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Mechanical enrichment of converted spodumene by selective sieving

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ABSTRACT

Spodumene ore can be concentrated in large particle size of 1–6 mm by a dense media separation (DMS) process. The concentrate typically contains relatively large amounts of impurities due to the incomplete liberation of spodumene and the quite narrow density difference between spodumene and gangue minerals. The extraction of lithium from spodumene requires the phase transformation of spodumene from α- to β-form which takes place at 1100 °C. After heat treatment the Li_2O content of spodumene concentrate can be improved by particle size separation. In this work the technical and economical possibilities of producing first low grade concentrates by DMS method and increasing the grade afterwards by particle size separation were studied. Various DMS spodumene concentrates were mechanically enriched after heat treatment by selective sieving. Autogenous and ball mill grinding were used to increase the separation efficiency between the spodumene and the gangue minerals. The Li_2O contents of the concentrates were increased from 5.1%, 3.6%, 3.1% and 1.4% to 6.8%, 5.8%, 5.9% and 5.0%, respectively. The energy economy of the sieving method was evaluated from the perspective of increased energy consumption in the heat treatment process.

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Abbreviations: DMS, dense media separation; AG, autogenous grinding; BM, ball mill grinding; t_{sp}, spodumene ton.

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1. Introduction

Lithium is a relatively rare element which has some distinctive features, such as having a very small ionic radius and the highest electrochemical potential of all metals. Because of its special features it has been used for wide variety of applications. Nowadays lithium is mainly used for various lithium chemicals in the lithium battery industry and as a lithium carbonate and as a low iron mineral concentrate additions in the glass and ceramics industry (USGS, 2016; Garrett, 2004). Lithium occurs in some rocks and brines in very low concentrations. The most important economically exploitable lithium mineral is spodumene ($LiAlSi_2O_6$) which contains 8.03% Li_2O stoichiometrically. Spodumene occurs in pegmatites associated with quartz (SiO_2), albite ($NaAlSi_3O_8$), microcline ($KAlSi_3O_8$) and muscovite ($KAl_2(Si_3Al)O_{10}(OH,F)_2$). Typical pegmatitic spodumene ore contains 1–2% Li_2O. Commercial spodumene concentrates are usually classified according to their lithium content as a high-grade concentrate with at least 7.25% Li_2O and as a glass grade concentrate at 5.00% Li_2O. Most commonly, spodumene concentrates are processed into the form of lithium carbonate. The suitable spodumene concentrate for lithium carbonate production contains approximately 6–7% Li_2O which corresponds at least 75% spodumene.

Spodumene ore can be concentrated after mining and crushing by flotation or dense media separation (DMS) (Amarante et al., 1999). Flotation requires fine grinding to a particle size of <100–400 μm (Amarante et al., 1999; Menéndez et al., 2004; Xu et al., 2016), which increases the energy consumption of the process, and part of the material is lost during the desliming process which is required prior the flotation. The fine grained concentrate may also cause difficulties in the form of dusting during the following heat treatment process. Dense media separation can be carried out with larger particle size (1–6 mm) but the selectivity of the method is not as good due to the lower liberation rate of spodumene particles. In addition to a low liberation rate, the density difference is quite narrow between spodumene (~3.15 g/cm^3) and gangue minerals (~2.5–2.9 g/cm^3), which may impair the separation result. The larger particle size, however, reduces the energy consumption of the grinding process and decreases the loss of lithium into the slimes. High grade spodumene concentrates (~95% spodumene) have been achieved by a flotation process after several cleaning stages (Amarante et al., 1999; Menéndez et al., 2004). Slightly lower grade concentrates with spodumene contents of 86–89% have been obtained in fine particle size of 74–500 μm using the heavy liquid separation method (Tippin et al., 1970). However, a DMS process with larger particle size (2.0–6.7 mm) has resulted in considerably lower grade spodumene concentrates (~5% Li_2O) (Amarante et al., 1999).

The extraction of lithium from spodumene concentrates requires heat treatment at 1000–1100 °C to achieve the complete phase transformation from monoclinic α-spodumene into tetragonal β-spodumene. Due to this irreversible change of crystal structure the density of the spodumene decreases. The spodumene becomes very brittle and the particle size becomes smaller. During the heat treatment process, the gangue minerals which are present in the concentrate also undergo structural changes. The reversible phase transformation of quartz from α- to β-quartz occurs at 573 °C. The reversible phase transformations of both feldspars from triclinic into monoclinic form take place at elevated temperatures (Brown and Parsons, 1989; Cherry and Trembath, 1979). The complete dehydroxylation of muscovite occurs by 950 °C and the structure decomposes by 1100 °C resulting in the formation of a glass phase, in addition to which some spinel phase and γ-Al_2O_3 can form (Barlow and Manning, 1999; Mackenzie et al., 1987). Unlike in spodumene these structural changes do not result in significant embrittlement of the gangue minerals. The melting points of the minerals present in spodumene concentrate are above the heat treatment temperature of 1100 °C, but the melting of the mixture consisting of spodumene, quartz, albite, microcline and muscovite can begin from phase interfaces at lower temperatures during the heat treatment. According to phase equilibrium diagram examinations, the lowest melting temperature for the mixture spodumene, albite and quartz is as low as 975 °C (ACerS-NIST, Fig. 10174) and for the mixture of abite, microcline and quartz 990 °C (ACerS-NIST, Fig. 00786). This partial melting of phase interfaces could make the particles even more tenacious during the heat treatment.

Due to the friability of β-spodumene compared to the relatively hard gangue minerals, spodumene ore can be enriched after the heat treatment by particle size separation (Fraas and Ralston, 1937; Hevia et al., 2006). The drawback of the method is the fairly high energy consumption required for the conversion process as the whole ore mass is heat treated at 1100 °C. However, particle size separation could be applicable for additional enrichment alongside the DMS method, in which case the mass of the heat treated material would be lower. In this work the spodumene content of various DMS concentrates, as well as crushed ore, were improved after heat treatment by the selective sieving. Autogenous and ball mill grinding were used as pretreatments to enhance the separation efficiency between the spodumene and gangue minerals. The economics of the method were evaluated with regard to increased energy consumption in the heat treatment process.

2. Experimental

2.1. Materials

The spodumene ore used in the experiments was from the Kokkola-Kaustinen region in Central Ostrobothnia (Finland). The average lithium content of Kaustinen spodumene pegmatites is 1.2% and the spodumene from the deposit contained approximately 7% of Li_2O (Al-Ani and Ahtola, 2008). The ore was crushed and then concentrated in a pilot-scale DMS process (aqueous suspension of ferro-silicon, ρ = 2.4 g/cm^3). Three different DMS concentrates and one crushed ore were used in the experiments. The lithium content and particle size varied between the sample materials. The particle size distributions and average lithium contents of the pilot-scale DMS concentrates and crushed ore are presented in Table 1.

The mineral contents of the materials were determined by X-ray diffraction (XRD) and the obtained diffraction patterns are presented in Fig 1. In addition to spodumene, all samples contained quartz, albite, microcline and muscovite as gangue minerals. All three DMS concentrates, excluding the crushed ore, also contained some pure waste rock particles, hence minor peaks of waste rock originated schorl ($NaFe_3^{2+}Al_6(BO_3)_3Si_6O_{18}(OH)_4$), epidote ($Ca_2Fe_{2.25}^{3+}Al_{0.75}(SiO_4)_3(OH)$) and hematite ($Fe_2O_3$) were identified from the concentrate samples.

Table 1
Materials used in experiments.

Material	Li_2O	Particle size distribution [mm]			
		<1.0	1.0–2.8	2.8–6.0	>6.0
C48	4.8%	4%	51%	45%	
C35	3.5%		16%	73%	11%
C30	3.0%	4%	96%		
O12	1.2%[a]		35%	65%	

[a] Average Li_2O content of Kaustinen spodumene (Al-Ani and Ahtola, 2008).