Application of Ion Sieve Sorbent Prepared from Mineral Stream Associated with Critical Minerals in Direct Lithium Extraction

NATIONAL ENERGY TECHNOLOGY LABORATORY

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NETL Support Contractor








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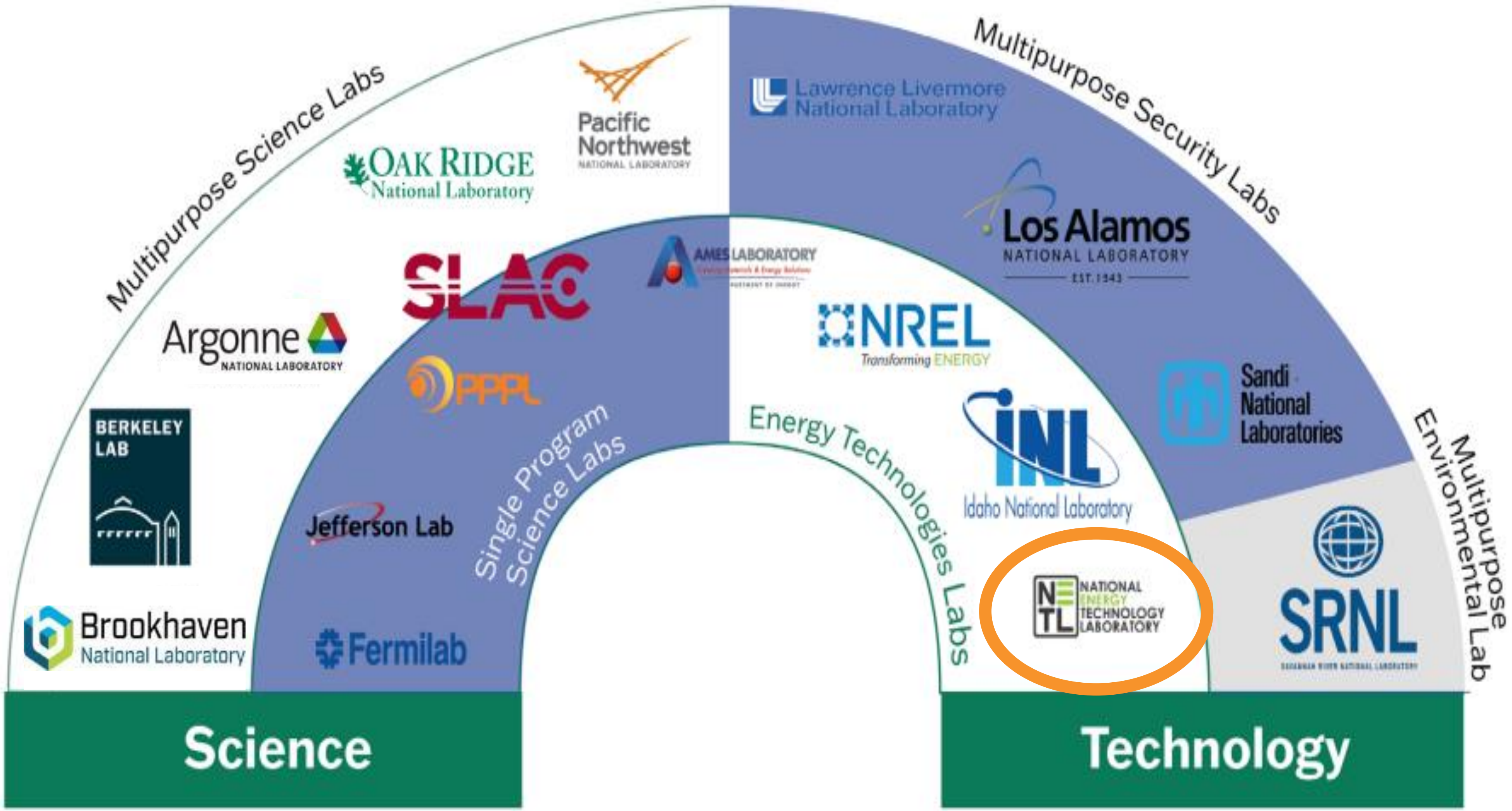
The DOE National Laboratory System



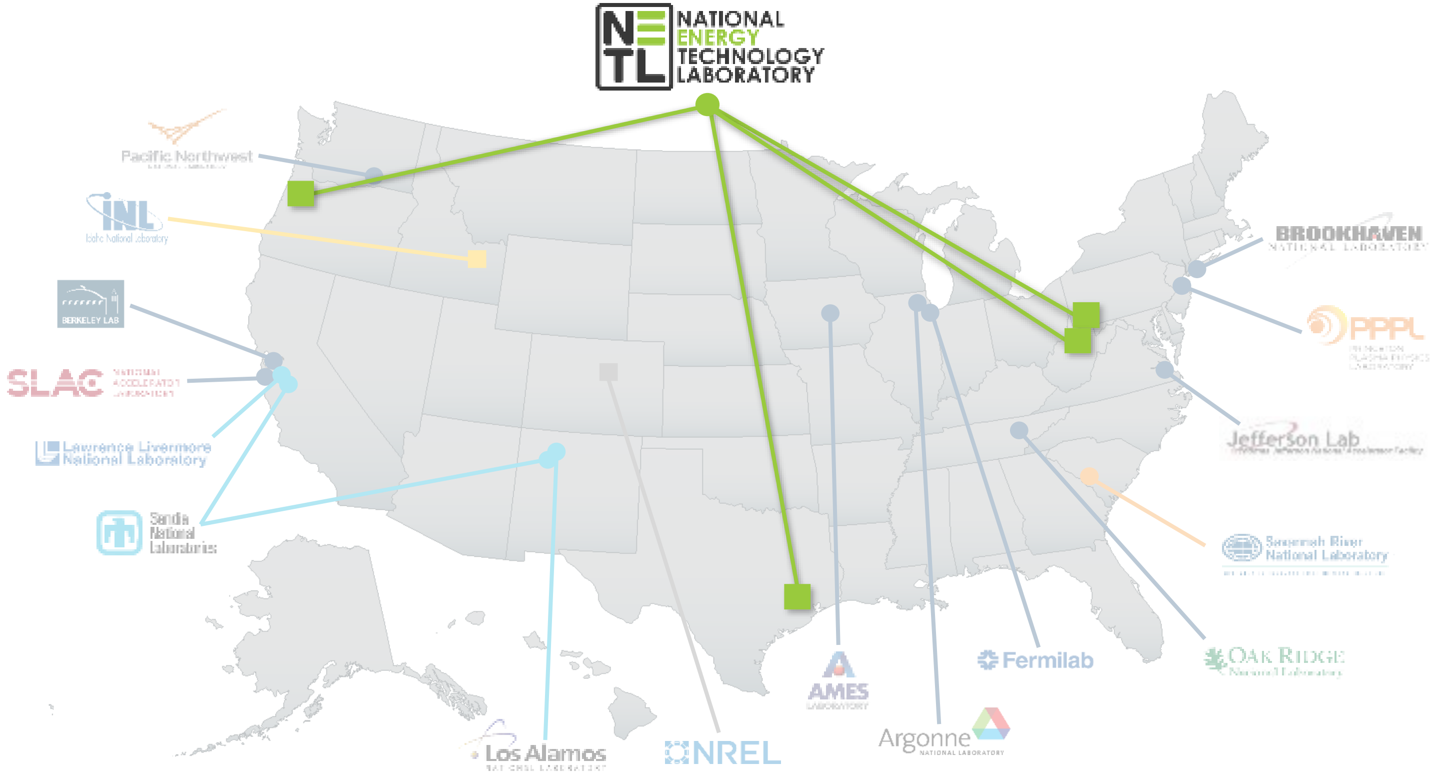
National Energy Technology Laboratory

NETL is:

- One of three applied energy DOE national labs
- The only DOE government owned & operated (GOGO) national lab

Two primary components:

- Research & Development
  - Carbon Management
  - Resource Sustainability
- DOE Program Deployment



NETL Supports U.S. Decarbonization Goals

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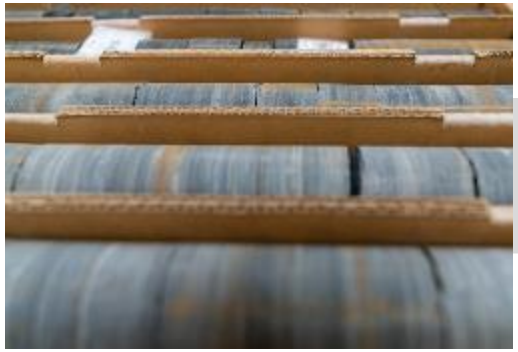
Carbon management to help decarbonize industry and power generation



Sustainable natural gas to meet our energy needs and support our allies

Critical minerals to build the clean energy and industrial economy and ensure national security

NETL R&D for Fossil Energy and Carbon Management Programs

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Carbon Management

Point Source Carbon Capture

Carbon Dioxide Conversion

Carbon Dioxide Removal

Carbon Transport & Storage

Hydrogen with Carbon Management

Carbon Dioxide Conversion Photo Courtesy of MicroBio

Resource Sustainability

Minerals Sustainability

Methane Mitigation Technology

Advanced Remediation Technologies

Natural Gas Decarbonization and Hydrogen Technologies

NETL's Vision & Mission

NATIONAL ENERGY TECHNOLOGY LABORATORY

VISION

Delivering a clean and secure energy future.

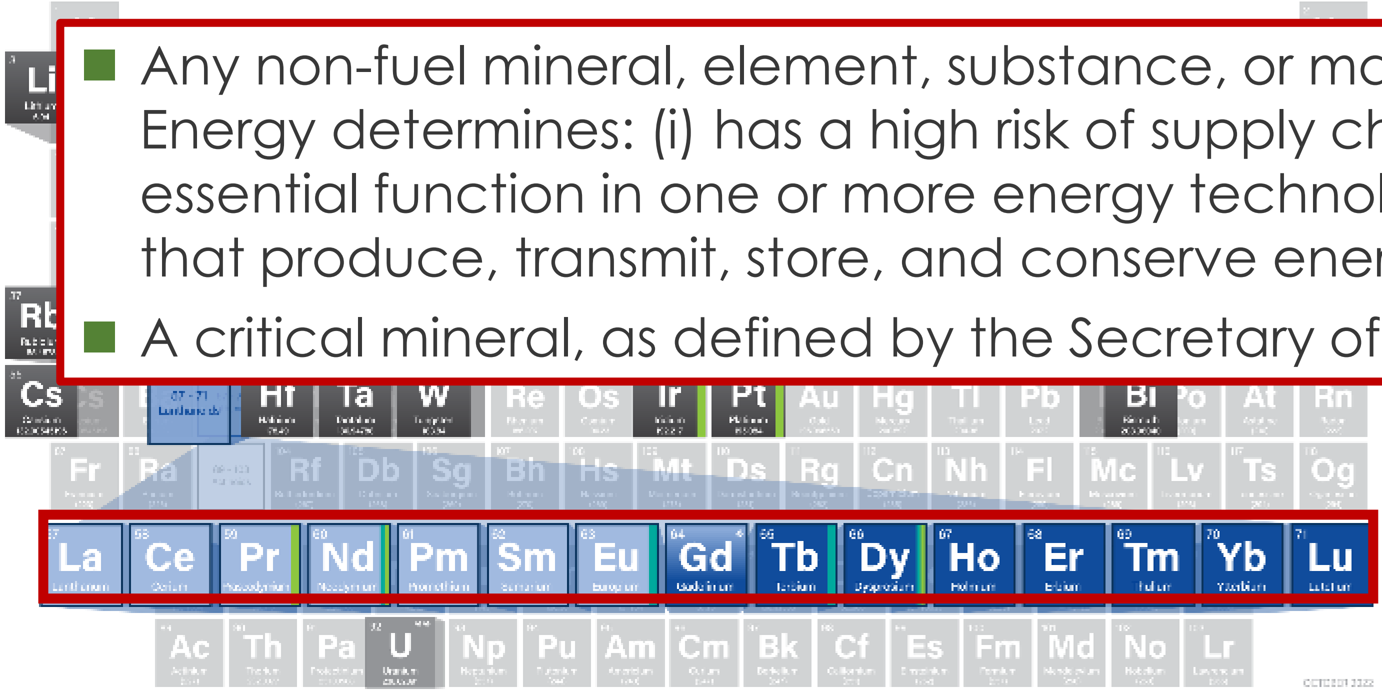
MISSION

To drive innovation and deliver solutions for a clean and secure energy future by advancing carbon management and resource sustainability technologies.

Critical Minerals

Critical to Emerging Technologies

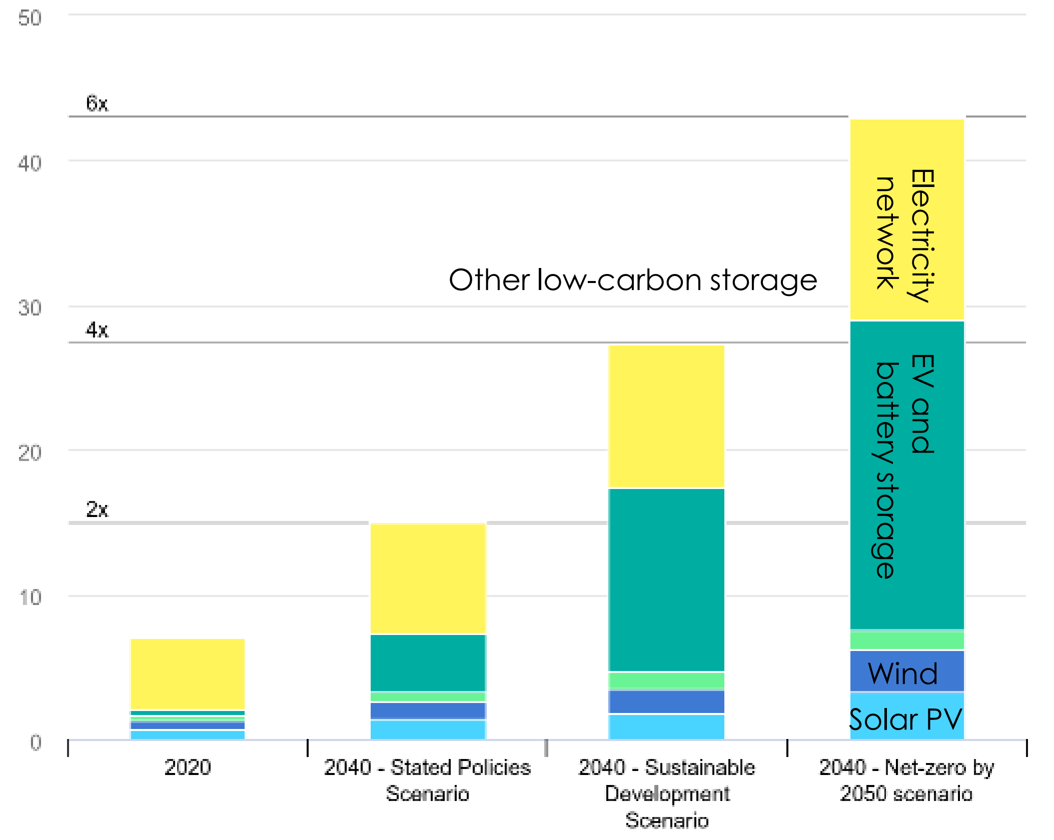
- Any non-fuel mineral, element, substance, or material that the Secretary of Energy determines: (i) has a high risk of supply chain disruption; and (ii) serves an essential function in one or more energy technologies, including technologies that produce, transmit, store, and conserve energy; or
- A critical mineral, as defined by the Secretary of the Interior



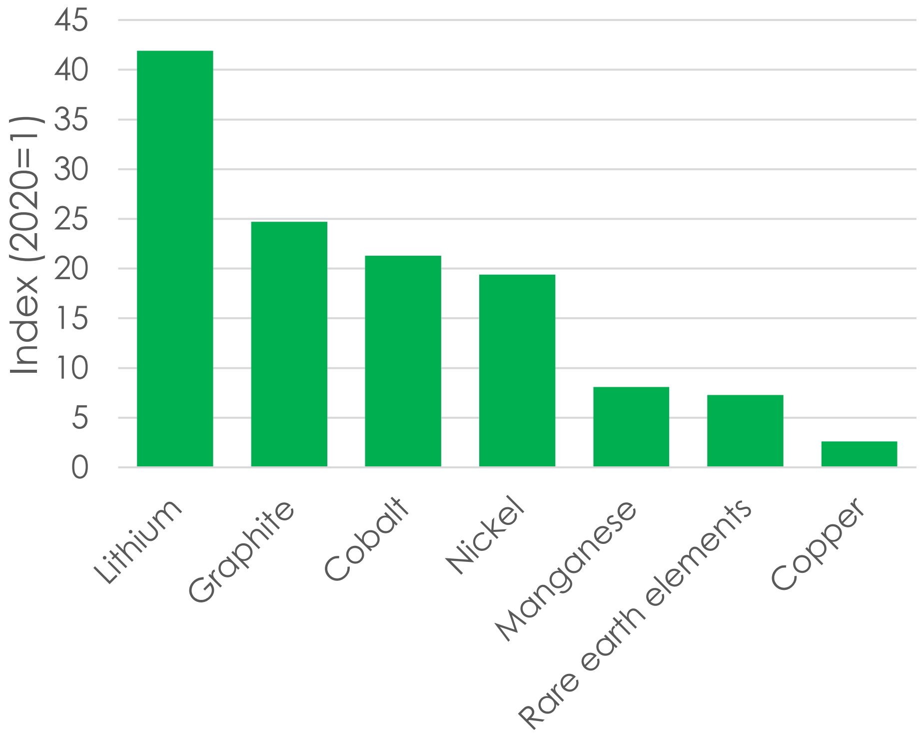
- Over 80% of U.S. rare earth element (REE) demand is import-dependent; at least 12 critical minerals (CM) are 100% from foreign sources.
- Executive Order 138176 recognized the strategic vulnerability of the nation's security created by the dependency on foreign sources.

Challenge: Clean Energy Technologies Drive Demand Growth

Increases 5-50x of Current CM Supplies in Next 20 Years



[Total mineral demand for clean energy technologies by scenario, 2020 compared to 2040 – Charts – Data & Statistics - IEA]



Source: IEA. Licence: CC BY 4.0 This data is subject to the IEA's terms and conditions: https://www.iea.org/t_c/termsandconditions/ Sustainable Development Scenario

Traditional Mining - Large Environmental Footprint

Environmental Impacts and Cost Drivers

- Expensive pre-treatment processing
- Strong inorganic acids and bases to crack minerals
- High temperature and pressure process conditions
- Hazards and cost associated with wastes:
  - Strong acid wastes containing unwanted elements and radioactive materials (e.g., Thorium, Uranium)
- High organic solvent use in the purification and separation of REE into individual product streams

https://www.bbc.com/future/article/20150402-the-worst-place-on-earth


(Image credit: Liam Young/Unknown Fields)


MICHAEL STANDAERT/YALE E360


Rare-earth mining in China comes at a heavy cost for local villages

https://e360.yale.edu/features/china-wrestles-with-the-toxic-aftermath-of-rare-earth-mining
https://www.theguardian.com/environment/2012/aug/07/china-rare-earth-village-pollution

Valorization of Fossil Energy Waste Streams

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Carbon Ore, Coal Byproducts, Oil & Gas Drill Cuttings, Produced Waters


Coal


Refuse


Fly Ash


AMD

COULD BE PROCESSED TO…


Produce Rare Earth Elements


Fortify National Security


Produce Feedstock for Advanced Materials


Produce Clean Water

Amrclearinghouse.org; fondriest.com; defenseimagery.mil; netl.doe.gov; energy.gov

Acid Mine Drainage (AMD)

Viable Alternative Source of REEs and CMs

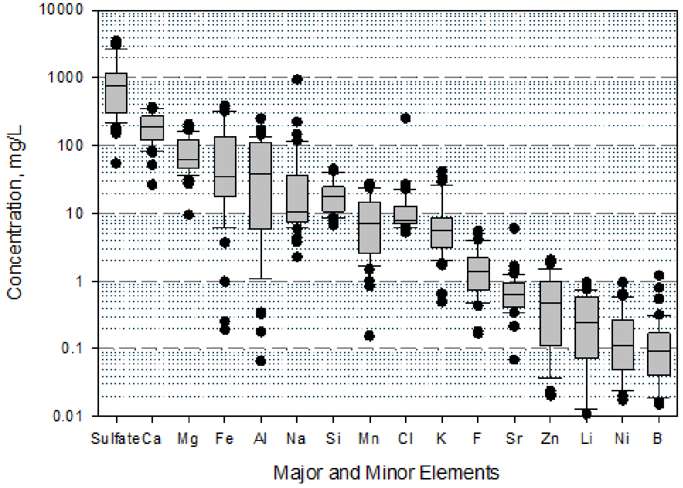
$$FeS_2 + {}^{7}/_{2}\,O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

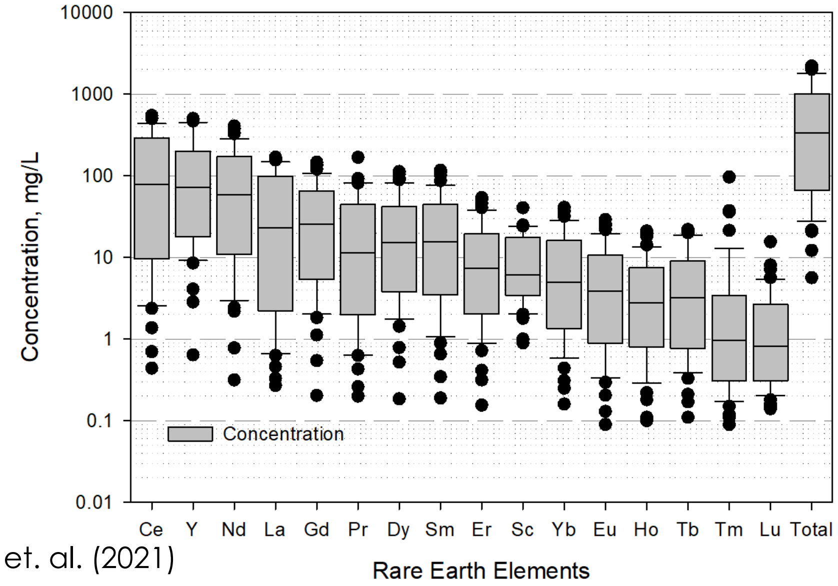
$$Fe^{2+} + {}^{1}/_{4}\,O_2 + H^+ \rightarrow Fe^{3+} + 3H^+$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

$$FeS_2 + 14Fe^{3+} + H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

- Over 5,400 km of streams in the Appalachian region are negatively impacted by AMD.
- Appalachian AMD is enriched in both critical and middle REEs.





Cheng et. al. (2021)

CMs from 140 discharges across Pennsylvania[2]

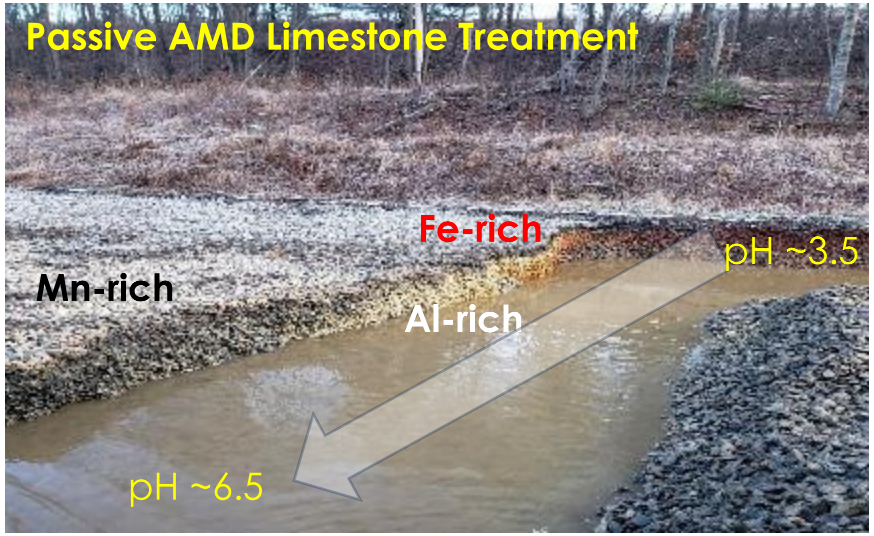
Element	Max conc. (ug/L)	Min conc. (ug/L)	Max loading (kg/year)	Min loading (kg/year)
Mg	210,000	3,600	3,541,140	40
Mn	74,000	19	215,522	4.5
Sr	3,600	27	83,321	0.23
Ni	3,200	2.6	10,428	0.3
REE	1,765	0.4	7,364	<0.01
Co	3,100	0.3	6,952	0.1
Cu	190	0.4	2,086	<0.1
Li	390	11.0	4,513	0.2

Cravotta (2008); Cravotta and Brady (2015)

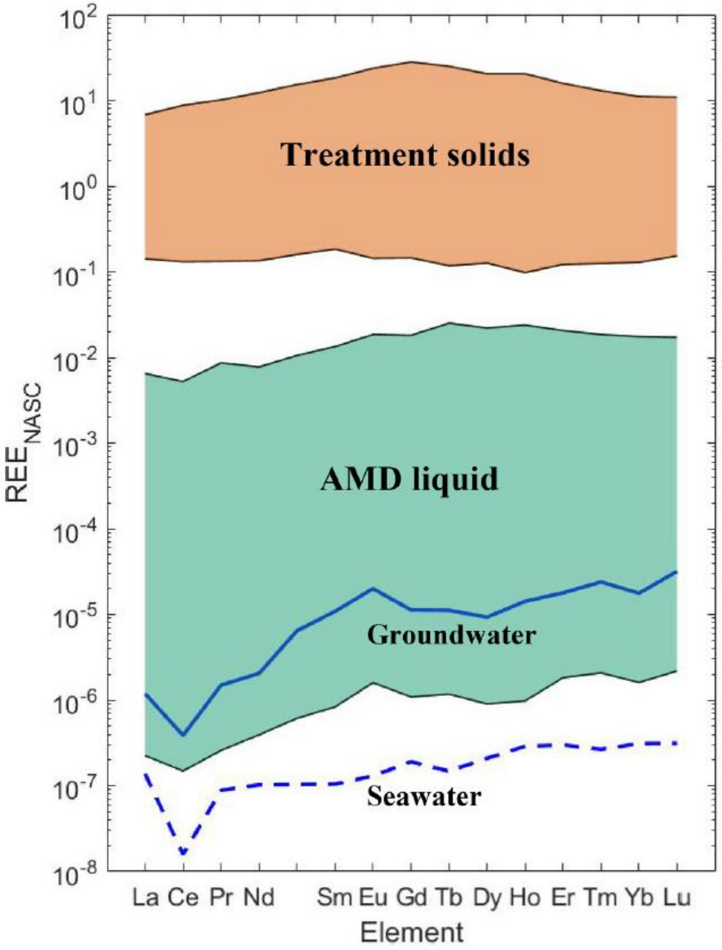
AMD Solids

Potential Sinks for CMs

- AMD solids are precipitates formed during acid neutralization by active or passive treatments.



Source: https://www.slideshare.net/MichaelHewitt4/bob-hedin-hedin-environmental-effective-passive-treatment-of-coal-mine-drainage

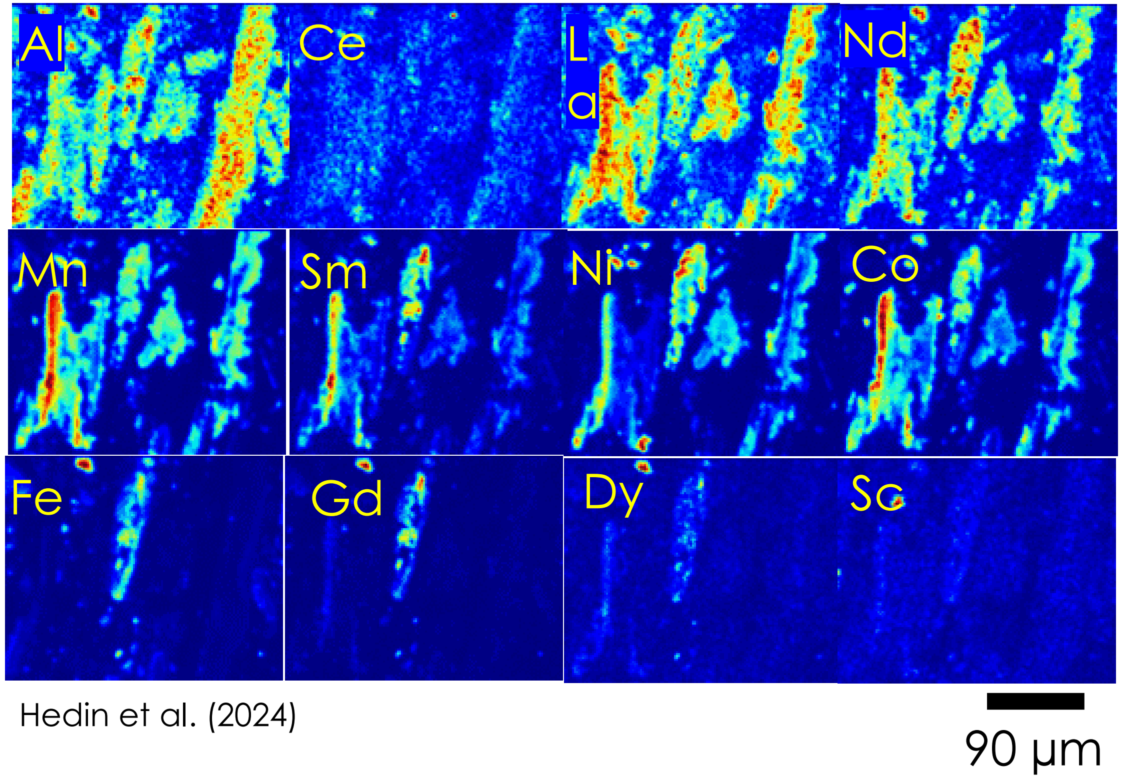


Hedin et al. (2019 & 2020, IJCG)

- Over 200 systems in PA treating ~240 million gallons per day (MGD) AMD.
- Elevates pH and sequentially precipitates metals.
- >90% REEs in AMD are trapped in the beds.
- ~1,100 tons/yr rare earther oxides (REOs) recovery potential (~40% U.S. annual demands).

Harvesting Rare Earths from AMD Solids

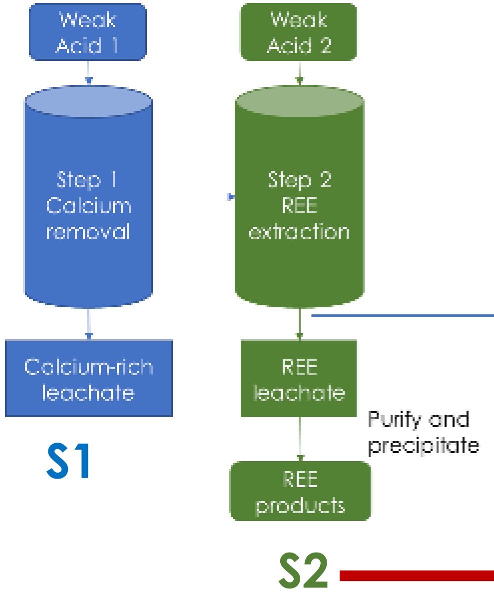
Targeted Rare Earth Extraction

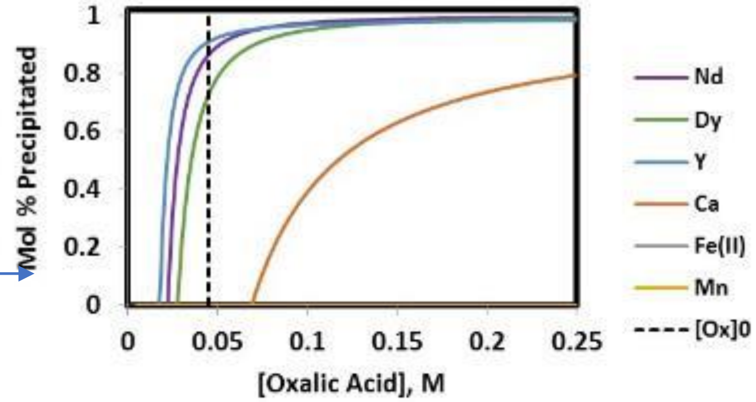


Hedin et al. (2024)

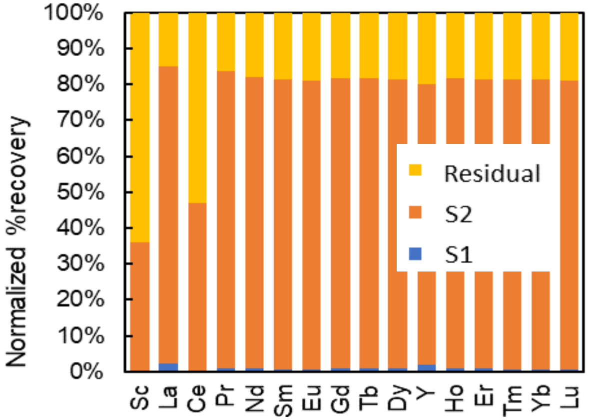
- REEs are mostly co-localized with Mn- and Al-rich solids.
- Heavy REEs (e.g., Sm and Gd) are co-localized with Fe.

Targeted Rare Earth Extraction (TREE)





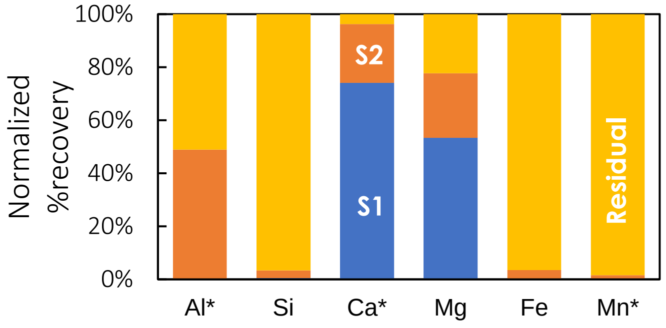
~45% Residual

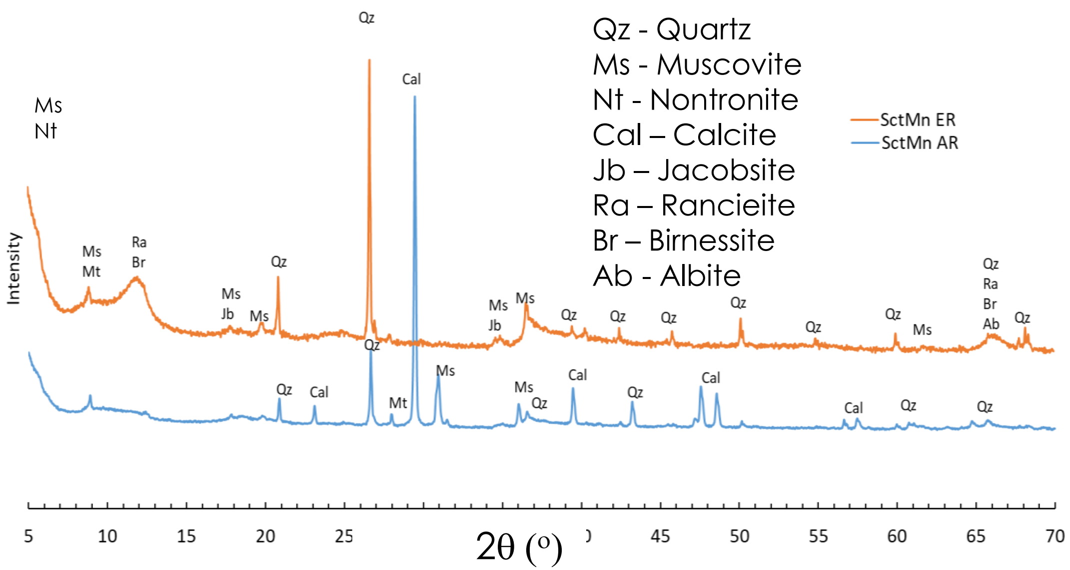


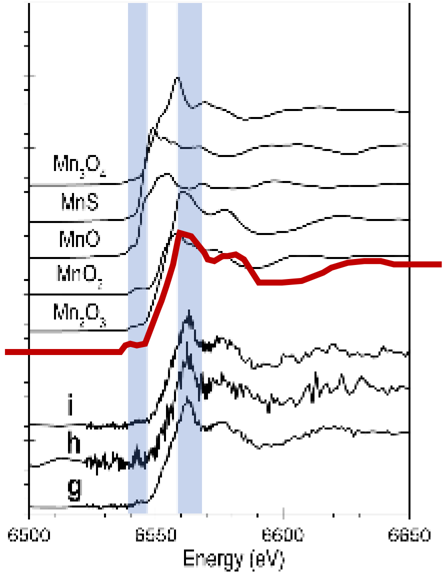
- Patent-pending, low acid consumption, TREE process extracts over 80% of REEs.
- Carried out under room temperature and pressure.
- Sequential direct oxalic precipitation recovers 99% of extracted REEs.

Extraction Residuals

Potential Feedstock to Prepare Ion Sieves for Lithium







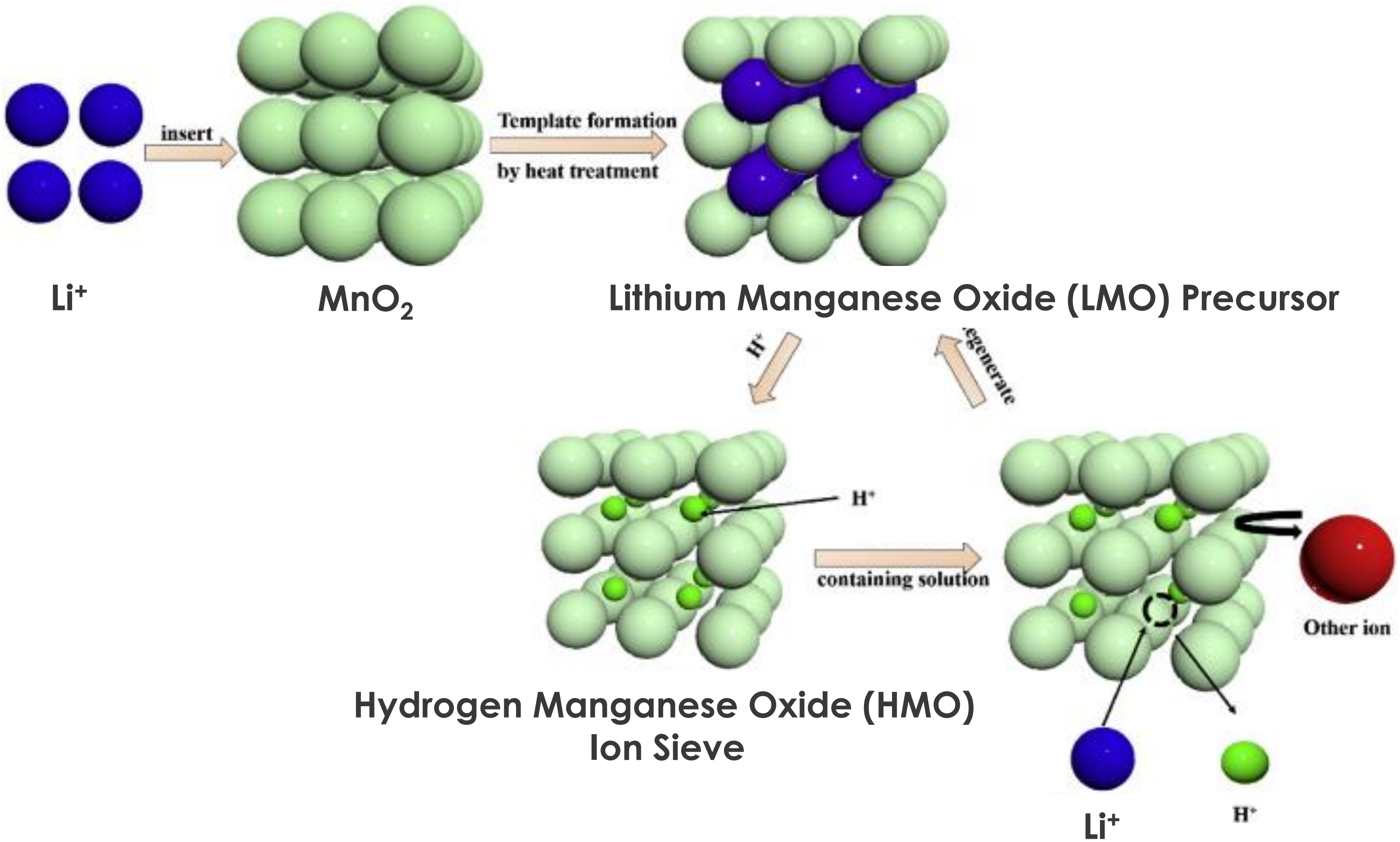
	Concentrating Factor after Extraction
Al	0.78
Si	1.33
Ca	0.05
Mg	0.35
Fe	2.45
Mn	2.11
Na	1.47
K	1.07

- Clay minerals (i.e., muscovite and nontronite), quartz, and calcite are the major crystallin minerals in the as-received Scootec Mn-rich AMD solids (SctMn).
- No calcite was found in SctMn-S2 residual. A mix of crystalline and amorphous rancieite, birnessite, and/or jacobsite were possible minerals bearing Mn.
- X-ray absorption near edge structure (XANES) analysis suggests Mn(IV) is the dominating species.
- Mn-rich AMD extraction residual is a potential feedstock to prepare **hydrogen manganese oxide (HMO)** sorbents.

HMO for Direct Lithium Extraction

Lithium Ion Sieves

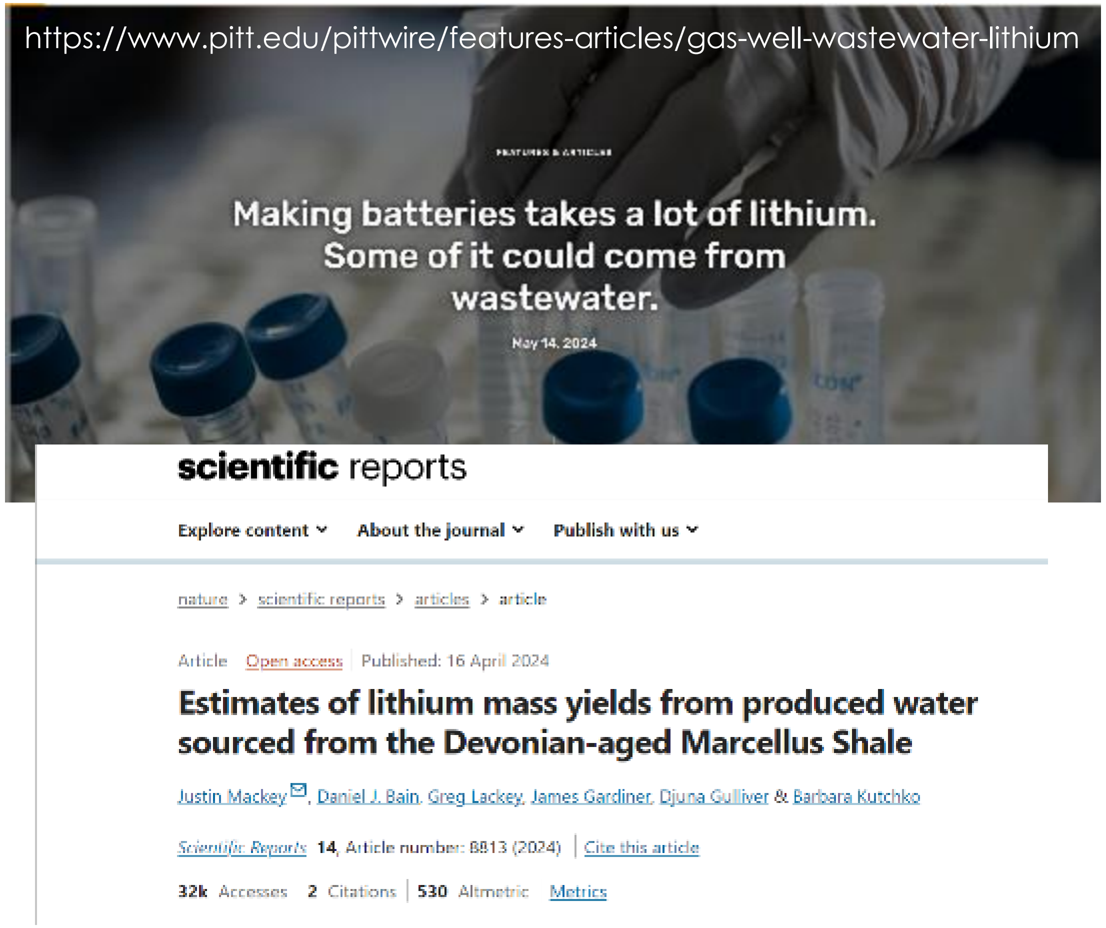
- Currently, inorganic ion sieve is the most technologically advanced approach for direct lithium extraction from geothermal brines (Stringfellow and Dobson, *Energies*, 2021).
- Current inorganic ion sieves showing high Li selectivity include:
  - MnO_2 (~8-~55 mg/g) (Li et al., *Johnson Matthey Technology Review*, 2018)
  - Layered double hydroxide (~8 mg/g) (Stringfellow and Dobson, *Energies*, 2021)
  - H_2TiO_3 sorbent (37 mg/g (Shi et al., *TNMSC*, 2013), 32.6 mg/g (Chitrakar et al., *J. Solid State Chem.*, 2014))



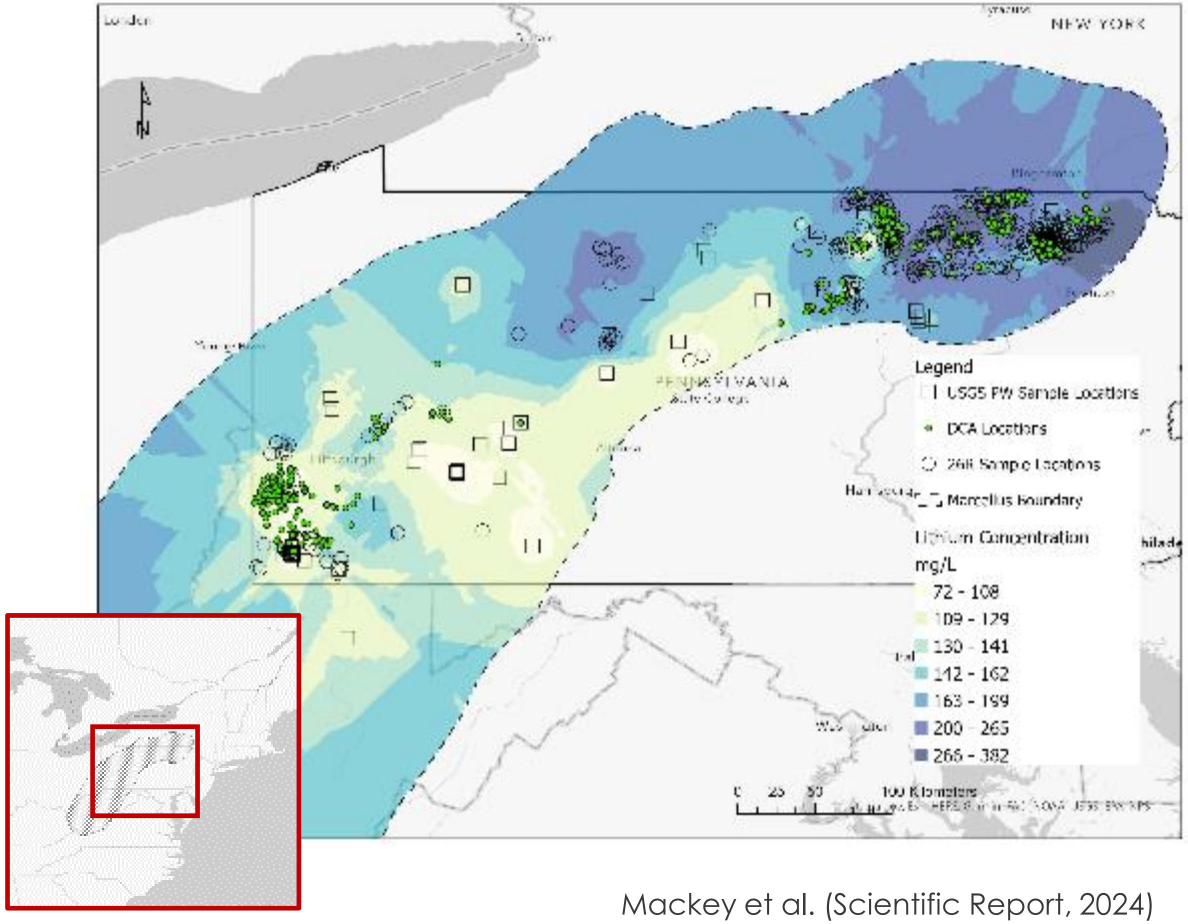
Modified from Weng et al., (*Prog. Nat. Sci.: Mater. Int*, 2020)

Direct Lithium Extraction from Oil and Gas Produced Waters

PW is a Viable Lithium Source



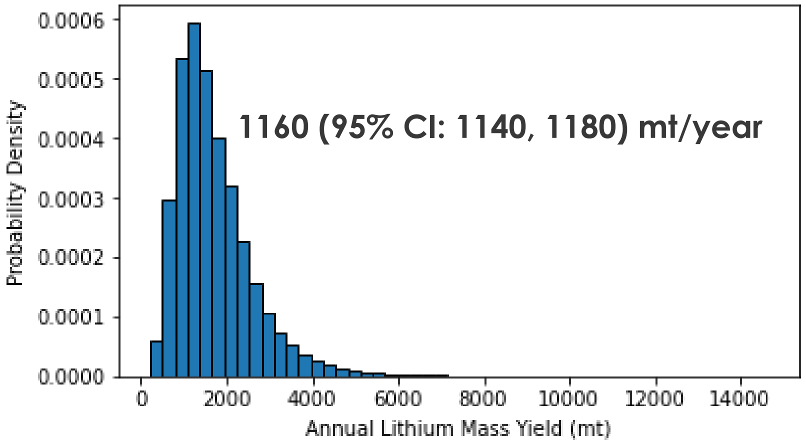
https://www.nature.com/articles/s41598-024-58887-x

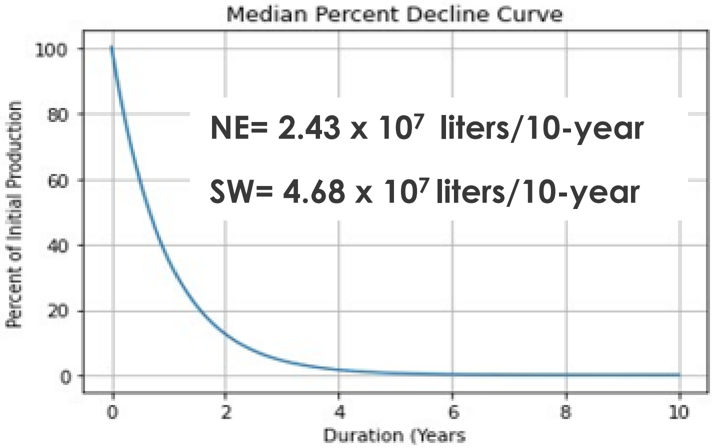


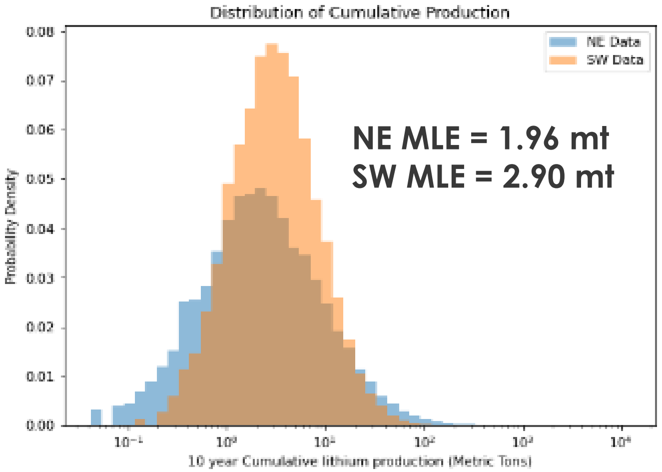
Mackey et al. (Scientific Report, 2024)

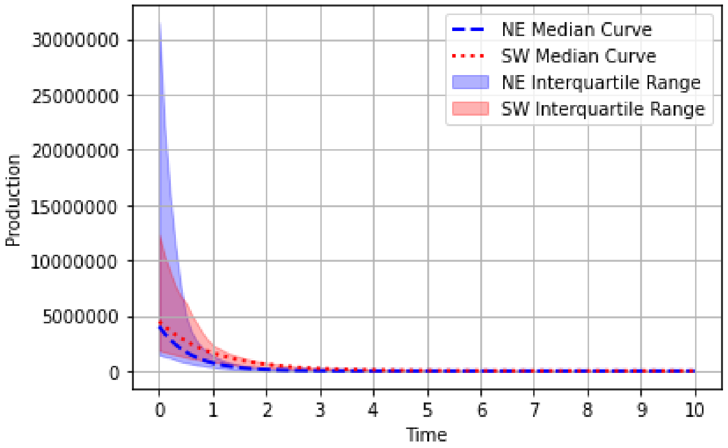
Direct Lithium Extraction from PW

PW is a Viable Lithium Source

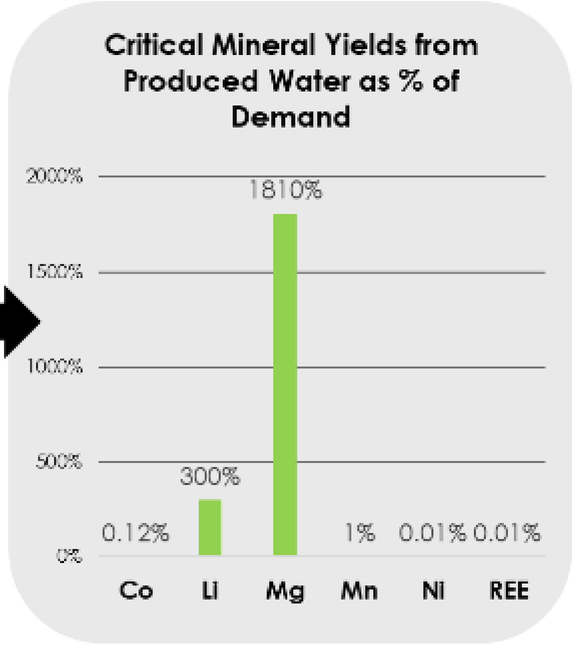








Mackey et al. (Scientific Report, 2024)



Key finding: Lithium in U.S. PW can meet 300% of current "USGS estimated" U.S. lithium demand

Smith et al. (Sci. Tot. Environ., 2024)

Lithium Ion Sieve from Acid Mine Drainage Residuals (LISA)

Solid State Method

SctMn-S2

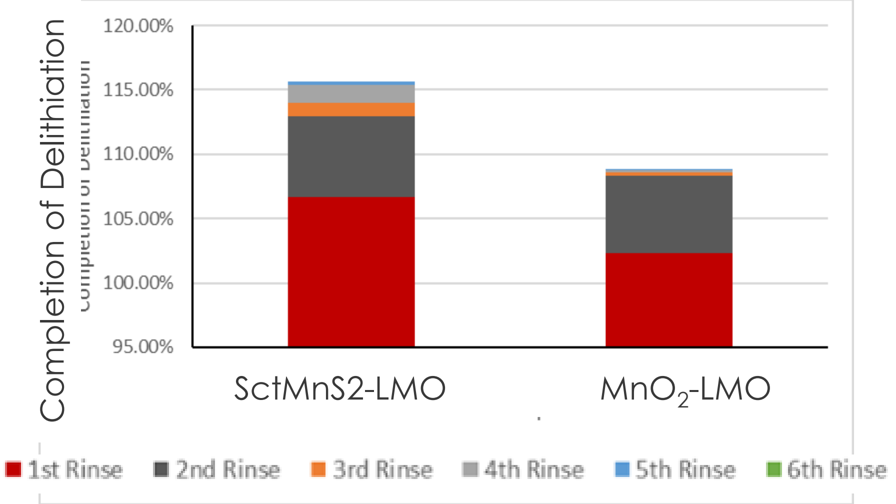
LiOH· H_2O

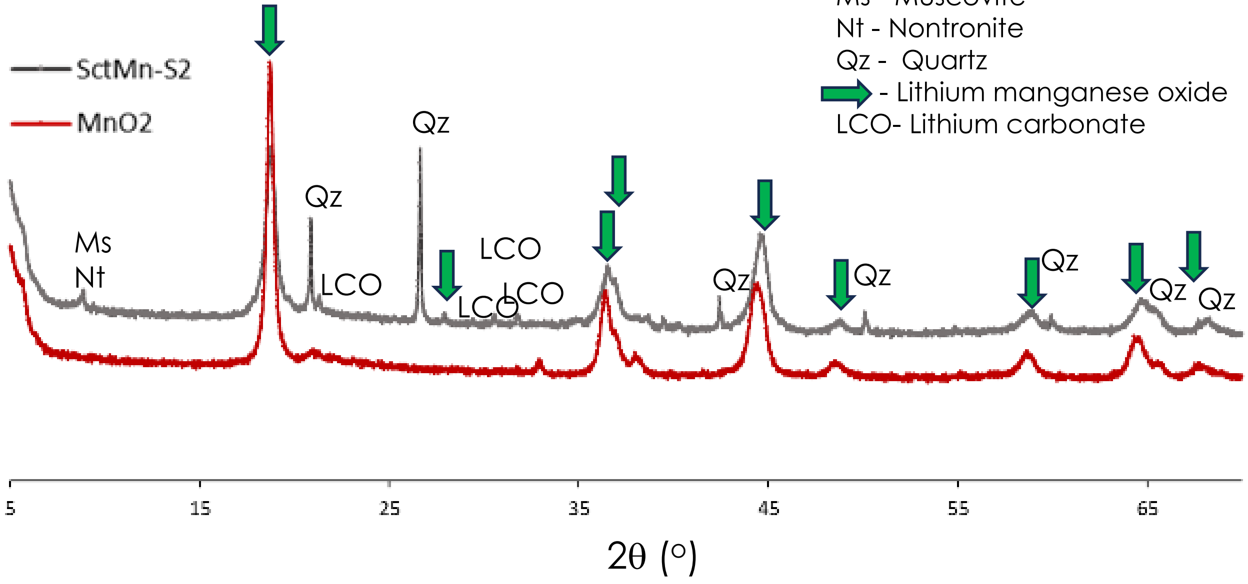
Solid State Reaction

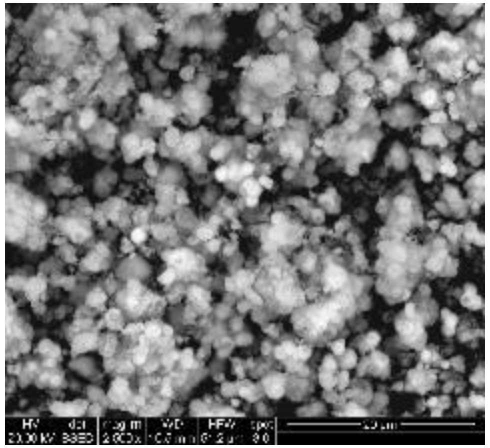
LMO Precursor

Delithiation

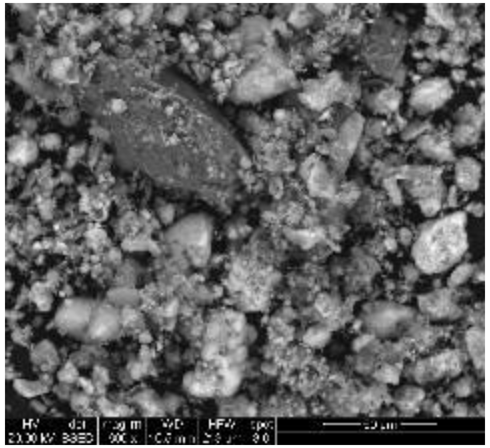
LISA (HMO)







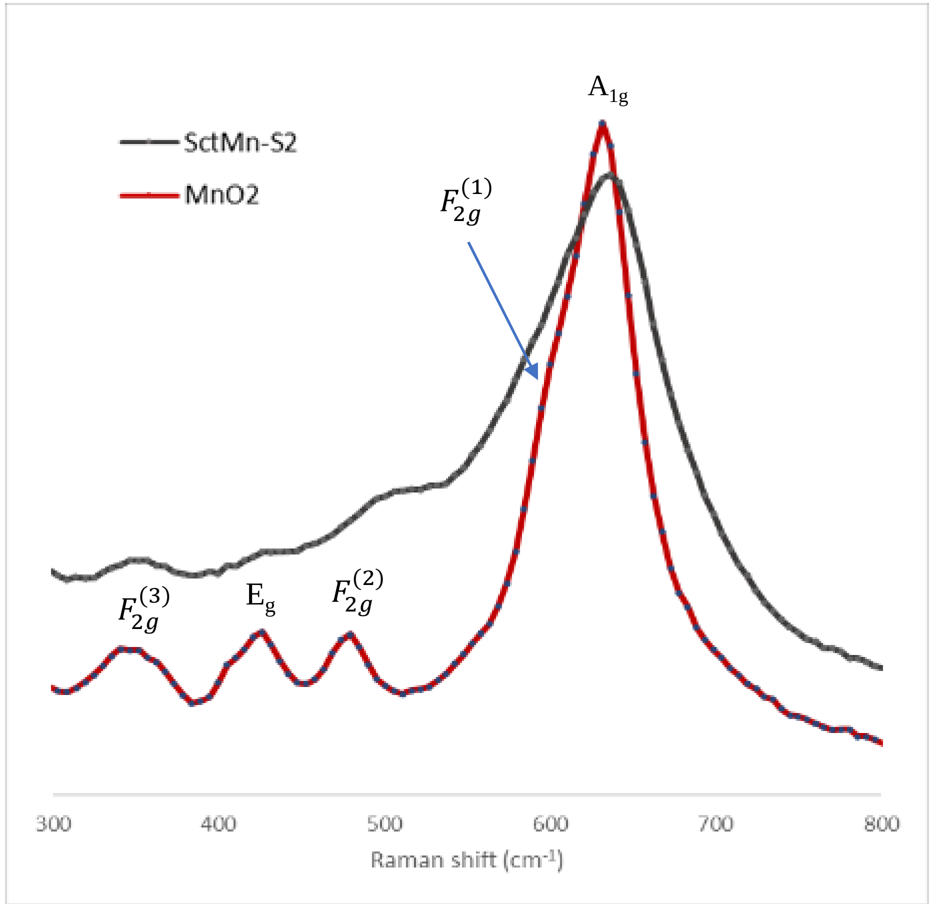
LMO prepared from MnO_2.



LMO prepared from SctMn-S2.

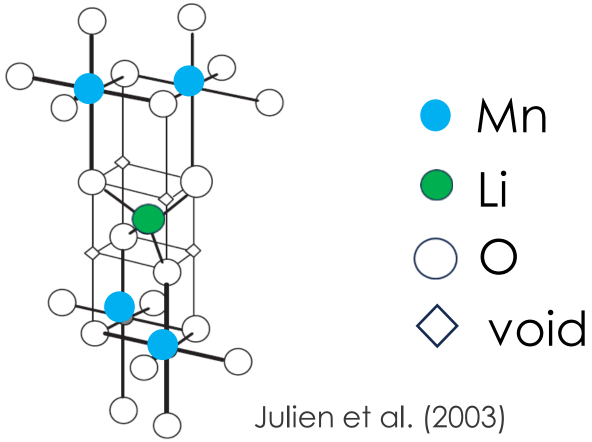
Lithium Ion Sieve from Acid Mine Drainage Residuals (LISA)

Spinel Lithium Manganese Oxide Precursor

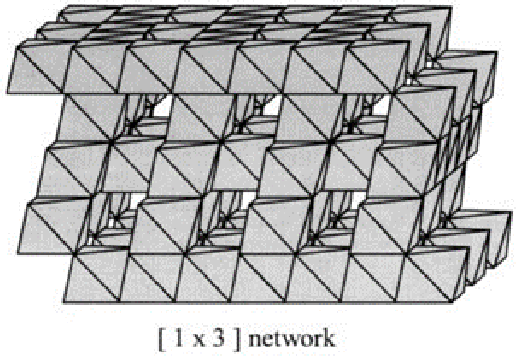


Raman Shifts (Unit: cm^{-1})

LMO	Mn-O			Li-O	Mn-O+Li-O	References
	A_{1g}	$F_{2g}^{(1)}$	$F_{2g}^{(2)}$	$F_{2g}^{(3)}$	E_g	
SctMn-S2-LMO	**636.4**	**-**	**~500.5**	**351.7**	**431.7**	**present**
MnO_2-LMO	**631.3**	**~600.1**	**479.4**	**351.7**	**426.5**	**present**
$LiMn_2O_4$	625-629	583-590	480-483	365-382	426-432	Ammundsen et al., 1999; Julien et al., 2003; Slautin et al. 2018
$Li_{1.33}Mn_{1.66}O_4$	634-653	600	491	376	434	Julien et al., 2003
$Li_2Mn_2O_4$	607	-	-	-	-	Julien et al., 2003



Julien et al. (2003)

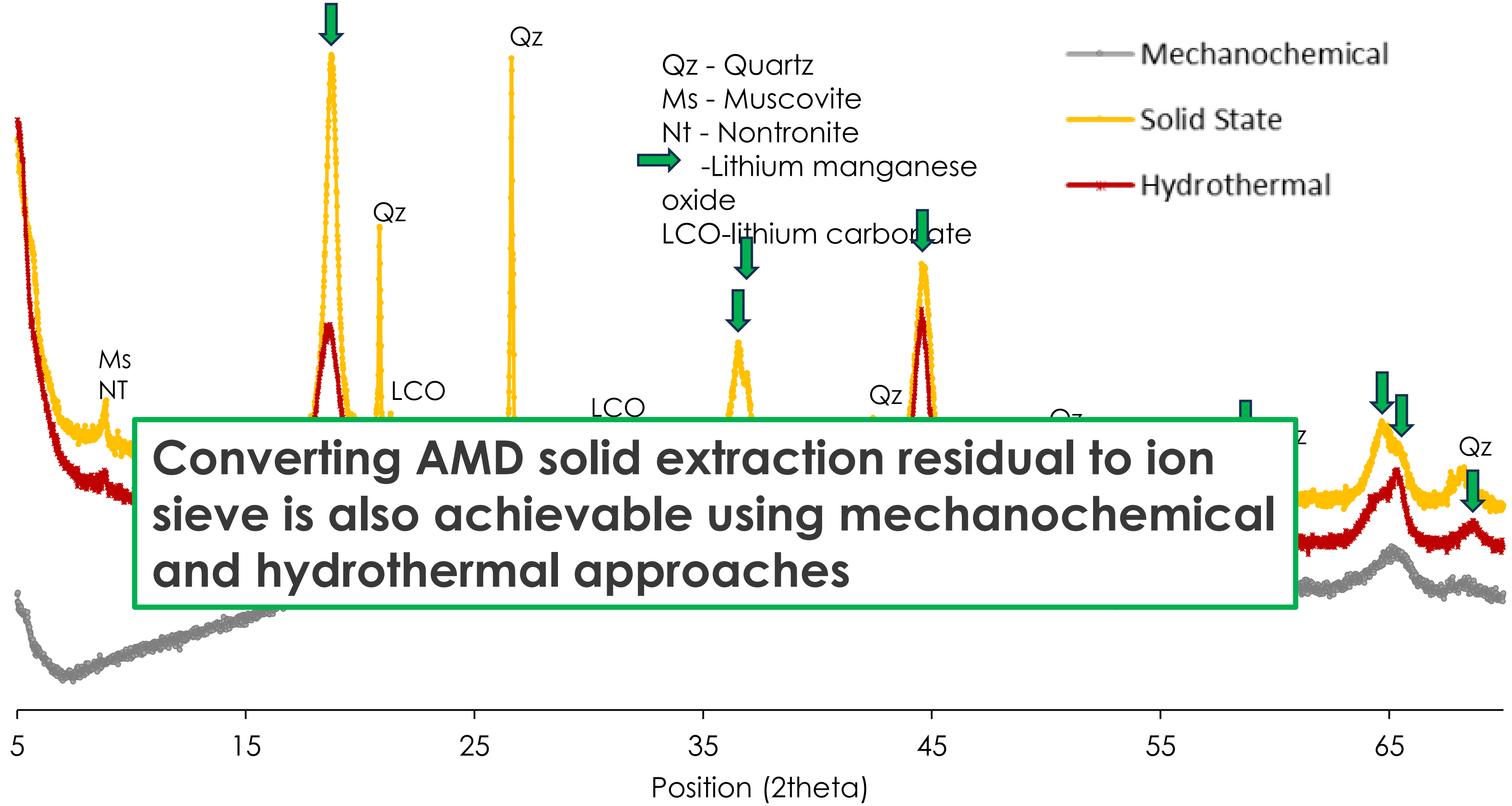


Feng et al. (1998)

Developing Alternative Synthesis Approaches

Hydrothermal Method

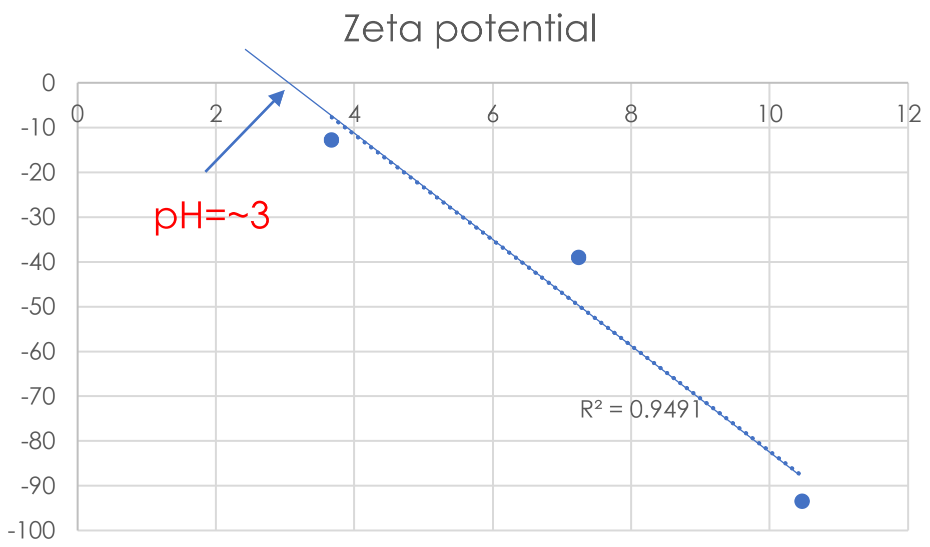
Mechanochemical Synthesis



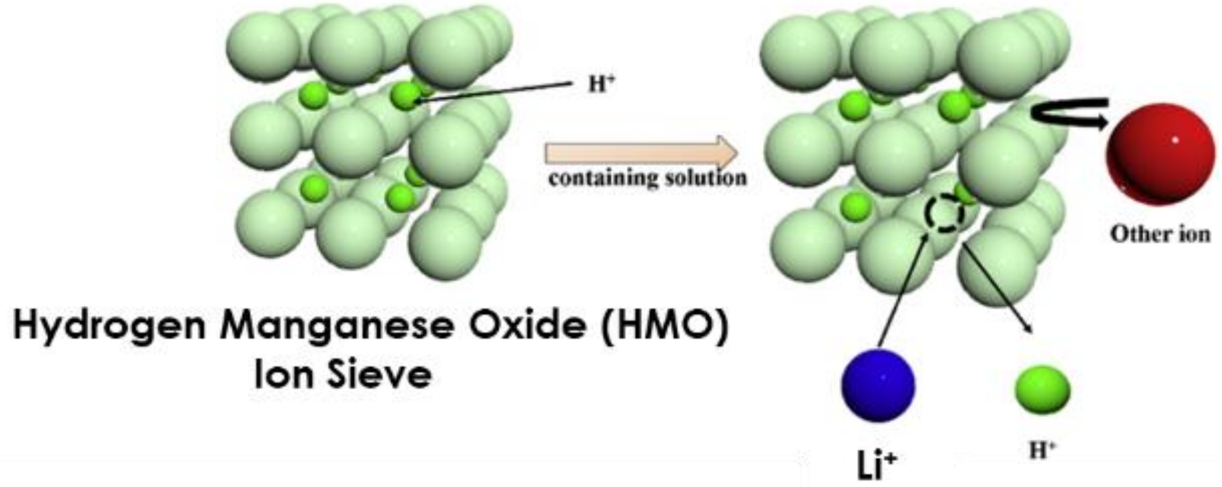
Converting AMD solid extraction residual to ion sieve is also achievable using mechanochemical and hydrothermal approaches

Adsorption Capacity of LISA

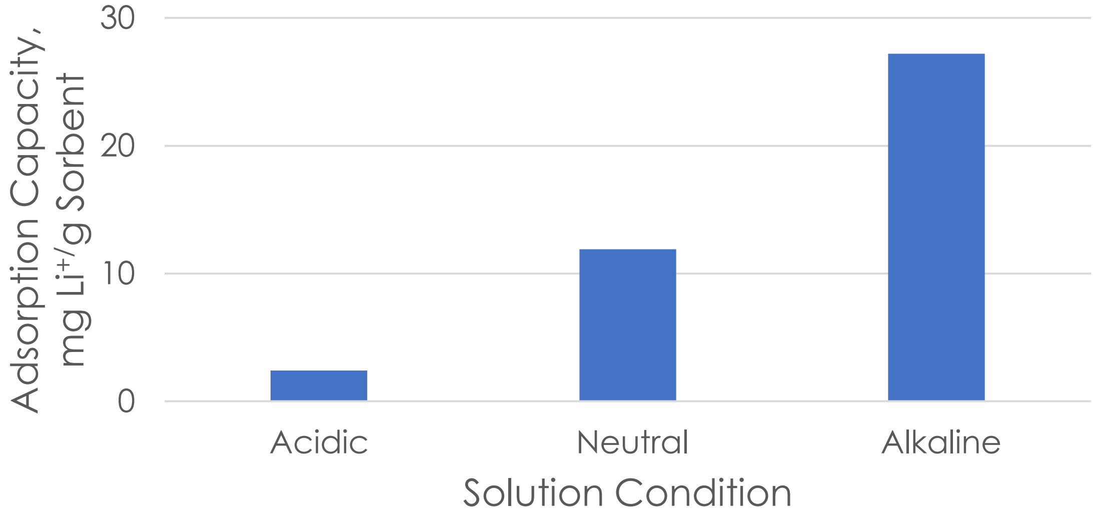
pH Dependent



- Zeta potential of LISA under various pH was characterized using an Electrophoretic Light Scattering (ELS) technique.
- Characterizing surface charge of LISA allows us to predict adsorption effectiveness and optimize operation condition for direct lithium extraction.



(Modified from Weng et al., *Prog. Nat. Sci.: Mater. Int*, 2020)



Adsorption Capacity of LISA

Comparing to HMO Ion Sieves Prepared by Others Using Chemical Reagents

Characterized Using Simple Li Solution

	Solution Matrix	pH	Adsorption Capacity (mg/g)
LISA-1	Li_2CO_3	9.7±0.5	**~30**
	Li_2CO_3	7.0±0.7	**~15**
LISA-2	Li_2CO_3	9.94±0.12	**~30**
LISA-3	Li_2CO_3	9.8±0.3	**~30**
Zhang et al. (2009)	LiCl	9.19	16.8
Zhang et al. (2010)	LiCl	10.1	20.5
Xiao et al. (2015)	LiCl	10.1	23.5
Wang et al. (2009)	LiCl	10.12	28.4
Wang et al. (2009)	LiCl	7.14	12.3

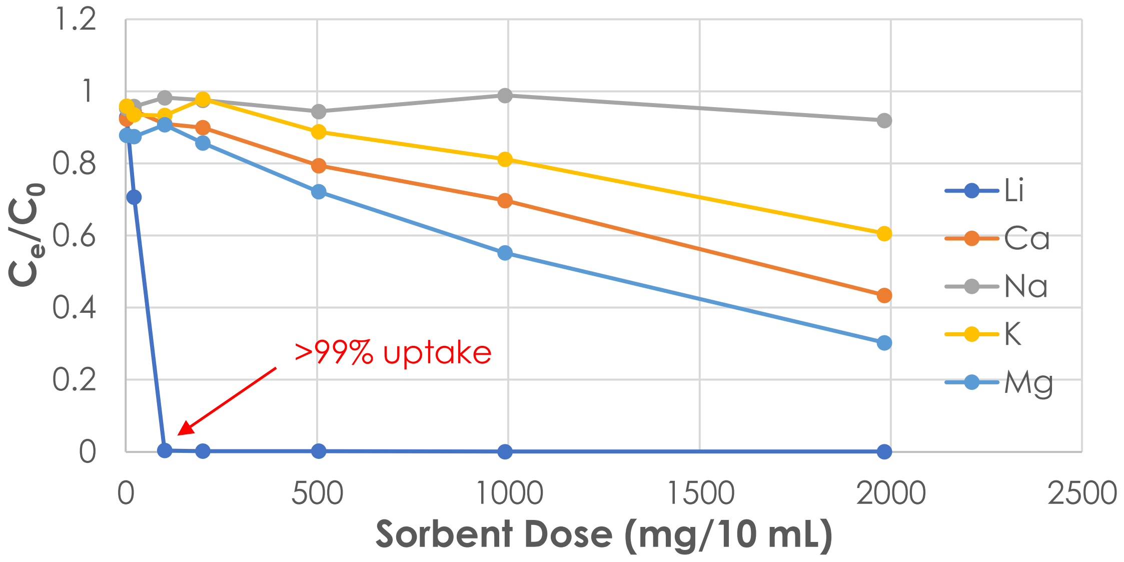
Characterized Using Solution with Complex Matrix

	Solution Matrix	pH	Adsorption Capacity (mg/g)
LISA-1	Tuttle Feedwater (Li^+ 106 mg/L; Na^+ 58.0 g/L; K^+ 1.03 g/L; Ca 12.5 g/L; Mg 1.7 g/L)	**9.92**	**~30**
Ma et al. (2011)	Salt Lake Brine (Li^+ 237 mg/L; Na^+ 3591 mg/L; K^+ 3118 mg/L; Mg^{+2} 109 g/L)	6	1.5
Sun et al. (2011)	Mixed solution with Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+} of 10.0 mmol/L	-	46.6
Chitrakar et al. (2001)	Seawater (Li^+ 0.17 mg/L)	8.1	40
Shi et al. (2011)	Simulated brine (Li^+ 270 mg/L)	5.35	27.2

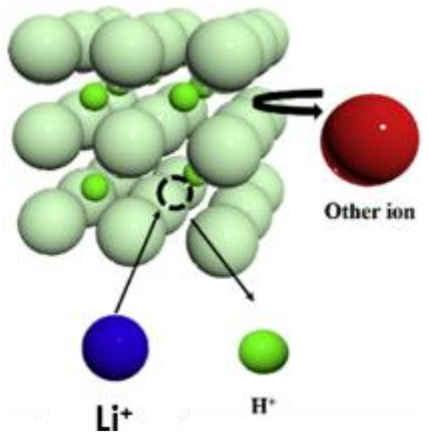
Selectivity of LISA

Distribution Coefficients, Kd ($wt._{sorbent}/wt._{solution}$)

- "Ion-sieve" effect enables LISA to have excellent screening and memory to target Li^+ from other coexisting cations.
- Adsorption of coexisting cations occurs due to electrostatic attraction.
- Relative significance of the ion-sieve effect and electrostatic attraction affects the selectivity treating oil and gas produced waters and geothermal brines with various salinities.



TF geothermal brine: Li ~100 mg/L; Ca:12,000 mg/L ; Na:~60,000 mg/L



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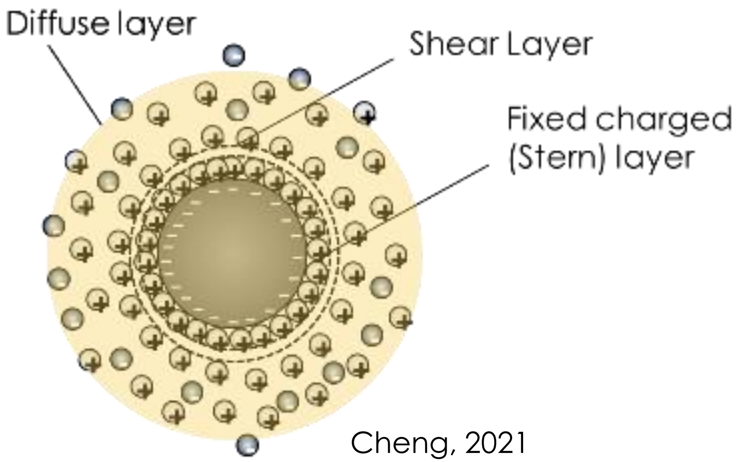
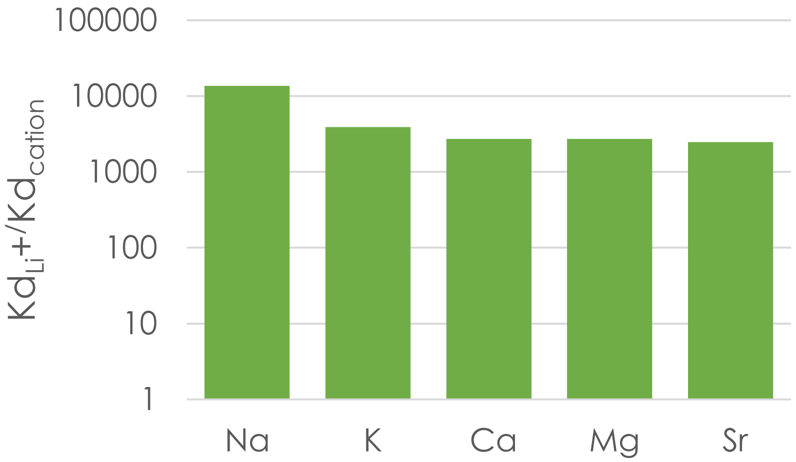
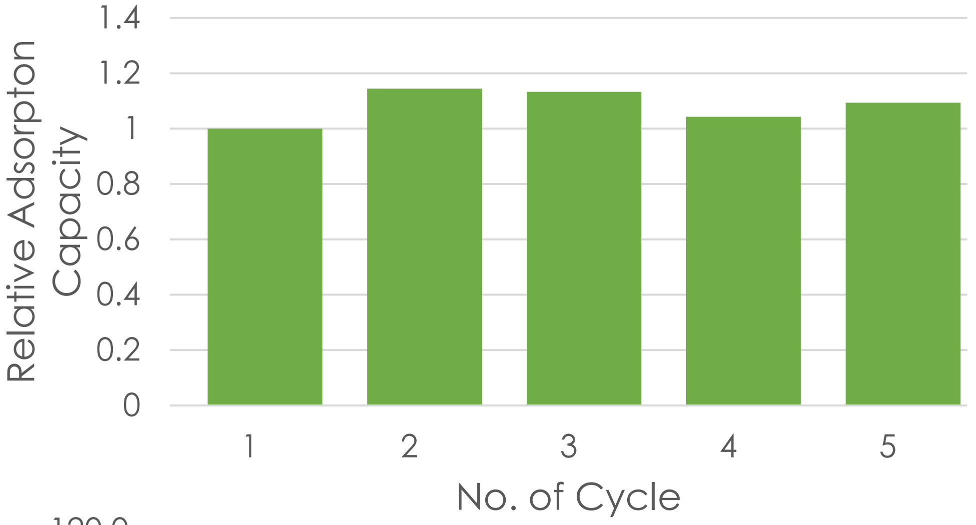


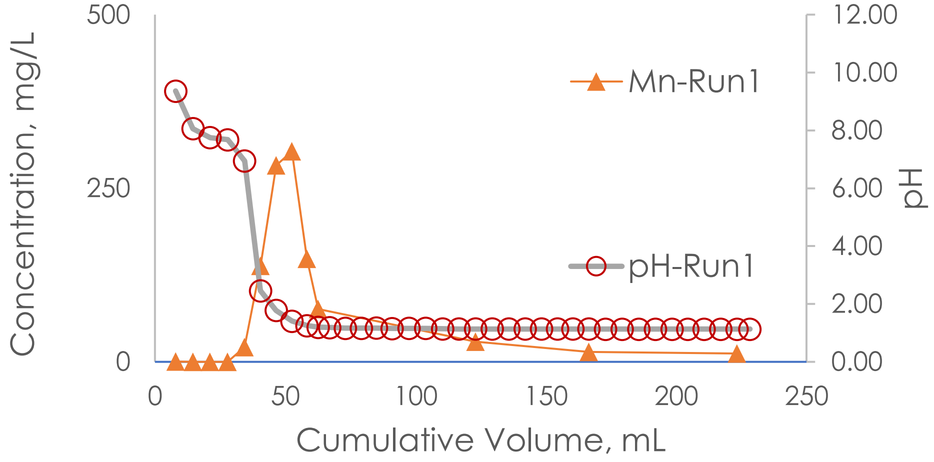
Cheng, 2021

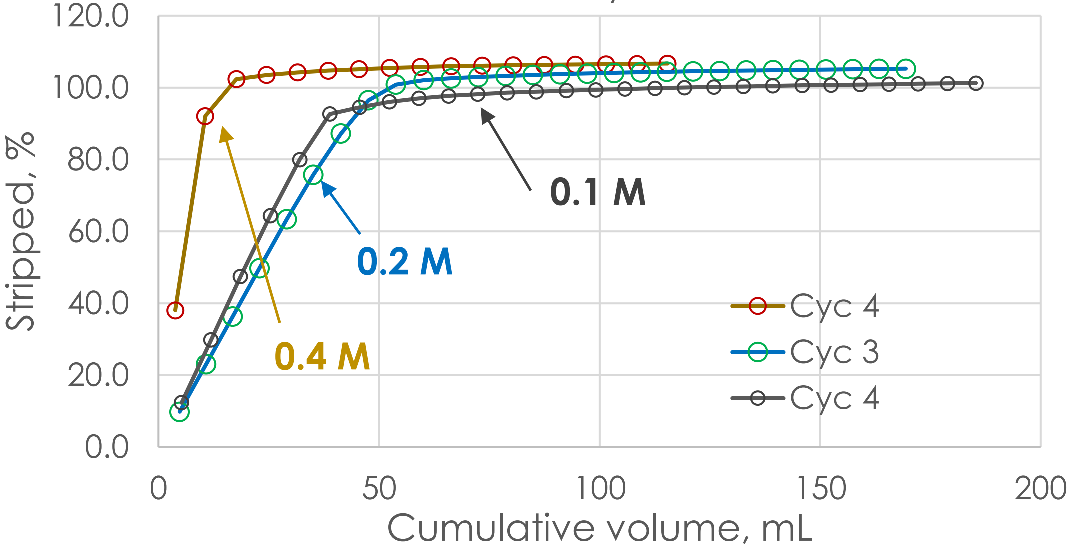


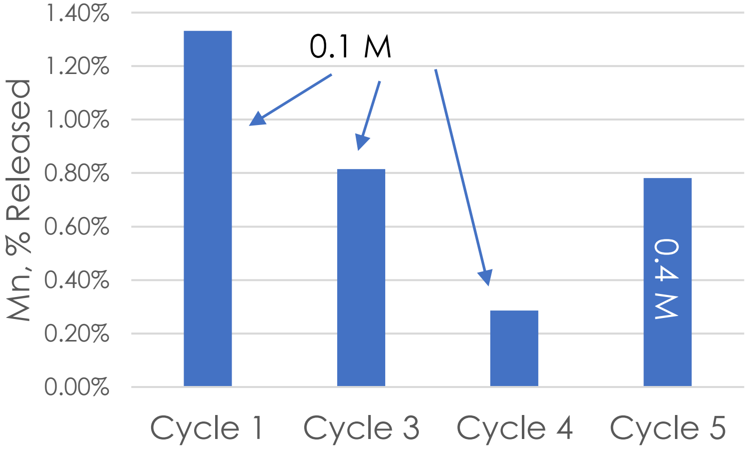
Durability of LISA

Adsorption/Regeneration Cycle Test



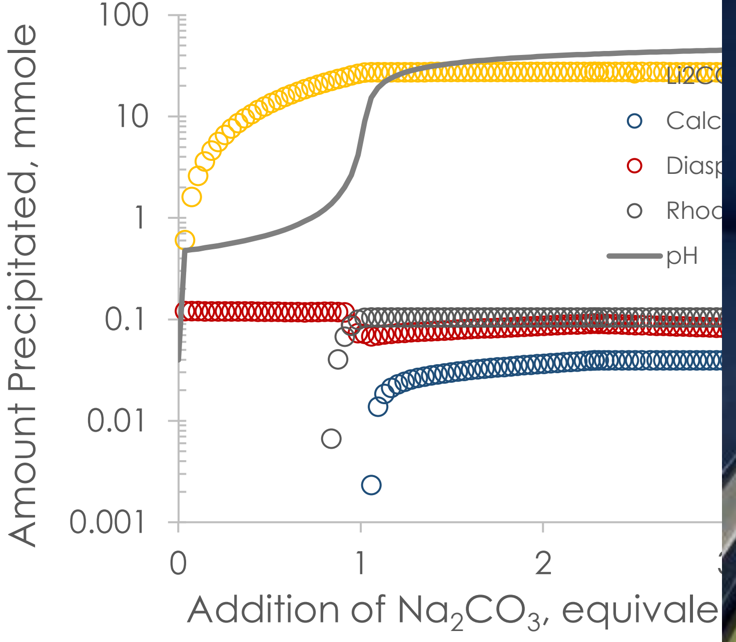


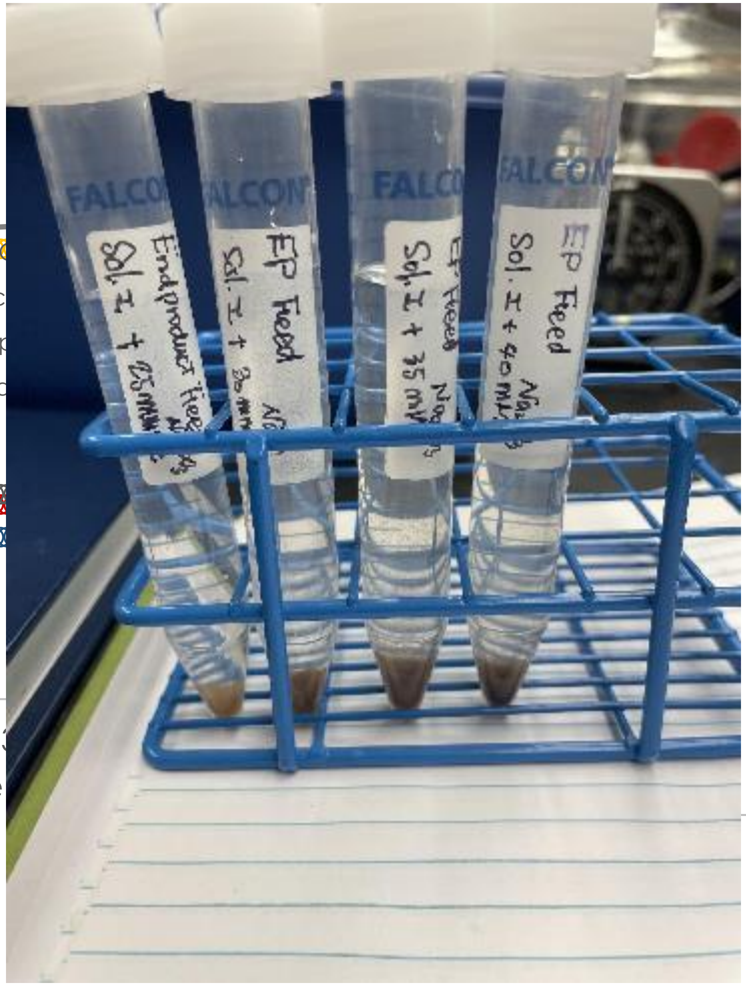


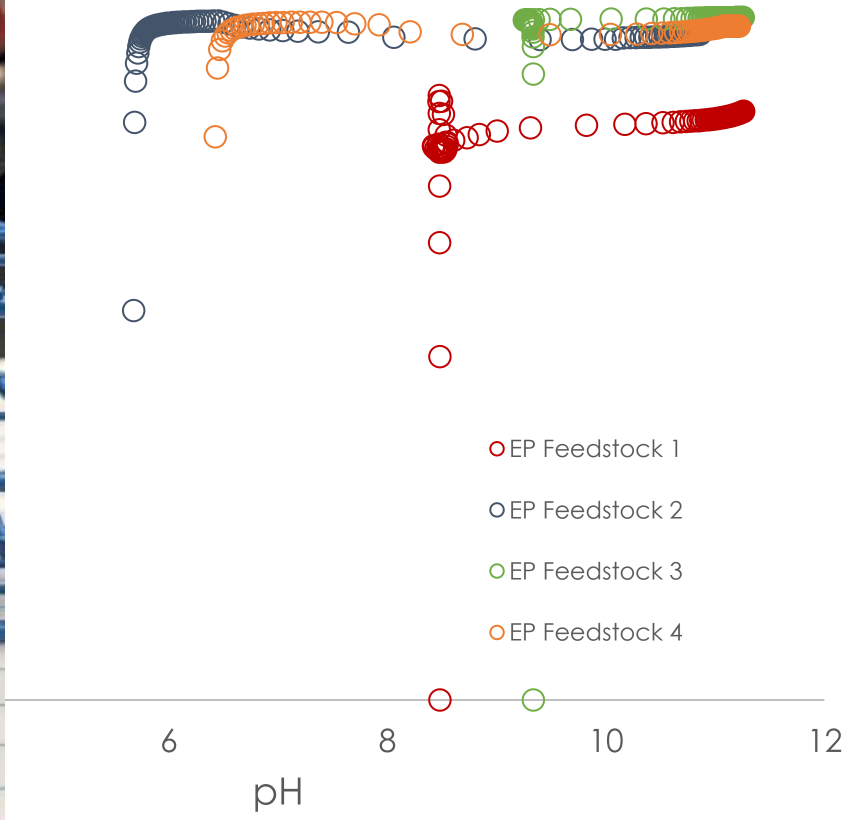


Recovering Lithium

Producing Li_2CO_3 as End Product

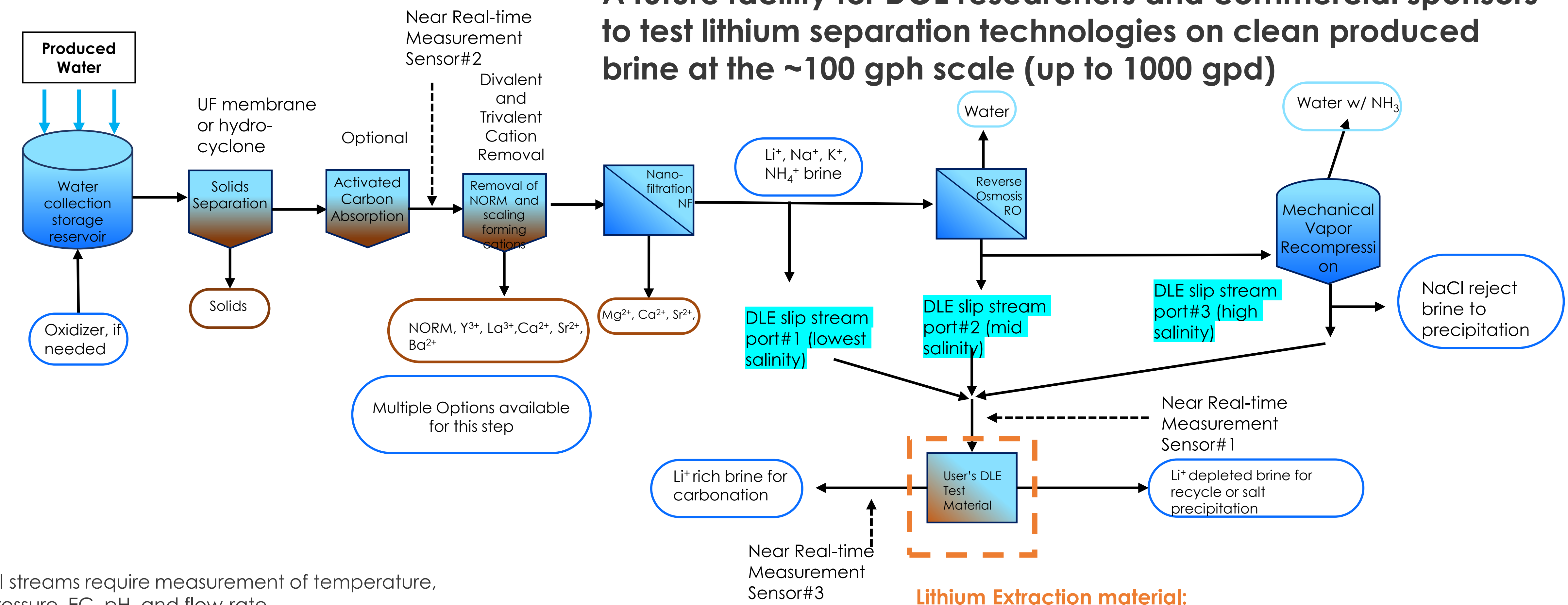






Accelerate Brine Lithium Extraction (ABLE) Facility

A future facility for DOE researchers and commercial sponsors to test lithium separation technologies on clean produced brine at the ~100 gph scale (up to 1000 gpd)



All streams require measurement of temperature, pressure, EC, pH, and flow-rate.

Lithium Extraction material: DOE, NETL or commercial sponsor

Summary

- **Using waste mineral streams associated with CMs to produce Spinel-type HMO sorbent (LISA) for DLE is technically feasible**
  - Demonstrated three potential chemical pathways, i.e., solid-state. microwave-assisted hydrothermal, and mechanochemical.
- **LISA performs promising adsorption characteristics for DLE**
  - High adsorption capacity (~30 mg/g or ~40 g/L).
  - High Li^{+} selectivity (e.g., ${Kd_{Li^+}}/{Kd_{Ca^{+2}}}$>2,500, ${Kd_{Li^+}}/{Kd_{Na^+}}$>12,000).
  - High chemical stability (maintain consistent adsorption capacity after 5 adsorption/regeneration cycle, <0.3% Mn loss per cycle).
  - Li+ captured by LISA can be effectively (>99.9%) stripped using diluted acid (0.1M HCl).
- **Techno-economic analysis for LISA in DLE is currently ongoing**
  - Sorbent preparation, adsorption/regeneration, and Li end-product production.

Partnering with NETL

The TOOLBOX

- Cooperative Research and Development Agreement (CRADA)
- Contributed Funds Agreement (CFA)
- Memorandums of Understanding (MOU)/ Memorandums of Agreement (MOA)
- Informal Discussions
- Non-Analysis Agreements (NAA)
- Small Business Innovation Research (SBIR) & Small Business Technology Transfer (STTR) Programs
- Licenses
- Non-Disclosure Agreement (NDA)
- Financial Assistance Awards (FA)

Available Technologies

Technologies and intellectual property available for licensing on NETL's website.
https://www.netl.doe.gov/business/tech-transfer/available-technologies

Funding Opportunity Announcement (FOA)

NETL uses FedConnect.net, EERE Program Information Center, Grants.gov, and Contract Opportunities to post FOAs.
https://www.netl.doe.gov/business/solicitations

Request for Collaboration

NATIONAL ENERGY TECHNOLOGY LABORATORY

NETL's Critical Mineral Multiple Year Research Planning Goal 5: Within 5 years, develop the basis needed to scale-up and pilot test modular processes for recovering multiple commodities from U&S feedstocks (both liquid and solid)

DOE Fossil Energy Carbon Management Goal:

By 2035, enable unconventional and secondary sourcing for half of the domestic critical mineral needs:

- **Demonstrate sufficient resources from domestic unconventional and secondary (U&S) feedstocks, including Oil and Gas produced waters and drill cutting wastes**
- **Demonstrate economically competitive and environmentally sustainable extraction and processing technologies**

NETL Critical Mineral MYRP

- National prospective Database (Goal 1)
- Resource Characterization (Goal 2)
- Technology Deployment Decision Support Tool (Goal 3)
- Advanced Critical Mineral and Carbon processing (Goal 4&5)
- In-situ recovery using fossil energy infrastructure (Goal 6)

Industry

- Existing Database
- U&S feedstocks (solid & liquid)
- Technology transfer or decision making
- Modular unit demonstration sites
- In-situ recovery collaboration

Acknowledgments

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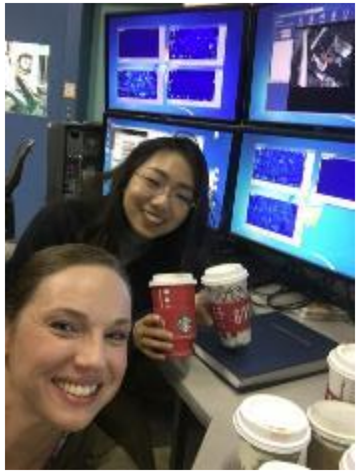
- This work was performed in support of the U.S. Department of Energy's (DOE) Fossil Energy and Carbon Management's Mineral Sustainability Program and executed through the National Energy Technology Laboratory (NETL) Research & Innovation Center's Critical Minerals Field Work Proposal.



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