

Advanced Manufacturing To Enable New Solvents and Processes For Carbon Capture

August 24, 2017

NETL CO₂ Capture Technology Meeting

Joshuah K. Stolaroff

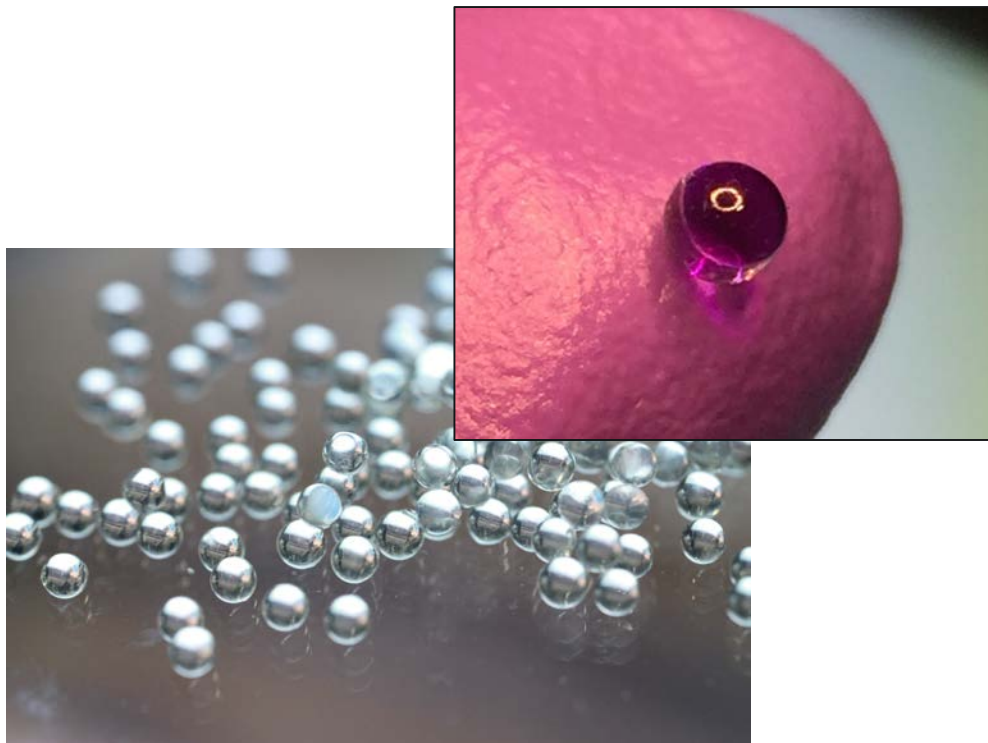
 Lawrence Livermore
National Laboratory



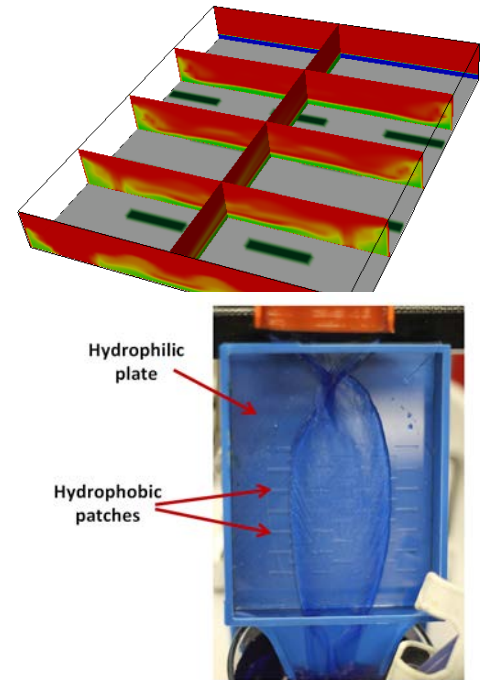
HARVARD
UNIVERSITY

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New fabrication techniques can enable new materials and processes to achieve transformational carbon capture.



Microencapsulated CO₂ Sorbents (MECS)

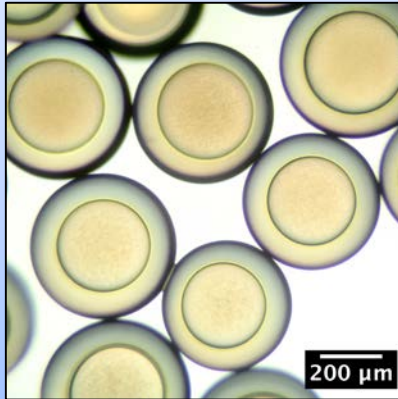


Functionalized packing

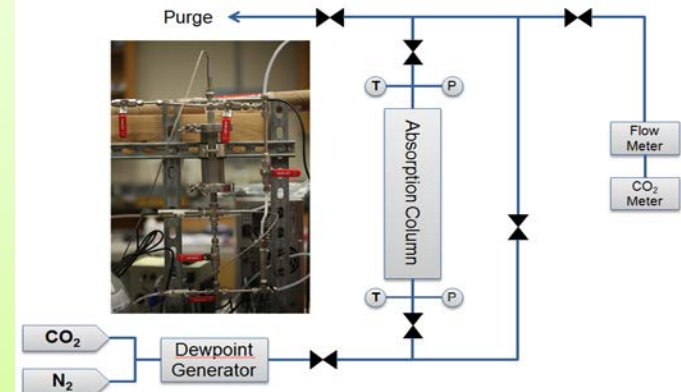
FEW0194: \$4.45M over 3 years (April 15, 2015 – April 14, 2018)

in five main tasks:

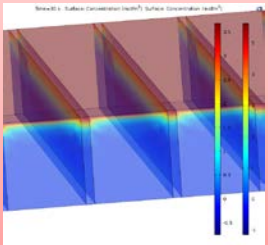
Encapsulation of Advanced Solvents \$475k/yr



Process design and scaleup with microcapsules -- \$475k/yr



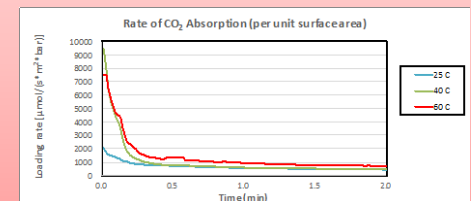
CO₂ absorber design with advanced manufacturing \$250k/yr



Rapid determination of solvent properties via microfluidic reactors \$133k/yr



Process modeling collaboration with CCSI \$250k



Project Team



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Collaborators



CCSI²
Carbon Capture Simulation for Industry Impact

Imperial College
London

Camille Petit

 **COLUMBIA UNIVERSITY**
IN THE CITY OF NEW YORK

Alissa Park

Spray-Tek
Jiten Dihora

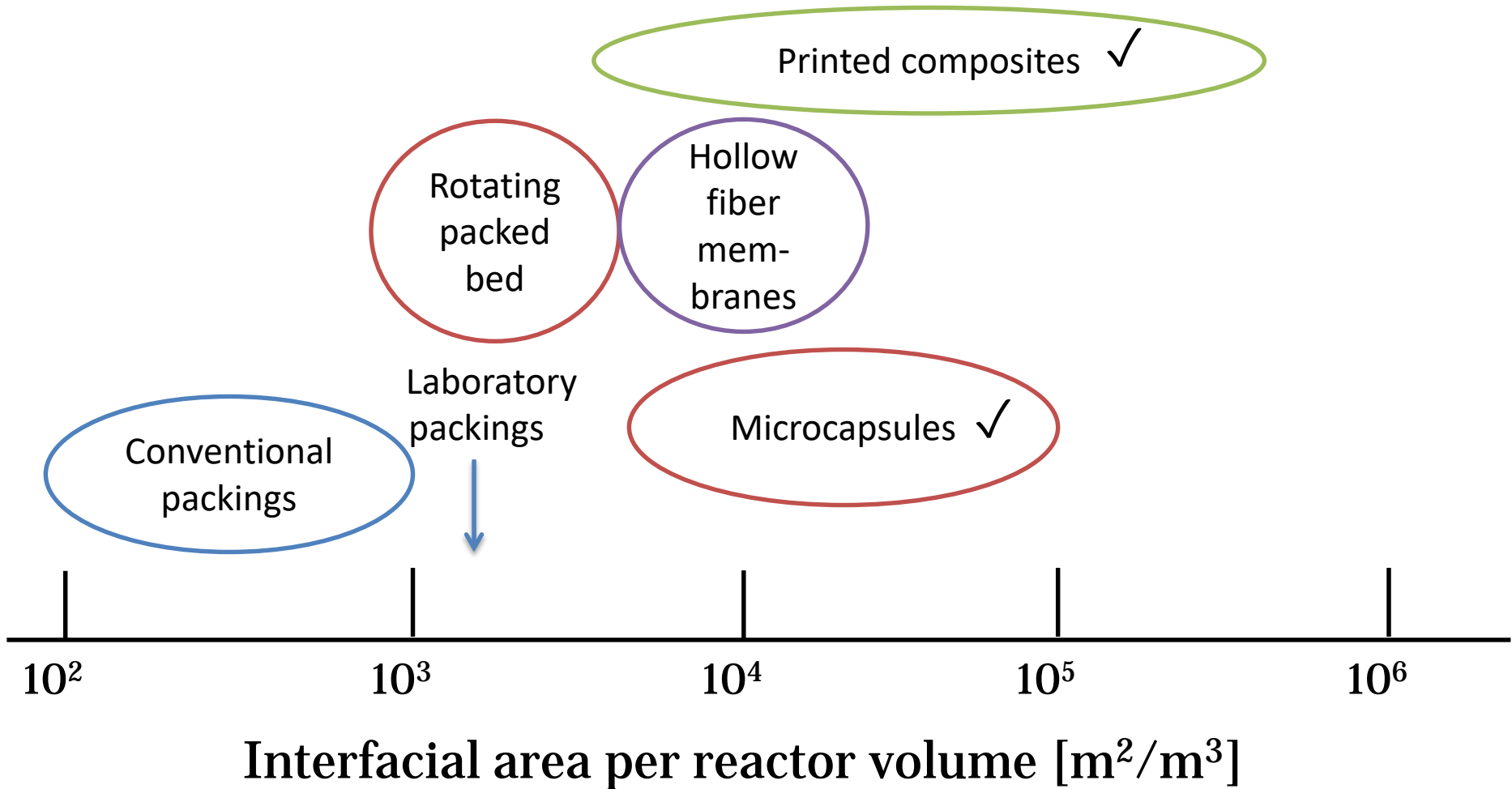


Joan Brennecke



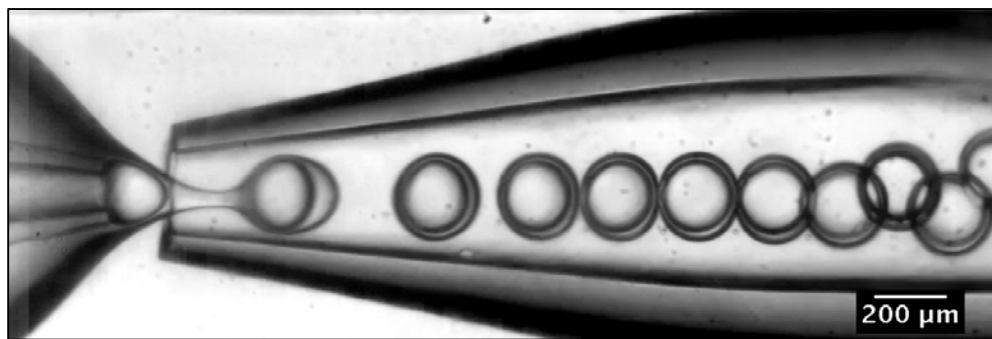
THE UNIVERSITY OF
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Permeable solids can form intensified gas-liquid reactors.



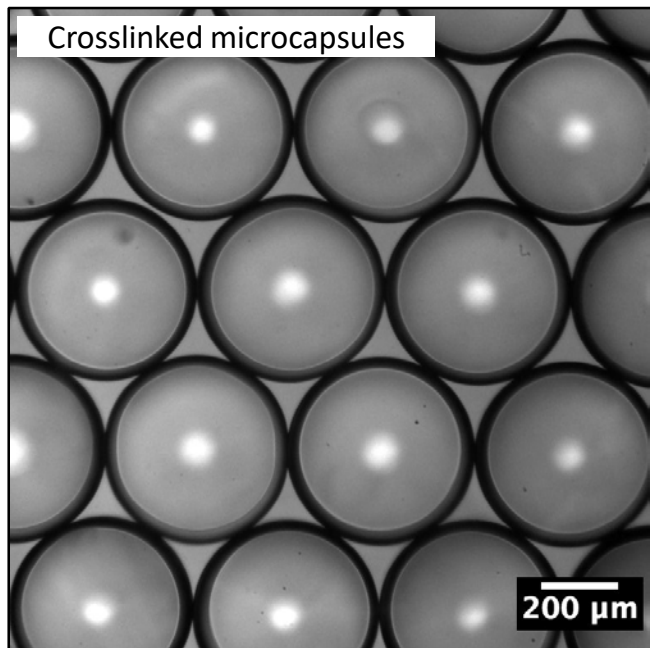
✓ Also tolerates phase changes!

Microcapsules are high surface area, permeable microreactors that enable advanced solvents

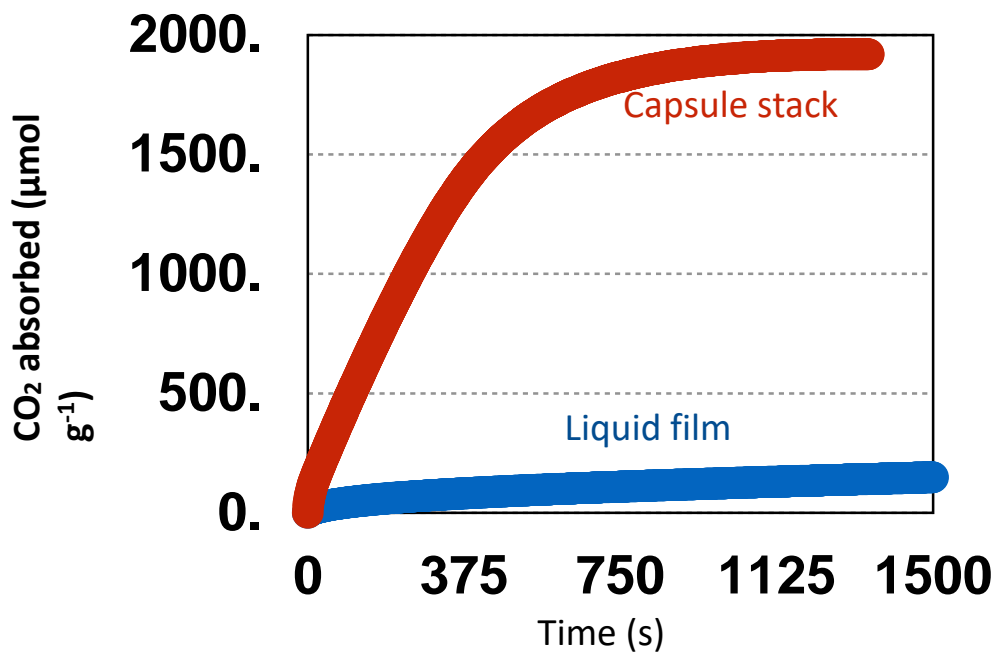


Video of typical drop generation
1/1000 speed

...but encapsulating new solvents takes development.



8–14X Faster Mass Transfer



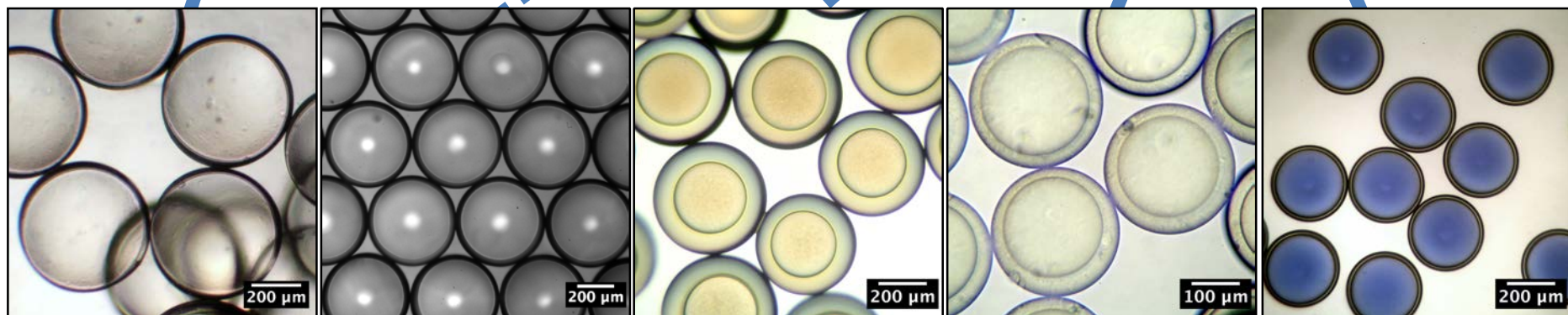
Many commercial and custom-developed shell materials tried with favorites now selected.

Name	Manufacturer	Material	Permeability (barrer)	Amine Compatibility	Mechanical Properties	Curing Time
Semicosil 949	Wacker	Silicone	3100	Poor	Elastic, strong, tacky	30 min
SiTRIS	LLNL	Acrylic	400	After curing	Stiff, strong, untacky	10 s
Thiol-eneQ	LLNL	Silicone	2700	Yes	Elastic, strong, tacky	30 s
Thio-leneQ (gen. 2)	LLNL	Silicone	2700	Yes	Elastic, strong, tacky	~0.1 s
Tego Rad 2650	Evonik	Silicone	3200	After curing	Elastic, friable, untacky	10 s

Many solvents screened across four classes of shell material.

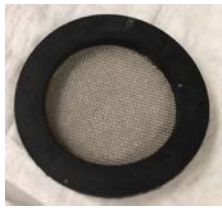
Good properties for encapsulation	Marginal properties for encapsulation	Not compatible
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	Koech-anol	Koech-anol w/ 1:1 wt. water	DBU/Hex-anol 1:1	NDIL 0274	NDIL 0252	NDIL 0231 w/ 1:1 wt. water	NDIL 0230	NDIL 0230 w/ 1:1 wt. water	NDIL 0309 (solid)	NDIL 0309 w/ 1:1 wt. water	Carbonate w/ water	NOHM -I-PEI w/ water	Sarcosine + carbonate
Semi-cosil						X		X			√	√	
Thiol-ene		√								√	√		√
SiTRIS						√		√ w/ 1:3			√		
T.R. 2650		√ (unstable)									√	√	√



Successful capsules cycled and measured for rate and capacity

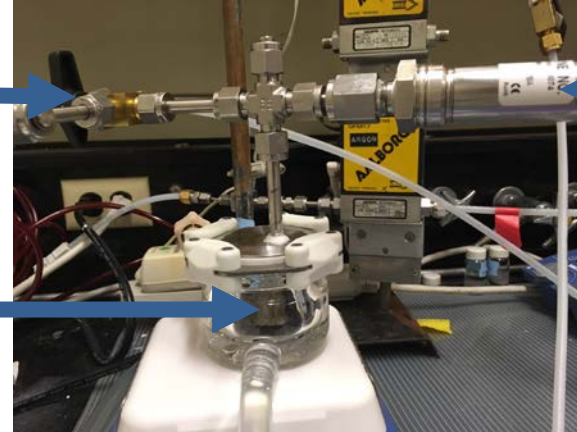
Absorption: measured by change in CO₂ partial pressure over time



Mesh platform

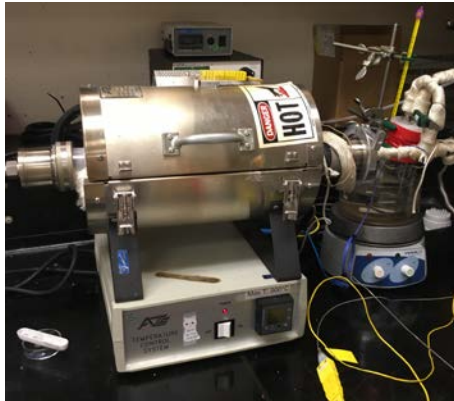
Valve for CO₂/vacuum

Capsules on mesh platform in jacketed vessel



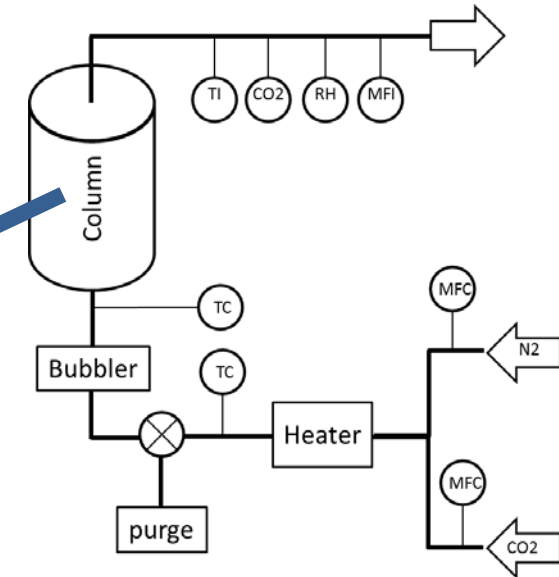
Pressure transducer

Regeneration: heat capsules to 100-120C for 1 hour then measure absorption capacity

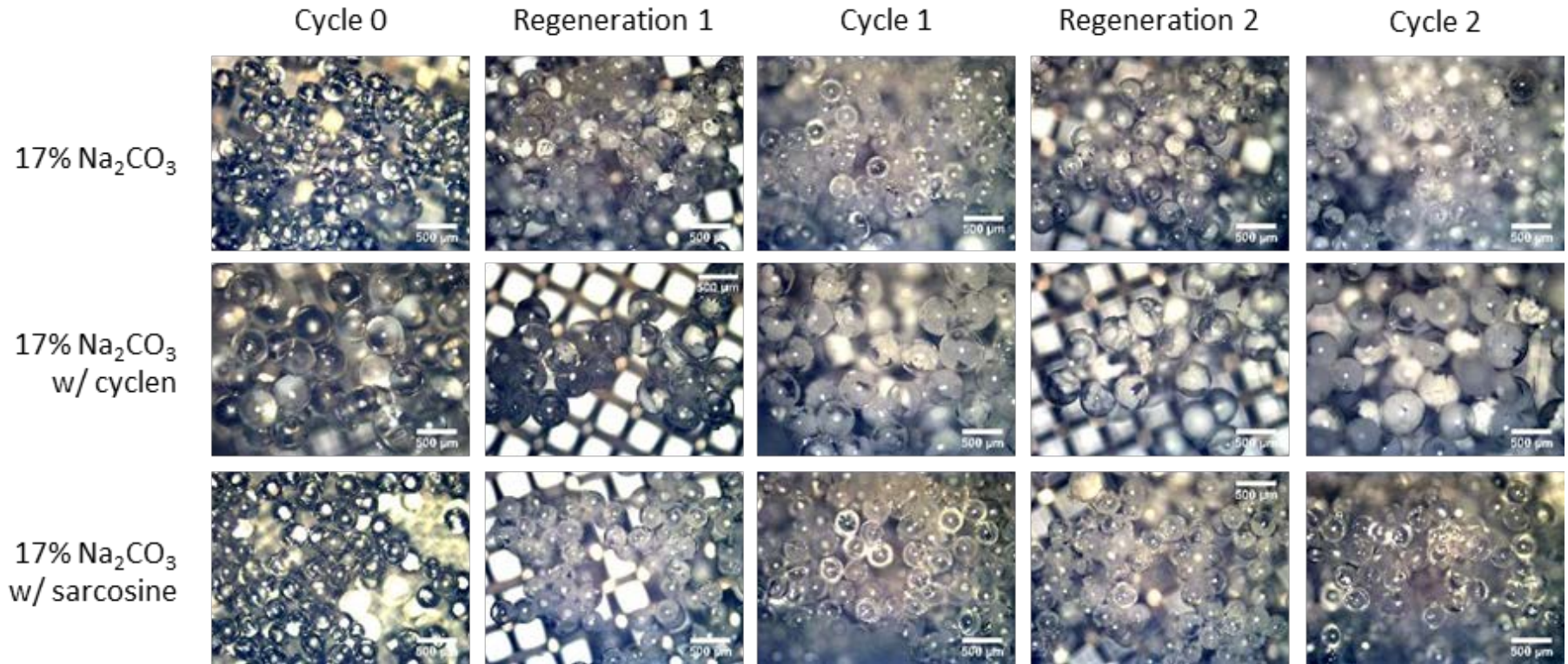


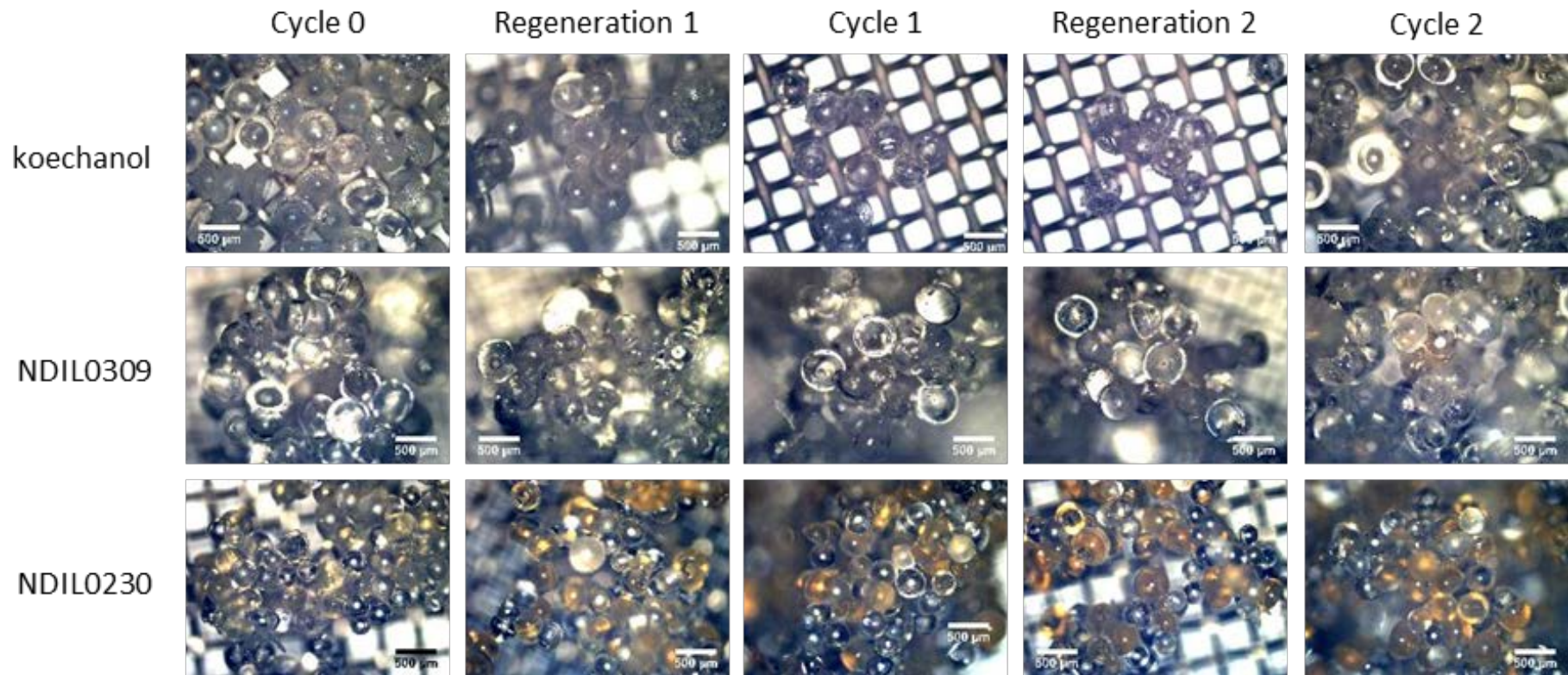
Left: tube furnace flowing wet nitrogen

Right: column flowing heated N₂ and/or CO₂

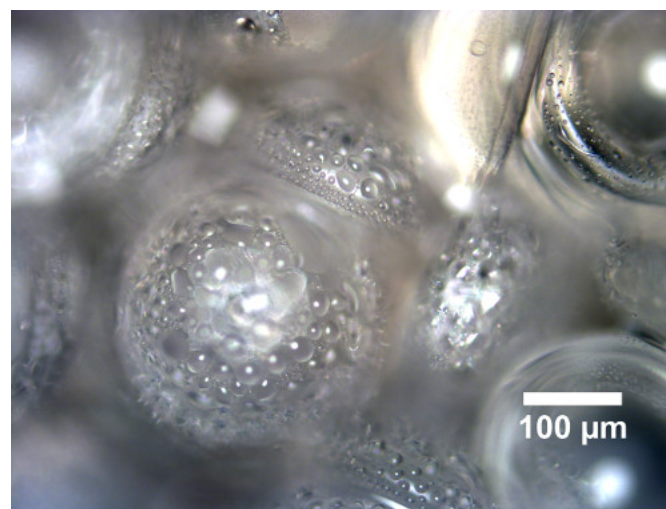


Rate, capacity, and morphology observed across cycles.

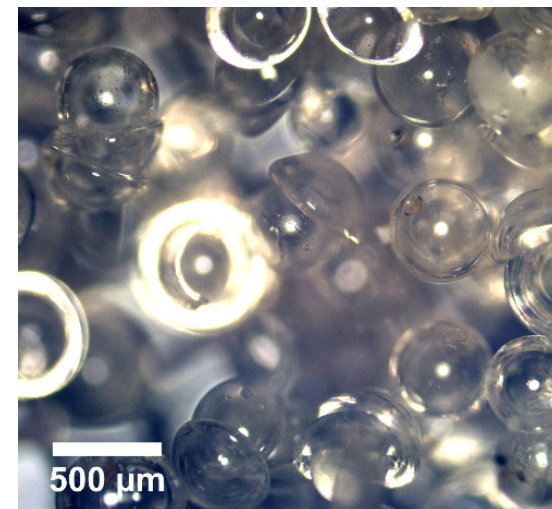




**Koechanol
appears to leak
from shell:**

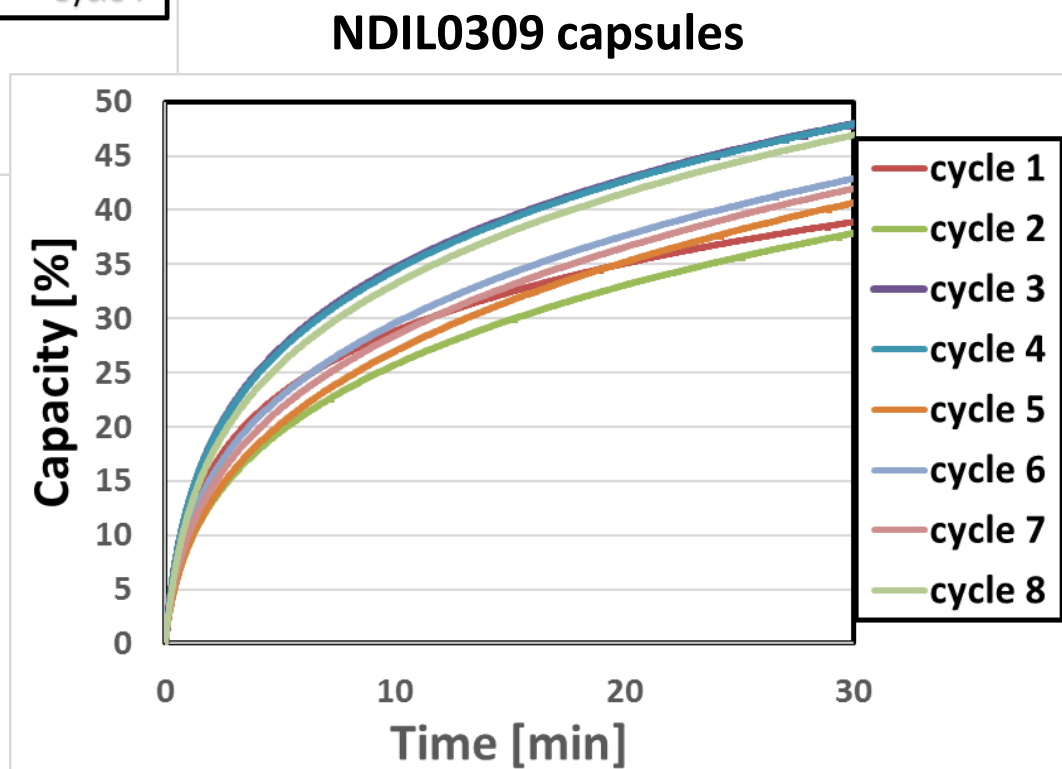
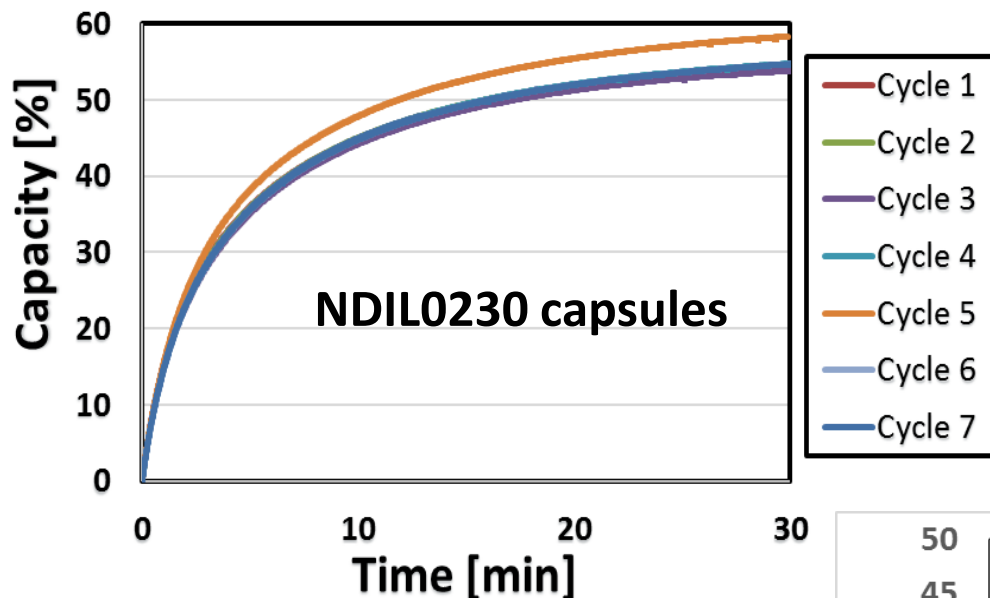


Solvent drops on capsule surface



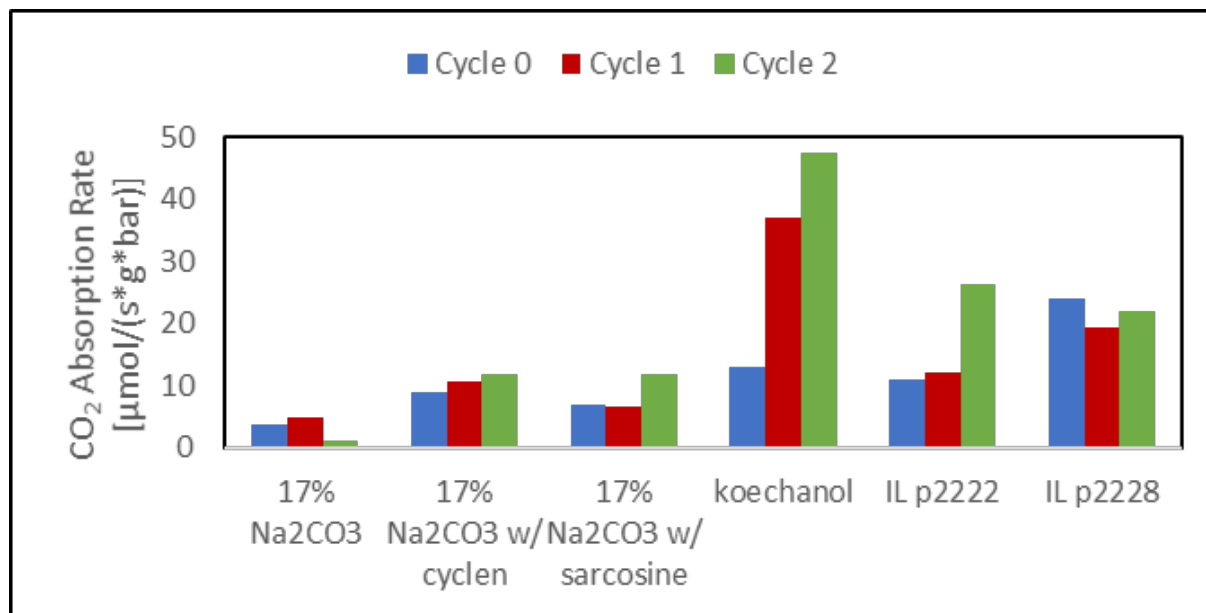
Collapsed capsules after cycling

Ionic liquids cycle like a charm; carbonate cycling is confounded by water transport.

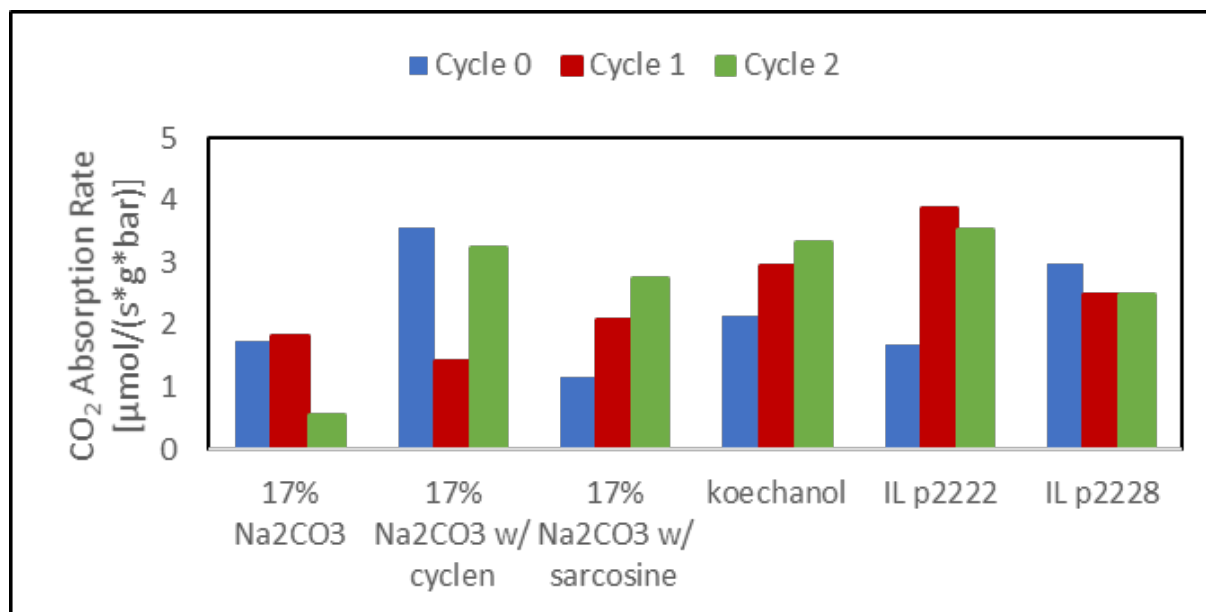


Initial rates vary a lot, full-loading rates are similar across solvents.

First 30 s

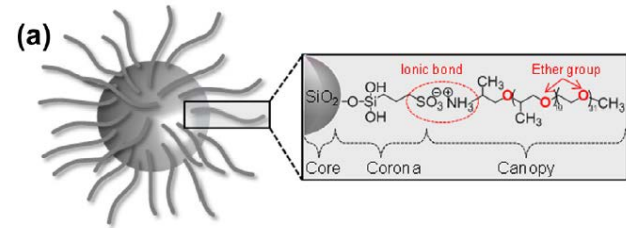


First 5 min



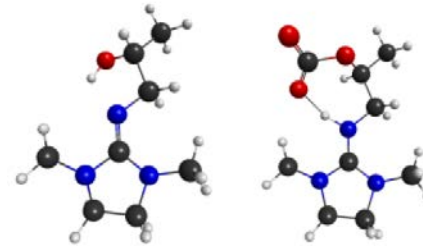
Summary of solvent classes encapsulated

X NOHMs: slower kinetics than carbonates in current formulations



X Amino acids / amino acid-promoted carbonates: poor kinetics in capsule form

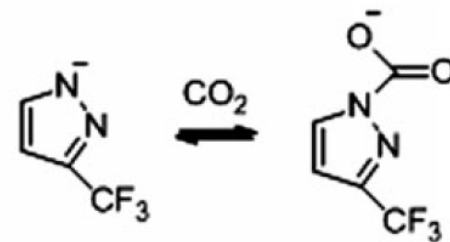
X CO₂BOLs: permeate shell / encapsulation may not be needed.



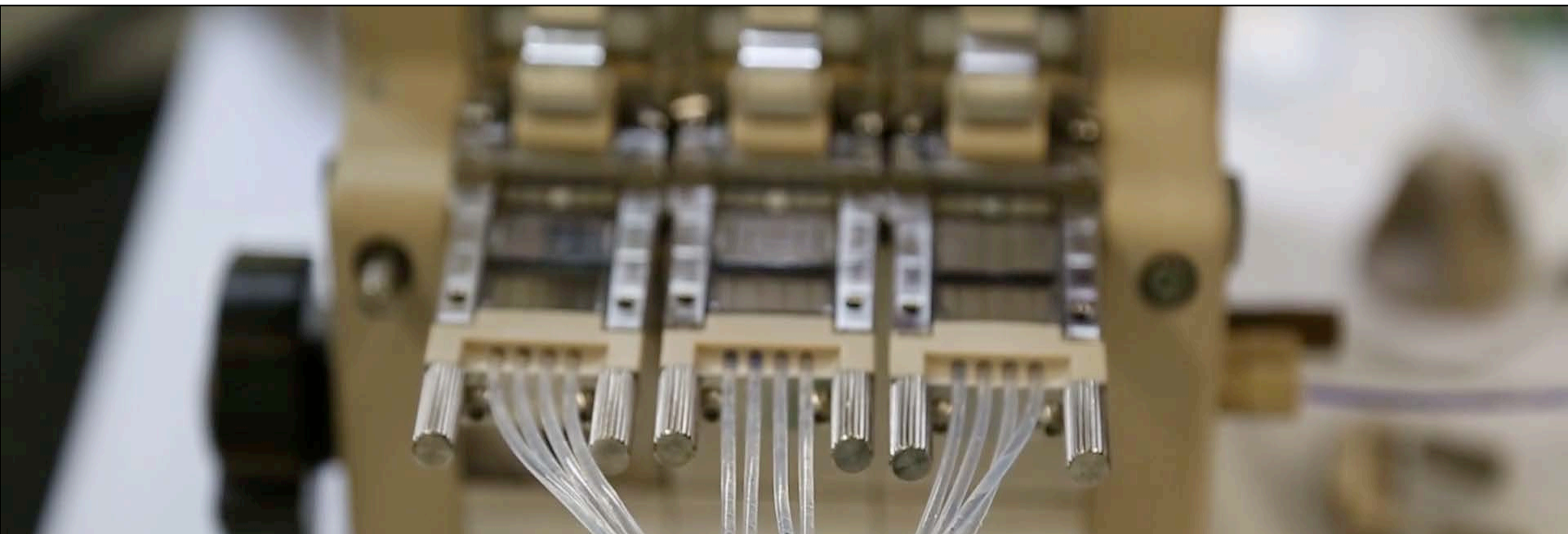
✓ Sodium carbonate with Cyclen catalyst: moderate kinetics / other advantages



✓ Ionic Liquids: NDIL0309 and NDIL0230 meet performance criteria.



Two scale-up methods selected: parallel glass chips and a proprietary system (IDEA)



Chip system:

- Demonstrated for carbonates and NDIL0309
- 4 g/hr per device
- finicky for industrial use

IDEA:

- Demonstrated for selected shell materials
- 250 g/hr per device
- More robust, scalable

Machine learning algorithms for automated quality control

Desired

Undesired

Dripping

Jetting

Broken

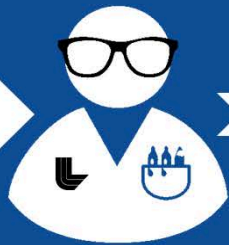
Wetting



Collect $\geq 10k$ images

Label images

Training set of images



Real-time image collection

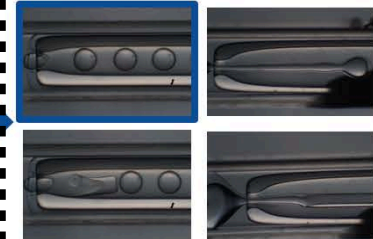


Machine Learning Algorithm



Fully trained detection algorithms operate at 98.6% & 99.5% accuracy

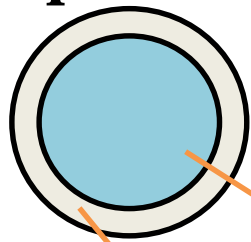
Detect



Trigger Response

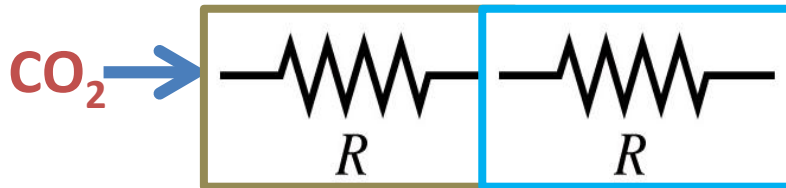


Semi-empirical process model estimates reactor size and cycle times.



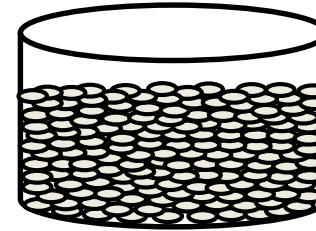
shell

solution

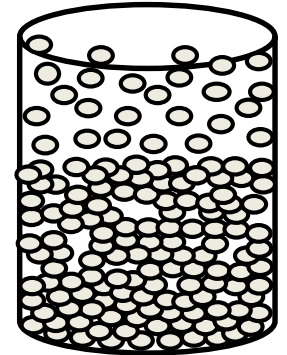


Packed bed

Fluidized bed



(plug flow)



(CFSTR)

$$K_{ov} * RT = \left[\frac{1}{K_{shell}} + \frac{1}{K_{solution}} \right]^{-1}$$

$$K_{shell} = P / L$$

$$K_{solution} = \frac{\dot{n}_{CO_2}}{AP_{CO_2}}$$

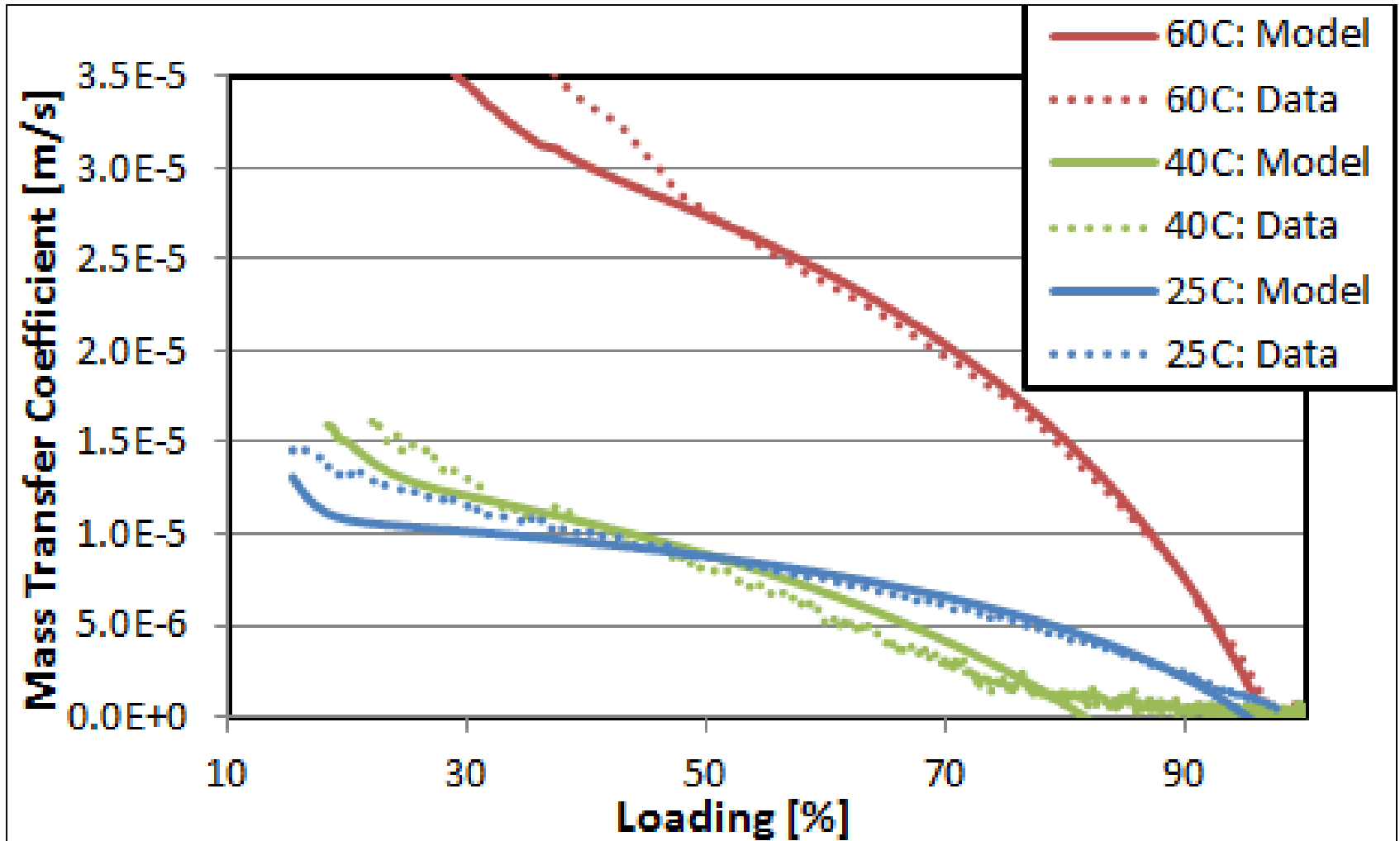
$$P = A_1 \exp[-B_1/RT]$$

$$\dot{n}_{CO_2} = k_f \sqrt{[OH^-]} - k_b [HCO_3^-]$$

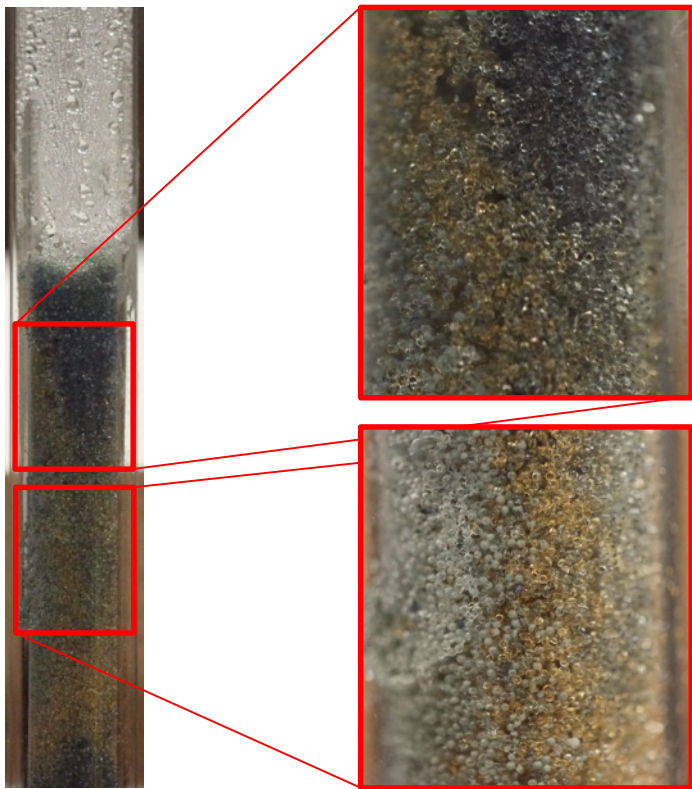
Constants from literature

Arrhenius fitting parameters

Extensive data collected on isolated capsules



Validated with fixed and fluidized column measurements.



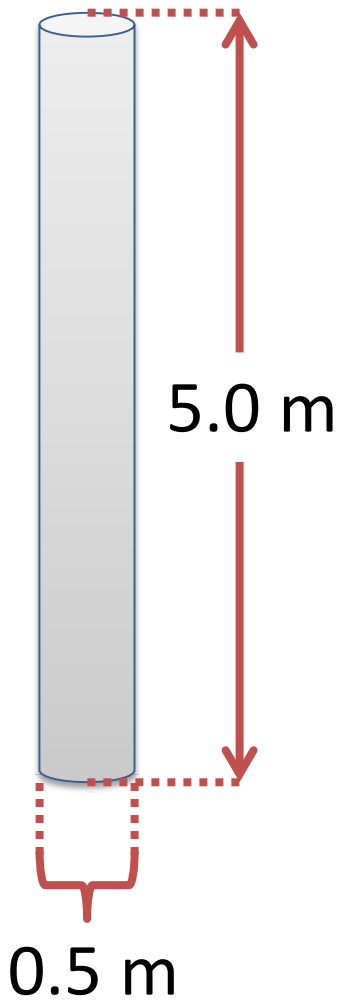
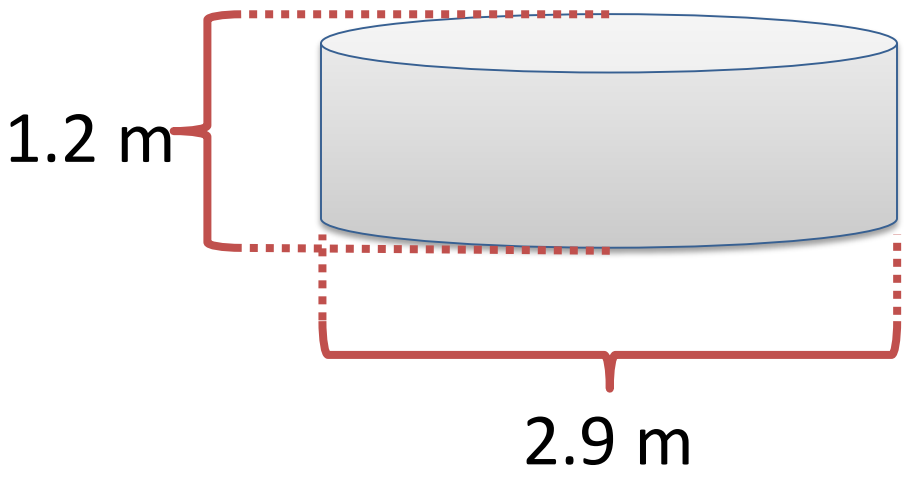
Color changes with loading during fixed bed testing

Initial results indicate reactor sizes are comparable to solvent systems.

MEA Absorber:

1 MW absorber sizing

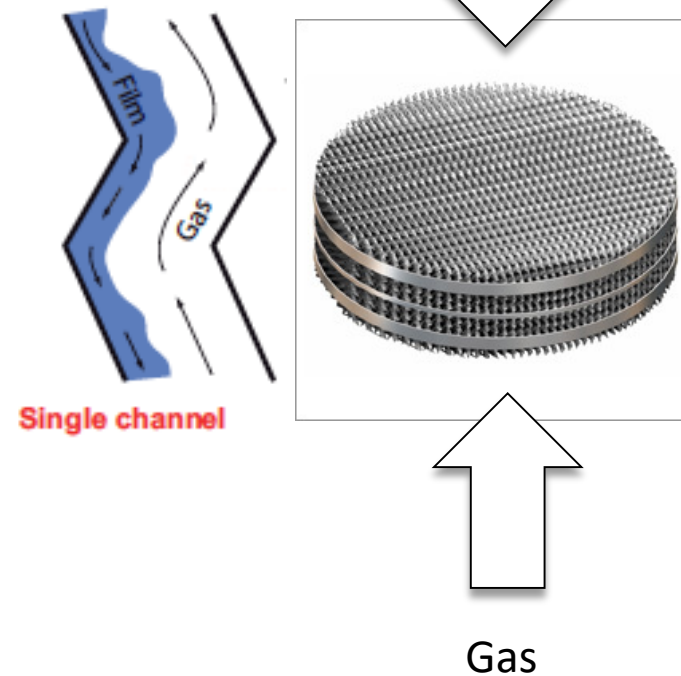
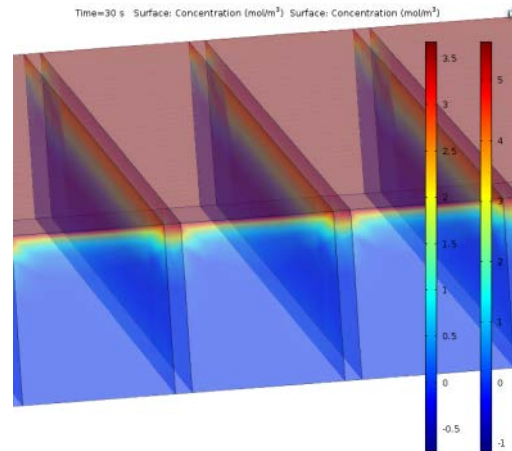
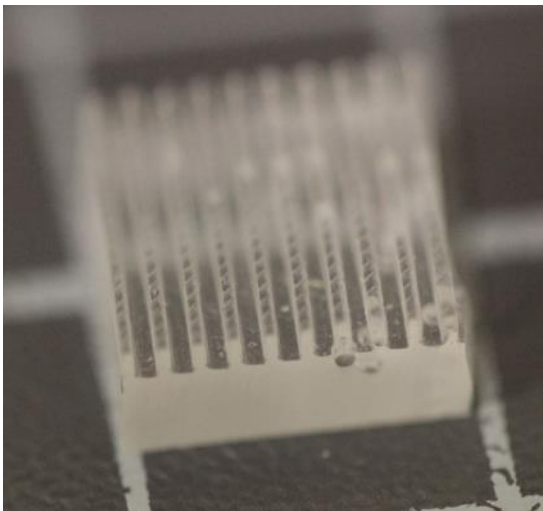
Single stage fixed bed



Advanced packings

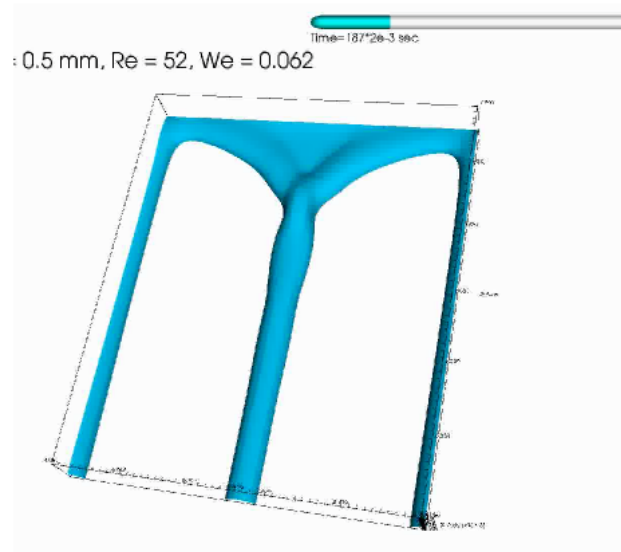
How to increase mass transfer at the gas-liquid interface?

Permeable solids help, but more so for slow solvents.

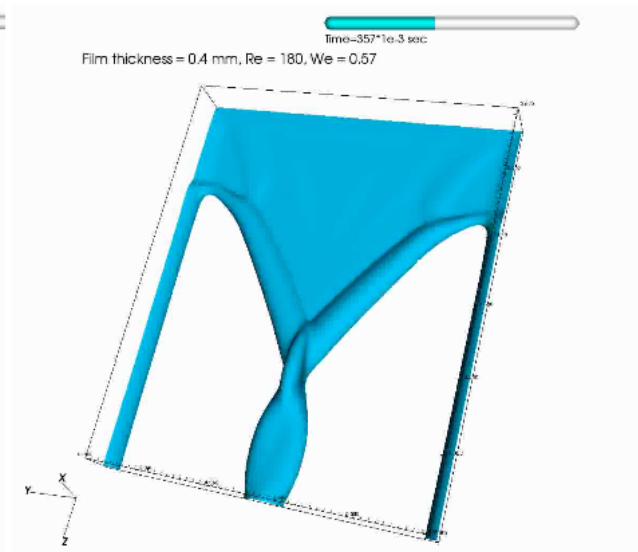


~15%
improvement with
carbonates.

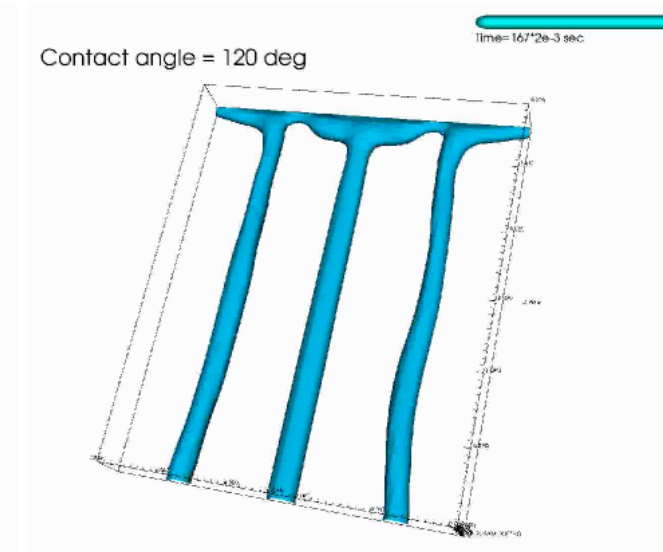
Surface wettability affects flow



Hydrophilic plate,
Low velocity



Hydrophilic plate,
High velocity

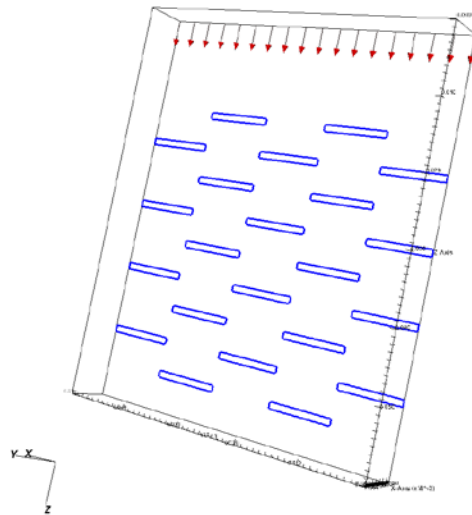
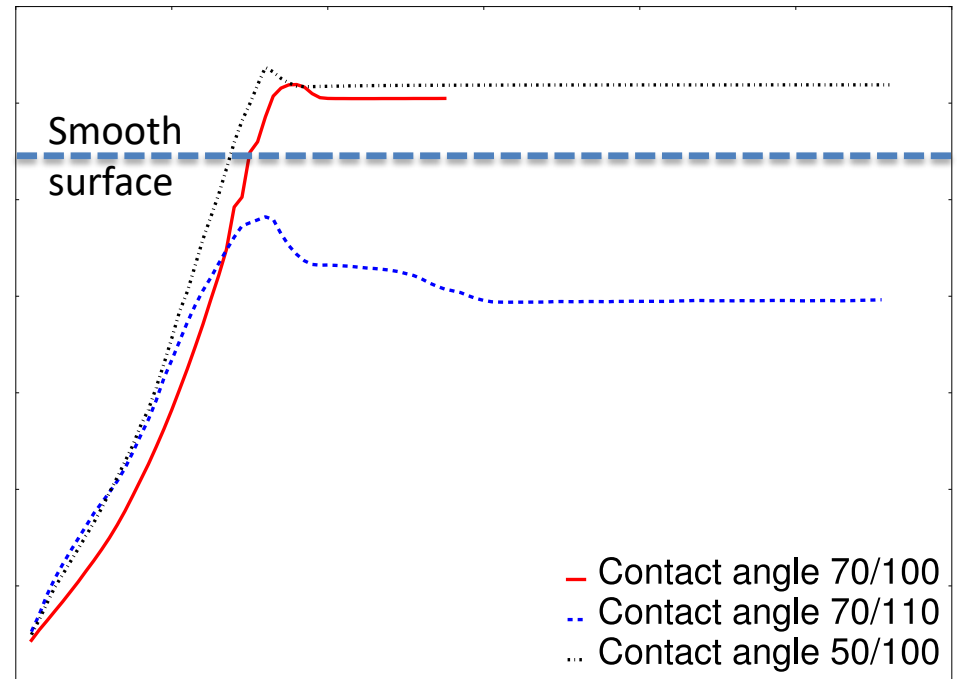
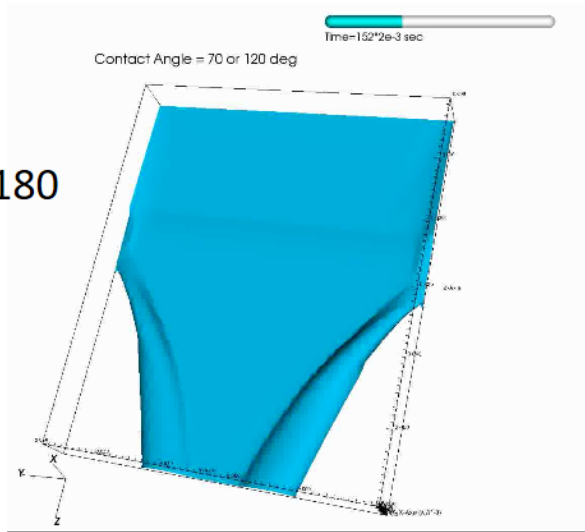


Hydrophobic plate,
High velocity

What if we combine the hydrophilic and hydrophobic zones?

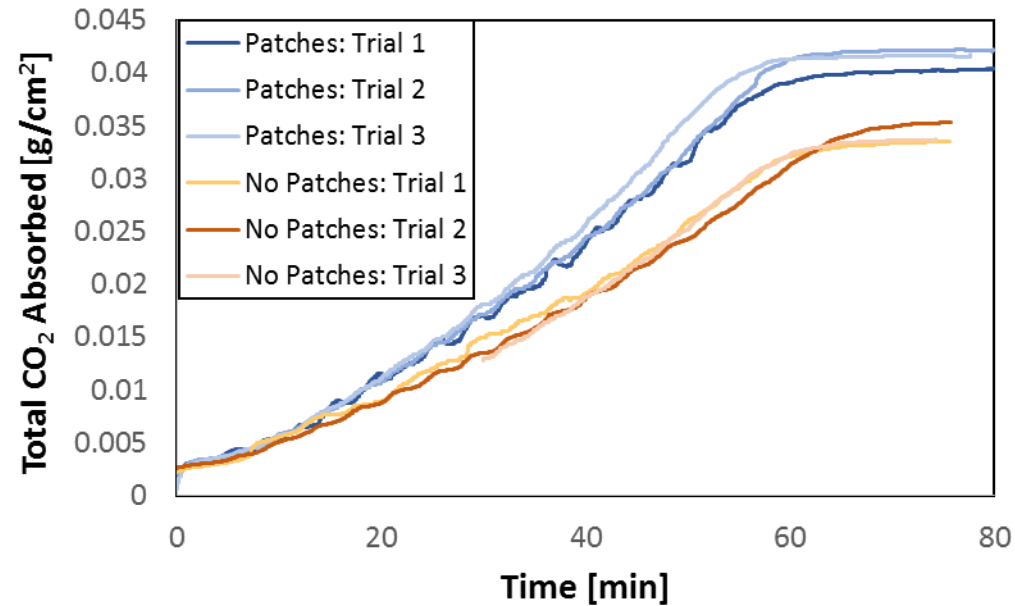
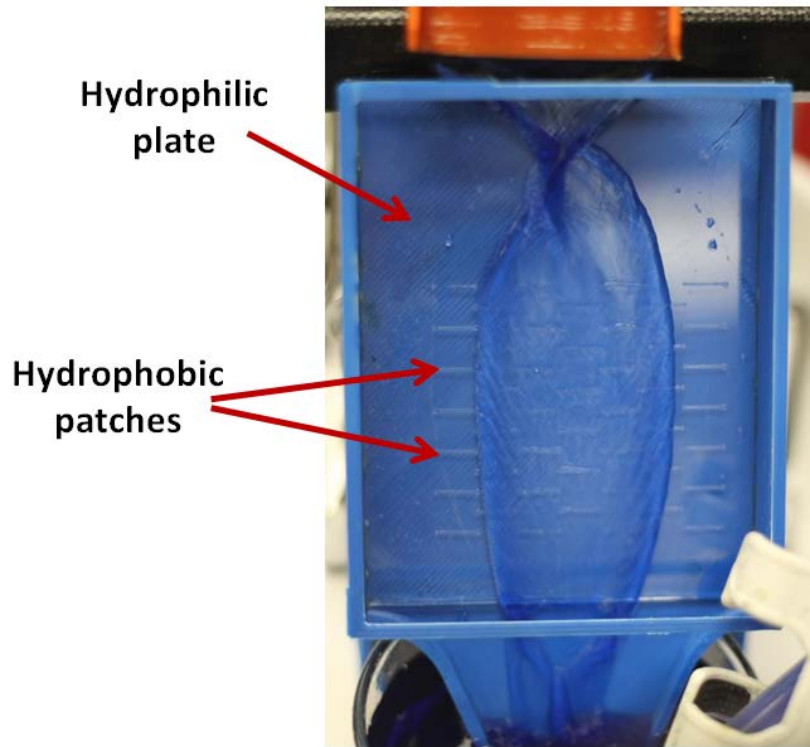
Flow in hydrophilic/ hydrophobic patches

Re = 180



~10% increase in interfacial area with hydrophobic patterns on hydrophilic plate.

Tailored surface wettability enhances mass transfer by 22%



This should hold across solvent classes.

Future plans

Primary objectives for Year 3:

- Top-level process design and cost estimate for Microencapsuled CO₂ Sorbents (MECS)
- Design of a small pilot with MECS
- Proof-of-concept demonstration with advanced packing motif

Acknowledgements



Lynn Brickett
Andy Aurelio

