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Technical note

A selective process for extracting antimony from refractory gold ore

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ABSTRACT

To avoid the adverse effects of antimony on the cyanide leaching process used for the recovery of gold from refractory gold ore, a cleaner production process was proposed that would selectively remove antimony as sodium pyroantimonate. The process included three steps: 1) leaching of antimony from the refractory gold ore with sodium sulfide solution; 2) pressure oxidation of the leaching solution containing sodium thioantimonite, transforming it to sodium pyroantimonate; and 3) concentration/crystallization to recover the sodium thiosulfate byproduct from the oxidized solution. The leaching recoveries of antimony, gold, and arsenic in the first step were 96.64%, 1.44%, and 0.41%, respectively. The precipitation ratio of antimony exceeded 99.80% during the second step. The synthesized sodium pyroantimonate product exhibited a regular tetragonal morphology. The purity of the sodium thiosulfate byproduct obtained during the third step reached 98.0%.

1. Introduction

Gold is a strategic precious metal that is widely used in ornamentation, currency reserves, and high-tech industries. According to the United States Geological Survey, globally identified gold reserves amount to 89,000 tons, with approximately one-third of that total contained in refractory ores (George, 2009). With the gradual depletion of high-grade resources, refractory gold ores have attracted increased attention.

Refractory gold ores are defined as minerals for which the cyanide-leaching recovery of gold is <80%, even after fine grinding. High-arsenic refractory gold ores constitute the largest reserves but are the most difficult from which to extract gold. Gold leaching recoveries can often be as low as 50% (Yang, 2005). These poor results can be attributed to the encapsulation of the fine gold particles—even at micron size—in pyrite or arsenopyrite. Therefore, refractory gold ores must be pretreated prior to the cyanide leaching process to liberate the gold. Currently, there are many methods for the pretreatment of refractory gold ores, including two-stage roasting (Dunn and Chamberlain, 1997), pressure oxidation (Gudyanga et al., 1999), bacterial oxidation (Hol et al., 2011), fixed arsenic roasting (Liu et al., 2000), microwave roasting (Amankwah and Pickles, 2009), chemical oxidation (Saba et al., 2011), and nitric acid catalytic oxidation (Gao et al., 2009).

Geochemical studies have shown that gold migrates easily and is concentrated, along with characteristic elements such as arsenic and antimony, during the endogenous mineralization of gold deposits (Nie and Suo, 1997). However, the coexistence of those elements increases the difficulty of extracting gold from refractory gold ores. During the direct cyanide leaching process, the dissolution of stibnite (Sb_2S_3) not only increases the consumption of OH^-, CN^-, and O_2, but also forms precipitates that coat the surfaces of the gold particles, which leads to low leaching recoveries (Yang, 2005). During the two-stage roasting pretreatment process, it is easy to fuse with each other due to the low melting points of antimony compounds, causing the gold particles to be encapsulated again (Cui et al., 2011). In pressure oxidation pretreatments, precipitates of antimony compounds are produced, which cover the surfaces of the gold particles and hinder further leaching reactions. In the biological oxidation pretreatment process, the antimony-containing minerals significantly affect the oxidation rates of gold-bearing minerals.

Due to the adverse effects of antimony on these pretreatment and direct cyanide leaching processes, it is necessary to remove it from antimonial refractory gold ores before gold extraction (Anderson, 2012). In general, the hydrometallurgical methods for removing antimony can be conducted in either alkaline (sodium sulfide, Na_2S) or acidic (hydrochloric acid, HCl) systems. In alkaline sodium sulfide solution, antimony is dissolved in the form of sodium thioantimonite (Na_3SbS_3). The antimony can be recovered from the leaching solution by neutralization, displacement, electrowinning, air oxidation, and so on. Owing to its excellent selectivity, this method has been widely used for removing antimony from stibnite (Ubaldini et al., 2000), jamesonite (Yang et al., 2005), enargite (Curreli et al., 2009), and refractory antimony ores (Celep et al., 2011). In HCl solution, antimony is dissolved in the form of $SbCl_3$ by adding oxidizing agents such as Cl_2, $FeCl_3$, $SbCl_5$, or H_2O_2 (Zhao, 1987). Methods for the recovery of antimony from the $SbCl_3$ leaching solution include hydrolysis, replacement, distillation, and electrowinning. Although the foregoing methods afford high antimony

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recoveries, they all focus on the unit leaching process or the recovery of antimony from the leaching solution. However, a complete technological process should consider many factors, including the recovery of sulfur, operational environment, and processing costs.

In our previous study, low-grade jamesonite concentrate was leached in sodium sulfide solution, affording an antimony recovery exceeding 91.0% (Yang et al., 2005). We have also shown that antimony can be precipitated as sodium antimonite from a solution of sodium thioantimonite by air oxidation (Yang et al., 2002). Based on these findings, a cleaner production process was proposed to selectively remove antimony in the form of sodium pyroantimonate from refractory gold ore. In this work, the complete process is presented in detail so as to provide guidance for the extraction of antimony from antimonial refractory gold ores.

2. Experimental

2.1. Materials

The raw material, antimonial refractory gold ore, was provided by the Jinchiling Gold Mine (Zhaojin Mining Industry Co., Ltd., Shandong Province, China). The chemical composition of the ore is given in Table 1. Before the experiments, the ore was dried at 383 K, and then ground and sieved to obtain a particle size below 74 μm. The main phases of the material were analyzed by XRD (Fig. 1). Many mineral components are observed in the refractory gold ore, including quartz (SiO_2), muscovite ($KAl_2Si_3AlO_{10}(OH)_2$), pyrite (FeS_2), and arsenopyrite (FeAsS). Antimony is present mainly in the form of stibnite (Sb_2S_3). All reagents were of analytical grade. The purity of the oxygen used during the pressure oxidation process exceeded 99.9%.

2.2. Process flowsheet

To avoid the adverse effects of antimony on gold extraction, a clean production process for removing and recovering antimony from refractory gold ore is proposed. The complete process flowsheet is shown in Fig. 2. First, the antimonial refractory gold ore is leached in alkaline sodium sulfide solution. Gold is extracted from the leaching residue by the cyaniding process. The leaching solution is subjected to a pressure oxidation process to prepare sodium pyroantimonate ($NaSb(OH)_6$). Finally, the oxidized solution is concentrated and crystallized to recover sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$).

2.3. Experimental procedure

The clean production process for extracting antimony from refractory gold ore involves sodium sulfide leaching, pressure oxidation, concentration, and crystallization steps. First, the stibnite in the refractory gold ore reacts with sodium sulfide, and antimony is dissolved into the leaching solution in the form of sodium thioantimonite (Eq. (1)). During the leaching process, a given amount of sodium hydroxide is added into the leaching solution to prevent the hydrolysis of sodium sulfide (Eq. (2)). The main chemical reactions can be described as follows:

$$Sb_2S_3 + 3Na_2S = 2Na_3SbS_3 \quad (1)$$

$$Na_2S + H_2O = NaOH + NaHS \quad (2)$$

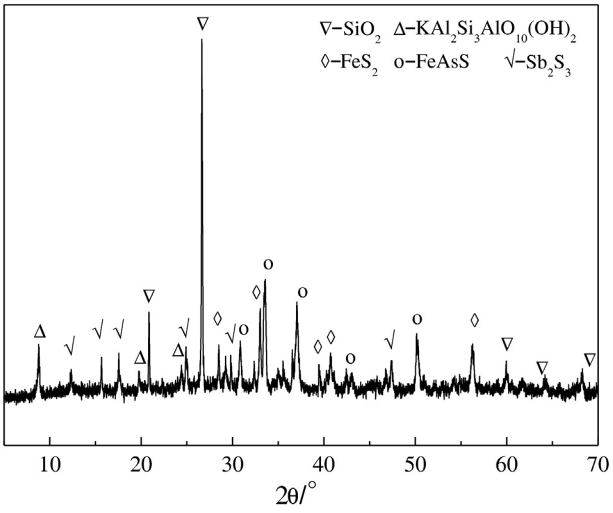

Fig. 1. XRD pattern of the antimonial refractory gold ore.

After completing the leaching process, the leaching solution is transferred into an autoclave to prepare sodium pyroantimonate. The reaction equation is expressed as:

$$2Na_3SbS_3 + 7O_2 + 2NaOH + 5H_2O = 2NaSb(OH)_6 + 3Na_2S_2O_3 \quad (3)$$

The oxidized solution is concentrated and hot filtered to remove the insoluble mixture of sodium sulfate and sodium sulfite. Finally, the sodium thiosulfate byproduct is crystallized from the solution by cooling.

2.4. Analysis and characterization

Samples with low antimony, arsenic, and gold contents were determined by ICP-AES (IRIS Intrepid II, XRS), and those with high contents of antimony and arsenic were determined by titration with ceric sulfate and potassium bromate, respectively. The gold and silver contents of the solid samples were determined by fire assay. The sulfur content in the solution was analyzed by the iodine-sodium thiosulfate dispersion method. The chemical composition of the solid samples was characterized using X-ray fluorescence (XRF, ZSX Primus II, Rigaku). The phases of the solid sample were identified by X-ray diffraction (XRD) using a Rigaku TTRAX-3 instrument (40 kV, 30 mA, 10°/min). Microstructures were characterized using a Japan Jeol JSM-6360LV instrument equipped with a spectrometer for microanalysis based on an energy dispersive X-ray spectroscopy (EDS) system (EDX-GENESIS 60 S, EDAX, USA) with an accelerating voltage of 0.5 kV to 30 kV.

3. Results and discussion

3.1. Sodium sulfide leaching

3.1.1. Leaching recoveries of antimony, gold, and arsenic

Several studies have reported that the cyanide leaching of gold from antimonial refractory gold ore can be enhanced significantly after removing the antimony. Therefore, the selective leaching of antimony before the conventional cyanidation treatment is necessary. Through

Table 1
Chemical composition of the antimonial refractory gold ore.

Component	Au/(g/t)	Ag/(g/t)	S	Fe	Sb	As	Cu	SiO_2	Al_2O_3	CaO	K_2O
wt%	58.8	42.0	17.68	15.74	6.30	5.50	0.04	36.58	11.94	3.76	2.45