

# Implementation of Ion Exchange Processes on Industrial Waste Streams for CO<sub>2</sub> Mineralization

Dante Simonetti<sup>1,3</sup>, Dale Prentice<sup>2</sup>, Erika Callagon La Plante<sup>2,3</sup>, Gaurav Sant<sup>2,3</sup>, Bu Wang<sup>3</sup>, Abdulaziz Alturki<sup>1</sup>, Steven Bustillos<sup>1</sup>

<sup>1</sup>Department of Chemical and Biomolecular Engineering, UCLA

<sup>2</sup>Department of Civil and Environmental Engineering, UCLA

<sup>3</sup>Institute for Carbon Management, UCLA

<sup>4</sup>Department of Civil and Environmental Engineering,  
University of Wisconsin-Madison

2019 AIChE Annual Meeting  
November 11, 2019

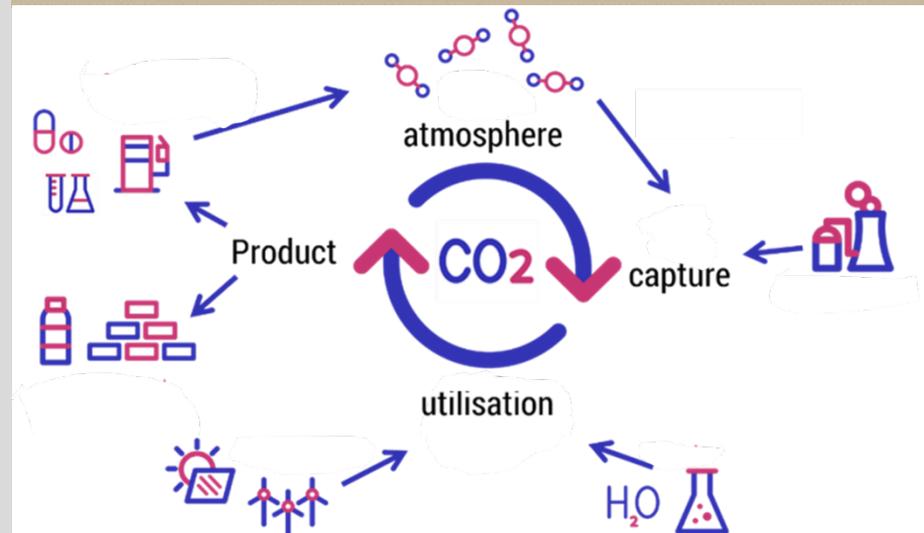
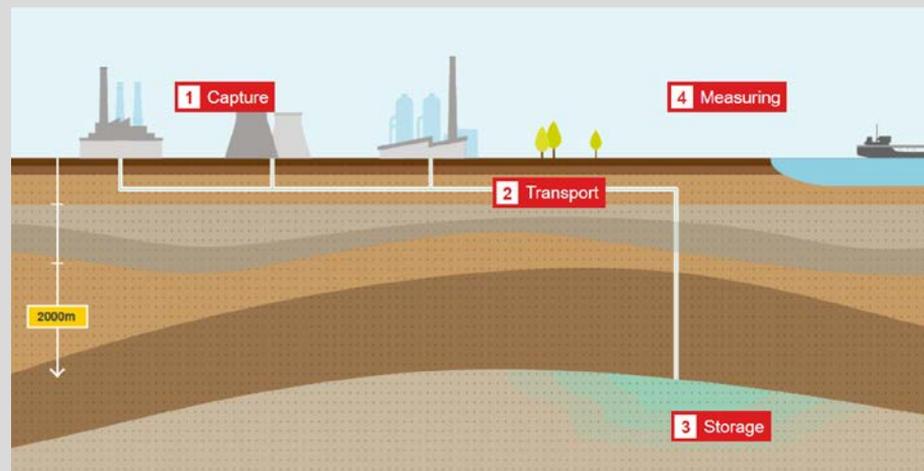
Novel Approaches to CO<sub>2</sub>  
Utilization

# Current models of carbon management

- CCS
  - 22,000 Gt potential capacity (North America)
  - Limited to  $\sim 1,000$  Mt  $\text{CO}_2$ /year
  - Risk of  $\text{CO}_2$  migration and leakage

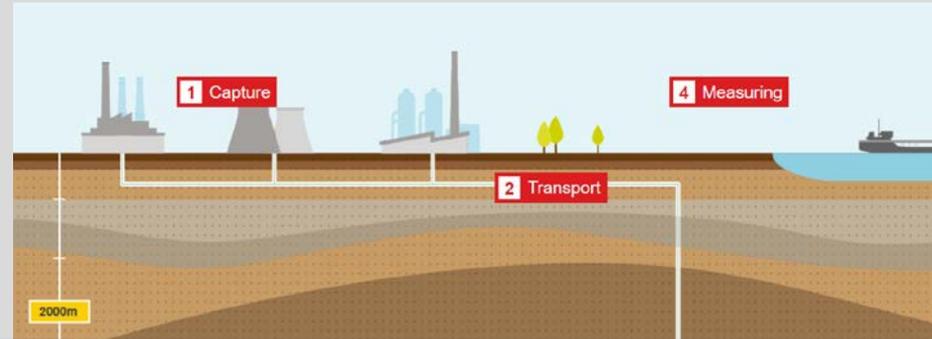
Shell, CARBON CAPTURE AND STORAGE, <https://reports.shell.com/sustainability-report/2016/energy-transition/our-work-to-address-climate-change/carbon-capture-and-storage.html>

- “Recycled”  $\text{CO}_2$ 
  - Potentially profitable for businesses
  - Need for co-feed molecules
  - Displaces only  $\sim 30\%$  need
    - Gasoline in the US would only account for 7% of need



# Thermodynamic, Kinetic, and Political Barriers

- CCS
  - 22,000 Gt potential capacity (North America)
  - Limited to ~1,000 Mt CO<sub>2</sub>/year
  - Risk of CO<sub>2</sub> migration and leakage



Shell, CARBON CAPTURE AND STORAGE, <https://reports.shell.com/transition/our-work-to-address-climate-change/carbon-capture-and-storage>

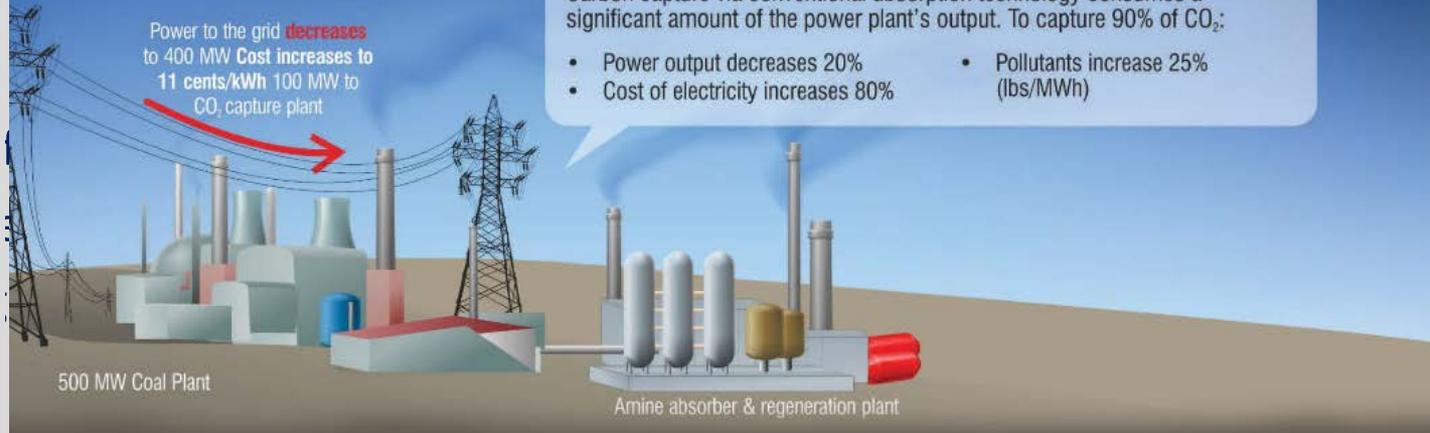
## Energy for separation/concentration

### Conventional CO<sub>2</sub> Capture

Carbon capture via conventional absorption technology consumes a significant amount of the power plant's output. To capture 90% of CO<sub>2</sub>:

- Power output decreases 20%
- Pollutants increase 25% (lbs/MWh)
- Cost of electricity increases 80%

Power to the grid **decreases** to 400 MW  
 Cost increases to **11 cents/kWh** 100 MW to CO<sub>2</sub> capture plant



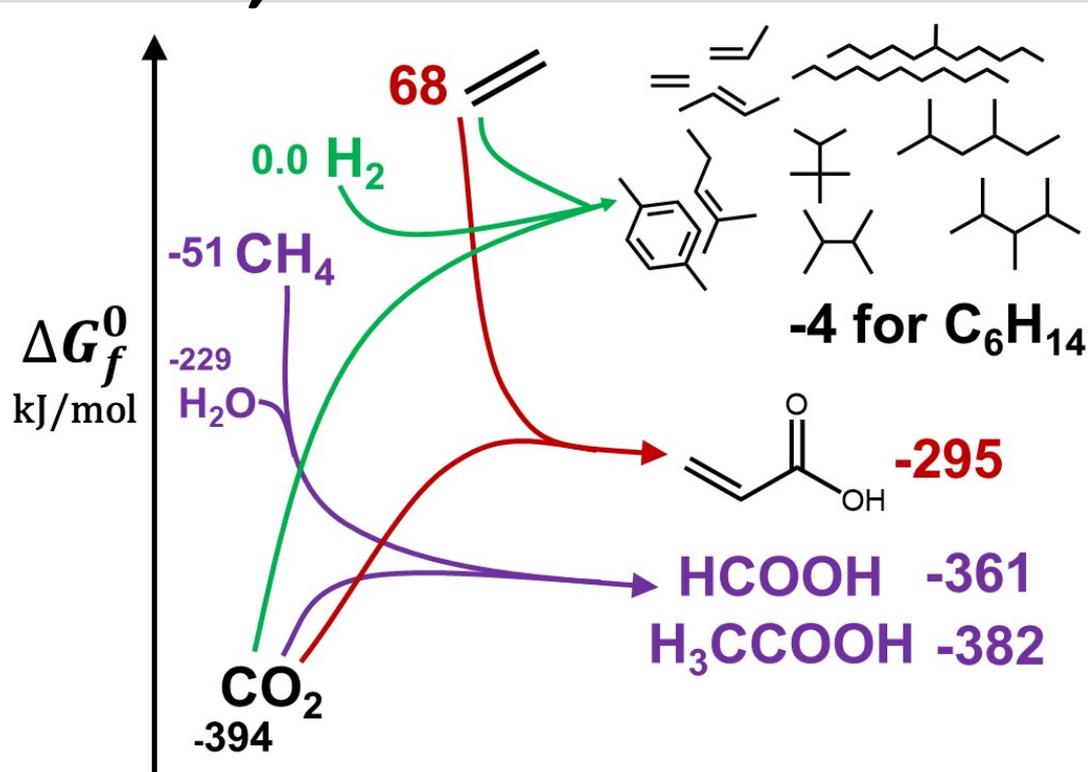
**0.11 kWh per kg CO<sub>2</sub> for optimum Amine unit**

# Thermodynamic, Kinetic, and Political Barriers

>390 kJ/mol CO<sub>2</sub> to overcome rxn energy

>415 kJ/mol average C-H BDE of methane

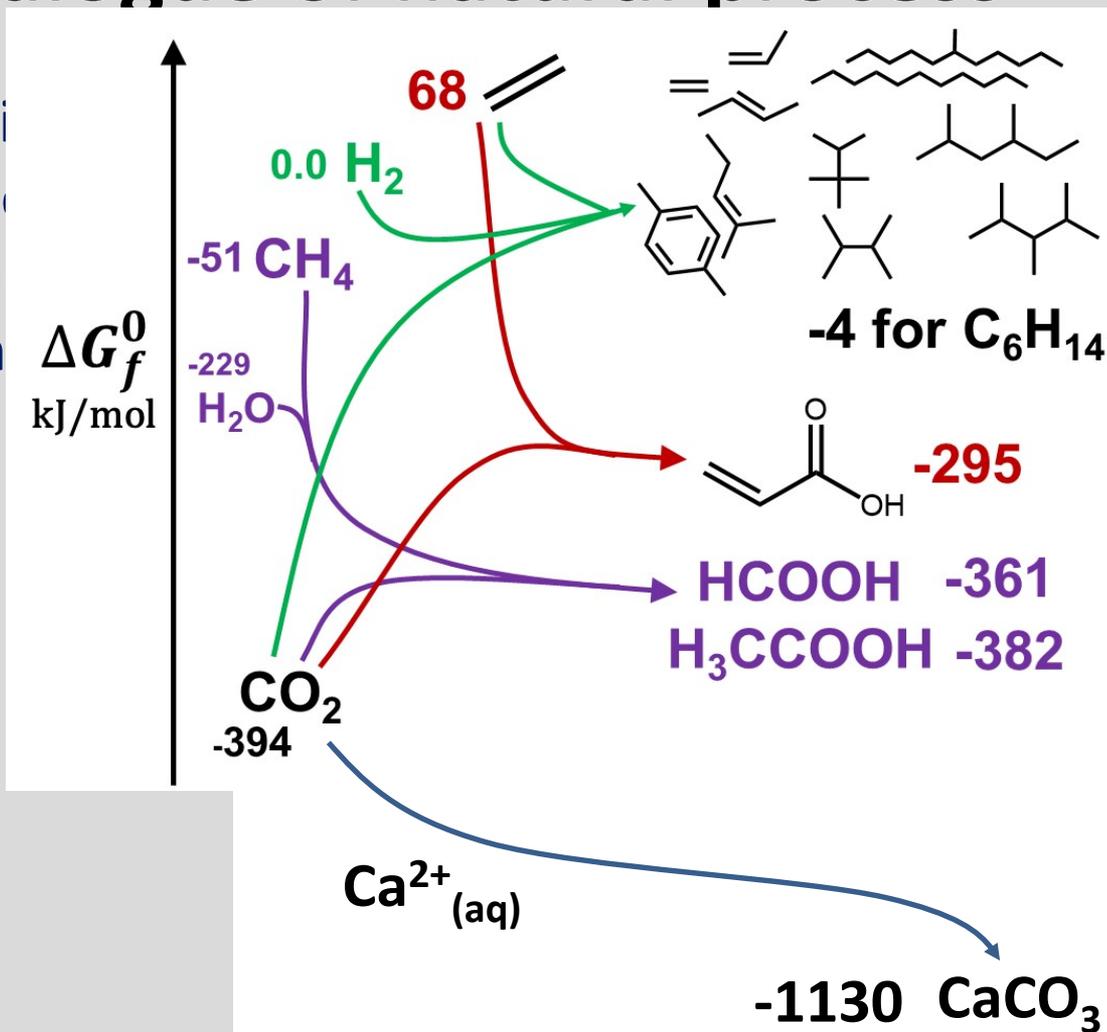
- “Recycled” CO<sub>2</sub>
  - Potentially profitable for b



**Can we develop additional processes with less severe science and engineering hurdles?**

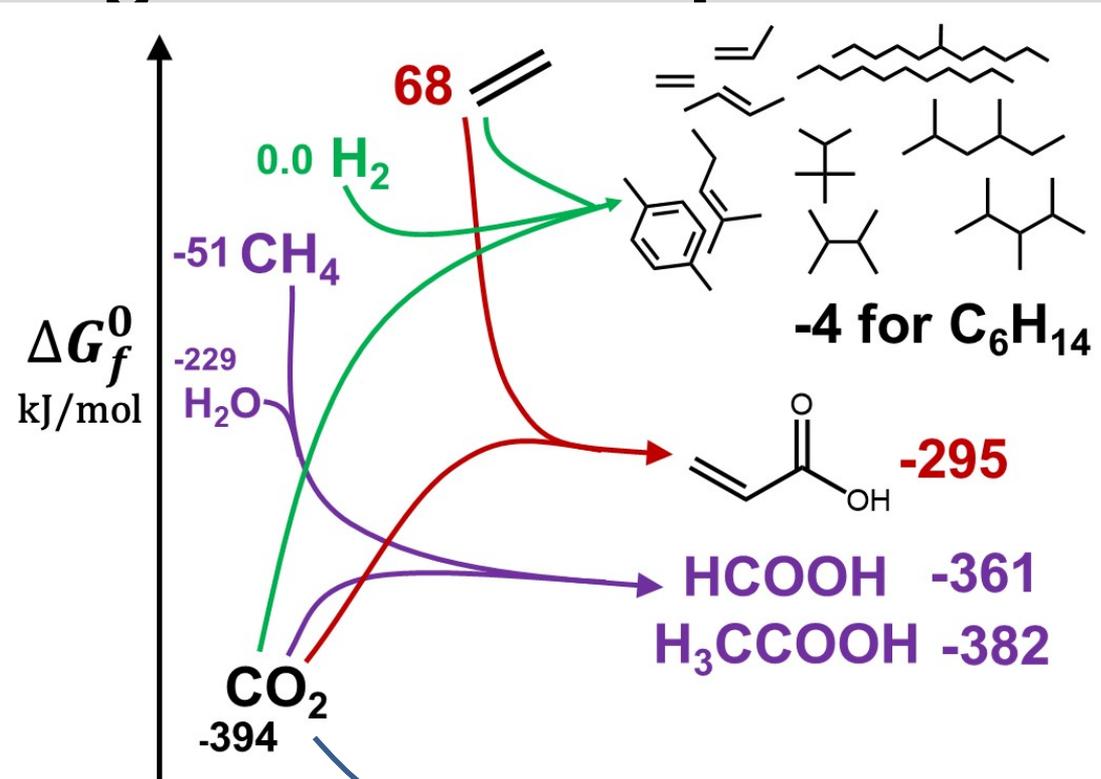
# A synthetic analogue of natural process

- CO<sub>2</sub> fixed within stable microprecipitated carbonates, mimicking the natural process of biogenic abiogenic limestone formation
- Thermodynamically favorable

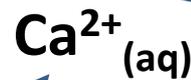


# A synthetic analogue of natural process

- CO<sub>2</sub> fixed within stable microprecipitated carbonates, mimicking the natural process of biogenic and abiogenic limestone formation
- Thermodynamically favorable
- Utilizes abundant and/or waste sources of Ca

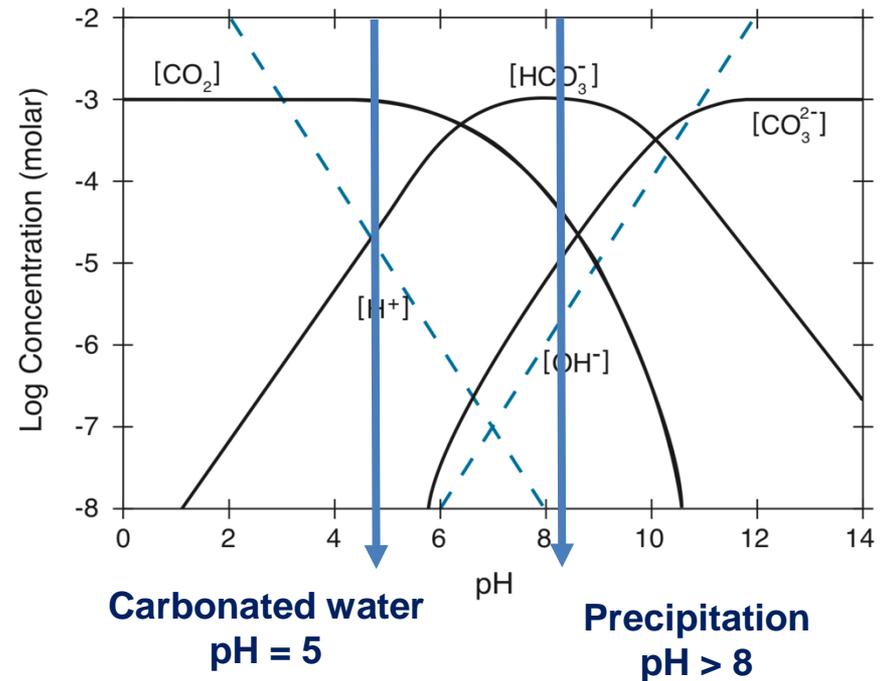


**Seawater, Desalination Brines,  
Industrial Wastewater,  
Produced Water**



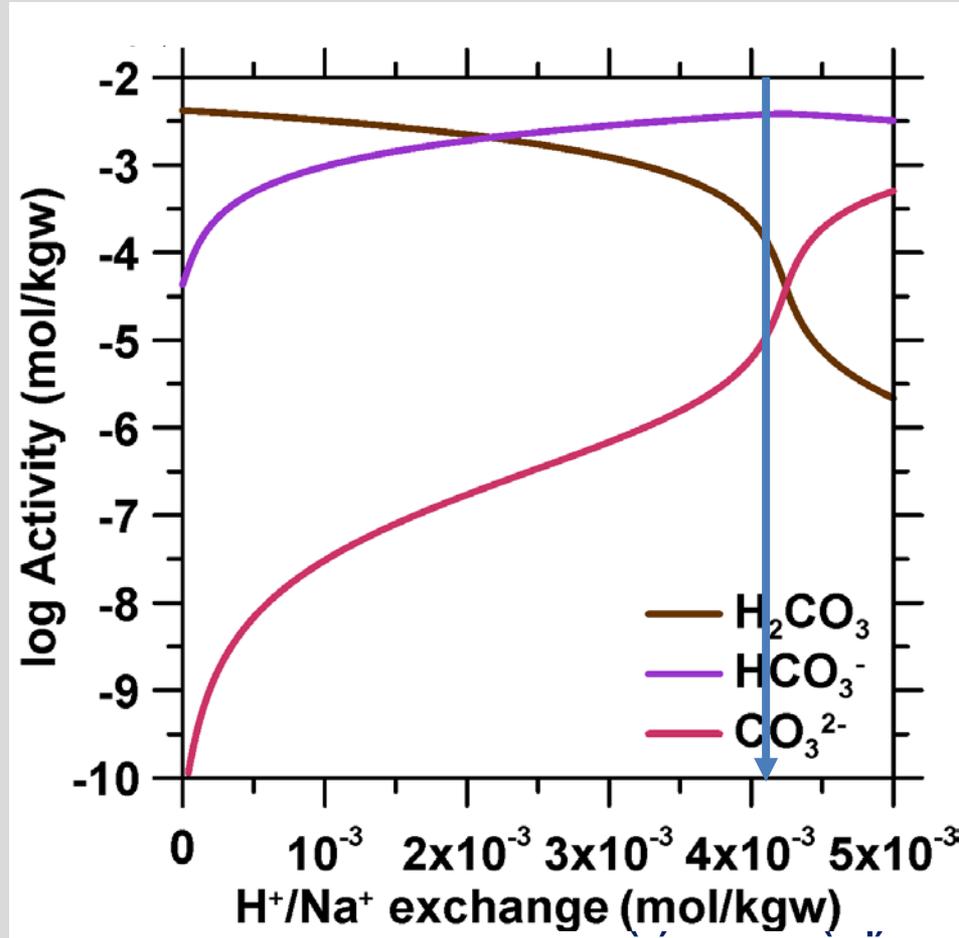
## Different thermodynamic barrier

- Alkalinity must be supplied to continuously precipitate  $\text{CaCO}_3$
- Inducing alkalinity with consumable bases (e.g.,  $\text{NaOH}$ ) is expensive and energy intensive



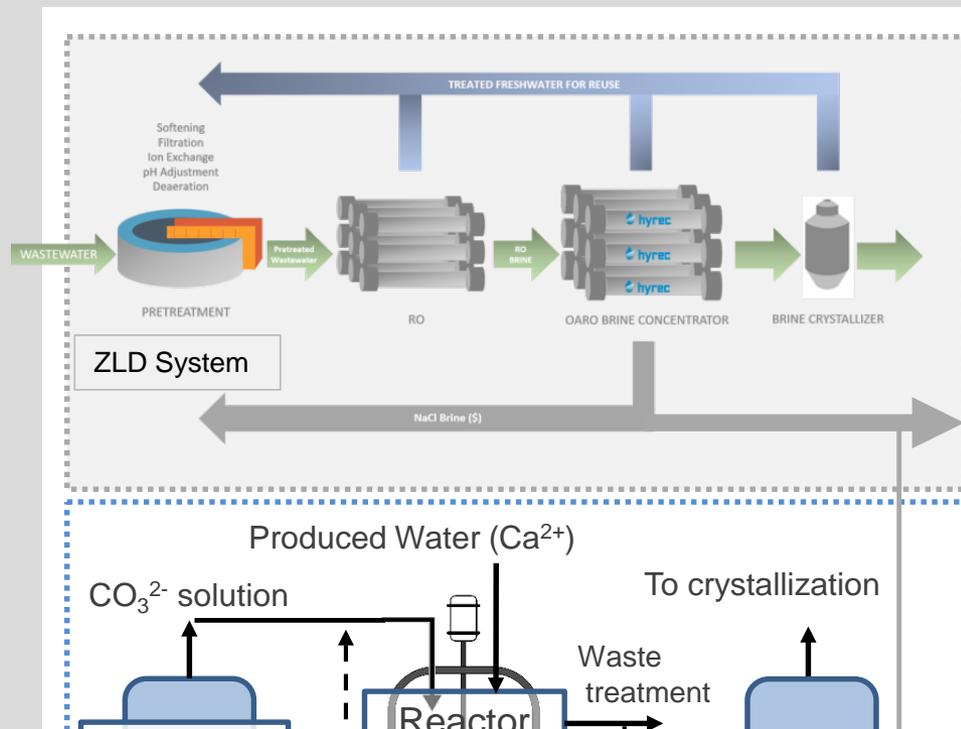
## Different thermodynamic barrier

- Alkalinity must be supplied to continuously precipitate  $\text{CaCO}_3$
- Inducing alkalinity with consumable bases (e.g.,  $\text{NaOH}$ ) is expensive and energy intensive
- Ion-exchange materials may be an attractive, reusable alternative



## Proposed process integrating ion-exchange

- Ion exchange reactor may be constructed in the form of packed columns (grain size considerations)
- Acidity is induced by  $\text{CO}_2$  dissolution, ion-exchange produces a  $\text{CO}_3^{2-}$ -rich solution
- Reaction of  $\text{CO}_3^{2-}$ -rich solution with  $\text{Ca}^{2+}$ -rich produced water

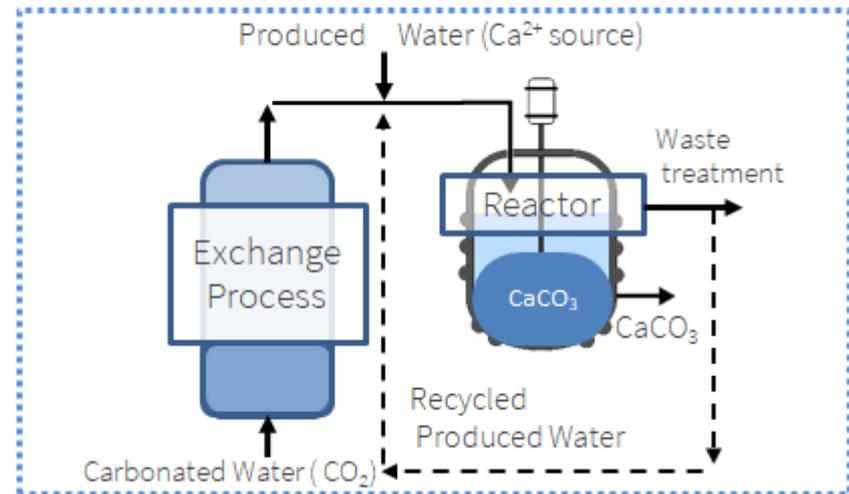
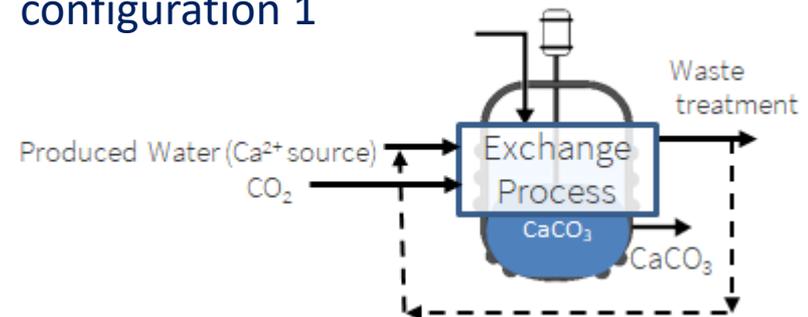


**What ion exchange materials deliver desirable exchange capacity, dynamics, and stability ?**

# Which process configuration?

- Two process configurations proposed:
  - 1)  $\text{CO}_2$  mixed with produced water in contact with ion exchange material for an increase in alkalinity
  - 2)  $\text{CO}_2$  mixed with fresh water in contact with ion exchange material for an increase in alkalinity

configuration 1

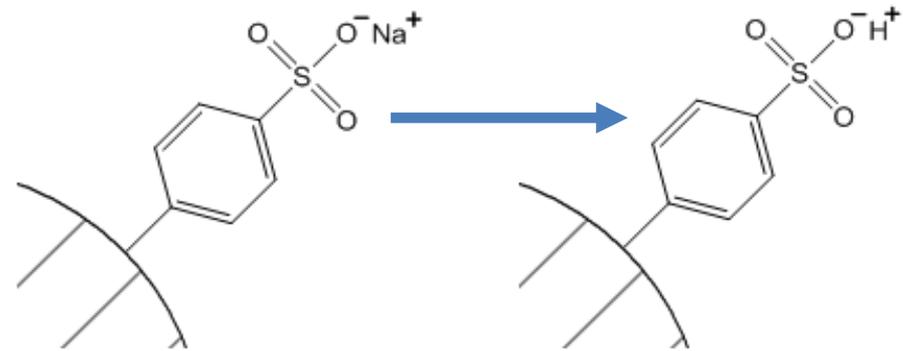


configuration 2

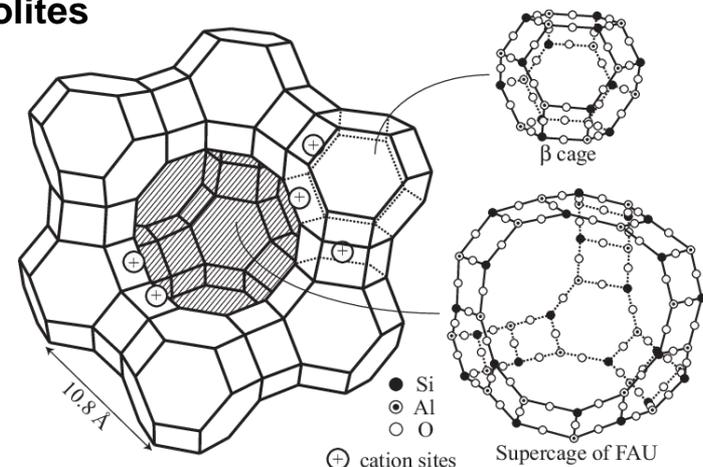
## Which ion-exchanger?

- Natural materials such as phyllosilicates (layered silicates/clays) and zeolites, and synthetic resins can be used as ion-exchangers
- Compare based on capacity for and kinetics of ion exchange and for stability/extent of regeneration

Ion exchange resins

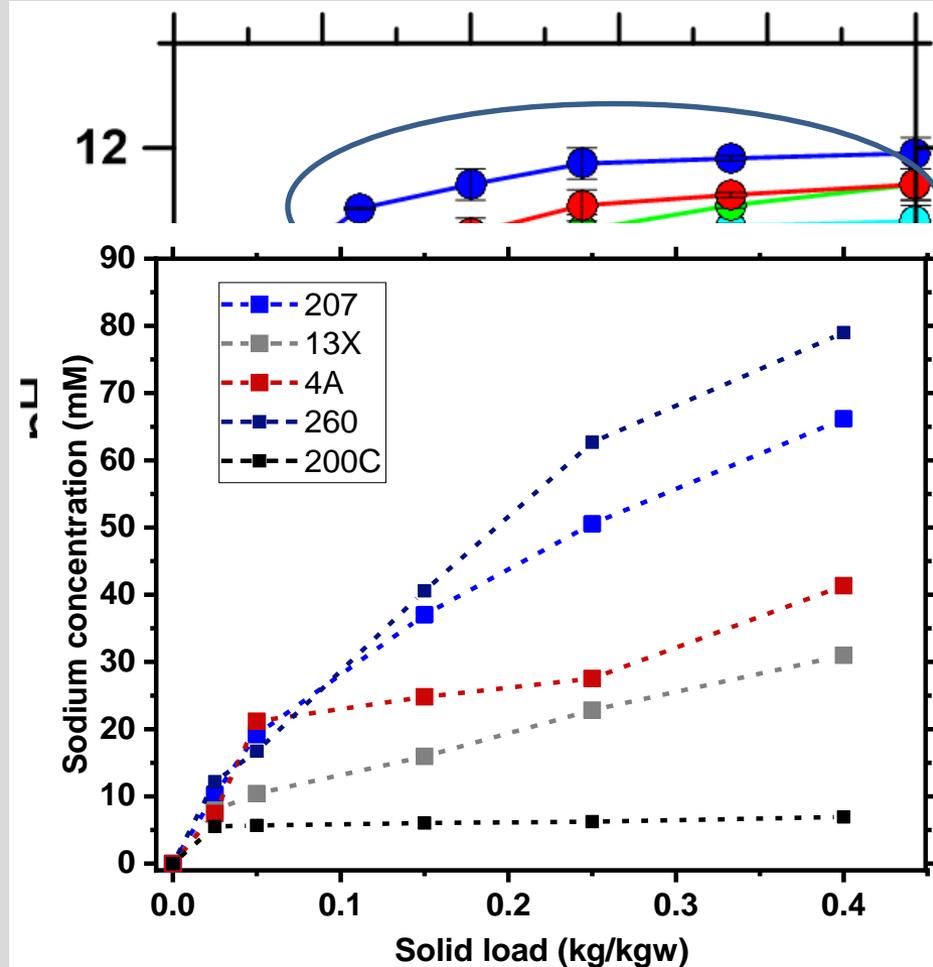


Zeolites



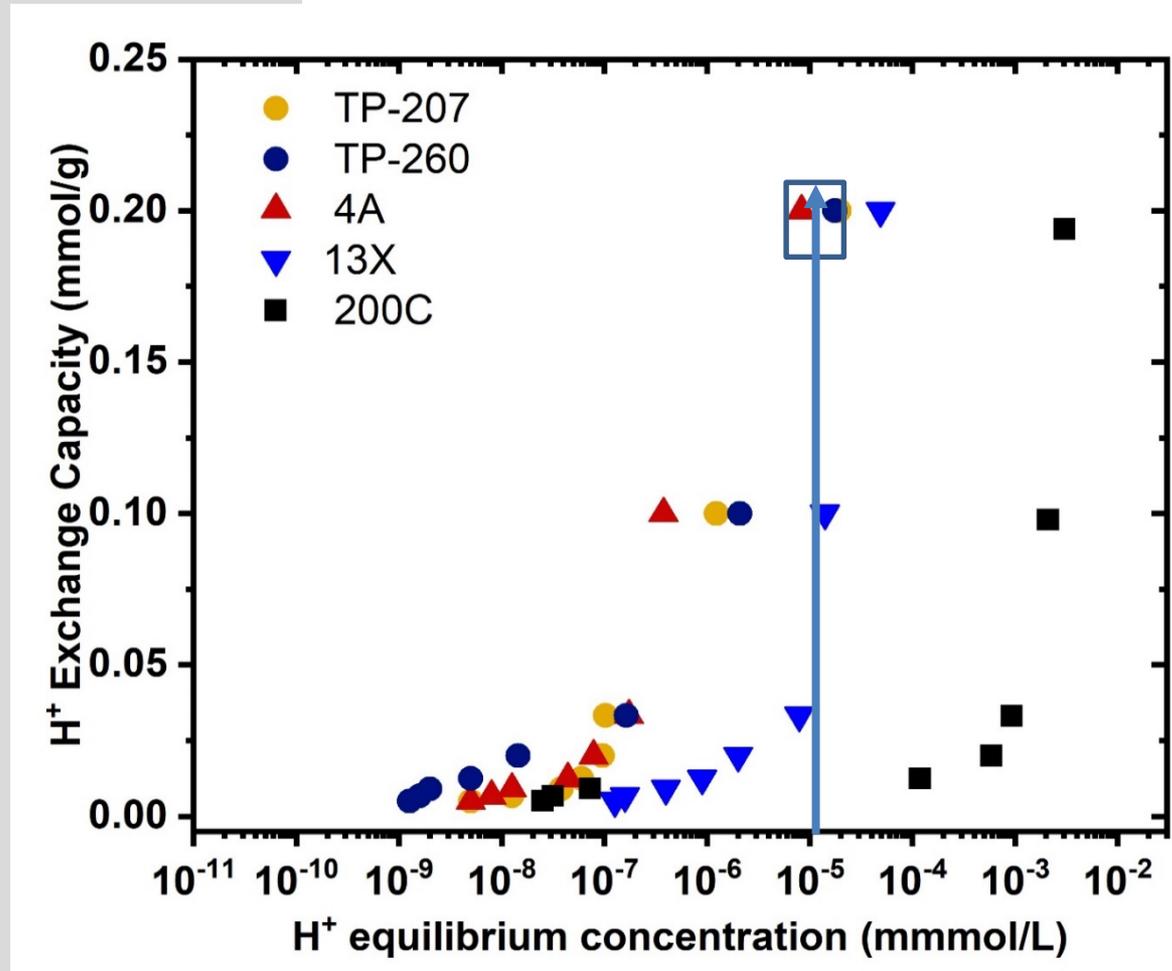
# Na<sup>+</sup>/H<sup>+</sup> exchange using resins, clays, zeolites

- Batch experiments: HCl or CO<sub>2</sub> solutions at initial pH = 4, then add ion exchanger and observe pH increase
- Two zeolites and two resins meet the “minimum” requirement of pH > 8
- Na<sup>+</sup> release appears to be unbalanced but follows the same trend as pH increase

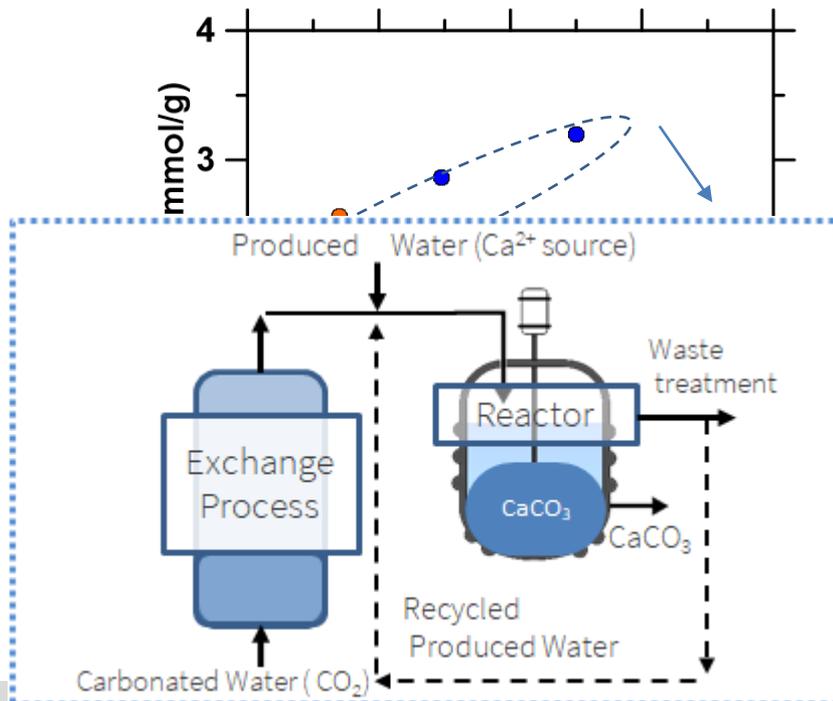


# H/Na exchange isotherms quantitatively identify resins and 4A

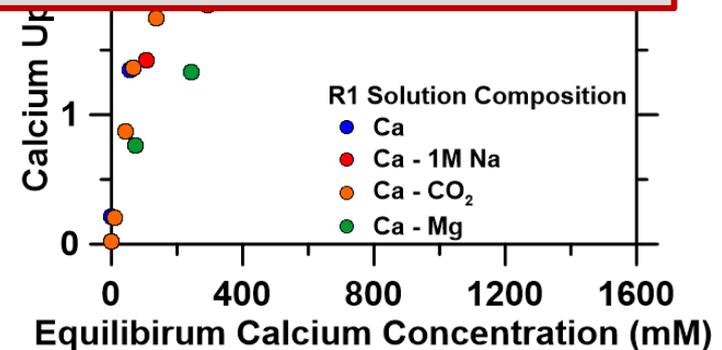
- At the equilibrium conditions of our feed solutions (i.e., pH 5), TP-207, TP-260, and 4A give highest capacities
- Potential for smallest bed sizes (or higher throughputs) without mass transfer restrictions



## Ca uptake is selective on ion exchange resins...

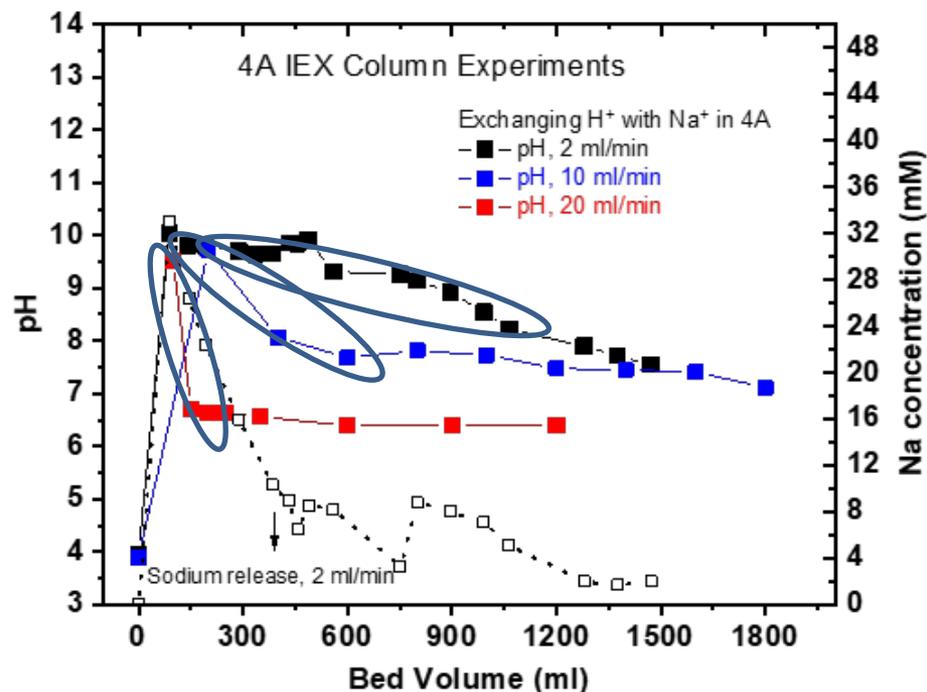
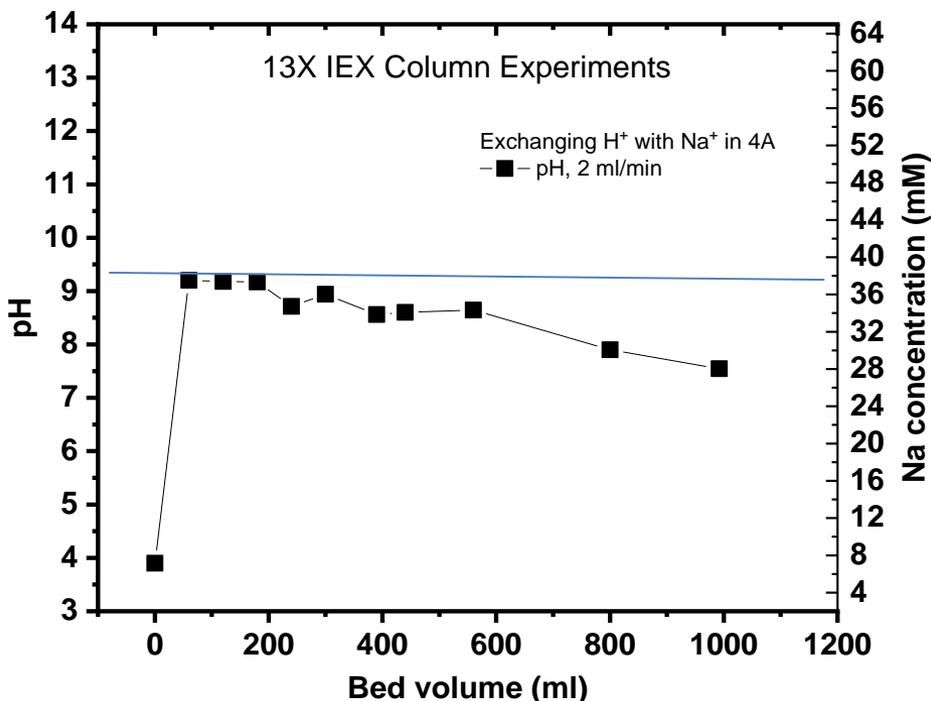


**Separate exchange and precipitation vessels will be required**



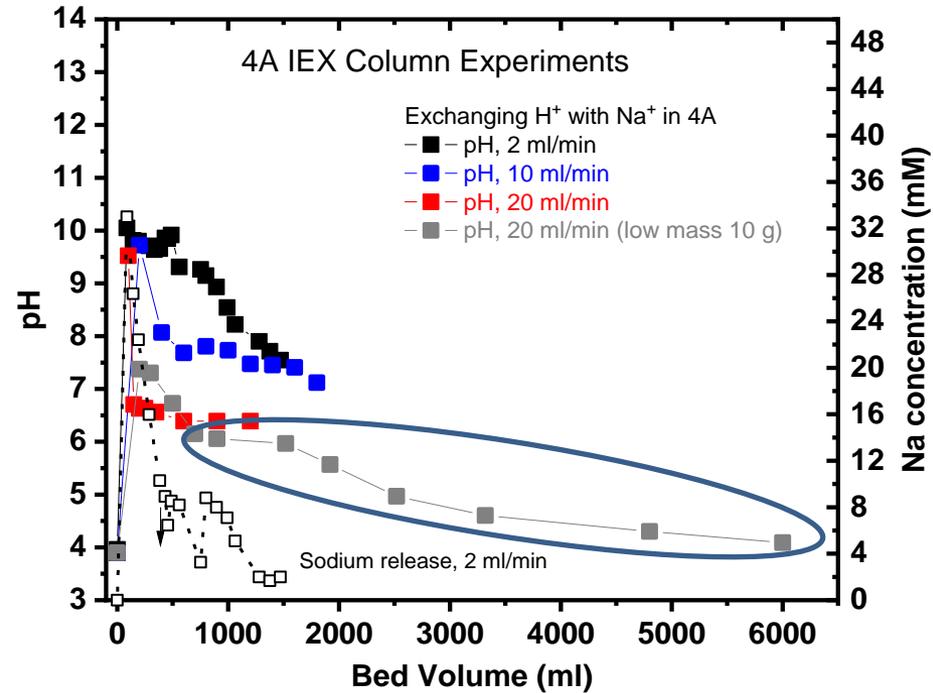
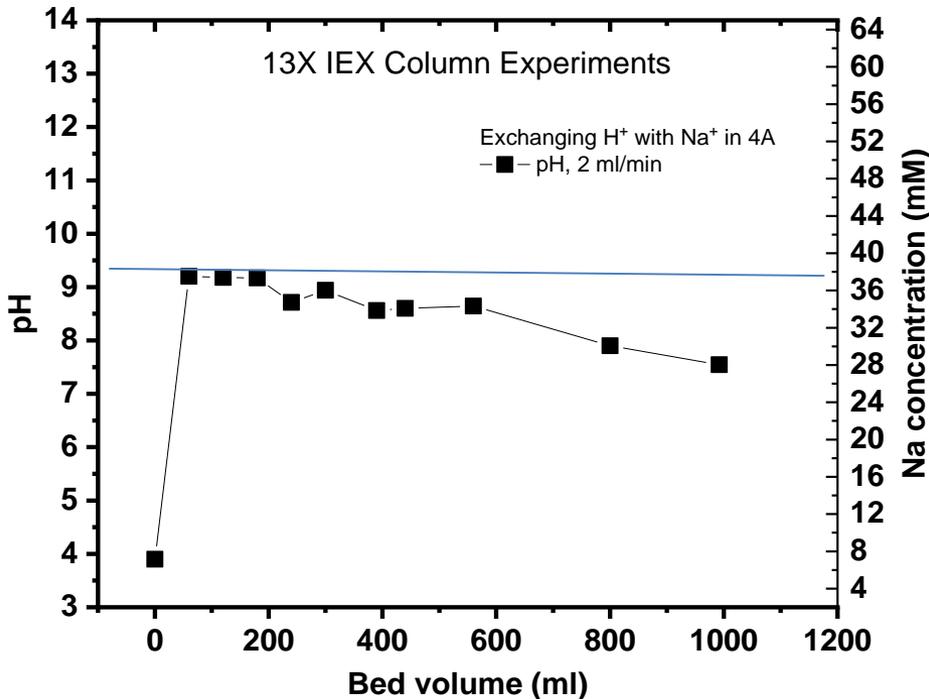
- Ca uptake independent of pH (within relevant range) or source of protons (HCl or CO<sub>2</sub>-saturated solution)
- Only other divalent cations (or large concentrations of monovalent ions) impact Ca ion uptake

## Dynamics of zeolites



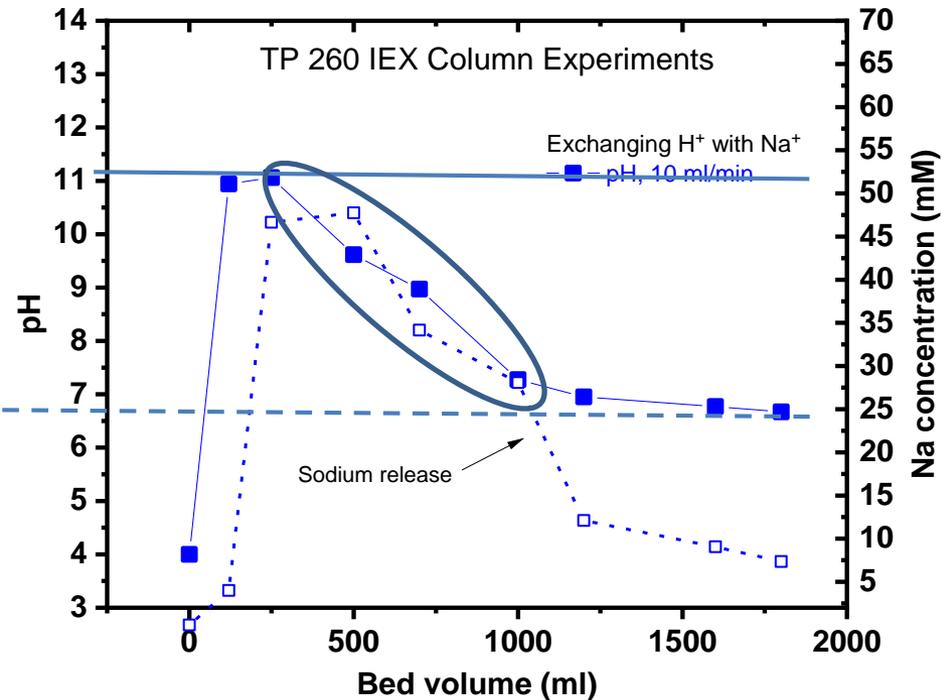
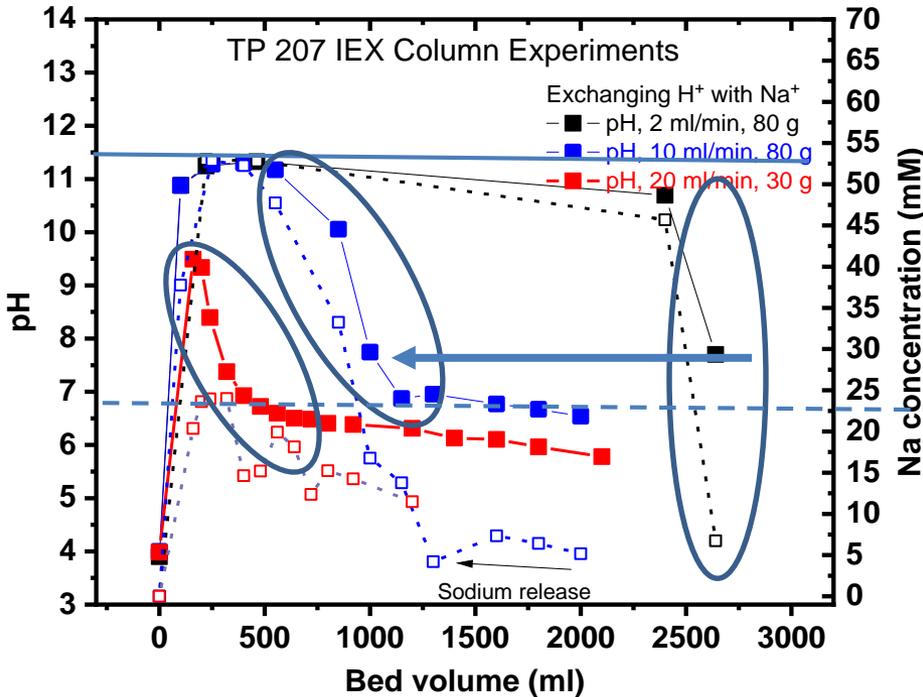
- No diffusion restrictions on exchange equilibrium
- Microporous structure may slow uptake kinetics (larger process vessel)

# Dynamics of zeolites



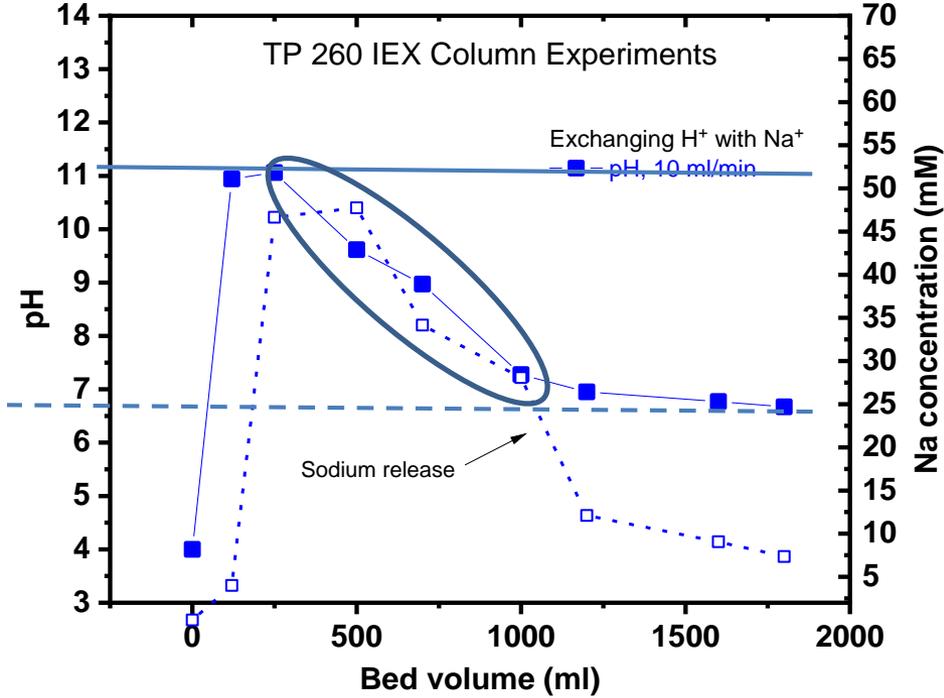
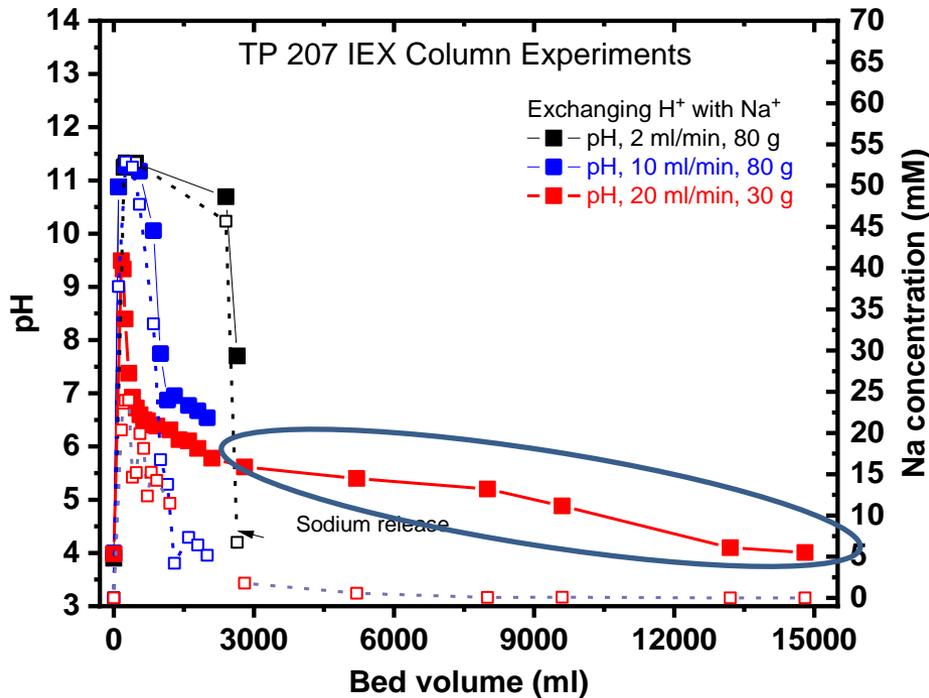
- No diffusion restrictions on exchange equilibrium
- Microporous structure may slow uptake kinetics (larger process vessel)...observe very long mass transfer zone

# Dynamics of resins



- Achieve equilibrium exchange capacities; Faster uptake kinetics
- Still observe a pH increase from 4 to 7
- Shift in breakthrough almost proportional with contact time

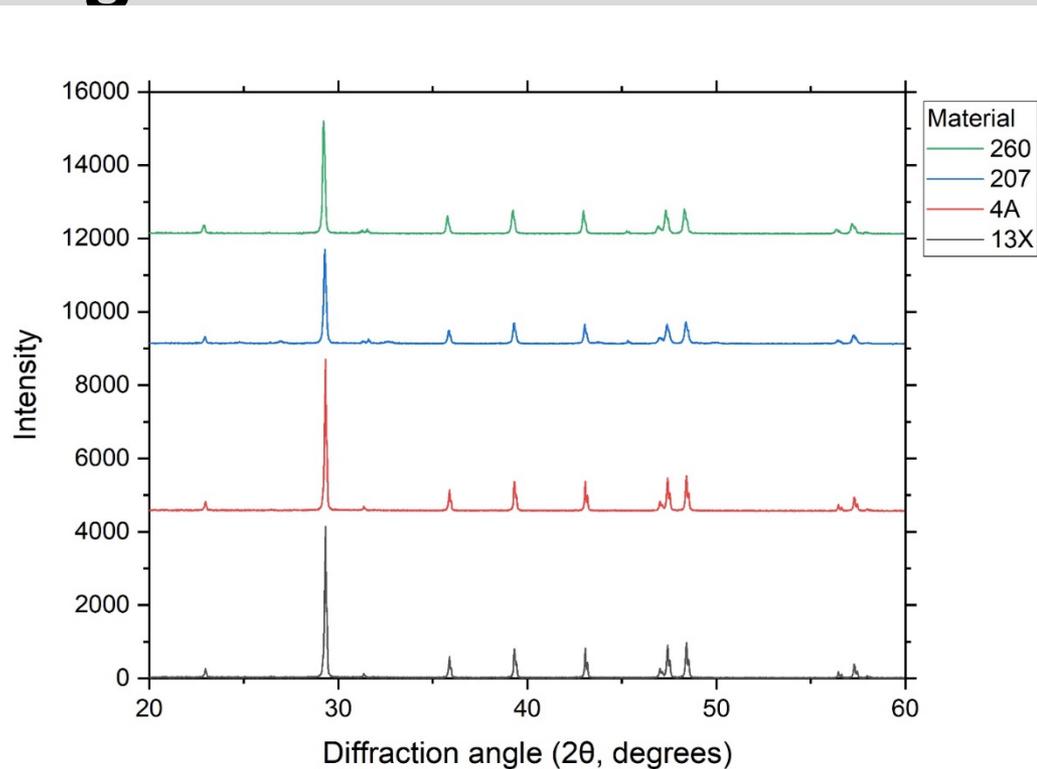
# Dynamics of resins



- Achieve equilibrium exchange capacities; Faster uptake kinetics
- Still observe a pH increase from 4 to 7
- Shift in breakthrough almost proportional with contact time

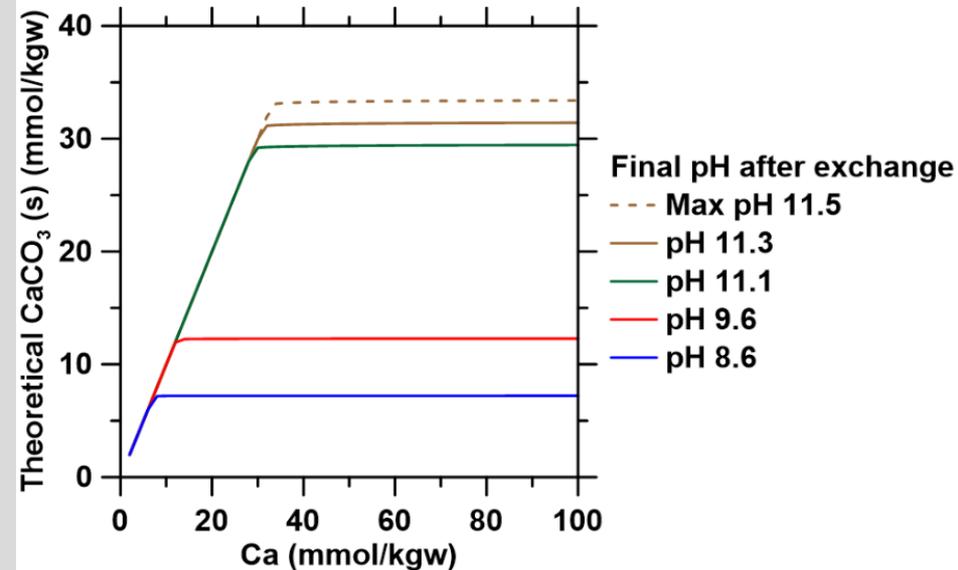
# Precipitation using column effluent

- CaCO<sub>3</sub> precipitation (XRD) following column ion exchange (using 0.10 M CaCl<sub>2</sub>)



# Precipitation using column effluent

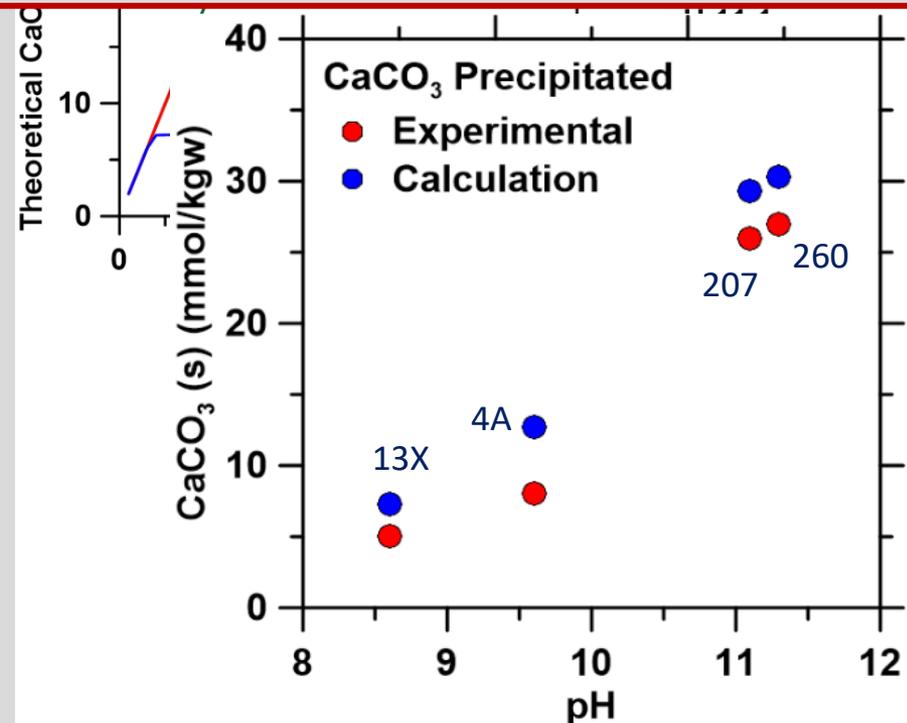
- $\text{CaCO}_3$  precipitation (XRD) following column ion exchange (using 0.10 M  $\text{CaCl}_2$ )



## Precipitation using column effluent

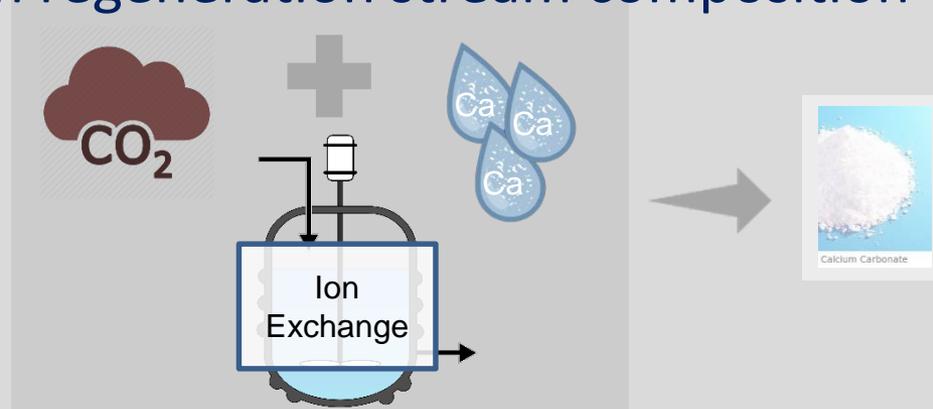
Known zeolites and resins can achieve thermodynamic production for overall process

- Achieve (close to) the thermodynamic maximum amount of  $\text{CaCO}_3$  (using PHREEQC minteq database)
- Small reaction time length or loss of  $\text{CO}_2$  may explain differences in calculated and experimental  $\text{CaCO}_3$  (s) values



## Conclusions

- Production of precipitated calcium carbonate using industrial waste brines presents substantial reductions in GHG emissions
- Various pathways have been identified, processes need to be characterized and controlled
- Ion-exchange produces a  $\text{CO}_3^{2-}$ -rich solution, Reaction of  $\text{CO}_3^{2-}$ -rich solution with  $\text{Ca}^{2+}$ -rich produced water forms calcite
- Resins exhibit higher “capacity” and better kinetics, but have capacities that will vary with regeneration stream composition



# Acknowledgements

- Department of Energy Award Number DE-FE0031705
- UCLA Institute for Carbon Management

# Questions?

Disclaimer: "This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."