Extraction of lithium from spodumene

By
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A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy in the Department of Engineering and Energy; College of Science, Health, Engineering and Education; Murdoch University

September 2019
I declare that:

a) The thesis is my own account of my research, except where other sources are acknowledged.

b) The extent to which the work of others has been used is clearly stated in each chapter and certified by my supervisors.

c) The thesis contains as its main content, work that has not been previously submitted for a degree at any other university

Nasim Khoshdel Salakjani

Date: 24/9/19

Statement of contribution of others

This thesis has been developed in the format of Thesis by Publications. Chapters 2, 3, 4 and 5 within this thesis have been published or submitted to specific journal. These chapters represent collaborative works; however, the PhD candidate for which this thesis represents has completed the majority of the study design, data collection, data analyses and interpretation, and drafting of the manuscript.

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Date: 24/9/19

Prof. Pritam Singh

Date: 24/9/15

A/ Prof. Aleksandar Nikoloski

Date: 24/9/19
“Nothing in life is to be feared, it is only to be understood. Now is the time to understand more, so that we may fear less.”

Marie Curie

To my Mum, Manijeh, who taught me to dream big and never give up. To my Dad, Mohammad, the person that I am today is thanks to the brave and sensitive soul that you are, you are a true role model to me.

To My husband, Mohammad, without whom this would not happen at all, thanks for always encouraging me to pursuit my dreams and believing in me. I am so grateful for the very patient and humble person you have been in all the ups and downs which came along this journey.

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Thanks to Ken Seymour, Stewart Kelly and Juita Hartanto for the technical support that they have done to this study.

To my students, you are brilliant and helped me learn and enjoy every second I have spent teaching you.

AND this is all for my Grandmother who is the strongest woman and the greatest soul I have ever known.

Nasim
September 2019
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Many thanks to Metrohm Australia for performing sizing analysis of the samples of this study.
Abstract

Spodumene is an important source of lithium, a key element of Li-ion batteries used in mobile communication and entertainment devices, hybrid and all electric cars and electric bikes.

Spodumene forms three different crystal structures, the naturally occurred $\alpha$-spodumene and $\gamma$ and $\beta$-spodumene which are the products of heat treatment at 700 to 1100 °C. Among these three modifications $\beta$-spodumene proven suitable for lithium extraction processes, hence the production of these phases should be closely monitored in feed preparation stage.

In order to extract lithium from spodumene, $\beta$ form of the mineral goes through acid roasting with concentrated sulfuric acid at 250 °C. This method remained unchanged for almost 50 years and limited information on the details of the process and effect of key factors is available.

This study will investigate the preparation of suitable spodumene phase for extraction process exploiting two different types of heating.

Then focuses on traditional acid roasting of spodumene and the key factors of the process and further on proposing a less energy intense method of acid roasting using microwaves.

Spodumene concentrate of the highest purity from Greenbushes Western Australia was studied for mineralogical changes with temperature in muffle furnace. The feed sample with particle size of 325 mm was heated at temperatures from 800 to 1100 °C for different durations of time and structural changes were closely monitored. At 950 °C after 30 minutes of heating $\gamma$ phase appeared on the XRD spectra which detected while $\beta$-spodumene was produced, after 2 hours of heating at 1100 °C. The crystal structure altered from monoclinic $\alpha$ to hexagonal $\gamma$ and finally tetragonal $\beta$-spodumene.

Physical properties of product heated at different temperatures and times were analyzed. The significant change was related to the particle size. Conversion of $\alpha$ to $\gamma$-spodumene is accompanied by shrinkage of the crystal units leading to contraction of particles. Moreover, particles go through substantial expansion with formation of $\beta$-spodumene. This leads to cracking of the particles and their dispersion to smaller particles. This phenomenon directly causes the reduction in particle size which increases the specific surface of the sample. Specific gravity of the sample was constantly reduced with order of changes of the crystal structure.
All these alterations positively affect the yields of lithium extraction from $\beta$ over $\alpha$-spodumene.

As an alternative process of calcination, a sample of $\alpha$-spodumene was subjected to microwave and hybrid microwave heating. The sample reached 98 °C after 10 minutes of microwave irradiation with power of 3 kW. This proved that spodumene is categorized in the group of non-absorbers of microwave. Next a hybrid microwave heating set up was designed which applied three SiC sticks to absorb microwave energy and conventionally heat the spodumene sample. After 32 minutes of hybrid microwave heating and temperature increase up to 643 °C a sudden increase in temperature was observed. Due to localized heat some spot of the sample heated up to the melting point of the spodumene and left sintered and/or melted parts. This suggested that $\alpha$-spodumene can start absorbing microwave at temperatures above 643 °C. The process was repeated for a sample of synthesized $\beta$-spodumene absorption of microwave energy started at 447 °C. This phenomenon made the complete conversion of the sample complicated.

As the next part of this study the common method of extraction of lithium from spodumene was studied. Sample of synthesized $\beta$-spodumene was mixed with concentrated sulfuric acid and roasted at temperatures between 200 and 300 °C. This process was followed by water leaching at 50 °C for 1 hour. In addition to temperature, the effects of acid dosage and roasting time were investigated. The highest extraction of 98% was achieved after roasting at 250 °C for 1 hour with 80% excess acid to the stoichiometry of the reaction of spodumene and sulfuric acid. Elongated roasting, roasting at temperatures close to boiling point of the acid and very high amount of excess acid negatively affected Li extraction. The residue after water leach was identified as aluminium silicon hydrate ($\text{H}_2\text{O}.\text{Al}_2\text{O}_3.4\text{SiO}_2$).

In order to reduce the energy consumption of the acid roast process application of microwave oven was proposed. Acid roasting of spodumene was replicated in benchtop microwave oven adjusted on 700 W power. Interestingly 96 % of lithium was extracted after 20 second of microwave irradiation in presence of 80% excess acid. After 30 seconds of roasting the extraction reduced and reached 49% after 4 minutes.

The residue of the water leach was aluminium silicon hydrate ($\text{H}_2\text{O}.\text{Al}_2\text{O}_3.4\text{SiO}_2$) for roasting under 30 seconds and after 4 minutes peaks of $\beta$-spodumene appeared in the XRD pattern. More studies on the residue showed that the residue has ion exchange properties and at elevated temperatures in presence of lithium the $\text{H}^+$ can be replaced with $\text{Li}^+$. With slight grinding the excess acid could be reduced to 15%. The energy consumption of microwave
acid roasting was 15.4 kJ which was 3 order of magnitude less than the energy consumption of conventional acid roasting. Microwave acid roasting of β-spodumene is a promising method with less energy consumption.
List of publication and presentations

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Conference presentations


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Figure D. 3 Different Magnification SEM Images of β-spodumene acid roasted with 80% excess concentrated H$_2$SO$_4$ in microwave oven for 20 second before water leach. The pores are due to Li$_2$SO$_4$ being dissolved in the course of polishing. The depth of the reaction seems more in this method.

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Chapter 1

General introduction

Lithium, the lightest metal in the periodic table, is a strategic element which has a broad range of application from manufacturing ceramic parts to additive to metallurgical operations, energy storage devices and even medical uses. These constantly growing applications of lithium put this commodity under spotlight and leads to active investigation on its geological occurrence and extraction processes.

This chapter outlines research questions of this project as well as its aims and objectives. It also shows the way this thesis is organized.
1.1 Background

It is interesting to note that in 1900s, the lithium market was “practically non-existent” (Ober., 2000). The significant growth happened during World War II. Lithium hydride was used to inflate antenna balloons for rescue radios and anhydrous lithium hydroxide was applied to absorb CO₂ in submarines (Ober., 2000).

Lithium eventually found its way into different industries and so its production increased. In 2010, ~150 kt Lithium Carbonate Equivalent (LCE) was mined and refined and in 2018 this amount reached ~450 kt LCE for mined and ~300 kt LCE for refined lithium (Figure 1).

In addition to growing application of Li in glass and ceramic industry, air conditioning, greases and lubricants, medicine and metallurgical processes (Bradley et al., 2017; Kavanagh et al., 2018), lithium industry has gone through a considerable change during the past couple of decades owing to Li-Ion batteries for mobile devices.

Development of hybrid and all electric cars (Bradley et. al., 2014), electric bikes and energy storage units create a considerable lithium market. Figure 2 shows the increase in demand of lithium for only one of the applications, batteries (both rechargeable and non-rechargeable from 2017 to 2025.)
Figure 1. 2 Demand of lithium (Lithium carbonate equivalent) for lithium batteries from to 2025 (Garside, 2019).

The rechargeable batteries will need ~213 kT Lithium Carbonate Equivalent (LCE) by 2025 which is ~130% increase to the demand for lithium for batteries in 2017. This market requires sufficient and stable supply of lithium and in fact supply security of lithium is a top priority for technology companies specially in Asia and the United States (Jaskula, 2019).

Lithium salts were initially extracted from brines and lake water. Extraction of Lithium from brines is a less energy consuming process, it relies on the solar energy and also produces less solid waste, Figure 3, shows the schematic of extraction from brines.
Figure 1. Schematic of extraction of lithium from brines (Cheminfo Services Inc., 2012)

Beside all the mentioned advantages of the extraction of lithium from brine, the process is slow and time consuming and to satisfy the world increasing demand for lithium, minerals and clays also became attractive recently.

Lithium can be found in many minerals (Bradley et al., 2017) due to its high reactivity but production from some of these minerals is not feasible. Table 1 summarizes the important minerals that contain lithium.

Table 1. Scientifically or chemically important minerals of lithium (Bradley et al., 2017).

<table>
<thead>
<tr>
<th>Mineral name</th>
<th>Chemical formula</th>
<th>Lithium (weight percent)</th>
<th>Geologic setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amblygonite</td>
<td>(Li,Na)Al(PO₄)(F,OH)</td>
<td>3.44</td>
<td>Pegmatite intrusions in orogenic belts; solid solution with montebrasite</td>
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<tr>
<td>Elbaite</td>
<td>Na(Li,Al)₂Al₆(BO₃)₃Si₄O₁₄(OH)₄</td>
<td>1.89</td>
<td>Tourmaline group. Pegmatite intrusions in orogenic belts. Includes the gem form watermelon tourmaline</td>
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<td>Eucryptite</td>
<td>LiAlSiO₄</td>
<td>5.51</td>
<td>Pegmatite intrusions in orogenic belts</td>
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<tr>
<td>Hectorite</td>
<td>Na₈(Mg, Li)₈Si₄O₁₂(OH)₂</td>
<td>0.54</td>
<td>Hydrothermal alteration of volcanic ash in arid, closed basins</td>
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<td>Jadarite</td>
<td>LiNaB₂SiO₅(OH)</td>
<td>3.38</td>
<td>Hydrothermal alteration of volcanic ash in arid, closed basins</td>
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<td>Lepidolite</td>
<td>KLi₂Al₂(Si₄Al₂O₁₀)(F,OH)₂</td>
<td>3.58</td>
<td>Pegmatite intrusions in orogenic belts</td>
</tr>
<tr>
<td>Montebasite</td>
<td>LiAl[(PO₄)₂(OH,F)]</td>
<td>4.74</td>
<td>Pegmatite intrusions in orogenic belts</td>
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<tr>
<td>Petalite</td>
<td>LiAlSi₂O₆</td>
<td>2.09</td>
<td>Pegmatite intrusions in orogenic belts</td>
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<tr>
<td>Spodumene</td>
<td>LiAlSi₂O₆</td>
<td>3.73</td>
<td>Pegmatite intrusions in orogenic belts. Gem forms are triphane (yellow), kunzite (pink), and hiddenite (green)</td>
</tr>
<tr>
<td>Zabuyelite</td>
<td>Li₃CO₃</td>
<td>18.79</td>
<td>Evaporite mineral (rare)</td>
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</table>
Among these minerals, spodumene is the most abundant (Talens Peiró et al., 2013). Although due to the small market extraction of lithium from spodumene has been limited for a while, with the drastic increase in lithium demand researchers once again focused on this mineral its beneficiation, flotation, calcination and extraction to produce lithium salts quicker and under less intense conditions. Chapter 2 of this study provides a comprehensive review on the available knowledge and literature on pre-treatment of spodumene and methods of extraction of lithium from this mineral. Study of the literature assisted the author to build the aims and objectives of the present project in relevance to the ongoing industry with the hope to contribute to the existing knowledge.

1. 2 Research Questions
After a comprehensive review on the available literature brought in chapter 2, the dominant questions in the process of extraction of Li from spodumene are related to the lengthy procedures and consumption of energy at different stages of the process. The first question is if it is possible to perform calcination at lower temperatures or shorter times? Therefore, it is necessary to know the effect of calcination on the physical properties of the mineral. What properties facilitate the extraction? Is it possible to activate α-spodumene with other methods?
Information on commercial process of extraction from spodumene, acid roasting is limited in literature, therefore, it is required to evaluate the important factors on acid roasting of spodumene. And are there any alternatives for conventional acid roasting?

1. 3 Aims and objectives of the project
After comprehensive study of the literature the aims and objectives of this work been proposed.
The study is divided into two main phases as following:
1. 3. 1 Phase 1- Calcination of spodumene
To enhance the process of extraction of lithium from spodumene study of the mineralogical changes of this mineral is necessary.
The aims of this phase are firstly to obtain a better understanding of the structural changes of spodumene while heating and secondly to look into lower the consumption of energy. This stage of extraction happens traditionally in a rotary kiln and to avoid use of unnecessary energy, it is necessary to understand the series of reactions occurs to the mineral and investigate the relevant physical properties of different products. This objective will be addressed in chapter 3 of this present thesis.
As the conversion stage is energy intense and therefore expensive, any improvement that can lower the working temperature and/or time would be beneficial. Therefore, to achieve the next aim of this study is the mineral will be subjected to a different type of heating. For that microwave energy is considered. Study of different conditions under electromagnetic field may assist the development of a less energy consuming conversion stage for preparation of active spodumene. The target is to either prepare an active spodumene feed without alteration of the crystal structure, only by producing voids and internal cracks and pores which opens up the structure for extraction reagents to access lithium species. Or to convert α-spodumene to β-spodumene at lower temperatures and/or faster. This has been covered in chapter 4.

1.3.2 Phase 2- Extraction of lithium from spodumene

Second phase of the projects focuses on detail study of conventional method of extraction of lithium from spodumene, roasting with sulfuric acid and water leaching. The aims of this phase are to suggest the optimal conditions of conventional method and finally to propose a novel process that is more economic and easier to operate.

To find the optimal condition of acid roasting the effect of key process factors need to be investigated and understanding the mechanisms can help improving the process. This objective is brought in chapter 5.

As to investigate a less energy consuming method of lithium extraction, application of microwave oven in acid roasting of spodumene as well as finding the optimum working condition is the objective of this part of the study which is explained in chapter 5.

References


Cheminfo Services Inc., 2012, Review of the Rare Earth Elements and Lithium Mining Sectors, Final report for Environment Canada Mining Section, Mining and Processing Division.

sources—industrial use and future in the electric vehicle industry: A Review. Resources, 7(3), 57.
Chapter 2

Literature review-

Production of lithium; Part 1 Pre-treatment of spodumene

Production of lithium; Part 2 Extraction of lithium from spodumene

As lithium became a strategic commodity in the past decade, different sources of this element also been under intense study. Spodumene as the main and most abundant source among hard rocks has been subject of many laboratory and industrial scale projects. Natural spodumene is a refractory mineral. Current extraction process is designed to activate the mineral and to extract Li in following stage.

This chapter reviews the literature in two parts. Part 1 focusing on pre-treatment of spodumene and Part 2 the extraction methods. Nasim Kh Salakjani wrote all the sections of this chapter. Co-Supervisor, Prof. Pritam Singh, provided feedback and comments on various drafts of the papers. A/Prof. Aleks Nikoloski as Principal Supervisor provided guidance and comments on the drafts of the papers and also edited the final manuscripts.

The outcome of this review is published as:


### Percentage contribution

**Literature review - Production of lithium; Part 1 Pre-treatment of spodumene**

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<th>Data analyses</th>
<th>Interpretation</th>
<th>Manuscript development</th>
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<td>Nasim Khoshdel Salakjani</td>
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<td>100%</td>
<td>100%</td>
<td>90%</td>
<td>80%</td>
</tr>
<tr>
<td>Pritam Singh</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5%</td>
<td>10%</td>
</tr>
<tr>
<td>Aleksandar Nikoloski</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>10%</td>
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**Literature review - Production of lithium; Part 2 Extraction of lithium from spodumene**

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<thead>
<tr>
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### Confirmation of contribution

As a contributor to this Chapter, I confirm that the level of contribution attributed to me is correct.

Nasim Khoshdel Salakjani [Signature]

Prof. Pritam Singh [Signature]

A/ Prof. Aleksandar Nikoloski [Signature]

Date: 29/9/19

Date: 29/9/18

Date: 29/9/19
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Chapter 3

Mineralogical transformations of spodumene through conventional heating

Spodumene is in the group of pegmatite. It occurs naturally in a mineral phase named α-spodumene which preserves lithium in a packed structure and makes the recovery of lithium complicated. Conversion of α-β-spodumene resolves the problem since β-spodumene crystallizes in a less packed expanded structure which allows the extraction of lithium to take place by substitution of Li ions with other ions. This chapter focuses on the three existing modifications of spodumene and the transformation by conventional heating and also discuss the physical properties of each structure.

Nasim Kh Salakjani carried all the practical work and wrote all the sections of this chapter. Co-Supervisor, Prof Pritam Singh, provided feedback and comments on results of the experiments and various drafts of the paper. A/Prof. Aleks Nikoloski as Principal Supervisor provided guidance on the test work as well as comments on the drafts of the paper and also edited the final manuscript.

The Manuscript is published as:


Supplementary information for this chapter can be find in Appendix B.
Percentage contribution

Mineralogical transformations of spodumene concentrate from Greenbushes, Western Australia. Part 1: Conventional heating

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Confirmation of contribution

As a contributor to this Chapter, I confirm that the level of contribution attributed to me is correct.

Nasim Khoshdel Salakjani Date: 24/9/19
Prof. Pritam Singh Date: 24/12/15
A/ Prof. Aleksandar Nikoloski Date: 27/3/15
Chapter 4

Mineralogical transformations of spodumene with application of microwave energy

As the energy to convert refractory α-spodumene to a the more reactive format is is significant, therefore any measurement that assist the reduction of the time and temperature necessary for the conversion can lower the production cost of lithium. Microwave ovens have been studied in minerals processing for the past couple of decades. In this case the mechanism of heating materials is different from conventional heating which may positively affect the consumption of energy in the conversion stage. In continuation of the pervious chapter this chapter covers the findings of microwave heating of spodumene and the transformations that occur in this different type of heating.

Nasim Kh Salakjani performed all the practical work and wrote all the sections of this chapter. Co-Supervisor, Prof Pritam Singh, provided feedback on the practical work and reviewed various drafts of the paper, A/Prof. Aleks Nikoloski as Principal Supervisor provided advice on the experiment and commented the drafts of the paper and also edited the final manuscript. The Manuscript is published as:


Supplementary information for this chapter can be find in Appendix C.
**Percentage contribution**

*Mineralogical transformations of spodumene concentrate from Greenbushes, Western Australia. Part 2: Microwave heating.*

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**Confirmation of contribution**

As a contributor to this Chapter, I confirm that the level of contribution attributed to me is correct.

Nasim Khoshide Salakjani

A/ Prof. Aleksandar Nikoloski

Prof. Pritam Singh

Date: 3/19/19

Date: 2/7/9

Date: 1/2/17
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Chapter 5

Microwave acid roasting of spodumene vs. Conventional acid roasting of spodumene

The commercial method of extracting lithium from spodumene is roasting the converted spodumene with concentrated sulphuric acid which leads to substitution of Li⁺ with H⁺ without decomposing the aluminosilicate framework. This method has been used since 1950 to produce lithium from spodumene. But the study of the process is limited to the commercial section and industrial scale. The process remained quite unchanged compared to the initial invention which made us think if we can improve the process by addition or substitution of any of the equipment used in the process. This chapter deals with the conventional acid roasting of concentrated spodumene and the impact of key factors on the recovery of lithium. And then follows the novel process of acid roasting in the microwave oven and compares the two methods. This chapter basically covers the second phase of the work. Overall it covers the two final objectives of this study.

Nasim Kh Salakjani carried all the test work and analysis and wrote all the sections of this chapter. Co-Supervisor, Prof. Pritam Singh, provided feedback on the experiments and comments on various drafts of the papers. Principal Supervisor A/Prof. Aleks Nikoloski provided guidance with practical section and reviewed the drafts of the paper and also edited the final manuscript. The final manuscript is published as:


Additional information for this chapter is brought in Appendix D.
### Percentage contribution

*Acid roasting of spodumene: Microwave vs. conventional heating*

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### Confirmation of contribution

As a contributor to this Chapter, I confirm that the level of contribution attributed to me is correct.

Nasim Khoshdel Salakjani  
Prof. Pritam Singh  
A/ Prof. Aleksandar Nikoloski  

Date $\underline{24/9/19}$  
Date $\underline{24/10/19}$  
Date $\underline{24/10/19}$
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Chapter 6

Overall Conclusion

With extraction of lithium from spodumene being a popular topic at the moment this work may be useful to improve different stages of the process. Apart from the novel procedures the review of the conventional method of extraction may assist promotion of the current process of production of lithium. This chapter summarizes the achievements of this study.
6.1 Outcome of the study

The comprehensive review over the existing knowledge on lithium extraction from spodumene contributed to highlighting the shortages of traditional methods and introduced the opportunity for us to create this study.

This work studied the characterization of the highest grade spodumene concentrate from Greenbushes Western Australia. Detailed XRD, SEM, FTIR and sizing analysis of the feed concentrate help us to better understand the initial structure and properties and changes down the track. Study of the feed then was followed by investigation of different stages of lithium extraction from spodumene which calcination and acid roasting of are the calcine.

Mineralogical changes of spodumene in calcination stage was investigated over a range of temperatures (800-1100 °C) and it is concluded that at higher temperature the changes took place at shorter time. Morphological changes were studied by means of XRD and SEM which showed transformation of pointy elongated particles to cracked and porous particles. The alteration of physical properties, particle size, specific surface, specific gravity was measured for product of different time and temperature. Reduction in particle size with conversion to β-spodumene was the significant finding. Specific surface was increased, and specific gravity faced reduction. The heat flow pattern was suggested.

Substitution of muffle furnace with microwave oven was explored. It was found that spodumene is not absorbent of microwave. Hybrid microwave heating of spodumene at powers below 3 kW had no effect on the structure and morphology of spodumene particles. Irradiation of 3 kW for 32 minutes led to rapid changes of temperature and melting of the sample at some spots. The temperature of the sample before the sudden raise which was 634 °C was nominated as the critical temperature at which α-spodumene starts absorbing microwave energy. This temperature for β-spodumene was 447 °C. Possible reasons were explained with TEM study of the sample.

Although hybrid microwave could not supply a uniform feed for the extraction process, the outcome may be very useful for other industries like ceramic industry. The energy consumed to melt the sample was less than the energy required to convert the entire α to β-spodumene.

As the main stage of extraction of lithium acid baking with concentrated sulfuric acid was studied. Detailed investigation of the key factors of the process, temperature, time and excess amount of acid to the stoichiometry of the reaction of spodumene and acid, shows that low and high values in the considered range of each factor can negatively affect the extraction. From the optimum conditions a baseline was extracted.
To enhance the traditional method of extraction, use of microwave oven was suggested. This method lowered the operation time and energy consumption significantly. The mechanisms of heating are proposed and explained. At microwave timing more than 30 seconds reduction of extraction was observed. Further investigation confirmed the reverse reaction of Li+ and H+ and reformation of β-spodumene. This was attributed to temperature rise in microwave. The conditions were replicated in muffle furnace and relevant reactions at elevated temperatures were proposed and discussed. Grinding of the sample was effective on extraction and assisted with reduction of excess acid while maximizing the extraction. With the energy consumption being 3 orders of magnitude less than the replicate process in muffle furnace, microwave acid roasting can positively affect the economic aspects of production of lithium salts from spodumene.

This work shows that the use of microwave ovens in production of lithium from spodumene is promising and is worth researching in bigger scales.

6.2 Significance of the study

In calcination of spodumene crystallization of γ-spodumene was not considered in previous studies. This study confirms the formation of γ-spodumene which remained in the calcined sample even at high temperatures. This would be important in adjustments of both upstream stages if complete conversion to β-spodumene is necessary and downstream stages to ensure existence of γ-spodumene does not negatively impact lithium extraction.

Application of microwave in both stages of processing spodumene is a novel procedure which is proposed previously. Microwave heating of spodumene resulted in measuring the critical temperatures of converting both α and β-spodumene to absorbers of microwave. This can be important not only for mineral processing of spodumene but also for glass and ceramic industry.

On the other hand, the acid roasting of spodumene by means of microwave energy was a successful process with a facile short operation, which may change the process of acid roasting in the long run.

6.3 Suggestions for further work

It is suggested to:

1. Consider extraction from γ-spodumene, this can be helpful in terms of calcination stage and if complete conversion to β-spodumene is necessary.

2. Can formation of γ-spodumene be limited by applying changes in beneficiation of spodumene
3. Survey of the effect of size distribution, mass and also existing impurity on temperature and time of calcination.

4. Study beneficiation of spodumene by means of calcination.

5. Investigate of mechanical agitation on microwave process of calcination.

6. Consider microwave acid roasting of spodumene without mixing acid and feed sample (as two separate layers).

7. Investigate the effect of particle size and size distribution on microwave acid roasting of spodumene and try to reduce the acid consumption.

8. Study the dilution of the acid with water in microwave process.

9. Study roasting with other reagents in microwave oven.
Appendix

Appendix A- Additional information on Feed material

Figure A. 1 SEM spectra of spodumene concentrate at different magnifications.

Figure A. 2 Camsizer digital images of spodumene feed sample of 150-250 μm with (a) basic camera and (b) zoom camera prepared with Camsizer X2.
Figure A. 3 Image and dimension measurements of smaller particles prepared with Camsizer X2.

Figure A. 4 Image and dimension measurements of the larger particles prepared with Camsizer X2.
Figure A. 5 Size distribution of the feed spodumene (150-250 mm) measured for width and length of the samples with Camsizer X2.
Appendix B- Supplementary material for Chapter 3

Figure B. 1 XRD patterns of spodumene heated at 800 °C for 10, 20, 30 and 60 minutes.

Figure B. 2 XRD patterns of spodumene heated at 850 °C for 10, 20, 30 and 60 minutes.
Figure B. 3 XRD patterns of spodumene heated at 900 °C for 10, 20, 30 and 60 minutes.

Figure B. 4 SEM images of calcination at 800 °C for a) 10, b) 20, c) 30, d) 60 minutes.
Figure B. 5 SEM images of calcination at 850 °C for a) 10, b) 20, c) 30, d) 60 minutes.

Figure B. 6 SEM images of calcination of spodumene at 900 °C for a) 10, b) 20, c) 30, d) 60 minutes.
Figure B. 7 SEM images of calcination of spodumene at 950 °C for a) 10, b) 20, c) 30, d) 60 minutes.

Figure B. 8 Higher magnification of the sample heated at 1050 °C for (a) 10, (b) 20, (c) 30 and (d) 60 minutes. Changes in particles vs time of heating are obvious from cracks to falling apart to smaller particle.
Figure B. 9 Changes of FTIR spectra of samples heated at 900, 950, 1000, 1050 and 1100 °C for 60 minutes.

Figure B. 10 Raman shifts of (a) spodumene feed, (b) initial point of structural change, (C) α, γ and β-spodumene and (d) γ and β-spodumene.
Figure B. 11 (a) and (c) TEM images of two different shape particles of spodumene calcined at 950 °C for 30 minutes. (b) and (d) Electron Diffraction patterns of the specified points. The images show two different patterns for the particles with different shapes ((a) similar to particles of α-spodumene and (c) similar to particles β-spodumene).
Figure B. 12 Structural changes of spodumene heated at 1100 °C for different amounts of time on a 2-gram sample of 150-250 μm. Structural changes are obvious after 1 minute of heating and complete conversion achieved after 15 minutes.

Figure B. 13 Changes of the shape of particles with changes in structure from asymmetric to symmetric specifically after 6 minutes measured by Camsizer X2.
Figure B. 14 Changes of the shape of particles with changes in structure after 4 minutes of heating at 1100 °C after appearance of β-spodumene the particles transform to more isometric and round shape particles. Data from Camsizer X2.

Figure B. 15 Size distributions of the samples heated at 1100 °C for different residence times in terms of 10, 50 and 90 % of the distribution.
Table B. 1 Particle size of the samples heated at 1100 °C for different residence time in terms of 10, 50 and 90 % of the distribution.

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Appendix C- Supplementary material for Chapter 4

Figure C. 1 Microwave oven used for heating to study the resulting mineralogical transformations of spodumene sample. This equipment has the ability of recording temperature and applied power Vs. time. The chamber is insulated which allows treatments at high temperatures. Power can be adjusted from 0.5 to 6 kW.

Figure C. 2 Colour changes of spodumene treated at 3 kW of microwave irradiation for different residence times.
Figure C. 3 (a) TEM image and HRTEM image of α-spodumene particle at (b) point 1 and (c) point 2, showing crystal structure of the particle.

Figure C. 4 (a) and (b) TEM image treated spodumene particle at 950° C for 30 minutes and HRTEM image of (c) point 1 and (d) point 2. The HRTEM shows disorder phase with no continues crystal structure. Pockets of random crystal structure is observed which can prove the fact that there is a transition trough amorphous phase which can change the absorption of microwave energy.
Appendix D- Supplementary material for Chapter 5

Figure D. 1 Final temperature of α-spodumene samples after a microwave roast with 80% excess acid. The lithium extraction for all times was around 3%. The temperature of the sample was not raised above the boiling point of the acid which means apart from heating up by acid no other reaction took place.

Figure D. 2 Different Magnification SEM Images of β-spodumene acid roasted with 80% excess concentrated H₂SO₄ in muffle furnace at 250 °C for 1 hour before water leach. The pores are due to Li₂SO₄ being dissolved in the course of polishing.
Figure D. 3 Different Magnification SEM Images of β-spodumene acid roasted with 80% excess concentrated H₂SO₄ in microwave oven for 20 second before water leach. The pores are due to Li₂SO₄ being dissolved in the course of polishing. The depth of the reaction seems more in this method.

Figure D. 4 Different Magnification SEM Images of β-spodumene acid roasted with 80% excess concentrated H₂SO₄ in microwave oven for 20 second after water leach.
Figure D. 5 Different Magnification SEM Images of β-spodumene acid roasted with 80% excess concentrated H$_2$SO$_4$ in microwave oven for 4 minutes before water leach.

Figure D. 6 Different Magnification SEM Images of β-spodumene acid roasted with 80% excess concentrated H$_2$SO$_4$ in microwave oven for 4 minutes after water leach. The residue and non-leached sample are similar which confirms the fact that reverse reaction took place at longer time and consequently higher temperatures.