CCSI²

Carbon Capture Simulation for Industry Impact

Contactor Design for Transformational Sorbents: Application to LBNL MOF

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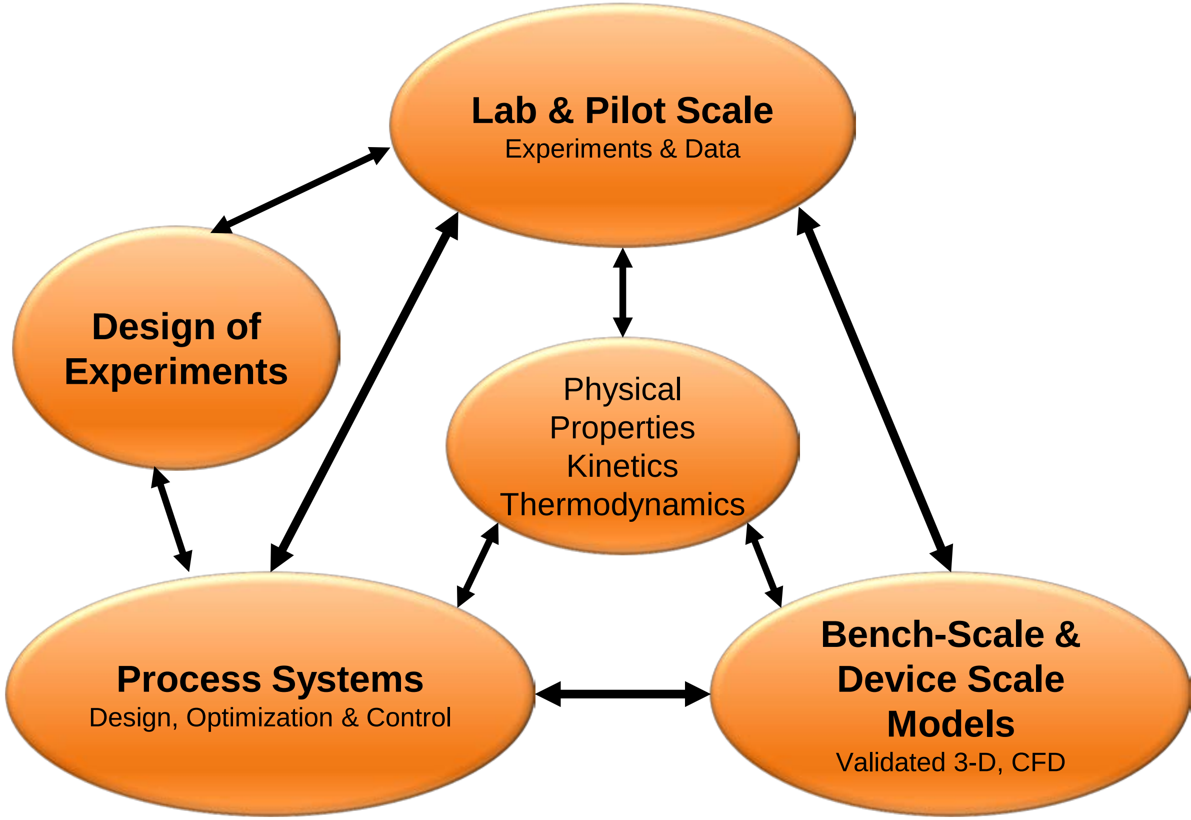
Outline

- ❑ Exploiting transformational sorbents: LBNL MOF
- ❑ Process Modeling
- ❑ CFD Modeling
- ❑ Design of Experiments
- ❑ Upcoming/Future Works

Exploiting Transformational Sorbents: LBNL MOF

- Complex and highly nonlinear equilibrium and kinetic characteristics
- Need to exploit the step-shaped isotherms
- Limiting mechanism is likely to be heat transfer, possibly along with mass transfer- both strongly depend on contactor type, design, and configuration
- Heat recovery from the hot solid is critical for reducing the energy penalty but can be challenging
- Lack of understanding of mass/heat transfer characteristics and hydrodynamics for different contactor types under various operating regimes
- Multiple spatial and time scales are of interest
- Strong tradeoff between CAPEX and OPEX



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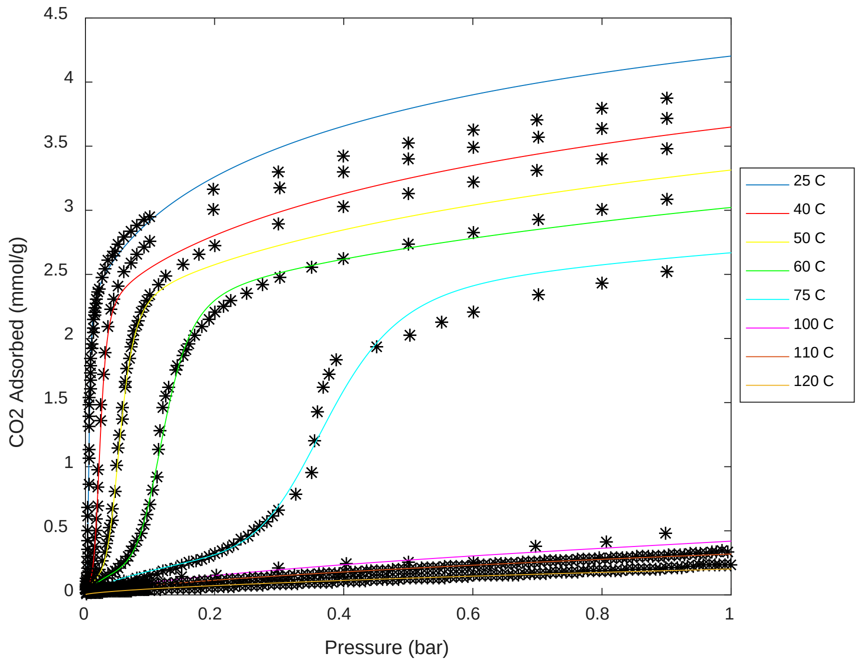
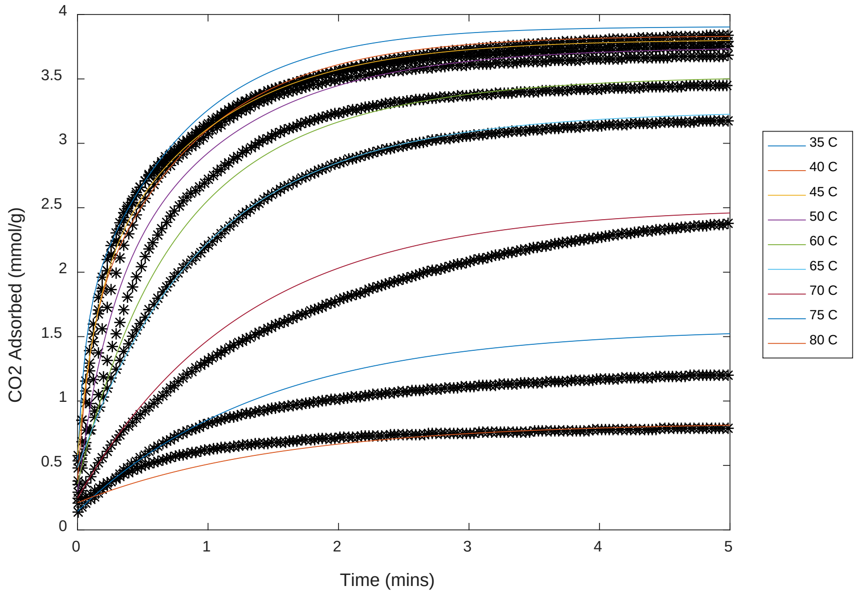
Isotherm Model

- Traditional isotherm models unable to predict experimental data
- Sips isotherms have been successfully used to model CO_2 adsorption on MOFs and activated carbons[1,2]
- Modified dual-site Sips isotherm developed taking into account both chemisorption and physisorption



Kinetic Model

- A kinetic model is developed by considering both the physisorption and chemisorption
- Model parameters are estimated using TGA data from LBL



1 - Bao, Z., Yu, L., Ren, Q., Lu, X., Deng, S. Adsorption of CO_2 and CH_4 on a magnesium-based metal organic framework. Journal of Colloid and Interface Science. 2011; 353, 549-556

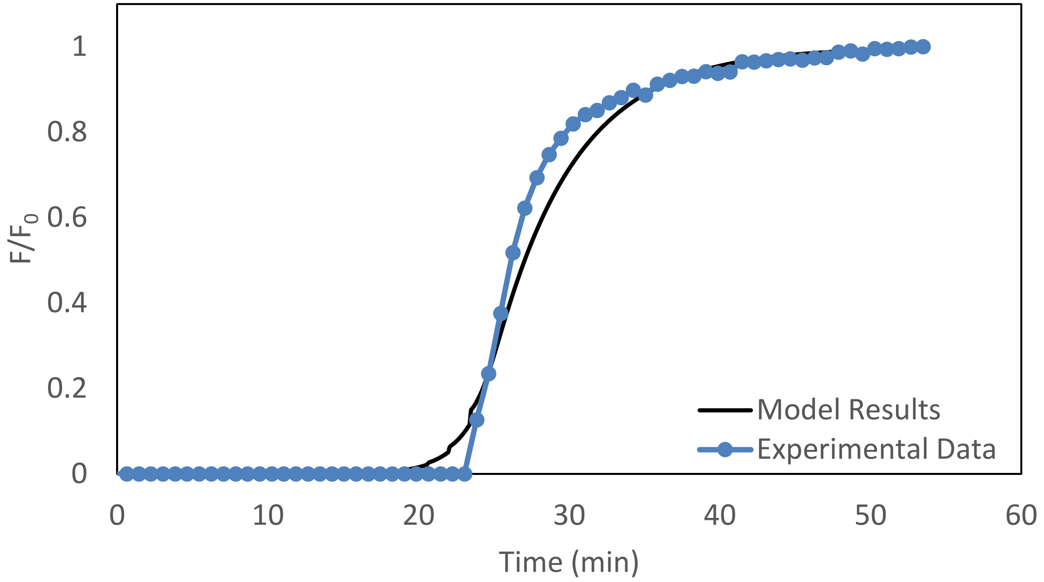
2 - Tzabar, N., Brake, H. Adsorption isotherm and Sips models of nitrogen, methane, ethane, and propane on commercial activated carbons and polyvinylidene chloride. Adsorption. 2016; 22, 901-914

Axial-Flow Fixed Bed Model

- Dynamic, 1-D, non-isothermal model
- Incorporates external and internal mass transfer resistances

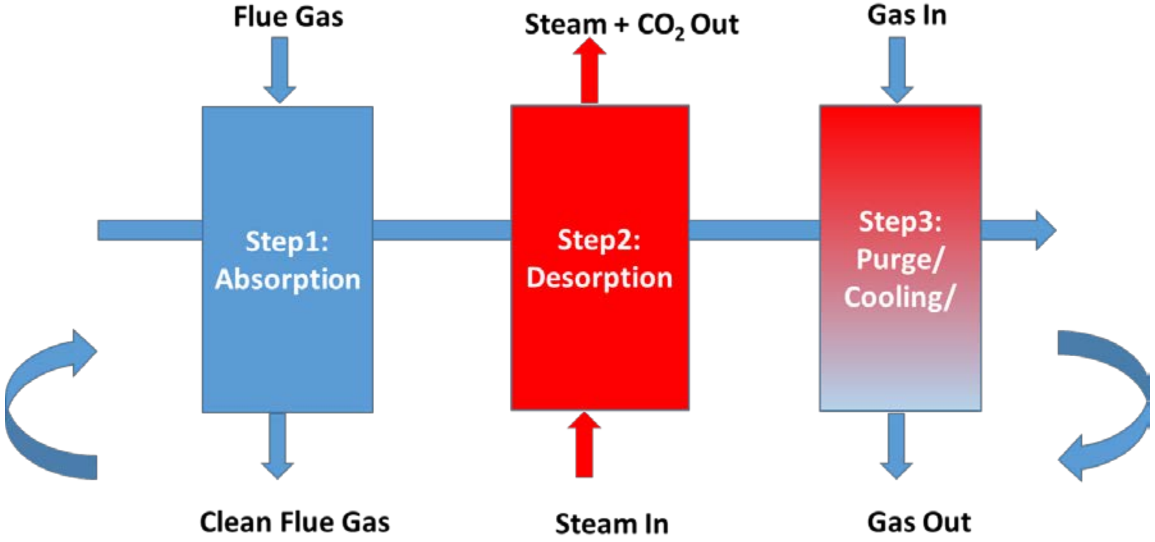
Lab-Scale Model Validation

•Lab scale experimental data from LBNL for the powdered material



Process Scale

- Temperature swing adsorption (TSA) cycle using an embedded heat exchanger
- Sized to process flue gas from a gross 644 MWe power plant[1]

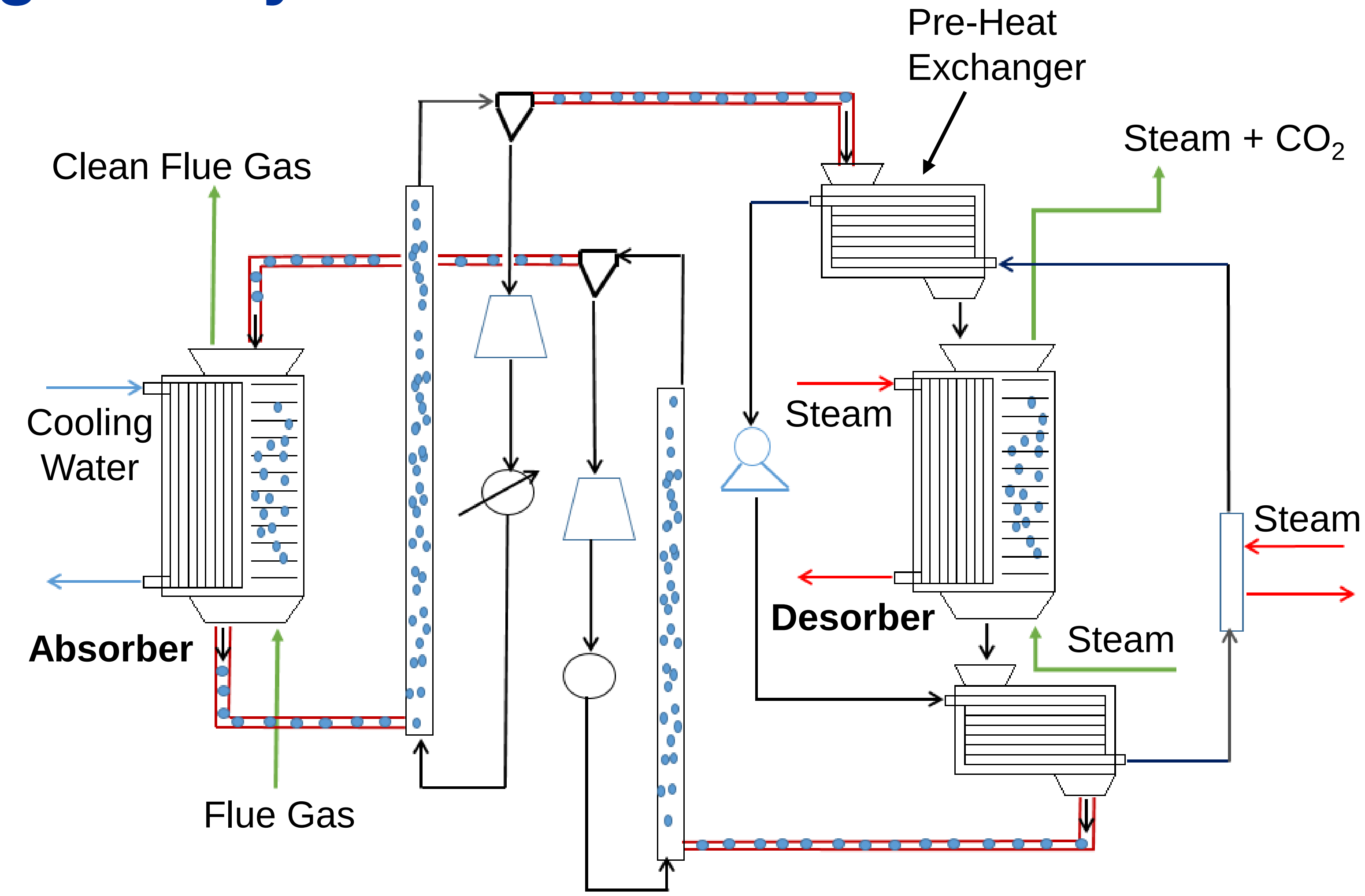


•**Key Observation**: Breakthrough time can increase by about 4 times for isothermal operation in comparison to adiabatic operation

1 - Fout et al., Cost and Performance Baseline for Fossil Energy Plants Volume 1. 2015. DOI: DOE/NETL-2015/1723.y

Moving Bed Dynamic Model

- 1-D two-phase pressure-driven non-isothermal dynamic model of a moving bed reactor
- Cooling water used in the adsorber while steam used in the desorber
- An integrated process is set up by including the adsorber, desorber, and heat recovery system
- Heat exchange among gas, solid and with the embedded heat exchanger considered



Techno-Economic Analysis

- Techno-economic analysis using equivalent annual operating cost (EAOC)

$$EAOC = Capital\ cost \left[\frac{i}{(1-(1+i)^{-n})}\right] + Yearly\ Operating\ Costs$$

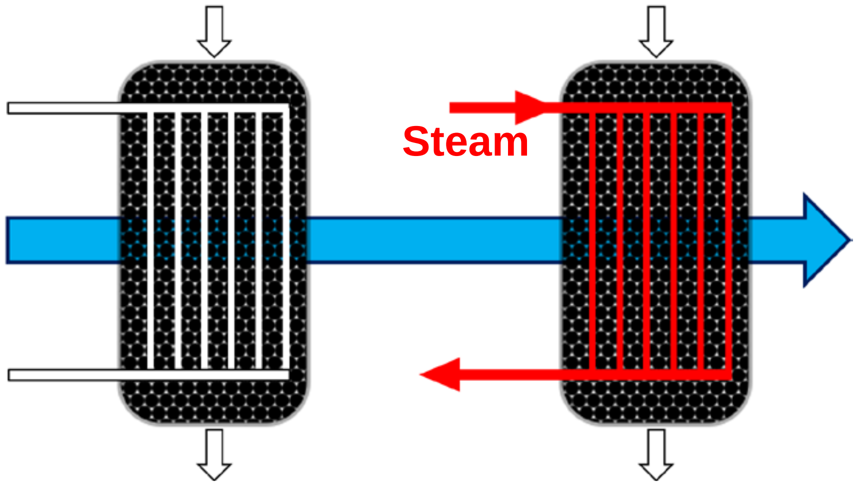
i = Discount Rate
n = Number of Years

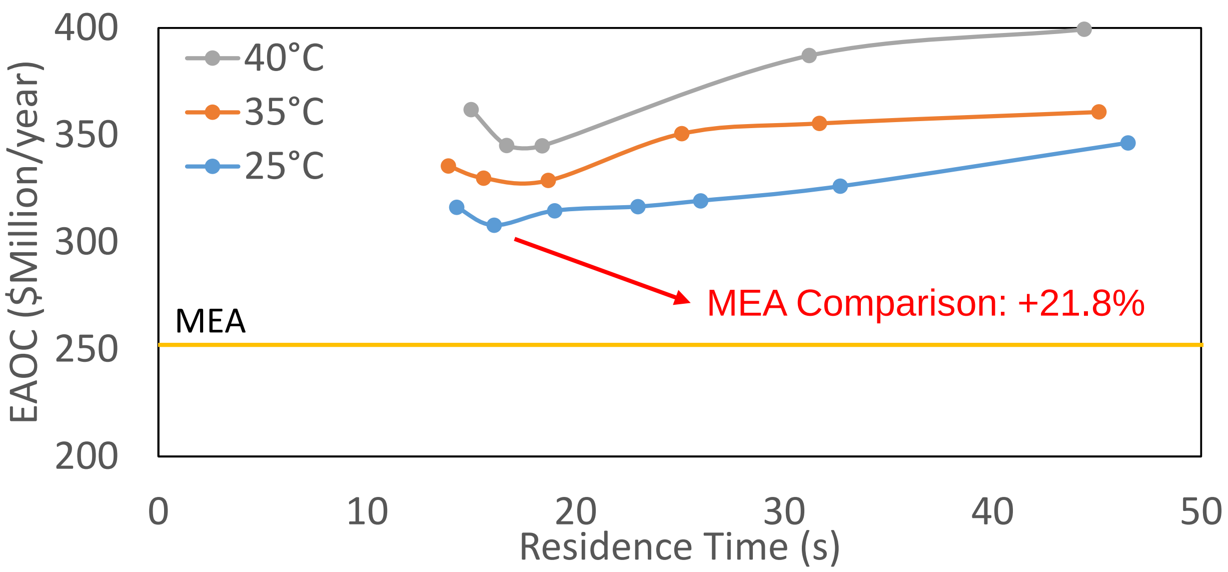
- Capital cost evaluated using Aspen Process Economics Analyzer (APEA) and standard correlations[1]
- Operating costs includes process utilities- steam, electricity, and cooling water
- Comparison to a traditional MEA system[2]

1 –Turton R, Shaeiwitz J A, Bhattacharyya D, Whiting W B, "Analysis, Synthesis, and Design of Chemical Processes", 5th Edition, 2018, Prentice Hall, NJ

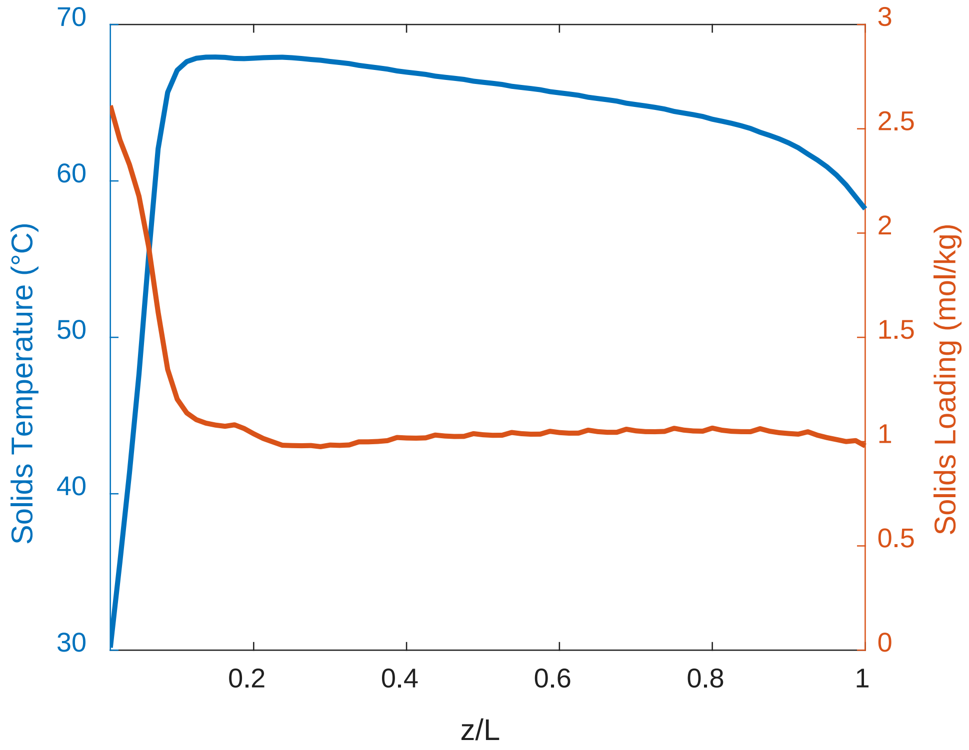
2 - Fout et al., Cost and Performance Baseline for Fossil Energy Plants Volume 1. 2015. DOI: DOE/NETL-2015/1723.y

Basic TSA Process





- No thermal management during adsorption results in sharp temperature spikes and low solid loadings



Temperature and loading profiles at end of adsorption step for a specific basic TSA process case

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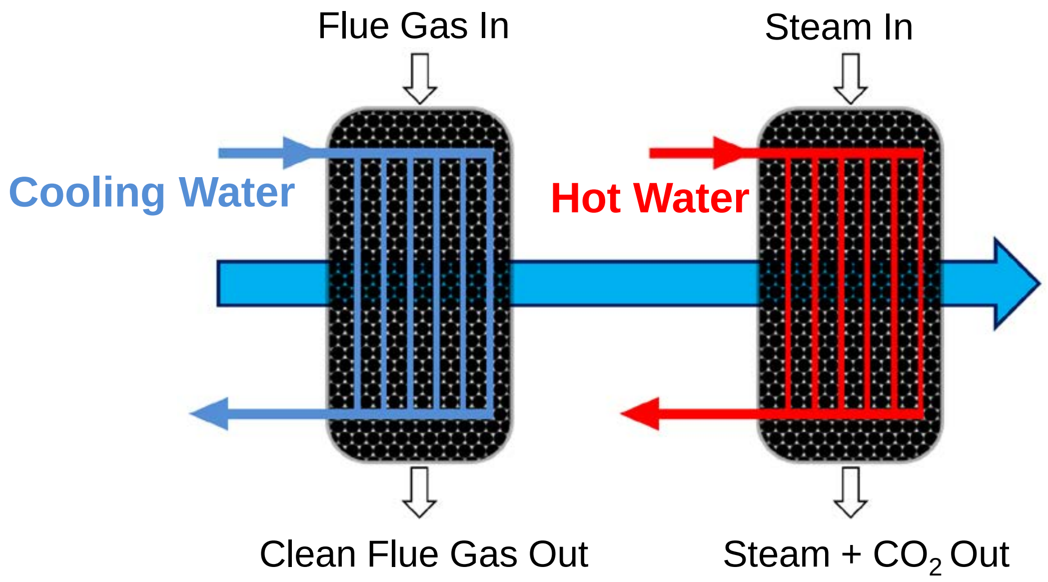
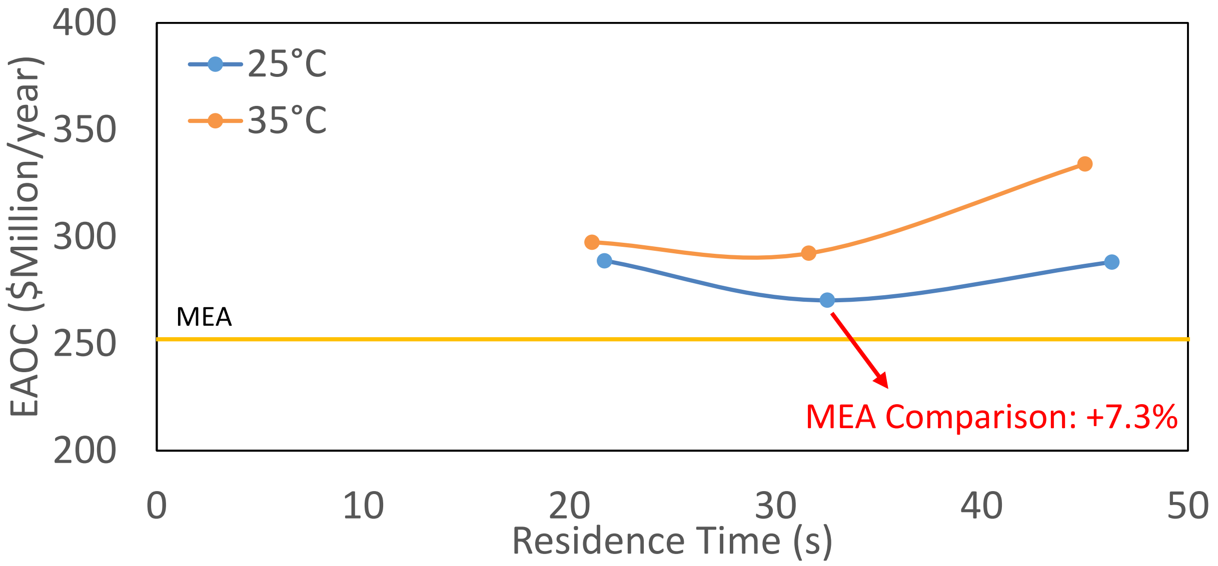
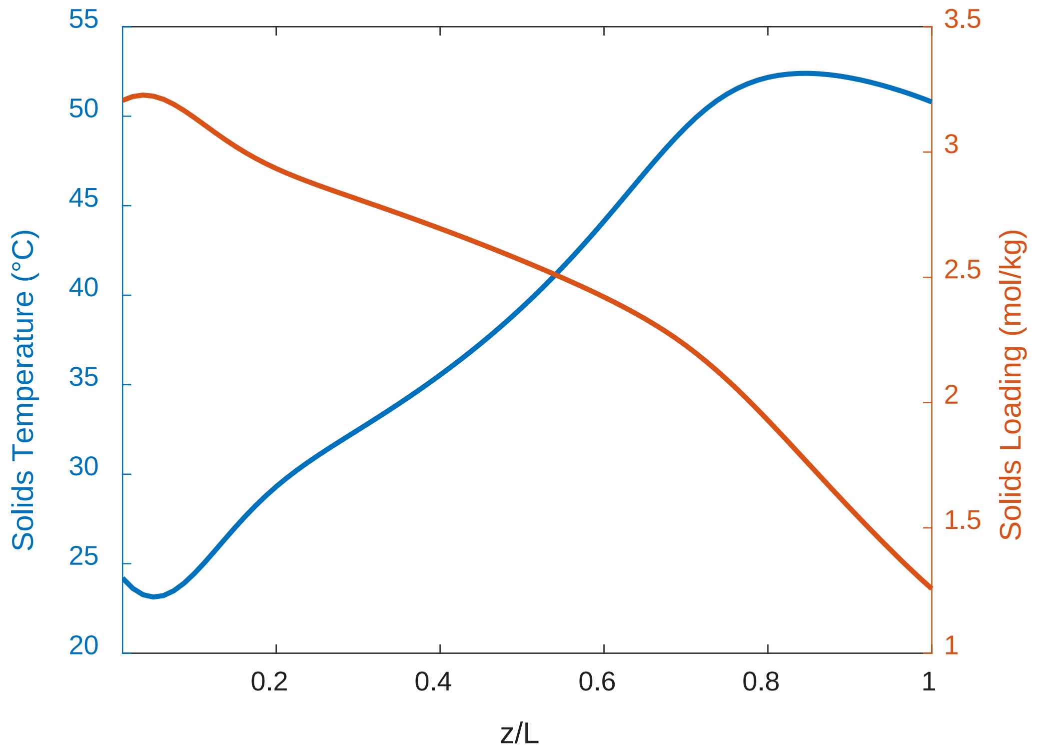
Modified TSA Process





Increase in average bed loading: 133%

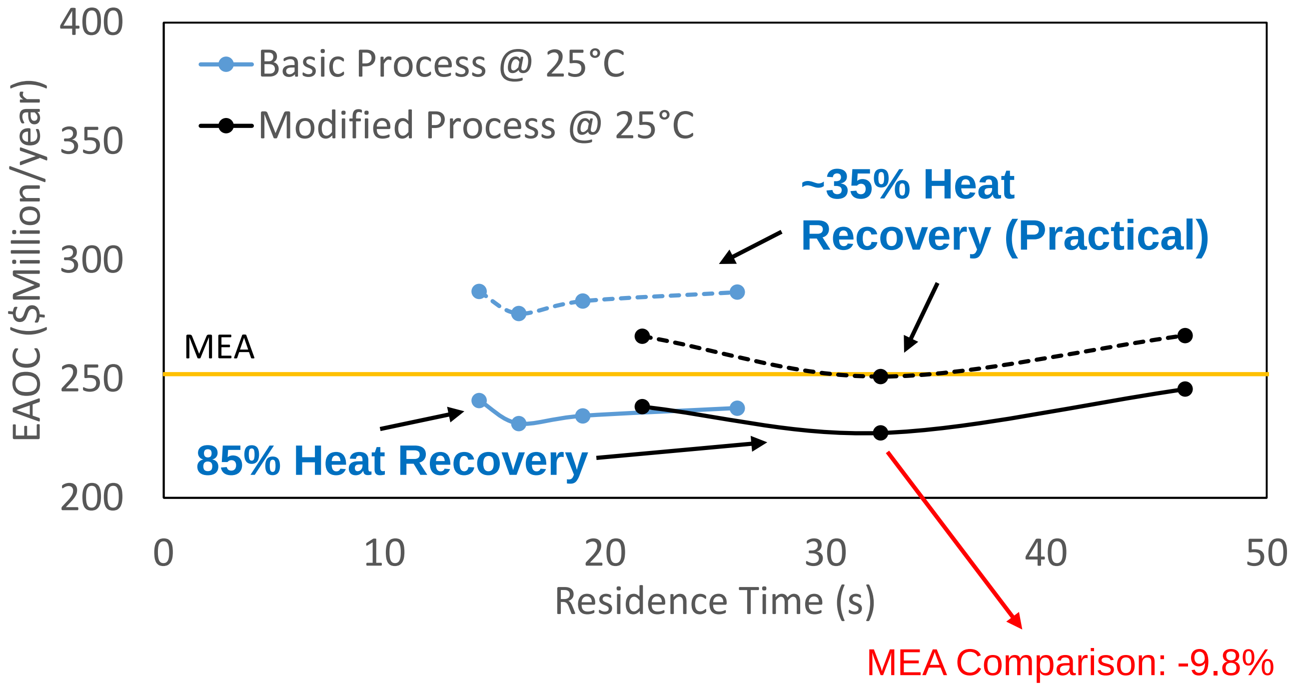


Temperature and loading profiles at end of adsorption step for a specific modified TSA process case

Modified TSA Process with Heat Recovery

Heat Recovery

- Utilizing remaining sensible heat at the end of desorption
- MEA systems can achieve about 85% heat recovery which may not be feasible for a gas-solid system

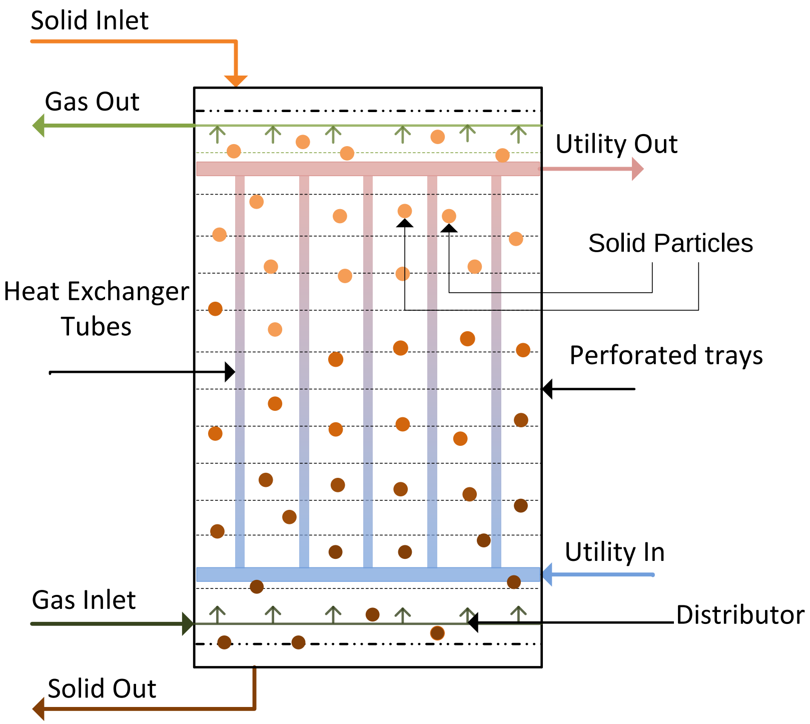


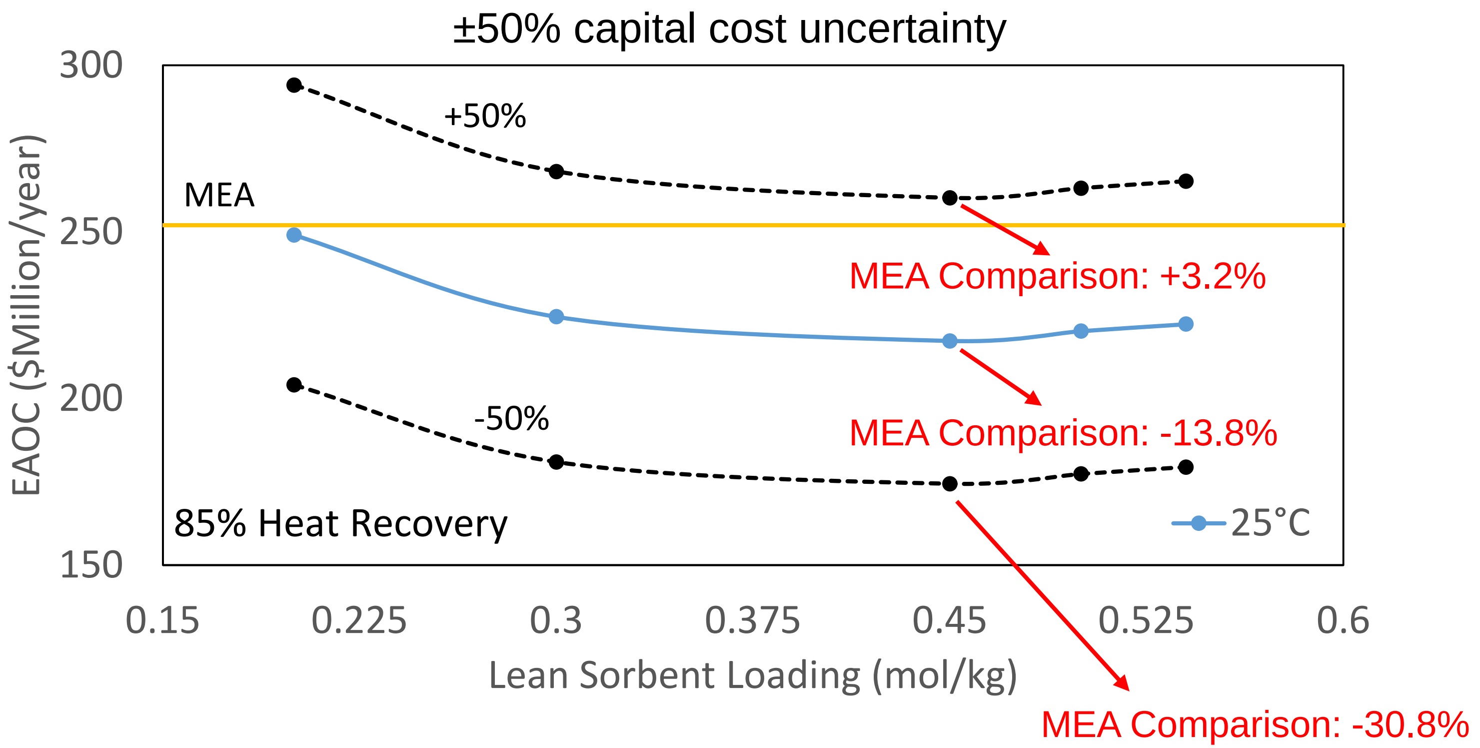
Energy Requirements	Basic TSA Process Using Steam	Modified TSA Process with Cold/Hot Water in Integrated HE*
Sensible Heat (MJ/kg CO_2)	0.76	0.39
Reaction Energy (MJ/kg CO_2)	1.48	1.48
Total Regeneration Energy (MJ/kg CO_2)	2.24	1.87

*For lowest EAOC cases with practical heat recoveries

Moving Bed Analysis

- Capital cost uncertainty
  - ±50% to account for uncertainties in the moving bed process equipment





Process Modeling Highlights

- Techno-economic analysis shows potential to improve when compared to traditional MEA system
  - **Fixed bed system**: cooling during adsorption and 35% heat recovery result in similar EAOC as the MEA system
  - **Fixed bed system**: cooling during adsorption and 85% heat recovery result in 10% decrease in EAOC compared to the MEA system
  - **Moving bed system**: For the nominal cost, about 14% decrease in EAOC compared to the MEA system can be achieved. If the capital cost is lower by 50%, then 30% reduction in EAOC may be possible.

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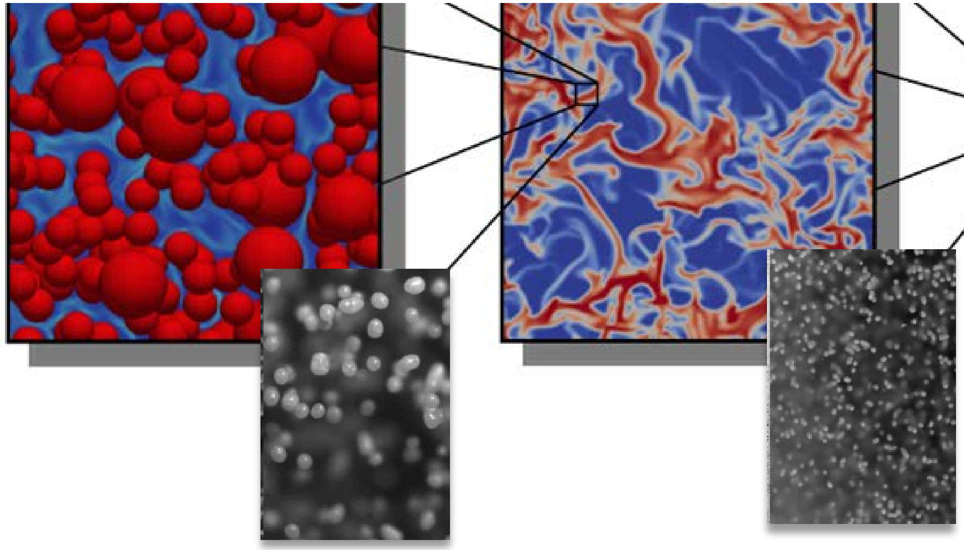
Multiphase Flow Modeling

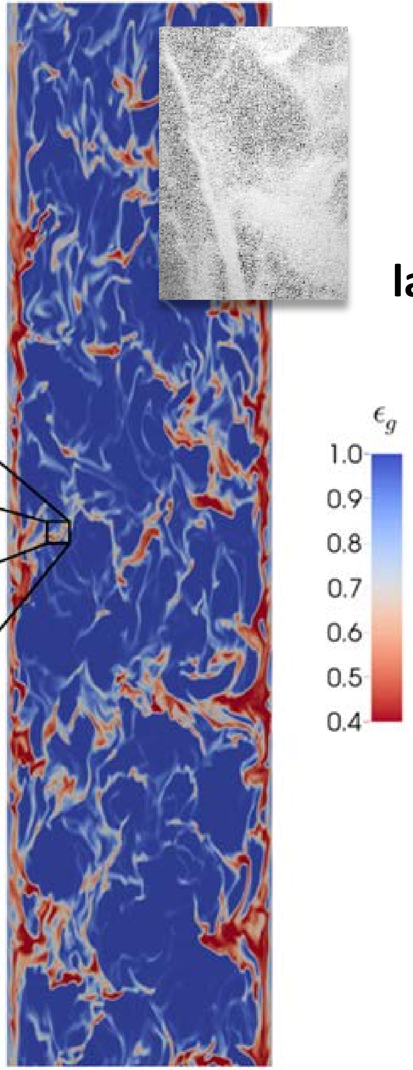
Why CFD for MOF?

Efficiency of CO_2 adsorption will depend on overall flow distribution and local inhomogeneity

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

Use MFIX to predict 3-D distributions in volume fraction, temperature and species concentration

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

Chemistry and Mass Transfer

$$\boldsymbol{CO_2(g) \Leftrightarrow CO_2(s)_{c,\,p}}$$

$$\mathcal{R}_{g,CO2} = -\sum \mathcal{R}_{m,CO2,\propto}$$

$$\mathcal{R}_{m,CO2,\propto} = \varepsilon_m \rho_m X_{m,MOF} \frac{dn_\propto}{dt}$$

$$\frac{dn_\propto}{dt} = k_{ov,\propto}\left(n_\propto^*(P,T) - n_\propto\right) \quad \propto = c, p$$

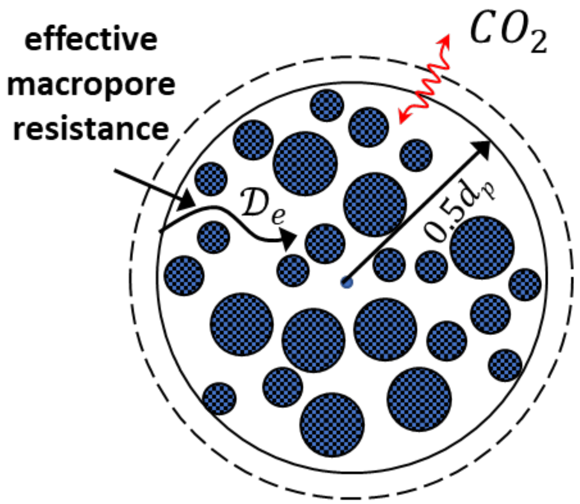


Fig. spherical porous adsorbent particle

$$\frac{1}{k_{ov,\propto}} = \frac{d_p^2}{60\varepsilon_p \mathcal{D}_e} + \frac{1}{k_\propto}$$

macropore resistance | reaction kinetics

Isotherm model for $n_\propto^*(P,T)$ based on WVU sub-model

- dual-Sips isotherm model for chemical/physical adsorption : parameterized with equilibrium data

Mass transfer model for $k_{ov,\propto}$ based on WVU sub-model*

- **reaction kinetics** : term introduced by WVU and parameterized with TGA data
- **macropore diffusion resistance** : parameterized with breakthrough data (molecular diffusion + Knudsen diffusion)
- **gas-film resistance** : neglected; looking to incorporate this term (separately like process model as opposed to within LDF)
- **micropore diffusion resistance** : neglected

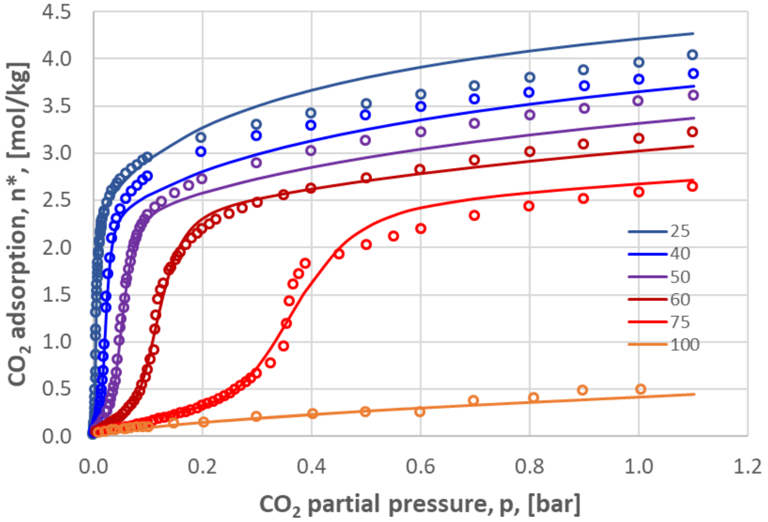
*Similar to the Linear Driving Force model of Farooq/Ruthven (1990)

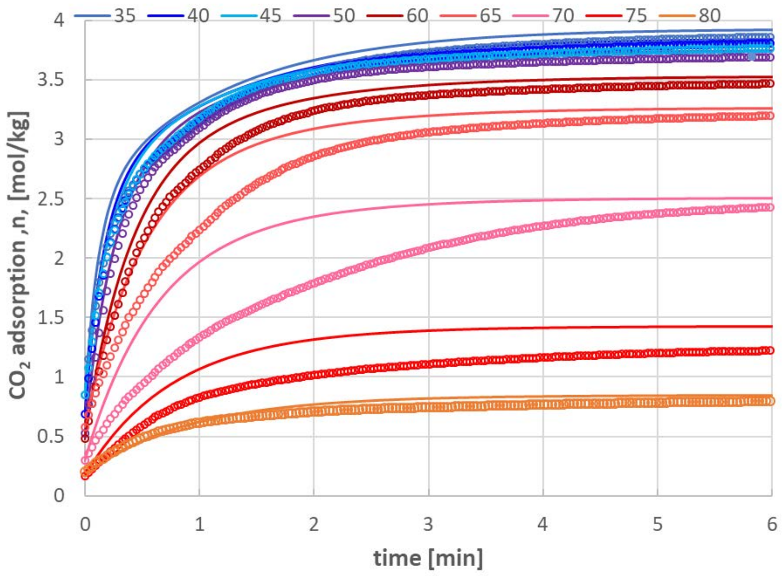
CFD Modeling Highlights

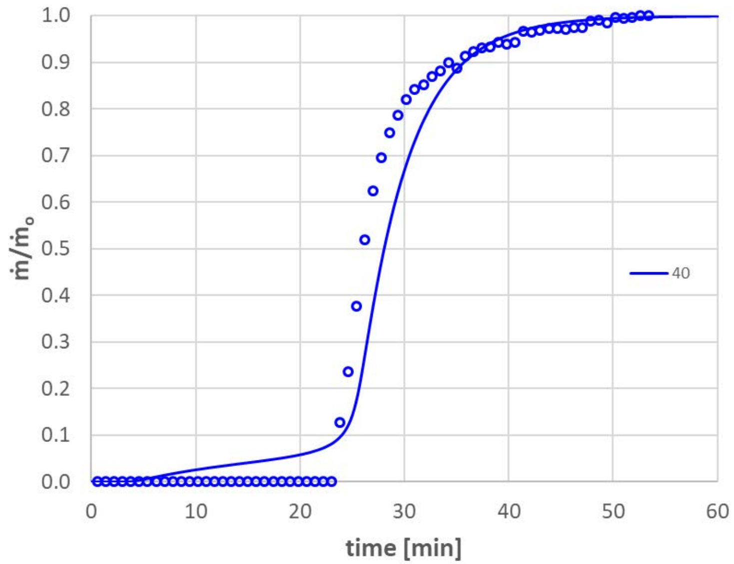
1. Incorporated chemistry, heat (preliminary) and mass transfer into CFD framework for diamine appended MOF : dmpn-Mg_2(dobpdc)

   Approach: CFD-TFM that includes adsorption isotherm and kinetics for CO_2 transfer and corresponding density changes.

2. Verified model with expected sub-model predictions and validated with data from LBNL: equilibrium isotherms, TGA and breakthrough experiments







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Design of Experiments for Sorbent Modeling and Characterization

Problem Statement: What experimental designs maximize useful information collection to:

- Create predictive models of sorbent processes and ultimately reduce uncertainty in technoeconomic optimization.
- Discern between proposed mechanisms to accelerate scientific understanding.

Accomplishments:

- U. Notre Dame joined CCSI^2 team in May 2019.
- Shared models from WVU to ND, creating software for parameter estimation.

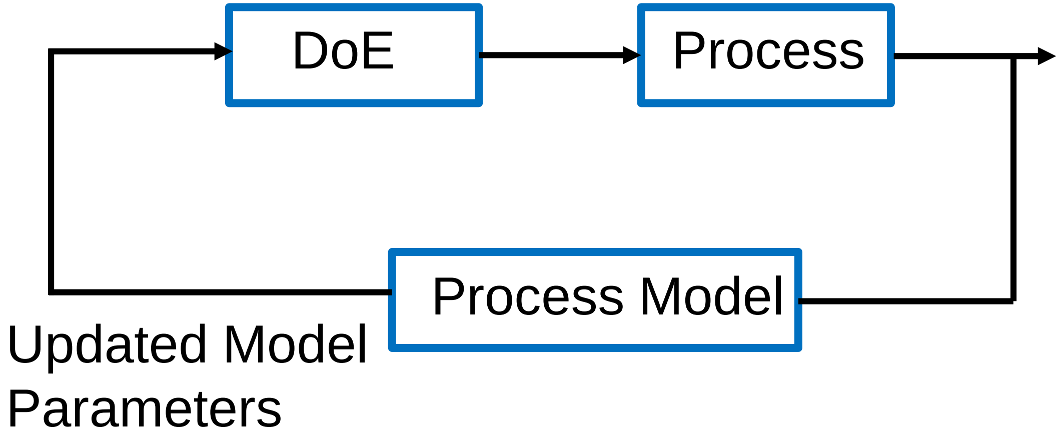
$$\frac{\partial C_{s,i}}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_{ma}\frac{\partial C_{s,i}}{\partial r}\right) + \frac{(1-\varepsilon_p)}{\varepsilon_p}\rho_s\frac{\partial q_i}{\partial t}$$

$$\frac{1}{D_{ma}} = \tau\left(\frac{1}{D_{k,i}} + \frac{1}{D_{g,i}}\right)$$

$$D_{k,i} = C_1 r_{pore}\left(\frac{T_S}{M_{w,i}}\right)^{C_2}$$

Parameters to be estimated

Local temperature inside particles cannot be measured



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Upcoming/Future Works

Process Modeling

- Further development of the kinetic model considering species other than CO_2
- Development of the mass transfer and heat transfer model using data from the shaped particles
- Radial flow fixed bed model development and optimization
- Rotary packed bed model development and optimization
- Bubbling/circulating fluidized bed model development and optimization

CFD Modeling

- Simulate/investigate contactor (packed/fluidized) performance under different conditions
- Finish extending to PIC-CFD & investigate $O(m)$ pilot scale adsorber
- Continue model refinement
- Add new sub-models as available : additional species mass transfer (H_2O/N_2)
- Incorporate gas-side mass transfer resistance : separately or part of LDF

Design of Experiments

- Complete identifiability analysis based on existing experimental capabilities
- Compute optimal experimental designs

Acknowledgements

- LBNL/UC, Berkeley (Jeffrey Long; Stephanie Didas; Rebecca Siegelman; Surya Parker; Alex Forse; Jeff Martell; Matthew Dods), Mosaic Materials (Thomas McDonald Carly Anderson, Graham Wenz) for the experimental data/support/valuable discussions