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Environmental assessment of an innovative lithium production process

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Abstract

The recent development towards a battery-powered electric vehicle industry has led to a significant rise in the demand for high-grade Lithium (Li). Global Li is predominately produced from brines (salar or geothermal) and from hard-rocks, while the amount of Li produced from recycling (e.g. from waste batteries) is still negligible, although it is expected to increase in the near future. Li extraction from hard rocks and brines is also associated with environmental issues, such as (i) consumption of a large quantity of reagents, (ii) high water footprint (especially in the case of brines). Therefore, ensuring a clean, stable and sustainable supply of Li is a key point in the European agenda to reach its ambitious climate targets by 2050.

Building on this need, a LiOH production process is under development at KU Leuven (C3 SOLVOLi+ project). This process concentrates technical grade LiCl from the roasting of low-content Li sources. Subsequently, it converts the concentrated technical grade LiCl into aqueous LiOH by mean of a series of processes. The presented environmental analysis, based on a ex-ante Life Cycle Assessment, highlights the potential environmental hotspots that can potentially hinder the breakthrough of the technology, providing useful insights on unit processes requiring optimizations during future upscaling. In particular, at this early stage of development, the optimization and the recycling of the chemicals used in the process seems to be the most efficient strategy to reduce the overall environmental impact of the process. Future studies foresee to enlarge the current analysis to the comparison with other processes for LiOH production. A lower environmental footprint can indeed help to strength the position of the proposed process into the future market for LiOH production.

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1. Introduction

The electrification of the transport and mobility sectors is considered a key element for transition toward future carbon-lean economy [1,2]. Lithium-ion batteries (LIBs) represent the dominant energy technology for electric vehicles, while their share in stationary energy systems is constantly increasing [3]. As a consequence, the demand for lithium (Li), the main component of LIBs, has dramatically risen, with the forecast demand expected to exceed 1 Mt in 2027, with a growth of over 18% per year to 2030[4]. Li can be found in small amounts in

igneous rocks, and in waters from mineral springs, lakes, seas and oceans [5]. Commercially available Li salts are lithium carbonate (Li_2CO_3), lithium chloride (LiCl), lithium hydroxide (LiOH) and lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$). In general, Li salts can be produced by two different technologies: (i) evaporation from brines, and (ii) extraction from minerals.

Li originating from brines represents 65% of global Li-production, mostly coming from Chile (60%), China (20%) and Argentina (14%) [6]. The Li extraction process from brines comprises consecutive stages, starting with concentration by evaporation, impurity removal and precipitation by

carbonation. The specifics of the process may differ at each plant, due to the different chemistry of brines around the world [5].

Li-bearing minerals are mainly spodumene, lepidolite, petalite and amblygonite, with spodumene being the most important commercial mineral for Li extraction at an industrial scale [7,8]. These minerals are first grounded to produce a Li-concentrate of approximately 6% Li content, which is subsequently calcinated or roasted, before entering the leaching and purification phases.

Previous environmental analyses comparing the different Li-production processes have highlighted the key differences between Li obtained from brines versus minerals. While brine evaporation predominantly uses solar energy to concentrate Li up to 6%, the mineral extraction relies on fossil fuels and electricity [9]. On the other hand, brine evaporation technology has been associated with high water depletion and biodiversity losses in the area surrounding the brines [10]. Along with production from brines and minerals, the recycling of Li from Li-bearing slags is a key factor to ensure the transition toward sustainable renewable energy. Therefore, the amount of recycled Li is expected to increase in the future. However, Li recycling is a challenging task, and the amount of Li currently recycled is negligible.

At the moment, Li_2CO_3 represents the most common lithium compound in the market for LIB applications. However, the expected growth of Ni-rich NMC-622 batteries is diverting the demand of Li towards LiOH, which is more suitable to synthesize cathode materials with more than 60% of nickel. The production of LiOH is typically a two steps process, using LiCl from brines to first produce Li_2CO_3 , and then converting the Li_2CO_3 into LiOH. One of the main advantages of mineral extraction compared to brines evaporation, is the possibility to directly produce LiOH, avoiding the intermediate production of Li_2CO_3 .

Moreover, although Europe has solid reserves of lithium-bearing minerals, it lacks refining capacity. Today the European demand for Li relies entirely on Li production from China and South America (although this is set to change by 2024 when

Keliber Oy’s new lithium refining plant is expected to start operating in Finland).

Considering all the above, the development of a Li production process that can directly produce LiOH from lithium bearing minerals, bypassing the Li_2CO_3 intermediate step, would be beneficial for the development of a European internal Li supply, reducing the dependency of Europe with respect to external import.

In this framework, a LiOH production process is currently under development at KU Leuven (C3 SOLVOLI+ project). This process concentrates technical grade LiCl from the roasting of low-content Li sources (hard rocks or Li bearing slags). Subsequently, it converts the concentrated technical grade LiCl into aqueous LiOH by mean of a series of processes (selective dissolution in organic solvent, ion-exchange in non-aqueous solvents, and solvent extraction).

Together with the ongoing investigation about the technical feasibility of the process, it is also important to assess its environmental performance. An environmental assessment of the process allows highlighting the most relevant environmental hotspots to be considered to reduce the environmental footprint of the process. In particular, ex-ante Life Cycle Assessment (LCA) is a methodology to evaluate the potential future environmental impacts of a process, already at its early stage of development [11]. An ex-ante LCA improves the understanding of the implications of initial design choices on the environmental performances of a technology [12]. Indeed, ex-ante LCA must be seen as a process that run in parallel to the technical development of the technology, allowing to prevent future environmental burdens at low cost. Building on these needs, the study presents an ex-ante LCA of an innovative and under-development process aiming to directly produce LiOH, bypassing the Li_2CO_3 intermediate.

2. Life Cycle Assessment

The LCA is conducted following the guidelines reported in the ISO standards (ISO 14040, ISO 14044) and the

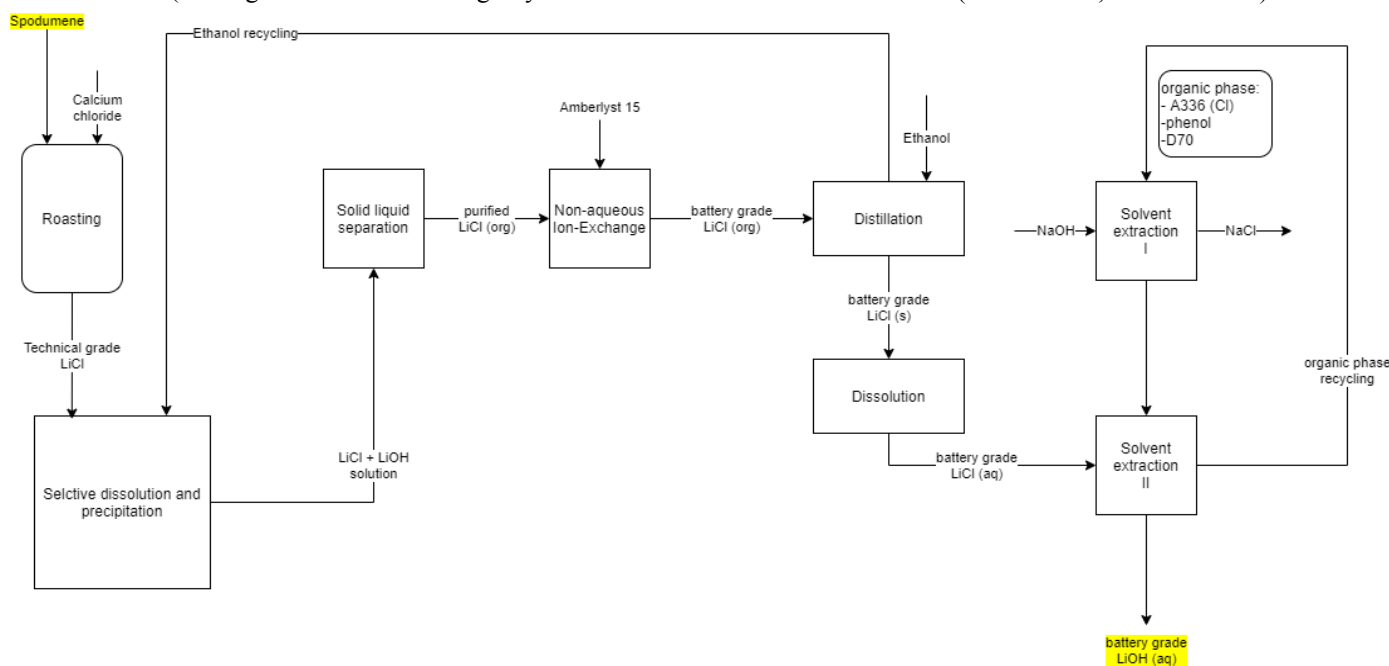


Figure 1: Flowsheet of the process

International Reference Life Cycle Data System (ILCD), published by the European Commission's Joint Research Centre (JRC) [13].

According to the ISO 14040, LCA is a four-phase framework, defined as (i) goal and scope definition, (ii) inventory analysis, (iii) impact assessment, (iv) results interpretation.

2.1. Goal and scope

In this first phase of LCA, the goal and scope of the assessment are defined, including the definition and description of the considered system boundaries, the functional unit, and the allocation rules (if needed).

The goal of the presented ex-ante LCA is to highlight the environmental hotspots of the novel proposed process to directly produce LiOH from low-content Li sources, providing information on which elements should be improved and optimized to effectively lower the environmental impact of the process.

Since the process is currently under development at a lab scale, the data used for this ex-ante LCA refers to lab experiment using spodumene as source of Li, with a Li content around 7%. For the future upscaling of the whole process, other Li sources are intended to be tested, such as lepidolite, petalite and Li bearing slags. The composition of the processed spodumene is reported in table 1.

Table 1: Composition of a ore 95% α -spodumene and 4,5% quartz [14]

Input	Quantity
SiO ₂	66%
Al ₂ O ₃	22%
Fe ₂ O ₃	0.95%
CaO	0.28%
MgO	0.25%
K ₂ O	0.03%
Na ₂ O	0.4%
Li ₂ O	7.2%
TiO ₂	0.06%

When defining the system boundaries of an LCA study, different perspectives can be considered. An analysis considering a full life cycle perspective of a product, from upstream (production phase) to downstream (disposal phase and recycling), is referred to as “cradle-to-cradle”. When an LCA study considers only the production phase and sets its boundaries at the gate of the factory, it is referred to as “cradle-to-gate”. For the present study, the focus is on the LiOH production phase, therefore a “cradle-to-gate” is used, and data

on the subsequent use and disposal phase of the LiOH are not included in the assessment.

The process steps under study are divided into three main stages: (i) Roasting of spodumene to 1100 °C, to concentrate technical grade LiCl, (ii) non-aqueous ion exchange (NAIX), to refine technical grade LiCl into battery-grade LiCl, and (iii) a double-step solvent extraction (SX), to convert aqueous LiCl into LiOH. A simplified flowsheet of the process is presented in figure 1.

In the flowsheet, A336 (Cl) stands for Aliquat® 336, and D70 is Shellsol® D70. Aliquat® 336 consists out of a mixture of quaternary ammonium chlorides, with 88.2–90.6% quaternary ammonium content. Sellsol® D70 consists predominantly of C11- C14 paraffins and naphthenes.

Finally, all data collected during the experiments referred to the production of only a few grams of LiOH. The whole process has been therefore mathematically upscaled to the treatment of 100 kg of spodumene, which represents the functional unit of the study. The functional unit is indeed the quantitative reference to which all inputs and outputs of the analysed system are calculated.

2.2. Inventory analysis

The core of the inventory analysis is the collection and the compilation of data from all physical and energy flows from the process under study. Therefore, the main output of the inventory analysis is a compiled table with all elementary flows (whose quantity is referred to as the functional unit), that is used as the basis of the subsequent impact assessment phase.

The inventory analysis has been carried out by mathematically upscaling the data at lab-scale to the treatment of 100 kg of spodumene as the main input. A complete list of all considered inputs, along with their quantities, is reported in Table 2.

Concerning the energy requirements of the process, no relevant data was available at the lab scale. Therefore the energy requirement of the roasting process has been calculated based on the heat capacity of all the compounds present in the spodumene. The calculated value has been doubled to consider all possible energy losses and inefficiencies during heat transfers in the roasting process. Electricity (from the Belgian electricity grid) has been assumed as the only source of energy. The complete calculation of the energy requirement in the roasting process is reported in supplementary note 1.

Finally, it was not possible to make any hypothesis on the energy requirements for the NAIX and the SX process steps, since data from energy requirements at a lab scale cannot be simply mathematically upscaled without adding significant uncertainty to the whole results. Therefore, for the present ex-ante LCA, no energy requirement is considered for the NAIX and SX process steps. Although this represents a limitation on the relevance of the results, it must be considered that roasting represents the main energy requirement in the whole process (roasting is a high-temperature process, reaching 1100 °C), while energy requirement in the NAIX and SX processes are incurred only by mixing and pumping.

All chemical production processes have been modelled using the Ecoinvent 3.7 database, one of the most used databases for inventories in LCA studies. However, for some of the inputs, it was not possible to find the production process in the Ecoinvent database. For those inputs, the production process has been modelled using proxies that were available in the database.

Table 2: Inventory table

Input	Quantity	Ecoinvent Proxy (if needed)	Source of data
Roasting			
Spodumene	100 kg		
Heat requirement	56.6 kWh	Electricity (Belgian electricity mix)	calculated (supplementary note 1)
Calcium Chloride	26.7 kg		calculated (supplementary note 1)
NAIX			
Technical-grade LiCl	13.3 kg		Lab experiment
Amberlyst 15	3.7 kg	Cationic resin	Lab experiment
Ethanol	55.4 kg		Lab experiment
SX			
Sodium hydroxide	63.5 kg		Lab experiment
A336	51.7 kg	Ethylamine	Lab experiment
D70	155.2 kg	50% Paraffin; 50% Cyclohexane	Lab experiment
Water	191.7 kg		Lab experiment

Output		
LiOH (aq)	0.3 kg	Lab experiment

2.3. Impact assessment

The third phase of an LCA is the Life Cycle Impact Assessment (LCIA), which translates the results of the inventory phase into different impacts on the environment, expressed in terms of several distinct environmental impact categories. A handful of LCIA calculation methods are available in the literature, and a thorough discussion on the characteristics of the several LCIA methods goes beyond the scope of this study.

For the presented LCA the Environmental Footprint 3.0 (EF 3.0) is selected as the LCIA method [15]. The EF 3.0 is an environmental impact calculation method developed by the European Commission, and it is built on recommended approaches and international standards (for more information, see Fazio et al. 2018 [16]).

The results for the LCIA by using EF 3.0 are shown in Figure 2. From the analysis of the results, it can be concluded that for a few environmental impact categories there is one process that has a predominant contribution to the final results. The use of ethanol, for instance, contributes 85% to the ecotoxicity of freshwater, 82.4% to the final land use, and 87% to the non-cancer human health effect. The electricity required for the roasting process is contributing 37.6% to the final impact in ionizing radiation. In all other environmental impact categories, the contribution of all processes is rather scattered, with predominant elements being the use of chemicals (cyclohexane, ethanol, sodium hydroxide and paraffin among others).

3. Conclusions and limitations

The study presents an ex-ante LCA of an innovative process to concentrate LiCl from spodumene, and then convert it to battery grade LiOH in aqueous solution, through Non-Aqueous Ion Exchange (NAIX) followed by Solvent Extraction (SX). The study has been performed by using data from lab-scale

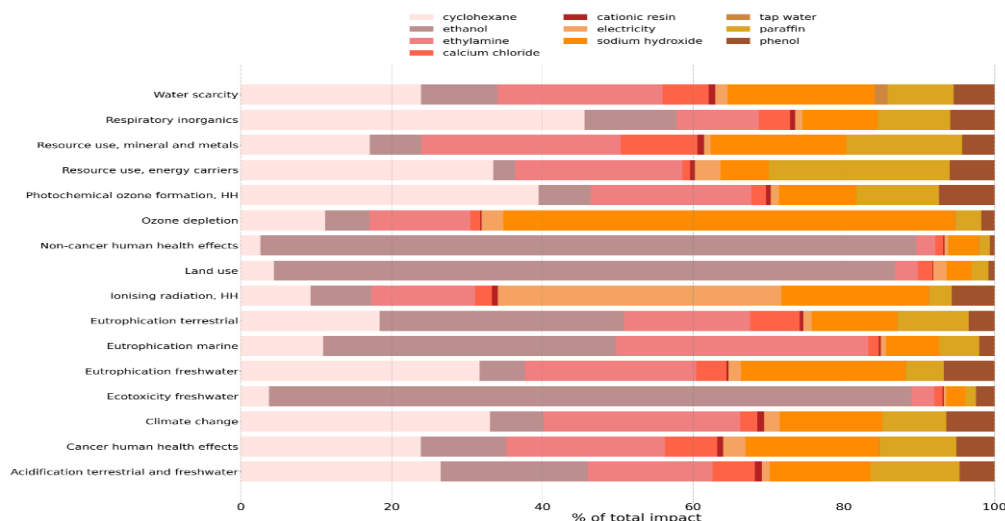


Figure 2: LCA results

experiments (based on the production of a few grams of LiOH) and mathematically upscaled to the processing of 100 kg of spodumene.

The results of this ex-ante LCA highlight the predominant role of chemicals in the final environmental footprint of the process. Therefore, for future upscaling, an optimization in the use of chemicals, especially cyclohexane, ethanol, sodium hydroxide and paraffin, may lead to significant environmental benefits for the whole process. At this stage of analysis, the energy requirement from roasting does not have a predominant effect on the final environmental footprint, despite the high temperature required (1,100 °C).

Some of the limitations encountered by the ex-ante LCA results are related to the early stage of the technical development of the process. In particular:

- Chemicals used within NAIX and SX can be recycled and recirculated (e.g. ethanol). On a lab scale, however, it was not possible to calculate the recycling rate of the chemicals. It can be foreseen that, during the industrial implementation of the process, chemicals will be recycled and their consumption will be significantly reduced.
- The real energy consumption for roasting may be different to the energy requirement calculated in this study. Parameters other than heat capacity must be also taken into account, such as the energy required for evaporation and other chemical reactions during the roasting process. All these parameters will be included in future assessments of energy consumption. Moreover, the source of energy strongly depends on the technology selected for the roasting at a larger scale.

Despite the limitations described above, the ex-ante LCA presents already some useful insights to guide future development of the process to lower the overall environmental footprint. Finally, for future studies, it is foreseen to enlarge the current analysis to the comparison with other processes for LiOH production, including Keliber Oy's LiOH process. A lower environmental footprint can indeed help to strengthen the position of the proposed process into the future market for LiOH production.

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6. Supplementary Note

Calculation of specific heat in Roasting

Composition	Percent	a	b (10 ³)	c (10 ⁻⁵)
	w/w			
SiO ₂	66.2%	10.49	0.24	-1.44
Al ₂ O ₃	22.3%	25.48	4.25	-6.82
Fe ₂ O ₃	1.0%	36		
CaO	0.3%	11.86	1.08	-1.66
MgO	0.3%	11.71	0.75	-2.8
K ₂ O	0.03%	22.86	-1.18	-2.64
Na ₂ O	0.4%	25		
Li ₂ O	7.2%	14.94	6.08	-3.38
TiO ₂	0.1%	17.97	0.28	-4.35

Temperature 1100 °C

Specific heat= a +b·T + c·T⁻² (cal/deg·mol)

Calculated Specific heat for 100 kg spodumene = 28.3 kWh

Calculation calcium chloride consumption in roasting



Mol Li ₂ O in 100 kg spodumene	240.9	mol
Mol CaCl needed	240.9	mol
Molar mass CaCl	110.98	g/mol
CaCl needed for 100 kg spodumene	26,742	g
	26.7	kg

Amount of LiCl produced

molar mass LiCl	42.394	g/mol
mol LiCl produced	313.9	mol
	13,306	g
	13	kg