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Direct Lithium Extraction (DLE): An Introduction

A report exploring the various technologies used for direct lithium extraction (DLE)

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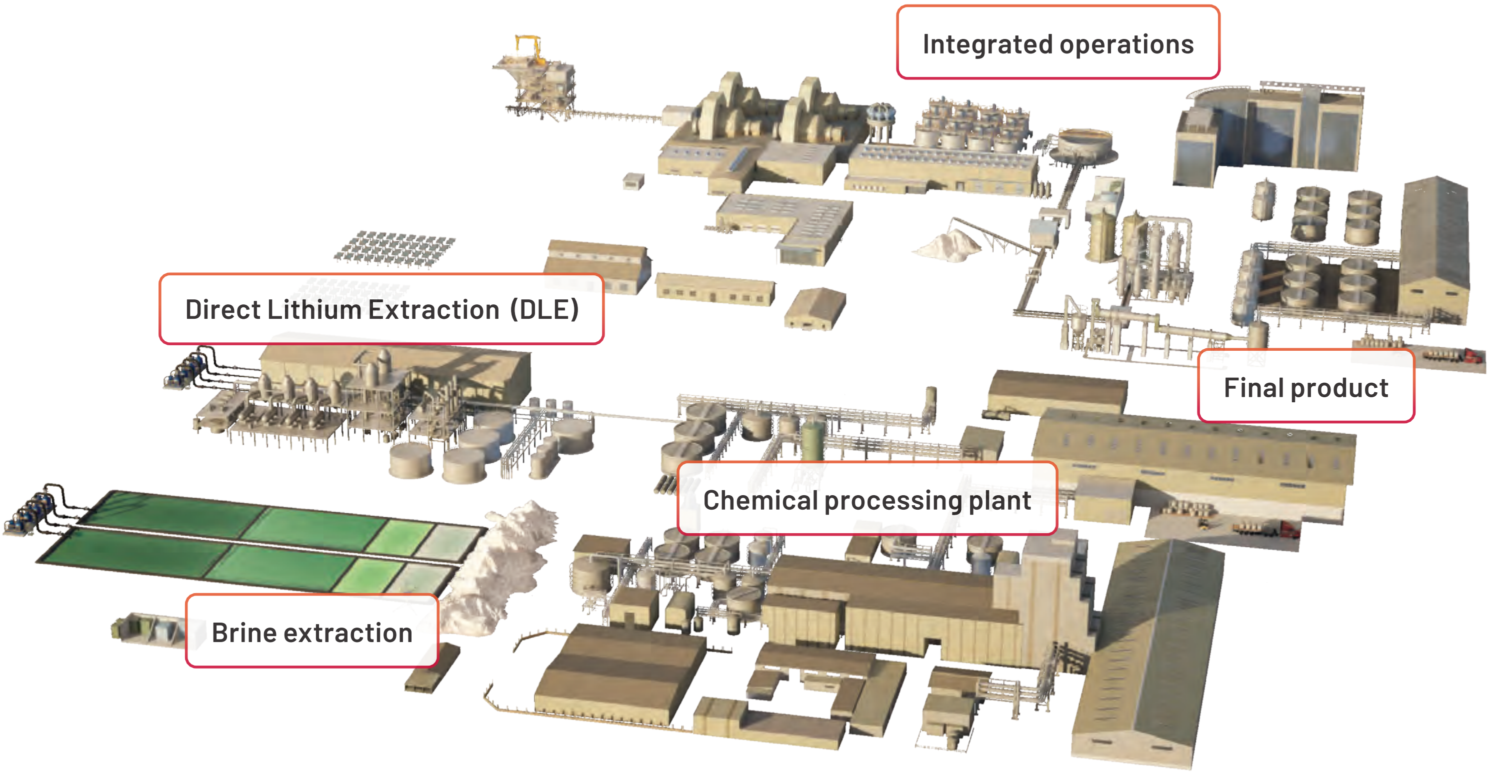

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Executive Summary

This report explores the various technologies used for direct lithium extraction (DLE) as they stand today. It explores various DLE methods, including sorption, ion exchange, solvent extraction, membrane, electrochemical, carbonation processes etc.

Each method's mechanisms, advantages, disadvantages, and technological readiness are analysed, along with a comparison of their commercial potential. This work also examines the economic viability of DLE compared to conventional extraction methods. Additionally, the potential sustainability benefits of DLE, such as lower carbon, water, and land footprints, are discussed.

It is important to appreciate that each brine is unique (lithium content, total dissolved solids (TDS), situation…) and while the techniques described here work well at certain sites, each brine requires a tailored approach.

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Direct Lithium Extraction (DLE): An introduction was written for the International Lithium Association in partnership with Rockwell Automation by Associate Professor Amir Razmjou.

Associate Professor Razmjou is an experienced academic and industry professional with over 20 years of expertise in desalination, water treatment, membrane technology, and mineral processing.

He received his docterate from the University of New South Wales (UNSW) in Sydney, Australia, in 2012. He is a Board Director of the Membrane Society of Australasia (MSA) and Founder of the Mineral Recovery Research Centre (MRRC) at Edith Cowan University (ECU), Western Australia. Dr Razmjou has made significant contributions to the fields of mining and resource extraction, particularly in lithium processing.

He has published over 200 peer-reviewed articles and secured research funding exceeding AUD9.2 million. Dr. Razmjou has received awards such as the 2024 WA FHRI Fund Innovation Fellow, the 2023 MSA Industry Innovation Award, and the 2021 UTS Chancellor Research Fellow. He has supervised more than 40 master's and Ph.D. candidates and serves in editorial roles for journals such as Desalination, DWT, and JWPE. At MRRC, he established a DLE line, including various processes such as membranes, ion exchange, and adsorption at laboratory and pilot scales. His research also includes developing and implementing advanced technologies for DLE's pretreatment and post-treatment to enhance the Li/TDS ratio and purify the final product to battery-grade quality.

Contents

Introduction

The long-term forecast for lithium demand is strongly positive, driven by the global push towards achieving net zero carbon emissions, the transition to e-mobility, the growing adoption of energy storage systems (ESS). As such it is important to consider all routes by which lithium might be produced.

Additionally, there is a growing awareness of the sustainability credentials and the production of lithium chemicals with lower carbon and water footprints. Consequently, of the sustainability credentials of any new technologies or processes capable of producing lithium are relevant to the wider discussion.

History has shown that when demand increases alongside public awareness, particularly regarding sustainability, two things tend to occur: industries adapt by redesigning, replacing, or altering their workflows, and new disruptive technologies emerge.

An illustrative example is desalination technologies. In the early 1950s, global demand for fresh water suddenly surged due to the rapid industrialization of developing countries, population growth, and urbanization [1]. However, the existing mainstream technologies for desalination such as Multi-Effect Distillation (MED) and Multi-Stage Flash (MSF) struggled to effectively address the increasing demand, especially for small-scale projects. Although the concept of desalination by Reverse Osmosis (RO) was discovered by Jean-Antoine Nollet in the year 1748, it took over 200 years for it to be technically utilized [2]. The first RO plant was implemented in Coalinga, California in 1965, marking the beginning of its disruptive influence worldwide [3]. According to a report by Straits Research [4], the 2022 global water desalination market was valued at USD 19.62 billion and RO technology accounts for over 69% of the market share [5].

Similarly, in the last decade the demand for lithium has increased rapidly and there has been considerable interest in potential new technologies that are capable of lithium production. DLE could potentially have a transformative impact on lithium production and several countries' national lithium strategies/Acts promote it, including in Bolivia, in Chile (National Lithium Policy, NLP), and in the USA (the Inflation Reduction Act (IRA)), as well as in the European Union (Critical Raw Materials Act).

Since 2020, there has been significant investment in DLE innovation, with both government and private entities showing keen interest. Notably, the US Department of Energy (DOE) granted USD50 million to support Lilac Solutions, a DLE startup, in 2022 [6]. Additionally, in Bolivia consortia from Russia and China committed to investing USD1.5 billion in two DLE processing plants located in the towns of Pasto Grande and Uyuni Norte. These plants were expected to produce a minimum of 45,000 tonnes of lithium carbonate annually [7]. In 2021, Vulcan Energy Resources has raised USD320 million for its Zero Carbon Lithium™ Project in the Upper Rhine Valley in Germany, followed by receiving USD76 million from Stellantis investment in 2022 [8]. Some of the other investments include Rio Tinto acquiring the Argentinian Rincon DLE project for USD825 million and Koch Minerals and Trading investing USD252 million in Compass Minerals in 2022 [6, 9, 10]. The next wave of investments appears to be coming primarily from the oil and gas industry, including companies such as Exxon Mobil, Koch Industries, Occidental Petroleum, SLB (formerly Schlumberger), and Chevron Corp. [8]. Numerous significant DLE projects are dispersed globally, as depicted in Figure 1 alongside their target annual lithium carbonate equivalent (LCE) output.

Company	Project	Capacity (ktpa LCE)	
Anson Resources	Paradox Lithium	–	■
Compass Minerals	Great Salt Lake	35	■
Berkshire Hathaway	Salton Sea	90	■
Energy Source Minerals	Salton Sea (Project ATLiS)	20	■
Controlled Thermal Resources	Salton Sea	25	▲
Controlled Thermal Resources	Hell's Kitchen	25	▲
Standard Lithium	Smackover (Lanxess Project)	22	▲
American Battery Materials	Lisbon Lithium Project	–	●

Company	Project	Capacity (ktpa LCE)	
Vulcan Energy Germany	Upper Rhine Valley	24 (P1)	■
Cornish Lithium UK		–	▲
Lithium de France France	TBC	–	–

Company	Project	Capacity (ktpa LCE)	
Lanke Lithium	Yiliping Lake	20	■
Zangge Lithium	Chalkhan Lake	20	■
Jintai Lithium	Mahai Lake	7	■
Tibet National	Qinghai	–	■
Yiwei Lithium	Qinghai Salt Lake	–	■

Company	Project	Capacity (ktpa LCE)	
E3 Metals Corp	Clearwater	20	▲
LithiumBank	Boardwalk	–	▲

Company	Project	Capacity (ktpa LCE)	
Albemarle	Atacama	-	●
SQM	Atacama	220-250	●
CleanTech Lithium	Laguna Verde	20	■
CleanTech Lithium	Fransisco Basin	–	●

Company	Project	Capacity (ktpa LCE)	
Eramet/Tsingshan	Centenario-Ratones	~24+50 (P1+P2)	■
RIO	Rincon	30	■
Lake Resources	Kachi Project	25 (P1)	▲
Eon Minerals	Amanecer	–	■
Tibet Summit Resources	Angeles	25 (P1)	■
Arcadium Lithium	Olaroz enhanced recoveries	–	●
Arcadium Lithium	Fenix (Hombre Muerto)	~80 (3 expansions)	■

Lithium Extraction Technology

- ▲ Ion exchange
- ■ Adsorption
- ● Solvent extraction

Figure 1: Worldwide distribution of the key DLE project developers and their target annual LCE output. (Source: Data obtained from [11-14])

Traditionally, there were two ways to produce lithium; from hard rock minerals or from ultra-salty brines. In 2022 approximately 60% of global lithium production came from hard rock deposits, primarily located in Australia, with the remainder (30% evaporation pond and 10% DLE) coming from brine resources mainly from Chile and Argentina [15].

From a technological perspective, brine is more attractive as lithium is already in an aqueous or water-based solution, whereas extracting lithium from hard rock requires leaching it into water. Lithium production from brine is currently dominated by traditional solar/evaporation pond-based lithium extraction. During this process, brine is pumped into vast ponds and allowed to evaporate until the lithium chloride (LiCl) concentration reaches approximately 6%. The solution is then treated to remove any remaining magnesium, calcium, and boron before being refined into lithium carbonate (Li_2CO_3) or lithium hydroxide (LiOH) [16]. In contrast, in a typical DLE process, lithium ions are selectively extracted from a brine while leaving most other salts in the brine solution [17].

This document will summarise the current types of DLE technology and consider their pros and cons, commercialization status, and technological readiness.

DLE Technologies

Recent advances in DLE technologies offer the potential to access lithium deposits that were previously hard to reach or too costly to extract using traditional methods. Over the last 20 years, many DLE methods have been developed to separate lithium from other elements in brine without needing to evaporate water. A recent study [18] evaluated the sustainability and potential scalability of 84 reports related to DLE technologies from the period 2017 to 2022. They found that only 30% of the reported DLE technologies were tested using real brine, while the rest were tested using simulated brines, single-component, or binary mixture-based brines. While these techniques work well at certain sites, they cannot be swapped out easily because brines vary in nature and purity. So, each project needs its own tailored approach. Technology developers worldwide are exploring different DLE methods, but only relatively few have progressed to commercial use with a high level of readiness so far [11].

The methods employed in DLE were originally conceived for desalination and wastewater treatment purposes, rather than being specifically tailored for lithium extraction, as is often misconceived. DLE essentially repurposes established technologies which were initially developed for desalination and wastewater treatment, to facilitate mineral recovery, including lithium. Acknowledging this historical context is pivotal in discussions regarding the advancement and integration of DLE. A comprehensive understanding of the genesis of these technologies and their applicability within DLE enables us to pinpoint areas ripe for improvement and innovation.

DLE is already producing lithium at industrial scale at a handful of sites. This plant in China, owned by EVE Energy Co. Ltd, extracts up to 10,000 tpa LCE (battery grade) from brines using DLE technology provided by Sunresin New Materials Co. Ltd. The lithium concentration in the brine which is treated at this plant is 100-120 mg/L (Photo: Sunresin New Materials Co. Ltd).

The DLE process begins with the collection of lithium-rich brine from underground reservoirs or salars, where it undergoes pre-treatment to remove impurities (see Figure 2). This purification step ensures optimal conditions for subsequent extraction processes [19]. DLE methods employ various techniques such as adsorption, ion exchange, solvent extraction, or membrane processes to selectively capture lithium ions from the brine while leaving other ions behind. These extraction methods offer efficient and selective separation of lithium from the brine, paving the way for high-purity lithium production. Following extraction, the captured lithium ions undergo post-treatment to recover them from the capturing material or phase. This typically involves processes after desorption or stripping processes of DLE to concentrate, refine, and convert the lithium salt, usually LiCl, to lithium compounds suitable for various applications. Additionally, post-treatment ensures proper management of the depleted brine, meeting environmental regulations before being reintroduced into the environment or reinjected into the reservoir [18].

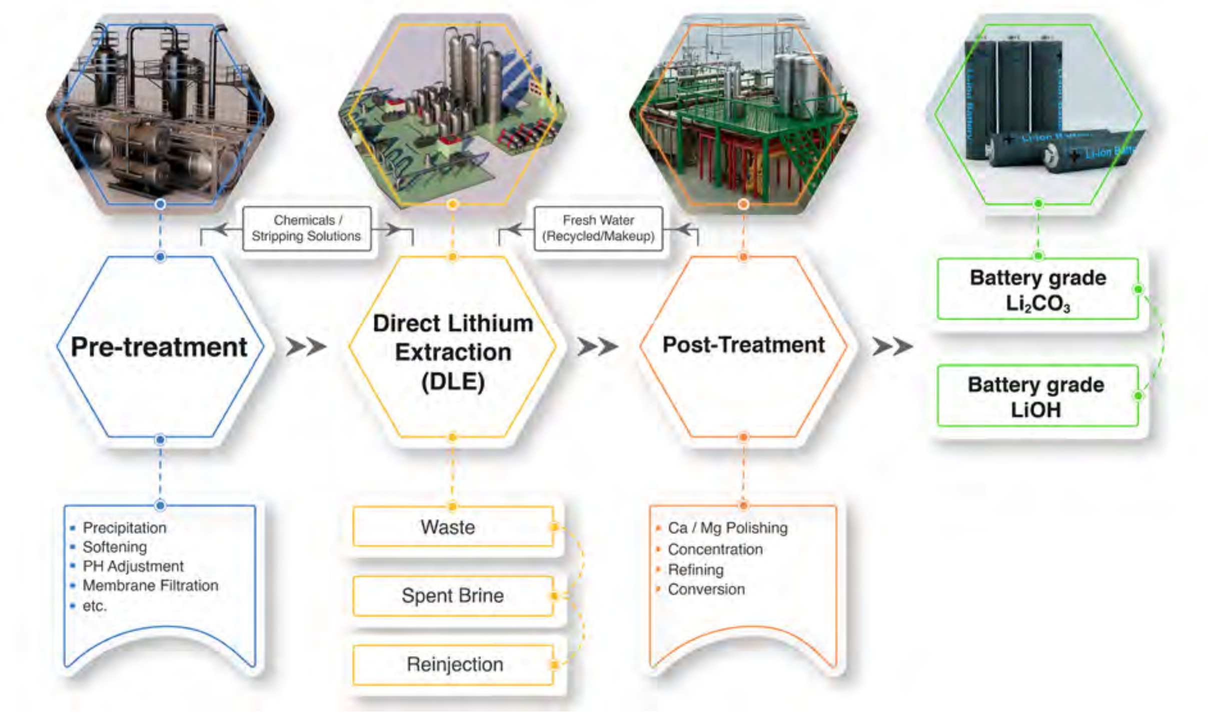


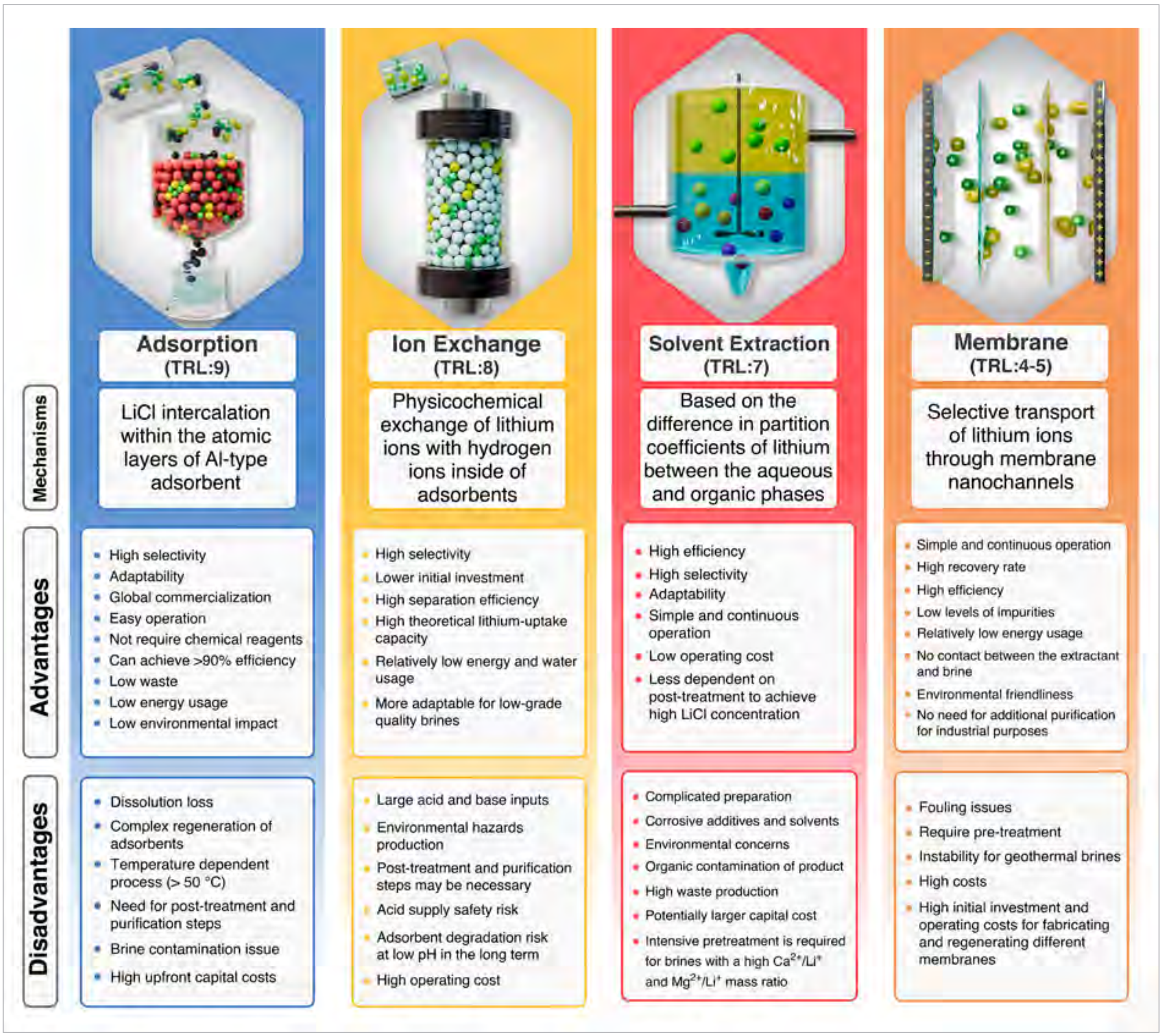
Figure 2: A schematic illustrating the Direct Lithium Extraction (DLE) process within the context of a complete processing scheme, including pre-treatment, DLE, and post-treatment.

DLE performance is typically evaluated against several indicators such as Li/ Total Dissolved Solids (TDS), lithium to sodium (Li/Na), lithium to magnesium (Li/Mg), and lithium to sulphates (Li/SO_4) before and after DLE processing. Additionally, parameters such as kilograms of fresh water required per kilogram of Li_2O_3 or LiOH, as well as Li recovery (extracted Li concentration / initial Li brine concentration), are assessed. Other parameters such as input energy in kilowatt-hours (kWh) and carbon produced per kilogram of Li_2O_3 or LiOH are also significant.

Among various DLE technologies, only a few, including adsorption, ion exchange, solvent extraction, and membranes, have progressed beyond Technology Readiness Level (TRL) of 4, while the majority are still in the early stages of development and refinement. Figure 3 provides an overview of these selected DLE techniques, showcasing their mechanisms, advantages, and disadvantages.

The leading DLE technologies can be broadly categorised into four groups (see Figure 3):

- Adsorption
- Ion exchange
- Solvent extraction, and
- Membranes



	Adsorption (TRL:9)	Ion Exchange (TRL:8)	Solvent Extraction (TRL:7)	Membrane (TRL:4-5)
Mechanisms	LiCl intercalation within the atomic layers of Al-type adsorbent	Physicochemical exchange of lithium ions with hydrogen ions inside of adsorbents	Based on the difference in partition coefficients of lithium between the aqueous and organic phases	Selective transport of lithium ions through membrane nanochannels
Advantages	High selectivity Adaptability Global commercialization Easy operation Not require chemical reagents Can achieve >90% efficiency Low waste Low energy usage Low environmental impact	High selectivity Lower initial investment High separation efficiency High theoretical lithium-uptake capacity Relatively low energy and water usage More adaptable for low-grade quality brines	High efficiency High selectivity Adaptability Simple and continuous operation Low operating cost Less dependent on post-treatment to achieve high LiCl concentration	Simple and continuous operation High recovery rate High efficiency Low levels of impurities Relatively low energy usage No contact between the extractant and brine Environmental friendliness No need for additional purification for industrial purposes
Disadvantages	Dissolution loss Complex regeneration of adsorbents Temperature dependent process (> 50 °C) Need for post-treatment and purification steps Brine contamination issue High upfront capital costs	Large acid and base inputs Environmental hazards production Post-treatment and purification steps may be necessary Acid supply safety risk Adsorbent degradation risk at low pH in the long term High operating cost	Complicated preparation Corrosive additives and solvents Environmental concerns Organic contamination of product High waste production Potentially larger capital cost Intensive pretreatment is required for brines with a high Ca^{2+}/Li^{+} and Mg^{2+}/Li^{+} mass ratio	Fouling issues Require pre-treatment Instability for geothermal brines High costs High initial investment and operating costs for fabricating and regenerating different membranes

Figure 3: A comparative schematic of the DLE techniques with a TRL of more than 4, including adsorption, ion exchange, solvent extraction, and membranes, with a focus on their respective mechanisms, advantages, and disadvantages. (Source: Data obtained from [12, 17, 19]).

Sorption-based DLE

Sorption-based DLE is a process where lithium ions are selectively captured from a liquid solution onto insoluble materials known as sorbents. This can happen through either adsorption (without involving ion exchange) or ion exchange processes. There is a common misconception about sorption-based DLE, often mistakenly associating it solely with adsorption onto aluminium-based (adsorption-Al) sorbents. It is crucial to clarify that sorption encompasses both adsorption and ion exchange processes [20]. In adsorption-Al based DLE, lithium ions intercalate into the surface of solid particles, typically aluminium-based sorbents. Meanwhile, ion exchange based DLE involves swapping lithium ions in a liquid phase with ions of the positive charge but different chemical properties e.g. H^+ on a solid ion exchanger, mainly manganese and titanium-based sorbents.

In the adsorption-Al type DLE process, lithium chloride is selectively extracted from multi-ion aqueous environments infiltrating within the atomic layers of the adsorbent, and then desorbed using a warm diluted lithium chloride solution. These adsorbents must meet specific criteria, including high lithium selectivity, sufficient adsorption capacity, and operational stability. Despite the success of adsorption in lithium recovery from complex brines, challenges remain in its applicability to specific brine conditions. While many brines are naturally quite saline, some may still require additional heat sources or adjustments in salinity to optimize the adsorption process. Although these adjustments may not lower the TRL of adsorption-Al type DLE, they highlight the need for situational adaptations to achieve optimal performance [17].

Studies indicate that adsorption technology can achieve optimal results in lithium recovery from brines under three critical conditions: a minimum lithium content in the brine typically over 100 mg/L, a specific salinity level to relax the hydration shell around lithium ions, and a reliable heat source affecting kinetics and efficiency. Therefore, if the essential conditions of lithium content, heat, and salinity are met, adsorption-Al type DLE methods can be considered at TRL 9, indicating commercial viability [17]. It is important to note that some brines require their specific pre-treatment methods to maximize the effectiveness of sorption-based DLE technology. This is especially true if impurities originate from non-ionic sources such as NOMs (Natural Organic Matters), hydrocarbons, oil, suspended solids, etc [19].

Ion exchange type DLE

The manganese and titanium-based ion exchange sorbents (also known as LMO and LTO, respectively) have garnered significant attention due to their superior lithium adsorption capacity and selectivity compared to aluminium-based sorbents. In ion exchange-type DLE, adsorbents with precisely adjusted porosity function as ion sieves, restricting mass diffusion solely to lithium and hydrogen ions. The absorbed lithium can subsequently be released using a low pH solution, facilitating the substitution of lithium ions with protons. Operational variables such as pH, temperature, and feed composition can be adjusted to optimize the process, achieving recovery rates of over 90%.

The aluminium-based sorbent can increase the lithium concentration by 2 times (with some reports of achieving 10 times [8]), while LMO and LTO-based sorbents in DLE can achieve lithium concentration increases of up to 10 times. It is important to mention that DLE technology is designed based on the principle that the lithium to TDS ratio should be increased as much as possible. The aluminium-based sorbent DLE could lower this ratio to approximately 30-20, whereas LMO and LTO sorbents in DLE have shown potential to decrease the ratio to around 15-5. Although there are no comprehensive reports (as far as we know) on the carbon footprints of sorbent-based DLEs, it is worth noting that the water consumption rate of aluminium-based sorbent DLE is nearly five times higher than that of LMO and LTO-based sorbents DLE [21]. Nonetheless, aluminium-based sorbent DLE eliminates the need for acid washing during stripping and base usage for post-treatment and neutralization thus it has lower operating cost and less waste. It is crucial to consider that water in aluminium-based sorbent DLE can be recycled within a closed-loop system, which allows for the repeated reuse of water [17]. Utilizing the adsorption-Al type DLE process, which necessitates heat, on naturally heated geothermal brines can conserve energy and decrease operational expenses.

In the industry, aluminium-based sorbents are sometimes referred to as generation one DLE, while manganese and titanium-based ion exchange sorbents are referred to as generation two DLE. Although LMO and LTO adsorbents have shown significantly higher lithium adsorption capacity, challenges for both types of sorbents include cost, acidic desorption processes, sensitivity to oxidation-reduction reactions, and dissolution loss. Modifications, such as altering synthesis conditions or introducing additives, aim to enhance efficiency for industrial-scale utilization. Further research and modification for practical industrial application are required to ensure they can sustain long-term performance.

Photo credit: E3 Lithium Ltd

Solvent extraction DLE

Solvent extraction DLE for lithium recovery relies on exploiting the different solubilities of compounds in aqueous and organic phases. This method involves several steps: combining the organic phase that has a Li selective extractant with brine to form lithium complexes, subjecting the complexes to a stripping step to extract lithium, and recycling the organic phase. Lithium extraction makes use of a range of organic solvents, including kerosene (the most common one), m-xylene, p-xylene, chlorobenzene, benzene, dodecane, chloroform, cyclohexane, ketone, methyl-tertbutyl ether, and acetic ether.

Three categories of lithium solvent extraction techniques exist based on the nature of extractant: multicomponent solvent systems, ionic liquids, and crown ethers. Multicomponent solvent systems involve extractants, co-extractants, and a bulk solvent.

They offer high efficiency but can lead to environmental contamination and increased operational costs. Ionic liquids provide high separation efficiency and selectivity but are limited by their high cost and solvent loss. Crown ethers selectively interact with lithium ions, with their efficacy depending on the crown ring cavity size. However, their commercialization is hindered by high costs and environmental concerns.

During extraction, lithium complexes are recovered using acidic stripping agents mainly HCl or H_2SO_4. The extraction efficiency increases above 90% with repeating extraction-stripping-extraction cycles, typically above 5 with operational temperature range of above 25°C. The extraction process duration varies, usually spanning between 10 minutes to 4 hours. Solvent extraction requires inputting fresh water but is self-sufficient in lithium pre-concentration. Tri-n-butyl phosphate (TBP) + $FeCl_3$ systems show promise, with China emerging as a major player in DLE-produced lithium supply (for example, the DLE plant in Qinghai Chaidamu Xinghua Lithium Salt Co., Ltd, produces 10,000 tonnes per annum lithium carbonate)[19].

While solvent extraction has demonstrated efficiency, it is not yet mainstream to compete with other DLE techniques on an industrial scale. However, solvent extraction has the potential to be utilised as a post-treatment step to purify the product and achieve battery quality grade.

Challenges include the complexity of lithium-rich brine, cost, environmental toxicity, risk of fire, and processing large volumes daily. Future research aims to improve extractants for industrial application.

Membrane technology

Membrane technology plays a crucial role in the advancement of DLE methods. Within membrane-based DLE, it is important to recognize two main types of membrane processes with high TRL>7: pressure-assisted membrane processes (such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) and potential-assisted membrane processes (including electrodialysis (ED), bipolar, and capacitive deionization (CDI)). MF, UF, NF, and RO are already utilized in various aspects of sorption based DLE systems.

Pressure-assisted membrane processes within DLE primarily contribute to water recycling (especially RO and NF), impurity removal (mainly NF, UF and MF), and LiCl concentration post-sorption columns (mainly RO). However, it is crucial to note that pressure-assisted membrane processes are originally designed for water treatment and desalination rather than ion separation, which may pose challenges when applied to ion separation. NF can effectively segregate monovalent ions like Li, Na, and K ions from multivalent ions like Al or Mg ions, thereby reducing the TDS/Li ratio. Nevertheless, many brines with significant lithium concentrations also exhibit high salinity, leading to severe scaling and fouling issues. Hence, relying solely on NF as the separation process without pretreatment might compromise the TRL of DLE[22].

Recently, applied potential-assisted membrane technologies like electrodialysis (ED) have been integrated into DLE flowsheets primarily for converting lithium chloride into lithium hydroxide and hydrochloric acid, resembling the chloralkali process. Additionally, bipolar membrane processes have shown promising results in the recovery of sodium sulphate, particularly in spodumene-based Lithium refinery processes. It should be pointed out here that by using only ED, lithium ions cannot be separated from monovalent ions such as sodium (Na) and potassium (K), although ED has shown promising performance for the separation of Li from Mg ions. It is important to clarify that none of the aforementioned membrane applications should be considered as "membrane-based DLE" since membranes have already been integrated into sorption based DLE processes. However, "membrane DLE" refers to the emerging technology involving the use of lithium-selective membranes in applied potential processes. Technically akin to electrodialysis, instead of employing ion exchange membranes like Nafion, lithium-selective membranes are utilized. This enables selective transport of lithium ions through the nanochannels of the membranes to increase the Li/Na and Li/K ratio after processing, facilitating the direct extraction of lithium from brine [23].

Although DLE membrane technology is still in the early stage, it holds the potential to disrupt sorption and solvent-based DLE methods, as it eliminates direct contact between the brine and product. Furthermore, membrane DLE enables modular design, resulting in a reduced water and carbon footprint, while also minimizing water loss and brine contamination. This facilitates the reinjection of lithium-depleted brine back into aquifers and underground reservoirs. Additionally, membrane DLE eliminates the need for water or acid stripping and reduces reagent usage for post-DLE processes or neutralization.

The primary challenge facing membrane DLE is the creation of a durable membrane exhibiting long-term chemical stability, capable of being applied across a wide spectrum of brines with varying compositions and TDS. Furthermore, developing a membrane with high Li/Na selectivity poses a challenge due to the chemical similarity between sodium and lithium in their transport through the nanochannels of ion-selective membranes.

Other DLE methods

Several other types of DLE approaches have been reported, which are still in the proof-of-concept stage and have low TRL [19]. One such approach is electrochemical or battery-based DLE, which relies on selectively capturing lithium on or inside electrodes in AC or DC power mode systems. While battery-based ion recovery processes have been utilized for separating valuable compounds like nickel, cesium, and copper, their application for lithium is relatively new. Battery-based DLE methods can also be integrated with membrane technology for lithium recovery, as seen in membrane capacitive deionization (MCDI) systems. MCDI demonstrates a substantially lower energy consumption rate compared to its close relative, electrodialysis ED, or DLE membrane methods. However, the technology is still in its early stages and requires further development. The utilization of carbon dioxide (CO_2) in the production of lithium carbonate through the carbonation process has emerged as a significant focus in recent years amidst the escalating global CO_2 emissions. This method presents an opportunity to capture and incorporate released CO_2 into the lithium recovery process, particularly in ores (mineral carbonation) and brines. In brines, CO_2 can be generated as both CO_2 and supercritical CO_2 (SC-CO_2), aiming to enhance lithium extraction efficiency while reducing operational costs due to their superior diffusivity and low viscosity.

Direct carbonation involves reacting lithium-containing brines with concentrated lithium directly with CO_2 at elevated temperatures, followed by separation of solid lithium carbonate from the solution. Indirect carbonation, a promising method proven effective in ion battery lithium recovery, treats lithium-containing brines with acid before introducing SC-CO_2 to dissolve lithium carbonate, which precipitates upon depressurization. Reverse carbonation, demonstrated in solar energy storage, reacts brines with a salt solution to isolate lithium carbonate, followed by further processing. Additionally, electrochemical carbonation, used in ion batteries, involves applying voltage to facilitate lithium ion migration to the electrode surface, where CO_2 induces lithium carbonate precipitation.

The effectiveness of these methods varies depending on factors such as starting material nature, processing conditions, and desired purity and yield. Direct carbonation stands out as the simplest and most effective method, boasting approximately 75-85% recovery rates. However, the electrochemical approach exhibits even higher Li_2CO_3 production with over 95% recovery rates [19]. Notably, carbonation processes offer environmental advantages over traditional methods like direct acid leaching, utilizing waste CO_2 and producing minimal toxic by-products. Comparative studies highlight significant reductions in energy usage, material consumption, wastewater generation, and emission rates with carbonation processes compared to conventional techniques for lithium extraction, further underscoring their environmental promise. Carbonation-based DLE processes are still in their early stages, and further development is necessary to transition them into mainstream technology for lithium recovery from brine.

Selective precipitation is sometimes referred to in the literature as one type of DLE. This technique relies on the low aqueous solubility of lithium phosphate (Li_3PO_4) [18]. The method requires that the brine has previously been depleted of multivalent species. While some individuals classify selective precipitation as a type of DLE, its concept differs slightly from the fundamentals of other DLE methods, which involve extracting only lithium and leaving other impurities behind. Therefore, it may not be entirely accurate to consider it as part of the DLE family.

Photo credit: ARTIS-Uli Deck for Vulcan Energy Resources

TRL analysis and Commercialization status

The Commercial Readiness Index (CRI) and Technology Readiness Level (TRL) are both metrics used to assess the readiness of technologies, but they focus on different aspects and serve different purposes. TRL, originating from NASA, measures technical maturity on a scale from 1 to 9. It tracks a technology's progression from basic principles to real-world operation, primarily through laboratory and field testing. TRL is commonly used in R&D to gauge a technology's advancement toward deployment.

In contrast, the Commercial Readiness Index (CRI) evaluates a technology's readiness for market entry, considering factors like market demand, regulations, and financial viability. CRI provides insights into whether a technology is poised for successful commercialization, complementing TRL's technical assessment with commercial readiness indicators.

Currently, DLE technologies are assessed based on their TRL, indicating their technological maturity. However, there is not a standardized CRI specific to DLE methods. While TRL assessments provide insights into technical readiness, the absence of a CRI means factors like market demand and cost-effectiveness are not systematically evaluated for commercial deployment of DLE. Thus, while DLE technologies may show technical progress, their commercial readiness requires broader assessment beyond TRL levels.

As mentioned, among 84 different reports on DLE technologies from the period 2017 to 2022 [18], only 30% of these technologies were tested using real (natural) brine. While using simulated brine solutions for technology validation might be acceptable if they accurately mimic ion concentrations found in real brines, this is not usually the case for those that used either single salts or binary mixtures, which don't fully replicate real-world conditions.

As presented in Figure 3, adsorption and ion exchange methods stand out as the most advanced, with adsorption reaching a TRL of 9, notably with aluminium-based sorbents already at full-scale deployment. However, other sorbents like manganese-based and titanium-based ones are still in the pilot stage 7-8 [17]. Lake Resources has recently announced the Definitive Feasibility Study for its ion exchange based DLE (using Lilac Solutions technology) at the Kachi lithium brine project in Argentina [24, 25]. The Adsorption-Al type DLE method was first implemented at a full commercial scale in Argentina by Arcadium Lithium (previously Livent), where it has been in operation for over two decades, on a salar brine at Hombre Muerto. Subsequently, the technology found application in China (e.g. Lanke Lithium, Zangge Mining, Jintai Lithium etc.) for the commercial production of lithium chemicals from continental brines.

Additionally, in 2015, Simbol Materials successfully operated the adsorption-Al type DLE in pilot plant scale using geothermal brine in southern California, USA. The technology has also been commissioning by Vulcan Energy to produce battery-quality lithium hydroxide from geothermal brine in the Upper Rhine Valley of Germany. The French-based company Eramet is also in the process of commissioning adsorption-Al type DLE technology in Argentina. Additionally, Albemarle and SQM are transitioning towards DLE technology in Chile and Arkansas, respectively. Major corporations such as Rio Tinto and ExxonMobil have plans to construct/expand DLE plants in their Argentina (Rincon) and Arkansas (Project Evergreen) respective projects, further showcasing the widespread adoption of this technology.

While Adsorption-Al type DLE is currently the dominant force in DLE, with companies like Arcadium and Albemarle achieving large-scale implementation, other innovative approaches are emerging. One such approach is the use of ion exchange nanomaterials by companies such as Litus, developing a line of tailored nanomaterial composites designed for lithium extraction. Their technology, though still under development, has shown the potential of up to 98.5% efficiency and over 90% selectivity. These nanomaterials leverage their tiny size and structure to facilitate selective lithium-ion exchange, offering the potential to further enhance ion exchange type DLE.

Solvent extraction processes typically fall within the range of TRL 7-8 [12]. However, the solvent extraction DLE plant operated by Qinghai Chaidamu Xinghua Lithium Salt Co., Ltd, producing 10,000 tonnes per annum of lithium carbonate, could potentially achieve a TRL of 8-9. Nonetheless, additional data from more plants is needed to confirm that the TRL for solvent extraction in DLE surpasses 8 [12, 19]. Membrane-based DLE, though at a lower TRL of 4-5, hold potential for lithium extraction from brines. It is worth noting that pressure-assisted membrane processes commonly used in DLE flowsheets, such as RO, NF and UF, have already attained a TRL of 9. Electrochemical methods like ED and MCDI are at the applied research level (TRL 4), with promising bench-scale validations but limited progress towards pilot-scale deployment [17, 19].

The GreenSpace Tech report by Deloitte [6] reports that approximately 38 technology developers and vendors are engaged in DLE, along with 57 lithium production projects either currently utilizing or intending to adopt DLE methods. The technology providers have the potential to unlock future revenue streams through technology licensing, or to acquire and develop their own lithium resources.

Figure 4 depicts the commercialization status of key DLE projects. Several are already operating at full-scale production, predominantly in Argentina and China, while others are undergoing commissioning, execution, or are in the pilot/feasibility stages [11].

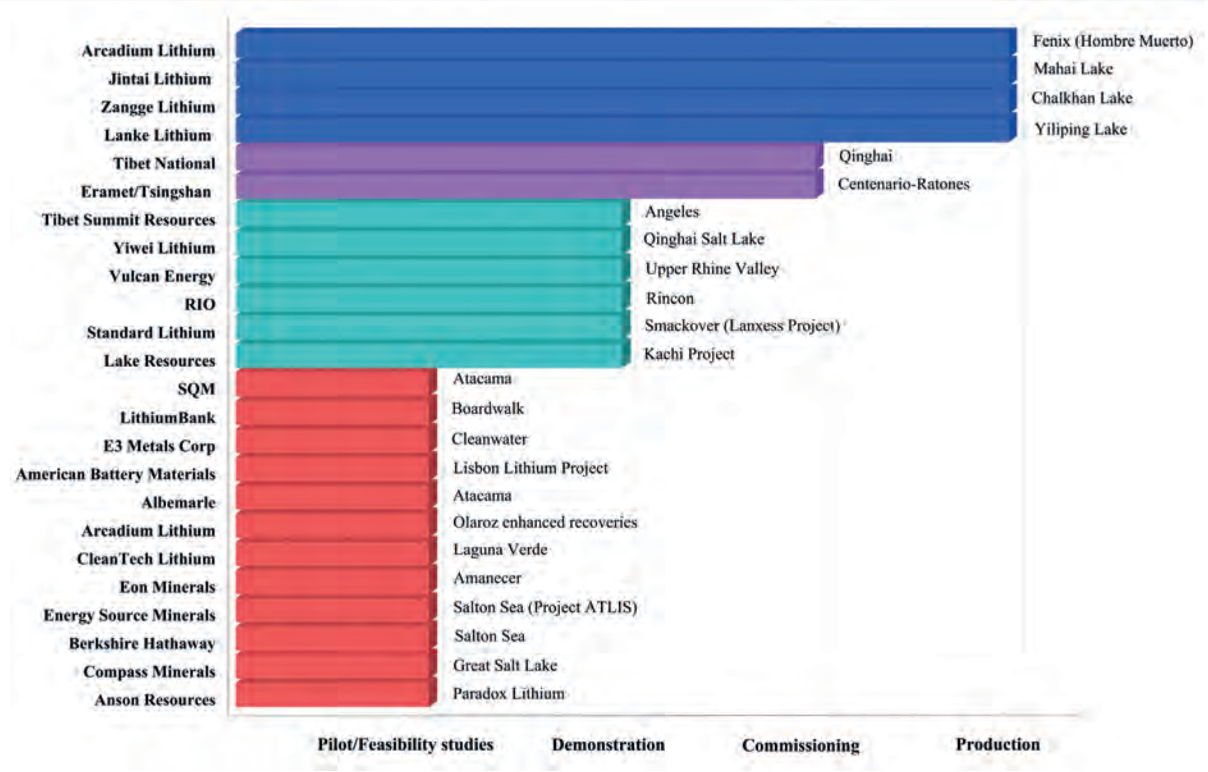


Figure 4: DLE projects and their project stage. (Source: Data obtained from [11, 12, 14]).

OPEX and CAPEX analysis

Alongside the technological aspects of lithium extraction, it's important to consider the capital and operational expenditures. DLE and solar evaporation have comparable initial costs, with DLE having higher capital expenditures (CAPEX) due to advanced technology and infrastructure requirements, ranging from USD45,000 to USD80,000 per tonne of lithium carbonate equivalent per annum (tpa LCE), compared to solar evaporation's USD23,000 to USD34,000 per tpa LCE (CPAEX for solar evaporation might be slightly higher due to inflation in 2024 and other factors) [11, 25-27]. Additionally, DLE also has comparable operational expenditures (OPEX), ranging from USD4,500 to USD7,500 per tonne of LCE [11, 25, 26], compared to solar evaporation's OPEX (ranging from USD4,800 to USD8,000 per tonne of LCE). In contrast, the OPEX of hard rock mining ranges from USD6000 to USD18000 per tonne of LCE [8, 28].

It is noteworthy that CAPEX and OPEX intensity may change as technology progresses beyond the initial phase. Despite higher capital intensity, DLE projects may benefit from selective removal of by-products into saleable products, potentially improving economics and shortening payback periods. It should be noted here that, akin to most new technologies, both capital and operational expenditures may decrease as DLE technology and its implementation progress beyond the initial phase.

Based on 2022 data, the upfront capital expenses for DLE projects may range from USD300 to USD900 million, compared to USD200 to USD500 million for traditional brine evaporation [11]. This is primarily because the equipment required might need customization based on the brine's composition, leading to higher costs. Additionally, not all DLE methods are suitable for every type of brine due to variations in brine conditions. Over time, although DLE projects have higher initial expenses, they might have lower overall costs per unit due to higher lithium recovery rates. In some areas, producers can utilize geothermal brine to power DLE operations, potentially reducing energy costs and OPEX.

When comparing the OPEX and CAPEX of different DLE technologies, ion exchange and adsorption are two prominent methods that warrant a closer examination. Ion exchange in principle may have lower CAPEX but higher OPEX than adsorption processes for lithium extraction. The higher OPEX for ion exchange is primarily attributed to the recurring costs associated with the use of acids and other chemicals required for the desorption process [25, 26]. Based on the recent DFS documents from Vulcan, Standard Lithium, and Lake Resources, it seems the difference between ion exchange and Al sorbent DLEs is marginal. Data from their future project developments will provide us with a better understanding of the differences between the two DLE technologies.

Sustainability benefits and analysis

DLE has the potential to offer environmental advantages over traditional extraction methods, and potentially improved sustainability credentials. These advantages include potentially lower perceived environmental risks, reduced land, carbon footprint and water usage (if recycled and reinject). These benefits may facilitate community and permitting approvals and have the potential to increase government revenue from projects.

DLE can significantly reduce the time required for lithium production compared to conventional methods. While solar evaporation typically takes over 18 months, and hard rock mining takes several months, DLE processes can accomplish extraction in a matter of hours or days [17]. This represents a crucial advancement, as DLE enables rapid production scaling, allowing stakeholders to adapt to market demands more effectively.

Figure 5 shows the sustainability analysis of DLE compared to solar evaporation and hard rock mining. The freshwater consumption and water footprint of lithium production should not be conflated, as the water footprint considers additional hidden waters, such as those used to make reagents. Likewise, the carbon footprint and carbon emission, which are partially linked to energy consumption, should not be confused. The carbon footprint encompasses various forms of carbon, including Scope 1-3 emissions. Also, the water and carbon footprint and consumption/emission of Li_2CO_3 and LiOH is different, however great care is needed when considering these factors since there can be discrepancies in measurement criteria, making like-for-like comparisons difficult. Multiple reports present contradictory or discrepant information regarding water and carbon footprints, consumption, and emissions.

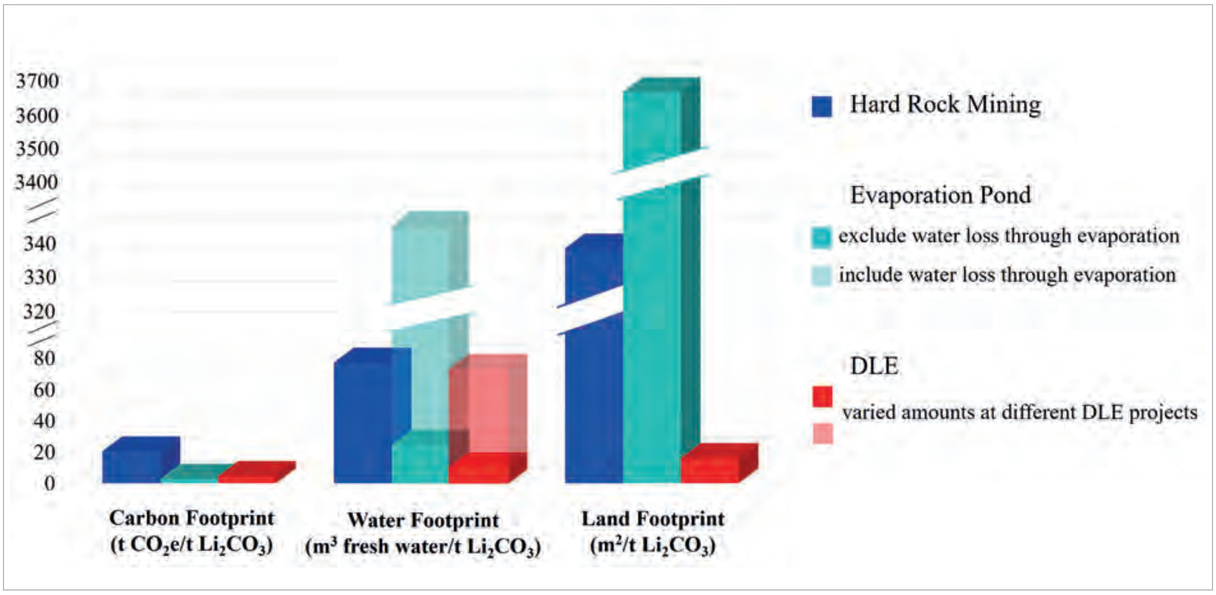


Figure 5: A comparative analysis of DLE with solar evaporation and hard rock mining in terms of sustainability, including carbon, water, and land footprints (the water consumption of evaporation ponds is considered both excluding and including water loss through evaporation. Additionally, due to the broad range of values from various sources, the water consumption of different DLE projects is shown in the graph. Finally, the average amount of carbon emission of solar pond has been considered) [29-31].

According to a life cycle analyses (LCA) by Kelly et al. [29], the production of Li_2CO_3 from brine using solar ponds requires 15.5−32.8 m^3 of fresh water per tonne of Li_2CO_3 (excluding water loss through evaporation), whereas that from ore requires 77 m^3 of fresh water per tonne of Li_2CO_3. This is while in some reports, the water loss through evaporation in solar ponds is considered, and the fresh water usage for the production of one tonne of Li_2CO_3 is reported between 100 and 800 m^3 (average around 450-480 m^3) [18, 29].

The LCA values for carbon emissions are 2.7−3.1 tonnes CO_2 per tonne of Li_2CO_3 from brine evaporation and 20.4 tonnes CO_2 per tonne of Li_2CO_3 from ore [15, 29]. In general, the carbon and water footprint of producing $LiOH{\bullet}H_2O$ from brine is slightly higher compared to that from Li_2CO_3 (e.g. 31−50 m^3 fresh water and 6.9 − 7.3 tonnes CO_2 per tonne of Li_2CO_3 [29]). However, the situation is reversed when it comes to the production of lithium chemicals from ore.

Reports on water consumption/footprint of DLE indicate a discrepancy in the literature. An analysis of 57 articles on DLE technology published in 2023 [18] revealed a wide range of water consumption rates (not water footprint). Some articles reported substantially lower water consumption rates for DLE compared to brine extraction and hard rock mining (less than one m^3 fresh water per tonne of Li_2CO_3), while others indicated rates exceeding 500 m^3 fresh water per tonne of Li_2CO_3, over 10-12 times greater than current practice. It is worth noting that water loss due to evaporation in DLE is small since it operates as a closed system with controlled volume. Also, it should mention here that academic records usually reference gross usage in stripping, not net usage in a project.

The evaluation based on the available data conducted in the present study estimates that DLE water consumption is below 100 m^3 fresh water per tonne of Li_2CO_3. Arcadium Lithium's DLE plant at Salar del Hombre Muerto, operational since 1996, reported an overall water use for its entire facility as 71 m^3 fresh water per tonne of Li_2CO_3 [32]. In some of the other DLE projects, the freshwater consumption is estimated to be lower. For instance, in the Lake Resources' Kachi ion exchange project, it is evaluated around 11 m^3 per tonne of Li_2CO_3, and Vulcan estimated the water consumption to below 2 m^3 per tonne of LiOH [8, 25]. It Seems that closed looped water recycling is an important approach to reduce DLE water consumption rate. Therefore, any DLE project requires effective water recycling measures and strategies to reduce water footprint. Reinjection of used brine can also substantially reduce the water footprint of DLE; however, environmental complications surrounding reinjection need to be thoroughly investigated and studied further, as there is limited practical information regarding reinjection.

Similarly, the carbon footprint/emission of DLE technologies is also unclear in the literature, with several reports presenting a broad range of data. Some studies have reported the energy consumption rate of the extraction part of DLE, which could be used to estimate carbon emissions or footprint. However, this information might not be accurate as the input energy of pretreatment and post-treatment processes of DLE have not been considered. Therefore, the carbon emissions and footprint may not be representative. Also, the source of energy may affect the DLE CO_2 emission. A study by Mousavinezhad et al. [30] on lithium extraction from brine in Clayton Valley, Nevada, demonstrated distinct emissions profiles when producing one tonne of lithium carbonate using the DLE method. Emissions amounted to approximately 22, 17.3, and 7.6 tonnes of CO_2 per tonne of Li_2CO_3 when electricity was sourced from a diesel generator, the Nevada grid, or solar panels, respectively. Based on the available data in literature, the direct CO_2 emissions of DLE seem to range between 2.5 and

7 CO_2 per tonne of LiOH•H_2O. For example, Arcadium Lithium reported GHG Intensity (tonne CO_2/tonne Li product) of 2.5 to 3 for its DLE plant [32]. DLE offers the advantage of modularity, enabling seamless integration with renewable energy sources to completely offset CO_2 emissions. When based on geothermal brine, DLE facilitates a significant reduction in carbon footprint, nearing zero emissions.

The information on land use varies across different reports. For a typical hard rock plant (such as Greenbushes and Mt. Catlin mines and Tianqi lithium plant in Western Australia), approximately 335 m^2 per tonne of Li_2CO_3 are required, including open-pit mining areas, tailing dams, and lithium refineries [30]. In brine evaporation pond systems, land is needed for evaporation ponds, wellfields, processing plants, and disposal areas. Direct land use for a brine evaporation pond resource is estimated to be approximately 3656 m^2 per tonne of Li_2CO_3 (based on Atacama) [30]. Conversely, direct land use in a typical DLE setup is lower, averaging around 16 m^2 per tonne of Li_2CO_3 for processing plants, and, if the wellfield area is also taken into account, approximately 493 m^2 per tonne of Li_2CO_3 [30]. Additionally, if the source of electricity shifts to solar panels, the land required for solar panel installation must be added to the total land use of DLE.

Credit: Adionics

DLE outlook

From a technical perspective, the outlook for DLE appears promising, with advancements in technology leading to improved efficiency and effectiveness in lithium recovery. Innovations in DLE processes can enable more selective extraction of lithium from brine sources, addressing challenges associated with co-extraction of other ions such as sodium and potassium with the bonus of ability to producing byproducts from DLE wastes.

From a sustainability standpoint, DLE offers several advantages. DLE processes typically have a smaller environmental footprint. They require less land area, have relatively low water usage (recycling and reinjection), and the potential to mitigate the risk of groundwater contamination. Furthermore, advancements in DLE technology have the potential to reduce greenhouse gas emissions associated with lithium production, particularly when renewable energy sources are utilized to power extraction processes.

The main challenge of DLE is the unique composition of each brine found across the world. Each new DLE method necessitates unique design and considerations. Furthermore, the complexity is compounded by differences in regulations and local environments, emphasizing the crucial role of conducting comprehensive pre-feasibility studies and thorough techno-economic evaluations for any new project.

Additionally, ongoing research and development efforts should be focused on optimizing operating conditions, enhancing selectivity, and reducing energy and water consumptions in DLE processes. Further studies need to be carried out to understand and assess the risks and benefits of reinjection of spent brine from DLE processing in salar basins. Currently, there is limited practical information regarding the potential implications of reinjection on the layered stratigraphic structure of these basins.

Salar de Uyuni in Bolivia is the largest salar and largest known lithium deposit in the world. The Bolivian government intends to extract lithium here using DLE.

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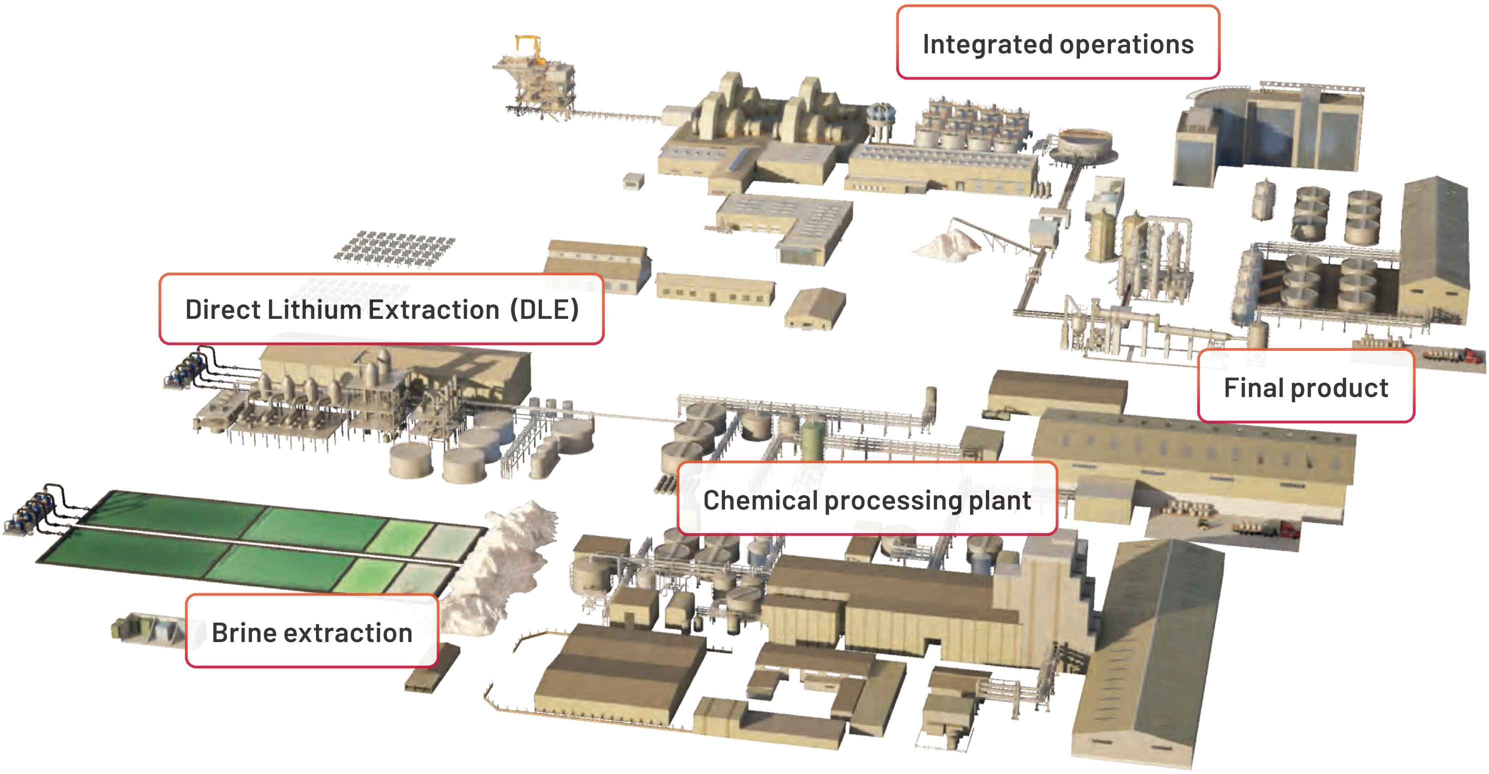

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