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Fine Calcium Carbonate Production by CO_2 Mineralization of Industrial Waste Brines

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DOE Office of Fossil Energy, NETL
UCLA Institute for Carbon Management

2019 Carbon Management Technology Conference

Carbon Utilization

CARBON MANAGEMENT TECHNOLOGY CONFERENCE

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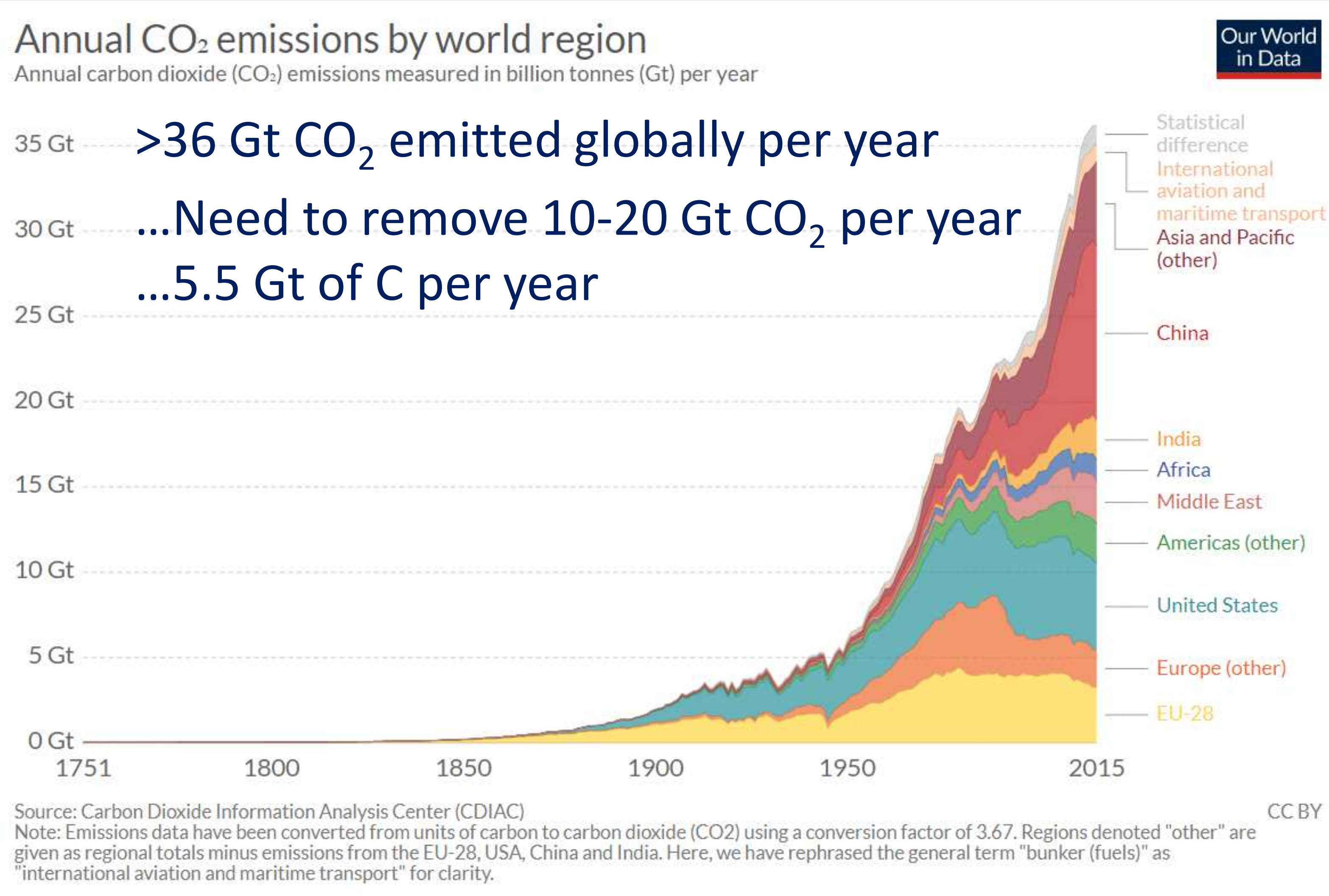
Need global strategy for carbon management



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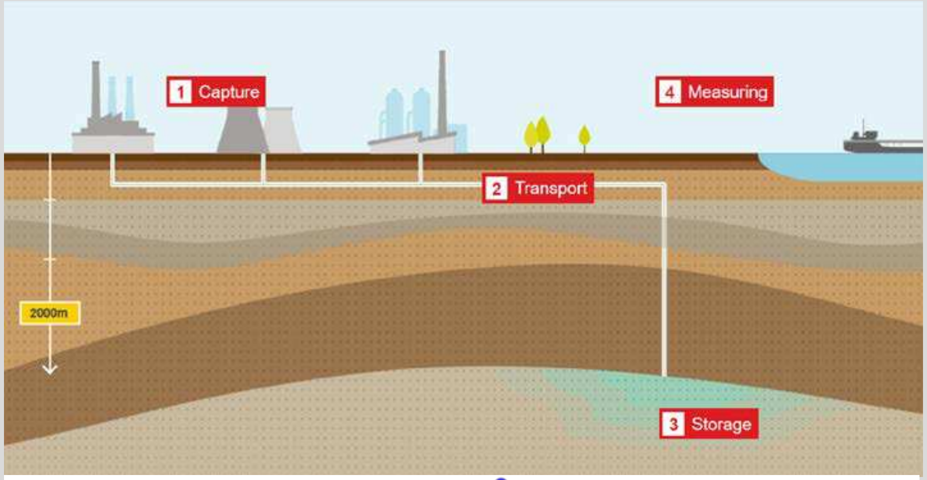
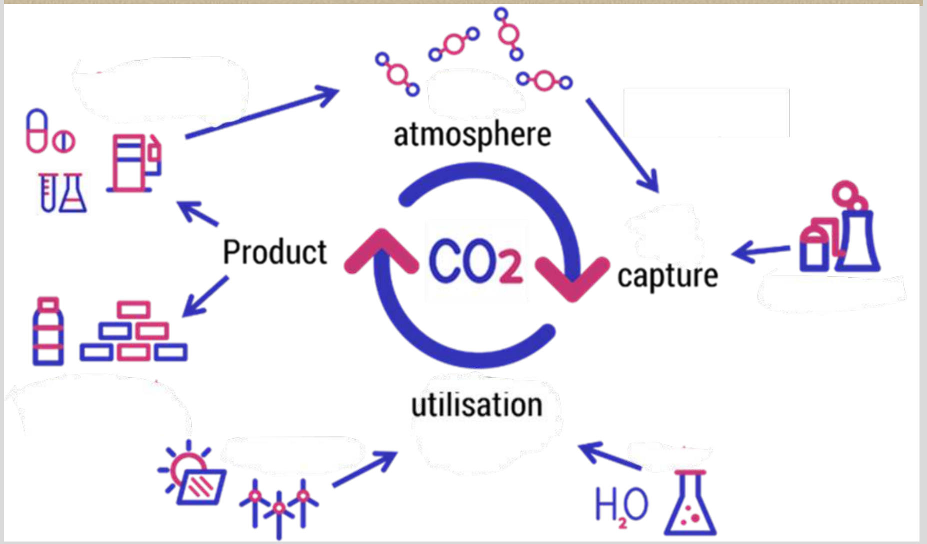
Current models of carbon management

- CCS
  - 22,000 Gt potential capacity (North America)
  - Limited to ~1,000 Mt CO_2/year
  - Risk of 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" CO_2
  - Potentially profitable for businesses
  - Need for co-feed molecules
  - Displaces only ~30% need
    - Gasoline in the US would only account for 7% of need



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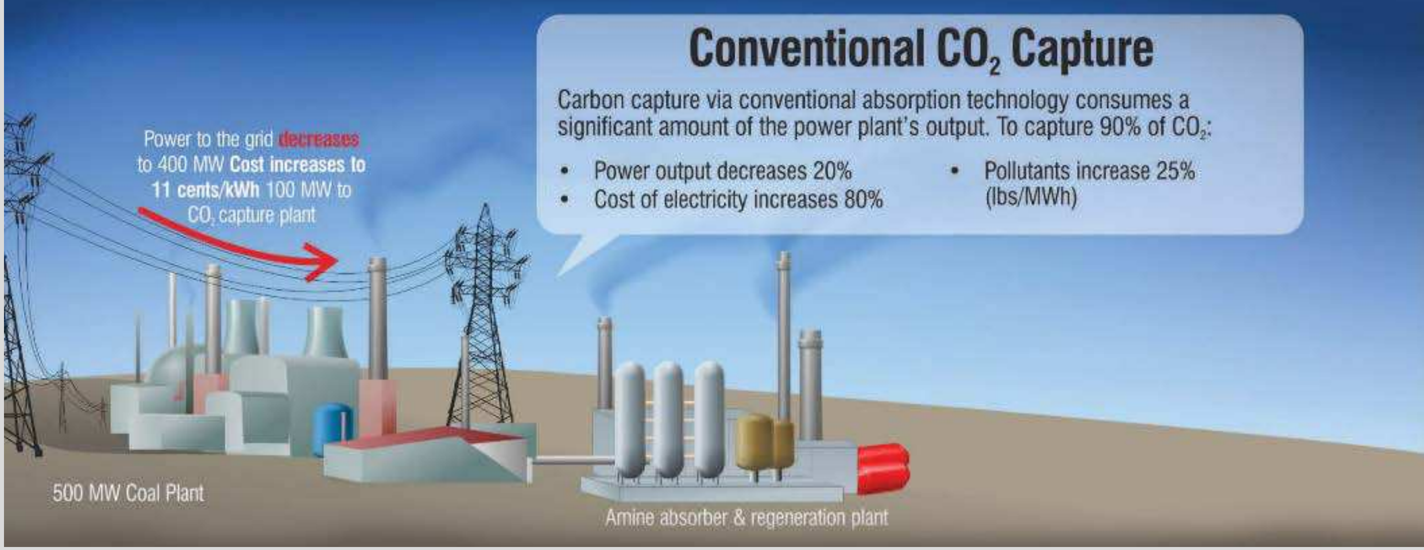
Thermodynamic, Kinetic, and Political Barriers

0.11 kWh per kg CO_2 for optimum Amine unit

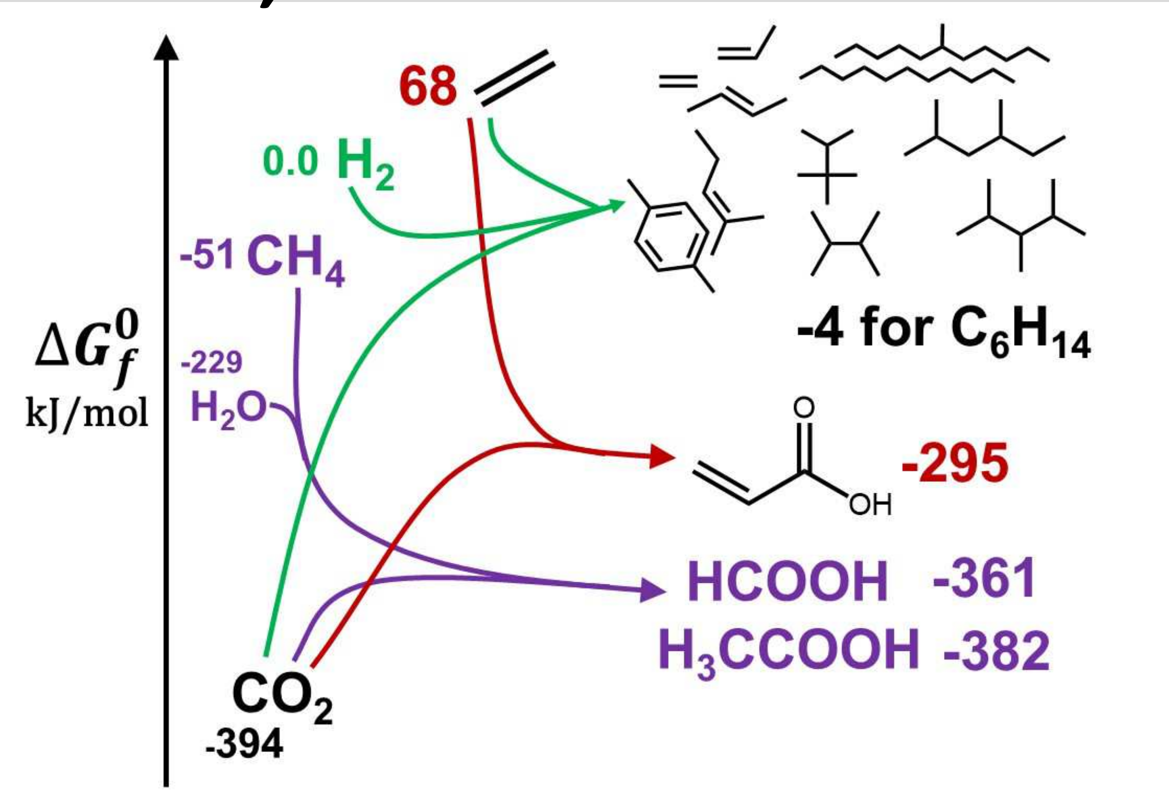
Energy for separation/concentration



Thermodynamic, Kinetic, and Political Barriers

>390 kJ/mol CO_2 to overcome rxn energy

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



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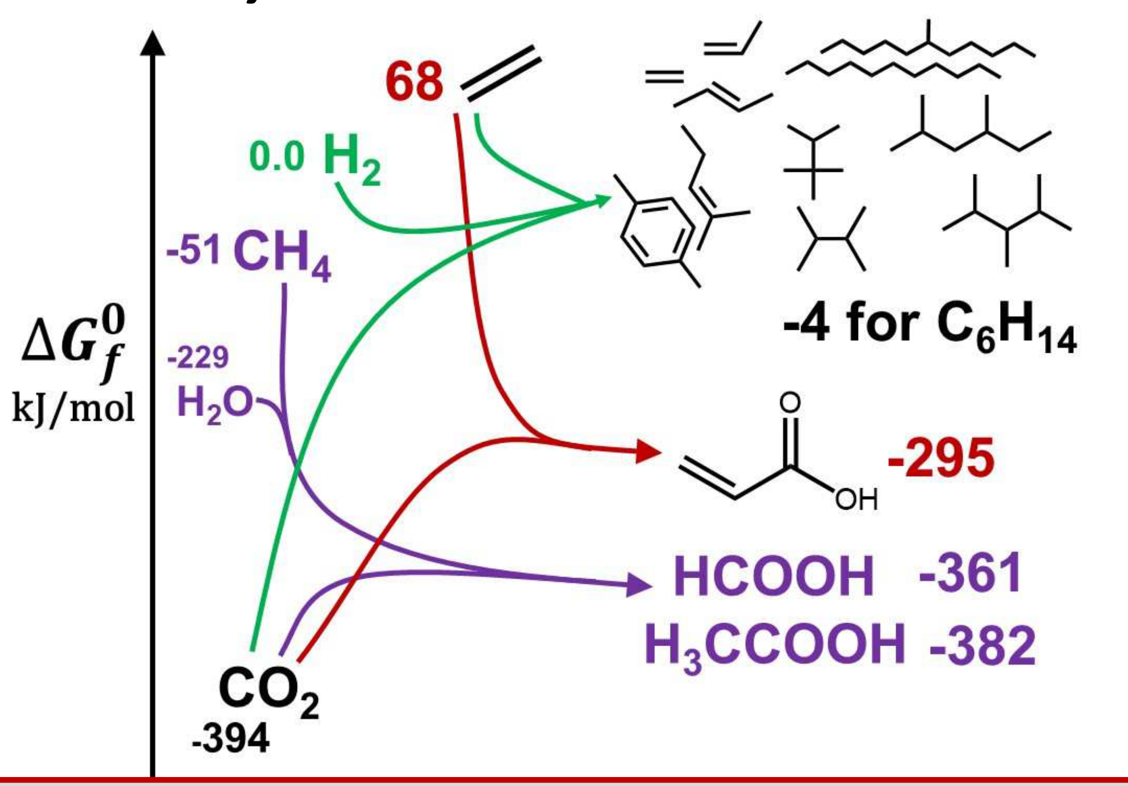
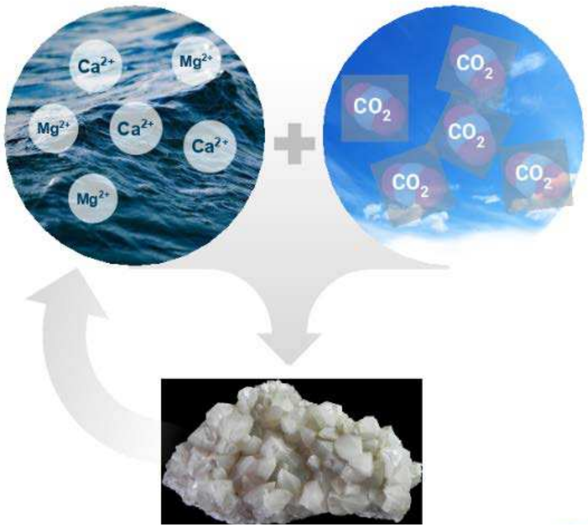


Can we develop additional processes with less severe science and engineering hurdles?

A synthetic analogue of natural process

- CO_2 fixed within stable mineral carbonates, mimicking the natural process of biogenic abiogenic limestone formation



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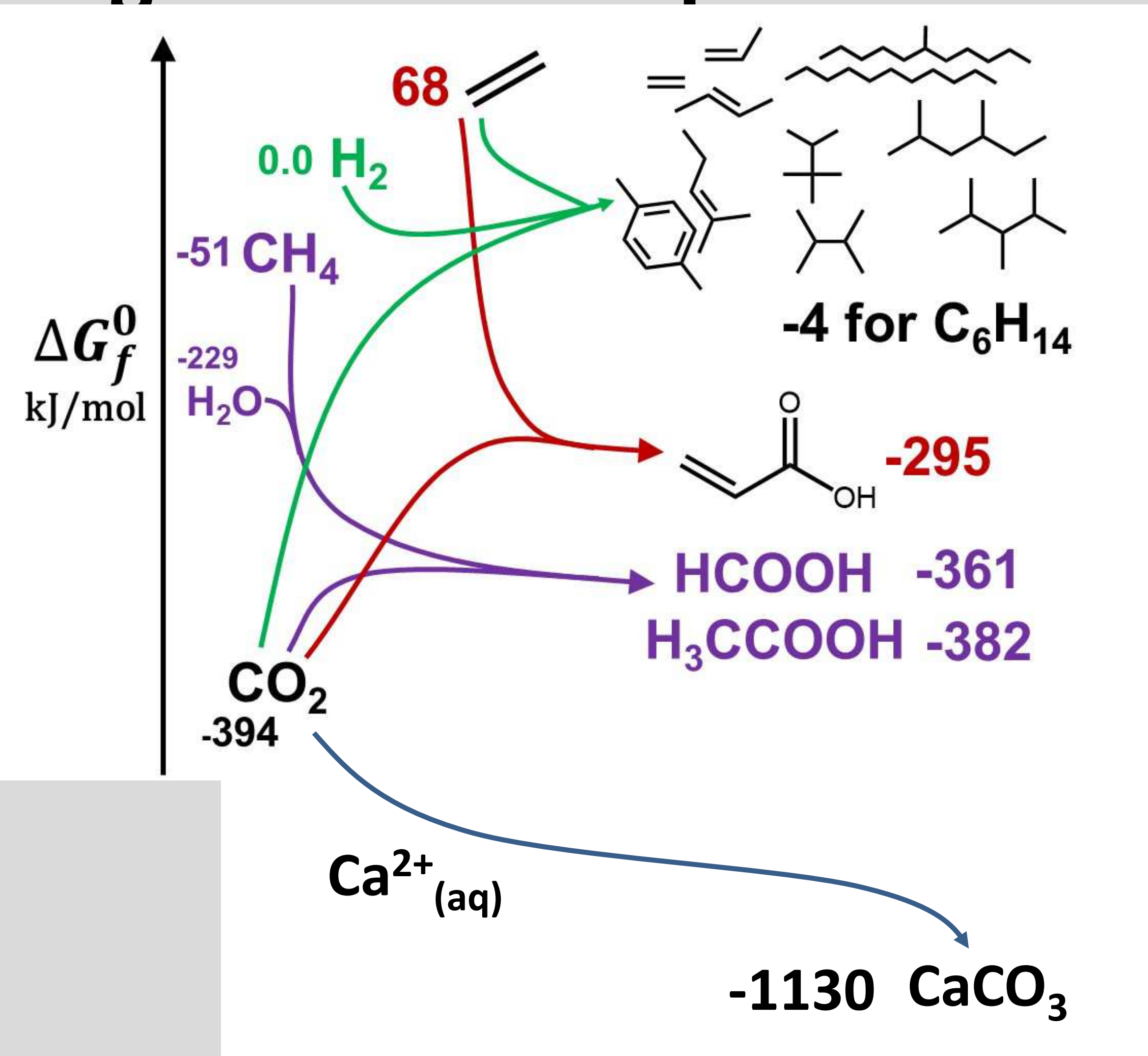
- Thermodynamically favorable



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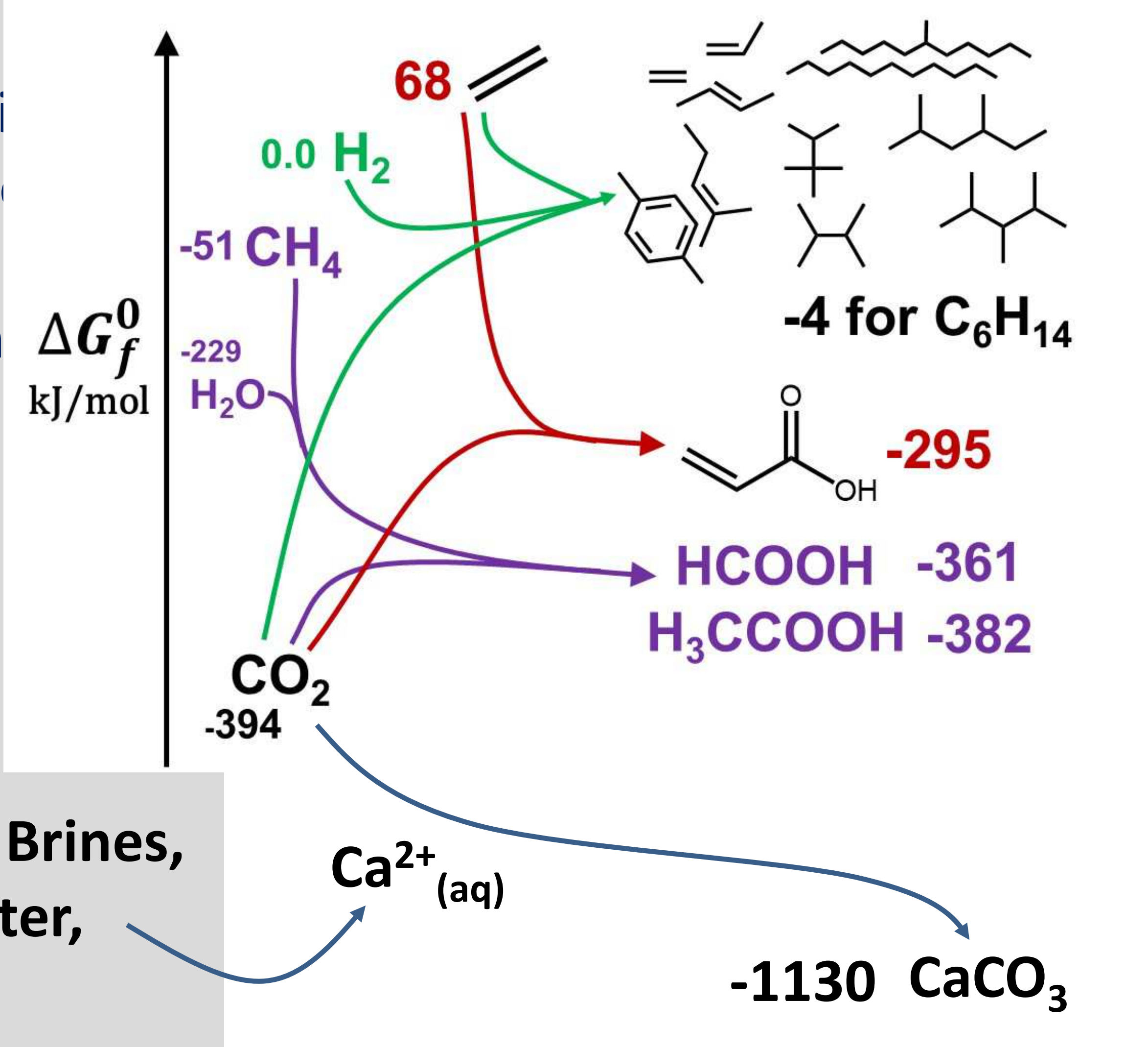
- Thermodynamically favorable
- Utilizes abundant and/or waste sources of Ca



Seawater, Desalination Brines, Industrial Wastewater, Produced Water

A synthetic analogue of natural process

- CO_2 fixed within stable mi
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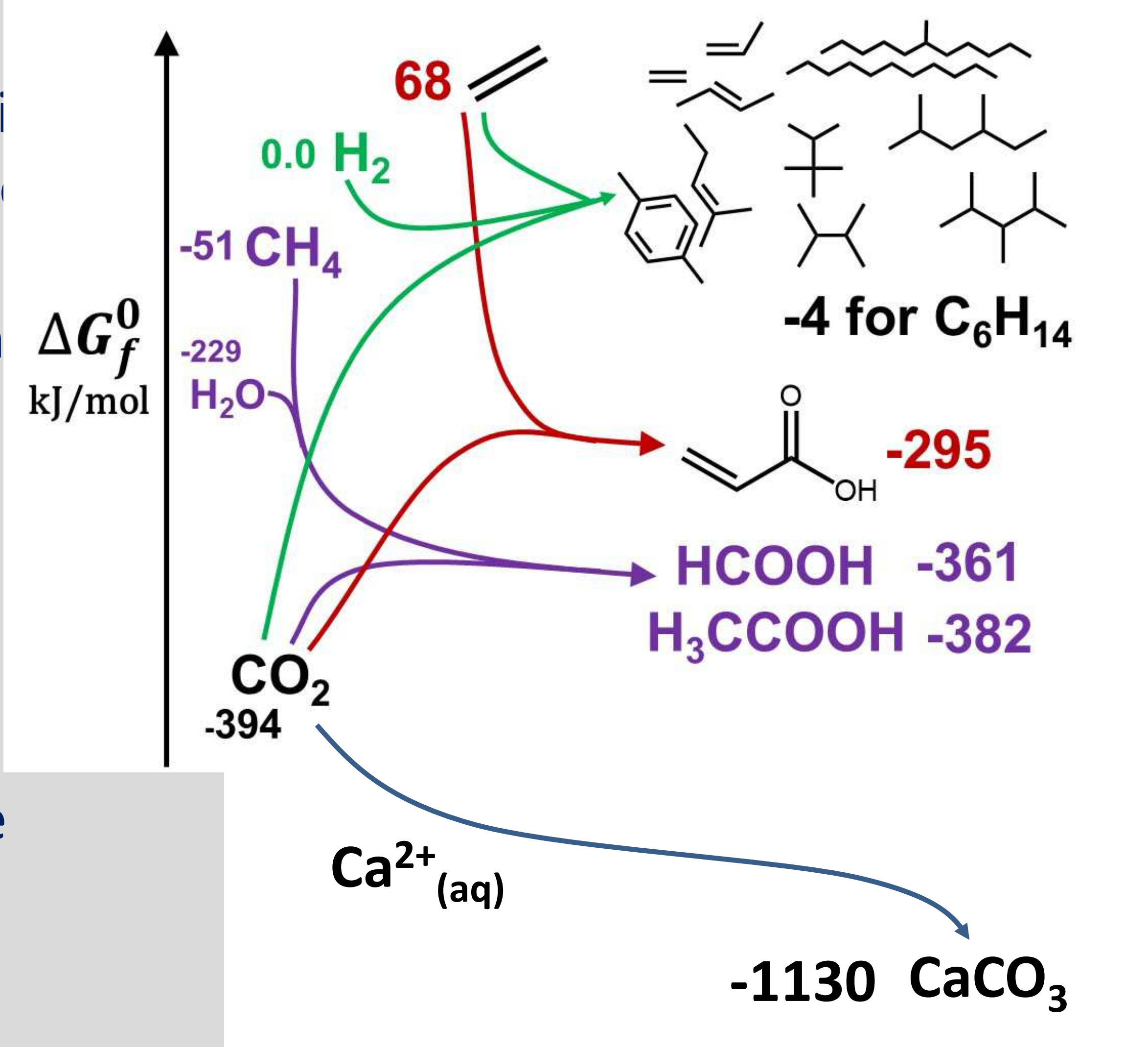
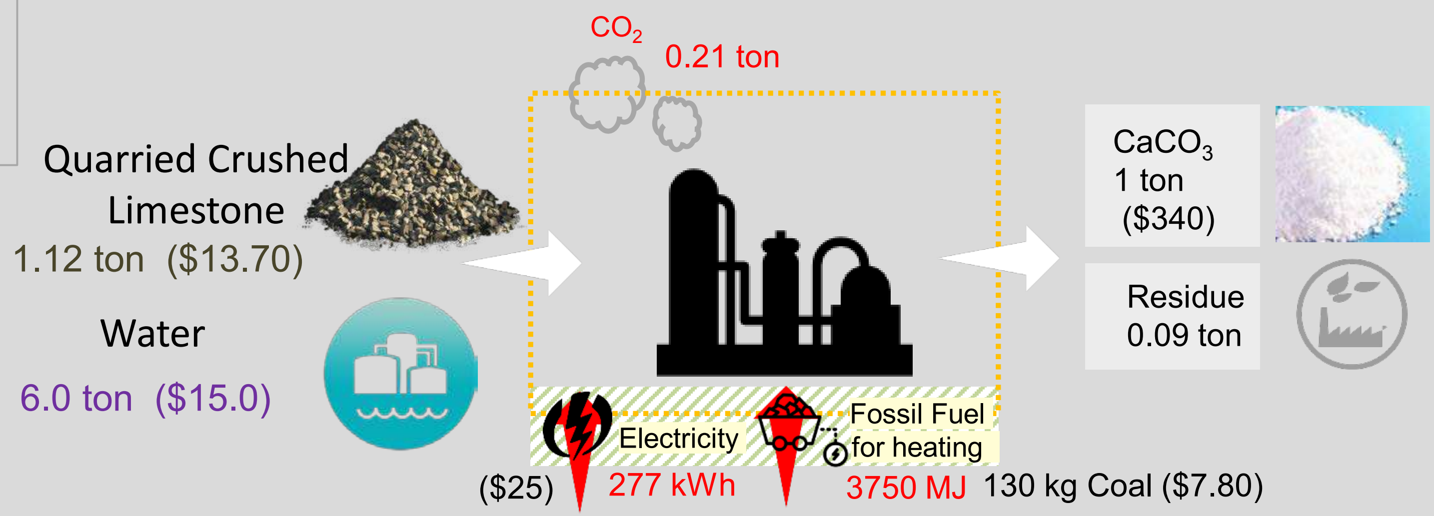
- Thermodynamically favorable
- Utilizes abundant and/or waste sources of Ca
- Economically competitive and environmentally "friendlier" process



Precipitated Calcium Carbonate Processes

Current Process



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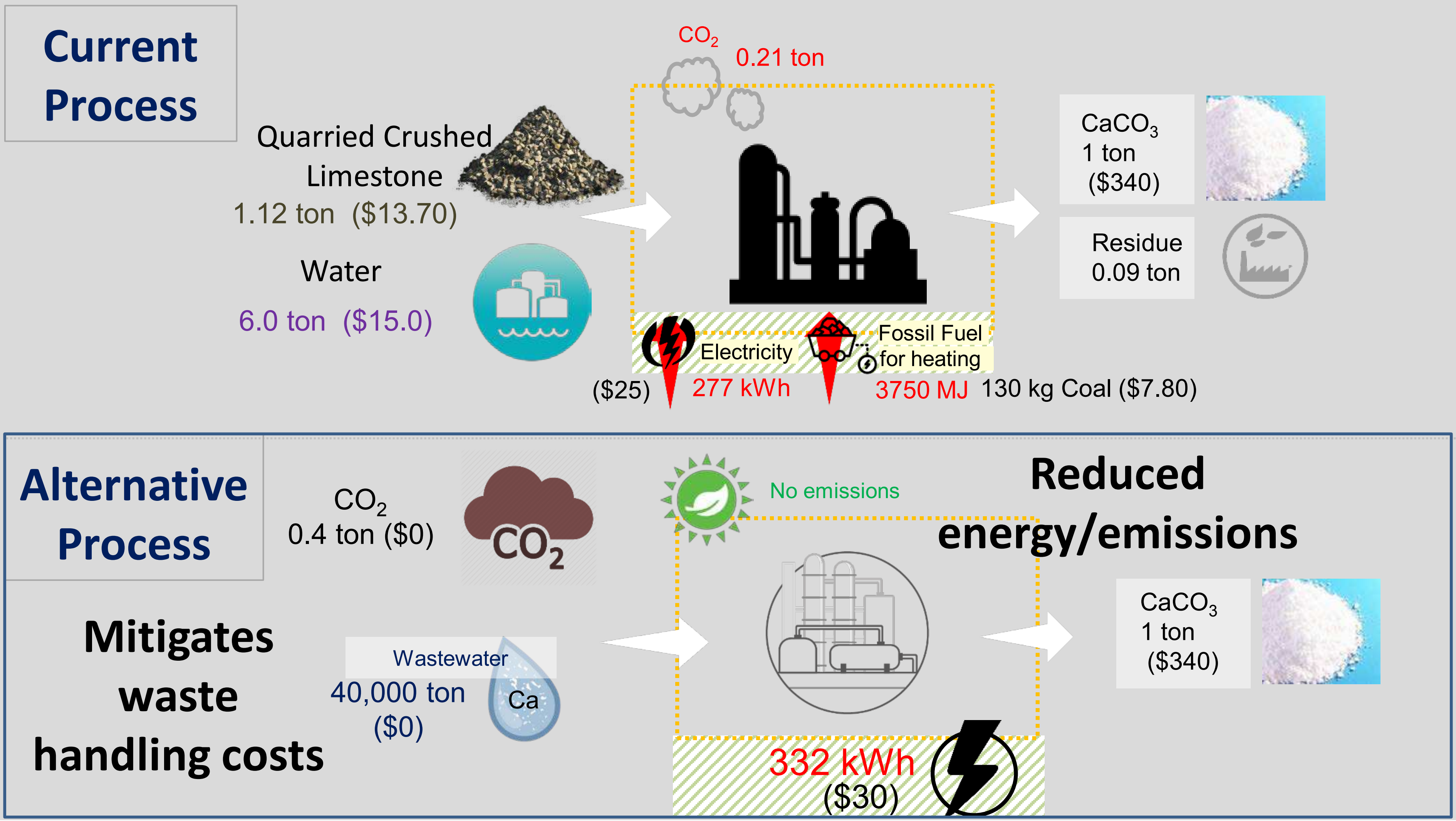
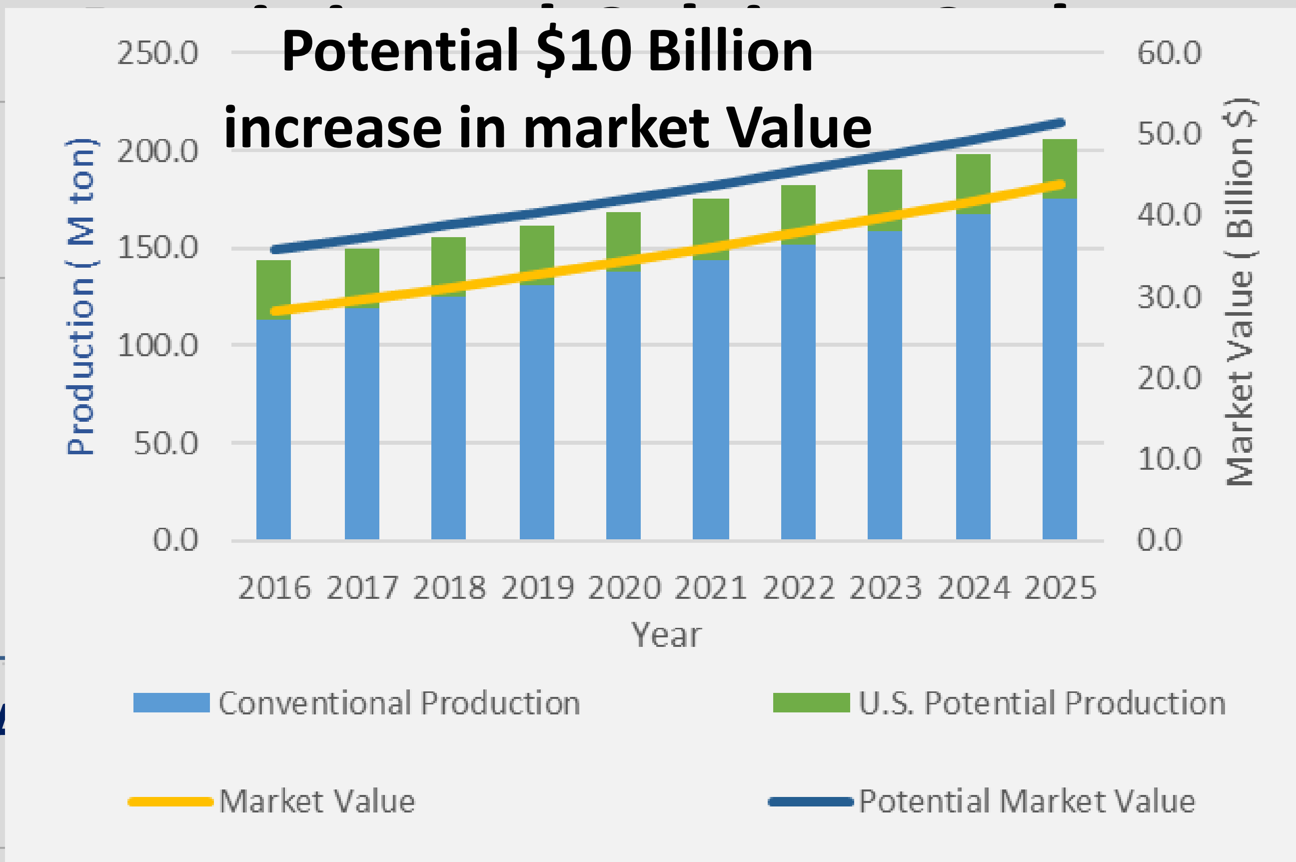
Precipitated Calcium Carbonate Processes



Alternative Processes for Precipitated Calcium Carbonate Production

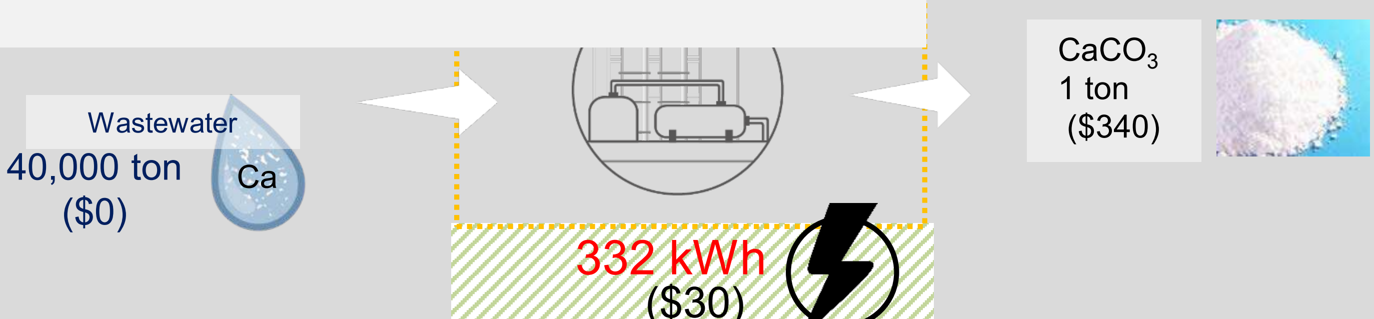
e Processes



g Coal ($7.80)

Reduced
gy/emissions

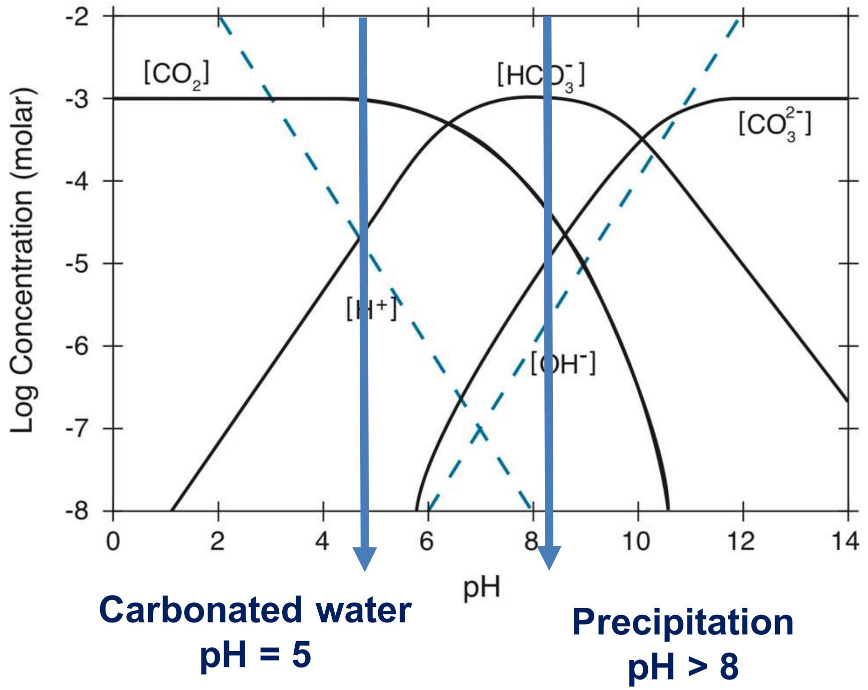
Mitigates waste handling costs



Different thermodynamic barrier

- Alkalinity must be supplied to continuously precipitate $CaCO_3$

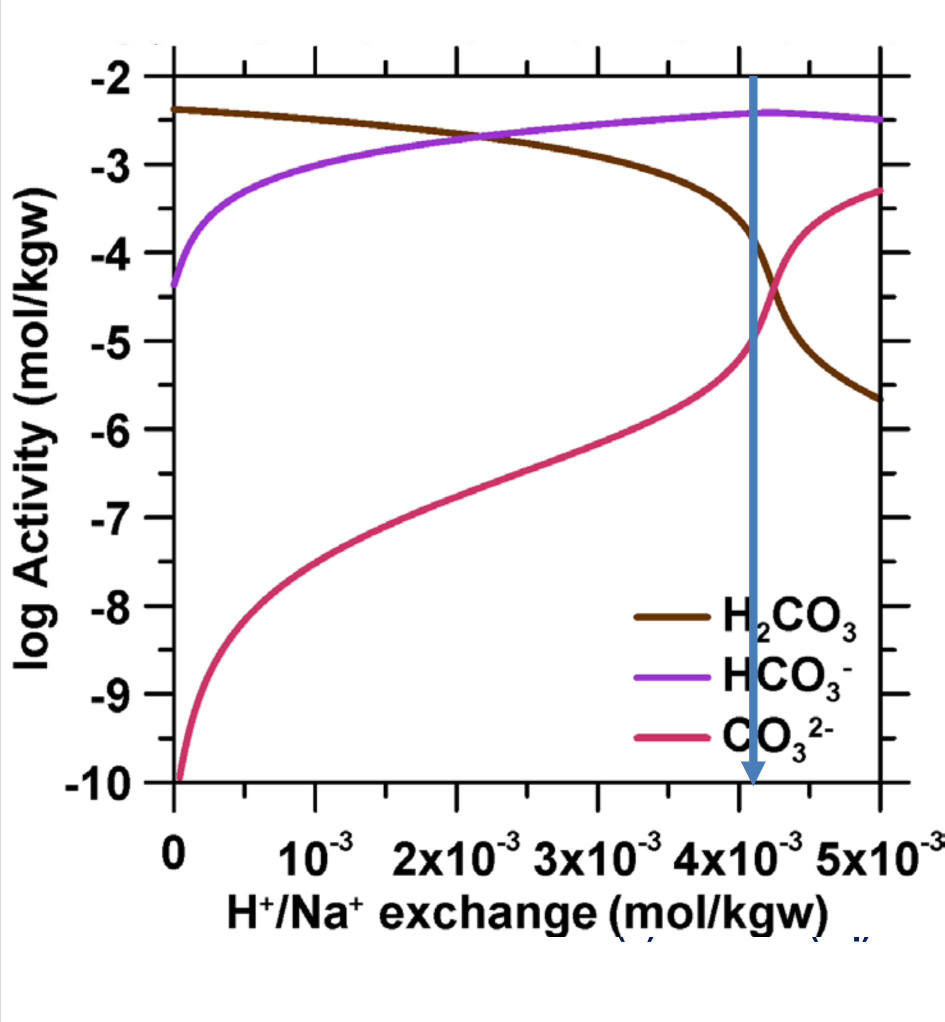
- Inducing alkalinity with consumable bases (e.g., NaOH) is expensive and energy intensive



$$Ca^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)} \rightarrow CaCO_{3(s)} + 2H^+_{(aq)}$$

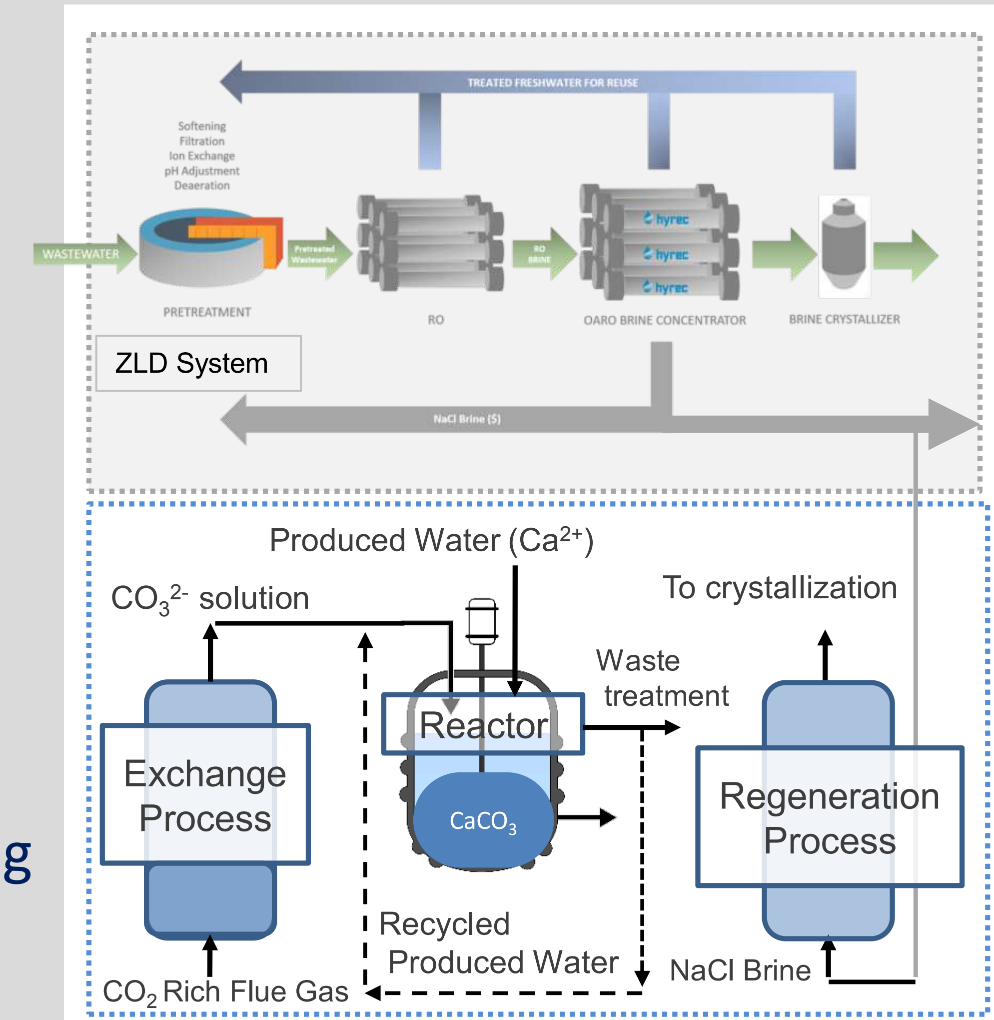
Different thermodynamic barrier

- Alkalinity must be supplied to continuously precipitate $CaCO_3$
- Inducing alkalinity with consumable bases (e.g., 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 CO_2 dissolution, ion-exchange produces a CO_3^{2-}-rich solution
- Reaction of CO_3^{2-}-rich solution with Ca^{2+}-rich produced water forms calcite
- Ion-exchanger regenerated using Ca-depleted produced water



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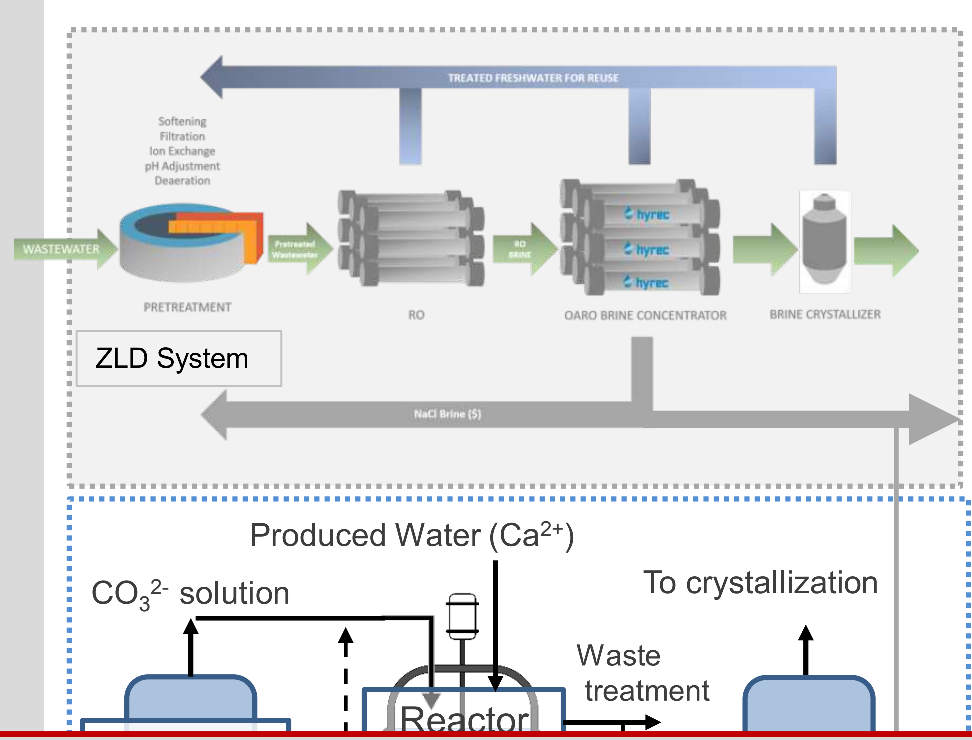
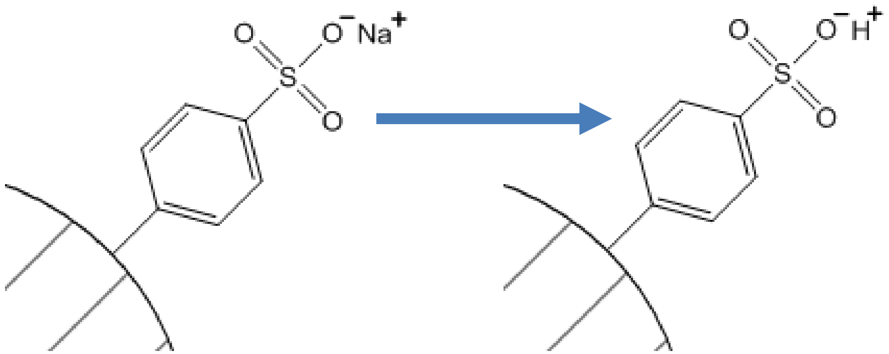


What ion exchange materials deliver desirable exchange capacity, dynamics, and stability ?

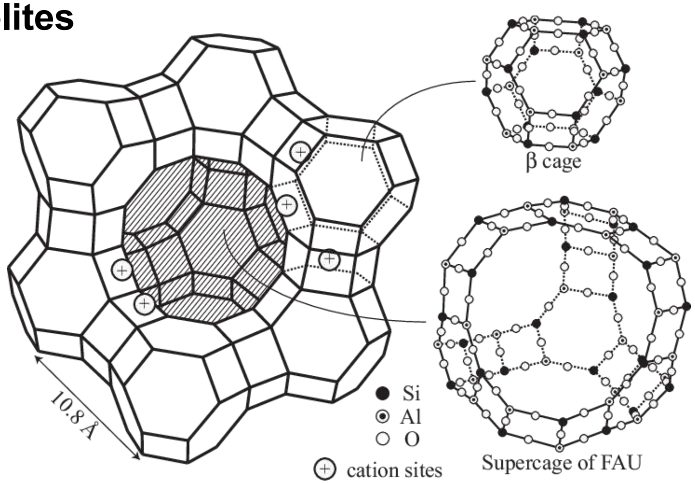
Regenerable ion-exchangers

- 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

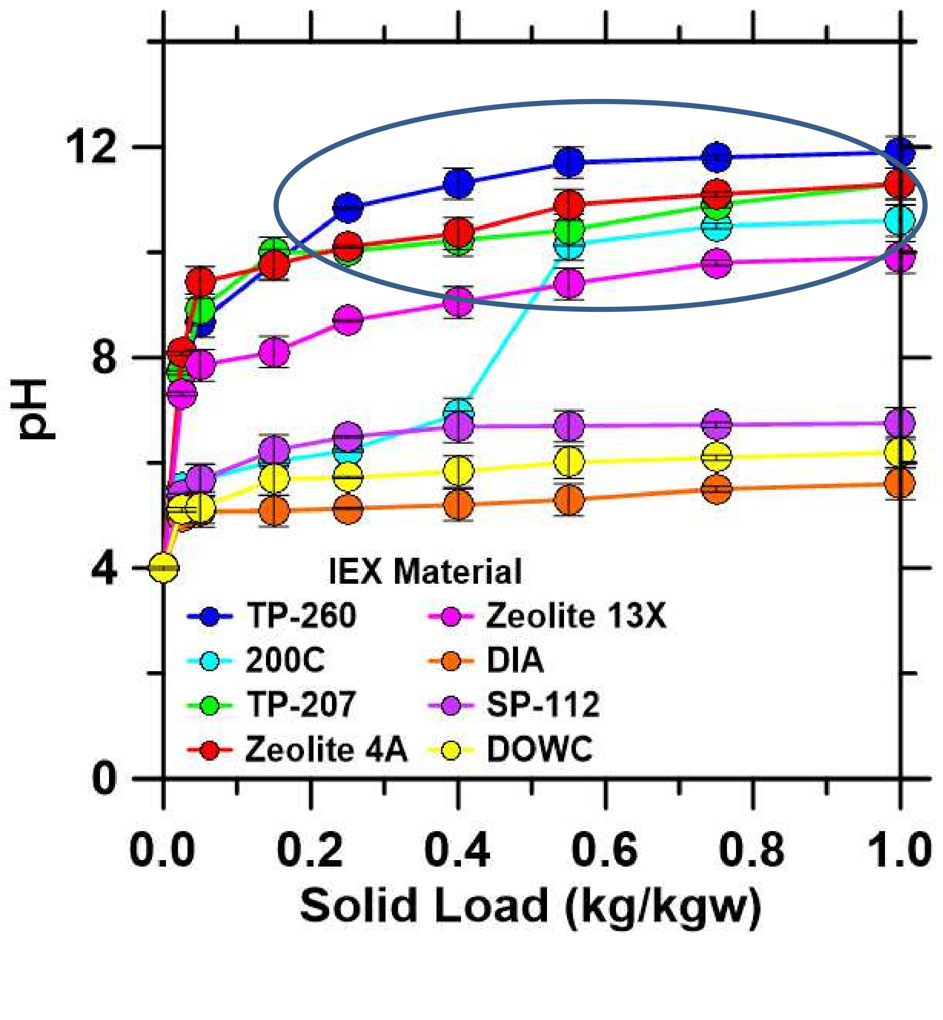


Zeolites



Na^+/H^+ exchange using resins, clays, zeolites

- Batch experiments: bubble CO_2 into DI water until pH 4, then add ion exchanger and observe pH increase
- Two zeolites and two resins meet the "minimum" requirement of pH > 8



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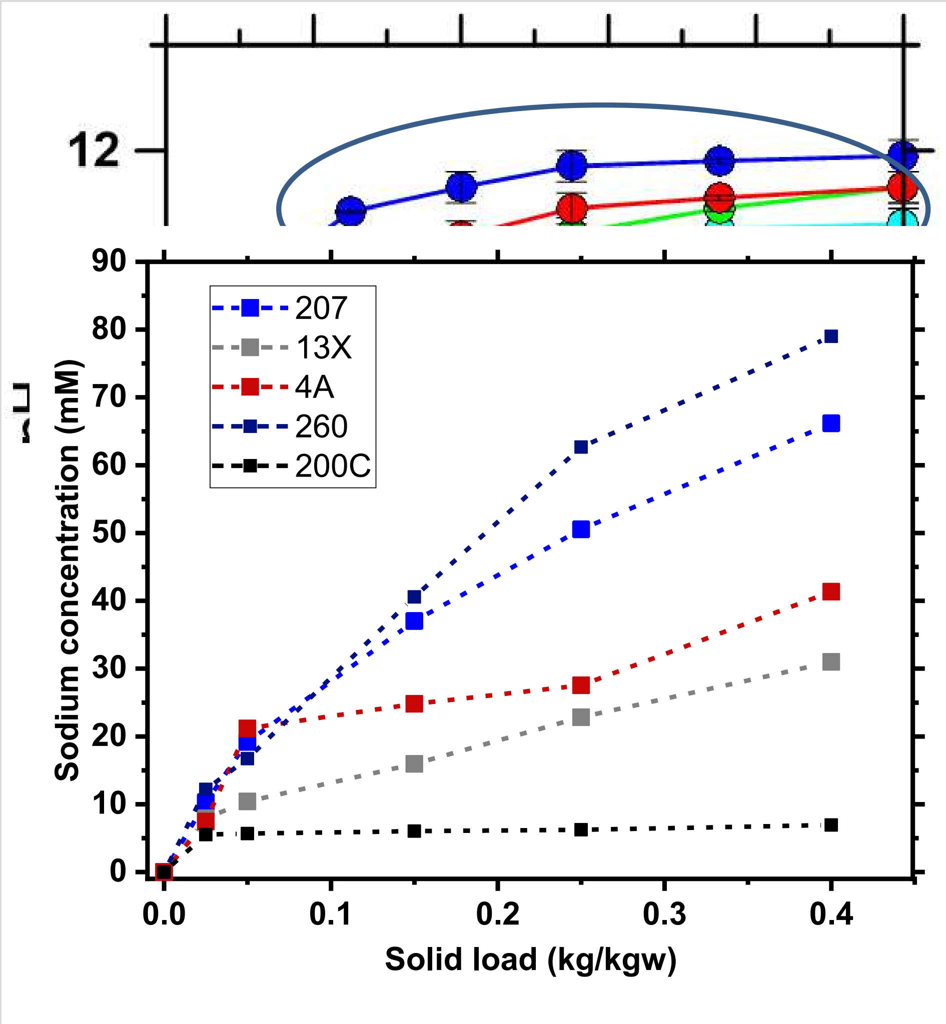
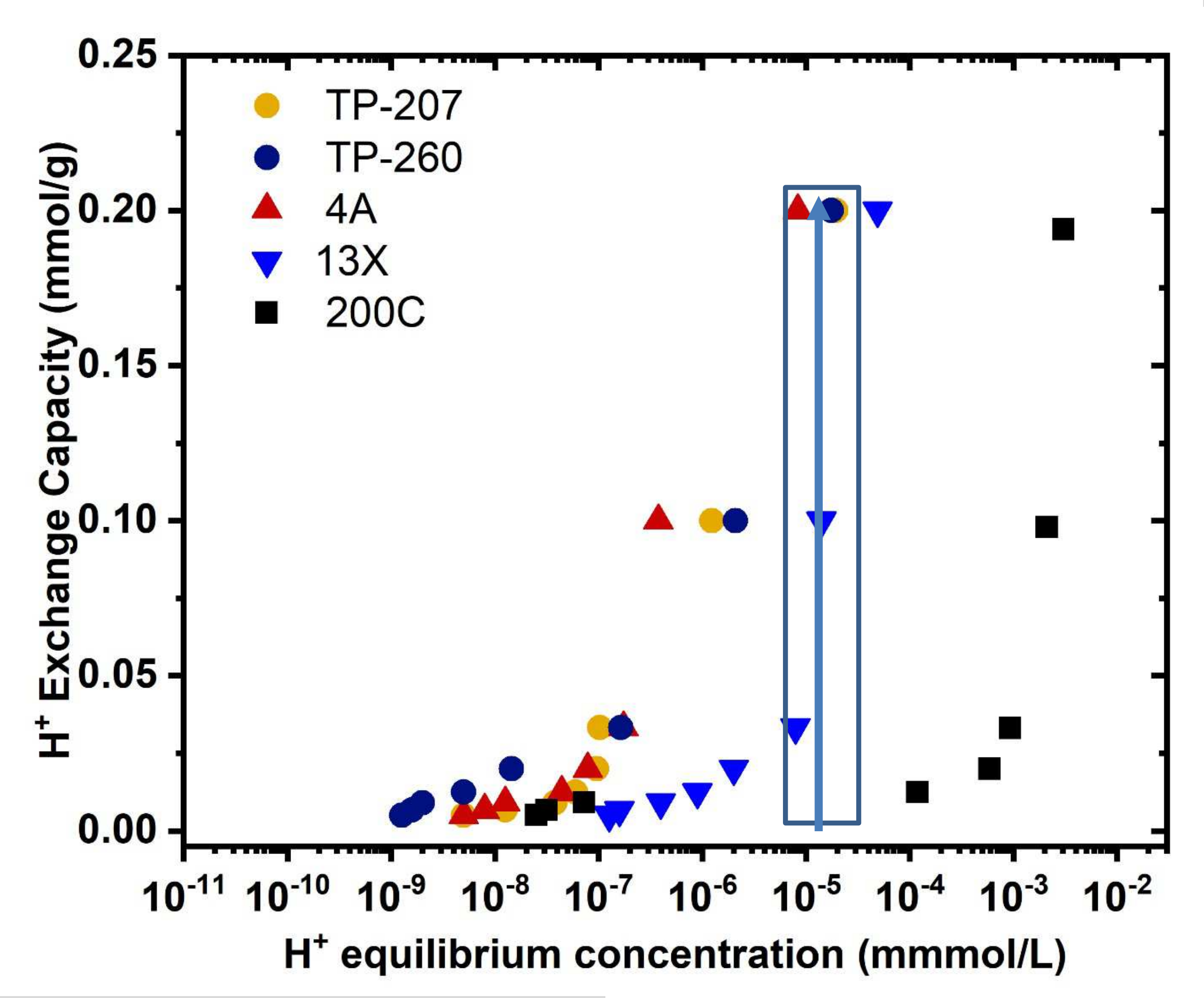
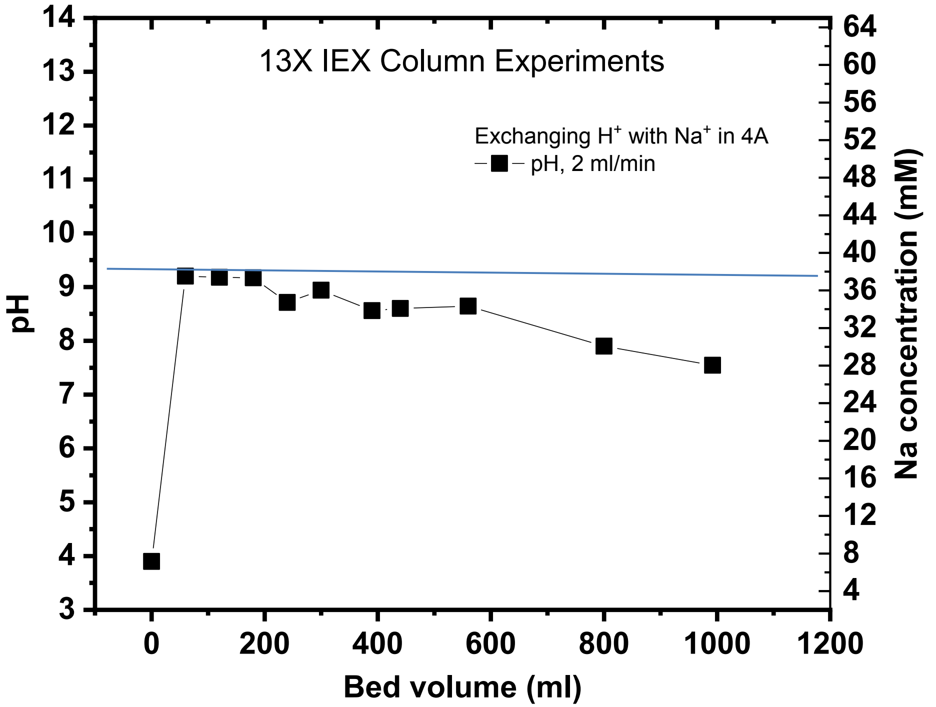
- Two zeolites and two resins meet the “minimum” requirement of pH > 8
- Na^+ release appears to be unbalanced but follows the same trend as pH increase

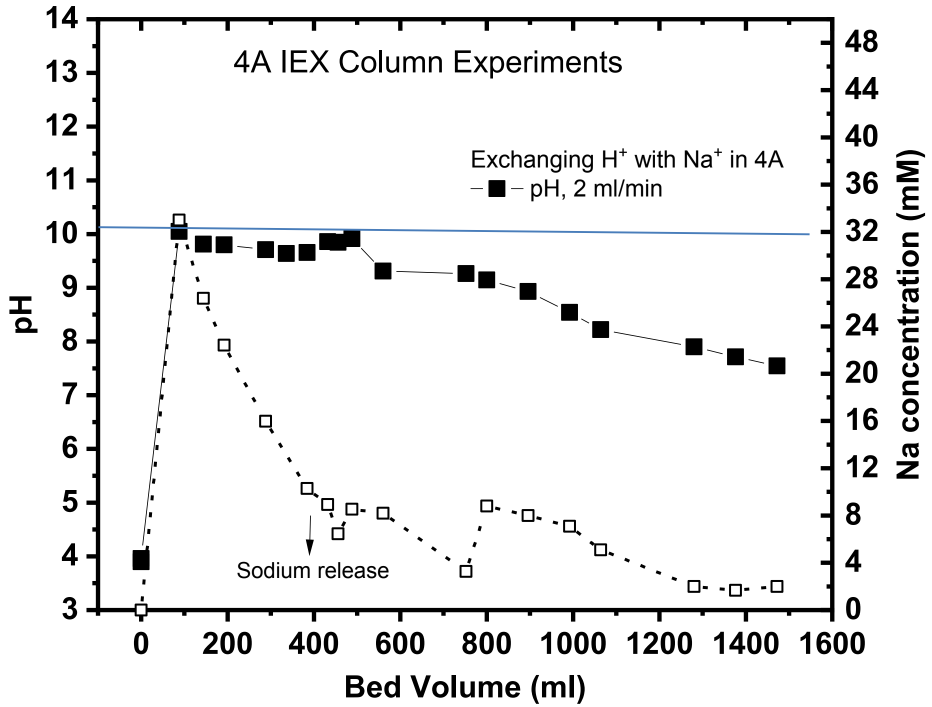


Exchange Isotherms point to the resins and 4A



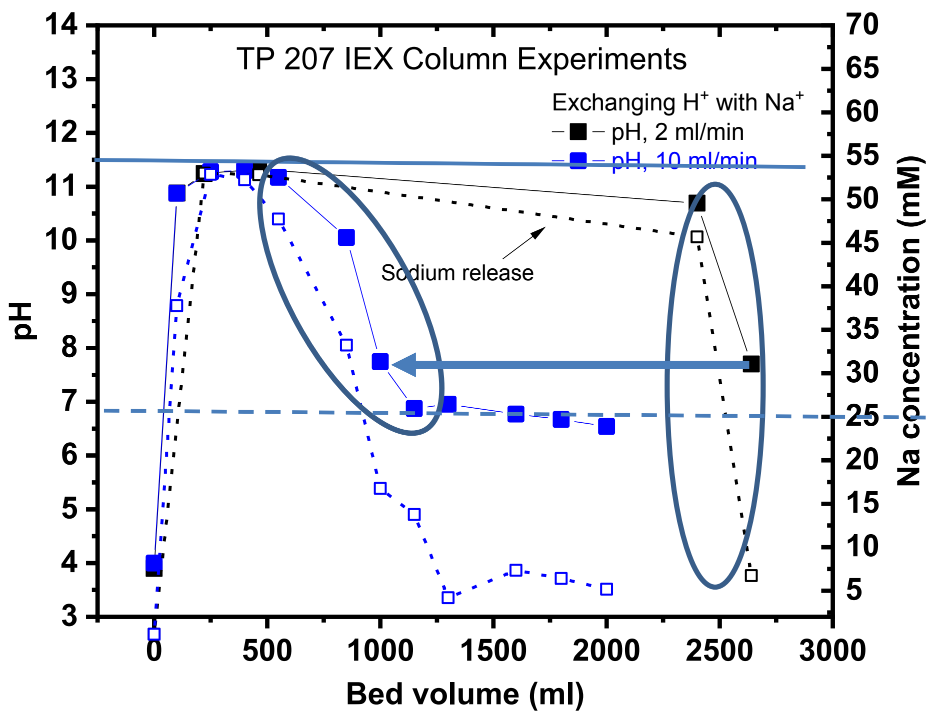
Dynamics of zeolites

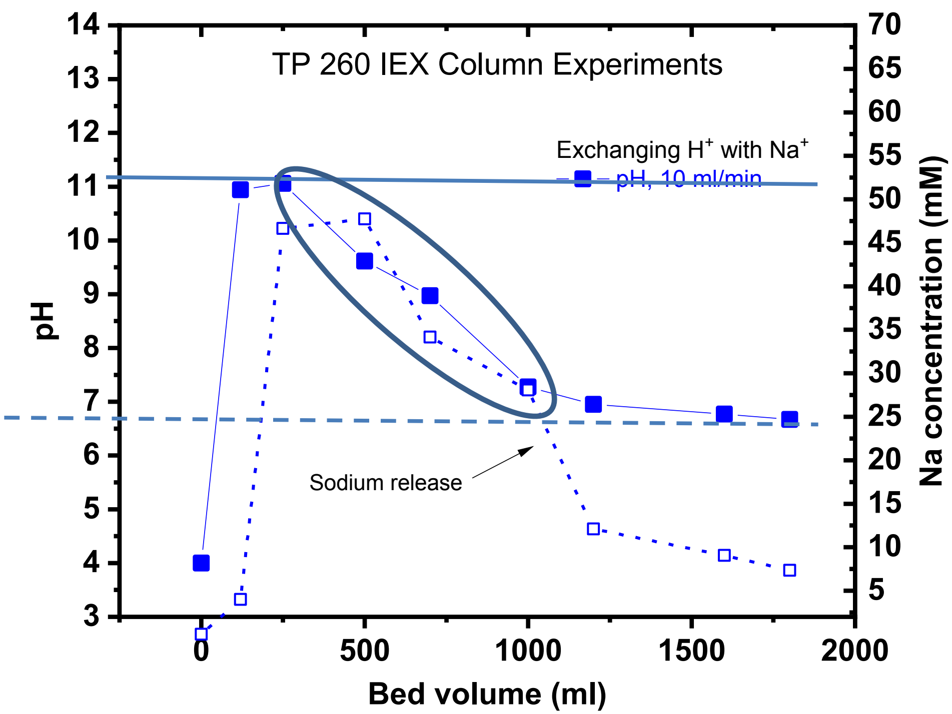




- No diffusion restrictions on exchange equilibrium
- Microporous structure may slow uptake kinetics (larger process vessel)

Dynamics of resins

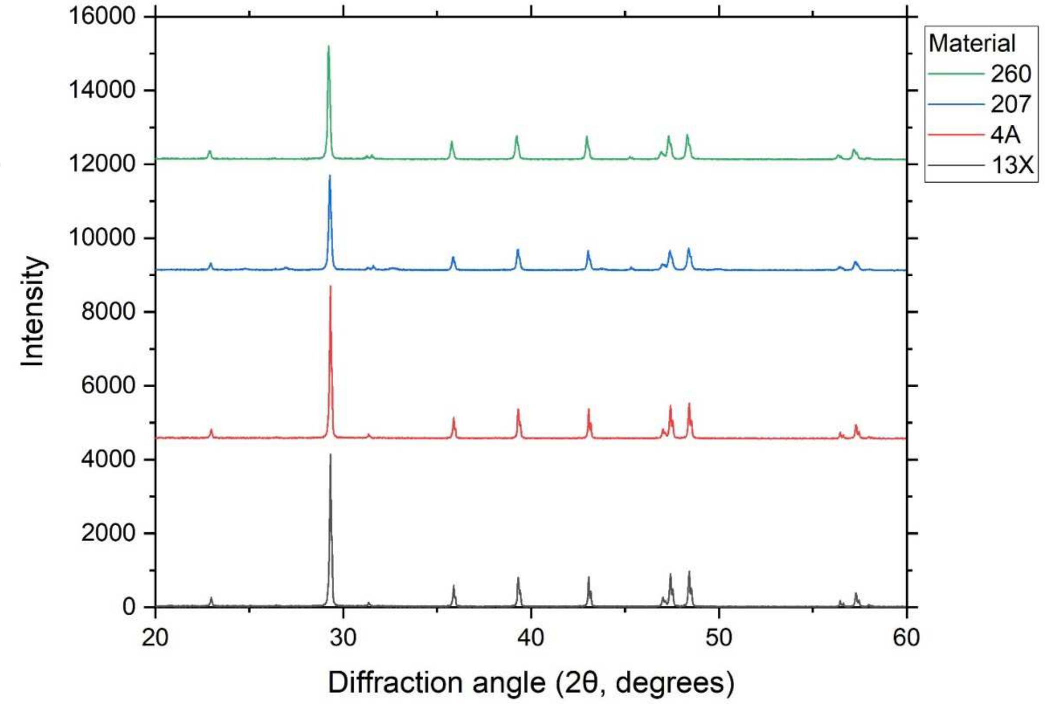




- Achieve equilibrium exchange capacities; Faster uptake kinetics
- Still observe a pH increase from 4 to 7
- Shift in breakthrough not proportional with contact time

Precipitation using column effluent

- $CaCO_3$ precipitation (XRD) following column ion exchange (using 0.10 M $CaCl_2$)



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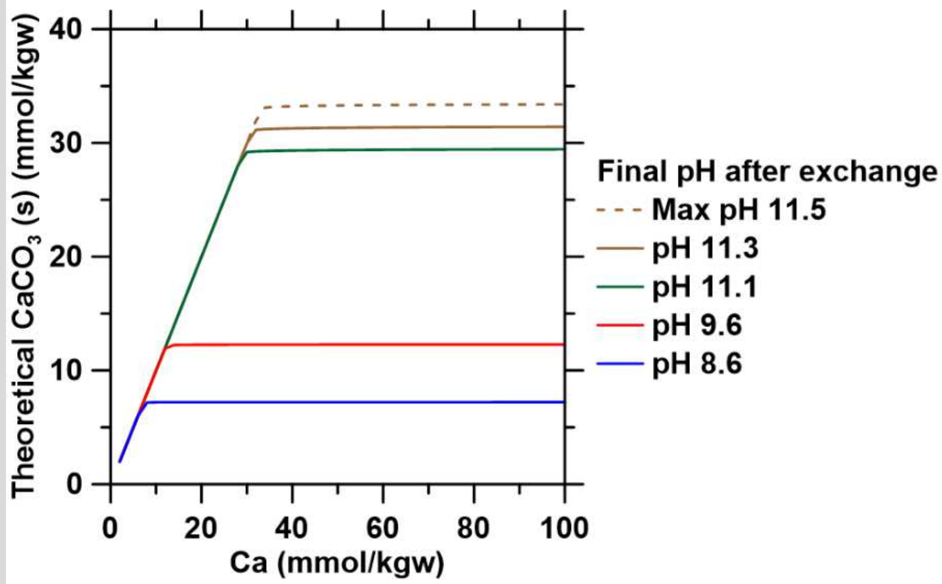
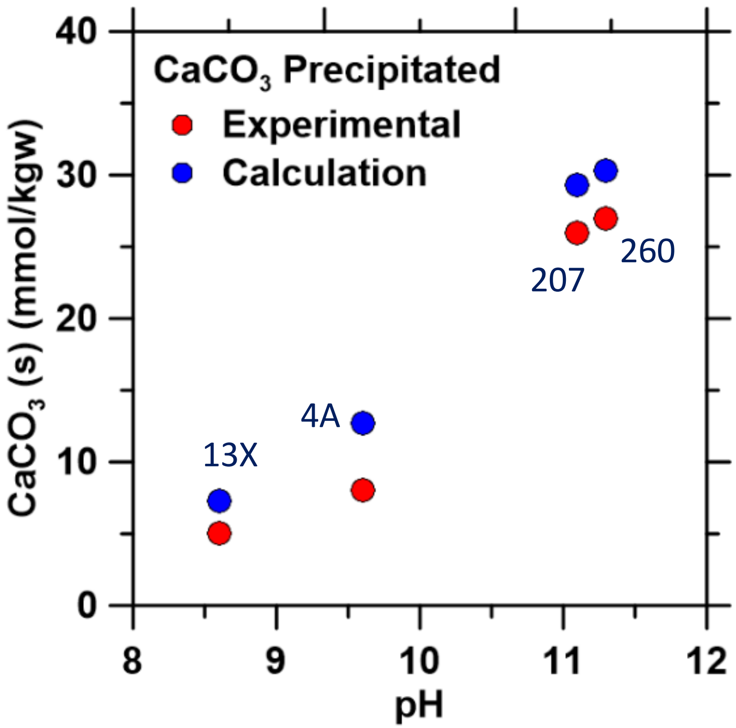


Precipitation using column effluent

- $CaCO_3$ precipitation (XRD) following column ion exchange (using 0.10 M $CaCl_2$)

- Achieve (close to) the thermodynamic maximum amount of $CaCO_3$ (using PHREEQC minteq database)

- Small reaction time length or loss of CO_2 may explain differences in calculated and experimental $CaCO_3$ (s) values



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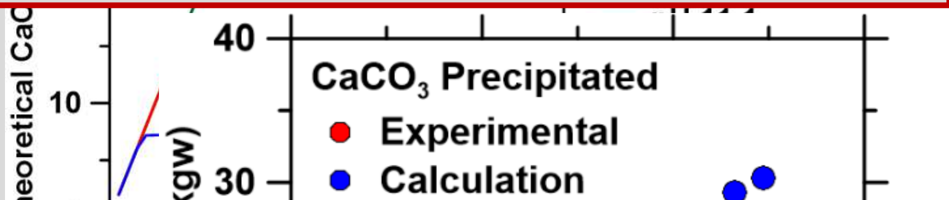
Precipitation using column effluent

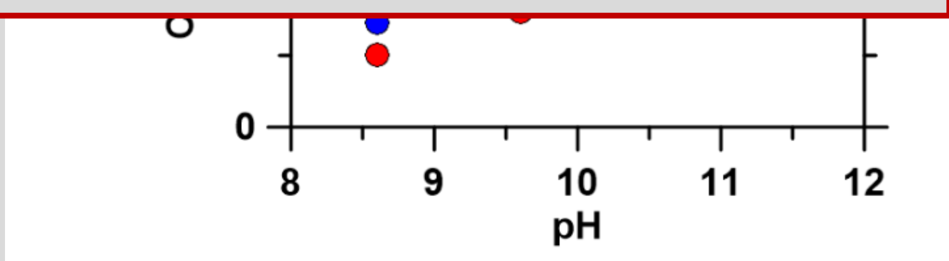
Known zeolites and resins can achieve thermodynamic maxima for overall process

- Achieve (close to) the thermodynamic maximum



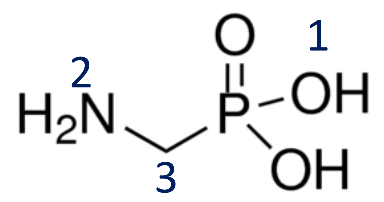
Regeneration? Higher than expected Na^+ during batch exchange? Post-breakthrough pH = 7?

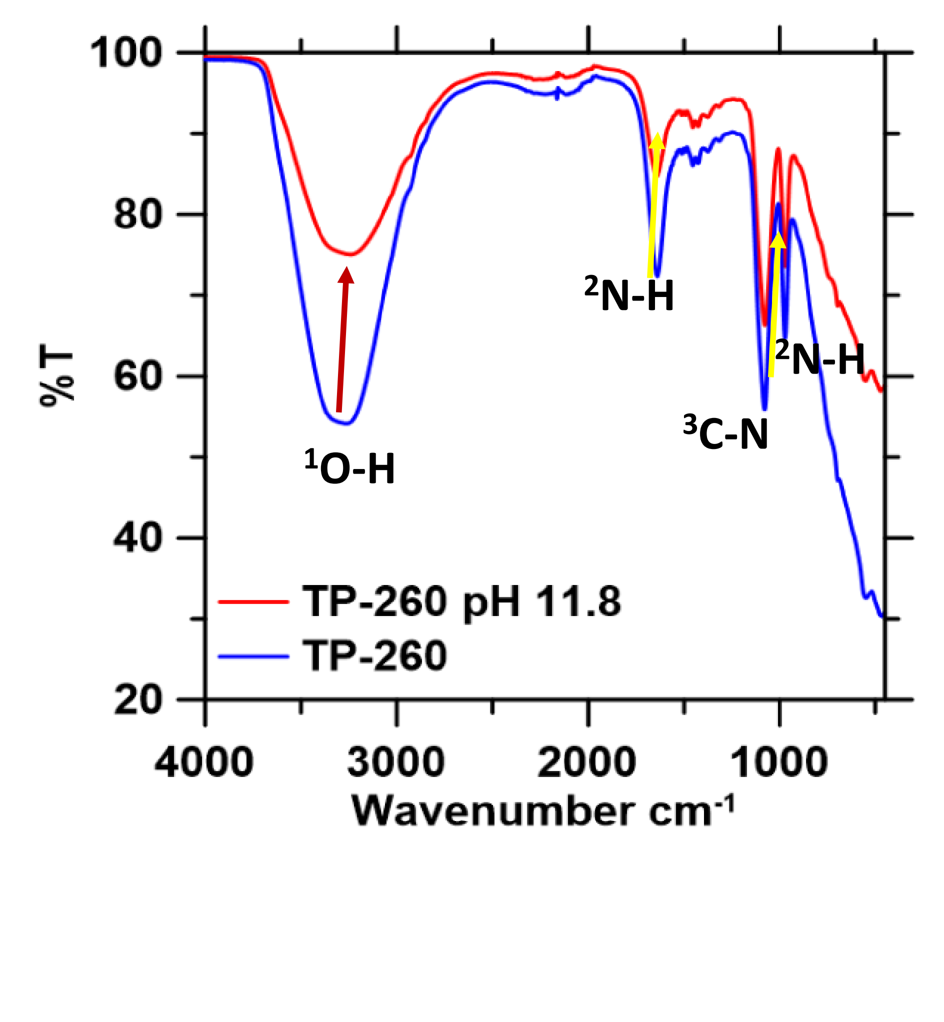
loss of CO_2 may explain differences in calculated and experimental $CaCO_3$ (s) values



FTIR characterization of organic ion exchange resins

- TP-260: Loss of amino methyl phosphonic acid after exposure to water at pH = 11.8





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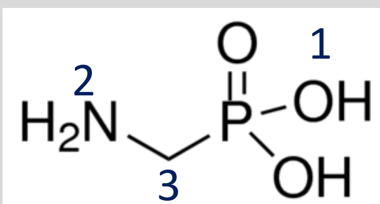
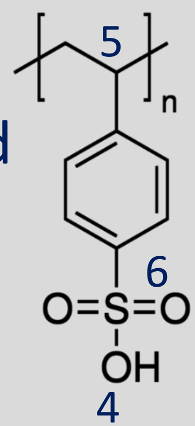
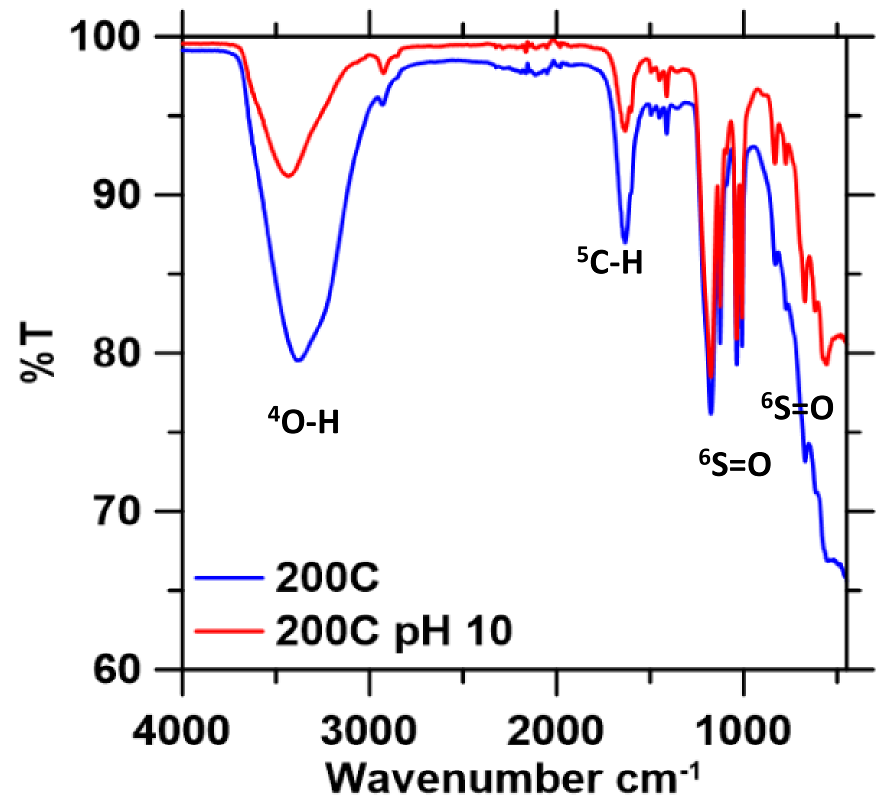


- 200C: Loss of sulfonic acid functional group





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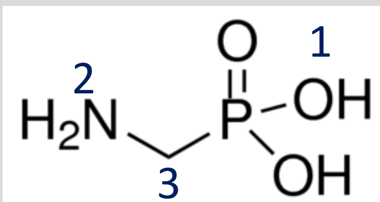
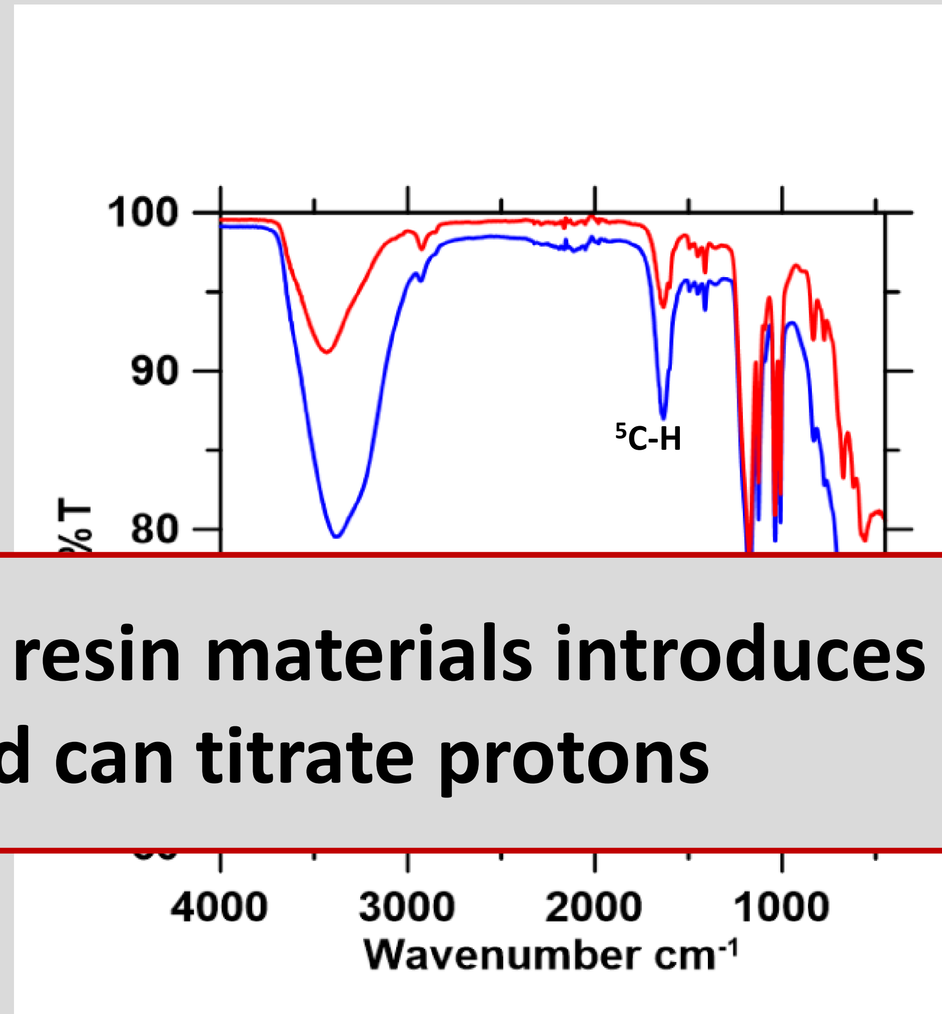
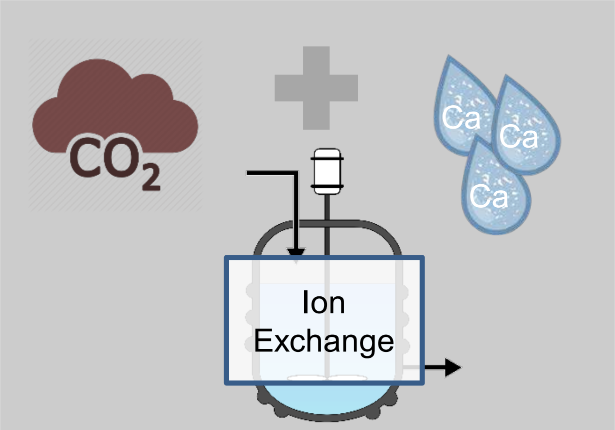




Leaching of active sites on resin materials introduces Na^+ into solution and can titrate protons

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 CO_3^{2-}-rich solution, Reaction of CO_3^{2-}-rich solution with Ca^{2+}-rich produced water forms calcite
- Resins exhibit higher "capacity" and better kinetics, but are unstable in water at low pH



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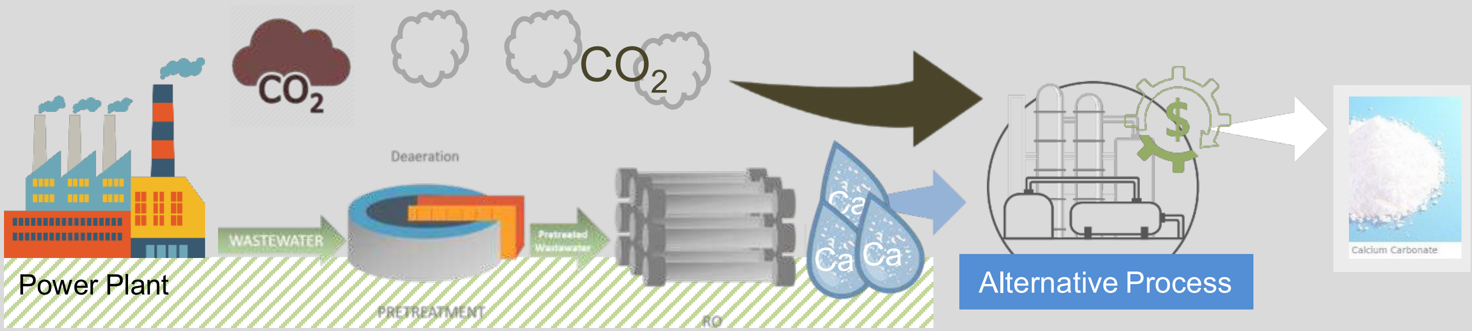
Acknowledgements

- UCLA Institute for Carbon Management
- Sant and Simonetti groups at UCLA; Wang group UW-Madison
- DOE/NETL for funding

Questions?



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