Advanced Mineral Separations with Novel Simulated Moving Beds

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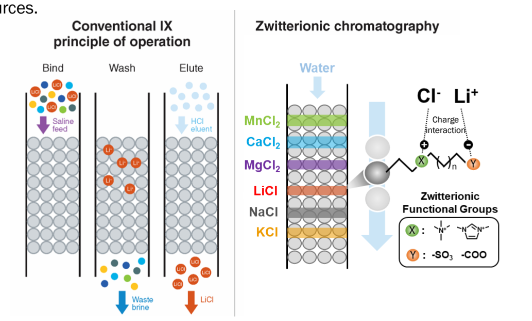
INDUSTRIAL EFFICIENCY AND DECARBONIZATION OFFICE

PROJECT SUMMARY

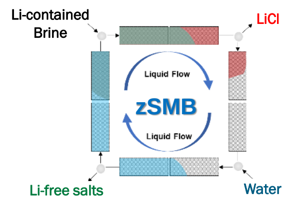
Zwitterionic chromatography separates LiCl from brine using only water as the eluent. This is different than traditional ion exchange (IX) used in direct lithium extraction (DLE). In DLE, IX resins selectively adsorb Li^+ ions that are then eluted with hydrochloric acid. In contrast, zwitterionic chromatography operates chromatographically using only water as the eluent and thus requires no added chemicals and increases throughput. This improves environmental stewardship and reduces operating expenditures (OPEX). The technology can also handle saline waters with high concentrations of hard minerals. Lastly, zwitterionic chromatography has the potential to simultaneously separate other minerals such as $MnCl_2$ and $CoCl_2$ that may be present in some brine resources.



Ref. Karp et al., WO 2021/119208 A1

TECHNOLOGY IMPACT

Zwitterionic simulated moving beds (zSMB) has the potential to be a paradigm-shifting technology from conventional IX used in mineral recovery from brines. It requires no added chemicals, increases throughput, and can separate many valuable minerals simultaneously in addition to LiCl.

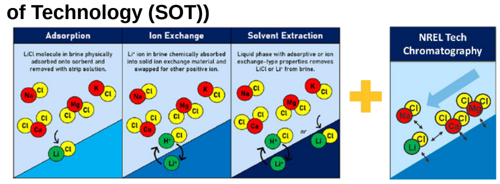


Case Study: Value Proposition

Salt	Salar de Pozuelos		Bakken, ND		Smackover, AR		Bryans Mill, Tx	
	g/L	Ratio (X / LiCl)	g/L	Ratio (X / LiCl)	g/L	Ratio (X / LiCl)	g/L	Ratio (X / LiCl)
LiCl	2.36	----	0.86	----	1.47	----	2.47	----
$MgCl_2$	8.3	3.5	5.2	6.1	11.1	7.6	10.7	4.3
NaCl	6.9	2.9	94.8	110.1	173.2	118.1	176.2	71.4
$CaCl_2$	4.5	1.9	103.3	119.9	93.9	64.1	78.4	31.8
TDS	22.1		204.2		279.6		267.7	

Ref. USGS National Produced Waters Geochemical Database v2.3, accessed 2022

Comparison to Dynamic Lithium Extraction (State of Technology (SOT))



	Hydrometallurgy	DLE (IEX, ADS, LLE)	NREL chromatographic technology
Yield of Li	40-60 %	70-90%	> 95%
No chemicals needed?	✗	✗	✓
Continuous process	✗	Semi-continuous	✓
Applicable to mineral conc. < 12000 ppm?	✗	✓	✓
Scalable?	✓	✓	✓
System flexibility for other minerals?	✗	✗	✓

Ref. Ian Warren, NREL Tech Report (2021) "Techno-Economic Analysis of Lithium Extraction from Geothermal Brines"

RESULTS AND ACHIEVEMENT

Synthesis of 18 Zwitterionic (ZW) Stationary Phase

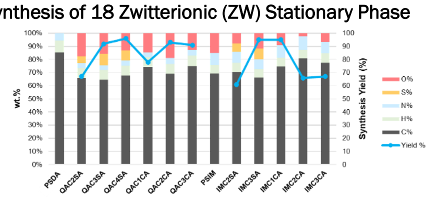


Fig. 1. Elemental analysis of prepared ZW stationary phase

Effect of Various ZW Groups on the Salt Retention

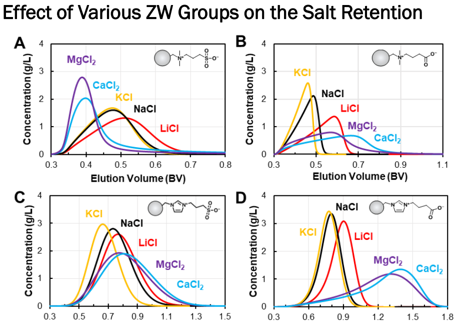
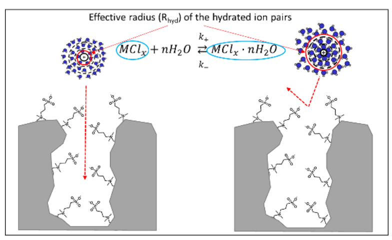


Fig. 2. Salt retention on (A) QAC3SA, (B) QAC3CA, (C) IMC3SA, and (D) IMC3CA



Separation Mechanism: Hydration reaction in the mobile phase (water) affects the retention of salts.

Hydration Shell Radius and $\Delta_{hyd}G$

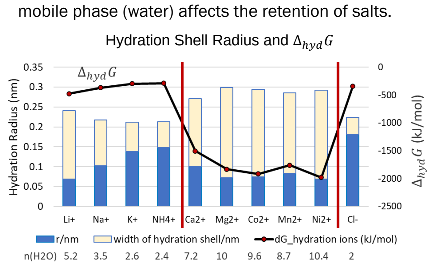


Fig. 3. Hydrated radius and the Gibbs free energy of hydration of ions

Ref. J. Chem. Soc. Faraday Trans., 1991, 87(18), 2995-2999
Sep. and Purif. Tech., 51 (2006) 40–47

Multicomponent Separation on the ZW Stationary Phase

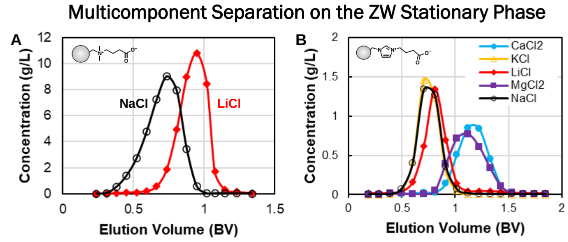
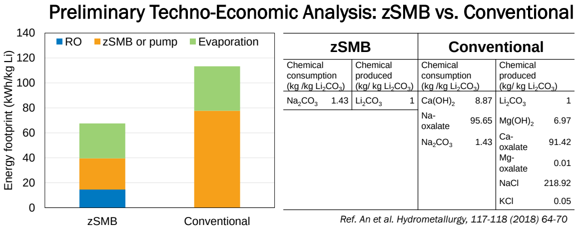


Fig. 4. (A) NaCl and LiCl (10 g/L) separation on QAC3CA and (B) five salt (5 g/L) separation on IMC3CA under water elution

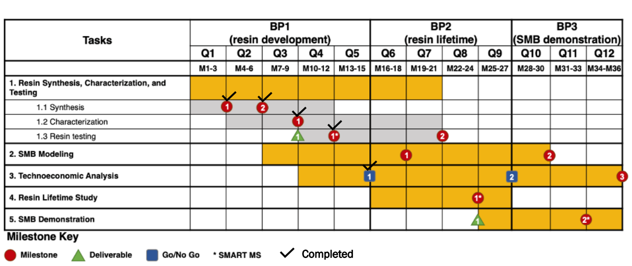
Preliminary Techno-Economic Analysis: zSMB vs. Conventional



Ref. An et al. Hydrometallurgy, 117-118 (2018) 64-70

Fig. 5. Estimated energy (left) and chemical (right) consumptions for lithium recovery from the brines (Li 300 ppm) in Smackover, AR: zSMB vs. conventional hydrometallurgy process. The conservatively estimated productivity of zSMB will be 0.27 kg Li/m^3/day (0.19 g Li/min/m^3).

PROJECT PROGRESS



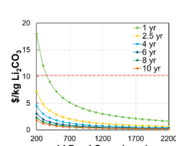
Task	Project Goals	Due	Completion
1	Systematic testing of 18 zwitterionic for LiCl separation	Sep 2023	90%
2	SMB simulation to achieve >99% purity & > 90% yield	Jun 2024	30%
3	TEA demonstrating >30% OPEX reductions over IX (SOT)	Dec 2025	20%
4	A resin lifetime study targeting lifetimes >5 years	Mar 2024	10%
5	SMB demonstration recovering >100 g LiCl	Dec 2025	0%

DELIVERABLES (Metrics)

1. Shell, Mines, and Standard lithium will deliver >55 gallons of Li-contained brines
2. Develop zSMB for >30% reduction in OPEX, an 15% increase in LiCl yield or x1.5 throughput compared to IX technology (SOT).
3. NREL will run zSMB for >20 gallons of brine to deliver 100g of LiCl with >90% yield and >95% purity

FUTURE WORKS

Feed Composition Analysis → Develop zSMB Modeling and Simulations → Optimize zSMB to Recover LiCl with >90% yield → Demonstrate Operation at Pilot Scale (TRL 5) → Scale up to Commercial Scale



ZW Resin Lifetime Analysis → Techno-Economic and Life Cycle Analysis → Scale up to Commercial Scale

Risk and Mitigation Strategies

Risk	Mitigation	Impact
Production of 5 kg resin for zSMB is cost-prohibitive within the project budget	Engage with industrial partners to assist in manufacturing the resins. Or pack smaller columns to use less material but still achieve continuous operation.	Moderate
Anions present in real brine feeds impact LiCl separation performance	A pretreatment using anion exchange resins will be employed to remove sulfate ions.	Moderate
Resin lifetime is less than 300 hours	Develop a regeneration method using high-salinity desorbents and incorporate that into zSMB operations.	Low
ZW LC model is not predictive with a conventional model	Do more experiments to get the solute retention at the feed concentration and match with simulations by trial and error.	Moderate -High

Acknowledgement

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