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Modeling of heat and mass transfer in $LaNi_5$ matrix during hydrogen absorption-desorption cycle

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Packed bed reactors using metal hydride are attracting a lot of attention as potential hydrogen storage systems. Some operational and design variables are major constraints to obtain a proper inflow/outflow of hydrogen into a metal hydride reactor. These variables include packed bed thermal conductivity, porosity, pressure and temperature distributions in the reactor during the absorption/desorption cycle. They also cause a mechanical stress induced by temperature gradient. In this paper, two dimensional models are implemented in COMSOL multiphysics to simulate the hydrogen flow, pressure and temperature distributions in the packed bed reactor during absorption/desorption cycle. Also, stresses in porous metal hydride induced by temperature variation in the heating/cooling cycle were evaluated. A possible effect of stress induced, porosity changes on diffusion and heating of hydrogen in both radial and axial direction in packed bed is discussed. The model consists of a system of partial differential equations (PDE) describing structural mechanics of stress, heat and mass transfer of hydrogen in the porous matrix of the packed bed reactor.

Keywords: Packed bed, reactor, stress, metal hydride, hydrogen, structural mechanics, heat transfer, mass transfer.

INTRODUCTION

Due to the high demand and a consistent usage of non-renewable carbonaceous fuels worldwide such as gasoline, there is a need to provide an alternative energy source that will serve the same purpose as gasoline[1].

Hydrogen has been receiving great boost throughout the world as an alternative energy to be used in a fuel cell. Hydrogen storage is one of the central technical barriers to the wide deployment of hydrogen, particularly for automotive application (e.g. hydrogen fuel cell vehicles). Current hydrogen storage methods including gas compression and liquefaction are not optimal for onboard application due to the associated large quantity of energy consumption and safety issues.

A promising alternative is solid-metal hydride storage utilizing metal hydrides to absorb/desorbs hydrogen at a relatively low pressure (< 20 bar>) which offers safety and cost advantage, however, the obvious disadvantage of weight for hydrogen onboard storage.

Efficient release of hydrogen gas in the metal hydride reactor should meet the need of fast load variation in order to build and satisfy such hydrogen systems, physics of the transport process coupled with reaction kinetics are very important such as hydrogen mass flow in the hydride bed, heat transfer within the bed and local hydrogen absorption rate.

In the previous years, several mathematical models for analyzing hydrogen absorption /desorption in metal hydride beds were presented in the literature.

Jemni and Nasrallah[2] presented a model for the two--dimensional transient heat and mass transfer within a cylindrical reactor. The influence of some parameters (reactor radius, temperature and inlet pressure) on the dynamic reactor performance was determined.

Aldas et al.[3] extended the mathematical model of Jemni and Nasrallah to three-dimensions demonstrating that hydrogen flow significantly influences the temperature profile in the system.

Mayer et al.[4] developed a one-dimensional model which showed that heat and mass transfer are key factors affecting the reaction rate in the reactor.

Nakawaga et al.[5] predicted the transient heat and mass transfer phenomenon through the hydride bed by using a two-dimensional mathematical model with hydriding and dehydriding kinetics.

Suda et al.[6] compared their mathematical model with the experimental data obtained from a cylindrical vessel. But in their experiments, the hydrogen bed was cooled or heated by water flowing in an annular shell around the vessel; as a result, their model was only compared with experimental results for validation as one- dimensional model.

Marty et al.[7] presented a two and three dimensional numerical simulation for the prediction of the characteristic of an industrial tank filled with hydrides. The comparison between 2D and 3D calculations showed that three-dimensional tank geometry is necessary to properly design the tank.

In this paper, a 2-dimensional reactor configuration has been simulated consisting of two rectangular enveloped with fins where there is discharge/charge of hydrogen in metal hydride. The experimental work of Jemni et al was also simulated to verify the model, and validate the experimental results.

Mathematical simulations have been achieved through the desorption of transient heat and mass transport phenomena by partial differential equations (PDE) using the COMSOL MULTIPHYSICS. The finite element approach allows easy adaptation of the model to different reactor geometrics, allowing accurate analysis and optimization of the design.

GEOMETRY

The cylindrical reactor presented by Jemni et al was re-configured as a rectangle as illustrated in the Figure1 below. The geometry consists of two rectangles which

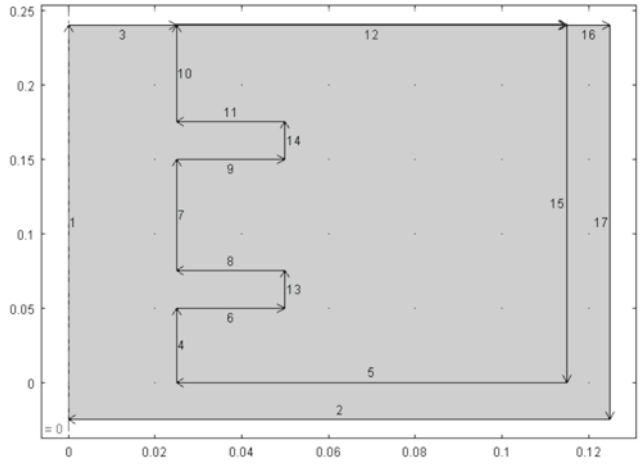

Figure 1. Geometry showing different boundaries in $LaNi_5$ Hydride Hydrogen Storage Tank (LHHST)

were built in COMSOL software and Boolean operation of union and difference was performed on the operation. One rectangle represents domain for hydrogen and metal hydride, the second rectangle represents the domain that supplies heat to the system which is copper. For the entire configuration hydrogen enters the reactor in axial direction.

The assumptions considered in developing the model are the following:

(1) The media is in thermal equilibrium (gas temperature is the same as solid temperature)

(2) The gas phase is ideal

(3) Velocity of hydrogen gas is calculated by Darcy's law

(4) Equilibrium gas pressure is calculated by Van't Hoff equation, disregarding hysteresis and plateau inclination of real pressure/concentration isotherms.

The governing equation consists of energy balances for hydrogen gas, metal hydride beds. Mass balances for hydrogen diffusion and momentum balances which includes Darcy's term to account for momentum transfer due to pressure gradient in the metal hydride porous media.

MODELING EQUATIONS

The following equations are incorporated in COMSOL Multiphysics to simulate hydrogen absorption/desorption in a metal hydride bed.

Mass balance

The mass conservation equation of the solid metal hydride:

$$(1-\varepsilon)\frac{\partial \rho_s}{\partial t} = m \tag{1}$$

Mass balance equation for hydrogen gas:

$$\varepsilon \frac{\partial \rho_g}{\partial t} + \nabla(\rho_g u_g) = m \tag{2}$$

where ϱ_g denotes the density of the hydrogen gas in the reactor during the desorption process. Hydrogen density is determined using the perfect gas law. The velocity of hydrogen gas (u_g) is calculated using the Darcy's law (Jemni *et al*., 1995):

$$u_g = \frac{K}{\mu_g}\nabla P_g \tag{3}$$

Where K is permeability, μg is gas viscosity, Pg is gas pressure.

Distribution of hydride powder particles by size and shape causes widening and smoothing of adsorption/desorption curves. The complex mechanism of hydrogen reaction with metal hydride is not well known, and macrokinetics expressions are obtained from the experimental data for each particular metal hydride powder.

The equation for hydrogen kinetics (hydrogen mass desorbed, *m*, per unit time and per unit volume) is given by (Dhaoua *et. al.* 2007):

$$m = C_d \exp\left(-\frac{E_d}{R_g T}\right)\frac{P_g - P_{eq}}{P_{eq}}\rho_s \tag{4}$$

For the $LaNi_5$–Hydrogen system C_d = 9.57 1/s; E_d = 16.420 KJ/ mol of H2.

Equilibrium pressure P_{eq} can be calculated from the modified van't Hoff equation (Nishizaki T., *et.al,* 1983)):

$$\ln(P_{eq}) = \frac{\Delta H}{RT} - \frac{\Delta S}{R} + (\phi - \varphi_0)\tan\left[\pi\left(\frac{C}{C_m} - \frac{1}{2}\right)\right] + \frac{\beta}{2} \tag{5}$$

where, φ (0.35) and β (0.25) are the plateau flatness factor and the plateau hysteresis factor.

Momentum balance

Momentum balance equation includes Darcy's term to account for momentum transfer due to pressure gradient in the metal hydride porous media:

$$\frac{\partial(\rho_g \varepsilon)}{\partial t} + \nabla\left(-\rho_g \frac{K}{\mu_g}\nabla P_g\right) = 0 \tag{6}$$

where:

Permeability K and porosity ε are related by equation:

$$K = C_k \cdot d_p^2\left(\frac{\varepsilon}{1-\varepsilon}\right)^2 \tag{7}$$

Where d_p is metal hydride particle diameter and constant C_k=2.37x10^{-3}.

Energy balance

Energy balance equation, describing temperature evolution of the hydrogen – porous bed system:

$$\frac{d}{dt}\left(\varepsilon\rho_g C_{pg} T + (1-\varepsilon)\rho_s C_{ps} T - \varepsilon\frac{\rho_g RT}{M_{H_2}}\right) \tag{8}$$

$$+\nabla(\rho_g C_{pg} uT - \lambda_e \nabla T) + (1-\varepsilon)(-\Delta H)\rho_s m = 0$$

The effective thermal conductivity of metal hydride bed traditionally expressed as:

$$\lambda_e = \varepsilon\lambda_g + (1-\varepsilon)\lambda_s \tag{9}$$

BOUNDARY CONDITIONS

The following boundary conditions are properly implemented in the software during the simulation:

Inlet/outlet, wall, flux, and isolation, and they are considered for heat, mass and momentum transfer for both absorption/desorption in the geometry used.

Initial Conditions:

Absorption

P-ini = P = 40bar,T-ini = 293K

Desorption

P-ini =P =10bar, T-ini = 333K

RESULTS AND DISCUSSION

Absorption / Desorption process was simulated for hydrogen storage tank filled with metal hydride. The geometry of the tank and boundary conditions are developed which is represented in figure 1 shown above. The simulation results of the model described above were presented. The distribution of gas pressure, temperature, mass flow rate, density of the gas in metal hydride for both absorption and desorption were presented in figures 2,3,4,5,6,7,8 and 9. Figures 10, 11, and 12, show

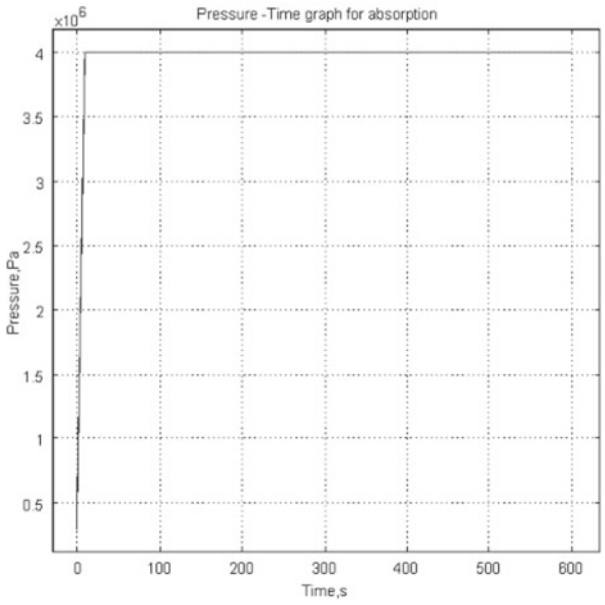

Figure 2. Relationship of hydrogen pressure in $LaNi_5$ Hydride Hydrogen Storage Tank (LHHST) versus time during absorption step T=0=600s

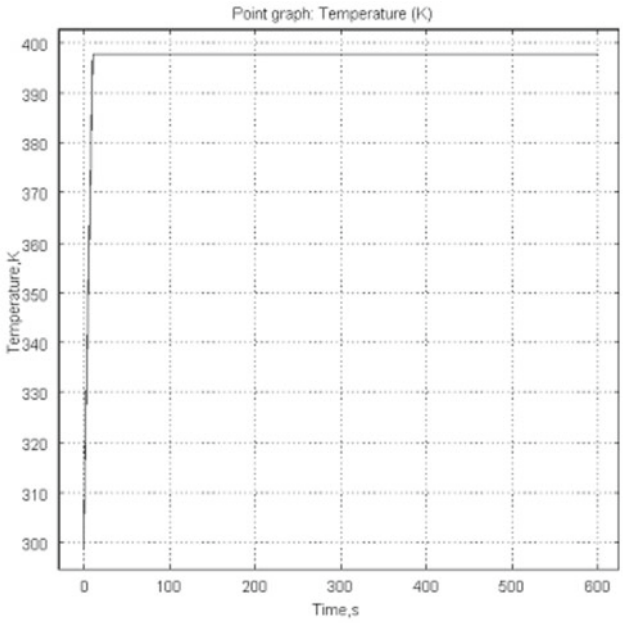

Figure 3. Relationship of hydrogen temperature in $LaNi_5$ Hydride Hydrogen Storage Tank (LHHST) versus time during absorption step T=0=600s

the Concentration, pressure, and temperature profile during the simulation of hydrogen absorption /desorption. Figure 10 shows the Concentration distribution profile of hydrogen in $LaNi_5$ Hydride. Figure 11 shows the pressure distribution profile of hydrogen in $LaNi_5$ Hydride. Figure 12 shows the temperature distribution

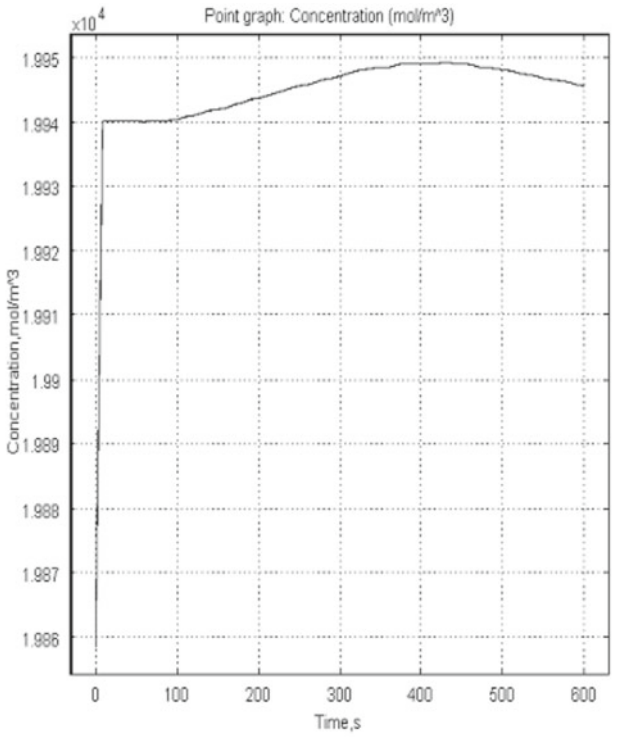

Figure 4. Relationship of hydrogen Concentration in $LaNi_5$ Hydride Hydrogen Storage Tank (LHHST) versus time during absorption step T=0=600s

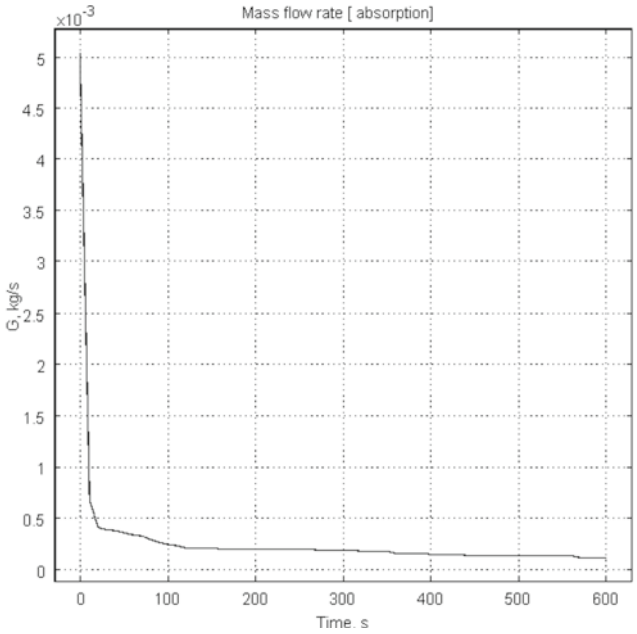

Figure 5. Relationship of hydrogen Flow rate in $LaNi_5$ Hydride Hydrogen Storage Tank (LHHST) versus time during absorption step T=0=600s

profile of hydrogen in $LaNi_5$ Hydride during absorption/ desorption. The simulation time for both absorption and desorption is set to be 600s. The absorption process is accompanied by heat of formation which is exothermic and occurs at high pressure and low temperature, and the desorption process is accompanied by endothermic reaction which occurs at high temperature and low pressure. The pressure in the bed increases as a result of increase in the temperature of the bed and the heating fluid, the equilibrium pressure strongly depends on the temperature. There is decrease in temperature, pressure and the concentration of hydrogen in metal hydride during desorption at different time intervals. The

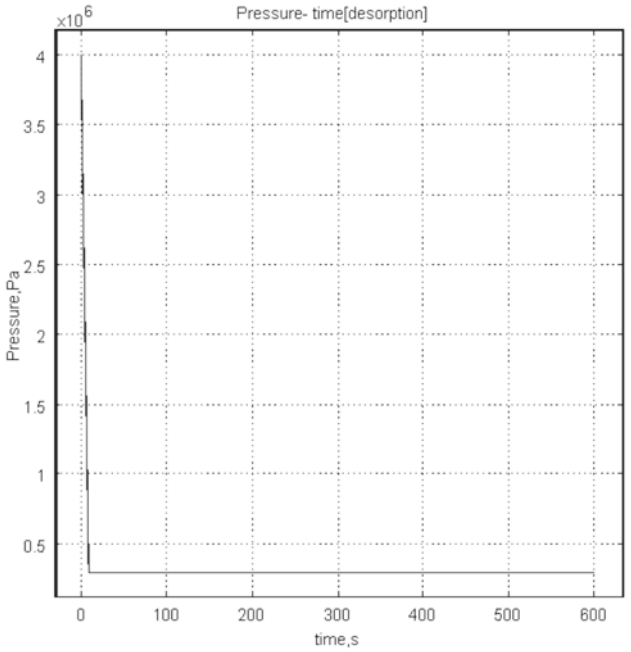

Figure 6. Relationship of hydrogen pressure in $LaNi_5$ Hydride Hydrogen Storage Tank (LHHST) versus time during desorption step T=0=600s

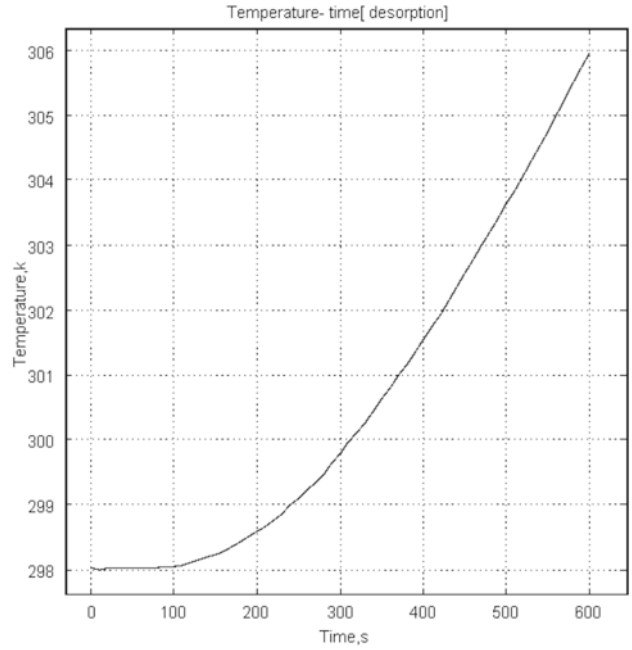

Figure 7. Relationship of hydrogen temperature in $LaNi_5$ Hydride Hydrogen Storage Tank (LHHST) versus time during desorption step T=0=600s

simulation results for both absorption and desorption were presented in the figures below.

Figure 2 shows the pressure distribution in the LHHST during absorption, the pressure in the bed increases with an increase in time during the simulation, in Figure 3 there is a gradual increase in temperature due to the exothermic nature of the reaction between hydrogen and $LaNi_5$.

Figure 4 shows the concentration of hydrogen in LHHST at different time intervals. The concentration of hydrogen in metal hydride increases with time, and more hydrogen is absorbed by $LaNi_5$ within the simulation time of 600s.

Figure 5 shows the mass flow rate of hydrogen in metal hydride during absorption, there is a gradual decrease

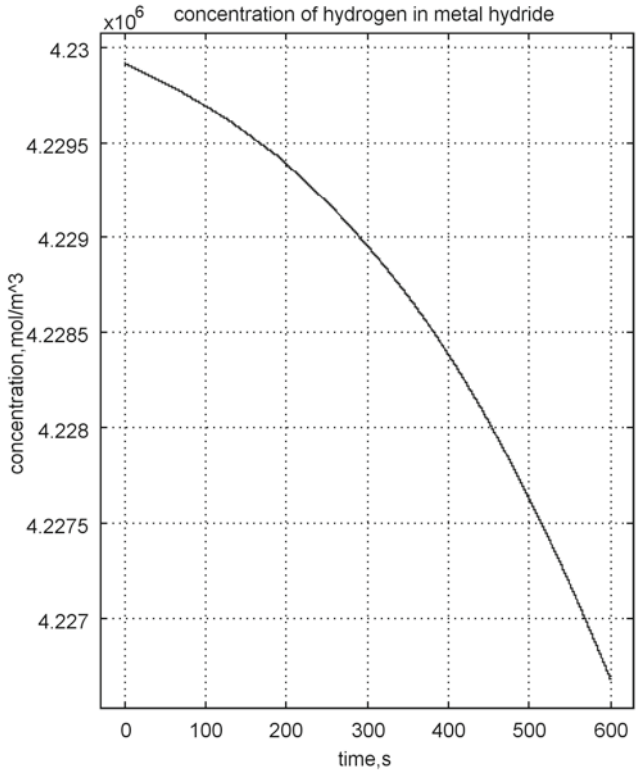

Figure 8. Relationship of hydrogen concentration in $LaNi_5$ Hydride Hydrogen Storage Tank (LHHST) versus time during desorption step T=0=600s

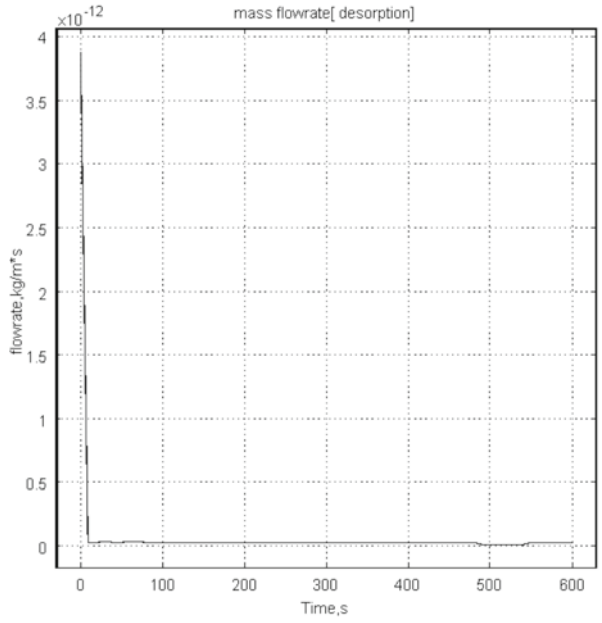

Figure 9. Relationship of hydrogen flow rate in $LaNi_5$ Hydride Hydrogen Storage Tank (LHHST) versus time during desorption step T=0=600s

in hydrogen concentration; more hydrogen is absorbed by $LaNi_5$Hydride within the simulation time of 600s.

Figure 6, 7, and 8 shows decrease in pressure, the temperature and concentration of hydrogen in $LaNi_5$ Hydride during desorption at different time intervals.

Figure 9 shows an increase in hydrogen released from metal hydride hydrogen storage tank at simulation time of 600s during desorption. As the tank is been heated up at higher temperature of 333K, larger percentage of hydrogen was released from LHHST, and it is evidence that at increasing simulation time and higher pressure, low pressure, more hydrogen will be released.

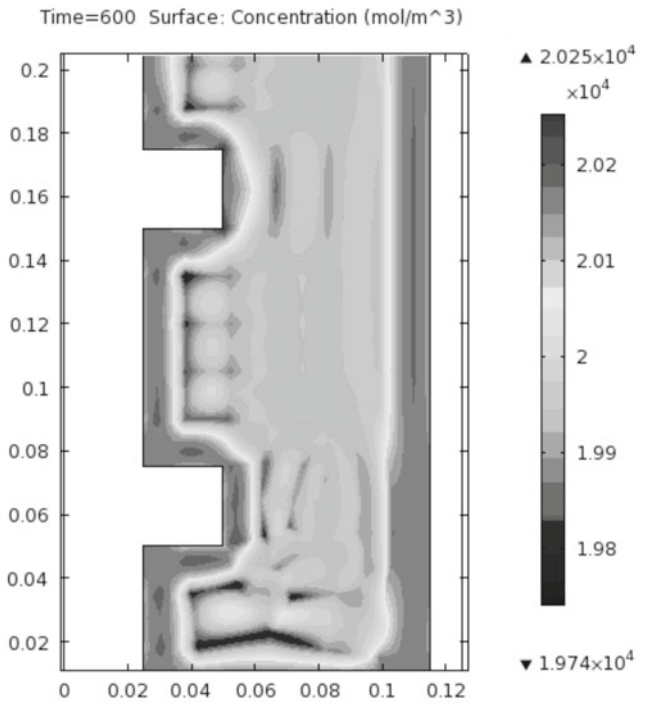

Figure 10. Concentration of Hydrogen in $LaNi_5$ hydride bed profile

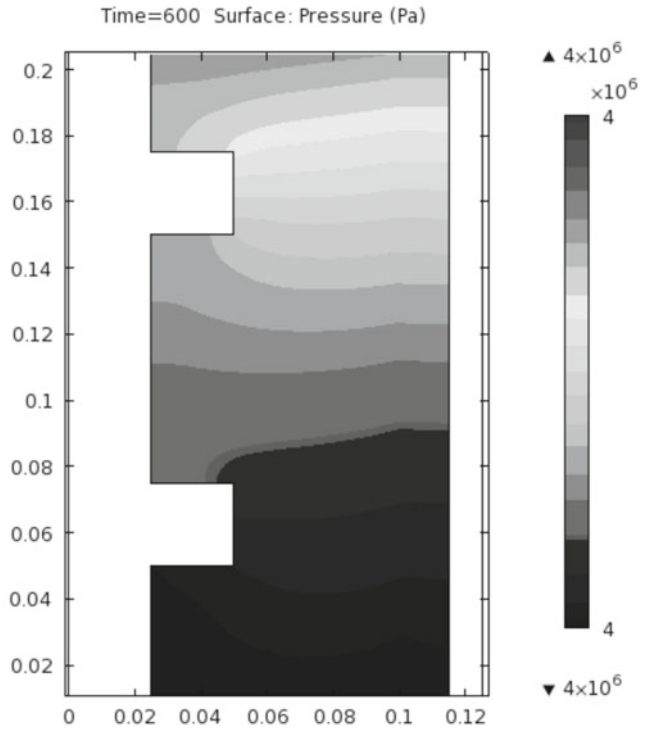

Figure 11. Pressure distribution of Hydrogen in $LaNi_5$ hydride bed profile

CONCLUSIONS

In this paper, the objectives of the work have been verified with the simulation results obtained. The simulation of heat and mass transfer for LHHST with internal geometry was done. Heat transfer, mass transfer, and momentum transfer modules were effectively incorporated in COMSOL Multiphysics 4.0a software.

Absorption of hydrogen in metal hydride occur faster at a lower temperature and higher pressure due to the exothermic nature of the reaction, and desorption occurs at higher temperature and lower pressure due to the endothermic nature of the desorption process. The

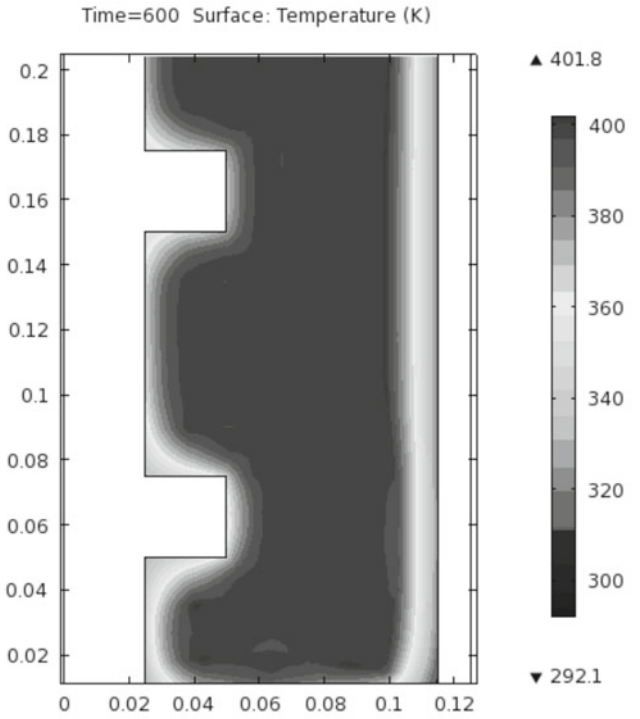

Figure 12. Temperature distribution of hydrogen in $LaNi_5$ hydride bed profile

concentration increases with the absorption of hydrogen and decreases with the desorption of hydrogen. The mass flow rate of hydrogen in metal hydride during absorption decreases with increasing the simulation time, and it increases with an increasing simulation time. More

Table 1. Values of model parameters used in the Simulation (COMSOL Software)

ρ_s	6360kg/m^3	Bulk density of $LaNi_5$ at saturation
ε	0.5	Porosity
ρ_g	0.089g/L	Density of gas
Cps	419J/Kg/K	Solid specific heat capacity
Pg	P[Pa]	Gas pressure
K	1e-08[m^2]	Permeability
T_ini	293K	Initial temperature
Rg	8.314J/mol/K	Universal gas constant
P_ini	40bar	Initial pressure
Ca	59.187[1/s]	Absorption constant
Cd	9.57[1/s]	Desorption constant
Cpg	14890J/Kg/K	Gas specific heat capacity
λe	1.32W/m/K	Effective thermal conductivity
ΔH	-1.539e+07[J/kg]	Heat of formation in absorption/desorption reaction
β	0.25	Plateau hysteresis factor
ϕ	0.35	Plateau flatness factor
Ed	15473[J/mol]	Desorption activation energy
Ea	21179.6[J/mol]	Absorption activation energy
$Peqa$	1000[Pa]*exp(17.6083704.6[K]/T)	Equilibrium gas pressure of absorption
$Peqd$	1000[Pa]*exp(17.4783704.6[K]/T)	Equilibrium gas pressure of desorption
H	150w/m^2/k	Heat source

hydrogen will be released from metal hydride hydrogen storage tank at higher temperature and low pressure.

Nomenclature

U	velocity [m/s]
K	permeability [m^2]
m	hydrogen mass desorbed [$Kgm^{-3}s^{-1}$]
P	pressure [Pa]
R	Universal gas constant [$J/mol^{-1}K^{-1}$]
T	temperature, K
t	time, s
E	activation energy,$JKg^{-1}K$
C_p	specific heat, J $kg^{-1}K^{-1}$
C_a	absorption constant [1/s]
C_d	desorption constant [1/s]
H	heat source [$w/m^2/k$]

Greek letters

λ	thermal conductivity [w/M/K]
β	Plateau hysteresis factor
φ	Plateau flatness factor
μ	dynamic viscosity, $kgm^{-1}s^{-1}$
ε	porosity
ΔH	reaction heat of formation
ΔS	entropy of reaction[J/mol-H2 K]
ρ	density [Kg/m^3]

Subscripts

e	effective
eq	equilibrium
g	gas
s	solid
a	absorption
d	desorption
ini	initial

LITERATURE CITED

1. Momirian, M. & Vesiroglu,T.N, Renewable Sustainable Energy (2002), Rev6, 141–179. Doi:10.1016/j.ijhydene.2011.01.008.6.

2. Jemni, A. & Nasrallah, B.S. Study of 2- Dimensional Heat transfer and Mass transfer during absorption in a metal – Hydrogen Reactor.Int.j.Hydrogen Energy(1995),20(1), 43–52 .Doi:10.1016/0360-3199(93) E0007-8.

3. Aldas, K., Mat, M.D. & Kaplan, Y. Three Dimensional mathematical model for absorption in a metal hydride bed. Int. J.Hydrogen Energy (2002), 27(10), 1049–1056.Doi:10.1016/j.ijhydene.2008.12.096.

4. Mayer, U., Grol, M. & Supper, W. Journal of less common metals (1987), vol44, 131–235.

5. Nakagawa, T., Inomata, A., Aoki, H. & Miura, T. Numerical analysis of heat and mass transfer characteristics in the metal hydride bed. Int. journal. Hydrogen Energy (2002).25(4), 339–350.Doi:-org/10.1016/so360-3199 (99) 0036-1.

6. Suda, S., Kobayashi, N., Morishita, E. & Takanmoto, N. Journal of less- common metals (1983), vol32, 89–325. Doi/abs/10.1111/j.1440.

7. Marty, P., Fourmigue, J.F, De Rango, P., Fruchart, D. & Charbouner, J., Numerical simulation of heat and mass transfer during the absorption of hydrogen in a magnesium hydride. Energy conversion and management (2006), Vol 47, 3632–3643.

8. www.comsol.com.

9. Jenni, A., Contribution a letude des transfer de chaleur et de masse dans inreacteur metal – hydrogen(1997).

10. Askri, F., ben Salam, M., Jenni, A. & ben Nasrallah, S., Optimization of hydrogen storage in metal hydride tanks, International journal of hydrogen Energy 34(899), (2009).doi:10.1016/j.ijhydene. 2008.11.021

11. Mahmut Mata, D. & Yuksel Kaplan, Numerical study of hydrogen absorption in an lm-Ni_5 hydride reactor, international journal of hydrogen Energy, 26, (2001) 957–963. Doi/10.1016/j.ijhydene.2008.11.021.

12. Chung, C.A., C,J, HO,Thermal fluid behavior of the hydriding and dehydriding processes in a metal hydride hydrogen storage. Doi/10.1016/SO360-3199 (01) 0030-1.

13. Aldas, K., Mat, M.D. & Kaplan, Y., A three dimensional mathematical model for absorption in a metal hydride bed. Int.J. Hydrogen Energy, 27, (2002) 1049–1056. Doi/10.1016/j.ijhydene.2011.12.140.

14. Dhaoua, H., Mlloulia, S., Askaria, F., Jemni, A. & Ben Nasrallaha, S. Int.J.Hydrogen Energy, 32, (2007) 1922. Doi:/10.1016/j.ijhydene.2006.08.045.

15. Forde, T., Modeling of Metal hydride storage Norstoreconference/workshop (2005), int.J.HydrogenEnergy32,1041(2007).Doi:/10.1016/j.ijhydene.2006.07.015.

16. Hahne, E. & Kallweit, J., thermal conductivity of metal hydride materials for storage of hydrogen Int.J.Hydrogen Energy 23, 107(1998).Doi:10.1016/so360-3199 (97) 00020-7.