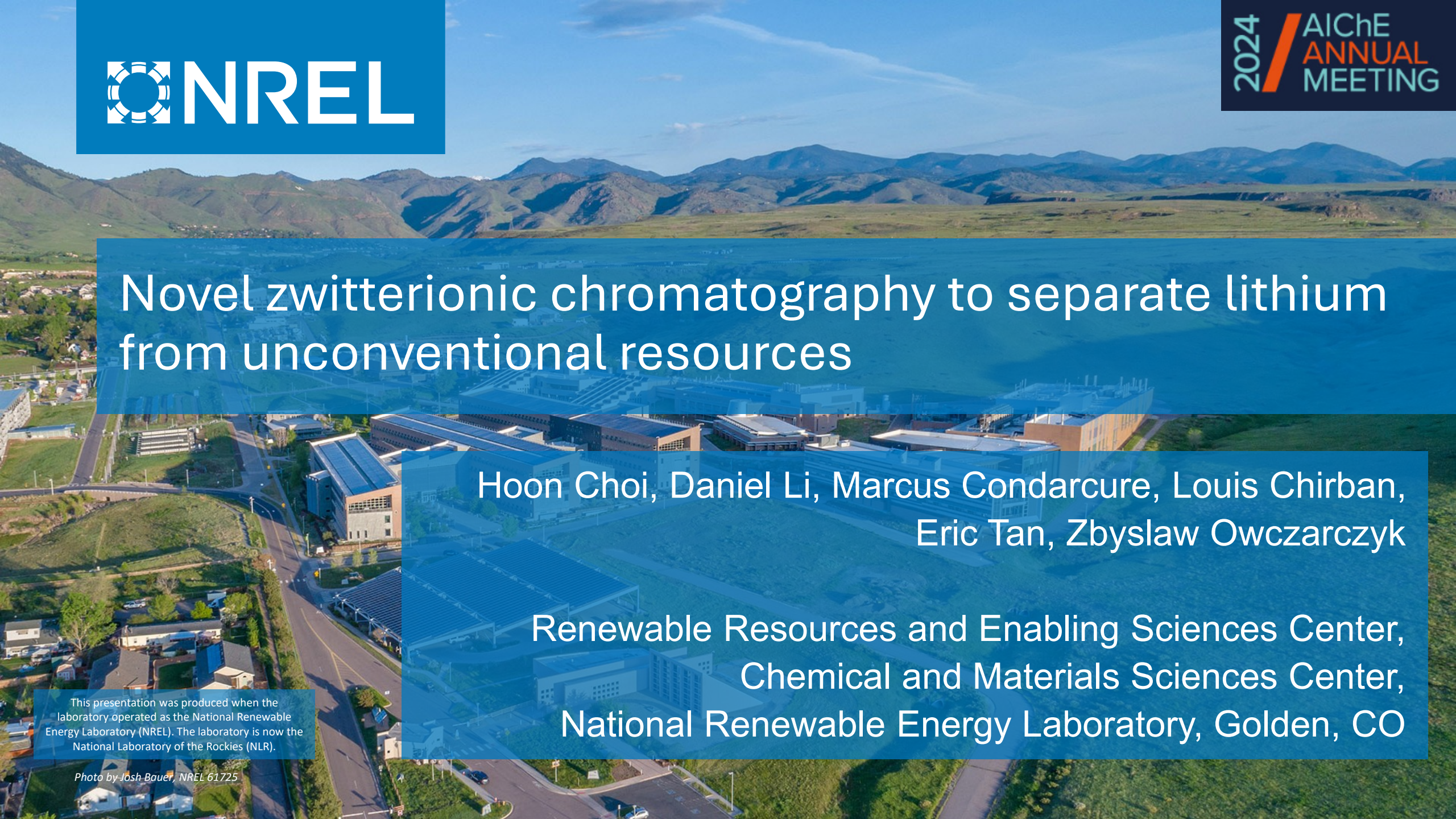

Novel zwitterionic chromatography to separate lithium from unconventional resources

Hoon Choi, Daniel Li, Marcus Condarcure, Louis Chirban, Eric Tan, Zbyslaw Owczarczyk

Renewable Resources and Enabling Sciences Center,
Chemical and Materials Sciences Center,
National Renewable Energy Laboratory, Golden, CO

This presentation was produced when the laboratory operated as the National Renewable Energy Laboratory (NREL). The laboratory is now the National Laboratory of the Rockies (NLR).

Photo by Josh Bauer, NREL 61725

Li extraction from unconventional resources

INSIGHTS

POLICY FORUM

ENERGY

Sustainable minerals and metals for a low-carbon future

Policy coordination is needed for global supply chains

By Benjamin K. Sovacool[1], Saleem H. Ali[2,3,4], Morgan Bazilian[5], Ben Radley[6], Benoit Nemery[7], Julia Okatz[8], Dustin Mulvaney[9]

Climate change mitigation will create new natural resource and supply chain opportunities and dilemmas, because substantial amounts of raw materials will be required to build new low-carbon energy devices and infrastructure (1). However, despite attempts at improved governance and better corporate management, procurement of many mineral and metal resources occurs in areas generally acknowledged for mismanagement, remains environmentally capricious, and, in some cases, is a source of conflict at the sites of resource extraction (2). These extractive and smelting industries have thus left a legacy in many parts of the world of environmental degradation, adverse impacts to public health, marginalized communities and workers, and biodiversity damage. We identify key sustainability challenges with practices used in industries that will supply the metals and minerals—including cobalt, copper, lithium, cadmium, and rare earth elements (REEs)—needed for technologies such as solar photovoltaics, batteries, electric vehicle (EV) motors, wind turbines, fuel cells, and nuclear reactors. We then propose four holistic recommendations to make mining and metal processing more sustainable and just and to make the mining and extractive industries more efficient and resilient.

Between 2035 and 2050, the global EV stock needs to jump from 1.2 million light-duty passenger cars to 965 million passenger cars, battery storage capacity needs to climb from 0.5 gigawatt-hour (GWh) to 12,380 GWh, and the amount of installed solar photovoltaic capacity must rise from 223 GW to more than 7100 GW (3). The materials and metals demanded by a low-carbon economy will be immense (4). One recent assessment concluded that expected demand for 14 metals—such as copper, cobalt, nickel, and lithium—central to the manufacturing of renewable energy, EV, fuel cell, and storage technologies will grow substantially in the next few decades (5). Another study projected increases in demand for materials between 2015 and 2060 of 87,000% for EV batteries, 1000% for wind power, and 3000% for solar cells and photovoltaics (6). Although they are only projections and subject to uncertainty, the World Bank put it concisely that "the clean energy transition will be significantly mineral intensive" (7) (see the figure).

Many of the minerals and metals needed for low-carbon technologies are considered "critical raw materials" or "technologically critical elements," terms meant to capture the fact that they are not only of strategic or economic importance but also at higher risk of supply shortage or price volatility (8). But their mining can produce grave social risks. A majority of the world's cobalt, used in the most common battery chemistries for EVs and stationary electricity storage, is mined in the Democratic Republic of Congo (DRC) (see the map), a country struggling to recover from years of armed conflict. There, women and sometimes children often work in or around mines for less pay or status than their male and adult counterparts, without basic safety equipment (see the photo). Owing to a lack of preventative strategies and measures such as drilling with water and proper exhaust ventilation, many cobalt miners have extremely high levels of toxic metals in their body and are at risk of developing respiratory illness, heart disease, or cancer.

In addition, mining frequently results in severe environmental impacts and community dislocation. Moreover, metal production itself is energy intensive and difficult to decarbonize. Mining for copper, needed for electric wires and circuits and thin-film solar cells, and mining for lithium, used in batteries, has been criticized in Chile for depleting local groundwater resources across the Atacama Desert, destroying fragile ecosystems, and converting meadows and lagoons into salt flats. The extraction, crushing, refining, and processing of cadmium, a by-product of zinc mining, into compounds for rechargeable nickel cadmium batteries and thin film photovoltaic modules that use cadmium telluride (CdTe) or cadmium sulfide semiconductors can pose risks such as groundwater or food contamination or worker exposure to hazardous chemicals, especially in the supply chains where elemental cadmium exposures are greatest. REEs, such as neodymium and the less common dysprosium, are needed for magnets in electric generators in wind turbines and motors in EVs, control rods for nuclear reactors, and the fluid catalysts for shale gas fracking. But REE extraction in China has resulted in chemical pollution from ammonium sulfate and ammonium chloride and tailings pollution that now threaten rural groundwater aquifers as well as rivers and streams. Several metals for green technologies are found as "companions" to other ores with differential value and unsustainable supply chains (9).

POLICY RECOMMENDATIONS

With these sobering social and environmental aspects of current mineral extraction in mind, we suggest four policy recommendations.

Diversify mining enterprises for local ownership and livelihood dividends

Although large-scale mining is often economically efficient, it has limited employment potential, only set to worsen with the recent arrival of fully automated mines. Mining can concentrate occupational hazards as well as environmental risk, as demonstrated most severely by tailings pond disasters and mining wastewater contamination. Even where there is relative political stability and stricter regulatory regimes in place, there can still be serious environmental failures, as exemplified by the recent global rise in dam failures at settling ponds for mine tailings. The level of distrust of extractive industries has even led to countryside monsoons on all new mining projects, such as in El Salvador and the Philippines.

Traditional labor-intensive mechanisms of mining that are possible to undertake with less mechanization and without major capital investments are called artisanal and small-scale mining (ASM). Although ASM is not immune from poor governance or environmental harm, it provides livelihood potential for at least 40 million people worldwide, with an additional three to five times more people indirectly supported by the sector (10). It is also usually more strongly embedded in local and national economies than foreign-owned, large-scale mining, with a greater level of

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1

US Critical Mineral assessment

2

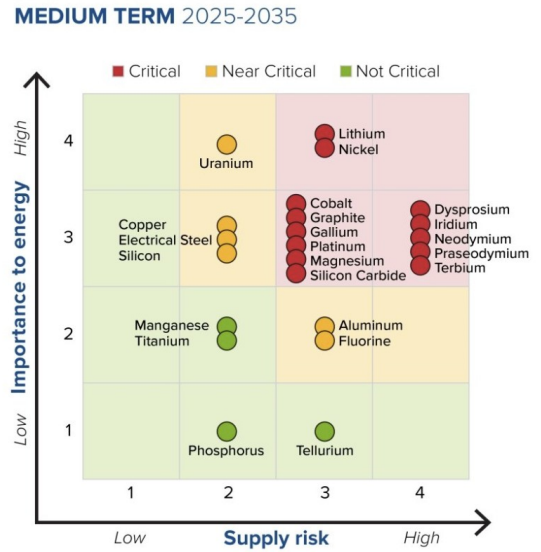


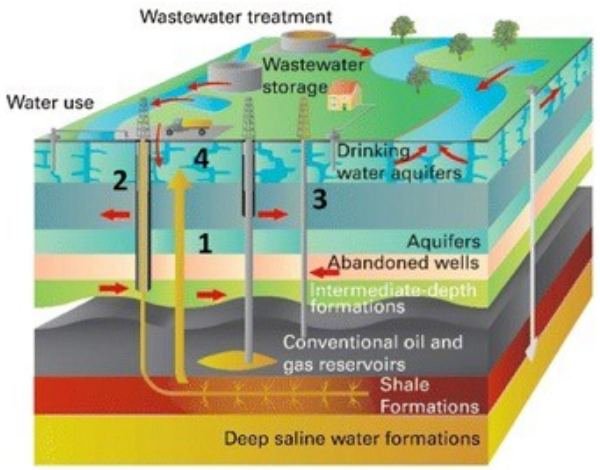
Figure 3. Medium-term (2025–2035) criticality matrix

High profile interest in exploiting U.S. based resources

1. DOE – Critical minerals in the circular economy (e.g. lithium)
2. IAS2023 – the highest supply chain index for Li
3. Recognize importance for sustainable lithium extraction technologies and exploiting waste resources

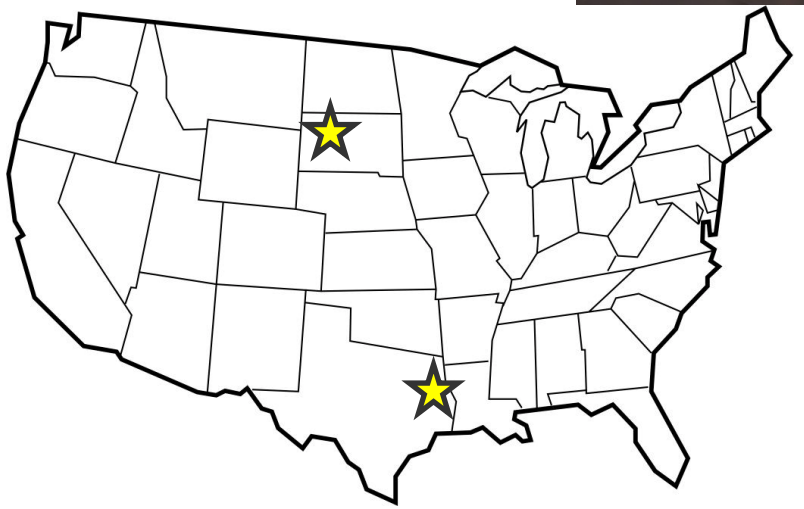
1. B.K. Sovacool, et. al. Science, 2020, 367, 6473, 30-33 2. Department of Energy, 2023

Opportunity in unconventional resources



Produced water

Inland brines



Salt	Salar de Pozuelos		Bakken, ND[1]		Bryans Mill, Tx[1]	
	g/L	Ratio (X / LiCl)	g/L	Ratio (X / LiCl)	g/L	Ratio (X / LiCl)
LiCl	2.36	----	0.86	----	2.47	----
$MgCl_2$	8.34	3.53	5.22	6.06	10.68	4.33
NaCl	6.89	2.91	94.81	110.10	176.19	71.40
$CaCl_2$	4.51	1.91	103.28	119.93	78.37	31.76
TDS (main salts)	22.09		204.2		267.7	

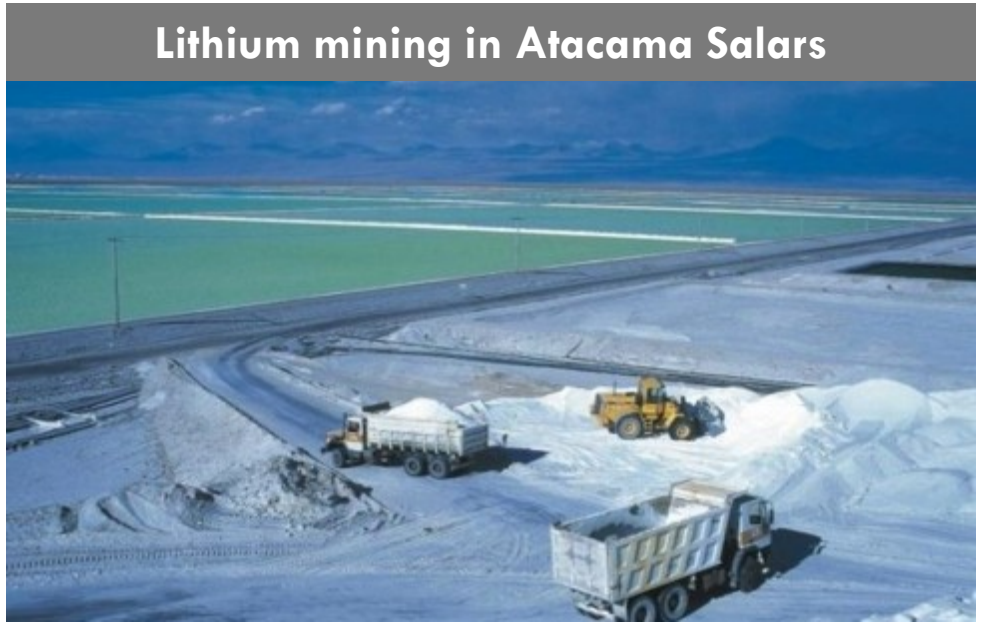
Exploiting U.S. resources w/ NREL tech.

- TDS, Ca, and Mg ratios to high for IX or hydrometallurgy
- Challenges with low Li concentrations in feed and complex compositions
- New technology is necessary to exploit these resources!

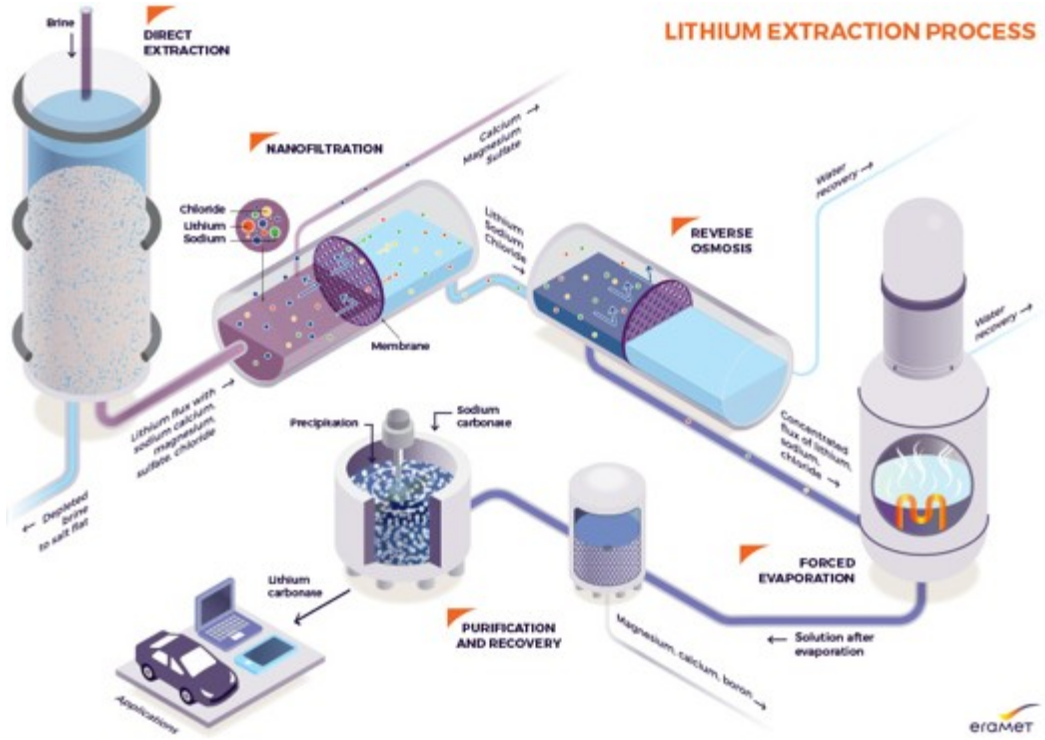
1. USGS National Produced Waters Geochemical Database v2.3, accessed 2020

Current State of the art technology

Hydrometallurgy[1]



Dynamic Lithium Extraction[2]



State of technology comes from lithium mining

- Hydrometallurgy from South American Salars (Mg ratio critical to Salar success)
- DLE - Ion exchange in non-traditional resources (e.g. Standard Lithium in AR)

1. J.W. An, et. al., Hydrometallurgy, 117-118, 2012, 64-70
2. https://www.eramet.com/en/activities/development-projects/lithium-project-new-growth-domain

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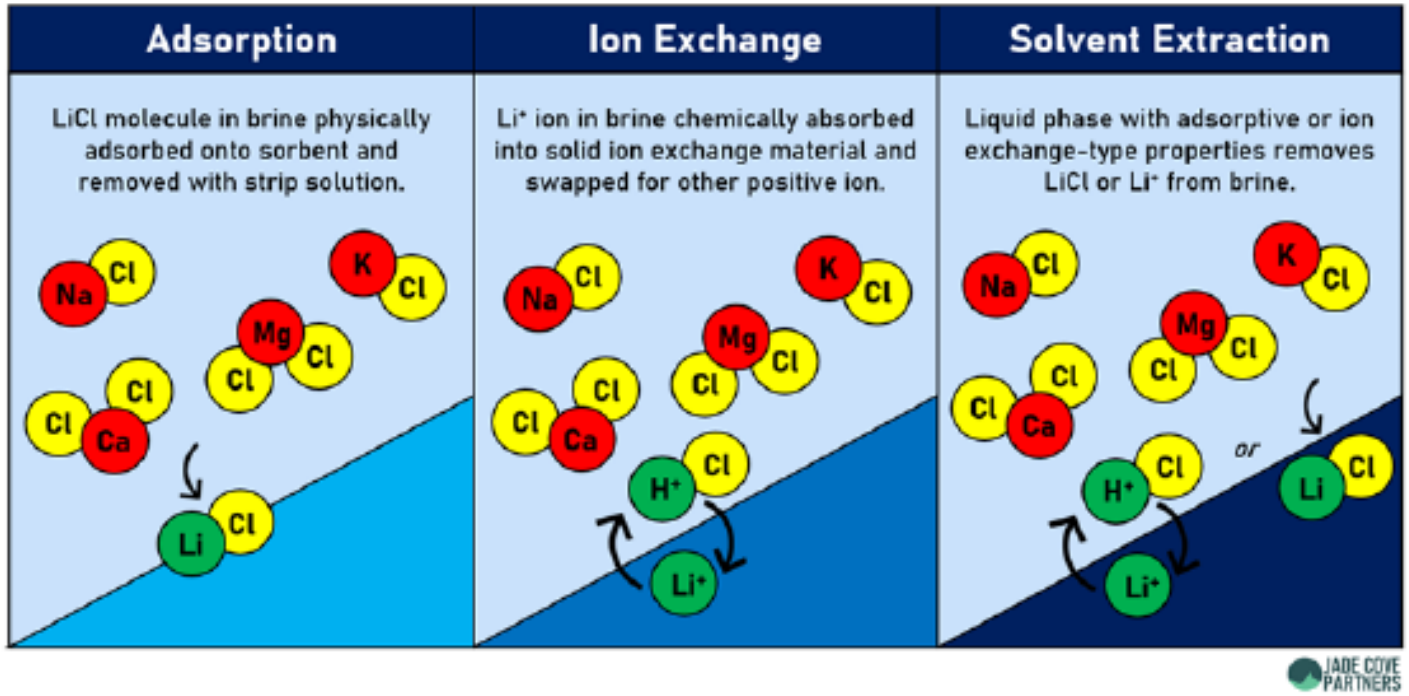
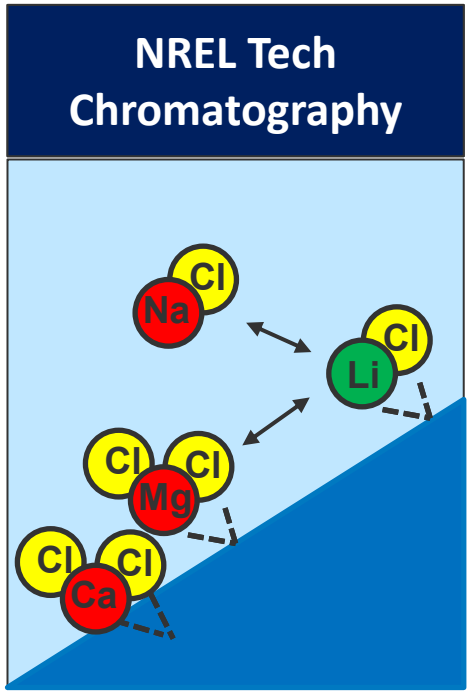
Direct Lithium Extraction (DLE) approach



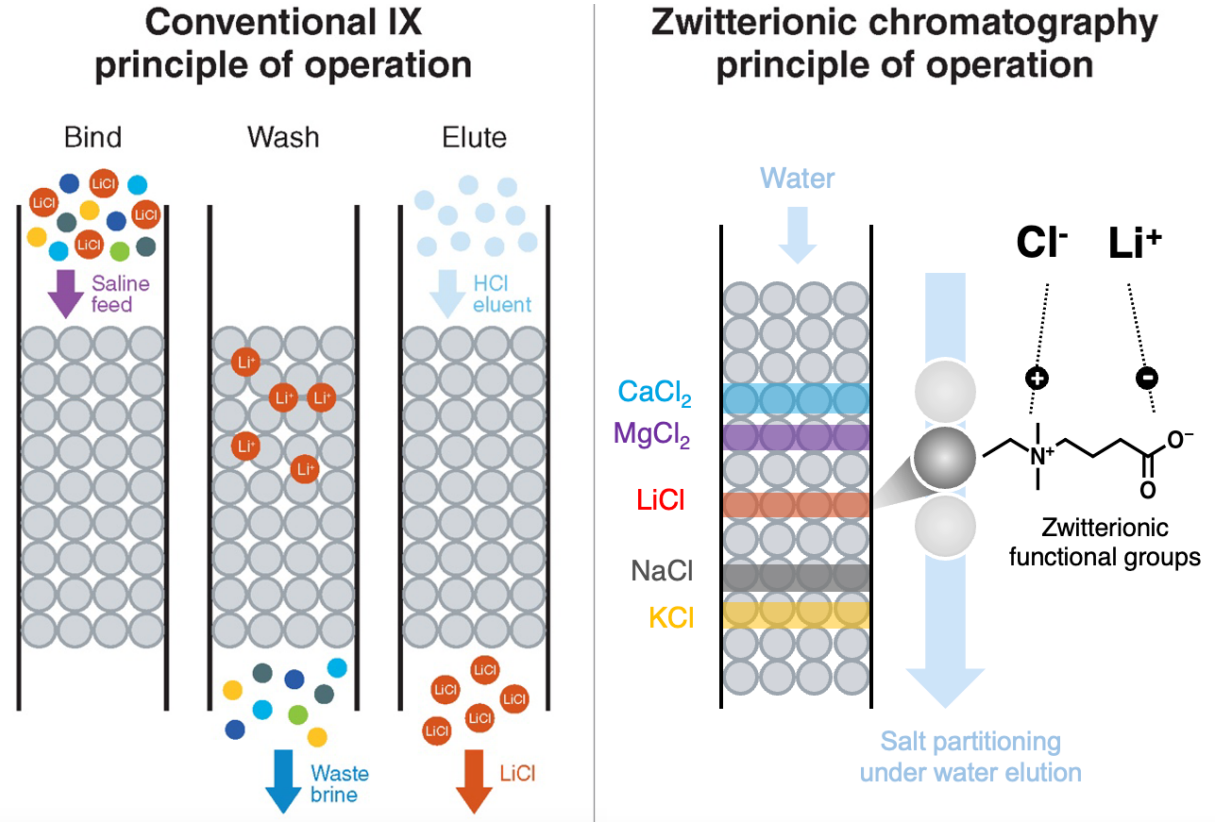


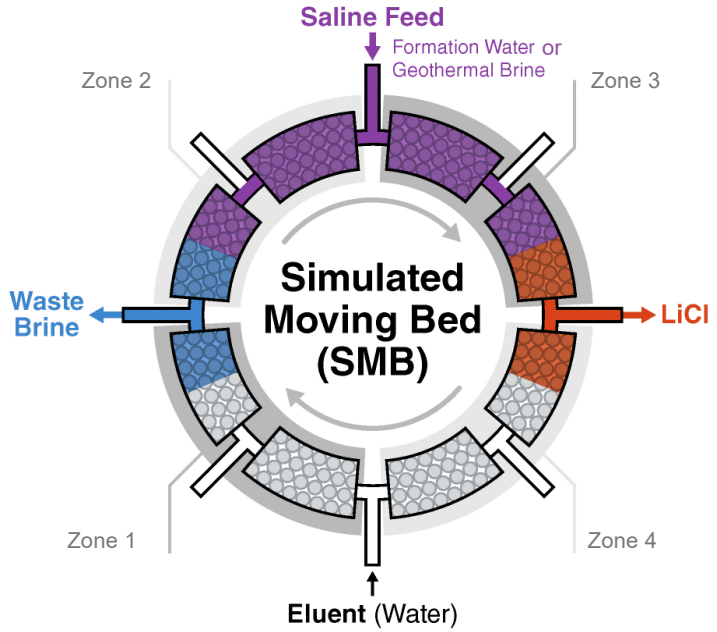
- Current IX or extraction approaches requires lower/equimolar amount of strong acids
- Adsorption is limited by low adsorption capacity and slow mass transfer rates

- We propose a new salt partitioning approach using chromatography process

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

Zwitterionic chromatography (ZIC) approach for DLE

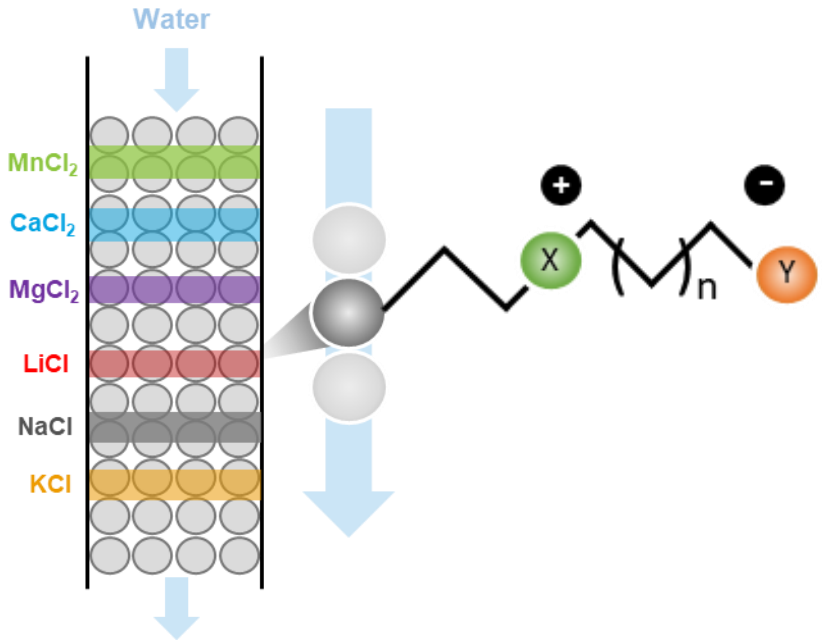


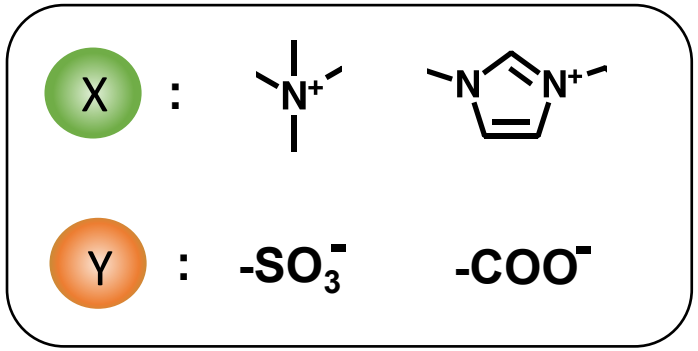


Zwitterionic chromatography – whole salt partitioning

- IX is semicontinuous bind, elute, wash steps with significant water footprints
- Handle high hardness solutions
- Continuous process to increase the recovery yield, purity, and productivity

ZIC process development





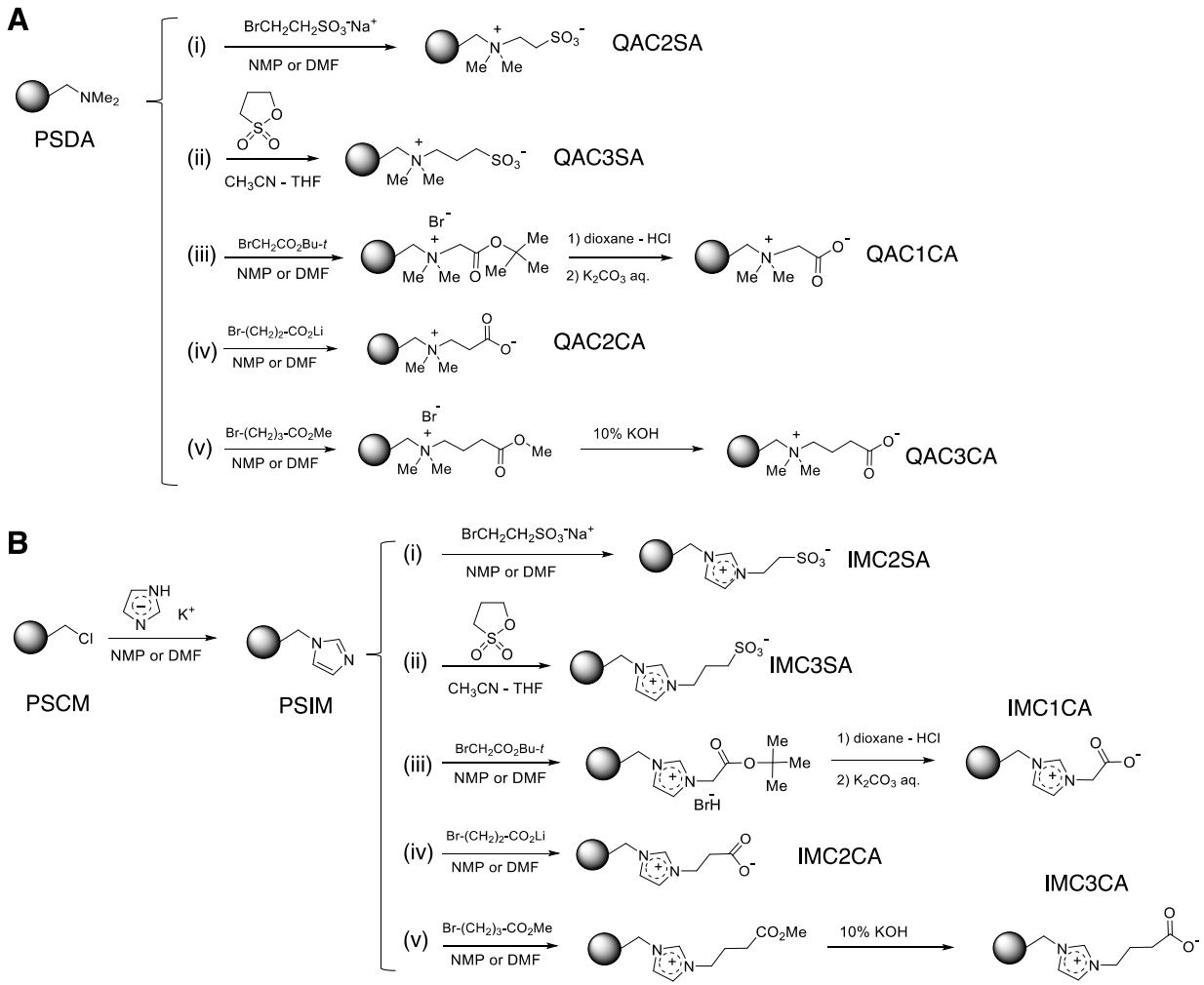
Design ZI resins → Screening ZI resins promising for Li separation → Single-column tests to develop a LC model → SMB model optimization & prediction → zSMB demonstration to produce >10 g Li products

1. S. N. Kalyakin, V. I. Kuz'min, *Mendeleev Comm.*, 2000, **10,(4),** 151-152

ZI Resins synthesized from commercially available ones

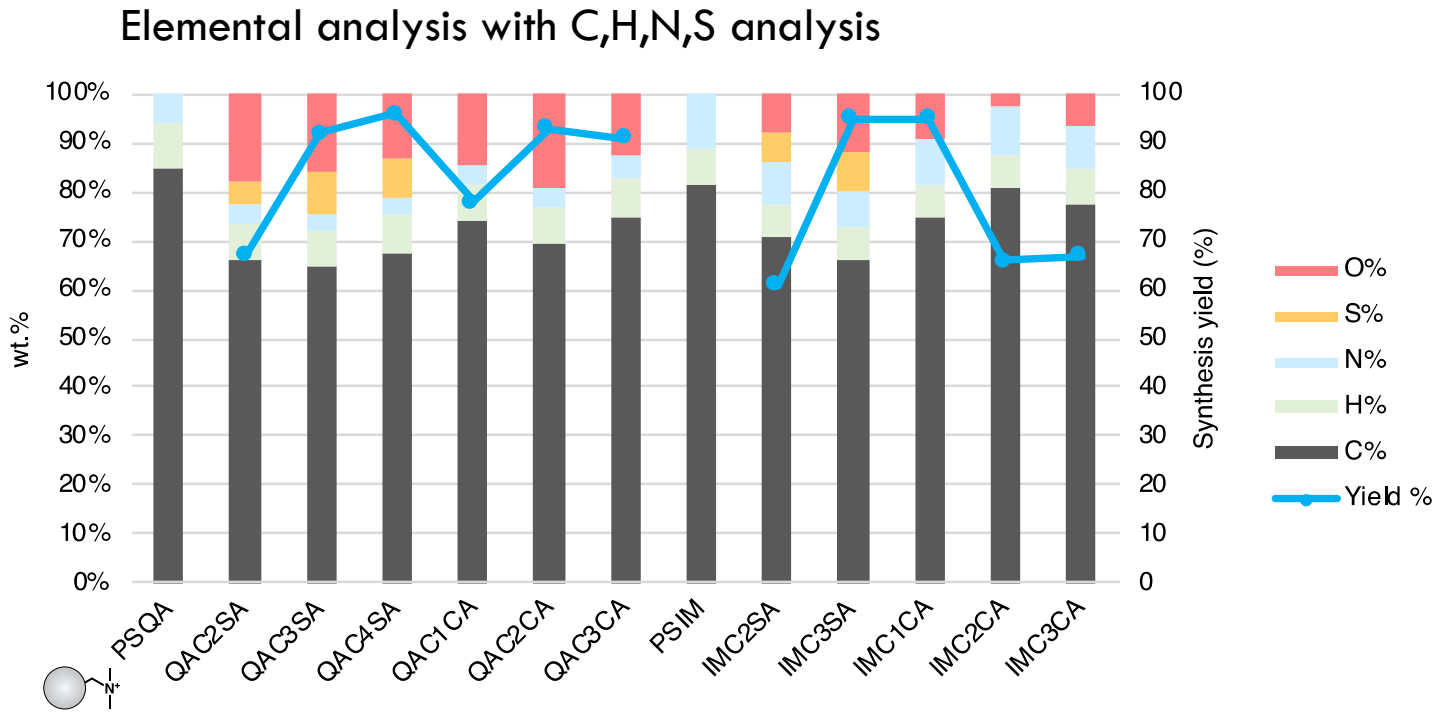
Synthesize and test >10 zwitterionic resins

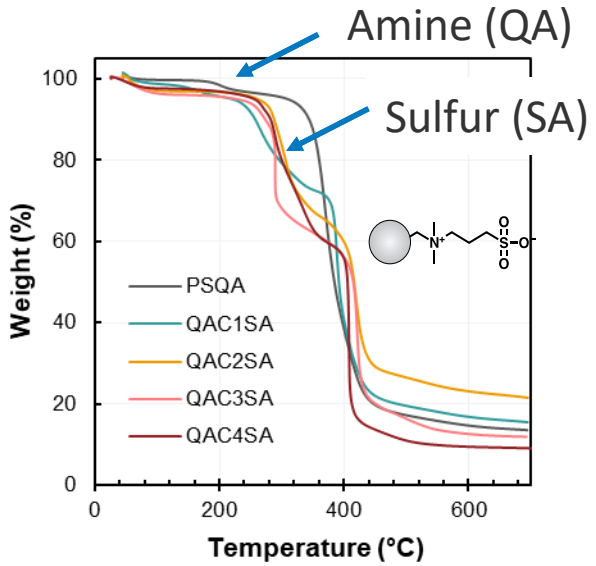
Base	Carbon chain	Acid
Quaternary Ammonium (QA)	C2	Sulfonic acid (SA)
QA	C3	SA
QA	C4	SA
QA	C1	Carboxylic acid (CA)
QA	C2	CA
QA	C3	CA
Imidazole (IM)	C2	SA
IM	C3	SA
IM	C1	CA
IM	C2	CA
IM	C3	CA

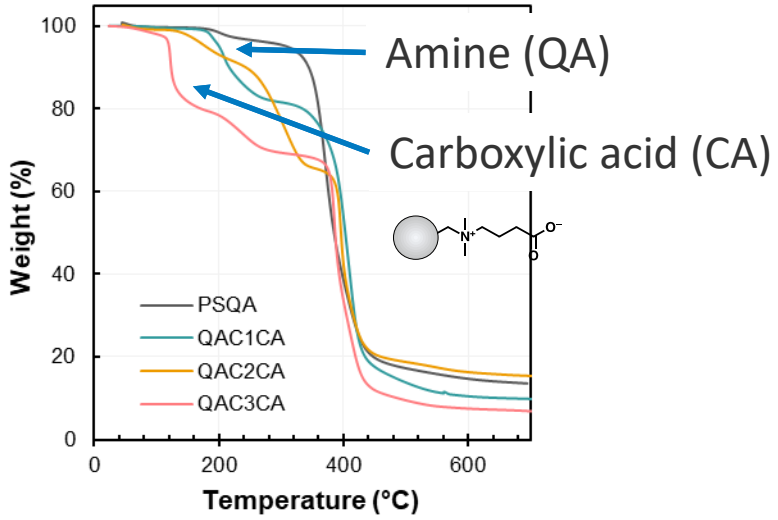


Choi et al., Sep and Purify Tech, *2024, in preparation*

ZI Resin preparation and Characterization



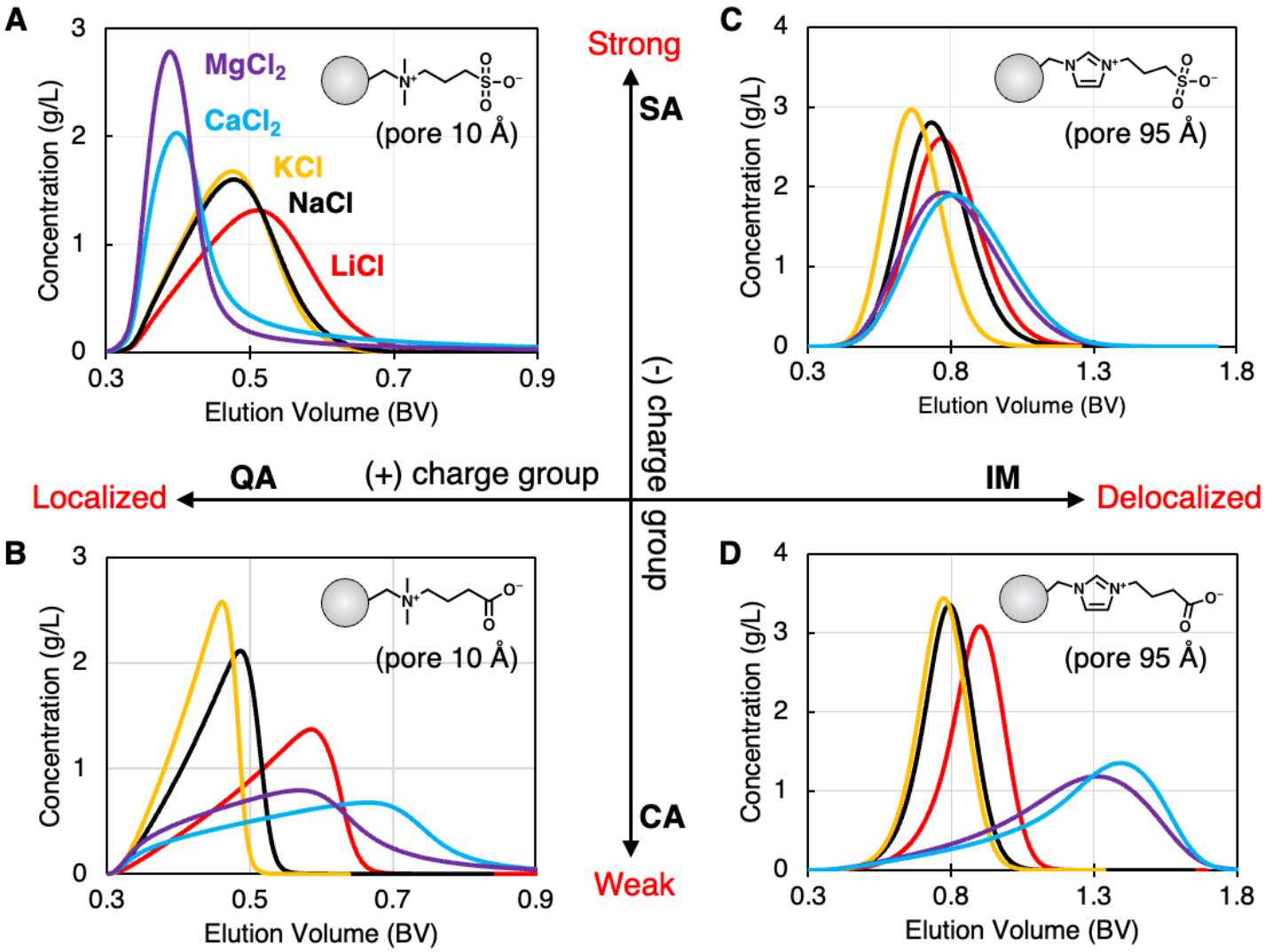




- Prepare ZI resin from commercial ion exchange resins
- Conversion yields were varied from 80~99% except QAC1SA
- TGA showed the existing functional groups

Choi et al., Sep and Purify Tech, *2024, in preparation*

Effect of ZW Groups on the Salt Elution

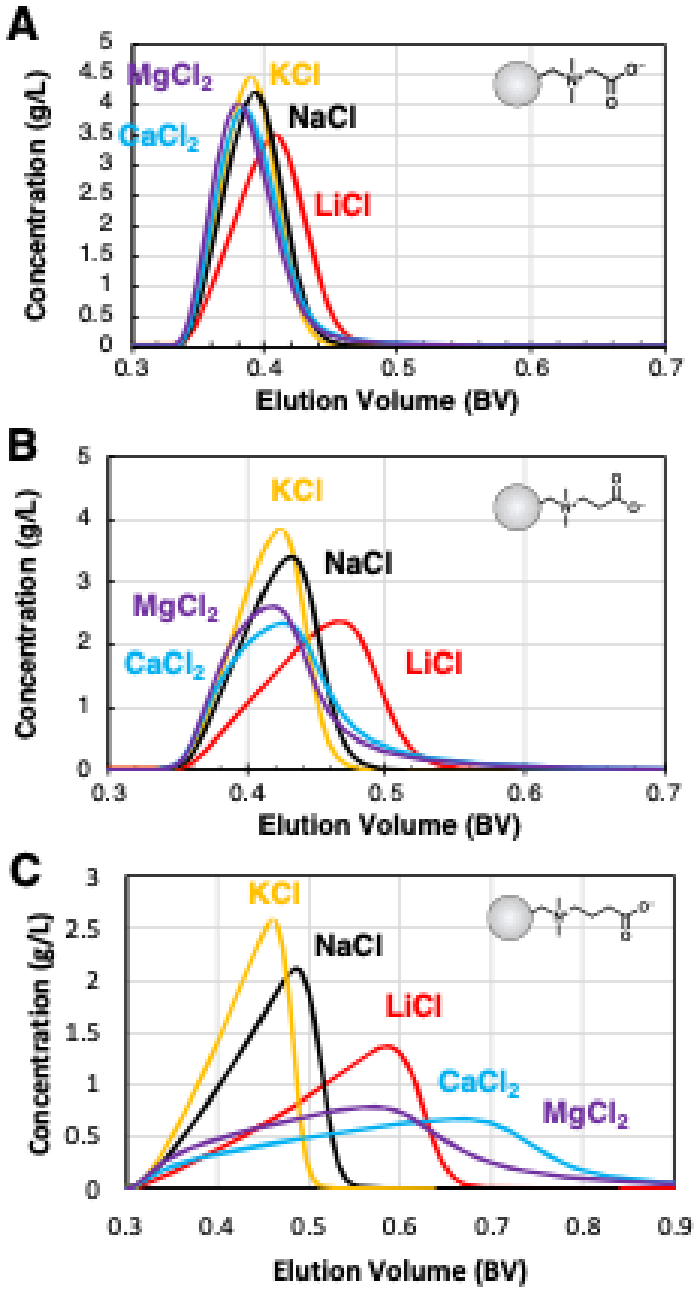


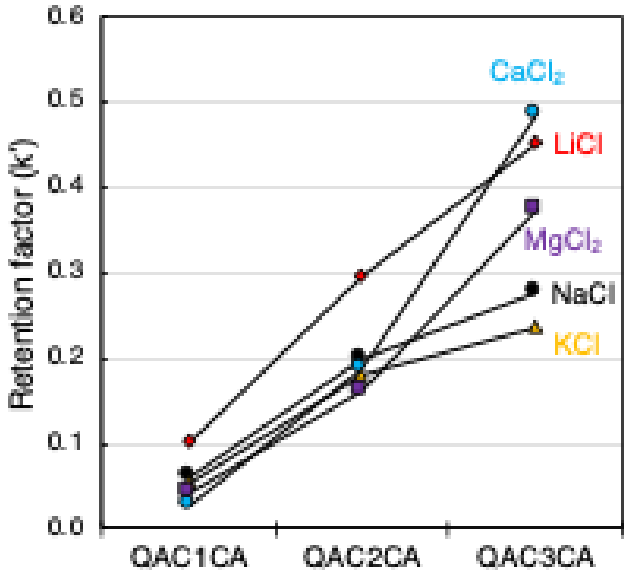
- Zwitterionic groups affect salt retention, synergistically with pore size control
- QA-SA increases size exclusion of divalent salts
- CA increases the retention of divalent salts

- Elution order: K, Na, Li, Mg, Ca

Choi et al., Sep and Purify Tech, *2024, in preparation*

Effect of Carbon Chain Length between ZW Groups on the Salt Elution

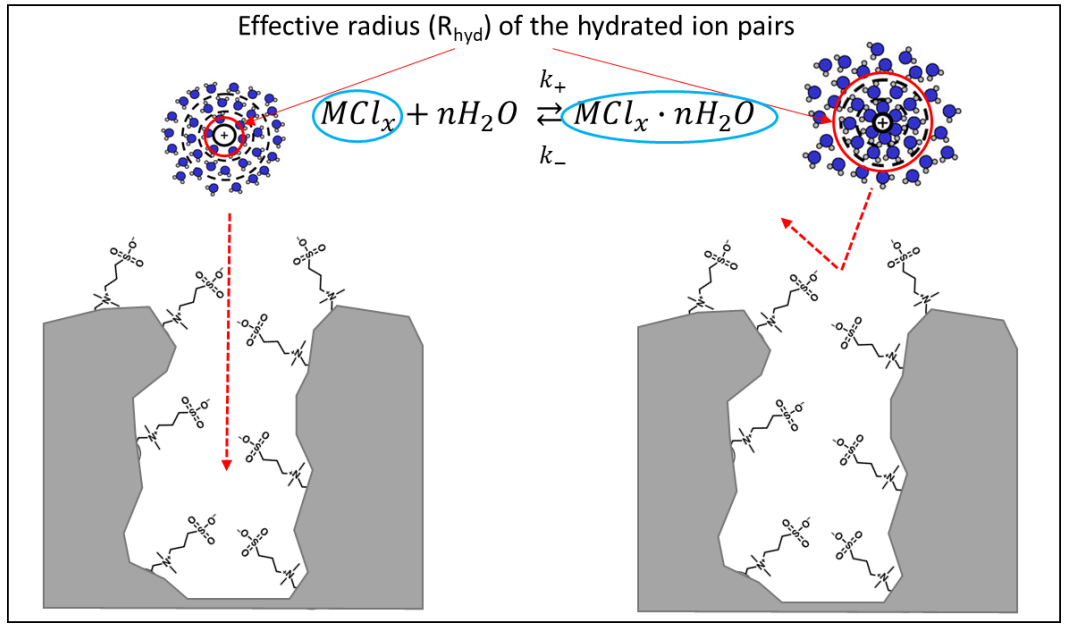


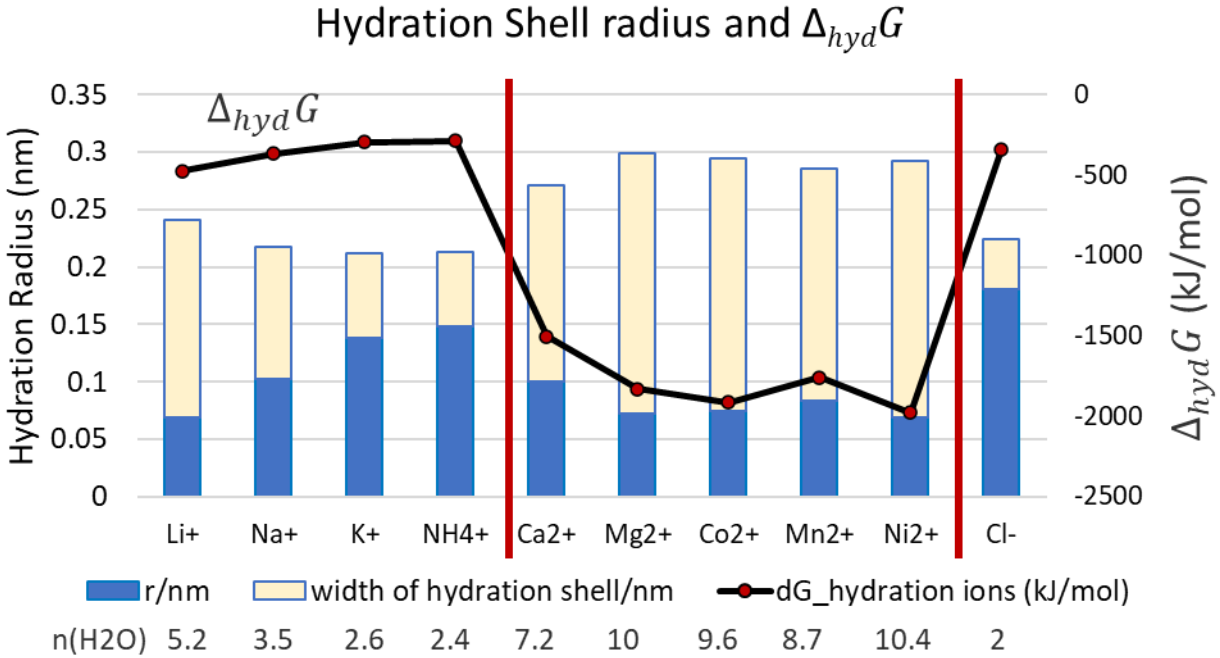


- Varying carbon chain length changes the retention time of salts
- C3 chain is the optimal length for separating LiCl from divalent salts in QACxSA

Choi et al., Sep and Purify Tech, *2024, in preparation*

Elution Behavior Relation to Hydration Shells on QAC3SA



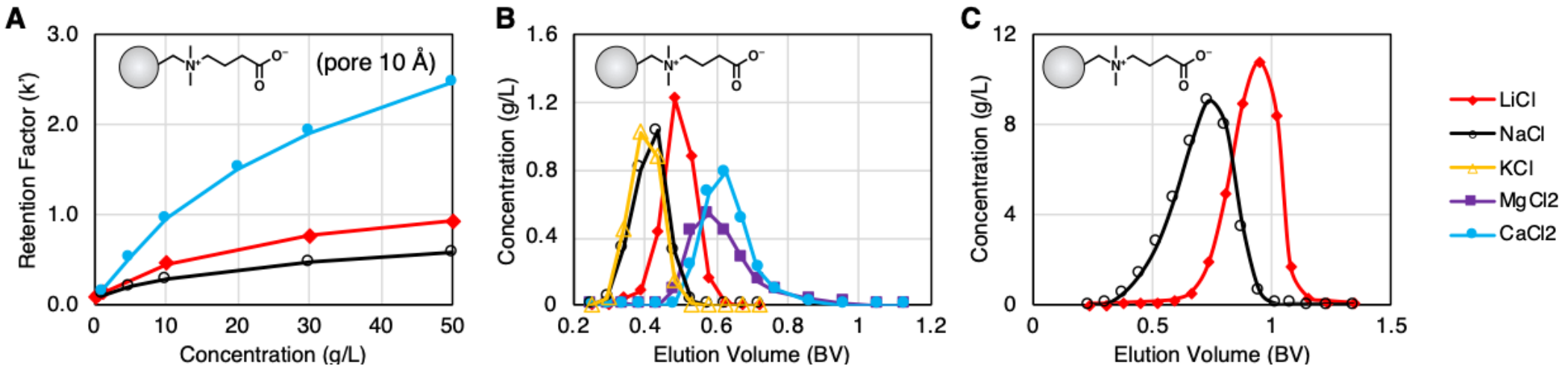


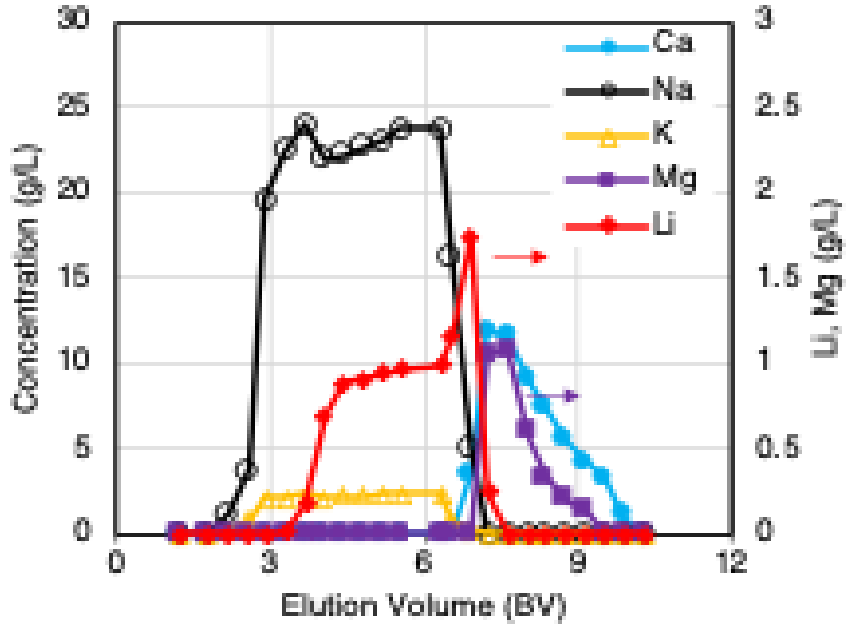
- With water eluent, M^+Cl^- is moving as one solute by ion-pairing effect to neutralize the charge balance
- In small pore, the ZW group density gets higher enough to screen hydrated ion pairs
- **Divalent cations:** favorable to form **strong hydration shells** (large r_{hyd}) with fast k+ → **Size-excluded**
- NaCl, KCl, LiCl: favorable to form **weak hydration shells** (small r_{hyd}) with slow k+ → Penetration into the pore phase

J. CHEM. SOC. FARADAY TRANS., 1991, 87(18), 2995-2999
https://dasher.wustl.edu/chem478/labs/lab-09/jcs-faraday-87-2995-91.pdf

Choi et al., Sep and Purify Tech, *2024, in preparation*

Mineral fractionation from real brine sample with QAC3CA





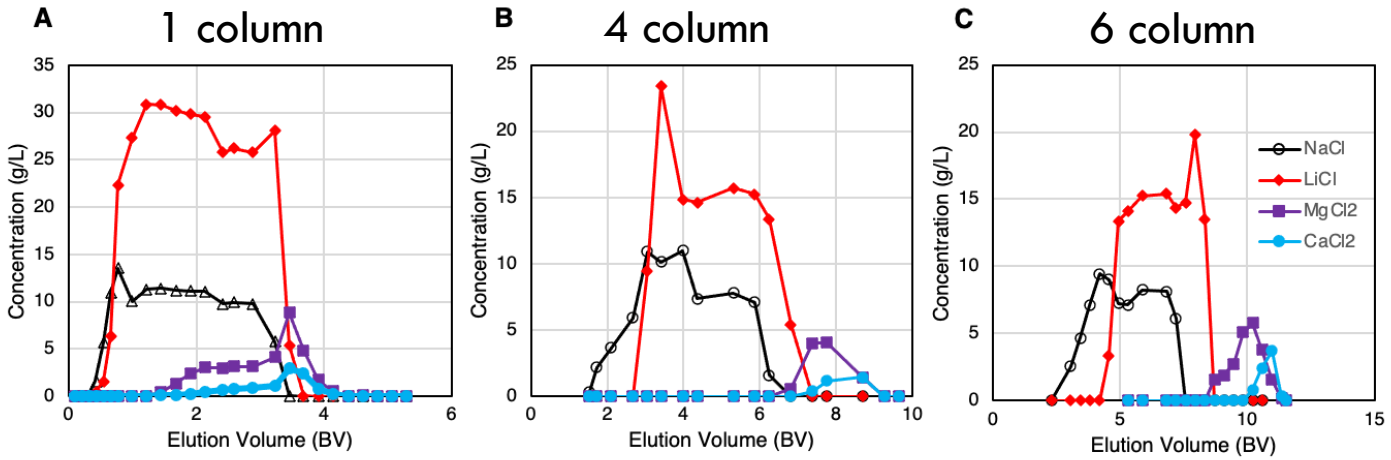
- Elution order from K, Na, Li, Mg, Ca
- Na/Li can be separated by water elution

- Long column can increase the separation window between Li and Mg/Ca
- In-land brackish water loading in 1m column and separated Li with >79% yield of 99% free of Ca and Mg
- Promising for continuous SMB mode

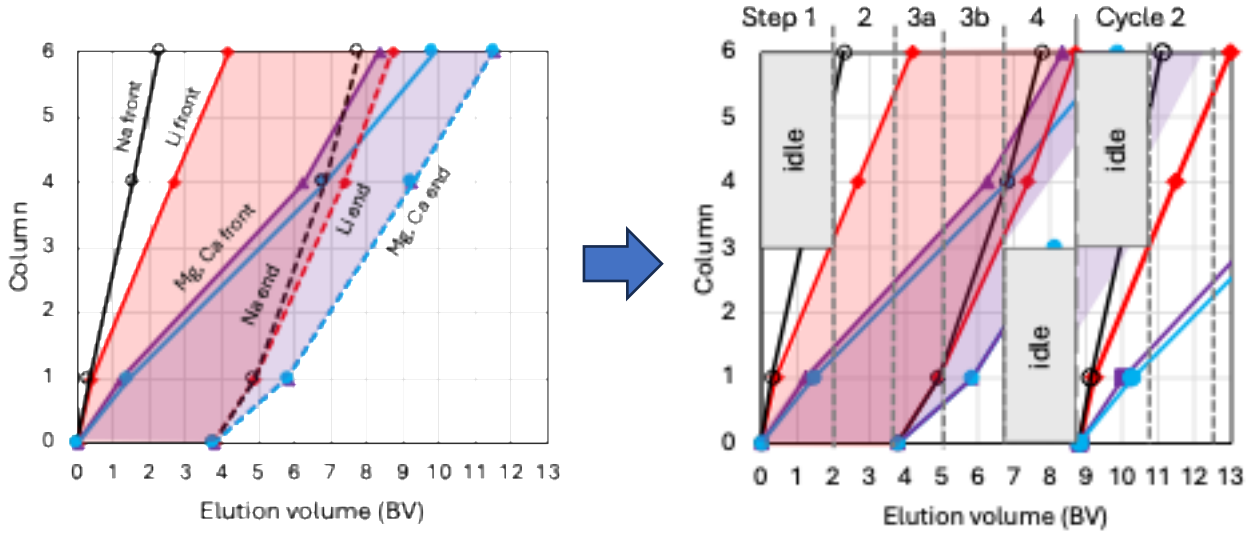
Choi et al., Sep and Purify Tech, *2024, in preparation*

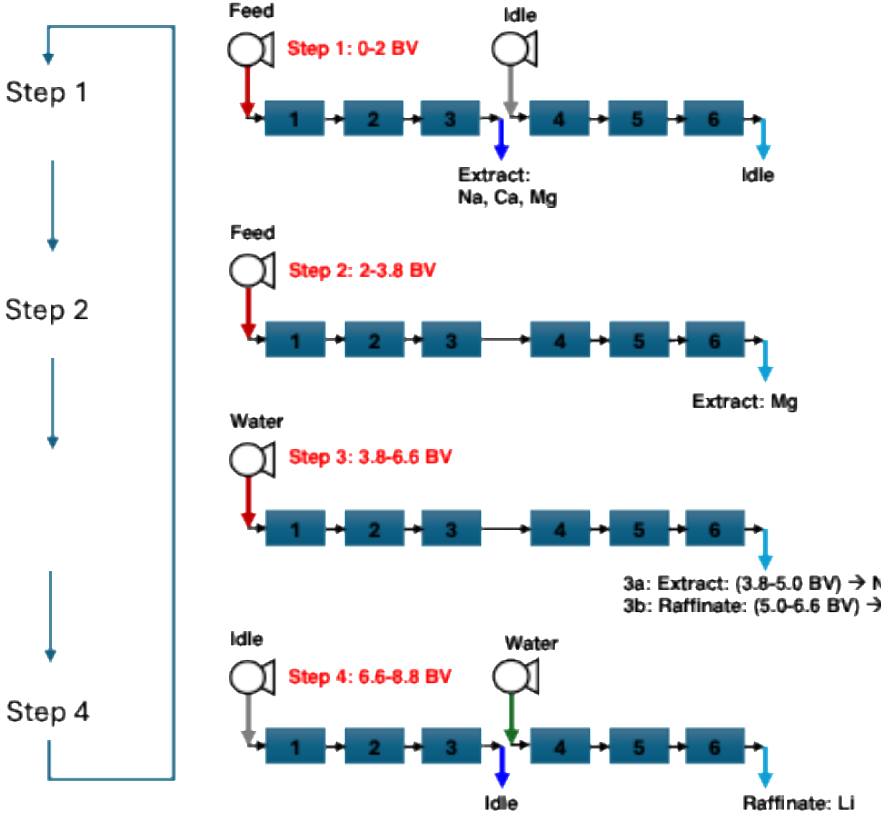
Mineral fractionation from real brine sample with QAC3CA

Mining water long loading test on QAC3CA



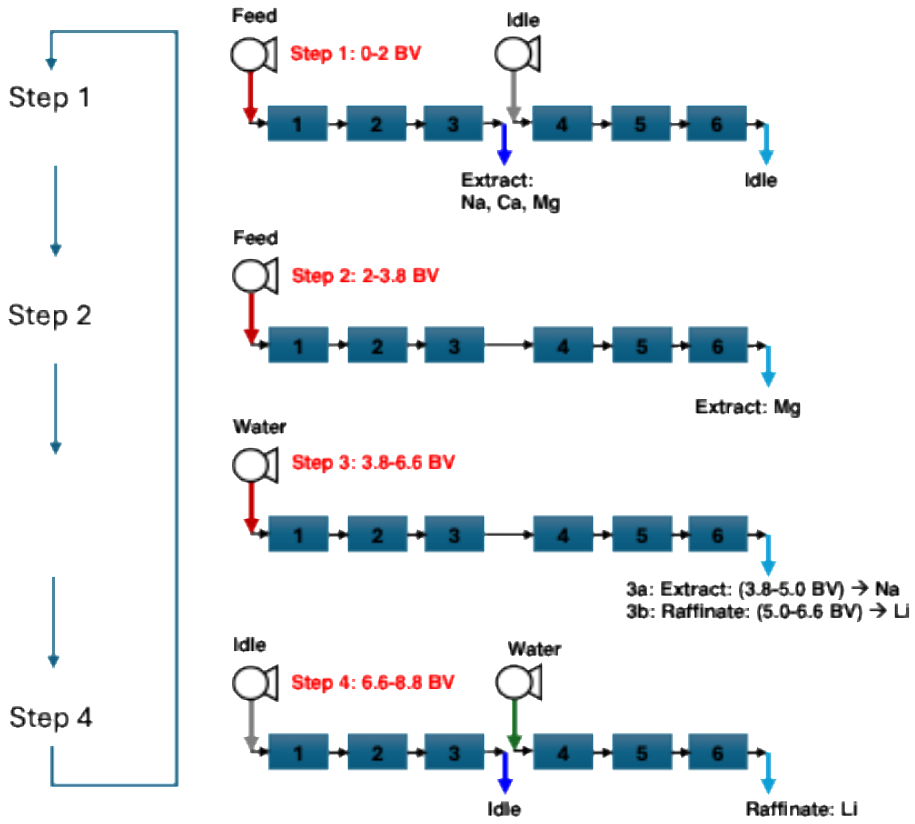
Short-cut design for Li fractionation

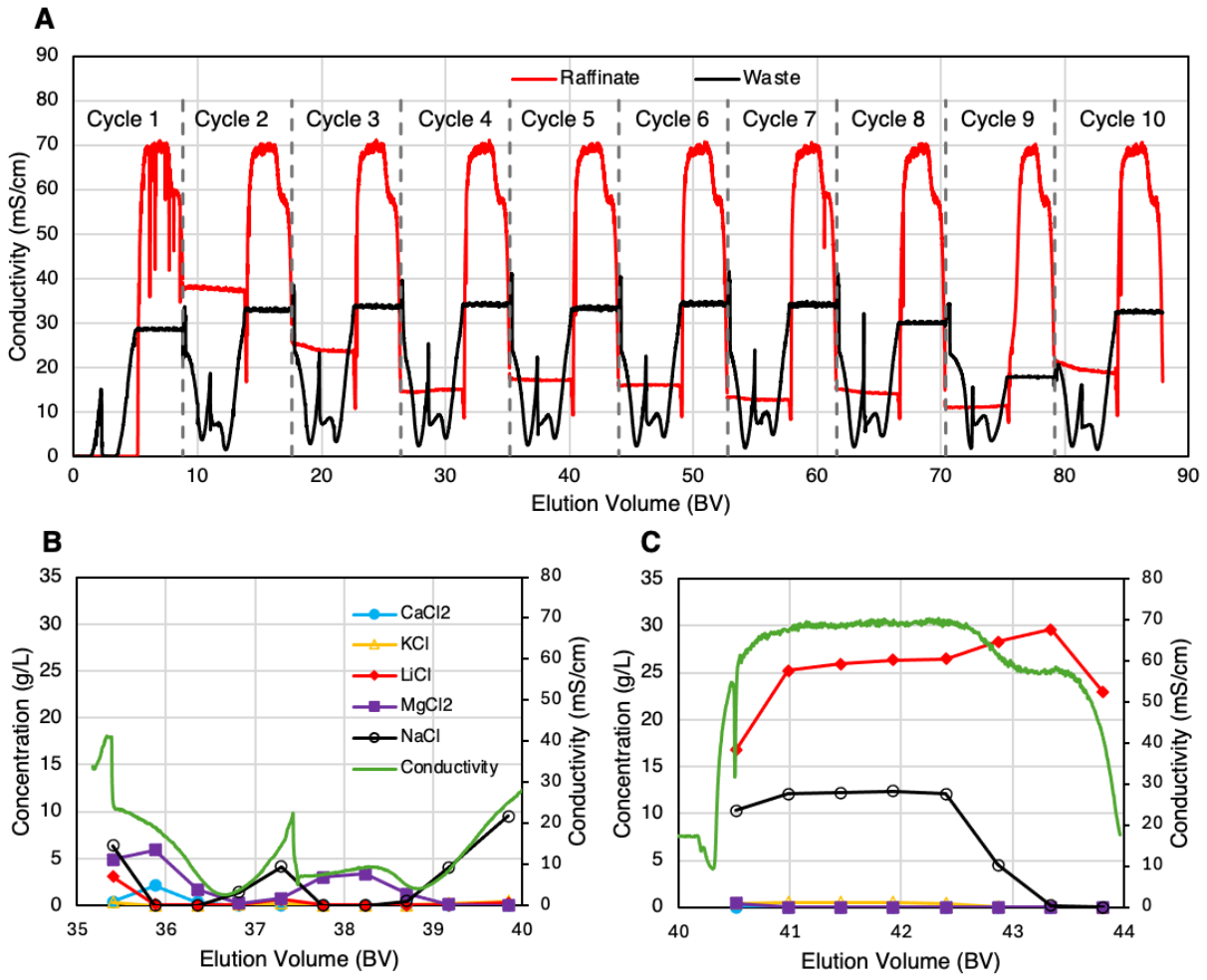




Choi et al., Sep and Purify Tech, *2024, in preparation*

Mineral fractionation from real brine sample with QAC3CA





- Multi-column ZIC in continuous mode separated Li from Ca and Mg, yielding >99% Li recovery
- Water consumption is reduced by >33% compared to batch operation
- Shortcut process design method is scalable

Purity (w/w)	52.0%
Yield	99.2%
D/F	1.6

Choi et al., Sep and Purify Tech, *2024, in preparation*

Conclusions

- Various zwitterionic functional groups resins were synthesized and characterized
- Effects of ZW groups, C chain, pore size were explored for separating LiCl from salt solution
- Ion pairing effect and ion hydration in the pore phase cause salt partitioning behaviors
- Li separation from divalent salts were demonstrated with multi-column ZIC, yielding >99% Li with free of Ca and Mg

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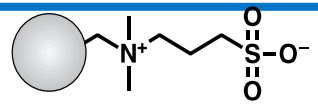
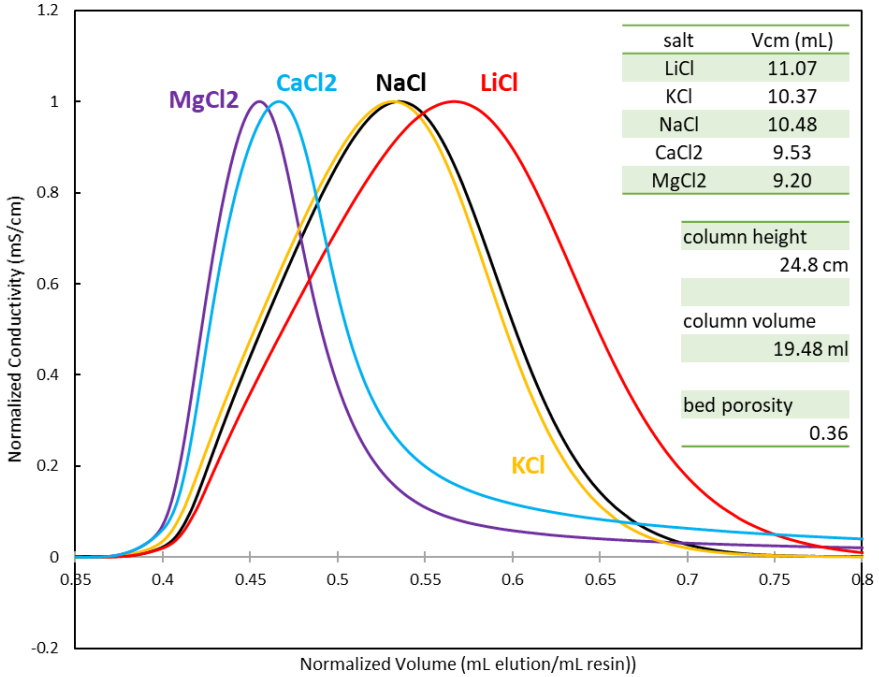
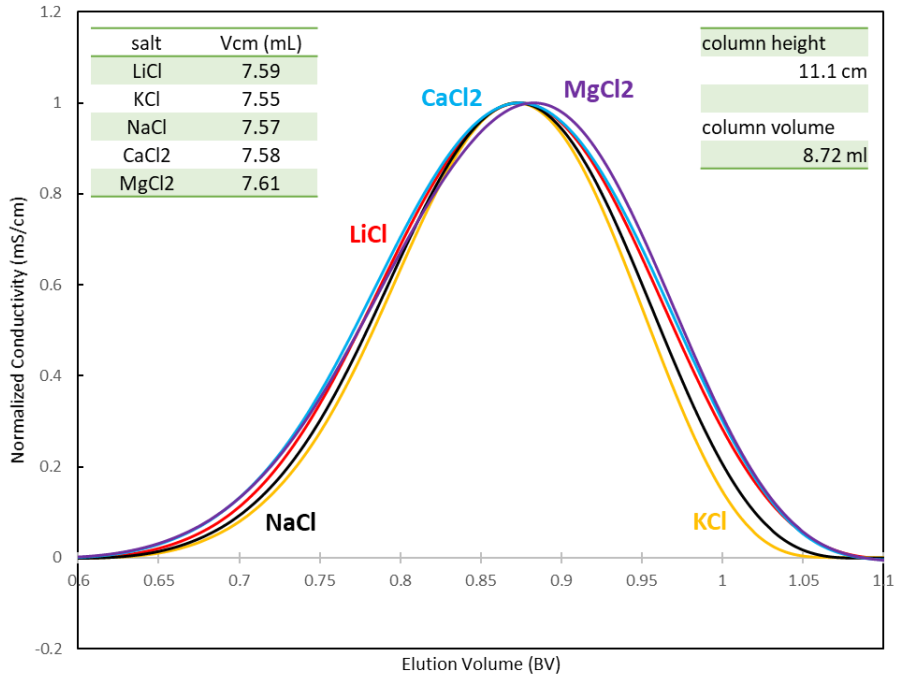
Pore size affects the salt elution behavior



Small Pore (size 5~20 nm)



Large Pore (size 10~60 nm)



- Functional group density at the pore surface gets higher in small pore size
- Dense functional groups at the particle surface causes the size-exclusion effect for divalent cations and partial penetration of monovalent cations