Speeding Carbon Dioxide Capture - The Key to Better Energetics

Lawrence Livermore National Laboratory

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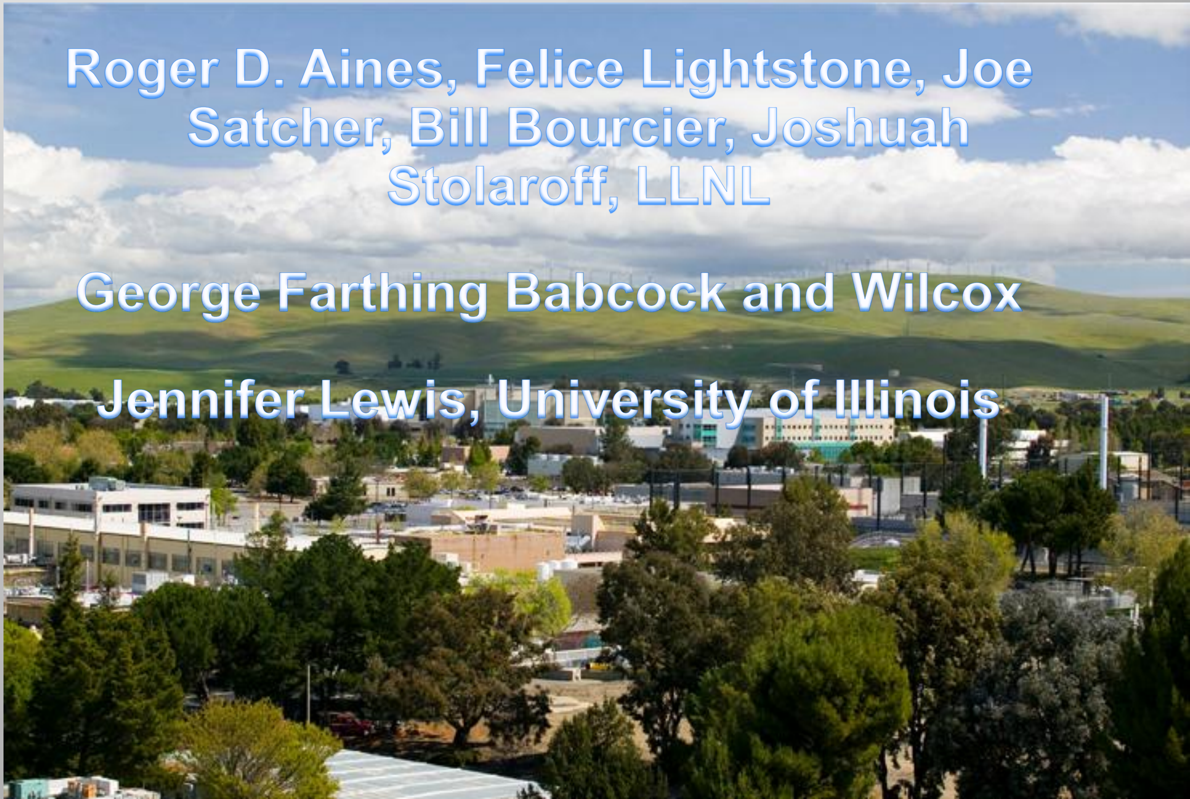
The Babcock and Wilcox Company



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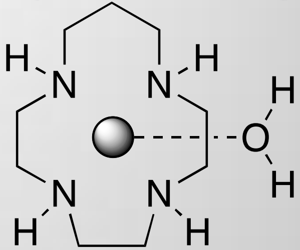
Carbonic anhydrase is one of the most rapid enzymes known – it was first discovered in human lungs, where it facilitates CO_2 exhalation

Carbonic anhydrase appears to have evolved independently five times, and has hundreds of structural variants

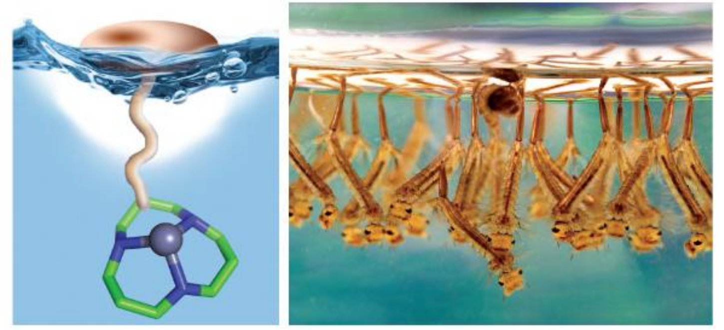
The problem for today – carbon dioxide separation is too slow

- Separating pure CO_2 from industrial sources, or from the atmosphere, is a slow chemical reaction
- This requires large process equipment and long times, leading to high costs
  - Separation from natural gas power is 3-4x slower than coal
  - Separation from air is 300x slower than from coal flue gas
- Water-based liquids separate CO_2 from other gases with very high efficiency because CO_2 is very soluble in water

We have focused on using natural analgues to beat the speed limit



- Faster, rugged catalysts that survive industrial conditions
- Tethering of catalysts to the air-water interface
- Encapsulation to provide high surface area and confine solvent

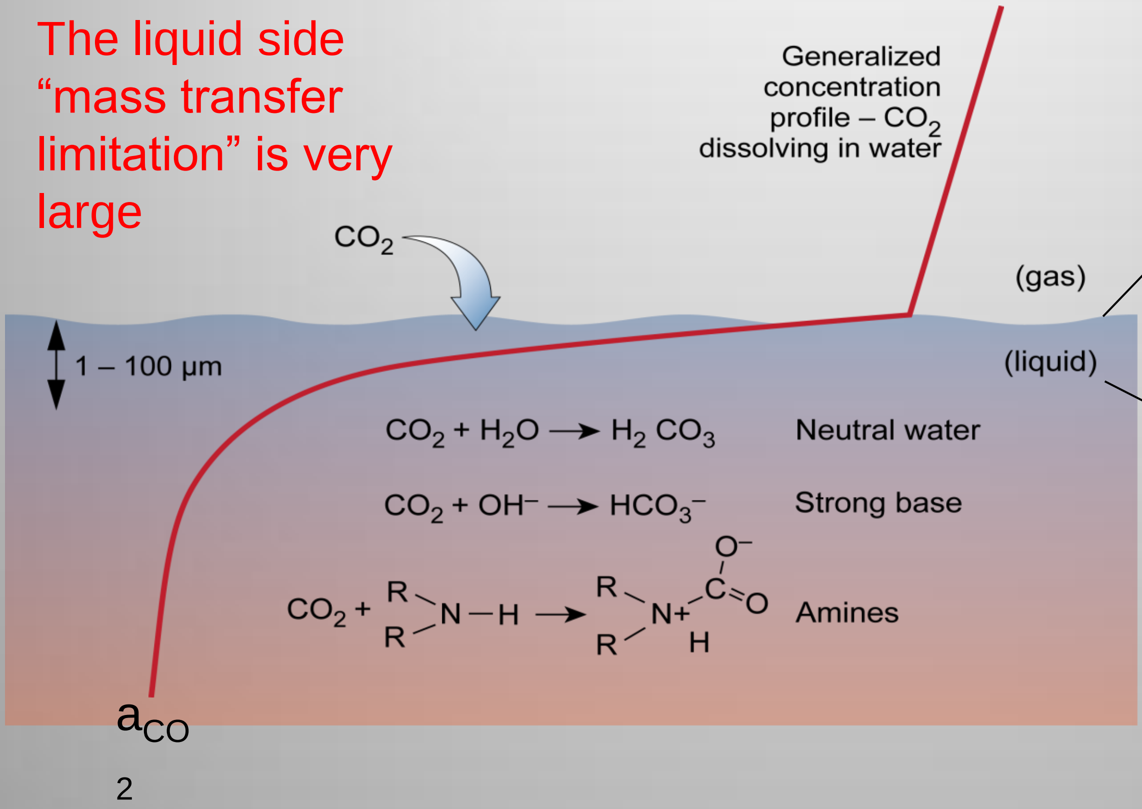


And we are examining processes that utilize solid bicarbonate

25% exchangeable CO_2 by weight

The transfer of CO_2 into water or other liquids is almost always dominated by chemical reactions at the liquid interface

The liquid side "mass transfer limitation" is very large



Generalized concentration profile – CO_2 dissolving in water

CO_2

(gas)

(liquid)

1 – 100 µm

$CO_2 + H_2O \longrightarrow H_2\,CO_3$ Neutral water

$CO_2 + OH^- \longrightarrow HCO_3^-$ Strong base

$CO_2 + R_2N{-}H \longrightarrow R_2N^{+}(H){-}C(=O)O^-$ Amines

a_{CO_2}

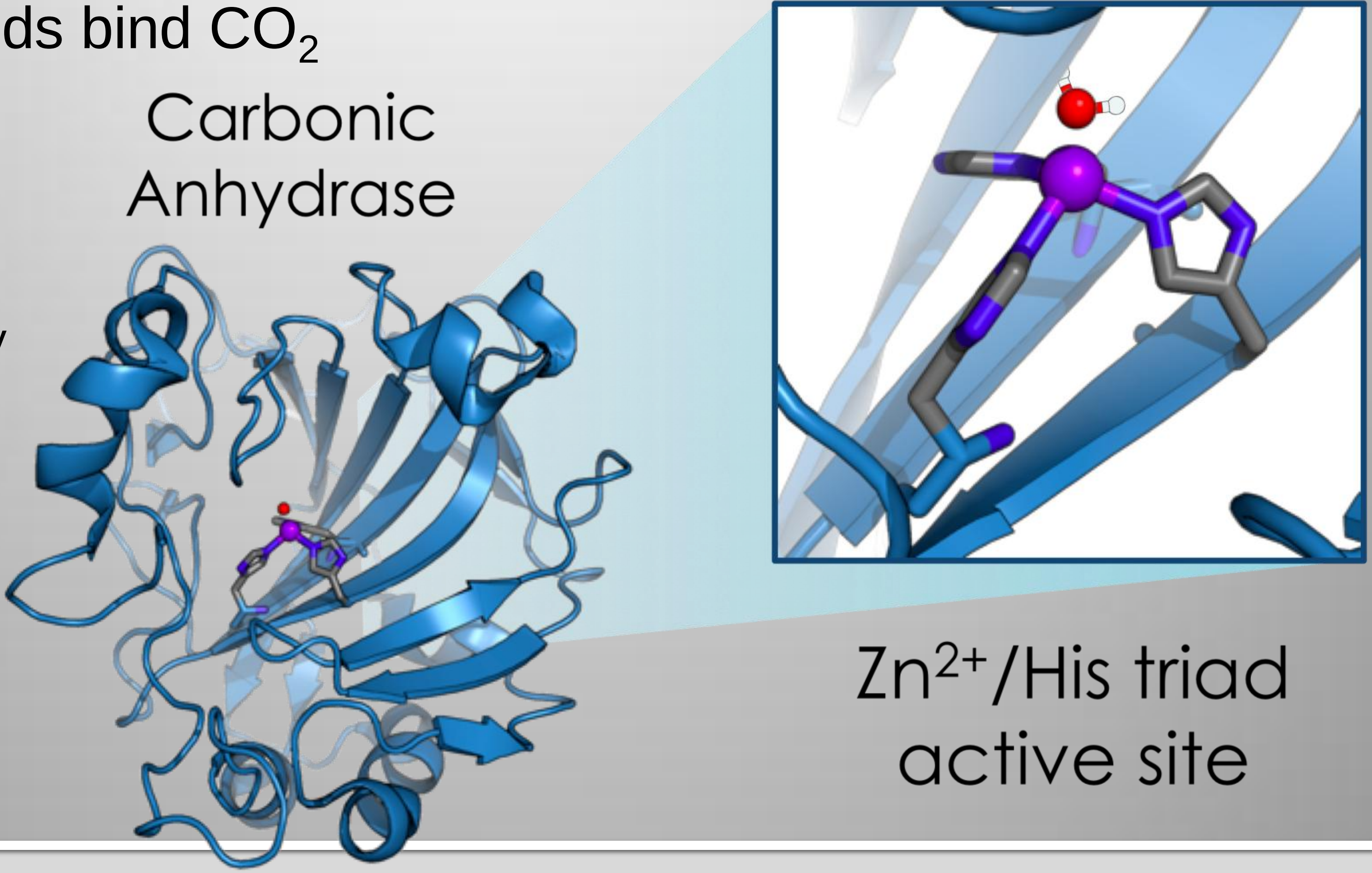
The rate of CO_2 uptake directly depends on the near-surface conversion rate of CO_2(aq) to another species

First we want a general approach for mimicking enzymes with small molecules - then to apply it to CO_2 capture

CA Structure & Function:
His triad, axial –OH, coordinate Zn^{2+} center,
key amino acids bind CO_2

Mimics:
optimize metal and ligand identity to improve kinetics

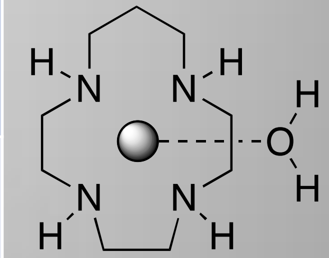
Carbonic Anhydrase



Zn^{2+}/His triad active site

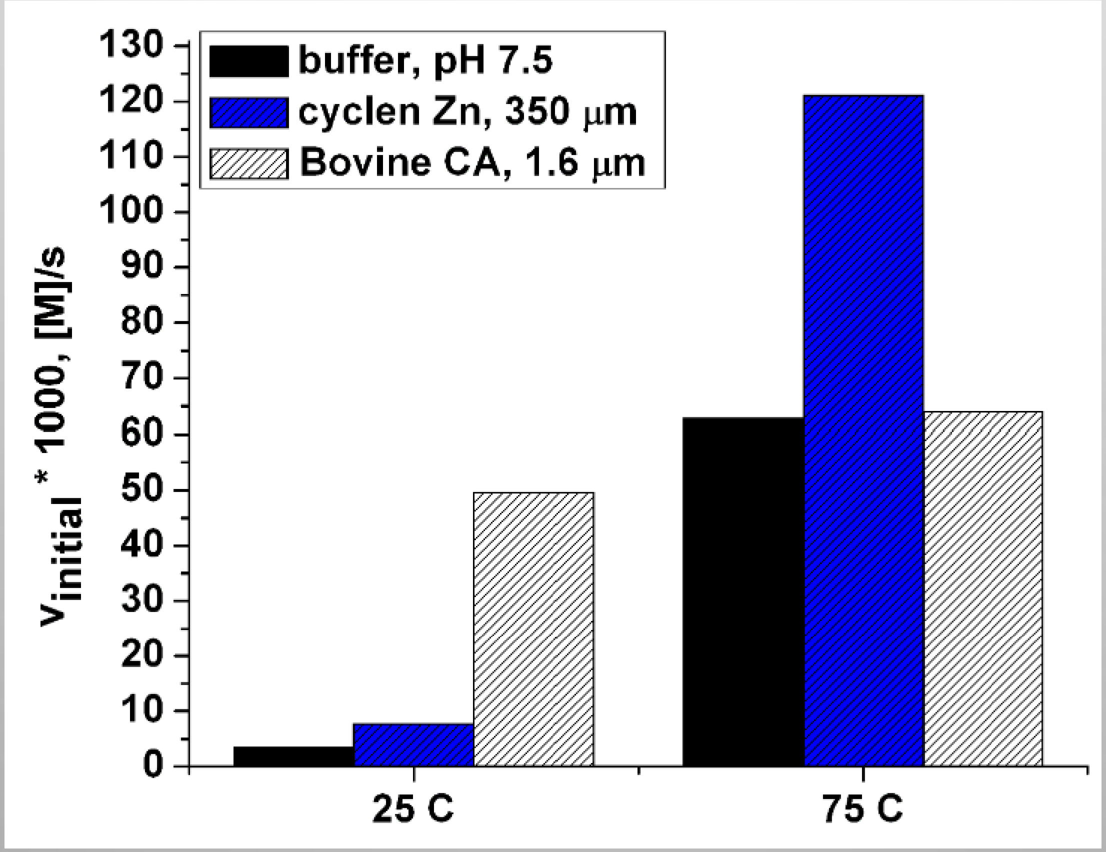
We have created mimic catalysts that they are stable at 100ºC, and their rate increases with temperature

Catalyst	Buffer	Temp (C)	K_{cat}
$Zn(BF_4)_2$ ctrl	Hepes, phenol red, pH = 7.5	T_r	7
Cyclen-Zn	Hepes, phenol red, pH = 7.5	T_r	540
Cyclen-Zn	Hepes, phenol red, pH = 7.5	Post 18 h, 100 C	900
Cyclen-Zn	AMPSO, thymol blue, pH = 9.0	T_r	2500
Cyclen-Zn	AMPSO, thymol blue, pH = 9.0	Post 18h, 100 C	2260
Cyclen-Zn	AMPSO, thymol blue	50C	11,500

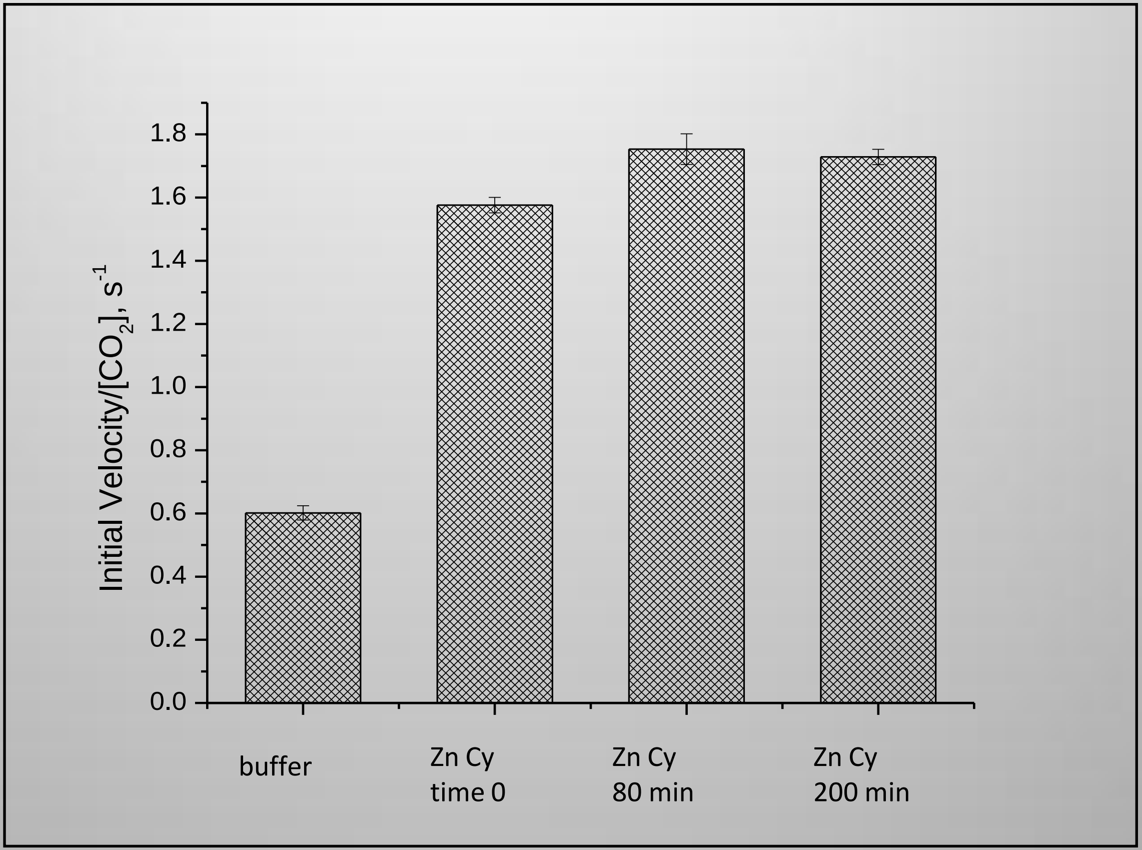


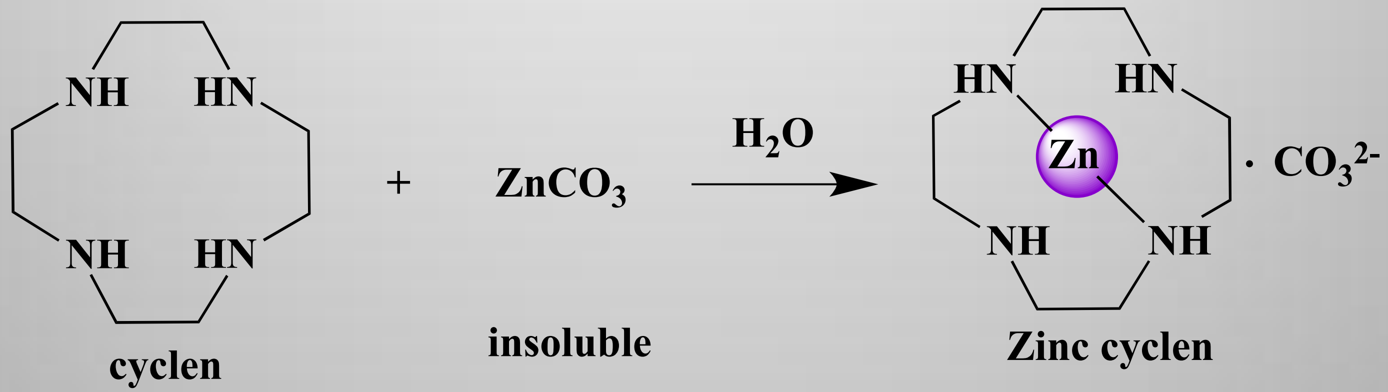
Demonstrated stability and enhanced kinetics for cyclen at elevated temperature and pH conditions

Our mimics are faster at higher temperatures



And stable up to at least 120ºC

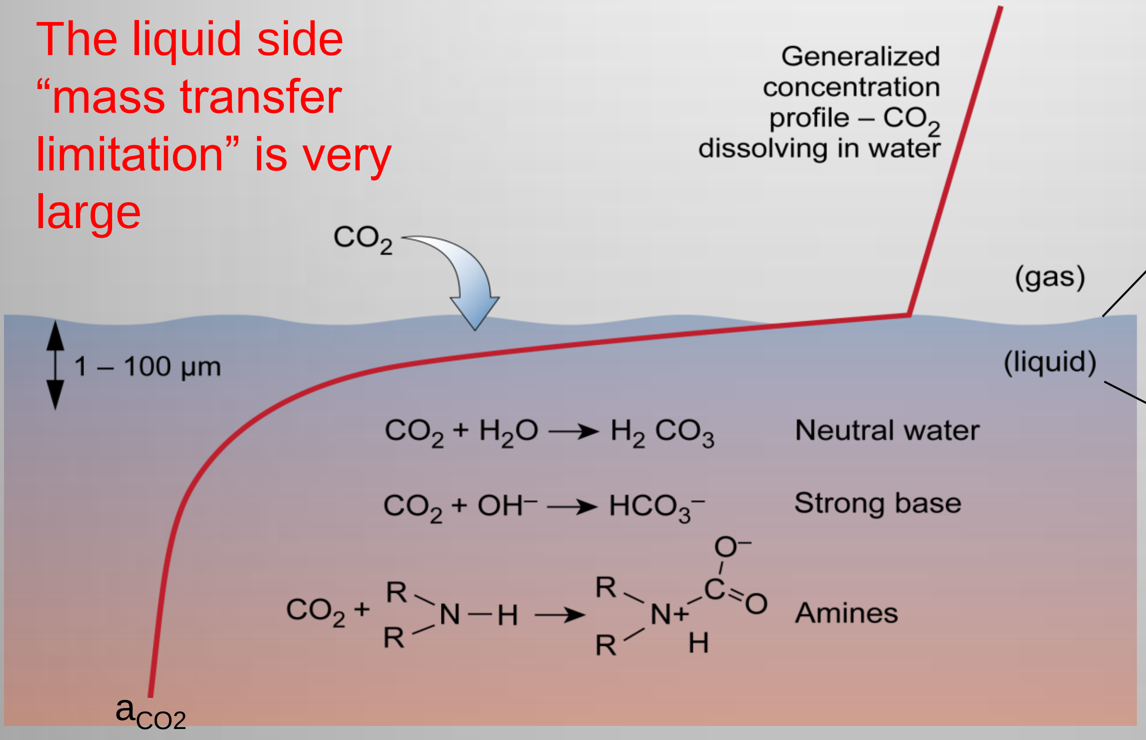




The catalyst can be formed from zinc carbonate, indicating that carbonate solutions will not scavenge the zinc

But we still have to deal with the surface transfer issue

The liquid side "mass transfer limitation" is very large



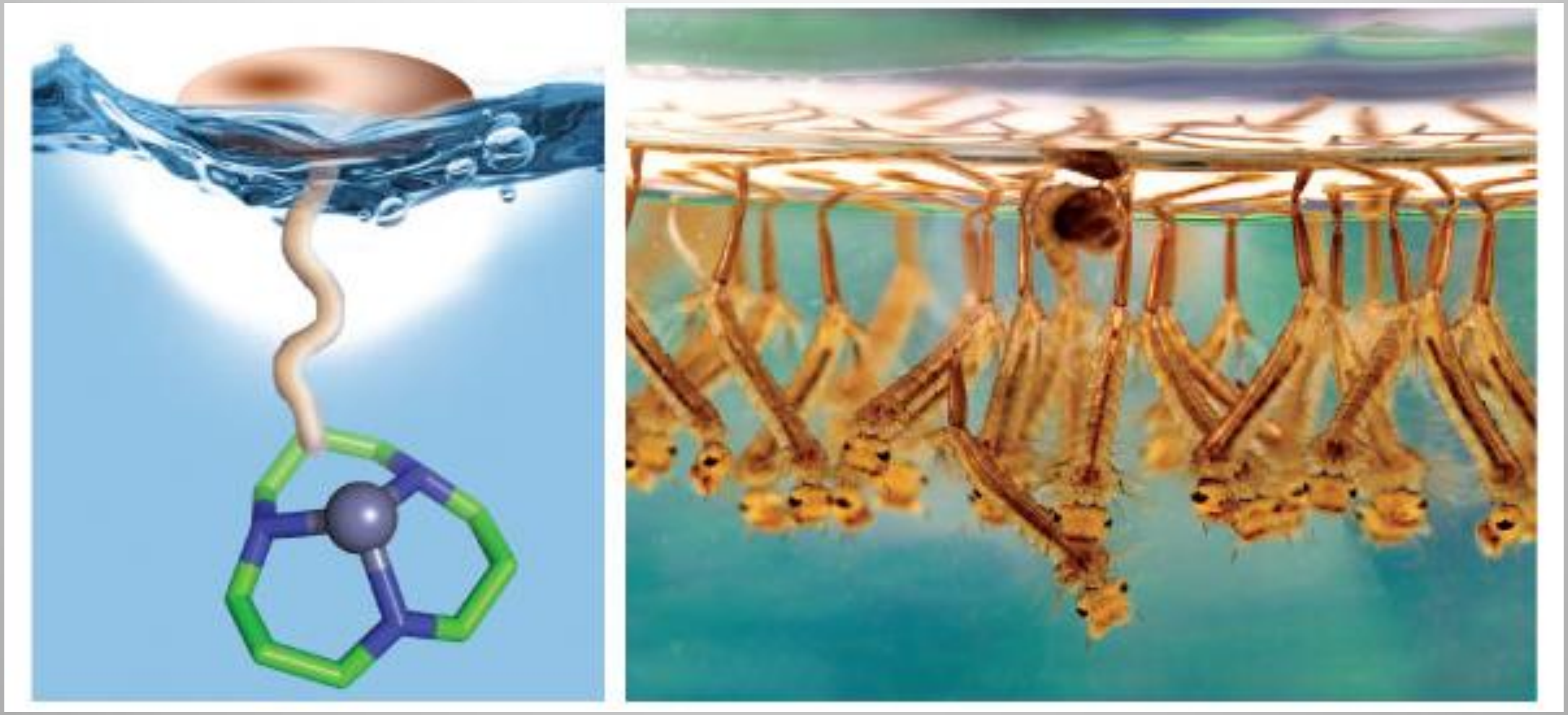
$CO_2 + H_2O \rightarrow H_2CO_3$

$CO_2 + OH^- \rightarrow HCO_3^-$

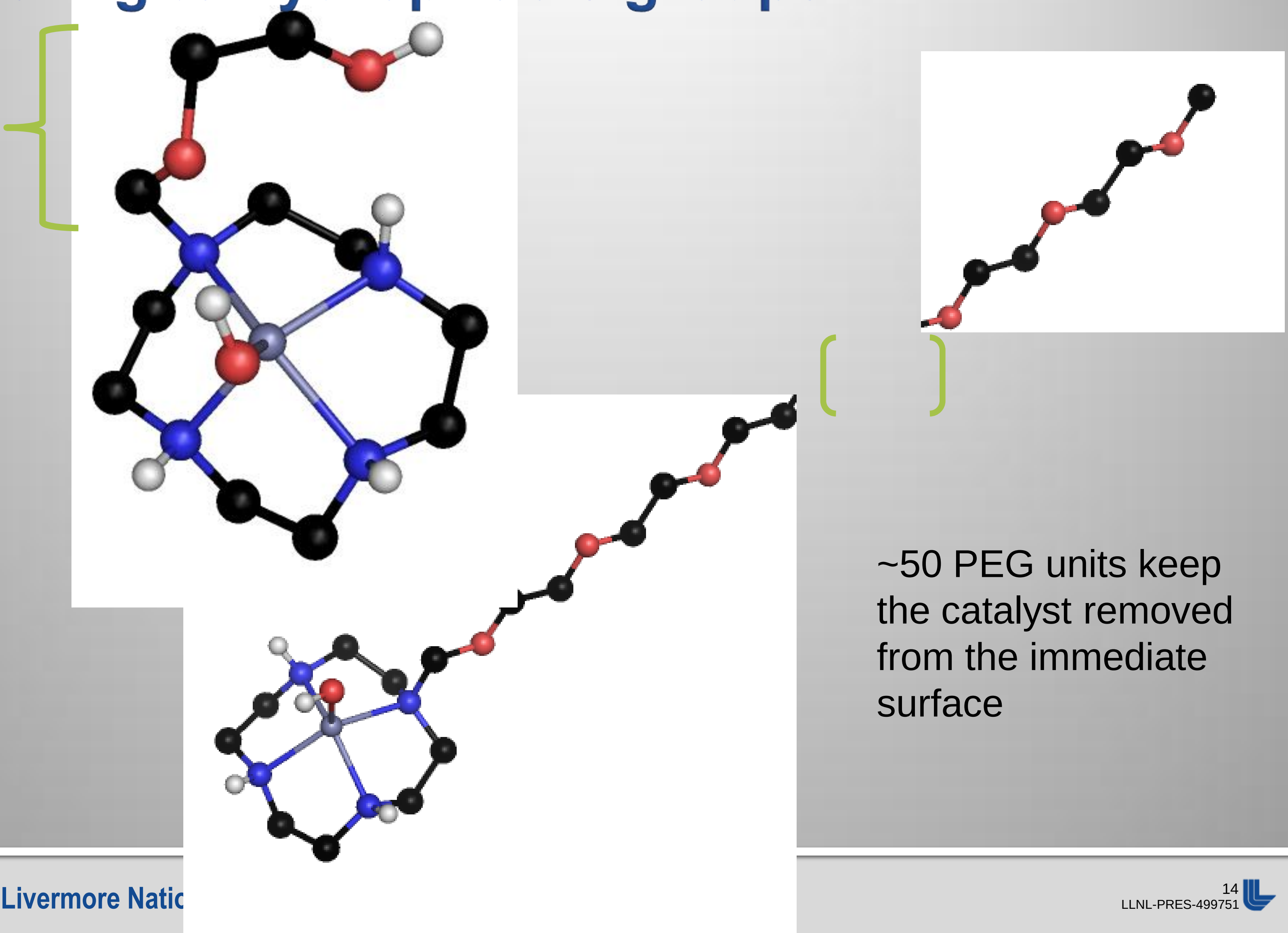
$CO_2 + R_2N{-}H \rightarrow R_2N^{+}(H){-}C(=O)O^-$

The rate of CO_2 uptake directly depends on the near-surface conversion rate of $CO_2(aq)$ to another species

The trick is tethering the catalyst to the liquid/gas interface – again nature is our example

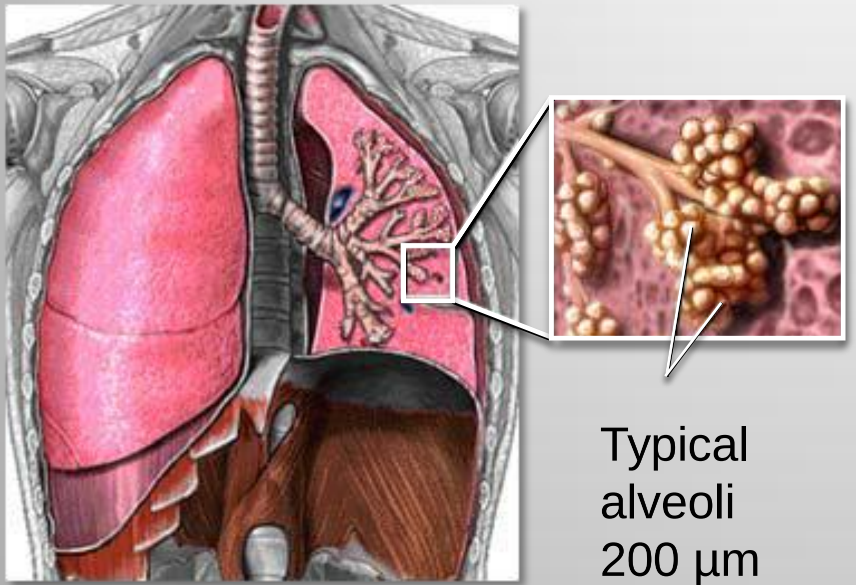


Polyethyleneglycol (PEG) linkers do not deform the catalysts and appear to be appropriate for tethering to hydrophobic groups

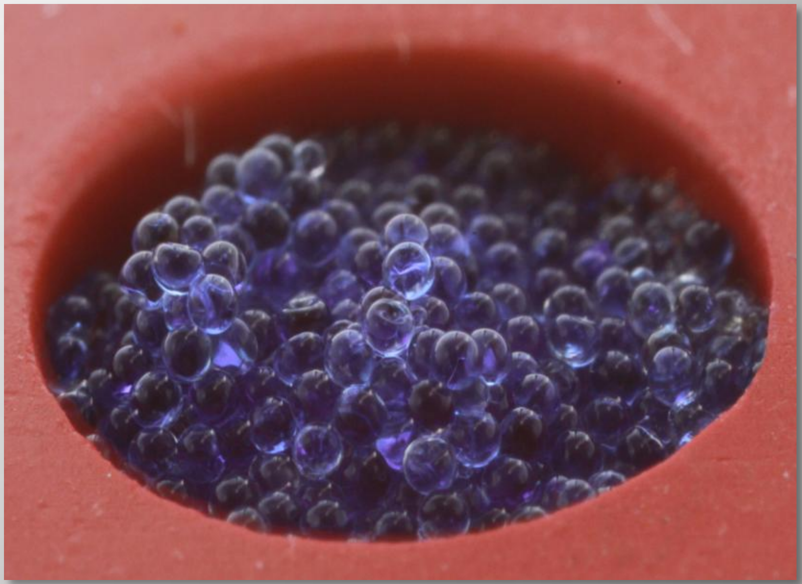


~50 PEG units keep the catalyst removed from the immediate surface

Catalysis is not the only speed-enhancer – surface area is critical



Typical alveoli 200 µm



We can create encapsulated solvents analogous to alveoli in size and function

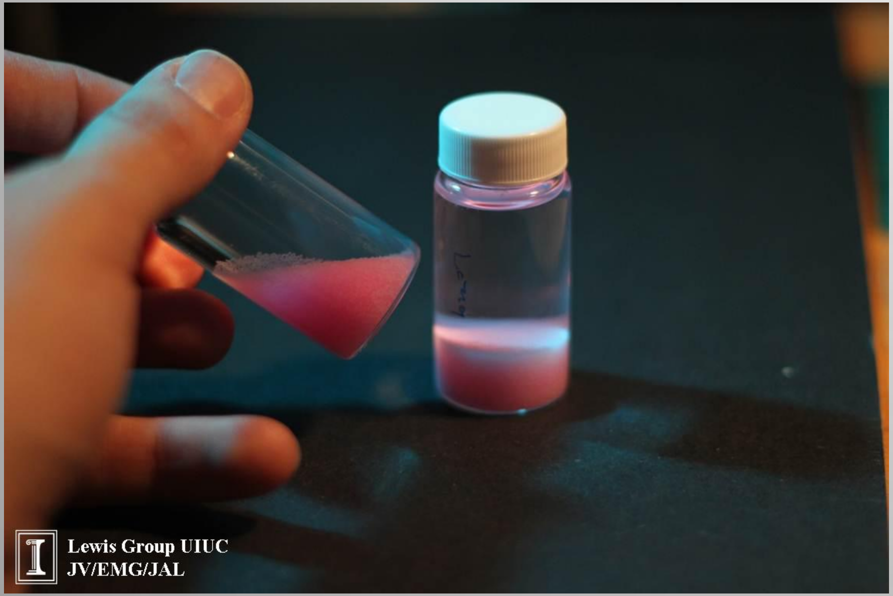
Concept: Encapsulate liquid solvents such as MEA in a thin, permeable, polymer shell.


MEA-filled Microcapsules

Initial Goals

✓Reduced volatility

✓Degradation products contained


Lewis Group UIUC
JV/EMG/JAL

Additional Benefits

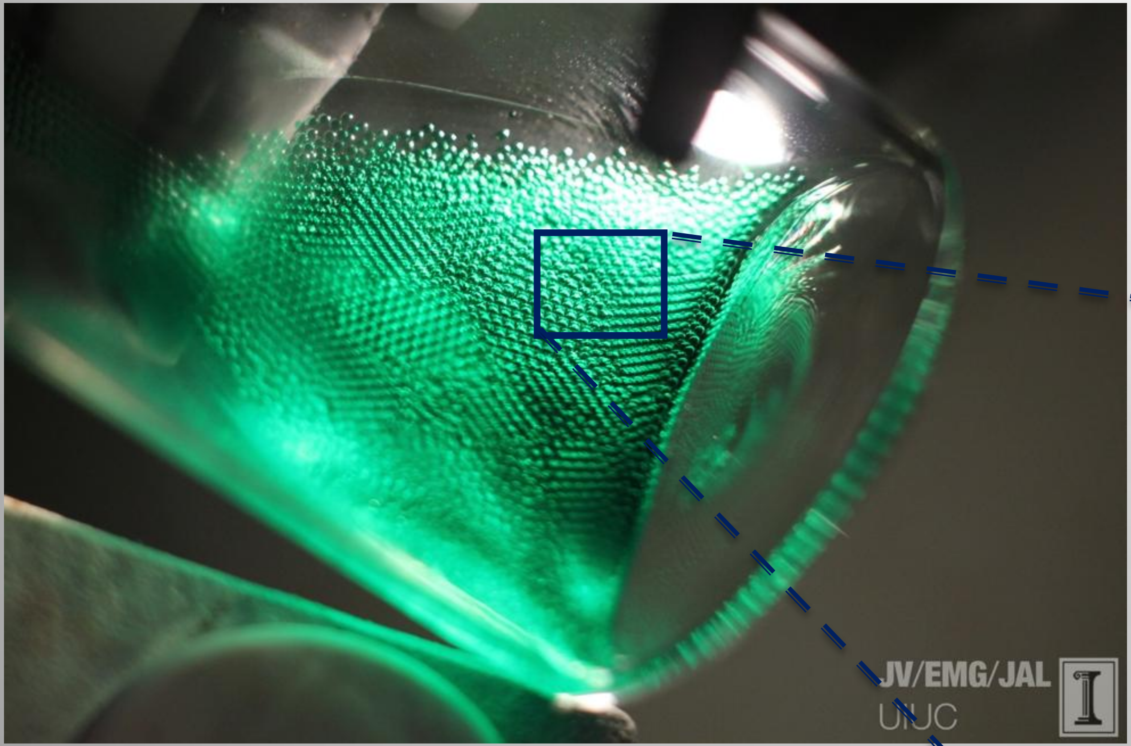
✓Increased surface area

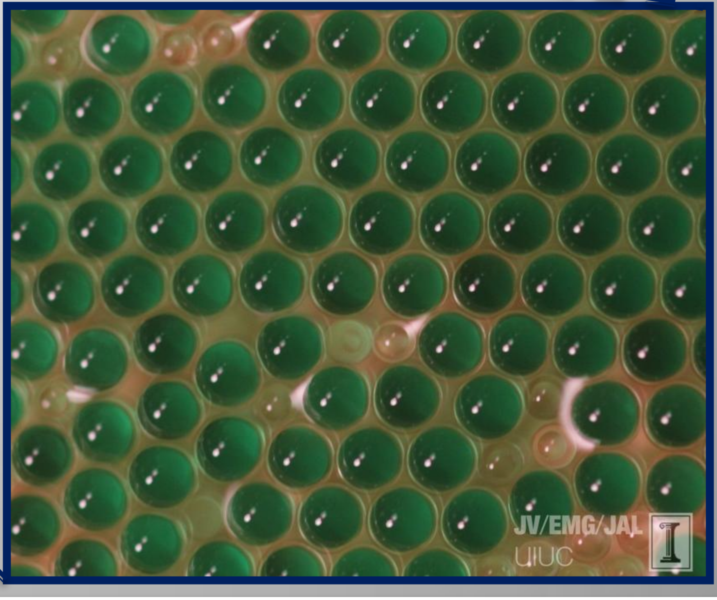
✓Good interface with capture catalysts

✓Facilitates new chemistries, especially high viscosity

We have pursued microcapsules made from a photocurable silicone (Semicosil)

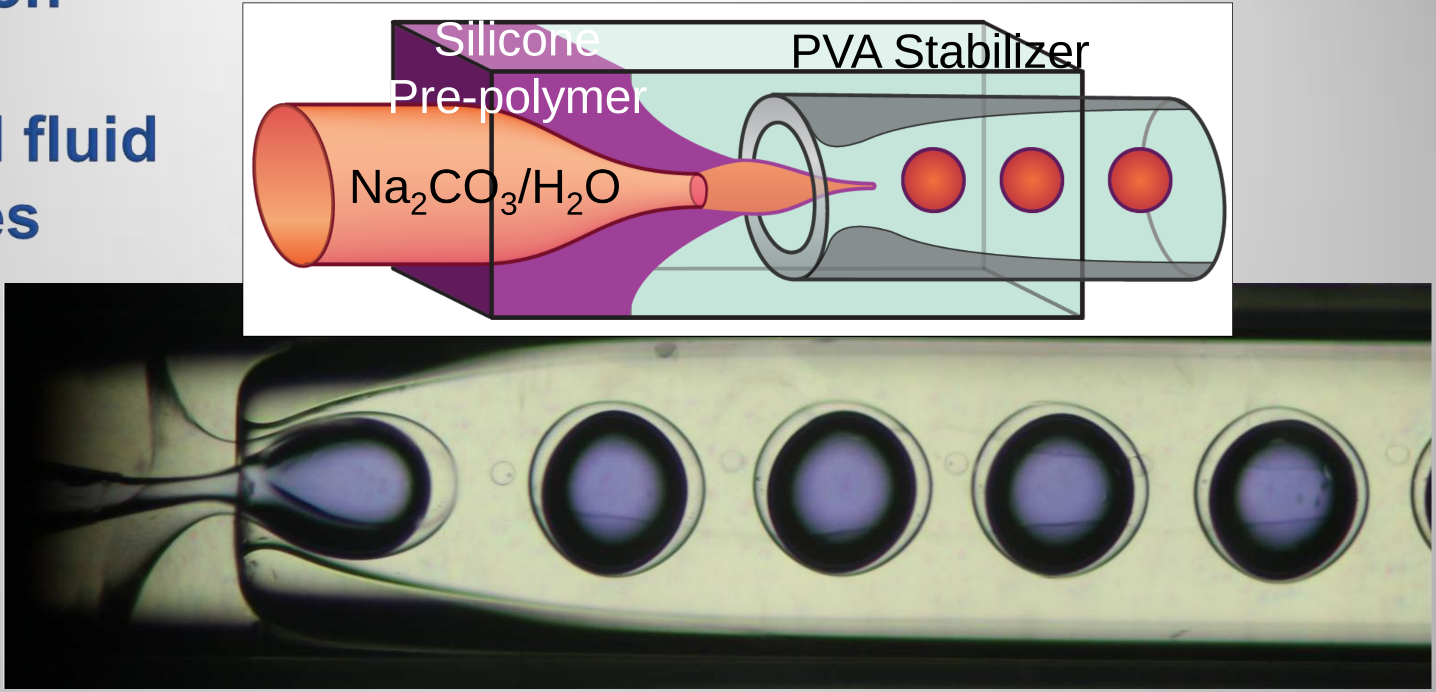
Inner fluid:
5 wt% PEO solution in water with green dye
Middle fluid:
Unmodified Semicosil A & B (10:1)
Outer fluid:
2 wt% PVA , 34 wt% H_2O, 64 wt% glycerol





Successful fabrication of microcapsules with Semicol UV curable silicon

Microcapsule production requires balanced fluid properties

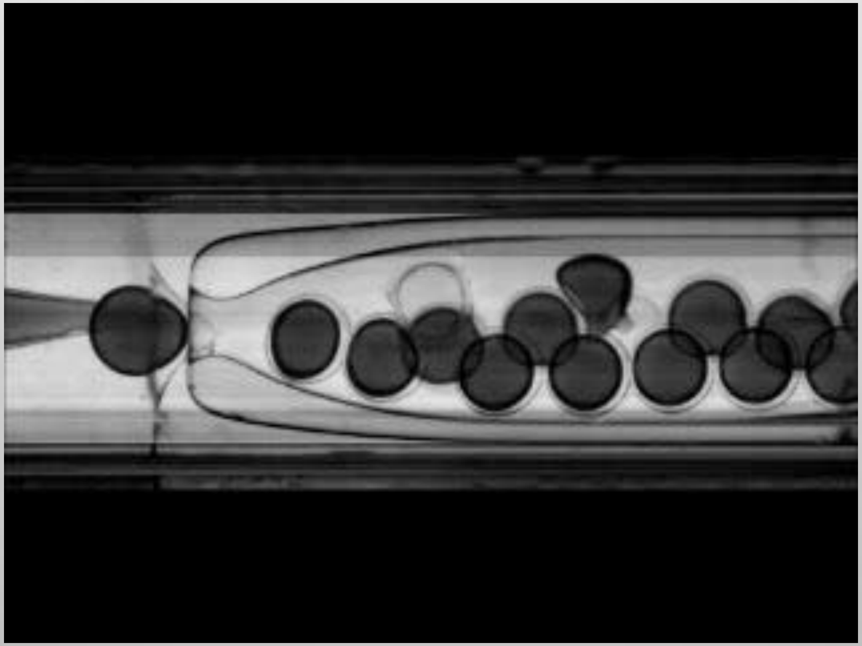


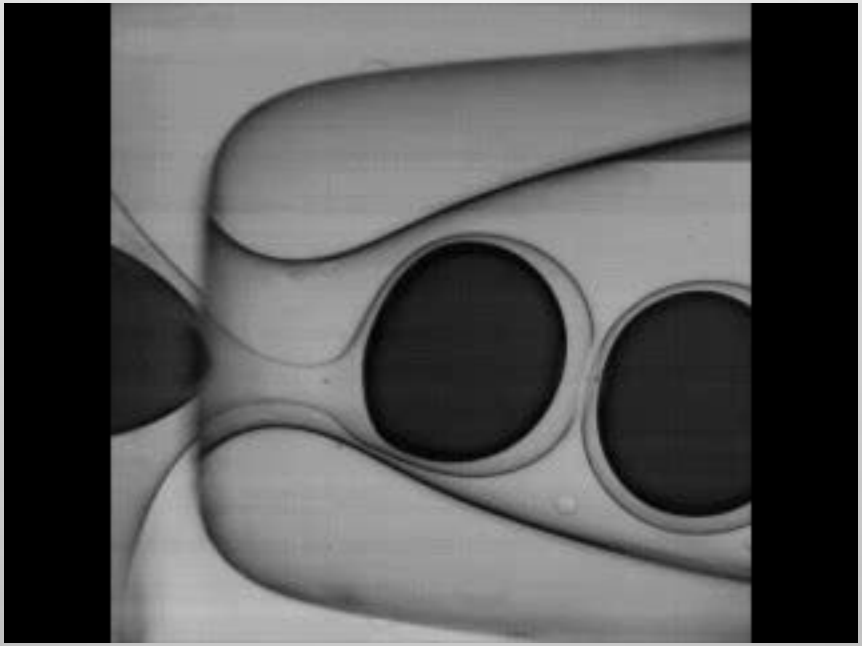
Capillary	ID (μm)	OD (μm)
Injection	50	1000
Collection	500	1000
Square	1000	1200

Fluid	Viscosity (cP)	Flow rate (μl h^{-1})
Inner Fluid	10-50	200-800
Middle Fluid	10-50	200-800
Outer Fluid	100-500	2000-3500

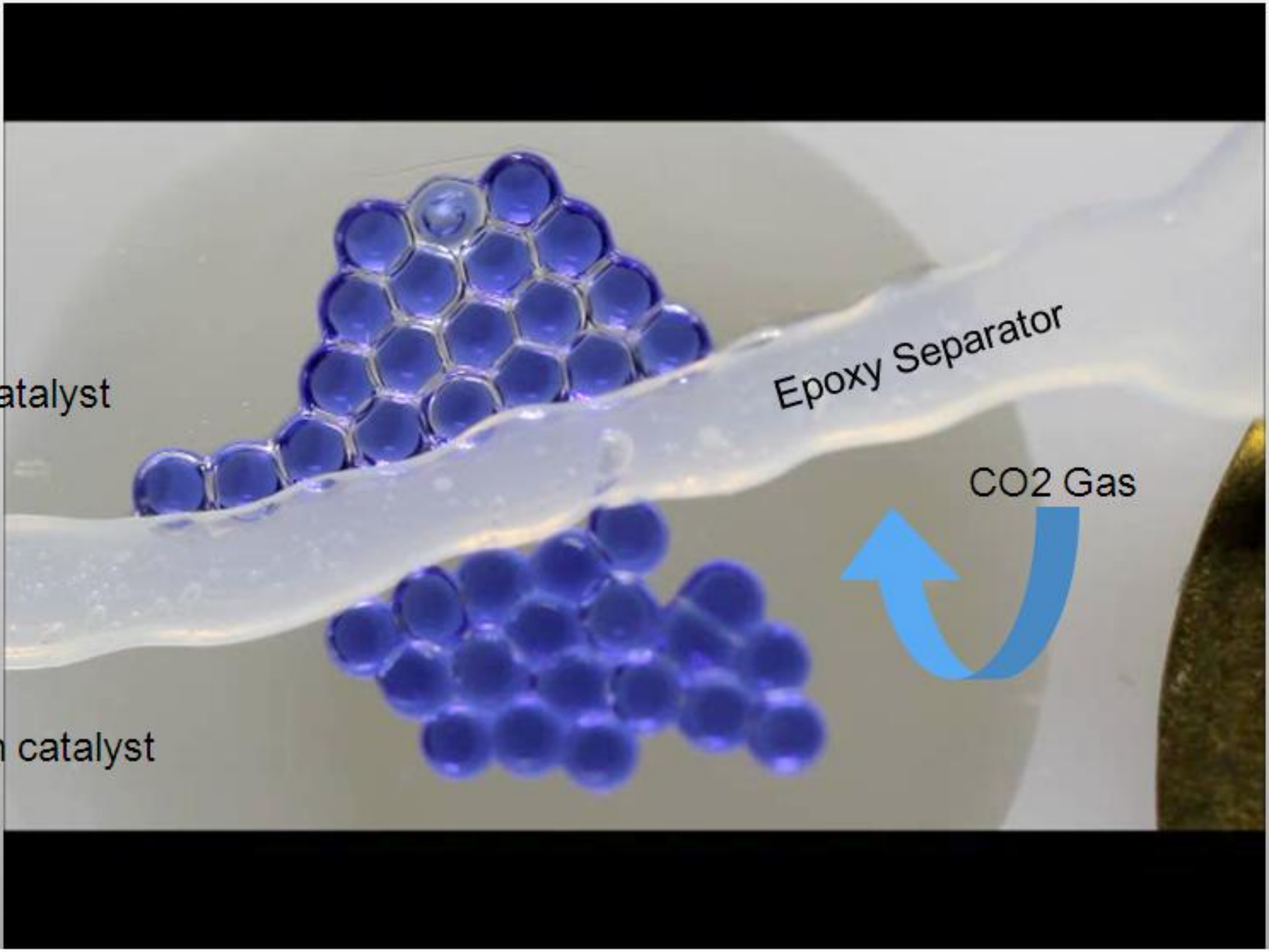
Formation of double emulsions within microfluidic device using methods as described by the Weitz group

Our current process runs at 250 capsules per second – too fast for this movie!



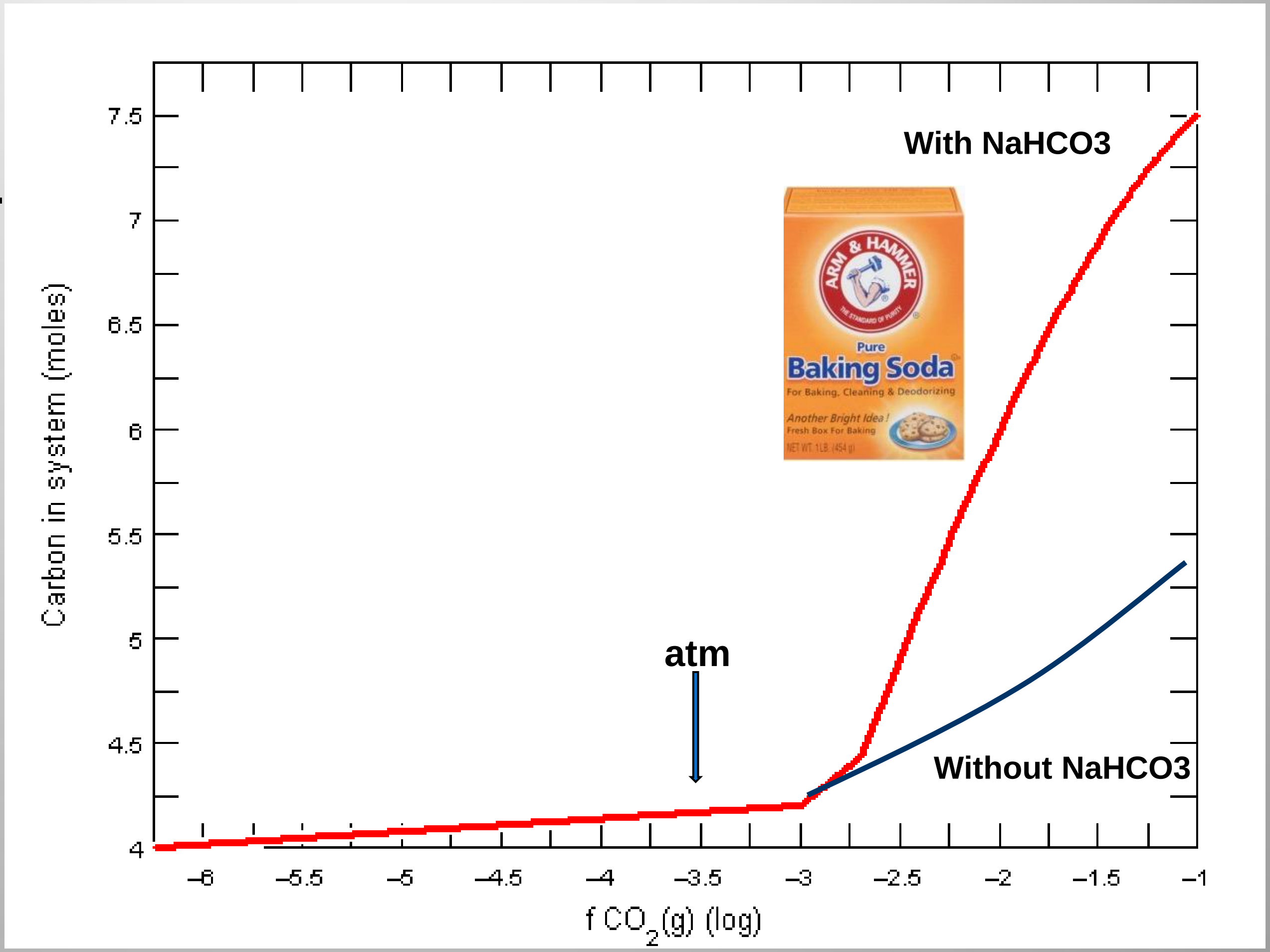


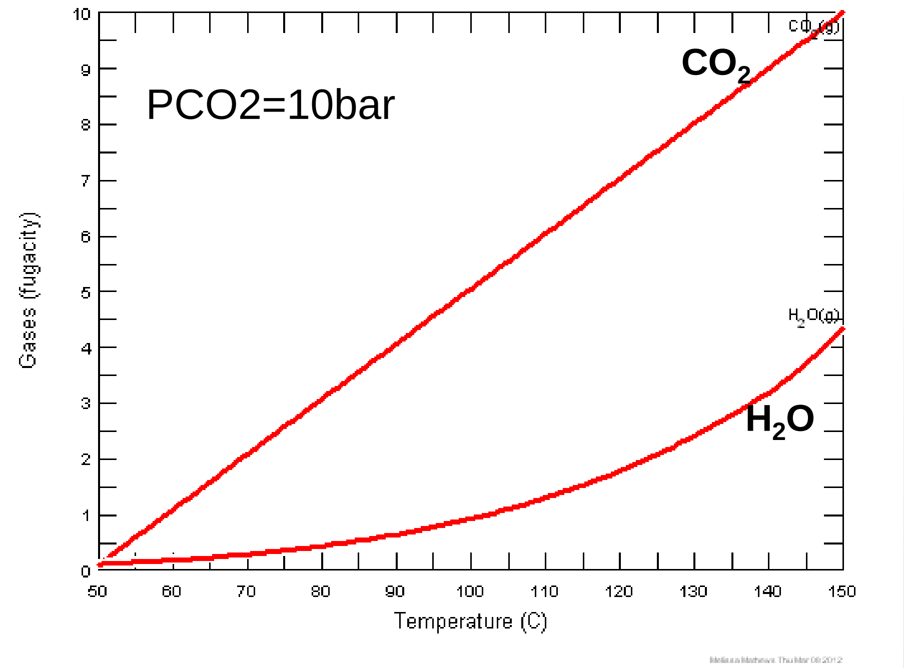
We have encapsulated multiple solvents in silicone capsules – with and without added catalyst

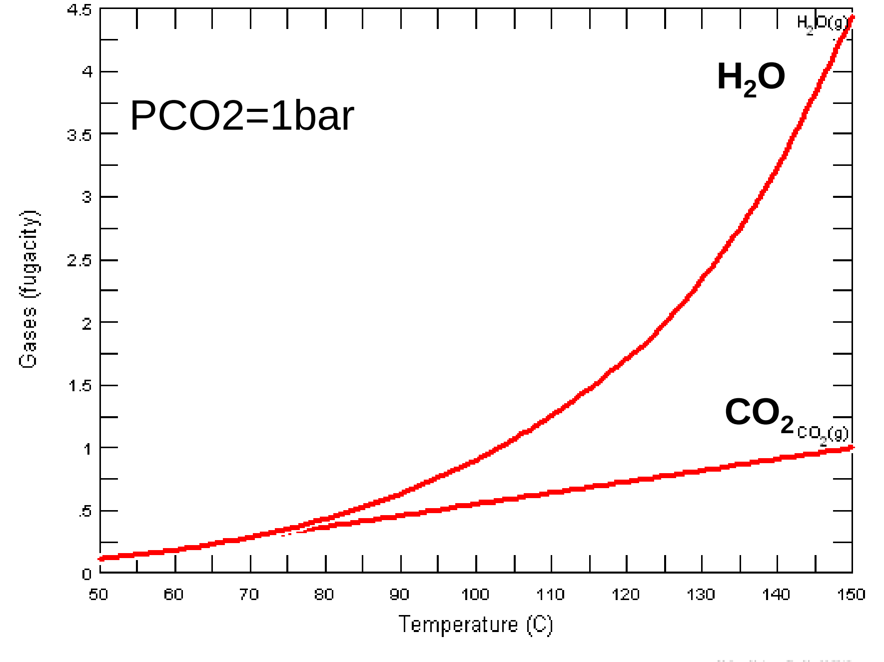


Carbonate solvents show carbon capture amounts of over 3 moles CO_2 per liter of solvent (13 wt % CO_2)

- Plot shows the increase in carbon content as 30 wt % (4m) Na2CO3 reacts with flue gas.
- Calculated carbon capacity is the maximum possible per 1000g H2O in solvent. Still need to get it back out.
- Most of the carbon capacity comes at $PCO_2 > 0.001$.
- Nahcolite doubles carbon capacity.



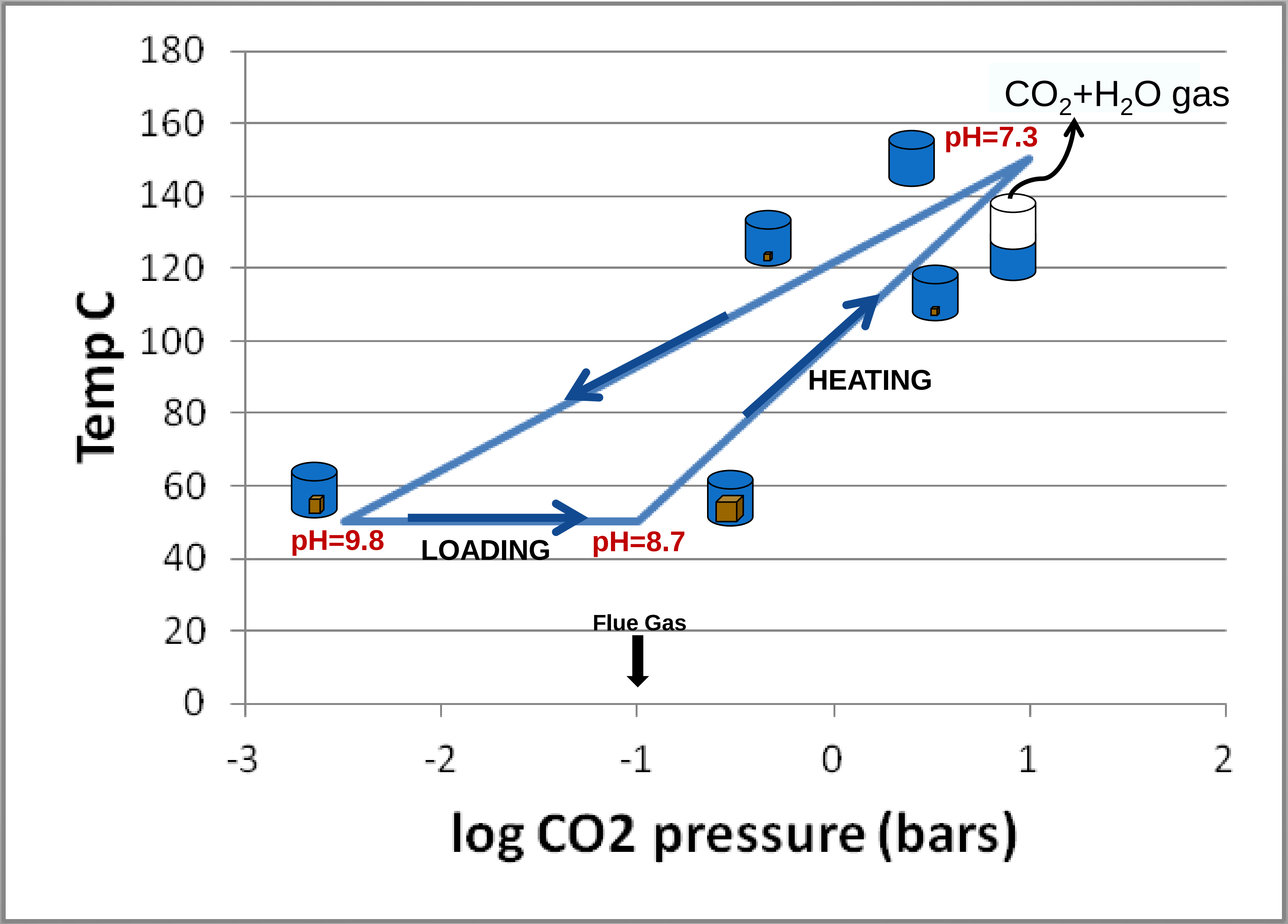




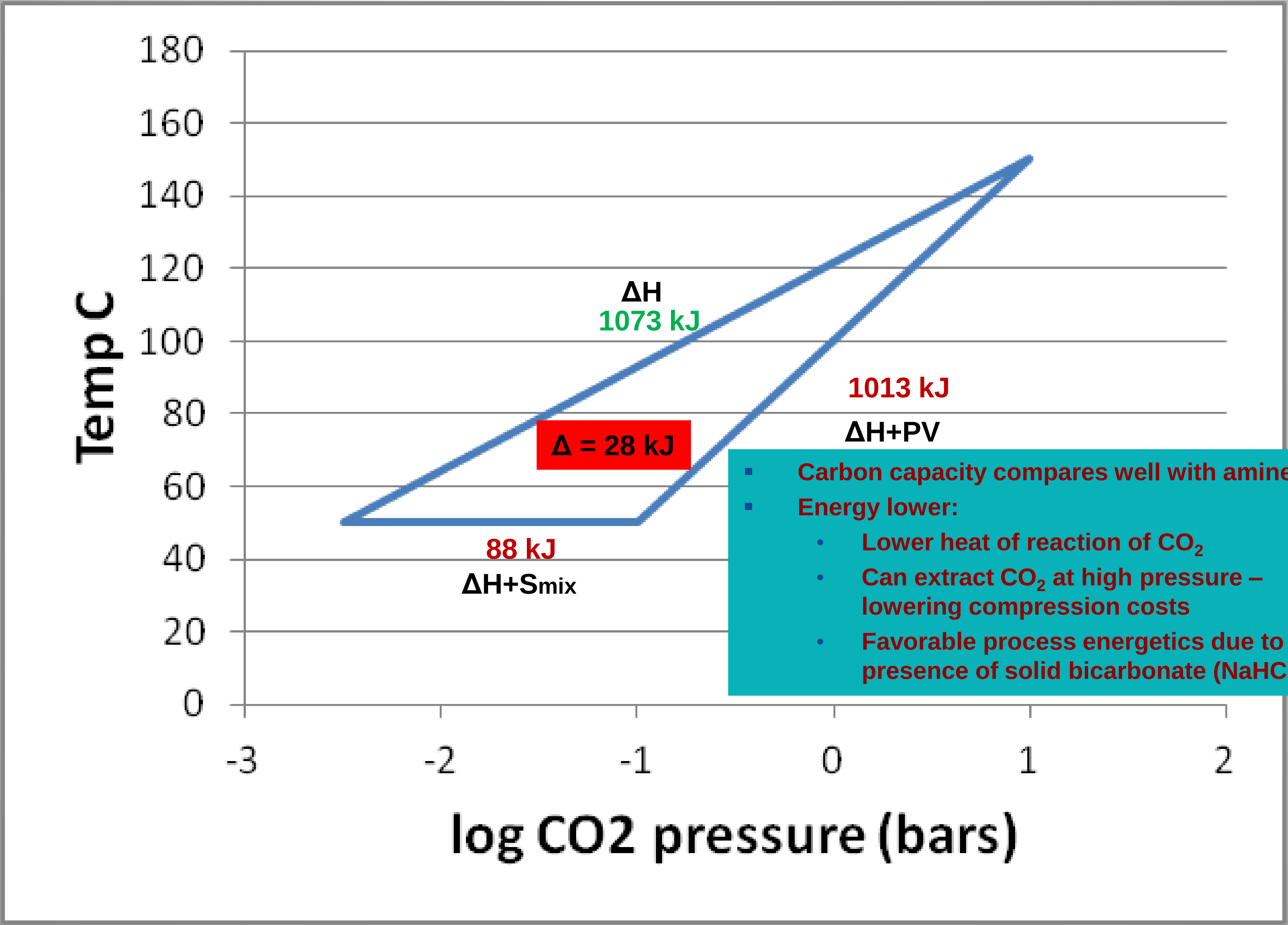
Why attempt high pressure recovery with solids present?

- High PCO2
  - Less energy to compress CO2
  - Less water boiled
  - Less carbon transfer per unit of solvent
- Low PCO2
  - More energy to compress gas
  - More water boiled
  - More carbon transfer per unit of solvent

30 wt % (4M) Sodium Carbonate (1) – Phase behavior



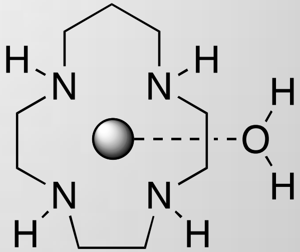
30 wt % (4M) Sodium Carbonate (3) - Energetics



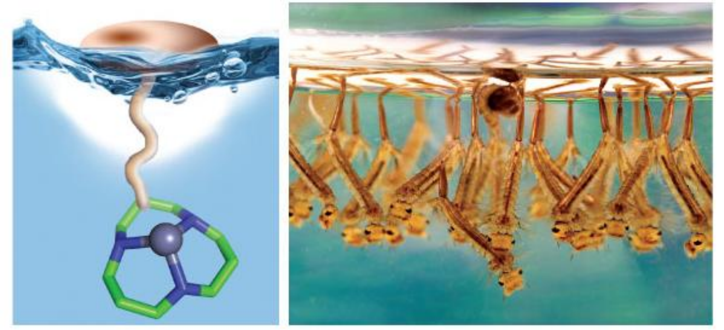
- Carbon capacity compares well with amines
- Energy lower:
  - Lower heat of reaction of CO_2
  - Can extract CO_2 at high pressure – lowering compression costs
  - Favorable process energetics due to the presence of solid bicarbonate ($NaHCO_3$)

in kJ per mole of CO2 removed

Speeding carbon dioxide absorption will enable low energy process approaches



- Faster, rugged catalysts that survive industrial conditions



- Tethering of catalysts to the air-water interface

- Encapsulation to provide high surface area and confine solvent, permit solids formation