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Numerical study of parametric effects on hydrogen storage using porous metal hydrides

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Abstract: -- Metal hydrides have been prompted as one of the most promising materials for hydrogen storage applications. The key challenges confronted with hydrogen storage using metal hydrides are to minimize the time of absorption and maximize the amount of hydrogen storage. The objectives of the present study are (i) to develop relationship between operating and design variables and (ii) predict, numerically, the performance of metal hydride system. The governing transport equations are solved with a fully implicit finite volume numerical scheme with the commercial software FLUENT. The heat transfer analysis of the metal hydride bed underlines that thermal conductivity of the bed material plays a significant role in the hydrogen absorption characteristics of the bed. Further, the study has lead to propose a new design of hydride bed with the inclusion of aluminium layers inside the LaNi5 hydride bed. The numerical analysis was further extended to study effect of wall thermal boundary conditions on absorption characteristics the of metal hydride bed. The results show that better heat transmission and reduction in time for charging is possible with the proposed new design of metal hydride bed.

Keywords: CFD simulation, hydrogen storage, metal hydride, Transport equations

I. INTRODUCTION

The continued use of fossil fuel threatens the energy supply and put our environment into high strain due to pollution and global warming. The increase in global temperature results in sinking shores and natural disasters. Moreover, fossil fuel reserves are finite- it's only a matter of when they run out. So, it's imperative that we need a clean and ecologically benign alternate energy source for the sustainable global economic growth. Moreover, the energy source must be safe, abundant, affordable and reliable.

Among the nonconventional fuels, hydrogen is an apt option for supplying these needs in clean and environmental friendly manner due to its fuel properties. Hydrogen can produce electrical energy by fuel cells or heat energy by combustion engines which allows conversion of the energy stored in hydrogen. It's the element with the highest mass energy density (141.8 MJ/kg) which is about three times more than gasoline fuels. It's the most plentiful element in nature, but its exist is not in free form. So, its extraction from the compounds has a prime consideration. But, nowadays better methods like electrolysis, steam reforming, biological productions, etc. are available for the extraction. So, the next problem deals with the storage which should be safe and economical for the transportation and other applications. The very low volumetric energy density of hydrogen results in storage difficulties due to large space at ambient conditions. The conventional storage methods like compressed gas at high pressure (700 bars) or liquid at cryogenic conditions (20 K) entail additional costs for high pressure containment or cryogenic conditions. In addition to the processing cost, these methods have serious safety issues as hydrogen have low minimum ignition energy which is about one order of magnitude less than that of gasoline.

So, due to economical and safety concerns, a better storage method required and solid state storage methods came into picture. They demonstrate better storage properties in low pressures by the reaction of hydrogen with transition metals. They have comparable volumetric densities with liquid hydrogen. They can absorb and desorb hydrogen at a constant pressure. They also provide storage under moderate temperatures with high volume efficient storage in safely manner. Metal hydrides are generally classified based on their operating temperature as low temperature, AB_5 (20- 100^{o}C) and high temperature, A_2B (200-400^{o}C) types. The AB_5 type hydrides have good hydrogenation capacities at ambient temperature than A_2B type hydrides. But, hydrogen capacity is high for A_2B (around 7%) than AB_5 (1-1.5%). $LaNi_5$ and Mg_2Ni are commonly using examples for AB_5 and A_2B type intermetallic hydrides.

The absorption reaction is exothermic in nature when the supply is high pressure hydrogen to the metal bed. The desorption reaction is an endothermic process by providing high temperature to hydride bed at ambient pressure conditions. In practical vehicular or fuel cell applications, the rate of reaction is evaluated by how quickly the heat is removed from or added to the hydride bed. So, most of the

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Vol 2, Issue 5, May 2017

researches are now focusing on the heat transfer enhancing methods for metal hydrides.

The amount of hydrogen absorbed and cycling time are the main parameters used to measure the overall performance of a metal hydride. Inlet temperature and pressure, reactor geometry, material properties, thermal management systems, operating conditions, etc. are the performance affecting variables of metal hydride system. The operating conditions include the porosity of metal bed, viscous effects, etc.

For every metal hydride, they have a specific equilibrium pressure at working condition. At equilibrium conditions, absorption neutralizes desorption. The driving force behind chemical reaction is the difference between equilibrium pressure and bed pressure. Absorption occurs only if loading pressure exceeds bed pressure and vice versa. As from equation (11), lower equilibrium pressure for the same bed pressure favors hydrogen absorption and the rate of absorption and similarly, higher equilibrium pressure enhances desorption.

Various experimental and numerical models were reported on the heat and mass transfer of metal hydride bed in order to describe their performance. The three dimensional models require more time and computing facility to run. So, 3-D studies are used to investigate when 2-D models are ineffective. Minko et al. [1] carried out 2-D analysis on cylindrical metal hydride tank and concluded that concentration gradient is the driving force behind hydrogen flow inside the hydride bed. The two dimensional model developed and evaluated by Jemni and Nasrallah [2] found that the hydrogen absorption rate highly depends on inside temperature. They validated the assumption that local thermal equilibrium exist between solid and gaseous zones. They also studied the radiation effects inside the bed and they showed radiation is prevailing only in high temperature hydrides. So, for low temperature hydrides like $LaNi_5$, radiation effects are negligible. Kumar et al. [3] analyzed thermal behavior inside MH bed using Fluent software indicated that at the beginning of absorption process, the speed of absorption in the system is high, but as time proceeds the absorption speed decreases due to the temperature increase of the bed. Besides, with the increase in inlet pressure of hydrogen at constant pressure, the absorption speed increases. Askri et al. [4] concentrated on the heat exchange designs for MH tanks and they concluded internal cooling using liquid fluid inside circular finned tubes are the best option. An experimental and theoretical study on the internal cooling using spiral heat exchanger was done by Mellouli et al. [5] found that spiral heat exchangers with fins are superior than that without fins. Muthukumar et al. [3] studied the effect of overall heat transfer coefficient and showed the increase in heat transfer coefficient has a least effect on heat transfer inside the system. Mohan et al. [6] introduced a $LaNi_5$ based hydrogen filters and heat exchanger tubes. A systematic numerical analysis identified the geometric and operational parameters associated with the performance characteristics. Aldas et al. [7] reported that the hydride formation near the cooled water tube boundary walls is notably higher than core region due to better heat transfer.

The present work is a continuation of the study done by Chabne et al. [8]. The aim of this study is to find the effect on heat transfer and mass stored by the implementing of two new designs by the inclusion of high conductive Aluminium layers inside the low conductive hydride bed and a constant temperature boundary with the help of heat pipe instead of cooling convective boundaries. The simulation models were developed using ANSYS Workbench and Fluent software.

II. GEOMETRY

Case 1: The reactor configuration consists of a cylindrical container of radius R = 10 cm and height L = 15 cm filled with $LaNi_5$ powder (Fig 1). Only half of the axisymmetric domain is considered here. Aluminium wall is provided on all boundaries. Hydrogen is supplied from top boundary and constant temperature of (a) 273 K and (b) 293 K are provided around the wall as separate cases.

Case 2: The reactor configuration consists of a cylindrical container with alternate layers of Aluminium and $LaNi_5$ powder with radius R = 10 cm and height L = 15 cm. The inner Aluminium layer has 0.4 cm and the Aluminium partition has 0.2 cm length (Fig 2). Only half of the axisymmetric domain is considered here. Aluminium wall is provided on all boundaries. Hydrogen is supplied only to hydride layers at constant pressure and a convective boundary is provided around the outer wall.

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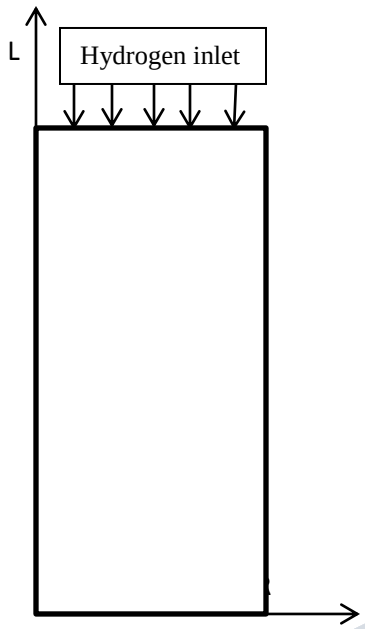

Fig. 1 - Geometry of hydride with isothermal wall

III. MATHEMATICAL FORMULATION

Considering the axisymmetry of the metal hydride bed, only half of the physical domain is selected. For simulation on hydride powder, the macroscopic differential equations are obtained from averaging the microscopic governing equations of the domain volume. For simplicity of problem, the following assumptions are taken.

- The gas phase is ideal
- Local thermal equilibrium between solid and gaseous phases.
- Porosity of MH bed is constant and uniform
- Solid phase is isotropic
- Convective term in heat transfer is neglected due to low speed of gas
- Radiative transfer inside porous medium is neglected.
- Laminar flow is considered (Darcy's law is valid)
- Hydrogen pressure within the bed is uniform

IV. GOVERNING EQUATIONS

To carry out the simulation, conservation equations of mass, momentum and energy were solved.

A. Energy equation

The energy conservation equations are solved by Fluent in single phase as:

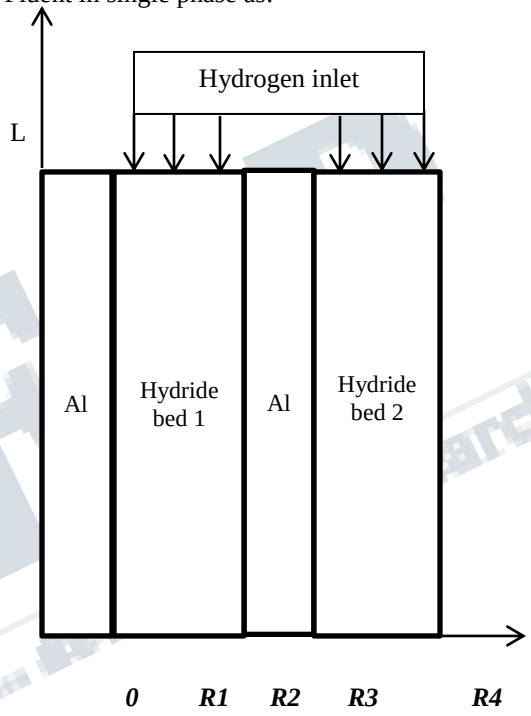

Fig. 2 - Geometry of aluminium layered hydride

$$(\rho C_p)_{eff}\frac{\partial T}{\partial t} + \rho_g C_{pg} \upsilon_g \nabla T = \nabla(\lambda_{eff}\nabla T) + S_m \quad (1)$$

Where S_m is the energy source term given by,

$$S_m = (1-\varepsilon)|\nabla H|\frac{\partial \rho_s}{\partial t} \quad (2)$$

The effective heat capacity and thermal conductivity of the hydride bed are expressed as,

$$\rho C_p = \varepsilon\rho_g C_{pg} + (1-\varepsilon)\rho_s C_{ps} \quad (3)$$

$$\lambda_{eff} = \varepsilon\lambda_g + (1-\varepsilon)\lambda_s \quad (4)$$

B. Mass balance equation

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Vol 2, Issue 5, May 2017

For hydrogen flow, the mass of hydrogen absorbed is determined by solving mass balance as,
For the gas,

$$\varepsilon \frac{d\rho_g}{dt} + div(\rho_g \vec{v}_g) = -\dot{m} \quad (5)$$

For the solid,

$$(1-\varepsilon)\frac{\partial \rho_s}{\partial t} = \dot{m} \quad (6)$$

C. Momentum kinetics

Porous media is modeled by the addition of momentum source term which includes a viscous resistance and an inertial resistance term to the fluid flow equation. Since, the flow through porous media

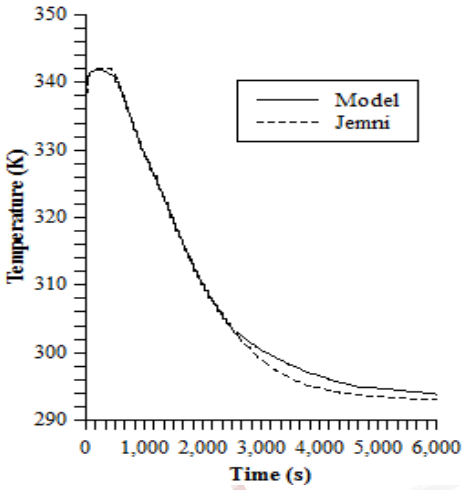

Fig. 3(a) - Bed temperature vs. time

is laminar, velocity of gas flow and pressure drop are proportional. Thus, inertial resistance is considered as zero. So, the gas velocity by Darcy's law states, $\overrightarrow{v_g} = \frac{-K}{\mu}\overrightarrow{\nabla p}$ (7)

$$K = \frac{\varepsilon^2 {d_p}^2}{150(1-\varepsilon)^2} \quad (8)$$

For hydrogen absorption reaction, $\frac{\partial \rho_s}{\partial t} = C_a \exp\left(\frac{-E_a}{RT}\right) \ln\left(\frac{P}{P_{eq}}\right)(\rho_{ss} - \rho_s)$ (9)

Mohammedshahi et al. [9] present some models for finding the equilibrium pressure, P_{eq} for the system. All relations were made on considering the experimental data which relates P_{eq} with hydrogen concentration and temperature. Some relations also considered account plateau features like hysteresis and the plateau slope, which are least considered. As all these relations are modifications of van't Hoff equation, for general cases van't Hoff relation is sufficient

$$\ln\frac{P_{eq}}{P_0} = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (10)$$

Van't Hoff equation can be simplified as,

$$\ln\frac{P_{eq}}{P_0} = A - \frac{B}{T} \quad (11)$$

Where A and B are Van't Hoff constants which depends on standard state enthalpy and entropy with values 12.919 and 3704.4 respectively [8].

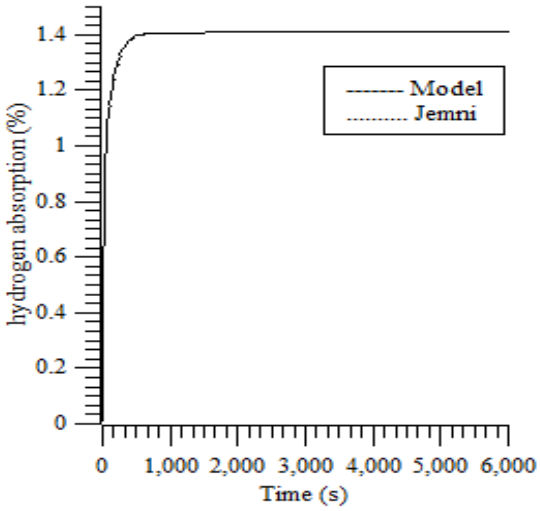

Fig. 3(b) - Hydrogen absorption vs. time

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V. INITIAL AND BOUNDARY CONDITIONS

For the constant temperature boundary condition at initially t = 0, the temperature, the hydride density and the pressure in the system are assumed to be constant.

$T(t_0, r, z) = T_0$

$P(t_0, r, z) = P_0 = 1$ bar

$\rho(t_0, r, z) = \rho_0$ (12)

The boundary conditions are expressed as:

At the top surface, inlet conditions are provided.

$T(r, H) = T_0$; $P(r, H) = P_{in}$ (13)

As symmetry is enabled at left boundary,

$$\frac{\partial P(0,z)}{\partial r} = 0 \; ; \; \frac{\partial T(0,z)}{\partial r} = 0 \quad (14)$$

Adiabatic conditions are enabled on lower boundary as,

$$\frac{\partial P(r,0)}{\partial r} = 0 \; ; \; \frac{\partial T(r,0)}{\partial r} = 0 \quad (15)$$

For case 1, isothermal condition of 273 K and 293 K is provided

$T(R, z) = K273$ or 293 K (16)

For case 2, convective heat transfer is provided at right boundary as

$$\frac{\partial P(R,z)}{\partial z} = 0 \; ; \; \frac{\partial T(R,z)}{\partial t} = h(T - T_{ext}) \quad (17)$$

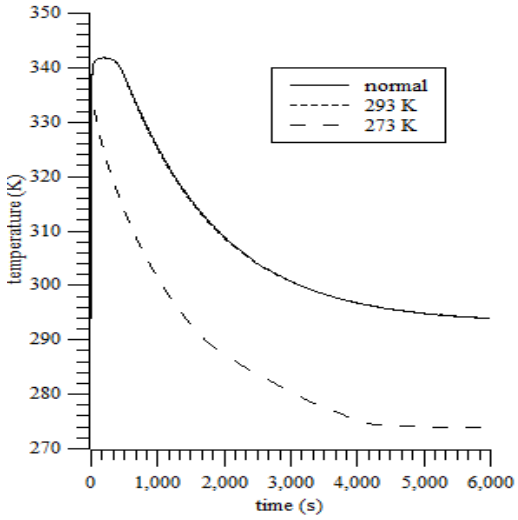

Fig. 4(a) - Temperature vs time

VI. METHOD OF SOLUTION

The volumetric heat source term and the rate of reaction are enabled by incorporating a user defined function to Fluent. Two user defined memories are created for storing the sources.

VII. RESULTS AND DISCUSSIONS

VIII.

For the sake of validation, fig (3) shows the comparison of our results with those of experimental results of Jemni et.al. [2] and are in agreement. The study is with a convective exchanging boundary. The increase in temperature is due to hydriding reaction and the further decreasing tendency is due to high temperature of bed. The cooling time is quite high due to the low thermal conductivity of hydride bed. The bed attains its maximum absorption capacity of

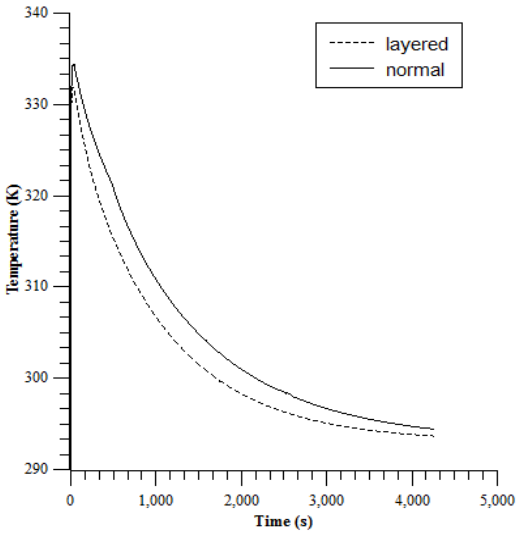

Fig. 5(a) - Temperature vs. time

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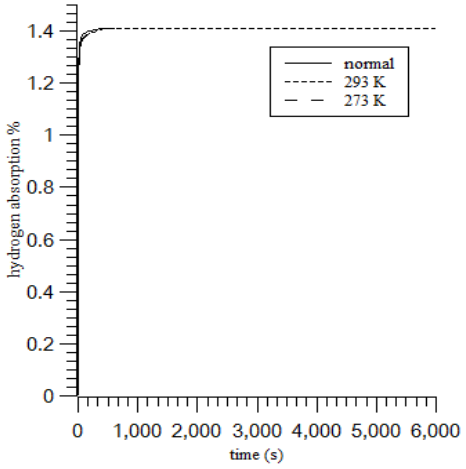

Fig. 4(b) - Hydrogen absorption vs time

1.41%. The sudden increase in absorption rate is due to the large pressure gradient between equilibrium pressure and applied.

1. Case 1

Fig 4 (a) and (b) depicts the temperature and absorption kinetics studies at the constant temperature boundary of 293 K stands almost equal effects with that of the convective boundary and 273 K stands better performance than the above two in heat transfer and absorption time. Temperature developed is about 10 K lower when wall is provided with a constant temperature of 273 K. It can be noted that a low constant temperature boundary with the help of heat pipes are an excellent alternative method for convective boundary.

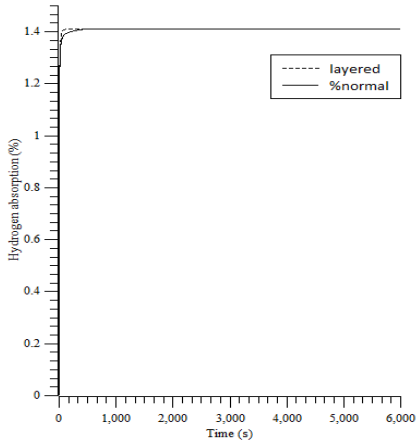

Fig. 5(b) - Hydrogen absorption vs. time

1. Case 2

Fig 5 (a) and (b) shows the temperature and hydrogen absorption amount when the hydride bed is separated by layered Aluminium films inside the bed. The bed attains its storage saturation in least time and lower temperature. The average temperature is about 5 K lower for the present study.

Table.1- Thermo physical properties and constants

Parameters	Symbol	Value
Initial pressure	P_0	1 bar
Initial pressure of hydrogen	P_{in}	8 bar
Temperature of hydrogen inlet	T_{in}	293 K
Activation energy	E_a	21170 J/ mol
Universal gas constant	R	8.314 J/ mol K
Density of solid	ρ_0	8400 kg/ m^3
Density of solid at saturation	ρ_{ss}	8520 kg/m^3
Enthalpy of formation	ΔH	30 kJ/kg K
Specific heat of solid	C_{ps}	419 J/kg K
Specific heat of hydrogen	C_{pg}	14890 J/kg K
Thermal conductivity of solid	λ_s	2.4 W/m K
Thermal conductivity of hydrogen	λ_g	0.16 W/ m K
Reaction constant	C_a	59.9 1/s
Porosity	ε	0.5
Heat transfer coefficient	h	1650 W/m^2 K
permeability	K	10^{-8} m^2
Particle diameter	d_p	10^{-6}m

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IX. CONCLUSION

Elaborate analysis of the charging process of hydrogen into a $LaNi_5$ metal hydride tank equipped with heat pipes for constant temperature boundary shows that a lower temperature of 273 K is more effective than a constant temperature boundary of 293 K and a convective boundary of 293 K with 1650 W/m^2K.. The temperature rise and time for cooling is very much lower as its effective for vehicular uses, while the absorption tendency almost remains the same.

Also, the study of hydride bed with thin Aluminium layers placed inside the hydride bed shows time has reduced for complete absorption and the temperature rise and cooling time has reduced

due to the high conductivity of the metal placed. So, both the studies show they are favorable for hydride systems.

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