ANL-22/73

Lithium Production from North American Brines

Energy Systems and Infrastructure Analysis Division

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ACRONYMS

$Al(OH)_3$	Aluminum Hydroxide
BHE Renewables	Berkshire Hathaway Energy Renewables
CTR	Controlled Thermal Resources
DLE	Direct Lithium Extraction
ESS	Energy Storage Systems
EV	Electric Vehicle
GREET®	Greenhouse gases, Regulated Emissions and Energy use in Transportation
HCl	Hydrochloric Acid
ILiAD	Integrated Lithium Adsorption Desorption Technology
JV	Joint Venture
KGRA	Known Geothermal Resource Area
LCE	Lithium Carbonate Equivalent
LDH	Lithium-Aluminum-Layered Double Hydroxide Chloride
Li	Lithium
Li_2CO_3	Lithium Carbonate
LIB	Lithium-Ion Batteries
LiCl	Lithium Chloride
LiOH	Lithium Hydroxide
$LiOH\text{-}H_2O$	Lithium Hydroxide Monohydrate
Na_2CO_3	Sodium Carbonate
NaOH	Sodium Hydroxide
PVDF	Polyvinylidene Fluoride
RO	Reverse Osmosis
SO_2	Sulfur Dioxide
TRL	Technology Readiness Level
USGS	United States Geological Survey

ABSTRACT

This memo documents a literature review and preliminary life-cycle inventory on producing lithium-based chemicals – lithium carbonate (Li_2CO_3) and lithium hydroxide (LiOH) – from North American brines, which has been incorporated into the GREET® 2022 model release. These brines are being considered for domestic production of these chemicals in the United States in light of the importance of their reliable supply to meet the increasing demand for lithium-ion batteries. If produced successfully at commercial scale, Li chemicals processed from these domestic brines are expected to substitute their imported counterparts, thus meeting a US strategic goal.

1 INTRODUCTION

Lithium is a key constituent of lithium-ion batteries (LIBs) that are used in several applications, particularly in consumer electronics, electric vehicles (EVs), and energy storage systems (ESSs) (Ambrose and Kendall, 2020; Stringfellow and Dobson, 2021; Warren, 2021). The global drive for clean energy and transportation has initiated a jump in sales of EVs and ESSs and is expected to accelerate it further (Stringfellow and Dobson, 2021; Toba et al., 2021). This will cause an increase in demand for lithium (Li), mainly as two battery-grade Li-based chemicals: lithium carbonate (Li_2CO_3) and lithium hydroxide ($LiOH.H_2O$) (Stringfellow and Dobson, 2021; Warren, 2021). Lithium is also important for other sectors, including in ceramics, glass, pharmaceuticals, polymers, metallurgy, and aerospace (Bradley et al., 2017; Stringfellow and Dobson, 2021). Given such significance, Li remains on the United States' list of critical materials whose sustained, reliable supply over the next few decades is important for both its economy and security (The White House, 2021; US Department of the Interior, 2022; US DOE, 2020).

Globally, Li is found in three types of deposits: brines, hard rock deposits (or pegmatite deposits), and sedimentary deposits (clay). The major commercial sources of these deposits are located outside the United States – saline brines (such as those in Chile) that collectively account for 50-75% of global Li production, and hard rock deposits in Australia and China (Stringfellow & Dobson, 2021; USGS, 2022). However, Li production from these sources has been known to fluctuate over the years for a variety of reasons (Stringfellow & Dobson, 2021; USGS, 2022). This, along with the supply chain issues during the CoVID-19 crisis and the critical importance of lithium, has generated concern about the likelihood of Li shortages in the future and its resultant negative effects on the US economy (The White House, 2021; US DOE, 2020). It has also sharpened the focus on exploring opportunities for domestic production of Li (The White House, 2021; US DOE, 2020).

While the US has historically led global Li production in the past, at present, it is a minor player (< 2% share) of global Li production (USGS, 2022). However, the prospects of Li production in US (and North America more generally) have increased recently owing to brines with considerable Li content. These include geothermal brines in the Salton Sea Known Geothermal Resource Area (KGRA), and of other brines located in Nevada, Utah, and Canada, with considerable Li content (Grant, 2019; Stringfellow & Dobson, 2021; Toba et al., 2021; Warren, 2021). Apart from their considerable potential for meeting Li-needs of various sectors and their favorable location from geographic and geopolitical perspectives, these reserves also present other advantages from the viewpoints of the US economy and environment. Compared to its extraction from saline (Salar) brines and hard rock deposits, Li production from these brines has lower land and water demands, is less carbon-intensive via use of geothermal energy for plant operation, and involves less turnaround time for Li supply (Warren, 2021). Also, after Li extraction, the barren brine is returned back to the reservoir, thereby addressing environmental and social concerns associated with brine evaporation in case of saline (Salar) brines (Pell et al., 2020; Stringfellow & Dobson, 2021). Estimates suggest that geothermal brine-based Li production lowers land requirement by ***a factor of ~10,000*** over evaporation-based projects for the same amount of Li produced (Grant, 2019; Pell et al., 2020). Lastly, Li production from both geothermal and non-geothermal brines involves the use of reserves that are being used for other economic purposes, meaning that these are brownfield investments that may not incur high costs for investors (Pell et al., 2020).

In this report, we briefly present a literature review of potential Li production in the United States and North America (as Li-based chemicals) through various brines. This will include the likelihood of Li production, the companies involved in this domain, and the technologies they are deploying to meet their objectives. We also provide a preliminary life-cycle inventory on the production of Li from such a resource, while also highlighting potential gaps that still need to be addressed.

2 LITERATURE REVIEW

2.1 Types of Brine Resources Available

Two kinds of brine reserves exist in the United States and North America: geothermal brines, and other saline brines (termed as “non-geothermal” brines in the rest of this document). Figure 1 shows a list of major geothermal and non-geothermal brines in the US and North America (Grant, 2019).

Figure 1 List of major lithium-containing brines in the United States and North America (reproduced from (Grant, 2019)) (Circle size indicates the number of companies in the location)

Geothermal brines refer to hot, concentrated saline solutions that flow through hot rocks and are used to generate electricity via geothermal power plants (Al Radi et al., 2022). These brines mostly consist of water, while also being rich in major elements and minerals such as potassium, arsenic, boron, silica, and most critically, lithium (Al Radi et al., 2022; Stringfellow & Dobson, 2021; Warren, 2021). The extraction of these elements and minerals from geothermal brines is useful as it provides alternative sources of their supply, as well as important in order to avoid their harmful impacts on geothermal power plant components (Al Radi et al., 2022). Examples of such harmful impacts are corrosion of power plant equipment and scaling inside pipes that can damage this equipment and reduce its heat transfer efficiency (Al Radi et al., 2022).

Neupane and Wendt (2017) analyzed the data for over 2,000 samples of geothermal fluids in the US from USGS (United States Geological Survey) and other sources, and reported that only 1% of samples showed significant Li content (> 20 mg/kg) (Stringfellow & Dobson, 2021). All these prominent Li-containing samples were from the Salton Sea KGRA in the Imperial Valley in California, with an average Li-content of 200 mg/liter of brine (Neupane & Wendt, 2017; Stringfellow & Dobson, 2021; Warren, 2021). Neupane and Wendt (2017) calculated the likely Li production from this resource, assuming an operating ratio of 90%, a recovery efficiency of 80% for Li from brine, and an average daily brine production of ~275,000 metric tons. This translated into ~76,500 metric tons of annual output of LCE (lithium carbonate equivalent) (Warren, 2021). Studies indicate this production potential to reach up to 600,000 metric tons of LCE output upon the complete development of this resource (Ventura et al., 2020), highlighting its significance in meeting the US's strategic imperatives.

Apart from geothermal brines, the United States also has other brines that contain lithium in substantial amounts (Figure 1). Currently, these brines are either in operation and being used to produce other materials and chemicals, or in certain cases, they are reserves that were used for commercial production of oil or other materials in the past, but are now unused (Grant, 2019). Prominent non-geothermal brines with notable Li content are located in Arkansas basin, Utah (Great Salt Lake), and Nevada in the US, and in Alberta in Canada (Figure 1) (Grant, 2019; Warren, 2021). On average, non-geothermal brines have lower Li content than their geothermal brine counterparts in the Salton Sea KGRA (Warren, 2021). However, since both geothermal and non-geothermal brines are brownfield brines they offer opportunities to use existing resources and infrastructure for production of Li-chemicals (Li_2CO_3 and $LiOH.H_2O$) from existing resources (Al Radi et al., 2022; Grant, 2019; Stringfellow & Dobson, 2021; Warren, 2021).

2.2 Extraction Technology

Conventionally, lithium is extracted from Salar brines through evaporative concentration, where brine water is evaporated using solar radiation, and the left-over concentrate is processed to obtain Li-chemicals (Kelly et al., 2021; Stringfellow & Dobson, 2021). However, Li extraction from both geothermal and non-geothermal brines utilizes a different group of technologies, collectively termed *direct lithium extraction* (DLE) (Grant, 2019; Pell et al., 2020; Stringfellow & Dobson, 2021; Warren, 2021).

Figure 2 shows a general schematic of the DLE process/technology (Grant, 2019). Initially, fresh brine (or brine obtained after geothermal power generation) is withdrawn from the reservoir, and processed chemically to selectively strip Li-containing material from it. The Li-containing material is subsequently processed further in multiple steps to produce the final Li-chemical (Li_2CO_3 or LiOH). The residual spent brine (after recovering the Li-containing material from it) is reinjected back into the brine using injection wells.

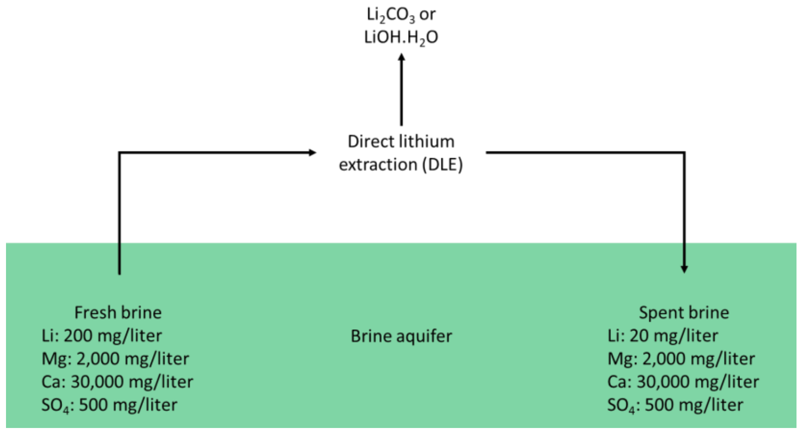

Figure 2 Schematic of Direct Lithium Extraction (DLE) technology (reproduced from (Jade Cove Partners, 2022))

The use of DLE technology for brines is beneficial compared to evaporative concentration on multiple counts. Evaporative concentration requires the brines to contain extremely high amounts of lithium (>> 2,000 mg/kg), limiting its applicability for most brines with much lower Li content (60-600 mg/kg) for which DLE can be used (Grant, 2019; Pell et al., 2020; Stringfellow & Dobson, 2021; Warren, 2021). Further, evaporative concentration can only be used in specific geographies and climatic regions that receive abundant sunshine and less rainfall over any time horizon, since a large amount of time is needed to extract the desired lithium (typically many months) (Grant, 2019, 2020b; Pell et al., 2020). In contrast, DLE process can be used to extract Li from brines in a matter of hours (Stringfellow & Dobson, 2021). Also, in case of Salar brines, almost all of the water from the brine is lost to evaporation, raising concerns (Grant, 2020a; Pell et al., 2020; Stringfellow & Dobson, 2021). However, DLE technology offers the option to re-inject the spent brine back into the reservoir, thus reducing these concerns (Pell et al., 2020; Warren, 2021).

DLE comprises a variety of technologies and techniques, including precipitation, sorption, ion-exchange, solvent separation/extraction, membranes (membrane separation), and electrochemical separation technologies (Stringfellow & Dobson, 2021; Warren, 2021). Table 1 gives a summary of major features of prominent DLE technologies.

Table 1 Major features of different DLE technologies (Stringfellow & Dobson, 2021; Warren, 2021)

Technique	Sub-type	Key features
Precipitation		• Involves the addition of alkaline reagents (such as sodium carbonate, sodium oxalate, aluminum salts, and lime) to precipitate Li • Oldest method, and useful for removing silica from geothermal brines • Not preferred today due to its high cost because of the extensive post-processing needed to both obtain Li from precipitate and to dispose off complex chemical wastes generated in the process
Organic sorbents	Ion-exchange resins	• Use of strong acid cation-exchange resins to selectively extract Li from seawater/brine solutions • Effective only when impregnated with inorganic, Li-selective sorbents
	Ion-imprinted polymers	• Use polymers with reactive/chelation sites to selectively absorb Li (and avoid other metal ions) • Currently under development, at a low technology readiness level (TRL)
Inorganic sorbents	Aluminum hydroxides	• Selectively absorb Li (like organic sorbents) at cation-exchange sites in crystal grid, with Li recovery done via acid stripping and the sorbent regenerated for repeated use • Under development for many years; used in commercial-scale DLE ventures • Require monitoring and control of interference from other metals during Li-extraction and sorbent stability over time
	Manganese oxides	• Preferentially adsorb Li from seawater (brines) through their spinel-type ion sieves • Highly selective for Li adsorption over multiple metal ions • Requires pre-treatment of silica and divalent cations to avoid any coating of sorbent that can prevent Li-sorption • Sorbed Li recovered with dilute acid solutions • Widely considered promising for future commercial projects
	Titanium oxides	• As effective as manganese oxide sorbents in Li-sorption • More acid stable and robust during cycling between sorption and stripping process • Considered more environment friendly, but its effectiveness is still under investigation
	Others	• Includes mixed metal oxides (lithium-aluminum oxide, lithium-manganese oxides, zeolite, etc.)

Table 1 (Cont.)

Technique	Sub-type	Key features
Solvent extraction	Crown ethers	• Well-established technology to separate metals from aqueous solutions; used for valuable/semi-valuable metals • May be used to separate Li quantitatively and selectively from aqueous solutions • Li typically recovered via aqueous stripping agent (usually HCl or other similar acids) • Crowns of ethers dictate Li-selectivity and sorption, through their steric properties and electrostatic interactions between Li and oxygens in these crowns • Can be used directly or by attaching crown ethers to other substances, such as carbon nanotubes, ionic liquids, or even supercritical fluids
	Multi-component solvents	• Use the combination of extractant (metal chelating/binding reagent, like ketones and organophosphates), co-extractant (a reagent that forms adducts, such as organic and inorganic compounds), and diluent (or bulk solvent, like kerosene and alkanes)
	Alternative diluents	• Involve ionic liquids (with ketones as extractant) and supercritical SO_2 (with crown ethers) as diluents for solvent extraction • Ionic liquids can lead to issues in the form of loss of ionic liquids and limited use due to their solubility in water, poor physical properties, and high costs
	Supported liquid membranes or surfaces	• Supported liquid membrane a variant of multi-component systems, where the membrane has the extractant in its pores
Membranes		• Primarily involves filtration membranes that allow Li ions to permeate and reject other ions via use of either surface charge of membrane, size exclusion, or other properties • Used mainly to pre-treat brines and remove metals, divalent cations, and other substances that can interfere in DLE • Includes two kinds of techniques: reverse osmosis (RO), and nanofiltration • RO: Typically applied to remove water and concentrate brines before use of precipitation, sorption, or other DLE technologies on brines • Nanofiltration: Used extensively for separating magnesium and other divalent cations before DLE use
Electrochemical separation		• Also known as “electrodialysis” • Uses electric field to aid ion movement across a semi-permeable membrane • Depends on use of Li-selective membrane, and uses anode and cathode (like in LIBs) • Can also use various solvent extraction-related modifications, as well as coatings of metal oxides on anodes/cathodes

2.3 Companies Involved in DLE

About six major DLE-based projects are currently in different stages of exploration, development, and production in the entire North American content (five in the United States, one in Canada) (Figure 1). While a brief summary of these major projects is given below, Table 2 lists the major features/aspects for each of these projects, as well as the projected demand of LCE over the years.

Table 2 Summary of key features of major DLE projects in North America

Company	**Location**	**Brine type[a]**	**Resource potential (LCE, in million metric tons)**	**DLE technology used**	**Projected annual production (LCE, kilo metric tons)**
EnergySource Minerals	Imperial, CA (Salton Sea)	G		ILiAD	13
Controlled Thermal Resources		G	15		300
BHE Renewables		G			90
Compass Minerals	Ogden, UT (Great Salt Lake)	I	2.4	Fast evaporation + DLE	20-25
US Magnesium		I			10
Standard Lithium	El Dorado, AK (LANXESS plant, Smackover Arkansas)	I (O earlier)	3.14	LiSTR	21
	25 miles of Smackover (Lafayette County, AK)	O	1.195		19.5
	San Bernardino, CA (Bristol Lake)	I			
E3 Metals Corporation	Alberta, Canada	O	7		13
Schlumberger	Clayton Valley, NV	N.A.			65.3 metric tons

[a]G: Geothermal brine; I: Industrial brine; O: Oil brine

<u>**Projected Demand**</u>: 500,000 metric tons in 2021; 3-4 million metric tons in 2030 (Azevedo et al., 2022)

2.3.1 EnergySource Minerals

EnergySource Minerals operates its project ATLiS on geothermal brines in the Salton Sea associated with the John L. Featherstone geothermal power plant (EnergySource Minerals, 2021). The project is located in Southern California – 200 miles east of Los Angeles and Port of Long Beach – and has a nominal land area of 30 acres (EnergySource Minerals, 2021). The company envisions annually producing 20,000 metric tons of LiOH (or ~13,000 metric tons of LCE), assuming commercial-level brine flow of 7,000 gallons per minute for over 9 years of its operation. Construction was slated to begin in the second quarter of 2022, and the company expects to begin its production in the second quarter of 2024 (EnergySource Minerals, 2021).

Based on public statements from EnergySource Minerals, they envision Li extraction using the spent brine from a geothermal power plant via proprietary Integrated Lithium Adsorption Desorption (ILiAD) technology (EnergySource Minerals, 2021). The company claims that ILiAD combines a superior Li-selective adsorbent with continuous bed processing to obtain the best recovery efficiency for Li from brines, while ensuring low capital and operating costs as well as minimal environmental footprint. The company aims to set up a processing plant that can produce 2,500-3,500 metric tons of LCE and intends to scale this up in phases over subsequent years (EnergySource Minerals, 2021). However, no details are available on the actual specifics of this technology.

The major challenge with the company's brine reserves, or for that matter, with all brine reserves in the Salton Sea, is the geology of this ore. These reserves contain high amounts of silica and transition elements (Rock Stock Channel, 2022). This is since these are deep brines, and the presence of these elements can render it difficult (and costlier) for DLE technologies to remove these elements to obtain Li-chemicals (Rock Stock Channel, 2022).

2.3.2 Controlled Thermal Resources

Controlled Thermal Resources (CTR) is building its flagship Hell's Kitchen Lithium and Power Project in the Salton Sea geothermal brines (Controlled Thermal Resources, 2022). Its inferred resource base is estimated at 15 million metric tons of LCE. Under its flagship project, CTR aims to set up a geothermal power plant (capacity: 49.9 MW) by 2023 and a Li-extraction DLE plant (production capacity: 25,000 metric tons/year) by 2024 (Controlled Thermal Resources, 2022). When operational, both plants (power plant and Li-extraction plant) will use the brine in Salton Sea to produce electricity, steam, and LCE. CTR intends to expand these plants and produce up to 1,100 MW of geothermal power and 300,000 metric tons of LCE annually by 2030 (Controlled Thermal Resources, 2022). CTR proposes using this high plant Li-extraction capacity to support the production of LIBs in a Gigafactory with an annual capacity of 54 GWh of battery production. CTR has signed a Letter of Intent with Statevolt on setting up this Gigafactory, and if this comes to fruition, it could serve up to ~650,000 EVs. Additionally, CTR has indicated that it will also explore opportunities to extract other critical mineral resources from its brine reserves, including potassium, manganese, rubidium, zinc, and rare earth elements.

2.3.3 Compass Minerals

Compass Minerals has identified a major Li-containing brine resource at its Ogden facility in Great Salt Lake, Utah (Compass Minerals, 2021, 2022; Compass Minerals International Inc., 2021). The brine is located in the North Arm of the Great Salt Lake, and is estimated to contain 2.4 million metric tons of LCE (Compass Minerals International Inc., 2021). Currently, a small portion of this brine undergoes accelerated evaporation using solar and wind energy to obtain crystallized concentrates of useful minerals, including salt, magnesium chloride, sulfates of potash, and other chemicals, with the residual brine left in evaporation ponds (Compass Minerals International Inc., 2021). The company now plans to use both this residual material left behind in evaporation ponds, as well as the flowing brine resource, for commercial Li production through a direct, separate chain, and expects to begin its Li sales by 2025 (Compass Minerals, 2021).

For initial Li production, Compass Minerals has estimated a resource base (indicated + inferred) of 127,000 metric tons of LCE in the interstitial brine (or the brine being used to produce various chemicals) (Compass Minerals, 2022). While other companies process spent brine (brine obtained after removing other useful materials), Compass Minerals proposes to reverse this chronology. In other words, the company intends to process fresh brine directly in its DLE plant to extract lithium, and then transfer the spent brine (after Li-extraction) to its existing facilities to remove other useful chemicals and materials. The company estimates annual production of 20,000-25,000 tons of LCE from this brine through its DLE technology (Compass Minerals International Inc., 2021).

In terms of order of resource use, Compass Minerals plans to initially extract Li from the left-over brine that has been concentrated at different stages in its evaporation ponds (Compass Minerals, 2021, 2022). This is due to the high Li content of this residual brine, be it the most recently accumulated brine in evaporation reservoir (205-318 mg/liter) or that accumulated in the evaporation reservoirs after three years of solar evaporation (1,000-1,600 mg/liter) (Compass Minerals, 2021, 2022). The company estimates that Li production from this residual brine will account for ~65% of its overall Li production over the DLE plant's operational lifetime. Over the later years, the company will switch to using its interstitial brine flow for Li extraction (Li content in ambient brine flow is 55-60 mg/liter) (Compass Minerals, 2021, 2022).

In terms of its timeline, Compass Minerals is in the last stages of finalizing a DLE partner after having completed an 18-month assessment of multiple DLE technologies via pilot projects (Compass Minerals, 2022). It has also established arrangements with Minviro Ltd. to conduct life-cycle analysis of its proposed technology (Compass Minerals, 2022).

From a geological perspective, the biggest advantage of Compass Minerals' reserves is that unlike the geothermal brines in Salton Sea, these brines are shallow and have a favorable geo-chemistry with very low concentrations of transition elements (Rock Stock Channel, 2022). This suggests that Li production via DLE should be relatively inexpensive for the company vis-à-vis geothermal brine-based projects.

2.3.4 Standard Lithium

Standard Lithium Inc. set up their demonstration DLE plant in 2020 to extract Li from pre-existing brines in the Smackover formation in Arkansas under their flagship project *Smackover Arkansas* (Standard Lithium, 2019, 2021, 2022). These brines first began operation as oilwells since 1921, and have been subsequently used for bromine production since 1957 (Standard Lithium, 2022). Currently, these bromine brines are operated by LANXESS Inc., with whom Standard Lithium has set up a joint venture (JV) to use the spent brine (after bromine extraction) to produce battery grade LCE over a 25-year duration (Standard Lithium, 2021, 2022). Standard Lithium estimates a total indicated resource base of 3.14 million metric tons in these brines, with a projected average annual production potential of 20,900 metric tons of LCE (Standard Lithium, 2022).

In terms of its geology, Standard Lithium's brines are based in an area with dominant limestone and dolomite geology formation, meaning that the brine has high calcium carbonate content (Rock Stock Channel, 2022). The advantage with this formation is that unlike the geothermal brines in Salton Sea that have high silica and transition element content, these brines have low amounts of these materials. This helps to avoid the technology-intensive processing needed to remove silica and transition elements, suggesting that the likely costs of DLE processing may be lower for these brines than for their geothermal counterparts.

A second key constituent of the flagship *Smackover Arkansas* project is an optional JV of Standard Lithium with TETRA Technologies Inc. for brine leases located 25 miles west of the LANXESS project (Standard Lithium, 2022). These brines are also associated with the Smackover formation (but are not owned by LANXESS), and have been used primarily for crude oil and natural gas production, with spent brines discharged as waste. Standard Lithium's focus is on exploration, production, and Li extraction from these brine leases. The company projects annual production of 30,000 metric tons of battery-grade LiOH ($LiOH.H_2O$ over a 20-year plant lifetime (or 0.20 million metric tons of LCE), assuming Li content of 400 mg/liter of brine (Standard Lithium, 2022).

Standard Lithium is also exploring the potential for Li extraction at Bristol Lake in San Bernardino county in California (Standard Lithium, 2022). Bristol Lake is a flat, dry salt lake over ~155 km^2 in a 2,000 km^2 arid drainage basin, with the actual brine covering over 45,000 acres in this lake (Standard Lithium, 2022). Standard Lithium is in process of establishing business relationships with brine processing companies for exploration and commercial development rights for lithium extraction from this resource.

Regarding its technology, Standard Lithium uses its patented LiSTR technology to extract Li from the spent brine received from the LANXESS plant (Standard Lithium, 2019, 2021, 2022). The company's demonstration plant is designed to process 50 gallons/minute of spent brine (~100-150 metric tons of LCE production per year), and monitors the flow of all inputs and resultant fluids (Standard Lithium, 2019, 2021). The spent brine (with a temperature of 160°F) is filtered and sent into loading reactors and mixed with Standard Lithium's proprietary absorbent for 10 minutes. The reactors enable a thorough mixing of spent brine and absorbent to enable Li-ions to move into the absorbent (which is a fine-grained solid material).

Next, the loaded absorbent (with Li) moves to a three-stage washing process. Here, excess brine is removed, and the slurry (Li-containing brine + absorbent) is washed to remove the absorbent material and thicken the Li-containing part. The final washing-related step is stripping, where dilute hydrochloric acid (HCl) is added to thickened brine in the reactor to obtain concentrated lithium chloride (LiCl) solution. In the final step, the stripped LiCl is ultra-purified by passing it through ion-exchange membranes into a final tank, with the final concentrated LiCl collected for subsequent conversion to battery-grade LCE. Using its patented process, Standard Lithium claims to recover more than 90% of Li from its brine resource within a few hours (Standard Lithium, 2019, 2021, 2022). LiCl obtained via this process could also be used directly as feedstock for producing Li metal via electrolysis. More details on the process schematic are given in (Standard Lithium, 2019, 2021, 2022; Warren, 2021).

2.3.5 E3 Metals Corporation

E3 Metals Corporation is a lithium resource and technology company in Alberta, Canada (E3 Metals Corp, 2022). The company has outlined three major resources in the Leduc Formation – an expansive ancient roof complex over 2 km in the subsurface of Clearwater Area – with a combined inferred reserve base of 7 million metric tons of LCE (E3 Metals Corp, 2022). Their plan is to achieve > 90% recovery efficiency for Li from brines and reduce the impurities in their Li by > 99% to produce high-purity, battery-grade Li-chemicals, while avoiding any freshwater use and using 97% lesser land than in Li production from Salar brines. More details on all three projects of E3 Metals are given in Table 2.

Of its three projects (Table 2), the most prominent project is the Clearwater Project located in the south-central portion of the company's permit area. The reserve has an inferred resource base of 2.2 million metric tons, and E3 Metals aims to produce 20,000 metric tons of LiOH-H_2O per year from this reserve (~13,000 metric tons of LCE) over a 20-year project life (E3 Metals Corp, 2022). The company's plan is to pump Li-rich saline formation water into a central process facility, where Li will be extracted and purified, with the spent formation water reinjected back into the brine. Subsequently, Li-rich water will be treated to produce a clean Li-concentrate, which will be processed into high-grade Li-chemicals via electrolysis and crystallization.

E3 Metals is currently constructing a prototype DLE facility in their Calgary testing location for this project, while their other two projects (listed in Table 2) are in exploration and testing stages (E3 Metals Corp, 2022). Like with Standard Lithium, the company's brine reserves are located in a geology with high dolomite and limestone content and low concentration of silica and transition elements, which can ease the process of Li-extraction via DLE (Rock Stock Channel, 2022).

2.3.6 Other Resources

In addition to the above-mentioned projects, there are projects being undertaken by other companies as well. However, most of their details are not available in the public domain. Some of these are presented below.

Regarding geothermal brines in the Salton Sea, another company (apart from above-mentioned ones) that is attempting Li extraction in this area is Berkshire Hathaway through its renewable energy arm, BHE Renewables (Berkshire Hathaway Energy, 2022; Seeking Alpha, 2022). The company intends to set up a demonstration facility sometime in 2022 to assess the commercial viability of Li extraction from their brine reserves, towards a full-scale plant setup by 2026 with a capacity of 90,000 metric tons of annual lithium production (Seeking Alpha, 2022). However, more details about the project could not be obtained.

Schlumberger has been permitted to operate its Clayton Valley Pilot Plant Project – a Li brine extraction and chemical processing facility – close to the existing Silver Peak Li brine operated by Albemarle in Nevada (State of Nevada, 2021). The company's plan is to produce 65.3 tons of Li-based chemicals over an anticipated duration of 18 months, based on a technology approach described to the State of Nevada (State of Nevada, 2021). Initially, pumped brine will be reacted with dilute HCl, after which the modified brine will be polished by removing several ions from it to make it Li-rich. Subsequently, the brine will be passed through an ion exchange system, with magnesium and calcium ions replaced by sodium ions, and the system will be degenerated periodically using dilute sodium hydroxide (NaOH) and HCl. Additional ions will be removed to obtain the final Li-concentrate, which will be treated using RO to obtain concentrated LiCl. This LiCl will be reacted with sodium carbonate (Na_2CO_3) to obtain lithium carbonate, with a secondary step enabling its conversion to LiOH-H_2O. Apart from Li-based chemicals, this process schematic will also produce limestone ($CaCO_3$). Overall, the key focus of this project seems to be about demonstrating Schlumberger's DLE capabilities and highlighting its ability to provide technological solutions in this domain for larger companies interested in Li-extraction via this technology.

Another company working on this area is US Magnesium, which aims to extract Li from brines in the Great Salt Lake region (similar to Compass Minerals) (Gillie, 2019). The company's plan was to begin LCE production from its existing brines (up to 10,000 metric tons) in 2020 (Gillie, 2019), and reports suggest that their production has begun with the extracted Li being sold to Japan, Korea, and China for further processing (Penrod, 2021). Further details are unavailable.

3 PRELIMINARY ENVIRONMENTAL ANALYSIS: LIFE-CYCLE INVENTORY

Li-extraction from geothermal (and non-geothermal) brines is touted as an excellent economic proposition compared to conventional Li production from brines via evaporative concentration, as it enables the use of brines with lower Li content (Grant, 2019; Pell et al., 2020; Warren, 2021). At the same time, this route is also highlighted for its numerous environmental benefits over the conventional evaporative technology. When used for geothermal brines, DLE uses geothermal energy (produced using the same brine) for plant operation, potentially reducing its net-energy usage to that of the solar-based evaporation route (Grant, 2019, 2020b; Stringfellow & Dobson, 2021). Moreover, while nearly all of the brine water is lost in solar-based evaporative concentration, in DLE, it is reinjected back as spent brine into the reserve, thereby avoiding water loss effects (Grant, 2019, 2020a; Pell et al., 2020; Stringfellow & Dobson, 2021; Warren, 2021). As mentioned earlier, *co-production of Li chemicals with geothermal power is estimated to reduce land requirement by almost ~10,000 times compared to evaporation-based projects*, assuming that both types of projects produce the same amount of Li chemicals (Grant, 2019; Pell et al., 2020).

Despite the aforementioned advantages, any holistic environmental analysis of Li-extraction from these brines requires evaluating the environmental impacts of the entire life-cycle of this process. This must include all the processes associated with Li extraction from brines, along with all the processes associated with the production of intermediate materials and energy sources used in Li extraction, beginning with the extraction and refining of their respective raw materials. However, despite the above-mentioned benefits claimed in favor of Li extraction via DLE, only one study of the life-cycle environmental analysis of DLE could be obtained in our literature review of this technology. Due to the lack of any alternative data, we use this study (Huang et al., 2021) to introduce the life-cycle inventory for DLE production from geothermal brines as a separate section in the updated GREET model (in the Li_Chemicals sheet of GREET2 model). Key details of this inventory analysis are provided below.

3.1 Process Flow

Huang et al. (2021) characterize the life-cycle inventory for DLE-based Li extraction from geothermal brines, based on laboratory-scale data and chemical stoichiometry along with empirical formulas for various processes to scale up these lab-scale results to industrial-scale production. Their research considers the production of both lithium carbonate (Li_2CO_3) and lithium hydroxide ($LiOH/LiOH.H_2O$) from geothermal brines.

Figure 3 shows the production pathway reported by Huang et al. (2021), consisting of four steps: (a) Sorbent synthesis; (b) Column extraction; (c) Forward osmosis; and (d) Li-chemical production.

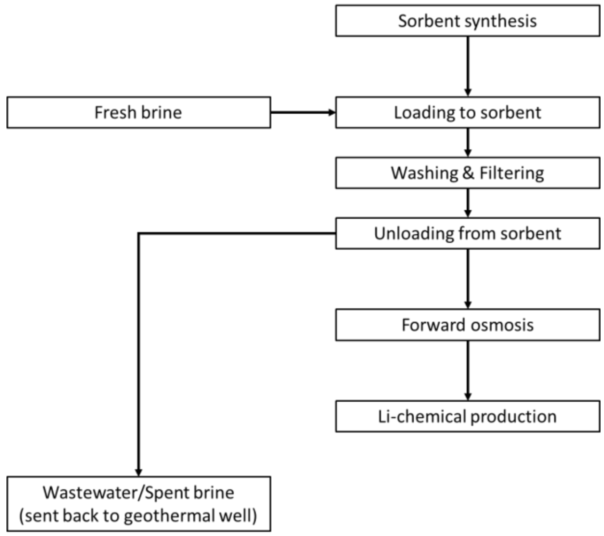

Figure 3 Production pathway for Li extraction from geothermal brines (based on (Huang et al., 2021))

In the first step, sorbent used for the DLE process is synthesized (LDH or lithium-aluminum-layered double hydroxide chloride) using lithium hydroxide (LiOH), hydrochloric acid (HCl), aluminum hydroxide ($Al(OH)_3$), and deionized water. Subsequently, in column extraction, lithium chloride (LiCl) from geothermal brine (Li content: 0.194 g/liter) is loaded onto this sorbent column, and then washed and stripped to unload the sorbent and remove concentrated LiCl. The spent brine (inclusive of wastewater) is reinjected back into the geothermal well. Next, stripped LiCl (Li content: 40 g/liter) is further concentrated into a denser solution (Li content: 174 g/liter) by absorbing water from it using a poly(vinylidene fluoride) (PVDF) hollow fiber membrane to absorb water. In the final step, concentrated LiCl is reacted with sodium carbonate (soda ash) at a 70% conversion rate to produce technical-grade lithium carbonate, which is purified further by converting it into a soluble bicarbonate and reconverting back to obtain battery-grade lithium carbonate (Li_2CO_3). To produce battery-grade lithium hydroxide (LiOH), technical-grade Li_2CO_3 is reacted with calcium hydroxide (lime), with the reaction byproduct (calcium carbonate) sent to waste stream. More details on the process flow and associated chemical reactions are provided in Huang et al. (2021).

3.2 Material and Energy Inputs

Table 3 provides the material and energy inputs for all four processes (sorbent synthesis, column extraction, forward osmosis, and Li-chemical production), as obtained from (Huang et al., 2021). For each process, these inputs are given on per US ton of intermediate material produced from the process (e.g., for LDH synthesis, inputs are given per US ton of LDH output; for column extraction, they are given per US ton of stripped LiCl solution; etc.). The inputs account for the water content that is present in the various solutions (geothermal brine, stripped and concentrated LiCl solutions).

Table 3 Material and energy inputs of DLE process (DLE from geothermal brines; values on US ton/US ton of intermediate)

Materials	**Processes**					**Total**	
	Sorbent synthesis	**Column extraction**	**Forward osmosis**	**Li-chemicals**		**Li-chemicals**	
Intermediate Output	LDH	Stripped LiCl	Concentrated LiCl	Li_2CO_3	LiOH	Li_2CO_3	LiOH
Material Inputs (US ton/US ton of intermediate output)							
Geothermal brine[a]		809				8,460	13,739
Sorbent		0.041					
Stripped solution[b]			1.110				
Concentrated LiCl solution[c]				9.421			
Li_2CO_3					1.624		
LiOH (not DLE output)	0.098					0.042	0.068
$Al(OH)_3$	0.641					0.275	0.446
HCl	0.150					0.064	0.104
Water	0.297	40.94			8.141	428.25	703.618
NaCl		0.117				1.224	1.987
PVDF			2.363×10^{-6}				
Na_2CO_3				2.049		2.049	3.328
$Ca(OH)_2$					1.628		1.628
Energy inputs (mmBtu/US ton of intermediate output)							
Electricity	1.862	0.254	0.281	1.079	6.146	7.181	17.808

[a]Geothermal brine (0.194 g/liter; rest assumed as water)
[b]Stripped solution (40 g/liter; rest assumed as water)
[c]Concentrated LiCl solution (174 g/liter; rest assumed as water)

4 CONCLUSIONS AND FUTURE WORK

Global demand for lithium has shown a considerable jump amidst the growing need for transport electrification to reduce greenhouse gas emissions. This has also sparked an increasing focus in the United States to strengthen its battery supply chain by developing economically viable resource pathways to explore its various Li-resources, including clays, hard rocks, and brines. Among these, brines have gained considerable traction due to their presence across multiple regions in the United States and North America, substantial Li-content (~100-200 mg/L), and the advent of DLE technology has accelerated the economic viability of Li extraction from such brines. DLE is advocated in particular for both its economic and environmental benefits, especially as it can extract Li from low Li-content brines and is estimated to use much lesser land than its evaporative processing counterpart. However, any environmental assessment of DLE is only possible through its holistic assessment across the entire life cycle.

In this report, we discuss the major domestic initiatives on commercializing Li extraction from existing brines within the United States and North America by different companies. We list important details of these projects, including brine locations, projected production levels (and the year in which these will be achieved), and the specifics of their respective DLE technology employed. We also report a preliminary life-cycle inventory of DLE technology based on an existing reference that is incorporated in this year's version of Argonne's GREET model to determine the energy use and emissions of implementing this technology for Li extraction.

Future efforts are needed to further improve upon the preliminary inventory reported here for DLE technology and to make it more robust. These efforts should both investigate more DLE pathways in both the United States and North America, as well as explore alternative pathways of domestic Li production, especially using clays. As and when such efforts are accomplished, future avenues to update the inventory for this technology in GREET will be explored.

REFERENCES

Al Radi, M., Al-Isawi, A. O., Abdelghafar, A. A., Qiyas, A. A. F., Almallahi, M., Khanafer, K., & Assad, M. E. H. (2022). Recent progress, economic potential, and environmental benefits of mineral recovery geothermal brine treatment systems. *Arabian Journal of Geosciences, 15*(9), 1–27. https://doi.org/10.1007/S12517-022-10115-4

Azevedo, M., Baczyńska, M., Hoffman, K., & Krauze, A. (2022). *How lithium mining is fueling the EV revolution*. https://www.mckinsey.com/industries/metals-and-mining/our-insights/lithium-mining-how-new-production-technologies-could-fuel-the-global-ev-revolution

Berkshire Hathaway Energy. (2022). *Berkshire Hathaway Energy*. Berkshire Hathaway Energy. https://www.brkenergy.com/

Compass Minerals. (2021, October 18). *Our Lithium Vision on Vimeo*. Vimeo. https://vimeo.com/635590099/944dd5f606

Compass Minerals. (2022). *Compass Minerals* . https://www.compassminerals.com/

Compass Minerals International Inc. (2021). *SEC Technical Report Summary - Initial Assessment Lithium Mineral Resource Estimate*. https://s22.q4cdn.com/834578860/files/doc_presentations/2021/07/Compass-Minerals-Ogden-Lithium-RE_Report_Final.pdf

Controlled Thermal Resources. (2022). *CT Thermal*. https://www.cthermal.com/

E3 Metals Corp. (2022). *E3 Metals Corp*. https://www.e3metalscorp.com/

EnergySource Minerals. (2021). *EnergySource Minerals*. EnergySource Minerals. https://www.esminerals.com/

Gillie, T. (2019, April 25). *US Mag breaks ground on lithium facility*. Tooele Transcript Bulletin. http://tooeleonline.com/us-mag-breaks-ground-on-lithium-facility/

Grant, A. (2019). *The Brownfield Lithium Brine Opportunities of North America*. Jade Cove Partners. https://www.jadecove.com/research/

Grant, A. (2020a, February). *Is Lithium Brine Water?* Jade Cove Partners. https://www.jadecove.com/research/

Grant, A. (2020b, April). *From Catamarca to Qinghai - The Commercial Scale DLE Operations*. Jade Cove Partners. https://www.jadecove.com/research/

Huang, T. Y., Pérez-Cardona, J. R., Zhao, F., Sutherland, J. W., & Paranthaman, M. P. (2021). Life Cycle Assessment and Techno-Economic Assessment of Lithium Recovery from Geothermal Brine. *ACS Sustainable Chemistry and Engineering*, *9*(19), 6551–6560. https://doi.org/10.1021/ACSSUSCHEMENG.0C08733/SUPPL_FILE/SC0C08733_SI_001.PDF

Jade Cove Partners. (2022). *Jade Cove Partners*. https://www.jadecove.com/

Kelly, J. C., Wang, M., Dai, Q., & Winjobi, O. (2021). Energy, greenhouse gas, and water life cycle analysis of lithium carbonate and lithium hydroxide monohydrate from brine and ore resources and their use in lithium ion battery cathodes and lithium ion batteries. *Resources, Conservation and Recycling*, *174*, 105762. https://doi.org/10.1016/J.RESCONREC.2021.105762

Neupane, G., & Wendt, D. S. (2017). Potential economic values of minerals in brines of identified hydrothermal systems in the US. *GRC Transactions*. https://www.osti.gov/servlets/purl/1402042

Pell, R., Grant, A., & Deak, D. (2020, May). *Geothermal Lithium: The Final Frontier of Decarbonization* . Jade Cove Partners. https://www.jadecove.com/research/

Penrod, E. (2021, December 10). *Lithium mining in Utah could be the next big industry* . Utah Business. https://www.utahbusiness.com/lithium-mining-in-utah-is-a-big-deal/

Rock Stock Channel. (2022, January 22). *E50: North America's Unconventional Lithium Promise*. Rock Stock Channel. https://www.youtube.com/watch?v=KrWeRQMvebs

Seeking Alpha. (2022, April 29). *Berkshire Hathaway: Lithium Prospector*. Seeking Alpha. https://seekingalpha.com/article/4504924-berkshire-hathaway-warren-buffett-lithium-prospector

Standard Lithium. (2019, August 1). *Standard Lithium LiSTR - Direct Lithium Extraction Demo Plant*. YouTube. https://www.youtube.com/watch?v=6XeZ2B9Hi6M

Standard Lithium. (2021, July 10). *LiSTR Direct Lithium Extraction Plant Full Video Tour 4 0 1*. Youtube. https://www.youtube.com/watch?v=QEGBc2znFdw

Standard Lithium. (2022). *Standard Lithium Ltd. (SLI)*. Standard Lithium. https://www.standardlithium.com/

State of Nevada. (2021). *FACT SHEET (Pursuant to Nevada Administrative Code [NAC] 445A.401) - Draft*. https://ndep.nv.gov/uploads/documents/NEV2020114dfsFY21.pdf

Stringfellow, W. T., & Dobson, P. F. (2021). Technology for the Recovery of Lithium from Geothermal Brines. *Energies 2021, Vol. 14, Page 6805*, *14*(20), 6805. https://doi.org/10.3390/EN14206805

The White House. (2021). *Building Resilient Supply Chains, Revitalizing American Manufacturing, and Fostering Broad-Based Growth*. https://www.whitehouse.gov/wp-content/uploads/2021/06/100-day-supply-chain-review-report.pdf

Toba, A. L., Nguyen, R. T., Cole, C., Neupane, G., & Paranthaman, M. P. (2021). U.S. lithium resources from geothermal and extraction feasibility. *Resources, Conservation and Recycling*, *169*, 105514. https://doi.org/10.1016/J.RESCONREC.2021.105514

US DOE. (2020). *Critical Minerals and Materials: U.S. Department of Energy's Strategy to Support Domestic Critical Mineral and Material Supply Chains (FY 2021-FY 2031)*. https://doi.org/10.3133/70194932

USGS. (2022). Mineral Commodity Summaries 2022. In *Mineral Commodity Summaries*. https://doi.org/10.3133/MCS2022

Ventura, S., Bhamidi, S., Hornbostel, M., & Nagar, A. (2020). *Selective Recovery of Lithium from Geothermal Brines*. https://www.sri.com

Warren, I. (2021). *Techno-Economic Analysis of Lithium Extraction from Geothermal Brines*. https://www.nrel.gov/docs/fy21osti/79178.pdf

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