Research status of refractory treatment technology of carbon-bearing gold ores

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Abstract: Carbon-bearing gold ore is one of the important refractory gold resources, which can not be effectively utilized by conventional treatment methods. In this paper, the main reasons for the difficult treatment of carbon-containing gold ore, the material composition of carbonaceous matter and the mechanism of carbonaceous matter "robbing gold" are analyzed. At the same time, the working principles of several pretreatment methods are summarized, and the advantages and disadvantages of each pretreatment method are analyzed, so as to provide strong technical support for the future development of carbon-bearing gold ores in China.

1 Introduction

In recent years, with the rising demand for gold, easy mining gold resources are increasingly poor, complex and difficult to deal with gold gradually become the main source of gold industrial production in the future. At present, refractory gold resources in the world's gold deposits account for 60% to 70% of global gold reserves, and about 1/3 of the world's total gold production comes from refractory gold deposits. Therefore, reasonable, efficient and environmentally friendly development and utilization of refractory gold resources have become the main technical problems faced by gold-producing countries in the world. About 30% of the proven gold resources in China belong to refractory gold deposits, which are mainly distributed in Shandong, Gansu and Henan provinces. How to process and treat refractory gold resources efficiently, green and low-cost is what most gold mines must face, which is also the key issue for the sustainable development of China's gold smelting industry at present.

Refractory gold ores are also known as refractory gold ores, refractory metallurgical ores or refractory gold ores. It is generally believed that gold ores with a gold leaching rate lower than 80% are refractory gold ores when they are directly extracted by traditional cyanide method after fine grinding without pre-treatment. Among them, the gold leaching rate is less than 50%, which is extremely difficult to treat. Therefore, according to the conventional cyanide gold leaching rate and chemical consumption, the refractory gold ore can be classified according to Table 1, and the ores that need to consume a large amount of chemicals to achieve satisfactory gold leaching rate are called low refractory gold ores, while the ores that cannot get higher gold leaching rate by increasing the dosage of chemicals are divided into medium refractory gold ores or high refractory gold ores.

Table 1 Classification of refractory gold ores

<table>
<thead>
<tr>
<th>Gold leaching rate</th>
<th>50%~80%</th>
<th>80%~90%</th>
<th>90%~100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorting difficulty</td>
<td>High difficulty in handling</td>
<td>Moderate difficulty to deal with</td>
<td>Low difficulty in handling</td>
</tr>
</tbody>
</table>

According to the occurrence state of gold in ores, refractory gold ores can be roughly divided into fine disseminated gold, complex symbiotic gold, carbonaceous gold and telluride gold. The reasons why the four types of gold deposits are difficult to handle are listed in Table 2:

Table 2 Causes of difficult treatment of four kinds of gold deposits

<table>
<thead>
<tr>
<th>Gold deposit type</th>
<th>Intractable cause</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine disseminated gold deposits</td>
<td>The gold coated gangue minerals in microscopic, submicroscopic or even lattice gold form is difficult to expose the wrapped gold particles to contact reaction with the leaching agent through grinding. Gold ore is often associated with harmful elements such as copper, zinc, antimony and mercury, and the leaching process consumes a lot of oxygen, alkali and leaching agent, which deteriorates the gold leaching effect, and at the same time, it is easy to form iron oxides, arsenic and antimony compounds to cause the secondary coating of gold.</td>
</tr>
<tr>
<td>Complex gold deposit</td>
<td></td>
</tr>
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</table>

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Among them, carbonaceous gold resources are widely distributed and are one of the important refractory gold resources in the world. In China's gold industrial reserves, carbonaceous gold deposits account for about 8% of the total gold resources in China, accounting for more than 20% of the current exploitation and proven gold reserves in China, mainly distributed in Sichuan, Northeast China and Shaanxi.\[4\] With the continuous development of gold sorting technology, this proportion will continue to increase, therefore, the development and utilization of carbon gold resources is of great significance to improve the production capacity of China's gold industry.

Generally, the carbonaceous gold deposit contains high carbon, sulfide ore and graphite, and its gold particle size is fine, and it has close symbiotic relationship with pyrite and gangue minerals. There are two main reasons for the difficult treatment of carbonaceous gold deposits: In the process of cyanide gold leaching, the carbonaceous matter can rob the dissolved gold through the adsorption of activated carbon, and the phenomenon of "gold robbing" appears. On the other hand, part of the gold in carbonaceous gold deposits is often locked by sulfide ores such as pyrite, resulting in the inability of conventional treatment methods to separate gold from minerals and affect the dissolution of gold. Due to these two problems, the leaching rate of gold is usually very low, so gold needs to be pre-treated before leaching to eliminate these harmful effects. At present, the main pretreatment methods of carbon-bearing gold ores are high temperature roasting, biological oxidation, chemical oxidation and carbon inhibition for gold extraction.

2 Material composition and coating effect of carbonaceous matter

2.1 Material composition

The existence of carbon is the main reason for the low gold leaching rate, and a clear understanding of carbon is the basis of pretreatment technology research. During the leaching of carbonaceous gold ore, many substances in the ore can show different degrees of "gold robbing" ability.

Common "gold robbing" substances in carbonaceous gold deposits include amorphous carbon, chalcopyrite, chlorite, and layered silicate minerals (pyrophyllite, kaolinite, mica and illite). Previous studies have found that different types of "gold robbing" substances have different "gold robbing" abilities. According to the adsorption results of gold in different minerals, it was found that quartz can only adsorb 1.7% of gold, while layered silicate minerals can adsorb about 18% of gold, among which pyrite, chalcopyrite and carbonaceous matter have a high degree of "gold robbing", gold can be fully adsorbed within half an hour. Although there are many kinds of "gold robbing" substances in ores, the "gold robbing" ability of other substances is often ignored as long as there are carbon substances.

2.2 Coating effect

The main element of solid carbon is C, which has the performance of activated carbon in the cyanide leaching process, and can adsorb the gold-cyanide complex ions in the solution. It is generally believed that there are two mechanisms of carbon adsorption of gold-cyanide complex: the first is that under electrostatic adsorption and chemical action, gold-cyanide complex is attached to the surface of carbon; The second is that gold is adsorbed on the active point of activated carbon in the form of M"+[Au(CN)\(_2\)]\(_n\) ion pairs, which is a widely recognized mechanism at present. \[12\]

Tan H.\[13\] et al. 's research results show that in the pyrite solution system polluted by carbon or graphite, carbon and graphite not only have a "gold robbing" effect, but also enhance the adsorption of gold on the pyrite surface, and non-graphite-like carbonaceous matter has a stronger promotion effect on the adsorption of gold on the pyrite surface. Due to the adhesion of carbon or graphite on the surface, the physical adsorption effect of gold-cyanide complex is enhanced. Although the "gold robbing" effect of other minerals can be eliminated in the environment of high concentration of cyanide, the "gold robbing" effect of carbon substances attached to pyrite still exists, and fine grinding will further enhance the pollution of graphite and carbon substances to mineral particles, so that the "gold robbing" effect of carbon-containing gold ores becomes more serious.

3 Pretreatment method of carbonaceous gold ore

At present, in addition to the "gold hijacking" effect of carbonaceous matter, gold wrapped in carbonaceous matter can not be leached, and the adsorption of fine carbon flocs and leached gold during grinding process will lead to a significant decrease in gold leaching rate. Therefore, it is necessary to adopt pretreatment method to solve the problem of "robbing gold" by carbon in ore. According to the existing mechanism of "robbing gold", the following solutions have been developed: first, the carbon is oxidized and decomposed to essentially remove the carbon, so as to eliminate its impact on gold, such as oxidation roasting. The other is to passivate the carbon, such as adding a passivator, through the chemical interaction between the passivator and the functional groups on the surface of the carbon, so that the activity of
these functional groups is greatly reduced, thereby reducing or even eliminating its "gold robbing" ability. Therefore, in addition to the common pretreatment methods of gold ore, this paper also introduces the competitive adsorption, oxidation and surface passivation/inhibition of carbon by adding gold adsorbent, among which oxidation treatment process is the most effective.

3.1 High-temperature roasting and oxidation

Roasting is the most common method for the pretreatment of carbonaceous gold ores. By roasting the carbonaceous gold ore in the air, the gold locked in the mineral can be effectively exposed, the adsorption of the carbonaceous matter to the gold cyanide complex can be eliminated, and the gold leaching rate can be successfully increased. Because of its strong applicability, simple process flow and high recovery rate, roasting method will still be widely used in the industrial production of carbonaceous gold mines for a long time in the future.

The research results of Azele et al. show that stratiform silicate minerals (pyrophyllite, kaolinite, mica and illite) in carbonaceous gold deposits can be decomposed into CaO and MgO at 690 ℃, and transformed into MgO, CaO and CO2 at 886 ℃. Dong Xiaowei et al. used oxidation roasting and cyanide leaching processes to treat a carbon-bearimg gold mine in Shaanxi province, and found that when the roasting condition was 680 ℃ for more than 2 h and the roasting equipment was liquid roasting furnace, the gold leaching rate was as high as 86.67%. Zhang et al. pretreated carbonaceous gold ore by reduction roasting, which increased the gold leaching rate from 2.43% to 73.7%, and the reaction formula of the reaction stage is shown in (1) ~ (2).

\[
\text{CaMg(CO}_3\text{)}_2 \rightarrow \text{CaCO}_3 + \text{MgO} + \text{CO}_2(g) \quad (1) \\
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2(g) \quad (2)
\]

In recent years, the transformation of roasting process and equipment, such as oxygen rich roasting, curing roasting and microwave roasting, especially the new curing roasting process, has basically eliminated the pollution of harmful gases to the environment and effectively improved the roasting efficiency. It can be seen that the development of new environmental protection roasting technology is the key direction of future research.

3.2 Biological Oxidation

The biological oxidation method is to oxidize the sulfide ore in the carbonaceous gold mine into the corresponding salt through the metabolism or metabolic products of the bacteria itself, and dissolve in the solution, so as to destroy the gold coating in the ore, and achieve the purpose of the contact reaction between gold and cyanide. At the same time, biological oxidation can also greatly reduce the adsorbability of active organic carbon, and the pretreatment effect of carbonaceous gold ores is obvious. The main strains of the biological oxidation method are mesothermal strains, such as thiobacillus ferrooxidans, thiobacillus phyllosus and thermophilic thiobacillus.

The results of Kojo T. Konadu et al. showed that lignin degrading enzymes preferentially attacked defective graphite and dissolved some decomposition byproducts in carbonaceous substances. After continuous biological treatment, the gold recovery rate increased from 44% to 93%. The advantages of biological oxidation method are: low investment cost, low energy consumption, simple process, small environmental pollution, and high gold leaching rate. The disadvantages of biological oxidation method: it is necessary to control the temperature, oxygen concentration, pulp concentration and pH to provide a suitable environment for bacteria; The oxidation process requires a long time and low efficiency, and the key to the promotion of biological oxidation is to cultivate high-performance strains.

3.3 Chemical Oxidation

Chemical oxidation method is a kind of pretreatment method which uses potassium permanganate, chlorine gas, hypochlorite, nitric acid, peroxide and other chemical oxidants to oxidize and remove the inclusions on gold surface under certain conditions. The chemical oxidation methods can be divided into chlorine oxidation method, nitric acid oxidation method, hypochlorite method and electrochemical oxidation method. Chlorine oxidation method is to oxidize gold ore by chlorine gas and strong oxidizing substances generated by the reaction of chlorine gas with water, which is especially suitable for pretreatment before cyanide leaching of carbonaceous gold ore. After chlorination oxidation treatment, a thin layer of chlorinated hydrocarbon or carbonyl (-COOH) structure organic matter is formed on the surface of the carbonaceous matter, thus reducing the adsorption activity of the carbonaceous matter. Under alkaline conditions, the functional groups generated by chlorination oxidation are ionized, and the surface of the carbonaceous matter is negatively charged, which will also repel the negatively charged gold-cyanide complex and reduce the adsorption of the carbonaceous matter to gold.

The Jerritt Canyon mine in the United States uses chlorination oxidation to pretreat part of the carbonaceous ore. The operation steps are as follows: first, use lime to neutralize and produce sulfuric acid, and then use chlorine gas to oxidize; Secondly, Na2CO3 or NaOH is used to adjust pH value and act as buffer. Finally, the treated pulp was treated by carbon leaching, and the recovery rate of gold reached 90%~93%. The advantages of this method are high efficiency and low investment, while the disadvantages are high oxidizer price and potential environmental pollution.

3.4 Carbon inhibition gold extraction method

Certain chemical agents can passivate and inhibit the carbonaceous matter, and when added before cyanide leaching, the effect of the carbonaceous matter can be reduced or eliminated when fully mixed with the pulp. The mechanism of these chemical agents to inhibit the
carbonaceous material is mainly: first, the chemical interaction with the carbonaceous material surface and hydrophobicity, forming electrostatic repulsion and inhibiting the adsorption of gold; Second, it preferentially adsorbs on the surface active points of carbonaceous matter, which reduces the ability of carbonaceous matter to adsorb gold-cyanide complex. Adding some flotation agents (turpentine, cresol acid, sulfonate, pine oil) and non-polar hydrocarbons (kerosene, heavy oil, petroleum, diesel oil) before cyanidation passivates or inhibits the activity of carbon, thereby reducing its adsorption capacity, which is also one of the commonly used pretreatment methods for carbon-containing gold ores.

A gold mine in Australia used diesel or kerosene (200mg/L) to passivate carbonaceous substances with "gold robbing" in the leaching process, aiming at the low grade and very fine gold granularity of carbon-containing gold ores, especially those containing graphite and organic carbon, and effectively eliminated the "gold robbing" effect of carbonaceous substances during leaching.\(^{[12]}\) In a gold mine in Kyrgyzstan Republic, diesel oil and alkyl sulfate were added as masking agents to inhibit carbon activity, which reduced the impact of carbon content on gold recovery, up to 86%. According to domestic reports, China's gold industry has developed a composite inhibitor of carbon, which can well inhibit the activity of carbon, and can replace the adsorbed gold from the carbonaceous matter, and the amount of agents is small, and the gold leaching rate can be increased by 6% to 25% compared with the conventional process.

4 Conclusion

As an important part of refractory gold ores, how to effectively extract gold from refractory gold ores is the main research direction of gold production in the future. In order to eliminate the "gold robbing" effect of carbon in carboniferous gold ores to the greatest extent, pretreatment methods such as oxidation roasting and chemical oxidation are commonly used at home and abroad to achieve industrial application worldwide, among which oxidation roasting pretreatment method is the most widely studied and applied. However, with the increase of environmental protection efforts and the increase of production costs, these pretreatment methods have their advantages and disadvantages and applicability. Therefore, it is crucial to select the appropriate method according to the process mineralogy of the ore. Therefore, it is necessary to know the composition of carbonaceous minerals in carbon-containing gold deposits and understand the mechanism of "gold robbing" and adsorption of carbonaceous minerals, so as to better select suitable pretreatment methods for carbon-containing gold deposits. In the future, the research of new equipment and new process combined with pretreatment process will be one of the main research directions in the future.

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