

# Thermally Programmable pH Buffers

## Programmable Materials for Reversible CO<sub>2</sub> Sequestration

Dara Van Gough, Bruce C Bunker, Mark E Roberts,\*  
Dale L Huber, and Diana Moore

Sandia National Laboratories, Albuquerque, NM

\*Clemson University, Clemson, SC



# Targets for CO<sub>2</sub> Sequestration

*Prevent Global Warming associated with the burning fossil fuels.  
(Fuels introduce  $6 \times 10^9$  metric tons (6 GT) of CO<sub>2</sub> into the air each year.)*

*Remove CO<sub>2</sub> from air.  
(Atmosphere =  $5.1 \times 10^{15}$  metric tons)*

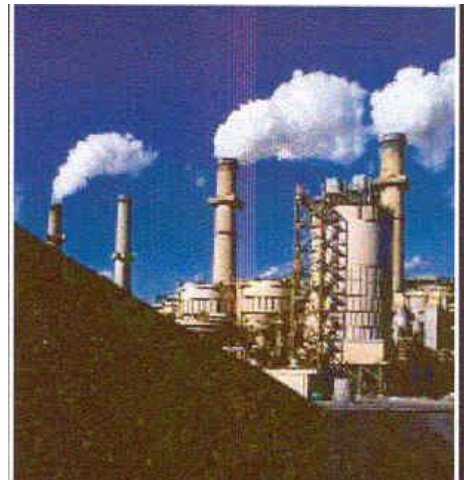
**Current CO<sub>2</sub>:** 377 ppm  
( $2 \times 10^{12}$  metric tons)

**Removal Goal:**  $10^9$  metric tons/yr  
(1 km<sup>3</sup> of liquid CO<sub>2</sub>)

**Disposal:** underground

**Desired Cost:** \$10/metric ton  
(4 kcal/mole)

**Alternate:** treat coal exhaust  
(10-15% CO<sub>2</sub>)



**Processes must be selective, reversible, cheap, and capable of handling billions of tons of CO<sub>2</sub>, preferably from air.**

# Nature Currently Mediates Atmospheric CO<sub>2</sub> Levels

*Natural processes for CO<sub>2</sub> capture/release all involve water.*

## Oceans (Capture/Release)



Ocean Volume =  
 $2 \times 10^9$  GT  
 $2 \times 10^9$  km<sup>3</sup>

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

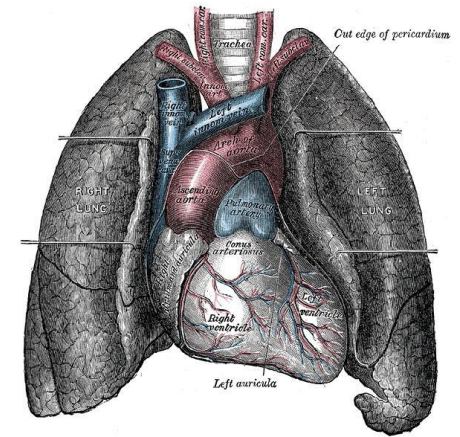
## Plants (Capture)



Land Biomass =  
11,000 GT

β-carbonic  
anhydrase

## Animals (Release)



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

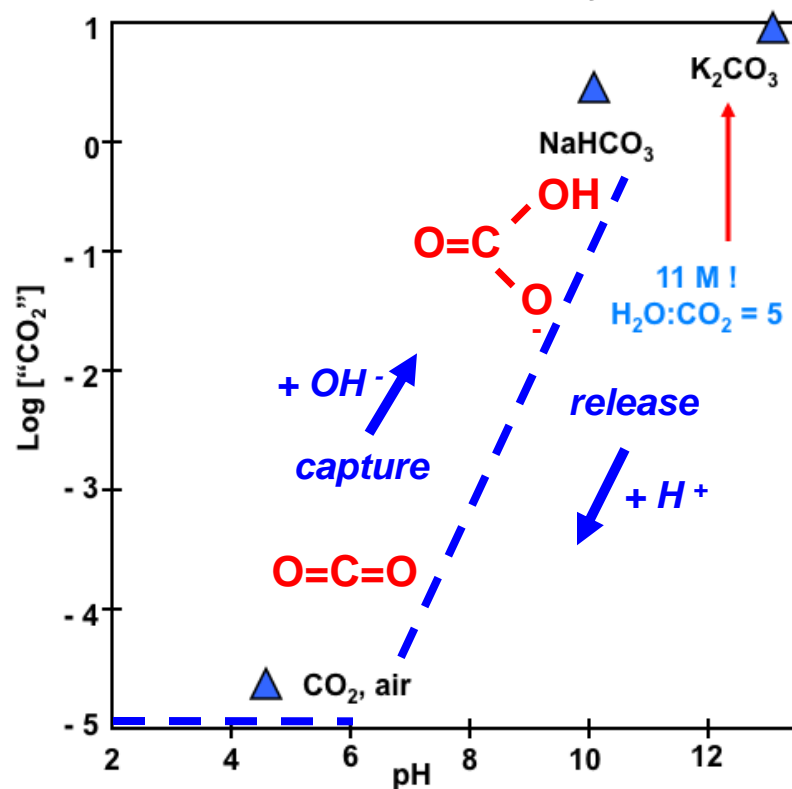
α-carbonic  
anhydrase

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

# Reversible Sequestration of CO<sub>2</sub> Requires the Inter-conversion from “Insoluble” and Soluble

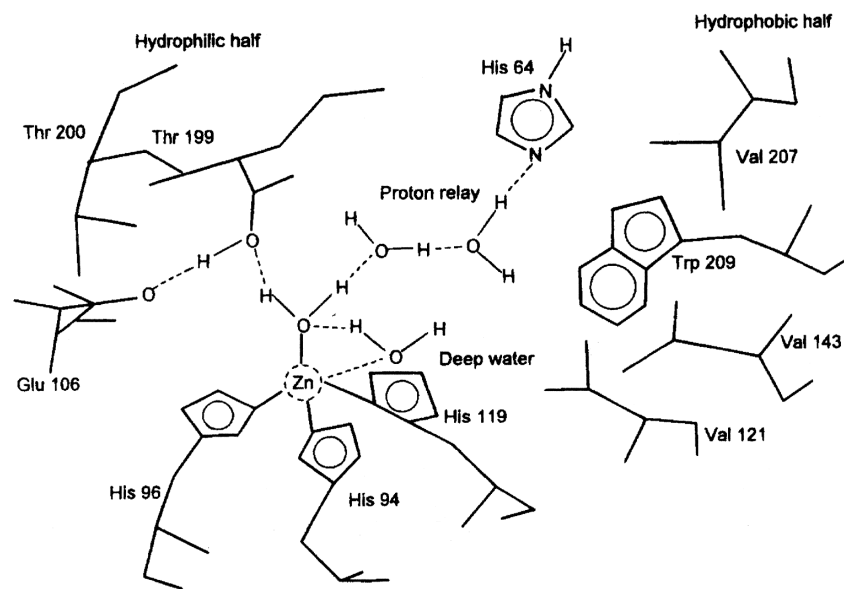
Carbonates for capture  $\leftrightarrow$  CO<sub>2</sub> for release

## Solubility



$\Delta$ [“CO<sub>2</sub>”] of 100,000 is possible.  
Requirement:  $\Delta$ “pH” = 4-5.

## Catalytic Enzymes (carbonic anhydrase)

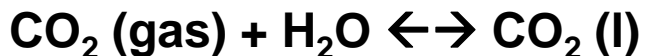


Same enzyme used for loading/unloading.  
Rapid, diffusion-controlled kinetics.  
Requirement:  $\Delta$ pH = 2 (around pH 7).

**Goal: Develop programmable pH buffers that can be used to promote CO<sub>2</sub>:carbonate inter-conversions via pH control.**

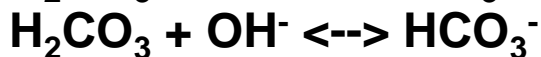
# Chemical Equilibria

## Carbon Dioxide in Water



$$K_{\text{Henry}} = 0.033 \text{ M/atm}$$

$$K_{\text{hyd}} = 2.6 \times 10^{-3}$$



$$K_{\text{a1}} = 1.7 \times 10^{-4} \text{ M}^{-1}$$

$$(K_{\text{app}} = 4.5 \times 10^{-7})$$

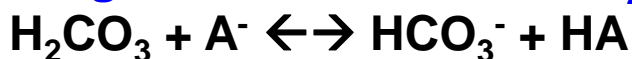
## Polymer Buffers in Water



$$\text{p}K_{\text{p}} = -\log K_{\text{p}}$$

$$K_{\text{p}} = \text{programmable}$$

## Programmable Buffer + CO<sub>2</sub>



loading →

← unloading

$$K_{\text{l}} = K_{\text{app}}/K_{\text{p}} \rightarrow \text{p}K_{\text{p}} > 8.5$$

$$K_{\text{u}} = 1/K_{\text{l}} \rightarrow \text{p}K_{\text{p}} < 5$$

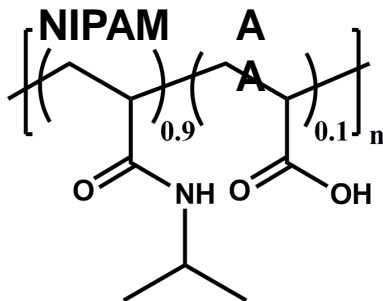
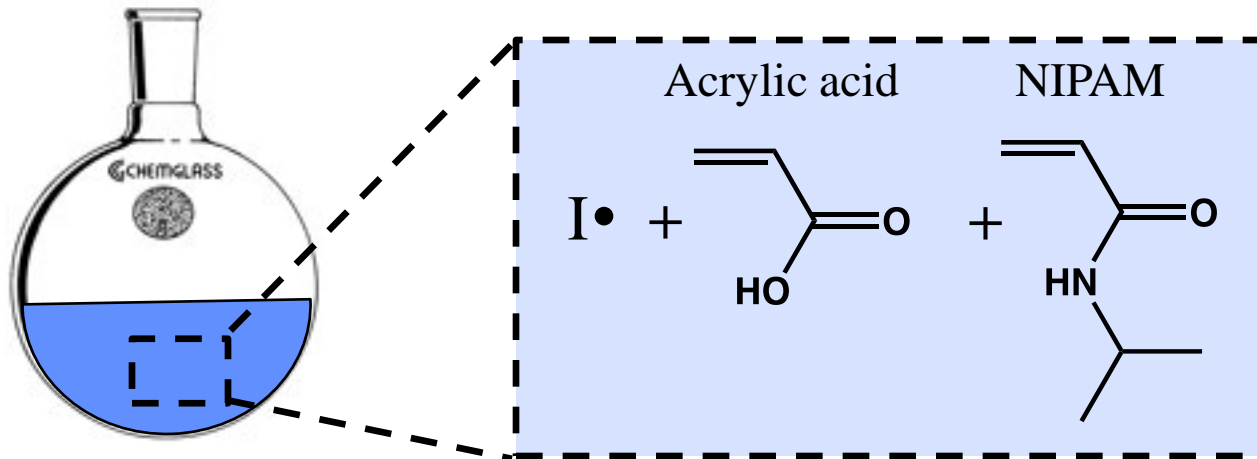
To reversibly load and unload CO<sub>2</sub> in water, a programmable pH buffer is required that can reversibly switch its acid dissociation constant by a factor of over 3000.

# Synthesis of Programmable Materials

*Switching mechanism: a reversible, thermally-activated swelling transition*

Below  $T_c$ : PNIPAM is swollen and hydrophilic.

Above  $T_c$ : PNIPAM is collapsed and hydrophobic.



Synthesis: free radical polymerization (MW = 25,000 g/mole)  
90% NIPAM (n-isopropylacrylamide) → provides programming  
10% Acrylic acid → provides acid-base activity

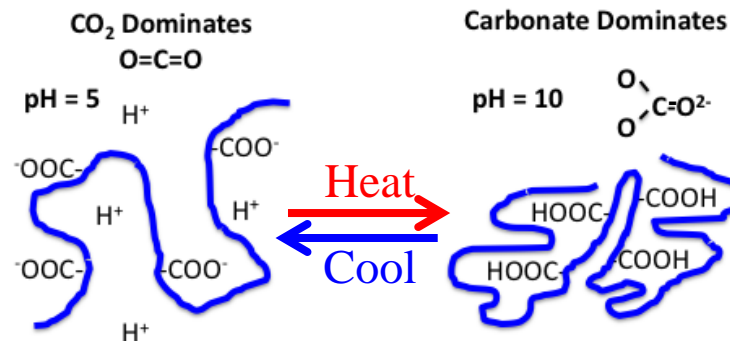
# Programmable pH Buffers: P(NIPAM-AA)

*Switching mechanism: a reversible, thermally-activated swelling transition*

Below  $T_c$ : PNIPAM is swollen and hydrophilic.

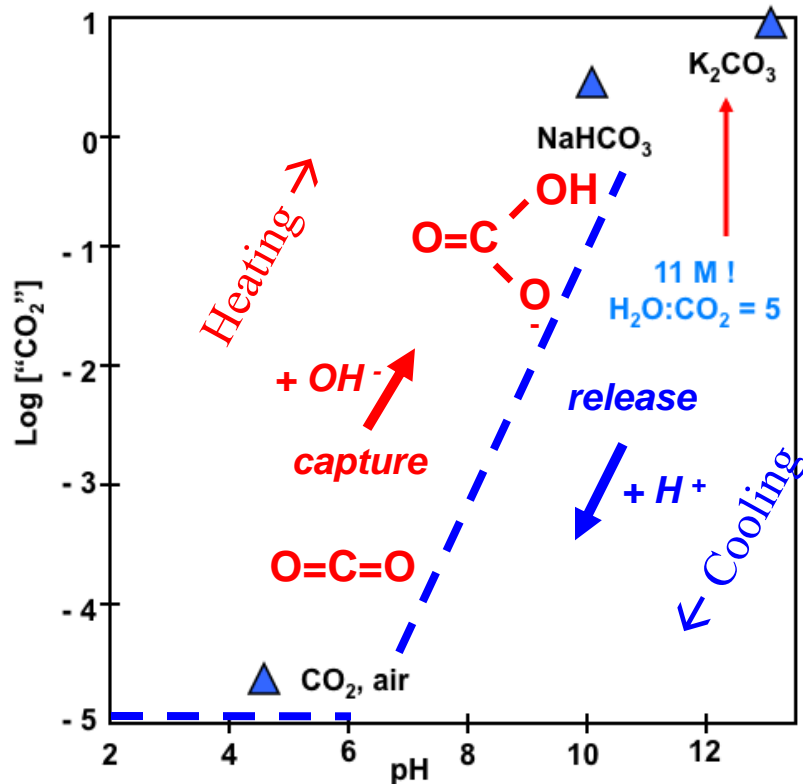
Above  $T_c$ : PNIPAM is collapsed and hydrophobic.

**Hydrophilic:**  
AA ionization promoted  $\rightarrow$   
Low  $pK_p$  for  $\text{CO}_2$  unloading  
 $\text{HA} \rightarrow \text{A}^-$   
 $\text{HCO}_3^- \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{CO}_2(\text{g})$

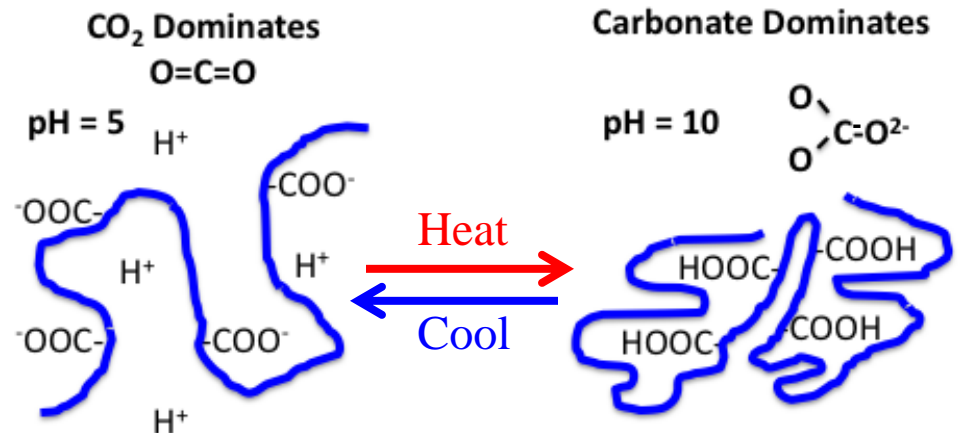


**Hydrophobic:**  
AA ionization suppressed  $\rightarrow$   
High  $pK_p$  for  $\text{CO}_2$  loading  
 $\text{A}^- \rightarrow \text{HA}$   
 $\text{CO}_2(\text{g}) \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{HCO}_3^-$

*The dissociation constant for acrylic acid is sensitive to the local polymer environment, facilitating reversible programming of the pH buffer system.*



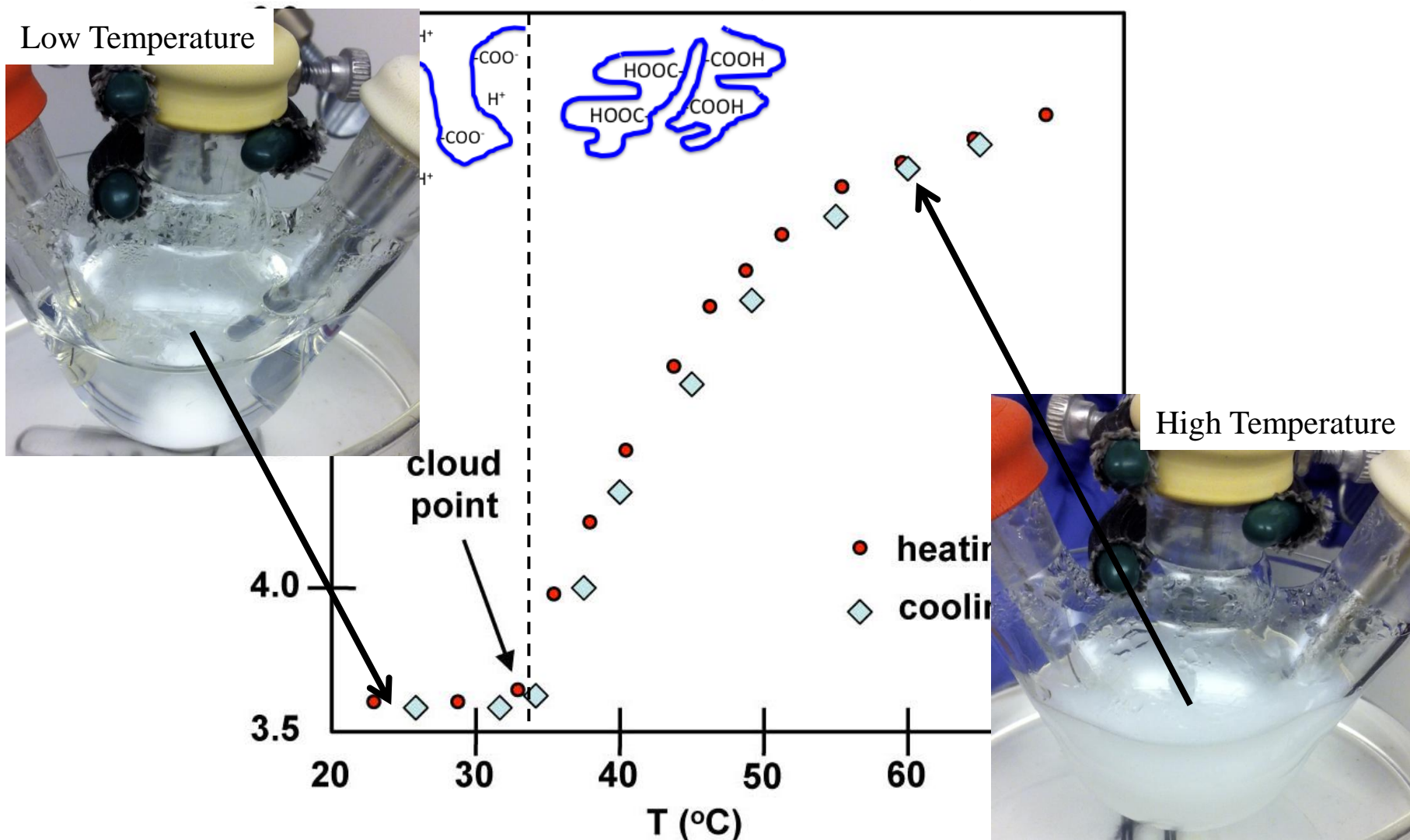
**High T:** PNIPAM is collapsed and hydrophobic



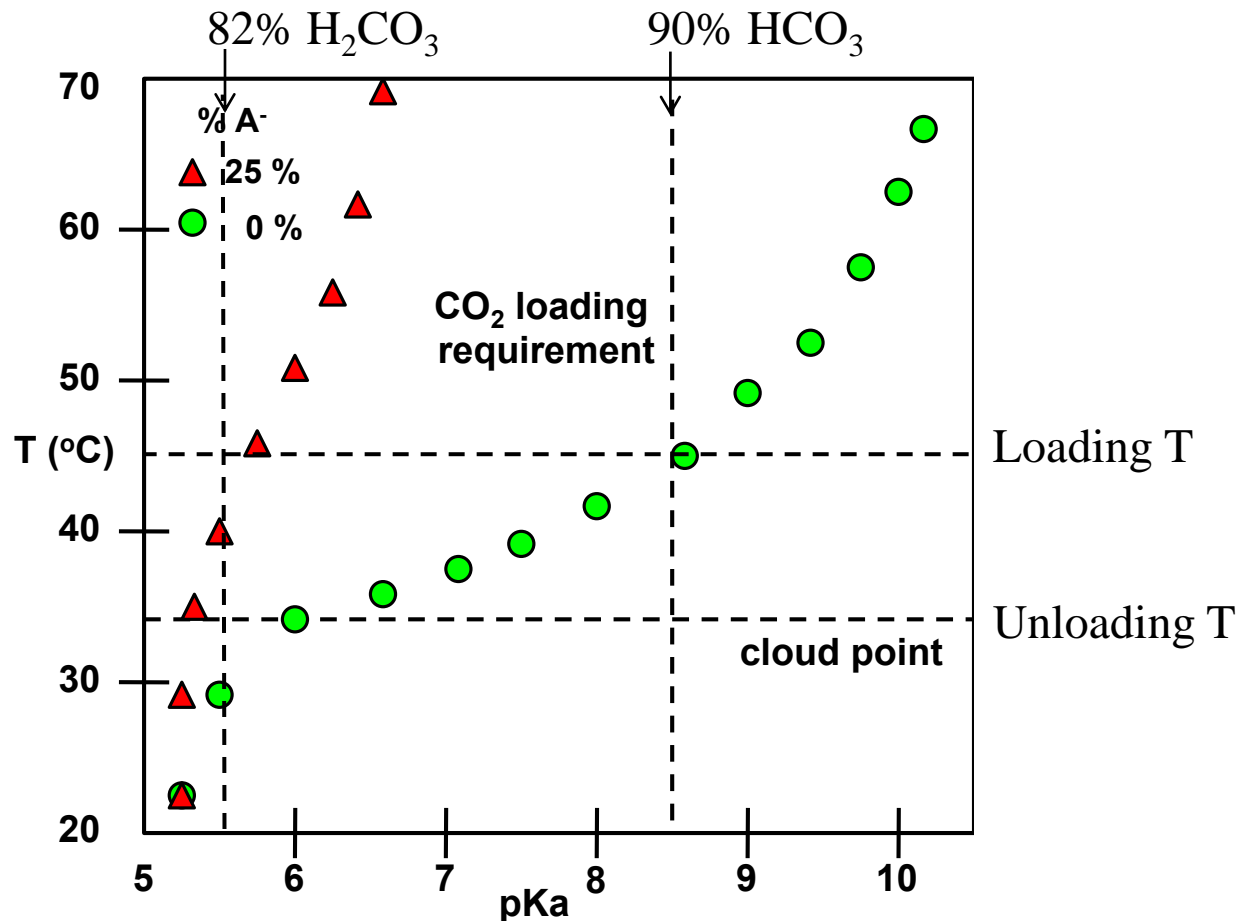
**Carbonates for capture  $\leftrightarrow$  CO<sub>2</sub> for release**

# Programming pH with Temperature

1 wt % solution of P(NIPAM-AA)



# Programming pK<sub>a</sub> with Temperature



- 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<sub>2</sub>.**

# Experimental Setup

Components:

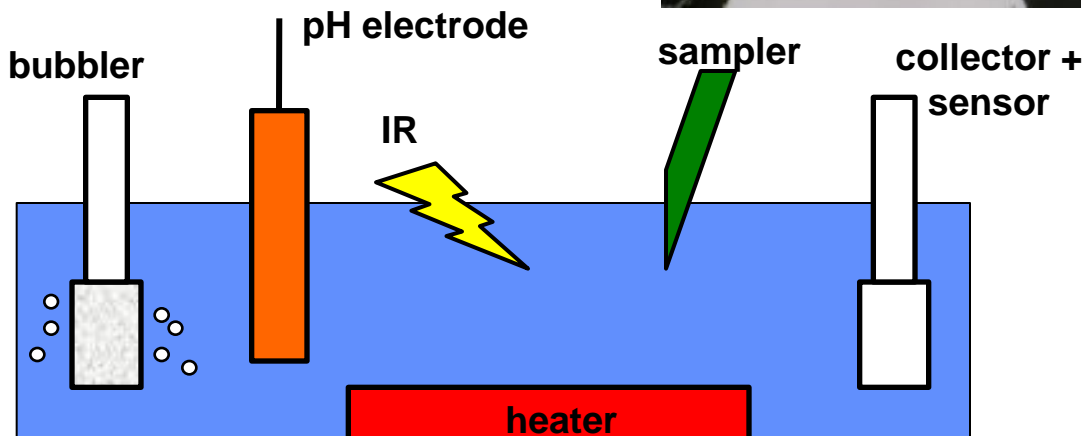
Gas handling hardware

CO<sub>2</sub> sensor

Solution reaction vessel

pH measurement/titration

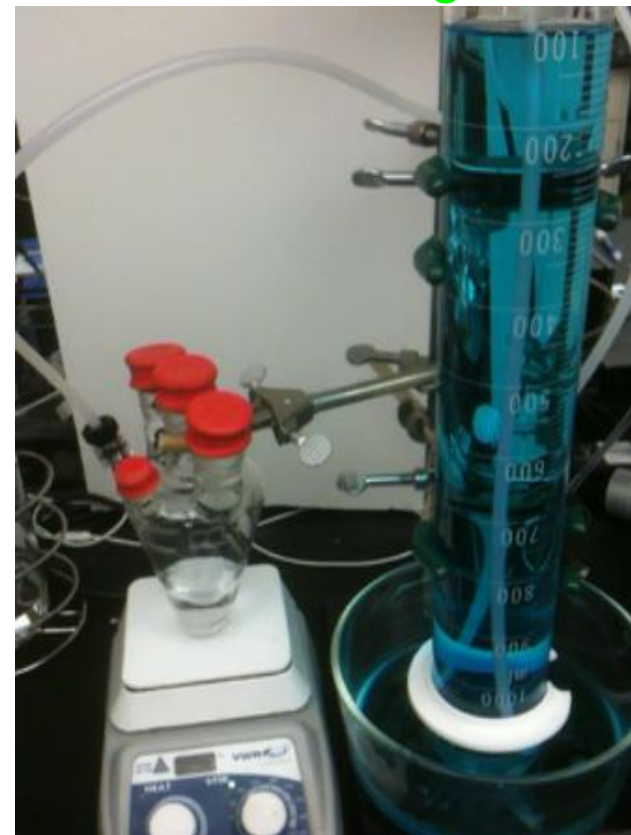
FTIR spectroscopy



**Loading**



**Unloading**



**Goal:** Methodologies have been developed to introduce CO<sub>2</sub> gas, measure dissolved CO<sub>2</sub> and carbonates, collect and measure CO<sub>2</sub> gas, and determine the kinetics of CO<sub>2</sub> loading/unloading.

# Initial Experiments on CO<sub>2</sub> Unloading/Loading

T = 63°C, 100% HCO<sub>3</sub><sup>-</sup>



T = 50°C



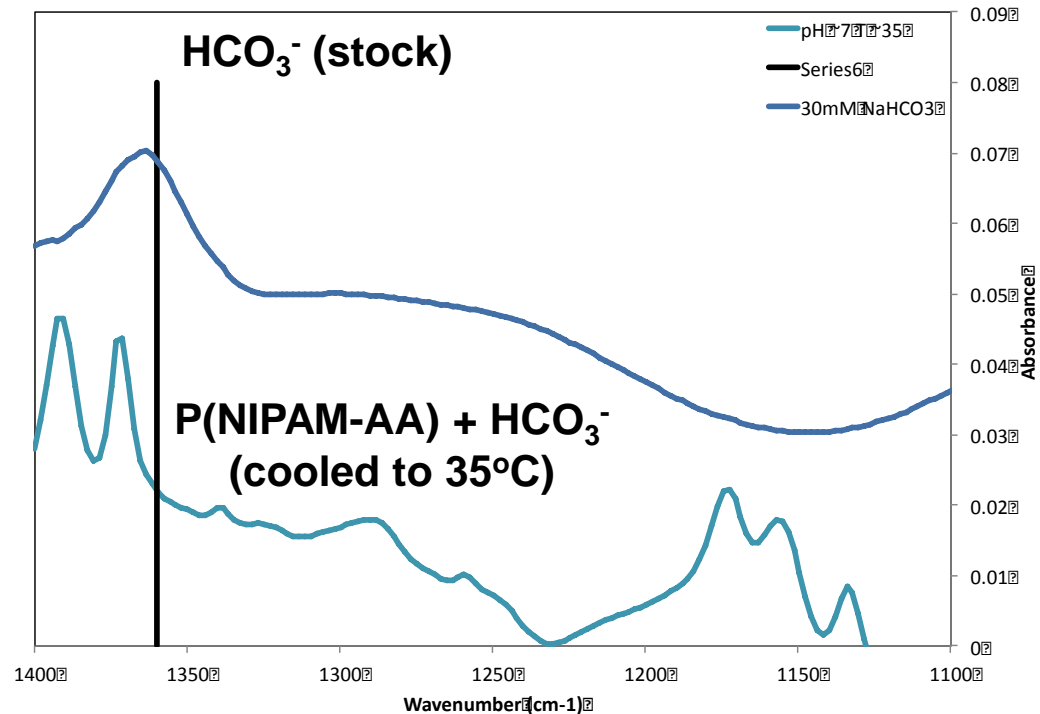
T = 47°C, 65% HCO<sub>3</sub><sup>-</sup>



T = 45°C, 0% HCO<sub>3</sub><sup>-</sup>



## Infrared Spectra for HCO<sub>3</sub><sup>-</sup> Unloading



**Good News** → Programmed CO<sub>2</sub> unloading is successful.

HCO<sub>3</sub><sup>-</sup> is stable in contact with P(NIPAM-AA) above T<sub>c</sub>.

HCO<sub>3</sub><sup>-</sup> completely decomposes to release CO<sub>2</sub>(g) as T drops below T<sub>c</sub>.

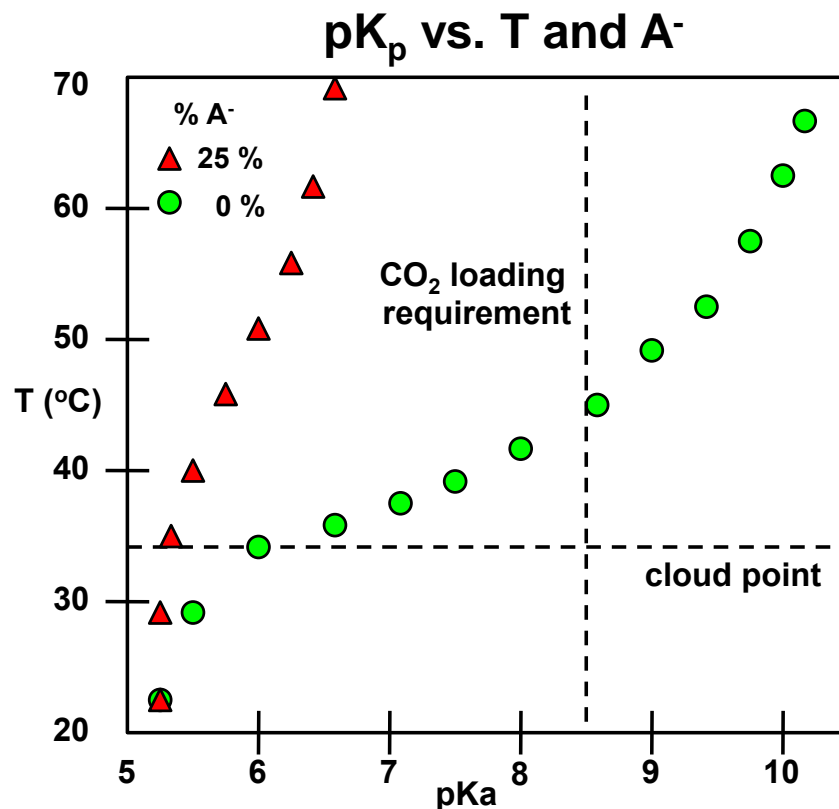
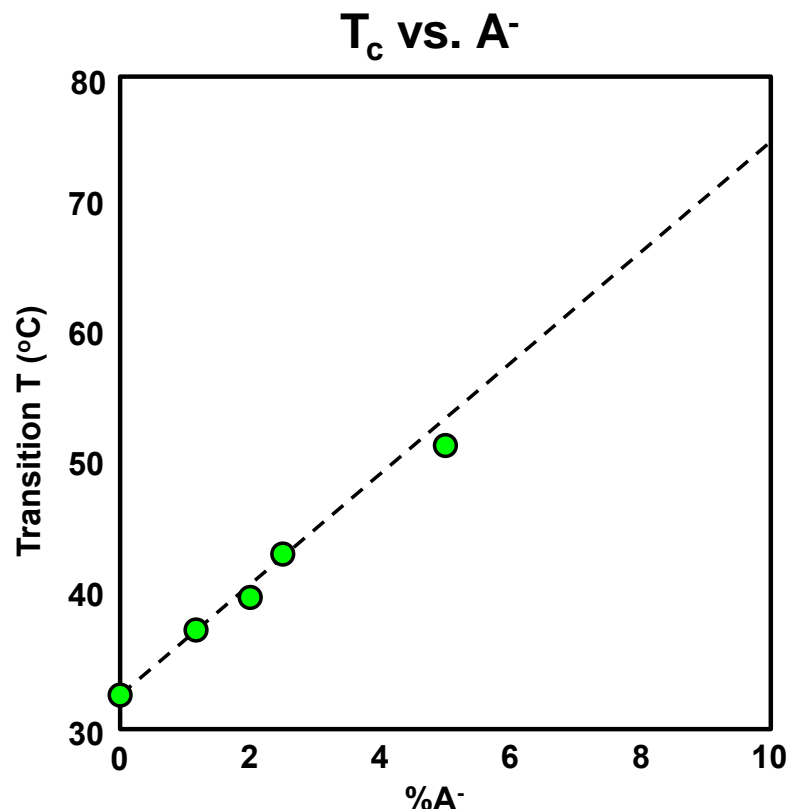
**Bad News** → Extensive reloading with CO<sub>2</sub> does not occur.

After complete unloading, P(NIPAM-AA) does not exhibit a phase transition.

Reheating “used” P(NIPAM-AA) does not result in significant pH or pK<sub>a</sub> increases.

# The Mechanism for Irreversible Polymer Behavior: Buffer Ionization Impacts Hydrophobic:Hydrophilic Switching

Introduction of  $A^-$  into the polymer makes the environment more hydrophilic. Hydrophilic groups suppress the phase transition and  $pK_p$  changes.



Loading/unloading is reversible if only a fraction of the buffer capacity is used. The maximum  $HCO_3^-$  attainable on loading scales with usable buffer capacity ( $A^-$ ).



## Summary

---

- Polymer-based programmable pH buffers have the potential for promoting the reversible loading and unloading of  $\text{CO}_2$  from water.
- Our initial P(NIPAM-AA) provides complete unloading of  $\text{HCO}_3^-$  to  $\text{CO}_2$ .
- $\text{CO}_2$  loading is limited by the maximum anion content the buffer can maintain and still support the required thermal phase transition.
- The current buffer will require modifications to achieve a buffer capacity that is sufficient to deploy in a practical process for the reversible capture and release of  $\text{CO}_2$  from air.

## Ongoing Work

- Varying polymer properties through composition
- Exploring properties of grafted copolymers

# Acknowledgements

## People:

- Bruce Bunker
- Dale Huber
- Mark Roberts
- Erik Spoerke
- Jill Wheeler
- Holly Zarick



## Funding:

- The authors are grateful for support from Laboratory Directed Research and Development funding from Sandia National Laboratories and the Division of Science and Engineering of the Office of Basic Energy Sciences.