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Selective flotation separation of spodumene from feldspar using new mixed anionic/cationic collectors

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ABSTRACT

The selectivity in flotation separation of spodumene from other pegmatic aluminosilicates such as feldspar and mica, using a single fatty acid anionic collector, is found to be very difficult. It is attributed to the same surface Al site for interaction with fatty acid. In this study, a collector mixture of sodium oleate (NaOL) and dodecyl trimethyl ammonium chloride (DTAC) demonstrates a high selectivity for the flotation of spodumene from feldspar. The influences of important factors such as molar ratio of the mixed collectors, dosages of calcium chloride, sodium hydroxide and sodium carbonate, and pulp temperature on spodumene and feldspar flotation using the mixed collectors have been investigated through micro-flotation tests. The optimum molar ratio of NaOL and DTAC is found to be 9:1. Sodium hydroxide has to be used as a pH regulator. Without the use of depressants, no selectivity is observed as the flotation of spodumene and feldspar are activated by Ca^{2+}. Sodium carbonate must be used as depressant of feldspar. A comparison of the flotation for a lithium pegmatite ore using mixed fatty acid soaps and mixed anionic/cationic collectors (NaOL/DTAC) was carried out by the batch flotation tests. The results indicated that NaOL/DTAC decrease collector consumption by two-thirds. The recovery and grade of Li_2O concentrates increase by 4.93% and 0.31%, respectively.

1. Introduction

Lithium has become a precious commodity since about a quarter of all lithium production is used for energy storage. The increased demand for lithium in batteries, especially for electric vehicles has focused attention on the adequacy of known and anticipated lithium resources (Gruber, 2010; Yaksic and Tilton, 2009). Spodumene, $LiAl(SiO_3)_2$, containing 8.03% Li_2O, 27.4% Al_2O_3, and 64.6% SiO_2, is the principal economic mineral of lithium-rich pegmatite ores. Spodumene belongs to a silicate group called clinopyroxene, one of the single-chain silicates (Zhu et al., 2015). In the polyhedral model of spodumene, the silicates $[SiO_3]^{2-}$ are represented by the chains of tetrahedra. The irregular six coordinations of Li^+ and Al^{3+} with oxygens are indicated by the octahedral linking the silicate tetrahedral chains (Moon and Fuerstenau, 2003).

The *Jiajika* pegmatite deposit in western Sichuan Province of China is the largest solid lithium deposit in Asia, and the spodumene-bearing pegmatite is reported to have a lithium reserve of 0.48 Mt. Another pegmatite in the area, *Barkam*, is reported to contain 0.22 Mt Li (Kesler et al., 2012; Li and Chou, 2015). For example, the lithium ore from *Jiajika*, contains 20.1% by weight of spodumene, 2.3% mica, 44.5% feldspar, and 31.0% quartz.

Flotation is the most widely used industrially for the beneficiation of spodumene from associated silicate minerals with fatty acid collectors such as sodium oleate, naphthenic soap, and oxidized paraffin soap, among which a combination of the two is used sometime (Amarante et al., 1999; Moon, 1986). The flotation separation of spodumene from other complex aluminosilicate minerals such as feldspar and mica, is problematic, due to their same active Al site for interaction with anionic collectors (Rai et al., 2011). In practice, the general method to accomplish effective spodumene flotation is to add amount of depressants associated with fatty acids in a large amount and to take some special treatments such as high-intensity agitating, pretreatment by strong alkali and heating.

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In recent years, many studies have been carried out to improve and strengthen spodumene flotation by adding activated ion such as Ca^{2+}, Mg^{2+}, Fe^{3+} (Jie et al., 2014; Liu et al., 2015). However, the ion activation has a poorly selective flotation of spodumene as the gangue minerals such as feldspar and quartz are activated simultaneously by metal ions. Fuerstenau and Rai have studied the anisotropic crystal chemistry of pegmatitic aluminosilicates with sodium oleate (Moon and Fuerstenau, 2003; Rai et al., 2011). It suggested that if more hydrophobicity exposed planes of minerals can be controlled by selective comminution, the wettability and floatability may be modified. This is a significant reference we can draw from at present.

However, the reports on more selective collectors for strengthening spodumene flotation are rare. A new single collector with a long development cycle has too high a cost to be used. A collector mixture is a good choice for this purpose. Recent researches showed that the flotation separation efficiency of minerals could be enhanced using a mixture of anionic collectors with anionic, nonionic and cationic collectors, respectively (Sis and Chander, 2003a; Vidyadhar and Hanumantha Rao, 2007; Von Rybinski and Schwuger, 1986; Von Rybinski et al., 1987; Xu et al., 2013). The mixed collectors demonstrated three synergetic effects, namely enhanced mineral recovery, improved adsorption behavior of the main collector on the target mineral surface, and enhanced adsorption selectivity (Holland and Rubingh, 1992; Rao and Forssberg, 1997).

Quaternary ammonium salts (QAS) are extensively used as an efficient collector for clay-type aluminosilicate minerals such as kaolinite, pyrophyllite and illite in Chinese diasporic bauxite reverse flotation (Longhua et al., 2015; Xu et al., 2004). It is reasonable to imply that it would interact with pegmatitic aluminosilicate such as spodumene and feldspar. In this study, DTAC was considered as a secondary collector, as DTAC has an excellent solubility, insensitivity for temperature and pH. An attempt to improve the selectivity for the flotation of spodumene from feldspar was made using the mixed anionic/cationic collectors NaOL/DTAC through micro-flotation and batch flotation tests.

2. Materials and methods

2.1. Mineral samples

The pure mineral samples of spodumene and feldspar (albite) were obtained from the *Jiajika* Lithium Mine, Ganzi District of Sichuan province, China. The samples were hand-picked, crushed and ground in a laboratory porcelain mill, and −0.074 mm fractions were used in the experiments. Chemical composition analysis (Table 1) and X-ray diffraction (XRD) (Fig. 1) were used to study chemical and mineral compositions. The results showed the as-prepared spodumene contained 7.86% Li_2O. And the purity of spodumene and feldspar is greater than 90%.

The lithium pegmatite ore for batch flotation was also from the *Jiajika* Lithium Mine. The multi-elemental chemical analysis of the ore was conducted by acid dissolution and Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and the analysis results are shown in Table 2. As shown in Table 2, the minerals contained 1.43% Li_2O, 70.52% SiO_2 and 14.36% Al_2O_3, and also contained others rare metals

Table 1
Chemical compositions of the purified samples (mass fraction, %).

Sample	Li_2O	Na_2O	K_2O	SiO_2	Al_2O_3	Fe_2O_3
Spodumene	7.86	0.15	0.043	62.48	27.43	0.13
Feldspar	–	11.99	0.14	66.43	20.58	0.25

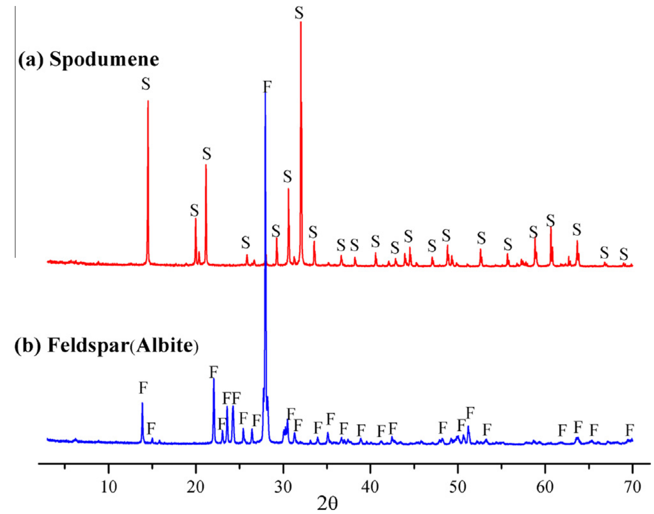

Fig. 1. XRD patterns of the purified samples (a) spodumene and (b) feldspar (S = spodumene and F = feldspar).

(e.g. Be). XRD and MLA analyses indicated lithium existed in the form of spodumene, and primary gauge minerals were feldspar (44.5%), quartz and mica in the ore (Table 3).

2.2. Reagents

In the microflotation tests, the anionic collector NaOL and cationic collector DTAC of analytical grade were obtained from Sinopharm Chemical Reagent Co., Ltd. The mixed NaOL/DTAC collectors were freshly prepared when used to avoid precipitation. Calcium chloride ($CaCl_2$) and sodium carbonate (Na_2CO_3) were used as regulators. HCl and NaOH were used to adjust the pH of the system. The deionized water (Resistivity = 18.3 MΩ cm) was used for the microflotation tests.

In the batch flotation tests, the home-made mixed collectors NaOL/DTAC were used as collector. As a contrastive study, mixed fatty acid soaps (oxidized paraffin wax soap and naphthenic soap) are employed as collector. Sodium carbonate, sodium hydroxide and calcium chloride were used as regulators. All reagents used in batch flotation were of industrial grade. Tap water was used for batch flotation tests.

2.3. Micro-flotation tests

The micro-flotation tests were carried out in flotation machine of XFG-1600 with a 40 ml hitch groove flotation cell. The impeller speed was fixed at 1700 rpm. The mineral suspension was prepared by adding 3.0 g of single mineral to 40 ml of solutions in single mineral flotation tests, and adding 1.0 g of spodumene and 2.0 g feldspar to 40 ml of solutions in artificially mixed minerals flotation. HCl or NaOH was added to adjust the pH. After adding the desired amount of reagents, the suspension was stirred for 5 min. The flotation was conducted for 5 min. The froth products and tails were weighed separately after filtration and drying, and the recovery was calculated based on the dry weight of the product. In artificially mixed minerals flotation, the flotation grades of the two products were assessed by chemical analysis. The results of each flotation test were measured tree times in the same experimental conditions. And the average was reported as the final value. The standard deviation, which is presented as an error bar, was obtained by using Origin 9.2 to calculate based on the three measurements.