



## Full Length Article

## Sustainable process design for lithium recovery from geothermal brines using chemical precipitation

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## ABSTRACT

Lithium demand is surging, necessitating efficient extraction methods. Geothermal brines offer a promising alternative feedstock, yet comprehensive systems-level analyses are lacking. We developed an industrial process model for a plant processing 2000 ton/h geothermal brine using chemical precipitation to produce lithium carbonate, coupled with techno-economic and life cycle assessments to evaluate process economics and environmental impacts. A novel recycling process for on-site reuse of precipitating agents is also proposed, increasing total investment cost by 23% while reducing CO<sub>2</sub> emissions by nearly 50% without extending the payback period. Additionally, we investigated the impact of feedstock concentration and water costs on process economics. Our findings show that low-concentration lithium brines (less than 200 mg/L) are economically viable only at high lithium carbonate selling prices. This study highlights the potential of geothermal brines as a sustainable lithium source and the benefits of integrating recycling processes to mitigate environmental concerns.

## 1. Introduction

The widespread electrification of various sectors plays a pivotal role in reducing carbon dioxide (CO<sub>2</sub>) emissions and combating climate change. In particular, nearly one-third of all greenhouse gas emissions (GHGs) in the United States come from the transportation sector, where roughly 200 billion gallons of gasoline are consumed annually (Soeder, 2022; Najafi et al., 2023; Verma et al., 2020). Electric vehicles (EVs) offer a solution by replacing conventional fossil fuel-powered vehicles with electric-powered ones, thereby mitigating GHG emissions (Su et al., 2022). Projections indicate a tenfold growth in the global EV market by 2030, with an anticipated sale of approximately 25.8 million EVs based on the International Energy Agency's stated policies scenario or 46.8 million EVs based on the sustainable development scenario (IEA, 2021). This projected growth is also expected to drive the lithium demand, an essential ingredient in battery storage systems, with an estimated amount of 3.3 million metric tons of lithium carbonate equivalent by 2030 (Kim et al., 2019; Azevedo et al., 2022). According to the United States Geological Survey's (USGS) 2023 report, approximately 80% of the global lithium supply is allocated for battery usage (U.S. Geological Survey, 2023), reflecting lithium's crucial role in lithium-ion batteries as well as its significant demand across diverse

industries, including light aviation alloys, glass production, catalyst manufacturing, cosmetics, and the nuclear industry (Xie and Lu, 2020; Tarascon, 2010; Nikkhah et al., 2023b; Kudryavtsev, 2016; Schenker et al., 2024). This substantial demand and usage of lithium drive the exploration of diverse resources to meet the growing need for lithium.

Lithium can be obtained from various sources, including ores, brines, and seawater. Although the oceans contain a vast reserve of approximately 231.4 trillion tons of dissolved lithium, its low concentration of about 0.178 mg/L (Song et al., 2017; He et al., 2020) renders lithium recovery from seawater economically nonviable. Therefore, lithium is currently only mined from hard rock ores (e.g., spodumene and lepidolite) and continental brines (e.g., salt lakes) (Vera et al., 2023; Zhang et al., 2019), with brines accounting for 61.8%, and minerals for 25% of the total resources (Meinert et al., 2016; Xu et al., 2021a; He et al., 2020). Based on the recent report of USGS (U.S. Geological Survey, 2023), approximately 98 million tons (Mt) of lithium resources are available globally, however, only 26 Mt of them are accessible for extraction (U.S. Geological Survey, 2023). Furthermore, with the rising environmental concerns over ore and salt lake brine processing, as well as these conventional feedstocks being concentrated in specific

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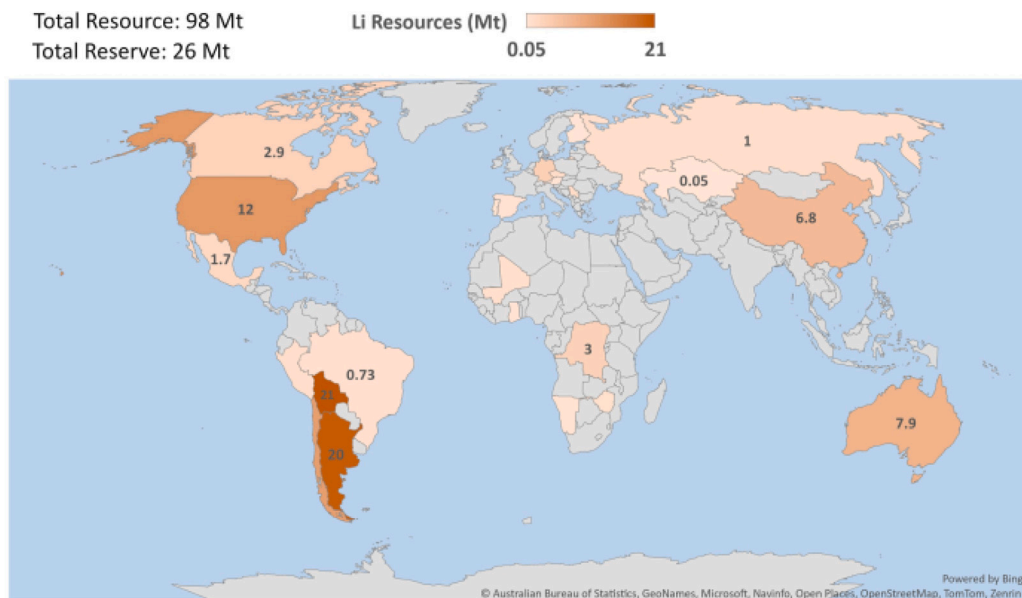


Fig. 1. Lithium resources around the world based on data from U.S. Geological Survey (2023).

geographical regions of the world (Fig. 1), there is a growing interest in the United States to extract lithium from unconventional sources such as geothermal brines found along the West coast, specifically in California and Nevada (Huang et al., 2021).

Geothermal brine is an emerging resource, delivering both renewable energy and essential minerals from a single operation. These hot saline solutions from the subsurface Earth generate electricity by turning turbines when pumped to the surface. They are also rich in minerals as the hot fluids circulating through mineral-bearing rock formations dissolve minerals and metals into the solution. High quantities of lithium (up to 100–1000 mg/L) (Khalil et al., 2022; Tabelin et al., 2021; Ventura et al., 2020), along with other valuable minerals like boron and potassium, make geothermal brines a desirable feedstock for lithium recovery (Office, 2021; Richter, 2021). Consequently, the United States Department of Energy recognized California's Salton Sea region as a domestic lithium resource in November 2023 (Dobson et al., 2023).

Membrane, solvent extraction, adsorption, and chemical precipitation are some of well-known lithium extraction methods for various kinds of brines (Nikkhah et al., 2024a). Among them, chemical precipitation (Zhang et al., 2019; Linneen et al., 2019; Alsabbagh et al., 2021; Battaglia et al., 2022; Lai et al., 2020; Grágeda et al., 2018) stands out as one of the well-known recovery methods, where the desired ionic components are separated from brine by decreasing their solubility through the addition of counter-ions. This approach is especially favored in industrial-scale facilities due to its simplicity, affordability, and scalability (Galhardi et al., 2022; Zhang et al., 2019; Alawa et al., 2022). The aim of chemical precipitation is to produce high-purity lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) or lithium hydroxide ( $\text{LiOH}$ ) (Sun et al., 2021; Liu et al., 2019). For battery applications, the final  $\text{Li}_2\text{CO}_3$  product should have a purity greater than 99.5 wt%, whereas, in the case of thermal nuclear systems, this goes up to 99.9 wt%. Hence, purification technologies play an important role in determining the suitability of the lithium compounds for their intended end uses (Linneen et al., 2019).

Various studies have explored the use of chemical precipitation to recover lithium using different types of precipitants (Grágeda et al., 2018; Battaglia et al., 2022; Lai et al., 2020; Nikkhah et al., 2024b; Stringfellow and Dobson, 2021; Paranthaman et al., 2017). Grágeda et al. (2018) used chemical precipitation to produce battery-grade lithium from lithium-concentrated brine on the lab scale. Their findings demonstrated efficient removal of  $\text{Ca}^{2+}$  (98.93%) and  $\text{Mg}^{2+}$  (99.93%).

In addition, advancements in precipitation methods, demonstrated in the studies conducted by Lai et al. (2020) and Battaglia et al. (2022), contributed to the enhancement of lithium extraction processes. These developments present potential opportunities for enhancing the effectiveness of large-scale operations. Lai et al. (2020) suggested a new crystallization-precipitation process for extracting lithium from salt lake brine with a high Mg/Li mass ratio.

The efficiency of  $\text{Mg}^{2+}$  removal was 99.6%, while the recovery rate of lithium was 93.2%. Battaglia et al. (2022) used  $\text{Na}_2\text{CO}_3$  and a gas-to-liquid ( $\text{NaOH}$ - $\text{LiCl}$ ) system where  $\text{Li}^+$  was precipitated using homogeneous and heterogeneous crystallization methods. The approach proved to be highly efficient, yielding high levels of lithium recovery (about 70%) and  $\text{Li}_2\text{CO}_3(\text{s})$  purity (around 80%). Stringfellow and Dobson (2021) also emphasized the efficiency of aluminum salts in extracting lithium from geothermal water by inducing lime precipitation. Paranthaman et al. (2017) successfully attained a recovery efficiency of around 91% for lithium from geothermal brine by utilizing lithium-aluminum layered double hydroxide chloride sorbents. The readers are further guided to notable review papers (Farahbakhsh et al., 2024; Vera et al., 2023; Zhang et al., 2023, 2019; Nikkhah et al., 2024b) to delve into the significance of chemical precipitation for lithium recovery.

While these studies have explored different precipitating agents and methods for lithium recovery from brine on the lab scale, most of these studies were only focusing on the specific part of the lithium recovery process (e.g., divalent ion removals such as  $\text{Mg}^{2+}$ , or removal of impurity such as boron). There are a few studies to show the full processes and steps to recover lithium. Moreover, there is a lack of in-depth process modeling and economic and environmental evaluations of the lithium recovery process. Integrating techno-economic assessment (TEA) and life cycle analysis (LCA) into assessing lithium recovery processes is crucial for understanding their economic feasibility and environmental impact. Although some studies look into environmental impact assessment of lithium recovery (Halkes et al., 2024; Mousavinezhad et al., 2024; Khakmardan et al., 2023) or techno-economic assessment of lithium recovery (Warren, 2021; Huang et al., 2021), these studies are still limited to lab-scale, and the details of the modeling approach have not been described completely.

Additionally, well-documented challenges in lithium recovery from brine, such as high water consumption, energy intensity, environmental impacts, and production costs, prompt key inquiries (Murodjon

et al., 2020; Linneen et al., 2019). Leveraging process system engineering expertise allows us to construct comprehensive process models for brine-based lithium recovery and address these critical queries. Therefore, synthesizing existing knowledge and proposing a framework for process modeling and economic and environmental analysis, this study seeks to develop the first end-to-end digital twin of a large-scale sustainable lithium production process from geothermal brines using chemical precipitation. This technique is used for final product recovery and purification from undesired divalent ions. Techno-economic and life cycle assessment of the proposed process is also performed to assess its economic viability as well as its environmental impacts, along with a detailed sensitivity analysis to characterize the effects of internal and external factors, such as the initial lithium concentration, water cost, and  $\text{Li}_2\text{CO}_3$  sale price on the process economics. Furthermore, we explore the potential benefits of on-site production of the chemical precipitating agent, aiming to enhance both the sustainability and cost-effectiveness of the process.

## 2. Methodology

### 2.1. General assumptions and modeling approach

For our analysis, we selected a geothermal brine from the Salton Sea well with the following composition given in Table C.1 (Ventura et al., 2020; Warren, 2021; Tabelin et al., 2021). SuperPro Designer® V13.02 (Intelligen, Inc., USA) is used to simulate the process with the following assumptions:

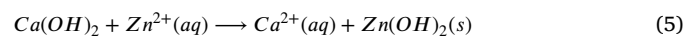
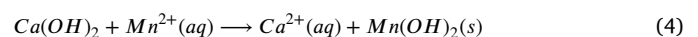
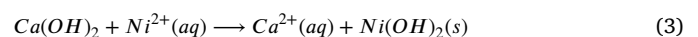
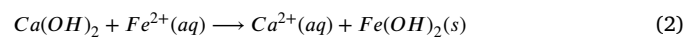
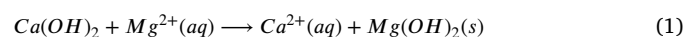
- All components of the process operate at steady-state.
- Input brine feedstock flows at 2000 mt/h.
- The process aims to produce battery-grade  $\text{Li}_2\text{CO}_3$  (99.5 wt%) (Linneen et al., 2019; Perez et al., 2014).
- We assume that 70% of water in brine is evaporated in solar ponds.
- We assume that effect of organic matter on the precipitation process is negligible, therefore not considered in the modeling.

### 2.2. Process description: Chemical precipitation

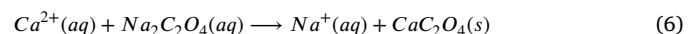
In this study, we employed chemical precipitation to recover solid lithium from brine as well as for purification of divalent ions in the pre-processing steps. Precipitation is a versatile and essential technique in the lithium extraction process, commonly utilized for purification and the removal of divalent ions, as well as for the production of solid lithium compounds. Specifically, we used lime ( $\text{Ca}(\text{OH})_2$ ) and sodium oxalate ( $\text{Na}_2\text{C}_2\text{O}_4$ ) to effectively precipitate and eliminate divalent ions from the brine. It is important to note that the choice of precipitation method, such as the use of lime, is highly dependent on the chemical composition of the brine being processed. Since not all brines are alike, the method must be carefully tailored to effectively remove specific impurities present in each brine.

The process begins with the extraction of geothermal brine from the well (Fig. 2). After being utilized in the geothermal plant to recover its energy and produce electricity, it is sent to solar evaporation ponds, where solar energy is harnessed to evaporate water, leading to the natural concentration of the brine solution. As the salt concentration reaches its saturation point, crystallization occurs, resulting in the formation of salt crystals, including NaCl and KCl. Solar ponds require large pieces of land, especially when they are designed to be shallow (Loganathan et al., 2017). Similar to the Cauchari-Olaroz project (Chagnes and Swiatowska, 2015; Tran and Luong, 2015), we assume a pond with specific dimensions (9000  $\text{m}^2$  in area and 1 m in depth) to handle a brine flow rate of 2000 mt/h. The solar pond helps to remove NaCl and other salts such as KCl, which can be considered for revenue generation (Boryta et al., 2011). Following the concentration of brine, the next step involves boron removal, and we use a process based on

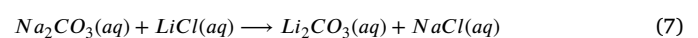
the method described in the work by Xu et al. (2021b). This technique utilizes monohydric alcohols to extract boron from the brine using a three-stage counter-current extraction process. The process involves the use of an organic solution containing 2.5 M isodecanol. Under specified conditions, the extraction of boron reach a rate of 99.07%, and water is employed as a stripping agent to recover the solvent. The effluent stream then proceeds to the first precipitation stage (Pr 1) to remove  $\text{Mg}^{2+}$  and other ions such as  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$  (Chagnes and Swiatowska, 2015; Karidakis et al., 2005; An et al., 2012). Lithium recovery processes face difficulties with handling large quantities of magnesium as it needs to be recovered as a by-product to enhance the economic efficiency of the process while minimizing the loss of lithium. Magnesium can be extracted by precipitating it as  $\text{Mg}(\text{OH})_2$  using dolime ( $\text{CaO} \cdot \text{MgO}$ ) or hydrated lime ( $\text{Ca}(\text{OH})_2$ ) (Chagnes and Swiatowska, 2015). In our study,  $\text{Ca}(\text{OH})_2$  is used as a precipitating agent. This chemical agent was also applied for Mg recovery from Uyuni salar brine (An et al., 2012). The following precipitation reactions take place in this part:



Following the precipitation stage, the process proceeds to a thickener (Th 1) designed to dewater and concentrate the solid. After that, the bottom output of the thickener is sent to the belt filter (F 1) to separate hydroxide solids (Viadero Jr. et al., 2006). The outlet-treated stream is sent back to the reactor as it contains LiCl. This recycling would help to avoid large lithium loss. Meanwhile, the clarified stream from the thickener is directed to the second precipitation stage (Pr 2), where we use sodium oxalate ( $\text{Na}_2\text{C}_2\text{O}_4$ ) to remove and precipitate  $\text{Ca}^{2+}$  with Reaction (6).  $\text{Na}_2\text{C}_2\text{O}_4$  is also previously used for removing  $\text{Ca}^{2+}$  from brine and seawater (Linneen et al., 2019; Natasha and Lalasari, 2017).



Similar to the previous precipitation stage, a thickener and filter are used to separate calcium oxalate ( $\text{CaC}_2\text{O}_4$ ). The treated stream from the thickener goes to the third precipitation step (Pr 3) where conversion of LiCl to  $\text{Li}_2\text{CO}_3$  happens. The reaction temperature is 80°C (Khalil et al., 2022).



The next step is the crystallization of  $\text{Li}_2\text{CO}_3$ . The crystallization yield is assumed to be 40%, and 60% of water is evaporated. With such an evaporation rate, the concentration of  $\text{Li}_2\text{CO}_3$  12 g/L of water, corresponding to 20%–30% supersaturation at 60–80°C which results in residual solution of 8g/L of  $\text{Li}_2\text{CO}_3$  (Cheng et al., 2013). Finally, the obtained product goes through vacuum filtration (VF) to separate solid  $\text{Li}_2\text{CO}_3$ , followed by a rotary dryer (RD) to remove water and get pure  $\text{Li}_2\text{CO}_3$ . The final purity of  $\text{Li}_2\text{CO}_3$  is designed to be 99.5%, making it suitable for battery applications, a goal that has been achieved in various studies through chemical precipitation (Perez et al., 2014; Linneen et al., 2019). Table C.2 summarizes the responsibility of different unit operations during the process.

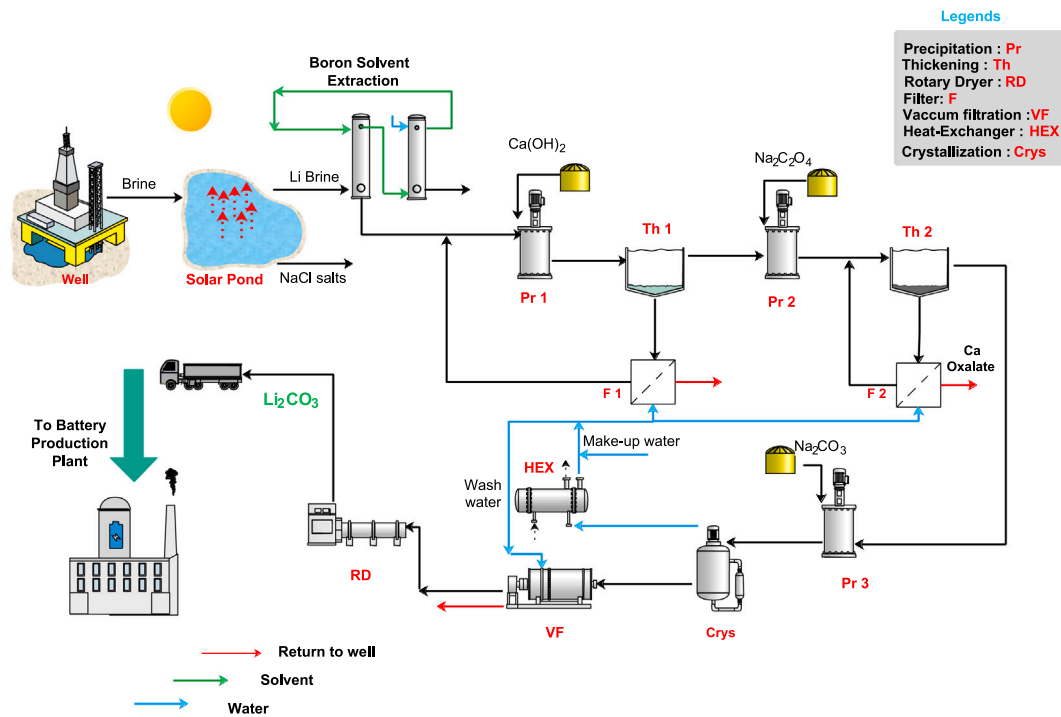


Fig. 2. Process flowsheet of lithium recovery from geothermal brine.

### 2.3. Techno-economic assessment (TEA)

The SuperPro Designer V13.02 is used to size the equipment and calculate the costs. The expenses for utilities such as electricity (measured in kilowatt-hours) and water (measured in cubic meters) are determined based on the fees set by the public utility companies for the industrial sector. We meticulously assessed raw material expenses, analyzed product pricing strategies, and conducted thorough supplier quote reviews and online research to ensure our pricing was accurate. Buildings and equipment were subject to the straight-line method of depreciation for 12 years (Gómez et al., 2020; Nikkhah and Beykal, 2023). We also performed sensitivity analysis on the price of  $\text{Li}_2\text{CO}_3$ , which ranged from \$5/kg to \$85/kg. This wide range is selected because of the fluctuations seen in its pricing in the last two years (Anon, 2024). The details of the techno-economic analysis are provided in Appendix A.

### 2.4. Life cycle analysis (LCA)

International standard life cycle assessment techniques (ISO14040:2006) are used to conduct the LCA for the lithium recovery process (International Organization for Standardization, 2006; Nikkhah et al., 2023a). We perform cradle-to-gate LCA (Fig. B.2) using SIMAPRO version 9.4.0.2 with ecoinvent 3.8 database (Kallitsis et al., 2022; Zalazar-Garcia et al., 2022) and Environmental Footprint 3.0 impact assessment method (Castellani et al., 2021). In our analysis, 16 impact categories, including climate change, ozone depletion, land use, water use, resource use (fossil fuel, mineral, and metals), eutrophication (marine), eutrophication (freshwater), eutrophication (terrestrial) acidification, human toxicity (cancer and non-cancer), photochemical ozone formation, particulate matter, ionizing radiation and ecotoxicity are assessed.

### 2.5. Performance metrics

To evaluate our performance metrics, we measured the lithium recovery rate across the entire process, from raw material to final

product. In this context, the term ‘recovery rate’ refers to the efficiency of the process in converting lithium from brine, which is initially in the form of  $\text{LiCl}$ , to the final product,  $\text{Li}_2\text{CO}_3$ . The following equation illustrates the calculation of this recovery rate.

$$\text{Recovery Rate} = \left( \frac{\text{Mass of Li produced}}{\text{Total Li in brine}} \right) \times 100 \quad (8)$$

## 3. Results and discussion

### 3.1. Base case results

#### 3.1.1. LCA and TEA results

Table C.3 presents the key findings of the base case design with a feed flowrate of 2000 mt/h and an initial concentration of 500 mg/L  $\text{Li}^+$  in brine. The plant has a capacity of producing 4.02 mt/h (equivalent to 31,680 mt/yr) of battery-grade  $\text{Li}_2\text{CO}_3$ . The lithium recovery process in our study demonstrated an acceptable recovery rate, achieving a recovery rate of 75.8%. This result not only underscores the effectiveness of our methodology but also aligns closely with findings from other investigations employing chemical precipitation techniques (Garcia et al., 2023; Liu et al., 2021; Nikkhah et al., 2024a; Yang et al., 2012). Liu et al. (2021) used facet engineered  $\text{Li}_3\text{PO}_4$  and they were able to recover 51.62% of lithium from brine. Yang et al. (2012) were able to achieve recovery rate of 75% using  $\text{Al}(\text{OH})_3$  precipitant. In terms of economic factors, the investment cost of the process is approximately \$1.354 billion, a figure that aligns with the investment costs of other lithium recovery processes. For example, according to the National Renewable Energy Laboratory report (Warren, 2021), the investment cost for the Upper Rhine Valley project with an annual capacity of 40,000 mt/yr was about \$1.287 billion. However, it is important to note that operational costs pose a significant challenge for chemical precipitation processes. Compared to other projects, such as the Kachi Project in Argentina, the reported operational cost was \$106 million, while in this study, the operational cost is roughly \$2.584 billion. The detailed list of equipment, their sizing, and costs are provided in the Supplementary Material.



Furthermore, Fig. B.1 illustrates the calculated % of the total impact of the utilities and chemicals used at different stages of the process across the 16 studied impact categories in LCA. The results show that  $\text{Na}_2\text{C}_2\text{O}_4$  has the highest contribution in each impact category, exceeding 80% in all cases. For instance, in the climate change category, the use of  $\text{Na}_2\text{C}_2\text{O}_4$  results in 464.12 kg  $\text{CO}_2$  eq, whereas lime contributes only 7.80 kg  $\text{CO}_2$  eq (detailed values for each impact category are provided in the Supplementary Material). This is because the synthesis of  $\text{Na}_2\text{C}_2\text{O}_4$  is characterized by its high energy consumption, which is attributed to the involvement of numerous chemical reactions, purification steps, and high temperatures. These measures contribute to a higher total energy consumption and an increase in  $\text{CO}_2$  emissions. Moreover, the acquisition and transportation of the primary substances employed in the synthesis of  $\text{Na}_2\text{C}_2\text{O}_4$  also add to the increased environmental impacts.

Moreover, the chemical precipitation process for lithium recovery shows significant water consumption, with nearly 200  $\text{m}^3$  depriv. per kg of  $\text{Li}_2\text{CO}_3$ , primarily due to the use of  $\text{Na}_2\text{C}_2\text{O}_4$ , which demands high water usage for filtration. To mitigate these environmental impacts, recovering, and regeneration of  $\text{Na}_2\text{C}_2\text{O}_4$  is proposed. This involves using the large amount of  $\text{Ca}_2\text{C}_2\text{O}_4$  (Fig. 2) which is produced during the process and can be recycled and converted back to  $\text{Na}_2\text{C}_2\text{O}_4$ . The effect of recycling will be examined in Section 3.2.

### 3.1.2. Sensitivity analysis

We perform sensitivity analysis to study the effects of lithium concentration in the feed, water cost, and selling price of  $\text{Li}_2\text{CO}_3$  on the economics of the process. The first analysis evaluates the revenue and NPV (Net Present Value) of the process at different selling prices of \$(5–85)/\text{kg}\$ for a constant feed lithium concentration of 250  $\text{mg/L}$  (Fig. 3(a)). The results show that the recovery process reaches a positive NPV for selling prices greater than \$70/kg  $\text{Li}_2\text{CO}_3$  at this initial lithium concentration. While a positive revenue is attainable for all studied price points, the NPV is negative for lower selling prices, showing that the designed process for lithium recovery from geothermal brines is only economical for relatively high selling prices.

However, it should be noted that the initial concentration of lithium in the geothermal brine also plays a vital role in the economics of the final design. Fig. 3(b) shows the effect of different concentrations of lithium in brine on the revenue and NPV at a constant  $\text{Li}_2\text{CO}_3$  selling price of \$40/kg. Lithium concentrations typically vary between 0.1–500  $\text{mg/L}$  in most geothermal wells (Herrmann et al., 2022; Tabelin et al., 2021). However, some studies report that a few wells may have up to 500–1000  $\text{mg/L}$  lithium (Neupane and Wendt, 2017). Hence, we examined a wide range of geothermal brine lithium concentrations of 50 to 850  $\text{mg/L}$ . The results show that for lithium concentrations greater than 450  $\text{mg/L}$ , the chemical precipitation process leads to positive NPV. Similar to the selling price analysis, positive revenues are attained for all studied concentrations, however, the highly negative NPV makes lithium recovery from this base case design economically unfavorable for lower-concentration wells.

Furthermore, Table 1 shows the effect of lithium concentration on the payback period and the annual capacity for production. In this table, the lithium concentration is for raw brine, and the  $\text{Na}_2\text{CO}_3$  refers to the amount of reagent used to precipitate lithium ions. During this analysis, the concentration of other ions remains constant.

As the lithium concentration in the brine increases, the annual  $\text{Li}_2\text{CO}_3$  production capacity also increases. With the initial lithium concentration of 50  $\text{mg/L}$ , the plant produces approximately 3,000 metric tons (mt) of  $\text{Li}_2\text{CO}_3$  compared to 54,252 mt for an initial lithium concentration of 850  $\text{mg/L}$ . As expected, this also substantially impacts the overall economic parameters of the process as well. For lower concentrations (50–250  $\text{mg/L}$ ), the ROI (Return on Investment) is negative which shows an unfavorable economic outlook. Even when the lithium concentration reaches 350  $\text{mg/L}$ , resulting in a positive ROI of 4.17%, the payback period is still 23 years. This suggests that although there is

some potential for profitability, the economic feasibility is significantly limited from a plant operations perspective. We also observe that there is a significant reduction in the payback period from processing 350  $\text{mg/L}$  to 450  $\text{mg/L}$  lithium in brine, where it drops from 23 years to 6.26 years, respectively. As expected, higher lithium concentration in the feed brine yields higher ROI and a lower payback period, whereas in the most concentrated feed streams, the payback period drops below 2 years.

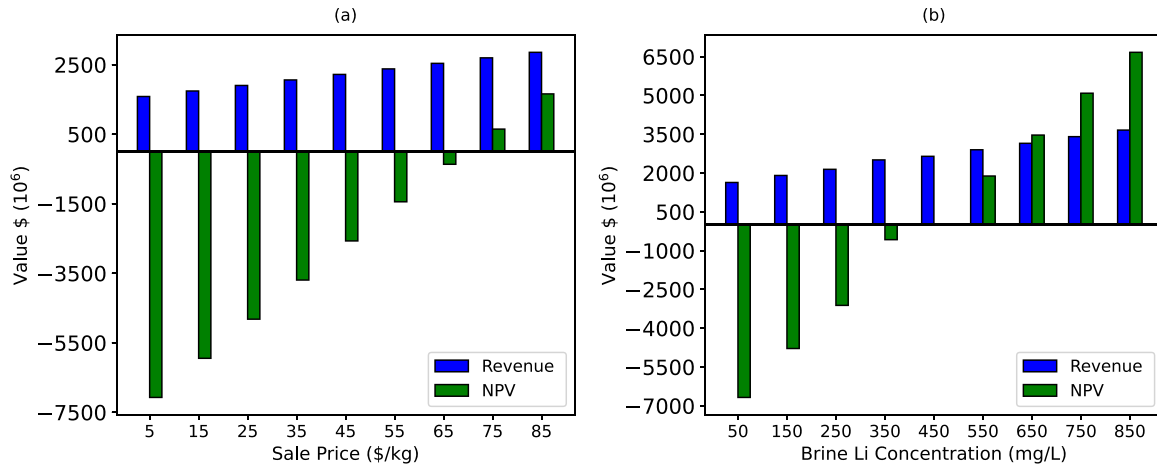
In addition, we explored solutions for achieving a more favorable payback period for processing geothermal brines with lithium concentrations of 150, 250, and 350  $\text{mg/L}$ . In this analysis, we set the payback period to 5 years, resulting in revised  $\text{Li}_2\text{CO}_3$  prices of \$123.7/kg, \$74.2/kg, \$53.28/kg, respectively. The obtained price for the 150  $\text{mg/L}$  concentration is astronomically high, considering lithium prices have consistently remained below \$100/kg (Anon, 2024). For concentrations of 250 and 350  $\text{mg/L}$ , the price falls within the recent range of \$60–80/kg. This demonstrates that lithium extraction from a lower-content lithium source becomes economically feasible only by significantly increasing the  $\text{Li}_2\text{CO}_3$  selling price, which will occur only in high demand-low supply scenarios in the lithium market. Therefore, it is important to navigate these economic parameters when designing processes for recovering commodities with highly volatile pricing such as the case for lithium.

Finally, the effect of water cost and the brine lithium concentrations is studied on the NPV and payback period. This analysis is essential because lithium recovery processes typically consume large amounts of water, particularly in the precipitation stages. Water is primarily used to wash and purify the precipitated solids, ensuring the removal of impurities and improving the quality of the final lithium product (Vera et al., 2023). Based on the available data (Holidu.de., 2021; Anon, 2023; Unger et al., 2023), the water cost also varies significantly in different regions of the United States, ranging from \$1/ $\text{m}^3$  – \$7/ $\text{m}^3$ . Given that geothermal wells could be located anywhere in the country, it is important to account for this variability. For this analysis, we investigated the water cost ranging from \$1–7/ton. The results in Fig. 4 show that the NPV and the payback period are not substantially affected by the changing water cost when the brine lithium concentration is high. For example, at 550  $\text{mg/L}$ , the payback period only varies approximately a year, from 2.5 to 3.47, even when the water cost increases by seven-fold. However, for a concentration of 450  $\text{mg/L}$ , the NPV is positive until \$4/ton but turns negative for higher water prices. This also impacts the payback period where it reaches 14.10 years for the highest water cost. This analysis shows that for lower lithium concentrations of brine, it is important to consider the water availability and cost to have a positive NPV.

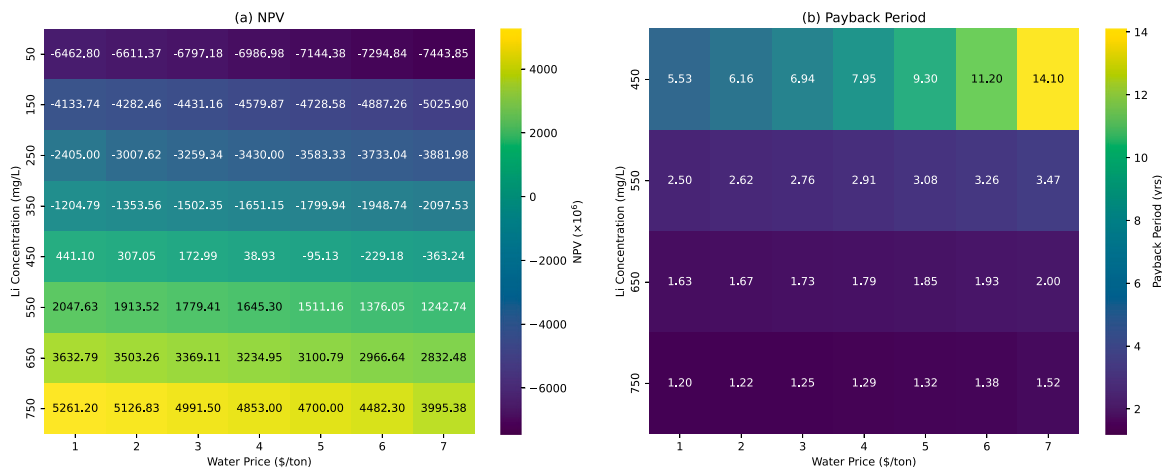
### 3.2. A new process for recycling and on-site precipitant production

One of the main drawbacks of chemical precipitation is the environmental impact of the agents used in the process. Especially, large-scale processing will require higher volumes of these precipitating agents and the impacts of the recovery process are going to be substantially higher. We have also observed this in our base case process, where our main precipitating agent,  $\text{Na}_2\text{C}_2\text{O}_4$ , had the largest contribution in every environmental impact category studied in LCA. Moreover, a large portion of the operational cost is also coming from the purchase of raw materials, which includes  $\text{Na}_2\text{C}_2\text{O}_4$ . Recycling, reusing, or having an on-site chemical production process may reduce the environmental impacts of these agents while reducing the operational costs. Therefore, we have added several new processing steps to recover  $\text{Ca}_2\text{C}_2\text{O}_4$ , which is a by-product of our base case process for removing  $\text{Ca}^{2+}$ , and convert it to  $\text{Na}_2\text{C}_2\text{O}_4$  for its reuse as a precipitating agent. Fig. B.3 shows the new recycling process that is added to the base case design (Process 1) in Fig. 2.

One of the procedures for producing  $\text{Na}_2\text{C}_2\text{O}_4$  is converting  $\text{Ca}_2\text{C}_2\text{O}_4$  into oxalic acid through sulfuric acid treatment, followed by the reaction of oxalic acid with  $\text{NaOH}$ , and the crystallization of  $\text{Na}_2\text{C}_2\text{O}_4$  from



**Fig. 3.** NPV and revenue at: (a) different selling prices of  $\text{Li}_2\text{CO}_3$  at a constant initial brine lithium concentration of 250 mg/L; and (b) different initial brine lithium concentrations at a constant  $\text{Li}_2\text{CO}_3$  selling price of \$40/kg.



**Fig. 4.** The effect of water cost and lithium concentration of the geothermal brine on the: (a) NPV and (b) payback period.

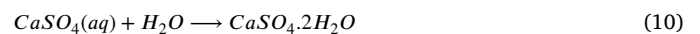
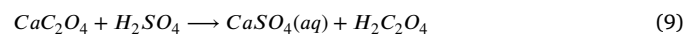
**Table 1**

Effect of lithium concentration on the ROI, payback period, and the annual production capacity of the plant. N/A indicates payback periods with negative ROI. Selling price for  $\text{Li}_2\text{CO}_3$  is taken as \$40/kg.

Lithium (mg/L)	ROI (%)	Annual Capacity (mt)	$\text{Na}_2\text{CO}_3$ (mt)	Payback period (yrs)
50	-79	3168.0	0.65	N/A
150	-53.37	11 404.8	2.2	N/A
250	-30.51	15 998.4	3.35	N/A
350	4.17	22 413.6	4.45	23
450	15.93	28 749.6	5.48	6.26
550	37.71	32 709.6	6.55	2.65
650	59.19	39 600.0	7.7	1.7
750	81	47 836.0	8.93	1.25
850	102.48	54 252.0	10.1	1

the resulting solution (Wilson, 1927). We use this procedure in the new process where at the first stage  $\text{CaC}_2\text{O}_4$  is sent to a filter (F 3) to concentrate it further, and the filter wash stream is sent back to the thickener (Th 2). The concentrated  $\text{CaC}_2\text{O}_4$  goes to the sulfuric acid treatment reactor (R 1) as shown in Fig. B.3. In our process, we used 40%–60% sulfuric acid, and Reactions (9) and (10) take place in the reactor. The primary rationale for selecting  $\text{Na}_2\text{C}_2\text{O}_4$  over oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) is that the use of oxalic acid can negatively impact subsequent processing stages due to its tendency to lower the pH. Additionally, the desired

recovery of a solid precipitate is hindered by the high solubility of oxalic acid, necessitating supersaturation to induce precipitation, which significantly increases energy requirements.



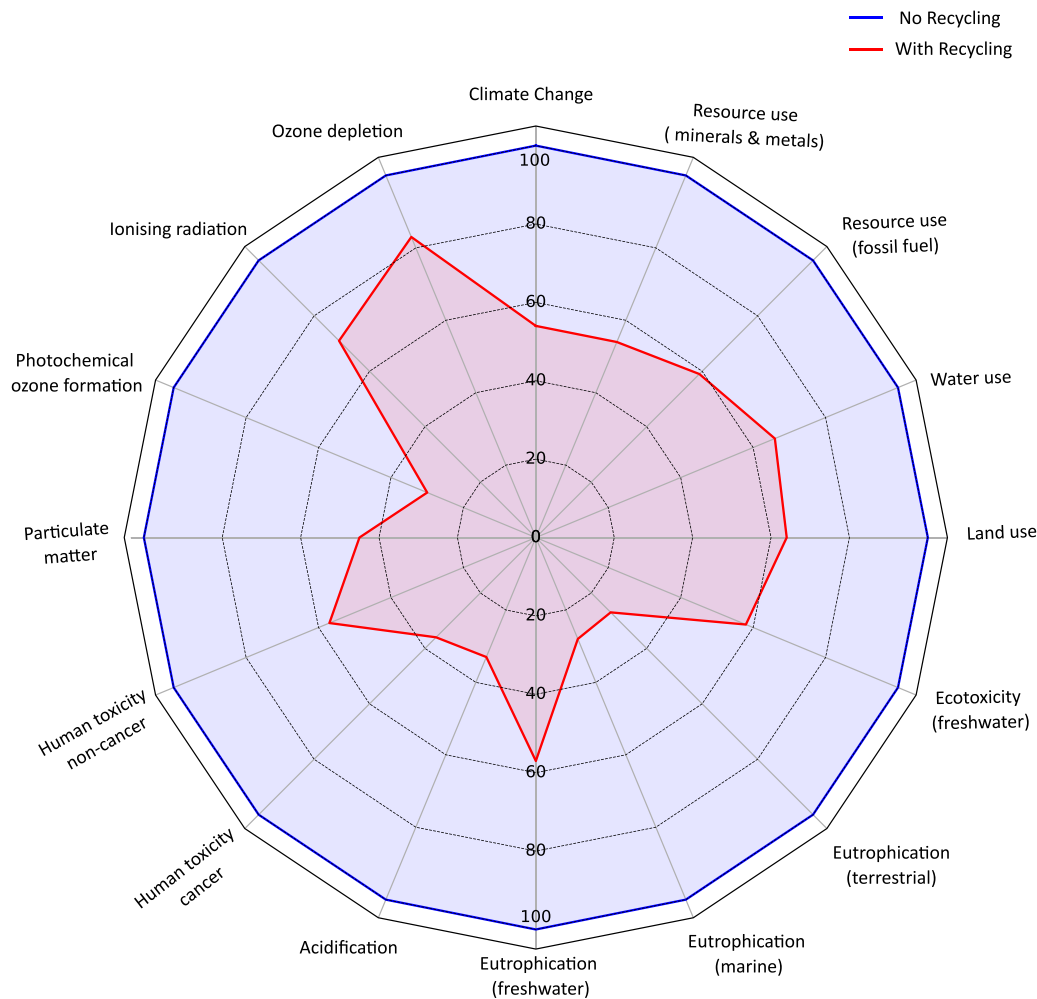
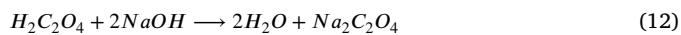
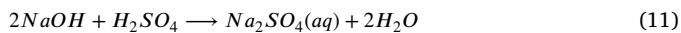


Fig. 5. Comparison of the LCA results between the two processes.

The next step is the separation of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) through the vacuum filter (VF 2). After that, the produced oxalic acid is sent to the second reactor (R 2), where we produce  $\text{Na}_2\text{C}_2\text{O}_4$ . Reactions (11) and (12) take place in the second reactor.



This step is followed by the crystallization to produce solid sodium oxalate. Finally, a vacuum filtration (VF 2) is used to separate  $\text{Na}_2\text{C}_2\text{O}_4$ , which is then ready to be reused in the lithium recovery process. The make up  $\text{Na}_2\text{C}_2\text{O}_4$  is also added to compensate for the loss throughout the new process.

### 3.2.1. LCA and TEA results for the recycling process

Fig. B.4 shows the results of LCA for the new process, which indicates that recycling  $\text{CaC}_2\text{O}_4$  helps reduce the negative impacts caused by  $\text{Na}_2\text{C}_2\text{O}_4$ . We observe that the contribution of other chemicals such as NaOH and  $\text{H}_2\text{SO}_4$  start to play an important role in the total impact. However, even with the on-site production of  $\text{Na}_2\text{C}_2\text{O}_4$ , we still observe that its contribution to total environmental impact is high. This is due to the make up amount we need to add for the process, as it is impossible to convert all  $\text{CaC}_2\text{O}_4$  to  $\text{Na}_2\text{C}_2\text{O}_4$ . This analysis indicates

that although oxalate is a good precipitating reagent, its negative impacts on the environment are also a hotspot for the process and should not be ignored. The detailed values for each impact category are provided in the Supplementary Material.

Furthermore, Fig. 5 compares the LCA results of the two processes in all 16 studied impact categories. The recycling and reusing of oxalates in the process results in more than 50% reduction for some impact categories including, acidification, eutrophication (marine), and photochemical ozone depletion. Especially in the climate change impact category, we observe that the recycling process results in approximately a 50% decrease in  $\text{CO}_2$  emissions, which is a significant improvement compared to the base case design and a more environmentally friendly way of recovering lithium from geothermal brines.

We also perform TEA for the new process with results shown in Table C.4. A noticeable change is in the substantial decrease in the operational and material costs compared to the base case process without recycling. While in initial process where the material cost is nearly \$2,243 million, the recycling of chemical waste and on-site production of the sodium oxalate decreases this by almost fourfold. Despite this reduction, the NPV of the recycling process is lower which results in the payback period of the recycling process to increase to 5.7 years. Moreover, the total capital investment cost is also higher due to the addition of more unit operations, such as an additional

crystallization unit. A detailed list of other economic factors is provided in the Supplementary Material.

Generally, although the recycling process would be more environmentally friendly, it will inevitably increase the cost of the process. Moreover, the analysis shows a possibility of more lithium loss, probably due to the use of lower-quality precipitant.

#### 4. Conclusions

This study designed and simulated the first end-to-end digital twin of a large-scale sustainable lithium production process from geothermal brines using chemical precipitation. We obtained battery grade  $\text{Li}_2\text{CO}_3$  with a purity of 99.5% and investigated the effect of initial geothermal brine concentration,  $\text{Li}_2\text{CO}_3$  selling price, water cost, and the recycling and on-site production of precipitating agents on the process economics. Techno-economic and life cycle analyses showed that the on-site production of the precipitating agents and recycling of chemicals increases the total capital investment cost and will lead to lower NPV. However, it also reduces  $\text{CO}_2$  emissions by approximately 50% compared to the case where no recycling is considered. In addition, the results show that the process economics is tightly interlinked to the initial lithium concentration in brine and the selling price of  $\text{Li}_2\text{CO}_3$ . The process has favorable economics for geothermal brines with at least 450 mg/L for a \$40/kg  $\text{Li}_2\text{CO}_3$  selling price. However, water cost plays an important role in the payback period for lower lithium concentrations, whereas the recovery from geothermal brines with 550 to 750 mg/L lithium is less sensitive to changes in the water cost. Future studies will focus on the optimal selection of processing routes and precipitating agents to improve economics and reduce environmental impacts, and perform cradle-to-grave or cradle-to-cradle LCA to understand the full life cycle impacts of lithium recovery from geothermal brines.

#### CRediT authorship contribution statement

**Hasan Nikkhah:** Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation. **Andrea Di Maria:** Writing – review & editing, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation. **Giuseppe Granata:** Writing – review & editing, Methodology, Formal analysis, Supervision, Software, Conceptualization. **Burcu Beykal:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

#### Declaration of Generative AI in Scientific Writing

During the preparation of this work the authors used OpenAI's ChatGPT in order to improve readability and language of the paper. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of this publication.

#### Declaration of competing interest

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

#### Acknowledgments

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**Table A.1**

Parameters used for the techno-economic assessment of the process.

Parameters	Value
Project life (yrs)	15
Depreciation period (yrs)	12
Construction period (yrs)	2.5
Inflation (%)	4
NPV interest (%)	9
Salvage value	0.1 Direct Fixed Cost
Income taxes (%)	10

**Table A.2**

Purchase and selling price of raw material, products and utilities.

Material/Utility	Price (\$/kg)	Material/Utility	Price (\$/kg)
$\text{Ca(OH)}_2$	0.2	$\text{Na}_2\text{CO}_3$	2
Water	0.002	Solvent	10
$\text{Na}_2\text{C}_2\text{O}_4$	1.5	Steam	0.032
$\text{H}_2\text{SO}_4$	2	Kerosene	0.1
$\text{Li}_2\text{CO}_3^a$	45	Electricity	0.11 (\$/kWh)
$\text{H}_3\text{BO}_3^a$	0.5	NaOH	0.3
$\text{NaCl}^a$	0.1	$\text{CaC}_2\text{O}_4^a$	1

<sup>a</sup> Main revenue streams of the process.

#### Appendix A. Equations and parameters for techno-economic analysis

As part of the economic evaluation, SuperPro Designer creates a list of equipment together with the size and quantity of each item. Afterward, the cost of the equipment ( $C_{PE}$ ) is determined using the in-built power law model. The total ( $C_{TC}$ ) and fixed capital ( $C_{FC}$ ) costs are determined by multiplying the cost of the equipment purchase by the relevant cost factors. The annual operating cost can be determined using SuperPro by calculating the number of labor-hours and the utility requirement. The material balances determine the amount of various input streams that are needed (Rouf et al., 2001). Finally, the economic viability is evaluated using return on investment (ROI), and net present value (NPV). The ROI measures the return on investment that can be regained within one year of earning profits (Granata et al., 2022). The NPV is a measure of the entire worth of future net cash flows that will be received throughout a project, calculated at the beginning of the project. Eq. (A.1) and Eq. (A.2) show how ROI and NPV are calculated, respectively:

$$ROI(\%) = \frac{\text{Net Profit}}{\text{Total Investment}} \quad (\text{A.1})$$

$$NPV = \sum_{t=0}^T \frac{Cf_t}{(1 + DR)^t} \quad (\text{A.2})$$

where  $Cf_t$  is cash flow at a specific time within the project lifetime,  $DR$  is discount rate,  $t$  is specific time within a project lifetime and  $T$  is project lifetime (see Tables A.1 and A.2).

#### Appendix B. Additional figures

See Figs. B.1–B.4.



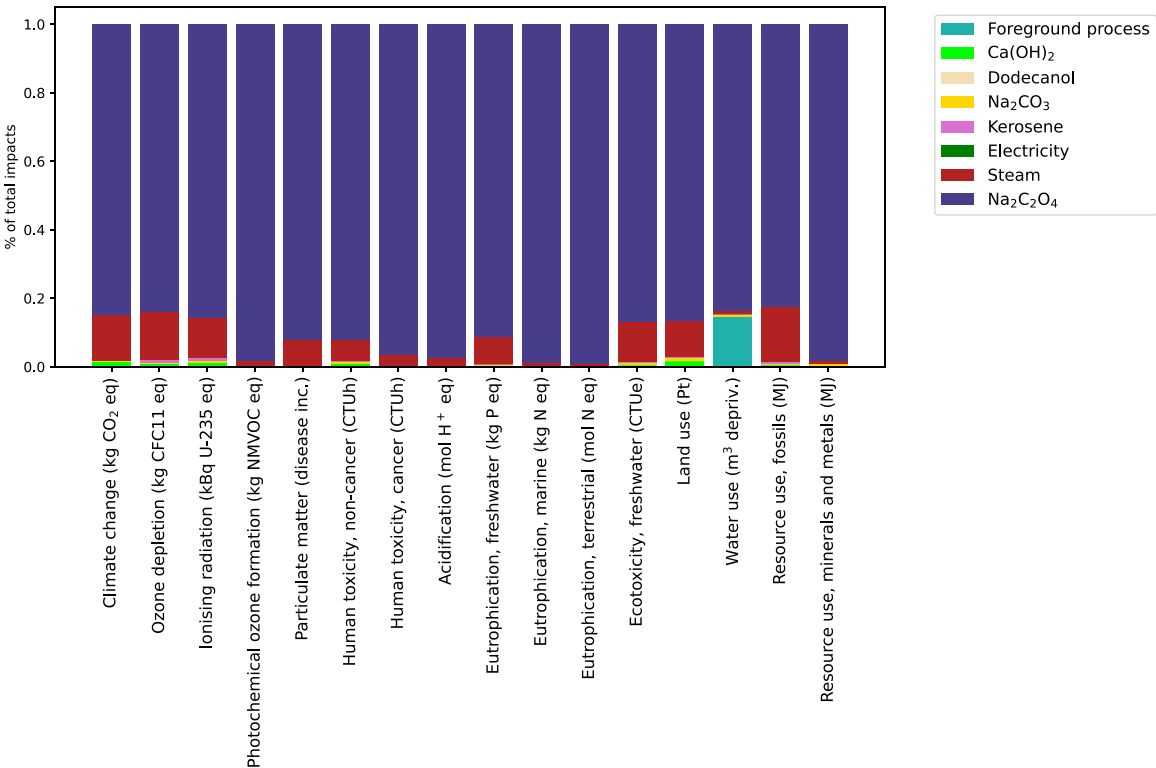


Fig. B.1. LCA results for each environmental impact category and the breakdown of contributions from each chemical/utility used in the lithium recovery process.

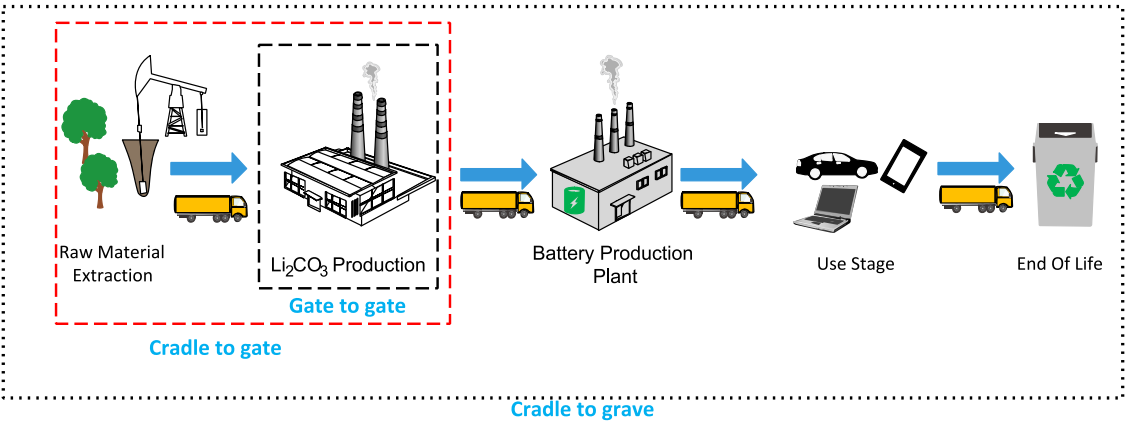


Fig. B.2. Boundaries of life cycle analysis of battery production from raw material extraction to end use of a battery. In this work, we used cradle-to-gate for evaluating the life cycle impact of Li<sub>2</sub>CO<sub>3</sub> production from geothermal brines.

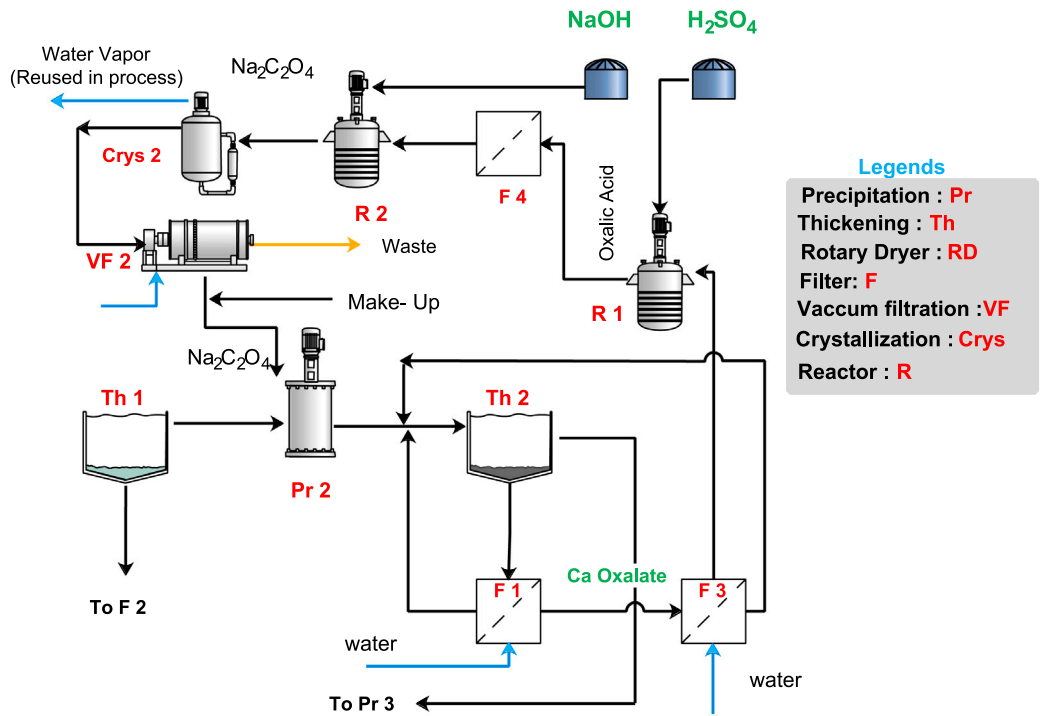


Fig. B.3. Process flowsheet of lithium recovery from brine with recycling of calcium oxalate.

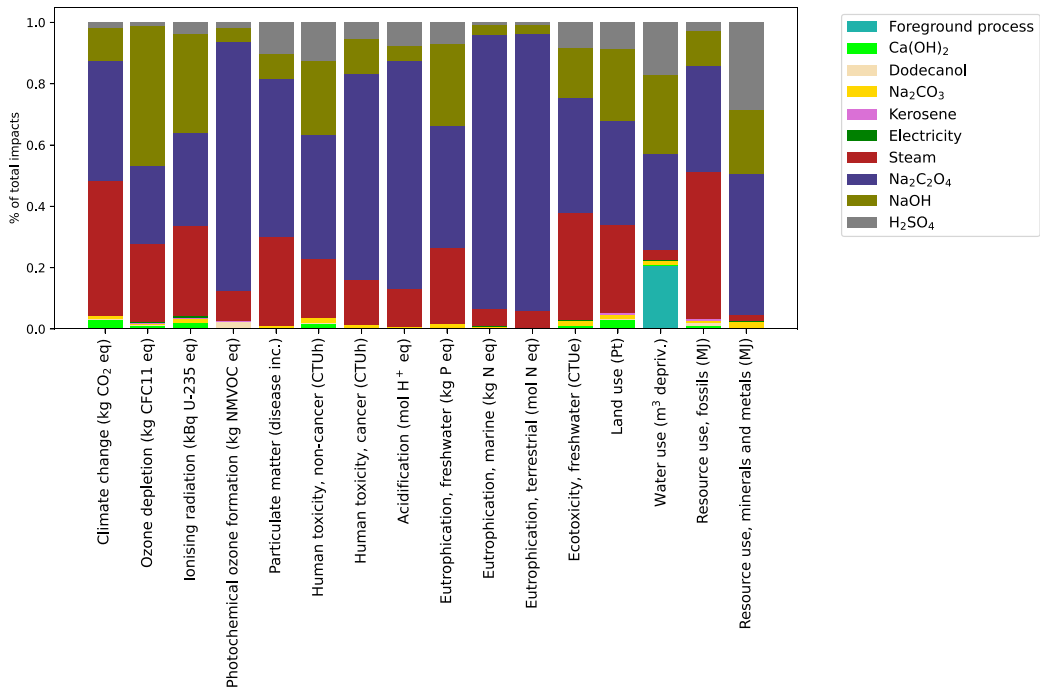


Fig. B.4. LCA results for different environmental impact categories and contribution of different material for proposed process.

Appendix C. Additional tables

See Tables C.1 and C.4.

Appendix D. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.resconrec.2024.107980>.

Data availability

The datasets and the simulation files generated during this study are available from the corresponding author upon request. Additionally, the simulation files are accessible at the SuperPro Designer library.

**Table C.1**  
The feed brine composition used in this analysis is based on Salton Sea brine (Ventura et al., 2020).

Ions	Value (mg/L)	Ions	Value (mg/L)
Ca <sup>2+</sup>	24 100	Fe <sup>2+</sup>	2400
Mg <sup>2+</sup>	530	Sr <sup>2+</sup>	600
Na <sup>+</sup>	52 450	Ba <sup>2+</sup>	433
K <sup>+</sup>	14 300	As <sup>3+</sup>	11
Li <sup>+</sup>	250	Mn <sup>2+</sup>	1480
B <sup>-</sup>	380	Ni <sup>2+</sup>	4
Cl <sup>-</sup>	145 189	Pb <sup>2+</sup>	100
SO <sub>4</sub> <sup>2-</sup>	84	Zn <sup>2+</sup>	660
CO <sub>3</sub> <sup>-</sup>	140	F <sup>-</sup>	9
Cu <sup>2+</sup>	4	TDS	241,611

**Table C.2**  
Different unit operations in the process and their responsibility.

Treatment stage	Note
Solar pond	Removal of NaCl and KCl
Solvent Extraction	Isodecanol (1:1 organic to aqueous) for removal of boron Use water for stripping stage
Precipitation 1	Removal of Mg <sup>2+</sup> , Mn <sup>2+</sup> , Fe <sup>2+</sup> , Ni <sup>2+</sup> using calcium hydroxide
Precipitation 2	Removal of Ca <sup>2+</sup> using sodium oxalate <sup>2+</sup>
Precipitation 3	Precipitation of LiCl as Li <sub>2</sub> CO <sub>3</sub>
Thickening 1	Dewatering hydroxide solids
Thickening 2	Dewatering calcium oxalate solids
Belt Filter	Removing of solid waste
Rotary Dryer	Removing water from Li <sub>2</sub> CO <sub>3</sub>
Crystallization	Crystallization of Li <sub>2</sub> CO <sub>3</sub>

**Table C.3**  
Base case results for lithium recovery from geothermal brine (NPV: Net Present Value; ROI: Return on Investment).

Parameters	Values
Final Purity (wt.%)	99.5
Li <sub>2</sub> CO <sub>3</sub> Production Capacity (mt/h)	4.02
Total Capital Investment (\$) [×10 <sup>6</sup> ]	1,354.168
NPV (\$) [×10 <sup>6</sup> ]	1,189.879
Payback Period (yrs)	4.10
Operational Cost (\$/yr) [×10 <sup>6</sup> ]	2,584.676
Material Cost (\$/yr) [×10 <sup>6</sup> ]	2,243.409
ROI (%)	24.36
Recovery Rate (%)	75.80

**Table C.4**  
TEA results for the recycling process.

Parameters	Values
Final Purity (wt.%)	99.5
Li <sub>2</sub> CO <sub>3</sub> Capacity (mt/h)	3.48
Total Capital Investment (\$) [×10 <sup>6</sup> ]	1,669.536
NPV (\$) [×10 <sup>6</sup> ]	657.656
Payback Period (yrs)	5.7
Operational Cost (\$/yr) [×10 <sup>6</sup> ]	962.216
Material Cost (\$/yr) [×10 <sup>6</sup> ]	535.378
ROI (%)	17.57
Recovery Rate (%)	65.26

References

Alawa, B., Galodiya, M.N., Chakma, S., 2022. Source reduction, recycling, disposal, and treatment. In: *Hazardous Waste Management*. Elsevier, pp. 67–88. <http://dx.doi.org/10.1016/B978-0-12-824344-2.00005-7>.  
Alsabbagh, A., Aljarrah, S., Almahasneh, M., 2021. Lithium enrichment optimization from dead sea end brine by chemical precipitation technique. *Miner. Eng.* 170, 107038. <http://dx.doi.org/10.1016/j.mineng.2021.107038>.  
An, J.W., Kang, D.J., Tran, K.T., Kim, M.J., Lim, T., Tran, T., 2012. Recovery of lithium from uyuni salar brine. *Hydrometallurgy* 117, 64–70. <http://dx.doi.org/10.1016/j.hydromet.2012.02.008>.  
Anon, 2023. Cooling water cost and industrial utilities retrieved from : Intratec. <https://www.intratec.us/products/water-utility-costs/commodity/cooling-water-cost>.  
Anon, 2024. Metal spot price charts. <https://www.dailymetalprice.com/metalpricecharts.php?c=li&u=kg&d=240>.  
Azevedo, M., Baczyńska, M., Hoffman, K., Krauze, A., 2022. Lithium mining: How new production technologies could fuel the global EV revolution. *McKinsey Co.* 12.

Battaglia, G., Berkemeyer, L., Cipollina, A., Cortina, J.L., Fernandez de Labastida, M., Lopez Rodriguez, J., Winter, D., 2022. Recovery of lithium carbonate from dilute li-rich brine via homogenous and heterogeneous precipitation. *Ind. Eng. Chem. Res.* 61 (36), 13589–13602. <http://dx.doi.org/10.1021/acs.iecr.2c01397>.  
Boryta, D.A., Kullberg, T.F., Thurston, A.M., 2011. Production of lithium compounds directly from lithium containing brines. *US Patent* 8, 057, 764.  
Castellani, V., Sanyé-Mengual, E., Sala, S., 2021. Environmental impacts of household goods in europe: a process-based life cycle assessment model to assess consumption footprint. *Int. J. Life Cycle Assess.* 26, 2040–2055. <http://dx.doi.org/10.1007/s11367-021-01987-x>.  
Chagnes, A., Swiatowska, J., 2015. *Lithium Process Chemistry: Resources, Extraction, Batteries, and Recycling*. Elsevier.  
Cheng, W., Li, Z., Cheng, F., 2013. Solubility of Li<sub>2</sub>CO<sub>3</sub> in Na–K–Li–Cl brines from 20 to 90 C. *J. Chem. Thermodyn.* 67, 74–82. <http://dx.doi.org/10.1016/j.jct.2013.07.024>.  
Dobson, P., Araya, N., Brounce, M., Busse, M., Camarillo, M.K., English, L., Humphreys, J., Kalderon-Asael, B., McKibben, M., Millstein, D., et al., 2023. Characterizing the Geothermal Lithium Resource at the Salton Sea. *Tech. rep.*, Lawrence Berkeley National Laboratory (LBNL), Berkeley, CA (United States), <http://dx.doi.org/10.2172/2222403>.  
Farahbakhsh, J., Arshadi, F., Mofidi, Z., Mohseni-Dargah, M., Kök, C., Assefi, M., Soozanipour, A., Zargar, M., Asadnia, M., Boroumand, Y., et al., 2024. Direct lithium extraction: A new paradigm for lithium production and resource utilization. *Desalination* 575, 117249. <http://dx.doi.org/10.1016/j.desal.2023.117249>.  
Galhardi, J.A., Luko-Sulato, K., Yabuki, L.N., Santos, L.M., da Silva, Y.J., da Silva, Y.J., 2022. Rare earth elements and radionuclides. In: *Emerging Freshwater Pollutants*. Elsevier, pp. 309–329. <http://dx.doi.org/10.1016/B978-0-12-822850-0.00011-9>.  
Garcia, L.V., Ho, Y.-C., Myo Thant, M.M., Han, D.S., Lim, J.W., 2023. Lithium in a sustainable circular economy: A comprehensive review. *Processes* 11 (2), 418. <http://dx.doi.org/10.3390/pr11020418>.  
Gómez, J.A., Sánchez, Ó.J., Correa, L.F., 2020. Techno-economic and environmental evaluation of cheesemaking waste valorization through process simulation using SuperPro designer. *Waste Biomass Valoriz.* 11, 6025–6045. <http://dx.doi.org/10.1007/s12649-019-00833-4>.  
Grágeda, M., González, A., Grágeda, M., Ushak, S., 2018. Purification of brines by chemical precipitation and ion-exchange processes for obtaining battery-grade lithium compounds. *Int. J. Energy Res.* 42 (7), 2386–2399. <http://dx.doi.org/10.1002/er.4008>.  
Granata, G., Altamari, P., Pagnanelli, F., De Greef, J., 2022. Recycling of solar photo-voltaic panels: Techno-economic assessment in waste management perspective. *J. Clean. Prod.* 363, 132384. <http://dx.doi.org/10.1016/j.jclepro.2022.132384>.  
Halkes, R.T., Hughes, A., Wall, F., Petavratzi, E., Pell, R., Lindsay, J.J., 2024. Life cycle assessment and water use impacts of lithium production from salar deposits: Challenges and opportunities. *Resour. Conserv. Recy.* 207, 107554. <http://dx.doi.org/10.1016/j.resconrec.2024.107554>.  
He, X., Kaur, S., Kostecki, R., 2020. Mining lithium from seawater. *Joule* 4 (7), 1357–1358. <http://dx.doi.org/10.1016/j.joule.2020.06.015>.

- Herrmann, L., Ehrenberg, H., Graczyk-Zajac, M., Kaymakci, E., Kölb, T., Kölb, L., Tübke, J., 2022. Lithium recovery from geothermal brine—an investigation into the desorption of lithium ions using manganese oxide adsorbents. *Energy Adv.* 1 (11), 877–885. <http://dx.doi.org/10.1039/d2ya00099g>.
- Holidu.de., 2021. Prices of tap water in selected cities in the United States in 2021 (in U.S. dollars per cubic meter) [graph]. In *statista*. Retrieved from. <https://www.statista.com/statistics/1232861/tap-water-prices-in-selected-us-cities/>.
- Huang, T.-Y., Perez-Cardona, J.R., Zhao, F., Sutherland, J.W., Paranthaman, M.P., 2021. Life cycle assessment and techno-economic assessment of lithium recovery from geothermal brine. *ACS Sustain. Chem. Eng.* 9 (19), 6551–6560. <http://dx.doi.org/10.1021/acssuschemeng.0c08733>.
- IEA, 2021. Global EV sales by scenario, 2020–2030. <https://www.iea.org/data-and-statistics/charts/global-ev-sales-by-scenario-2020-2030>, IEA, Paris. Licence: CC BY 4.0.
- International Organization for Standardization, 2006. *Environmental Management: Life Cycle Assessment; Principles and Framework*. ISO.
- Kallitis, E., Korre, A., Kelsall, G.H., 2022. Life cycle assessment of recycling options for automotive li-ion battery packs. *J. Clean. Prod.* 371, 133636. <http://dx.doi.org/10.1016/j.jclepro.2022.133636>.
- Karidakis, T., Agatzini-Leonardou, S., Neou-Syngouna, P., 2005. Removal of magnesium from nickel laterite leach liquors by chemical precipitation using calcium hydroxide and the potential use of the precipitate as a filler material. *Hydrometallurgy* 76 (1–2), 105–114. <http://dx.doi.org/10.1016/j.hydromet.2004.09.007>.
- Khakmardan, S., Rolinck, M., Cerdas, F., Herrmann, C., Giurco, D., Crawford, R., Li, W., 2023. Comparative life cycle assessment of lithium mining, extraction, and refining technologies: a global perspective. *Procedia CIRP* 116, 606–611. <http://dx.doi.org/10.1016/j.procir.2023.02.102>.
- Khalil, A., Mohammed, S., Hashaikheh, R., Hilal, N., 2022. Lithium recovery from brine: Recent developments and challenges. *Desalination* 528, 115611. <http://dx.doi.org/10.1016/j.desal.2022.115611>.
- Kim, S., Joo, H., Moon, T., Kim, S.-H., Yoon, J., 2019. Rapid and selective lithium recovery from desalination brine using an electrochemical system. *Environ. Sci. Process. Impacts* 21 (4), 667–676. <http://dx.doi.org/10.1039/C8EM00498F>.
- Kudryavtsev, P., 2016. Lithium in nature, application, methods of extraction. *Sci. Isr. Technol. Advant.* 18 (3).
- Lai, X., Xiong, P., Zhong, H., 2020. Extraction of lithium from brines with high Mg/Li ratio by the crystallization-precipitation method. *Hydrometallurgy* 192, 105252. <http://dx.doi.org/10.1016/j.hydromet.2020.105252>.
- Linneen, N., Bhavre, R., Woerner, D., 2019. Purification of industrial grade lithium chloride for the recovery of high purity battery grade lithium carbonate. *Sep. Purif. Technol.* 214, 168–173. <http://dx.doi.org/10.1016/j.seppur.2018.05.020>.
- Liu, D., Li, Z., He, L., Zhao, Z., 2021. Facet engineered Li<sub>3</sub>PO<sub>4</sub> for lithium recovery from brines. *Desalination* 514, 115186. <http://dx.doi.org/10.1016/j.desal.2021.115186>.
- Liu, G., Zhao, Z., Ghahreman, A., 2019. Novel approaches for lithium extraction from salt-lake brines: A review. *Hydrometallurgy* 187, 81–100. <http://dx.doi.org/10.1016/j.hydromet.2019.05.005>.
- Loganathan, P., Naidu, G., Vigneshwaran, S., 2017. Mining valuable minerals from seawater: a critical review. *Environ. Sci. Water Res. Technol.* 3 (1), 37–53. <http://dx.doi.org/10.1039/C6EW00268D>.
- Meinert, L.D., Robinson Jr., G.R., Nassar, N.T., 2016. Mineral resources: Reserves, peak production and the future. *Resources* 5 (1), 14. <http://dx.doi.org/10.3390/resources5010014>.
- Mousavinezhad, S., Nili, S., Fahimi, A., Vahidi, E., 2024. Environmental impact assessment of direct lithium extraction from brine resources: global warming potential, land use, water consumption, and charting sustainable scenarios. *Resour. Conserv. Recy.* 205, 107583. <http://dx.doi.org/10.1016/j.resconrec.2024.107583>.
- Murodjón, S., Yu, X., Li, M., Duo, J., Deng, T., 2020. Lithium recovery from brines including seawater, salt lake brine, underground water and geothermal water. *Thermodyn. Energy Eng.* 90371, <http://dx.doi.org/10.5772/intechopen.90371>.
- Najafi, A.M., Soltanali, S., Khorashe, F., Ghassabzadeh, H., 2023. Effect of binder on CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> adsorption behavior, structural properties, and diffusion coefficients on extruded zeolite 13X. *Chemosphere* 324, 138275. <http://dx.doi.org/10.1016/j.chemosphere.2023.138275>.
- Natasha, N.C., Lalasari, L.H., 2017. Calcium extraction from brine water and seawater using oxalic acid. In: *AIP Conference Proceedings*. 1805, (1), AIP Publishing, <http://dx.doi.org/10.1063/1.4974443>.
- Neupane, G., Wendt, D.S., 2017. Assessment of mineral resources in geothermal brines in the US. In: *Proceedings of the 42nd Workshop on Geothermal Reservoir Engineering*, Stanford, CA, USA. pp. 13–15.
- Nikkhah, H., Beykal, B., 2023. Process design and technoeconomic analysis for zero liquid discharge desalination via LiBr absorption chiller integrated HDH-MEE-MVR system. *Desalination* 558, 116643. <http://dx.doi.org/10.1016/j.desal.2023.116643>.
- Nikkhah, H., Beykal, B., Stuber, M.D., 2023a. Comparative life cycle assessment of single-use cardiopulmonary bypass devices. *J. Clean. Prod.* 425, 138815. <http://dx.doi.org/10.1016/j.jclepro.2023.138815>.
- Nikkhah, H., Ipekçi, D., Xiang, W., Stoll, Z., Xu, P., Li, B., McCutcheon, J.R., Beykal, B., 2024a. Challenges and opportunities of recovering lithium from seawater, produced water, geothermal brines, and salt lakes using conventional and emerging technologies. *Chem. Eng. J.* 498, 155349. <http://dx.doi.org/10.1016/j.cej.2024.155349>.
- Nikkhah, H., Nikkhah, A., Ghalavand, Y., 2023b. Acid gas preparation for enhanced oil recovery: techno-economic analysis of different dehydration processes. *Sep. Sci. Technol.* 58 (11), 2064–2076. <http://dx.doi.org/10.1080/01496395.2023.2219379>.
- Nikkhah, A., Nikkhah, H., Shahbazi, A., Zarin, M.K.Z., Iz, D.B., Ebadi, M.-T., Fakhroleslam, M., Beykal, B., 2024b. Cumin and eucalyptus essential oil standardization using fractional distillation: Data-driven optimization and techno-economic analysis. *Food Bioprod. Process.* 143, 90–101. <http://dx.doi.org/10.1016/j.fbp.2023.10.005>.
- Office, G.T., 2021. Can geothermal energy solve the lithium shortfall? <https://www.energy.gov/eere/geothermal/articles/can-geothermal-energy-solve-lithium-shortfall#footnotes>.
- Paranthaman, M.P., Li, L., Luo, J., Hoke, T., Ucar, H., Moyer, B.A., Harrison, S., 2017. Recovery of lithium from geothermal brine with lithium–aluminum layered double hydroxide chloride sorbents. *Environ. Sci. Technol.* 51 (22), 13481–13486. <http://dx.doi.org/10.1021/acs.est.7b03464>.
- Perez, W., Barrientos, H.A.C., Suarez, C., Bravo, M., 2014. Method for the production of battery grade lithium carbonate from natural and industrial brines. *US Patent* 8, 691, 169.
- Richter, A., 2021. Geothermal lithium, its extraction and impact on clean energy. <https://www.thinkgeoenergy.com/geothermal-lithium-its-extraction-and-impact-on-clean-energy/>.
- Rouf, S., Douglas, P., Moo-Young, M., Scherer, J., 2001. Computer simulation for large scale bioprocess design. *Biochem. Eng. J.* 8 (3), 229–234. [http://dx.doi.org/10.1016/S1369-703X\(01\)00112-7](http://dx.doi.org/10.1016/S1369-703X(01)00112-7).
- Schenker, V., Bayer, P., Oberschelp, C., Pfister, S., 2024. Is lithium from geothermal brines the sustainable solution for li-ion batteries? *Renew. Sustain. Energy Rev.* 199, 114456. <http://dx.doi.org/10.1016/j.rser.2024.114456>.
- Soeder, D., 2022. Zero carbon vehicles. In: *Energy Futures: The Story of Fossil Fuel, Greenhouse Gas, and Climate Change*. Springer, pp. 185–204. [http://dx.doi.org/10.1007/978-3-031-15381-5\\_8](http://dx.doi.org/10.1007/978-3-031-15381-5_8).
- Song, J.F., Nghiem, L.D., Li, X.-M., He, T., 2017. Lithium extraction from Chinese salt-lake brines: opportunities, challenges, and future outlook. *Environ. Sci. Water Res. Technol.* 3 (4), 593–597. <http://dx.doi.org/10.1039/C7EW00020K>.
- Stringfellow, W.T., Dobson, P.F., 2021. Technology for the recovery of lithium from geothermal brines. *Energies* 14 (20), 6805. <http://dx.doi.org/10.3390/en14206805>.
- Su, H., Tan, B., Zhang, J., Liu, W., Wang, L., Wang, Y., Zhu, Z., Qi, T., 2022. Modelling of lithium extraction with TBP/P507–FeCl<sub>3</sub> system from salt-lake brine. *Sep. Purif. Technol.* 282, 120110. <http://dx.doi.org/10.1016/j.seppur.2021.120110>.
- Sun, Y., Wang, Q., Wang, Y., Yun, R., Xiang, X., 2021. Recent advances in magnesium/lithium separation and lithium extraction technologies from salt lake brine. *Sep. Purif. Technol.* 256, 117807. <http://dx.doi.org/10.1016/j.seppur.2020.117807>.
- Tabelin, C.B., Dallas, J., Casanova, S., Pelech, T., Bournival, G., Saydam, S., Canbulat, I., 2021. Towards a low-carbon society: A review of lithium resource availability, challenges and innovations in mining, extraction and recycling, and future perspectives. *Miner. Eng.* 163, 106743. <http://dx.doi.org/10.1016/j.mineng.2020.106743>.
- Tarascon, J.-M., 2010. Is lithium the new gold? *Nat. Chem.* 2 (6), 510. <http://dx.doi.org/10.1038/nchem.680>.
- Tran, T., Luong, V.T., 2015. Lithium production processes. In: *Lithium Process Chemistry*. Elsevier, pp. 81–124. <http://dx.doi.org/10.1016/B978-0-12-801417-2.00003-7>.
- Unger, S.R., Kilgannon, E.M., Elliott, D.B., Cort, K.A., Stoughton, K.L., 2023. *Water and Wastewater Annual Price Escalation Rates for Selected Cities across the United States*. Tech. rep., Pacific Northwest National Lab.(PNNL), Richland, WA (United States).
- U.S. Geological Survey, 2023. Mineral commodity summaries 2023. p. 108. <http://dx.doi.org/10.3133/mcs2023>.
- Ventura, S., Bhamidi, S., Hornbostel, M., Nagar, A., International, S., 2020. Selective Recovery of Lithium from Geothermal Brines: Final Project Report. California Energy Commission, <https://www.energy.ca.gov/sites/default/files/2021-05/CEC-500-2020-020.pdf>.
- Vera, M.L., Torres, W.R., Galli, C.I., Chagnes, A., Flexer, V., 2023. Environmental impact of direct lithium extraction from brines. *Nat. Rev. Earth Environ.* 4 (3), 149–165. <http://dx.doi.org/10.1038/s43017-022-00387-5>.
- Verma, A., Johnson, G.H., Corbin, D.R., Shiflett, M.B., 2020. Separation of lithium and cobalt from LiCoO<sub>2</sub>: a unique critical metals recovery process utilizing oxalate chemistry. *ACS Sustain. Chem. Eng.* 8 (15), 6100–6108. <http://dx.doi.org/10.1021/acssuschemeng.0c01128>.
- Viadero Jr., R.C., Wei, X., Buzby, K.M., 2006. Characterization and dewatering evaluation of acid mine drainage sludge from ammonia neutralization. *Environ. Eng. Sci.* 23 (4), 734–743. <http://dx.doi.org/10.1089/ees.2006.23.734>.
- Warren, I., 2021. Techno-economic analysis of lithium extraction from geothermal brines. Tech. rep., National Renewable Energy Lab.(NREL), Golden, CO (United States), <http://dx.doi.org/10.2172/1782801>.
- Wilson, J.M., 1927. *The system: calcium oxalate-sulphuric acid*.
- Xie, J., Lu, Y.-C., 2020. A retrospective on lithium-ion batteries. *Nat. Commun.* 11 (1), 2499. <http://dx.doi.org/10.1038/s41467-020-16259-9>.
- Xu, P., Hong, J., Qian, X., Xu, Z., Xia, H., Tao, X., Xu, Z., Ni, Q.-Q., 2021a. Materials for lithium recovery from salt lake brine. *J. Mater. Sci.* 56, 16–63. <http://dx.doi.org/10.1007/s10853-020-05019-1>.



- Xu, Z., Su, H., Zhang, J., Liu, W., Zhu, Z., Wang, J., Chen, J., Qi, T., 2021b. Recovery of boron from brines with high magnesium content by solvent extraction using aliphatic alcohol. *RSC Adv.* 11 (26), 16096–16105. <http://dx.doi.org/10.1039/D1RA01906F>.
- Yang, H.-j., Li, Q.-h., Li, B., Guo, F.-q., Meng, Q.-f., Li, W., 2012. Optimization of operation conditions for extracting lithium ions from calcium chloride-type oil field brine. *Int. J. Miner. Metall. Mater.* 19 (4), 290–294. <http://dx.doi.org/10.1007/s12613-012-0553-y>.
- Zalazar-Garcia, D., Fernandez, A., Rodriguez-Ortiz, L., Torres, E., Reyes-Urrutia, A., Echegaray, M., Rodriguez, R., Mazza, G., 2022. Exergo-ecological analysis and life cycle assessment of agro-wastes using a combined simulation approach based on cape-open to cape-open (COCO) and SimaPro free-software. *Renew. Energy* 201, 60–71. <http://dx.doi.org/10.1016/j.renene.2022.10.084>.
- Zhang, J., Cheng, Z., Qin, X., Gao, X., Wang, M., Xiang, X., 2023. Recent advances in lithium extraction from salt lake brine using coupled and tandem technologies. *Desalination* 547, 116225. <http://dx.doi.org/10.1016/j.desal.2022.116225>.
- Zhang, Y., Hu, Y., Wang, L., Sun, W., 2019. Systematic review of lithium extraction from salt-lake brines via precipitation approaches. *Miner. Eng.* 139, 105868. <http://dx.doi.org/10.1016/j.mineng.2019.105868>.