U.S. DEPARTMENT OF ENERGY

Sandia National Laboratories

Clean Energy States Alliance

Domestic Lithium:

What The US Government is Doing to Increase Supply

October 10, 2023

A Presentation of the Energy Storage Technology Advancement Partnership (ESTAP)

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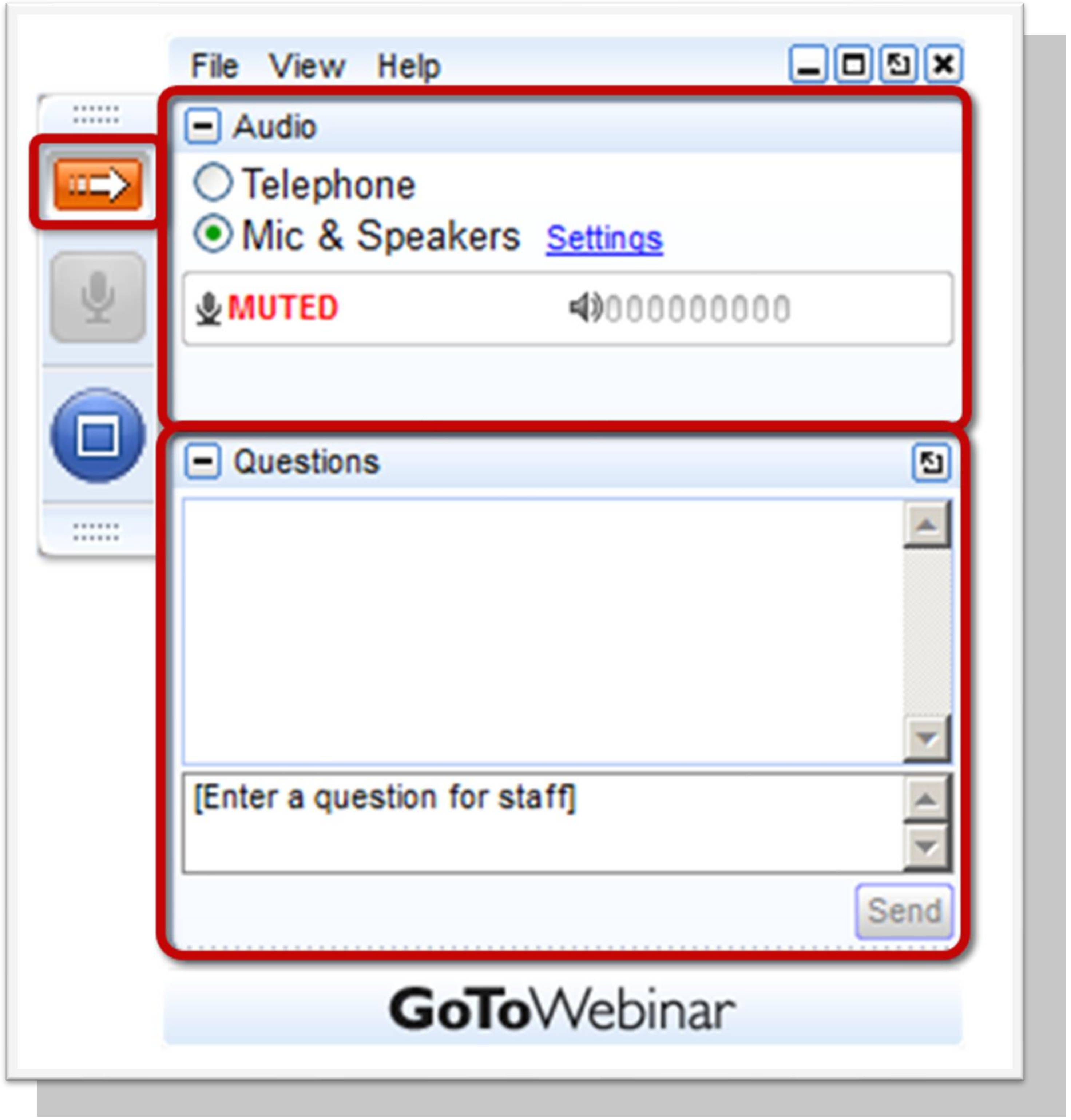

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20 CleanEnergy States Alliance

The Clean Energy States Alliance (CESA) is a national, nonprofit coalition of public agencies and organizations working together to advance clean energy.

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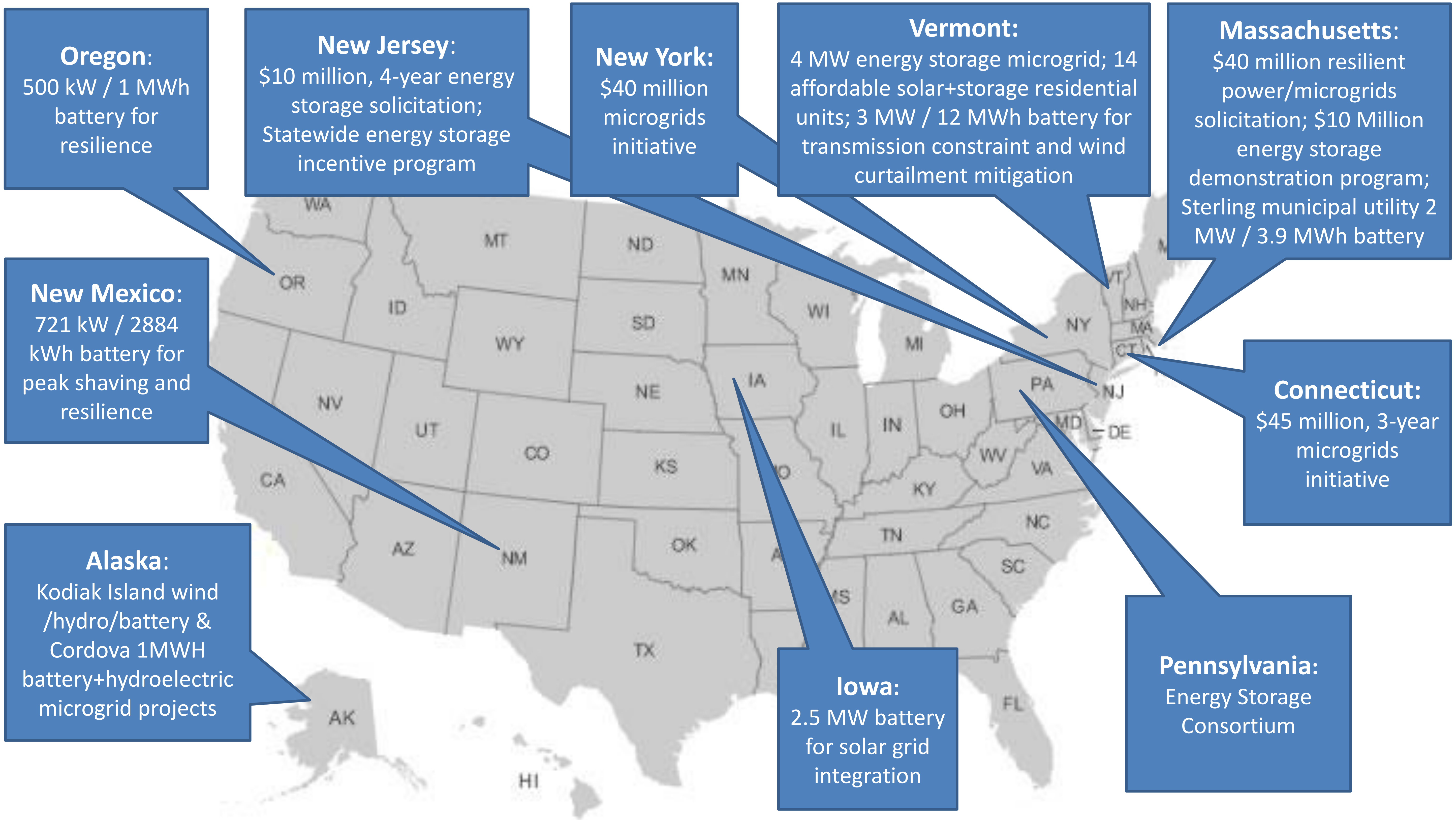
Energy Storage Technology Advancement Partnership (ESTAP)

Conducted under contract with Sandia National Laboratories, with funding from US DOE Office of Electricity.

- Facilitate public/private partnerships to support joint federal/state energy storage demonstration project deployment
- Support state energy storage efforts with technical, policy and program assistance
- Disseminate information to stakeholders through webinars, reports, case studies and conference presentations

www.cesa.org/ESTAP

Technical & Policy Support for Energy Storage Across the Nation



Oregon: 500 kW / 1 MWh battery for resilience

New Jersey: $10 million, 4-year energy storage solicitation; Statewide energy storage incentive program

New York: $40 million microgrids initiative

Vermont: 4 MW energy storage microgrid; 14 affordable solar+storage residential units; 3 MW / 12 MWh battery for transmission constraint and wind curtailment mitigation

Massachusetts: $40 million resilient power/microgrids solicitation; $10 Million energy storage demonstration program; Sterling municipal utility 2 MW / 3.9 MWh battery

New Mexico: 721 kW / 2884 kWh battery for peak shaving and resilience

Connecticut: $45 million, 3-year microgrids initiative

Alaska: Kodiak Island wind /hydro/battery & Cordova 1MWH battery+hydroelectric microgrid projects

Iowa: 2.5 MW battery for solar grid integration

Pennsylvania: Energy Storage Consortium

Thank You!

Dr. Imre Gyuk
Director, Energy Storage Research,
U.S. Department of Energy

Waylon Clark
Energy Storage Program Demonstration Team Lead,
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NYSERDA's State Energy Financing Fund and DOE's Loan Programs Office: Financing Clean Energy at the State Level (11/1)

Building the Foundation for Energy Resilient Communities: Clean Energy Group's Resilient Power Funding Programs' 2022 Impact (11/14)

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Energy Storage -
With Lithium and Without

IMRE GYUK, CHIEF SCIENTIST
ENERGY STORAGE RESEARCH, DOE-OE

10-10-23

Energy Storage has finally reached National Scale

NORTH AMERICAN BATTERY INITIATIVES

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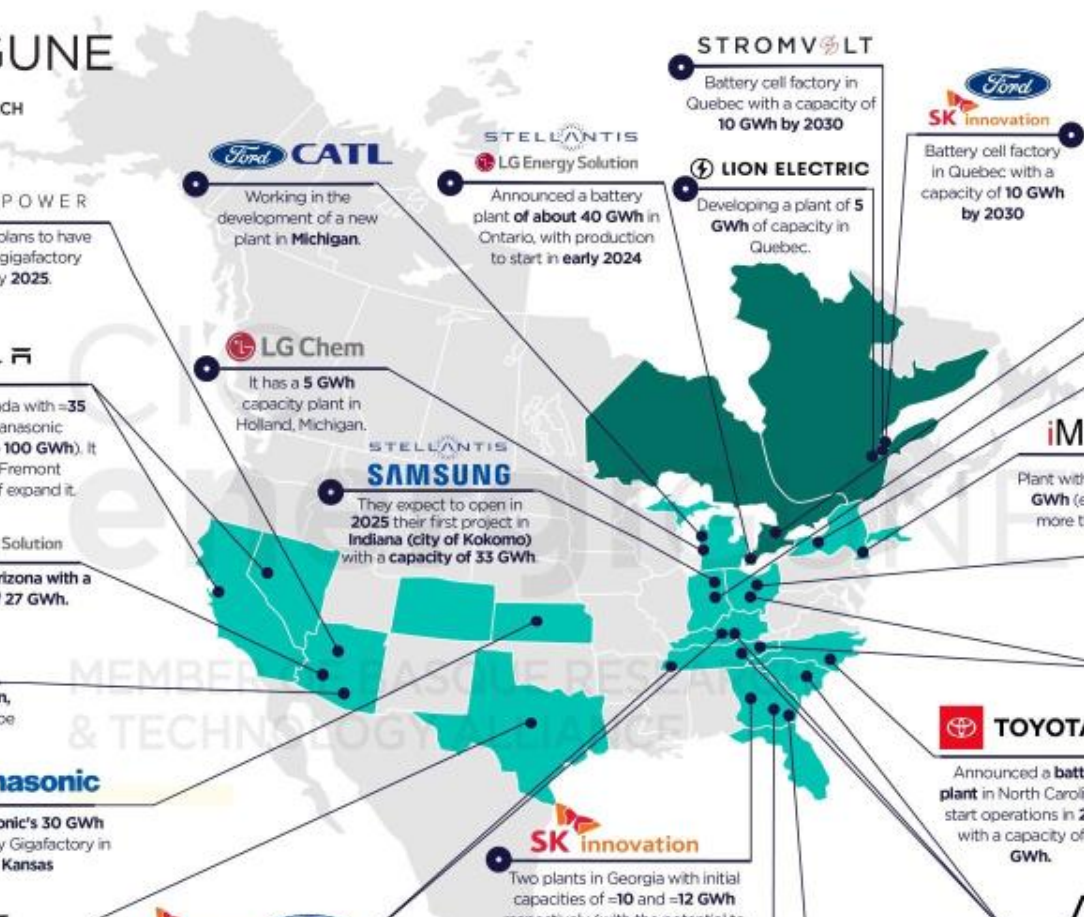

KOREPOWER
Kore Power plans to have its **12 GWh** gigafactory open by **2025**.

TESLA
Operational plant in Nevada with ≈**35 GWh** operated with Panasonic (expected to expand up to **100 GWh**). It also has a pilot line in Fremont (California) with plans of expand it.

LG Energy Solution
Gigafactory **Arizona with a capacity of 27 GWh.**

ABF
Gigafactory in **Tucson, Arizona** (capacity to be defined)

Panasonic
Panasonic's 30 GWh capacity Gigafactory in **Kansas**

TESLA
Tesla expects to expand the gigafactory in Austin (Texas) which is already operating up to **100 GWh**.

SK innovation **Ford**
Development of the **"Blue Oval City"** project in Kentucky with **two gigafactories** and a third one in Staton (Tennessee), each one with a capacity of **43 GWh**

Ford **CATL**
Working in the development of a new plant in **Michigan**.

LG Chem
It has a **5 GWh** capacity plant in Holland, Michigan.

STELLANTIS
SAMSUNG
They expect to open in **2025** their first project in **Indiana (city of Kokomo)** with a **capacity of 33 GWh**.

STELLANTIS
LG Energy Solution
Announced a battery plant **of about 40 GWh** in Ontario, with production to start in **early 2024**

STROMVOLT
Battery cell factory in Quebec with a capacity of **10 GWh by 2030**

LION ELECTRIC
Developing a plant of **5 GWh** of capacity in Quebec.

Ford
SK innovation
Battery cell factory in Quebec with a capacity of **10 GWh by 2030**

SK innovation
Two plants in Georgia with initial capacities of ≈10 and ≈**12 GWh** respectively (with the potential to increase beyond **25 GWh**) to supply OEMs such as Hyundai.

FREYR **KOCH**
They have announced a **joint venture (50% each)** to start building a **gigafactory in Georgia**

HYUNDAI
LG Chem
Starting a new facility in 2025 with 30GWh of capacity **in Savannah, Georgia.**

Volkswagen
Volkswagen's Canadian Gigafactory in **St. Thomas (Ontario)**, with a planned capacity of **90 GWh**.

gm
SAMSUNG
Developing a new plant for 2026 in Indiana.

TESLA
Operational plant in Buffalo dedicated to solar cells of ≈ **2 GWh**).

iM3NY
Plant with a capacity of **1 GWh** (expandable to more than **15 GWh**)

LG Chem **HONDA**
New facility to be completed in 2025 in **Ohio** (40 GWh).

ultium cells
This joint venture between LG Energy solutions and GM involves a plant in Lordstown (Ohio, with **30-35 GWh**) and in Spring Hill (Tennessee) (with similar capacity).

TOYOTA
Announced a **battery plant** in North Carolina to start operations in **2025** with a capacity of **12 GWh.**

AESC
Currently working in 3 different initiatives in for several OEMs (**BMW, Nissan and Mercedes** respectively).

STELLANTIS
SAMSUNG
A **second project** has been announced, location to be defined. It will open in **2027** and will have a **capacity of 34 GWh**.

Source: Own elaboration from public information

Version 6. Last update: 09/2023

…. also in Europe
Australia, China, Korea ….

EUROPEAN GIGAFACTORIES MAP

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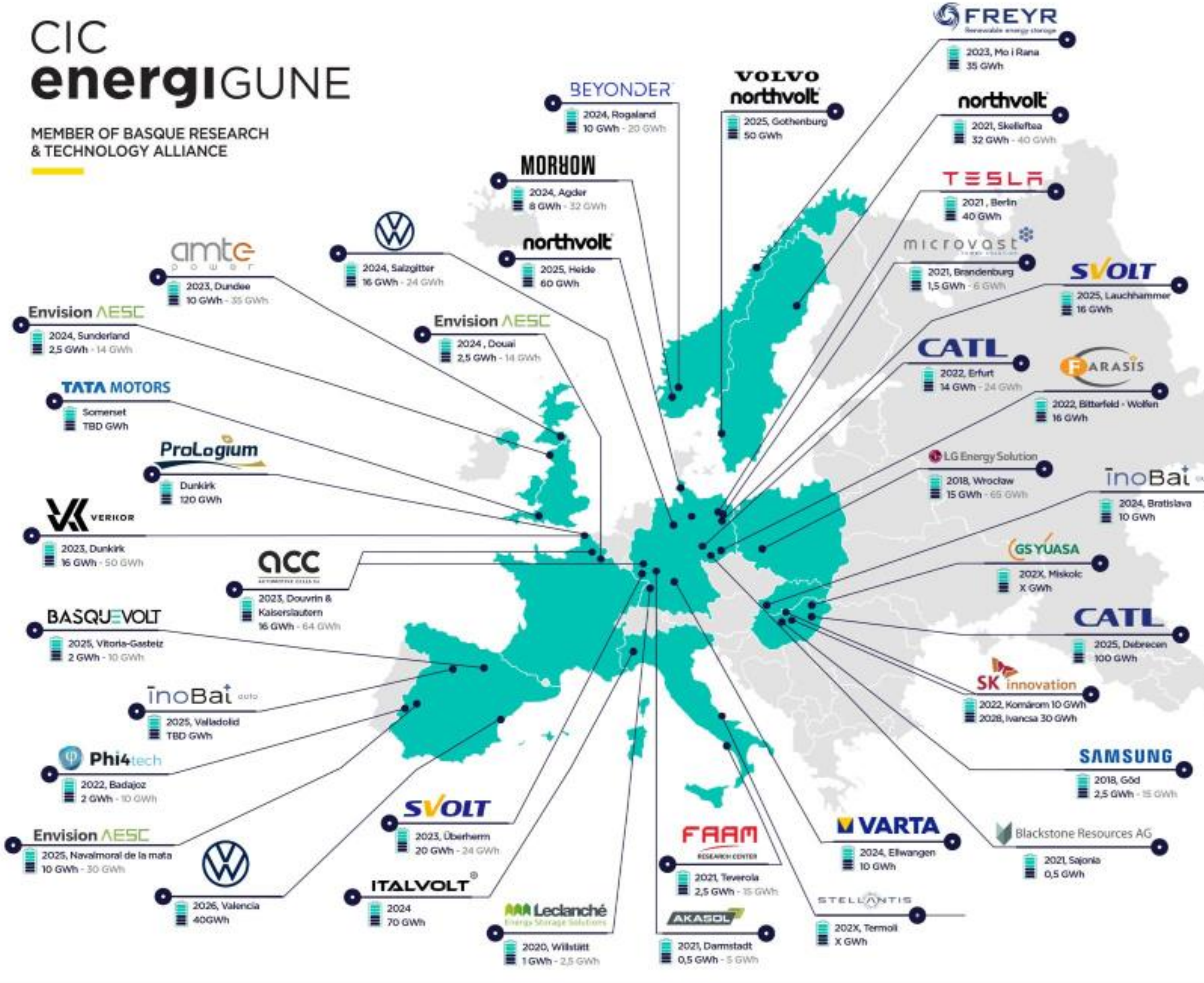


amte power
2023, Dundee
10 GWh - 35 GWh

Envision AESC
2024, Sunderland
2,5 GWh - 14 GWh

TATA MOTORS
Somerset
TBD GWh

ProLogium
Dunkirk
120 GWh

VERKOR
2023, Dunkirk
16 GWh - 50 GWh

acc
2023, Douvrin &
Kaiserslautern
16 GWh - 64 GWh

BASQUEVOLT
2025, Vitoria-Gasteiz
2 GWh - 10 GWh

inoBat auto
2025, Valladolid
TBD GWh

Phi4tech
2022, Badajoz
2 GWh - 10 GWh

Envision AESC
2025, Navalmoral de la mata
10 GWh - 30 GWh

VW
2026, Valencia
40GWh

SVOLT
2023, Überherrn
20 GWh - 24 GWh

ITALVOLT®
2024
70 GWh

Leclanché Energy Storage Solutions
2020, Willstätt
1 GWh - 2,5 GWh

VW
2024, Salzgitter
16 GWh - 24 GWh

Envision AESC
2024 , Douai
2,5 GWh - 14 GWh

MORROW
2024, Agder
8 GWh - 32 GWh

northvolt
2025, Heide
60 GWh

BEYONDER
2024, Rogaland
10 GWh - 20 GWh

VOLVO northvolt
2025, Gothenburg
50 GWh

FREYR Renewable energy storage
2023, Mo i Rana
35 GWh

northvolt
2021, Skelleftea
32 GWh - 40 GWh

TESLA
2021 , Berlin
40 GWh

microvast
2021, Brandenburg
1,5 GWh - 6 GWh

SVOLT
2025, Lauchhammer
16 GWh

CATL
2022, Erfurt
14 GWh - 24 GWh

FARASIS
2022, Bitterfeld - Wolfen
16 GWh

LG Energy Solution
2018, Wroclaw
15 GWh - 65 GWh

inoBat auto
2024, Bratislava
10 GWh

GS YUASA
202X, Miskolc
X GWh

CATL
2025, Debrecen
100 GWh

SK innovation
2022, Komárom 10 GWh
2028, Ivancsa 30 GWh

SAMSUNG
2018, Göd
2,5 GWh - 15 GWh

Blackstone Resources AG
2021, Sajonia
0,5 GWh

VARTA
2024, Ellwangen
10 GWh

STELLANTIS
202X, Termoli
X GWh

FAAM RESEARCH CENTER
2021, Teverola
2,5 GWh - 15 GWh

AKASOL
2021, Darmstadt
0,5 GWh - 5 GWh

BYD
202X
34 GWh

ROSATOM
2025, Location in Russia
(TBD) 2 GWh

VW
2 gigafactories announced
to upcoming years
(locations TBD)

EUROCELL
2025, Location in
Netherlands (TBD)

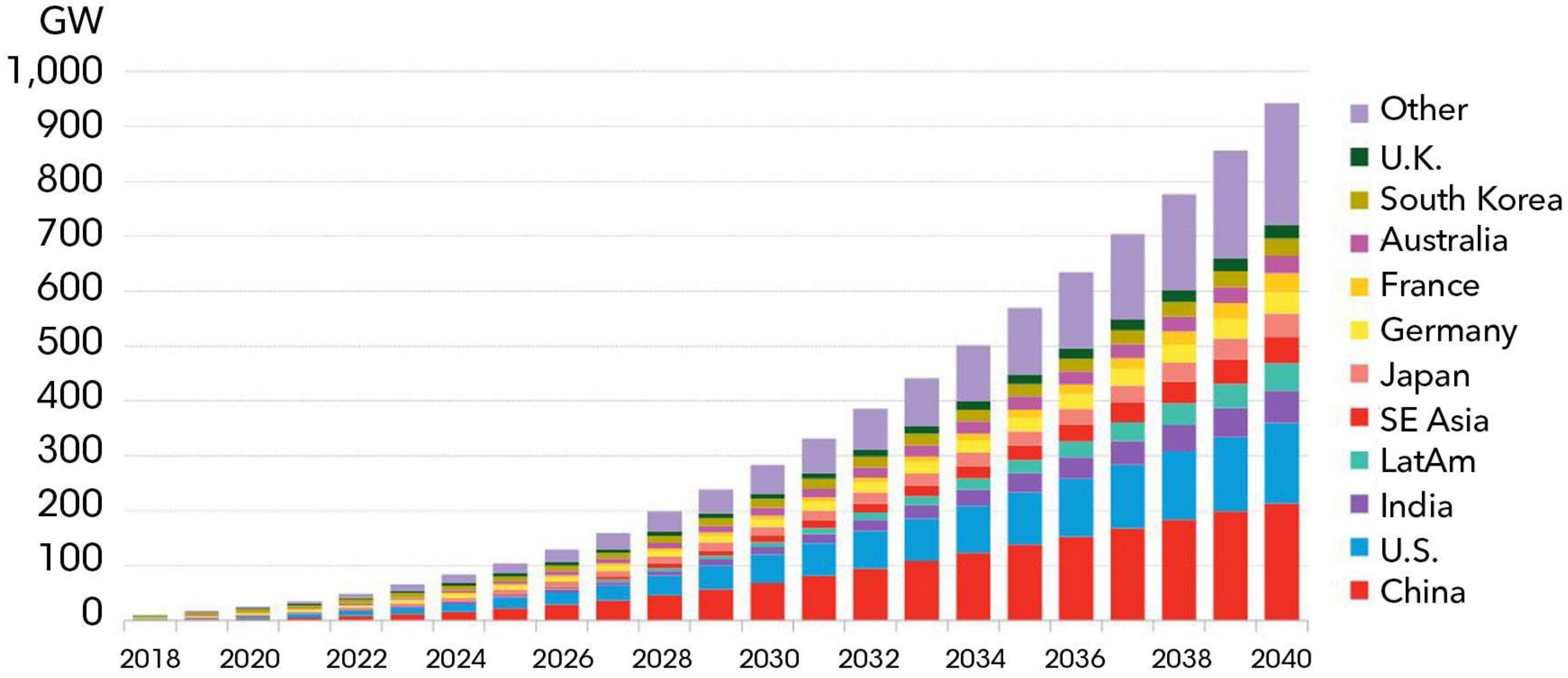
LG
Location, year and
capacity to be defined

Source: Own elaboration from public information

Version 13. Last update: 09/2023

Cumulative Deployment of Storage
is continually Increasing
around the World.

Global cumulative storage deployments



Source: BloombergNEF

Lithium Demand vs Supply Forecast

source: Benchmark Minerals

Lithium Supply and Production
will become Constant
and fall short of Demand!

By 2040, Demand will be
twice the available Supply!

Lithium Dominates both
Stationary and
Vehicle applications

However,
with increasing Penetration
and Limited Resources
there will be Competition
and increasing Prices!

Vehicle Batteries
must have high Energy Density
while
Stationary Applications
must have Low Price

Lithium supply cannot cover
Vehicular and Stationary Supply.
In a Resource Competition
Vehicle Applications will win!

Unless domestic Li sources
in huge amounts
suddenly become available
Stationary Applications
will have to turn to new;
cheaper types of Batteries
Relying on more
Earth abundant Materials

ZnBr Flow Batteries,
Redox Flow Batteries, V, Zn, Fe,
Organic Electrolytes
Solid State, Na-ion, L/A

Invinity: Oxford 5 MWh
Commiss. July 5, 2022
Planned: Australia 8MWh
+6MWh PV ► 10GWh/year
Vanadium supply line!

ESS: Stanwell Power Station
Queensland, Australia
150MW / 8-10 hours
Option for 200MW total
Iron Flow Battery

Such Batteries
will be appropriate
for medium Duration Use -
4 hours to 12 hours.

Meanwhile,
Lithium-ion Batteries
will find Application
For Transportation:
Cars, Trucks, Trains, and Planes

But I may be Wrong,
and the Future is in Na-ion
for both Stationary and Vehicle
Applications!

JAC EV powered by 25kWh Na-ion Battery – 250 km/charge

Direct lithium extraction (DLE) from geothermal brines and clay minerals

M. Parans Paranthaman, J. Kumar, I. Popovs, B. A. Moyer,
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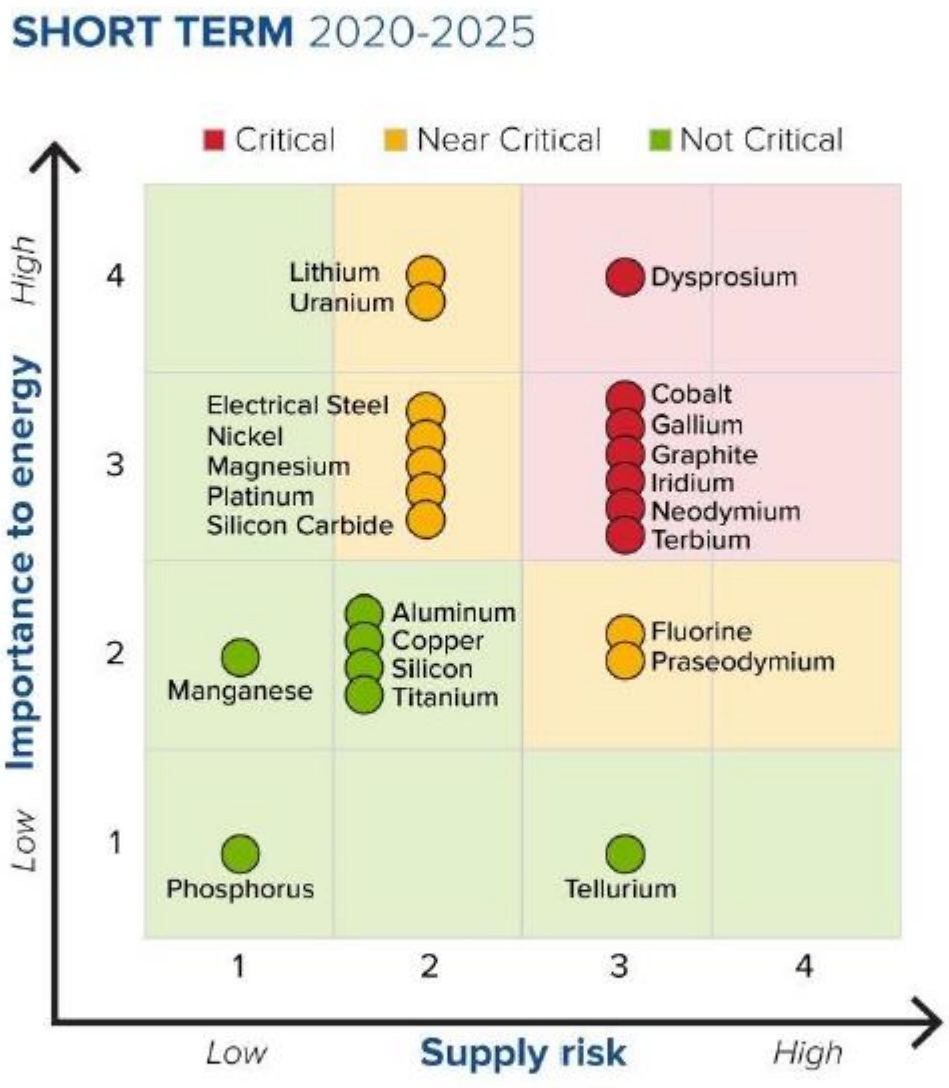
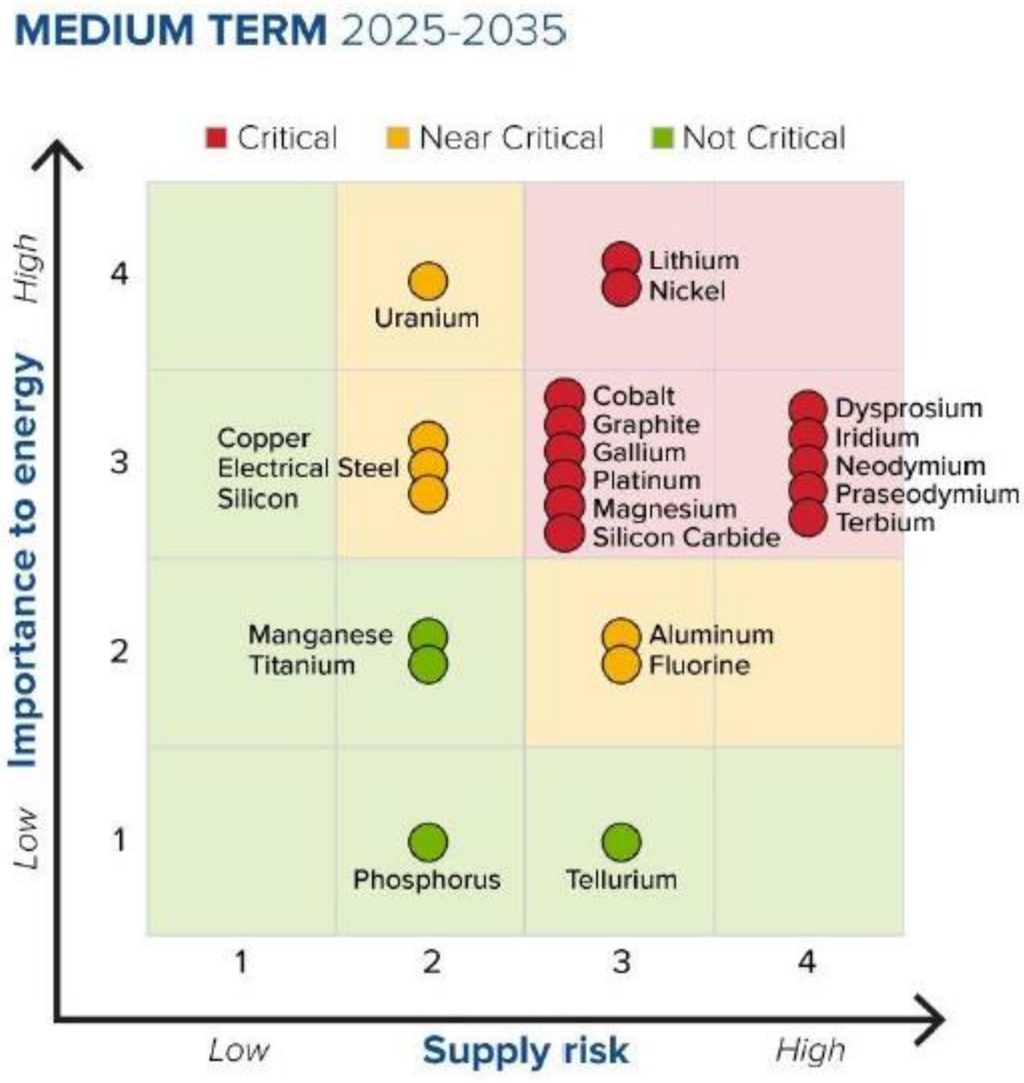
This research was supported by the Critical Materials Institute, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office. Part of sorbent research was supported by EERE, GTO TCF program.

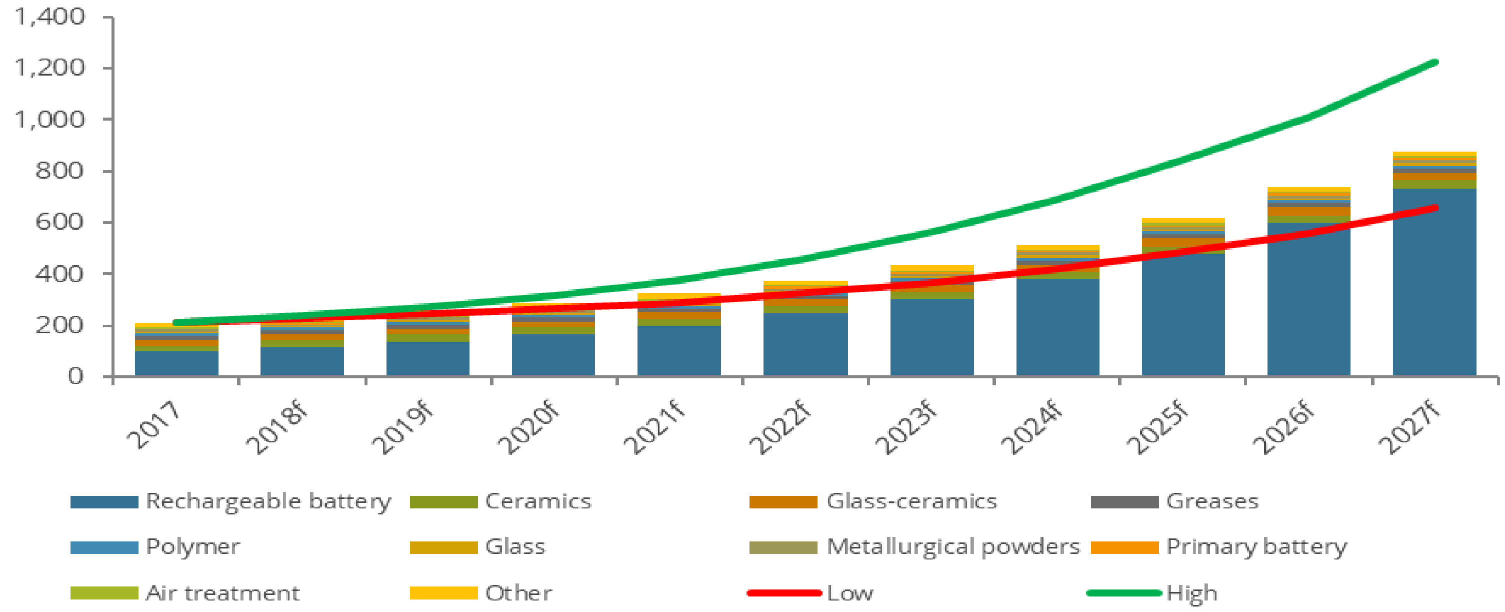
What are Critical Materials and Critical Minerals?





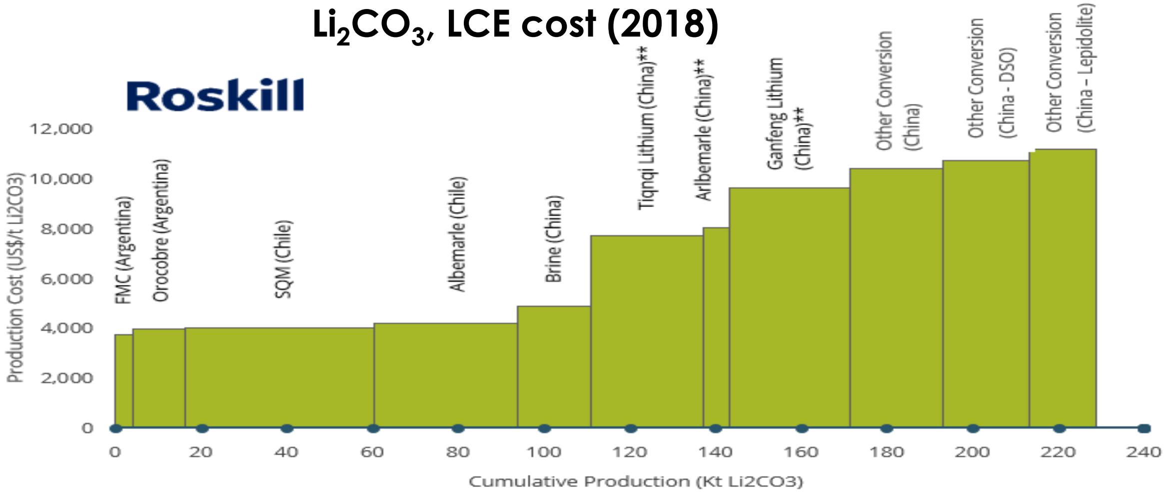
U.S. Department of Energy Releases 2023 Critical Materials Assessment to Evaluate Supply Chain Security for Clean Energy Technologies, July 31, 2023

Lithium forecast (x 1000t LCE)

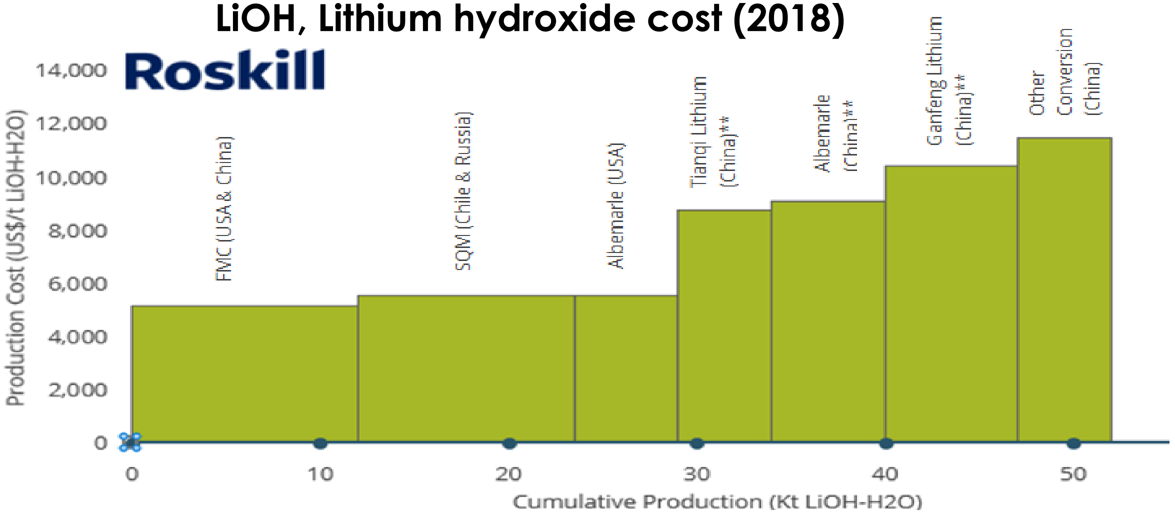


Goldman expects lithium carbonate prices to fall to **$US53,000** a ton in 2023 before plunging to $US11,000/t in 2024 and 2025, and lithium hydroxide prices to ease to $US58,650/t and then $US12,500/t over the same period.

Li_2CO_3, LCE cost (2018)

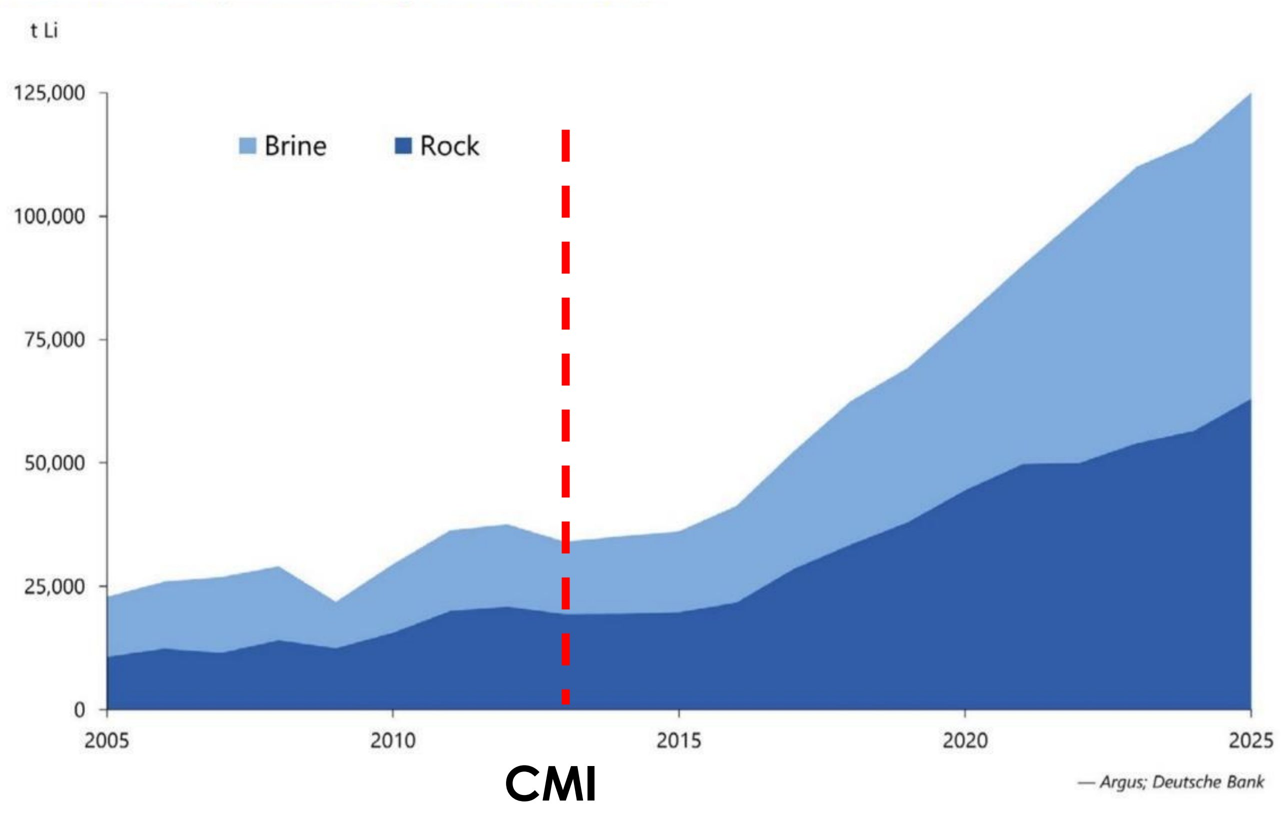


LiOH, Lithium hydroxide cost (2018)



Source: Roskill (2018) Lithium: Global Industry, Markets and Outlook

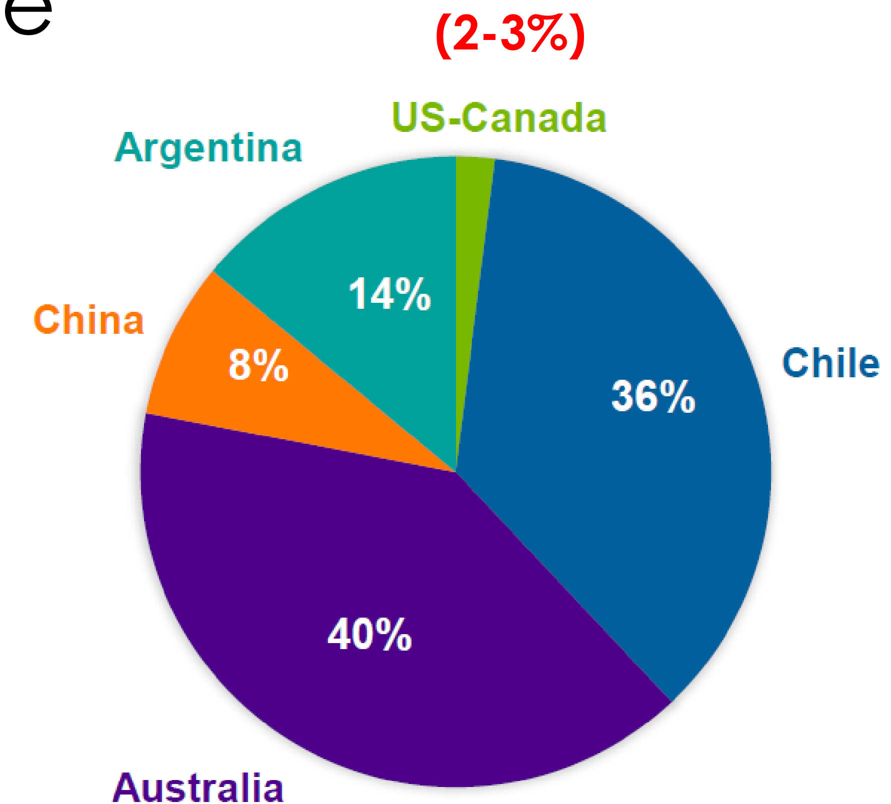
Global lithium production by source



— Argus; Deutsche Bank

Brines play a major role in lithium production

Citation: Stringfellow, W.T.; Dobson, P.F. Technology for the Recovery of Lithium from Geothermal Brines. Energies **2021**, 14, 6805. https://doi.org/10.3390/en14206805



AUSTRALIA
Greenbushes
Mt. Cattlin
Mt. Marion
Wodgina (starting)

CHINA
Sichuan (Jiajika, Maekang, Lijiagu)
Jiangxi (Yichun, Heynan)
Xinjiang (Koktokay)

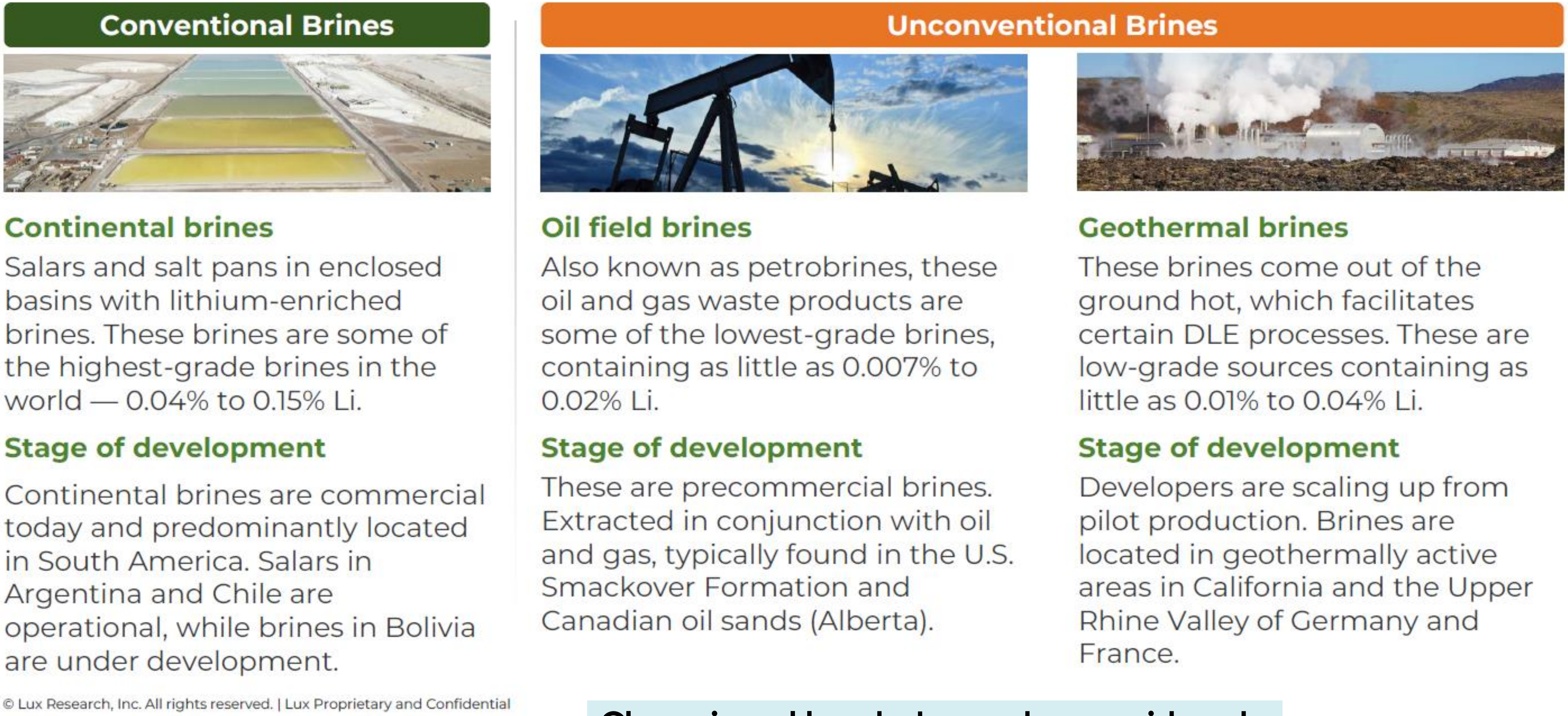
CHINA
Taijinar (Citic, QLL)
Zhabuye (Tibet)
Chaerhan (QSLG)

ARGENTINA
Salar de Hombre Muerto (FMC)
Olaroz (ORE)

CHILE
Salar de Atacama (SQM, ALB)

Source: SQM

DLE can target conventional and unconventional brines



Conventional Brines

Continental brines

Salars and salt pans in enclosed basins with lithium-enriched brines. These brines are some of the highest-grade brines in the world — 0.04% to 0.15% Li.

Stage of development

Continental brines are commercial today and predominantly located in South America. Salars in Argentina and Chile are operational, while brines in Bolivia are under development.

Unconventional Brines

Oil field brines

Also known as petrobrines, these oil and gas waste products are some of the lowest-grade brines, containing as little as 0.007% to 0.02% Li.

Stage of development

These are precommercial brines. Extracted in conjunction with oil and gas, typically found in the U.S. Smackover Formation and Canadian oil sands (Alberta).

Geothermal brines

These brines come out of the ground hot, which facilitates certain DLE processes. These are low-grade sources containing as little as 0.01% to 0.04% Li.

Stage of development

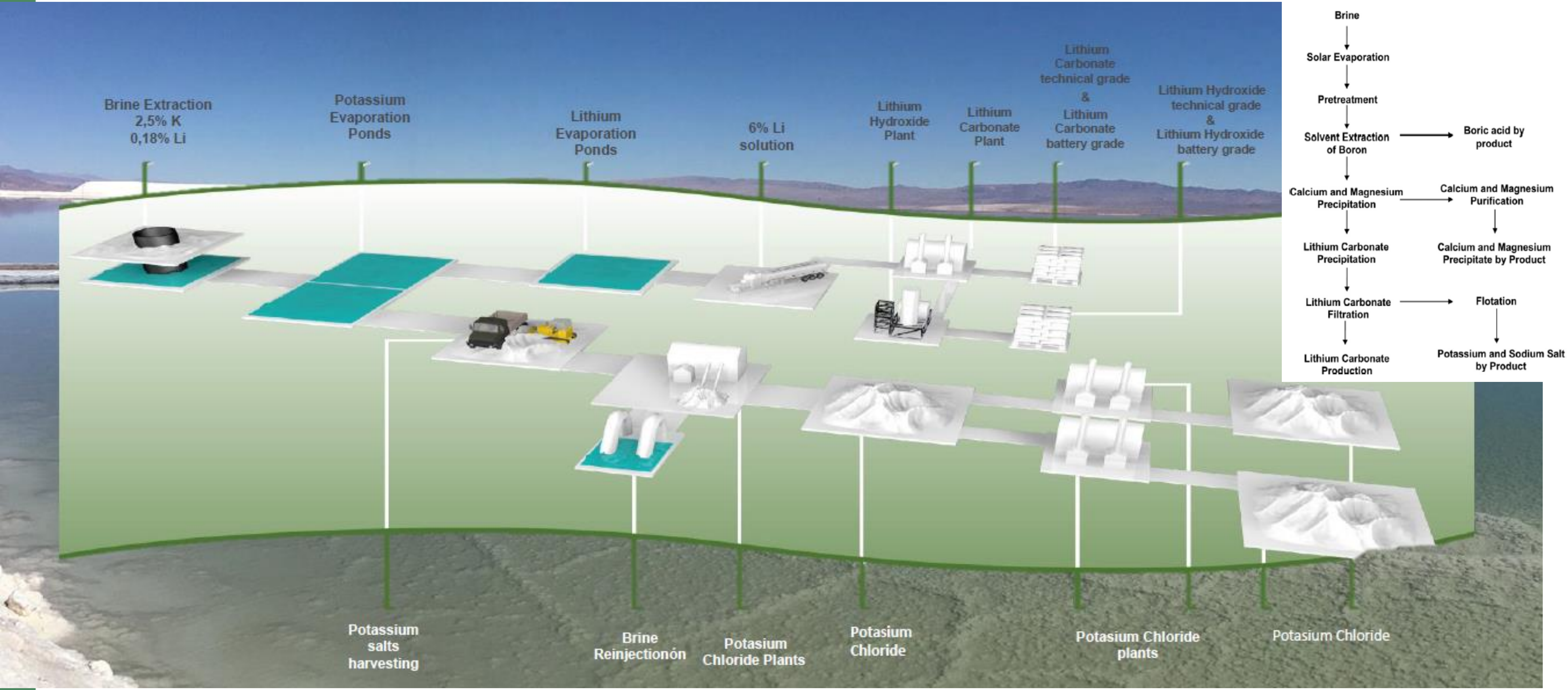
Developers are scaling up from pilot production. Brines are located in geothermally active areas in California and the Upper Rhine Valley of Germany and France.

Clay mineral leachate can be considered as unconventional brines as well

DLE comes in many approaches

- **Adsorbents:** Adsorbents physically capture LiCl molecules on their surface while water acts as a stripping solution. This technology is at commercial scale today and is used for brines in South America.
- **Ion-exchange resins:** Lithium ions in the brine are chemically adsorbed onto the ion-exchange material and swapped for other positive ions from the resin. Ion exchange uses acidic reagents like HCl to strip lithium. The technology is nearing commercialization for continental and geothermal brines.
- **Solvent extraction:** Not unlike the solvents used in hard-rock mining, DLE solvents are organic chemicals with adsorptive or ion-exchange capabilities that strip the brine of lithium to form either LiCl or lithium ions in solution. No commercial operations use solvents today, but the technology has been demonstrated in pilots.
- **Membranes:** Lithium extraction relies on membrane selectivity and pore size as brine is pushed across the membrane surface. It's an early stage technology with innovations in using metal organic frameworks (MOFs) infused with polymer substrates and chemically modified ion-exchange membranes. Companies testing membranes are currently in lab or early pilot testing.
- **Electrolysis:** Like membrane technology, electrolysis can extract lithium from brines using ion-selective membranes or adsorbents, but most companies will likely end up using electrolysis as a lithium-refining step to convert LiCl to LiOH and recycle water.

Li recovery process from Salar brines



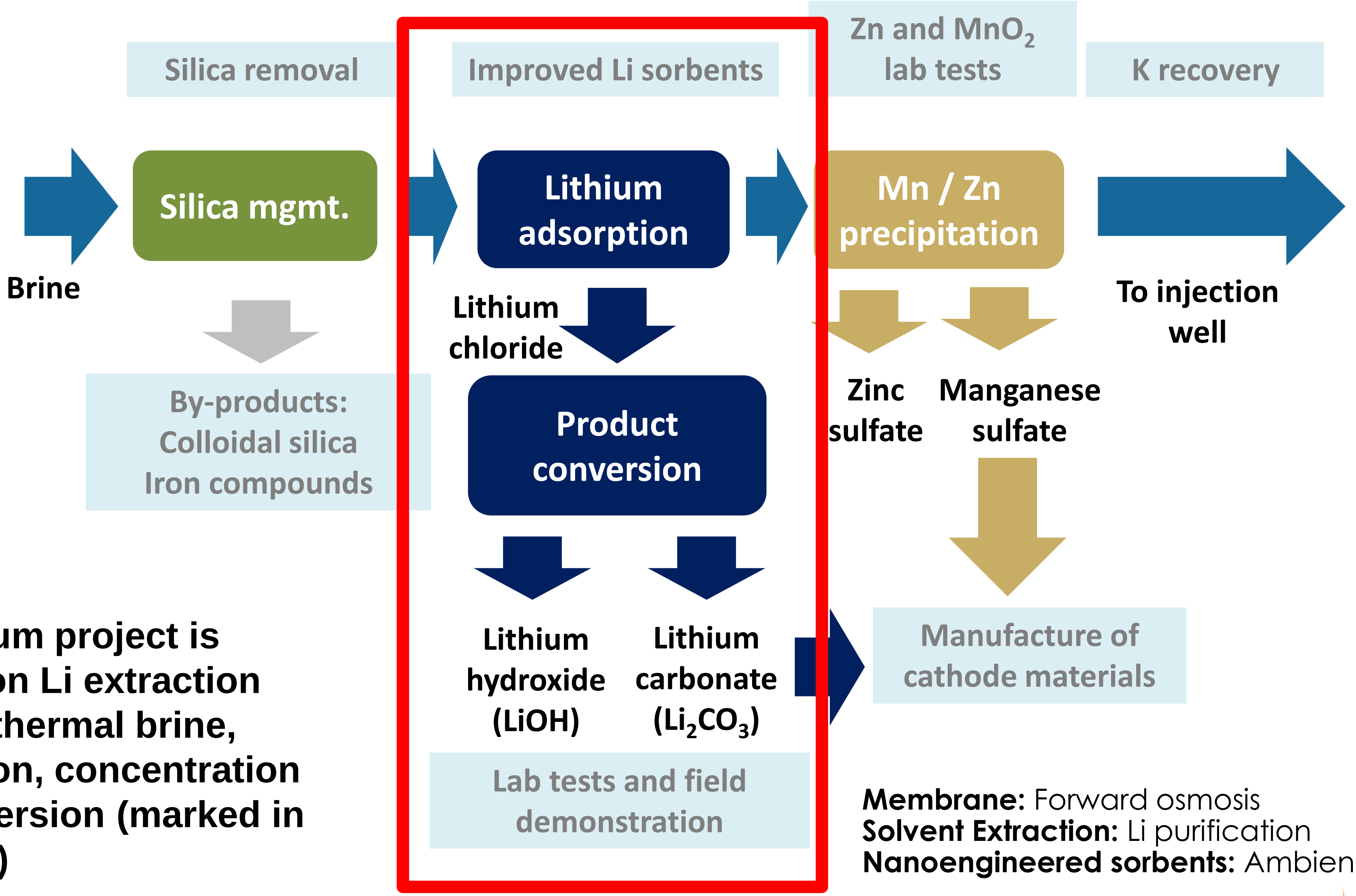
Flow-chart

Brine
Solar Evaporation
Pretreatment
Solvent Extraction of Boron → Boric acid by product
Calcium and Magnesium Precipitation → Calcium and Magnesium Purification
Calcium and Magnesium Precipitate by Product
Lithium Carbonate Precipitation
Lithium Carbonate Filtration → Flotation
Potassium and Sodium Salt by Product
Lithium Carbonate Production

Li recovery time: 18-24 months

Source: SQM

Lithium removal process flow from geothermal brine



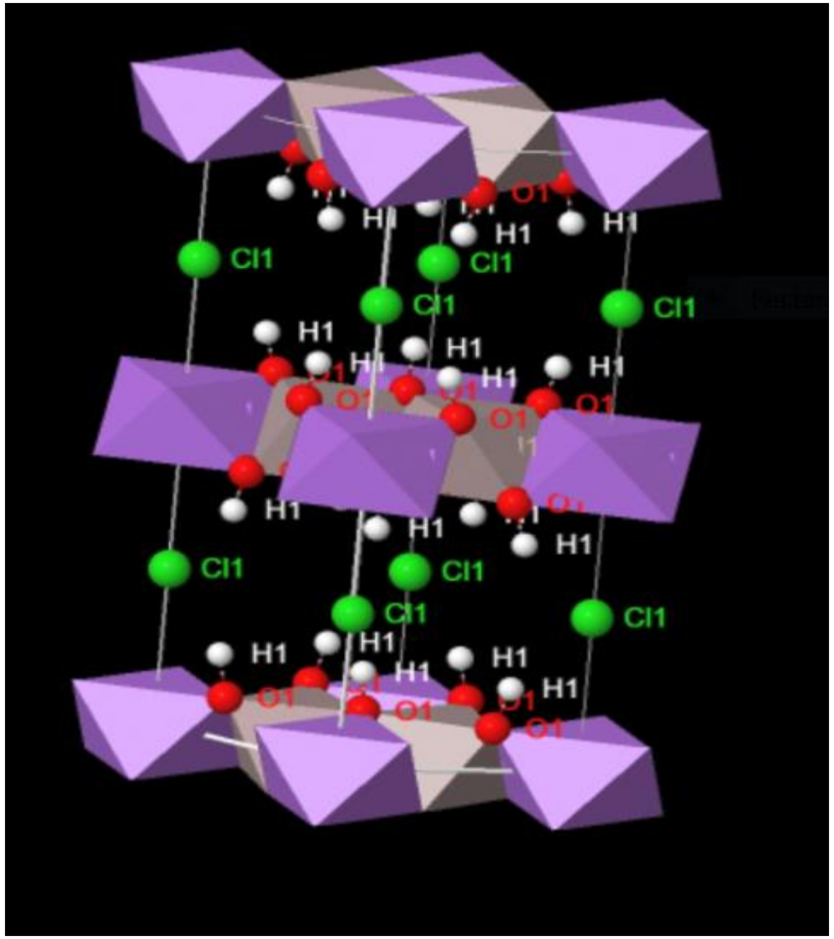
CMI Lithium project is focused on Li extraction from geothermal brine, purification, concentration and conversion (marked in a red box)

Membrane: Forward osmosis
Solvent Extraction: Li purification
Nanoengineered sorbents: Ambient temp. brines

Source: S. Harrison, Simbol Final DOE GTO DE-EE0002790 Report (2014)

LDH based sorbents

- Lithium layered double aluminum hydroxide chloride (LDH) is an attractive candidate for application in large-scale industrial plants due to its various advantages, including low cost, environmental-friendliness, easy regeneration.
- LDH has a general formula $[LiAl_2(OH)_6]^+Cl^- \cdot nH_2O$.
- Crystallized in the hexagonal symmetry with the Li^+ located in the vacant octahedral sites within the $Al(OH)_3$ layer.
- $[LiAl_2(OH)_6]^+$ layers are separated by water molecules and chloride ions.
- Li/Al LDHs can be synthesized by intercalating LiCl into gibbsite (α-$Al(OH)_3$)

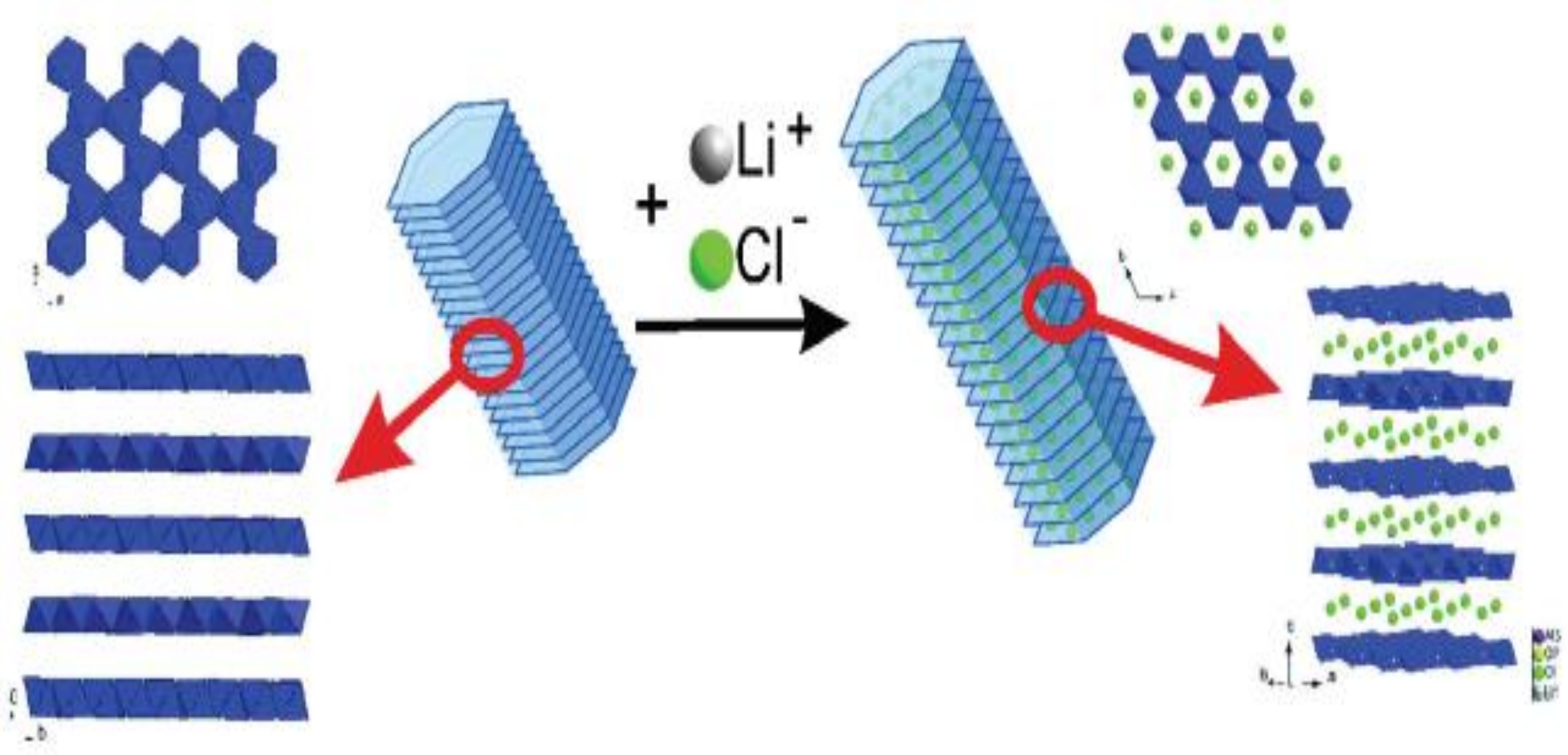


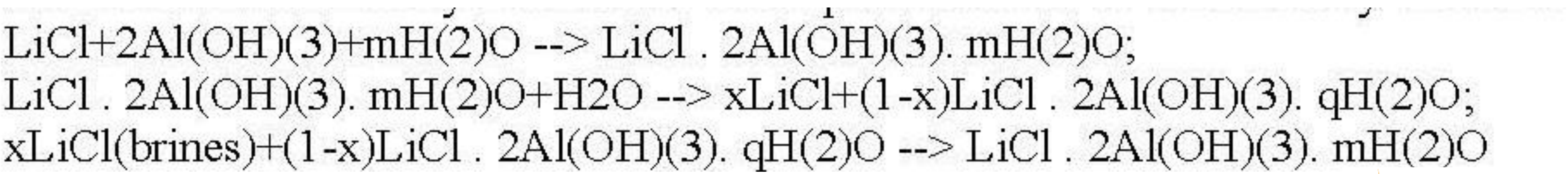
Source: M. P. Paranthaman, L. Li, J. Luo, T. Hoke, H. Ucar, B. A. Moyer, S. Harrison, "Recovery of lithium from geothermal brine with lithium aluminum layered double hydroxide chloride sorbents," *Environmental Science and Tech.* **2017**, 51, 13481. DOI: 10.1021/acs.est.7b03464.

Li, L.; Deshmane, V.; Paranthaman, M.P.; Bhave, R.; Moyer, B.; Harrison, S. Lithium Recovery from Aqueous Resources and Batteries – A Brief Review. *Johnson Matthey Technol. Rev.* **2018**, *62* (2), 161-176. https://doi.org/10.1595/205651317X696676

Li/Al layered double hydroxide chloride (LDH) sorbents

- Lithium chloride is intercalated into interlayers of hexagonal gibbsite.

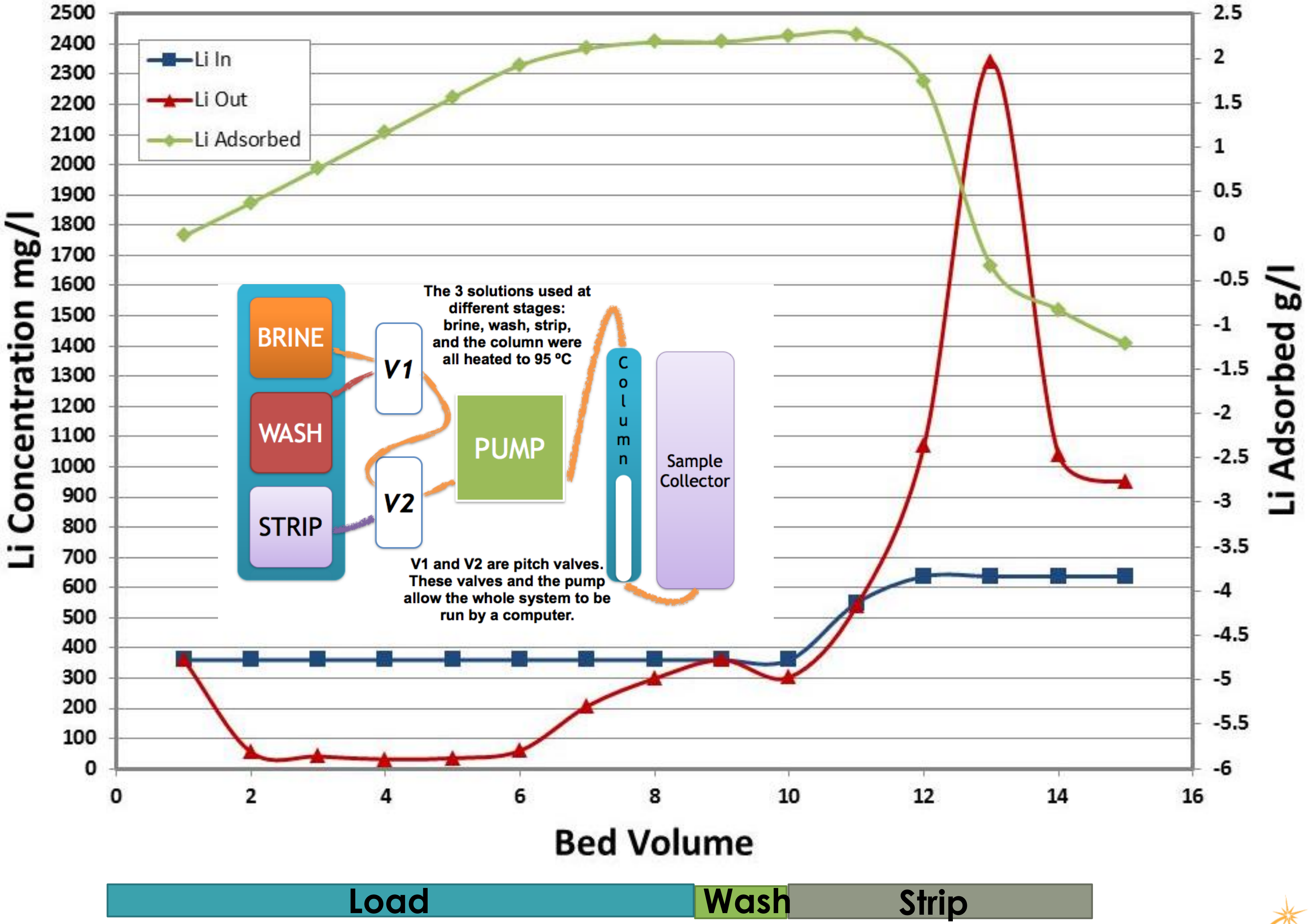




LiCl+2Al(OH)(3)+mH(2)O --> LiCl . 2Al(OH)(3). mH(2)O;
LiCl . 2Al(OH)(3). mH(2)O+H2O --> xLiCl+(1-x)LiCl . 2Al(OH)(3). qH(2)O;
xLiCl(brines)+(1-x)LiCl . 2Al(OH)(3). qH(2)O --> LiCl . 2Al(OH)(3). mH(2)O

Source: C.J. Wang and D. O'Hare, Topotactic synthesis of layered double hydroxide nanorods, J. Mater. Chem. 22, 23064-23070 (2012). DOI: 10.1039/C2JM34670B

Bench-scale selective column extraction of LiCl from simulated geothermal brine using LDH sorbents



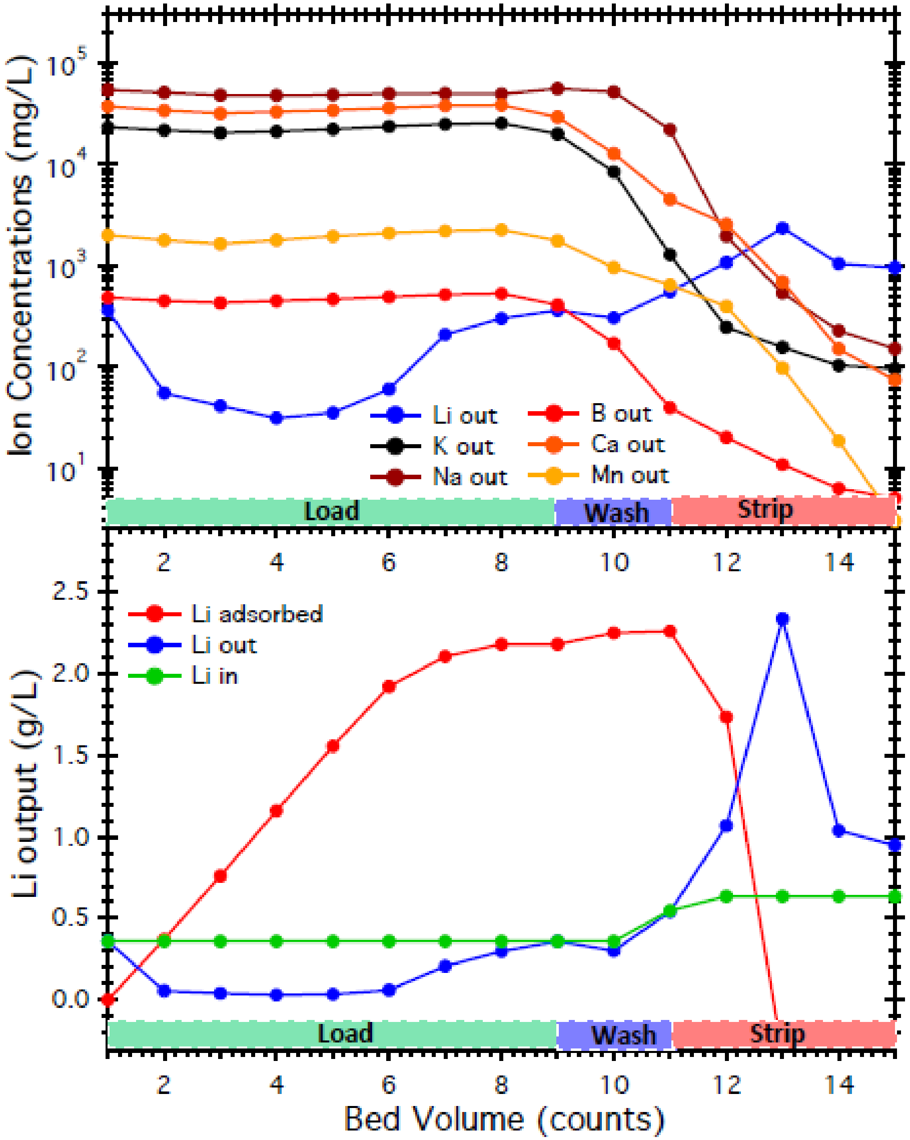
The 3 solutions used at different stages: brine, wash, strip, and the column were all heated to 95 °C

V1 and V2 are pitch valves. These valves and the pump allow the whole system to be run by a computer.

Operation at 95°C

Source: M. P. Paranthaman, L. Li, J. Luo, T. Hoke, H. Ucar, B. A. Moyer, S. Harrison, “Recovery of lithium from geothermal brine with lithium aluminum layered double hydroxide chloride sorbents,” *Environmental Science and Tech.* **2017**, 51, 13481. DOI: 10.1021/acs.est.7b03464.

ICP data on the strip eluate solution with LDH sorbents



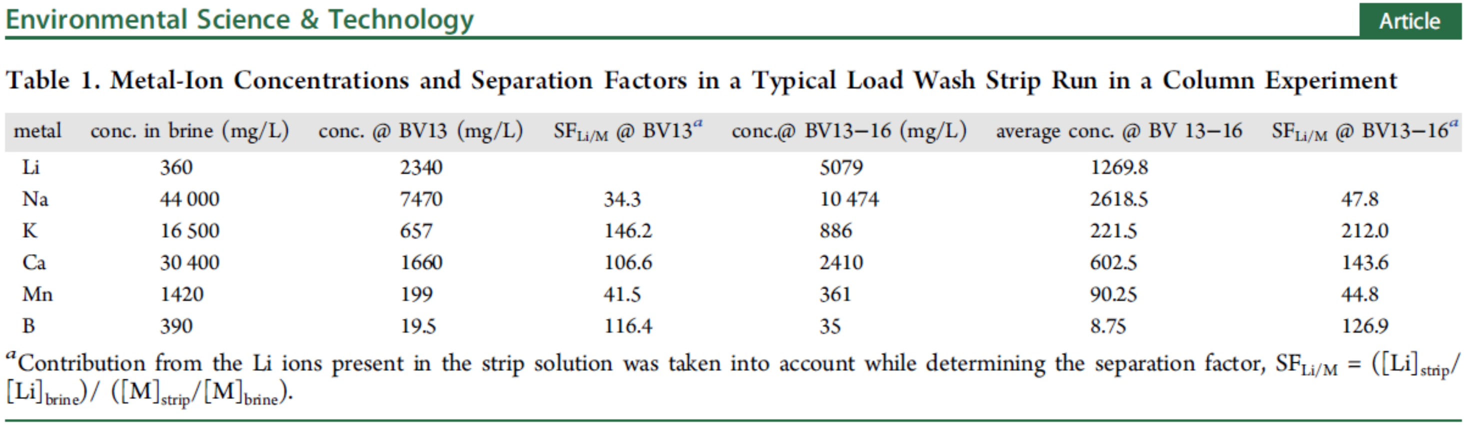

Environmental Science & Technology Article

Table 1. Metal-Ion Concentrations and Separation Factors in a Typical Load Wash Strip Run in a Column Experiment

metal	conc. in brine (mg/L)	conc. @ BV13 (mg/L)	$SF_{Li/M}$ @ BV13[a]	conc.@ BV13–16 (mg/L)	average conc. @ BV 13–16	$SF_{Li/M}$ @ BV13–16[a]
Li	360	2340		5079	1269.8	
Na	44 000	7470	34.3	10 474	2618.5	47.8
K	16 500	657	146.2	886	221.5	212.0
Ca	30 400	1660	106.6	2410	602.5	143.6
Mn	1420	199	41.5	361	90.25	44.8
B	390	19.5	116.4	35	8.75	126.9

[a] Contribution from the Li ions present in the strip solution was taken into account while determining the separation factor, $SF_{Li/M} = ([Li]_{strip}/[Li]_{brine})/([M]_{strip}/[M]_{brine})$.

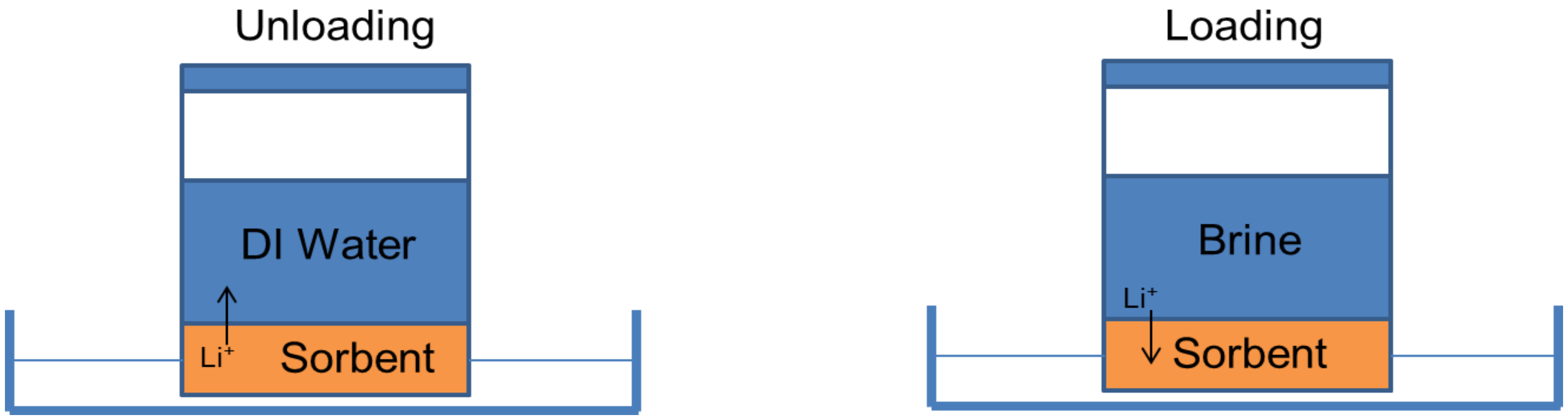
Summary: LDH is effective in extracting Li from geothermal brine. However, ~ 180 ppm of K and ~ 520 ppm of Na are still present in the strip eluate solution. Further purification process is needed to selectively remove Li from K and Na.

- Alternate methods are being explored in CMI to address this issue

Source: M. P. Paranthaman, L. Li, J. Luo, T. Hoke, H. Ucar, B. A. Moyer, S. Harrison, “Recovery of lithium from geothermal brine with lithium aluminum layered double hydroxide chloride sorbents,” *Environmental Science and Tech.* **2017**, 51, 13481. DOI: 10.1021/acs.est.7b03464

Loading and unloading trials (Batch process)

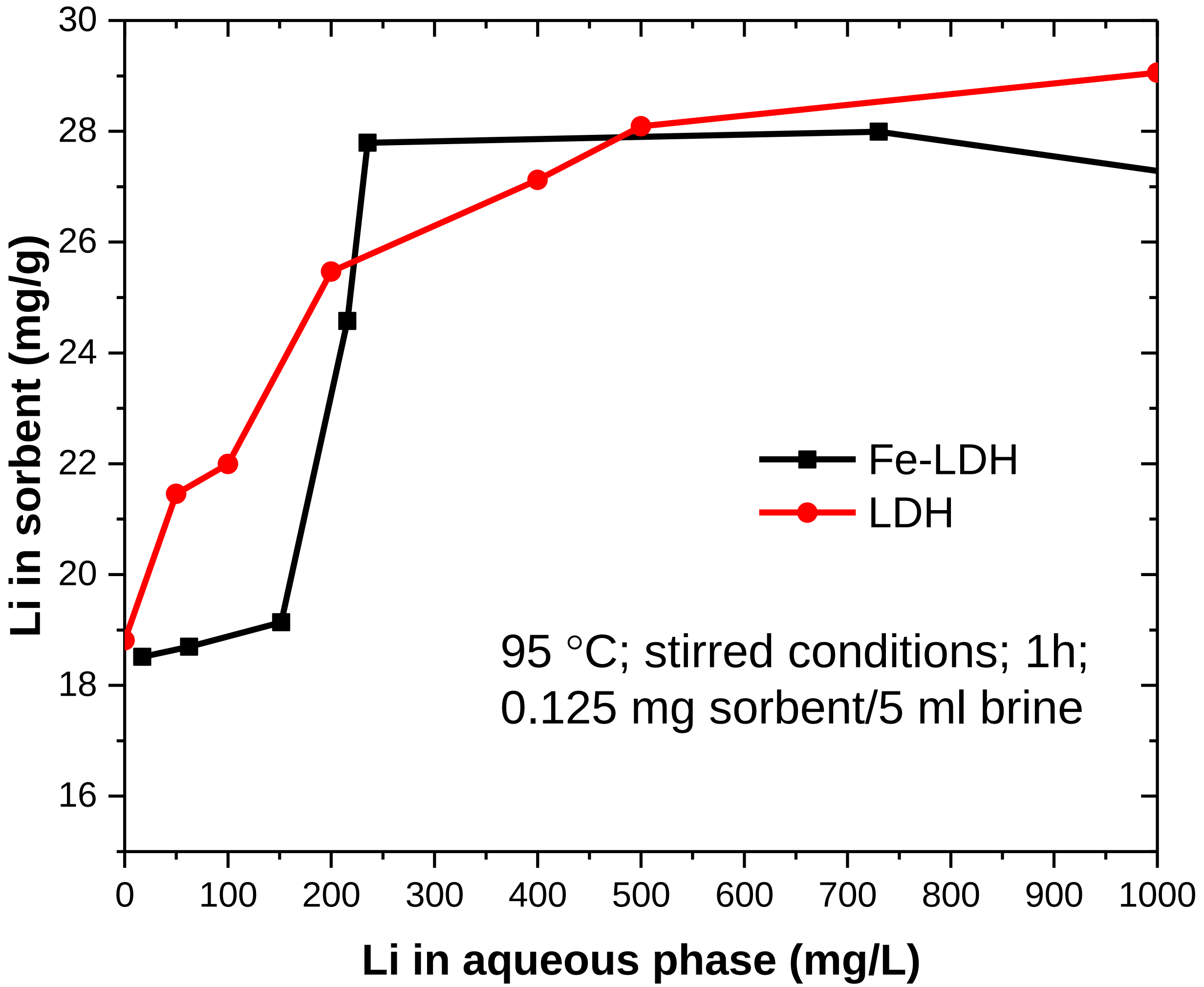
- LDH or Fe-LDH sorbent is mixed with DI water in order to “unload” Li from the structure in a well sealed container at 95°C.
- This unloaded LDH is used in trials to load Li from the brine solution
- Sorbent structure studied using X-Ray Diffraction



Trials

- 0.5 g sorbent, 10 mL brine at different concentrations placed in a well sealed vial
- Agitated and kept at room temperature for 24 hours
- Filtered, Diluted, Run with Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

Developed isotherms of Li absorption for LDH sorbents



95 °C; stirred conditions; 1h;
0.125 mg sorbent/5 ml brine

- Lithium in geothermal brine is ~ 300 ppm
- Absorption capacity in LDH and Fe-LDH is similar : 6 mg/g
- Also determined the stability of LDH phase of up to 125 °C

- TCF – GTO Funded: Sorbent scale up and test it at the geothermal site

US Patent Issued: Composition for Recovery of Lithium from Brines, and Process of Using Said Compositions, Paranthaman, M.P. (ORNL); Bhave, R. (ORNL); Moyer, B.A. (ORNL); Harrison, S. (AAL) – U.S. Patent # 10,266,915; Issued on April 23, 2019.

Forward-Osmosis Technology Concentrates Lithium Chloride Enabling Recovery from Geothermal Brine

Achievement

- Energy-efficient concentration of LiCl recovered from geothermal brine has been achieved, where LiCl concentration increases from 35 g/L to 175 g/L.

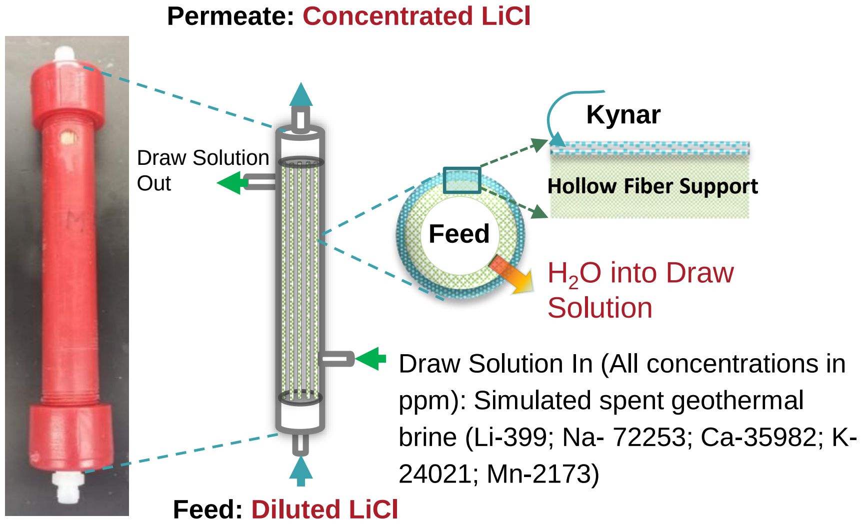
Significance and impact

- The technology concentrates high-purity LiCl for efficient conversion into Li_2CO_3 or Li(OH), feedstocks for fabrication of lithium-ion batteries. Energy savings of >90% vs thermal evaporation or > $60/m^3 of water removal can be obtained.

Details and next steps

- Stable performance for >500 hours.
- No cation transfer from draw solution.
- LiCl purity: >99.99 wt.%.
- Hot operating temperature: 75–80°C.
- Optimize process to increase water flux.
- Work with industry partner to scale up for demonstration and commercialization.

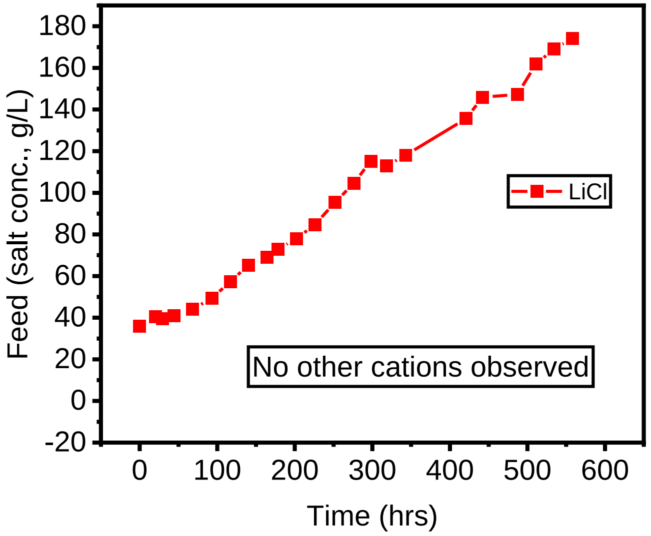
Wagh, P.; Islam, S. Z.; Deshmane, V. G.; Gangavarapu, P.; Poplawsky, J.; Yang, G.; Sacci, R.; Evans, S. F.; Mahajan, S.; Paranthaman, M. P.; Moyer, B. A.; Harrison, S.; and Bhave, R., "Fabrication and characterization of Composite Membranes for the Concentration of Lithium Containing Solutions using Forward Osmosis, *Adv. Sustainable Sys*. 4, 2000165 (2020). https://doi.org/10.1002/adsu.202000165; Bhave, Ramesh et al., U.S. Patent application no. 16/535585, Aug 9, 2019.


Permeate: Concentrated LiCl

Draw Solution Out

Draw Solution In (All concentrations in ppm): Simulated spent geothermal brine (Li-399; Na- 72253; Ca-35982; K-24021; Mn-2173)

Feed: Diluted LiCl



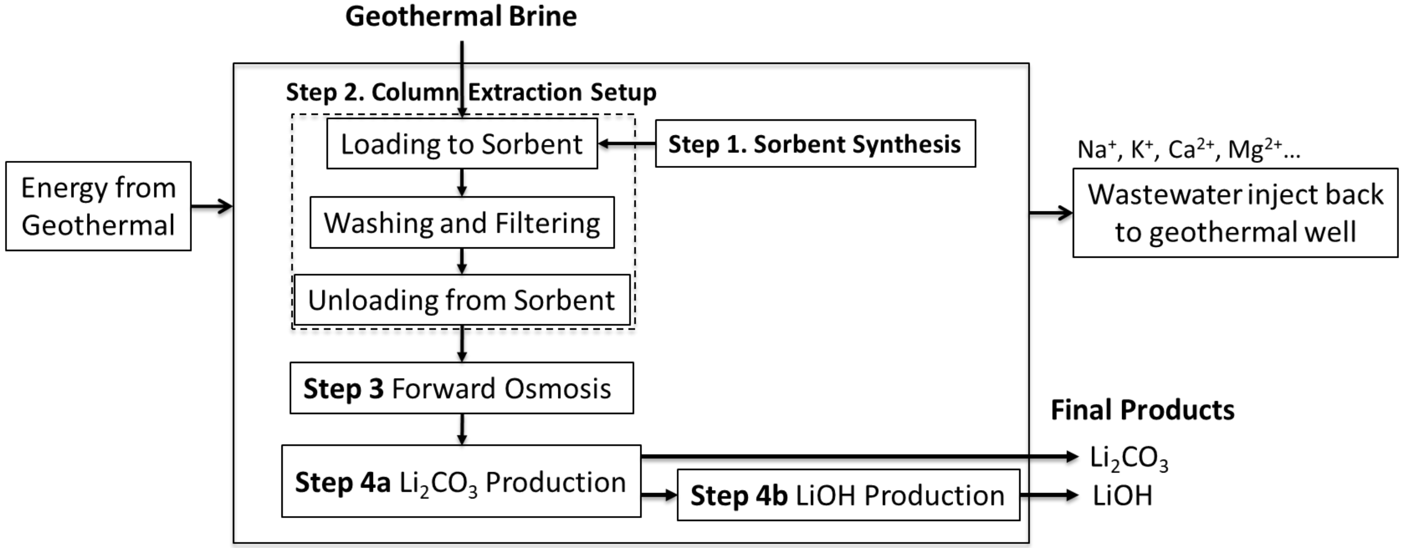
Increase in LiCl concentration as water diffuses across the membrane into the draw solution.

OAK RIDGE
National Laboratory

CMI sorbents and forward osmosis reduce environmental impacts

- Achievement
- Life cycle analysis (LCA) of LiOH and Li_2CO_3 production from geothermal brines shows up to 91% reduction in environmental impacts compared to mining or salar brine.

- Significance and impact
  - LDH sorbents recover >91% of LiCl from geothermal brines.
  - Forward osmosis membrane technology concentrates 3% LiCl eluate to 20%.



LCA schematic of lithium recovery from geothermal brines using CMI innovations in sorbent and membrane technology.

- Li_2CO_3 produced from geothermal brines has a carbon footprint that is 34% lower than production from salt flats and 26% lower than production from the mineral spodumene.
- LiOH production from geothermal brines can achieve 48% reduction on greenhouse gas emissions.

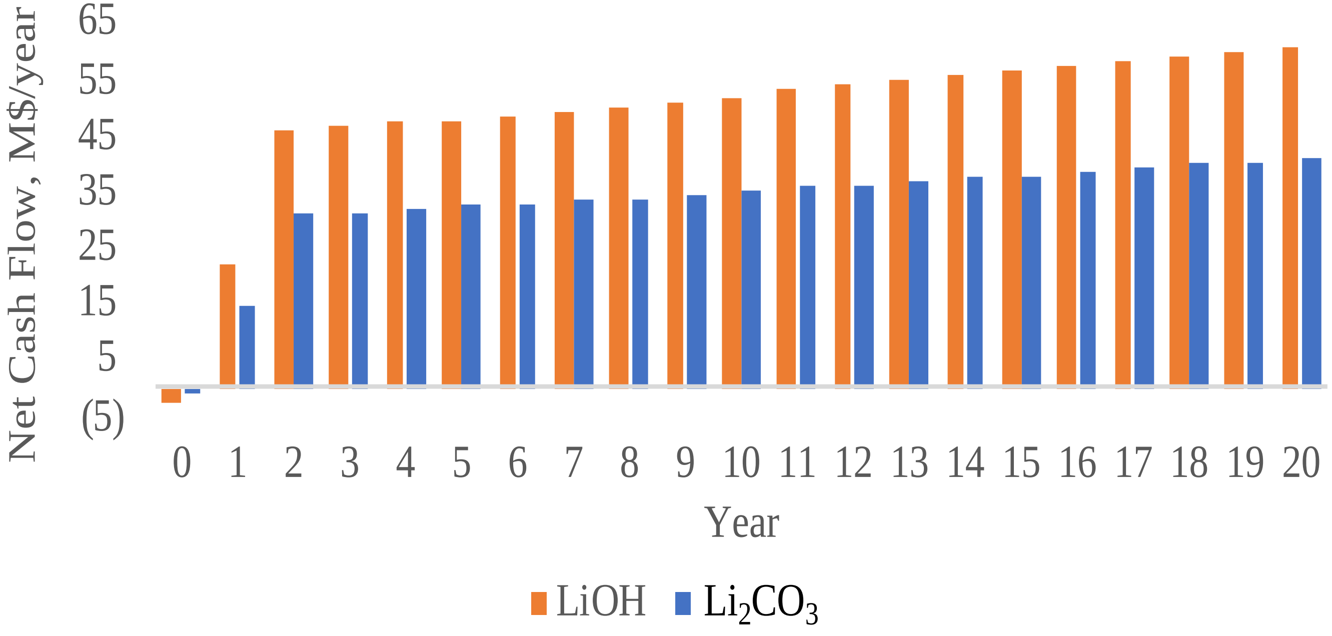
Details and next steps

- This work is coupled with technoeconomic analysis and extended to recovery of lithium from other sources.

Tai-Yuan Huang, Jesus Ramon Perez-Cardona, Fu Zhao, John W. Sutherland, and Mariappan Parans Paranthaman, “Life Cycle Assessment and Techno-economic Analysis of Lithium Recovery from Geothermal Brine” *ACS Sustainable Chem. Engg*. 9, 6551-6560, 2021. https://doi.org/10.1021/acssuschemeng.0c08733

CMI sorbents and forward osmosis boost lithium economics

- Achievement
  - Techno economic analysis (TEA) of LiOH and Li_2CO_3 production using CMI sorbent and membrane technologies points to a green and profitable approach for recovering lithium from geothermal brines.
- Significance and impact
  - ➢ Geothermal brine is one of the promising resources to enable a sufficient domestic supply of lithium for batteries for electric vehicles.
  - ➢ Based on the CAPEX and OPEX, the pay back period is only one year.



Net Cash Flow for LiOH and Li_2CO_3 production (for augmented geothermal plant across its life).

➢ TEA coupled with LCA project the respective production of Li_2CO_3 and LiOH to be 16,000 tpa and 10,372 tpa by assuming plant operation of 330 days in a year and plant life of 20 year for each 50 MW geothermal plant.

Details and next steps

➢ This work has been extended to recovery of lithium from clay minerals.

Tai-Yuan Huang, Jesus Ramon Perez-Cardona, Fu Zhao, John W. Sutherland, and Mariappan Parans Paranthaman, "Life Cycle Assessment and Techno-economic Analysis of Lithium Recovery from Geothermal Brine" *ACS Sustainable Chem. Engg*. 9, 6551-6560, 2021. https://doi.org/10.1021/acssuschemeng.0c08733

Summary and outlook

- Extraction of lithium from geothermal brine seems to be economically and environmentally attractive
- LDH and Fe modified LDH sorbents are promising – high selectivity; high capacity
- Membrane and solvent extraction are good for further purifying the eluate downstream solution for achieving high purity LiCl
- Sorption method and solvent extraction are good for direct lithium extraction from sulfate stream
- **FA1 hub level goal: Industry adoption of CMI lithium technology – Licensed CMI/ORNL lithium technologies to Lithos Industries LLC/Element3 for recovering lithium from produced water from oil and gas fields**

U.S. DEPARTMENT OF ENERGY

Clean Energy States Alliance

Diversifying Lithium Supply from Brines to Hard-Rock Minerals: Mechanochemical Extraction of Lithium at Low Temperature (MELLT) from α-Spodumenes

Ihor Hlova

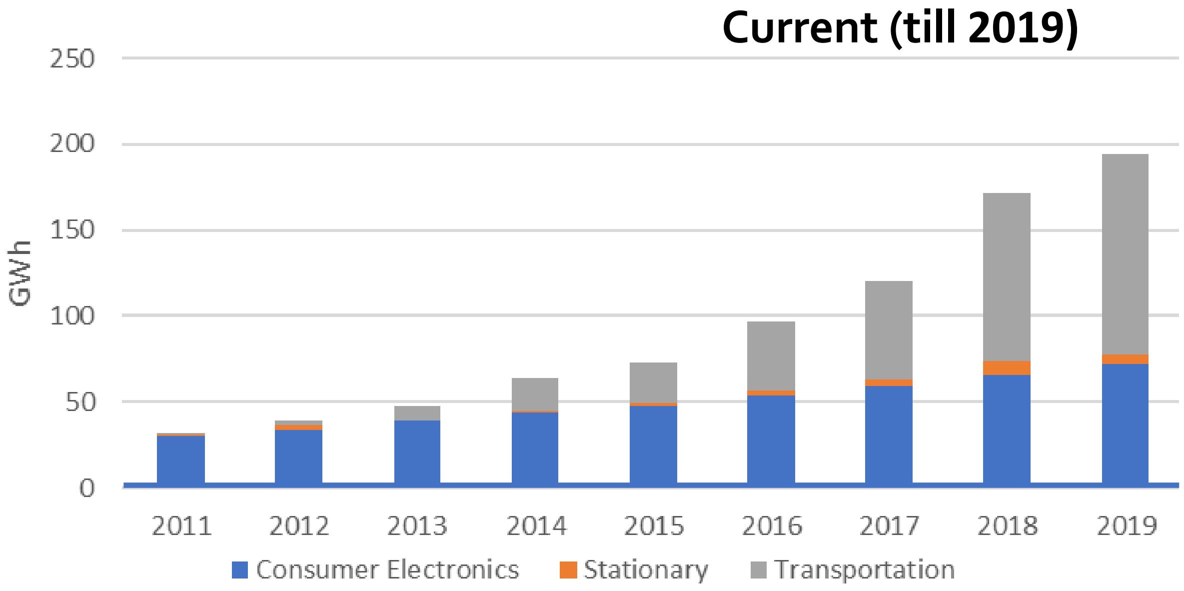
CMI Critical Materials INSTITUTE

AMES NATIONAL LABORATORY
Creating Materials & Energy Solutions

PIEDMONT LITHIUM

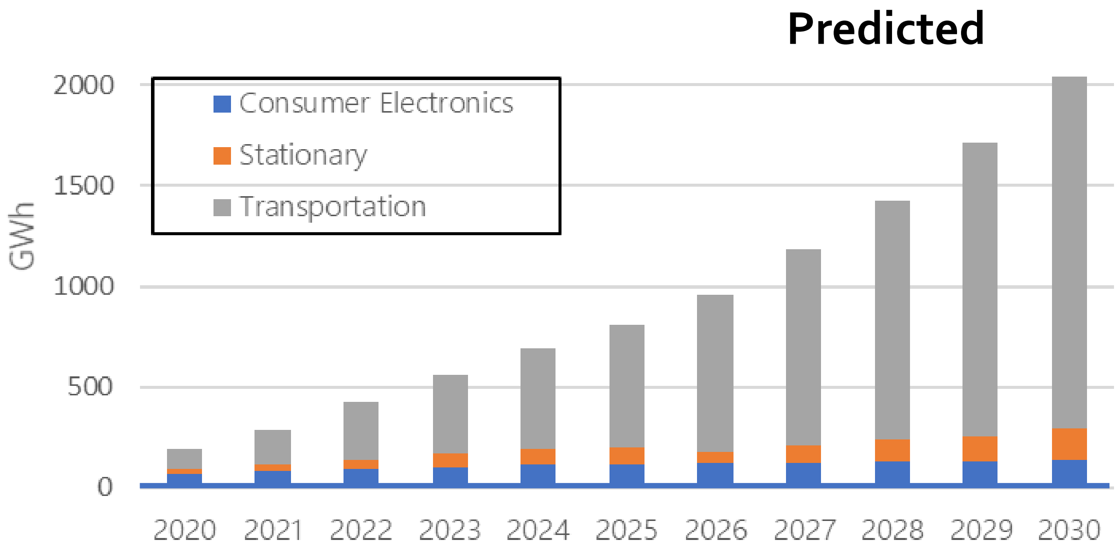
Is Lithium demand underestimated?

- Transportation sector **dominates** the Li-ion market and is also the fastest growing



Historical annual global Li-ion deployment – all markets

Source: Bloomberg New Energy Finance, "Electric Vehicle Outlook 2020," BloombergNEF, New York, 2020.



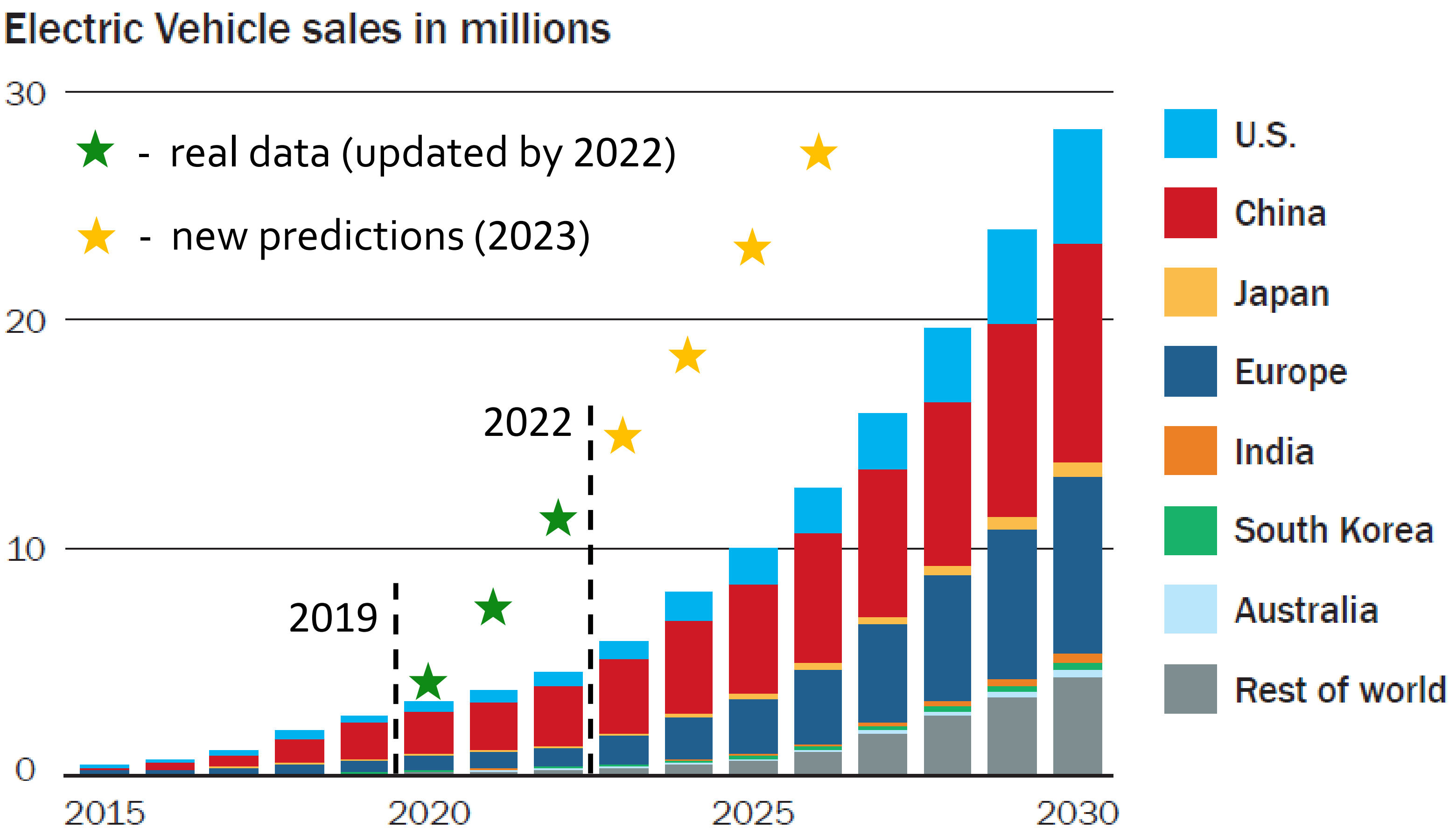
BNEF projected global Li-ion deployment – all markets

Source: Bloomberg New Energy Finance, "Electric Vehicle Outlook 2020," BloombergNEF, New York, 2020.

- Mann, Margaret, Susan Babinec, and Vicky Putsche. Energy storage grand challenge: Energy storage market report. No. NREL/TP-5400-78461. National Renewable Energy Lab.(NREL), Golden, CO (United States), 2020

Is Lithium demand underestimated?

- In 2022, EVs accounted for 18.6% of total vehicle sales
- Will the predictions hold? Will it underestimate?
- **Demand is exceeding the expectations, so we must ensure we will meet it**



Annual Sales of Passenger EVs (Battery Electric Vehicles (BEVs) and Plug-in Hybrid Electric Vehicles (PHEVs))

Source: BloombergNEF Long-Term Electric Vehicle Outlook 2019

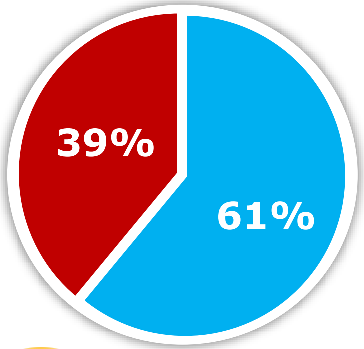
- Granholm, Jennifer M. "National Blueprint for Lithium Batteries 2021–2030." (2021)
- BloombergNEF Electric Vehicle Outlook 2023

Hard-rock minerals vs Brines

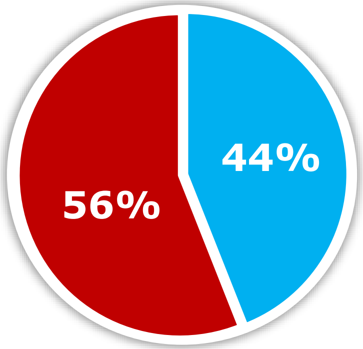
❖ Hard-rock minerals

~71% is spodumene

- Majority – Australia (~80%, reserve: 6.2 Mt);China, Brazil
- 20 US sites, with Kings Mountain (5.0 Mt) – the largest deposit
- 6–8 wt.% Li_2O
- Energy-demanding and waste-generating extraction



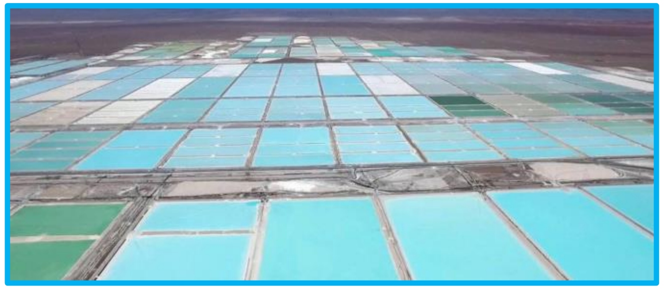
Global Reserves



Global Production

The production of Li-from **brines** is strongly influenced by climate, as the concentration of brine is primarily based on evaporation in open air using shallow wells. In addition, the long well-to-market times, which typically range between **8–16 months**, **lack flexibility to address the rapidly rising <u>demand</u>**.

❖ Brines

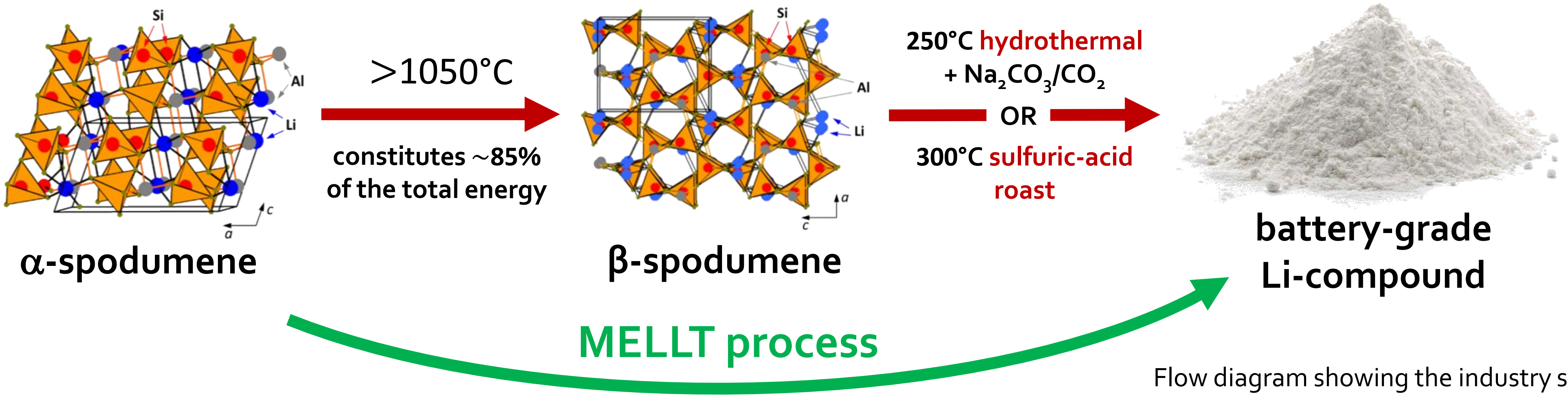


- Majority – Chile (~70%, reserve: 9.3 Mt); Argentina, China
- Brines are main source of Li for US, both on import and domestic
- 0.09–0.32 wt.% Li_2O
- Cost-effective solar evaporation process

- Karl, N.A., Reyes, J.L. and TA Scott, P.C., 2019. Lithium deposits in the United States
- Kesler, S.E., et. al, 2012, Global lithium resources—relative importance of pegmatite, brine and other deposits: Ore Geology Reviews, v. 48, October ed., p. 55—69
- U.S. Geological Survey, Mineral Commodity Summaries, Lithium, January 2023

Industrial methods for Li-extraction from Spodumene

- Spodumene ($LiAlSi_2O_6$) mineral occurs naturally as **stable, tightly packed α-spodumene**
- Industrial methods utilize an **energy intensive decrepitation**, thus converting stable naturally-occurring α-spodumene into β-spodumene (more susceptible to chemical attack), followed by harsh leaching conditions, **generating green-house gases and hazardous waste streams**



α-spodumene

>1050°C

constitutes ~85% of the total energy

β-spodumene

250°C hydrothermal + Na_2CO_3/CO_2

OR

300°C sulfuric-acid roast

battery-grade Li-compound

MELLT process

mechanochemical extraction of lithium at low temperatures

Flow diagram showing the industry standard processes and the MELLT approach for Li-extraction from α-spodumene

- Salakjani, N.K., Singh, P. and Nikoloski, A.N., 2021. Production of lithium–A literature review. Part 2. Extraction from spodumene. Mineral Processing and Extractive Metallurgy Review, 42(4), pp.268-283.

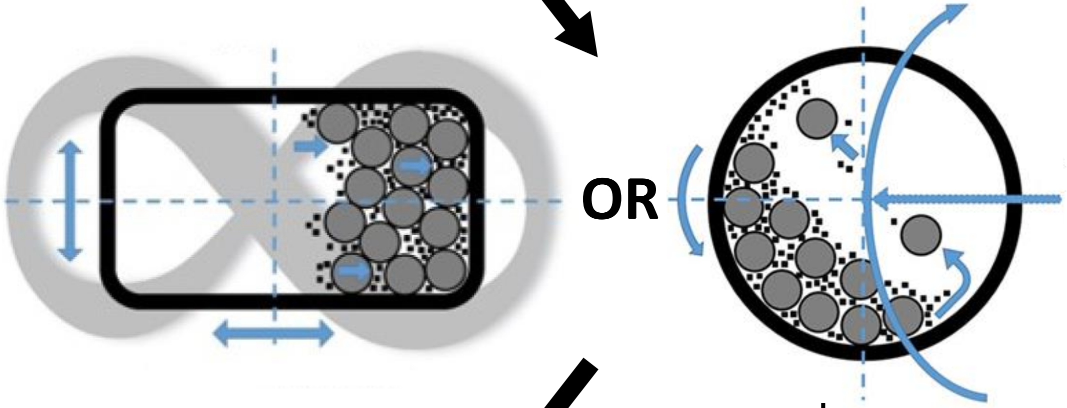
Concept and Advantages

α-spodumene (e.g. Na_2CO_3)

$\alpha\text{-}LiAl(SiO_3)_2$ + solid reactant(s)

MELLT

milling

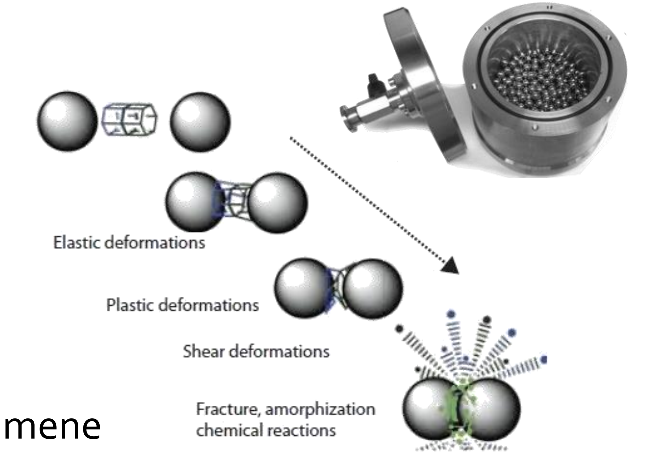


water wash

$X{\cdot}Al_2O_3{\cdot}SiO_2 + Li_2CO_3/LiOH$

Schematics of the MELLT concept where mechanochemical processing is followed by water or diluted acid extraction of the target Li-containing compounds

Mechanochemistry

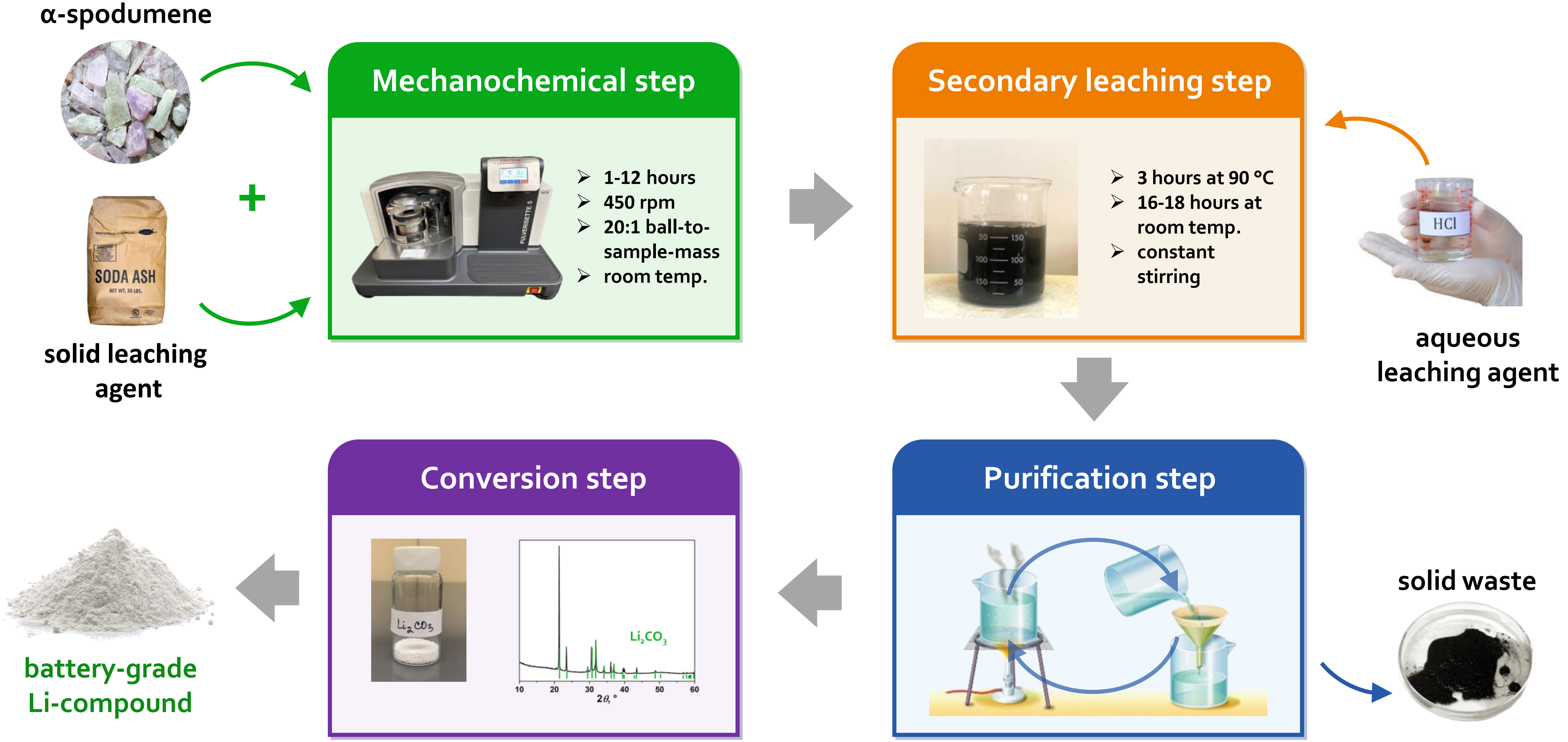


Cumulative effects of rapid, repetitive application of shear and impact stresses leads to metastable high-energy states which are relaxed via chemical transformations between α-spodumene and common solid reactants, leading to ion-exchange and formation of water-soluble Li-compounds

Benefits

- Energy-intensive decrepitation step is eliminated
- Li leaching performed with water or dilute acids like HCl
- Environmentally benign by-products and leaching agents
- Eliminates or substantially reduces acidic and corrosive waste streams

MELLT procedure



α-spodumene

+

solid leaching agent

Mechanochemical step

- 1-12 hours
- 450 rpm
- 20:1 ball-to-sample-mass
- room temp.

Secondary leaching step

- 3 hours at 90 °C
- 16-18 hours at room temp.
- constant stirring

aqueous leaching agent

Purification step

solid waste

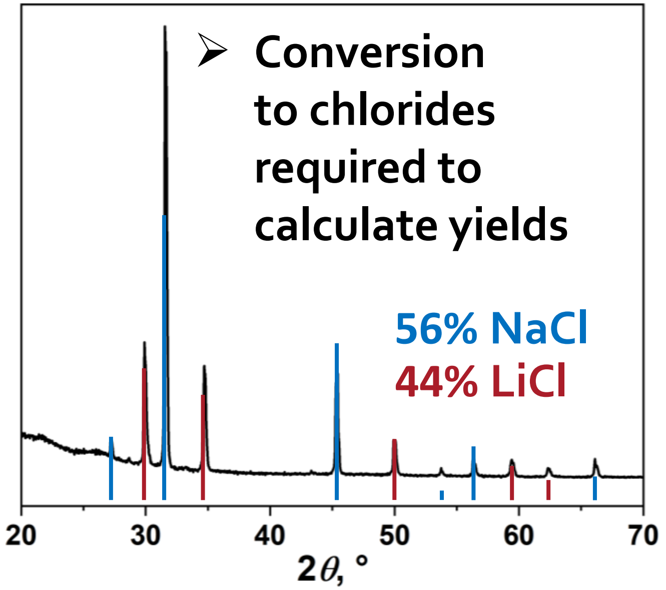
Conversion step

battery-grade Li-compound

Feasibility and Scalability

❖ Small scale (~2g)

~94% Li extraction yield



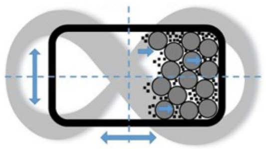
- ➢ **Conversion to chlorides required to calculate yields**

Quantitative powder X-ray diffraction analysis of the soluble product after reaction with 5% HCl

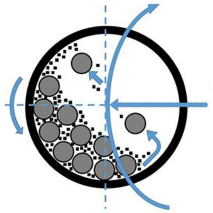
❖ Large scale (~250g)

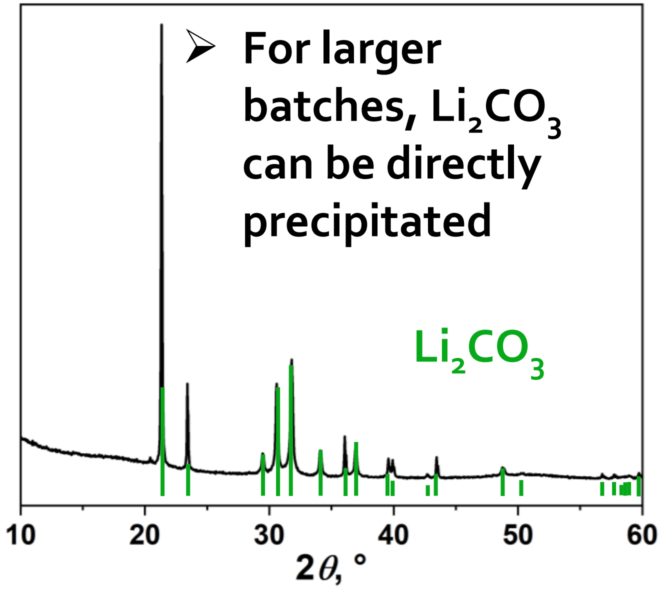
~75% Li extraction yield

Shaker-type milling (SPEX)



Planetary-type milling (Fritsch)





- ➢ **For larger batches, Li_2CO_3 can be directly precipitated**

Powder X-ray diffraction pattern of Li_2CO_3 extracted from α-spodumene demonstrating product purity

Technology comparison

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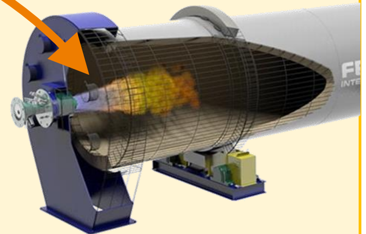
❖ Industrial process

α-spodumene

α to β decrepitation
in direct-fired kiln
at 1075-1100°C



$10/ton

Sulfuric-acid digestion
at 300°C

$8/ton

battery-grade Li-compound

❖ MELLT process

α-spodumene

+

Mechanochemical reaction
at room temperature

$8/ton

Preliminary TEA

~45% energy cost savings
(factoring in 75%
Li-extraction yields)

Thank you!

AMES
NATIONAL LABORATORY
Creating Materials & Energy Solutions

- Ihor Hlova
- Vitalij Pecharsky
- Tyler Del Rose
- Jordan Schlagel
- Long Qi
- Yuting Li
- Shalabh Gupta
- Mykola Abramchuk
- Nagaraj Nandihalli

U.S. DEPARTMENT OF
ENERGY

PIEDMONT
LITHIUM

- Austin Devaney
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- Dave Buckley

STATE

- Taylor Schlagel
- Alexandra Petzke
- Alexandra Vosburgh

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AN ENERGY INNOVATION HUB

This work was supported by the Critical Materials Innovation Hub

U.S. DEPARTMENT OF
ENERGY

Office of
ENERGY EFFICIENCY &
RENEWABLE ENERGY

Geothermal Technologies Office Critical Materials Portfolio

Alexandra Prisjatschew
Staff Engineer – Hydrothermal Resources Subprogram

GTO's Critical Materials History

Lawrence Berkeley National Laboratory Retrospective Report

- Summarizes findings from 2014 and 2016 GTO Rare Earth Extraction FOAs
  - Lithium is profitable; rare earths are not
  - Reporting of results should be standardized
  - Benchmarks for techno-economic analysis should be established
  - Actual geothermal fluid samples should be used

National Renewable Energy Laboratory Geo-Mining Report

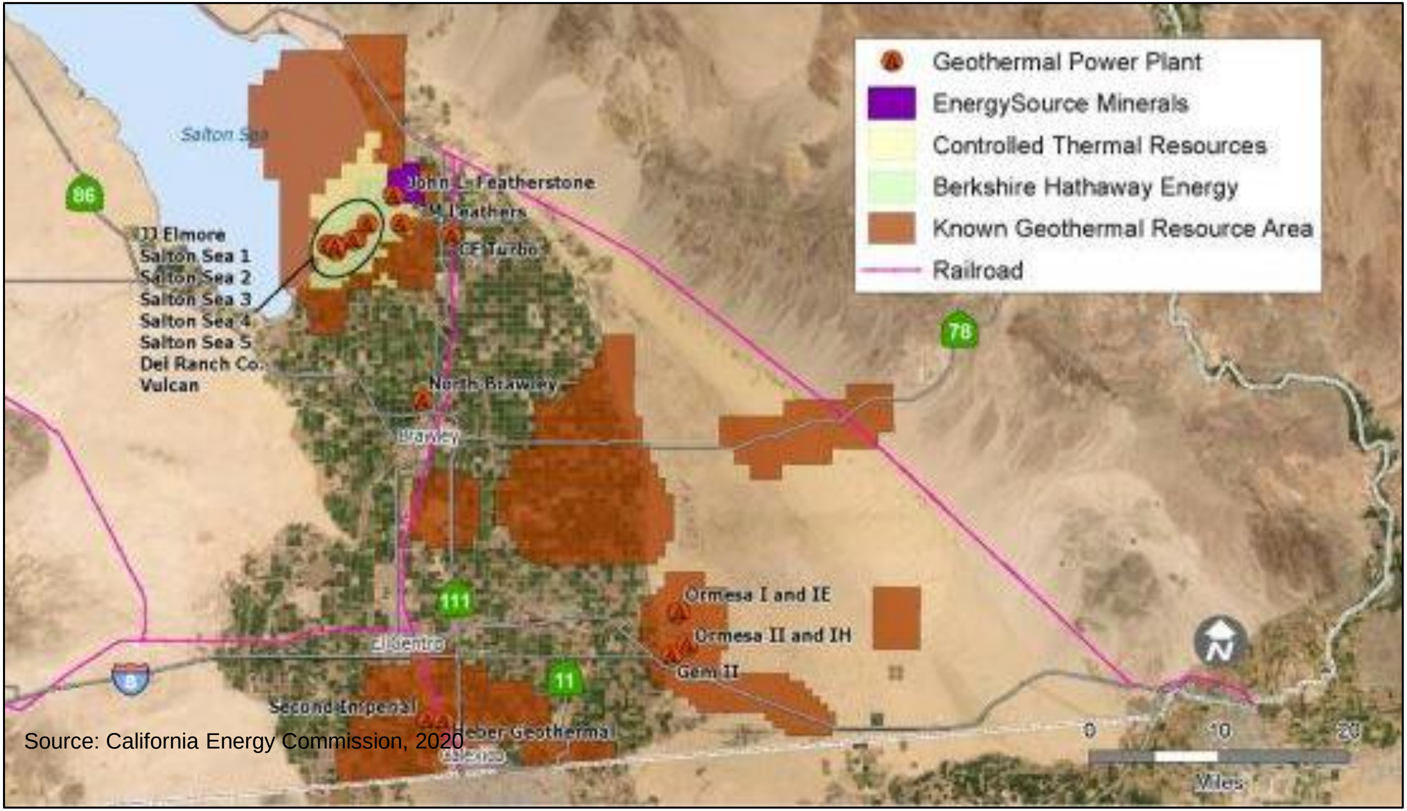
- Investigate potential synergies between the Mining and Geothermal industries

National Renewable Energy Laboratory State of Lithium Production Report

- Produce a techno-economic analysis and benchmarking for lithium extraction from domestic geothermal brines

Lithium is the most feasible, abundant, and economic critical mineral that can be extracted from geothermal brines.

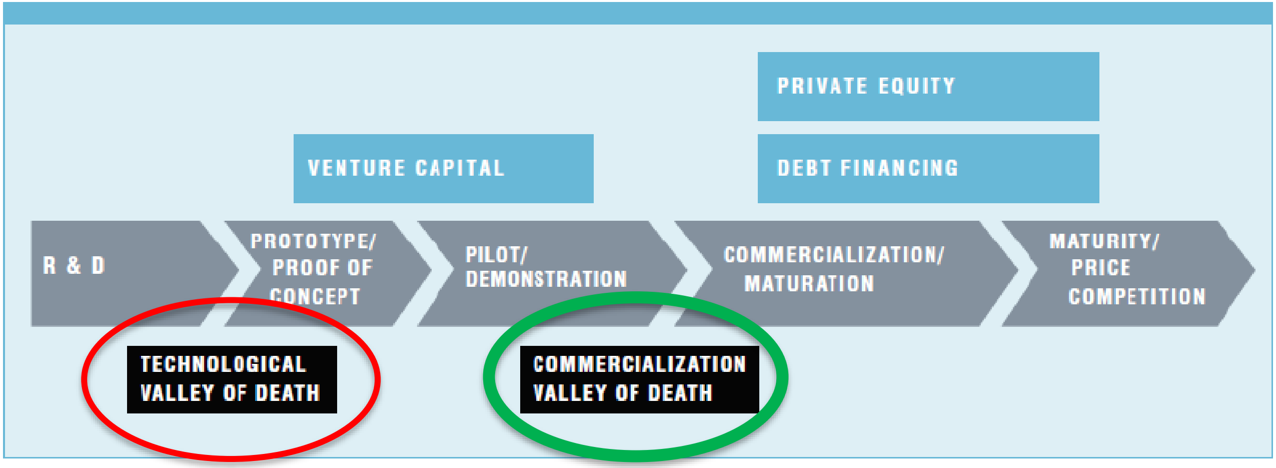
America’s Greatest Lithium Resource: Salton Sea Basin, California



Source: California Energy Commission, 2020

Domestic Geothermal Lithium: Overcoming The 2nd 'Valley Of Death'

THE ENERGY INNOVATION CYCLE AND THE CLEAN ENERGY VALLEYS OF DEATH



Source: Jesse Jenkins and Sara Mansur, "Bridging the Clean Energy Valleys of Death," Breakthrough Institute, November 2011

AMERICAN MADE
GEOTHERMAL PRIZE
U.S. DEPARTMENT OF ENERGY

GEOTHERMAL LITHIUM EXTRACTION PRIZE

WHY IS THIS PRIZE IMPORTANT?

Catalyze

Catalyzes efforts in the U.S. to identify, develop, and test solutions that improve the profitability of DLE from geothermal brines.

Incentivize

Incentivizes the nation’s academic community to rapidly discover, research, iterate, and deliver new DLE solutions while developing a safe, domestic, cost-competitive source of lithium to ensure American leadership in the transition to a carbon-free economy.

Transform

Transforms innovative research and ideas into early-stage concepts and then tests proposed designs to demonstrate their ability to improve DLE from geothermal brines.

Enable

Enables the rapid development of technology and builds critical connections for new avenues of technology commercialization.

$4M Geothermal Lithium Extraction Prize

PHASE 1: IDEA & CONCEPT

$600,000

UP TO **15** SEMIFINALISTS

PHASE 2: DESIGN & INVENT

$1.4 MILLION

UP TO **5** FINALISTS

PHASE 3: FABRICATE & TEST

$2 MILLION

UP TO **3** WINNERS

Prize YouTube Playlist!

https://www.youtube.com/playlist?list=PLnc7qHIiD-9w5yDXvde8EBKT0EQ5uyv3i

Industry Advisory Panel (IAP)

- A team of industry advisors who are experts in state-of-the-art of lithium extraction technology to serve as mentors during the competition.
- Phase 1 – IAP members participated in panel discussions about lithium extraction from geothermal brines. **Checkout the interviews on our YouTube Playlist!**
- IAP members and prize teams meet throughout Phase 2 and Phase 3 to discuss team progress and receive feedback to refine their designs.

AMERICAN LITHIUM

geo40

Controlled Thermal Resources

GEOKEM

BHE RENEWABLES

Standard LITHIUM

ENERGY SOURCE

VULCAN ENERGY RESOURCES Zero Carbon Lithium®

THERMOCHEM®

VEIZADES & ASSOCIATES, INC. CONSULTING ENGINEERS

Winning Team ($1 million)
University of Illinois Urbana-Champaign—Team SelectPureLi, A Redox Membrane for Lithium Hydroxide Extraction

Runner-Up ($500,000): University of Virginia—Team TELEPORT, Targeted Extraction of Lithium with Electroactive Particles for Recovery Technology (TELEPORT)

Runner-Up ($500,000): George Washington University—Team Ellexco, Chemical-Free Extraction of Lithium from Brines

Improved quantification of Li resources for Lithium Valley – A research proposal

Pat Dobson, Will Stringfellow, Eric Sonnenthal, Jenn Stokes-Draut, Dev Millstein, Nic Spycher, Ram Kumar, Verónica Rodríguez Tribaldos, Nori Nakata, Avinash Nayak (LBNL), Mike McKibben, Maryjo Brounce, Jen Humphries (UC Riverside), Sabodh Garg (Geologica)

History of Salton Sea Li Estimation

- Numerous studies that have estimated the Li resource potential of these fluids, consisting of two approaches –
  - Estimate of Li production derived from geothermal well flow rates and Li concentrations, and
  - Li contents and the fluid volume of Salton Sea geothermal reservoir.
- As part of the USGS review Williams et al. (2009) used heat flow data, sediment thickness, and the distribution of permeable sediments to derive power potential.

Where is the lithium coming from and how much is there?

Improved Quantification of Li at Salton Sea

LBNL will quantify the sources and amounts of Li present in geothermal brines within the Salton Sea

(Lab Direct, FY22 $1.5M, 12 months)

- Develop a better constrained geologic model of the reservoir.
- Understand what is controlling the concentration of Li including analysis of the reservoir rock, and other sources of Li.
- How do the Li concentrations decrease over time?

Environmental Impacts at The Salton Sea

FRESH WATER USAGE

CHEMICAL USAGE

AIR QUALITY AND EMISSIONS

INDUCED SEISMICITY

American-Made Challenge | Geothermal Lithium Extraction Prize

Community Impact

ENVIRONMENTAL JUSTICE

COMMUNITY OUTREACH

EDUCATION

CROSS GOVERNMENTAL COLLABORATION

AMMTO-GTO Lithium Extraction and Conversion from Geothermal Brines

Awarded $10.9 million for 10 projects in Lithium Extraction and Conversion from Geothermal Brines

Topic Area 1: Field Validation of Lithium Hydroxide Production from Geothermal Brines: Pilot or demonstration projects to validate cost-effective, innovative lithium extraction and lithium hydroxide conversion technologies.

Topic Area 2: Applied Research & Development for Direct Lithium Extraction from Geothermal Brines: Research and development projects to advance emerging direct lithium extraction (DLE) process technologies to increase efficiency, reduce waste generation, and/or reduce cost of DLE.

https://www.energy.gov/eere/ammto/funding-selections-fy22-ammto-gto-lithium-extraction-and-conversion-geothermal-brines

Thank You!

the
drill down

Get the hottest geothermal news from *The Drill Down*, GTO's monthly newsletter!
Sign up today: geothermal.energy.gov

Check out GTO's Lithium Storymap!
energy.gov/eere/geothermal/lithium-storymap

Interested in serving as a merit reviewer for GTO RD&D projects?

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