Research article

Influence of calcination temperatures on lithium deportment by screening hard rock lithium

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ABSTRACT

Calcination of spodumene is a pre-treatment stage in preparation for sulfation roasting and leaching in lithium recovery. During calcination, α-spodumene (less reactive, monoclinic crystal structure) is converted to β-spodumene (more reactive, tetragonal crystal structure). A third, metastable γ-phase has been identified at lower temperatures than full conversion to the β-phase. It has been previously observed that calcination greatly alters the physical properties of the various minerals in pegmatite ores, impacting comminution energy and liberation. Thus, this work investigates the relationships between calcination temperatures and the physical behaviour of hard rock lithium ores. The results showed that the increase in calcination temperature resulted in a higher lithium deportment in the finest size fraction (−0.6 mm) and thus a higher lithium grade and recovery. The samples calcined at 813.15 K and 1223.15 K did not show a significant increase in lithium grades in the finest size fraction. This work shows the incremental change in the physical properties of various minerals in the ore with increasing calcination temperature.

1. Introduction

Spodumene ($LiAlSi_2O_6$) is a lithium aluminosilicate that acquired its name from the Greek word "spodumene" (burnt to ashes) due to its post-grinding ash-like grey colour. Spodumene is the most important lithium mineral to produce lithium compounds from hard rock lithium ores because of its significant Li_2O content [1–3]. This mineral is found in association with other minerals like quartz, albite, and beryl traces [4].

There are three known phases of spodumene: α, β, γ. Naturally occurring α-spodumene has the highest density (3.27 g/cm^3) due to its monoclinic crystal structure [5]. β-Spodumene has an open tetragonal structure [6,7] while γ-Spodumene [8,9] has a hexagonal structure; however, both β-Spodumene and γ-Spodumene have the same density (2.45 g/cm^3). It should be noted that γ-spodumene is recently discovered as a meta-stable phase [8,10–12].

α-Spodumene is weakly reactive in the presence of strong acids and thus a common practice is to convert α to β-spodumene through a thermal treatment [13]. The extraction process of lithium from spodumene was patented in 1950 [14] using the heat treatment to transform α-spodumene to β-spodumene which is a less dense tetragonal allotrope of spodumene. The phenomenon of thermally activated phase transition is known as calcination or decrepitation [14]. During calcination, crushed spodumene concentrate is heated

in a furnace at temperatures above 1223.15 K for more than 30 min. This thermal treatment allows α-spodumene to convert completely to β-spodumene, leading to a crystal lattice expansion of β-spodumene. The lattice volume of γ-spodumene is 8% more than that of α-spodumene while that of β-spodumene is 17% more than γ-spodumene [5]. It means that the lattice volume of β-spodumene is the highest while the lattice volume of α-spodumene is the lowest. For energetics, α-spodumene to β -spodumene and γ -spodumene to β-spodumene transition are reported to be endothermic [10,11,15,16] while the transition from α-spodumene to γ-spodumene is exothermic [17].

Numerous authors have investigated the phase transformations that takes place during calcination of spodumene [5,10–12,18,19]. A study by Salakjani et al. [11] showed that the dislocation of Al^{+3} during calcination is responsible for the volumetric expansion of spodumene crystal structure making lithia species mobile and reactive with strong acids [19]. Comminution was observed to be improved as a result of this phase transformation attributed to a flaky and softer structure of β-spodumene [8,12]. With the recent discovery of a third meta-stable γ-phase, the sequence of the phase transformation during calcination is now described as α→γ→β [5,8, 10]. The interlocking gangue associated with spodumene can play a detrimental role in downstream beneficiation process, but some studies have shown that the presence of these impurities can expedite the heat conduction and thus effective phase transition of spodumene [18,20].

Moore et al. [21] observed that the mass fraction of transformed phases during calcination was unaffected by the heating temperature and the heating method, however, Salakjani et al. [11] showed that the temperature and residence time are the major factors to define the phase transformation during calcination of spodumene. Various studies [5,10,12,21] have shown that a number of factors can influence the phase transformation during the calcination of spodumene at elevated temperature, that include the heating technique, the morphology of the spodumene sample after initial comminution, and the quantity of gangue materials present in the sample.

Most research work and studies have focused on two stable phases of spodumene that are α and β. These two phases got more attention due to their known reactions with strong inorganic acids. Our previous work showed that calcination altered the physical properties of spodumene, reducing comminution energy requirements and thus improving lithium grade and recovery [22]. However, it has not been quantified the effect of different calcination temperatures on the deportment of lithium to the finest size fraction by screening. Therefore, this study aims to examine the effect of calcination temperatures on lithium grade and recovery by screening hard rock lithium ores.

2. Materials and methods

2.1. Ore

A spodumene ore (Bald Hill Mine Eastern Goldfields, Western Australia) was used in this work. The ore had quartz and albite as main gangue minerals with spodumene as a valuable mineral as found using XRD (X-ray diffraction). The ore grade was 0.3% lithium (i.e., 8.5% of spodumene), and the particle size was −15 mm.

2.2. Calcination

The ore (see Fig. 1) was split into four samples, and the mass of each sample was 1500 g. All these samples were calcined at 813.15, 1223.15, or 1373.15 K in a muffle furnace (Cupellation furnace, Carbolite Sheffield England) for 1 h, which was sufficient for complete phase transformation at the given temperature; the air atmosphere was used for calcination. After calcination, the mass of the sample was reduced by 0.6% (at 813.15 K), 1% (at 1223.15 K), and 1.4% (1373.15 K). It should be noted that one sample was not calcined. Fig. 2a, b, 2c and 2d show the photos of both non-calcined and calcined samples. The increase in temperature affected the physical appearance of the samples. For example, the fracturing of the sample calcined at 1373.15 K was evident due to the conversion of α to β-spodumene, which agrees well with the literature [18,23].

After calcination at 1373.15 K, the variations in ore properties were characterized by MLA (mineral liberation analysis) and
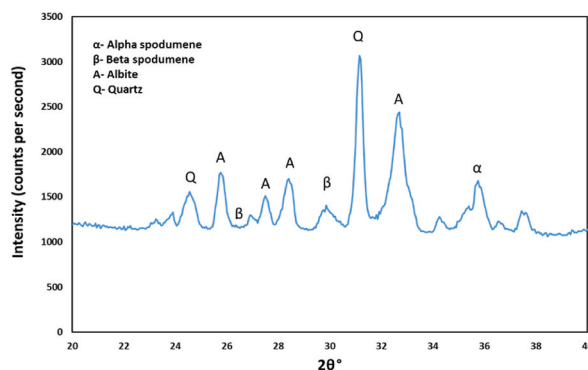

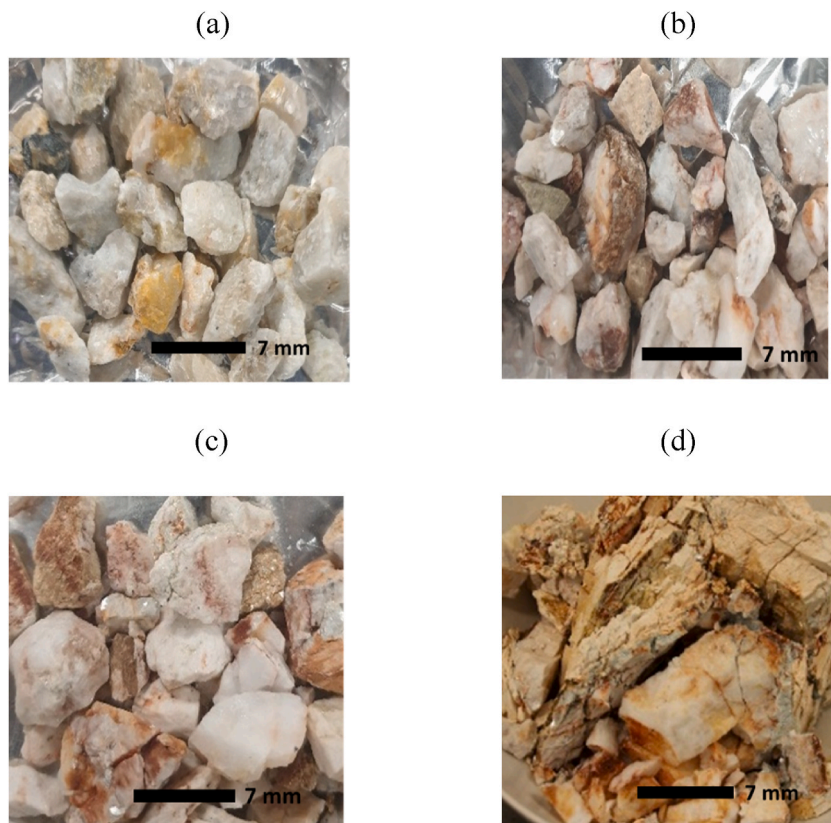**Fig. 1.** XRD for the non-calcined spodumene ore.

(a)

(b)

(c)

(d)

Fig. 2. The images of a) non-calcined ore, b) calcined ore at 813.15 K, c) calcined ore at 1223.15 K and d) calcined ore at 1373.15 K.
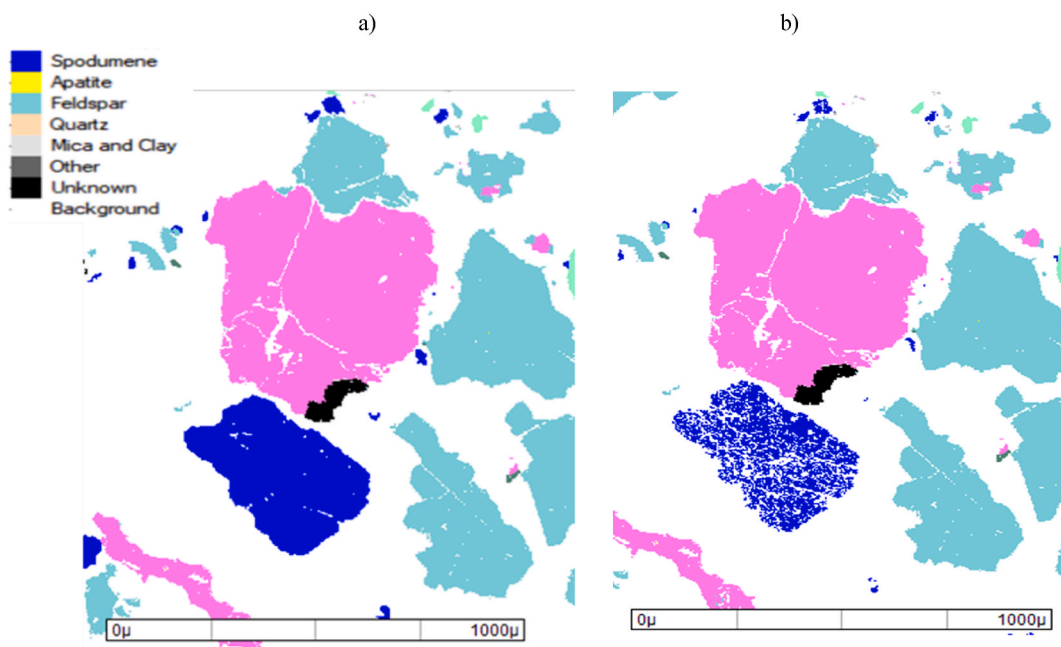
a)

b)

Fig. 3. Estimation of particle properties a) before calcination and b) after calcination [24].

represented in Fig. 3a and b. The MLA contains a FEI Quanta 600F field emission SEM (US, Oregon), two Bruker Quantax X-Flash 5010 EDX detectors (US, Massachusetts), and FEI's MLA software 3.1.3 for data acquisition and processing. Fig. 3 shows that spodumene was more fractured after calcination due to the complete conversion of α to β spodumene [10,23].

2.3. Grinding

Both non-calcined and calcined samples (1500 g of the ores) were ground in a laboratory mill. The mill had 12 forged balls that had 27.3 mm in diameter, and a sample mass of 1060 g (the ratio of the forged balls to the ore was 0.7). The mill speed was 70 rpm. Each sample was ground for 20 min and subsequently screened in the following fractions: +3.35 mm, −3.35 + 2.36 mm, −2.36 + 1.7 mm, −1.7 + 1.18 mm, −1.18 + 0.6 mm, −0.6 mm. The lithium content of each size fraction was determined by preparing a fusion glass bead, digesting in 10% citric acid, and using ICP-OES (Agilent Technologies, US).

2.4. X- ray diffraction (XRD)

Mineralogical analyses of the lithium ore samples were performed using an Olympus BTX™ III Benchtop (Co-Kα) X-ray diffrac-tometer (XRD) to study the phase transformation of spodumene in the range between 20 and 40° (2θ) as a function of different calcination temperatures; this instrument is a transmission XRD and it does not have steps. The AMCSD database cards for the phases are: α-spodumene – Set 1 (file 408), β-spodumene Set 2 (file 2119), quartz – Set 2 (file 1936), albite – Set 1 (file 2289).

The XRD experiments were conducted on fine fractions (−0.6 mm) and coarse fractions (+0.6 mm) of all four products obtained after calcination and grinding. It should be noted that the maximum lithium content was found in the finer size fraction after calci-nation. The finest fraction is generally the most relevant for coarse gangue rejection since lithium tends to deport to the finest fractions.

3. Results and discussions

3.1. Effect of calcination temperature on ore retention

Fig. 4 shows the influence of different calcination temperatures on particle size distribution. The vast majority of the non-calcined material was oversized, reporting to the +3.35 mm fraction. However, the minimum ore retention was obtained for the grinding product calcined at the highest temperature (i.e., 1373.15 K); the ore retention represents the amount of the ore retained on each screen after sieving. Fig. 4 also shows that calcination shifted the particle size distributions toward the finer fraction and to a greater extent with higher temperatures.

The reason is that the increase in calcination temperature made spodumene and albite more brittle, resulting in more efficient grinding and thus more deportment of the grinding products to the finest screen size.

3.2. Effect of calcination temperature on lithium grade and lithium recovery

Fig. 5 shows the influence of calcination temperature on cumulative lithium grade; the cumulative lithium grade represents the accumulation of lithium in the finest size fraction (−0.6 mm). As seen in Fig. 5, for the non-calcined sample (i.e., 298.15 K), the higher the lithium grade, the largest the screen size. It means that the lithium deportment to the finest screen did not happen after the grinding
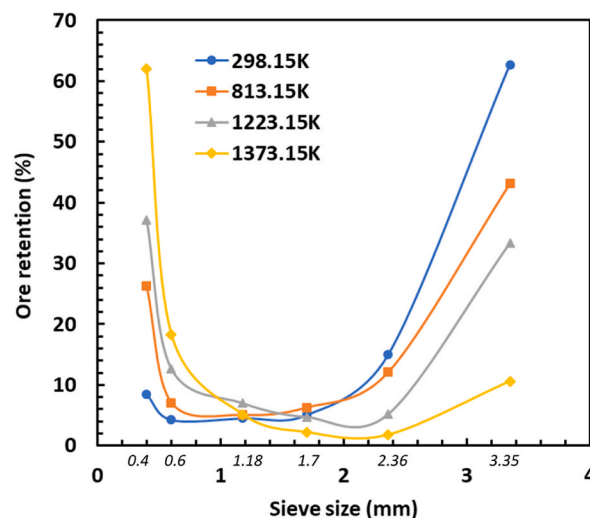

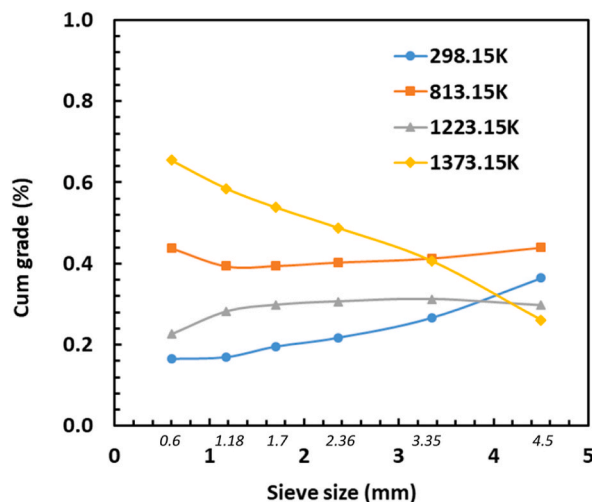**Fig. 4.** The influence of calcination temperature on ore retention.

Fig. 5. Effect of calcination temperature on cumulative lithium grade.

of the non-calcined sample. However, in the case of the sample calcined at 1373.15 K, the opposite trend was observed, indicating an improvement in coarse gangue rejection. In other words, the maximum lithium grade was obtained in the smallest screen size (0.6 mm) while the minimum lithium grade was achieved in the coarsest screen size (3.35 mm). The reason is that when the sample was calcined to 1373.15 K, α-spodumene was completely transformed to β-spodumene, making the sample very brittle and thus leading to coarse gangue rejections after grinding and screening operation.

However, when the sample is calcined to 813.15 or 1223.15 K, the lithium content was similar across the screen sizes, demonstrating some shift from the non-calcined sample behaviour was achieved but not to the extent of the sample treated at 1373.15 K. This observation could be due to the incomplete transformation from α to β-spodumene and dilution in the fines due to greater grinding of other phases. It is worth mentioning that the lithium grade in the case of the sample calcined to 1223.15 K was lower than that in the case of the sample calcined to 813.15 K. The reason is that at 1223.15 K albite deported to the fine fraction, leading to a lower lithium grade of the sample in all the screen sizes (see Fig. 6).

Fig. 6 shows the mineralogy of the fine size (−0.6 mm) and coarse size (+0.6 mm) fractions which are required to understand the lithium deportment as a function of temperature. As seen in Fig. 6a, the maximum amount of β-spodumene was found when the calcination temperature was 1373.15 K. The amount of β-spodumene in the non-calcined sample was almost the same as that in the samples calcined at 813.15 K and 1223.15 K because α-spodumene did not transform to β-spodumene at these temperatures. Fig. 6a also shows that the higher the calcination temperature, the higher the amount of albite in the fine size fraction. As a result, the lithium grade in the fine size fraction for the sample calcined at 813.15 K was higher than that for the sample calcined at 1223.15 K. However, due to a complete phase transformation from α to β-spodumene at 1373.15 K, most of β-spodumene deported to the fine size fraction, leading to the highest lithium grade in the fine size fraction.

Fig. 6b shows that the amount of β-spodumene in the coarse size fractions followed the same pattern as that in the case of fine size fractions. However, the amount of albite for the coarse size fraction was the highest at 1223.15 K. Therefore, due to a significant amount of albite present in the finest size fraction at 1223.15 K, the lithium grade for the sample calcined at this temperature was lower than that at 813.15 K.

Fig. 7 shows the influence of calcination temperature on cumulative lithium recovery with size fraction; the cumulative lithium recovery is the sum of the recovered lithium (i.e., the sum of the mass of lithium on each screen divided by the mass of lithium in feed) for each size fraction. As seen in Fig. 7, in the finest size fraction (−0.6 mm), the increase in calcination temperature led to a higher lithium recovery due to the department of lithium to the finest size fraction. A similar trend was also observed for particle sizes higher than 0.6 mm. However, when the screen size was higher than 0.6 mm, the recovery for the sample calcined at 1223.15 K was slightly higher than the sample calcined at 1373.15 K. The reason is that the transformation from α to β spodumene at 1223.15 K was not complete.

This work shows the correlations between calcination temperature, coarse gangue rejections and physical properties of the spodumene ore. A similar correlation may exist for other minerals in which there are phase transformations during the calcination process, leading to the change in the physical properties of these minerals.

4. Conclusions

This work investigates the influence of calcination temperature on lithium grade and recovery by screening a spodumene ore. It was found that the lithium grade in the finest size fraction (−0.6 mm) was the lowest when the sample was not calcined. A strong lithium department to fines was observed at 1373.15 K but not after calcination conducted at temperatures lower than 1223.15 K. The reason is due to incomplete transformation from α to β spodumene at temperatures below 1223.15 K, leading to a higher amount of non-brittle
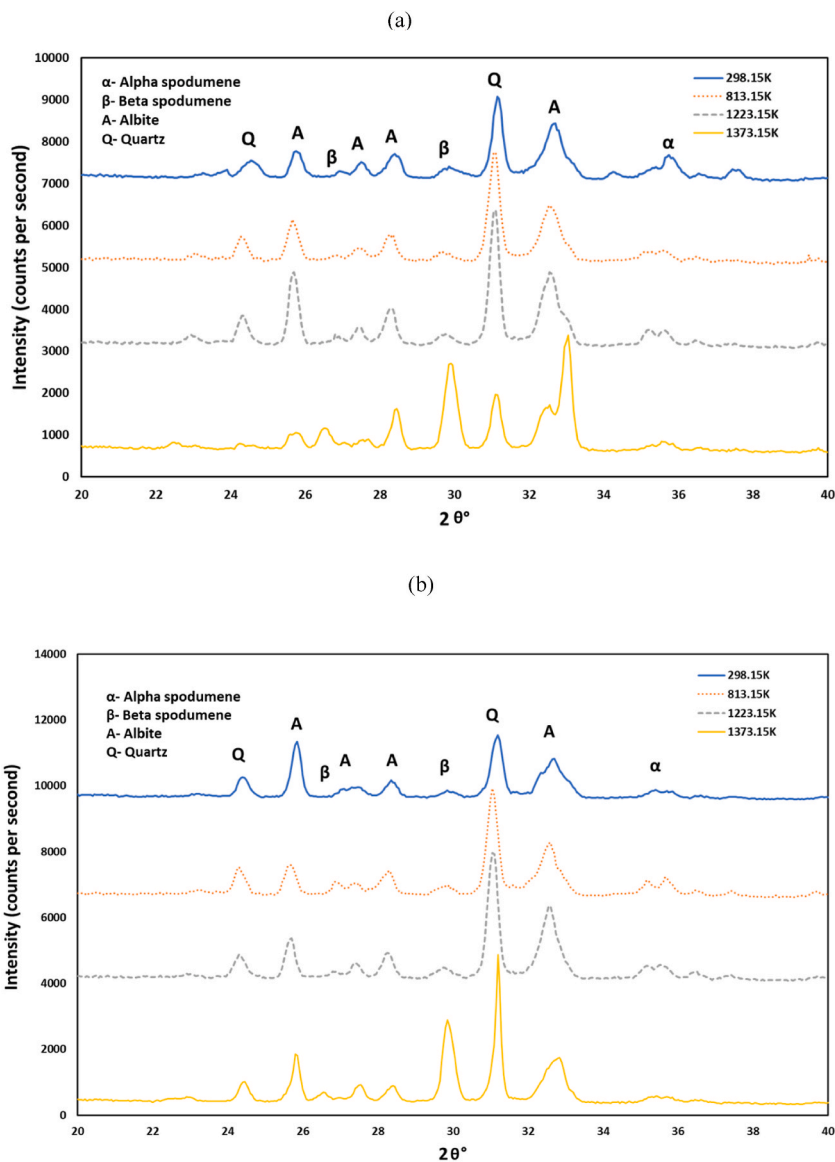
(a)

(b)

Fig. 6. Mineralogy of a) the fine size fraction (−0.6 mm) and b) the coarse size fraction (+0.6 mm).

spodumene phase (i.e. α-spodumene). The lithium grade in the finest size fraction when the sample was calcined at 813.15 K was slightly higher than that when the sample was calcined at 1223.15 K. The reason is that at 1223.15 K albite deported to the finest size fraction, reducing the lithium grade. The highest lithium grade in the finest size fraction was obtained when the sample was calcined at 1373.15 K due to the complete transformation from α to β spodumene. The highest lithium recovery was also achieved at the same temperature in the case of the finest size fraction. Further work is required to investigate calcination as a potential treatment for increasing grade and recovery by screening hard rock ores in which phase transformations of some minerals occur as a function of calcination temperature.

Declarations

Author contribution statement

Muhammad Kashif Nazir: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.Laurence Dyer: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.Bogale Tadesse: Conceived and designed the experiments; Analyzed and interpreted the data.Boris Albijanic: Analyzed and interpreted the data; Wrote the paper.Nadia Kashif: Performed the experiments.
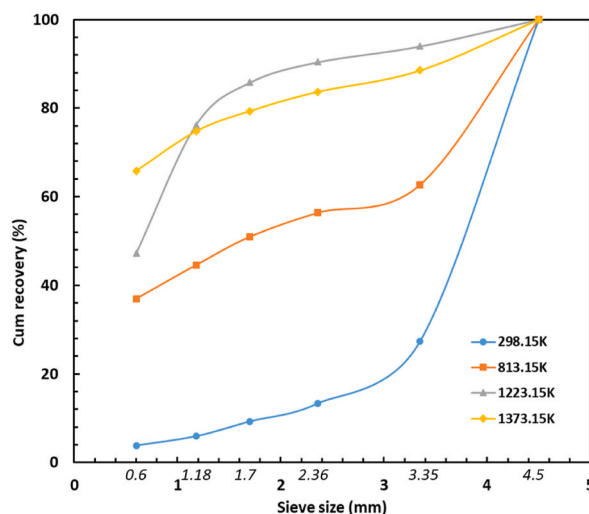
Fig. 7. Effect of calcination temperature on lithium recovery.

Data availability statement

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

References

[1] P.K. Choubey, K.-S. Chung, M. Kim, J. Lee, R.R. Srivastava, Advance review on the exploitation of the prominent energy-storage element lithium. Part II: from sea water and spent lithium ion batteries (LIBs), Miner. Eng. 110 (2017) 104–121, https://doi.org/10.1016/j.mineng.2017.04.008.

[2] D.E. Garrett, Handbook of Lithium and Natural Calcium Chloride", Elsevier, 2004 https://doi.org/10.1016/B978-0-12-276152-2.X5035-X.

[3] F. Habashi, Handbook of Extractive Metallurgy", vol. IV, Wiley, Weinheim, 1997.

[4] J.W. Anthony, R.A. Bideaux, K.W. Bladh, M.C. Nichols, Handbook of Mineralogy", Mineralogical Society of America, Chantilly, VA, USA, 2015. Available online: http://www.handbookofmineralogy.org/. (Accessed 12 March 2019). accessed on.

[5] C. Dessemond, G. Soucy, J.-P. Jean-Philippe Harvey, P. Ouzilleau, Phase Transitions in the α-γ-β Spodumene Thermodynamic System and Impact of γ-Spodumene on the Efficiency of Lithium Extraction by Acid Leaching", Minerals, 2020.

[6] C.T. Li, D.R. Peacor, The crystal structure of LiAlSi2O6-II (B-spodumene), Z. Kristallogr. 126 (1967) 46–65.

[7] P.P. Keat, A new crystalline silica Science" 120 (1954) 328–330.

[8] O. Peltosaari, P.A. Tanskanen, E.P. Heikkinen, T. Fabritius, α- β- γ-phase transformation of spodumene with hybrid microwave and conventional furnaces, Miner. Eng. 82 (2015) 54–60.

[9] C.T. Li, The crystal structure of LiAlSi2O6 III (high-quartz solid solution), Z. Kristallogr. 127 (1967) 327–334.

[10] N.K. Salakjani, P. Singh, A. Nikoloski, Mineralogical transformations of spodumene concentrate from Greenbushes, Western Australia. Part 1: conventional heating, Miner. Eng. 98 (2016) 71–79.

[11] N.K. Salakjani, A. Nikoloski, P. Singh, Mineralogical transformations of spodumene concentrate from Greenbushes, Western Australia. Part 2, Microwave heating. Miner. Eng. 100 (2017) 191. –199.

[12] A.A. Abdullah, H.C. Oskierski, M. Altarawneh, G. Senanayake, G. Lumpkin, B.Z. Dlugogorski, Phase transformation mechanism of spodumene during its calcination, Miner. Eng. 140 (2019), 105883, https://doi.org/10.1016/j.mineng.2019.105883.

[13] G.D. Rosalesa, A.C.J. Resenteraa, J.A. Gonzalezc, R.G. Wuilloudb, M.H. Rodriguez, Efficient extraction of lithium from -spodumeneby direct roasting with NaF and leaching, Chem. Eng. Res. Des. 150 (2019) 320–326.

[14] R.B. Ellestad, K.M. Leute, Method of extracting lithium values from spodumene ores, U.S. Patent Application 2 109 (1950) 516.

[15] I.L. Botto, S.C. Arazi, T.G. Krenkel, Aplicación de la teoría de Delmon al estudio des mecanismo de latransformación polimórfica espodumeno I en espodumeno II, Boletin Sociedad Española Cerámica Vidrio 15 (5–10) (1976).

[16] H. Gasalla, E. Pereira, Activation-deactivation mechanisms in spodumene samples, Solid State Ionics 42 (1–6) (1990).

[17] R.J. Brook, Concise Encyclopedia of Advanced Ceramic Materials", Pergamon Press, Oxford, England, 1991.

[18] N.K. Salakjani, P. Singh, A.N. Nikoloski, Production of lithium – a literature review Part 1: pretreatment of spodumene, Miner. Process. Extr. Metall. Rev. 41 (5) (2019) 335–348, https://doi.org/10.1080/08827508.2019.1643343.

[19] A. Changes, A.Y. Fosu, Retrieved from, 2020, https://encyclopedia.pub/3834.

[20] G.D. White, T.N. McVay, Some Aspects of the Recovery of Lithium from Spodumene", Oak Ridge National Laboratory, Oak Ridge, TN, USA, 1958.

[21] R.L. Moore, J.P. Mann, A. Montoya, B.S. Haynes, In situ synchrotron XRD analysis of the kinetics of spodumene phase transitions, Phys. Chem. Chem. Phys. 20 (2018) 10753–10761, https://doi.org/10.1039/C7CP07754H.

[22] M.K. Nazir, L. Dyer, B. Tadesse, B. Albijanic, N. Kashif, Effect of calcination on coarse gangue rejection of hard rock lithium ores, Sci. Rep. 12 (2022), 12963.

[23] O. Peltosaari, P. Tanskanen, S. Hautala, E.P. Heikkinen, T. Fabritius, Mechanical enrichment of converted spodumene by selective sieving, Miner. Eng. 98 (2016) 30–39.

[24] M.K. Nazir, L. Dyer, B. Tadesse, B. Albijanic, N. Kashif, Flotation performance of calcined spodumene, Adv. Powder Technol. 33 (11) (2022), 103772.