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Study of Hydrogen Release from a Metal Hydride Bed Adiabatic Conditions

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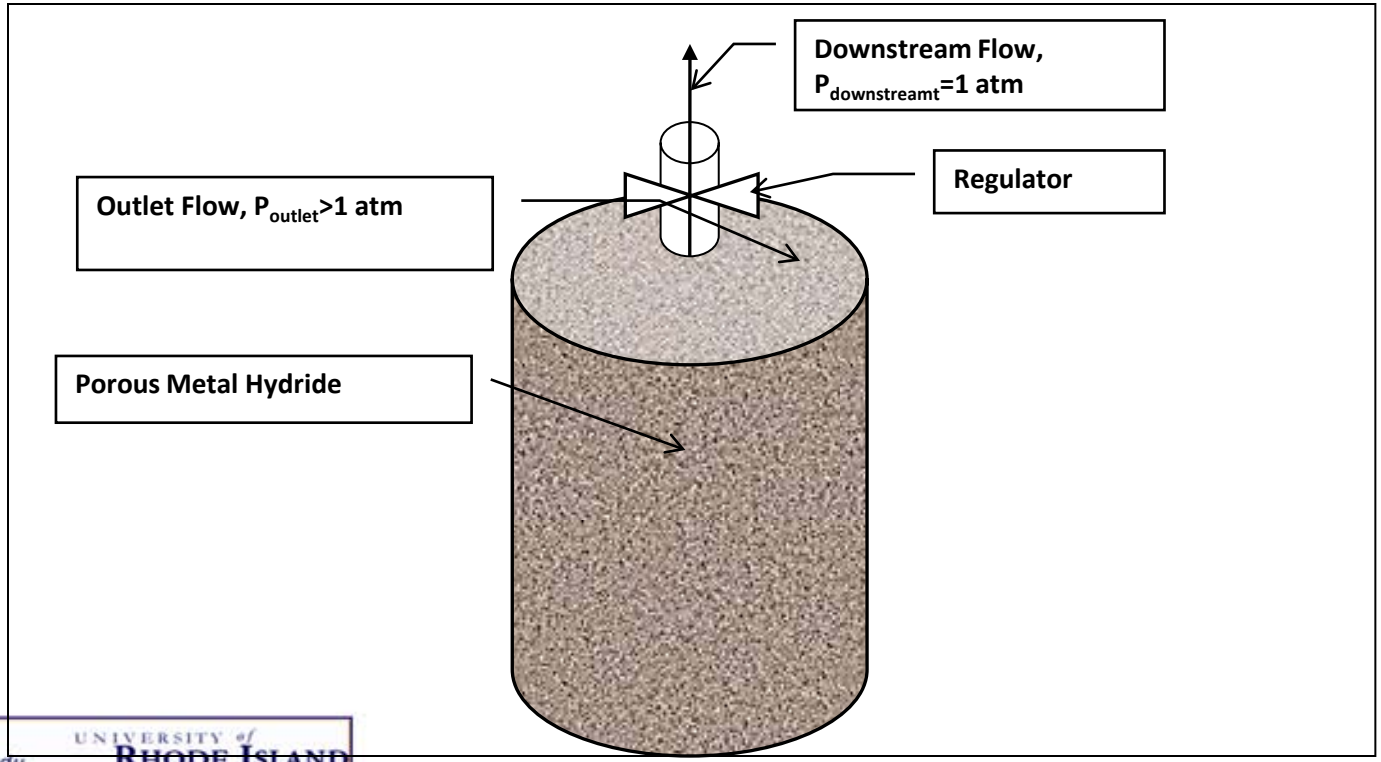
Objective

- Construct Metal Hydride Bed (MHB) Model using COMSOL
- Simulation the dynamic H_2 releasing process at adiabatic operating condition
- Provide a guideline for MHB Design

Metal Hydride Bed Design

- Cylinder Metal Hydride Bed (MHB) with 5 kg H_2 loading
- Supply continuous hydrogen to a Fuel Cell through a regulator at **adiabatic** condition and specified power loading 10kWe
- Restrain applied: $P_{outlet} > P_{downstream}$
- Height: 0.570 m; diameter: 0.248 m



Operating Conditions

Fuel Cell	
Power Requirement	10 kWe
Pressure	1 atm
Operating Point	0.66V, 3000A/m^2
Hydrogen Utilization	95%

MHB	
Initial Temperature	298 K
Initial Gas Pressure	5 MPa
Initial Pressure of Simulation	156 kPa
Maximum Hydrogen Storage	5 kg
Hydrogen Storage Capacity	6%
Outlet Flow Rate	0.0826 mol/s
Theoretical Supply Period	8.37 hrs

Model Analysis Methods

1. Darcy's Law: Momentum Balance in Porous Material
2. Mass Balance: H_2 in gas phase/MH
3. Desorption Rate: Endothermic; MH→Gas Phase
4. Energy Balance: Lumped Model

Darcy's Law for H_2 in thePorous Media

- The gas velocity within the pores of the MHB can be calculated using

Darcy's Law

$$V_g = -\frac{K}{\mu_g}\nabla P_g$$

K: Permeability of the Porous MHB

μ_g: Dynamic Viscosity of Hydrogen in gas flow

P_g: Pressure of Hydrogen in the pores

V_g : volumetric flow rate per cross sectional area

Continuity Equation for the Gas Phase (H_2) in the Pores

- Darcy's Law is coupled with the **Continuity Equation** to solve for the gas phase transient process

$$\varepsilon \frac{d\rho_g}{dt} + \nabla \bullet (\rho_g V_g) = -m$$

ρ_g: Density of Hydrogen

m: Hydrogen Desorption Rate

ε: Porosity of Metal

Mass Balance for the H_2 in the Solid Phase (MH)

- Solid volume is fixed; hydrogen diffusion in solid is neglected
- Hydrogen density variation in the metal:

$$(1-\varepsilon)\frac{d\rho_{H_2M}}{dt} = m$$

- Where the density in the derivative is just the mass of H_2 in the MH divided by the Volume of the tank times the one minus the porosity

H_2 Desorption Rate from MH to Gas Phase

- The *m* is the hydrogen mass desorbed per unit volume which can be estimated from equation below, **the desorption only happened when $P_g < P_{eqd}$, otherwise the *m* is 0 (a judging equation is applied in COMCOL)**:

$$m = C_d \exp\left(-\frac{E_d}{R_g T}\right)\left(\frac{P_g - P_{eqd}}{P_{eqd}}\right)\rho_{H_2M}$$

C_d: Desorption Constant

E_d: Activation Energy for Desorption

P_{eqd}: Equilibrium Pressure for Desorption in the Gas Phase

ρ_{H_2M}: Hydrogen Density in Solid Phase

Ref: J. Less Common Metals 1987, 131, 235-244

Energy Balance Equation for a Homogenous Mixture (Lumped Model)

- The Lumped Energy Balance Equation is build for Gas/Solid Mixture:

$$(\boldsymbol{\rho C_p})_e \frac{\boldsymbol{\partial T}}{\boldsymbol{\partial t}} = \boldsymbol{k_e \nabla^2 T + m \Delta H^o + S_{th}}$$

C_p: Specific Heat

k_e: Effective Thermal Conductivity

ΔH^o: Reaction Heat of Desorption

S_{th}: Heat Source

Estimation of Parameters & Variables

- Hydrogen Density (Ideal Gas Law)

$$\rho_g = \frac{M_g P_g}{R_g T}$$

where M_g is the molecular weight of hydrogen gas

- Dynamic Viscosity of Hydrogen: 9.05*10-6 kg/(m.s^2) at 298K
- Equilibrium Pressure of Hydrogen Desorption: 156kPa at 298K

ref: DOE Hydride Material Listing Database

Estimation of Parameters & Variables (cont)

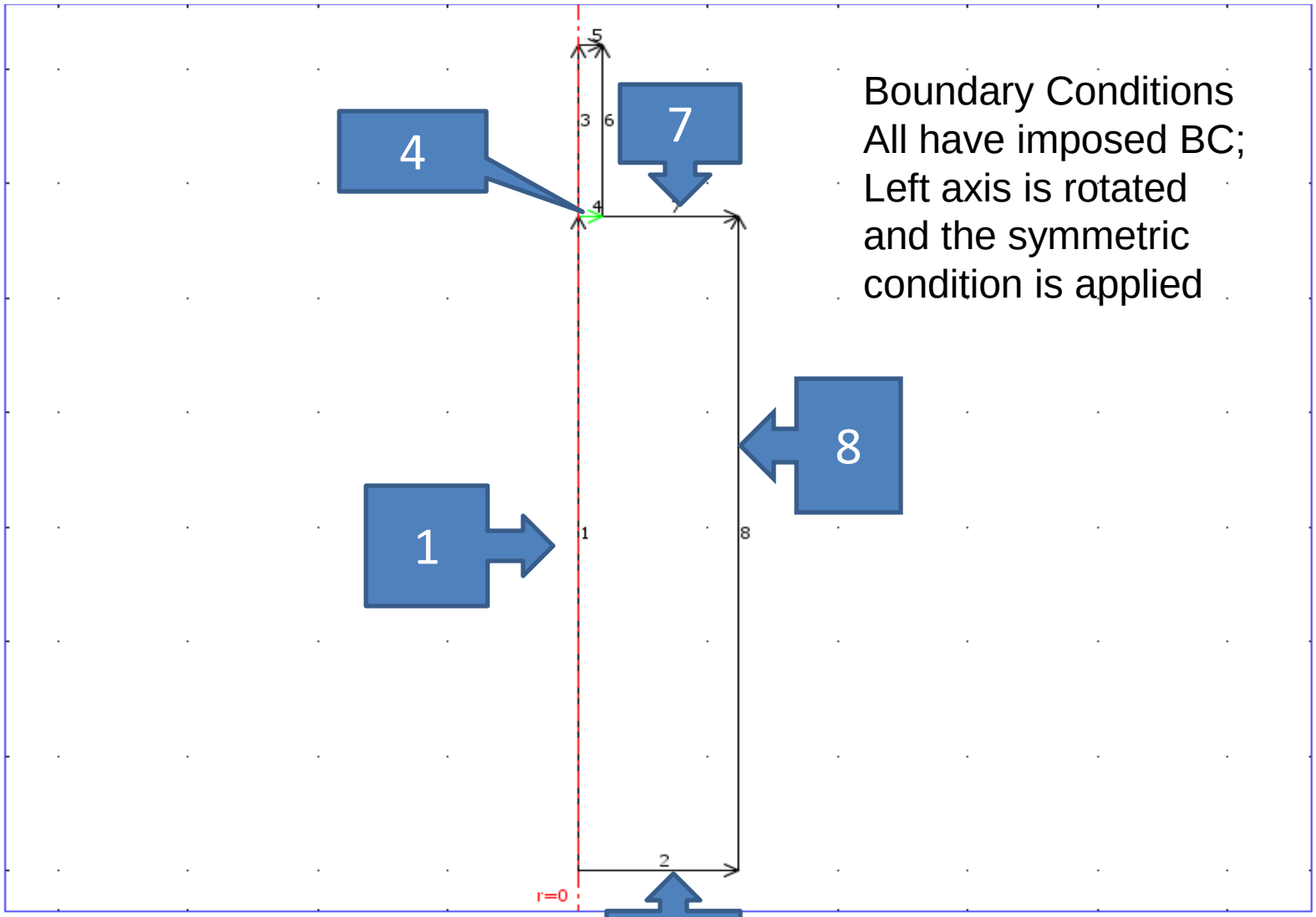
- The effective specific heat term in energy equation:

$$\left(\boldsymbol{\rho C_p}\right)_{\boldsymbol{e}} = (\boldsymbol{\varepsilon \rho_g C_{pg}} + (\mathbf{1} - \boldsymbol{\varepsilon})\boldsymbol{\rho_s C_{ps}})$$

  Where subscript *g* represent gas, *s* represent solid

- S_{th} is zero in adiabatic model

Boundary Schematic Setting



Boundary Conditions
All have imposed BC;
Left axis is rotated
and the symmetric
condition is applied

Initial and Boundary Conditions

Initial Condition, t=0	$p=p_{eqd}$ $\rho_{H2M}=\rho_{H2M\_S}$ $\boldsymbol{T=T\_ini}$
Boundary 1, center axis	$dp/dr=0$ $d\rho_g/dr=0$ $d\rho_{H2M}/dr=0$ $dT/dr=0$
Boundary 8, wall	$dp/dr=0$ $d\rho_g/dr=0$ $d\rho_{H2M}/dr=0$ $dT/dr=0$
Boundary 2,7, top and bottom	$dp/dz=0$ $d\rho_g/dz=0$ $d\rho_{H2M}/dz=0$ $dT/dz=0$
Boundary 4, outlet	$\boldsymbol{v_g=v_{g\_outlet}}$ $\boldsymbol{N=n_{outlet}}$ *(Fixed)* $d\rho_{H2M}/dz=0$ $T=T\_out$

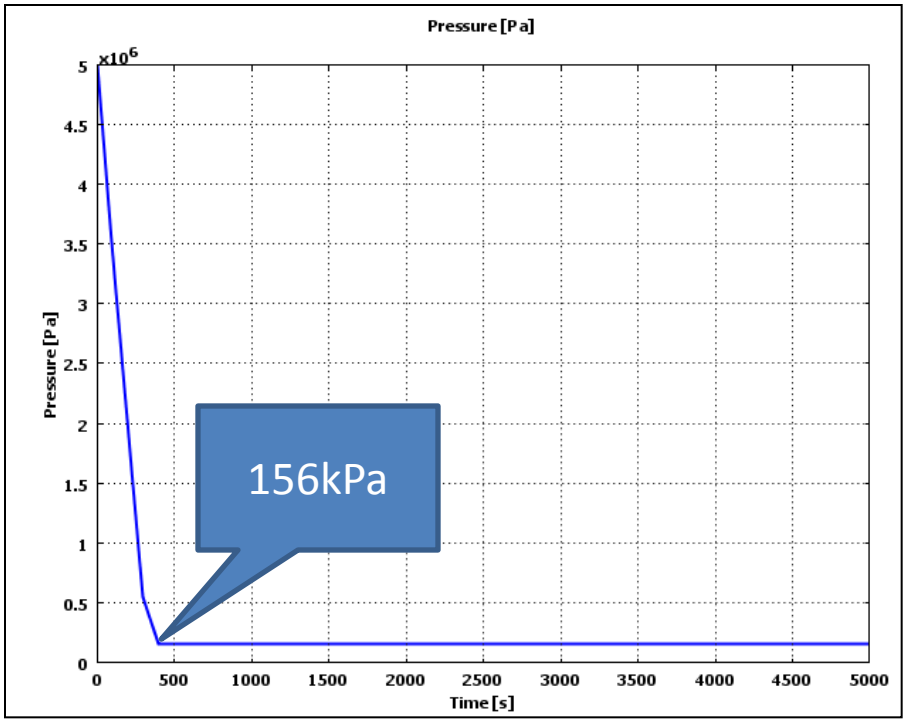
Parameters Used in Simulation

	Value	Range:	Comments
Metal Properties:			
Metal Density, ρ_{emp} [kg/m^3]	6000	4000-8000	Pure Metal
Metal Density at Saturation, ρ_s [kg/m^3]	6360		
Saturated Hydrogen Density in Metal Hydride, ρ_{H2M_S} [kg/m^3]	360		
H_2 Storage Capacity, h [kg H_2/kg Metal]	6%	DOE 2010	Hydrogen Loading Ratio
Permeability, K [m^2]	10^-8	10^{-6}-1.1*10^{12}	Experiment
Porosity, ε	0.5	0.5	Void Fraction of Metal Hydride
Specific Heat of Hydrogen, C_{pg} [J kg^{-1}K^{-1}]	14890		
Specific Heat of Metal, C_{ps} [J kg^{-1}K^{-1}]	500	490-1000	Pure Metal
Effective Thermal Conductivity, k_e [W m^{-1}K^{-1}]	1.32	0.34-1.6	Gas and Metal Mixture
Desorption Properties:			
Desorption Active Energy, E_d [J mol^{-1}]	16000	15000-30000	Active Energy
Desorption Heat, ΔH_d [J mol^{-1}]	1.6*10^7 [J kg^{-1}]	27500-36000	Desorption Energy
Desorption Coefficient, C_d, [s^{-1}]	10	10	Experiment
Desorption Equilibrium Pressure, P_{eqd} [kPa]	156		

Initial Pressure Drop

- The simulation show there is an initial pressure drop from 5MPa to the equilibrium pressure (156 kPa).
- This process last about 321s (5mins) without desorption.

  Thus we choose the 156 kPa as our simulation initial condition (t=0) to analyze the desorption process.

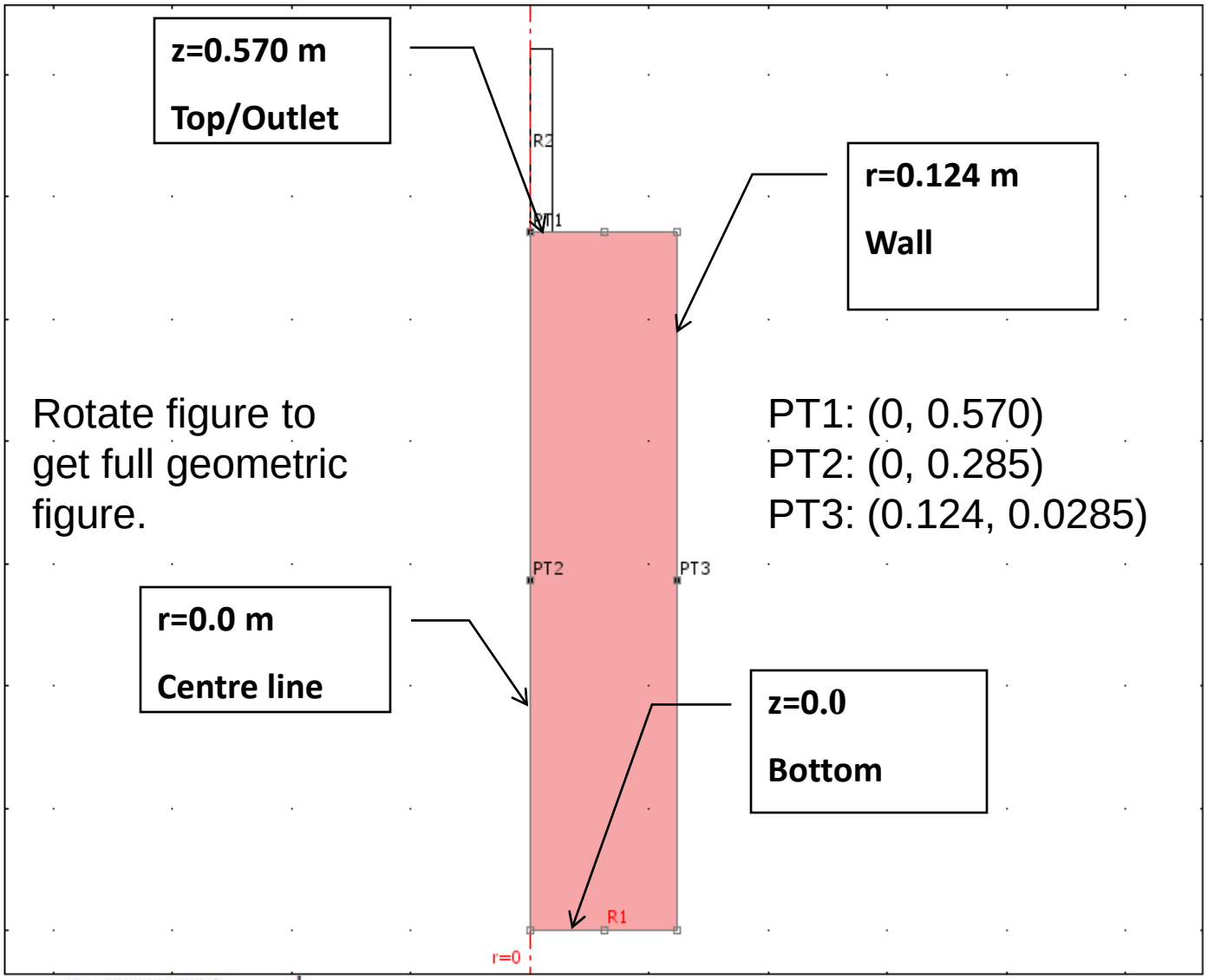


Pressure Variation at P_{ini}=5 MPa

Apply in COMSOL

1. Choose **2D** symmetric mode
2. Choose the appropriate PDE mode: **Darcy's Law** for porous material and **mass diffusion mode** for solid phase; **heat conduction mode** for lumped energy model
3. Draw the geometry
4. Set the initial and boundary condition
5. Set scalar expressions and constants
6. Initialize the mesh
7. Choose time dependent solver and solve the problem

Modeling Geometry



Summary of Basic Model Equations

Momentum Balance: Darcy' Law	$$v_g = -\frac{K}{\mu_g}\nabla P_g$$
Mass Balance: Gas Phase	$$\varepsilon\frac{\partial(\rho_g)}{\partial t} + \nabla\cdot\left(\rho_g v_g\right) = -m$$
Mass balance: Solid Phase	$$(1-\varepsilon)\frac{\partial(\rho_s)}{\partial t} = m$$
Energy Balance: Gas/Solid	$$(\rho C_p)_e\frac{\partial T}{\partial t} = k_e\nabla^2\mathrm{T} + \mathrm{m}\Delta\mathrm{H}^{\mathrm{o}} + \mathrm{S}_{\mathrm{th}}$$

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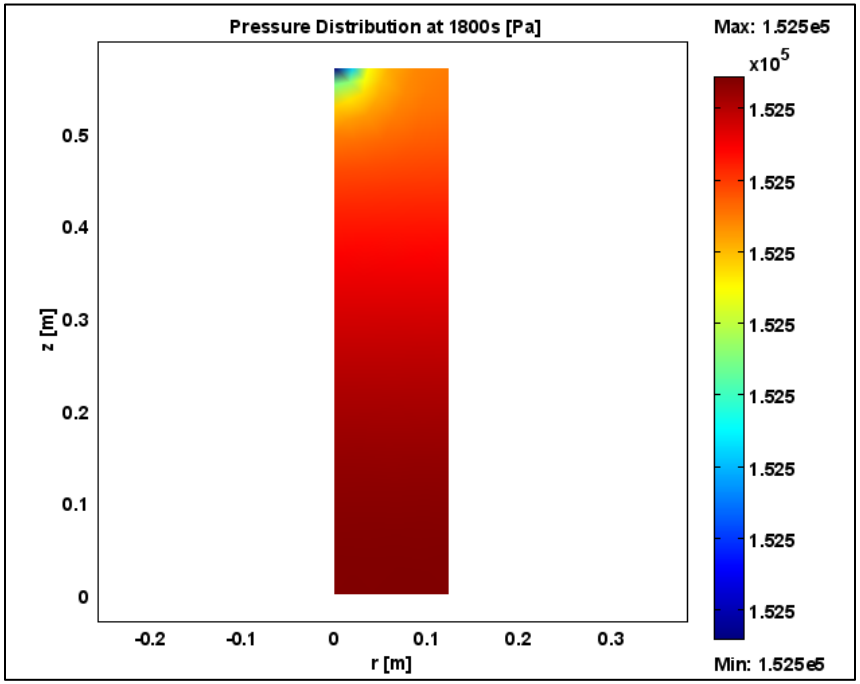
Simulation Results

Adiabatic Model

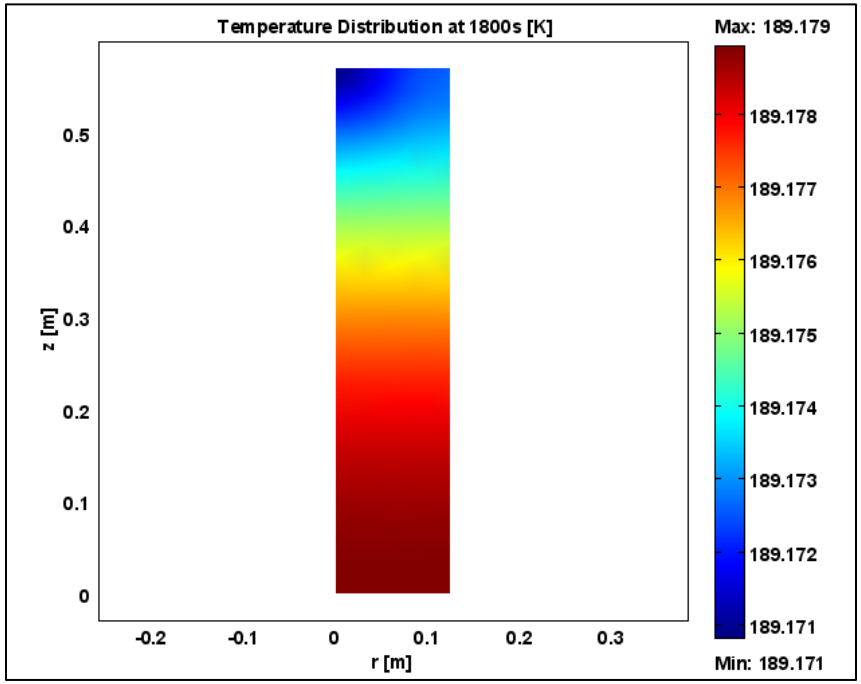
Endothermic Desorption

Simulation Results at 1800s

Pressure

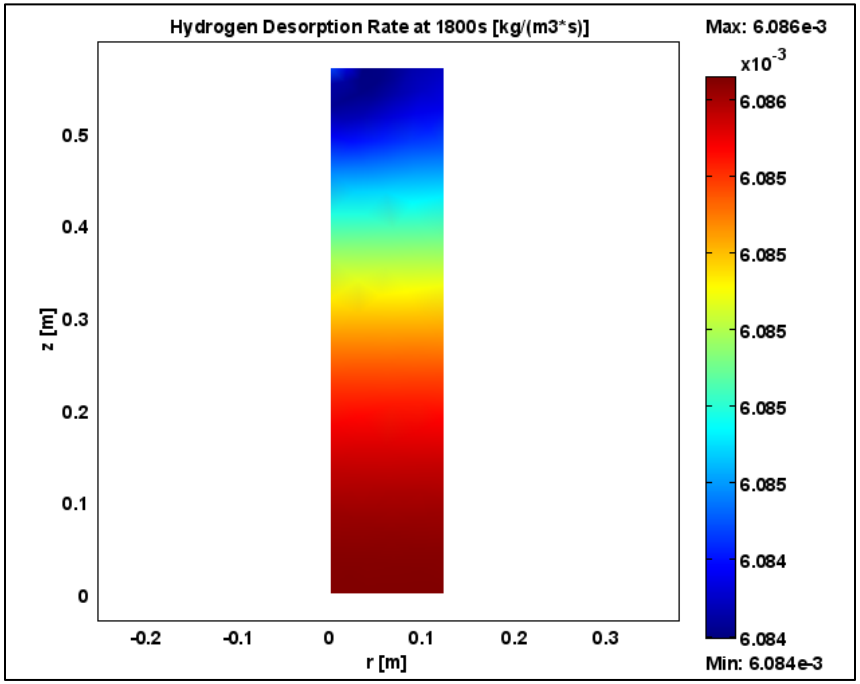


Temperature

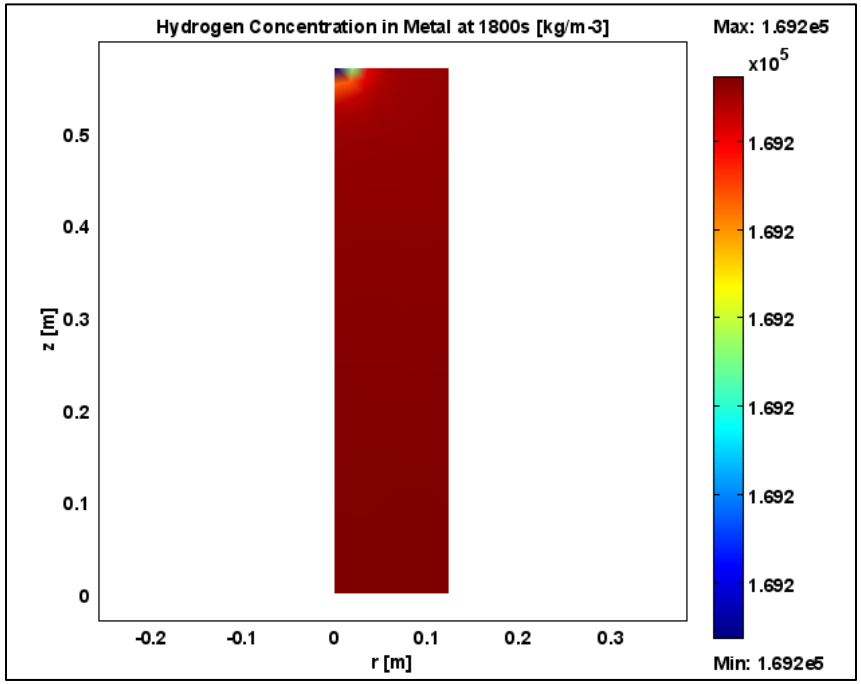


Simulation Results at 1800s

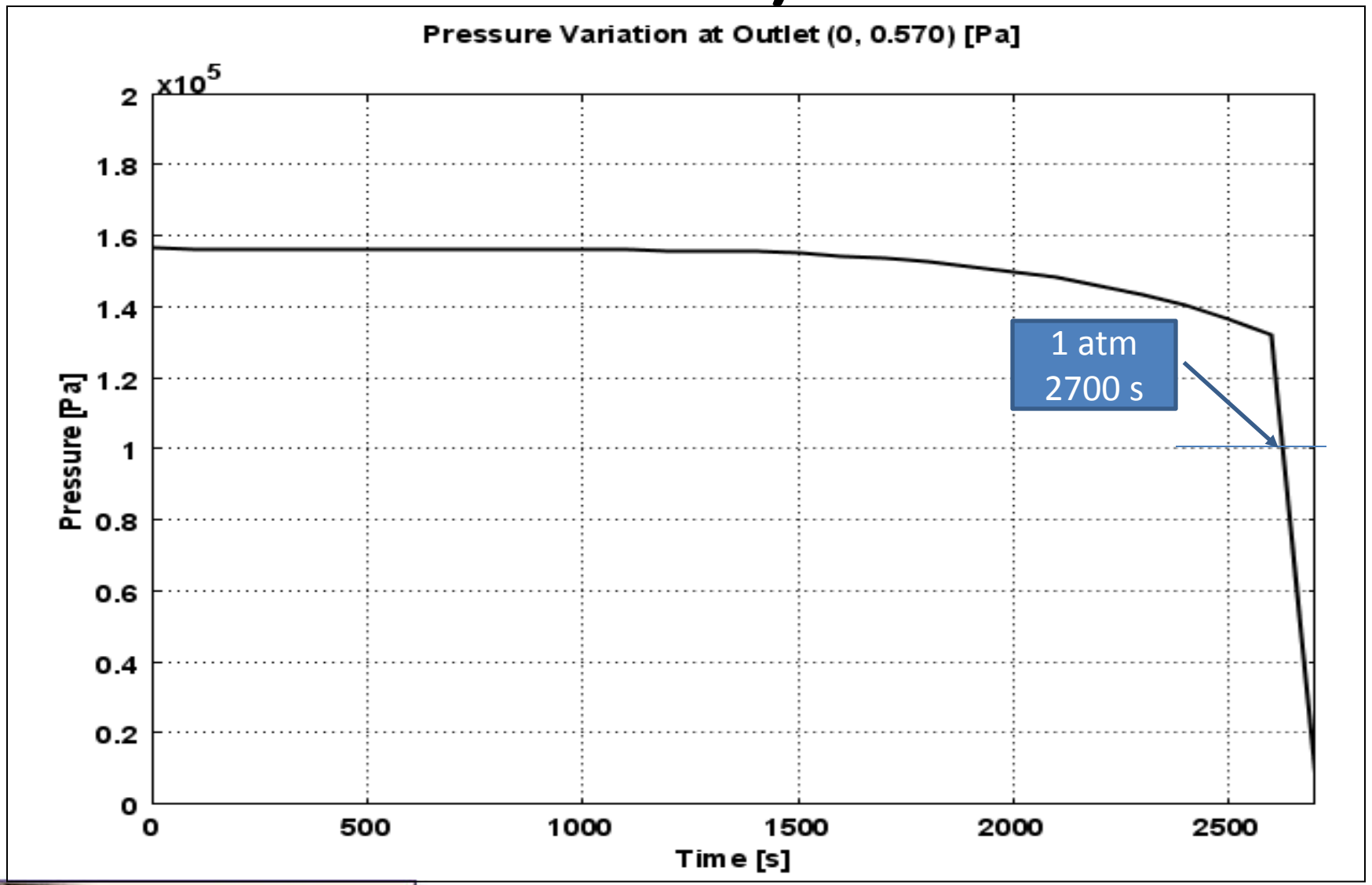
H2 Desorption Rate



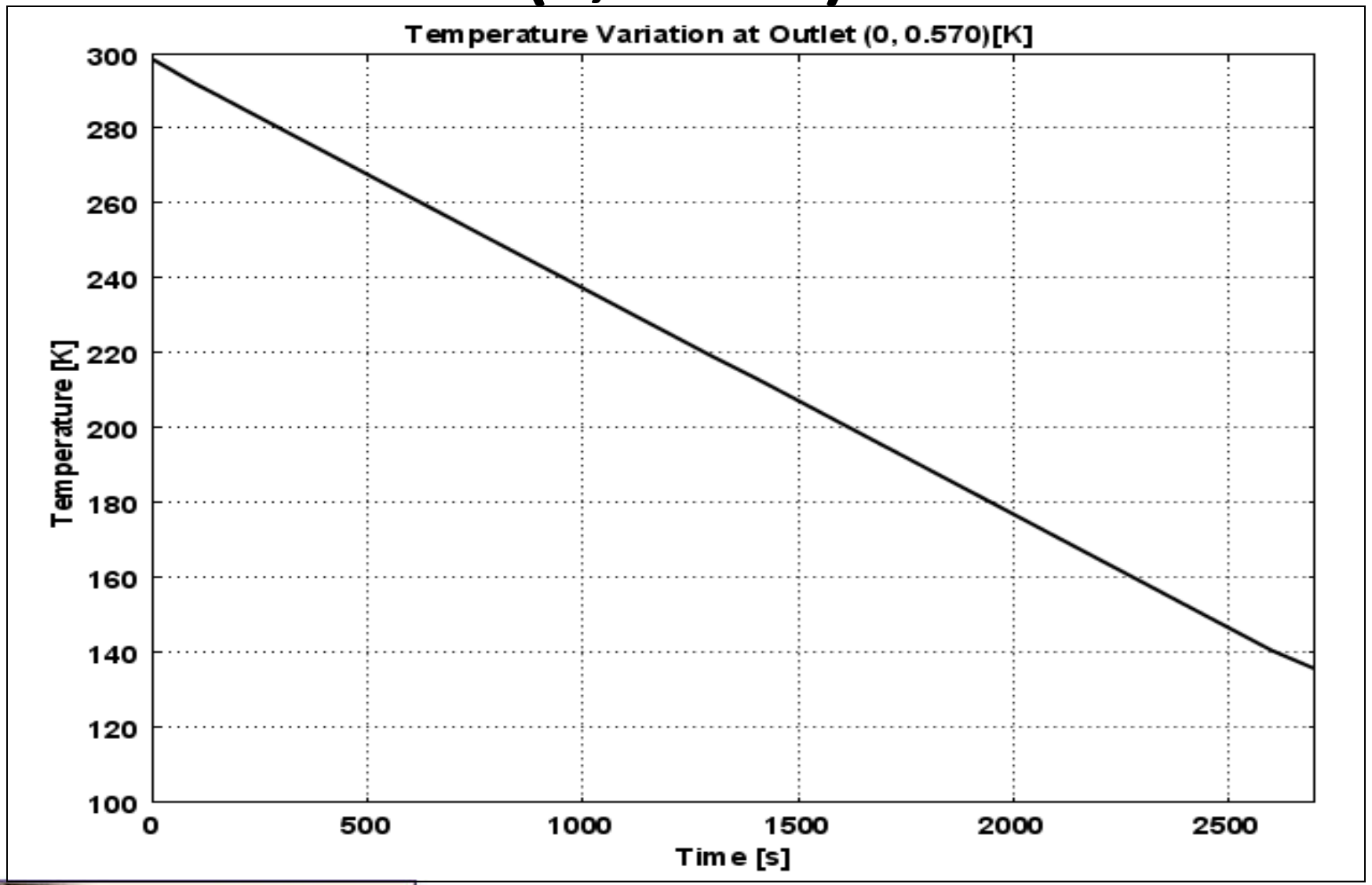
H_2 Concentration in MH



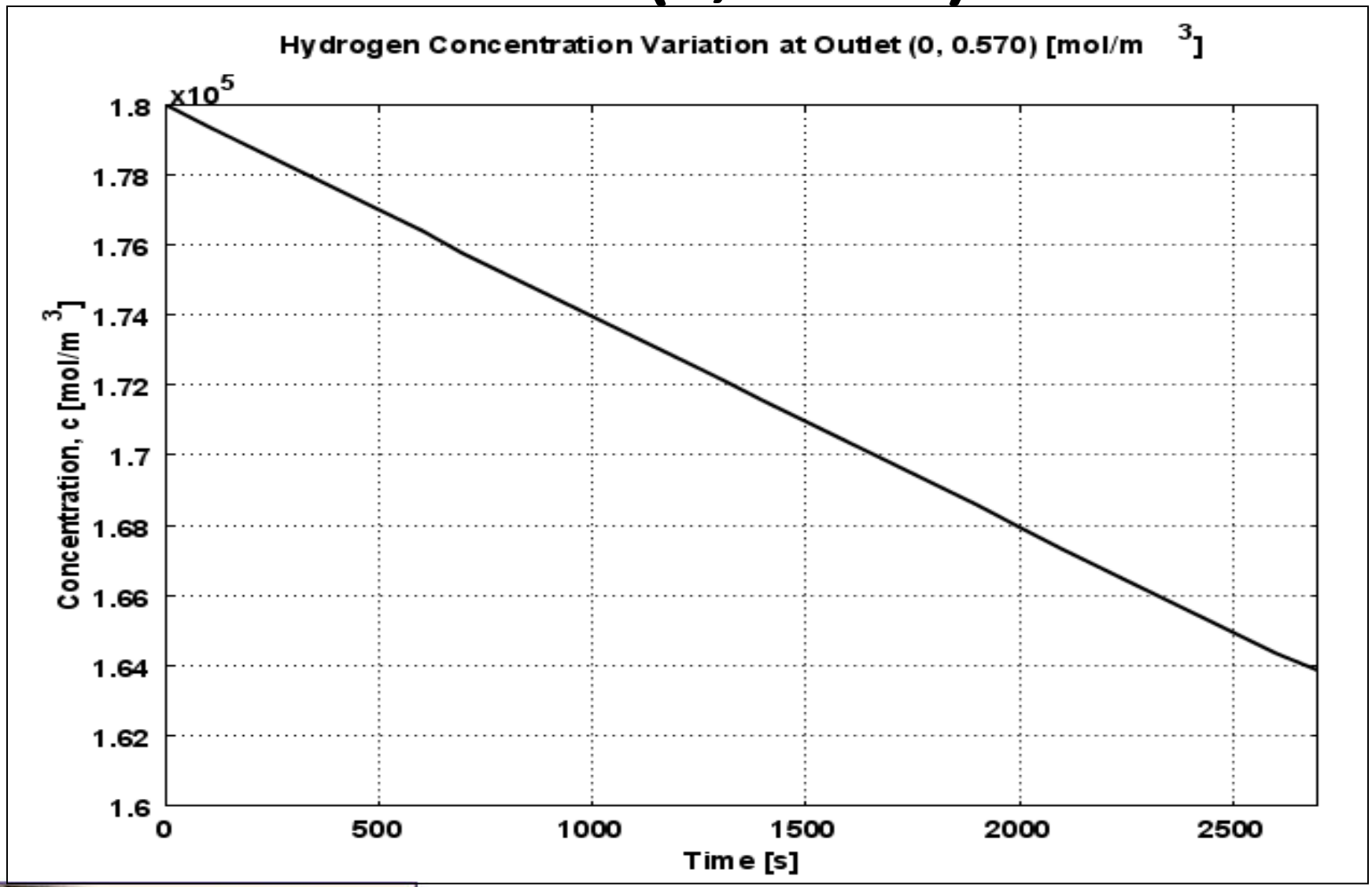
Pressure Variation at Outlet (0, 0.570)



Temperature Variation at Outlet (0, 0.570)



Hydrogen Concentration in MH at Outlet (0, 0.570)



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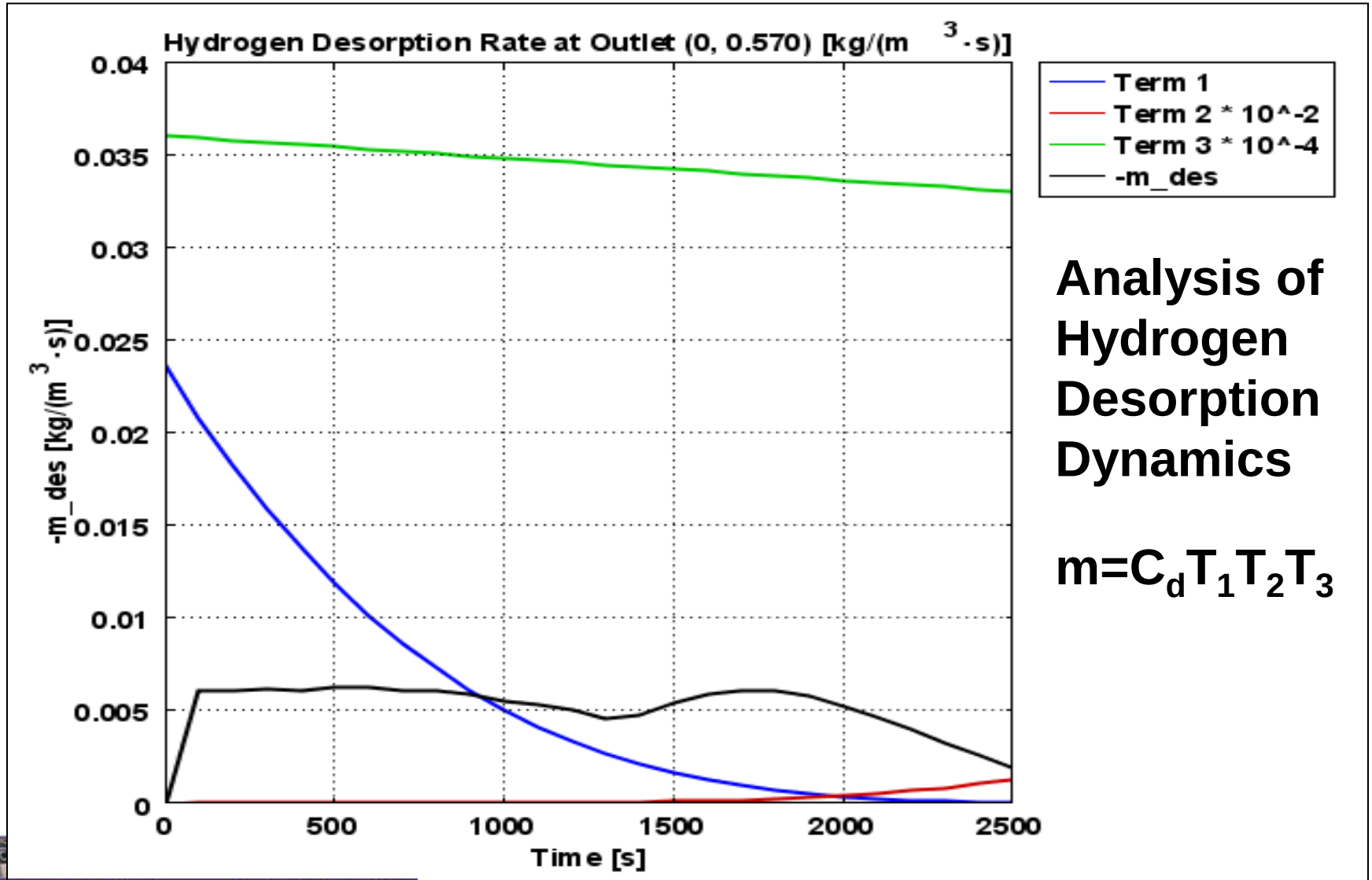
$$m = C_d \exp(-\frac{E_d}{R_g T})(\frac{P_g - P_{eqd}}{P_{eqd}})\rho_{H_2M}$$



Analysis of Hydrogen Desorption Dynamics

$m=C_dT_1T_2T_3$

Results and Conclusions

- The model successfully simulates the dynamic process of MHB H_2 releasing
- A basic template for future modeling is built
- The simulation indicates:

  For adiabatic situation, the gas pressure could be considered relative spatially constant after initial drop although there is small variation along the surface; the gas pressure in the tank varies with time obviously;

  Same conclusions can be applied on hydrogen concentration in MH, hydrogen desorption rate and temperature in tank

Results and Conclusions (cont)

- The simulation indicates:

  In order to maintain the downstream flow at fixed fuel cell pressure (1 atm), the pressure at upstream of valve must be greater than 1 atm. Under this condition, the adiabatic model can last around 2700s because the endothermic desorption reduces the tank temperature and limits the desorption rate which causes the inner pressure to fall below the required value to maintain the flow rate;

  There is still plenty H_2 left in the cold tank

Future Works

- The model can be expanded to different operating conditions:

  1) Isothermal; 2)External heat source; 3) Inner heat source

- Parameters investigation will be applied:

  Permeability, Active Energy, Heat Transfer Coefficient …