Synthesizing Lithium Sorbents Using Acid Mine Drainage Solids

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Chin-Min Cheng
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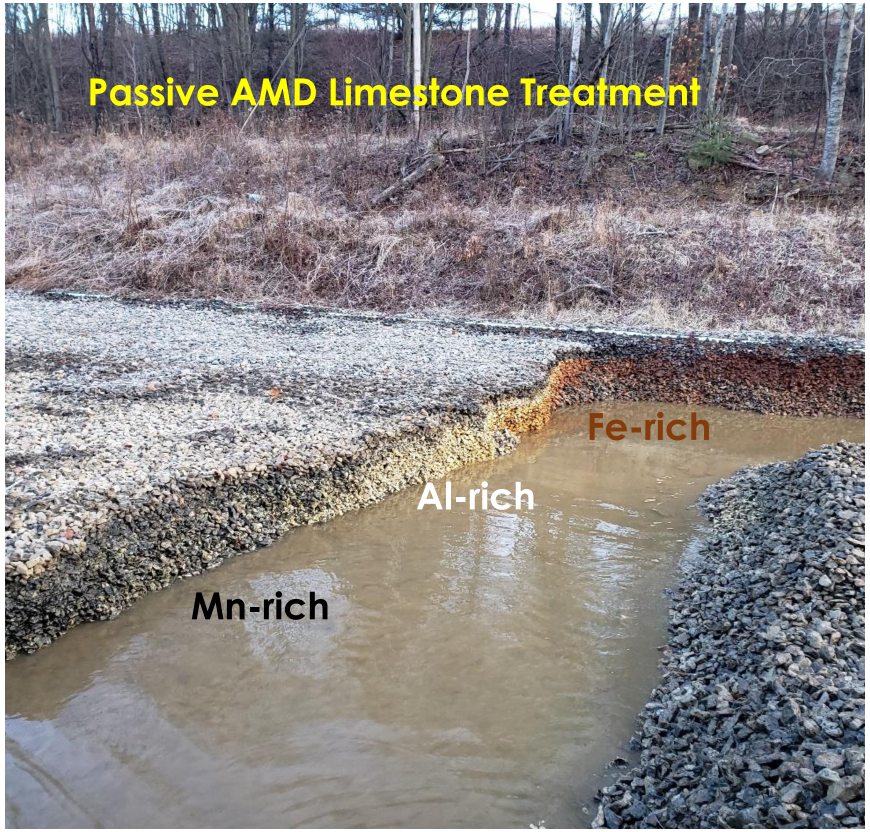

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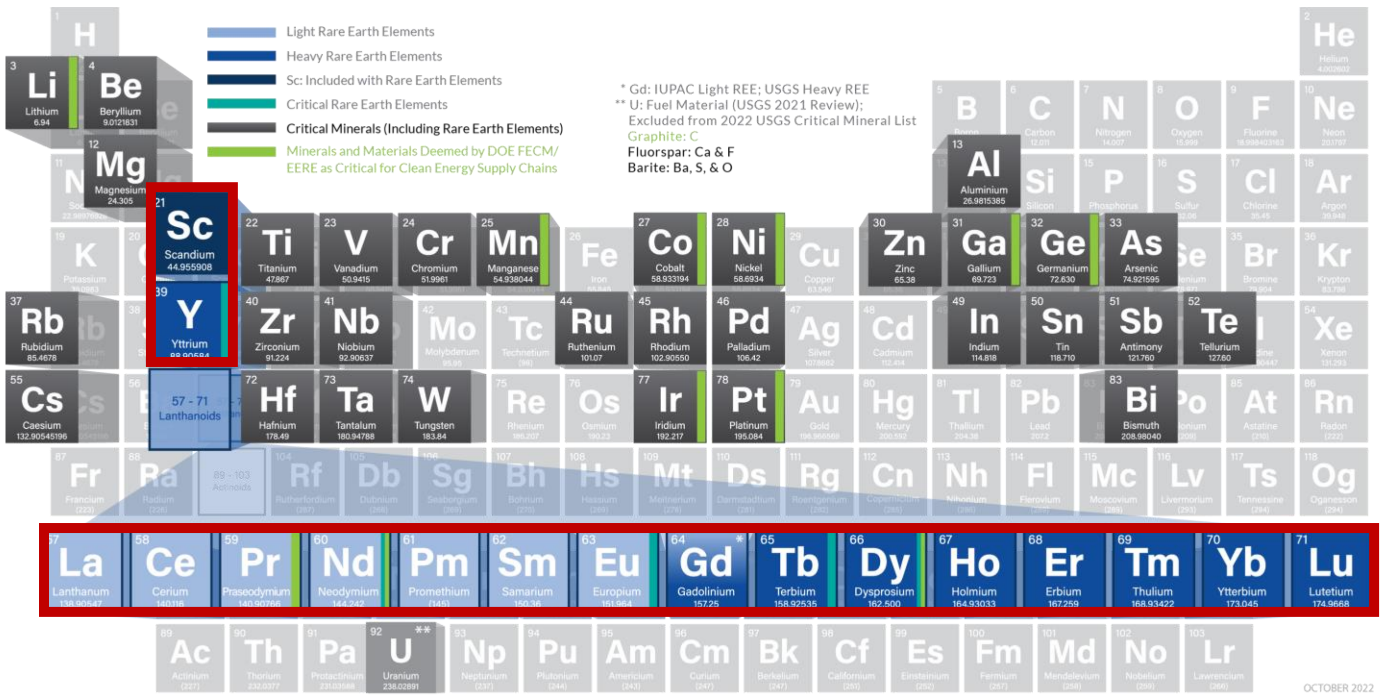
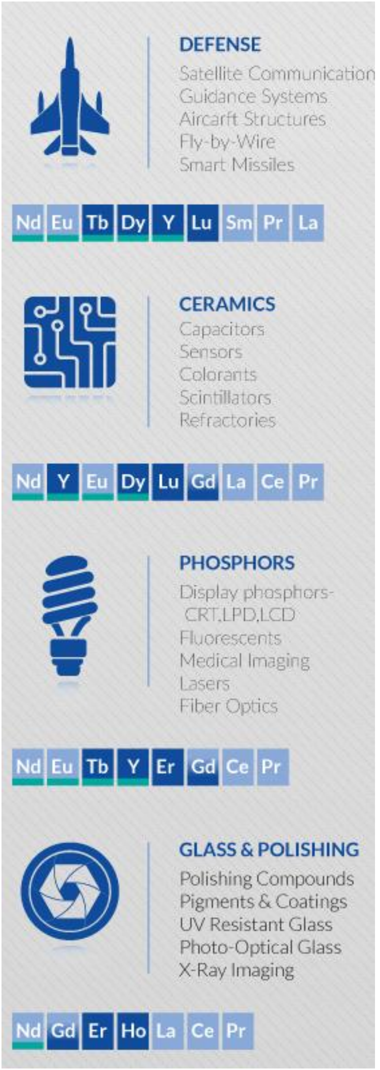
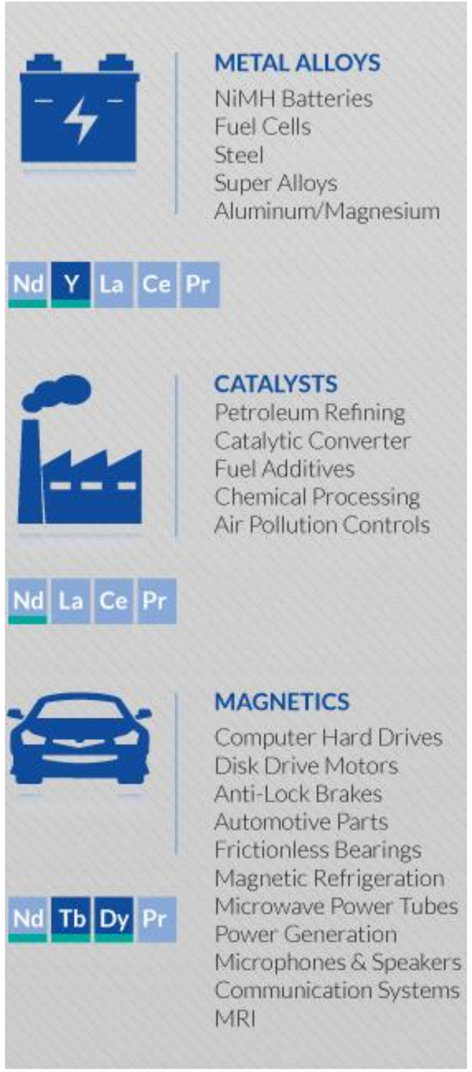
Critical Minerals

Critical to Emerging Technologies







- 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 nation's security created by the dependency on foreign sources.

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 CM

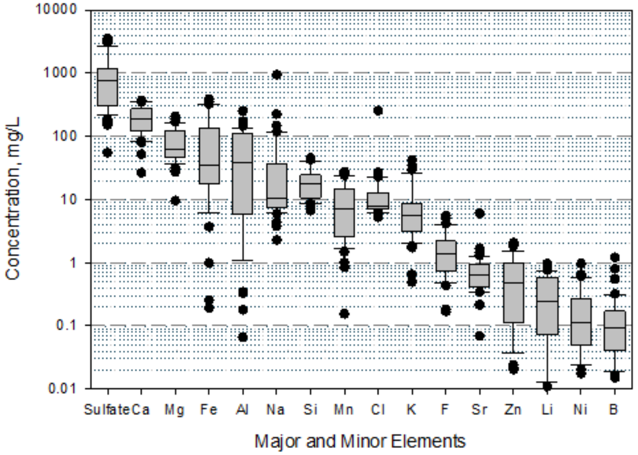
$$FeS_2 + {}^{7}/_{2}\,O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

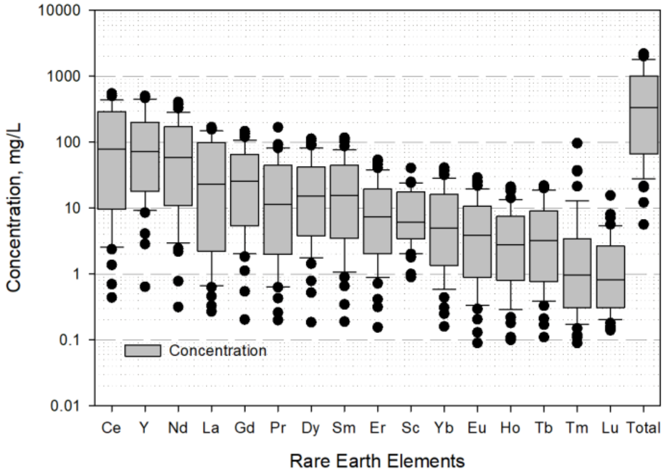
$$Fe^{2+} + {}^{1}/_{4}\,O_2 + H^+ \rightarrow Fe^{3+} + 3H^+$$

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

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

- 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]

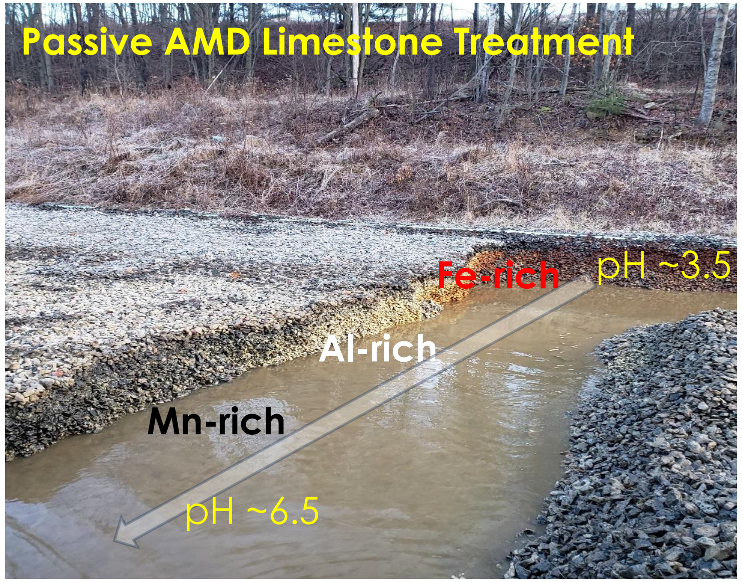
Element	Max conc. (ug/L)	Min conc. (ug/L)	Max loading (kg/year)	Min loading (kg/year)
Mg	210,000	3,600	3,541,140	40
Mn	74,000	19	215,522	4.5
Sr	3,600	27	83,321	0.23
Ni	3,200	2.6	10,428	0.3
REE	1,765	0.4	7,364	<0.01
Co	3,100	0.3	6,952	0.1
Cu	190	0.4	2,086	<0.1
Li	390	11.0	4,513	0.2

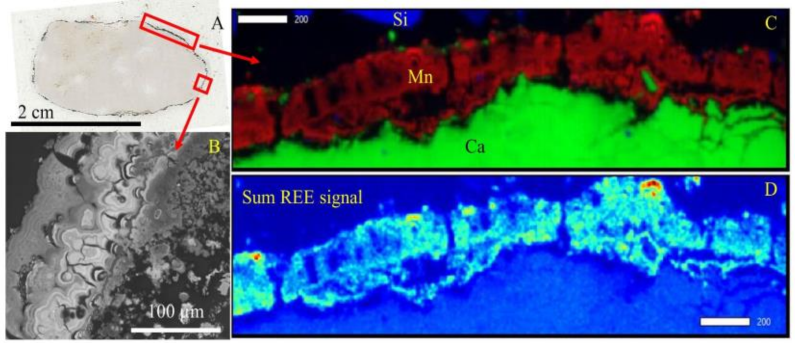
Cravotta (2008); Cravotta and Brady (2015)

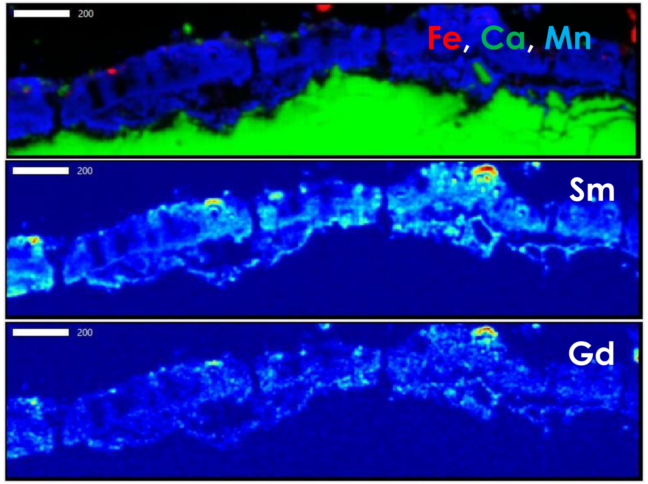
AMD Solids

Potential Sinks for CM

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





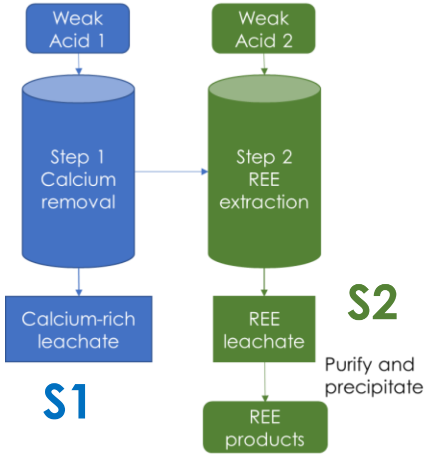


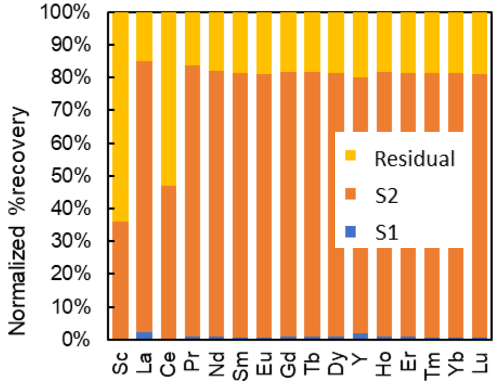
Hedin et al. (2019, 2024)

- REEs are mostly co-localized with Mn- and Al-rich solids (Hedin et al. 2019).
- Heavy REEs (e.g., Sm and Gd) are co-localized with Fe (Hedin et al., 2024).

Scootec Mn-rich AMD solids

Targeted Rare Earth Extraction (TREE)





- Patent-pending TREE process extracts over 80% of REEs.
- Extraction residuals contain high Mn and/or Al.

Deriving Sorbent for Li from AMD Extraction Residuals

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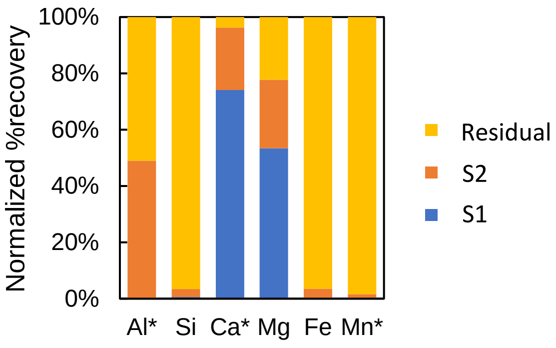
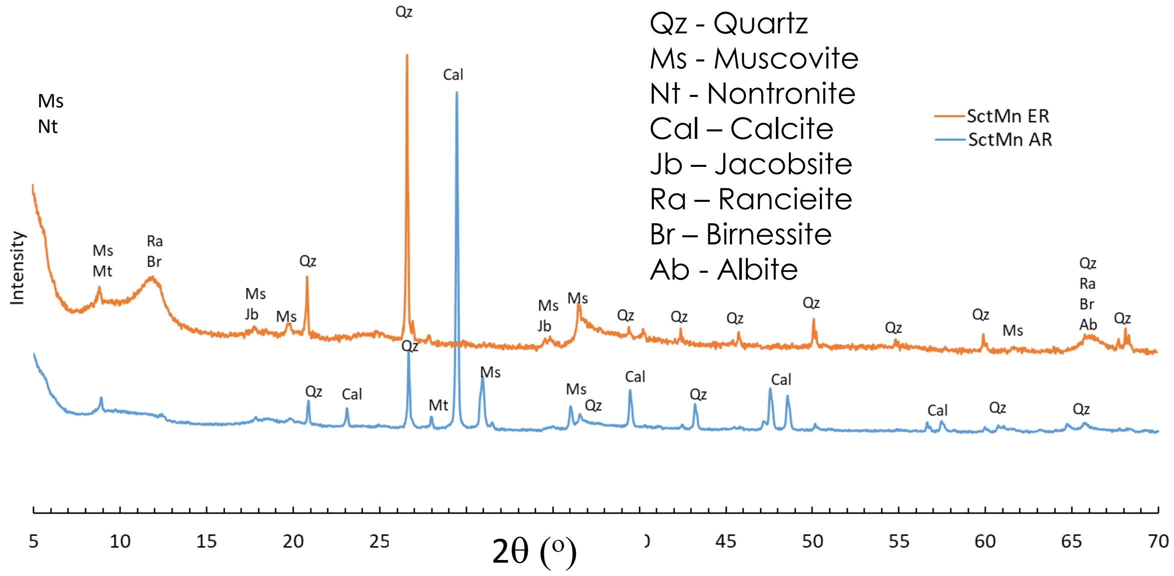
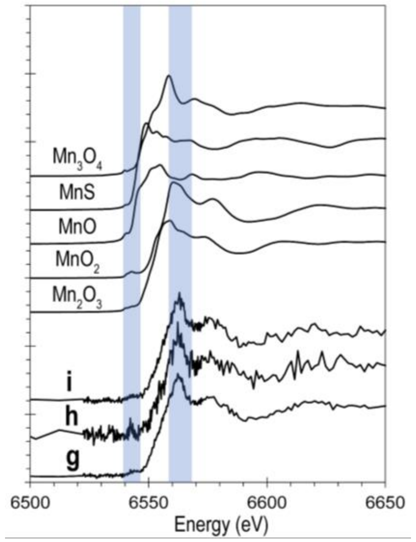
Potential Feedstock to Prepare Ion Sieves for Lithium



		Scootac Mn As Received	Scootac Mn S2 Extraction Residual
Al	%	3.2±0.6	2.5±0.4
Si	%	5.3±1.4	7.04±0.04
Ca	%	16.3±1.9	0.8±0.8
Mg	%	0.68±0.13	0.24±0.11
Fe	%	0.49±0.03	1.2±0.5
Mn	%	18±6	38±7
Na	%	0.3±0.2	0.44±0.06
K	%	0.6±0.2	0.64±0.18

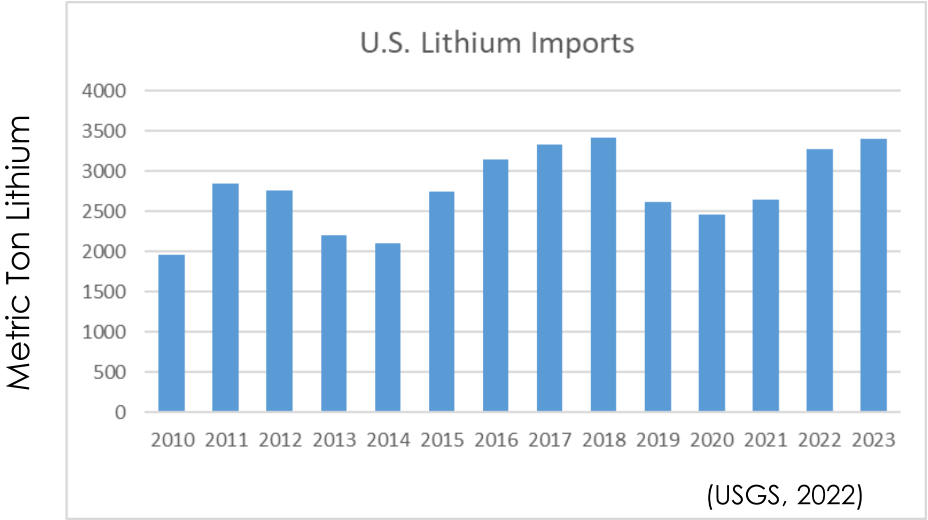




- Clay minerals (i.e., muscovite and nontronite), quartz, and calcite are the major minerals in the as-received SctMn.
- No calcite was found in SctMn-S2 residual. A mix of crystalline and amorphous racieite, birnessite, and jacobsite were possible minerals bearing Mn.
- X-ray absorption near edge structure (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.

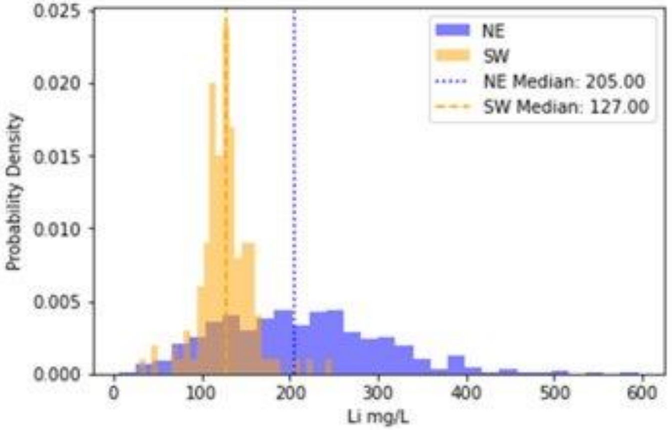
Recovering Lithium from Energy-Related Mineral Streams

Producing Value-Added Products from REE/CM Associated Mineral Streams

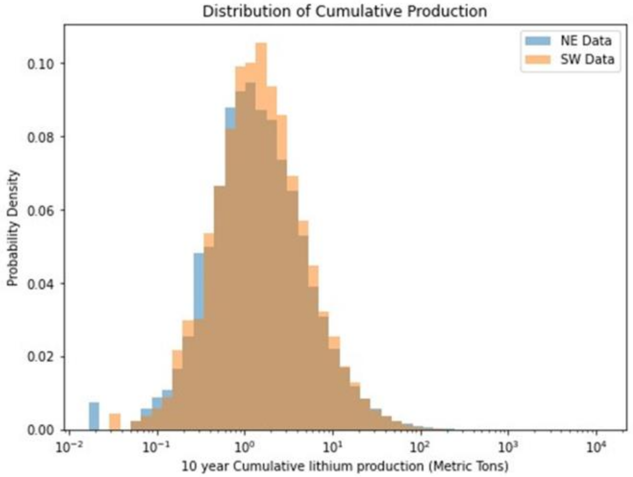


- Global demand for lithium is expected to increase by 500% by 2050 (World Bank, 2020).
- U.S. imports most of the lithium demand (70%)(USGS, 2017).
- U.S. is not a major producer but has significant lithium resources (12.2% of total world reserve), including continental brines, geothermal brines, and oilfield brines (USGS, 2023).

- Producing a low-cost sorbent to recover lithium from energy-related mineral streams, e.g., O/G produced water, geothermal brine and AMD, offsets AMD treatment costs for communities and regions impacted by legacy coal mining.



Concentration of Li from 553 well locations in Pennsylvania

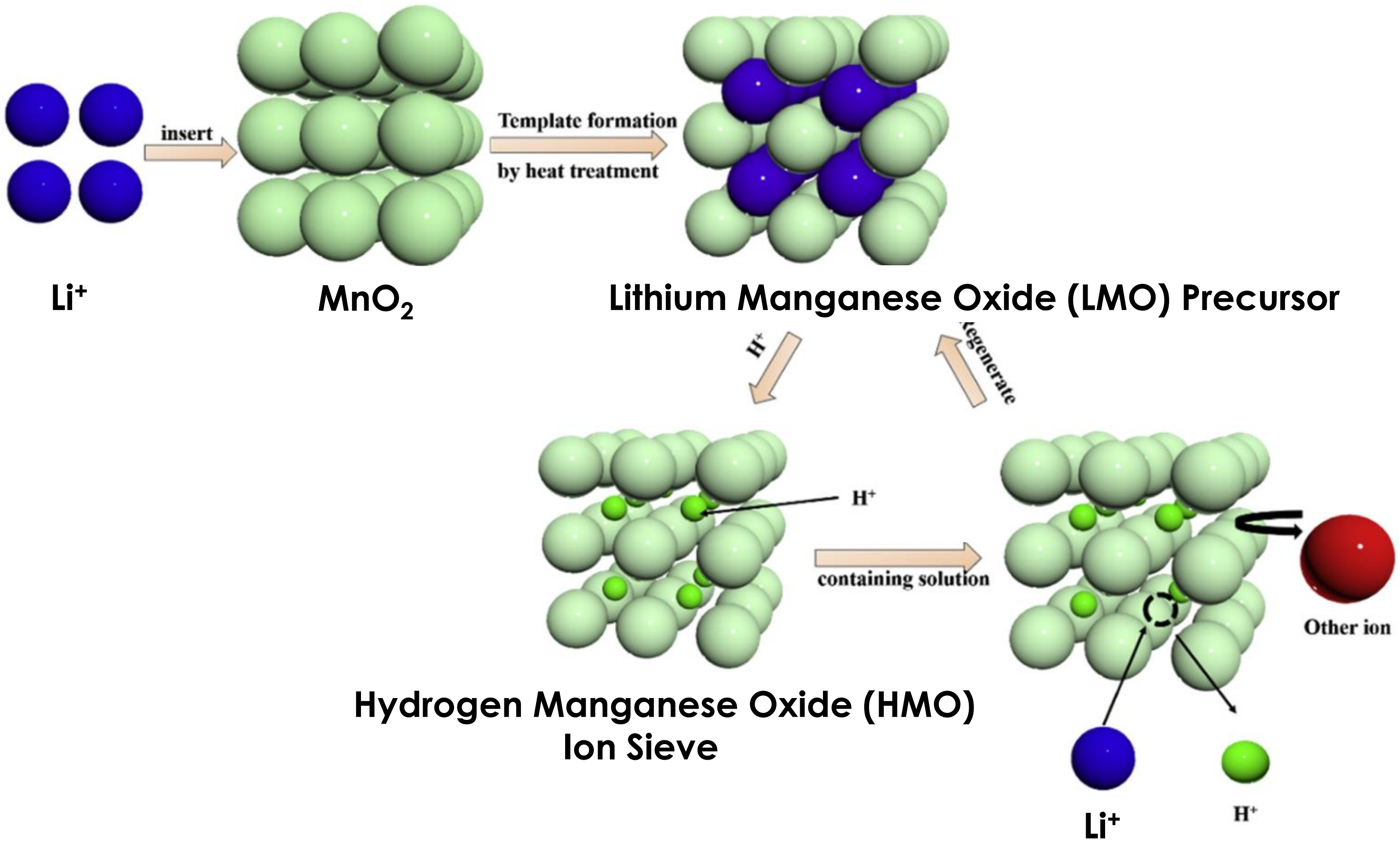


Estimated total lithium mass yields from a single Marcellus well over a 10-yr time frame.

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, 2021).
- Current inorganic ion sieves showing high Li selectivity include:
    - MnO_2 (α-, β-, γ-, δ-, and λ-types) (~8-~55 mg/g) (Li et al., 2018)
    - Layered double hydroxide (~8 mg/g)
    - H_2TiO_3 sorbent (37 mg/g (Zhang et al., 2013), 32.6 mg/g (Chitrakar et al., 2014))



(Modified from Weng et al., 2020)

Lithium Ion Sieve from Acid Mine Drainage Residuals (LISA)

Solid State Method

SctMn-S2

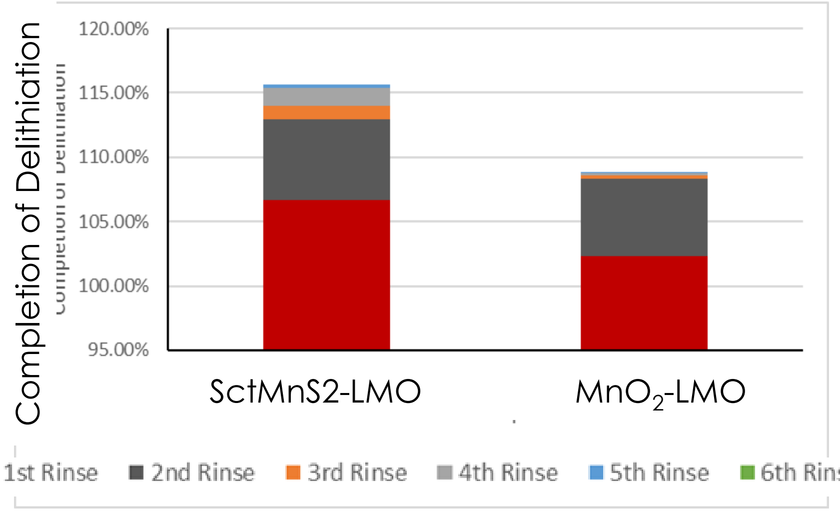
LiOH· H_2O

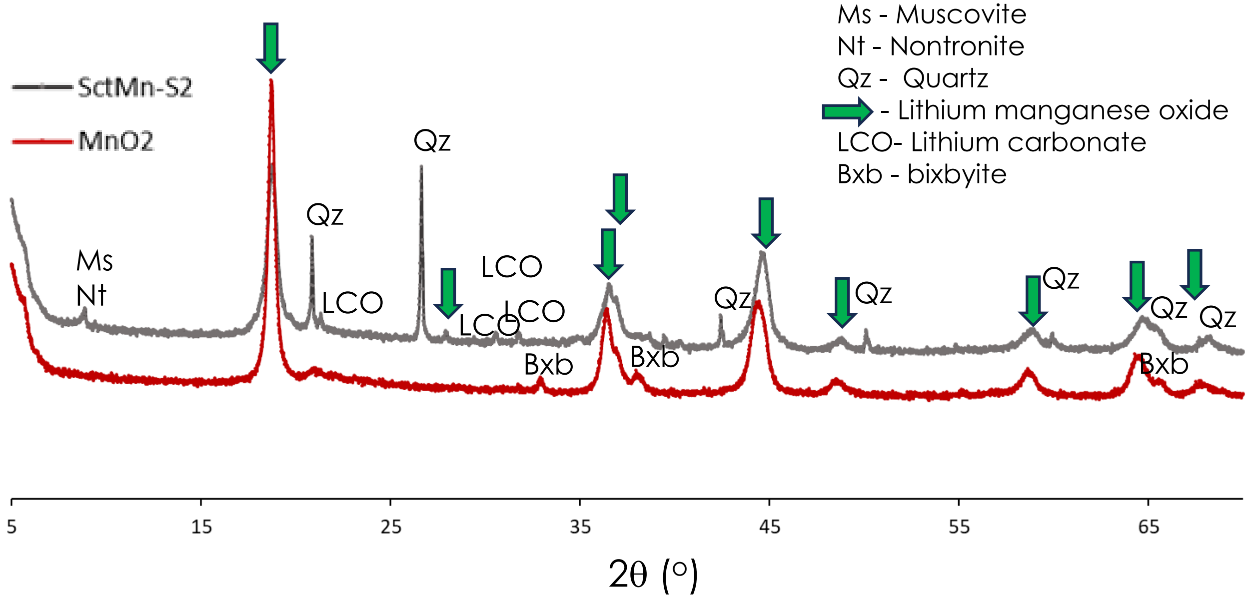
Solid State Reaction

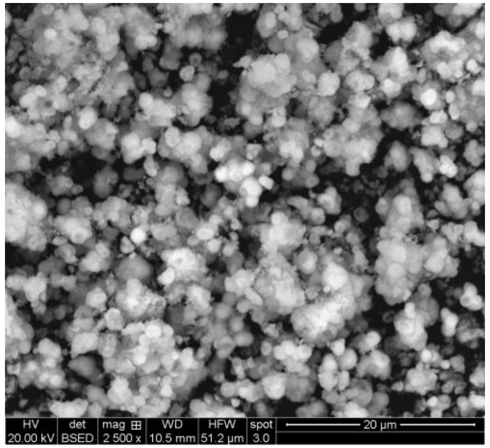
LMO Precursor

Delithiation

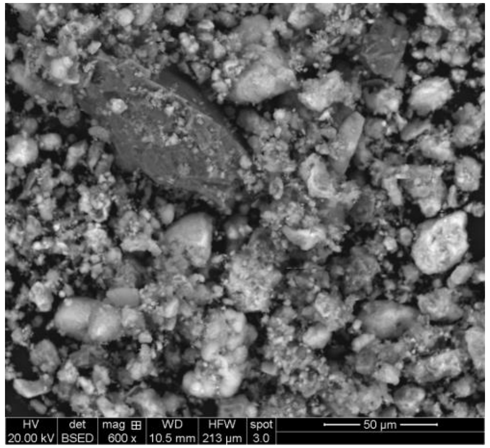
LISA (HMO)







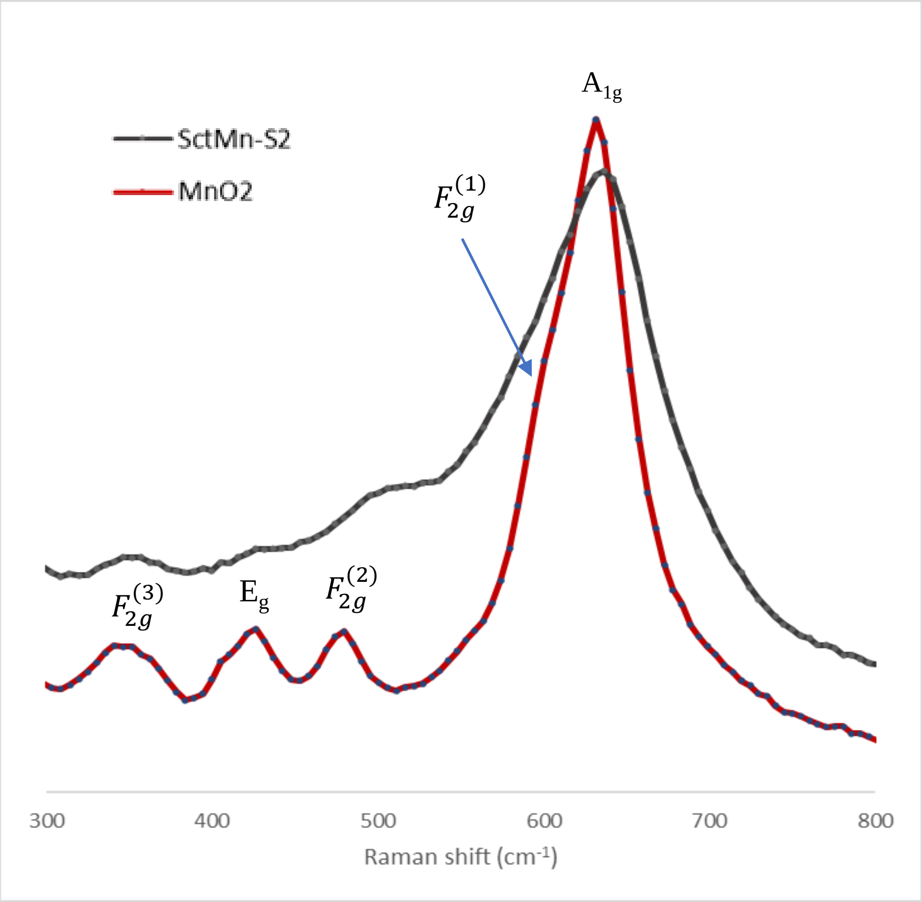
LMO prepared from MnO_2



LMO prepared from SctMn-S2

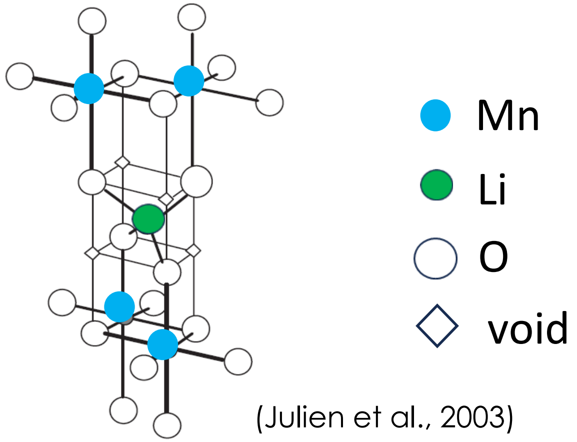
Lithium Ion Sieve from Acid Mine Drainage Residuals (LISA)

Spinel Lithium Manganese Oxide Precursor

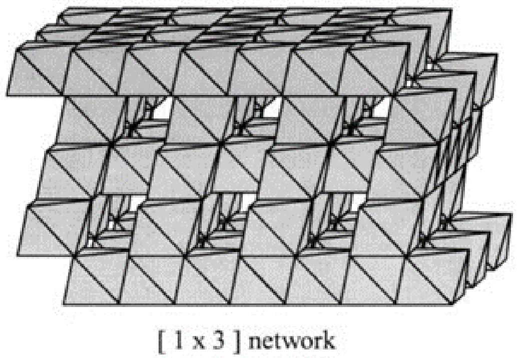


Raman Shifts (Unit: cm^{-1})

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



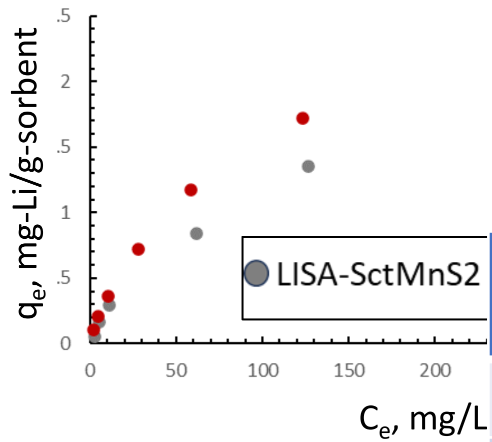
(Julien et al., 2003)



(Feng et al., 1998)

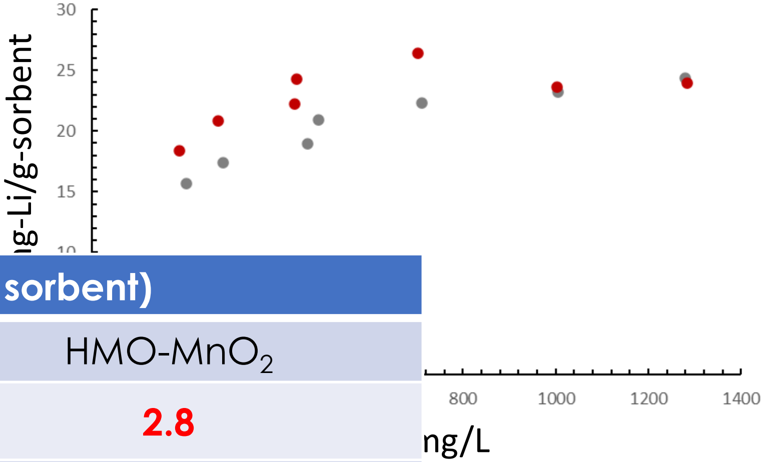
Adsorption Capacity

pH 2.8±0.3



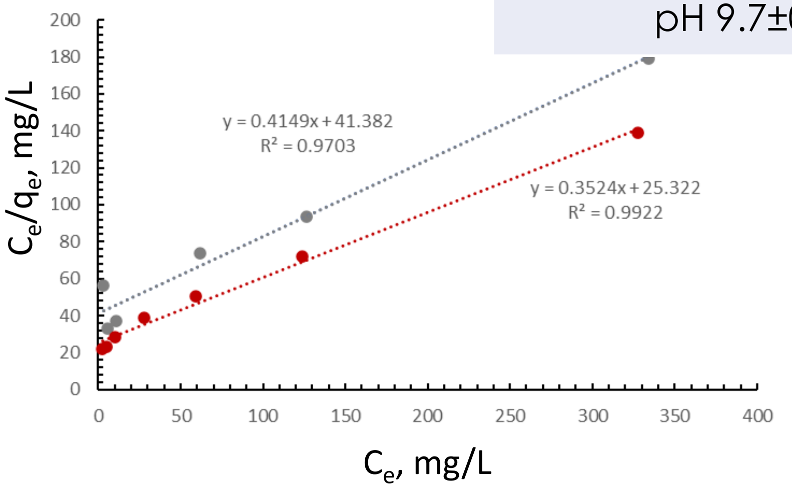
pH 7.0±0.7

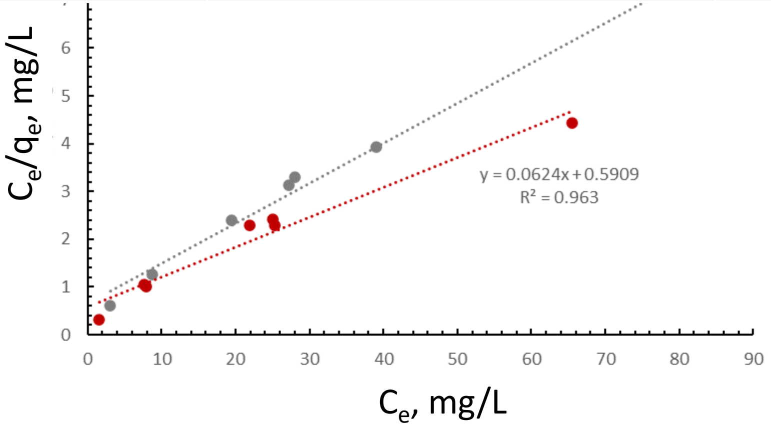
pH 9.7±0.5

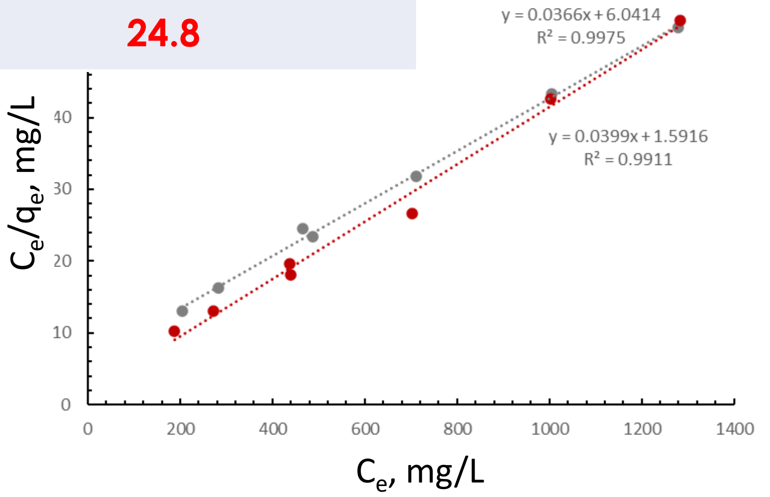


$$\frac{C_e}{q_e} = \frac{1}{K \cdot Q_a^0} + \frac{C_e}{Q_a^0}$$

	Q_a^0 (mg-Li/g-HMO sorbent)	
	HMO-SctMnS2	HMO-MnO_2
pH 2.8±0.3	**2.4**	**2.8**
pH 7.0±0.7	**11.9**	**16.0**
pH 9.7±0.5	**27.2**	**24.8**







Adsorption Capacity

Sensitivity to Factors in Preparation

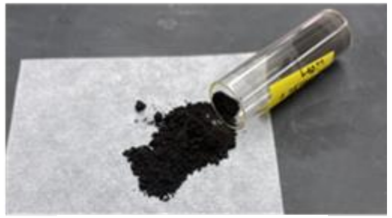
SctMn-S2

LiOH· H_2O

Solid State Reaction

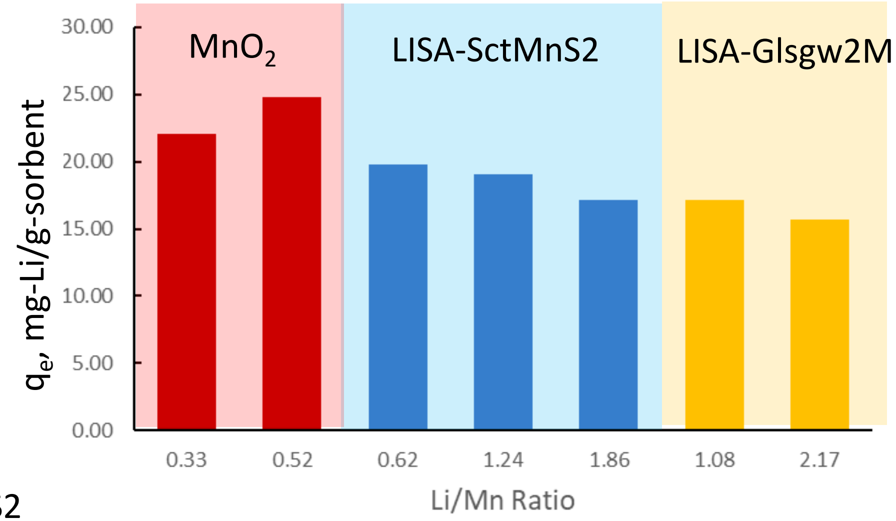
LMO Precursor

Delithiation



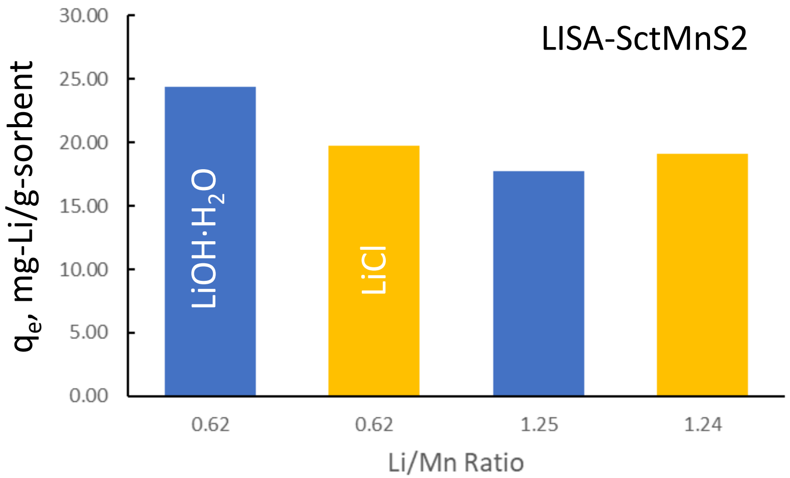
LISA (HMO)

Feedstock Elemental Composition/Mn Content

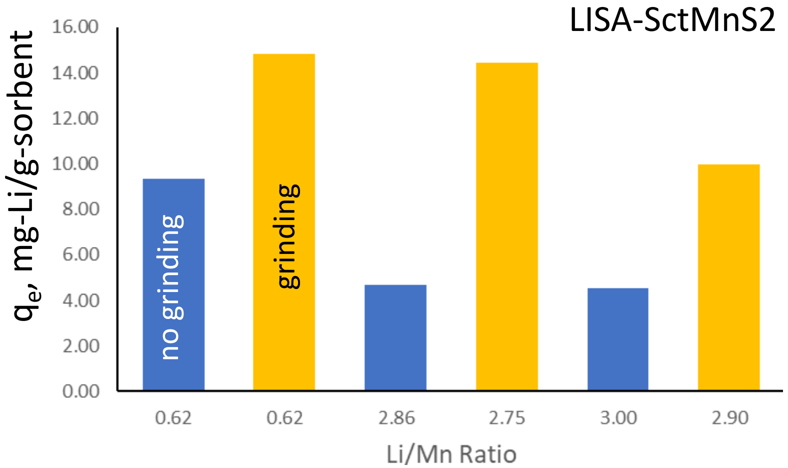


Dry Base		SctMn- S2	Glsgw -2M
Al	%	2.5±0.4	5.04
Si	%	7.04±0.04	16.67
Ca	%	0.8±0.8	0.04
Mg	%	0.24±0.11	0.52
Fe	%	1.2±0.5	3.26
Mn	%	38±7	24.42
Na	%	0.44±0.06	0.05
K	%	0.64±0.18	3.30

Source of Li



Mixing During Calcination



Adsorption Capacity

Comparing to HMO Ion Sieves Prepared by Others Using Chemical Reagents

Characterized Using Simple Li Solution

	Solution Matrix	pH	Adsorption Capacity (mg/g)
Present (LISA- SctMnS2)	Li_2CO_3	9.7±0.5	**27.2**
	Li_2CO_3	7.0±0.7	**11.9**
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

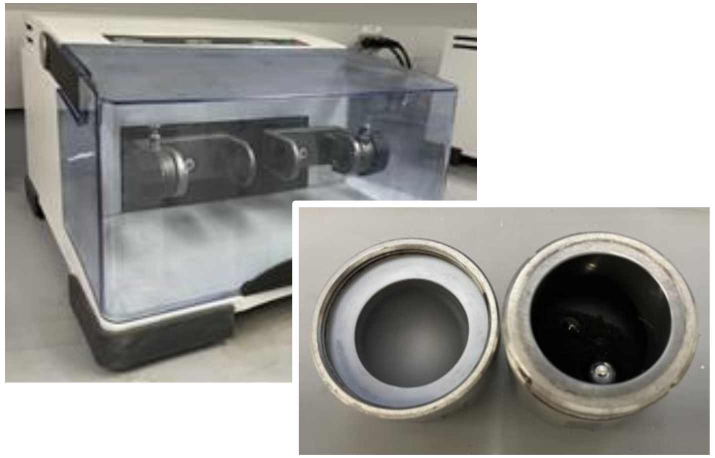
Characterized Using Solution with Complex Matrix

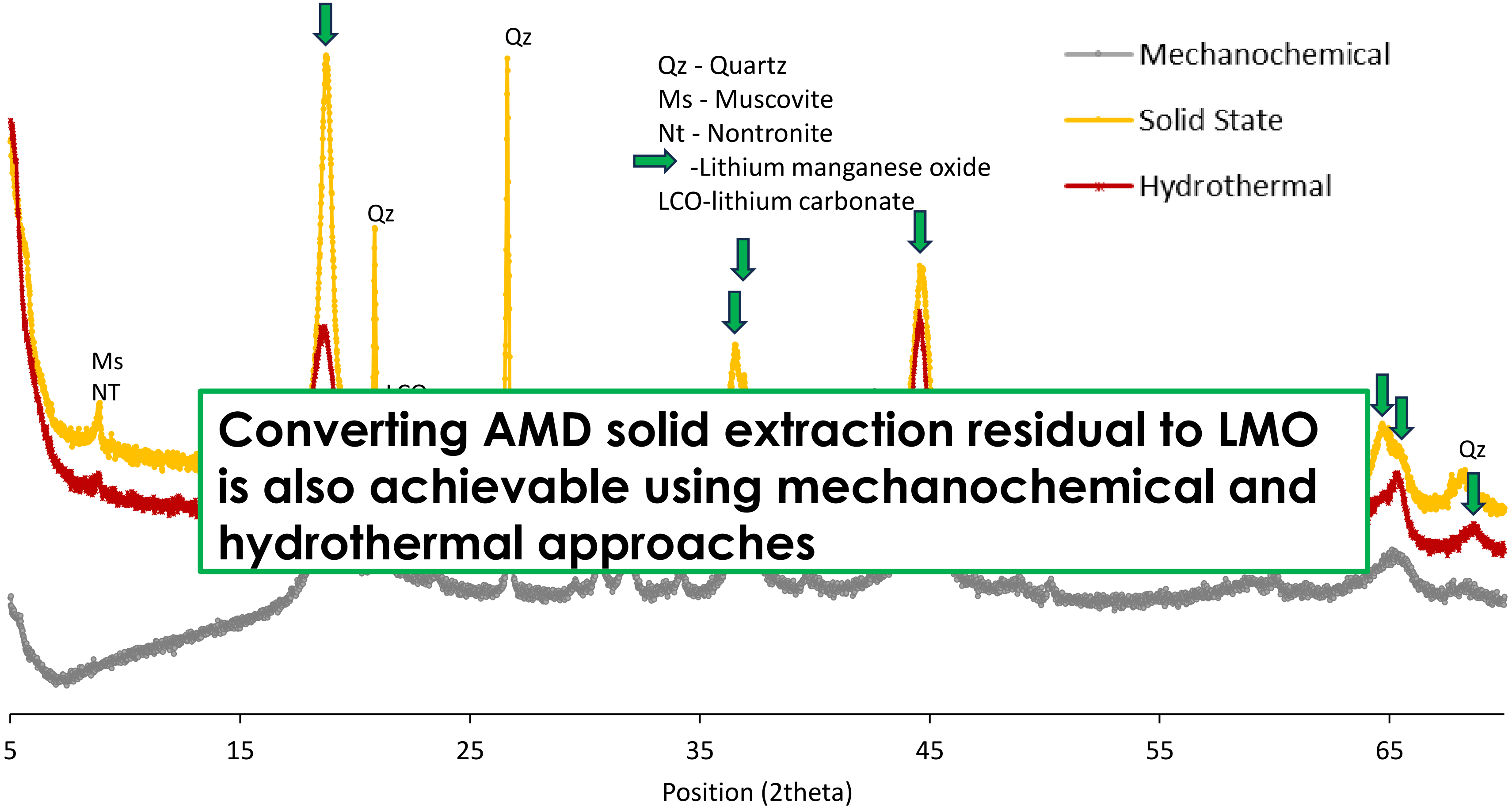
	Solution Matrix	pH	Adsorption Capacity (mg/g)
Present (LISA-SctMnS2)	Synthetic Brine (Li^+ 1.34 g/L; Na^+ 116.1 g/L; K^+ 20.4 g/L)	9.52	**7.5**
Ma et al. (2011)	Salt Lake Brine (Li^+ 237 mg/L; Na^+ 3591 mg/L; K^+ 3118 mg/L; Mg^{+2} 109 g/L)	6	1.5
Sun et al. (2011)	Mixed solution with Li^+, Na^+, K^+, 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

Searching for Ideal Synthesis Approach

Hydrothermal Method

Mechanochemical Synthesis





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

Summary

- **Preparing spinel-type HMO sorbent using coal mine drainage solids after being extracted for CM is technically feasible.**
    - Synthesis process is to be optimized to either increase the adsorption capacity and/or reduce consumptions of resources.
- **Adsorption capacity of lithium by the AMD-derived HMO (LISA) is comparable to that of HMO prepared from high-purity MnO_2.**
    - Adsorption characterization to determine the selectivity toward other cations (i.e., Na+ and K+) is ongoing.
    - Chemical stability of the sorbent will be investigated using a packing bed setting.

Acknowledgments

NATIONAL ENERGY TECHNOLOGY LABORATORY

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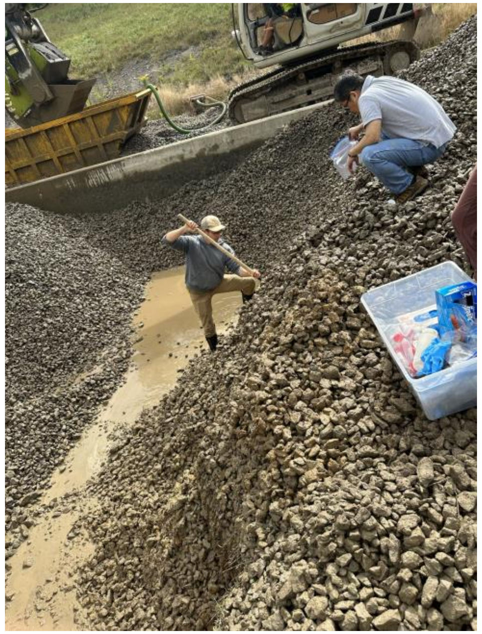

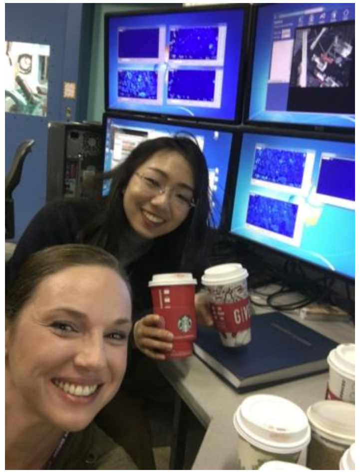

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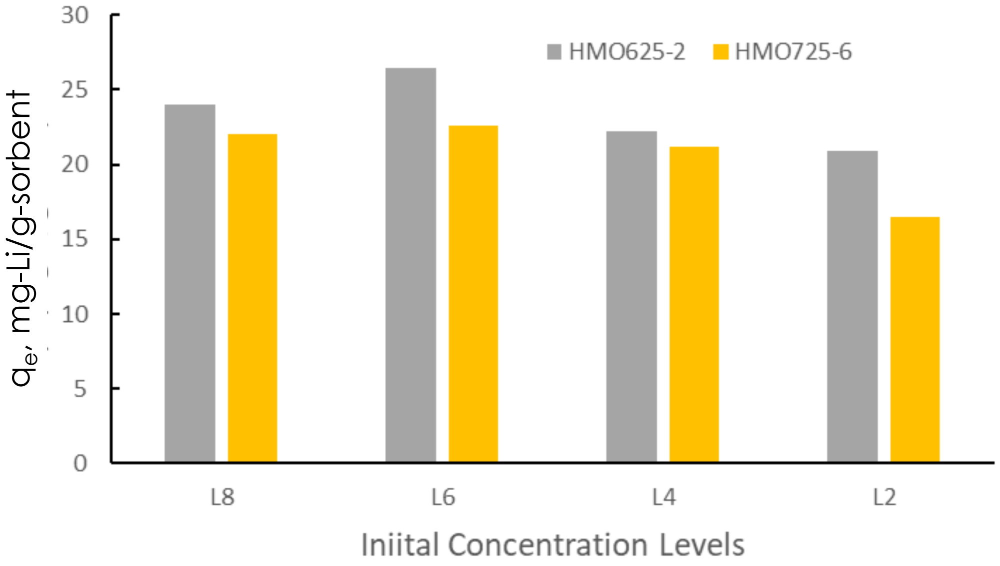
Adsorption Capacity

Reproducibility

Adsorption Tests



Sorbent Preparation