Numerical Simulation of Hydrogen Transport in Metal Hydride Based Coupled Beds

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ABSTRACT

Metal hydride based sorption heat pump is witnessing an increased acceptance due to its environment friendliness and energy efficiency. These systems provide a wide operating temperature range and use low grade thermal energy to produce high quality thermal energy and cooling outputs. Further, these systems contain no moving parts, have a compact structure and offer noise free operation. Heat transfer effectiveness and kinetics are the major challenges to be addressed in these devices. Even though several studies were reported on the thermal performance of metal hydride based reaction beds, only a few deals with the hydrogen transport during their operation. In the present study, a transient heat and mass transfer model for the coupled beds with $LaNi_5$ - $LaNi_{4.7}Al_{0.3}$ alloy pair has been developed. The numerical simulations were carried out using COMSOL Multiphysics® commercial code. The influence of refrigeration and regeneration temperatures on the hydrogen transport between the two beds and its influence on the sorption performance has been studied.

Keywords: Metal Hydride, $LaNi_5$, $LaNi_{4.7}Al_{0.3}$, Hydrogen, Simulation

1. INTRODUCTION

With the world heavily impacted by the effects of climate change there is an urgent need to switch over to cleaner sources of energy to meet the growing energy demand. Hydrogen is a potential zero-emission secondary energy carrier. The use of which can reduce the usage of fossil fuels for transportation, heating and cooling applications. Therefore, the possibility of an increased use of hydrogen in the near future is high.

Storage of hydrogen in metal hydrides has several advantages over compressed and liquefied forms of hydrogen storage. The metal hydride systems also have a good potential for heating and cooling applications. Metal hydride-based sorption heat pump is witnessing an increased acceptance due to its environment friendliness and energy efficiency. These systems use low grade thermal energy to produce high quality thermal energy and cooling outputs.

The performance of the metal hydride-based heat pump mainly depends upon the selection of the alloy pairs for the required operating conditions. The metal hydride pair of $LaNi_5$ and $LaNi_{4.7}Al_{0.3}$ offers advantages such as easy activation at moderate temperatures and pressures, desorption of hydrogen at a temperature less than 100C and satisfactory absorption or desorption kinetics. Pressure difference is the major sorption rate controlling factor in these devices.

2. LITERATURE REVIEW AND OBJECTIVE

Nishizaki et al [1], proposed a model for the analysis of a metal hydride based chemical heat pump consisting $LaNi_5$ and $LaNi_{4.7}Al_{0.3}$. They introduced the concept of sensible heat exchange between the reactors containing the same metal hydride for improving the COP of the system. The working pairs reported favourable outputs. Performance analysis of a single stage metal hydride-based heat transformer, operating at temperatures of 423K, 383K and 303K, using the same alloy pair was carried out by Muthukumar et al [2]. They found that for the bed having thermal conductivity of 4W/mK, the cycle time can be decreased by 30% by reducing the bed thickness. Effect of operating temperature on the COP of system were also reported. Later, Muthukumar and Satheesh [3] studied the operating feasibility of a crossed van't Hoff single stage metal hydride heat pump working with two different hydride alloy pairs and presented the optimum operating temperatures. They reported that crossed van't Hoff systems yielded 60% higher COP than conventional single stage systems.

Sharma et al [4], conducted studies on La based intermetallic hydrides to determine their suitability in metal hydride based cooling systems. A major finding of the study was the effect of the metal hydride bed composition on the driving potential and hydrogen transfer rate during cooling and regeneration. Mohan et al [5] analysed the performance of a metal hydride based simultaneous cooling and heat transformation system. They also studied the variation in pressure during hydrogen transfer process between the metal hydride beds. Murthy et al [6] conducted a study on thermodynamic compatibility criteria for the selection of metal hydride pairs for the application in coupled metal hydride based thermal energy storage systems. The simulations were done using COMSOL 5.4, using alloy pair of Mg_2Ni and $LaNi_5$. They reported that the pressure variation in beds were consistent in the three cycles studied during charging and discharging processes at an energy storage efficiency of 89.4%.

Gopal and Murthy [7] conducted a study on the hydriding and dehydriding characteristics of $LaNi_{4.7}Al_{0.3}$ using a one dimensional mathematical model. The outcome of the study

was that the performance of the metal hydride system depends on the heat transfer characteristics, which could be improved by increasing the thermal conductivity of the bed. Mohan et al [8] conducted a study to identify the influence of operating parameters in the hydriding performance of a metal hydride storage device with embedded filters and heat exchanger tubes. Muthukumar et al [9] conducted studies on hydriding kinetics of LaNi5, LaNi4.7 Al0.3 and LmNi4.91Sn0.15 at different temperatures. They presented the variation in bed and cooling fluid temperatures, hydrogen concentration and equilibrium pressure in axial direction. Sakintuna et al [10] presented a review on the developments of metal hydrides on properties including hydrogen storage capacity, kinetics, cyclic behaviour, toxicity, pressure and thermal response. They reported that though Mg based hydrides have slow kinetics and high hydrogen desorption temperature, it is a promising candidate for hydrogen storage with a reversible hydrogen storage capacity up to 7.6wt%. Sharma et al [11], investigated the effect of measurement parameters on the thermodynamic properties of La based metal hydrides. They concluded that with increase in Al substitution, the unit cell volume of the alloy, plateau slope and reaction enthalpy increased while hydrogen capacity and plateau pressure decreased.

3. MATERIALS AND METHODS

3.1 physical model
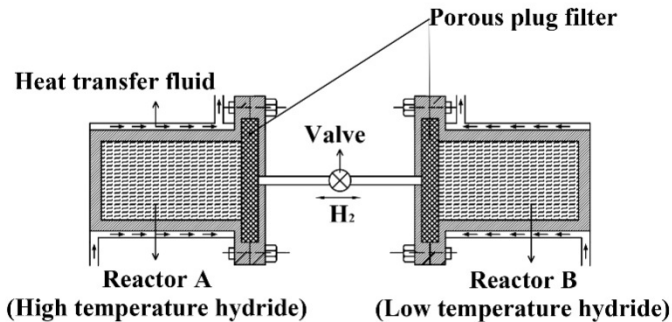
Fig.1.Schematic of coupled bed metal hydride reactors

Figure 1 shows the schematic of the metal hydride-based coupled bed reactor. The device consists of two cylindrical reactors joined together by a flange coupling with a porous plug filter inserted between them. The low temperature hydride (LaNi5) and the high temperature hydride (LaNi4.7Al0.3) are packed on either sides of the filter.
The operating principle of a single stage metal hydride based coupled beds on van't Hoff plot is shown in figure 2. The operating cycle consists of two heat and mass transfer processes (1-2 and 3-4) and two sensible heat transfer processes (1-4 and 2-3). The device works across three temperatures namely, high temperature (T_h), intermediate temperature (T_m) and refrigeration temperature (T_c). Initially the valve is closed. The high temperature alloy filled with LaNi4.7Al0.3 is kept at 365K and the low temperature alloy filled with LaNi5 is kept at 313K. There exists an equilibrium

pressure difference, which is a function of the bed temperature, between the reactors.
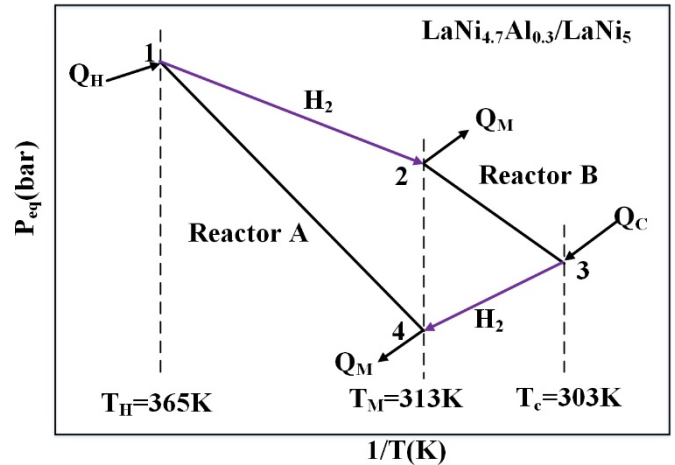
Fig.2.van't Hoff plot for a single stage metal hydride based coupled beds

Once the valve is opened, hydrogen gets desorbed from the high temperature bed, taking in the heat of desorption from the bed and heat transfer fluid and flows to the low temperature bed and gets absorbed, liberating heat to the bed and heat transfer fluid. The process continues until a certain amount of hydrogen is transported between the reactors. This process is called regeneration. The valve is then closed and both the reactors are sensibly cooled to T_m and T_c. When the valve is opened, hydrogen gets desorbed from the low temperature alloy bed, where the refrigeration effect is achieved and gets absorbed in the high temperature alloy. After refrigeration, the valve is closed and the reactors are heated to the initial conditions.

The following assumptions were made to simplify the problem
1. Hydrogen behaves as an ideal gas at the existing pressure and temperature in the hydride bed.

2. Plateau slope and hysteresis factors have negligible effect on sorption kinetics.

3. Thermo-physical properties are independent of the pressure, bed temperature and concentration.

4. Conduction is the prevalent mode of heat transfer within the bed. Natural convection and radiation effects within the bed are neglected.

5. Hydride bed is assumed to have uniform porosity and is isotropic.

6. Boundary walls of the bed are assumed to be impermeable for any mass flow.

3.2. Problem formulation

Mass Balance

Conservation of mass for the solid phase of the reactor in polar co-ordinates [8] is expressed as:

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$$(1\text{-}\varepsilon)\frac{\partial \rho_s}{\partial t} = \dot{m} + (1\text{-}\varepsilon)\, D\frac{1}{r}\frac{\partial}{\partial_r}\left(r\frac{\partial \rho_s}{\partial r}\right) + (1\text{-}\varepsilon)\, D\frac{1}{r^2}\frac{\partial}{\partial \theta}\left(\frac{\partial \rho_s}{\partial \theta}\right) \qquad (1)$$

ρ_s-denotes the density of hydride, D denotes the diffusion coefficient and $\dot{m}$ represents the reaction term. Convection term is not considered

Reaction kinetics

The amount of hydrogen absorbed is expressed as [2]:

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

The amount of hydrogen desorbed per unit time and unit volume is expressed as [2],[12],[13];

$$\dot{m} = -C_d \exp\left(-\frac{E_d}{RT}\right)\left(\frac{P - P_{eq}}{P_{eq}}\right)\rho_s \qquad (3)$$

C_a, C_d are material dependant constants for absorption and desorption, E_a, E_d are the activation energies for absorption and desorption of the material, ρ_{sat} is the density of hydride at saturation. The change in volume, due to hydrogen sorption is not considered.

The equilibrium pressure is determined by the van't Hoff relationship [1]:

$$\ln(P_{eq}) = A - \frac{B}{T} \qquad (4)$$

Where A and B are van't Hoff constants

Energy Balance

Energy balance in porous hydride bed is governed by the equation [8]:

$$(\rho C_P)_e \frac{\partial T}{\partial t} = k_e \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + k_e \frac{\partial}{\partial z}\left(\frac{\partial T}{\partial z}\right) - \dot{m}\Delta H^0 \qquad (5)$$

C_p is the specific heat, k_e is the effective thermal conductivity and ΔH^0 is the heat of formation.

The left-hand term represents the heat of reaction and the right-hand term includes the spatial variation of temperature

Momentum Balance

The momentum balance for the flow of hydrogen can be expressed by the Brinkman equation

$$-\nabla \cdot \eta (\nabla u + (\nabla u)^T) + \frac{\eta}{k}u + \nabla p = g\beta_T(T - T_c) \qquad (6)$$

$$\nabla \cdot u = 0 \qquad (7)$$

P is the pressure, k is the permeability, β_T is the co-efficient of thermal expansion, Tc is the initial temperature, T is the temperature from heat transfer application and u is the vector of directional velocities.

Simulation Methodology

The mass and energy conservation of the hydride bed was implemented using the inbuilt modules in COMSOL Multiphysics namely Transport of diluted species and heat transfer in porous media respectively. The UMFPACK solver was used for solution.

Table 1: Thermo-physical properties of the alloy pair

Properties		LaNi$_5$	LaNi$_{4.7}$Al$_{0.3}$
Effective density(kg/m^3)		3975	3900
Activation energy(J/mol)	Abs	21170	30000
	Des	16420	28000
Specific heat(J/kgK)		419	419
Permeability(m^2)		10$^{(-12)}$	10$^{(-12)}$
Reaction rate constant(s^{-1})	Abs	59.18	43.27
	Des	9.57	8.2
Porosity		0.5	0.5
Effective thermal conductivity of the bed(W/mK)		1.32	1.32
A		13.44	12.92
B		3780	4068

Table 2: Parameter values used in simulation

| Parameters	Values
Heat source temperature(K)	365-353
Intermediate temperature(K)	313
Evaporator temperature(K)	295-307
Heat transfer co-efficient at outer wall(W/m^2 K)	1000
Bed thickness (mm)	20
Length of each reactor (mm)	70

4. RESULTS AND DISCUSSION

Results are obtained for a coupled bed metal hydride module with LaNi$_5$ and LaNi$_{4.7}$Al$_{0.3}$ as the working alloy pairs. Reaction constants and thermo-physical properties of the alloys used in the simulation are given in Table 1. Range of the operating parameters are shown in Table 2.The operating cycle is divided into regeneration (2000s) represented by 'a', sensible cooling (120s) represented by 'b', refrigeration (2000s) represented by 'c' and sensible heating processes represented by 'd'. The time limit for each process is taken as a constant. The variation of temperature of the heat transfer fluid along the length of the reactor is neglected.
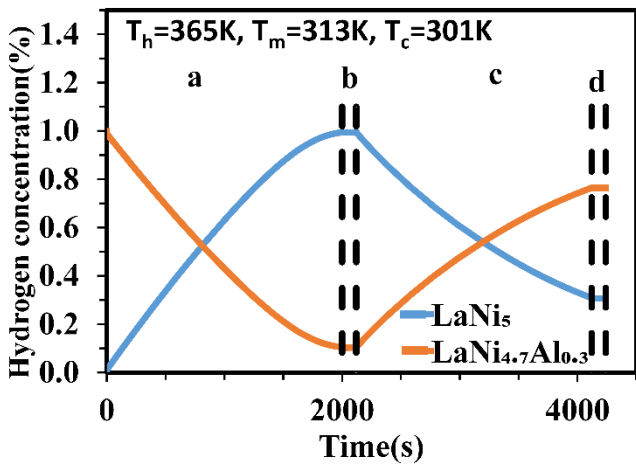
Figure 3 represents the variation of pressure, temperature and concentration of a coupled bed reactor operating at temperatures of 365/313/301, with time, over a complete cycle.
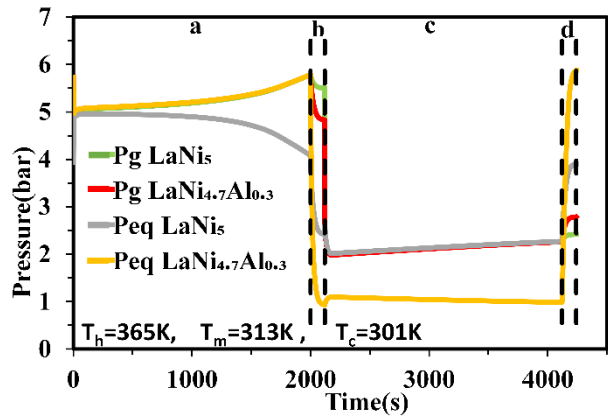
[A]
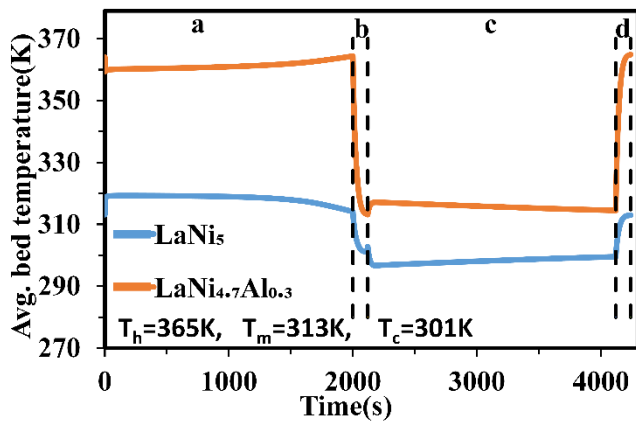
[B]

[C]

Figure 3: Variation of A-gas pressure, B-average bed temperature and C-hydrogen concentration of the coupled bed reactor over a cycle

The LaNi$_{4.7}$Al$_{0.3}$ bed desorbs hydrogen during the regeneration process. The heat transfer rate between the bed and the heat transfer fluid is not fast enough to match the reaction kinetics due to its low effective thermal conductivity. Therefore, the energy required for the reaction is mostly supplied by the sensible heat of the bed. The bed temperature suddenly drops and then gradually reaches the heat transfer fluid temperature. The temperature is brought down to the intermediate temperature during sensible cooling process. The temperature suddenly shoots up during the start of refrigeration process, as hydrogen is absorbed, then gradually reaches the heat transfer fluid temperature. It is then sensibly heated to the initial condition. Similarly, for LaNi$_5$ bed, as the effective thermal conductivity is less, there is a sudden increase in bed temperature during absorption and sudden drop during desorption.

The concentration of hydrogen in the low temperature alloy changes from 0.1 to 0.99 during regeneration due to hydriding and changes from 0.99 to 0.3 during refrigeration as hydrogen gets desorbed in this process. The concentration in the high temperature alloy changes from 0.99 to 0.1 during regeneration due to dehydriding and changes from 0.1 to 0.7 during refrigeration due to hydriding.
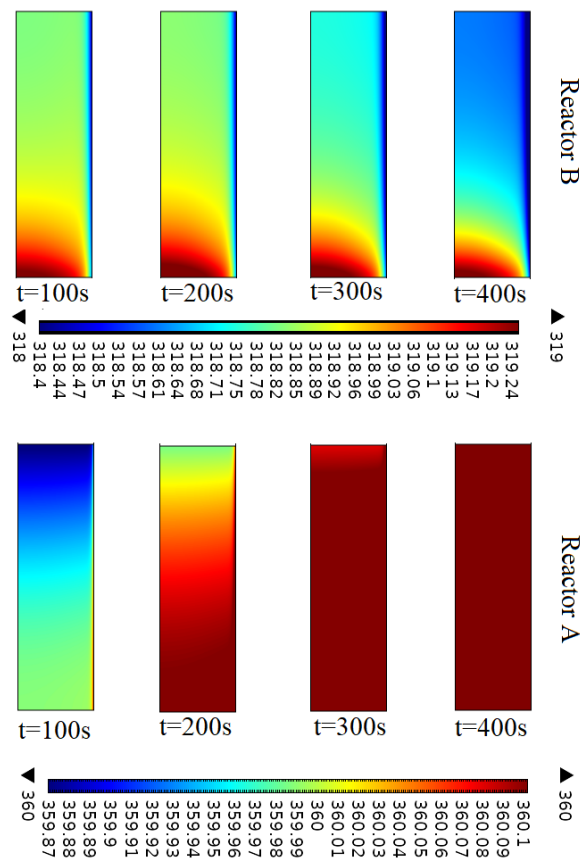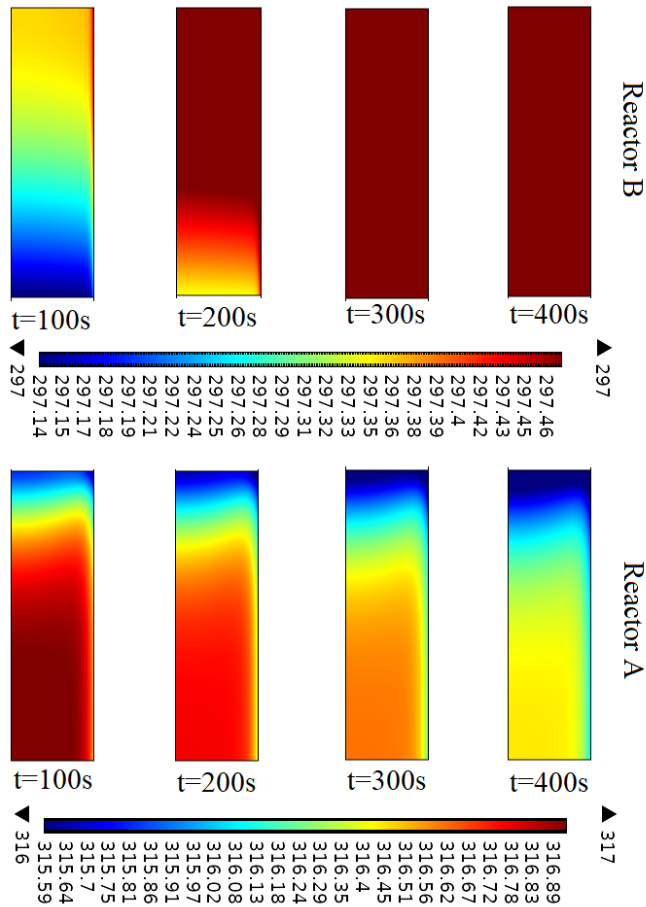

Figure 4: Variation in the bed temperature at different instants during regeneration

Figure 4 shows the variation of bed temperatures of the reactors during regeneration at 100s, 200s, 300s and 400s.

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Figure 5: Variation in the bed temperature at different instants during refrigeration

Figure 5 shows the variation of bed temperatures of the reactors during regeneration at 100s, 200s, 300s and 400s.

The pressure difference is the driving potential for the transport of hydrogen. The equilibrium bed pressures are functions of the bed temperatures. It is observed that the equilibrium pressure of the desorbing bed is the driving potential as the gas pressure in both the beds obtain the same value as that of the equilibrium pressure of the desorbing bed. The axial variation of gas pressure is plotted from one end to the other. 0-70mm is the high temperature alloy region and 70-140mm is the low temperature alloy region. The gas pressure is plotted for different time durations.

Figure 6 represents the gas pressure along the axial direction of the coupled beds during regeneration. It is observed that there is only marginal variation in gas pressure along the axial direction. The gas pressure decreases along the length. The gas pressure in reactor A is more than that of reactor B as hydrogen is added due to desorption. Once the valve between them is opened, a small pressure gradient is observed as hydrogen moves between the reactors. The pressure drop is maximum at the exit of the desorbing bed as the flow of hydrogen is maximum at this position. The pressure drop decreases as the pressure in both beds reaches equilibrium. The gas pressure increases with time. This is because the rate of desorption in reactor A is greater than the rate of absorption in reactor B.
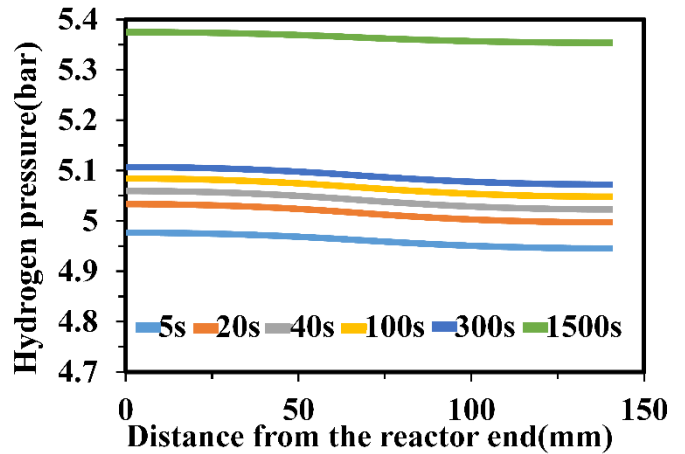
Figure 6: Axial Variation of gas pressure of a coupled bed reactor during regeneration at different time intervals

Figure 7 represents the gas pressure along the length of the reactor during refrigeration. There is small variation in gas pressure along the axial direction. The gas pressure increases along the axial direction. The gas pressure in reactor B is more than A due to desorption of hydrogen. A pressure gradient is observed as hydrogen flows between the reactors once the valve is opened. Maximum pressure drop is observed at the exit of desorbing bed as the hydrogen flow is maximum at this position. The gas pressure decreases with time initially and then increases. This is because, during the initial reaction, the rate of desorption in reactor B is less than the rate of absorption in reactor A. After which, the rate of absorption in reactor A decreases.

Effect of T_c on axial variation of gas pressure of a coupled metal hydride bed reactor

Figure 8 represents the effect of T_c on axial variation of gas pressure during refrigeration. The effect of increase in T_c predominantly affects the pressure during refrigeration. It is noted that as the T_c increases, the gas pressure also increases. Increase in T_c causes an increase in the equilibrium pressure of the LaNi$_5$ bed. As the driving potential increases, the rate of desorption of hydrogen from the LaNi$_5$ bed also increases. As the rate of desorption is more than the rate of absorption there is a pressure build up. This causes the increase in gas pressure in the reactors. Figure 9 shows the effect of T_c on axial variation of gas pressure during regeneration. As the T_c increases the gas pressure increases marginally. The change is minimal compared to the variation in gas pressure in the refrigeration process.
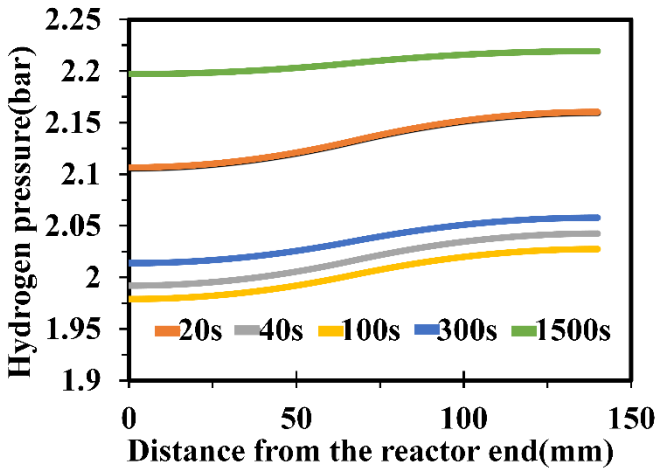
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Figure 7: Axial Variation of gas pressure of a coupled bed reactor during refrigeration at different time intervals
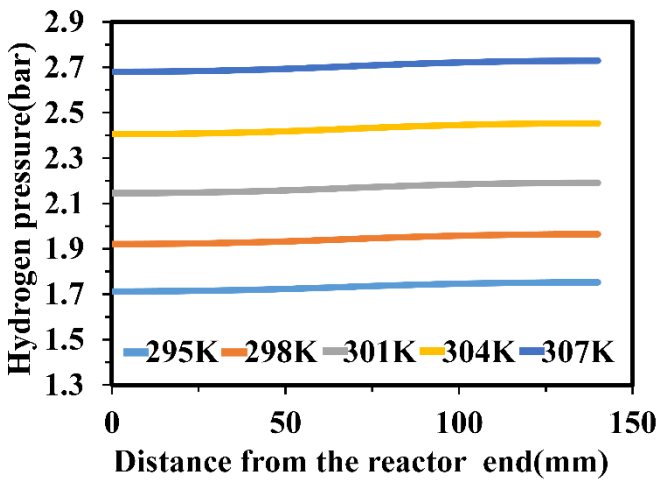

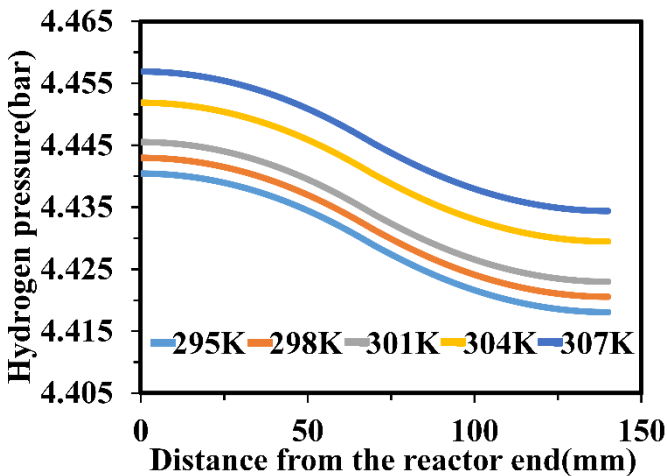**Figure 8: Effect of T_c on axial variation of gas pressure during refrigeration (t=20s,T_h=365K)**

Figure 9: Effect of T_c on axial variation of gas pressure during regeneration (t=20s,T_h=365K)

Effect of T_h on axial variation of gas pressure of a coupled metal hydride bed reactor

Fig 10 represents the effect of T_h on axial variation of gas pressure during regeneration. The effect of increase in T_h predominantly affects the pressure during the regeneration process. As T_h increases, the equilibrium pressure in the $LaNi_{4.7}Al_{0.3}$ bed increases. The difference in the equilibrium and gas pressures in this bed acts as the driving potential which causes an increase in the rate of desorption. The amount of hydrogen desorbed and transported to the $LaNi_5$ bed is increased. As there is a mismatch between the rates of desorption and absorption, there is pressure build-up. This increases gas pressure in the reactors.

Fig 11 represents the effect of T_h on axial variation of gas pressure during refrigeration. Hydrogen transfer during the refrigeration process doesn't change significantly with increase in T_h, hence the increase in T_h, is beneficial only up to a certain limit beyond which T_c controls the amount of hydrogen transferred.
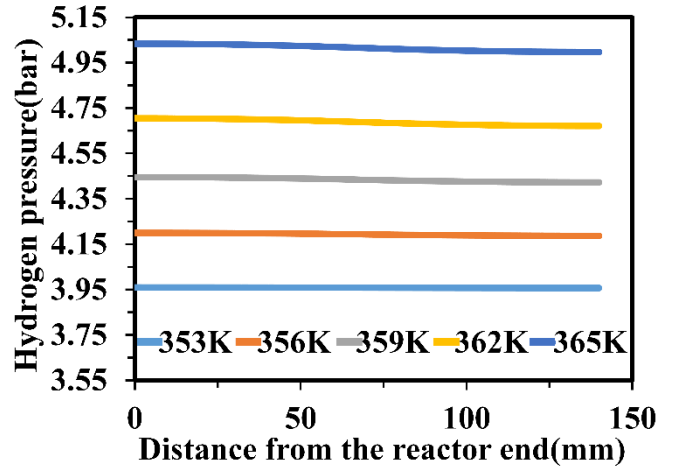

Figure 10: Variation of a pressure profile of a coupled bed reactor for different T$_h$ during regeneration
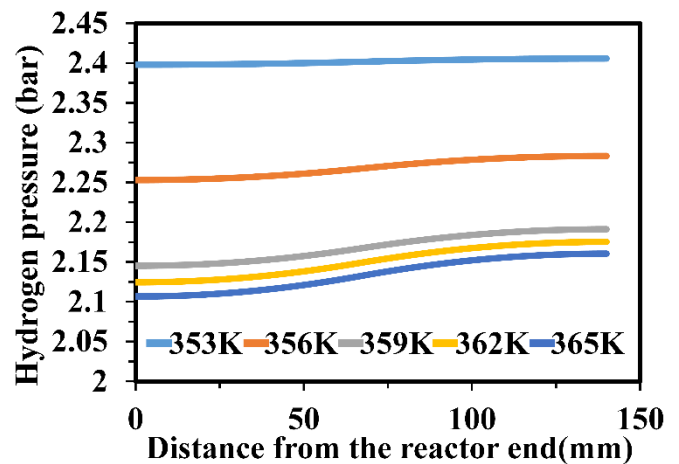

Figure 11: Variation of a pressure profile of a coupled bed reactor for different T$_h$ during refrigeration

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5. CONCLUSIONS

The equilibrium pressure of the desorbing bed plays a vital role in the transport of hydrogen. While T_c affects the gas pressure during refrigeration, T_h affects this during regeneration. The mismatch between desorption/absorption rates lead to pressure build up and affect capacity utilisation of the device.

NOMENCLATURE

T_h	High temperature		[K]
T_m	Intermediate temperature		[K]
T_c	Refrigeration temperature		[K]
C_p	Specific heat,		[J/kgK]
D	Diffusion coefficient		[m²/s]
R	Universal gas constant		8.314[J/mol K]
Subscripts			
ε	Porosity	s	solid
eq	Equilibrium	sat	saturation

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