Feasibility of lithium recovery from geothermal brines in the Netherlands

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Abbreviations

CLP = Central Lithium(hydroxide) Plant
DLE = Direct Lithium Extraction
IEM = Ion Exchange Membrane
LCE = Lithium Carbonate Equivalent
LEP = Lithium Extraction Plant
LHM = Lithium Monohydrate
Ppm = parts per million
RO = Reverse Osmosis
TDS = Total Dissolved Solids
TRL = Technology Readiness Levels

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SAMENVATTING

Aanleiding

De EU Critical Raw Materials Act moet een veilige en duurzame levering van essentiële grondstoffen binnen de EU waarborgen. Eén van deze kritieke materialen is lithium, een cruciale grondstof voor de productie van batterijen, die voornamelijk geïmporteerd wordt door EU-lidstaten uit Chili en Australië. Om de geopolitieke afhankelijkheid van import te verminderen en in de toenemende vraag te voorzien, onderzoekt de EU alternatieve bronnen van lithium binnen haar grenzen. Een potentiële bron van lithium is het water dat opgepompt wordt voor aardwarmte[1], afkomstig uit watervoerende lagen (reservoirs) op dieptes vanaf 500 meter. Een aantal aardwarmteboringen in Europa bevatten aanzienlijke hoeveelheden lithium, en de technologie om lithium uit het water te winnen ontwikkelt zich wereldwijd snel. De winning van lithium uit aardwarmtewater zou daarnaast ook de business case van aardwarmteprojecten kunnen verbeteren.

In dit kader is in 2022 een Kamervraag gesteld om de haalbaarheid van het winnen van lithium uit aardwarmtewater in Nederland te beoordelen[2]. Dit rapport beschrijft de verschillende technologieën en evalueert de huidige technische en economische haalbaarheid voor de toepassing in Nederland voor enkele aardwarmtebronnen. Deze opdracht is uitgevoerd met ondersteuning van een projectteam bestaande uit EBN, Ennatuurlijk, Shell en het Ministerie van Economische Zaken en Klimaat.

Hoe werkt lithiumwinning uit aardwarmte?

In conventionele winning wordt lithium via verdampingsprocessen uit (ondergrondse) zoutmeren of uit erts gewonnen. In het algemeen is dit kostbaar, energie intensief en is veel water nodig om het lithium te winnen. De laatste jaren wordt in Zuid-Amerika en China ook een nieuwe techniek in een aantal projecten op industriële schaal toegepast. Deze directe lithium extractie technologie is een alternatief voor verdampingsprocessen met als groot voordeel om het waterverbruik en energiegebruik te verminderen.

Deze relatief nieuwe technologie kan ook in aardwarmte-installaties gebruikt worden als er voldoende lithium aanwezig is het aardwarmtewater. Hierbij wordt het lithium met hoge selectiviteit uit het aardwarmtewater gehaald, en kan het water- zonder het verwijderde lithium- weer terug worden geïnjecteerd in het reservoir. In een aantal projecten in Europa en de Verenigde Staten van Amerika wordt op pilot schaal lithium gewonnen uit aardwarmteboringen. Dit kan in potentie de mogelijkheid bieden om de aardwarmteboringen te gebruiken als warmtebron én voor lithiumwinning.

Voor directe lithiumwinning worden meerdere technologieën ontwikkeld, waarvan de volgende drie het verst doorontwikkeld zijn:

- adsorbentia;
- ion-exchange materialmen;
- vloeistof scheiding.

De extractie van lithium via deze methoden resulteert in een lithiumchloride-oplossing, die na zuivering en concentratie leidt tot een halffabricaat. Deze initiële stappen van lithiumwinning (directe winning, zuivering en concentratie) vormen de upstream-processen. Vervolgens wordt het halffabricaat omgezet in grondstoffen voor batterijproductie, namelijk lithiumcarbonaat of lithiumhydroxide. Deze omzetting wordt

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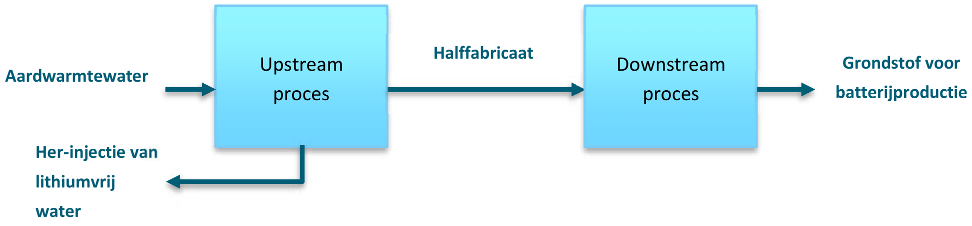
[1] Voor meer informatie over aardwarmte, zie www.hoewerktaardwarmte.nl.

[2] *Aanhangsel Handelingen I 2021/22, nr. 28.*

het downstream-proces genoemd. De kosten van het uiteindelijke product (met batterijkwaliteit) worden doorgaans uitgedrukt als de prijs per Lithium Carbonate Equivalent (LCE). Een schematisch overzicht van dit proces wordt hieronder weergegeven.

Afbeelding 1.1 Schematisch overzicht van de lithium extractie en processen



Uitgangspunten, scope en aanpak van het onderzoek

In het kader van deze studie wordt de haalbaarheid van lithiumwinning uit aardwarmteboringen onderzocht voor de combinatie van warmte- en lithiumwinning voor een aardwarmte installatie. In deze studie is de focus gelegd op het onderzoek naar de techniek van het upstream proces om een eerste inschatting van de haalbaarheid te maken van lithium winning uit aardwarmtewater. Er is een literatuurstudie naar de huidige technologie van het upstream proces uitgevoerd, tevens zijn interviews gehouden met mogelijke leveranciers. Daarnaast is de economische haalbaarheid van het upstream proces ingeschat, rekening houdend met de verwachte toekomstige marktprijs. Tenslotte zijn de ecologische en juridische aspecten op hoofdlijnen beschreven. Buiten de onderzoeksopgave van deze studie vallen het downstream proces, de potentie van innovatieve technieken, het inschatten van scenario's van geopolitieke en marktontwikkelingen op de lithiumprijs, en een gedetailleerde business case analyse. Ook is de economische haalbaarheid van schaalvergroting door het koppelen van meerdere aardwarmteboringen niet onderzocht.

In deze studie is de technische en economische haalbaarheid voor 3 boringen bekeken, die geboord zijn in twee verschillende reservoirs. Deze boringen (aangeduid als Boring A, B en C om vertrouwelijkheid te waarborgen) zijn geselecteerd in overleg met EBN. Hiervoor is de watersamenstelling van bestaande aardwarmteboringen beoordeeld door het projectteam en zijn de boringen geselecteerd die de hoogste (gemeten) lithiumconcentratie bevatten. Hierbij moet worden opgemerkt dat het aantal beschikbare metingen van de lithium concentraties in boringen in Nederland beperkt is. Hogere concentraties dan de drie beschouwde boringen worden niet verwacht: gemeten lithiumconcentraties in de reservoirs die momenteel gebruikt worden voor aardwarmte zijn lager dan deze drie boringen. Het valt niet uit te sluiten dat bij toekomstige aardwarmteprojecten hogere concentraties worden gevonden. Zo zijn er locaties in België waarbij de lithiumconcentratie hoger is dan tot nu toe gemeten is in Nederland. Dezelfde reservoirs lopen ook door in Nederland, en het is dus mogelijk dat ook in Nederland hogere concentraties kunnen worden aangetroffen.

De lithiumconcentraties in deze boringen (A, B,C) - respectievelijk 13, 24 en 22 mg/l - zijn relatief laag in vergelijking met (onderzoeks)projecten in bijvoorbeeld Duitsland, Frankrijk en België waarbij lithiumwinning uit aardwarmte is onderzocht. De buitenlandse projecten verwerken doorgaans water met meer dan 150 milligram per liter aan lithium, een factor 5-10 hoger dan de tot nog toe in Nederland maximale gemeten concentratie.

In de analyse is een gemiddelde productiecapaciteit (debiet) van 250 m^3/uur water per aardwarmte-installatie aangehouden. Dit debiet is representatief, aangezien de meeste aardwarmte-installaties tussen de 100 en 450 m^3/uur verwerken. Ter beeldvorming: bij een lithiumconcentratie concentratie van 22 mg/l, een extractie efficiëntie van 90 % en een gemiddeld debiet van 250 m^3/uur kan er jaarlijks omgerekend 211 ton LCE in een aardwarmte-installatie gewonnen. Dit is genoeg voor de productie van ongeveer 6.000 autobatterijen per jaar. In de praktijk zal dit niet allemaal gewonnen kunnen worden door verliezen tijdens verwerkingsstappen. Ook zal op den duur de lithiumconcentratie in het reservoir dalen, omdat het teruggepompte water geen lithium meer bevat.

Onderzochte winningstechnologieën

De state-of-the-art technologieën voor directe lithiumwinning, -zuivering en -concentratie zijn beoordeeld aan de hand van literatuuronderzoek en interviews met leveranciers. De belangrijkste directe lithiumwinningstechnieken zijn gebaseerd op de toepassing van adsorbentia, ion-exchange materialen en vloeistof scheiding. Het zuiveren en concentreren tot halffabrikaat kan worden gedaan met ionen-wisseling materialen, nanofiltratie, en concentratie met membraandestillatie en verdampingstechnieken.

Alleen leveranciers die hun technologie minimaal op pilotschaal hebben bewezen, zijn benaderd voor interviews. Er zijn ongeveer 20 leveranciers in dit onderzoek benaderd. Een groot aandeel daarvan concludeerde dat de lithiumconcentraties van de drie boringen te laag waren voor economisch haalbare lithiumwinning met hun technologie bij de huidige lithiumprijs. Er zijn twee technologieleveranciers, die wel aangeven dat -in potentie - hun technologie geschikt zou kunnen zijn voor het Nederlandse aardwarmtewater. Beide leveranciers extraheren het lithium met sorbentia, één op basis van aluminaten (adsorptie) en één op basis van titanaten (ionen-wisseling).

Een overzicht van de toepassing van de twee technologieën, gebaseerd op een aluminaten-gebaseerde adsorbents en titanaten-gebaseerde ion exchange sorbent, is weergegeven in tabel 1.1 Hierin zijn de kenmerken van de technieken toegelicht, zijn de toepasbaarheid gegeven voor de Nederlandse boringen, en tenslotte is de indicatieve kostprijs gegeven, uitgedrukt in euro per ton LCE. De kostprijs is alleen voor extractie uit aardwarmtewater tot aan halfproduct (het upstream proces). Kosten voor het downstreamproces zijn niet meegenomen en er is aangenomen dat de kosten voor de benodigde aardwarmte-installatie gedekt zijn via de warmtelevering. De kostprijs is gerelateerd aan de marktprijs van gemiddeld EUR 30.000,-- per ton LCE, die over de komende periode tussen 2026 en 2045 verwacht wordt. In het rapport is dit verder toegelicht. Deze marktprijs is gebruikt om de financiële haalbaarheid aan te toetsen.

Tabel 1.1 Overzicht van twee potentiële technieken voor lithiumextractie uit Nederlandse aardwarmtebronnen

Basismateriaal van absorbent	Kenmerken	Toepasbaarheid	Indicatieve kostprijs per ton LCE in EUR
adsorbent gebaseerd op aluminaten	goede lithium selectiviteit bij neutrale pH, mits de sulfaat concentratie niet te hoog is	Alleen voor boring C. In boringen A en B is het sulfaatgehalte te hoog, waardoor de lithium selectiviteit beperkt wordt.	> 22.700,-- - 33.700,--
ion exchange sorbent gebaseerd op titanaten-	vereist een pH van het water van 10, terwijl de pH van het aardwarmtewater in Nederland tussen 5 en 6 ligt	Beperkte toepasbaarheid. Verhogen van pH vereist veel additieven, wat hoge kosten met zich meebrengt. De pH moet vervolgens weer verlaagd worden naar de originele pH, omdat het teruggepompte water gelijk moet zijn aan het opgepompte water volgens de Mijnbouwwet. Ook resulteert dit in een extra toevoeging van NaCl in het geothermisch water.	> 23.000,--

De tabel maakt duidelijk dat voor beide technieken de indicatieve kostprijs voor het upstream proces van lithiumwinning dicht in de buurt komt van de marktprijs.

Ter referentie: andere aardwarmteprojecten rondom lithiumwinning wereldwijd hebben geschatte kosten van EUR 3.000,-- - EUR 5.000,-- per ton LCE, een factor 5-10 keer lager dan in dit rapport is berekend voor de Nederlandse situatie. De belangrijkste redenen hiervoor zijn de lagere lithiumconcentratie en de hogere gehaltes aan (andere) zouten, die de lithium extractie en de zuiveringsstappen in Nederland bemoeilijken.

Ecologische en milieuaspecten

Voor de winning van lithium uit aardwarmtewater is een relatief klein productie oppervlak nodig, is de CO_2 uitstoot beperkt door een laag energiegebruik, en het watergebruik is beperkt. Voor de winning is natuurlijk wel een installatie nodig, maar de CO_2 emissie als gevolg van toevoeging van de lithiumwinning - aan een bestaande aardwarmtewinning - zal beperkt zijn. Ook andere emissies zullen beperkt zijn. Milieutechnisch zien we geen bijzondere issues, maar wel relevante aandachtspunten. Zo zou het zinvol zijn om de milieubelasting (bijvoorbeeld emissies, energieverbruik, chemicaliënverbruik) van lithiumwinning af te wegen tegen de te bereiken reductie in CO_2-emissie door het beschikbaar komen van extra lithium. Verder kan er gekeken worden naar het vrijkomen van reststromen en het effect daarvan op de omgeving. Dit is in dit onderzoek niet meegenomen.

Juridische aspecten

De vraag of lithiumwinning onder de Mijnbouwwet valt, kan bevestigend worden beantwoord. Lithium is een mineraal en valt als zodanig onder de Mijnbouwwet, maar wordt niet expliciet genoemd. Wel is de vraag of de Mijnbouwwet de lithiumwinning uit aardwarmtewater goed kan beschrijven, en of de systematiek zoals nu in de Mijnbouwwet wordt gehanteerd daarvoor geschikt is. In dit onderzoek is daar nu geen antwoord op gegeven.

Conclusies en kanttekeningen

Geconcludeerd kan worden dat- met de huidige beschikbare technieken- lithiumwinning uit water van de huidige operationele aardwarmte-installaties in Nederland op dit moment (in 2023) economisch uitdagend is. De kosten voor alleen het upstream proces zijn in dezelfde grootte als de marktprijs. Wanneer ook het downstreamproces toegevoegd, is de kans groot dat de kostprijs hoger uitkomt dan de marktprijs. De kwaliteit van het Nederlandse aardwarmtewater maakt daarnaast dat de Nederlandse aardwarmtereservoirs minder geschikt zijn om lithium uit te winnen dan in (nabije) buitenlandse projecten.

Bij deze conclusies zijn de volgende kanttekeningen te plaatsen:

- de huidige analyse is gebaseerd op de watersamenstelling van drie aardwarmteboringen in Nederland. Hoewel dit de boringen zijn met de hoogst gemeten lithiumconcentraties, valt niet uit te sluiten dat bij toekomstige aardwarmteprojecten hogere concentraties worden gevonden. We adviseren om in de toekomst bij analyses van aardwarmtewater ook standaard de lithiumconcentratie te meten. Daarnaast adviseren we ook om verder onderzoek te doen naar de geologische omstandigheden voor aardlagen waarin hogere lithium concentraties te verwachten zijn;
- naast het meten van lithiumconcentraties, kan het ook lonen om concentraties van andere waardevolle en kritieke mineralen zoals bijvoorbeeld zeldzame aardmetalen te meten. Dat wordt op dit moment weinig gedaan. Deze mineralen zouden de business case kunnen versterken, deze zijn in deze studie echter niet onderzocht;
- er is een verwachte marktprijs van EUR 30.000,-- per ton LCE gehanteerd, gebaseerd op huidige prognoses in 2023. Gezien de wereldwijde elektrificering en de groeiende vraag naar lithium voor batterijen is het denkbaar dat de marktprijs in de nabije toekomst stijgt, alhoewel de volatiliteit ook groot is. In dat geval kan lithiumwinning uit Nederlandse aardwarmte toch financieel of strategisch interessant worden. Wel moet worden opgemerkt dat - in Europees verband - het voor de hand ligt om dan eerder op andere locaties (bijvoorbeeld Duitsland, Frankrijk) lithium te winnen, vanwege de hogere lithium concentraties en, als gevolg daarvan, lagere kostprijs;
- de haalbaarheid is gebaseerd op de huidige beschikbare technieken die in de markt worden ingezet. Deze technieken worden momenteel in snel tempo doorontwikkeld. Nieuwe technieken worden op laboratorium- of pilotschaal getest. Het is denkbaar dat er in de toekomst technologieën ontwikkeld worden die tegen lagere kosten lithium uit Nederlands aardwarmte kunnen winnen, wat de (financiële) haalbaarheid kan vergroten. Lithiumwinning in Nederland zou dan relatief ten opzichte van buitenlandse bronnen nog steeds kostbaarder zijn door de relatief lage lithiumconcentraties;
- in dit rapport is gekeken naar lithiumwinning voor individuele aardwarmteprojecten. Er zijn ook lithium winningsprojecten opgestart rond een groot aantal aardwarmtebronnen op een centrale locatie zoals Vulcan in Duitsland, Cornish Lithium in Engeland of E3 Lithium in Amerika. Als op dit soort grote schaal lithium wordt gewonnen zullen de investeringen, uitgedrukt in de productprijs voor lithium (uitgedrukt in prijs per ton geproduceerd LCE), lager zijn dan voor een kleinschalig project. Dit zou lithiumwinning

mogelijk interessanter maken in Nederland. Maar ook hier geld: in Europees verband ligt het voor de hand om dan eerder op andere locaties (bijvoorbeeld Duitsland, Frankrijk) lithium te winnen, vanwege de hogere lithiumconcentraties en, als gevolg daarvan, lagere kostprijs;

- we adviseren om de relevante vragen rond de juridische en de ecologische aspecten verder uit te diepen. We adviseren een verder onderzoek naar de toepasbaarheid van de Mijnbouwwetgeving op deze specifieke winning van lithium uit aardwarmte. Zo kan het zinvol zijn om de milieubelasting van lithiumwinning af te wegen tegen de te bereiken reductie in CO_2-emissie door het beschikbaar komen van extra lithium, of kan een Life Cycle Assement (LCA) opgesteld. Verder kan er gekeken worden naar het vrijkomen van afval- en reststromen bij de lithiumwinning, en wat het effect daarvan is op de omgeving.

2

SUMMARY

Motivation

The EU Critical Raw Materials Act focuses on a safe and sustainable supply of essential raw materials within the EU. One of these critical materials is lithium, a crucial raw material for battery production, mainly imported by EU member states from Chile and Australia. To reduce geopolitical dependence on imports and meet increasing demand, the EU is exploring alternative sources of lithium within its borders. A potential source of lithium is the brine pumped for geothermal energy, originating from aquifers (reservoirs) at depths of 500 meters or deeper. A number of geothermal wells in Europe contain significant amounts of lithium, and the technology to extract lithium from water is developing rapidly worldwide. The extraction of lithium from geothermal water could also improve the business case of geothermal projects.

In this context, a parliamentary question was posed in 2022 to assess the feasibility of extracting lithium from geothermal water in the Netherlands. This report examines the different technologies and evaluates the current technical and economic feasibility for application in the Netherlands for some geothermal heat sources. This assignment was carried out with the support of a project team consisting of EBN, Ennatuurlijk, Shell and the Ministry of Economic Affairs and Climate.

How does geothermal lithium extraction work?

In conventional mining, lithium is extracted from (underground) salt lakes or from ore via evaporation processes. In general, this is expensive, energy intensive and requires a lot of water to extract the lithium. In recent years, a new technique has also been applied in a number of projects on an industrial scale in South America and China. This direct lithium extraction technology is an alternative to evaporation processes with the major advantage of reducing water and energy consumption.

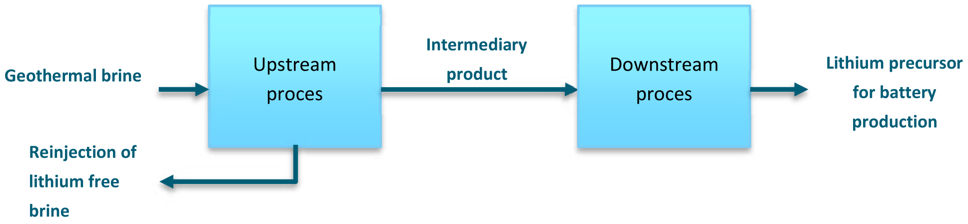
This relatively new technology can also be used in geothermal installations if there is sufficient lithium present in the geothermal water. The lithium is extracted from the geothermal water with high selectivity, and the water - without the removed lithium - can be injected back into the reservoir. Lithium is being extracted from geothermal wells on a pilot scale in a number of projects in Europe and the United States of America. This could potentially offer the opportunity to use geothermal both as a heat source and for lithium extraction.

Several technologies are being developed for direct lithium extraction, of which the following three are the most fully developed:

- Adsorbents.
- Ion exchange materials.
- Liquid separation.

The extraction of lithium via these methods results in a lithium chloride solution, which after purification and concentration, leads to an intermediary product. These initial steps of lithium extraction (direct extraction, purification and concentration) constitute the upstream processes. The intermediary product is then converted into raw materials for battery production, namely lithium carbonate or lithium hydroxide. This conversion is called the downstream process. The cost of the final product (with battery quality) is usually expressed as the price per Lithium Carbonate Equivalent (LCE). A schematic overview of this process is shown below.

Figure 1.1 Schematic overview of lithium extraction and processes.



Principles, scope and approach of the research

In the context of this study, the feasibility of lithium extraction from a geothermal source is investigated for the combination of heat and lithium extraction for a geothermal installation. In this study, the focus was on research into the technology of the upstream process to make an initial estimate of the feasibility of lithium extraction from geothermal water. A literature study was carried out into the current technology of the upstream process, and interviews were also held with possible suppliers. In addition, the economic feasibility of the upstream process has been estimated, taking into account the expected future market price. Finally, ecological and legal aspects are discussed in broad terms. Outside the scope are the downstream process, the potential of innovative techniques, the assessment of scenarios of geopolitical and market developments on the lithium price, and a detailed business case analysis. The economic feasibility of scaling up by linking multiple geothermal wells has also not been investigated.

This study examines the technical and economic feasibility for 3 wells, drilled in two different reservoirs. These boreholes (referred to as Bore A, B and C to ensure confidentiality) have been selected in consultation with EBN. For this purpose, the water composition of existing geothermal wells was assessed by the project team and the wells containing the highest (measured) lithium concentration were selected. It should be noted that the number of available measurements of lithium concentrations in geothermal wells in the Netherlands is limited. However, higher concentrations than found in the three considered boreholes are not expected: measured lithium concentrations in the reservoirs currently used for geothermal heat are lower than these three boreholes. However, it cannot be ruled out that higher concentrations will be found in future geothermal projects. For example, there are locations in Belgium where the lithium concentration is higher than has been measured so far in the Netherlands. The same reservoirs also extend into the Netherlands, and it is therefore possible that higher concentrations can also be found in the Netherlands.

The lithium concentrations in these wells (A, B, C) - 13, 24 and 22 mg/l respectively - are relatively low compared to (research) projects in, for example, Germany, France and Belgium where lithium extraction from geothermal energy is being investigated. The projects abroad usually process water with more than 150 mg/l of lithium, a factor 5-10 higher than the maximum concentration measured so far in the Netherlands.

The analysis used an average production capacity (flow rate) of 250 m^3/hour of brine per geothermal installation. This flow rate is representative, as most geothermal installations process between 100 and 450 m^3/hour. To illustrate that: with a lithium concentration of 22 mg/l, an extraction efficiency of 90 % and an average flow rate of 250 m^3/hour, 211 tons of LCE can be extracted annually in a geothermal installation. This is enough for the production of approximately 6,000 car batteries per year. In practice, not all the lithium can be harvested by losses in the processing steps. The lithium concentration in the reservoir will also eventually decrease, because the pumped back water no longer contains lithium.

Studied lithium extraction techniques

The state-of-the-art technologies for direct lithium extraction, purification and concentration have been assessed based on literature research and interviews with suppliers. The main direct lithium recovery techniques are based on the application of adsorbents, ion-exchange materials and liquid separation.

Purification and concentration into semi-finished products can be done with ion-exchange materials, nanofiltration, and concentration with membrane distillation and evaporation techniques.

Only suppliers who have proven their technology at least on a pilot scale were approached for interviews. Approximately 20 suppliers were approached in this study. A large proportion of these concluded that the lithium concentrations from the three wells were too low for economically viable lithium extraction with their technology at the current lithium price. There are two technology suppliers who indicate that - potentially - their technology could be suitable for Dutch geothermal water. Both suppliers extract the lithium with sorbents, one based on aluminates (adsorption) and one based on titanates (ion exchange).

An overview of the application of the two technologies, based on an aluminate-based adsorbent and titanate-based ion exchange sorbent, is shown in table 2.1. This explains the characteristics of the techniques, their applicability for Dutch geothermal wells. Finally, an indicative cost price is given, expressed in euros per ton of LCE. The cost price mentioned here refers only to the extraction from geothermal water up to semi-product (the upstream process). Costs for the downstream process are not included and it is assumed that the costs for the required geothermal installation are covered by the heat supply. The cost price is compared to the expected market price of an average of EUR 30,000.-- per ton of LCE, which is estimated over the coming period between 2026 and 2045. This is explained further in the report. This market price is used to assess the economic feasibility.

Tabel 2.1 Overview of two potential techniques for the lithium extraction out of Dutch geothermal wells

Basic absorbent	**Characteristics**	**Applicability**	**Indicative costs per ton LCE in EUR**
adsorbent based on aluminates	good lithium selectivity at neutral pH, provided the sulphate concentration is not too high	only for borehole C. In boreholes A and B, the sulphate content is too high, which limits the lithium selectivity	> 22,700.-- - 33,700.--
ion exchange sorbent bases on op titanates	requires a water pH of 10, while the pH of geothermal water in the Netherlands is between 5 and 6.	limited applicability. Increasing pH requires many additives, which require high costs. The pH must then be lowered back to the original pH, because the pumped brine must be equal to the pumped water according to the Mining Act. This also results in an effective addition of NaCl to the geothermal water	> 23,000.--

The table makes it clear that for both techniques the indicative cost price for the upstream process of lithium extraction is close to the market price.

For reference: other geothermal projects involving lithium extraction worldwide have an estimated costs of EUR 3,000.-- - EUR 5,000.-- per ton LCE, a factor 5-10 times lower than calculated in this report for the Dutch situation. The main reasons for this are the lower lithium concentration and the higher levels of (other) salts, which complicate lithium extraction and purification steps in the Netherlands.

Ecological and environmental aspects

The extraction of lithium from geothermal water requires a relatively small production surface, CO_2 emissions are limited by low energy use, and water use is limited. An installation is of course required for extraction, but the CO_2 emissions resulting from the addition of lithium extraction will be limited. Other emissions will also be limited. We do not see any special environmental issues, but we do see relevant points of attention. For example, it would be useful to consider the environmental impact (e.g., emissions, energy consumption, chemical consumption) of lithium extraction against the reduction in CO_2 emissions that can be achieved by making extra lithium available. Furthermore, the release of residual flows and their effect on the environment can be examined in the future. This was not included in this study.

Legal aspects

The question is whether lithium mining falls under the Mining Act can be answered affirmative. Lithium is a mineral and as such falls under the Mining Act but is not explicitly mentioned as such. The question is whether the Mining Act can properly describe lithium extraction from geothermal water, and whether the system currently used in the Mining Act is suitable for this. This study does not provide an answer to this question.

Conclusions and remarks

It can be concluded that - with the currently available techniques - lithium extraction from water from the currently operational geothermal installations in the Netherlands is currently (in 2023) economically challenging. The costs for just the upstream process are already the same as the expected market price. When the downstream process is also added, there is a good chance that the cost price will be higher than the market price. The quality of Dutch geothermal water also means that Dutch geothermal reservoirs are less suitable for extracting lithium than in (near) foreign projects.

The following remarks can be made about these conclusions:

- The current analysis is based on the water composition of three geothermal wells in the Netherlands. Although these are the wells with the highest measured lithium concentrations, it cannot be ruled out that higher concentrations will be found in future geothermal projects. In the future, we recommend that the lithium concentration also be measured as standard when analyzing geothermal water. In addition, we also recommend further research into the geological conditions for earth layers in which higher lithium concentrations are expected.
- In addition to measuring lithium concentrations, it can also be worthwhile to measure concentrations of other valuable elements and to measure critical minerals such as rare earth metals. This is rarely done at the moment. These minerals could strengthen the business case, but they were not investigated in this study.
- An expected market price of EUR 30,000.-- per ton of LCE has been used, based on current forecasts in 2023. Given global electrification and the growing demand for lithium for batteries, it is conceivable that the market price will increase in the near future, although volatility is also high. In that case, lithium extraction from Dutch geothermal energy could become financially or strategically interesting. It should be noted that - in a European context - it would be obvious to extract lithium sooner at other locations (for example Germany, France), because of the higher lithium concentrations and, as a result, lower costs.
- The feasibility is based on the currently available techniques used in the market. These techniques are currently being developed at a rapid pace. New techniques are tested on a laboratory or pilot scale. It is conceivable that technologies will be developed in the future that can extract lithium from Dutch geothermal heat at lower costs, which could increase the (financial) feasibility. However, lithium extraction in the Netherlands would still be more expensive compared to foreign sources due to the relatively low lithium concentrations.
- This report looked at lithium extraction for individual geothermal projects. Lithium extraction projects have also been started around a large number of geothermal sources at a central location such as Vulcan in Germany, Cornish Lithium in England or E3 Lithium in the United States of America. If lithium is extracted on this type of large scale, the investments expressed in the product price for lithium (expressed in price per ton of LCE produced), will be lower than for a small-scale project. This could possibly make lithium mining more interesting in the Netherlands. But this also applies here: in a European context, it makes sense to extract lithium earlier in other locations (for example Germany, France), because of the higher lithium concentrations and, as a result, lower costs.
- We advise you to further explore the relevant questions surrounding the legal and ecological aspects. For example, it may be useful to weigh the environmental impact of lithium extraction against the reduction in CO2 emissions that can be achieved by making additional lithium available, or a Life Cycle Assessment (LCA) can be made. Furthermore, the release of waste and residual flows during lithium extraction and its effect on the environment can be examined.

3

INTRODUCTION

3.1 Background

In Europe and the Netherlands, the demand for sustainably and locally sourced raw materials has increased. The EU's Critical Raw Materials Act aims to ensure a safe and sustainable supply of essential raw materials within the EU [1] . One of these critical materials is lithium, a crucial component for battery production, which is mainly imported by the EU from Chile and Australia.

In the energy transition of the Netherlands and Europe as a whole, alternative strategic renewable heat sources are investigated to become less dependent on fossil fuels for heating. Geothermal energy holds the promise to become an important reliable and local source of renewable heat. However, the business case for geothermal heat, despite its advantages for the energy system, is not always easy to make [2]. The geothermal energy is still developing, and cost reductions will be made in the future. Lithium extraction could provide an added value and strengthen the geothermal energy development. Combining the development of geothermal heat production with extraction of lithium from the geothermal brine could provide a synergy, simultaneously improving the overall business case for the overall geothermal production site. Additionally, it would reduce the EU's and The Netherlands' dependence on import from non-European countries for critical raw materials that are required for their industry and renewable energy systems.

To reduce geopolitical dependence on imports, the EU is exploring alternative sources of lithium within its borders [1]. After all, lithium is an important raw material in the energy transition. Geothermal brine is considered a potential source of lithium. For example, in a number of places in Europe, research is being done into the possibilities of the combination of geothermal energy and the extraction of lithium. A number of geothermal resources in Europe contain significant amounts of lithium, and the extraction technology called direct lithium extraction (DLE) is developing rapidly worldwide [3]. The business case for lithium extraction from geothermal brines has improved by the increasing demand and rising prices. Also, the extraction technologies have developed rapidly in the last years [4].

Worldwide several lithium extraction projects from geothermal reservoirs are currently under development. Typically, these reservoirs have a lithium concentration greater than 150 ppm Li [5]. An overview of typical projects in Europe is given in Appendix III. In the Netherlands, the lithium concentrations found so far are lower. The highest lithium concentrations in the Netherlands are found in the North (Akkrum: 47-48 ppm Li) and the South (California Geothermie: 20-28 ppm), as was elaborated by Biagini (2023) [6].

In this context, a Parliamentary Question has been asked in 2022 in the Netherlands to assess the feasibility of extracting lithium from geothermal sources in the Netherlands [7]. This report investigates the technology of direct lithium extraction and evaluates the technical and economic feasibility for implementation in the Netherlands, based on the current available technologies, the available data of Dutch geothermal brine compositions, and a fixed lithium market price (given in paragraph 4.2).

3.2 Project scope

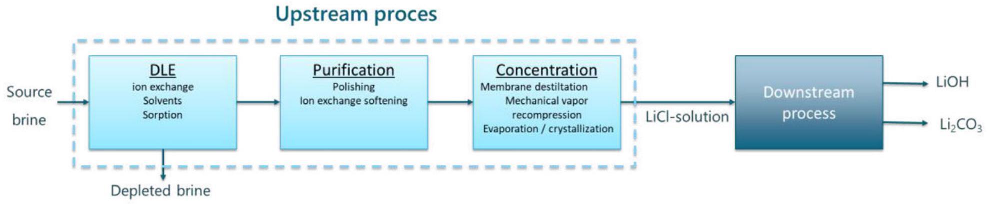
In this study, the feasibility of lithium extraction from geothermal wells is investigated for the combination of heat and lithium extraction for the basic case of a single geothermal installation. The focus was on research into the technology of the upstream process in order to assess the feasibility of lithium extraction from geothermal water. A literature study into the current technology of the upstream process is undertaken, and possible suppliers are interviewed. In addition, the economic feasibility of the upstream process is estimated, taking into account the current market price. Outside the scope are the downstream process, the potential of innovative techniques, the assessment of scenarios of geopolitical and market developments on the lithium price, and a detailed business case analysis. The economic feasibility of scaling up by linking multiple geothermal wells has also not been investigated.

In this study, the focus was on research into the technology of the upstream process. For this purpose, a Finally, ecological and legal aspects are mentioned in a high-level survey. Not examined are the downstream process, the potential of innovative techniques for, scenarios of geopolitical and market developments on the lithium price, a detailed business case analysis. and the analysis of the economic feasibility of scaling up by connecting multiple geothermal heat wells.

This study examines the technical and economic feasibility for 3 wells in the Netherlands. The water composition of existing geothermal wells was assessed and the wells containing the highest lithium concentration were selected. This concerns wells drilled in two different aquifers.

The upstream process relates to the extraction of lithium from the geothermal brine into a LiCl-solution, which is then purified and concentrated towards a concentrated LiCl solution, as shown in figure 3.1. The downstream process converts the LiCl-solution into lithium hydroxide (LiOH) or lithium carbonate (Li_2CO_3).

Figure 3.1 Schematic overview of upstream and downstream processes for direct lithium extraction



The downstream process is only reviewed briefly in a literature study. No suppliers were contacted, as the feasibility of the downstream process was out of scope of this report. This report focusses on the following scope items:

1 Technical analysis of upstream lithium extraction process by:
  - Literature review of the existing extraction and processing technologies.
  - Evaluation of the upstream DLE processes of existing geothermal projects.
  - Consultation with technology providers of DLE methods. The selection of suppliers is based on their Technology Readiness Levels (TRL). Only suppliers were contacted that have proven their technology at least on pilot scale.
  - Selection and detailed analysis of 2-most feasible DLE methods for three geothermal doublets in the Netherlands. The selection is based on interviews with suppliers and internal technical analyses.
  - Dimensioning the upstream lithium processing for three geothermal wells in the Netherlands, based on a flow rate of the geothermal well of 250 m^3/h. This is an average flow rate in operational geothermal doublets, typically between 100 and 450 m^3/h.

2 Analysis of ecological and jurisdictional implications of lithium extraction the geothermal wells in the Netherlands.

3 Economic analysis of the two most feasible DLE methods for the three geothermal brines in the Netherlands:
  - CAPEX estimate of equipment and installation, required for the lithium extraction.
  - OPEX estimate related to the DLE extraction installation.
  - Business case analysis of upstream lithium extraction process.

4 Literature analysis of the downstream extraction process:

- Literature review of the downstream processing technologies.
- Assessment of composition and quality of the preferred battery grade lithium precursor ($LiOH.H_2O$ or Li_2CO_3).

3.3 Reading guide

The remaining of the report is structured as follows:

- Chapter 4 describes the context of the current lithium market, including the global use of lithium, and different extraction methods.
- Chapter 5 reviews the available upstream processes for extraction from geothermal brines, including lithium extraction, purification and concentration, resulting in a semi-finished product, namely a lithium-chloride solution.
- Chapter 6 describes the available downstream processes. Here the lithium-chloride solution is converted into the final product, a battery grade lithium product.
- Chapter 7 gives an overview of technologically feasible upstream processes for lithium extraction from Dutch geothermal brines, including the ecological and jurisdictional implications.
- Chapter 8 shows the economic feasibility of these upstream processes.
- Chapter 9 concludes the results of this report.

4

CONTEXT

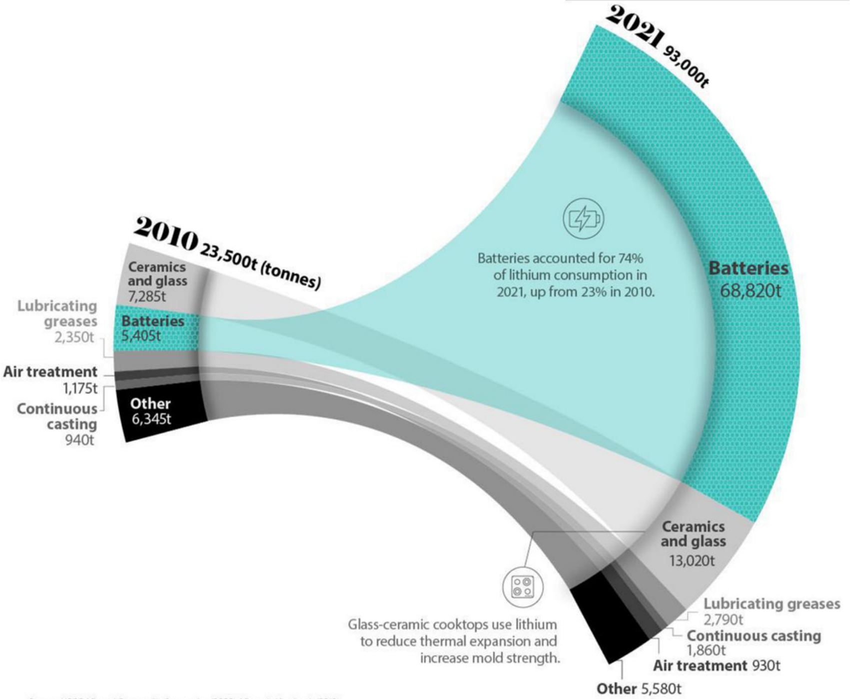
4.1 Global use of lithium

The demand for lithium has seen a significant increase from 2010 onwards, driven by the growing demand for rechargeable batteries used in various applications. Figure 4.1 shows that the global lithium demand in 2010 was approximately 23,500 metric tons of lithium, and it increased to 93,000 metric tons of lithium in 2021 [8].

The demand trend for lithium has been influenced by the rapid growth of the electric vehicle market, which has resulted in a surge in demand for lithium-ion batteries. The global electric vehicle fleet has been growing at a compound annual growth rate of over 50 % in the last few years, and this trend is expected to continue [8]. As a result, the demand for lithium-ion batteries is projected to increase significantly, driving the demand for lithium. The EU and the Netherlands are currently mostly dependent on non-European countries for the supply of lithium.

Apart from the electric vehicle market, the demand for lithium is also driven by the growing popularity of consumer electronics such as smartphones, laptops, and tablets. Additionally, the increasing need for energy storage solutions, such as grid-scale batteries, is also contributing to the growth of the lithium market.
In conclusion, the demand for lithium has seen a substantial increase from 2010 onwards, driven by the growing demand for rechargeable batteries used in various applications, including electric vehicles, consumer electronics, and energy storage systems.

Figure 4.1 The growth of Lithium global consumption from 2010 to 2021 [8]

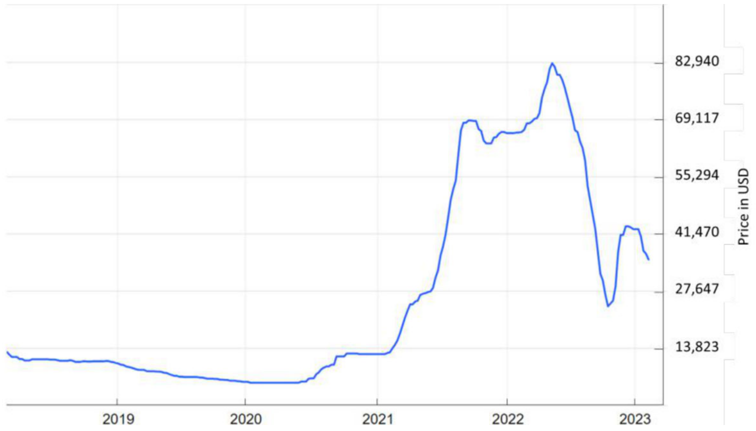


Source: USGS Mineral Commodity Summaries (2022), Minerals Yearbook (2010)

4.2 Price development of lithium

The price of lithium is generally expressed per tonne lithium carbonate equivalent (LCE). Figure 4.2 shows the price of LCE in US dollars from 2019 to August 2023. In 2021 the price of LCE raised rapidly to a maximum of $ 80,000.-- USD in 2022, due to a large demand for electrical vehicles. A drop is seen after this peak, which was mainly caused by a halt of subsidies for electrical vehicles.

Figure 4.2 Price development of lithium carbonate equivalent from 2019 to August 2023 [9]. Prices converted from Chinese Yen to US Dollars



In the near future, the lithium price could decline, and the gradually rise to EUR 37,000.-- in 2040. With the current estimates from Fastmarket in the period of 2026-2045 and specialists in the market, the average price of one tonne lithium hydroxide is expected to be around EUR **30,000.-- [10] [11],** as is illustrated in Figure 4.1. Between 2026 and 2031 a decline is expected in pricing, following a gradual increase until 2040. A price of EUR 30,000.-- per tonne LCE is used in this report to assess the current economic feasibility.

Figure 4.1 Expected price development of lithium hydroxide between 2026 and 2045, as expected by Vulcan [], based on analysis of Fastmarket data and long term offtake price agreements

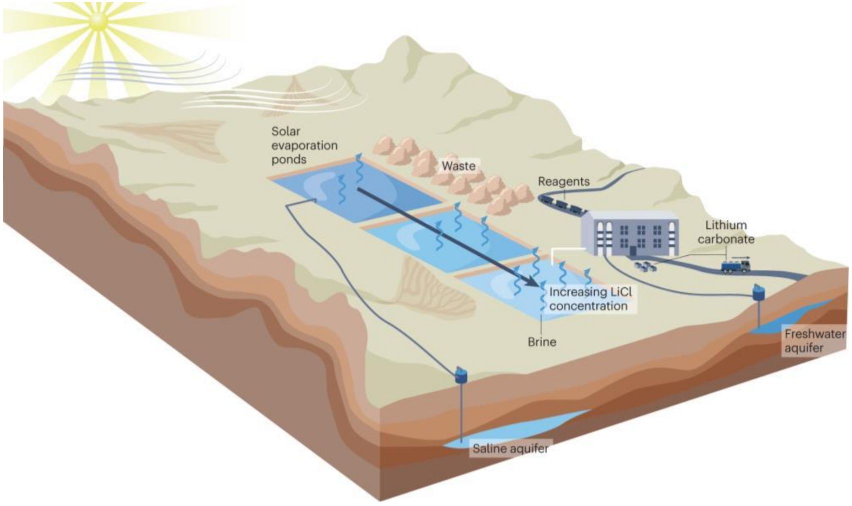
4.3 Current lithium mining methods

Most of the global lithium production comes currently from two main sources: salar brine extraction and hard rock mining. A relatively new method for lithium extraction is by Direct Lithium Extraction, which can be applied on typical lithium salar brines, but also on other sources such as geothermal brines.

Salar brine extraction

Salar brine extraction is the most common method for producing lithium globally, accounting for around two-thirds of total production. The lithium is extracted from saline aquifers, by using solar evaporation ponds to concentrate the salar brine. The largest brine operations are located in South America's 'Lithium Triangle' in Argentina, Bolivia, and Chile, which together account for over 50 % of global lithium production [12]. Other significant brine producers include China, Australia, and the United States of America. The process is visualized in figure 4.3.

Figure 4.3 Process of lithium mining by brine extraction [12]



Hard rock mining

Hard rock mining, on the other hand, accounts for around one-third of global lithium production. The main hard rock mines are located in Australia, Canada, and the United States.of America The largest hard rock mine is the Greenbushes mine in Western Australia, which produces over one-third of the world's lithium from hard rock mining [13]. Lithium is present in the mineral spodumene in pegmatites, and is extracted by grinding, milling and froth flotation processes.

Direct Lithium Extraction

The direct lithium extraction method (DLE) is a relatively new process used to extract lithium from various sources, including salar brines, clays, and geothermal brines. Unlike the traditional brine extraction method, which relies on evaporation and precipitation to extract lithium, DLE uses selective sorbents, ion exchange or solvents to directly capture lithium ions from the source material.

The DLE process for most geothermal brines can divided into upstream and downstream processes, which is visualized in the Introduction of this report in figure 3.1. In the upstream process, lithium is extracted from (saline) geothermal brine into concentrated LiCl solution. The LiCl solution is converted into a purified lithium compound, such as battery grade Li_2CO_3 or LiOH in the downstream process.

Table 4.1 shows a summary of the three lithium recovery methods. It shows that DLE is the best option for most parameters such as recovery rates, water consumption and required area. LE technology is still in its early development phase, and therefore not widely applied. The DLE market has however been expanding rapidly over the last few years, as is discussed in paragraph 5.6.

Table 4.1 Lithium extraction methods comparison [14] (edited)

	Direct lithium extraction (DLE)	**Lithium brine extraction in evaporation ponds**	**Hardrock mining (mineral ore)**
land area requirement	low	high	high
weather dependence	no	yes	yes
water consumption	low	high	high
energy Consumption	++	+	++++
lithium recovery rates / contained	70-99 %	~50 %	6 %-7 % Li2O in ~80 % spodumene
GHG impact (Scope 1 emissions)	low	low	high
dominant Process	adsorption, Ion Exchange, Solvent Extraction	staged atmospheric evaporation	crushing, heating, leaching and precipitation
costs	$$	$	$$

4.4 Lithium extraction from geothermal brines

Geothermal brines are an increasingly recognized source of lithium, as they may contain high concentrations of lithium and other valuable minerals. While the exact resource potential of geothermal brines for lithium extraction is not well understood, there is growing interest in exploring this resource due to the potential for low environmental impact and the increased opportunities due to the development of the DLE technology.

One of the challenges in assessing the lithium resource potential of geothermal brines is the variability in brine chemistry and lithium concentrations across different geothermal systems. In some cases, lithium concentrations in geothermal brines are higher, i.e., at 150 ppm or higher, making them an attractive resource for lithium extraction. However, in other cases, the lithium concentrations may be too low to be economically viable for extraction.

Despite these challenges, there are several regions around the world that are known to have high lithium concentrations in their geothermal brines, including the Salton Sea region in California, USA, the Rhine Valley in Germany, and the Taupo Volcanic Zone in New Zealand. In addition, there are numerous other geothermal systems around the world that are being explored for their lithium and other mineral resources [15] [14]. An overview of selected geothermal European sites with high lithium concentrations is given in Appendix III.

Overall, the lithium resource potential of geothermal brines is still being explored, and much more research is needed to fully understand the extent and variability of this resource. Given the growing demand for lithium and the potential advantages of extracting lithium from geothermal brines, it is likely that more attention will be paid to this resource in the coming years.
Table 4.2 shows example compositions of geothermal and salar brines. Although geothermal brines typically have lower lithium concentrations compared to some traditional lithium deposits, they offer several advantages. For instance, they already have high temperatures and are not weather dependent for processing like salar brines. Additionally, some geothermal brines are situated closer to infrastructure and power sources, providing a distinct advantage. Furthermore, the geothermal energy available from geothermal sources can enhance Direct Lithium Extraction (DLE) technologies, resulting in more efficient and cost-effective lithium recovery. As a result, geothermal brines may be economically viable even with lower lithium grades compared to non-heated, salar-type deposits, and without the need for fossil fuel consumption. [16]

Table 4.2 Typical examples of a geothermal and salar brine compositions [16]

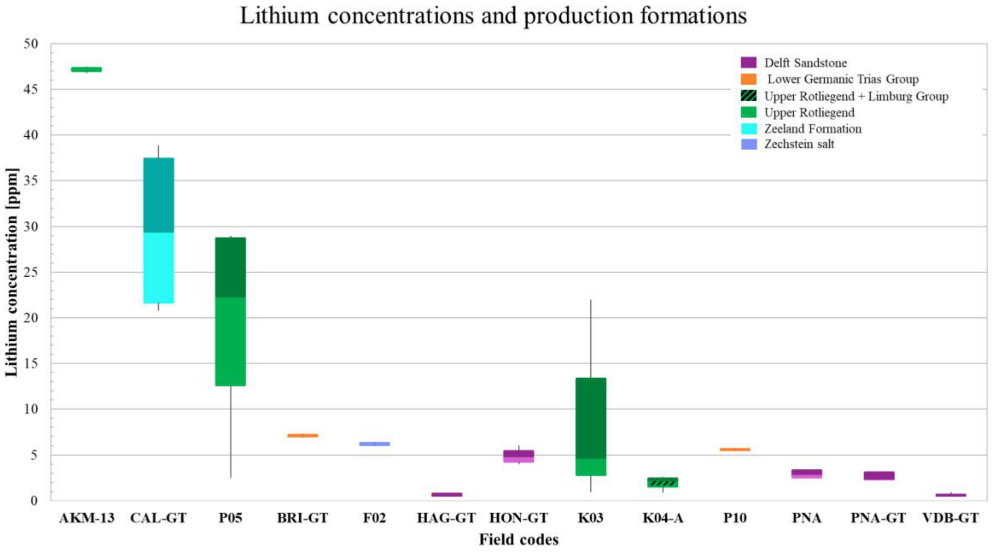
Element	Salton Sea geothermal brine (USA) (mg/L)	Salar de Atacama brine (Chile) (mg/L)
Li	100 - 400	1570
Mg	700 - 5700	9650
Ca	22600 - 39000	450
Na	50000 - 70000	91000
K	13000 - 34200	23600
Cl	142000 - 209000	189500
SO_4	42 - 50	15900
B	40	400

In the Netherlands, the lithium concentrations in geothermal, gas and oil wells are range from close to no lithium to 48 ppm based on public available well data, as shown in figure 4.4. AKM-13 is a Chevron gas field, closed in 1980, and P05, K03 and KO4-A are all offshore gas fields. This data was summarised in a concise overview by Biagnini [6].

In this study, the feasibility of lithium extraction from three different geothermal doublets is investigated. The wells, designated as Well A, B, and C to protect confidentiality, have been selected based on factors such as an average representation of the brines, the lithium concentration, total dissolved solids (TDS) and location.

The brine compositions of these three wells are given in Appendix II. While there are more wells in the Netherlands, the wells in figure 4.4 are ones where an average to relatively elevated lithium concentration is present. It should be noted that the number of available measurements on the lithium concentration is limited. Given the current geological knowledge and given the fact that the currently studied reservoirs are fairly homogeneous, it is not expected that significant higher lithium concentrations will be measured in the current reservoirs. Of course, this does not necessary hold for the -not yet studied- deeper reservoirs or specific geological conditions (intrusions, faults etc.). The analysis of geothermal brines, which include lithium, is important for future wells to gain more knowledge on the lithium variation in geothermal brines in the Netherlands.

Figure 4.4 Variability of lithium concentrations in geothermal brines the Netherlands based on field data results and the reservoir formation, Biagnini 2022 [6]



For comparison, the concentration of selected geothermal reservoirs in the world that have a high content of lithium are listed in the table below.

Table 4.3 Selection of geothermal pilot plants with high lithium concentration, and comparison with the brine composition in this study

Geothermal pilot plant	Lithium concentration [ppm]	Total dissolved solids (TDS) [g/L]
selected wells in the Netherlands in this study	13-24	84-228
Salton Sea (USA) [15]	141-278	200-278
Innsheim, Germany (Vulcan Energy Resources) [17] [18]	168	106
Redruth, United Down, Cornwall, UK (Cornish Lithium) [19]	220	29

4.5 Environmental and legal implications of lithium extraction from geothermal wells in the Netherlands

The environmental impact of lithium recovery using DLE extraction from geothermal brine is, compared to conventional lithium mining methods (salar brine evaporation or hardrock mining), much lower [14].
In general, the extraction of lithium from geothermal brine is a better option than conventional lithium mining: A smaller production area is required, significant CO_2 savings are possible due to lower energy use. Also, environmental harm, such as groundwater pollution, dust and impact on habitat is significantly lower. Also, the water consumption and required power is lower than conventional mining technologies [12] . The footprint of the surface installations is limited, and the water consumption for the lithium harvesting is typically <1 % of that of hardrock mining or salar mining, as was calculated by Vulcan for their production facilities [10].

To prevent environmental harm from the processes of geothermal lithium extraction, mainly leakage to groundwater should be prevented. This is already the general practice in geothermal operations but combining it with lithium extraction increases the risk due to an increasing number of processes and increasing surface area. Where chemicals are stored and used, leakage into the soil should be prevented by using impermeable floors and spill containments for storage. This also is standard practice and is being supervised by the State Supervision of the Mines (SODM). Clean energy for the extraction is readily available, as part of the low temperature geothermal heat can be used in the processes. In this respect, Vulcan claims to have a net-zero CO_2 emission in their planned lithium extraction from geothermal brine. Here it should be noted that Vulcan utilizes high enthalpy sources that generate also electricity. This electricity is also used in the further processing and purification of the lithium salts [10] .

Regarding the legal aspects of the lithium extraction: the Dutch Mining Act is not tailored yet for lithium extraction from geothermal wells in combination with geothermal heat production. The law is applicable for extraction of hydrocarbons, geothermal heat, subsurface storage, salts or limestone [20]. A legal obstacle is the structure of the current Dutch Mining Law. Lithium is a mineral and as such falls under the Mining Act. As such, a lithium compound (or to be more specific: lithium chloride) is a mineral and salt but is not explicitly mentioned in the Dutch Mining Act. Lithium is owned by the state before extraction. After extraction, ownership is transferred to the permit holder. An exploration and extraction permit is required for the extraction of lithium in accordance with the Mining Act. The question is whether an analogous application of the system as included in the current Mining Act is suitable for the extraction of lithium. An extra exploration permit would be required for the extraction of lithium, according to article 6 in the Mining Law.

An extra point of attention is the brine composition, especially the mass balance. The composition of the reinjected geothermal brine should not differ too much from the extracted source brine. It is, in general, the practice that additives in the brine may be utilized in the processing, and as such no removal is required, as long as it can be proven that the there are no negative consequences for the geothermal wells and reservoir. It is expected that in some cases the added additional chemicals and volumes should be at least lowered. before brine reinjection, and that the pH may be adjusted again. The need for the removal of excess water is of course necessary in order to prevent additional pressure build-up in the geological reservoir.

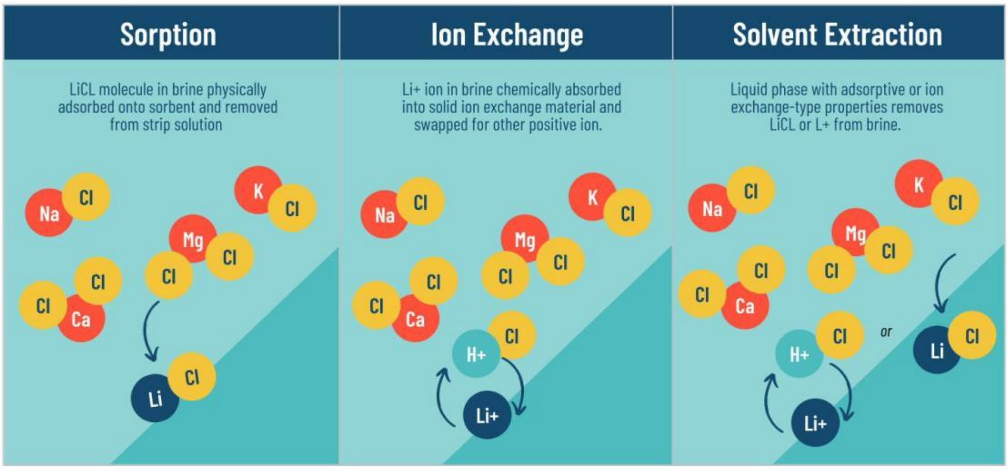
5

TECHNOLOGY REVIEW OF UPSTREAM PROCESS

Although there are numerous potential approaches to the extraction and recovery of lithium from brines, the to this date most thoroughly investigated technologies include adsorption of lithium to **inorganic mineral sorbents, ion exchange compounds** and the extraction of lithium from brines using **solvents** [21]. The principles of these three methods are shown in figure 5.1 [22].

These three methods are described in paragraphs 4.1-4.3. Besides these three methods, potential alternative technologies and supporting processes are described in this chapter in 5.4 and 5.5 respectively.

Figure 5.1 Principles of sorption, ion exchange and solvent extraction for direct lithium extraction [22]



5.1 Organic sorption

In the sorption process, LiCl molecules are adsorbed onto a sorbent surface. When the surface is saturated, the sorbent is regenerated (stripped), and the LiCl molecules are transferred to the strip solution, which subsequently requires further concentration.

Several investigators have investigated the synthesis and application of organic polymers that selectively extract lithium in preference to other metal ions. Metal selectivity may be imparted by including reactive or chelation sites in steric structures specifically sized, using an ion-imprinting process, to allow entry of lithium and not competing ions. Smaller crown ether structures have been shown to selectively bind lithium, even in complex solutions. Cyclic siloxanes appear to function in a similar manner to crown ethers but have not been investigated to any significant extent in the context of geothermal lithium recovery. Lithium-imprinted polymers are in development by startup companies but are still at a very low technology readiness level [21].

5.2 Inorganic and Ion exchange sorbents

With ion exchange adsorbents, lithium ions are chemically adsorbed into solid ion exchange material and swapped for another positive ion. Afterwards the lithium ion is recovered by using an acid.

Inorganic crystalline solids, including various alumina-based adsorbent (AlOH), manganese oxide-based ion exchange sorbent (MnOx), and titania-based ion exchange sorbent (TiOx), have been shown to be selective lithium sorbents [23] [24]. Also, studies based on lithium iron phosphate are ongoing. Crystalline metal structures are selective for the sorption of lithium because they have numerous cation-exchange sites that are protected inside a crystal matrix that serves as a molecular sieve. The molecular sieve selectively allows small lithium ions to access internal ion-exchange sites, whereas larger cations are excluded from internal sites. [21] Adsorbed lithium is typically recovered by use of an acid stripping solution, such as. hydrochloric acid, and the sorbent is regenerated or cycled for repeated use. Typically, these sorbents have high selectivity (ratio of > 100) against other ions, and high extraction efficiencies (> 90 %) [3].

Manganese oxide-based ion exchange sorbents

Studies have shown that manganese oxide-based ion exchange sorbents are very selective for lithium over calcium, strontium, barium, sodium, and potassium [23] [24]. Also, some experience has been gained at the Bruchsal geothermal power plant of EnBW [5]. It has been established that MnOx materials made with magnesium or lithium as the template metal offer the best selectivity for lithium over monovalent and divalent cations. Sorbed lithium can be recovered with dilute acid solutions; however, in some cases the adsorptive capacity for lithium ions decreased through repeated adsorption/elution cycles. A high initial brine lithium concentration favours the extraction efficiency. Thus, with the appropriate amounts of sorbent, up to 90 % of lithium have been extracted from different brines in the laboratory, with a loading capacity of 62 mg lithium per gram MnOx. Typically, in this class of materials the extraction pH is between 10-13 [[23] [24], which requires needed raising of the pH of the geothermal brine by adding a base. The stability of MnOx under acidic conditions is considered a limiting property for long term operation [21].

Titania-based ion exchange sorbent

Titania-based ion exchange sorbent are very similar to manganese oxide-based ion exchange sorbents in their mechanism of action [23] [24]. Studies have demonstrated that TiOx were at least as effective as MnOx for the sorption of lithium ions from solution. TiOx may have some advantages over MnOx, including being considered more environmentally friendly, but TiOx is still being investigated at a fundamental level in the laboratory. It shows higher stability over multiple loading and unloading cycles but are less selective. For an optimal pH range of 8-13, their loading capacities are in the range of 20-30 mg/g. Typically, in this class of materials the extraction pH is between 10-13 [21].

Alumina-based adsorbents

Alumina-based adsorbents (AlOH) have been shown to preferentially adsorb lithium. AlOH-based sorbents have been in development since the 1970s and have served as the lithium extraction technology for a number of pilot and proposed full-scale direct lithium extraction ventures.

Compared to the above sorbents, the loading is much lower, reaching less than 8 mg/g [23] [24]. The extraction can be performed at neutral or slightly acidic pHs, which makes this technology directly applicable for many geothermal brines. No acid is required for desorption, which minimizes the loss of sorbent. However, large amounts of water in a water-to-sorbent ratio of 100:1 are required. In a sensitivity analysis (Jiang et al. 2020), an optimal pH of 7 was determined, as well as a loading time of 60 min for 50 % loading and 600 min for reaching equilibrium. Considering these parameters, up to 90 % of lithium could be recovered from brines in the laboratory and in practical operations [3] [21].

5.3 Organic Solvent Separations

Solvent extraction is a well-established technology for the separation of metals from aqueous solutions in the mining industry. The CAPEX is relatively low due to the simplicity of the equipment and operation, but

OPEX (chemical costs) are significant. Some common types of organic solvent for lithium applications are described below. Companies like Tenova and Adionics are developing technologies based on solvent separation.

Crown ethers

The most lithium-selective solvents are in the family of crown ethers. Crown ethers have been shown to have selective reactivity with lithium. Although crown ethers have been successful for this application in the laboratory, there are significant barriers to commercial application of crown ethers for the extraction of lithium from geothermal brines. Crown ethers are expensive to manufacture and the selectivity of crown ethers for lithium in complex solutions has not been proven [21].

Multicomponent solvent systems

Organic solvent processes for metal extraction and purification frequently use a mixture of chemicals that include: 1) an extractant, such as a metal chelating or binding reagent; 2) a co-extractant, such as an adduct-forming synergistic reagent; and 3) a diluent or bulk solvent. Experience in the lithium battery recycling industry specifically and mining applications generally show that solvent extraction systems favour the complexation of transition metals, such as cobalt and copper, and divalent alkaline earth metals over lithium. While solvent systems have been successfully tested on lab-scale on geothermal brines, is has not been applied on larger scales [21].

5.4 Other processes

There are other processes that could potentially be applicable for direct lithium extraction. However, these technologies are at this moment less developed and facing limitation to scale up.

Electrochemical

Electrochemical ion-pumping technology is based on materials that are highly specific for Li+ cations, similar to the case for ion exchange resins. However, in electrochemical ion pumping, Li+ is inserted in an electrode material subjected to a potential gradient, which undergoes an electrochemical reaction. No chemicals are needed, and no species are concomitantly liberated to the brine. Subsequently, Li+ is de-inserted from the electrode material using recovery solutions requiring fresh water, producing a diluted LiCl solution. Electrochemical ion pumping is often coupled to ion-selective membranes. While tested on lab-scale, this method has not been proven on larger scale [21].

Electrodialysis

Li et al. [25] reviewed selective electrodialysis in the context of lithium extraction from water. They noted that the extraction of lithium ion from salt lake brines can be achieved by electrodialysis using commercially available anion-exchange membranes and lithium iron phosphate electrodes. Parameters such as pH and salt content influenced lithium extraction and that lithium adsorption as high as 38.9 mg/g could be achieved. The applied voltage, feed velocity, feed lithium to magnesium ratio and pH significantly influenced the lithium to magnesium separation factor. It was concluded that selective electrodialysis was superior to nanofiltration for the fractionation of lithium to magnesium in solutions with a high initial mass ratio. However, the poor durability of ionic membranes is a major issue preventing electrodialysis from becoming a widely applied technology for the recovery of lithium from brines.

Precipitation

Selective precipitation is based on the very low aqueous solubility of lithium phosphate (Li_3PO_4). A large proportion of lithium from brines can often be recovered by the addition of different phosphates, provided that the brine has previously been depleted of multivalent species [21]. Precipitation reactions are routinely used in geothermal power production, especially for the control of silica, but precipitation reactions may not be practical for direct extraction of lithium from geothermal brines.

The non-selective nature of these types of reactions and the numerous competitive co-precipitates (such as calcium carbonates, iron hydroxides, etc.) will influence chemical reagent costs and may cause waste disposal problems. In addition, lithium extracted by precipitation will require extensive post-extraction purification and processing to meet standards for lithium battery production or other uses.

5.5 Purification and concentration processes

The capture or concentration of Li^+ ions is a crucial processing step. However, brine pre-processing (for example, heating or adjusting the pH of the brine) is often needed for the key DLE process to work. Furthermore, most proposed DLE technologies do not directly produce a pure lithium product but instead a lithium chloride solution that requires additional processes to purify and concentrate the solution. In the current practice, the lithium chloride solution is concentrated to ~6 % Li concentration, which is a semi-finished product. This solution can then be converted into Li_2CO_3 and LiOH in the downstream process.

Geothermal fluids are complex solutions. Even the most selective molecular sieves adsorb undesirable minerals from lithium leachates or brines. The initial brine composition determines the production process, which typically includes pretreatment steps (to prepare the brine for lithium extraction), the lithium extraction process, and post-treatment processing (to remove impurities from the recovered lithium and for concentration).

For geothermal brines, typical materials that must be removed or reduced in concentration before lithium extraction include silica, magnesium, calcium, sulphates, and other metals. Major elements and compounds found in geothermal brines that can interfere with lithium extraction include other alkali metals (Na, K), alkaline earth metals (Mg, Ca, Sr, Ba), iron and base metals (Fe, Mn, Pb, Zn), and metalloids (B, Si, As). Lithium is a minor element in a concentrated brine and the majority of the other more abundant elements may need to be removed or controlled before lithium can be adsorbed or otherwise extracted and recovered. Also, after lithium extraction, the produced concentrate with need to be purified and concentrated for further downstream processing.

Below we describe the typical processes involved.

Table 5.1 Overview of the available technologies for purification and concentration

Technology	Conditions	Used as	Energy consumption	Chemicals needed	TRL
reverse Osmosis [26]	TDS< 70 g/l	concentration	1.5-4 kWhe/m3 permeate (dependent on TDS)	pH adjustment and/or anti-scalants, cleaning agents	9 (for general desalinisation)
nanofiltration	TDS < 20 g/l	purification (removal divalent ions)	0.5-2 kWhe/m3 permeate (dependent on TDS)	pH adjustment and/or anti-scalants, cleaning agents	9 (for general desalinisation)
polishing (sorption)	Any TDS	removal divalent ions	no	acid for regeneration	9 (general)
electrodialysis [26]	Limited TDS	purification	++	cleaning agents	6 [27]
evaporators/crystallisers [28]	Any TDS	concentration	40-60 kWhe/m3 (more efficient at concentrated brines)	limited	9 (general)

Reverse Osmosis

Reverse Osmosis (RO) uses semi-permeable membranes to separate water molecules from other substances, by applying pressure to overcome the osmotic pressure in the solution. It is known for drinking water purification and desalinisation of water.

RO can be applied for concentration of the product resulting from the Direct Lithium Extraction. This is generally a lithium chloride solution. In this case, water molecules are removed from the solution, thereby increasing the concentration of lithium chloride and other salts. The pure water effluent can be reused [29]. The major costs for RO systems result from its energy consumption, 1.5-4 kWhe/m^3 permeate, dependent on the feed TDS.

Nano filtration

Nanofiltration, as an example of membrane technology, enables the selective separation of multivalent from monovalent ions. Nanofiltration treatment is particularly useful for magnesium-rich fluids, as Mg competes with Li in many methods due to similar ionic radii. Separation occurs in a pressure-driven process via pore size as well as membrane charge. Nanofiltration systems are already available on an industrial scale and are also used for water upgrading. The use of nanofiltration for lithium separation is always in combination with a pre- or post-treatment to separate the interfering ions, since other monovalent cations such as Na or K also pass through the membrane [30].

Membrane distillation

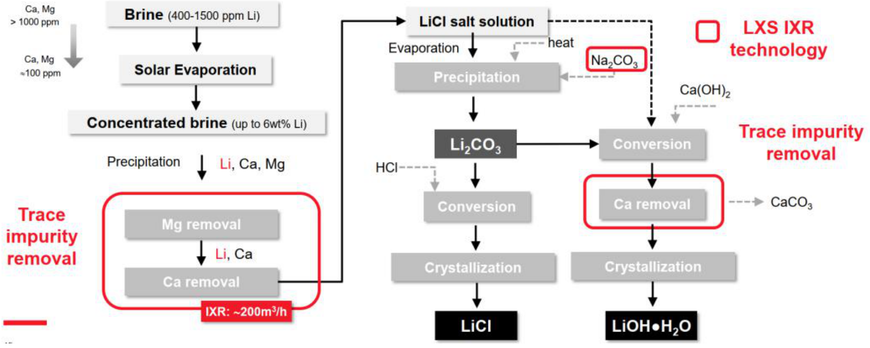
Another approach is the combination of membrane distillation and crystallizers. Membrane distillation is a temperature-driven process that provides contactless concentration up to the crystallization limit via a water repellent membrane. The temperature-driven process enables net energy-neutral water treatment for geothermal systems.

A warm input solution is passed past a hydrophobic membrane with a cold permeate stream on the other side, creating a vapor pressure gradient along the membrane, which allows the water to pass through as vapor and condense in the permeate stream. The removal of water molecules in the form of the separated vapor results in the relative enrichment of solids in the feed water stream. The permeate tower water could even be used to recover fresh water as a co-product. Similar to nanofiltration, membrane distillation only allows enrichment of mineral phases up to the saturation limit [30].

Softening with Ion exchange

After the extraction of lithium with one of the lithium extraction methods, the resulting lithium chloride solution might need to be polished. For the removal of calcium and magnesium ion exchange softening can be applied. Water softening is a widely applied technology to produce soft water but can be applied here to produce a purer lithium chloride concentrate. Ion exchange is applied on already concentrated brine, as shown in figure 5.2 [31] as IXR.

Figure 5.2 Typical process for lithium recovery by solar evaporation, ion exchange (IXR) and downstream processing to Li_2CO_3 [31]



Forced evaporation

A final method for lithium recovery comprises processes in which the main objective is to concentrate native brines with concomitant water recovery. Brine concentration is also the objective of open-air evaporation ponds, except that in this case the evaporated water is lost to the atmosphere. Examples of these processes include membrane distillation and solar evaporators.

With the evaporation technology, salt-crystals NaCl and gypsum ($CaSO_4$) are precipitated, while Li remains in solution. Crystallization takes place in modules; from there it will need to be processed with a solid discharge unit. This unit consists of a salt clarifier or head tank, followed by a centrifuge where the salt crystals are separated from the brine. The brine is then depleted from NaCl and $CaSO_4$, while the lithium remains. The energy consumption is significant: for the modules alone, it is estimated that 9,000-9,500 Kilowatt (kW) of electrical power is required, and this large power consumption makes the use the solid discharge unit not likely [32].

Crystallization could be used for purification and further concentration of already concentrated LiCl-solutions. The final LiCl-solution should have a concentration of several g/l LiCl for further downstream processing into LiOH or Li_2CO_3.

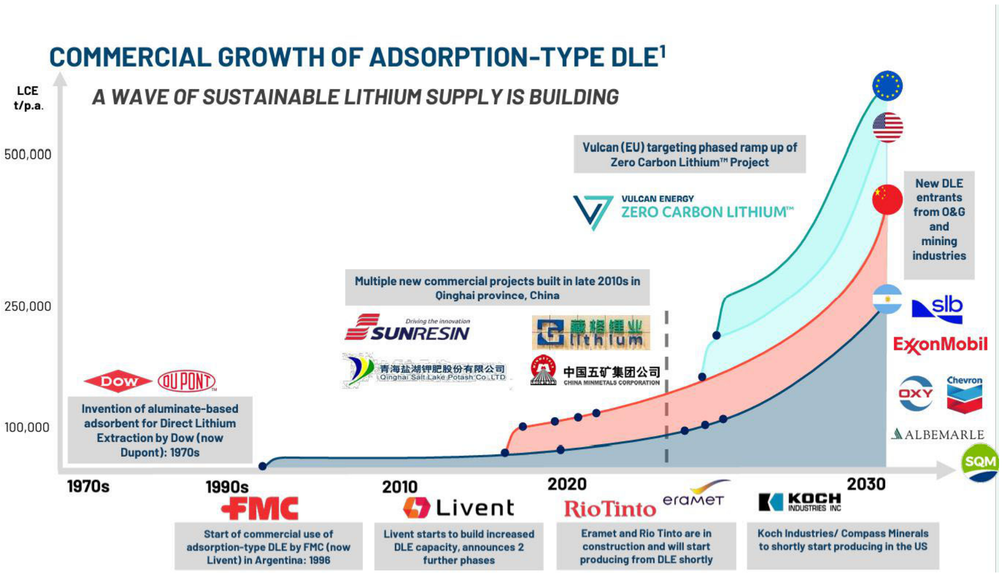
5.6 Current DLE technology market

The first development of DLE sorbent material was initiated by DOW Chemicals in the 1970s, which was an alumina-based sorbent. Livent has been operating lithium extraction with alumina-based sorption since 1996 and is planning to expand its operations in Argentina with 20,000 tonnes per year in 2024. Also, in China several projects are launched, most of them based on an alumina-based adsorbent by the Chinese company Sunresin. These are all brine operations, not combined with geothermal energy [4].

The oil and gas industry is also investing in integrating lithium extraction in their operations. ExxonMobil Corp has announced the acquisition of an adsorption-type DLE project in the Smackover Formation of Arkansas, and SLB (formerly Schlumberger) is building a portable Adsorption-type DLE plant [4].

In Europe, Vulcan Energy is developing its geothermal Zero Carbon Lithium™ Project on the French-German border since 2018 and is now ready to move into the execution phase, using its own alumina-based adsorbent. Vulcan is targeting start of production from geothermal brines by end of 2025, and ramping up production during 2026, with 24,000 tonne per year LCE capacity for Phase One of production. An overview of the DLE market of the last 50 years is given in figure 5.3 [4].

Figure 5.3 Growth and prospects of DLE market in tonne LCE per year, from 1970 to 2030 [4]



6

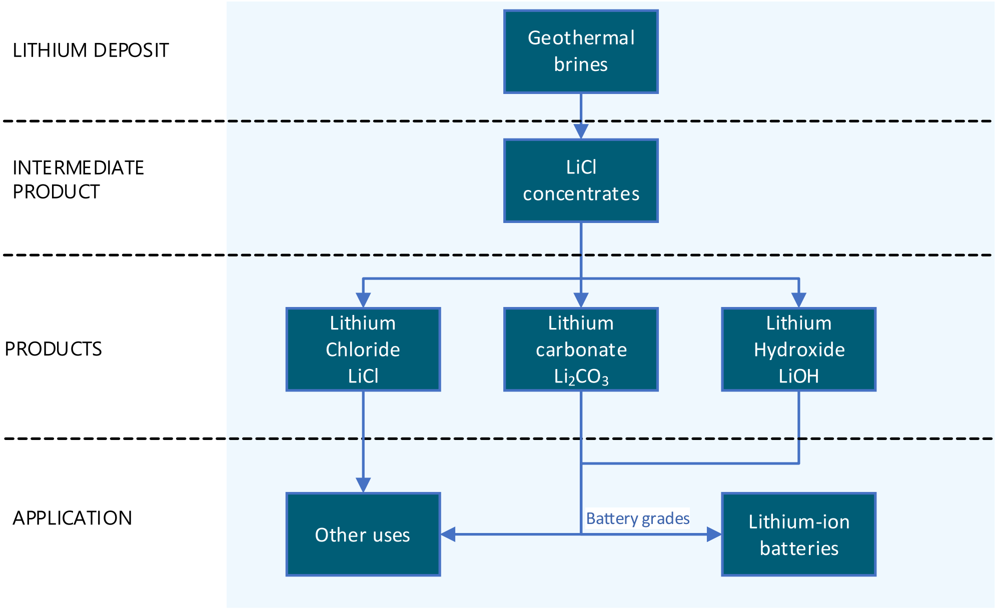
SURVEY OF DOWNSTREAM LITHIUM CONVERSION

6.1 Conversion routes into battery grade

After lithium extraction, purification and concentration, the intermediate product is a LiCl concentrate. This concentrate requires downstream processing to produce battery grade products such as lithium chloride (LiCl), lithium carbonate- (Li_2CO_3) or lithium hydroxide (LiOH). This process is described in this chapter, based on literature research. This research is however in lower detail than the research on DLE, as DLE is the main focus of this report.

Figure 6.1 shows different routes to produce lithium-ion battery from geothermal brines. LiOH and Li_2CO_3 are the precursor of lithium for Li-ion battery applications. We limit the process for lithium-ion battery applications.

Figure 6.1 Different routes to battery grade products



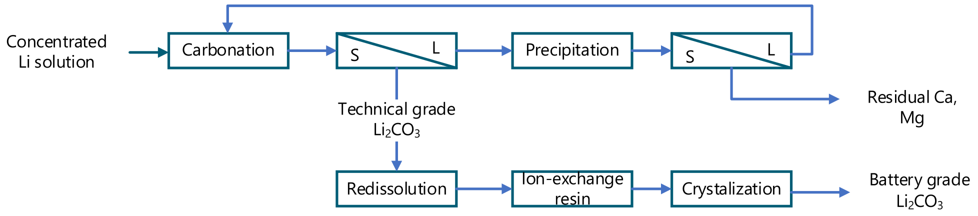
6.1.1 LiCl concentrate conversion into Li_2CO_3 precursors

The conversion of lithium chloride from brine into battery-grade lithium carbonate typically involves the following steps:

1. Lithium chloride purification: the brine is first processed to remove impurities, such as magnesium and calcium, which can interfere with the subsequent steps. This is typically done by adding chemical agents that selectively precipitate the impurities, which can then be removed by filtration or sedimentation.
2. Sodium carbonate addition: Sodium carbonate (Na_2CO_3) is added to the purified lithium chloride solution, which reacts with the lithium chloride to form lithium carbonate (Li_2CO_3) and sodium chloride (NaCl): $2LiCl + Na_2CO_3 \rightarrow Li_2CO_3 + 2NaCl$.
3. Lithium carbonate precipitation: the lithium carbonate precipitates out of the solution and is separated from the remaining solution using a variety of methods, such as filtration or centrifugation.
4. Lithium carbonate washing and drying: the lithium carbonate is washed with water to remove any remaining impurities, and then dried to produce battery-grade lithium carbonate.

The purity and quality of the final product can be controlled by adjusting the parameters of the process, such as the concentration of the starting brine, the amount of sodium carbonate added, and the conditions of precipitation and drying. The process is shown in figure 6.2.

Figure 6.2 Process for LiCl concentrate conversion into Li_2CO_3 precursors [33]



6.1.2 LiCl concentrate conversion into LiOH precursors

Battery grade LiOH can be converted into LiCl by converting the technical grade Li2CO3 or by electrolysis of the LiCl solution.

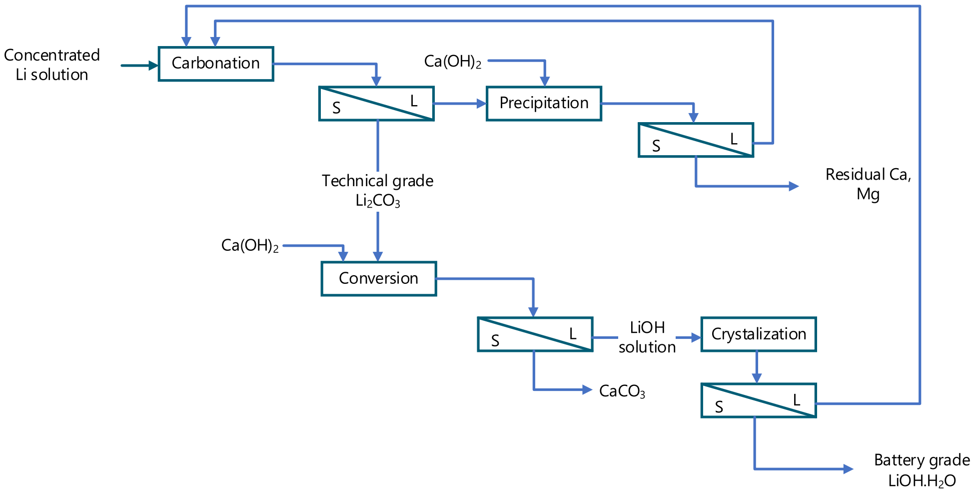
Via Li_2CO_3 route

The process involves the following steps:

1. Lithium carbonate carbonation: Lithium carbonate is reacted with carbon dioxide (CO_2) in the presence of water (H2O) to form lithium bicarbonate ($LiHCO_3$):
   - $Li_2CO_3 + CO_2 + H_2O \rightarrow 2LiHCO_3$.
2. Lithium bicarbonate separation: The lithium bicarbonate solution is separated from any remaining solids, such as calcium and magnesium carbonates, using filtration or sedimentation.
3. Lithium bicarbonate conversion to lithium hydroxide: The lithium bicarbonate solution is then heated to drive off carbon dioxide, leaving behind lithium hydroxide monohydrate:
   - $2LiHCO_3 \rightarrow Li_2CO_3 + CO_2 + H_2O$ $LiOH + H_2O \rightarrow LiOH.H_2O$.

The resulting lithium hydroxide monohydrate can then be washed, dried, and further processed into battery-grade lithium hydroxide. The process is shown in figure 6.3.

Figure 6.3 Process for LiCl concentrate conversion into LiOH precursors, via Li_2CO_3 [33]



Electrolysis

Conversion of LiCl into LiOH can be achieved by membrane electrolysis via a process that is similar to the production of NaOH from NaCl, as shown in figure 6.4. Typically, a fluorinated cation-exchange membrane with sulfonic acid groups is being used (e.g., Nafion membrane). The main drawbacks of the membrane electrolysis process are the high price of membranes, the loss in energy efficiency due to the internal resistance of the ion-exchange membrane and the fact that the membranes are susceptible to fouling and scaling. When LiCl is used as electrolyte, Cl_2 gas is released at the anode during electrolysis which requires additional HSE procedures. Moreover, the Cl_2 gas can also attack the membrane. Membrane electrodialysis is a technique that is similar to membrane electrolysis.

Figure 6.4 Membrane electrolysis for LiOH production from LiCl [34]

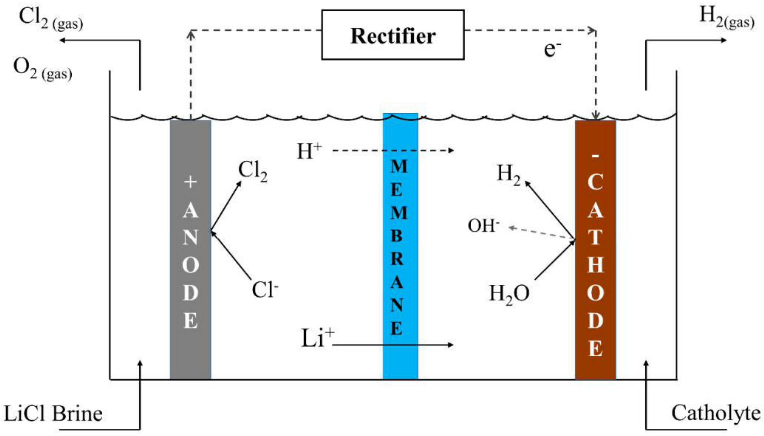
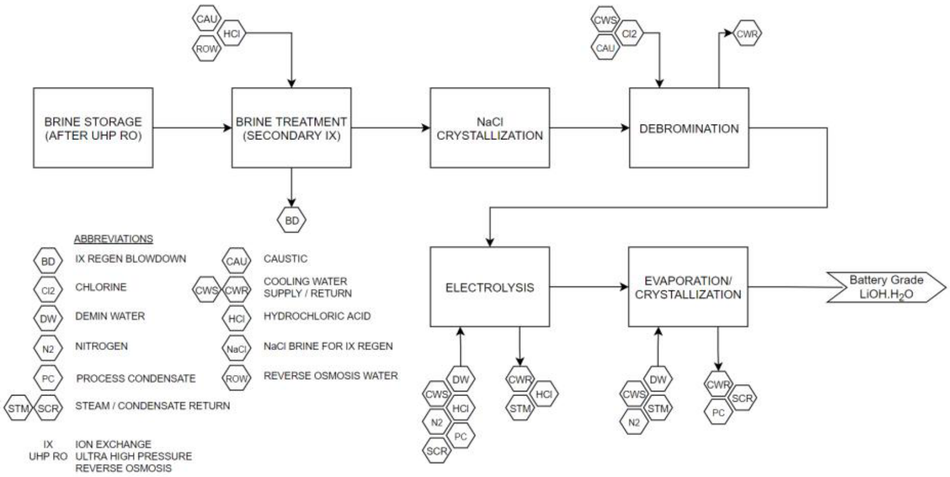


Figure 6.5 shows an example block diagram of processing Lithium Chlorine into battery grade Lithium Hydroxide Monohydrate (LHM). The steps involved are:

1 An additional stage of ion exchange to remove any residual calcium and magnesium.
2 Further concentration of the lithium chloride concentrate and separation of sodium chloride.
3 From the solution using an evaporative crystallization process.

4 Electrolytic conversion of lithium chloride to lithium hydroxide.
5 Further evaporative crystallization of the lithium hydroxide into LHM; and
6 Drying and packaging in an inert atmosphere to produce dry LHM crystals.

Figure 6.5 Process for LiCl concentrate conversion into LiOH precursors by electrolysis [35]



Sodium chloride produced from the NaCl evaporator-crystallizer is dissolved to provide the pure brine required for regeneration of the ion exchange resin in the strong-acid-cationic (SAC) ion exchange process. Chlorine gas produced from the electrolysis of lithium chloride to lithium hydroxide will be reacted with hydrogen, also produced by the electrolysis process, to produce hydrochloric acid. The hydrochloric acid is used in the sorbent stripping stage in the lithium extraction process and for regeneration in the weak-acid-cationic ion exchange process. Condensate produced from the evaporation is used for washing in the lithium extraction process.

6.2 Requirements for Battery Grade

Table 6.1 and table 6.2 show a typical specification of battery grade lithium carbonate and lithium hydroxide respectively, with the minimum lithium concentration, and maximum concentrations of impurities. The definition of battery grade may slightly vary depending on the manufacturer.

Table 6.1 Battery grade lithium carbonate specification [36]

Component	Composition	Component	Composition	Component	Composition
Li_2CO_3	>99.9 %	Na	<20 ppm	Mn	<5 ppm
Si	<40 ppm	Cl	<20 ppm	Al	<2 ppm
SO_4	<30 ppm	Mg	<10 ppm	Cu	<2 ppm
Ca	<25 ppm	Pb	<5 ppm	Fe	<2 ppm

Table 6.2 Battery grade lithium hydroxide monohydrate specification [36]

Component	Composition	Component	Composition	Component	Composition
$LiOH.H_2O$	>99.3 %	SO_4^{2}-	<100 ppm	Insol (HCl)	<50 ppm
Na	<50 ppm	CO_2	<3000 ppm	Insol (H_2O)	<50 ppm
K	<50 ppm	Ca	<20 ppm		
Cl-	<30 ppm	Fe	<7 ppm		

7

TECHNOLOGICAL FEASIBILITY OF UPSTREAM DLE TECHNOLOGIES IN THE NETHERLANDS

This chapter gives an overview of available Direct Lithium Extraction (DLE) technologies and their feasibility for geothermal brines in the Netherlands, based on a processing capacity of 250 m^3 brine per hour. Several DLE technologies are investigated by consulting suppliers and by modelling to estimate CAPEX and OPEX. Only the upstream processes are taken into account, where the final product is a Lithium-Chloride concentrated solution. The downstream process, where the solution is processed into solid lithium carbonate (Li_2CO_3) or lithium hydroxide (LiOH), is out of the scope. A scheme with up- and downstream processes is given in the Introduction in figure 3.1.

The price of the battery grade product (either lithium carbonate or lithium hydroxide) is expressed as price per Lithium Carbonate Equivalent (LCE). The OPEX of the DLE technologies are referred to as costs per tonne LCE, to be able to compare it with the market price of LCE and determine the economic feasibility. As stated in paragraph 4.2, the assumed LCE market price is about EUR 30,000.-- for the current market conditions (2023).

In paragraph 7.1, the composition of three selected geothermal brines in the Netherlands are given, anonymized as Well A, B and C. Paragraph 7.2 gives descriptions of the investigated DLE technologies, including their feasibility for the three brines.

7.1 Geothermal brine composition in the Netherlands

Table 7.1 shows the most important parameters of the geothermal brine compositions for three sites in the Netherlands: Well A, B and C. These wells were pre-selected for this study as they were considered to have the highest potential for lithium extraction, based on among others location and lithium concentration. The brines of these wells differ in lithium concentration, but also in other important parameters for DLE technologies, such as sulphate content, pH and total dissolved solids (TDS). A table with the complete compositions of the brines is given in Appendix II.

Table 7.1 Geothermal brine compositions for three sites in the Netherlands

		Well A	Well B	Well C
Li	**mg/l**	**13**	**24**	**22**
Na	mg/l	43,000	74,769	21,933
K	mg/l	880	3,047	1,633
Ca	mg/l	8,100	3,799	3,627
Mg	mg/l	1,100	1,469	471
Fe	mg/l	59	70	28
Cl	mg/l	110,000	133,210	52,000
SO_4	mg/l	470	579	39
HCO_3-	mg/l	130	222	360
pH (as received)	-	5.64	5.73	6.4
Conductivity at 25 °C	mS/cm	67.0	234.5	125.0
TDS	mg/l	164,164 (calculated*)	228,375 (measured)	84,550 (measured)

*Calculated by summing al cations and anions

7.2 Available technologies

More than 20 technology suppliers of DLE and supporting technologies have been contacted to discuss the technological and economic feasibility of lithium extraction from the Dutch geothermal brines with their technology. Current state-of-the-art technologies for direct lithium extraction, purification and concentration have been assessed through literature research and interviews with suppliers. Only suppliers who have proven their technology at least on a pilot scale were approached for interviews. Approximately 20 suppliers were approached in this study. Most suppliers concluded that the lithium concentrations from the three wells were too low for economically feasible lithium extraction with their technology at the current lithium price. These suppliers have requested to stay anonymous, and therefore are not mentioned by name. The suppliers provided the following technologies:

- Alumina-based adsorbent.
- Titania-based ion exchange sorbent.
- Solvent extraction.
- Ion exchange membrane.
- Combination of membranes, solvents and adsorbents.
- Evaporation/crystallization.
- Ion exchange resin for purification.

There are two technology suppliers who indicate that - potentially - their direct lithium extraction technology could be suitable for Dutch geothermal water. Both suppliers extract with sorbents, one based on aluminates (adsorption), and one based on titanates (ion exchange).

7.2.1 Alumina-based adsorbent

This supplier has developed a DLE technology which is based on alumina-based adsorbent (AlOHx) material. The AlOHx material selectively sorbs lithium, which can be regenerated with demineralized water, therefore no reagents are required. The optimal pH for the DLE is around 4.5. The technology is generally combined with ion exchange softening for removal of calcium/magnesium (Ca/Mg) and other multivalent ions after DLE, and finally Reverse Osmosis (RO) for concentration of the brine to a lithium chloride (LiCl) solution. Additionally, crystallization with solid liquid separation can be used for further concentration and purification. After reverse osmosis, the demineralized water can be reused for regeneration of the AlOHx material. The depleted geothermal brine is reinjected in the reservoir after lithium recovery [29].

The Dutch Mining Law states that the reinjected brine needs to have the same composition and volume compared to the source brine. This means that in this process, the concentrated Ca/Mg solution from the ion exchange softening will need to be mixed and reinjected. Furthermore, it is necessary to remove added volume (such as demineralized water) before reinjection to prevent pressure buildup in the reservoir.

The supplier has stated that the DLE is less efficient at higher TDS, as other metals will compete with Li sorption. Especially sulphate (SO_4) will compete with Li, therefore sulphate concentration must be at least lower than the Li concentration. Typically, a Li concentration of 150 ppm feeds the sorption process. The lowest Li concentrations at which the DLE has been tested, was on a case with 80 ppm Li and 80 ppm SO_4 [29].

The supplier currently operates a pilot installation with a capacity of 1000 tonne LCE/ year (approximately 100 m^3 brine/h) with a Li concentration of 250 ppm. The scope in this case was:
- DLE for selective adsorption of lithium over other ions, and desorption using water.
- Ion Exchange Softening to remove multivalent ions coming from the DLE step. Regeneration of ion exchange using salt.
- Reverse Osmosis for preconcentration to about 2,500 ppm of Li [29].

Reviewing the performance alumina-based technology for the three Dutch geothermal brines.

Well A

It is concluded that **Well A brine is too high in sulphate content compared to lithium** for the alumina-based sorption technology**.** Due to the low Li content, multiple passes through the DLE equipment are required, therefore large-scale equipment will be required, raising the CAPEX significantly.

Well B

Well B brine has an even higher sulphate content than the Well A brine, and the sulphate concentration is higher than the lithium concentration. As sulphate competes with lithium for sorption, **this DLE technology technically is not feasible for Well B either.**

Well C

The supplier concluded that their DLE technology could be technically feasible for Well C brine, as the sulphate concentration is significantly lower than for Well B and Well A. However, it is still higher than the lithium concentration (39 ppm SO_4 and 22 ppm Li), where the DLE requires the sulphate content to be equal to the lithium content or lower. It was also stated that as the lithium concentration is relatively low, large DLE units are required, as multiple extraction steps are required. This increases the CAPEX significantly.

The cost analysis for the technology on Well C brine is covered in the next chapter.

7.2.2 Titania-based ion exchange adsorbent

Another supplier has developed a DLE technology based on ion exchange, where titania-based ion exchange sorbent (LiTiOx) with inorganic material selectively sorbs lithium ions. The supplier uses cartridges, which are assembled in racks. These racks can be assembled in modules, including pumps, pipes, valves, and programmable logic controller. With these modules the plant size is scalable for the required capacity [37].

The titania-based ion exchange sorbent selectively sorbs lithium from the brine. For effective sorption, a pH of 10 is required. This means that the pH of brine first needs to be increased from 5.6 to 10 by adding reagents. Extraction of lithium from the titania-based ion exchange sorbent is done with a HCl solution, which can partially be recycled. The extraction process typically takes up to 3 hours and generates a 1 g/l Li solution [37].

The pH of the Li depleted brine will need to be lowered to its original pH before reinjecting it in the reservoir, as required by the Dutch Mining Law [38]. This means that another reagent is required to lower the pH. For increasing and decreasing the pH, sodium hydroxide (NaOH) and HCl respectively are the most used reagents. A flow diagram with these reagents is given in figure 7.1. Due to addition of NaOH, solids will precipitate. These will need to be filtered and returned to the Li depleted brine before the brine is reinjected.

The Li-depleted brine also requires post-treatment before reinjection in the well. As NaOH and HCl are added, and the resultant Na and Cl will need to be removed before reinjection, but also the total volume needs to be lowered because the reagents are added in liquid form. Although the volume increase would be marginally increased, this extra volume needs to be removed in order to prevent pressure buildup in the reservoir. Blending the depleted brine in the reservoir could also result in scaling in the wells or reservoir, however this is not further investigated.

Figure 7.1 Flow diagram for DLE with the Ion Exchange technology based on titania-based ion exchange sorbent

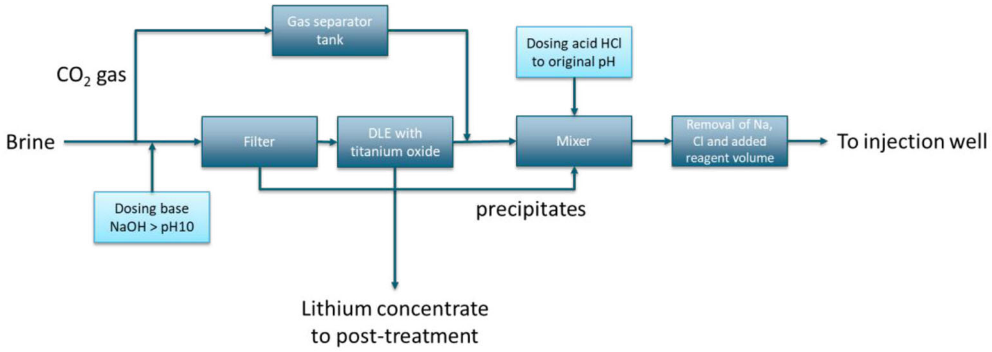


Table 7.2 shows the design information and chemical consumption for the three brines as determined by the supplier. Note that due to the low lithium concentration, cycle times are significant (75 and 40 hours), resulting in large installations.[1] The titania-based ion exchange sorbent filters have a lifetime of 2,000 cycles (10-20 years), after which they need to be replaced [37].

The chemical consumption for pH adjustment (NaOH and HCl) is not taken into account in this table. These chemicals will increase the OPEX, but also additional steps will need to be taken into account after chemical addition. The chemical consumption and corresponding costs are covered per location in the following paragraphs.

Table 7.2 DLE Design information and chemical consumption for the three Dutch brines. Shared by the supplier. Excluding chemical consumption for pH adjustments, delivery and utilities [37]

		Well A	Well B	Well C *
Li-sorption capacity of titania-based ion exchange sorbent filter	g Li/kg filter	10	10	10
volume one filter	L	188	188	188
production yield	%	90	90	90
flow rate geothermal brine	m3/h	250	250	250

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[1] In comparison: for brine with a Li concentration of 3500 ppm, the processing time is 3 hours.

		Well A	Well B	Well C *
brine Li-concentration	mg/L	13	24	22
# of filters	-	813	800	800
plant availability	h/year	8,000	8,000	8,000
cycle time	h	75	40	40
lifetime of filter	# cycles	2,000	2,000	2,000
lifetime of filter	years	18,8	10,0	10,0
Li extraction	kg/year	23,400	43,200	39,600
LCE production	tonne/year	124.6	230.0	210.8

**# of filters, cycle time, CAPEX, Acid for Li recovery, water consumption assumed to be similar to Well B.*

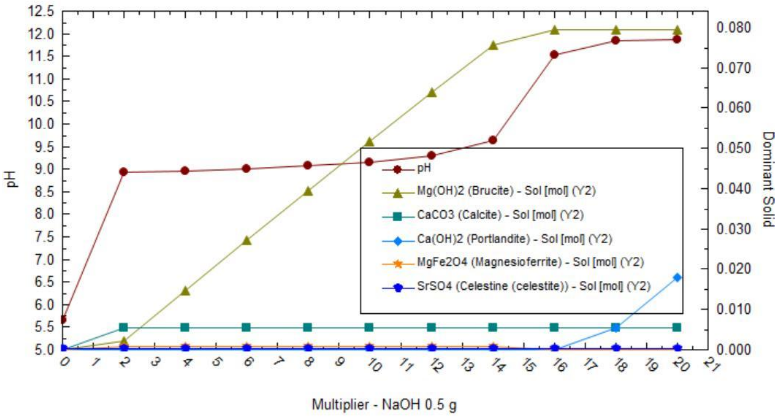
Chemical consumption for pH adjustment

Well B

The required NaOH to raise the pH of the brines to pH10 is simulated with OLI software. The required dosing of HCl to lower the pH back to the original brine pH is determined stoichiometrically based on the NaOH dosing.

The OLI simulation for the brine composition of Well B brine is given in figure 7.2. On the x-axis the added NaOH in steps of 0.5 g/L is given, with the pH on the y-axis on the left, and solubility of solids in mol/L on the right. pH 10 is reached after adding 7,131 mg NaOH/L to the brine. This high consumption of NaOH is mainly caused by the precipitation of magnesium hydroxide, which forms brucite ($Mg(OH)_2$) after adding NaOH. The graph shows that after adding approximately 7 g/l NaOH, the majority of the magnesium ions are precipitated, therefore OH^- is not consumed anymore, and the pH of the brine increases.

Figure 7.2 OLI simulation at 30 °C and 8 barg. pH and dominant solids plotted against addition of NaOH for Well B brine



For Well B brine with a capacity of 250 m^3/h, adding 7,131 mg/L results in a yearly consumption of 15,500 tonne solid NaOH or 31,000 tonne NaOH (50 %) solution. After the DLE, HCl is required to return the pH to the original value of 5.6. This would require another 43,000 tonne 32 % HCl solution, on top of the HCl that is needed for lithium recovery.

The chemical consumption for this process is extensive, and would result in significant costs, more than $ 70,000.-- USD per tonne LCE, more than twice the current market price (see figure 4.2). It would also be difficult to practically operate (supply and storage). Based on the chemical consumption, this technology is practically unfeasible for Well B brine.

Well A

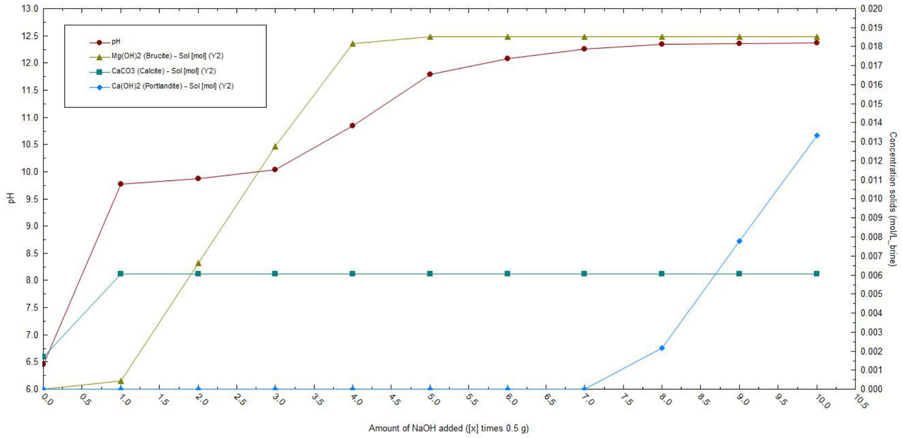
Well A has a similar Mg concentration compared to Well B (1,100 and 1,469 ppm respectively), therefore the buffering effect would also be significant for Well A. Similar consumption rates for NaOH and HCl can be expected. The lithium concentration of Well A brine however is much lower than for Well B (13 ppm versus 23 ppm), and therefore the production of LCE will be lower than for Well B.

This technology is also deemed unfeasible for the Well A brine, due to very high chemical demand.

Well C

Well C brine has a Mg concentration of 471 mg/l, lower than Well B and Well A. The OLI simulation (figure 7.3) shows that to raise the pH from 6,4 (brine pH) to 10, 1500 mg NaOH/L is required. Again, Mg precipitates as $Mg(OH)_2$, but the buffering effect is smaller due to a lower Mg concentration compared to Well B.

Figure 7.3 OLI simulation at 30 °C and 8 barg. pH and dominant solids plotted against addition of NaOH for Well C brine



For a capacity of 250 m^3/h, 6570 tonne NaOH (50 %) and 9,099 tonne HCl (32 %) per year would be required for pH adjustment. The chemical demand for Well C brine is significantly lower than for the other two brines.

7.2.3 Solvent extraction

The following supplier has developed a technology that is based on selective extraction of salts. It uses liquid-liquid extraction with a patented media to produce a purified lithium chloride concentrate. No reagents such as acids are required, and the water can be recycled to reduce the water consumption to a minimum. After consultation with the supplier and sharing the characteristics of the Dutch geothermal brines, the supplier concluded that the lithium concentrations in the brines are too low to deliver a high efficiency with the DLE technology. The supplier considers a minimum concentration of 50 ppm as a prerequisite to investigate feasibility [39].

It was noted that the technology might work on pre-concentrated brine where the concentration is above 50 ppm. However, pre-concentration of the Dutch brines is challenging on its own; due to the high TDS, membranes are no viable option, and evaporation would require a high energy consumption [39].

7.2.4 Ion exchange membrane

Ion Exchange Membrane (IEM) can separate monovalent and divalent ions. After consultation with the supplier, it became clear that due to the high TDS in the Dutch brines, this technology would not work. Another issue is that Na and Li are similar in charge and ionic radius, and therefore cannot be separated by IEM, therefore only a concentrated Na/Li streams could be reached with this technology [40].

7.2.5 Nanotechnology membranes

This supplier uses a combination of nanotechnology membranes, solvents and adsorbents for DLE. After sharing the Dutch brine composition, experts from the supplier concluded that the Li concentrations are too low, as their technology requires concentrations higher than 100 ppm [41].

7.3 Technical feasibility of Direct Lithium Extraction from Dutch geothermal brines

From consultation with the DLE suppliers, it has become clear that several DLE technologies are not feasible for the three Dutch geothermal brines, due to multiple reasons such as low lithium content or high TDS. The two most promising DLE technologies for the Dutch brines are the sorption technologies based on alumina-based adsorbent and titania-based ion exchange sorbents.

In summary, the following conclusions can be drawn from this study:

1. The brine of Well C is technically most suited for lithium recovery, due to relatively low TDS and high lithium concentration compared to the other two brines.
2. The sorption technology with titania-based ion exchange sorbent is technically feasible, but rising the pH of the geothermal brine with reagents is required for the lithium extraction process, followed by lowering the pH again before injection. This requires a huge chemical reagent consumption, and that has to be removed before reinjecting the brine.
3. The sorption technology with alumina-based adsorbent is feasible, however the efficiency may drop as SO_4 competes with Li for sorption. However, it does have the benefit that no reagents are required in the direct lithium extraction.

An overview of the technical feasibility per brine for these two DLE technologies is given in table 7.3. Feasibility of post-treatment of the brine, to return the reinjected brine into the same composition and volume as the source brine, is excluded. This post-treatment is required to comply with the Dutch Mining Law.

Table 7.3 Summary of technical feasibility of DLE with titania-based ion exchange sorbent and alumina-based adsorbent
Green text = feasible, red text = not feasible

	Alumina-based adsorbent			**Titania-based ion exchange sorbent**		
	Well A	**Well B**	**Well C**	**Well A**	**Well B**	**Well C**
technical feasible?	no, SO_4 content too high, competes with Li for sorption	no, SO_4 content too high, competes with Li for sorption	yes, but still high in SO_4 content, which competes with Li for sorption	no, pH adjustment to pH 10 requires extensive amounts of chemicals, which will practically and financially will be unfeasible	no, pH adjustment to pH 10 requires extensive amounts of chemicals, which will practically and financially will be unfeasible	yes, pH adjustment to pH 10 required, adding more Na, Cl and volume to brine. Removal necessary before reinjection (brine post-treatment)

8

ECONOMIC FEASIBILITY OF DLE IN THE NETHERLANDS

The previous chapter gives an overview of the technical feasibility of DLE technologies on Dutch geothermal brines. The two technically feasible technologies are the ion exchange adsorbent materials, based on titania-based ion exchange sorbent and alumina-based adsorbent, only for the Well C brine. The economic feasibility of these two technologies on for the Well C brine with a capacity of 250 m^3/hour are assessed in the following chapter. Here it is considered that the combination of lithium extraction and the heat production of geothermal wells are combined. Therefore, the construction costs for the geothermal installation and filtering are not included in the economic analysis.

8.1 Upstream processes

8.1.1 Alumina-based adsorbent

A cost indication is retrieved from the supplier on the OPEX and CAPEX for one of their pilot installations. The pilot installation treats a brine with 250 ppm Li and has an OPEX of $ 2,000.---$ 3,000.-- USD/tonne LCE, or $ 2-$ 3 million USD/year. The brine was already prefiltered with ultrafiltration that was available on-site, this is not included in the costs. Purification with ion exchange and concentration with reverse osmosis is included in these costs. The CAPEX was about $ 7 -$ 9 million USD for a capacity of 95 m^3/h [29].

Of the three observed locations, the technology is only technically feasible on brine from Well C because the sulphate concentrations of Well A and Well B are too high. Assuming the same OPEX per m^3 treated brine for Well C as for the pilot, but with a Li concentration of 22 ppm instead of 250 ppm, this would result in an OPEX of $ 23,000.-- - $ 35,000.-- USD/tonne LCE for Well C. This excludes the costs for pre-filtration with ultrafiltration, and further downstream processing of the LiCl solution to create the solid LCE. As the LCE market price is expected to be around EUR 30,000.-- per tonne LCE, this technology based on alumina-based adsorbent will be economically challenging for Well C brine at the current market prices.

An overview of indicative cost for the pilot plant and the technology for Well C is given in table 8.1.

Table 8.1 Indicative costs for a pilot plant and application on Well C for an alumina-based sorbent. This includes additional polishing with ion exchange and concentration with Reverse Osmosis and crystallisation

	unit	Suppliers pilot plant [29]	Application on Well C brine
Lithium concentration	ppm	250	22
Capacity	m3/h	95	250
OPEX	USD $/tonne LCE	$ 2,000.-- -3,000.--	$ 23,000.-- -30,000.00
CAPEX	USD $	$ 7-9 million	17-22 million (based on capacity)

8.1.2 Titania-based ion exchange sorbent

Table 8.2 shows the OPEX and CAPEX for Well C as communicated by the supplier. However, the chemical consumption for pH adjustment (NaOH and HCl) is not taken into account in this table. These chemicals will increase the OPEX, but also additional steps and equipment will need to be taken into account after chemical addition. The chemical consumption and corresponding costs are covered per location in the following paragraphs. The Dutch Mining Law requires that brine that is reinjected is similar in amount and composition compared to brine before processing. This means that the Li-depleted brine requires post-treatment before reinjection in the well. As NaOH and HCl are added, mainly Na and Cl will need to be removed before reinjection, but also the volume needs to be lowered because the reagents are added in liquid form.

The filters have a lifetime of 2,000 cycles, replacement of these filters is included in the OPEX. CAPEX includes engineering, filter racks, pipes & pumps, first supply of filters and site support[1]. Delivery, utilities (i.e., the building), post-treatment of brine and downstream processing of LiCl-solution is excluded.

Table 8.2 Indicative OPEX and CAPEX for titania-based ion exchange sorbent DLE technology for Well C brine. Data have been shared by the supplier. Excluding chemical consumption for pH adjustments, delivery and utilities [37]

	Well C brine
CAPEX	
filter racks. piping/fittings	$ 1,000,000.--
filters	$ 6,000,000.--
design & engineering	$ 520,000.--
site support	$ 130,000.--
delivery & Utilities	excluded
OPEX	
filter replacement	$ 600,000.--
chemicals and energy consumption	see below

Significant amounts of chemicals are required to raise the pH before DLE and lower the pH afterwards. The OPEX of chemical consumptions for the three brines are given in the following paragraphs, based on the OLI simulations as given shown in figure 7.2 and figure 7.3.

Chemical consumption

For a capacity of 250 m^3/h, 6570 tonne NaOH (50 %) and 9,099 tonne HCl (32 %) per year would be required to lower the pH back to the original brine pH (6.4). With cost prices of $ 350.-- and $ 128.-- USD per tonne for NaOH (50 %) and HCl (32 %) respectively, this results in $ 3.64 million USD per year for these chemicals. The resultant OPEX indication is given in table 8.3.

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[1] Building, site works, electrical works, cabling, permits, financing costs, unforeseen all not included. CAPEX will likely be 2.5-3 times higher than give in the table.

Table 8.3 Indicative costs for chemicals for DLE for Well C with titania-based ion exchange sorbent based DLE technology

	Chemical	Consumption per year in tonne	Cost price USD / tonne (NaOH or HCl)	Cost per year in USD
pH from 6.4 > 10	NaOH (50 %)	6,57	$ 350.--	$ 2,299,500.--
Li recovery	HCl (32 %)	190	$ 128.--	$ 24,284.--
pH from 10 > 6.4	HCl (32 %)	9,099	$ 128.--	$ 1,164,631.--
filter replacements				$ 600,000.--
total costs per year				$ 4,088,415.--
costs per tonne LCE				**$ 19,396.--**

Well C contains a lithium concentration 22 mg/l, and assuming a yearly up-time of 8,000 hours, a flowrate of 250 m^3/h and an overall extraction efficiency of 90 %, that this would correspond to an overall Li-extraction of 39,600 kg. When converted from Li to LCE (with a conversion factor 5,32) this would corresponds to a yearly production of 211 ton LCE per year. The number of 211 ton LCE/y would be sufficient to produce roughly 6,000 car batteries per year, assuming that an electric car contains 40 kWh storage capacity, and that a 0,85 kg LCE is needed for the production of 1 kWh battery storage capacity. We note that these are indicative numbers for the produced batteries, as the storage capacity per car model, the type of battery and the production process of the car may differ.

In total a volume of 211 tonne LCE per year would be produced for a geothermal doublet. This results in an OPEX of $ 19,396.-- USD/tonne LCE produced. This however excludes the energy consumption of the DLE technology, CAPEX depreciation, polishing and concentration, downstream processing from the LiCl solution to LCE, and post-treatment of the brine for Na and Cl removal prior to reinjection.

The chemistry added for lowering and rising the pH need to be extracted from the brine. This means that added Na and Cl will need to be removed before reinjecting the brine. For Well C, this means that yearly 1,888 tonne Na and 2,912 tonne Cl (enrichment of brine with 3 % and 4 % respectively) will need to be removed. Furthermore around 9.470 m^3 of water that is added (0.5 % of total processed brine) with the NaOH and HCl solutions will need to be removed/recycled, to prevent pressure buildup in the brine reservoir. The cost for these are not included in the cost estimate, but this means that the indicative OPEX would increase even further.

The costs for further polishing, concentration and downstream processes are estimated below. The energy consumption of the DLE technology is unknown and is not taken into account in these costs.

Polishing

Ion exchange polishing can be applied to remove the Ca and Mg concentrations from the LiCl-solution resulting from the DLE technology. During polishing, Ca and Mg are bound to the resin, which needs to be regenerated afterwards with HCl.

Before the DLE, the pH is raised with NaOH for an effective lithium extraction. The majority of the Mg, and part of the Ca in the brines precipitates when NaOH is added to raise the pH (figure 7.2 and figure 7.3). These precipitates are filtered before DLE (figure 7.1). The remaining Mg and Ca remains in solution and ends up in the LiCl-solution resulting from the DLE.

The DLE technology results in a LiCl-solution of around 1 g/l. This means that the volume yield of the DLE technology is around 2.5 %, and 5 m^3 of LiCl-solution is produced per hour. The capacity for polishing with ion exchange is therefore 5 m^3 per hour.

With the Mg and Ca concentrations of the LiCl-solution, it can be estimated how much HCl (32 %) is required to regenerate the ion exchange resin. Table 8.4 gives the Mg and Ca concentrations after DLE, the required

HCl for regeneration and the costs corresponding to this HCl consumption. Assuming a cost price of $ 120.--USD/tonne HCl (32 %), this results in approximately $ 110,000.-- USD per year for HCl consumption for Well C brine.

Table 8.4 HCl consumption and corresponding costs for ion exchange polishing of Well C brine concentrate after DLE

	Well C brine
Ca concentration in mg/L	3,386
Mg concentration in mg/L	155
total load Ca/Mg in equivalent/hour	910
HCl (32 %) consumption in kg/day	2347
costs for HCl consumption in USD/year	$ 109,650.--
costs (USD) for HCl for polishing in USD per tonne LCE	$ 520.--

Concentration: reverse osmosis and evaporation

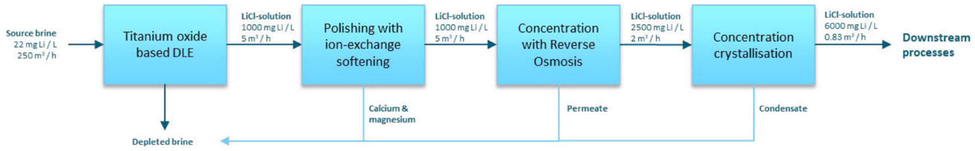
After polishing of the LiCl-solution, the solution needs to be concentrated to reduce the volume and reach a LiCl concentration of several grams per litre for further downstream processing into LiOH or Li_2CO_3.

The costs for reverse osmosis and evaporation are mainly related to the high energy consumption of both steps. For reverse osmosis, the energy consumption is estimated to be 2-4 kWh/m^3 permeate, for crystallization this is 20-60 kWh/m^3 feed.

The feed flowrate (resulting from the ion-exchange) of the RO system will be around 5 m^3/hour. Assuming a recovery rate of 60 % for the RO, the flowrate of the permeate is 3 m^3 per hour, which is clean water. The production of concentrated LiCl-solution is then 2 m^3 per hour, with a lithium concentration of 2.5 g/l.

The crystalliser increases the concentration of the LiCl-solution up a lithium concentration of 6 g/l, which is required for the downstream process. The feed of the crystalliser is 2 m^3/hour. An overview of the processes including concentrations and flowrates is given in figure 8.1.

Figure 8.1 Overview of upstream processes, including concentrations and flowrates



The energy costs also need to be accounted for as well. Assuming a price of $ 0.25 per kWh, this result in energy costs per year of $ 12,000.-- -$ 24,000.-- USD for reverse osmosis and $ 80,000.-- -$ 240,000.-- USD for crystallization. In costs per tonne LCE, this equals energy prices of $60.-- - $120.-- USD for RO and $ 380.-- - $1,140.-- USD for crystallization.

Concentration by RO and crystallization will increase the costs $ 440.-- - $ 1,260.-- USD per tonne LCE. Assuming the average, this means a costs per tonne of $ 850.-- USD.

Footprint

For a plant size with 800 cartridges, it is estimated that the required surface area for the modules would approximately 500 m^2. Next to the modules, also storage for NaOH and HCl is required. Per day, 18 ton of

NaOH is consumed. For NaOH, this requires another 150 m^2, assuming 3 tanks of 56 ton and sufficient room to fill the tanks, for pumps and pipes. The 30 % HCl consumption is around 1 ton per day, the required area for this is limited.

For dosing of NaOH and HCl, mixing tanks will be required. For these another 400 m^2 is assumed, based on 1,000 m^3 tanks. Furthermore, polishing and concentration of the concentrate is required, with ion exchange softening, reverse osmosis and crystallization. Also, post-processing of the brine is required before reinjection. This including sufficient transport area, storage facilities and a service building, would result in a rough estimate of **4,000 m^2.**

8.2 Downstream processes

The final lithium product at the geothermal is a purified and concentrated LiCl-solution. This solution will need to be treated at an external site, to produce a battery grade product, either LiOH or Li_2CO_3. For this downstream process, no financial analysis is made in this report. However, from other reference projects an estimate can be made for the downstream processing costs.

Table 8.5 gives an overview of economics of several projects. In the technical report of E3 Metals Corp [42], it is stated that the DLE process costs $ 414.-- USD per tonne LiOH, and the lithium production (concentration, polishing, electrolysis and crystallization) costs $ 564.-- USD per tonne LiOH. The total of $ 3,656.-- USD/tonne LiOH also includes the brine production itself (well, pumps and pipeline) and hydrogen sulphide removal (this is necessary as here the lithium is recovered from oil instead of geothermal brine).

Vulcan Energy Resources gives the separate OPEX of downstream processing in their technical report [10]. Their total production cost is estimated at EUR 4,359.-- per tonne LiOH. This includes upstream processes of EUR 2,656,-- and downstream processes EUR 1,704,-- per tonne LiOH. A further analysis of the Vulcan Energy project is given in the next paragraph.

For downstream processes of the Dutch geothermal brine, we assume the same OPEX as estimated by Vulcan Energy; EUR 1,704,--/tonne LCE. However, this is likely an underestimation, as Vulcan will have a much larger production capacity, thereby reducing the costs per tonne LCE. For the Well C brine, only 211 tonne LCE is produced per year (see paragraph 8.1.2), compared to 40,000 tonne LCE that Vulcan will produce. A separate downstream processing plant for Well C will be unlikely, therefore the LiCl-solution will need to be treated externally in a larger downstream processing plant. This of course results in transportation costs, depending on the location of the downstream processing plant. Currently, such a plant does not exist in North-West Europe.

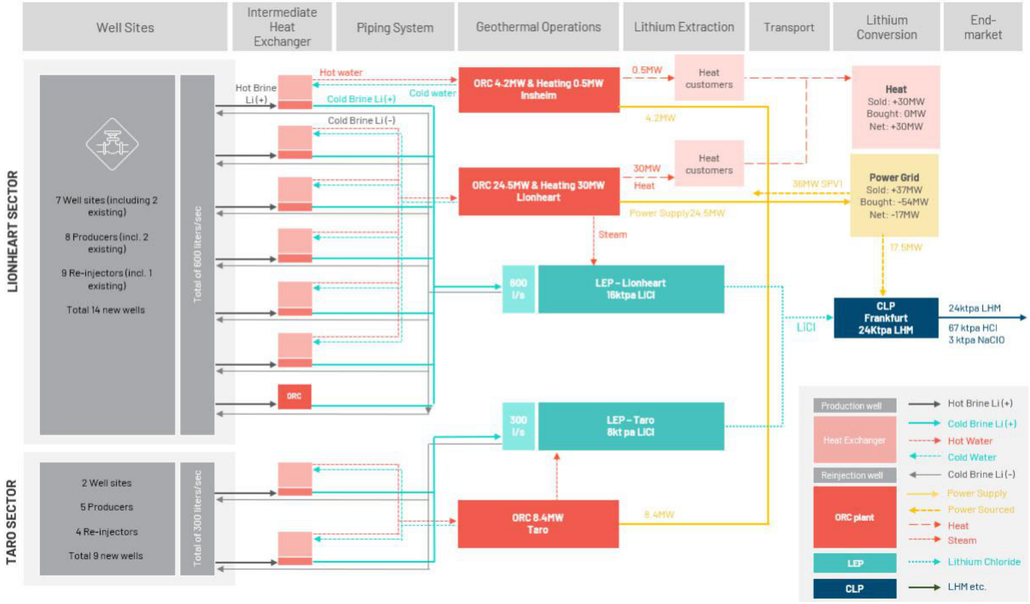
Table 8.5 Summary of DLE project economics [12]

Company	**SRI International**	**Vulcan Energy Resources**	**Standard Lithium**	**E3 Metals Corp**	**Anson Resources**	**Pure Energy Minerals**	**Lake Resources**
Project	Salton Sea	Upper Rhine Valley	Lanxess Smackover	Clearwater	Paradox Stage 3 (Li)*	Clayton Valley	Kachi
Location	California, USA	SW Germany	Arkansas, USA	Alberta, Canada	Utah, USA	Nevada, USA	Argentina
Brine type	Geothermal	Geothermal	Evaporite (Br tail brine)	Oilfield	Evaporite	Evaporite	Salar
Resource (1,000 kg LCE)	NA	15,850,000	3,140,000	2,200,000	192,000	217,700	1,010,000
Lithium concentration (mg/L)	400	181	168	74.6	100–500	65–221	289
Production (mt/yr)	20,000**	40,000	20,900	20,000	15,000	11,500	25,500
Production cost ($/mt)	3,845	3,217***	4,319	3,656****	4,545	3,217*****	4,178
CAPEX ($1,000)	52,300	1,287,600	437,162	602,000	120,000	358,601	544,000
OPEX ($1,000/yr)	76,900	128,688	90,259	73,200	68,180	36,516	106,539
Technology	Ion exchange	Adsorption	Ion exchange	Ion exchange	Ion exchange	Solvent extraction******	Ion exchange
Lithium recovery	90%	90%	90%	>90%	75%	90%	83.20%
Product	Li_2CO_3	$LiOH \cdot H_2O$	Li_2CO_3	$LiOH \cdot H_2O$	Li_2CO_3	$LiOH \cdot H_2O$	Li_2CO_3
Comments	Bench-scale testing and ASPEN modeling of hybrid sorbent with nanostructured manganese oxide-based ion exchange embedded within Li-imprinted polymer beads using synthetic brine.	Known geothermal resource with measured chemistry and temperature. Bench-scale testing of two commercially available adsorbents using Upper Rhine Valley brine.	Bench- and mini-pilot-scale confirmation of process using ceramic adsorbent and crystallization process to convert concentrated LiCl into high-purity Li_2CO_3.	Bench-scale testing demonstrated high Li electivity and recovery. Full process yet to be tested.	Multi-stage development with stage 3 producing 60,000 mt/yr NaBr and 15,000 mt/yr Li_2CO_3. production cost reported as All-in Sustaining Cost.	Bench-scale testing of brine and synthetic equivalents informed the solvent extraction process developed by Tenova.	Nano-coated, porous ion exchange beads, tailored composition, and continuous column process.

8.3 Reference case study: Vulcan Energy in Germany

Vulcan Energy plans to extract lithium from geothermal brines in the Upper Rhine Valley in Germany, with an average lithium concentration of 181 ppm. An overview of the project flow process is given in figure 8.2.

Figure 8.2 Project flow diagram of Vulcan in Germany [10]

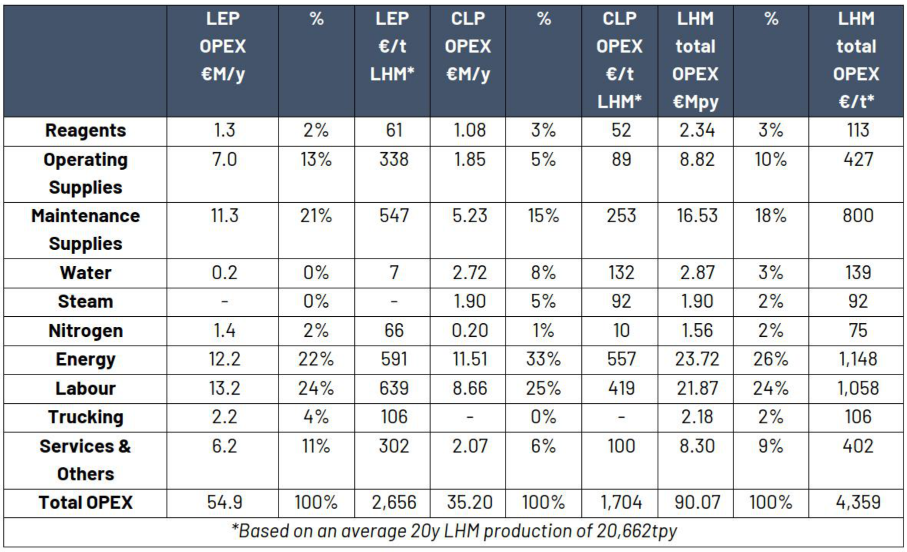


Lithium is extracted at different Lithium Extraction Plants (LEP), where the upstream processes take place, with DLE technology using alumina-based sorbents, combined with purification and concentration including evaporation. From there the LiCl-solutions from both LEPs are transported to the Central Lithium(hydroxide)Plant (CLP) in Frankfurt, where the downstream processing takes place, and the LiCl solution is converted into lithium hydroxide.

OPEX

The average OPEX over 20 years for the LEPs and CLP are given in figure 8.3. The estimated OPEX for the LEP (upstream processes) is EUR 2,656.--/ton LiOH. For the downstream processes, the OPEX is EUR 1,704.--/ton LiOH, resulting in a total OPEX of EUR 4,359.--/ton LiOH.

Figure 8.3 Vulcan's key estimated lithium extraction and conversion operating cost inputs. [10] LHM = Lithium Hydroxide Monohydrate



	LEP OPEX €M/y	%	LEP €/t LHM*	CLP OPEX €M/y	%	CLP OPEX €/t LHM*	LHM total OPEX €Mpy	%	LHM total OPEX €/t*
Reagents	1.3	2%	61	1.08	3%	52	2.34	3%	113
Operating Supplies	7.0	13%	338	1.85	5%	89	8.82	10%	427
Maintenance Supplies	11.3	21%	547	5.23	15%	253	16.53	18%	800
Water	0.2	0%	7	2.72	8%	132	2.87	3%	139
Steam	-	0%	-	1.90	5%	92	1.90	2%	92
Nitrogen	1.4	2%	66	0.20	1%	10	1.56	2%	75
Energy	12.2	22%	591	11.51	33%	557	23.72	26%	1,148
Labour	13.2	24%	639	8.66	25%	419	21.87	24%	1,058
Trucking	2.2	4%	106	-	0%	-	2.18	2%	106
Services & Others	6.2	11%	302	2.07	6%	100	8.30	9%	402
Total OPEX	54.9	100%	2,656	35.20	100%	1,704	90.07	100%	4,359

**Based on an average 20y LHM production of 20,662tpy*

8.4 Economic feasibility of DLE in the Netherlands

A comparison between the OPEX of Vulcan Energy and the treatment of Well C brine with alumina-based adsorbent- and titania-based ion exchange sorbent DLE technology is given in table 8.6. Where previously the costs for the Dutch brines were expressed in US dollars, these are now expressed as Euros for comparison with Vulcan Energy. The two Dutch brines Well A and Well B are not shown, as their treatment is either not technologically feasible (alumina-based adsorbent) or require vast amounts of chemicals that already cost over EUR 60,000 per tonne LCE (titania-based ion exchange sorbent).

The post-treatment of the depleted Well C brine, to return the reinjected brine into the same composition and volume as the source brine, is excluded in the table. This post-treatment is required to comply with the Dutch Mining Law.

Table 8.6 Indicative OPEX comparison between the plans for production of Vulcan Energy in Germany [10] and Well-C geothermal doublet alumina-based adsorbent- and titania-based ion exchange sorbent for the Well C brine in the Netherlands

		Vulcan Energy, Germany	**Well C, DLE by an alumina-based adsorbent**	**Well C, DLE by titania-based ion exchange sorbent.**
design parameters	capacity in LCE / year	40,000*	211**	211**
	brine lithium concentration in ppm	188	22	22
OPEX in EUR/tonne LCE **LCE market price :** **EUR 30,000.--/tonne** **(August 2023)**	DLE technology	EUR 2,660.--	>EUR 21,000.-- - 32,000.--	>EUR 20,000.--
	purification			EUR 480.--
	concentration			EUR 790.--
	downstream process	EUR 1,700.--	EUR 1,700.--***	EUR 1,700.--*
	total OPEX per tonne LCE	**EUR 4,360.--**	**>EUR 22,700.--- 33,700.--**	**>EUR 22,970.--**

** Estimated production of Vulcan in full operation for a large number of geothermal wells.*
*** The calculation of the production capacity is listed in paragraph 8.1.2.*
****Assumed same OPEX costs as for Vulcan, but likely much higher due to low production capacity, as compared to Vulcan.*

The large difference between the OPEX of Vulcan and the indicative OPEX costs for Well C brine is mainly caused by the difference in lithium concentration of the brines. The concentration of the brines treated by Vulcan is 8.5 times higher, meaning that also around 8.5 times more LCE is produced per treated m^3 brine. Another factor is the capacity of Vulcan is much higher, benefiting an economy of scale. Vulcan plans to build two DLE plants, which each treat brines from multiple geothermal wells. The LiCl-solution from both DLE plants will then be processed in one central plant to produce battery grade LiOH.

While worldwide projects are initiated to extract lithium from geothermal brines, and are estimated to be economically viable, this seem to be currently economically rather challenging in the Netherlands for these three wells, based on the current available technologies. This is mainly due to the following reasons:

- Relatively low lithium concentrations in the Netherlands. While the productions costs will be similar to other projects, the revenue will be much lower, due to low lithium concentrations.
- High TDS in Dutch geothermal brines. This limits the current available extraction technologies.
- Low production capacity, which hampers the realization of economies of scale. Higher capacities result in lower costs per m^3, for example by treating brines from different geothermal wells, as done by Vulcan. Some operators in the Netherlands already exploit multiple doublets at a single location with a combined flowrate of several thousands cubic meters per hour. If the combined flowrates increase further, this could lower the production costs of lithium extraction, if the technical feasibility has been proven.

9

CONCLUSION

This report gives an overview of the currently available technologies for lithium recovery from geothermal brines and investigates technological and economic feasibility to recover lithium from three selected Dutch geothermal brines. Lithium recovery is divided in upstream and downstream processes. Upstream processing includes the Direct Lithium Extraction (DLE), purification and concentration, resulting in a lithium-chloride solution. Downstream processing converts the lithium-chloride solution into battery grade lithium hydroxide or lithium carbonate, both referred to as lithium carbonate equivalent (LCE).

The following conclusions can be drawn from this study:

- The current main DLE technologies are based on sorbents, ion-exchange material or by solvent separation. Of these, sorption and ion-exchange are most widely applied.
- Some geothermal brines in Europe that are being investigated and developed for DLE have a lithium concentration of >150 ppm. The three anonymized investigated Dutch geothermal brines have concentrations of 13, 24 and 22 ppm. Up to date, higher concentrations (up to 48 ppm) have been measured in the Netherlands, but only in (offshore) gas fields.
- Most technology providers indicate that the lithium concentration was too low for utilizing their technology. From the consulted DLE technology providers, two suppliers stated that their technology could work for the lithium concentrations between 13 and 24 ppm that are present in the selected Dutch brines. One offers an alumina-based adsorbent, the other a titania-based ion exchange sorbent. Further analysis shows that only one Dutch geothermal brine, namely that of Well C, could be technologically feasible with utilizing these sorbents.
- Lithium extraction from Well C is technologically feasible, but economically challenging under the current lithium market conditions. For both technologies, the indicative operating costs are near. the current market price of LCE, which is in the range of EUR 30,000.--:
  - Alumina-based adsorbent DLE technology: the indicative OPEX is EUR 22,700.---33,700.-- per tonne LCE. It is noted that in the current estimates, the costs on the energy consumption of DLE, and the post-treatment of brine before reinjection, are excluded.
  - Titania-based ion exchange sorbent DLE technology: the indicative OPEX is more than EUR 23,000.-- per tonne LCE. The high costs are mainly caused by chemical requirements for pH adjustment.
- The proposed geothermal extraction from the site of Vulcan Energy in Germany is taken as a reference project. Here, the total costs per tonne LCE are estimated to be EUR 4,360.-- per tonne LCE. The large difference compared to cost estimate of Well C is caused the following factors:
  - The lithium concentration of the brines treated by Vulcan Energy is on average 188 ppm, 8.5 times higher than Well C.
  - Vulcan Energy designed for a much higher capacity, 40,000 tonne LCE per year delivery, based on the drilling of several tens of geothermal doublets in a central location. Brines from multiple wells are treated in two facilities for DLE, from which the downstream processing takes place in one central plant. The expected LCE production for the single Well C is 211 tonne LCE per year, more than 300 times lower than Vulcan Energy.
- While worldwide projects are initiated to extract lithium from geothermal brines, and are estimated to be economically viable in the current market, this is currently not yet the case in the Netherlands, mainly due to the following reasons:
  - The lower lithium concentrations in the currently studied geothermal wells in the Netherlands compared to other European geothermal DLE projects. While the productions costs will be similar to other projects, the revenue will be much lower due to low lithium concentrations.

  - The high TDS in the Dutch geothermal brines. This limits the operation window of currently available extraction technologies.
  - Low production capacity, which hampers the realization of economies of scale. Higher capacities result in lower costs per m^3, for example by treating brines from different geothermal wells, as is done e.g., by Vulcan.
- From an environmental perspective, lithium extraction from geothermal brines is much better option than hardrock mining or evaporation, in terms of footprint, energy and water consumption, CO_2 emissions and possible environmental impact.
- Regarding the juridical aspects of the lithium extraction, it is the Dutch Mining Act is not tailored yet for lithium extraction from geothermal wells in combination with geothermal heat production. The question is whether an analogous application of the system as included in the current Mining Act is suitable for the extraction of lithium.

Outlook

While this study shows that lithium extraction from geothermal brines in the Netherlands is economically challenging, this might change over time, because of the following reasons:

- The current analysis is based on the available water composition of three geothermal wells. It should be noted that the number of available measurements of lithium concentrations in the Netherlands is limited, although it is already known that a number of reservoirs used in geothermal energy are very contain low lithium concentrations. It is also possible that other reservoirs will be assessed in the future, where a higher concentration of lithium could be found. For example, an increased lithium concentration has been found in a number of locations in Belgium, and it is therefore advisable to further investigate the related strata in the Netherlands. It is also recommended that standard lithium be measured in future analyses of geothermal water. In addition to measuring lithium concentrations, it may also be worthwhile to measure concentrations of other valuable and critical minerals such as rare earth metals. This is rarely done at the moment. These minerals could strengthen the business case, but they were not investigated in this study.
- A market price of EUR 30,000.-- per tonne of LCE has been used, based on current forecasts in 2023. Given global electrification and the growing demand for lithium for batteries, it is conceivable that the market price will increase in the near future, although volatility is also high. In that case, lithium extraction from Dutch geothermal wells could still become financially interesting. It should be noted that - in a European context - it would be obvious to extract lithium at other locations (e.g., Germany, France) instead, due to the high lithium concentrations and lower cost price.
- The feasibility is based on the currently available techniques used in the market. These techniques are currently being developed at a rapid pace. New techniques are tested on a laboratory or pilot scale. It is conceivable that technologies will be developed in the future that can recover lithium from Dutch geothermal water at lower costs, which could increase the (financial) feasibility.
- The scope of the current study considered the extraction of lithium in a single geothermal doublet, and that is on a relatively small scale. It is conceivable that a large-scale geothermal project with a many centrally located doublets will be developed in the future, and lithium can therefore be extracted from multiple wells. Costs could be further reduced if brines from multiple wells are treated in a central lithium recovery, which provides economies of scale. This requires local infrastructure to be developed and the distance between the wells also plays a role. It should be noted that operating costs are expected to be higher than other locations in Europe (e.g., Germany, France).

Appendices

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II

APPENDIX: GEOTHERMAL BRINE COMPOSITIONS IN THE NETHERLANDS WITH MODERATE LITHIUM CONCENTRATIONS

Table II.1 Brine compositions for Well A, Well B and Well C

		Well A	**Well B**	**Well C**
Na	mg/l	43,000	74,769	21,933
K	mg/l	880	3,047	1,633
Ca	mg/l	8,100	3,799	3,627
Mg	mg/l	1,100	1,469	471
Sr	mg/l	400	136	188
Ba	mg/l	3.7	3	8
Mn	mg/l		5	2
Fe	mg/l	59	70	28
Ni	mg/l	0.018		<0.1
Cu	mg/l		0.30	<0.1
Zn	mg/l	7.5	58	<0.2
Si	mg/l		16	16
Li	**mg/l**	**13**	**24**	**22**
Pb	mg/l	0.37	10	0
B	mg/l		34	<0.1
NH4+	mg/l		89	
Cl	mg/l	110,000	133,210	52,000
Br	mg/l		126	<50
SO4	mg/l	470	579	39
HCO3-	mg/l	130	222	360
CO3	mg/l	<2.5	-	<10
PO4	mg/l		<60	<50
Density @ 20 °C	kg/m3	1,167	1,168	1,054
pH (as received)		5.64	5.73	6.4
Conductivity at 25 °C	mS/cm	67	234.5	125.0
TDS	mg/l	164,164 (calculated*)	228,375 (measured)	84,550 (measured)
Total alkalinity	mg/L		371.5	200

*Calculated by summing al cations and anions

III

APPENDIX: LIST OF SELECTED DLE PROJECTS IN EUROPE

Table 2 List of selected direct lithium extraction projects in Europe

Project	**Lithium (ppm)**	**TDS (g/L)**	**T(°C)**	**Location**
Bruchsal [17]	163	130 g/L [43]	124	Karlsruhe, Baden-Württemberg, Germany
United Downs Deep Geothermal Power	>250 [44]	29 g/L, Mg <5mg/L [19]	175 [45]	Redruth, Cornwall, United Kingdom
Blackwater geothermal [46]	~100s ppm	Low	>100	Cornwall, United Kingdom
Rodda/North Downs. geothermal	Unknown (~100s ppm?)	Unkown (Low?)	>100	Cornwall, United Kingdom
Vendenheim - GEODEEP	~200 [47]	ca. 100 g/L [47]	200 [48]	Vendenheim, Rhine Graben, France
Rittershofen (Eugeli)	190 [17]	100 g/L [49]	177	Rittershofen, Upper Rhine Graben, France
Soultz Sous Forêt (Eugeli)	173 [17]	97 [50]	200 [51]	Soultz Sous Forêt, Upper Rhinge Graben, France
Landau [52]	168 [17]	106-107 [18]	160	Landau, Upper Rhine Graben Germany
Insheim	168 [17]	106-107 [18]	165	Insheim, Upper Rhine Graben, Germany
Les Cigognes	ca. 214 [53]	-	-	Haguneau Upper Rhine Graben, France
Cesano (Campagnano & Galeria)	likely 100s, up to 480 [54]	80 [55]	145 (1800m), 300 (3080m) [56]	Latium, Italy
Viterbo (Ferento)	likely 100s ppm, up to 480 [54]	-	-	Latium, Italy
Puy-de-dome [57]	likely >80 ppm [57]	-	-	Riomt, Massif Central, France
Les Sources (4 licenses)	unknown, likely > 100 ppm	-	50°C at 500 m depth	Upper Rhine Graben, France
Groß Schönebeck [58]	215 mg/L	265 [59]	150	Brandenburg, Germany

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