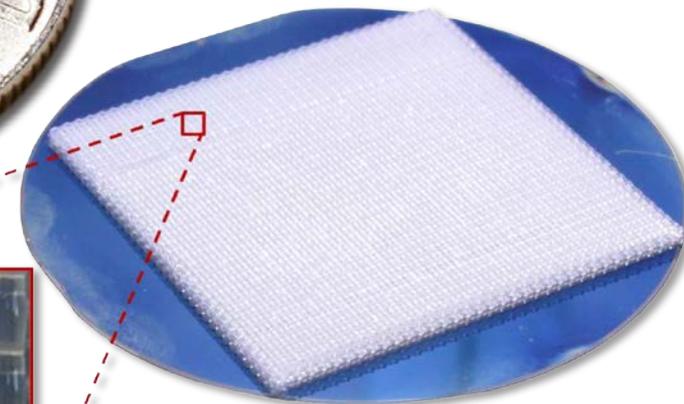
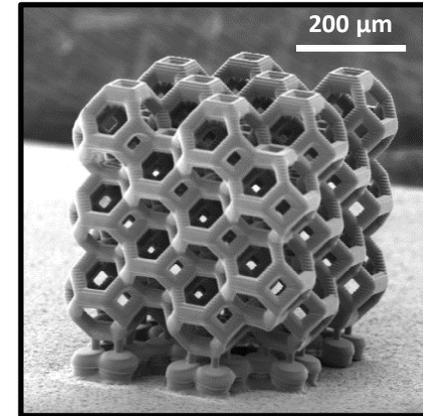
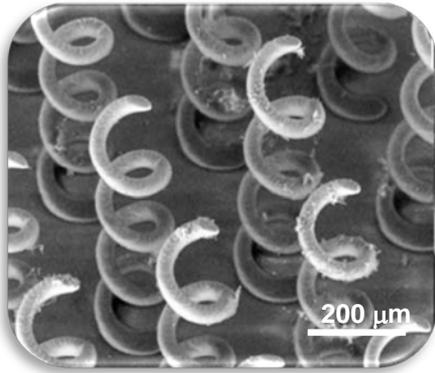


# Advanced Manufacturing To Enable New Solvents and Processes For Carbon Capture

August 10, 2016

NETL CO<sub>2</sub> Capture Technology Meeting

Joshuah K. Stolaroff



 Lawrence Livermore  
National Laboratory

Carnegie Mellon University



HARVARD  
UNIVERSITY

LLNL-PRES-555917

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC

**New fabrication techniques can enable new materials and processes to achieve low-cost carbon capture.**

**Designer solvents  
and sorbents + Advanced  
Manufacturing**

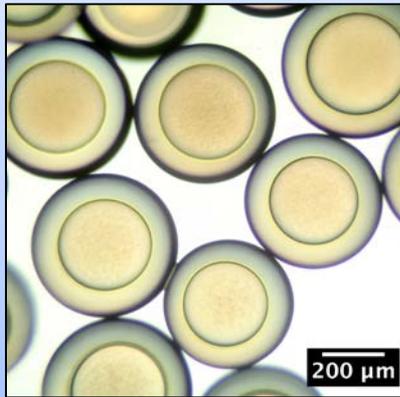
**Energy  
efficiency + Process  
innovation**

**Transformational Carbon Capture**

# FEW0194: Advanced Manufacturing To Enable Enhanced Processes And New Solvents For Carbon Capture

\$4.15M over 3 years (April 15, 2015 – April 14, 2018)

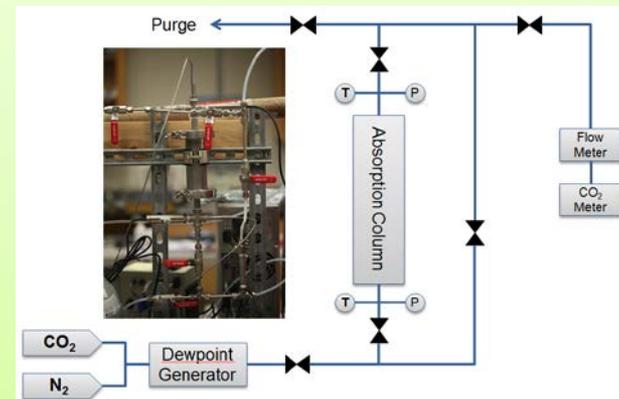
## Encapsulation of Advanced Solvents



\$475k/yr

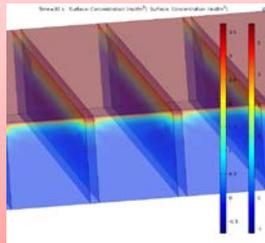
## Process design and scaleup with microcapsules

\$475k/yr



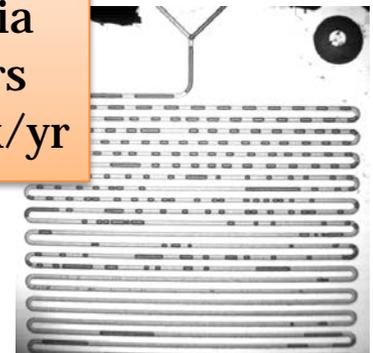
## CO<sub>2</sub> absorber design with advanced manufacturing

\$250k/yr



## Rapid determination of solvent properties via microfluidic reactors

\$133k/yr



# Project Team



Joshuah K. Stolaroff, Congwang Ye, Du Nguyen, Sarah E. Baker, William L. Smith, James S. Oakdale, Eric B. Duoss, Bill Bourcier, Pratanu Roy, Christopher M. Spadaccini, and Roger D. Aines

**Carnegie Mellon University**

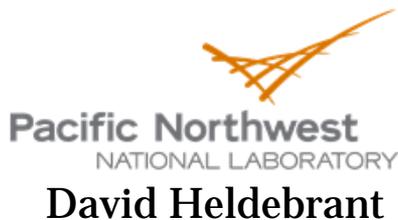
John Kitchen  
Elif Erdinc



**HARVARD**  
UNIVERSITY

David Weitz  
Saraf Nawar

## Collaborators



**Imperial College**  
London

Camille Petit

**Spray-Tek**

Jiten Dihora



Joan Brennecke



THE UNIVERSITY OF  
MELBOURNE

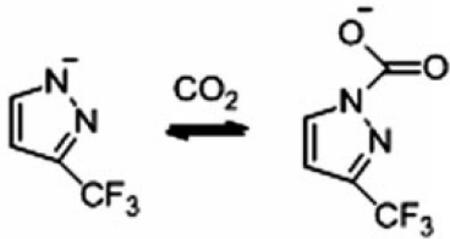
Kathryn Mumford



Alissa Park

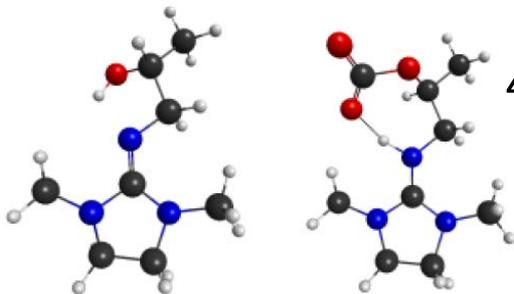
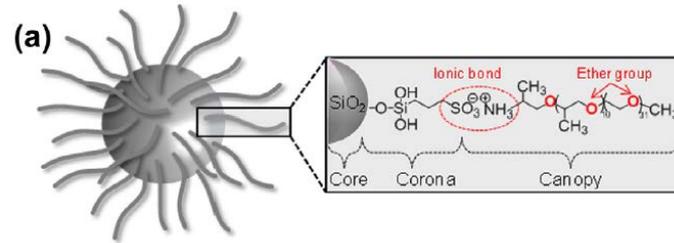
# Some solvents with potential for 30–50% energy savings and specific challenges:

1. **Sodium carbonate** solution: slow CO<sub>2</sub> absorption, precipitates solids.



2. **Ionic Liquids**: water intolerance, precipitate solids (PCIL's)

3. **NOHMs**: high viscosity, slow CO<sub>2</sub> absorption.



4. **CO<sub>2</sub>BOLs**: poor heat transfer rates (high viscosity).

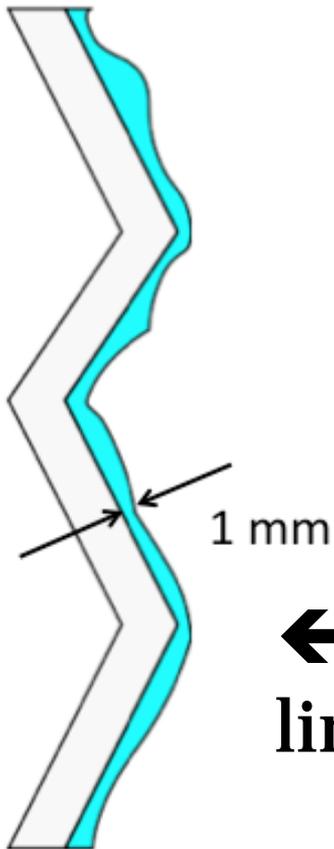
# Can packed towers be improved?



Raschig rings:  
“Since 1894”

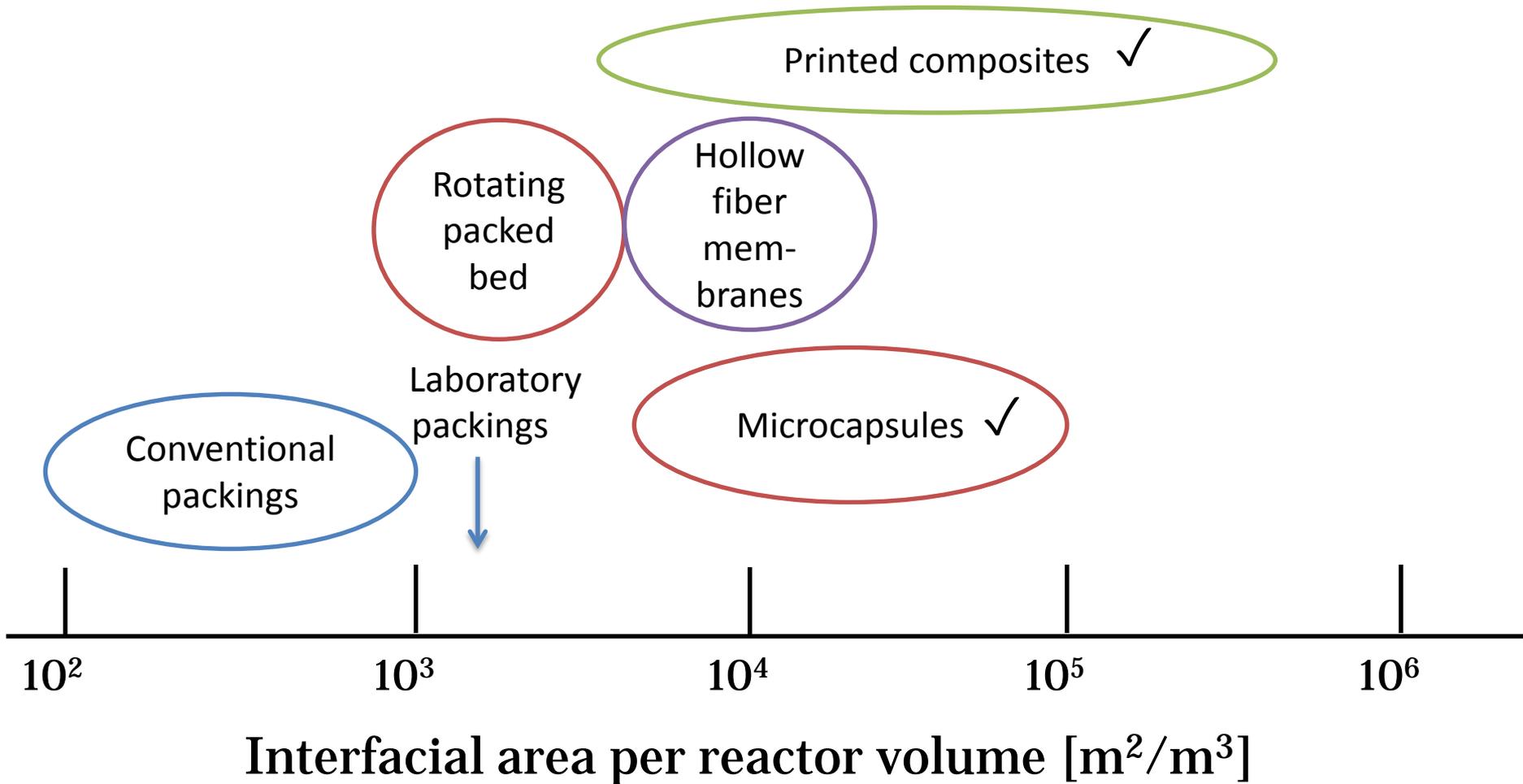


Structured packing:  
“A little better”



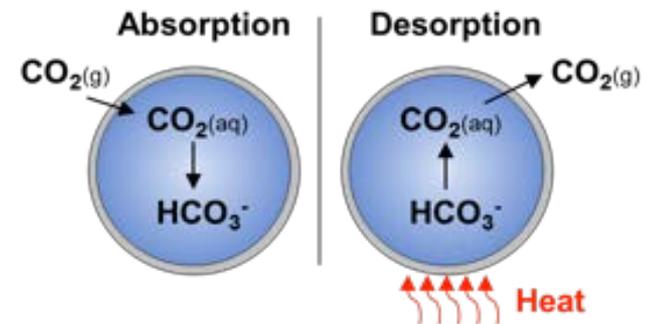
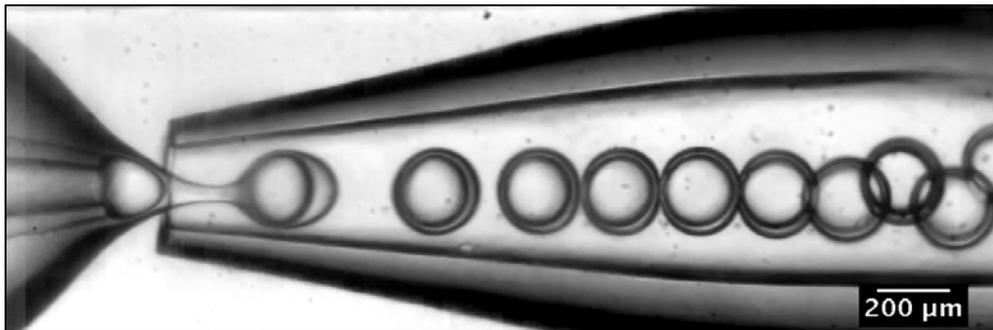
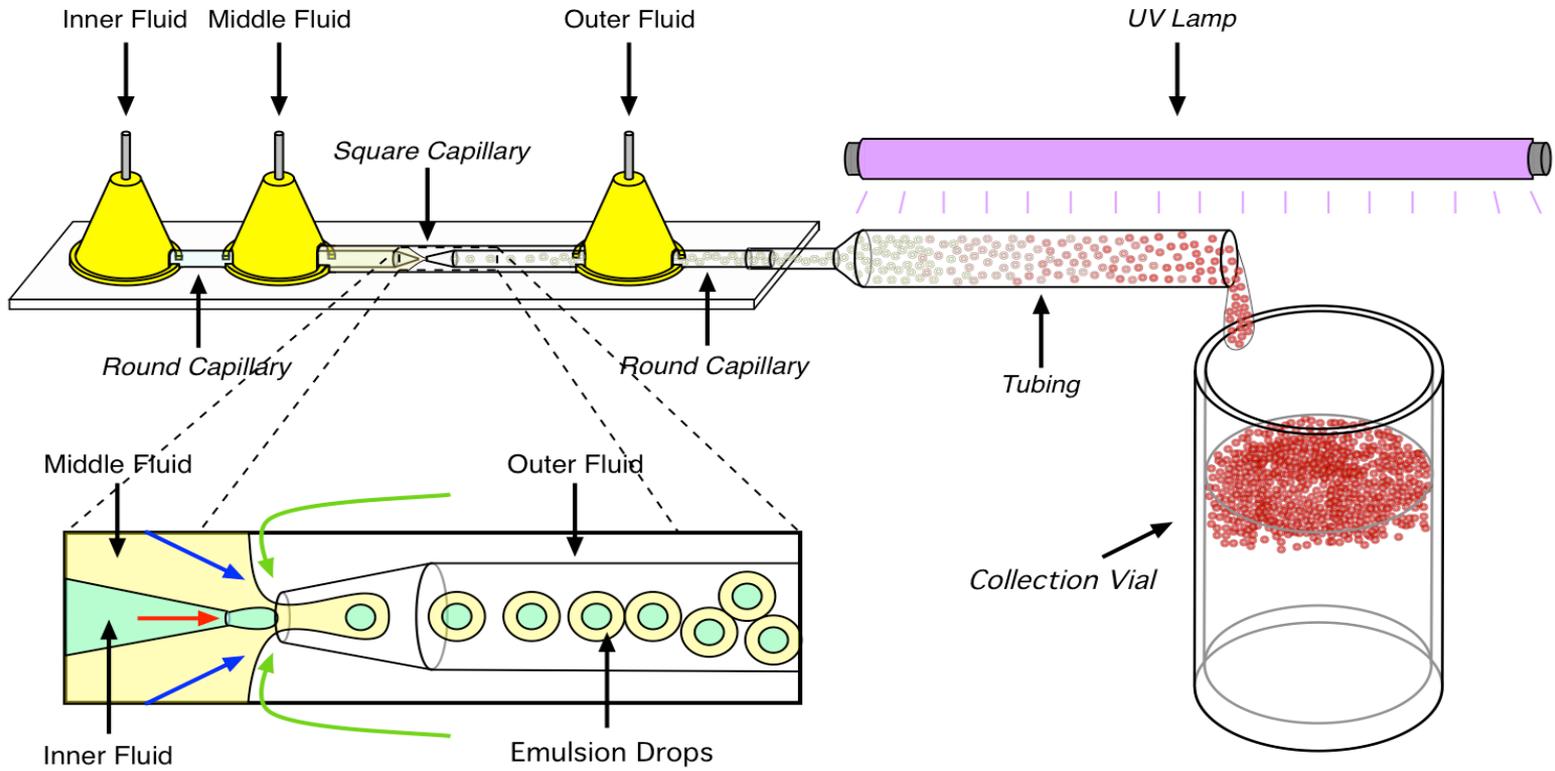
← Process intensification  
limited by film thickness  
... and fabrication technology?

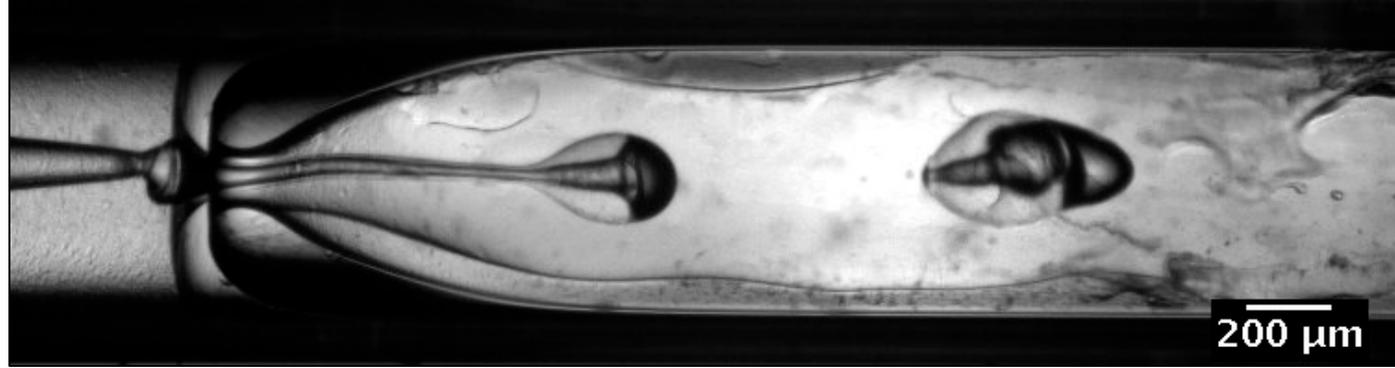
# Additional surface area can be formed by permeable solids.



✓ Also tolerates phase changes!

# Microencapsulation: an enabling technology for CO<sub>2</sub> solvents.





## Major challenges for encapsulation:

- Shell material-solvent compatibility
- Microfluidic-solvent compatibility
- Production scale-up
- Process design and evaluation

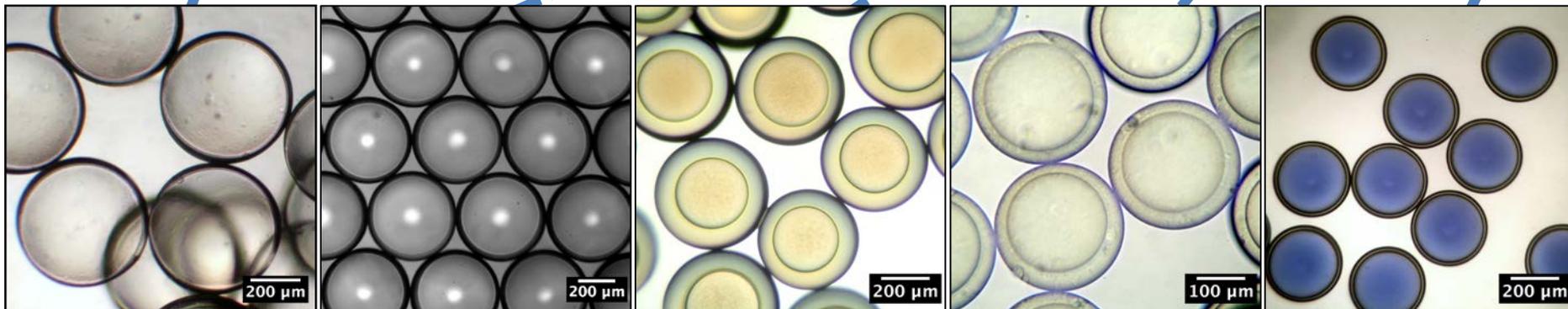
# We now have four permeable shell materials (two formulated in-house).

Name	Manufacturer	Material	Permeability (barrer)	Amine Compatibility	Mechanical Properties	Curing Time
Semicosil 949	Wacker	Silicone	3100	No	Elastic, strong, tacky	30 mins
Thiol-ene	LLNL	Silicone	2700	Yes	Elastic, strong, tacky	30 secs
SiTRIS (80:20)	LLNL	Acrylic	400	After curing	Stiff, strong, untacky	10 secs
Tego Rad 2650	Evonik	Silicone	3200	After curing	Elastic, friable, untacky	10 secs

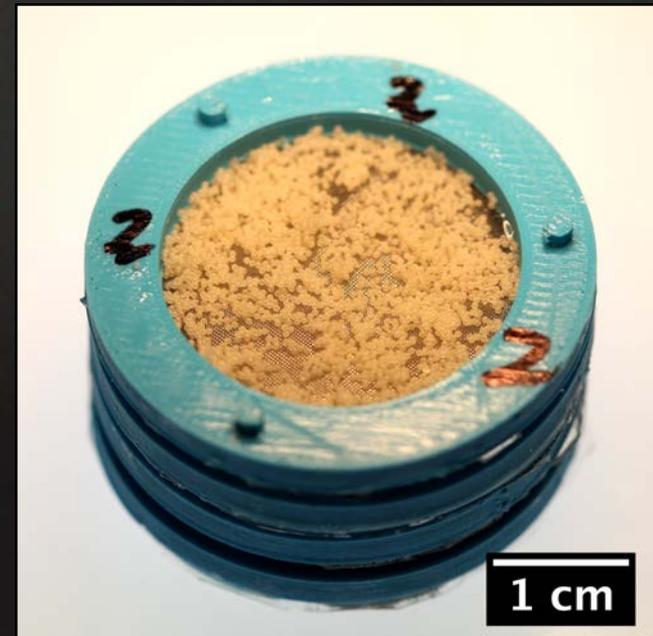
# Extensive screening indicates viable candidates for encapsulation.

Good properties for encapsulation	Marginal properties for encapsulation	Not compatible
-----------------------------------	---------------------------------------	----------------

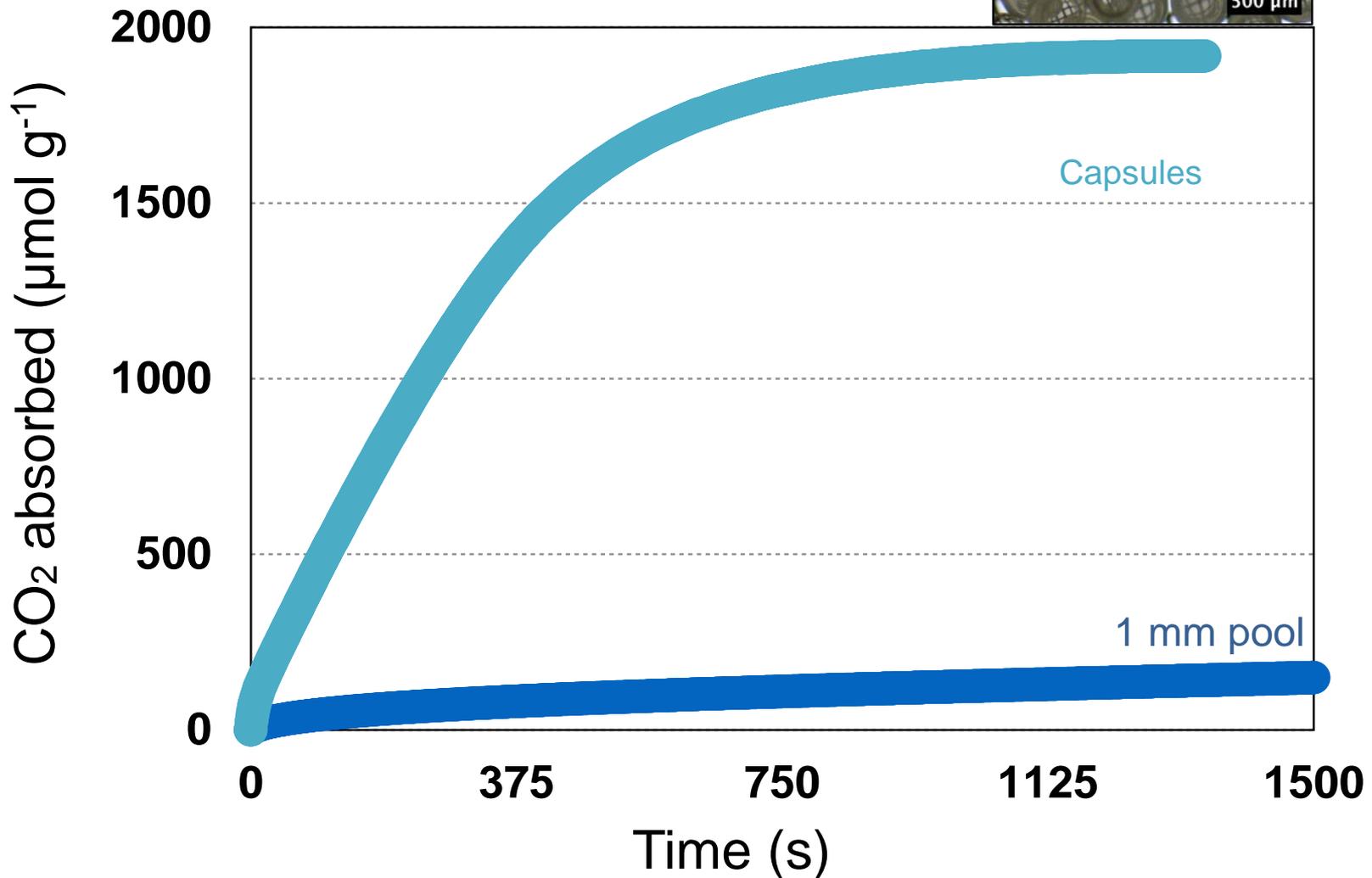
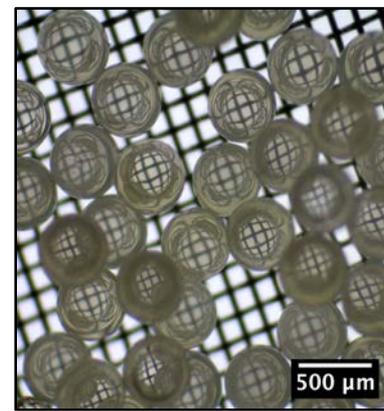
	Koech-anol	Koech-anol w/ 1:1 wt. water	DBU/Hex-anol 1:1	NDIL 0274	NDIL 0252	NDIL 0231	NDIL 0231 w/ 1:1 wt. water	NDIL 0230	NDIL 0230 w/ 1:1 wt. water	NDIL 0309 (solid)	NDIL 0309 w/ 1:1 wt. water	Carbon-ate w/ water
Semi-cosil							X		X			✓
Thiol-ene		✓									✓	✓
Si-TRIS							✓		✓ w/ 1:3		✓	✓
T.R. 2650		✓ (un-stable)									✓	✓



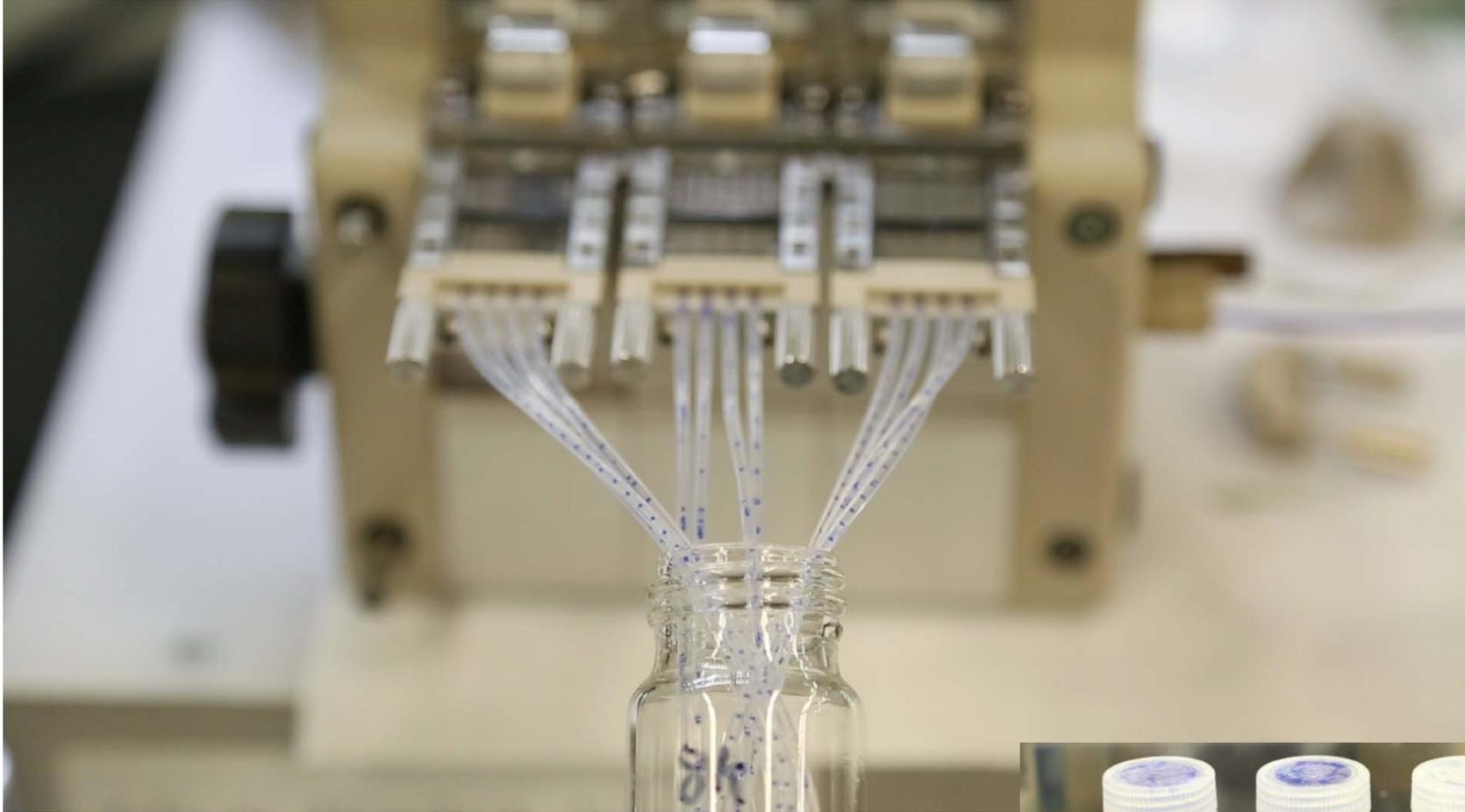
IL-SiTRIS  
capsules  
dried and tested  
for CO<sub>2</sub>  
absorption



Enhanced absorption rate compared to liquid film is confirmed.



# Microcapsule production scaled up by parallelization.

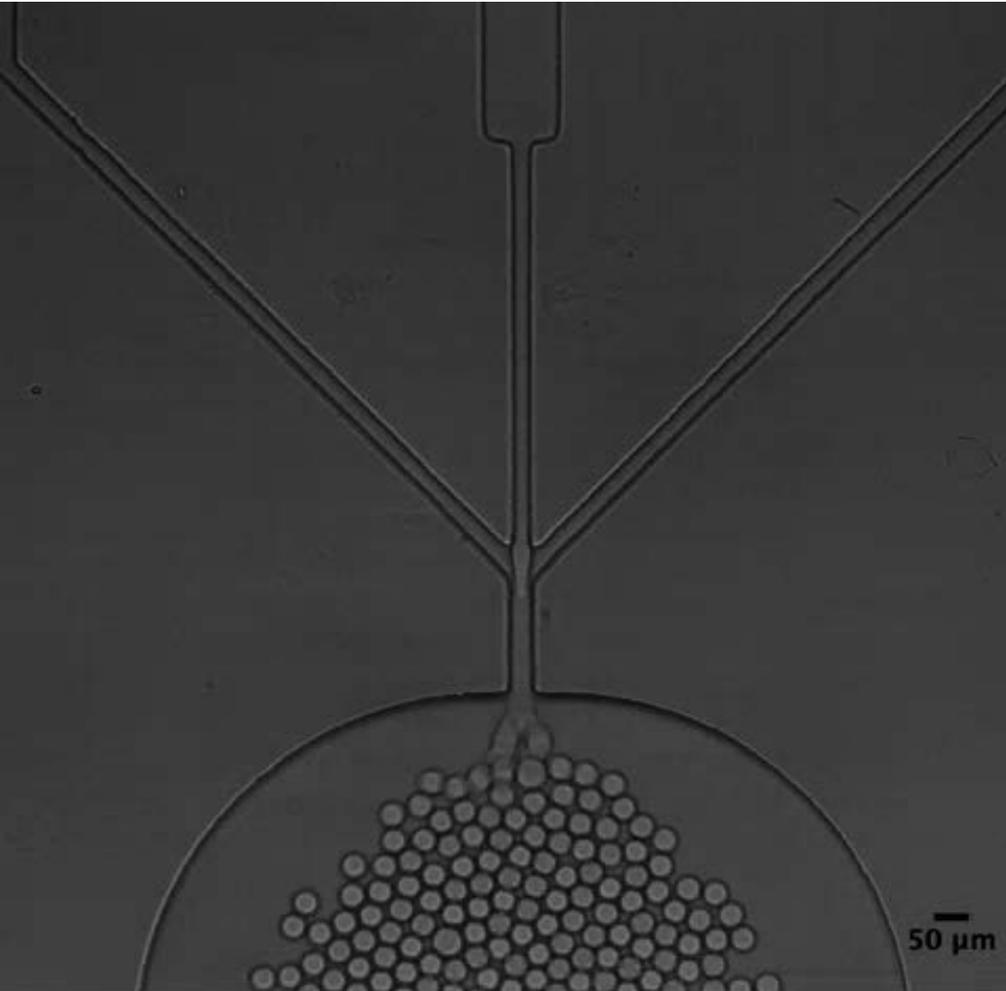


→ 500 g/day



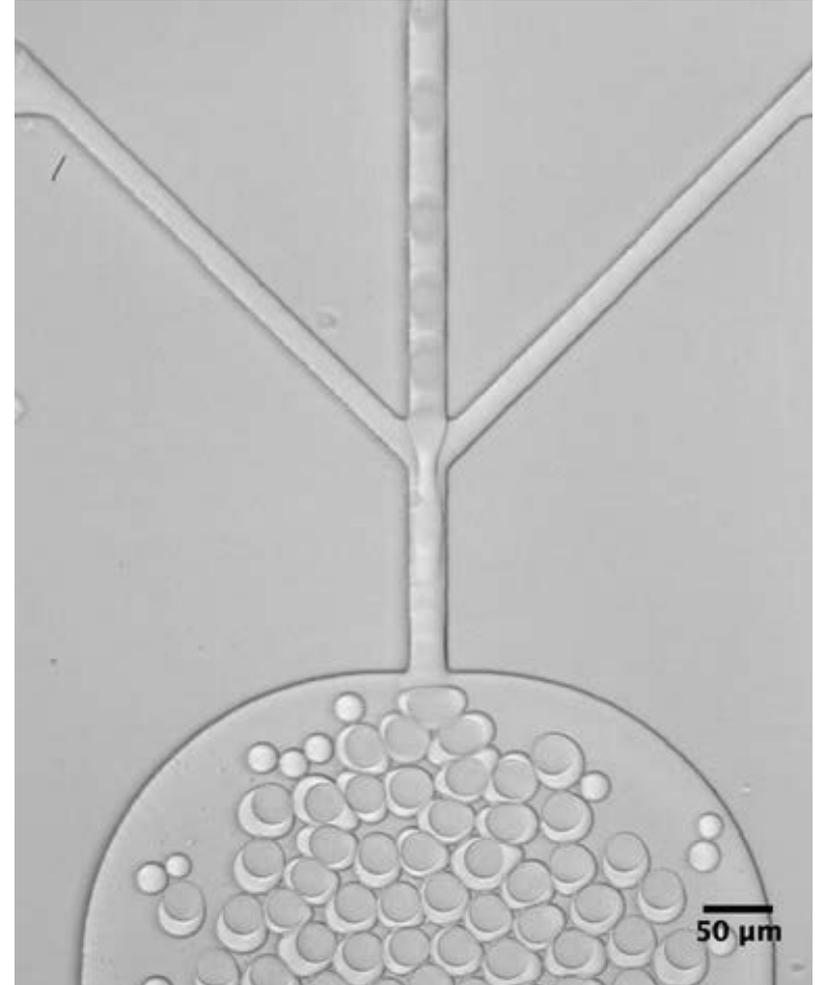
# Alternative scale-up technique: 2-part production

Device 1 - hydrophobic



Inner phase: DI water 500 ul/h  
Outer phase: HFE 7500 w/ 1 wt.% Krytox

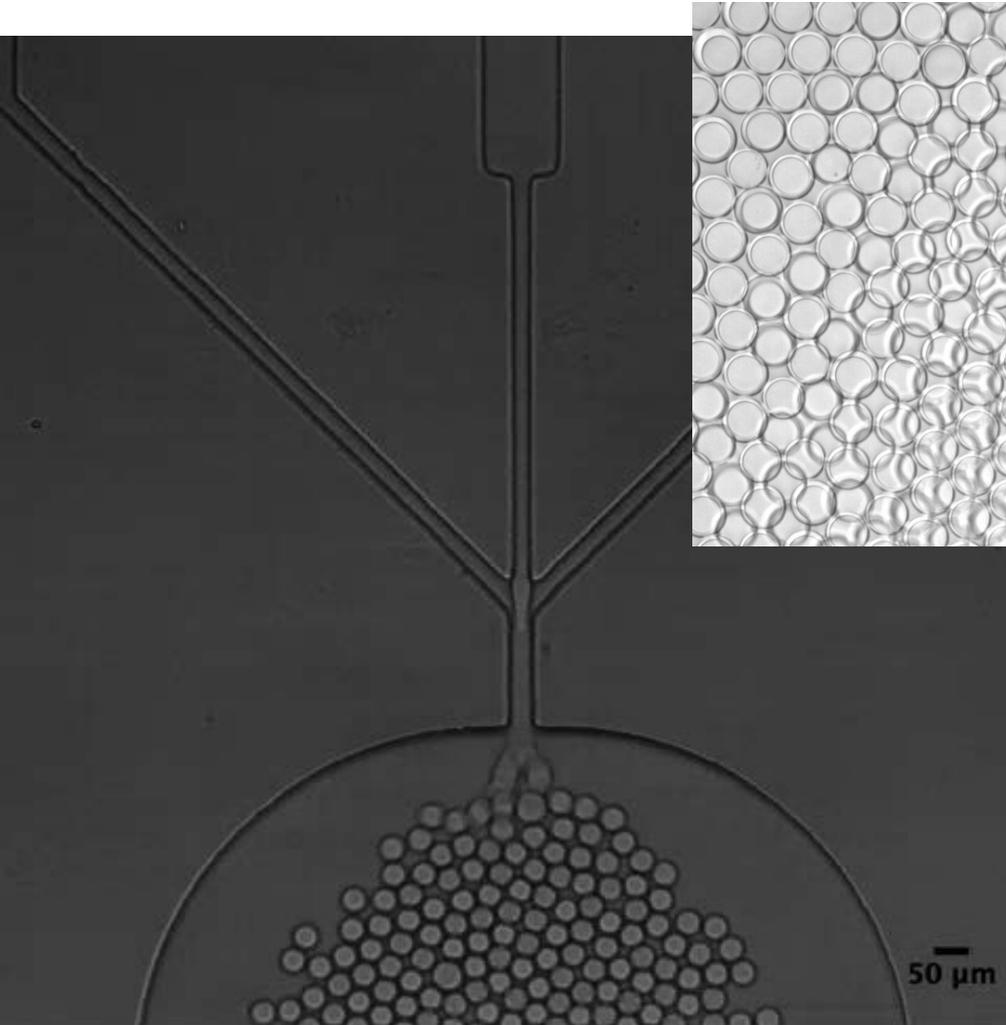
Device 2 - hydrophilic



Inner phase: DI water 500 ul/h  
Middle phase: HFE 7500 w/ 1 wt.% Krytox 500 ulh  
Outer phase: DI water w/ 1 wt.% Triton-X100 1000 ulh

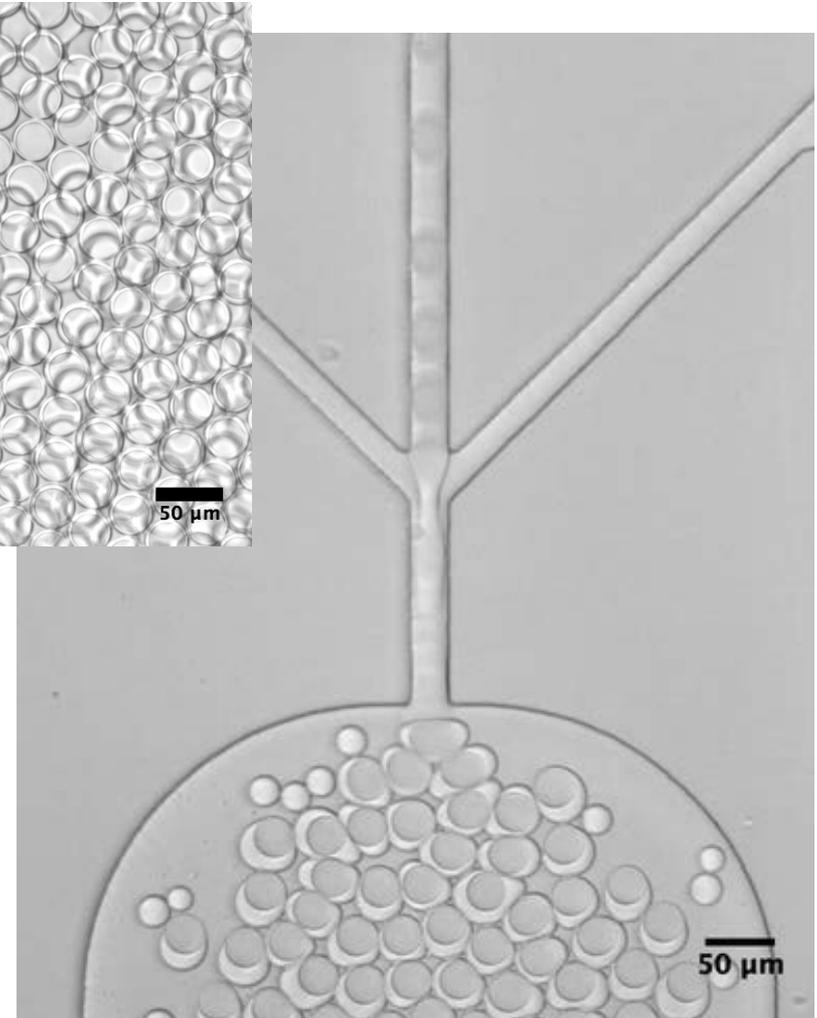
# Alternative scale-up technique: 2-part production

Device 1 - hydrophobic



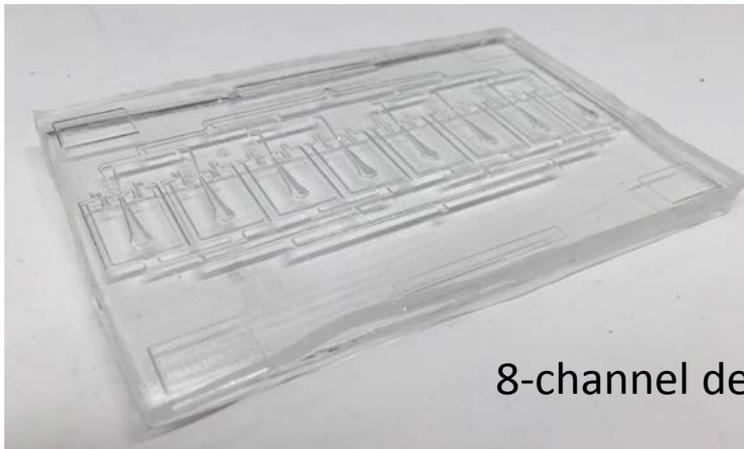
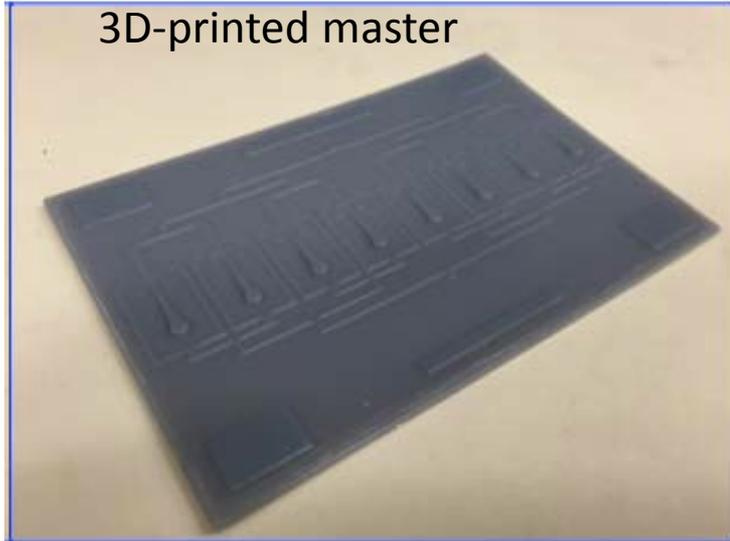
Inner phase: DI water 500 ul/h  
Outer phase: HFE 7500 w/ 1 wt.% Krytox

Device 2 - hydrophilic

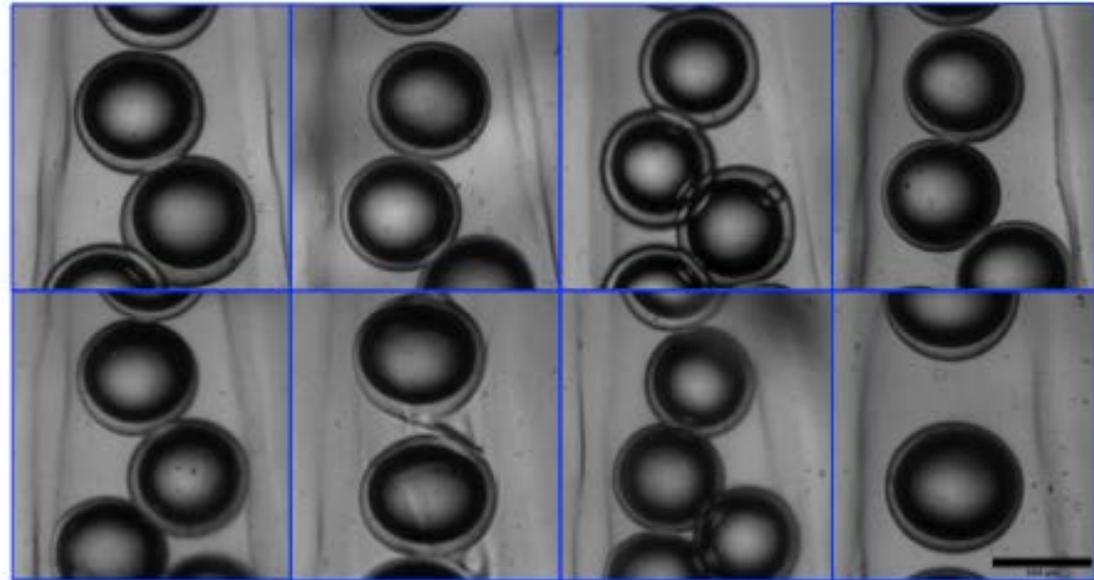


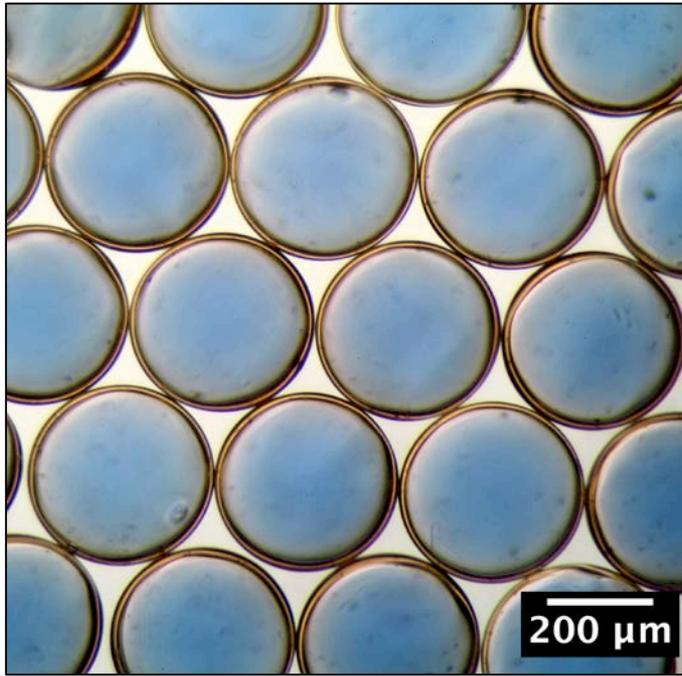
Inner phase: DI water 500 ul/h  
Middle phase: HFE 7500 w/ 1 wt.% Krytox 500 ulh  
Outer phase: DI water w/ 1 wt.% Triton-X100 1000 ulh

# We used 3D printing to rapidly prototype microfluidic devices

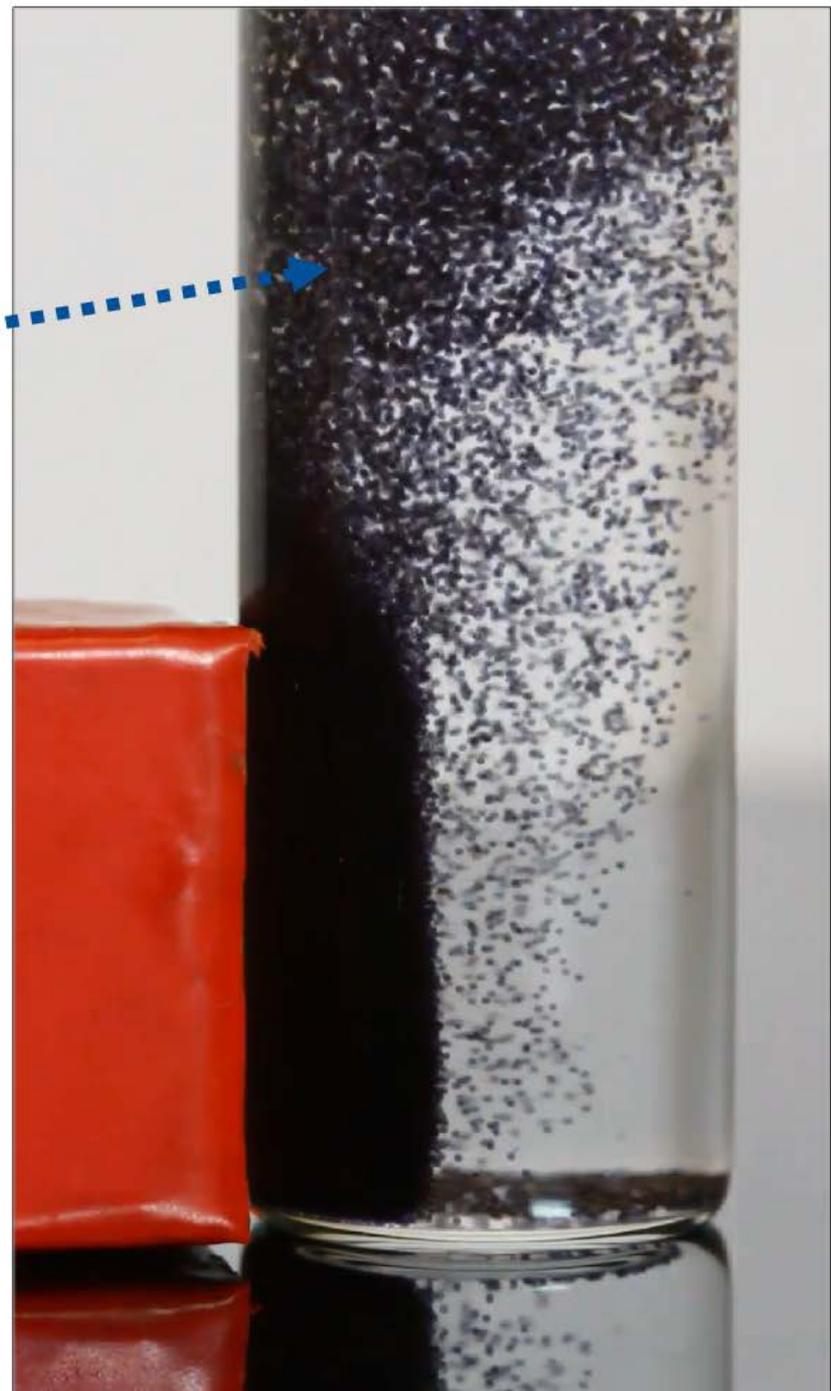
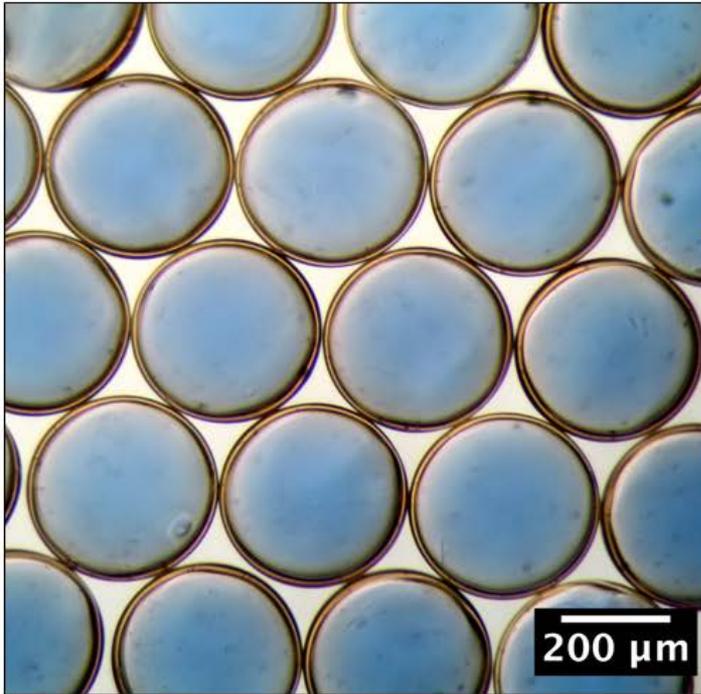


8-channel device in PDMS





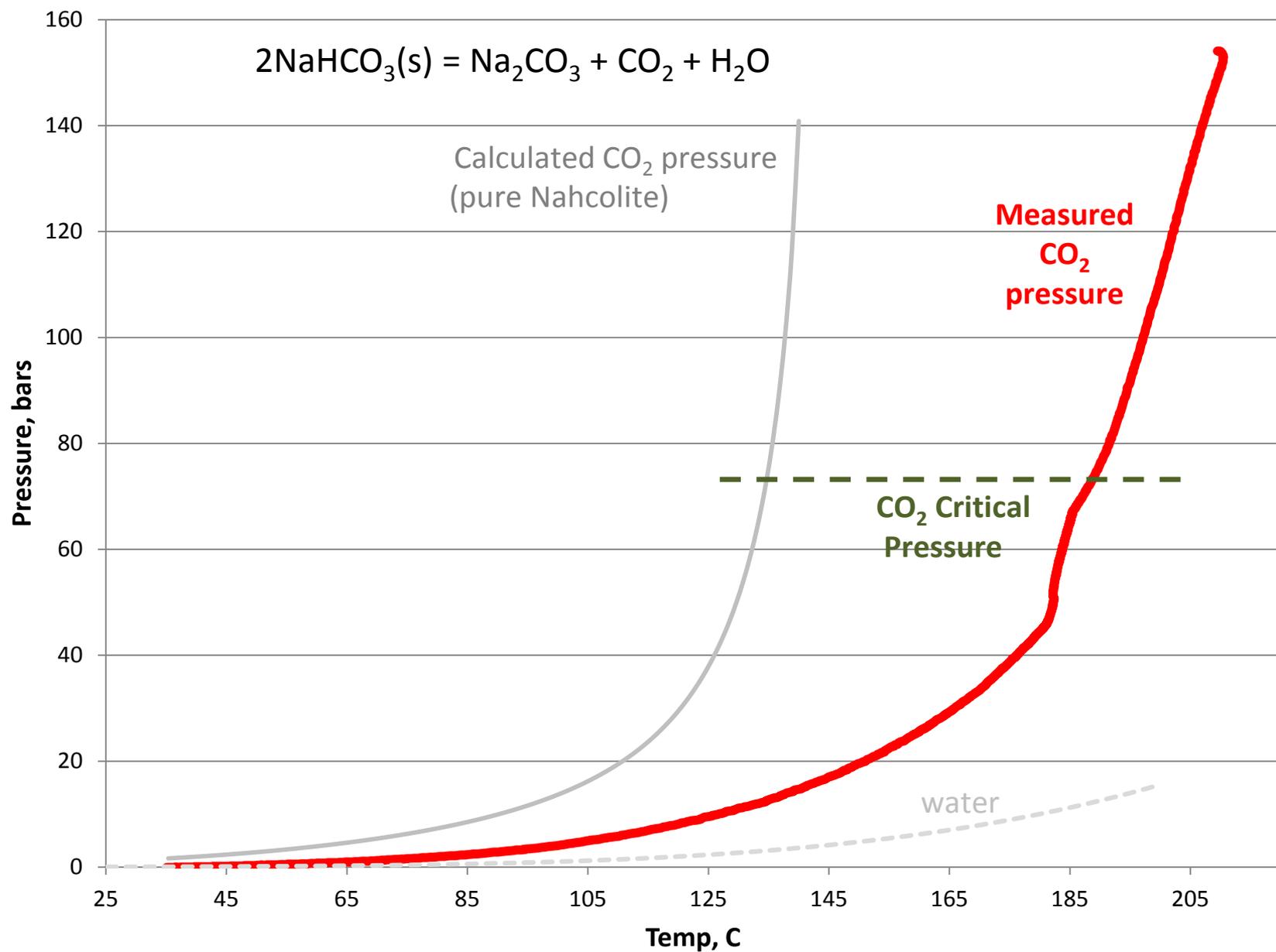
**Capsules doped  
with magnetic  
nanoparticles**



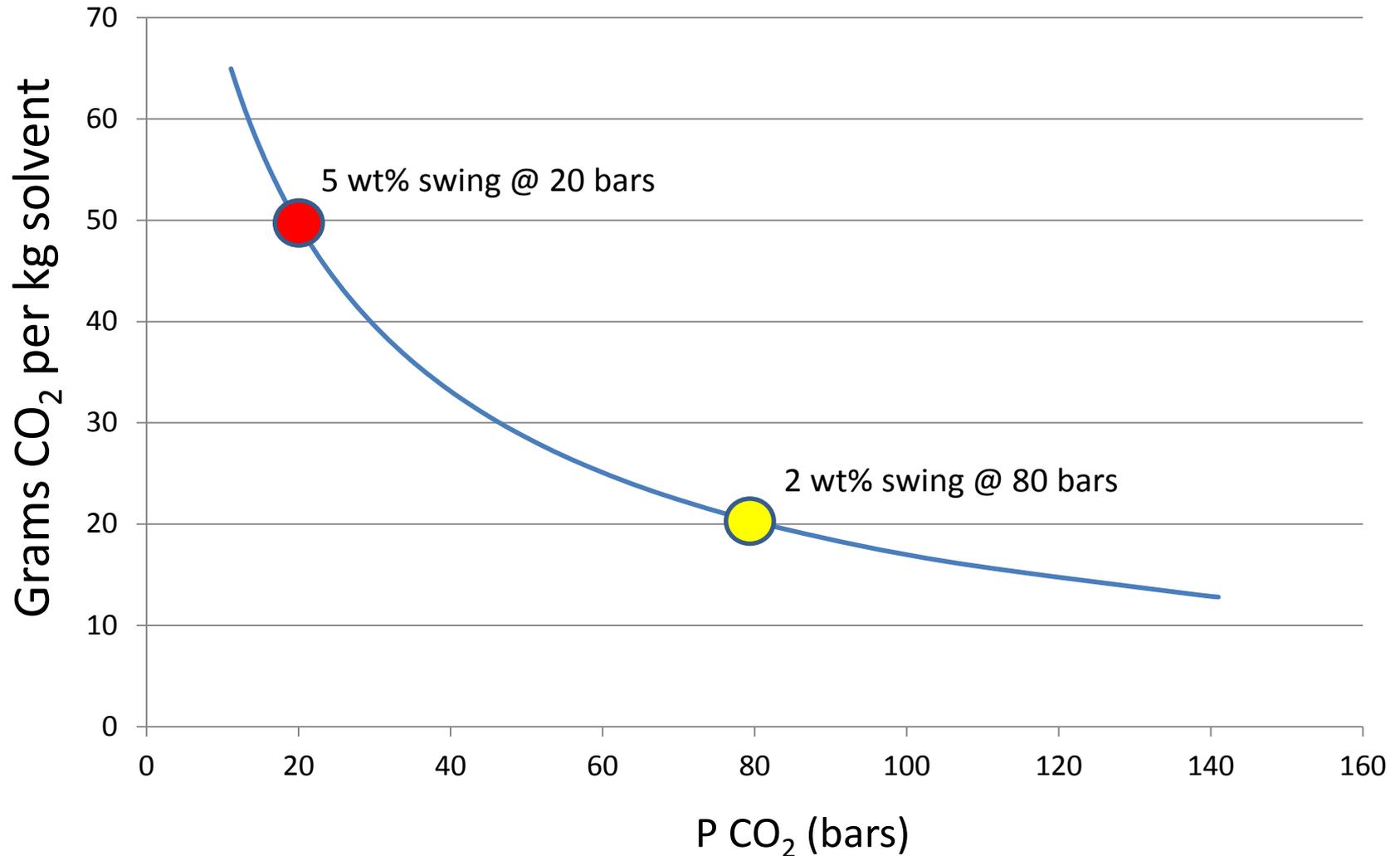
Capsules doped  
with magnetic  
nanoparticles

# **New reactor concepts**

# Sodium carbonate: supercritical CO<sub>2</sub> without a compressor

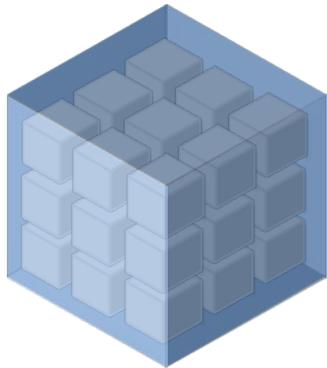


# Swing capacity depends on release pressure.

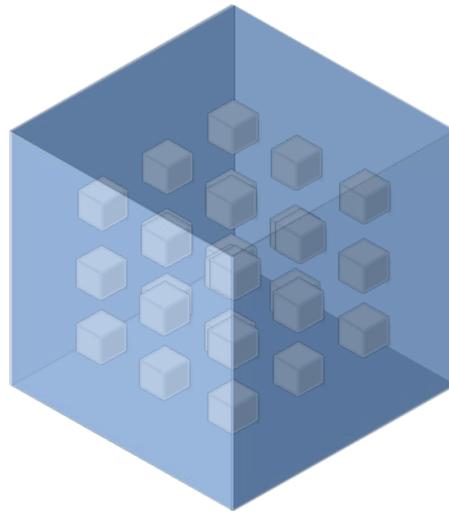


# Sorbent-polymer Composites

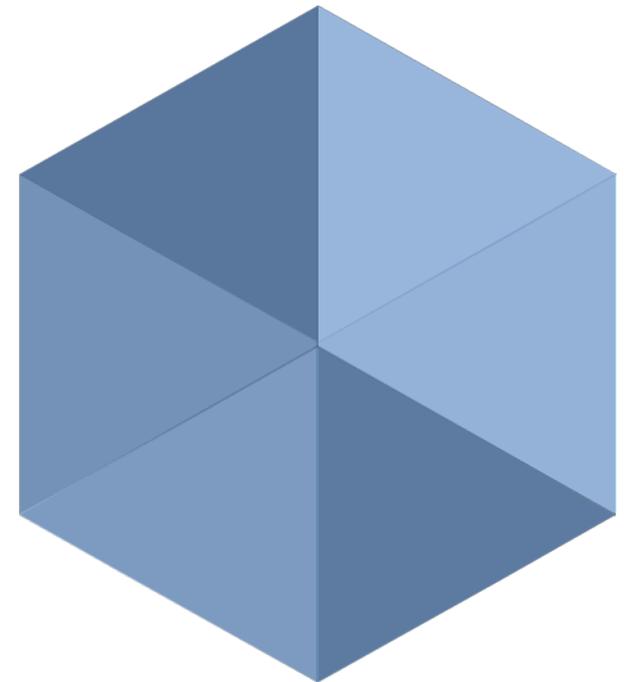
- Carbonate particles embedded within a CO<sub>2</sub> permeable polymer (silicones)
- Composited will capture water and swell



Polymer-Carbonate  
Composite

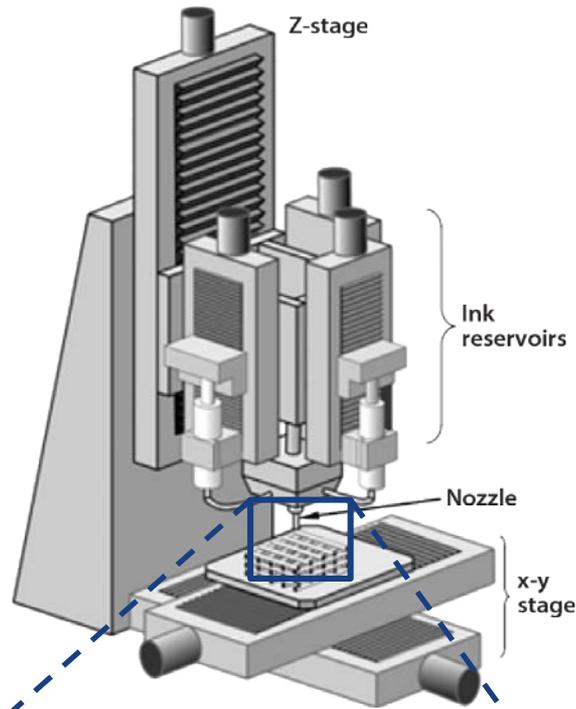


Water

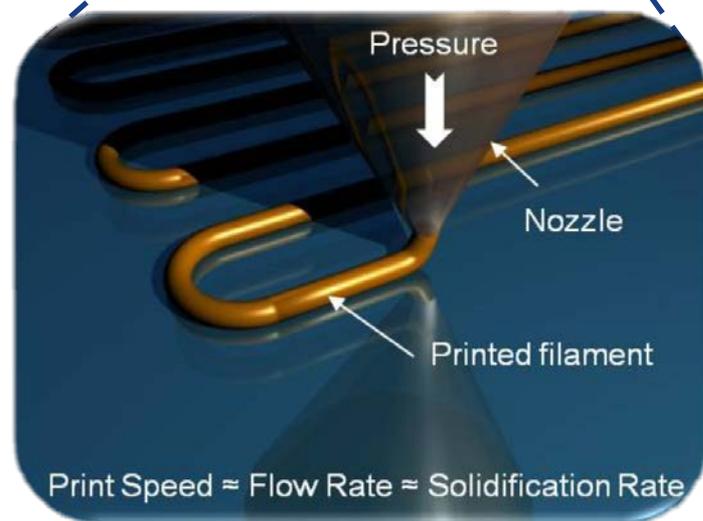


Hydrated Polymer-Carbonate  
Composite

# 3D Printed Composites



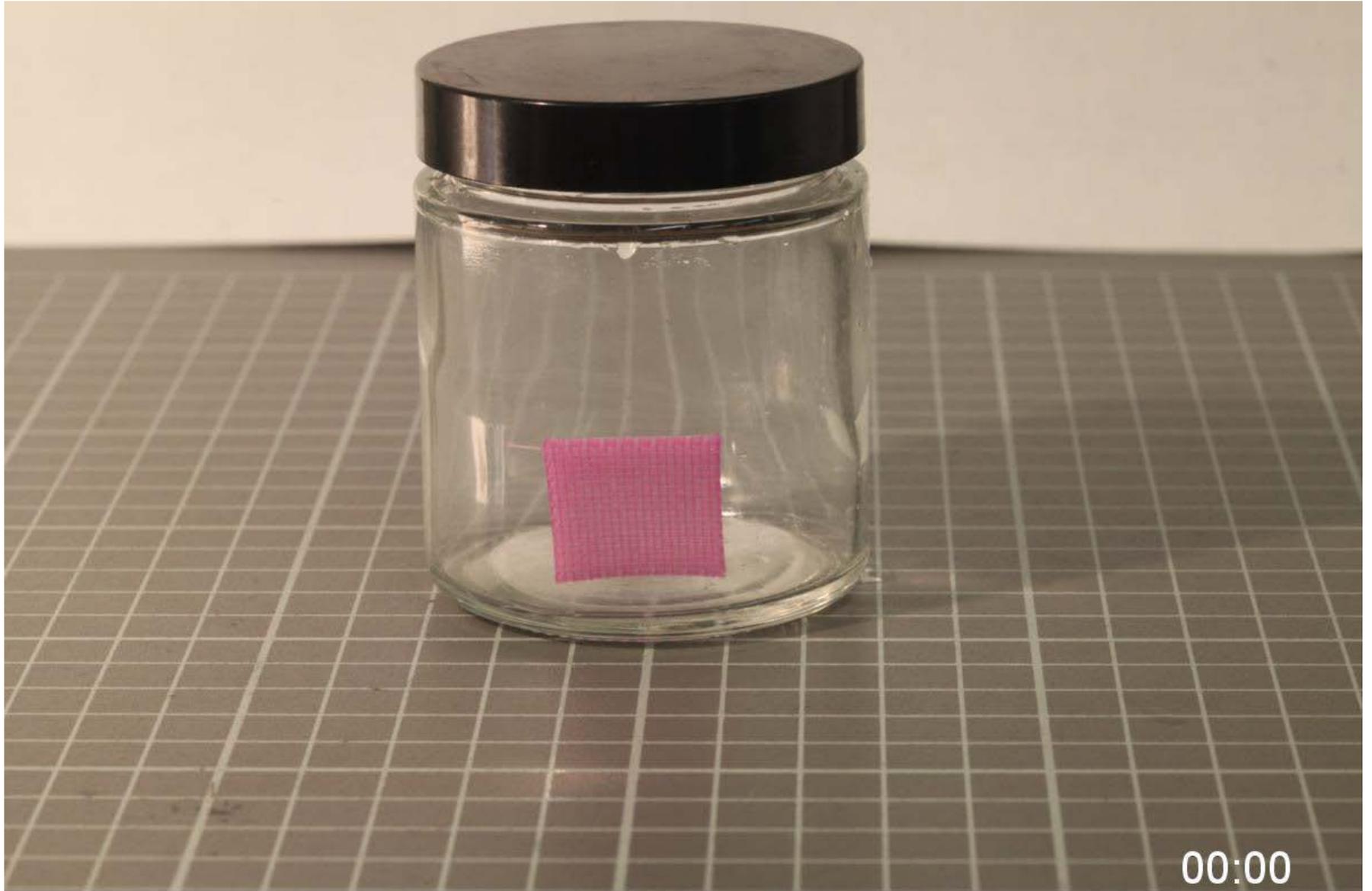
- Shear-thinning polymer allows for Direct Ink Write (DIW) of composites
- Can include color indicating dyes to identify CO<sub>2</sub> loading



CO<sub>2</sub> →

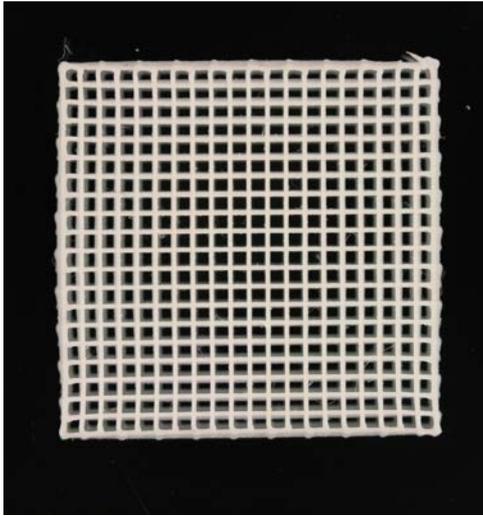


# The Breath Test

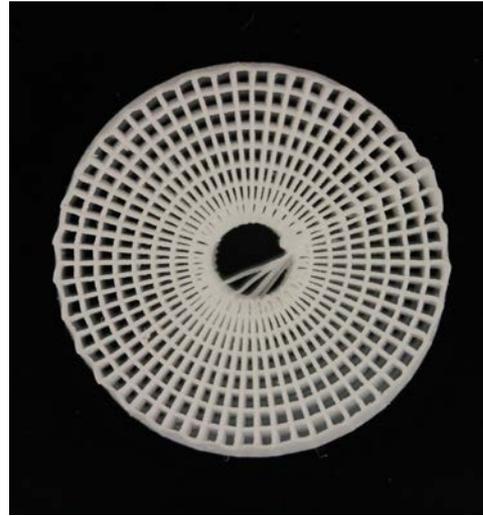


00:00

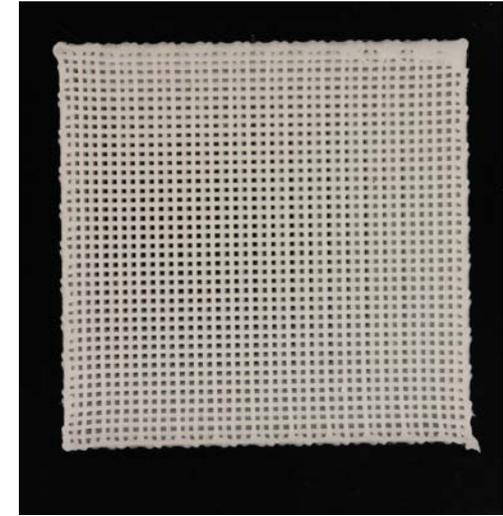
# Geometries can be optimized for gas flow and reactor shape



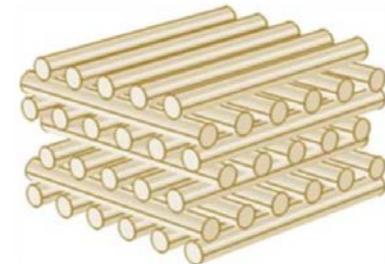
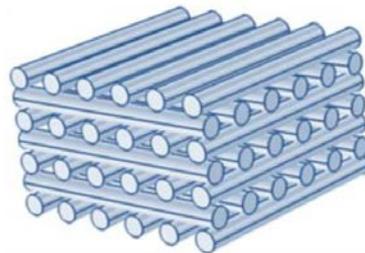
Simple Cubic

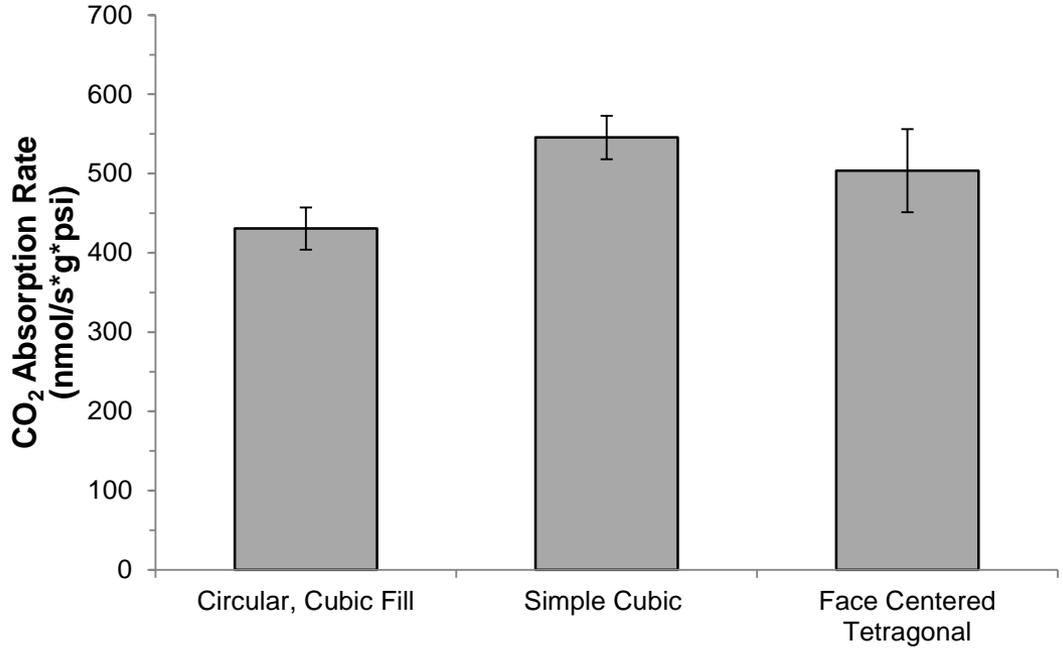


Radial Simple Cubic

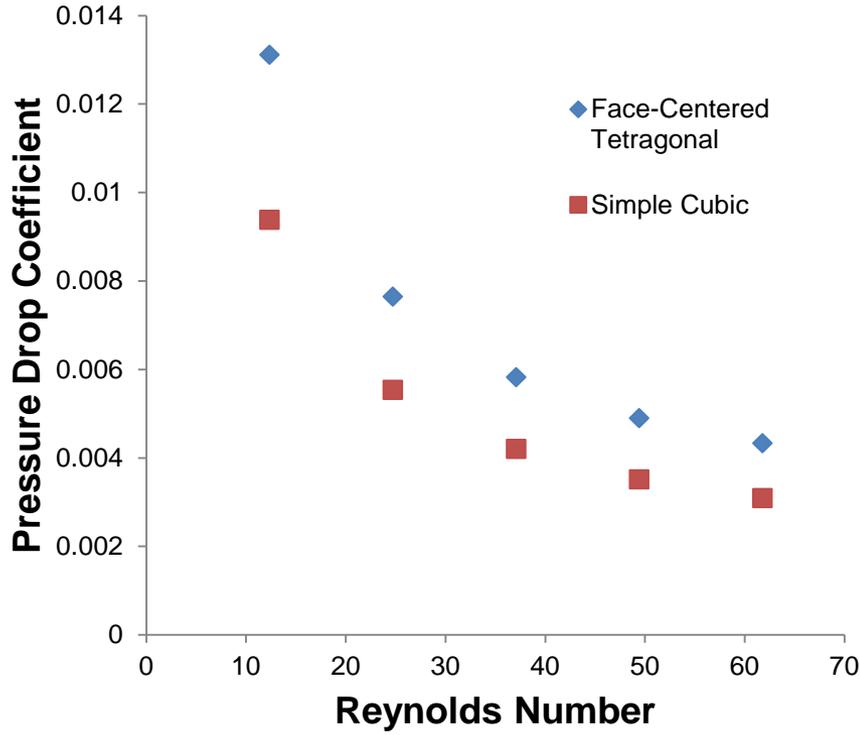
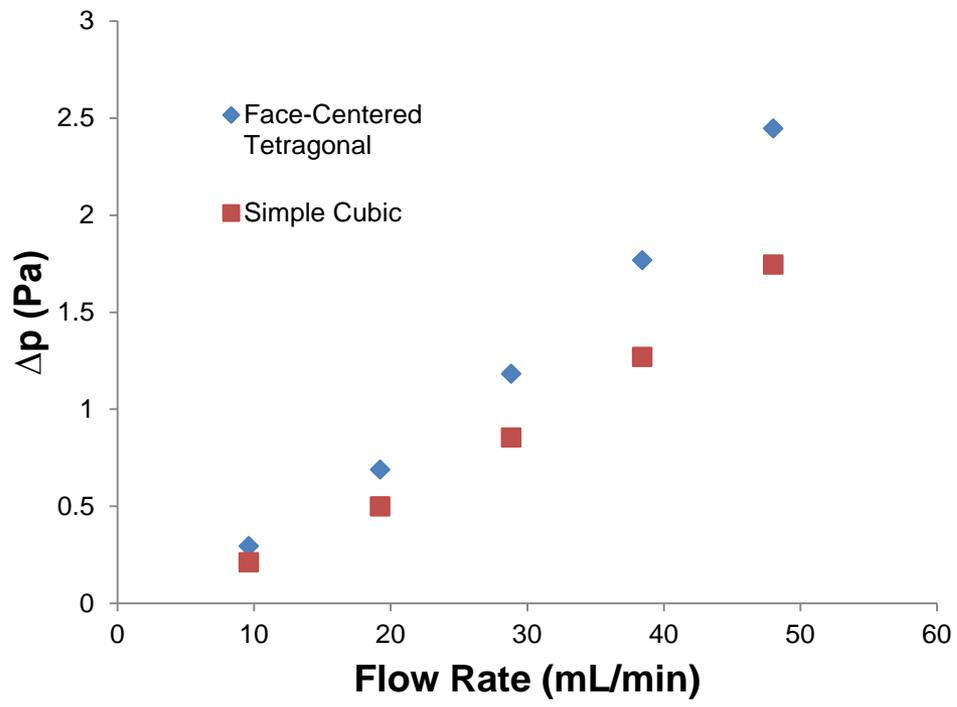


Face Centered Tetragonal

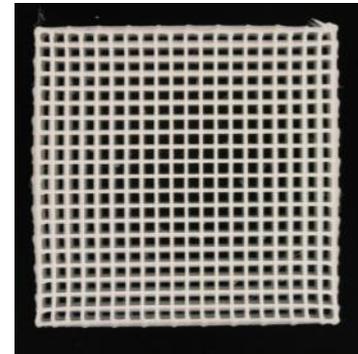
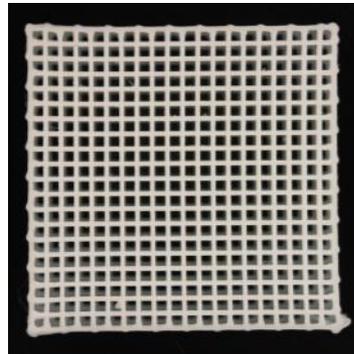
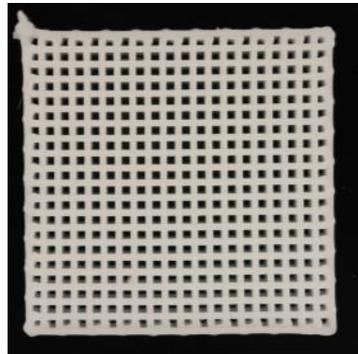
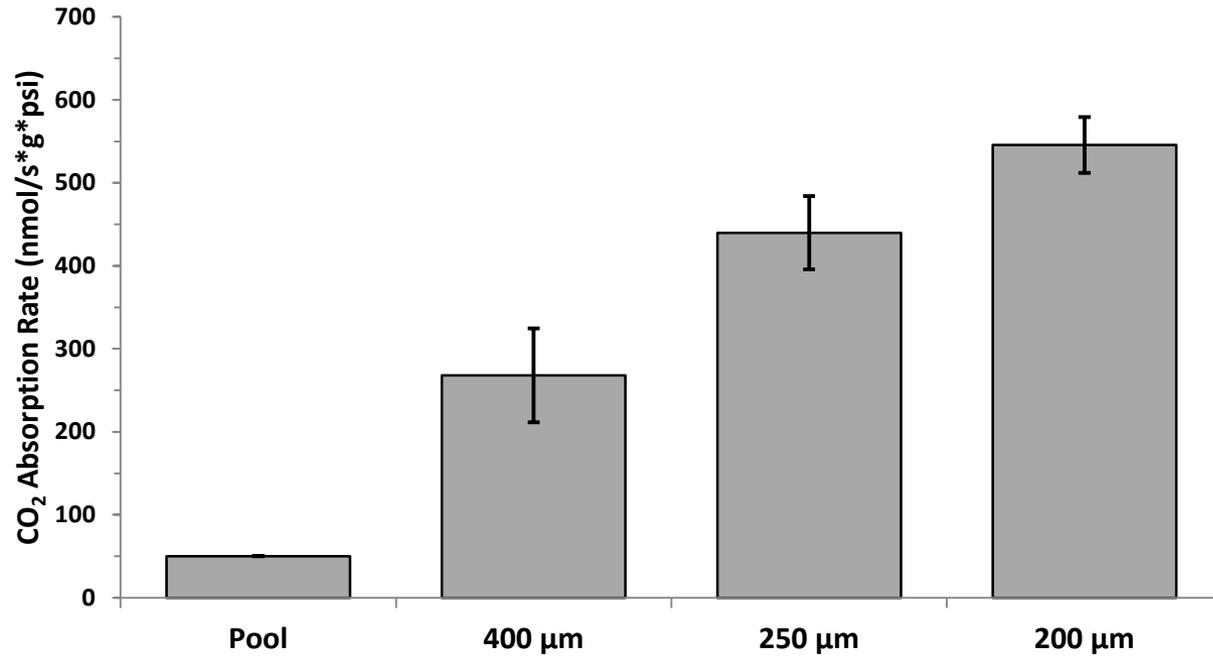




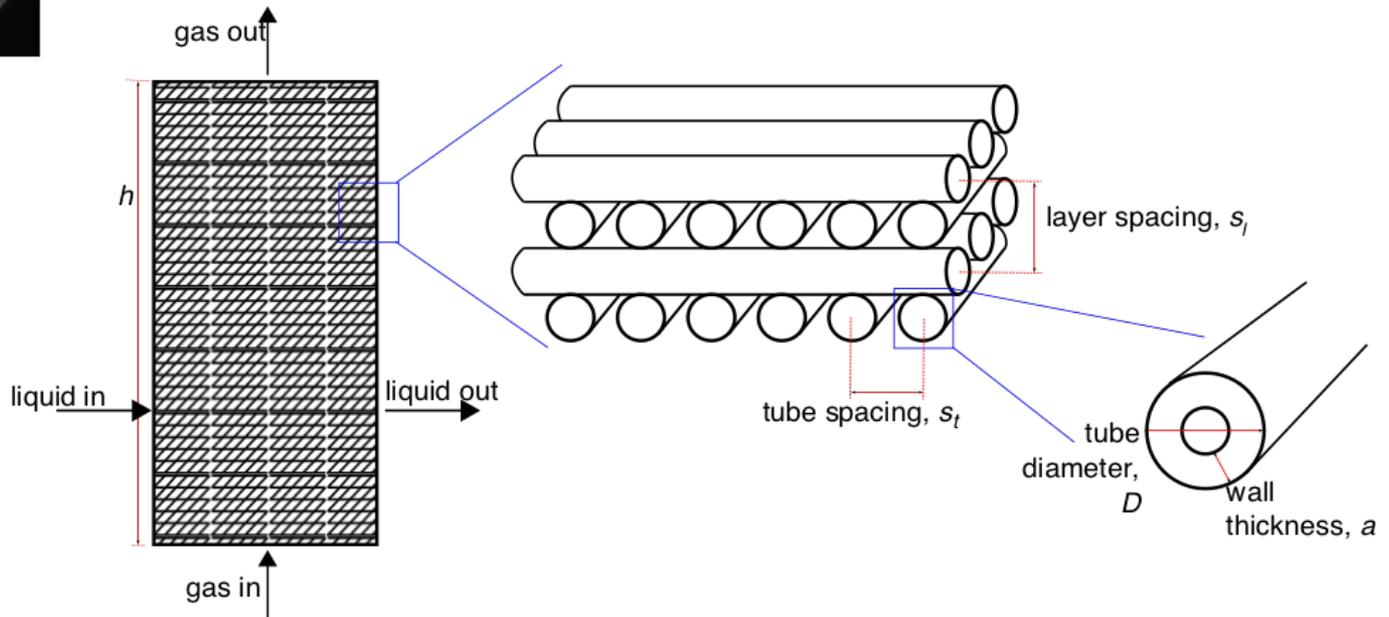
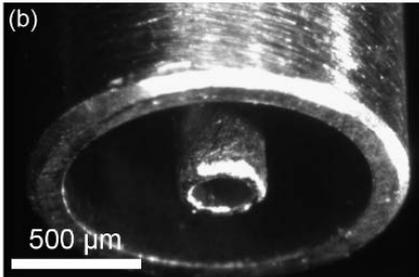
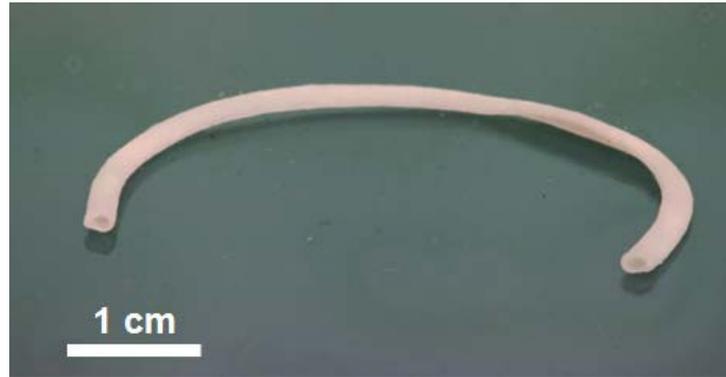
**Geometry affects mass transfer and pressure drop.**



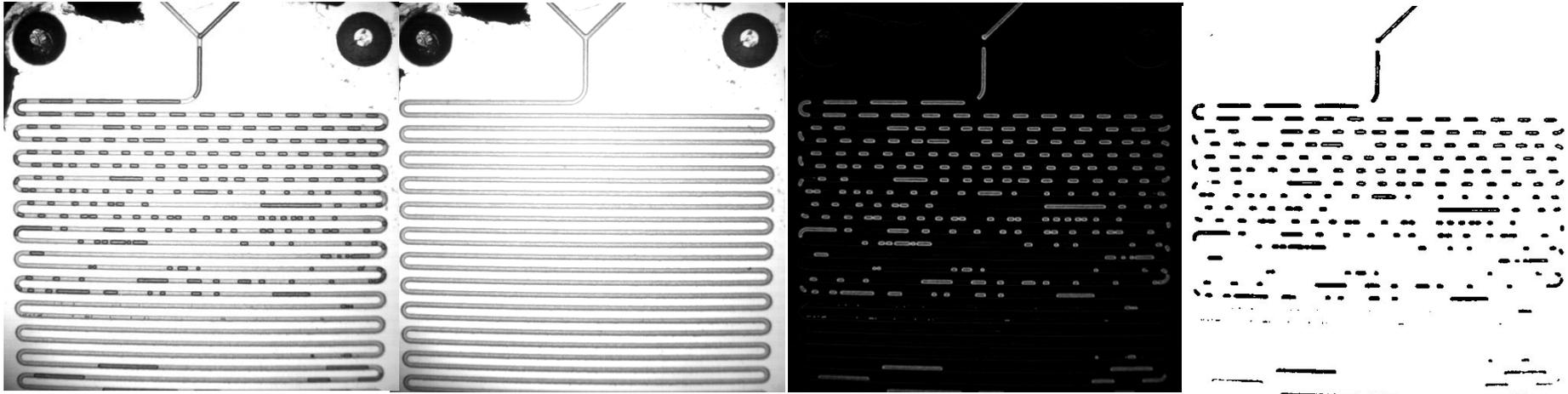
# Smaller struts yield higher absorption rates.



# Tube-lattice reactors expand the process options.

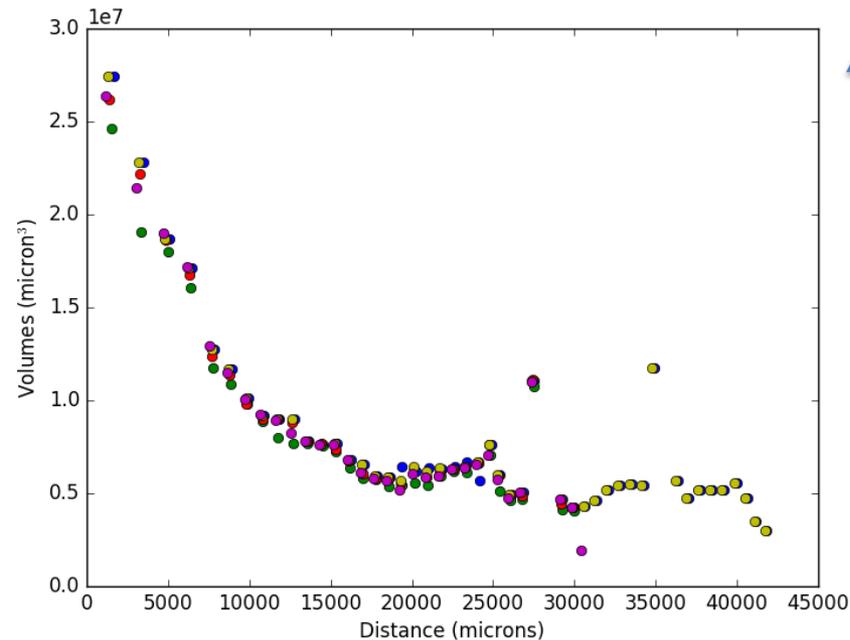


# Microfluidic determination of solvent properties: New “snapshot” approach

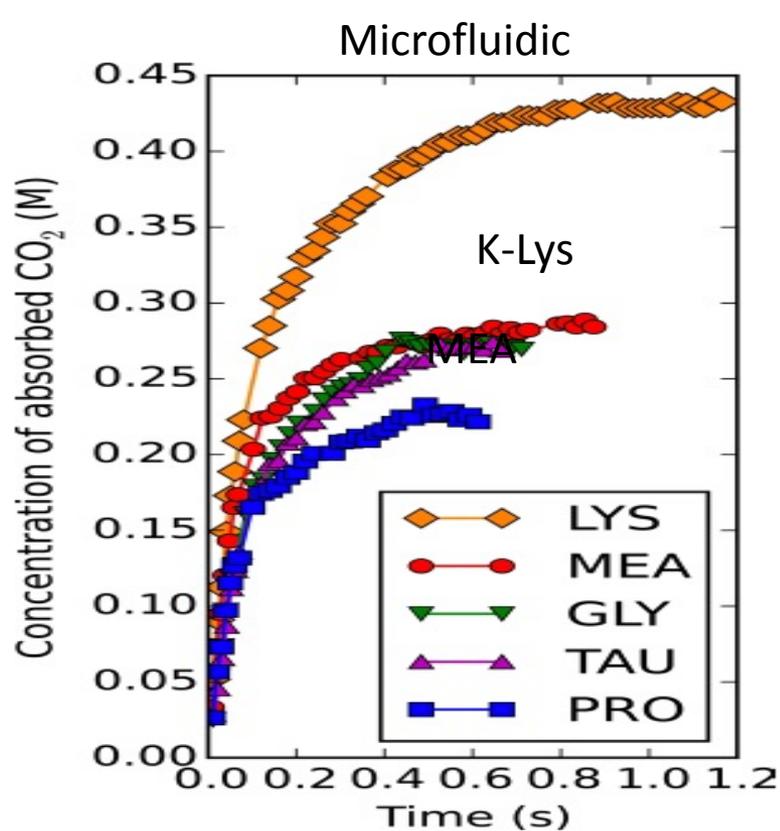


Bubble volume vs.  
distance traveled

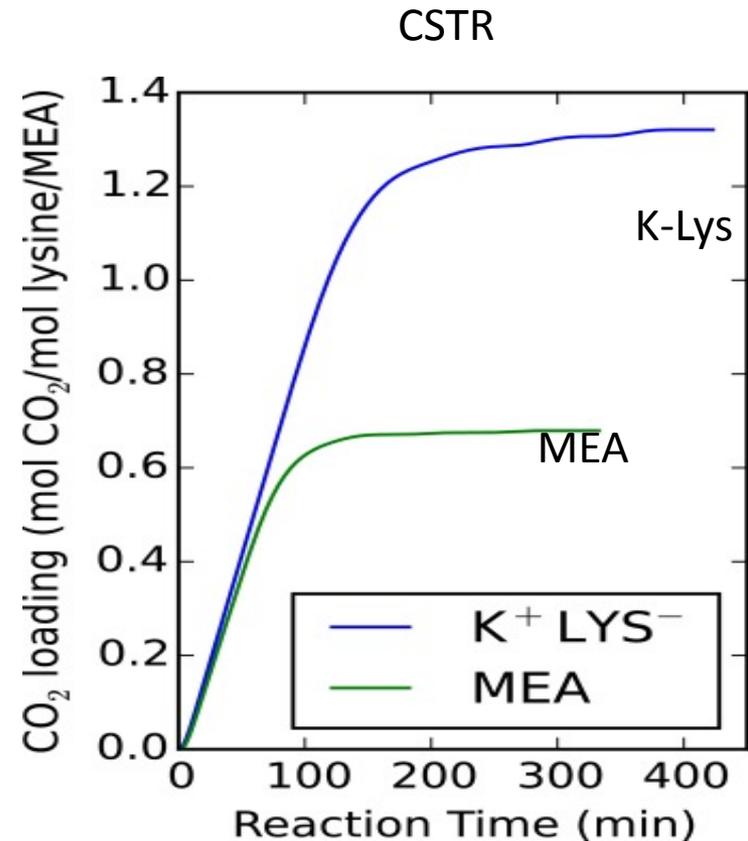
⇒ CO<sub>2</sub> absorbed  
vs. time



# Microfluidics used to characterize amino acid-based solvents.



Potassium lysinate outperforms MEA



Results consistent with CSTR.

# Acknowledgements



Lynn Brickett  
Andy Aurelio



# Questions