Developing a High-Fidelity CFD Model for CO_2 Separation by Adsorption

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Background & Objective

- CO_2 separation by adsorption is based on the selective adsorption of CO_2 from a feed gas on a solid adsorbent to produce a gas stream that is CO_2-lean
- For continuous operation, this is typically carried out in a chemical looping system with interconnected fluidized beds
- High-fidelity computational fluid dynamics (CFD) simulation of a chemical looping system for CO_2 separation requires accurate modeling of both the adsorption/desorption reaction kinetics and the hydrodynamics of the system
- CFD model for the full system is developed using a "bottom-up" approach to ensure the highest degree of accuracy whereby each of these aspects is verified against experiments independently and only then assembled into one comprehensive model

Computational Setup

- All simulations in this presentation are performed using the National Energy Technology Laboratory (NETL) open-source solver Multiphase Flow with Interphase Exchanges (MFiX)
- The solids phase is resolved using the Discrete Element Model (DEM) where the position, velocity, and angular velocity of each particle is calculated via Newton's equations of motion

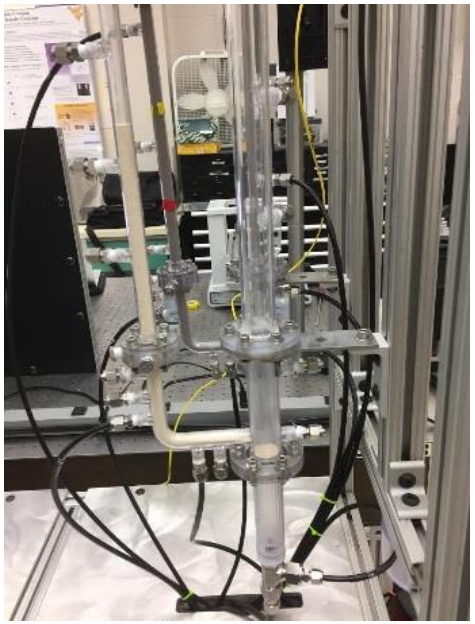
$$\frac{d}{dt}(\mathbf{X}(t)) = \mathbf{V}(t)$$

$$m\frac{d}{dt}(\mathbf{V}(t)) = \mathbf{F}_{\mathrm{T}} = m\mathbf{g} + \mathbf{F}_{\mathrm{D}}(t) + \mathbf{F}_{\mathrm{C}}(t)$$

- $\mathbf{F}_{\mathrm{C}}(t)$ is the net contact force from collisions and is calculated explicitly in the DEM framework based on the soft-sphere model
- The simulations are run on the NETL supercomputer Joule (and later Joule 2.0) using distributed memory parallel (DMP) through message passing interface (MPI)
- Kinetics are calibrated using the open-source Nodeworks Optimization Toolset developed by NETL to perform automated parameter sweeps of the MFiX simulations

Step 1: Simple Circulating Fluidized Bed

- Cold-flow experiments are conducted on a simple circulating fluidized bed (CFB) consisting of a riser, crossover, cyclone, and standpipe, and L-valve
- 2 conditions are tested and used for CFD validation of the hydrodynamics
- Total solids loading of 80.0 g



Flow (cm^3/s)	Case 1	Case 2
Riser	1,333.33	1,166.67
Standpipe	33.33	33.33
L-valve	33.33	33.33

Solids: 13X Zeolite	
ρ_p (kg/m^3)	1,140±49
d_p (μm)	793±11
Φ	0.95±0.002
ε_{packed}	0.34±0.020
$\varepsilon_{fluffed}$	0.39±0.005
u_{mf} (cm/s)	18.87±2.442
# particles	~268,700

Gas: Air	
P_{std} (Pa)	101,325
T_{std} (K)	293.15
$\rho_{g,std}$ (kg/m^3)	Ideal Gas
$\mu_{g,std}$ (Pa-s)	$1.85 \cdot 10^{-5}$
MW_{avg} (g/mol)	29

DEM Properties	
k_n (N/m)	1,000[1]
$e_{n,p\leftrightarrow p}$	0.90
$e_{n,p\leftrightarrow w}$	0.90
$\mu_{p\leftrightarrow p}$	0.50
$\mu_{p\leftrightarrow w}$	0.50

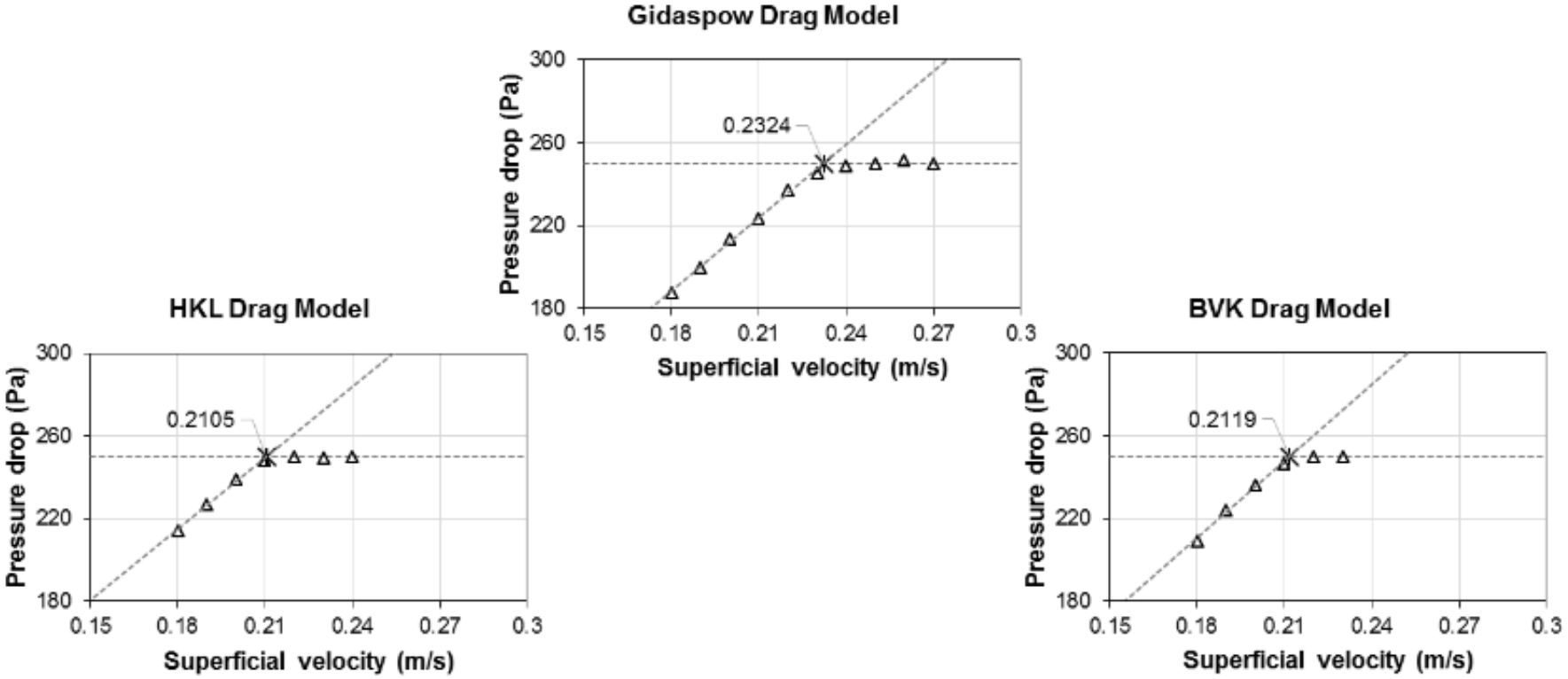
[1]Bakshi, A. et al. 2017. Multivariate sensitivity analysis of CFD-DEM: Critical model parameters and their impact on fluidization hydrodynamics, *2017 AIChE Annual Meeting*, October 29-November 3, Minneapolis, MN

Determining u_{mf} in Simulation

- u_{mf} is the minimum superficial fluid velocity (U_g) needed to fluidize the bed
- As gas is injected into a packed bed the pressure drop (Δp) across the bed increases until the minimum fluidization condition
- At the minimum fluidization condition the net weight of the bed is exactly balanced by Δp
- Further increase in the superficial velocity results in no further increase in the pressure drop
- Simulations are conducted on a bed of dimensions 0.5" × 0.5" × 5" filled with 14,700 particles (~4.375 g) fluidized from the bottom over a range of U_g

Effect of Drag Model on u_{mf}

- 3 different drag models are considered: Gidaspow[1], Hill-Koch-Ladd[2], and Beetstra-van der Hoef-Kuipers[3]



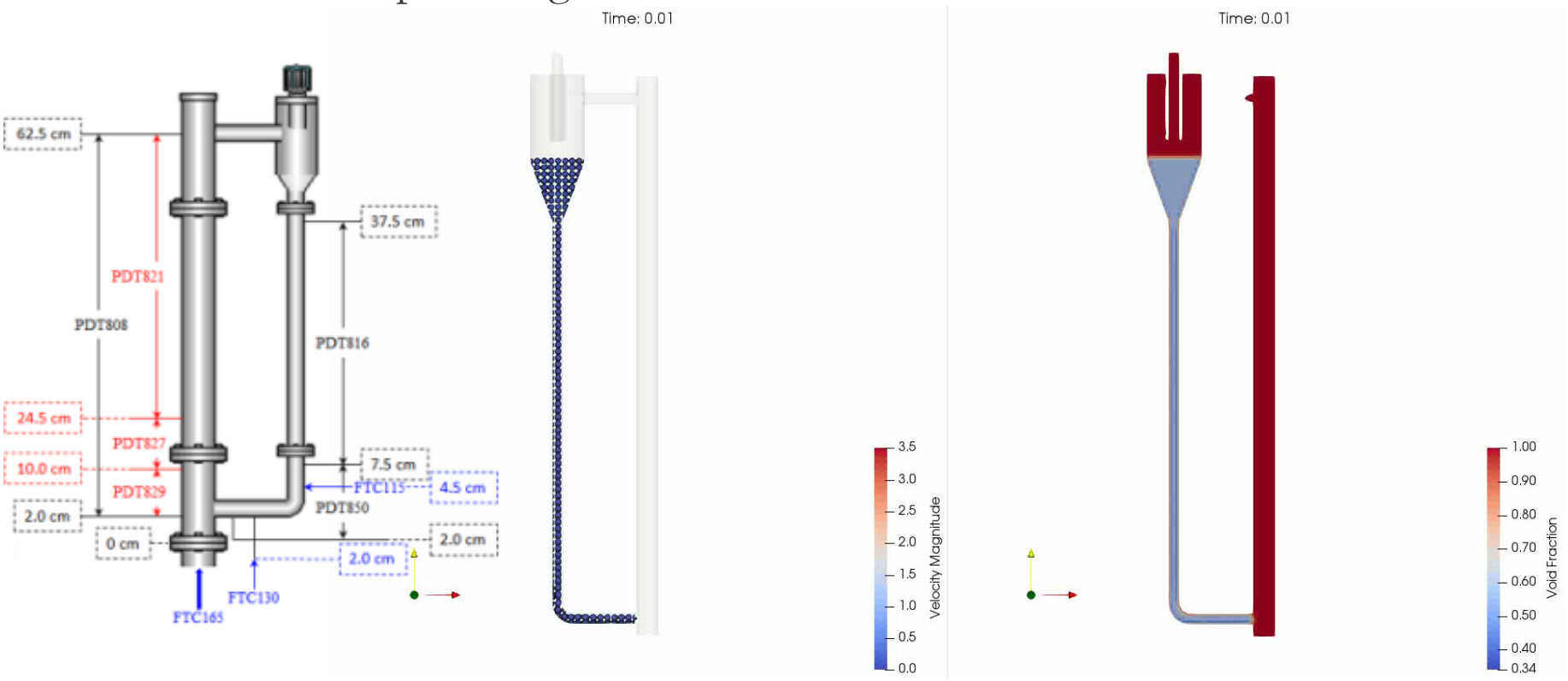
[1]Ding, J. and Gidaspow, D. 1990. A bubbling fluidization model using kinetic theory of granular flow, *AIChE J.*, 36, 523-538

[2]Hill, R.J., Koch, D.L. & Ladd, A.J.C. 2001. Moderate-Reynolds-number flows in ordered and random arrays of spheres, *J. Fluid Mech.*, 448, 243-278

[3]Beetstra, R., van der Hoef, M.A. & Kuipers, J.A.M. 2007. Numerical study of segregation using a new drag force correlation for polydisperse systems derived from lattice-Boltzmann simulations, *Chem. Eng. Sci.*, 62(1-2), 246-255

Simple CFB Hydrodynamics

- Case 1 is modeled using 3 different drag models: Gidaspow, HKL, BVK
- Results with Gidaspow drag model shown



[1]Ding, J. and Gidaspow, D. 1990. A bubbling fluidization model using kinetic theory of granular flow, *AIChE J.*, 36, 523-538

[2]Hill, R.J., Koch, D.L. & Ladd, A.J.C. 2001. Moderate-Reynolds-number flows in ordered and random arrays of spheres, *J. Fluid Mech.*, 448, 243-278

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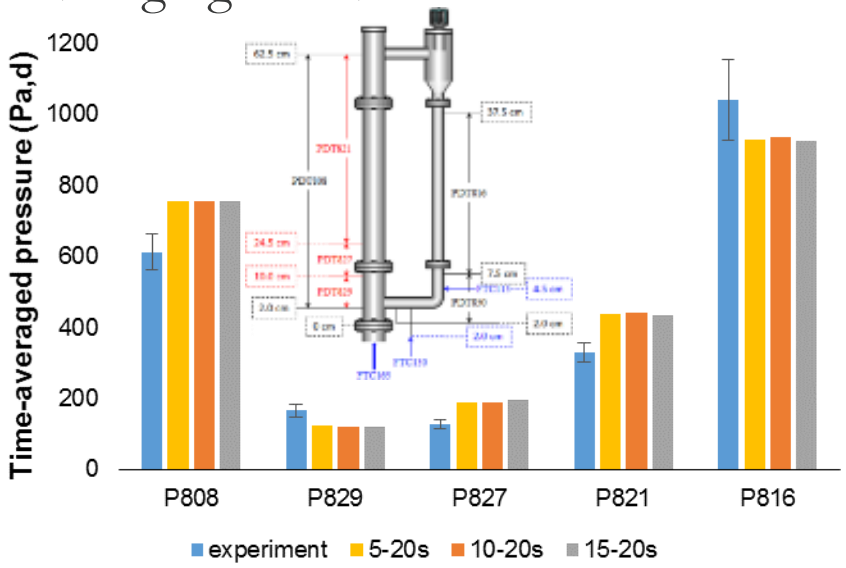
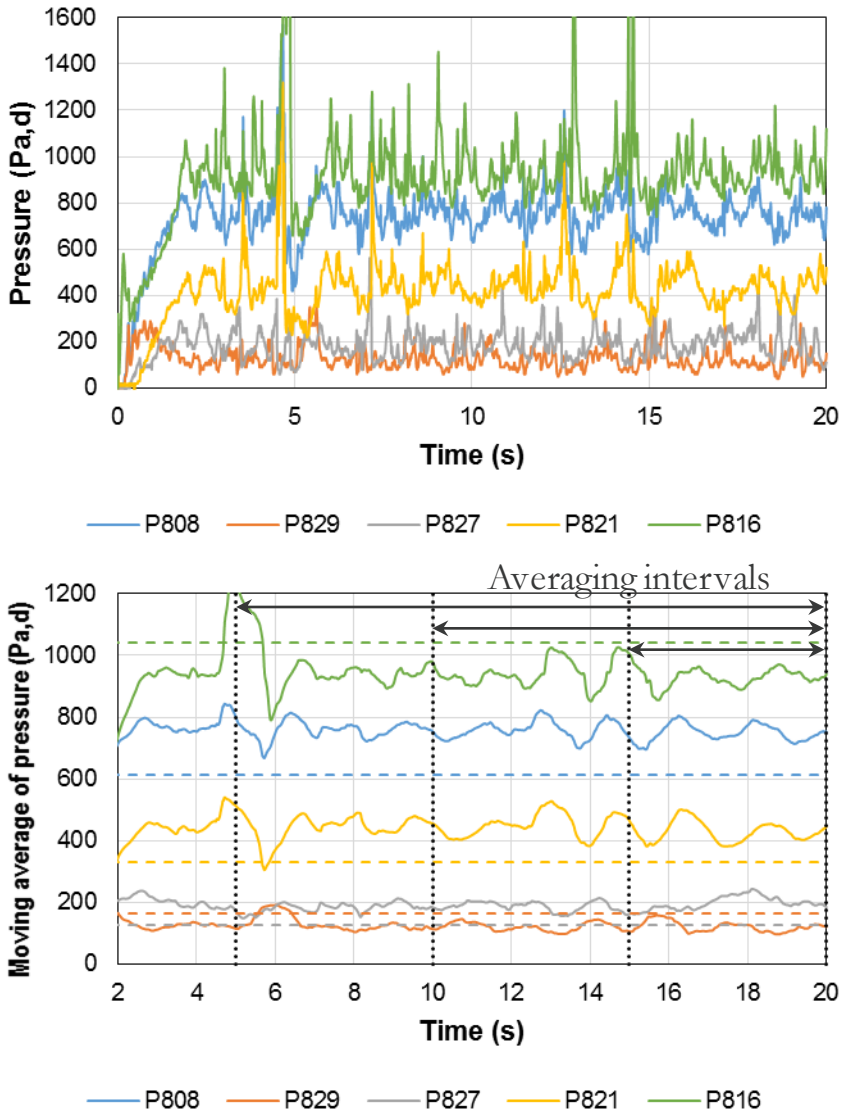
Simple CFB Hydrodynamics

- *Δp*'s across 5 sections are monitored and compared against experiment
- Moving average of pressure drop shows that the flow reaches quasi-steady state quickly
- Medium frequency fluctuations persist but final average is insensitive to the averaging interval





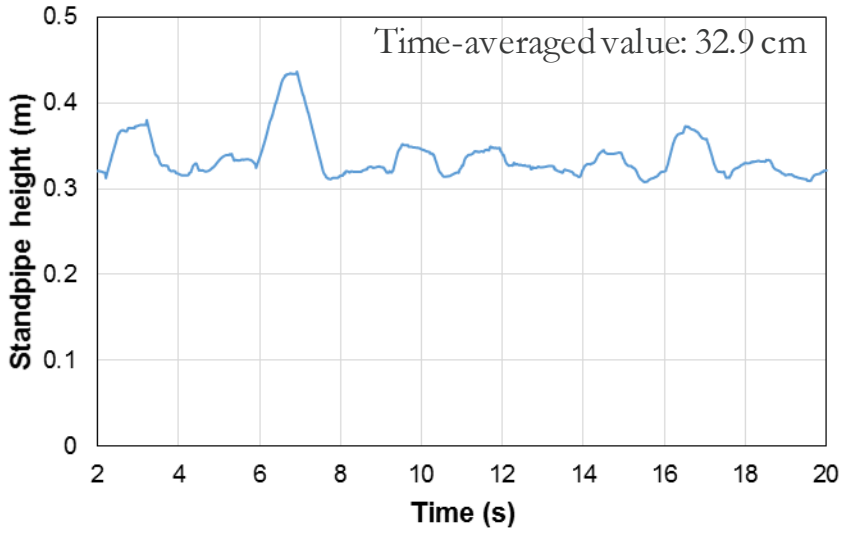
Simple CFB Hydrodynamics

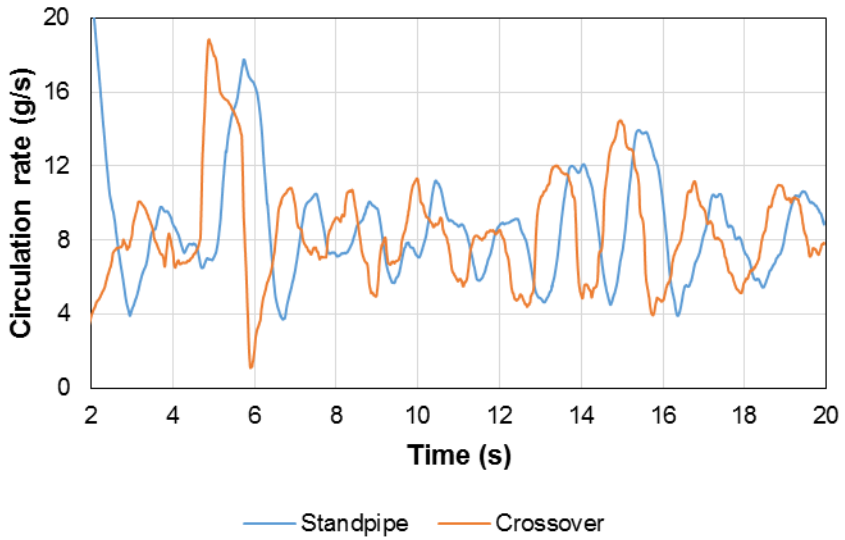
- Standpipe height is calculated from ε_g values and compared to the reported value of 33.6 cm
- Solids circulation rate is obtained by

$$\dot{m} = \rho u A \Rightarrow \dot{m}_s = \rho_p \sum_{i=1}^{N} u_{p\perp,i} A_{p,i}$$

- The solids circulation rate is calculated at the center of the crossover and at 2 locations in the standpipe just below the cyclone for cross-verification

Location	$\dot{m}_s$ (g/s)
Crossover	8.30
Standpipe @ 42.5 cm	8.41
Standpipe @ 37.5 cm	8.37

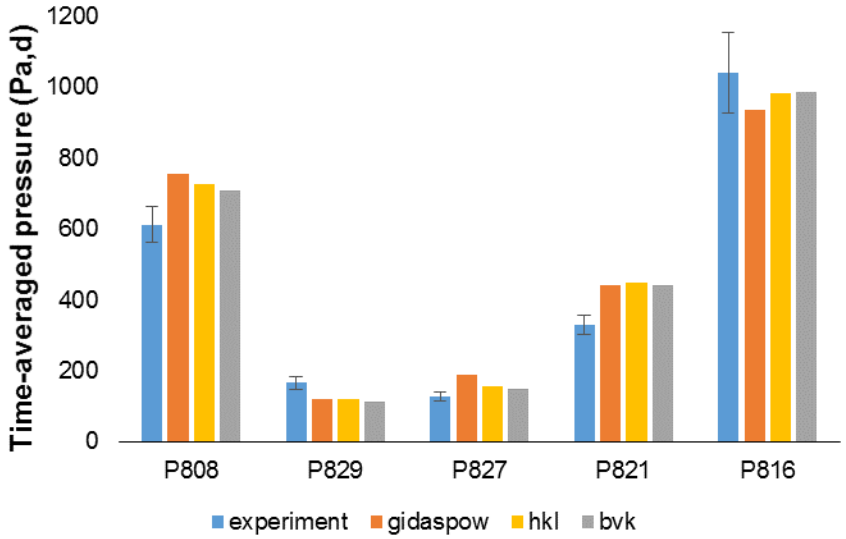


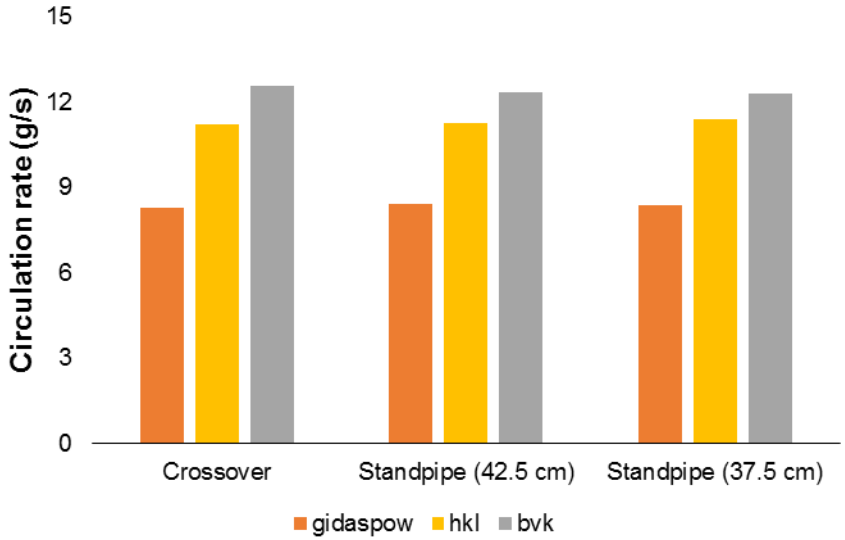


Comparison of Drag Models

- Gidaspow drag produces the best match for standpipe height but worst for pressure drop; the inverse for BVK
- Upshot is that the HKL drag model provides the best results overall
- Sensitivity to drag models in line with the results of Xu et al.[1]

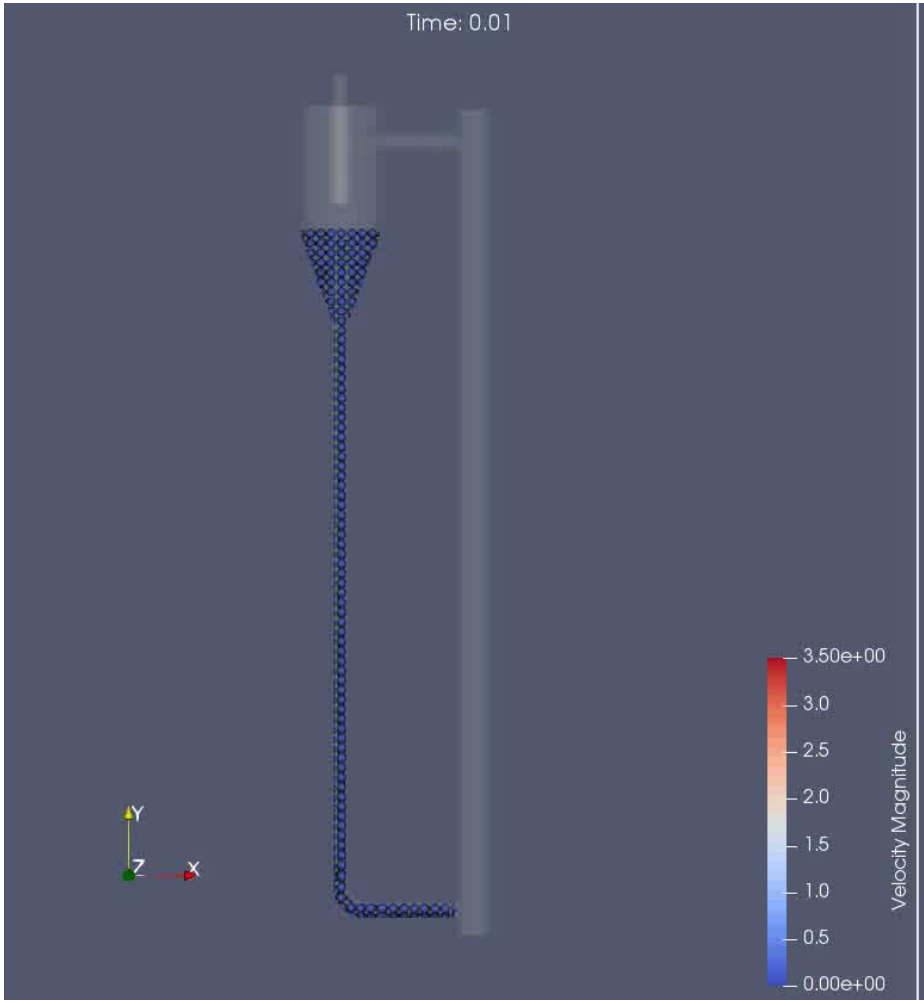
Standpipe height	cm
Experiment	33.65
Gidaspow	32.95
HKL	32.62
BVK	31.68

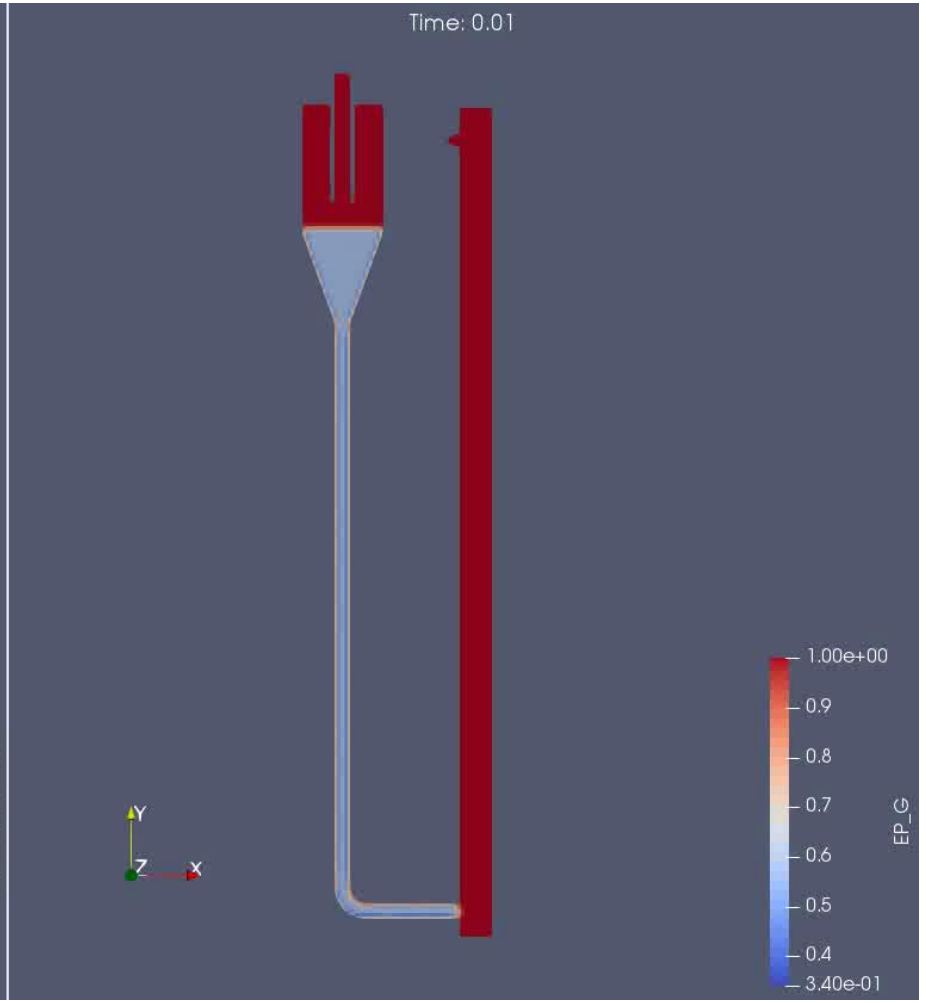




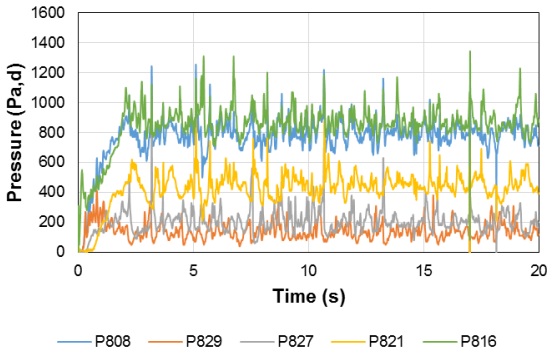
[1]Xu, Y. et al. 2017. Numerical simulation and experimental study of the gas-solid flow behavior inside a full-loop circulating fluidized bed: evaluation of different drag models, *Ind. Eng. Chem. Res.*, 57 (2), 740-750

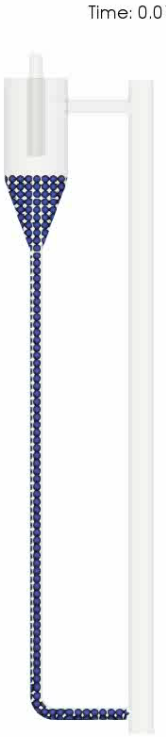
Case 1 Simulation: HKL Drag Model

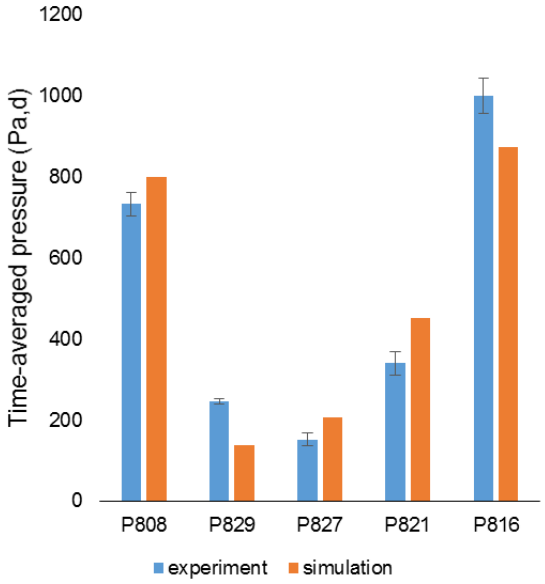


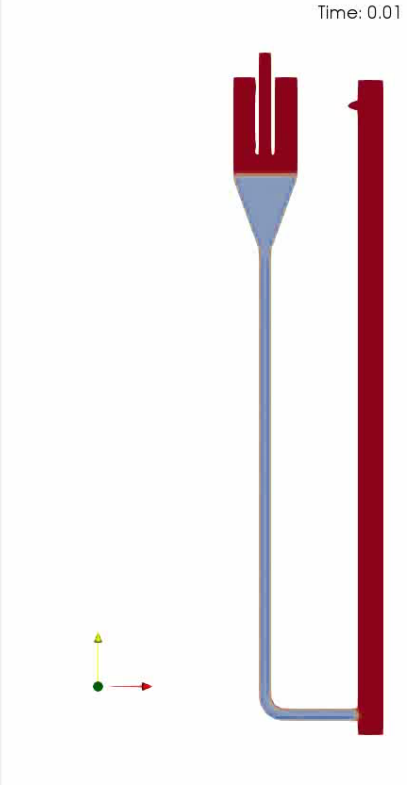


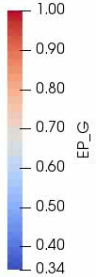
Case 2 Simulation







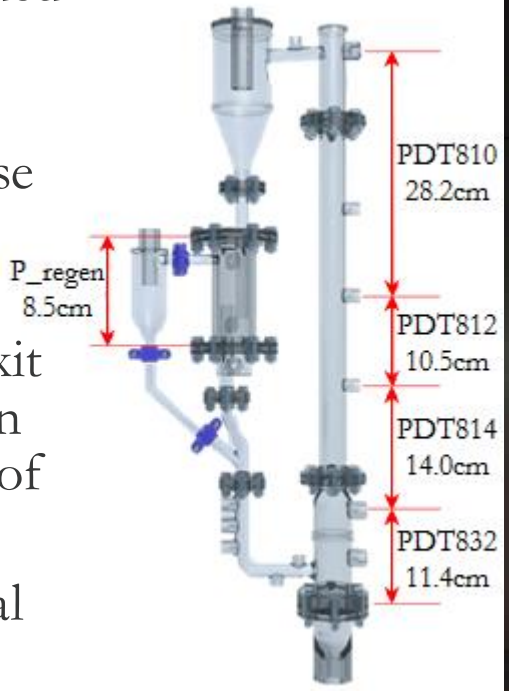




Circulation rate	$\dot{m}_s$ (g/s)
Crossover	4.68
Standpipe @ 42.5 cm	4.81
Standpipe @ 37.5 cm	4.81
Standpipe height (cm)	35.9

Step 2: Chemical Looping System w/ Regenerator

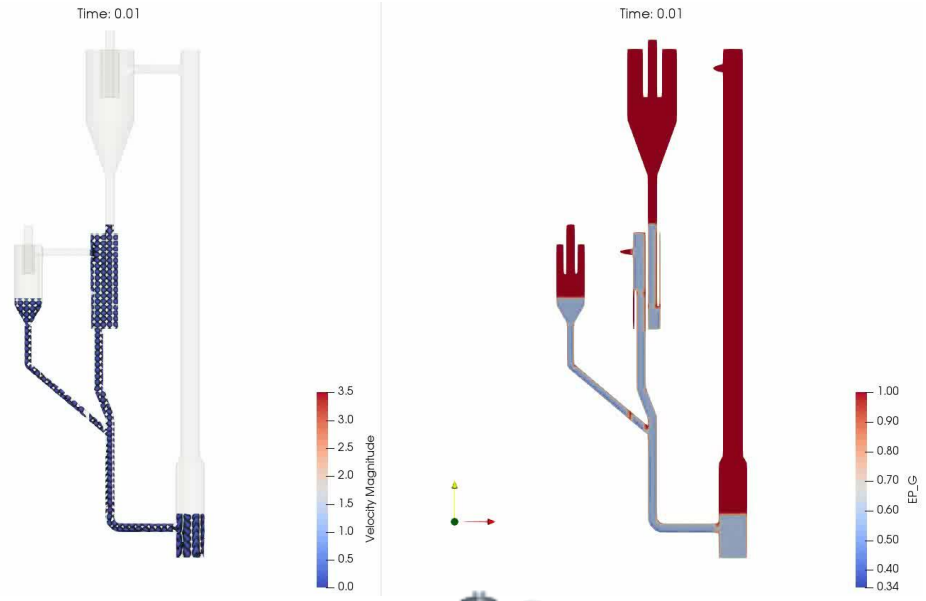
- A bubbling bed regenerator is added to the simple CFB setup after the cyclone
- Base of riser is widened to increase residence time of zeolite particles for increased adsorption
- The pressure at the regenerator exit is found to be unstable resulting in frequent "upsets" and elutriation of particles
- A second iteration of the chemical looping setup adds a secondary cyclone after the regenerator to maintain stable pressure at exit and retrieve particles in case of upset
- Total solids loading of 150.0 g

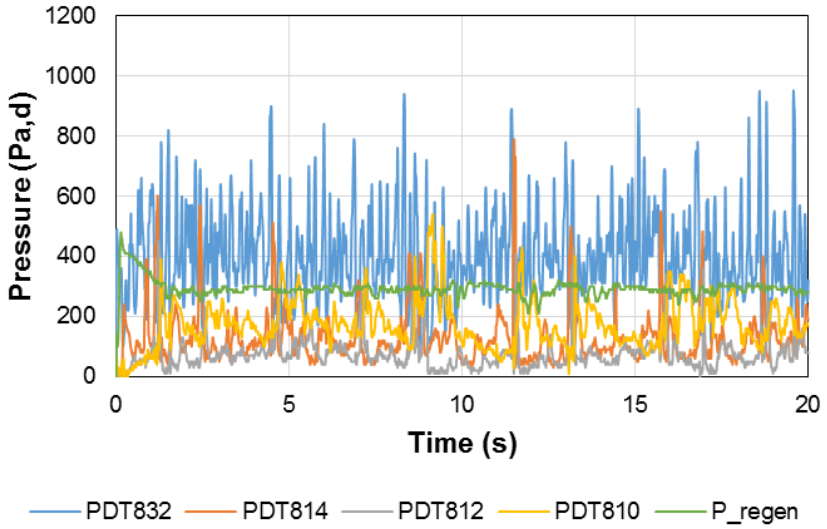


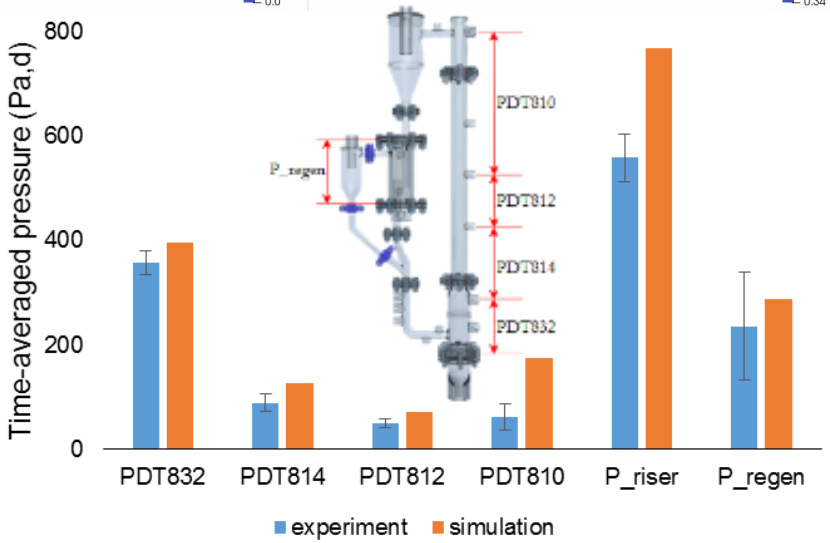
Location	Flow (cm^3/s)
Riser	1,666.67
Regenerator	283.33
Standpipe	50.0
L-valve	50.0

Chemical Looping System Hydrodynamics

- Fluidization at the bottom of riser is turbulent by design so significant pressure fluctuations are observed; high frequency fluctuations do not get attenuated by averaging
- The regenerator is a gently bubbling bed and shows minimal fluctuations in pressure

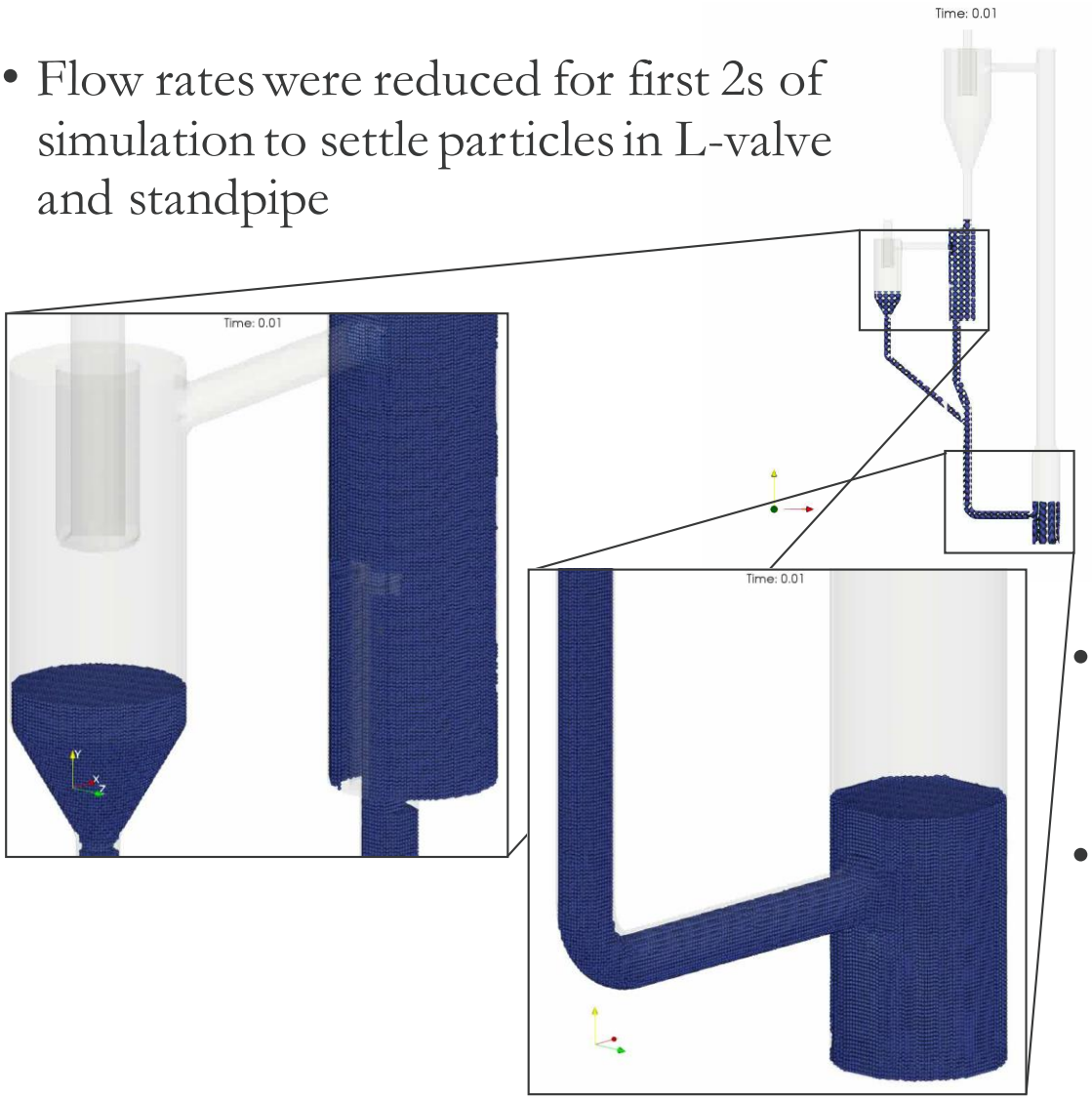


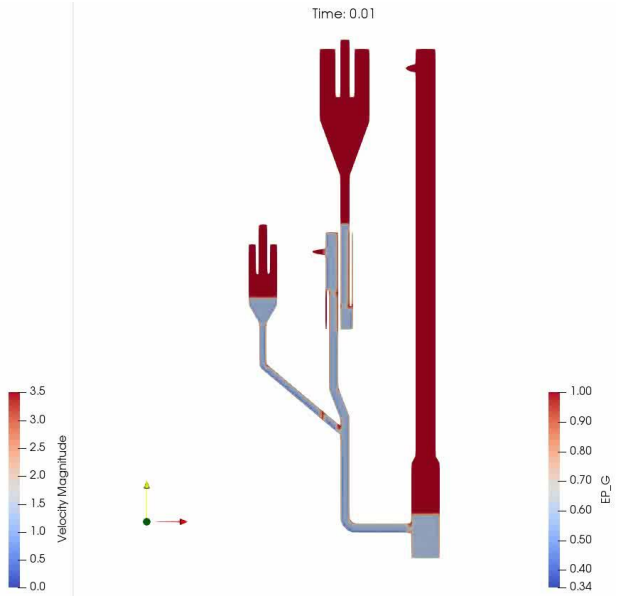




Chemical Looping System Hydrodynamics

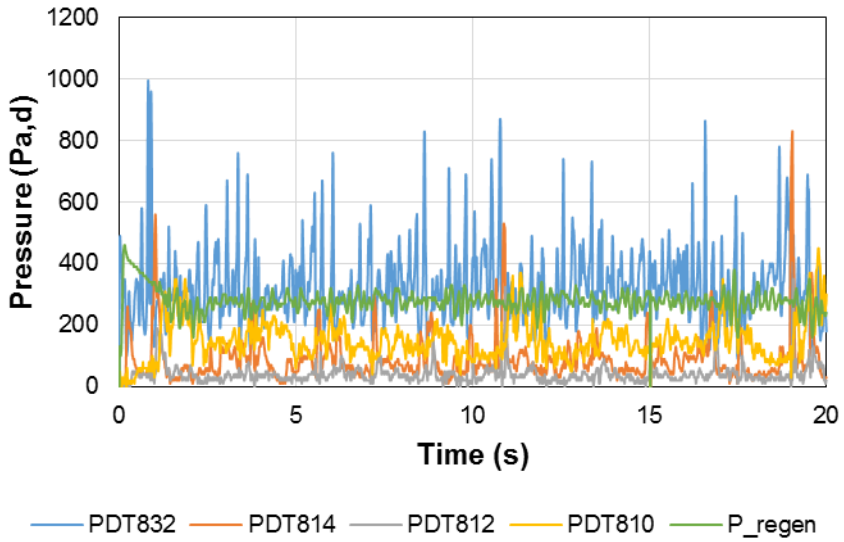
- Flow rates were reduced for first 2s of simulation to settle particles in L-valve and standpipe

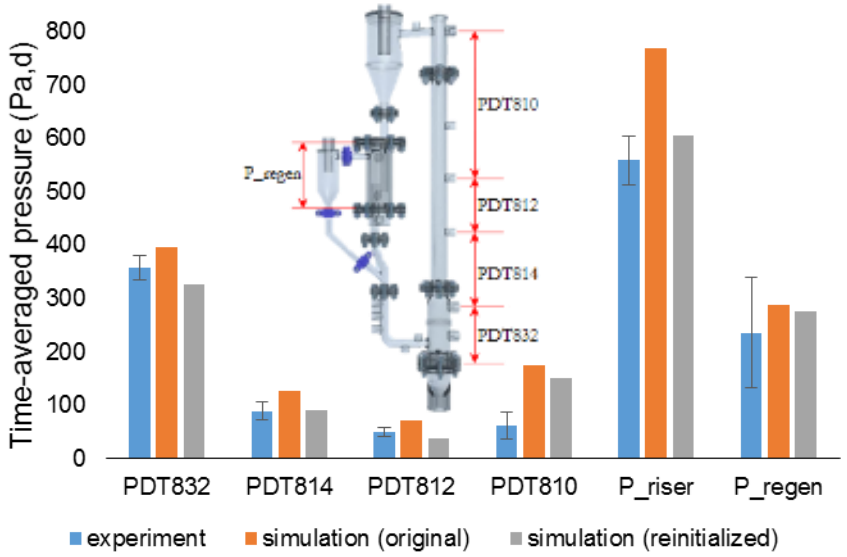




- The settled particles in the secondary cyclone/dipleg remain in place for longer
- The chemical looping setup is more sensitive to initial particle distribution than the simple CFB

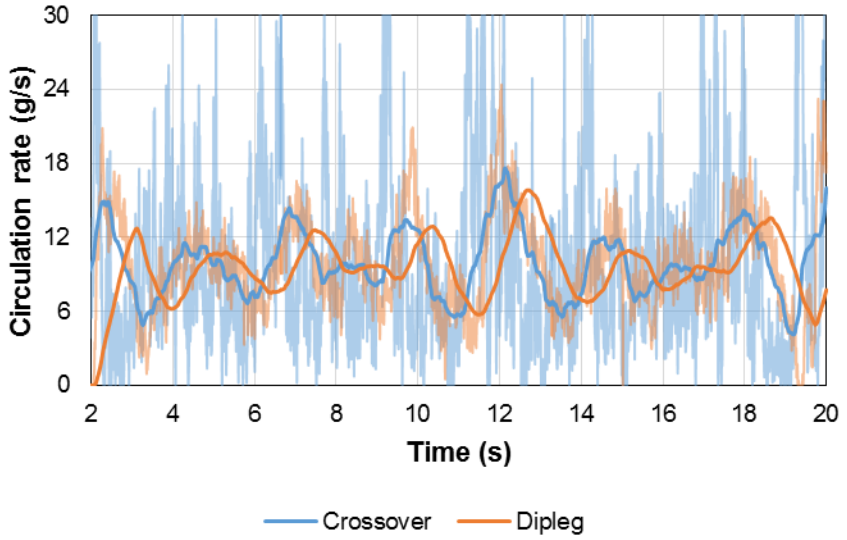
Chemical Looping System Hydrodynamics





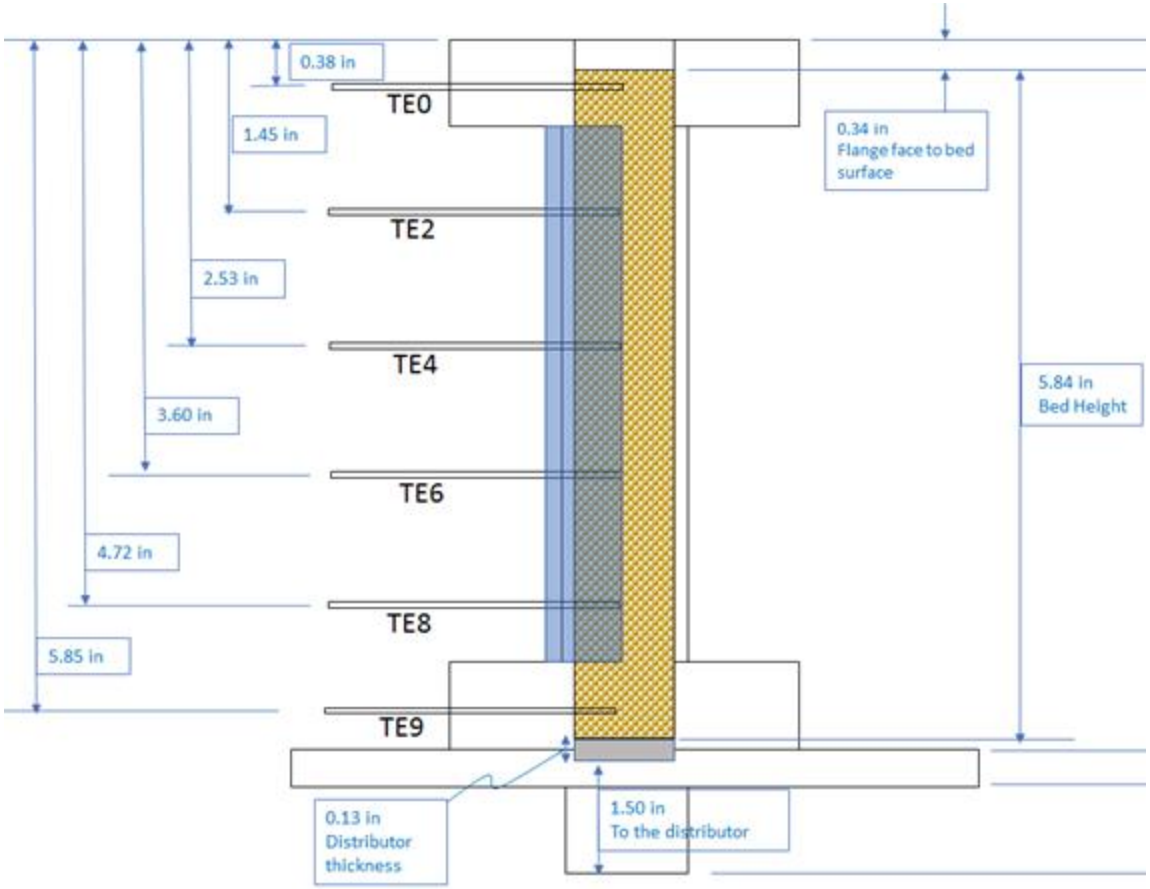
- Circulation rate is calculated in the middle of the crossover and in the dipleg just below the primary cyclone

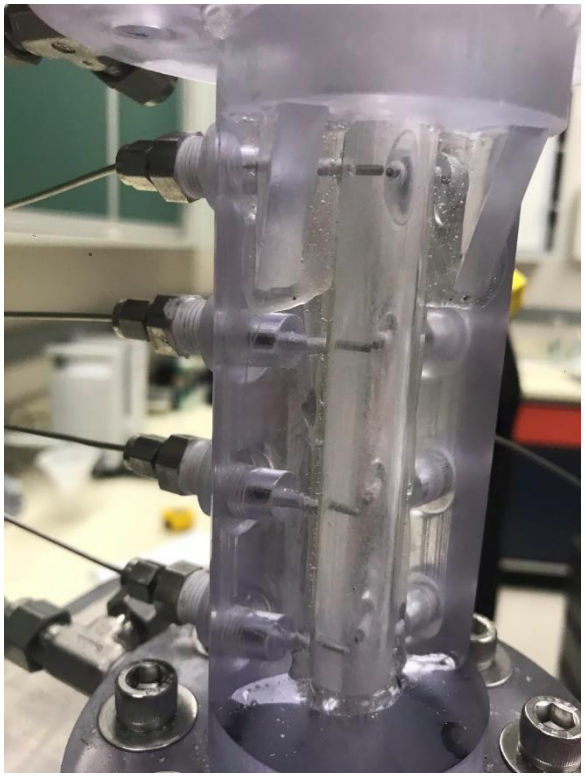
Circulation rate	$\dot{m}_s$ (g/s)
Crossover	10.30
Dipleg @ 48.5 cm	9.86



Step 3: Zeolite Adsorption Kinetics

- A 0.5”Ø × 6” cylinder was filled with a fixed bed of 13X zeolite in a downflow configuration of 10 vol. % CO_2 / rest N_2 to determine the CO_2 adsorption kinetics





Determining Kinetics from Experiment

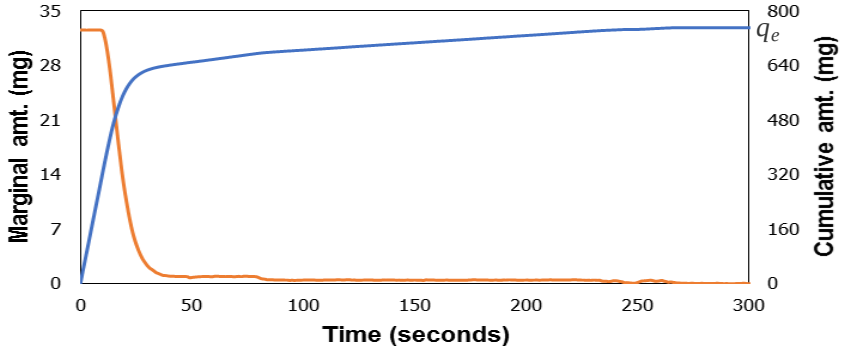
- Experiment is conducted at 3 temperatures
- The difference between inlet and outlet CO_2 flow gives the CO_2 amount adsorbed in the fixed bed column
- The linear driving force model is used to fit the experimental data

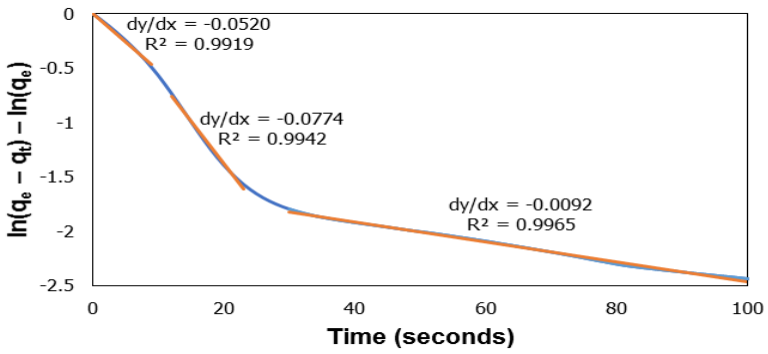
$$\frac{dq_t}{dt} = k(q_e - q_t)$$

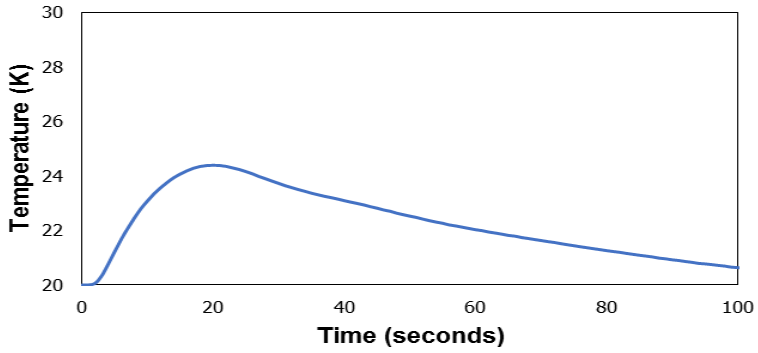
$$\Rightarrow \ln(q_e - q_t) - \ln(q_e) = -k \cdot t$$

Temp. (K)	q_e (mg)	k (1/s)
293.15	405.66	0.0763
303.15	323.17	0.1455
308.15	295.70	0.1806

- Plotting k vs. T and q_e vs. T, nominal relations between these variables are obtained







Calibrating Kinetics from Simulation

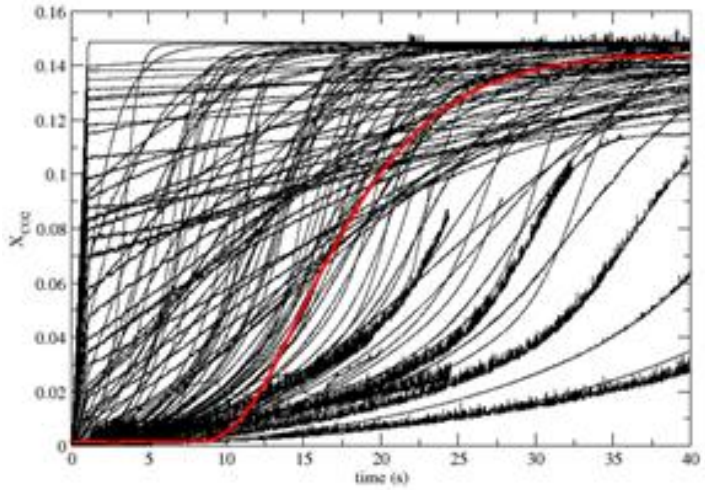
$$k = \exp(15.4184 - 5270.3515/T_p)$$

$$q_e = -7.4620\,T_p + 2591.1727$$

- Due to uncertainties in the temperature measurements, simulations of the fixed bed setup are conducted implementing a parameter sweep of the reaction kinetics coefficients around their nominal values (in red)
- The input parameter space is sampled with a 128-point space-filling design using the Latin Hypercube optimized genetic algorithm in Nodeworks
- The final "optimized" reaction scheme is given by

$$k = \exp(16.0 - 4928.0/T_p)$$

$$q_e = -7.6\,T_p + 3268.0$$



Step 4: Chemical Looping System w/ Reactions

- The next step is to incorporate the optimized adsorption reaction rate scheme into the validated cold flow simulation of the full chemical looping system
- The CO_2 concentrations at the riser outlet (primary cyclone) and the regenerator outlet (secondary cyclone) will be used to validate the comprehensive model
- This work is currently ongoing

Conclusions

- Solid-gas hydrodynamics and reaction rate kinetics for CO_2 adsorption on 13X zeolite are individually validated/calibrated against experimental data
- Simulation results of cold-flow in the simple CFB and the full chemical looping setup using the Hill-Koch-Ladd drag model show excellent match with experimental data
- The "optimized" reaction kinetics scheme is able to predict the CO_2 adsorption performance of the 13X zeolite sample accurately
- The utility of MFiX-DEM as a high-fidelity simulation tool capable of predicting key performance parameters for challenging multiphase applications is demonstrated

Acknowledgements & Disclaimer

- **Acknowledgements**

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- **Disclaimer**