# Polymer-Encapsulated Carbonate Solvents for Improved Bicarbonate Solids Utilization with Minimal Liquid Water

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**Award:**
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DE---AR0000099 (University of Illinois and Babcock & Wilcox)
**Lead Recipient:**
Lawrence Livermore National Security, LLC (LLNS)
**Project Title:**

Catalytic Improvement of Solvent Capture Systems

Lawrence Livermore National Laboratory
ILLINOIS
arpa·e

**The Babcock and Wilcox Company**
**Harvard University**

LLNL-PRES-555917

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# Our quest for dramatic improvement in capture cost started with *speed*

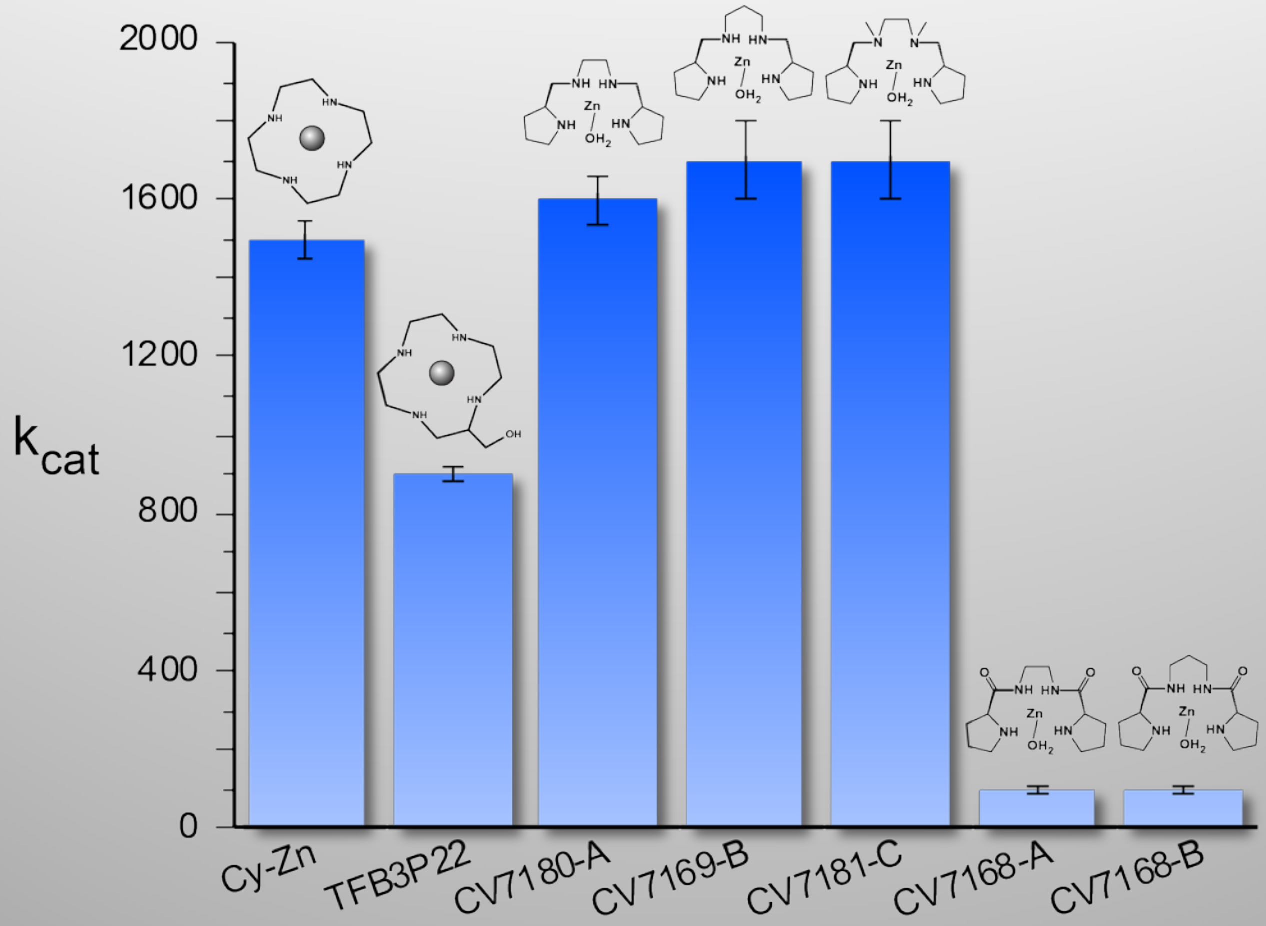
WHY?

- Enable lower energy solvent systems

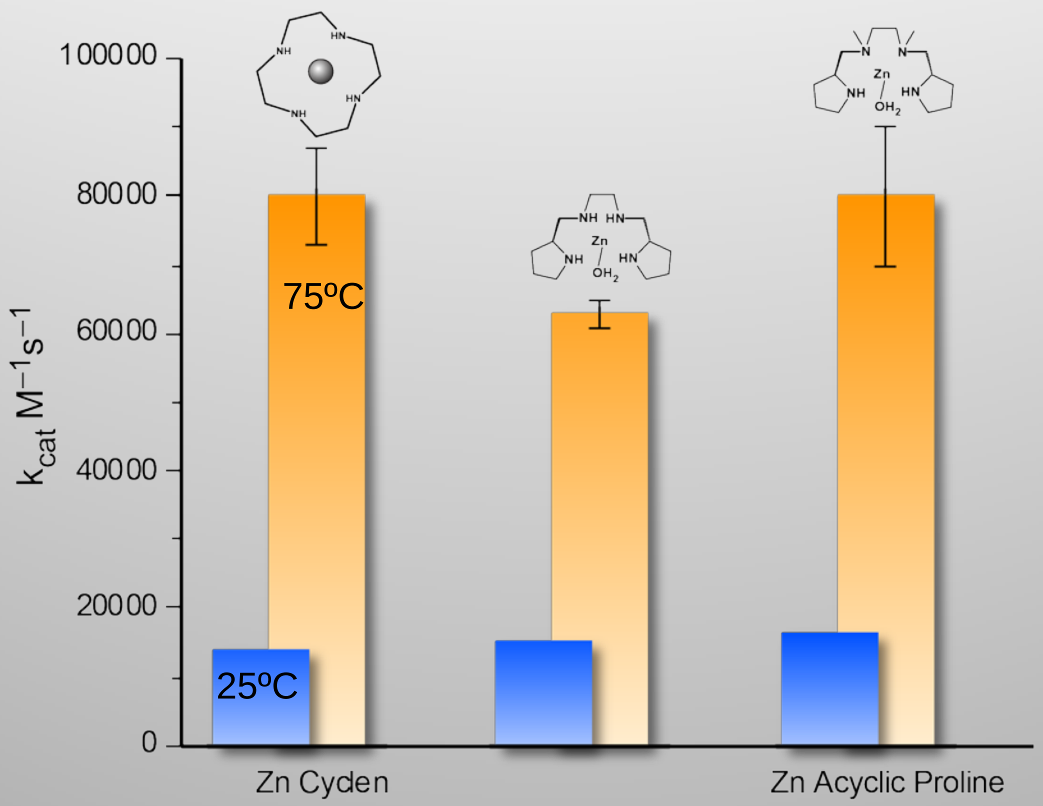
WHAT?

- Rugged synthetic catalysts
- Surface area enhancement

# We developed a family of catalysts that speed capture in hindered amines and carbonates



# And all are dramatically better during incubation at 75 C (>40✕)



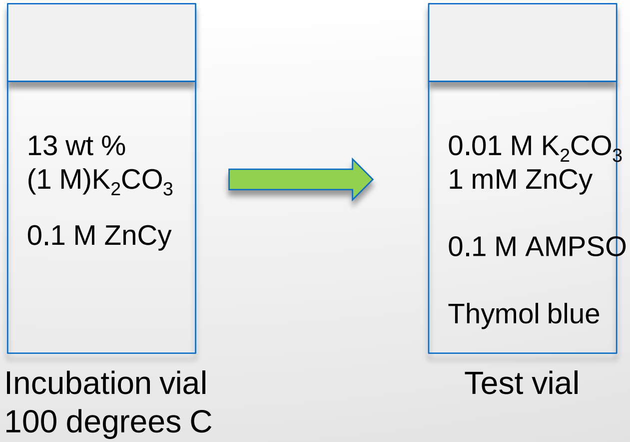

Bovine Carbonic Anhydrase

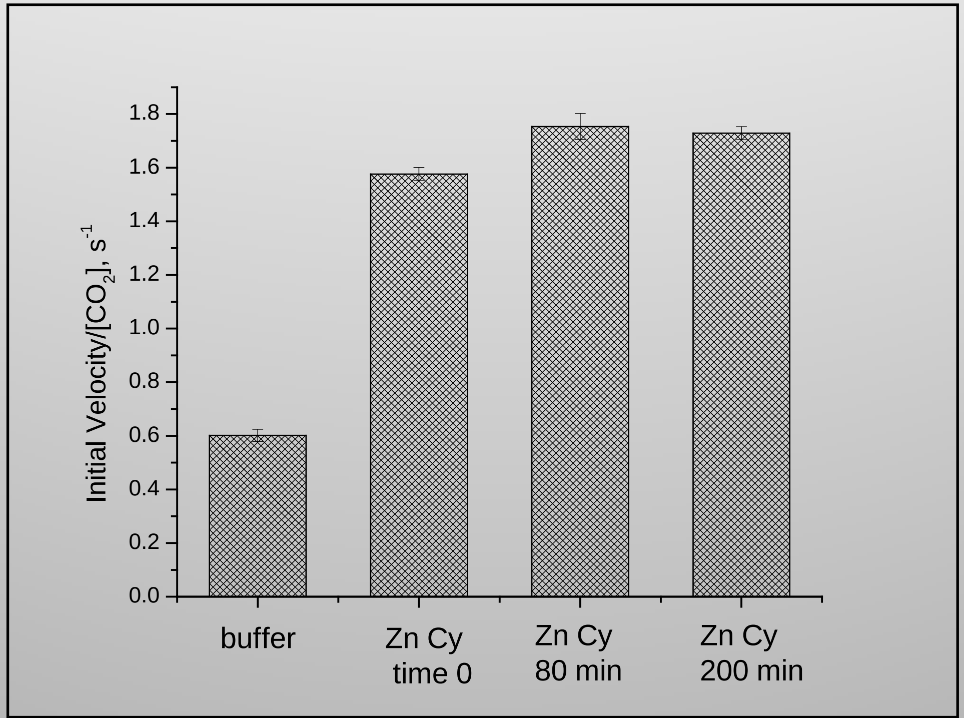
# 5) Kinetic activity of Zn cyclen exposed to hot $K_2CO_3$

**Experiment:**

**1) incubate catalyst in $K_2CO_3$**

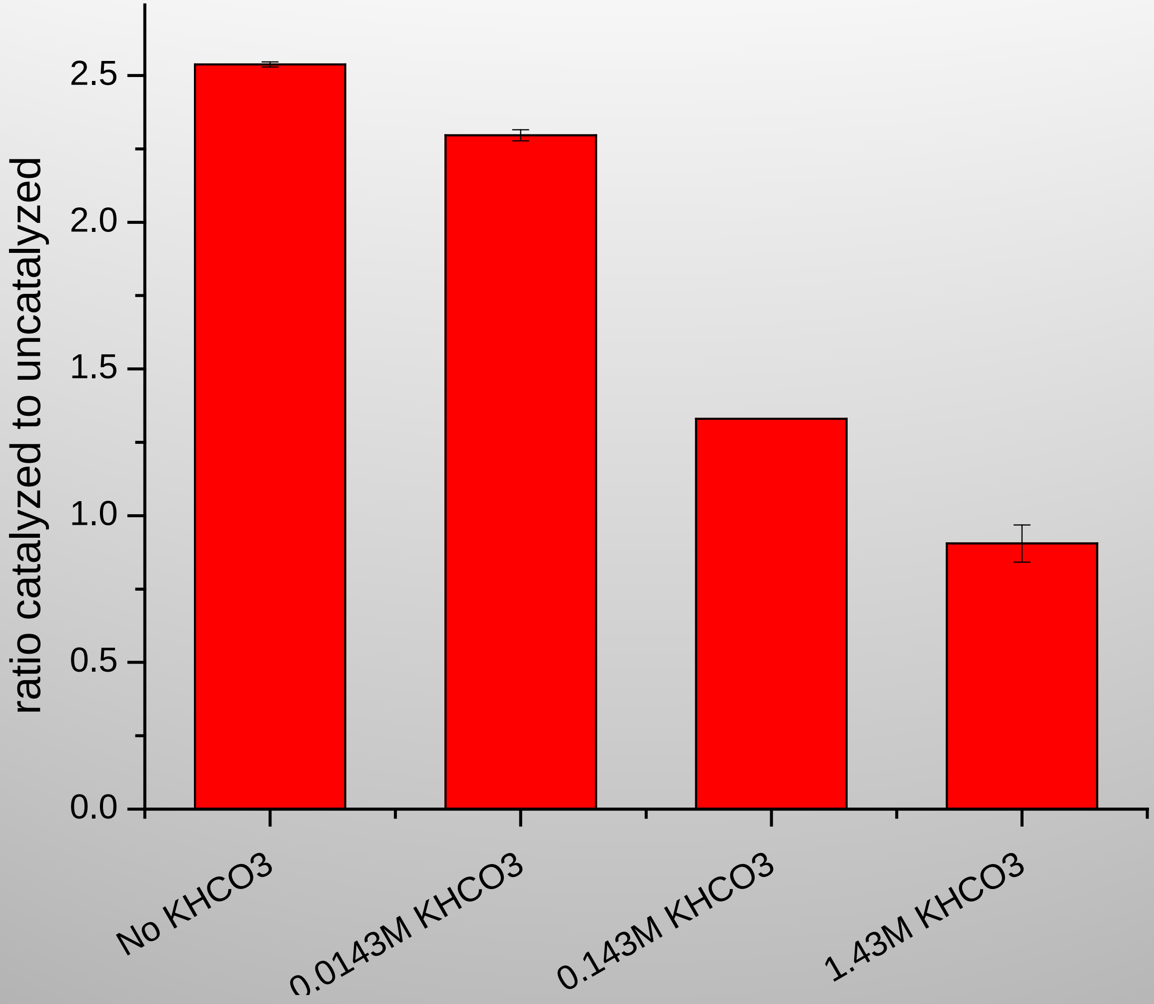
**2) dilute and measure $CO_2$ hydration rate**




- **Incubation of Zn Cyclen in hot $K_2CO_3$ *improves* catalytic activity**

# Cyclen-Zn is rugged and catalyzes $CO_2$ hydration but is inhibited by bicarbonate



# Inhibition affects all carbonic anhydrase isoforms.

$K_I$:inhibition constant. Lower $K_I$=more inhibition

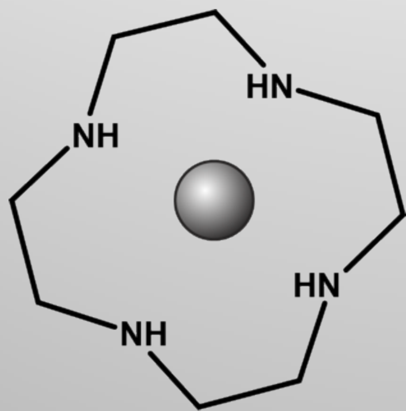
| **α-CA** | **$K_I$** | **β-CA** | **$K_I$** | **γ-CA** | **$K_I$** | **ζ-CA** | **$K_I$** |
|---|---|---|---|---|---|---|---|
| HCA I | 12 | Can2 | 0.75 | Zn-Cam | 42 | Cd-R1 | 0.12 |
| HCA II | 85 | scCA | 0.78 | Co-Cam | 0.10 | Zn-R1 | 0.10 |
| HCA III | 0.74 | cgNce103 | 0.086 | | | | |
| HCA VA | 82 | Cab | 44.9 | | | | |
| HCA VII | 0.16 | PCA | 0.33 | | | | |
| mCA XIII | 140 | stCA I | 0.64 | | | | |
| mCA XV | 0.008 | stCA II | 27.9 | | | | |

DeSimone, G., Supuran, C.T., *J. Inorg. Biochem*., **2011**,

•Carbonic anhydrases are subject to bicarbonate inhibition.
•Widely varying degree of inhibition depends on the degree to which the active site is “buried” within the protein.

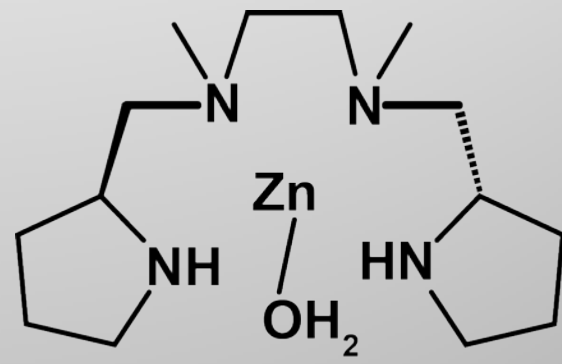
# And the winning catalysts are:

Best for:
High T cycles – stable to 120ºC
Low carbonate concentrations




Zn Cyclen
$K_{cat}$ 700 $M^{-1}s^{-1}$

Best for:
High carbonate concentrations
Lower T recycle – to 80ºC




Zn Acyclic Proline
(N,N'-dimethylethylenediamine)
$K_{cat}$ 900 $M^{-1}s^{-1}$

# But the Rochelle work has shown that water is the hidden cost in $CO_2$ capture

| **Solvent Heat of Absorption** | **Moles Water Evaporated in Stripper @80C** |
|---|---|
| 30 KJ/mole $CO_2$ *(e.g. carbonates)* | 3.5 |
| 80 KJ/mole $CO_2$ *(e.g. piperazine)* | 0.6 |

Schoon and VanStraelen TCCS-6

Low-enthalpy liquid solvents produce net increases in energy due to the high vapor pressure of water

**So:**

**Low-enthalpy solvents don’t improve on amine energy cost (due to water)**

**But:**

**Amine systems are too expensive for large scale use.**

# Let's not give up – zero-water capture is possible, and at low enthalpy

Thermonatrite
$Na_2CO_3 \cdot$H2O

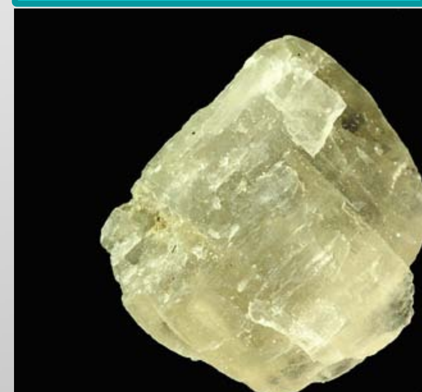
+ $CO_{2(g)}$ → 2

Nahcolite
$NaHCO_3$

Sodium Carbonate

ΔH -18
KJ/mole CO2

**This is ¼ of the intrinsic energy cost of amines**



Sodium Bicarbonate

# This reaction is well known in nature – but slow, and messy to engineer

Mixed carbonate/bicarbonate (Trona) Searles Lake

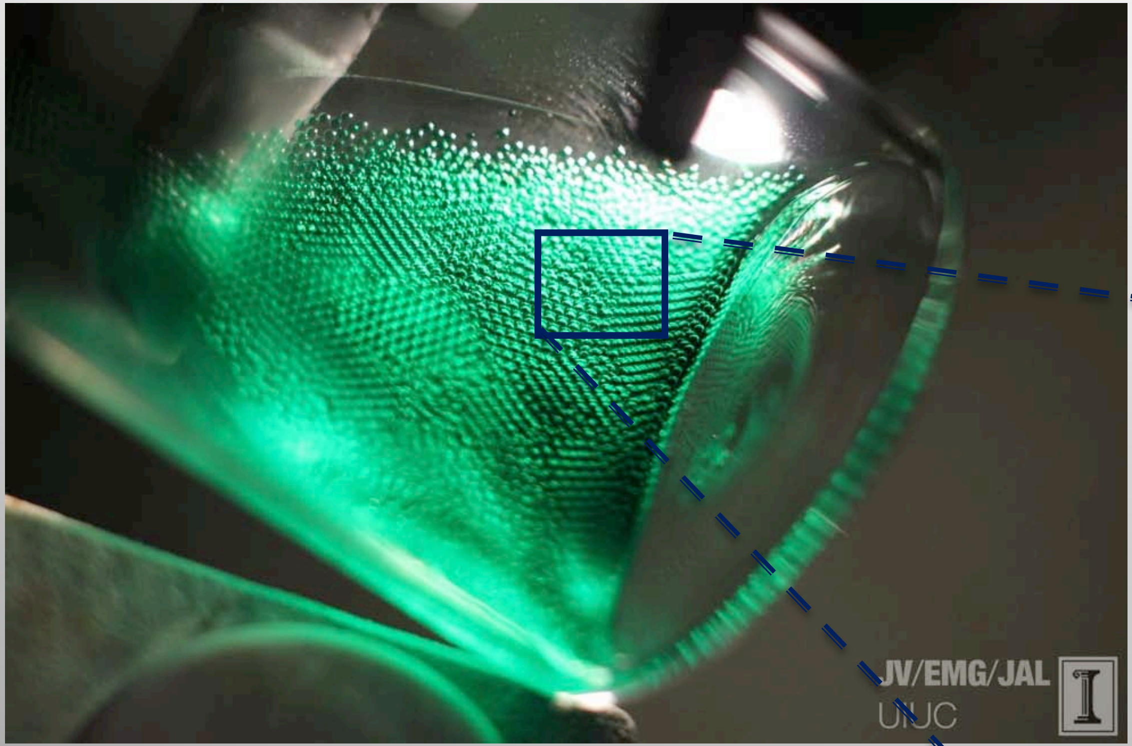
Water is required as a flux – making a difficult crystal mush

Rates of uptake are still limited by carbonate solution kinetics – very slow

# What if….

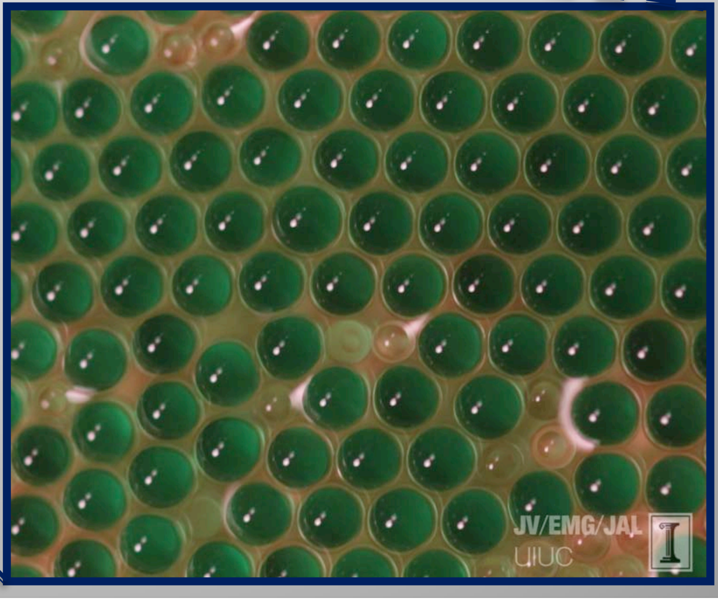
- ✓ **We could achieve acceptable reaction speeds, and**
- ✓ **Manage the solids with minimal water?**

# Our second innovation –microencapsulated solvents made from a photocurable silicone




**Multiple solvents and solids**
- MEA
- Carbonates
- Fluorescein

**And shell materials**
- Silicones (Semicosil)
- NOA



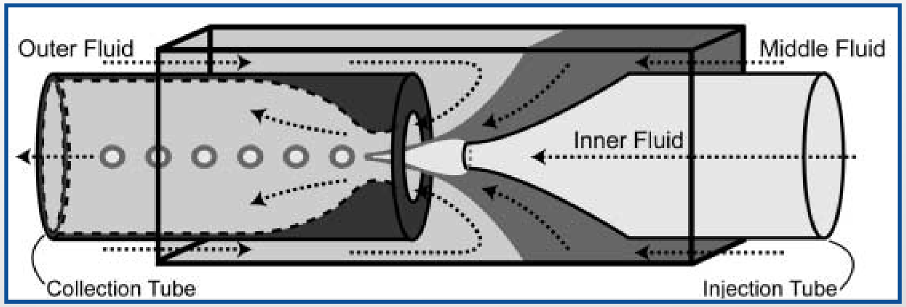
# Production requires balanced fluid properties – almost any polymer and fluid can work

Size control: shell diameter & thickness

Encapsulates ~100% of inner fluid

Core fluid can also have solids, or no liquid at all

Production rate: 1-100 Hz



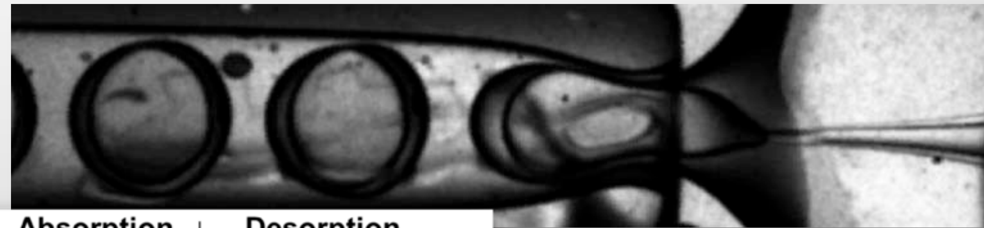

A.S. Utada, *et al.*, *Science* **308**, 537 (2005)


| Capillary | ID (μm) | OD (μm) |
|---|---|---|
| Injection | 50 | 870 |
| Collection | 500 | 870 |
| Square | 900 | 1000 |

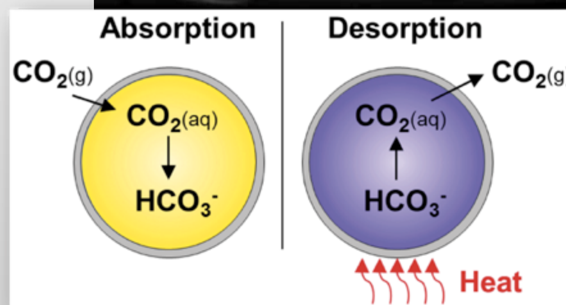
| Fluid | Viscosity (cP) | Flow rate (μl $h^{-1}$) |
|---|---|---|
| Inner Fluid | 10-50 | 1200-2500 |
| Middle Fluid | 10-50 | 800-1700 |
| Outer Fluid | 100-500 | 2000-5500 |

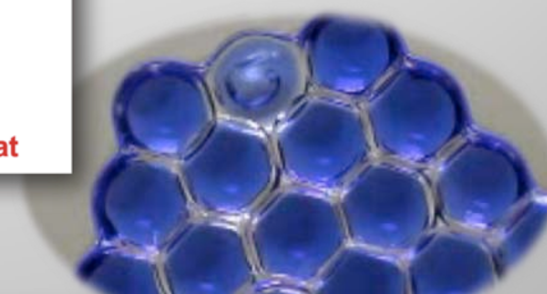
# Created originally as recyclable, high surface area liquid reactors for $CO_2$ concentration

Created by microfluidic "inkjet"



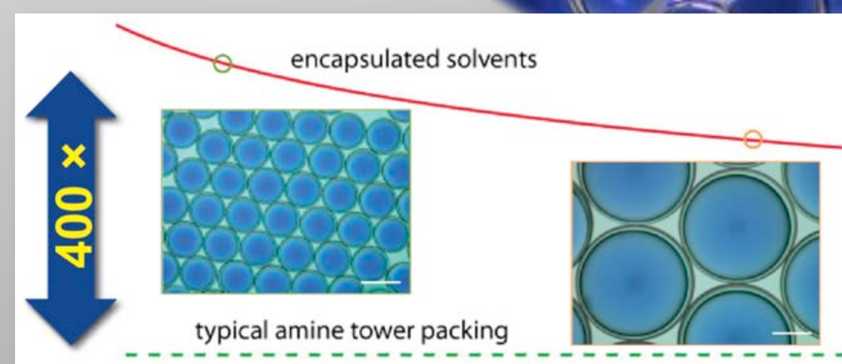
$CO_2$ absorbs through wall



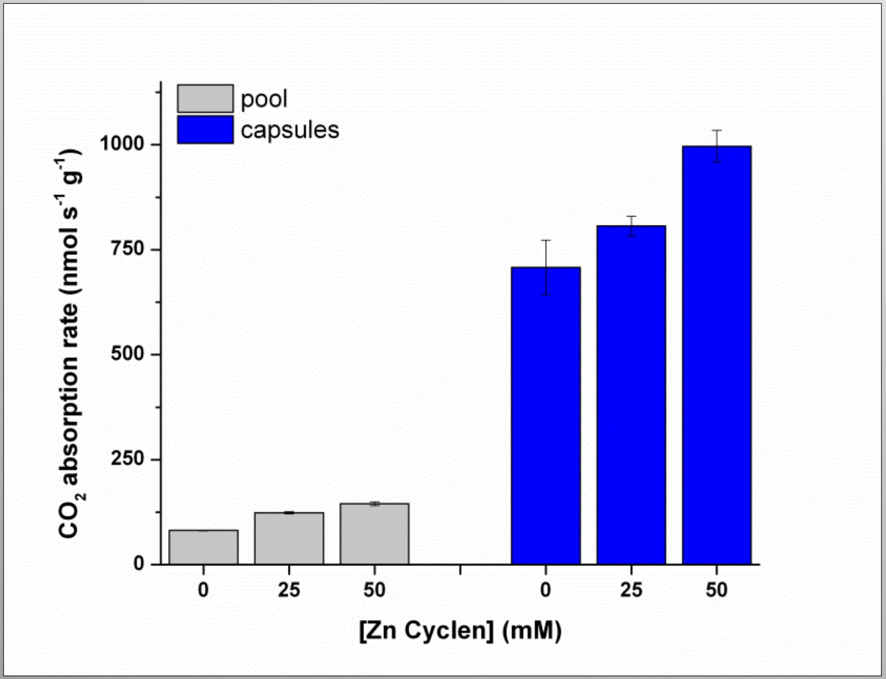



Fully recyclable

Surface area formed by capsule, not an expensive packed tower



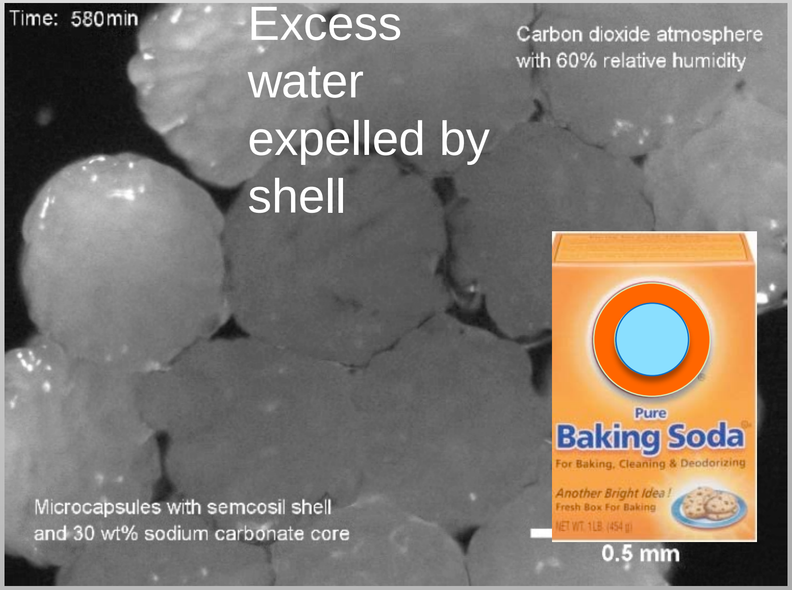
# Capsules increase carbonate capture rate by 10x (compared to same volume of liquid)




**(This is still about 10x slower than amine systems – more on that later)**

# And they provide really simple handling for solids

- Sodium bicarbonate precipitates *inside* shell
- Water is expelled
- Shrink wrapped solids are all identical

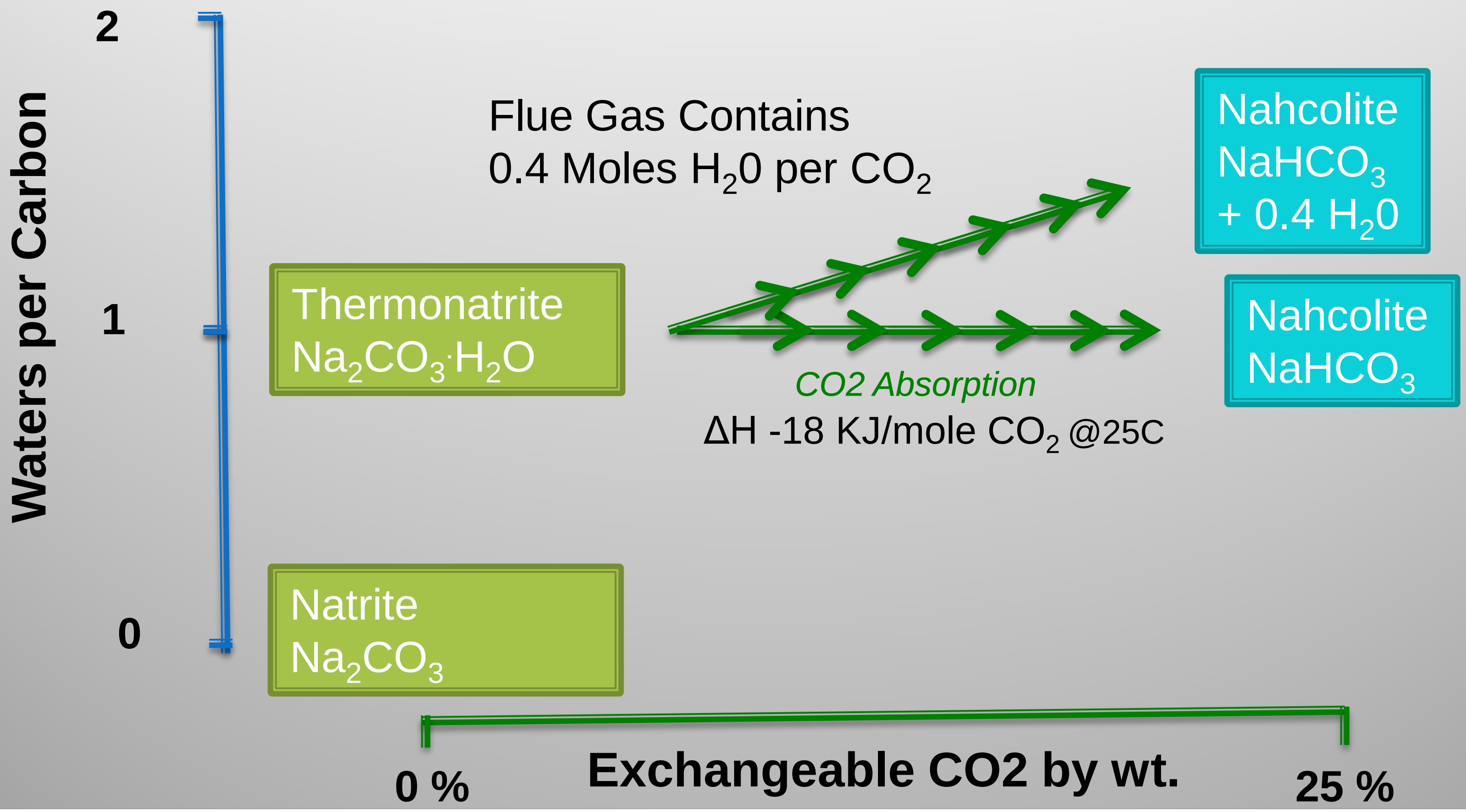


# Three dramatic improvements

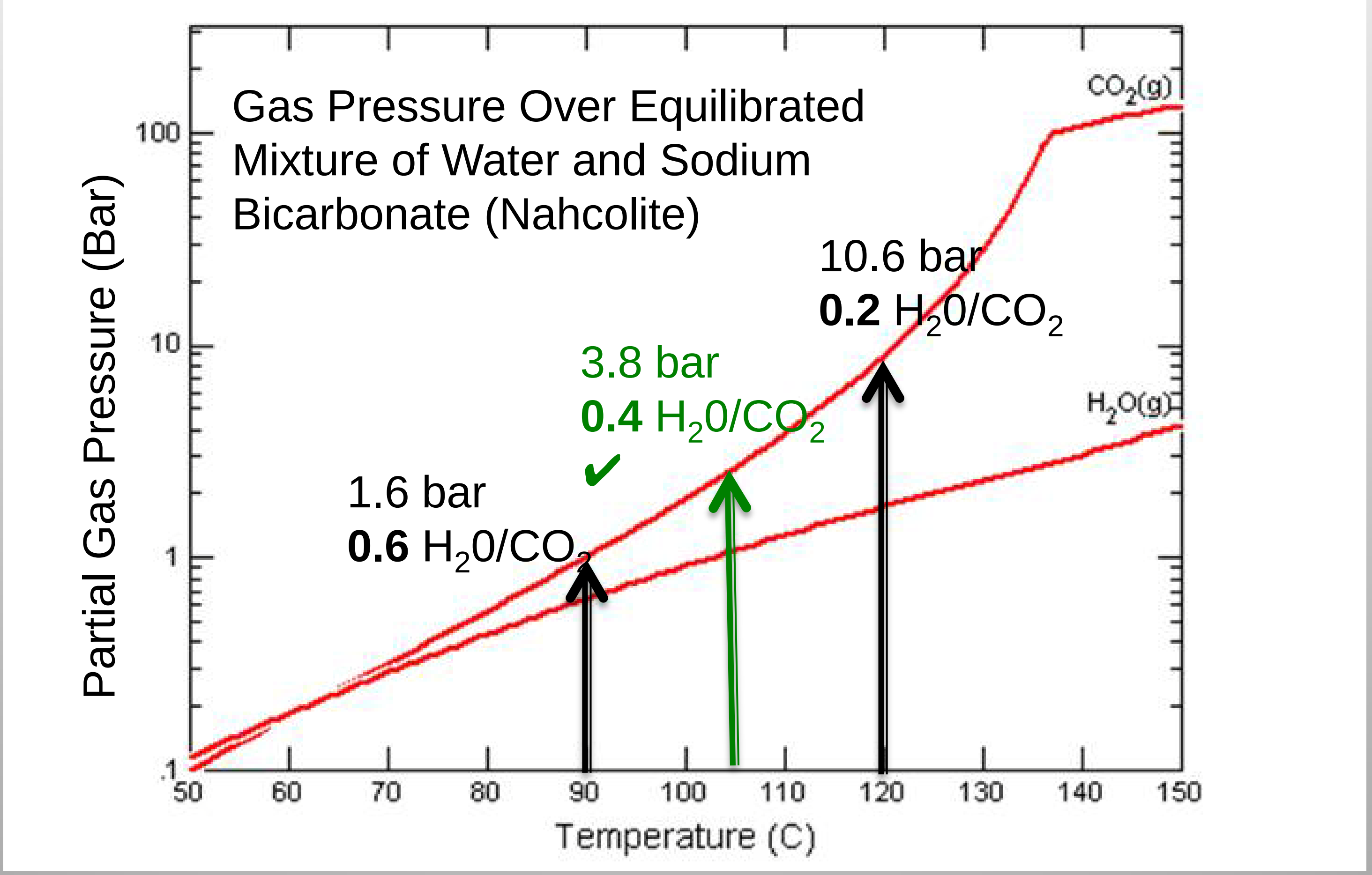
- ✓Encapsulation to control solids and speed capture
- ✓Catalysts to further speed capture
- ✓Automatic water exclusion for slurries

**But will it work in flue gas? Again water is the key – it is always present.**

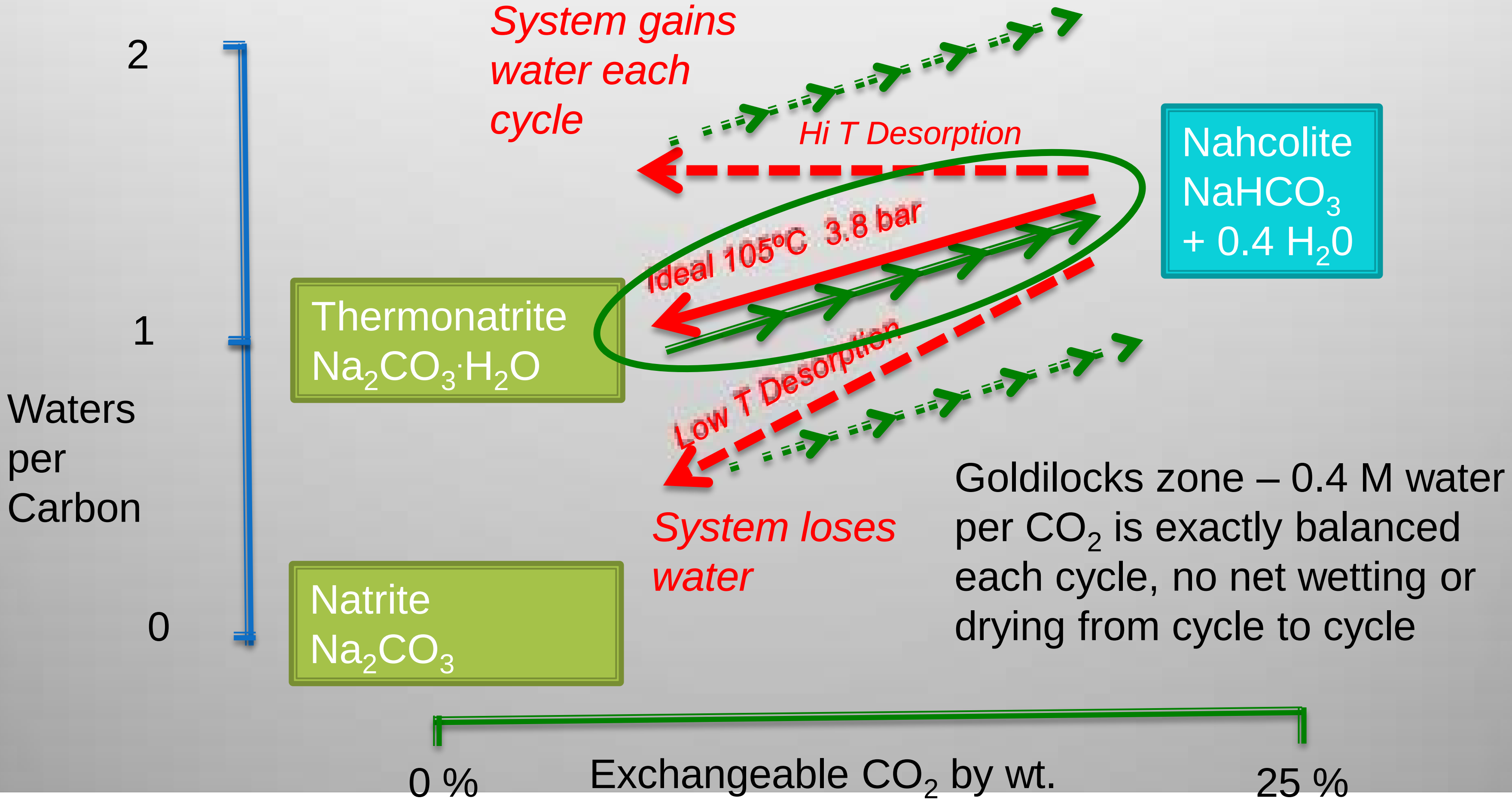
# Our encapsulated carbonate/bicarbonate swing is activated by water added from flue gas



# On heating, $CO_2$ pressure is *higher* than water due to sublimation from the solid



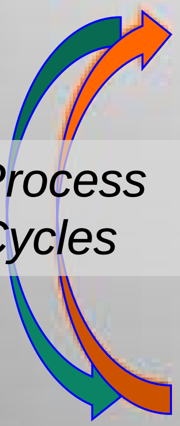
# Minimum equilibrium water content is a function of desorption temperature



# Let's review the cycle:

*Bed Charging*

1. Capsules are dried after production to precipitate a dry, encapsulated sodium carbonate.

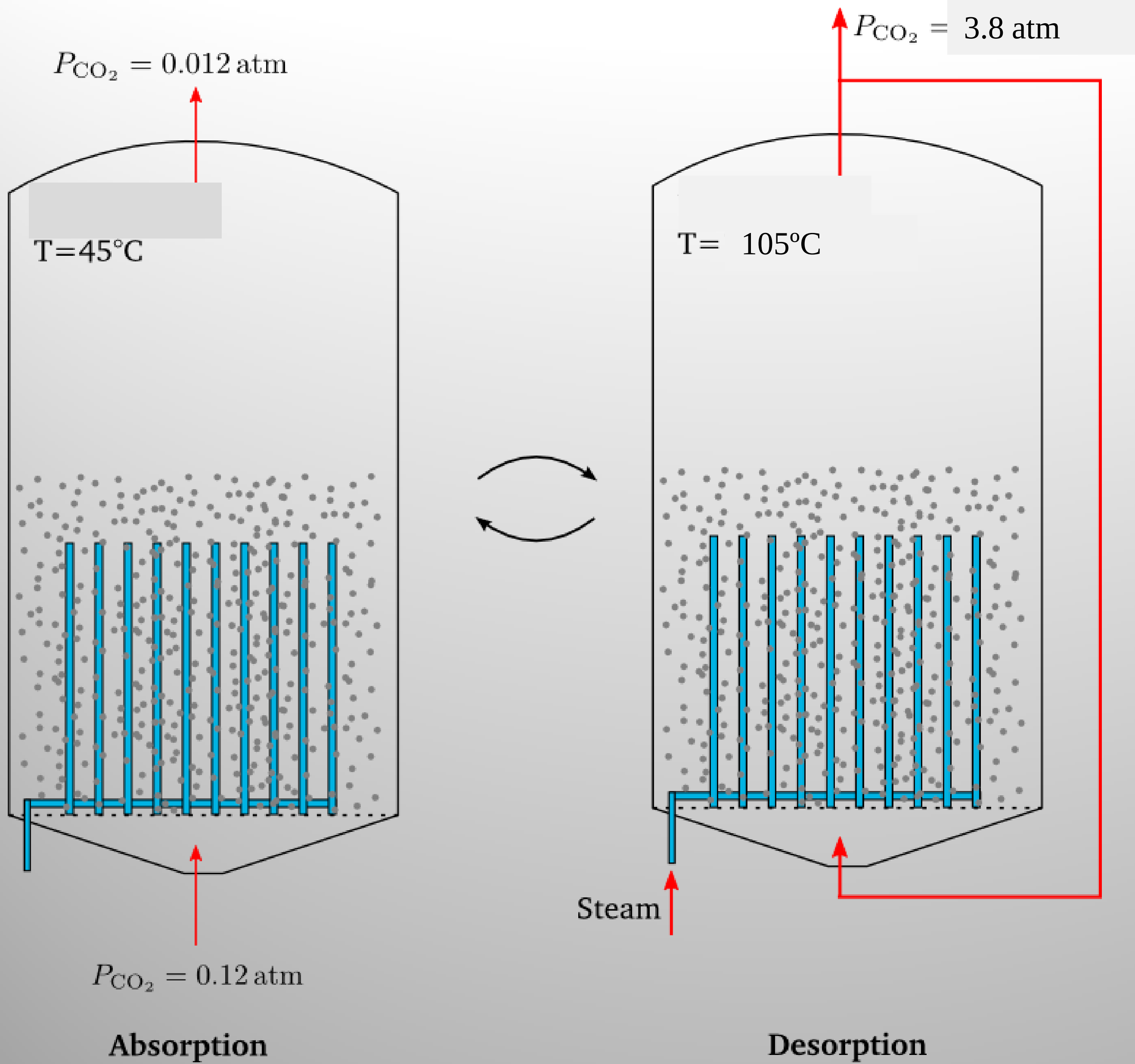


*Process Cycles*

2. Capsules absorb $CO_2$ and $H_2O$, converting to sodium bicarbonate slurry.

   *Heat with indirect steam*

3. Heat to 105ºC, desorb $CO_2$ at 3.8 bar. Capsules revert to dry, encapsulated sodium carbonate.




Operating concept is being refined:
one option is dual fluidized beds.

# What about…..

- SOx and NOx
  - Permanently absorbed – potential for fertilizer use
- Lifetime of capsules
  - >100 cycles (thermal testing to date)
  - Abrasion expected to be small, testing underway
  - Limited by SOx and NOx in some cases
- Cost of capsule production
  - Estimated $0.10/lb (mostly capsule wall material)
  - For 100 cycle lifetime, capsule cost $2/ton $CO_2$ captured
- Size of facility
  - Larger footprint than amine stripper

# What is needed next?

- Material optimization
  - Minimal abrasion
  - Good fluidization
  - Recycling when SOx or NOx build up
- Improved kinetics (always!)
  - Crystal seeding
  - Minimum capsule wall
- Bench scale process evaluation

# Engineering a truly low-energy capture system appears possible

- ✓ Desorption enthalpies ¼ of current solvents
- ✓ Minimal water evaporation
- ✓ Optimal for coal or natural gas
- ✓ Environmentally friendly materials


- ◆ Absorption will be slower