

Pore scale Simulation of Hydrogen Absorption of Metal Hydride Storage Bed Aravind V.K., Vishnu K., Akshay R.B., Ali Shabeeb K.K., Mohan G*.

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ABSTRACT

In solid sorption based storage systems, metal hydrides assumed a prominent role with advantages like compactness, safety and zero maintenance. However, their performance is affected by non-favourable material characteristics such as low thermal conductivity, powdering and densification during hydrogen sorption. Sorption performance of metal hydride based devices depends on heat transfer as the major rate controlling factor. During hydrogenation-dehydrogenation cycles, the morphology of the bed changes drastically due to powdering of the particles and its consequent settling and densification at the bottom of the container. Even though several studies were reported on the heat and mass transfer of metal hydride beds, the studies on the effects of bed morphology on its performance is less. In the present study, effect of this on the sorption performance of the bed is studied. Discrete element method is used to capture the particle mechanics of storage bed during charge discharge cycles. The consequent effect of this on the sorption performance of the bed is simulated using COMSOL Multiphysics®.

Keywords: Metal hydride, Simulation, Heat and mass transfer, LaNi₅, Discrete element method.

1. INTRODUCTION

Several metals, alloys and intermetallic compounds react reversibly with hydrogen at suitable temperatures and pressures to form metal hydrides. As hydrogen storage media, they offer high volumetric storage capacity, favourable sorption kinetics, good cyclic stability and safety. Metal hydride based hydrogen storage is a promising alternative to competing storage technologies in terms of energy and volume requirements. The optimized design of these storage devices is important for their possible deployment in mobile applications. Heat transfer is the major factor that controls hydrogen sorption in these devices. Other issues include lattice expansion of the alloy particles eventually leading to fragmentation into fines and subsequent settling at the bottom of the container. This can lead to stress concentration in those regions and eventual failure of the device upon charge-discharge cycles. The resultant structure and porosity of the bed can also affect hydrogenation performance of the device.

The hydrogenation performance of the storage device is affected by geometric parameters such as the bed thickness and operating parameters such as hydrogen supply pressure and coolant temperature. Heat transfer is the major rate controlling factor.

2. LITERATURE REVIEW AND OBJECTIVE

Gravimetric storage capacity and charging rates are important considerations in the thermal design of solid state hydrogen storage devices and effective solutions to these issues are required for the realization of hydrogen economy (Srinivasa Murthy [1]). Several studies were conducted on the numerical simulation of heat and mass transfer of metal hydride bed. Most such studies used effective properties for the modelling and simulation the alloy bed. However mechanical characteristics of the alloy bed and the associated porosity variations are not aptly represented in these models.

Okumura et al. [2] showed that the porosity of the metal hydride bed is reduced at the bottom due to the settling of pulverized metal hydride particles. Charlas et al. [3, 4] studied the real time measurements of change in volume of hydride bed in relation to swelling and shrinkage of hydride. The cyclic change of gradual settlement, porosity and global reduction in porosity was also studied. Lin and Chen [5] studied the decrease in particle size with progressive cycles of hydriding/dehydriding. Hu et al. [6] modeled a cyclic compression effect in clustering of hydride powders towards the reactor bottom. Saito et al. [7] studied the relation between volume expansion and hydriding/dehydriding reactions and associated agglomeration of fine particles at the bottom of the container.

New modeling and simulation methods needs to be developed to address the effects of pulverization, settling and agglomeration of the hydride bed on heat transfer and sorption performance of the storage device. The present study deals with the application of discrete element method to model the hydride bed on a pore scale. The heat and mass transfer performance of these pore scale models were studied using COMSOL Multiphysics® [8] commercial code. Effect of porosity variations in the alloy bed upon charge-discharge cycling on the hydrogenation performance of the device is studied.

3. MODEL AND METHODOLOGY

A schematic of vertically placed hydrogen storage container with filter tube at its center and outer cooling jacket is shown in Fig 1. The device is filled with alloy particles (LaNi₅) to the given height. Hydrogen inducted at the given supply pressure to the container is distributed through the centrally located filter tube. Filter tube is provided throughout the length of the container to avoid pressure variation in the bed. Sorption heat liberated during hydrogenation is transferred to the coolant circulated through the outer jacket. As heat transfer at the outer boundary of the storage bed is higher than the rest of the bed,

the sorption rate in this region will be higher. Due to this, particles in these regions will be hydrided earlier than the remaining bed. As reaction proceeds, hydrogenation of the inner regions will be completed progressively towards the centre of the bed. In the meanwhile, the hydride particles expand due to increase in lattice volume. The fragmented alloy particles gradually settle towards the bottom and finally agglomerate at the prevailing pressure and temperature inside the container.

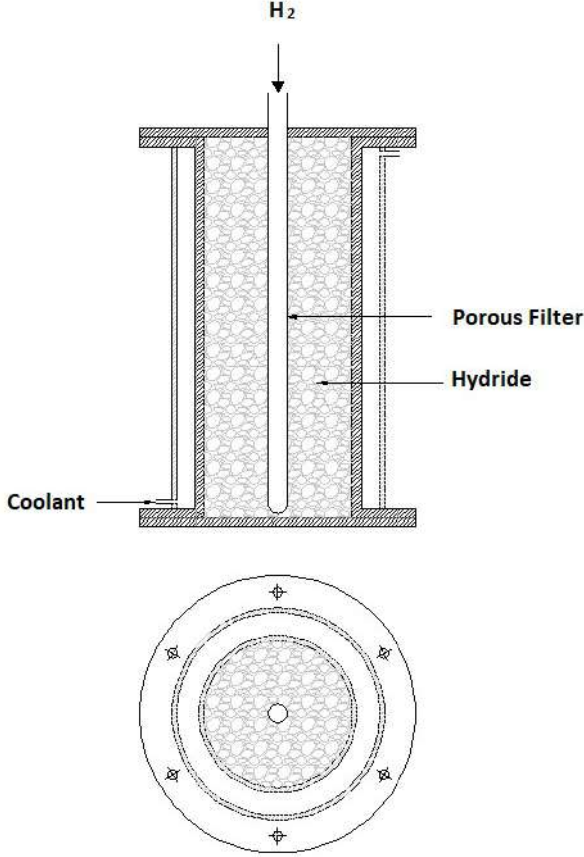


Figure 1: Schematic of liquid cooled metal hydride storage device

True representation of the fragmentation, settling and agglomeration of the particles coincident with hydrogen sorption in the alloy bed is unfeasible due to complexity. Therefore, following assumptions are used to simplify the mathematical model:

1. Hydrogen behaves as an ideal gas since the pressure within the bed is moderate and temperature value is taken to be more than the critical value.
2. Plateau slope and hysteresis factors for LaNi₅ don't have any significant effect on sorption and so they are neglected.
3. Radiation is not significant at the prevailing operating temperatures.
4. The thermo-physical properties like thermal conductivity, permeability and young's modulus of

bed are independent of bed temperature, pressure and concentration, but dependent on porosity.

5. The pressure drop within the hydride bed is negligible.
6. The hydride bed can be treated as homogenous and isotropic across given cross section.
7. The particles are treated as spherical, smooth and rigid and inter-particle collisions are considered pseudo-elastic.
8. The particle size variation is taken to be uniform and particle settling is gravity driven.

3.1 Problem Formulation

Mass balance

The conservation of mass for the metal alloy is given by equation 1.

$$\frac{\partial \rho}{\partial t} = \dot{m} \quad (1)$$

Absorption kinetics

The hydrogen absorbed is proportional to the reaction rate and is given in Equation 2.

$$\dot{m} = -C_a \exp\left(-\frac{E_a}{RT}\right) \ln\left(\frac{P}{P_{eq}}\right) (\rho_{sat} - \rho_s) \quad (2)$$

C_a is material constant for absorption. E_a represents activation energy of the material. ρ_{sat} is the density of hydride at saturation.

The equilibrium pressure is determined by the van't Hoff relationship as given below:

$$\ln P_{eq} = A - \frac{B}{T} \quad (3)$$

Where A and B are van't Hoff constants.

Darcy's Law

Flow of hydrogen through the porous hydride bed can be represented by combining the mass conservation equation for hydrogen with Darcy's law [9] which is given below.

$$\varepsilon \frac{\partial \rho_H}{\partial t} + \varepsilon \left(\frac{-\kappa}{\mu}\right) \frac{1}{r} \frac{\partial(r \rho_H \frac{\partial p}{\partial r})}{\partial r} + \left(\frac{-\kappa}{\mu}\right) \frac{\partial(\varepsilon \rho_H \frac{\partial p}{\partial z})}{\partial z} = -\dot{m} \quad (4)$$

The permeability κ , porosity ε and particle size d_p are correlated by the Kozeny-Carman relation [10] as given below.

$$\kappa = \frac{d_p^2 \varepsilon^3}{C(1-\varepsilon)^2} \quad (5)$$

Energy balance

Energy balance in the hydride bed is governed by the correlation given in Equation 6.

$$(\rho C_p) \frac{\partial T}{\partial t} = \lambda \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \lambda \frac{\partial}{\partial \theta} \left(\frac{\partial T}{\partial \theta} \right) - \dot{m} \Delta H^\circ \quad (6)$$

Initial and Boundary Conditions

Initially the pressure and temperature of reactor bed are assumed uniform and constant. Therefore,

$$\rho_s = \rho_{s0} \quad ; \quad p = p_0 \quad ; \quad T = T_0 \quad \text{at } t = 0 \quad (7)$$

Reactor wall:

$$\frac{\partial \rho_s}{\partial r} = 0 \quad ; \quad \frac{\partial p}{\partial r} = 0 \quad ; \quad \frac{\partial T}{\partial r} = 0 \quad \text{at } t > 0 \quad (8)$$

Cooling tube wall:

$$\frac{\partial \rho_s}{\partial r} = 0 \quad ; \quad \frac{\partial p}{\partial r} = 0 \quad ; \quad -k_e \frac{\partial T}{\partial r} = h_f (T_f - T) \quad \text{at } t > 0 \quad (9)$$

Filter wall:

$$\frac{\partial \rho_s}{\partial r} = 0 \quad ; \quad p = p_{in} \quad ; \quad \frac{\partial T}{\partial r} = 0 \quad \text{at } t > 0 \quad (10)$$

3.2 Simulation Methodology

The numerical simulation of metal hydride bed is based on the particle bed configurations created using LIGGGHTS, an open source discrete element method particle simulation code.

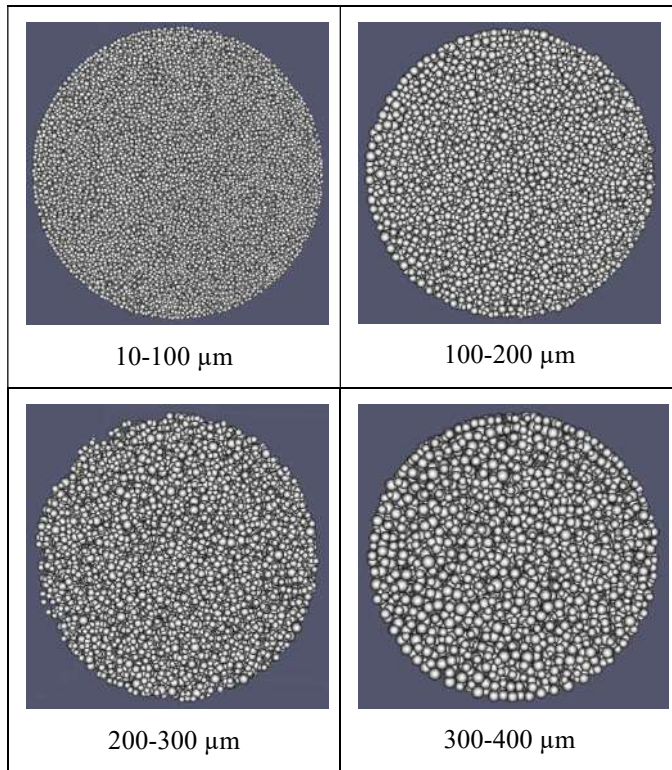


Figure 2: Alloy bed configurations at different particle size ranges (without filter)

The configurations are taken at different bed packing as reported by Okumura et al. [2] in their investigations. The filling of particles (of given size range) under gravity followed with swelling upon hydrogenation and subsequent settling of the fines to the bottom of the container is simulated in LIGGGHTS. Alloy bed configurations at different particle size ranges are shown in Fig. 2. The resultant configurations at given bed sections in 2D were exported to COMSOL Multiphysics commercial code for heat and mass transfer simulations.

The fully coupled conservation equations of mass, and energy were applied to the hydride particles along with the conservation of mass, momentum and energy to the gas domain. The boundary and interface conditions as per the problem formulation are also applied. Unstructured mesh of triangular elements of given element size and quality is generated with suitable mesh parameters. Grid independent test was conducted to validate the mesh. Solving the model with the given set of non-linear equations demands the application of time-dependent, iterative solver for convergence.

4. RESULTS AND DISCUSSION

The present simulation demands the use of LaNi₅ as the hydriding material which is well characterized and can operate at low temperatures and pressures. The application of LaNi₅ also offers fast sorption kinetics, reversibility, good cycle life and safety. The hydrogen sorption and alloy treatment of LaNi₅ is controlled by heat transfer. The thermo-physical properties of LaNi₅ are listed in Table 1. The Simulations are conducted on different parametric ranges as given in Table 2.

Table 1: Thermo-physical properties of materials (Lekshmi et al. [9]; Charlas et al. [4] ; *Pons and Dantzer et al. [11])

Property	LaNi ₅	Hydrogen
Density, ρ (kg m ⁻³)	8200	0.0838 at NTP
Specific heat, C_p (J kg ⁻¹ K ⁻¹)	419	14.890
Thermal conductivity, λ (W m ⁻¹ K ⁻¹)	30*	0.1825
Activation energy (abs), E_a (J mol ⁻¹)	21170	-
Constants in reaction kinetics equation		
C_a , s ⁻¹	59.187	-
A	12.99	-
B	3704.59	-
Modulus of elasticity, E (G Pa)	140	-
Poisson's Ratio, ν	0.31	-
Coefficient of thermal expansion, α	1.23e-5	-

Table 2: Parameter ranges used in simulation

Parameter	Range of values
Initial temperature of hydride bed, K	300 (Constant)
Supply pressure of hydrogen, bar	8-16
Coolant temperature, K	295-315
Overall heat transfer coefficient, $W\ m^{-2}\ K^{-1}$	500 (constant)
Inner radius of container, mm	2.5
Height of the hydride bed, mm	10-80
Porosity of hydride bed	0.45-0.6
Particle size, μm	10-400

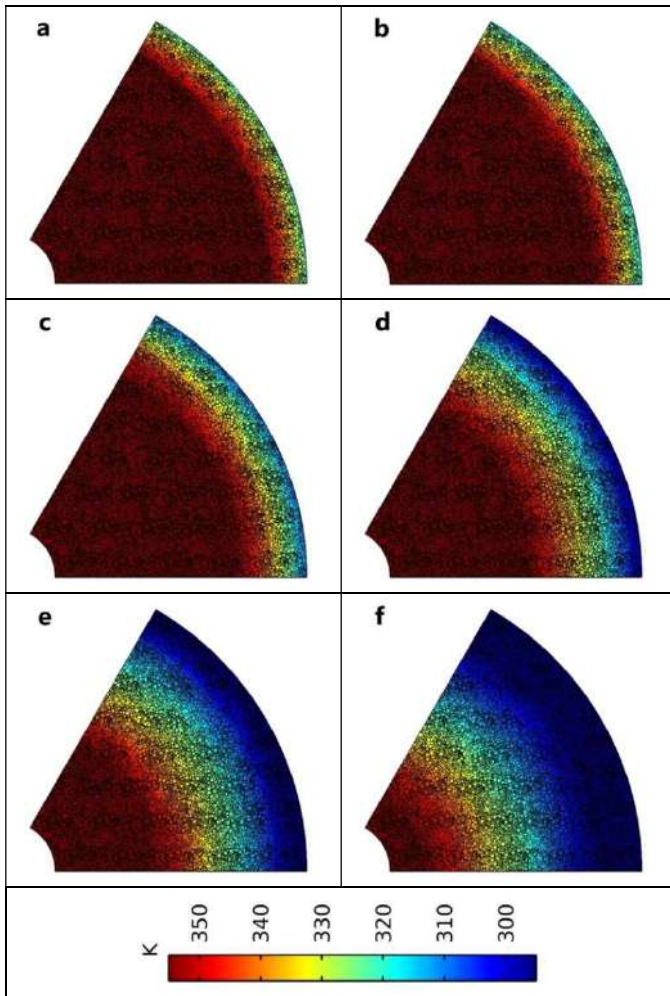
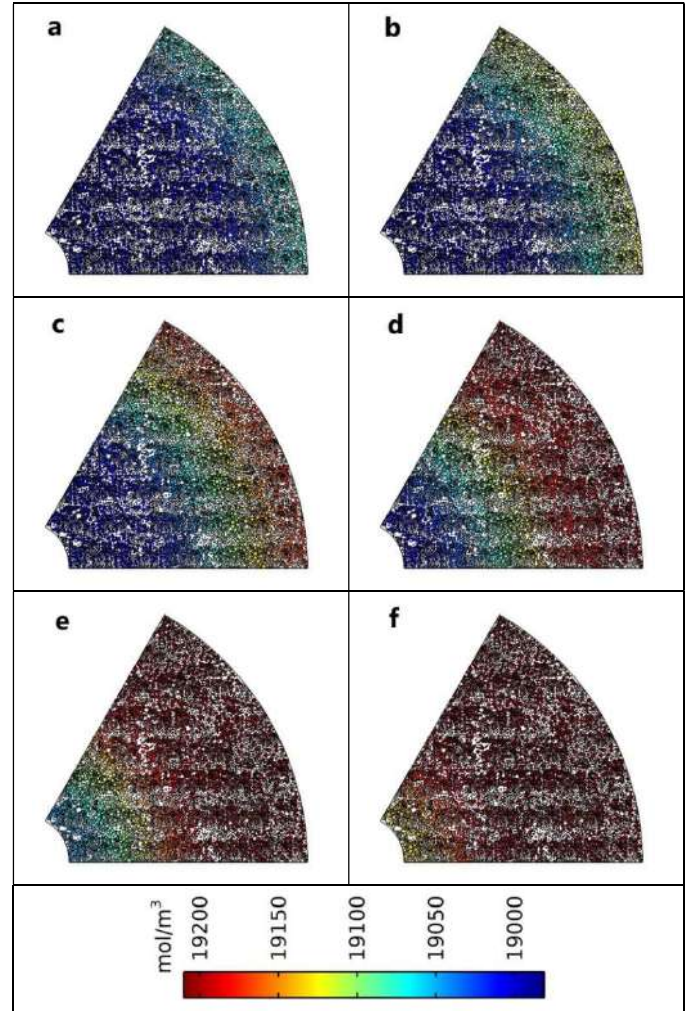
**Figure 3: Spatial variation of bed temperature during hydrogenation a) 50s b) 100s c) 200s d) 400s e) 600s f) 800s**

Figure 3 shows the spatial variation of temperature of the porous hydride bed during hydrogenation at different time intervals. The temperature observed at the inner core of the device is higher than that at the periphery which is cooled

externally. The substantial difference between these temperatures is due to low effective thermal conductivity of the porous bed.

Spatial variation of hydride concentration of the particle bed during hydrogenation at different time intervals is depicted in Fig. 4. Concentration in the inner regions is less than the externally cooled peripheral regions. As equilibrium pressure depends on hydride temperature, higher pressure differential exists near the periphery. This explains the higher hydride saturation in those regions.

**Figure 4: Spatial variation of hydride concentration during hydrogenation a) 50s b) 100s c) 200s d) 400s e) 600s f) 800s**

4.1 Effect of bed thickness

Effect of bed thickness on alloy bed temperature is shown in Fig. 5. Temperature increases drastically due to higher sorption rates during initial time periods followed with a gradual decrease later. This fall in temperature is found to be rapid initially followed with a gradual exponential decrease later. Higher bed thickness leads to markedly lower rate of temperature fall which is attributed by low effective thermal conductivity.

Fig.6 shows the effect of bed thickness on hydride concentration at different bed thickness. Hydrogenation rate is significantly higher initially which becomes more gradual later as this becomes more heat transfer dependant. Low effective thermal conductivity can be the major attribute which affects heat transfer in the hydride bed.

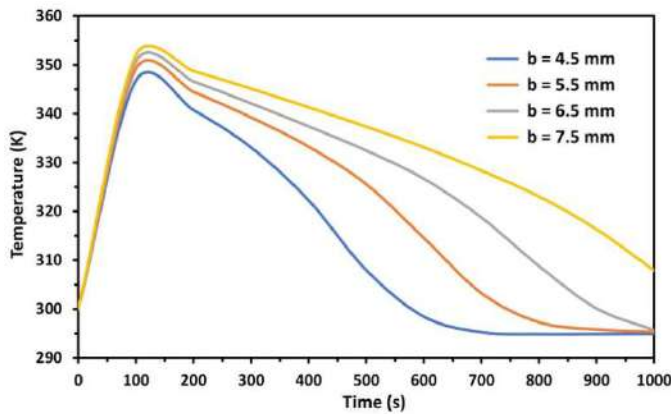


Figure 5: Effect of bed thickness on average bed temperature during hydrogenation

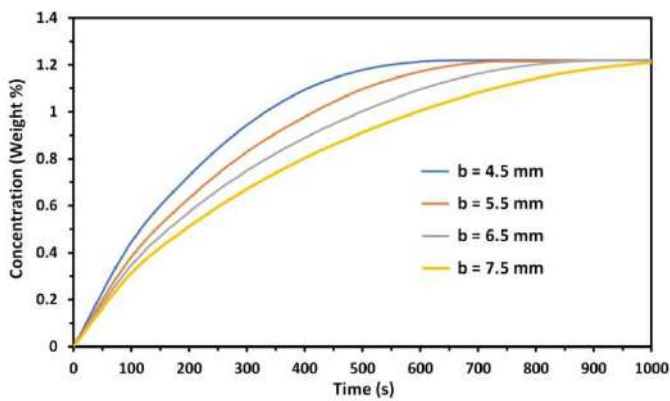


Figure 6: Effect of bed thickness on hydride concentration during hydrogenation

4.2 Effect of particle size

Fig.7 shows the effect of particle size on average temperature of hydride bed. The effect is not evident during the temperature rise in the bed as sorption heat generation is significant during this phase due to high sorption kinetics. However, during cooling the effect is more notable as this is more dependent on effective thermal conductivity bed which reduces with bed porosity.

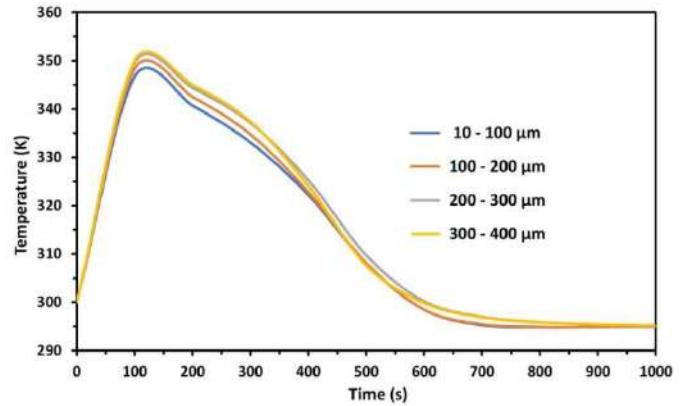


Figure 7: Effect of particle size on average bed temperature during hydrogenation

Effect of particle size on hydride concentration during hydrogenation is shown in Fig. 8. As observed above, effect of particle size and resultant porosity is not evident during the initial phase of hydrogen sorption as this is controlled by fast hydrogenation kinetics of LaNi_5 . However the effect is noted during later reaction which is dependent on heat transfer. Higher rate of reaction is observed for the bed with higher porosity and vice versa. This is due to high average temperature of denser bed which adversely affects hydrogenation.

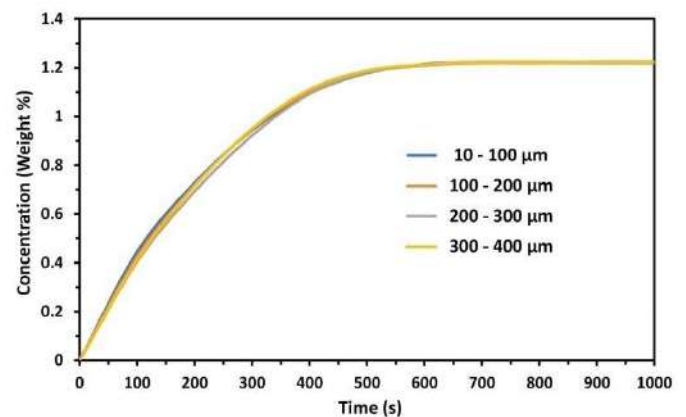


Figure 8: Effect of particle size on hydride concentration during hydrogenation

4.3 Effect of operating parameters

Hydrogen supply pressure and coolant temperature are salient operating parameters controlling the bed temperature and hydrogen sorption in metal hydride bed. Fig.9 shows that average temperature of the hydride bed decreases with the temperature of the coolant. The effect is more notable during later period when the temperature of the bed falls. The corresponding effect on hydrogenation is shown in Fig. 10. As reported earlier by Mohan et al. [12], higher rate of hydrogenation is attributed to lower bed temperature resulted from lower temperature of coolant circulated through the jacket.

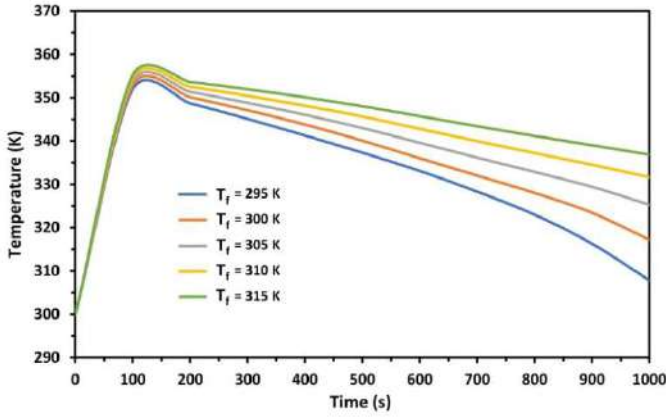


Figure 9: Effect of coolant temperature on average bed temperature during hydrogenation

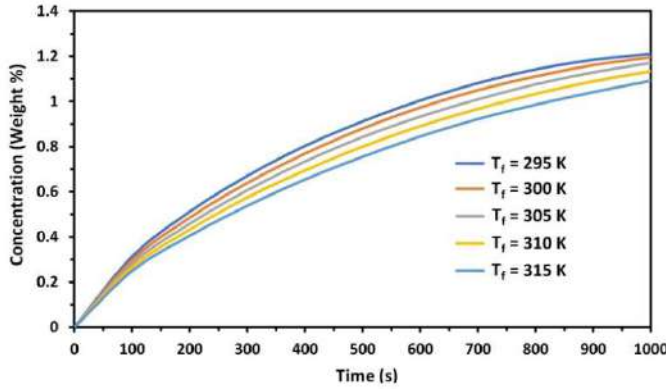


Figure 10: Effect of coolant temperature on hydride concentration during hydrogenation

Effect of supply pressure on average bed temperature is given in Fig.11. As hydrogen sorption is directly controlled by the supply pressure, the heat generation and the corresponding bed temperature directly depends on supply pressure. As reported earlier by different investigators [1], higher supply pressure increases the rate of hydrogen sorption which leads to higher concentration of hydride as shown in Fig.12.

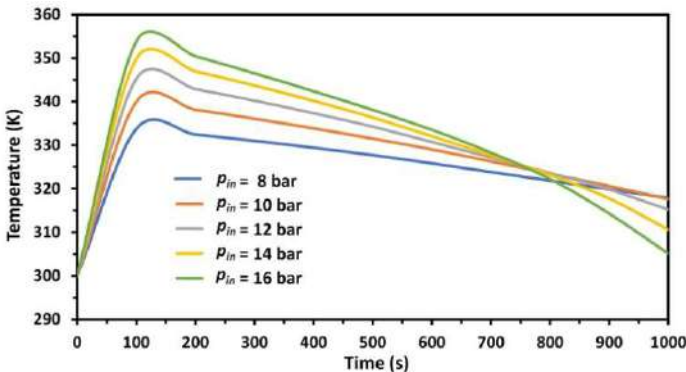


Figure 11: Effect of supply pressure on average bed temperature during hydrogenation

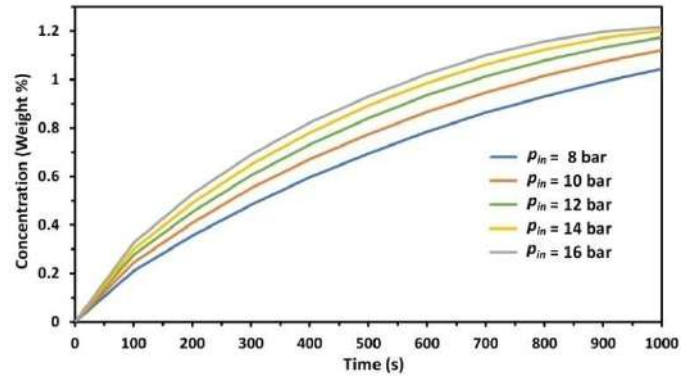


Figure 12: Effect of supply pressure on hydride concentration during hydrogenation

5. CONCLUSIONS

Pore level numerical simulation of LaNi_5 based metal hydride hydrogen storage bed is conducted. Simulation results reveal that the powdering of the alloy particles has less effect on hydrogenation performance. Bed thickness is the most salient parameter that control hydrogenation rate. Coolant temperature and supply pressure are the major operating parameters affecting the sorption performance of the device.

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NOMENCLATURE

b	Bed thickness	[m]
C_p	Specific heat	[J/kgK]
D	Diffusion coefficient	[m ² /s]
d	Diameter	[m]
E_a	Activation energy	[J/mol]
h	Heat transfer coefficient	[Wm ² /K]
m	Rate of hydrogen absorbed	[kgm ³ /s]
p	Pressure	[Pa]
R	Universal gas constant	[8.314J/mol K]
t	Time	[s]
T	Temperature	[K]

Greek letters

ΔH°	Heat of formation	[J/kg]
ε	Porosity	--
κ	Permeability	[m ²]
λ	Thermal conductivity	[W/mK]
θ	Polar coordinate	radian
ρ	Density	[kg/m ³]
μ	Dynamic viscosity	[kg/ms]

Subscripts

e	effective
eq	equilibrium
f	cooling fluid
in	inlet
s	solid
sat	saturated

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