Separation and Purification Technology 169 (2016) 33–42

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Surface crystal chemistry of spodumene with different size fractions and implications for flotation

Longhua Xu [a,b,*], Yuehua Hu [b,*], Houqin Wu [a], Jia Tian [a], Jing Liu [a], Zhiyong Gao [b], Li Wang [b]

[a] Key Laboratory of Solid Waste Treatment and Resource Recycle Ministry of Education, Southwest University of Science and Technology, Mianyang, Sichuan, PR China
[b] School of Resources Processing and Bioengineering, Central South University, Changsha, Hunan, PR China

ARTICLE INFO

Article history:
Received 14 April 2016
Accepted 2 June 2016
Available online 3 June 2016

Keywords:
Spodumene
Particle size
Anisotropic adsorption
Flotation
Molecular dynamics

ABSTRACT

The flotation and adsorption of sodium oleate (NaOL) on spodumene with four different particle size fractions (45–75 μm, 38–45 μm, 19–38 μm and 0–19 μm) were investigated. The flotation recovery increases upon slightly decreasing the size fraction, reaching a peak value at a size fraction of 38–45 μm. The recovery then decreases gradually upon further decreasing the particle size over the entire investigated range of solution pH values. The specific chemisorption sites for the anionic NaOL collector are the Al sites on the surface of negatively charged spodumene, which is confirmed by FTIR and zeta potential measurements. Anisotropic surface energies and broken bond densities are calculated based on density function theory (DFT) to characterize the surface chemistry of spodumene crystal planes. The anisotropic adsorption behavior of NaOL on different crystal planes of spodumene is studied in terms of adsorption conformations and interaction energies by molecular dynamics (MD) simulations. It is demonstrated that NaOL prefers to bind in a monodentate chelating complex configuration to the most stable surface plane, the (1 1 0) plane, which has two broken Al—O bonds. The (1 1 0) plane of spodumene is more favorable for chemisorbing NaOL than the (0 0 1) plane, which has one broken Al—O bond. The flotation behavior of spodumene with different particle sizes is well explained by the surface crystal chemistry. Based on the findings of this work, further improvement in spodumene flotation is possible if a selective comminution or grinding process is used that favors the production of (1 1 0) planes.

1. Introduction

Lithium (Li) is known to have excellent properties for energy storage applications and has become a precious commodity. The availability of known and anticipated lithium resources has gained considerable attention due to the increased demand for Li in batteries, especially for electric vehicles [1]. Pegmatites currently account for 38% of known global Li resources. Li-containing pegmatites are predicted to dominate future markets in China [2]. Spodumene ($LiAl(SiO_3)_2$), containing 8.03% Li_2O, is the principal economic mineral of lithium-rich pegmatite ores. The largest solid lithium deposit in Asia is located in the western Sichuan Province of China. Two pegmatite deposits in the area, *Jiajika* and *Barkam*, have reported lithium reserves of 0.48 Mt and 0.22 Mt, respectively [3,4].

Flotation is the most widely used industrial method for the beneficiation of spodumene from associated silicate gangue minerals, employing fatty acid collectors such as oleate, naphthenic soap, oxidized paraffin soap, or a combination of two such reagents [5]. The flotation separation of spodumene from other complex aluminosilicate minerals, such as feldspar and mica, is problematic due to the minerals' common active Al site that interacts with anionic collectors [6]. The challenge of the flotation system is that the separation process relies on seemingly imperceptible differences in the mineral crystal surface chemistries of the exposed and cleaved surfaces of various aluminosilicate minerals [7]. Several researchers have investigated the flotation and adsorption of NaOL on aluminosilicate minerals and found that the chemisorption of NaOL on the Al sites of the mineral surfaces is responsible for their flotation behavior [8–10]. Therefore, the availability of surface Al sites for the interaction of NaOL is essential for the selective flotation separation of aluminosilicate minerals. The surface chemical properties of aluminosilicate minerals such as surface charge, surface hydrophobicity and surface free energy are governed by the cleavage edges and basal planes [11–14]. It is also known that the surface properties of aluminosilicate mineral edges

* Corresponding authors at: Key Laboratory of Solid Waste Treatment and Resource Recycle Ministry of Education, Southwest University of Science and Technology, Mianyang, Sichuan, PR China (L. Xu).
E-mail addresses: neuxulonghua@163.com (L. Xu), huyuehuacsu@126.com (Y. Hu).

http://dx.doi.org/10.1016/j.seppur.2016.06.005
1383-5866/

and basal planes differ greatly [15]. Rai et al. have recently performed detailed molecular dynamics simulations to study the interaction of NaOL with different crystal planes of jadeite and spodumene [9]. The difference in flotation behaviors of wet and dry ground spodumene was attributed to their crystal structures by Zhu et al. [16]. These investigations have provided us with a great deal of useful information. We demonstrate in this work how these important observations about the anisotropic adsorption properties of aluminosilicate minerals influence the flotation of spodumene with different size fractions.

The reduction of particle size by mechanical crushing and grinding is closely related to the mineral flotation process. It is well known that as the mineral particle size is gradually reduced during processing, the mineral's shape and surface properties become more important [17–20]. Meanwhile, it is worth noting that as the mineral particle size is varied, different crystal planes determine the surface properties. Consequently, the anisotropic surface properties of a mineral are dependent on the mineral particles' size factors [21]. In practical flotation applications, the comminution or grinding mechanisms are related to the final shape and surface properties of the product particles. Therefore, selective comminution or grinding should be employed during mineral processing whenever possible to expose more planes that favor the collector [22].

Because the particle size factor can affect the surface crystal chemistry properties of spodumene, flotation tests of NaOL on spodumene with four different particle size fractions were carried out. Various surface chemistry characterization techniques, including zeta potential measurements, infrared spectroscopy of the NaOL-spodumene system and adsorption measurements of NaOL on spodumene, were conducted. In addition, the anisotropic surface energies and broken bond densities were calculated based on density function theory (DFT) to characterize the surface crystal chemistry for spodumene planes. The anisotropic adsorption behavior of NaOL on different crystal planes of spodumene is studied in terms of adsorption conformation and interaction energy by molecular dynamics (MD) simulations. Furthermore, the aim of this work is elucidate how the anisotropic surface chemistry properties of spodumene and its anisotropic adsorption of NaOL influence the flotation of spodumene with different particle sizes.

2. Materials and methods

2.1. Materials

A pure mineral sample of spodumene was obtained from the *Jiajika* Lithium Mine in the Ganzi District of Sichuan Province, China. The sample was handpicked, crushed and ground in a laboratory porcelain mill. Then, the powder samples were screened to four different size fractions (45–75 μm, 38–45 μm, 19–38 μm and 0–19 μm). Chemical composition analysis (Table 1) and X-ray diffraction (XRD) (Fig. 1) were used to study the chemical and mineral compositions. The results showed that the as-prepared spodumene contained 7.86% Li_2O and the purity of the spodumene was greater than 90%.

The particle size distribution of sieved fractions of spodumene was determined using a laser diffraction particle size analyzer (Beckman Coulter, LS13320). The specific surface area (SSA) of spodumene powders was determined by N_2 adsorption analysis using a Micromeritics ASAP 2010C instrument. The size distribution of the different fractions and their specific surface areas are presented in Table 2, and the latter decreases with increasing particle size.

Table 1
Chemical composition of the purified sample (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

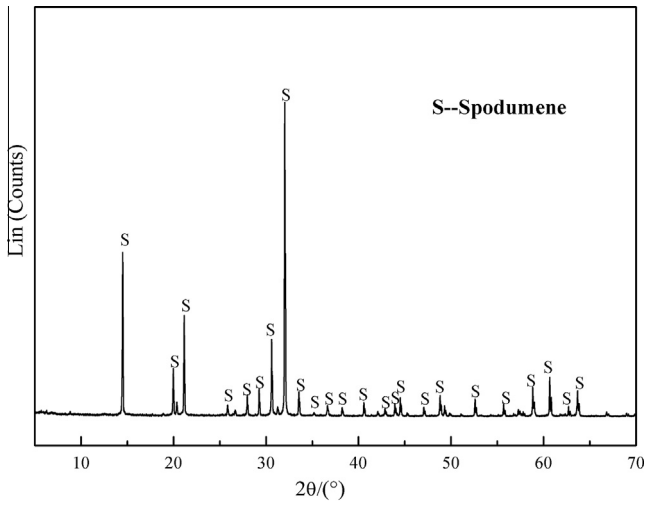

Fig. 1. XRD pattern of the purified spodumene sample.

The anionic collector NaOL of analytical grade was obtained from Sinopharm Chemical Reagent Co., Ltd. Ferric trichloride ($FeCl_3{\cdot}6H_2O$) was used as an activator. HCl and NaOH were used to adjust the pH of the system. Deionized water (resistivity = 18.3 MΩ cm) was used for all experiments.

2.2. Micro-flotation tests

Flotation tests were carried out in a 40-mL hitch groove flotation cell. Prepared mineral particles (3 g) were placed in a plexiglass cell, and then the cell was filled with deionized water. HCl or NaOH was added to adjust the pH. After adding the desired amount of reagents, the suspension was agitated for 3 min. The flotation test duration was 4 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 products. The result of each flotation test was measured three times under the same experimental conditions, and the average value is reported. The standard deviation, which is presented as an error bar, was calculated based on the three measurements using Origin 9.0.

2.3. Zeta potential measurements

A suspension containing 0.1 wt% mineral particles (ground to 5 μm in an agate mortar) was prepared in 1 mM NaCl solution and conditioned by magnetic stirring for 5 min. After allowing the solution to settle for 10 min, the supernatant of the dilute fine particle suspension was removed for zeta potential characterization. The zeta potentials were measured using a Malvern Zetasizer

Table 2
Particle size analysis and specific surface area analysis of different size fractions.

	Spodumene sample			
	45–75 μm	38–45 μm	19–38 μm	0–19 μm
D10 (μm)	48.729	40.562	22.369	2.215
D50 (μm)	70.623	43.237	35.473	10.872
D90 (μm)	105.768	73.456	50.675	36.968
Vol. weighted mean D[4,3] (μm)	65.543	41.369	29.461	15.74
SSA (m^2/g)	0.448	0.856	1.267	1.845