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Investigation of two-stage depressing by using hydrophilic polymer to improve the process of fluorite flotation

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ABSTRACT

Fluorite is a non-renewable mineral that is used for anhydrous hydrofluoric acid and aluminum fluoride purposes. In China, along with the excellent fluorite resource, which is over-exploited, many off-specification fluorites ($CaF_2 > 93$, under 97%; $SiO_2 > 1.5\%$) are produced. Improving the grade of fluorite instead of costly technologies of the Buss and CHEMCO are conducted. To improve the grade of fluorite, an excessive amount of sodium silicate is commonly used. However, this approach cannot stably produce high-quality fluorite and result in excessive reagent consumption, poor selectivity and high-water content of the fluorite concentrate. To solve these problems, suitable hydrophilic polymer depressants, which are highly stable, safe, non-toxic, hydrophilic, biodegradable and low processing cost because of abundant in nature, are selected to replace sodium silicate. To make the study practical, the testing location chosen was in Chenzhou (Hunan, China) and was operated by Xinyuan mining Co. Ltd., the largest monolithic fluorite ore producer in Asia. Meanwhile, to prevent the above problems from occurring, the focus throughout this study was achieving separation in the flotation process through the successful occurrence of two sub-processes. The first process was desilicication using dextrin, and the second process was decalcification using tannin.

A tech-economic assessment based on the pilot program showed that compared with sodium silicate, the new technology (dextrin + tannin) improved fluorite recovery by 19.23%, removal rate of $CaCO_3$ by 13.43% and SiO_2 by 8.93% and reduced production costs by $2914.8 per day. The technology (dextrin + tannin) produced an excellent result, simplifying the flow during fluorite flotation, which can led to a reduction in power consumption as well as reduction in production costs for each ton of 105% sulfuric acid of $3.24 (t/t) for the entire production chain lifecycle. The new technology was an efficient, economic and environmentally friendly and has widespread applications and promising market prospects.

1. Introduction

Fluorite minerals have been found on every continent, but they are mainly concentrated in the circum-pacific metallogenic belt and make up approximately half of the global fluorite ore reserves. The main producers are South Africa (0.2 Mton), China (3.8 Mton), Mongolia (0.38 Mton) and Mexico (1.1 Mton), and estimated reserves ($CaF_2 = 100\%$) are mainly located in South Africa (41 Mton), China (24 Mton) and Mexico (32 Mton) (Gocha, 2015). China is the world's largest fluorite producer and has an annual production that accounts for 60.8% of global production. In China, all companies and institutions are increasing their efforts to improve resource utilization and reduce drainage of industrial sewage, which will eventually lead to the entire production chain to meet sustainability standards.

For now, fluorite is the main material in the manufacture of anhydrous hydrofluoric acid and aluminum fluoride in China. To our knowledge, the fluorite powder quality index is commonly $CaF_2 \geq 97\%$, $SiO_2 < 1\%$. However, along with the constant excellent fluorite resource development, the side effects of resource exploitation in China are increasing daily. Many off-specification fluorites ($CaF_2 > 93$, under 97%; $SiO_2 > 1.5\%$) are produced because of the low grade, complex properties and extremely fine dissemination size of the raw fluorite ore. Fortunately, the aluminum fluoride process

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described by (Ying and Ying, 2010) is being rapidly developed by the introduction of Buss and CHEMCO technology in China (Ying and Ying, 2010), which is widely used for aluminum fluoride in the electrolytic aluminum industry. Off-specification fluorite can be used by the Buss and CHEMCO technology, but the cost of it use is restricted because of the presence of impurities. Even so, there are still challenges that must be faced when utilizing a lower grade of fluorite than before ($CaF_2 < 93$).

Currently, flotation is the most common method for enriching fluorite and is well documented (Aliaga et al., 2006; Song et al., 2006; Zawala et al., 2008). Silicate (such as quartz, sericite) and carbonate (calcite) are recognized as the least valuable components and must be removed from fluorite ore (Tian et al., 2017). (Bo et al., 2015) reported that the method of depressing can achieve the flotation separation of scheelite from calcite (Shi et al., 2014). further demonstrated that added lattice ions change reactivity of the calcite surface and improve depressants actions on calcite flotation.

Sodium silicate is a widely used depressant for worthless minerals (Rao et al., 1989) and has advantages over flotation, including low cost, simple operation, adjustable pulp properties (Sis and Chander, 2003) and effective depressing of silicate minerals (Zhang and Anderson, 2017). However, when used for fluorite flotation, it produces a number of problems that cannot be neglected, such as large reagent consumption, poor selectivity, high SiO_2 content and high water content of the fluorite concentrate. The production of fluorite is becoming increasingly common at a lower grade than before ($CaF_2 < 93$).

The focus throughout this study is to prevent these problems from occurring through separation in the flotation process, which is achieved through successful application of two sub-processes. The first process involves enriching ore in such a way that the silicate minerals can be rapidly removed. The second process requires the ore to have a similar solubility and the same active Ca^{2+} site so that it can interact with the anionic collectors of fluorite and calcite, which should be effectively separated. Thus, the primary goal of this study was to select suitable depressants to replace sodium silicate to depress the two impurities.

As always, organic depressant reagents are cleaner than conventional inorganic reagents. Some researchers have focused their attention on the application of a polymer (starch, dextrin, CMC, guar gum and other polysaccharide polymers as a depressant for alum inosilicate minerals present as impurities in sulfide ores) (Beattie et al., 2006; Bessière and Etahiri, 1993; Kapu et al., 1999; Turrer and Peres, 2010; Wie and Fuerstenau, 1974; Wiese et al., 2007). Most of the achievements of previous studies have been restricted to laboratory research and may not be suitable for industrial applications. However, the use of dextrin as a commercial depressant for flotation separation of calcite and sericite minerals from fluorite ores has not been reported nor has it been used in practical applications.

In addition, another challenge is that the efficient calcite depressant should be inexpensive and must not affect the subsequent treatment of hydrofluoric acid production. References to the use of tannin in froth flotation have been found recently for the depression of pyrite (Castro and Hoces, 1993; Sarquís et al., 2014). Tannin is a non-toxic, biodegradable reagent that is approved for use as a flocculent in water purification plants in several countries and also as a dispersant in mud drilling due to its surfactant properties on particles in a water suspension (Anirudhan and Ramachandran, 2006; Oats et al., 2010). Tannin is a significant reference that we can draw from.

Consequently, developing a new flotation technology to decrease the damage from water glass and increase the removal efficiency of impurities as well as recovery of fluorite are worthwhile objectives. To our knowledge, no data have been published on the application of hydrophilic polymers (dextrin + tannin) to separate fluorite, calcite and sericite in the fluorite industry. Based on these considerations, this work provides details regarding a process that applies dextrin for the removal of sericite and tannin for the removal of calcite in the fluorite flotation process. To assess the superiority and sustainability of the new system, indicators for the recovery and grade of fluorite were obtained and compared to those of the old fluorite flotation system. The technical treatment and cost–benefits were evaluated in detail by testing the work at the plant.

2. Materials and methods

2.1. Materials and reagents

This study was implemented at Hunan Xinyuan Minerals Corporation in Chenzhou city, China, as seen in Fig. 1. This mine contains beryllium fluorite ore deposits, which is the most common monolithic fluorite ore in Asia, and includes 15.38 million tons of fluorite mineral resources reserves. The fluorite ores (containing sericite and calcite) used for the batch flotation tests and industrial flotation tests were from the Hunan Xinyuan Mining Limited-liability Company.

Multi-elemental chemical analysis of the sample was conducted by Atomic Adsorption Spectroscopy (AAS) and an Inductively Coupled Plasma Optical Emission Spectrometer (ICPOES), and the analysis results are shown in Table 1. As shown in Table 1, the main components of the sample were 40.32% CaF_2, 15.11% $CaCO_3$, and 16.8% SiO_2. Relative content analysis of the minerals indicated that the silicate was sericite and muscovite based and carbonate was calcite based (Table 2, Fig. 2).

The reagents used for all of the tests were obtained from the following sources: oleic acid $C_{18}H_{34}O_2$), tannin ($C_{76}H_{52}O_{46}$) and dextrin $(C_6H_{10}O_5)n$ were from Reagent Technology Ltd., Zhuzhou, China; sodium carbonate and water glass were supplied by HongYuan chemical co., LTD. All of the chemicals (AR) used for the industrial tests were purchased from a local supplier (Guoyao, China) and were used without further purification.

2.2. Methods

2.2.1. Batch flotation tests

In the batch flotation tests, the ore (500 g, crushed to −2 mm during sampling) was ground to the desired proportions by passing

Fig. 1. The precise geographic location of Hunan Xinyuan Mining Limited-liability Company.