CCSI^2

Carbon Capture Simulation for Industry Impact

Multiscale Modeling and Simulation of Micro-Encapsulated Carbon Sorbent (MECS) Technology

Debangsu Bhattacharyya[1], Goutham Kotamreddy[1], Ryan Hughes[1]
Janine Carney[2], Justin Finn[2,3]
Zhijie (Jay) Xu[4] , Chao Wang[4]

[1]West Virginia University
[2]NETL
[3]AECOM
[4]PNNL

Outline

- What is MECS and what is CCSI^2 trying to do for improving the understanding and economics of this technology?
- Process Modeling of MECS
- Bench-Scale CFD Model for MECS
- Device-Scale Model for MECS

MECS Technology

- Being developed by LLNL
- Shell
  - -made of silicone

- Core fluid/material
  - -contains solvent (encapsulated by the shell)
  - -solvent can be highly viscous and/or form solid precipitate upon CO_2 absorption

- Typical diameters 100 µm – 600 µm

Currently studying: Sodium carbonate as the encapsulated solvent

OH^-(aq)

$Na_2CO_3(s)$

$CO_3^{--}(aq)$

$H_3O^+(aq)$

$H_2O(l)$

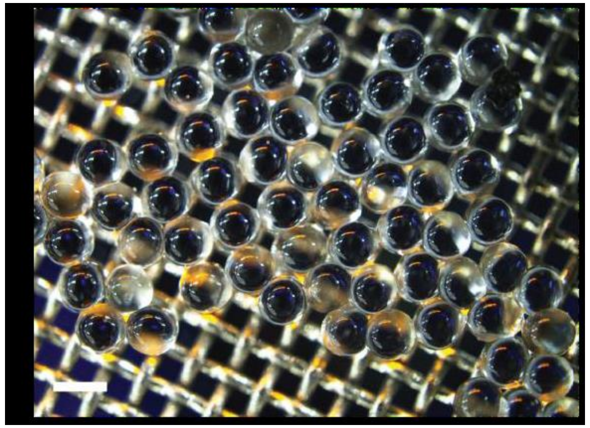
$CO_2(aq)$

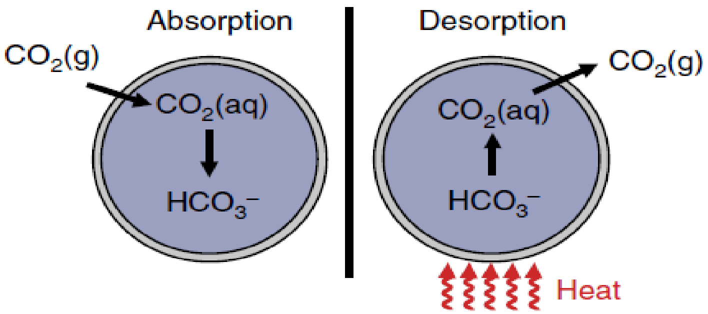
$HCO_3^-(aq)$

Na^+(aq)

$NaHCO_3(s)$

Species in chemical equilibrium in sodium carbonate solutions





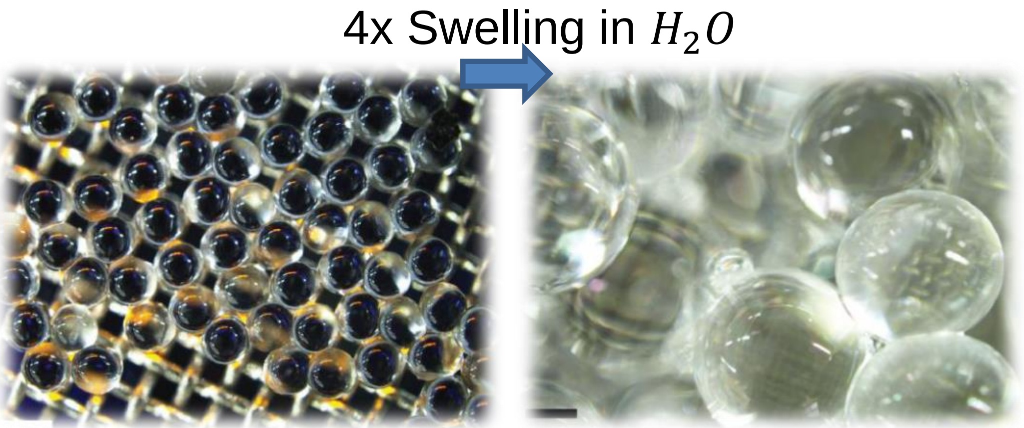
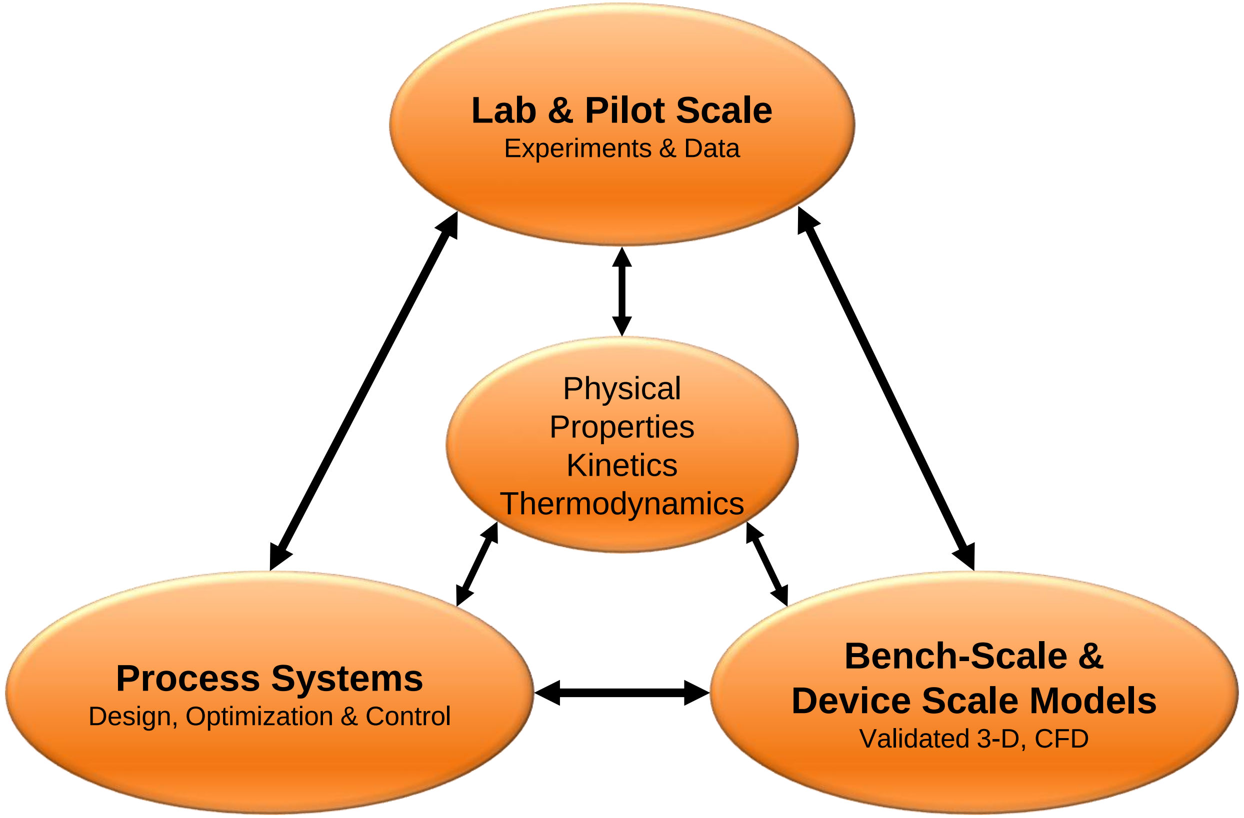


FIG: Swelling of MECS capsules in water[1]

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

Challenges of the MECS System where Models can Help



Lab & Pilot Scale
Experiments & Data

Physical
Properties
Kinetics
Thermodynamics

Process Systems
Design, Optimization & Control

Bench-Scale &
Device Scale Models
Validated 3-D, CFD

- Elastic, deformable shell
- Capsule size/density change
- Precipitation inside capsule
- Water loss/uptake during capture and regeneration
- State of the solvent inside the capsule in a location at a given instant is practically impossible to measure
- Hydrodynamics of gas-particle flow
- Disparity in scales
- Optimal selection and design of the contactor

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Reactions

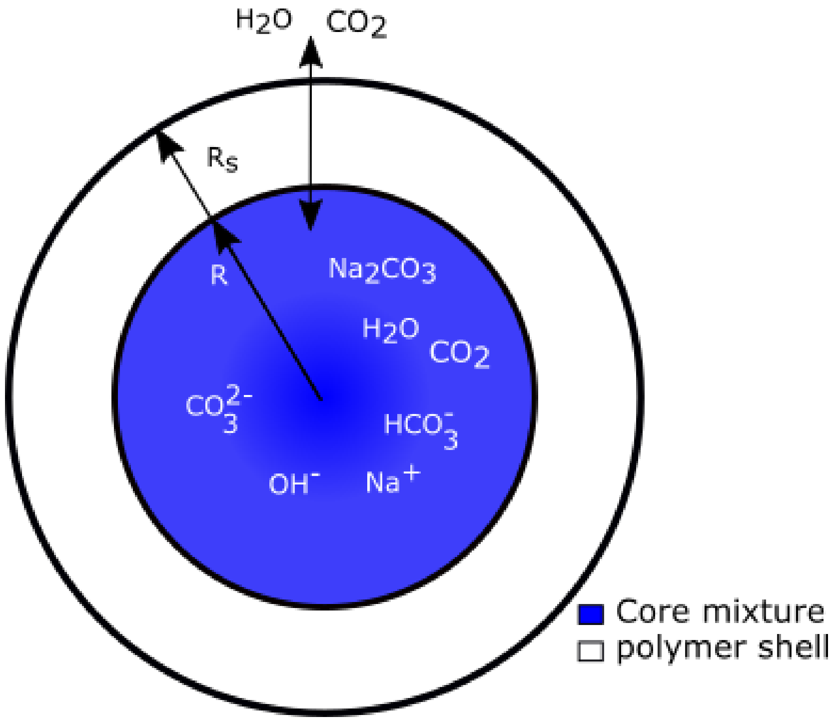
- Kinetically controlled:

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

- Equilibrium Limited:

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

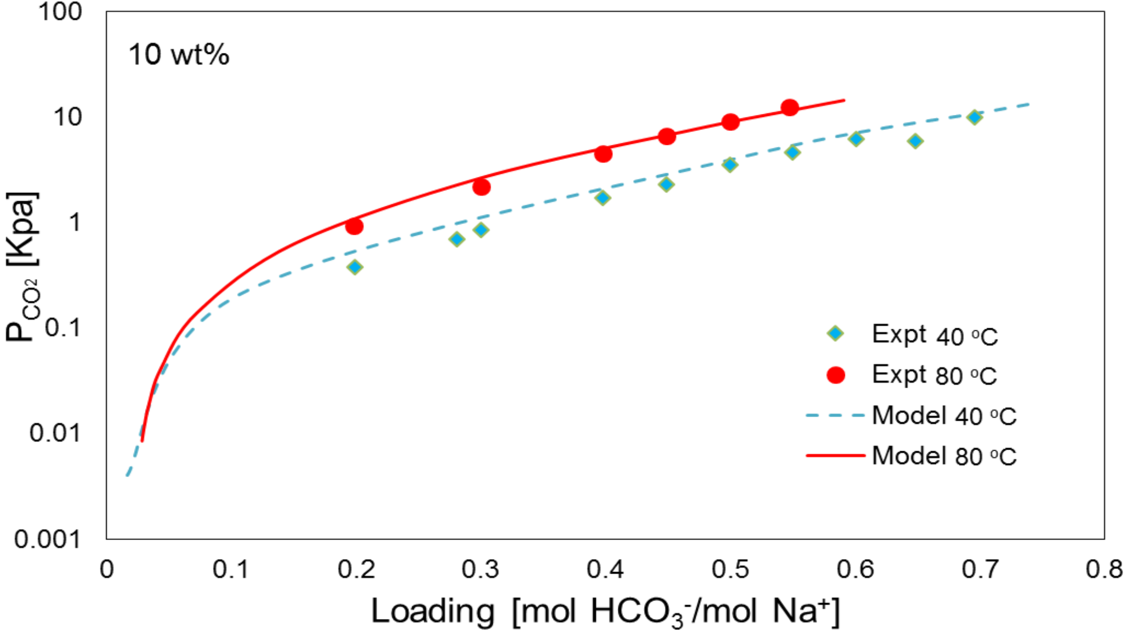
  R3: $Na_2CO_3 \leftrightarrow 2Na^+ + CO_3^{2-}$

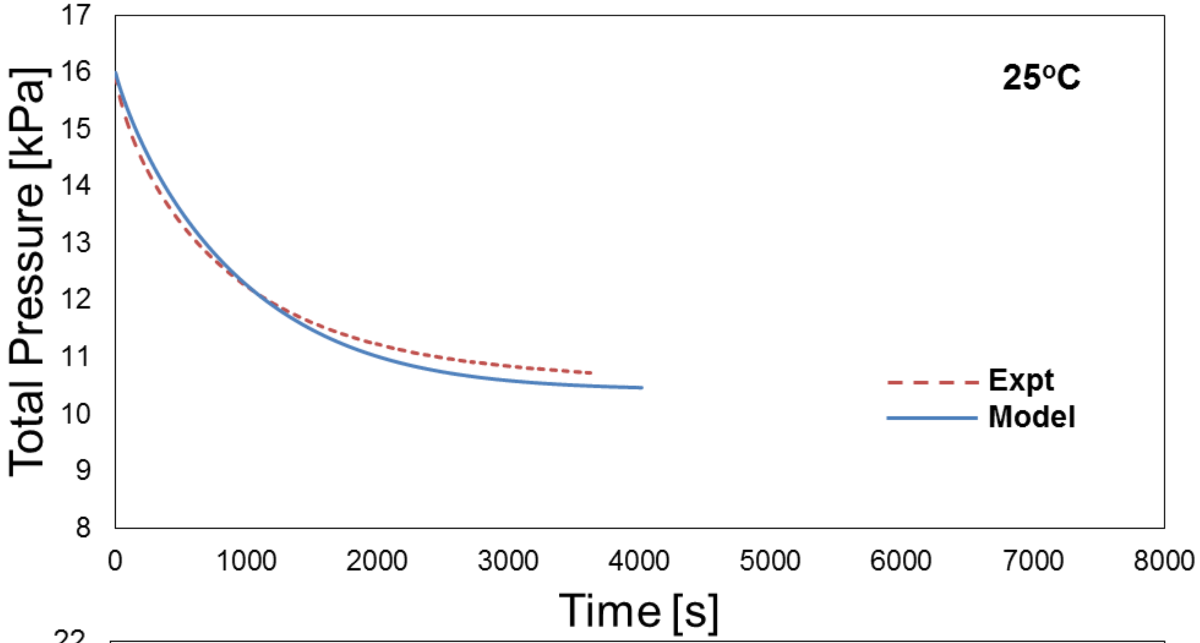


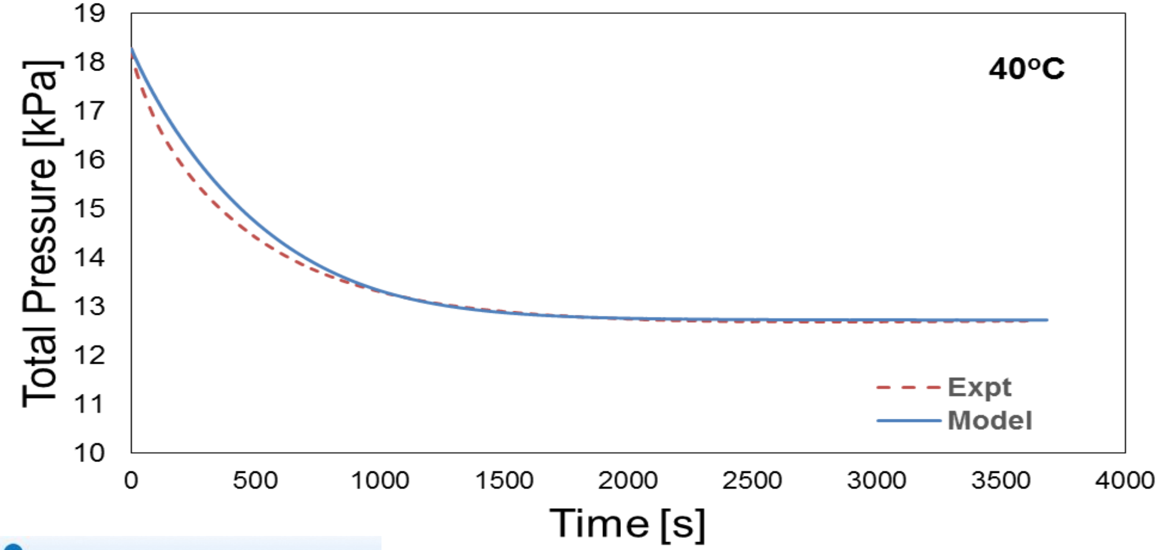
Pinsent B.R., Pearson L. , Roughton F.J.W., “The Kinetics of Combination of Carbon Dioxide with Hydroxide Ions”, Trans. Faraday Soc., 52, 1512-1520, 1956

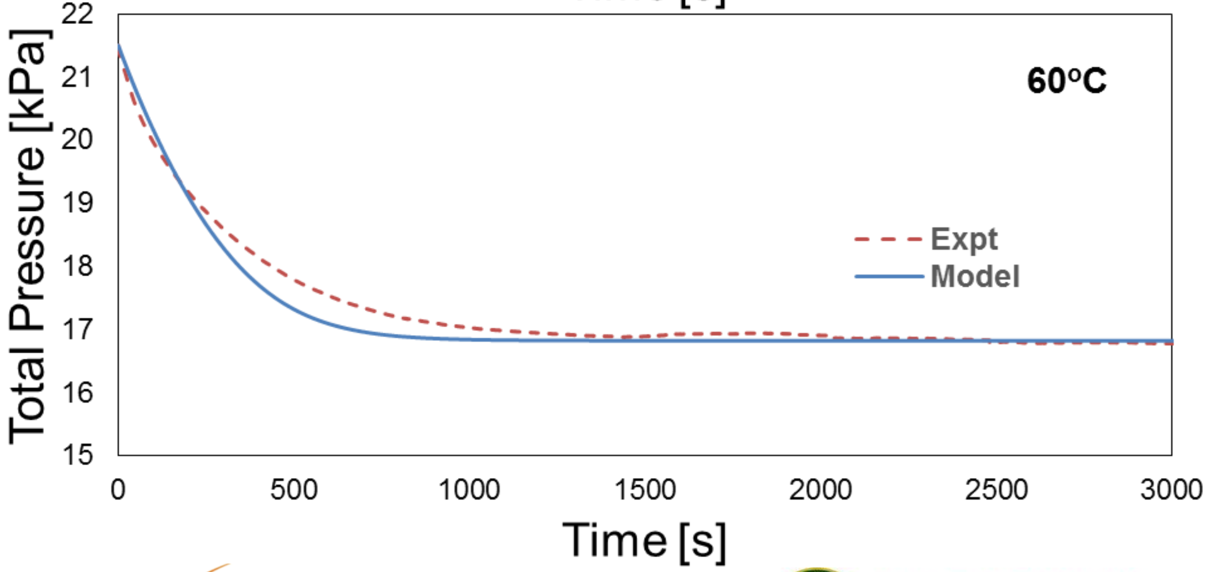
Astarita G., Savage, D. W., Longo, J. M., “Promotion of Mass Transfer in Carbonate Solutions”, Chemical Engineering Science, 36, 581, 1981

Thermodynamic and Capsule Model Validation

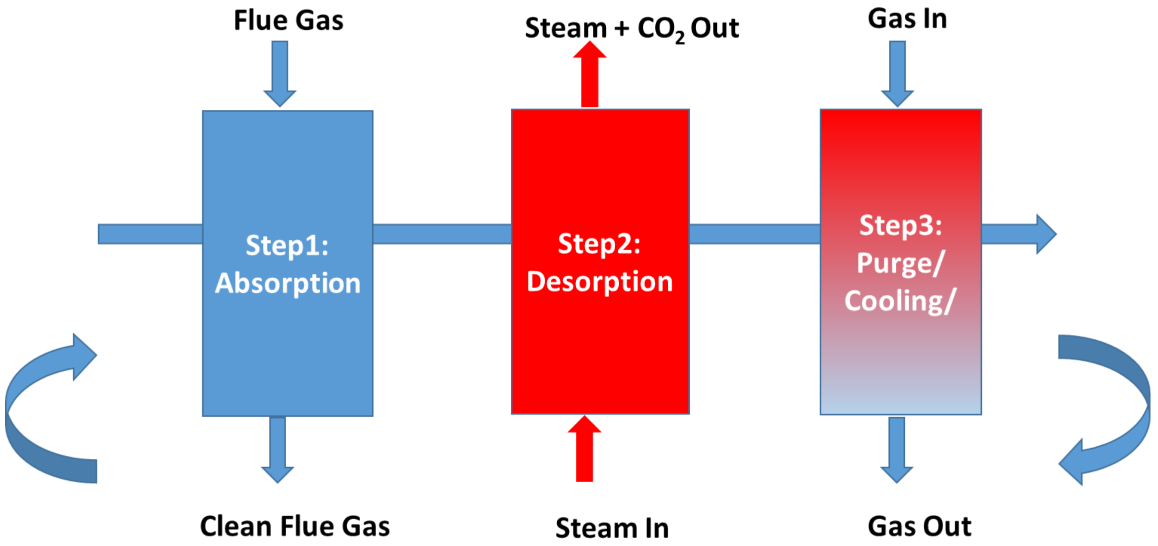


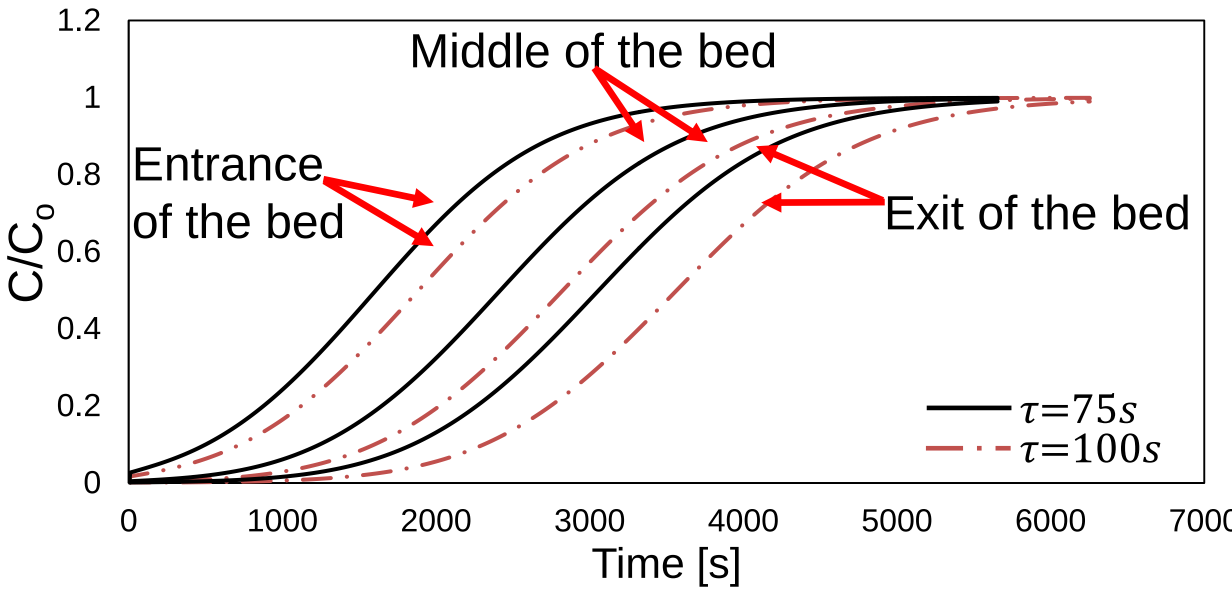


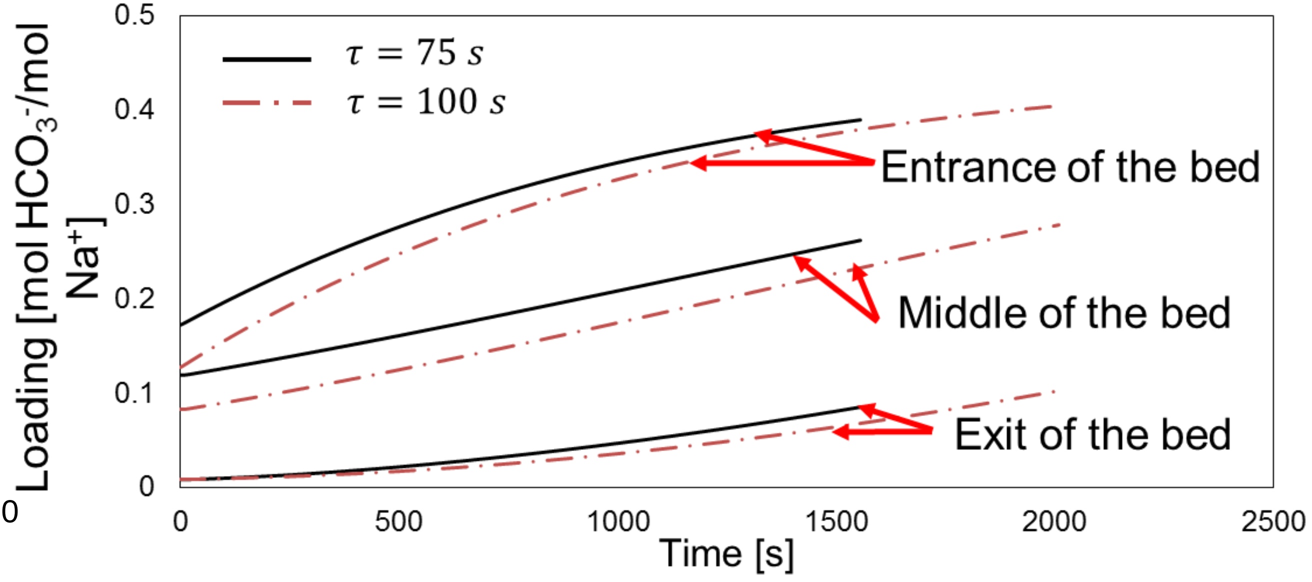




Fixed Bed Cycle Modeling: Impact of the Residence Time







Energy Breakdown for MECS (Na_2CO_3) vs MEA
(w/o considering heat loss due to steam leaving the desorber/desorption cycle)

Basis (1 kg of solvent)	MEA	MECS (Na_2CO_3) τ = 100 s	MECS (Na_2CO_3) Similar to MEA
Sensible heat for liquid (kJ)	**320**	**359**	**359**
Sensible heat for shell (kJ)	**0**	**51**	**51**
Solvent (wt.%)	**30**	**20**	**30**
Solvent (mol)	4.91	1.88	2.83
Abs. outlet loading(mol CO_2/mol solvent)	0.41	0.15	0.41
Des. outlet loading(mol CO_2/mol solvent	0.17	0.01	0.17
Relative loading change	**0.24**	**0.14**	**0.24**
CO_2 released (mol)	1.17	0.26	0.67
Heat of desorption (kJ/mol CO_2)	**90**	**25.2**	**25.2**
Heat of desorption (kJ)	106.09	6.65	17.11
Sensible to total heat ratio	**0.751**	**0.984**	**0.960**

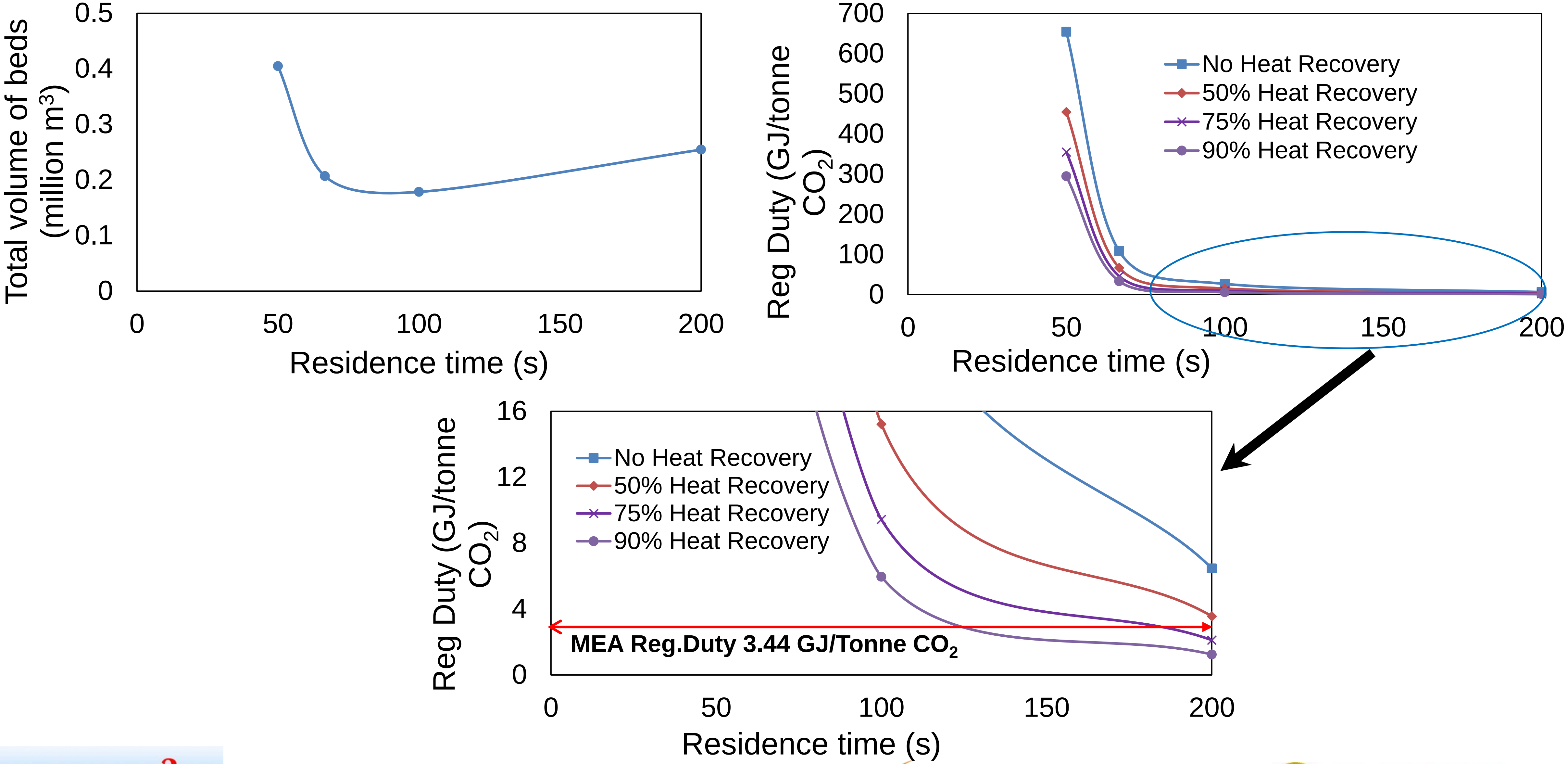
Similar to MEA: Assuming same solvent concentration and same relative loading change as MEA

Impact of Heat Recovery [20 wt% Na_2CO_3]

	Current Reaction Rate		**10X Current Raction Rate**	
	τ = 75 s	**τ = 100 s**	**τ = 75 s**	**τ = 100 s**
Total duty (GJ/tonne CO_2) No heat recovery	64.5	25.7	43.3	18
Total duty (GJ/tonne CO_2) 50% heat recovery	34.4	15.21	21.1	8.8
Total duty (GJ/tonne CO_2) 75% heat recovery	18.7	9.41	10.9	4.55
Total duty (GJ/tonne CO_2) 80% heat recovery	16.6	8.09	8.76	**3.3**
Total duty (GJ/tonne CO_2) 90% heat recovery	9.29	5.95	4.53	**2.0**
Sensible heat (%)	99.1	98.9	98.7	98.4

MEA Regeneration duty:~ **3.4 GJ/tonne CO_2**

Tradeoff between Capital and Operating Costs



Conclusions & Future Work (Process Modeling)

- High temperature absorption/desorption data (beyond 60^{o}C) and data reflecting water transport through the shell are currently not available. When these data are available from LLNL, further modification in the model may be necessary.
- Heat recovery: critical, but difficult to obtain high heat recovery for fixed bed processes due to the cyclic nature of the process
- Both high heat recovery and higher loading can be obtained using other types of beds such as moving beds
- Development of moving bed and bubbling fluidized bed models is in progress

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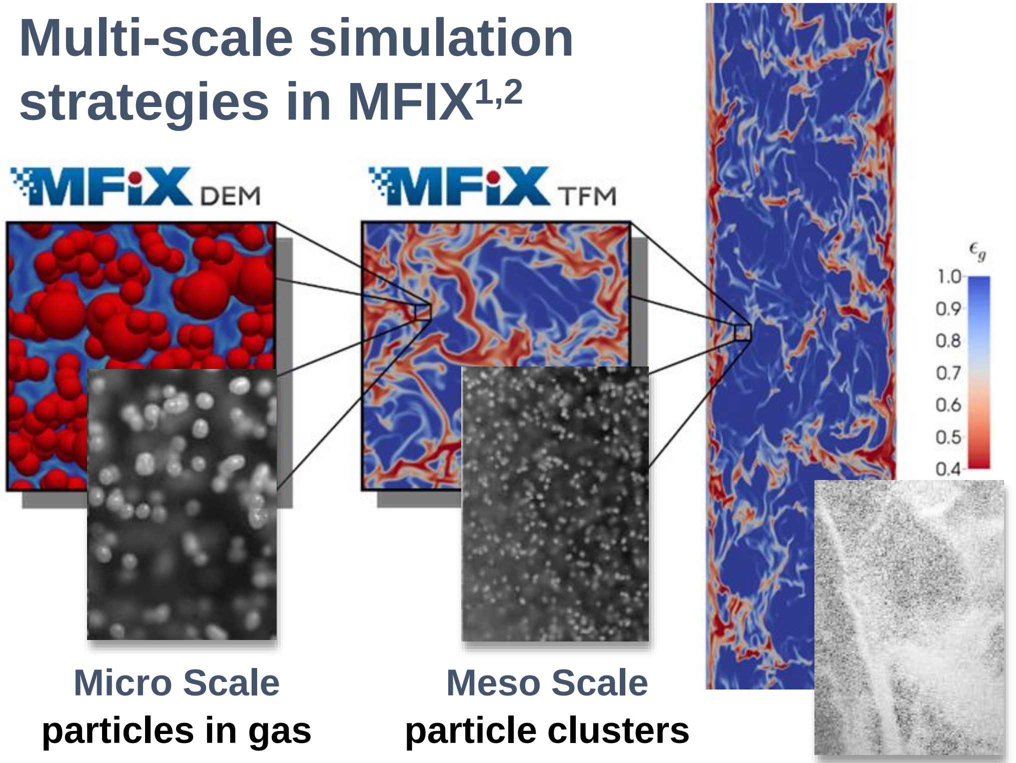
- ☐ Device-Scale Model for MECS

CFD Models for Simulating MECS Unit Operations

Multi-scale simulation strategies in MFIX[1,2]



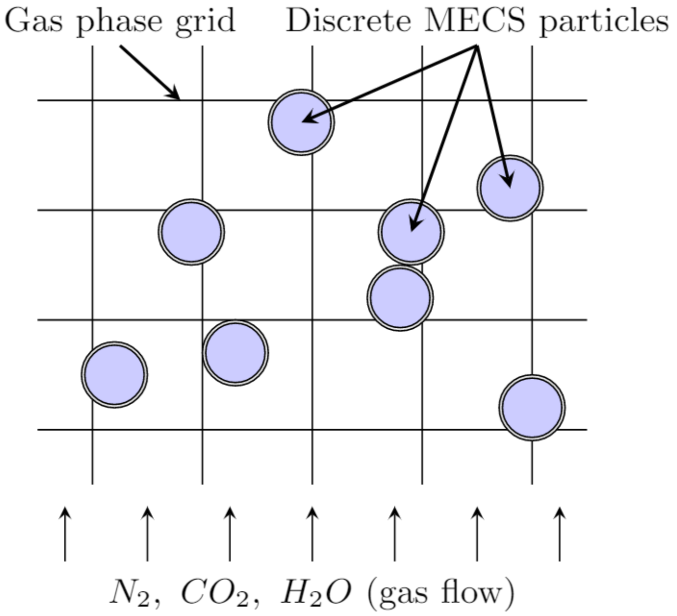
Micro Scale
particles in gas
(~100's microns)

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

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

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

MECS representation in MFIX-DEM

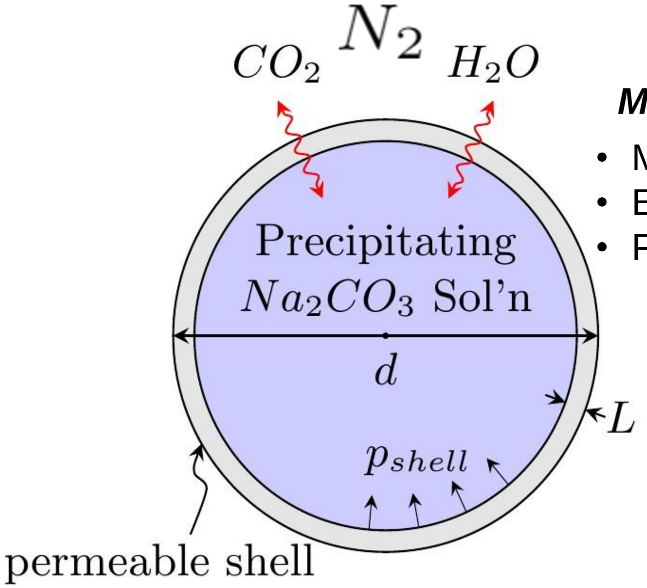


***3-D distributions** in volume fraction, temperature and species concentration are predicted*

GOAL: Develop and validate a predictive CFD tool for MECS behavior under fixed/fluidized bed unit operations.

1) https://mfix.netl.doe.gov/experimentation/
2) Shaffer, F., et al., NETL MFSW, 2010. Image: Streamers, clusters, particles in CFB

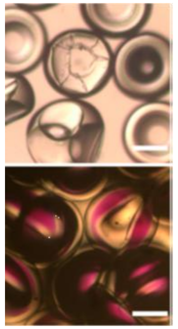
Mass Transfer Model for Encapsulated Carbonate Solutions



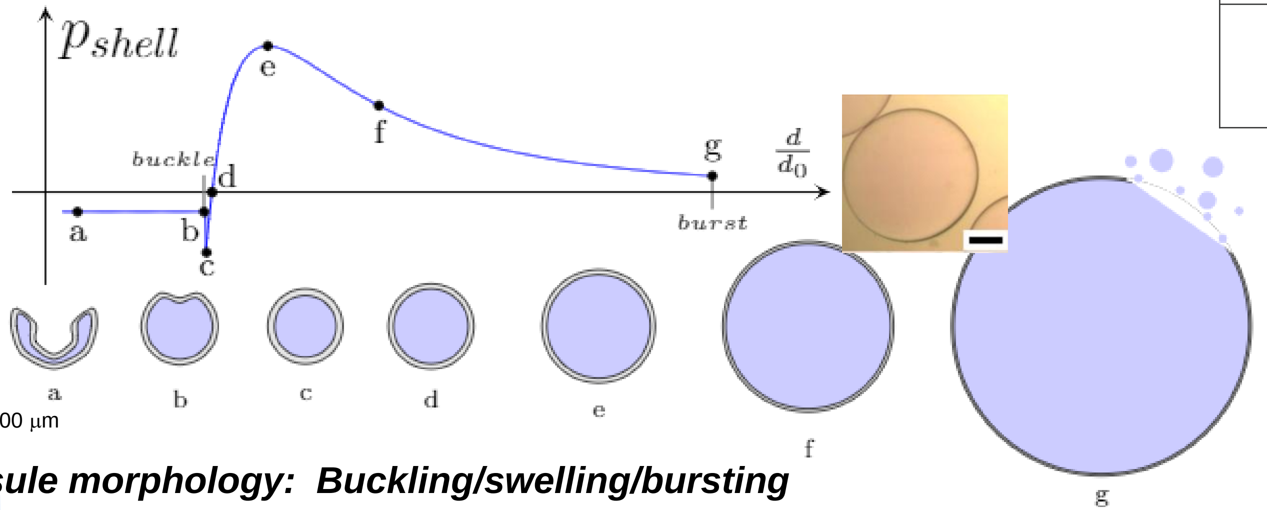
Mass Transfer Model

- Modified two film theory for CO_2 & H_2O
- Elastic swelling/buckling due to H_2O transfer
- Physical & chemical prop. sub-models

Resistance in series representation
$\dot{n}_{CO_2} = \frac{a}{RT}\cdot k_{ov,CO_2}\left(p_{CO_2} - H_{CO_2}[CO_2] - p_{shell}\right)$
$k_{ov,CO_2} = \frac{1}{\frac{1}{k_{g,CO_2}} + \frac{1}{k_{shell,CO_2}} + \frac{1}{k_{l,CO_2}}\cdot\frac{H_{CO_2}}{RT}}$
$k_{g,CO_2} = \frac{Sh\cdot\mathcal{D}_{CO_2,g}}{d}$
$k_{shell,CO_2} = \frac{\mathcal{G}_{CO_2}}{L}\cdot RT$
$k_{l,CO_2} = E\cdot k_l^o = C_1\cdot\sqrt{\mathcal{D}_{CO_2,sol}k_{OH^-}[OH^-]}$



Image[1]; scale bar = 200 µm



Image[3]; d_p~480 µm

Capsule morphology: Buckling/swelling/bursting

1) Nabavi et al., Langmuir, v. 32, 2016;
2) Quilliet, The Eup. Phys. J. E., v. 35, 2012.
3) Panday, R. & Rogers, B., private communication, 2018.

Extensive Model Validation

- ✓ Vapor-liquid equilibrium for carbonate solutions[1]
- ✓ Onset of precipitation for loaded carbonates[2]
- ✓ Vacuum chamber CO_2 absorption rate[3,4,5]
- ✓ Bench scale fluidized bed CO_2 capture[6]

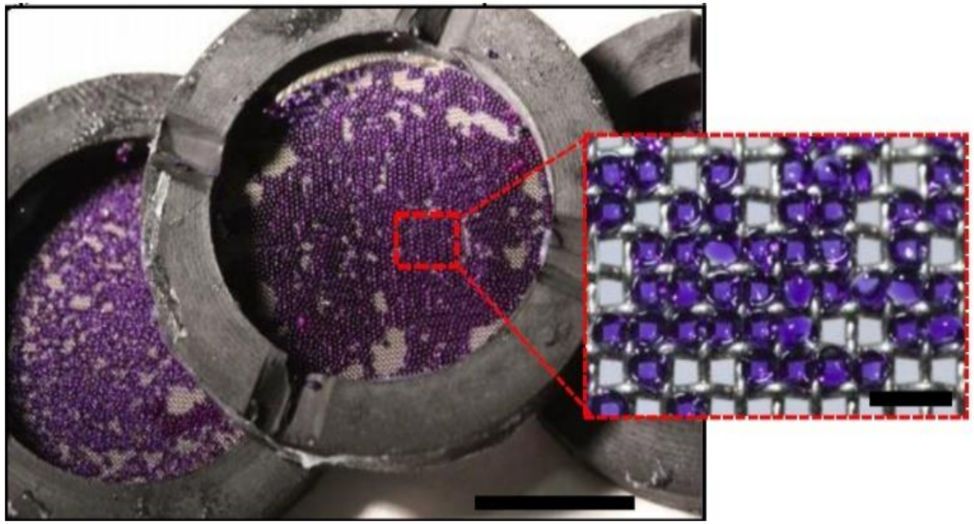


FIG: Vacuum chamber absorption[3,4]

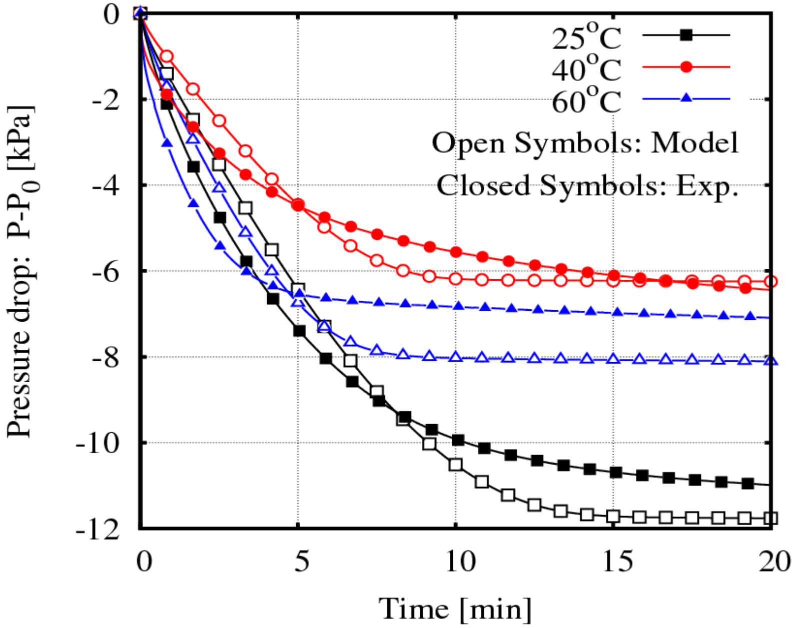


FIG: Bench scale fluidized bed[5]

[1]Knuutila et al., CES, 2010; [2]Gartner et al, 2004; [3]Vericella et al., Nature Comms; [4]Hornbostel et. al, submitted;. [5]Finn & Galvin, IJGGC, 2018; [6]Finn et al., in preparation

Simulation & Experiment of Bench-Scale Absorber

LLNL Experiment:

$T_{g,in}$ [^oK]	313
$y_{N_2,in}[-]$	0.811
$y_{CO_2,in}$ [$-$]	0.113
$y_{H_2O,in}$ [$-$]	0.076
P_{out} [Pa]	101325
$v_{g,in}/u_{mf}$	1.24

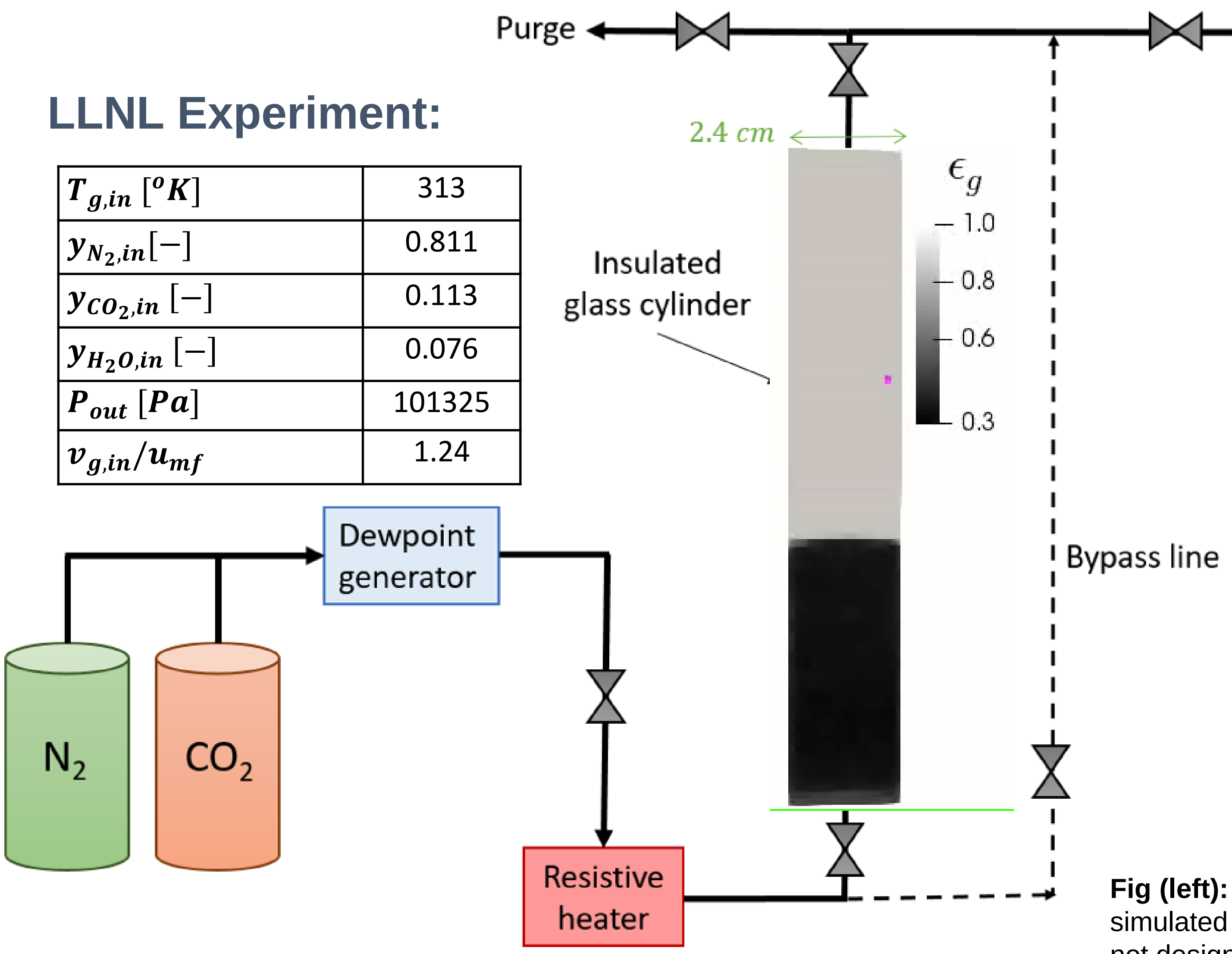


Fig (below): Experiment & Model Comparison

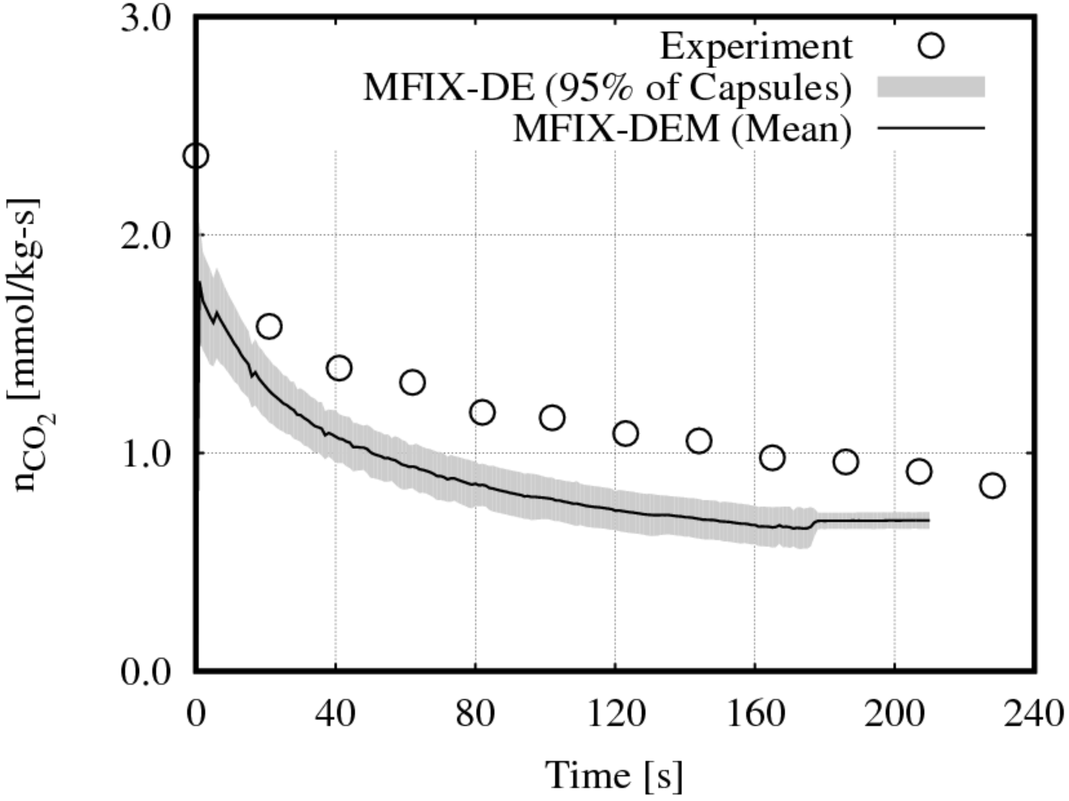


Fig (left): Schematic of experiment and model setup. Animation shows simulated gas fraction in the bubbling bed. Note, bench-scale absorber not designed for actual CO_2 capture requirements.

Conclusions (Bench-Scale CFD Model)

1. MECS technology: **Combine benefits of solvents and sorbents** for carbon capture.
2. Predictive models needed to aid process design process. **Our approach: MFIX-DEM.**
   ✓ Precipitating carbonate chem. ✓ CO_2 & H_2O mass transfer ✓ Elastic size change
3. Validation with controlled MECS CO_2 absorption experiments & literature data for carbonates.
4. Ongoing studies of **fluidized bed** absorber/regenerator unit operations.

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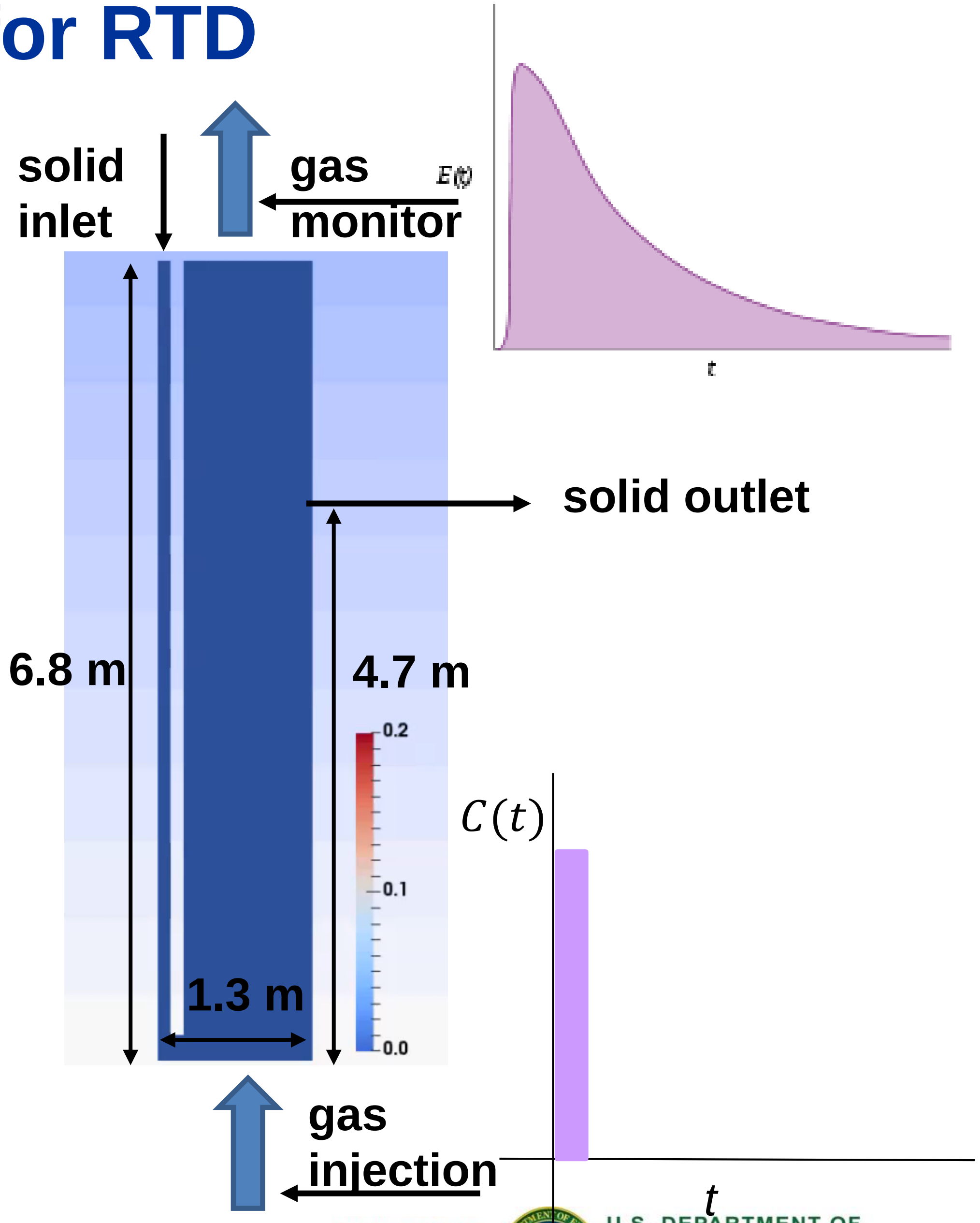
Device-Scale CFD for RTD

- **Device-scale CFD Model**
  - MFIX-TFM for multiphase gas/solid flow
  - MECS chemistry from bench-scale MFIX-DEM model

- **Testing Conditions**
  - Pulse experiments
  - MECS are fully packed at designed bed height
  - Entire absorber reaches a hydrodynamic steady state

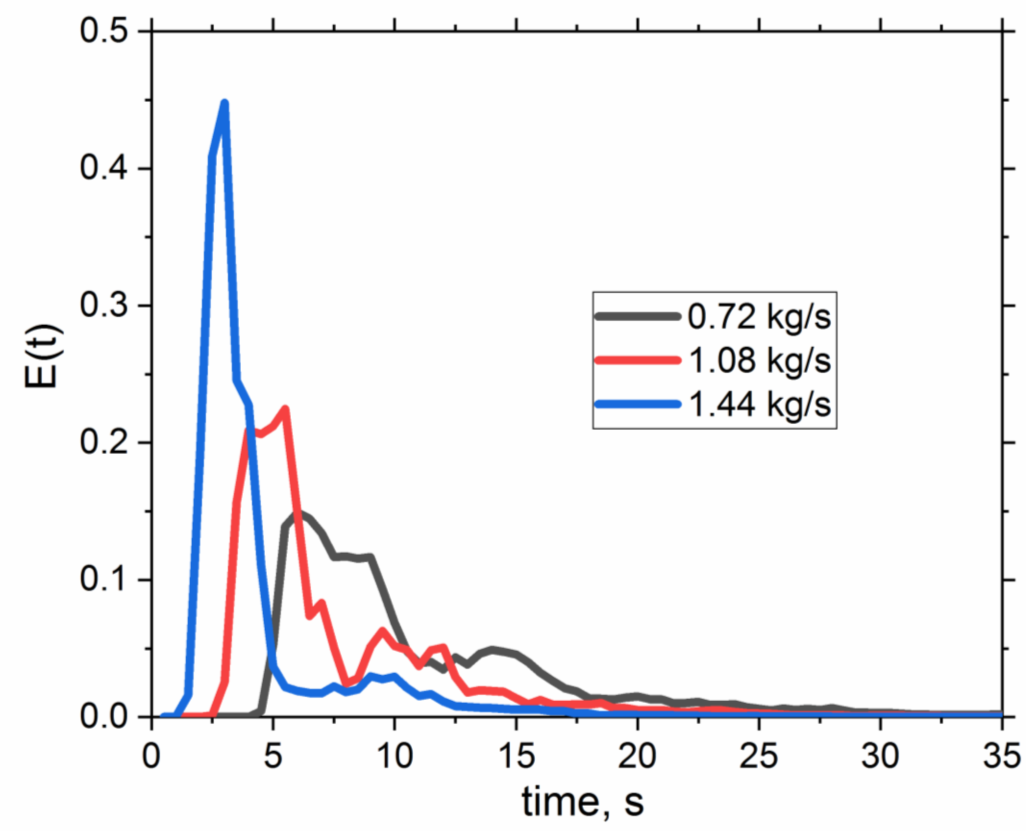
- **RTD Computation**
  - Residence time distribution function $E(t) = \frac{C(t)}{\int_0^\infty C(t)dt}$

    $C(t)$ is change of gas concentration with time
  - Mean residence time $\bar{t} = \int_0^\infty t \cdot E(t)dt$
  - Variance $\sigma^2 = \int_0^\infty (t - \bar{t})^2 \cdot E(t)dt$

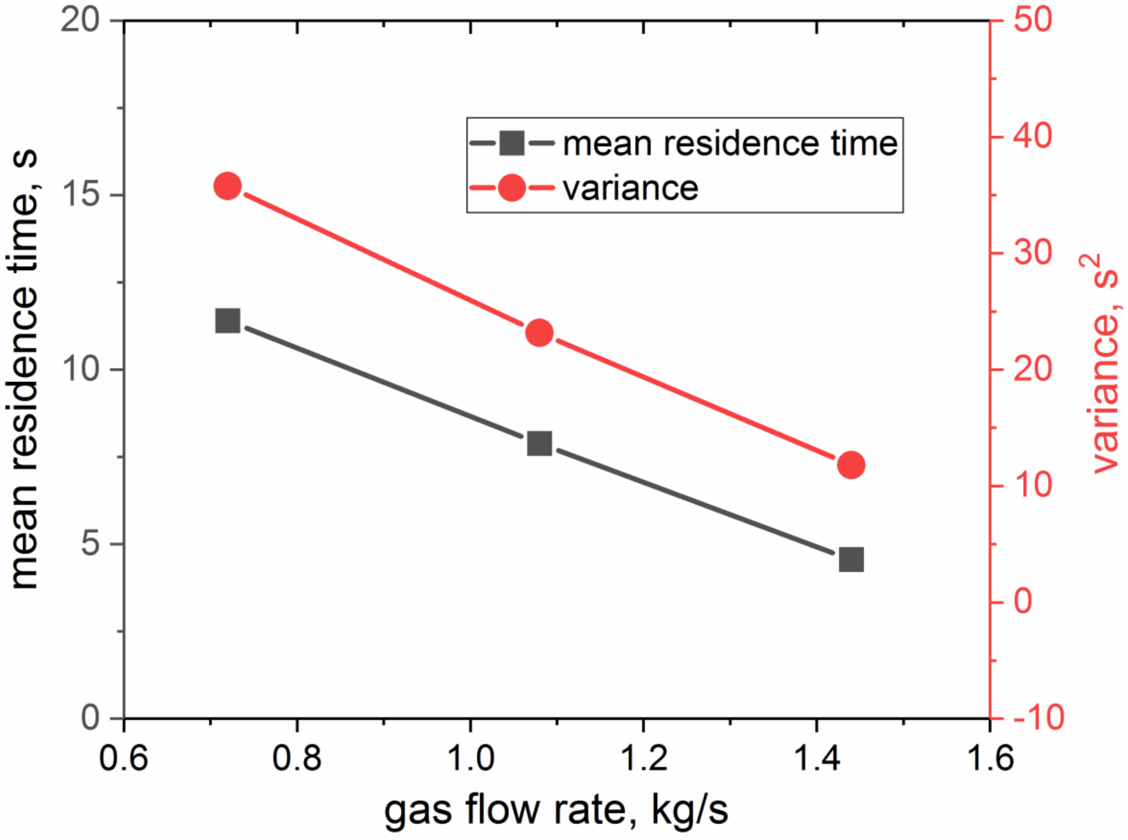


RTD Results

- **Effect of gas flow rate**
    - 120 µm MECS size



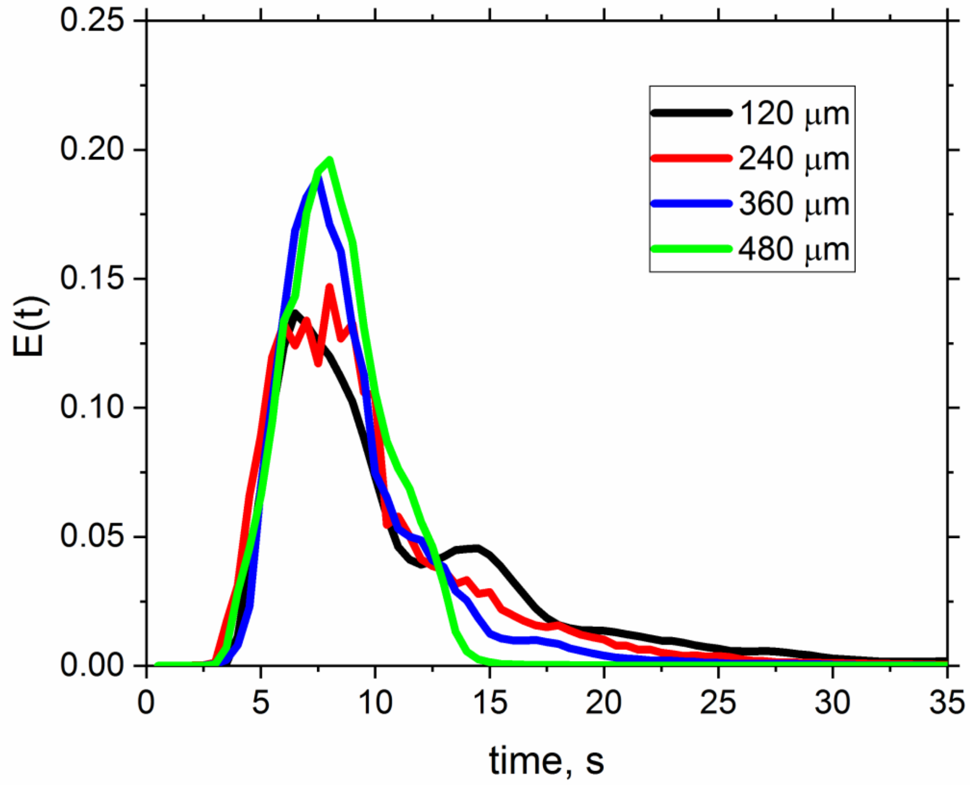
Residence time distribution gets wider with decreasing gas flow rate



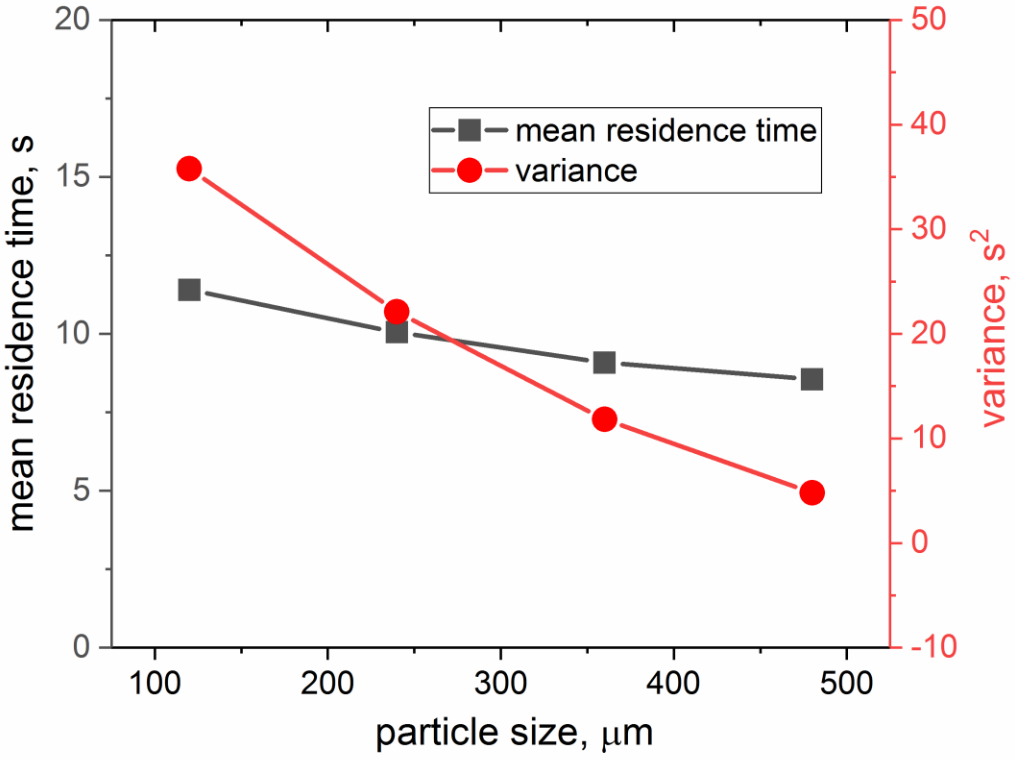
Mean residence time and variance decrease with increasing gas flow rate

RTD Results, cont'd

- **Effect of MECS size on gas phase RTD**
  - 0.72 kg/s gas flow rate



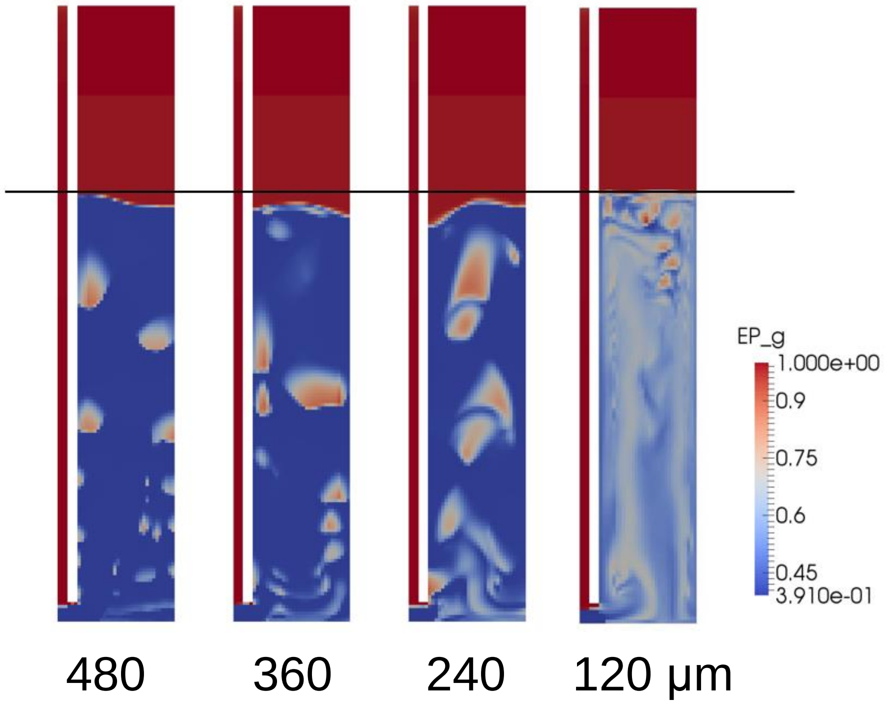
Residence time distribution gets slightly narrower with increasing particle size



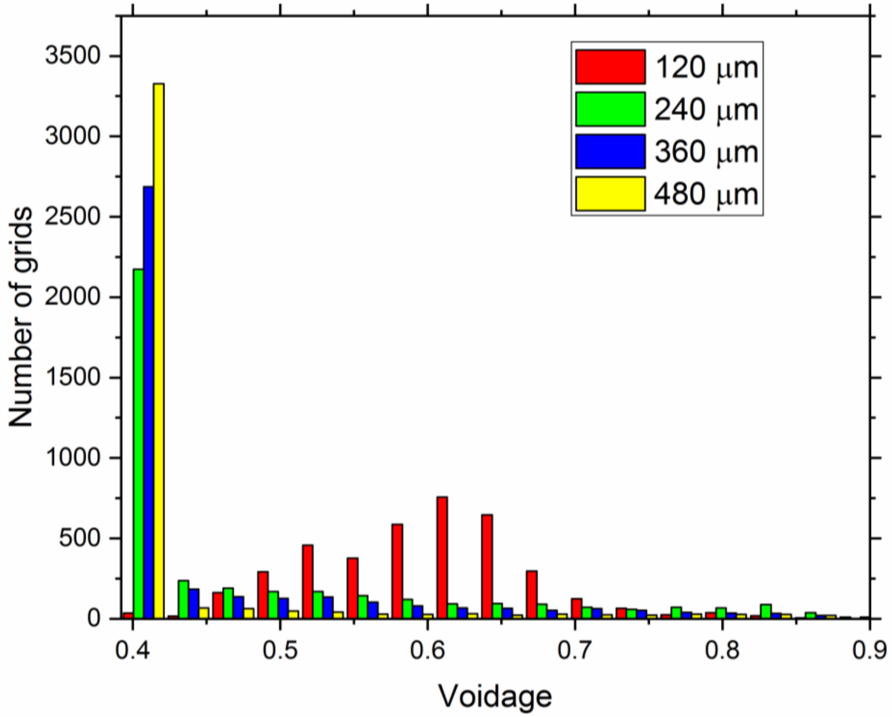
Mean residence time and variance decrease with increasing particle size

Characterize Gas/Solid Mixture

- Gas flow rate: 0.72 kg/s; particle size: 120, 240, 360, and 480 µm
- Steady state when all beds reach a constant holdup
- Smallest particle follows Gaussian distribution with better homogeneity--more gas/solid drag and longer mean residence time



Quantify gas/solid mixture by voidage distribution



Summary

- Effect of particle size and gas flow rate on mean residence time and variance
- Statistical characterization of gas/solid mixture homogeneity
- CFD results as guidance to improve MECS and device-scale absorber design
  - Assist in process modeling
  - Optimize bed height, MECS size, etc.

Acknowledgements

- LLNL (Joshua Stolaroff, Pratanu Roy, Katherine Mary Ong, William R. Bourcier and others from LLNL) for the experimental data and support

CCSI^2

Carbon Capture Simulation for Industry Impact

For more information
https://www.acceleratecarboncapture.org/

Debangsu Bhattacharyya
West Virginia University
Debangsu.Bhattacharyya@mail.wvu.edu

Janine Carney
NETL
Janine.Craney@netl.doe.gov

Zhijie Xu
PNNL
Zhijie.Xu@pnnl.gov