Master Thesis Report

Ex-Ante Comparative Life Cycle Assessment of Membrane Distillation-Crystallization for Lithium Extraction

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Abstract

Lithium is an energy-critical-element (ECE) that is a fundamental component of lithium-ion batteries which are projected to surge in demand in the coming years to meet the rising demand for battery electric vehicles (BEVs), variable renewable energy storage systems (RESS) and personal electronics. Supplying the projected amount of lithium for lithium-ion batteries in the near future is challenging due to the geographical concentration of lithium reserves and resources, complexity of recovering lithium from brines and the environmental impacts associated with lithium extraction in general. Several emerging technologies are being investigated to determine if they can provide additional lithium production capacity with improved efficiency and applicability to varying brine chemical compositions.

In this study, membrane distillation-crystallization (MCr) is investigated as a potentially environmentally preferable alternative to the current lithium extraction process from continental brines. An ex-ante life cycle assessment (LCA) was conducted to measure the potential environmental impacts of using MCr as an alternative to the brine inspissation process. The midpoint impact assessment methodologies used were global warming potential (GWP), water use, acidification potential (AP), resource use (metals and minerals) and cumulative energy demand (CED). To conduct the study, an early-stage lab study of MCr by (Cerda et al., 2021) for lithium recovery was scaled using processing modeling at the Advanced Mining Technology Center in Chile to create a life cycle inventory (LCI) of MCr in addition to an annual operational mass and energy balance. The MCr LCI was coupled with existing datasets for Li_2CO_3 production to model a theoretical MCr-Li_2CO_3 production facility and measure the environmental impacts associated with producing the functional unit (FU) of 1 ton Li_2CO_3.

Additionally, a narrative literature review was conducted to determine the current environmental impacts associated with brine inspissation in the Salar de Atacama, Chile. A second narrative literature review was conducted to determine the criteria upon which an improved lithium extraction technique can be measured. Lastly, the land use, land use intensity (LUI) and production intensity of the current brine inspissation route and the MCr route were explored.

The most salient results of this study indicate that an MCr lithium extraction facility has the potential to produce the equivalent of 100 kilotons Li_2CO_3, 76 kilotons of potassium chloride (KCl) and 14 megatons of freshwater per year with an annual raw brine input of 22 megatons per year. This results in a 64% water recovery efficiency and 75% lithium recovery efficiency. However, the main drawbacks are the exceptional amount of energy required which amounts to 5.43 TWh per year and would require approximately 50 km^2 of land if powered by solar photovoltaic (PV) energy. The other main drawback found was that the MCr-Li_2CO_3 production route had 4.5 times the amount of GWP than the brine inspissation route and 2.5 times the GWP when using 100% solar PV for electricity supply. Lastly, considering MCr uses 94% less water than the brine inspissation route, it is a trade-off worth further evaluation and future research.

List of Abbreviations

ADP	Abiotic Depletion Potential
AE	Accumulated Exceedance
AP	Acidification Potential
AMTC	Advanced Mining Technology Center
AGMD	Air Gap Membrane Distillation
AWARE	Available Water Remaining
BEV	Battery Electric Vehicle
PSAB	Biotic Environmental Monitoring Program
$MgCl_26H_2O$	Bischofite
$CaSO_4$	Calcium Sulfate
CO_2	Carbon Dioxide
CF	Characterization Factor
CL	Chile
CED	Cumulative Energy Demand
DOD	Department of Defense
DCMD	Direct Contact Membrane-Distillation
DLE	Direct Lithium Extraction
ECE	Energy Critical Element
EF	Environmental Footprint
EoL	End-of-Life
FU	Functional Unit
GJ	Gigajoule
GLO	Global
GWP	Global Warming Potential
GHG	Greenhouse Gas
GREET	GHGs, Regulated Emissions, and Energy Use in Technologies Model
IPCC	Intergovernmental Panel on Climate Change
IEA	International Energy Agency
ISO	International Standards Organization
$KMgCL_26H_20$	K-Carnallite
kt	kilotons
kWh	kilowatt-hour
LULUCC	Land Use & Land Cover Change
LUI	Land Use Intensity
LCA	Life Cycle Assessment
LCIA	Life Cycle Impact Assessment
LCI	Life Cycle Inventory
Li_2CO_3	Lithium Carbonate
LCE	Lithium Carbonate Equivalent
LDH	Lithium-aluminum layered double hydroxide chloride
LiOH	Lithium Hydroxide
$LiOH \cdot H_2$	Lithium Hydroxide Monohydrate

$Mg(OH)_2$	Magnesium Hydroxide
MRL	Manufacturing-Readiness-Level
MCr-PV	MCr coupled with PV electricity
MJ	Megajoule
Mtons	Megatons
MWh	Megawatt-hour
MD	Membrane Distillation
MCr	Membrane Distillation-Crystallization
NDVI	Normalized Difference Vegetation Index
PM	Particulate Matter
PV	Photovoltaic
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl Chloride
PVDF	Polyvinylidene fluoride
KCl	Potassium Chloride
K_2SO_4	Potassium Sulfate
PRISMA	Preferred Reporting Items for Systematic Reviews and Meta-Analyses
RESS	Renewable Energy Storage Systems
RoW	Rest of World
RBMP	River Basin Management Plan
SdA	Salar de Atacama
SQM	Sociedad Química & Minera
NaCl	Sodium Chloride
SWE	Surface Water Extent
SGMD	Sweep Gas Membrane Distillation
SLR	Systematic Literature Review
TEA	Techno-Economic Assessment
TRL	Technology-Readiness-Level
TWh	Terawatt-hour
t	tons
TDS	Total Dissolved Solids
TWS	Total Water Storage
TWSA	Total Water Storage Anomaly
US	United States
USGS	United States Geological Survey
VMD	Vacuum Membrane Distillation

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1 Introduction

1.1 Background

Achieving net-zero carbon emissions requires energy critical elements (ECEs) which are fundamental for advanced energy production, transmission and storage but exposed to supply chain disruption risk (Hurd et al., 2012). Lithium, a highly reactive alkali metal with unique chemical and physical properties (Kavanagh et al., 2018) is an ECE that provides the basis for superior battery storage capabilities (Habib et al., 2020). Lithium-ion batteries provide high-capacity storage for variable renewable energy production and provide the basis for battery electric vehicles (BEVs) and consumer electronics (Li et al., 2019). The demand for Li-ion batteries is expected to grow at an annual compound rate of approximately 30% for the next ten years, and Li-ion batteries are expected to account for 95% of lithium demand by 2030 (McKinsey, 2022). Lithium resources and reserves are usually presented in tons of lithium carbonate equivalent (LCE) which serve as a useful metric in the lithium market which deal with different lithium compounds such as lithium hydroxide (LiOH), lithium hydroxide monohydrate ($LiOH{\cdot}H_2$) and lithium carbonate (Li_2CO_3). Worldwide consumption of lithium in 2021 increased 33% from 70,000 tons in 2020 to 93,000 tons in 2021 (USGS, 2022). Importantly, there is a large supply shortage foreseen in the future due to expected lithium demand in 2030 to be between 3,000 and 4,000 kilotons LCE with confirmed supply by 2030 estimated at only 1,200 kilotons (McKinsey, 2022). Therefore, increased lithium production is needed alongside new production methods to mitigate a supply shortage and advance decarbonization goals through a more sustainable procurement of lithium (AltaLey, 2022; McKinsey 2022).

Providing lithium production capacity which can meet forecasted demand by 2030 requires careful consideration of the environmental, socio-economic, and technological implications of a buildout of production capacity. A ‘wicked problem’ or ‘burden-shifting’ emerges when technologies necessary for the global energy transition which reduce climate footprints in one region, contribute to environmental issues such as water scarcity in other regions of the world (Schomberg et al., 2021). Recently, the lithium industry has received notable scrutiny because of soaring prices (IEA, 2022a), supply constraints (McKinsey, 2022) and environmental and social sustainability concerns (Marazuela et al., 2019; Quinteros-Condoretty et al., 2020; Liu and Agusdinata, 2021; IEA, 2021; Yang et al., 2021; IEA, 2022b; Moran et al., 2022). Part of this scrutiny relates to the ways in which lithium is extracted and produced around the world.

Primary lithium is commercially extracted in two ways, either through ore and clay deposits or through brine deposits. Brines are water solutions with a salinity content higher than seawater and can be categorized as geothermal brines, oilfield brines and continental brines (Baudino et al., 2022). This research focuses specifically on continental brine deposits. Approximately 65% of primary lithium production originates from continental brine deposits (USGS, 2017) while 35% originates from pegmatite ores (primarily in Australia) and clay deposits (Peiró et al., 2013). The Puna Plateau which includes Argentina, Bolivia and Chile are estimated to have the largest lithium reserves worldwide with Chile having the most at 10.5 million metric tons (AltaLey, 2022). In Chile, lithium-rich brine is extracted primarily from the Salar de Atacama (SdA) which is a dry salt flat that contains underground continental brine deposits. After the brine is extracted, it is evaporated through a process known as ‘brine inspissation’ which is also referred to as brine evaporation. Part of the reason that lithium extraction has been scrutinized is because it is estimated that up to 95% of the water content in extracted brines is lost during the evaporation process (Heubl, 2019) and approximately 2.2 million liters of water are needed to produce 1 ton of LCE from lithium brine (IEA, 2022). When contextualizing this water loss within one of the driest deserts on the planet (Romero et al. 2012), it raises concerns about the long-term sustainability of lithium. A study by Schomberg et al. (2021) calculated the water scarcity footprint related to Li-ion battery production and found that brine inspissation in Chile and China are responsible for the greatest evapotranspiration losses along the supply chain of Lithium-ion batteries. Furthermore, the evapotranspiration losses from brine inspissation occur in regions of Chile and China that have a 'very high' probability of natural freshwater scarcity for humans and nature (Schomberg et al., 2021). In addition to water scarcity issues, Liu and Agusdinata (2019) found a strong correlation between lithium extraction activities in the SdA and local environmental degradation. However, several studies indicate that more detailed and exploratory research is needed to fully understand the sustainability implications of lithium extraction via brine inspissation on the surrounding environment (Agusdinata, 2018; Heubl, 2019; Liu et al., 2019; Gajardo and Redon, 2019; Marazuela et al., 2020).

Fortunately, industry stakeholders and governments are committed to developing alternative and improved lithium extraction processes which can improve environmental and social sustainability while still being economically feasible (Quinteros-Condoretty et al., 2020; Albemarle, 2021; AltaLey, 2022; McKinsey, 2022; SQM, 2022). In fact, experimentation with different technologies for lithium extraction has been studied for several years but have not been widely developed commercially due to cost and technical challenges. These technologies are known as direct-lithium-extraction (DLE) technologies which include adsorption methods, ion-exchange and sorption, solvent extraction, electrochemical separation, membrane processes and other hybrid methods such as ion-imprinted membranes, Li ion sieve membranes, membrane capacitive deionization and membrane distillation-crystallization (MCr) (Flexer et al., 2018; Sun et al., 2021; Xu et al., 2021; Khalil et al., 2021). Recently, Cerda et al. (2021) and Quilaqueo et al. (2022) conducted lab-scale studies at the Advanced Mining Technology Center (AMTC) in Santiago, Chile which validated the feasibility of using MCr for lithium recovery from continental brines in the SdA. Based on their lab-scale studies, this research seeks to evaluate the implications of using MCr at a commercial scale for lithium extraction in the SdA.

1.2 MCr Benefits

Importantly, MCr has the potential to be a notable improvement for brine-based extraction of lithium for several key reasons. First, MCr for lithium extraction shows the capacity to recover 95% of water contained in lithium brines (Cerda et al., 2021). This potential recovery rate is possible due to the fact that MCr is based on membrane distillation (MD) which can produce freshwater as permeate. Secondly, MCr eliminates the need for evaporation ponds and the 12-24 months required for the inspissation process because the concentration of the lithium brine occurs inside of the membrane modules. Third, the land area required for brine concentration may be substantially reduced because the evaporation ponds are no longer needed. Fourth, MCr does not require the use of reagents or anti-solvents to recover other by-products from the lithium brine such as potassium chloride (KCl), magnesium (Mg) or sodium chloride ($NaCl$). Fifth, MCr can operate with low pressures (Lawson and Lloyd, 1996) and temperatures (Banat et al., 2002) and can therefore be integrated with low-grade waste heat sources (Guan et al., 2012; Kim et al., 2017; Lu and Chung, 2019; Ghaffour et al., 2019).

1.3 Previous Lithium LCA Literature

Previous studies and reviews (Stamp et al., 2012; Peters et al., 2017; Ambrose and Kendall, 2020; Jiang et al., 2020; Li et al., 2020; Kelly et al., 2021; Manjong et al., 2021; Sadhukhan and Christensen, 2021; Schomberg et al., 2021; Arshad et al., 2021; Lai et al. 2022; Schenker et al., 2022; Chordia et al., 2022) have tried to determine the environmental impact of lithium extraction via brine inspissation by using life cycle assessment (LCA) which is a standardized and quantitative tool used to evaluate the potential environmental impacts of a product or service. Part of the difficulty in understanding and anticipating the potential environmental impact of 'emerging technologies', as is the case with MCr, is due to the high uncertainty associated with scaling lab-scale technology to commercial scale production (Moni et al., 2020; Tsoy et al., 2020; Giesen et al., 2020). To date, only a few studies have studied the life cycle environmental impacts of various emerging technologies that could be used for lithium production which are nanofiltration (Li et al., 2020), lithium-aluminum-layered double hydroxide chloride (LDH) sorbent and forward osmosis (Huang et al., 2021), and the C3 SOLVOLi+ process developed at KU Leuven (Maria et al., 2022). However, studies exploring the LCA of MCr for lithium recovery and LCE production have yet to be conducted. Given the aforementioned benefits of MCr as a lithium recovery method, this research seeks to provide the first preliminary understanding of the potential environmental impact of producing Li_2CO_3 at a commercial scale MCr facility.

1.4 Problem Definition

Achieving decarbonization goals will require significant amounts of lithium in the coming years and it is not yet fully understood how meeting lithium demand will be accomplished or if it will be produced in a sustainable manner. It is unknown whether MCr is an environmentally preferable technology or what the trade-offs might be at commercial scale for producing Li_2CO_3. Substantial research exploring the socio-economic, environmental, political and technological implications is needed. This research seeks to address one facet of the problem by providing scientific knowledge about the environmental impact of commercial scale LCE via MCr.

1.5 Research Aims

The research aims of this study are to:

(1) Provide an overview of the known environmental impacts resulting from brine inspissation in the SdA.
(2) Provide an overview of criteria for improved lithium brine extraction technologies.
(3) Perform an ex-ante comparative LCA to examine the differences between brine inspissation and MCr.
(4) Calculate and compare the land-use intensity of brine inspissation and MCr.

Such an analysis can provide the basis for informed decision-making regarding the improvement and deployment of MCr as an alternative for brine inspissation or as a supplement to existing production capacity. This ex-ante comparative LCA can lead to new insights and can help support process engineers, chemists and other technologists in the development of the MCr technology at a commercial scale by identifying hotspots and points of improvement.

1.6 Scope

The scope of this research pertains specifically to the SdA in Chile because the research carried out by Cerda et al. (2021) and Quilaqueo (2022) exploring MCr for lithium recovery rely on brine compositions that are modeled after the SdA brine composition. Secondly, the largest brine reserves in the world are in Chile and it is sensible to assess emerging technologies within this context as this is a region that will continue to create more production capacity (AltaLey, 2022). Lastly, the brine inspissation data used for the comparison is derived from operational data of Sociedad Química y Minera de Chile SA (SQM) which is the largest producer of lithium products in Chile. Figure 1-1 below depicts a topographical map illustrating the SdA.

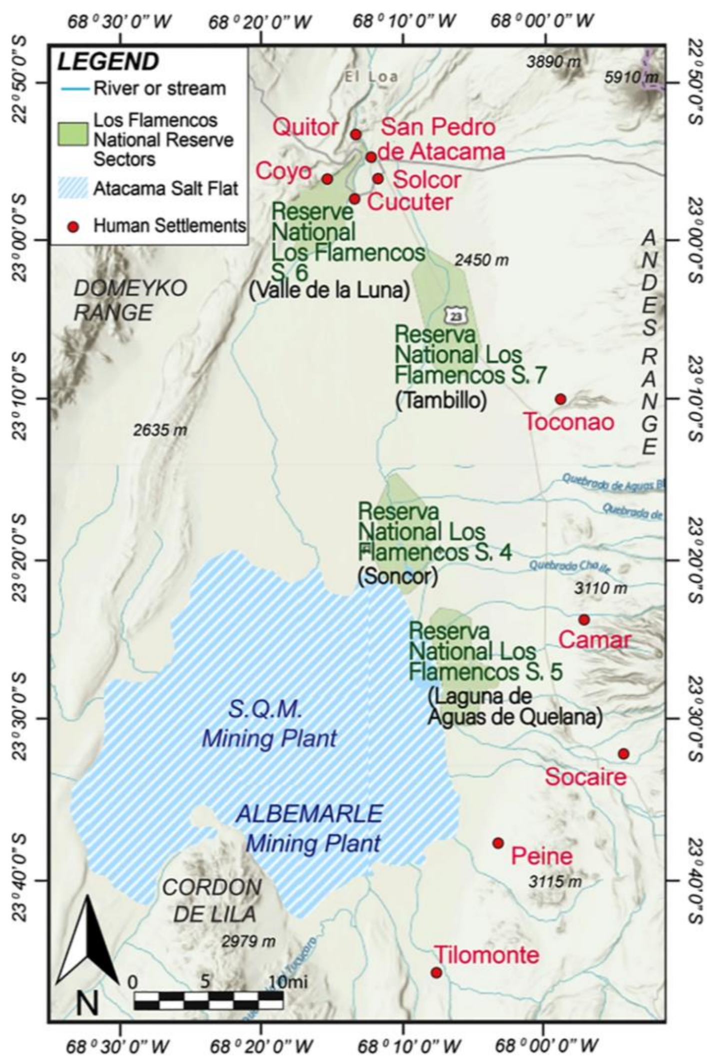


Figure 1-1: Topographical map of Salar de Atacama, adapted from Liu and Agusdinata (2019).

1.7 Research Questions

Consistent with the stated research aims and scope of this study, the following main research question and sub questions have been formulated below.

What are the potential environmental sustainability implications of producing LCE via MCr in the Salar de Atacama?

1. **What are the environmental impacts of brine inspissation in the Salar de Atacama?**
2. **What are the criteria for improved lithium brine extraction technologies?**
3. **How does a commercial MCr plant compare to a brine inspissation facility regarding environmental impacts?**

1.8 Relevance

This study is being done in collaboration with the Advanced Mining Technology Center (AMTC) in Santiago, Chile. AMTC is the main research center in Chile for the mining industry and it is also a part of the Faculty of Physical and Mathematical Sciences at the University of Chile. This study is relevant for several key reasons. First, it provides the first comparative ex-ante LCA of MCr used for lithium recovery. Secondly, it adds to the nascent and understudied domain of ex-ante LCA literature. Lastly, it advances our understanding of the potential trade-offs and limitations of MCr as an environmentally sustainable alternative for continental brine-based lithium extraction.

1.9 Research Structure

Section 1 'Introduction' provides a general overview of the societal relevance of lithium extraction and focuses on MCr as the object of study along with research questions consistent with the stated research aims. Section 2 'Theoretical Background' introduces the theoretical framework which provides the background to understand the research including an overview of LCA, ex-ante LCA, scale-ups of emerging technologies, MCr, brine inspissation and land-use intensity (LUI). Section 3 'Methodological Framework' introduces the methods used to answer the research questions which detail the scale-up process, life cycle inventories (LCI), life cycle impact assessment (LCIA) methodologies used and the approach used to calculate land use and land use intensity of producing LCE via MCr and brine inspissation. Section 4 'Results' provides the discoveries that were made following the methods used in Section 3. Section 5 'Discussion' integrates the results to answer the main research question and discuss the implications, trade-offs, main foreseen limitations and risks of the technology and finally, ideas for further research. Section 6 'Conclusion' provides a brief summary of the entire research.

2 Theoretical Background

2.1 Life Cycle Assessment

LCA methodology is a commonly used tool for industry, scientific research and policymaking to understand the potential environmental impacts that may occur throughout the entire product system life cycle. In other words, LCA assesses the potential environmental impacts that occur during the raw material acquisition, production, use phases and End-of-Life (EoL) phase of a product. In doing so, LCA provides decision-support to different stakeholders by creating an overview of potential environmental impacts which are often considered in conjunction with other strategic values that are of interest to a given stakeholder (Lindahl et al., 2014). For this reason, the decision-making context should be made clear to prevent results from being used out of context (Sandin et al., 2015). In the last two decades, the International Standards Organization has produced ISO 14040:2006 and ISO 14044:2006 (ISO, 2006a; 2006b) to provide a standardized approach and guidance for constructing LCAs. Moreover, different LCAs address different aims depending on if they are consequential, attributional, dynamic, anticipatory or ex-ante (Giesen et al., 2020). There are four main iterative phases of an LCA including (1) the goal and scope definition, (2) the life cycle inventory analysis, (3) the life cycle impact assessment and (4) the interpretation phase.

(1) Goal & Scope Definition: The goal defines the purpose of the LCA and the scope determines the functional unit that is assessed along with the system boundaries regarding spatial and temporal criteria and the methods that will be used for the impact assessment. Importantly, in comparative studies, conclusions are drawn based on measured differences observed in the same functional unit which serves as the object of study and standard from which a comparison can take place.

(2) Life Cycle Inventory Analysis (LCI): This phase gathers quantitative data about energy and material inputs, emissions, wastes and other outputs. Primary data can be obtained first-hand through interviews, surveys, experiments, questionnaires or similar means. Secondary data can be retrieved from publications, journal articles, records etc. Often times to construct an LCI, secondary data is utilized for different processes with the use of databases such as Ecoinvent.

(3) Life Cycle Impact Assessment (LCIA): The LCIA phase compiles the inventory data which is characterized by chosen impact assessment methodologies to determine their environmental significance. LCIA typically consists of the following steps: (1) selecting relevant impact categories, (2) assigning elementary flows to the impact categories (classification), (3) modeling potential impacts using characterization factors to obtain an indicator for the impact category (characterization), and finally, (4) normalization, grouping and weighting which are optional steps and depend on the goal and scope of the study (Hauschild et al., 2018).

(4) Interpretation: The final phase of the LCA is to identify potentially significant issues, and check for completeness, sensitivity and uncertainty for each of the identified issues. Significant issues are sources of uncertainty such as input parameters, unit processes or characterization factors used in the analysis that contribute to uncertainty in LCA results (Hauschild et al., 2018). Due to the nature of LCA, sensitivity and uncertainty analyses provide an important means of evaluating changes in outcomes of the system and refining results. It also involves determining whether or not the LCA phases have been designed to adequately attend to the goals defined in the goal and scope definition.

LCAs are most commonly conducted either as attributional or consequential and there are stark differences between the two. The objective of attributional LCA is to determine what environmental burdens can be attributed to a certain product or service throughout its lifecycle (Hauschild et al., 2018). The objective of consequential LCAs is to provide information about the environmental burdens that may occur, directly or indirectly, as a consequence of a decision which is usually represented as a change in demand for a product or service (Hauschild et al., 2018). The type of LCA conducted also has important implications for dealing with multifunctionality, whereby a product system creates multiple outputs. Multifunctionality poses a methodological challenge because it requires informed judgement to determine the method by which environmental burdens are attributed to different co-products. Approaches for dealing with multifunctionality follow a hierarchical approach and can be further reviewed in Schrijvers et al. (2016), Hauschild et al. (2018) and Schaubroeck et al. (2021). Further information regarding the methodology and nuances within LCA can be found in ISO (2006a), ISO (2006b), Hauschild et al. (2018), and ILCD (2010) in addition to relevant academic literature. Like any tool, there are several benefits and limitations of using LCA. The following subsection provides a brief overview of the main benefits and limitations of LCA.

2.1.1 LCA Strengths & Benefits

Life cycle thinking provides the ability to identify environmental issues that are beyond our immediate attention, which may occur in another place or another form and might therefore be ignored or devalued (Klopffer, 2014). LCA also highlights potential environmental trade-offs based on complex interactions between various systems that may be located in different regions (e.g., battery supply chains). Importantly, LCA can also challenge conventional wisdom by quantifying products or services that might have been commonly held as environmentally preferable but in fact, are worse than alternatives (Klopffer, 2014). However, although LCA provides a tool for decision-making and communication among stakeholders to improve products and services, there are several limitations that are still being addressed in the academic and professional community.

2.1.2 LCA Challenges & Limitations

Delineating the challenges and limitations of LCA is important both for practitioners and stakeholders involved in decision-making. It is also important to catalog and understand the current limitations so that future research can be targeted towards rectifying known issues. Depending on the LCA study, the nature of the challenges or limitations differ and therefore the most common limitations will be addressed. First, uncertainty plays a substantial role throughout the entire LCA process and there are several different types of uncertainty. An epistemological discussion around uncertainty can be found in Sigel et al. (2010) but for the purpose of this research, Hauschild et al. (2018) provides a useful summary of the different types of uncertainty and limitations present in LCA studies. The types of uncertainty are broadly categorized as parameter, model, scenario and relevance uncertainty.

Parameter uncertainty is constituted by the inaccuracy, lack or non-representativeness of input data and model parameters (Hauschild et al., 2018). Model or ‘structure’ uncertainty relates to the uncertainty of the setup of the model including the initial and boundary conditions defined, equations used and the variables and indicators accounted for (Hauschild et al., 2018). Scenario uncertainty pertains to uncertainty in the use and application of the model and its results under predefined conditions and assumptions which may also contribute to uncertainty in the interpretation of the model results (Hauschild et al., 2018).

Lastly, relevance uncertainty is associated with the relevance and representativeness of the indicators that are used to represent a given environmental problem (Hauschild et al., 2018). Considering the different types of uncertainty together, the uncertainty during the decision-making process is dependent not only on the variability of parameters but also how results are interpreted and whether the model is representative and complete. Importantly, there is no formal guideline or standard to explain how uncertainty should be dealt with in LCA and in many studies, uncertainty is dealt with piece-meal or not at all. However, the approach used for dealing with uncertainty and sensitivity in this research is further discussed in Section 3 'Methodological Framework'.

2.2 Ex-Ante Life Cycle Assessment

An increasing number of studies apply LCA to emerging or future technologies which is commonly referred to as prospective or ex-ante LCA (Giesen et al., 2020). Although prospective LCA and ex-ante LCA are similar, the term ex-ante LCA will be used for this research. Following the definition of Giesen et al. (2020), ex-ante refers to an LCA that is carried out 'before a product or technology is commercially deployed at scale and information about the technology under assessment is not yet available'. In contrast to conventional LCA, ex-ante LCA endeavors to study an emerging technology or product system that is at an early stage of development but is modeled at a future, more-developed stage i.e., commercial production (Arvidsson et al., 2018). The purpose of an ex-ante LCA is to help guide research and development and avoid environmental lock-in effects thereby creating an environmentally competitive technology compared to the current incumbent technology. Environmental lock-in effects occur when technology pathways embed certain designs that commit themselves to certain associated environmental impacts that are difficult to diverge from (Chester et al., 2014). Therefore, ex-ante LCA can help provide a more rigorous understanding of how emerging technology systems may affect long-term sustainability goals (Chester et al., 2014; Reyna and Chester, 2015).

2.2.1 Ex-Ante LCA Strengths & Benefits

One reason ex-ante LCAs play an important role in technology development, scale-up and environmental guidance is because they might help ameliorate the Collingridge dilemma (Collingridge, 1980). This dilemma supposes that at an early stage of technological development, ample room for alteration and control of the process exists but the knowledge about the technology is sparse however, at a later stage of development, more knowledge exists about the process but there is less room for alteration hence the lock-in effect (Arvidsson et al., 2018). Ostensibly, early stages of development can be improved with information provided by the results of an ex-ante LCA. Ex-ante LCAs are similar to conventional LCAs in that they are still composed of a goal & scope definition, a life cycle inventory, an impact assessment and an interpretation phase. However, the greatest difference associated with ex-ante LCAs is the high levels of uncertainty, lack of data availability and quality and challenges regarding comparability and scaling effects (Hetherington et al., 2014; Moni et al., 2020; van der Giesen et al., 2020; Thonemann et al., 2020). In addition, the potential environmental impacts of new technologies may not be covered by existing impact categories and there may also be an absence of specific characterization factors because many biosphere flows are left unclassified due to a lack of adequate data and modeling (Giesen et al., 2020).

2.2.2 Ex-Ante LCA Challenges & Limitations

Aside from the challenges previously mentioned, there are also some methodological differences that pose a challenge for the LCA practitioner. Ideally, the emerging technology should be modeled at a late stage of technical development to accurately reflect the technology's environmental performance at a mature stage (Arvidsson et al., 2018). Two important concepts to help describe this process are the technology readiness level (TRL) (US DOD, 2011 as cited in Arvidsson et al., 2018) and manufacturing readiness level (MRL) (US DOD, 2015 as cited in Arvidsson et al., 2018). The TRL indicates the extent to which the technology has evolved from its early stages until demonstration while MRL indicates production volumes from lab-stage (low volume) to commercial production (high volume). Additionally, a distinction can be made between intra-technology comparisons and inter-technology comparisons. Intra-technology comparisons consist of a comparison between different scenarios of one emerging technology while inter-technology comparisons delineate a comparison between an emerging technology and a conventional or incumbent technology (Thonemann et al., 2020).

An example of an inter-technology comparison would compare an emerging technology modeled at a high TRL and a conventional technology (high TRL) at a future point in time. This avoids the pitfall of comparing a lab-scale technology with low TRL with an incumbent technology with a high TRL which would not be ex-ante as it compares the status quo at different scales while neglecting technological development of the emerging technology (Thonemann et al., 2020). Therefore, the LCI foreground data of both the emerging technology and the incumbent technology should be modeled at the same TRL but importantly, the LCI background data for both product systems should also be modeled at the same TRL. This is a methodological challenge and is further described in section 2.3 Scale-Up where data scaling is discussed. Importantly, by addressing the TRL for both background and foreground data, the technological scope and temporal scope of the LCA are consistent. Moni et al. (2020) provides a useful framework for assessing the TRL and MRL of a given technology which has been adapted in Figure 3 below. In Section 3 'Methodological Framework', the TRL framework presented by Moni et al. (2020) will be used to assess the TRL and corresponding MRL of MCr for lithium recovery in addition to the TRL and MRL of lithium brine inspissation.

2.2.3 Ex-Ante LCA Problem-Solving Strategies

Perhaps the most important aspect of conducting an ex-ante LCA is to explicitly communicate the various uncertainties, assumptions and challenges encountered throughout the analysis. Doing so provides transparent information for decision-makers, technologists and future LCA practitioners which might help with future iterations of the scale-up, design and evaluation process. Moni et al. (2020) suggests some key strategies for supporting the development of an ex-ante LCA which include developing a LCI data repository for various emerging materials, processes and technologies which include uncertainty distributions, TRL and MRL indicators as well as data collection methods, assumptions and information regarding spatial and temporal variation. In addition, integrating ex-ante LCA with techno-economic analysis (TEA) allows for the simultaneous evaluation of environmental and economic performance of an emerging technology which may reduce inconsistencies which could arise when performed separately (Moni et al., 2020). However, due to time constraints of this study, a TEA will not be conducted but is recommended for future research in Section 5. The framework provided by Moni et al. (2020) in Figure 2-1 is useful for discerning what TRL and MRL a given technology under assessment may be. In this study it is used to determine the current TRL and MRL of brine inspissation and MCr as well as the future TRL and MRL that are theorized in this study.

TRL	Question to determine TRL	Technological advancement	Corresponding MRL	Available Data for LCA	Decision support from LCA	Methodological challenges of LCA of emerging technologies
TRL1: Basic principle observed and reported	Have basic principles of new technology been observed and reported and methodologies been developed for applied R&D?	Identification of scientific principles underlying potential useful technology	MRL 1: Identification of basic manufacturing implications	Published research articles or other references	Major screening (e.g., raw materials, energy mix); environmental impacts based on thermodynamic principles	Uncertain functions and system boundaries, very limited inventory data
TRL 2: Technology concept and/or application formulated	Have paper studies confirmed the feasibility of system or component application?	Identification of potential practical applications of the technology	MRL 2: Identification of new manufacturing concepts	As above	As above	As above
TRL 3: Proof of concept	Have analytical and experimental proof-of-concept of components of technology been demonstrated in a laboratory environment?	Laboratory validation of different technology components	MRL 3: Proof of manufacturing concepts through analytical or laboratory experiments	Laboratory scale data of technology components	Environmental impacts of technology components; selection from component alternatives	Systems not integrated; overall material and energy balance data is not available
TRL 4: Component and/or system validation in laboratory environment	Has performance of components and interfaces between components been demonstrated in lab environment?	Laboratory validation that all components work together	MRL 4: Production of laboratory prototype	Laboratory scale data of integrated system	Comparison between process alternatives based on mass and energy balance	Comparability, scale up issues, data and model uncertainties
TRL 5: Laboratory scale system validation in relevant environment	Have laboratory to engineering scale scale-up issues been identified and resolved?	Validation of the capability of integrated systems in simulated environment	MRL 5: Production of prototype in simulated environment	Simulation data	Selection of promising alternatives for further research and comparison with existing technologies	As above
TRL 6: Engineering/pilot scale system validation in relevant environment	Have engineering scale to full scale scale-up issues been identified and resolved?	Scale up from laboratory scale to engineering scale	MRL 6: Production of prototype system in simulated environment	Pilot scale data.	As above	As above
TRL 7: Full scale, similar system demonstrated in relevant environment	Has the actual technology been tested in relevant operational environment?	Demonstration of actual system prototype in relevant environment	MRL 7: Production of prototype in production environment	Full scale prototype testing data.	Full scale LCA results which will provide updated environmental assessment as technology maturity increases and process parameters are optimized	Scale up issues due to change in material and energy efficiency; data and model uncertainty
TRL 8: Actual system completed and qualified through test and demonstration	Has the actual technology successfully operated in a limited operational environment?	Final form of the technology and proof of applicability under expected condition	MRL 8: Ready to begin low rate initial production	Small scale production data	As above	As above
TRL 9: Actual system operated over full range of expected conditions	Has the actual technology successfully operated in the full operational environment?	Fully developed technology operated under full range of operating conditions	MRL 9: Capable to begin full rate production	Full scale production data	As above	As above
Mass production	TRL 10 does not exist.		MRL 10: Lean mass production	Mass scale production data	As above	As above

Figure 2-1: Technological Readiness Level Framework, adapted from Moni et al. (2020)

2.3 Scale-Up of Emerging Technologies

An integral part of ex-ante LCA requires the scaling of a technology to a given TRL and MRL so that it can be appropriately compared with other technologies at similar TRL and MRL. However, for emerging technologies, industrial scale data is likely non-existent and therefore data from lab-scale processes must be used which likely do not adequately represent the environmental or economic implications at commercial scale production (Shibasaki, 2007). Part of the reason for this is that there is an incongruence in data from lab-scale to commercial-scale technology which is often due to a difference in efficiencies (waste heat reutilization, reuse and recycling of raw materials, continuous vs. batch processes) as well as the types of equipment used at different scales (Moni et al., 2020). Additionally, different raw materials (reactants, solvents, eluents) may be used which could contribute to a different profile of co-product or by-product output as well as a change in emissions and waste generation (Maranghi et al., 2020).

Without commercial-scale data for the emerging technology, various approaches are utilized to model commercial-scale operational data however, a standard approach for upscaling in ex-ante LCA does not currently exist (Tsoy et al., 2020). Perhaps the most common approach to obtain LCI data is to perform process simulation and modeling using process engineering calculations which include mass and energy balances in addition to stoichiometric calculations (Morgan-Sagastume et al., 2016; Tsoy et al., 2020). Parvatker and Eckelman (2019) found that using process simulation tools for LCI data generation provides similar results compared to data from operational plants. While there are several frameworks that have been developed for scale-ups of technologies (Shibasaki, 2007; Piccinno et al., 2016; Simon et al., 2016; Villares et al., 2016; Schulze et al., 2018; Elginoz et al., 2022), the framework used by Tsoy et al. (2020) is the approach that is generally followed in this research. The decision to use the framework developed by Tsoy et al. (2020) is based on the fact that they conducted a systematic review of upscaling methods used for ex-ante LCA between 1990 and 2019 and presented a simplified framework that integrates the main characteristics of previous ex-ante LCA scale-up approaches.

The framework proposed by Tsoy et al. (2020) consists of three steps. The first step involves designing a conceptual scenario for the new technology. This may involve using predictive scenarios or scenario ranges (Arvidsson et al., 2018) or it may be developed through literature review and expert interviews depending on the goal and scope of the analysis at hand. Second, LCA and technology experts should develop a flow chart for the LCA and thirdly, data for unit processes should be estimated or modeled to generate LCIs. For this research specifically, process simulation is used because it provides the mass and energy balances for which elementary and reference flows can be established. Technical knowledge, process modeling and chemical engineering expertise is provided by the process engineering team at AMTC in Santiago, Chile. Specific details regarding the scale up process for MCr are covered in Section 3 "Methodological Framework".

2.3.1 Scale-Up Limitations

One of the limitations of most ex-ante LCA results is that most often they are not validated after the assessed technologies are created at industrial scale (Tsoy et al. 2020). Secondly, simulating a possible future commercial scale scenario involves several assumptions about the process (Piccinno et al., 2016) and also requires extensive expert knowledge about the technology that is not always readily available. For this reason, several authors (Piccinno et al. 2016; Tecchio et al. 2016; Arvidsson et al., 2018; Thonemann et al., 2020; Giesen et al., 2020; Tsoy et al., 2020) highly suggest performing sensitivity or uncertainty analyses to effectively manage uncertainty throughout the process and further understand the implications of assumptions. Lastly, it is probably preferable to assess and model the emerging technology system using conservative assumptions to ensure that the results are likely higher that what is potentially achievable, therefore assuring that known impacts are not underestimated (Piccinno et al., 2016).

2.4 Membrane Distillation Crystallization (MCr)

This section provides a brief discussion regarding the key characteristics of MCr and is divided into three sections which comprise the basics of MCr used in this research which are membrane distillation, crystallization and hollow fiber membranes.

2.4.1 Membrane Distillation

Membrane distillation crystallization (MCr) integrates MD and crystallization which can provide high-quality freshwater from the MD stage and valuable salts derived from highly saline solutions during the crystallization and settling stage (Wan Osman et al., 2022). As previously discussed in Section 1.2 'MCr Benefits', the theoretical advantages of MCr include the reduction of energy consumption, raw material use and waste emissions while simultaneously maximizing freshwater and crystal product output (Quist-Jensen et al., 2016). In addition, MCr may enhance process control while allowing for the manipulation of crystal size, shape, growth rate and purity (Balis et al., 2022) however, refining the manipulation of these variables is still under investigation.

There are several types of membranes including flat-plate, spiral-wound, multi-bore and hollow fiber membranes. The membranes can be used in different configurations depending on the application but for membrane distillation (MD) the configurations primarily include direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweep gas membrane distillation (SGMD) and vacuum membrane distillation (VMD). For this research, only DCMD will be discussed because it is the configuration used in Cerda et al. (2021) and Quilaqueo et al. (2022) which this research report is based upon, and it is also the most studied MD configuration. DCMD is a thermally driven separation process involving the transport of vapor molecules across a hydrophobic porous membrane which is positioned between a high temperature feed solution and a low temperature permeate stream. The major driving force for this process is the vapor pressure difference, $\Delta P = Pf - Pp$ resulting from a temperature difference $\Delta T = Tf - Tp$ between the feed (f) and permeate (p) streams (Yadav et al., 2022). The feed stream is also referred to as the retentate stream and the permeate stream can be referred to as the distillate stream. The properties of the membrane such as the hydrophobicity, porosity and pore size distribution substantially affect the transmembrane flux and the degree of supersaturation (Di Profio et al., 2009). During the MD stage, the feed solution becomes supersaturated due to the continuous removal of solvent via solvent evaporation across the membrane surface and the simultaneous decline in feed temperature thereby increasing the concentration of solutes in the feed (Choi et al., 2019). The supersaturated solution can then be transported to a settler or filter whereby crystallized salts precipitate. The basic mechanics of the MD process are depicted in Figure 2-2 below. Figure 2-3 below illustrates a basic process flowsheet of the MCr process.

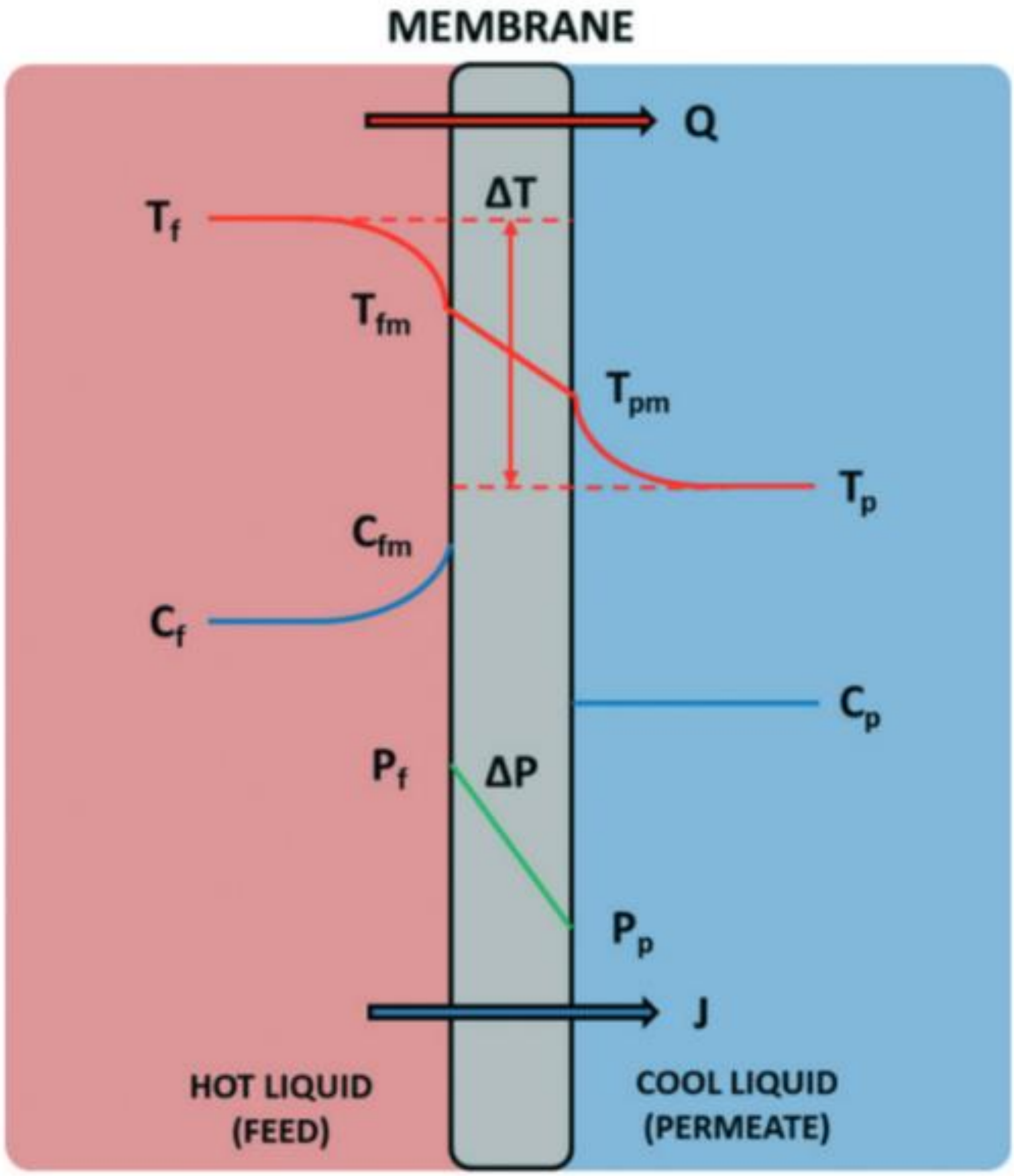


Figure 2-2: Profile of temperature, concentration and hydraulic pressure across the membrane in the DCMD process (image adapted from Choi et al. (2019). (T_f is the temperature in the feed solution, T_{fm} is the temperature on a membrane surface in the feed solution stream, T_p is the temperature in the permeate stream, T_{pm} is the temperature on the membrane surface in the permeate stream, C_f is the concentration in the feed solution stream, C_{fm} is the concentration on the membrane surface in the feed solution side, C_p is the concentration in the permeate stream, P_f is the hydraulic pressure of the feed solution, and P_p is the hydraulic pressure of the permeate).

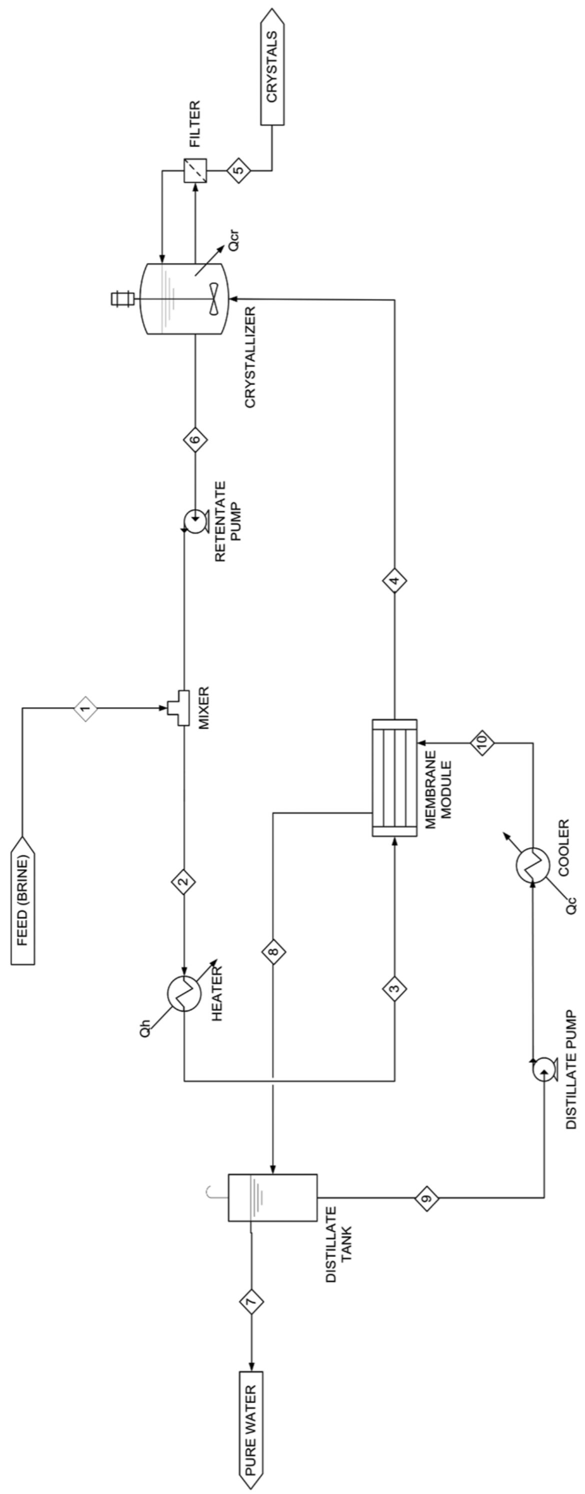


Figure 2-3: Process flowsheet of membrane distillation crystallization, adapted from Pantoja et al. (2015).

2.4.2 Crystallization

Crystallization is a fundamental process in a wide range of scientific disciplines which intersect chemistry, physics, biology, materials science and geology. Within industrial applications, crystallization is a separation and purification technique whereby a crystalline product is obtained from a solution. Crystallization is a complex process which requires several stages the first of which is supersaturation. To create a population of crystals from a solution, supersaturation must be induced as it serves as the driving force of crystallization, whereby the solute concentration exceeds the equilibrium solute concentration at a given temperature (Myerson et al., 2019). The most common methods for generating supersaturation are achieved through a temperature change (cooling), evaporation of the solvent, changing the solvent composition, inducing a chemical reaction or increasing the pressure of the solution (Myerson et al., 2019). Once supersaturation is achieved, the growth of crystals can be understood as a two-step process involving nucleation and crystal growth. Nucleation occurs when molecules dissolved within a solution begin to aggregate to relieve supersaturation and move the system back towards equilibrium which eventually leads to the formation of nuclei that act as centers of crystallization (Myerson et al., 2019). Nucleation can occur spontaneously or it can be achieved with external influences but the two primary mechanisms of nucleation are primary nucleation and secondary nucleation. The final crystal size distribution within a system is dependent upon both nucleation and the growth rate of crystals. For the purpose of this research and the complex nature of the various theories regarding nucleation and crystal growth, in depth information can be found in Byrappa and Ohachi (2002), Tung (2009), Van Driessche et al. (2017) and Myerson et al. (2019).

Importantly, MCr is unique in that the process generates a crystal slurry via solvent evaporation within the membrane modules as opposed to being generated within a separate crystallizer unit. Due to the fact that crystallization occurs within the retentate/feed stream resulting from the MD process, collecting crystallized solids is made possible with the use of gravity sedimentation using settlers, decanters, thickeners or clarifiers which rely on the gravitational force to induce the separation between crystals and the retentate solution (Tarleton and Wakeman, 2007).

2.4.3 Hollow Fiber Membranes

Hollow fiber membranes will be discussed in this section because they are the membranes used in the research by Cerda et al. (2021), Quilaqueo et al. (2022) and they are the membrane type that is modeled for process simulation in this research. Hollow fiber membrane modules are comprised of several membrane fibers which can be called fiber bundles. The fiber bundle is embedded within a tube sheet to create a barrier and allow for separate fluid communication with the fiber interior (lumen) and exterior (shell) spaces. Fluid streams can then be introduced to the lumen and shell spaces whereby volatile compounds can evaporate through the porous membranes into the shell space as permeate. A permeate sweep is also used to dramatically improve the module performance (Mat et al., 2014) and in the case of Cerda et al. (2021), the permeate sweep creates the temperature differential which allows the MD process to occur. A cut-away view of a typical hollow fiber membrane module can be seen in Figure 2-4 below.

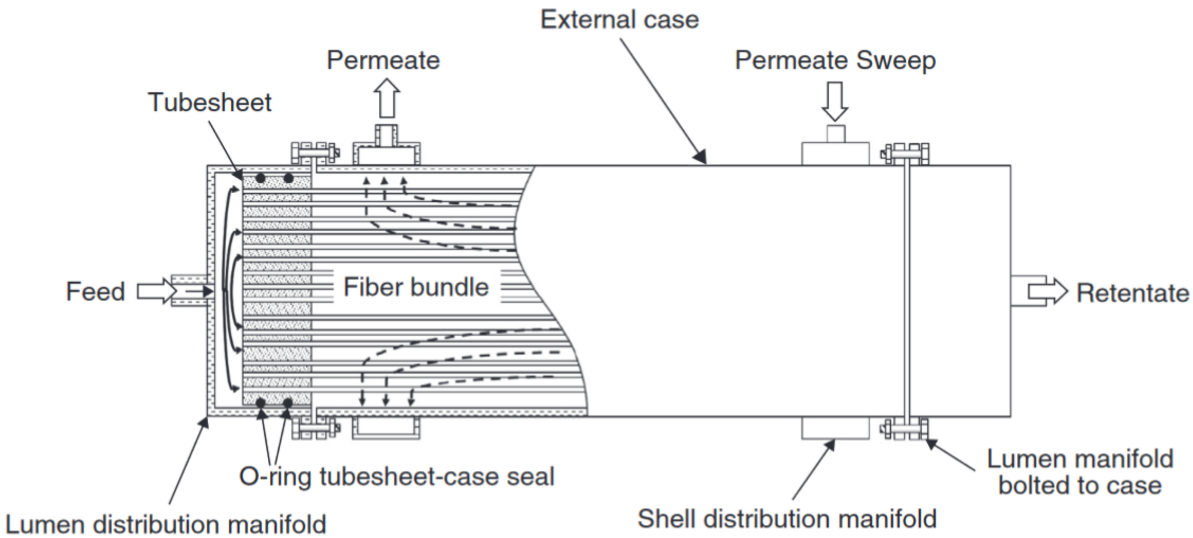


Figure 2-4: Cut-away view of a hollow fiber membrane module, adapted from Mat et al. (2014).

Hollow fiber membranes used for membrane distillation or other filtration applications are typically made of polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polypropylene (PP) or polyvinyl chloride (PVC) and an image depicting the membrane structures can be found in Figure 2-5 below. Generally, the membranes used for MCr need good mechanical performance, thermal and chemical stabilities and low resistances to mass and heat transfer (Jiang et al., 2017). However, the major limitation of membrane contactor technology is due to membrane fouling.

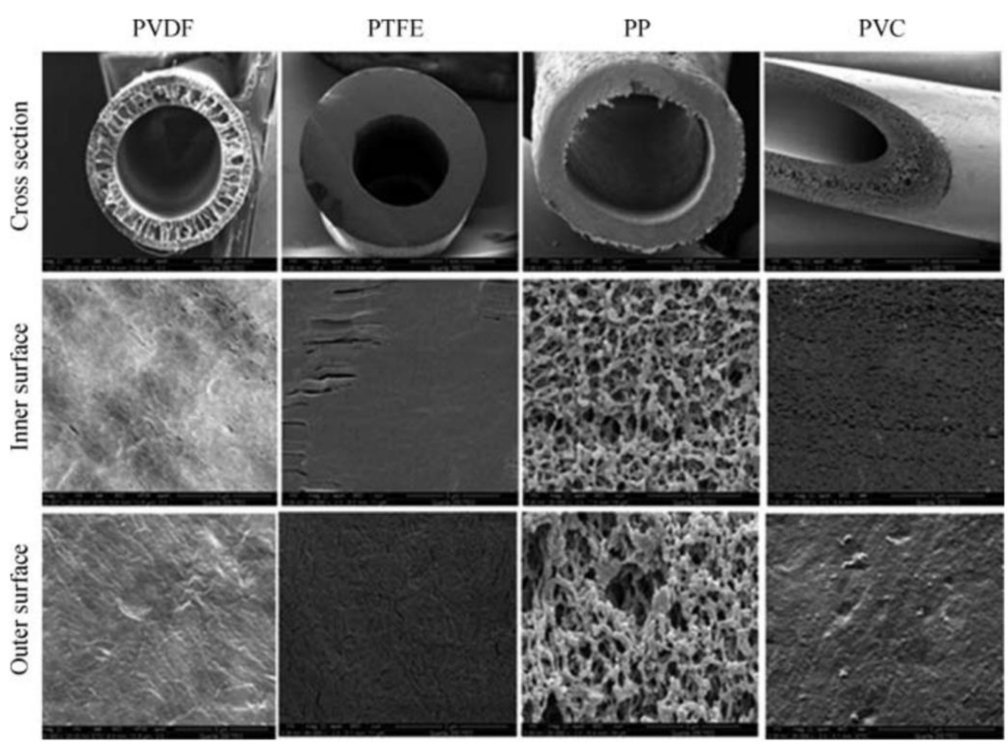


Figure 2-5: Scanning Electron Microscopy image of various hollow fiber membrane structures, adapted from Jiang et al. (2017).

2.4.4 Membrane Fouling

Membrane fouling occurs when particles, colloidal particles, or solute macromolecules are adsorbed or deposited onto the membrane surface or membrane pores by physical or chemical interactions causing the membrane pores to be blocked and therefore impinge transmembrane flux (Luo and Deng, 2019). Severe flux drops affect the quality of the MD application and can affect operational parameters of the entire process which have implications in terms of the operating cost of the membrane system, including power requirements, costs of power, labor, materials, membrane cleaning, membrane life and replacement (Bennett, 2005). Membrane foulants can be classified into four categories namely, particulates, organic, inorganic and micro-biological organisms which each pose their own challenges (Guo et al., 2012). In addition, there are six primary fouling mechanisms that have been identified which are pore blocking, cake formation, concentration polarization, organic adsorption, inorganic precipitation and biological fouling (Guo et al., 2012). Ongoing research is exploring how to mitigate membrane fouling because it is the primary barrier limiting membrane technologies from being widely adopted for commercial applications. Bagheri and Mirbagheri (2018), Nasrollahi et al. (2021) and Al Sawaftah et al. (2021) provide recent comprehensive reviews of different techniques for mitigating membrane fouling however for the purpose of this research, this phenomenon is neglected due to the difficulty of obtaining process modeling data that incorporates this behavior.

2.5 Brine Inspissation

Currently, two thirds of commercially extracted lithium originates from continental brines which are extracted via brine inspissation which is also referred to as brine evaporation. Brine inspissation is a relatively mature technology in addition to being more cost-effective (Grosjean et al. 2012) and less intensive on the environment than rock-based extraction (Jiang et al. 2020). Brine inspissation is a passive process whereby brines are first pumped out of salt flats and then held in large evaporation ponds. While in the evaporation ponds, wind and solar evaporation concentrate the brines to approximately 6000mg_{Li} L^{-1} and often include successive stages where – depending on the brine processed – other ions that did not spontaneously precipitate are removed with chemical treatments. However, current brine inspissation technology requires specific conditions that are difficult to replicate and therefore primarily occur in the Puna Plateau which comprises Bolivia, Argentina Chile as well as the Qinghai-Tibet Plateau in China. The specific conditions that are difficult to replicate yet fundamental to the process are the climatic behavior and the hydro-geological makeup of the salt flats which affect the composition of the brine, the time needed for evaporation and separation and the refining process (Baudino et al., 2022). A section of the evaporation ponds used for lithium recovery in the SdA can be seen in Figure 2-6 below.

Figure 2-6: Evaporation ponds in the Salar de Atacama (adapted from Tom Hegen, 2022).

A generalized process diagram provided by Cerda et al. (2021) in Figure 2-7 illustrates the various stages of brine inspissation that occur in the SdA. There are several ions present in the raw brine which precipitate out as different compounds with the addition of chemicals throughout the process. The specific chemicals used are provided in Section 3 when constructing the life cycle inventory analysis.

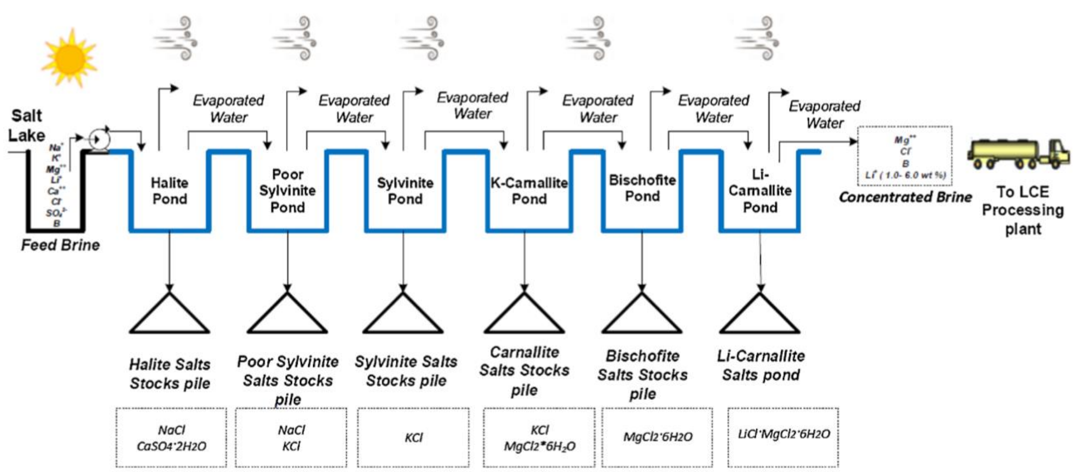


Figure 2-7: General process to concentrate raw lithium brine in the Salar de Atacama (adapted from Cerda et al., 2021).

2.6 Land Use & Land Cover Changes (LULUCC)

Changes in natural environmental conditions and anthropogenic activities affect global land use and land cover changes (LULUCC). Land cover is defined as the physical and biotic character of the land surface such as forests, water bodies, grasslands and mangroves while land use denotes anthropogenic activities which transform land cover into the built environment (Kelly-Fair et al., 2022). The exploitation of natural resources contributes to land-cover changes which can degrade ecosystems and the services that they provide (Foley et al., 2005) and can have long-term climatic impacts due to the alteration of the planet's biophysical, biogeochemical and energy exchange processes (Kelly-Fair et al., 2022). Within the context of decarbonizing our world, the increase in demand of ECEs invariably results in LULUCC as a result of mining activities that transform the land to extract minerals. Within the context of the SdA, the land use for lithium extraction via brine inspissation, shown in Figure 2-8, has expanded at an average annual rate of 7.07% from 1997-2017 (Liu and Agusdinata, 2019). With plans to increase lithium production output (SQM, 2022) there is the possibility for further increase of land use for lithium extraction operations and potential environmental impacts. Therefore, limiting or reducing the amount of land needed to produce lithium products may be an environmentally friendly alternative and can be evaluated by calculating the current land-use intensity of brine inspissation operations and comparing it with the expected land use intensity of a commercial MCr facility and processing plant. Importantly, increased land-use intensity is not always a net benefit (Felipe-Lucia et al., 2020) but in the context of land use in the SdA, identifying the current LUI of brine inspissation compared to MCr may be valuable for future research.

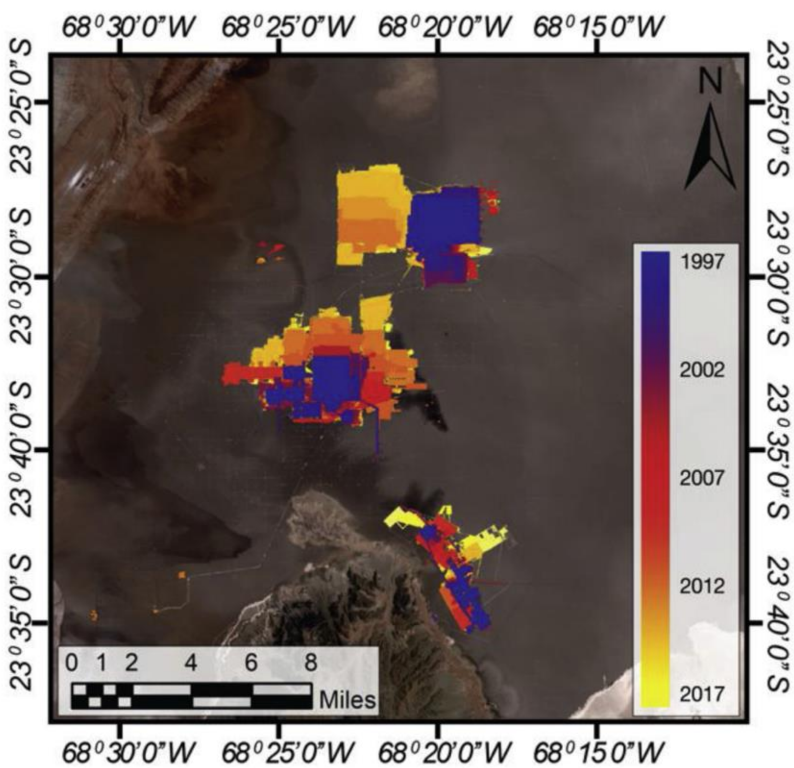


Figure 2-8: Spatial map of lithium extraction land use increase from 1997-2017 (adapted from Liu and Agusdinata, 2019).

3 Methodological Framework

Section 3 'Methodological Framework' is divided into four sections which each correspond to the 3 sub-research questions. Section 3.1 'SdA Brine Inspissation Environmental Impacts' discusses the method used to answer sub-research question 1 by using a narrative literature review to provide a succinct understanding of the currently known environmental impacts due to brine extraction in the SdA. Section 3.2 'Improved Lithium Technologies Criteria' also uses a narrative literature review to determine the most salient criteria for which new lithium extraction technologies should aim to improve. Section 3.3 'Potential Environmental Impacts of MCr' discusses the methodological approach used for the scale up process and the ex-ante LCA. Section 3.4 'Land Area & Land Use Intensity' discusses the methodological approach used to (1) calculate the land area used for current brine inspissation and processing facilities in the SdA (2) calculate the land-use intensity (LUI) of current brine inspissation and processing facilities (3) calculate the land area needed to supply the MCr facility with solar photovoltaic (PV) energy and (4) calculate the theoretical LUI of the MCr plant and processing facility.

3.1 SdA Brine Inspissation Environmental Impacts

3.1.1 Narrative Literature Review Methodology

Assessing the environmental impacts of brine inspissation in the SdA was accomplished using a narrative literature review. A narrative literature review aims to assess what has been already published and also seeks to identify new study areas not already addressed (Ferrari, 2015). While PRISMA (Preferred Reporting Items for Systematic Reviews and Meta-Analyses) provides reporting guidelines for systematic literature reviews (SLRs), no codified guidelines exist for narrative literature reviews (Ferrari, 2015).

3.1.1.1 Limitations of Narrative Literature Reviews

Tranfield et al. (2003) suggests that because of the informality, implicit biases of the author are difficult to avoid. Additionally, Snyder (2019) suggests that narrative reviews can lack thoroughness and systematicity due to selective assumptions of the author. While these are important considerations, for the purpose and goal of this research, the narrative review has been chosen based on a preliminary search that revealed a relatively small body of articles that fit the criteria needed for this research. The selection criteria of this research will be elaborated upon in Section 3.1.2.

3.1.1.2 Search Terms

The literature search strategy that was used for this narrative review aimed to gather articles focusing on the environmental impacts in the SdA or near the SdA that were attributable to lithium brine extraction, inspissation and processing. The databases that were searched were Scopus and Google Scholar with the date filter set to 2000 to 2022 and articles could be in English and Spanish. Concepts included in the search are provided in Table 3-1 below.

Table 3-1: Search terms used for narrative review of environmental impacts related to lithium extraction in the SdA.

Lithium mining impacts Salar de Atacama	*Lithium evaporation ponds environmental impacts Salar de Atacama*	*Lithium mining impacts Salar de Atacama*	*Lithium evaporation ponds environmental impacts Salar de Atacama*
Lithium mining environmental impacts Salar de Atacama	*Lithium industry environmental impacts Chile*	*Lithium mining environmental impacts Salar de Atacama*	*Lithium industry environmental impacts Chile*
Lithium mining environmental damage Salar de Atacama	*Lithium industry environmental impacts Salar de Atacama*	*Lithium mining environmental damage Salar de Atacama*	*Lithium industry environmental impacts Salar de Atacama*
Lithium extraction impacts Salar de Atacama	*Lithium Extraction LCA*	*Lithium extraction impacts Salar de Atacama*	*Lithium Extraction LCA*

3.1.1.3 Selection Criteria

The selection criteria for literature that constitutes the narrative review are articles that specifically discuss and provide qualitative and quantitative peer-reviewed evidence of environmental impacts are attributable to lithium extraction from the SdA. First, articles with titles that included at least some or all of the keywords listed in Table 1 were collected. Afterwards, article abstract and conclusion sections were read to ensure the articles pertained to environmental impacts of lithium extraction in the SdA. Of the articles that met those criteria, they were cataloged, read and critically examined to gather information which met the overarching selection criteria. In addition, the reference lists of articles that met the overarching selection criteria were also read to further obtain information about the known environmental impacts of lithium extraction in the SdA. The selected articles constitute the narrative review and provides a current and succinct understanding of the known environmental impacts in the SdA related to lithium extraction.

3.2 Criteria for Improved Lithium Extraction Technologies

A narrative literature review was also used to identify the criteria for improved lithium extraction technologies specifically as they relate to lithium rich brine sources.

3.2.1 Search Terms

The literature search strategy that was used for this narrative review aimed to gather articles focusing on discussions regarding improved lithium extraction techniques from brine and the criteria upon which they are measured as improvements. Although the aim of this research is to evaluate the potential environmental impact of MCr, addressing the potential trade-offs or burden shifts of different lithium extraction techniques from brine should be well understood. The databases that were searched were Scopus and Google Scholar with the date filter set to 2000 to 2022 and articles were in English. Concepts included in the search are provided in Table 3-2.

Table 3-2: Search terms used for narrative review of improved lithium brine extraction technology criteria.

Improved lithium brine extraction technologies	Advances in lithium brine extraction technologies	Sustainable lithium brine extraction technologies	Emerging technologies for lithium brine extraction
Efficient lithium brine extraction technologies	Green technologies for lithium brine extraction	New lithium brine extraction technologies	Future lithium brine extraction technologies

3.2.2 Selection Criteria

The selection criteria for literature that constitutes the narrative review are articles that specifically discuss and provide qualitative and quantitative peer-reviewed evidence or theories of improved lithium brine extraction techniques. First, articles with titles that included at least some or all of the keywords listed in Table 2 were collected. Afterwards, article abstract and conclusion sections were read to ensure the articles pertained to discussions regarding improved lithium brine extraction technologies. Of the articles that met those criteria, they were cataloged, read and critically examined to gather information which met the overarching selection criteria. In addition, the reference lists of articles that met the overarching selection criteria were also read to further obtain information regarding improved lithium brine extraction technologies. The selected articles constitute the narrative review and provides a current and succinct understanding of the main criteria upon which improved lithium brine extraction techniques can be measured or theorized.

3.3 Potential Environmental Impacts of MCr

This section describes the methodological steps taken to identify the potential environmental impacts of using MCr for lithium brine concentration coupled with the lithium carbonation process. Section 3.3.1 discusses the scale-up process that was used to generate the mass and energy balance of a commercial scale MCr plant and provides the LCI of producing 1 ton of concentrated lithium brine using MCr. Section 3.3.2 provides the methodological approach for the ex-ante comparative LCA. Section 3.3.3 discusses the methodological approach used to determine the land use intensity of current lithium brine extraction operations in the SdA as well as the approach used to determine the potential land use intensity of a commercial scale MCr operation powered by solar photovoltaic energy.

3.3.1 MCr Scale-Up

This section discusses the methods used to construct a reasonable scale-up scenario which generally follows the framework proposed by Tsoy et al. (2020). The first step involves designing a conceptual scenario for the new technology which is detailed in Section 3.3.1.1. The second step was to develop an LCA flowchart. The third step involved process modeling to determine the energy and mass balance for the entire plant based on the scenario defined in Section 3.3.1.1 as well as the LCI for producing 1 ton of concentrated lithium brine. Important assumptions and limitations are discussed throughout each subsection.

3.3.1.1.1 Technological Consistency

As previously discussed in Section 2.2.2, scale-ups used for LCA benefit from clearly indicating the current TRL and MRL of the technologies being compared as well as the future scenario TRL and MRL at which they will be compared. Additionally, the background and foreground datasets should be temporally, geographically and technologically consistent as possible. Therefore, the first step was to determine the current TRL and MRL of MCr technology for lithium brine concentration. Based off of the framework presented in Figure 2 by Moni et al. (2020), MCr for lithium recovery is currently at a TRL and MRL of 5. The TRL and MRL of 5 is based on the fact that there is ‘laboratory scale system validation in a relevant environment’ as shown in Cerda et al. (2021) and Quilaqueo et al. (2022), and there is a ‘production of prototype in a simulated environment’ with simulation data which has been gathered during this research from AMTC. To appropriately compare MCr and brine inspissation, they must both be compared at the same TRL and MRL. Brine inspissation is already at the highest TRL which corresponds to an MRL of 10 because it is characterized by ‘lean mass production’. Therefore, the MCr scenario must be constructed to be equivalent to MRL 10.

Temporal Consistency

Providing the temporal consistency between the two product systems is important because they are both modeled at a future point in time. Since a dramatic increase in production is needed before 2030 (AltaLey, 2022; McKinsey, 2022) and all of the necessary planning, validation, permitting, construction and production take significant amounts of time, the chosen operational year is 2027, five years from now. The brine inspissation and processing facilities are already constructed and scheduled to expand in the coming years with output steadily increasing (SQM, 2022). To account for the temporal change in the ex-ante LCA, the electricity mix was modeled based on Chilean government reports which aim to have 70% renewable energy in their electricity mix by 2030 (International Trade Administration, 2022). While there are several other considerations for foreground and background system changes in 2027-2030, due to the time constraints and difficulty of obtaining such data, only the change in electricity mix is accounted for.

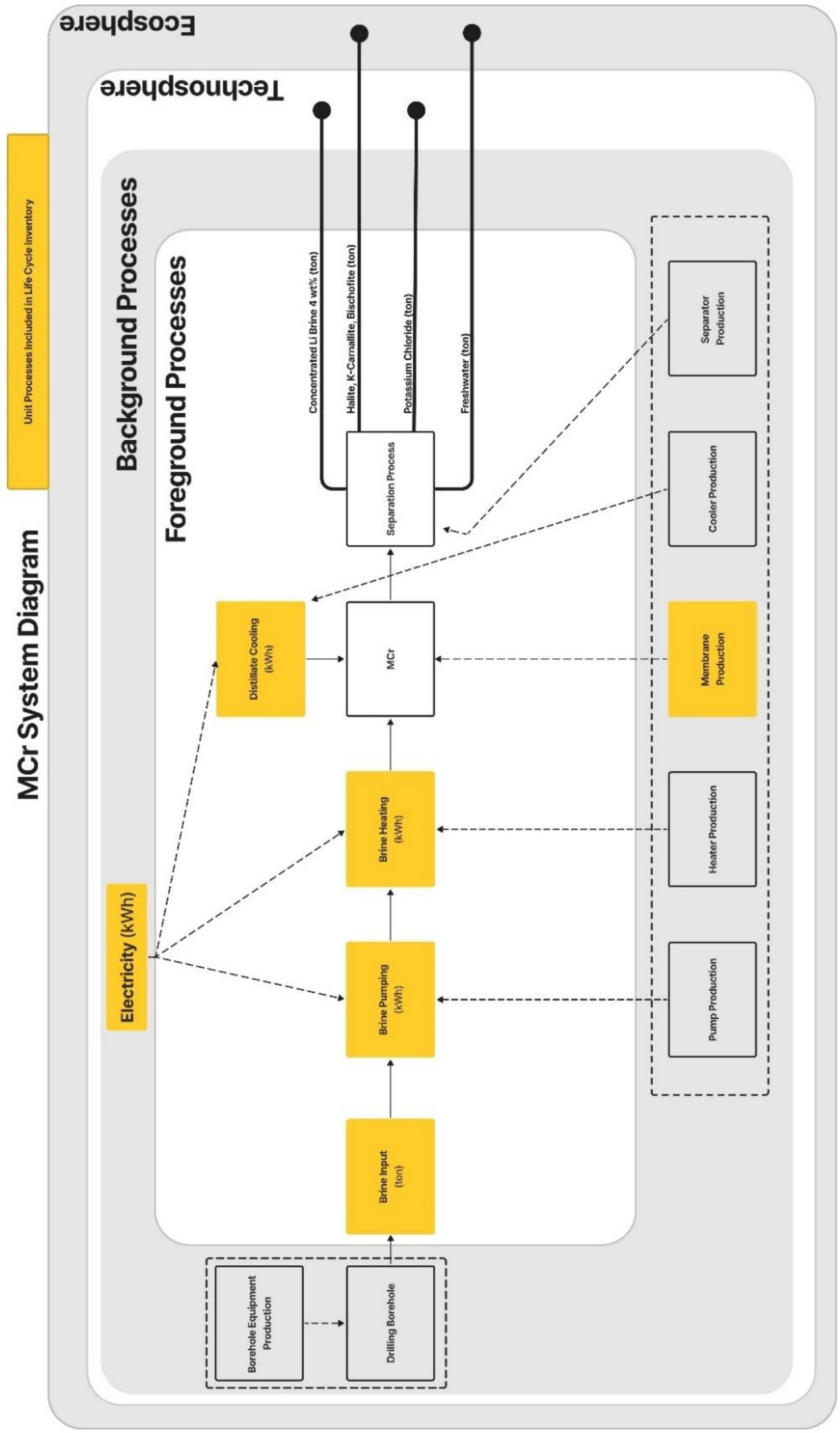
3.3.1.2 Conceptual MCr Commercial Plant Scenario

To construct the scenario, several assumptions and choices were made. The most important assumption that was made was that the MCr plant would operate without major challenges related to membrane fouling or the feasibility of mass production however in reality, these are challenges that still need to be resolved. The second assumption made pertains to the capacity of the MCr facility which is reflected in the chosen raw brine input flow rate for the MCr plant. An input flow rate of 1000 kg/s of raw brine was chosen based on the fact that the environmental permits currently allocated to SQM and Albemarle for brine pumping are 1600 L/s and 442 L/s, respectively (AltaLey, 2022). An input flow rate of 1000 kg/s was chosen for the MCr plant due to the fact that pumping at the same rate as SQM is likely unfeasible due to the precariousness of water and brine extraction in the SdA and because the MCr facility is meant to be a supplement to existing production and not a complete substitute.

There were several other assumptions that were made for the scenario which will be elaborated upon for transparency of this research. Besides the absence of membrane fouling modeling, the construction of the MCr facility infrastructure was not accounted for which includes among other things, the pumping equipment, pipes, valves, holding tanks, gravitational settlers, lighting, electrical equipment etc. However, because membranes play a central role in the technology and their environmental impact from manufacturing is not insignificant (Yadav et al., 2022), an estimate of their contribution to the LCA impacts is accounted for in the LCI. Additionally, the constructed scenario also supposes that the MCr plant which would be built in the SdA would also include a Li_2CO_3 processing facility alongside it. The construction and operation of the processing facility is also not accounted for but since it would be next to the MCr facility, transportation is considered negligible.

Importantly, potassium chloride (KCl) is a co-product during the MCr process but it cannot be subdivided due to the nature of the process and therefore to deal with this in the LCA, system expansion is used. Furthermore, the remaining solutes that precipitate as by products include the crystals halite (NaCl), K-Carnallite ($KMgCl_26H_2O$) and bischofite ($MgCl_26H_2O$) which are treated as waste. The software application Figma was used to illustrate the LCA flowchart which represents the MCr process and system boundaries and is provided in Figure 3-1 below. The unit process 'MCr' and 'Separation Process' on the flowchart are not included in the life cycle inventory because during those processes, brine is flowing through the membranes and crystallizing which do not require inputs but are nonetheless a unit process. During the separation process, gravity is used to separate the component crystals and concentrated brine and although it may require inputs or electricity, they were not modeled by AMTC.

Figure 3-1: System diagram of MCr process for ex-ante LCA.



3.3.1.3 Mass and Energy Balance of MCr

The model was developed by the process development team of AMTC, University of Chile. In addition to the assumptions and constraints previously mentioned, the modeling of the MCr process depended on the composition of the input brine (Appendix 8.1) modeled after the composition used in the study by Cerda et al. (2021) and acutely reflects the native brine composition at the SdA. The model was also constrained by the input parameters for the membrane modules which are represented in Appendix 8.2. In addition, the default transmembrane flux was set at 2.5 kg/m^2/hr. The capacity factor of the plant was also assumed to be 70%. There were also several electrical efficiencies and a coefficient of performance assumed in the model to account for brine heating, pumping and distillate cooling which are provided in the Appendix 8.3.

To simulate water recovery and crystal formation in realistic conditions, the model was based on a configuration of multiple membrane modules in series with stages in series. The multiple stages indicate that there is consecutive heating of the brine flow because after passing through membrane modules, the brine temperature decreases due to conductive heat losses between the cold permeate/distillate side and the hot brine feed side in each membrane module. Several mathematical expressions were programmed in the software MATLAB and implemented using numerical solver to simulate the entire MCr process to obtain results including water recovery, temperatures, mass of crystals, and required electrical energy needed for the pumping, heating and cooling processes of the entire commercial scale process.

The module is assumed to be a steady state process of two phases with transfer of mass and energy. The main equations used in the process modeling are shown in Table 3-3 below. The equations listed correspond to the mass and energy transfer diagram shown in Figure 3-2 and Table 3-4 below.

Table 3-3: Equations used by AMTC for the mass and energy balances of MCr scale-up.

Mass Balance	Energy Balance	Heat Transfer
$F_2 = F_1 + F_w$ $F_W = F_1 \cdot (1 - \sum \boldsymbol{w}_1) \cdot \frac{\%Rec}{100}$ $F_3 + F_w = F_4$	$F_1 \cdot cp_b \cdot T_1 = F_2 \cdot cp_b \cdot T_2 + Q$ $F_4 \cdot cp_w \cdot T_4 + Q = F_3 \cdot cp_w \cdot T_3$	$Q = \frac{Q_{ev} - \phi \cdot Q_{ev}}{\phi} + F_w \cdot H$ $H = 1.7535 \cdot T_{avg} + 2024.3$ $T_{avg} = \frac{(T_2 - T_3) - (T_1 - T_4)}{\mathrm{Ln}\frac{T_2 - T_3}{T_1 - T_4}}$
Other	1.7535 (heat capacity of water vapor)	2024.3 (enthalpy of water vapor)

Figure 3-2: Mass & Energy balance diagram corresponding to Table 3-3 and Table 3-4.

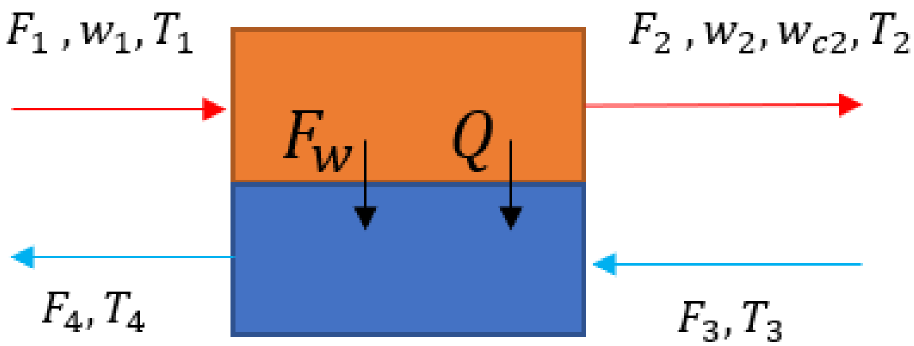


Table 3-4: Description of different variables in mass and energy balance modeling.

Variable	Description	Subindex	Description	Ions	Crystals
F	Mass Flow	*1*	Inlet Brine	Na+	NaCl
w	Vector of ions	*2*	Outlet Brine	K+	KCl
w_c	Vector of crystals	*3*	Inlet Distillate	Mg+2	KMgCl3· 6H2O
T	Temperature	*4*	Outlet Distillate	Li+	MgCl2 · 6H2O
Q	Heat Transfer	*w*	Water	Cl-	LiCl · MgCl2·7H2O
cp	Heat capacity	*b*	Brine		
ϕ	Thermal Efficiency	*avg*	Average		

The formation of crystals was estimated according to the saturation index (SI) of each crystal component according to the following expressions in Table 3-5 which were used to obtain the ion activities as a function of the brine concentration and temperature. The saturation index is used to determine if the conditions are appropriate for each crystal formation and if the SI is greater than zero, the respective aqueous ions will assemble themselves into crystals.

Table 3-5: Equations used to model crystal formation.

Saturation Index	Ionic Activity Product	Constant Solubility Product
$SI = \log \frac{IAP}{K_{sp}}$	$IAP = \frac{\prod_i a_P^i}{\prod_j a_R^j}$	$K_{sp} = K_{sp_0} \cdot \exp\left(\frac{\Delta H_{rx}}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right)\right)$

The following section presents the results of the model including the input and output parameters on an annual basis. The choice to present the results of the scale up in this section is based on the fact that they are used in the ex-ante LCA methodological section and providing them after the methodological section would interrupt the flow of the report.

3.3.1.4 Annual MCr Operational Parameters

Table 3-8 on the following page illustrates the annual inputs and outputs of a commercial scale MCr plant. The Li_2CO_3 equivalent output was calculated based on the mass composition of Li_2CO_3 and the concentration of the lithium brine output which is 4 wt. %. Importantly, the energy consumption of producing Li_2CO_3 is not included in Table 3-8 because that data is part of the Kelly et al. (2021) dataset which the MCr brine is used in, however that energy usage is accounted for in the LCA. Building on the assumption that 4 tons of raw brine at a Li concentration of 5-6 wt. % are needed to produce 1 ton of Li_2CO_3 according to the LCI dataset of Kelly et al. (2021), it is likely that more brine with less concentration would be needed to produce 1 ton of Li_2CO_3. To calculate this the mass percent composition of Li_2CO_3 was calculated in Table 3-6 and the percentage of lithium in Li_2CO_3 was divided by the weight percentage of Li in the output brine and shown below:

$$\frac{\%\,Li\ per\ Li2CO3}{Weight\ Percentage\ Li\ in\ Brine} = \frac{.188}{.04} = 4.697$$

Table 3-6: Mass Percent Composition of Li_2CO_3

Mass Percent Composition of Li_2CO_3	Atoms	Mass (g)	Total Mass (g)	%
Lithium	2	6.941	13.882	18.79
Carbon	1	12.011	12.011	16.26
Oxygen	3	15.999	49.997	64.96
Total			73.89	100

Table 3-7 shows the relative proportion of brine needed to produce 1 ton of Li_2CO_3 depending on the brine concentration.

Table 3-7: Proportion of brine needed depending on concentration.

Technology	Brine Concentration	Required input (tons)	Li_2CO_3 (ton)
Brine Inspissation	5-6 wt. %	4	1
MCr	4 wt. %	4.697	1

Table 3-8: Annual Mass & Energy Balance of Commercial Scale MCr Facility.

Annual Mass & Energy Balance of MCr Facility		
Inputs	**Unit**	**Value**
Aqueous		
Raw Brine	Mton/year	22.08
Energy		
Brine Pumping	TWh/year	0.1
Distillate Cooling	TWh/year	1.81
Brine Heating	TWh/year	3.51
Total Energy	TWh/year	5.42
Outputs		
Crystals		
Halite Crystal (NaCl)	Mton/year	4.14
Sylvinite Crystal (KCl)	Mton/year	0.76
K-Carnallite Crystal ($KMgCl_26H_2O$)	Mton/year	0.23
Bischofite Crystal ($MgCl_26H_2O$)	Mton/year	0.74
Aqueous		
Freshwater	Mton/year	14.13
Concentrated Brine 4% wt.	Mton/year	0.61
Other		
Membrane Modules	-	46,080
Lithium Recovery Efficiency	%	74.7
Water Recovery Efficiency	%	64
Li_2CO_3 Equivalent	Mton/year	0.1

Table 3-9 below provides the basis of the LCI for producing 1 ton of lithium brine via MCr. The weight of the solutes contained in the brine were calculated based on the brine composition in Appendix 8.1 and the input of raw brine calculated by the model. Importantly, this table does not represent the exact inputs and outputs that are used in Simapro because it does not include the type of electricity used or the inputs of the membrane material used in the process. The LCIs that are used for the ex-ante LCA are provided in Section 3.4.4.

Table 3-9: Scaled LCI values derived from annual mass & energy balance.

* Indicates part of the raw brine, which together replace the 'raw brine' flow		
Product Material Input	**Normalized to 1 ton Brine**	**Unit**
Raw Brine	3.63E+01	t
Sodium*	2.77E+00	t
Potassium*	7.70E-01	t
Lithium*	5.40E-02	t
Magnesium*	3.48E-01	t
Calcium*	0.00E+00	t
Sulfate*	0.00E+00	t
Chlorine*	5.79E+00	t
Boron*	2.10E-02	t
Water Content in Brine*	2.43E+01	m3
Energy Input		
Brine Pumping	169.86	kWh
Distillate Cooling	2964.91	kWh
Brine Heating	5769.43	kWh
Output		
Concentrated Brine 4 wt. %	1.00E+00	t
Freshwater	2.32E+01	t
Halite Crystal Output (NaCl)	6.8E+00	t
Sylvinite Crystal Output (KCl)	1.24E+03	t
K-Carnallite Crystal Output (KMgCl26H20)	3.80E-1	t
Bischofite Crystal Output (MgCl26H20)	1.22E+00	t

3.4 Ex-Ante Comparative Life Cycle Assessment

This section discusses several steps included in the methodological approach for the ex-ante comparative LCA including the goal and scope definition, the life cycle inventory analysis of the two product systems, the impact assessment methodologies used, and the interpretation stage which deals with the sensitivity analysis.

3.4.1 Goal Definition

The goal of this study is to compare the potential environmental impacts associated with producing the functional unit of 1 ton of Li_2CO_3 via MCr and via brine inspissation. Although it is advised to refrain from using only a quantity as a functional unit, 1 ton of Li_2CO_3 is molecularly the same as another ton of lithium carbonate assuming their purities are the same, which is likely given that they are processed to be inputs into lithium battery production and other end-uses. This study provides a comparison between a theoretical commercial scale MCr plant which produces lithium rich brine concentrated to 4 wt. % coupled with a processing facility and the traditional brine inspissation process which concentrates lithium brine between 5 and 6 wt. %, also coupled with a processing facility. While the brines themselves could serve as a functional unit, in both cases they differ in concentration potential, and so the functional unit of Li_2CO_3 is chosen which allows for a more practical comparison because ultimately, LCE products are the main products in the worldwide market and not concentrated lithium brines. The reason this study is being conducted is because it may provide micro-level decision support for process engineers, chemical engineers and other technologists to improve the MCr process in terms of what may be environmentally preferable. The additional target audience of this study includes academics, LCA practitioners and technologists within the lithium extraction industry. While AMTC participates in the study to provide process data for the scale-up it was not explicitly commissioned by them. Furthermore, this study will not be disclosed to the public as it will not undergo a third-party independent review.

The standardized methodological approach for this LCA uses the ISO 14040 (2006) and ISO 14044 (2006) guidelines. This study also draws on recommendations and methodological tips found in Hauschild et al. (2018). The LCA process was assisted by the software SimaPro 9.2.0.2 which utilized the Ecoinvent v3 database and the Environmental Footprint 3.0 (EF) Impact Assessment Methodology. The specific midpoint categories that were chosen for this research are global warming potential, acidification, water use, resource use (metals and minerals) and cumulative energy demand (CED). These midpoint categories are focused on because it is expected that the global warming potentials of the two different brine concentration routes will vary significantly due to the fact that brine inspissation relies mainly on solar energy to evaporate and concentrate the brine whereas MCr relies heavily on electricity used for pumping, heating and cooling throughout the process. Water use is focused on because of the stark differences in water recovery expected between the two technologies, due to the fact that MCr has the potential to recover a significant amount of freshwater while brine inspissation is unable to recover freshwater. Resource depletion is considered because both technologies extract significant resources from the SdA and elsewhere to process Li_2CO_3. Acidification is measured because the use of chemicals in the technologies could have the potential to pose an adverse environmental impact. Other midpoint indicators found in EF were omitted so that the key midpoint categories that are anticipated to be important are focused on. Lastly, to assess the land use and land use intensity, a different methodological approach was used which is discussed in Section 3.5.

3.4.2 Scope Definition

The scope of this study can be subdivided into the geographic, temporal and technological scope. Handling of multifunctional processes will also be discussed.

3.4.2.1 Geographic Scope

The geographic scope of this study applies to the SdA located in northern Chile and depicted in Figure X. In the SdA the brine is extracted and concentrated, either through the evaporative process during brine inspissation or in the case of MCr, the brine is extracted and then concentrated in the membrane modules. As previously discussed, brine from the inspissation process is transferred to a processing facility near Antofagasta. Based on the MCr scenario described in the previous section, the processing facility would also be constructed next to the MCr facility within the SdA, to minimize transportation impacts.

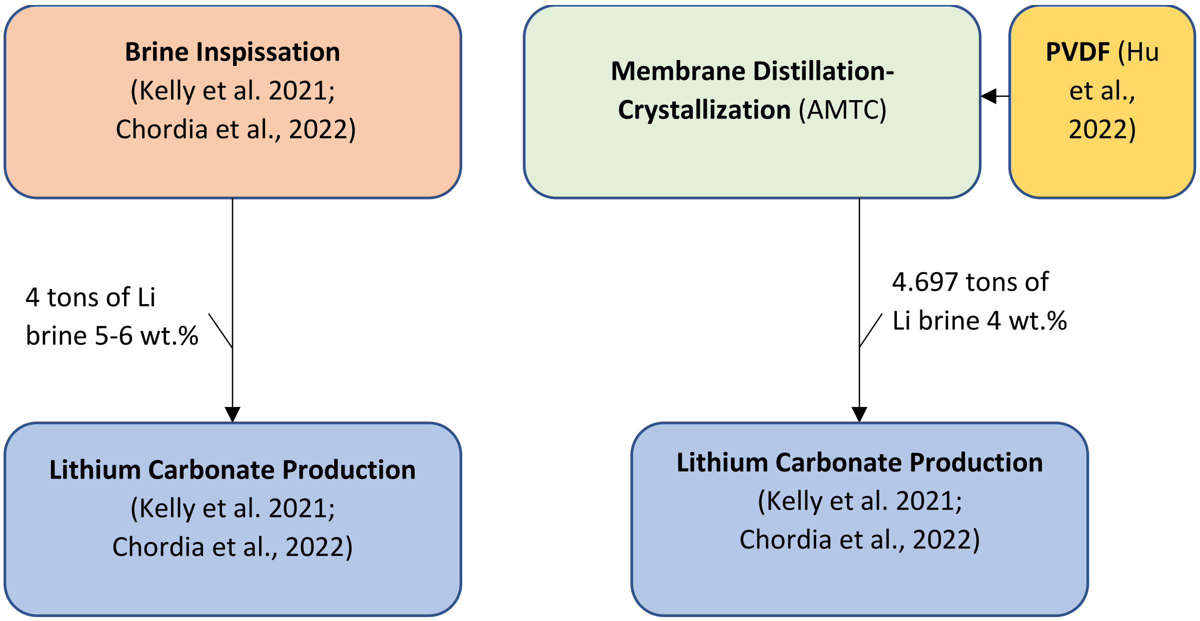
3.4.2.2 Temporal Scope

The temporal scope of this study is particularly important due to the nature of an ex-ante LCA study. As previously discussed, the MCr scenario operates in year 2027, and the brine inspissation process is also compared in the same year. It is exceedingly difficult to obtain industry datasets of lithium extraction due to the proprietary nature of their businesses. However, the datasets that are used are retrieved from the most recent academic LCA studies by Kelly et al. (2021) and Chordia et al. (2022) in addition to the data gathered from AMTC for the scale-up. These datasets are explained further in Section 3.4.3.

3.4.2.3 Technological Scope

Two different technologies can produce two identical products despite being associated with different sets of unit processes and related flows (Hauschild et al., 2018). In this research, the two main technologies under study are the brine inspissation process and the MCr process, both of which concentrate brine to slightly different concentrations. These concentrated brines are the input to the next process which is the Li_2CO_3 production process. Due to the fact that Ecoinvent's data for brine inspissation and lithium carbonate production are 10 years outdated, the dataset provided by Kelly et al. (2021) and further adapted by Chordia et al. (2022) for Li_2CO_3 production is the dataset used. The figure below shows how the different datasets are used with each other. In addition, the dataset by Hu et al. (2022) for the manufacturing of PVDF. The reason to include PVDF in the MCr LCI is because it is used throughout the lifetime of the plant, serves as the basis of the technology and may have considerable environmental impacts (Yadav et al., 2022). Figure 3-3 illustrates the datasets that were linked for this research.

Figure 3-3: Linking of datasets that were used for the LCA.



3.4.2.4 Multifunctionality

Both MCr and brine inspissation produce potassium chloride (KCl) as a co-product however, the two technologies are different and Kelly et al. (2021) handled multifunctionality by subdividing the process into lithium brine production and potash production. Therefore, the unit process data for producing lithium brine from Kelly et al. (2021) attributes all environmental burdens to the lithium brine production because the potash production was subdivided out. However, with MCr technology, the process cannot be subdivided due to the nature of the technology and although system expansion would be used if subdivision is not possible, the choice was made to allocate all environmental burdens during the MCr process to lithium brine concentration.

3.4.3 Life Cycle Inventory Analysis

This section describes the LCI analysis divided into three sections. The first section discusses the LCI for producing brine via MCr and the different methods used model the electricity mix and account for membrane module impacts. The second section discusses the LCI for brine inspissation and the third section discusses the LCI for Li_2CO_3 processing which both brine inspissation and MCr feed into.

3.4.4 MCr

3.4.4.1 Electricity Mix

Since the electricity mix is forecasted to be 70% renewable by 2030, the electricity mix used for the background process was remodeled based on the market mix for electricity in Chile and is used for the 2027 scenario. This was decided because the current electricity market mix in Chile is based off of 2017 data and would therefore not be representative of a 2027 scenario. The process of relinking the remodeled electricity market mix is shown in Figure 3-4 below. The high voltage mix was remodeled to be composed of 70% renewable energy sources which were divided between wind, solar and hydro. The LCI dataset for the original high voltage mix is provided in Appendix 8.4. The remodeled 70% mix is provided in Table 3-10 below. Importantly, most data needed for the Chilean electricity mix was not available for Chile specifically, so {RoW} and {GLO} data was used, which is also what is used in the original Ecoinvent process and therefore may not be entirely representative of Chile.

Figure 3-4: Diagram illustrating how Chilean electricity mix was re-modeled for 2030.

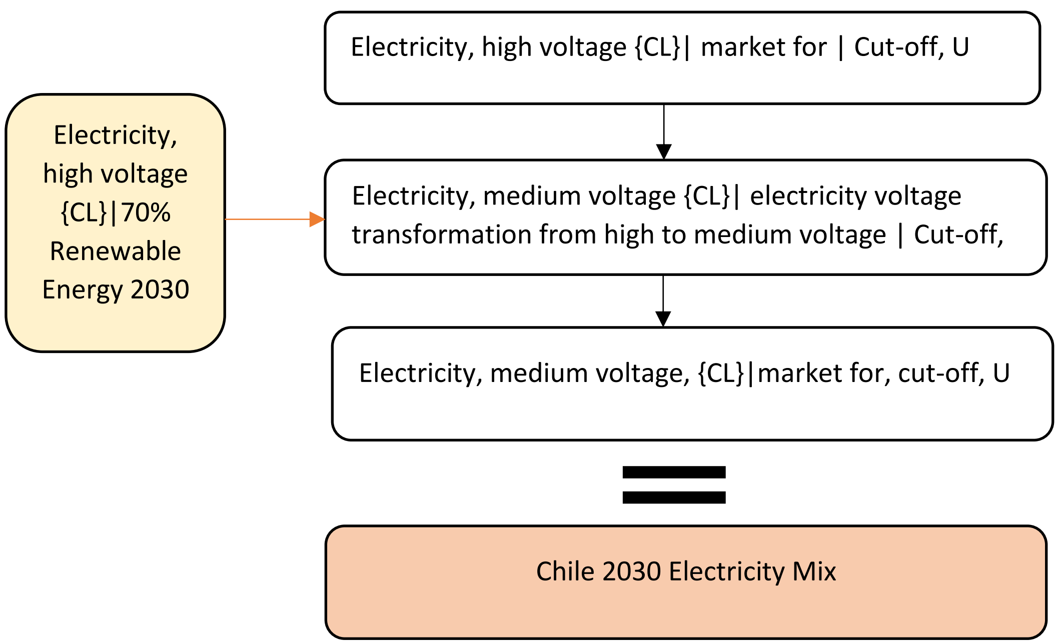


Table 3-10: Chile 2030 Electricity Mix Unit Process Data.

Product Material Input	Normalized to Unit Process	Unit	Category	Notes
Transmission network, electricity, high voltage {GLO}| market for | Cut-off, U	6.58	km	GLO	
Transmission network, long-distance {GLO}| market for | Cut-off, U	3.17E-10	km	GLO	
Electricity, high voltage {RoW}| electricity production, hydro, run-of-river | Cut-off, U	0.3	kWh	RoW	
Electricity, high voltage {RoW}| electricity production, natural gas, conventional power plant | Cut-off, U	0.3	kWh	RoW	
Electricity, high voltage {RoW}| electricity production, solar tower power plant, 20 MW | Cut-off, U	0.2	kWh	RoW	
Electricity, high voltage {CL}| electricity production, wind, >3MW turbine, onshore | Cut-off, U	0.2	kWh	CL	
Output				
Chile 2030 High Voltage Electricity 70% RE	1	kWh		Re-modeled based on electricity, high voltage {CL}| market for | Cut-off, U
Dinitrogen monoxide	5.00E-06	kg		pollution from high voltage lines ionizing air molecules
Ozone	4.15	kg		pollution from high voltage lines ionizing air molecules

3.5 PVDF Membranes

To account for the use of membranes in the lithium concentration process, assumptions were made based on the following. The commercial plant requires 46,080 membrane modules, which are a result of the process modeling and module specifications. Assuming a 20% replacement rate of modules every 5 years and a plant lifetime of 20 years, 9,216 membrane modules will need to be replaced every 5 years. Over the 20-year lifetime of the plant, 82,944 membrane modules are required. However, the membrane modules which were used in the process modeling, which provided the constraints in the model are no longer being manufactured (Jinhuimo Intl. Trading, Personal communication, July 7, 2022). However, a similar membrane is offered by the membrane manufacturer which has an interior of 50 m^2 instead of 20 m^2. Assuming the membranes operate similarly, and the transmembrane flux of 2.5 $kg/m^2/hr$ stays the same, less membranes would be required for the same output because 20 m^2 is 40% of 50 m2. Therefore, the amount of membrane modules needed with an interior membrane area of 50 m^2 is 33,178.

According to the manufacturer, Jinhuimo, the membrane model UFcOA2860, made of PVDF, has a net weight when empty of 48 kg. Multiplying the amount of membrane modules used over the 20-year plant lifetime with the net empty weight of the PVDF module results in 1,592,544 kg of PVDF or 1.59 kilotons of PVDF. To determine how many kgs of PVDF is used per ton of Li brine, two calculations are required. First, 33,178 membrane modules are divided by the lifetime output of brine which according to Table 3-8 is 610,000 kilotons which results in .054 membrane modules per ton of lithium brine. Secondly, .054 membrane modules multiplied by 48 kg results in 2.61 kg of PVDF per ton of Li brine.

To account for the use of membrane modules per 1 ton of lithium brine, the recent and only dataset for PVDF production is used which was obtained from Hu et al. (2022). Importantly, two different routes of producing PVDF are explored in the study by Hu et al. (2022), and route 1, which has larger environmental impacts is chosen because it provides a more conservative estimate of the impact of using PVDF membrane modules in MCr for lithium extraction. Importantly, the dataset by Hu et al. (2022) found in Appendix 8.5, does not specify the regions for the various inputs including materials and energy, so {RoW} and {GLO} were chosen when re-modeling it. The dataset created for this research, based on Hu et al. (2022) can be found below in Table 3-11 below.

Table 3-11: Unit Process for Producing 1 kg PVDF (Route 1)

Unit Process for Producing 1 kg PVDF (Route 1)								
Reactants	**Amount**	**Unit**	**Materials**	**Ecoinvent Source**	**Amount**	**Unit**	**Electricity (kWh)**	**Source**
R-132b	2.17	kg	trichloroethylene	Trichloroethylene, at plant/WEU U	2.17	kg	7.5516	Electricity, medium voltage {GLO}| market group for | Cut-off, U
			hydrogen fluoride	Hydrogen fluoride, at plant/GLO U	1.085	kg		
			ultrapure water	water, ultrapure {RoW}| market for water, ultrapure | Cut-off, U	0.217	kg		
hydrogen	0.13	kg	hydrogen	hydrogen, gaseous {GLO}| market for hydrogen, gaseous | Cut-off, U	0.13		30	Electricity, medium voltage {GLO}| market group for | Cut-off, U
tri-isobutyl borane	0.1	kg	butene	Butene, mixed {RoW}| market for butene, mixed | Cut-off, U	0.4782	kg	12	Electricity, medium voltage {GLO}| market group for | Cut-off, U
			decarbonized water	water, decarbonized {RoW}| market for water, decarbonized | Cut-off, U	0.1536	kg		
			sodium tetrahydridoborate	Sodium tetrahydridoborate {GLO}| market for | Cut-off, U	0.1			
			acetic acid	Acetic acid, at plant/kg/RNA	0.1			

After creating the datasets to account for membrane module usage and the electricity mix, the LCI data table was constructed for producing 1 ton of concentrated lithium brine via MCr which can be found in Table 3-12 below. The total raw brine amount is shown and is composed of water content and the constituent elements which are denoted with an asterisk and are used as inputs to represent the raw brine input.

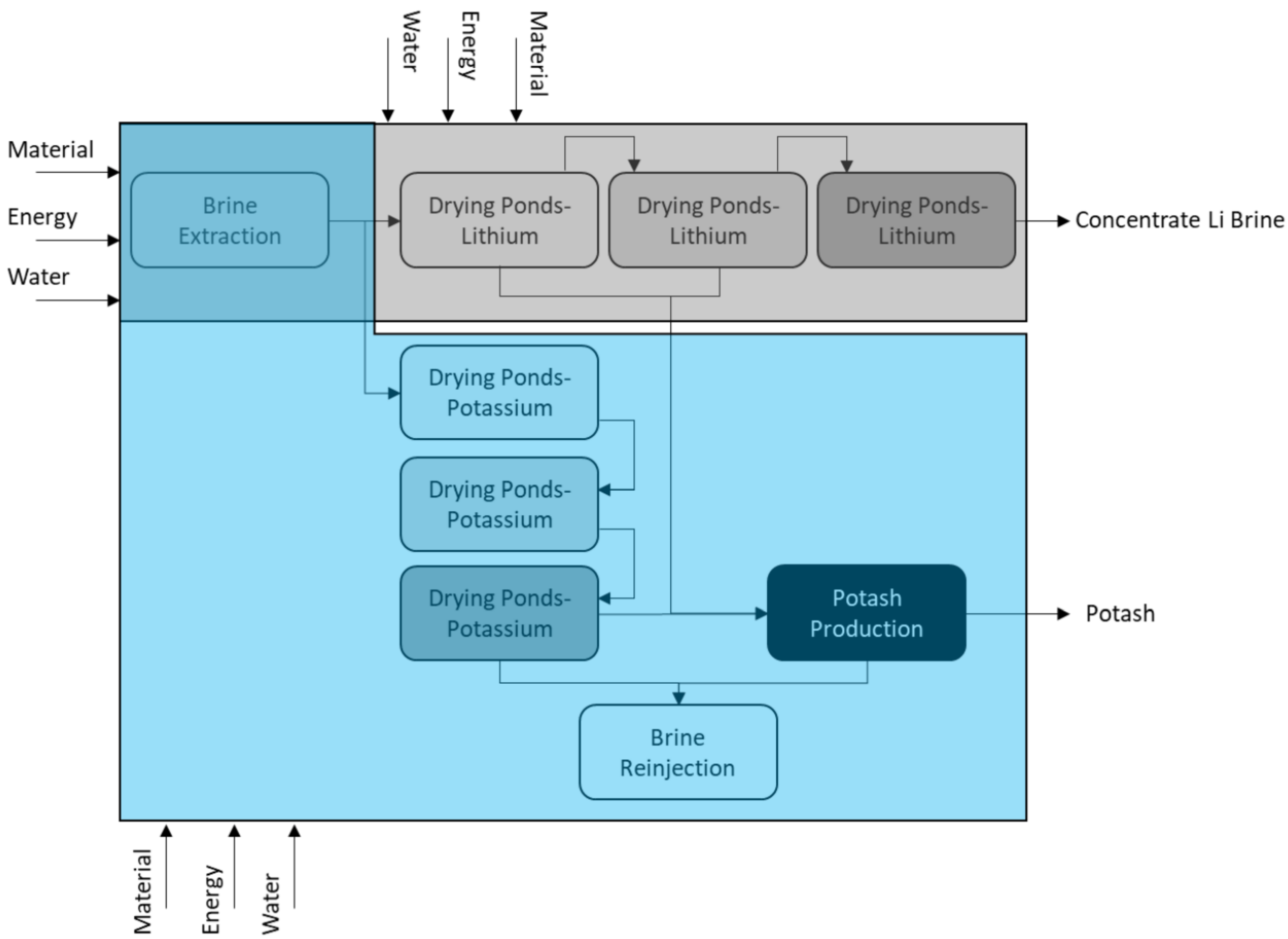
Table 3-12: LCI of producing 1 ton lithium brine 4 wt%. via MCr.

LCI of Concentrated Brine Production via MCr					
Product Material Input	**Normalized to Unit Process**	**Unit**	**Provider in Ecoinvent**	**Category**	**Notes**
Raw Brine	36.30	t			
Sodium*	2.77	t	Sodium	Resource/ in ground	
Potassium*	0.77	t	Potassium	Resource/ in ground	
Lithium*	0.05	t	Lithium	Resource/ in ground	
Magnesium*	0.35	t	Magnesium	Resource/ in ground	
Chlorine*	5.79	t	Chorine	Resource/ in ground	
Boron*	0.02	t	Boron	Resource/ in ground	
Water Content in Brine*	24.27	m3	water, unspecified natural origin, CL	Resource/ in water	Used to account for water extraction
PVDF (Route 1)	2.16	kg	-	-	(Hu et al., 2022)
Energy Input	**Normalized to Unit Process**	**Unit**	**Provider in Ecoinvent**	**Category**	**Notes**
Brine Pumping	169.87	kWh	-	-	*Chile 2030 Electricity Mix
Distillate Cooling	2964.92	kWh	-	-	
Brine Heating	5769.43	kWh	-	-	
Output	**Normalized to Unit Process**	**Unit**	**Provider in Ecoinvent**	**Category**	**Notes**
Concentrated Brine 4 wt%.	1.00	t	-	-	Input for Li_2CO_3 Production
Freshwater	23.2	t	water, CL	emissions to water	
Salts	8.4	t		Final Waste Flows	Bischofite, Halite, K-Carnallite

3.5.1.1 *Brine Inspissation*

A system diagram of the brine inspissation process can be seen below in Figure 3-5. It closely follows the general process explained in the theoretical background which includes consecutive evaporation ponds however Kelly et al. (2021) did not report any chemical usage during the inspissation process. In addition, the data was adapted by Chordia et al. (2022) to be used in Ecoinvent instead of GREET. The blue square denotes potash production which was subdivided while the grey squares denote lithium brine production from which the LCI dataset is based on.

Figure 3-5: System diagram of brine inspissation (adapted from Kelly et al., 2021).



The LCI dataset for lithium brine production via brine inspissation is in Table 3-13 below. Similar to the LCI dataset for the MCr process, the material inputs denoted with an asterisk represent the constituent components of the brine which include the water and solutes contained in the brine.

Table 3-13: LCI of 1 Ton lithium brine 5-6 wt%. via brine inspissation.

LCI Concentrated Brine Production via Inspissation					
Product Material Input	**Normalized to Unit Process**	**Unit**	**Provider in Ecoinvent**	**Category**	**Notes**
Raw Brine	2.30E+02	t		Resource/ in ground	* Items replace raw brine flow
Sodium*	1.75E+01	t	Sodium	Resource/ in ground	
Potassium*	4.26E+00	t	Potassium	Resource/ in ground	
Lithium*	3.91E-01	t	Lithium	Resource/ in ground	
Magnesium*	2.21E+00	t	Magnesium	Resource/ in ground	
Calcium*	7.13E-02	t	Calcium	Resource/ in ground	
Sulfate*	3.80E+00	t	Sulfate	Resource/ in ground	
Chlorine*	3.69E+01	t	Chorine	Resource/ in ground	
Boron*	1.47E-01	t	Boron	Resource/ in ground	
Water Content in Brine*	1.65E+02	m3	water, unspecified natural origin, CL	Resource/ in water	Used to account for water extraction
Energy Input	**Normalized to Unit Process**	**Unit**	**Provider in Ecoinvent**	**Category**	**Notes**
Electricity	7.60E+02	MJ	Chile 2030 Electricity Mix*		
Diesel	6.57E+02	MJ	market for diesel, burned in building machine	GLO	Processes/Energy/ Mechanical
Water Input	**Normalized to Unit Process**	**Unit**	**Provider in Ecoinvent**	**Category**	**Notes**
Freshwater	5.94E+00	t	Water, lake, CL	Resource/ in water	

Output	Normalized to Unit Process	Unit	Provider in Ecoinvent	Category	Notes
Concentrated Li Brine 5-6 wt%.	1.00E+00	t	-	-	Input for Li_2CO_3 Production

3.5.2 Li_2CO_3 Processing

The flowchart of the Li_2CO_3 production process has been adapted from Kelly et al. (2021) and is shown in Figure 3-6 below. The LCI dataset for Li_2CO_3 production is based on the dataset by Kelly et al. (2021) however it was adapted by Chordia et al. (2022) to be used with Ecoinvent and that dataset is found in Table 3-14 below. There are a few important things to note, first, the brine input amount is variable depending on the concentration of brine that is used as an input. As previously mentioned, for the inspissation brine, 4 tons are used whereas for the MCr brine, 4.697 tons are used. Another important note is that in the dataset by Kelly et al. (2021), the authors did not indicate what proportion of materials were used and so they were evenly divided by Chordia et al. (2022), which is the same approach used in this research. In addition, the Li_2CO_3 production dataset includes the 2030 Chile electricity mix that was modeled for the electricity input. Lastly, the type of alcohol was not determined by Kelly et al. (2021) or Chordia et al. (2022) and so 'market for chemical, organic' is used in place of alcohol.

Figure 3-6: System diagram of Li_2CO_3 Production (adapted from Kelly et al., 2021).

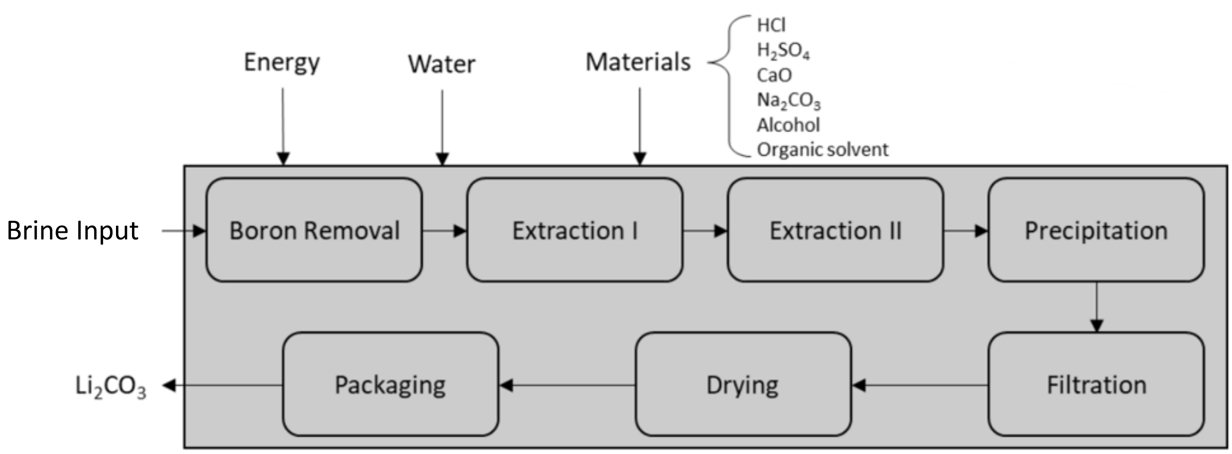


Table 3-14: LCI of 1 ton Lithium Carbonate Production.

Life Cycle Inventory of Lithium Carbonate Production					
Product Material Input	**Normalized to Unit Process**	**Unit**	**Provider in Ecoinvent**	**Category**	**Notes**

Concentrated Brine	4 or 4.697	t	-	-	Variable, depending on brine concentration
Chemical and reagent input	**Normalized to Unit Process**	**Unit**	**Provider in Ecoinvent**	**Category**	**Notes**
Sodium Carbonate	2.00E+00	t	market for soda ash, dense	GLO	
Sulfuric Acid	1.60E-02	t	market for sulfuric acid	RoW	
Hydrochloric Acid	1.60E-02	t	market for HCl acid, without water, in 30% solution state	Row	
Calcium Oxide	1.60E-02	t	market for lime, hydrated, packed	RoW	
Solvent	1.60E-02	t	market for chemical, organic	GLO	
Alcohol	1.60E-02	t	market for chemical, organic	GLO	
Energy Input	**Normalized to Unit Process**	**Unit**	**Provider in Ecoinvent**		**Notes**
Electricity	1.50E+03	MJ	*Chile 2030 Electricity Mix	CL	
Diesel	4.00E+02	MJ	market for diesel, burned in building machine	GLO	
Heat	2.80E+03	MJ	market group for heat, district or industrial, natural gas	GLO	
Emission to air (non-combustion)	**Normalized to Unit Process**	**Unit**	**Provider in Ecoinvent**		**Notes**
PM 10	7.00E+02	g	particulates, >2.5 µm and <10 µm	Emission to air/ unspecified	

PM 2.5	4.00E+02	g	particulates, <2.5µm	Emission to air/ unspecified	
Output	**Normalized to Unit Process**	**Unit**			**Notes**
Lithium Carbonate	1.00E+00	t	-	-	-

3.5.3 Impact Categories

The impact categories that were chosen to evaluate the environmental impact of producing Li_2CO_3 via brine inspissation and MCr for this research are climate change, water use, resource use (minerals and metals and acidification. These impact categories are chosen based on previous studies as well as the criteria that were determined as measures for improvement for new lithium extraction technologies. The impact categories and the models they are based on are shown in Table 3-15 below.

Table 3-15: List of impact categories used in the LCA.

Impact Category	Indicator	Unit	Model
Climate change	Global Warming Potential (GWP)	Kg $CO_{2eq.}$	IPCC (2013) baseline model of 100 years
Resource use (minerals & metals)	Abiotic resource depletion (ADP ultimate reserves)	Kg $Sb_{eq.}$	Based on van Oers et al. 2002, as implemented in CML v.4.8 (2016)
Water use	Weighted water deprivation potential for humans & ecosystems	m^3 water deprivation	Available WAter REmaining (AWARE) based on Boulay et al. (2018)
Acidification	Accumulated exceedance (AE)	Mol $H^+{}_{eq.}$	Accumulated exceedance (Seppälä et al. 2006, Posch et al. 2008)
Climate Change	Cumulative Energy Demand (CED)	GJ (based on higher heating values)	Based on Frischknecht et al. (1998)

Global Warming Potential (GWP)

GWP is a measure of the potential warming caused by greenhouse gas (GHG) emissions that trap heat in the atmosphere and increase radiative forcing. GHGs differ in their ability to absorb heat and how long they stay in the atmosphere. The impact assessment methodology proposed in the IPCC GWP 2013 edition accounts for the variations in GWP of different GHGs and represents GWP as a score expressed in terms of kg CO2 eq.

Abiotic Resource Depletion Potential (ADP)

While there are several approaches that are heavily debated for assessing abiotic resource depletion potential, this research adopts the characterization model implemented in CML v4.8 (2016). The ADP method was originally developed by Guinée and Heijungs (1995) and was later updated by van Oers et al. (2002). Guinée and Heijungs (1995) method is based on a scarcity indicator that combines production and reserves where production is in terms of world annual production P expressed in kg/year of a given element and reserves R which is the estimated ultimate global reserve expressed in kg of a given element. The CF is ADP quantified as kg of antimony-equivalent (SB-eq) per kg of extraction.

Water Use

In this research, Available Water Remaining (AWARE) is the water use midpoint indicator that is used. The indicator represents the relative available water remaining per area in a watershed, after the demand of humans and aquatic ecosystems has been met. Importantly, it assesses the potential for water deprivation to either humans or ecosystems, by assuming that the less water remaining available per area in a watershed, the more likely another user (humans or ecosystems) will be water deprived (WULCA, 2022). The AWARE characterization factors (CF) are between 0.1 and 100, with a value of 1 representing the world average whereas a CF of 10, would represent a region where the available water per area is 10 times less than the world average (WULCA, 2022).

Acidification

The acidification impact category is a measure of acidification potential (AP) which can occur either in terrestrial or freshwater ecosystems and accounts for the ability of contaminants to affect the pH level of those ecosystems. The calculated score is expressed in mol H^+ eq.

Cumulative Energy Demand

CED measures the energy demand, measured as GJ primary energy, during the life cycle of a product and is a useful indicator of global warming potential due to the fact that fossil energy demand is primarily responsible for GWP and the depletion of fossil resources (Frischknecht et al., 1998).

3.6 Interpretation

3.6.1 Uncertainty Analysis

An intrinsic part of ex-ante LCAs are their high degree of uncertainty due to data often being estimated by experts or created by models despite the technology not yet existing at a large scale. This research chose to deal with uncertainty by using a pedigree matrix adapted from Hauschild et al. (2018) to describe the level of uncertainty for each of the datasets used within the LCA. Table 3-16 below classified the different levels of uncertainty.

Table 3-16: Uncertainty Analysis Matrix Table (adapted from Hauschild et al., 2018).

Data Specificity	Reasoning
Very Low	Judgement by expert or LCA practitioner
Low	Generic LCI database process or data from literature, e.g., covering a mix of technologies in a country or region obtained from measurements at process site and scaled via modeling
Medium	LCI database process or data from literature specific to actual process, e.g., according to best available technology standard or country average. Specificity may be improved by modifying a process with site specific data
High	Derived from measurements at specific process site via modeling
Very High	Measured directly at specific process site or scaled from measurement

Based on an evaluation of the datasets used for the LCIs and unit process data in this research, Table 3-17 provides a data specificity indicator of the datasets used.

Table 3-17: Uncertainty analysis of datasets used throughout this research.

Dataset	Source	Data Specificity
MCr Annual Mass & Energy Balance & Brine LCI	AMTC	Low
Brine Inspissation & Li_2CO_3 Production LCIs	Kelly et al. (2021)	Low
PVDF Membrane Production Data	Hu et al. (2022)	Low
Chile Electricity Mix 2030	Edited Ecoinvent Processes	Low
SQM Land Use & Li_2CO_3 Production	SQM (2022)	Very High

3.6.2 Sensitivity Analysis

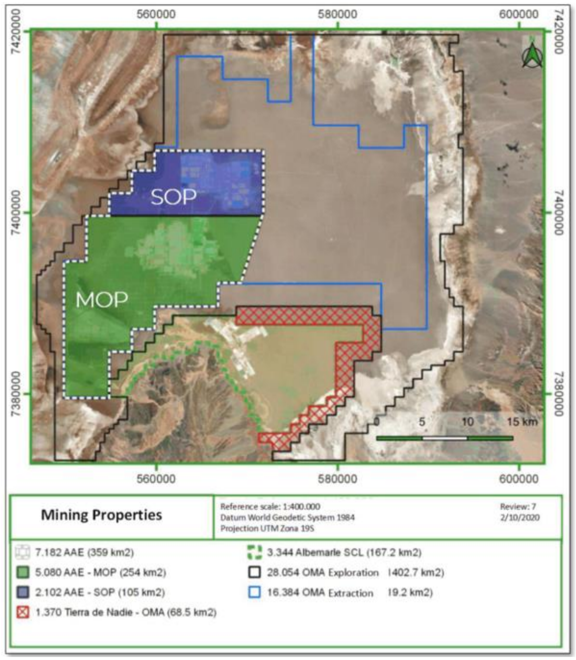
Due to the fact that the main difference between the brine inspissation and the MCr technology is the energy usage, a sensitivity analysis was conducted to explore the difference in environmental impacts if 100% renewable electricity was used for the MCr facility and the processing facility. Importantly, since the facilities for brine inspissation and processing are already constructed, the sensitivity analysis only models the MCr and processing facility with 100% renewable electricity because they have not been built yet. Due to the fact that the SdA has one of the highest amounts solar PV potentials, the sensitivity analysis uses solar PV for the electricity background process. However, Ecoinvent does not have utility-scale solar PV processes so Argentina was used as a proxy based on regional similarity. The electricity process chosen was "electricity, low voltage {AR}| electricity production, photovoltaic, 570kWp open ground installation, multi-Si | Cut-off, U" which is interchanged in the MCr LCI for the electricity used in brine pumping, distillate cooling and brine heating. The Argentinian solar PV process was also interchanged with the electricity required in the Li_2CO_3 production LCI. The results of this sensitivity analysis will be presented in Section 4 'Results'.

3.6.3 Land Use & Land Use Intensity (LUI)

3.6.3.1 Brine Inspissation

To calculate the land use and LUI of brine inspissation and Li_2CO_3 processing, data was collected from the technical report recently released by SQM (2022). The report indicates sector 'MOP' is used exclusively for potash and lithium brine production and is adapted from SQM's report in Figure 3-7 below.

Figure 3-7: SQM land usage report for lithium brine production and potash (adapted from SQM, 2022).



According to SQM, the MOP sector encompasses 254 km^2 however, to determine the land use specifically associated with lithium production, an assumption was made that mass allocation could be used and the land area could be divided according to the share of projected product output reported in year 2027. According to Figure 3-8 adapted from the technical report, it is expected that there are 220 kilotons of Li_2CO_3 produced per year and 1,224 kilotons of potassium chloride produced per year in 2027.

Figure 3-8: SQM production forecasts (adapted from SQM, 2022).

		2022	2023	2024	2025	2026	2027	2028	2029	2030
Lithium Carbonate	ktpy	95	130	150	220	220	220	220	220	200
Lithium Hydroxide	ktpy	21	25	30	30	30	30	30	30	30
Potassium Chloride	ktpy	1,548	1,483	1,406	1,380	1,305	1,224	1,139	1,050	960

In total, 1444 tons of product will be produced, with 15.2% of it being Li_2CO_3 and 84.8% being potash. To calculate the LUI the following formula was used:

$$LUI = \frac{Lithium\ Mining\ Area\ (km^2)}{Annual\ Production\ (tons)}$$

Therefore, 15.2% of 254 km^2 is equal to 40 km^2 which is divided by 220 tons of Li_2CO_3 which equals .18 km^2 per ton of Li_2CO_3. If no allocation method was used, 254 km^2 divided by 220 tons of Li_2CO_3 would equal 1.15 km^2 per ton of Li_2CO_3. The processing facility itself is roughly 2 km^2 (personal communication) and was therefore not considered in the calculation because the difference is negligible.

3.6.3.2 MCr

The primary contribution to land area usage for MCr relates to the scenario in the sensitivity analysis in which 100% of electricity use is from solar PV. The land area used for the MCr facility is considered to be negligible compared to the evaporation ponds because the concentration occurs within the membrane modules and approximately 40,000 will likely not take more than 1 km^2. To determine the land area associated with the amount of electricity required per year at the MCr facility, recent data from Bolinger and Bolinger (2022) was used. The authors provide the most up-to-date empirical study of land requirements for utility-scale PV based on 90% of all utility-scale PV plants built in the United States through 2019. While the data is not exactly representative of the solar PV potential of SdA, it provides a conservative estimate of the land area requirements for the MCr facility.

Based on findings from Bolinger and Bolinger (2022), the energy density for fixed-tilt utility scale PV plants is 447 MWh/year/acre. This is equivalent to 0.11175 TWh/year/km^2 based on the calculation that 1 acre is equal to .004 km^2. Dividing the yearly electricity consumption required at the MCr plant, which is 5.42 TWh, the required land area needed is 48.5 km^2. Using the previous LUI formula, and the mass allocation approach the LUI can be determined for Li_2CO_3 production. The required land area for utility-scale solar PV is 48.5 km^2, the annual Li_2CO_3 equivalent output of the MCr facility is 100 kilotons and the potash production is 76 kilotons. Therefore, 56% of the product mass output is Li_2CO_3 and 44% is potash. Using the previous formula and the mass allocation approach, 56% of 48.5 km^2 is equal to 27.16 km^2 which results in a LUI of .0002 km^2 per ton of Li_2CO_3. The results of the required land area and land use intensity of MCr and brine inspissation are provided in Table 3-18 below.

Table 3-18: Land Use Intensity & Production Intensity

Technology	Total Land Area (km^2)	Lithium Land Area (km^2)	Li_2CO_3 Output (tons)	LUI (km2/ton Li_2CO_3)	Production Intensity (tons Li_2CO_3 /km^2)
Brine Inspissation	254	40	220,000	.0001	10,000
MCr	48.5	27.16	100,000	.0002	5000

The results show that the production intensity of brine inspissation is twice as much as MCr which is likely due to the fact that based on the operational data of the MCr plant, it only produces 6% the amount of potash that the MOP sector produces during brine inspissation and therefore the mass allocation approach allocates more land to potash production making the land required for lithium production seem much less. Obtaining higher quality data about the exact land required for solely lithium production would make the results more robust.

4 Results

4.1 Environmental Impacts of Brine Inspissation

4.1.1 Narrative Review

Lithium brine extraction and associated freshwater use in arid regions such as the SdA has been scrutinized by diverse stakeholders seeking to understand the environmental impacts of extracting lithium for the lithium-ion battery supply chain (Gajardo and Redón, 2019; Kalazich et al., 2019; Marazuela et al., 2019; Kaunda 2020; Heredia et al., 2020; Gutiérrez et al., 2022; Moran et al., 2022). Determining the specific environmental impacts of lithium brine extraction has been markedly difficult due to the paucity of studies exploring and conceptualizing the complex hydrogeological, geochemical, and biophysical systems that comprise the SdA (Flexer et al., 2018; Moran et al., 2022). Moreover, this topic is particularly sensitive due to the livelihoods of different stakeholders that have been adversely affected in the region (Heredia et al., 2020; Lorca et al., 2022). However, while the social impacts of lithium extraction are of equally vital importance, the aim of this narrative literature review is to focus solely on the environmental impacts of lithium extraction in the SdA. In doing so, different foreseen and measured environmental impacts may be properly attributed to their origin and therefore avoid the mischaracterization of environmental impacts and their respective causes.

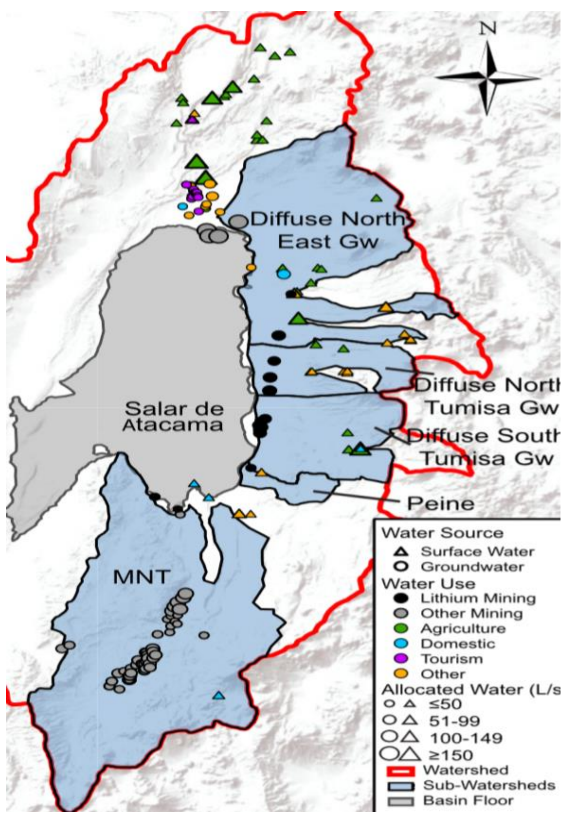
Recent studies have attributed environmental degradation to the operation and expansion of lithium extraction activities. Liu et al. (2019) attributed degrading vegetation cover, hotter local climate and increasing dry conditions to lithium extraction operations in the SdA. Liu et al. (2019) also argue that climatic variabilities such as rare precipitation events may contribute considerably less than the impact-intensive anthropogenic stressors such as lithium extraction. However, Moran et al. (2022) point out that the remote sensing methodology used by Lui et al. (2019) is not justified in their article and improperly applies the Normalized Difference Vegetation Index (NDVI) by not applying specific thresholds for vegetation identification and differentiation. Furthermore, the Liu et al. (2019) study includes the built evaporation ponds in their NDVI assessment which biases the NDVI towards negative numbers because water bodies result in negative values and therefore overestimates the land cover change due to lithium extraction. Moreover, Moran et al. (2022) argues that the conclusion put forth by Lui et al. (2019) is not grounded in the SdA basin's hydrological regime and is inconsistent with observations made by Moran et al. (2022) who constructed the most up-to-date hydrological assessment using geochemical tracer data.

Similarly, Liu and Agusdinata (2020) argue that brine extraction in the SdA in the past decades has led to a direct decline in terrestrial water storage in the SdA basin however, as Moran et al. (2022) point out, the methods used by Lui and Agusdinata (2020) are flawed because the methodology they used to process GRACE Total Water Storage (TWS) data was not explained and therefore not reproducible. Furthermore, the data which Liu and Agusdinata (2020) used encompasses a domain dozens of kilometers larger than the SdA basin and errantly assume that the trends observed over the much larger domain reflect changes in water storage in the SdA basin (Moran et al., 2022). Lastly, the analysis of water availability by Montecino et al. (2016) and Moran et al. (2022) show a strong increase in total water storage anomaly (TWSA) over the same time period. Therefore, the confidence in conclusions reached by Lui et al. (2019) which attribute lithium extraction as the cause of degrading vegetation cover, hotter local climate and increasing dry conditions in the SdA is not very strong. Similarly, there is not strong confidence in results of Lui and Agusdinata (2020) which attribute a decline in terrestrial water storage to lithium extraction in the SdA.

One important implication of these findings is due to the fact that according to Google Scholar, at the time of this writing, Lui et al. (2019) has been cited 93 times and Lui and Agusdinata (2020) has been cited 61 times which illustrates the point that while those authors may have important contributions, a careful consideration is needed when attributing water availability and scarcity in the SdA to lithium extraction. While it is entirely appropriate to be prudent and closely examine the developments of lithium extraction in the SdA to limit or mitigate environmental impacts, it is also recommendable to avoid propagating misinformation regarding the water-lithium nexus in the SdA.

Moran et al. (2022) provide a more recent and nuanced understanding of water sustainability as it relates to lithium extraction in the SdA. The entire hydrogeological assessment they conducted will not be explained but a few important conclusions provide value to the discussion. First, most of the water use permits granted by the Chilean government are allocated to copper mining and agriculture, which claim approximately 47% and 37% of total water rights, respectively, while lithium and potash mining companies are allocated 10% and 'other' uses comprise 7%, and domestic use totaling 2% of total allocations for water (Moran et al., 2022). Importantly, publicly available water extraction amounts based on government permitting do not necessarily equal actual extraction in the basin because water use has been historically monitored for industrial users but not for private, non-industrial users such as agriculture (AMPHOS21, 2018; Moran et al., 2022). Therefore, it is not entirely known the extent to which agricultural users draw water. Figure 4-1 provides a map of the freshwater allocation among different users in the SdA basin.

Figure 4-1: Map of freshwater extraction locations in SdA (adapted from Moran et al., 2022).



Using tritium, stable oxygen and hydrogen isotopes to create geochemical tracer data paired with remote sensing data and terrestrial hydroclimate data, Moran et al. (2022) distinguished sources of water within the SdA based on their residence time, physical characteristics and connectivity to modern climate and found that surface water extent (SWE), vegetation and total terrestrial water storage have increased substantially since 2015 due to short-term climate variations from drought and extreme rainfall events. Moreover, although it may seem reasonable to attribute decline in surface waters, wetland vegetation and groundwater levels in the SdA to lithium brine extraction, Moran et al. (2022) also show that the fresh groundwater zones where lithium and potash mining extractions are most concentrated, experienced the smallest groundwater storage declines, whereas the largest groundwater storage declines have occurred in the aquifers where freshwater is extracted for copper mining, agricultural and domestic uses. Importantly, Moran et al. (2022) highlight the importance of contextualizing water extraction in terms of rate, location and water source in addition to climatic conditions to properly assess the causes of environmental impacts in the SdA. Furthermore, as global climate change continues to accelerate, assessing environmental impacts within the SdA in the context of these changes becomes even more important (Moran et al., 2022).

Research by Guzmán et al., (2021) also found that lithium brine extraction had a minor impact on the availability of water in the SdA basin. They argue that an increase in water recharge within the SdA is occurring due to an ‘exohydric’ mechanism whereby large volumes of water contained in extracted lithium brines are evaporated from the lithium production ponds and return as freshwater in the form of precipitation within the SdA basin. This finding may be a potential positive consequence of lithium extraction however further investigation is required (Guzmán et al., 2021). Interestingly, this finding begs the question of whether the extreme rainfall events witnessed in the SdA basin in the past several years (Moran et al., 2022) could be linked to the large volumes of water being evaporated during lithium extraction. The findings by Guzmán et al., (2021) suggest that lithium extraction may have contributed to increased freshwater availability in the SdA basin through the exohydric mechanism previously discussed.

Environmental concerns have also been raised regarding the impact lithium extraction may have on lagoon systems located in the marginal zone within the SdA, an area between the alluvial fans and the salt flat nucleus. Garcés and Álvarez (2020) suggest that operations could affect the lagoon ecosystems and consequently reduce flora and fauna (Gajardo and Redón, 2019). However, a recent study conducted by Guzmán et al. (2022) found that the lagoon systems have not significantly changed from 1986 to 2018 despite increasing lithium production, even during years of large brine extraction. Moreover, the findings reinforce the notion that lithium extraction had minimal or no impact on the surface area of the lagoon systems and that the lagoons exhibit the ability to adapt to changing environmental conditions (Tejeda et al., 2003; Marazuela et al., 2020). However, it is not the case that propagating current brine extraction levels or increasing them would not have an effect on the lagoons and in addition, potential impacts on the lagoon systems may take a long time to be noticed (De la Fuente et al., 2021).

However, Gutiérrez et al. (2022) found that flamingo populations within the lagoon systems in SdA fluctuated significantly over a 30-year time span from 1985-1988 and 1997-2019. The main contributing factors influencing flamingo abundance were predicted by precipitation, minimum temperature, potential evapotranspiration and surface water levels via their effects on food availability indicating that water and food availability are key drivers of flamingo abundance (Gutiérrez et al., 2022). Importantly, the authors mention the extreme variability of the regions climate with annual precipitation varying three-fold to five-fold and rates of run-off differed by 150-fold during the study period.

While Gutiérrez et al. (2022) acknowledge the role of climate change related declines in surface water, they conclude that the decrease in flamingo abundance – a function of water and food availability – is due to lithium extraction. However, given the findings by Moran et al. (2022), which posit that recent extreme climate variability has affected surface water bodies and soil moisture in the basin, coupled with the fact that lagoon system surface area has not changed, a careful degree of skepticism is warranted when evaluating the claim that flamingo population decline is attributable to lithium extraction (Gutiérrez et al., 2022) because climatic variability (Moran et al., 2022) may confound that conclusion.

A study by Marazuela et al. (2019) found that lithium extraction in the SdA salt flat nucleus had decreased the phreatic evaporation rate based on a 'damping capacity' of the salt flats. When a certain volume of brine is extracted from the salt flat nucleus, a drawdown in the water table occurs however, the phreatic evaporation rate subsequently reduces due to an increase in the unsaturated zone between the surface of the salt flat and the reduced water table. So, although the brine extraction may reduce the water table, the water loss associated with phreatic evaporation is also reduced, thereby partially counteracting the effects of brine pumping (Marazuela et al., 2019). From an ecological perspective, the damping effect may affect the mixing zone of brine and freshwater within the marginal zone which could affect the wetland and lake ecosystems, however more research is needed to assess that implication (Marazuela et al. 2019). Building off of their previous work, Marazuela et al. (2020) suggest that to take better advantage of the damping capacity of the salt flat which counteracts the drawdown caused by lithium extraction, optimizing the location of brine pumping locations should be distributed within the largest possible area in the salt flat. In effect, the damping capacity is optimized to decrease the phreatic evaporation rate across the largest possible area and therefore offset the impacts of brine pumping on the water table and water balance (Marazuela et al., 2020). Another point of contention raised in the debate regarding the environmental impacts of lithium extraction is the definition of water as dictated by current Chilean law. Due to the fact that brine is unfit for human consumption and impossible to use for agriculture (Flexer et al., 2018), the continuous extraction of brine has continued without adequate investigations exploring how it may be interacting with freshwater in the SdA basin (Kalazich et al., 2019). However, as Moran et al. (2022) points out, there is notable uncertainty between permitted water use and actual extraction rates (Babidge et al., 2019) and a considerable over allocation of water in the basin has occurred based on assumptions that overestimate water resource sustainability.

A final point is the issue of waste production and disposal during the lithium extraction process. Due to the high content of TDS in extracted brine, the evaporitic process requires the removal of different salts such as NA and K throughout the process. For example, a brine with a TDS 300 g L^{-1}, a Li^{+} content of 700 ppm and a recovery rate of 70% means that creating 1 ton of Li_2CO_3 will produce 115,041 kg of waste including Na, $Mg(OH)_2$ and $CaSO_4$ (Flexer et al., 2018). Fortunately, this waste is non-toxic however, currently it accumulates in large quantities at the outskirts of the operational area and will eventually require waste management and if 20 kilotons of Li_2CO_3 are produced per year, after 10 years, it amounts to 2.3 E 10^7 tons of waste (Flexer et al., 2018). Moreover, when accounting for volumetric density of the salt mixtures, that mass will translate into a volume of 1.15 E 10^7 m^3 of waste which at a height of 1 meter, will occupy a land area of 11.5 km^2 (Flexer et al., 2018). Contextualizing these numbers according to SQM's technical report detailing their expected Li_2CO_3 production (SQM, 2022), 220 kilotons will be produced every year until 2030, which is approximately 11 times the amount of waste discussed previously which makes the process of waste management more difficult and energy intensive and has its own set of implications for environmental impacts which should be further researched.

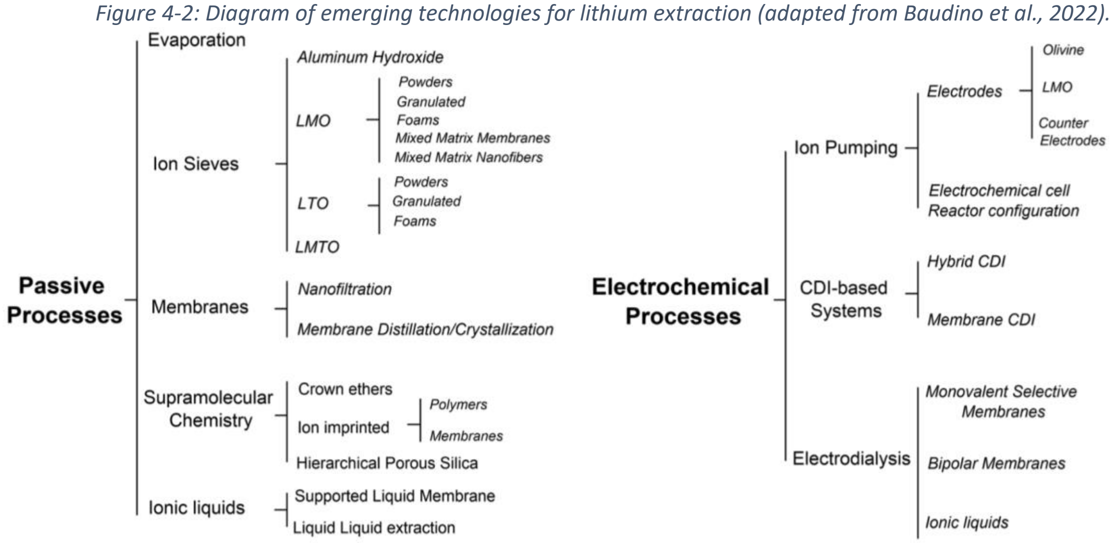
1.1 Recommendations

Based on the literature review, some recommendations are made for further consideration to limit any potential environmental impacts associated with lithium extraction in the SdA via brine inspissation. Probably the most important is to enhance and build on the hydrological assessment conducted by Moran et al. (2022) by further incorporating geochemical tracer data into physical hydrological models to better understand and monitor the water budget within the SdA. Floyd (2020) also proposes that more monitoring wells should be constructed within the alluvial fans where freshwater is pumped from. The addition of more monitoring wells throughout the basin including the salt nucleus and the regions around it will help provide more data points for an improved and robust hydrogeological model. Efforts should also be channeled towards scientific research that evaluates how climate change impacts will affect the basin in the future. Additionally, more scientific research is needed to monitor and evaluate the ecosystems and biodiversity within the SdA. To further bolster the monitoring of the basin, Floyd (2020) proposes the development of a river basin management plan (RBMP) which would expand the network of stakeholders involved in monitoring and maintaining the SdA basin. Additionally, the Biotic Environmental Monitoring Program (PSAB) which is the environmental monitoring program of SQM might benefit from independent evaluation of findings from researchers who are experts in relevant fields. The final recommendation is that to avoid environmental impacts associated with lithium extraction, new methods should be commercially developed which require less intensive land use, freshwater and brine extraction which is the subject of the following section.

4.2 Improved Lithium Extraction Criteria

To meet projected lithium demand, a large increase in production capacity is needed (Flexer et al., 2018; McKinsey, 2022; Khalil et al., 2022). Since continental brine lithium resources and reserves are much larger than those in hard rock ores (Kesler et al., 2012; Vikström et al., 2013; USGS, 2017), several efforts are underway to optimize the exploitation of continental brine reserves. There are several technologies being developed to recover lithium from brines which can be broadly categorized as passive processes and electrochemical processes (Baudino et al., 2022). While not all of the different technologies will be discussed, the schematic in Figure 4-2 indicates that substantial research is underway to improve the lithium extraction process from brines. The primary reasons that alternative technologies are being developed to extract lithium is because there are several intractable shortcomings with the brine inspissation process and evaporitic techniques in general.

Figure 4-2: Diagram of emerging technologies for lithium extraction (adapted from Baudino et al., 2022).



4.2.1 Water Use

First, the most obvious problem is that brine inspissation relies on an evaporation process that usually takes almost 24 months to complete (Flexer et al., 2018), and not much can be done to accelerate the evaporation process because it is highly contingent upon the climate of the region where the evaporation ponds are located. In the case of the SdA and other salt flats, the aridity of the environment makes it a feasible process but outside of these climates it is unfeasible. In addition, the brine composition is highly variable between different salars even within the Lithium Triangle but also globally, which further complicate the feasibility of the evaporation process (Kesler et al., 2012; Flexer et al., 2018). However, the main advantage of the evaporation process is that it relies on solar irradiation and is therefore not as energy intensive as lithium extraction from ores occurring in pegmatite formations such as spodumene, petalite and lepidolite (Vikström et al., 2013). Importantly, the most salient problem with the evaporative process is that up 95% of water contained in the extracted brine is lost during evaporation (Heubl, 2019). As previously mentioned in the environmental impact literature review, identifying sustainable withdrawals of freshwater and brine are still an unresolved issue and therefore prioritizing the recovery of water is arguably the most important criteria for an improved lithium extraction process (Flexer et al., 2018; Heredia et al., 2020; Bustos-Gallardo et al., 2021; Jerez, 2021; Moran et al., 2022; AltaLey, 2022; Schomberg et al., 2022).

4.2.2 Energy Consumption

Another key indicator of an improved lithium extraction process which doesn't rely on the evaporation process is the energy consumption required to recover lithium. Common to all lithium extraction technologies, is the requirement of energy for brine pumping however, the specific energy requirements of different technologies differ. Studies of emerging technologies for producing lithium carbonate at various TRL's have been conducted but their energy requirement profiles are often only reflective of lab-scale efficiencies and do not reflect the actual consumption at commercial scale (Li et al., 2020; Maria et al., 2022, Torres et al., 2020). Electrochemical processes for example, all require the presence of an external voltage (Baudino et al., 2022). Similarly, some passive processes which require membranes, such as nanofiltration, require hydraulic pressure which is generated with external energy sources. The concern is that technologies which are rated to be more versatile and increase water recovery might have a substantially larger GWP footprint. This could pertain to the energy needed throughout the process or the energy needed to create various materials used in the process. Therefore, the second key criterion for an improved lithium extraction process is the minimization of energy consumption and associated global warming potential (AltaLey, 2022).

4.2.3 Chemical Usage

A third criterion for improved lithium extraction technologies is to avoid or limit the incorporation of chemicals that affect the sustainability of the process (AltaLey, 2022). There are several implications regarding the involvement of chemical intensive technologies for lithium extraction. First, technologies which require the use of chemicals such as organic solvents, acids, bases, eluents, or ionic liquids will require enormous quantities transported to the salt flat operations (Flexer et al., 2018). More importantly, the addition of chemicals introduces their own set of environmental implications related to proper handling, spills and emissions to the environment. Moreover, with the addition of chemicals to extract lithium, the spent brines and left-over chemical compounds pose their own set of challenges for waste management. Importantly, according to Flexer et al. (2018), an ongoing unpublished discussion is occurring among scientists and industry stakeholders that propose to re-inject spent brines into the salt flat nucleus. This approach could be overwhelmingly problematic without serious consideration and studies examining the anticipated effects and would likely further complicate the already elusive understanding of the hydrological regime in the SdA. Many of the technologies that include the addition of chemicals to recover lithium will likely produce a treated brine that will be left over with traces of chemicals that are exogenous to the native brine such as aluminum, titanium (Chitrakar et al., 2014), manganese (Song et al., 2017), iron derivatives (Pasta et al., 2012), phosphates, silver (Pasta et al., 2012), organic solvents (Song et al., 2017) or ionic liquids (Shi et al., 2016; Flexer et al., 2018). Re-injecting spent brine containing trace elements would likely affect any ecosystem within the SdA and therefore should be avoided until the implications of doing so are further studied. Even if spent brine does not containing any trace elements foreign to the native brine, it is likely that a diluted brine re-injected back into the salt flat could dilute the brine deposit (Houston et al., 2011).

4.2.4 Resource Efficiency & Circularity

A fourth criterion for an improvement in lithium extraction technology is for the possibility to recover as much resources as possible from the brine and thereby improve circularity and resource efficiency. Water recovery could provide a supply of process water to the mining companies within the SdA and thereby avoid the additional withdrawal of freshwater (Flexer et al., 2018). In addition, water recovery from improved lithium technologies could also potentially provide water for domestic purposes or irrigation in the nearby communities (Flexer et al., 2018) which have long been in conflict with mining companies over their lack of water (Lorca et al., 2022). Interestingly, with potentially enormous volumes of freshwater being recovered, there may be a potential for new agricultural production within the desert landscape due to the availability of freshwater for irrigation (Flexer et al., 2018). In addition to water, the solutes contained in the raw brines also contain other potentially valuable resources such as Na, K, Mg, B, and even Cs and Rb (Garret, 2004). Due to the current market value of salts that are precipitated out during the evaporative process and the difficulty in transporting such large amounts, they are left unused on the periphery of the salt flat operations. However, if those resources were able to be cascaded into another process, or sold on the market, the overall resource efficiency of the brine extraction might be improved. This already occurs during lithium extraction at SQM with recovery of KCl and K_2SO_4 (SQM, 2022). By improving the recovery rates of water and solutes within the brine and cascading them into subsequent processes or products, economic value is created while achieving the minimization of waste and raw material extraction.

4.2.5 Efficiency, Scalability & Land Use

A fifth criterion should evaluate whether the extraction technology is able to process brines much faster than the current evaporative process, due to the fact it takes almost 24 months to create 1 ton of concentrated brine. While there are several technologies being developed, improved technologies must be able to handle large amounts of brine in a relatively quick manner in order to scale commercially (Flexer et al., 2018). Ideally, they should also be applicable and scalable in diverse locations which may have differing brine compositions because the incumbent evaporative process is really only applicable and scalable within the SdA and a few other locations (Flexer et al., 2018). Lastly, the land required for extraction operations should also be minimized as much as possible to improve land use efficiency and avoid encroachment on natural habitats. Although Guzmán et al. (2022) did not find a change in surface area of lagoon systems within the SdA despite increasing land use for lithium extraction, it is appropriately cautionary to limit the amount of land that is required for operations, especially since production capacity will need to be substantially increased and land cover is increasingly being changed for anthropogenic activities (Winkler et al., 2021).

4.2.6 Economic Feasibility

Lastly, the economic feasibility of a new technology is undeniably critical however, it is unlikely that many technologies will be able to achieve the economic effectiveness of the evaporative process. However, identifying technologies which may be more expensive but have the ability to use less land, recover more water, minimize chemical usage, cascade by-products into other processes and be readily applied to most regions may compensate for the increased cost. However, the scope of this research will not include an economic assessment of MCr for lithium extraction but is recommended for future research.

In conclusion, the criteria for an improved lithium extraction technique can be evaluated in terms of water use and recovery, energy usage, chemical usage, efficiency and circularity, scalability, land usage and economic feasibility.

4.3 Ex-Ante Life Cycle Assessment

This section presents the results of the LCA based on the chosen impact categories at a midpoint indicator level for 1 ton of Li_2CO_3 production. Section 4.4 discusses the results between Li_2CO_3 production via MCr which is compared to the brine inspissation route. Section 4.5 discusses the results between L Li_2CO_3 production via MCr using 100% solar PV which is compared to the brine inspissation route. Section 4.5 provides a brief comparison of the brine concentration technologies. Section 4.6 discusses PVDF impacts.

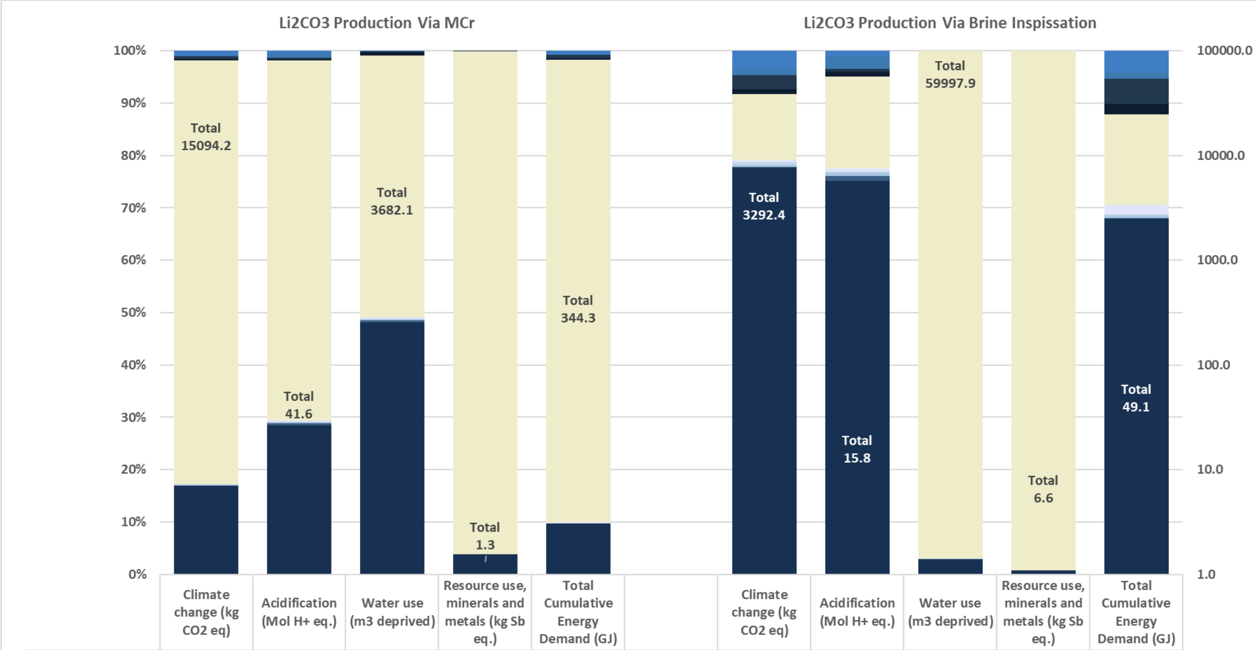
4.3.1 Li_2CO_3 via MCr vs. Li_2CO_3 via Brine Inspissation

Figure 4-3 displays the LCA results of comparing 1 ton Li_2CO_3 production.

4.3.1.1 Global Warming Potential & Cumulative Energy Demand

Producing 1 ton of Li_2CO_3 via MCr has a GWP of 15,094 kg CO_2 eq. per FU which is more than 4.5 times higher than producing it via brine inspissation which has a GWP of 3292 kg CO_2 per FU. This large increase is due to the fact that MCr uses much more electricity for brine production and the remainder of the GWP is due to the use of soda ash during the Li_2CO_3 processing. This is difference is also reflected in the total CED of the MCr route which is 344.3 GJ per FU which is 7 times higher than the brine inspissation route for Li_2CO_3.

Figure 4-3: LCA results comparing Li_2CO_3 production via MCr and brine inspissation.

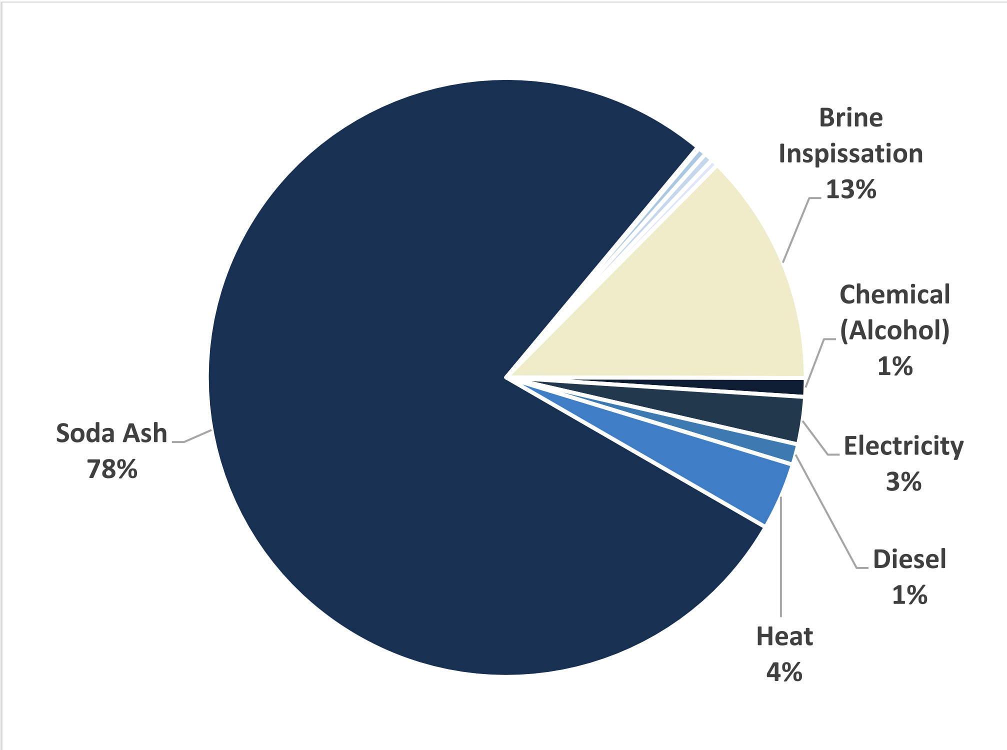


	Climate change (kg CO2 eq)	Acidification (Mol H+ eq.)	Water use (m3 deprived)	Resource use, minerals and metals (kg Sb eq.)	Total Cumulative Energy Demand (GJ)		Climate change (kg CO2 eq)	Acidification (Mol H+ eq.)	Water use (m3 deprived)	Resource use, minerals and metals (kg Sb eq.)	Total Cumulative Energy Demand (GJ)
Heat	119.4	0.2	3.5	0.0	2.1		119.4	0.2	3.5	0.0	2.1
Diesel	36.6	0.4	0.7	0.0	0.5		36.6	0.4	0.7	0.0	0.5
Electricity	84.2	0.1	6.0	0.0	2.4		84.2	0.1	6.0	0.0	2.4
Chemical (Alcohol)	33.2	0.1	22.1	0.0	1.0		33.2	0.1	22.1	0.0	1.0
Brine Production	12216.1	28.6	1844.6	1.3	303.6		414.3	2.8	58160.5	6.5	8.5
Organic Solvent	12.7	0.1	7.5	0.0	0.9		12.7	0.1	7.5	0.0	0.9
Lime	15.6	0.0	0.5	0.0	0.1		15.6	0.0	0.5	0.0	0.1
Hydrochloric Acid	14.8	0.1	12.9	0.0	0.2		14.8	0.1	12.9	0.0	0.2
Sulfuric Acid	3.0	0.1	11.2	0.0	0.1		3.0	0.1	11.2	0.0	0.1
Soda Ash	2558.7	11.9	1773.0	0.0	33.3		2558.7	11.9	1773.0	0.0	33.3
Total	15094.2	41.6	3682.1	1.3	344.3		3292.4	15.8	59997.9	6.6	49.1

Soda Ash · Sulfuric Acid · Hydrochloric Acid · Lime · Organic Solvent · Brine Production · Chemical (Alcohol) · Electricity · Diesel · Heat · Total

In the brine inspissation route for Li_2CO_3, the GWP contributions differ considerably which is shown represented in a pie chart in Figure 4-4 below. Since the GWP in the brine inspissation route is much lower, the relative contribution of other chemicals especially soda ash is much higher.

Figure 4-4: Pie Chart of GWP percentage contribution to Li_2CO_3 production via brine inspissation.



4.3.1.2 Water Use

Another important result is the magnitude of difference in water usage between the two production routes which was expected due to the aforementioned water recovery potential of MCr. Compared to the brine inspissation route which uses nearly 60,000 m^3 of water per 1 ton of Li_2CO_3, the MCr route uses about 3,700 m^3 of water which is nearly a 94% decrease in water consumption. However, this result is likely based on the modeling decision to allocate the recovered water as a water emission to water. This could change significantly if it was modeled as a co-product or re-injected into the salt flats.

4.3.1.3 Acidification Potential

In terms of acidification potential, the MCr route is approximately 2.7 times higher than the brine inspissation route. This is likely due to the PVDF membrane modules which require several chemicals for their manufacturing whereas the brine inspissation route does not use membranes and relies on solar energy for most of the brine production.

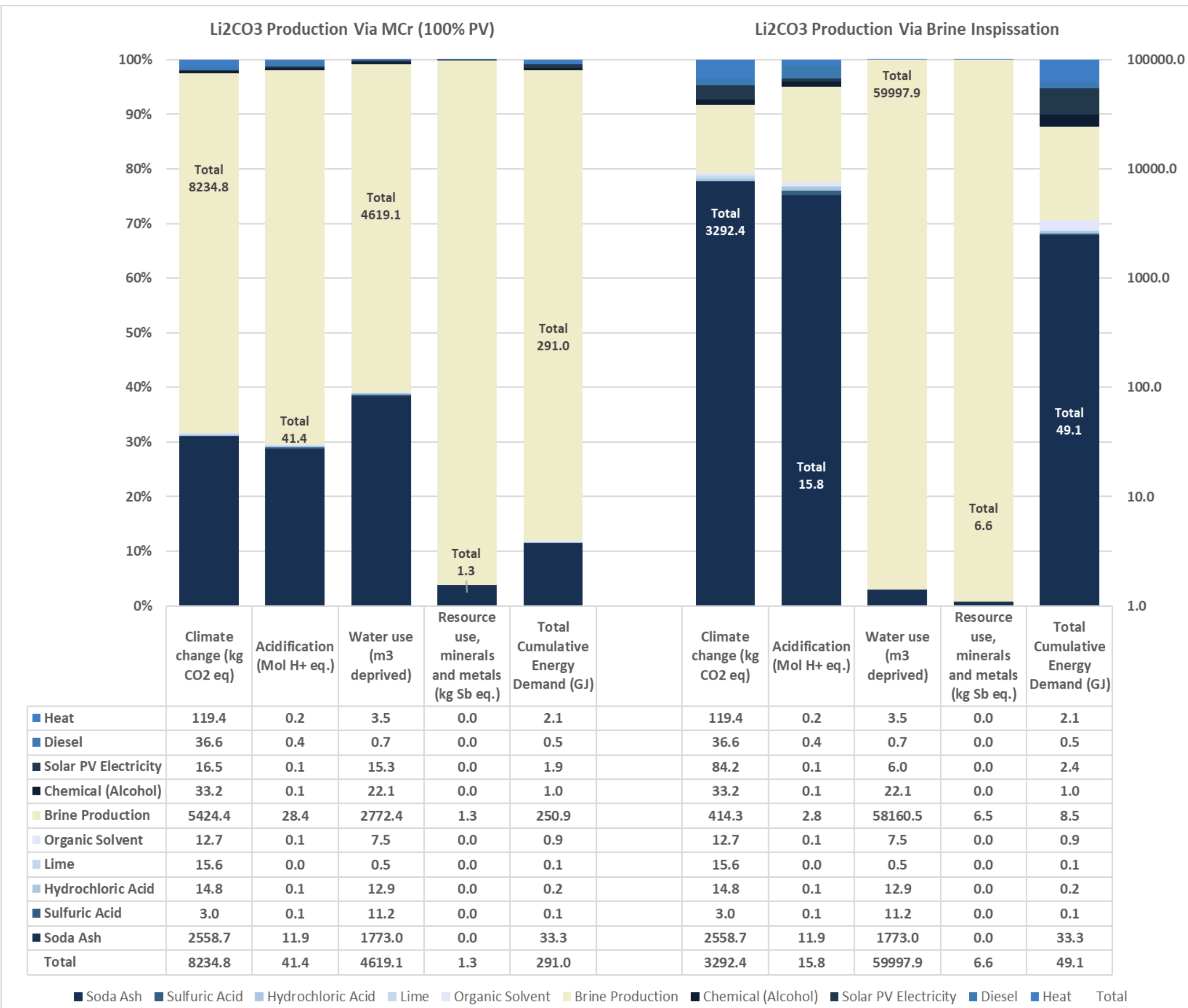
4.3.1.4 Resource Use (Metals & Minerals)

In terms of metal and mineral resource use, the brine inspissation route is 5 time higher which could be due to the fact that water is not recovered from the process at all. However, a more in-depth analysis in future research could determine theories why it is much larger than the MCr route. One potential reason is because the process modeling carried out at AMTC did not have calcium or sulfate in their model inputs which also meant that it was not included in the LCI for MCr brine production whereas for the brine inspissation process, calcium and sulfate are accounted for in the dataset by Kelly et al. (2021).

4.3.2 Li_2CO_3 via MCr with 100% solar PV vs. Li_2CO_3 via Brine Inspissation

This section provides the results of the sensitivity analysis which evaluates the MCr route for Li_2CO_3 production based on 100% solar PV for electricity input which is compared with the brine inspissation Li_2CO_3 production route in Figure 4-5.

Figure 4-5: LCA results comparing Li_2CO_3 production via MCr using 100% solar PV and brine inspissation.



	Climate change (kg CO2 eq)	Acidification (Mol H+ eq.)	Water use (m3 deprived)	Resource use, minerals and metals (kg Sb eq.)	Total Cumulative Energy Demand (GJ)		Climate change (kg CO2 eq)	Acidification (Mol H+ eq.)	Water use (m3 deprived)	Resource use, minerals and metals (kg Sb eq.)	Total Cumulative Energy Demand (GJ)
Heat	119.4	0.2	3.5	0.0	2.1		119.4	0.2	3.5	0.0	2.1
Diesel	36.6	0.4	0.7	0.0	0.5		36.6	0.4	0.7	0.0	0.5
Solar PV Electricity	16.5	0.1	15.3	0.0	1.9		84.2	0.1	6.0	0.0	2.4
Chemical (Alcohol)	33.2	0.1	22.1	0.0	1.0		33.2	0.1	22.1	0.0	1.0
Brine Production	5424.4	28.4	2772.4	1.3	250.9		414.3	2.8	58160.5	6.5	8.5
Organic Solvent	12.7	0.1	7.5	0.0	0.9		12.7	0.1	7.5	0.0	0.9
Lime	15.6	0.0	0.5	0.0	0.1		15.6	0.0	0.5	0.0	0.1
Hydrochloric Acid	14.8	0.1	12.9	0.0	0.2		14.8	0.1	12.9	0.0	0.2
Sulfuric Acid	3.0	0.1	11.2	0.0	0.1		3.0	0.1	11.2	0.0	0.1
Soda Ash	2558.7	11.9	1773.0	0.0	33.3		2558.7	11.9	1773.0	0.0	33.3
Total	8234.8	41.4	4619.1	1.3	291.0		3292.4	15.8	59997.9	6.6	49.1

4.3.2.1 Global Warming Potential & Cumulative Energy Demand

In terms of GWP, using 100% solar PV electricity for the MCr-Li_2CO_3 production results in approximately 8,325 kg CO_2 eq. per FU which is 2.5 times higher than the brine inspissation route per FU. Fortunately, it is an improvement compared to the MCr-Li_2CO_3 route that used the electricity mix modeled for 2030 because the 100% PV MCr-Li_2CO_3 route amounts to roughly half of the GWP potential that was observed previously. This is likely due to the fact that the MCr process is powered entirely by solar PV electricity which reduces the GWP of the process. The other improvement of the 100% PV MCr-Li_2CO_3 route compared to the MCr-Li_2CO_3 route is that there is 15% less CED per FU. However, the 100% PV MCr-Li_2CO_3 route still has a CED that is nearly 6 times higher than the brine inspissation- Li_2CO_3 production route.

4.3.2.2 Water Use

A trade-off observed in the results is the increased water use per FU for the 100% PV MCr-Li_2CO_3 compared to the original MCr-Li_2CO_3 route which is 4,619 m^3 of water per FU compared to 3,682 m^3. Fortunately, it is still a 93% decrease in water usage compared to the brine inspissation-Li_2CO_3 route. One potential reason why the water usage is higher because substantial amounts of water are needed to produce solar panels and their constituent components.

4.3.2.3 Acidification Potential

The acidification potential observed between the two technologies is predictably similar based on the fact that the only main difference was the change in electricity mix which had previously already been composed of 70% renewable sources. However, determining why a larger change was not observed could potentially be determined in future research.

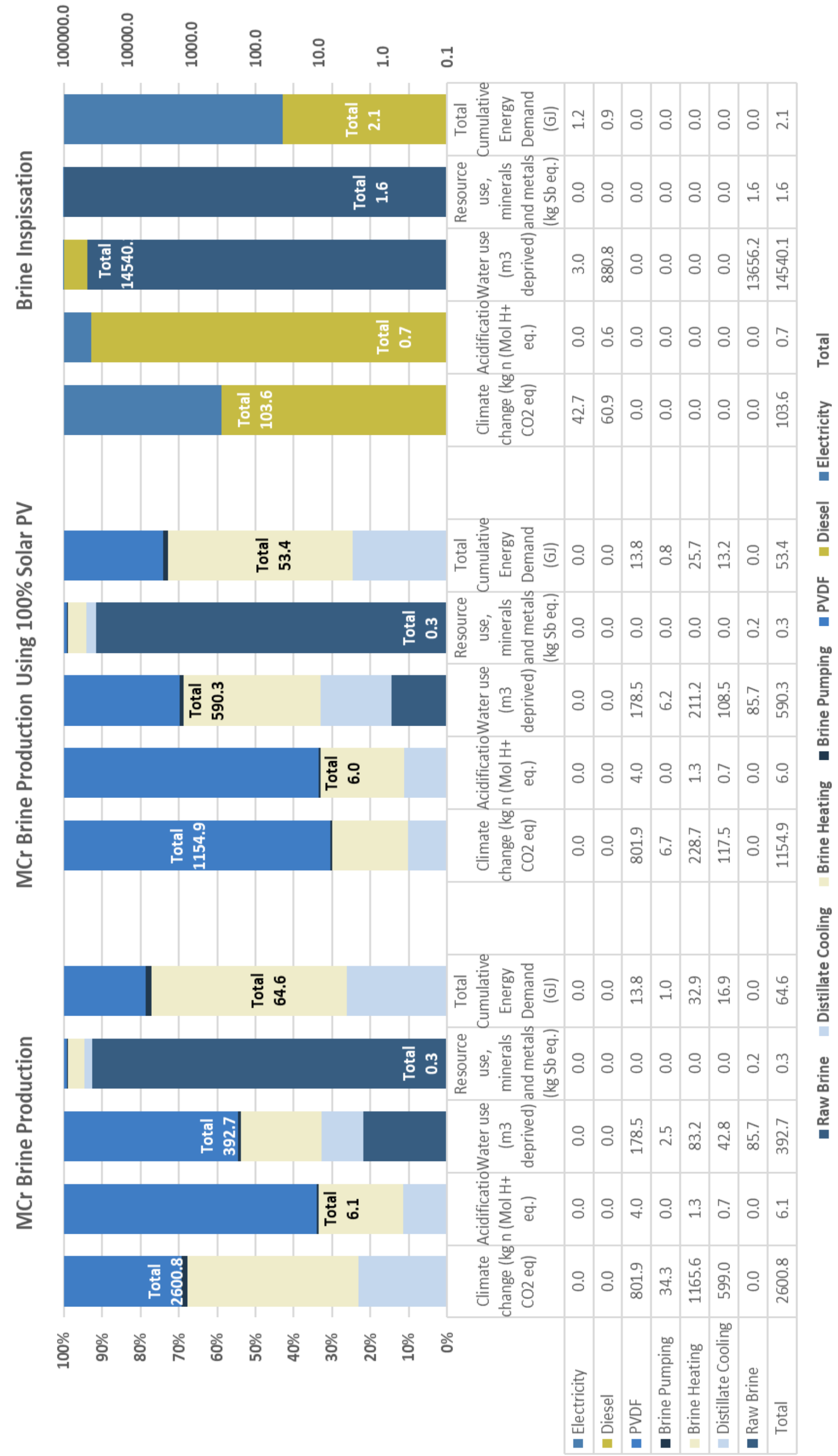
4.3.2.4 Resource Use (Metals & Minerals)

It would be reasonable to expect that more metals and minerals would be needed if the MCr-Li2co3 process relies on 100% PV because the solar panels and battery systems accompanied with them require ECEs and other elements. The result is confounding because it is the same as the previous comparison and therefore warrants deeper analysis in future research.

4.3.3 Brine Concentration Technology Comparison

This section aims to provide a brief overview of the main contributing factors to the environmental impacts observed in the two previous sections. To do so, all three brine concentrations are compared below in Figure 4-6 based on the impact categories previously discussed.

Figure 4-6: LCA Results of 1 ton brine production via three production routes.



MCr Brine Production

	Climate change (kg CO2 eq)	Acidification (Mol H+ eq.)	Water use (m3 deprived)	Resource use, minerals and metals (kg Sb eq.)	Total Cumulative Energy Demand (GJ)
Electricity	0.0	0.0	0.0	0.0	0.0
Diesel	0.0	0.0	0.0	0.0	0.0
PVDF	801.9	4.0	178.5	0.0	13.8
Brine Pumping	34.3	0.0	2.5	0.0	1.0
Brine Heating	1165.6	1.3	83.2	0.0	32.9
Distillate Cooling	599.0	0.7	42.8	0.0	16.9
Raw Brine	0.0	0.0	85.7	0.2	0.0
Total	2600.8	6.1	392.7	0.3	64.6

MCr Brine Production Using 100% Solar PV

	Climate change (kg CO2 eq)	Acidification (Mol H+ eq.)	Water use (m3 deprived)	Resource use, minerals and metals (kg Sb eq.)	Total Cumulative Energy Demand (GJ)
Electricity	0.0	0.0	0.0	0.0	0.0
Diesel	0.0	0.0	0.0	0.0	0.0
PVDF	801.9	4.0	178.5	0.0	13.8
Brine Pumping	6.7	0.0	6.2	0.0	0.8
Brine Heating	228.7	1.3	211.2	0.0	25.7
Distillate Cooling	117.5	0.7	108.5	0.0	13.2
Raw Brine	0.0	0.0	85.7	0.2	0.0
Total	1154.9	6.0	590.3	0.3	53.4

Brine Inspissation

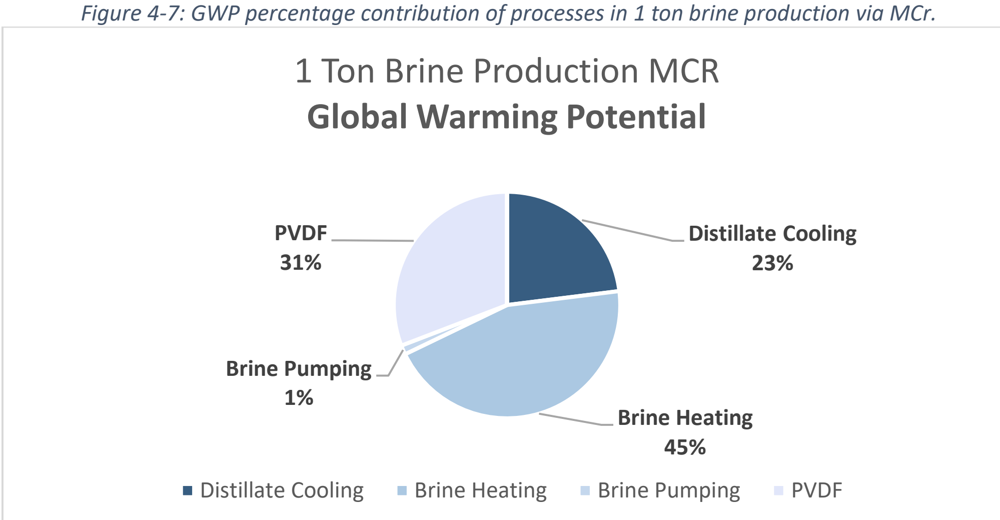
	Climate change (kg CO2 eq)	Acidification (Mol H+ eq.)	Water use (m3 deprived)	Resource use, minerals and metals (kg Sb eq.)	Total Cumulative Energy Demand (GJ)
Electricity	42.7	0.0	3.0	0.0	1.2
Diesel	60.9	0.6	880.8	0.0	0.9
PVDF	0.0	0.0	0.0	0.0	0.0
Brine Pumping	0.0	0.0	0.0	0.0	0.0
Brine Heating	0.0	0.0	0.0	0.0	0.0
Distillate Cooling	0.0	0.0	0.0	0.0	0.0
Raw Brine	0.0	0.0	13656.2	1.6	0.0
Total	103.6	0.7	14540.1	1.6	2.1

Based on Figure 4-6, several observations can be made about the different trade-offs in terms of impact categories. However, it should be noted that the brine inspissation brine is between 1 and 2 wt%. more concentrated and for that reason it was not chosen as the FU for the LCA study but this section hopes to provide some information about the different contributions to the impact category scores. A reminder that 4.697 tons of concentrated brine are used for 1 ton Li_2CO_3 in the MCr route and 4 tons of concentrated brine are used for 1 ton Li_2CO_3 in the brine inspissation route.

4.3.3.1 Global Warming Potential & Cumulative Energy Demand

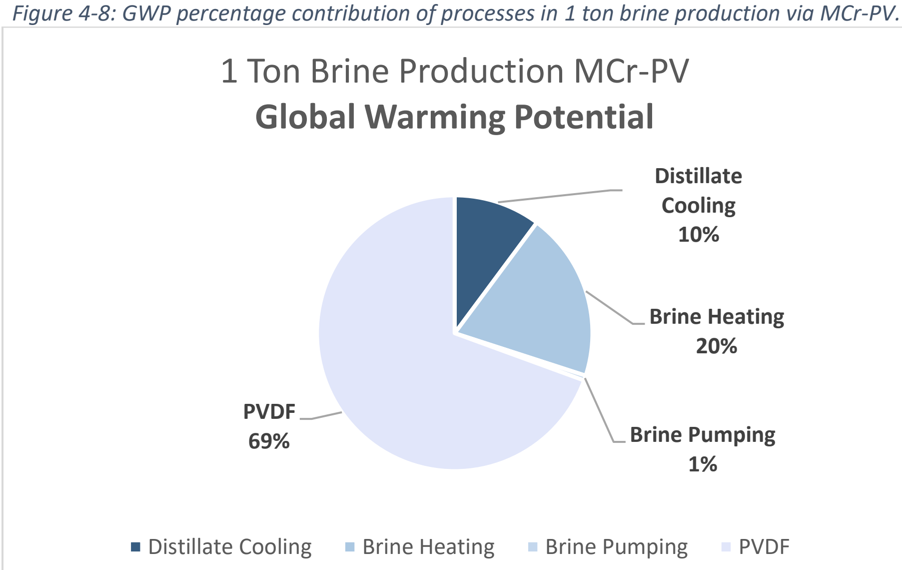
In the MCr route, the GWP is primarily due to the use of PVDF and brine heating. Figure 4-7 shows the percentage contribution of each process to the total GWP.

Figure 4-7: GWP percentage contribution of processes in 1 ton brine production via MCr.



However, in the 100% PV scenario, the GWP of the MCr brine production process has a slightly different percentage contribution which can be seen in Figure 4-8 below. This is due to the fact that the background electricity process for distillate cooling, brine heating and brine pumping rely on solar PV instead of the electricity mix for 2030.

Figure 4-8: GWP percentage contribution of processes in 1 ton brine production via MCr-PV.



The GWP for the brine inspissation process is 96% less than the MCr process and 90% less than the MCr-PV process because it does not require nearly as much energy. It is almost split evenly between electricity use and diesel use. The CED of producing 1 ton of lithium brine via brine inspissation is 2.1 GJ which is 96% less than the CED of MCr which is 64.6 GJ per 1 ton of lithium brine. The CED does not decrease significantly in the MCr-PV scenario but the GWP does due to the use of Solar PV.

4.3.3.2 Water Use

The water use results for producing 1 ton of concentrated brine are similar to the LCA results of 1 ton Li_2CO_3 production. The most water intensive route is brine inspissation which uses 14,540 m^3 per ton of brine produced which is approximately 25 times more than the amount needed for MCr-PV brine which is 590.3 m^3 per ton of brine. Compared to MCr using the electricity mix, which uses 392.7 m^3 per ton of brine, brine inspissation requires 37 times more water. Asides from the water loss from the raw brine extraction during inspissation, the other contributor to water usage is diesel. Figure 4-9 below shows the percentage contribution of water usage for producing 1 ton of brine via MCr.

Figure 4-9: m^3 water deprived percentage contribution of 1 Ton Brine Production MCr

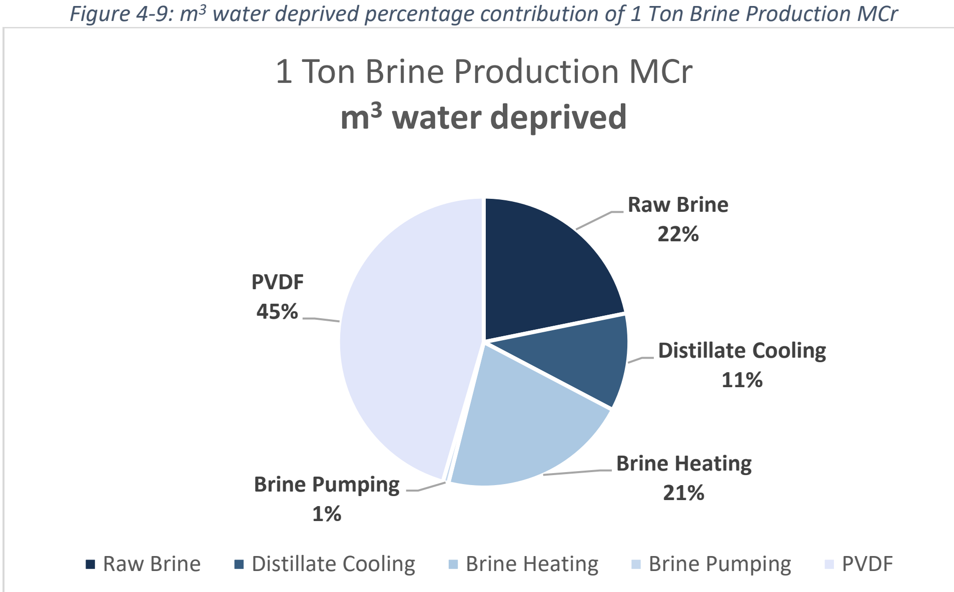
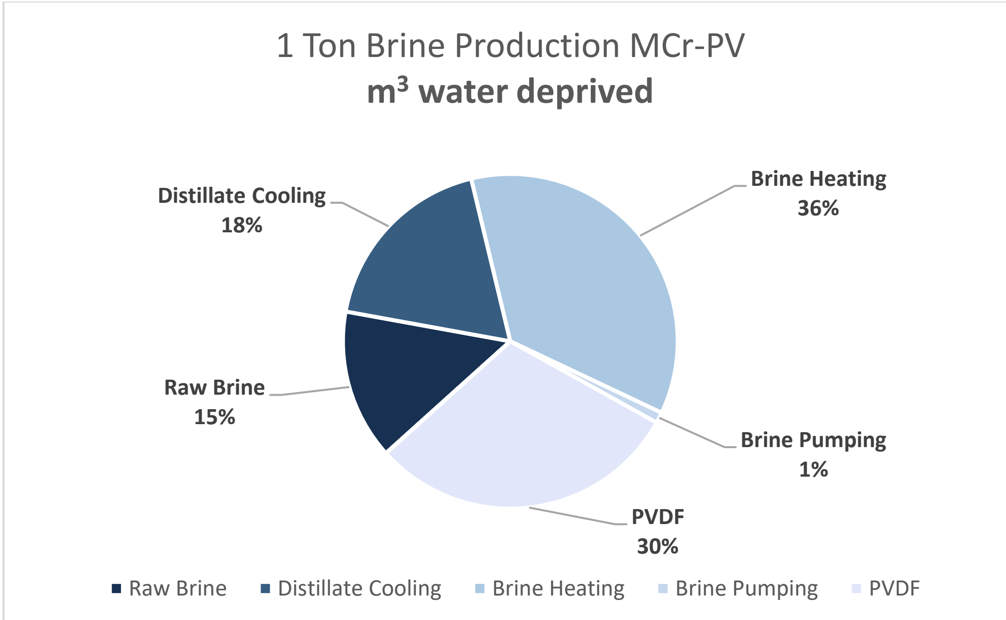


Figure 4-10 below shows the percentage contribution of water usage for producing 1 ton of brine via MCr-PV.



4.3.3.3 Acidification Potential

The acidification potential for both MCr technologies is the same based on PVDF use and brine heating which requires electricity. However, the acidification potential for brine inspissation is due to the use of diesel in their process.

4.3.3.4 Resource Use (Metals & Minerals)

The resource use is decidedly low per 1 ton of brine produced by MCr and MCr-PV and is slightly higher in the brine inspissation process. As previously theorized and based on the available data in this research, the resource use must be higher in brine inspissation because calcium and sulfate are included in the LCI.

5 Discussion

This section discusses the limitations of the research, implications related to the results of the research and the broader problem definition discussed in the beginning of the research. Recommendations for future and improved research are also given.

5.1 Limitations

5.1.1 Data Availability & Reliability

The most prominent limitation of this study is the lack of data availability and reliability. This is due to a few different reasons. First, the nature of ex-ante LCAs are characterized by a high degree of data uncertainty based on the fact that many of the processes have not been operational at a commercial or pilot level and therefore the data for LCIs are based on modeling, scaling or expert judgement. Moreover, usually a lab study like the one this research is based off of would first be further validated at pilot stage levels and move incrementally further towards a TRL 9 and MRL 10. In addition, not all processes and inputs are fully accounted for and gross assumptions are made which infer that the process will operate without any catastrophic failures or setbacks. In the case of this research, the main foreseeable setback is the data used in this research does not account for challenges associated with membrane fouling which is the most prominent reason membrane technologies are not as widely adopted yet. Another limitation pertains to the settling/separation stage where the crystal slurries are collected, however this was not modeled because the process engineering team had not yet determined how that process should be modeled or what it would consist of. In addition, there was not an indication what condition the potassium chloride produced would be in.

Yet another limitation was the fact that freshwater was modeled as waste to water when in fact, it could theoretically be modeled as a co-product, but AMTC was not entirely sure what the fate of the freshwater would be. This sentiment is also echoed in the academic community because no one is sure whether spent brines or water should be re-injected back into the salt flats. An additional limitation of the representativeness of the study is that potassium chloride was not credited to the system because a conservative approach was taken to allocate all environmental burdens to the lithium production. Another limitation of the study pertains to the lack of plant construction data and all of the infrastructure that would be required including pumps, pipes, valves, settlers, lighting, buildings, electronics, membrane cleaning etc. for the product system to be fully represented. In addition, the transportation was not accounted for MCr- Li_2CO_3production because an assumption was made that the Li_2CO_3 facility would be constructed next to the MCr facility in the SdA. In actuality, the LCI dataset for MCr brine production mainly focuses on foreground processes which is similar to Kelly et al. (2021)'s lithium brine and lithium carbonate processing datasets.

Another limitation of the study relates to how crystal output was modeled as salts in final emission flows. This was done because the constituent salt outputs did not exist in the ecoinvent database. Another major limitation of the study relates to the electricity mix that was modeled, the solar PV electricity process that was used and the modeling of the PVDF. The electricity mix was modeled with a coarse level of detail because the 70% renewable energy target set forth by the Chilean government cannot be modeled using datasets for Chile. Furthermore, many of the processes in Ecoinvent are already based on quite old, so to model electricity 5 years into the future, there is a lack of data representativeness. In addition, there are very few datasets for large scale solar PV electricity production besides concentrated solar tower production. Moreover, of the existing datasets for solar PV, most of them are for building integrated or residential use and very few options are available for Chile. That is why Argentina was chosen for the ground-mounted 570 kWp installation.

Alongside the electricity modeling and solar PV, battery usage was also not accounted for which is imperative for any large-scale renewable energy facility such as the one that would need to be constructed for the MCr facility. An attempt was made to collect datasets from Raugei et al. (2020) to determine what the environmental impacts would be of a utility scale solar PV field coupled with battery storage would be, but they could not be retrieved and were not available in supplementary materials.

The choice of plastic polymer for the membrane module also likely affects the LCA results significantly. For this research, PVDF was used in the LCI based on the membrane module that was modeled in the scale-up as well as a personal communication with the membrane manufacturer. However, there are several types of plastic polymers that can be used in membranes, each with their own trade-offs.

5.2 Literature Comparison

This section briefly compares the results of this LCA with other recent ex-ante LCA results for lithium extraction. Li et al. (2020) reports that to produce 1 ton of Li_2CO_3 via nanofiltration, 546. 51 tons of water were required. 546.51 tons of water per FU is much smaller than the brine inspissation route but the MCR-PV-Li_2CO_3 process requires about 10 times the amount of water as reported by Li et al. (2020) for producing 1 ton of Li_2CO_3. However, the nanofiltration approach presented by the authors report that 180.83 L, 59.35 L and 11.89 L of water are recovered in various stages throughout the process of producing 1 kg Li_2CO_3. Scaling these values to 1 ton Li_2CO_3 would equate to .25 m^3 recovered per 1 ton of Li_2CO_3. This value is 98% less than the water recovery potential that was reported in this research per ton of Li_2CO_3, which was 23.2 m3, based on Table 3-9. In terms of energy usage, Li et al. (2020) reports that 8674 kWh are required per 1 ton of Li_2CO_3 production which is very close to the electricity required via MCr. Since lithium rich brines exist in arid and water-scarce areas and the previous discussion, it seems that MCr may be more beneficial than nanofiltration due to the fact that MCr can recover much more freshwater per FU while still using the same amount of electricity.

The other ex-ante LCA for lithium technologies was published by Maria et al. (2022) however in this study they use a novel process to create 0.3 kg of lithium hydroxide and therefore this study will not be compared to theirs.

5.3 Recommendations

The recommendations of improving environmental impacts of brine inspissation and the lithium-water nexus in the SdA have already been discussed in Section 4.1. The recommendations for an improved lithium extraction process are also derived in Section 4.2 based on the improvement criteria. The remainder of recommendations in this research pertain to suggestions for improving future iterations of the LCA which are mainly based off of the limitations previously discussed. The main recommendation is to update the process model to include membrane fouling which will provide more representative data for the LCI. Additionally, it should also be determined what type of equipment will be used so that the LCI can also accurately reflect the entirety of the system process. Lastly, the electricity mix should be better modeled and the solar PV data could be dramatically improved if datasets are obtained from Raugei et al. (2020), or newly created. A final recommendation would be to conduct a techno-economic analysis alongside the next iteration of LCA for MCr as well as an energy-payback time study for the required solar PV field.

6 Conclusion

Based on the research conducted, the current understanding of the potential environmental implications of using MCr for lithium extraction coupled with a processing facility, is that the GWP is 4.5 times higher than brine inspissation per FU but when MCr and the lithium carbonate facility are using 100% solar PV, the GWP is only 2.5 times higher. However, the trade-off is that MCr can recover water and therefore there is an approximate 93% reduction in water usage per FU in the MCr-Li_2CO_3 route. In terms of CED, the MCr-Li_2CO_3 route is approximately 7 times higher than the brine inspissation route however if the MCr-Li_2CO_3 uses solar PV, the CED is reduced by 15%. The acidification potential of both of the MCr-Li_2CO_3 routes is nearly 3 times larger than the brine inspissation route which is likely due to the use of the PVDF membranes. This could potentially be reduced if green chemistry is used to manufacture membrane modules for MCr but further research is needed. One confounding aspect of this research was the metal and mineral resource use results, which were approximately 5 times higher for the brine inspissation route. The only explanation for this is the inclusion of calcium and sulfate in the LCI dataset for brine inspissation whereas the MCr dataset did not include it because it was not modeled in the scale-up and further research should be targeted towards understanding the confounding result.

In terms of modeled production output, the results show – assuming a MRL 10 – that an MCr-Li_2CO_3 facility could produce the equivalent of 100 kilotons of Li_2CO_3 and 76 kilotons of KCl per year which amounts to a 75% lithium recovery efficiency. The Li_2CO_3 and KCl output require the equivalent of 22 Mtons per year of raw brine however 64% of it is recovered as freshwater, amounting to 14.13 Mtons per year. The main benefit of this operation, which is also the main limitation of the brine inspissation process is the water recovery potential. Determining what should be done with the vast amount of freshwater that is recovered is a focus for further research however, it could be cascaded into the existing brine inspissation process which would thereby offset the freshwater withdrawal. Alternatively, it could potentially be used for irrigation in agricultural production in the area or provided as drinking water to local communities. Similarly, 4.14 Mtons of NaCl, 230 kilotons of $KMgCl_26H_20$ and 740 kilotons of $MgCl_26H_2O$ are recovered which could also be potentially cascaded into other processes to increase circularity however more research is needed to identify their potential use cases.

In terms of land use, the MCr-Li_2CO_3 facility would require approximately 50 km^2 to include the MCr facility, processing facility and utility-scale solar field. However, this value should be taken with a degree of uncertainty and could likely increase or decrease by 10%. Due to the method used for LUI and production intensity, the LUI for MCr is greater than brine inspissation but has a smaller production intensity. However, different methods for estimating LUI of the SQM operations would sharpen the results.

In conclusion, based on the results of this research, MCr provides an alternative to the current brine inspissation process with the capability of providing an additional 100 kilotons per year of Li_2CO_3 while achieving an exceptional water recovery rate compared to brine inspissation. However, the main limitation is the GWP associated with the process. Based on the reviewed criteria for improved lithium extraction techniques and current environmental impacts of brine inspissation, this result indicates that MCr is an emerging technology for lithium extraction that is worth further research due to its significant potential for water recovery.

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8 Appendix

8.1 Native Brine Composition

Elemental Composition of Brine				
Element	**Value**	**Unit**	**Value**	**Unit**
Na	7.66	wt%	2.78	t
Ca	0	wt%	0.00	t
K	2.12	wt%	0.77	t
Mg	0.96	wt%	0.35	t
Li	0.15	wt%	0.05	t
Cl	15.97	wt%	5.79	t
So	0	wt%	0.00	t
B	0.06	wt%	0.02	t
Total Molality	6.14	(mol salt, kg h20)	2.23	t
		Total Mass of Solutes	**11.99**	
		Total Mass of Water	**24.27**	

8.2 Membrane Module Specifications

Notes	Parameter	Unit	Value
module specification	Membrane module model	DDPT-BQ-10-20Z	
module specification	Membrane inner diameter	mm	1.3/2.3
module specification	Membrane area inside	m^2	20
module specification	Membrane pore size	µm	0.2
module specification	Module length	m	1,43
operational criteria	Feed brine circulation	lumen	lumen
operational criteria	Distillate flow circulation	shell	shell
operational criteria (must fit to the manufacturer range)	Feed brine flow	L/h	[variable]
operational criteria (must fit to the manufacturer range)	Distillate flow	L/h	[variable]
operational criteria (must fit to the manufacturer range)	Feed Temperature of brine input module	°C	50
	Feed Temperature of brine outlet module	°C	40
	Feed Temperature distillate input module	°C	20
operational criteria (must fit to the manufacturer range)	Feed Temperature distillate output module	°C	[variable]
Assumption	Water concentration of distillate	%	100

8.3 Electrical Efficiencies and Coefficient of Performance

Assumption	COP (refrigeration performance)	-	5
Assumption	Efficiency of the electric Pump	%	80
Assumption	Efficiency of the electric heating	%	100
Assumption	Efficiency of the Heat Recovery	%	60

8.4 Chilean High Voltage Mix (Ecoinvent)

Inputs from technosphere: electricity/heat	Amount	Unit
Electricity, high voltage {CL}| electricity production, deep geothermal | Cut	0.0008762817	kWh
Electricity, high voltage {CL}| electricity production, hard coal | Cut-off, U	0.4318344715	kWh
Electricity, high voltage {CL}| electricity production, hydro, run-of-river | Cu	0.3178432893	kWh
Electricity, high voltage {CL}| electricity production, natural gas, combined	0.1124351651	kWh
Electricity, high voltage {CL}| electricity production, natural gas, conventior	0.0692098347	kWh
Electricity, high voltage {CL}| electricity production, oil | Cut-off, U	0.0132467382	kWh
Electricity, high voltage {CL}| electricity production, wind, <1MW turbine, c	0.0008581993	kWh
Electricity, high voltage {CL}| electricity production, wind, 1-3MW turbine,	0.0517531501	kWh
Electricity, high voltage {CL}| heat and power co-generation, biogas, gas e	0.0001450195	kWh
Electricity, high voltage {CL}| heat and power co-generation, wood chips,	0.0017978502	kWh
Electricity, high voltage {CL}| market for | Cut-off, U	0.0221473542	kWh

8.5 LCI Dataset for Producing 1 kg PVDF (Route 1) (adapted from Hu et al., 2022)

Table 4. Summary of LCI Data to Produce 1 kg of PVDF (Route 1)

process	reactants	amount (kg)	materials	database	amount (kg)	electricity (kW h)	data source
Route 1: synthesis of PVDF	R-132b	2.170	trichloroethylene	Ecoinvent 3	2.17	7.5516	stoichiometric calculations based on the study.[63]
			hydrogen fluoride	Ecoinvent 3	1.085		
			ultrapure water	Ecoinvent 3	0.217		
	hydrogen	0.13		Ecoinvent 3		30	stoichiometric calculations based on the study.[62]
	tri-isobutyl borane	0.1	butene	Ecoinvent 3	0.4782	12	stoichiometric calculations are based on the study of organometallic polymerization.[61] For the initiator, the calculations are based on the study.[67]
			decarbonized water	Ecoinvent 3	0.1536		
			sodium tetrahydridoborate	Ecoinvent 3	0.1		
			acetic acid	Ecoinvent 3	0.1		

Table 5. Summary of LCI Data to Produce 1 kg of PVDF (Route 2)

process	reactants	amount (kg)	materials	database	amount (kg)	electricity (kW h)	data source
Route 2: synthesis of PVDF	VDF	1.0652	activated carbon	Ecoinvent 3	0.1065	1.3097	stoichiometric calculations based on the study.[64]
			HFC-152a	Ecoinvent 3	1.0993		
			chlorine	Ecoinvent 3	25.9493		
			copper	Ecoinvent 3	0.0107		
			palladium	Ecoinvent 3	0.0001		
			nitrogen	ELCD	0.1332		
			hydrogen	Ecoinvent 3	0.2663		
			potassium hydroxide	Ecoinvent 3	0.0053		
			ultrapure water	Ecoinvent 3	0.0479		
			cadmium sulfate	Ecoinvent 3	0.1065		
	di-*tert*-butyl peroxide (DTBP)	0.0084	hydrogen peroxide	Ecoinvent 3	0.02107	0.00249	stoichiometric calculations based on the study.[68]
			sulfuric acid	Ecoinvent 3	0.01704		
			butene	Ecoinvent 3	0.0149		
			decarbonized water	Ecoinvent 3	0.0048		
			sodium hydroxide	Ecoinvent 3	0.00285		
			ultrapure water	Ecoinvent 3	0.04554		
			magnesium sulfate	Ecoinvent 3	0.00475		
	ultrapure water	3.0458		Ecoinvent 3		12.3691	stoichiometric calculations based on the study.[69]
	wax	0.0017		Ecoinvent 3			

8.6 Outlet Brine Composition

Outlet Brine Composition (%)	Ion
.0009	Na+
.002	K+
9.96	Mg+2
4.06	Li+
0	Ca+2
1.62	B+3
0	SO4-2
49.82	Cl-