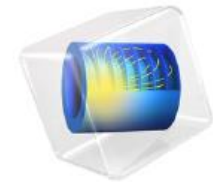


Modeling and Simulation of Carbon dioxide Adsorption on Silica Aerogel Storage System



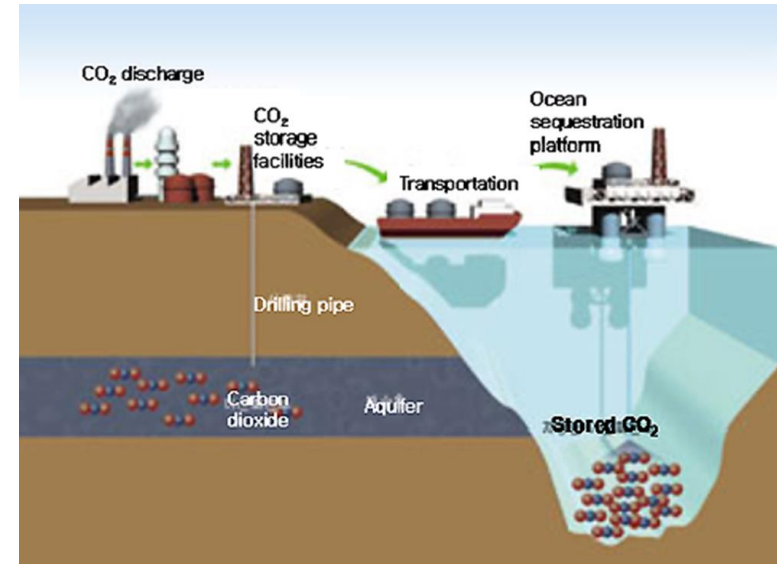
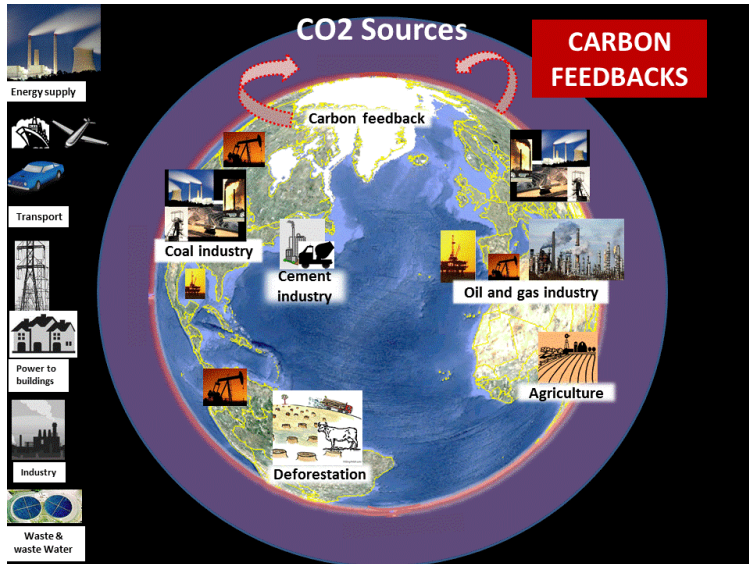
Minju N & S. S. Savithri


Materials Science and Technology Division
CSIR-National Institute for Interdisciplinary Science and
Technology (NIIST)
Trivandrum, Kerala, India.

Objectives

- Development of a predictive model for better understanding of new adsorbent for CO₂ during adsorbent-desorption cycle including all transport phenomena.
- Validation of the model with literature results for H₂ storage
- Prediction of pressure, temperature distribution at various locations in the storage tank

CO₂ Capture and Sequestration (CCS)



- Safe strategy for permanent storage are **porous materials** which ensures safer transportation from industries to long distance storage sites without leakage.
- The storage of CO₂ in **porous materials**  Safe and easy access to CO₂ for different applications

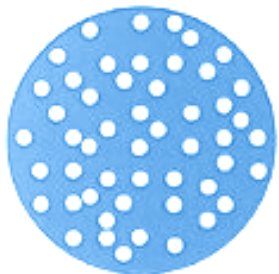
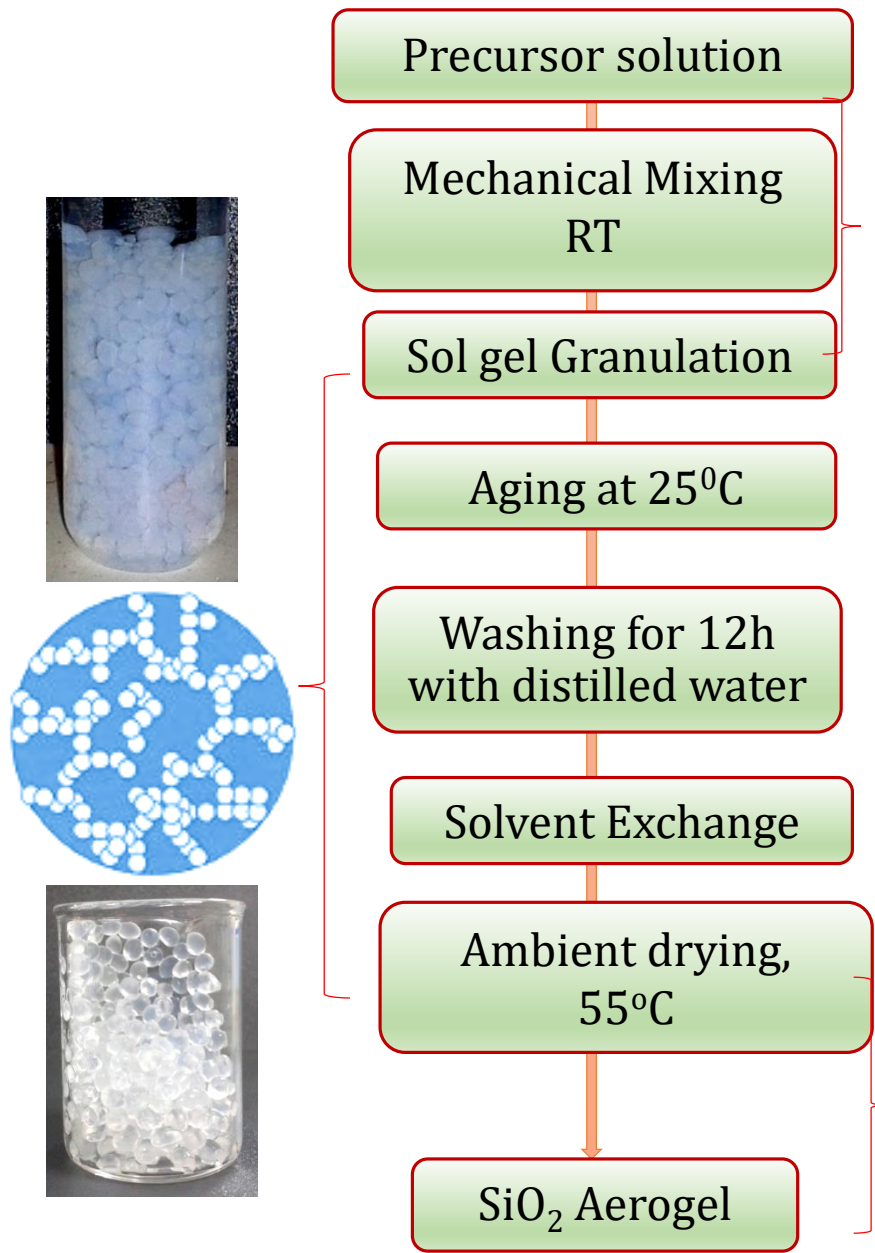
Porous materials as solid sorbents

- Zeolite, Activated carbons, Mesoporous silica, Metal organic frameworks (MOFs), Porous polymers

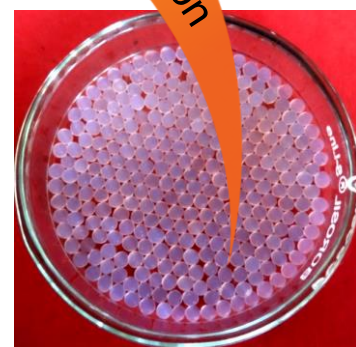
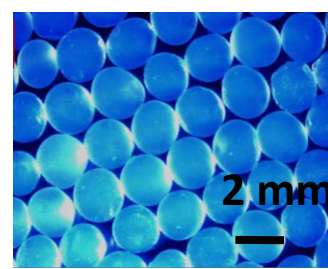
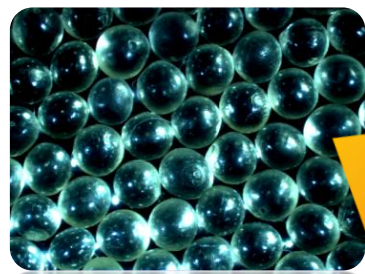
Material	Adsorption temperature/ °C	Adsorption pressure/ atm	CO₂ adsorption capacity/ mmol g⁻¹
Carbon based	≤ 80	1	≤ 3.5
Zeolite based	≤100	1	≤ 4.9
MOF based	≤100	1	≤ 4.5
Alkali metal carbonate based	≤120	1	≤ 9.4
Amine based	≤60	1	≤ 5.5

Surface engineered silica mesospheres – A promising adsorbent for CO₂ Capture, (N. Minju, Balagopal N. Nair, A. Peer Mohamed , S. Ananthakumar) Separation and Purification Technology, 181 (2017), 192-200.

Functionalized Silica aerogel as solid adsorbent for CO₂



- ✓ Low-cost water-glass as silica source
- ✓ Ambient pressure drying



Problem formulation

Simulation of heat and mass transfer process for CO₂ storage during adsorption-desorption cycle in a fixed column filled with modified silica aerogels.

- *More realistic storage tank is used as computational domain*
- *Darcy's law for charging of CO₂ in the storage tank*
- *Considering the heat transfer between the bed and the walls of the container and convective heat transfer between the outer wall and surroundings of the storage tank*
- *The adsorption isotherm in the adsorbent - The Dubinin-Astakov (D-A) micropore volume filling adsorption model*

$$n_a = n_{max} \exp \left[- \left[\frac{RT}{\varepsilon} \right]^m \ln \left(\frac{P_o}{P} \right)^m \right] \quad \varepsilon = \alpha + \beta T$$

- *Variational isosteric heat of adsorption based on DA model*

$$q_{st} = \alpha \sqrt{\ln(n_{max}/n_a)}$$

n_{max} (mol kg ⁻¹)	α (J mol ⁻¹)	β (J mol ⁻¹ K ⁻¹)	P_o (Pa)
5.714	3000.1	177.46	5.0001E8

Geometry

- Selection of dimension
- Creation of computational domain

Physics

- Subsurface flow module – Darcy's law
- Heat transfer in porous media
- Time dependent

Material Properties

- Properties of CO₂
- Properties of silica aerogel (matrix)
- Wall properties

Initial

- Inlet – mass source
- Initial conditions for temperature, pressure etc
- Heat flux, heat source term etc

Meshing

- Extremely fine mesh option

Analysis of Results

- Pressure, temperature, velocity
- Adsorption capacity, isosteric heat etc.,
- 2-D plots and contours

- Parameters

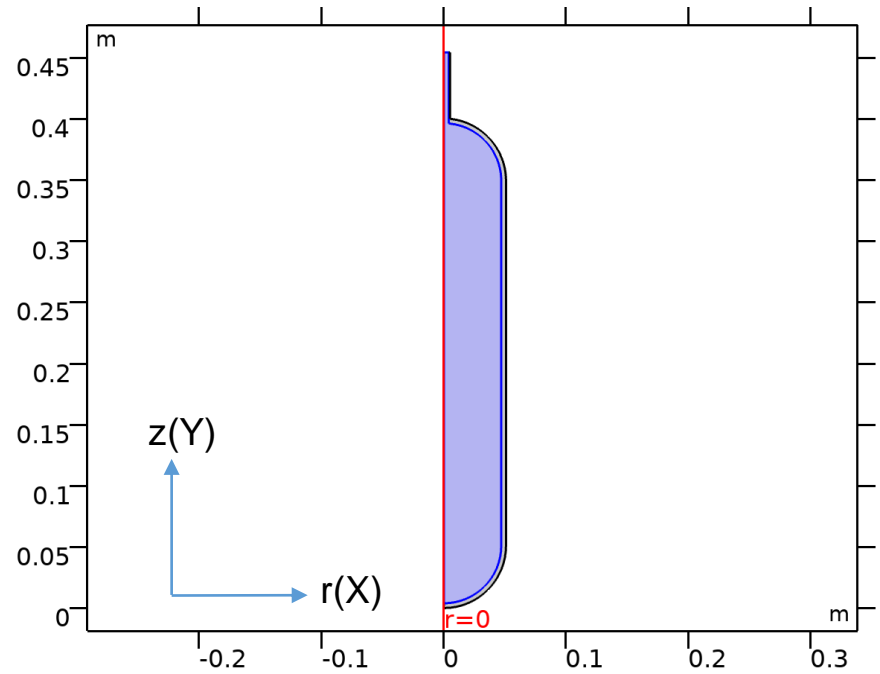
Name	Value
sigmab	0.752
p_initial	1.0133E5 Pa
ht	36 W/(m ² ·K)
alpha	3000.1 J/mol
beta	177.46 J/(mol·K)
nmax	5.714 mol/kg
R1	8.314 J/(mol·K)
R2	188.92 J/(kg·K)
P0	5.0001E8 Pa
k_CO ₂	0.0187 W/(m·K)
k_silica	0.125 W/(m·K)
Cp_CO ₂	871 J/(kg·K)
Cp_silica	2300 J/(kg·K)
Dp	0.002 m
rho_silica	656 kg/m ³
MCO ₂	0.04401 kg/mol
T_initial	323 K
T_amb	293.15 K

- Variables

Name	Expression	Unit
rho_H ₂	$(p \cdot MCO_2) / (R1 \cdot T)$	kg/m ³
na	$nmax \cdot \exp(-(R1 \cdot T / (\alpha + \beta \cdot T))^2 \cdot \log(P0/p)^2)$	mol/kg
K	$(Dp^2 / 150) \cdot (\text{sigmab}^3 / (1 - \text{sigmab})^2)$	m ²
Qst	$((1 - \text{sigmab}) \cdot d(\text{na}, t) \cdot \text{rho_silica} \cdot \text{qst})$	W/m ³
qst	$\alpha \cdot (\text{sqrt}(\log(nmax/na)))$	J/mol
Qm	$-(1 - \text{sigmab}) \cdot \text{rho_silica} \cdot MCO_2 \cdot d(\text{na}, t)$	kg/(m ³ ·s)
temp	int4(t)	
velocity	int5(t)	



2D - axisymmetric



CO₂ storage tank with steel walls

- Mass conservation

$$\frac{\partial}{\partial t} (\varepsilon_b \rho_{CO_2}) + \nabla \cdot (\rho_{CO_2} \mathbf{u}) = Q_m$$

$$\mathbf{u} = - \left(\frac{K}{\mu} \right) \nabla P$$

$$Q_m = -M_{CO_2} (1 - \varepsilon_b) \rho_{silica} \frac{\partial n_a}{\partial t}$$

where

- ε_b - porosity of the adsorbent bed
- ρ_{CO_2} - fluid density
- \mathbf{u} - Darcy velocity of CO_2
- K - permeability (m^2)
- μ - dynamic viscosity of fluid
- Q_m - mass source term which accounts for the mass added from the gas phase to the absorbed phase in unit volume per second.
- ρ_{silica} - particle density
- M_{CO_2} - molecular mass of CO_2 gas

- Momentum conservation

- The Darcy's flow model predicts the total pressure distribution over time thereby defining the time dependent velocity field distribution.
- Combining Darcy's law and continuity equation provides the conservation of mass and momentum.

$$\frac{\partial}{\partial t}(\varepsilon_b \rho_{CO_2}) + \nabla \cdot \left[\rho_{CO_2} \left(-\frac{\kappa}{\mu} \nabla P \right) \right] = -M_{CO_2} (1 - \varepsilon_b) \rho_{silica} \frac{\partial n_a}{\partial t}$$

- The permeability κ is dependent on the particle diameter ($D_{silica} = 2 \text{ mm}$) and bed porosity ($\varepsilon_b = 0.752$)

$$\kappa = \frac{1}{150} \frac{D_{silica}^2 \varepsilon_b^3}{(1 - \varepsilon_b)^2}$$

- Energy conservation

During the carbon dioxide adsorption process, the heat of the system is transferred by conduction and convection in porous media. The partial differential equation representing energy balance can be written as

$$(\varepsilon_b \rho_{CO_2} + \rho_{CO_2} n_a M_{CO_2} C_{pg} + \rho_{silica} C_{ps}) \frac{\partial T}{\partial t} + \rho_{CO_2} C_{pg} \vec{v} \cdot \nabla T = \nabla \cdot (k_{eff} \nabla T) + Q + \Phi$$

$$k_{eff} = \varepsilon_b k_{CO_2} + (1 - \varepsilon_b) k_{silica}$$

$$Q = Q_a + Q_p = (1 - \varepsilon_b) \rho_{silica} \frac{\partial n_a}{\partial t} q_{st} + \gamma T \left[\varepsilon_b \frac{\partial p}{\partial t} + (\vec{v} \cdot \nabla) p \right]$$

C_{pg} - specific heat capacity of CO_2 ($J \text{ kg}^{-1} \text{ K}^{-1}$)

\vec{v} - Darcy velocity (m s^{-1})

k_{eff} - effective thermal conductivity ($\text{W m}^{-1} \text{ K}^{-1}$)

Q - energy source term which combines the adsorption (Q_a) and compression (Q_p) heat source terms (W m^{-3})

γ - volumetric thermal expansion coefficient which equals $(1/T)$ for ideal gas (K^{-1})

q - isosteric heat of adsorption (J mol^{-1})

Φ - viscous dissipation term (W m^{-3})

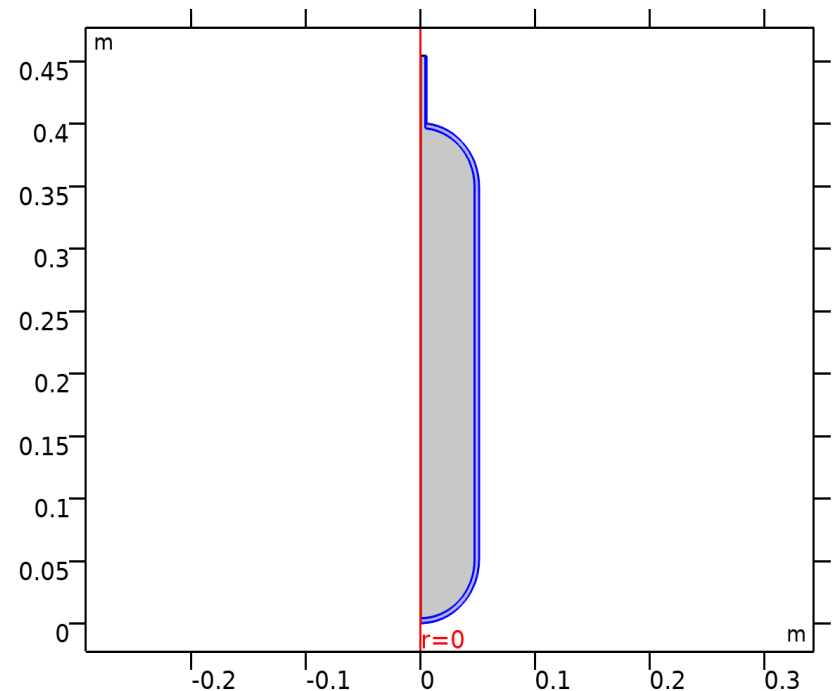
Initial and boundary conditions

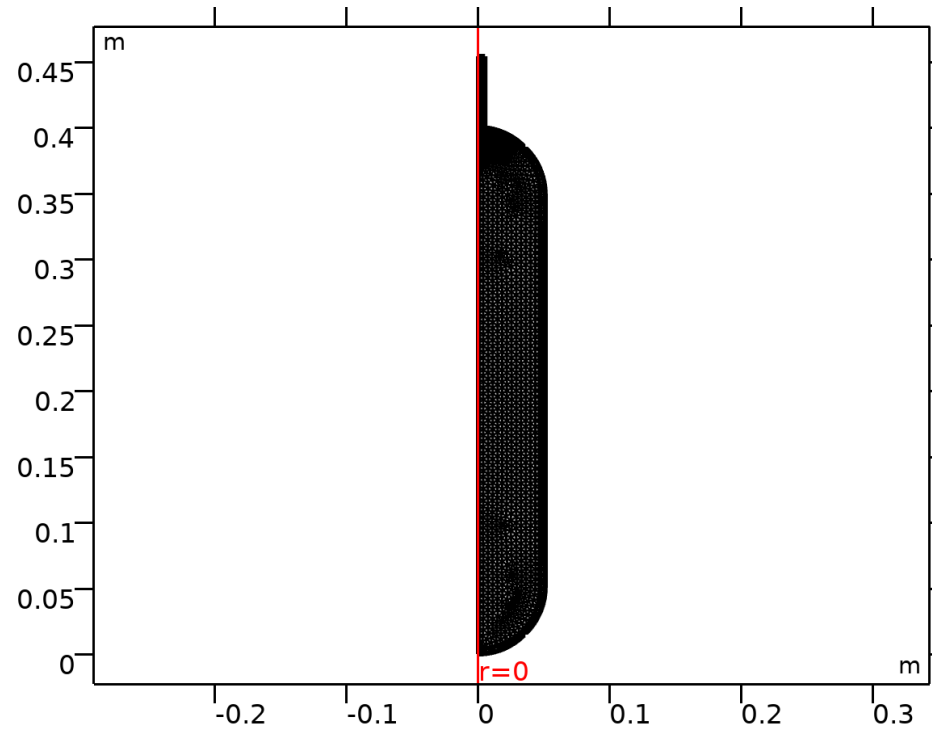
- Initial pressure – 0.1 MPa
- Inlet gas velocity – 0.15 m/s
- Initial temperature inside tank– 323 °K
- Inlet gas temperature – 323 °K
- Heat flux = $-ht*(T_{amb}-T)$, T_{amb} - 293.15 °K, ht – 36 [W/m² K]

Solid

Steel wall

- Thermal conductivity = 13 W m⁻¹ K⁻¹
- Density = 7830 kg m⁻³
- Specific heat capacity = 468 J kg⁻¹ K⁻¹





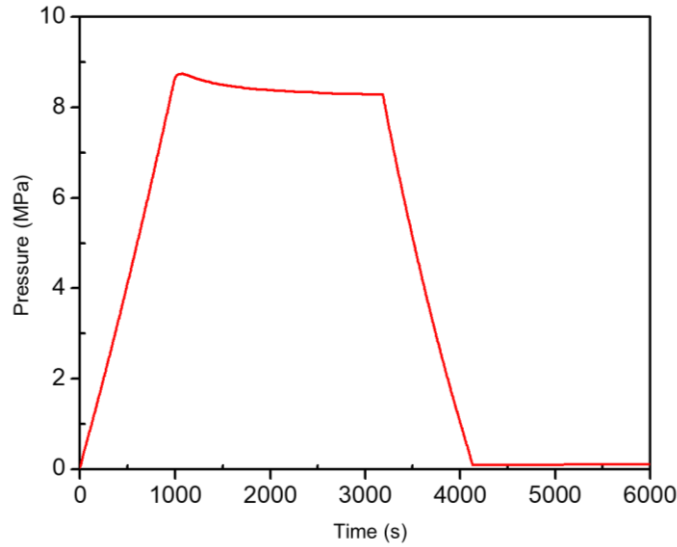
Study

- Time dependent
- Range (0,0.1,3603)s
 - 0 – 1200 s – charging of CO₂ gas
 - 1201 – 2401 s – holding
 - 2402 – 3002 s – discharge
 - 3003 – 3603 s – holding

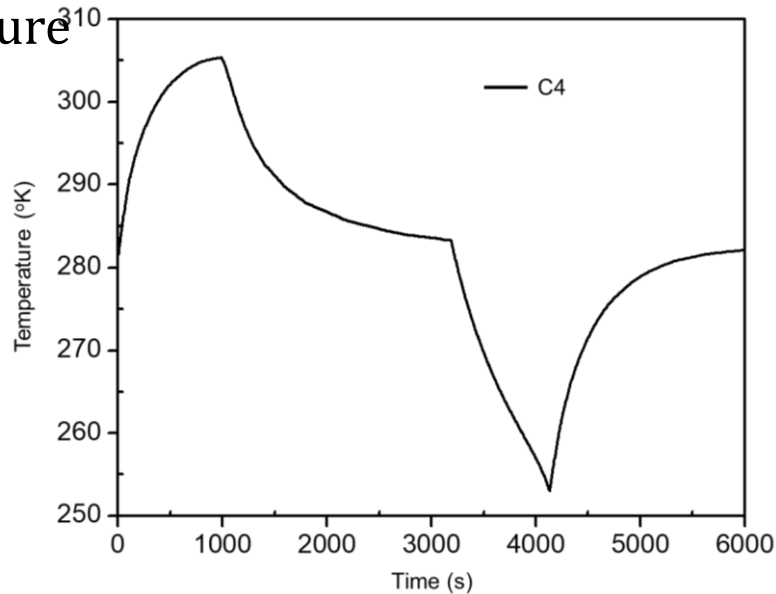
Validation studies

Current model

- Pressure



- Temperature



Finite element model for charge and discharge cycle of activated carbon hydrogen storage

Jinsheng Xiao^{a,b,*}, Jijuan Wang^a, Daniel Cossement^b, Pierre Bénard^b, Richard Chahine^b

^a School of Automotive Engineering, Wuhan University of Technology, Hubei 430070, China

^b Hydrogen Research Institute, Université du Québec à Trois-Rivières, QC G9A 5H7, Canada

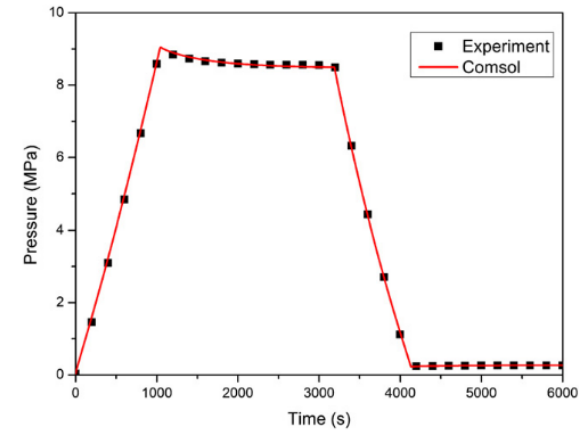


Fig. 3 – Comparison between simulated and experimental pressure.

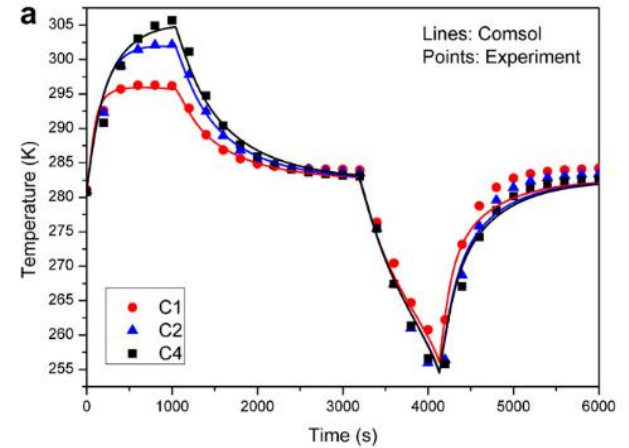
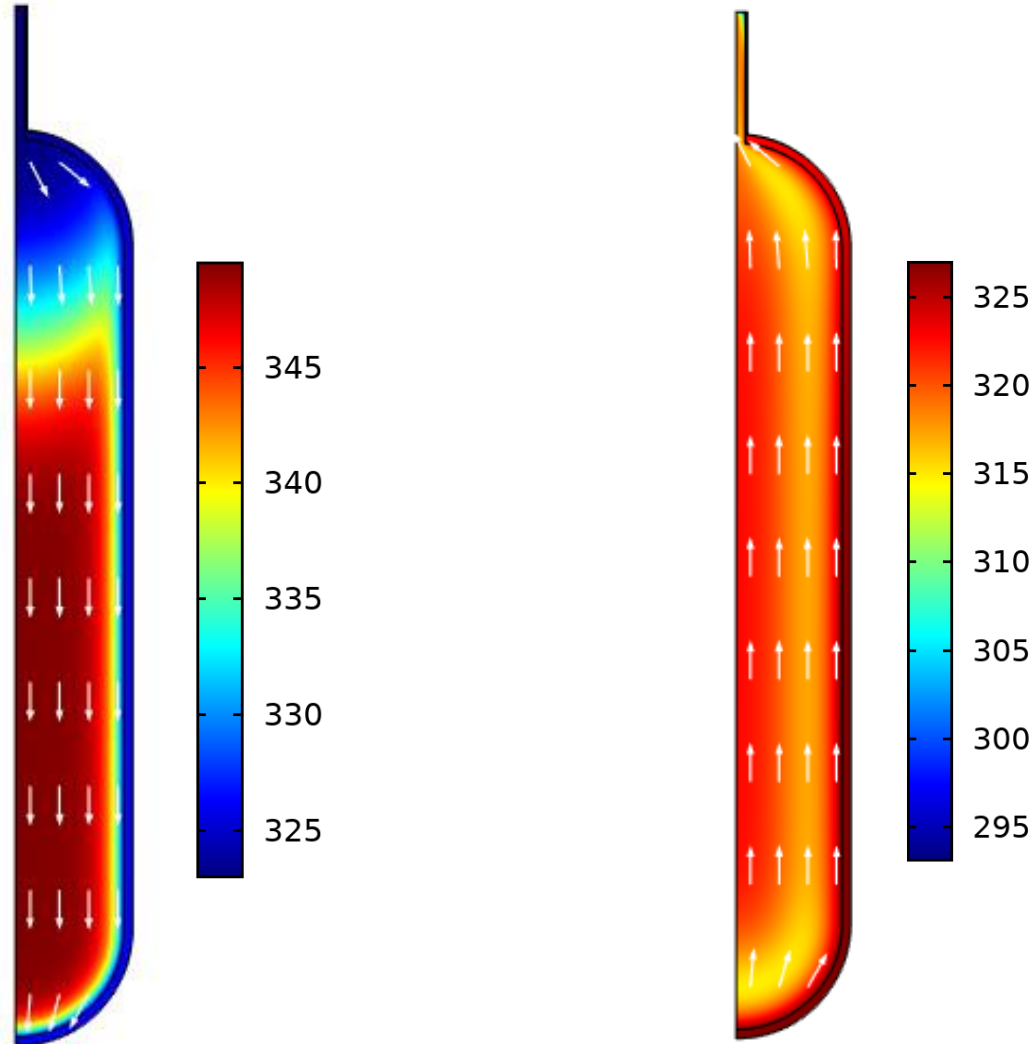


Fig. 4 – Comparisons between simulated and experimental temperatures along (a) axial direction

Temperature contour

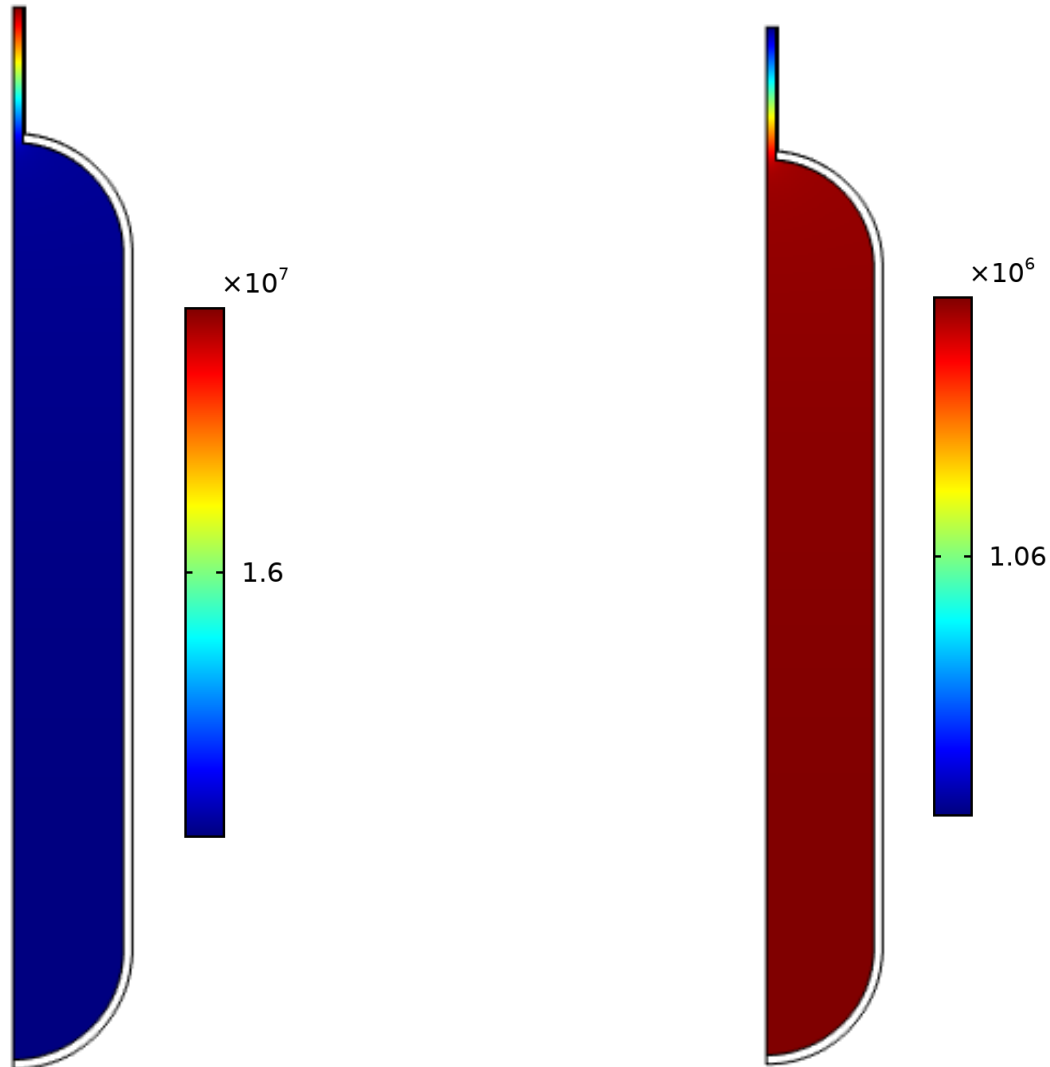
Temperature at the end of charging (1200 s) and discharging (3002 s)



Surface: Temperature (°K); Arrow Surface: Darcy's velocity field

Pressure contour

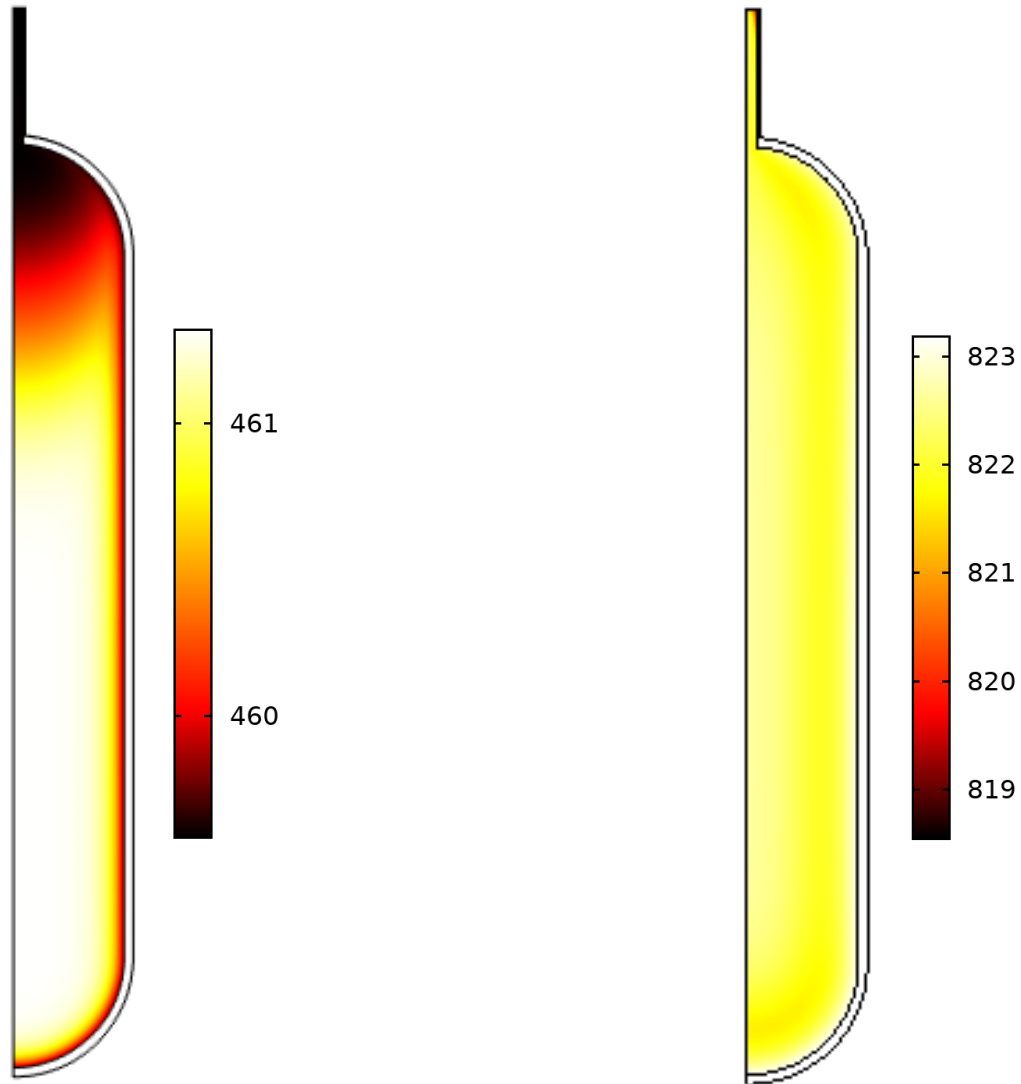
Pressure at the end of charging (1200 s) and discharging (3002 s)



Surface: Pressure (Pa)

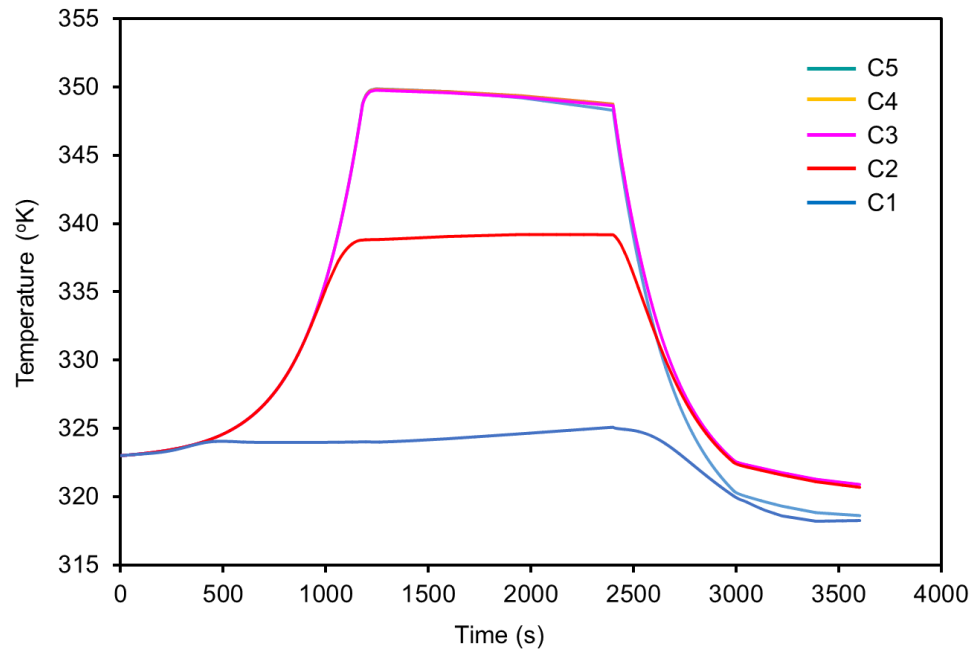
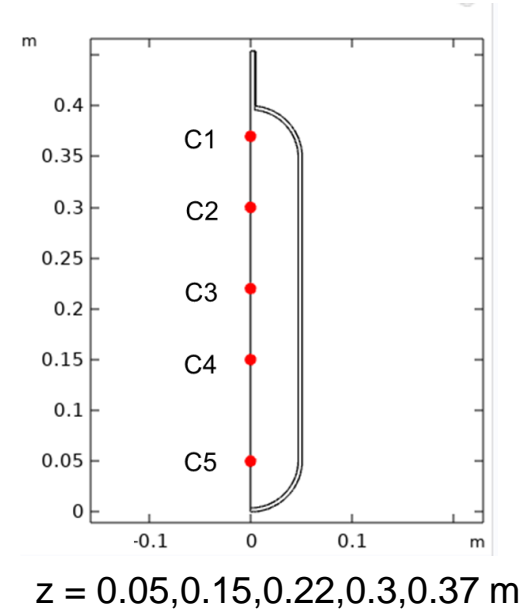
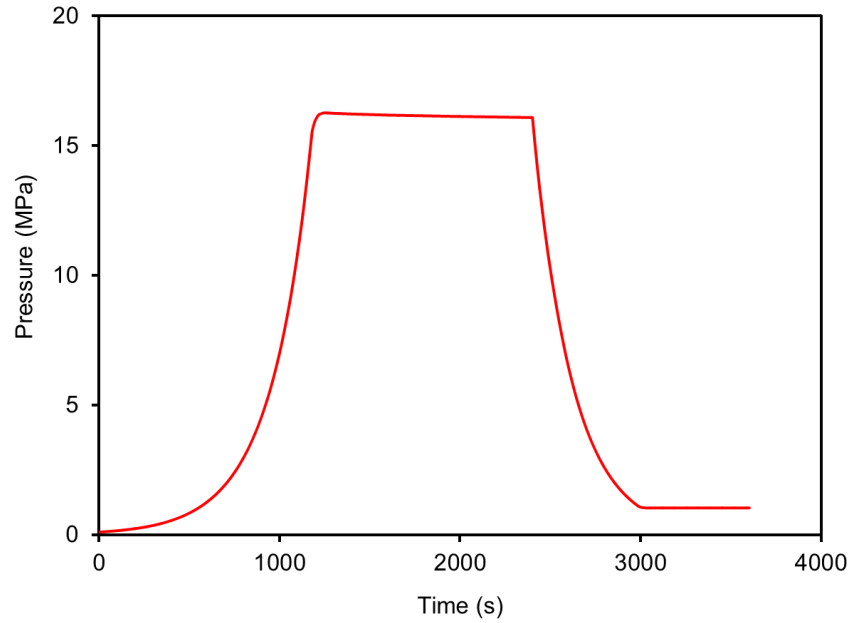
Isosteric contour

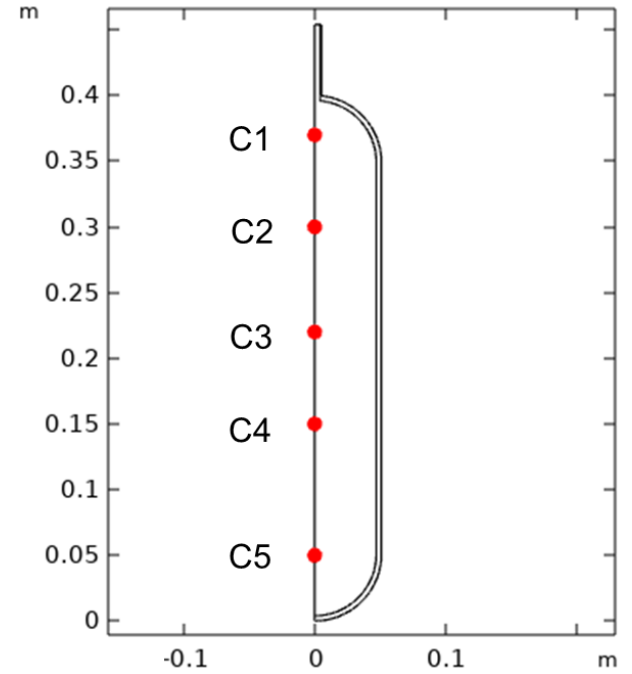
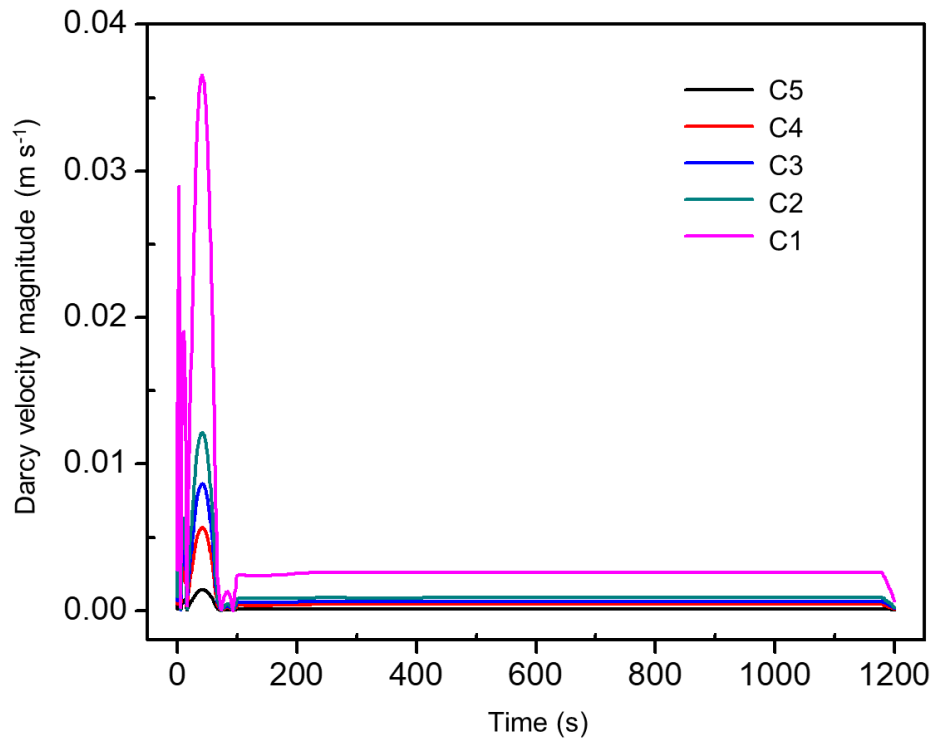
Isosteric heat at the end of charging (1200 s) and discharging (3002 s)



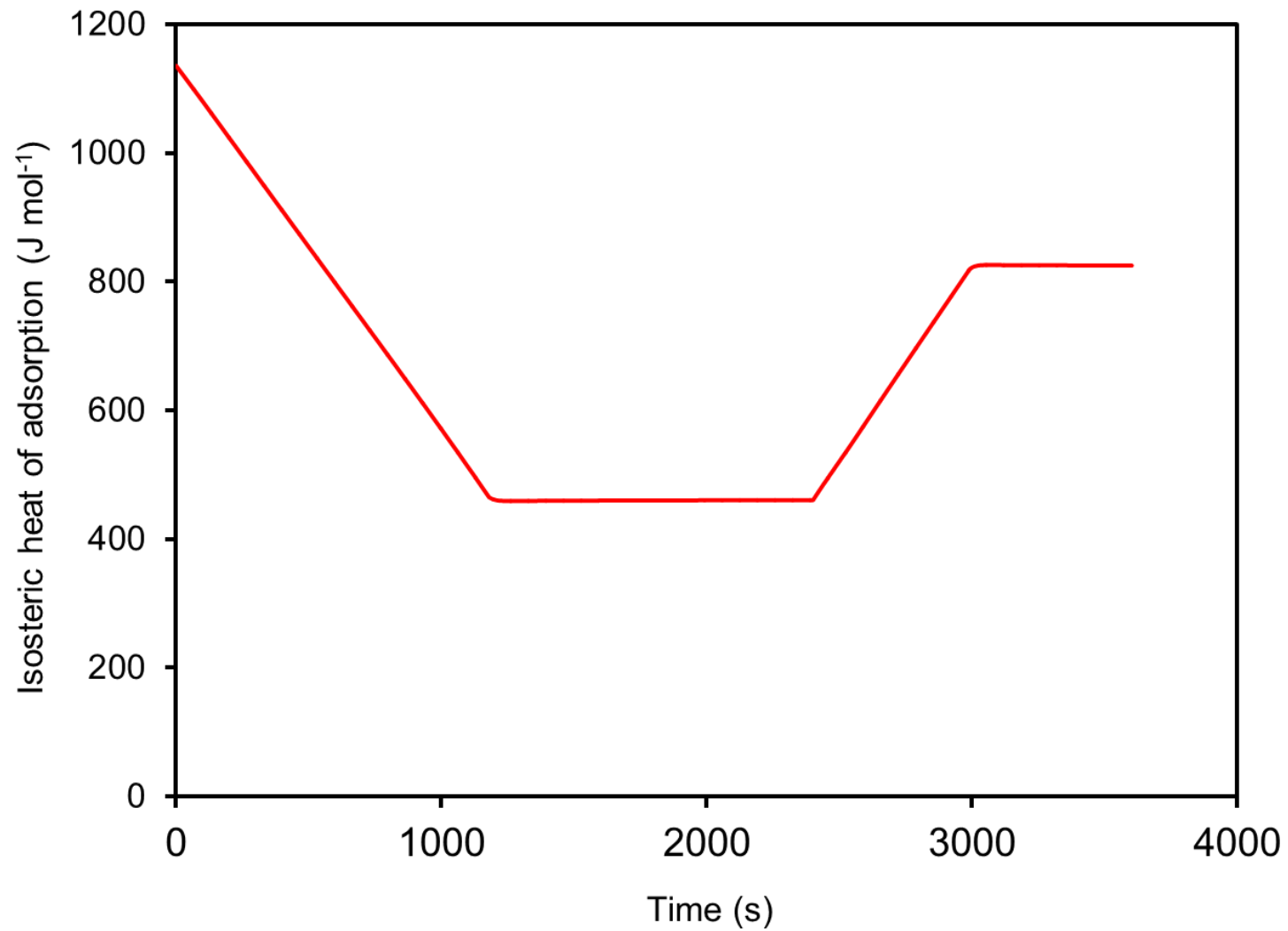
Surface: Isosteric heat ($J mol^{-1}$)

2D Plots

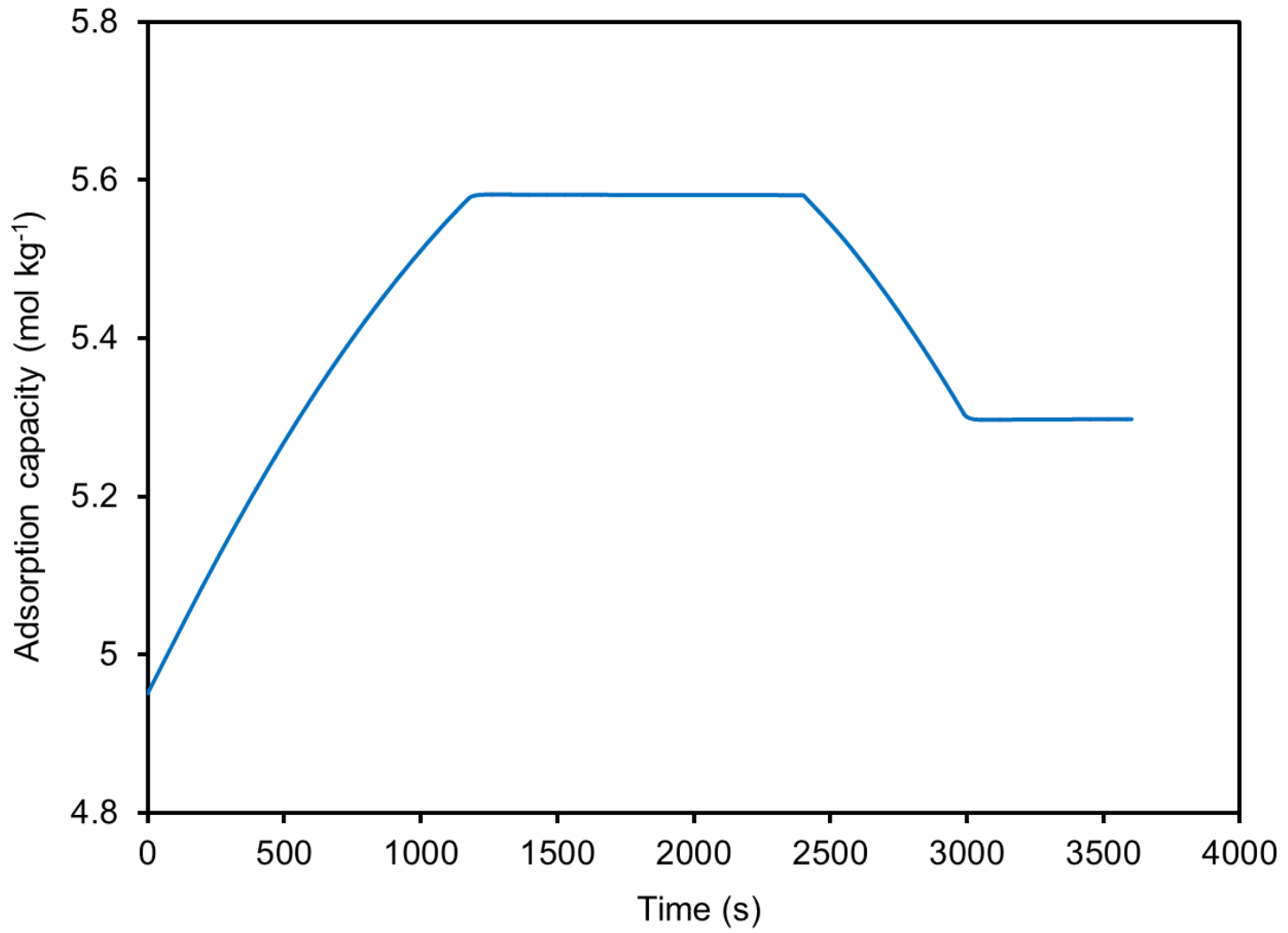




Darcy velocity along axial direction during charging



Isosteric heat of adsorption at $z = 0.22$ m



Adsorption capacity at $z = 0.22$ m

Conclusions

- The finite element simulation of the heat and mass transfer studies on CO₂ storage tank packed with amine functionalised silica aerogel were performed using Comsol Multiphysics software.
- An axisymmetric model was established with a set of PDE to define the system.
- Modified D-A model was used to define the isotherm.
- The pressure and temperature of the tank rises rapidly with time during the charging process and decreases during discharge.
- The maximum heat is observed at the center of the tank where the adsorption capacity is minimum.
- An increase in pressure favours increase in adsorption capacity.
- An increase in thermal conductivity may help in heat removal of the system thereby improving the adsorption capacity.