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A significant improvement of scheelite flotation efficiency with etidronic acid

Jianhua Kang, Yuehua Hu**, Wei Sun*, Runqing Liu, Zhigang Yin, Honghu Tang, Xiangsong Meng, Qingpeng Zhang, Hang Liu

School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China

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ABSTRACT

This research demonstrates an effective application of etidronic acid to improve the scheelite flotation efficiency and reduce the consumptions of energy and reagents. The cleaning recovery is significantly increased by 7%, and the cleaning cost is reduced by 17% accompanied with the efficient improvement of roughing grade from 1.22% to 1.68% compared with that in previous month. The depression abilities of etidronic acid, normal water glass, and acidified water glass for the scheelite roughing flotation are studied using laboratory-scale experiments. Etidronic acid shows an improved selective performance in improving the roughing grade. This performance is further verified by industrial test. The use of etidronic acid in the roughing circuit improves the product grade from 24.66% to 28.26%. The daily product output is also increases by 1.54 t. Economic evaluation results indicate that the heating cost is reduced by 28%, and the water glass consumption is decreased by 14%. An increased product profit of $1,248,000 and a reduced cost of $20,841 are also obtained.

1. Introduction

Mineral resources are the main raw material sources of industrial production and manufacturing and the basis of human survival and development. High-efficiency exploitation and utilization of mineral resources are important for the sustainable and stable development of economy and society (Dubiński, 2013). In recent years, the consumptions of energy, steel, copper, and aluminum in China all ranked first place worldwide (Wang et al., 2016). Population growth, industrialization, urbanization, and technological developments are accompanied with significant increase in the consumptions of minerals, energy, water, and land (Kok and Benli, 2017; Tamaki et al., 2017). In the last century, resource consumption is one of the most important factors that plays an active role in promoting economic development (Buus, 2017). However, the rapid consumption pattern has caused a series of problems, such as resource waste and environmental pollution. With the realistic pressure of resource shortage and environment protection, the improvement of resource utilization and the reduction of energy consumption and waste emission are considerable challenges and urgent tasks in the current modern mining (Freire-González and Font Vivanco, 2017).

The fine dissemination size and complex associated minerals are the dominant factors causing low efficiency and high energy consumption of low-grade scheelite ($CaWO_4$) flotation. For the type of scheelite–calcite–fluorite ores, separating scheelite from Ca-bearing gangue minerals, such as calcite ($CaCO_3$) and fluorite (CaF_2), by flotation is difficult because of their similar floatability in the fatty acid system (Chen et al., 2017a, 2017b). Normal roughing and heating cleaning are required processes to achieve effective enrichment and access-qualified products. In the heating cleaning circuit, the roughing concentrates should be concentrated to 60%–70%, heated to 85 °C–95 °C, and stirred strongly with large amounts of water glass ($Na_2O \cdot mSiO_2$) to depress the Ca-bearing gangue minerals. Although the Petrov cleaning method can effectively separate scheelite, the large consumptions of energy and reagents, high costs, and complicated operation are the main problems of scheelite flotation. Accordingly, a series of measures has been adopted to improve the scheelite flotation efficiency and reduce the cost. For example, the development and application of a flotation column significantly improve the enrichment efficiency and simplify the flotation process (Peng et al., 2016; Şahbaz et al., 2017). In the heating cleaning circuit, the selective addition of

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* Corresponding author.
** Corresponding author.
E-mail addresses: hyh@csu.edu.cn (Y. Hu), sunmenghu@csu.edu.cn (W. Sun).

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sodium hydroxide or sodium sulfide in combination with water glass can strengthen the depression of Ca-bearing gangue minerals and sulfide ores and reduce the water glass consumption. Research on the precipitation treatment of water glass in mineral processing wastewater improves the reuse of flotation wastewater (Kang et al., 2017b) and eliminates the influence of residual water glass in recycled water on scheelite roughing (Kang et al., 2017a). Nevertheless, the recovery of low-grade scheelite from molybdenite (MoS_2) flotation tailings in Luanchuan still suffers from low roughing efficiency and high heating cleaning cost.

The scheelite flotation plant in Luanchuan is owned and operated by China Molybdenum Co. Ltd. (CMOC), which is the largest producer of molybdenum and tungsten in China. The ores are mined and processed to recover molybdenite and scheelite by sequential selective flotation. The molybdenite flotation tailing is directly used to recover scheelite without concentration and grind by the roughing and cleaning flotation circuits. In the roughing circuit, sodium carbonate (2000 g/t) is used as the regulator, and fatty acid (250 g/t) is used as the collector for scheelite flotation. In recent years, the continuous research and experiment on the collector has increased the roughing recovery to 83%–85%. Nonetheless, the roughing enrichment ratio is relatively low due to the influence of Ca-bearing gangue minerals, such as calcite and fluorite. The concentration and heating of roughing concentrates cause the large consumption of energy and water glass. In addition, the WO_3 loss of overflow from thickener reaches 120 t annually, which is a significant waste of resources. In the heating cleaning circuit, the combined use of flotation column and flotation machine considerably shortens the cleaning process and improves the cleaning efficiency. The combination of sodium hydroxide and water glass also effectively reduces the dosage of water glass and improves the cleaning recovery. Nonetheless, in practice, the calcite and fluorite in the ore are abundantly enriched during the scheelite roughing. The calcite and fluorite grades in the roughing concentrate reach 30% and 25%, respectively; calcite and fluorite are the main factors causing the low roughing efficiency and high cleaning cost. Therefore, the investigation and application of effective depressants to depress the flotation of calcite and fluorite in the roughing may be a useful method to improve the scheelite roughing efficiency.

Water glass has been widely used as the dispersant and depressant to separate scheelite (Han et al., 2017), phosphate ore (Dho and Iwasaki, 1990), and rare-earth element (Zhang and Anderson, 2017). This compound can effectively improve the pulp properties and reduce the entrainment of gangue minerals. The acidified and salinization water glasses are modified products mixed with sulfuric acid and aluminium salt, respectively, to enhance the selective depression ability of water glass. The acidified water glass is used as a selective depressant in scheelite, ilmenite and fluorite flotations. The use of acidified sodium silicate as depressant can achieve the flotation separation of scheelite from calcite; the preadsorption of acidified sodium silicate interferes with the adsorption of sodium oleate on calcite surface, but not with its adsorption on scheelite surface (Feng et al., 2015). The selective flotation of ilmenite from olivine can be remarkably achieved using acidified water glass as the depressant (Yang et al., 2016). Fluorite flotation with acidified water glass can improve the fluorite recovery, accelerate the sedimentation rate of fine particles in tailing slurry, and consequently produce a clean recycled water (Zhou et al., 2013). Organic depressants, such as citric acid and tannin, are used to separate collophanite, jamesonite, and chalcopyrite. The combined use of citric acid and sulfuric acid can effectively improve the collophanite flotation performance and reduce the sulfuric acid dosage by 30% (Liu et al., 2017). The larch tannin extract improves the jamesonite flotation to depress marmatite, pyrrhotite, arsenopyrite, pyrite, calcite, and quartz (Chen et al., 2011). The quebracho extract (tannin) shows a good performance on the chalcopyrite flotation to depress pyrite (Sarquís et al., 2014). Scale inhibitors, such as amino trimethylenephosphonic acid and etidronic acid, are rarely used in flotation, but they possess excellent chelate ability to coordinate with calcium and form a stable complex compound. The amino trimethylenephosphonic acid shows an excellent performance in disturbing the normal growth of calcium carbonate and inhibiting its deposition (Tang et al., 2008); this performance is attributed to the excellent ability of this acid to chelate with Ca^{2+}, prevent the layer stacking in forming calcite, and induce lattice distortion of $CaCO_3$ from calcite to vaterite at considerably low concentration (Ji et al., 2017). Etidronic acid strongly affects the inhibition of crystal growth, the morphology of $CaCO_3$ crystals, and the coverage of the metallic surface (Garcia et al., 2001; Ukrainczyk et al., 2013). Scale inhibitors with excellent chelating ability may be utilized as selective depressants to achieve the flotation separation of calcic minerals.

In this paper, we provide details on the application of etidronic acid to improve the scheelite flotation efficiency. The roughing grade is significantly improved, which results in the increased product output and reduced heating cleaning cost. The technical and economic feasibility of the application of etidronic acid is also investigated by industrial tests at the plant.

2. Materials and methods

2.1. Materials and reagents

The ores used in the experiments are molybdenite flotation tailings collected from a molybdenite plant in Luanchuan. The molybdenite flotation tailings are processed by the roughing and cleaning flotation circuits to recover scheelite. Sodium carbonate, fatty acid (FX-6), and the water glass, which are used as the regulator, collector, and depressant, respectively, were obtained from the reagent preparation workshop in the scheelite plant. Etidronic acid was obtained from a scale inhibitor plant in Xinxiang.

2.2. Characterization of molybdenite flotation tailings

The main chemical elements of the molybdenite flotation tailings were analyzed by X-ray fluorescence spectrometry (AxiosmAX, PANalytical, Holland), and analysis results are shown in Table 1. The main valuable element is W, and the main impurity elements are Ca, Si, and Fe. Phase analysis results of tungsten minerals are shown in Table 2. The finding indicated that scheelite is the main mineral, and its ratio reaches 94.53%. The X-ray diffraction analysis (Rigaku D/max 2500, Japan) was conducted on raw tailings to identify the main mineral components. The XRD results and the analysis results of the minerals' relative contents are presented in Fig. 1 and Table 3. These results confirmed that the predominant gangue minerals are quartz, garnet, feldspar, calcite, fluorite, and mica. In the molybdenite flotation tailings, the calcite and fluorite grades reach 9.68% and 8.56%, respectively, which maybe the main factor influencing scheelite flotation.

The tailings are pumped from the molybdenite flotation circuit, and they directly enter the scheelite roughing circuit without concentration and grind. The particle size is completely determined by the grinding fineness of molybdenite flotation. Recent studies (Bazin and Proulx, 2001; Santana et al., 2008) investigated the influence of particle size on the separation performance of valuable minerals. The grind fineness is the key factor for valuable mineral flotation; an appropriate grind fineness guarantees the release of valuable minerals and influences the separation efficiency. The