# Encapsulated Solvents for Carbon Dixode Capture

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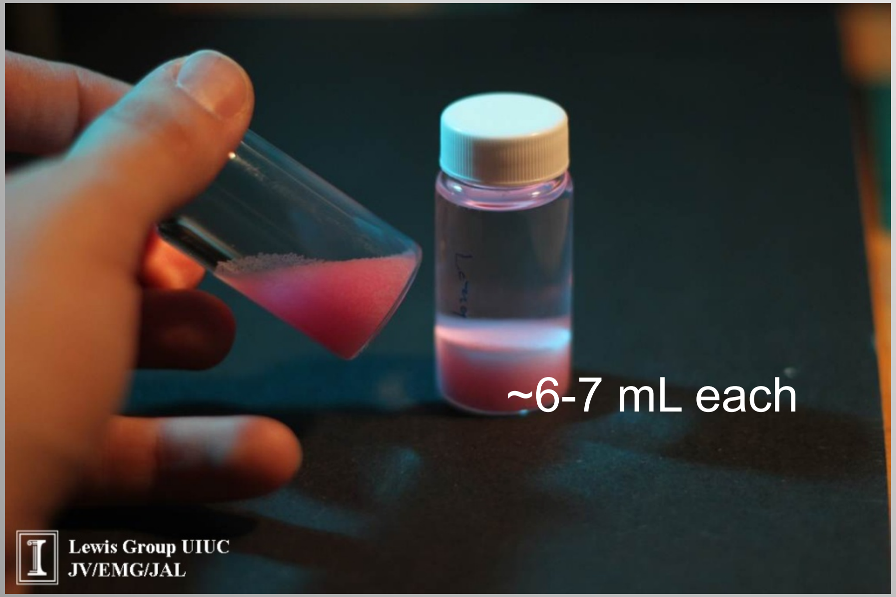
# ***Concept***: Encapsulate liquid solvents such as MEA in a thin, permeable, polymer shell.


### Initial Goals

✓Reduced volatility

✓Degradation products contained




### Additional Benefits

✓Increased surface area

✓Good interface with capture catalysts

✓Facilitates new chemistries, especially high viscosity

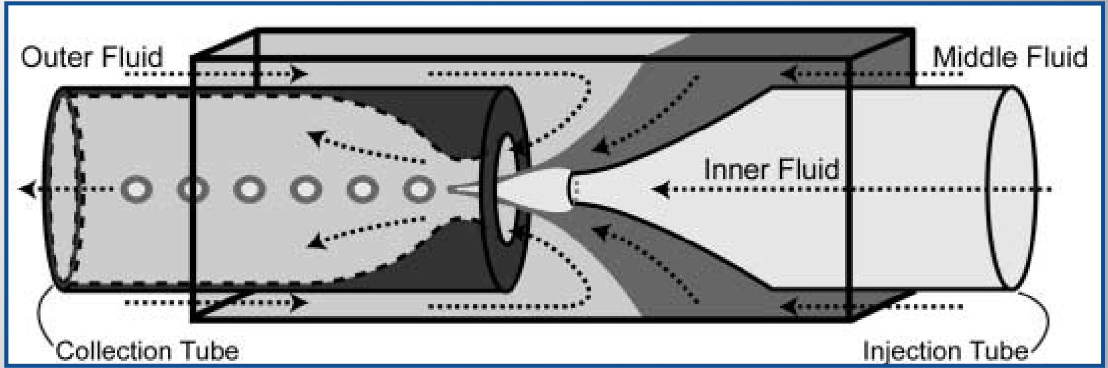
# Fabricating Double-Emulsion Microcapsules with a Flow-Focusing Microfluidic Geometry

Size control: shell diameter & thickness

Encapsulates nearly 100% of inner fluid

Embed catalyst in shell wall or inner fluid

Production rate: 1-5000 Hz




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

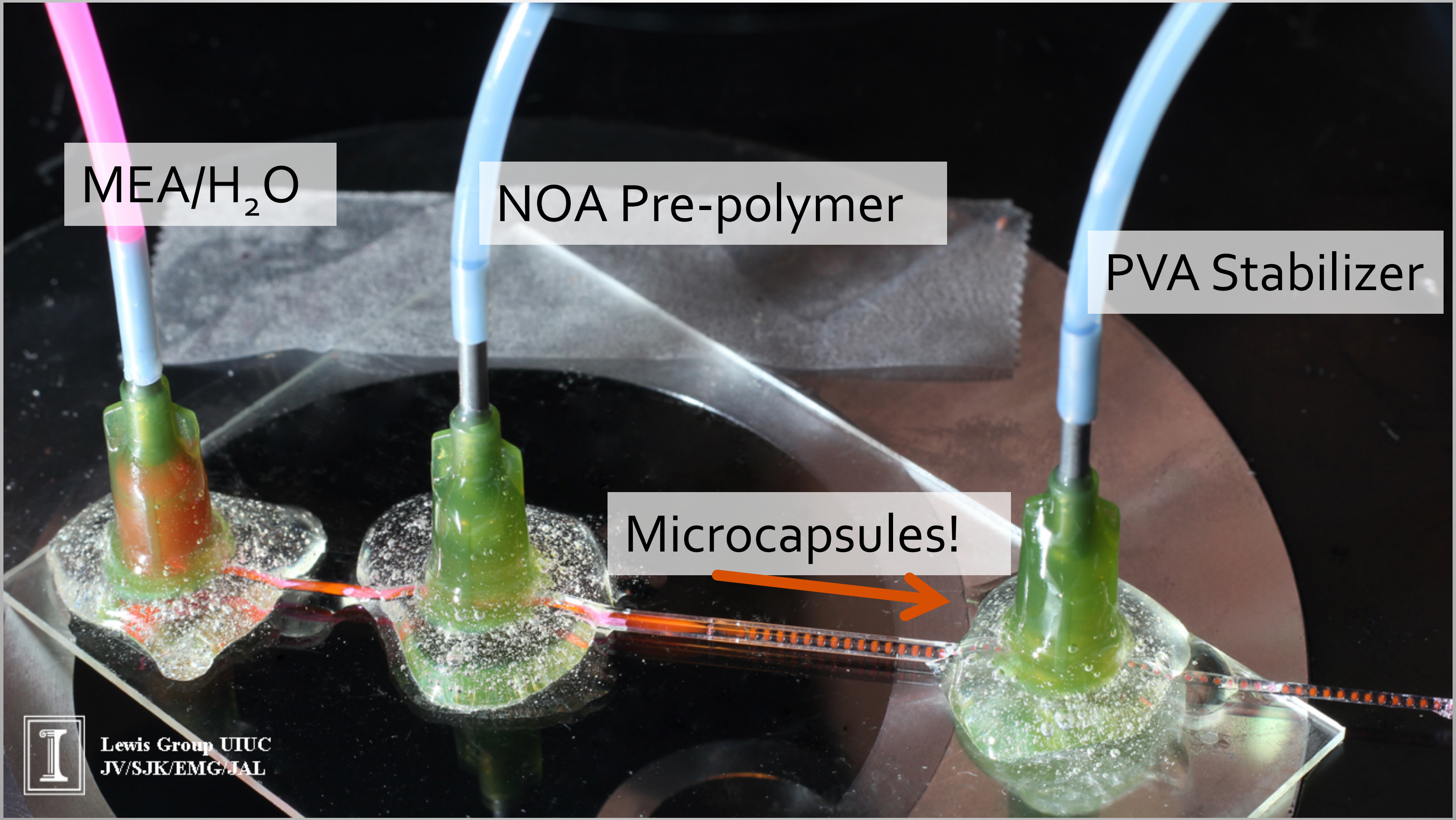
| Capillary | ID (μm) | OD (μm) |
|---|---|---|
| Injection | 50 | 1000 |
| Collection | 500 | 1000 |
| Square | 1000 | 1200 |

| 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 |

# Microcapsule Production - Movie

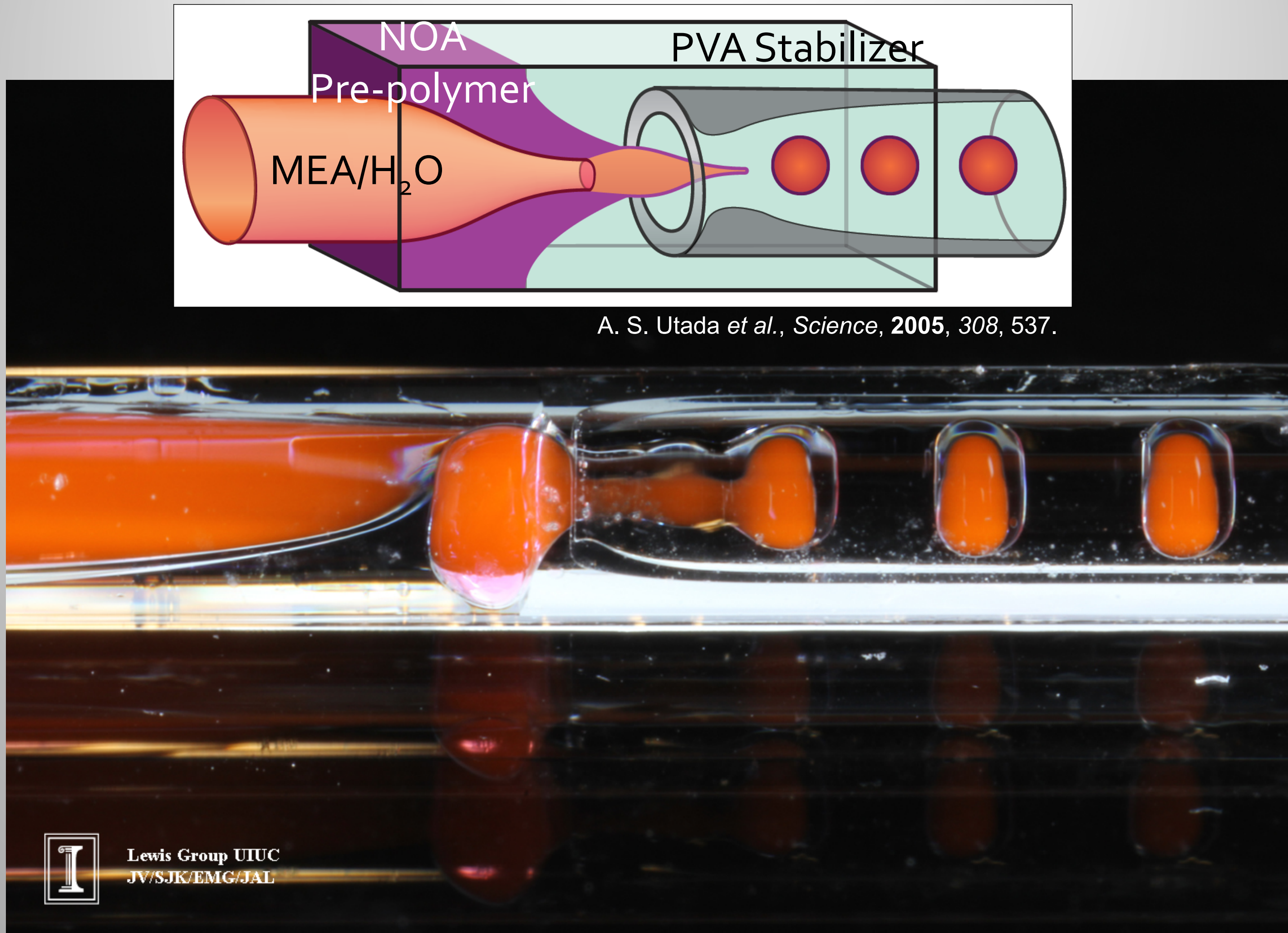
Playback 1/10th speed

# Parallel Production Can Provide Scale-up For These Simple Devices



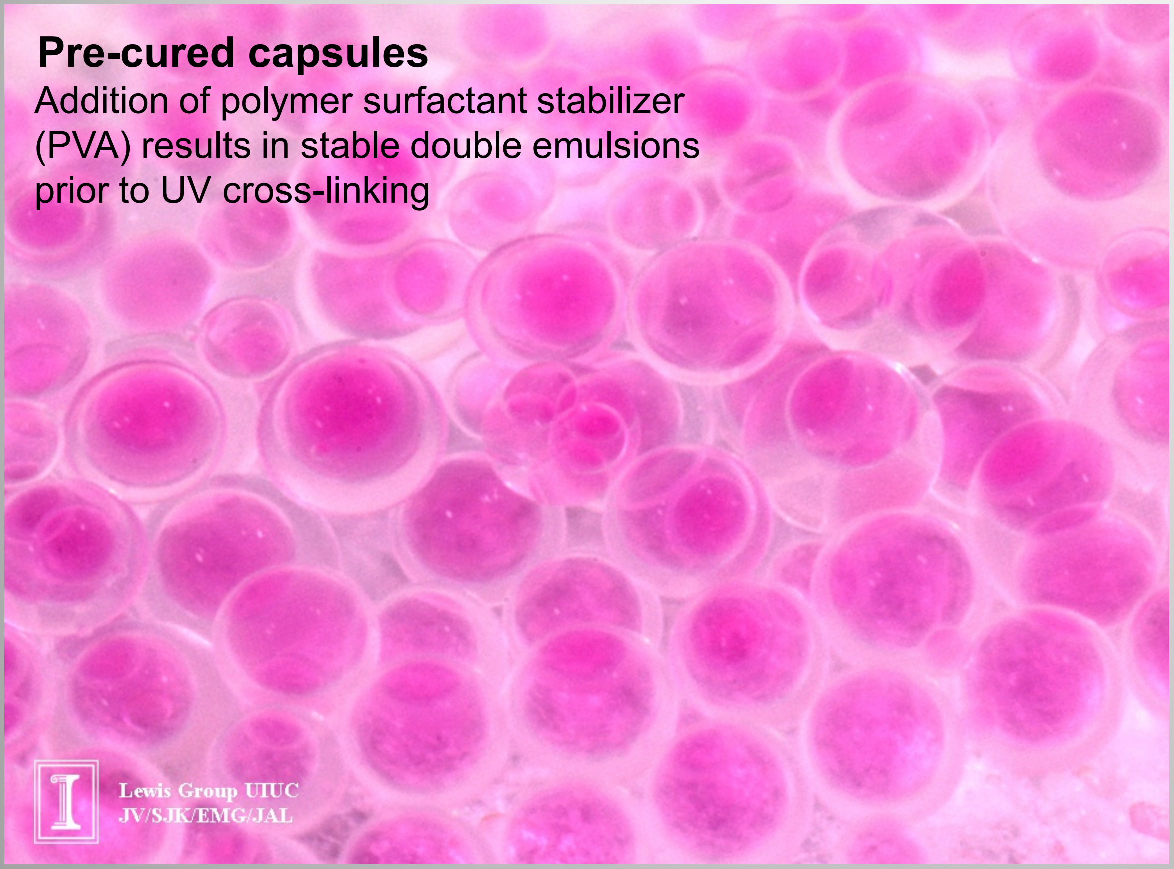

Real-time image of capsule production – John Vericella, UIUC

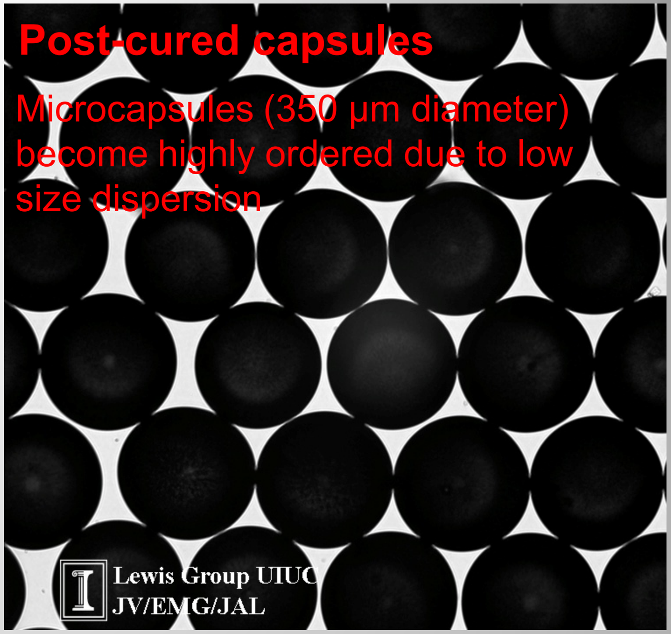
# Microcapsule Production

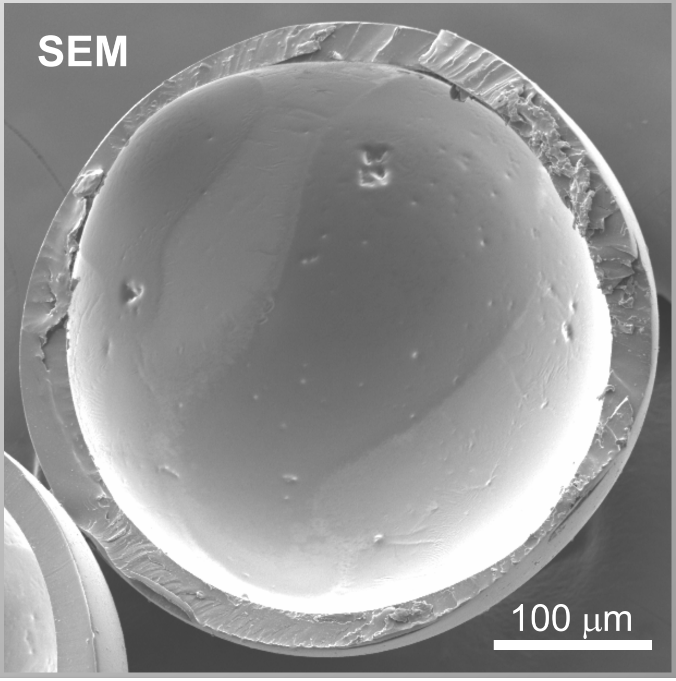



Formation of double emulsions within microfluidic device using methods described by the Weitz group

# NOA/MEA Microcapsules




Lewis et al. 2011

# Encapsulated solvents design parameters

- Encapsulation provides large surface area and new process designs in exchange for slower $CO_2$ absorption per unit surface area
- Goal: system that compares favorably to MEA packed tower

**Capsules** with sufficient:

- permeablity
- structural integrity
- loading capacity, etc

Viable **system design** in terms of:

- pressure drop
- capital expense
- capsule retention, etc.

# Required Microcapsule Properties

What are the chemical constraints for the shell material?

- Formed via photo-polymerization or interfacial polymerization
- Cured material is compatible with amines (or other solvents of interest) and resistant to corrosion
- Thermally resistant to 120$^oC$

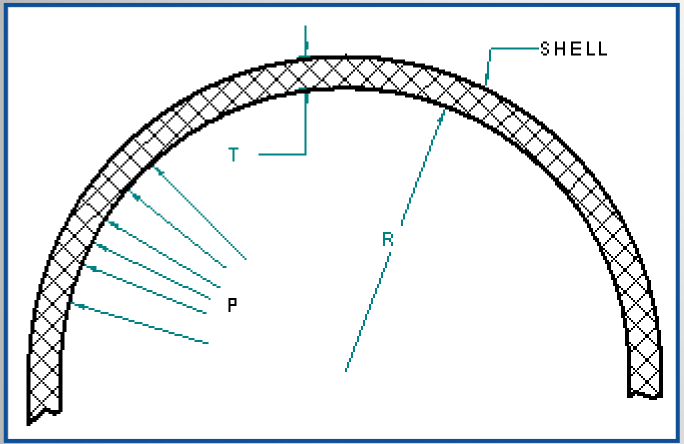
What are the permeation constraints?

- Solvents and catalysts must remain encapsulated
- Shell materials must be permeable to $CO_2$
- Requires optimal shell thickness for mass transfer/mechanical stability

What are the mechanical constraints?

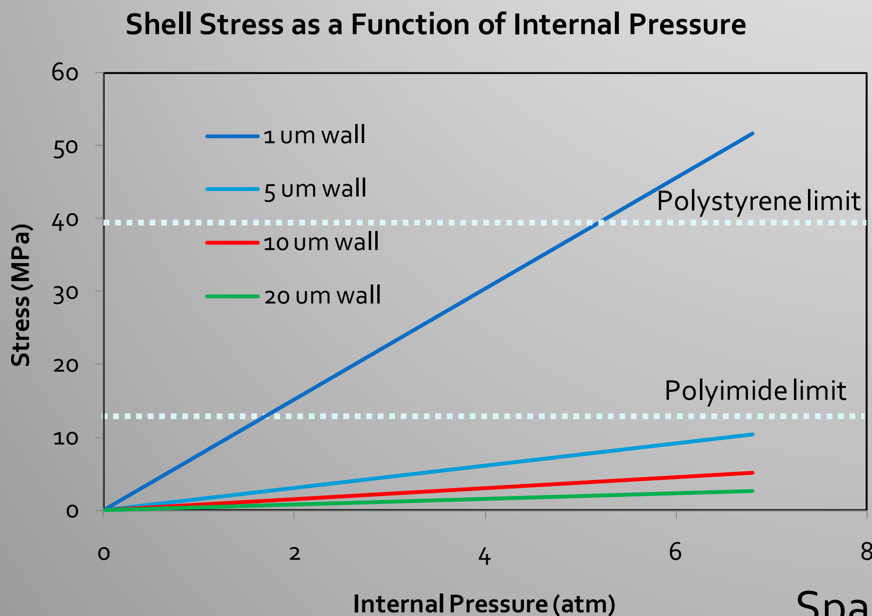
- Microcapsules must not rupture during $CO_2$ uptake/regeneration or during handling in packed/fluidized bed

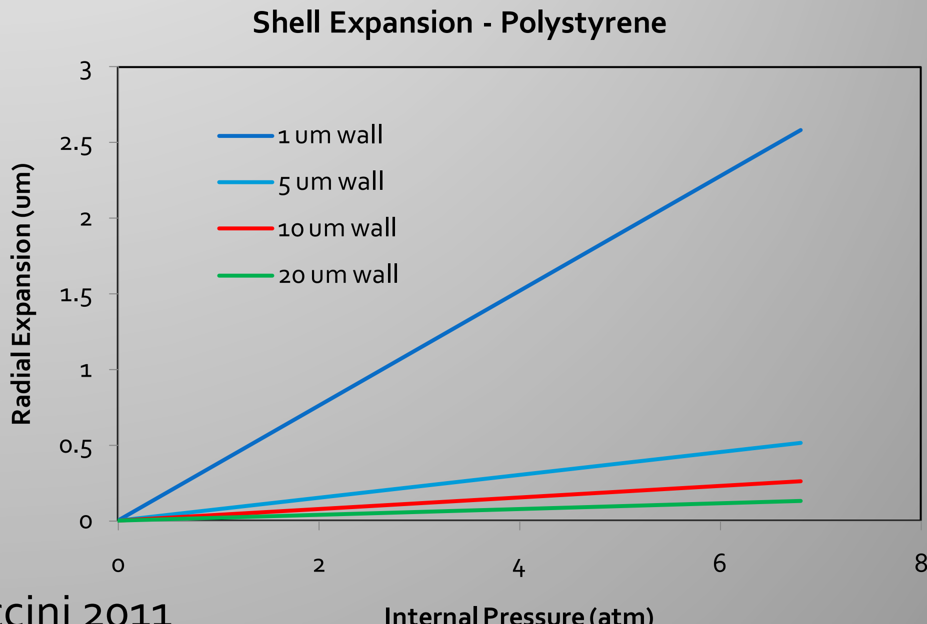
# Mechanical Constraints: Examining Hoop Stress of Polymer Shells using a Pressure Vessel Approximation




- 300 μm diameter capsule assumed
- Hoop stress over a range of pressures compared to yield
- Radial growth estimated

***For capsule geometries and internal pressures of interest, no apparent issues***




Spadaccini 2011

# We can calculate an "equivalent permeability" for membrane shells

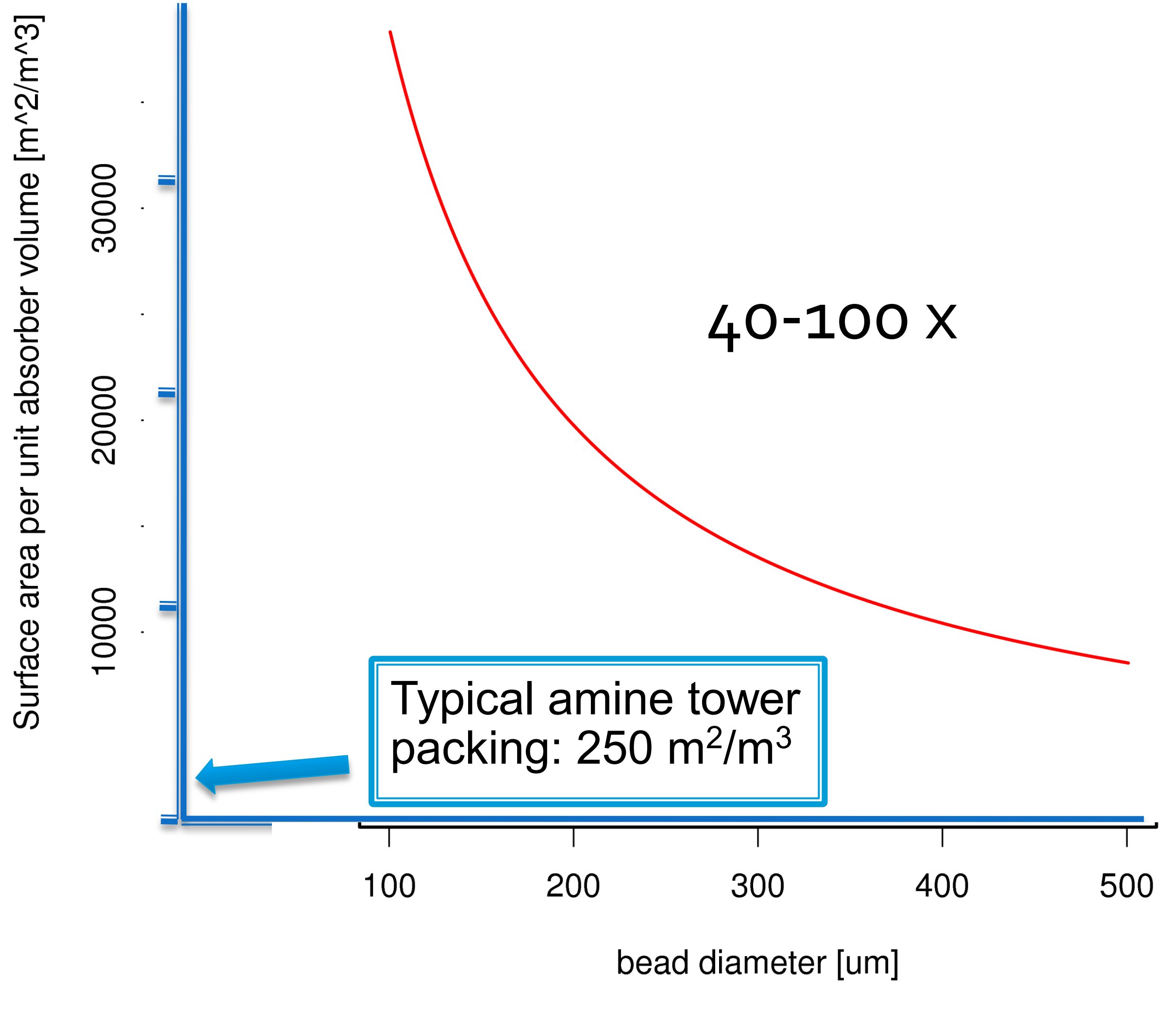
*The point at which mass transfer resistance across the shell equals that for the liquid it contains*

| Case | K (m/s) | Equiv. Permeability (barrer) @ 5 µm thickness | Reference for K |
|---|---|---|---|
| 5M MEA | $4.0 \times 10^{-3}$ | 26,000 | Dang and Rochelle (2003) |
| 5M NaOH | $2.6 \times 10^{-3}$ | 17,000 | Stolaroff et al. (2008) |
| 1N $Ca_2CO_3$ | $1.5 \times 10^{-5}$ | 430 | Harte and Baker (1933) |

This equivalent permeability presents a target mass transfer resistance bead systems

Stolaroff 2011

# Surface area in bed of randomly-packed spherical beads is roughly 40-100x that in an amine tower (void space, ϵ = 0.38)




Stolaroff 2011

⇒Increased surface area roughly compensates for shell resistance at permeability of ~100 to 400 barrer (4000 to 40,000 on previous slide)

⇒Our minimum target shell permeability is ***100 barrer***

# A literature survey revealed promising candidate shell materials with high $CO_2$ permeabilities

| Shell Material | $CO_2$ permeability (barrer) | Photocurable? |
|---|---|---|
| Poly(1-trimethylsilyl propyne) | 28,000 | Yes |
| Vinyl alcohol/acrylate copolymer | 6,100 | Yes |
| Polydimethylsiloxane (PDMS) | 4,500 | Yes |
| Semicosil silicone | 3500 | yes |
| Polyimide with 6FDA groups | 900 | Yes, but lowers permeability |
| Cellulose acetate | 400 | Yes |
| Poly(vinyl alcohol) | 160 | Yes |

C. E. Powell & Greg G. Qiao, "Polymeric CO2/N2 gas separation membranes for the capture of carbon dioxide from power plant flue gases," *J of Membrane Science*, **279** (2006) 1–49.

C. A. Scholes, S. E. Kentish, & G. W. Stevens, "Carbon dioxide separation through polymeric membrane systems for flue gas applications," *Recent Patents on Chem Eng*, **1**, (2008), 52-66.

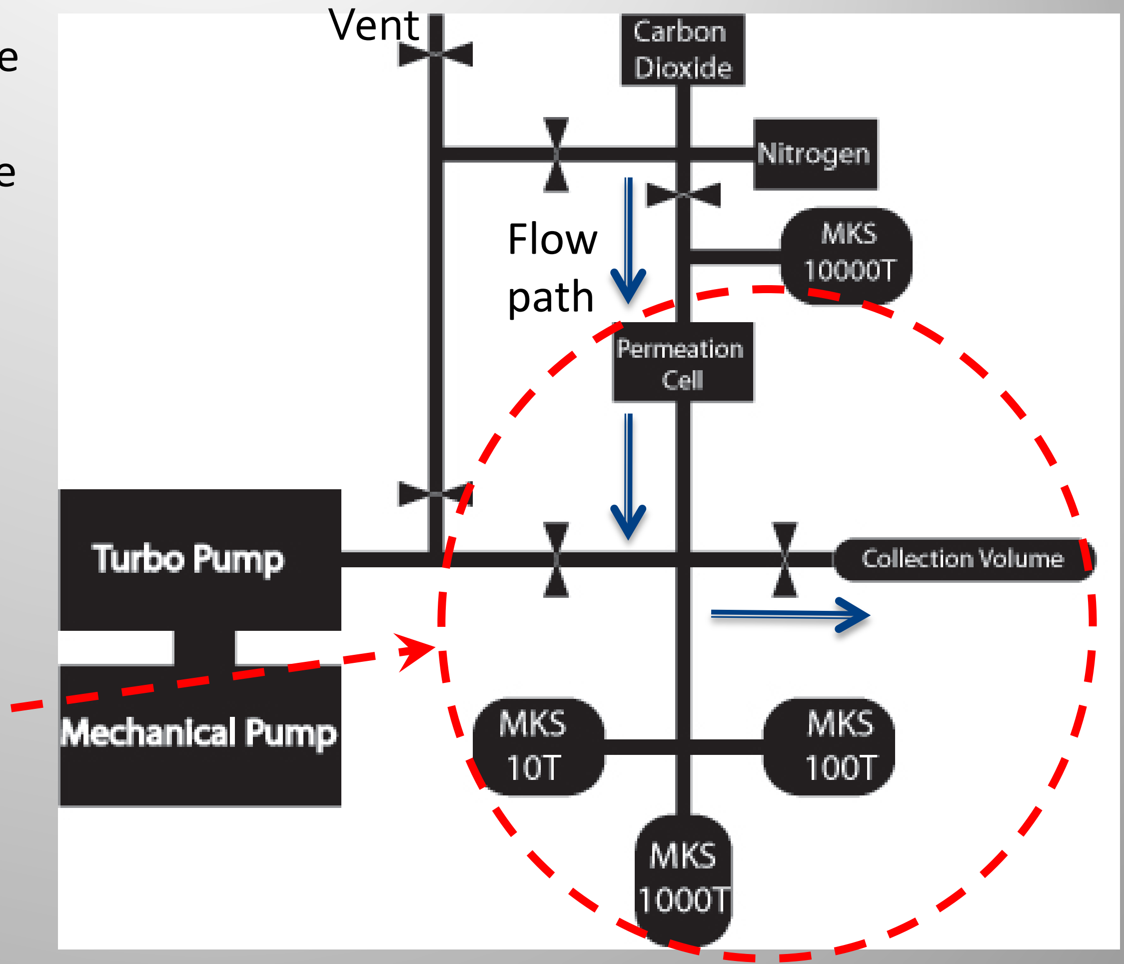
# We have assembled an apparatus to test gas permeability of shell materials in membrane form

LabView data acquisition:

- Collection volume temperature
- Upstream inlet pressure
- Downstream collection volume pressure
  - 1-10 torr
  - 10-100 torr
  - 100-1000 torr

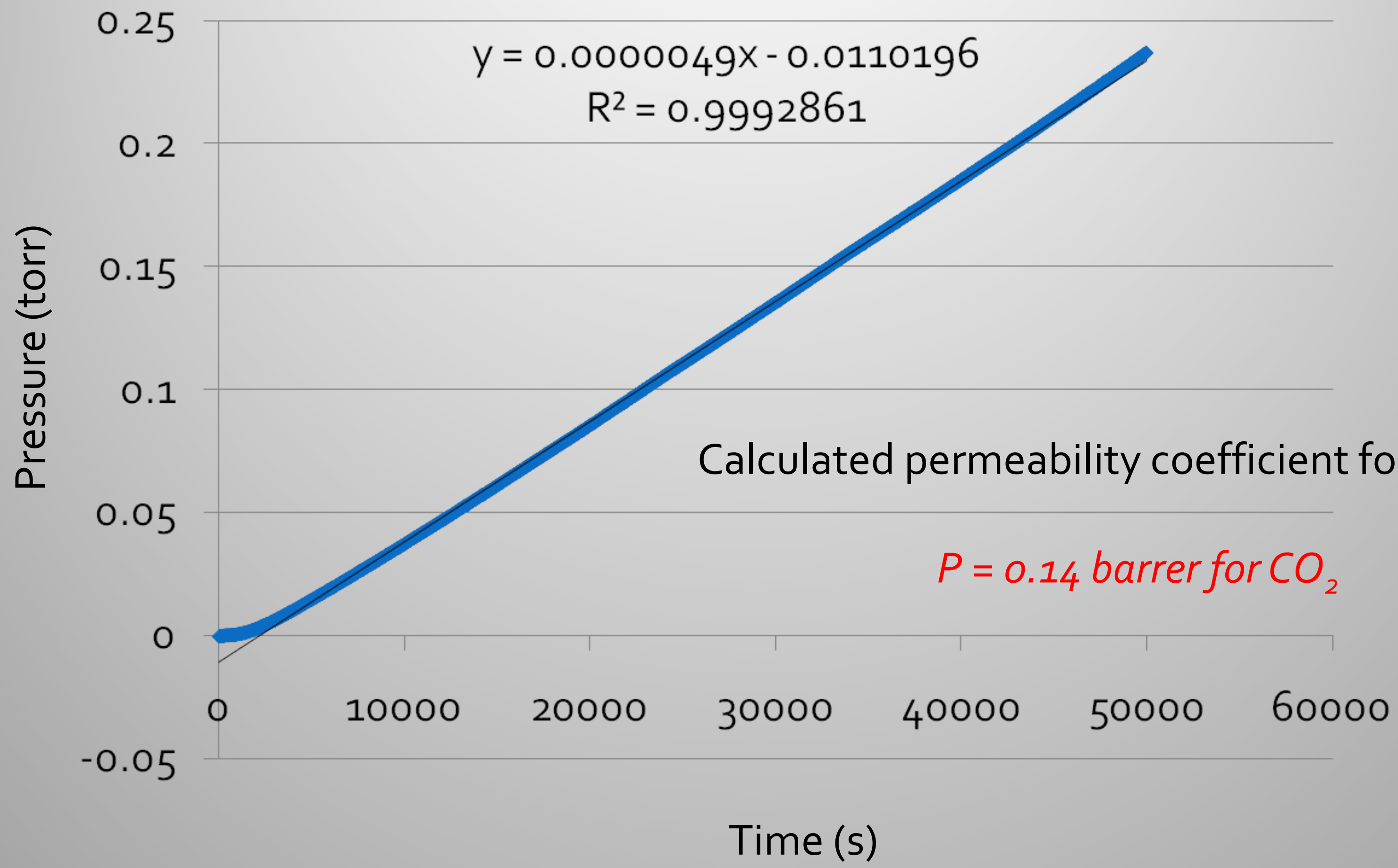
Test apparatus capable of single gas and binary gas permeation experiments

*GOAL:* Measure leak-up rate, *dP/dt*, through membrane into collection volume.




Spadaccini et al. 2011

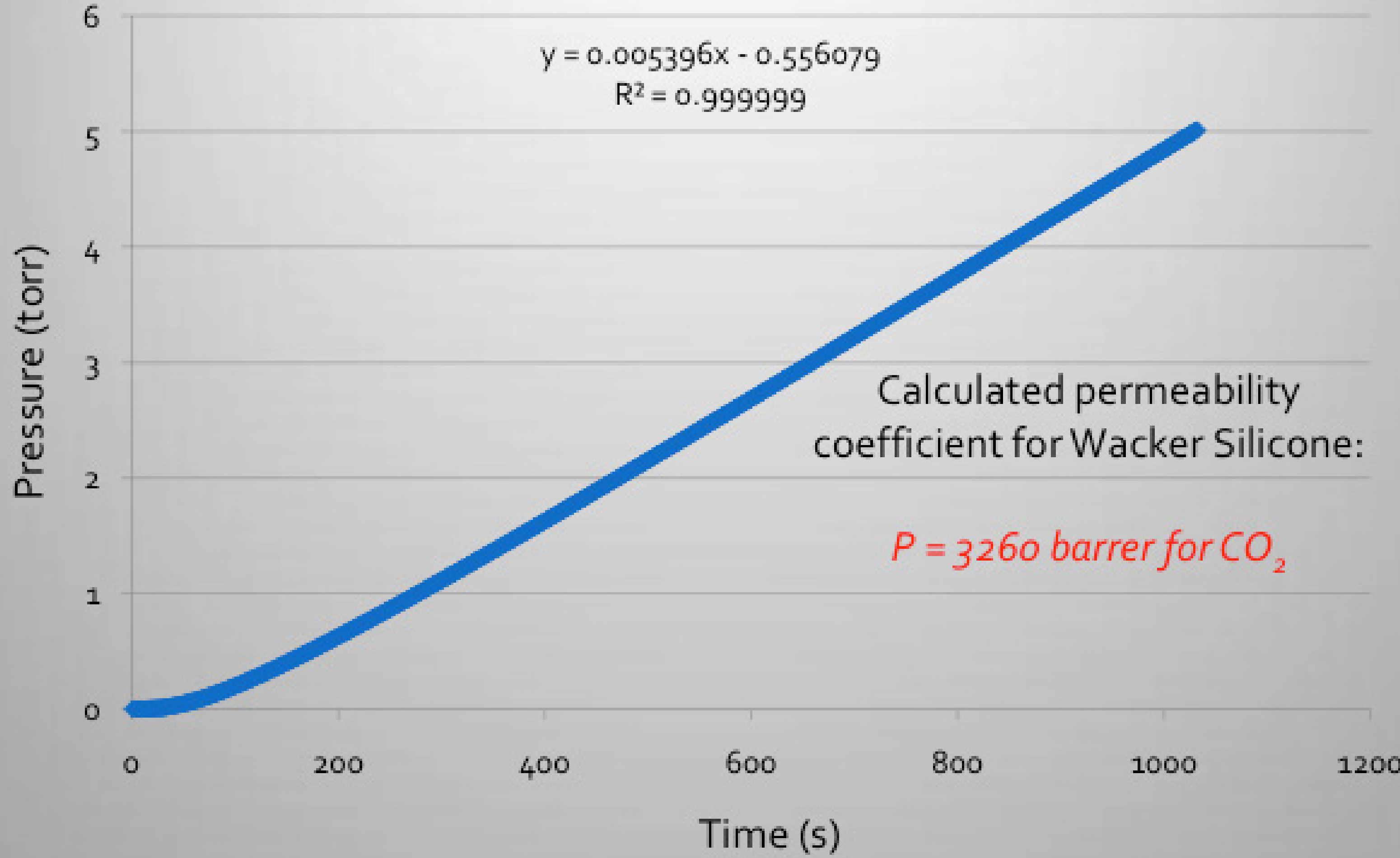
# Our first test shell material, Norland Optical Adhesive 61, helped set fab procedure but has a low CO2 permeability




Calculated permeability coefficient for NOA 61:

*P = 0.14 barrer for $CO_2$*

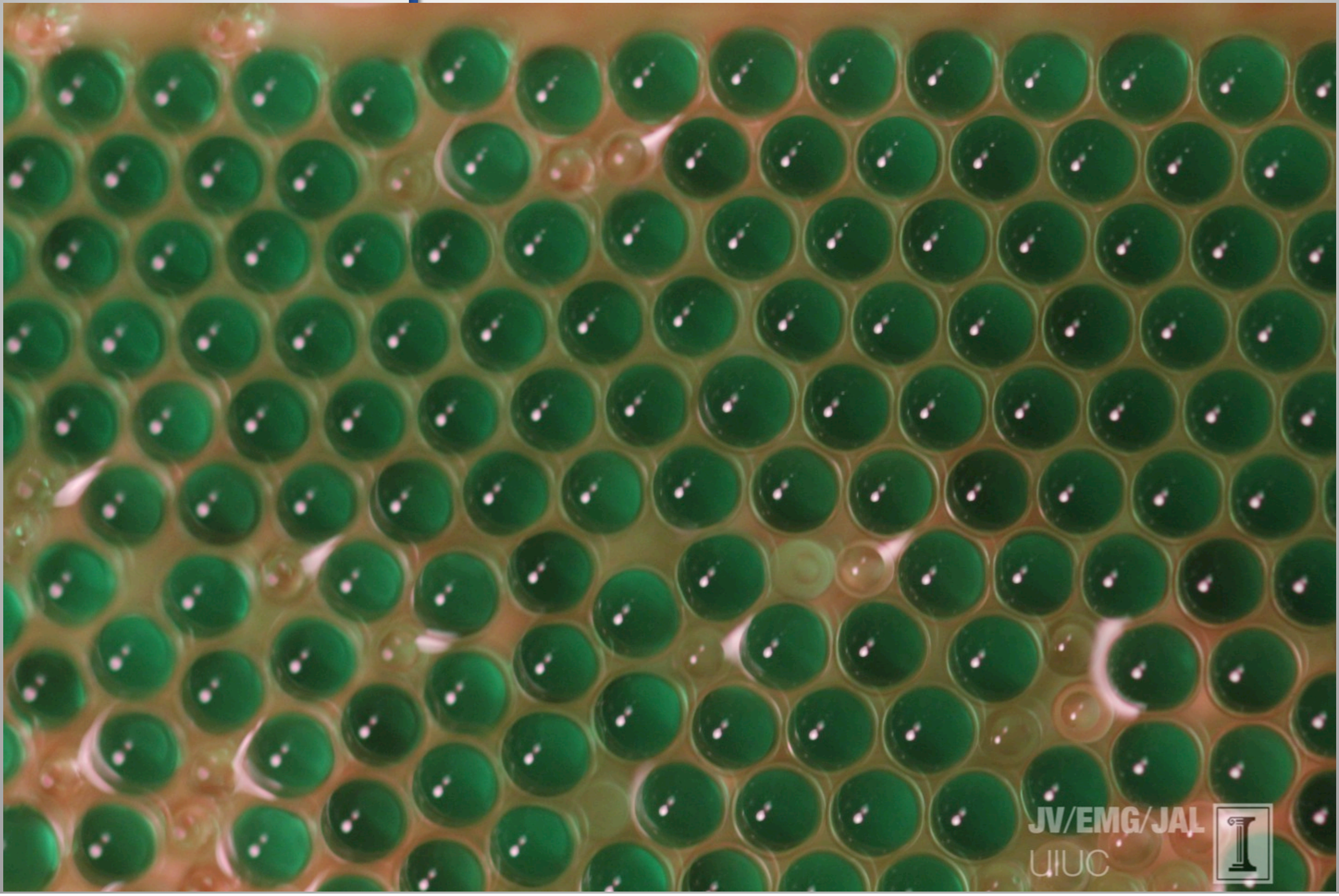
# But Wacker Semicosil silicone appears very suitable



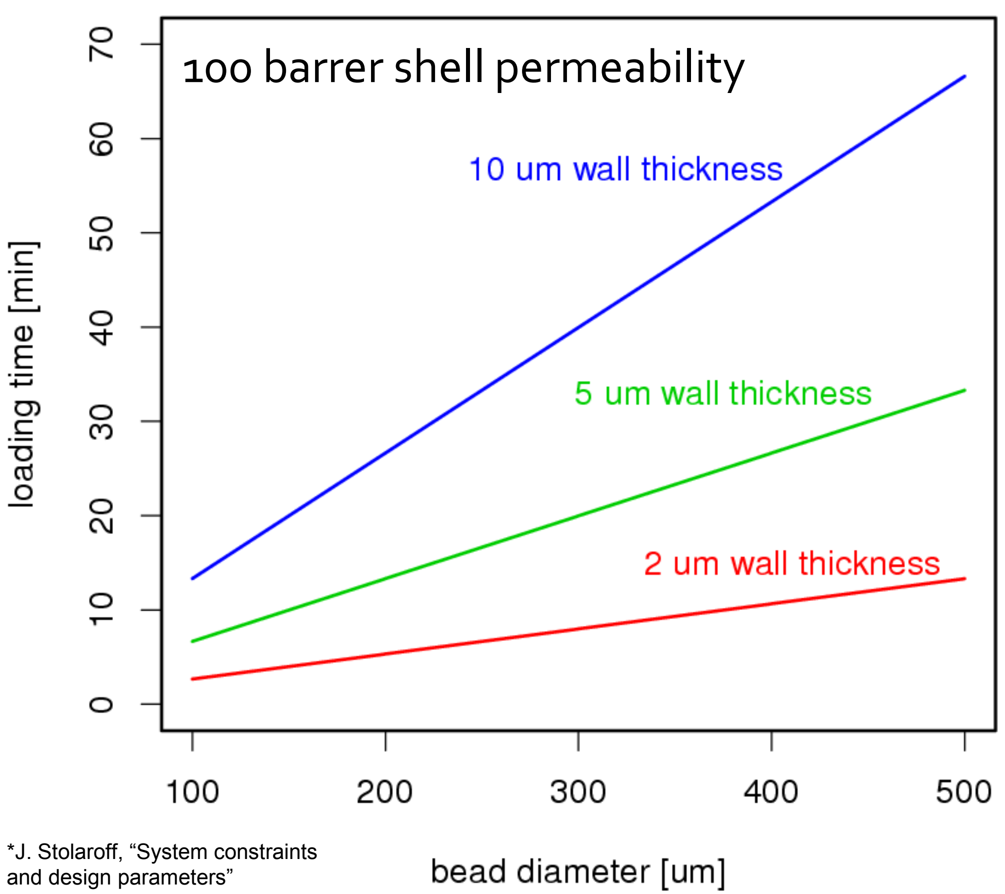

Calculated permeability coefficient for Wacker Silicone:

*P = 3260 barrer for $CO_2$*

# Semicosil Capsules



# Simple diffusion models indicate loading times can be comparable to MEA residence time in conventional stripping towers

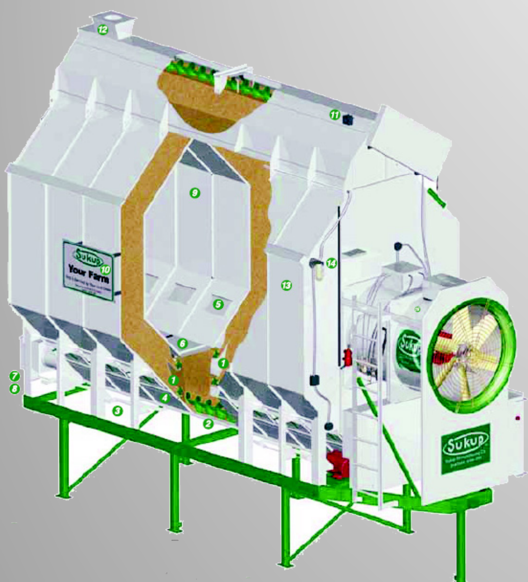



*J. Stolaroff, "System constraints and design parameters"

- Calculation performed for*:
  - 30% MEA in water
  - 15% $CO_2$ in gas stream
- The capsule must remain in contact with flue gas at ~50°C for 5-10 minutes in order to fully load the amine with $CO_2$.

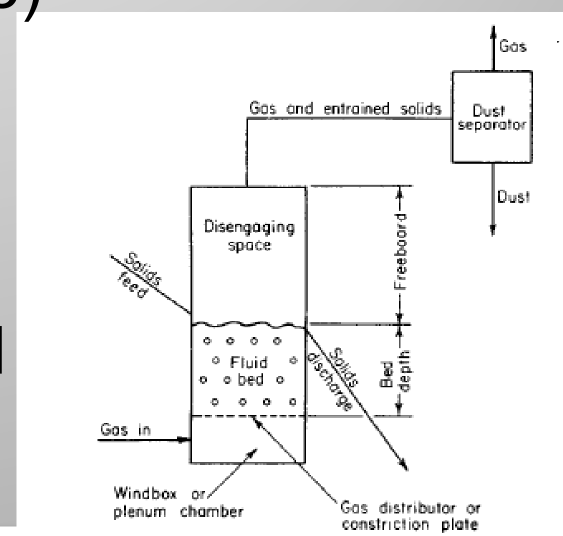
# We are evaluating possible process configurations

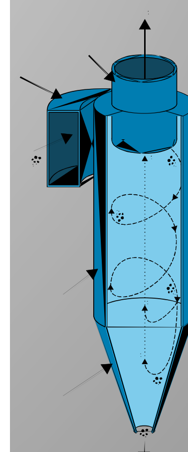
Packed bed




Moving bed
(grain dryer-type)

Fluidized bed



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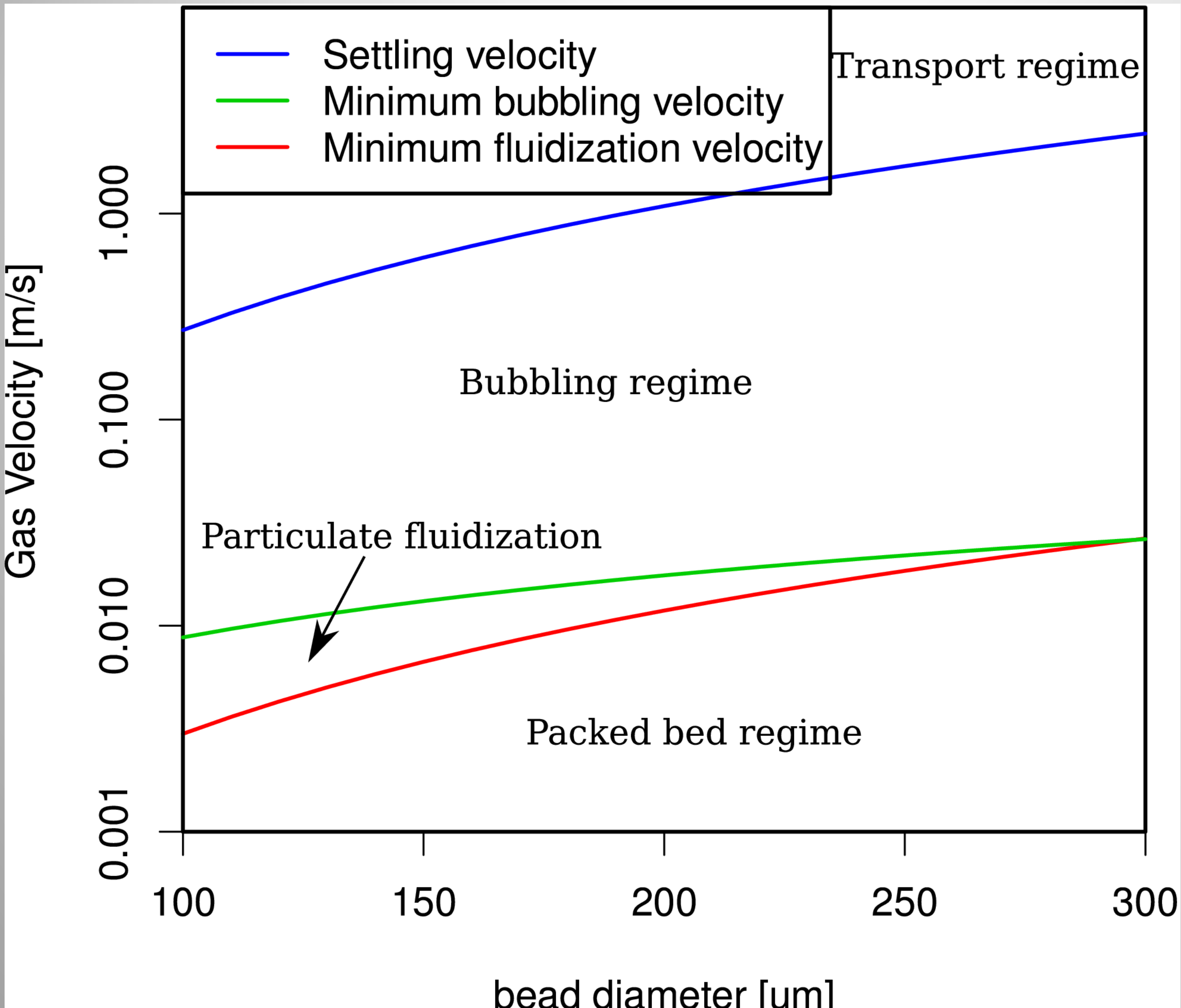
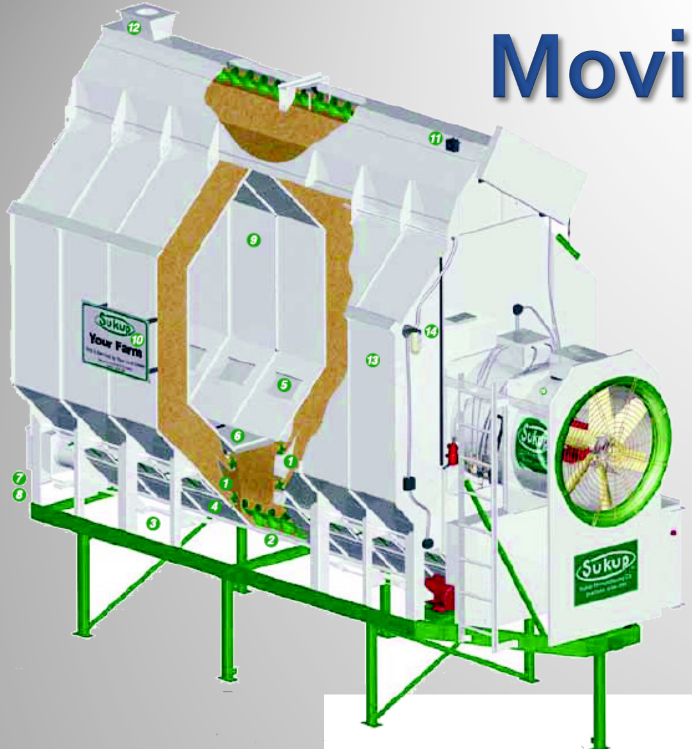
# Realistic beads are light – only transport regime appears feasible in fluidized beds



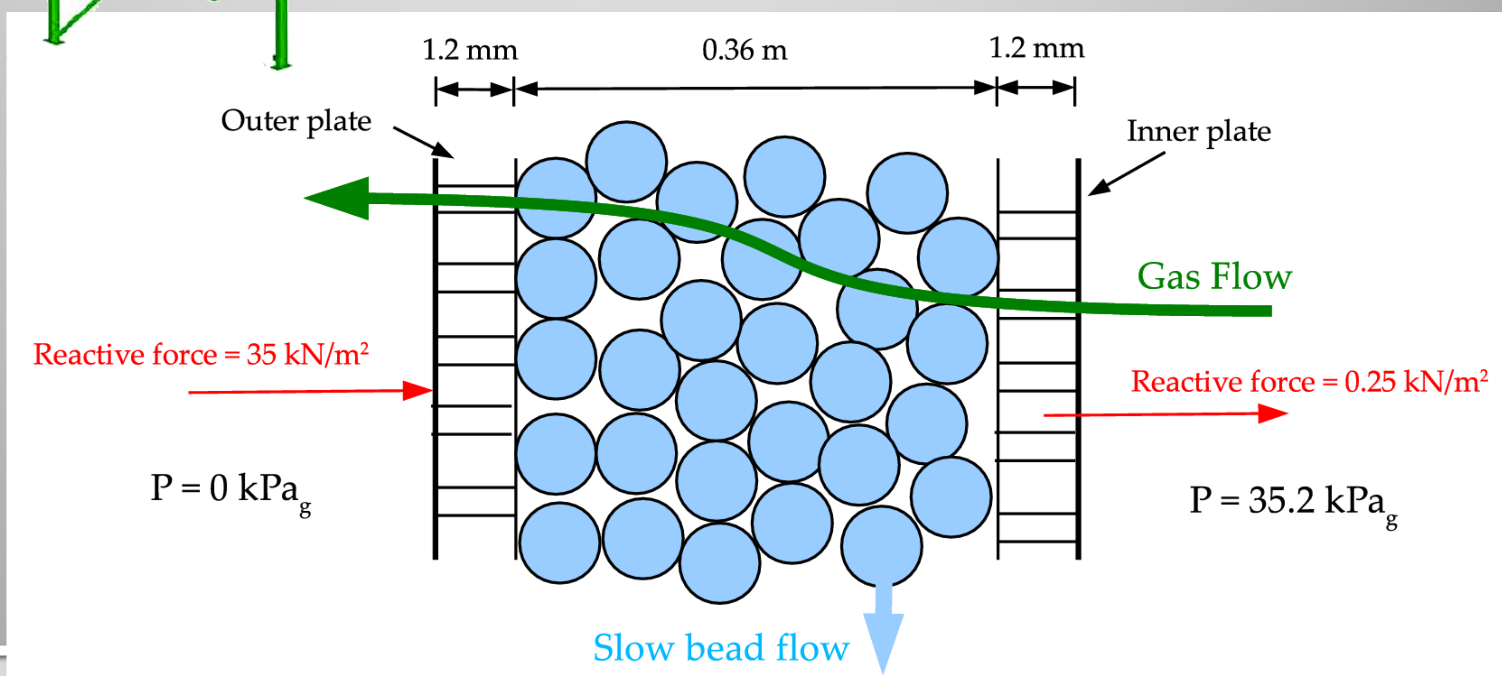

⇒Probably need to be in the transport or fast-fluidization regime (harder to model).

Particle separation may be controlling feature.

# Moving bed systems




- Low velocity and large cross-section is another route to lower pressure drop.



# Encapsulation appears promising – evaluation continues at LLNL and UIUC

**Working requirements for encapsulated solvents**

- Shell permeability > 100 barrer
- ~30 kPa compression tolerance
- Abrasion resistance for fluidization and cyclone separation

**Current testing and synthesis**

- MEA, Piperazine, $K_2CO_3$
- Silicone and other membrane materials

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