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Comprehensive recovery of metals from cyanidation tailing

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ABSTRACT

Cyanidation tailing is the residue produced in gold plants which use cyanidation to extract gold. It can be used as a secondary resource to recover residual metals that are of great economic value. The cyanidation tailing investigated in this paper was obtained from Shandong Province, China. It contained valuable metals such as chalcopyrite, galena, sphalerite and pyrite. In this study, alkaline sodium hypochlorite was used as a regulator in the pretreatment stage. It was proved that the sodium hypochlorite played two roles in the flotation pulp: oxidant and pH regulator. On one hand, sodium hypochlorite oxidized cyanide to cyanate, eliminating the negative effect of residual cyanide towards the environment. On the other hand, with the pH of flotation pulp exceeding 10, sphalerite and pyrite were depressed enormously, which was beneficial to the recovery of chalcopyrite and galena. With the Cu–Pb bulk flotation flowsheet, the cyanidation tailing was processed to obtain qualified Cu concentrate with grade of 13.17% and recovery of 70.00% compared with the original Cu grade of 0.21%. The Cu–Pb tailing was processed to obtain qualified Zn concentrate with grade of 34.72% and recovery of 69.58% compared with the original Zn grade of 0.33%, constituting the comprehensive recovery routing for the cyanidation tailing.

1. Introduction

Tailings, generated from mineral processing, used to be regarded as deserted byproducts. However, with the exploitation and gradual depletion of the mineral resources all over the world, the reuse of tailings for recycling their residual valuable minerals become a necessity. Cyanidation tailing is the residue produced from gold plants which use cyanidation (direct cyanide leaching process) to extract gold. In China, It is estimated that more than 2.45 million tons of cyanidation tailings are discharged into tailing ponds every year (Zhu et al., 2010). Most of these cyanidation tailings contain some valuable minerals, such as copper minerals, lead minerals, zinc minerals and sulfide minerals. For example, the cyanidation tailing from Penglai Gold Smelting Plant (in Shandong Province, China) contains 38.07% Fe, 41.22% S. This tailing was used to prepare nano-iron red oxide pigment by an ammonia process with urea as precipitant (Li et al., 2008). The cyanidation tailing from Yindongpo Gold Plant (in Henan Province, China) contains 0.14% Cu, 6.40% Pb, 2.83% Zn, 33.06% Fe and those valuable minerals were recovered by flotation using pretreatment method and YO reagent (He et al., 2003). The cyanidation tailing from Tianshui Gold Plant (in Gansu Province, China) contains 1.94% Cu, 5.96% Pb, 0.27% Zn, 24.62% Fe. With the combination of a new activator and copper sulfate in the flotation, qualified Cu concentrate can be acquired (Gao and Li, 2005).

However, the residual cyanide in cyanidation tailing depresses the recovery of copper minerals, lead minerals, zinc minerals and sulfide minerals (Popov et al., 1988; Grano et al., 1990; Cao and Liu, 2006). Besides, the redundant cyanide is highly toxic to the environment and a threat to human health if not well treated (Shifrin et al., 1996; Mudder and Botz, 2004; Botz et al., 2005; Donato et al., 2007). So the elimination of cyanide (including free cyanide and cyanide complexes) is imperative before retrieving valuable minerals.

There are many physical and chemical methods that have been tested for the removal of cyanide from gold mill effluents, including natural degradation, ozonation, bacterial oxidation, SO_2 process, acidification, ion exchange, hydrogen peroxide, alkaline chlorination, which are commonly used in treating waste water in gold plants (Botz, 2001; Ritcey, 2005; Kuyucak and Akcil, 2013). Khodadad et al. used sodium and calcium hypochlorite to oxidize cyanide to cyanate and the residual cyanide was under the detection limit under the optimal conditions. They indicated that the removal of cyanide by sodium hypochlorite cost less compared with by calcium hypochlorite, considering operational factors such as transportation and conditioning tanks (Khodadad et al., 2008). Ingles and Scott also pointed out that the oxidation

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of sodium hypochlorite was accepted as a technique for cyanide waste water treatment (Ingles and Scott, 1993). However, all these cyanide destruction methods were used to treat cyanide-containing liquid wastes rather than to treat the cyanide-containing solid wastes. In this study, sodium hypochlorite was chosen as an adjuster to treat the solid waste of cyanidation tailing considering the oxidability and the oxidation condition of sodium hypochlorite.

The feed for this study was the cyanidation tailing obtained from Shandong Province in China. It contained some valuable minerals, such as chalcopyrite, galena, sphalerite, and pyrite, so it can be used as a secondary resource to recover these minerals. However, the cyanidation tailing had the following features, bringing about much difficulty to the recovery of valuable minerals:

(1) The grades of chalcopyrite, galena, and sphalerite in the tailing were very low.
(2) Residual cyanide and reagents in the tailing depressed the recovery of chalcopyrite, galena, and sphalerite to some extent.
(3) The particle size was very fine, detrimental to flotation process.

2. Experimental

2.1. Ores characterization

The cyanidation tailing in this study was stored in stout polyethylene containers in the dark to minimize the loss of cyanide. The solid content measured was 20% averagely. After filtration, approximately 100 g of sample was dried at about 90 °C in drying oven for 6 h. Then the lumps were broken and thoroughly mixed. Next, the sample was analyzed by chemical analysis methods using atomic absorption spectrophotometer (AAS, WFX-130A, Beijing, China). The result is shown in Table 1. The mineralogical determination of the feed sample was detected by X-ray diffraction (XRD, Smartlab-201307, Rigaku Corporation, Japan) and scanning electron microscope (SEM, JSM-7001F, JEOL, Japan, operating at 15 kV), as shown in Fig. 1.

From the chemical composition analysis and the XRD result, it can be seen that the pyrite and quartz were the major minerals in the cyanidation tailing. The valuable metals were mainly copper mineral (grade 0.21%), lead mineral (grade 0.33%), zinc mineral (grade 0.35%) and sulfide mineral (grade 24.98%), which mainly existed in the form of chalcopyrite, galena, sphalerite, separately. The gangues were mainly quartz and silicate. Thus, the goal of the study was to recover Cu, Pb, Zn, and S (representing chalcopyrite, galena, sphalerite and pyrite, the same below) while depressing quartz and silicate. From Fig. 1(b), it can be seen that the minerals were mostly in the form of particle, sheet, and irregular granular.

For the particle size analysis, the feed was sieved into different size fractions by wet sieving. Table 2 shows the particle size distribution and the chemical grades of Cu, Pb, Zn, and S in the different size fractions.

It was shown in Table 2 that nearly 99% of the cyanidation tailing was less than 74 μm, indicating that the tailing was already very fine and there was no need to further grind it. Besides, Cu, Pb and Zn distributed relatively equally among different size fractions with similar grades. What is more, there were 78.66% of Cu, 80.95% of Pb, and 81.92% of Zn in the −30 μm size fraction. The results showed that these metals cannot be separated by elutriation to different size fractions, and the particle size were also a big problem for the treatment of cyanidation tailing. It is believed that fine particles typically show slow recovery rates, and are prone to entrainment, which have a considerable impact on grades and recoveries of valuable minerals (Trahar, 1981; Feng and Aldrich, 1999; Graeme, 2012). As a result, the recovery of valuable metals from cyanidation tailing would be of great difficulty.

2.2. Flotation reagents and flowsheet

The flotation experiments were conducted with iso-butyl ethionine (Z200), sodium diethyldithiocarbamate (SN9), and sodium n-butyl xanthate (SNBX) as collectors, which were acquired from Jiangxi Copper Corporation. These collectors were all in industrial grade and were diluted in water to a concentration of 1%. Sodium hypochlorite solution (purchased from Sinopharm Chemical Reagent Beijing Co., Ltd.) was added to the pulp as a regulator. Copper sulfate pentahydrate (purchased from Sinopharm Chemical Reagent Beijing Co., Ltd.), in analytical pure, was used to activate sphalerite in the flotation of sphalerite. CP mixture (composed by sulfurous acid, sodium silicate, and carboxy methylated cellulose), was prepared in laboratory. Terpenic oil (acquired from Jiangxi Copper Corporation), with monohydric alcohol content more than 40%, was used in the whole flowsheet as frother.

The flotation flowsheet is shown in Fig. 2, following the principle of Cu–Pb bulk flotation. In the Cu–Pb flotation stage, sodium hypochlorite was used as an adjuster, followed by SN9 and Z200 as collectors. At the optimal conditions, Cu–Pb concentrate was collected. Then ultrasonic device and CP mixture was used to separate the Cu–Pb mixture to acquire Cu concentrate and Cu tailing. The Cu–Pb tailing served as the Zn raw material. With the activation of copper sulfate pentahydrate, Zn concentrate can be collected. Zn tailing served as S concentrate. The keypoint would be how to get the Cu concentrate and Zn concentrate from cyanidation tailing in this study.

The following tests were designed in the Cu–Pb bulk flotation stage by choosing the primary affecting factors. The effect of sodium hypochlorite dosage, reaction time and the synergism of collectors on the flotation of Cu–Pb bulk flotation were studied through one roughing flotation test.

A 300 g of cyanidation tailing sample was transferred into a 1L XFD series single flotation cell (Jilin Exploring Machinery Plant, Jilin, China) and pulped to 30 wt.% solids using city water. It was agitated at 1220 rpm for 1 min before any reagents were added. Then add sodium hypochlorite solution into the pulp for a certain time, followed by SN9 and Z200. As there were residual reagents from former leaching process, there was no need to add frother in the roughing flotation. Thereafter, the pulp was aerated and flotation was carried out. Froth height was maintained at the same level by adding water periodically throughout the test. The bulk concentrate and tailing collected were filtered, dried, and weighed, and the samples were analyzed by chemical analytical method. The results analysis was done with the recoveries of Cu, Pb, Zn and S.

3. Results and discussion

3.1. Influence of sodium hypochlorite on the flotation

As shown in Fig. 3, about 83% of Zn was collected without the pretreatment of sodium hypochlorite, while the recoveries of

Table 1
Result of chemical composition analysis of the cyanidation tailing.

Elements	Au	Ag	Cu	Pb	Zn	S	As	Fe	Mg	Ca	Al	Si
Content/%	1.10 g/t	18.81 g/t	0.21	0.33	0.35	24.98	0.03	25.08	2.19	2.19	6.50	16.77