Performance Simulation of Hydrogen Sorption in Metal Hydride Based Storage Bed Using 2d Lattice Boltzmann Method

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Abstract - *Metal hydrides are formed on exposure of certain metals or alloys to hydrogen at ordinary temperatures and pressures. Metal hydrides as hydrogen storage media offer various beneficial features such as high volumetric storage capacity, fast reaction kinetics, large number of charge-discharge cycles and safety. Hydrogen sorption rate in metal hydride bed is controlled by heat transfer.*

Experimental investigation of hydrogen sorption and heat transfer in metal hydride bed is complicated and expensive. In such circumstances, numerical study of such storage beds offers reliable results. Conventional numerical schemes employing FDM, FEM and FVM have been used to simulate continuum-based governing equations with suitable boundary conditions. However in the last decade, the Lattice Boltzmann method (LBM) has met with significant success for the numerical simulation of a large variety of problems in science and engineering. As a different approach from the conventional numerical methods, the LBM has been demonstrated to be successful in simulation of complex physical systems where the continuum approach has failed. It also offers lower computational time. The LBM is a mesoscopic approach that incorporates microscopic physics with affordable computational expense. Unlike the conventional methods that directly simulate the continuum based governing equations, the LBM is based on a mesoscopic kinetic equation.

In this project, the heat and mass transfer in metal hydride based storage bed is studied using 2D Lattice Boltzmann method. The effects of different parameters such as supply pressure, coolant temperature and bed thickness on the sorption performance are analysed. The results are compared with the experimental results.

1. INTRODUCTION

Hydrogen is stored in gaseous, liquid and solid forms. Gaseous form of storage is the simplest in which compressed hydrogen gas is stored in strong containers. These containers are all metal or composite tanks with appropriate

liners. Storage of hydrogen in liquid form ensures higher energy density than the gaseous form. Liquefied hydrogen is stored in sophisticated cryogenic tanks with suitable controls. Boil-off losses need to be restricted with appropriate measures. Safety is the main concern in both these cases.

Hydrogen storage in solid form involves either physisorption or chemisorption of hydrogen in suitable storage materials which include metal hydrides, complex hydrides, carbon based materials, zeolites, silica etc. Gravimetric hydrogen density of metal and complex metal hydrides is higher than other storage forms.

Hydrogen storage in inter-metallic compounds is capable of absorbing and releasing hydrogen without compromising its own structure. Hence, metal hydride based hydrogen storage systems deserve attention as they possess higher storage density than that of the compressed gas storage. Besides larger hydrogen capacity, metal hydrides offer several other practical advantages. Their formation does not require any special processes / machinery as they are formed simply by coming in close contact with the hydrogen gas. Unlike compressed hydrogen and liquid hydrogen, metal hydrides can be kept for a long period in simple metal containers at atmospheric conditions. They are quite stable below their dissociation temperatures and since the dissociation of metal hydride is an endothermic reaction, the self cooling effect limits the evolution of hydrogen in the event of a leak developing accidentally in the storage tank. Storage of hydrogen in metal hydrides does not require thick walled containers or special thermal insulation and, therefore the possibility of explosion in hydride containers is minimal.

1.1 Metal Hydride

Metals, intermetallic compounds and alloys generally react with hydrogen and form mainly solid metal-hydrogen compounds. Hydrides exist as ionic, polymeric covalent, volatile covalent and metallic hydrides. The binary hydrides of the transition metals are predominantly metallic in character and are usually referred to as metallic hydrides. The lattice structure is that of a typical metal with hydrogen atoms on the interstitial sites; and for this reason they are also called interstitial hydrides. Since the adsorption of hydrogen will increase with the size of the lattice.

The sorption mechanism of metal hydride is, M (solid) + (X/2) H2 MHX (solid) + HEAT,   H= 25-30 KJ/mol Molecular hydrogen is dissociated at the surface before absorption; two H atoms recombine to H2 in the desorption process. The thermodynamic aspects of hydride formation from gaseous hydrogen are described by pressure composition isotherms.

The host metal initially dissolves some hydrogen as a solid solution (α-phase). As the hydrogen pressure together with the concentration of H in the metal is increased, interactions between hydrogen atoms become locally important, and we start to see nucleation and growth of the hydride (β) phase. While the two phases coexist, the isotherms show a flat plateau, the length of which determines how much H2 can be stored reversibly with small pressure variations.

In the pure β-phase, the H2 pressure rises steeply with the concentration. At higher H2 pressure, further plateau and further hydride phases may be formed. The two-phase region ends in a critical point TC, above which the transition from α- to β- phase is continuous. The plateau or equilibrium pressure depends strongly on temperature and is related to the changesH and S of enthalpy and entropy, respectively.

As the entropy change corresponds mostly to the change from molecular hydrogen gas to dissolved hydrogen, it is roughly 130 J K-1mol–1 for all metal–hydrogen systems under consideration. The enthalpy term characterizes the stability of the metal–hydrogen bond. To reach an equilibrium pressure of 1 bar at 300 K, H should amount to 19.6 kJ molH-

1. The operating temperature of a metal hydride system is fixed by the plateau pressure in thermodynamic equilibrium and by the overall reaction kinetics
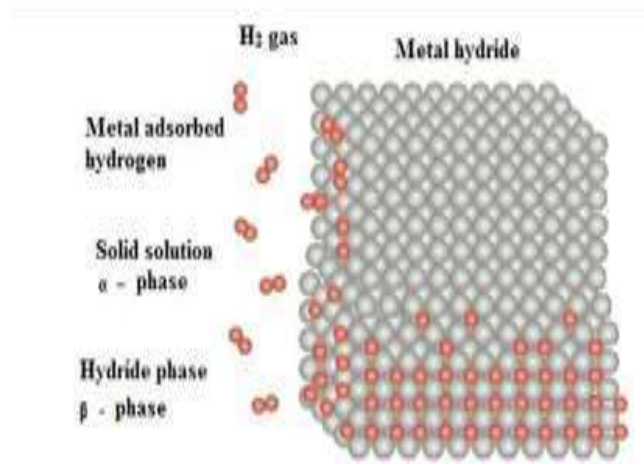

Fig. 1.1 Schematic representation of hydrogen sorption

The pressure–composition isotherm is created on basis of Van'tHoffequation.The equilibrium pressure Peq as a function of temperature is related to the changes H and S of enthalpy and entropy, respectively, by the Van't Hoff equation:

The pressure–composition isotherms is shown in fig. 1.2 comprises of the solid solution (α-phase), the hydride phase (β-phase) and the region where the two phases coexist.

The coexistence region is characterized by the flat plateau and ends at the critical temperature Tc. The construction of the Van't Hoff plot is shown on the right hand side. The slope of the line is equal to the enthalpy of formation divided by the gas constant and the interception is equal to the entropy of formation divided by the gas constant.
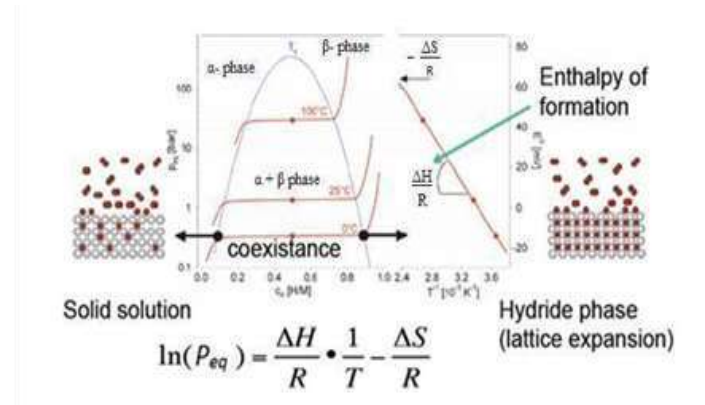

$$\ln(P_{eq}) = \frac{\Delta H}{R} \cdot \frac{1}{T} - \frac{\Delta S}{R}$$
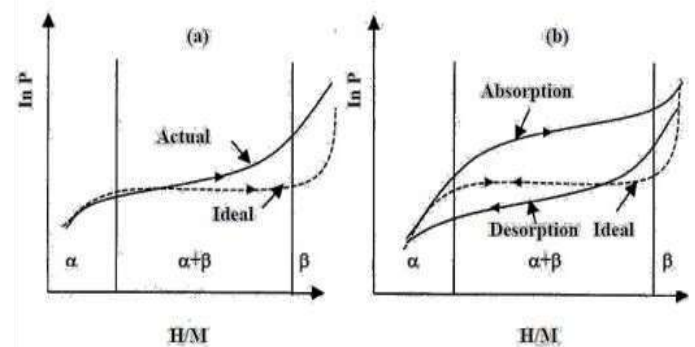
Fig. 1.2 Ideal PCI diagram of metal hydride

Fig 1.3 Comparison of actual and ideal cases

1.2 Heat and Mass Transfer in Metal Hydride

The study of heat and mass transfer characteristics in metal hydride beds is a crucial step in designing the metal hydride energy conversion systems. Heat and mass transfer study also helps to optimize the enhancement techniques and to select the operational and bed related parameters .The bed temperature increases rapidly during the initial phase of the reaction and then gradually reaches the equilibrium temperature at which the equilibrium absorption pressure of the hydride is equal to the applied hydrogen pressure. Heat transfer from the bed to the cooling media dissipates the heat generated in the process. Due to very low effective thermal conductivity of the hydride bed, the heat transfer rate between the heat transfer media and the bed is not fast enough to match the reaction rate. Initially the absorption rate is higher than the heat transfer rate and as a result most of the energy released due to hydrogen absorption is absorbed by hydride bed itself.

Therefore the bed temperature climbs almost instantly to peak values. The differential between the supply pressure and the equilibrium pressure is the major driving force for

hydrogen sorption. Steep rise in bed temperature causes a rise in equilibrium pressure and a corresponding decrease in pressure differential. Therefore sorption rate falls. The generated heat is removed instantaneously by the circulating coolant and the rest of the reaction is controlled by heat transfer.

1.3.Effect of Geometric Parameters

Important geometric parameters that depend on the hydriding in metal hydride beds include bed thickness, cooling channel dimensions and the overall dimensions of the bed. Heat transfer is the dominant limitation for unenhanced hydride beds. However, if effective thermal conductivity is increased above 5 W/m-K, hydrogen flow and reaction kinetics become the rate limiting processes. In applications where system weight is a critical parameter, the effect of the additional weight for conductivity enhancement must be assessed. Heat transfer limitation is more significant for thicker beds. The optimal bed thickness of an enhanced bed is larger than that of an unenhanced bed. For bed thickness less than 5 mm and pressures greater than 2 bar, pressure drop due to hydrogen flow is not a rate limiting factor .

1.4Effect of Operating Parameters

Hydrogen supply pressure, cooling media temperature are independent operating parameters which influence the performance of the hydride bed. The time needed for the reactor saturation is small when the inlet pressure is higher. The increase in hydrogen pressure results in the decrease of the mean free path of hydrogen, leading to increase in conductivity of hydrogen. The charging time increases rapidly as the charging pressure approaches absorption plateau pressure. control the transport of exothermic heat generated within the bed. The reaction velocity is faster when the inlet temperature of the media is less. At any given supply pressure, lower coolant temperature causes a lower bed. temperature and thereby lower equilibrium pressure. This consequently increases the driving potential for mass transfer, resulting in a higher rate of reaction. Impact of heat transfer coefficient on hydrogen sorption is substantial at small flow rates but is very limited at higher ranges.

2 BOLTZMANN METHOD

There are two main approaches in simulating the transport equations (heat, mass, and momentum), continuum and discrete. In continuum approach, ordinary or partial differential equations can be achieved by applying conservation of energy, mass, and momentum for an infinitesimal control volume. Since it is difficult to solve the governing differential equations for many reasons(nonlinearity, complex boundary conditions, complex geometry, etc.), therefore finite difference, finite volume, finite element, etc., schemes are used to convert the differential equations with a given boundary and initial conditions into a system of algebraic equations. The

algebraic equations can be solved iteratively until convergence is insured. Let us discuss the procedure in more detail, first the governing equations are identified (mainly partial differential equation). The next step is to discredited the domain into volume, girds, or elements depending on the method of solution. We can look at this step as each volume or node or element contains a collection of particles (huge number, order of 1016). The scale is macroscopic. The velocity, pressure, temperature of all those particles represented by a nodal value, or averaged over a finite volume, or simply assumed linearly or bi-linearly varied from one node to another. The phenomenological properties such as viscosity, thermal conductivity, heat capacity, etc. are in general known parameters (input parameters, except for inverse problems). For inverse problems, one or more thermo-physical properties may be unknown.

On the other extreme, the medium can be considered made of small particles (atom, molecule) and these particles collide with each other. This scale is micro scale. Hence, we need to identify the inter-particle (inter-molecular) forces and solve ordinary differential equation of Newton's second law (momentum conservation). At each time step, we need to identify location and velocity of each particle, i.e, trajectory of the particles. At this level, there is no definition of temperature, pressure, and thermo-physical properties, such as viscosity, thermal conductivity, heat capacity, etc. For instance, temperature and pressure are related to the kinetic energy of the particles (mass and velocity) and frequency of particles bombardment on the boundaries, respectively.

This method is called molecular dynamics (MD) simulations. Fundamentally, MD is simple and can handle phase change and complex geometries without any difficulties and without introducing extra ingredients. However, it is important to specify the appropriate inter -particle force function. The main drawback or obstacle of using MD in simulation of a relatively large system is the computer resource and data reduction process, which will not be available for us in the seen future.
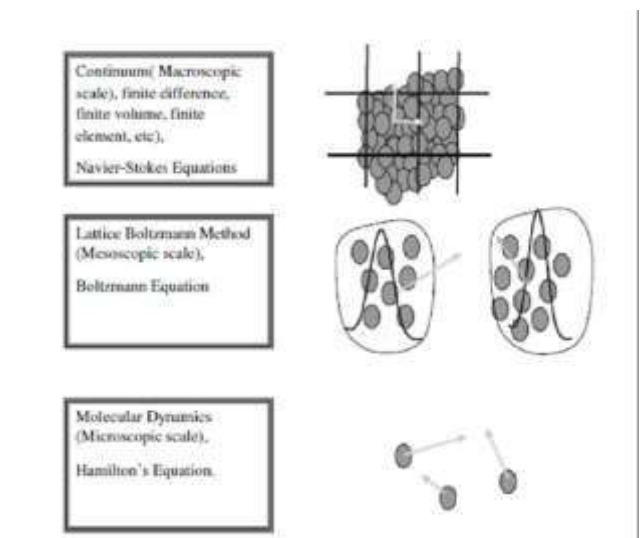

Fig. 2.1 Techniques of simulations

What about a middle man, sitting at the middle of both mentioned techniques, the lattice Boltzmann method (LBM). The main idea of Boltzmann is to bridge the gap between micro-scale and macro-scale by not considering each particle behaviour alone but behaviour of a collection of particles as a unit, Fig. . The property of the collection of particles is represented by a distribution function. The keyword is the distribution function. The distribution function acts as a representative for collection of particles. This scale is called meso-scale. LBM enjoys advantages of both macroscopic and microscopic approaches, with manageable computer resources. flows without a need to trace the interfaces between differe adapted to parallel processes computing.Moreover, there is no need to solve Laplace equation at each time step to satisfy continuity equation of incompressible, unsteady flows, as it is in solving Navier – Stokes (NS) equation. However, it needs more computer memory compared with NS solver, which is not a big constraint. Also, it can handle a problem in micro - and macro-scales with reliable accuracy.LBM has many advantages. It is easy to apply for complex domains,easy to treat multi-phase and multi-component nt phases. Furthermore, it can be naturally

2.1 PHYSICAL MODEL

The metal hydride storage device considered in the present study is shown in Fig. 3.2. It is a rectangular alloy bed having four boundary walls. Hydrogen storage material is evenly packed within this storage bed. Hydrogen enters the bed through appropriate filtering and distribution mechanism provided at the top and bottom of the bed. The side walls are duly cooled/ heated with heat exchanger (HX).

Initially, as hydrogen enters the bed, the reaction commences and the temperature of the bed increases due to exothermic heat generation. This heat is transported out of the bed by the heat exchanger and the temperature falls. As the temperature in the vicinity of the heat exchanger is low, the reaction rate will be faster at this location. Therefore, the boundary close to the heat exchanger gets saturated faster. As reaction proceeds, the saturated region progress gradually to the unsaturated region until

Reiterating the fact that absorption process will be faster in the close vicinity of heat exchanger and it will be saturated earlier than the rest, we can visualize a smooth interface, known as a reaction front which demarcates the fully hydrided portion from the unhydrided/ unsaturated regions

As time proceeds, these reaction fronts move outwards from the periphery of HX to the unsaturated areas of the alloy.

The computational domain used in this study is shown in fig. 6.3

2.2 ASSUMPTIONS

Exact mathematical formulation of heat and mass transfer in metal hydride beds is complicated due to the random nature of bulk material. Hence it is generally assumed that the packed bed is a homogeneous and isotropic porous medium where permeability, effective thermal conductivity and mass diffusivity of the bed are independent of position and direction. The convective heat transfer and inter-particle radiation are negligibly small compared with the conduction heat transfer in the hydride bed.

Thermo -physical properties such as density, viscosity, thermal conductivity and specific heat are nearly constant at the pressure, temperature and hydrogen concentration prevailing inside the bed. The equilibrium pressure is determined using van't Hoff's law. Velocity of hydrogen inside the hydride bed is very small as the particle diameter is small compared with the characteristic length of the problem. Darcy's law may be used to model fluid flow through packed beds where viscous forces dominate inertia forces.

2.3 RESULTS AND DISCUSSION

LaNi5 is selected as the hydriding material for the present simulation. The reaction rate of LaNis is extremely fast. Reaction kinetics and thermo-physical property date of LaNi5 are given in Table. 2.1. The parametric ranges used in simulation is given in Table. 2.2

Table 2.1 Thermo-physical properties of LaNis and H2

Parameter	LaNis	H2
Density. Kg/m^2	8200	0.0838 at
Specific heat, Cp, J/kg K	419	14,890
Effective thermal	1.2	0.12
Activation energy, Ea, J/mol	21170	-
Reaction energy , Ca,l/s	59.187	-
A	12.99	-
B	3704.59	-

Table 7.2 Parameter alues used in simulation

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2.3.1 Heat and Mass Transfer in Metal Hydride Bed

The heat transfer rate is maximum at the boundaries. So the temperature evolved at the boundaries will be minimum when compared to other areas in the bed. Temperature rises towards the centre of the bed. When it is the case with density, density of hydride bed is maximum at the boundaries. This is because heat transfer rate is maximum at boundaries.

As time elapses the density increases towards center and on reaching saturation there will be uniform density over the entire bed. The density and temperature profile and shown in fig.2.4 and fig.2.5

2.3.2 Effect of Bed Thickness on Hydride Formation

Bed thickness is an important geometric parameter that influences the performance of any hydrogen storage device. For thinner beds , the conduction path is relatively short. If the thickness exceeds an optimum value, the gain due to higher quantity of hydride is negated by the increased resistance to heat and mass transfer. Hence it results in a higher charging duration for the entire bed to het saturated. Figure shows the influence of bed thickness on absorption of hydrogen. In all cases, the same saturated state of about 1.2 weight % H2 is achieved after different time intervals. It is obvious that, at lower bed thicknesses the hydra bed reaches saturation earlier.

2.3.3 Effect of Operating Parameters on Hydrogen sorption Effect of supply pressure

Supply pressure is an importance operating parameter controlling the hydriding rates because the differential between equilibrium pressure and imposed pressure controls the absorption process. The figure fig shows the effect of supply pressure on hydride formation. From the graph, as pressure suppolied is imcreased keeping coolant temperature, thickness of the bed and heat transfer coefficient constant the time required to rach saturation decreases.

For LaNi5 the saturation concentration is about 1.2%. The initial sudden rise in concentration is dependent on material selected.

2.3.4 Effect of coolant temperature

Cooling media temperature control the transport of exothermic heat generated within the bed. effect of cooling media temperature on hydriding is shown in Fig. At any given supplu pressure, lower coolant temperature causes a lower bed temperature and thereby lower equilibrium pressure.

It consequently increasese the driving potential for mass transfer resulting in a higher rate of reation.
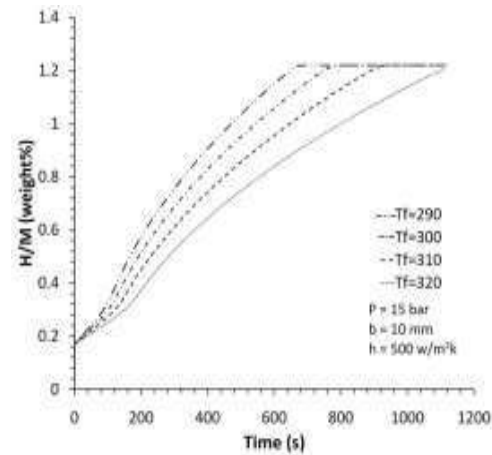

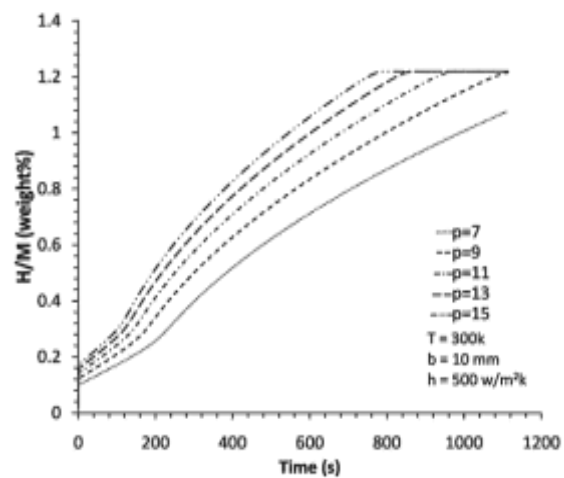Fig.2.3 Effect of coolant temperature on hydride formation

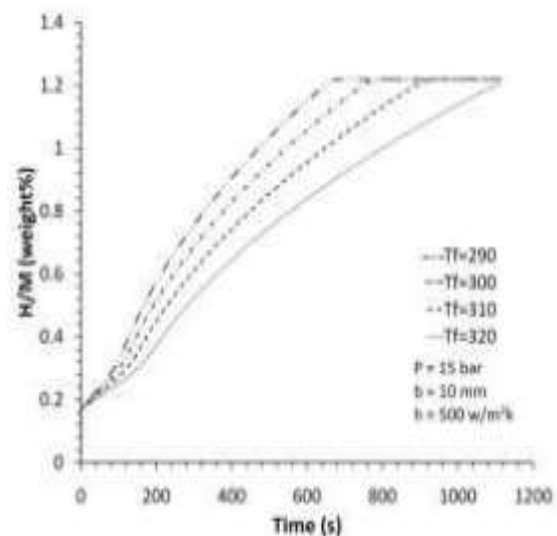Fig. 2.4 Effect of supply pressure on hydride formation

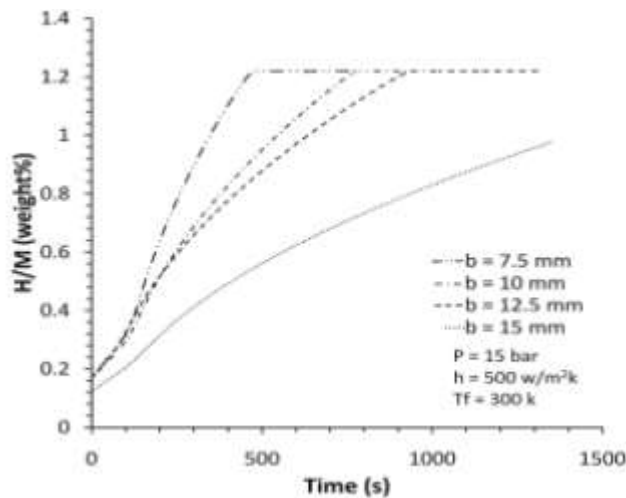Fig.2.4 Effect of coolant temperature on hydride formation

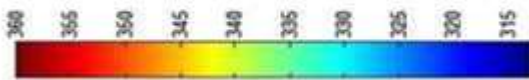Fig. 7.5 Influence of bed thickness on absorption of hydrogen

Fig. 2.1 Evolution of temperature in metal hydride bed at different time   intervals (T= 300 k, p= 15 bar, h = 500 W/m2k, b=10mm)
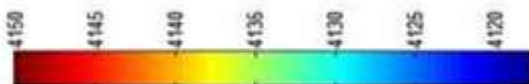
Fig. 2.2 Density profile in metal hydride bed at different time in steps (T=300 K, p=15 bar, h=500W/m2K, b=10mm)

3 CONCLUSIONS

In this project, numerical simulation o hydrogen sorption in metal hydride based storage bed using lattice Boltzmann method is presented. Simulations are carried out in MATLAB. The hydriding material selexted is LaNi5. Based on the hydrogenation pergormance of metal hydride bed it is found that

1. Due to higher heat transfer rate at the boundaries, concentration is higher at the boundaries.

2. At a particular time, the concentration will be higher for higher gressure, lower temperature and lesser bed size. The time to get saturated increases with decrease in pressure, increase in temperature or the increase in bed size.

3. The supply pressure, coolant temperature of the hydride ned and the size of the bed are he major

parameters that influence the concentration of hydrogen in the metal hydride bed.

LBM can be used as the powerful tool to LBM is a powerful method to simulate the complex heat and mass transfer phenomena in hydride bed, especially where the continuum approach fails. the LBM code is simple and computationally efficient.

REFEREMCES

1. A.A. Mohammad (2011), lattice Boltzmann method. Springer Publications

2. Chih-Hao-Liu, Kuen-Hau Lin, Hao-Chueh Mai, Chao-An-Lin (2010), Thermal boundary conditions for thermal lattice Boltzmann simulations,Computers and Methematics with Applications

3. F.Askri, M. Ben Salah, A.Jemni, S.Ben Nasrallah (2009), A new algorithm for solving transient eat and mass transfer in metal –hydrogen reactor, International journal of hydrogen energy

4. G. Mohan, M. Prakash Maiya, S. Srinivasa Murthy (2007) Performance simulation of metal hydride hydrogen storage device with emdedded filters and heat exchaer tubes, International Journal of Hydrogen Energy G. Mohan, M. Prakash Maiya, S. Sriniv