

Western Australian School of Mines

Mechano-activation and Acid
Leaching of Li from Alpha
Spodumene

Norman Lim

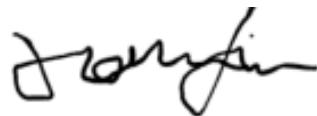
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Master of Research
of
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Author's Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

To the best of my knowledge and belief, this thesis contains no materials previously published by any other person except where due acknowledgement has been made.

A handwritten signature in black ink, appearing to read 'Norman Lim', written in a cursive style.

Norman Lim

Date: 5th December 2023

Abstract

Spodumene, a double silicate of lithium (Li) and aluminum (Al), has become an important resource for Li as the metal's demand has consistently increased with market growth driven by battery applications and the increasing global conscious consumerism. The traditional source of Li is continental brines but it is expected that the supply shortage will be met mainly by hard rock sources, particularly spodumene.

The conventional processing technique for spodumene for Li extraction is based on an energy intensive process of calcination in combination with sulphation baking followed by water leaching. This process leaves a big volume of leach residue which is currently being tested industrially as supplementary cementitious material.

Mechano-activation is a technique in which mechanical action by attrition and impact is used to activate mineral surface to render them reactive. There are no known industrial applications for mechano-activation although its variant mechano-chemical activation, which is incorporates chemicals as added activation medium on top of mechanical action, has been used in industry for activating fly-ash and also in iron oxides for mechanical alloying.

Mechano-activation as an alternative to current conventional processing of Li from spodumene would provide for a process simplification by enabling a direct leaching of Li from mechano-activated spodumene. There are very few studies on the mechano-activation of spodumene, particularly on alpha spodumene, the stable and refractory form of the mineral. The degree of mechano-activation is highly dependent on the type of the activator mill used and in all of the studies done on this subject matter, details fo the activator mill and activation conditions are not

fully disclosed. This is the reason why successful mechano-activation of alpha spodumene with Li recoveries as high as 95% as conducted by Russian researchers was never replicated. The mill used was a planetary mill, and of patented design and was reported to deliver a centrifugal acceleration of 100 g.

There is then a research opportunity to characterize mechano-activation of alpha spodumene using a known commercial planetary mill. The effect of mechano-activation as measured from Li recoveries by direct sulphuric acid, can also be evaluated by an alternative citric acid leaching. As Li is one of the green metals, there is an expectation that processing techniques for this metal should be consistently come from a green process as well. Equally important, the co-leaching of Al will need to be characterize to look at options from which other elements can be extracted commercially from spodumene, for a circular economic processing of the mineral and without having to generate a large volume of leach residue. The above are the set-out objectives of this research work.

In this research work, mechano-activation was carried out on an alpha spodumene concentrate sample using a laboratory size planetary mill PM 100 (Restch) which delivers a centrifugal acceleration of 33.3 g. Basing on the broad peak intensities of XRD diffractograms (measured at 14.5 two theta angle), highest degree of amorphisation at greater than 60% on a normalized scale resulted from activation done at highest milling speed of 600 rpm and dry milling. It was also found out that there is no direct correlation on the particle size distribution (PSD) of mechano-activated samples to the degree of activation. This was contrary to common notion that a finer PSD after mechano-activation would mean a higher degree of activation was effected. This was not the case for alpha spodumene. This simply means that mechano-activation is mainly dependent on the distortion of crystal lattices to effect a metastable highly activated state. From a combination of XRD and SEM-EDS analyses, it was also observed that the degree of mechano-activation was not uniform, in that there are large grains of alpha spodumene which appeared

to have not been subjected to mechano-activation. This was a consequence on the use of only one size of grinding balls. A combination of ball sizes will need to be used to improve the uniformity of mechano-activation.

The mechano-activated samples were subjected to a comparative direct leaching using (a) sulfuric and (b) citric acid. The sulfuric acid leaching resulted in Li leaching of 34%-56% and highest leaching was observed from the sample subjected to most intense of activation conditions: highest milling speed of 600 rpm, dry milling and highest ball: spodumene concentrate ratio of 50:1. The concentration of sulfuric acid also played a significant role in increasing Li lixiviation. Analysis using Main Effects plot confirmed that the highest milling speed incurred the highest Li leaching. This finding confirms that mechano-activation of alpha spodumene is effected by inducing structural damage (by impact). This will then facilitate Li leaching. From the leaching results, Li leaching was highest from samples which showed higher degree of amorphisation.

Aluminium codissolved to as much as 26% in the sulfuric acid leaching of mechano-activated alpha spodumene. It formed alunogen ($\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$) which is a hydrated aluminium sulfate. These products of hydrolysis were observed via SEM to precipitate randomly and at times covering spodumene surfaces and may have a contributory factor to limiting Li lixiviation from mechano-activated alpha spodumene. In contrast, the co-dissolution of Si is nil. The relatively higher co-leaching of Al is a good indicator on the degree of mechano-activation. Li and Al both sit at about the same level in the monoclinic structure of alpha spodumene, leaching of both Li and Al is an indicator of a good level of mechanical activation. Significant Si co-dissolution would mean an excessive mechanical activation, as the strongest bond energy in the spodumene structure lies in the silicate chains.

To contrast, the citric acid leaching suffered from a very slow kinetics and Li leaching was only 9% and increased to 17% after a month-long reaction time. This was an improvement though of the recent studies done using the same activator

mill in which the Li recoveries was 1.69%. Consistently, there was higher Li leaching from samples with a higher degree of amorphisation. Li/Al ratio wise, there was higher co-leaching of Al at 14.7% but the Si-codissolution was consistently nil.

Over-all, while there was relatively lower Li recovery from direct leaching of mechano-activated alpha spodumene shown from this research study, there are ways wherewith these can be improved further. Mechano-activation can then present as an alternative to conventional processing techniques by calcination. The greatest challenge at this point is the commercial design of activator mill that can deliver the forces effectively to lower energy consumption for such technique.

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Most importantly, to my wonderful family, for their tireless support and sacrifices. This journey certainly would not have been possible without the encouragement of my loving wife Hazel, who has always been part of my life adventure. From university days to our first work in a gold mine and our ten years stint in a copper refinery, to us completing the Group 12 family of elements with our kids Au,Cu,Ag and Rg and now to my studies of spodumene of which she was truly instrumental in discussing the subtle concepts with me- can't imagine metallurgy without you.

To my kids who tirelessly and unconditionally accept me as their weird father.

To Eistein and to his most truthful view on experimentation which has guided me throughout: "Insanity is doing the same thing over and over again and expecting different results."

It is with the thought of these wonderful people that I find the will to *keep moving forward*.

And most importantly to God, the source and author of all truth.

List of Publications

The following publications have resulted from the research presented in this thesis:

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Chapter 1

Introduction

1.1 Spodumene: demand and processing

Spodumene, $\text{LiAlSi}_2\text{O}_6$, is gaining popularity over the dominant resource of continental brines as a source of lithium (Li) (Kesler, et al., 2012). While extraction of Li from brines entails a relatively cheaper cost (Wietelmann & Steinbeld, 2014), Li extraction from pegmatites have shorter processing times, and offers economic benefit via a time-based strategy to take advantage of soaring Li prices (Kavanagh, Keohane et al. 2018). The increasing demand for Li chemicals most particularly Li carbonate and Li hydroxide is mainly triggered by rising demands for Li-ion batteries (LIBs) as applied in consumer products driven mainly by electric vehicles (Figure 1-1) (Theng 2018). Although there has been recent market disruption as caused by the global pandemic from COVID-19 (Wills 2020), the market growth projection for spodumene is still estimated to be at 10-20% compounded annual growth rate (Volta Foundation & Intercalation, 2022). The projected demand is expected to be met exceedingly by supply mainly from hard rock sources (Latham and Kilbey 2019).

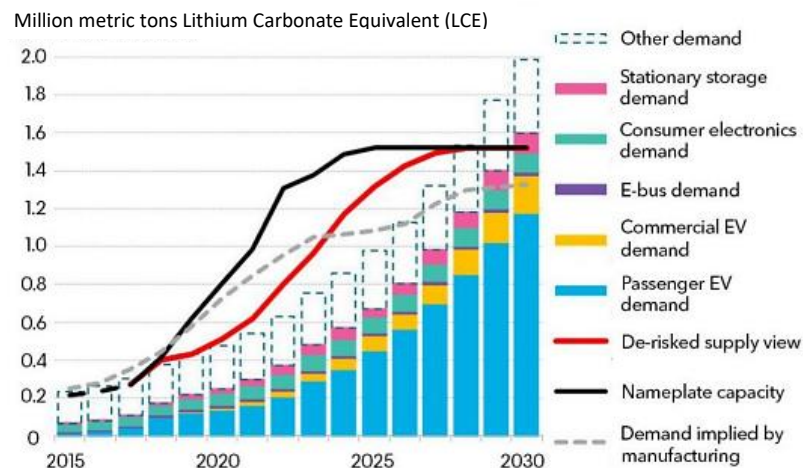


Figure 1-1. Supply and demand curve for Li chemicals (BloombergNEF, 2021).

The conventional processing of spodumene is energy intensive (Dlugogorski, 2018). It relies on decrepitation of alpha spodumene, in which high temperatures of 1000-1100 °C is utilised to convert the monoclinic structure to tetragonal structure (ANZAPLAN, 2022). The resulting open structure renders the mineral amenable to leaching (Chagnas & Swiatowska, 2015). This is realised by subsequent sulphation baking of converted spodumene at 250 °C followed by water leaching (Figure 1-2). While this conventional process is highly energy intensive, it has been adopted by many refineries as the technologies and equipment involved are commercially available and reliable (Galaxy Resources Ltd, 2008). Further, Li recoveries from this traditional treatment are very high at more than 95% (Rioyo, Tuset et al. 2020).

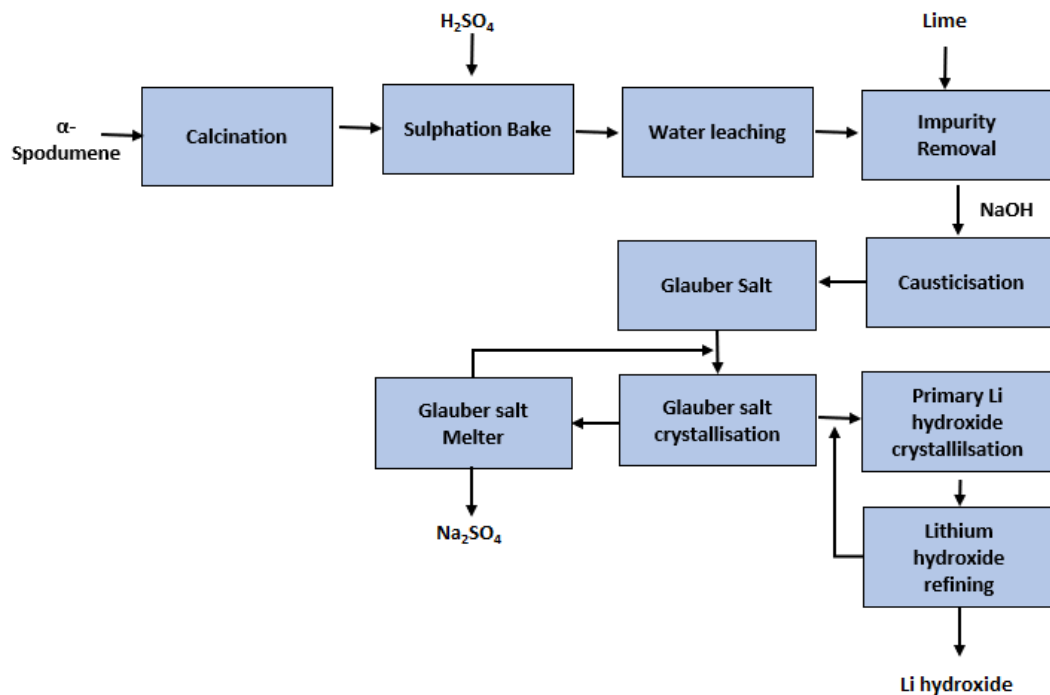


Figure 1-2. Typical flowsheet for processing of Li hydroxide from spodumene (Griffith, 2019)

This process however leaves a huge volume of residue which is currently being researched and promoted for use of supplementary cementitious material (Karrech, Azadi et al. 2020, Karrech, Dong et al. 2021).

1.2 Mechano-activation process

Mechanical activation, otherwise known as mechano-activation is a technique which relies on the use of mechanical energy to effect surface and structural changes in minerals, and

results in a metastable state which provides advantages in the subsequent process (Juhas and Pockzy 1990). It is carried out using high intensity milling. It differentiates itself from the usual size reduction step as crushing, grinding and pulverizing, in that these processes simply refers to size reduction without the loss of crystallinity. The end result of mechano-activation is an amorphous phase, and therefore increased free energy which makes the mineral reactive to metals recovery, e.g. leaching (Hennart et al. 2009).

The concept of mechanical activation can also be viewed from the point of view of energetics. While the conventional pre-treatment of alpha spodumene relies on the conversion of a refractory alpha phase to a more metallurgically treatable beta phase, by provision of heat on calcination (thermal activation), the same amount of energy can be supplied via milling. Thus, the design of the activator mill is crucial in any study of mechano-activation.

The use of mechano-activation can provide environmentally friendly alternatives to spodumene processing as opposed to the direct use of fossil fuel on calcination, as is in the traditional process. Mills can be easily run from green electricity. Successful application of mechano-activation for spodumene processing also offers benefits to process simplification, e.g. sulphation baking can be eliminated if direct leaching of mechano-activation can be implemented commercially.

The earliest studies on mechano-activation of spodumene was conducted on a monomineral beta spodumene, and showed very promising results (Berger, Boldyrev et al. 1990). This was on a use of an M3 centrifugal planetary mill and the intention was to lower the roasting temperature of mechano-activated beta spodumene. There was a succeeding study on the mechano-activation of a monomineral of alpha spodumene with very high leaching recovery of 90% (Kotsupalo, Menzheres et al. 2010). An alkaline leach after mechano-activation showed lower impurity co-dissolution and other by-products such as alum was proposed to be co-produced in the process. The successful mechano-activation was also conducted using an M3 centrifugal planetary mill.

The exceptional results reported above was never replicated. This was likely due to the different activator mills used in subsequent studies. More importantly, the design of the

M3 planetary mill used in the above researches was never commercialized but the design was patented.

The more recent studies on mechano-activation of spodumene concentrate using Restch planetary mill PM 100 have very poor results. Hwang (2019) researched on the citric acid leaching of mechano-activated alpha spodumene using low sample:ball ratio of 1:10 g/g and activation time of 30 min and Li recoveries were reported to be very low at 3%. Purba (2019) has explored the use of much longer activation times of 120 mins, still at spodumene concentrate to ball ratio of 10:1g/g, still with very poor Li recovery of less than 2%. The above results suggested that the milling conditions have not been optimized to promote activation.

Other studies on the mechano-activation of other Li-bearing silicate minerals petalite and lepidolite have reported activating these minerals using very long activation times of 2-4h. This was with the use of commercially available disc or ring mills (Vieceli 2017).

1.3 Motivation of the study

Mechano-activation provides an alternative route to extracting Li from spodumene. By breaking aluminum and silicate chains on mechano-activation, direct leaching of Li can be done. Such processing technique can simplify existing industrial treatment for alpha spodumene, which currently suffers from utilization of high energy on calcination and sulphation roasting.

While activation by milling also requires intensive energy, it is desired that understanding the conditions for effective mechano-activation of spodumene will result in a design (in future research work) for an activator mill that could deliver a lower energy requirement than heat-activation in calciners and kilns.

It is also desired that the co-leaching of Al and/or Si from leaching of mechano-activated spodumene samples will open more researches for the production of other by-products than Li and will promote effective resource utilization. The cost of alpha spodumene feed constitutes roughly 50% of the overhead cost of Li refineries (Gao, Fan et al. 2023). For example, alum or silica can be co-produced with Li chemicals if the alumino-silicate

structure is effectively destroyed and Al and Si values can be recovered from the leach solution.

1.4 Motivation of Investigation

This research aims to investigate the mechano-activation of alpha spodumene concentrate. Specifically, this study aims to:

- Investigate conditions for effectively activating alpha spodumene by use of Retsch planetary mill (PM100);
- Characterise the leaching behavior of mechano-activated alpha spodumene samples by direct sulphuric acid leaching;
- Investigate the citric acid leaching of mechano-activated alpha spodumene samples;
- Characterise the co-leaching of Al, Fe and Si in the leaching of mechano-activated spodumene, from both (i) direct sulfuric acid leaching and (ii) citric acid leaching. It is also aimed to look at ways from which the co-leaching of these elements paves way for its co-extraction and production of other by-products.

1.5 Structure of the Thesis

This thesis has 7 chapters.

Chapter 2 provides a thorough review of studies on mechano-activation of spodumene minerals. As these studies are limited, this chapter also provides a review on mechano-activation as applied to other Li-bearing silicate minerals petalite $\text{LiAlSi}_4\text{O}_{10}$ and lepidolite $\text{LiAl}_3\text{Si}_4\text{O}_{10}\cdot\text{OH}_2$.

Chapter 3 provides a narrative on the methodologies used in this research, from characterization of the spodumene concentrate samples, mechano-activation procedures, as well as characterization of the leach residue samples.

Chapter 4 discusses results of mechano-activation of the spodumene concentrate samples used as well other characterization done on the mechano-activated samples.

Chapter 5 discusses results of the direct sulfuric acid leaching of the mechano-activated alpha spodumene samples.

Chapter 6 discusses results of citric acid leaching of mechano-activated alpha spodumene samples.

Chapter 7 concludes the study and describes further possible areas of research following developments made in the present study.

Chapter 2

Review of Related Literature

2.1 Introduction

Mechanical activation, known commonly by its shortened term *mechano-activation*, is a technique which relies on the use of mechanical energy to generate surface and structural changes in minerals, and results into a metastable state (Juhasz and Opoczky 1990). The term was originally introduced by Smekal in 1952 (Smekal.A.G., 1952). It is commonly carried out using high intensity milling in an activator mill. It differentiates itself from the usual size reduction step as crushing, grinding and pulverizing, in that these processes simply refers to a size reduction without a significant loss of crystallinity in a mineral subjected to such treatment. The end-result of mechano-activation is an amorphous phase, and therefore results in an increased free energy. This increase in free energy provides for the activation that makes the minerals more reactive to a chemical treatment, e.g. higher leaching recoveries (Hennart et al. 2009).

The forces inside a planetary mill is caused by the motion of grinding media and processed material and includes impact forces when milling media falls at high speed in contact with processed material; attrition forces when material rubs with other particles or with milling media; and very high centrifugal forces (Tole, Habermehl-Cwirzen et al. 2019).

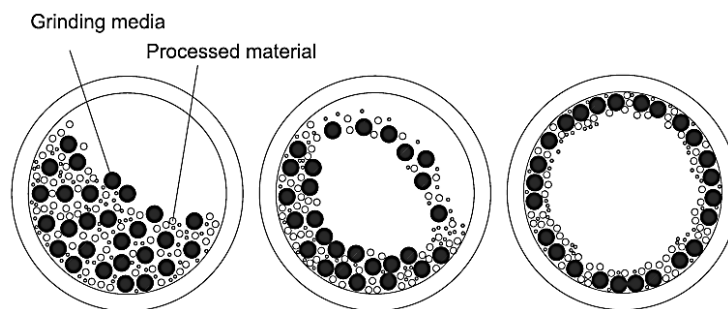


Figure 2-1. Diagram of the relative motion of grinding media and processed material: cascading, cataracting and rolling (Burmeister and Kwade 2013)

The effect of mechano-activation can be classified into two categories: (1) primary process which is characterized by a general increase in the reactivity of the mineral as brought about by an increase of surface area, surface energy and decrease of coherence energy of solids; (2) secondary processes which can proceed spontaneously in an activated system and may show up during mechanical activation (e.g. grinding) or even after activation has been completed. This secondary effect can be seen as aggregation, adsorption or recrystallisation of new phases (Juhasz 1974, Boldyrev, Pavlov et al. 1996, Boldyrev 2018).

A variant to *mechano-activation* treatment is *mechano-chemical* activation. The latter technique relies in the synergistic effect of mechanical and chemical treatment to effect physicochemical changes in minerals (Boldyrev 2018).

In this chapter, previous studies on the mechano-activation of spodumene mineral is reviewed along with a review of mechano-activation of common silicate minerals. To date, there appears to be some inconsistencies on the definition of mechano-activated samples, and thus, this chapter will endeavor to define the term based on current arguments. Addressing the ambiguities early on will help clarify the objectives and will set the tone for the analysis of the test results generated from this study.

2.2 Defining amorphicity

The measure for incurring mechano-activation in a mineral sample is the production of an amorphous phase from a crystalline structure. From literature, there seems to be a lot of ambiguity when defining amorphous materials. In general terms, amorphous materials are characterised by a short-range order, or have loose long-range order. This definition lacks a sharp distinction between short and long range as to what really constitutes an amorphous or a crystalline material. To complicate things further, it has even been reported that even crystalline materials have amorphous surface layers to the thickness of 3 crystallographic units.

A clearer definition of amorphicity is given by Klug & Alexander (1974), "Amorphous solids must be reserved for substances that show no crystalline nature whatsoever by any of the means available for detecting it." This definition provides a relative perspective from the point of reference to the analytical methods used in determining amorphicity. For example,

the use of conventional XRD loses its resolution on nano-scale and gives rise to the phrase, 'Xray-amorphous' to highlight the limitations of X-ray diffraction technique.

In this research work, the same definition will be applied. The measure for defining a mechano-activated sample will be based on the diffractograms of an XRD. The specifications and equipment details used in this research work will be disclosed in the next chapter.

2.3 The mechano-activation of spodumene

As popularly known in technical literature, spodumene belongs to pyroxene group of minerals and exist in 3 polymorphs. Spodumene exist in its natural state alpha spodumene $\text{LiAlSi}_2\text{O}_6$ which has a density of 3.184 g/cm^3 and has a monoclinic crystal structure (Salakjani, Singh, & Nikoloski, 2020). Beta spodumene $\text{LiAlSi}_5\text{O}_{12}$ has a tetragonal structure and is the most reactive form of spodumene. The expanded crystal structure of beta spodumene caused a reduction of its density to 2.374 g/cm^3 . From Chapter 1, the irreversible transition of alpha to beta form is easily done by calcination at temperature range of $950\text{-}1100 \text{ }^\circ\text{C}$, and this conversion is more sensitive to temperature rather than heating rate (Rioyo, Tuset et al. 2020). The third polymorph of spodumene is gamma phase, $\text{LiAlSi}_5\text{O}_{12}$ which has a hexagonal structure and a density of 2.399 g/cm^3 . The gamma phase is a metastable state. Due to this, only very little is known of the gamma state of spodumene.

From the above background information, it easily follows that the mechano-activation of alpha spodumene would require higher energetics as compared to beta spodumene. This is not surprising as a study based on first principles revealed that alpha spodumene has the highest largest bulk shear, Young's modulus and hardness, making it the most stable form of spodumene (Zhang, Duan, & Li, 2017). To understand better the comparative differences, previous studies on mechano-activation of alpha spodumene is discussed and compared to that of mechano-activation of beta spodumene in the succeeding sections.

Generally, the amount of mechanical activation effected can be described mathematically using the following equation (Torres, Sanchez et al. 1989):

$$G(X) = X_0 + F(x) \quad \text{Equation 1}$$

Where $G(x)$ is the overall kinetic model on leaching, X_0 is the mechanical conditions and $F(x)$ represents both the mechanical and kinetic conditions (e.g. temperature and concentration on leaching).

The above equation simply means that dissolution reaction rates of a mechano-activated sample is a complicated function of many variables that includes external factors as the dissolution environment (solvent and its constituents, pressure, agitation speed, temperature) and internal factors as crystal condition (crystal structure of minerals present, impurities present in the crystals, crystallographic orientation, presence of microcracks, dislocations) (Eggleston 1988). Mechano-activation can be viewed as a pre-treatment procedure to induce structural damage which can then be largely classified into three:

- (i) Damage resulting in the generation of finer particles and/or low radius of curvature which can dissolve relatively quickly;
- (ii) Damage resulting in distortion but not breakage of bonds, e.g. XRD line broadening which could mean either reduction in crystallite size and/or distortion of crystal structure;
- (iii) Damage resulting from breakage of bonds, e.g. formation of microcracks; microcracks provides additional access to exterior reactants to aid on dissolution

Due to the condensed and stable structure of alpha spodumene, earlier studies noted that dominance of third type of structural damage as listed above is ideal for spodumene for Li lixiviation to occur.

2.3.1 Mechano-activation of alpha spodumene

There was only one literature which claimed the successful mechanical activation of alpha spodumene. Kotsupalo et al. (2010) reported the mechanical activation of monomineral alpha spodumene using an M-3 centrifugal planetary mill and the subsequent extraction of Li with high recoveries of 96-99% on sulfuric acid leaching and a comparative recovery using alkaline leach. Their research claimed that complete amorphization of the spodumene in aqueous medium took place after 30 min of milling in aqueous medium or milling in air for 10 min. It was reported that alpha spodumene milled in air is more amorphous and tends to be agglomerated while alpha spodumene

milled in water is more dispersed but less amorphous. Due to the high solubilization rates of Li, it was believed that the mechano-activation was able to induce cleavage on the Li,Al-O sites

The details of the milling condition were not disclosed in the report. No technical literature can be found with regards to similar studies, replication of such study or a follow-up study from the researchers themselves. This is quite surprising given the high Li recoveries and the potential for processing simplification with replacement of mechano-activation over the use of calcination with sulphation baking to solubilise Li from spodumene.

It is to be noted that Kotsupalo et al. used M3 centrifugal planetary mill in effecting the mechanical activation of spodumene. The only reference that can be found with regards to such design is a schematic drawing of Avvakumov (1986) in Kheifes and Lin's Energy transformation (1996) (see Figure 2-2 below). The principle is very similar to a Retsch planetary mill but the jars are resting horizontally rather than vertically. The net effect is a higher impact energy generated as the balls will be thrown at a longer axis as compared to the vertical sitting jars in Restch planetary mills. This design is patented by Avvakumov but there are no commercial units of this type of mill activators. This may could have explained why the results of the study made by Kotsupalo et al. (2010) was never replicated.

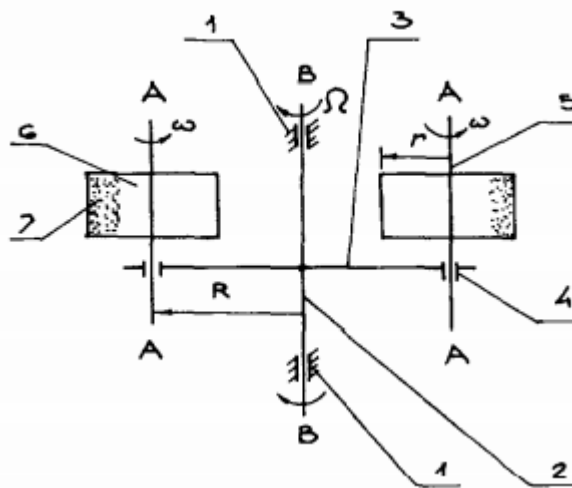


Figure 2- 2. Schematic diagram of the planetary mill structure A chamber axis; B central axis; R radius of movement of translation (radius of carrier); r radius of relative movement (chamber radius); Ω angular velocity of translation; ω relative angular velocity; 1 central bearing; 2 central shaft; 3 carrier; 4 chamber bearing; 5 chamber shaft; 6 chamber; 7 grinding medium (Avvakumov 1986)

Another potential reason why there was effective activation on this research work was due to the use of mono-mineral alpha spodumene. The sample used was 99 wt. % spodumene as compared to 70-75% spodumene content in spodumene concentrate. The energy dispensed on milling was utilized only on the activation of spodumene and not on other minerals which could have been present if the material used was a spodumene concentrate. In other words, the energy ratio to spodumene (not accounting for the losses) was higher in this study.

A study by Torres et al. (1989) on mechano-activation of alpha spodumene using Herzog HSM 100 oscillating mill claimed that there was increased in Li peak intensities on the surface of mechano-activated alpha spodumene after 50 min of milling. Herzog oscillating mills works like ring mills and are relatively gentler than a planetary mills (Table 2-1). The intensities were measured by X-ray Photo Spectroscopy. There was doubling of intensities of Al 2p and Si 2p while Li 1s intensities increased in multiples of 12. These means that the milling action was able to expose these surfaces. However, the investigation reported on the solubilization of Al only, and there was no disclosure on Li solubilization. The Si in the leach residue increased in expense of Al dissolution. The degree of amorphization of the activated samples via the conventional method of XRD was not measured.

Table 2- 1. Summary of Activator mills and milling mechanisms from technical papers.

Equipment	Conditions	Milling mechanism/Notes	References
TsMA-06 centrifugal activator	2-6 kg/h	Not available	Borisov et al. (1982)
Ago 10	30 kg/h	Not available	Avvakumov (2006)
HERZOG HSM 100 oscillating mill	20 min with 20s interval -some peaks still exist	Similar to a ring pulveriser. Works through friction and the impact caused by the relative movement of a ring and a concentric cylinder, placed within a casing containing the material to be ground	Torres et al. (1989)
Disc mill	15 min on lepidolite	Compression, shear, and impact	(Vieceli 2017)
M3 centrifugal planetary mill		Material is subjected to impact, shearing, and friction forces as brought about by ball-ball and ball-wall collision; G is 50-60	Avvakumov (1986); Berger et al. (1990) Kotsupalo et al. (2010)

Both studies were able to establish that activation by mechanical means is significantly a function of the design of the activation mill and that a higher degree of activation is expected from a high energy mill as long as the energy is utilized for activation and there is less losses in the form of heat.

A variant approach to mechanical activation of alpha spodumene is activating the mineral concentrate followed by heating (Kotsupalo, Menzheres et al. 2010). The energy accumulated during mechanical activation is released on heating and increases the exothermic reaction, which often results in lowering of calcination temperature. The converted beta spodumene can then be directly leached with sulfuric acid and does not have to undergo sulphation roasting (Samoilov, Borsuk et al. 2009).

2.3.2 Mechano-activation of beta spodumene

The earliest studies on mechano-activation of spodumene was conducted on beta spodumene, and such topic is the widely investigated area. Berger et al. (1990) performed mechanical activation of a mono-mineral of beta spodumene using an M3- two drum planetary mill using the following conditions: 600 ml, rotation speed of jars in its own axis at 1000 rpm and rotation of drum on the general planetary axis is 425 rpm, charge to ball ratio of 1:50. The steel balls used was 3.5 mm. The centrifugal acceleration was 90 g. It was claimed that after 10-15 min in the mill activator, the beta spodumene samples was X-ray amorphous (Figure 2-3). The Li recovery on subsequent leaching was 90-98% on samples activated for 3-10 min. The study also showed that plane {400} is the most responsive to mechano-activation as shown in Figure 2-3, while plane {201} is the least responsive. Plane {201} is normally the growing plane for beta spodumene(Wang, Hon et al. 1988). Plane {400} on the other hand represents d-spacing of 1.884 with peak intensity of 8. It is to be noted that the planes described in here are planes in a tetragonal crystal system for beta spodumene and not for a monoclinic alpha spodumene.

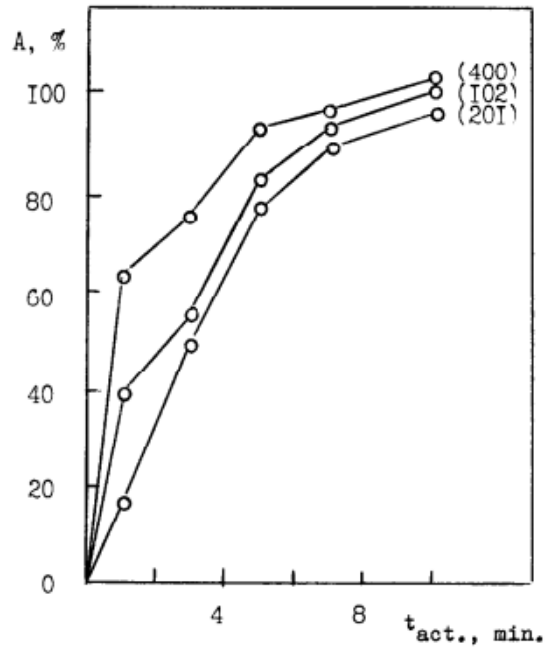


Figure 2- 3. Degree of amorphization on mechano-activated beta spodumene samples as a function of activation time (Berger, Boldyrev et al. 1990).

Torres et al. (1989) performed mechano-activation of beta spodumene using a Herzog HSM 100 oscillating mill with a milling time of up to 50 min with 20 s interval for mixing the sample. The activation was measured by titration to locate the point of zero charge (PZC). Results showed that PZC values vary depending on the content of Li and Al oxides in the surface, e.g. PZC was found at pH 8 for samples with high aluminum oxide. Li can also shift the PZC to a higher pH (Figure 2-4). It was also reported that the increase of iron oxide from mill contamination does not affect the PZC values. The main finding of the study is that there is an increase on concentrations of Li, Al and Si on the surface in direct proportion of mechanical treatment time.

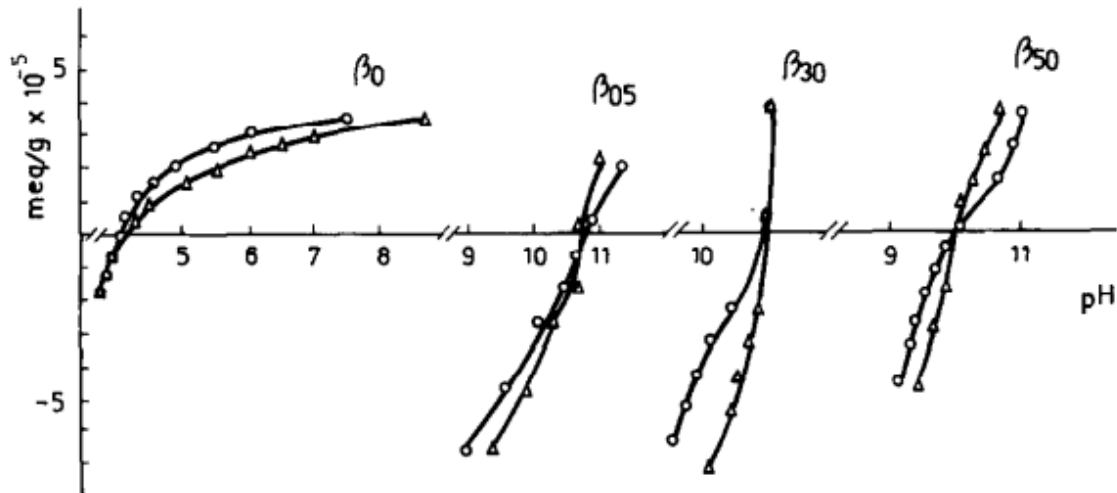


Figure 2-4. Titration curves for mechano-activated beta spodumene samples as a function of time (Torres, Sanchez et al. 1989).

2.3.3 Mechano-activation of other Li-bearing minerals

Not only does mechano-activation technique been tested on spodumene minerals but recently, there has been a few studies which have explored the use of this technique to other Li-bearing minerals, petalite $\text{LiAlSi}_4\text{O}_{10}$ and lepidolite $\text{LiAl}_3\text{Si}_4\text{O}_{10} \cdot \text{OH}_2$

Petalite and lepidolite are both in monoclinic crystal system and their silicate structure is classified as phyllosilicate. Phyllosilicates are sheet silicates which render to easy leaching. In contrast, spodumene is a chain silicate or inosilicates which are established to be refractory.

The mechano-activation of petalite with the work conducted by Setoudeh et al. (2020) involved the use of sodium sulfate in the 5 h milling of petalite, followed by calcination at 1000°C for an hour and then hot water leaching at 80°C to recovery Li values. The Li recovery was very high at 99%. However, it appears that this process defeats the purpose of mechano-activation as a replacement of thermal treatment. The lixiviation of Li follows after petalite converted to LiNaSO_4 after mechano-chemical activation with sodium sulfate followed by thermal treatment.

The mechani-activation of lepidolite was done with high Li leaching recoveries of $>85\%$ (Vieceli, Nogueira et al. 2017). The concentrate was activated for 15 min, followed by acid baking at 165°C for 4 h at a dosage of 650 g sulfuric acid/kg lepidolite concentrate. This

was followed by water leaching. The effect of mechano-activation was mainly to reduce the sulphation temperature.

Results show that activation or milling time was directly proportional to Li recovery up to an activation time of 15 min at which Li recovery stabilizes at 80% from activation time of 15 min even up to 45 min. For reference, Li recovery was low at 60% for 5 min grinding time and was at 55% when no activation was used.

Recently, a patented process of using planetary mill as an activator mill for mechano-chemical activation of clay minerals was published. The patent reported using PM 100 and activating for 2 h at 500 rpm and adding NaCl as source of Cl for lixiviating Li through the subsequent leaching process (USA Patent No. US2021/0207243A1, 2021). The described process suffers from low Li recovery of < 65% and prolonged activation times.

2.4 Chapter Summary

Mechano-activation is a technique of using mechanical energy to generate surface and structural changes in minerals, resulting in a meta stable state, and thus, a reactive state. Mechano-activation is highly dependent on the milling conditions and thus, on the type of mill activator used. The mill that could provide a more intense or high energy milling would effect the highest activation. As there is ambiguity in the definition of amorphicity, the best definition adopted is referenced to the analytical method used to determine it, e.g. X-ray amorphous.

The previous studies done for mechano-activation of alpha spodumene and beta spodumene has been done using different activator mills as summarized in Table 2-1. As the type of mill used can significantly affect the outcome, identifying this as a major variable could explain why the results from each studies are different and that why a replicated study could not be found. For example, the use of M3 planetary mill from Kotsupalo's work was reported to have very high Li mobilization on leaching. The M3 planetary mill design is patented and is limited to lab-scale only. It was never commercialized.

Chapter 3

Materials and Methods

3.1 Introduction

Mechano-activation of spodumene relies mainly on the destruction of the spodumene lattice using mechanical energy. The lattice distortion creates a meta stable state of the mineral and renders the mineral reactive. The degree of activation is dependent on the degree of destruction of the crystallite lattice as the microcracks induced on activation would provide for enhanced penetration of lixiviants on leaching (Gasalla and Pereira 1990).

To understand the degree and extent of mechanical activation, it is imperative that a sound characterization of the spodumene sample as well as mechano-activated samples, particularly understanding the sample's chemical and physical properties must be undertaken. This chapter thus provides details on the materials and methods used in the conduct of this study. The objective of this chapter is to provide discussion on the following:

- (1) Procedures of sampling and characterization of spodumene concentrate sample;
- (2) Mechano-activation of spodumene including details of milling condition;
- (3) Leaching procedure base on traditional sulfuric acid leach and compared with citric acid leach;
- (4) Analytical techniques utilized to characterize the mechano-activated samples and leach residue samples.

3.2 Sample preparation and characterization of spodumene concentrate

A 2-kg spodumene concentrate sample was sourced from Bald Hill, Western Australia. The spodumene concentrate was produced from a beneficiation process via dense media separation.

The sampling method used in the study is shown in Figure 3-1. First, the bulk spodumene concentrate sample was subjected to homogenization by mat rolling and sample splitting using Jones riffle splitter (Sepor). Sample from split A was then crushed using disc pulverizer (Rocklabs) and the pulverized concentrate was again subjected to riffle splitting. Sample from split A.1 was used for physical and chemical characterization while samples from split A.2 was used for mechano-activation test work.

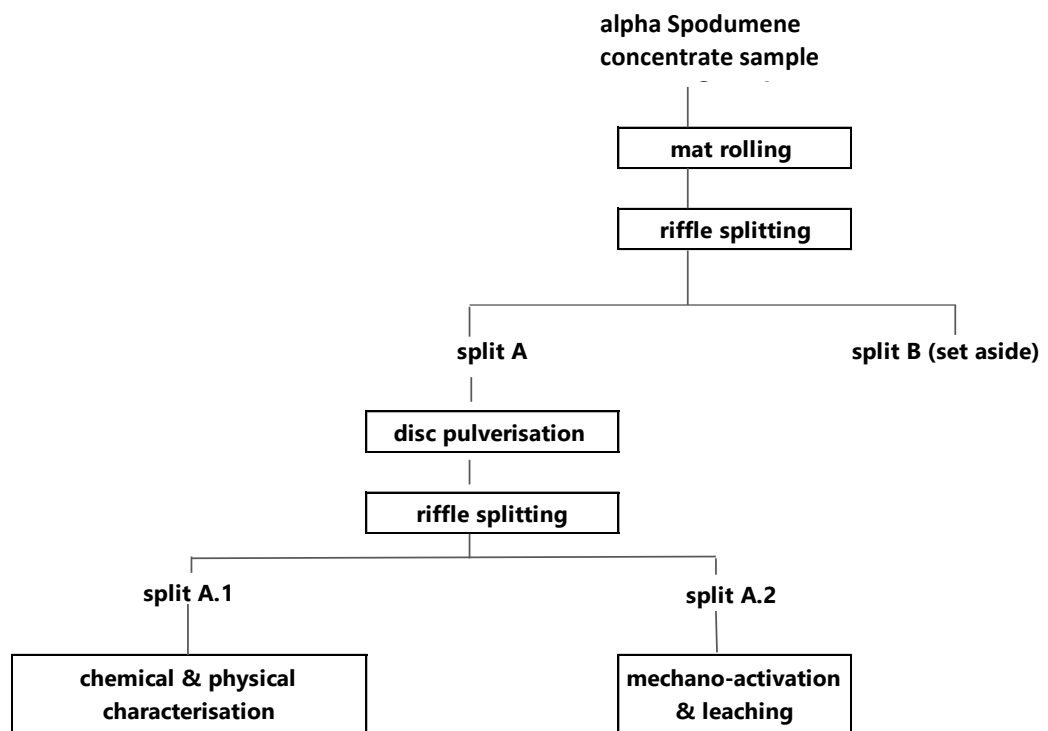


Figure 3- 1. Sampling Method.

Physical characterization of the 'as received' spodumene concentrate sample was mainly sizing analysis which was done by screen analysis (SM200, IMP Innovative Solutions). Visual examination by the naked eye and by light microscope (Meiji MTL93) was also used to examine some of the physical attributes of the mineral components in the sample.

Chemical analysis of the spodumene concentrate was done by XRF (S8 Tiger Bruker) peroxide fusion with Li analysed by ICP-OES (Agilent 5800). Mineral composition of the concentrate was analysed by XRD (Rigaku MlniFlex), as done commercially by Microanalysis Australia.

3.3 Mechano-activation

Mechano-activation of samples was done at WASM laboratory in Kalgoorlie using a planetary mill PM100 (Retsch) (Figure 3-2). Specification of the planetary mill is provided in Appendix A. The mechano-activation was done using 5-mm stainless steel balls. No zirconia beads were available for use; some sighter test using alumina balls were also explored to prevent contamination, but there was flaking and popping of alumina balls due to the heat generated on mechano-activation.



Figure 3- 2. Planetary mill PM 100 used in mechano-activation of spodumene sample (RETSCH, 25 Jan 2023, Planetary Ball Mill PM 100 - RETSCH - highest fineness)

The experimental plan table for the testwork was designed using Minitab 10.2. A definitive screening design was used with four factors and three settings of low, medium and high for each factor (Table 3-1).

Table 3- 1. Definitive screening design for initial testwork on mechano-activation.

Factors	high	medium	low
ball: spodumene concentrate ratio, g/g	50:1	30:1	20:1
solids density, %	100	30	10
Milling speed, rpm	600	500	300
milling time, min	15	10	5

The objective of the test work was to explore milling conditions with a consideration of the following factors: solids density (wet milling versus dry milling), milling speed, ball to spodumene concentrate ratio (abbreviated in here as spod. conc.), and milling time. In detail, the experimental plan table for initial test work is as below (Table 3-2). The sample weight used was 20 g. This means that for a solids density of 10 % (Table 3-1), the amount of water added was 180 g.

Table 3- 2. Experimental plan table generated from the definitive screening design using Minitab 11.2.

Run Order	Ball: Spod conc. ratio, g/g	Solids density, %	RPM	Milling time, min
A	30:1	10	500	10
B	50:1	10	600	5
C	20:1	10	300	15
D	50:1	100	600	10
E	20:1	30	600	5
F	30:1	100	300	5
G	20:1	30	300	10
H	20:1	100	500	5
I	50:1	100	300	15
J	50:1	30	500	15
K	20:1	100	600	15
L	30:1	30	600	15
M	50:1	30	300	5

For wet-milled samples, the slurry was collected in glass beakers and the residual slurry in the milling jar was collected by washing with water and collecting the washings. Excess water was decanted, and the paste was collected in deep aluminum trays and dried overnight in an oven (Labcon) at 40 °C. The drying was purposely done at low temperature to avoid potential de-activation by heat (Gasalla and Pereira 1990).

Assessment on mechano-activation of spodumene mineral samples was done by XRD (Olympus BTX II, Cu X-Ray source), reading from the peak intensities and indicated by the change of diffractogram signatures from crystalline to amorphous. XRD equipment settings: radiation by $\text{CuK}\alpha$ ($\lambda = 1.54 \text{ \AA}$), an angular range of $7\text{-}100^\circ 2\theta$, step size of 0.015° . The software used to determine the phases was X Powder Ver.2010.35.PRO.

Particle size analysis of the mechano-activated spodumene was done using Mastersizer 3000 (Malvern) using water as medium. Sample was slurried in water, chemical dispersant was added (5% Decon solution) and the slurry was ultrasonicated (Unisonics) to correct for potential agglomeration of fine particles.

A sample of mechano-activated material was sent to Microanalysis Australia for SEM (Carl Zeiss EVO50) and XRD (Rigaku, Co X-Ray source) analysis. The search match software used was Eva 4.3.

3.4 Leaching

Mechano-activated samples were subjected to a comparative leaching tests using a) sulfuric acid (H_2SO_4) and b) citric acid ($\text{C}_6\text{H}_8\text{O}_7$).

Leaching tests were conducted using the following reagents: sulfuric acid (Analar, 98%), sodium bicarbonate (Rowe Scientific, 84.01 g/mole) and citric acid (Rowe Scientific, 192.12 g/mol). Deionized water of 18 Ω purity was used to prepare solutions.

The following equipment was used in the conduct of leaching test: Thermo Fisher Scientific 2200 hotplate ($0\text{-}350^\circ\text{C}$), 3-L IEC magnetic stirrer hotplates with PTFE top, alcohol thermometer ($0\text{-}110^\circ\text{C}$), TPS Aqua pH meter and centrifuge (C28A, Boeco Germany).

In the leaching test following mechano-activation test work, the following factors and settings were investigated:

Table 3- 3. Conditions for the comparative leaching tests.

Lixiviant	Concentration	Solids: liquid ratio	Temperature, $^\circ\text{C}$	Leaching time, h
Citric acid	3 M, pH adjusted by sodium bicarbonate	1 kg:20 L	70 +/- 5	1-3
Sulfuric acid	50% w/w	1 kg:20 L	70 +/- 5	1

At termination of leaching, slurries were decanted to centrifuge tubes and were centrifuged for 10 mins at 400 rpm. On some occasions when the centrate was still not clear, the centrifugation was repeated. The centrate was then collected and filtered using syringe filter fitted with 5 μm filters, final filtrate were then submitted for assays.

3.5 Analysis of leach solutions and characterization of leach residue

Leach solutions were analysed for Al,Ca, Fe, K,Li, Na, Si and S by ICP-OES (Agilent 5800). The leach residues were fused in sodium peroxide and potassium hydroxide bead and analysed by XRF (S8 Tiger Bruker) for Al,Ca, Fe, K, Na, Si and S. The fused bead is digested with HCl for analysis of Li by ICP-OES (Agilent 5800). The leach residues were also sent for semi-quantitative XRD and SEM analysis (by Microanalysis Australia) and TGA (IMP Innovative Solutions).

3.6 Scope and Limitations

This research focuses on conditions for activation of α spodumene by mechanical means and focuses on the use of Restch planetary mill (PM 100) to carry out the activation. The design of the activator mill has a profound effect on the degree of activation of mineral samples.

Due to the limitation in the available equipment for use in the study, the use of stainless balls on mechano-activation was the only explored route. The use of stainless steel balls for an intensive milling regime for such an abrasive material as α spodumene is expected to cause some form of contamination from the grinding media. The amount of contamination is specified in the study as well as the likely impact of Fe contamination on the leaching behavior of Li from mechano-activated samples.

The mechano-activation of β spodumene was not explored in this research work. Moreover, mechano-chemical activation of α spodumene is also not included in this research as the main objective is to understand the conditions for effectively inducing mechanical activation only, as measured by the subsequent leaching of Li into aqueous solutions.

This study focuses on conditions for mechano-activating alpha spodumene and not on enhancing leaching conditions. Leaching was used to gauge and compare degree of mechano-activation induced on alpha spodumene concentrate sample.

3.7 Summary

The schematic diagram below summarises the methodology used in this research work to study the mechano-activation of spodumene and its direct leaching of Li comparatively using citric and sulfuric acid.

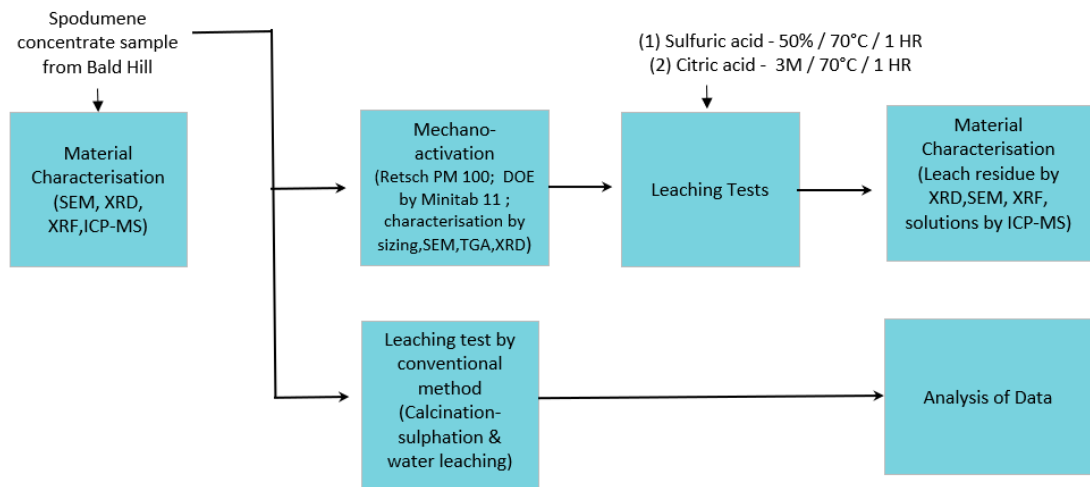


Figure 3- 3. Schematic diagram of the methodology used in the study.

Chapter 4

Mechano-activation of spodumene

4.1 Introduction

Alpha spodumene is lithium aluminosilicate crystallised in a stable monoclinic crystal structure (Figure 4-1). It belongs to mineral group pyroxene, in which the silicate (SiO_4) tetrahedrons polymerizes to form one-dimensional chains of indefinite length (Deer et al., 1997). Because of this and its monoclinic crystal structure, alpha spodumene is hard, abrasive and resistant to chemical treatment. The weakest plane of alpha spodumene is $\{101\}$ (Moon and Fuerstenau 2003). This plane exposes both Si and Al.

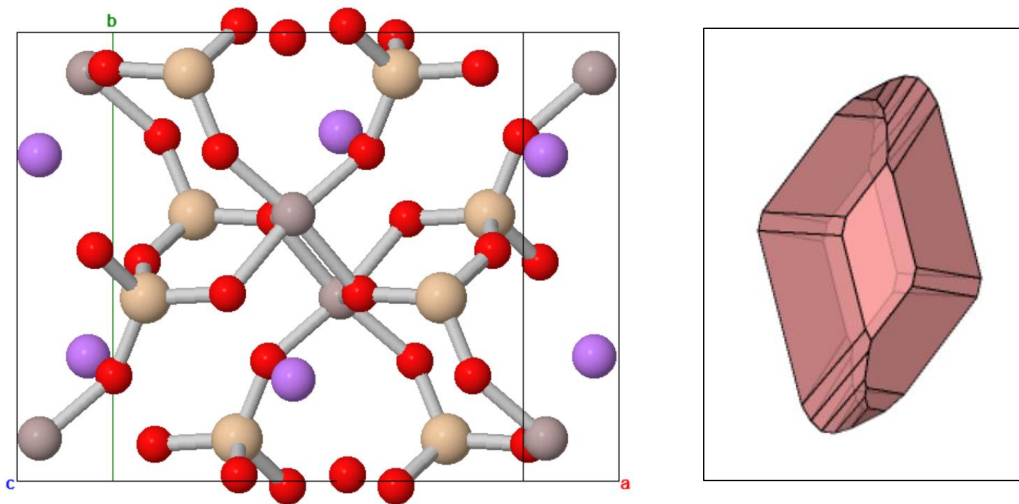


Figure 4- 1. Crystal structure of spodumene showing arrangement of Si (light brown), Al (gray) and O (red) atoms, lithium depicted as purple spheres; spodumene crystallizes in monoclinic structure (right)

This chapter discusses the experimental results of the mechano-activation of alpha spodumene sample. Firstly, the physical and chemical characteristics of the spodumene sample used in this study is discussed. Secondly, the milling conditions which resulted in mechanical activation of spodumene samples are discussed. This is gauged mainly on XRD diffratograms of the activated samples. Assessment on the efficacy of mechano-activation as measured by Li solubilization on leaching which will be discussed separately in the next chapter.

4.2 Aims of the Chapter

This chapter discusses investigations to the following:

- Characterisation of spodumene sample;
- Mechano-activation of alpha spodumene using stainless steel balls in a Retsch PM 100 planetary mill;
- Physical and chemical characterisation of mechano-activated samples.

4.3 Characterisation of alpha spodumene sample

The spodumene sample was sourced from Bald Hill and was produced by dense media separation (DMS). From the XRD analysis done, the major minerals in the sample are spodumene, quartz, muscovite, and some feldspars (Figure 4-2). Spodumene constituted about 90% of the concentrate sample (Table 4-1). The spodumene peaks are evident on the $14.5^\circ 2\theta$ which represents the $\{110\}$ plane- the main cleavage plane of the mineral (Moon and Fuerstenau 2003) (Figure 4-2).

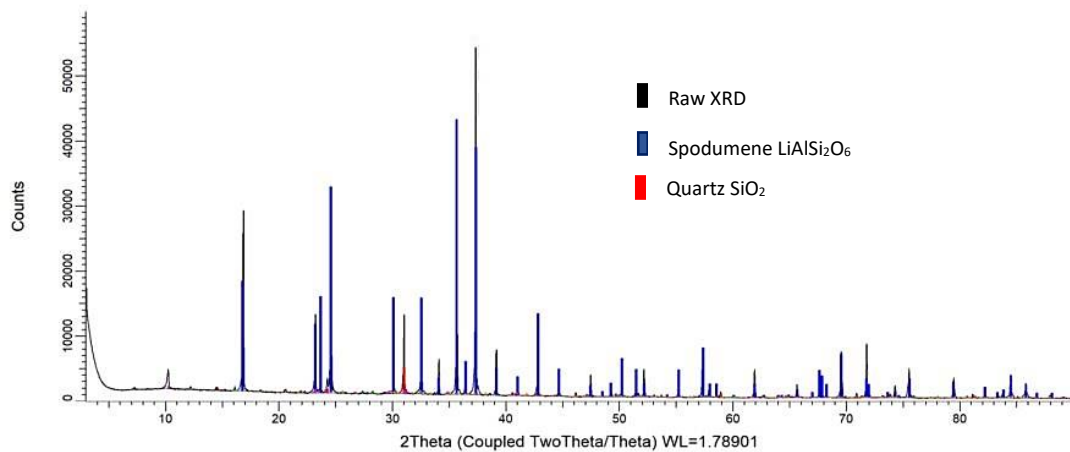


Figure 4-2. XRD diffractogram of alpha spodumene sample

Table 4.1. Semi-quantitative XRD analysis of spodumene feed sample used in this research, analysed using EVA 4.3 software

Crystalline mineral phase	Concentration (%)
Spodumene (LiAlSi ₂ O ₆)	90
Muscovite-2M1, Fe+3-bearing (K _{0.92} Na _{0.08} Al _{1.88} Fe _{0.12} Mg _{0.04} (Al _{1.08} Si _{2.92} O ₁₀)(OH) _{1.89} F _{0.11})	2
Quartz, syn (SiO ₂)	3
Amphibole, syn Sodium Magnesium Silicate Hydroxide (Na _{1.6} Mg _{6.2} Si ₈ O ₂₂ (OH) ₂)	2
Albite (Na _{0.98} Ca _{0.02} Al _{1.02} Si _{2.98} O ₈)	2
Clinochlore-1MIIb, Fe+2-bearing ((Mg,Fe) ₆ (Si,Al) ₄ O ₁₀ (OH) ₈)	1

Some of the minerals can be easily identified by the naked eye: spodumene minerals are the white grains with a greenish tinge typical of hiddenite variant of spodumene, flaky shiny grains of muscovite, vitreous quartz grains while the black minerals are mainly basalt (Figure 4-3).



Figure 4-3. Alpha spodumene sample showing coarse size fractions of green spodumene

From XRF analysis (Table 4-2), the Li content of the spodumene sample was 2.98% which is the usual chemical grade of spodumene used as feed to refineries producing battery grade Li chemical. The Si and Al content are at the comparable values at 29.8% and 13.4% respectively. It is to be noted that the feed sample has an Fe content of 0.84%.

Table 4- 2. XRF analysis of the feed spodumene sample used in the study (prior to mechano-activation)

Sample Description	XRF assays, %							
	Al	Ca	Fe	K	Li	Mg	Na	Si
Sample 1	13.3	0.30	0.79	0.59	2.98	0.21	0.40	29.6
Sample 2	13.4	0.29	0.88	0.58	2.98	0.21	0.41	30.0
Average	13.4	0.30	0.84	0.59	2.98	0.21	0.41	29.8

The particle size distribution of the as-received sample was not profiled. The as-received sample was ground using jaw crusher followed by pulverization using disc pulveriser. The PSD of the pulverized sample was D_{80} 106 μm and form as a feed for mechano-activation treatment.

4.4 Mechano-activation using stainless steel balls in a planetary mill

4.4.1 Degree of Amorphicity

A stack of the XRD diffractograms is shown in Figure 4-4. It can be easily observed based on the characteristics of the peaks that only four samples were mechanically-activated as can be seen by its characteristic broad peaks: samples D, J, K and L. This can be evaluated by comparing the intensity or peak height at the dominant plane at angle of 14.5° 2θ (Table 4-3). As can be seen in Figure 4-4, samples D, J, K and L all experienced broadening of peaks at 14.5° 2θ while the rest of the samples have this peak still highly recognizable. Evidence on the loss of crystallinity in the samples is summarized in Table 4-3, in which a comparison of the intensity counts of the peaks at 14.5° 2θ , and the estimated normalized degree of amorphization is provided. The estimation is based on the decrease of peak at 14.5° 2θ as effected by milling, and normalized for easy comparison. As shown in Table 4-3, for the 14.5° , sample K has the lowest intensity count at 15 or the highest degree of amorphization, followed by sample L at 63 counts, then sample D at 81 and sample J at 137 counts. In summary, samples D, J, K and L have degrees of amorphization (normalized) greater than 50%. Sample M is interesting in that while the peak signatures are somewhat in between broad and crystalline, these peaks were also slightly offsetted to the left, notably observable at 31° 2θ (Figure 4-4). Degrees of amorphicity on other angles is shown in Appendix B and showed the same relative pattern of amorphicity on other planes. It is also very interesting to note that the highest peak for

all samples shifted to the $30.35^\circ 2\theta$ instead of 26.30° and $27.95^\circ 2\theta$ for non-milled alpha spodumene (Figure 4-5.) A qualitative assessment of the comparative peaks in Figure 4-4 is shown in Table 4-4.

The peak at $14.7^\circ 2\theta$ represents the plane {110} (Figure 4-4). This plane exposes the Al and silica tetrahedron (Xu, Hu et al. 2016)(Figure 4-5). It is expected that with the mechano-activation, this plane would have some distortion, as it is the exposed surface. From the XRD diffractograms shown in Figure 4-4, it appeared to be the case.

Table 4 -3. Summary of intensity counts on the processed samples.

Sample code	Mechano-activation conditions: Ball charge per g of sample (g)/ solids density (%)/ RPM / activation time (min)	Intensity at $14.5^\circ 2\theta$, counts	Normalised degree of amorphization, %
A	30/10/500/10	188	47.25
B	50/10/600/5	232	34.90
C	20/10/300/15	291	18.35
D	50/100/600/10	81	77.27
E	20/30/600/5	229	35.75
F	30/100/300/5	344	3.48
G	20/30/300/10	299	16.11
H	20/100/500/5	298	16.39
I	20/100/600/15	332	6.85
J	30/30/600/15	137	61.56
K	20/100/600/15	15	95.79
L	30/30/600/15	63	82.32
M	50/30/300/5	148	58.47

In reference to the milling conditions shown in Table 3-2 (Chapter 3), samples J,K and L were all subjected to the longest milling time of 15 min and the highest rpm of 600 while sample D was also at 600 rpm but a lesser milling time of 10 min. Samples D and J have the highest ball: spodumene concentrate ratio of 50:1 g/g. In contrast, K has the lowest ball: spodumene concentrate ratio of 20:1 g/g while L is at intermediate ball ratio of 30:1 g/g. To compare with samples which still retained some crystalline XRD signatures, the conditions of milling were characterized mainly by relatively lower milling time with higher rpm or higher milling time but lower rpm. It appears from results of the XRD characterization that mechano-activation of spodumene is affected mainly by milling time and higher rpm.

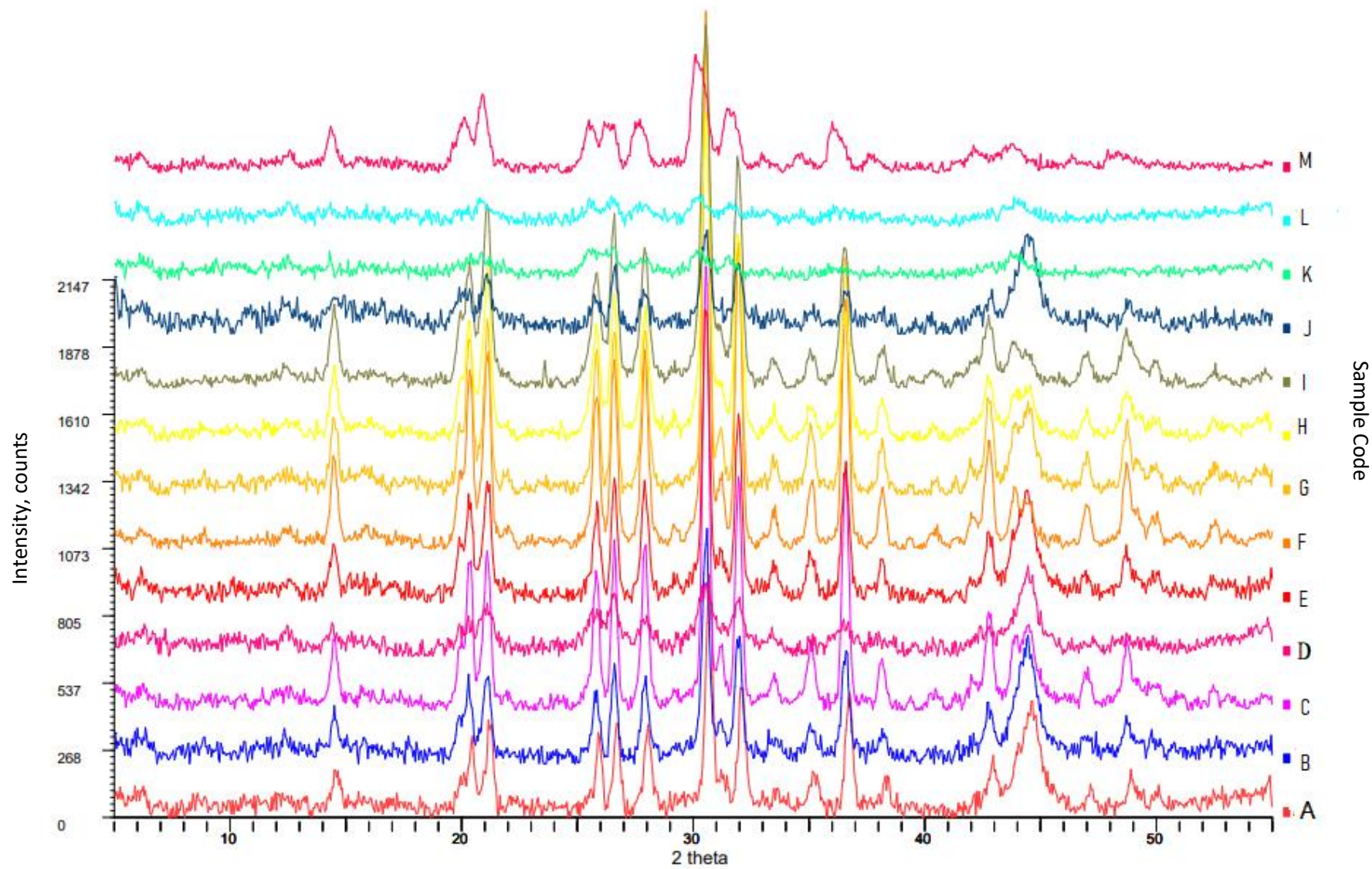


Figure 4- 4. Stack of XRD diffractograms and a tabulated decription of peak characteristics.

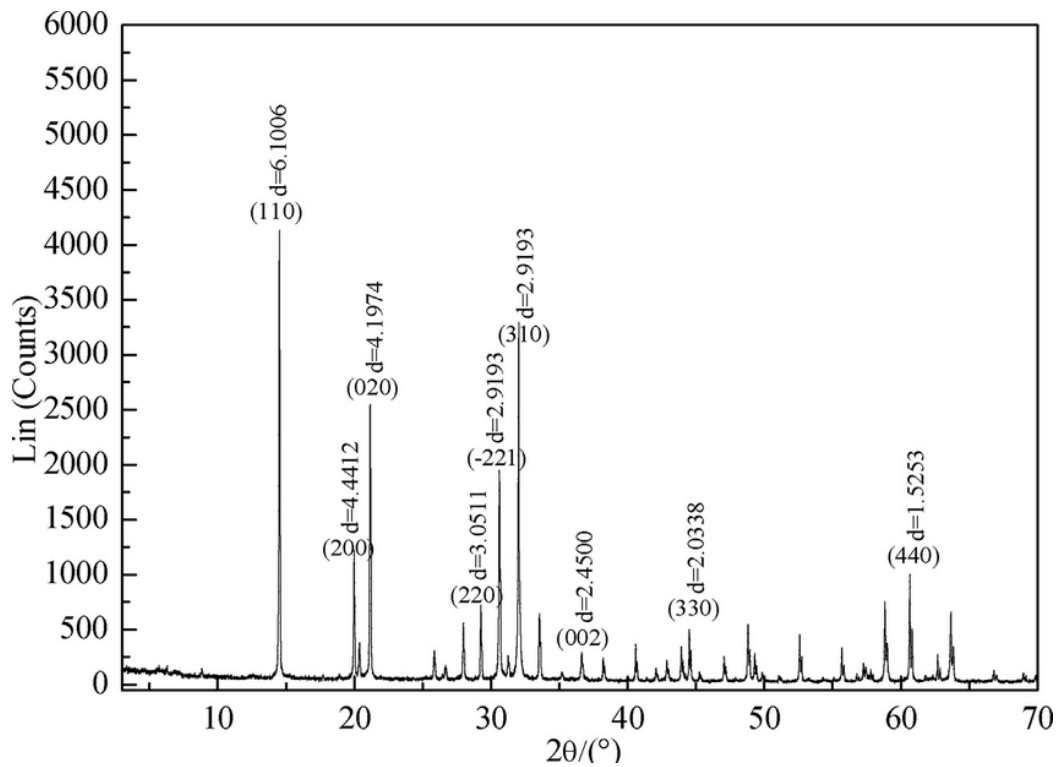


Figure 4-5. XRD diffractogram of raw alpha spodumene, unmilled (Xu, Peng et al. 2017)

Table 4 -4. Qualitative characterisation of XRD peaks based on mechano-activation conditions, referenced from Figure 4-4.

Sample Code	Mechano-activation conditions: Ball charge per g of sample (g)/ solids density (%) / RPM / activation time (min)	Characteristics of XRD peaks
A	30/10/500/10	crystalline
B	50/10/600/5	crystalline
C	20/10/300/15	crystalline
D	50/100/600/10	broad peaks
E	20/30/600/5	crystalline
F	30/100/300/5	crystalline
G	20/30/300/10	crystalline
H	20/100/500/5	crystalline
I	20/100/600/15	crystalline
J	30/30/600/15	broad peaks
K	20/100/600/15	highly amorphous
L	30/30/600/15	broad peaks
M	50/30/300/5	broad and offset

4.4.2 Particle size distribution

The particle size distribution of the samples subjected to mechano-activation is shown in Table 4-5. The table provides a comparative sizing results with ultrasonication on laser sizing versus no ultrasonication prior to laser sizing. The intention is to show the agglomeration effect based on the mechano-activation conditions. From the results, it can be seen that sample L has the highest agglomeration effect of 567%. This sample was prepared using highest rotation speed of 600 rpm for 15 min. Sample K was also treated using the same condition but showed a lower agglomeration effect of 152% only, Sample K was prepared without any water and it was believed that the agglomeration in sample J was convoluted by the presence of water. The water on milling should not cause agglomeration but the subsequent drying, even done at low temperature of 40 °C can also effect agglomeration effects (Kotsupalo, Menzheres et al. 2010). It can also be deduced from the results that samples prepared at higher speed of 500 rpm (samples B, J) suffered more agglomeration as compared to sample prepared at lower rpm of 300 (samples C,G,I).

Basing on the ultrasonicated laser sizing result, data showed that there is no direct correlation of grind size with the intensity of the milling conditions. For example, a milling condition of 20:1 g/g ball: spodumene concentrate ratio, 30% solids density, 600 rpm and 5 min milling time resulted in particle size of D_{80} of 16 μm . On the other hand, more intense milling condition of 20:1 g/g ball to ore ratio, 100% solids density, 600 rpm and 15 min milling time, resulted in particle size of D_{80} of 42 μm . Even if the samples were treated with dispersant and ultrasonicated prior to particle size analysis, the tendency of particle agglomeration cannot be ruled out and that agglomeration of particles may have caused the lack of correlation between particle size and milling conditions. This is highly likely as some of the samples were dried in the oven, scraped off the container, pulverized by mortar and pestle and then re-slurried for PSD analysis.

Table 4- 5. Summary of PSD of the milled samples, comparative between ultrasonicated and non-ultrasonicated on lasersizing.

Sample Code	Particle size, μm				Agglomeration effect, in % of ultrasonicated D_{80} results
	Ultrasonicated on lasersizing			Non-ultrasonicated on lasersizing	
	D_{10}	D_{50}	D_{80}	D_{80}	
A	1.3	8.6	23.7	69	191
B	1.4	9.2	25.4	89	251
C	1.9	12.4	30.9	83	167
D	1.5	15	48.3	87	80
E	1.1	6.1	16.4	54	229
F	1.2	9.1	24.4	26	7
G	1.5	8.3	20.8	50	140
H	0.9	8.2	27.9	83	197
I	0.9	9.3	40.7	120	195
J	0.9	5	18.6	105	465
K	1.1	12.4	41.7	105	152
L	0.9	4.6	16.5	110	567
M	1.2	7.2	19.2	35	83

Mechanoactivation conditions	Sample Code												
	A	B	C	D	E	F	G	H	I	J	K	L	M
30/10/500/10													
50/10/600/5													
20/10/300/15													
50/100/600/10													
20/30/600/5													
30/100/300/5													
20/30/300/10													
20/100/500/5													
50/100/300/15													
50/30/500/15													
20/100/600/15													
30/30/600/15													
50/30/300/5													

Thus, judging plainly from the results of the particle size analysis, there is no direct correlation of the particle size to amorphicity, case in point, samples D,J,K and L have a particle size distribution of D_{80} : 48 μm , 19 μm , 42 μm , and 17 μm respectively. Samples E, F and G which still bear crystalline XRD signatures have a particle size distribution of D_{80} 16-25 μm , finer than samples D and K. This observation is interesting as it is contrary to the popular notion that inducing mechano-activation milling can be gauged by fineness of the output grind size, e.g. finer PSD is a result of higher intensity of mechano-activation and therefore subjects itself to easy lixiviation.

The above is a very interesting observation. The common notion is that there is a direct correlation of size to mechano-activation effects. This is not surprising though as the literature has been flooded with reports on the direct correlation of grinding and structural damage. For example, Dempster and Ritchie (1952) showed that crystallinity of quartz decreases with grinding time. Steinke (1985)

also showed that the number of paramagnetic centers of quartz, which bears correlation to broken Si-O bonds, increases with grinding time. However, with mechano-activation of a hard mineral as spodumene, correlating grind size to mechano-activation is not enough. In addition to the observations presented in the previous paragraph, a sighter test done on using Restch Emax mill (2000 rpm, 60 mins) produced an alpha spodumene sample with D_{80} at 1 μm but this treated sample still bore a crystalline XRD signature (Appendix C).

In summary, for mechano-activation of spodumene, it is important that the gauge for determining activation is through X-ray and not mainly on size.

4.4.3 Chemical and morphological characterization of mechano-activated samples

Results of SEM-EDS showed that the mechano-activated sample, particularly K, resulted in varied sizing of spodumene (Figure 4-5) which suggested that not all of the spodumene particles in sample K were subjected to activation effects. This also suggest that a combination of ball sizes needs to be used for a more uniform effect of mechano-activation.

Planetary mills as characterized by their high intensity milling function suffers from a major drawback: high rate of wear and consequently, incurring impurities particularly if there is a mismatch on the grinding balls used to that of the material being treated (Kheifets 1994).

Alpha spodumene is known to be an abrasive mineral with a Mohs hardness of 6.5-7.0. The milling media used in the study was stainless steel balls with a hardness of 7-8. Due to the close hardness of the grinding media and spodumene, there was abrasion of grinding media and/or milling jar (see weight loss of grinding balls, Appendix D-1 and distinct color of leachate on highly contaminated samples, Appendix D-2) which subsequently resulted in contamination of spodumene. Semi-quantitative XRD analysis confirms the presence of iron (Table 4-5). Metal contamination can be easily seen in the SEM micrograph in Figure 4-6, note the shiny rounded particle at the top right. The occurrence of contamination is also supported by the increased of Cr content in the mechano-activated samples in the EDS spectra of Figure 4-6 (Appendix E).

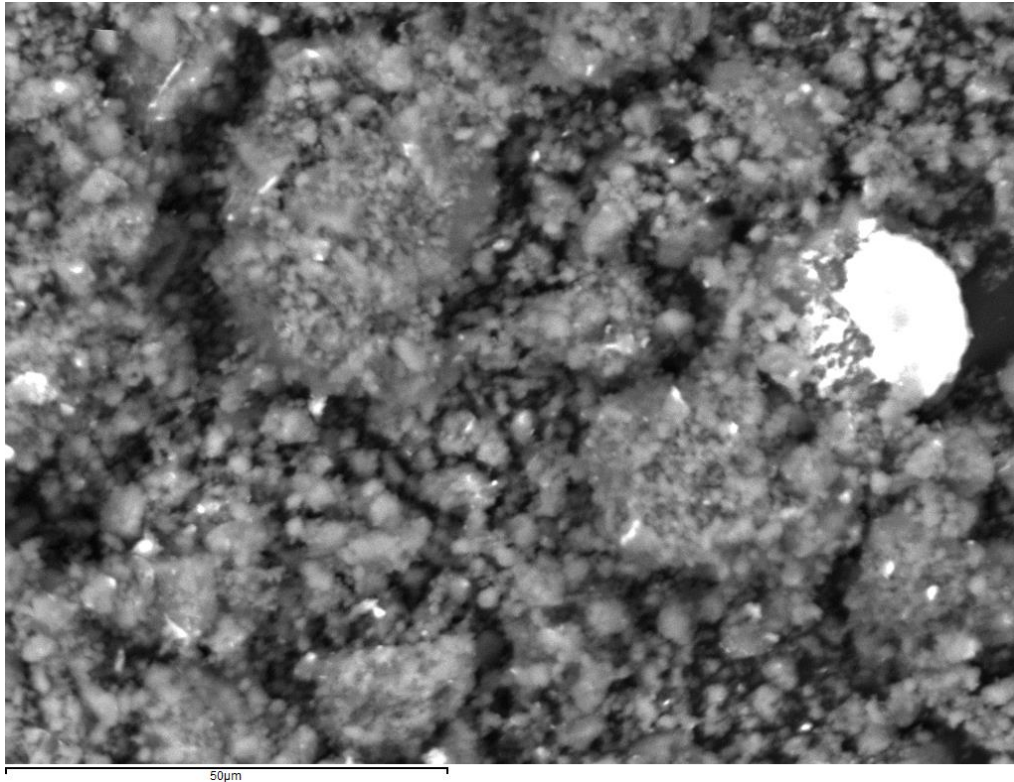


Figure 4- 6. SEM micrograph of mechano-activated sample

Table 4-6. Comparative semi-quantitative XRD results on a mechano-activated sample K

Crystalline mineral phase	Concentration %	
	Pre-mech act.	Post mech. act.
Spodumene (LiAlSi ₂ O ₆)	90	85
Muscovite-2M1,Fe+3-bearing (K _{0.92} Na _{0.08} Al _{1.88} Fe _{0.12} Mg _{0.04} (Al _{1.08} Si _{2.92} O ₁₀)(OH) _{1.89} F _{0.11})	3	ND
Quartz, syn (SiO ₂)	3	9
Amphibole, syn Sodium Magnesium Silicate Hydroxide (Na _{1.6} Mg _{6.2} Si ₈ O ₂₂ (OH) ₂)	2	ND
Albite (Na _{0.98} Ca _{0.02} Al _{1.02} Si _{2.98} O ₈)	2	ND
Clinocllore-1M1lb, Fe+2-bearing ((Mg,Fe) ₆ (Si,Al) ₄ O ₁₀ (OH) ₈)	1	ND
Iron, syn(Fe)	ND	6

An XRF analysis of the mechano-activated samples is provided in Table 4-6 in which the assays shows elevated levels of Fe oxide content of > 5%. Such contamination has considerably diluted the relative concentration of Li, Al and Si, and as can be seen in Table 4-5, the assays of Li,Al and Si have reduced compared to the non-activated sample (control). In this testwork, Fe contamination can result to higher consumption of acid but in relation to extracting Li, Fe can easily be removed by neutralization of the Li pregnant solution. The contamination encountered in this research can

be avoided by using a harder milling balls such as zirconia and that the milling jars should be ensured to be of top-grade quality Mn steel which are much more resistant to wear.

It is interesting to note, that while the Fe content of the mechano-activated samples have increased significantly due to contamination from the grinding media, the loss of ignition (LOI) values as shown in Table 4-6 are very variable. The negative LOI are related mainly to the oxidation of Fe in the samples (weight gain) and the large variability can be explained by the inhomogeneity of the sample with regards to contamination. This means that Fe (&Cr) incorporation to spodumene occurs by chance depending on the intensity of the milling action in the planetary mill. The TGA plots for the samples are shown in Figures 4-7 to 4-9 in which there was a very high LOI 3.7% and 3.3% respectively on samples A and B. These samples were subjected to the highest milling speed of 600 rpm but did not result in mechano-activation as these samples were subjected to activation as a slurry and not as a powder. Samples D, J, K and L which resulted in mechano-activation, all have relatively high LOI.

Contamination of Fe from milling media was also reported in earlier studies (Torres, Sanchez et al. 1989). In theory, such contamination is not ideal and that a relatively harder grinding media should be utilized for the purpose, e.g. alumina beads or zirconia beads. However, such contamination presents an opportunity to learn if mechano-activation in synergy to alloying would create more lattice strain that will aid more in leaching. This will be considered as well in the analysis of the leaching results as will be discussed in the next chapter.

Table 4- 7. XRF analysis of alpha spodumene samples subjected to mechano-activation using different activation conditions

Sample Label*	XRF assays, % (m/m)										% (m/m)
	Li ₂ O	Al ₂ O ₃	CaO	Cr ₂ O ₃	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	SiO ₂	TiO ₂	LOI
Spodumene feed**	6.5	25.7	0.261	0.009	0.572	0.679	0.246	0.584	65.1	<0.026	0.61
A: 30/10/500/10	5.5	22.3	0.259	2.22	>4.784	0.641	0.232	0.524	56.1	<0.026	-3.7
B: 50/10/600/5	5.5	22.2	0.272	2.34	>4.784	0.647	0.241	0.538	55.3	<0.026	-3.3
C:20/10/300/15	5.8	24.2	0.285	0.859	>4.784	0.686	0.237	0.593	60.7	<0.026	-0.9
D:50/100/600/10	5.9	23.2	0.273	1.5	>4.784	0.651	0.253	0.574	58.6	<0.026	-1.6
E:20/30/600/5	5.8	22.9	0.274	1.75	>4.784	0.64	0.231	0.569	58	<0.026	-2.4
F:30/100/300/5	6.4	25.2	0.293	0.295	2.43	0.693	0.256	0.578	62.8	<0.026	0.26
G:20/30/300/10	6.1	24.5	0.288	0.813	>4.784	0.691	0.262	0.598	61.4	0.026	-0.8
H:20/100/500/5	6.2	24.8	0.298	0.539	3.96	0.697	0.249	0.612	62.2	<0.026	-0.01
I:50/100/300/15	6.3	25.2	0.306	0.129	1.36	0.700	0.260	0.602	64.1	0.026	0.89
J:50/30/500/15	4.9	19.8	0.239	>2.750	>4.784	0.541	0.204	0.455	49.6	<0.026	-3.5
K:20/100/600/15	5.7	23.2	0.279	1.5	>4.784	0.669	0.257	0.592	58.7	<0.026	-1.6
L:30/30/600/15	4.9	19.8	0.248	>2.750	>4.784	0.518	0.192	0.479	50.4	<0.026	-4.5
M:50/30/300/5	6.0	24.6	0.285	0.6	4.34	0.706	0.259	0.646	61.9	<0.026	-0.1

*Sample Label: ball charge per g of sample (g)/ solids density (%)/RPM /activation time (min)

** assay of spodumene prior to mechano-activation

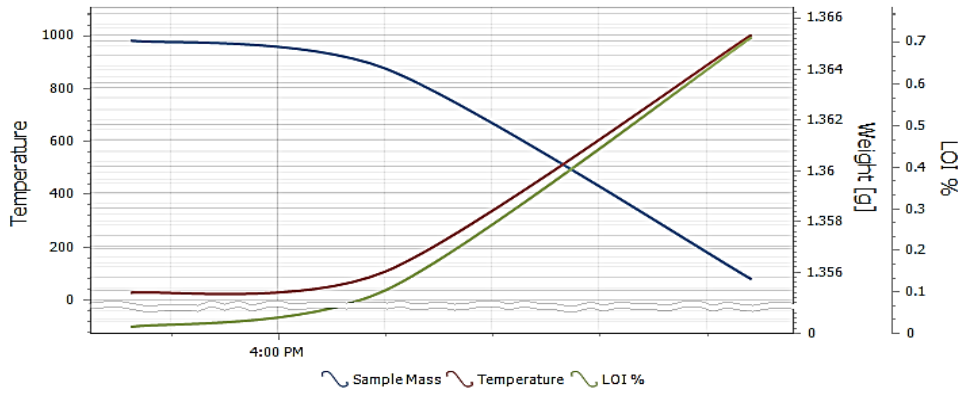


Figure 4- 7. TGA graph of untreated alpha spodumene sample

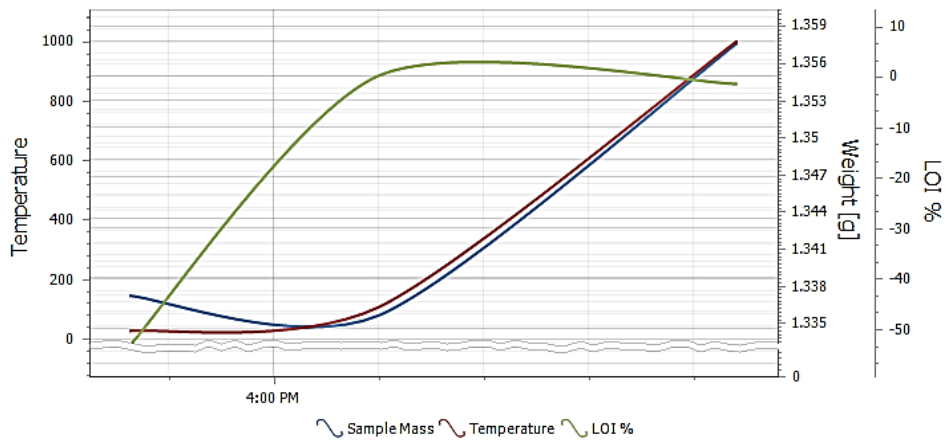


Figure 4- 8. TGA plot for samples B. The same trend was observed for samples C,D,E,G,H,J,K,L and M.

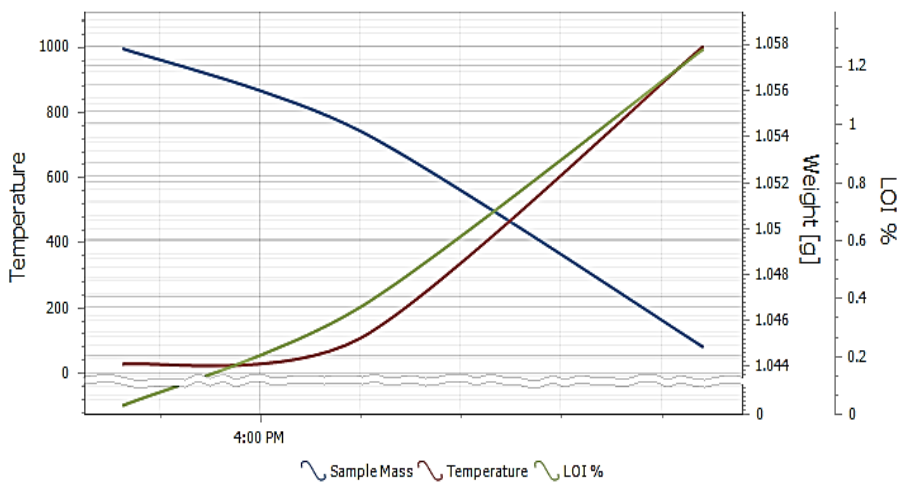


Figure 4- 9. TGA plots for sample A, the same trend observed for samples F and I.

4.5 Summary

This chapter summarizes the characterization results of spodumene and mechano-activated samples and the following are the main results:

- XRD and XRF analysis confirms spodumene concentrate was used in this research work, concentrate contains about 90% spodumene with grade of 2.9% Li.;
- Mechano-activation of spodumene using planetary mill (Retsch PM 100) and using one size diameter balls (5 mm) resulted in a wide range of particles size distribution;
 - SEM micrographs shows large particles of spodumene;
 - Against common notion, size is not a reliable indication of amorphicity;
 - Mechano-activation is dependent on the energy of impact received by a particle.

It appears that mechano-activation is highly affected by type of activation mill and that discussion of mechano-activation should always be qualified with the type of activator mill used.

- The use of stainless steel balls as well as use of high intensity milling conditions resulted in significant Fe contamination.
 - XRF assays showed iron content of > 3.3% from spodumene sample of 0.4%; SEM –EDS and TGA analysis confirmed the presence of high Fe contamination;
 - XRD analysis showed that the spodumene content of the mechano-activated sample reduced to 85% from 90% in spodumene concentrate;
 - Although there was high iron contamination, the effect of Fe on leaching will be limited to an increase in acid consumption; Fe as an impurity in leaching can be removed from the pregnant leach solution on neutralization stage.
- Judging by its XRD peak intensities, only samples J,K,L and D were amorphised and showed the lowest relative peak intensities (broad peaks rather than sharp).
 - These samples were processed in the planetary mill using highest revolution of 500-600 rpm and activation time of 10-15 min.
- Degree of mechano-activation is highly dependent on the design or type of activation mill used and the utilization of milling energy to activating spodumene; e.g. higher activation resulted from horizontal mill as compared to a vertical mill; there was also higher activation for spodumene mono-mineral as compared to spodumene concentrate;

Chapter 5

Direct sulfuric acid leaching of mechano-activated alpha spodumene

5.1 Introduction

The conventional processing of alpha spodumene would require a calcination step to effect a change of crystal structure from monoclinic spodumene (alpha) to tetragonal crystal structure (beta spodumene) followed by sulphation roasting. The calcination would effect a 27% volume expansion which renders the Li atoms more mobile to react with sulphuric acid and produces a water soluble Li sulfate compound (Moore, Mann, Montoya, & Haynes, 2018). Such approach is highly energy intensive in that 655 KJ/mol of spodumene of heat is needed for the phase conversion to occur (Fuso, et al., 2021). This is more than five times the energy requirement for Li extraction from either brines or from clay (Dry & Tijsseling, 2022).

The direct sulfuric acid leaching of spodumene would provide for an interesting option from the point of view of energetics. Kotsupalo et al. (1998) reported on the sulfuric acid leaching of mechano-activated alpha spodumene with favourable results on Li extraction at 96-99%. The tested sulfuric acid concentration was 10 wt. % and 20 wt. %. Like any other studies on mechano-activation of spodumene, the milling conditions used to produce the sample for the leaching test was not detailed with respect to ball:solids ratio and milling speed. The mill used by Kotsupalo et al. was also a planetary mill but of a different design than existing commercial planetary mills and was reported to be of a patented design.

The mechano-activated samples as prepared via procedures outlined in Chapter 3.3 was subjected to direct sulphuric acid leaching. This chapter aims to define the milling conditions necessary to effect mechanical activation that will solubilize Li into solution on reaction with sulphuric acid as well as the results of the leaching tests.

5.2 Aims of the Chapter

This chapter aims to discuss the following:

- Characterise leaching of Li from mechano-activated alpha spodumene samples;
- Characterise the co-leaching of impurities from these mechano-activated samples.

5.3 Conventional treatment of alpha spodumene

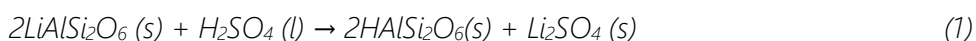
To provide for a baseline data, samples of alpha spodumene were prepared according to conventional method (see Appendix F-1 for details of procedures). The same alpha spodumene concentrate was subjected to calcination at 1000 °C for an hour in a muffle furnace followed by sulphation baking at 250 °C for an hour at 20 % stoichiometric acid equivalent. Leaching was done at 35% solids density.

Results of this test work showed that the Li recovery is high, as expected from this conventional method of treatment: > 90% Li solubilization on leaching (Appendix F-2.).

5.4 Direct sulphuric acid leaching of mechano-activated alpha spodumene

5.4.1 Leaching of Li

The sulphuric acid leaching of spodumene has proven effective on the beta phase of the mineral. In the conventional process, the high temperature of the roasting step enhances the kinetics of ion exchange reactions between sulfuric acid and spodumene to form lithium sulfates (Reaction 1) (Ellestad & Leute,1950; Hader et.al.,1951):

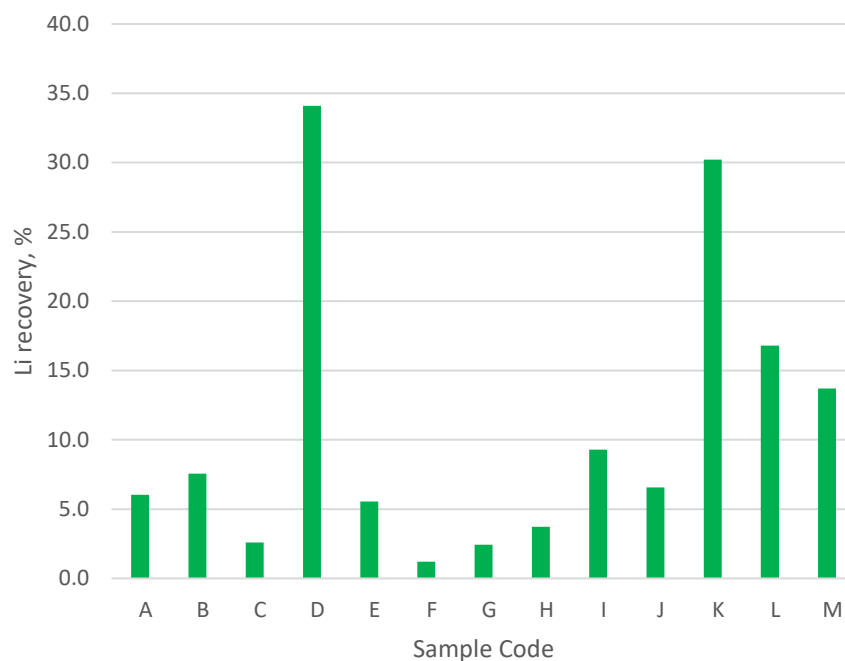


The lithium sulfate formed is easily solubilised on the subsequent water leaching step. As the acid is always dosed on a surplus, it is expected that excess sulfate ions and bisulfates also exist in the pregnant solution (Lajoie-Leroux, Dessemond et al. 2018)

From the sighter test conducted on the direct sulphuric acid leaching of mechano-activated spodumene using sample D, 12% Li solubilization on leaching was observed with the use of 20%

sulfuric acid (see Appendix G). To this regard, the concentration of sulphuric acid for the official test work was increased to 50 wt. %.

The results of the leaching test (Figure 5.1) showed that on direct sulphuric acid leaching of mechano-activated alpha spodumene, the amount of Li leached out is still very low compared to conventional method of sequential calcination-roasting-leaching, e.g. 34% Li extraction versus 90% Li extraction using conventional method. The highest Li recovery was 34.1% from sample D and 30.2% from sample K. These samples were mechanically activated at the highest milling speed of 600 rpm and 100% solids density. While these Li recovery results are comparative low, they are relatively higher than the leaching results from use of 20 wt. % sulfuric acid in which Li solubilization was 16% and 12.4% respectively for samples K and D (sighter test, Appendix G). It appears that acid concentration plays a significant factor as well in the leaching of Li from mechano-activated samples. The highest Li assays was 939 mg/L for a 5% solids density on leaching, at 50 wt.% sulphuric acid.



Mechanoactivation conditions	Sample Code												
	A	B	C	D	E	F	G	H	I	J	K	L	M
30/10/500/10													
50/10/600/5													
20/10/300/15													
50/100/600/10													
20/30/600/5													
30/100/300/5													
20/30/300/10													
20/100/500/5													
50/100/300/15													
50/30/500/15													
20/100/600/15													
30/30/600/15													
50/30/300/5													

Figure 5- 1. Li solubilization on direct sulphuric acid leaching of mechano-activated samples

It should also be noted that Li recoveries as calculated from the liquor stream, as is done for above (Figure 5.1), represents a very conservative Li accounting. There were significant volume losses encountered during liquid-solid separation: e.g. use of centrifugation to separate very fine solids from the liquid stream, followed by decantation and syringe filtration would make it hard to account with good accuracy the volume of the Li-bearing filtrate. Li recovery calculation made on solid assays will then be compared in the following section.

It can be recalled that from the 12 samples subjected to mechano-activation, only samples D, J, K and L have broad peaks while the rest still registered crystalline peak signatures. Samples K (D_{80} 42 μm) and D (D_{80} 48 μm) were both milled dry at 600 rpm, 15 min for sample K but at a ball: sample ratio of 20:1 while sample D was milled for 10 min but at a higher ball: sample ratio of 50:1. Sample M (D_{80} 19 μm) was also noted to have more of broad peaks than crystalline and notably had a shifted peak (shifted to the left).

As can be seen from the leaching results in Figure 5.1, relatively the highest Li solubilization came from samples which have been mechano-activated.

It is interesting to note that the results of this research study is very different from reported results by Kotsupalo et al. in which there was higher than 90% recovery of Li on direct leaching of mechano-activated samples using 10-20 wt. % sulphuric acid. As different types of mills were utilized in each study, the logical reason is that each mill would have produced a different state of activation. For example, in the earlier study by Kotsupalo et al. (2010), a horizontal mill was used with a high angular momentum which means that the intensity of milling is expected to be high (see Figure 2.1), expectedly much higher than the result of this study. Reports on confirmatory studies on Kotsupalo et al.'s results could not be found.

It needs to be noted as well that in the earlier study, a monomineral of spodumene was used for the study which means that the energy utilized for mechano-activation was utilized all for activating spodumene. In this present study, as a spodumene concentrate was used, the energy on milling is also used for milling other minerals in the concentrate such as quartz, feldspar, and albite and not mainly on spodumene only.

The above differences, (1) different design of planetary mill and (2) use of monomineral spodumene as opposed to spodumene concentrate could explained the differences in results of previous research to this current study. The effect of differences in design of activator mill (planetary mill) is therefore believed to be more significant.

This recent study consistently shown that dry milling resulted in higher activation as compared to wet milling, the same observation was reported by Kotsupalo et al.

5.4.2 Characterisation of leach residue

Results of XRD semi-quantitative analysis on the leach residue showed that the main component of the leach residue is Alunogen which is an aluminum sulfate. This phase was not existent prior to leaching and could have formed as a precipitation product on leached aluminium reacted with sulfuric acid. Aluminium sulfates are known to easily form hydration products (Singh, 1969).

The semi-quantitative XRD results also showed that the spodumene content has reduced to 37% (Table 5.1) from 85% on unleached sample (Table 4.4). This represents a spodumene content reduction of 56.5% which should also represent the amount of Li that was leached out on sulfuric acid treatment. Compared to Li recovery calculated from solution streams, the huge difference in Li recoveries could be interpreted in the form of non-uniform degree of activation, which is likely the case in this present study. As only one size of grinding balls was used and the ratio of ball to solids ratio was not optimised, it is highly likely that not all of the spodumene charge has been subjected successfully to mechano-activation.

Guided by the thoughts above, it is therefore suggested that Li recoveries on leaching can then be enhanced by mechano-activation using combination of grinding ball sizes; higher milling speed (although this factor is limited on the type and design of activator mill), or a sequential mechano-activation in which leach residue will be subjected to a secondary mechano-activation step.

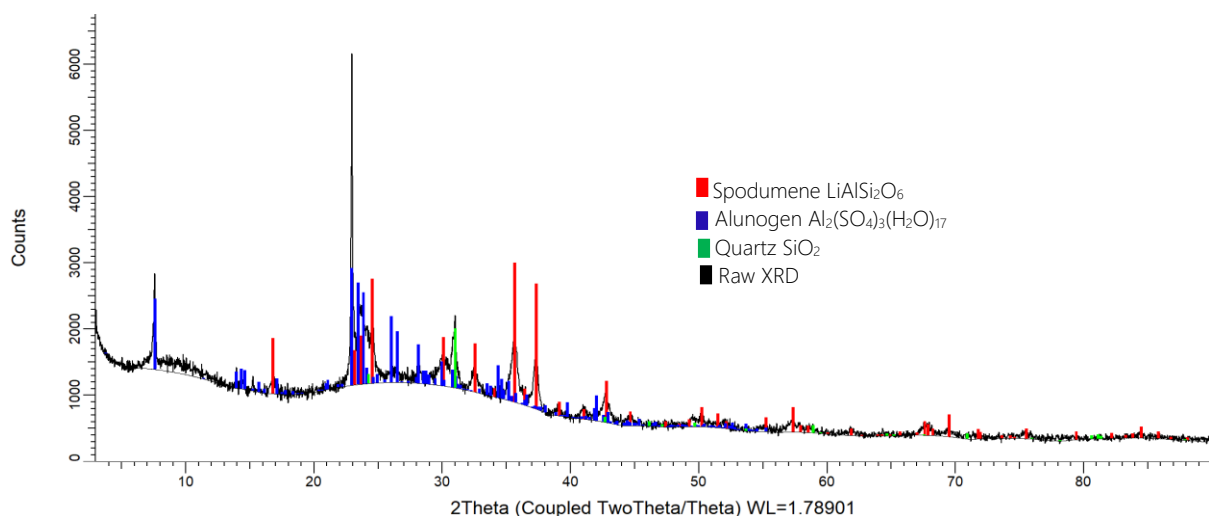


Figure 5- 2. XRD diffractogram of leach residue from sulfuric acid leaching of sample K

Table 5- 1. Semi-quantitative XRD analysis on leach residue from sulfuric acid leaching of sample K.

Crystalline mineral phase	Concentration (%)
Alunogen ($\text{Al}_2(\text{SO}_4)_3(\text{H}_2\text{O})_{17}$)	58
Spodumene ($\text{LiAlSi}_2\text{O}_6$)	37
Quartz, syn (SiO_2)	5

An SEM micrograph of leach residue of sample K after it underwent sulfuric acid leaching is shown in Figure 5.3. An EDS spectrum analysis reported the alunogen precipitated on various surfaces of spodumene (Appendix H) and may have limited the leaching of Li when these hydrolysis products prevented contact of sulfuric acid to spodumene surfaces.

From analysis on the relative ratio of Si/Al on the various portions of leach residue subjected to EDS analysis, it can be shown that the leaching of Li from mechano-activated appeared to be random. The ratio of Si/Al in unleached but mechano-activated sample was 2.2. In Table 5.2, the Si/Al ratio varied from 1.83-2.82. The lower Si/Al ratio, and notably very low Al assays seems to suggest that these are the precipitates of alunogen as suggested by the S assays associated with it. Si/Al ratio higher than the reference ratio of 2.2 is suggestive of Al and Si enrichment (but mainly Al) due to leaching of Li. The varying relative ratios of Si/Al supports the earlier argument on the varying degree of mechano-activation within a sample. Due to the limited sample volume generated on mechano-activation, the variability effect was not included in this study. Nonetheless, this variability in Li leaching within a sample leads to a realization on the randomness of the mechano-activation and that a mixture of ball sizes should be explored in future studies, for an improvement of activation and the subsequent Li recoveries on leaching.

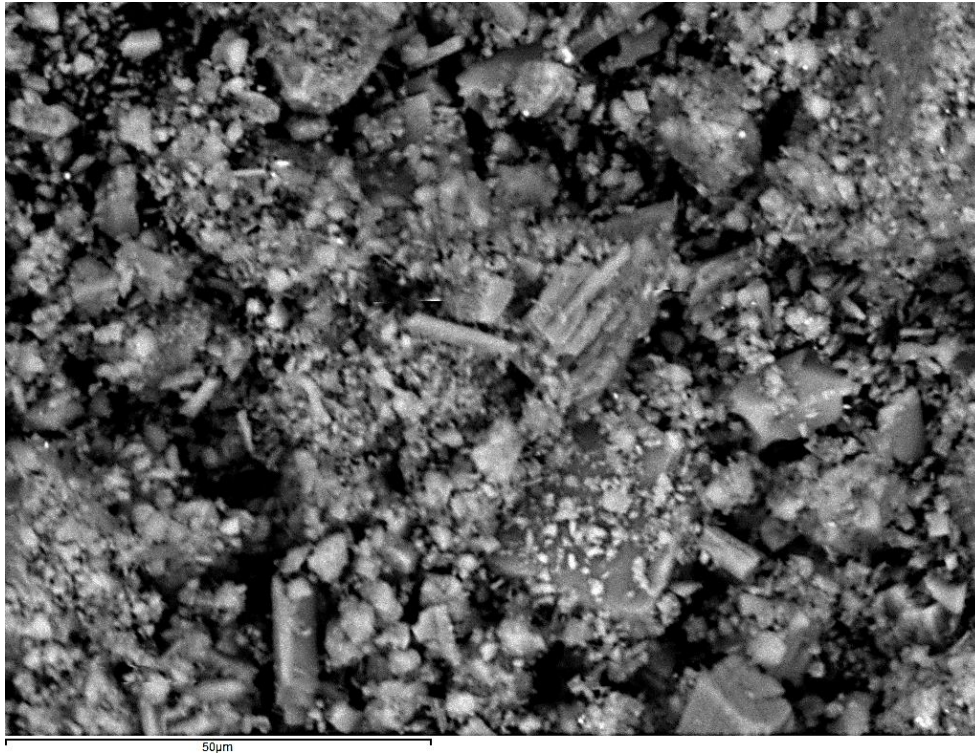


Figure 5- 2 SEM micrograph of Sample K leach residue post sulfuric acid leaching.

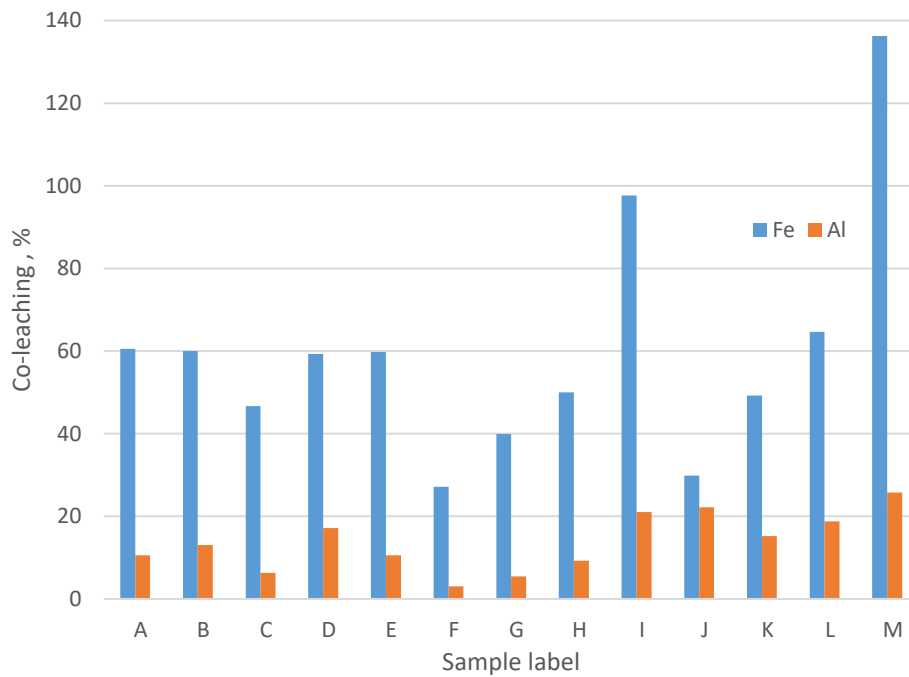
Table 5- 2. Typical EDS spectrum of Sample K.

Spectrum	In stats.	O	Na	Al	Si	S	K	Cr	Fe	Total	Si/Al
Spectrum 1	Yes	59.43	0.48	9.93	27.98	0.21	0.49	0.39	1.10	100.00	2.82
Spectrum 2	Yes	46.64	0.45	16.14	36.78					100.00	2.28
Spectrum 3	Yes	72.51	3.70	5.90	10.78	7.11				100.00	1.83
Spectrum 4	Yes	55.78		13.74	30.49					100.00	2.22
Spectrum 5	Yes	44.58		16.48	38.94					100.00	2.36
Max.		72.51	3.70	16.48	38.94	7.11	0.49	0.39	1.10		
Min.		44.58	0.45	5.90	10.78	0.21	0.49	0.39	1.10		

All results in weight%

5.3 Co-leaching of impurities on direct sulphuric acid leaching of mechano-activated alpha spodumene samples

With regards to co-dissolution of other impurities, Fe has the highest mobilisation, with deportment figures higher than 100%. It can be recalled that there was high Fe on the mechano-activated samples due to the contamination from the grinding media. The co-leaching of Fe and Al does not appear to be consistent with the degree of mechano-activation on each sample, for example, Fe and Al were dissolved the highest from sample M although sample M did not show higher Li lixiviation (Figure 5.4).



Mechanoactivation conditions	Sample Code												
	A	B	C	D	E	F	G	H	I	J	K	L	M
30/10/500/10													
50/10/600/5													
20/10/300/15													
50/100/600/10													
20/30/600/5													
30/100/300/5													
20/30/300/10													
20/100/500/5													
50/100/300/15													
50/30/500/15													
20/100/600/15													
30/30/600/15													
50/30/300/5													

Figure 5- 3. Co-leaching of Fe and Al on direct sulphuric acid leaching of mechano-activated samples at various mechano-activation conditions (see Table 3.2).

It should be noted that Al was also solubilized in the leach solution but not Si. The mobilization of Al, along with Li, is a good sign in that this means that the Me-O bond (Me: Li, Al) is ruptured to some extent, leading to the mobilization of these elements. The same explanation was offered from previous studies (Kotsupalo, Menzheres et al. 2010, Berger et al., 1990, Torres, Sanchez et al. 1989) in which there was co-leaching of Al first prior to Si. As the results of the earlier investigation showed higher Al mobilization as an effect of total cleavage of the Me-O bond, it can be deduced that for this study, that the samples were not fully and/or uniformly mechanically-activated against the amorphous signatures on the XRD diffractograms for samples D, J, K and L. The co-dissolution of Si was nil (Appendix I)

It should be noted that above trends on co-dissolution of impurities is consistent to the reported relative bond strengths for the Si-O, Al-O and Li-O bonds which are as follows: 1.17, 0.69 and 0.15. This means that it is expected to have higher co-dissolution of Al than Si. By mentioning this, if there

is significant co-dissolution of Si, it follows that there is a very high degree of mechano-activation and that Li lixiviation should also be very high. Such degree though is not ideal in that it means that the applied mechano-activation is excessive if only Li is only the target metal of interest. Co-dissolution of Al provides an opportunity for exploring the production of other by-products.

5.4 Main Effects Plot for significant factors

Statistical analysis using Minitab software to show the Main Effects plot and highlight significant factor/s for the leaching of Li from mechano-activated samples is provided in Figure 5.5. Easy to see in the Main Effects plot that milling speed is the most significant factor with higher revolutions effecting the highest Li leaching (shown as average of all Li extractions with 600 rpm setting on mechano-activation). High revolutions would relate to the high impact and thus, more damage to the crystalline structure.

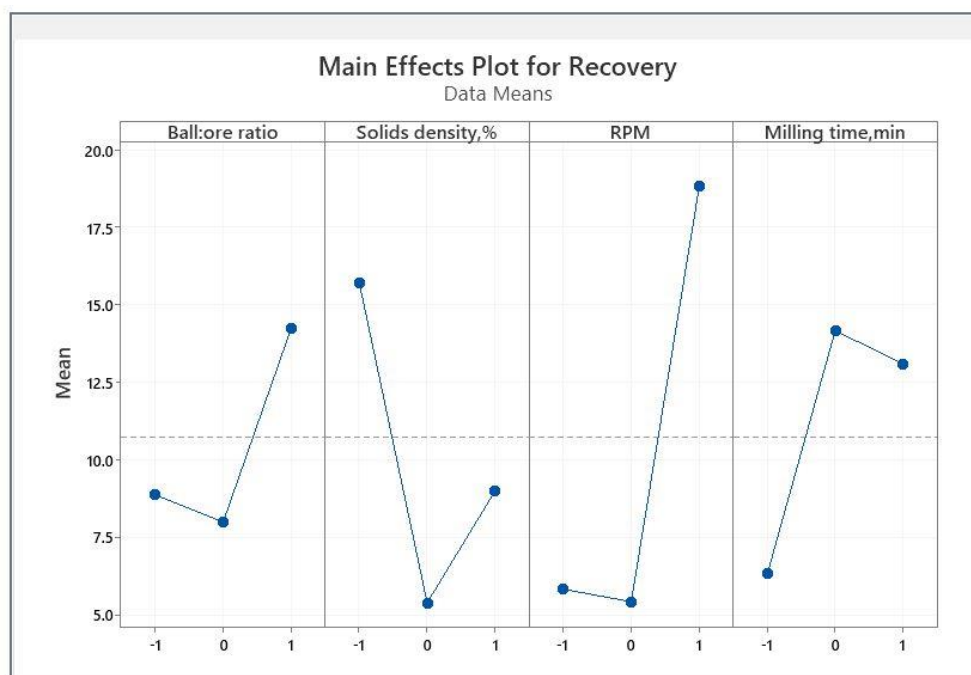


Figure 5- 4. Main Effects plot for the sulfuric acid leaching of mechano-activated samples

After rpm, the factor that affects highly the degree of mechano-activation is solids density. In the Main Effects plot, 100% solids (dry milling) has higher Li lixiviation compared to activation using slurry (wet milling). This is understandable as the impact energy would be higher on solids-load only condition due to the drag effect of liquid on grinding media.

Higher ball-to ore ratio is favored but this factor represented the least effect. It is understandable that the effect of ball to solids ratio would affect mechano-activation differently if the ball sizes used are of mixed sizes.

5.5 Summary

In this chapter, the following learnings are achieved; all in reference to the use of PM 100 planetary mill as an activator mill:

- Li leaching from spodumene concentrate activated in a vertical planetary mill and using 50 wt. % sulfuric acid is 35%; the milling conditions to produce the mechano-activation were as follows: dry milling at 600 rpm and for 10 min with a ball: sample ratio of 50:1;
- The co-leaching of Fe impurities is high, with higher iron in the mechano-activated samples as a result to contamination from the grinding media; future test work should consider the hardness of spodumene and the grinding media to be used;
- The co-leaching of Al for the mechano-activated samples is low at 20-25% however, the co-leaching of Al has direct correlation with the co-leaching of Fe;
 - It appears that Fe contamination and its effect on distortion of lattice is only limited to the level of Al; it should be recalled that in alpha spodumene, the Li sits lower than the Al atoms in the polyhedral structure;

Chapter 6

Citric acid leaching of mechano-activated alpha spodumene

6.1 Introduction

The citric acid leaching of mechano-activated spodumene is a relatively new area of research. Spodumene has always been extracted by inorganic acid, most popularly by sulfuric acid. The intention on the use of organic acid is mainly to test the lixiviation properties of spodumene using inorganic acid and potentially find a green alternative to the use of sulphuric acid. This will have increasing significance in the future, more so that there is a growing drive for lower Green House Gases emissions from battery metals processing, inarguably as battery metals are at the fore front of green and sustainable manufacturing initiatives.

Recent studies on the mechano-activation of alpha spodumene using PM 100 followed by the use of organic acid showed very unfavourable results of less than 3% Li lixiviation (see Appendix J-1 and J-2). Purba (2019) used mechano-chemical activation using sodium sulphate and calcium chloride. The tested conditions include 5:1 to 10:1 ball-solid ratio, 30-120 minutes milling time followed by water leaching at ambient conditions. The reagent dosage was varied from 35-65% and the Li lixiviation was nil (Appendix J-1) . On the other hand, Hwang (2019) explored citric acid leaching of mechano-activated spodumene using 1M – 3M citric acid with leaching time of 1-3h. The milling conditions were as follows: ball:solid ratio of 1:5 to 1:10, and milling time of 5-30 min. Li lixiviation using citric acid and these mechano-activation conditions were very low at less than 3% (Appendix J-2).

6.2 Aims of the Chapter

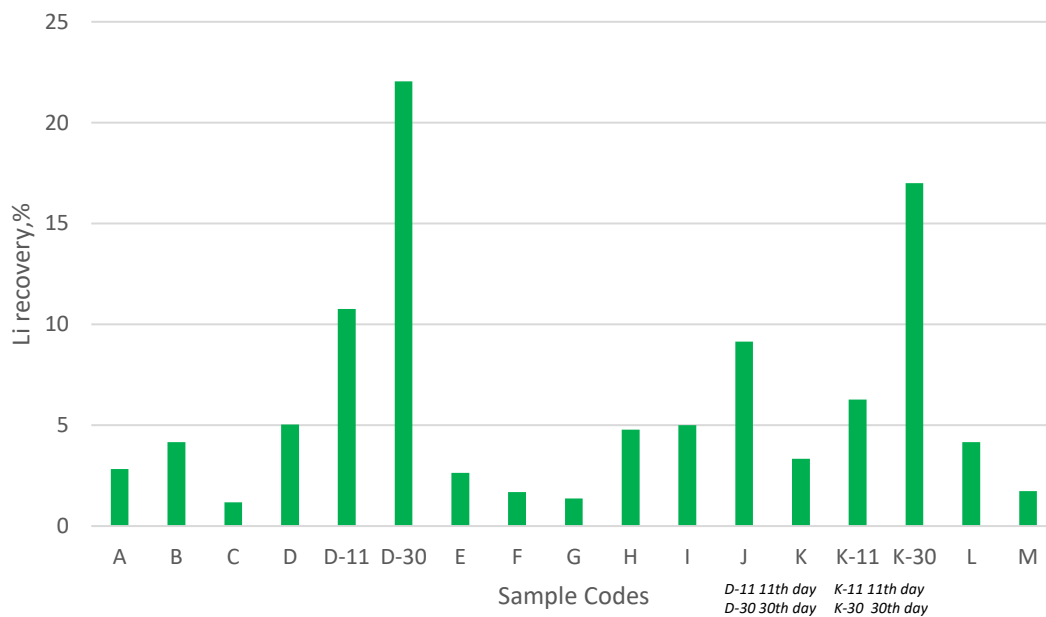
This chapter aims to discuss the following:

- Milling conditions to effect mechano-activation using planetary mill PM 100 and subsequent leaching of Li by citric acid leaching;
- Characterise the co-leaching behavior of impurities Al, Fe and Si;

6.3 Li recoveries on citric acid leaching of mechano-activated samples

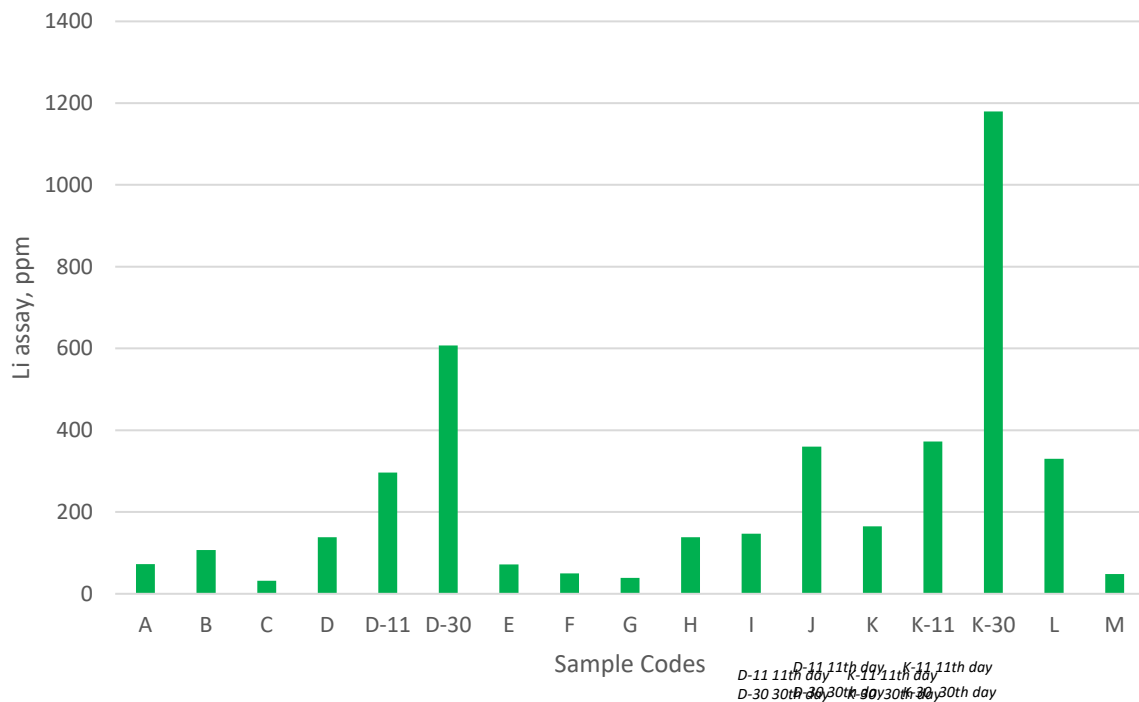
The leaching recoveries of Li via citric acid leaching (3 M concentration) of mechano-activated samples is comparably low at < 10%, with the highest Li leaching resulted from sample J (Figure 6-1). The activation conditions for samples J are as follows: 50: 1 ball to sample ratio, 15 min milling time at 500 rpm and 30% solids density. Samples D and K showed the next highest Li leaching at 5-7%. Sample D and K were samples which were mechanically activated at the highest milling speed of 600 rpm and 100 % solids density. The Li assay from sample J was very low at 200 mg/L (Figure 6-2).

The data provided in Figure 6-1 included data from both D and K samples which were resampled on the 11-day and 30-day slurries (unfiltered). From the results, it can be seen that citric acid leaching is characterized by very slow kinetics in that Li recoveries seemed to double from 5% to 11% on the 11-day sample and increased again to 22% on the 30-day sample (refer to D, D-11 and D-30



Sample Code	
Mechanoactivation conditions	A
	B
	C
	D
	E
	F
	G
	H
	I
	J
	K
	L
	M

Figure 6- 1. Li recoveries on citric acid leaching of mechano-activated samples.



		Sample Code												
		A	B	C	D	E	F	G	H	I	J	K	L	M
Mechanoactivation conditions	30/10/500/10													
	50/10/600/5													
	20/10/300/15													
	50/100/600/10													
	20/30/600/5													
	30/100/300/5													
	20/30/300/10													
	20/100/500/5													
	50/100/300/15													
	50/30/500/15													
	20/100/600/15													
	30/30/600/15													
	50/30/300/5													

Figure 6- 2. Li assays on citric acid leaching of mechano-activated samples

on Figure 6-1). Similarly, the same pattern was observed for sample K in which Li recoveries increased from 3% to 6% on the 11-day sample and then to 17% on the 30-day sample (see K, K-11 and K-30, on Figure 6-1). Regardless, the highest assays on the 30-day sample for sample K was still relatively low at 1.18 g/L at 5% solids density on leaching (Figure 6-2). Based on these results, it can be easily concluded that citric acid leaching of mechano-activated spodumene suffers from very slow kinetics. The results of this present study though was an improvement to the earlier studies done by Purba (2019) and Jisu (2019) for which Li recoveries were really low at less than 3%. The improvements can be attributed to a more intense mechano-activation conditions used in this present study, mainly higher ball: spodumene ratio and higher milling speed of 500 rpm.

In consideration of the various complexes that citric acid can form in solution (in increasing order of pH): H_3Cit , H_2Cit^- , $HCit^{2-}$ and Cit^{3-} (Tevebaugh 1947) and the pH of the leach solution derived from

citric acid leaching of mechano-activated spodumene which were in the ranges of 1.6-2.0, it is believed that the likely form of the citrate complex dominant at this condition is H_2Cit^{-1} or $H_2C_6H_5O_7^{-1}$. The lixiviation of Li is then believed to be as follows:



The most stable citrate compounds of Li are formed from Cit^{-3} ions at pH of 4 and higher (Golmohammadzadeh, Rashchi et al. 2017). The low Li lixiviation and hence lower Li recovery by citric acid leaching as compared to sulfuric acid leaching can also be attributed to the decomposition of citrate ions at higher temperature (Li, Ge et al. 2010).

Main Effects analysis as ran through Minitab showed that for citric acid leaching of mechano-activated spodumene concentrate sample, the effect of factors were as follows: milling speed > solids density > ball: spodumene ratio > milling time (Figure 6-3). From the combination of milling speed and dry milling, it can be easily deduced that mechano-activation highly depends on the intensity of energy and utilizing that energy to break crystalline structures.

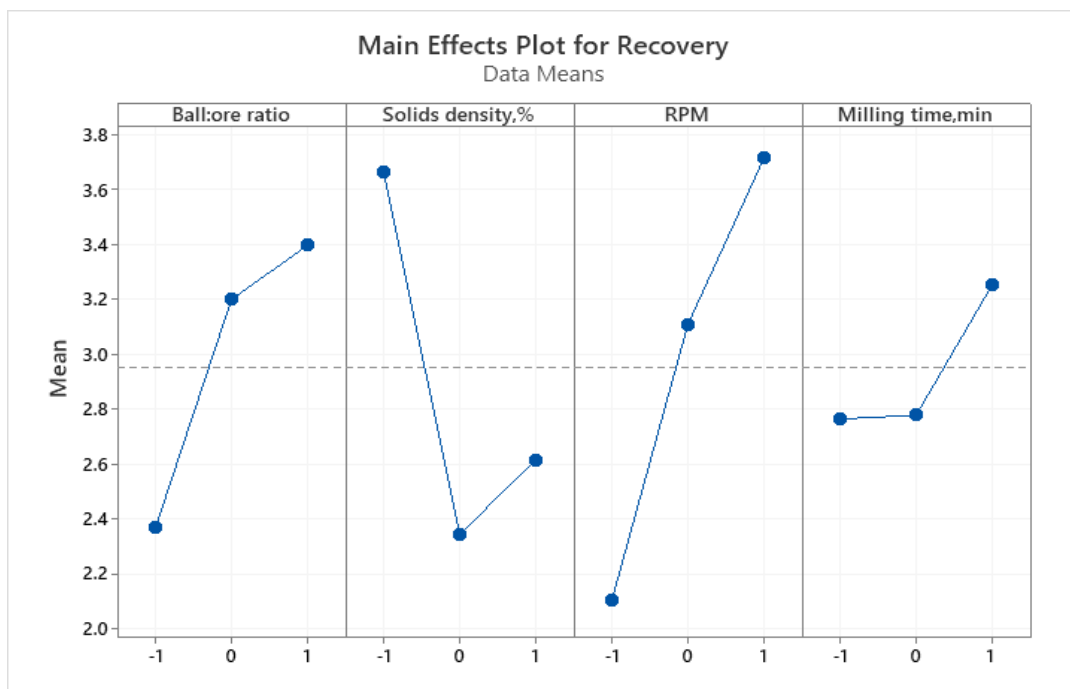


Figure 6- 3. Main Effects plot on Li recovery by citric acid leaching of alpha spodumene subjected to mechano-activation by PM 100.

The outcome of the Main Effects plot analysis on citric acid leaching is consistent with the Main effects plot analysis done for the sulfuric acid leaching of mechano-activated samples. The comparative leaching results of both lixiviants consistently showed a similar pattern as shown in

Figure 6-4 in which mechano-activated samples D,J, K and L have relatively the highest Li leaching. Comparatively sample J showed a slightly higher Li leaching on use of citric acid than sample D which was the opposite scenario on use of sulfuric acid leaching.

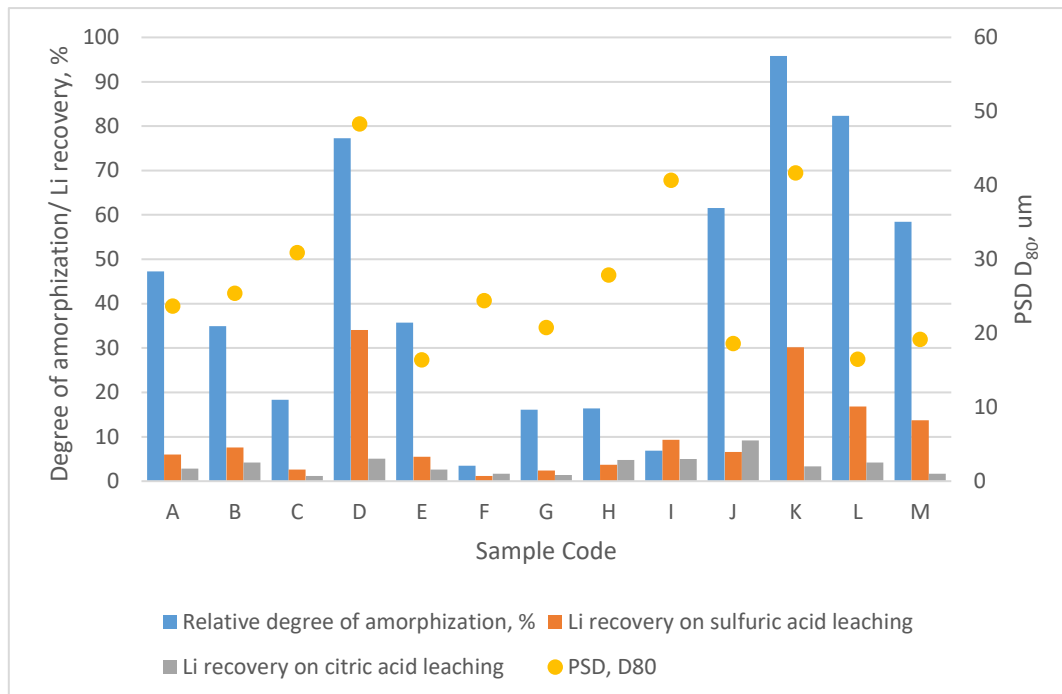


Figure 6-4. Summary graph showing degree of amorphization(normalised, based on intensity at 14.5 two theta, blue bar graph), Li recoveries on sulfuric acid leaching (orange bar graph), Li recoveries on citric acid leaching (gray bar graph) and PSD of the mechano-activated samples (scatter plot).

6.4 Co-leaching of impurities on citric acid leaching of mechano-activated samples

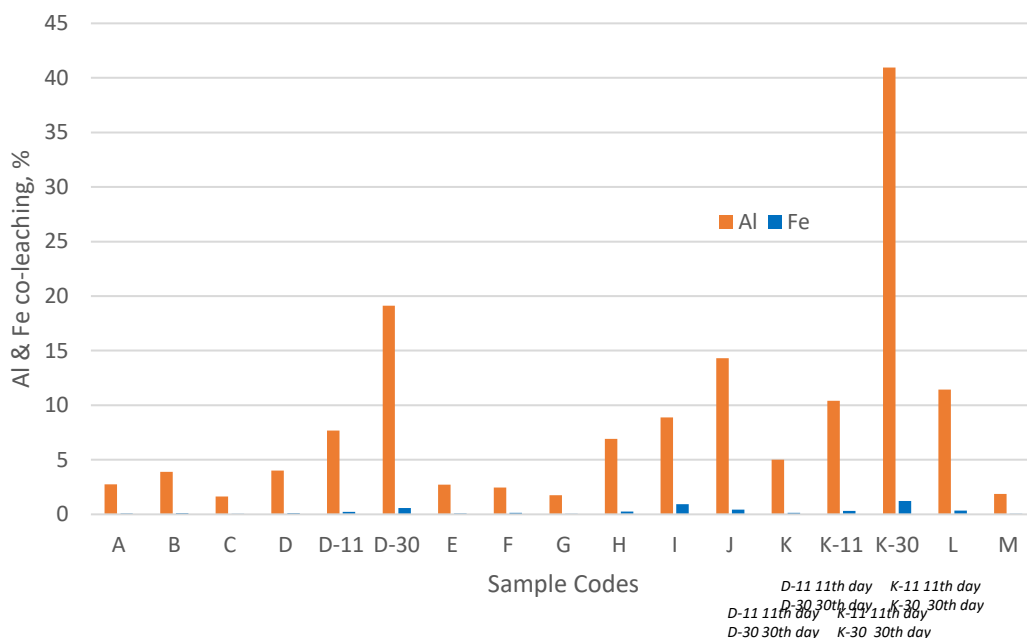
Figure 6-4 summarizes the co-leaching of Al and Fe on citric acid leaching of mechano-activated spodumene concentrate. The co-leaching of Al is higher than Fe on citric acid leaching which is the reverse pattern compared to sulfuric acid leaching. The co-leaching of Al and Fe seemed to be consistent with mobilization of Li in each sample, for example, highest Al and Fe co-leaching came from sample K-30 which consistently had the highest Li leaching from among the samples. It has to be recalled that the main cause for high Fe co-dissolution was mainly from high Fe contamination during mechano-activation as pointed out in Chapter 4.

Based on Al speciation at low Al concentrations in solution, the dominant Al ions are $Al(OH)_2^+$ and $Al(OH)_4^-$ (Yokel & McNamara,2006). Al once solubilised, is known to readily undergo hydrolysis

(Kuan, Wang et al. 2005) reactions which supports the proposed ionic forms of Al at the solution pH of 1.6-2.0. The proposed reaction for Al co-dissolution on citric acid leaching is as follows:



Of the three major impurities monitored, the levels of Si in the leach solution was nil (Appendix K). This came about as the dissolution of Si ions by citric acid has been known to be of slow kinetics and proceeds by chelation with the carboxyl ion (-COOH) (Kong, Huang et al. 2014). Moreover, the solubility of silica in citric acid is known to be relatively low. This is due to a competing ions in which active citrate anions exist in a pH at which silicic acid exists also as anions (Plettinck, Chou et al. 1994).



Sample Code		A	B	C	D	E	F	G	H	I	J	K	L	M
Mechanoactivation conditions	30/10/500/10													
	50/10/600/5													
	20/10/300/15													
	50/100/600/10													
	20/30/600/5													
	30/100/300/5													
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	30/30/600/15													
	50/30/300/5													

Figure 6- 5. Al co-leaching on citric acid leaching of mechano-activated spodumene concentrate

The relative higher co-leaching of Al and Fe compared to Si on the use of citric acid leaching of treated alpha spodumene was consistent with the trends observed on sulfuric acid leaching of the same sample (Chapter 5.3). This confirmed that the mechano-activation at the conditions tested in this study was able to effect activation at the initial layers of the Si-Al bond only and that a more

severe condition would be needed to get into the deeper structure of the Si-Al bond and eventually release the Li values. A similar observation was reported by Torres et al. (1989) in which Al values were reported much higher than Si.

6. 5 Summary

The citric acid leaching of mechano-activated spodumene concentrate provided the following main learnings:

- Citric acid leaching of mechano-activated alpha spodumene concentrate is characterized by very slow kinetics and as such, more studies need to be done on this regard; from this study, Li lixiviation from sample K was only 5% but increased to 22% after 30 days;
- The Li recoveries are comparatively very low at less than 10%;
- The spodumene concentrate would need more intense activation conditions to increase Li mobilization;

Chapter 7

Conclusions and Recommendations

The aims of this thesis were to:

- Define the mechano-activation conditions in a PM 100 planetary mill which favors direct sulfuric acid leaching of Li from alpha spodumene;
- Characterise the mechano-activated samples;
- Explore the use of citric acid for leaching Li from mechano-activated alpha spodumene;
- Characterise the co-leaching of Al, Si and other impurities in the leaching of mechano-activated alpha spodumene samples in a) sulfuric acid leaching and b) citric acid leaching;
- Analyse Li recoveries and conduct statistical analysis as to which factor/s on mechano-activation affect significantly the leaching of Li from mechano-activated spodumene samples;
- Propose methods of improvement to enhance mechano-activation and increase Li yield in the subsequent leaching process.

The conclusions derived from the conduct of research and laboratory work in the pursuit of the above objectives are discussed in detail in the following sections.

7.1 Characterisation of Mechano-activated samples

It is important to qualify that the activator mill used in this research work was a planetary type ball mill (Restch PM 100) in which stainless steel balls were used. This mill has one milling jar and operates on a G-force of 33.3 g with the main forces acting are friction and impact (Appendix A).

A study by Kotsuplao et al. (1998) reported high Li leaching recoveries from mechano-activated alpha spodumene, the results were never replicated by other researchers. This is most likely due to the different design of the planetary mill used. The activator mill used in the study by Kotsupalo et al. was an M3 centrifugal planetary mill of patented design and details are not available in the public domain. As a point of reference, a mechano-activation study on a beta spodumene using a

Herzog planetary mill utilizes a centrifugal acceleration of 90 g (Berger et al., 1990). The main objective of this research study then is to characterize mechano-activation of alpha spodumene using Restch PM 100.

XRD diffractogram patterns showed that intense milling conditions characterized by highest milling speed of 600 rpm and dry milling (as opposed to slurry milling) resulted in highest degree of amorphization on a normalized scale. This was shown in the XRD diffractograms of samples D, J, K and L (Chapter 4, Figure 4-4 and Table 4-3). The peak intensities were normalized prior to measuring and were measured at 14.5° two theta, which represents the {110} plane- the characteristic peak of alpha spodumene.

Particle size distribution (PSD) did not correlate reliably to the degree of amorphisation and contrary to common notion and cannot be used as a quick measurement to assess the degree of mechano-activation. For example, sample M with 59% degree of amorphisation has a finer PSD of 19 μm while sample K with about 96% degree of amorphisation has a coarser PSD of 42 μm (Chapter 4, Table 4-4).

Notably for this research work, there was significant contamination of Fe, from the milling balls and jar used. In some occasions as in the case of mechanical alloying, presence of impurities can aid in providing dislocation sites (Neikov 2019) which as applied to this research work, could work in favor for mechanically activating spodumene by intensifying the stressed lattices at which impurities elements are accommodated in the crystal lattices. However, this was not the case as the Fe contamination can be seen as abraded metas shown evidently in Chapter 4, Figure 4-6 (also Appendix E). This means that Fe was not fused into the alpha spodumene structure. The main learning then is to ensure that milling balls should have a significantly higher hardness than the material to be treated. Care must also be taken care of using coated zirconia or alumina beads. Due to the significant heat generated on mechano-activation specially using intense conditions, these beads tend to expand rapidly as observed in the sighter tests done in relation to this research. An improvement to the design of these mills is an appropriate cooling mechanism.

7.2 Li leaching of mechano-activated samples by a) sulfuric and b) citric acid

Li recoveries from direct sulfuric acid leaching of mechano-activated alpha spodumene samples showed that Li leaching is higher in samples with a higher degree of mechanical activations. The highest recoveries were from samples ran at highest milling speed of 600 rpm and 100% solids density at 34.1% and 30.2%. Sample that was mechanically activated at 600 rpm but solids density of 30 % had 16.8% Li recovery. The effect of ball:concentrate ratio and milling time were secondary to the impact of milling speed and solids density. The highest Li recovery (calculated from assays of concentrate) was 34%, which is relatively much lower Li recoveries by conventional method (calcination, roasting and leaching). A higher recovery of 55% is achieved when recovery calculations are made from the leach residue. It is therefor believed that the Li recoveries derived from this work could be in the range of 34% -55% and the variability is believed to be contributed mainly to the expected inhomogeneity in the degree of mechano-activation incurred in a charge of sample subjected to such treatment. This has been realized as resulting from the use of single size of milling balls. A combination of ball sizes charge should be used as an improvement to the processing technique.

Semi-quantitative XRD analysis coupled with SEM-EDS analysis on the leach residue from sulfuric acid leaching of mechano-activated alpha spodumene showed that there was formation and precipitation of alunogen, an aluminium sulphate hydrate, on the residue and at times covering surfaces of alpha spodumene. The co-leaching of aluminum is a good sign of some crystalline lattice breakage, in consideration of the refractory nature of alpha spodumene, and confirms that sample K (as a case in point) was indeed subjected to mechano-activation.

On the other hand, the citric acid leaching of Li from mechano-activated alpha spodumene returned a much lower Li recovery of only 9.2%. It was found out that citric acid leaching is characterised by very slow kinetics. While the Li recoveries are very low, this is an improvement to earlier studies on mechano-activation on alpha spodumene using PM 100 for which the Li recoveries were nil (Hwang, 2019) (Purba, 2019).

Consistently for both sulfuric and citric acid leaching of alpha spodumene samples subjected to mechano-activation treatment, Li lixiviation responds well to samples with higher degree of

amorphisation, e.g. degree of amorphisation as measured by XRD peak intensities greater than 60%.

Statistical analysis by Main Effects plot has showed consistently that milling speed was the main factor affecting the mechano-activation of alpha spodumene using PM 100 planetary mill. It has become more obvious that mechano-activation relies simply on the destruction of crystal lattices for effecting activation.

From analysis of co-dissolution of impurities, it was observed that for samples which had incurred greater than 60% relative amorphization, as measured by XRD peak intensities on the 14.5 two theta angle, that Al co-dissolves to as much as 48% while there was nil co-dissolution of Si.

The co-dissolution of Fe was significant for this research study but this was mainly due to Fe contamination from the mill materials and can be avoided with proper choice of materials.

7.3 Conclusions

From results gathered through this research work, the main conclusions are derived:

- Using a planetary mill with a lower acceleration of gravity at 33.3 g, mechano-activation of alpha spodumene can be carried out using intense milling conditions. This was best carried out using the highest milling speed of 600 rpm and dry milling as opposed to activation using a slurry charge. The highest ball to ore ratio used in this study was 50:1 and milling times of 15 mins. From Main effects plot analysis, milling speed was the most critical factor for the activation to effect;
- In a PM 100 planetary mill, the effect of factors in decreasing significance are as follows: milling speed, solids density, ball:spodumene concentrate ratio and milling time.
- Mechanical activation relies mainly on the design of mill; previous studies which reported high mechano-activation results and Li lixiviation from mechano-activated alpha spodumene utilized a planetary mill of patented design that could deliver an acceleration of gravity to about 100 g. As the impact forces in a PM 100 planetary mill used in this research work can only deliver an acceleration of gravity of 33.3 g; there was lower Li lixiviation on direct sulphuric acid leaching at 34-56%. The high variance on Li leaching was a result of non-uniform activation of alpha spodumene in the planetary mill used and also due to the use of one size of milling balls;

- Mechano-activation using a simpler design planetary mill (PM 100) can deliver mechano-activation and high Li lixiviation by improving the uniformity of mechano-activation: use of two different sizes of milling balls or the use of sequential mechano-activation.
- The main challenge of mechano-activation is the energy requirement to deliver such forces to destroy crystalline structure and relies on the design of the mill;

7.4 Recommendations

- There is a potential for the use of mechano-activation in combination with direct leaching of Li from mechano-activated alpha spodumene. More studies needs to be done on designing an industrial size activator mill for this purpose.
- For futher studies using PM 100 planetary mill, it is recommended to revisit the same activation conditions but with the use of a combination of sizes of zirconia balls. This is to avoid contamination and at the same time, to study the effect of a more sequential impact caused by different sizes of milling media.

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Appendix

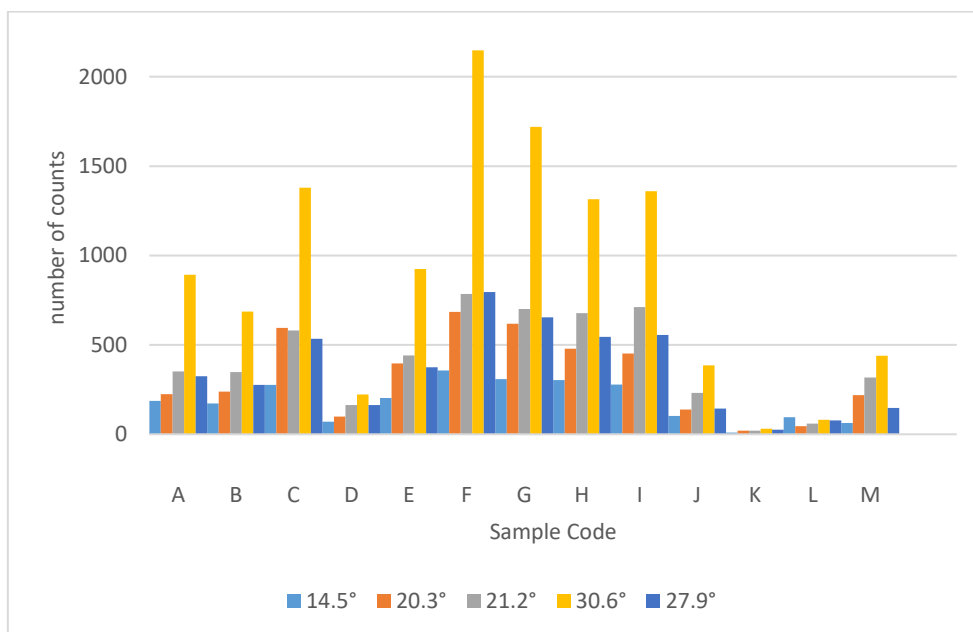
Appendix A. Technical specifications of Retsch PM 100 planetary mill (see [Planetary Ball Mill PM 100 - RETSCH - highest fineness](#))

Size reduction principle	impact, friction
Material feed size	< 10 mm
Final fineness	< 1 µm, for colloidal grinding < 0.1 µm
Batch size / feed quantity	max. 1 x 220 ml, max. 2 x 20 ml with stacked grinding jars
No. of grinding stations	1
Speed ratio	1: -2
Sun wheel speed	100 - 650 min ⁻¹
Effective sun wheel diameter	141 mm
G-force	33.3 g (for reference RM 400 26.8 g, PM 200 is 37.1 g)
Material of grinding tools	Stainless steel
Grinding jar sizes	12 ml / 25 ml / 50 ml / 80 ml / 125 ml / 250 ml / 500 ml
Drive	3-phase asynchronous motor with frequency converter
Drive power	750 W
Power consumption	~ 1250W (VA)
W x H x D closed	640 x 480 (780) x 420 mm
Net weight	~ 86 kg

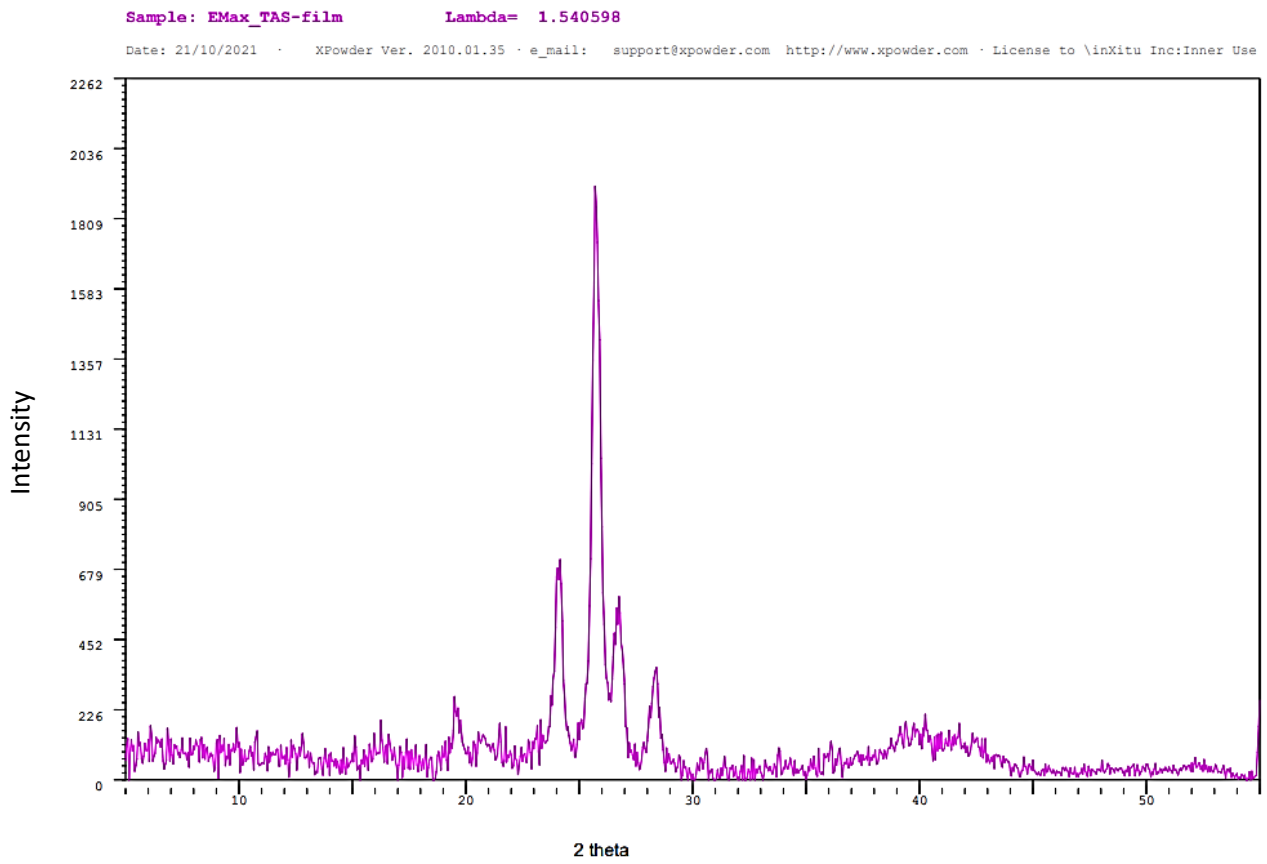
Appendix B. Degree of amorphicity on other angles (table and chart presentation)

Sample Code	2 theta angle				
	14.5°	20.3°	21.2°	27.9°	30.6°
A	187	224	351	325	892
B	172	239	348	277	687
C	276	595	581	534	1380
D	71	99	164	163	222
E	204	397	441	375	925
F	357	684	785	795	2147
G	309	619	701	654	1720
H	304	479	678	545	1315
I	278	452	712	556	1359
J	102	139	231	144	386
K	9	20	21	26	31
L	95	45	59	77	81
M	63	219	317	147	439

2 theta angle and its equivalent crystal plane in alpha spumene: 14.5° (110); 20.3° (-111); 21.2°(020);27.9°(021); 30.6°(-221)



Appendix C. XRD diffractogram of alpha spodumene ground to 1 μm using Restch Emax



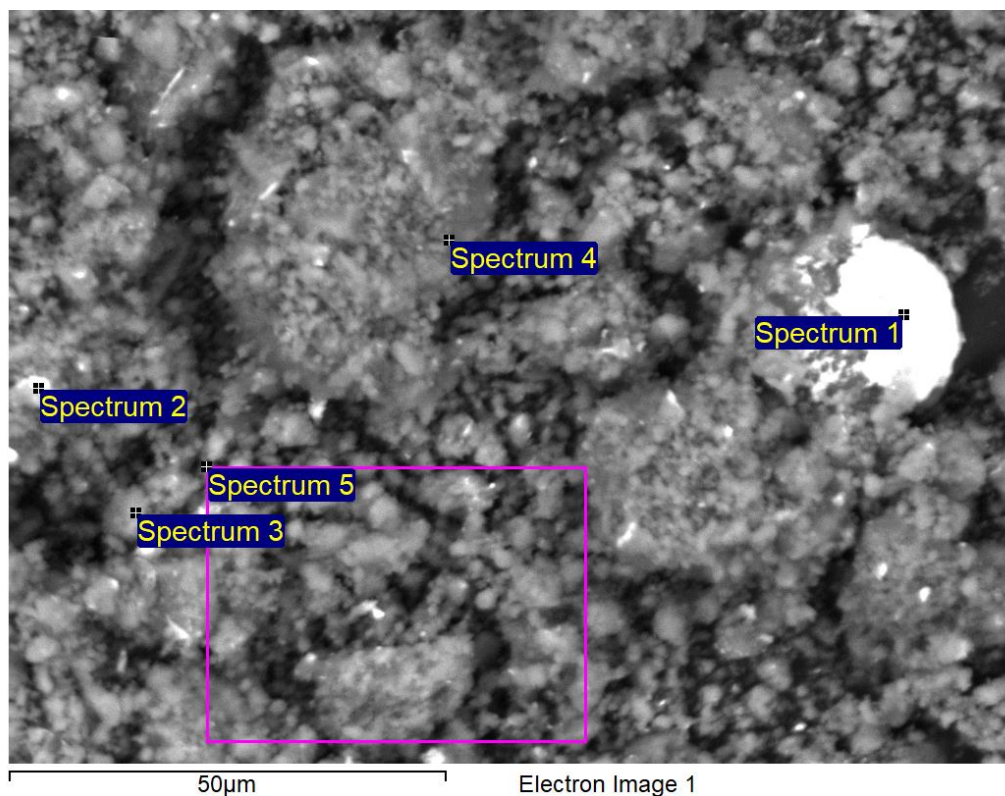
Appendix D-1. Table showing loss of weight of grinding media

Sample Code	Wt of grinding media		wt. loss, %	Milling Conditions			
	in, g	out, g		Ball:spod. Conc. ratio, g/g	Solids density, %	Milling speed, rpm	Milling time, min
A	600	592	1.33	30:1	10	500	10
B	1002	1000	0.20	50:1	10	600	5
C	401	400	0.25	20:1	10	300	15
D	999	996	0.30	50:1	100	600	10
E	400	398	0.50	20:1	30	600	5
F	603	603	0.00	30:1	100	300	5
G	403	402	0.25	20:1	30	300	10
H	400	400	0.00	20:1	100	500	5
I	1002	1002	0.00	50:1	100	300	15
J	1000	997	0.30	50:1	30	500	15
K	401	399	0.50	20:1	100	600	15
L	603	603	0.00	30:1	30	600	15
M	1000	999	0.10	50:1	30	300	5

Appendix D-2. Differences in colour of the milled sample



Appendix E. EDS spectra of the SEM micrograph shown in Figure 4-6, metal contamination in mechano-activated samples



Spectrum	In stats.	O	Na	Al	Si	S	K	Ca	Cr	Mn	Fe	Cu	Total
Spectrum 1	Yes	6.70		1.54	2.69				10.58	0.56	77.92		100.00
Spectrum 2	Yes	24.91		6.22	13.06	4.96	0.29		5.35		37.63	7.56	100.00
Spectrum 3	Yes	60.98	0.53	10.59	23.77		0.40	0.18	0.46		3.08		100.00
Spectrum 4	Yes	44.38		10.13	23.00		1.07		2.40		19.03		100.00
Spectrum 5	Yes	55.25	0.63	11.25	24.92		0.51	0.25	0.98		6.19		100.00
Max.		60.98	0.63	11.25	24.92	4.96	1.07	0.25	10.58	0.56	77.92	7.56	
Min.		6.70	0.53	1.54	2.69	4.96	0.29	0.18	0.46	0.56	3.08	7.56	

All results weights %

Appendix F-1. Procedure for conventional processing of spodumene sample

- Spodumene sample (concentrated by DMA) was splitted using Jones-riffle splitter.
- Samples were pulverised using Retsch Mill 200 down to size -3.5 mm, milling time of 2 min.
- Calcination was done in a muffle furncae at 1000 °C for an hour.
- Sizing was done using Endecotts Octagon 200, 10 mins, power 8 M1.
- Sulphation baking at 250 °C for 1 h using 0.5 g/g acid: solid ratio.
- Leaching done at 35% solids density for an hour.
- Solid-liquid separation done by buchner filtration.
- Samples dried overnight in the oven at 105 °C prior to analysis.

Appendix F-2. ICP-OES analysis of the leach solution using conventional processing

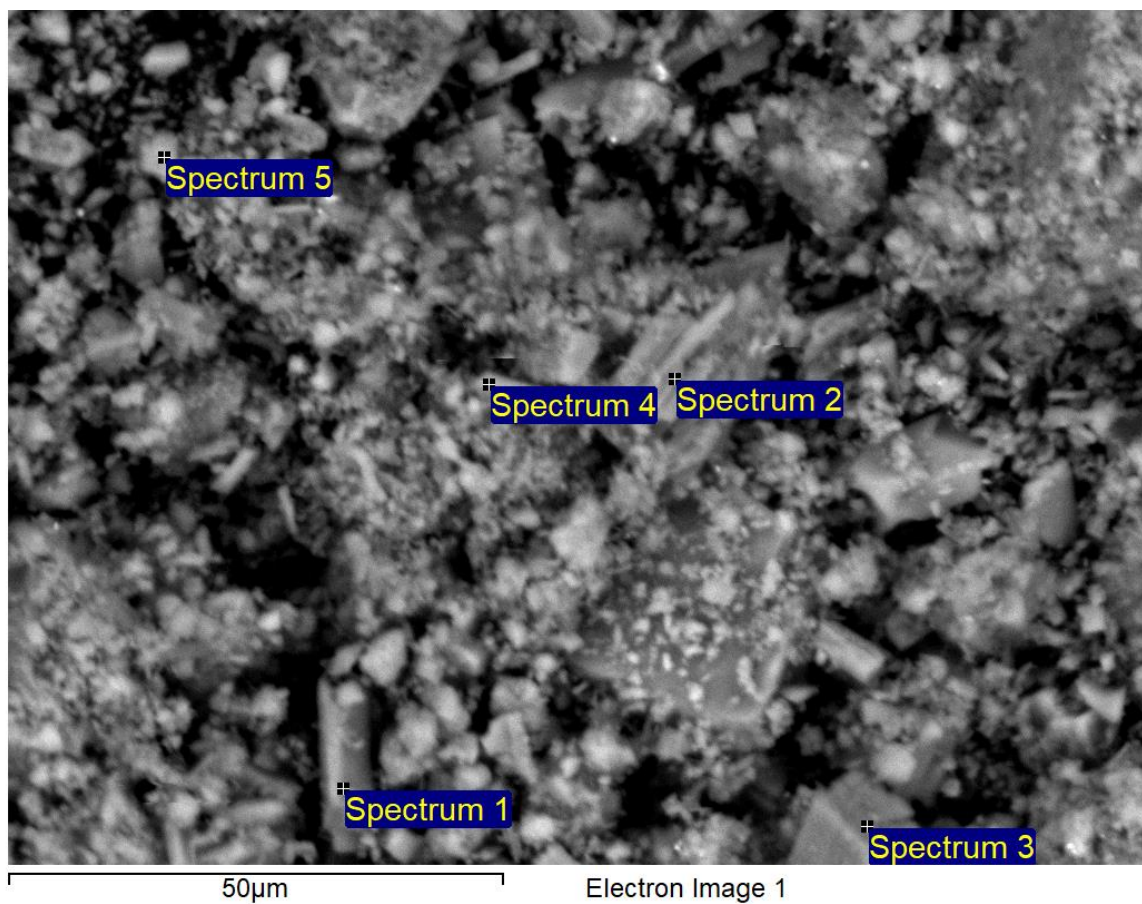
Sample Description	mg/L							
	Al	Ca	Fe	K	Li	Na	S	Si
Leach filtrate 1	424	780	376	600	8930	696	27680	56
washate 1	168	270	138	240	3552	308	10640	38
Leach filtrate 2	486	735	492	660	10302	762	31770	69
washate 2	92	130	88	120	1878	172	5560	22

Sample Code	In, Li (mg)	out,Li in filtrate (mg)	out,Li in washate (mg)	Recovery, %
Trial 1	196.4	64.54	35.52	100.1
Trial 2	26.22	64.68	18.78	83.5
			average	91.8

Appendix G. Sighter test, acid leaching of mechano-activated samples

Sample Code	20% sulfuric acid		50% sulfuric acid	
	Li assay,ppm	Li, recovery, %	Li assay,ppm	Li, recovery, %
D	342	12.4	939	34.1
K	426	16.0	804	30.2
L	266	11.6	384	16.8

Appendix H. SEM-EDS of aluminogen found in leach residue of mechano-activated sample after sulfuric acid leaching



Spectrum	In stats.	O	Na	Al	Si	S	K	Ca	Cr	Fe	Total
Spectrum 1	Yes	47.30		14.68	36.35	0.58	0.56	0.53			100.00
Spectrum 2	Yes	51.88		14.27	33.33	0.28	0.25				100.00
Spectrum 3	Yes	53.91		13.80	32.30						100.00
Spectrum 4	Yes	45.81	0.52	12.58	38.53	0.30	1.75			0.50	100.00
Spectrum 5	Yes	57.17	0.54	10.60	28.74	0.18	0.43		0.74	1.61	100.00
Max.		57.17	0.54	14.68	38.53	0.58	1.75	0.53	0.74	1.61	
Min.		45.81	0.52	10.60	28.74	0.18	0.25	0.53	0.74	0.50	

All results in weight%

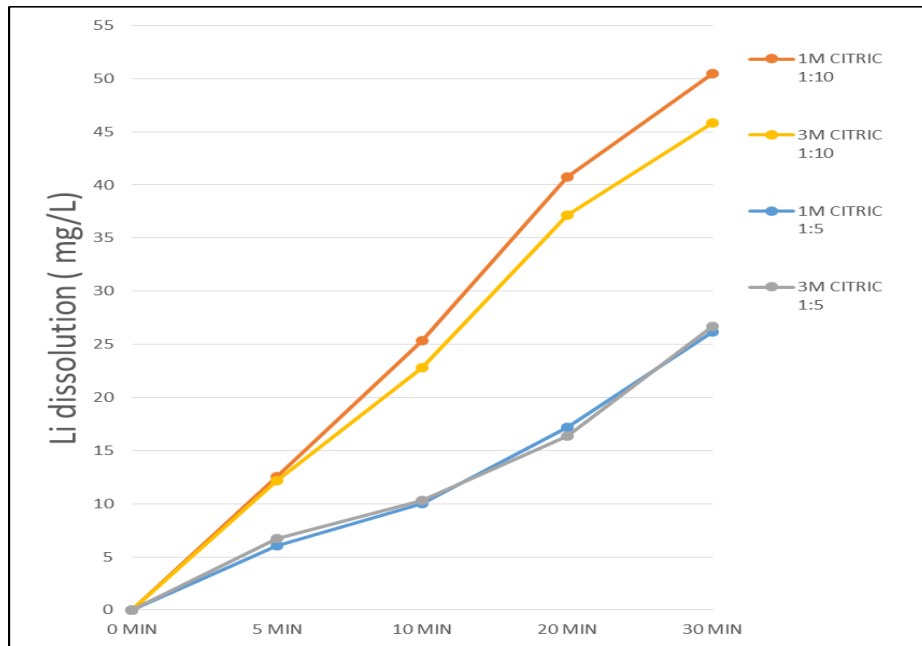
Appendix I. Co-leaching of Al, Fe and Si on mechano-activation samples after H₂SO₄ leaching

SAMPLE CODE	METALS EXTRACTION, %			
	Li	Fe	Al	Si
A	6.0	60.6	10.6	0.0
B	7.6	60.0	13.0	0.0
C	2.6	46.6	6.3	0.0
D	34.1	59.3	17.1	0.0
E	5.5	59.8	10.5	0.0
F	1.2	27.2	3.0	0.0
G	2.4	40.0	5.4	0.0
H	3.7	50.0	9.2	0.0
I	9.3	97.7	21.0	0.0
J	6.6	29.9	22.2	0.0
K	30.2	49.3	15.3	0.0
L	16.8	64.7	18.8	0.0
M	13.7	136.3	25.7	0.0

Appendix J-1. Li recoveries on mechano-chemical activation of alpha spodumene using PM 100 (Purba, 2019)

Sample Treatment	Lithium Concentration (mg/L)	Recovery, %
Feed sample	2980	n.a.
No reagent, 5:1 ball-mineral ratio, 120 minutes	15.37	0.52
No reagent, 10:1 ball-mineral ratio, 120 mins	26.52	0.89
Na ₂ SO ₄ , 5:1 ball-mineral ratio, 30 minutes	8.88	0.30
Na ₂ SO ₄ , 5:1 ball-mineral ratio, 60 minutes	13.11	0.44
Na ₂ SO ₄ , 5:1 ball-mineral ratio, 120 minutes	21.00	0.70
Na ₂ SO ₄ , 10:1 ball-mineral ratio, 30 minutes	11.68	0.39
Na ₂ SO ₄ , 10:1 ball-mineral ratio, 60 minutes	20.48	0.69
Na ₂ SO ₄ , 10:1 ball-mineral ratio, 120 minutes	40.30	1.35
CaCl ₂ , 5:1 ball-mineral ratio, 30 minutes	3.58	0.12
CaCl ₂ , 5:1 ball-mineral ratio, 60 minutes	15.40	0.52
CaCl ₂ , 5:1 ball-mineral ratio, 120 minutes	20.14	0.68
CaCl ₂ , 10:1 ball-mineral ratio, 30 minutes	15.69	0.53
CaCl ₂ , 10:1 ball-mineral ratio, 60 minutes	21.70	0.73
CaCl ₂ , 10:1 ball-mineral ratio, 120 minutes	33.04	1.11

Appendix J-2. Citric acid leaching test results on mechano-activated alpha spodumene samples using PM 100 (Hwang, 2019)



Li leaching recovery,						
Citric acid concentration	ball: spod. conc. ratio	leaching time	milling time, min			
			5	10	20	30
1M Citric acid	5:01	1h	0.20	0.34	0.58	0.88
	5:01	3 h	0.24	0.42	0.60	0.95
	10:01	1h	0.39	0.77	1.21	1.49
	10:01	3 h	0.42	0.85	1.37	1.69
3M Citric acid	5:01	1h	0.22	0.30	0.53	0.83
	5:01	3 h	0.23	0.35	0.55	0.89
	10:01	1h	0.35	0.71	1.14	1.40
	10:01	3 h	0.41	0.77	1.25	1.54

Appendix K. Al and Si co-dissolution on citric acid leaching of alpha spodumene samples subjected to mechano-activation

Sample Codes	Assays, ppm			Dissolution		
	Li	Al	Si	Li	Al	Si
A	72.5	324.8	159.6	2.4	2.8	0.1
B	106.7	456.7	191.4	3.6	3.9	0.1
C	31.8	208.6	112.7	1.1	1.6	0.0
D	138.7	493.2	131.6	4.6	4.0	0.0
D-11	296.3	944.0		9.9	7.7	NA
D-30	607.2	2350.0	85.0	20.2	19.1	NA
E	71.4	328.7	162.3	2.4	2.7	0.1
F	50.3	329.3	127.9	1.7	2.5	0.0
G	38.7	227.8	110.4	1.3	1.8	0.0
H	138.2	907.1	226.4	4.6	6.9	0.1
I	146.9	1183.6	212.3	4.9	8.9	0.1
J	360.0	1500.0	900.0	12.0	14.3	0.4
K	164.7	616.2	155.5	5.5	5.0	0.1
K-11	372.6	1279.9	NA ¹	12.4	10.4	NA
K-30	1180.0	5030.0	NA	39.3	41.0	NA
L	330.0	1200.0	890.0	11.0	11.4	0.4
M	48.6	243.7	110.8	1.6	1.9	0.0

¹ NA – not analysed