

24th Annual Conference Proceedings

Lithium Processing Conference

Including

Novel Lithium Processes Forum

Sponsored by



3rd Annual Lithium Processing Event

ALTA Metallurgical Services, Melbourne, Australia www.altamet.com.au

PROCEEDINGS OF

ALTA 2019 LITHIUM PROCESSING SESSIONS

Including Novel Lithium Processes Forum

24 May 2019

Perth, Australia

ISBN: 978-0-9946425-9-2

ALTA Metallurgical Services Publications

All Rights Reserved

Publications may be printed for single use only. Additional electronic or hardcopy distribution without the express permission of ALTA Metallurgical Services is strictly prohibited.

Publications may not be reproduced in whole or in part without the express written permission of ALTA Metallurgical Services.

The content of conference papers is the sole responsibility of the authors.

To purchase a copy of this or other publications visit www.altamet.com.au



Celebrating 33 years of service to the global mining and metallurgical industry.

ALTA Metallurgical Services was established by metallurgical consultant **Alan Taylor** in 1985, to serve the worldwide mining, minerals and metallurgical industries.

Consulting: High level metallurgical and project development consulting.

Conferences: ALTA conferences are established major events on the international metallurgical industry calendar. The event is held annually in Perth, Australia. The event comprises three conferences over five days: Nickel-Cobalt-Copper, Uranium-REE-Lithium and Gold-PM.

Short Courses: Technical Short Courses are presented by Alan Taylor, Managing Director.

Publications: Sales of proceedings from ALTA Conferences, Seminars and Short Courses.

MetBytes: Free technical articles offering metallurgical commentary and insights.

Free Library: Conference proceedings and technical papers. The library is expanded regularly, providing a major ongoing resource to the industry.

THE NATURE OF LITHIUM MINERAL PHYSICAL PROPERTIES IN SELECTING CALCINATION AND ROASTING EQUIPMENT

By

Grant Harman

Lithium Consultants Australasia, Australia

Presenter and Corresponding Author

Grant Harman grant.harman@lithiumconsultants.com

ABSTRACT

Until recently, Talison was essentially the sole supplier of spodumene concentrate to the world. The bulk of the spodumene concentrate had a grade of 6 wt% Li₂O and still remains the bench mark for chemical grade. In addition, the combined spodumene and quartz content comprised roughly 90 wt% and other minerals only 10wt%.

The newer spodumenes being offered to the market typically have a lower amount of spodumene and quartz and behave differently in the calcination and/or roasting operations which are typically the first steps in the processing of lithium concentrate to extract the lithium. Furthermore, many of the new ores require flotation of a significant portion of the ore in order to achieve the grade and this results in a finer concentrate. Similarly, the secondary lithium mineral concentrates, such as lithium micas and clays, are also fine (compared with the median particle size of the Talison SC6.0) and contain a larger percentage of other minerals. They are generally more reactive, for example to acids at low temperature.

There are a suite of tests that can be performed on a lithium concentrate to determine which equipment is the most suitable for the calcination and or roasting of the ore. The tests that can be considered include elemental analysis, mineralogy, PSD (particle size distribution), TGA (thermogravimetric analysis), DSC (Differential Scanning Calorimetry) and the Heating Microscope Dilatometer.

Based on the physical properties a selection of the best equipment can be made for the application with the melting point and PSD of the concentrate being the two main factors to consider. Typically, the range of calciners and roasters available include rotary kilns, fluidised bed kilns, flash calciners, tunnel kilns and multiple hearth furnaces. This paper provides guidance for the selection of the most suitable equipment based on the physical properties of the lithium concentrate.

Keywords: Lithium ores, spodumene, calcination, calciner, roaster, TGA/ DSC, PSD, rotary kiln, fluidised bed kiln, flash calcination, multiple hearth furnace.

INTRODUCTION

All operating lithium conversion plants of spodumene involve calcination and roasting as the first processing steps to extract lithium. The calcination involves heating the ore up to a temperature of around 1,100°C causing the spodumene to be converted from the α -spodumene to β -spodumene form. The structure of the spodumene is irreversibly changed from monoclinic to tetragonal and causes the mineral to shatter. The volume increases by about 30% and makes the lithium in the ore amenable to reaction with acid to form lithium sulphate which can be extracted from the ore in a water leach.

Secondary lithium minerals are largely proposed to be extracted using an alkali salt roast at temperatures in the region of 800° C – 1,000°C. The roasted calcine is water leached to extract the lithium. Due to the higher reactivity of the secondary minerals, there are technologies that use acid at temperatures around 100°C. These technologies are outside the scope of this paper.

In order to design the equipment for the calcination and roasting of the ore, a selection needs to be made of the best type of kiln for the application. In order to make the selection the properties of the ore or mixture being fed to the kiln needs to be considered. This also involves in knowing what tests can be conducted and what equipment is available for conducting these tests.

Definitions of calcination and roasting:

- Calcination in this application refers to the process of bringing about thermal decomposition of solid material in the presence of limited supply of air or oxygen.
- Roasting refers to the process of mixing ore and reagents and heating the mixture up to a temperature, usually lower than the calcination temperature to promote the reactions between the ore and the reagents.

FACTORS INFLUENCING THE DESIGN AND SELECTION OF CALCINATION AND ROASTING EQUIPMENT

The key properties of the feed material that affect the selection of the calcination and roasting kilns are the melting characteristics of the material at high temperature, the feed PSD (particle size distribution), abrasiveness and ability to handle dust. Each of these properties of the feed are discussed in greater details in this section.

Clinker Formation and Slagging

The temperature at which spodumene conversion starts is typically 960°C with pure spodumene melting at 1,430°C as shown in Table 1. The higher the temperature the better are the kinetics for the conversion but the smaller is the margin before the material will melt which also makes the selection of the best equipment as well as the design and operation of the equipment more challenging.

An added problem in heating the ore, or mixture, is that the ore is not a single mineral but a combination of minerals each with their own melting characteristics. A mineral that is partially or fully molten in contact with another solid mineral can form a eutectic mixture and result in the solid mineral melting well below the melting temperatures of the individual minerals.

In sintering experiments, it has been observed that as the temperature increases a number of minerals disappear and new phases appear. The new, lower melting point phases tend to coat the particles which is detrimental to the extraction of the lithium and requires grinding to disturb this coating or layer around the particle to allow for the acid to contact the ore. Additionally, this coating may prevent the required conversion reaction from taking place by acting as a barrier.

Various correlations have been developed to predict the fusion point, mainly for fly ash in the power generation industry. A typical empirical fusibility correlation is:

S.T. = f([Fe203 + Ca0 + Mg0 + Na20 + K20) / [Si02 + Al203])

where S.T. is the softening temperature defined in Figure 4.

In Table 1 the transformations of lithium minerals and roasting reagents is shown.

Table 1: Mineral transformat	ions at different temperatures
------------------------------	--------------------------------

Mineral	Temperature [°C]	Comments
Tourmaline	950	Dehydroxylation (>980 with higher Mg content), melting, F and B_2O_3 escape
Amphibole	400-800 >850	Fe→Fe ²⁺ (oxidative conditions) Dehydroxylation, meta phase transformation
Orthoclase KAlSi₃O ₈	>680	Can form low melting eutectic with albite of other feldspars
Albite (NaAlSi₃Oଃ)	1,100-1,120 (1)	Melting
Apatites	~1,600 (2)	Melting
Biotite	500-600 900-1,200	Oxidation of bivalent Fe, dehydroxylation Phlogopite decomposition
Muscovite	820-920 1,100-1,200	Dehydroxylation Recrystallisation to cristobalite and mullite
Quartz	573 870	$\alpha \rightarrow \beta$ transformation $\beta \rightarrow$ Tridimite transformation
α-Spodumene‡	>200 950-1,150 1,430	Dehydroxylation $\alpha \rightarrow \beta$ transformation Melts
Limestone CaCO₃	~900	Decomposes to Cao + CO ₂ influenced by CO ₂ partial pressure
Gypsum CaSO ₄ .2H ₂ O	60 -150 105 – 240 >1,200	Forms hemihydrate (CaSO ₄ .0.5H ₂ O) Forms anhydrite (CaSO ₄) CaSO ₄ \rightarrow CaO + SO ₂ + 0.5 O ₂
Na ₂ SO ₄	884	Melts
Clays	530 - 630	Dehydroxylation
Zinnwaldite	300 300- 800 800 900	Oxidation of Fe2+ followed by dihydroxylation Release of HF Precipitation of hematite observed Decomposition of Zinnwaldite accompanied by the liberation of SiF4

While several converters believe the main cause of clinker formation is iron, as Fe_2O_3 , the reason for clinker formation and slagging is more likely to be the combination of iron with the other oxides. Currently, several converters have set the maximum alkali content (Na₂O and K₂O) in the concentrate to 3wt%. Very little work appears to have been done in the lithium industry to develop a typical correlation for the fusibility for spodumene while it is reported that there are over 4,000 papers written on the behaviour of fly ash in coal fired Power Stations.

In general, calcination results in the product calcine having a PSD (particle size distribution) which is finer than the feed. If the kiln temperature is too high or if the spodumene is exposed directly to the flame, clinker can be formed. If the over-temperature in the kiln is limited, the clinker will be lighter in colour and soft, and if ground to around 200 microns can still achieve a lithium extraction of 75%. However, clinker formed at higher temperature with a corresponding darker brown colour and considerably harder will have a far lower lithium extraction. Typically, the design would assume a 1% lithium loss in the calciner due to clinker formation.

Particle Size Distribution

The particle size distribution of the feed largely depends on:

- 1) The beneficiation flowsheet which involves crushing and grinding the ore until the spodumene is liberated from the gangue. The finer the spodumene crystals the greater the liberation required to separate the gangue from the spodumene and the finer the PSD.
- 2) The nature of the comminution equipment can affect the number of fines produced
- 3) Whether the feed is pelletised or agglomerated.
- 4) The particle size of the reagents, which can be influenced by the PSD on the solid reactions.

A typical PSD graph of a spodumene concentrate is shown in Figure 1 where the Beneficiation plant flowsheet consists of a DMS (Dense Media Separation) and the flotation of the DMS rejects (overflow) showing the bimodal distribution.

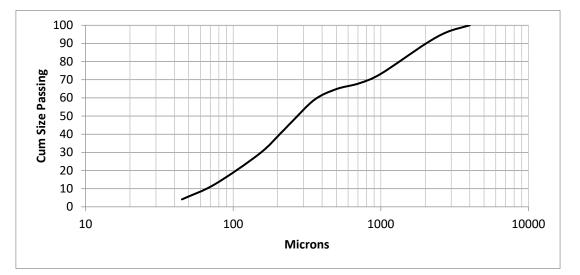


Figure 1: PSD of a Typical Spodumene Produced by the Combination of DMS and Flotation, showing the bimodal distribution.

The DMS typically produces a concentrate with a size distribution between 15mm - 0.5mm while the flotation produces a contrate with a PSD < 0.250 mm (250 microns). The PSD of the resulting concentrate has a major impact on the amount of dust elutriated from the kiln as well as heat transfer rate.

Dust

Fines in the feed to a calciner are likely to be elutriated out of the kiln with the offgases, especially in a rotary kiln. In a rotary kiln the amount of dust elutriated has been reported as being around 30% of the feed and poses significant issues if the dust handling equipment is not sized large enough.

In the case of a spodumene rotary kiln the dust is predominantly unreacted α -spodumene which should be recycled back the calciner feed. The β -spodumene although finer, is less dense compared with the α -spodumene and exposed to higher gas velocities is not elutriated to the same extent mainly due to the stickiness of the β -spodumene at thigh temperature.

As a result, the un-converted spodumene is recycled back to the calciner feed which reduces the overall capacity of the plant as the dust load increases in the kiln.

To get around the dusting problem, testwork has been done to use agglomerates, as proposed by Western Lithium, for the feed of a lithium clay mixture to the roaster.

Heat Transfer

The fines heat up faster than the coarser particles. The calciner and roaster need to be designed for the correct particle size distribution and specifically to have enough residence time for the heating up and soaking of the coarser particles at reaction temperature. Increasing the feed size to the calciner and or roaster can result in lower conversion or reaction extent. Retrofitting the kiln, for example, installing lifters or increasing the damming before discharge, to increase heat transfer may have limited beneficial effect as both changes may cause a significant increase in the amount of dust entrained with the offgas.

Abrasion

Spodumene is very abrasive and abrasion is pronounced at high temperature when metals are relatively soft. An example of this, was acid and β -spodumene plough mixer at RB Energy where the shell failed prematurely due to abrasion. Problems are also experienced in the refractory lined preheat cyclones in areas exposed to higher localised velocity such as cyclone inlets.

In contrast zinnwaldite and other lithium micas are softer as well as having a platelet shape which results in lower abrasion.

Bond abrasion indices (Ai's) vary from a low of 0.026 for limestone through 0.18 for quartz and 0.25 for magnetite to 0.69 for quartzite and taconite. Spodumene typically has a value around 0.3.

ANALYTICAL EQUIPMENT

Elemental Analysis

Elemental analysis is achieved using a combination of the following instruments:

<u>XRF</u> is an analytical technique used to measure the elemental composition of a sample but cannot measure lithium. XRF can distinguish important elements such as P, Ca, Mg, Fe, Al, Si and Sr.

Four acid digests followed by ICP-OES or peroxide fusion are industry standards as they can be used to analyse a full suite of elements at the same time and are accurate. As a note, it is important to calibrate the machine when analysing for high lithium tenors, using high and low grade CRMs (certified reference materials).

AAS used widely in operating plants for the analysis of Group I elements. That is Li, Na and K. The modern style of machine, such as the Analytic Jena AAS, can analyse Group I elements successively without the need to change the flame settings or the lamp. This is preferred as it is quick and considered by most converters to be more accurate for the detection of high tenors of lithium.

ISE used widely in laboratories for the for chloride and fluoride.

Mineral Analysis XRD

X-ray diffraction (XRD) is a technique used to determine the mineralogy of a solid sample and is able to infer the crystal structure of a material. This becomes very useful when structural changes have occurred in a material rather than elemental changes. In this case, XRD can determine the temperature at which the $\alpha \rightarrow \beta$ spodumene reaction occurs.

TGA/ DSC/ MS

TGA/ DSC/ MS is the commonly abbreviated form referring to Thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC) and Mass Spectrometry (MS). TGA and DSC are typically in a single machine which is coupled (connected by a pipe) to the MS.

Thermogravimetric analysis (TGA) involves recording the changes in the mass of a sample as it is heated up from ambient.

Differential Scanning Calorimetry (DSC) is a measure of the difference between the heat flow of the sample against a reference sample. It provides quantification of the chemical and physical changes occurring in the sample.

Mass Spectrometry (MS) analyses the purge gas from the sample holder of the TGA/ DSC and confirms qualitatively what gases have been generated as well as at what temperature the generation occurred. The MS is able to monitor up to 60 channels. Each channel is a molecular weight of the gases generated from which the most likely compound can be inferred.

The analysis by TGA and DSC of a mineral sample is only applicable to samples that contain thermally active minerals. Most mineral samples consist of a mixture of minerals that are thermally active over the typical TGA and DCS temperature range but there can also be a considerable part of the minerals that don't show any thermal reactivity in response to heating.

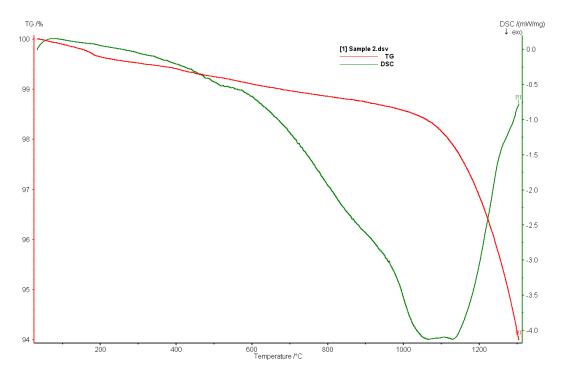


Figure 2: TGA and DSC results for spodumene. Ramping rate of 10 °C per minute to 1300 °C.

The TGA/DSC results in Figure 2 are typical for a spodumene. Common observations from this chart are:

- For spodumene concentrate with a high lithium grade it is expected that there will be small levels of dehydroxylation of minor minerals, but a more pronounced endothermic peak corresponding to the structural change of α-spodumene to β-spodumene. At high enough temperature, minor minerals may melt. If the temperature reaches ~1,430°C (the typical melting temperature of spodumene) the whole sample would be melted.
- A sudden endothermic process (a sudden rise in the DSC curve) in the material will then
 occur at some temperature >1100 °C depending on the chemical makeup. This indicates that
 some of the material has begun to melt. Any further spikes in the DSC indicate further melting
 of certain compounds.

Heating Microscope Dilatometer

A heating microscope dilatometer (HMD) is an instrument used to measure shape changes of materials over a range of temperatures. Essentially a sample of material (compacted lithium mineral cube) is placed into a heating furnace and as the temperature increases there are quantifiable changes that occur to the sample shape. The HMD comprises of three sections:

- The furnace, where the sample is placed and temperature ramping occurs.
- The camera, which records the changing shape of the sample.
- The lamp, which shines light on the sample making a silhouette for image capture.

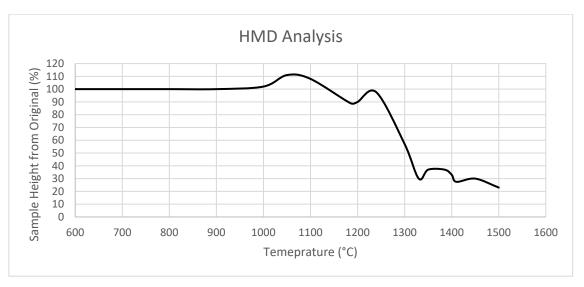


Figure 3: Typical Spodumene HMD analysis of sample height over a range of sintering temperatures.

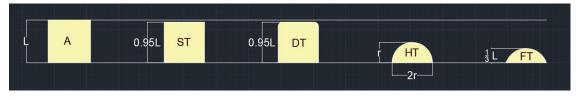


Figure 4: Typical sample silhouette at various temperatures adapted from (3).

Figure 4 illustrates how a materials' shape changes during the sintering process. The typical abbreviations relating temperature to sample shape are:

A – Original shape

ST – The temperature where the sample size has decreased by 5 % (softening temperature)

DT – The temperature where the sample corners begin to round (deformation temperature)

HT – The temperature where the sample shape begins to resemble a half sphere (hemispherical temperature)

FT – The temperature where the sample has melted and spreads (fluid temperature)

The HMD is able to analyse the sample height in real time and produce a graph typical to that in Figure 3. The HMD shows that the sample height begins to rise at approximately 950 °C which corresponds to the conversion of α -spodumene (3.2 g/cm³) to β -spodumene (2.4 g/cm³). Following expansion, the sample begins to decrease in size as the sample begins to melt (DT) however another small spike can be observed indicating the completion of the spodumene conversion.

After this, the rapid drop in height indicates that a large portion of minerals in the sample are beginning to melt. Again, sudden small spikes may indicate the formation of lighter phases. The height is expected to continue to drop after about 1430 °C (spodumene melting point).

HMD is an important analytical tool as it can indicate the deformation temperature (DT), where the material will typically start to become sticky⁽³⁾. Mineral impurities such as amphibole, micas and albite will begin to melt below the spodumene conversion temperature. A material, such as shown in Figure 3, with significant low melting mineral present poses a significant challenge in selecting a suitable kiln.

KILN TYPES

Rotary Kiln

The rotary kiln is the only kiln successfully commercialised for the calcination of spodumene and is also widely used for the sulphation roasting of beta spodumene. A rotary kiln is a long cylindrical shaped shell supported on riding rings (tyres) that continuously rotate as illustrated by Figure 5. The drum is lined with refractory brick (or cast) and set at a slight angle to help continuously move the material to the discharge end. Typically, the drum is at an incline of 2- 6° with a rotary speed of 0.5 - 5 rpm ⁽⁴⁾. A calciner for a 20,000 tpa LCE (lithium carbonate equivalent) plant is around 60 metres in length and has an outer diameter around 5 metres. Hot discharge product requires cooling, usually in a rotary cooler roughly 75% the length of the kiln.

Gas velocities through the kiln can be significant and because of the tumbling action in the kiln, significant dust is generated and requires dust control. In the flame radiation zone dust can be overheated, which can result in lower recovery. Dust recovery equipment on the exhaust adds considerably to the cost of the kiln.



Figure 5: Direct Fired Rotary Kiln

The most common type of rotary kiln is the direct fired type, where a single burner is located at discharge end of the kiln and the hot gasses counter-currently exchange heat with the feed which enters at the feed end.

The fuel is commonly either natural gas or pulverised coal but also fuel oil has been used.

In contemporary design, the incoming feed is preheated in a series of cyclones with the hot gases from the calciner, as is common practice in the cement industry. This has the benefits of better energy utilisation and lower cost to capture the fines. Downstream dust collection is still required. However, incorrectly designed pre-heaters may result in off-gas discharge to the baghouse that may be too hot or cold, with each of these conditions able to greatly reduce plant availability.

The other type rotary kiln typically used in lithium industry is the indirect type in which there are several smaller burners along the length of the shell and heat is transferred through the shell to the material inside. This is commonly used for sulphation roasters where the roasting temperature is moderate and the residence time short.

The properties of the feed which have the largest impact on the design and operation of the rotary kiln are the PSD and melting point. These are discussed in greater detail below.

Effect of PSD

Increasingly the spodumene concentrates entering the market contain higher amounts of fines than the historical Talison 6.0 as a result of increased use of flotation that requires grinding the material fine to achieve the required liberation.

The increased number of fines result in higher carry over (entrainment) of fines with the offgas which requires larger offgas handling equipment as well as having an adverse effect on the capacity of the plant.

The issue of PSD is being addressed in industry with a combination of:

- 1) Blending of coarse and fine feed. This is being done in one Chinese plant where coarse Galaxy concentrate is being blended with fine Mineral Resources flotation concentrate.
- 2) Reducing the spread of size. One spodumene producer has reduced the top size to 2 mm and reduced the amount of fines by making process changes to the beneficiation plant.
- 3) Agglomerating the feed. An example is the proposed agglomeration of a lithium bearing clay ore with the roast reagents. The agglomerates were proposed to be dried using waste heat prior to being fed to the Roaster.

Clinker Formation and Melting

The rotary kiln typically serves more than one purpose. That is the feed material is dried, preheated up to the calcination or roasting temperature, soaked (held at the reaction temperature for the required time) and then cooled. In the kiln the gas is hottest in the area adjacent to the burner and decreases towards the off-gas outlet. In the hottest section of the kiln, the temperature will exceed the melting temperature of some of the feed and clinker will form, and if the temperature of the solids is high enough, glassing will occur.

Clinker formation is almost impossible to prevent in a rotary kiln and is not limited to the formation of large masses, but also to the PSD of the whole feed becoming larger in the calciner or roaster. For clarity, fines fuse together to form larger particles. In general, provided that temperature is not too high and the calcined or roasted product is ground, lithium extraction is not detrimentally affected.

In some cases, lithium plant operators have had to shut down the kiln and remove the molten material in the area of the burner tip on fortnightly basis. Glassing build up has been reported to be up to 100 mm thick but is reported to be reasonably easy to remove.

Flash Calciner

A flash calciner (otherwise known as gas suspension calciner) is a relatively new technology in the lithium industry but is commonly used in the alumina industry. Significant testwork has been done at ThyssenKrupp and FL Smidth to commercialise this technology for the lithium industry with the first commercial flash calciner expected to be installed at the Nemaska plant.

The core of the unit is the u-shaped cylindrical "pipe" as illustrated by Figure 6. The mineral feed is first pre-heated in a series of cyclones using recycled exhaust gas from the calciner. The pre-heated feed is mixed with hot gases around 1,200°C which pneumatically convey the solids to the Product Cyclone where the calcined solids are separated from the hot gas. Key aspects of the flash calciner are:

- The hot gas is limited to the melting temperature of the solids. Typically, this is set around 1,200°C.
- The device is a co-current contactor in that the gas temperature decreases and the solids temperature increases along the length of the calciner with both approaching the same outlet temperature.
- The outlet temperature needs to be higher than the conversion temperature for the conversion of the α -spodumene to β -spodumene. This is around 960°C.
- The mass of hot gas required is roughly 4 times the mass or ore fed to the calciner.
- There is significant heat consumption (process heat and heat loss) through the calciner and supplementary burners are required which create hot spots.
- Melting of the feed results in blocking of the "pipe" and increases the pressure drop across the unit making it more susceptible to blockage than a rotary kiln.
- Melted material in the pipe is expected to be more difficult to remove than in a rotary kiln.

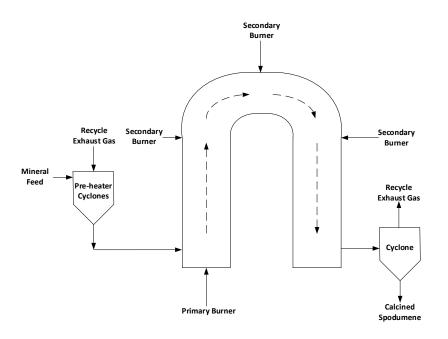


Figure 6: Simplified diagram of a multi stage flash calciner/ gas suspension calciner.

Compared to rotary kiln, the flash calciner has a number of advantages such as lower CAPEX (indicated to be around 30% less), lower OPEX (indicated to be around 30% less), good heat recovery and a smaller footprint. Despite this, there are several critical issues that must be considered.

Fluidised Bed Calciner

A fluidised bed calciner was installed in the Talison plant in 1995 but there were significant problems with the operation of the unit mainly due to the abrasive nature of spodumene. A fluidised bed roaster has been considered for lower temperature operation with less abrasive feed mainly as it is thought to offer better temperature control.

The operation of a fluidised bed roaster is shown in Figure 7. The feed is pre-heated in several cyclones using recycled exhaust gas from calcination. The pre-heated material then enters the bottom of the calciner where hot combustion gases fluidise and calcine the particles. The calcine is pneumatically transported to a cyclone where the calcine is separated from the gases and dust. The described process is typical for a circulating fluidised bed calciner.

Key aspects of the flash calciner are:

- Spodumene is very abrasive and a fluidised bed calciner does not appear to be a viable option.
- PSD needs to be narrow to allow fluidisation of the bed without excessive elutriation of the fines from the bed. A spodumene concentrate with a bimodal PSD as shown in Figure 1.
- Spodumene is notoriously difficult to fluidise.
- Would not appear to be suitable for a roaster in which solid-solids reactions occur and the solids are not in close contact with each other.
- Maximum temperature is around 1,200 °C.
- The fluidised bed has as a small footprint.
- Precise temperature control.

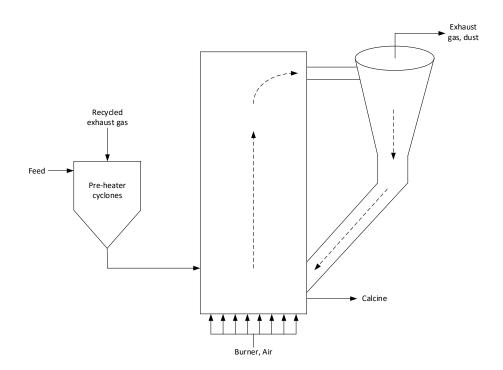


Figure 7: Typical circulating fluidised bed calciner configuration

Tunnel Kiln

A tunnel kiln is a long continuously operated kiln consisting of tunnel kiln with potentially hundreds of burners mounted along its side. A typical tunnel kiln used in the brick industry is shown in Figure 8. Material to be fired is loaded onto kiln cars that carry the material being fired through the kiln. The cars are unloaded and returned to the filling station. The kiln is heated electrically or direct fired using natural gas, LPG, producer gas, fuel oil or coal fuels. The atmosphere is normally oxidizing, but can be neutral or reducing if required. The maximum firing temperature is $1,750^{\circ}$ C with temperature control to $\pm 5^{\circ}$ C anywhere in the kiln.

To accommodate higher production, heat transfer to the solids can be increased by circulating hot gases through the solids. Material is briquetted to optimise heat transfer through the material while minimising the pressure drop through the bed. Because there is no solids movement, there is no abrasion and no observable dust.



Figure 8: Tunnel Kiln

Tunnel kilns are a very energy efficient and inexpensive choice which allow for good temperature control throughout each chamber. This is particularly important for roasting where there can be a small temperature difference between mineral softening and melting temperatures. Some of the advantages to the tunnel kiln are:

- High maximum temperature
- Excellent temperature control
- Minimal dust (dust recovery not necessary)
- Thermally efficient with little maintenance, i.e. low OPEX

However, the tunnel kiln can have a very large footprint, up to approx. 140 m long.

For a more detailed description of a tunnel kiln, the reader is recommended to read the companion paper presented at ALTA 2019 by Dr Jeff Claflin.

Multi-Hearth

A multi-hearth kiln is a tower like structure containing a central shaft which drives multiple rabble arms/ rakes as illustrated by Figure 9. The feed material enters from the top of the kiln and is raked by the rabble arms to mix the material and move it to the hearth discharge allowing it to fall downwards from upper hearth to the hearth below. Multiple burners are installed at each hearth levels to maintain the required temperature. Typically, the bottom section of the kiln does not have heating which allows the calcine to be cooled.

The most significant issue with the multi-hearth kiln are the rotating parts, which have historically required a high level of maintenance. The softening and melting of minerals in this kiln can be especially problematic as the rabble arms may struggle to shift the material. Multi-hearth kilns are quite outdated and not being considered seriously for any of the current lithium projects.

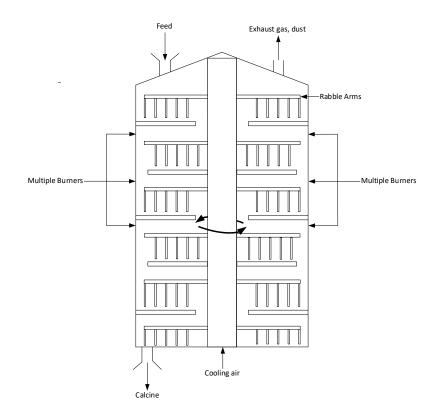


Figure 9: Diagram of a typical multi-hearth kiln

SUMMARY

There are many different criteria that must be considered when selecting an appropriate kiln for calcination or roasting. PSD, footprint and melting are some of these key parameters and are included in Table 2.

Criteria	Rotary – Direct Fired	Rotary – Indirect Fired	Flash	Fluidised	Multi-hearth	Tunnel
Footprint	Can be >60 m long, >6 m diameter	Limited in length	Small - tall standing unit	Small - tall standing unit	Typically, < 10 m diameter	Large. Can be >140 m and 4 m wide (includes cooler)
Energy Efficiency	Low in the rotary kiln but can be improved with a pre-heat section	Lower than direct type, relies on heat transfer through shell	Considered to be better than a rotary kiln but relies on pre- heating the feed	Continuous production, short residence time, high throughput	Limited output rate	Very good and does not require a separate cooler of the solids
Maximum Temperature	>1,600 °C	Approx. 1,150 °C	Approx. 1,450 °C	Approx. 1,200 °C	Approx. 1,200 °C	> 1,750 °C achievable
Overheating	Will occur in burner area and impact depends on the nature and amount of low melting minerals present	Good control – burners along length of kiln ±20 °C control	Can be held constant with burners through the calciner	Precise control and uniform temperature	Precise control, ±5°C	Excellent uniformity, precise temperature control, ±5°C due to multiple burners throughout kiln
Melting	Clinker formation will occur but should be possible to minimise glassing. In the event of glassing can be chipped out without major impact on operation.	Should be able to prevent glassing but cake build up in the feed area of an acid roaster is likely but can be mitigated with knockers.	Maintaining heat in the "pipe" is potentially an issue and supplementary burners likely to result in hot spots causing melting. Melting is a real problem.	Good temperature control although bed being eroded can result in significant localised overheating.	Good temperature control however major issue to remove	The good temperature control should prevent melting but would be a significant issue if briquettes formed a solid mass and have to be mechanically removed from baskets.
Abrasion	Minor issue due to higher air flow through kiln	Low issue - limited air flow hence low particle velocity	High particle velocity may cause abrasion	High particle velocity may cause abrasion	Low -slow moving system	No material movement thus no abrasion
PSD	5 mm > PSD > 0.2 mm	Smaller PSD than direct type is allowable	Grinding required, < 2 mm, sometimes <4 mm	Grinding required, 0.5< PSD < 5 mm	Suitable for all sizes <40 mm	Uses briquette or agglomerated form

Table 2: Key kiln selection criteria

Criteria	Rotary – Direct Fired	Rotary – Indirect Fired	Flash	Fluidised	Multi-hearth	Tunnel
Dust/offgas equipment sizing	Small PSD means fines caught in kiln air flow hence large off gas equipment sizing	No air flow thus fines not captured hence small offgas system	Dust loses if too fine a feed	Dust loses if too fine a feed	Small - limited dust loses, small system	Small – limited fines usually no requirement for dust collection
Capital Cost	High	High	Low	Low	High	Low
Operating Cost	High fuel consumption	Higher fuel consumption than direct type, high maintenance on burners and rotating parts	Low due to hot exhaust gas recycle, minimum moving parts	Low due to hot exhaust gas recycle, minimum moving parts	Low operating cost due to heat recycle but high maintenance of moving parts	Good fuel economy due to heat recycle, low maintenance and low labour requirement
Spodumene Calcination (Y/N)	Y	Ν	Y	N	Y	Ν
Alkali Salt/ Acid Roasting (Y/N)	Y	Y	Ν	Ν	Y	Y

CONCLUSION

Historically the hard rock conversion was effectively only done in China and using spodumene concentrate sourced from the Talison mine in Western Australia. Several new mines have come on line that now offer spodumene concentrates to converters. These are different to the standard Talison SC6.0 in several key aspects. These are:

- 1) Different PSD- typically greater percentage of fines
- 2) A greater amount of other minerals present with a higher propensity to melt at lower temperature
- 3) Lower grade

In addition, there are a growing number of projects looking to establish the viability of secondary lithium minerals such as lithium clays and micas.

In order to select the best kilns for the application an assessment needs to be made of the physical properties of the concentrate. Techniques to evaluate the physical properties include chemical and mineral analysis, TGA, DSC abrasion index measurement and the HMD. Based on the data from these tests it is possible to predict melting behaviour as well as dust formation and guide the designer towards the kiln which is best suited to the specific application.

ACKNOWLEDGMENTS

The author thanks Jeff Claflin for reviewing the paper and Anthony Yannakis, Lithium Consultants Australasia for collating data for this report and preparing graphics.

REFERENCES

- 1. Congruent melting kinetics of albite: Theory and Experiment. Greenwood, James P and Hess, Paul C. Rhode Island : Journal of Geophysical Research, 1998, Vol. 103.
- 2. *The melting points of synthetic apatites*. **Pandya, J R and Mehta, B J.** 288, Baroda : Mineralogical Magazine, 1969, Vol. 37.
- 3. *Fusion Characteristics of Volcanic Ash Relevant to Aviation Hazards.* **Song, Wenjia, et al.** 2014, Geophysical Research Letters, pp. 2326-2332.
- 4. Office of Air Quality Planning. Calciners and Dryers, in Mineral Induestries Background Information for Proposed Standards. Springfiled : U.S Environmental Protection Agency, 1985.
- 5. **Bryers, Richard W.** *FIRESIDE SLAGGING, FOULING, AND HIGH-TEMPERATURE CORROSION OF HEAT-TRANSFER SURFACE DUE TO IMPURITIES IN STEAM-RAISING FUELS.* New Jersey : Foster Wheeler Development Corporation, 1995.
- 6. *Mechanical enrichment of converted spodumene by selective sieving.* **Peltosaari, Olli, et al.** 2016, Minerals Engineering, pp. 30-39.