

A new extraction process of refractory gold arsenosulfide concentrates

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(Received 2002-11-15)

Abstract: A new hydrometallurgical process for the refractory gold arsenosulfide concentrates under normal temperature and pressure was presented. The experimental results of a refractory gold concentrate show that the total consumption of NaOH in alkaline leaching is only 40% of those theoretically calculated under the conditions of full oxidization at the same oxidation of arsenic to arsenate and sulfur to sulfate. After alkaline leaching, cyanidation and adsorption were carried out for 24 h. The dissolution of gold by NaCN is increased to 95.3% from 12.8% before pretreatment, and meanwhile 99.3% of the adsorption of gold by activated charcoal. The consumption of NaCN for one ton ore is 10 kg, which is 1.2 times less than that before pretreatment. As it is carried out under normal temperature and pressure, the investment of installations is also decreased.

Key words: refractory gold arsenosulfide concentrates; normal temperature and pressure; pretreatment

[This project is jointly supported by the Creative Foundation of the National Northeast Research and Developing Base of High-Performance and New Materials of China (No.CX9906-3), the Natural Science Foundation of Liaoning Province of China (No. 2001101015).]

The gold can be effectively recovered only after the pretreatment for refractory gold ores, which depends on the mineralogical and liberation characteristics of gold in the ores. In many instances the gold contained in an arsenosulfidic concentrate is in solid solution within arsenopyrite (FeAsS), ultra-fine grinding may not result in complete liberation, and the oxidative destruction of arsenosulfide may be necessary. The options are roasting, pressure oxidation and bacterial oxidation, *etc.* [1,2]. The conventional methods of alkaline leaching of arsenosulfide concentrates in an autoclave require expensive equipment as well as high-cost energy and reagents. Rossovsky [3] reported a method of alkaline leaching, which includes grinding of the concentrate to $<40\ \mu\text{m}$, leaching in sodium hydroxide solution at the ratio of liquid/solution of 5-6:1, flotation, ultra-fine grinding of the froth product to $<10\ \mu\text{m}$ and to return to alkaline leaching, and cyanidation of the flotation tailings. In practice, it is not easy to complete fine particle flotation and to ultra-fine grind the froth product to $<10\ \mu\text{m}$ by the use of any type mill available now. Moreover, the flotation tailings containing practically no sulfides leached by cyanide, in the meantime means that the consumption of NaOH in alkaline leaching is very high.

In this paper, a hydrometallurgical method was described for processing refractory gold arsenosulfide concentrates, including the fine grinding while intensified alkali-leaching (FGWIAL) was first performed in a tower-type pulverizing-leaching mill, then the enhanced agitation alkali-leaching (EAAL) was carried out in the enhanced agitation tanks under normal temperature and pressure, and then followed by cyanidation and adsorption without flotation [4]. This technology was tested in laboratory by 11 sorts of concentrates from typical refractory gold deposits in China, and resulted in consistent extractions of gold in the range of 93%~98% from 0~20% before pretreatment.

1 Experimental

1.1 Experimental materials

The raw material used in this work is a refractory gold concentrate, produced from Yangjingou deposit in Jilin Province in China, which one ton ore contains 66.5 g Au, 90 g Ag, and mass fraction of elements were 12.4% As, 24.9% S, 28.5% Fe, 1.5% Cu and 0.17% Pb. By conventional method of cyanide leaching for 24 h, the dissolution of gold was only 12.8% at

the consumption of 22 kg NaCN. This is one of typical refractory gold concentrate.

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

1.2 Experimental flowsheet and apparatus

The experimental flowsheet is shown in **figure 1**, in which the main apparatus used include feeder, stirring-type pulverizing-leaching tower mill [5] of $\phi 159\text{mm}\times 840\text{mm}$ unit, enhanced agitation tank [6] of $\phi 190\text{mm}\times 285\text{mm}$ unit, laser particle size analyzer (Mastersizer Ver.2.15), XRD, pH gauge, air compressor, flow meter, cyanidation-adsorption tank, and filter, etc..

1.3 Experimental conditions

The basic experimental conditions are shown in **ta-**

Table 1 Conditions for fine grinding while intensified alkali-leaching (FGWIAL)

Content / kg·d ⁻¹	Water / L·d ⁻¹	Grinding size / μm	Aerating air / $\text{m}^3\cdot\text{h}^{-1}$	NaOH mass (1 t ore) / $\text{kg}\cdot\text{t}^{-1}\text{ore}$	Ambient Temperature / $^{\circ}\text{C}$	Ambient pressure / MPa	Solid content of pulp / %
24	24	<35.6 (96.6%)	0.1	12	10	0.1	50

Table 2 Conditions for enhanced agitation alkali-leaching (EAAL)

Water of modifi- cation / L·d ⁻¹	Solid content of pulp/ %	Ambient tempera- ture / $^{\circ}\text{C}$	Ambi- ent pres- sure/ MPa	Flow of air / $\text{m}^3\cdot\text{h}^{-1}$	Speed of agi- tation/ $\text{m}\cdot\text{s}^{-1}$	NaOH mass (1 t ore) / $\text{kg}\cdot\text{t}^{-1}\text{ore}$	pH	Time of leaching / h	Temperature of pulp* / $^{\circ}\text{C}$
12	40	10	0.1	0.3-0.4	10-13	184	~11	48	24(beginning) 65 (peak) 40 (end)

Note: Without preheating and incubation.

Table 3 Conditions for cyanidation-adsorption

CaO mass (1 t ore) / kg	Solid content of pulp / %	Charcoal mass / $\text{g}\cdot\text{L}^{-1}$	NaCN mass (1 t ore) / kg	pH	Temperature of pulp/ $^{\circ}\text{C}$	Time/ h
140	40	30	10	~11	10-15	24

2 Results and discussion

2.1 Fine grinding while intensified alkali-leaching (FGWIAL)

When the FGWIAL completed in a tower mill, *i.e.* at the beginning of enhanced agitation alkali-leaching (EAAL), the oxidation of As and S (mass fraction) are 40% and 8.43%, respectively. The corresponding dissolution of gold by cyanide for leaching 24 h is increased to 48% from 12.8% at the same grinding size of <35.6 μm of 96.6% under the conditions of no NaOH and air introduced while grinding. Due to the precipitation of FeAsO₄, there is only Fe 0.65 mg/L, but As 0.22 g/L and S 1.1 g/L in solution. The con-

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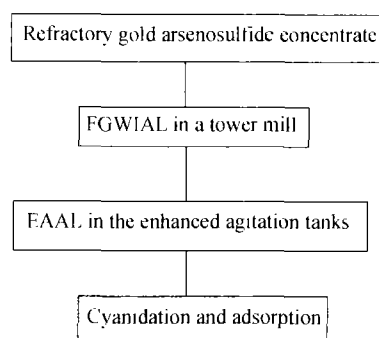


Figure 1 Flowsheet of gold extraction.

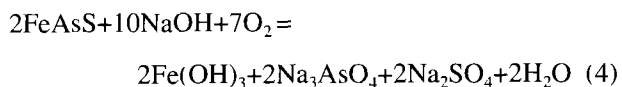
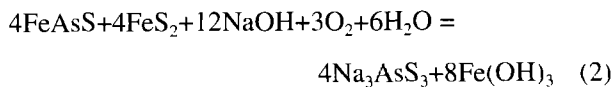
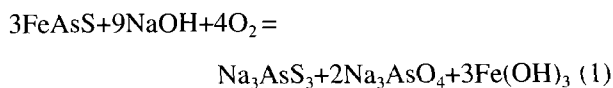
tribution to the arsenic oxidation in the tower mill is quite obvious at a lower consumption of 12 kg NaOH.

An important feature of the pulverizing-leaching tower mill is that it enables chemical leaching with the size reduction while pulverizing [4,7-10] so that the tower mill can be used as a pre-reactor [4,10], which contributes to the oxidation of arsenopyrite (FeAsS) and hence cuts down the oxidation course remarkably, due to the intensive and active functions [5,7,10,11]. The reasons are as follows.

(a) The coarse arsenosulfide particles are fine ground, increasing their surface area as well as the active points of reaction; (b) the freshly liberated arseno-

sulfide particles are subjected to O₂ and NaOH; (c) the enhanced mass transfer conditions increases the contact probabilities among arsenosulfide particles, NaOH and O₂; (d) the surface coating and tarnishing are removed from the arsenosulfide particles under the high shear conditions so that the passivation of surface is not possible; (e) the diffusion film is smashed or thinned, reinforcing the diffusion; (f) the heat generated from grinding and oxidation increases the oxidation rate.

Thus, the combination of FGWIAL with EAAL can substantially increase the reaction kinetics of alkaline leaching so that the oxidation probabilities of FeAsS can be induced under normal temperature and pressure instead of under high ones. The reactions are as follows:



Under certain conditions, the anions S₂O₃²⁻ and AsS₃³⁻ can be further oxidized to SO₄²⁻ and AsO₄³⁻, and the Fe(OH)₂ is oxidized to Fe(OH)₃, and the Fe(OH)₃ is decomposed to Fe₂O₃, etc. The occurring extent of reaction (5) will depend on the reactivity of FeS₂. Due to the generation of thiosalts, a small amount of NaOH compared to those theoretically calculated under the conditions of full oxidization at the same oxidation of arsenic to arsenate and sulfur to sulfate is required.

2.2 Enhanced agitation alkali-leaching (EAAL)

(1) Selective oxidation of arsenic and sulfide.

As shown in **figure 2**, after the FGWIAL completed and with the EAAL going on in the enhanced agitation tanks, the arsenic and the sulfide are selectively oxidized, and the arsenic is oxidized faster than the sulfide. When EAAL for 6, 12, 24, 36 and 48 h, the oxidation of As are 71%, 83.1%, 90.3%, 94.6% and 95.9%, but 15.7%, 18.9%, 26.1%, 32.9% and 34.1% of S respectively. The corresponding dissolution of gold by cyanide for leaching 24 h are enhanced to 65.4%, 82.6%, 88.6%, 93.7% and 95.3% respectively. There is a linear relationship between the dissolution of gold and the oxidation of As. Without ultra-fine

grinding, this technology can meet the requirements of mineralogical and liberation characteristics of refractory gold arsenosulfide concentrate, and high dissolution of gold can be attained.

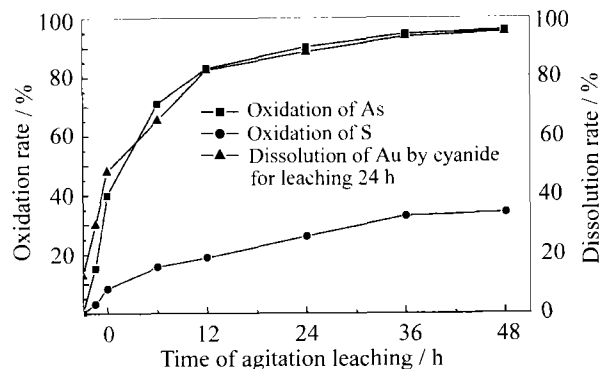


Figure 2 Selective oxidation kinetics of arsenic and sulfur and corresponding dissolution of gold.

The selective oxidation of arsenic and sulfide during EAAL combining with the generation of thiosalts mean that a smaller amount of NaOH is required. After EAAL for 48 h, the total consumption of NaOH for one ton ore accumulated 12 kg in grinding-leaching is 196 kg, which is only 40% of those theoretically calculated under the conditions of full oxidization at the same oxidation of arsenic to arsenate and sulfur to sulfate.

(2) Consumption kinetics of NaOH and change of pulp temperature.

As more heat given out from the oxidation of arsenic and sulfide in EAAL, the temperature of pulp rises quickly, as shown in **figure 3**. When EAAL for 1.5 h, temperature increases from initial 24°C to the peak value of 65°C. After maintaining for 0.5 h at the peak, it drops quickly. After EAAL for 6 h, temperature falls slowly from 49°C. During EAAL for 30-48 h, temperature keeps 40°C.

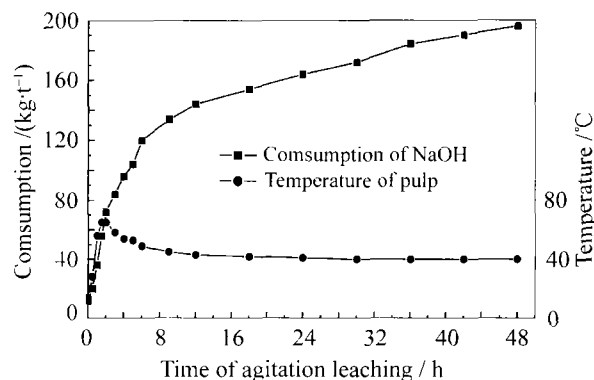


Figure 3 Consumption kinetics of NaOH and change of pulp temperature.

Compared with the consumption of NaOH at the same time of EAAL in figure 3, the changing tendency of the temperature of pulp is very consistent with it. During EAAL for 0-1.5 h, 2-6 h, 6-30 h and 30-48 h,

the consumption rate of NaOH are 32, 12, 2.2 and 1.3 kg/h respectively, and 28°C/h, -4°C/h, -0.4°C/h and 0°C/h of the rising or dropping rate of the temperature of pulp. From the meanwhile oxidation of As and S in figure 2, it shows that the rapid and preferential oxidation of As and the heat given out from which in the initial stage of EAAL is the main reason for the rising of pulp temperature. After the temperature of pulp reaches the maximum, the small amount of As and the smaller amount of S are continuing to be oxidized, which results in the decrease of the heat generation at the unit time and hence the falling of pulp temperature. During EAAL for 30~48 h, there is a balance between the heat generation and radiation of the reactor. But anyhow, the heat generation from the oxidation is keeping on so that the temperature of pulp is always higher than that of its ambience. This results in a higher adaptability for this process, especially for the application in the cold areas.

(3) Property changes of pulp and solution.

During EAAL, the color of the solid phase is changing fast. When EAAL for 6 h, the yellow color of solids has got obvious, which shows the presence of Fe_2O_3 . But the liquor color is getting brown and brown.

Figure 4 and 5 show the property changes of pulp and solution. The ϕ_h of pulp is rising gradually before EAAL for 36 h. This means that the reducibility of pulp is weakening little by little with the oxidization of As and S. After that, the ϕ_h of pulp has a little fall.

Before EAAL for 12 h, the contents of As, S and Fe in solution are all increasing gradually. Afterwards, they fluctuate up or down a little. At the end of EAAL, the solution contains As 47 g/L, S 52.9 g/L and Fe 22 g/L, respectively.

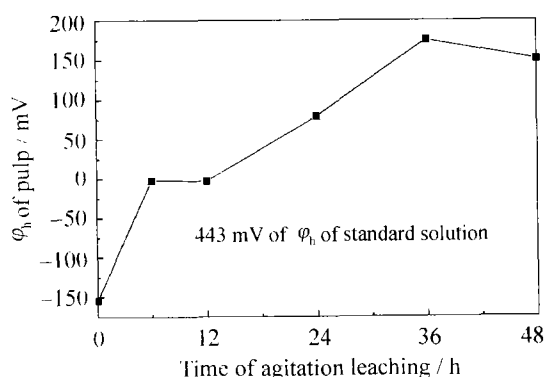


Figure 4 ϕ_h change of pulp under pH=11 at 15°C.

Due to the precipitation while the generation of ions Fe^{3+} and AsO_4^{3-} in the solution of EAAL, most of the oxidized As is again turned into the solid phase. At the end of EAAL, the solid residue contains 6.3% As and 16.4% S. After the regulation of pulp by 140kg

CaO/t ore, the contents of As and Fe in solution decrease to 8.7 g/L and 0.12 g/L respectively, but S 53.7g/L with a little change.

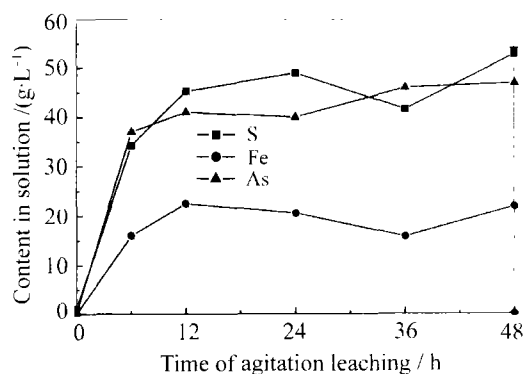


Figure 5 Content changes of S, As and Fe in solution.

(4) Change of particle size.

Due to the selective oxidation of arsenic and sulfide in EAAL, the arsenic is almost completely oxidized, but most of the sulfide is non-oxidized and remaining its primitive phase. This is further verified by the analysis results of XRD, as shown in figure 6. After EAAL, there is no FeAsS but FeS_2 in the solid residue. Thus, most of the skeletal structure of particles before EAAL can be remained. As shown in figure 7, the particle size is a little reduced at the end of EAAL, which is <35.6 μm of 98.1% contrasted to <35.6 μm of 96.6% before EAAL and even with a little coarsening change between 6~26 μm . This is very profitable for the subsequent extraction of gold.

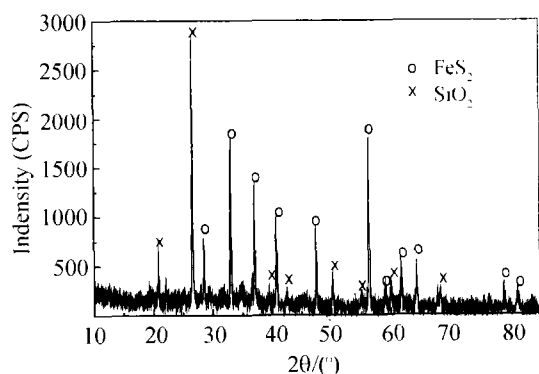


Figure 6 XRD patterns of solids after alkaline leaching.

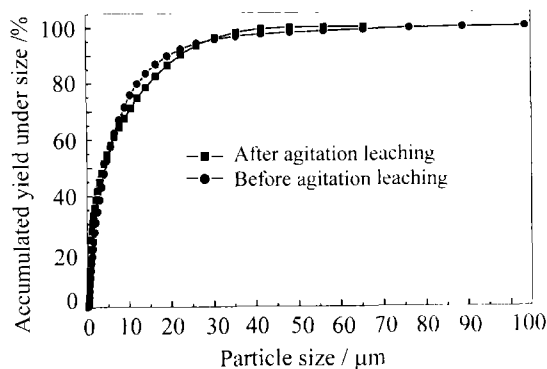


Figure 7 Grain size distribution after alkaline leaching.

(5) A new phenomenon on self-leaching of gold.

Thiosulfate is a good and non-toxic reagent for the extraction of gold. Up to now, there have been reported many results in this field and still as a hot spot on the gold extraction [2]. But this method is defined by the high cost of reagents, which needs to be recycled. In this process, as the generation of anions $S_2O_3^{2-}$ during EAAL, the gold liberated from minerals can be simultaneously self-leached by thiosulfate. At the end of EAAL, the gold dissolution of self-leaching is 88%. The liquid phase contains $S_2O_3^{2-}$ 52 g/L. To other certain refractory gold concentrates, the self-leaching dissolution of gold in EAAL can be 91.5%~92.8%. In this field, some further research could lead to a breakthrough of non-cyanide extraction of gold as well as the pretreatment of refractory gold ores or concentrates.

2.3 Gold extraction

After EAAL, the CaO and NaCN are added to the slurry in order. The filterability of slurry can be improved greatly as the introduction of CaO so that the slurry can be filter-pressed before cyanidation to make the liquor return to the alkaline leaching stage. Cyanidation-adsorption and other recovery methods of gold, such as thiosulfate and cementation by zinc, can also be used.

Due to the equilibrium constant [12] of anions $Au(CN)_2^-$ about 10^{10} times larger than that of anions $Au(S_2O_3)_2^{3-}$, the anions $Au(S_2O_3)_2^{3-}$ can be quickly and perfectly turned into anions $Au(CN)_2^-$ at the beginning of cyanidation. At the same time of cyanide leaching, the activated charcoal of 30 g/L is also introduced to the pulp. After 24 h, the gold dissolution by NaCN is 95.3%, and the gold adsorption by activated charcoal is 99.3%. The consumption of NaCN is 10 kg/t ore, which is 1.2 times less than that before pretreatment.

2.4 Environmental control

After the extraction of gold, the $Ca(ClO)_2$ of 12kg/m³ is added to the pulp in the conventional agitation tanks. The cyanide can be oxidized to CO₂ and N₂. Afterwards, the Fe₂(SO₄)₃ of 8 kg/m³ is added to the slurry. And the arsenic in solution is precipitated and existing in a stable mixture of ferric arsenate and calcium arsenate. The contents of As and NaCN in solution are all decreased below 0.5 mg/L, which can not cause the pollution to the environment.

2.5 Techno-economic assessment

A preliminary techno-economic assessment of this technology shows that the cost of treating 1 t of the objective concentrate is about 520 yuan, including 30

yuan in grinding-leaching. The investment of the 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 oxidation or bacterial oxidation processes.

3 Conclusions

(1) After fine grinding while intensified alkali-leaching in a pulverizing-leaching tower mill and enhanced agitation alkali-leaching for 48 h in the enhanced agitation tanks at the ambient temperature (10°C) and the ambient pressure (0.1 MPa), the dissolution of gold by cyanidation of the objective refractory concentrate is increased to 95.3% from 12.8% before pretreatment. The consumption of NaCN is decreased to 10 kg/t ore, which is 1.2 times less than that before pretreatment.

(2) Fine grinding while intensified alkali-leaching results in 40% of the arsenic oxidized in the tower mill at a lower consumption of NaOH and hence the oxidation course of arsenic cut down. The selective oxidation of arsenic and sulfide and the generation of thiosalts during enhanced agitation alkali-leaching further decrease the consumption of NaOH and the cost of this process. The total consumption of NaOH in this technology is only 40% of those theoretically calculated under the conditions of full oxidization at the same oxidation of arsenic to arsenate and sulfur to sulfate.

(3) The new phenomenon on self-leaching of gold during enhanced agitation alkali-leaching could lead to a breakthrough of non-cyanide extraction of gold as well as the pretreatment of refractory gold ores or concentrates.

Acknowledgements

Some analysis work completed by the State Key Laboratory of Commercial Test of the CAS's Institute of Metal Research should be acknowledged.

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