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Scale Up of Pyrometallurgical Processes in the Extraction of Lithium from Minerals

Presented at IChemE, Perth 26 June 2017

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Introduction

- Roughly 40% of the world's lithium is sourced from spodumene.
- The Chinese chemical converters all use the sulphation route to extract lithium and the upfront treatment of the spodumene is with pyrometallurgical processes.
- There are a few projects at present looking at commercializing secondary lithium mineral projects.
- The clay, zinnwaldite and jadarite project are all looking at pyrometallurgical processes.
- This presentation will discuss the design of a spodumene calciner and a zinnwaldite roaster and the steps from concept through to commercialization.

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Spodumene Calcining

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Calcining Spodumene

- “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.”
- α-spodumene which has a monoclinic structure is transformed into β-spodumene which has a tetragonal structure.
- Spodumene undergoes an irreversible phase transformation at about 1,000°C. This transformation is accompanied by a 30% volume increase as the specific gravity changes from 3.1-3.2 to about 2.4.

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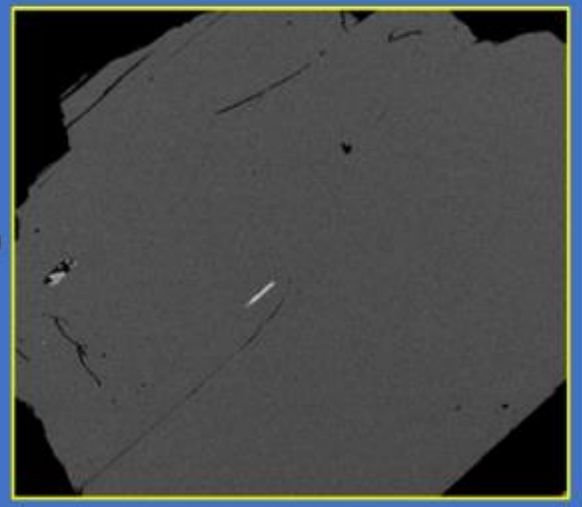
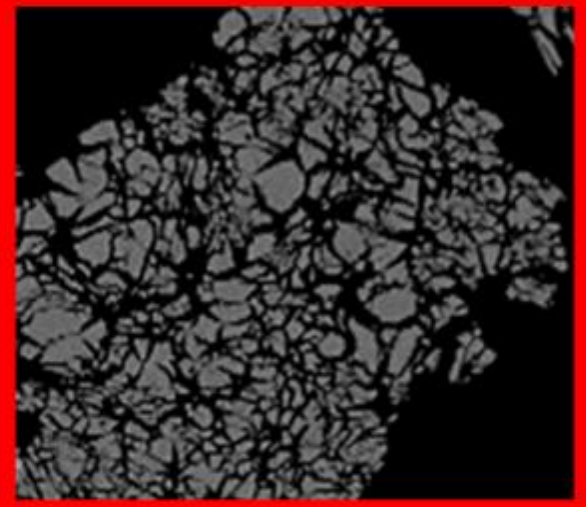
Calcination of Spodumene

α -



1,080°C

β -



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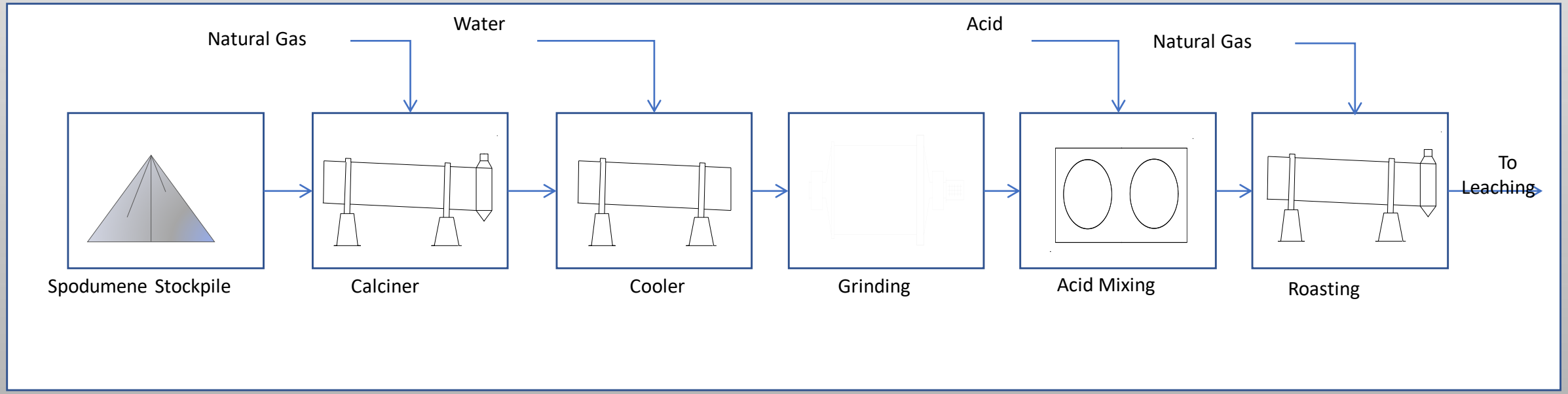
Sulphation Flowsheet for Spodumene

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Factors Affecting Calciner Design

- Grade - capacity
- Temperature – faster kinetics with increasing temperature
- Residence Time – adequate time to be converted
- Particle size – smaller particles convert faster
- Impurities – clinker formation


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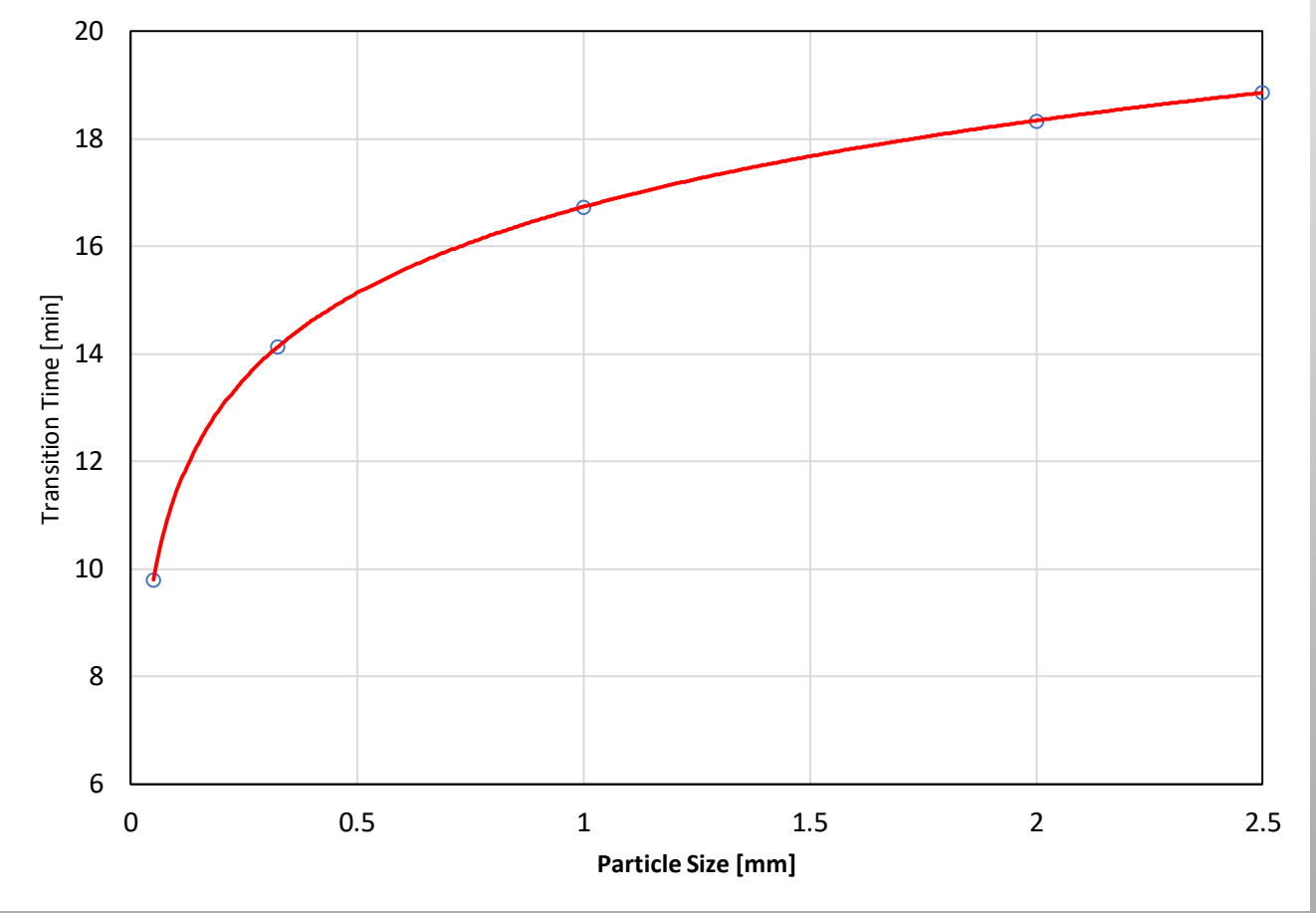
Effect of Particle Size on Transition Time




Effect of Particle Size on Entrainment

- The hot off gas typically entrains an amount of dust.
- In general the finer the calciner feed the greater is the entrainment.
- Some calciners have a scroll on the inlet which is there to minimize the entrainment.
- Most of the dust entrained is not transformed from α to β and therefore it tends to be returned to the feed end.
- Heat transfer is augmented by fitting lifters in the feed end as well as refractory bricks which extend a bit further into the calciner.

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Effect of Impurities

Minerals Present	Spodumene A	Spodumene B
Spodumene	77.2	77
Quartz	11.3	2
Albite	3.8	5
K-feldspar	3.1	1
Muscovite (Mica)	0.8	8
Phosphates	0.2	1
Iron Minerals	3.6	
Amphibolite		6

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Effect of Impurities

Mineral	Melting Temperature [°C]
Amphibole	800
Micas	700-1,000
Albite	1,100
K-Feldspar	1,250
Spodumene	1,420
Quartz	1,670

Spodumene Conversion Temperature [1,080 °C]


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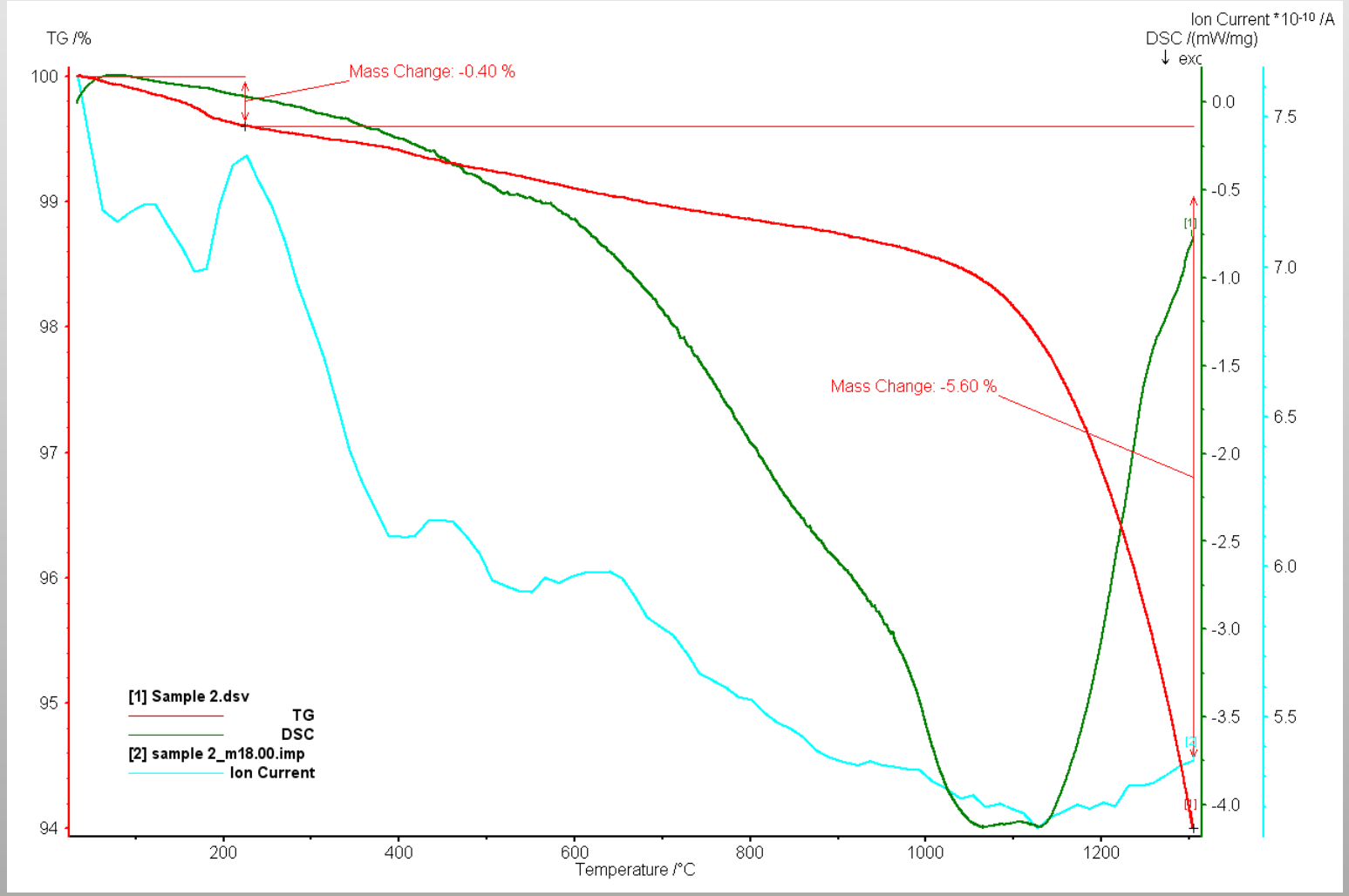
Role of Iron in Spodumene Processing

- Iron is present in a number of minerals as well as in spodumene lattice.
- White spodumene contains 0.02-0.1% Fe_2O_3, green contains 0.3-0.5% Fe_2O_3 .
- Iron containing minerals associated with spodumene include:
  - Micas such as Muscovite and Biotite,
  - Phosphate minerals such as ambylgonite, montebrasite and apatite, tourmaline, and mining waste such as amphibole
- Removal of iron can be achieved by magnetic, chlorination and acid washing.

Properties of Spodumene



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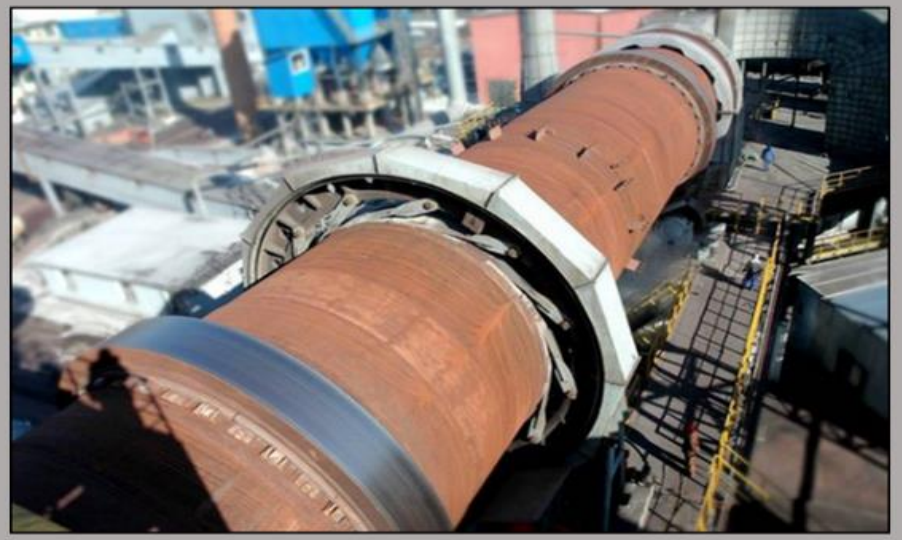
Scale Up

Laboratory

Pilot Plant



Calciner

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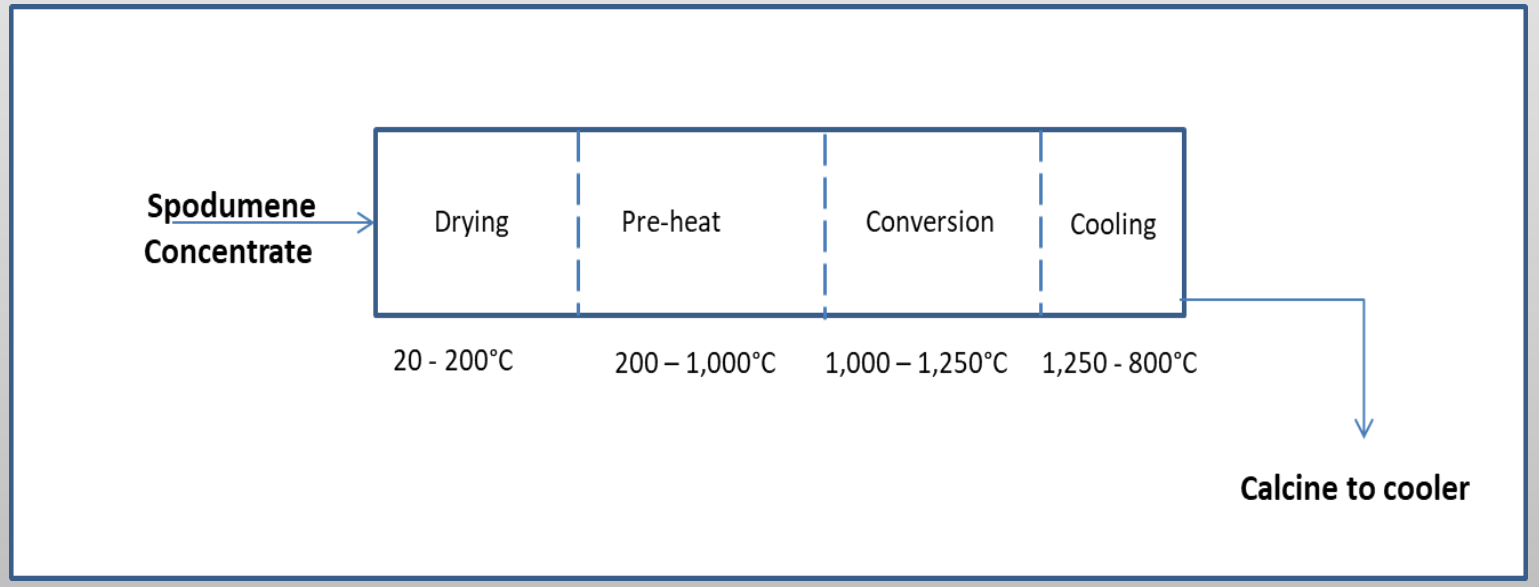
Calciner Design



The challenge is how to design a single unit that is capable of achieving all four steps within a single device.

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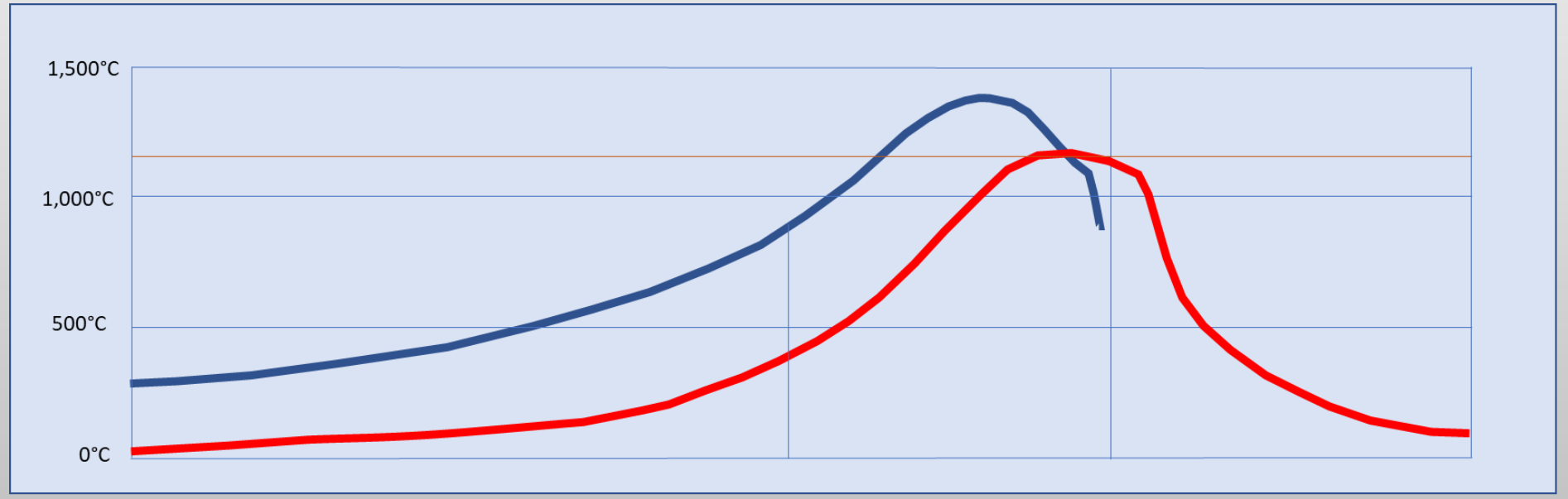
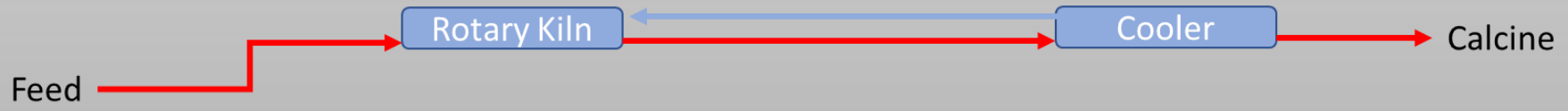
Calciner Design





Gas Retention Time	
10 seconds	
Material Retention Time	
180 minutes	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Summary

- Testwork for a calciner is straight forward to establish the time/ temperature relationship to achieve 99% conversion.
- Spodumene concentrates from different beneficiation plants have different impurities, size distribution and grade and influence the design of the calciner.
- The rotary kiln is not the best choice for achieving the combined drying, pre-heating, conversion and cooling.

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Zinnwaldite Roasting

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Roasting Zinnwaldite

- **Roasting** is a process of heating of concentrated **ore** to a high temperature in presence of air.
- **Roasting** consists of thermal gas–liquid reactions, which can include oxidation, reduction, chlorination, sulfation, and pyrohydrolysis.
- Roasting of zinnwaldite converts the lithium to lithium sulphate which can be extracted in a water leach.
- Roasting technologies include:
  - Sodium sulphate roast
  - Gypsum Roast
  - Acid Bake

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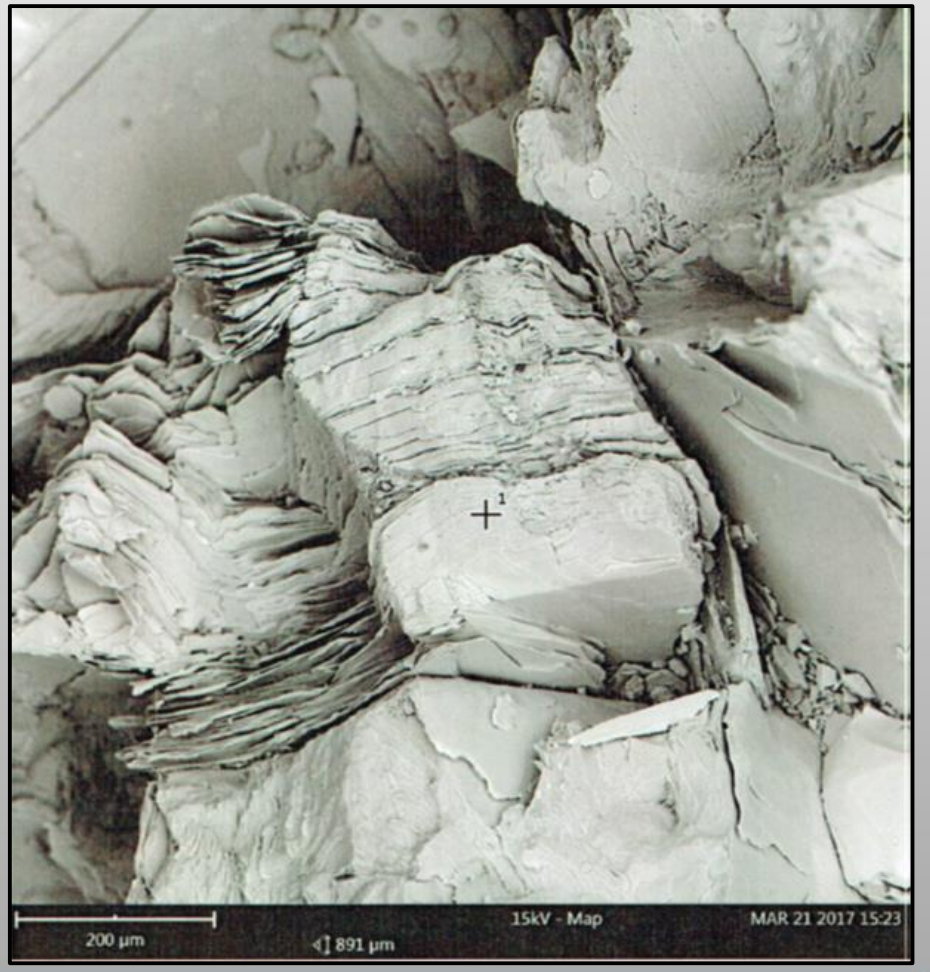
What is Zinnwaldite?

- Zinnwaldite can be considered to be part of a solid solution series of the ferrous lithium micas.
- The series is characterized by the progressive replacement of Li^{+1} by Fe^{+2}, with an average replacement ratio of 2.0 Li^{+1} for 1.5 Fe^{+2}.



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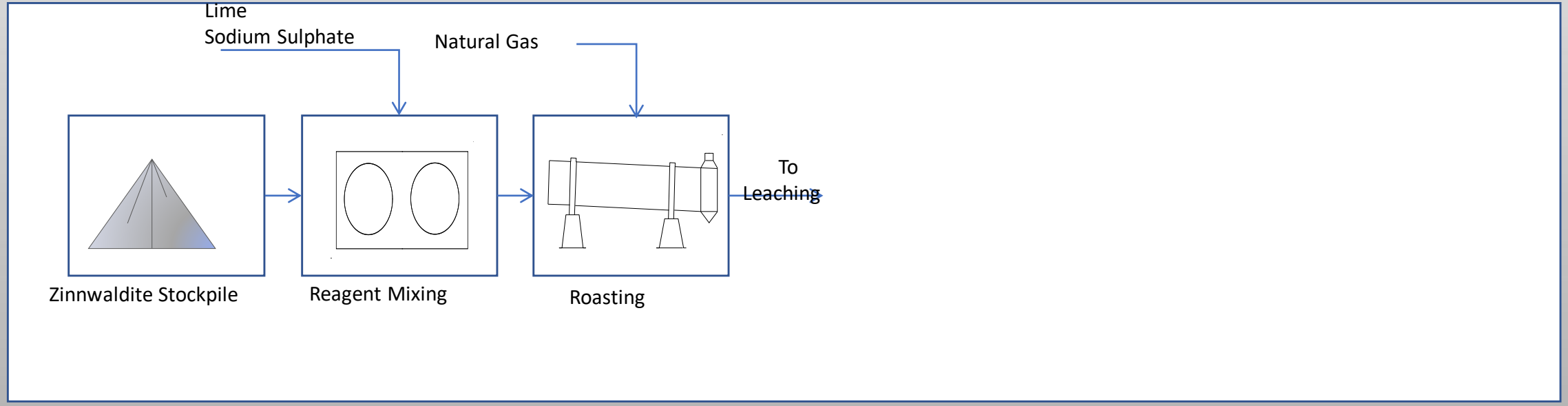
EMH Zinnwaldite Flowsheet




Theory of Sodium Sulphate Roasting

- The most accepted theory is that of Haas & Khalafalla in which sodium sulphate acts as a carrier of SO_3.
- There is no evidence of SO_2 formation.
- For a gypsum/ sodium sulphate/ lime roast it is proposed that:

  $CaSO_4 \rightarrow CaO + SO_3$.

  $Na_2SO_{4(s)} + SO_3 \leftrightarrow Na_2S_2O_{7\ (l)}$

  $Na_2S_2O_{7\ (l)} + Li_2O \rightarrow Li_2SO_{4(s)} + Na_2SO_{4(s)}$

  - It is suggested pyrosulphate forms between 300 – 400°C and is molten.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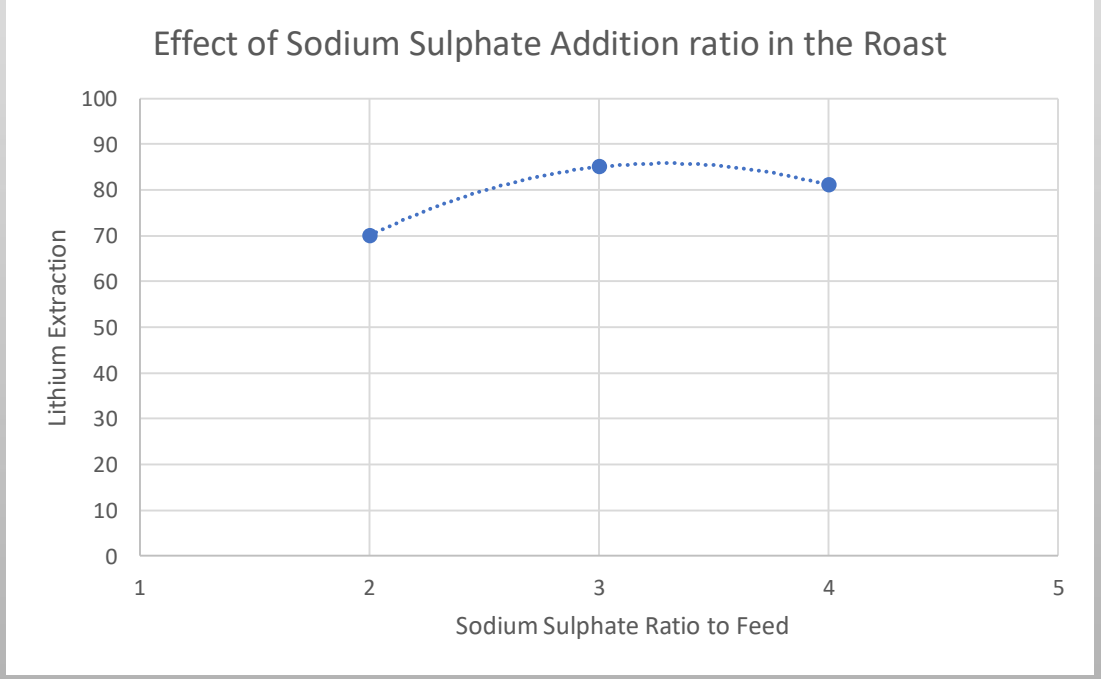
Theory of Sodium Sulphate Roasting



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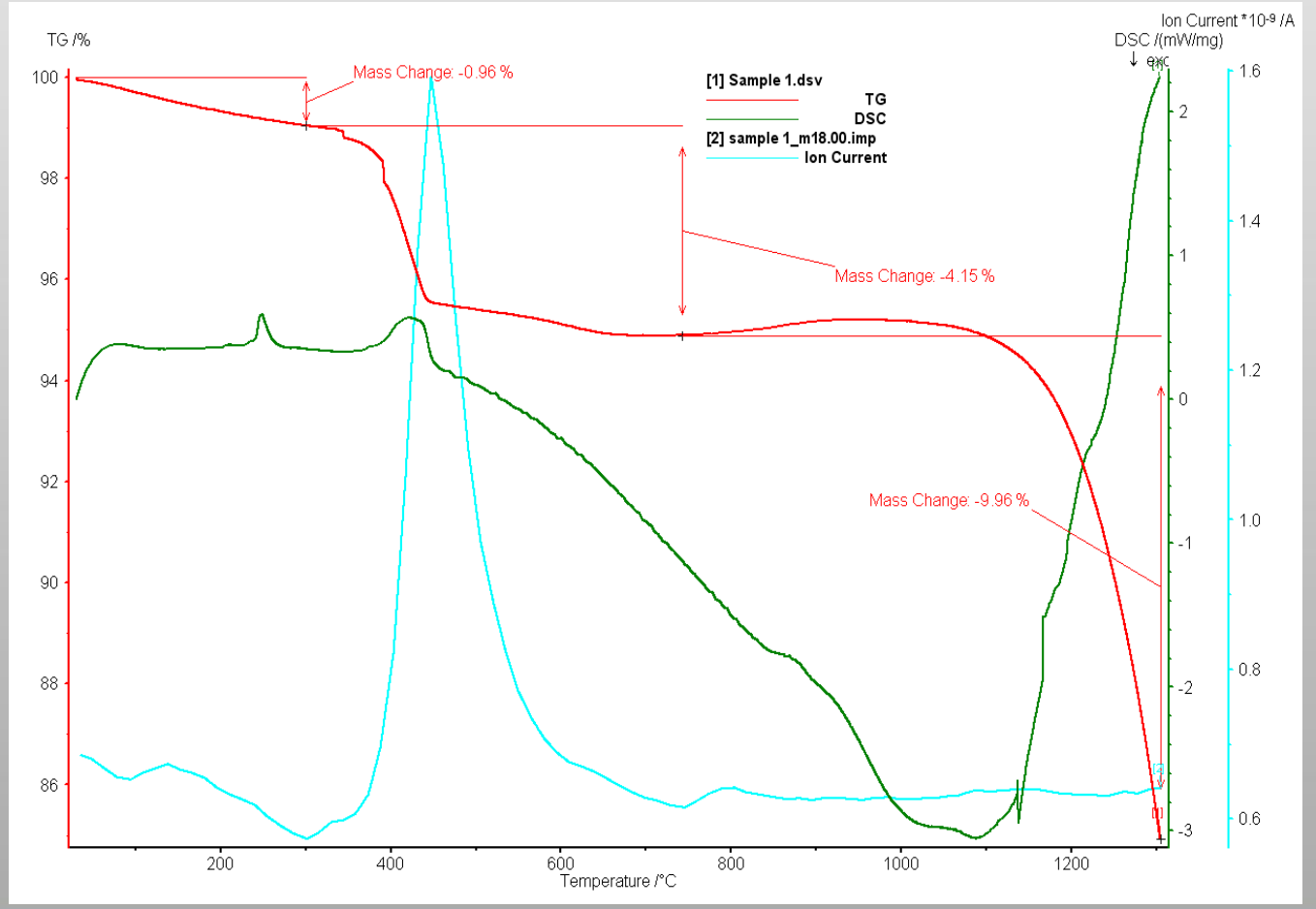
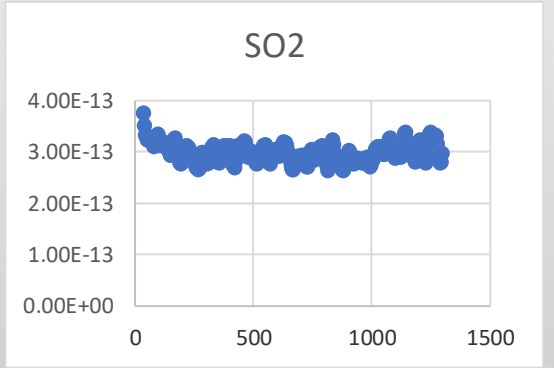
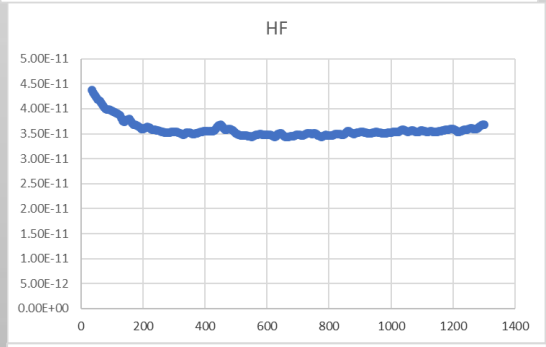
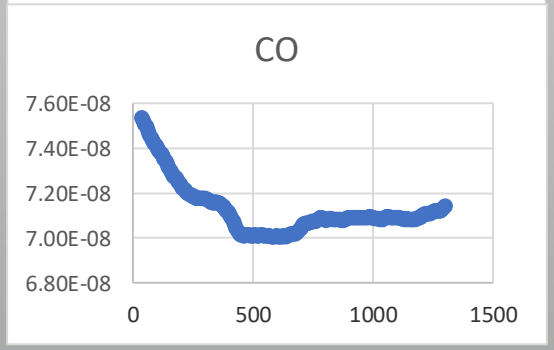
Properties of Zinnwaldite

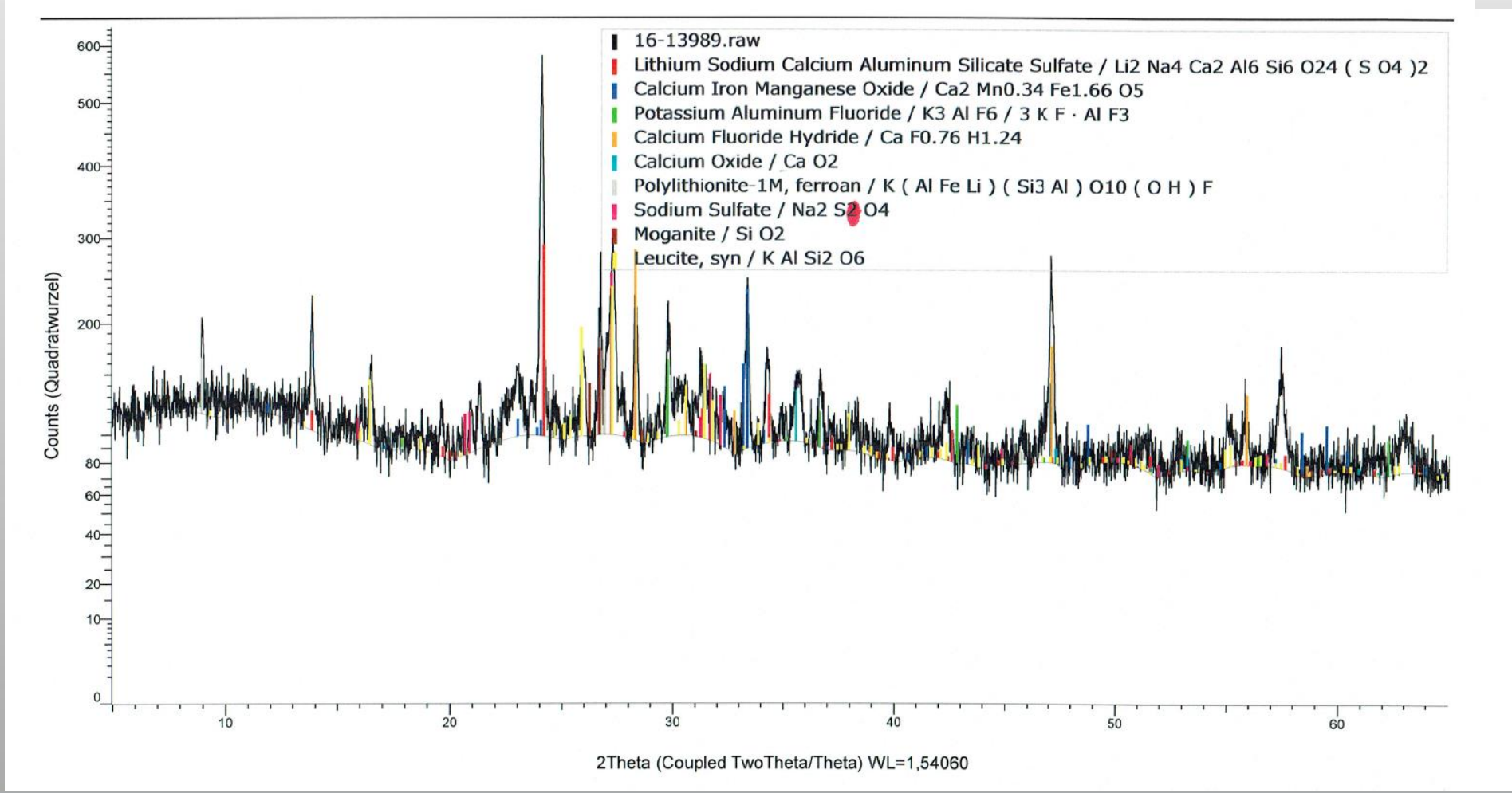








XRD of Sodium Sulphate Calcine




Results of the XRD Analysis

- The fluoride is bound typically as calcium fluoride and cryolite.
- The iron is bound as hematite or with calcium.
- There is excess calcium.
- Lithium is converted to soluble lithium sulphate compounds.

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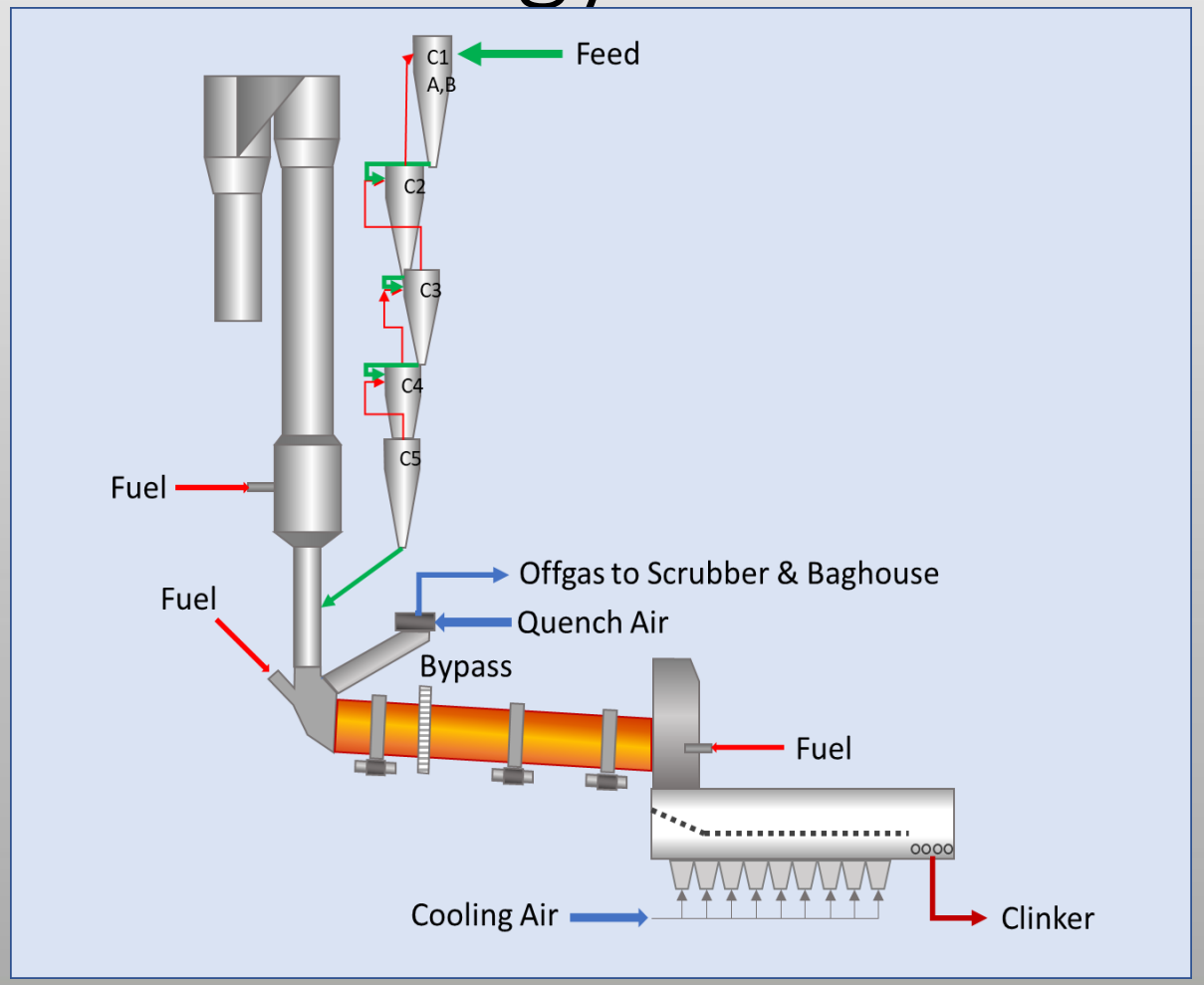
Cement Technology for Clinker Production



Cement Industry

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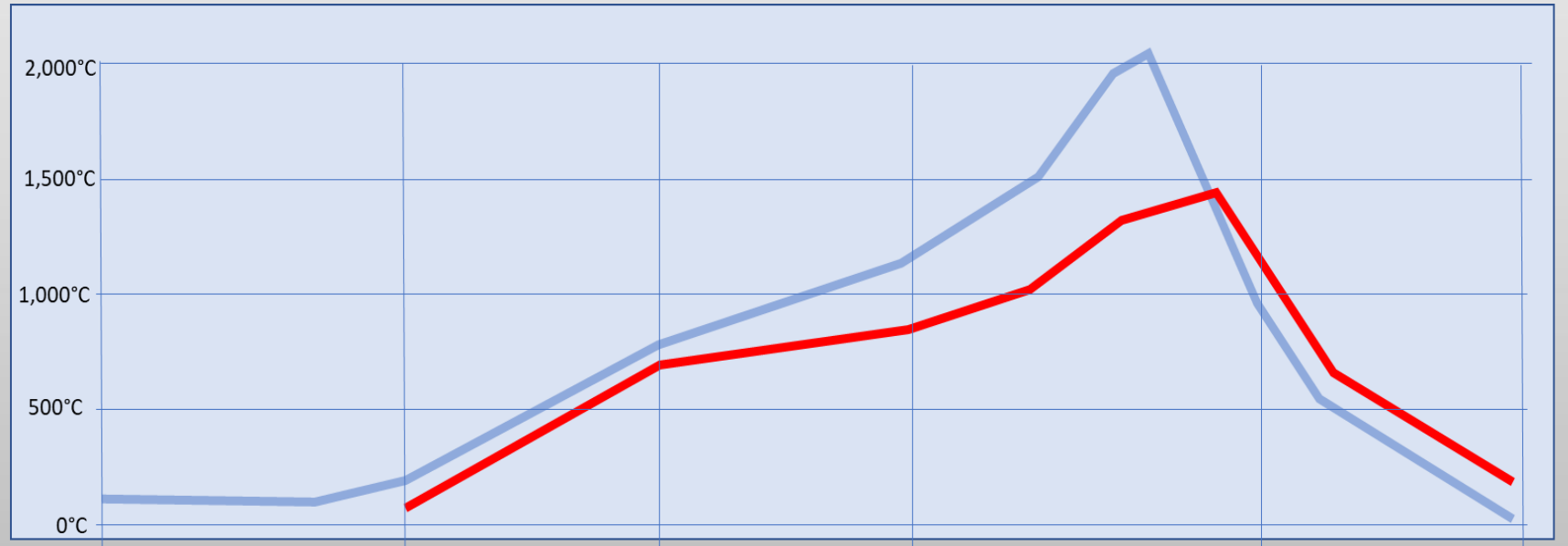

Gas Retention Time				
10 seconds	15 seconds	3 seconds	10 seconds	1 second
Material Retention Time				
	1 minute		30 minutes	30 minutes

Current Roaster Design

- The current design temperature for the roast is 850°C which is extremely close to the temperature at which the calcine would melt and therefore a standard rotary kiln as typically used for spodumene calcination is not suitable. Instead a device/s is required that will better prevent the overheating of the calcine.

- The options being explored with Hatch are:
  - A preheat tower with and indirectly fired rotary kiln, and
  - A preheat tower with a fluidized bed calciner.

Summary

- For the Cinovec Zinnwaldite European Metals Holdings Project a sodium sulphate roast has been selected.
- The advantage of the process is that sodium sulphate is recycled as the main reagent for the roast.
- The roast temperature of 850°C is very close to the melting temperature and a direct fired traditional rotary kiln is not suitable.
- Most likely roasting configuration is a pre-heat tower with either a rotary of fluidized bed kiln.