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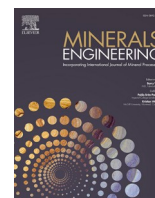
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Environmental impacts of lithium hydroxide monohydrate production from spodumene concentrate – A simulation-based life cycle assessment

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ABSTRACT

The demand for lithium hydroxide monohydrate (LHM) is likely to increase in the future due its growing use in the manufacturing of high-nickel lithium-ion batteries (LIB), such as NMC811. Conventional production of LHM is largely based on spodumene ore that is refined using sulfuric acid roasting processes, which have been shown to be environmentally straining. Decarbonization of LIB production as part of the green transition requires careful evaluation of all the material production steps. In this work, the environmental impacts of the conventional sulfuric acid roasting process of LHM production were compared to a recently launched soda leaching process using simulation-based life cycle assessment (LCA). This comparison can help in finding the environmentally most competitive process option as well as in identifying the pain points of the processes. The results show that the soda leaching process has lower environmental impacts in all the impact categories observed, notably in global warming, acidification, smog formation, and ozone layer depletion. The global warming potential in the soda leaching process was approximately 33% lower compared to the sulfuric acid roasting process. The other impact categories also showed lower indicator values, the reduction ranging from approximately 16% to 72% when compared to the sulfuric acid roasting process. The largest sources of environmental impacts inside the soda leaching process were the production of heat, soda ash, and quicklime, whereas in the sulfuric acid roasting process, heat, sulfuric acid, and sodium hydroxide were the main contributors in all the impact categories observed.

1. Introduction

Due to the increasing use of lithium-ion batteries (LIBs) in electric vehicles and energy storage systems lithium is currently one of the most important battery metals. The International Energy Agency (IEA) has estimated that by 2040 the demand for lithium will see approximately a 12–42 fold increase compared to that of 2020, even in the case of adopting alternative battery chemistries in the market (IEA, 2021). It is clear that lithium will play an important role in the green transition for decades to come and, thus, its sustainable production must be ensured. LIB recycling is suggested as an approach to provide some of the lithium required, but it will likely cover only a fraction of the growing demand

(Martin et al., 2017; Ziemann et al., 2018). It is estimated that Li from recycled EV and energy storage batteries would cover only approximately 5–7 % of the demand in 2040 (IEA, 2021; Pommeret et al., 2022), so primary production needs to be increased significantly. Lithium as such is an abundant element in the Earth's crust, but is currently extracted only from lithium rich brines and pegmatite ores, specifically from spodumene (Salakjani et al., 2020). Lithium markets include a variety of products, of which the most important include both battery- and technical-grade lithium carbonate (Li_2CO_3 , LC) and lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$, LHM), battery grade LHM usually reaching purity levels of over 99 % in commercial products (Nanografi, 2023; Targray, 2023). Currently, most lithium (over 60 %) is extracted

Abbreviations: AP, Acidification potential; CAM, Cathode active material; DLE, Direct lithium extraction; EP, Eutrophication potential; FAETP, Freshwater aquatic ecotoxicity potential; GHG, Greenhouse gas; GS, Glauber's salt; GWP, Global warming potential; HTP, Human toxicity potential; IEA, International Energy Agency; LC, Lithium carbonate; LCA, Life cycle assessment; LCI, Life cycle inventory; LCIA, Life cycle impact assessment; LHM, Lithium hydroxide monohydrate; LIB, Lithium-ion battery; MVR, Mechanical vapor recompression; ODP, Ozone layer depletion potential; PLS, Pregnant leaching solution; POCP, Photochemical ozone creation potential; SSA, Sodium sulfate anhydrous.

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from brines in South America, conventionally producing LC (Dessemond et al., 2019). Spodumene is mined dominantly in Australia, Canada, and China, and refined to LC or LHM mainly in China (Dessemond et al., 2019).

Large investments in lithium production in the 2010 s created a global supply chain for LHM, which relies largely on Australian spodumene mining and Chinese sulfuric acid roasting refining (Grant et al., 2020). LHM provided by this supply chain exhibits a greatly increased CO₂ footprint for the lithium product compared to brine-based LC products, which were previously the dominant lithium source in LIB manufacturing (Grant et al., 2020). In previous studies, it has been estimated that the share of the environmental impacts of LHM can be 5–15 % of the total impacts of LIB manufacturing (Chordia et al., 2022). Today, LIB manufacturers are moving toward low-cobalt/high-nickel cathode chemistries, such as NMC811, and in these production lines LHM is the favored lithium chemical (Grant et al., 2020). In fact, it has been predicted that the demand for LHM will reach 1.6 million metric tons per year in lithium carbonate equivalents (LCE) by 2031, showing an increase of approximately 20 times that of 2021 (Dupéré et al., 2018).

Lithium hydroxide is conventionally manufactured either from brine or from spodumene using sulfate roasting processes (Grant et al., 2020), where spodumene concentrate is roasted with sulfuric acid and then leached with water to produce lithium sulfate, which is then converted into LHM. Depending on the process, the conversion from lithium sulfate happens directly into LHM or through an intermediate form, such as LC (Rioyo et al., 2022). This process relies on the use of fossil fuels and large amounts of sulfuric acid. Consequently, large amounts of sodium hydroxide are also needed to precipitate the sulfate ions out of the solution, a feature that generates excess solid waste (Rioyo et al., 2022). To reduce the environmental burden of LHM products, new production methods are emerging around the world; one of the most prevalent is the soda leaching process, which produces high-purity LHM in an acid- and sulfate- free hydrometallurgical process (Tiihonen et al., 2019).

Decarbonizing and reducing the environmental impacts of LIB production is encouraged on many levels of industry and legislation, creating a need to be able to evaluate and compare the environmental footprints of different lithium products and production processes. For example, a digital “battery passport” (Berger et al., 2022) has been suggested to enhance circularity in the battery metals value chains, but this requires detailed knowledge of the impacts of alternative or parallel production processes. Currently, the environmental impacts of lithium products have been studied using life cycle assessment (LCA), but many studies have previously assumed that LHM is produced mainly by sulfate roasting processes (Chordia et al., 2022; Grant et al., 2020; Kelly et al., 2021). As new spodumene-based LHM production methods are being developed, it is important that the environmental impacts of the novel production routes are carefully evaluated in the early stages of development.

In previous studies, simulation-based LCA has been successfully applied to evaluate the environmental impacts of metals production from primary (Rinne et al., 2021a) and secondary (Aromaa et al., 2022; Rinne et al., 2021b) raw materials, and to evaluate existing and novel process flowsheets (Rinne et al., 2022). In this work, a flowsheet simulation-based gate-to-gate LCA is performed on the production of LHM from spodumene concentrate using both the soda leaching and sulfate roasting processes. The aim of the study is to investigate the environmental impacts of each process, and to identify the most important sources of impacts in the upstream processes. A better understanding of the environmental impacts of these two processes would help the decision makers and process designers and could help in finding the most sustainable route to produce LHM.

2. Methodology

The comparative LCA studies conducted in this work followed the ISO standards 14040:2006 (ISO 14040, 2006) and 14044:2006 (ISO

14044, 2006). Firstly, the goal and scope of the study were defined. This comprised formulating the research questions and determining the boundaries for the studied systems. Secondly, a life cycle inventory (LCI) was built for each process from the mass and energy balances of the flowsheet models, which were simulated with HSC Sim version 10.2.2.0 (Metso:Outotec, 2023). Thirdly, the life cycle impact assessment (LCIA) results were calculated using OpenLCA version 1.10.3 (GreenDelta, 2023) software and Ecoinvent 3.6 (Wernet et al., 2016) database. And finally, the results were interpreted and examined against the goal and scope of the study, and the process was refined and repeated iteratively if necessary.

2.1. Goal and scope

The goal of the study was to investigate the environmental impacts of LHM from two alternative production routes, specifically by comparing the more traditional sulfate roasting process to the recently launched soda leaching process. The processes were evaluated as gate-to-gate LCA studies so that the systems only contained metallurgical refining plants. The scope of the study and the system definitions were chosen to make the environmental impacts of the two systems comparable and so that no differences arising from the background processes or material transportation affected the comparison. The simulation models were built on literature data and publicly available descriptions of suitable process plants. The functional unit chosen for the study was 1 metric ton (t) of battery-grade LHM. Battery-grade in this work is defined as having a purity over 99.5 %.

Two systems were defined, each consisting of one of the studied processes (i.e. the *sulfate roasting process* and *soda leaching process*), including the pyrometallurgical and hydrometallurgical processes involved at the lithium refinery plants. The starting material for both processes is a spodumene ore concentrate with identical amount and composition, and the product is battery-grade LHM delivered to the factory gate. The system boundaries for the sulfate roasting process and soda leaching process are presented in Fig. 1. More detailed simulation flowsheets are presented in the [supplementary information](#). The solid side streams from either process are not considered as side products, although that could be a possible scenario in a real plant. The sulfate roasting process produces aluminosilicate waste and sodium sulfate anhydrous (SSA), while the soda leaching process produces inert analcime sand. SSA is possibly a tradeable product, albeit with a low economic value, while analcime sand could possibly be used as a construction material, for example. However, no multifunctionality based on these assumptions was applied in this study to limit the comparison to only the metallurgical processes themselves.

No streams outside the system boundaries were treated further in the simulations or in the LCA part of the study. All input flows were taken as background processes from the Ecoinvent database in the LCA part, and all output flows treated as emissions or inert waste. Europe was chosen as the geographic boundary. The starting material, α -spodumene concentrate, was assumed to come from a mineral processing plant outside of the system. No transportation was considered in the study, as the system boundaries only contain the lithium refinery plant. The cut-off streams in the systems comprise small or difficult-to-handle streams and have no significant impact on the LCIA results. The cut-off streams are defined in the [supplementary information](#).

2.2. Process descriptions

The studied processes include the steps that are assumed to be present in the metallurgical refining plants (Fig. 1). More detailed flow diagrams are presented in the [supplementary material](#). Both processes start with the calcination of the spodumene concentrate that is delivered from the mineral processing plant, and end with delivering the dried LHM product to the factory gate. In both processes, there should be a milling step after calcination. However, because details about this step

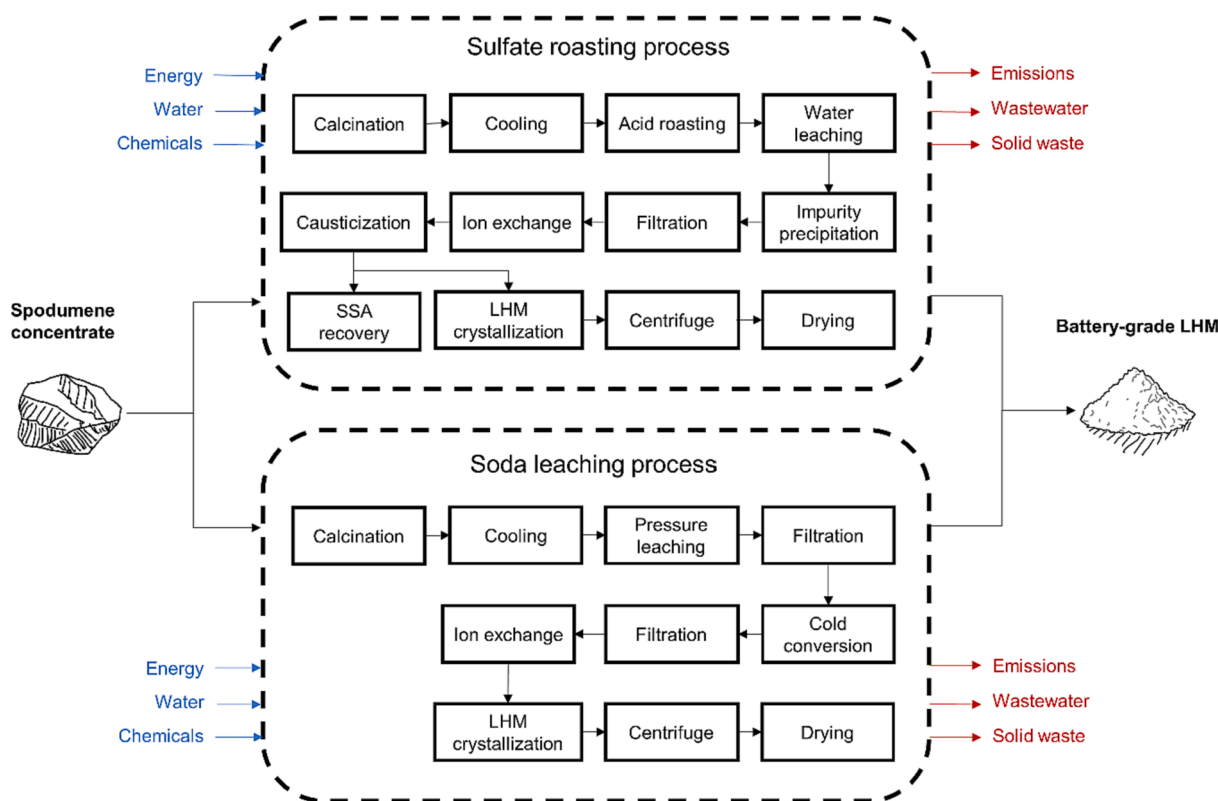


Fig. 1. Simplified flow diagrams for the studied *sulfate roasting process* and *soda leaching process*. System boundaries are presented with dotted lines. General input and output flows are presented at the boundaries; the main feed material (spodumene concentrate) and the product are underlined.

were not available in the literature, it was left out of the models. This does not affect the comparison, because the input material flow amount and composition are identical at this stage in both processes. However, it will produce a systematic error in the electricity consumption in both processes. Consequently, the estimated electricity consumption in both of the modeled processes will be too low, and therefore the electricity related values should not be compared to other estimations outside of this work without critical evaluation of the missing contribution from the milling process.

The raw material composition of the spodumene concentrate used as the feed is presented in Table 1. The composition was chosen so that the lithium content is suitable for both processes, i.e., having a Li_2O content of approximately 5%. It should be noted that the processes investigated in this work are designed and optimized to process only the given raw material, and applying different raw materials would require alteration of the flowsheet models.

The sulfate roasting process is loosely based on the Piedmont process flowsheet provided in a pre-feasibility study for a chemical plant in

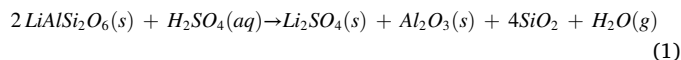
Table 1

Mineralogical composition of the spodumene concentrate (Peltosaari et al., 2017) adopted in this work.

Mineral	Chemical formula	wt%
Spodumene	$\text{LiAlSi}_2\text{O}_6$	75.12
Quartz	SiO_2	8.95
Albite	$\text{NaAlSi}_3\text{O}_8$	8.00
K-feldspar	KAlSi_3O_8	2.63
Muscovite	$\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$	3.14
Apatite	$\text{Ca}_3(\text{PO}_4)_2$	0.64
*Hematite	Fe_2O_3	2.03
*Magnesium oxide	MgO	0.06
*Manganese oxide	MnO	<0.01

*The Fe, Mg, and Mn oxide amounts were calculated from the reported amounts of tourmaline (0.12 wt%) as approximate values.

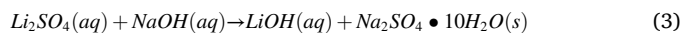
North Carolina, USA (Piedmont Lithium Limited, 2023). The process starts with calcination, where natural gas is used as fuel to heat the spodumene to $1050\text{ }^\circ\text{C}$ in order to convert the crystal structure into a β -form that is more accessible for the leaching agents (Salakjani et al., 2020). After calcination, the concentrate is roasted with sulfuric acid at $250\text{ }^\circ\text{C}$ and consequently leached with water. The main reaction (1) is slightly exothermic, and is taking place in the roasting unit is the conversion of spodumene into lithium sulfate and an aluminosilicate:



The aluminosilicate is represented as individual oxides, as suggested by Fosu et al. (Fosu et al., 2020). Other reactions taking place in the roasting unit are similar sulfate formation reactions from the other minerals presented in Table 1. In the water leaching step, most of the sulfates formed are dissolved, the most important reaction being the dissolution of lithium sulfate (2):



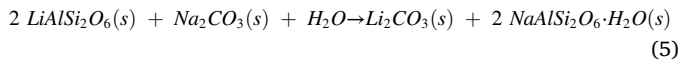
The remaining solids are filtered out and the pregnant leaching solution (PLS) is neutralized and treated with lime and soda ash to precipitate magnesium and calcium from the solution. The precipitated Mg and Ca residues are filtered out and the solution is purified using ion exchange that removes any remaining two valent ions, such as Ca, Mg, and Mn. The purified lithium sulfate solution is then concentrated and causticized to precipitate the sulfate ions as Glauber's salt (GS), which is crystallized and filtered out, according to reaction (3):



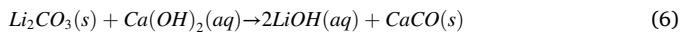
The GS cake enters the SSA crystallization circuit, which produces SSA as solid waste. From GS filtration, the lithium hydroxide solution is routed to the LHM crystallization circuit, which produces the final product, LHM, according to reaction equation (4):



The soda leaching process follows the alkaline leaching concept introduced by Metso (Tiihonen et al., 2019) and is loosely based on the Sibanye-Stillwater Keliber lithium project (Sibanye-Stillwater, 2023) that will start operating in Finland in 2025. The process starts with a calcination step which is identical to that in the sulfate roasting process. After calcination, the concentrate is cooled and pulped with soda ash to form a slurry, which is then pressure leached at 220 °C and 20 bar. The main reaction (5) of spodumene conversion into LC and analcime sand is slightly exothermic and takes place in the autoclave:



After leaching, the hot slurry is cooled and filtered. The solids fraction, containing the LC, is routed to cold conversion, where LC is mixed with lime in ambient conditions. The main reaction in the cold conversion is the conversion of LC into lithium hydroxide (6):



After cold conversion, the solids are filtered out and the lithium hydroxide solution is purified in ion exchange, which removes divalent ions, mainly Ca. After purification, the lithium hydroxide solution enters a crystallization circuit similar to that at the end of the sulfate roasting process, the end product being battery-grade LHM.

2.3. Simulation parameters

The simulation parameters are presented in Table 2. In addition to the listed parameters, heat and process water were recycled in both processes so that all outgoing non-contaminated process water was collected and circulated back into the processes. The same was done for all outgoing heat, which included direct heat flows and heat that was recovered from condensed water vapors. All condensed water was also recycled back as process water. Excess water vapor was treated as off-gas. All crystallizers, except the GS crystallizer, were assumed to be mechanical vapor recompression (MVR) crystallizers. They were modeled in a manner that emulates the MVR working principle by circulating the heat through vapor compression and heat exchange.

In this study, the term “battery-grade” is defined as having a purity equal to or larger than 99.5 wt% of LHM. The impurity levels were not controlled rigorously due to the lack of details about additional purification steps in the processes and knowledge about the initial side reactions leading to impurity formation.

2.4. Sensitivity analysis

Many simulation parameters could not be found in the literature and had to be estimated, especially in the sulfate roasting process, therefore there are some built-in uncertainties in the models. The robustness of the models and the reliability of the results were evaluated by conducting a sensitivity analysis, where sets of chosen simulation parameters were varied in each model and the LCIA results were re-calculated for each simulation run. Each set of values for the chosen parameter consisted of the base case with default parameters, as well as two other values that were either lower or higher than in the base case. These parameter sets are presented in Table 3. The non-base case simulation runs provide information about the robustness of the flowsheet models and reveal volatile simulation parameters, which could possibly have a large effect on the LCIA results.

2.5. Life cycle inventory

The life cycle inventories gathered from the flowsheet models are presented in Table 4.

Table 2

Simulation parameters for the soda leaching and the sulfate roasting processes.

Sulfate roasting process			
Unit	Parameter	Value	Ref.
Calcination	Temperature	1050 °C	(Tiihonen et al., 2019)
Calcination	Cooling temperature after calcination	65 °C	(Rioyo et al., 2022)
Acid roasting	Temperature	250 °C	(Rioyo et al., 2022)
Acid roasting	Sulfuric acid stoichiometric excess	35 %	(Dupéré et al., 2018)
Acid roasting	Side reactions progress*	30 %	Estimate
Water leaching	Temperature	90 °C	(Karrech et al., 2020)
Lime slaking	Temperature	85 °C	(Radaker, 2023)
Lime slaking	Water-to-lime ratio	4:1	(Radaker, 2023)
GS crystallization	Temperature	25 °C	Estimate
SSA crystallization	Na ₂ SO ₄ solubility	281 g/l	(NCBI, 2023)
SSA crystallization	Temperature	60 °C	Estimate
SSA centrifuge	Cake moisture	10 %	Estimate
SSA dryer	Temperature	80 °C	Estimate
LHM crystallization	Temperature	70 °C	(Dupéré et al., 2018)
LHM crystallization	Li effective concentration	35 g/l	Estimate
LHM crystallization	Solids-%	20 wt%	Estimate
LHM centrifuge	Cake moisture	10 %	Estimate
LHM dryer	Temperature	80 °C	Estimate
Soda leaching process			
Unit	Parameter	Value	Ref.
Calcination	Temperature	1050 °C	(Tiihonen et al., 2019)
Calcination	Cooling temperature after calcination	65 °C	(Rioyo et al., 2022)
Pulping	Na concentration in recycled filtrate**	4 g/l	(Tiihonen et al., 2019)
Pulping	pH	11.5	(Tiihonen et al., 2019)
Autoclave	Temperature	220 °C	(Tiihonen et al., 2019)
Autoclave	Pressure	20 bar	Estimate
Slurry cooling	Li concentration***	2 g/l	(Tiihonen et al., 2019)
Lime slaking	Temperature	85 °C	(Radaker, 2023)
Lime slaking	Water-to-lime ratio	4:1	(Radaker, 2023)
Filter 1	Cake moisture	21.5 %	(Tiihonen et al., 2019)
Cold conversion	Li concentration	10 g/l	(Tiihonen et al., 2019)
Cold conversion	Al concentration	20 mg/l	(Tiihonen et al., 2019)
Cold conversion	Si concentration	50 mg/l	(Tiihonen et al., 2019)
Cold conversion	K concentration	50 mg/l	Estimate
Cold conversion	Fe, Mg, Mn and PO ₄ ³⁻ concentrations	0.5 mg/l	Estimate
Filter 2	Cake moisture	30 %	(Tiihonen et al., 2019)
LHM crystallization	Temperature	70 °C	(Dupéré et al., 2018)
LHM crystallization	Li concentration	35 g/l	Estimate
LHM crystallization	Solids %	20 wt%	Estimate
LHM centrifuge	Cake moisture	10 %	Estimate
LHM dryer	Temperature	80 °C	Estimate

*Side reaction progress means the formation of sulfates of Na, K, Ca, Mg, Mn, and Fe from the minerals present in the feed other besides spodumene.

**Na concentration in the pressure leaching circuit is used to control the amount of soda ash feed.

***Li concentration in slurry cooling is used to control the formation of lithium carbonate.

Table 3
Parameter sets for sensitivity analysis.

Case	Sulfate roasting process	1	2 (Base case)	3
SF A	Sulfuric acid excess (%)	30	35	40
SF B	Sulfation side reactions progress rate (%)	10	30	50
SF C	Li concentration in evaporation (g/l)	7	12	18
SF D	Li loss in GS crystallization, solid formation reaction progress rate (%)	0	3.5	7
SF E	Effective Li concentration in LHM crystallization (g/l)	30	35	40
	Soda leaching process	1	2 (Base case)	3
SL A	Na concentration in pressure leaching circuit (g/l)	1	4	7
SL B	Effective Li concentration in LHM crystallization (g/l)	30	35	40

Table 4
Life cycle inventories for the soda leaching and sulfate roasting processes. The values are expressed in terms of the functional unit, i.e., per metric ton of LHM.

Flow	Unit / t LHM	Sulfate roasting process	Soda leaching process
INPUTS			
Spodumene concentrate	t	6.59	6.61
Soda ash	t	6.99·10 ⁻³	1.37
Quicklime	t	1.27	0.821
Sulfuric acid	t	3.61	–
Hydrochloric acid	t	2.10·10 ⁻⁴	1.07·10 ⁻²
Sodium hydroxide	t	1.00	–
Carbon dioxide (liquid)	t	–	0.170
Anionic resin	t	1.55·10 ⁻⁶	6.90·10 ⁻⁵
Process water (tap water)	t	3.88	9.82
Deionized water	t	0.500	0.500
Cooling water (from ocean)	t	1150	313
Natural gas (liquid)	t	0.308	0.264
Steam	t	14.5	5.42
Electricity	kWh	849	845
OUTPUTS			
Battery-grade LiOH·H ₂ O	t	1	1
Carbon dioxide	t	0.123	0.716
Carbon monoxide	t	4.60·10 ⁻³	4.60·10 ⁻³
Water vapor	m ³	2380	6460
Cooling water (to ocean)	m ³	943	315
Wastewater	m ³	14.1	7.20
Solid waste	t	15.7	12.7

2.6. Impact assessment

The environmental impacts were investigated using the CML-IA baseline LCIA method (CML, 2023) through the following impact categories: Global warming potential (GWP, kg CO₂-eq), Eutrophication Potential (EP, kg PO₄-eq), Acidification Potential (AP, kg SO₂-eq), Freshwater Aquatic Ecotoxicity Potential (FAETP, kg DCB-eq), Human Toxicity Potential (HTP, kg DCB-eq), Photochemical Ozone Creation Potential – or smog formation – (POCP, kg ethane-eq), and Ozone Layer Depletion Potential (ODP, kg CFC11-eq).

3. Results and discussion

3.1. Processing and impact results

Both flowsheet models achieved a lithium recovery yield of > 89 %, with the target product purity of > 99.5 %. The flowsheet simulations were fully converged, except in the sensitivity analysis case SL B1, in which the simulation was unable to converge completely.

The base case LCIA results for both processes are presented in Table 5 and further illustrated in Fig. 2 as relative impact results.

The LCIA results show that the environmental impacts of the soda leaching process are significantly lower in all categories compared to the sulfate roasting process, the difference ranging approximately from 16 % to 72 %, depending on the impact category. For example, the GWP of the soda leaching process is over 33 % lower than that of the sulfate roasting process.

The internal contributions within the processes are further illustrated in Fig. 3. The figures show that heat production is generally a large contributor in both processes, especially in GWP and ODP. In the sulfate roasting process, heat production is clearly the biggest contributor to GWP. Besides heat production, other major sources of environmental impacts are sodium hydroxide and sulfuric acid production, sodium hydroxide being the largest contributor to EP and ODP. Sulfuric acid is the largest contributor to AP, FAETP, HTP, and POCP. Electricity generation is also a notable contributor to EP and FAETP. Similarly, quicklime is a large contributor to GWP. In the soda leaching process, the production of soda ash is the largest contributor to the environmental impacts in EP, AP, FAETP and HTP. In the other categories, it is the second largest contributor after heat production. Quicklime contributes significantly to GWP and POCP, and electricity can also be considered a major general contributor after heat and soda ash production.

Overall, heat production in these processes is generally a major source of environmental impacts. This, however, depends on the heat production route. Different energy sources can be used to generate steam that provides the heat. The Ecoinvent 3.6 database used in this work assumes a 2016 average European energy mix for the steam production, so it is largely based on fossil fuels. The large share of heat production in the LCIA results encourages the consideration of adopting waste heat sources from nearby industrial partners, for example, or using renewable energy to produce the steam. Production of chemicals – in this case soda ash, quicklime, sulfuric acid, and sodium hydroxide – is also a major source of environmental impacts. One possibility to lower the environmental impacts of the studied processes would be to find alternative, less burdening chemical production processes or even alternative, less burdening chemicals to use in the reactions. However, this might not be easy to achieve for practical or fundamental reasons. To lower the environmental impacts caused by these chemicals, their manufacturing processes should be reviewed, and if possible, greener providers and manufacturers could be chosen to contribute to the improvements of the LHM environmental performance. In the LCA part of the calculations, synthetic soda ash was used for the soda ash in both processes. By using natural soda ash instead, the environmental impacts could be reduced, especially in the soda leaching process. It can also be

Table 5
LCIA results for the sulfate roasting and soda leaching processes.

Impact category	Units / t LHM	Sulfate roasting process	Soda leaching process
GWP	t CO ₂ -eq	8.15	5.44
EP	t PO ₄ -eq	8.06·10 ⁻³	6.77·10 ⁻³
AP	t SO ₂ -eq	0.0601	0.0164
FAETP	t DCB-eq	2.78	1.81
HTP	t DCB-eq	4.16	3.13
POCP	t ethane-eq	2.80·10 ⁻³	9.62·10 ⁻⁴
ODP	t CFC11-eq	1.56·10 ⁻⁶	5.01·10 ⁻⁷

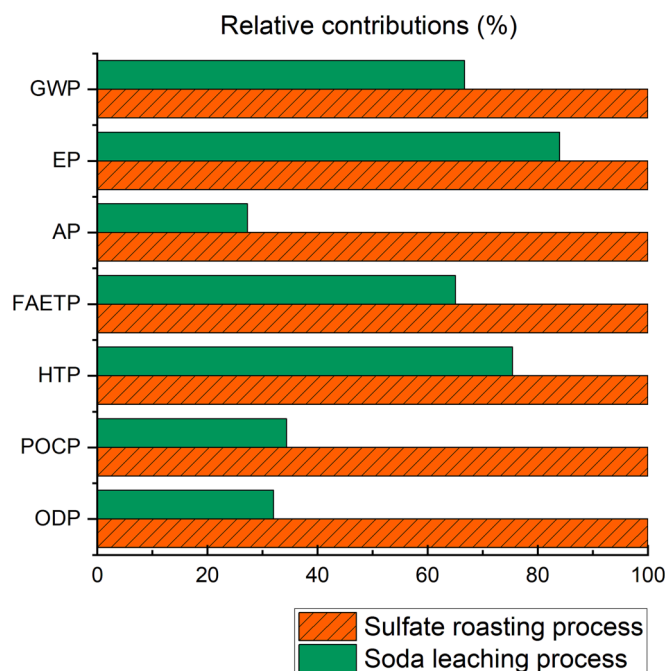


Fig. 2. Relative contributions from the sulfate roasting and soda leaching processes in the selected impact categories. Impact categories: global warming potential (GWP), eutrophication potential (EP), acidification potential (AP), freshwater aquatic ecotoxicity potential (FAETP), human toxicity potential (HTP), photochemical ozone creation potential (POCP), and ozone depletion potential (ODP).

speculated that heat production in general is a large contributor to the environmental impacts in the production of these chemicals, and that the transition towards renewable energy will also reduce the contribution of background processes related to heat and chemical production.

3.2. Sensitivity analysis

The results of the sensitivity analysis are presented in Fig. 4. The case studies used in the sensitivity analysis are listed in Table 3. The sulfate roasting process case groups SF A-E and the soda leaching process case groups SL A-B in Fig. 4 show the cases 1 (blue), 2 (orange), and 3 (green) presented in Table 3. Dotted lines for the base cases (in orange) for both processes are highlighted with horizontal dotted lines. The results presented in Fig. 4 show that, in many cases, there is no significant qualitative difference, suggesting that the major conclusions of the study are unaffected. The most significant outcome was seen in case SF C where the water evaporation rate prior to causticization was varied in the sulfate roasting process. This was shown to have a significant impact on the total heat consumption of the process and therefore the evaporation rate should be considered a volatile parameter. However, the qualitative outcome remains unchanged: the environmental impacts of the sulfate roasting process are higher compared to the soda leaching process in all categories, albeit only slightly in the GWP and EP in the case SF C1. It could be interpreted from the SF C case results that the GWP and EP of the sulfate roasting process depend highly on the actual heat consumption of the process.

3.3. Critical considerations

LHM production from Australian spodumene with Chinese sulfuric acid conversion has previously been reported to have a GWP of 15 t CO₂-eq/t LHM (Grant et al., 2020), whereas the GWP of the current study for the sulfate roasting process (8.15 t CO₂-eq/t LHM) is somewhat lower. The difference might be explained by different system boundary and

scope definitions, but it could also indicate that the simulated process in this work is over-optimized, and the LCIA results of the sulfate roasting process are underestimated. Some of the difference might be explained by the exclusion of milling steps in the simulated process.

Surprisingly, the soda leaching process in this study shows an even lower GWP (5.44 t CO₂-eq/t LHM) than that of the Argentinian brine process that has been reported to have a GWP of 8 t CO₂-eq/t LHM (Grant et al., 2020). These brine extraction methods are based on the direct lithium extraction (DLE) process, which consumes a lot of natural gas to heat the brine. Opposite to Argentinian brine process, Chilean brine processes have been reported to have only 5 t CO₂-eq/t LHM, but this is for technical grade LHM, not battery grade (Grant et al., 2020). Again, part of the difference between the simulated soda leaching process and the Argentinian brine process might come from the too low electricity consumption due to the missing milling steps. Nevertheless, the results indicate that the soda leaching process could be comparable to the South American brine processes in terms of environmental impacts.

However, it should be noted that such direct comparison of GWP indicator values from different studies should be considered critically, as the system definitions, functional units, assumptions, and methods might be different. Also, the processes compared here are very different, and in reality, they vary from plant to plant.

LCIs for similar processes are scarce in the literature, but Chordia et al. (Chordia et al., 2022) have presented some LCI data for a sulfate roasting process, originally reported by Kelly et al. (Kelly et al., 2021), and for a soda leaching process. The reported sulfate roasting process appears to be similar to the sulfate roasting process defined in this work, and the reported soda leaching process describes the same Keliber process on which the soda leaching flowsheet in this work is based on. The LCI data for these two reported processes, as well as the corresponding LCIs from the current work are listed in Table 6. The sulfate roasting process described by Kelly et al. is quite similar to that in this work, but not enough to be considered identical. However, it should give a good indication about some of the material consumptions in the sulfate roasting process. The data reported for the Keliber process should be close to the soda leaching data acquired in this work, because they represent essentially the same process.

The data shows that the values acquired in the current work are in many cases lower than those reported, indicating a systematic error or over-optimization of the processes. This may be explained, for example, by the fact that the electricity consumption was grossly underestimated in the current study compared to that reported by Kelly et al. However, this was to be expected because of missing milling operations in the flowsheet studied in this work. The heat consumption is also lower in the current study, possibly due to over-optimized heat recovery and recycling. In processes reported earlier in the literature, heat is very likely not recovered from all outgoing off-gas streams, and the water vapor condensation is likely less efficient in real applications. On the other hand, in their supplementary material, Kelly et al. (Kelly et al., 2021) state that the Tianqi Lithium lithium hydroxide plant in China would have a steam consumption of 12 t/t LHM, which is close to the 14.5 t/t LHM acquired in this work.

The chemical consumptions are similar to the values reported earlier, except for the sulfuric acid consumption, which is more than twice as high in the current work when compared to the data reported in the published literature. This suggests that the processes are different. The sulfuric acid amount used in the flowsheet model in the current work is based on the stoichiometric lithium amount and the required 30 %–40 % excess that has been reported elsewhere (Rioyo et al., 2022; Dupéré et al., 2018) for such processes. Thus, it could not be significantly reduced without affecting the yield. The notably higher amount of spodumene used in the reported Keliber process likely comes from assuming a lower ore grade or yield %. Nonetheless, the data shows that overall, the LCI data acquired from the flowsheet models seems reasonable, providing some confidence in the calculated LCIA results.

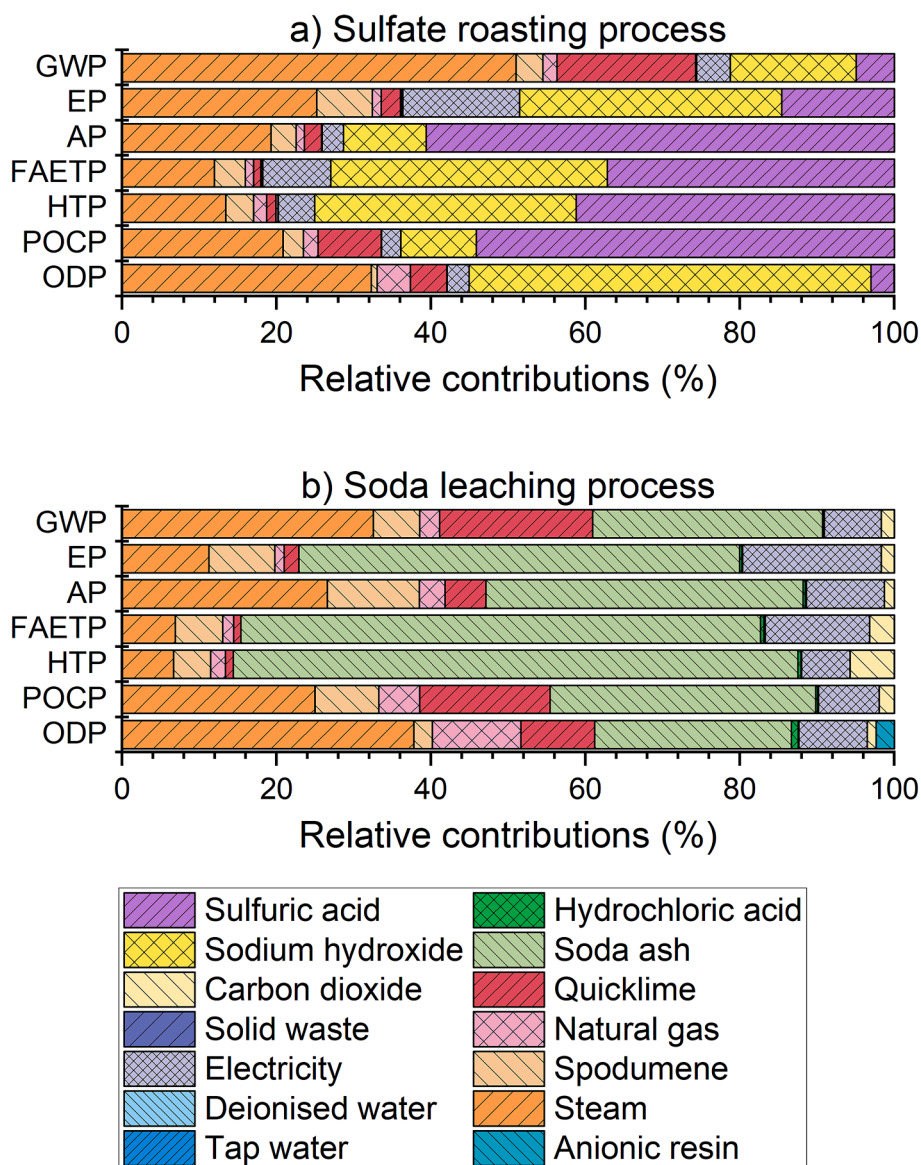


Fig. 3. Relative internal contributions of (a) sulfate roasting process and (b) soda leaching processes in all chosen environmental impact categories. Impact categories: global warming potential (GWP), eutrophication potential (EP), acidification potential (AP), freshwater aquatic ecotoxicity potential (FAETP), human toxicity potential (HTP), photochemical ozone creation potential (POCP), and ozone depletion potential (ODP).

In the sulfate roasting process, lithium sulfate roasting is converted into lithium hydroxide in the causticization step, where sodium hydroxide is fed into the process, causing precipitation of GS crystals. Lithium is partly lost in the step because some of it is captured inside the GS crystals. When dissolved, the GS forms an aqueous solution of Li^+ , Na^+ , K^+ , SO_4^{2-} and OH^- and consequently, lithium is difficult to recover from the solution due to the other alkali metal ions. However, this has been shown to be technologically possible with solvent extraction methods (Zhang et al., 2022), increasing the total lithium yield in sulfuric acid processes, but is not considered in this work. The yields of both processes were on the same level, so the losses were assumed small and comparable.

4. Conclusions

Lithium hydroxide monohydrate (LHM) production is likely to increase in the future due to its rising demand as a battery chemical, especially in high-nickel/low-cobalt LIB chemistries, such as NMC811. Conventional production lines designed to produce LHM from

spodumene ore rely heavily on sulfuric acid roasting and fossil fuels. More novel process routes include a hydrometallurgical alkaline soda leaching process, which is rapidly emerging as an alternative for the conventional sulfate roasting process. For decarbonizing the LIB manufacturing lines, it is important to evaluate the environmental impacts of different battery chemical production routes. This will enable newly developed production plants to be designed based on the best available technologies and existing plants to be reviewed and possibly converted to use technologies with better environmental performance.

In this work, the conventional sulfate roasting process was compared to the soda leaching process, and the environmental impacts of the two processes were evaluated. The two processes were first modeled as flowsheet simulations and life cycle inventories (LCI) were built from the mass and energy balances of the simulations. Life cycle assessment (LCA) was conducted to compare the environmental impacts of the processes using the Ecoinvent database for the background processes. Sensitivity analysis was performed to evaluate the robustness of the simulation models and the reliability of the results. The results as well as the constructed LCI were compared to those found in the literature for

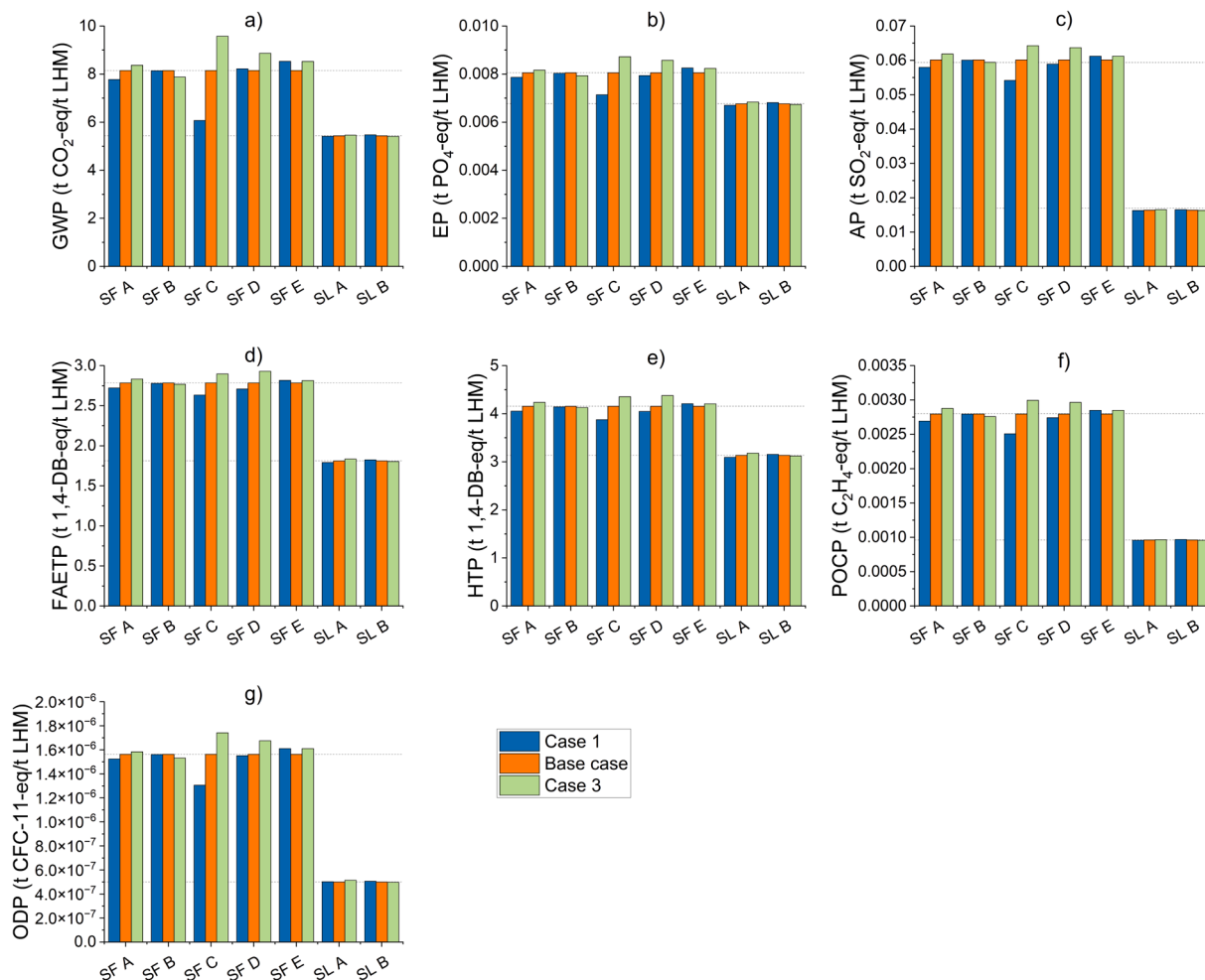


Fig. 4. Sensitivity analysis results for the sulfate roasting process and soda leaching process. The subfigures present the impact categories (a) global warming potential (GWP), (b) eutrophication potential (EP), (c) acidification potential (AP), (d) freshwater aquatic ecotoxicity potential (FAETP), (e) human toxicity potential (HTP), (f) photochemical ozone creation potential (POCP), and (g) ozone depletion potential (ODP) indicator values for all the simulation runs performed for the sulfate roasting process (SF A-E) and soda leaching process (SL A-B) cases. Each bar represents a single simulation, and the case groups represent the parameter runs listed in Table 3. Each group comprises cases 1 (blue), 2 (orange), which is the base case, and 3 (green). The base cases for both processes are highlighted with dotted lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 6

LCI data reported by Chordia et al. (Chordia et al., 2022) in the literature for similar processes.

Geography INPUT	Unit / 1 t LHM	Kelly et al. 2021 (Kelly et al., 2021)	Keliber	This work	
		Sulfate roasting China	Soda leaching Finland	Sulfate roasting Europe	Soda leaching Europe
Spodumene	t	6.42	10.4	6.59	6.61
Electricity	MWh	3.50	1.49	0.849	0.845
Heat*	GJ	71.3	20.7	39.7	14.9
Sodium hydroxide	t	1.18	0.112	1.00	–
Soda ash	t	0.0250	1.58	0.00699	1.37
Sulfuric acid	t	1.52	–	3.61	–
Hydrochloric acid	t	–	0.0720	0.000210	0.0107
Other chemicals	t	0.600	1.82	1.27	0.821

*Heat was converted between energy content and mass with a 2.75 MJ/kg ratio, as suggested in the Ecoinvent 3.6 database steam provider description.

similar processes. Based on the comparison, the results can be considered reliable at least qualitatively.

According to the results, the soda leaching process – which does not produce sulfates and contains no major greenhouse gas (GHG) releasing steps apart from spodumene calcination – showed reduced impact indicator values in all observed impact categories. The reduction ranged from approximately 16 % to over 72 %, depending on the impact category. The carbon footprint of LHM production can be reduced by over 33 % with the soda leaching process compared to the conventional sulfate roasting process. The largest relative reductions were seen in ozone layer depletion, acidification, and smog formation, but significant reductions could also be seen in global warming potential and freshwater ecotoxicity. The major contributors to environmental impacts within the sulfate roasting process were heat production, as well as production of sulfuric acid and sodium hydroxide. In the soda leaching process, the largest contributions came from the production of heat, soda ash, and quicklime. Reducing the environmental impacts of heat production by process optimization, utilizing waste heat, or transitioning toward renewable energy would reduce the environmental impacts of both processes and, arguably, also reduce the impacts from the production of the input chemicals: soda ash, quicklime, sulfuric acid, and sodium hydroxide. The contribution from heat is especially pronounced in the sulfate roasting process, where steam consumption through, e.g.

process optimization, would be a straightforward way to reduce the environmental impacts. One way to lower the environmental impacts of the soda leaching process would be to use natural soda ash instead of synthetic one.

CRedit authorship contribution statement

Heikki Lappalainen: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Marja Rinne:** Writing – review & editing, Validation, Methodology, Data curation. **Heini Elomaa:** Writing – review & editing, Validation, Methodology, Formal analysis, Data curation, Conceptualization. **Jari Aromaa:** Writing – review & editing, Validation, Writing – review & editing. **Mari Lundström:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

All relevant data is included in the article and in the [supplementary material](#).

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mineng.2024.108632>.

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