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 (72) Inventeur/Inventor:
LI, DENGXING, CN
 (73) Propriétaire/Owner:
DONGHUA UNIVERSITY, CN
 (74) Agent: CASSAN MACLEAN

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REFRACTAIRE RICHE EN SOUFFRE ET EN ARSENIC
 (54) Title: A METHOD FOR CATALYTIC OXIDATION OF REFRACTORY GOLD CONCENTRATE WITH HIGH
CONTENTS OF SULFUR AND ARSENIC UNDER ORDINARY PRESSURE

(57) **Abrégé/Abstract:**

An atmospherically catalyzing and oxidizing method of refractory gold concentrate with high arsenic and high sulfur, comprises ① adding predefined ore, solid catalyst, acid and water into reaction container with stirrers to form ore pulp; ② continuously introducing gas oxidizer such as ozone and oxygen, or ozone and air into the pulp at 60-100°C, continuously stirring the mixture to form oxidized ore pulp, reacting for 6 to 18 hrs, then cooling to room temperature and filtering; ③ In accordance with traditional extracting and filtering process, mixing the residue from the filtering step with calcium hydroxide solution to regulate its pH value to 11 ~ 12, adding sodium cyanide, stirring for 24 hrs, and filtering to extract noble metals from filtrate. The method improves the extraction rate of noble metals such as gold and silver in the refractory gold concentrate while reducing the environment pollution.

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(71) 申请人 (对除美国外的所有指定国): 东华大学 (DONGHUA UNIVERSITY) [CN/CN]; 中国上海市松江区人民北路 2999 号, Shanghai 200041 (CN)。**(72) 发明人: 李登新 (LI, Dengxing);** 中国上海市松江区人民北路 2999 号, Shanghai 200041 (CN)。**(74) 代理人: 上海金盛协力知识产权代理有限公司 (SHANGHAI CO-EFFORT IPR AGENT CO., LTD.);** 中国上海市陆家嘴环路 958 号华能联合大厦 31 楼陈益奇, Shanghai 200120 (CN)。**(81) 指定国 (除另有指明, 要求每一种可提供的国家保护):** AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB,

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本国际公布:

— 包括国际检索报告(条约第 21 条(3))。

(54) Title: ATMOSPHERICALLY CATALYZING AND OXIDIZING METHOD OF REFRACTORY GOLD CONCENTRATE WITH HIGH ARSENIC AND HIGH SULFUR**(54) 发明名称:** 一种高硫高砷难选金精矿常压催化氧化方法**(57) Abstract:** An atmospherically catalyzing and oxidizing method of refractory gold concentrate with high arsenic and high sulfur, comprises ① adding predefined ore, solid catalyst, acid and water into reaction container with stirrers to form ore pulp; ② continuously introducing gas oxidizer such as ozone and oxygen, or ozone and air into the pulp at 60-100°C, continuously stirring the mixture to form oxidized ore pulp, reacting for 6 to 18 hrs, then cooling to room temperature and filtering; ③ In accordance with traditional extracting and filtering process, mixing the residue from the filtering step with calcium hydroxide solution to regulate its pH value to 11~12, adding sodium cyanide, stirring for 24 hrs, and filtering to extract noble metals from filtrate. The method improves the extraction rate of noble metals such as gold and silver in the refractory gold concentrate while reducing the environment pollution.**(57) 摘要:**

一种高硫高砷难选金精矿常压催化氧化方法,包括如下步骤: 1、在带有搅拌器的反应釜中一次性加入适量矿样、固体催化剂、酸和水,配置成浆液; 2、在 60~100°C 的温度条件下,向浆液中连续通入气体氧化剂例如臭氧和氧气或臭氧和空气,连续搅拌形成氧化矿浆,反应时间 6~18 小时,然后降至室温过滤得滤液和滤渣; 3、根据传统提取工艺,滤渣与氢氧化钙溶液混合,调至 pH 值 11~12,加入氰化钠搅拌 24 小时后过滤,从滤液中提取贵金属。该方法提高了难选金精矿中金、银等贵金属的提取率,同时在提取过程中,减少环境污染。

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A Method for Catalytic Oxidation of Refractory Gold Concentrate with High Contents of Sulfur and Arsenic Under Ordinary Pressure

TECHNICAL FIELD

The invention relates to a method for catalytic oxidation of refractory gold concentrate with high contents of sulfur and arsenic under ordinary pressure.

BACKGROUND

The treatment processes for refractory gold concentrate with high contents of sulfur and arsenic in the art mainly include roasting oxidation, pressure oxidation, ordinary pressure oxidation, bacteria oxidation, nitric acid catalytic oxidation, etc. The major disadvantages are low extraction rate of the noble metals such as gold, silver, platinum, palladium and the like, low comprehensive utilization rate of other elements, environmental pollution in the process of noble metal extraction, complicated processes and high cost.

If there exists a catalyst which not only can be regenerated in gaseous phase but also has high solubility in water, and the catalyst also has high cathode potential when the catalyst is deoxidized on the surface of a fluid bed, therefore, the required temperature and oxygen pressure for the oxidation acid leaching of sulfide concentrate can be markedly reduced. This is an important research direction in hydrometallurgy.

SUMMARY OF THE INVENTION

The objects of the invention are to improve the extraction rate of noble metals, such as gold, silver, platinum, palladium, etc., and the comprehensive utilization rate of other elements in the refractory gold concentrate, and to reduce environment pollution in the process of the extraction; in addition, the invention has simple process and low equipment cost.

For the objects, the invention provides an ordinary pressure catalytic oxidation method for the refractory gold concentrate with high contents of sulfur and arsenic. The working principle of the invention is: the combination bond energy of most molecules is 25 to 35 kcal per mol, but the redox potential of ozone is about 2.07V, and the combination bond energy of ozone is 47 kcal per mol; thus, ozone has enough power to break the combination bond of most molecules, so iron pyrites and arsenopyrite wrapped over the noble metals of gold, silver, etc. can be broken, and the noble metals can be exposed; in addition, the elements of iron, copper and manganese have the functions of catalysis and helping oxygen and ozone to be dissolved and transformed in water.

The key of the invention is the adoption of oxidants and catalyst, and the invention has the following reaction steps:

$$O_3 + O_2 + \text{deoxidization state [solid catalyst]} \rightarrow O^+ + \text{oxidation state [solid catalyst]}$$

$$O^+ + \text{oxidation state [solid catalyst]} + FeS_2 \rightarrow FeSO_4 + \text{deoxidization state [solid catalyst]}$$

The deoxidization state [solid catalyst] can be oxidized again for recycling use, and the oxidization speed for oxygen can be indirectly enhanced.

The method of the invention has the following steps:

Step 1: proper amounts of the concentrate sample, solid catalyst, acid and water are added into a reactor with an agitator at one time, wherein the concentration of the solid catalyst is from 151 to 280 grams per liter, the weight ratio of the concentrate sample to the water is from 1:6 to 1:10; add acid until the pH value reaches 1 to 3 and then a slurry of the refractory gold concentrate is prepared;

Step 2: under the temperature condition of 60 to 100 degrees centigrade, gas oxidants, namely ozone and oxygen, are pumped into the slurry continuously with continuous agitation and react for 6 to 18 hours, wherein the speed of the ozone is 0.8 to 1.2 grams per hour, and the speed of the oxygen is 0.1 to 1.0 cubic meter per hour; or namely ozone and air, wherein the speed of the ozone is 0.8 to 1.2 grams per hour and the speed of the air is 0.1 to 1.0 cubic meter per hour; and then filter liquor and filter residue are obtained by filtration after the slurry is cooled to room temperature;

Step 3: using extraction process know in the art, the filter residue and calcium hydroxide are mixed and the pH value of the mixture is adjusted to 11 to 12, then sodium cyanide is added into the mixture for agitation for 24 hours before filtration, and noble metals are extracted from filter liquor.

The preparation process of the solid catalyst is as follows: industrial iron, copper, hydrochloric acid or chlorine, manganese oxide, alumina and silicon oxide are evenly mixed by agitation under the conditions of ordinary temperature and ordinary pressure, and the chlorine is continuously pumped if the chlorine is adopted in the process so that the weight percentages of the contents of final product are respectively 30% of iron, 30% of chlorine, 15% of oxygen, 10% of copper, 5% of manganese, 5% of silicon and 5% of aluminum.

The acid in the slurry of the refractory gold concentrate can be hydrochloric acid or sulphuric acid.

The invention has the advantages that the extraction rate of the noble metals, such as gold, silver, etc. and the comprehensive utilization rate of other elements in the refractory gold concentrate are improved; simultaneously, environment pollution is

reduced in the process of the extraction, and the invention has simple process and low equipment cost. According to measurement based on national standard, the leaching rates of gold and silver are 68-98.5% and 80-96% respectively, while the corresponding leaching rates out of direct cyanidation are less than 40% and 50-60% respectively without the steps in the invention.

SPECIFIC EXAMPLES OF THE INVENTION

The invention is further illustrated in details with following examples:

Example 1

The refractory gold concentrate with high contents of sulfur and arsenic, concentrate sample, the solid catalyst, water and sulphuric acid are put into a reactor with an agitator for one time, wherein the concentration of the solid catalyst is 151 grams per liter, and the weight proportion of the concentrate sample to the water is 1:10; then the slurry of the refractory gold concentrate is prepared by adding the sulphuric acid into the mixture until the pH value of the mixture becomes 1. The preparation process of the solid catalyst in the Example is that industrial iron, copper, manganese oxide, alumina and silicon oxide are evenly mixed by agitation under the conditions of ordinary temperature and ordinary pressure, and chlorine is continuously pumped in the process so that the weight percentages of the contents of final product are respectively 30% of iron, 30% of chlorine, 15% of oxygen, 10% of copper, 5% of manganese, 5% of silicon and 5% of aluminum.

Under the temperature condition of 90 degrees centigrade, ozone and oxygen are pumped into the slurry continuously, wherein the speed of the ozone is 0.8 grams per hour, and the speed of the oxygen is 0.1 cubic meter per hour; then oxidized slurry is formed by continuous agitation; the reaction takes 8 hours, and then filter liquor and filter residue are obtained by filtration after the slurry is cooled to room temperature. Based on the traditional extraction process, the filter residue and calcium hydroxide are mixed together and the pH value of the mixture is adjusted to 11, and then sodium cyanide is added into the mixture for agitation for 24 hours before filtration, and noble metals are extracted from filter liquor. According to measurement based on national standard, the leaching rates of gold and silver are 82.65% and 88.77%, respectively.

Example 2

Operation steps are exactly the same as the steps in Example 1, wherein the preparation process of the solid catalyst is that industrial iron, copper, hydrochloric acid, manganese oxide, alumina and silicon oxide are evenly mixed by agitation under the conditions of ordinary temperature and ordinary pressure so that the weight percentages of the contents of final product are respectively 30% of iron, 30% of chlorine, 15% of oxygen, 10% of copper, 5% of manganese, 5% of silicon and 5% of

aluminum.

In the Example, the concentration of the solid catalyst is 280 grams per liter, and the weight proportion of the concentrate sample to the water is 1:10; then hydrochloric acid is added until the pH value of mixture becomes 1. Under the temperature condition of 100 degrees centigrade, ozone and air are pumped into the slurry continuously, wherein the speed of the ozone is 1.2 grams per hour, the speed of the air is 0.4 cubic meter per hour, and the reaction takes 16 hours; based on the traditional extraction process, the filter residue and calcium hydroxide are mixed together and the pH value of the mixture is adjusted to 12, and then sodium cyanide is added into the mixture for agitation for 24 hours before filtration. According to measurement based on national standard, the leaching rates of gold and silver are 98.45% and 95.27%, respectively.

Example 3

Operation steps are exactly the same as the steps in Example 1, wherein the preparation process of the solid catalyst is that industrial iron, copper, hydrochloric acid, manganese oxide, alumina and silicon oxide are evenly mixed by agitation under the conditions of ordinary temperature and ordinary pressure so that the weight percentages of the contents of final product are respectively 30% of iron, 30% of chlorine, 15% of oxygen, 10% of copper, 5% of manganese, 5% of silicon and 5% of aluminum.

In the Example, the concentration of the solid catalyst is 170 grams per liter, and the weight proportion of the concentrate sample to the water is 1: 6; then sulphuric acid is added until the pH value of mixture becomes 3. Under the temperature condition of 70 degrees centigrade, ozone and air are pumped into the slurry continuously, wherein the speed of the ozone is 1.0 grams per hour, the speed of the air is 0.8 cubic meter per hour, and the reaction takes 12 hours; based on the traditional extraction process, the filter residue and calcium hydroxide are mixed together and the pH value of the mixture is adjusted to 11, and then sodium cyanide is added into the mixture for agitation for 24 hours before filtration. According to measurement based on national standard, the leaching rates of gold and silver are 68.32% and 81.02%, respectively.

Example 4

Operation steps are exactly the same as the steps in Example 1, wherein the preparation process of the solid catalyst is that industrial iron, copper, chlorine, manganese oxide, alumina and silicon oxide are evenly mixed by agitation under the conditions of ordinary temperature and ordinary pressure, and chlorine is continuously pumped in the process so that the weight percentages of the contents of

final product are respectively 30% of iron, 30% of chlorine, 15% of oxygen, 10% of copper, 5% of manganese, 5% of silicon and 5% of aluminum.

In the Example, the concentration of the solid catalyst is 230 grams per liter, and the weight proportion of the concentrate sample to the water is 1: 8; then hydrochloric acid is added until the pH value of mixture becomes 3. Ozone and oxygen are pumped into the slurry continuously, wherein the speed of the ozone is 0.9 grams per hour, the speed of the oxygen is 1.0 cubic meter per hour, and the reaction takes 8 hours; based on traditional extraction process, the filter residue and calcium hydroxide are mixed together and the pH value of the mixture is adjusted to 12, and then sodium cyanide is added into the mixture for agitation for 24 hours before filtration. According to measurement based on national standard, the leaching rates of gold and silver are 76.25% and 92.19%, respectively.

Claims:

1. A method for catalytic oxidation of refractory gold concentrate with high Contents of sulfur and arsenic under ordinary pressure, wherein the method comprises the following steps:

Step 1: proper amounts of the concentrate sample, solid catalyst, acid and water are added into a reactor with an agitator at one time, wherein the concentration of the solid catalyst is from 151 to 280 grams per liter, the weight ratio of the concentrate sample to the water is from 1:6 to 1:10; add acid until the pH value reaches 1 to 3 and then a slurry of the refractory gold concentrate is prepared;

Step 2: under the temperature condition of 60 to 100 degrees centigrade, gas oxidants, ozone and oxygen, are pumped into the slurry continuously with continuous agitation and react for 6 to 18 hours, wherein the speed of the ozone is 0.8 to 1.2 grams per hour, and the speed of the oxygen is 0.1 to 1.0 cubic meter per hour; or ozone and air, wherein the speed of the ozone is 0.8 to 1.2 grams per hour and the speed of the air is 0.1 to 1.0 cubic meter per hour; and then filter liquor and filter residue are obtained by filtration after the slurry is cooled to room temperature;

Step 3: using extraction process known in the art, the filter residue and calcium hydroxide are mixed and the pH value of the mixture is adjusted to 11 to 12, then sodium cyanide is added into the mixture for agitation for 24 hours before filtration, and noble metals are extracted from filter liquor.

2. The method for catalytic oxidation of refractory gold concentrate with high contents of sulfur and arsenic under ordinary pressure according to Claim 1, wherein the acid in Step 1 is hydrochloric acid or sulphuric acid.

3. The method for catalytic oxidation of refractory gold concentrate with high contents of sulfur and arsenic under ordinary pressure according to Claim 1, wherein the preparation process of the solid catalyst in Step 1 is: industrial iron, copper, hydrochloric acid or chlorine, manganese oxide, alumina oxide and silicon oxide are mixed by agitation under ordinary temperature and ordinary pressure; and if chlorine is adopted in the process the chlorine is continuously pumped so that the mass percentages of the elements of the final catalyst are respectively 30% of iron, 30% of chlorine, 15% of oxygen, 10% of copper, 5% of manganese, 5% of silicon and 5% of aluminum.