NETL Carnegie Mellon PENNSTATE University of Pittsburgh VirginiaTech WestVirginiaUniversity URS

A Novel Sub-pore Modeling Methodology for CO2 Capture in Meso-porous Particle Systems

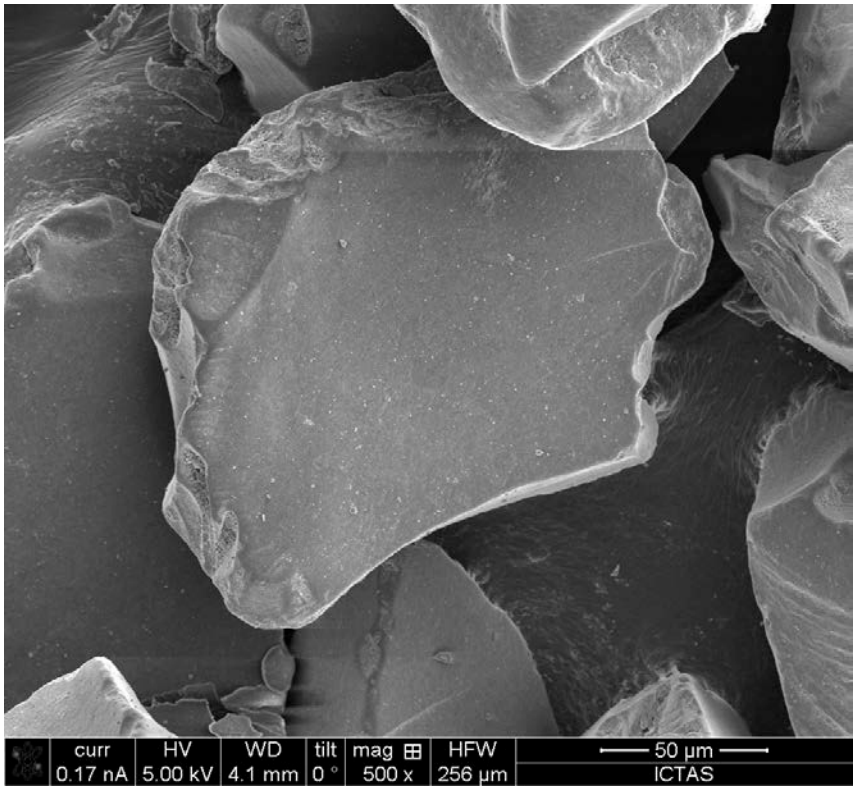
Nagendra Krishnamurthy & Danesh Tafti
HPCFD Lab, Virginia Tech.

U.S. DEPARTMENT OF ENERGY

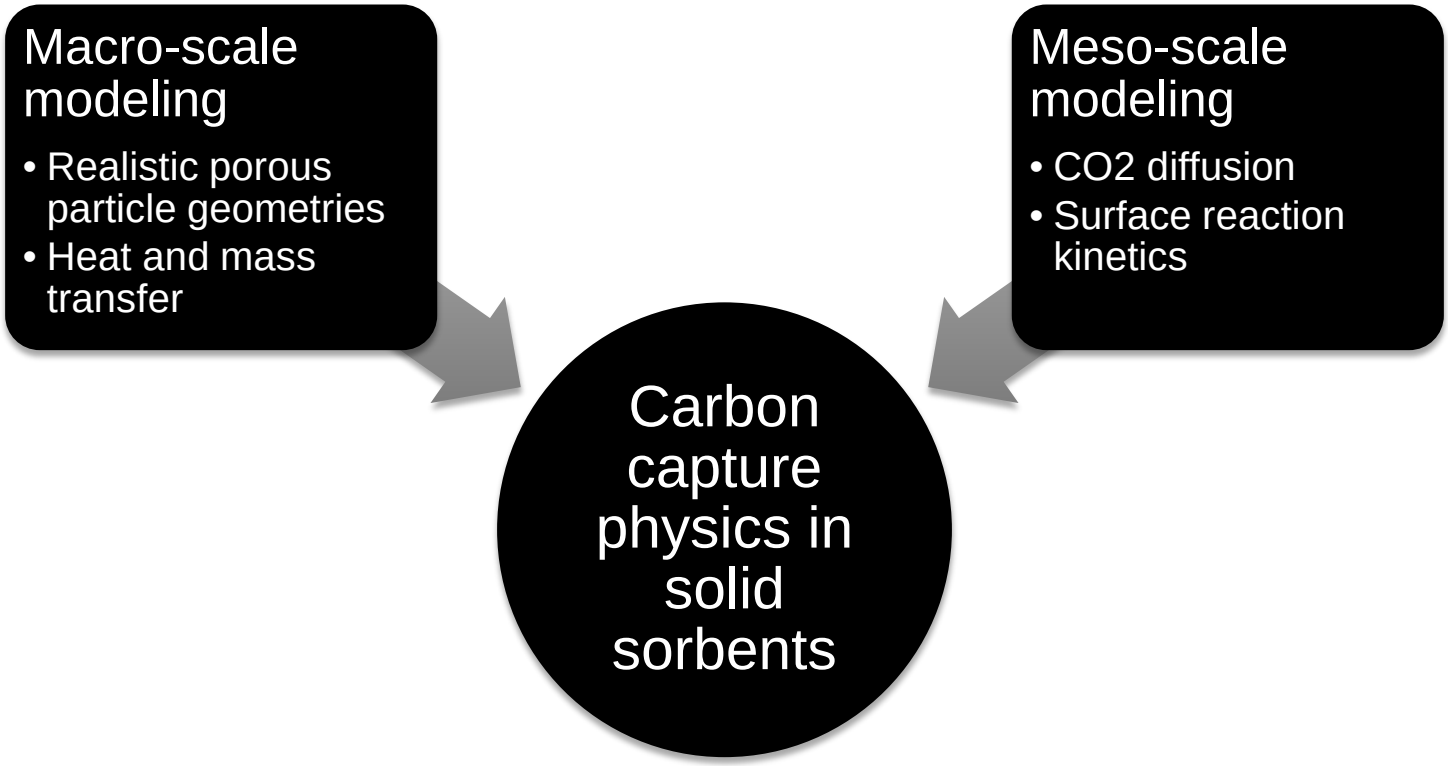
Motivation

- Sorbent particles for post-combustion carbon capture – PEI loaded **porous silica particles**

- Challenges in porous sorbent particle simulations
  - Complex porous **microstructures**
  - **Multi-scale** nature
    - 3-4 orders of magnitude
  - A variety of **physical phenomena** involved
    - Heat and mass transfer
    - Surface kinetics
    - …

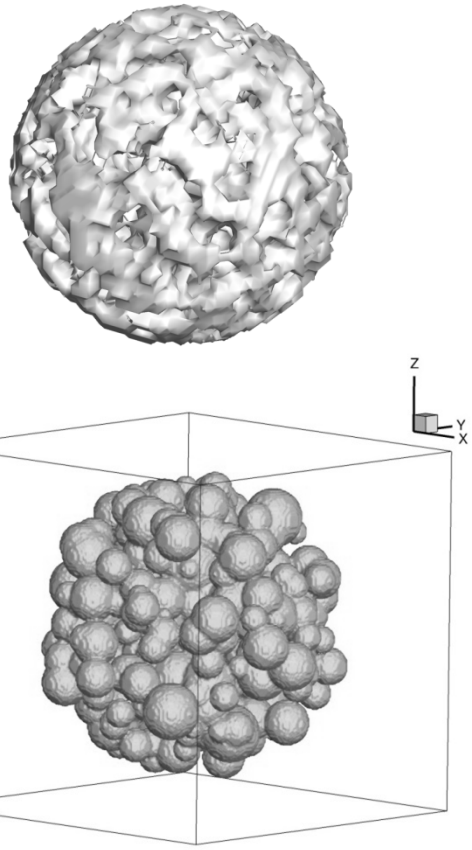


Approach


Macro-scale modeling
• Realistic porous particle geometries
• Heat and mass transfer
Meso-scale modeling
• CO2 diffusion
• Surface reaction kinetics
Carbon capture physics in solid sorbents

Macro-scale Effects

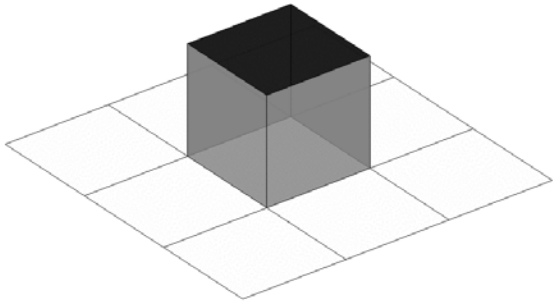
- IBM framework
  - Model flows through **intricate porous microstructures**
  - **Conjugate heat and mass transfer** capability.
- Sorbent geometry creation
  - Use experimentally obtained **statistical descriptors** such as porosity and autocorrelation functions.
  - **Stochastic** reconstruction procedure to match actual sorbent particles



Reconstructed porous spherical particles with porosities of 0.55 and 0.40, respectively

Meso-scale Effects

- Underneath the macro-pores, implementation of a fractal-type **‘sub-pore’** system
- Desired **porosity** and/or specific **surface area**
- Analogous to **sub-grid scale modeling** employed for turbulent flows
- Applicable to any surface underneath which **unresolved pore-scale effects** are to be modeled

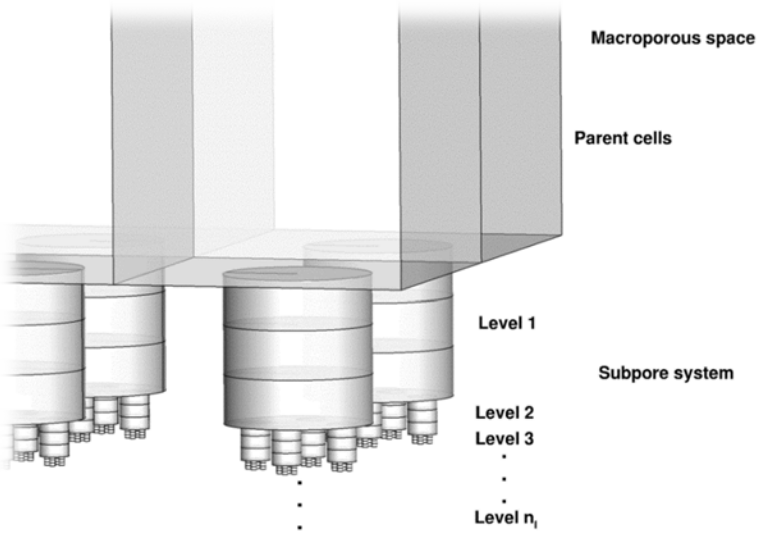


*Example Van Koch surface with cubic structures***

*** Source: Wikipedia*

Sub-pore Model

- A multi-level **fractal system** composed of structures of specified shape
- Within the sub-pore system, solve equations for
  - CO2 diffusion
  - Surface adsorption kinetics
  - Heat transfer
- Coupling with macro-pore system for **mass conservation**



Sub-pore model with cylindrical branching

Fractal Network

- **Multi-level subpore system**
  - Additional area per subpore:

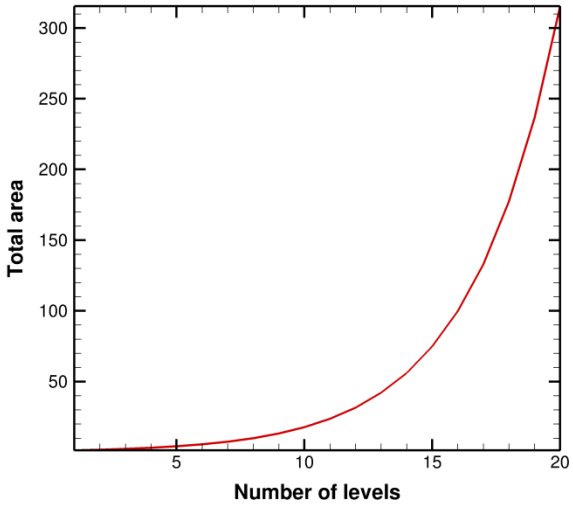
$$\Delta A = \sum_{i=1}^{n_l} n_b^{i-1} A_i = \frac{A\left((\mathrm{r_a^2 n_b})^{\mathrm{n_l}} - 1\right)}{\mathrm{r_a^2 n_b} - 1}$$

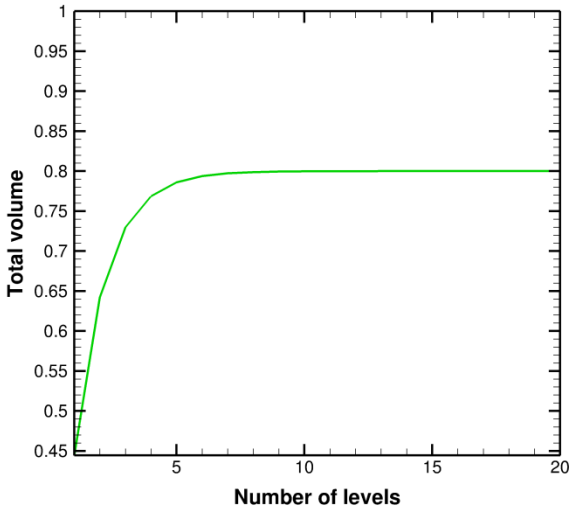
  - Total additional area due to all subpores

$$\Delta A_t = \left(A_{mp} n_{sp}\right) \Delta A$$

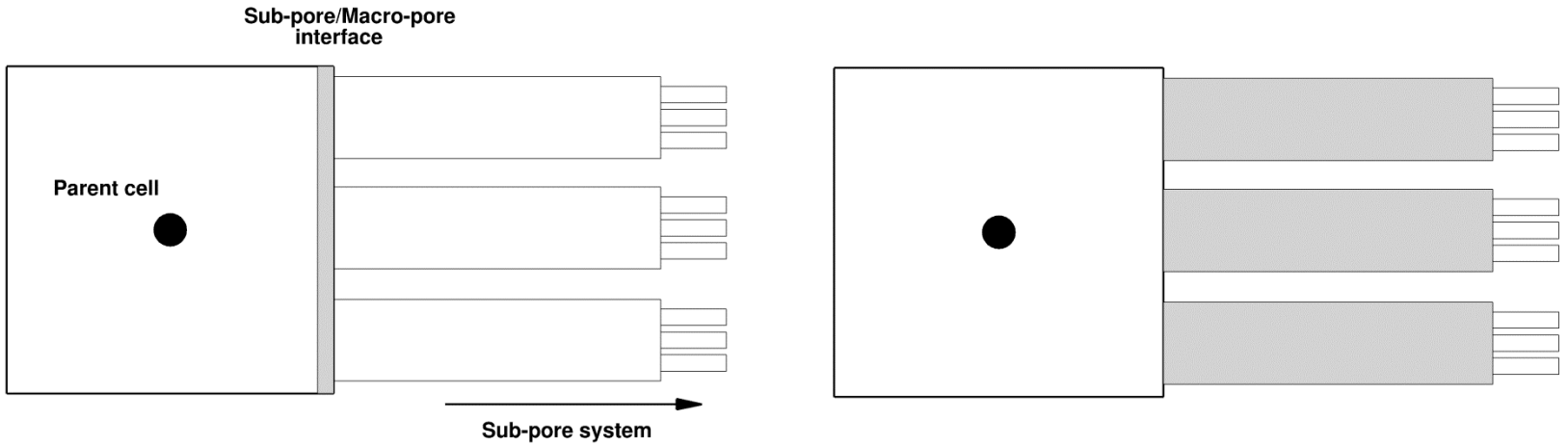
  - Increase in specific area of the particle due to introduction of subpore system

$$A_s = \frac{(A_{mp} + \Delta A_t)}{\rho V_p \left(1 - \epsilon_{mp} - \epsilon_{sp}\right)}$$





Sub-pore Model



Adsorption/Desorption Modeling

- **Rate equation derived from first principles**
  - Molecular wall impact rate

$$F = \frac{p}{\sqrt{2\pi m R_u T}}$$

  - Sticking model

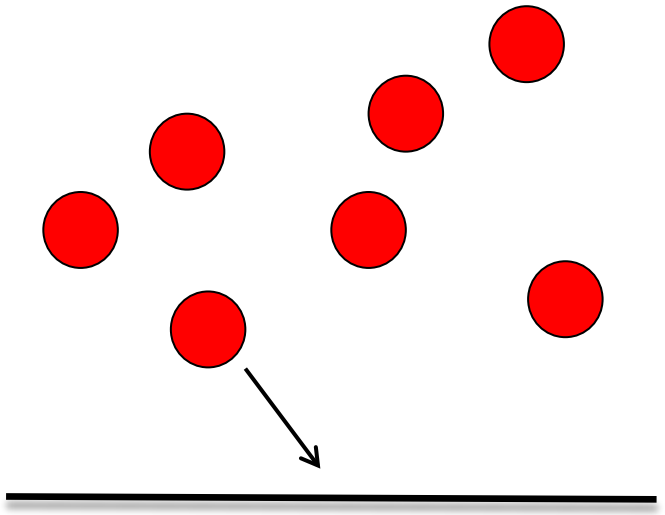
$$S = \mathrm{f}(\theta) \cdot \exp\left(-\frac{E_a}{R_u T}\right)$$

  - Rate of adsorption

$$R_{ads} = S \cdot F$$

  - Rate of desorption

$$R_{des} = f(T) \cdot g(\theta)$$



Surface with adsorption sites

  - Final form for rate equation

$$\frac{d\theta}{dt} = R_{ads} + R_{des}$$

Adsorption/Desorption Modeling

- **CO2 adsorption/desorption model**
  - Linear sticking model for CO2 molecules is used
  - Second order rate equation
  - Resulting equation is **non-linear** in θ
  - Parameters $N_S, E_{ads}, \Delta S, E_{des}$ will be from **experimental calibration**
  - Calibration using equilibrium surface coverage values (θ_{eq} obtained by using $\frac{d\theta}{dt} = 0$)

$$\frac{d\theta}{dt} = K_{ads}(1-2\theta)^2 - K_{des}\theta^2$$

$$k_{ads} = \frac{p}{\sqrt{2\pi m k_B T}} \cdot \frac{1}{N_s} \cdot \exp\left(-\frac{E_{ads}}{R_u T}\right)$$

$$k_{des} = -\frac{e\kappa k_B T}{h} \cdot \exp\left(\frac{\Delta S}{R_u}\right) \cdot \exp\left(-\frac{E_{des}}{R_u T_s}\right)$$

θ	surface coverage
p	partial pressure of CO2
N_s	no. of ads. sites per unit area
E_{ads}	Activation energy for adsorption
E_{des}	Activation energy for desorption
ΔS	Entropy of adsorption reaction
T_s	Surface temperature

Diffusion Modeling

- **Solve a 1D unsteady diffusion equation**

$$\frac{\partial(\rho y_i)}{\partial t} = \frac{\partial}{\partial x}\left(\rho D_{eff}\frac{\partial y_i}{\partial x}\right) + \omega_i$$

- **Diffusion coefficient computed using Bosanquet formula**

$$\frac{1}{D_{eff}} = \frac{1}{D_{bulk}} + \frac{1}{D_{Kn}} + \cdots$$

- **Temperature dependence of diffusion coefficients**
  - Chapman and Cowling correlation:

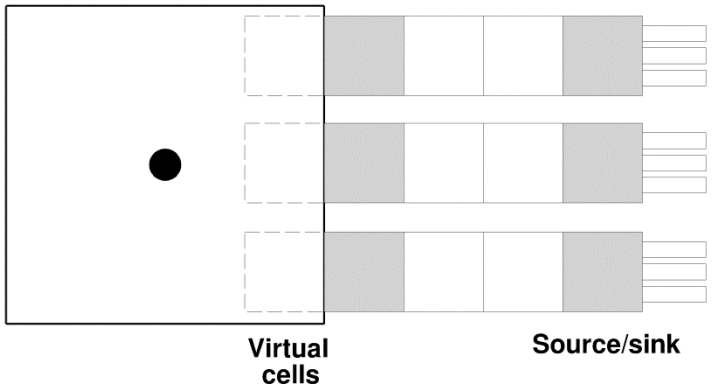
$$D_{bulk} = 0.001858\, T^{\frac{3}{2}} \sqrt{\frac{M_1 + M_2}{M_1 M_2}}$$

  - Knudsen diffusion:

$$D_{Kn} = \frac{1}{3} d_p \sqrt{\frac{8R_u T}{\pi M}}$$

Coupling Methodology

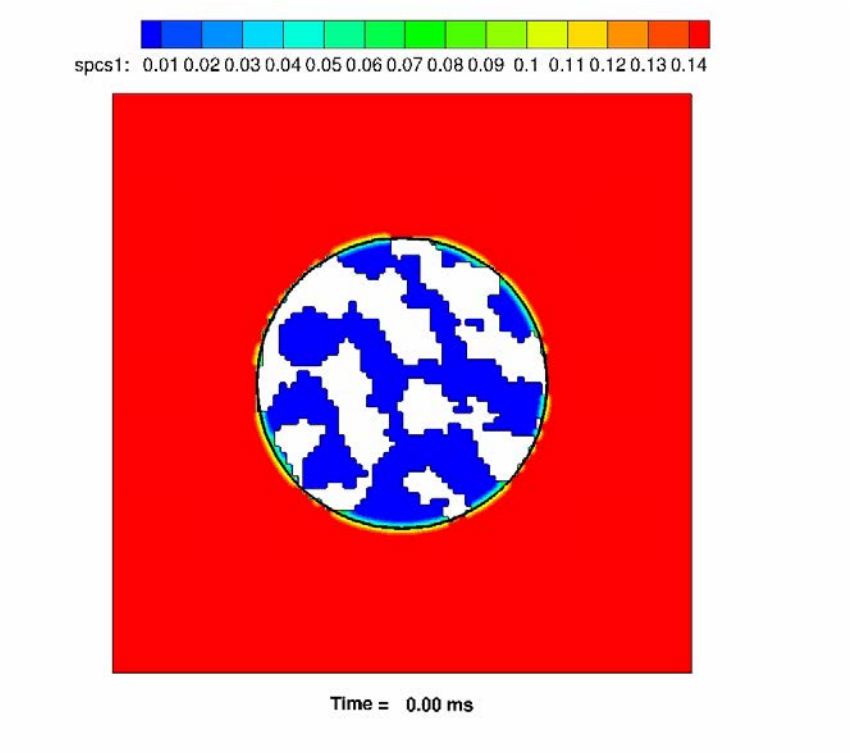
- Concept of **virtual cells**
  - If a neighboring cell is bigger, assume a virtual cell with same properties
- Mass **source/sink** term
  - If a neighboring cell is smaller, a zero flux BC and use a source/sink term



- Adsorption/desorption
  - Every cell has an additional source/sink

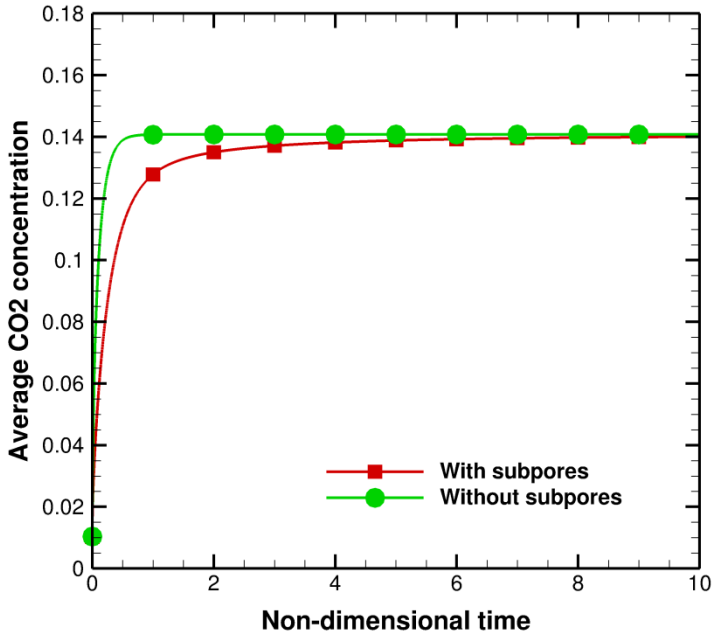
Results – 2D Particle

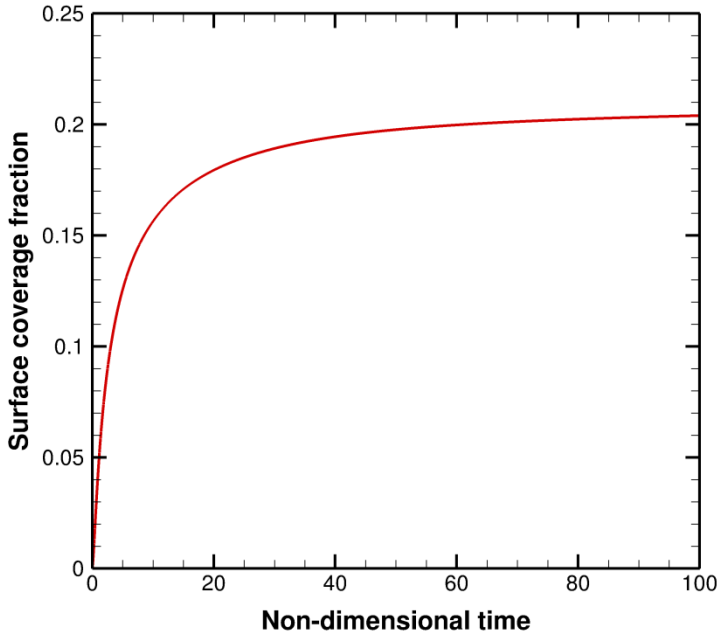
- 2D particle simulations
  - 100 microns diameter
  - 60% porosity
  - Initially 0% CO2
  - Surface area increase – 50
- Ambient conditions
  - 15% CO2 (and 85% N2)
  - Temperature – 300K
- Saturation times
  - Attain 95% of the asymptotic value



Results – 2D Particle

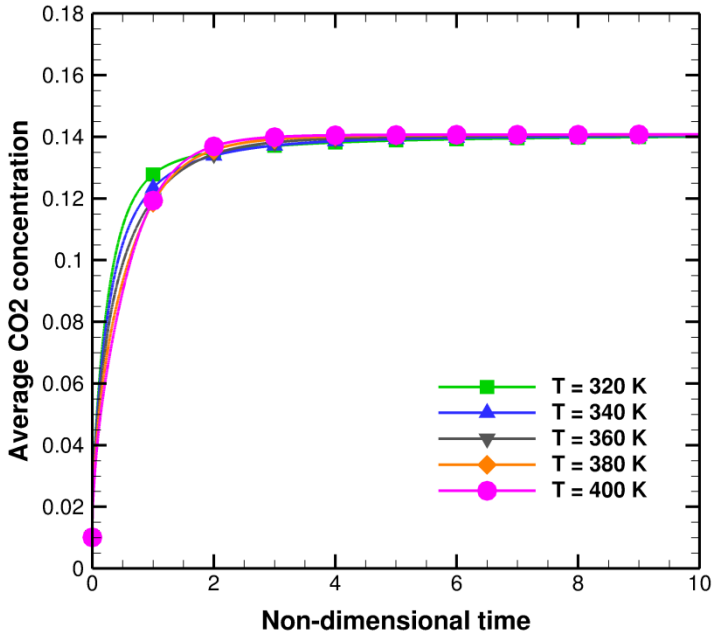
- Diffusion into particle pore space
- Adsorption on particle surface



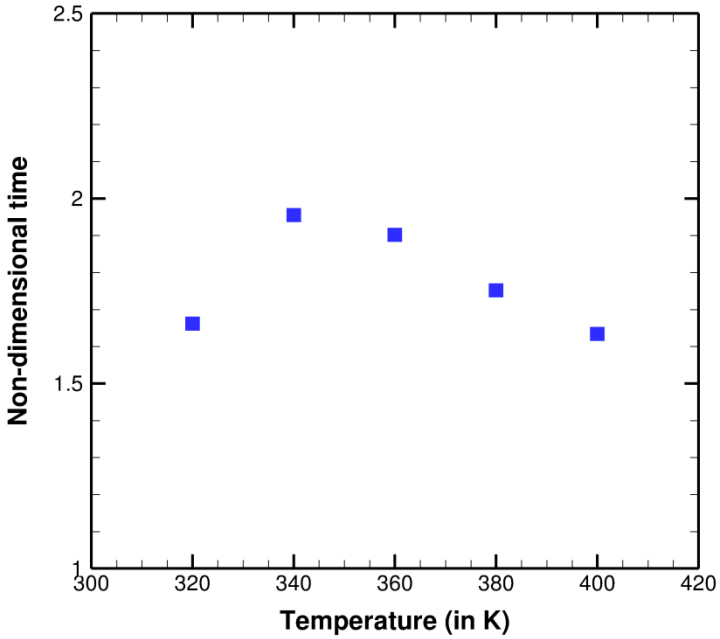


Results – Effect of Temperature

- Diffusion into particle pore space

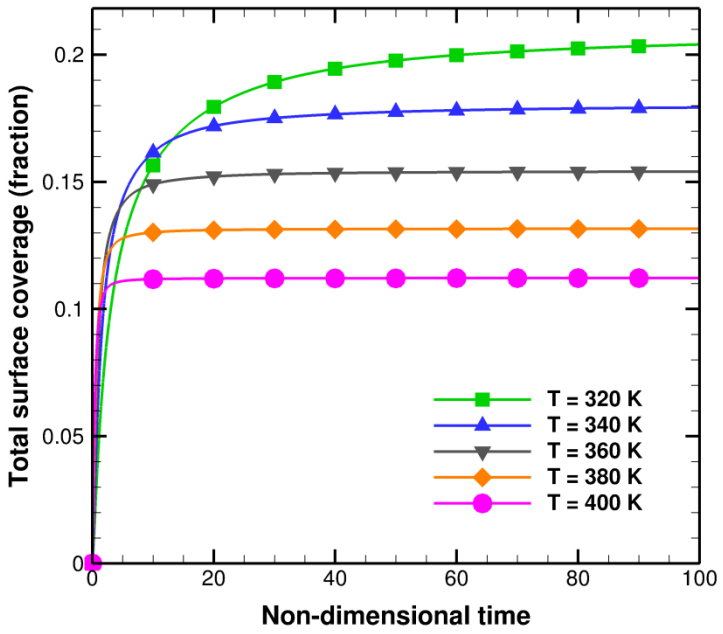


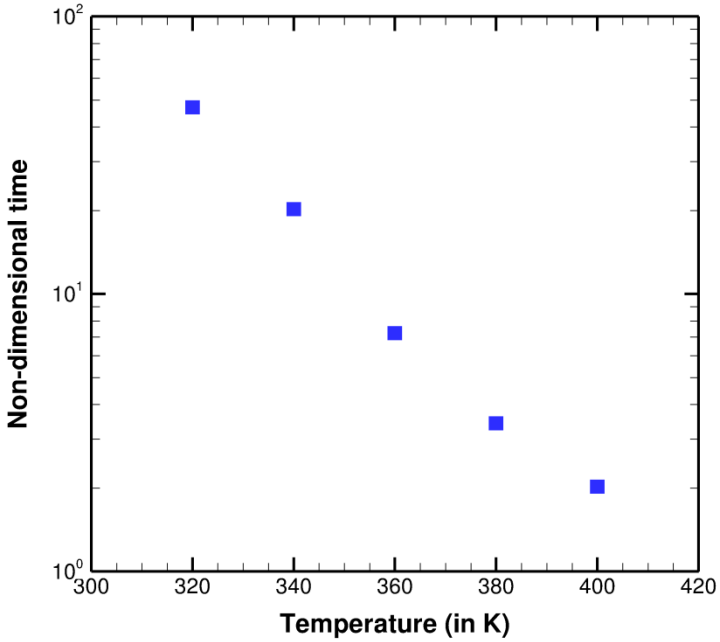
- Effect of temperature on saturation time



Results – Effect of Temperature

- Adsorption on the particle surface
- Effect of temperature on saturation time





Summary

- A novel **‘sub-pore’ modeling** methodology to account for meso-scale effects in porous particles
- Takes into account the **diffusion and surface adsorption** phenomena occurring at smaller scales
- IBM + sub-pore – enables simulation of single-particle systems
- A **general method** that is applicable to a wider range of diffusion-dominated problems involving multi-scale porous media

Future work

- Solution to **energy equation** with the sub-pore system to include localized heat of reaction effects
- **Calibration of parameters** using available experimental results for known diffusion-reaction systems
- Simulation of CO2 capture in single-particle systems using **3D sorbent particles**
- Obtain **adsorption/desorption correlations** for use in larger scale simulations

Acknowledgements

- As part of the National Energy Technology Laboratory's Regional University Alliance (NETL-RUA), a collaborative initiative of the NETL, this technical effort was performed under the RES activity number 4000.3.672.238.001.

NETL-RUA
Regional University Alliance

NETL Carnegie Mellon PENNSTATE University of Pittsburgh VirginiaTech WestVirginiaUniversity URS

Thank you!

Questions?

U.S. DEPARTMENT OF ENERGY