The problem of the refractory nature of gold bearing arsenide ores is described. The basic principle, characteristics and application of pretreatment technique of arsenic-bearing gold ores are presented in this paper. Several different classes of process options for pretreating refractory ores are considered. These options include: roasting oxidation; wet chemical treatment; bacterial peroxidation; and other pretreatments such as: eliminating arsenic in vacuum, volatile smelting, segregation of roasting, electrolychemical oxidation. Its development tendency in the future is also looked ahead.

KEY WORDS: arsenic-bearing gold ore; pretreatment process; refractory gold ore.

1. Introduction

Gold ores are considered refractory if gold extractions from a conventional cyanidation process are less than 80% even after fine grinding. Arsenic-bearing refractory gold ore has stones extremely difficult to deal with. In the stones, gold is locked up in arsenic mineral matrix as the form of microscopic or submicroscopic lattice. If use conventional cyanidation gold extraction process, the gold leaching rate is very low. Because gold in such ores is very fine particle form wrapped with arsenic, the leach reagents are unable to reach it in cyanide leaching process. The gold ores with As must be broken or decomposed in the gold particles scales, so that gold is fully exposed, and then extracted with the appropriate gold leaching agent. The process of crushing or decomposition before gold leaching is called pretreatment of refractory gold.

Statistics show that, in the world, about 2/3 gold resource belongs to the difficult processing ores, and about 1/3 total output of world gold is produced from refractory gold. This proportion will further increase in future. Therefore, pretreatment of arsenic-bearing refractory gold has an extremely important significance. In recent years, researches are mainly about the refractory gold leaching easily through arsenic removal to expose gold, changing the composition, physic-chemical and electro-chemical properties of the ore. Currently, there are four main methods of pretreatments of refractory gold ores with As. Pretreatment options for dealing with refractory gold ores are illustrated in Fig. 1 and described in detail in the subsequent sections.

2. Roasting Oxidation Pretreatment

So far, the application of roasting oxidation pretreatment has a history of 70 years. The principle is to destroy the ores tissue to make gold exposed by the means of roasting the flotation concentrate. The main chemical reactions are:

\[
12\text{FeAsS} + 29\text{O}_2 \rightarrow 4\text{Fe}_2\text{O}_3 + 3\text{As}_2\text{O}_5 + 12\text{SO}_2
\]

\[
2\text{FeAsS} + 6\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{As}_2\text{O}_3 + 2\text{SO}_2
\]

In solidification roasting, solid sulphate and arsenate are produced by oxidation of sulphur and arsenic with added limestone or dolomite decomposition in ores.

\[
2\text{CaO} + 2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{CaSO}_4
\]

\[
3\text{CaO} + \text{As}_2\text{O}_3 \rightarrow \text{Ca}_3(\text{AsO}_4)_2
\]

It can dramatically improve gold cyanide leaching rate. Roasting has advantages of mature and reliable technology, simple operation, adaptability, etc. But it is easy to form secondary wrapping to reduce leaching rate of gold in the roasting process, and at the same time produces gases of SO2 and As2O3 polluting environment seriously. In ores with a high sulphide content this treatment involves the production of sulphuric acid. This is an undesirable feature, due to the already saturated market for sulphuric acid. In ores with low sulphide content it requires gas purification equipment. In some cases, this method of preoxidation can result in a poor metal recovery. The process flow diagram is as show in Fig. 2.

In order to solve under-burning, over-burning and environmental pollutions and other defects, scientific and technical workers have been researching to explore to improve and develop the roasting process and equipment for many years. For devices, they developed furnace from single to multiple, roasting from fixed to fluidized bed up to flash roasting. For technology, it developed from a roasting to two, from air to oxygen-enriched roasting. In addition, reduction roasting, chlorination roasting, salt sulfur fixation and arsenic roasting are developed on the base of the traditional process.

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Roasting oxidation inevitably will emit a certain amount of toxic and harmful gases in the process. Microwave roasting is a new pretreatment to solve the problem. It uses mineral absorption properties to heat minerals. In this way, gold, arsenic and sulfur can be separated from ores. The technical advantages of microwave roasting are selectively heating materials, fast heating rate and high heating efficiency. Microwave heating has the effect of reducing the temperature of chemical reaction. So it can avoid generating gases of SO₂ and As₂O₃ by controlling the temperature appropriately.⁵⁻⁷

Kyuesi and Haque, etc. have studied the role of microwave in the gold extraction process of arsenic-bearing refractory gold ore.⁸⁻⁹) Haque K E used microwave to dispose of arsenical pyrite and gold concentrate with pyrite, the gold leaching rate reached 98%.¹⁰) Liu Quanjun etc. made a test for a gold mine in Guizhou province. The ore without microwave pretreatment could be hardly leached in cyanide. On the other hand the cyanide leaching of gold ore increased to 86.53%.¹¹) WeiMingan, Ma Shaojian, etc. also researched microwave pretreatment of gold concentrate, and achieved good results.

### 3. Chemical Treatment

Chemical treatment is another branch of ore pretreatment and has the advantages roasting process doesn’t have. Those are no difficult secondary leaching issues caused by under-burning and over-burning, well-adapted and selecting different reagents according to different ores. The process of chemical treatment is as show in Fig. 3.

Reagent availability and cost, materials of construction, environmental concerns and development progress all contribute to limiting the application of these techniques.¹²) According to the different media, the pretreatment can be divided into alkali-ne and acid leaching pretreatments. Depending on the reaction conditions, it can be divided into atmospheric pressure and hot pressure pretreatments.

#### 3.1. Alkaline Leaching Pretreatment

Alkaline leaching pretreatment is a chemical pretreatment process which can oxidize and dispose of components of the ore through adding chemical reagents. Meng Yuqun, Wu Minjie, etc. have researched to strengthen...
the alkaline leaching pretreatment on a gold concentrate with As at normal temperature and pressure. The gold concentrate has many metallic minerals with sulfides as major ones. They are mainly pyrite, arsenopyrite, iron ore and so on. In the experiment, the ore is separated by physical and chemical methods and is in ultrafine grinding. Then, use stirred tank to strengthen the alkaline leaching pretreatment at normal temperature and pressure. Sulfur and arsenic removal separates gold and sulfide fully. Finally, leach gold with cyanide and reach the purpose of gold extraction efficiently. The main chemical reactions are:

\[
3\text{FeAsS} + 9\text{NaOH} + 4\text{O}_2 \\
= \text{Na}_3\text{AsS}_3 + 2\text{Na}_2\text{AsO}_4 + 3\text{Fe(OH)}_3 
\]........ (5)

\[
4\text{FeAsS} + 4\text{FeS}_2 + 12\text{NaOH} + 3\text{O}_2 + 6\text{H}_2\text{O} \\
= 4\text{Na}_3\text{AsS}_3 + 8\text{Fe(OH)}_3 
\]........ (6)

\[
2\text{FeAsS} + 4\text{NaOH} + 7\text{O}_2 = 2\text{FeAsO}_4 + 2\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} 
\]........ (7)

\[
2\text{FeAsS} + 10\text{NaOH} + 7\text{O}_2 \\
= 2\text{Fe(OH)}_3 + 2\text{Na}_3\text{AsO}_4 + 2\text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} 
\] .... (7)

\[
2\text{FeS}_2 + 4\text{NaOH} + 3\text{O}_2 = 2\text{Na}_2\text{S}_2\text{O}_7 + 2\text{Fe(OH)}_2 
\] .... (9)

Under a certain condition, Na₂S₂O₇ and Na₃AsS₃ are further oxidized to Na₃AsO₄ and Na₃AsO₄, Fe(OH)₃ is oxidized to Fe(ΟH)₄, Fe(OH)₃ decomposes to Fe₂O₃.

This method is environmental protection, simple process, short flow, small investment, etc.\(^{13-17}\)

3.2. Acid Treatment

Atmospheric acid treatment usually uses permonosulfuric acid to oxidize refractory gold ore with As. It’s said that the method is not suitable for all refractory gold ores, but has good results in dealing with symbiotic arsenopyrite gold ore. Because arsenopyrite is easily oxidized.

Compared with roasting pretreatment and pressure oxidation, acid treatment has low expense. Even so, this method has not yet been used in industrial applications because of some technology and equipment problems.\(^{18}\)

3.3. Wet Chlorination

Wet chlorination uses chlorine (or chlorine oxidant) to dispose of Arsenic-bearing refractory gold ore. It is an effective method for the carbon refractory gold ore and is used in preprocess of high arsenic gold ore. Beijing General Research Institute of Mining and Metallurgy has studied a refractory gold ore bearing high arsenic in Guizhou. It used water chlorination to leach gold and gold leaching rate reached 91.48%.\(^{17}\)High cost of chlorides and serious corrosion of equipment are the key factors to restrict the application of wet chlorination.

3.4. HNO₃ Catalyzing Oxidation Decomposition Method

Nitric acid is the most efficient oxidant for pyrite, arsenopyrite and nonferrous metal sulfide. In this method, nitric acid oxidizes pyrite and arsenical pyrite as a catalyst under the condition of low temperature and pressure. The reactions are as follows:\(^{19}\)

\[
3\text{FeAsS} + 8\text{HNO}_3 \\
= 3\text{Fe}^{3+} + 3\text{AsO}_4^{3-} + 2\text{S}^2 + 4\text{H}_2\text{O} + 8\text{NO} 
\] .... (10)

\[
6\text{FeS}_2 + 30\text{HNO}_3 \\
= 3\text{Fe}_2\left(\text{SO}_4\right)_3 + 3\text{H}_2\text{SO}_4 + 12\text{H}_2\text{O} + 30\text{NO} 
\] .... (11)

\[
2\text{FeS} + 6\text{HNO}_3 + \text{H}_2\text{SO}_4 = \text{Fe}_2\left(\text{SO}_4\right)_3 + 4\text{H}_2\text{O} + 6\text{NO} 
\] .... (12)

HNO₃ oxidation is an improving pretreatment technology. Cigna corporation has made experiments on gold ore of most deposit in the world.\(^{20}\) The result showed that the effect on ore bearing sulphur of 1%–50% was good and time of oxidation pretreatment was short. But it is not beyond the scope of high temperature and pressure. And the problem of nitric acid regeneration hasn’t been solved. The superiority of technology hasn’t yet been confirmed by the practices of industrialized production.\(^{21,22}\)

3.5. Pressure Oxidation

Pressure oxidation process is more mature. It oxidizes and decomposes gold bearing sulfide to make gold exposed from ores under conditions of high temperature and pressure.\(^{23}\) The main chemical reactions are:

\[
4\text{Fe}_2\text{AsS}_3 + 13\text{O}_2 (g) + 6\text{H}_2\text{O} = 4\text{FeSO}_4 + 4\text{H}_2\text{AsO}_4 
\] .... (13)

\[
4\text{FeAsS} + 7\text{O}_2 (g) + 4\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O} \\
= 4\text{FeSO}_4 + 4\text{S}(l) + 4\text{H}_2\text{AsO}_4 
\] .... (14)

\[
2\text{S}(l) + 3\text{O}_2 (g) + 2\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 (l) 
\] .... (15)

Sulphur may wrap releasing gold again in the reaction, and is bad for cyanidation leaching. High temperature and pressure are good for avoiding the generation of sulphur.

The process can be carried on not only in acidic medium but also in alkaline medium. It also deals with raw ores and concentrates. It has following advantages: first, soluble oxidation product and completely decomposition reaction; second, not releasing harmful gases; third, suitable for large gold factory. The disadvantages are high requirements for equipment and materials’ quality, security risks, careful operation and maintenance. When conditions are controlled badly, it may produce sulfur, affect the process and reduce the gold’s recovery. The method is not appropriate for refractory gold ore bearing organic carbon.

4. Bacterial Preoxidation

The research of bacterial peroxidation is quite active. The technology started to process ores in the 1950 s, and at first leached to recovery copper from the low-grade copper ore or marginal copper ore. In the mid-1980 s, the first commercial plant which applied bacterial oxidation to pretreat refractory gold ores was built in South Africa. After bacterial oxidation, sulphide decomposition, arsenic comes into the solution, so as to remove arsenic. The process is showed in Fig. 4. The reactions are as follows:
Ferric sulphate is a strong oxidant produced in the reaction, and reacts with arsenious sulfide. The advantages are small investment, low cost, simple method, easy operation, no environmental pollution, etc. Bacterial oxidation process to leach gold is roughly divided into three stages: (1) using bacteria culture medium to cultivate thiobacillus ferroxidans, etc. and prepare sulfuric acid bacteria leaching solution of Ph=1.5–2.5; (2) bacteria catalyzing, oxidizing and removing arsenic and sulfur; (3) the residue from pretreatment cyaniding (or other methods) to leach gold, solution of pretreatment can be recycled after bacterial activation. The process flow diagram is as follows.

However, Bacterial oxidation process still has some defects to be improved such as low pulp density, easy to corrode the iron, requirements of temperature tolerance of bacteria, low processing speed.

A. D. Bailey, etc. have come up with a batch biooxidation to increase pulp density. It made pulp density reached 40% even 50%, was applied to refractory gold ore bearing low-grade sulfide.

A. Mazuelos, etc. have designed a flooded packed bed reactor. The reactor separates bacterial oxidation on Fe$^{3+}$ from bacteria and ferric iron oxidation on refractory gold ores, and improves the efficiency of bioreactor.

The institute of Microbiology of Chinese Academy of Sciences has done many researches on bacterial oxidation. In 1980, the institute did tests on arsenic gold ore concentrate to remove arsenic in Guangxi. On the condition of arsenic content <6%, solid-to-liquid ratio of 1:5, temperature of 30–35°C, Ph=1.5–2.5, bacterial count greater than 1 0^8 5/ml, stir pulp 5–6 day and night, use HCL to wash leached residue, the elimination efficiency of As reaches 90%, recycle rate of Au is over 90%.

5. Others

In addition to the above pretreatment processes, some new type of pretreatments of refractory gold ore have been developed such as eliminating arsenic in vacuum, volatile smelting, segregation of roasting, electrochemical oxidation, etc.

The process of eliminating arsenic in vacuum is that arsenopyrite is heat to decompose into As in vacuum. It is an effective method to remove arsenic. If there is pyrite, sulfide or arsenide formed by precipitating S and As can be condensed and deposited by condenser. So eliminated gas doesn’t need special purification. Volatile smelting removes As more completely and has good technical and economic indicators. It has so large processing capacity as to deal with different intermediate product of smeltery. But smoke of the method contains much Au to pollute environment seriously.

Segregation roasting is to dead roast gold ore concentrate with As to remove As. High concentration of flue gas generated during the procedure should be recycled to further process. The calcine of output makes separate-on with a certain amount of reductant and chlorating agent. And separating product is selected to get high grade concentrate. The advantage of the method is largely reducing energy consumption, but it is a big challenge for environment to handle the high con-centration of flue gas.

Electrochemical oxidation uses electrodereaction to oxidize gold ore bearing arsenide and sulfide in a certain media. The dielectric system contains vitriol, nitric acid and hydro-chloric acid, etc. The result of reaction is similar to pressure oxidation. The process can change microstructure of refractory gold ore to improve porosity of ore. So it becomes easily to leach gold. At the same time, peroxidation and leaching can be completed in one system. Compared with bacterial peroxidation of Harbuor Light, it is feasible to practice economically.
6. Prospect

The pretreatment technology of high arsenic gold ore is becoming more and more appreciable and is an inevitable trend to gold development. Through the continuous efforts of scientists in recent years, people have paid high attention to the technology and have obtained quite significant progress. In the future, the goal of development of the pretreatment technology is reusing, recyclable, low input, low consumption, low emission and high efficiency. Its developing tendencies are as follows:

First, it calls for further researches on energy saving and high efficiency. Liquid membrane for extracting gold is researched innovatively to gold ores with lower grade and more complexities.

Second, the development directions of gold extraction must be met the demand of energy saving and emission reduction. Therefore, trends of floatation of refractory gold ores are not only how to improve recovery rate but also how to solve the problem of raffinate’s recycle and emission.

Third, the researches are developed and utilized for low grade refractory gold resources. With the development of refractory gold ores step by step, the proportion of low grade ores is larger and larger. It is significant to develop technologies for lower cost and higher recovery rate.

Finally, systematic technical studies are doing to improve recovery of refractory gold. Original flotation has low loss rate of gold because of refractory ore’s bad floatability. So, ‘flotation with high production rate and recovery will be a main development direction.

In a word, pretreatment before leaching of refractory gold ores is one of technical problems in gold industry. The research of pretreatment has been constantly improved in recent years. The prospect of refractory gold ores’ development and utilization will be wider.

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