Programmable Nanomaterials for Reversible CO_2 Sequestration

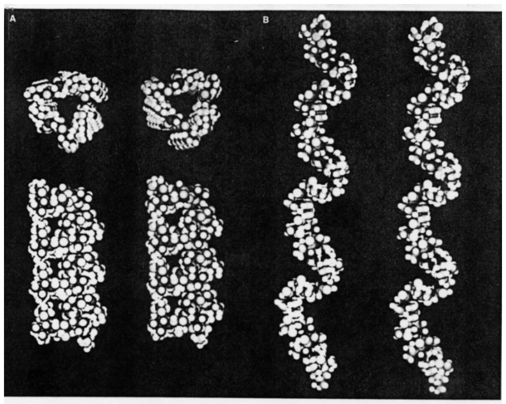
Bruce Bunker, Dale Huber, George Bachand, Bill Smith, Mark Roberts, Pat Brady, Susan Rempe, and Dian Jiao

CO_2 Capture

CO_2 Release

Programmable Polymers

Programmable Enzymes



Angew. Chem. Int. Ed. Engl., 32, 819 (93)

Biochem. J., 385, 715 (05)

Goal: Develop nano-materials that can be used to facilitate the programmable capture and release of CO_2 from water.

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Targets for CO_2 Sequestration

Prevent Global Warming associated with the burning fossil fuels.
(Fuels introduce 6 x 10^9 metric tons (6 GT) of CO_2 into the air each year.)

Remove CO_2 from air.
(Atmosphere = 5.1 x 10^{15} metric tons)

Current CO_2:	**377 ppm (2 x 10^{12} metric tons)**
Removal Goal:	**10^9 metric tons/yr (1 km^3 of liquid CO_2)**
Disposal:	**underground**
Desired Cost:	**\$10/metric ton (4 kcal/mole)**
Alternate:	**treat coal exhaust (10-15% CO_2)**

Processes must be selective, reversible, cheap, and capable of handling billions of tons of CO_2, preferably from air.

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Nature Currently Mediates Atmospheric CO_2 Levels

Natural processes for CO_2 capture/release all involve water.

Oceans (Capture/Release)

Ocean Volume =
2×10^9 GT
2×10^9 km^3

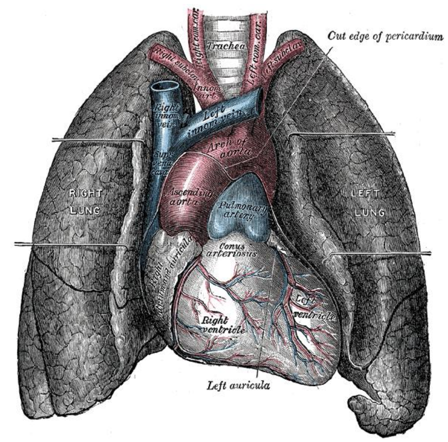
"Dissolved C"
(solubility + biomass) =
37,000 GT

Plants (Capture)

Land Biomass =
11,000 GT

β-carbonic
anhydrase

Animals (Release)



100 kg/yr/liter blood
(Humans exhale 6 GT/yr)

α-carbonic
anhydrase

Question: Can we adopt Nature's processing schemes in artificial systems?

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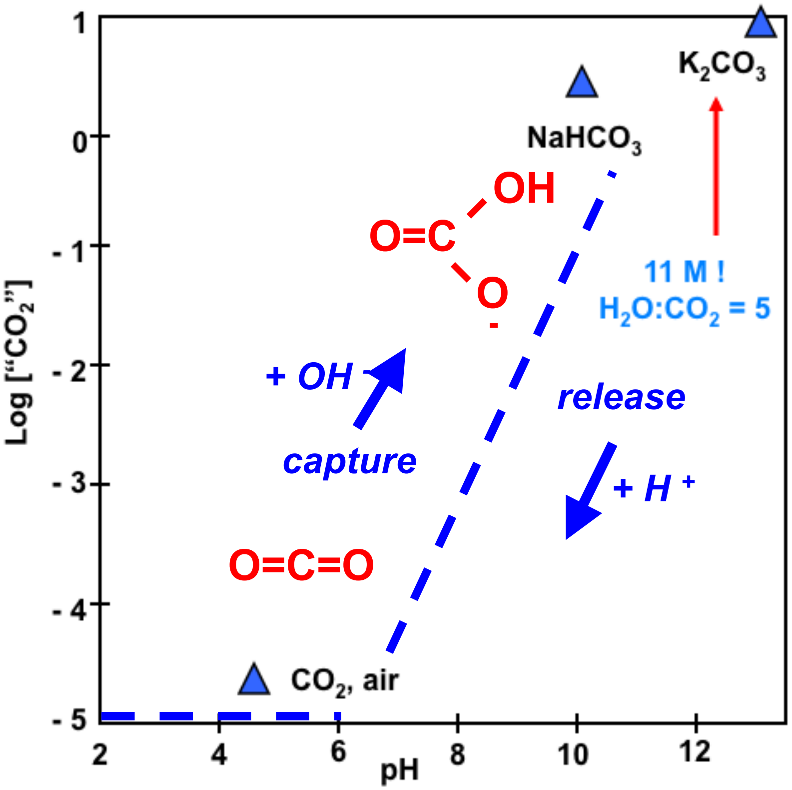
Reversible Sequestration of CO_2 by Water Requires the Inter-conversion between "Insoluble" CO_2 and Soluble Carbonates

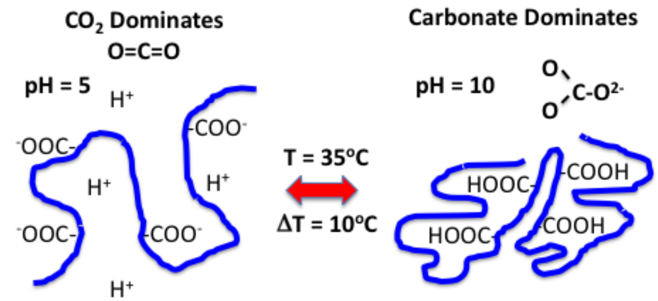
Carbonates for capture <-> CO_2 for release

Solubility



Materials and Mechanisms

Programmable Polymers



Catalytic Enzymes

Nature has developed a process!
Can we adapt it to our needs?

Research Goal: Develop nano-materials that can be used to catalyze reversible CO_2:carbonate inter-conversions.

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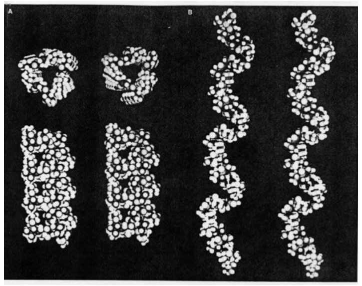
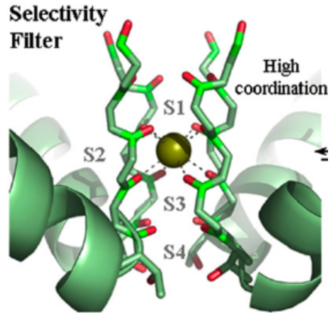
Program Components and Staffing

Programmable Polymers



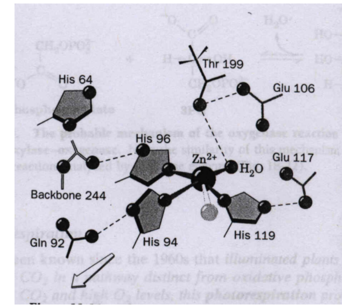
Dale Huber

Theory/Modeling



Susan Rempe, Dian Jiao

Programmable Enzymes



George Bachand

CO_2 Loading/Unloading Experiments

Mark Roberts, Bill Smith

CO_2 Chemistry

Capture

$CO_2(g) \rightarrow CO_2(l)$

$CO_2(l) + OH^- \rightarrow HCO_3^-$

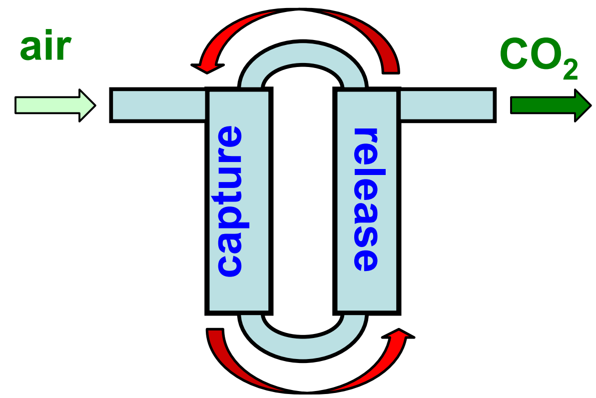
Release

$HCO_3^- + H^+ \rightarrow CO_2\ (l) + H_2O$

$CO_2(l) \rightarrow CO_2(g)$

Bruce Bunker

Process Development



Bill Smith, Pat Brady

Developing understanding and processes for reversible CO_2 capture and release requires the efforts of a multidisciplinary team.

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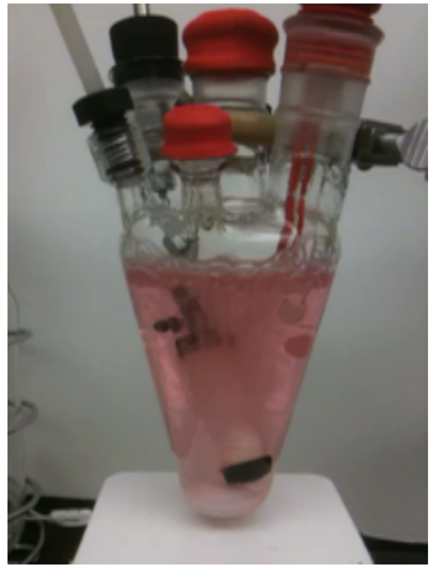
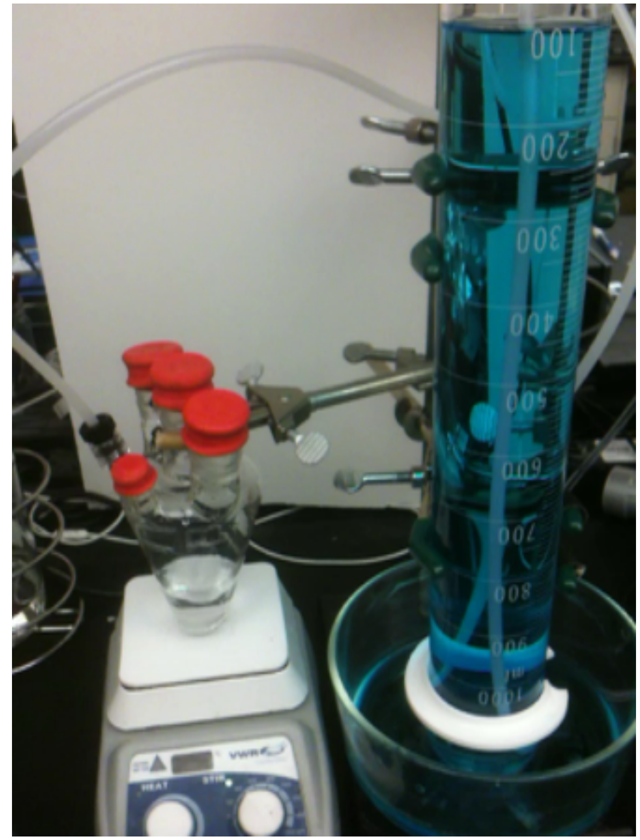
Process Development: Bench Scale Systems

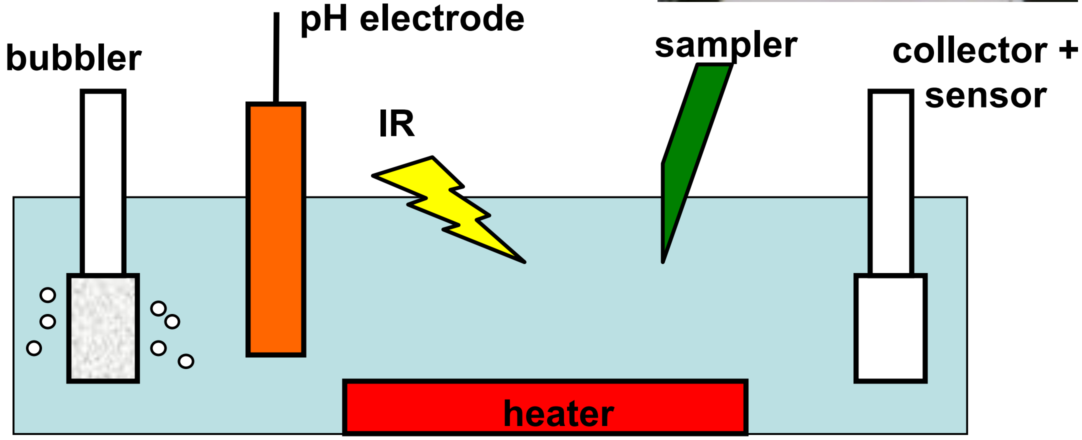
Loading



Components:
Gas handling hardware
CO_2 sensor
Solution reaction vessel
pH measurement/titration
FTIR spectroscopy

Unloading





Goal: Methodologies have been developed to introduce CO_2 gas, measure dissolved CO_2 and carbonates, collect and measure CO_2 gas, and determine the kinetics of CO_2 loading/unloading.

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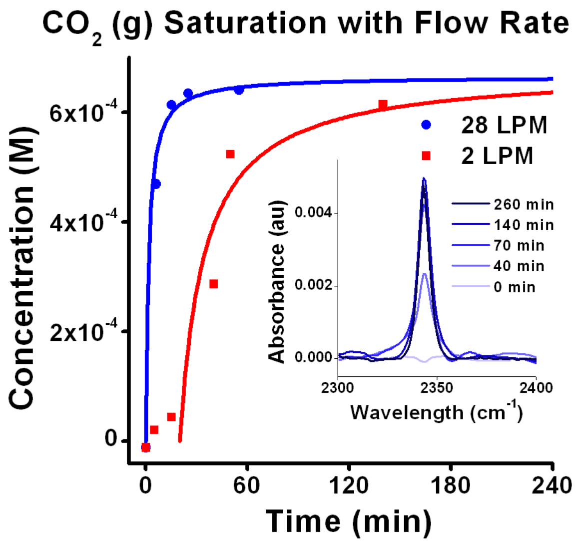
Reversible CO_2 Sequestration: Baseline Experiments

CO_2 Loading

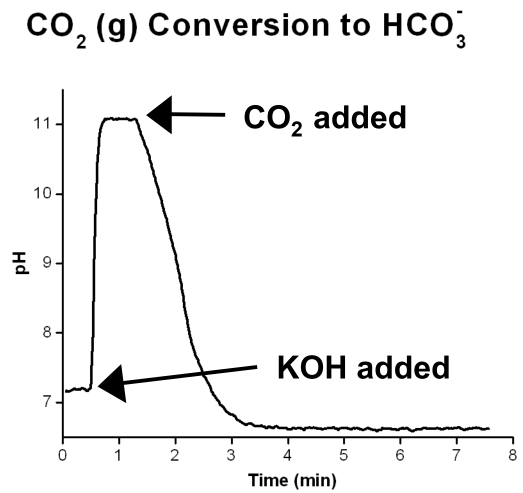
$CO_2(g) \rightarrow CO_2(l)$



- CO_2 dissolution in water can be rate limiting.
- Bubbler design is critical.
- Rate vs. efficiency

CO_2 to Carbonates

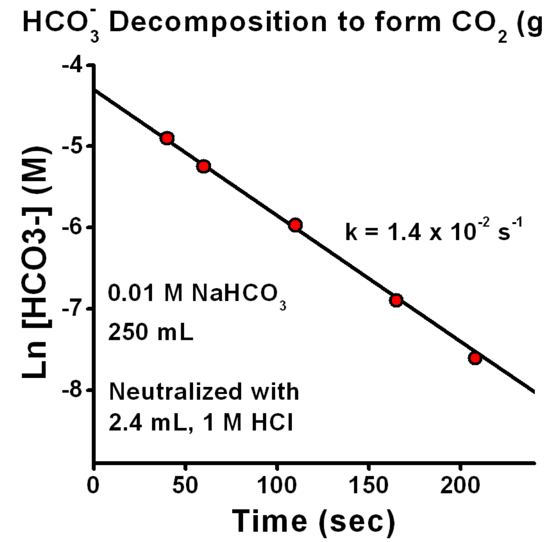
$CO_2(l) + OH^- \rightarrow HCO_3^-$



- High CO_2 loadings are achieved in base.
- Rates increase by 10 for unit increase in pH.
- Reaction self limits as base is consumed and pH drops.

CO_2 Unloading

$HCO_3- + H^+ \rightarrow CO_2(g) + H_2O$



- Acid promotes decomposition.
- Decomposition is rapid until acid is consumed.
- CO_2 is released until concentration drops to CO_2 solubility limit.

The rate and extent of CO_2 loading and unloading in water have been measured in the absence of programmable materials (enzymes and polymers).

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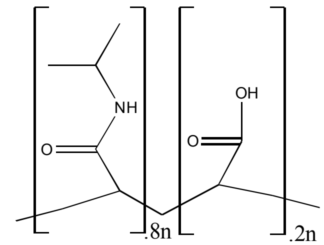
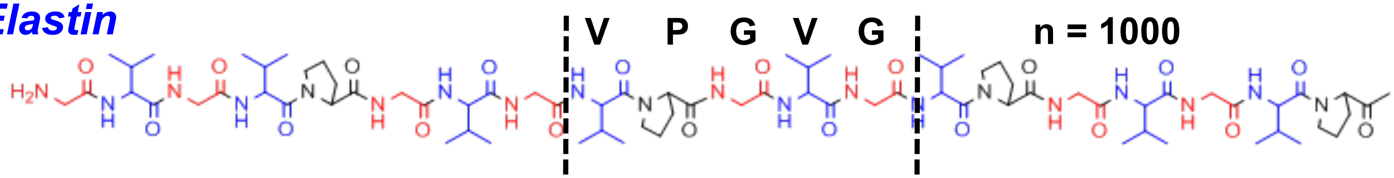
Proposed Research: Programmable Polymers

Polymer formulations will be based on elastin or PNIPAM.
Polymer compositions will be formulated and tested for:

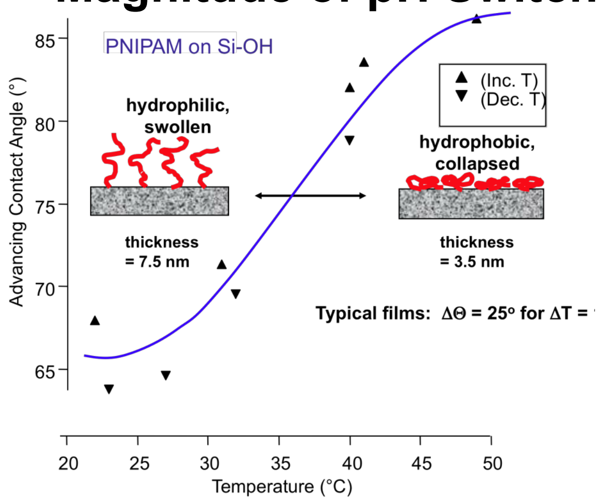
PNIPAM



Elastin



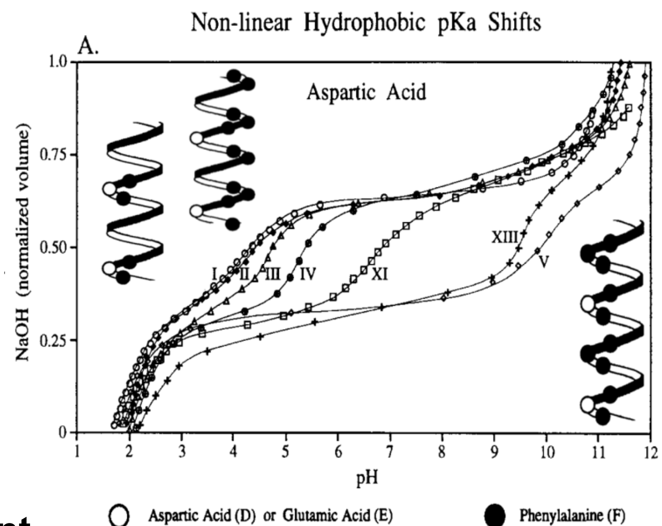
Magnitude of pH Switch



Substitutions to maximize the change in the polymer environment (hydrophilic to hydrophobic).

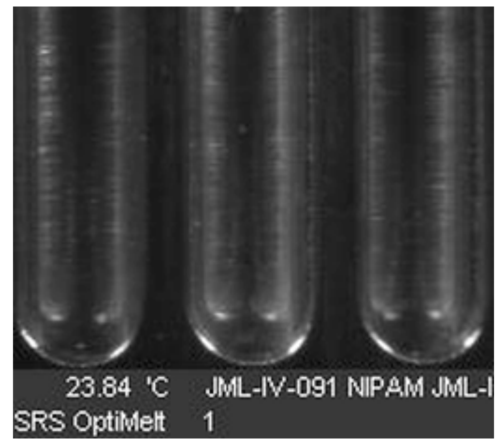
Hydrophilic → low pH (H^+ release)
Hydrophobic → high pH (H^+ capture)

Range of pH Switch



Substitutions in the acid group and local environment to tune the pKa.

Tethering/Deployment



Tune molecular weight to control dispersion in solution, or groups to anchor polymer to substrate and/or enzymes.

Goal: Determine the extent to which polymers can program pH to promote CO_2:carbonate conversions or switch enzyme activity.

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Programmable Polymers: Results to Date

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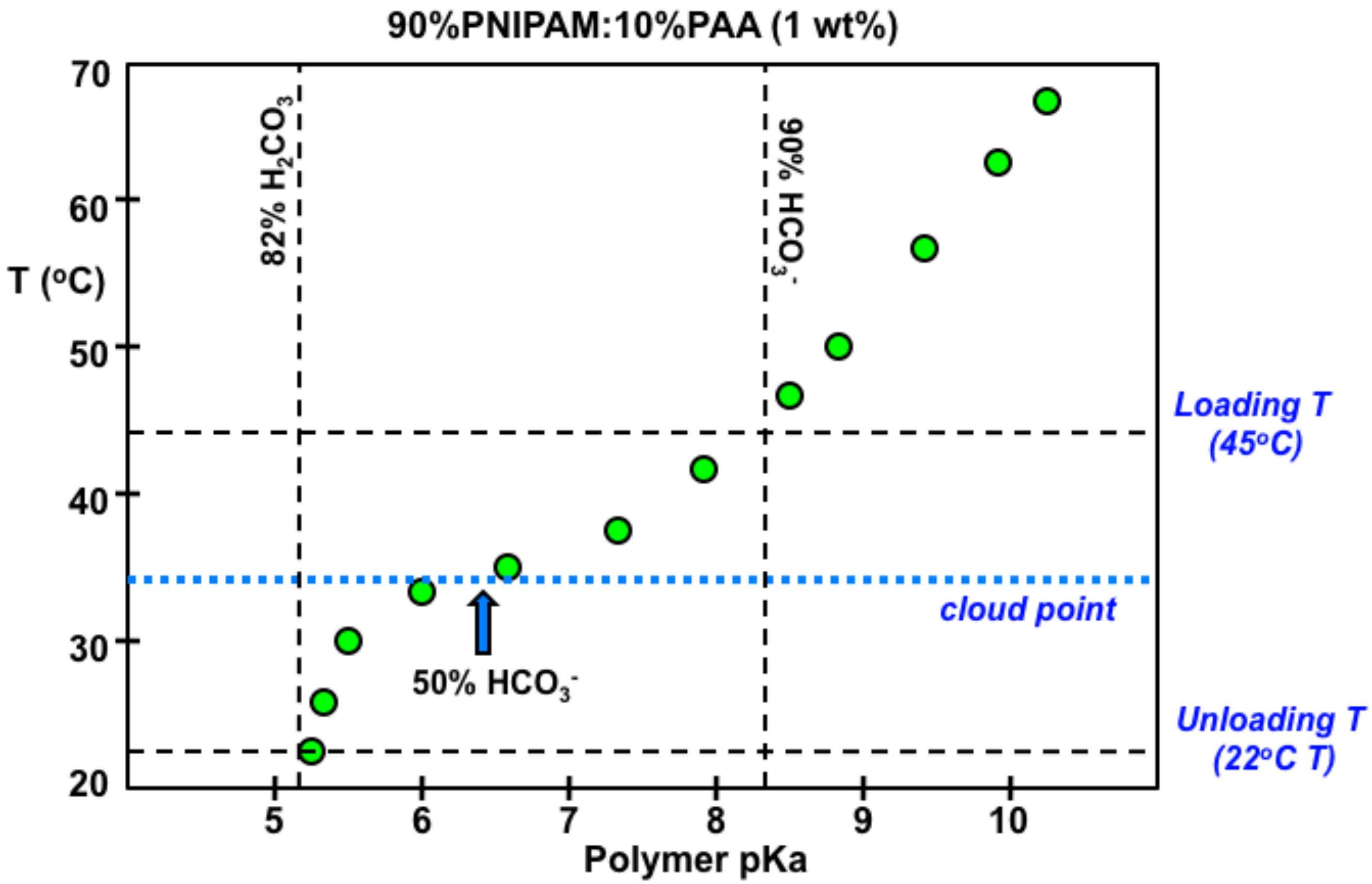
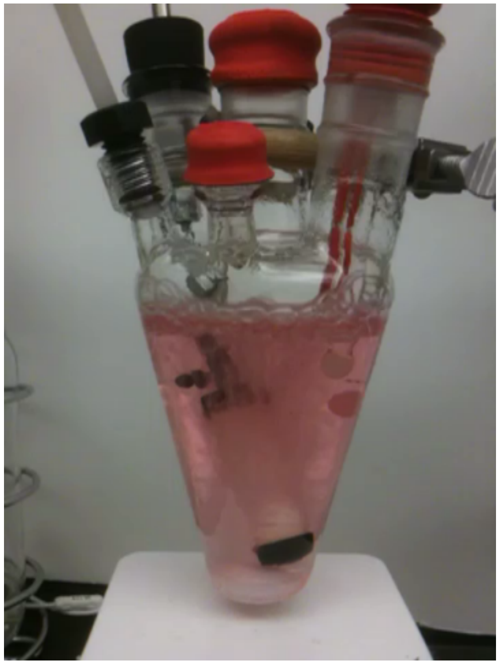


1) The initial polymer formulation (PNIPAM/PAA) has been synthesized.
2) Large concentrations of the polymer can be dissolved into water (> 5%).
3) The polymer transition temperature in water is 34°C.
4) The transition induces large, reversible changes in solution pH.
5) *Programming of the polymer should suffice for loading/unloading of CO_2.*

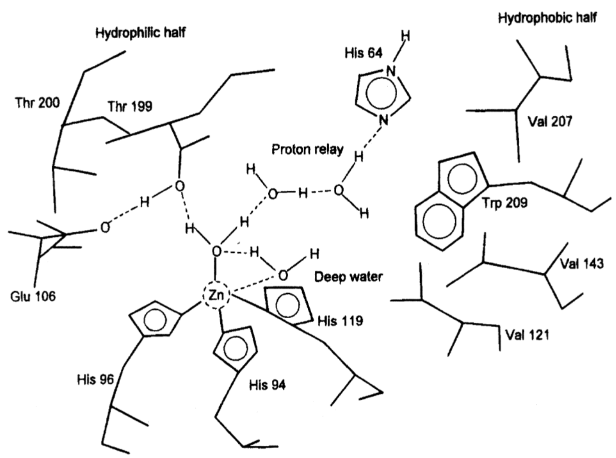
Proposed Research: Switchable Enzymes

Test Enzyme Activity



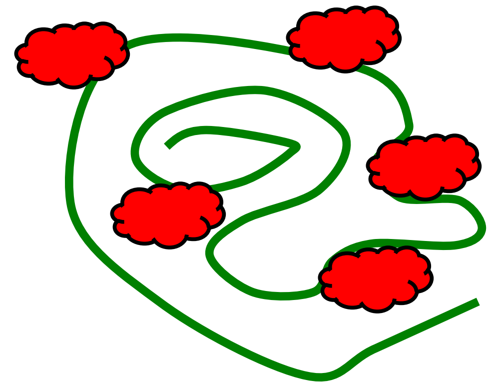
- Determine conversion kinetics
- Determine processing window
- Evaluate stability

Engineer Enzymes for Processes



- Improve stability
- Optimize switching
- Provide tethering

Develop Enzyme:Polymer Hybrids



- Enzyme + polymer
- Match performance

Goal: Explore the incorporation of carbonic anhydrase into reversible CO_2 sequestration processes.

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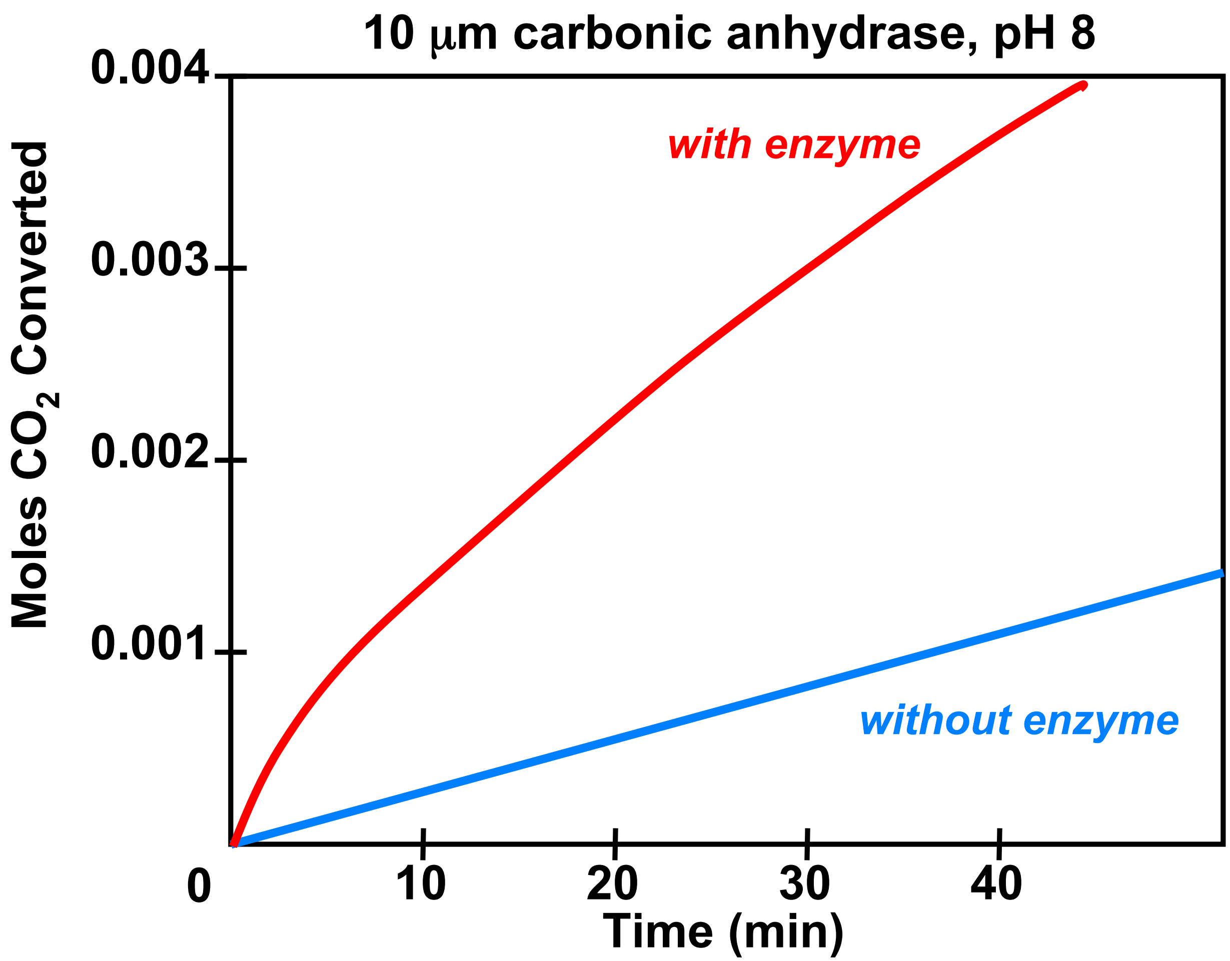
Switchable Enzymes: Results to Date

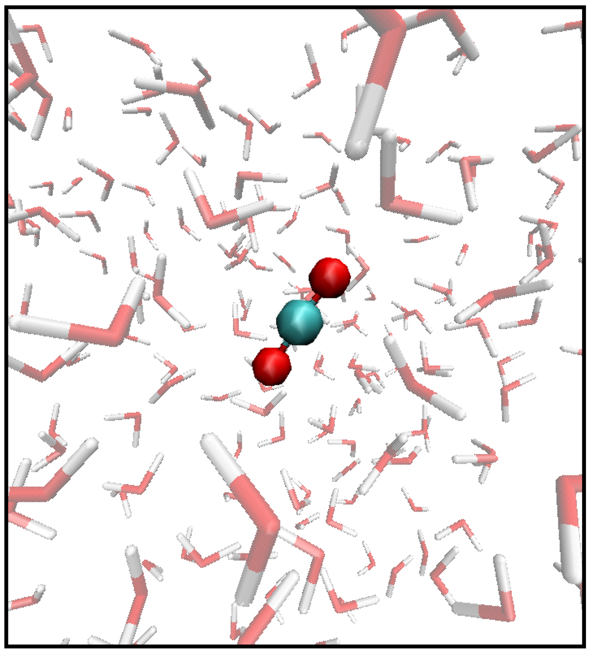


1) Small enzyme concentrations (10^{-5} M) triple CO_2-to-HCO_3^- conversion rates.
2) High enzyme concentrations should provide order-of-magnitude increases.

Modeling Results: CO_2 Hydration and Hydrolysis Mechanisms

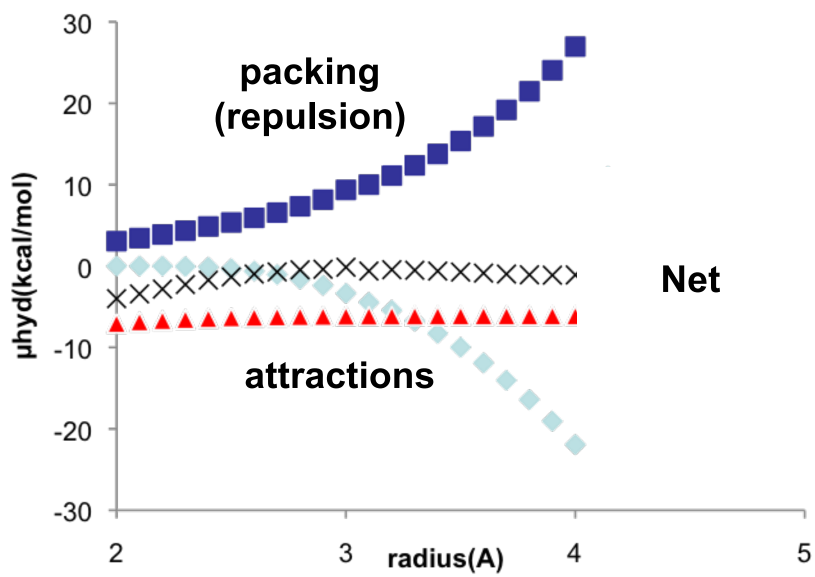
Methodologies have been developed to study CO_2:water interactions.
Example: Hydration energies calculated using Quasi-chemical theory.

CO_2 Interacting with H_2O Molecules



Contributions to CO_2 Solvation Energy

ΔG_{qct} = 0.4 kcal/mole
ΔG_{exp} = 0.2 kcal/mole



Results show why solvation of hydrophobic CO_2 in water is unfavorable.
Repusive molecular packing off-sets ionic and van der Waals attractions.

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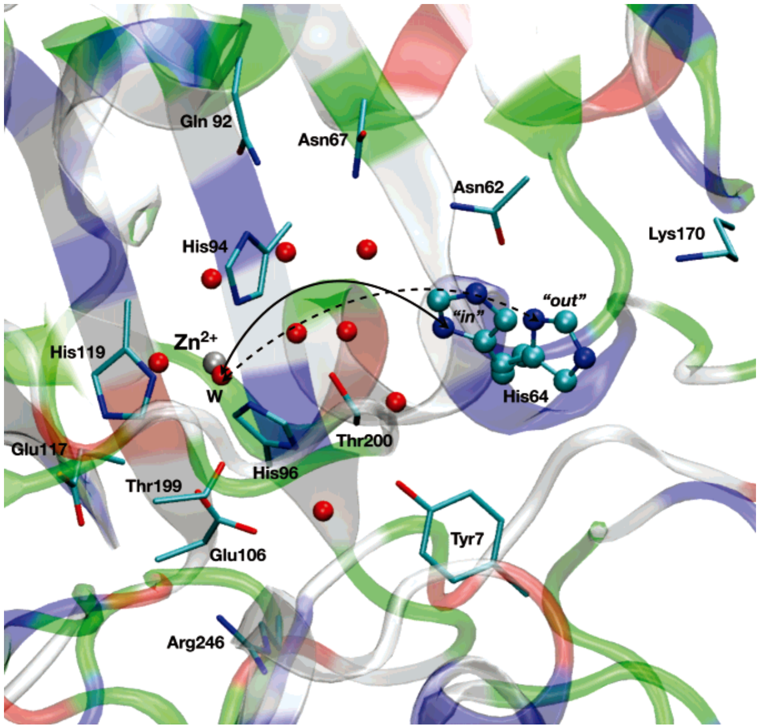
Proposed Research: Theory and Modeling

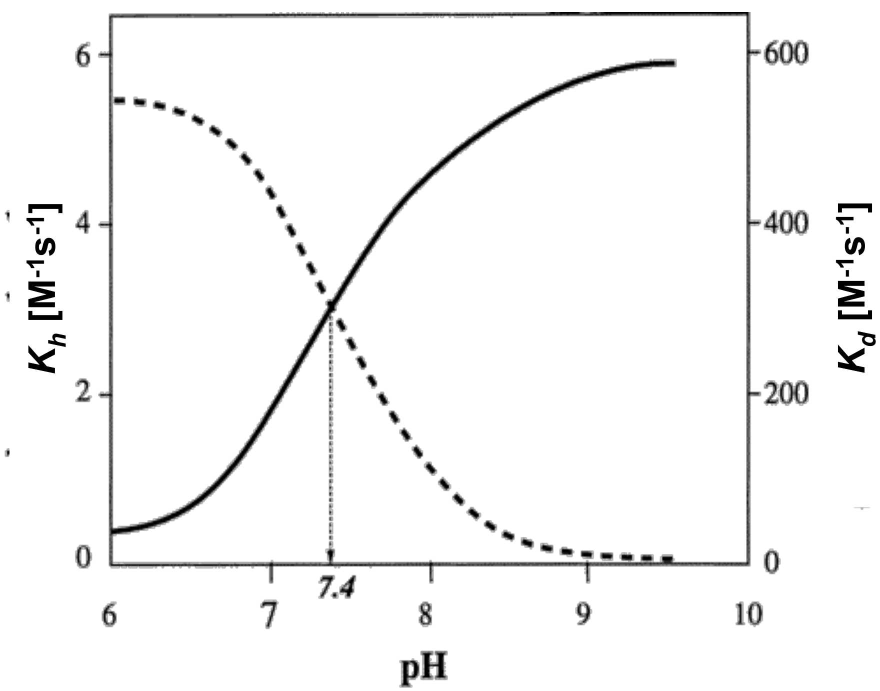
Goal: Predict rate constants for CO_2:carbonate conversions in water.

$$CO_2 + EnZn{-}OH^- \underset{K_d}{\overset{K_h}{\longleftrightarrow}} [EnZn{-}^{-}OCO_2H] \longleftrightarrow HCO_3^- + EnZn{-}OH_2$$

Zn-Complex in Carbonic Anhydrase



Forward/Reverse Rate Constants vs. pH



Example: Model the kinetics of CO_2 hydration and dehydration by the Zn-containing active site in carbonic anhydrase.

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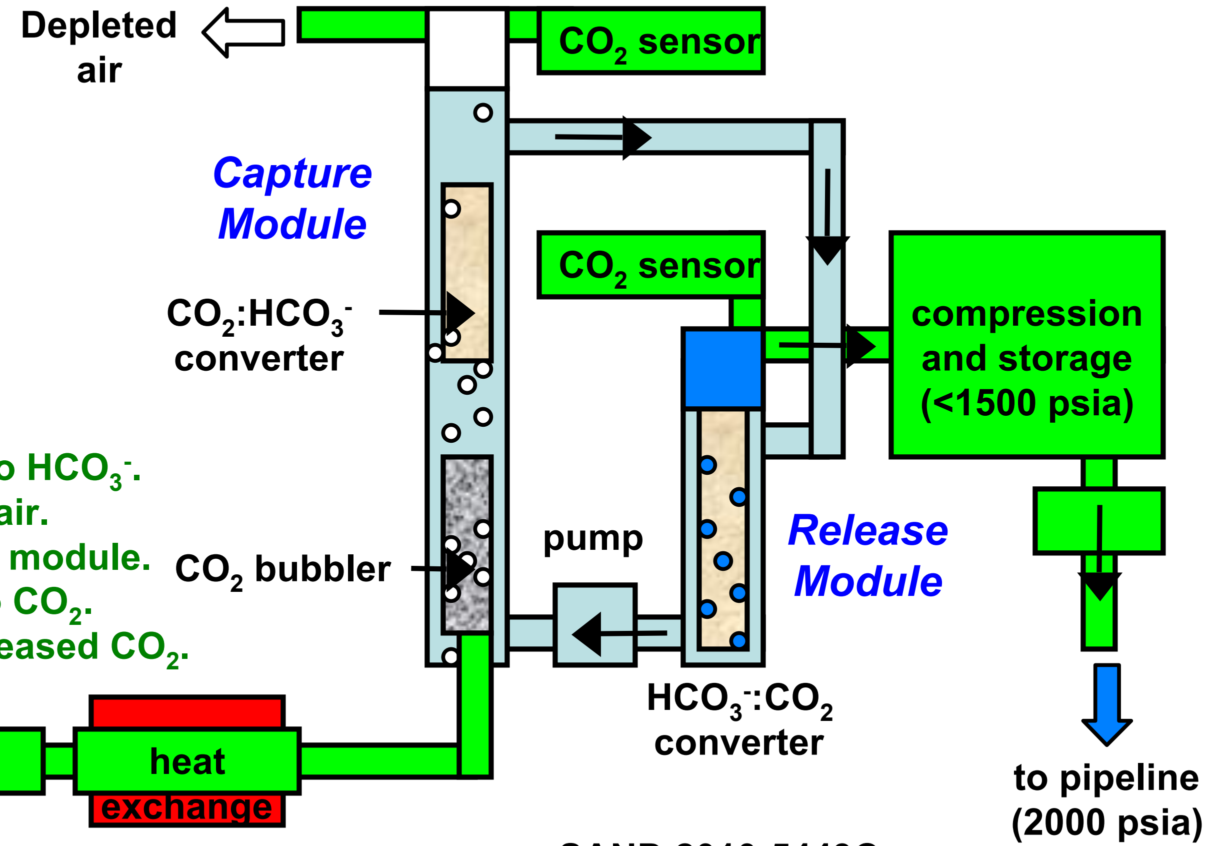
Proposed Research: Process Development

Prototype system explores reversible CO_2 capture using batch and continuous processes. Switchable materials could either be supported or dispersed in the liquid.

Step 1: Air input, conditioning.
Step 2: CO_2 capture, conversion to HCO_3^-.
Step 3: Removal of CO_2-depleted air.
Step 4: Water transport to release module.
Step 5: HCO3- conversion back to CO_2.
Step 6: Collection, handling of released CO_2.



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Goal: Provide a test bed for exploring a wide range of reversible CO_2 sequestration processes that deploy switchable nanomaterials.

Examples: Process Development Options

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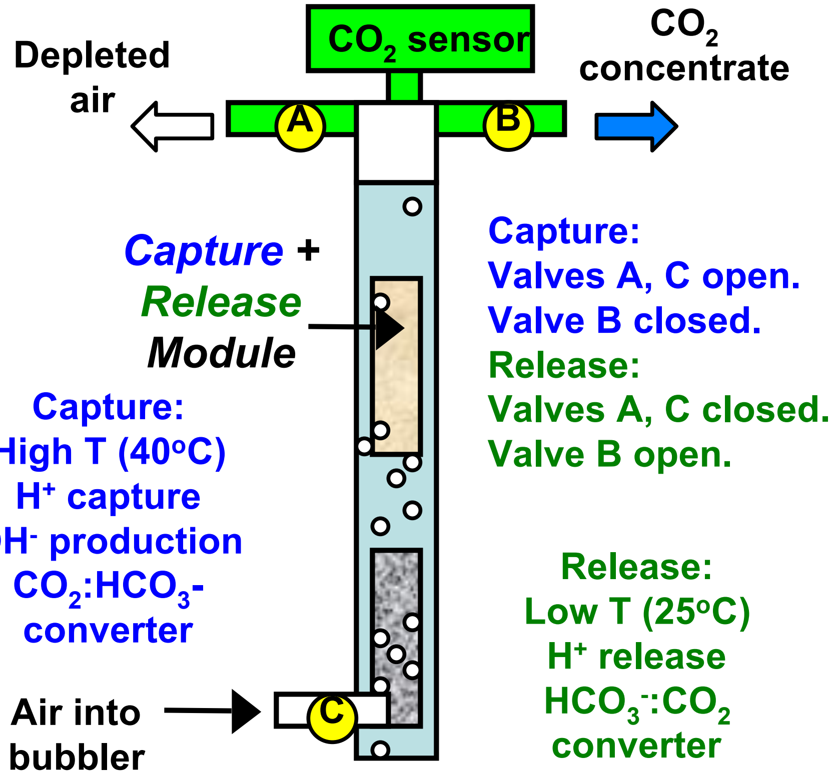
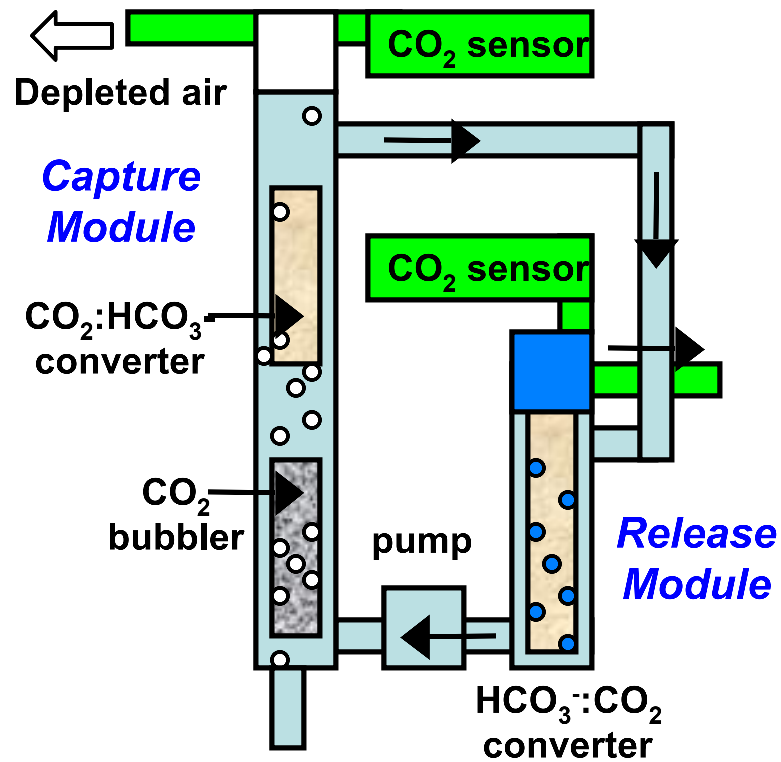
Batch Process: Temperature Programming of Polymer pH



Continuous Process: Enzymes + pH Control



Process A:
Single module contains programmable polymer.
Polymer triggers capture or release with modest Δ T.

Process B:
At intermediate pH, one enzyme continuously loads, while the second enzyme unloads.

Goal: Provide a test bed for exploring a wide range of reversible CO_2 sequestration processes that deploy switchable nanomaterials.

Program Benefits

Scientific and Technical Merits:

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Exploring water as a reversible agent for CO_2 capture.

1) Water is cheap, abundant, and "process-friendly".
2) Our programmable materials are "green" and benign.
3) The work could impact other technologies (e.g. artificial lungs).

Programmatic Merits:

Technical visibility and funding opportunities in key research areas.

1) Programmable materials (for CO_2, pH, etc.).
2) Hybrid nanomaterials.
3) Complements Sandia's "Sunshine-to-Petrol" Grand Challenge.
4) Complements Columbia/SNL ARPA-E proposal.
5) Promotes competing for Federal CO_2 sequestration funding (BES).

Establish Sandia as a leader in developing the science and technology needed to mitigate Global Warming while allowing for the safe use of fossil fuels.