881-1
Research Report

Chances for lithium from reservoir waters -
Germany & Austria as production location

DGMK

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Chances for lithium from reservoir waters - Germany & Austria as production location

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Report: Chances for lithium from reservoir waters - Germany & Austria as production location.

Part 1

1. Introduction

In order to meet the increasing demand for lithium, it is necessary to establish alternative process concepts and extraction methods in addition to conventional extraction technologies, which do not provide an ecological footprint that meets the requirements of a sustainable economy. One possibility could be the extraction of lithium from reservoir waters, especially for countries like Germany and Austria, which do not have significant mining lithium sources.

This additional milestone report focusses on an overview of basic methods of Direct Lithium Extraction (DLE). Thus, a large amount of possible DLE methods exist, most of them are in a low TRL (Technical Readiness Level) that do not go beyond a laboratory or demonstration state. But there are also some real “technologies” beyond the prove of concept around TRL 5-6 using prototypes in operation environment. Additionally, a rough economical estimation is provided based on Li-content/flow rates. More precise statements can only be made once further analysis values have been obtained

2. Chances for lithium from reservoir waters – Germany & Austria as production location

Lithium as an economic factor:

The current trend in the price development of lithium carbonate has a high volatility starting at a high level in 2021 (Fig. 1) and decreasing due to market acceptance problems with electromobility, inflation and the global destabilisation.

In line with the European Union's agreement to phase out combustion engines, demand will increase immensely in the near future (Fig.2). Lithium based energy storage will be the solution of choice for both electromobility and storage provision.

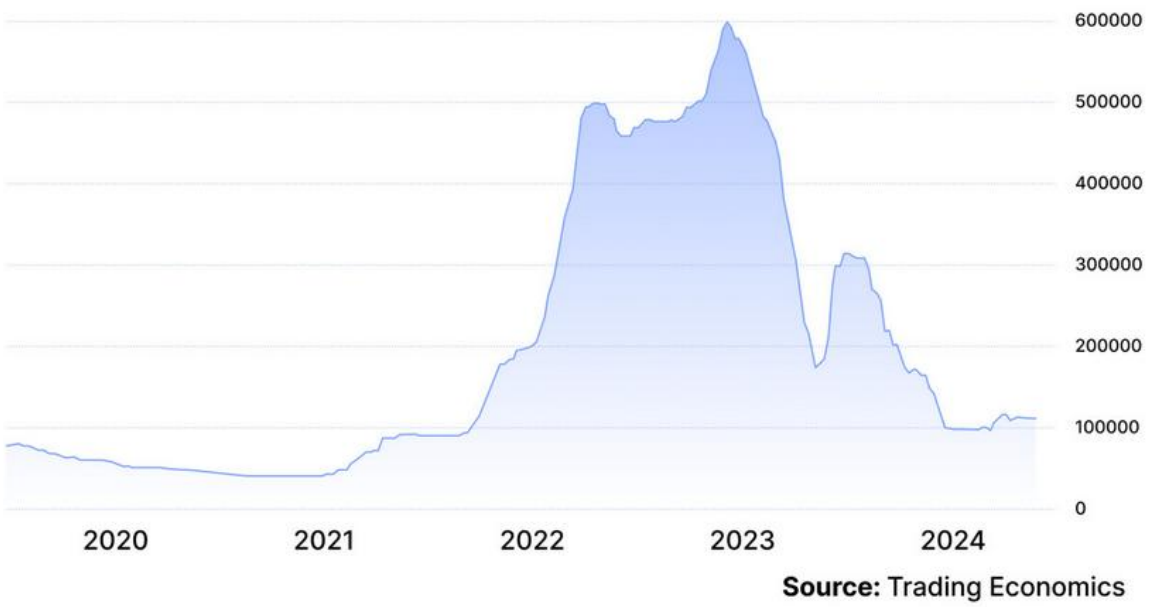


Figure 1: A glance on Lithium price development [100.000CNY=14.000USD][1]

Despite of the current decrease in lithium prices may cause concern, there are several factors that suggest potential for prices to rise again in the future. As of the latest trends, some industry analysts expect lithium prices to stabilize and potentially rise due to the following reasons:

- **Long-Term Demand Growth**: Continued growth in the EV market and energy storage solutions is expected to drive long-term demand for lithium.
- **Supply Constraints**: Some existing lithium producers may face challenges in ramping up production quickly enough to meet the rising demand.
- **Investment in New Projects**: While new lithium mining projects are being developed, there can be delays and challenges in bringing these projects to production, affecting short-term supply. There are numerous upcoming lithium mining projects and investments aimed at boosting supply. In the U.S. and Canada, there are several projects set to advance, which could help stabilize the market and potentially increase prices as production scales up.
- **Technological Advancements**: Improvements in battery technology and energy storage solutions are expected to sustain high demand for lithium. The transition towards renewable energy and the need for efficient storage solutions will further bolster lithium's importance in the energy sector.

[1] https://www.techopedia.com/investing/lithium-price-forecast

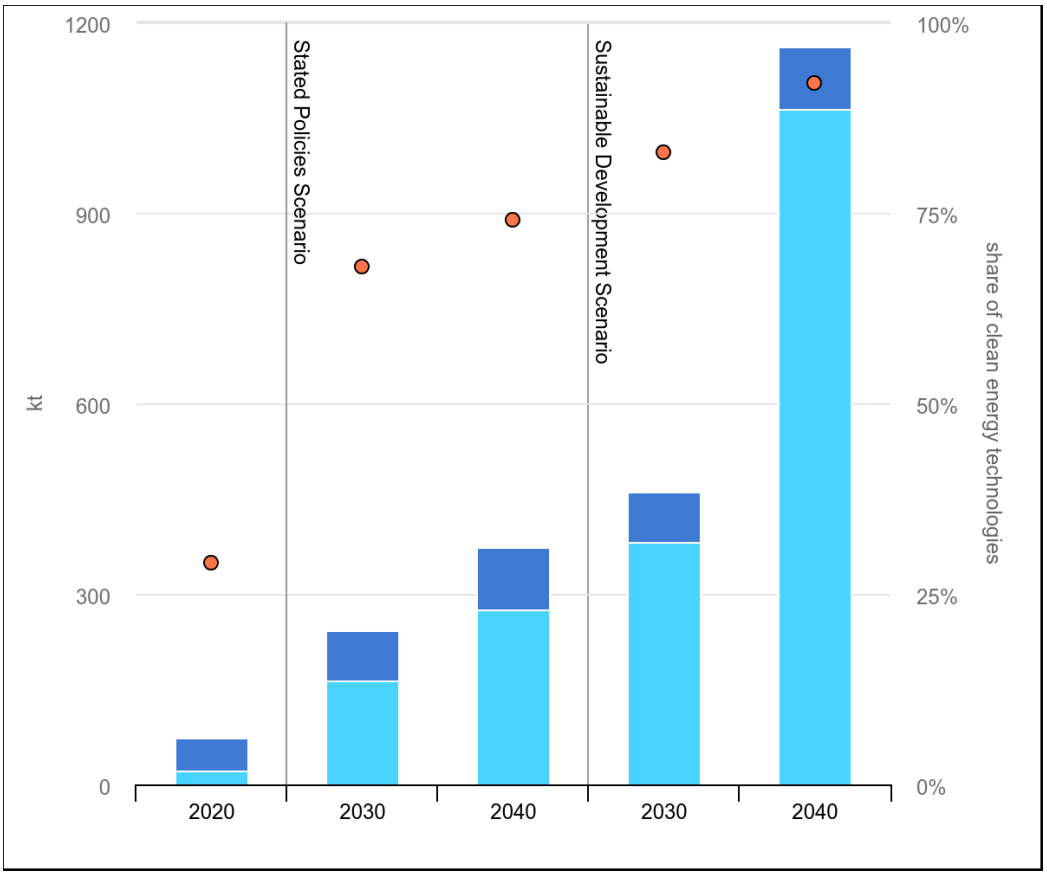


Figure 2: Total Lithium demand by sector and scenario 2020-2040 [2]

The forecast demand for lithium is set to surge dramatically, driven by the accelerating adoption of electric vehicles and renewable energy technologies. By 2040, lithium demand could increase up to 16 times from 2020 levels.

The economic viability of alternative extraction is coupled to price development, determined by exporting nations and demand. Global lithium production is mainly concentrated in Australia, Chile, and Argentina, which, despite not being problematic geopolitically, leaves demand as the dominant factor in price development (Fig. 3). The greatest risks to lithium availability include the concentration of supply in a few countries, geopolitical tensions, and environmental concerns related to mining practices.

Given these risks, diversifying lithium sources through alternative methods, such as extracting lithium from oil and gas reservoirs, could enhance supply security and reduce environmental impact. Investing in this project leverages existing infrastructure and expertise in oil and gas extraction, providing a cost-effective and environmentally friendly solution to meet the growing

[2] https://www.iea.org/data-and-statistics/charts/total-lithium-demand-by-sector-and-scenario-2020-2040

lithium demand. By supporting this initiative, investors can capitalize on the booming lithium market while contributing to sustainable resource development.[3]

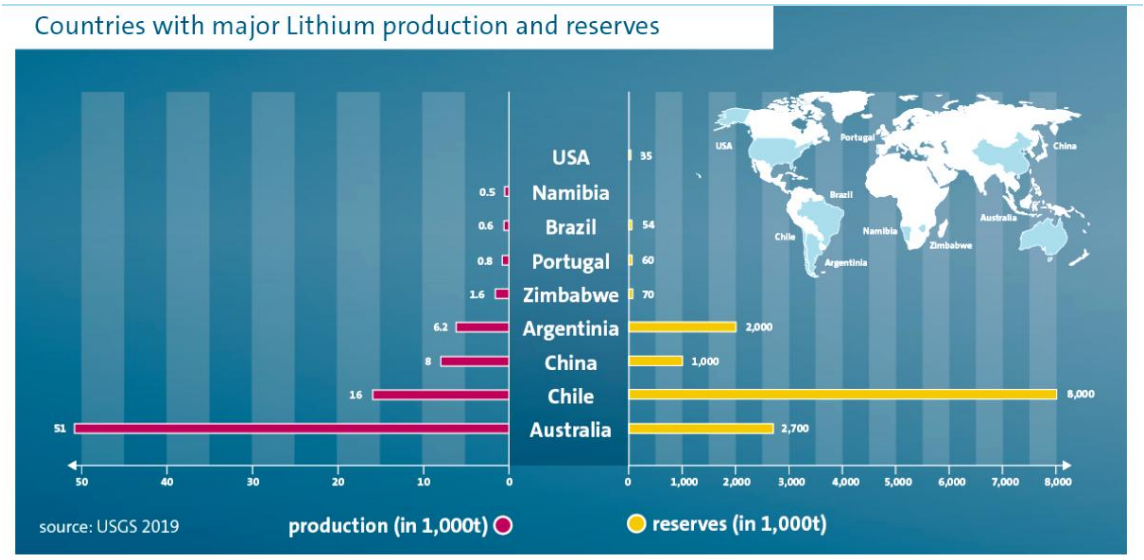


Figure 3: Li-producing countries [USGS 2019]

Can lithium extraction by separation from reservoir waters besides geothermal sources be economically feasible and reduce dependence on external/international suppliers?

2.1. Extraction from geothermal, gas and oil deposits:

The number of existing implementations for the utilisation of so-called sources with ionogenic ingredients is increasing worldwide. Mostly it is a mixture of standard ions and strategic elements. The challenge here is the selective extraction of the valuable elements while taking into account the scaling characteristics of the accompanying elements. However, the content of lithium salts in the aqueous phase and the flow rate is the first decisive factor for a rough economic assessment. Figure 4 shows some relevant sites in Germany.

A wide variety of physicochemical approaches are available as separation methods, which must be adapted depending on the characteristics of fluid material flows. A very simplified overview of the state of the art can be seen in Figure . The trend goes towards hybrid methods in order to realise the necessary selectivity. Most of the proposed technologies are at a low technology ready level (TRL) of around 4-6.

[3] (https://www.iea.org/reports/lithium#dashboard, kein Datum)

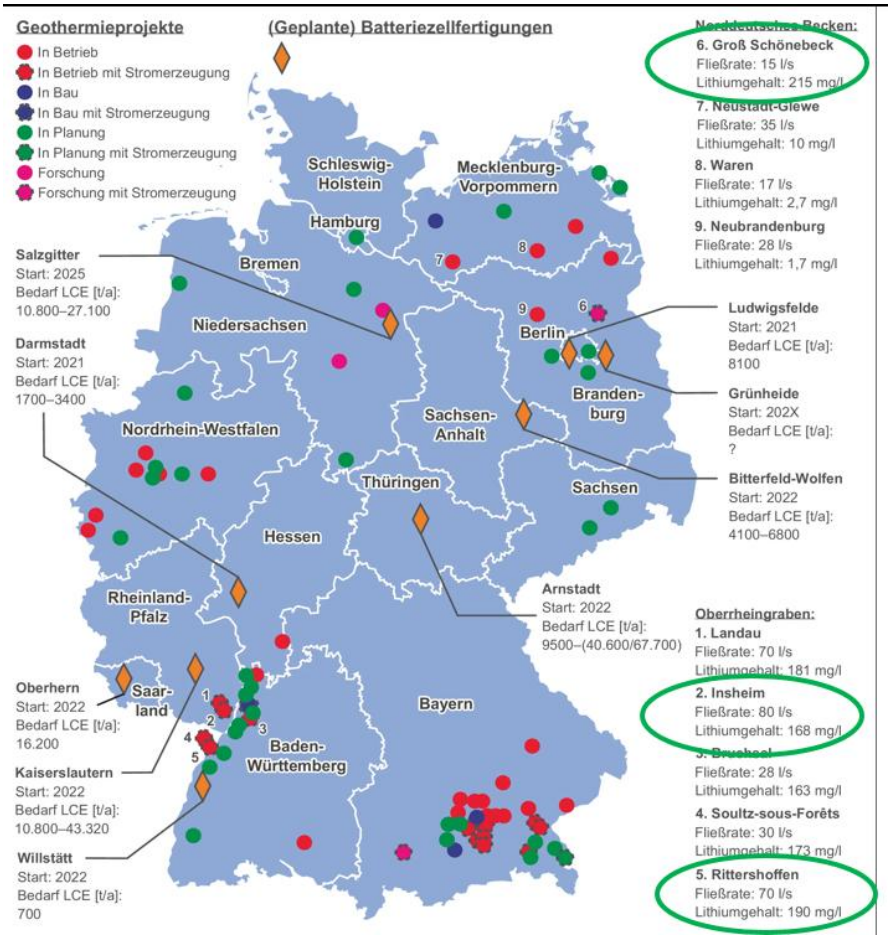


Figure 4. Geothermal sites with lithium contents, flow rates and planned battery cell production in Germany[4]

The exact data regarding the concentrations of the target elements is usually not directly available or is not published. For example, various literature searches have provided data for lithium concentrations from Smackover Brines between 50 and 572 mg/l, Texas Cretaceous reservoirs between 132 and 333 mg/l and North Dakota Devonian Formations between 100 and 288 mg/l. The Canadian Energy Research Institute (CERI) sees good opportunities for extraction at various deposits in the gas and oil industry. [5]

Few available data sets from the German/European area provide values around 161 mg/l for the known project on the Upper Rhine Graben (ERAMET) at the geothermal power plant in Rittershofen, France, which should prove exploitable from a current perspective. The Altmark gas field delivers concentrations of a maximum of 263 mg/l. The former natural gas production well Munster-Südwest Z3 (EXXON) [6] appears to be highly interesting with 353 mg/l of Li in the

[4] (Goldberg, 2022)
[5] (Kumar, 2019)
[6] (Dirk Weißenborn, 2021)

reservoir water. In addition, there are various research projects at selected locations throughout Europe.

Gazprom started a large-scale project for lithium extraction at the Kovyktinskoye deposit, the largest deposit in eastern Russia (1.8 trillion cubic metres),[7] at the beginning of 2022. Unfortunately, due to the current conflicts, no information can be obtained here.

The project starts at this point. In the first phase of the project, comprehensive data compilation and evaluation will be carried out according to process engineering and economic aspects.

Field tests of an economic lithium extraction is planned for phase 2 - 3.

2.2. Project structure

Phase 1: Analysis of the potential of lithium-bearing waters in existing geothermal, gas and oil reservoirs (bottom-up or top-down changing WP1 and 2)

WP1 Data acquisition & analysis

- Data acquisition on existing wells - what analytical data has been collected so far - use of scaling parameters - provision of data by project partners - sampling and analysis of selected samples - creation of a database

WP2 Recording of the plant technology currently available on the market

- Plant technologies for the separation of the ionogenic solutes - especially for the selective separation of lithium from the reservoir waters - which concepts are feasible (including the Influence of the concentration of the target element(s) as well as influence of accompanying elements and system parameters on the separation success - temperature, pH-value, organic content, flow rate affecting the separation success)?

WP3 Evaluation of the acquired data

- Data evaluation with focus on conception of possible system configurations - cost consideration (incl. energy, residues, etc.) - economic efficiency consideration (system efficiency, break-even, risk analysis)

WP4 Conception of possible system configurations

- Design of a mobile container solution with a maximum of flexibility

[7] (Adams, 2022)

2.3. Gantt chart phase 1

WP	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul
WP1 Data acquisition & analysis													
WP2 Recording of the plant technology currently available on the market													
WP3 Evaluation of the acquired data													
WP4 Conception of possible system configurations													
Milestone M						M0.5		M1					M2

Milestone 0.5: Summary of current project results

Milestone 1: Database containing relevant datasets (effluent parameters and extraction technologies)

Milestone 2: Design (concept) of mobile container device

3. Methods of Direct Lithium Extraction (DLE)

Overview of the methods

Direct Lithium Extraction methods have gained attention as an alternative to traditional lithium extraction processes, such as those used in lithium brine and hard rock mining. DLE methods aim to extract lithium from various sources more efficiently. Here is an overview of some common methods of Direct Lithium Extraction (Figure 2):

1. **Solvent Extraction** relies on the use of selective solvents to extract lithium ions from a solution. The solvent is chosen to selectively bond with lithium, allowing separation from other ions.
2. **Adsorption** involves the adhesion of lithium ions to a solid surface, typically an adsorbent material. This method is often used with clay minerals or synthetic adsorbents.
3. **Ion Exchange** involves replacing lithium ions in the source material within other ions, typically sodium ions. After extraction, lithium is then recovered from the ion exchange resin.
4. **Membrane Separation** methods use selective membranes to allow the passage of lithium ions while blocking other ions.
5. **Direct Precipitation** involves inducing the precipitation of lithium compounds from a solution. By adjusting the pH-value or adding specific reagents, lithium compounds

(such as lithium carbonate or lithium hydroxide) can be precipitated. The precipitate is then separated and processed to obtain lithium.

6. **Electrochemical Extraction** methods involve using an electric current to selectively extract lithium ions.

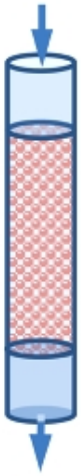
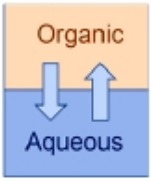
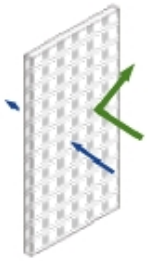
Technology	Mechanism	Developer
Solar evaporation	 Lithium-containing solutions in ponds are concentrated by solar heating; lithium carbonate precipitated on addition of soda ash (sodium carbonate). $2LiCl + Na_2CO_3 \rightarrow Li_2CO_3 + 2NaCl$	Conventional
Phosphate precipitation	Lithium phosphate precipitated on addition of phosphoric acid. $3LiCl + H_3PO_4 \rightarrow Li_3PO_4 + 3HCl$	POSCO[8–10]
Ion exchange resin	 Lithium ions intercalated into layers of aluminum hydroxide on ion exchange resins. $LiCl+NaCl \cdot 2Al(OH)_3 \cdot nH_2O \rightarrow NaCl+LiCl \cdot 2Al(OH)_3 \cdot nH_2O$	Dow[11–13]
Aluminum based adsorbent	Lithium ions adsorbed onto aluminum hydroxide with the almost same mechanism as ion exchange resin above.	FMC[14–16] Simbol[17,18] Eramet[19]
Manganese based adsorbent	Lithium ions adsorbed within layers of manganese oxide such as $H_{1.6}Mn_{1.6}O_4$ and λ-MnO_2.	JOGMEC[20]
Titanium based adsorbent	Lithium ions adsorbed into layers of titanium oxide such as H_2TiO_3.	Neometals[21]
Solvent extraction	 Lithium ions extracted from water phase by oil phase. $R\text{-}H_{sol} + LiCl_{aq} \rightarrow R\text{-}Li_{sol} + HCl_{aq}$	Tenova[22,23]
Nanofiltration	 Lithium ions concentrated through differences in ion rejection ratios and water flow rejection by membrane	MGX[24,25]

Figure 2. Overview of Lithium Extraction Methods. [8]

[8] (Kumar, 2019)

Following this, a more comprehensive elucidation of each methodology will be presented, drawing upon the most current literature sources available up to the present moment.

3.1. Solvent extraction

The process of solvent extraction, wherein dissolved substances transition from a liquid starting medium into a different liquid solvent, hence earning the appropriate title of "solvent extraction." The fundamental requirement for this process is that the starting medium doesn't amalgamate with the solvent but rather exchanges the substance to be extracted by contact. Organic solvents like tributyl phosphates (TBP) diluted with methyl isobutyl ketone or paraffin, crown ethers, or the utilization of ionic liquids have the capacity to absorb significant quantities of lithium chloride while also exhibiting selectivity towards other cations.[9,10] Thus, the different types of extraction agents operate through various mechanisms. In TBP (tributyl phosphate) extraction, in addition to solvents, a co-extraction reagent is used, such as $FeCl_3$. In chloride-rich waters, a complex is formed from $FeCl_3$ together with the solvents and lithium is bounded through a cation exchange process. In crown ethers, oxygen acts as a donor atom, forming a strong base and exhibiting very high reactivity with dissolved alkali metal cations such as lithium, which in turn represent strong acids.[9,11,12] After absorbing lithium, it can be dissolved from the organic ether phase using acid. This process involves multiple steps as lithium requires a different pH condition for release compared to other ions like Na, K, Ca, and Mg, which remain in the organic phase during extraction. Therefore, the dissolution of Li from the ether must take place in several steps. Na and K can initially be dissolved out of the ethers at a pH value of 7-8. Li is only released at a lower pH value, while Ca and Mg remain in the organic phase. Ionic liquids are a further medium for lithium extraction. These are salts with a melting temperature of below 100 °C that contain organic cations in combination with organic or inorganic anions.

3.2. Adsorption and Ion exchange

A highly effective extraction method is adsorption. For the application of inorganic sorbents for selective ion separation, various approaches and materials are being investigated, such as

[9] (Liu, 2019)
[10] (Stringfellow, 2021)
[11] (Swain B. , 2016)
[12] (Zhang, 2021)

titanium oxides, manganese oxides, aluminium hydroxides, or zeolites. The current focus of research projects is to optimize the performance of sorbents concerning their loading capacity and reusability.[9,10] Manganese oxides feature a spinel structure and demonstrated notably efficient abilities in extracting lithium (Figure 3). The manganese oxides are synthesized with addition of lithium, allowing to be incorporated into the crystal structure. After the extraction of lithium, a gap remains, leading to the term "ion sieves" (specifically for lithium ions). The binding of lithium occurs through redox reactions and ion exchange on and within the crystal lattice. [13]

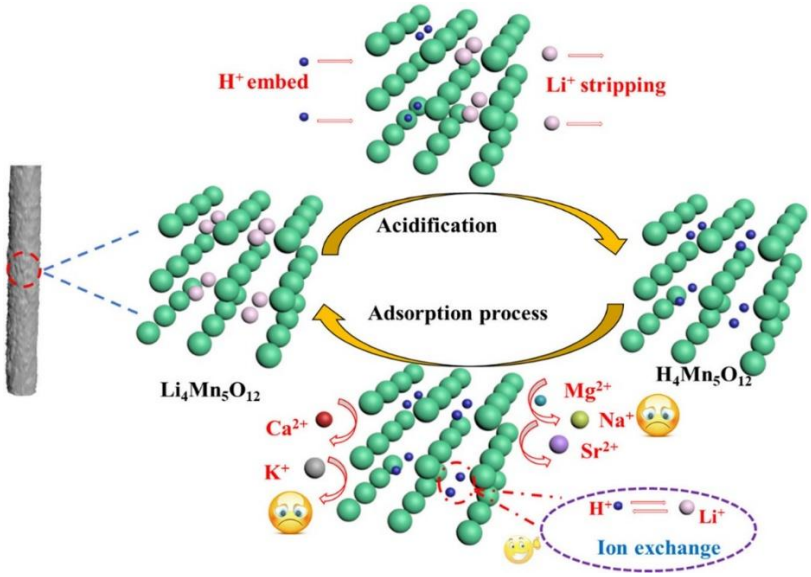


Figure 3. Functioning of the lithium extraction process with manganese oxides. [14]

For sorbents based on titanium oxides the mechanism of action is quite similar to manganese oxide sorbents. However, they exhibit greater stability over multiple charge and discharge cycles but they are less selective.[9]

The extraction of lithium using aluminium hydroxides involves the incorporation of lithium into octahedral gaps within layered aluminium hydroxide minerals (such as gibbsite), resulting in the formation of Lithium Aluminium Double Hydroxide Chloride (LADH-CL) [15,16,10,17]. Simultaneously, chloride is bound between the individual layers, simplifying the production of lithium chloride during the dissolution process.[18] Another method of lithium extraction involves

[13] (Weng, 2020)
[14] (Qiu, 2021)
[15] (Isupov, 1999)
[16] (Paranthaman, 2017)
[17] (Wu, 2019)
[18] (Jiang, 2020)

the utilization of both naturally occurring and artificially synthesized zeolites. Zeolites, characterized by their porous crystalline structures, have the capacity to contain lithium among various other chemical compounds. The process typically includes treating zeolites with acids or bases to dissolve the lithium content, subsequently isolating and purifying the lithium through a series of procedures. However, while this method shows promise, it may not currently match the economic viability or efficiency of other extraction methods, such as those involving salt lakes or ores.

3.3. Membrane Separation

Extensive focus has been directed towards researching membrane separations for direct lithium extraction. Numerous methodologies have been investigated to create membranes (Figure 4) capable of selectively permitting the transit of lithium ions while repelling other ions or concentrating lithium from brines or solutions. Nanofiltration, as an example of membrane technology, allows selective separation of multivalent from monovalent ions. This pressure-driven separation technique is based on pore size and charge of the membrane. [9,19,20] Nanofiltration systems, also used in a wide spectrum of water treatment processes, are already available on an industrial scale. Nanofiltration for lithium separation is always coupled with pre- or post-treatment processes to separate interfering ions because other monovalent cations such as Na or K can also permeate through the membrane [9,21,19]. Further approaches include the combination of membrane distillation and crystallisers [20,22,23], "Supported Liquid Membranes" and membranes functionalized with ion sieves.

Membrane distillation is a temperature-driven process that enables contactless concentration up to the crystallisation limit via a water-repellent membrane. Here, a vapour pressure gradient along the hydrophobic membrane is created by a higher tempered feed and a cooled permeate stream on the other side of the membrane. This allows water to pass through the membrane as vapour and condense within the permeate stream. As a result of the removal of water molecules as vapour, the inlet water stream is relatively enriched in ions.[24] The economic viability of water extraction using membrane distillation has been proven for high-salinity water (approx. 100g/l) among others by shale gas extraction.[25]

[19] (Sun, 2015)
[20] (Li, 2019a)
[21] (Somrani, 2013)
[22] (Quist-Jensen C. A., 2016a)
[23] (Quist-Jensen C. A., 2016b)
[24] (Winter, 2017)
[25] (Tavakkoli, 2017)

In the "Supported Liquid Membrane" method, membranes loaded with liquids are used during liquid-liquid extraction. These membranes, which function like conventional systems, offer advantages such as lower solvent and space requirements. Under laboratory conditions, this method has achieved high extraction rates of over 90 % for lithium extraction with low salt solutions within 120 minutes at pH values of 9.5 and 12.5. Similar techniques can also be applied to membranes by equipping them with ion exchange resins, combining large [20] membrane surface areas and selectivity of sorbents to keep the sorbent stationary and ensure low energy consumption.[20] These sorbent-loaded membranes achieved loadings of 30 mg/g. Most of the loading takes place within 60 minutes, demonstrating relatively fast kinetics compared to other extraction processes.[19,20]

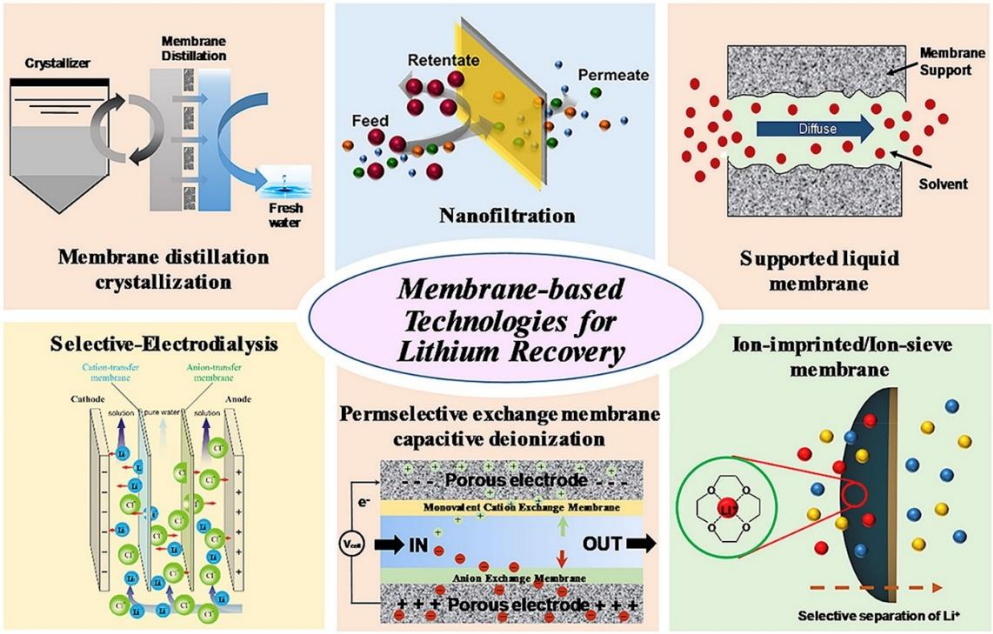


Figure 4. Overview to lithium extraction by Membrane technology.[26]

3.4. Electrochemical methods

Electrochemical methods stand out as a promising route for Direct Lithium Extraction. Despite demonstrating high selectivity even at low initial lithium concentrations of 7 mg/l, these methods are constrained to a maximum concentration of approximately 350 mg/l lithium.[27, 28] The most commonly debated techniques encompass the electrochemical ion pump and electrodialysis.

[26] (Li, 2019)
[27] (Battistel, 2020)
[28] (Palagonia, 2017)

In an ion pump, the lithium is bound by applying a voltage to the working electrode and chloride to the counter electrode, which is made of nickel or silver, for example .[9, 27, 29, 30] In a second step, the brine is flushed out of the chamber and replaced with a recovery solution (seawater or brine). In a third step, the bound lithium is released by voltage reversal. [27, 30] In electrodialysis, electrochemical and membrane-based methods are combined.[9,10,20,31] Ion-selective membranes separate lithium cations and chloride anions when applying a voltage and allowing enrichment.[31] In a second step, through a voltage reversal, the raw material to be extracted can be released back into a carrier solution.[9,20,27]

Electrochemical methods, akin to those in lithium-ion batteries, are well comprehended, offering shorter charging durations (<20 minutes) and requiring no additional chemicals for dissolution. The energy demand varies from 1 to 60 Wh/mol, exclusive of pump energy. [27,9](Lithium extraction in geothermal power plants may necessitate 0.2 to 12.4% of the generated electrical energy, depending on the method, excluding pump energy. Ion pumps are considered more efficient, while upscaling electrodialysis using selective membranes presents challenges. Limited electrode loading capacity and the corrosive nature of thermal waters are primary concerns. Furthermore, pH fluctuations and membrane blockages can adversely affect performance.

3.5. Efficiency of current approaches

The following tables (Table 1-2) summarize some important parameters regarding lithium extraction methods. [4]

Table 1. Required pH values, extraction efficiency in the laboratory and loading capacity for various methods, including solvent extraction, adsorption/ion exchange with various sorbents, membrane separation and electrochemical methods

Methods	Required pH-value	Extraction efficiency (laboratory)	Load capacity
Solvent extraction	> 7-8	up to 90%	
Adsorption and ion exchange			
1. manganese sorbent	1. 10-13	up to 90 %	20–60 mg/g
2. titanium oxide-based sorbents	2. 8-13		
3. (LADH-Cl)	3. -		< 8 mg/g
4. Zeolites	4. -		5 mg/g
Membrane with ion sieves	-	-	30-34 mg/g
Electrochemical methods	-	-	30–40 mg/g

[29] (Romero, 2021)
[30] (Zhao, 2019)
[31] (Mroczek, 2015)

Table 2. Overview of the advantages and disadvantages of the various methods of lithium extraction.[4]

Method	Advantages	Disadvantages
Solvent extraction	- Solvents regeneration and reuse - Low solvent losses by contact with carrier fluid and during subsequent reprocessing	- high corrosiveness of acids and alkalis require high material standards especially in reaction tanks and pipework
Adsorption and Ion exchange	- high efficiency (Manganese oxides) - High stability over several charging and discharging cycles (Titanium dioxide) - No acid requirement, minimises sorbent losses (LADH-Cl)	- High material consumption - Long reaction times (24–120 h for complete loading, large reaction vessels) - Degradation during desorption - Potential environmental impacts - Use of chemical buffers and acids - Risk of layer formation and inclusion of competing ions - Low maximum loading of 8mg/g - High water demand (LADH-Cl)
Membrane separation	- Enable selective separation based on ion size, surface charge, or chemical/physical properties - High ion selectivity is promising for extracting lithium from magnesium-rich fluids (Nanofiltration) - Industrial scale applications for water treatment adaptable for lithium extraction (Nanofiltration) - Energy-efficient process	- Expensive membrane production - Potential for membrane scaling (hardness builder) reducing process efficiency - Disposal/recycling challenges exist for acids or solvents used, adding to environmental concerns and costs - For complete ion separation, additional treatments required - These technologies are still in development, needing refinement for large-scale use
Electrochemical methods	- Rapid binding of lithium and redissolution without the use of chemicals - Selectivity even with low initial lithium content	- Limited to a maximum concentration of approx. 350 mg/l lithium

3.6. Alternative sources for lithium extraction

After exploring potential methods for extracting lithium, the objective is to develop the most efficient mechanism and technique for obtaining lithium from oil and gas reservoir waters. It is widely recognized that the most challenging aspect of this process lies in the separation of lithium from the organic phase containing aqueous streams.

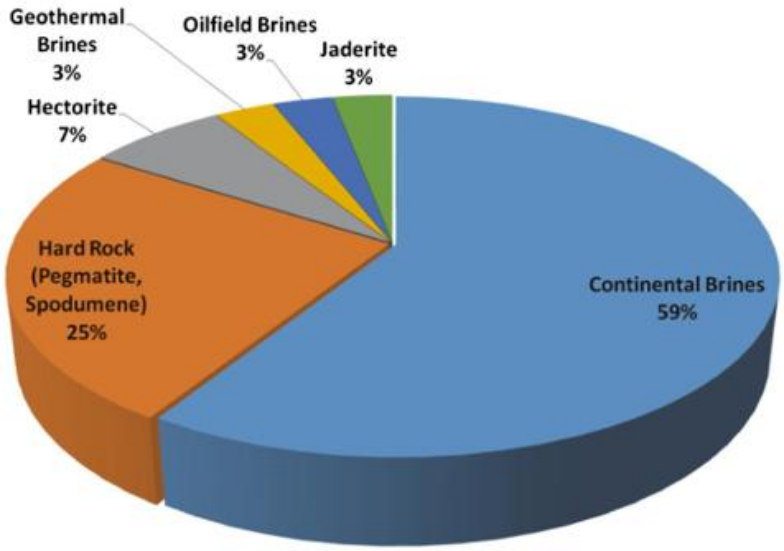


Figure 5. Lithium spread across multiple raw material sources.[32]

While the methods presented have commonly been used to extract lithium from geothermal systems, they can also be equally applicable for extracting lithium from shale gas-produced water [33] and oilfield brines. [34]Due to the significance and relevance of lithium resources, extensive research has already been conducted to explore lithium extraction from various natural systems (Figure 5) [32]. However, the field of study regarding DLE from geothermal, gas- and oilfield brines is relatively new, and ongoing research continues to investigate different approaches, resulting in the proposal of several solutions and techniques for lithium extraction.

One basic pretreatment structure is displayed in Figure 6.

[32] (Swain B. , 2017)
[33] (Lee, 2020)
[34] (Knapik, 2023)

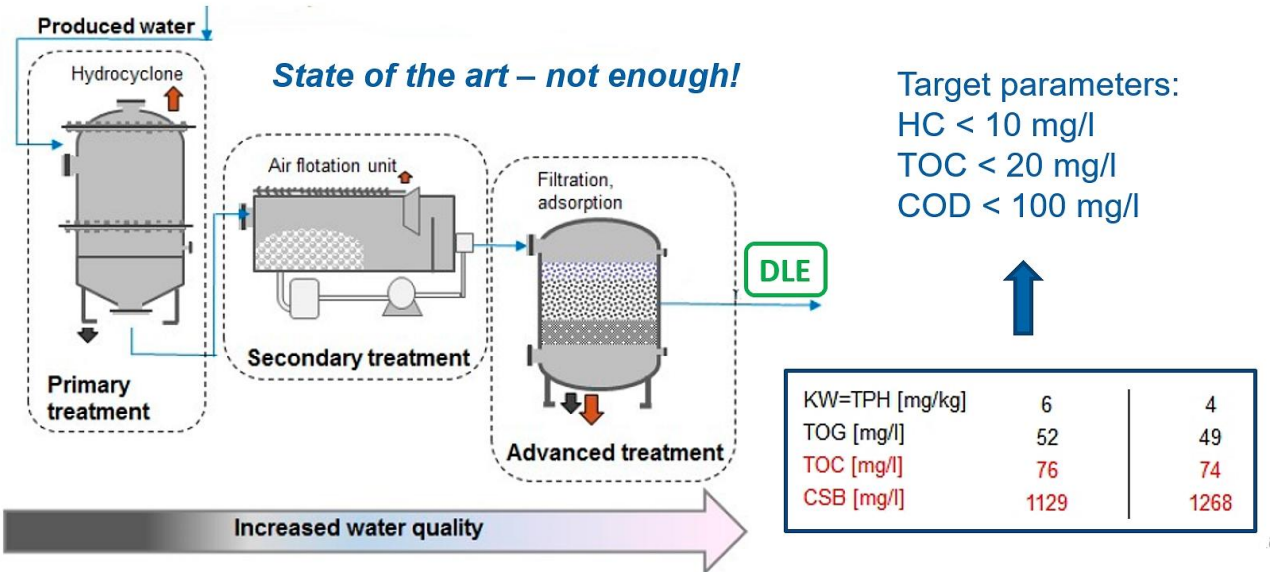


Figure 6. Diagram illustrating the process of crude oil dehydration and treatment of produced water. [34],[35]

The aim is the reduction of hydrocarbon content lower than 10 mg/l, a TOC < 20 mg/l and a COD < 100 mg/l. Pretreatment is followed by the DLE-process, with highest efficiency to the solute combination of regarded produced water effluent.

4. Analytical values of regarded produced water - Evaluation of the parameter sets

For a correlating of DLE processes with the datasets provided, there are still missing basic hydrochemical parameters, especially for Company B cases (see chapter 6). Without these values, no evaluation is realistic.

5. Estimation of DLE feasibility

A statement on the feasibility of the various DLE processes cannot yet be made at the present time.

[35] (Tian, 2022)

6. Rough economic assessment

Table 3. Dataset Company A

Field	LaWa Li Content [mg/l]	LaWa Volume [m^3/d]	LaWa Volume [l/d]	Li Mass [kg/d]
1	130	6,271	6271	0,82
2	208	16	16000	3,33
3	74	8	8000	0,59
4	69	6	6000	0,41
5	61	281	281000	17,14
6	NA	39	39000	-
7	NA	147	147000	-
8	0,01	414	414000	0,00
9	0,01	955	955000	0,01
10	-	1036	1036000	-

Rough calculation:

“Field 5” example: Li^+ yield 17.14 kg/d (extraction rate 90%, availability 330d, Li to $LiCO_3$ factor 5.3)

Amount of $LiCO_3$ 27t/a → Earnings ~ 1.000.000 $/a (with LCE 36.000$/t)

Table 4. Dataset of Company B

Probe	Field 1	Ionic content (in kg/d)
Sampling details	~1100m^3/h = 26,400,000 l/d	
Sample location	Water from Oilfield	
pH-value	7,10	
m-value[mmol/l] (alkalinity pH4,3)	18,3	
Hardness [ºdH]	49	
TDS calculated form ionic balance	23760	
Chloride [mg/l]	13558	357931,2
Bromide [mg/l]	52	1372,8
Jodide [mg/l]	32	844,8
Sulfate [mg/l]	6	158,4
Lithium [mg/l]	2,2	58,08
Sodium [mg/l]	8466	223502,4
Ammonium [mg/l]	70	1848
Potassium [mg/l]	82	2164,8
Magnesium [mg/l]	76	2006,4
Calcium [mg/l]	207	5464,8
Strontium [mg/l]	30	792
Barium [mg/l]	15,6	411,84
Iron [mg/l]	0,7	18,48
HC [mg/kg]	1-10	-
TOC [mg/l]	NA	-
COD [mg/l]	NA	-

Rough calculation (as in the previous example):

„Field 1“

2.2mg/l → 1100m^3/h → 2.4kg/h → $LiCO_3$ 91 t/a → Earnings ~ 3.300.000$/a

7. Vulcan Energy Phenomenon

Vulcan Energy was founded in 2018 by geologists Dr. Francis Wedin, who now acts as managing director and CEO, and Dr. Horst Kreuter. Wedin started his career in the Australian mining industry and began exploring ways to mine lithium using environmentally friendly geothermal resources in 2014. Kreuter, has been developing and implementing geothermal projects around the globe for over 20 years. In June 2018, Vulcan Energy Resources went public on the Australian stock market.

Some press releases:

SPIEGEL 12.2021: Vulcan's German subsidiary is purchasing a geothermal power plant in the Upper Rhine Valley for around 31.5 million euros. As the company announced, it is taking over the power plant from the regional energy supplier Pfalzwerke. A first pilot plant for the extraction of lithium hydroxide is to be put into test operation at the Insheim geothermal power plant in the Palatinate.

Vulcan is working on supplying lithium to Volkswagen and other European car manufacturers such as the Opel parent company Stellantis. They have already placed orders, as lithium is needed in the production of batteries for electric cars. However, experts believe that the company still has to prove that its idea for extracting lithium is actually financially lucrative enough to work on a large industrial scale.

In the Upper Rhine Graben, there is a lot of lithium dissolved in thermal water thousands of metres below the surface. The water is already being extracted to generate electricity and heat. Vulcan Energy wants to utilise the high lithium content of the salty liquid to extract the element and make it usable. At the same time, the extracted thermal water is to be used to generate energy, making lithium production CO2-neutral. Vulcan Energy is planning an extraction process that uses less land, groundwater and energy than the existing methods of open-cast mines and brine evaporation ponds.

However, investors are also sceptical as to whether Vulcan Energy's idea will work at all. High investments are necessary to make it a viable business. Volkswagen also tied its long-term supply agreement with the company to the condition that the German Vulcan subsidiary can also successfully start commercial production of lithium in 2026.[36]

CHARGED Magazine 01.2023 – original quotation: “Vulcan Energy Resources has successfully developed, tested and demonstrated its in-house lithium extraction sorbent, VULSORB, for use in lithium extraction from the Upper Rhine Valley Brine Field in Germany.

VULSORB is a variation of the type of lithium extraction sorbents developed thirty years ago, but the company says its process is faster and more efficient than the legacy method of using large-scale evaporation and large quantities of chemical reagents to extract the lithium and

[36] (Vulkan Energy kauft deutsches Geothermiekraftwerk für Lithium-Produktion, 2021)

process it into lithium hydroxide. The sorbent extraction happens in hours, rather than up to 18 months.

The company says VULSORB has demonstrated higher performance and lower water consumption in lithium extraction compared to commercially available sorbents. Testing has been carried out on live brine from Vulcan's geothermal renewable energy plant in Insheim, Germany.

Vulcan says it plans to use VULSORB for lithium extraction in its phase 1 commercial development, and first commercial production is targeted for Q4 2025. The company is also testing other sorbents from commercial suppliers for potential use in future phases of development.

Vulcan's CEO, Dr. Francis Wedin, said, "Until now, there have been no commercially available sorbents for lithium extraction manufactured in Europe, thus making the region dependent on foreign supply chains. VULSORB will enable Europe to extract lithium from its own brine fields, without being exposed to geopolitical risk. Vulcan will assess the potential of VULSORB to be used in other lithium brines in Europe and globally."" [37]

Scientific information:

Vulcan Energy is actively engaged in exploring adsorption-type Direct Lithium Extraction (A-DLE) technology for lithium extraction, utilizing geothermal brines to minimize environmental impact and resource usage. This innovative method involves the adsorption of lithium ions onto a porous material, in contrast to dominating conventional and resource-intensive evaporation ponds. A-DLE's use of water instead of acid for recovery, further minimizes its environmental footprint.

DuPont, a renowned French company known for its expertise in providing aluminate-based sorbents (as detailed on their website: https://www.dupont.com/water/applications/lithium-brine-purification.html), operates as a leading supplier in the sphere relevant to Vulcan Energy. They offer versatile options in the realm of lithium brine purification, showcasing their commitment to innovation and advancement in the field. Their emphasis on high-purity lithium aligns with the growing demand for advanced batteries, particularly within the electric vehicle sector.

[37] (Burkley, 2023)

Regarding the extraction of lithium from deep geothermal waters through Vulcan Energy's pursuit of the DLE technique, utilizing aluminum hydroxide, there's promising potential around a mid-level TRL.[4] However, significant uncertainties persist, particularly regarding its practicality within large-scale industrial operations, which remains unverified.[38]

Furthermore, within the domain of lithium adsorbance, there is a scarcity of published papers and patents.[39,40] Vulcan Energy's technology isn't groundbreaking; rather, it relies on an adsorption method employing aluminum hydroxide, a technique established two decades ago [41]. This aligns closely with the research detailed in Isupov's paper.[42] Furthermore, within the domain of lithium adsorbance, there is a scarcity of published papers and patents.

Stringfellow's findings reveal that crystalline aluminum trihydroxides like gibbsite, bayerite, and nordstrandite possess the ability to create layered intercalation matrices with lithium. Additionally, amorphous $Al(OH)_3$ can undergo a reaction with lithium chloride at higher temperatures, resulting in the formation of crystalline $LiCl \bullet 2Al(OH)_3$. This compound demonstrates the capacity to adsorb lithium ions from brines containing lithium. $Al(OH)_3$ can be added to zeolite, resins, and other materials to make lithium sorbents. Stringfellow's description of aluminum hydroxide's role as a lithium sorbent aligns closely with other explanations found in the field. His findings reveal that various crystalline aluminum trihydroxides and even amorphous $Al(OH)_3$ demonstrate the ability to adsorb lithium ions from brines containing this element. This characterization and mechanism of action for $Al(OH)_3$ as a lithium sorbent share similarities with other studies and established explanations within the field. The incorporation of Al(OH)3 into various materials for lithium sorbents highlights the adaptability and potential widespread application of this approach in lithium extraction technologies.

Apart from the usual PR publications on the high performance of Vulcan Technology and a large number of reports in stock exchanges and financial portals on the advantages of this technology, there is no reliable information available. Diagrams or tables with scientific data sets are nowhere to be found. Benchmarking is therefore not feasible.

The only existing “dataset” with reliable information [43] is a 2021 LCA on the footprint of Vulcan's lithium hydroxide production conducted by Minviro Ltd. According this data, the result confirm

[38] (Stringfellow, 2021)
[39] (U.S. Patentnr. 11,247,189.)
[40] (U.S. Patentnr. 4,472,362, 1984)
[41] (A-DLE)
[42] (Isupov, 1999)
[43] (Vulcan Energy: Industry-leading Life Cycle Assessment results, 2021)

that Vulcan's Zero Carbon Lithium™ Project has the lowest planned carbon footprint in the world compared to any LCA results previously published in the lithium industry. Unfortunately, no scientific datasets for this are accessible!

A company that merely claims to be better is difficult to categorise.

8. Opportunities for public funding

A rough scanning of current public funding programs shows different possible opportunities. Here, of course, the corresponding boundary conditions must be observed.

EIT RawMaterials:[44] EIT regularly offers funding programmes in the field of raw materials research. It is advisable to regularly review the calls for proposals and to study the funding conditions in detail with regard to the partner structure.

HORIZON-CL4-2024-RESILIENCE-01-01:[45] RESILIENT VALUE CHAINS 2024 Projects outcomes will enable achieving the expected impacts of the destination by increasing access to primary raw materials and secondary raw materials, in particular critical raw materials for EU industrial value chains and strategic sectors. There are new calls in March 2024 where possible matches can be identified.

BMBF and **BMWi**: no current programs available

[44] (Call for Innovation & Education Projects)
[45] (Funding & tender opportunities)

Part 2

1. Introduction to part 2

In the first part of this report, we presented the possibilities of extracting lithium from reservoir waters in Germany and Austria, discussed the extraction possibilities from geothermal, gas, and oil deposits, and presented non-conventional direct lithium extraction methods, including the currently existing methods of lithium extraction. The efficiency of the current approaches was also discussed. An assessment of the feasibility of DLE was made based on the data determined by Company A and B. We then discussed and presented our findings from the literature research on Vulcan Energy. The information about this company is particularly important for finding the most productive adsorbents in this field. It turns out that DuPont is the provider of these adsorbents and the leading supplier to Vulcan Energy. An extended list of funding companies and organizations is important for the next steps of this project. There are a few public programs that can be promising, but appropriate boundary conditions must be considered.

2. Project meeting Company B as host

After our additional milestone report from December 2023, on 7 February 2024, we had our next meeting with our project partners, where we shared our new findings in connection with the project. However, as there was no major time interval between the report and the meeting, there was no extended gain in knowledge. We mainly discussed the findings and research results and collected ideas for further investigations. One of the main points of discussion was the company Vulcan Energy LLC, specifically the adsorbent it uses to extract lithium. This may sound strange, but it is not, as this company claims to be the best at extracting lithium from geothermal water. Furthermore, it apparently has entire reserves of the most effective adsorbent, which it obtains from DuPont.

3. Gain of new useful information

In our search for the suitable extraction method, we found some new useful papers and sources[46, 47, 48, 49] that helped us to optimize the structure of the future pilot plant. Some details were important for understanding the existing current possibilities and the TRL (Technology Readiness Level). In the first part, we have already discussed the various methods that can be used to extract lithium. Some details that are important will be presented here, as these were obtained later thanks to the sources mentioned above. According Farabakhsh et al.48 the ion exchange method has already reached TRL 8, but this method requires high operating costs and environmental risks during production. Solvent extraction, which has already reached TRL 7 nowadays, has high efficiency, high Li^+ selectivity and good manageability, but is not favoured for our objectives as it has disadvantages such as fire hazard in a high temperature environment, high cost compared to other technologies, high waste production, production of toxic materials. Membranes, with a lower TRL (4-5), have advantages such as simple and continuous operation, high recovery rates, relatively low energy consumption, and environmental friendliness. However, they also have disadvantages, including pre-treatment requirements and high costs, which could lead to other potential issues. According to this work, the sorption of LiCl on the adsorbent already reaches TRL 9, which seems somewhat exaggerated. This method of separating and extracting lithium is an important part of the pilot plant. It is important to mention that the term sorption refers to adsorption and ion exchange. Both processes are characterised by high selectivity, relatively low energy consumption and low environmental impact/high environmental friendliness (Table 5). At this point, the important question arises as to which adsorbent is best suited. There are three main adsorbents under discussion (Table 6), which are based on complex aluminium-, manganese- and titanium-structures. Through literature research we came to conclusion that the Al-based adsorbent is most promising. Manganese or titanium-based adsorbents can be used in combination with aluminium-based adsorbents to increase the efficiency of lithium extraction. Liu Q. Y. et al. have summarised the intensity of the properties these adsorbents offer in a table with a unique presentative way (Table 6).

[46] (Lee K. &., 2011)
[47] (Liu Q. Y., 2023)
[48] (Farahbakhsh, 2023)
[49] (Miranda, 2022)

Table 5. The overview of TRL of possible Li-Extraction methods.

DLE -Method	**TRL**	**Mechanism**
Adsorption	(TRL:9)	Sorption of LiCl onto the adsorbent
Ion-exchange	(TRL:8)	Sorption of Li+ into the ion-exchanger
Solvent Extraction	(TRL:7)	Based on the difference in partition coefficients of lithium between the liquid and organic phases
Membranes	(TRL:4-5)	Pressure-driven (nanofiltration) or electrical potential driven (electrodialysis) methods
Electrochemical	(TRL:3-4)	Reversible electrochemical process, such as lithium- ion intercalation in electrodes

Table 6. Comparison of metal-based adsorbents for lithium extraction. (The number of plus points corresponds to the intensity of the respective property, with the three plus points representing the maximum.)

Performance	**Al-based**	**Mn-based**	**Ti-based**
Li adsorption capacity	+	++	+++
Li selectivity	+	+++	++
Technology maturity	+++	++	+
Stability and regeneration performance	+++	+	++
Facile operation condition	+++	+	++
Environmental safety	+++	+	++
Low preparation cost	+++	+	++

We also carried out literature research on the produced water. It was useful to understand what kind of mixtures we are dealing with when extracting lithium from the produced water. As we know produced water is a by-product of oil and gas extraction, and it typically contains a complex mixture of organic and inorganic compounds, including salts, heavy metals,

hydrocarbons, and various other chemicals. The oil fraction that contains these compounds

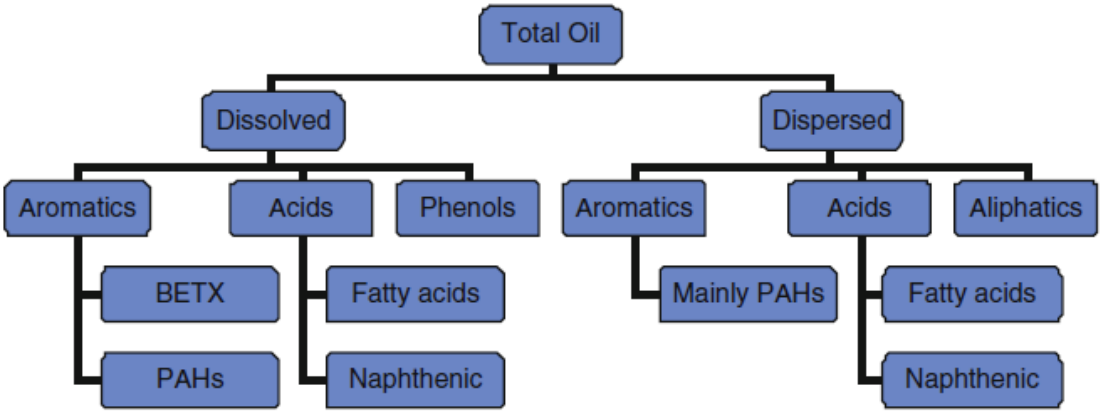


Figure 7 The variety of different compounds arearing in oil classified to the two classes: Dissolved and Dispersed.

can be dissolved and dispersed (Figure 7). In the case of “dissolved”, the oil is usually existing in a soluble form. In the case of “dispersed”, the oil is present as emulsion in the form of small droplets. However, this is only general information and not the actual produced water that we will be dealing with as part of our project, which may even differ from the picture presented here, as it was obtained at different locations as part of this project. Figure 8 shows a possible sequence of steps for separating and extracting Li from production water. However, this is again a more general scheme that contains some interesting and helpful details.

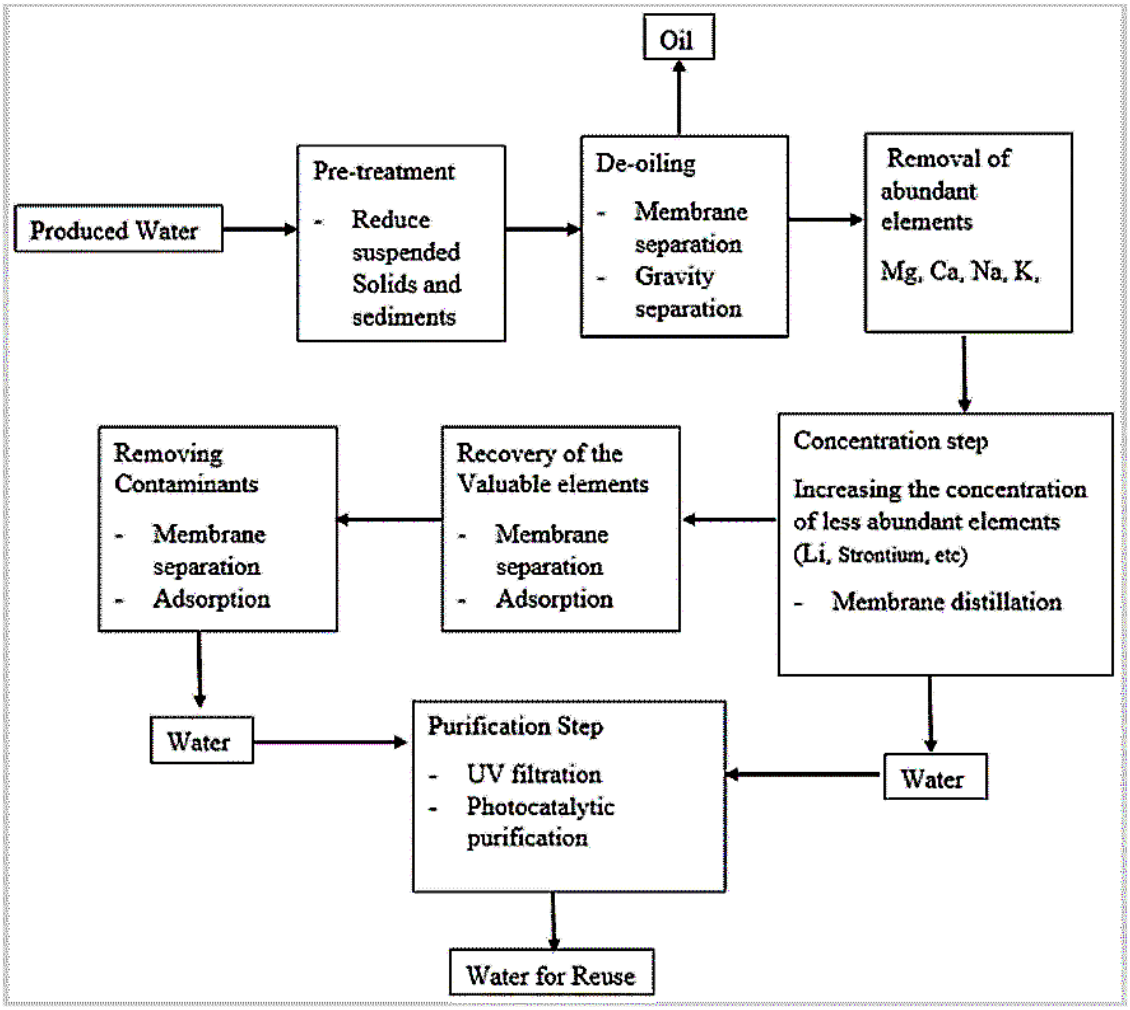


Figure 8 . A general process train for the separation and recovery of high-value elements. [49]

4. The way to the DLE flow chart for the Li extraction pilot system

After extensive literature research, a crucial step in our project was identifying the available methods for extracting lithium from oil and gas deposits. We used May 15, the start date of the DGMK conference in Celle, as an internal deadline, where we later presented the project and its advantages to the expert community. This was important for attracting additional investors (i.e. project partners) who could support the project with the aim of mutual benefit. As a result, we developed our first promising extraction scheme.

5. DGMK conference and the success among potential new project partners

As previously mentioned, we had the opportunity to present the current situation based on our literature research and the resulting successful flow chart of the Li extraction pilot plant at the conference organized by DGMK on May 15 and 16 (see Figure 12). Overall, the presentation attracted a highly interested audience, and we were able to engage a few potential new project partners.

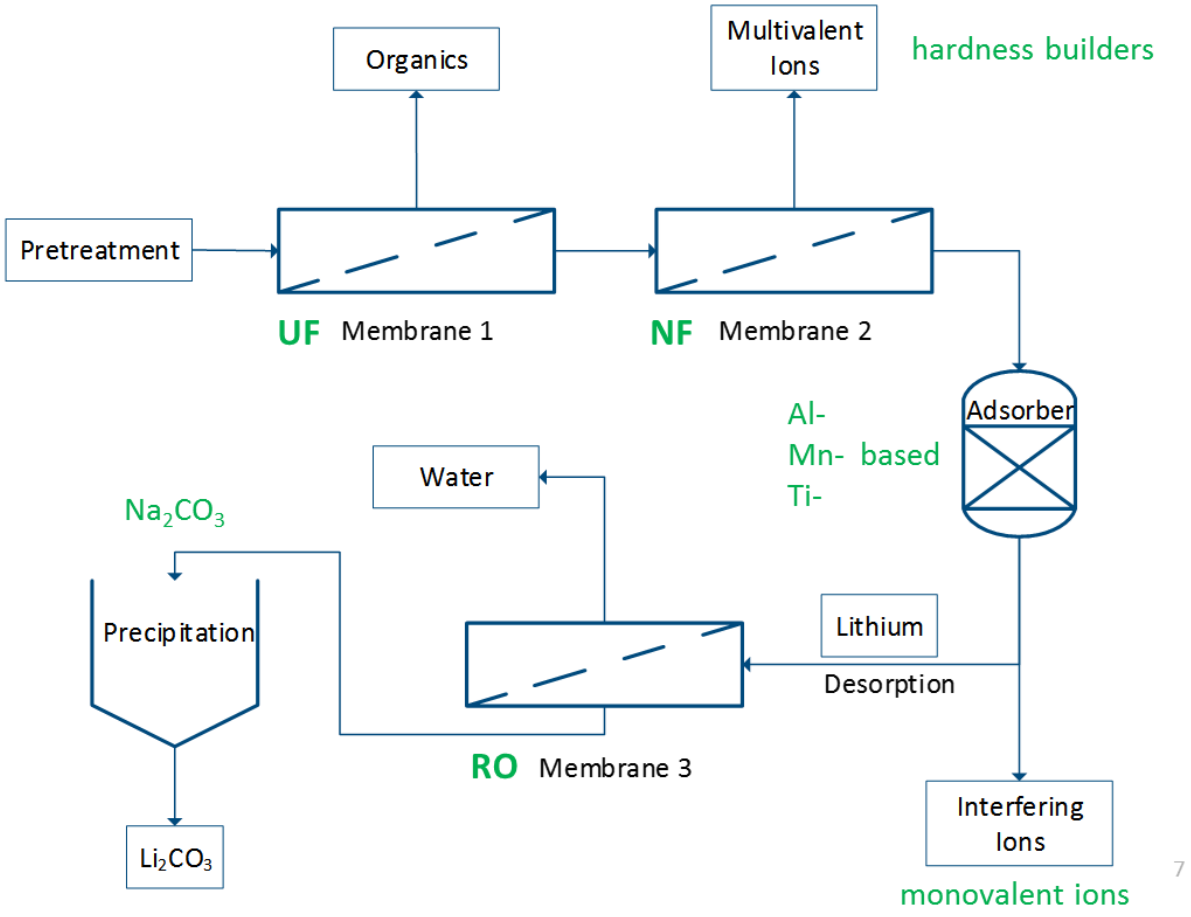


Figure 9. Flow chart of the Li extraction pilot plant

6. Starting with experiments

Since the middle of the project, we have realized the crucial importance of selecting a suitable adsorbent. This led us to identify aluminium hydroxide as the most widely used and currently most efficient adsorbent. Another key development was discovering that DuPont, the most well-known provider of this adsorbent, was virtually “out of stock” – this means there is an artificial unavailability of the material (politically caused by Vulcan Energy). We, therefore,

decided to synthesize our own aluminium-based adsorbent based on information available in the literature. [50, 51]

The experiments began on April 15, 2024. Additionally, we obtained produced water samples from Company A and B, from which lithium was extracted using the adsorbent synthesized by a master student. These samples were also analysed to gather information about other solutes, with a particular focus on defining the TOC (Total Organic Carbon) value.

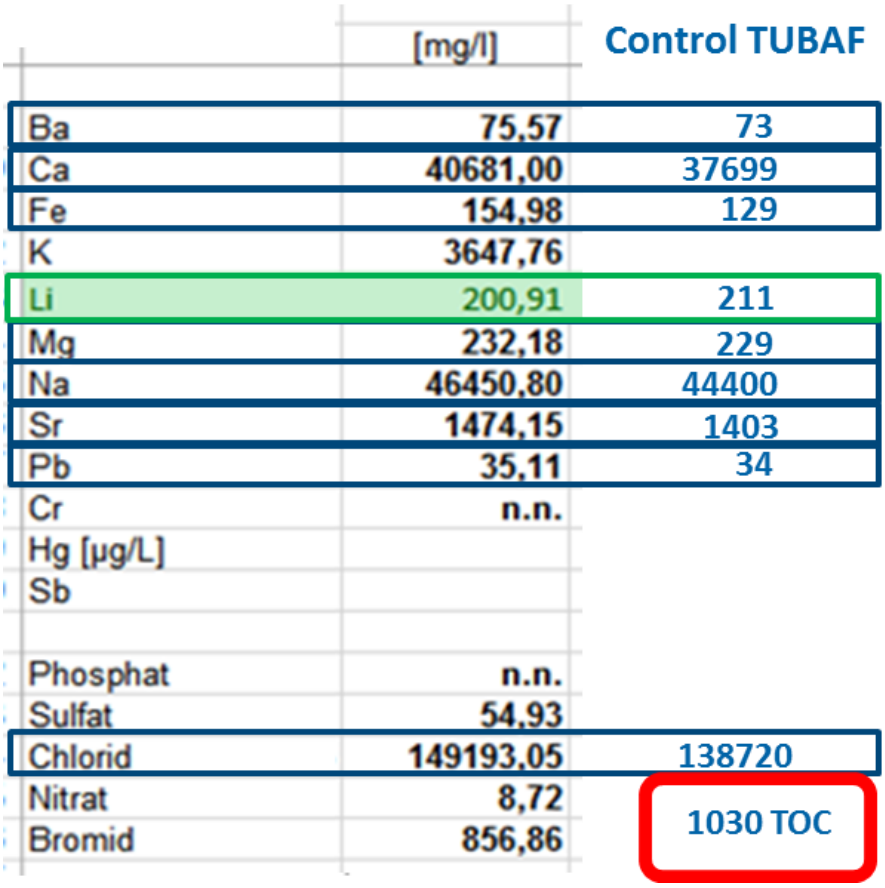
7. Data sets from analytical values of PW-samples

To verify the results of former analyses, the most relevant solutes in the samples provided by Company A and B have been analysed. The comparing results are shown in figure 13 to 15.

pH-Wert	7,10	
m-Wert [mmol/l] (Alkalinität pH4.3)	18,3	control TUBAF
Gesamthärte [°dH]	49	
TDS berechnet aus Ionenbilanz [mg/l]	23760	
Chlorid [mg/l]	13558	12960
Bromid [mg/l]	52	
Jodid [mg/l]	32	
Sulfat [mg/l]	6	
Lithium [mg/l]	2,2	5,2
Natrium [mg/l]	8466	8529
Ammonium [mg/l]	70	
Kalium [mg/l]	82	
Magnesium [mg/l]	76	78,3
Calcium [mg/l]	207	199
Strontium [mg/l]	30	29,6
Barium [mg/l]	15,6	15,6
Eisen [mg/l]	0,7	
KW=TPH [mg/kg]	6	
TOG [mg/l]	52	
TOC [mg/l]	76	41,8
CSB [mg/l]	1129	

Figure 13. Parameters of solute contents in Company B water sample x

[50] (Zhong, 2021)
[51] (Jayanthi, 2023)



	[mg/l]	Control TUBAF
Ba	75,57	73
Ca	40681,00	37699
Fe	154,98	129
K	3647,76	
Li	200,91	211
Mg	232,18	229
Na	46450,80	44400
Sr	1474,15	1403
Pb	35,11	34
Cr	n.n.	
Hg [µg/L]		
Sb		
Phosphat	n.n.	
Sulfat	54,93	
Chlorid	149193,05	138720
Nitrat	8,72	1030 TOC
Bromid	856,86	

Figure 104. Parameters of solute contents in Company A water sample y

Feld			
Wasser-Typ			
Datum			
Probenehmer			
Dichte	[kg/l]	1,1563	
pH		4,9	
ELF	[mS/cm]	227	
Härte	[°dH]	3081	control TUBAF
Al^{3+}	[mg/l]	0,04	
$Fe^{3+/2+}$	[mg/l]	130	78
Mn^{2+}	[mg/l]	19	
Ba^{2+}	[mg/l]	32	77
Sr^{2+}	[mg/l]	1400	635
Ca^{2+}	[mg/l]	19400	7778
Mg^{2+}	[mg/l]	1420	1691
K^{+}	[mg/l]	1200	
Na^{+}	[mg/l]	60700	57158
Li^{+}	[mg/l]	61	36
HCO_3^{-}	[mg/l]	189	
SO_4^{2-}	[mg/l]	178,5	
Cl^{-}	[mg/l]	143179	105540
Br^{-}	[mg/l]	909	
Acetat	[mg/l]	0	
Bor	[mg/l]	28	
BTEX			
Benzol	[µg/l]	59	
Toluol	[µg/l]	27	
Ethylbenzol	[µg/l]	12	
m,p-Xylol	[µg/l]	< 5	
o-Xylol	[µg/l]	7	50,4 TOC
Summe BTEX	[µg/l]	105	
KW-Index	mg/l	< 0,2	
Summe PAK	mg/l	6,32	

Figure 115. Parameters of solute contents in Company A water sample z

8. Project meeting in Freiberg

On July 4th, we were pleased to host our final project meeting in Freiberg. As before, we had a very interesting and productive exchange of ideas, primarily aimed at continuing this project. The current status of the project was presented, including the status of the ongoing experiments and the expected results. As mentioned earlier, the final results are expected to be available at the range of September/October.

9. Planning the extension of the research project in phases 2 and 3 with additional project partners

Focussing on the construction of a multifunctional container system at pilot scale for on-site investigation of the most efficient DLE-method related to the site-specific speciation of the reservoir waters. The resulting treatment system with as many degrees of freedom as possible should enable the 'best case' for deriving a production process. The results obtained provide site-specific parameters that can be used to plan a DLE plant on a pilot scale. Thanks to its multifunctionality, the treatment system can be flexibly adapted to the site-specific material flows and thus derive the key parameters for the scale-up for the co-operation partners involved.

10. Relevant results from Master's thesis

Design of Experiments

The experiments are based on the process flow diagram (Figure 12). This work focusses on the membrane and sorption methods.

The plan is to first remove the organics from the sample using ultrafiltration. Subsequently, the multivalent ions (Ca^{2+}, Mg^{2+}) are separated using nanofiltration, as these interfere with adsorption. The sample containing the remaining monovalent ions is then sent to the absorption stage, where lithium ions are extracted from the solution. An aluminate-based material is used as the sorbent, which selectively absorbs lithium from the solution. The sorbent is washed with deionised water for lithium desorption. The lithium-rich water is then transferred into a reverse osmosis device, where the lithium is further concentrated as a retentate. Deionised water is regenerated again as permeate. The lithium carbonate is then precipitated in an open tank by adding sodium carbonate.

Membrane Experiments

The experimental setup for the membrane experiments is shown in Figure 16. The membranes are placed in a cleaning solution for one hour for conditioning and then in deionised water for at least one hour. The membranes are also stored in deionised water, shielded from light. To remove suspended particles, all samples are pre-treated with a pleated filter before membrane-filtration.

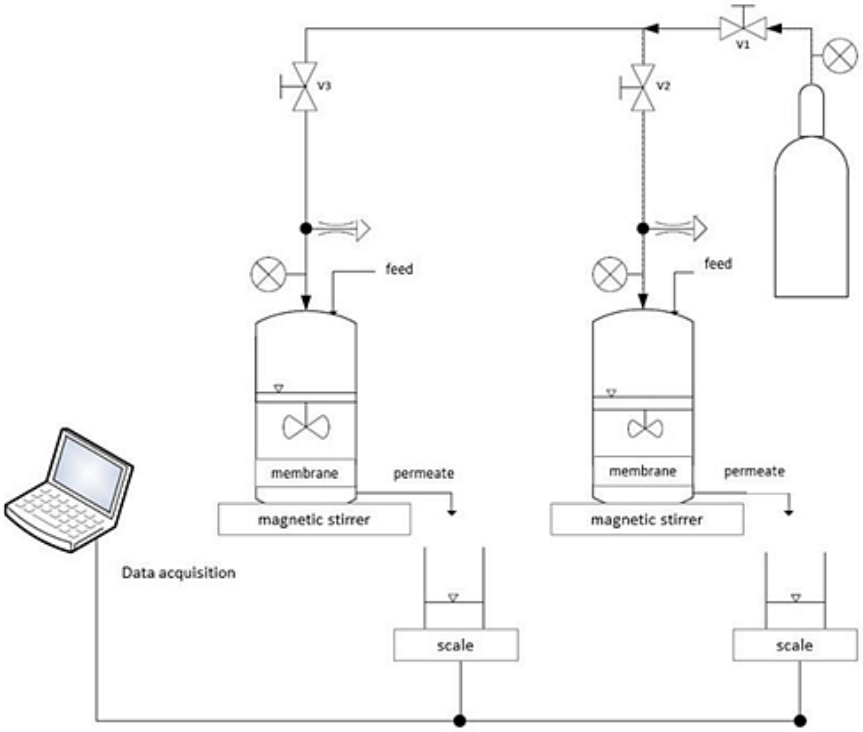


Figure 16: Experimental setup for membrane experiments in batch mode

For ultrafiltration, a pressure of 5 bar is set by N_2. 300 ml of sample water is filled into the membrane cells. The valves are then opened, and the membrane cells are pressurised. The experiment is stopped at a permeate volume of 150 ml, which corresponds to a recovery rate of 50 %. Permeate and retentate are both analysed. Membranes tested are listed in Table 7.

Table 7: Membranes used for ultrafiltration, data from institute data sheet and manufacturer

Membrane	Type	Manufacturer	MWCO (Da)	pH-range	T-range
RM UH030	hydrophile	Microdyn Nadir	30000	0-14	5-95°C
RM UP005	hydrophile	Microdyn Nadir	5000	0-14	5-95°C
RM UH004	hydrophile	Microdyn Nadir	4000	0-14	5-95°C
PES 5	hydrophile	Schleicher und Schüll	5000	-	-
ETNA 01PP	hydrophobe	Alfa Laval	1000	1-11	0-60°C
GR60PP	hydrophobe	Alfa Laval	25000	2-10	5-70°C
GR95PP	hydrophobe	Alfa Laval	2000	2-10	5-70°C

Membranes from table 8 are used for nanofiltration. The membranes are designed for hydrophilic applications. The operating pressure is 20 bar. The membrane cells are filled with 300 ml of sample water (same procedure as in ultrafiltration experiments). The test ends at a recovery rate of 50% or a test duration of 5 hours.

Table 8: Membranes used for nanofiltration, data from manufacturer

Membrane	Active Material	Manufacturer	MWCO (Da)	pH-range	T-range
NFT50	Polyamide	Alfa Naval	200400	2-10	5-50°C
NP030]	Polyethersulfone	Microdyn Nadir	500-600	0-14	5-95°C
NF99HF	Polypiperazine	Alfa Naval	300	3-9	5-50°C

In order to close the gap to a real process, nanofiltration tests are also carried out on a cross-flow system. The P&I diagram is shown in Figure 17. The NF99HF membrane is used. The operating pressure is 20 bar and the sample mass is 10 kg. The recovery rate is around 50 %. The procedure is carried out according to the operating instructions.

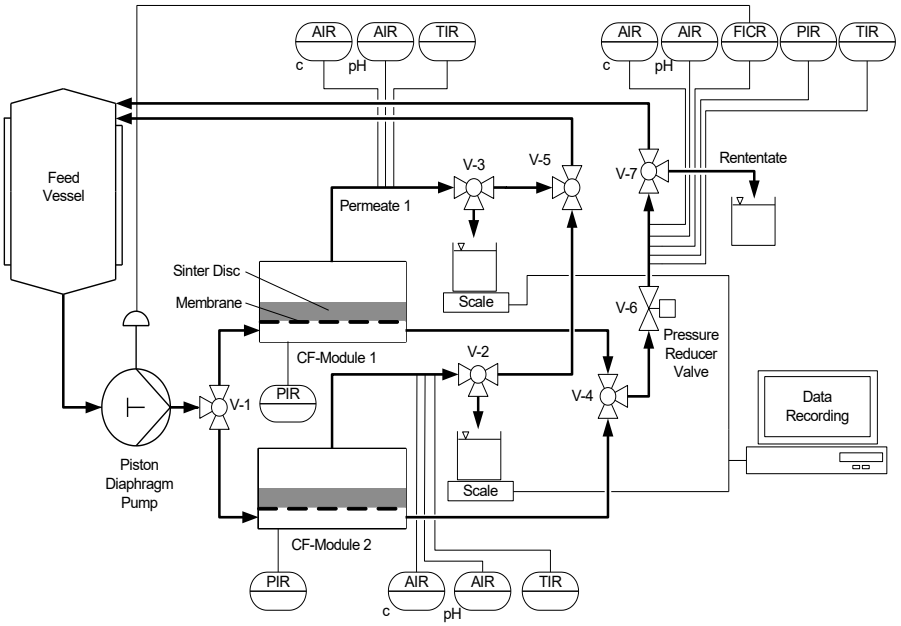


Figure 17: P&I flow diagram of the cross-flow system

Production of the Li/Al-LDH sorbent

As already mentioned in chapter 3.2, the aluminium-based sorbent Li/Al-LDH is used for the sorption experiments. As the sorbent is not available for purchase, it is produced in-house. It is produced using a precipitation reaction with subsequent washing according to Zhong [Zhong 2021].

First, an aqueous solution containing a Li^{+}/Al^{3+} molar ratio of 1:2 is mixed. To prepare the sorbent (Figure 18 left), the NaOH is weighed out and dissolved in 150 ml $water_{demin}$. The beaker is heated to 45°C on the heater with magnetic stirrer. The stirrer speed is 250 min^{-1}. The 1 g LiCl and 11.4 g $AlCl_3$ $6H_2O$ are also weighed out and dissolved in 150 ml $water_{demin}$. The solution is then poured into a drip apparatus. When the sodium hydroxide solution has heated up, the precipitation reaction starts. Initially, the dripping rate is set to around 60 drops per minute. The pH value is measured at regular intervals. Care is taken to ensure that the pH value does not fall below 5.5 according to Paranthaman [Paranthaman 2017]. A white precipitate forms relatively quickly in the solution. After about 10 minutes, the solution becomes cloudy. After the last drop, the stirrer is left on for another 10 min and then the solution is allowed to settle for 10 min. The liquid phase without solids is then poured off. The residue is washed into a filter paper with one litre of deionised water. Finally, the solids are placed in the drying cabinet at 50°C overnight.

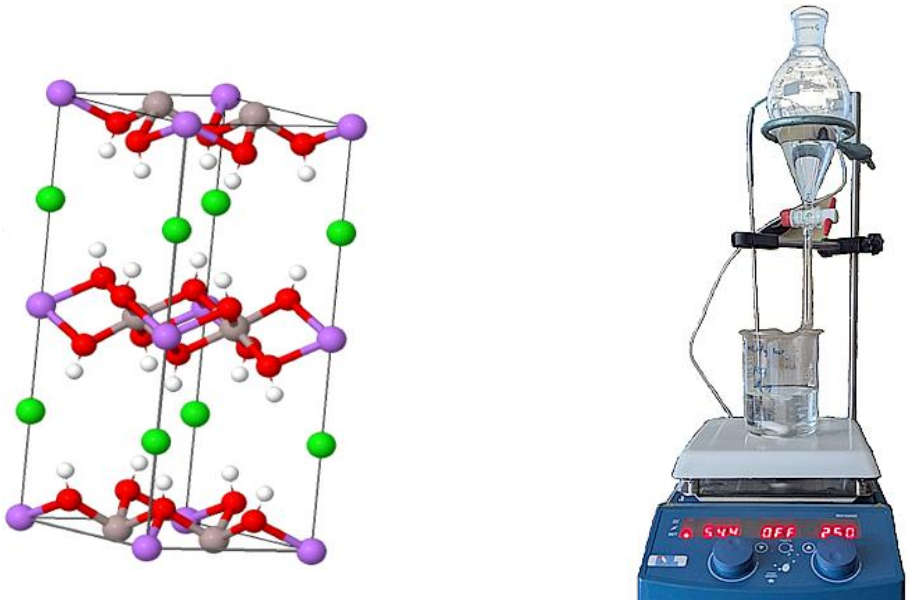


Figure 18: Structure of lithium aluminate; red - O2, white - H2, green - Li, purple - Al, grey – Cl (left) [Wu 2019], and experimental setup (right)

Results and discussion

Three samples from different locations were analysed for the experimental tests, relevant analytical values are shown in Table 9. The complete analysis data from the university's internal analyses and those from the companies can be found in Chapter 7. The composition of the samples in both analyses is similar.

Table 9: Extract of relevant analysis values of the starting materials (own measurements)

Sample	Company	Li-content mg/l	TOC mg/l	Salinity g/l	pH-value
x	Company B	5,2	41,8	22	7,3
z	Company A	36	50,4	222	5,8
y	Company A	211	1030	236	4,3

Membrane Filtration - Ultrafiltration

Ultrafiltration is used here for the separation of organic compounds (TOC). The membranes tested cover a wide range of different manufacturers, types and separable molecular masses.

The tests are initially carried out as screening experiments in order to shortlist suitable membrane systems. The tests are intended to provide an overview of how the samples interact with the various ultrafiltration membranes. To summarise, TOC removal by ultrafiltration is not efficient. The hydrophilic membrane with the most promising performance is the UH030, the hydrophobic membrane is the GR95PP (see table 7). The two membranes will be analysed more intensively in a two-stage ultrafiltration process and in a heated membrane cell using double determination.

As the single-stage process delivers unsatisfactory results, a two-stage ultrafiltration process (Figure 19) is used to test the extent to which each stage can remove some of the organic compounds in order to increase the TOC retention. The permeate from the first stage serves as feed for the second stage.

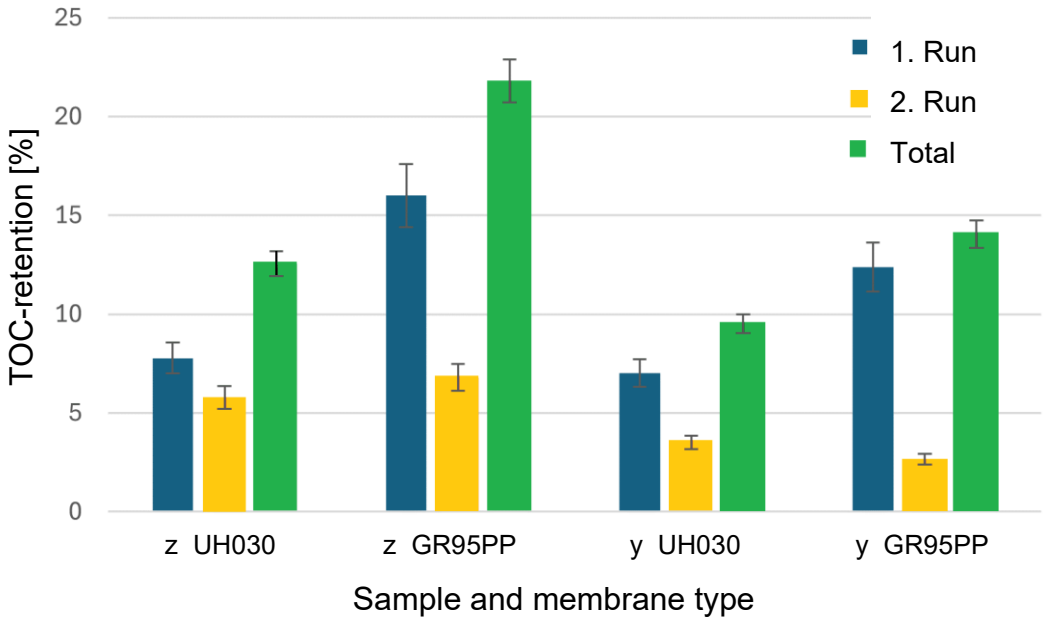


Figure 19: Two-stage ultrafiltration with samples y and z using membrane UH030 and GR95PP

Another approach to improving TOC separation is to use a heated membrane cell. Heating changes the membrane structure as well as the properties of the samples. For this purpose, a membrane cell is connected to a thermostat and a temperature of 50°C is set (Figure 20).

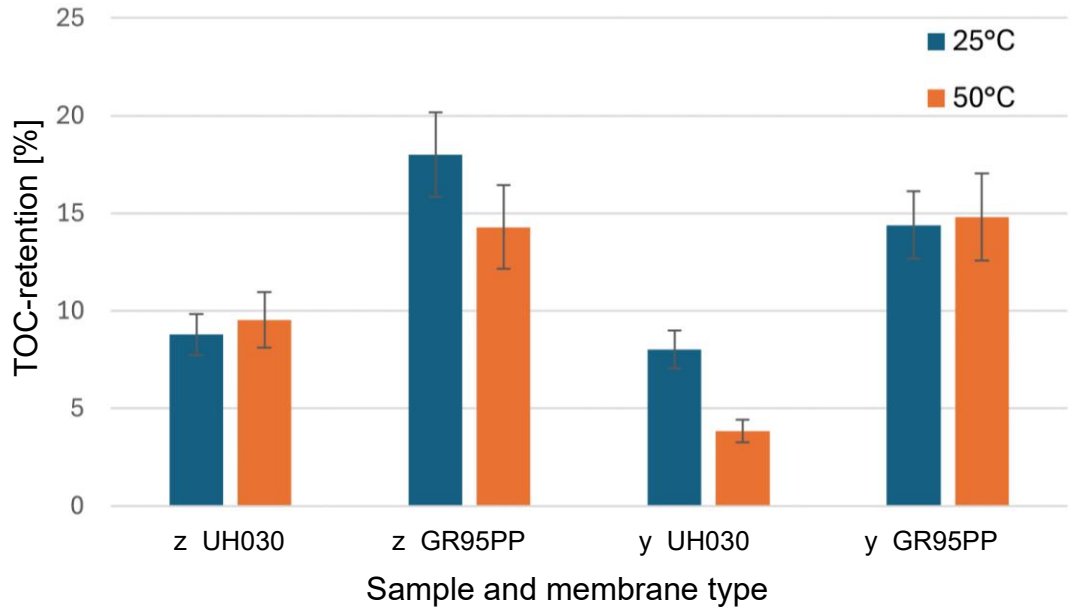


Figure 20: Comparison of the UF membranes at two temperatures: hydrophilic membrane UH030, hydrophobic membrane GR95PP

Overall, ultrafiltration was not successful in reducing the TOC content significantly. Both two-stage and heated ultrafiltration show no clear performance improvements. However, it can be deduced from the results that a large proportion of the organics must have a MWCO of less than 1000 Da. For this reason, an attempt is now being made to separate the organics together with the polyvalent ions in nanofiltration. The extent to which the organics increase the fouling of the membranes must be investigated in long-term experiments.

Membrane Filtration - Nanofiltration

In order to separate molecular masses smaller than 1000 Da, experiments are carried out using nanofiltration. As the membranes mark the transition area between pore membranes and solution diffusion membranes, they are used for the separation of multivalent ions (e.g. Ca^{2+}, Mg^{2+}, SO_4^{2-}) in addition to the separation of organic compounds, whereby the corresponding separation mechanisms are very complexly dependent on physicochemical parameters. For nanofiltration, the focus is set on three membranes (Table 9). Firstly, the separation of organics is addressed. The results for the y and z samples are shown in Figure 21.

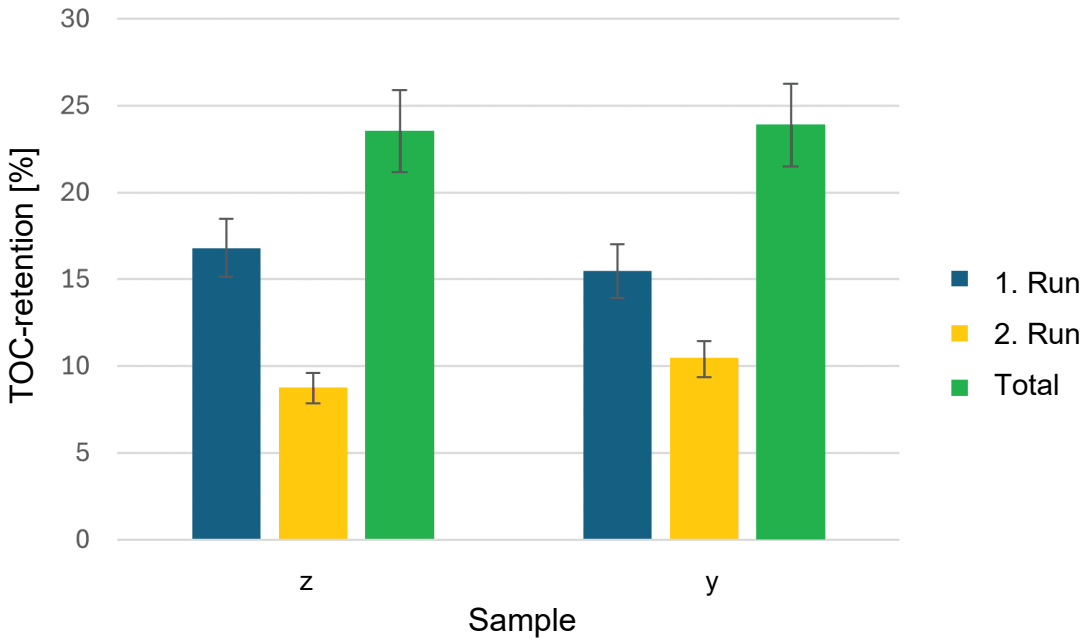


Figure 21: TOC separation of the y and z samples with the NF99HF membrane

Nanofiltration shows better separation of organics than ultrafiltration. Nevertheless, the separation is lower than expected.

In addition to TOC separation, the focus in nanofiltration is on ion selectivity. The aim is to retain as many multivalent ions as possible on the retentate side. At the same time, the

monovalent ions should be forced to the permeate side. Overall, the separation of the polyvalent ions in the single-stage process is not satisfactory (not shown). For this reason, two-stage nanofiltration was investigated. Figures 22 and 23 are intended to illustrate this. In the diagrams, the retention of the relevant ions when using the NF99HF membrane is considered to be the one with the best performance.

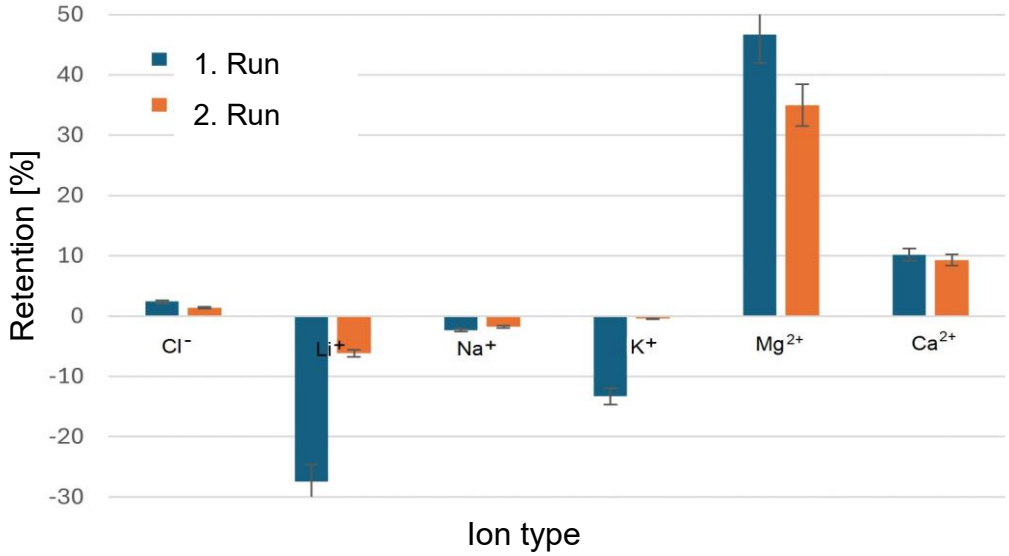


Figure 22: Separation of ions in two-stage nanofiltration for sample z with membrane NF99HF

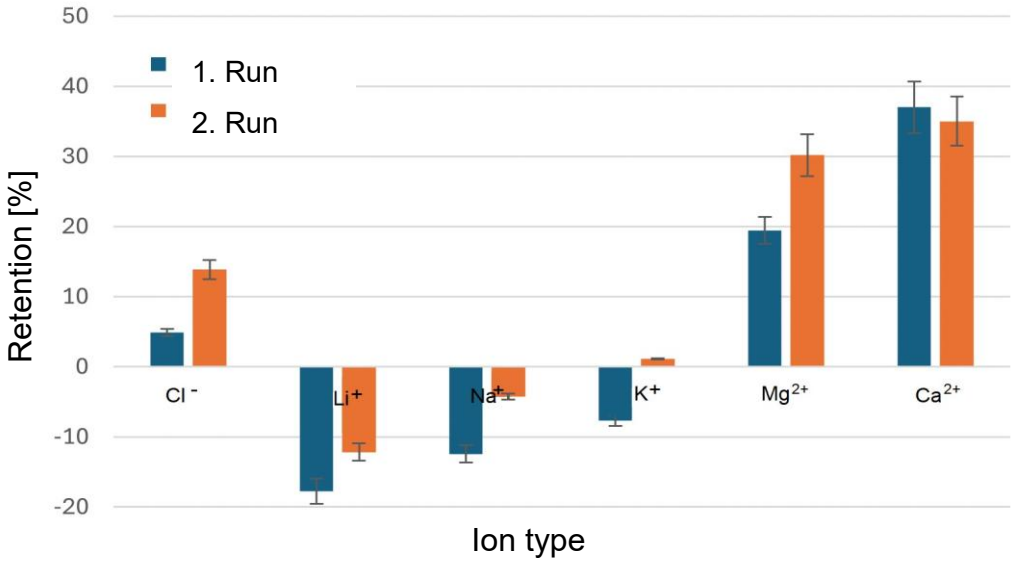


Figure 23: Separation of ions in two-stage nanofiltration for sample y with membrane NF99HF

The trends in the separation characteristics of the ions are promising in the combination of the two stages. In the z sample, a total of 80 % of the initial magnesium and 20 % of the calcium are removed after the second stage. In sample y, 50 % of the initial magnesium and 70 % of the calcium are retained. Further filtration stages are therefore required to increase the retention of multivalent ions. Monovalent ions, especially the target element Lithium can pass the membrane to permeate side and could be transferred to the adsorption step.

Adsorption Experiments

The aim of the adsorption experiments is to develop an ion-selective sorbent for lithium (Figure 18 and 24). The first three sorbents produced follow the pattern described in the chapter “Production of the Li/Al-LDH sorbent”. The differences lie in how quickly the LiCl/AlCl3 solution is dripped into the sodium hydroxide solution. Different particle sizes of the sorbent should be achieved with different feeding velocities. During crystallisation at low dripping speeds, only a few crystallisation nuclei are formed initially, which form the basis for particle growth as the solution becomes more supersaturated. Many crystallisation nuclei inhibit particle growth due to competition between the ions.

Based on the bulk density, it can be demonstrated that larger particles can be produced with a low feed rate. The sorption tests (Figure 25) include one loading and three discharges. Loading (stage 0) is carried out with the stock solution (Li^+ content approx. 1050 mg/l). The discharge (stages 1-3) is carried out with deionised water. The developed sorbents A2 and A3 turned out to be unstable. The substances desorb much more lithium than they can actually absorb. This indicates a dissolution of the Li/Al structure. The sorbent A1 does not absorb any lithium at all - stage 0 still has a Li^+ content of 1050 mg/l after loading. Desorption of lithium in stages 0-3 is probably due to desorption of existing lithium ions in the adsorbent material. Accordingly, sorbent A1 is also not relevant.

Figure 24: Li/Al-LDH sorbent after drying

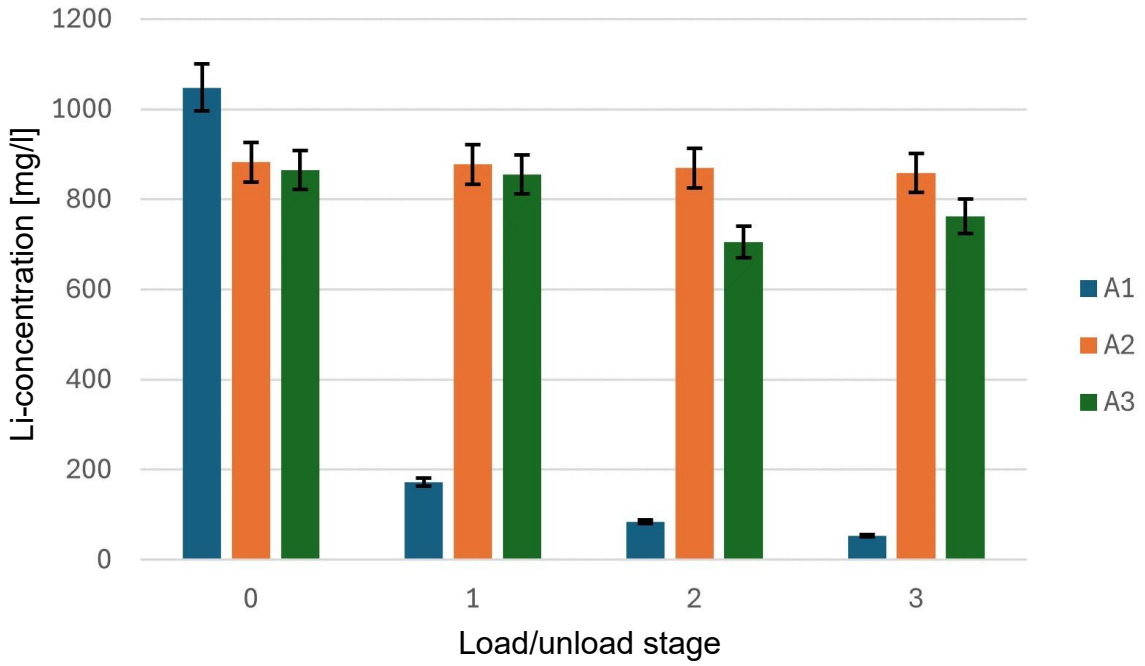


Figure 25: Sorption tests A1-A3

The pH value is regarded as a critical parameter for the development of the sorbent. For this reason, sorbents A4 and A5 are produced with improved pH control in order not to damage the Li/Al structure. The pH value at the end of the synthesis is pH 10.5 for A4 and pH 9.5 for A5. The sorption experiments are shown in Figure 26.

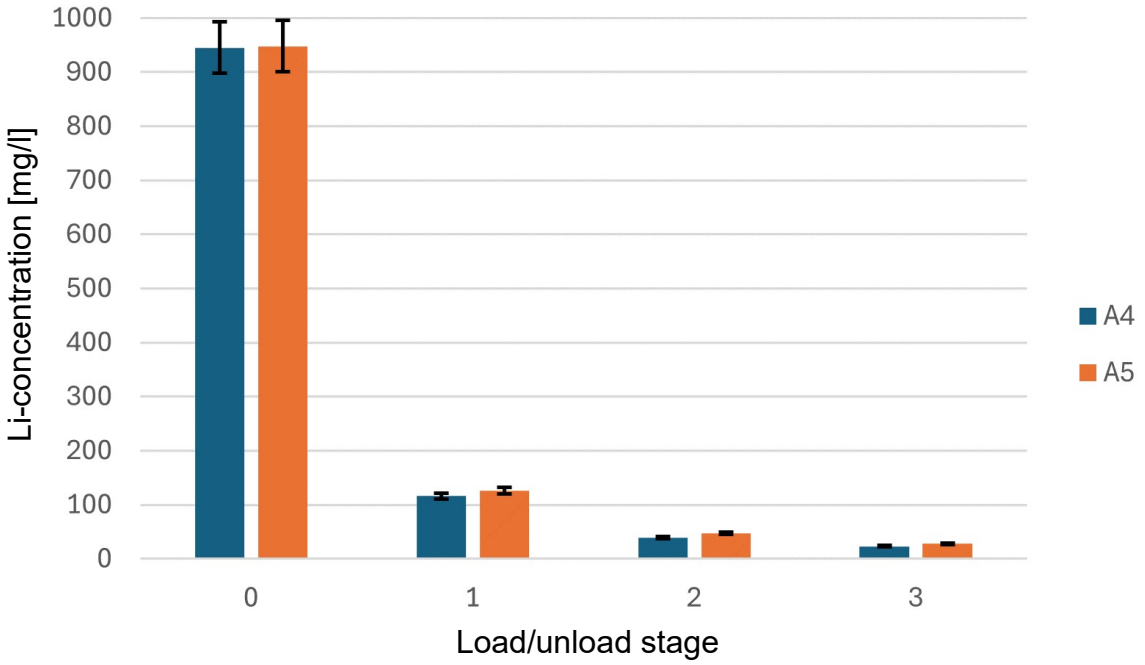


Figure 26: Sorption tests A4 and A5

To test the stability of the substances, A4 and A5 are placed in deionised water overnight after synthesis and washing. A lithium content of around 25 mg/l was found in the water in each case. The reason for this is probably that lithium desorbs from the sorbent because the material is still loaded with lithium from the synthesis.

During loading (stage 0), a clear lithium adsorption could now be determined, the lithium content of the stock solution drops from 1050 to 950 mg/l. This corresponds to an absorbed quantity of 100 mg/l lithium. In the subsequent desorption (stages 1-3), approx. 110 mg/l lithium is released. This may be due to lithium still contained in the lattice structure of the sorbent from the synthesis. With 38 ml of stock solution, this would result in a loading capacity of around 4 mg of lithium per 1 g of sorbent.

In order to investigate the stability of the sorbent, further loading and unloading tests are carried out on previously used material (Figure 27). Furthermore, the assumption can also be checked whether unreacted lithium is present in the lattice structure after synthesis. As a result, the sorption behaviour proves to be stable with a loading capacity of 100 mg/l.

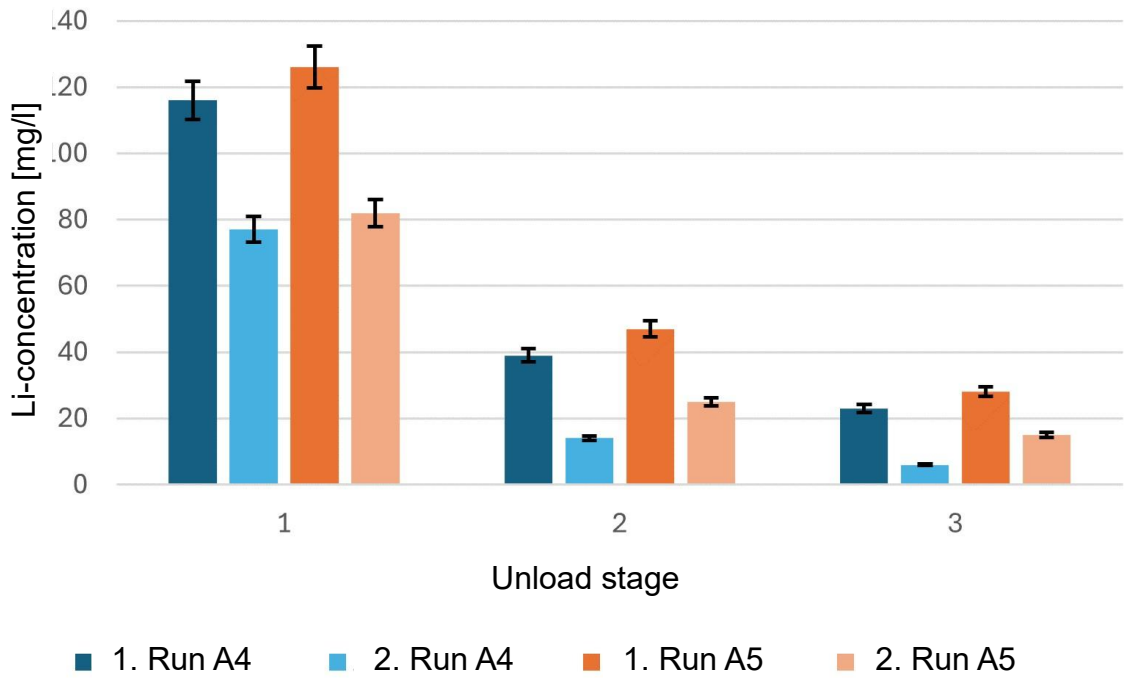


Figure 27: Reproducibility of sorption tests A4 and A5

Zhong [Zhong 2021] stated a loading capacity of 7 mg/l for his synthesised sorbents. The reasons for a deviation may be a lack of information on the washing of his synthesised

sorbentia and also a different procedure for the loading and unloading tests. A major factor here is the retention time.

In this work, the loading and unloading tests were carried out in one hour, while the author used six hours for each stage. The Karlsruhe Institute of Technology [Goldberg 2022] estimates dwell times of ten hours each. For retention times of one hour, they only describe a loading of 50%, whereby the maximum possible loading capacity remains below 8 mg/g. This would correspond to the self-synthesised sorbents with 4 mg/g.

The relatively short loading and unloading times in the tests are based on an economic consideration. Long residence times mean large plant technology. The space required for sorption tanks would be enormous. Assuming a volume flow of 80 l/s (according to Goldberg [Goldberg 2022]), a tank volume of around 300 m3 would be required for a retention time of one hour. This does not yet include the enhanced treatment plants. The large volumes are still one of the main problems for lithium extraction from wastewater and still require a great deal of research.

Summary

From the initial situation, a consortium of two industrial partners was formed in project phase1 to collect information by summarising current technologies and new research findings of the DLE community. A further focus was set on the data sets of oil and gas deposit waters. The composition regarding valuable solutes was analysed and interfering substances identified. After collecting all relevant data sets, a concept for a possible multifunctional system configuration for DLE was derived. Additional experiments (currently running) should validate the concept to optimize the configuration suggested.

Results from the experimental applications lead to the following results. Overall, ultrafiltration was not really successful in reducing the TOC content significantly. Both two-stage and heated ultrafiltration show no clear performance improvements. However, it can be deduced from the results that a large proportion of the organics must have a MWCO of less than 1000 Da (phenols and fatty acids). For this reason, an attempt is now being made to separate the organics together with the polyvalent ions in nanofiltration.

Due to the high salt content, multi-stage nanofiltration is recommended to separate polyvalent ions. The flux is mainly determined by the selected membrane, the salt content and pressure. The trends in the separation characteristics of the ions are promising in the combination of the two stages. In the sample z, a total of 80 % of the initial magnesium and 20 % of the calcium are removed after the second stage. In sample y, 50 % of the initial magnesium and 70 % of

the calcium are retained. Further filtration stages are therefore required to increase the retention of multivalent ions. Monovalent ions, especially the target element Lithium can pass the membrane to permeate side and could be transferred to the adsorption step.

A stable modification of Li/Al-LDH sorbent could be synthesised and loading/unloading performance as well as stability could be proven as suitable.

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