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Lithium extraction from α-spodumene by hydroalkaline treatment: Recent progress and outstanding considerations

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Presentation outline

1. Introduction

- Decarbonisation of spodumene refineries
  - ➢ Decrepitation (calcination)
  - ➢ Evaporation/crystallisation
- Spodumene reactivity
- Sulfuric acid process
- Technologies that avoid decrepitation

2. Hydroalkaline processes

- Filtrate based

  Li partitions mostly to leach solution
  - ➢ Digestion conditions
  - ➢ Sellable byproducts in residue
  - ➢ Li separation and recycling
- Residue based

  Li partitions mostly to leach residue
  - ➢ Digestion conditions and byproduct species in residue
  - ➢ Acid leach
  - ➢ Li separation and recycling

3. Quantities that matter

- Lithium recovery
- Feedstock intensity
- Byproduct intensity
- Energy intensity
- Capex

4. Conclusions

- Comparison with the sulfuric acid process
- Problems solved
- Outstanding problems

Decarbonisation of spodumene refineries

Decrepitation (calcining), evaporation and crystallisation

- The *embodied* emissions of CO_2 from the supply chain of lithium chemicals, especially lithium hydroxide ($LiOH·H_2O$) refined from spodumene, exceed those from brines, by about a factor of three, i.e., 15 t CO_2/(t $LiOH·H_2O$) for processing spodumene, in comparison to 5 t CO_2/(t $LiOH·H_2O$) for the Chilean production from brines.

- The EU will commence implementing carbon tariffs starting from 2023.

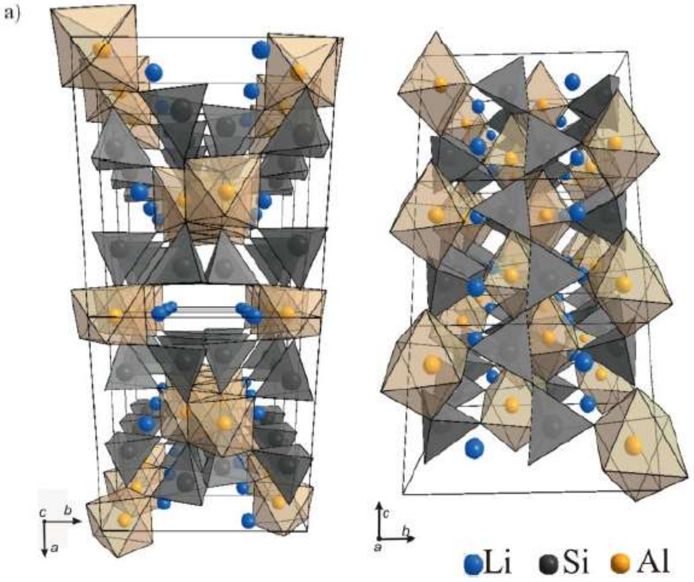
- These tariffs have potential to discriminate against electric vehicles equipped with batteries containing lithium chemicals refined from spodumene, because of their high embodied emissions of CO_2.

- The most CO_2 intensive steps in the supply chain of lithium hydroxide monohydrate (or Li_2CO_3) refined from spodumene concentrates are the decrepitation (calcining) and evaporation/crystallisation steps.

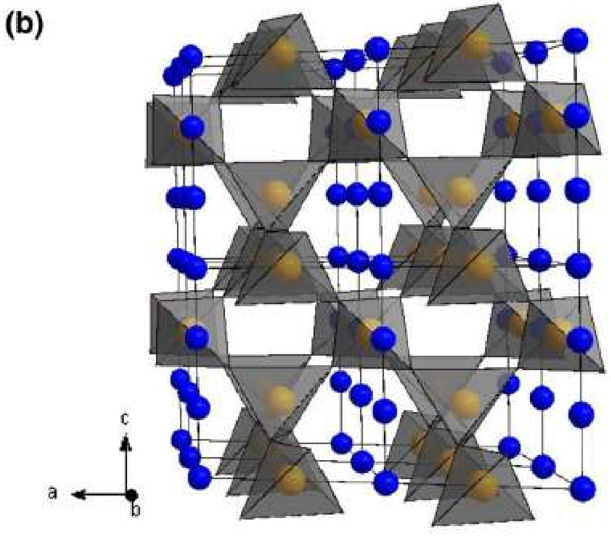
- The decrepitation step involves phase inversion of α-spodumene (aka spodumene) to β-spodumene; a question naturally arises about circumventing this step or change the design of the kiln to operate on renewable energy (outside the scope of this presentation).

Grant A, Deak D, Pell R, *The CO2 Impact of the 2020s' Battery Quality Lithium Hydroxide Supply Chain* (2023); https://www.jadecove.com/research/liohco2impact (assessed 3 May 2023)

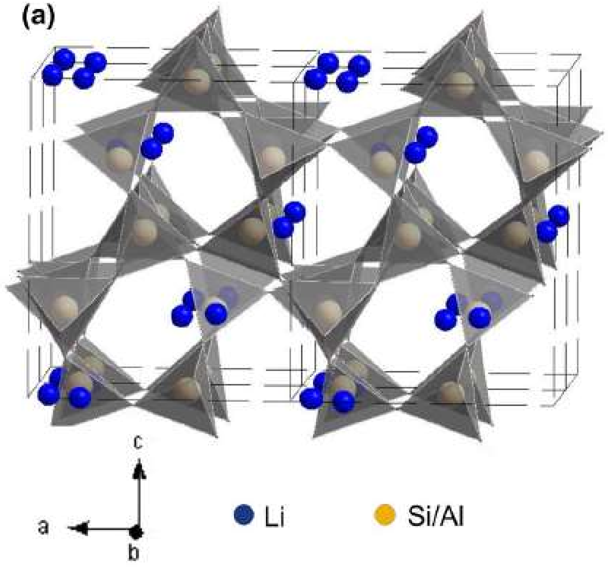
Reactivity of spodumene



α-spodumene: monoclinic



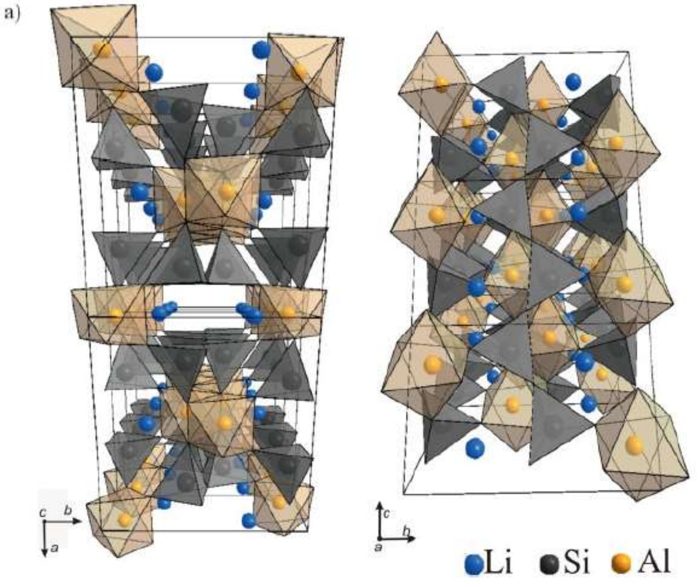
γ-spodumene: hexagonal



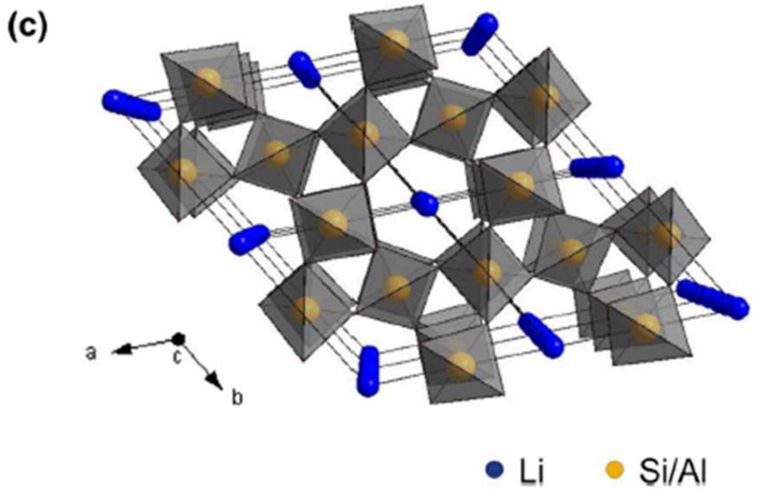
β-spodumene: tetragonal

Diagrams from Welsch et al., 2012, *Z Phys Chem* 226, 491-511; Welsch et al., 2015, *Phys Chem Minerals* 42, 413-420

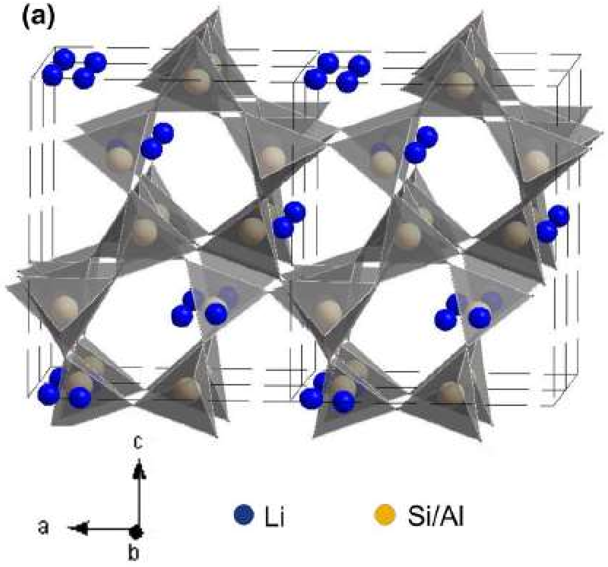
Reactivity of spodumene



α-spodumene: monoclinic



γ-spodumene: hexagonal



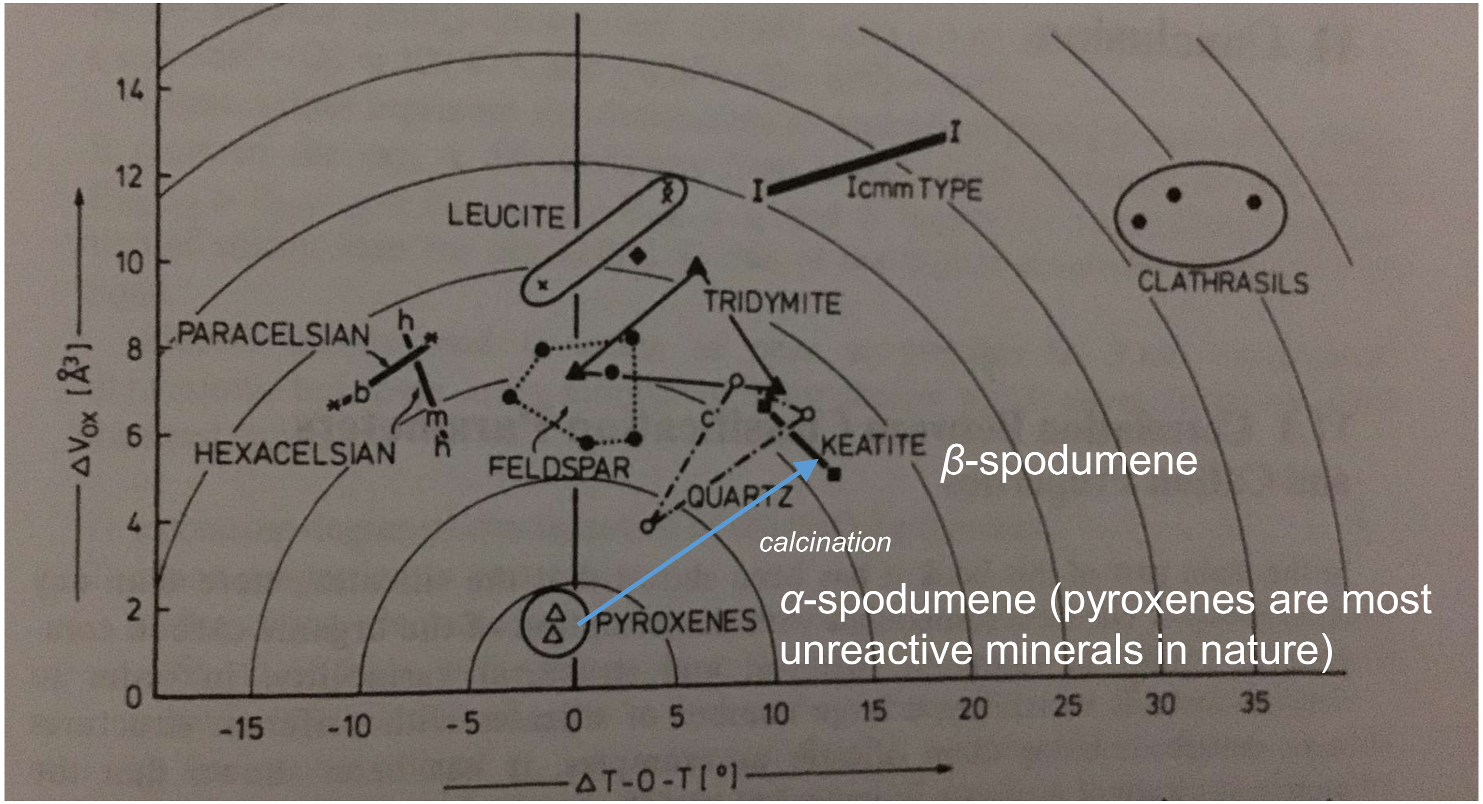
β-spodumene: tetragonal

- Natural *α*-spodumene is dense and unreactive
- *β*-spodumene is less dense and reactive with hot sulphuric acid
- *γ*-spodumene is intermediate phase, reactivity not known, but structure is "open"

Diagrams from Welsch et al., 2012, *Z Phys Chem* 226, 491-511; Welsch et al., 2015, *Phys Chem Minerals* 42, 413-420

Reactivity of spodumene, and, in more general, pyroxenes

Volume per framework oxygen minus 15 Å^3; 0 Å^3 denotes good space filling (i.e., minimum free energy)



β-spodumene

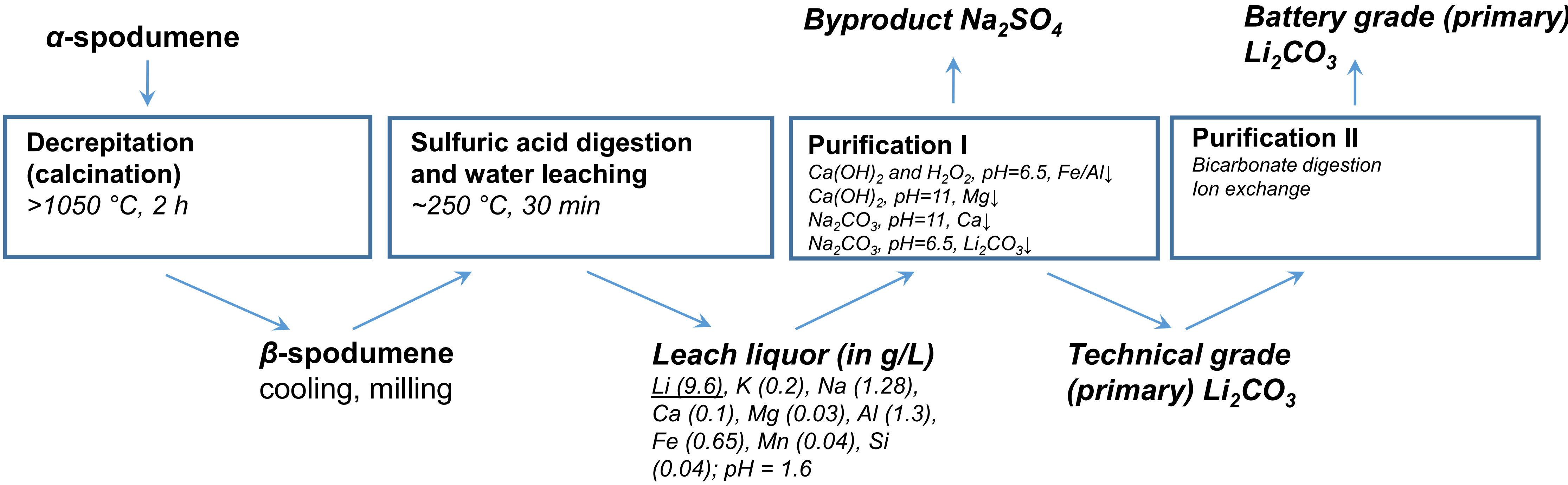
calcination

α-spodumene (pyroxenes are most unreactive minerals in nature)

Si – O – Si bond angle minus 140˚; O˚ denotes strain-free Si – O – Si bond

Fig. 10.40 from *Structural Chemistry of Silicates* by F Liebau, Springer-Veralg, 1985

Sulfuric acid process (SAP)



α-spodumene

Decrepitation (calcination)
>1050 °C, 2 h

β-spodumene
cooling, milling

Sulfuric acid digestion and water leaching
~250 °C, 30 min

Leach liquor (in g/L)
Li (9.6), K (0.2), Na (1.28), Ca (0.1), Mg (0.03), Al (1.3), Fe (0.65), Mn (0.04), Si (0.04); pH = 1.6

Purification I
$Ca(OH)_2$ and H_2O_2, pH=6.5, Fe/Al↓
$Ca(OH)_2$, pH=11, Mg↓
Na_2CO_3, pH=11, Ca↓
Na_2CO_3, pH=6.5, Li_2CO_3↓

Byproduct Na_2SO_4

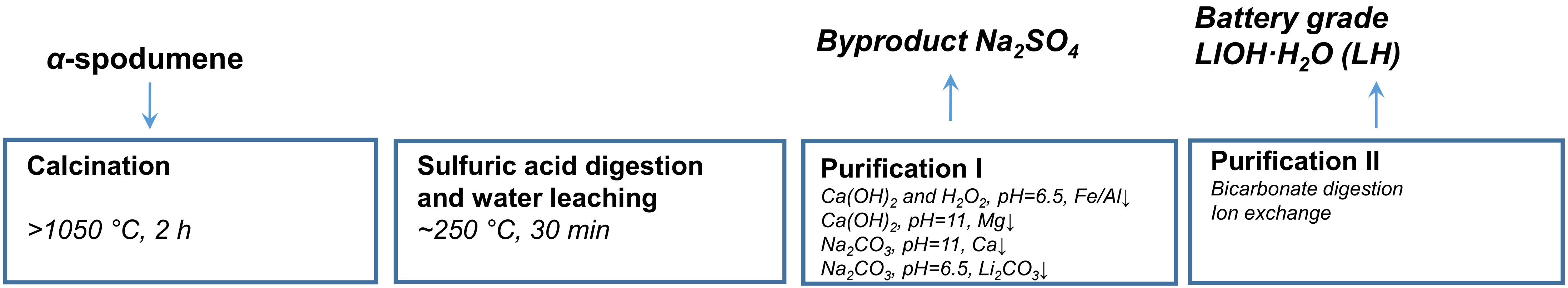
Technical grade (primary) Li_2CO_3

Purification II
Bicarbonate digestion
Ion exchange

Battery grade (primary) Li_2CO_3

Tan I K S, Process for Production of Lithium Carbonate, WO 2011/082444 A1
La Brooy S and Harman G, “Removal of minor and trace impurities from lithium leach liquors”, ALTA 2018, 19-26 May, Perth, Australia

Sulfuric acid process (SAP)



α-spodumene

Calcination

>1050 °C, 2 h

Sulfuric acid digestion and water leaching

~250 °C, 30 min

Purification I

$Ca(OH)_2$ and H_2O_2, pH=6.5, Fe/Al↓
$Ca(OH)_2$, pH=11, Mg↓
Na_2CO_3, pH=11, Ca↓
Na_2CO_3, pH=6.5, Li_2CO_3↓

Byproduct Na_2SO_4

Purification II

Bicarbonate digestion
Ion exchange

Battery grade $LiOH \cdot H_2O$ (LH)

Problem 1

Energy intensity

Problem 2

Waste disposal: acidic aluminosilicates from leaching and impurities precipitated in Purification I, SO_x

Problem 3

Energy intensity
Feedstock intensity: concentrated H_2SO_4, $Ca(OH)_2$, Na_2CO_3 (in addition to Na_2CO_3 needed for precipitation of Li_2CO_3)

Problem 4

Byproduct recycling: Na_2SO_4

SAP works well; steep-learning curve to produce battery-grade LH; well-oiled technology.

Technologies that avoid decrepitation

(no phase inversion of α-spodumene to β-spodumene)

1. Leaching α-spodumene with HF (Kuang et al, 2012) or HF/H_2SO_4 (Guo et al, 2019)
2. Roasting α-spodumene with NaOH at 320 °C (Han et al, 2022)
3. Digesting α-spodumene concentrated solution of NaOH (hydroalkaline treatment; today's presentation)

Guo H, Yu H, Zhou A, Lu M, Wang Q, Kuang G, Wang H, Kinetics of leaching lithium from α-spodumene in enhanced acid treatment using HF/H_2SO_4 as medium, *Trans Nonferrous Met Soc China 29*(2), 407−415 (2019).

Han s, Sagzhanov D, Pan J, Vaziri Hassas B, Rezaee M, Akbari H, Mensah-Biney R, Direct extraction of lithium from α-spodumene by salt roasting-leaching process, *ACS Sustain Chem Eng* 10, 13495-13504 (2022).

Kuang G, Chen Z, Guo H, Li M, Lithium extraction mechanism from α-spodumene by fluorine chemical method, *Adv Mat Res 524−527*, 2011−2016 (2012).

Outside the scope: alkaline treatment of lepidolite

Mulwanda J, Senanayake G, Oskierski H, Altarawneh M, Dlugogorski B Z, Leaching of lepidolite and recovery of lihium hydroxide from purified alkaline pressure leach liquor by phosphate precipitation and lime addition, *Hydrometallurgy 201*, 105538 (2021).

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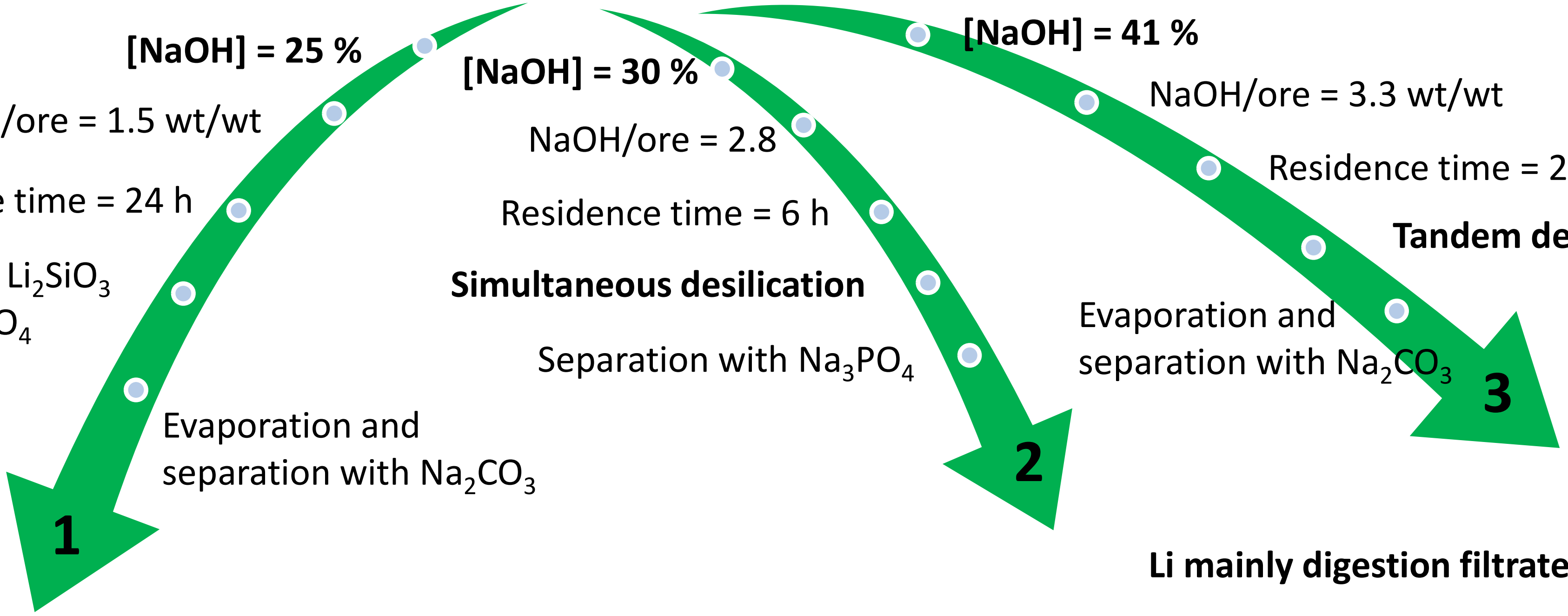
Strategies



Spodumene + NaOH in autoclave reactor at 250 °C

[NaOH] = 25 %

NaOH/ore = 1.5 wt/wt

Residence time = 24 h

Leaching Li_2SiO_3 with H_2SO_4

Evaporation and separation with Na_2CO_3

1

Li mainly in digestion residue, as Li_2SiO_3

[NaOH] = 30 %

NaOH/ore = 2.8

Residence time = 6 h

Simultaneous desilication

Separation with Na_3PO_4

2

[NaOH] = 41 %

NaOH/ore = 3.3 wt/wt

Residence time = 2 h

Tandem desilication

Evaporation and separation with Na_2CO_3

3

Li mainly digestion filtrate, as Li^+

Hydroalkaline processes

1. (Residue based with tandem leaching) Qiu S, Liu C, Yu J, Conversion of α-spodumene to intermediate product of Li_2SiO_3 by hydrothermal alkaline treatment in the lithium extraction process, *Miner Eng* 183, 107599 (2022)

2. (Filtrate based with simultaneous desilication) Song Y, Zhao T, He L, Zhao Z, Liu X, A promising approach for directly extracting lithium from α-spodumene by alkaline digestion and precipitation as phosphate, *Hydrometallurgy* 189, 105141 (2019)

3. (Filtrate based with tandem desilication) Xing P, Wang C, Zeng L, Ma B, Wang L, Chen Y, Yang C, Lithium extraction and hydrosodalite zeolite synthesis by hydrothermal conversion of α-spodumene, ACS Sustain Chem Eng 7, 9498-9505 (2019)

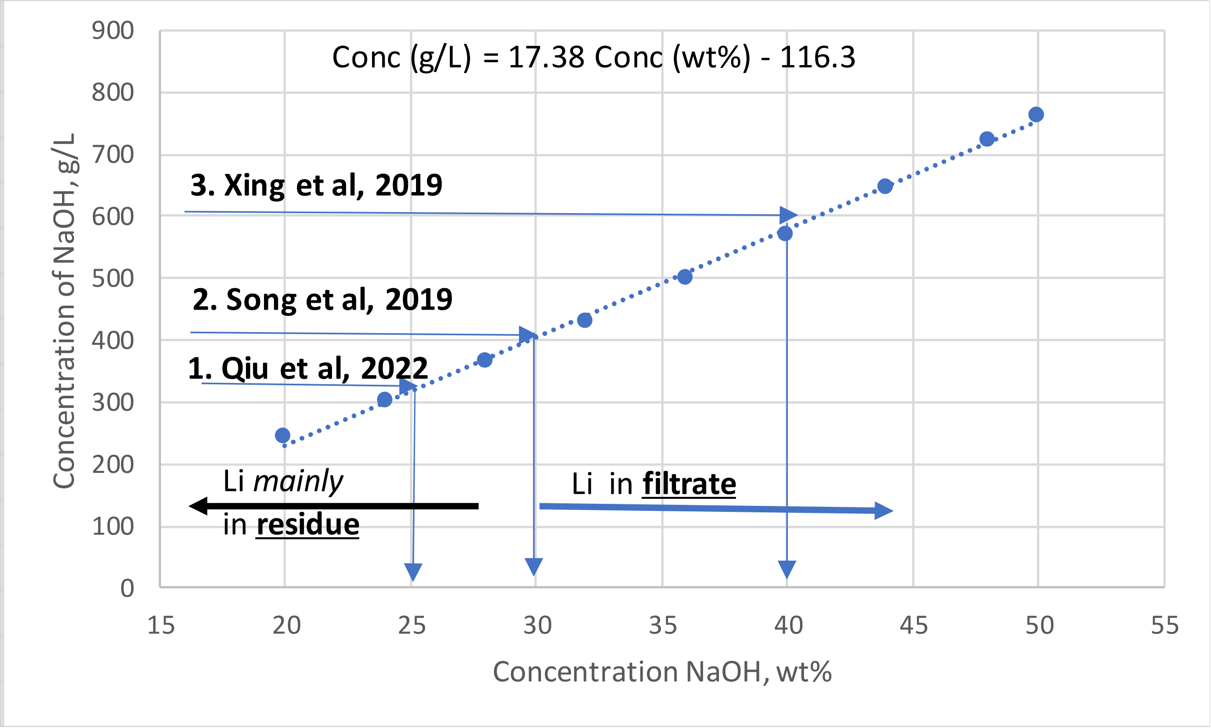
Patents

- Catovic E, *Caustic Digestion Process*, AU 2017306576 B2, Date of filing 2 Aug 2017
- Napier A, Griffith C, Caustic Conversion Process, US 2021/0180155 A1, PCT filed 24 July 2019

Hydroalkaline processes

Three process

- Qiu et al, 25 % NaOH
- Song et al, 30 % NaOH
- Xing et al, 41 % NaOH



24 h 6 h 2 h

Digestion time

Li_2SiO_3 in residue

Li^+ in filtrate

Similarities:
T = 250 °C for all
Small particle size

Key differences:

1. [NaOH] (%)
2. Residence time (h)
3. Li in filtrate or (mainly) in residue

---- *next slide* ----

4. NaOH/ore (g/g)
5. S/L (mL/g)
6. Desilication (yes/no, if yes, simultaneous or tandem)
7. Li separation

Hydroalkaline processes

	T, °C	[NaOH], %	t, h	Li part in digestion	NaOH/ore, g/g
1. Qiu et al	250	25	24	Mainly residue	1.5
2. Song et al	250	30	6	Filtrate	2.8
3. Xing et al	250	41	2	Filtrate	3.3
	S/L, mL/g	Desilication, Y/N	Li separation		Leaching, Y/N
1. Qiu et al	4.7	?	Evaporation, Na_2CO_3		Y
2. Song et al	7.0	Y (simul)	Na_3PO_4		N
3. Xing et al	5.0	Y (tandem)	Evaporation, Na_2CO_3		N
		Particle size, µm			
1. Qiu et al		D_{50} = 17.2			
2. Song et al		D_{50} = 15.3			
3. Xing et al		≈ 30			

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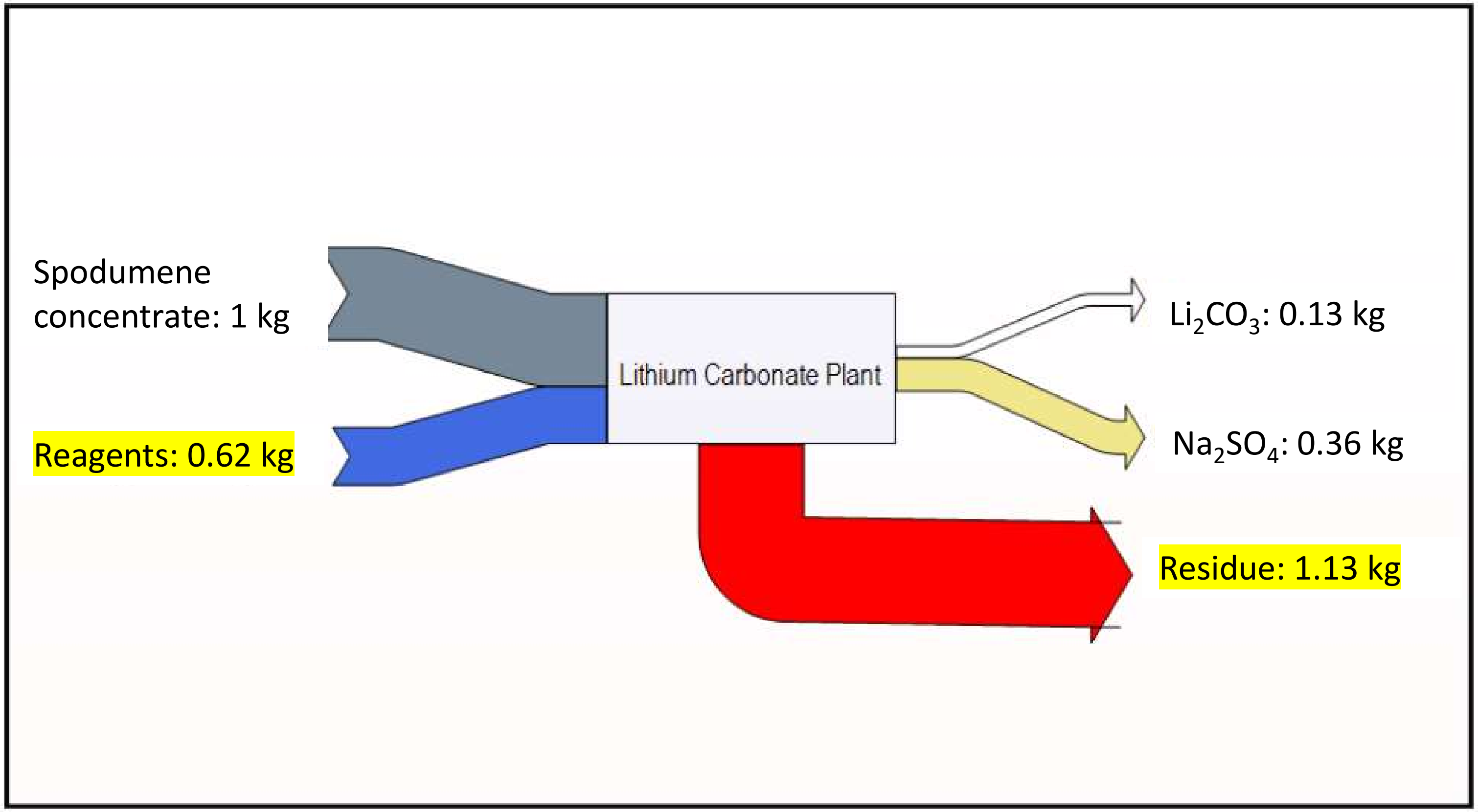
Overall refinery mass balance for sulfuric acid process

Energy intensity

Decepitation: 1.53 ± 0.05 MJ/kg ore (thermodynamic value)

Compare to 2.3 MJ/kg to evaporate or 4.2 kJ/(kg °C) to heat water. Average heat capacity of spodumene is 1.2 kJ/(kg °C).

Abdullah A, *Thermal Treatment of Spodumene (LiAlSi2O6) for Lithium Extraction*, PhD Dissertation, Murdoch University, 2018



Spodumene concentrate: 1 kg

Reagents: 0.62 kg

Li_2CO_3: 0.13 kg

Na_2SO_4: 0.36 kg

Residue: 1.13 kg

Harman G, Trends and developments in lithium processing, ALTA 2022

Feedstock, byproduct and energy intensity of Process 2

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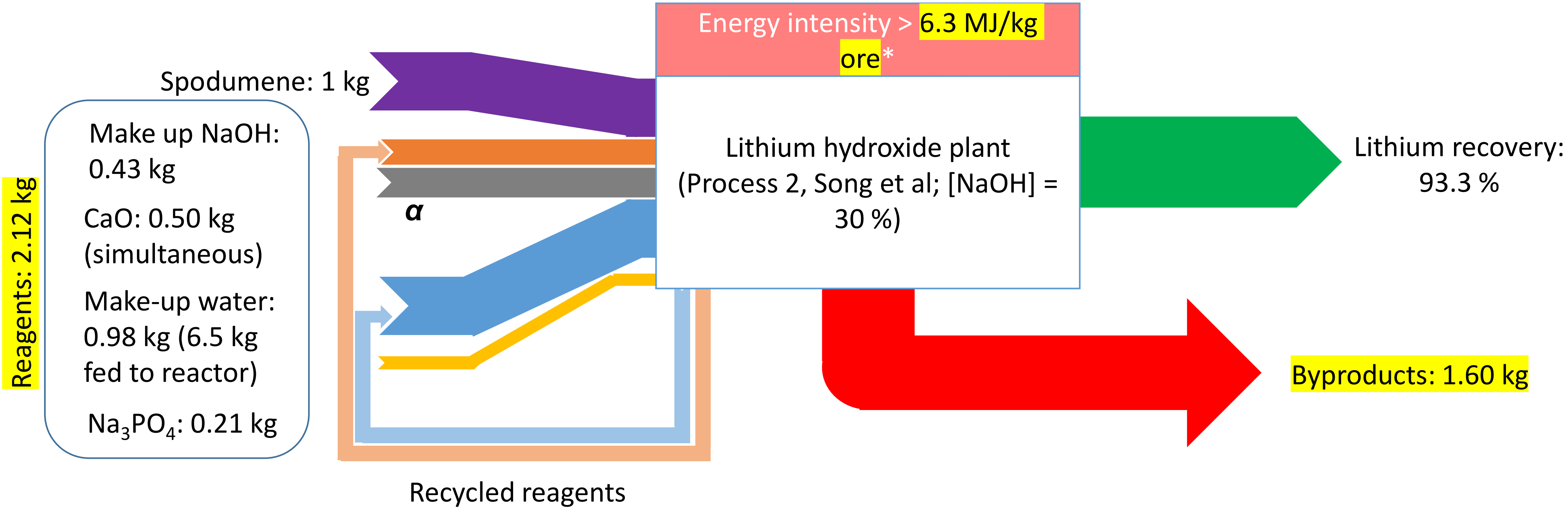


Energy intensity > 6.3 MJ/kg ore*

Spodumene: 1 kg

Reagents: 2.12 kg

Make up NaOH: 0.43 kg

CaO: 0.50 kg (simultaneous)

Make-up water: 0.98 kg (6.5 kg fed to reactor)

Na_3PO_4: 0.21 kg

Lithium hydroxide plant (Process 2, Song et al; [NaOH] = 30 %)

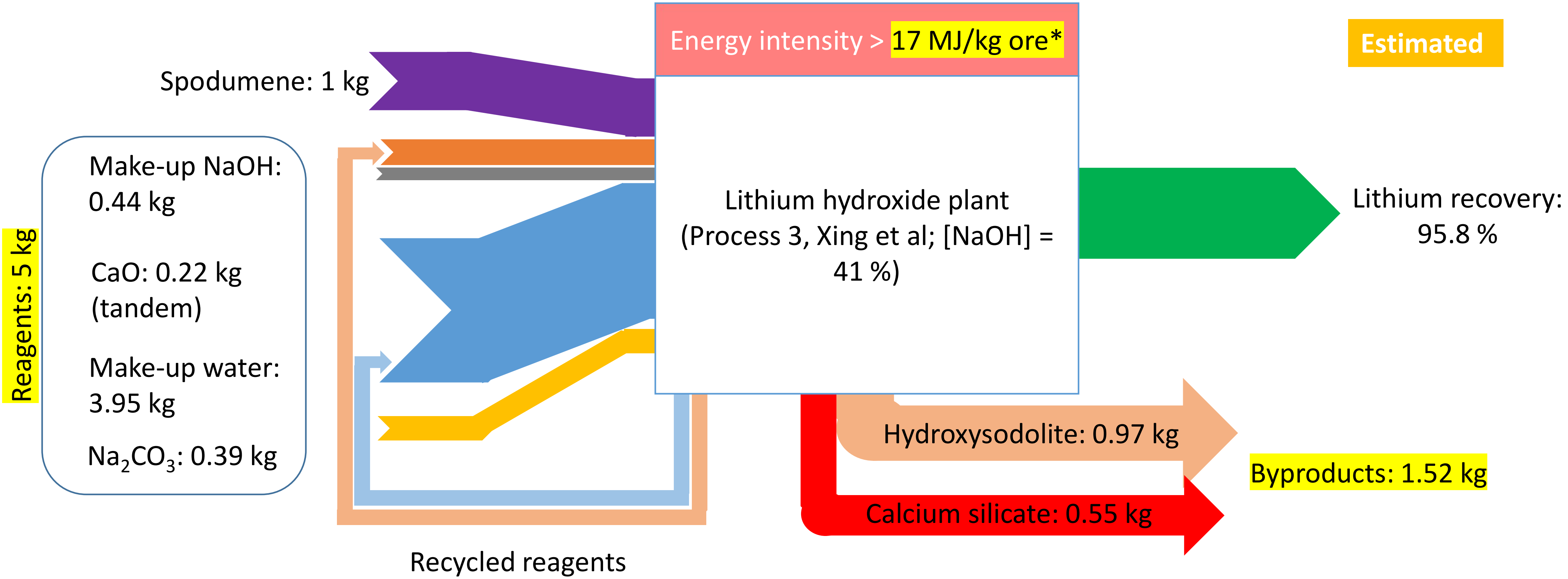
Lithium recovery: 93.3 %

Byproducts: 1.60 kg

Recycled reagents

*Based on heating the water between 20 °C and 250 °C.

Feedstock, byproduct and energy intensity of Process 3



Energy intensity > 17 MJ/kg ore*

Estimated

Spodumene: 1 kg

Reagents: 5 kg

Make-up NaOH: 0.44 kg

CaO: 0.22 kg (tandem)

Make-up water: 3.95 kg

Na_2CO_3: 0.39 kg

Lithium hydroxide plant (Process 3, Xing et al; [NaOH] = 41 %)

Lithium recovery: 95.8 %

Hydroxysodolite: 0.97 kg

Calcium silicate: 0.55 kg

Byproducts: 1.52 kg

Recycled reagents

*Based on heating the water between 20 °C and 250 °C and evaporating the water to concentrate the filtrate.

Cost of evaporation and concentration of Li

In present lithium refineries, [Li] from the sulfuric acid bake and water leaching is about 10 g/L.

If a hydroalkaline treatment requires to concentrate Li from, say, around 2.7 g/L to 10 g/L, this incurs significant operating cost

2 kg H_2O	2.3 MJ	\$10	7 g Li	10^6 g $LiOH\cdot H_2O$	=	\$770
10 g Li	1 kg H_2O	1000 MJ	42 g $LiOH\cdot H_2O$	1 t $LiOH\cdot H_2O$		1 t $LiOH\cdot H_2O$

Once one accounts for efficiencies in energy and Li extraction, the cost > \$1000/1 t LH.

If evaporation is required as part a process replacing the decrepitation kill, this defeats the purpose of decreasing the emission of embedded CO_2.

Capex

1. Industry appears to settle on multiples of 25 kt $NaOH \cdot H_2O$/y trains
2. This translates to ≈190 kt spodumene, concentrate treated per year, or 542 t/day;
3. Process 2 has 10.5 t charge per 1 t concentrate, with two runs a day, a 200 t autoclave can process 38 t SC a day, considering 6 h residence time and time for charging, heating and discharging
4. This corresponds to a battery of 15 autoclaves, each with charge capacity of 200 t

Residence time appears to be critical for capex; perhaps Process 2 can be accelerated by digestion with solutions of > 40 % NaOH.

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Conclusions

1. Comparing with the sulfuric acid process: (i) New technology; dramatic break with arnings since 1950s; (ii) Feedstock intensive (by ≈ 70 %, excluding process water, for Process 2); (iii) Byproduct intensive (by ≈ 40 %, for Process 2); (iv) Recycle – consumption of NaOH ≈ 15 % per pass, for Process 2; (v) Long residence time increases CAPEX; (vi) *There is no energy savings!*

2. Problems solved: (i) Chemistry works well; (ii) Nearly complete data set available for at least one process (Process 2; Song et al.); (iii) Desilication and NaOH recycling required; (iv) Identified weak points of the technology; (v) Evaporation needed to produce (low purity) Na_2CO_3 for further separation is a major energy requirement; (vi) Lithium recovery > 90 %

3. Outstanding problems: (i) Optimisation of residence time; (ii) Integration of separated lithium (low purity Na_2CO_3) into the purification circuits of existing refineries, or development of industrial technologies for converting Li_3PO_4 to LH or LC; (iii) CAPEX – number and cost of unit operations, recycling; (iv) Handling of byproducts; (v) Future research should focus on recycling and separation of Li from the filtrate, and on more detailed economic assessment; (vi) Unclear mechanisms at atomic level, their knowledge would help optimise the process