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Li Extraction from a-Spodumene Concentrate via Carbonizing Calcination †

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Abstract: The conventional lithium extraction method involves the calcination of a-spodumene at 1050 °C so that it can be converted to the more-reactive b-spodumene and then a sulfuric acid roasting step at 250 °C. Lithium is finally extracted via leaching with water. This method is energy-intensive, leading to high capital and operational costs. In this study, the direct calcination of a-spodumene with the use of sodium carbonate and calcium oxide was examined, aiming to significantly reduce the calcination temperature and completely omit the sulfuric acid roasting step, thereby radically redesigning the lithium extraction process. The calcination product was then leached with different leaching agents, such as water and sulfuric acid, and at different temperatures. The efficiency of the additives was evaluated through the results of lithium extraction achieved during the leaching step. Different leaching agents and temperatures were investigated. The maximum lithium extraction achieved was 96%, obtained after calcination using a sodium carbonate/spodumene mixture and leaching with sulfuric acid at 90 °C. High lithium extractions, up to 83%, can also be achieved under the same calcination conditions and after leaching with sulfuric acid at lower temperatures, such as 40 °C, and for shorter leaching times.

Keywords: spodumene; industrial minerals; critical raw materials; extractive metallurgy; decrepitation; roasting; leaching; lithium

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1. Introduction

Lithium is an excellent electrical conductor due to its atomic structure and is heavily used in batteries [1]. The value of the global market of Li-ion batteries is predicted to exceed USD 100 billion by 2025. Therefore, the need for lithium is ever increasing [2].

Today, lithium is found in two distinct deposit types: (a) brine deposits and (b) hard rock deposits [3]. The extraction of lithium from minerals is more efficient compared to extraction from brines or through the recycling of lithium batteries [4]. However, lithium processing may have higher environmental footprint compared to lithium extraction from brines, according to LCA studies [5]. Lithium is found in the minerals spodumene, lepidolite, and zinnwaldite, of which spodumene is the most abundant, and it also contains the largest amount of this element (consisting of about 8% Li_2O) [6,7].

Spodumene is naturally present in a stable α-monoclinic (highly packed crystal structure) form with high grindability; hence, this mineral is difficult to leach without pretreatment. It is made amenable to lixiviation via calcination at 1000 °C that causes it to assume the β-tetragonal form [8]. The current practice in industry is the extraction of lithium from b-spodumene through sulfating roasting. The ore is mixed with sulfuric acid in a rotary kiln at 250 °C for about 1 h, and thus water-soluble Li_2SO_4(s) is formed. Lajoie-Leroux et al. achieved 97% recovery of lithium from b-spodumene through the sulfate process [9].

New methods for bypassing the critical step of acid roasting have been studied. After calcination, b-spodumene can be roasted with Cl_2 (a chlorination process), $CaCO_3$ (an alkaline process), Na_2CO_3 (a carbonizing process), or HF (a fluorination process) to obtain a soluble lithium phase [10]. Barbosa et al. studied the chlorination of b-spodumene using pure chlorine gas as well as $CaCl_2$ [11,12]. They noticed that lithium is extracted from b-spodumene as lithium chloride gas and that the maximum conversion of lithium to LiCl reached 90.2%. In the alkaline process, the lithium-bearing ore is calcined with $CaCO_3$ at 825 °C–1050 °C, forming Li_2O(s), which is water-soluble. Because of the high amount of energy required, calcination with limestone is limited. Yan et al. applied a novel technique involving the liming process in lepidolite, achieving 98.9% lithium recovery [13]. The roasting of b-spodumene with Na_2CO_3 can be carried out through the reaction between the solid and Na_2CO_3 solution in an autoclave, forming Li_2CO_3. In the autoclave process, a lithium carbonate conversion efficiency of about 94% was achieved [14]. The fluorination process has been studied by Rosales et al., mixing b-spodumene with HF solution. The optimum experimental conditions led to about 90% lithium recovery. They also investigated the kinetics and proposed a mechanism for the dissolution of b-spodumene with HF [15,16].

The conversion of a- to b-spodumene is a high-energy process; thus, many researchers are focused on the more economical and environmentally friendly method of lithium extraction from a-spodumene. Furthermore, alternative methods for sulfate-roasting are being studied to avoid the special equipment needed and the emission of acid gasses [7].

Fosu et al. [17] studied the chlorination process on a-spodumene directly, using $CaCl_2$ and applying aqueous leaching to the product. The optimum conditions resulted in 90% recovery of lithium (85% in solution and the rest in gas phase). Song et al. [18] employed a method similar to Bayer alkaline treatment to extract lithium from a-spodumene, followed by the precipitation of Li with Na_3PO_4 solution in the form of Li_3PO_4. Experiments were carried out in an autoclave, leading to 93.3% extraction of Lithium. Xing et al. [19] mixed a-spodumene with NaOH solution in an autoclave so as to manage hydroxysodalite zeolite synthesis along with lithium extraction. The lithium extraction reached 95.8% (recovered through precipitation with Na_2CO_3).

In the present study, lithium was extracted directly from a-spodumene, avoiding the energy-consuming calcination step; additionally, sodium carbonate was used as an alternative to the current industrial process. The process took place in a muffle furnace heated to 850 °C, followed by leaching with sulfuric acid at temperatures ranging from 40 °C to 90 °C for 3 to 5 h, achieving lithium extraction ranging from 83% to 99.8%.

2. Materials and Methods

In this study, spodumene concentrate was supplied by European Lithium LTD. The samples were prepared using a Jones splitter. The concentrate was divided into samples weighing approximately 500 g, and all samples were passed through a 300 µm sieve. Analytical-grade Na_2CO_3 and CaO were supplied by Chem-Lab NV, Zedelgem, Belgium.

Experimental Procedure

The spodumene samples were calcined with Na_2CO_3 in graphite crucibles at 850 °C for 1 h in a mass ratio of 1:1, using Ar in order to create an inert environment. An additional batch of samples was calcined; in this process, CaO was also added along with Na_2CO_3 in a mass ratio of 1:1:1 under the same conditions. After calcination, the cooling of samples took place inside the furnace after almost 8 h.

After the pulverization of the samples, leaching tests were carried out in a 500 mL reactor for all the samples. The leaching solutions used were composed of H_2SO_4 1.5 M at temperatures of 40 °C and 90 °C and H_2O at 90 °C for a total retention time of 5 h. Hourly samples were taken, and lithium concentration was analyzed in AAS.

3. Results and Discussion

3.1. Characterization of Spodumene Concentrate

The sample was subjected to a series of physicochemical and mineralogical analyses, namely, chemical analysis via fusion and inductively coupled plasma–optical emission spectrometry (ICP-OES) using Optima 8000; Atomic Absorption Spectroscopy (AAS) using PinAAcle 900T; X-ray diffraction (XRD) using Rigaku MiniFlex; and particle size distribution determined using Malvern Mastersizer Micro-P. Table 1 presents the chemical analysis of spodumene concentrate. It is an alumino-silicate material with a lithium oxide content of 6.5%. The particle size distribution (Table 2) indicates that the sample is fine, varying between 1 μm and 300 μm, with 50% of the particles being below 115 μm and 90% being below 249 μm. No further pulverization was needed in order to increase the interface between the different mineral phases and accelerate the chemical reactions that took place.

Table 1. Chemical analysis of the spodumene concentrate.

Oxide	**Li_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**	**SnO_2**	**Na_2O**	**K_2O**	**LOI**	**SUM**
%	6.50	0.53	30.35	56.82	1.94	0.14	0.09	0.86	0.07	0.87	0.52	1.32	100

Table 2. Particle size distribution statistics of the spodumene concentrate.

Mean diameters	D (v, 0.1)	D (v, 0.5)	D (v, 0.9)
Particle size (μm)	38.16	115.63	249.22

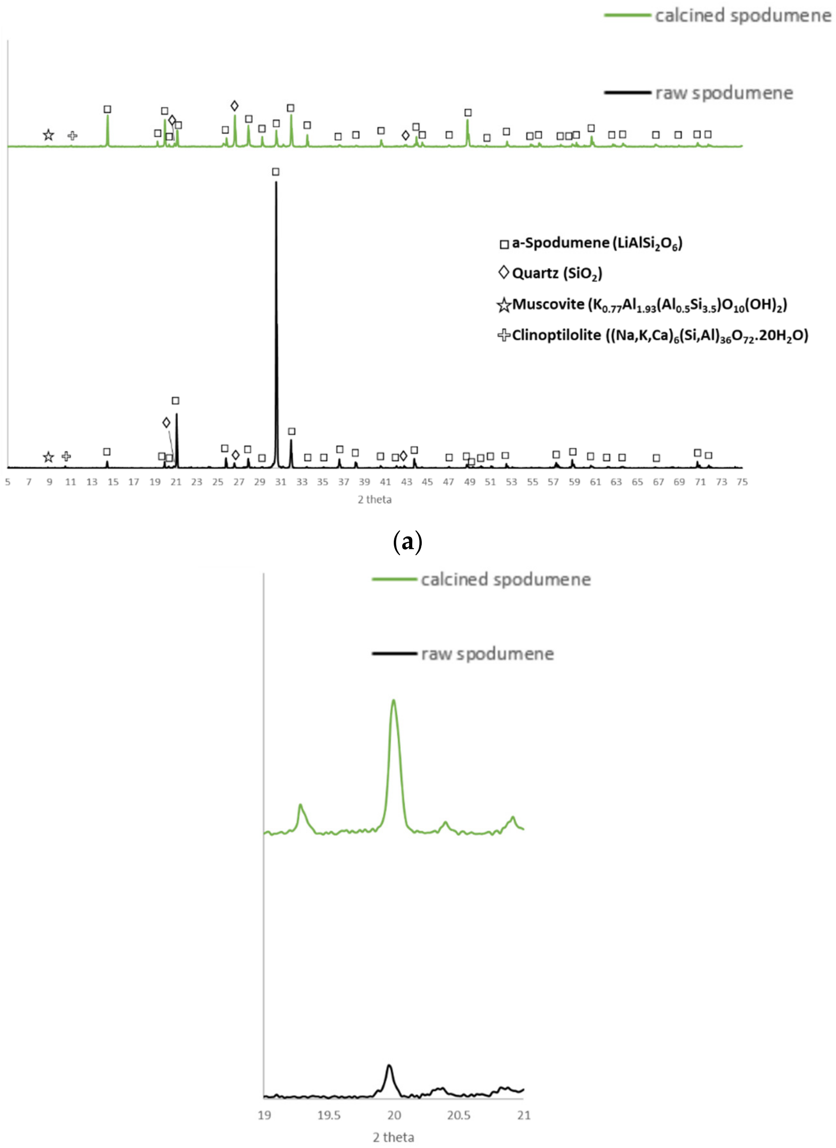
3.2. Calcination Results

The mineralogical analyses of the calcined samples are shown in Figures 1 and 2. Raw and calcined spodumene concentrate are presented in Figure 1, while the calcined mixtures of spodumene with Na_2CO_3 and spodumene with Na_2CO_3 and CaO are presented in Figure 2. The XRD analyses showed, as seen in Figure 1a, that the raw spodumene concentrate consisted of a-spodumene, quartz, muscovite, and clinoptilolite.

Spodumene is naturally present in the stable a-monoclinic (highly packed crystal structure) form, from which lithium is difficult to leach without pretreatment. During the conventional thermal process (1000–1100 °C), there is a dislocation of Al^{3+} in a-spodumene, leading to a b-spodumene crystal structure with a relatively larger crystal volume. This transformation increases the mobility of lithium atoms, which then become easily accessible. Recently, an intermediary metastable c- phase was discovered during calcination. Therefore, the sequence of the phase transformation after calcination is as follows: a→c→b-spodumene [10].

Figure 1 shows the XRD spectra of a-spodumene concentrate before and after calcination. The figure shows that after calcination, even though the main a-spodumene peak at 2θ of 30.5 decreased, all the peaks attributed to a-spodumene were still detected. The spectrum shows no amorphous background or significant broadening of peaks, revealing that the transformation of a-spodumene leading to b-spodumene has not occurred. The decreased intensities in the calcined sample reveal lower crystallinity [20].

The XRD patterns for the calcined a-spodumene sample also show a broadening of the peak at 2θ of 19.99°, which is a sign of internal stress indicating the partial recrystallization of spodumene in the form of c-spodumene [21]. The most obvious evidence of the formation of c-spodumene is the peak located at 19.5° at the 2θ-scale after heating, as this is the strongest peak of c-spodumene, which does not overlap with the peaks of the other phases (a- and b-) [22].



(**a**)

(**b**)

Figure 1. Mineralogical analysis of raw and calcined spodumene concentrate: (**a**) 2theta 5–75 and (**b**) 2theta 19–21.

In Figure 2, the XRD spectra of the calcined mixtures of spodumene with additives are presented. It is shown that in case of Na_2CO_3 addition, Li_2SiO_3 is produced after calcination; this compound is insoluble in water but is soluble in acid. The dominant phase of the calcined product of spodumene with Na_2CO_3 is sodium aluminum silicate ($Na_{1.15}Al_{1.15}Si_{0.85}O_4$), while the Na_2CO_3 that did not react was also detected. In the spodumene–Na_2CO_3–CaO mixtures, as seen in Figure 2, lithium is detected in a mixture of two phases: Li_2O/Li_2CO_3. The dominant phases of the calcined products are: a different type of sodium aluminum silicate ($Na_{1.55}Al_{1.55}Si_{0.45}O_4$) and calcium silicate. The Na_2CO_3 that did not react was also detected.

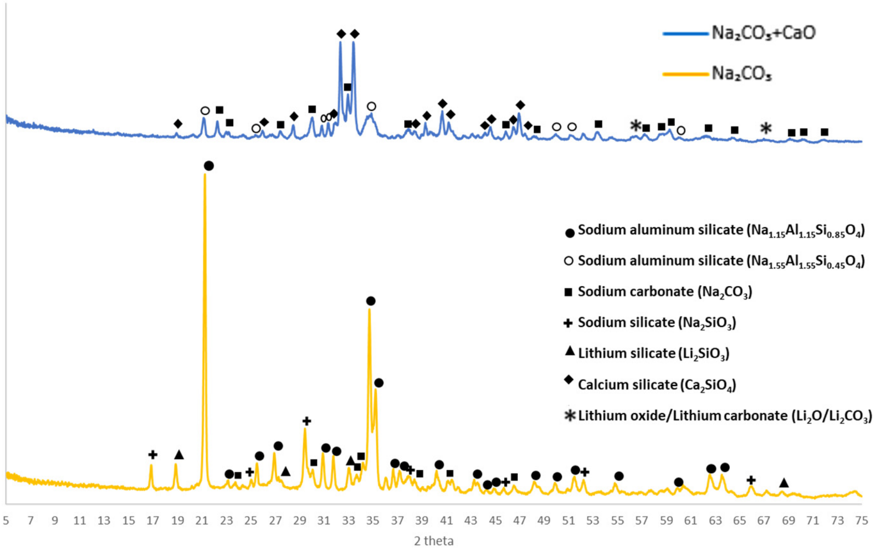


Figure 2. Mineralogical analysis of calcined spodumene–Na_2CO_3 and spodumene–Na_2CO_3–CaO mixtures.

3.3. Leaching Results

The results of Li extraction from calcined spodumene after leaching with H_2SO_4 are presented in Figure 3. It is evident that the lithium extraction yield from spodumene after calcination without any additive is very low, equal to 3.8%, even under intensive leaching conditions (acid concentration of 1.5 M; 90 °C). It is the use of Na_2CO_3 at the calcination stage that renders the lithium extraction not only feasible but also capable of reaching high levels ranging from 83 to 99.8%.

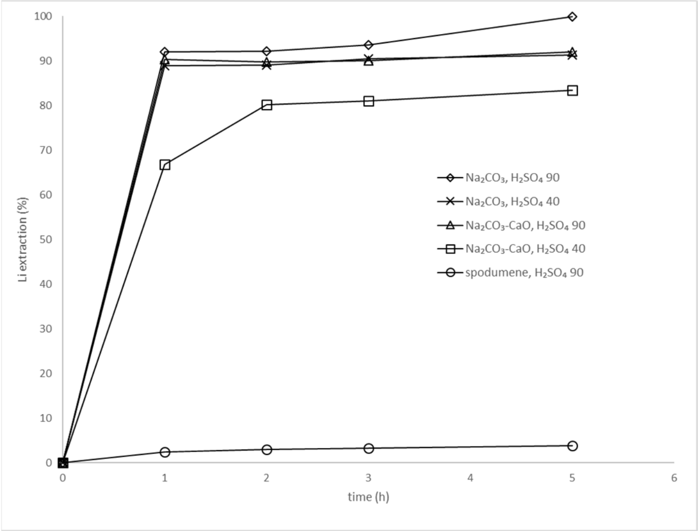


Figure 3. % extraction of Li from calcined spodumene with additives using H_2SO_4 at 40 °C and 90 °C.

The addition of CaO at the calcination stage does not seem to benefit Li extraction. When leaching occurred at 90 °C, the extraction achieved was 92% with CaO and 99.8% without CaO. When leaching was performed at 40 °C, the extraction achieved was 83.4% with CaO and 92% without CaO. Higher extraction was achieved at 90 °C. The leaching results show that the percentage of lithium extraction achieved during leaching at 90 °C when CaO is added at the calcination step is equal to the lithium extraction rate achieved at 40 °C when only Na_2CO_3 is used as an additive during calcination.

Figure 4 presents the Lithium extraction from calcined spodumene after leaching with H_2O at 90 °C. The use of H_2O as the leaching agent was not effective, even at high temperatures, resulting in a Li extraction yield no higher than 15%. Nevertheless, the use of Na_2CO_3 during calcination enhances lithium extraction from 1%, which is the Lithium extraction of calcined spodumene without additives, to 15%.

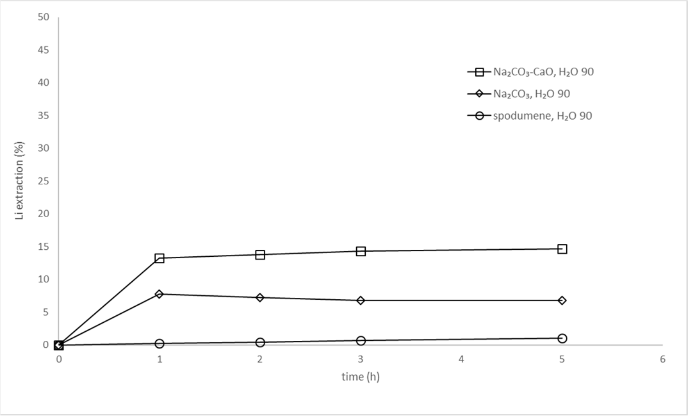


Figure 4. % extraction of Li from calcined spodumene with additives using H_2O at 90 °C.

4. Conclusions

The lithium extraction yields from a-spodumene in a sulfuric acid solution and in water were very low (below 5%) and practically unfeasible, even when using intensive leaching conditions. The study presented shows that the use of proper additives during the calcination stage of spodumene can render Li extraction efficient, even from a-spodumene. The use of Na_2CO_3 and CaO as additives enabled the maintenance of the calcination temperature of a-spodumene at low levels (850 °C), which are significantly reduced compared to the conventional process, which takes place at 1000–1100 °C. Furthermore, after the carbonizing calcination, the lithium extraction ranges between very high rates, even though the transformation to b-spodumene has not taken place.

Using sulfuric acid as the leaching agent of the carbonized calcined mixtures, Li extraction from a-spodumene concentrate can reach 99,8%, whereas a-spodumene thermally treated without additives cannot generate a Li extraction yield higher than 4%. The leaching temperature was 90 °C, which was reduced by 64% compared to that in acid roasting, which is the conventional method, taking place at 250 °C.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Kogel, J.E.; Trivedi, N.C.; Barker, J.M.; Krukowski, S.T. *Industrial Minerals & Rocks: Commodities, Markets, and Uses*, 7th ed.; Society for Mining, Metallurgy, and Exploration: Littleton, CO, USA, 2006.
2. Global Lithium Batteries Market Size 2017–2025. Available online: https://www.statista.com/statistics/235316/global-lithium-battery-market/ (accessed on 2 October 2023).

3. Gourcerol, B.; Gloaguen, E.; Melleton, J.; Tuduri, J. Xavier Galiegue Re-assessing the European lithium resource potential—A review of hard-rock resources and metallogeny. *Ore Geol. Rev.* **2019**, *109*, 494–519. [CrossRef]
4. Meng, F.; McNeice, J.; Zadeh, S.S.; Ghahreman, A. Review of Lithium Production and Recovery from Minerals, Brines, and Lithium-Ion Batteries. *Miner. Process. Extr. Metall. Rev.* **2021**, *42*, 123–141. [CrossRef]
5. Kelly, J.C.; Wang, M.; Dai, Q.; Winjobi, O. Energy, greenhouse gas, and water life cycle analysis of lithium carbonate and lithium hydroxide monohydrate from brine and ore resources and their use in lithium ion battery cathodes and lithium ion batteries. *Resour. Conserv. Recycl.* **2021**, *174*, 105762. [CrossRef]
6. Salakjani, N.K.; Singh, P.; Nikoloski, A.N. Production of Lithium—A Literature Review Part 1: Pretreatment of Spodumene. *Miner. Process. Extr. Metall. Rev.* **2019**, *41*, 335–348. [CrossRef]
7. Li, H.; Eksteen, J.; Kuang, G. Recovery of lithium from mineral resources: State-of-the-art and perspectives—A review. *Hydrometallurgy* **2019**, *189*, 105129. [CrossRef]
8. Salakjani, N.K.; Nikoloski, A.N.; Singh, P. Mineralogical transformations of spodumene concentrate from Greenbushes, Western Australia. Part 2: Microwave heating. *Miner. Eng.* **2017**, *100*, 191–199. [CrossRef]
9. Lajoie-Leroux, F.; Dessemond, C.; Soucy, G.; Laroche, N.; Magnan, J.F. Impact of the impurities on lithium extraction from β-spodumene in the sulfuric acid process. *Miner. Eng.* **2018**, *129*, 1–8. [CrossRef]
10. Fosu, A.Y.; Kanari, N.; Vaughan, J.; Chagnes, A. Literature Review and Thermodynamic Modelling of Roasting Processes for Lithium Extraction from Spodumene. *Metals* **2020**, *10*, 1312. [CrossRef]
11. Barbosa, L.I.; Valente, G.; Orosco, R.P.; González, J.A. Lithium extraction from b-spodumene through chlorination with chlorine gas. *Miner. Eng.* **2014**, *56*, 29–34. [CrossRef]
12. Barbosa, L.I.; González, J.A.; del Carmen Ruiz, M. Extraction of lithium from b-spodumene using chlorination roasting with calcium chloride. *Thermochim. Acta* **2015**, *605*, 63–67. [CrossRef]
13. Yan, Q.; Li, X.; Yin, Z.; Wang, Z.; Guo, H.; Peng, W.; Hu, Q. A novel process for extracting lithium from lepidolite. *Hydrometallurgy* **2012**, *121–124*, 54–59. [CrossRef]
14. Chen, Y.; Tian, Q.; Chen, B.; Shi, X.; Liao, T. Preparation of lithium carbonate from spodumene by a sodium carbonate autoclave process. *Hydrometallurgy* **2011**, *109*, 43–46. [CrossRef]
15. Rosales, G.D.; del Carmen Ruiz, M.; Rodriguez, M.H. Novel process for the extraction of lithium from β-spodumene by leaching with HF. *Hydrometallurgy* **2014**, *147–148*, 1–6. [CrossRef]
16. Rosales, G.D.; Ruiz, M.C.; Rodriguez, M.H. Study of the Extraction Kinetics of Lithium by Leaching β-Spodumene with Hydrofluoric Acid. *Minerals* **2016**, *6*, 98. [CrossRef]
17. Fosu, A.Y.; Kanari, N.; Bartier, D.; Vaughan, J.; Chagnes, A. Novel extraction route of lithium from α-spodumene by dry chlorination. *RSC Adv.* **2022**, *12*, 21468–21481. [CrossRef] [PubMed]
18. Song, Y.; Zhao, T.; He, L.; Zhao, Z.; Liu, X. A promising approach for directly extracting lithium from α-spodumene by alkaline digestion and precipitation as phosphate. *Hydrometallurgy* **2019**, *189*, 105141. [CrossRef]
19. Xing, P.; Wang, C.; Zeng, L.; Ma, B.; Wang, L.; Chen, Y.; Yang, C. Lithium extraction and hydroxysodalite zeolite synthesis by hydrothermal conversion of α-spodumene. *ACS Sustain. Chem. Eng.* **2019**, *7*, 9498–9505. [CrossRef]
20. Abdullah, A.A.; Oskierski, H.C.; Altarawneh, M.; Senanayake, G.; Lumpkin, G.; Dlugogorski, B.Z. Phase transformation mechanism of spodumene during its calcination. *Miner. Eng.* **2019**, *140*, 105883. [CrossRef]
21. Salakjani, N.K.; Singh, P.; Nikoloski, A.N. Mineralogical transformations of spodumene concentrate from Greenbushes, Western Australia. Part 1: Conventional heating. *Miner. Eng.* **2016**, *98*, 71–79. [CrossRef]
22. Peltosaari, O.; Tanskanen, P.; Heikkinen, E.-P.; Fabritius, T. α→γ→β -phase transformation of spodumene with hybrid microwave and conventional furnaces. *Miner. Eng.* **2015**, *82*, 54–60. [CrossRef]