurry can be filter-pressed before cyanidation.

3.2.3 Change of particle size

Due to the selective oxidation of As and S in the IAL process, the As is almost oxidized completely. But most of S is nonoxidized and remains its primitive phase. This is verified by XRD analysis, as shown in

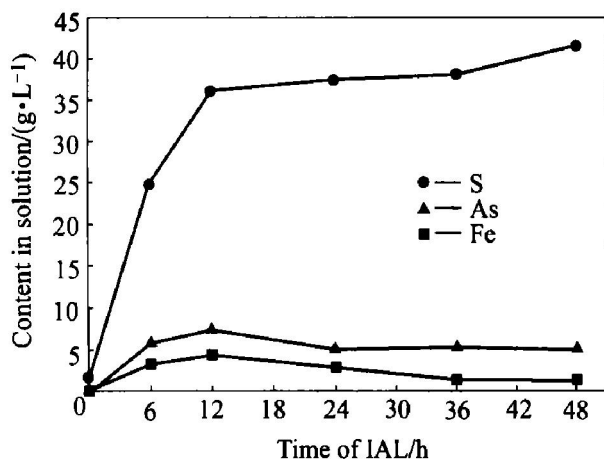


Fig. 4 Content changes of S, As and Fe in solution

Fig. 5. In the solid residue, there is no FeAsS but FeS₂. Thus, most of the skeletal structure of particles can be remained. After IAL for 48 h, the particle size is reduced slightly, from < 35.6 μm of 95.5% before IAL to < 35.6 μm of 98.5%, as shown in Fig. 6. This is very profitable for the subsequent extraction of gold.

3.2.4 Change of pulp temperature

As more heat given out from the oxidation reac -

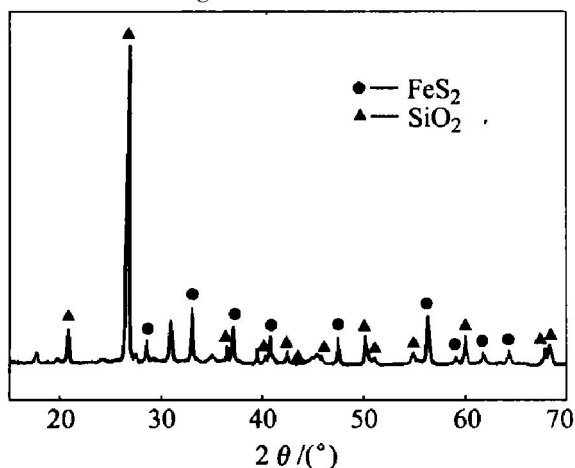


Fig. 5 XRD pattern of solids after IAL

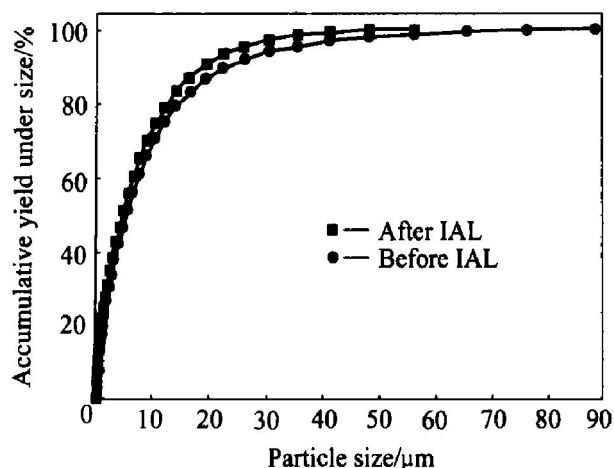


Fig. 6 Change of particle distribution after IAL

tions in IAL, the temperature of pulp rises quickly, as shown in Fig. 7. When IAL for 6 h, it reaches the peak value of 63 °C from 26 °C at the beginning. Then it quickly drops. After IAL for 12 h, it slowly falls in the range from 48 °C to 43 °C in the end.

Compared with the oxidation course of As and S in Fig. 2 and the consumption kinetics of NaOH in Fig. 7, the changing tendency of the pulp temperature is very consistent with them. During IAL for 0 - 1.5 h, 1.5 - 6 h, 6 - 12 h, and 12 - 48 h, the consumption speeds of NaOH are respectively 8 kg/(t·h), 10 kg/(t·h), 2 kg/(t·h), and 1 kg/(t·h). Meanwhile the rising or dropping speeds of the pulp temperature are respectively 16 °C/h, 3 °C/h, - 2.5 °C/h, and - 0.14 °C/h. When IAL for 6 h, the oxidation rate of As is 77.9 %, but only 28.6 % for S. These results show that the rapid oxidation of As in the initial stage of IAL and the generated heat is the main reason for the pulp temperature rising. After the pulp temperature reaches the peak, a small quantity of As and S continues to be slowly oxidized, which results in the decrease of heat generation and hence the falling of pulp temperature. But anyhow, the heat generation from oxidation is keeping on so that the temperature of the pulp is always higher than that of its environment. This results in a higher adaptability for the IAL process, especially to the application in the cold areas.

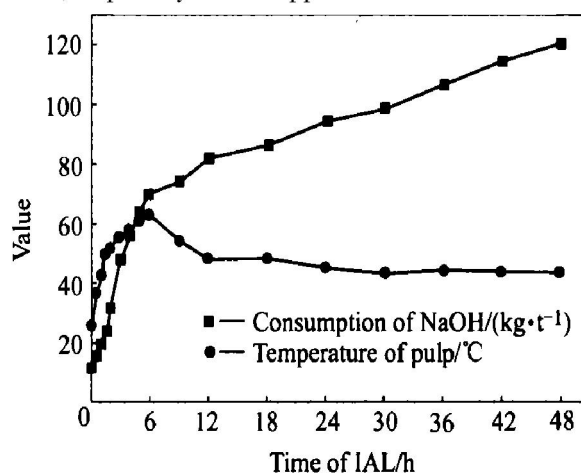


Fig. 7 Consumption kinetics of NaOH and temperature change of pulp

3.2.5 A new find on self-leaching of gold

Thiosulfate is a good extraction reagent for gold with less poison. Due to the generation of anions $S_2O_3^{2-}$ during IAL, the gold liberated from minerals can be simultaneously self-leached by anions $S_2O_3^{2-}$. After IAL for 48 h, the self-leaching rate of gold is 58.1%. The liquid phase contains $S_2O_3^{2-}$ 58 g/L. To other refractory gold concentrates, the self-leaching rate of gold in IAL was 91.5% - 92.8%. In this field, some further research should lead to a breakthrough at the pretreatment of refractory gold ores and the non-cyanide extraction of gold.

3.3 Gold extraction

After IAL, CaO and NaCN are added into the slurry in order. Because the equilibrium constant^[11] of anions $\text{Au}(\text{CN})_2^-$ is about 10^{10} times larger than that of anions $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$, the anions $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$ can be quickly turned into anions $\text{Au}(\text{CN})_2^-$ at the beginning of cyanidation. And this conversion is very complete. During cyanide leaching, the activated charcoal of 30 g/L is added into the pulp. After 24 h, the gold leaching rate is 94.2%, and 99.1% of adsorption. The consumption of NaCN is 7.5 kg/t, which is one times less than that before pretreatment.

3.4 Environmental control

After gold extraction, in conventional agitation tanks, $\text{Ca}(\text{ClO})_2$ of 5 kg/m³ and $\text{Fe}_2(\text{SO}_4)_3$ of 6 kg/m³ are respectively added in the pulp. The contents of As and NaCN in the solution are all decreased to < 0.5 mg/L, which can not cause the pollution to the environment.

3.5 Techno-economic assessment and new progresses

A preliminary techno-economic assessment of the proposed technology shows that the cost of treating 1 t of the objective concentrate is about 422 Yuan including 30 Yuan in grinding-leaching. The investment of whole installations of treating 50 t of concentrate per day is about 3.5–4 million Yuan, which is about 4–5 times less than those of pressure or bacterial oxidation.

Now a pretreatment plant treating 10 t refractory gold concentrate per day has been built up successfully in Liaoning Province in China. Other two extraction plants treating 10 t refractory gold concentrates per day and 30 t per day are now being built in Shandong and Hunan Provinces in China. This proposed process is valid for some certain types of refractory gold arsenosulfide concentrates.

4 CONCLUSIONS

1) Fine grinding while alkaline leaching in a pulverizing-leaching tower mill and intensified alkaline leaching for 48 h in enhanced agitation tanks at the environmental temperature of 9.5–13.5 °C and the environmental pressure of 10^5 Pa result in a consistent gold recovery by cyanide of 94.2% of the objective refractory concentrate. The consumption of NaCN is decreased to 7.5 kg/t, which is one times less than that before pretreatment.

2) Pretreating at common temperature and pressure has no danger of high pressure and oxygen in comparison with the autoclave and no gas and dust in comparison with roasting.

3) Grinding-leaching results in 22 % of arsenic

oxidized in the tower mill and cuts down its oxidation course. The combination of grinding-leaching, selective oxidation of arsenic and sulfide, and the generation of thiosalts results in a higher oxidation rate of As of 94.9% and a lower oxidation rate of S of 47.6% at a lower consumption of NaOH of 120 kg/t. The amounts of NaOH is only 20% of those theoretically calculated under the conditions of full oxidation at the same oxidation rates of arsenic to arsenate and sulfur to sulfate.

4) The new find on self-leaching of gold during intensified alkaline leaching can lead to a significant progress in the non-cyanide extraction of gold meanwhile the pretreatment of refractory gold ores.

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