CCSI^2

Carbon Capture Simulation for Industry Impact

Multiscale Modeling: Micro-Encapsulated Carbon Sorbent (MECS) Technology

Debangsu Bhattacharyya, Goutham Kotamreddy, Ryan Hughes, West Virginia University
Janine Carney (NETL) and Justin Finn (ORISE - NETL)
Zhijie (Jay) Xu and Chao Wang, Pacific Northwest National Laboratory (PNNL)

Outline

❑ What is MECS & Challenges for Modeling MECS

How Can CCSI^2 Help?

❑ Process Modeling of MECS

- Screening the design of reactor
- Developing optimal design of process

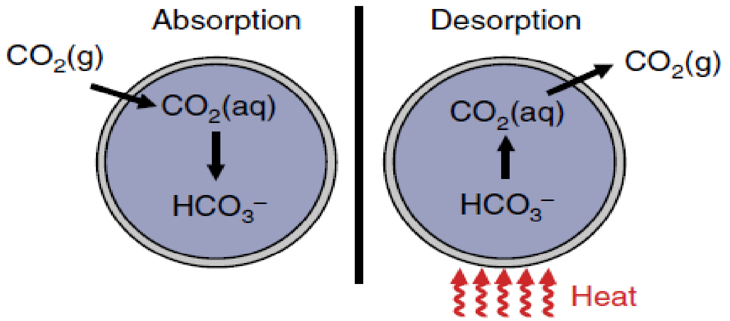
❑ Bench-Scale CFD Model for MECS: A Discrete Particle Model

- Understanding the MECS behavior at particle scale
- Calibrating models/parameters at bench-scale for use at device-scale
- Experiment test bed for validation of device scale

❑ Device-Scale Model for MECS Performance in Absorber

- Enabling device-scale prediction of MECS (~100µm) in Absorber (~10m)
- Understanding complex flow and adsorption kinetics to support process design

MECS Technology



- Shell*

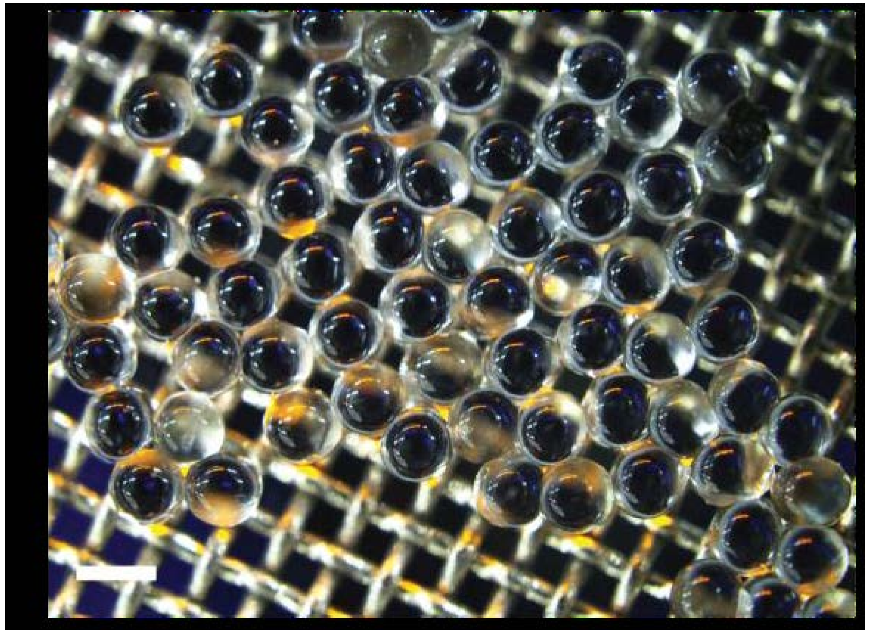
  -made of silicone

  -commercially available as Semicosil

- Core fluid/material

  -contains solvent (encapsulated by the shell)

  -Strong potential for solvents that are highly viscous and/or form solid precipitate upon CO_2 absorption



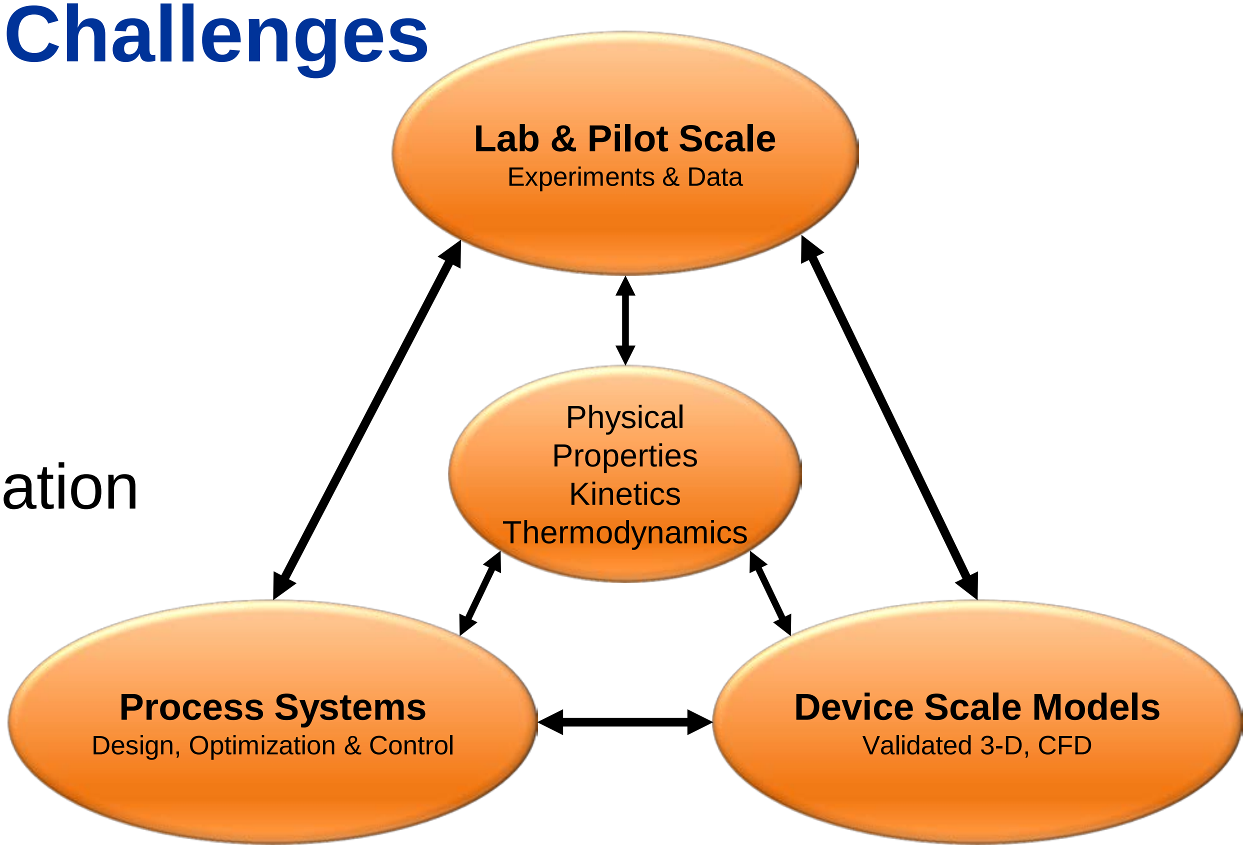
Polymer microcapsules filled with sodium carbonate

---

* Vericella, J. J. et al. Encapsulated liquid sorbents for carbon dioxide capture. Nat. Commun. 6:6124 doi: 10.1038/ncomms7124 (2015).

Modeling Challenges

- Elastic, deformable shell
- Capsule size/density change
- Precipitation inside capsule
- Water loss/uptake during capture regeneration
- Hydrodynamics of gas-particle flow
- Disparity in scales
- Impractical to measure solvent concentration and loading-difficulty in parameter estimation and model validation
- During operation, solvent concentration and loading need to be estimated



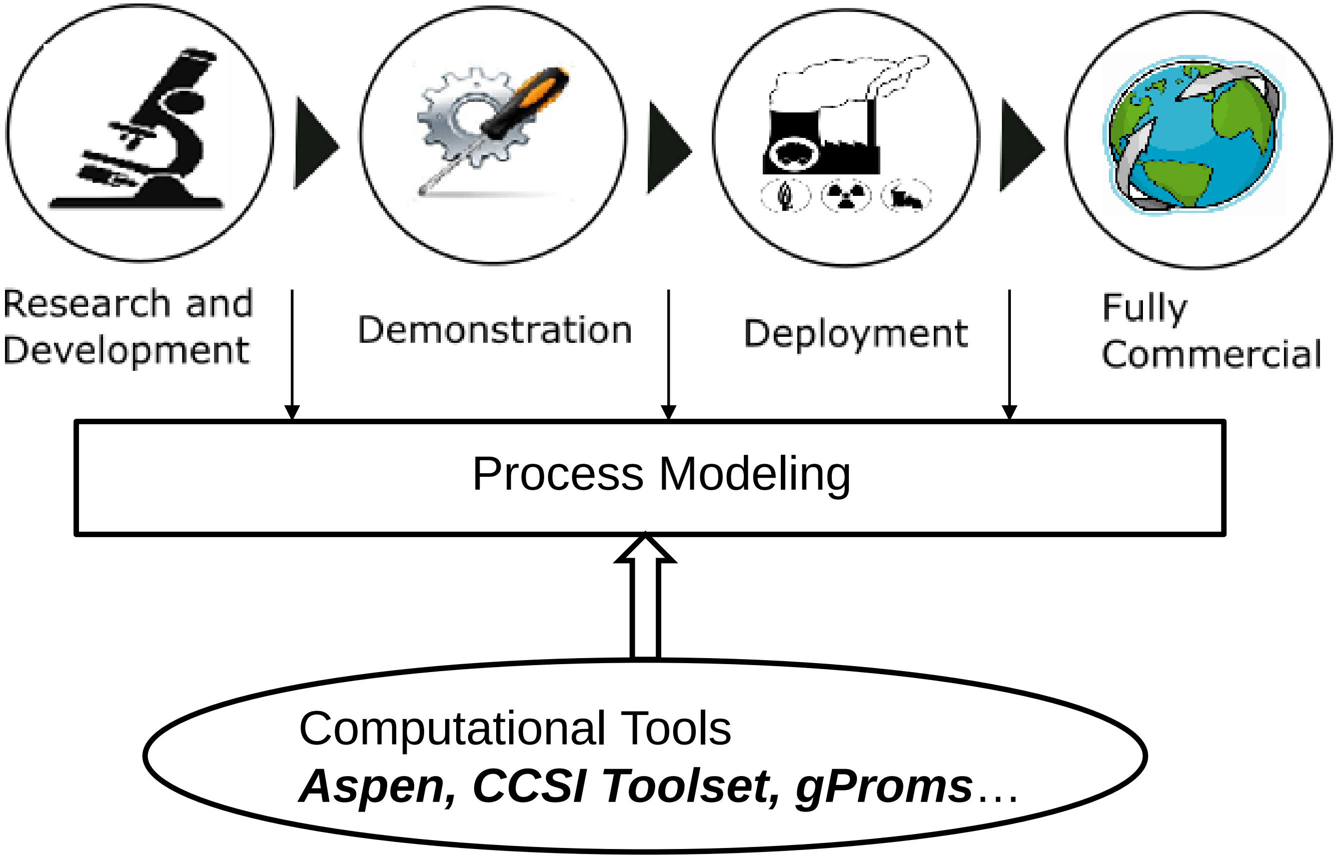
Lab & Pilot Scale
Experiments & Data

Physical
Properties
Kinetics
Thermodynamics

Process Systems
Design, Optimization & Control

Device Scale Models
Validated 3-D, CFD

Specific Objectives of Process Modeling for MECS



Research and Development

Demonstration

Deployment

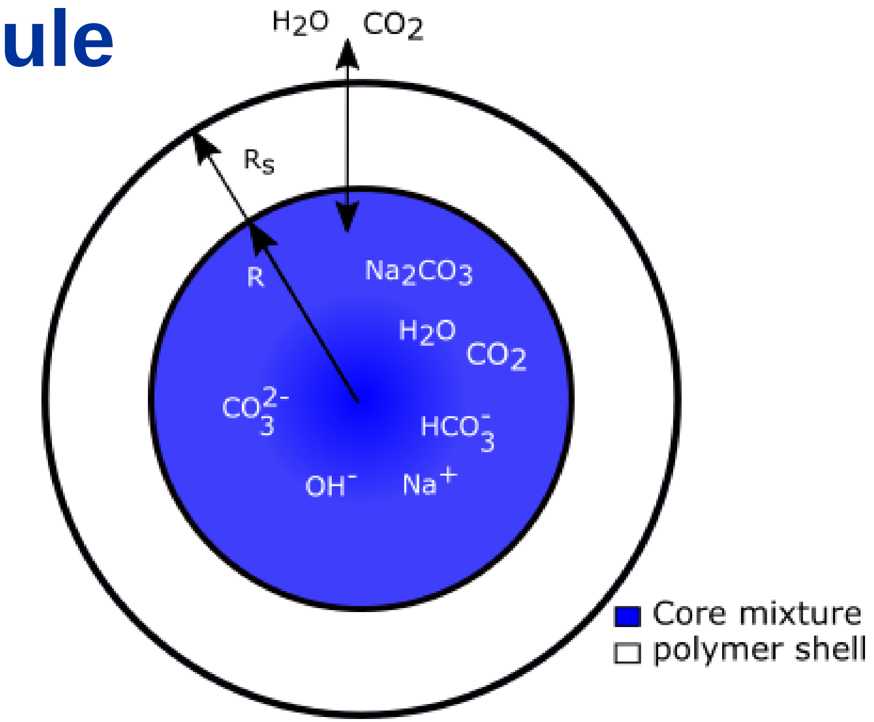
Fully Commercial

Process Modeling

Computational Tools
Aspen, CCSI Toolset, gProms…

- Understand rate-limiting mechanisms at the commercial scale to identify where resources should be focused
- Estimate model parameters
- Develop optimal contactor type and design
- Synthesize optimal configuration and operating conditions
- Helps to develop optimal design of experiments
- Study transient performance and develop control strategies

Model of a single capsule



Schematic of microcapsule

<u>Assumptions:</u>

- All capsules are perfectly spherical.
- No accumulation in the shell.
- Core is well mixed.
- Shrinking or swelling is neglected (initial version).
- Uniform ambient conditions.
- Mass transfer through the shell only through diffusion.
- No loss of the solvent through the membrane.

Reactions

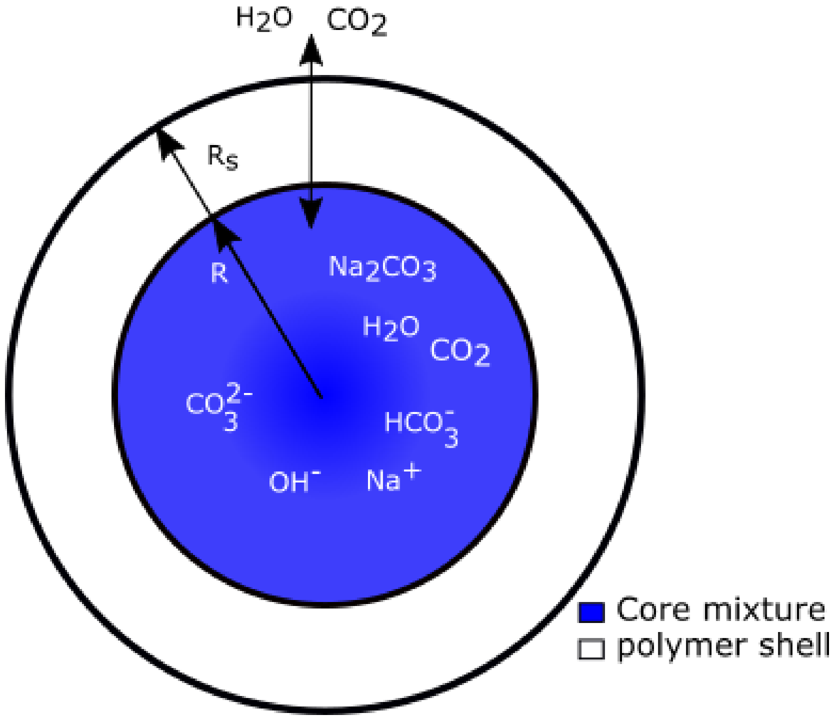
- Kinetically controlled:

  R1: $CO_2 + OH^- \leftrightarrow HCO_3^-$

- Equilibrium Limited:

  R2: $CO_3^{2-} + H_2O \leftrightarrow HCO_3^- + OH^-$

  R3: $Na_2CO_3 \leftrightarrow 2Na^+ + CO_3^{2-}$



Pinsent B.R., Pearson L. , Roughton F.J.W., “The Kinetics of Combination of Carbon Dioxide with Hydroxide Ions”, Trans. Faraday Soc., 52, 1512-1520, 1956
Astarita G., Savage, D. W., Longo, J. M., “Promotion of Mass Transfer in Carbonate Solutions”, Chemical Engineering Science, 36, 581, 1981

Capsule Model Overview

- **Mass transfer from the bulk to the capsule surface:**

$$N_{i,surf} = -k_{i,G}(C_{i,G,bulk} - C_{i,surf})$$

- **Mass transfer through the shell:**

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(D_{i,shell}\, r^2 \frac{\partial C_{i,shell}}{\partial r}\right) = 0 \qquad D_{i,shell} = C_{1,i}\exp\left(-\frac{C_{2,i}}{\mathrm{T}}\right)$$

- **Mass transfer from the interface to the liquid core :**

$$N_{i,L} = E k_{i,L} C_{tot,L}(x_{i,int} - x_i^*) \qquad E = Ha = \frac{\sqrt{k_1 C_{OH^-} D_{CO_2,L}}}{k_{CO_2,L}} \qquad D_{CO_2,L} = f(\mu_L, \mathrm{x}, \mathrm{T}, C_{1L,CO_2}, C_{2L,CO_2})$$

- **Chemical Equilibrium:**

$$K_{eq1} = \frac{[C_{HCO_3^-}]}{[CO_2^*][C_{OH^-}]};\ K_{eq2} = \frac{[C_{HCO_3^-}][C_{OH^-}]}{[CO_3^{2-}][H_2O^*]};\ K_{eq3} = \frac{[C_{Na^+}]^2[C_{CO_3^{2-}}]}{[C^*_{Na_2CO_3}]}$$

- **Phase Equilibrium at interface**:

$$\phi_{CO_2} P y_{CO_2,int} = He_{CO_2}\gamma_{CO_2} x_{CO_2,int}$$

$$\phi_{H2O} P y_{H_2O,int} = x_{H_2O,int}\gamma_{H_2O} f^L_{H_2O}$$

Model of a Single Shell (contd.)

- **Mass transfer Coefficients*:**

Liquid Phase

$$\frac{k_{i,L} d_{int}}{D_{i,L}} = C_L \left(\frac{d_{int}^3 \Delta\rho g}{\rho_L \mu_L^2}\right)^{\frac{1}{3}} \left(\frac{\mu_L}{D_{i,L}}\right)^{\frac{1}{2}}$$

Gas Phase

$$\frac{k_{i,G} d_{surf}}{D_{i,G}} = 2 + C_G \left(\frac{d_{surf}^3 d^3 \Delta\rho g}{\rho_G \mu^2}\right)^{\frac{1}{4}} \left(\frac{\mu_G}{D_{i,G}}\right)^{\frac{1}{3}}$$

- **Diffusion coefficients:**

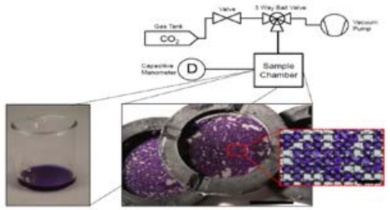
Diffusivity of CO_2 in liquid:

$$D_{CO_2,L} = f(\mu_L, \mathrm{x}, \mathrm{T}, C_{1L,CO_2}, C_{2L,CO_2})$$

Cussler, E. L. *Diffusion: Mass transfer in fluid systems*. (Cambridge, 1984).

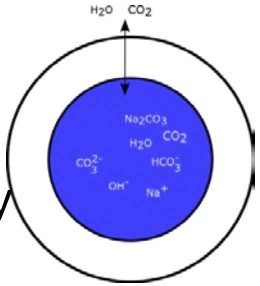
Estimation of Model Parameters

Experiments



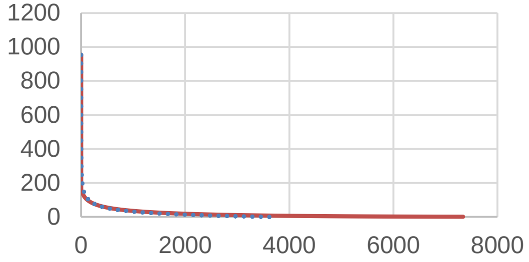
Capsule Model

- Input capsule properties
- Initial values of boundary conditions



Estimation

- Parameter identifiability analysis
- Maximum likelihood estimate of model parameters



$$\max_{\theta,\gamma}\left\{-\frac{1}{2}\sum_{i=1}^{Nmeas}\left(n_i\log(2\pi+1)+n_i\log\left[\frac{1}{n_i}\sum_{j=1}^{NDyn}\sum_{k=1}^{M_{ij}} w_j^2\frac{\left(Z_e(t_{ijk})-Z_m(t_{ijk})\right)^2}{Z_{m,ijk}^{\gamma_i}}\right]+\gamma_i\sum_{j=1}^{NDyn}\sum_{k=1}^{M_{ij}}\log w_j\, Z(t_{ijk})\right)\right\}$$

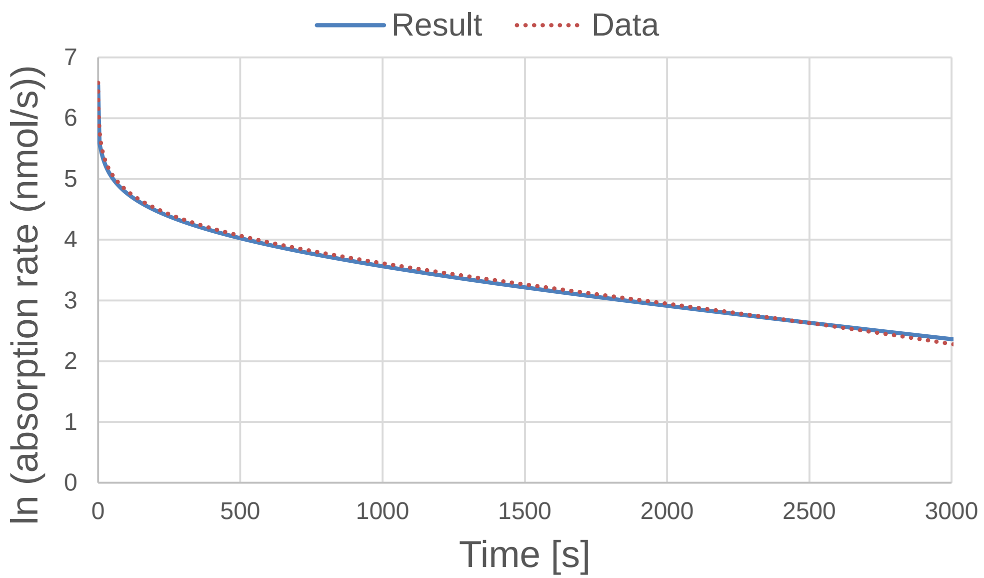
Subject to $\dot{x}=f(x,Z,u,\theta)$

$$g(x,Z,u,\theta)\le 0$$

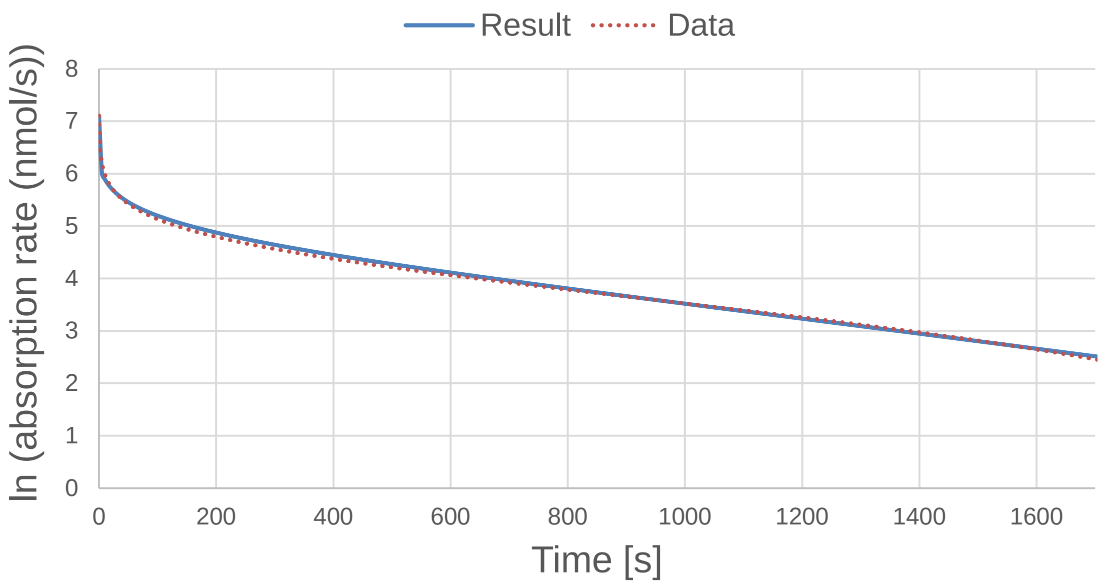
$$g(x,Z,u,\theta)\le 0$$

Validation of Capsule Model

25°C



40°C



Development of a Fixed Bed Model

- Can be used for studying mass and heat transfer characteristics, especially through the membrane and into the core
- Investigate feasibility of a fixed bed contactor
- Mass and energy balance for the gas phase:

$$\epsilon_{bed}\frac{\partial C_{i,g}}{\partial t} = -\frac{\partial(u_g C_{i,g})}{\partial z} + \epsilon_{bed}\frac{\partial}{\partial z}\left(D_{ax}\frac{\partial C_{i,g}}{\partial z}\right) - (1-\epsilon_{bed}) * n_{capsules} * a_v * N_{i,surf}$$

$$\epsilon_{bed} C_{T,g} C_{v,g}\frac{\partial T_g}{\partial t} = -u_g C_{T,g} C_{p,g}\frac{\partial T_g}{\partial z} + \frac{\partial}{\partial z}\left(\lambda\frac{\partial T_g}{\partial z}\right) - (1-\epsilon_{bed}) a_p h_{gs}(T_g - T_s) - \frac{4h_{gw}}{D_r}(T_g - T_w)$$

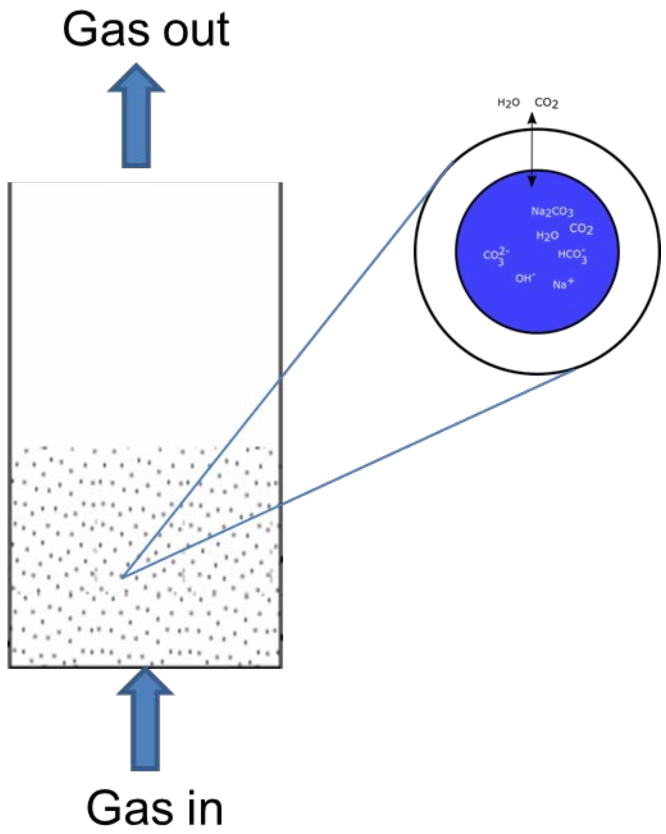
- Momentum balance:

$$-\frac{\partial P_g}{\partial z} = \frac{150\,\mu(1-\varepsilon)^2 u_g}{\varepsilon^3\, d_p{}^2} - \frac{1.75(1-\varepsilon)\rho_g |u_g| u_g}{\varepsilon^3\, d_p}$$

- Energy balance between wall and gas:

$$\rho_w \widehat{C_{p,w}}\frac{\partial T_w}{\partial t} = a_{w1} h_{gw}(T_g - T_w) - a_{w2} U(T_w - T_{amb}) = 0$$

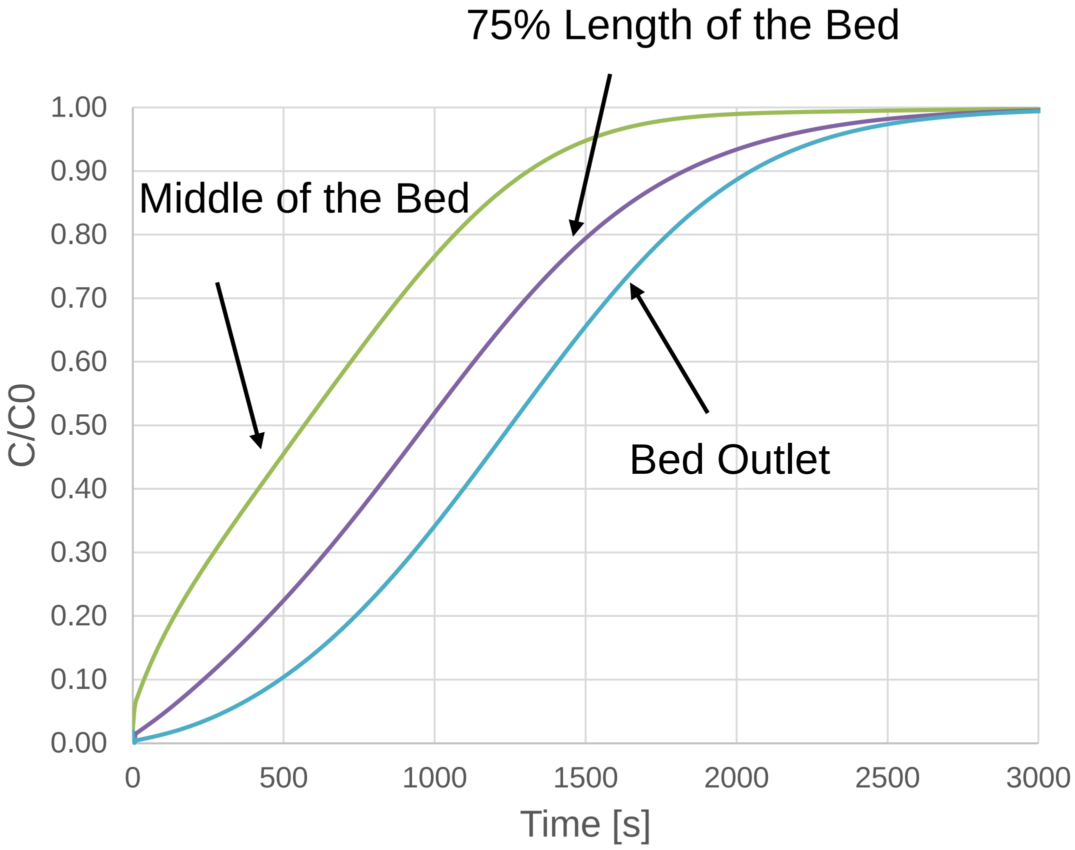
- Capsule model is embedded in the contactor model



Fixed Bed Results- Base Case

Operating conditions

Pressure	1.1	bar
Temperature	40	ºC
Bed Length	10	m
Bed Diameter	3	m
Flowrate	150	mol/s
Solvent loading	10%	wt



Breakthrough Curves at Different Sections of the Bed

Breakthrough Time

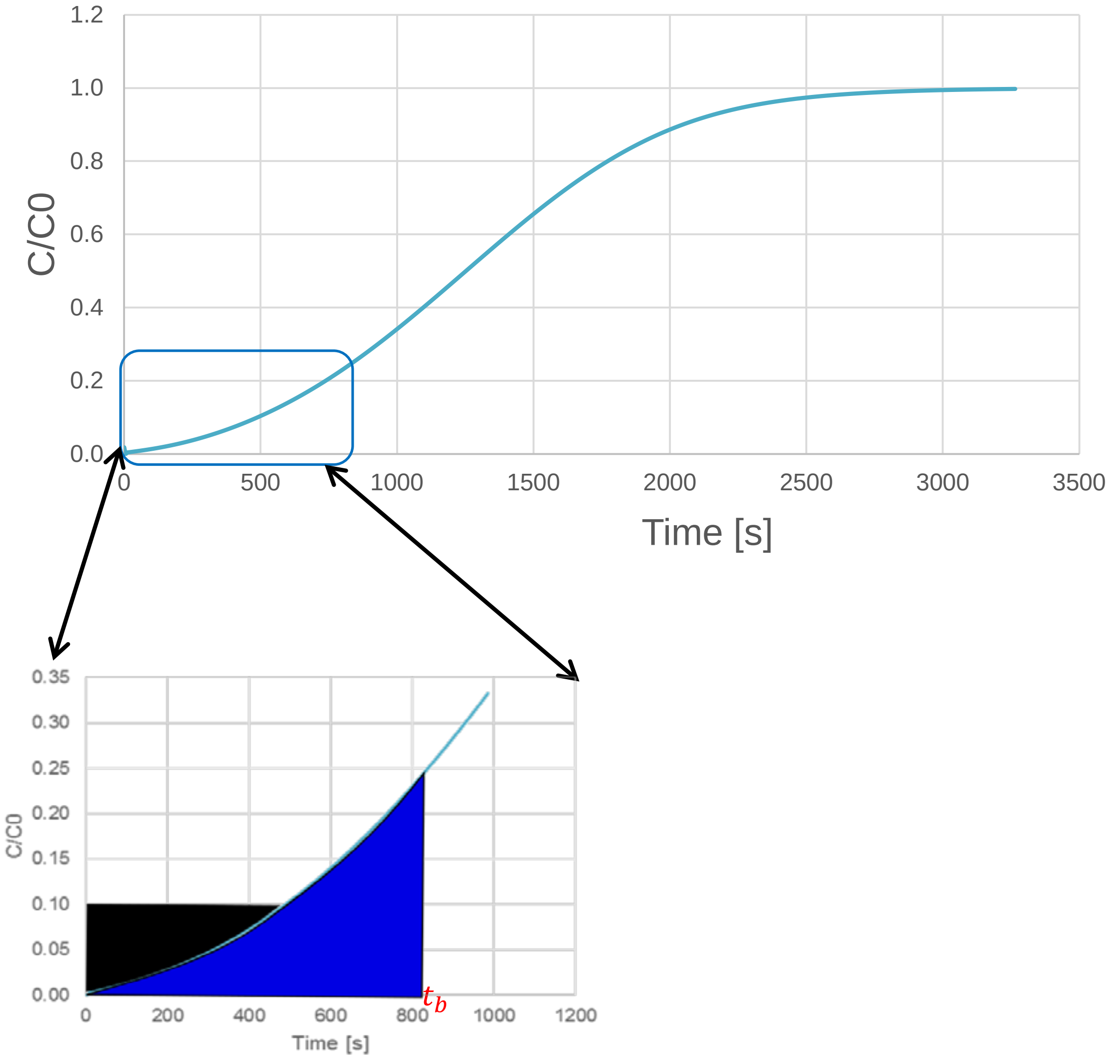
- Breakthrough Time for Overall 90% CO_2 Capture:

$$F_{in} z_{CO_2,in} * 0.1 * t_b = \sum_{i=1}^{n} F_{out,i}\, z_{CO_2,out,i} \Delta t$$

Where $n = \frac{(t_b - t_o)}{\Delta t}$

- Approximate number of beds for a 550 MWe net subcritical PC plant:

182



Fixed Bed Results-Possible Scenarios

- Assuming mass transfer resistance do not increase with solids formation-best case scenario analysis

Solvent Concentration (wt%)	Bed length (m)	Bed diameter (m)	No of parallel Beds
10	10	3	~182
10	15	3	~ 83
20	15	3.5	~ 67
30	15	3.5	~ 60
50	15	3.5	~ 55

- At 105°C, number of beds decreases to around 50
- Fixed bed may not be right configuration for the MECS under consideration

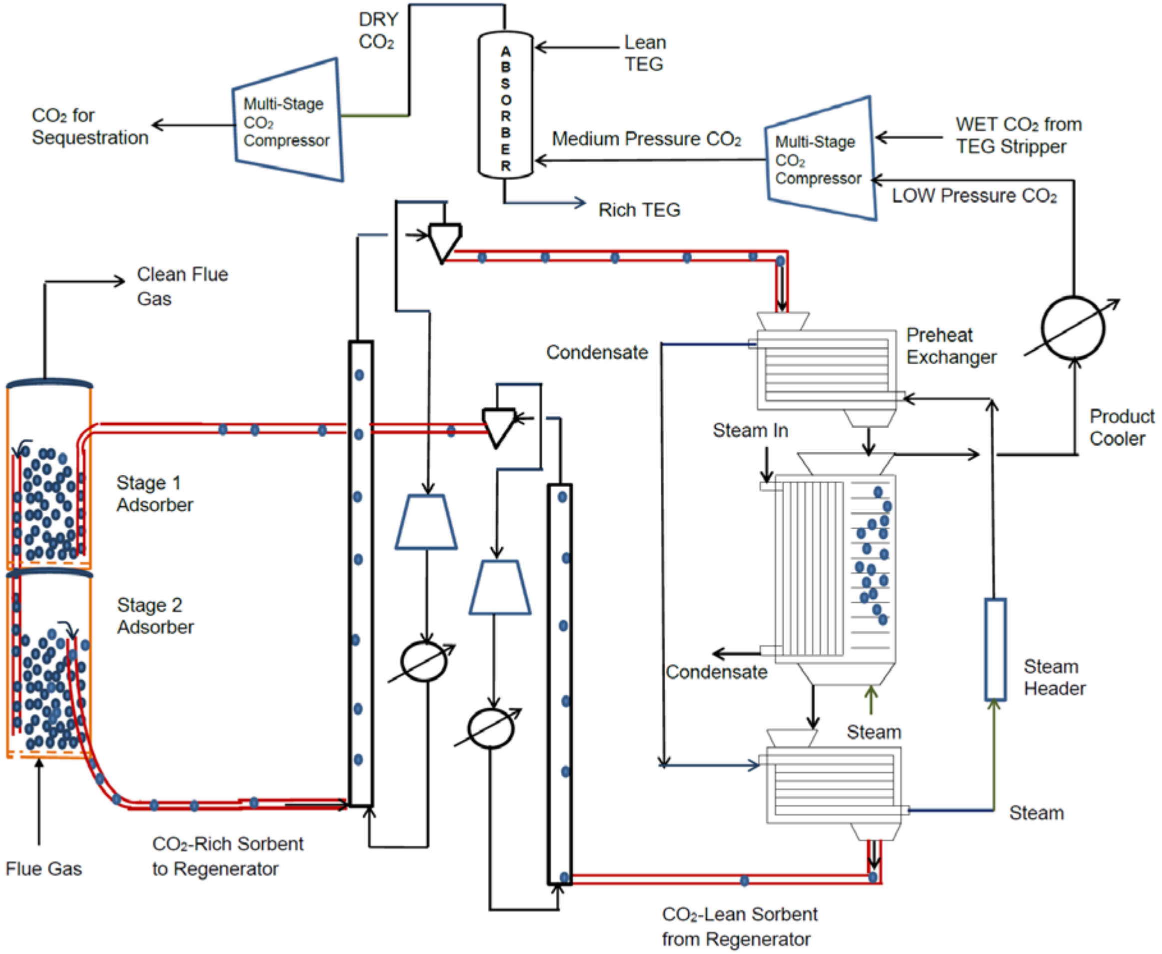
Conclusions and Future Work

- Based on our preliminary analysis, it appears that the fixed bed contactors are not suitable for the MECS system with carbonate solutions. Conclusions may change for other solvents and if a highly active catalyst is available.

- Investigate other types of contactors such as BFB, MB, CFB

- Synthesize optimal configuration and operating conditions

- Quantify uncertainty leveraging the CCSI toolset.



Objective of CFD Modeling for MECS

CCSI^2 Goal: ***Enable device-scale predictive capability for CO2 capture using MECS technology to accelerate development and deployment.***

FIG: MECS Fluidization Demonstration[1]

Design Considerations

Capsule size?

Shell Thickness?

Solvent type?

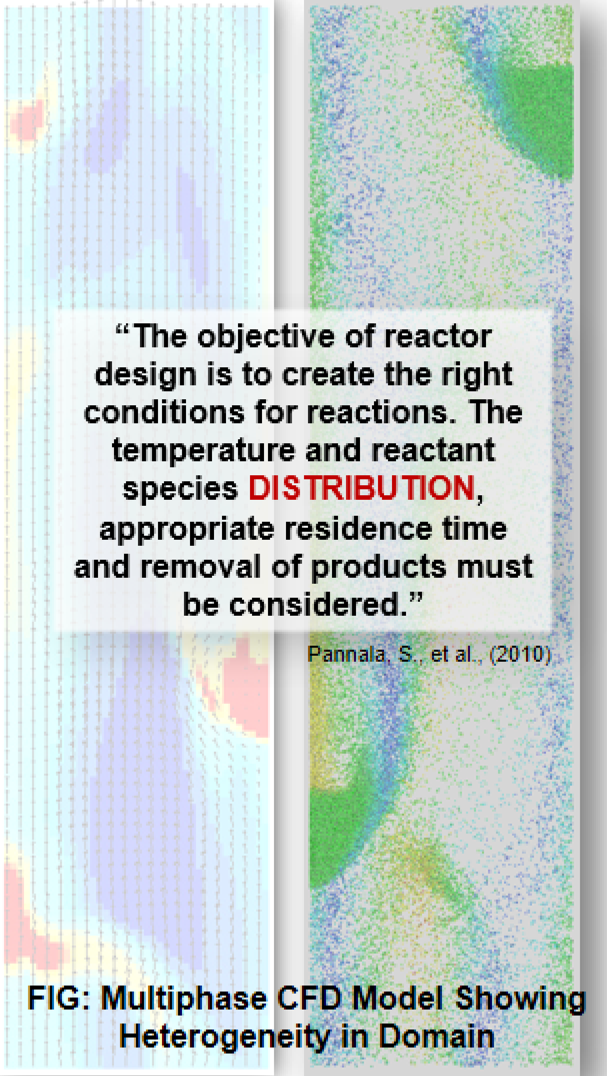
Circulating solids?

Fixed bed?

Fluidized bed?

Reactor Dimensions?

Cooling tubes?



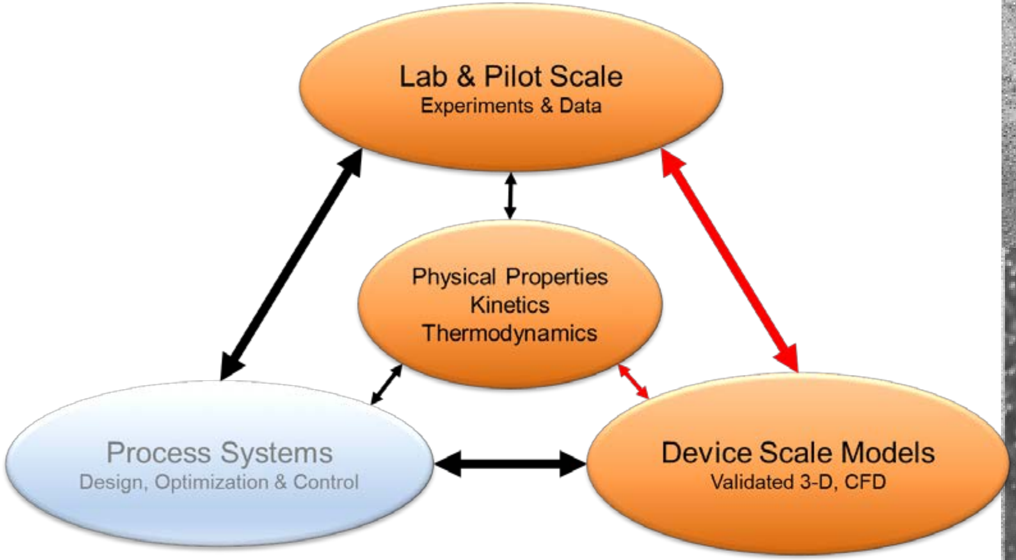
> **"The objective of reactor design is to create the right conditions for reactions. The temperature and reactant species DISTRIBUTION, appropriate residence time and removal of products must be considered."**

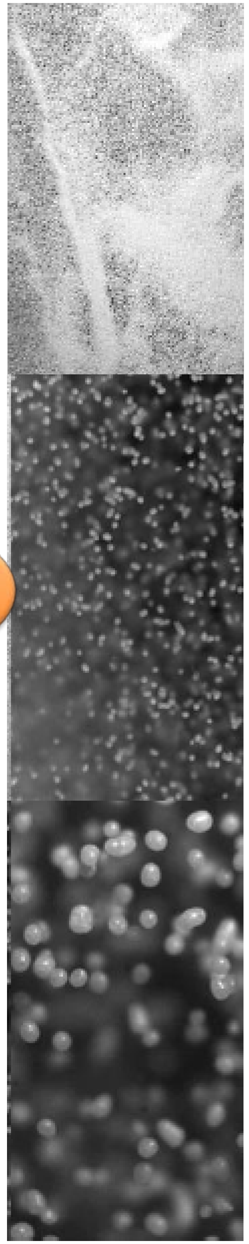
Pannala, S., et al., (2010)

FIG: Multiphase CFD Model Showing Heterogeneity in Domain

[1] Vericella et al., Nature Comms, v. 6, 2015;

Approach





IMG: Streamers, clusters, particles in CFB[2]

Requires

- **Integration of accurate physics and chemistry models**
- **A comprehensive understanding of all the significant competing and interacting mechanisms:**

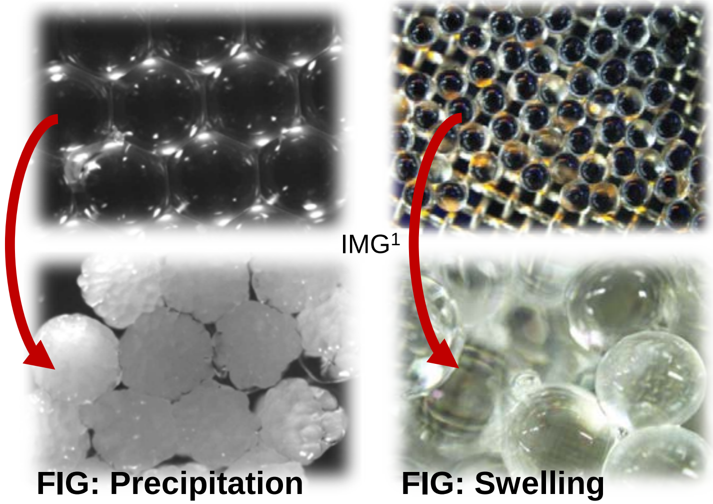
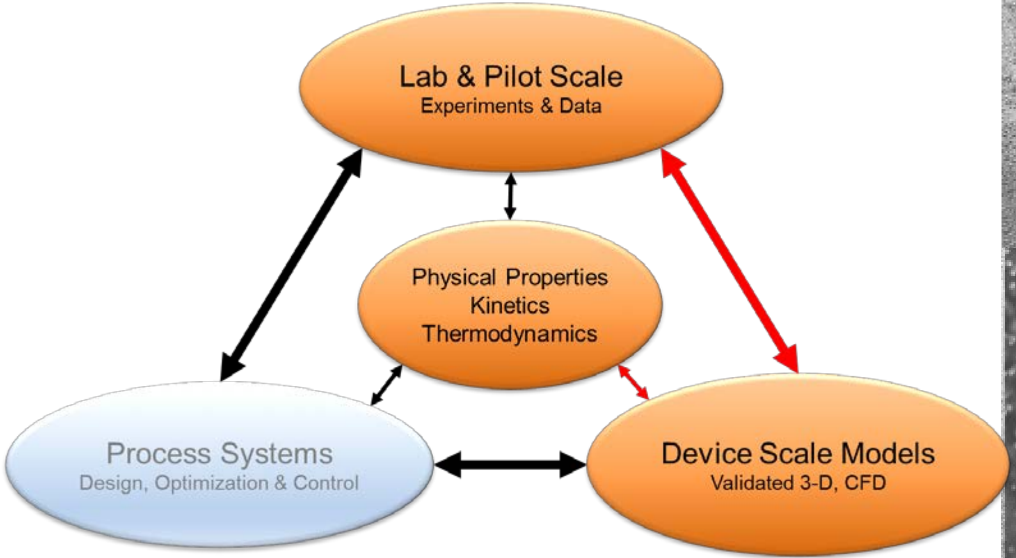


FIG: Precipitation **FIG: Swelling**

[1]Vericella et al., Nature Comms, v. 6, 2015;
Shaffer, F., et al., NETL MFSW, 2010.

Approach



Lab & Pilot Scale
Experiments & Data

Physical Properties
Kinetics
Thermodynamics

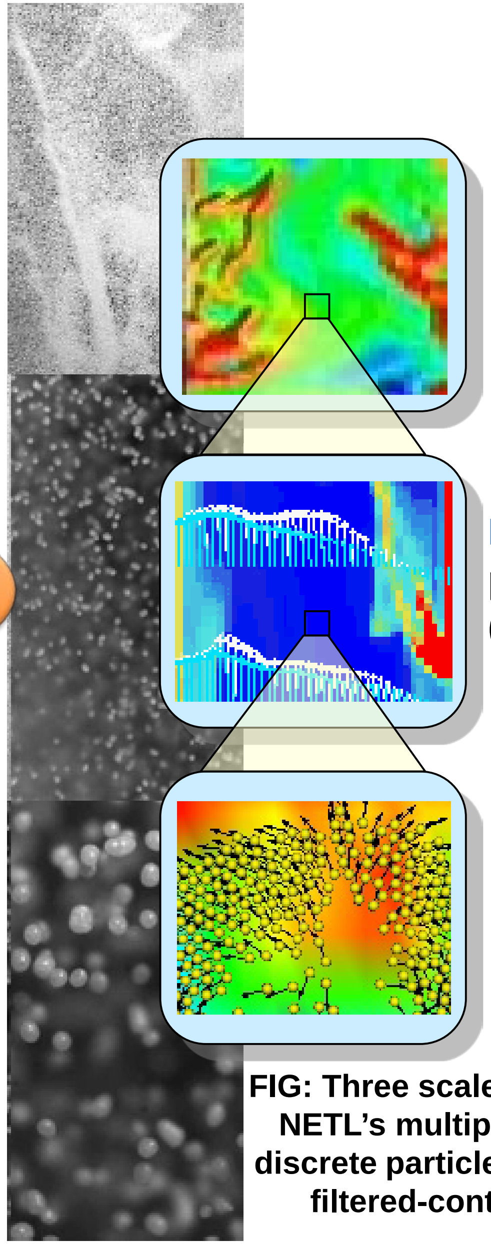
Process Systems
Design, Optimization & Control

Device Scale Models
Validated 3-D, CFD

Requires

- **Integration of accurate physics and chemistry models**
- **A comprehensive understanding of all the significant competing and interacting mechanisms:**

Model the effect of small-scale fluctuations that are too expensive to simulate directly



Device Scale
large flow structures in a CFB (~10's meters)

Meso Scale
particle clusters (~ mm's to meters)

Micro Scale
particles in gas (~100's microns)

FIG: Three scales of description in NETL's multiphase code MFIX: discrete particles to continuum to filtered-continuum models

IMG: Streamers, clusters, particles in CFB[2]

Model Challenges

- **Elastic, deformable shell**
- **Capsule size/density change**
- **Precipitation inside capsule**
- **Water loss/uptake during capture regeneration**
- **Hydrodynamics of gas-particle flow**
- **Disparity in scales**

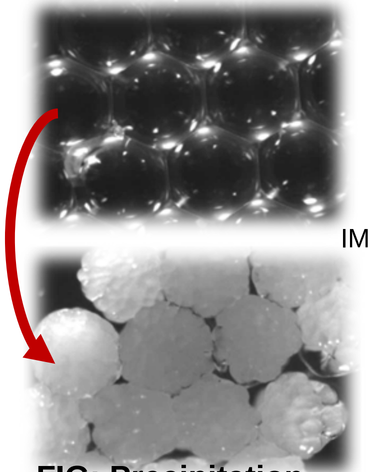


FIG: Precipitation

IMG[1]

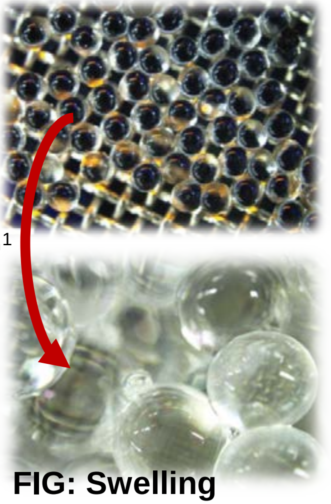


FIG: Swelling

[1]Vericella et al., Nature Comms, v. 6, 2015;
Shaffer, F., et al., NETL MFSW, 2010.

Accomplishments: Tool Development

✓ **Implemented chemistry, heat and mass transfer into a CFD-DEM simulation model/framework**

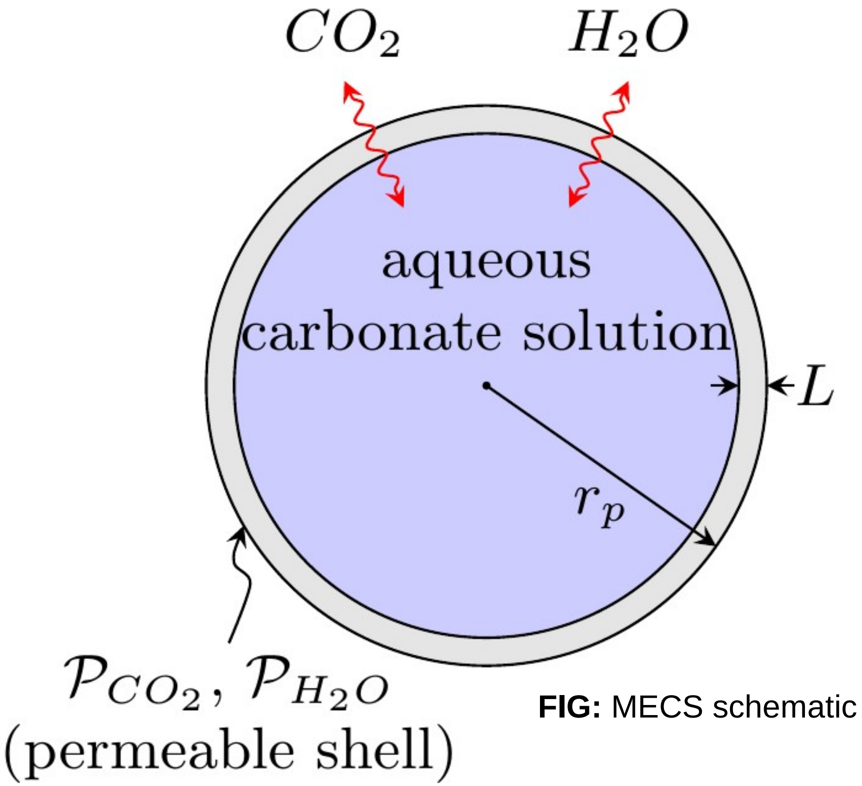


FIG: MECS schematic

Considerations

- Shell permeable to CO_2 and H_2O
- Solvent: aqueous Na_2CO_3
- Bulk liquid composition governed by 5 equilibrium reactions
- $NaHCO_3$ precipitate when solubility limit exceeded
- Capsule size/density changes
- Physical properties *mostly* available from literature

OH^-(aq)

$Na_2CO_3(s)$

$CO_3^{--}(aq)$

$H_3O^+(aq)$

$H_2O(l)$

$CO_2(aq)$

$HCO_3^-(aq)$

Na^+(aq)

$NaHCO_3(s)$

Species in chemical equilibrium in sodium carbonate solutions

$CO_2(g) \Leftrightarrow CO_2(aq)$ Chemically Enhanced Mass Transfer
$N_{CO_2} = k_{ov,CO_2} a_p (p_{CO_2} - H_{CO_2}[CO_2] - p_{shell})$
$\frac{1}{k_{ov,CO_2}} = \frac{1}{k_g} + \frac{1}{k_{shell}} + \frac{1}{k_l}$
$k_g = f(Re_p, Sc_p)$
$k_{shell} = \mathcal{P}_{shell}^{CO_2} / L_{shell}$
$k_l = k_l^0 E / H_{CO_2}$

$H_2O(g) \Leftrightarrow H_2O(l)$ Physical Mass Transfer
$N_{H_2O} = k_{ov,H_2O} a_p (p_{H_2O} - y_{H_2O}^{liq} p_{H_2O}^{sat}(T_p) - p_{shell})$
$\frac{1}{k_{ov,H_2O}} = \frac{1}{k_g} + \frac{1}{k_{shell}}$
$k_g = f(Re_p, Sc_p)$
$k_{shell} = \mathcal{P}_{shell}^{H_2O} / L_{shell}$

Accomplishments: Tool Development

✓ Developed a model to represent particle size and density changes

- At equilibrium the shell pressure (p_{shell}) balances mass transfer pressure gradient(s).[1]
- Direction of H_2O transfer depends on solution strength and gas relative humidity (RH).
- CO_2 absorption can also drive H_2O desorption.

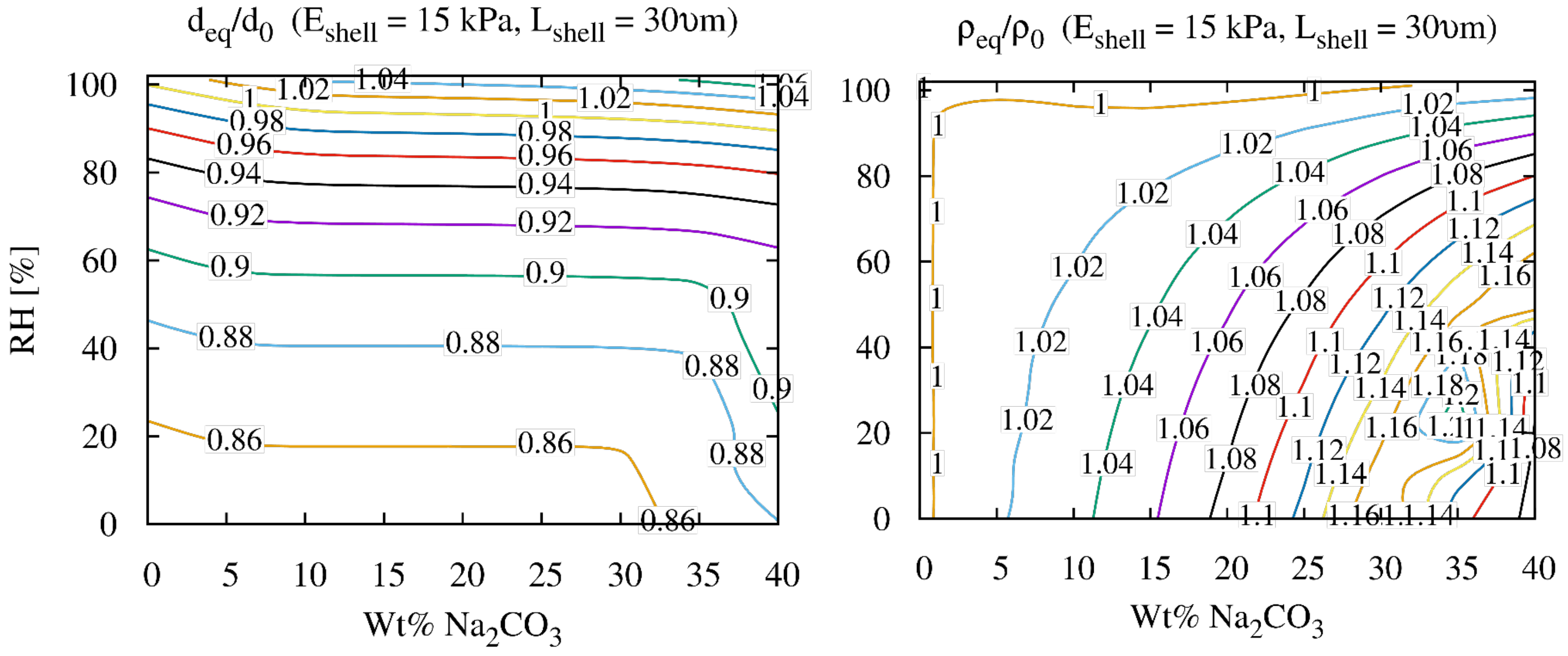


FIG: Predicted Eq. capsule size (left) and density (right) after exposure to flue gas at 1atm pressure and T=40C.

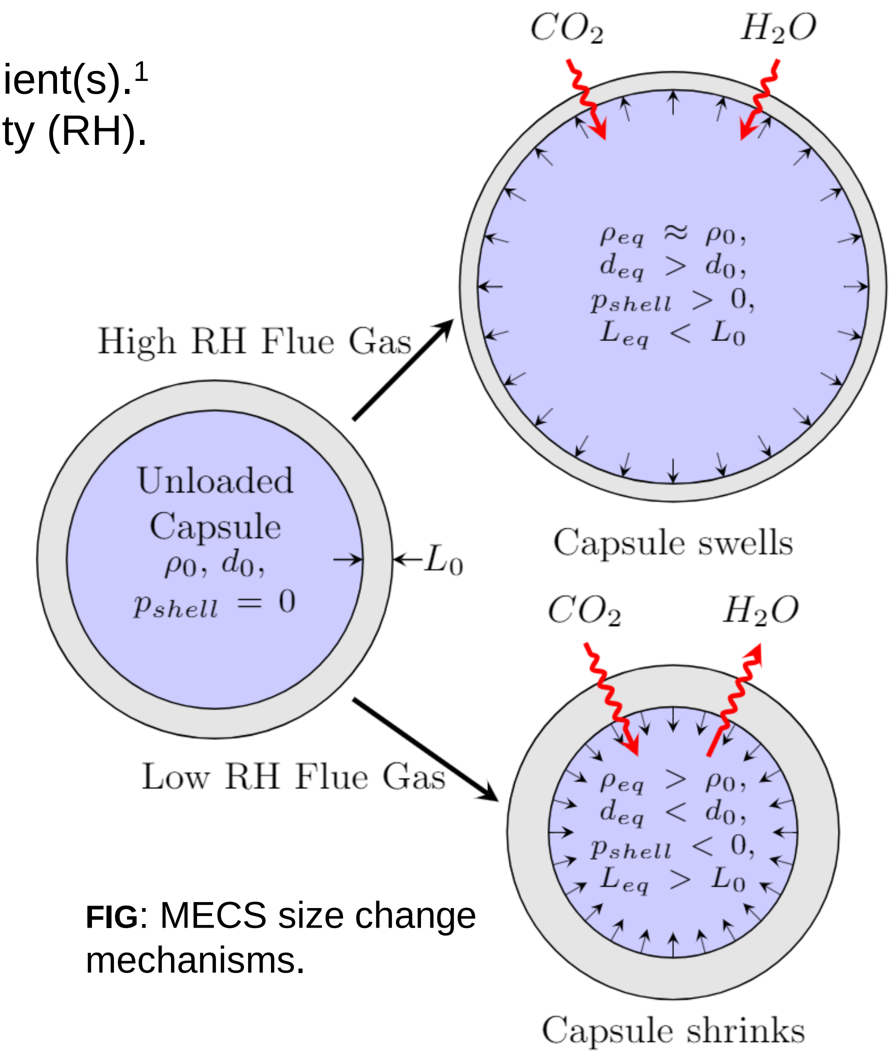


FIG: MECS size change mechanisms.

[1] Nabavi et al., Langmuir, v. 32, 2016;

Accomplishments: Validation

- ✓ Conducted limited validation studies on *chemistry* using literature data and LLNL experimental data

Onset of precipitation for loaded carbonate solution[2]

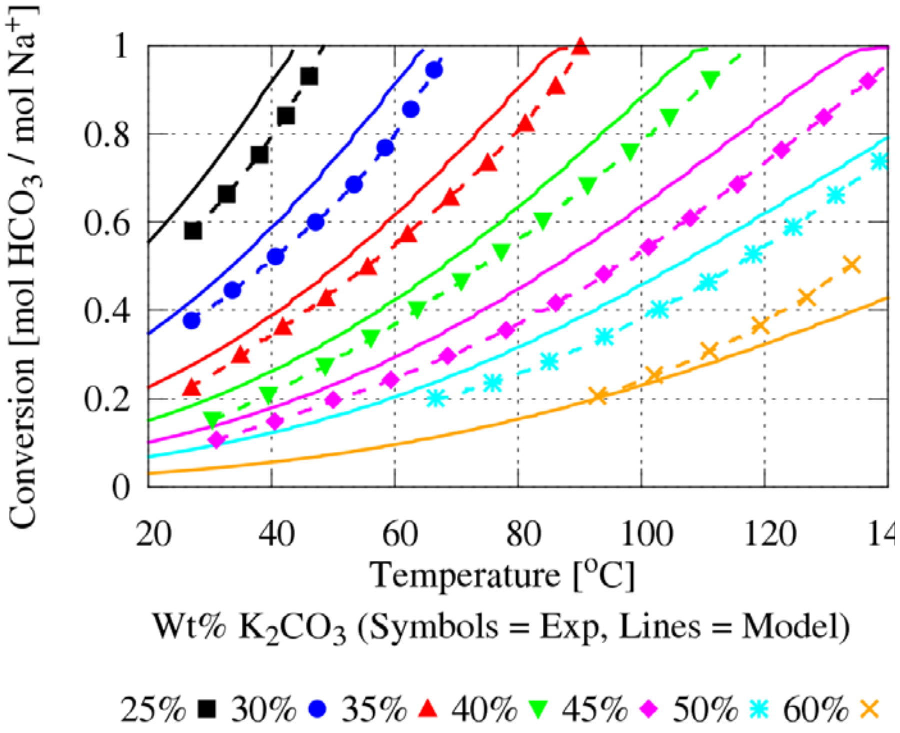


FIG: Threshold of potassium bicarbonate precipitation comparison with Kohl & Nielsen[2]

Vapor-liquid equilibrium (composition of loaded carbonate[1])

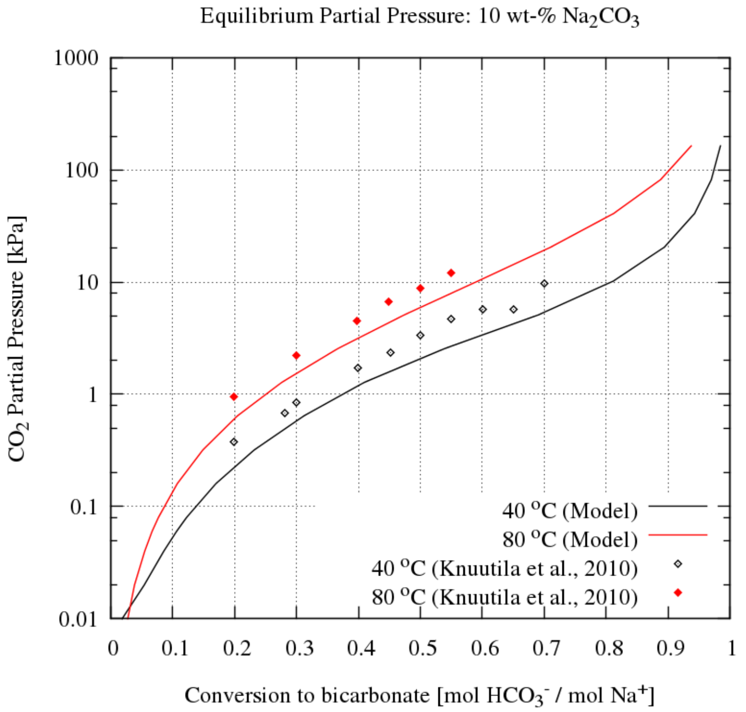
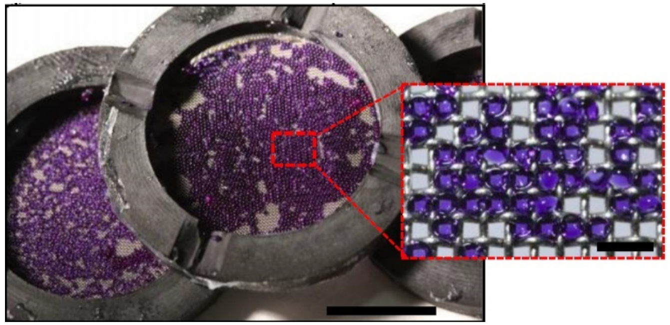


FIG: VLE comparison with Knuutila et al[1]

CO_2 absorption rate measurements[3]

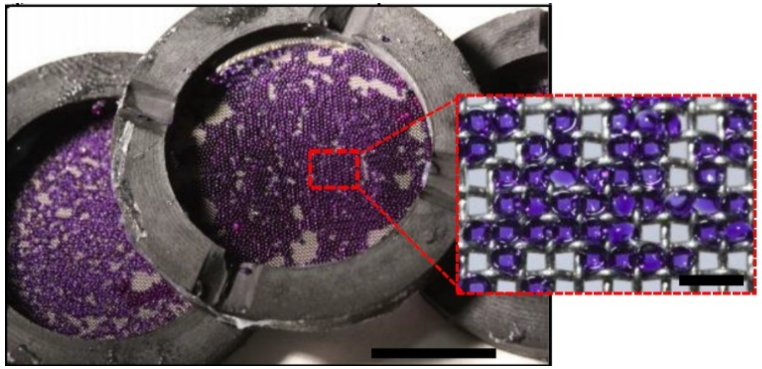


IMG: MECS in LLNL absorption chamber[4]

---

[1] Knuutila et al., CES, v. 65, 2010(a,b,c);
[2] Kohl and Nielsen, Gas Purification, 1997;
[3] LLNL Data, Private Communication, July 2017;
[4] Vericella et al., Nature Comms, v. 6, 2015

Accomplishments: Validation

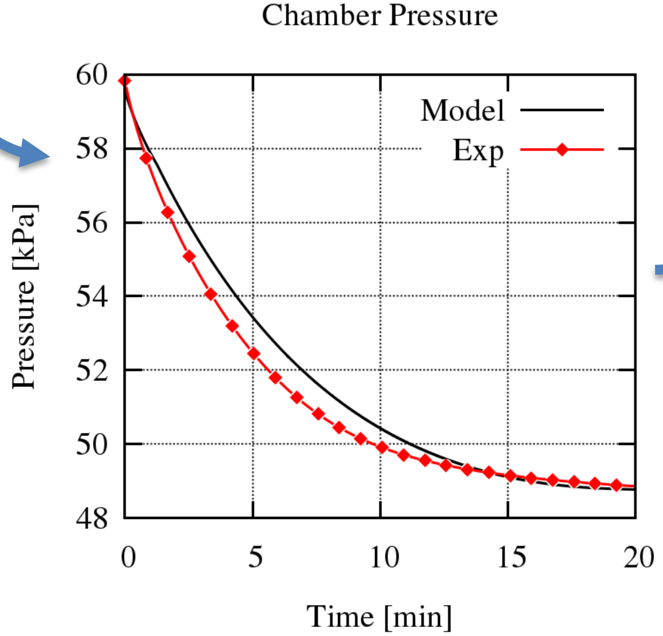


IMG: Vericella/LLNL[1,2]

1. LLNL absorption measurements

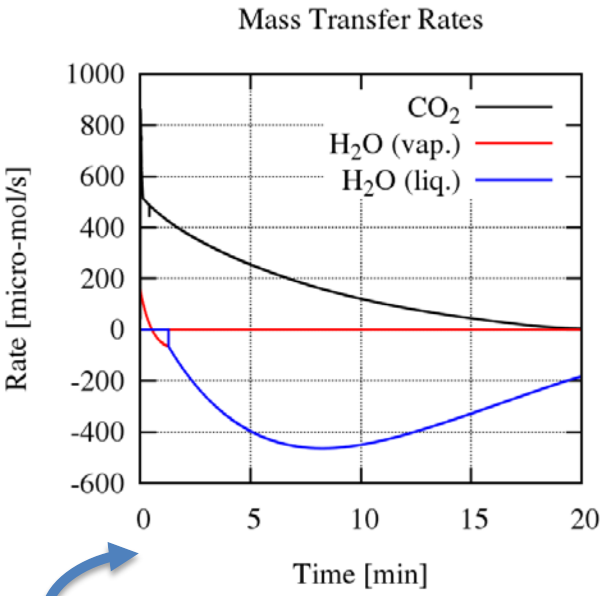
- MECS exposed to high CO_2 pressures in a sealed chamber.
- 17wt% Na_2CO_3
- $d_p = 480\mu m$
- $L_{shell} = 30\mu m$
- 100% RH in chamber

2. Tune Enhancement Factor*

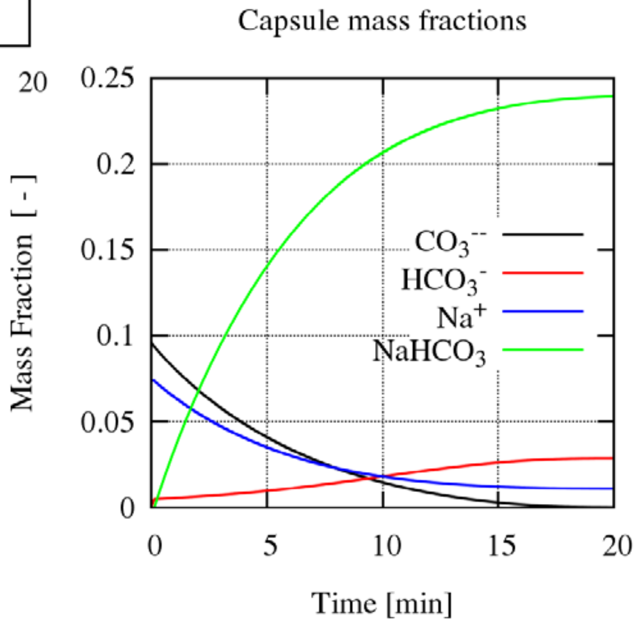


*E is tuned by adjusting k_{OH^-} and $\mathcal{D}_{CO_2}$

3. Use calibrated model to infer MECS behavior



- $NaHCO_3$ precipitates
- p_{shell} buildup as CO_2 is absorbed forces H_2O out.
- H_2O leaves first as vapor, then liquid as gas become saturated.

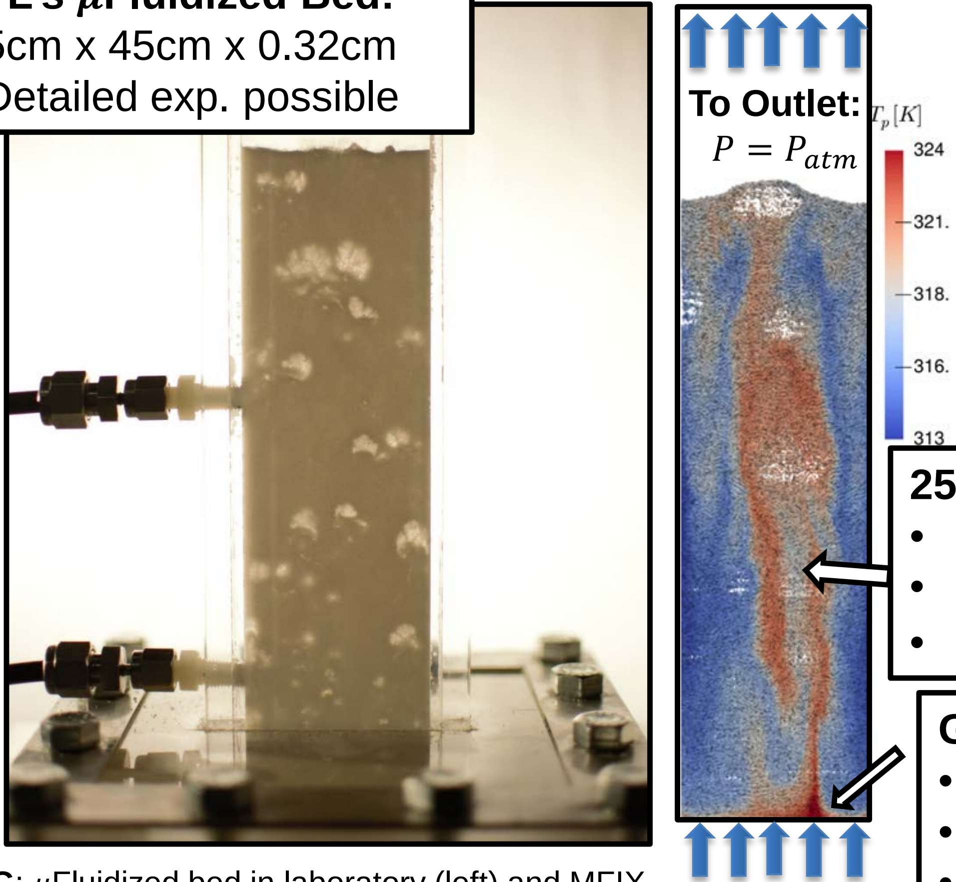


[1] LLNL Data, Private Communication, July 2017;
[2] Vericella et al., Nature Comms, v. 6, 2015

Bench Scale Simulation of MECS Carbon Capture

Bubbling fluidization in NETL's μFluidized Bed

NETL's μFluidized Bed:
- 5cm x 45cm x 0.32cm
- Detailed exp. possible



To Outlet:
$P = P_{atm}$

250,000 MECS:
- $17\ wt\%\ Na_2CO_3$
- $d_{po} = 480\mu m$
- $L_0 = 15\mu m$

Gas Inlet:
- T=40C
- 12% CO_2
- 20% RH
- $U_g = 1.3U_{mf}$

FIG: μFluidized bed in laboratory (left) and MFIX-DEM simulation setup with MECS particles (right) colored by temperature.

CFD Setup:

- Pseudo-3D domain: $L_z = 6.67d_p$
- 32x288x1 Grid $\Rightarrow \Delta_x, \Delta_y \approx 3.2d_p$
- Hertzian contact model for soft silicon capsules:
  - $E = 15GPa, \nu = 0.5$
  - $e_n, e_t = 0.9$
- Isothermal walls (T=313K)
- Enhanced kinetics (100 x k_{OH})
- $\Delta t_p \approx 3x10^{-6}s,\ \ \Delta t_f \approx 1x10^{-4}s$

FIG: Simulated bubbling behavior

Bench Scale Simulation of MECS Carbon Capture

- 75% capture efficiency in bubbling regime with a bed height of 15cm using enhanced kinetics $(100\ x\ k_{OH})$.
- Interesting effects during CO_2 absorption:
  - Rapid H_2O loss that humidifies the gas.
  - $NaHCO_3$ precipitation is very exothermic.
  - H_2O condenses as gas cools above the bed region.

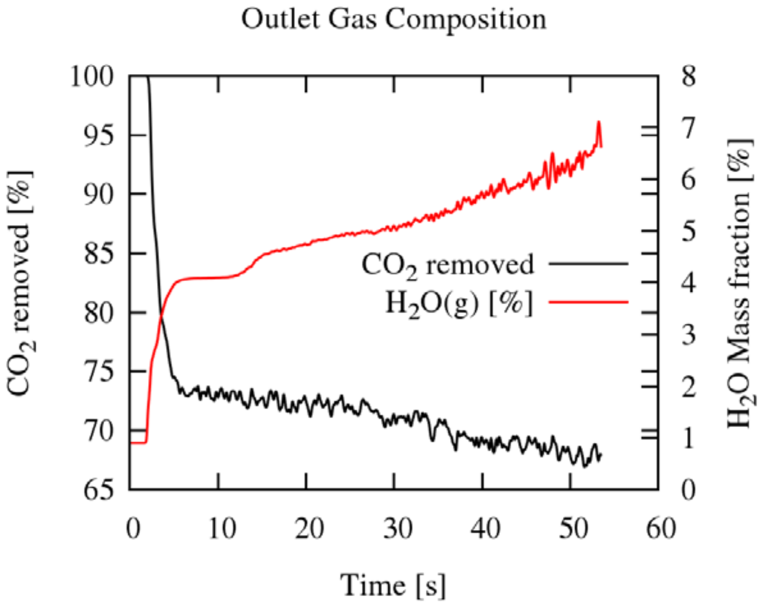


FIG: Time evolution of outlet gas composition

H_2O Vapor

Condensed H_2O

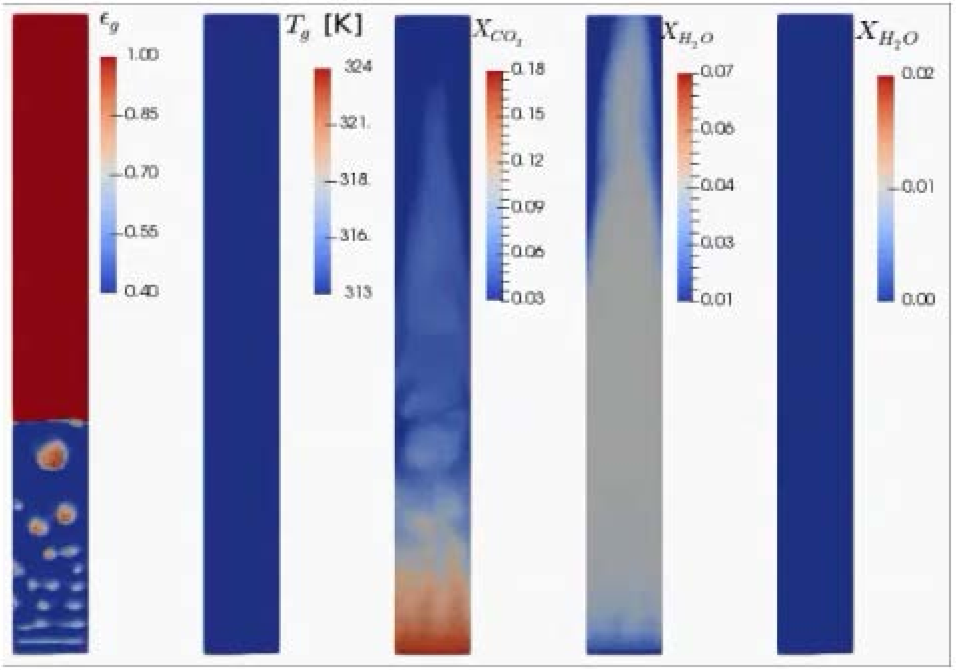


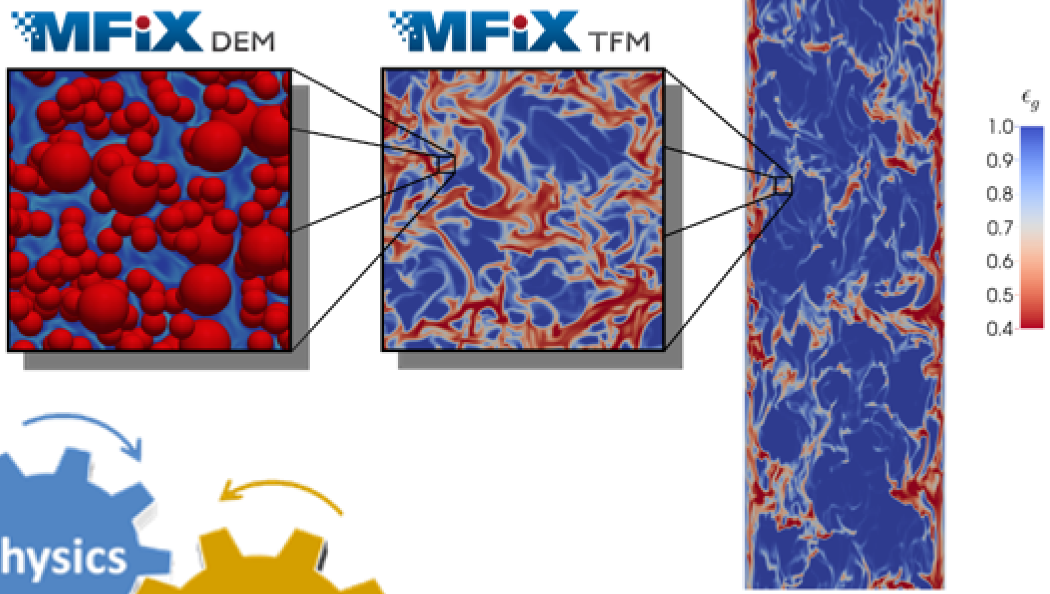
FIG: From left to right: gas vol. fraction, gas temp., CO_2 mass fraction, H_2O vapor mass fraction, condensed H_2O mass fraction.

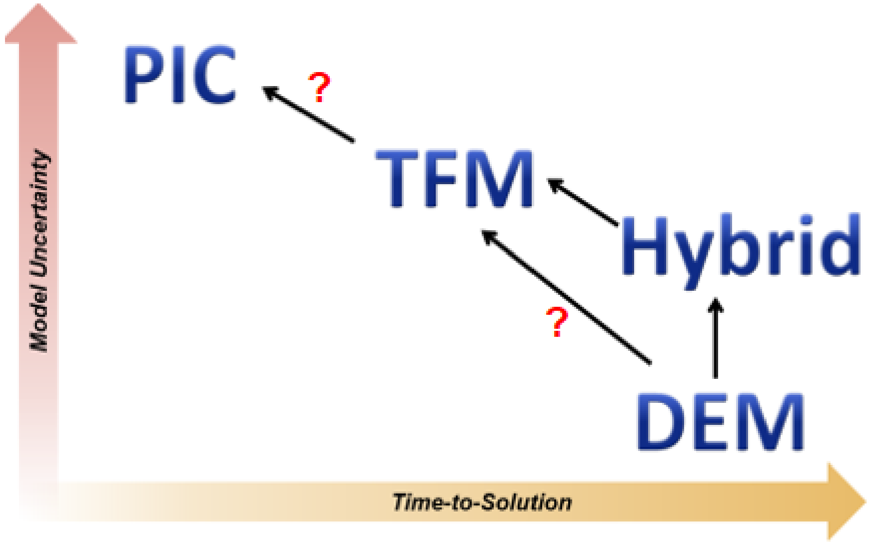
Tools and Capabilities

- ✓ Incorporated chemistry, heat and mass transfer into CFD framework for base case solvent (carbonate)
- ✓ Incorporated size and density changes into CFD framework
- ✓ Validated model with literature data nd new data from LLNL
- ⚠ Perform simulations of MECS technology in different reactor configurations

> ***"The open-source MFIX code … is technically mature to predict well fluidization phenomena based on the Eulerian-Eulerian method."***

Herzog et al. (2012) Comput. Chem. Eng. v39, p46





PIC

?

TFM

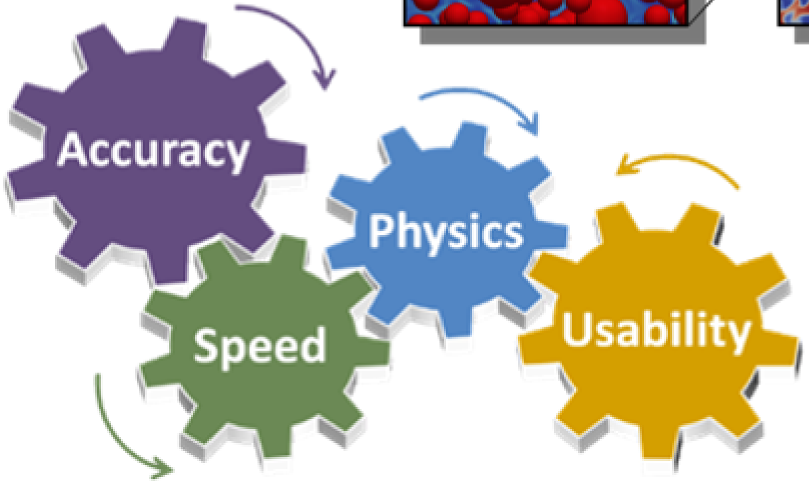
Hybrid

?

DEM

Model Uncertainty

Time-to-Solution



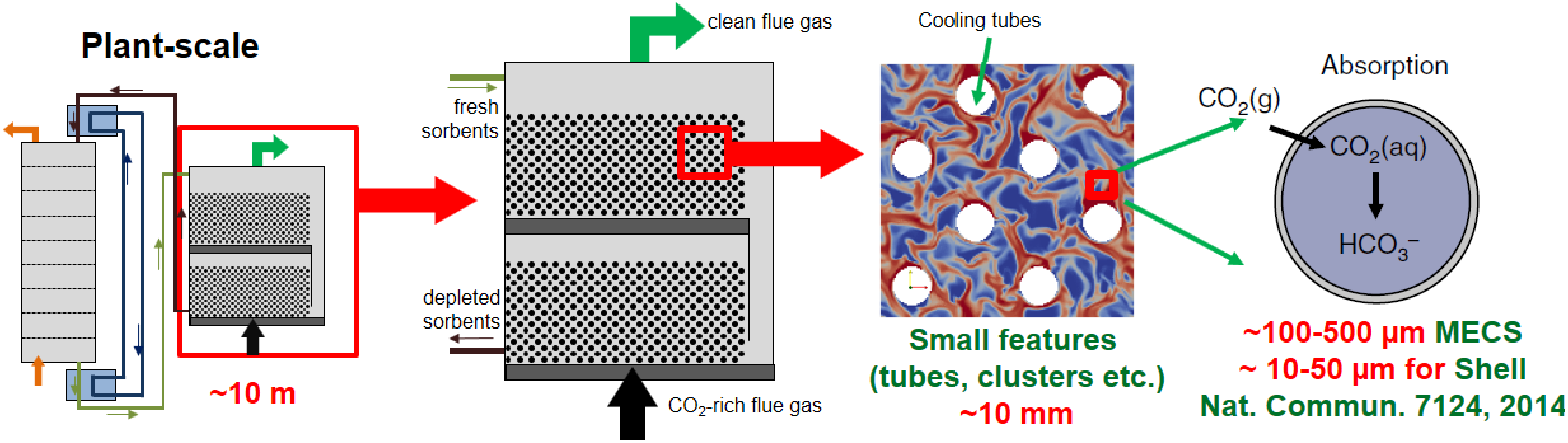
Accuracy

Physics

Speed

Usability

Objective & Challenges for MECS at Device-Scale



~10 m

Small features (tubes, clusters etc.)
~10 mm

~100-500 µm MECS
~ 10-50 µm for Shell
Nat. Commun. 7124, 2014

Objectives

- ☐ Development of Framework for Device Scale MECS
- ☐ Understanding MECS behavior in absorber
- ☐ Virtual experiment with different operating conditions
  - ➢ Effect of MECS particle size
  - ➢ Effect of gas flow rate

Challenges

- ☐ Multicale (scale disparity ~$10^{4\sim5}$)
  - ▪ Tubes and particles
- ☐ Multiphysics+chemical absorption /desorption
- ☐ Lack of device-scale design for MECS
- ☐ Particle size/density variation with loading

CFD Model Geometry and Dimension

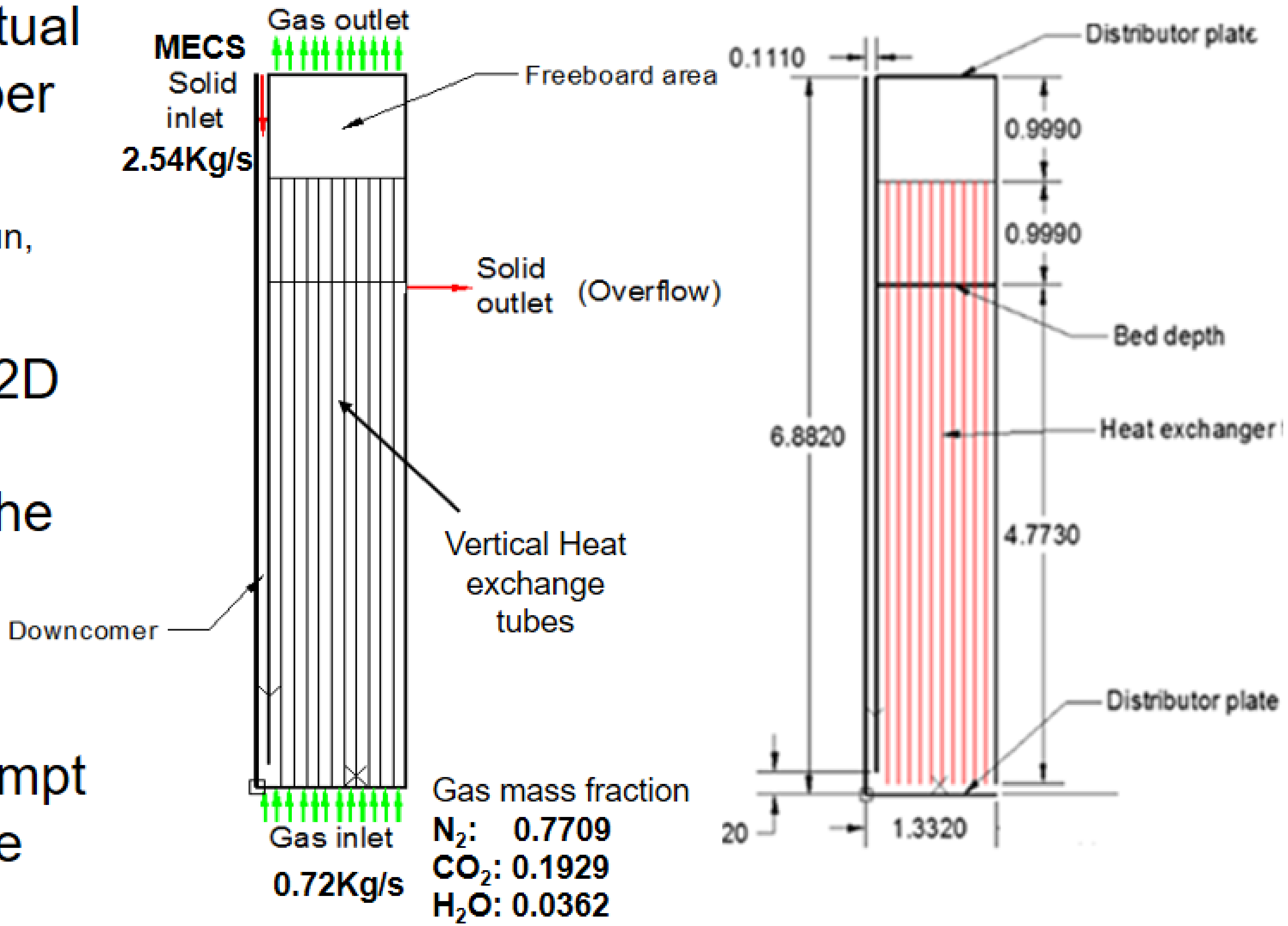
- Using 1MW pilot scale conceptual design for fluidized bed absorber

Zhijie Xu, Canhai Lai, Peter William Marcy, Jean-François Dietiker, Tingwen Li, Avik Sarkar, Xin Sun, ***Powder Tech. 312 (2017) 58***

- Originally designed for NETL32D

- Using the same chemistry as the bench-scale discrete particle model for MECS

- Though preliminary, a first attempt to model MECS at device-scale fluidized bed (CCSI^2 value)



Model geometry and dimension (m)

Properties for MECS

Physical Parameters	MECS
Particle size	120, 240, 360 and 480 μm
Particle density	1000 kg/m3
Shell thickness	7.5, 15, 22.5 and 30 μm
Shell permeability (Highly permeable)	10^{-12} mol / (m s pa) (10^{-14} ~10^{-13} for polymeric membranes)
Minimum fluidization velocity (u_{mf})	0.0122~0.1952 m/s
Solvent: Na_2CO_3	13 wt%

MECS: CO_2/Na_2CO_3

$$CO_2(l) + 2H_2O(l) \overset{K_1}{\Leftrightarrow} HCO_3^- + H_3O^+$$

$$HCO_3^- + H_2O \overset{K_2}{\Leftrightarrow} CO_3^{2-} + H_3O^+$$

$$2H_2O(l) \overset{K_3}{\Leftrightarrow} + OH^- + H_3O^+$$

$$Na_2CO_3(s) \overset{K_4}{\Leftrightarrow} 2Na^+ + CO_3^{2-}$$

$$NaHCO_3(s) \overset{K_5}{\Leftrightarrow} Na^+ + HCO_3$$

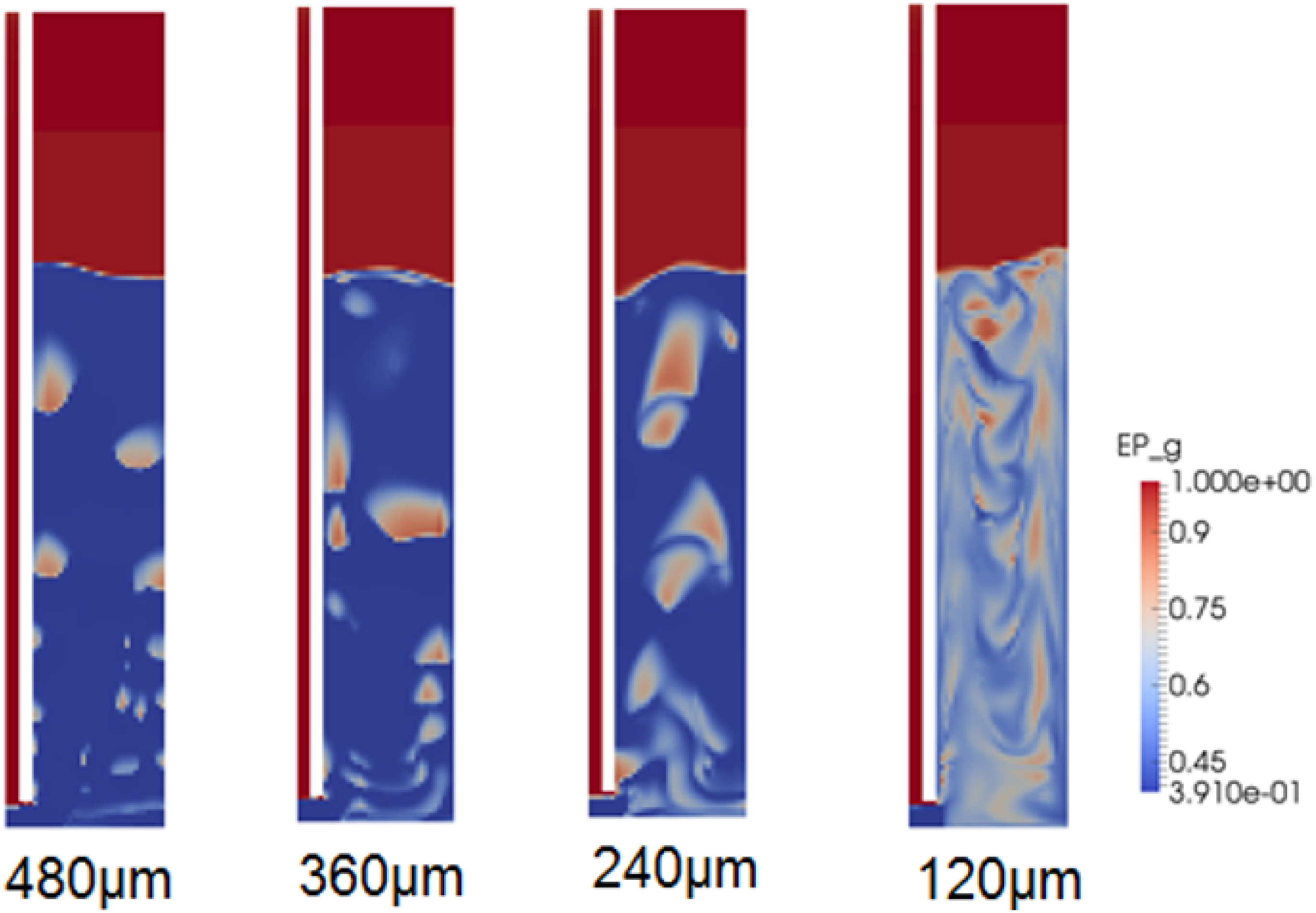
$$H_2O(g) \overset{K_6}{\Leftrightarrow} H_2O(l)$$

$$CO_2(g) \overset{K_7}{\Leftrightarrow} CO_2(l)$$

$$\boxed{u_{mf} = \frac{d_s^2(\rho_s - \rho_g)g{\varepsilon_{mf}}^3}{150\mu_g(1 - \varepsilon_{mf})}}$$

Hydrodynamics Only

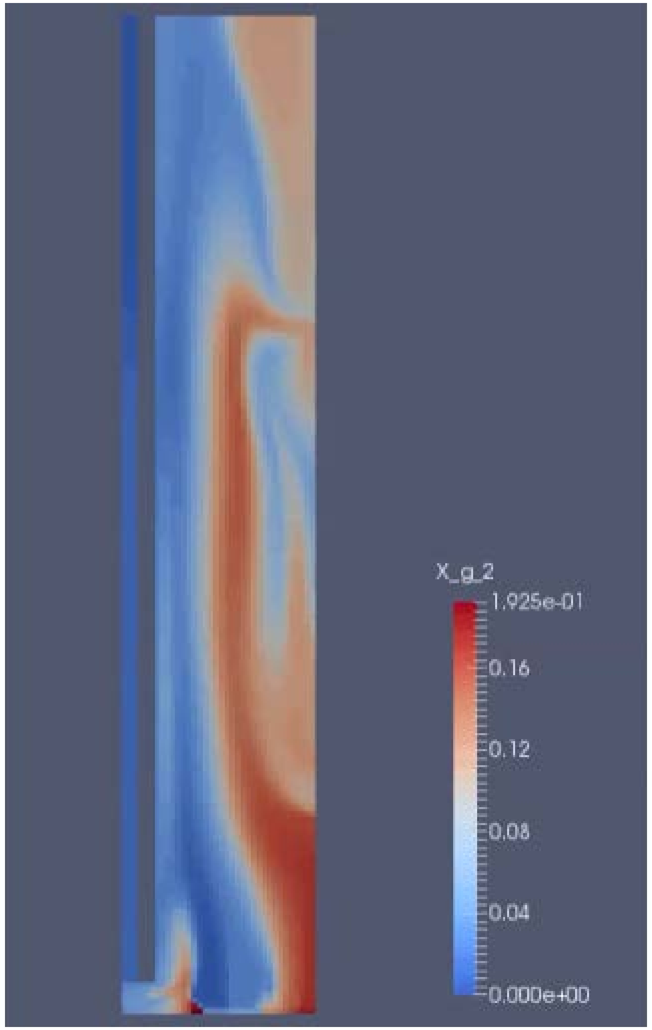
Gas phase volume fraction for gas flow 0.72kg/s



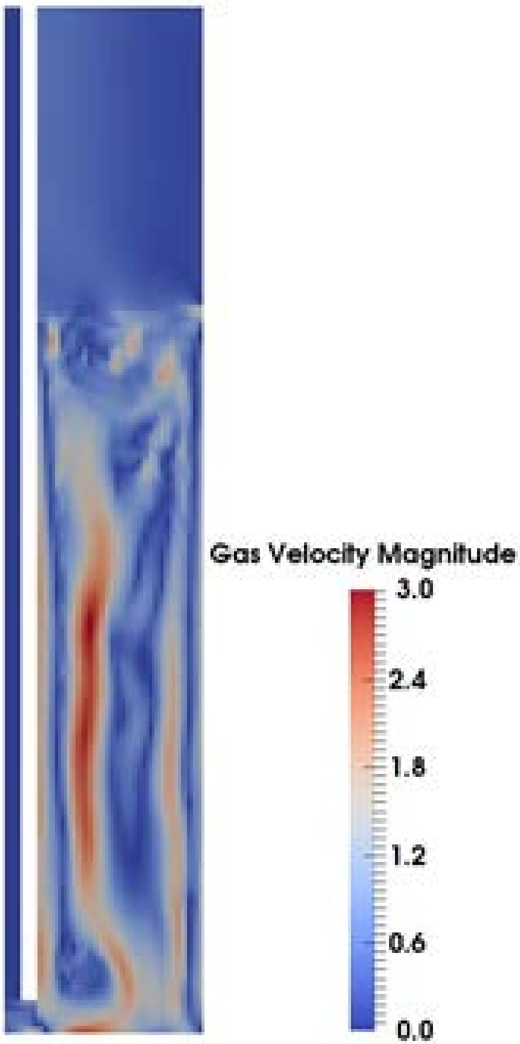
Particle size decrease

Hydrodynamics + Chemical Absorption

CO2 Mass Fraction



Gas Velocity



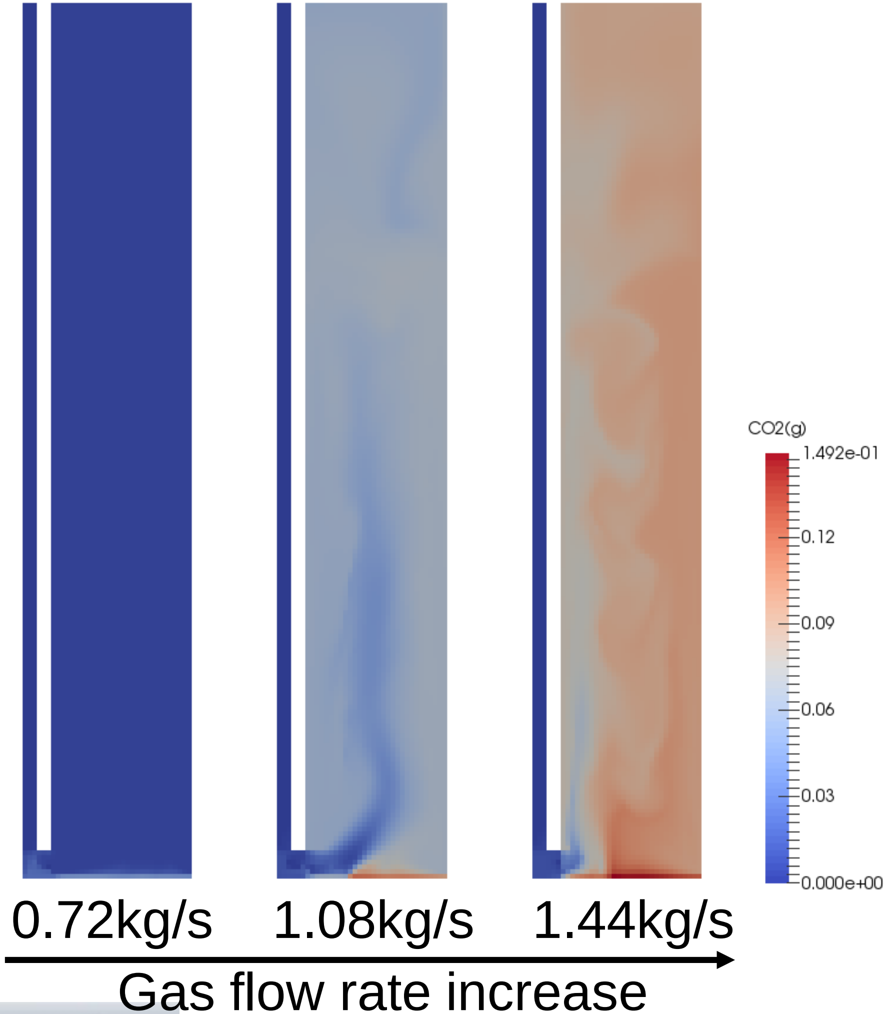
Particle size: 120 µm
Gas flow rate: 0.72kg/s
CO_2 at gas inlet: 19%

CFD value: effect of tubes (size, spacing, orientation…)

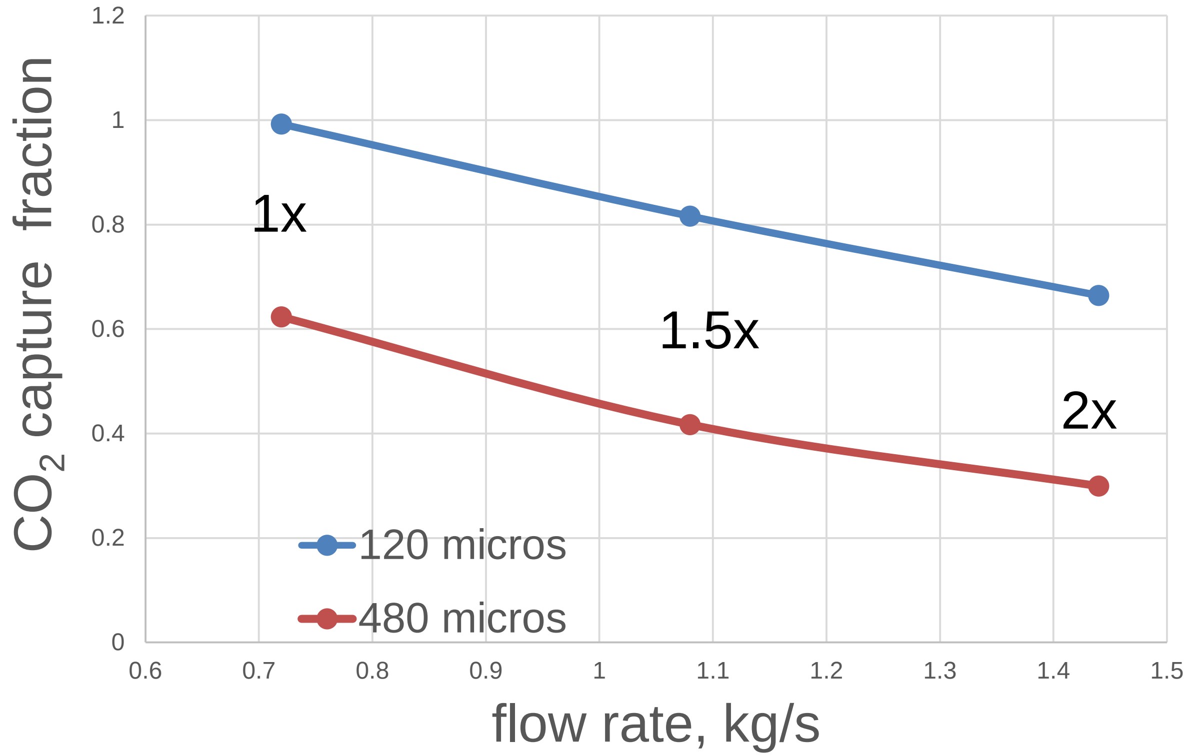
- Vertical cooling tubes affects hydrodynamics /absorption
- Gas forms fast flow channels along tubes: channeling

Chemical Reactions + Hydrodynamics cont’d

Distribution of CO_2 Mass Fraction in absorber for 120 µm MECS



- Baseline gas flow rate: 0.72kg/s
- MECS particle sizes: 120 µm and 480µm
- Capture fraction decreases with gas flow rate
- Absorption better with smaller particle size



Conclusions

- ❑ Models built for MECS particles in a conceptual absorber
  - 1MW conceptual design of absorber for MECS
  - Filtered method to resolve large scale disparity for tubes
  - Fully coupled chemistry module for absorption/desorption
  - Limitations and future work:

    size/density variation, heat transfer, heat of reaction, drag models ……

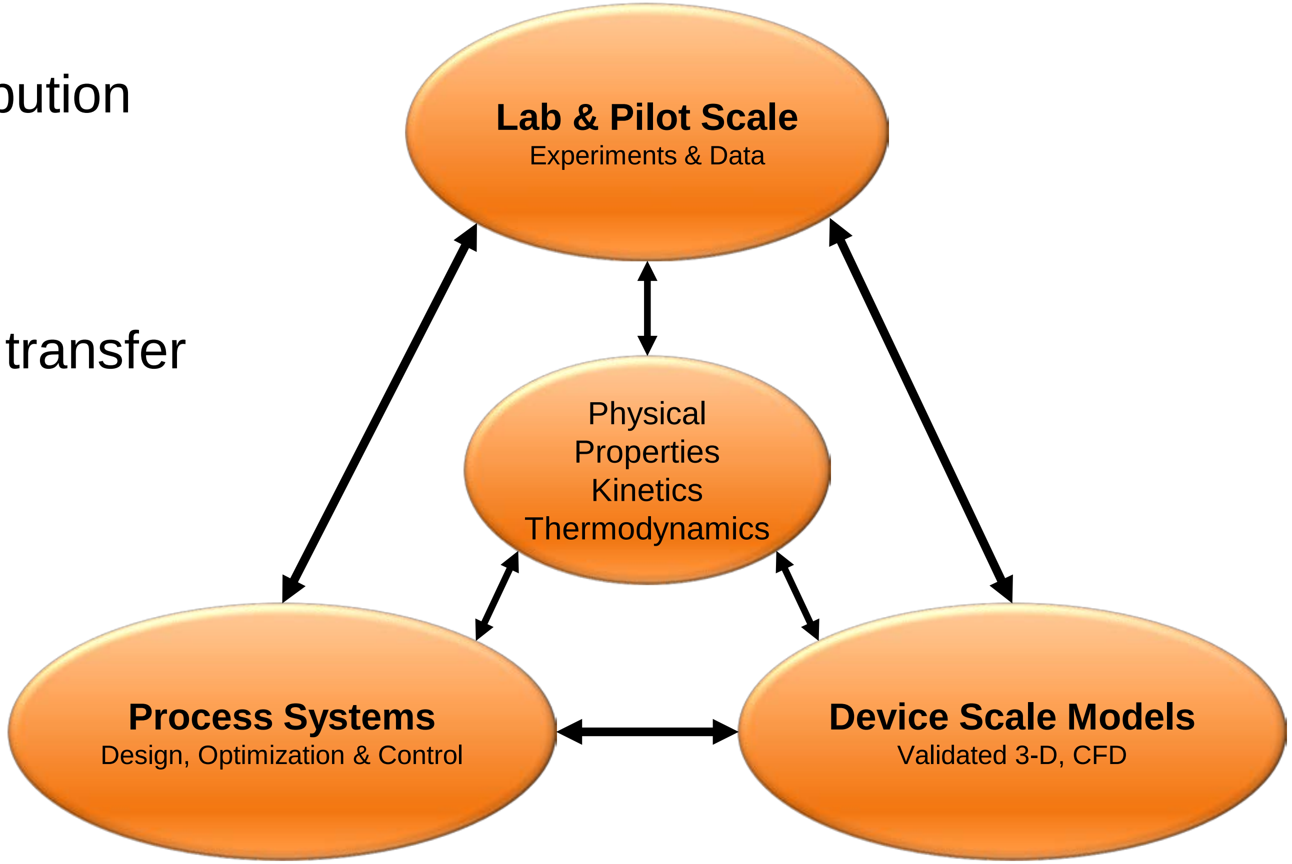
- ❑ Virtual experiment for MECS
  - Preliminary results on effects of MECS size and gas flow rate
  - CO_2 absorption decreases with gas flow rate
  - Smaller MECS particle might lead to a better performance

CCSI^2 Value

☐ Enabling predictive capability for MECS based CO_2 capture

- Overall CO_2 capture depends
  - Particle fluidization and spatially distribution
  - CO2 partial pressure
  - Temperature
  - Physical Properties: shell & solvent
  - Reaction parameters – kinetics, mass transfer

☐ Different tiers of modeling used together to advance/screen new technology for CO2 capture



Lab & Pilot Scale
Experiments & Data

Physical
Properties
Kinetics
Thermodynamics

Process Systems
Design, Optimization & Control

Device Scale Models
Validated 3-D, CFD

CCSI^2

Carbon Capture Simulation for Industry Impact

For more information

https://www.acceleratecarboncapture.org/

Debangsu Bhattacharyya, Ph.D.
debangsu.bhattacharyya@mail.wvu.edu

Janine Carney, Ph.D.
Janine.Carney@NETL.DOE.GOV

Zhijie (Jay) Xu, Ph.D.
Zhijie.Xu@pnnl.gov