

# Study of Hydrogen Release from a Metal Hydride Bed

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**Abstract:** In this paper we present a study of the time dependent analysis of a metal hydride bed (MHB) which provides constant flow to a fuel cell at required power loading and pressure. The hydrogen gas phase pressure, the hydrogen concentration in the metal hydride and the hydrogen desorption rate are considered as key variables in this study. Both the space scale and time scale analysis are performed. Parametric investigations are also conducted. All the simulations are treated at adiabatic conditions and applied using COMSOL software.

**Keyword:** Hydrogen Release, MHB, Adiabatic, Darcy's Law

## 1. Introduction

Due to advantages such as high volumetric density and relative low operating temperature, metal hydrides are considered as promising candidates for hydrogen storage (1, 2). In this work, a metal hydride bed (MHB) is used as a hydrogen source which provides constant hydrogen flow to a fuel cell stack at constant power loadings for a stand-alone plant or a vehicle propulsion usage. The schematic of the MHB is carefully selected based on our early work. In our work the metal hydride is treated as a porous material when modeling. The time dependent analyses of gas phase pressure, hydrogen concentration in the metal hydride, hydrogen desorption rate and temperature distribution are performed at constant flow rate release when operated adiabatically. Parametric investigation is carried out to meet the power loading requirement. The COMSOL package is used for all simulations.

Beside this adiabatic model we discuss below, the model can be expanded to a wider range of conditions such as isothermal model and external heat source model.

## 2. Design of a Metal Hydride Bed (MHB)

A cylindrical MHB is used to provide hydrogen to a fuel cell stack which operates at 10 kWe power requirement. This MHB is designed with 5 kg hydrogen loading. The hydrogen storage capacity is chosen as 6% based on DOE 2010 target. The inner volume and the size of the MHB can be determined based on our previous work (3). The porosity ( $\epsilon=0.5$ ) of the metal

hydride is taken into account also in the calculations. In this paper, the thickness of the wall is neglected. Figure 1 is the schematic of such a MHB. The inner volume of the MHB is 0.02747 m<sup>3</sup>. The height of the MHB is 0.570 m. The diameter of the MHB is 0.248 m. In the MHB gas phase and solid phase (metal hydride) coexist and the hydrogen is mainly stored in the metal hydride (around 4.945 kg). A pipe with a diameter of 1.5 inch is used to release the hydrogen. A regulator is attached on the releasing pipe in order to maintain the outlet flow constant at our specified power requirement.

Table 1 summarizes the basic operating conditions for the fuel cell stack and the MHB. The required hydrogen flow rate can be estimated (4) and the value is 0.0826 mol/s. Theoretically the MHB mentioned above can last 30120 seconds (8.37 hr) until the MHB has been emptied. However, in the practical situation, the downstream pressure which should equal to fuel cell pressure limits the hydrogen releasing. The  $P_{\text{outlet}}$  can't be smaller than the  $P_{\text{downstream}}$  which is 1 atm in this paper. Otherwise the regulator wouldn't be able to maintain a constant flow rate because the loss of pressure driving force. The release will stop before the MHB is empty. Thus the lasting time of the MHB can be predicted if the dynamic response of the outlet pressure is obtained. Table 1 also shows the MHB will be operated adiabatically.

**TABLE I.** Fuel Cell Operating Conditions.

<b>Fuel Cell</b>	
Power Requirement	10 kWe
Pressure	1 atm
Operating Point	0.66V, 3000A/m <sup>2</sup>
Hydrogen Utilization	95%
<b>MHB</b>	
Initial Temperature	298 K
Initial Gas Pressure	5 MPa
Maximum Hydrogen Storage	5 kg
Hydrogen Storage Capacity	6%
Outlet Flow Rate	0.0826 mol/s

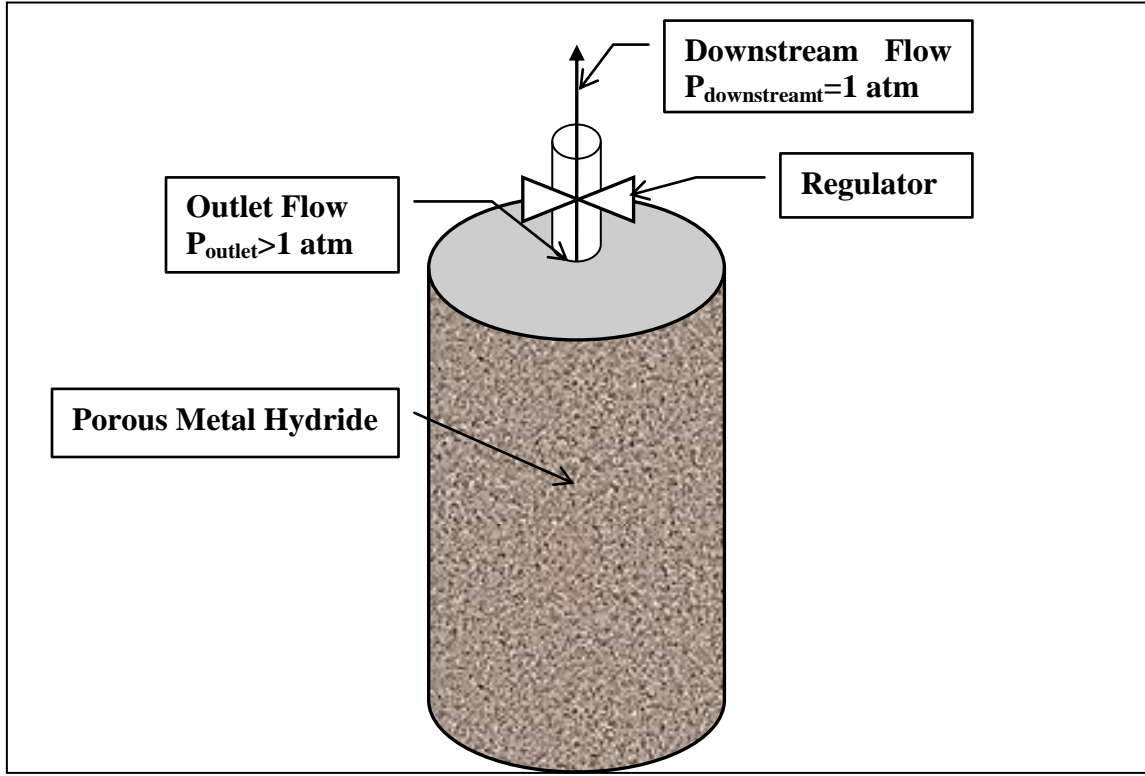


Figure 1. Schematic of a Metal Hydride Bed

### 3. Modeling

A two dimensional axis symmetric model is applied on the MHB described above. The model equations are solved for the  $r$  and  $z$  direction both. This model concern mass transport, gas momentum and hydrogen desorption in the MHB.

#### 3.1 Momentum Balance of the Gas Phase

The velocity profile of the gas phase in the porous MHB can be expressed by Darcy's Law below:

$$v_g = -\frac{K}{\mu_g} \nabla P_g \quad [1]$$

where  $K$  is the permeability of the porous metal hydride;  $\mu_g$  is the dynamic viscosity of hydrogen;  $P_g$  is the hydrogen pressure of the gas phase;  $v_g$  is the hydrogen velocity. The dynamic viscosity of hydrogen is temperature dependent variable which can be calculated by following equation (5).

$$\mu_g = 9.05 \times 10^{-6} \left(\frac{T}{293}\right)^{0.68} \quad [2]$$

#### 3.2 Mass Balance

Equation 1 can be coupled with the continuity equation to solve the mass balance of the gas phase.

$$\varepsilon \frac{d\rho_g}{dt} + \nabla \cdot (\rho_g v_g) = -m_d \quad [3]$$

where  $\rho_g$  is the density of hydrogen gas;  $m_d$  is hydrogen desorption rate of metal hydride;  $\varepsilon$  is the porosity of metal hydride. The  $\rho_g$  is determined by ideal gas law:

$$\rho_g = \frac{M_g P_g}{R_g T} \quad [4]$$

where  $M_g$  is the molecular weight of hydrogen.

Since the solid volume is fixed, the hydrogen density in the metal hydride can be expressed below:

$$(1 - \varepsilon) \frac{\partial(\rho_{H_2M})}{\partial t} = m_d \quad [5]$$

where the density in the derivative ( $\rho_{H_2M}$ ) is the mass of hydrogen in the metal hydride

divided by the volume of the tank times the one minus the porosity.

### 3.3 Hydrogen Desorption Rate

The hydrogen desorption rate  $m_d$  described in equation 3 and 5 can be obtained by solving the formula below (6):

$$m_d = -C_d \exp\left(-\frac{E_d}{R_g T}\right) \left(\frac{P_{eqd} - P_g}{P_{eqd}}\right) \rho_{H_2M} \quad [6]$$

where  $C_d$  is the desorption constant;  $E_d$  is the activation energy for desorption;  $P_{eqd}$  is the equilibrium pressure of desorption;  $\rho_{H_2M}$  is the hydrogen density in metal hydride. The value of equilibrium pressure of desorption is given by van't Hoff equation:

$$\ln P_{eqd} = A - \frac{B}{T} \quad [7]$$

where A and B are chose from the DOE Hydride Material Listing Database (7). In our work, A is 17.478 and B is 3704.60 respectively.

Since desorption only starts when the gas phase pressure is below the equilibrium pressure, a logical statement is applied to equation 6 which guarantees the desorption stops when gas pressure approach equilibrium value. Adsorption is not considered in this work.

### 3.4 Energy Balance

Since the model is simulated under adiabatic condition, the lumped energy balance equation is introduced for gas and solid mixture below. The temperature of hydrogen and metal is assumed at same value anytime in bed.

$$(\rho C_p)_e \frac{\partial T}{\partial t} = k_e \nabla^2 T + m \Delta H^0 + S_{th} \quad [8]$$

where  $(\rho C_p)_e$  is the effective specific heat term which is determined by equation 9;  $k_e$  is effective thermal conductivity;  $\Delta H^0$  is reaction heat of desorption;  $S_{th}$  is heat source which is zero in adiabatic model.

$$(\rho C_p)_e = (\varepsilon \rho_g C_{pg} + (1 - \varepsilon) \rho_s C_{ps}) \quad [9]$$

where g represents gas and s represents solid.

### 3.5 Initial and Boundary Conditions

The initial hydrogen density in the metal hydride for this time dependent study is equal to

the saturated hydrogen density  $\rho_{H_2M,S}$  because the MHB is fully loaded before it starts to release hydrogen. In this work,  $\rho_{H_2M,S}$  is chose as 360 kg/m<sup>3</sup>.

The initial gas phase pressure is set to 156.49 kPa which is equal to equilibrium pressure at 298K (initial bed temperature). Although the MHB is operated at 5 MPa at the start, the simulation shows before the average pressure approaches the equilibrium value, only the small amount of hydrogen in gas phase is released and there is no desorption in this period. From figure 2, we can see there is initial pressure drop from 5MPa to the equilibrium pressure. This process last only 321s (5mins) without desorption. Thus, we discard this period and focus on what happened when desorption starts (t=0).

Table II is a summary of the initial and boundary conditions used by our isothermal model. The center axis, wall, top surface and bottom surface are all set as insulation boundaries. For boundary 4 (figure 3), the outlet, constant flow rate is used as the boundary setting. Combined with the ideal gas law, the boundary velocity can be derived.

**TABLE II.** Initial and Boundary Conditions for Isothermal Model.

Initial Condition, t=0	$p = P_{eqd}$ $\rho_{H_2M} = \rho_{H_2M,S}$ $T = T_{ini}$
Boundary 1, center axis	$dp/dr = 0$ $d\rho_g/dr = 0$ $d\rho_{H_2M}/dr = 0$
Boundary 8, wall	$dp/dr = 0$ $d\rho_g/dr = 0$ $d\rho_{H_2M}/dr = 0$ $dT/dr = 0$
Boundary 2,7, top and bottom	$dp/dz = 0$ $d\rho_g/dz = 0$ $d\rho_{H_2M}/dz = 0$ $dT/dz = 0$
Boundary 4, outlet	$v_g = v_{g,outlet}$ $N = n_{outlet}$ $d\rho_{H_2M}/dz = 0$ $T = T_{out}$

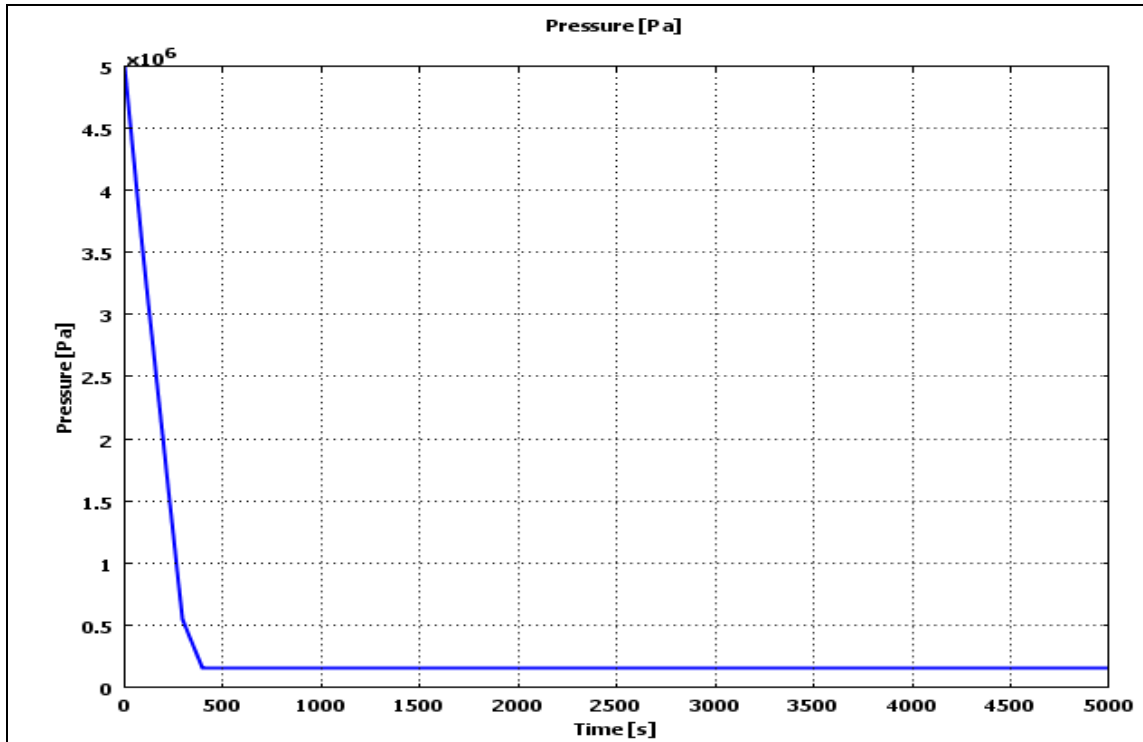


Figure 2. Gas Phase Pressure Variation when Simulation Start at Initial Pressure is 5Mpa

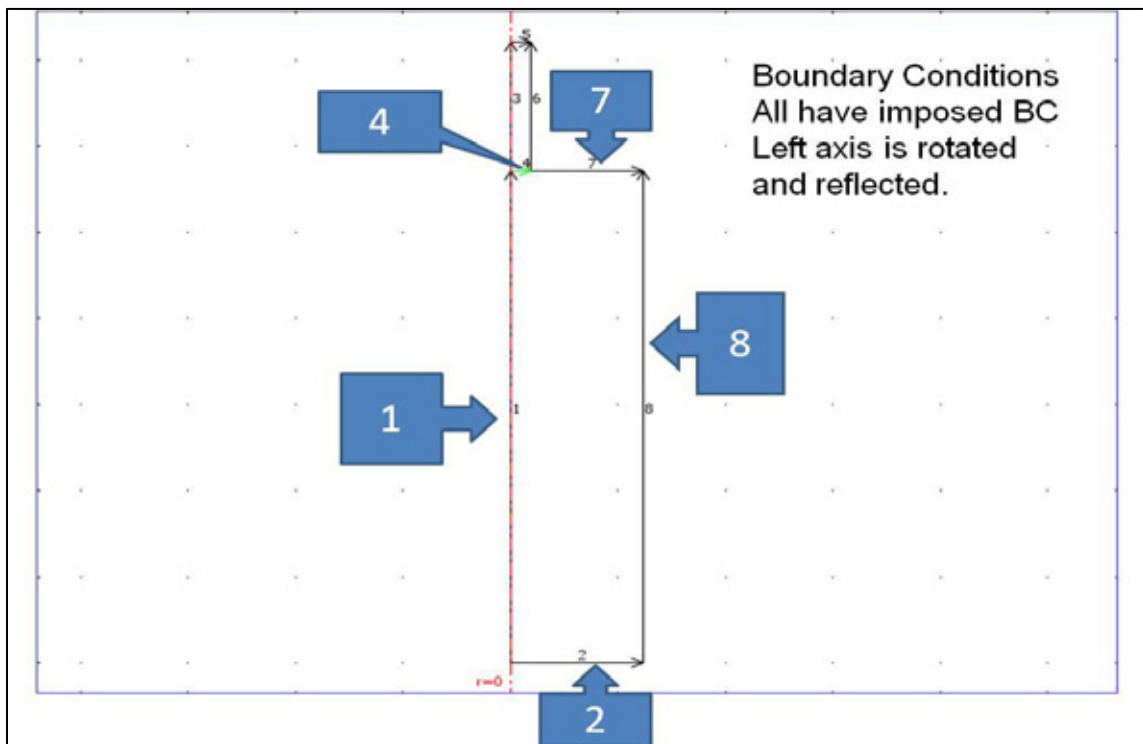


Figure 3. Boundary Setting for Isothermal Model

### 3.6 Parameters Investigation

TABLE III. Parameters Used in Simulation.

	Value	Range:	Comments
<b>Metal Properties:</b>			
Metal Density, $\rho_{emp}$ [kg/m <sup>3</sup> ]	6000	4000-8000	Pure Metal
Metal Density at Saturation, $\rho_s$ [kg/m <sup>3</sup> ]	6360		
Saturated Hydrogen Density in Metal Hydride, $\rho_{H2M_s}$ [kg/m <sup>3</sup> ]	360		
H <sub>2</sub> Storage Capacity, h [kg H <sub>2</sub> /kg Metal]	6%	DOE 2010	Hydrogen Loading Ratio
Permeability, K [m <sup>2</sup> ]	10 <sup>-8</sup>	10 <sup>-6</sup> -1.1*10 <sup>12</sup>	Experiment
Porosity, $\epsilon$	0.5	0.5	Void Fraction of Metal Hydride
Specific Heat of Hydrogen, $C_{pg}$ [J kg <sup>-1</sup> K <sup>-1</sup> ]	14890		
Specific Heat of Metal, $C_{ps}$ [J kg <sup>-1</sup> K <sup>-1</sup> ]	500	490-1000	Pure Metal
Effective Thermal Conductivity, $k_e$ [W m <sup>-1</sup> K <sup>-1</sup> ]	1.32	0.34-1.6	Gas and Metal Mixture
<b>Desorption Properties:</b>			
Desorption Active Energy, $E_d$ [J mol <sup>-1</sup> ]	16000	15000-30000	Active Energy
Desorption Heat, $\Delta H_d$ [J mol <sup>-1</sup> ]	1.6*10 <sup>7</sup> [J kg <sup>-1</sup> ]	27500-36000	Desorption Energy
Desorption Coefficient, $C_d$ [s <sup>-1</sup> ]	10	10	Experiment
Desorption Equilibrium Pressure, $P_{eqd}$ [Pa]	Van't Hoff equation: A=17.478, B=3704.61		

The parameters used in modeling are widely investigated. One of the purposes of this paper is to set a guide for following MHB design. Thus, we select appropriate values to optimize the results. Table III shows the parameters used in this work (8).

- 4) Set the initial and boundary condition (Table II).
- 5) Set scalar expressions and constants
- 6) Initialize the mesh.
- 7) Choose time dependent solver and solve the problem.

### 3.7 Modeling Procedure

The model described above is applied using COMSOL software which solves partial differential equation by the finite element method. The calculation procedure includes:

- 1) Choose 2D symmetric mode.
- 2) Choose the appropriate PDE mode: Darcy's Law for porous material and mass diffusion mode; heat conduction mode.
- 3) Draw the geometry (figure 4).

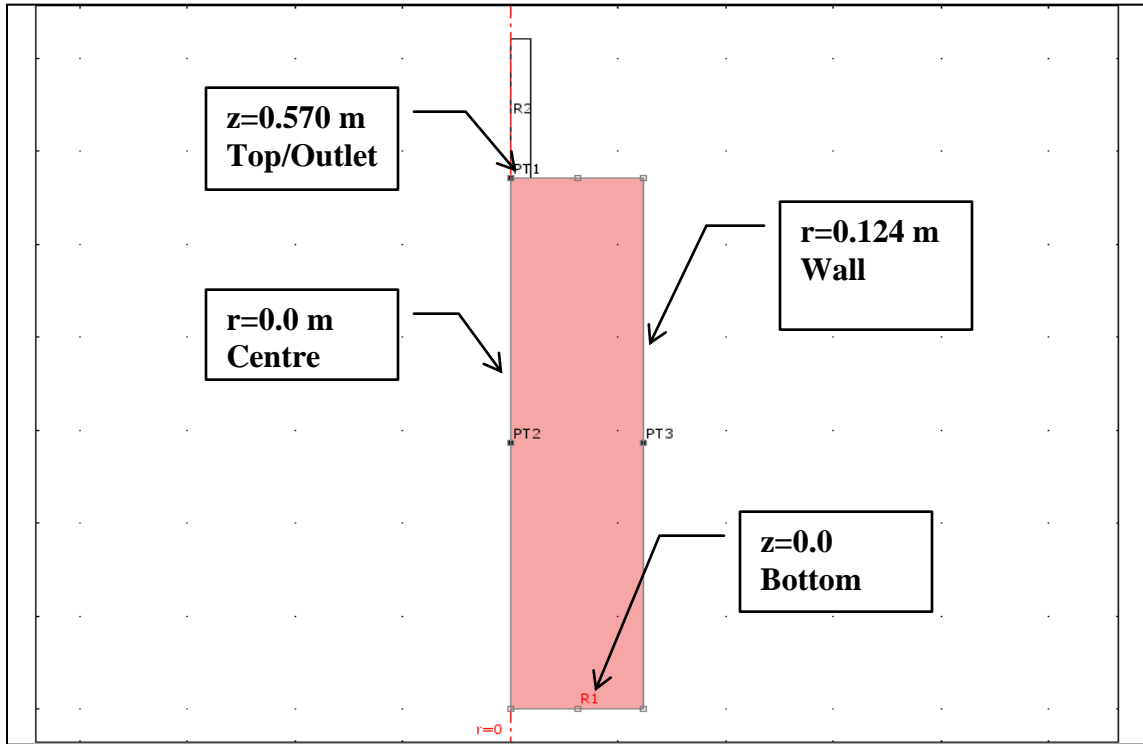


Figure 4. Schematic of Modeling Area

#### 4. Results and Discussion

This section presents the simulation results of the adiabatic model described above. The variation of hydrogen gas phase pressure, hydrogen concentration in the metal hydride, hydrogen desorption rate and temperature are calculated as key variables.

The distribution of hydrogen gas phase pressure, hydrogen concentration in the metal hydride, hydrogen desorption rate and temperature are shown in Figure 5, 6, 7 and 8 respectively. It can be seen that these variables could be consider as essentially spatially constant for the parameters chosen in the study.

Figure 9 shows hydrogen gas phase pressure at the outlet ( $r=0$ ,  $z=0.570$ ) varied along time. It can be seen, the pressure drops quickly with time. The sharp drop happens at 2600s. The inner pressure approach 1 atm at around 2700s. As we discussed before, due to the downstream hydrogen pressure setting ( $1 \text{ atm} = 1 \cdot 10^5 \text{ Pa}$ ) the outlet pressure should be kept higher than downstream pressure in order to maintain the constant flow requirement. Therefore, for the adiabatic model we are simulating the hydrogen supply can last only 2700s mostly which is a very small value compared to the theoretical value of 30,120s. There is plenty of hydrogen

left in the MHB at the end of releasing because of losing drive force.

Figure 10 shows the hydrogen concentration in the metal hydride at the outlet ( $r=0$ ,  $z=0.570$ ) varied lineally along time. The plot also shows the hydrogen concentration in metal is still high at the end of releasing.

Figure 11 shows the results of the analysis of the hydrogen desorption rate at the outlet ( $r=0$ ,  $z=0.570$ ). The equation 6 is divided by three terms which are presented in one plot. Term 1 represents the Ahhrenius temperature effect. Term 2 is the gas pressure effect on the desorption rate. Term 3 is the effect of hydrogen concentration in the metal hydride. Obviously, for the adiabatic model, the temperature effect dominates the desorption performance from the beginning. When the value of term 1 approach zero, desorption stopped even there are still plenty hydrogen in metal.

$$\text{Term 1} = -C_d \exp\left(-\frac{E_d}{R_g T}\right) \quad [10]$$

$$\text{Term 2} = \left(\frac{P_{eqd} - P_g}{P_{eqd}}\right) \quad [11]$$

$$\text{Term 3} = \rho_{H_2M} \quad [12]$$

Figure 11 represents inner temperature at the outlet ( $r=0, z=0.570$ ) varied along time. It can be observed the temperature dropped quickly in the MHB. At the end of releasing the inner

temperature is close to 140K which is a very low value. This explained why desorption stopped even there is a lot of hydrogen in metal.

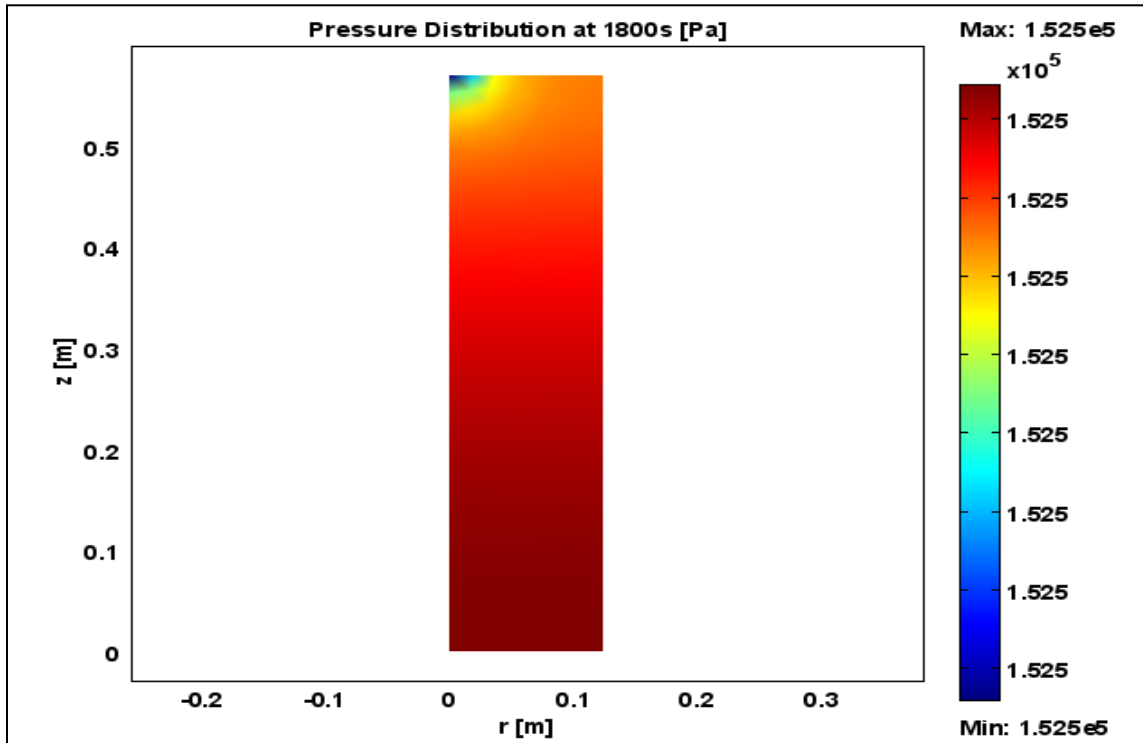


Figure 5. Gas Phase Pressure Distribution in MHB at 1800 s (0.5 hr)

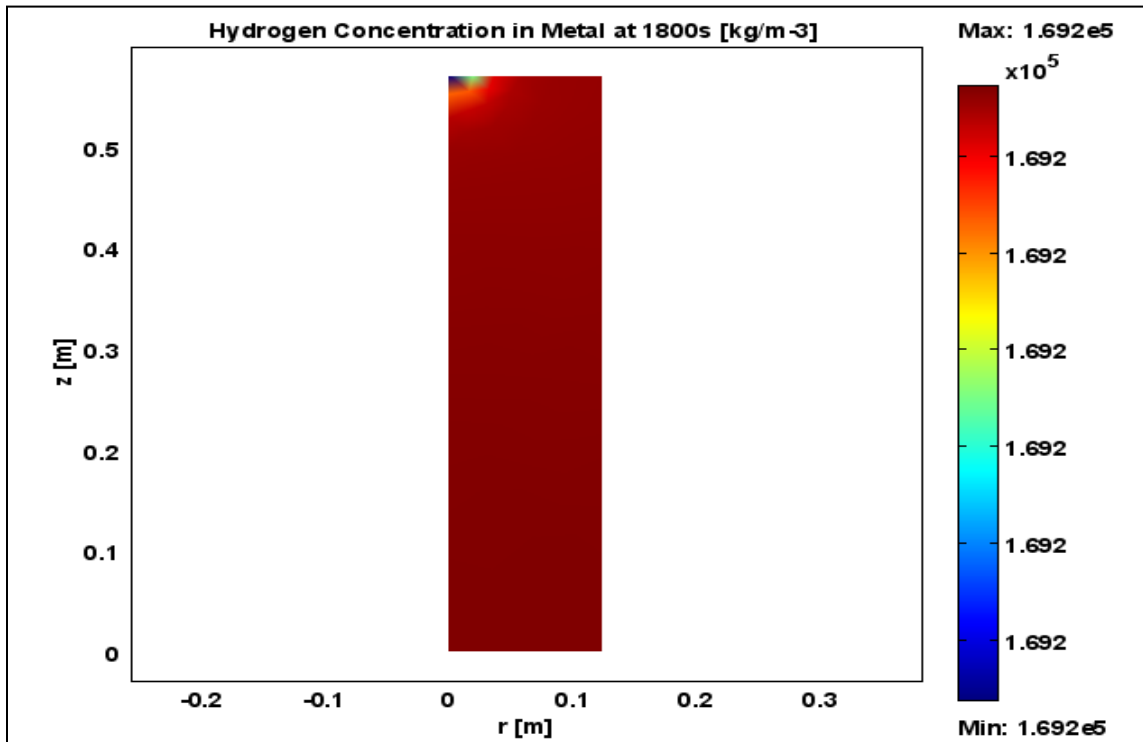


Figure 6. Hydrogen Concentration Distribution in Metal Hydride at 1800 s (0.5hr)

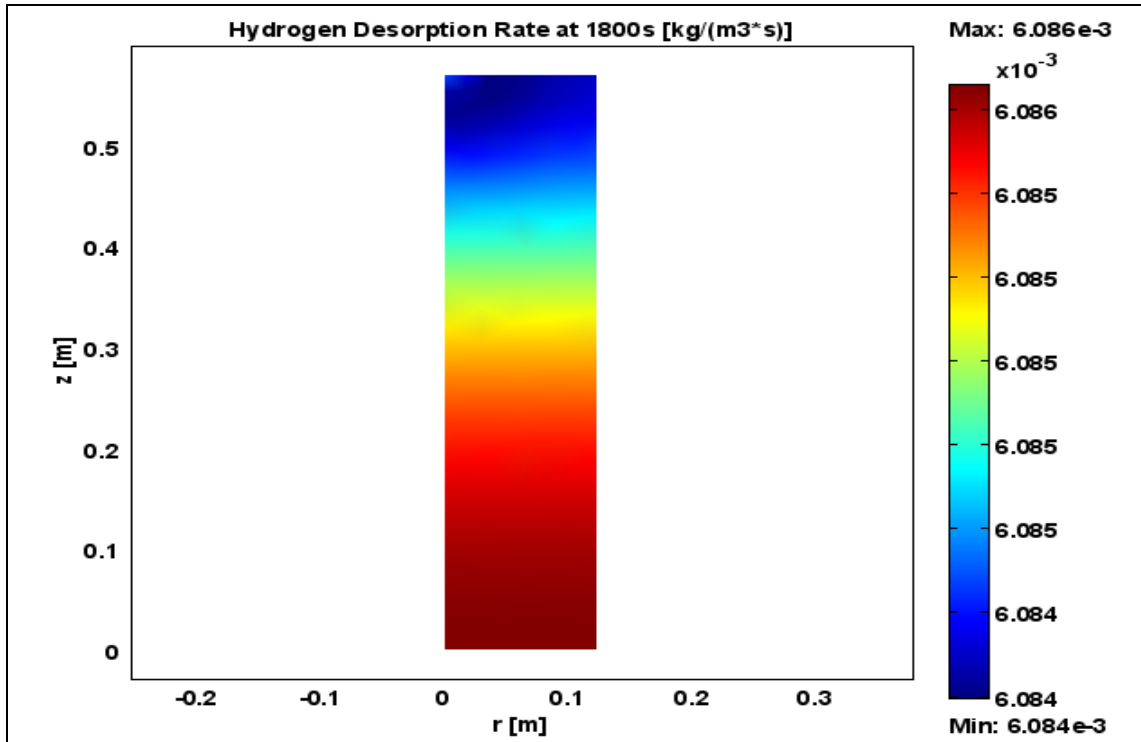


Figure 7. Hydrogen Desorption Rate Distribution at 1800 s (0.5 hr)

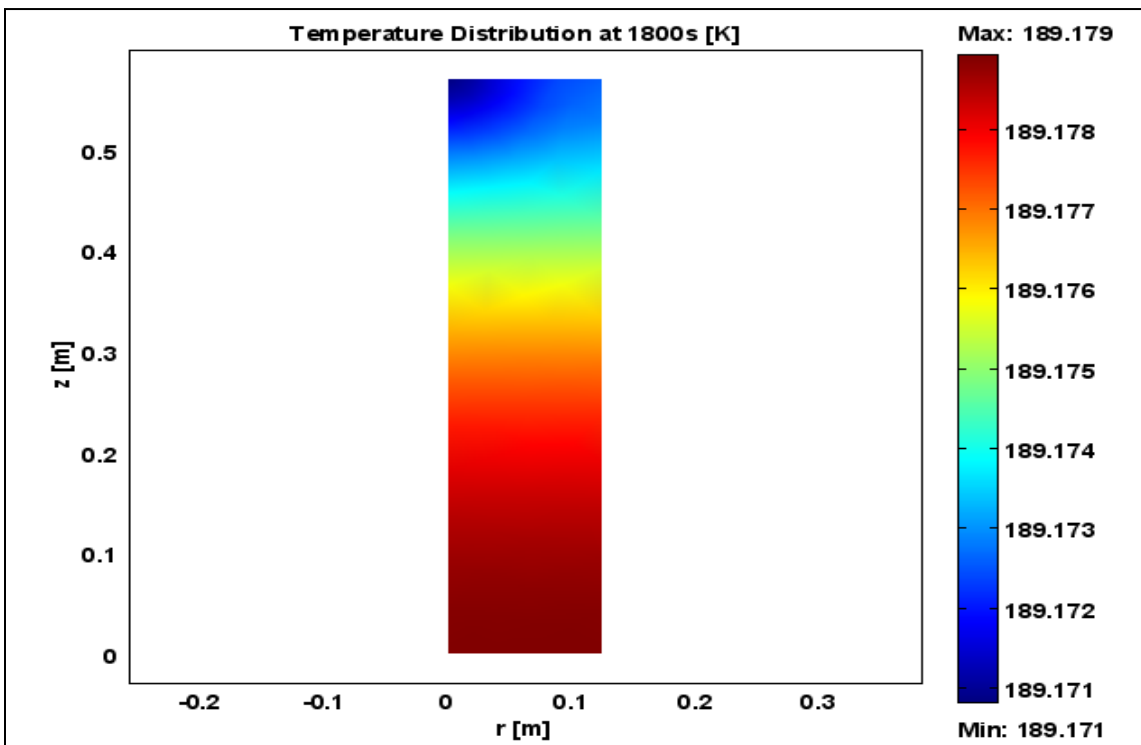


Figure 8. Inner Temperature Distribution at 1800 s (0.5 hr)



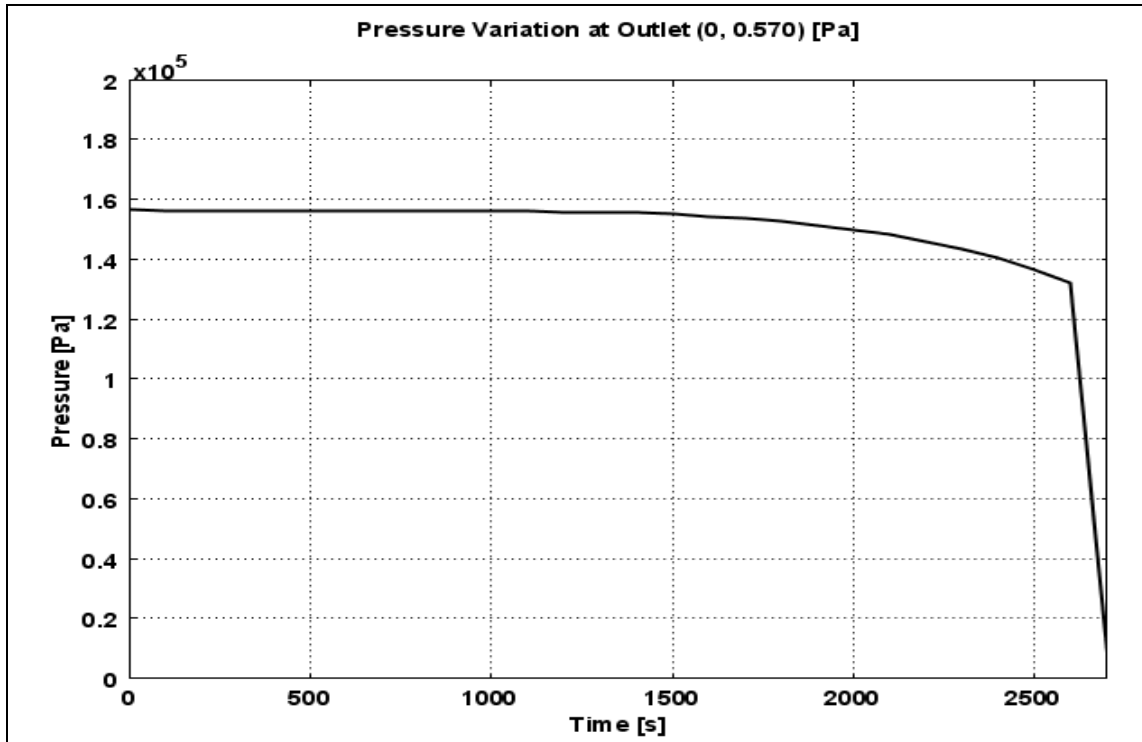


Figure 9. Hydrogen Gas Phase Pressure Variation at Outlet ( $r=0, z=0.570$ )

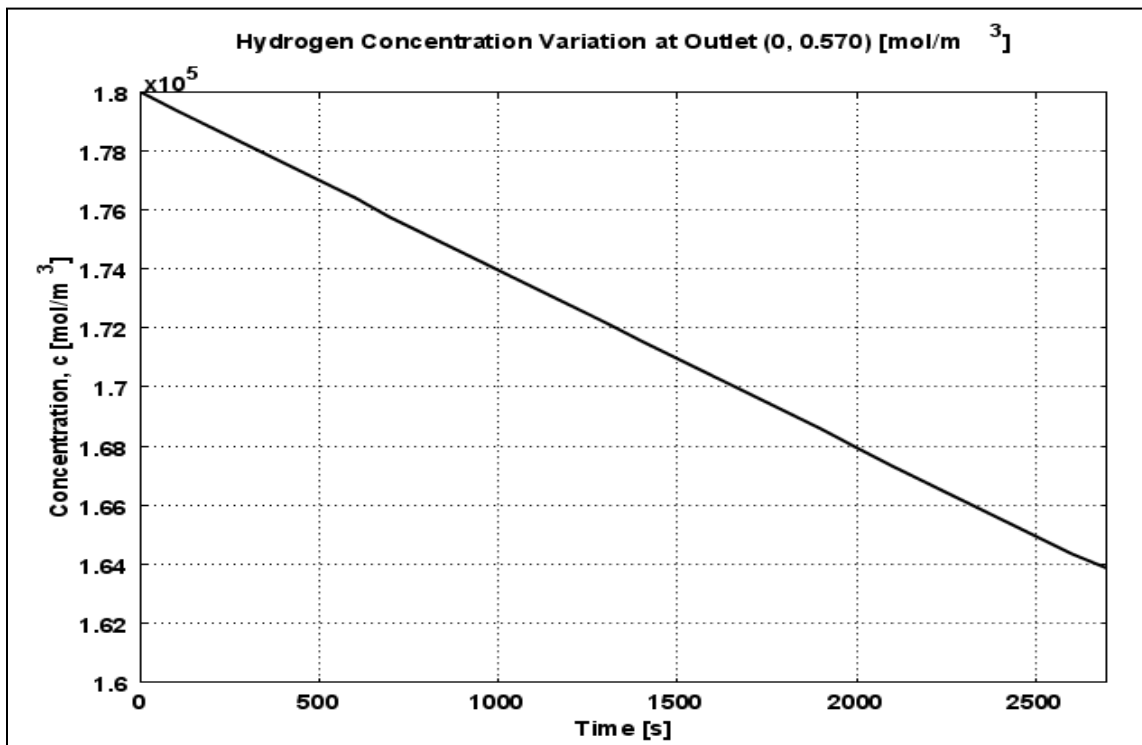


Figure 10. Hydrogen Concentration in Metal Hydride Variation at Outlet ( $r=0, z=0.570$ )

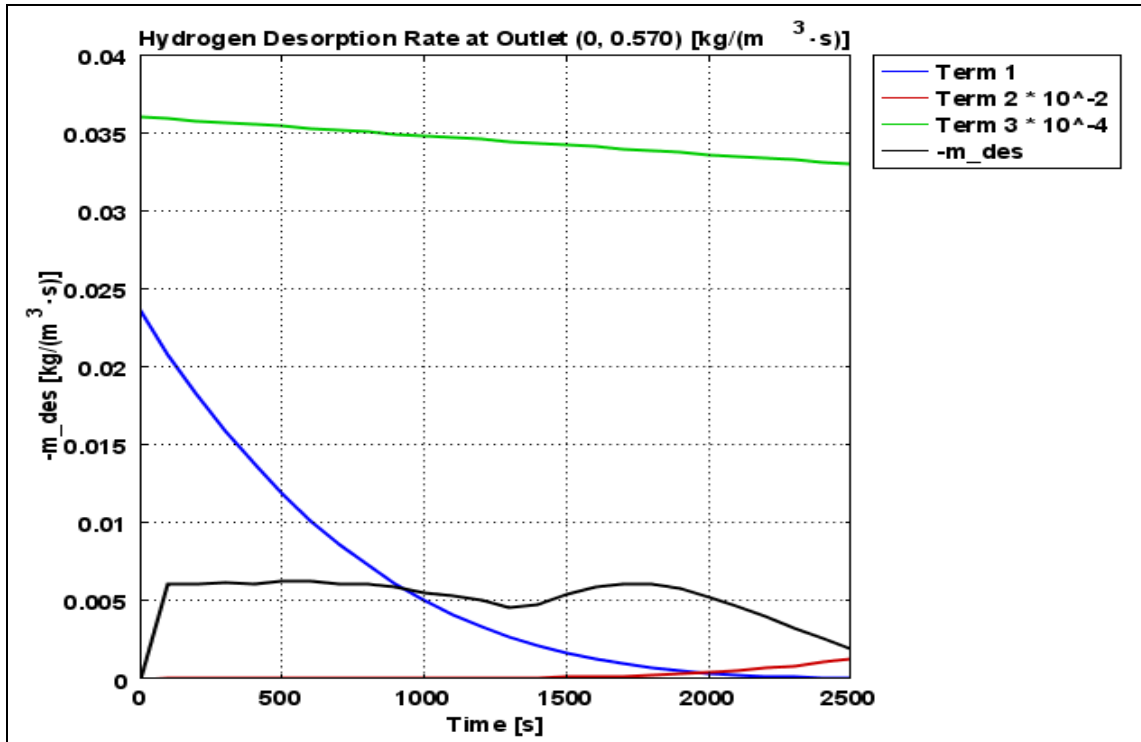


Figure 11. Hydrogen Desorption Rate Variation at Outlet ( $r=0, z=0.570$ )

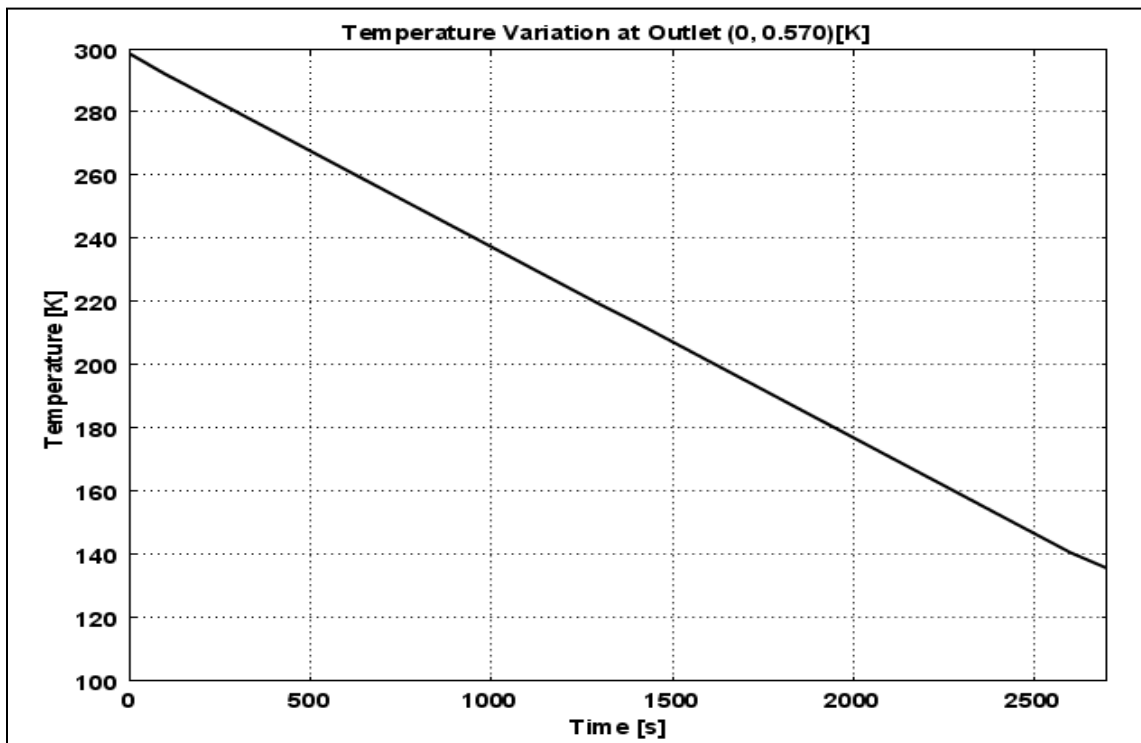


Figure 12. Inner Temperature Variation at Outlet ( $r=0, z=0.570$ )

## 5. Conclusion

In this paper, we analyze a metal hydride bed system which provides hydrogen to a fuel cell at certain power and pressure requirements. Darcy's Law is coupled with the continuity equation to estimate the hydrogen gas phase profile. The mass balance equation is used to calculate the hydrogen concentration profile. The lumped energy balance equation is applied also to analyze the temperature distribution in MHB. Hydrogen desorption is taken into account. These equations are applied in COMSOL to run simulations under adiabatic conditions.

The simulation result suggests: 1) hydrogen gas phase pressure is essentially spatially constant, it varies along time until the end of the hydrogen release; 2) the hydrogen concentration in metal hydride is spatially constant, it decrease along time linearly; 3) the hydrogen desorption rate appears term by term varied along time; the temperature in metal hydride is spatially constant, it decrease along time linearly.

In order to maintain the downstream pressure at 1 atm, the pressure at outlet must be greater than 1 atm. The simulation indicates, for the adiabatic case we are discussing above, the MHB can maintain constant hydrogen gas flow to only 2700 s. The fast decreasing temperature limit the hydrogen desorption.

In future work, the heat source term be taken into account. The current adiabatic model could be expanded to external heat and constant heat source conditions. Parameter investigation will be conducted.

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