National Alliance
for Water Innovation

NAWI Research Spotlight: Technoeconomic Assessment of Brine Valorization from Brackish Groundwater

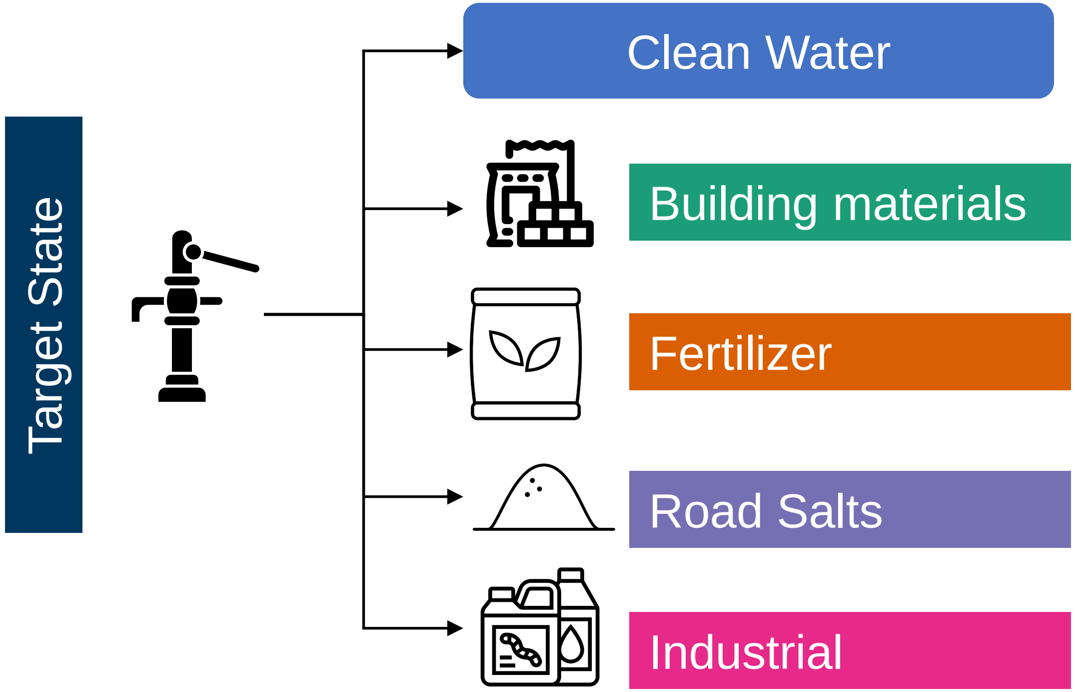
NAWI Seminar Series

Alison Fritz, Casey Finnerty, Alex Dudchenko, Haleigh Heil, Caroline Adkins, Meagan Mauter, Adam Atia, Chad Able, Erik Shuster

June 27, 2024

Objective: Review market opportunities for valorization during brackish water desalination

- Overview of NAWI 3.26
- Product market overview
- Geospatial assessment of markets
- Emerging markets
- Challenges and opportunities



NAWI 3.26 Technoeconomic Assessment of Brackish Groundwater Brine Valorization

October 2023-September 2025

Assess technical feasibility and long-term reliability of industrial ecosystems for brackish groundwater desalination with markets for reverse osmosis brine constituents.

Stakeholder Input

1. Understand supply and demand, commodity specifications and key trends of material markets
2. Connect brine composition to potential byproduct markets and perform mass balance on constituents and endpoints
3. Assess cost and emissions of 2-5 flowsheets for byproduct recovery from brine

Objectives

Objective 1. Develop geospatially resolved market assessment to identify existing and potential markets for bulk constituents recovered from waste brine with stakeholder input. Pair brine composition resource assessments with market data on building materials, fertilizer, road salts, and chemicals including caustic soda and sulfuric acid.

Objective 2. Conceptualize and develop process models for brackish groundwater treatment and valorization and perform an economic and life cycle assessment of the proposed treatment trains (WaterTAP with PHREEQC or other electrolyte modeling software).

3.26 Technoeconomic Assessment of Brine Valorization from Brackish Water Desalination Overview

October 2023-September 2025 (24 Months)

Objective 1.

Task 1. Coordinate Stakeholder Board

Menachem Elimelech (PI, Yale), Casey Finnerty (Yale)

Task 2. Perform market analysis to identify current utilization of priority byproducts

Erik Shuster (PI, NETL), Haleigh Heil (NETL)

Task 3. Connect brine composition to potential byproduct markets and perform mass balance on all constituents and endpoints

Alison Fritz (PI, NETL), Meagan Mauter (Stanford), Caroline Adkins (Stanford)

Objective 2.

Task 4. Process Scoping Assessment

Alexander Dudchenko (PI, SLAC), Menachem Elimelech (Yale), Caroline Adkins (Stanford)

Task 5. Perform technoeconomic analysis of extracting byproducts from brines using promising treatment train schema

Alexander Dudchenko (PI, SLAC), Carson Tucker (Stanford), Chad Able (NETL)

Task 6. Perform life cycle analysis

Menachem Elimelech (PI, Yale)

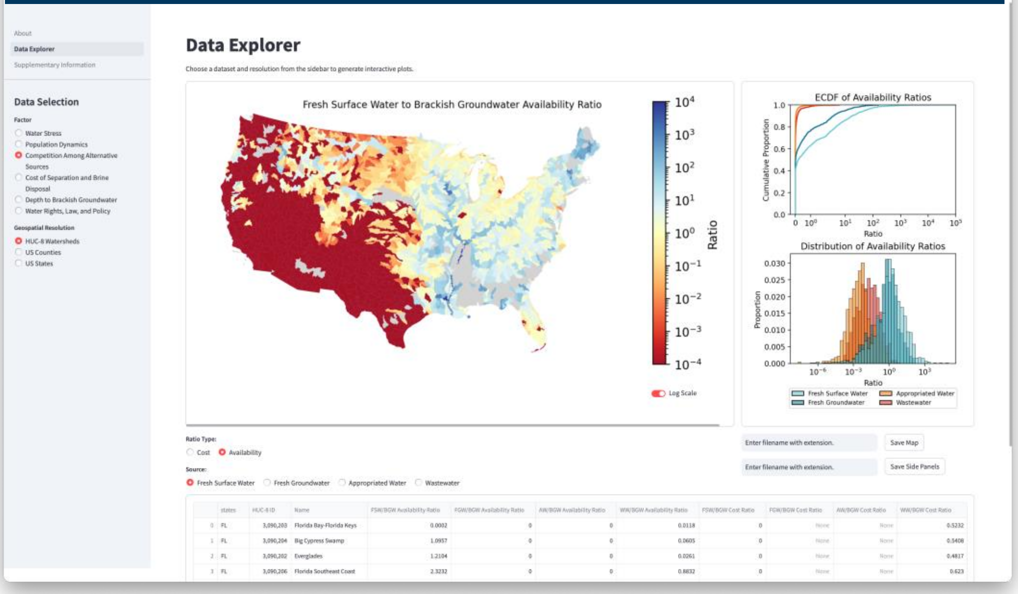
NAWI NATIONAL ENERGY TECHNOLOGY LABORATORY Yale University SLAC NATIONAL ACCELERATOR LABORATORY Stanford University

Stakeholder Board

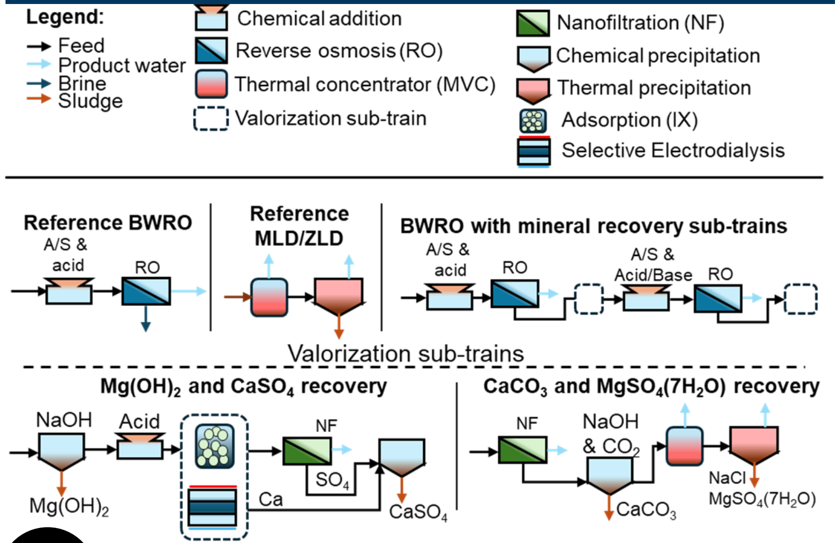
ASU Arizona State University
Sublime Systems
Ansys
Gradiant
Texas Tech University
Zero Brine
NM State
UC Davis
Olokun Minerals
Department of Transportation United States of America
Partanna — Building a World That Breathes
Texas
Michigan State University Founded 1855
Partnership International Sustainable Development
New Logic Research
CDM Smith
UCLA
DuPont
Burnt Island Ventures
BlueTech Research
ChemTreat, Inc.
Mickley & Associates — Integrating Science and Engineering
Miami
Euro Gypsum
Hazen
FTS H2O Fluid Technology Solutions
Capture6
United States Lime & Minerals
Saint-Gobain

What progress have we made to date?

Data explorer for regional prioritization of brackish groundwater treatment

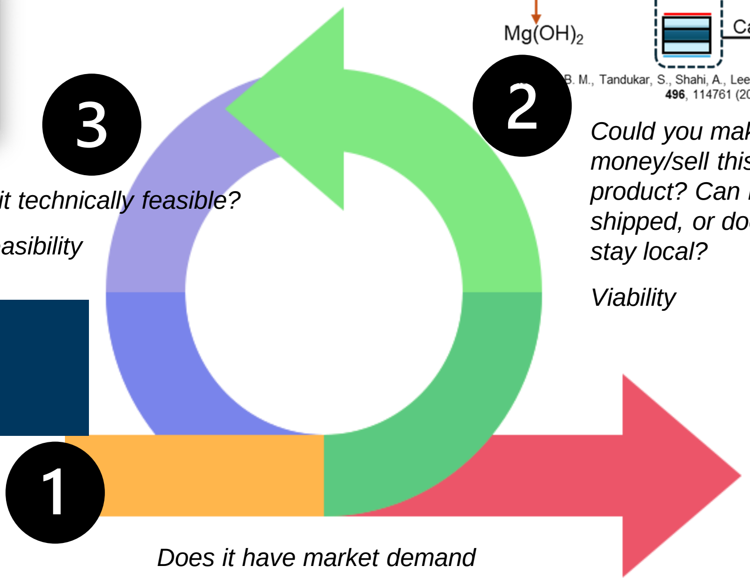


Literature review of mineral recovery processes and available models



B. M., Tandukar, S., Shahi, A., Lee, C. O. & Howe, K. J. *Desalination* **496**, 114761 (2020).

Drioli, E., Curcio, E., Criscuoli, A. & Profio, G. D. *Journal of Membrane Science* **239**, 27–38 (2004).



Is it technically feasible?

Feasibility

Could you make money/sell this product? Can it be shipped, or does it stay local?

Viability

Desirability and feasibility analysis for product markets

Does it have market demand

Desirability

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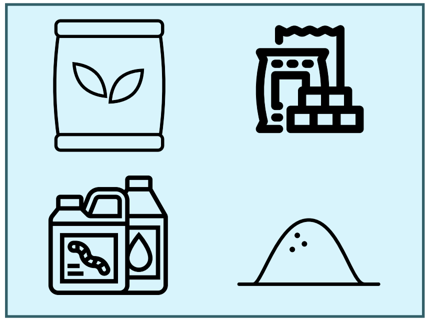
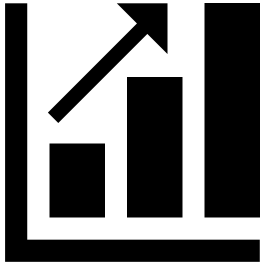
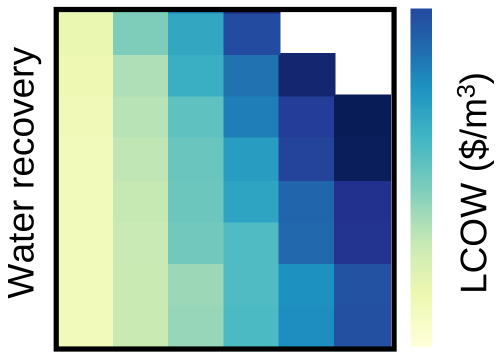
Our future products

Summary of promising products for valorization





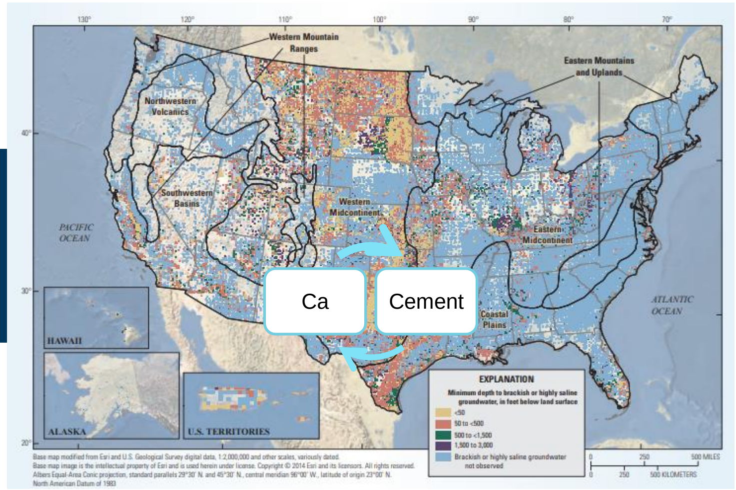
WaterTAP flowsheets demonstrating cost and emissions of treatment and valorization processes



Source: Tim Bartholomew

Read more on WaterTAP here:

Map pairing product markets and brackish groundwater ion compositions



Source: USGS

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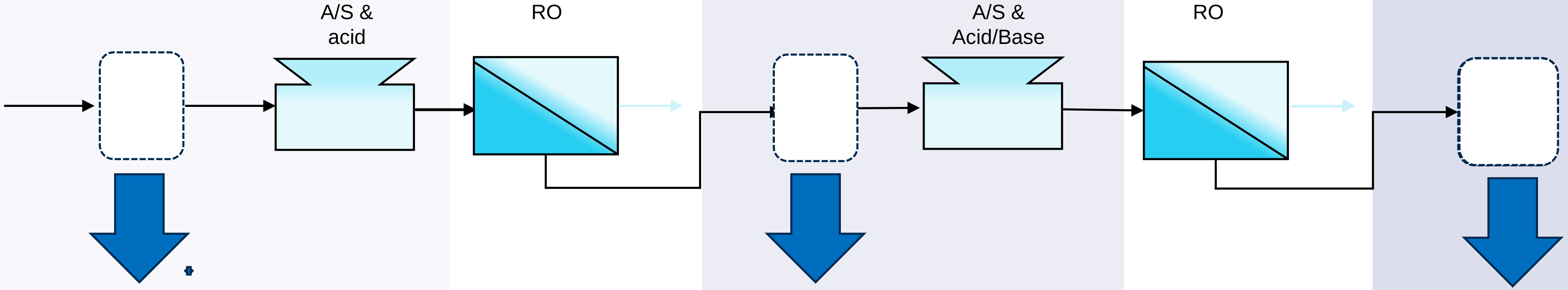
Valorization within the treatment train

BWRO with mineral recovery sub-trains*



Pre-treatment 1. Separate compounds of interest, send to market

Pre-treatment 2. Separate compounds of interest, or send brine directly to market

Post-treatment. Separate compounds of interest, or send brine directly to market

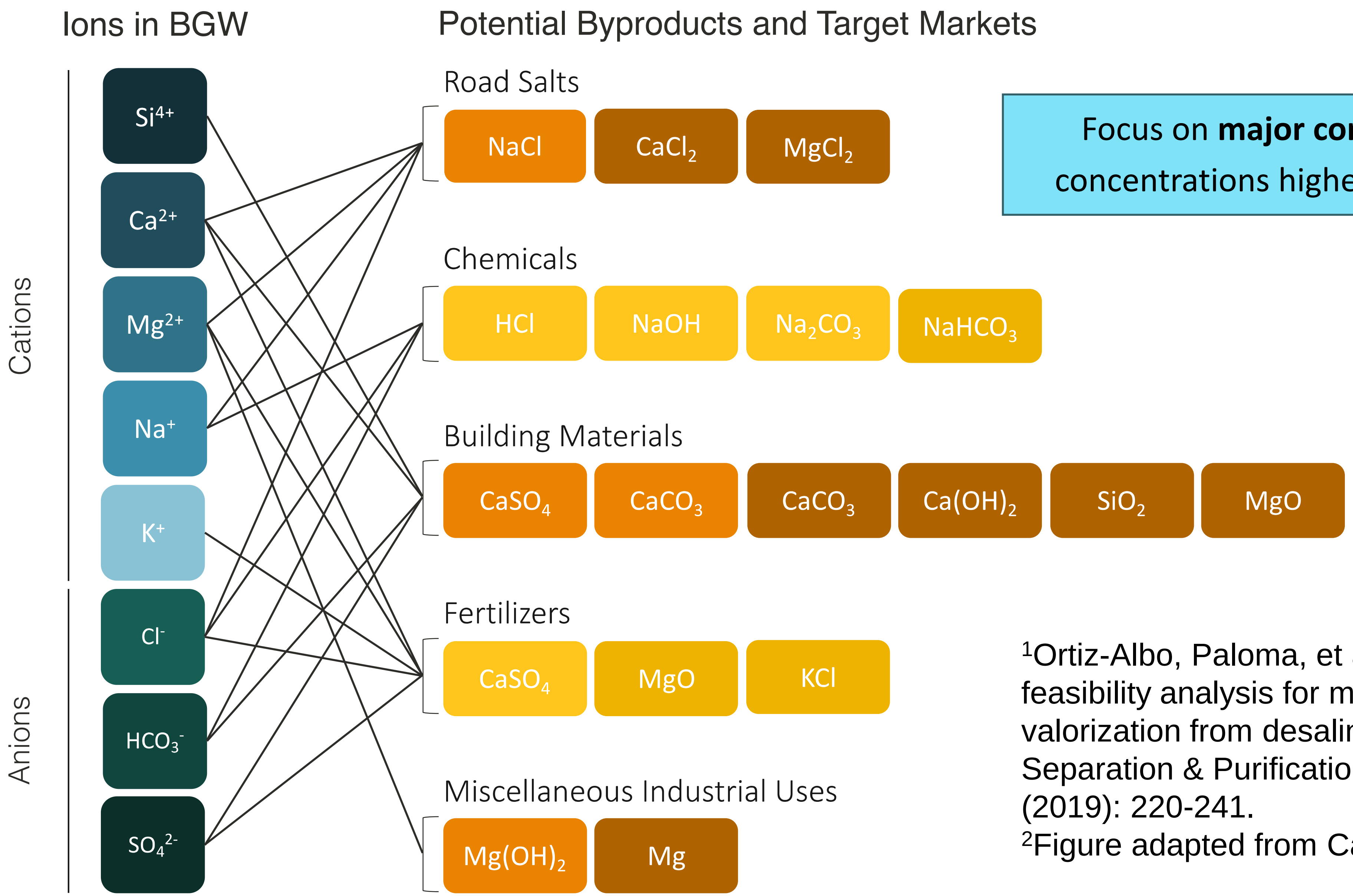
Valorization processes: Chemical precipitation, thermal precipitation, selective separation (ion exchange, nanofiltration, and selective electrodialysis), membrane or diaphragm electrolyzers, bipolar membrane electrodialysis

*Adapted from Alex Dudchenko

Valorization processes

	Reports in the prior art		Unit model status in WaterTAP and supporting packages	
Chemical produced	**Unit operation**	**References**	**Available**	**Modification needed**
Na_2SO_4	Thermal crystallizer	[4–6]	In WaterTAP	Needs chemistry and enthalpy surrogate models
NaCl	Thermal crystallizer	all	In WaterTAP	Needs chemistry and enthalpy surrogate models
NaOH	Membrane electrolyzer		In WaterTAP	None
	Direct electrolyzer	[1,6–9]	In WaterTAP	Can use standard electrolyzer model with assumptions
	Bipolar membrane electrodialysis		Under development in WaterTAP	
$Ca(OH)_2$	Chemical precipitator	[10]	In WaterTAP	Needs chemistry and enthalpy surrogate models
$CaSO_4$	Nanofiltration	[2]	In WaterTAP	None
	Ion exchange		In WaterTAP	Only for single species/needs an extension for multi-species
	Thermal crystallizer	[11]	In WaterTAP	Needs chemistry and enthalpy surrogate models
$CaCO_3$	Chemical precipitator	[3]	In WaterTAP	Needs chemistry surrogate
$Mg(OH)_2$	Chemical precipitator	[10,12]	In WaterTAP	Needs chemistry surrogate
MgCl	Thermal crystallizer	[4]	In WaterTAP	Needs chemistry and enthalpy surrogate
$MgSO_4$(7H2O)	Thermal crystallizer	[3]	In WaterTAP	Needs chemistry and enthalpy surrogate
KCl	Chemical precipitation	[4]	In WaterTAP	Needs chemistry and enthalpy surrogate
HCl	Bipolar membrane electrodialysis	[1,7–9]	Under development in WaterTAP	N/A
	Direct electrolyzer		In WaterTAP	Can use standard electrolyzer model with assumptions

Products for Major Components



Focus on **major components** with concentrations higher than 1.0 mg/L[1]

[1]Ortiz-Albo, Paloma, et al. "Techno-economic feasibility analysis for minor elements valorization from desalination concentrates." Separation & Purification Reviews 48.3 (2019): 220-241.

[2]Figure adapted from Caroline Adkins

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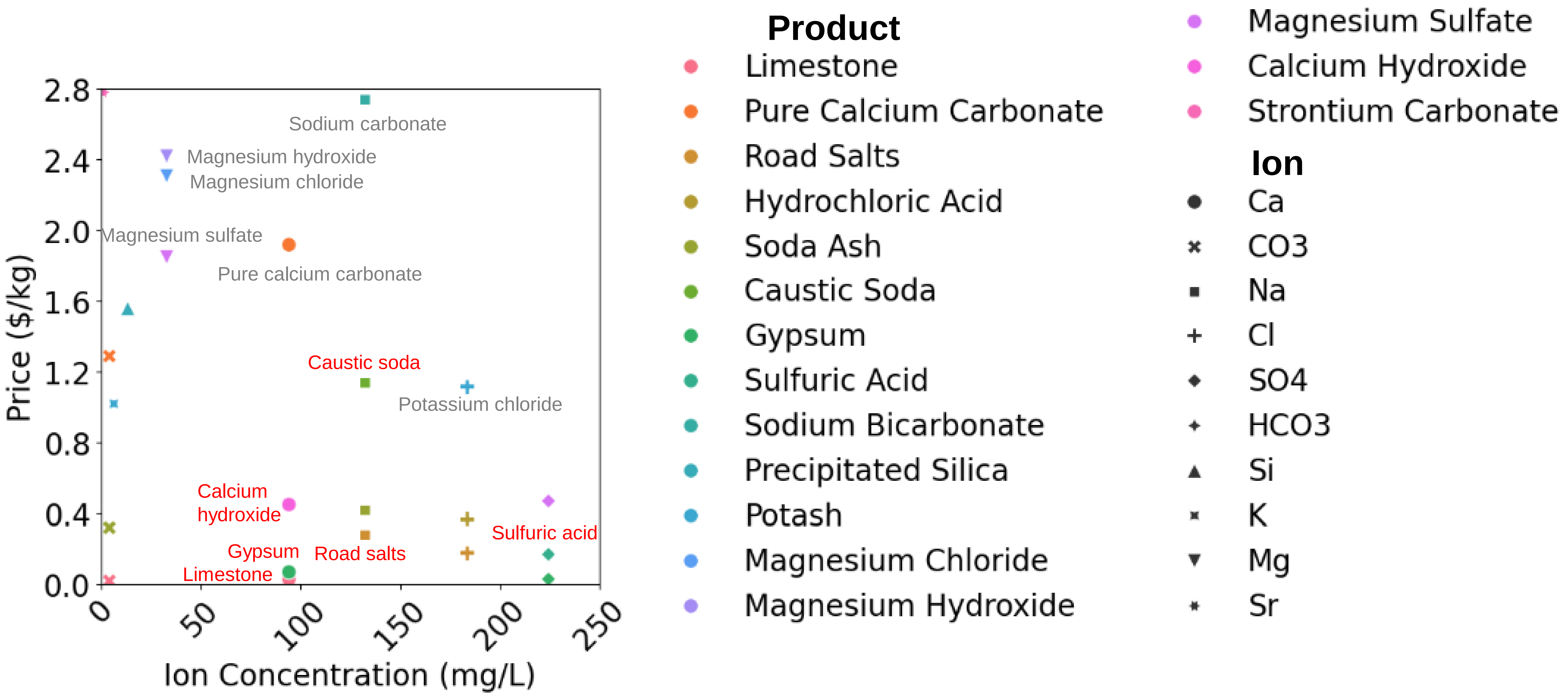
Tension between high demand markets and high value markets

Products for bulk constituents are generally under $3/kg



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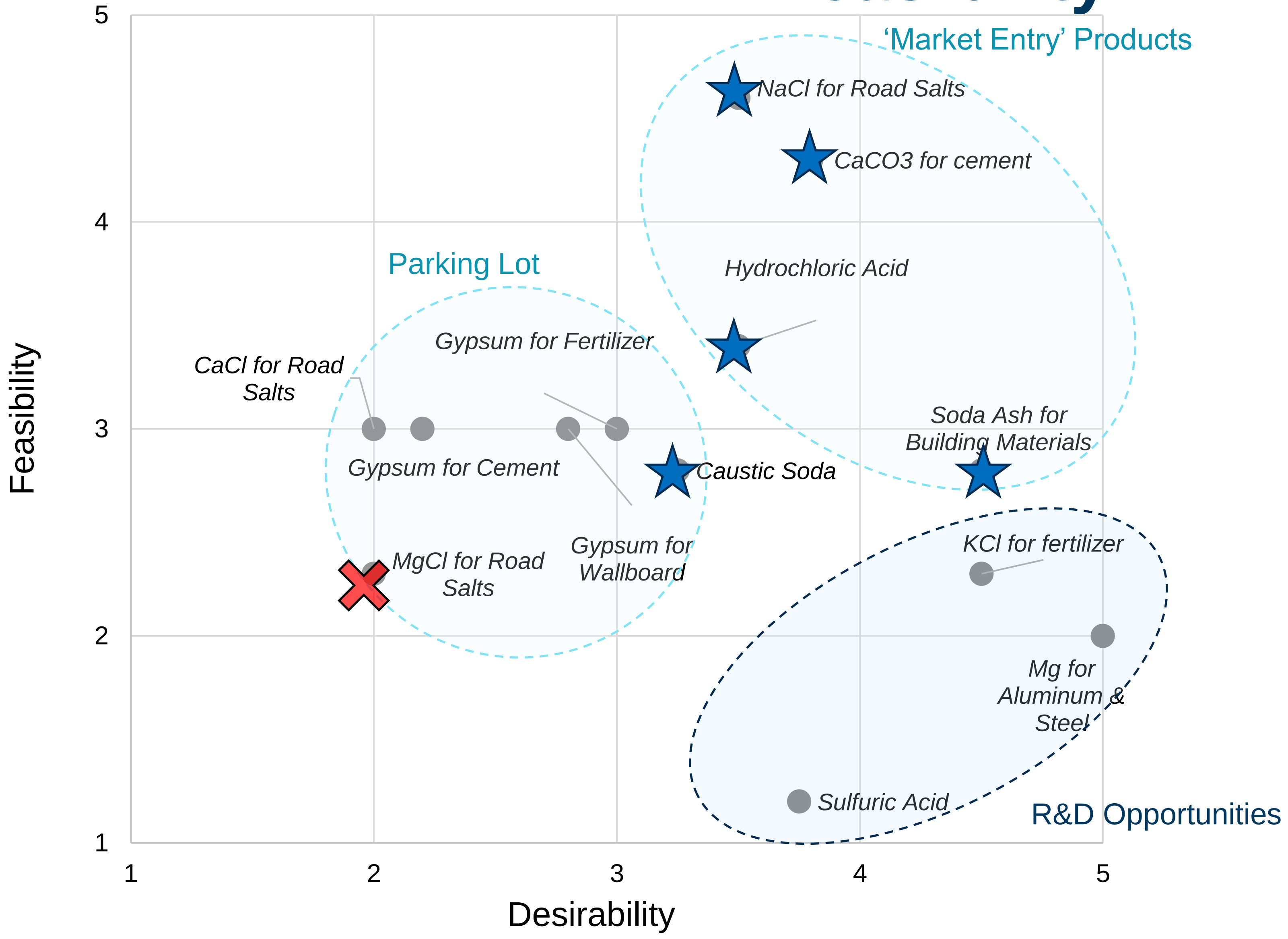
Selection of products based on desirability and feasibility



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*Adapted from Haleigh Heil

Understanding of Technical Specifications

- Gathered list of end markets/constituents, standards for end use constituents.

ASTM Standards Portland Cement (C150/C150M – 22)

TABLE 1 Standard Composition Requirements

Cement Type[A]	Applicable Test Method	I and IA	II and IIA	II(MH) and II(MH)A	III and IIIA	IV	V
Aluminum oxide (Al_2O_3), max, %	C114	. . .	6.0	6.0	. . .	. . .	. . .
Ferric oxide (Fe_2O_3), max, %	C114	. . .	6.0[B]	6.0[B,C]	. . .	6.5	. . .
Magnesium oxide (MgO), max, %	C114	6.0	6.0	6.0	6.0	6.0	6.0
Sulfur trioxide (SO_3),[D] max, %	C114						
When (C_3A)[E] is 8 % or less		3.0	3.0	3.0	3.5	2.3	2.3
When (C_3A)[E] is more than 8 %		3.5	F	F	4.5	F	F
Loss on ignition, max, %	C114						
When limestone is not an ingredient		3.0	3.0	3.0	3.0	2.5	3.0
When limestone is an ingredient		3.5	3.5	3.5	3.5	3.5	3.5
Insoluble residue, max, %	C114	1.5	1.5	1.5	1.5	1.5	1.5
Equivalent alkalies (Na_2O + 0.658 K_2O), %	C114	G	G	G	G	G	G
Tricalcium silicate (C_3S),[E] max, %	See Annex A1	. . .	. . .	. . .	. . .	35[C]	. . .
Dicalcium silicate (C_2S),[E] min, %	See Annex A1	. . .	. . .	. . .	. . .	40[C]	. . .
Tricalcium aluminate (C_3A),[E] max, %	See Annex A1	. . .	8	8	15	7[C]	5[B]
Sum of C_3S + 4.75(C_3A),[H] max, %	See Annex A1	. . .	. . .	100[C,I]	. . .	. . .	. . .
Tetracalcium aluminoferrite plus twice the tricalcium aluminate (C_4AF + 2(C_3A)), or solid solution (C_4AF + C_2F), as applicable, max, %	See Annex A1	. . .	. . .	. . .	. . .	. . .	25[B]

Type I and II most commonly used cement types in the US.
Type I accounts for 92% of cement used in the US

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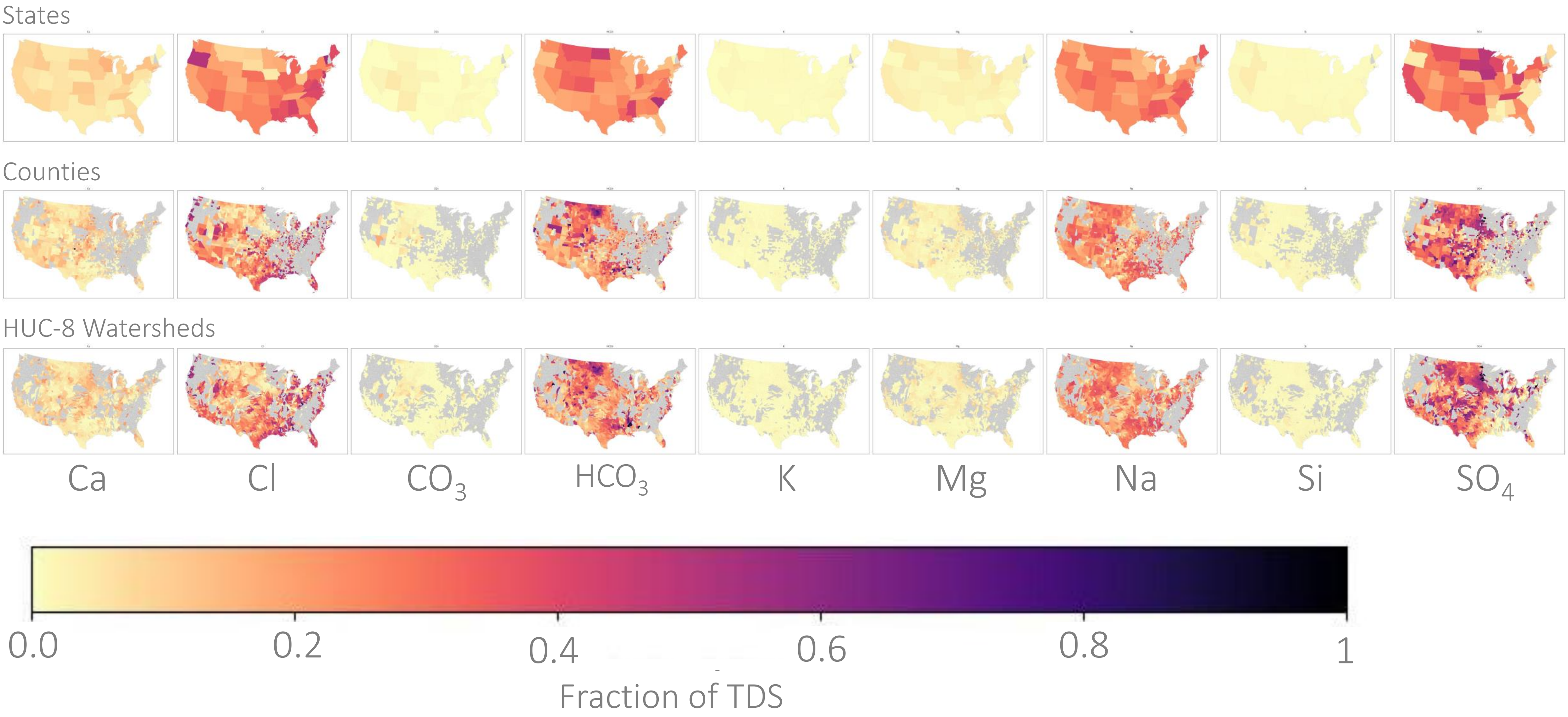
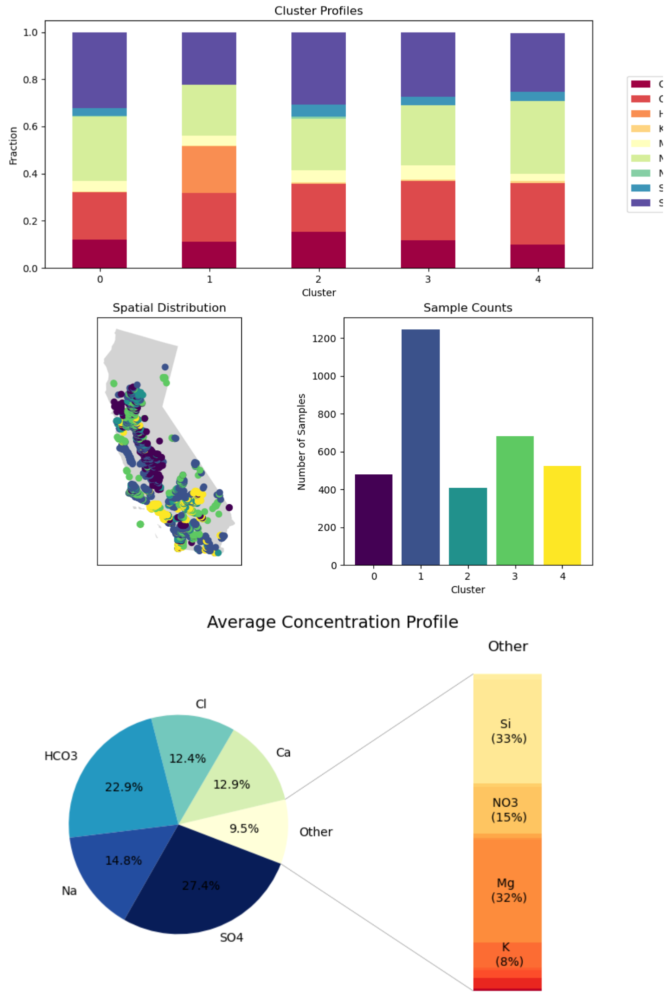
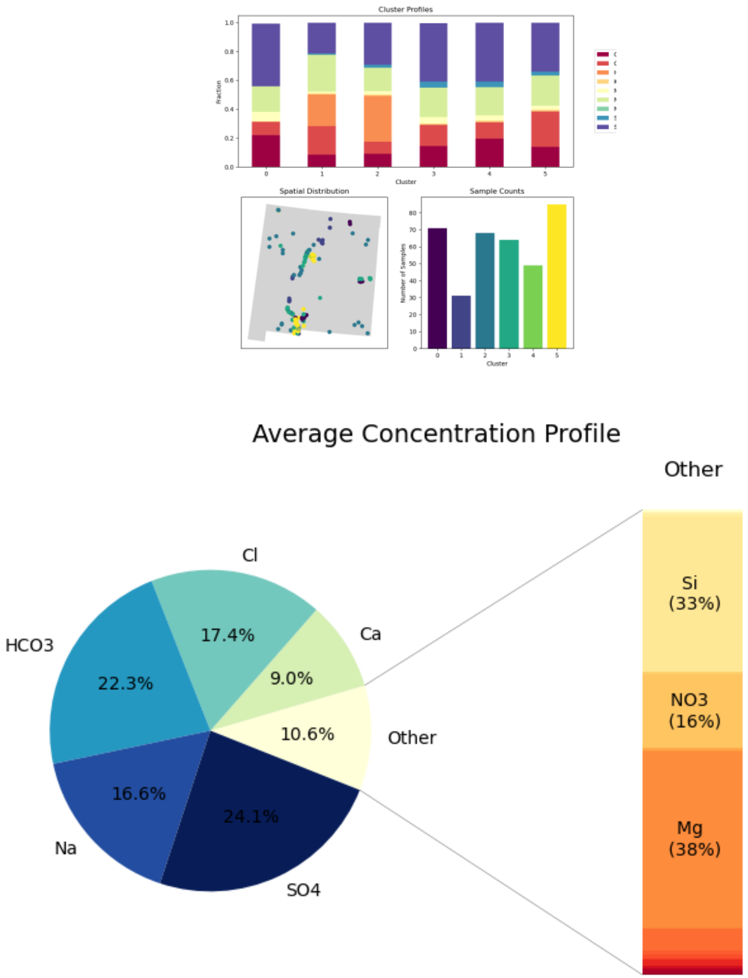
Geospatial Variation in Ion Composition

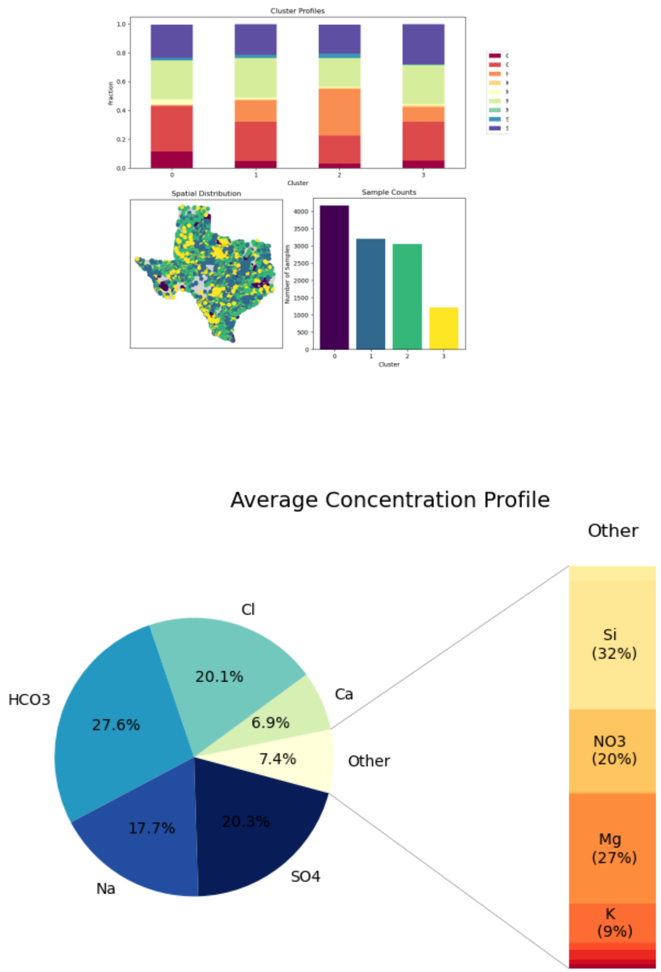


*Adapted from Caroline Adkins

Ion Composition profiles by state







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Geographic Market Trends

Product	California			Texas			Kansas			Arizona		
	Demand	Forecast range	Comments	Demand	Forecast range	Comments	Demand	Forecast range	Comments	Demand	Forecast range	Comments
Cement			*Current population: 39M Population growth: ~40M through 2060, slow population growth*			*Current population: 29.5M Population growth: By 2060 - 50-55M*			*Current Population: 2.9M Population growth: 3.3M by 2060*			*Current Population: 7.2M Population growth: 10.6M by 2060*
Gypsum / Gypsum Board			*High population, low growth*			*High/growing population, growing construction*			*Low population, low projected population growth*			*Relatively low population, relatively low projected population growth*
Plasters / Mortars												
Fertilizer / potash			*Spent $2.17B in 2020- Highest spender for fertilizer*			*spent $1.1 B in 2020, one of highest spenders*			*$1 billion in 2020 on fertilizer*			*~$220M in 2020 on fertilizer*
Sulfuric acid			*490 establishments – high exporter of chemicals*			*453 businesses*			*47 chemical manufacturing establishments in Kansas*			*70 chemical manufacturing establishments in Arizona*
Caustic / caustic soda						*Texas top exporter of chemicals in the US, 30% of all chem exports*						
Road Salts			*21K tons of rock salt*			*Applied 28K tons,*			*83K tons*			*20K tons Lowest road salt use of the 4 states*

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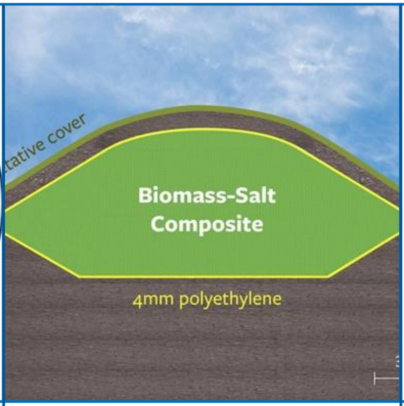
*Adapted from Haleigh Heil

Emerging brine markets

CAPTURE6	PARTANNA		BRINE MINERS		
Carbon capture. Use electrodialysis with bipolar membranes to separate brine into NaOH and HCl, and react NaOH with CO_2 to form Na_2CO_3.	**Direct cement production.** Concrete formula uses brine instead of fresh water to cure various concrete products (simultaneously sequester CO_2 through carbonation).	**Carbon sequestration.** Use salt to preserve biomass and bury in a dry environment within an engineered biolandfill.[1]	**Green hydrogen production**. Electrolysis of brine (powered by renewables)	**Cooling systems.** Use of brine as a refrigerant after adding buffer/ inhibitors (also an opportunity to use brine for softening for conventional cooling)	**Sodium Ion batteries.** Electrolysis to separate battery-grade NaOH.

[1]Yablonovitch, Eli, and Harry W. Deckman. "Scalable, economical, and stable sequestration of agricultural fixed carbon." Proceedings of the National Academy of Sciences 120.16 (2023): e2217695120.

Key Challenges for Valorization

Understand supply and demand dynamics	• Will salts from brine overrun the market OR not make a dent?
Resolve Delivery / Transport Considerations	• How can bulk shipping be made more cost-effective, can shipments be combined from multiple supplier? • What can be produced onsite?
Improvements to regulations and standards	• Resolve policy challenges for cross-state transport. • Standardize national regulatory process for approving the beneficial use of waste products. • Communicate consistent set of specifications for products that are easily understandable by brine generators. • Establish liability for innovation for new products (e.g. structural cement strength for new cement chemistries)
Quality Specifications	• Moisture content is import for product offtake. • Consider radioactivity, and PFAS concentration. • Impurities are often product specific and need to be screened for each brine.

Enabling Opportunities for Valorization

Look for opportunities for disruption across multiple industries.

Develop regional processing centers that are vertically integrated with product manufacturers.

Leverage government momentum on critical minerals and clean energy for more increased discussion on value/ incentives for salts.

Connect brine users with end users

- Landfills as key stakeholders- they are a natural hub with incentive to be more sustainable.
- Opportunities to collaborate across sectors (industrial effluents from mining sector, O&G)

Feedback opportunities

- **Provide us with feedback on our framework for byproduct market opportunities.** We welcome data, experiences, or recommendations on how to make this framework most usable.
- **Contribute to the brackish water brine valorization whitepaper.** A whitepaper summarizing this workshop will be released with key insights about requirements, challenges, and opportunities for the treatment and valorization of brackish groundwater. ***We would welcome review of this whitepaper if any individuals are interested in engaging further.***
- **Participate in the stakeholder board.** The stakeholder advisory board will meet at least quarterly to maintain connections between industrial and academic partners by providing updates and soliciting input for specific aspects of the project .
- **Join stakeholder workshop 2**. Opportunity to provide feedback on the framework and receive a demonstration of how WaterTAP can be used to support industries interested in the treatment and valorization of brackish groundwater. Models will be distributed to participants. (May 2025)

Questions?

Contact: Alison.Fritz@netl.doe.gov

Markets for major elements

Compound	Product	Industrial Uses
$CaCO_3$	Limestone	Cement production
$CaCO_3$	Pure Calcium Carbonate	Pulp and paper, food additive
NaCl	Sodium Chloride	Road salts
CaCl	Calcium Chloride	Road salts
HCl	Hydrochloric Acid	Internal reuse, water treatment
Na_2CO_3	Soda Ash	Glass, detergents
NaOH	Caustic Soda	Pulp and paper, food processing, detergents, water treatment
$CaSO_4 \cdot 2H_2O$	Gypsum	Wallboards, plaster, soil additive
H_2SO_4	Sulfuric Acid	Chemical production, cleaning agent
$NaHCO_3$	Sodium Bicarbonate	Baking soda
SiO_2	Silica	Thickener, glass and silicon
KCl	Potash	Fertilizer
MgCl	Magnesium Chloride	Precursor to magnesium metal, road salts (but issues with corrosion)
$Mg(OH)_2$	Magnesium Hydroxide	Antacids, cement preparation
$MgSO_4$	Magnesium Sulfate	Medical (epsom salt), cement preparation, desiccant, fertilizer
$Ca(OH)_2$	Calcium Hydroxide	Lime mortar, water treatment, pesticide
SrCO3	Strontium Carbonate	Fireworks, electronics, ceramics