

Studies on Metal Hydride Based Heat Transformer

A thesis submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

by

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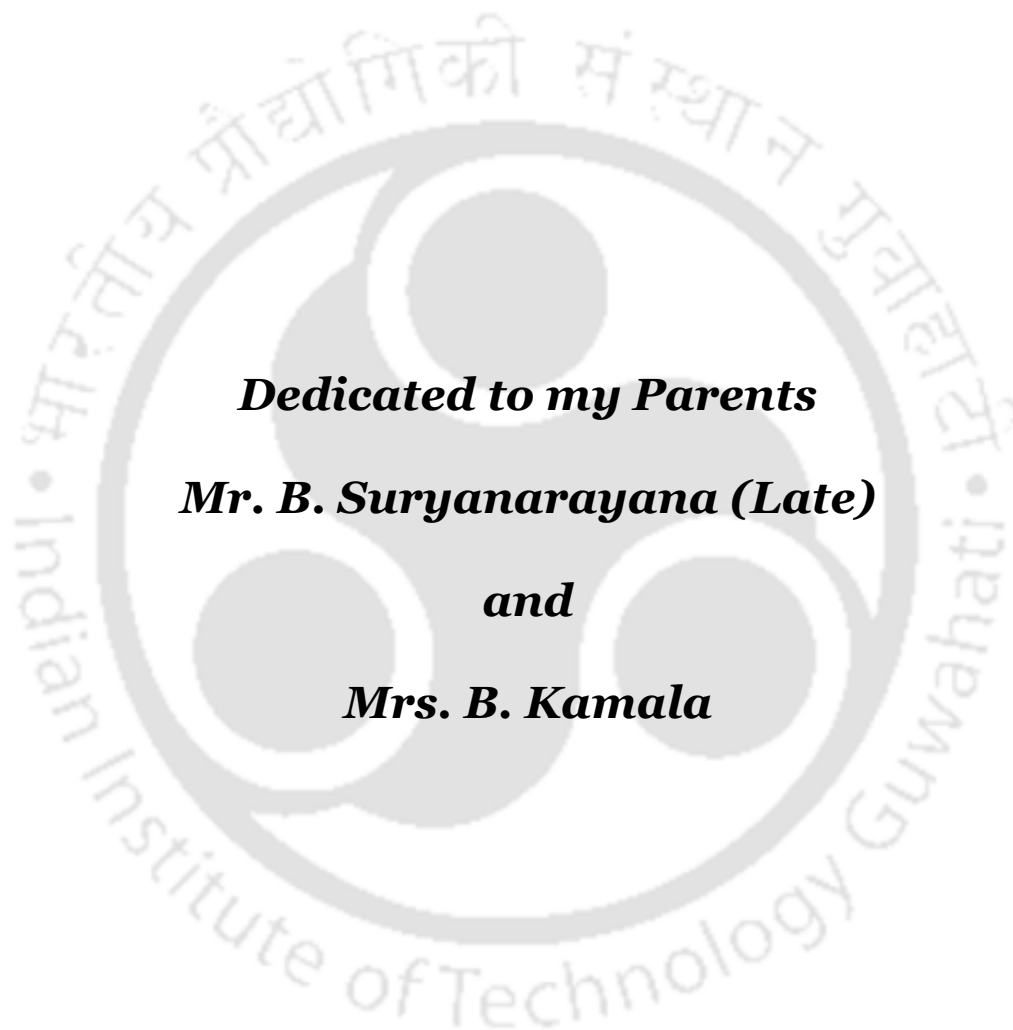


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THESIS CERTIFICATE

This is to certify that the work contained in the thesis entitled **Studies on Metal Hydride Based Heat Transformer** by **Bhogilla Satya Sekhar**, a student of the Department of Mechanical Engineering, Indian Institute of Technology Guwahati, for the award of the degree of **Doctor of Philosophy** has been carried out under my supervision and that this work has not been submitted elsewhere for any degree.

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Dedicated to my Parents

Mr. B. Suryanarayana (Late)

and

Mrs. B. Kamala

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Abstract

The global energy consumption has been increasing steadily due to the rapid industrialization and improvement in the living standard of the mankind. The predominant part of power is still produced from the fossil fuels. But, these fuel resources are limited and thus the mankind is forced to find the alternatives for resolving the critical issues associated with the use of fossil fuels such as environmental pollution and global warming. On the other side, most of the power producing industries release thousands of MW of low grade heat into atmosphere in the form of sensible heat in gaseous and liquid effluents, latent heat in vapour effluents, radiation and convection from hot objects. The alternate energy sources like solar energy, geothermal energy, etc. are not used directly because of their relatively low grade. If these low grade heats are upgraded to high temperature, it can be again used as inputs for thermal machines and several industrial applications. The utilization of low grade heat would contribute not only to lower energy consumption, but also reduces the environmental pollution and creates a better working environment. Therefore, the research and development on the waste heat utilization is of great interest to the present scientific community. Hence, an attempt is being made in this direction to develop an energy conversion system, which upgrades the quality of industrial waste heat, solar energy, geothermal energy, etc. to the higher temperature levels.

Unlike the conventional vapor compression systems, solid-gas sorption systems do not contribute to the depletion of ozone layer or global warming as they employ environment friendly refrigerants such as hydrogen, water, methanol, ammonia, etc. Further, these systems can effectively utilize the low-grade waste heat as an input for producing cold or upgraded heat outputs. When compared with the conventional liquid-gas absorption systems, solid-gas sorption systems have higher heat storage capacity, wide range of working temperatures and no crystallization problem. Metal hydride based heat pump is a type of solid-gas sorption system, in which the heat effect accompanied by absorption/desorption reaction is utilized for generating heat/cold. Metal hydride based heat pump works in three different operating modes: refrigeration, heat amplification and heat upgrading. Metal hydride based heat transformer is the third mode of heat pump which can upgrade the temperature of low grade heat from 120-140 °C

to 160-220 °C. The performance of such device highly depends on the rate at which the heat is removed/ supplied from/to the metal hydride beds during absorption/ desorption of hydrogen. Hence, the development of an efficient and economic design of such devices requires highly sophisticated computational models.

The performances of metal hydride based single-stage metal hydride based heat transformer (SS-MHHT) and double-stage metal hydride based heat transformer (DS-MHHT) are predicted by solving the unsteady, two-dimensional coupled heat and mass transfer processes in metal hydride bed of cylindrical configuration using a fully implicit finite volume method. Effects of hysteresis and plateau slope on the PCT characteristics of the metal hydrides and variation in the heat transfer fluid temperature along the axial direction of the reactor are considered in the model. The system of equations are solved by fully implicit finite volume method (FVM) using the central difference scheme. The computational results obtained from the simulation of SS-MHHT are compared with the experimental data reported in the literature for $\text{LaNi}_5/\text{LaNi}_{4.7}\text{Al}_{0.3}$ hydride pair and a good agreement between the two is observed. The variation of reaction bed temperature, hydride concentration, cooling fluid temperature and equilibrium pressures of the reactors are investigated over a complete cycle. The heat interactions (cooling/heating) between the hydride beds and heat transfer fluids are also studied for a complete cycle.

The mathematical model developed for a SS-MHHT is extended to study the performance of the system working with four different alloy pairs, namely $\text{LaNi}_5/\text{LaNi}_{4.7}\text{Al}_{0.3}$ (AP1), $\text{LaNi}_{4.6}\text{Al}_{0.4}/\text{MmNi}_{4.15}\text{Fe}_{0.85}$ (AP2), $\text{LaNi}_{4.61}\text{Mn}_{0.26}\text{Al}_{0.13}/\text{La}_{0.6}\text{Y}_{0.4}\text{Ni}_{4.8}\text{Mn}_{0.2}$ (AP3) and $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.9}\text{Fe}_{1.1}/\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.6}\text{Fe}_{1.4}$ (AP4). The effects of the operating temperatures, such as heat output (T_H), heat input (T_M) and heat sink (T_L) temperatures on the coefficient of performance (COP_{HT}), specific heating power (SHP) and second law efficiency (η_E) are presented. The optimum operating temperatures of all the selected metal hydride pairs are found out. From the selected hydride alloy pairs, the maximum COP_{HT} of 0.436 and SHP of 54 W/kg are obtained for $\text{LaNi}_{4.61}\text{Mn}_{0.26}\text{Al}_{0.13}/\text{La}_{0.6}\text{Y}_{0.4}\text{Ni}_{4.8}\text{Mn}_{0.2}$ pair. It is observed from the present investigation that $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.9}\text{Fe}_{1.1}/\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.6}\text{Fe}_{1.4}$ alloy pair provides a maximum temperature lift of about 50 K at the operating conditions of $T_H = 408$ K, $T_M = 358$ K and $T_L = 298$ K.

The performance investigation of a DS-MHHT working with $\text{LaNi}_{4.7}\text{Al}_{0.3}$, LaNi_5 and $\text{MmNi}_{4.6}\text{Al}_{0.4}$ (low/intermediate/high pressure hydride alloy) is also carried out. The variation in reaction bed temperatures, hydride concentrations, and equilibrium pressures over a complete cycle are presented. Further, the variations in the net amount of heat exchange between the reaction bed and the heat transfer fluid temperature over a cycle are presented. The performance parameters of the DS-MHHT such as coefficient of performance (COP_{HT}), specific heating power (SHP), second law efficiency (η_E) and HTF temperature difference (ΔT_{HTF}) are investigated at different heat output (T_H), heat input (T_M) and heat rejection (T_L) temperatures. The effect of half cycle time on COP_{HT} , SHP , total heat output and amount of hydrogen exchanged between the paired reactors are also presented. At the given operating conditions of heat output temperature 403 K, heat input temperature 353 K and heat sink temperature 303 K, the COP_{HT} , SHP and η_E of the system are found to be 0.35, 30 W/kg and 0.62, respectively.

Prototypes of both SS-MHHT and DS-MHHT have been developed. Experiments were performed on both SS-MHHT and DS-MHHT to validate the mathematical models developed and also to study the performance of the actual systems.

Single – stage MHHT's lab-scale prototype has been built and tested for upgrading the waste heat available from 393 - 413 K to about 428 - 440 K using LaNi_5 / $\text{LaNi}_{4.35}\text{Al}_{0.65}$ metal hydride pair. The transient behavior of hydrogen exchange and associated heat transfer of both the reactors were presented. The effects of heat source and heat rejection temperatures on the COP_{HT} , SHP and η_E were investigated. The numerical results were found to agree reasonably well with the experimental data. At the given operating conditions of heat output temperature 428 K, heat input temperature 413 K and heat sink temperature 308 K; the experimentally estimated values of COP_{HT} and SHP of the MHHT were 0.318 and 44 W/kg, respectively. For a given heat output and heat sink temperatures, the COP_{HT} and SHP of the system were found to increase with heat source temperature, while the η_E found to decrease with heat source temperature.

For developing a DS-MHHT, three metal hydrides namely, A, B and C with different thermo-physical properties are required. Hydrides A and B together act as hydrogen compressor and hydride C upgrades the quality of heat input. Therefore, a double-stage metal hydride based hydrogen compressor (DS-MHHC) was also developed for building a prototype of DS-MHHT. The metal hydrides chosen for the study were $\text{LaNi}_5/\text{La}_{0.35}\text{Ce}_{0.45}\text{Ca}_{0.2}\text{Ni}_{4.95}\text{Al}_{0.05}$. The effects of supply pressure and heat source (desorption) temperature on the delivery pressure and isentropic efficiency were investigated. It was observed that increase in supply pressure up to 10 bar significantly increase the delivery pressure and however, which reduced the compressor efficiency. A maximum compression ratio of 22 was obtained when the DS-MHHC operated at 2 bar supply pressure and 140 °C heat source temperature for $\text{LaNi}_5/\text{La}_{0.35}\text{Ce}_{0.45}\text{Ca}_{0.2}\text{Ni}_{4.95}\text{Al}_{0.05}$ alloy pair. At supply conditions of 10 bar supply pressure and 140 °C heat source temperature, a maximum delivery pressure achieved was 74 bar.

Experimental investigations on DS-MHHT were carried out at different heat source and heat sink temperatures. The waste heat was upgraded from 393 - 413 K to about 463 K employing LaNi_5 , $\text{La}_{0.35}\text{Ce}_{0.45}\text{Ca}_{0.2}\text{Ni}_{4.95}\text{Al}_{0.05}$ and $\text{LaNi}_{4.35}\text{Al}_{0.65}$. At the given operating conditions of heat output temperature 463 K, heat input temperature 403 K and heat sink temperature 308 K; the experimentally estimated values of COP_{HT} , SHP and η_E of the DS-MHHT were 0.217, 19.33 W/kg and 0.29 respectively. The COP_{HT} and the η_E were found to increase with heat sink temperature, while SHP of the system decreased with heat sink temperature. The total true temperature lift achieved was about 70 K.

Based on the above discussions, one can conclude that MHHT can be effectively used as a potential alternative device for upgrading the temperature of low grade heat input (393 - 413 K) up to the temperature range of 428 - 463 K. Further, the results presented in this thesis will be more useful for developing the commercial scale system for utilizing the waste heat from the industries. By using the developed thermal models one can predict the optimum operating parameters ranges of SS-MHHT and DS-MHHT, such as heat source, heat output and heat sink temperatures and half cycle time without conducting the expensive experimental studies.

Nomenclature

C_p	Specific heat, J/kg-K
E	Activation energy, J/mol H_2
h	Over all heat transfer coefficient, W/m^2-K
K	Permeability, m^2
m	Mass flux of hydrogen, kg/m^3-s
m_f	Mass flow rate of the heat transfer fluid, kg/s
M_g	Molecular weight of hydrogen, kg/kmol
n	Number of moles of hydrogen, mol
P	Pressure, bar
P_o	Reference pressure, bar
Q	Heat transfer, J
R	Reaction rate constant, s^{-1}
r_o	Outer radius of the reactor, m
R_u	Universal gas constant, J/mol-K
t	Time, s
T	Temperature, K
u	Velocity, m/s
V	Volume, m^3
X	Hydrogen concentration, (H/M ratio)
Z	Compressibility factor

Greek symbols

ε	Porosity
β	Hysteresis factor
ΔH	Enthalpy of reaction, J/mol H ₂
ΔS	Entropy of reaction, J/mol H ₂ -K
ν_g	Kinematic viscosity, m ² /s
λ	Thermal conductivity, W/m-K
ϕ, ϕ_0	Slope factors
μ_g	Dynamic viscosity, kg/m-s
ρ	Density, kg/m ³
γ	Isentropic compression index

Subscripts

a	Absorption
d	Desorption
e	Effective
eq	Equilibrium
f	Fluid, Final
hf	Half cycle time
fi	Heat transfer fluid inlet
fo	Heat transfer fluid outlet
g	Gas
i	Inner, initial
m	Metal

max	Maximum
min	Minimum
P	Connecting tube
s	Supply, solid
ss	Saturation solid

Abbreviations

CD	Compressor driven
COP	Coefficient of performance
DS	Double-stage
HTF	Heat transfer fluid
MHHC	Metal hydride based hydrogen compressor
MHHP	Metal hydride based heat pump
MHHT	Metal hydride based heat transformer
MHT	Metal hydride tank
PCT	Pressure-concentration-temperature
SCP	Specific cooling power
SHP	Specific heating power
SS	Single-stage

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Chapter 1

INTRODUCTION

1.1 Sorption Systems

Energy plays a vital role for economic growth and technological development of any nation. In the recent years, the amount of energy consumed has been increasing rapidly, and the energy shortage has become a major limiting factor for the economic and social development. Thus, it is crucial and imperative to improve the energy utilization efficiency and simultaneously to develop some advanced energy-saving technologies. Therefore, the key elements of the future energy conversion technology mainly include energy-saving, high-efficient technique, diversified development and environment protection. Proper utilization of energy is the only solution to solve the inconsistency between the energy supply and the energy consumption. Every year, enormous amount of low-grade thermal energy in the form of industrial waste heat, exhaust gases from engines and combustion devices, etc. is being wasted due to the low energy

conversion efficiency of the available devices. Further, a large amount of waste heat is directly released to the atmosphere or to the surface water without rational reutilization. This low-grade waste heat would become useful energy resources if they can be efficiently reutilized. This can significantly reduce the consumption of primary energy and also to promote the economic and social sustainable development by developing some advanced energy systems, such as the distributed energy system and the advanced integrated energy technologies. Figure 1.1 shows the amount of waste heat released to the environment in the global electricity system. About two-thirds of the primary energy which is used to produce electricity is being rejected as “waste” heat. This waste heat is left unused due to its relatively low-grade.

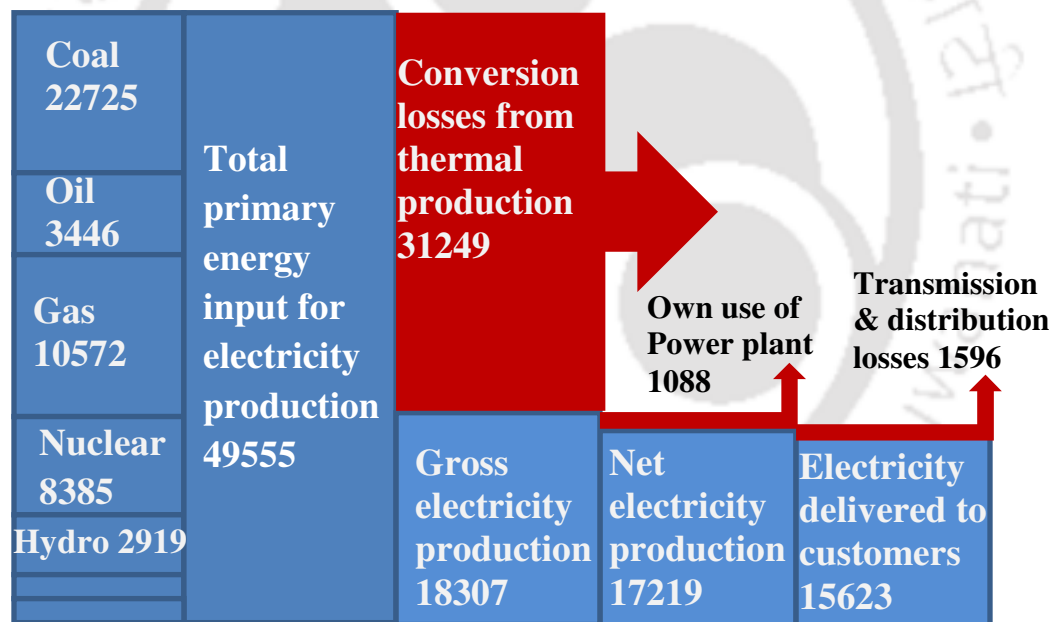


Fig. 1.1 Energy flows (TWh) in the global electricity system (IEA, 2011)

Though the exploitation and utilization of primary energy resources promotes the economic development, it also causes the serious environmental problems, such as ozone depletion potential (ODP) and the global warming potential (GWP). The chlorofluorocarbons (CFCs) and

the hydro chlorofluorocarbons (HCFCs), widely used in refrigeration, air conditioning and heat pump equipment's, are the major contributors to the ODP. Considering the environment pollution and energy shortage, in the recent years, progressive attention is focused on the study of new environment friendly refrigerants and the development of high-efficient heating and cooling systems. Thus, increasing the recognition of environmental problems, associated with issues related to the CFCs and HCFCs, has opened favorable opportunities for the development of environmental friendly heating and cooling technologies. As one of the environment friendly technologies, solid-gas sorption system has been regarded as an effective energy saver. They utilize low-grade thermal energy or renewable energy for upgrading the input heat or to produce cooling.

Solid-gas sorption system is a heat-powered carbon free heating and cooling technology, and it has a number of advantages over the conventional heat pumps or refrigeration machines. For example, in comparison with the vapor compression systems, solid-gas sorption systems have zero ozone depletion potential (ODP) as well as zero global warming potential (GWP) as they employ environment friendly substance as refrigerant such as hydrogen, water, methanol, ammonia, etc. Further, these systems can effectively utilize the low-grade waste heat or renewable energy for their operation and thus have a large energy- saving potential (Wang and Oliveira, 2006). When compared to the existing heat-powered liquid-gas absorption systems, solid-gas sorption systems have a wider range of working temperature and possess no crystallization problem. The energy storage capacity of these systems is also much higher than the liquid absorption heat pumps due to larger reaction heat; consequently heat /cold can be stored for longer time periods with low energy losses. In addition, solid sorption systems can be

applied to more extensive locations owing to their high reliability as compared with the liquid absorption systems.

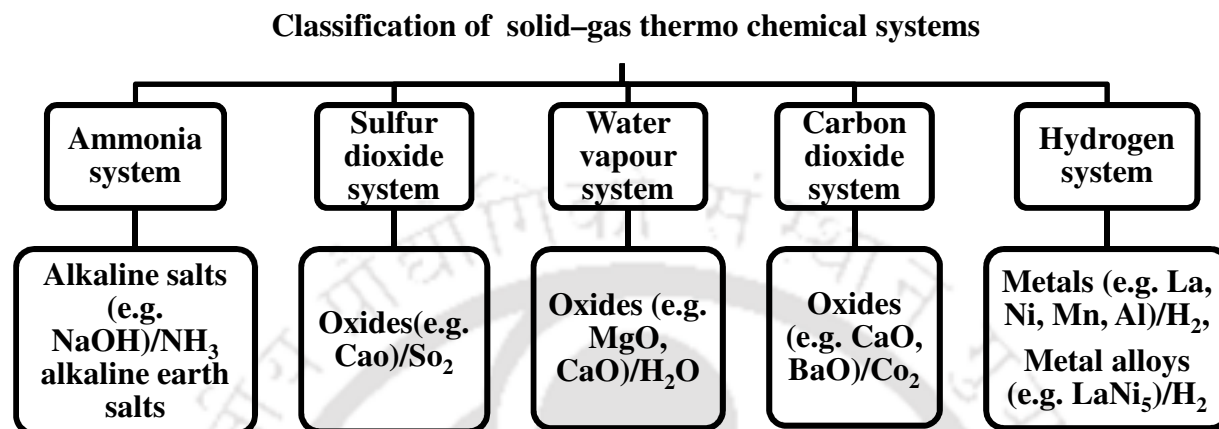


Fig. 1.2 Classification of solid-gas thermo chemical systems (Yu *et al.* 2007)

The performance of the solid sorption systems is mainly depends on the selection of sorption material, coupled heat and mass transfer characteristics of the sorption bed and its sorption thermodynamic cycle (Meunier, 1998). The solid sorption systems can be divided into physical sorption systems and thermo-chemical sorption systems in terms of the constraining force during the sorption process. The working principle of the former sorption is based on the Van der Waals force between the sorbent and the refrigerant, and the adsorption heat of the sorbent is almost equal to the condensation heat of the refrigerant. For the thermo-chemical sorption system, the operation principle is based on the thermal effect of reversible chemical reaction between the reactive sorbent and the refrigerant, and the adsorption heat of the sorbent is higher than the condensation heat of the refrigerant. Usually, chemical working pairs have the advantages of large sorption capacity and high volumetric heating or cooling density over physical adsorbents. Various chemical substances used in the solid-gas sorption systems are listed in Fig. 1.2.

In the solid sorption systems based on hydrogen-metal hydride, hydrogen is used as the working fluid and a pair of metals or alloys are used as absorbent and desorbent. Since, hydrogen is the working fluid, metal hydride systems are environmentally safe. The specific advantages of metal hydride systems are:

- Utilize low grade thermal energy as input.
- Extreme compactness due to high energy densities.
- Wide operating temperature ranges.
- Completely eliminate the use of moving parts and offer noise and vibration free operation.
- Cooling and heating rates, temperatures and pressure ranges can be varied easily by varying the metal alloy compositions.

1.2 Metal Hydrides

Metal hydrides are metallic or inter metallic compounds, formed by either milling or melting routes. They have the ability to reversibly absorb and desorb relatively large amounts of hydrogen at a certain temperature and pressure. This technology allows hydrogen to be stored in a solid form. It is observed that metal hydride based system can store about 20 to 80 % greater than that of liquid hydrogen at 20 K. Whereas, for gas storage requires very high pressures and thick walled vessels to approach these densities. Further, the performance of metal hydride based hydrogen storage system can be easily controlled by adjusting the supply pressure of hydrogen and varying the absorption temperature.

Metal hydride based hydrogen storage system offers several advantages over traditional hydrogen storage systems such as safe delivery of hydrogen at a constant pressure, higher

volumetric storage capacity, no mechanical losses due to the absence of moving parts, easy to handle and store for a longer period of time. The metal hydrides are generally classified as follows:

- i. Ionic hydrides
- ii. Covalent hydrides
- iii. Metallic hydrides

They differ in their chemical and physical properties, crystal structures and hydrogen storage capacities. Unlike the ionic and metallic hydrides, the covalent hydrides have practical limitations for hydrogen storage, as they cannot be formed by the direct reaction of hydrogen with metals except under special conditions. All ionic hydrides except magnesium hydride are highly stable. Metallic hydrides are important for practical applications because of their moderate operating temperatures, ease of hydride formation and recovery of hydrogen.

Large number of metals react with H_2 , forming metal hydrides. However, the practical applications of most of the metals are restricted due to their inconvenient thermodynamic properties. For example, only a few elements such as Pd, V, etc., can be considered, if the elements should be reversibly hydrogenated and dehydrogenated under a technically appropriate pressure and within a temperature range from ambient to about 300 °C. Fortunately, the number of practical hydriding metals has been greatly increased by the development of reversible hydrides of intermetallic compounds, which have a moderate affinity towards the hydrogen. The intermetallic compounds are formed by combining an element “A” which is a strong hydride former with an element “B” which is a weak hydride former. Either element “A” or “B” can be

substituted by one or more elements. The intermetallic compounds can be divided into four types:

Structure	Examples
A_2B	Zr_2Cu , Ti_2Pd , Mg_2Ni
AB	$MgNi$, $TiFe$
AB_2	$TiMn_2$, $ZrMn_2$, $ZrCr_2$
AB_5	$LaNi_5$, $CaNi_5$

1.3 Thermodynamics of Metal Hydride Formation

The chemical bonding of hydrogen to metal can be described by the following overall reaction.



The formation of metal hydrides is called absorption, which is an exothermic reaction. The endothermic reverse reaction is defined as desorption. Gaseous hydrogen can be stored in the form of solid metallic compounds (hydrides) which can be decomposed by heat input.

Actually the formation of metal hydrides by the direct reaction of hydrogen with metals or intermetallic compounds (Eq. 1.1) involves a number of sub-reactions. The sequence of sub-reactions is as follows, Fig. 1.3

- i. Physisorption of hydrogen molecules;
- ii. Dissociation of hydrogen molecules into atoms (chemisorption);
- iii. Diffusion of hydrogen atoms from the surface into the bulk through a surface layer;
- iv. Diffusion of hydrogen atoms through the hydride;

- v. Hydride formation at the metal hydride interface.

Desorption is essentially the reverse process. The mechanism can be better understood when associated with the pressure-concentration isotherms. As soon as hydrogen molecules are dissociated into atoms, they can penetrate into the metal surface and diffuse through the metal lattice. As the hydrogen pressure increases, a small amount of hydrogen is absorbed by the metal (trapped in interstitial sites) to form a solid solution. This phase is called α -phase (Fig. 1.3). The correlation between the pressure and the amount of absorbed hydrogen obeys the Sieverts' law. In the PCI figures, the pressure is plotted logarithmically.

$$x_{H_2} = \sqrt{P_{H_2}} \quad (1.2)$$

According to Eq. (1.2), a strong increase in pressure only leads to a rather small amount of dissolved hydrogen (α -phase). Within this range, there exist two components, metal and hydrogen, and two phases, a gaseous phase (hydrogen) and a solid phase (metal). Therefore according to Gibbs' phase rule (Eq. 1.3), the number of degrees of freedom is two, viz. temperature and pressure. If the temperature is determined to be constant, i.e. during an isothermal experiment, the amount of absorbed hydrogen is only related to the pressure. After the hydrogen saturation is reached, a metal hydride (β -phase) is formed. During the formation of metal hydride, there exist three phases, viz. one gaseous phase (hydrogen) and two solid phases (metal and metal hydride).

$$F = C - P + 2 \quad (1.3)$$

According to Eq. (1.3), there is only one degree of freedom. If the temperature is considered as an independent variable, the other variables are completely determined by a function of T under

equilibrium conditions. Under isothermal conditions ($T = \text{constant}$ and $f = 0$), the formation of metal hydride will take place under a constant equilibrium pressure.

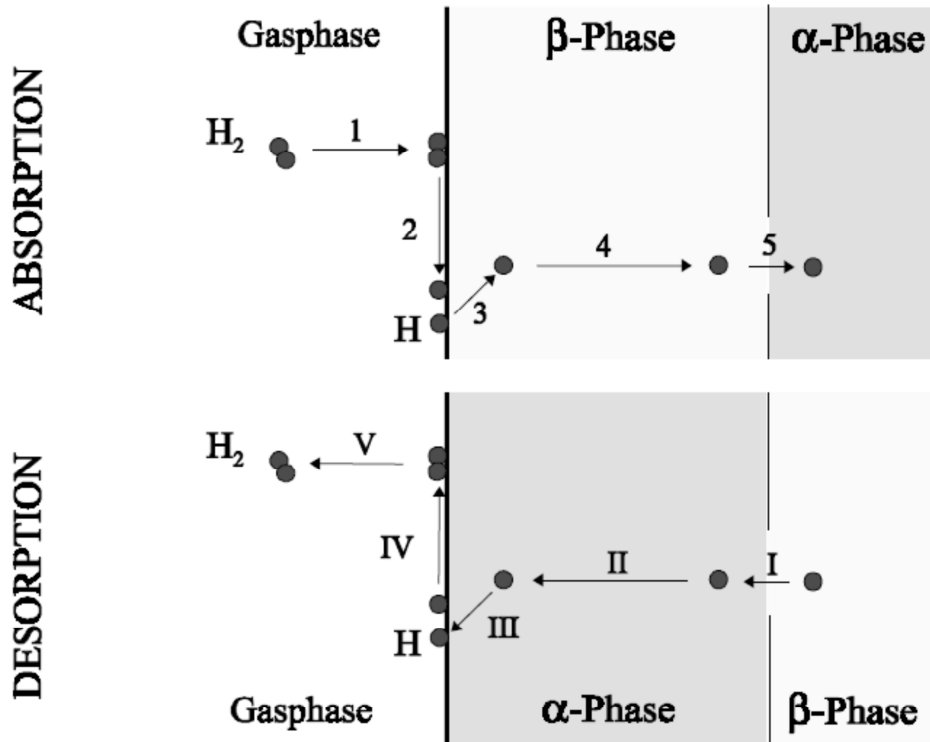


Fig. 1.3 Different steps involved in the hydriding kinetics (Klien, 2007).

The pressure plateau represents the formation of the metal hydride, where the width of the plateau illustrates the stoichiometry and thus the powder density (by weight) of metal hydrides, (see Fig. 1.4, points A $\rightarrow$ B, transformation $\alpha \rightarrow \beta$).

As soon as the hydride formation is completed, there is only one solid phase (hydride or β -phase). If additional hydrogen is introduced, still some hydrogen would be solved in the metal hydride. Again the increase of pressure obeys the Sieverts' law in Eq. (1.2). In the pure β -phase,

the hydrogen pressure rises steeply with the concentration. In the ideal case, desorption is the reverse process to absorption.

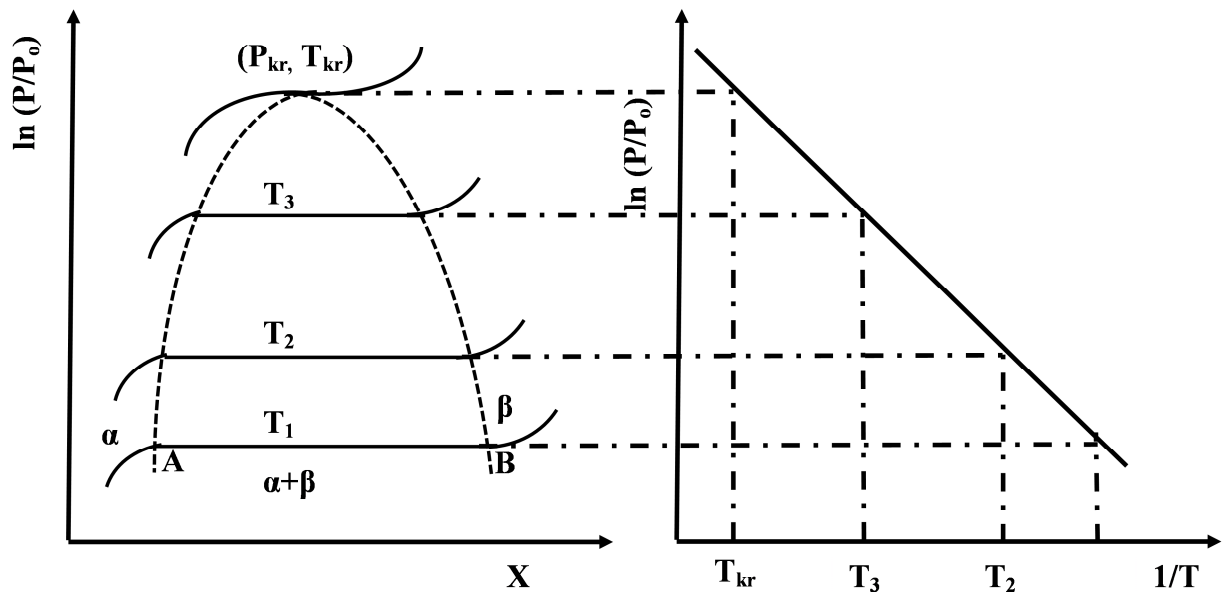


Fig. 1.4 Ideal pressure-concentration isotherms and van't Hoff plot

As shown in Fig. 1.4, with increasing reaction temperature the equilibrium pressure becomes higher and the plateaus become shorter. The two - phase region ends at a critical point T_{kr} . Above this temperature, the transition from the α - β -phase is continuous, and no metal hydride will be formed. Many metal hydrides deviate from the ideal behavior by exhibiting a hysteresis effect and a sloped plateau as shown in Fig. 1.5. Hysteresis effect is not desirable in practical applications as at the same temperature, hydrogen is released at a pressure slightly lower during desorption than that during absorption.

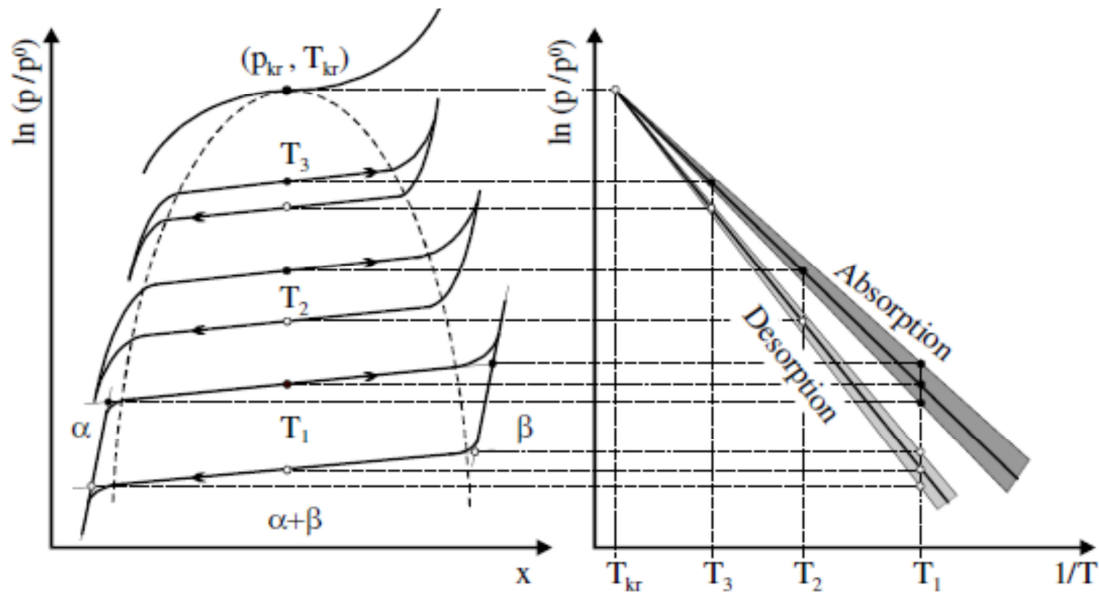


Fig. 1.5 Actual pressure-concentration isotherms and van't Hoff plot (Klien, 2007)

Apart from hysteresis, another irreversibility that reduces the system efficiency is the sloped plateau. In actual systems, all the hydrides possess sloped plateaus, the magnitude of which varies greatly from material to material. Because of the plateau slope, the equilibrium pressure in the $(\alpha+\beta)$ increases with concentration during absorption, and decreases with concentration during desorption. This reduces the usable hydrogen capacity, the heat and mass transfer rates also reduce with plateau slope, as a result the system performance is reduced. As already mentioned, the magnitudes of hysteresis and plateau slope vary greatly from material to material. It is possible to reduce these irreversibility's by varying the alloy composition.

1.4 Applications of Metal Hydrides

Metal hydrides can be effectively utilized as working materials for several engineering applications. Some of important applications are hydrogen storage, heat pump, heat transformer, heat storage, hydrogen compressor, metal hydride batteries, etc.

1.4.1 Hydrogen storage

Metal hydride based hydrogen storage is the most safe and a better option for hydrogen storage. Hydrogen can be stored by combining the hydrogen with solid state material through chemisorption. Metal hydrides have high volumetric hydrogen density compared to liquid hydrogen. Based on hydrogen desorption temperature, metal hydrides can be classified as

- Low temperature hydrides, which desorb hydrogen at room temperature (e.g. Rare earth metals, Zirconium, Titanium based intermetallic hydrides etc.). However the hydrogen storage capacity of these hydrides is less than 2 wt%.
- High temperature hydrides, which desorb hydrogen above 300 °C (e.g. Magnesium, Magnesium based intermetallic hydrides etc.). The hydrogen storage capacity of these hydrides is high up to 7 wt%.

Another class of solid state hydrogen storage materials is complex metal hydrides. These are prepared by chemical reaction and release more than 5 wt% hydrogen in the temperature range of 100 °C – 200 °C. However these materials are not reversible and hence cannot be used for cyclic hydrogen storage applications. One more option for solid state storage of hydrogen is physisorption, in which hydrogen is absorbed on the surface of materials such as carbon nano tubes, carbon nanofibers and activated carbon. The molecular hydrogen physisorption is demonstrated at cryogenic temperatures and extremely high surface area carbons are required. Out of all the options available today, metal hydrides are found suitable for cyclic hydrogen storage nearly at atmospheric conditions.

1.4.2 Hydrogen compressor

A thermally operated hydrogen compressor can be constructed without moving parts using metal hydride bed. The systematic dependence of absorption and desorption pressures on temperatures facilitates the absorption of hydrogen at low pressure, when metal hydride is cooled to low temperature and desorption of hydrogen at high pressure when the metal hydride bed is heated to a higher temperature. The advantages of metal hydride based hydrogen compressors over other compressors are utilization of low grade energy, absence of mechanical moving parts, compactness and discharging hydrogen with improved purity. The metal hydrides used for compression works in an open cycle and requires the following qualities (Sandrock, 1999)

- Good resistance to impurities
- Fast kinetics
- Cyclic stability
- High desorption pressure at moderate temperature ranges.

1.4.3 Thermal energy storage

Thermal energy can be stored as sensible heat or latent heat or in a thermo chemical way. The specific storage capacity increases in the same sequence. The latter is based on a reversible chemical reaction. In metal hydrides, heat energy is stored thermo-chemically in the form of enthalpy of formation. A pair of hydride beds is used for heat storage and recovery. A high temperature metal hydride bed receives heat input from the source and undergoes endothermic dehydrogenation. The second hydride absorbs the hydrogen desorbed by the first one. When heat is to be regenerated, the second hydride desorbs hydrogen using atmospheric heat and the heat is

liberated from first hydride by exothermic reabsorption. The advantages of using metal hydrides for heat storage are higher energy density, long term storage and adaptability to heat transformation process like heat transformers, heat pumps etc. The metal hydride required for energy storage should possess the following properties.

- High enthalpy of formation
- Good heat transfer characteristics
- Good kinetics
- Moderate operating pressures at high temperatures.

1.4.4 Metal hydride batteries

Nickel metal hydride battery (Ni-MH) is a well commercialized product. It uses a hydride forming metal alloy as negative electrode, $\text{Ni}(\text{OH})_2$ as positive electrode and alkaline solution as electrolyte. The advantages of Ni-MH batteries when compared to other batteries are compact cell assembly, higher energy density per unit cell voltage and environmental safety. These batteries are widely used in low cost consumer applications such as cameras, camcorders, mobile phones, medical instruments, automotive batteries and electric razors etc.

1.4.5 Heating and cooling systems

Metal hydrides release heat during absorption and absorb heat during desorption. Therefore, by constructing a closed thermodynamic device with two different suitable metal hydrides and hydrogen as transfer fluid, cooling or heating or heat up gradation can be achieved. The metal

hydrides for these applications require the following properties (Sastri et al., 1998; Muthukumar et al., 2003)

- High enthalpy of formation (particularly for refrigeration hydride)
- Moderate pressures and less pressure change with temperature
- High hydrogen capacity
- Low cost
- Low density and specific weight

Depending on the temperatures at which heat is supplied to or rejected from the system, the heat conversion systems can be classified as heat transformers, heat pumps and refrigerators.

Figure 1.6 shows the basic working principle of solid-gas chemisorption refrigerators, heat pumps and heat transformers. In refrigerators, the required output is cooling at low temperature T_L (system extracts heat at low temperature), while input heat is supplied by a high temperature T_H and the system rejects heat to the ambient. Heat pumps are similar to refrigerators, but the requirement is heating at the intermediate temperature T_M , while heat input to the system is at high temperature T_H and also from the ambient. Refrigerators and heat pumps are energy downgrading systems, as they provide cooling and/or heating by using the high temperature heat. Heat Transformers, on the other hand, are energy upgrading systems as these systems deliver useful heat at high temperature by using the heat available at the intermediate temperature (also called as temperature amplifiers). Thus heat transformers are reverse heat pumps, as in these systems, heat is supplied at the intermediate temperature, while the system rejects heat at high and low temperatures.

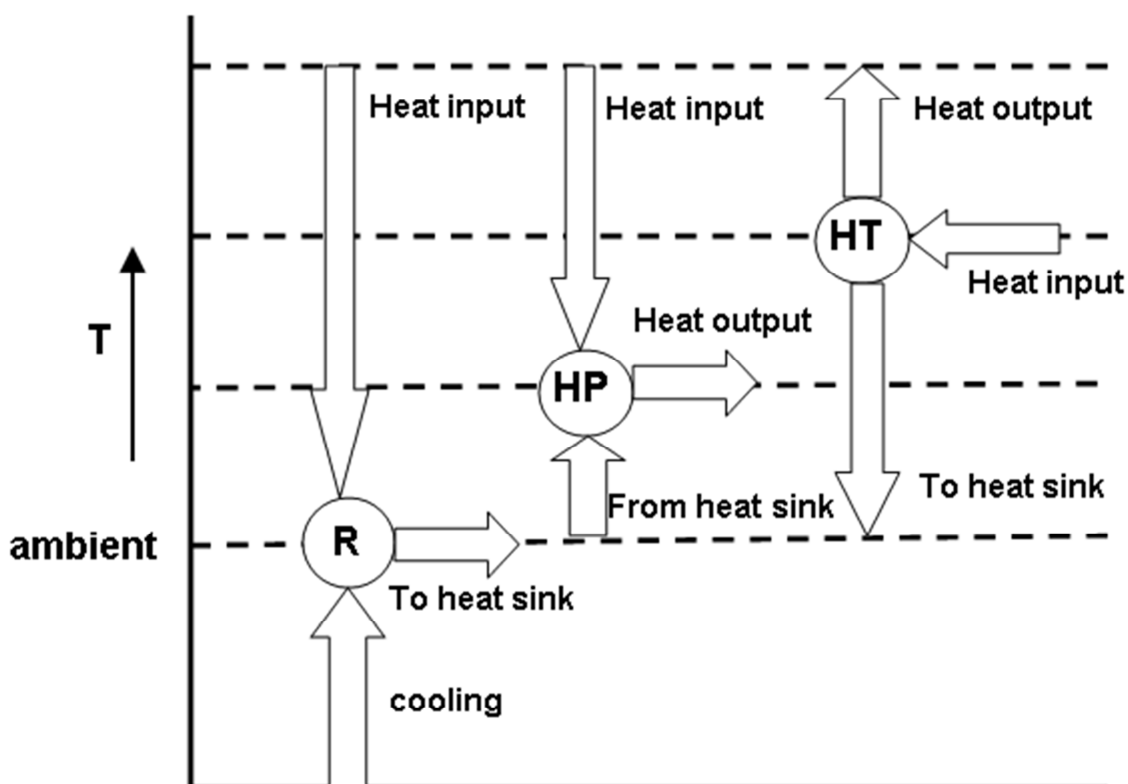


Fig. 1.6 Comparison of refrigerators (R), heat pumps (HP) and heat transformers (HT)

Since hydrogen absorption and desorption by metal hydrides are followed by heat generation and heat absorption, respectively, metal hydrides can be used for heating and cooling by allowing them to absorb or desorb hydrogen at required temperatures and pressures. This is the principle behind the metal hydride heating and cooling systems. Metal hydride heating and cooling systems normally consist of a pair of reactors filled with hydriding alloys of different chemical stabilities. These two reactors are connected in such a way that hydrogen gas can freely flow between them when there is sufficient driving force in the form of pressure difference between the reactors. Owing to the difference in the chemical stabilities, under certain temperatures, the equilibrium pressure of one hydride reactor would be higher than that of the other reactor. As a result, when connected to each other, the reactor with the higher equilibrium pressure would

release hydrogen gas. Since desorption requires enthalpy of formation, heat has to be supplied to the desorbing reactor externally. The reactor with the lower equilibrium would absorb the hydrogen gas released by the desorbing bed. Since heat is released during absorption due to the formation of hydride, it has to be rejected to an external sink, so that the absorption can proceed. Depending on the temperatures at which the heat transfer between hydride beds and the surroundings takes place, metal hydride systems can be used as refrigerators, air conditioners, heat pumps or heat transformers.

Metal hydride based heat pumps and refrigerating systems

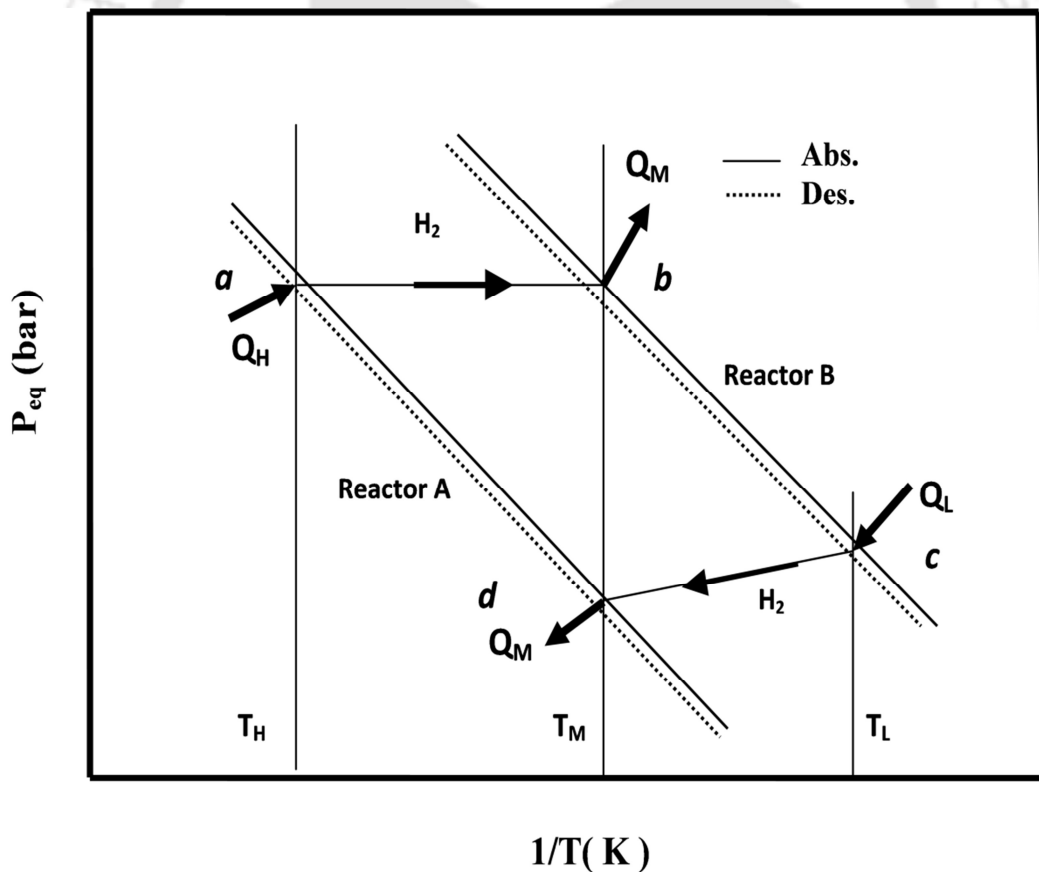


Fig. 1.7 van't Hoff plot for a single stage metal hydride heat pump.

Figure 1.7 shows the operating cycle of metal hydride heat pump (MHHP) on van't Hoff plot. It consists of two reactors containing a high temperature and a low temperature hydride, A and B respectively. It consists of four processes, which are explained below.

Process ab

Initially, the reactor A is fully hydrided (X_{max}) and B is fully dehydrided (X_{min}) at their respective operating temperatures of T_H and T_M . Two reactors are coupled by a connecting tube with a valve. Since the operating valve is initially closed, the equilibrium pressure difference exists between the reactors. Once the valve is opened, due to the difference in pressure, hydrogen gas starts to desorb from the reactor A by taking the heat from the reaction bed and the heat transfer fluid, and reactor B starts to absorb hydrogen gas by rejecting the heat of absorption to the reaction bed and the heat transfer fluid. This process continues till the fixed amount of hydrogen transfers from the reactor A to the reactor B.

Process bc

During this process, the valve between the reactors A and B is closed and no hydrogen transfer between the reactors takes place. Only the heat transfer takes place between the hydride bed and the cooling/heating fluids. This process is continued till the reactors A and B reach temperature T_M and T_L , respectively.

Process cd

Once the reactors A and B reach their respective operating temperatures (medium and low temperatures), the valve between the reactors is opened. Due to the existence of pressure difference, the hydrogen starts to desorb from the reactor B at temperature T_L by extracting the

heat of desorption from the reaction bed and heat transfer fluid, yielding refrigeration effect. Simultaneously, the hydride A absorbs this hydrogen by rejecting the heat of absorption to the reaction bed and cooling fluid at the medium temperature, T_M . This process continues till the fixed amount of hydrogen is transferred (same as during the process *ab*).

Process *da*

During this process the valve is closed. Reactors A and B are sensibly heated to T_H and T_M , respectively. Thus the first cycle operation is completed.

Depending upon the temperatures T_M and T_L , a hydride heat pump system can be used for cooling at low temperature T_L , and/or heating at the intermediate temperature T_M . By convention, the system is called as refrigerator/air conditioner if it is used for cooling and it is called as a heat pump if it is used for heating. The system is known as a dual effect system if it is used for both cooling as well as heating.

Metal hydride based heat transformer

Figure 1.8 shows the operating cycle of metal hydride heat transformer, which consists of the following four processes.

Process *ab*

Initially, the reactor A is fully hydrided and B is fully dehydrided at their respective operating temperatures of T_M and T_H . The operating cycle shows that the two reactors are connected with each other with a connecting valve. Since the connecting valve is initially closed, the equilibrium pressure difference exists between the reactors. Once the valve is opened, due to the difference in

pressure, hydrogen gas starts to desorb from the reactor A by taking heat from the reaction bed and the heat transfer fluid, and reactor B starts to absorb hydrogen gas by rejecting the heat of absorption to the reaction bed and the heat transfer fluid. This process continues till the fixed amount of hydrogen gas transfers from A to B.

Process *bc*

During this process, the valve between A and B is closed and no hydrogen transfer between the reactors takes place. Only the heat transfer takes place between the hydride bed and the cooling/heating fluids. This process is continued till the reactors A and B reach T_L and T_M , respectively.

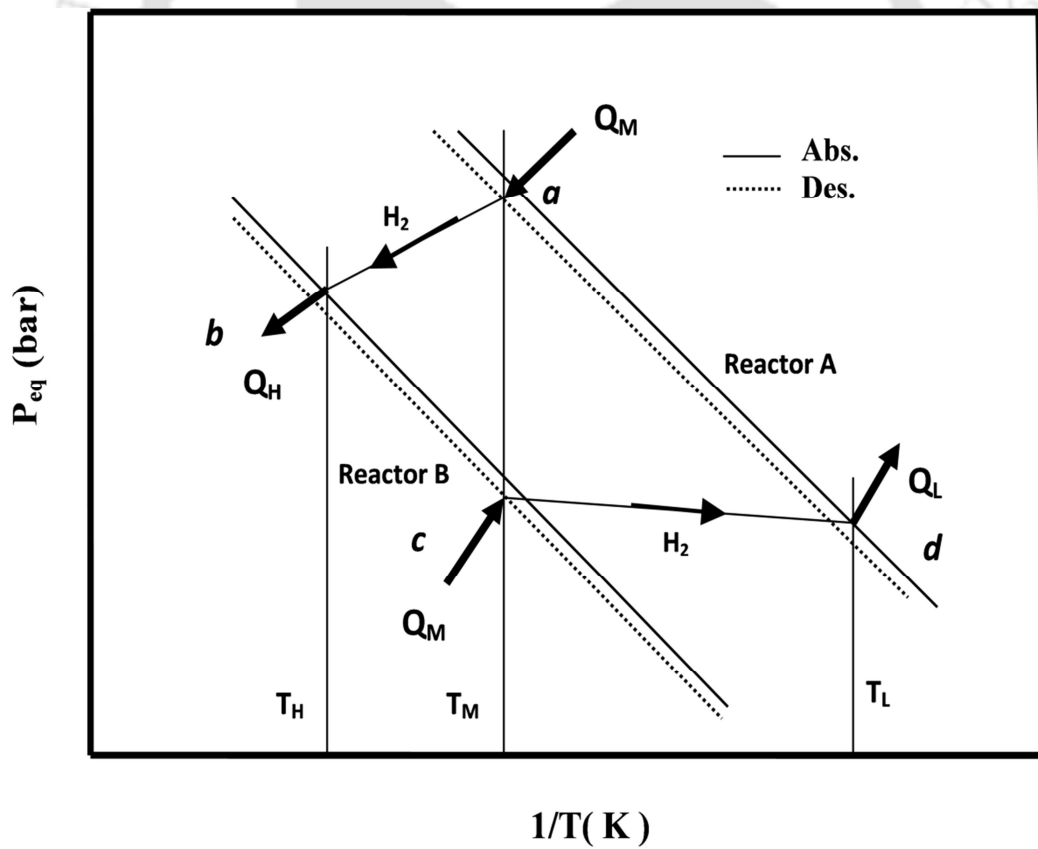


Fig. 1.8 van't Hoff plot for a single stage metal hydride heat transformer

Process cd

Once the reactors A and B reach the low and intermediate temperatures, the valve between the reactors is opened. Due to the existence of pressure difference, the hydrogen starts to desorb from the reactor B at medium temperature T_M by extracting the heat of desorption from the reaction bed and heat transfer fluid. Simultaneously, the hydride A absorbs this hydrogen rejecting the heat of absorption to the reaction bed and cooling fluid at the low temperature, T_L . This process continues till the fixed amount of hydrogen is transferred (same as during process ab).

Process da

During this process the connecting valve is closed. Reactors A and B are sensibly heated to the intermediate temperature T_M and high temperature T_H , respectively, so that at the end of this process the reactors A and B reach the initial conditions of the cycle.

In heat transformers, the heat input is at an intermediate temperature T_M , while heat is rejected both at the high and low temperatures T_H and T_L respectively. The heat rejected at T_H is the useful output of the system. Thus the quality of the heat is upgraded in heat transformer systems to higher levels.

1.5 Motivation of the Present Work

Secure, reliable and affordable energy supplies are very essential for the economic stability and development of any nation. Coal fired thermal power plants and transport sectors have produced nearly two-thirds of global CO₂ emissions in 2010: electricity and heat generation accounted for

41 % while transport accounted for 22 % (Fig. 1.9 (a)). Between 2009 and 2010, total CO₂ emissions from the generation of electricity and heat increased by 5.6 % (Fig. 1.9 (b)). The CO₂ emissions are projected to rise by 55 % from 27 Gt in 2005 to 42 Gt in 2030 (IEA 2012). Hence, this issue urgently needs to be addressed, using a portfolio of existing and emerging technologies particularly in relation to the production and consumption of heat and electricity.

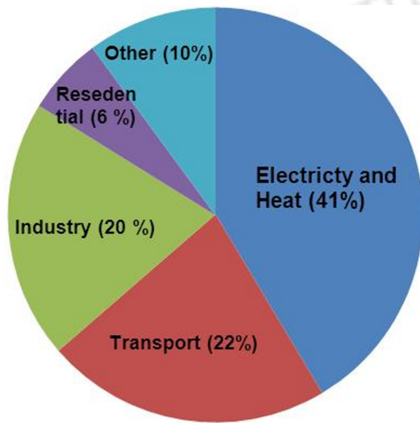


Fig. 1.9 (a) World CO₂ emissions by sector in 2010 (IEA 2012)

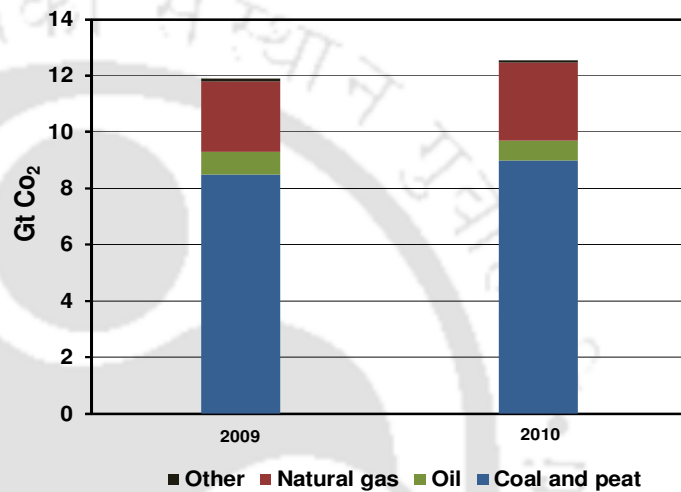


Fig. 1.9 (b) CO₂ emissions from electricity and heat generation in 2009 and 2010 (IEA 2012)

The losses in the global power system shown in Fig. 1.1 demonstrate that 63 % of total energy input is lost in the form of waste heat. On the other hand, there is a lot of low-grade heat from the renewable energy (e.g. solar energy, geothermal energy, etc.) left unused due to their relatively low-grade. If the low-grade heat can be upgraded to higher temperatures, it can be used as heat source for many industrial applications. The utilization of low-grade heat would contribute not only to lower energy consumption, but also reduces the global CO₂ emission and thus creates better environment. Therefore, the research and development on the waste heat utilization is of great interest to the present scientific community. Hence, an attempt is being made in this

direction to develop an energy conversion system, which can upgrade industrial waste heat, solar energy, geothermal energy, etc., to higher temperature levels for enabling them to use as an input for several thermally operated machines.

Metal hydrides have many technical applications as discussed in section 1.4. Metal hydride based heat transformer (MHHT) comes into the category of dry sorption systems and it can upgrade heat from medium temperature (100 - 150 °C) to high temperature (170 - 200 °C). It also provides higher heat storage capacity and wide range of working temperatures as compared to other conventional heat pumps / heat transformers. In addition, MHHTs use hydrogen as working fluid which is environment friendly and offer noise free and vibration less operation. Hence, in this thesis, the main focus is given to the development of metal hydride based heat transformer for upgrading the heat input from 120 - 140 °C to 160 - 200 °C.

1.6 Structure of the Thesis

As discussed earlier, the performance of metal hydride based hydrogen compressor and heat transformer depends on the proper selection of alloys and the heat and mass transfer aspects of the reaction bed. The objective of the present thesis is to study the performance of single-stage and double-stage metal hydride heat transformers based on the coupled heat and hydrogen transfer between the reaction beds and heat transfer fluid. To begin with, in this chapter an introduction on metal hydrides and their engineering applications are discussed.

In Chapter 2 a state-of-art on various aspects of metal hydride technology is presented. The literature published on the reaction kinetics of some selected categories of metal hydride alloys, coupled heat and hydrogen transfer studies during absorption and desorption of hydrogen to

/from the metal hydride beds and the literature published on some specific engineering applications, such as, hydrogen storage system, metal hydride based heat pump, heat transformer, and hydrogen compressor are also reviewed.

Chapter 3 describes the thermal modeling and performance investigation of single-stage and double-stage metal hydride based heat transformers.

Chapter 4 describes, the reactor configuration, the experimental setup, and the procedure followed for testing the double-stage hydrogen compressor, single-stage and double-stage metal hydride based heat transformers.

In Chapter 5, the results obtained from both theoretical and experimental studies are discussed.

Chapter 6 concludes the major outcomes from both theoretical and experimental studies on single and double – stage metal hydride based heat transformers.

Chapter 2

STATE OF THE ART

Use of hydrogen as a fuel in day to day applications is limited due to the problems associated with storage and transport. Recently, metal hydride based hydrogen storage systems have drawn attention over the conventional methods due to their high volumetric storage capacity, utilization of low-grade thermal inputs, compact in construction, absence of moving parts and high safety. Further, it also delivers pure hydrogen irrespective of the input quality of hydrogen. In addition to hydrogen storage, metal hydride systems also provide a variety of engineering applications such as heat pump, heat transformer, thermal energy storage, hydrogen compression, water pumping, etc. Therefore, several experimental and numerical works exist on different aspects of the metal hydrides.

In this chapter a detailed literature survey on reaction kinetics on some metal hydride alloys based on La, Mm, Ti and Zr and some of selected metal hydride applications such as hydrogen storage, hydrogen compressor, heat pump and heat transformer are presented.

2.1 Reaction Kinetics

Reaction kinetic studies, which involve basically the determination of absorption and desorption reaction rate constants and activation energy, are important for identifying the most favourable hydride alloy combination for a given application. A wide range of papers related to reaction kinetics have been reported in literature. Some of the important papers are discussed in this section.

Miyamoto *et al.* (1983) developed an experimental setup for studying the reaction kinetics of hydrogen absorption in a LaNi_5 under constant hydrogen pressure. The reaction rate was measured in the temperature range of 15 - 80 °C. Activation energy of 32.24 kJ/mol of H_2 was observed from the Arrhenius plot which showed good agreement with the data obtained from energy formation.

Goudy *et al.* (1984) performed the reaction kinetics studies on LaNi_5 , $\text{LaNi}_{4.7}\text{Al}_{0.3}$, $(\text{CFM})\text{Ni}_5$ (CFM = cerium-free misch metal) and $\text{MmNi}_{4.5}\text{Al}_{0.3}$ during desorption of hydrogen. Desorption of hydrogen from LaNi_5 hydride was observed to be first order kinetics at low temperature range of 25 - 45 °C with the activation energy in the range of 35 to 40 kJ/mol of H_2 . In the high temperature range of 70 - 90 °C, a second order kinetic was observed.

Huang *et al.* (1989) studied the effects of aluminium and iron substitution on the reaction kinetics of MmNi_5 (Mm = misch metal). Experiments were conducted in the temperature range of 0 - 50 °C. It was concluded that aluminium and iron substitution have a deleterious effect on the reaction kinetics of Mm nickel alloys.

Wang and Suda (1990) characterized the dehydriding kinetics of $\text{LaNi}_{4.7}\text{Al}_{0.3}$ using a stepwise method under both constant and variable pressure conditions. They developed the rate equation by considering both hydrogen pressure and concentration. They showed that the rate constants were independent of pressure and concentration in the $(\alpha+\beta)$ -phase region.

Bronfman *et al.* (1991) studied the hydriding kinetics of $\text{Zr}(\text{Al}_{0.2}\text{Fe}_{0.8})_2$ at four different temperatures between 238 - 298 K and an approximately constant pressure of 10 atm. Activation energy of about 27 kJ/mol of H_2 was estimated for the hydrogenation process.

Kesavan *et al.* (1996) studied the absorption kinetics of $\text{Zr}_{0.4}\text{Ho}_{0.8}\text{Fe}_{0.2}$ in the temperature and pressure ranges of 28 - 150 °C and up to 70 bar, respectively. The maximum hydrogen concentration of 8.1 hydrogen atoms per formula unit was attained at the equilibrium pressure of 67 bar at room temperature. The reported average activation energy in the two phase region was 24 kJ/ mol- H_2 .

Mungole *et al.* (1998) investigated the hydrogen desorption kinetics of $\text{MmNi}_{4.2}\text{Al}_{0.8}$ at three temperatures of 15, 25 and 35 °C. The reaction rate was based on the first order equation. The estimated the activation energy for hydrogen desorption reaction was 48.09 kJ/mol of H_2 .

Anilkumar *et al.* (2009) studied the absorption kinetics of MmNi_5 , $\text{MmNi}_{4.7}\text{Al}_{0.3}$, $\text{MmNi}_{4.5}\text{Al}_{0.5}$, $\text{MmNi}_{4.2}\text{Al}_{0.8}$ and MmNi_4Al in the temperature range of 20 - 80 °C by maintaining the ratio of operating pressure to the equilibrium pressure as constant at 2. It was found that an addition of Al decreases the absorption kinetics and increases the activation energy.

Muthukumar *et al.* (2009a) estimated the reaction enthalpies and entropies of LaNi_5 , $\text{LaNi}_{4.7}\text{Al}_{0.3}$ and $\text{LaNi}_{4.91}\text{Sn}_{0.15}$ during absorption and desorption processes and also expressed the reaction enthalpies as a function of hydrogen storage capacity by a polynomial equation of order three. Later, Muthukumar *et al.* (2009b) investigated the reaction kinetics of the above mentioned alloys by employing two popular reaction kinetics models at nearly isothermal condition. The experimentally obtained reaction kinetics data have been further analysed and reported the most reliable values of the activation energy of these hydrides. Subsequently, Muthukumar and his research team presented the Pressure–Concentration–Temperature (PCT) characteristics of three Ti based, five Mm based and eight La based metal hydride alloys at different operating temperatures (2013). The average enthalpy of formation during dehydriding process of the investigated titanium and lanthanum based alloys were about 3 -18 % higher than their respective hydriding enthalpies. The variation in reaction enthalpies during the initial and final stages of hydriding process of titanium based alloys was in the range of 7 - 9 %, while the respective ranges for misch metal and lanthanum based alloys were about 3 - 7.5 % and 2.1 - 8.5 %, respectively.

2.2 Heat and Mass Transfer Studies in Metal Hydride Devices

When the hydriding alloys are exposed to hydrogen at a certain pressure and temperature, they absorb hydrogen by releasing heat conversely, when they are heated to certain temperature, they release the same amount of hydrogen. Based on the reversible exothermic and endothermic reactions, several energy conversion devices have been built and tested. Some of the important metal hydride based devices are:

- Hydrogen storage
- Hydrogen compression
- Refrigeration and heat pumping
- Heat transformation, etc.

The absorption and desorption of hydrogen in metal hydrides are exothermic/endothermic processes, i.e. associated with release of heat from the reaction bed or uptake of heat into the reaction bed. The performance of any metal hydride based thermal device is essentially determined by these heat and mass transfer processes. Some key issues related to the metal hydride bed heat and mass transfer aspects reported are hydrogen storage, heat pump, heat transformer and hydrogen compressor are addressed in the following sections.

2.2.1. Hydrogen storage (absorption and desorption)

The performance (rates of hydrogen absorption and desorption) of hydrogen storage system depends on the heat and mass transfer characteristics of the hydride bed. Modeling of hydriding and dehydrating processes in metal hydride system is quite complicated since it involves coupled heat and mass transfer with chemical reaction. Many investigators attempted to study such coupled heat and mass transfer phenomena encountered in the hydride bed, particularly focused on the improvement of absorption and desorption rates. In this sub-section, important literature published on coupled heat and mass transfer aspects during the absorption and desorption of hydrogen to/from metal hydrides are presented.

Few decades ago, several investigators attempted to study the coupled heat and mass transfer phenomena encountered in the hydride bed using one-dimensional mathematical model (Lucas and Richards, 1984; Sun and Deng, 1988; Gopal *et al.*, 1992; 1993). Lucas and Richards (1984) developed a one-dimensional mathematical model for predicting the performance of hydrogen storage in a metal hydride reaction bed. Sun and Deng (1988) presented a one-dimensional model for calculating the temperature and hydrogen concentration profiles in planar, cylindrical (annular) and spherical hydride beds. Gopal *et al.* (1992) presented a one-dimensional mathematical model for predicting the heat and mass transfer characteristics of metal hydride beds of annular cylindrical configuration. They concluded that the best way to improve the heat transfer characteristics of metal hydride systems was by keeping the bed thickness as small as possible and improving the thermal conductivity of the bed and subsequently they extended their work to the metal hydride beds of rectangular configuration (1993).

Because of the importance of heat transfer rate which is identified as a main limiting factor for controlling the hydrogen charging/discharging in a metal hydride reactor, there have been many numerical works published on the design of innovative compact reactor-heat exchangers to address the heat transfer limitations in metal hydride based hydrogen storage. In general, there are two active heat transfer improvements techniques namely, internal heat transfer improvement and external heat transfer improvement techniques. MacDonald and Rowe (2006) numerically studied the effects of addition of fins on metal hydride storage tank for improving the external heat transfer rates. It was noted that the mere increase of external heat convection coefficient beyond a certain value will no longer affect much the charging/discharging time of metal hydride systems. Mohan *et al.* (2007) carried out a simulation of a metal hydride hydrogen storage

device with embedded filters and cooling tubes employing LaNi_5 . They also studied the effects of geometric and operating parameters on the hydriding performance of the storage reactor. Due to the low thermal conductivity of metal hydride powder, the bed thickness was an important geometric parameter which affects the heat transfer rate. Therefore, internal heat transfer enhancements have become more attractive.

At IIT Guwahati, Muthukumar's research group have developed several thermal models for predicting the performances of the metal hydride hydrogen storage devices during absorption (2007; 2009c) and during desorption (2009d). Muthukumar *et al.* (2007; 2009c; 2009d) presented a two-dimensional computational investigation of coupled heat and mass transfer process in annular cylindrical hydrogen storage device filled with $\text{MmNi}_{4.6}\text{Al}_{0.4}$ during absorption of hydrogen. Hydrogen storage performance of the device was studied by varying the operating parameters such as hydrogen supply pressure, absorption and desorption temperature. Further, the effects of various bed parameters such as hydride bed thickness and overall heat transfer coefficient on the storage performance of the device were also studied. Later, the same research group presented the changes in hydrogen concentration, hydride equilibrium pressure, and average hydride bed temperature at different axial locations by considering the variation in cooling fluid temperature along the axial direction (Muthukumar and Ramana, 2009e; 2010). Recently, Muthukumar *et al.* (2012a) presented the performance analysis of a metal hydride based hydrogen storage container with embedded cooling tubes during absorption of hydrogen. A 2-D mathematical model in cylindrical coordinates was developed using the commercial software COMSOL Multiphysics 4.2. Numerical results obtained were found in good agreement with experimental data available in the literature. Different container geometries, depending

upon the number and arrangement of cooling tubes inside the hydride bed, were considered to obtain an optimum geometry. The effects of various operating parameters viz. supply pressure, cooling fluid temperature and overall heat transfer coefficient on the hydriding characteristics of $\text{MmNi}_{4.6}\text{Al}_{0.4}$ are presented for the optimized geometry of the reactor. Industrial-scale hydrogen storage container with the capacity of about 150 kg of alloy mass was also modeled.

Few researchers studied the thermal conductivity enhancement by insertion of metal matrices of high thermal conductivity, such as copper or aluminum foam (Laurencelle and Goyette, 2007; Mellouli *et al.*, 2009; Tsai and Yang, 2010). Laurencelle and Goyette (2007) developed a model to evaluate the various designs of metal hydride reactors with planar, cylindrical and spherical geometries. The model simulates a cycling loop (absorption–desorption) focusing the attention on the heat transfer inside the hydride bed, which was considered the rate limiting factor. They have shown that a storage tank without heat exchanger must be small (less than 8 mm of diameter) to allow a fast reaction (< 15 min). It was concluded that if the storage tank contains aluminium foam, this limit can be extended to a diameter of 6 cm. Mellouli *et al.* (2009) presented a two-dimensional mathematical model to evaluate the transient heat and mass transfer in a metal hydride tank (MHT) with metal foam heat exchanger. After that, the model was used as a tool for predicting the performance of the hydrogen-charging process of two configurations of MHTs with metal foam heat exchangers. Their results showed that the reduction of the storage time due to the metal foam heat exchanger can be more important when the MHT was equipped with a concentric heat exchanger tube. Tsai and Yang (2010) developed a model that accounts for the mass and energy balance and the hydrogen absorption kinetics in a cylindrical MHT. They have examined how the charging time and hydrogen-to-metal weight percentage (wt %) of

an MHT were affected by the volume fraction of a metal foam installed in the MHT to enhance heat conduction.

Few investigators studied the integration of heat exchanger inside the bed, such as finned tube heat exchanger (Askri *et al.*, 2009a) and finned spiral heat exchanger (Mellouli *et al.*, 2010). Askri *et al.* (2009a) presented a 2-D theoretical model describing the hydrogen storage in MHTs. The model was used to evaluate the impact of the tank wall thermal mass on the absorption process. Steel and brass walls were tested and the obtained results have shown that i) the tank wall thermal mass can be neglected and heat transfer between hydride powder and cooling fluid can be described by a thermal conductance, ii) the use of MHTs with a large wall conductivity has no significant effect on hydrogen storage time. In addition, the established model was used to study the dynamic behavior inside various designs of MHTs and optimization results indicated that almost 80 % improvement of the storage time can be achieved when the design includes a concentric heat exchanger tube equipped with fins. Mellouli *et al.* (2010) presented a two-dimensional mathematical model to optimize the heat and mass transfer processes in a metal hydride storage tanks for fuel cell vehicles equipped with finned spiral tube heat exchangers. The effect of geometric parameters, such as, fin thickness, length, pitch and the arrangement of fins on the charging process was studied. They showed that the use of circular fins enhanced the heat transfer by about 66 % compared with the case without fins. The predicted numerical results of hydride pressure were compared with the experimental data reported by them and a reasonably good agreement was observed between the two.

The optimization of hydrogen storage in metal hydride beds have been investigated by few researchers (Kikkinides *et al.*, 2006; Melnichuk *et al.*, 2009; Visaria *et al.*, 2011; Raju and Kumar, 2012). Kikkinides *et al.* (2006) presented a systematic approach for modeling, optimization and control of metal hydride beds used for hydrogen storage. A detailed 2-D mathematical model was developed and validated against the experimental and theoretical literature results. Optimization results indicate that almost 60 % improvement of the storage time can be achieved, over the case where the system was not optimized, for a minimum storage capacity of 99 % of the total bed capacity. In order to fulfill the performance criteria, optimization will always be required at some stage in a design of hydrogen storage systems. Melnichuk *et al.* (2009) optimized the aluminum fraction of heat transfer fins for a LaNi_5 hydrogen storage container, at different absorption times and container diameters. The absorption capacity of a container of 120 mm was evaluated numerically and experimentally at different situations. A very good agreement between the simulations and the experimental results was observed.

Visaria *et al.* (2011) presented a methodology for the design of a plate type heat exchanger for hydrogen storage using high-pressure metal hydrides (HPMHs). The primary function of the heat exchanger was to remove the large amounts of heat released from the hydriding reaction as the system was being filled with hydrogen at the station. The heat exchanger design must adhere to several design criteria including removing the heat in less than 5 min, compact and lightweight design, and cost and ease of manufacturability. Raju and Kumar (2012) presented a systematic study to optimize the heat exchanger design using computational fluid dynamics (CFD) modeling. Three different shell and tube heat exchanger designs were chosen. In the first design,

metal hydride is present in the shell and heat transfer fluid flows through straight parallel cooling tubes placed inside the bed. The cooling tubes were interconnected by conducting fins. In the second design, heat transfer fluid flows through helical tubes in the bed. The helical tube design permits use of a specific maximum distance between the metal hydride and the coolant for removing heat during refueling. In the third design, the metal hydride was present in the tubes and the fluid flows through the shell. They found out that heat exchanger design II consisting of a helical coil heat exchanger gives better gravimetric and volumetric densities as compared to the other two shell and tube designs.

Few authors studied the heat and mass transfer aspects of a hydride bed using three-dimensional mathematical model (Askri *et al.*, 2009b; Nam *et al.*, 2012). Askri *et al.* (2009b) presented a transient, three-dimensional computational investigation of coupled heat and mass transfer in an annular cylindrical hydrogen storage tank, equipped with fins and filled with $\text{MmNi}_{4.6}\text{Fe}_{0.4}$. The effects of different parameters such as length, thickness and thermal conductivity of fins and overall heat transfer coefficient on the hydrogen storage performance of the tank are studied. Nam *et al.* (2012) developed a 3-D hydrogen absorption model to study precisely the hydrogen absorption reaction and the resultant heat and mass transport phenomena in metal hydride hydrogen storage vessels. The detailed 3-D simulation results showed that at the initial absorption stage, the vessel temperature and H/M ratio distributions were uniform throughout the entire vessel, indicating that hydrogen absorption was very efficient early during the hydriding process. In addition, a parametric study was carried out for various designs and hydrogen supply pressures. This numerical study further revealed that for the efficient design of the storage vessel and external surface to volume ratio of a metal hydride vessel and cooling system was critical.

They demonstrated the importance of considering the effect of plateau slope in the equilibrium pressure curves in hydrogen absorption simulations. They also presented detailed multidimensional contours for key parameters, such as the temperature, H/M atomic ratio, and hydrogen velocity.

2.2.2 Heat pump

The use of Chloro-Fluro-Carbon refrigerants is a significant source of pollution to the global environment and it is attempted to minimize this problem through the promotion of the alternative refrigeration and air-conditioning systems. One of the most promising alternatives is the use of hydrogen as refrigerant in the thermally driven metal hydride based cooling systems. Few researchers investigated the performances of the heat pump using numerical simulation of heat and mass transfer characteristics of the paired reactors. In the following sub-sections, a detailed literature review on single-stage and also more complex systems, such as multi-stage, thermal wave concept and compression driven systems are discussed.

Thermodynamic studies on single-stage metal hydride based heat pump (SS-MHHP)

Few researchers have presented the thermodynamic analysis of MHHPs (Dantzer and Orgaz, 1986; Altinisik and Veziroglu, 1991; Murthy and Sastri, 1992; Kim and Feldman, 1997a). Dantzer and Orgaz (1986) presented a model of the hydride chemical heat pump based on the classical thermodynamic analysis. The first step of the model was to describe a reference system which can be compared with other chemically driven heat pumps. The next step in the model was introducing the chemical constraints; these constraints were correlated to different process

encountered at the different steps of the cycle. The model was developed for two operating modes: isotherms and isobars, and was tested with $\text{LaNi}_{4.77}\text{Al}_{0.22}/\text{LaNi}_5$ system.

Altinisik and Veziroglu (1991) discussed the thermodynamics of hydrides and their application to heat pumps. They compared the performances of the MHHP with conventional heat pumps. Some of the possible and more promising applications of MHHPs in industrial and residential fields were discussed. Murthy and Sastri (1992) presented the thermodynamic analysis of MHHP using three alloys. The comparative performance of different alloys was presented. Kim and Feldman (1997a) presented the thermodynamic analysis of a heat driven hydride slurry heat pump by using different combinations of six refrigeration and three regeneration alloys. They showed that $\text{Zr}_{0.8}\text{Ti}_{0.2}\text{Cr}_{0.6}\text{Fe}_{1.4}$ and $\text{Zr}_{0.8}\text{Ti}_{0.2}\text{MnFe}$ hydride pair provides the highest coefficient of performance of about 1.59 with the desorption temperature nearly 0 °C.

Performance studies on SS-MHHP systems

Many authors have investigated the performance of the SS-MHHPs using one-dimensional mathematical model without considering the effect of hysteresis and plateau slope (Nishizki *et al.*, 1983; Gopal and Murthy, 1995a; 1995b; Kang and Kuznetsov, 1995; Fedorov *et al.*, 1999; Fateev *et al.*, 2000; Jang *et al.*, 2001). Nishizki *et al.* (1983) presented a model for calculating the COPs of MHHP with four reactors. The dependence of COP on various design parameters was discussed. From the numerical calculations they came to the conclusion that low reactor heat capacities and high efficient heat transfer are essential to achieve high COP.

Gopal and Murthy (1995a, 1995b) discussed a SS-MHHP system working with $\text{ZrMnFe/MmNi}_{4.5}\text{Al}_{0.5}$. For a fixed amount of the hydrogen transfer, the specific alloy output improves as the heat transfer for effectiveness increases and pressure drop between the reactors decreases. For a given refrigeration and heat rejection temperatures, the performance of the MHHP increases with heat source temperature. They have also studied the performance characteristics of the system by varying the bed thicknesses, thermal conductivity and overall heat transfer coefficient. The bed thickness and effective thermal conductivity were found to influence the cycle time and the specific alloy output significantly. For the bed thickness of 3 mm, an optimum effective thermal conductivity was reported as 4 W/m-K. The refrigeration temperature has considerable effect on the cycle time and specific alloy output. They also predicted the performance of the MHHP working with the same hydride pair (Gopal and Murthy, 1995b). Of the three operating temperatures, heat source and refrigeration temperatures were found to have the greatest influence on the performance of MHHP. The analysis was carried out for 1 kg of hydride in each reaction bed. The average COP was found to lie between 0.45 and 0.5.

Kang and Kuznetsov (1995) numerically predicted the performance of the metal hydride chiller by solving the transient transport processes of heat and hydrogen transfer between $\text{LaNi}_{4.5}\text{Al}_{0.5}$ and LaNi_5 reaction beds. They solved the system of five first-order ordinary differential equations using the Runge-Kutta method. The effects of heat source, cooling water and chiller water temperatures on the system performance were studied. The reported optimum operating cycle time for the regeneration and refrigeration processes were 500 s and 700 s, respectively for the operating temperatures of 423 /303 /282 K. Each reactor was filled with of 1.13 kg hydride

mass. For the above-mentioned operating temperatures, the reported COP and SCP of the system were 0.7 and 40 W/kg of desorbing hydride, respectively. Fedorov *et al.* (1999) presented the mathematical model of a MHHP using $\text{LaNi}_{4.5}\text{Al}_{0.25}\text{H}_x$ / $\text{TiFe}_{0.8}\text{Mn}_{0.2}\text{H}_y$ hydride pair. They carried out simulations without considering the effect of hysteresis and plateau slope on PCT isotherm. They predicted the time dependent hydride bed temperatures and equilibrium pressures over a complete cycle. They reported the minimum refrigeration temperature was -5°C .

Fateev *et al.* (2000) studied both numerically and experimentally the optimization of the operation processes of MHHP. The numerical study was carried out by using AB_2 alloys namely $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{1-y}\text{Fe}_{1+y}$ with y varying from 0 to 0.4. On the other hand, the experiment was conducted using only $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.6}\text{Fe}_{1.4}$. It was noticed that the heat transfer limitation played a major role in the cooling power of the system. The numerical results generated were compared with the experimental values which showed a good corresponding between the two. Jang *et al.* (2001) developed an unsteady, one-dimensional mathematical model of MHHP working with $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.9}\text{Fe}_{1.1}$ / $\text{Zr}_{0.9}\text{Ti}_{0.15}\text{Cr}_{0.6}\text{Fe}_{1.45}$ hydride pair. Their model was designed to operate at the heat source, heat sink and refrigeration temperatures of 200, 30 and 10°C , respectively. Duration of one cycle time was 12 min and the thermal conductivity of the hydride bed was taken as 1 W/m-K. They compared the predicted numerical results of hydriding kinetics over a cycle time with their own experimental data and obtained reasonably a good agreement between the two.

Recently, few investigators have studied the transient heat transfer and hydrogen exchange between the coupled reactors of MHHP using two-dimensional model by considering the effect of hysteresis and plateau slope (Satheesh *et al.*, 2009; 2010a; Mellouli *et al.*, 2009; Yang *et al.*,

2010; Paya *et al.*, 2011). Satheesh *et al.* (2009) carried out a computational study of MHHP working with $\text{MmNi}_{4.6}\text{Al}_{0.4}$ / $\text{MmNi}_{4.6}\text{Fe}_{0.4}$ hydride pair. The unsteady, two-dimensional mathematical model in an annular cylindrical configuration was solved numerically for predicting the time dependent conjugate heat and mass transfer characteristics between coupled reactors. It was reported that cycle time for the constant and variable wall temperature boundary conditions of a SS-MHHP were found to be 1470.0 s and 1765.6 s, respectively. Subsequently, the same research group have discussed the performance of a SS-MHHP working with five different alloy pairs, namely, $\text{MmNi}_{4.6}\text{Al}_{0.4}$ / $\text{MmNi}_{4.6}\text{Fe}_{0.4}$, $\text{LaNi}_{4.61}\text{Mn}_{0.26}\text{Al}_{0.13}$ / $\text{La}_{0.6}\text{Y}_{0.4}\text{Ni}_{4.8}\text{Mn}_{0.2}$, $\text{LaNi}_{4.91}\text{Sn}_{0.15}$ / $\text{Ti}_{0.99}\text{Zr}_{0.01}\text{V}_{0.43}\text{Fe}_{0.09}\text{Cr}_{0.05}\text{Mn}_{1.5}$, $\text{LaNi}_{4.6}\text{Al}_{0.4}$ / $\text{MmNi}_{4.15}\text{Fe}_{0.85}$ and $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.9}\text{Fe}_{1.1}$ / $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.6}\text{Fe}_{1.4}$ (2010a). The influences of operating temperatures such as heat source (T_H), heat sink (T_M) and refrigeration (T_C) temperatures on the coefficient of performance (COP) and specific cooling power (SCP) of the system were presented.

Mellouli *et al.* (2009) investigated the performance of MHHP employing $\text{MmNi}_{4.5}\text{Al}_{0.5}$ / $\text{MmNi}_{4.2}\text{Al}_{0.1}\text{Fe}_{0.7}$ hydride pair using a thermal model by solving a set of equations. Their model was focused on determining the optimum operating temperature range for the above selected hydride pair. Depending on the operating temperature ranges of 67 - 52 / 20 - 0 / -8 - -23°C (heat source/ heat sink/ refrigeration temperature), the COP and SCP of the system varied from 0.45 to 0.5, and 45 to 120 W/kg of desorbing hydride, respectively. Yang *et al.* (2010) investigated the influence of heat transfer enhancement measures in a thermally driven MHHP. Three types of reactors packed with metal hydride powder, metal hydride powder/Al foam and metal hydride compact were considered for the discussion. The results were shown that the

MHHP adopting heat transfer enhancement, the coefficient of performance reduced slightly, while the specific heating power increased significantly. Paya *et al.* (2011) presented both dynamic model and experimental results of a SS-MHHP working with $\text{LaNi}_{4.91}\text{Sn}_{0.15}$ (hot reaction bed) and $\text{Ti}_{0.99}\text{Zr}_{0.01}\text{V}_{0.43}\text{Fe}_{0.09}\text{Cr}_{0.05}\text{Mn}_{1.5}$ (cold reaction bed). The simulation results were validated with experimental measurements. Using this model, a sensitivity analysis was carried out, showing that the operating conditions (temperature sinks/sources, hydrogen charge, cycle duration) have a sensible impact on the cooling performance. The results showed a large deviation between the static and dynamic P-C-T conditions, and the systematic plot of the actual and static P-C-T curves helps to understand the internal behavior of the system.

Heat and mass recovery

In conventional wet absorption systems with solution circuit, the weak solution-strong solution heat exchanger recovers the heat between the hot solution from the generator and the cold solution from the absorber. This heat recovery significantly enhances the COP of the system. Studies on heat and mass recovery also have been reported for MHHP systems. Abraham and Murthy (2003a; 2003b; 2003c) studied the influence of mass recovery on the performance of SS-MHHP. Mass recovery between hydride reactors was found to improve system performance compared to that of a basic system. In another study, influence of heat recovery on the performance of SS-MHHP system was studied (2003b). Later, they studied the effects of combined heat and mass recovery on the performance of a SS-MHHP system. It was described that combined recovery cycle which effectively utilizes the advantages of both heat recovery and mass recovery. It was reported that at an intermediate temperature of 30 °C and a low temperature of 0 °C, when the heat source temperature was varied from 85 to 100 °C, the

improvement in mass recovery, heat recovery and combined recovery cycles compared to that of the basic cycle were 24 to 8 %, 43 to 15 % and 48 to 15 %, respectively. It was found that combined recovery was more effective at lower heat source temperatures and also at higher intermediate temperatures (2003c).

Multistage systems

The systems discussed so far are SS-MHHP systems. The actual COP of these systems is much smaller than the ideal one (1.0 maximum). COP of the MHHPs can be improved by using multistage systems. Very few studies on multi-stage systems have been reported in the literature (Ahmed and Murthy, 2004; Satheesh *et al.*, 2010b; 2010c). Ahmed and Murthy (2004) proposed a novel metal hydride alloy cycle for refrigeration, heat pumping and heat transformation using three metal hydrides alloy A- $\text{LaNi}_{4.6}\text{Sn}_{0.4}$, B- $\text{LaNi}_{4.7}\text{Al}_{0.3}$ and C- $\text{MmNi}_{4.5}\text{Al}_{0.5}$. The effects of operating temperatures on the COP, half cycle time and specific alloy output were studied based on the thermodynamics and simple reaction kinetic equations.

Satheesh *et al.* (2010b) presented the operational characteristics of a double-stage metal hydride based heat pump (DS-MHHP) working with $\text{LaNi}_{4.1}\text{Al}_{0.52}\text{Mn}_{0.38}$ / $\text{LaNi}_{4.91}\text{Sn}_{0.15}$ / $\text{Ti}_{0.99}\text{Zr}_{0.01}\text{V}_{0.43}\text{Fe}_{0.09}\text{Cr}_{0.05}\text{Mn}_{1.5}$ as high / medium / low temperature alloys. The performances of the DS-MHHP were predicted by solving the transient, two-dimensional, conjugate heat and mass transfer characteristics between the paired metal hydride reactors of cylindrical configuration using the finite volume method (FVM). The variations in hydrogen concentrations, hydride equilibrium pressures, and temperatures within the hydride beds, and the heat exchange between the hydride beds with the heat transfer fluids were presented for a complete cycle. Later,

the same research group investigated the performance of the DS-MHHP working with $\text{LaNi}_{4.1}\text{Al}_{0.52}\text{Mn}_{0.38}$, $\text{LaNi}_{4.91}\text{Sn}_{0.15}$ and $\text{Ti}_{0.99}\text{Zr}_{0.01}\text{V}_{0.43}\text{Fe}_{0.09}\text{Cr}_{0.05}\text{Mn}_{1.5}$ hydride alloys. The effects of half cycle time, hydride mass ratio, sensible heat exchange factor and operating temperatures, viz. heat source, heat sink, and refrigeration temperatures on the amount of hydrogen transferred between the paired reactors, coefficient of performance and specific cooling power of the DS-MHHP system were investigated (2010c). It was observed that decrease of mass ratio, which is the ratio between the reactor material mass to the alloy mass, from 1.35 to 0.3, enhances the COP and SCP of about 17.5 % and 46.3 %, respectively.

Compressor driven metal hydride cooling systems (CD-MHHP)

Compared to work-operated systems, the main disadvantages with heat-operated systems are: low COPs and low specific alloy outputs. In this context, the compressor-driven metal hydride systems for cooling and heating applications seem to be very promising. CD-MHHP is comprised of two reactors, each filled with the same metal hydride, and connected by a compressor. Bedbak and Gopal (2005) analyzed a compressor-driven metal hydride cooling system in terms of its energetic and exergetic efficiencies. Applying the first and second laws of thermodynamics, the system COP, contribution of individual irreversibility and the second law efficiency of the system were obtained. Effects of important design and operating parameters on system performance were presented. Studies revealed that the system performance depends mainly on the temperature drops at the high- and low-temperature reactors and compressor efficiency.

A summary of above-mentioned literature on numerical studies of MHHP is given in Table 2.1.

2.2.3 Heat transformer

Metal hydride based heat transformer (MHHT) is a type of heat pump which can upgrade the temperature of low grade heat such as industrial waste heat, solar energy, geothermal energy, etc. up to the temperature range of 150 - 220 °C. It also provides higher heat storage capacity and offers wide range of working temperatures as compared to other conventional heat pumps / heat transformers. In addition, MHHTs use hydrogen as working fluid which is environment friendly and offer noise free and vibration less operation. Numerical studies on MHHT are presented in this section.

Few authors reported on the thermodynamic analysis of MHHT (Kumar *et al.*, 1985; Gambin, 1989; Choi and Mills, 1991; Sun *et al.*, 1992; 1996). Kumar *et al.* (1985) carried out a comparative thermodynamic study of the MHHTs and MHHPs for different alloy pairs. The results were presented in the form of nomograms to yield the operation temperatures, COPs, and exergetic efficiencies. Based on the nomograms, the suitable alloy pairs were selected for specific applications.

Gambini (1989) developed a thermodynamic model for analyzing the performance of MHHP in heat upgrading mode under dynamic conditions using $\text{LaNi}_{4.7}\text{Al}_{0.3}/\text{MmNi}_{4.5}\text{Al}_{0.5}$ alloy pair. The reported COP and power output were about 0.36 and 40 W/kg hydride. The results provided by this model were in good agreement with the experimental results. It was shown that by lengthening the cycle time with respect to the previous value, the power output decreases while the heat output and the efficiency increase as a consequence of the increase of transferred hydrogen. Choi and Mills (1991) analyzed the performances of MHHP for upgrading space craft

waste heat. Dynamic response of two coupled hydride beds was also modeled accounting for heat transfer, reaction kinetics, and hydrogen flow. Parametric calculations were reported for the $\text{Mg}_{2.4}\text{Ni}/\text{LaNi}_{4.9}\text{Al}_{0.1}$ pair, which shows an optimal cycle time of about 10 to 12 min.

Sun *et al.* (1992) presented a practical method to select the hydride alloys to be used in a DS-MHHT. They introduced three different evaluation criteria to compare the operating characteristics of heat transformers working different alloy combinations, namely, COP, specific alloy output and temperature output. The influence of some metal hydride properties on the operating characteristics was also discussed. Further, Sun *et al.* (1996) performed a comparative study of a DS-MHHT working with six different operating cycles and presented the thermodynamic analysis of the systems. The effects of hydrogen exchange amount, weight ratio, specific heat capacity of the reactor vessel, and sensible heat exchange factor, and the various operating temperatures, such as, heat source, heat sink and refrigeration temperatures on COP of DS-MHHT systems were reported. They showed that the low-pressure-side two-stage heat pump was suitable for heat upgrading and the high-pressure-side two-stage heat pumps for heat amplifying and refrigeration applications.

The performance of the SS-MHHT was investigated by Kang and Yabe (1995) and Gopal *et al.* (1995c) using one-dimensional mathematical model. Kang and Yabe (1995) carried out a thermal analysis on a module type of MHHT to predict the performance of the system. Cylindrical tube module hydride reactor was considered in the modeling. The effects of various operating conditions, as well as the design parameters, on the system performance were extensively investigated. Gopal *et al.* (1995c) predicted the performance of a MHHT based on

heat transfer and reaction kinetics of the paired hydride beds. Results were computed for a MHHT working with a $\text{ZrCrFe}_{1.4}/\text{LaNi}_5$ pair. The results showed that due to the low effective thermal conductivity of the hydride beds, the performance of the system was controlled initially by heat transfer. For the $\text{ZrCrFe}_{1.4}/\text{LaNi}_5$ system the coefficient of performance lies between 0.27 and 0.30 and the second-law efficiency lies between 0.37 and 0.44.

Recently, Yang *et al.* (2011) developed a 2-D mathematical model to simulate the performance of the SS-MHHT. The predicted temperature gain was about 6.8 K using waste heat source available at 358 K using $\text{LaNi}_5/\text{LaNi}_{4.7}\text{Al}_{0.3}$ pair. The achieved COP and SHP were about 0.407 and 70.5 W/kg. Later, the same research group (2012) presented a parametric study on SS-MHHT employing $\text{LaNi}_5/\text{LaNi}_{4.7}\text{Al}_{0.3}$ pair. It was found that the amount of hydrogen exchanged between the coupled reactors was crucial to achieve high COP, while specific heating power was very sensitive to the cycle time.

A summary of above-mentioned literature on numerical studies of metal hydride heat transformer is given in Table 2.2.

2.2.4 Hydrogen compressor

Compressing hydrogen gas to high pressures by conventional methods demands high-grade energy input and also requires special sealing between the moving parts. Since, metal hydride based hydrogen compressor utilizes low-grade energy input and also offer vibration free and noiseless operation, it may be a better alternative to conventional compressor particularly for high delivery pressure in the range of 50 – 200 bar. Few authors investigated the influence of

operational and reactor bed related parameters on the performance of metal hydride based hydrogen compressor (MHHC) by analysing the heat and mass transfer aspects of the hydride bed. Numerical studies on MHHC were carried out by Silva (1993); Muthukumar *et al.* (2002, 2012b) and Wang *et al.* (2010). Silva (1993) proposed a prototype model for industrial hydrogen compression system. The authors have selected the FeTi metallic alloy which absorb the hydrogen at 1 MPa at room temperature and desorbs the pressurized hydrogen at 10 MPa at 120 °C heat source temperature.

Muthukumar *et al.* (2002) presented the parametric studies on a SS-MHHC. They also studied the influences of operating parameters such as heat source and sink temperatures, operating pressures, pressure ratios, cycle time, and bed parameters such as overall heat transfer coefficient, bed thickness and thermal conductivity, on the performance of a SS-MHHC. They have chosen AB₂ type Ti_{0.98}Zr_{0.02}V_{0.43}Fe_{0.09}Cr_{0.05}Mn_{1.5} alloy for their study. They observed that the heat transfer fluid temperature, bed thickness and supply pressure were found to exert significant influence on the compressor performance. Recently, Muthukumar *et al.* (2012b) presented a mathematical model for predicting the performance of a three-stage MHHC. The performance of MHHC was predicted by solving the unsteady heat and mass transfer characteristics of the coupled metal hydride beds of cylindrical configuration. Using three-stage compression, a maximum pressure ratio of 28 was achieved for the supply conditions of 20 °C absorption temperature and 2.5 bar supply pressure. A maximum delivery pressure of 100 bar was obtained for the operating conditions of 20 °C absorption temperature and 120 °C desorption temperature.

Wang *et al.* (2010) numerically studied the SS-MHHC. In order to analyze the dynamic working process of the reactor, a numerical simulation based on non-local thermal equilibrium model was presented.

2.3 Experimental Studies on Metal Hydride Devices

Several experimental studies have been reported on metal hydride based hydrogen storage device's thermal behavior, including the reactors ability to absorb or desorb hydrogen at various pressures, temperatures and flow rates. Based on the principle of reversible chemical reactions between the hydride alloy and hydrogen gas, several researchers experimentally developed different thermal machines and tested their performances. Some of important studies on this topic are discussed in the following sections.

2.3.1 Hydrogen storage

Several experimental studies have been reported on metal hydride based hydrogen storage device with simple reactor design; where the metal hydride is filled in the reactor and heat transfer fluid flows around the outer periphery of the tube. Some of the important papers are discussed in this sub-section (Supper *et al.*, 1984; Groll *et al.*, 1987; Gopal and Murthy, 1995d; Muthukumar *et al.*, 2005a). Supper *et al.* (1984) presented the experimental investigations of the reaction kinetics of various AB₅ type alloys and also studied the influences of different heat and mass transfer enhancement techniques on the reaction kinetics of LaNi_{4.7}Al_{0.3}. They studied the effects of bed thickness ranging from 1.0 mm to 6.0 mm and absorption temperatures ranging from 20 - 50 °C. Groll *et al.* (1987) experimentally investigated the reaction kinetics of LaNi_{4.7}Al_{0.4} and CaNi₅ alloys and observed that the improvement in the hydrogen flow and the heat transfer in the

reaction bed play an important role in reaction kinetics. Gopal and Murthy (1995d) presented the experimental results of $\text{LaNi}_{4.7}\text{Al}_{0.3}$ during both absorption and desorption processes at different absorption and desorption temperatures. They have studied the hydride bed performance for different cooling/heating fluid temperatures. The experimental results were compared with the numerical model and showed a good agreement between them.

Muthukumar *et al.* (2005a) experimentally investigated the performance of $\text{MmNi}_{4.6}\text{Fe}_{0.4}$ and $\text{MmNi}_{4.6}\text{Al}_{0.4}$ based hydrogen storage devices at different supply pressures, cooling fluid temperatures and overall heat transfer coefficient. Performance studies were carried out by varying the supply pressure, absorption temperature, and overall heat transfer coefficient. At any given absorption temperature, hydrogen absorption rate and storage capacity were found to increase with supply pressure for both the alloys. Cold fluid temperature was found to have a significant effect on hydrogen storage capacity at lower supply pressures. The overall heat transfer coefficient has a negligible influence on the hydrogen storage capacities of both the alloys. It was reported that at a supply pressure of 35 bar and a cold fluid temperature of 15 °C, $\text{MmNi}_{4.6}\text{Fe}_{0.4}$ alloy stored about 1.6 wt%, while $\text{MmNi}_{4.6}\text{Al}_{0.4}$ stored 1.3 wt%.

Recently, few investigators tested the hydrogen storage tank with different heat exchanger designs to further reduce the absorption and desorption time by enhancing the external heat transfer (Kaplan, 2009) and internal heat transfer (Dhaou *et al.*, 2010; Souahlia *et al.*, 2011; Visaria *et al.*, 2011). Kaplan (2009) studied the effects of heat transfer mechanisms on the charging process in metal hydride reactors under various charging pressures. Three different cylindrical reactors with the same base dimensions were designed and manufactured. The first

one was a closed cylinder cooled with natural convection, the fins were arranged around the second reactor and the third reactor was cooled with water circulating around the reactor. The third reactor showed the lowest temperature increase with the fastest charging time under all charging pressures investigated.

Dhaou *et al.* (2010) carried out an experimental study of a finned spiral heat exchanger based hydrogen storage device filled with LaNi_5 . The experimental results showed that the charge time of the reactor was considerably reduced, when finned spiral heat exchanger was used. In addition, the effects of different parameters (flow mass and temperature of the cooling fluid, applied pressure, and hydrogen tank volume) on the storage performance were also discussed. The reported maximum hydrogen storage capacity was about 1.4 wt%. Souahlia *et al.* (2011) built two metal hydride containers with a simple and modular design, one container having a cylindrical shape and equipped with concentric heat exchanger with fins and the other container without internal heat exchanger. They presented a description of the containers and an investigation of the parameters influencing the hydrogen storage performance. Different experiments were carried out on the two containers and obtained results concerning the hydrogen mass stored and the hydride bed temperature were compared. In addition, the effect of the cooling/heating fluid temperatures and the applied pressure on the storage time of the proposed containers was experimentally investigated. It was reported that the maximum hydrogen storage capacity was about 0.5 wt%.

Visaria *et al.* (2011) discussed the experimental setup and testing of a prototype heat exchanger using $\text{Ti}_{1.1}\text{CrMn}$ as high-pressure metal hydride (HPMH) storage material. Tests were performed

to examine the influence of pressurization profile, coolant flow rate and coolant temperature on metal hydride temperature and reaction rate. The prototype heat exchanger successfully achieved a fill time of 4 min 40 s with a combination of fast pressurization and low coolant temperature.

2.3.2 Heat pump

In the following sub-sections, a detailed literature review on experimental studies of SS-MHHP systems and also of the more complex systems, like thermal wave concept, cascading systems and compression driven systems are discussed.

Single-stage systems

Many researchers developed the prototypes of MHHPs and tested their performances (Nagel *et al.*, 1984; Suda, 1984; Lee *et al.*, 1995; Imoto *et al.*, 1996; Izhvanov *et al.*, 1996; Gopal and Murthy, 1999; Chernikov *et al.*, 2002; Ni and Liu, 2007; Payá *et al.*, 2009). Nagel *et al.* (1984) developed a MHHP system for refrigeration purpose employing $\text{MmNi}_{4.0}\text{Fe}_{1.0}$ / $\text{LaNi}_{4.65}\text{Al}_{0.3}$ hydride pair. The actual output of the system was found to be 1.7 kW. The system consists of two heat exchangers filled with high pressure hydride and low pressure hydride. Each heat exchanger consists of 18 reaction cells filled with aluminum foam with void fraction of 92 %. This arrangement yielded an effective thermal conductivity 5.5 W/mK and the optimum cycle time was found to be 13 min.

Suda (1984) developed a metal hydride refrigeration system for producing cold air of 1.75 kW capacity using $\text{LaNi}_{4.65}\text{Al}_{0.3}$ and $\text{MmNi}_{4.0}\text{Fe}_{0.1}$ hydride pair. The four reactors of 25 mm outer diameter and 360 mm length each filled with 0.55 kg of hydriding alloy. A total mass of about 10

kg hydride was filled in each heat exchanger (reactor). The maximum reported COP at 140 °C was 0.4. The optimum cycle time of the system was found to be 13 min.

Lee *et al.* (1995) constructed a prototype of a MHHP using $Zr_{0.9}Ti_{0.1}Cr_{0.9}Fe_{1.1}$ and $Zr_{0.9}Ti_{0.1}Cr_{0.6}Fe_{1.4}$ as regeneration and refrigeration alloys, respectively. Tubular type reactors (each of 210 mm length and 19.1 mm inner diameter) were filled with the hydride masses of 2 kg (regeneration alloy) and 2.5 kg (refrigeration alloy). For enhancing the heat transfer characteristics 120 mesh brass screens were inserted in the hydride beds at the intervals of 2 mm. The reported maximum power output of 272 W/kg of desorbing hydride was obtained at the optimum operating conditions of 12.8 - 13.2 mol hydrogen exchange, 4 min heating time and 7-8 min cooling time. The lowest cooling temperature was found to be 18 °C using 200 °C heat source temperature and 30 °C ambient air temperature. They found that the plateau pressure and reaction kinetics can be controlled by changing the relative composition of Cr and Fe.

Imoto *et al.* (1996) built a refrigeration system to generate temperature below -20 °C using $La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2} / LaNi_{4.6}Mn_{0.3}Al_{0.3}$ pair. Total inventory of the hydride alloys were 90 kg. A heat source temperature range of 130 - 150 °C was obtained from a solar collector. They employed the cylindrical reactors with internal aluminum fins. The maximum values of COP and SCP of the system were approximately 0.4 and 22.2 W/kg of total hydride mass for the cycle time of 40 min. Izhvanov *et al.* (1996) developed a MHHP with a cooling capacity of 150 - 200 W using $LaNi_{4.6}Al_{0.4}$ and $MmNi_{4.85}Fe_{0.15}$ hydride pair. They employed two pairs of cylindrical reactors (32 mm diameter and 560 mm length), each filled with 1.5 kg of respective hydride. Corrugated aluminum foils were employed for heat transfer enhancement. The estimated COP of

the system varied from 0.17 - 0.2 at the operating temperatures of 158 °C heat source temperature, 30 °C heat rejection and 0 °C refrigeration temperature. Gopal and Murthy (1999) tested a MHHP working with $\text{ZrMnFe} / \text{MmNi}_{4.5}\text{Al}_{0.5}$. They employed cylindrical reactors of 50 mm outer diameter and 250 mm length. The metal hydride was filled in the annular gap between Cu and filter tube, thus forming a thin bed of 5 mm thickness. External heat transfer was accomplished by a copper coil which was wrapped around the reaction bed. Depending upon the operating conditions (110 – 130 °C, 25 – 35 °C, and 10 – 20 °C); the SCP was between 30 and 45 W/kg of desorbing alloy for the whole cycle, and the COP varied between 0.2 and 0.35.

Chernikov *et al.* (2002) demonstrated a MHHP for producing ice from water available at 21.1 °C using $\text{LaNi}_{4.6}\text{Al}_{0.4}$ and $\text{MmNi}_{4.15}\text{Fe}_{0.85}$ as high and low temperature alloys, respectively. Total hydride mass of 3 kg (each hydride mass of 1.5 kg) was used for the model. The reported COP and SCP of the system were 0.33 and 66.67 W/kg of total alloy masses, respectively for the whole cycle time at the operating temperatures of 130 /25 /1.5 °C. Further they have also reported that an improvement of hydride bed thermal conductivity increases the rate of cold production and reduces the cycle time considerably. Ni and Liu (2007) experimentally investigated the performance of a SS-MHHP under the operating temperature of 150 /30 - 32 /20 °C. The high pressure reaction bed was filled with $\text{LaNi}_{4.61}\text{Mn}_{0.26}\text{Al}_{0.13}$ while the low pressure reactor was filled with $\text{La}_{0.6}\text{Y}_{0.4}\text{Ni}_{4.8}\text{Mn}_{0.2}$ hydride alloys. They observed the lowest refrigerating temperature of 1.9 °C for 150 °C driving heat temperature. They found that the COP and cooling power output increase with an increase in the heat source temperature. For the selected operating temperatures of 150 /30 /20 °C, the maximum COP and cooling capacity were found to be 0.3 and 240 W, respectively.

Payá *et al.* (2009) developed an experimental setup for a SS-MHHP employing $\text{LaNi}_{4.91}\text{Sn}_{0.15}$ and $\text{Ti}_{0.99}\text{Zr}_{0.01}\text{V}_{0.43}\text{Fe}_{0.09}\text{Cr}_{0.05}\text{Mn}_{1.5}$ hydride pairs. Using capillary tube bundle reactors, fast reaction kinetics (95 s during desorption and 80 s for absorption) were achieved. The predicted numerical results were compared with their own experimental data and a reasonably good agreement was observed between the two. Their scopes were limited by solving a set of theoretical equations for approaching the approximate solutions. For the selected operating temperatures, maximum and mean cooling powers of 736 W and 485 were reported during the refrigeration period. The average SCP and COP of the whole system were approximately 42 W/kg of total hydride mass and 0.22, respectively.

Few researchers tested the MHHP for air-conditioning applications (Ron, 1984; Jiu Jian and Hongmin, 2007; Qin *et al.*, 2007; Linder and Kulenovic, 2011). Ron (1984) built a MHHP employing $\text{LaNi}_{4.7}\text{Al}_{0.3}$ / $\text{MmNi}_{4.15}\text{Fe}_{0.85}$ hydride pair for utilizing the waste heat of exhaust gases from a bus as the heat source temperature for air-conditioning the bus. Total alloy inventory was about 70 to 80 kg for achieving 3.6 kW cooling capacity. A special aluminum matrix was used for enhancing the thermal conductivity of hydride alloy. The specific cooling capacity (cooling capacity per unit hydride mass) of 680 to 900 W/kg of desorbing hydride mass was predicted with 2 min cooling time. The low temperature units were located within the space to be air-conditioned. The high temperature units were heated via arrangements simulating the hot exhaust gas of a bus. Compared to the conventional vapour compression systems, this heat pump reduces the fuel consumption of the bus up to 30 %. Jiu Jian and Hongmin (2007) developed a MHHP to provide air conditioning for a bus employing $\text{LaNi}_{4.61}\text{Mn}_{0.26}\text{Al}_{0.13}$ and $\text{La}_{0.6}\text{Y}_{0.4}\text{Ni}_{4.8}\text{Mn}_{0.2}$. The lowest achievable refrigerating temperature was 1.9 °C. With increasing heat source temperature,

the pressure difference between the high-pressure bed and the low-pressure bed becomes large and enhances the hydrogen transfer rate during the heating process, which contributes to the improvement of COP and cooling power output.

Qin *et al.* (2007) employed the same hydride pair ($\text{LaNi}_{4.61}\text{Mn}_{0.26}\text{Al}_{0.13}$ / $\text{La}_{0.6}\text{Y}_{0.4}\text{Ni}_{4.8}\text{Mn}_{0.2}$) reported by Ni and Liu (2007) for developing the exhaust gas driven automotive air conditioner. The selected heat source, heat sink and refrigeration temperature ranges were 120 – 200 / 20 – 50 / -10 – 0 °C, respectively. The overall dimensions of the stainless steel reactors employed for their investigations were 75 mm outer diameter and 500 mm length. The reactors were filled with hydride mass of 2.75 kg each. Oil and water were used as the heat transfer fluids for the high and low temperature reactors, respectively. A maximum cooling power of 639 W was achieved. For the selected operating conditions and the reactor geometries, the operating times of various processes were fixed as 850 s for regeneration, 1300 s for refrigeration, 650 s for sensible cooling and 800 s for preheating. The average cooling power and system COP were reported as 84.6 W and 0.26, respectively, at the operating temperatures of 150 / 30 / 0 °C. Linder and Kulenovic (2011) developed a prototype air-conditioning system for hydrogen driven cars. The system was experimentally investigated on a laboratory prototype using $\text{Ti}_{0.99}\text{Zr}_{0.01}\text{V}_{0.43}\text{Fe}_{0.09}\text{Cr}_{0.05}\text{Mn}_{1.5}$ as working metal hydride. With a hydrogen supply pressure of 53 bar and a desorption pressure of 6 bar (supply pressure for the consumer), a quasi-continuous cooling power of around 900 W was reached.

Thermal wave concept

Willer *et al.* (1999a) built a multi hydride thermal wave device for simultaneous heating and cooling using seven metal hydrides on the high temperature side and two metal hydrides on the

low temperature side. The cooling power of the modules with three reactor beds was about 230 W for outlet temperature of 10 °C and 500 W for outlet temperature 0 °C with an average of 360 W. The reported COP was about 0.6 at cooling temperatures between 0 °C and 10 °C.

Cascading systems

The performance of the MHHP can be improved by coupling with other systems like vapour compression systems or vapour absorption systems. Cascading systems offer a greater flexibility and improved performance in terms of COP. Klein and Groll (2002) and Klein (2007) analyzed the possibility of a two-stage MHHP system, working with $\text{LaNi}_{4.91}\text{Sn}_{0.15}$, $\text{LaNi}_{4.1}\text{Al}_{0.52}\text{Mn}_{0.38}$ and $\text{Ti}_{0.99}\text{Zr}_{0.01}\text{V}_{0.43}\text{Fe}_{0.09}\text{Cr}_{0.05}\text{Mn}_{1.5}$ as a topping cycle with a single effect lithium bromide water cycle as a bottom cycle. They employed 24 stainless steel reactors (8 reactors for each metal hydride), having 27 mm inner diameter with 1.5 mm thickness. Stainless steel porous sinter metal tube of 3 mm inner diameter (1.5 mm thickness, 1 mm pore size) was used as filter. Aluminum foam with 92 % porosity was employed for heat transfer enhancement ($k_e = 8 \text{ W/m-K}$). The system was designed to operate at a driving temperature of 310 °C, heat release temperature for driving a bottoming cycle at 125 °C and producing cold temperature of 2 °C. The estimated cold production was about 1.8 kW and the heat generation was about 1.5 kW. The MHHP system COP is in the range of 0.9 and heat amplification was about 0.75.

Compressor driven metal hydride cooling systems

Experimental studies on compressor driven metal hydride cooling systems were carried out by Kim *et al.* (1997b) and Park *et al.* (2001; 2002). Kim *et al.* (1997b) studied the performance of compressor driven metal hydride heat pumps. The reactors were copper tubes (diameter 12.7

mm, length 165 mm) with external fins for enhancing the outside heat transfer. Experiments were carried out with reactors employing copper coated porous metal hydride compacts of LaNi_5 and $\text{Ca}_{0.4}\text{Mm}_{0.6}\text{Ni}_5$. The SCP was about 1.5 kW/kg of desorbing hydride (130 s cooling time) for the LaNi_5 reactor, while, for $\text{Ca}_{0.4}\text{Mm}_{0.6}\text{Ni}_5$ reactor (150 s cooling time) was about 2.2 kW/kg (high desorption equilibrium pressure of $\text{Ca}_{0.4}\text{Mm}_{0.6}\text{Ni}_5$). Pressure ratio of the compressor was about 7.0.

Park *et al.* (2001) developed a CD-MHHP using $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.55}\text{Fe}_{1.45}$. The maximum compressing pressure and minimum suction pressure were 20 and 0.5 atm, respectively. They employed a finned reactor of 15 mm diameter. Cooling power was found to increase by about 25 % when the airflow was increased from 8 m³/min to 11 m³/min. The effect of room temperature beyond 24 °C and the effect of airflow rate beyond 11 m³/min had no significant influence. The maximum SCP of 0.29 kW/kg of desorbing hydride was obtained under the optimum operating conditions of cycle time 2.6 min and air flow rate 11 m³/min. The same research group (Park *et al.* 2002) built an experimental set up (using 3.5 kg of $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.55}\text{Fe}_{1.45}$) employing a commercial compressor and demonstrated the practical applicability for air-conditioning applications. The experimental results showed that the system could produce a maximum SCP of 0.41 kW/kg of alloy at 6 °C cooling temperature and 7 m³/min airflow rate. COP of the above system is about 1.8 with an optimum cycle time of 6 min.

A summary of above-mentioned literature on experimental studies of metal hydride heat pump is given in Table 2.3.

2.3.3 Heat transformer

A few experimental studies reported in the literature on metal hydride based heat transformers (MHHT) are presented in this section.

Three decades ago, Tüscher *et al.* (1984) presented the operating concept of MHHT and investigated the dynamic sorption behavior of different hydrogen storage materials viz., $\text{MmNi}_{4.5}\text{Al}_{0.5}$, LaNi_5 and $\text{LaNi}_{4.7}\text{Al}_{0.3}$ for heat pump applications and a temperature lift of about 17.6 K was achieved in heat up gradation mode with $\text{MmNi}_{4.5}\text{Al}_{0.5}/\text{LaNi}_{4.7}\text{Al}_{0.3}$ alloy combination. It was found that the operation of the devices were sensitive to the characteristics of the hydride materials (e.g. hysteresis, plateau slope) as to those of the hydride bed and the container design (heat conductivity and heat capacity).

The first experimental proto-type of DS-MHHT was built by Suda *et al.* (1991) during 1991. They developed a DS-MHHT demonstration unit of capacities 7.72 kW and 77 kW. The metal hydrides employed in these units were: $\text{LaNi}_{4.28}\text{Al}_{0.23}$ as low pressure hydride, $\text{MmNi}_{4.57}\text{Al}_{0.46}\text{Fe}_{0.05}$ as intermediate pressure hydride and $\text{MmNi}_{3.98}\text{Fe}_{1.04}$ as high pressure hydride. The total weight of these three hydrides was 230 Kg. The actual COP obtained was 0.21 against ideal COP 0.36.

Subsequently, a series of experimental studies on MHHT have been carried out at IKE, University of Stuttgart, Germany (Werner and Groll 1991; Isselhorst and Groll 1995; Willers and Groll 1999b). Werner and Groll (1991) synthesized three different misch metal-nickel type alloys for MHHT application. They carried out absorption and desorption tests with individual

reaction beds under various temperature and pressure conditions to study the dynamic behavior of the reaction beds. The amount of hydrogen absorbed and desorbed was measured via the pressure change in an external constant volume. It was observed that charging and discharging times showed an inverse relationship with respect to the dynamic pressure difference (DPD). The experiments showed that for a given reaction bed, the DPD during absorption and desorption should be above 2 atm to obtain reasonably small cycle times (10- 15 min) i.e. the difference between absorption and desorption equilibrium pressures should be greater than 4 atm.

Isselhorst and Groll (1995) developed a prototype MHHT with a capacity of about 8 kW employing $\text{LmNi}_{4.85}\text{Sn}_{0.15}$, $\text{LmNi}_{4.49}\text{Co}_{0.1}\text{Mn}_{0.205}\text{Al}_{0.205}$ and $\text{LmNi}_{4.08}\text{Co}_{0.2}\text{Mn}_{0.62}\text{Al}_{0.1}$ as high, medium and low temperature hydrides, respectively. They showed that an upgrading of thermal energy from temperatures of about 130 - 140 °C up to temperatures of more than 200 °C with a heat sink temperature of 30 – 40 °C could be possible. The reported COP and specific alloy output were 0.27 and of 38 W/kg of total hydride mass. Later, Willers and Groll (1999b) built a prototype of DS-MHHT in star-scheme using six reactors to obtain quasi-continuous power output of about 7 kW. The operating temperatures were 190 - 200 °C for the useful heat, 130 - 135 °C for the driving heat and 40 °C for the waste heat. The specific power output was about 30 W/kg hydride. They have also explained the potential application of heat transformer in the petrochemical industry with schematic figure.

A summary of above-mentioned literature on experimental studies of MHHT is given in Table 2.4.

2.3.4 Hydrogen compressor

In this section, few of important experimental studies on metal hydride based hydrogen compressor (MHHC) are presented.

Some of experimental studies on SS-MHHC have reported in the literature are Muthukumar *et al.*, 2005b; Dehouche *et al.*, 2005; Wang *et al.*, 2006 and Kim *et al.*, 2008. Muthukumar *et al.* (2005b) tested the performance of the MHHC employing $\text{MmNi}_{4.6}\text{Al}_{0.4}$ by varying the operating parameters such as supply pressure and heat source temperature. They found that for a given hot fluid temperature, the influence of supply pressure on system performance was prominent up to about 10 bar. Maximum efficiency of 7.3 % was obtained at a pressure ratio of 8.8 at 95 °C heat source temperature. Results obtained by a simulation compared well with the experimental data. Dehouche *et al.* (2005) studied the hydride alloys properties for MHHC application. Three intermetallics, $\text{LaNi}_{4.8}\text{Sn}_{0.2}$, $\text{LmNi}_{4.9}\text{Sn}_{0.1}$ and $\text{MmNi}_{4.7}\text{Al}_{0.3}$ were selected among various alloys of the AB_5 family have used in a thermal hydrogen compressor. Hydrogen absorption and desorption kinetics and PCT characteristics of these alloys at ambient temperature were measured and compared.

Wang *et al.* (2006) studied the hydrogen storage properties of $\text{Ti}_x\text{Fe} + y \text{ wt. \% La}$ ($x = 1.0 - 1.2$; $y = 0 - 5$) alloys. The results showed that over stoichiometry of Ti and addition of small amount of La remarkably improve the activation behavior of TiFe alloy, and the mechanism was discussed briefly for $\text{Ti}_{1.1}\text{Fe} + 5 \text{ wt. \% La}$ alloy, which has admirable activation characteristics and hydrogen storage properties, and it was selected as the alloy for MHHC. With this alloys two SS-MHHC prototypes were designed and built, and the compression characteristics were tested. The

test result showed that, the delivery pressure of 45 MPa was achieved. Kim *et al.* (2008) studied a hydrogen-compression system using porous metal hydride pellets of $\text{LaNi}_{5-x}\text{Al}_x$. They have chosen LaNi_5 and $\text{LaNi}_{4.75}\text{Al}_{0.25}$ for their study. They observed that $\text{LaNi}_{4.75}\text{Al}_{0.25}$ had a faster absorption rate than LaNi_5 . In addition, the compression ratio was found to be primarily dependent on the temperature difference between cooling and heating. The compression work and the efficiency of the LaNi_5 reactor were slightly larger than those of the $\text{LaNi}_{4.75}\text{Al}_{0.25}$ reactor.

Few researchers experimentally developed DS-MHHC and tested their performances (Wang *et al.*, 2007; Hopkins *et al.*, 2010; Li *et al.*, 2010). Wang *et al.* (2007) carried out an investigation on high-pressure MHHCs. They studied AB_5 and AB_2 type multi-component hydrogen storage alloys for the purpose of high-pressure hydrogen compression. A SS-MHHC with hydrogen compression rate of 40 l/min and a DS-MHHC with hydrogen compression rate of 20 l/min were designed to produce high-pressure hydrogen. The SS-MHHC produces high-pressure hydrogen around 45 MPa from 4 MPa feed gas, when hot oil at 170 °C was used as the heat source. The DS-MHHC rather needs only hot water to produce 45 MPa hydrogen.

Hopkins *et al.* (2010) experimentally investigated the DS-MHHC system. The metal hydrides used in this study were LaNi_5 and $\text{Ca}_{0.6}\text{Mm}_{0.4}\text{Ni}_5$. A Finite time thermodynamics (FTT) model was also developed and the model proved useful in determining how the compression results and energy requirements for the system change with variations in the system parameters. DS-MHHC system results showed a final compression ratio of approximately 12 when using cooling and heating temperatures of 10 °C and 90 °C, respectively. Li *et al.* (2010) investigated the

performances of a high pressure hydrogen compressor up to 70 MPa. To reach these pressure limits hydrogen storage properties of La-Ce-Ca-Ni-Al family AB_5 type and Ti-Zr-Cr-Fe-V family AB_2 type alloys have been investigated. $La_{0.35}Ce_{0.45}Ca_{0.2}Ni_{4.95}Al_{0.05}$ and $Ti_{0.8}Zr_{0.2}Cr_{0.95}Fe_{0.95}V_{0.1}$ were chosen for first and second stage compressions. With these two alloys, a DS-MHHC with hydrogen compression capacity of around 2000 l/cycle was designed and built; oil was used as the cooling and heating medium. When hot oil of 423 K was used as the heat source, hydrogen with pressure of 74.5 MPa was obtained.

Recently, Laurencelle *et al.* (2009) developed a prototype of three-stage MHHC. It has been designed for a hydrogen production facility using a low-pressure alkaline electrolyser. The compression system should transfer heat recovered from the electrolyser into the hydride beds to allow hydrogen desorption flow. The three-stage MHHC achieves a compression ratio of 20:1 atm. It performs a thermal cycling of three AB_5 hydrides between 20 and 80 °C. Its flow rate, for 25 g of each hydride bed, reaches about 20 liter (NTP) of hydrogen per hour. The three metal hydrides chosen for the experiment were $LaNi_{4.8}Sn_{0.2}$, $LaNi_5$ and $MmNi_{4.7}Al_{0.3}$.

Table 2.1 Summary of literature on numerical studies of metal hydride based heat pump.

Author(s) and Year	Contribution
Nishizaki <i>et al.</i> (1983)	Presented a numerical model for calculating the COP of a MHHP with four reaction beds using LaNi_5 / $\text{LaNi}_{4.7}\text{Al}_{0.3}$ hydride alloys.
Murthy and Sastri (1992)	- Basic thermodynamic analysis of DS-MHHP for five hydride pairs was presented. - The overall COP was reported as 2.4 for MnNi_5, FeTi and CaNi_5 hydride pair at the operating temperatures of 185/ 50/ -2 °C.
Gopal and Murthy (1995a & 1995b)	- SS-MHHP working with ZrMnFe / $\text{MmNi}_{4.5}\text{Al}_{0.5}$ hydride alloy pair using a one-dimensional mathematical model was numerically investigated. - The average COP obtained for this system was approximately 0.45 to 0.50.
Kang and Kuznetsov (1995)	- The performance of the metal hydride chiller was numerically predicted by solving the transient transport processes of heat and hydrogen between $\text{LaNi}_{4.5}\text{Al}_{0.5}$ (regeneration alloy) and LaNi_5 (refrigeration alloy) reaction beds. - The system COP and SCP were reported to be 0.7 and 40 W/kg of desorbing hydride, respectively.
Kim <i>et al.</i> (1997)	- The thermodynamic analysis and experimental study of a heat driven hydride slurry heat pump was studied employing $\text{Zr}_{0.8}\text{Ti}_{0.2}\text{Cr}_{0.6}\text{Fe}_{1.4}$ / $\text{Zr}_{0.8}\text{Ti}_{0.2}\text{MnFe}$ hydride pair. - The highest coefficient of performance of about 1.59 was reported.
Fedorov <i>et al.</i> (1999)	- Reported the mathematical modelling of a SS-MHHP working with $\text{LaNi}_{4.5}\text{Al}_{0.25}\text{H}_x$ and $\text{TiFe}_{0.8}\text{Mn}_{0.2}\text{H}_y$ hydride pair. - Operating temperatures: 80/ 20/ 10 °C ($T_H/T_M/T_C$).
Willers <i>et al.</i> (1999a)	- The performance of three combinations, namely, single-stage (SS), double-stage (DS) and multi hydride thermal wave (MHTW) heat pumps for heating and cooling applications is theoretically evaluated. - Using a high performance reaction bed (capillary tube bundle reactor), SCP of 100 to 200 W/kg (SS) and 150 to 300 W/kg (DS) can be achieved.
Fateev <i>et al.</i> (2000)	- Discussed the optimization of the processes of MHHP. - It was found that the heat transfer problem played a decisive role in cooling power of the system.

Jang <i>et al.</i> (2001)	- An unsteady, one-dimensional mathematical model of MHHP system working with $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.9}\text{Fe}_{1.1}$ / $\text{Zr}_{0.9}\text{Ti}_{0.15}\text{Cr}_{0.6}\text{Fe}_{1.45}$ hydride pair was developed. - Operating temperatures: 200/ 30/ 10 °C ($T_H/T_M/T_C$).
Abraham and Murthy (2003a, 2003b, 2003c)	- Studied the concept of heat and mass recovery on the performance of a single-stage multi-bed cooling system. - It was found that combined recovery was more effective at lower heat source temperatures and also at higher intermediate temperatures.
Ahmed and Murthy (2004)	- Analyzed the multi-effect thermodynamic cycle for simultaneous heating and cooling using metal hydrides. - Operating temperatures: 225/ 175/ 60/ 5 °C ($T_H/T_M/T_W/T_C$).
Bedbak and Gopal (2005)	- Analyzed a compressor-driven metal hydride cooling system in terms of its energetic and exergetic efficiencies - Effects of important design and operating parameters on system performance were presented.
Mellouli <i>et al.</i> (2009)	- A set of theoretical equations was solved for predicting the performance of MHHP employing $\text{MmNi}_{4.5}\text{Al}_{0.5}$ / $\text{MmNi}_{4.2}\text{Al}_{0.1}\text{Fe}_{0.7}$ hydride pair. - The COP and SCP of the system were in the range of 0.45 to 0.5 and 45 to 120 W/kg of desorbing hydride mass, respectively.
Satheesh <i>et al.</i> (2009, 2010a, 2010b, 2010c)	- Developed a mathematical model for predicting the performance of a SS-MHHP considering the variation in cooling fluid temperature along axial direction and slope and hysteresis factors of the PCT characteristics of the hydride pairs. - Extended this model for predicting the performance of DS-MHHP at different operating conditions.
Yang <i>et al.</i> (2010)	- Investigated the influence of heat transfer enhancement measures in a thermally driven MHHP. - It was found that adopting heat transfer enhancement, the SCP increases remarkably.
Paya <i>et al.</i> (2011)	- Presented both dynamic model and experimental results of a SS-MHHP working with $\text{LmNi}_{4.91}\text{Sn}_{0.15}$ and $\text{Ti}_{0.99}\text{Zr}_{0.01}\text{V}_{0.43}\text{Fe}_{0.09}\text{Cr}_{0.05}\text{-Mn}_{1.5}$. - A comparison between the actual and static P-C-T curves provided for important information on the operating parameters.

Table 2.2 Summary of literature on numerical studies of metal hydride based heat transformer.

Author(s) and Year	Contribution
Kumar <i>et al.</i> (1985)	• A comparative thermodynamic study of metal hydride heat transformer (heat upgrading) and heat pump using different alloy pairs were carried out.
Gambini (1989)	• Developed a procedure for the evaluation of the performance of MHHT (heat upgrading mode) under dynamic operation. • The results showed that the thermal power output attains a maximum value for a definite cycle time and hydrogen amount.
Sun <i>et al.</i> (1992)	• Presented a practical method to select suitable hydrides to be used in a DS-MHHT. • The performance of the system was compared for different alloy pairs.
Kang and Yabe (1995)	• Presented a thermal analysis on a module type of MHHT to predict the performance of the system. • The effects of various operating conditions on the system performance were investigated using 1-D mathematical model. The results are not validated.
Gopal and Murthy (1995)	• Presented 1-D model for predicting the performance of the MHHT based on heat transfer and reaction kinetics. • It was reported that the performance of the system improves significantly with input temperature. • The COP of the system was in the range of 0.27 to 0.3.
Yang <i>et al.</i> (2011, 2012).	• A 2-D unsteady model was developed and numerically solved by using FVM. • Investigated the effect of different operating parameters on system performance in terms of COP and SHP. • The effect of operating temperatures on second law efficiency is not analyzed.

Table 2.3 Summary of literature on experimental studies of metal hydride based heat pump.

Author(s) and Year	Contribution
Ron (1984)	• A MHHP was designed and built for a bus air conditioner. Two pairs of $\text{LaNi}_{4.7}\text{Al}_{0.3}$ / $\text{MmNi}_{4.15}\text{Fe}_{0.85}$ hydride units were employed. • Total alloy inventory was about 70 to 80 kg for achieving the cooling capacity of 3.5 kW.
Suda <i>et al.</i> (1984)	• A metal hydride refrigeration system was developed for producing cold air of 1.75 kW capacity using $\text{LaNi}_{4.65}\text{Al}_{0.3}$ and $\text{MmNi}_{4.0}\text{Fe}_{0.1}$ hydride pair. • The maximum reported COP at 140 °C heat source temperature was 0.4.
Lee <i>et al.</i> (1995)	• A prototype SS-MHHP operating with $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.9}\text{Fe}_{1.1}$ and $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.6}\text{Fe}_{1.4}$ as regeneration and refrigeration alloys, respectively, was constructed. • The reported maximum specific power output of 151 W/kg of desorbing hydride was obtained at the optimum operating conditions of 12.8 - 13.2 mol hydrogen exchange.
Imoto <i>et al.</i> (1996)	• SS-MHHP working with $\text{La}_{0.6}\text{Y}_{0.4}\text{Ni}_{4.8}\text{Mn}_{0.2}$ / $\text{LaNi}_{4.6}\text{Mn}_{0.3}\text{Al}_{0.3}$ hydride pair was built and tested. • The maximum values of COP and SCP of the system were about 0.4 and 22.2 W/kg of total hydride mass (with a cycle time of 40 min)
Izhvanov <i>et al.</i> (1996)	• A MHHP with heating and cooling capacity of 150 - 200 W using $\text{LaNi}_{4.6}\text{Al}_{0.4}$ (high temperature alloy) and $\text{MmNi}_{4.85}\text{Fe}_{0.15}$ (low temperature alloy) hydride pair was developed and tested. • The estimated COP of the system varied from 0.17 - 0.2 at the operating temperatures of 158 °C, 30 °C and 0 °C.
Willers <i>et al.</i> (1999a)	• Built a multi hydride thermal wave system for simultaneous heating and cooling using seven metal hydrides. • The reported COP was about 0.6.
Gopal and Murthy (1999)	• An experimental study was carried out on MHHP with the working pair ZrMnFe / $\text{MmNi}_{4.5}\text{Al}_{0.5}$. • The SCP was between 30 and 45 W/kg for the whole cycle, and the COP varied between 0.2 and 0.35.

Park <i>et al.</i> (2001, 2002)	- Developed a compressor driven MHHP. - The maximum SCP of 0.29 kW/kg of desorbing hydride was obtained.
Chernikov <i>et al.</i> (2002)	- A SS-MHHP was built and tested for producing ice from water available at 21.1 °C. - The reported COP and SCP of the system were 0.33 and 66.67 W/kg of total alloy mass, respectively for the whole cycle time.
Klein and Groll (2002)	- DS-MHHP working with $\text{LaNi}_{4.91}\text{Sn}_{0.15}$, $\text{LaNi}_{4.1}\text{Al}_{0.52}\text{Mn}_{0.38}$ and $\text{Ti}_{0.99}\text{Zr}_{0.01}\text{V}_{0.43}\text{Fe}_{0.09}\text{Cr}_{0.05}\text{Mn}_{1.5}$ hydride alloy pair was built and tested. - The system was designed to operate at a driving temperature of 310 °C, releasing heat at 125 °C and producing cold temperature of 2 °C.
Ni and Liu (2007)	- The performance of a SS-MHHP was analyzed experimentally by employing $\text{LaNi}_{4.61}\text{Mn}_{0.26}\text{Al}_{0.13}$ / $\text{La}_{0.6}\text{Y}_{0.4}\text{Ni}_{4.8}\text{Mn}_{0.2}$ hydride alloy pair. - The maximum COP and cooling capacity were 0.3 and 240 W, respectively.
Qin <i>et al.</i> (2007)	- For developing the exhaust gas driven automotive air conditioner, the same hydride pair used by Ni and Liu (2007) was adopted. - The average cooling power and system COP was reported as 84.6 W and 0.26, respectively, at the operating temperatures of 150/ 30/ 0 °C.
Paya <i>et al.</i> (2009)	- An experimental setup for a SS-MHHP system operating with $\text{LaNi}_{4.91}\text{Sn}_{0.15}$ / $\text{Ti}_{0.99}\text{Zr}_{0.01}\text{V}_{0.43}\text{Fe}_{0.09}\text{Cr}_{0.05}\text{Mn}_{1.5}$ hydride pairs was developed. - The average SCP and COP of the whole system were about 42 W/kg of total hydride mass and 0.22, respectively.
Linder and Kulenovic (2011)	- Developed prototype of air-conditioning system for hydrogen driven cars. - A quasi-continuous cooling power of around 900 W was reached.

Table 2.4 Summary of literature on experimental studies of metal hydride based heat transformer.

Author(s) and Year	Contribution
Tusher <i>et al.</i> (1984)	• Tested the SS-MHHP in heat upgrading mode. • Achieved temperature lift about 17 K at heat source temperature of 353 K and heat rejection temperature of about 286 K.
Werner and Groll (1991)	• Tested three types of Mm-Ni based alloys at different driving pressures and temperatures to evaluate the thermal behavior of the reaction beds. • Using these three alloys, they proposed double-stage MHHT scheme.
Suda <i>et al.</i> (1991)	• Built a double-stage metal hydride heat transformer employing $\text{LaNi}_{4.88}\text{Al}_{0.23}$ / $\text{MmNi}_{4.57}\text{Al}_{0.46}\text{Fe}_{0.05}$ / $\text{MmNi}_{3.98}\text{Fe}_{1.04}$ hydride alloys. • The actual COP of the system was 0.21 and the specific alloy output was 33 W/kg of total alloy mass.
Isselhorst and Groll (1995)	• A prototype heat transformer was developed for continuous power output of about 8 kW. • Upgrading temperatures from about 130 - 140 °C to temperatures of more than 200 °C with a heat sink temperature of 30 to 40 °C were the design parameters.
Willers and Groll (1999)	• Developed a prototype of DS-MHHT in star-scheme using six reactors to obtain quasi-continuous output. • It was also explained the potential application of heat transformer in the petro-chemical industry with schematic figure.

2.4 Literature Closure

From the literature survey, the following conclusions are arrived.

- Many investigators predicted the heat and mass transfer characteristics of hydride bed during absorption and desorption of hydrogen.

- Considerable research work on the thermal modeling of the metal hydride based heat pumps have been reported in the literature [Dantzer and Orgaz (1986), Gopal and Murthy (1995a & 1995b), Kim *et al.* (1997), Fedorov *et al.* (1999), Fateev *et al.* (2000), Jang *et al.* (2001), Abraham and Murthy (2003a, 2003b, 2003c), Mellouli *et al.* (2009) Yang *et al.* (2010), Satheesh *et al.* (2009,2010a, 2010b, 2010c) , Paya *et al.* (2011)].
- Few experimental studies on metal hydride based heat pump [Nagel *et al.* (1984), Imoto *et al.* (1996), Willers *et al.* (1999a), Park *et al.* (2001, 2002), Klien and Groll (2002), Paya *et al.* (2009), Linder and Kulenovic (2011)], hydrogen compressor [Muthukumar *et al.* (2005), Wang *et al.* (2006, 2007), Hopkins *et al.* (2010)] have been reported in the literature.
- The design of hydride based heat transformer should be based on the heat and mass transfer rates and reaction kinetics aspects of coupled beds operating under dynamic conditions. Very few studies have been reported in the literature on this important aspect with simplifying assumptions. Hence, there is a need for more theoretical work in this area.
- No mathematical model on double-stage metal hydride heat transformer reported in the literature. Therefore, a detailed numerical investigation is required for predicting the performance of the system.
- Only two research groups developed the prototypes of metal hydride based heat transformer [Suda *et al.* (1991), Groll *et al.* (1991, 1995, and 1999)]. However, no one

has investigated the effects of various operating parameters on the performances of the system.

In the view of above literature closure, the following aspects are taken in to this Ph.D. work;

- To develop a detailed mathematical model for predicting the performance of a single-stage metal hydride heat transformer. To extend this model for comparing the performance of the system using different alloy combinations at different operating conditions.
- To develop a detailed mathematical model for predicting the performance of double-stage metal hydride heat transformer at different operating conditions.
- To test the performances of metal hydride based single-stage and double-stage heat transformers at different operating conditions.
- To validate the numerical results.

Chapter 3

HEAT AND MASS TRANSFER MODELS

Metal hydrides can be effectively utilized as the working materials for various thermal driven sorption machines. Recently, metal hydride based thermal driven sorption machines have received much research attention due to their compactness, low grade thermal energy utilization and other remarkable environmental benefits. One can make use of the hydrogen storage mechanism in metal hydrides for developing many engineering applications such as heat pump, refrigerator, thermal energy storage, hydrogen compressor, etc. Metal hydride based heat pump is a type of solid-gas sorption system, in which the heat effect accompanied by absorption/desorption reaction is utilized for generating heat/cold. Metal hydride based heat pump works in three different operating modes: refrigeration, heat amplification and heat upgrading. Metal hydride based heat transformer (MHHT) is the third mode of heat pump which can upgrade the temperature of low grade heat from 120 - 140 °C to 160 - 200 °C. The performance of such devices highly depends on

the rate at which the heat is removed/ supplied from/to the metal hydride beds during absorption/desorption of hydrogen. Hence, the development of an efficient and economic design of such devices requires highly sophisticated computational models. In the following sub-section, the details of thermal modeling of single-stage and double-stage metal hydride based heat transformers are presented.

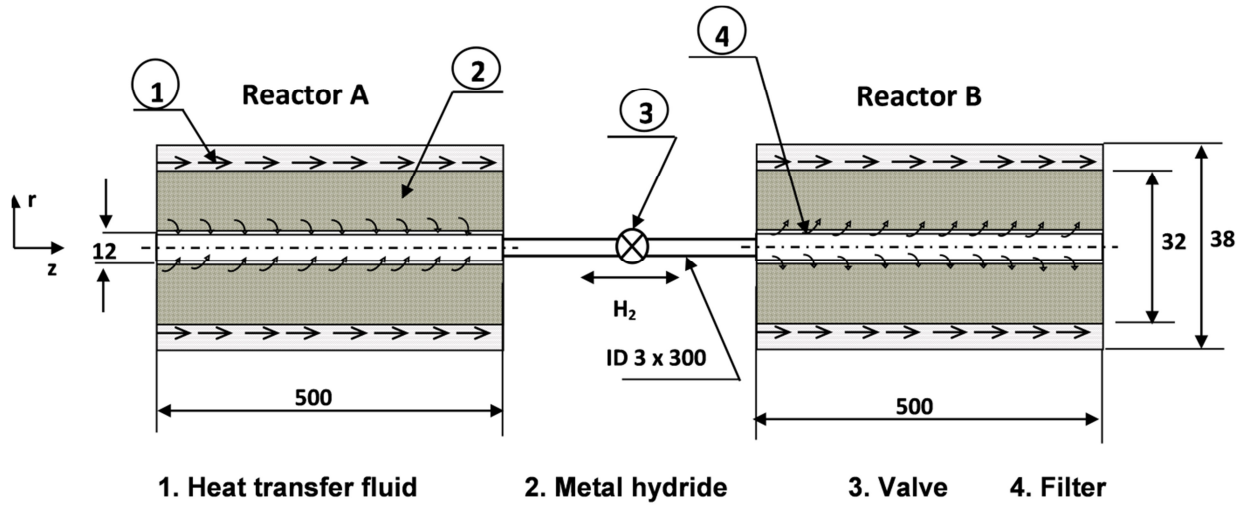
3.1 Single-Stage Metal Hydride Based Heat Transformer (SS-MHHT)

The system of equations are solved computationally for predicting the time dependent conjugate heat and mass transfer characteristics between the coupled reactors. The objectives of the thermal modeling are

- To investigate the variation of hydride bed temperature, hydrogen concentration and equilibrium pressures during coupled desorption and absorption processes.
- To find the temperature lift, the amount of hydrogen exchange between the paired reactors, cycle time, coefficient of performance, specific heating power and the second law efficiency of the system at different operating temperatures.
- To investigate the effects of various operating temperatures, such as heat source (T_M), heat output (T_H) and heat sink (T_L) temperatures on the performances of the SS-MHHT system.

3.1.1 Physical model and principle of operation

Figure 3.1 shows the design details of the coupled metal hydride reaction beds that consists of a pair of similar metal hydride reactors A and B, filled with LaNi_5 and $\text{LaNi}_{4.7}\text{Al}_{0.3}$ respectively.



All dimensions are in mm (not to scale)

Fig. 3.1 Schematic of coupled metal hydride reactors

Each reactor is of 32 mm outer diameter and 500 mm length. The inner porous bed of 12 mm outer diameter and 6 mm internal diameter acts as hydrogen filter. It ensures the instantaneous availability of hydrogen throughout the reaction bed during initial stage of absorption process and also it prevents the hydride particle from being carried away by the hydrogen gas during the desorption process. Metal hydride is filled in the space between the filter and the reactor wall. The heat transfer fluid flows around the the reactor tube (in the annular gap of 3 mm shown in Fig. 3.1). The two reactors are connected by a tube of 3.0 mm inner diameter (1.5 mm thickness) and 300 mm length with a control valve through which the hydrogen is exchanged freely between the reactors. The oprating principle of a SS-MHHT on van't Hoff plot is shown in Fig. 3.2. The operating cycle consists of two coupled heat and mass transfer processes (ab and cd) and two sensible heat transfer processes (bc and da). The system operates in three temperature limits viz., heat output (T_H), heat input or driving heat (T_M) and heat rejection (T_L) and two pressure limits ($P_H > P_L$). The cycle of operation consists of the following four processes.

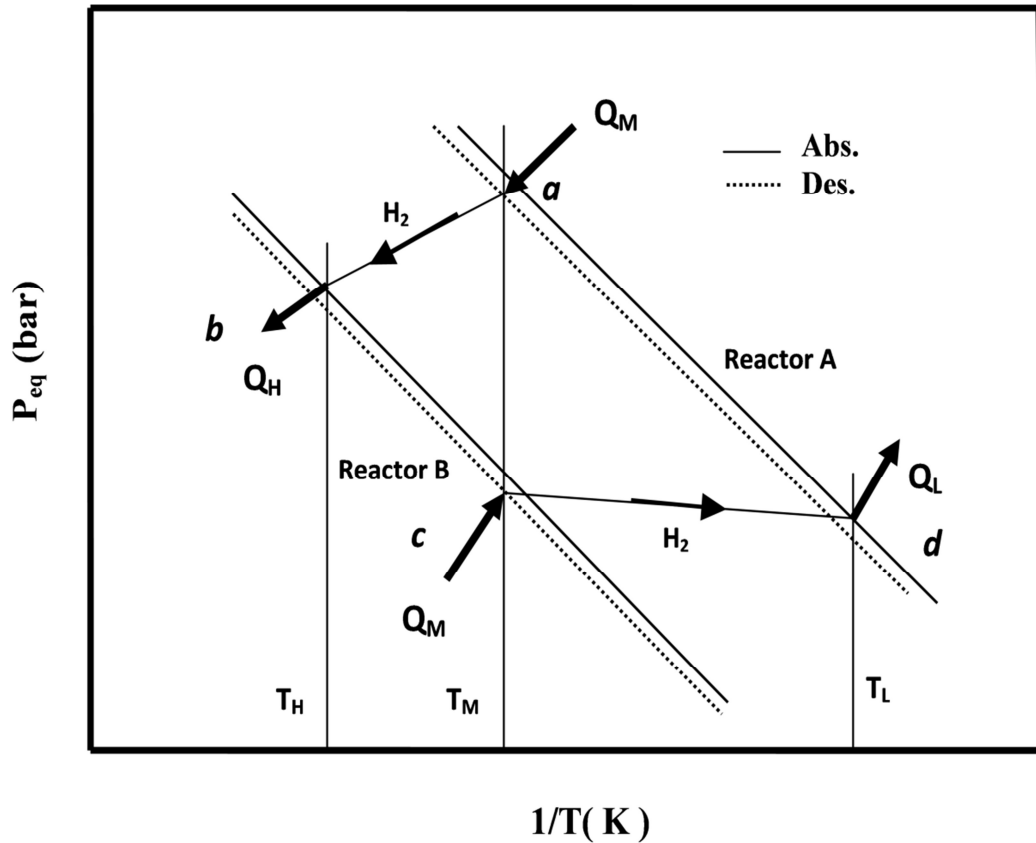


Fig. 3.2 Operation of SS-MHHT on van't Hoff plot

Process *ab* : Initially, the reactor A is fully hydrided and B is fully dehydrided at their respective operating temperatures of T_M and T_H . The operating cycle shows that the two reactors are connected with each other with a connecting valve and the reactor. Since the operating valve is initially closed, the equilibrium pressure difference exists between the reactors. Once the valve is opened, due to the difference in pressure, hydrogen gas starts to desorb from the reactor A by taking heat from the reaction bed and heat transfer fluid, and reactor B starts to absorb hydrogen gas by rejecting the heat of absorption to the reaction bed and heat transfer fluid. This process continues till the fixed amount of hydrogen gas transfers from A to B.

Process *bc* : During this process, the valve between A and B is closed and no hydrogen transfer between the reactors takes place. Only the heat transfer takes place between the hydride bed and

the cooling/heating fluids. This process is continued till the reactors A and B reach T_L and T_M , respectively.

Process *cd* : Once the reactors A and B reach the low and intermediate temperatures, the valve between the reactors is opened. Due to the existence of pressure difference, the hydrogen starts to desorb from the reactor B at medium temperature T_M by extracting the heat of desorption from the reaction bed and heat transfer fluid. Simultaneously, the hydride A absorbs this hydrogen rejecting the heat of absorption to the reaction bed and cooling fluid at the low temperature, T_L . This process continues till the fixed amount of hydrogen is transferred (same as during process *ab*).

Process *da* : During this process the valve is closed. Reactors A and B are sensibly heated to the intermediate temperature T_M and high temperature T_H , respectively, so that at the end of this process the reactors A and B reach the initial conditions of the cycle. Thus the first cycle operation is completed.

3.1.2 Selection of metal hydride pairs

The dependence of the equilibrium pressure, P_{eq} on the reciprocal of the absolute temperature, $1/T$, which is an important characteristic of the two hydrides, is shown in Fig. 3.2. The selected hydride pairs are supposed to operate within the range of specified operating temperatures. In order to ensure good system performance, metal hydrides should meet the following requirements:

High hydrogen storage capacity, low specific heat, high thermal conductivity and fast reaction kinetics. Favorable equilibrium pressure, small hysteresis and flat plateau slope in P - C - T curve are essential. Further, the selected alloy pairs should satisfy the following conditions.

- The minimum desorption pressure of the low temperature alloy (hydride A) at T_M should be greater than the maximum absorption pressure of the high temperature alloy (hydride B) at T_H .
- The minimum desorption pressure of high temperature alloy at T_M should be greater than the maximum absorption pressure of low temperature alloy at T_L .

Based on the above requirements and also the availability of the hydride properties in the literature, four alloy pairs, namely, LaNi₅/ LaNi_{4.7}Al_{0.3} (AP1), MmNi_{4.15}Fe_{0.85} / LaNi_{4.6}Al_{0.4} (AP2), LaNi_{4.61}Mn_{0.26}Al_{0.13}/ La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2} (AP3) and Zr_{0.9}Ti_{0.1}Cr_{0.9}Fe_{1.1} /Zr_{0.9}Ti_{0.1}Cr_{0.6}Fe_{1.4} (AP4) are selected for present investigation. The enthalpy and entropy of formations for the four selected alloy pairs during absorption and desorption processes are given in Table 3.1.

Table 3.1: Enthalpy and entropy of formations of the selected hydride alloy pairs for SS-MHHT

Alloy pairs		ΔH (kJ/mol H ₂)		ΔS (J/mol H ₂ K)		Ref.
		Abs.	Des.	Abs.	Des.	
AP1	LaNi ₅ (A)	28.5	30	103.2	104.7	(Muthukumar <i>et al.</i> 2009)
	LaNi _{4.7} Al _{0.3} (B)	33.9	34.9	105	106.4	
AP2	MmNi _{4.15} Fe _{0.85} (A)	25.3	24.7	105.0	107.0	(Chernikov <i>et al.</i> 2002; Izhvanov <i>et al.</i> 1996)
	LaNi _{4.6} Al _{0.4} (B)	34.8	35.8	113.9	115.6	
AP3	LaNi _{4.61} Mn _{0.26} Al _{0.13} (A)	36.9	37.6	109.7	108.2	(Ni and Liu 2007; Qin <i>et al.</i> 2007)
	La _{0.6} Y _{0.4} Ni _{4.8} Mn _{0.2} (B)	26.9	26.6	102.3	97.4	
AP4	Zr _{0.9} Ti _{0.1} Cr _{0.9} Fe _{1.1} (A)	29.65	34.71	92.0	104.97	(Lee <i>et al.</i> 1995; Park <i>et al.</i> 1990)
	Zr _{0.9} Ti _{0.1} Cr _{0.6} Fe _{1.4} (B)	24.55	29.77	92.0	104.13	

3.1.3 Mathematical model

For simplifying the thermal modeling of the SS-MHHT, the following assumptions are made.

- The local thermal equilibrium between the hydride bed and hydrogen is valid. The assumption of local thermal equilibrium is verified by Jemni and Nasrallah, 1995 by considering two separate energy equations for gas and solid. They observed that the results obtained from the combined energy equation match reasonably well with those obtained from the separate energy equations representing solid and gas mediums.
- Due to the moderate temperature, the heat transfer by radiation within the hydride bed is neglected. Effect of convection term in the energy equation is more significant during the initial stages of the reaction and becomes insignificant as the reaction proceeds.
- Hydrogen is assumed as an ideal gas. Hydrogen gas can be assumed as an ideal gas if the operating pressure is in the range of 0-20 bar (Werner and Groll, 1991). For SS-MHHT, we have assumed hydrogen is an ideal gas. However, for DS-MHHT (operating pressure is in the range of 60 bar), hydrogen is treated as a real gas.
- The thermo-physical properties of hydride alloy are independent of concentration and pressure. The thermo-physical properties such as effective thermal conductivity and specific heat capacity of the hydride beds are the function of hydride concentrations. Due to the non-availability of the data, most of the investigators have considered these properties as constants during absorption and desorption processes (Gopal and Murthy, 1995; Askri et al., 2009; Yang et al., 2011; Mellouli et al., 2009a; Muthukumar and Ramana, 2009; 2010).
- The temperature (T_g) and hydrogen gas pressure (P_g) in the combined space are uniform throughout the connecting tube but they are time dependent.

- Heat transfer between the reactors and the surroundings is neglected.

The hydride equilibrium pressure (P_{eq}) is calculated using the van't Hoff equation [Nishizaki *et al.*, 1983].

$$\frac{P_{eq}}{P_o} = \exp \left[\frac{\Delta S}{R_u} - \frac{\Delta H}{R_u T} + (\phi \pm \phi_o) \tan \left[\pi \left(\frac{X}{X_f} - \frac{1}{2} \right) \right] \pm \frac{\beta}{2} \right] \quad (3.1)$$

where '+' sign is used for hydriding process and '-' used for dehydriding process, X and X_f are the concentration at the given time (t) and final hydrogen concentration in the hydride bed, respectively.

The gas pressure and temperature in the combined gas space immediately after opening the valve are calculated from the following expressions;

$$P_{g,P} = \frac{P_{g,A} V_A + P_{g,B} V_B}{V_A + V_B}, \quad T_{g,P} = \frac{n_A T_A + n_B T_B}{n_A + n_B} \quad (3.2)$$

where V_A and V_B are the volumes of the reactors A and B, respectively. The number of moles of hydrogen in the respective reactors n_A and n_B are calculated using the following perfect gas equation;

$$n_A = \frac{P_A V_A}{R_u T_A}, \quad n_B = \frac{P_B V_B}{R_u T_B} \quad (3.3)$$

The number of moles of hydrogen (n_g), gas temperature (T_g) and pressure (P_g) in the combined gas space at any time ($t+\delta t$) during the hydrogen transfer process are calculated using the following equations;

$$n_{g,t+\delta t} = n_{g,t} + n_d - n_a \quad (3.4)$$

$$T_{g,t+\delta t} = \frac{\left(n_{g,t} - n_a\right)T_{g,a} + n_d T_{g,d}}{n_{g,t} - n_a + n_d} \quad (3.5)$$

$$P_{g,t+\delta t} = \frac{n_{g,t+\delta t} R_u T_{g,t+\delta t}}{V_A + V_B + V_P} \quad (3.6)$$

where, $n_{g,t}$ denotes the number of moles of hydrogen in the connecting tube immediately after opening the valve, and n_a and n_d are the number of moles of hydrogen absorbed by the reactor B and the number of moles of hydrogen desorbed from the reactor A during $t = \delta t$.

As stated in the physical model, the operating cycle consists of two hydrogen transfer processes (ab and cd) and two sensible heat transfer processes (bc and da). The heat and mass transfer rates during the processes ab and cd are estimated by simultaneously solving the continuity and energy equations in both the reactors. The heat transfer rates during the processes bc and da are estimated by solving only the energy equation. These equations are discretized using finite volume method and the details of discretization are presented in Appendix A. In the following sections, the details of heat and mass transfer processes between the coupled reactors are explained.

Process ab

During the process ab , hydrogen is desorbed from the reactor A by taking the heat of desorption from the heat transfer fluid temperature at T_M and the same hydrogen is absorbed by the reactor B by releasing the heat of absorption to the heat transfer fluid at upgraded temperature T_H . In the following subsection, the modeling of coupled heat and hydrogen transfer process between the reactors A and B are discussed.

Reactor A (desorption): Rate of hydrogen (mass flow rate per unit volume) desorption from the reactor A is estimated using following equation (Mayer *et al.*, 1987)

$$\dot{m}_A = C_d \exp\left(\frac{-E_d}{R_u T_A}\right) \left(\frac{P_{eq,A} - P_{g,t+\delta t}}{P_{eq,A}}\right) \rho_{m,A} \quad (3.7)$$

where, P_g is the gas pressure in the combined gas space at any given time (Eq. 3.6) and $\rho_{m,A}$ denotes the density of hydride at any given time t .

Due to the assumption of local thermal equilibrium between the hydrogen and the hydride bed, a combined energy equation is considered for predicting the temperature in the reaction bed (Jemini *et al.*, 1995).

$$(\rho C_p)_e \frac{\partial T}{\partial t} + (\rho C_p)_g \vec{u} \cdot \nabla T = \lambda_e \nabla^2 T - \dot{m}_A \left[\frac{\Delta H}{M_g} - T(C_{p,g} - C_{p,m}) \right] \quad (3.8)$$

where

$$(\rho C_p)_e = (\varepsilon \rho C_p)_g + ((1 - \varepsilon) \rho C_p)_m \quad (3.9)$$

and the effective thermal conductivity is given by;

$$\lambda_e = \varepsilon \lambda_g + (1 - \varepsilon) \lambda_m \quad (3.10)$$

The hydrogen mass balance is expressed as;

$$\varepsilon \frac{\partial (\rho_g)}{\partial t} + \nabla \cdot (\rho_g \vec{u}_g) = \dot{m}_A \quad (3.11)$$

where ρ_g denotes the density of the hydrogen in the reactor A and it is calculated using the perfect gas law. The velocity of hydrogen gas is determined using the Darcy's law (creeping flow);

$$\vec{u}_g = -\frac{K}{\mu_g} \nabla P_g. \quad (3.12)$$

By substituting the values of u_g and ρ_g in Eq. (3.11), the gas pressures (P_g) inside the reactor at different radial and axial location are calculated using the following equation.

$$\left(\frac{\varepsilon M_g}{R_u T} \right) \frac{\partial P_g}{\partial t} + \left(\frac{\varepsilon M_g P_g}{R_u} \right) \frac{\partial}{\partial t} \left(\frac{1}{T} \right) - \frac{K}{v_g r} \frac{\partial}{\partial r} \left(r \frac{\partial P_g}{\partial r} \right) - \frac{K}{v_g} \frac{\partial}{\partial z} \left(\frac{\partial P_g}{\partial z} \right) = \dot{m}_A. \quad (3.13)$$

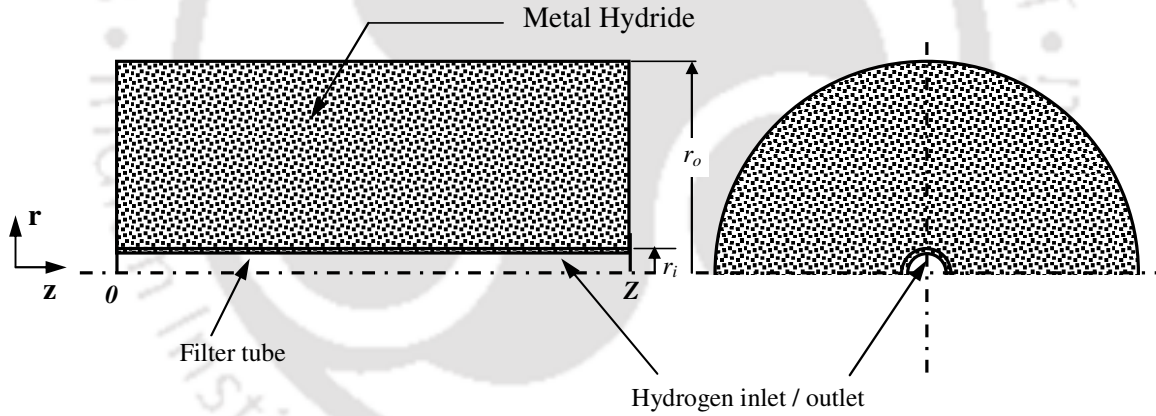


Fig. 3.3 Boundary conditions used for the numerical analysis.

Initial and boundary conditions: Initially at time $t = 0$; the hydride concentration, the temperatures of the hydrogen gas and metal hydride and the density of the metal hydride are assumed to be uniform throughout the reactor bed. They are given by;

$$\rho_{m,A}(z, r) = \rho_{ss}; \quad T_{m,A}(z, r) = T_{g,A}(z, r) = T_M; \quad X_A(z, r) = X_{\max,A}. \quad (3.14)$$

The right and left boundaries of the reactor are considered as adiabatic (shown in Fig. 3.3)

$$\frac{\partial P_g}{\partial z}(z, r, t)_{z=0} = 0; \quad \frac{\partial P_g}{\partial z}(z, r, t)_{z=Z} = 0; \quad \frac{\partial T}{\partial z}(z, r, t)_{z=0} = 0; \quad \frac{\partial T}{\partial z}(z, r, t)_{z=Z} = 0. \quad (3.15)$$

At the bottom wall (along the porous filter), gas pressure is uniform throughout the length of the reactor;

$$P_g(z, r_i, t) = P_g. \quad (3.16)$$

The heat transfer fluid flows around the reaction bed tube and therefore the convective boundary condition is applied at top boundary $r = r_o$.

$$-\lambda_e \frac{\partial T}{\partial r}(z, r_o, t) = U (T_{z, r_o, t} - T_f) \quad (3.17)$$

where T_f and $T_{(z, r_o, t)}$ denote the temperature of the heat transfer fluid and the temperature of the bed at the interface of its convective boundary, respectively. Most of the investigators assumed that the temperature of the heat transfer fluid is constant along the axial direction (Kang *et al.*, 1995, Gopal and Murthy 1995c and Yang *et al.* 2011). However, in practice, due to the limitation of heat transfer fluid flow rate, there will be a variation in the heat transfer fluid temperature along the axial direction and hence, the variable wall temperature convective boundary condition (non-isothermal convective boundary condition) is considered in the present study. The variation in the heat transfer fluid along the axial direction is updated using the following equation (Muthukumar and Ramana, 2009e).

$$\frac{dQ}{dt} = m_f C p_f (T_{f_o} - T_{f_i}) \quad (3.18)$$

$$\frac{dQ}{dt} = UA\Delta T_{lm} = UA \frac{T_{fo} - T_{fi}}{\ln \left[\frac{T_{z,r_o,t} - T_{fi}}{T_{z,r_o,t} - T_{fo}} \right]} \quad (3.19)$$

$$T_{z,r_o,t} - T_{fo} = (T_{z,r_o,t} - T_{fi}) \exp \left(-\frac{UA}{m_f C p_f} \right) \quad (3.20)$$

$$T_{fo} = T_{fi} + [T_{z,r_o,t} - T_{fi}] \left[1 - \exp \left(-\frac{UA}{m_f C p_f} \right) \right]. \quad (3.21)$$

Reactor B (Absorption): The rate of hydrogen absorption by the reactor B is expressed as (Mayer *et al.*, 1987)

$$\dot{m}_B = C_a \exp \left(\frac{-E_a}{R_u T_B} \right) \ln \left(\frac{P_{g,t+\delta t}}{P_{eq,B}} \right) (\rho_{ss} - \rho_{m,B}). \quad (3.22)$$

The hydride equilibrium pressure (P_{eq}) is calculated from Eq. (3.1). The temperature of the reactor B is updated by solving the following energy equation;

$$(\rho C_p)_e \frac{\partial T}{\partial t} + (\rho C_p)_g \vec{u} \cdot \nabla T = \lambda_e \nabla^2 T + \dot{m}_B \left[\frac{\Delta H}{M_g} - T (C_{P,g} - C_{P,m}) \right]. \quad (3.23)$$

The mass balance during absorption of hydrogen in the reactor B is given by;

$$\epsilon \frac{\partial (\rho_g)}{\partial t} + \nabla \cdot (\rho_g \vec{u}_g) = -\dot{m}_B \quad (3.24)$$

Hydrogen gas pressure in the reactor B is calculated in the same way as for the reactor A using Eq. (3.13).

Initial and Boundary Conditions: The initial condition of the reactor B at time $t = 0$ is given as

$$\rho_{m,B}(z,r) = \rho_i; \quad T_{m,B}(z,r) = T_{g,B}(z,r) = T_H; \quad X_B(z,r) = X_{\min,B}. \quad (3.25)$$

The boundary conditions of reactor B are similar to those for the reactor A. The initial conditions stated above are used only at the first cycle.

Process bc

During this process, the control valve remains closed. Hence, there is no hydrogen transfer between the reactors A and B and only sensible heat exchange takes place between the hydride bed and the heat transfer fluid. The change in the hydride bed temperature during the sensible cooling process is estimated using the following energy equation. The final condition of process *ab* is taken as the initial condition of the process *bc*.

$$(\rho C_p)_e \frac{\partial T}{\partial t} + (\rho C_p)_g \vec{u} \cdot \nabla T = \lambda_e \nabla^2 T. \quad (3.26)$$

Process cd

During this process, the hydrogen is exchanged from the reactor B to the reactor A at low pressure. The governing equations and boundary conditions used in this process are similar to those for the process *ab* and however, the boundary temperatures are different. The final condition of the process *bc* is taken as the initial condition of the process *cd*.

Process da

During this process, the reactors A and B are sensibly heated to T_M and T_H , respectively. Using Eq. (3.26), the temperature of the hydride bed is updated. The final condition of this process is the initial condition of the process *ab* of second cycle.

3.1.4 Performance analysis

The performance of a SS-MHHT is defined in terms of coefficient of performance (COP_{HT}), specific heating power (SHP) and second law efficiency (η_E). The COP_{HT} is defined as follows;

$$COP_{HT} = Q_H / Q_M \quad (3.27)$$

$$\text{where } Q_H = Q_{B,ab} - Q_{B,da} \quad (3.28)$$

Q_H denotes the heat output obtained at the heat output temperature, T_H . Q_M is the heat input at T_M . $Q_{B,ab}$ and $Q_{B,da}$ are the energy transfers between the heat transfer fluid and the hydride bed B during the processes ab and da , respectively. These quantities are defined as;

$$Q_{B,ab} = n_{B,ab} \Delta H_{B,ab} \quad (3.29)$$

$$Q_{B,da} = (m_B + m_r) C_{pB} (T_H - T_M) \quad (3.30)$$

where, m_B and m_r denote the masses of metal hydride and reactor, respectively and the ratio between them is assumed to be 2. The energy supplied at the medium temperature, T_M is given by

$$Q_M = Q_{A,ab} + Q_{A,da} + Q_{B,cd} \quad (3.31)$$

where, $Q_{A,ab}$, $Q_{B,cd}$ and $Q_{A,da}$ are the energy supplied to the reactors A and B during the processes ab , cd and da , respectively and the respective quantities are defined as follows;

$$Q_{A,ab} = n_{A,ab} \Delta H_{A,ab} \quad (3.32)$$

$$Q_{B,cd} = n_{B,cd} \Delta H_{B,cd} \quad (3.33)$$

$$Q_{A,da} = (m_A + m_r) C_{pA} (T_M - T_L) \quad (3.34)$$

The specific heating power (*SHP*) plays a significant role in the performance of SS-MHHT. It is defined as the net heat output obtained over a cycle per unit mass of alloy.

$$SHP = Q_H / m \times t_{cy} \quad (3.35)$$

where m is total hydride mass (mass of hydride A and hydride B) and t_{cy} is the total cycle time.

The second-law efficiency (η_E), which expresses the performance of the system with reference to its performance under reversible conditions, is defined as;

$$\eta_E = \frac{COP_{HT}}{COP_{Carnot}} \quad (3.36)$$

The COP_{Carnot} for SS- MHHT is defined as

$$COP_{Carnot} = \frac{\left(1 - \frac{T_L}{T_M}\right)}{\left(1 - \frac{T_L}{T_H}\right)} \quad (3.37)$$

3.1.5 Solution methodology

The solution of the above-mentioned mathematical model is obtained using the fully implicit finite volume method. The solution procedure of this system begins with the process ab and ends with the process da , so that the simulation of one complete cycle is carried out. Initially, the metal hydride heat transformer system is in equilibrium and pressures inside the reactors A and B are found by using Eq. (3.1). Once the valve is opened, hydrogen gas is desorbed from the reactor A and it is absorbed in the reactor B. This process is continued until a predefined quantity of hydrogen gas is desorbed from the reactor A.

The following convergence criteria's are employed in the mathematical model.

- For the coupled heat and hydrogen transfer processes (ab and cd), the hydrogen exchange between two consecutive time steps becomes less than 0.001 g.
- For the sensible heat transfer processes (bc and da), the difference between the average hydride bed temperature and the heat transfer fluid temperature becomes less than 1°C.

Time-dependent study for the present analysis is carried out for different time steps ($\Delta t = 10^{-5}$ s, 10^{-4} s and 10^{-3} s) and a negligible deviation is observed. Hence, a time step of 10^{-3} s is taken for further analyses. To find the variation in the cycle time between constant and variable convective wall temperature boundary conditions, the average hydride bed temperature is calculated at $z/Z = 0.95$. The end conditions of the sensible heating process are taken as the initial conditions of the first process of the next cycle. The cycle is repeated till the processes reach stable state and then the computed values are presented. Further, the effects of operating temperatures, such as heat source (T_M), heat output (T_H), heat rejection (T_L) temperatures on the performance of SS-MHHT are also presented.

Table 3.2: Operating temperature range for the selected alloy pairs of SS-MHHT

Parameters	AP1	AP 2	AP 3	AP 4
$*T_H$ (K)	413/428	403/388	393/378	408/393
$*T_M$ (K)	378/393	383/368	368/353	373/358
$*T_L$ (K)	298/313	298/313	298/313	298/313

* Operating range (maximum/minimum temperatures)

Table 3.2 lists the operating parameter ranges used in the present analysis. Specific heat capacity (419 J/kg K) and porosity (0.5) of the hydride beds are assumed as constant during both absorption and desorption processes. The initial density of the hydride alloy (with minimum

hydride concentration) is taken as 8400 kg/m^3 and this value is updated in each time step during the absorption and desorption processes. Table 3.3 lists the reaction rate constants and the activation energies of the selected alloy pairs. The properties of hydrogen are listed in Table 3.4.

Table 3.3 The reaction rate constants and activation energies of the selected metal hydrides for SS-MHHT (Satheesh, 2011)

Alloy pairs		Reaction rate constant (s^{-1})		Activation energy (kJ/mol H_2)	
		Abs.	Des.	Abs.	Des.
AP1	LaNi ₅ (A)	150	75	32.0	32.0
	LaNi _{4.7} Al _{0.3} (B)	250	120	30.0	30.0
AP2	MmNi _{4.15} Fe _{0.85} (A)	300	40	26.0	25.0
	LaNi _{4.6} Al _{0.4} (B)	185	20	35.0	32.0
AP3	LaNi _{4.61} Mn _{0.26} Al _{0.13} (A)	230	25	35.0	32.5
	La _{0.6} Y _{0.4} Ni _{4.8} Mn _{0.2} (B)	180	55	30.0	27.0
AP4	Zr _{0.9} Ti _{0.1} Cr _{0.9} Fe _{1.1} (A)	145	20	30.0	25.5
	Zr _{0.9} Ti _{0.1} Cr _{0.6} Fe _{1.4} (B)	265	45	26.0	23.5

Table 3.4 Properties of hydrogen gas (NTP condition)

Thermal conductivity of hydrogen (W/ m-K)	0.1272
Specific heat hydrogen (J/ kg-K)	14283
Density of hydrogen (kg/m^3)	0.0838

3.2 Double-Stage Metal Hydride Based Heat Transformer (DS-MHHT)

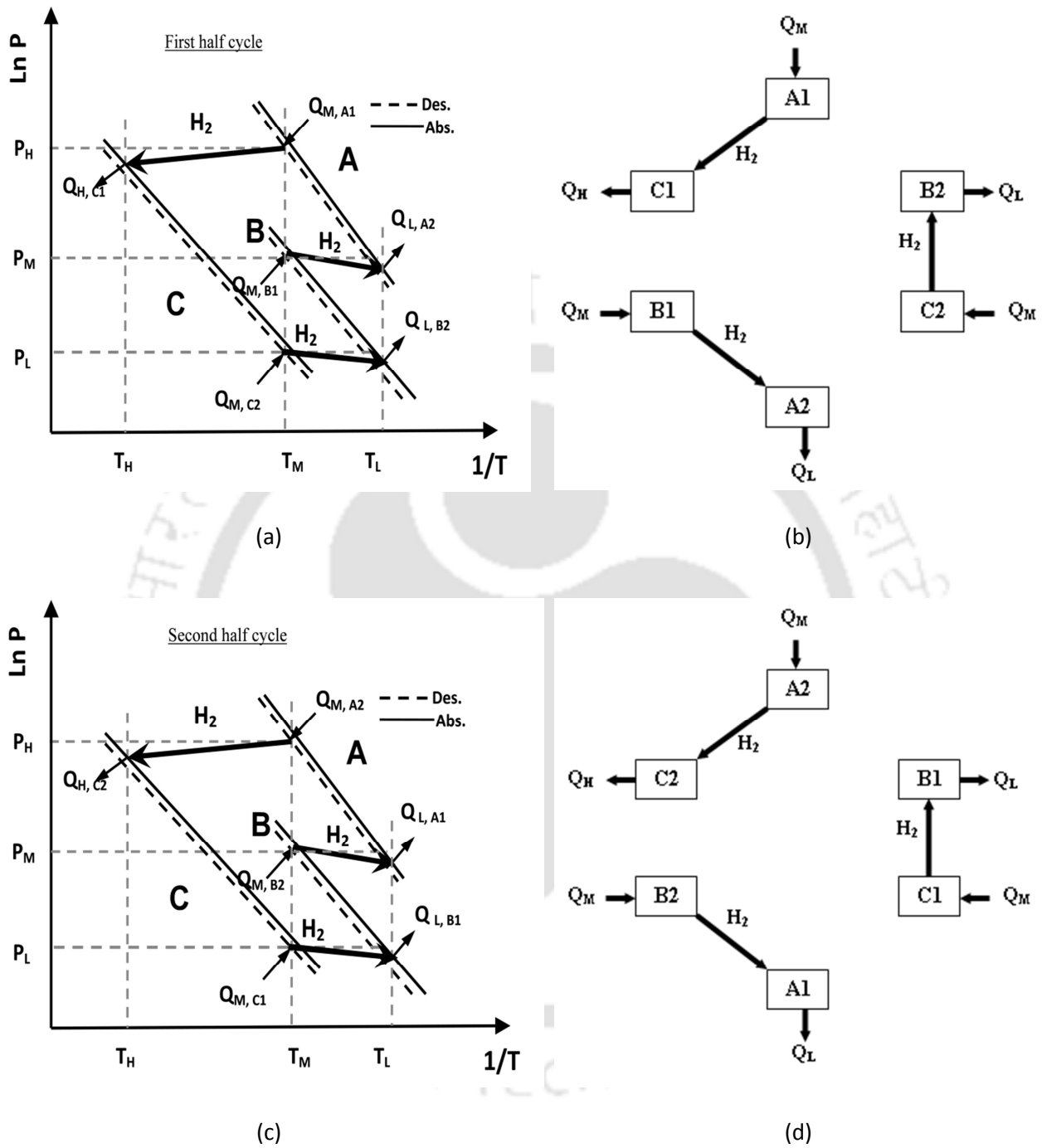
The SS-MHHT is restricted to the temperature lift of about $< 50^\circ\text{C}$. For high temperature lift ($> 50^\circ\text{C}$), multi-stage metal hydride based heat transformer is required. The performance of a DS-

MHHT is predicted by simultaneously solving the continuity and energy equations. Similar to the modeling of SS-MHHT, the effects of both conduction and convection heat transfers are included in the energy equation. The variation in the heat transfer fluid temperature along the axial direction is also considered.

3.2.1 Physical model and principle of operation

Figure 3.4 shows the operating principle of a DS-MHHT on ideal van't Hoff plot. The system consists of six reactors, namely, A1, A2, B1, B2, C1 and C2. Each alloy is filled in two reactors. Reactors A1 and A2 contain high pressure alloy $\text{MmNi}_{4.6}\text{Al}_{0.4}$, reactors B1 and B2 contain medium pressure alloy LaNi_5 and reactors C1 and C2 contain low pressure alloy $\text{LaNi}_{4.7}\text{Al}_{0.3}$. The operation of the cycle is explained below:

Step1: Fig. 3.4 (a, b) illustrates the operating of DS-MHHT during first half cycle. Initially, reactors A1, B1 and C2 are fully hydrided at heat source temperature T_M , reactors B2 and A2 are fully dehydrided at heat sink temperature T_L and reactor C2 is fully dehydried at heat output temperature T_H . To begin with, reactors A1 and C1, C2 and B2, and B1 and A2 are connected to each other so that the hydrogen transfer can take place freely between them. Reactor A1 desorbs hydrogen by taking the heat ($Q_{M, A1}$) at T_M which gets absorbed by reactor C1 at high pressure, thereby forming the hydride and releasing the heat of absorption at high temperature, T_H . This high temperature heat ($Q_{H, C1}$) is the output from the system. During the same period, reactors C2 and B1 desorb hydrogen by taking the heat ($Q_{M, C2}$ and $Q_{M, B1}$) at temperature, T_M and the desorbed hydrogen are respectively absorbed by reactors B2 and A2 at T_L by releasing $Q_{L, B2}$ and $Q_{L, A2}$.



(a) Ideal van't Hoff plot for first half cycle (b) Hydrogen transfer in the first half cycle
(c) Ideal van't Hoff plot for second half cycle (d) Hydrogen transfer in the second half cycle

Fig. 3.4 Operation of DS-MHHT on van't Hoff plot

This process will continue till a pre-determined amount of hydrogen exchange takes place between the paired reactors. Thus, the system completes the first half cycle. Now, the valves between the coupled reactors are closed.

Step 2: In this sensible heat transfer process, reactors A2 and B2 are heated to T_M , while reactor C2 is heated to T_H . The other reactors, A1 and B1 are cooled down to T_L , while reactor C1 is cooled to T_M . At the end of this process, reactors positions will be interchanged. i.e. A1 to A2, B1 to B2 and C1 to C2.

Step 3: The hydrogen transfer processes during the second half cycle are similar to the first half cycle (shown in Fig. 3.4 (c, d)). Heat input ($Q_{M, A2}$) is supplied at T_M to desorb the hydrogen from reactor A2, which is absorbed by reactor C2 liberating the useful heat ($Q_{H, C2}$) at high temperature, T_H . During the same period, reactors C1 and B2 desorb hydrogen by taking heat ($Q_{M, C1}$ and $Q_{M, B2}$) at T_M and the desorbed hydrogen are respectively absorbed by reactors B1 and A1 by rejecting the heat at T_L . This process will continue till a pre-determined amount of hydrogen exchange takes place between the paired reactors. Now, the valves between the coupled reactors are closed.

Step 4: Finally, reactors A1 and B1 are heated to T_M , while reactor C1 is heated to T_H . The other reactors, A2 and B2 are cooled down to T_L , while reactor C2 is cooled to T_M . All the reactors come to their initial respective operating temperatures for continuing the next cycle of operation.

3.2.2. Selection of alloys

Performance of the DS-MHHT system is characterized by COP_{HT} and SHP . These parameters mainly depend on the thermo-chemical properties of the alloys employed and also the coupled

heat and mass transfer characteristics of the paired reaction beds. In general, the low pressure alloy should have high enthalpy of formation and the high and medium pressure alloy must have low enthalpy of formation. All the three alloys should have high hydrogen storage capacity, low specific heat, high thermal conductivity and fast reaction kinetics. Favorable equilibrium pressure, small hysteresis and flat plateau slope in P - C - T curve are essential. Based on the above requirements and also the availability of the hydride properties in the literature, three alloys namely $\text{LaNi}_{4.7}\text{Al}_{0.3}$, LaNi_5 and $\text{MmNi}_{4.6}\text{Al}_{0.4}$ are selected for present investigation.

3.2.3. Mathematical model

The following assumptions are made for simplifying the thermal modeling of the DS-MHHT.

- The local thermal equilibrium between the hydride bed and hydrogen is valid.
- Due to the moderate temperature, the heat transfer through the hydride bed is mainly by conduction and convection. The radiation heat transfer is neglected.
- Initially all the reactors are in equilibrium with the hydrogen gas.
- The thermo-physical properties of hydride alloy and hydrogen are constant.
- There is no heat transfer between the hydride reactor and the surroundings.
- There is no heat transfer through the inner most tube (porous filter).

First half cycle

As explained in the operating principle, hydrogen exchange takes place between three pair of reactors simultaneously during the first of cycle.

- Reactor A1 desorbs hydrogen by taking the heat ($Q_{M, A1}$) at T_M and reactor C1 absorbs by liberating heat ($Q_{H, C1}$) at T_H .
- Reactor B1 desorbs hydrogen by taking the heat ($Q_{M, B1}$) at T_M and reactor A2 absorbs by liberating heat ($Q_{L, A2}$) at T_L .
- Reactor C2 desorbs hydrogen by taking the heat ($Q_{M, C2}$) at T_M and reactor B2 absorbs by liberating heat ($Q_{L, B2}$) at T_L .

In the following section the mathematical modeling of the hydrogen exchange process between the reactors A1 and C1 is explained. The same procedure is repeated for the remaining hydrogen exchange processes between the reactors C2 and B1 and, B2 and A2. The above-mentioned processes are modeled by simultaneously solving the continuity and energy equations for the respective reactor pairs. As already stated, initially all the reactors are assumed to be in equilibrium with respect to the hydrogen gas. Therefore, the equilibrium pressure P_{eq} (bar) is calculated using the van't Hoff equation (Eq. 3.1).

After opening the valve, the gas pressure and temperature in the combined gas space are calculated from the following expressions;

$$P_{g,P} = \frac{P_{g,A1}V_A + P_{g,C1}V_{C1}}{V_{A1} + V_{C1}}, \quad T_{g,P} = \frac{n_{A1}T_{A1} + n_{C1}T_{C1}}{n_{A1} + n_{C1}} \quad (3.38)$$

where V and n denote the free volume (m^3) and the number of moles of hydrogen gas in the respective reactors (A1 and C1). n_{A1} and n_{C1} can be calculated using the real gas equation.

$$n_{A1} = \frac{P_{A1}V_{A1}}{Z R_u T_{A1}}; \quad n_{C1} = \frac{P_{C1}V_{C1}}{Z R_u T_{C1}}; \quad (3.39)$$

where, Z denotes the compressibility factor and it is expressed as a function of pressure and temperature

$$Z = f(p, T) = 1 + (B_0 + B_1T + B_2T^2)P + (C_0 + C_1T + C_2T^2)P^2 \quad (3.40)$$

where the constants B_0 , B_1 , B_2 , C_0 , C_1 and C_2 were taken from the literature (Friedlmeier, 1997)

$$\begin{aligned} B_0 &= 0.00962 \text{ MPa}^{-1} & B_1 &= -15.446 \times 10^{-6} \text{ MPa}^{-1} \text{ K}^{-1} & B_2 &= 82.314 \times 10^{-10} \text{ MPa}^{-1} \text{ K}^{-2} \\ C_0 &= 18.167 \times 10^{-5} \text{ MPa}^{-2} & C_1 &= -83.222 \times 10^{-8} \text{ MPa}^{-2} \text{ K}^{-1} & C_2 &= 9.527 \times 10^{-10} \text{ MPa}^{-2} \text{ K}^{-2} \end{aligned}$$

Eq. (3.40) is valid in the pressure and temperature ranges $0.1 < P \leq 10 \text{ MPa}$ and $280 \leq T \leq 573 \text{ K}$, respectively.

The number of moles of hydrogen present in the gas space (n_g), gas temperature (T_g) and gas pressure (P_g) in the connecting pipe at any time during the hydrogen transfer process are calculated using Eqs. (3.4 to 3.6) (similar to SS-MHHT's model). As explained in the physical model, desorption of hydrogen and temperature of the hydride bed A1 are estimated using the reaction kinetics (Eq. 3.7) and energy equations (Eq. 3.8). Gas pressure at the reactor A1 is calculated using the mass balance equation (Eq. 3.11). By substituting the values of density and velocity of hydrogen gas into the hydrogen mass balance equation, the gas pressure in the hydride bed can be estimated using Eq. (3.41).

$$\begin{aligned} &\left(\frac{\varepsilon M_g}{Z R_u T} \right) \frac{\partial P_g}{\partial t} + \left(\frac{\varepsilon M_g P_g}{Z R_u} \right) \frac{\partial}{\partial t} \left(\frac{1}{T} \right) - \left[\frac{2a}{T} (1 + P_g) \right] \frac{\partial^2 P_g}{\partial r^2} - \left[\frac{a}{T} (1 + P_g) \right] \frac{\partial^2 P_g}{\partial z^2} - 2a P_g \frac{\partial P_g}{\partial r} \frac{\partial}{\partial r} \left(\frac{1}{T} \right) \\ &- a P_g \frac{\partial P_g}{\partial z} \frac{\partial}{\partial z} \left(\frac{1}{T} \right) - \frac{2a P_g}{r T} \frac{\partial P_g}{\partial r} = \dot{m}_A \end{aligned} \quad (3.41)$$

where,

$$a = \frac{KM_g}{Z\mu_g R_u} \quad (3.42)$$

where, M_g , K and μ_g denote the molecular weight of the hydrogen gas, the permeability in Darcy's law and the dynamic viscosity of the hydrogen gas, respectively.

Initial and Boundary Conditions (Desorption): Initially ($t = 0$), all the reactors (A1, A2, B1, B2, C1 and C2) are in the equilibrium with hydrogen at their respective operating temperatures. Hydride density, temperature and concentration of the reactor A1 are given by

$$\rho_{m,A1}(z, r) = \rho_{ss}; \quad T_{m,A1}(z, r) = T_{g,A1}(z, r) = T_M; \quad X_{A1}(z, r) = X_{\max,A1}. \quad (3.43)$$

The boundary conditions applied at the left, right and bottom walls are similar to the SS-MHHT (Eqs. 3.15 to 3.16). The effect of variation in heat transfer fluid temperature along the axial direction during absorption and desorption of hydrogen was studied in the SS-MHHT (Sekhar *et al.*, 2012). It was observed that the constant wall temperature convective boundary condition over predicts the numerical results. Hence, the variable wall temperature convective boundary condition is considered in the DS-MHHT. The mass flux, temperature of the hydride bed and gas pressure at the reactor C1 are found in the same way as for the absorbing hydride (reactor B) in the SS-MHHT.

Initial and boundary conditions (Absorption): The initial condition of the reactor C1 at time $t = 0$ is given as

$$\rho_{m,C1}(z, r) = \rho_i; \quad T_{m,C1}(z, r) = T_{g,C1}(z, r) = T_H; \quad X_{C1}(z, r) = X_{\min,C1}. \quad (3.44)$$

The boundary conditions of the reactor C1 are same as like reactor A1.

Sensible heat transfer process

The change in the hydride bed temperature during the sensible heating/cooling process is estimated using the following energy equation.

$$\left(\rho C_p\right)_e \frac{\partial T}{\partial t} + \left(\rho C_p\right)_g \vec{u} \cdot \nabla T = \lambda_e \nabla^2 T. \quad (3.45)$$

The initial conditions of the sensible heat transfer processes are used as the final conditions of the previous desorption/absorption processes.

Second half cycle

Modeling of second half cycle is similar to the first half cycle, however hydrogen exchange between the paired reactors will takes place in the following sequence;

- Reactor A2 desorbs hydrogen by taking the heat ($Q_{M, A2}$) at T_M and reactor C2 absorbs by liberating heat ($Q_{H, C2}$) at T_H .
- Reactor B2 desorbs hydrogen by taking the heat ($Q_{M, B2}$) at T_M and reactor A1 absorbs by liberating heat ($Q_{L, A1}$) at T_L .
- Reactor C1 desorbs hydrogen by taking the heat ($Q_{M, C1}$) at T_M and reactor B1 absorbs by liberating heat ($Q_{L, B1}$) at T_L .

The governing equations and the boundary conditions are similar to first half cycle. Finally all the reactors are sensibly heated/ cooled to respective temperatures. Using Eq. (3.45), the temperature of the hydride bed is updated. The final condition of first cycle is the initial condition of the next cycle.

3.2.4 Performance analysis

The performances of the DS-MHHT system are defined by the coefficient of performance (COP_{HT}) and the specific heating power (SHP). These parameters are defined as;

$$COP_{HT} = \frac{Q_{H,C1}}{Q_{M,A1} + Q_{M,B1} + Q_{M,C2}} \quad (3.46)$$

where, $Q_{H,C1}$ denotes the heat output obtained from reactor C1 ($Q_{H,C2}$ during second half cycle). $Q_{M,A1}$, $Q_{M,B1}$ and $Q_{M,C2}$ are the heat supplied to the reactors A1, B1 and C2, respectively.

Heat output from reactor C1 is calculated as;

$$Q_{H,C1} = n_{a,C1} \Delta H_{a,C1} - [C_{p,C1} m_{C1} (T_H - T_M)] \quad (3.47)$$

where, $n_{a,C1}$ denotes the number of moles of hydrogen absorbed in reactor C1. Similarly, the heat output obtained from the reactor C2 can be estimated.

Heat supplied to reactor A1 is calculated as;

$$Q_{M,A1} = n_{d,A1} \Delta H_{d,A1} + [C_{p,A1} m_{A1} (T_M - T_L)] \quad (3.48)$$

Similarly, the heat supplied to the reactors B1 and C2 are calculated. The net COP_{HT} of the system is estimated as;

$$COP_{HT} = \frac{(Q_{H,C1} + Q_{H,C2})}{(Q_{M,A1} + Q_{M,B1} + Q_{M,C2}) + (Q_{M,A2} + Q_{M,B2} + Q_{M,C1})} \quad (3.49)$$

The specific heating power (SHP) is defined as the net heat output obtained over a cycle per unit mass of alloy.

$$SHP = \frac{(Q_{H,C1} + Q_{H,C2})}{m \times t_{cy}} \quad (3.50)$$

where, m denote the hydride mass and t_{cy} denotes the total cycle time.

The second-law efficiency (η_E) is defined as

$$\eta_E = \frac{COP_{HT}}{COP_{Carnot}} \quad (3.51)$$

The COP_{Carnot} for DS-MHHT is defined as

$$COP_{Carnot} = \frac{\left(1 - \frac{T_L}{T_M}\right)}{\left(1 - \frac{T_L}{T_H}\right)} \quad (3.52)$$

HTF temperature difference (ΔT_{HTF})

The difference between heat output temperature (T_H) and heat source temperature (T_M) is usually called “temperature lift”. However, this definition does not provide any practical usability of the heat output. It is well known that the HTF outlet temperature varies temporally due to dynamic heat effects from the absorption/desorption reaction kinetics. Hence, the HTF temperature difference (outlet-inlet) varies from zero at the start of the cycle to maximum; and then again it reaches to zero at the end of the process. Yang *et al.* (2012) introduced a new terminology called “true temperature lift”, which is defined as the difference between outlet and inlet temperatures of the HTF during the heat output process. However, this temperature difference solely depends on the mass flow rate and specific heat capacity of the heat transfer fluid. Therefore, the transient HTF temperature difference (ΔT_{HTF}) is also predicted at different operating temperatures from the thermal model.

Table 3.5 lists the physical and thermo-physical properties of the selected metal hydride alloys, and constants employed in the mathematical model.

Table 3.5: Physical and thermo-physical properties of the metal hydrides and constants employed in the model (Kodama, 1999; Muthukumar *et al.*, 2012b)

Properties		LaNi ₅	MmNi _{4.6} Al _{0.4}	LaNi _{4.7} Al _{0.3}
Enthalpy of reaction (kJ/mol H ₂)	abs	28.5	29	33.9
	des	30	28	34.9
Entropy of reaction, (J/mol H ₂ -K)	abs	103.2	107.2	105
	des	104.7	108.7	106.4
Effective density, kg/m ³		4150	4200	4200
Molecular weight, kg/k mole of alloy		432.45	434	422.9
Activation energy, kJ/mole		32	30	31.4
Specific heat, (J/kg K)		419	419	419
Permeability (m ²)		10 ⁻¹²	10 ⁻¹²	10 ⁻¹²

Chapter 4

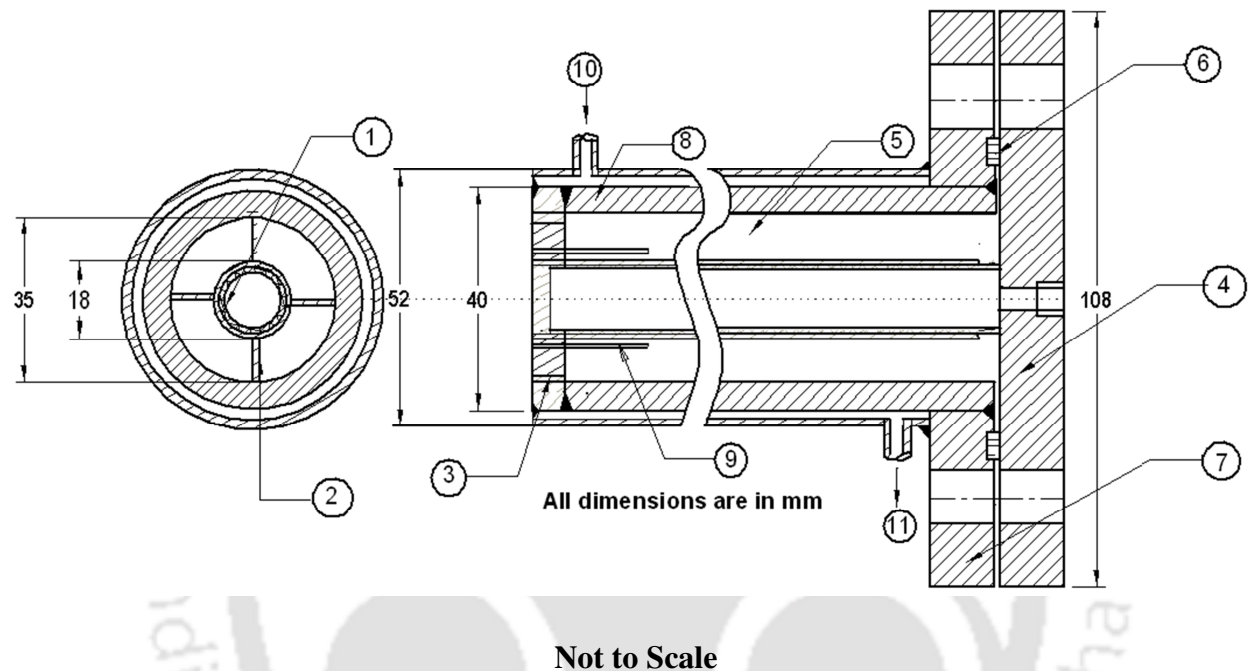
EXPERIMENTAL SET UP

In this chapter, the details of experimental setup used for testing the performances of metal hydride based heat transformer and hydrogen compressor are presented. The major objectives of these studies are:

- To validate the thermal model developed for predicting performance of single-stage metal hydride based heat transformer.
- To study the performance of a single-stage metal hydride based heat transformer.
- To study the performance of a double-stage metal hydride based hydrogen compressor.
- To study the performance of a double-stage metal hydride based heat transformer.

4.1 Details of Metal Hydride Reactor

4.1.1 Design of the reactor



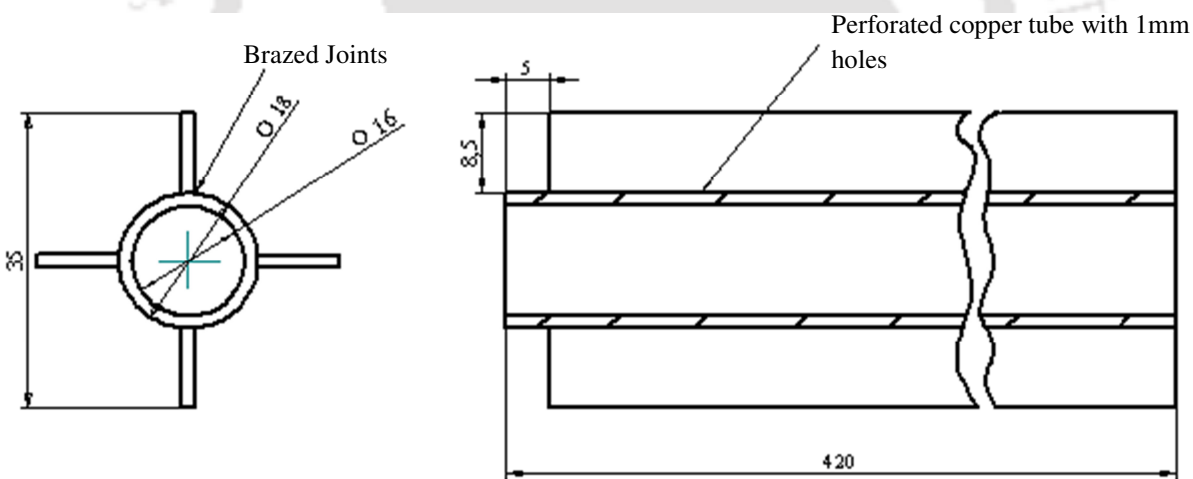
- | | | | | |
|----------------------------|-----------------------------|--------------------------|-----------------|------------------|
| 1. Filter | 2. Copper fins | 3. End plate | 4. Outer flange | 5. Metal hydride |
| 6. Teflon washer | 7. Inner flange | 8. Reactor (SS-316 tube) | 9. Thermocouple | |
| 10. Heat transfer fluid in | 11. Heat transfer fluid out | | | |

Fig. 4.1 Schematic diagram of the metal hydride reactor.

Figure 4.1 shows the schematic of the cylindrical metal hydride reactor used for the experimental study. The reactor body is made with stainless steel tube (SS-316) of inner diameter 35 mm and outer diameter 40 mm. Provisions to hold two thermocouples are given at the end plate, which is permanently TIG welded with the main body. The holes for the thermocouples are provided so that the thermocouples will be fitted at a distance of 8.5 mm each from the radial center of the stainless steel tube. The thermocouples are sealed and attached to the end plate using Swagelok

weld connector fittings. The other end of the reactor is welded to an outer flange which can be fitted to an inner flange with stainless steel nut and bolts. A Teflon washer is used in between the two flanges to provide a leak proof joint. The flanges have a central hole for supply of hydrogen from the cylinder through stainless tube of 6.5 mm diameter.

Copper fin matrix is used for enhancing heat transfer within the reactor. The schematic illustration of the copper fin matrix is shown in Fig. 4.2. Four copper strips of length 415 mm and width 8.5 mm are brazed horizontally each at an angular distance of 90 degrees to a copper tube of outer diameter 18 mm and thickness 1 mm. The tube is perforated with innumerable holes of diameter 1 to 2 mm.



All dimensions are in mm

Fig. 4.2 Schematic of the copper fin matrix

The pictorial views of the copper fin matrix and sintered metal filter are respectively given in Figs. 4.3 and 4.4.



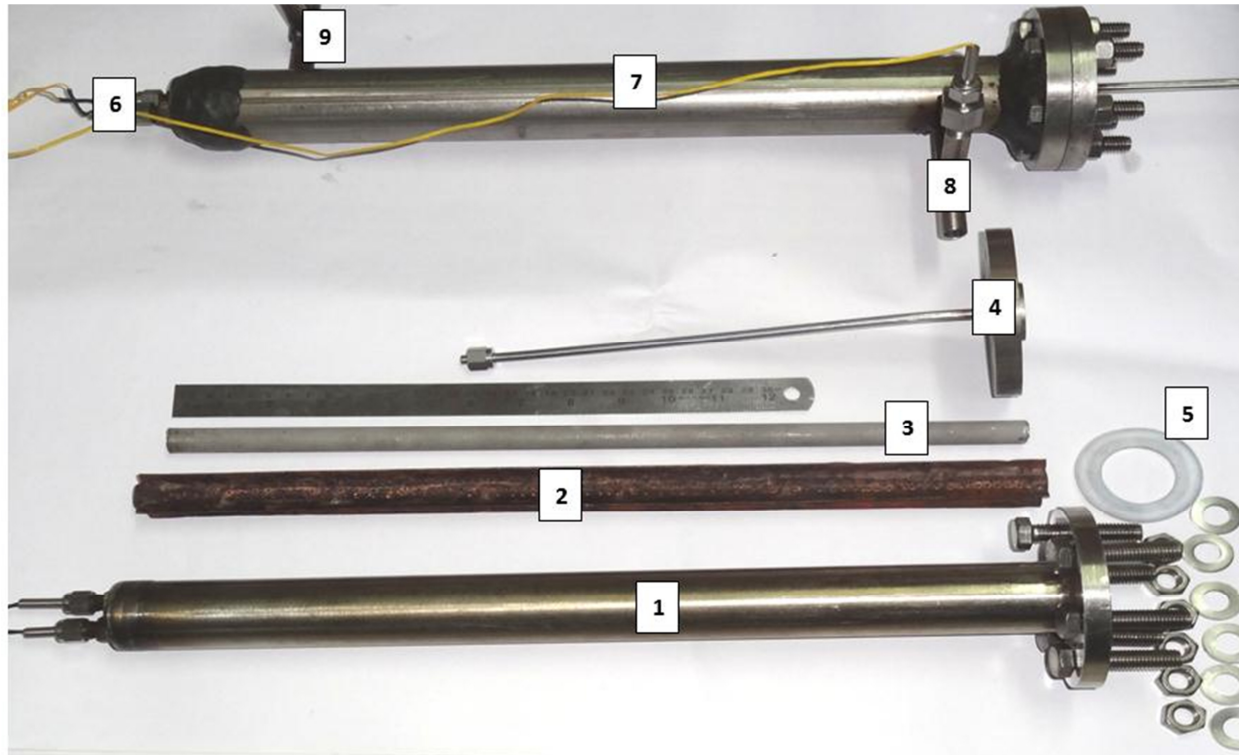
Fig. 4.3 Photograph of copper fin matrix.



Fig. 4.4 Photograph of SS filter brazed to inner flange.

4.1.2 Assembling the reactor

The copper fin matrix is inserted into the reactor tube to cover the entire length except 30 mm at the bottom so as to provide space for the Swagelok weld connectors to attach the thermocouples. A stainless steel tubular filter of 420 mm length and 16 mm (shown in Fig. 4.4) diameter is brazed to the inlet of the inner flange with precise alignment with the gas inlet hole. The other end of the filter is plugged by brazing it with a piece of stainless steel. The filter is then carefully inserted into the copper tube of the copper fin matrix and the inner flange is bolted to the outer flange with a Teflon washer. Fig. 4.5 shows the photograph of the dismantled and assembled views of the reactor employed in the experimental study. The reactor is insulated with polyurethane foam to reduce the heat transfer between the reactor and surroundings.



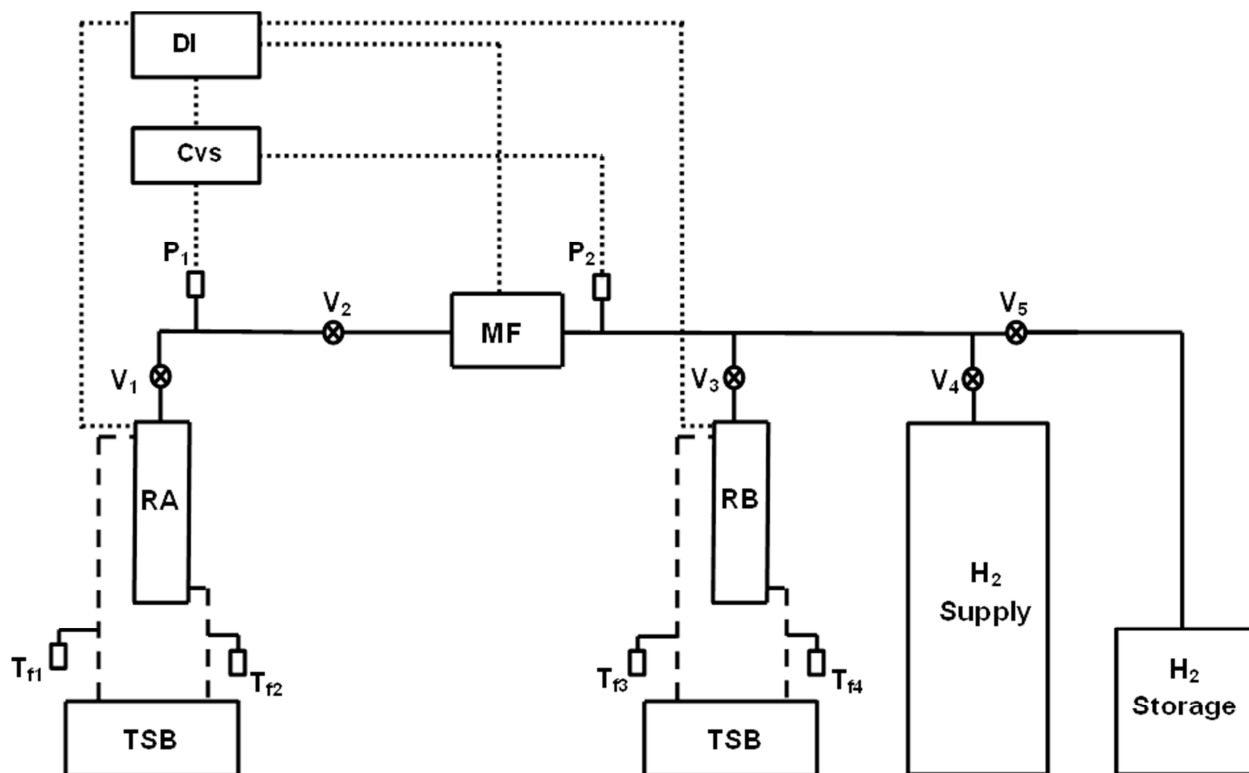
1. Reactor body 2. Copper fin matrix 3. SS sinter filter 4. Outer flange 5. Teflon washer
6. Thermocouples 7. Assembled reactor with HTF jacket 8. HTF inlet 9. HTF outlet.

Fig. 4.5 Pictorial views of the dismantled reactor and assembled reactor

4.2 Single-Stage Metal Hydride Based Heat Transformer

4.2.1 Experimental setup and procedure

Figure 4.6 shows the experimental set up of a single-stage metal hydride based heat transformer (SS-MHHT). Two constant temperature baths of temperature range 20 - 250 °C are used for supplying heat transfer fluid (HTF) (thermic oil: Thermal HS code: 8940102) to the reactors during absorption /desorption processes. Piezo resistive type pressure transducers (sensitivity 0.01 bar) in the range 0 - 160 bar are used for measuring pressures (P_1 , P_2). The flow rate of HTF is fixed at 2.5 l/min.



T_{f1-4} - Heat transfer fluid temperature, $\otimes$ Bellow valve, T_{1-4} - Thermocouple “K” type, M.F- Mass flow meter, R-Reactor, TSB-thermostatic bath, DI- Data logger, CVS- Constant voltage source, - - - Heat transfer fluid line, — Hydrogen gas flow line, Electrical line

Fig. 4.6 Schematic of SS-MHHT experimental setup

The amount of hydrogen transferred during the absorption/desorption processes is measured with the help of a coriolis mass flow meter (sensitivity of 0.001 g). High-pressure (120 bar) bellow valves are used for controlling and directing the flow of hydrogen gas. The desired vacuum level of about 1×10^{-3} mbar during the activation of hydride is achieved with the help of a vacuum pump assembly consisting of diffusion and a rotary pump.

Experimental procedure

Heat transfer fluid (HTF) is supplied to reactor A at 25 °C and then valves V_1 , V_2 and V_4 are opened. Hydrogen gas (purity 99.99 %) at a specified pressure is supplied from the hydrogen

supply cylinder to the reactor A. The total amount of hydrogen absorbed is measured from the coriolis mass flow meter. After completion of absorption process, the valves V_1 , V_2 and V_4 are closed and reactor A is heated to heat source temperature T_M and reactor B is heated to heat output temperature T_H . Valves V_1 , V_2 and V_3 are now opened and the hydrogen gas is desorbed from reactor A, which is absorbed by reactor B. Heat rejected by reactor B (useful output, Q_H) is removed by circulating the HTF. This coupled desorption-absorption process is stopped when there is no change in the totalized flow observed in the mass flow meter. Then, all the valves are closed again and the reactors A and B are sensibly cooled down respectively to T_L and T_M ($T_L < T_M$) and the valves V_1 , V_2 and V_3 are opened. Since, the equilibrium pressure of reactor B is higher than reactor A, hydrogen gas flows from reactor B to A. This process is stopped when there is no change in the totalized flow observed in the mass flow meter. After completion of this process, the reactors A and B are sensibly heated to T_M and T_H , respectively. The bed temperatures (T_1 , T_2 , T_3 and T_4), HTF inlet and outlet temperatures (T_{f1} , T_{f2} , T_{f3} and T_{f4}) and hydrogen flow rate are recorded at every 1 s with help of a data acquisition system. Experiments are repeated at different heat input temperatures (T_M) and heat rejection temperatures (T_L). Temperatures T_H , T_M and T_L are defined with respect to HTF inlet temperatures.

4.2.2 Selection and activation of metal hydride alloys

The alloy pair used for SS-MHHT should fulfill the following requirements.

- The minimum desorption pressure of the low temperature alloy (hydride A) at T_M should be greater than the maximum absorption pressure of the high temperature alloy (hydride B) at T_H .
- The minimum desorption pressure of high temperature alloy at T_M should be greater than the maximum absorption pressure of low temperature alloy at T_L .

Further, one of the important objective of the development of this prototype is to upgrade the heat available from 393 - 413 K to about 423 - 440 K by rejecting heat at 298 - 308 K. Hence, $\text{LaNi}_5/\text{LaNi}_{4.35}\text{Al}_{0.65}$ pair fulfills the above mentioned requirement, they have been chosen for the present experimental study.

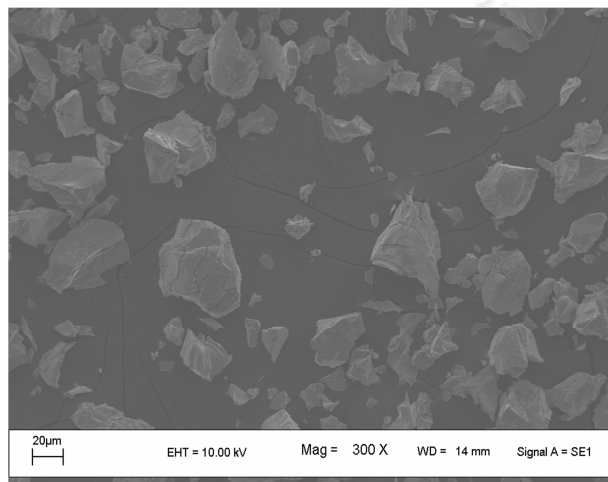
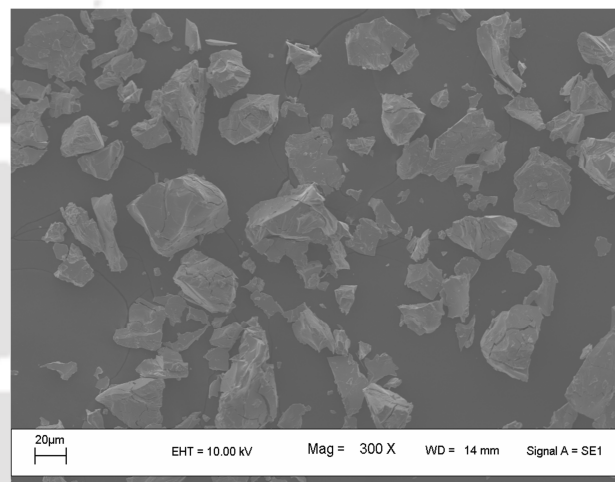
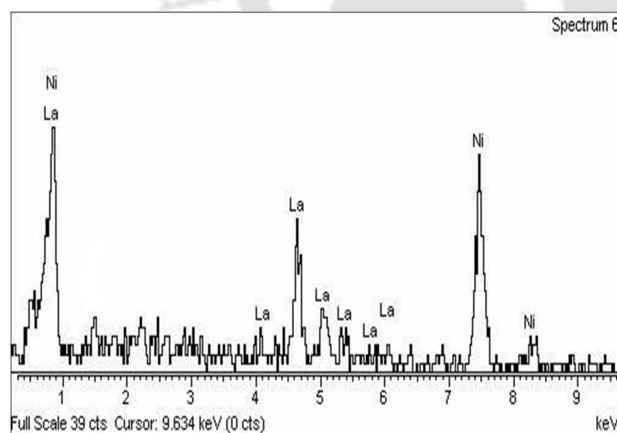
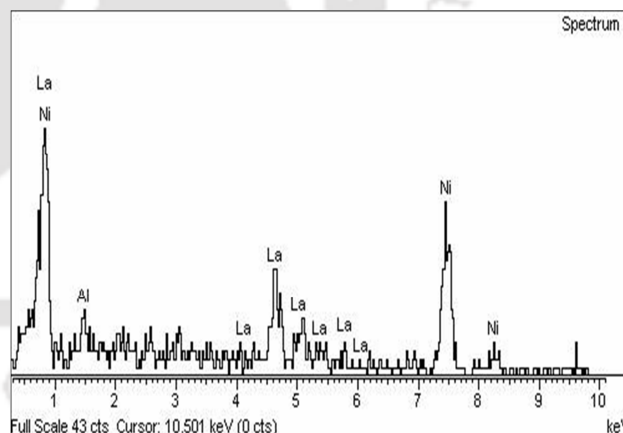
(a) LaNi_5 (b) $\text{LaNi}_{4.35}\text{Al}_{0.65}$ (c) LaNi_5 (d) $\text{LaNi}_{4.35}\text{Al}_{0.65}$

Fig. 4.7 SEM and EDAX images of LaNi_5 and $\text{LaNi}_{4.35}\text{Al}_{0.65}$

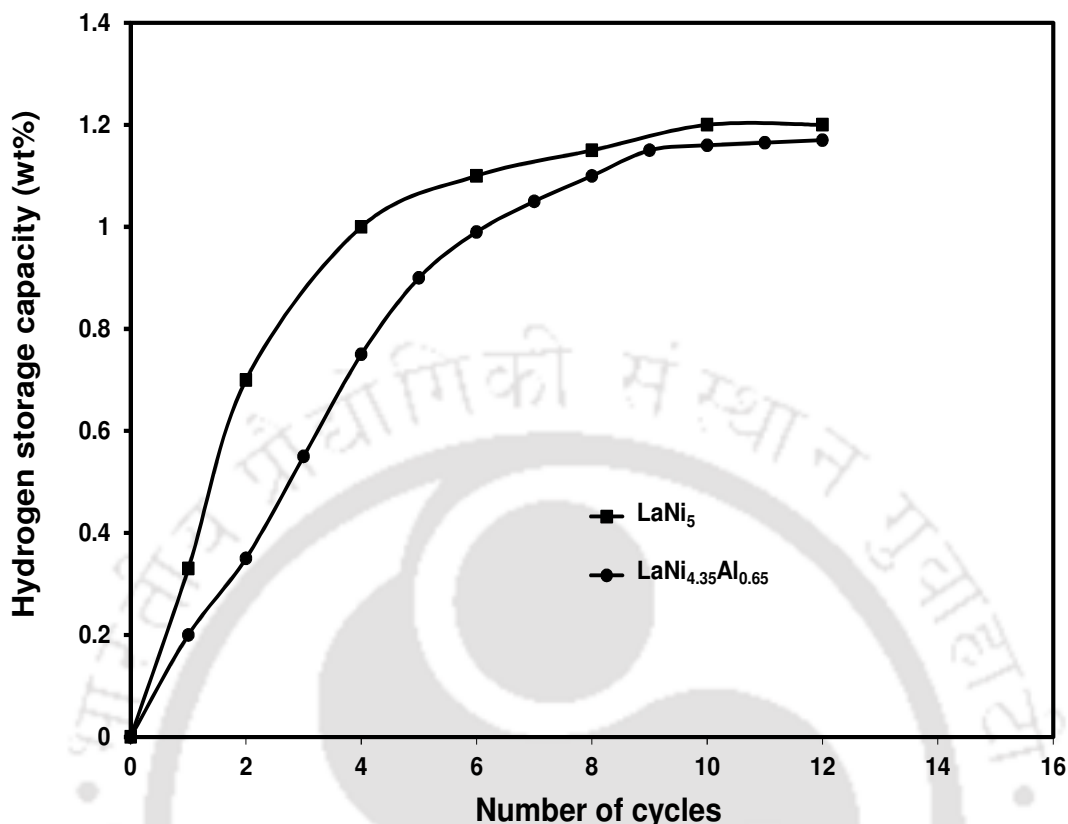


Fig. 4.8 Activation of LaNi₅ and LaNi_{4.35}Al_{0.65}

The amount of alloy taken in A and B are 600 g each (supplied by M/s. LABTECH Ltd, Sofia-1784, Bulgaria). The particle size and chemical composition of the procured material are confirmed through SEM and EDAX analyses. The SEM images shown in Fig. 4.7 (a) and (b) shows that the particle sizes vary between 10 μm and 100 μm . EDAX analyses shown in Fig. 4.7 (c) and (d) revealed that the chemical composition of metal hydride conferred to the specifications given by the supplier. Before starting the experiment, both the hydrides are activated at around 50 bar supply pressure, 25 °C absorption temperature and 50 °C desorption temperature. At the beginning of the cycles each reactor absorbs about 1 - 2 g of hydrogen. The hydrogen storage capacity increases with the number of absorption-desorption cycles. The absorption temperature and supply pressure are kept constant for all cycles. After 12 cycles,

LaNi₅ and LaNi_{4.35}Al_{0.65} based reactors reached their maximum storage capacities of 1.2 wt% and 1.13 wt%, respectively. Figure 4.8 shows the effects of number of absorption cycles on the storage capacity for LaNi₅ and LaNi_{4.35}Al_{0.65}. Amount of heat supplied / removed during experiments can be calculated as

$$Q = \int_{t_i}^{t_f} m_f C_{p,f} (T_{fo} - T_{fi}) dt \quad (4.1)$$

4.3 Double-Stage Metal Hydride Based Hydrogen Compressor

For developing a double-stage metal hydride based heat transformer (DS-MHHT), three metal hydrides namely, A, B and C with different thermo-physical properties are required. Hydrides A and B together act as a hydrogen compressor and hydride C upgrades the quality of heat input. Therefore, before developing a DS-MHHT, a double-stage metal hydride based hydrogen compressor (DS-MHHC) has been built and tested its performances at different operating conditions (within the range of heat transformer's operating temperatures).

4.3.1 Operating principle

The metal hydrides chosen for the present experimental study are LaNi₅ (reactor A) and La_{0.35}Ce_{0.45}Ca_{0.2}Ni_{4.95}Al_{0.05} (reactor B). The operation of a DS-MHHC shown in Figs. 4.9 and 4.10 consists of the following processes:

- I. Reactor A absorbs hydrogen from the supply cylinder at low supply pressure and releases the heat of absorption to the cooling fluid temperature (A-B).
- II. Reactor A is sensibly heated to the heat source temperature (B-C).

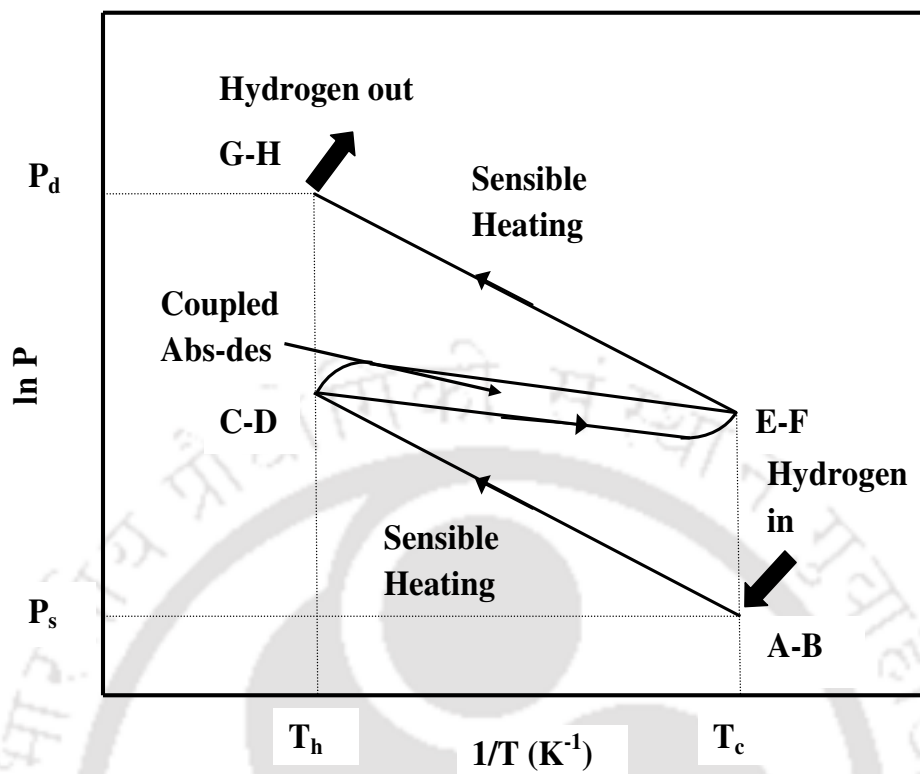


Fig. 4.9 Operation of DS-MHHC on van't Hoff plot

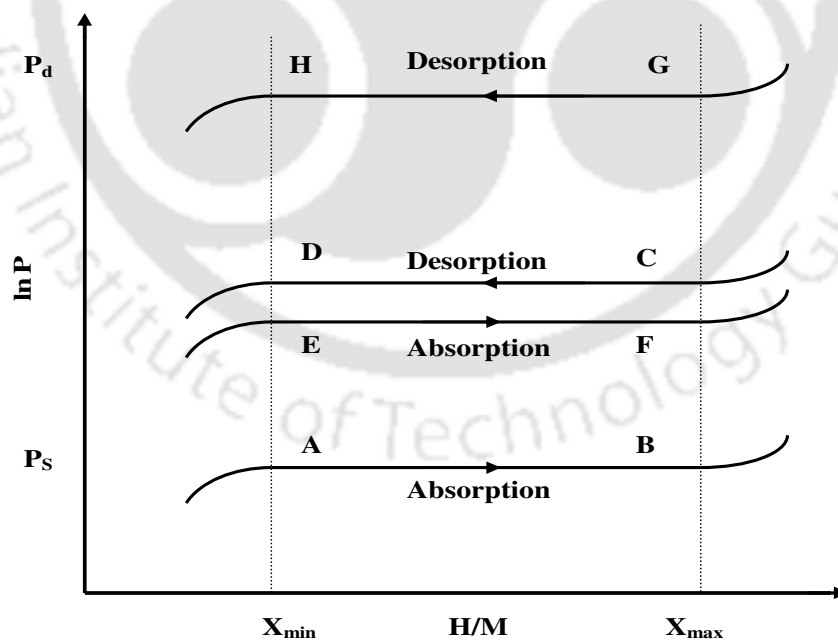
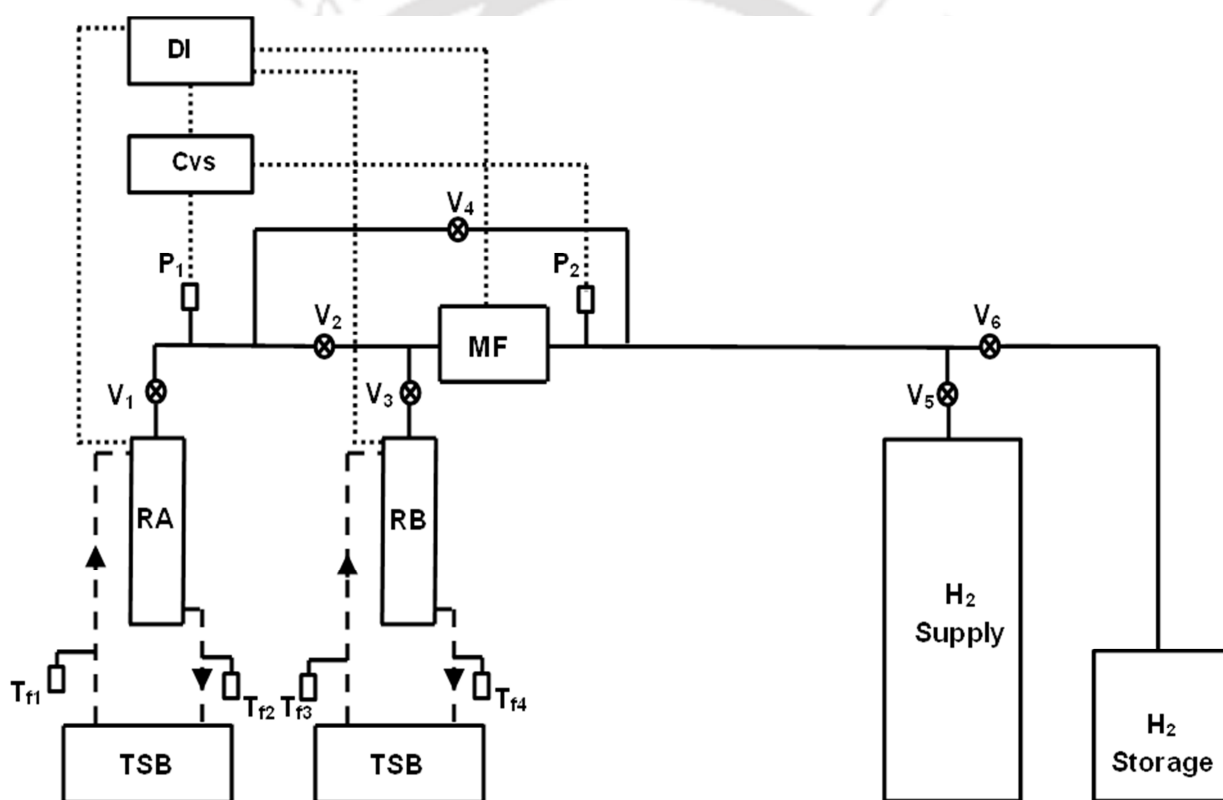


Fig. 4.10 Operation of DS-MHHC on P-C-T plot

- III. Reactor A desorbs hydrogen at T_h which is absorbed by reactor B at T_c . This coupled desorption (C-D) and absorption (E-F) process is represented in Fig. 4.9.
- IV. Reactor B is sensibly heated to the heat source temperature T_h (F-G).
- V. Desorption of hydrogen from reactor B at high pressure and collection of hydrogen into the storage cylinder (G-H).

4.3.2 Details of experimental set up and procedure



T_{f1-4} - Heat transfer fluid temperature, $\otimes$ Bellow valve, T_{1-4} - Thermocouple “K” type, M.F- Mass flow meter, R-Reactor, TSB-thermostatic bath, DI- Data logger, CVS- Constant voltage source, - - - - Heat transfer fluid line, ——— Hydrogen gas flow line, Electrical line

Fig. 4.11 Schematic of DS-MHHC experimental set up

In this section, the details of experimental procedure and alloy selection followed by the activation of alloy are presented. Figure 4.11 shows the schematic of the experimental set up of the DS-MHHC.

Experiment procedure

Before starting the experiment, both the reactors are activated at their respective operating temperatures. During the first absorption process (A-B), reactor A is cooled down to 25 °C by circulating the cold fluid and the valves V_1 , V_2 and V_5 are opened. Hydrogen is admitted to reactor A at low pressure (2 - 10 bar) and continued the supply of hydrogen till there is no appreciable change in the total amount of hydrogen absorbed (indicated in the coriolis mass flow meter). This indicates the thermal equilibrium of reactor A with the cooling fluid. Then, all the valves are closed and reactor A is heated to the heat source temperature (T_H) and reactor B is cooled down to the low temperature (T_C). Valves V_1 , V_4 and V_3 are opened and reactor A is allowed to desorb hydrogen which is absorbed by reactor B. This coupled desorption-absorption process is stopped when there is no change in the totalized flow observed in the mass flow meter. At the end of coupled desorption- absorption process, all the valves are closed and reactor B is reheated to the heat source temperature causing an increase of equilibrium pressure. Once reactor B reaches the thermal equilibrium with the heat source temperature, it desorbs hydrogen and the hydrogen is collected in the storage cylinder by opening the valves V_3 and V_6 . Desorption of hydrogen is continued till the storage pressure reach the equilibrium pressure of reactor B. The dynamic history of bed temperatures (T_1 to T_4), pressures (P_1 and P_2), and hydrogen flow rate are recorded for every 1sec by using the data acquisition system. The heat transfer fluid temperatures

at inlet and outlet of the reactors, and the hydrogen gas temperatures at the exit of supply cylinder and the storage cylinder are also recorded simultaneously.

4.3.3 Alloy selection

The purpose of this study is to develop a DS-MHHC for compressing the hydrogen from 2 - 10 bar to about of 50 - 80 bar. In order to reach such a delivery pressure target under mild conditions, the alloy selection is very crucial. It is clear from Eq. (3.1) that the equilibrium pressure of the hydride bed increase with bed temperature. For efficient compression, alloys must have high desorption pressure at moderate temperature ranges. The DS-MHHC alloys should satisfy the following conditions.

- First stage hydrogen compression alloy should have low absorption plateau pressure (~ 2 - 6 bar) at ambient temperature.
- Second stage hydrogen compression alloy must have high desorption plateau pressure (~ 50 - 80 bar) at 393 - 413 K temperature range.

LaNi_5 and $\text{La}_{0.35}\text{Ce}_{0.45}\text{Ca}_{0.2}\text{Ni}_{4.95}\text{Al}_{0.05}$ combination meets the above mentioned requirements for first and second stage hydrogen compression. The activation of $\text{La}_{0.35}\text{Ce}_{0.45}\text{Ca}_{0.2}\text{Ni}_{4.95}\text{Al}_{0.05}$ is carried out at 50 bar supply pressure, 298 K and 323 K absorption and desorption temperatures, respectively. During the consecutive absorption/desorption cycles increasing the amount of hydrogen absorption is absorbed and stabilized at a maximum storage capacity of 1.1 wt% after 12 cycles.

4.3.4 Data reduction

The amount of hydrogen desorbed/compressed (m_{H_2}) during desorption process is directly obtained from the mass flow meter. The supply and delivery pressures are obtained from the pressure transducers. Work done by the compressor is calculated using the following equation.

$$W = \frac{\gamma}{\gamma-1} m_{H_2} T_{ab} \left[\frac{R}{M_{H_2}} \right] \left[\left(\frac{P_d}{P_s} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (4.2)$$

where, P_d is the delivery pressure and P_s is the supply pressure.

The performance of a compressor depends on two important parameters; compressor efficiency and compression ratio. The efficiency of the compressor is given by

$$\eta_c = \frac{\text{Isentropic compression work}}{\text{Heat input to the compressure}} = \frac{W}{Q} \quad (4.3)$$

The heat supplied during the compression process is obtained by using the following relation.

$$Q_{\text{exp}} = m_f C_{p,f} \int_{t_{ab}}^{t_{de}} (T_{f1} - T_{f2}) dt \quad (4.4)$$

Q includes the heat of desorption and sensible heating of the hydride bed and reactor.

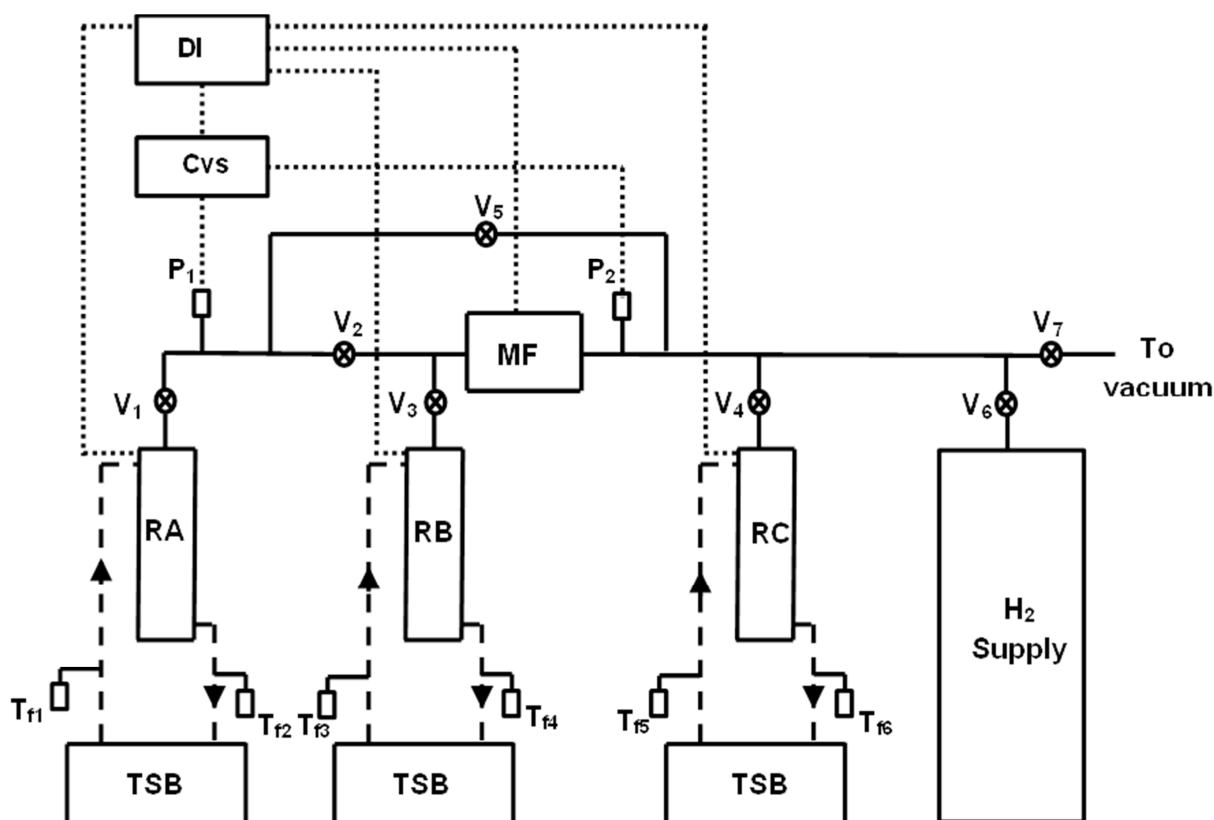
The compression ratio (CR) is defined by the following equation:

$$CR = \frac{P_d}{P_s} \quad (4.5)$$

An uncertainty analysis is made taking into account the errors of the various sensors. The maximum uncertainty in the estimation of compressor work and efficiency are $\pm 6.3\%$ and 10.7% , respectively.

4.4 Double-Stage Metal Hydride Based Heat Transformer

4.4.1 Experimental set up and procedure



T_{f1-6} - Heat transfer fluid temperature, $\otimes$ Bellow valve, T_{1-6} - Thermocouple “K” type, M.F- Mass flow meter, R-Reactor, TSB-thermostatic bath, DL- Data logger, CVS- Constant voltage source, - - - - Heat transfer fluid line ——— Hydrogen gas flow line
 Electrical line

Fig. 4.12 Schematic of DS-MHHT experimental setup

The experimental set up of a DS-MHHT is shown in Fig. 4.12. A coriolis mass flow meter (sensitivity of 0.001 g) is used for measuring the hydrogen flow rate and piezo resistive type pressure transducers in the range of 0-160 bar are used for measuring hydrogen pressure. High-pressure (120 bar) bellow valves are used for controlling and directing the flow of hydrogen gas.

During the activation of hydride the desired vacuum level of about 1×10^{-3} mbar is created using a vacuum pump, which consists of diffusion and a rotary pump. Three constant temperature baths of temperature ranges 20 - 250 °C are used for supplying hot and cold fluids during desorption and absorption processes, respectively.

Experimental procedure

Before starting the coupled desorption-absorption process, reactor A is charged by supplying the high pressure hydrogen (99.99 %) at a specified pressure from the hydrogen supply cylinder. During this process, the valves V_1 , V_2 and V_6 are opened and reactor A is cooled by circulating the HTF at 298 K, which continued till there is no appreciable change in the total amount of hydrogen absorbed (indicated in the coriolis mass flow meter). Then the valves V_1 , V_2 and V_6 are closed and the reactors A and C are heated to T_M and T_H , respectively. Now the valves V_1 , V_2 and V_4 are opened and reactor A is allowed to desorb hydrogen which is absorbed by reactor C. Heat rejected by reactor C (useful output, Q_H) is extracted by circulating the HTF. This coupled desorption-absorption process is stopped when there is no change in the totalized flow observed in the mass flow meter. At the end of coupled desorption- absorption process, all the valves are closed again and the reactors A and C are sensibly cooled down respectively to T_L and T_M . Now the valves V_4 and V_3 are opened. Since, the equilibrium pressure of reactor C is higher than reactor B, hydrogen gas flows from reactor C to B. This process is stopped when there is no change in the totalized flow observed in the mass flow meter.. After completion of this process, the reactors B and C are sensibly heated to T_M and T_H , respectively. Then, the valves V_3 , V_5 and V_1 are opened and the hydrogen gas is desorbed from reactor B which is absorbed by reactor A and this This process is stopped when there is no change in the totalized flow observed in the mass flow meter. After completion of this process, all the valves are closed again and the reactor

A is sensibly heated to T_M and reactor B is sensibly cooled down to T_L . The bed temperatures (T_{1-6}), HTF inlet and outlet temperatures (T_{f1-6}) and hydrogen flow rate are recorded at every 2 s with help of a data acquisition system. Experiments are repeated at different heat input temperatures (T_M) and heat rejection temperatures (T_L).

4.4.2 Selection and activation of metal hydride alloys

Performance of the DS- MHHT system is characterized by COP_{HT} and SHP . These parameters mainly depend on the thermo-chemical properties of the hydride alloys employed and the coupled heat and mass transfer characteristics of the paired reaction beds. In general, the low pressure alloy should have high enthalpy of formation and the high and medium pressure alloy must have low enthalpy of formation. All the three alloys should have high hydrogen storage capacity, low specific heat, high thermal conductivity and fast reaction kinetics. Favorable equilibrium pressure, small hysteresis and flat plateau slope in P - C - T curve are the other essential requirements. Further, one of the important objective of this prototype development is to upgrade the heat available from 393 - 413 K to about 453 - 473 K by rejecting heat at 298 - 308 K. Based on the above requirements $La_{0.35}Ce_{0.45}Ca_{0.2}Ni_{4.95}Al_{0.05}$, $LaNi_5$ and $LaNi_{4.35}Al_{0.65}$ are selected for present experimental study.

The amount of alloy taken in A, B and C are 600 g each (supplied by M/s. LABTECH Ltd, Sofia- 1784, Bulgaria). The SEM and EDAX analyses confirmed the particle size and chemical composition of the procured materials. The SEM image of $La_{0.35}Ce_{0.45}Ca_{0.2}Ni_{4.95}Al_{0.05}$ illustrated in Fig. 4.13 (a) shows that the particle sizes vary between 10 μm and 100 μm . EDAX analysis

shown in Fig. 4.13 (b) reveals the chemical composition of the metal hydrides as per specifications given by the supplier.

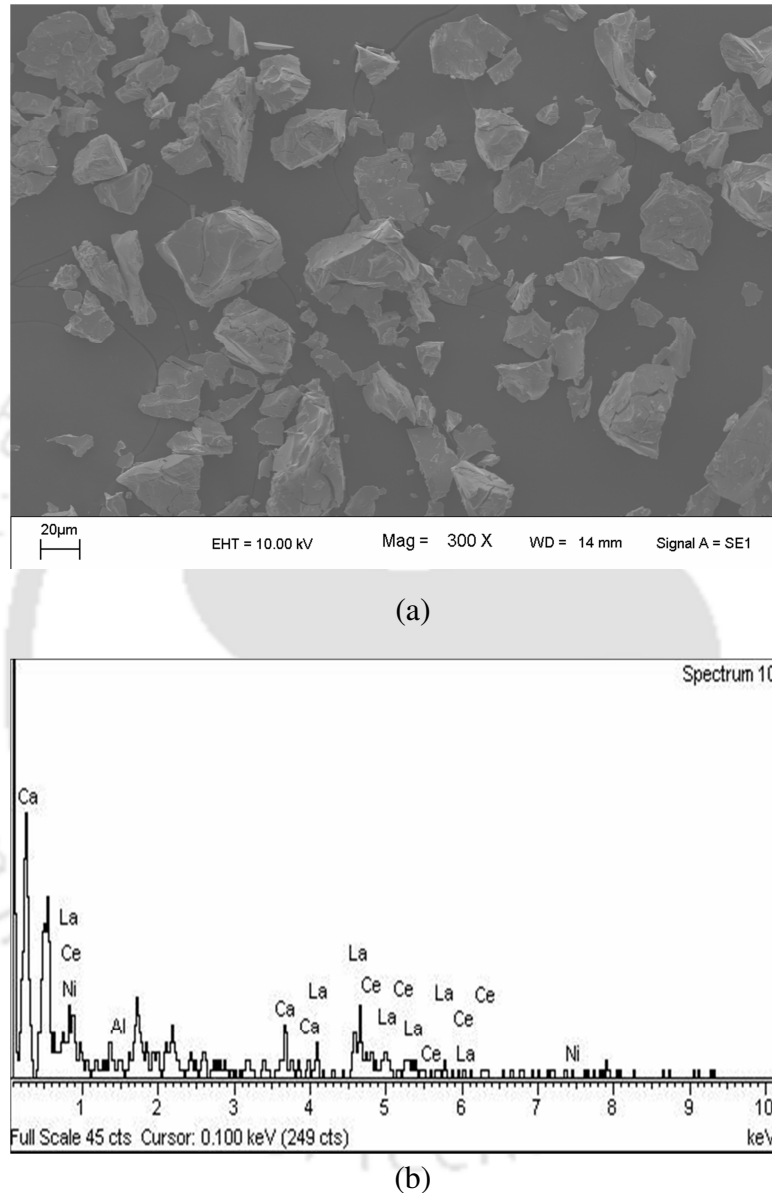


Fig. 4.13 SEM and EDAX images of $\text{La}_{0.35}\text{Ce}_{0.45}\text{Ca}_{0.2}\text{Ni}_{4.95}\text{Al}_{0.05}$

4.4.3 Performance parameters

For a DS-MHHT, coefficient of performance (COP_{HT}) is defined as

$$COP_{HT} = \frac{Q_H}{Q_M} \quad (4.6)$$

where, Q_H denotes the heat output obtained at T_H . Q_M is the heat input at T_M .

$$\text{where, } Q_H = Q_{C,ab} - Q_{C,de} \quad (4.7)$$

$Q_{C,ab}$ and $Q_{C,de}$ are the energy transfers between the HTF and hydride bed C during processes ab and de respectively. The energy supplied at T_M is given by

$$Q_M = Q_{A,ab} + Q_{C,cd} + Q_{B,de} + Q_{B,ef} + Q_{A,fa} \quad (4.8)$$

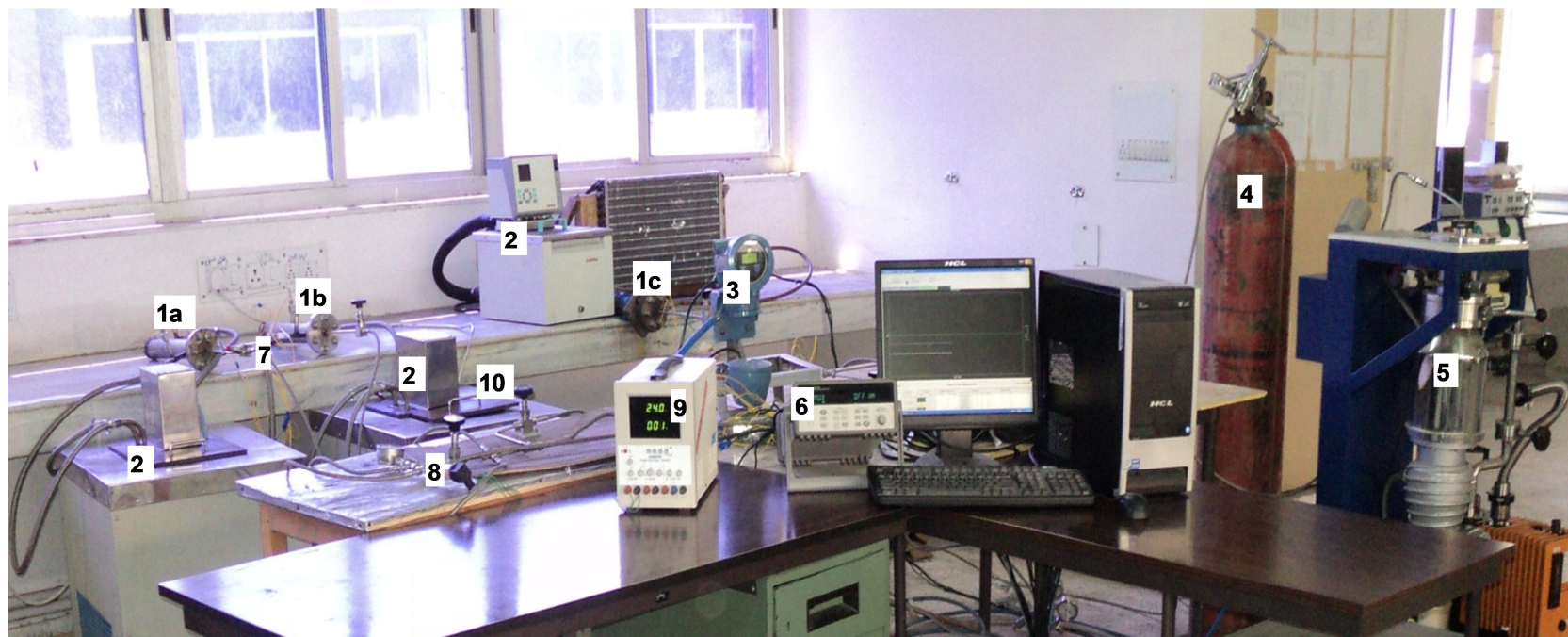
where, $Q_{A,ab}$, $Q_{C,cd}$, $Q_{B,de}$, $Q_{B,ef}$ and $Q_{A,fa}$ are the energy supplied to reactor A, B and C during the processes ab , cd , de , ef and fa respectively. Amount of heat interaction during any process can be calculated as

$$Q = \int_{t_i}^{t_f} m_f C_{p,f} (T_{fo} - T_{fi}) dt \quad (4.9)$$

Figure 4.14 shows the photographic view of the DS-MHHT experiment set up developed at Thermal Science Lab, Mechanical Engineering Department, IIT GUWAHATI. The experimental set up consists of three reactors, thermostatic baths, hydrogen cylinder, vacuum pump, coriolis mass flow meter, K-type thermocouples, constant DC power supply, piezo resistive pressure sensors and data acquisition system connected to a desk top computer. Welded ferrule joints make leak proof connection between the stainless steel pipes and other components. The positions of thermocouples and pressure transducers in the set up are illustrated in Fig. 4.14.

Hydrogen gas of high purity (99.99 %) is used in the experiment and argon gas of ultra-high purity (99.9%) is used for bleeding purpose. Piezo resistive type pressure sensors are used for measuring pressure. The thermocouples used in the setup are of 'K' type with an accuracy of ± 1.5 °C. The reactors are connected with thermostatic baths of range 20 – 250 °C for supplying the heat transfer fluid to the reactor during the absorption and desorption process. Hydrogen is supplied from the hydrogen reservoir during the initial absorption process. A vacuum pumping system consisting of a rotary pump and a diffusion pump is used for creating vacuum in the set-up. The vacuum is measured with the help of pirani gauges and penning gauge attached with the system. The maximum vacuum that can be created by this system is 5×10^{-5} mbar.

Particulars of various instruments and sensors used in this experimental study are detailed in Appendix C.



1-Reactors (1a- Reactor A; 1b- Reactor B; 1c- Reactor C); 2- Thermostatic baths; 3-coriolis mass flow meter;
4-Hydrogen cylinder; 5-Vacuum pump; 6-Data logger; 7- K-type thermocouples; 8-Pressure transducers
9-Constant voltage source; 10-Bellow valves.

Fig 4.14 Photographic view of the DS-MHHT experimental set up

Chapter 5

RESULTS AND DISCUSSION

In this chapter, the results obtained from the numerical simulation of SS-MHHT and DS-MHHT and experimental results of SS-MHHT, DS-MHHC and DS-MHHT are discussed.

5.1 Numerical Results of Single-Stage Metal Hydride Based Heat Transformer

System of equations is solved by using fully implicit finite volume method. A grid independence study for SS-MHHT is carried out by considering the effect of three different grid sizes on the hydride bed (Reactors A and B) concentrations. It is observed from Fig. 5.1 that there is no significant change in the concentration profile for a grid size greater than 41×41 . Therefore, all subsequent computations are performed by using the grid size of 41×41 .

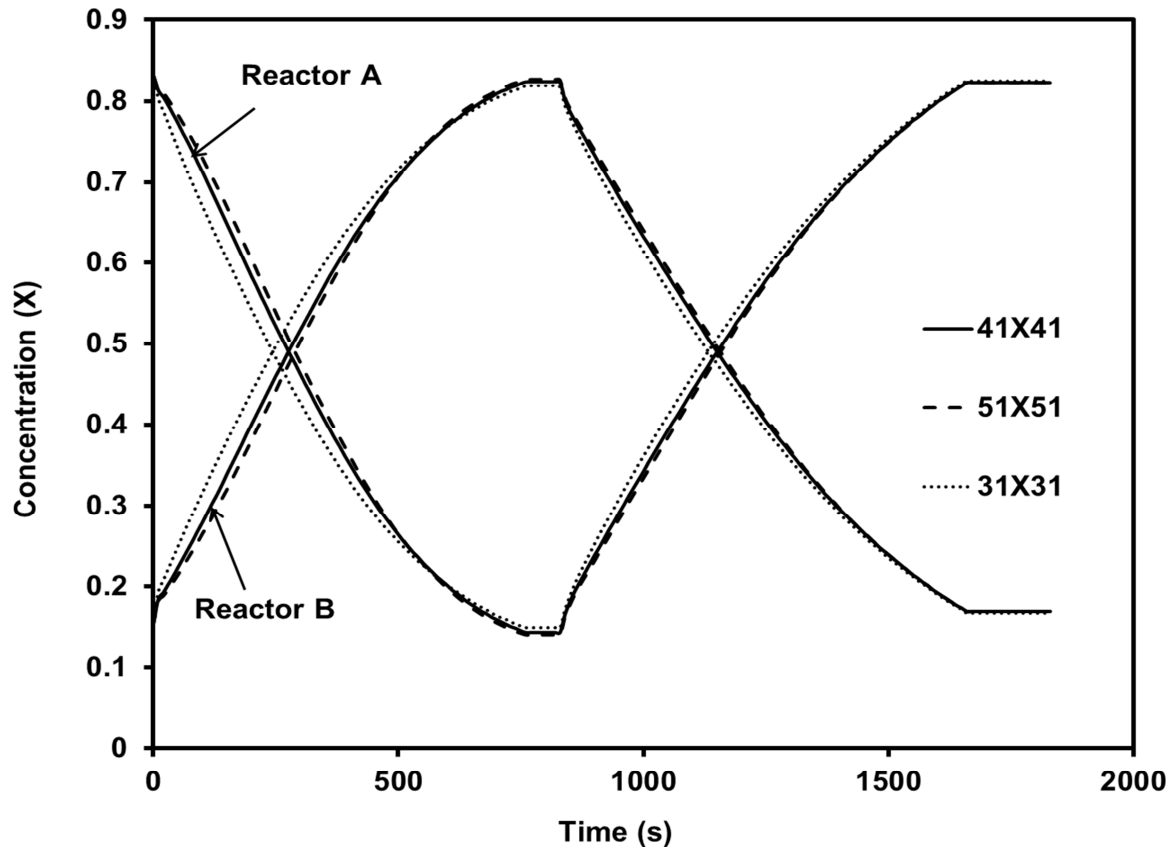


Fig. 5.1 Grid independent study

5.1.1 Numerical validation

For the validation purpose, the reactor geometry used by Ni and Liu (2007) was chosen and mathematical modeling was performed accordingly. The pair of metal hydrides chosen for the validation is $\text{LaNi}_{4.61}\text{Mn}_{0.26}\text{Al}_{0.13}$ (the high-pressure hydride) and $\text{La}_{0.6}\text{Y}_{0.4}\text{Ni}_{4.8}\text{Mn}_{0.2}$ (the low-pressure hydride). The hysteresis and plateau slope of the PCT for the corresponding high and low temperature alloys were determined from the experimental data reported by Ni and Liu (2007). The cycle time at different heat source temperatures, thermal conductivity and bed thickness of the reactors were selected based on the experimental conditions reported by Ni and Liu (2007). It is observed from Fig. 5.2 that the predicted regenerative (high temperature) hydride average bed temperature profiles at two heat source temperatures viz., 403 K and 423 K

match reasonably well with the experimental data reported by Ni and Liu (2007). For a heat source temperature of 423 K, the maximum deviation of numerical result from the experimental data is about 3.8 %.

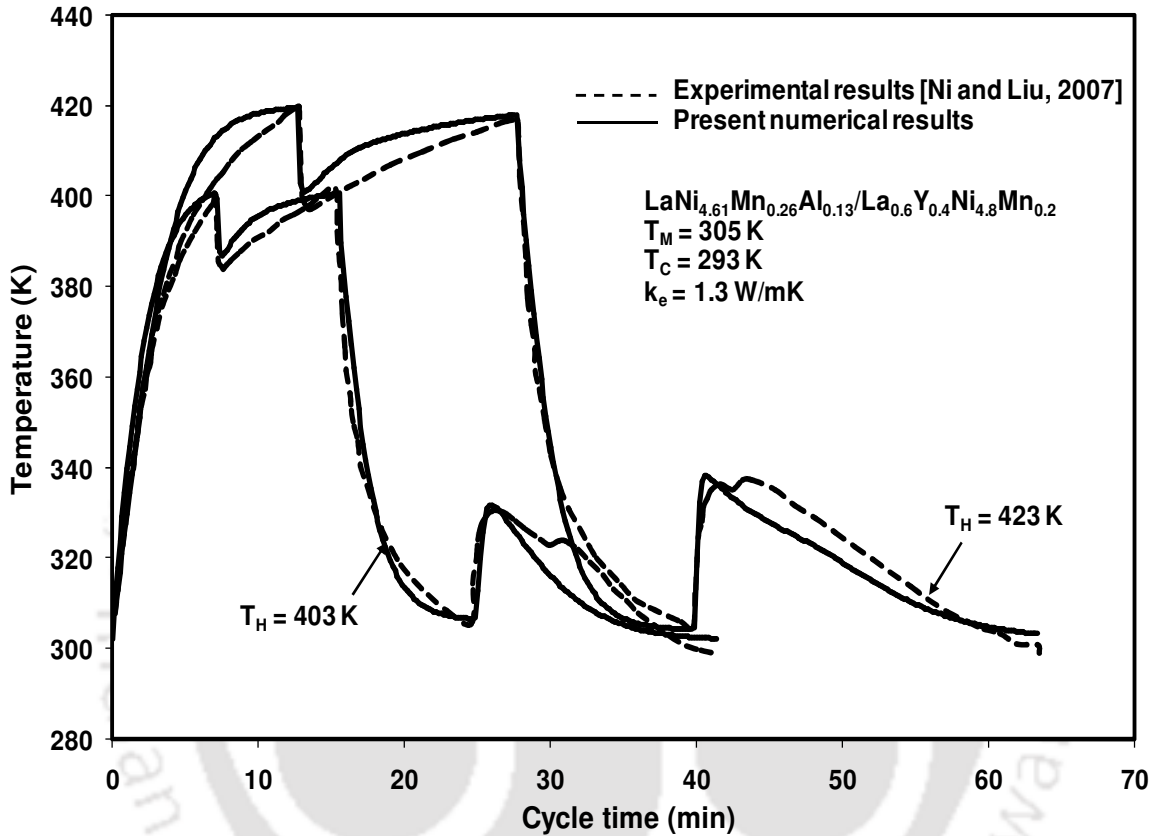


Fig. 5.2 Validation of predicted hydride bed temperature profiles of the regeneration reactor over a complete cycle

Hydride pair is chosen for the present numerical study is $\text{LaNi}_{4.7}\text{Al}_{0.3}/\text{LaNi}_5$ which is one among the best alloy pair for SS-MHHT reported in the literature (Tuscher *et al.*, 1984; Yang *et al.*, 2011; 2012) and also the reaction kinetics data of the two hydrides are relatively well known. In the following sections results obtained for a SS-MHHT working with $\text{LaNi}_{4.7}\text{Al}_{0.3}/\text{LaNi}_5$ are presented. For theoretical studies the bed temperature refers to the average bed temperature, whereas in experimental studies the bed temperature refers to the average temperature measured by the thermocouples.

5.1.2 Effect of convective boundary conditions on the variation of hydride concentrations

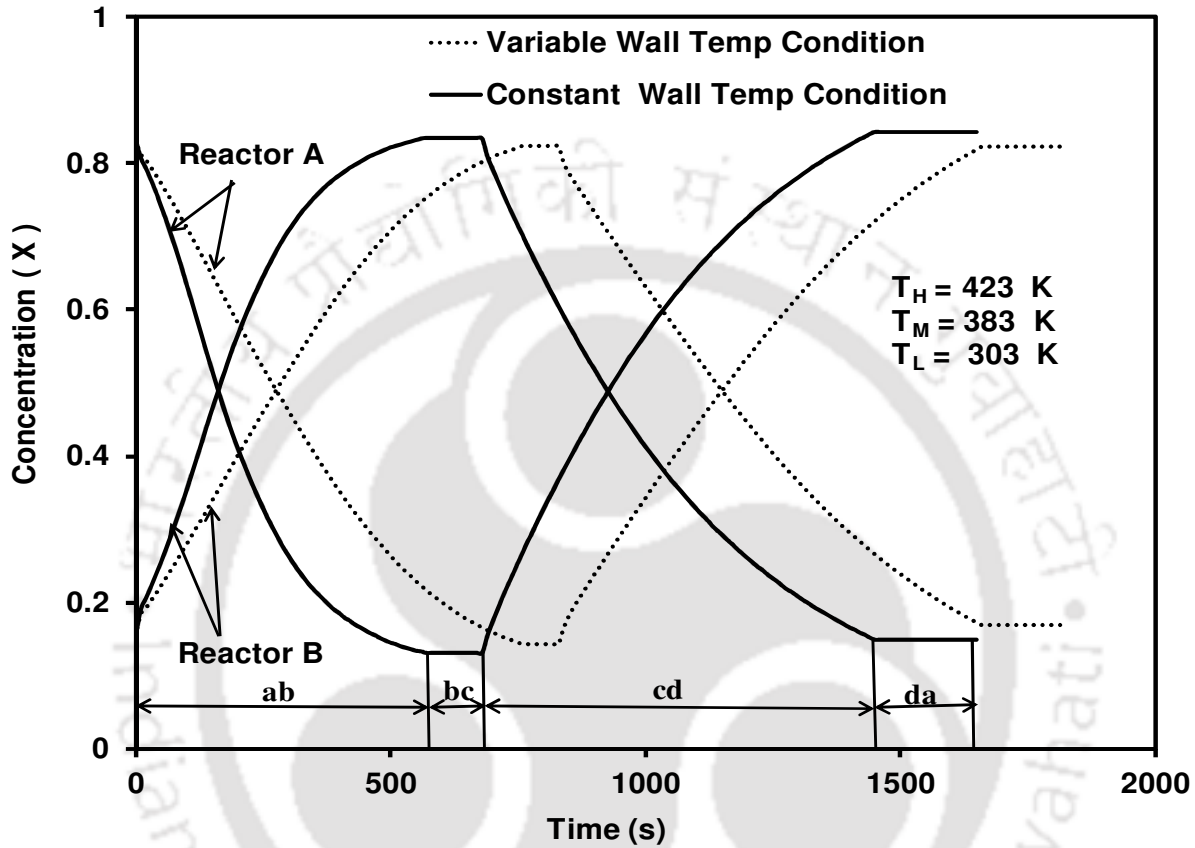


Fig. 5.3 Effect of convective boundary conditions on average hydride concentrations

The variations of the hydride concentration in the reactors A and B over a complete cycle are shown in Fig. 5.3. The four processes of the SS-MHHT are respectively indexed as *ab*, *bc*, *cd* and *dc*. During the processes *ab* and *cd*, (hydriding and dehydriding reactions occur respectively in A and B) the hydride concentration in the reactor A varies from 0.83 to 0.15 and in the reactor B varies from 0.15 to 0.83. Though, the same amount of hydrogen is transferred during the processes *ab* and *cd*, the time taken during the process *ab* (760 s) is shorter than that of the process *cd* (830 s). This is mainly due to higher pressure difference (higher driving potential)

between the equilibrium pressures of the reactor A and B during the processes *ab*. Since, there is no hydrogen transfer during the processes, *bc* and *da*, the time taken for these processes are in the order of 2 min.

During the process *ab*, the hydrogen starts desorbing from the reactor A. The heat transfer fluid enters at the left boundary ($z = 0$) and leaves from the reactor at the right boundary ($z = 500$ mm). Due to the heating of the hydride, there is a significant drop in the heat transfer fluid temperature when it reaches the right boundary. Hence, the rate of hydrogen desorption at the left boundary is higher in comparison with the right boundary. In case of the constant wall convective boundary condition, the transfer fluid temperature is assumed to be constant along the length of the reactor, resulting in uniform hydrogen desorption along length of the reactor. Therefore, the cycle time of the variable wall convective temperature boundary condition is higher by about 3 min compared to the constant wall convective temperature boundary condition.

5.1.3 Variation of average hydride bed temperature profiles over a cycle

The variation of average bed temperature of the reactors A and B over a cycle is illustrated in Fig. 5.4. Due to lower thermal conductivity of the hydride bed, the temperature of the absorbing bed increases sharply; while the desorbing bed drops rapidly during the initial stage of the process *ab* and then approach the heat transfer fluid temperature gradually at the end of the process *ab*. The sudden rise/drop in the bed temperature is undesirable as it reduces the driving potential (pressure difference) for the hydrogen transfer between the reactors. The temperature rise/drop depends upon the initial reaction rate, i.e., the equilibrium pressure difference between the hydride beds A and B. It is observed that the initial bed temperature drop/rise in the hydride

B is marginally greater than that of the hydride A. This is due to the higher heat of formation of the hydride B than the hydride A.

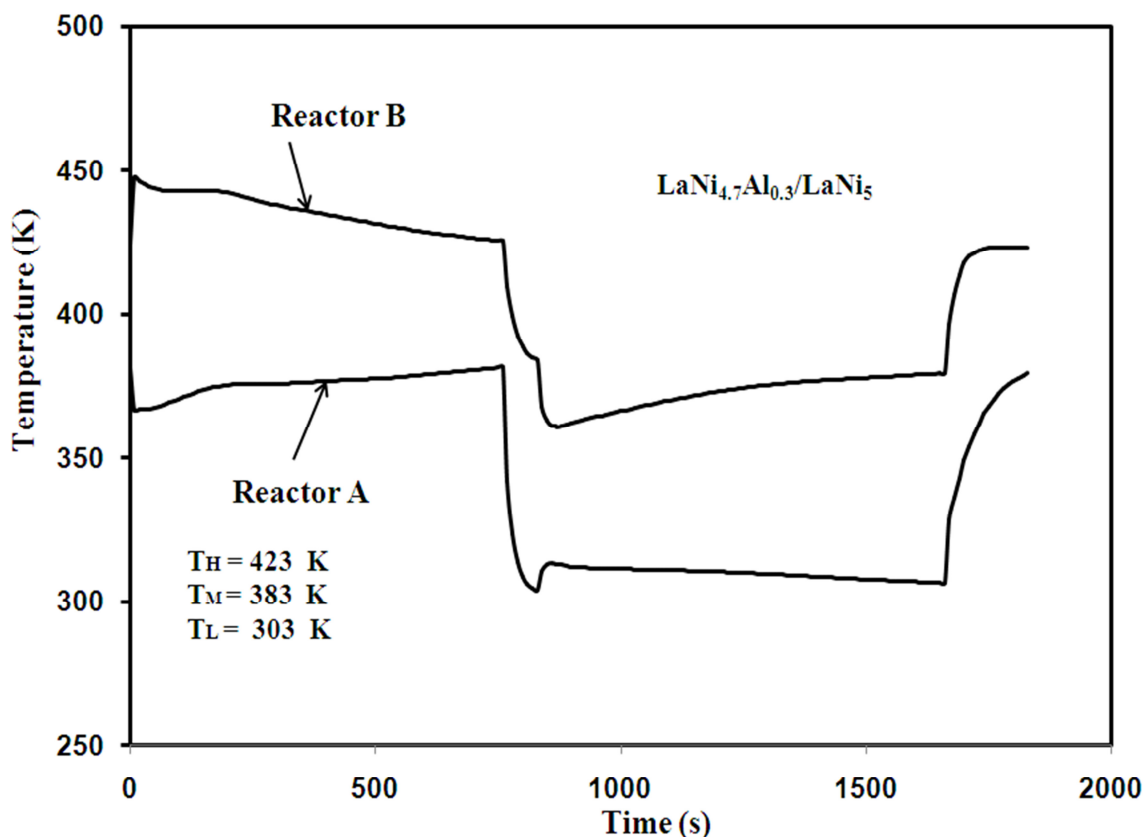


Fig. 5.4 Variation of average hydride bed temperature profiles over a complete cycle

5.1.4 Variation of hydride gas pressures over a complete cycle

Figure 5.5 shows the variation of hydride gas pressures in the reactors A and B over a complete cycle. Initially the system is in equilibrium with respect to the reactors A and B. Once the valve between the reactors is opened, due to the pressure difference, hydrogen starts to desorb from the reactor A and it is absorbed in the reactor B by releasing the heat of absorption. This process is continued till both the reactors reach the pressure equilibrium as illustrated in Fig. 5.5. During the sensible cooling process, the reactor A cools down from 383 K to 303 K and similarly reactor

B cools from 423 K to 383 K. Hence, the pressures of the high and low temperature reactors decrease to 5.3 and 2 bar, respectively. Similarly, during the process *cd* the hydrogen transfer takes place from B to A. This process terminates when both the reactors reach the pressure equilibrium state. Finally the heating process completes the cycle and the pressures of reactors reach the initial condition for continuing the next cycle.

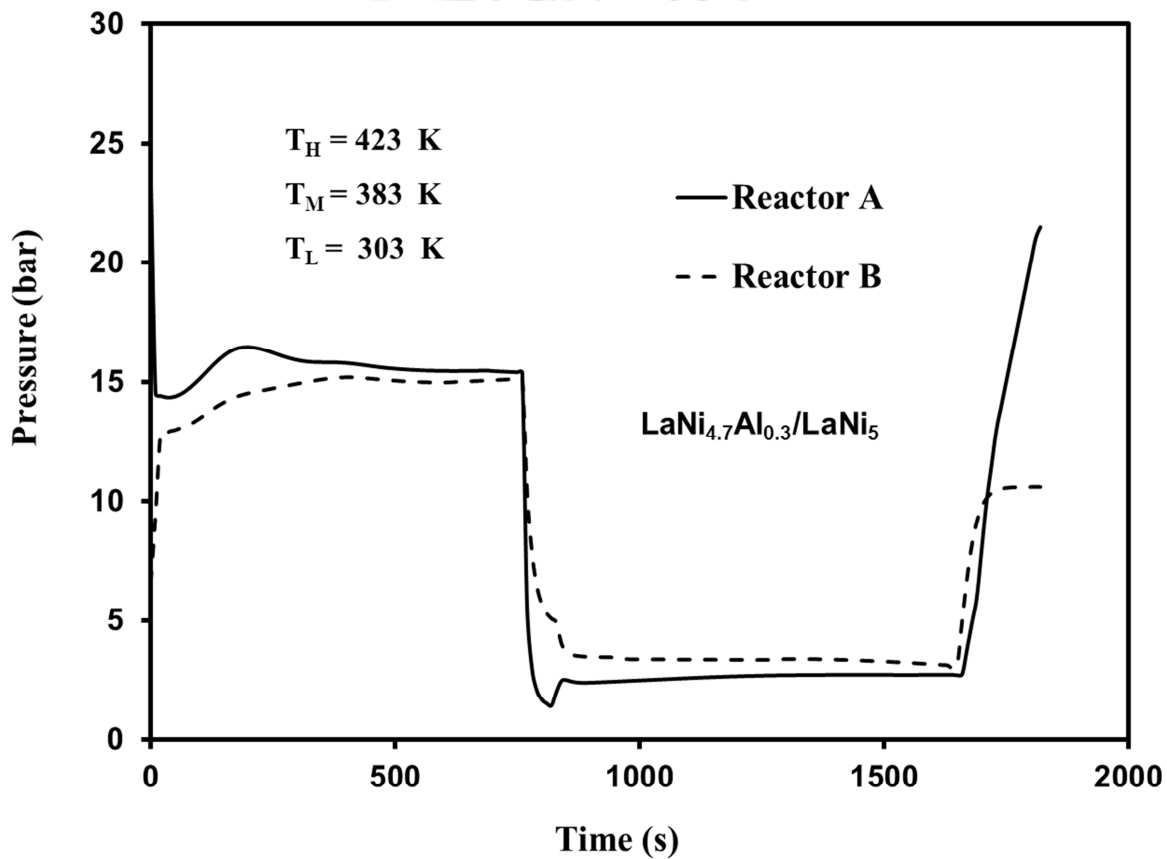


Fig. 5.5 Variation of hydride gas pressures over a complete cycle

5.1.5 Variation of heat transfer fluid temperature at different axial locations

The variations in heat transfer fluid temperature over a cycle at different axial locations are presented in Fig. 5.6. At the beginning of the absorption process (reactor B), the reaction starts rapidly due to large driving potential, resulting in sudden rise in the bed temperature. Owing to a

larger temperature difference, the heat transfer fluid gains more heat from the bed during the initial rapid absorption process.

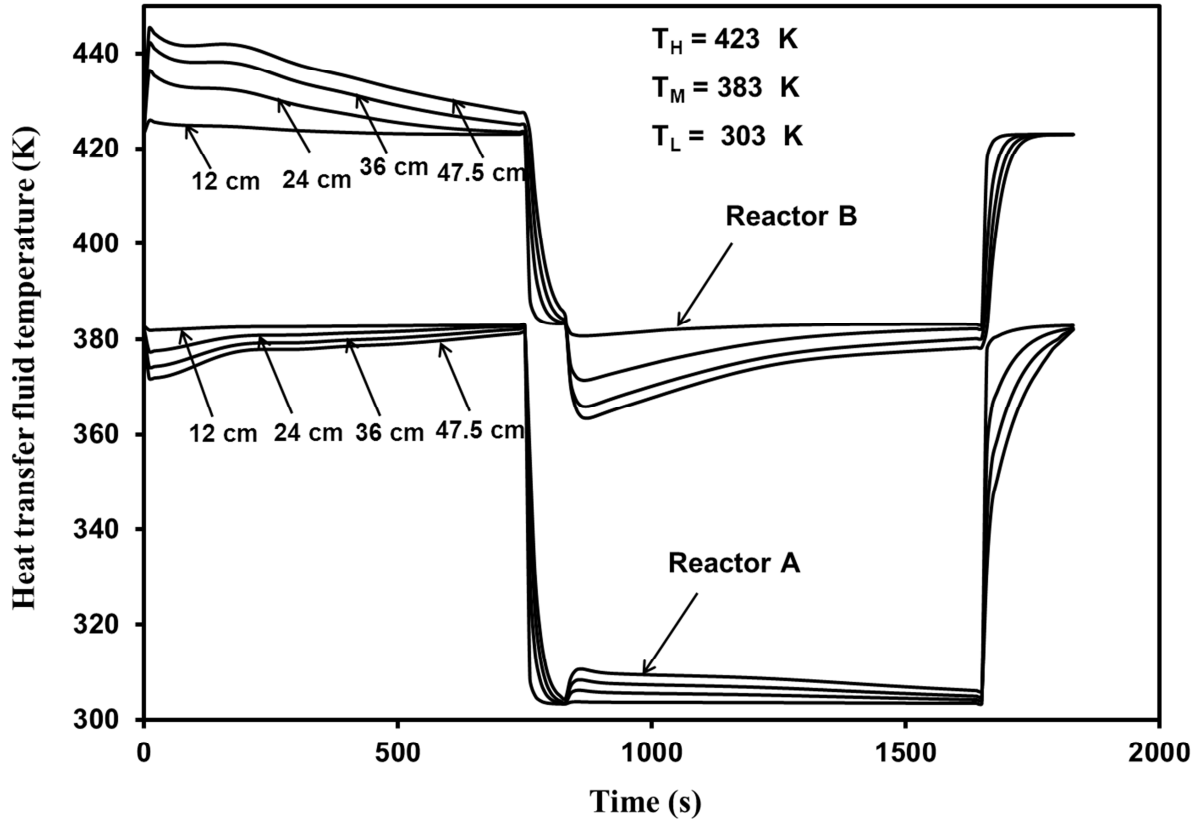


Fig. 5.6 Variations of heat transfer fluid temperature at different axial locations

The difference in temperatures between the heat transfer fluid at the inlet ($z \cong 12$ cm) and at the outlet ($z \cong 47.5$ cm) is about 23 K. Later, this difference decreases gradually due to the fall in reaction rate and it approaches zero at the end of the absorption process. During the desorption process, the heat transfer fluid temperature at the right boundary is found to be lower than that of the left boundary. When the heat transfer fluid reaches the right boundary, it loses the heat to the bed, resulting in temperature fall. As explained in Fig. 5.4, due to large heat of formation of the

hydride B, the difference in temperature of the heat transfer fluid flowing around the reactor B is higher than the respective value of the reactor A.

5.1.6 Heat interactions during the operation of SS-MHHT

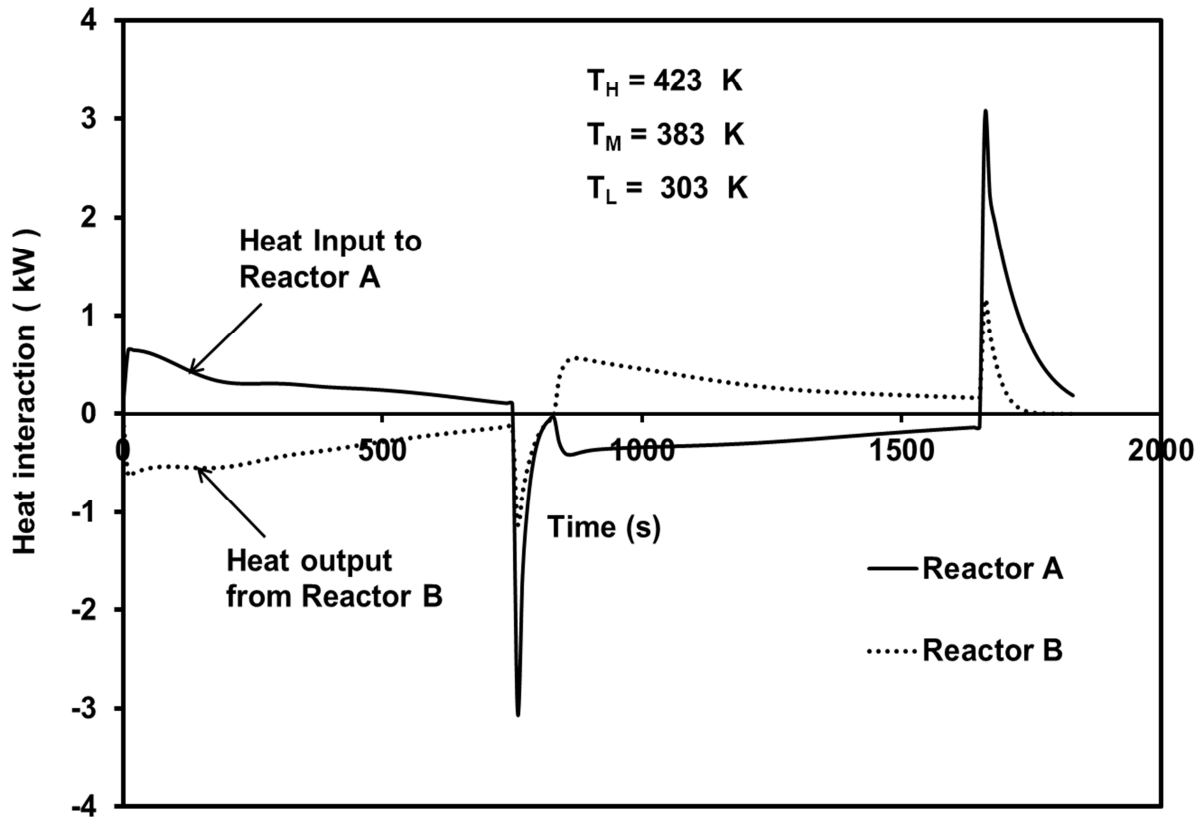


Fig. 5.7 Heat interactions during the operation of SS-MHHT

The heat interaction between the heat transfer fluid and the hydride bed during the four processes is illustrated in Fig. 5.7. Initially ($t = 0$), the variation in the heat transfer fluid temperature along the axial direction is zero. Due to the rapid absorption/desorption processes at the initial stage, the amount of heat is removed from/supplied to the reactor is very high. As the time progresses, the heat interaction is found to decrease gradually and becomes zero at the end of the process. This is due to the reason that owing to a large driving potential for heat and mass transfer

between the coupled reactors, most of the hydrogen is transferred within few minutes from the beginning of the process. As the bed begins to absorb/desorb the hydrogen, the driving potential decreases gradually and hence, the hydrogen transfer rate also drops. Since, the rate of hydrogen exchange between the reactors decreases with time, the heat interaction is also found to decrease. The amount of energy interaction from/to the reactor B is higher in comparison with the reactor A. This is due to the lower heat of formation of the hydride A. The heat transferred during the sensible heat transfer processes *bc* and *da* are much smaller than during the coupled heat and mass transfer processes *ab* and *cd*.

5.1.7 Performance investigation of SS-MHHT

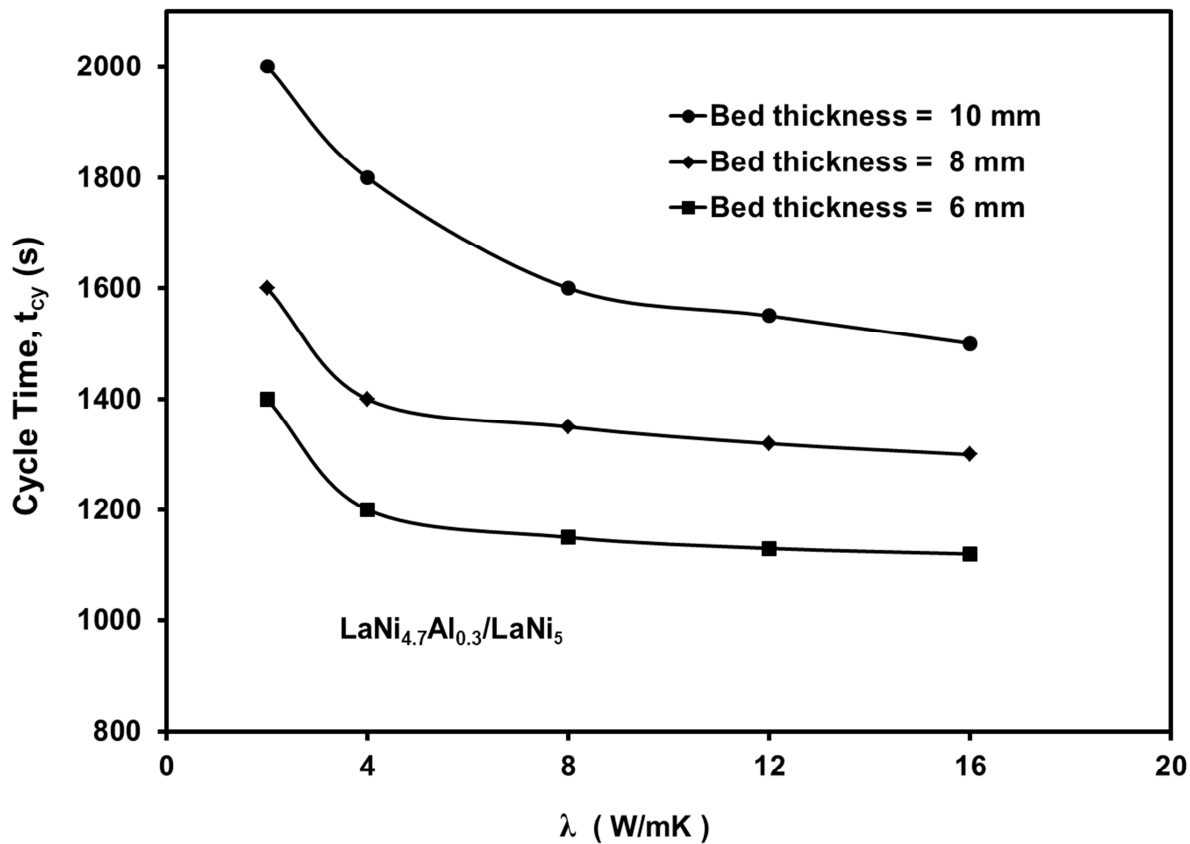


Fig. 5.8 Effect of thermal conductivity on cycle time

Figures 5.8 and 5.9 show the effect of thermal conductivity on cycle time and SHP . It is observed that for a given bed thickness, the cycle time (t_{cy}) is found to decrease significantly with hydride bed effective thermal conductivity (λ) up to about 12 W/m K. With further increase in λ , there is no significant change in the t_{cy} . Similarly the effect of λ on the SHP is limited up to about 12 W/mK. It can also be seen that this optimum value increases with bed thickness. The effect of bed thickness on t_{cy} and SHP are also presented in Figs. 5.8 and 5.9. Thicker bed increases the t_{cy} which leads to the lower SHP .

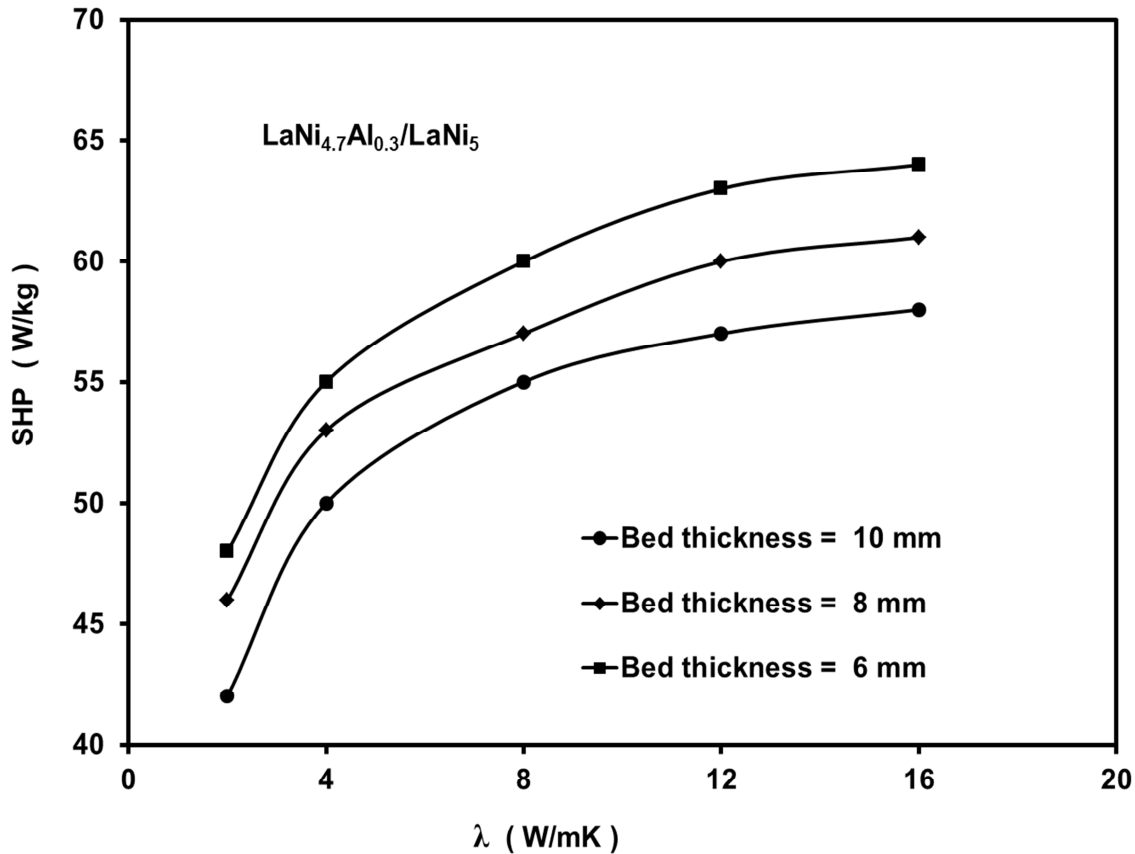


Fig. 5.9 Effect of thermal conductivity on SHP

The effects of the heat output temperature T_H and the heat source temperature T_M on the COP_{HT} and SHP are presented in Figs. 5.10 and 5.11. For a given T_H , higher T_M 's improve both the

COP_{HT} and SHP . The increase in COP_{HT} and SHP with T_M is mainly due to the more amount of hydrogen exchange between the coupled reactors. While for a given T_M , higher T_H 's reduce the driving potential for hydrogen transfer, resulting in higher cycle time and lesser hydrogen exchange between the paired reactors. As a result both the COP_{HT} and SHP decrease with T_H . At the operating conditions of $T_M = 383$ K and $T_L = 303$ K, the increase in T_H from 413 K to 428 K, reduce the COP_{HT} and the SHP by about 12.3 % and 22 %, respectively. The COP_{HT} and SHP are found to increase by about 8.75 % and 20 %, when the T_M is increased from 378 K to 393 K at $T_H = 423$ K and $T_L = 303$ K.

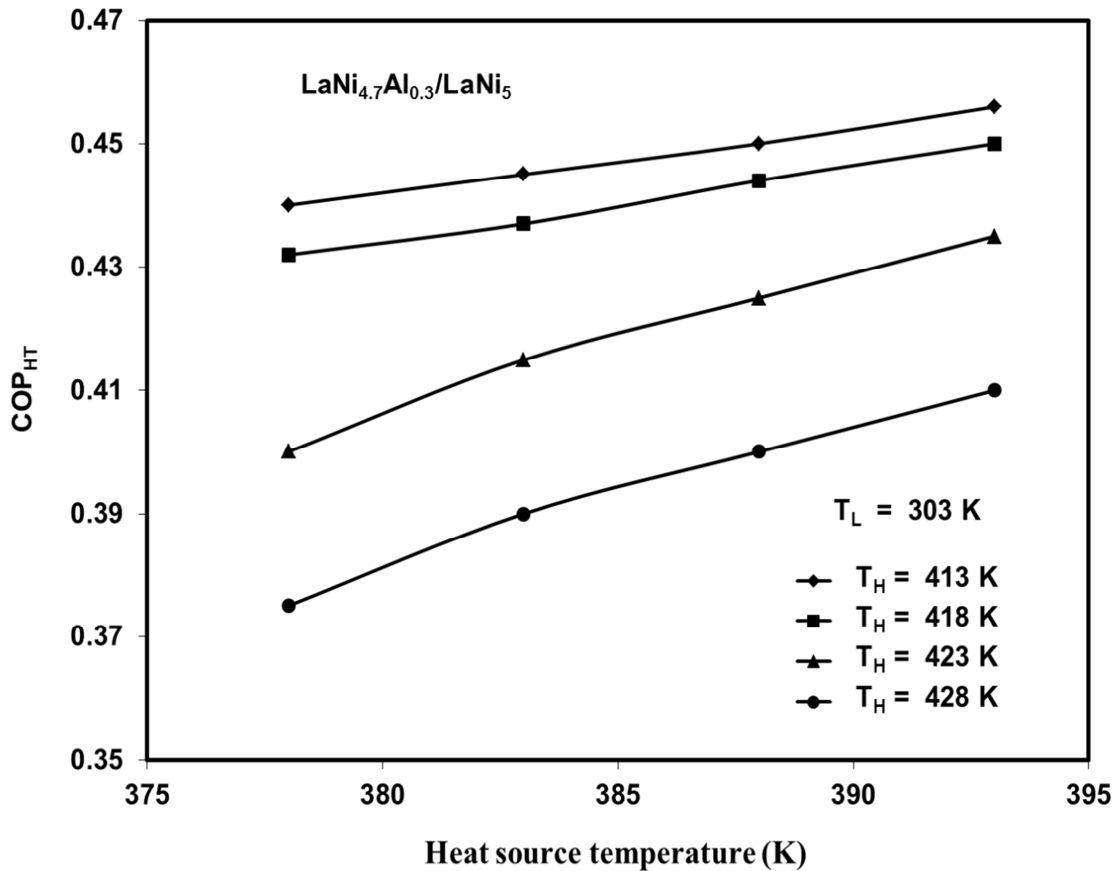


Fig. 5.10 Effect of heat output and heat source temperatures on COP_{HT}

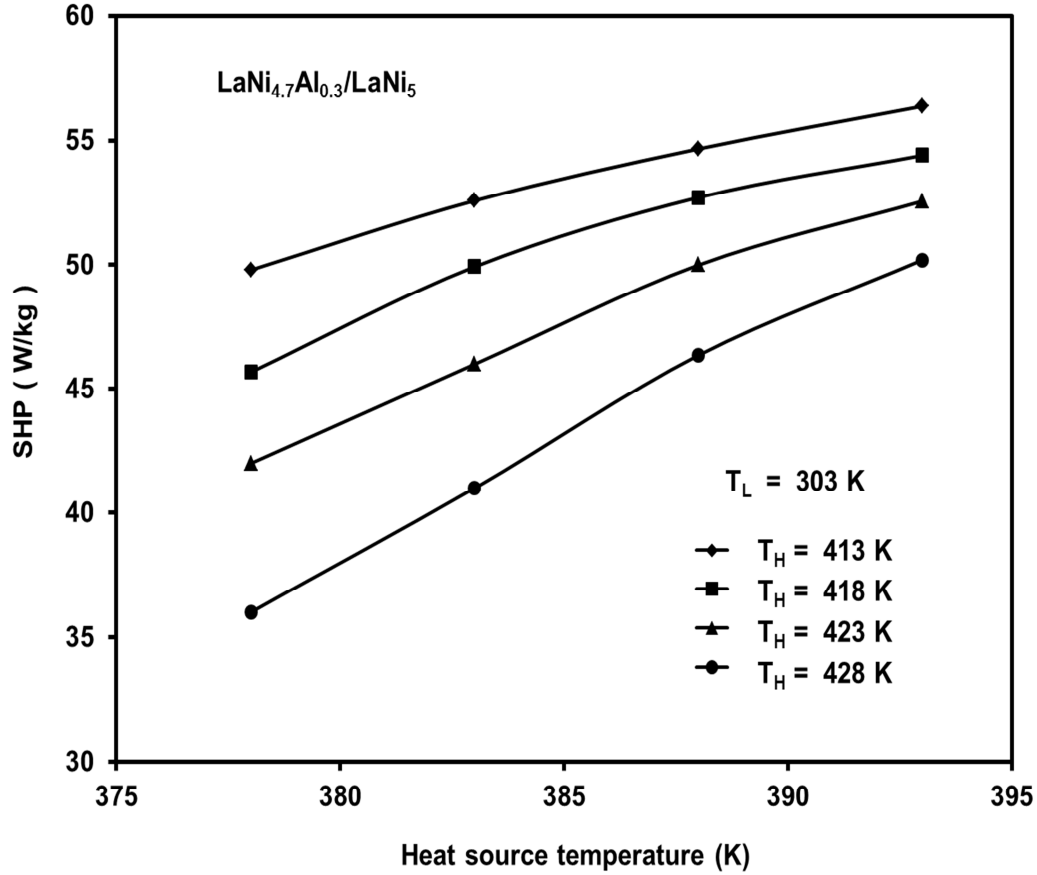


Fig. 5.11 Effect of heat output and heat source temperatures on *SHP*

The mathematical model developed for a SS-MHHT is extended for studying the performance of the system working with four different alloy pairs, namely LaNi₅/ LaNi_{4.7}Al_{0.3} (AP1), MmNi_{4.15}Fe_{0.85}/ LaNi_{4.6}Al_{0.4} (AP2), LaNi_{4.61}Mn_{0.26}-Al_{0.13}/ La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2}(AP3) and Zr_{0.9}Ti_{0.1}Cr_{0.9}Fe_{1.1} /Zr_{0.9}Ti_{0.1}Cr_{0.6}Fe_{1.4} (AP4). The optimum operating temperatures of all the selected metal hydride pairs are found out. From the selected hydride alloy pairs, the maximum COP_{HT} of 0.436 and *SHP* of 54 W/kg are obtained for LaNi_{4.61}Mn_{0.26}Al_{0.13}/La_{0.6}Y_{0.4}Ni_{4.8}Mn_{0.2} pair. It is observed from the present investigation that the Zr_{0.9}Ti_{0.1}Cr_{0.9}Fe_{1.1} /Zr_{0.9}Ti_{0.1}Cr_{0.6}Fe_{1.4} alloy pair provides a maximum temperature lift of about 50 K at the operating conditions of $T_H =$

408 K, $T_M = 358$ K and $T_L = 298$ K. Table 5.1 shows the optimum operating temperatures, COP_{HT} , SHP and maximum temperature lift for all the selected alloy pairs.

Table 5.1 Performance comparison of different alloy pairs

Metal hydride pairs	Operating temperatures (K) ($T_H / T_M / T_L$)	COP_{HT}	SHP (W/kg)	Temperature Lift (K)
LaNi ₅ (Alloy A) LaNi _{4.7} Al _{0.3} (Alloy B)	423 / 383 / 303	0.415	46	40
MmNi _{4.15} Fe _{0.85} (Alloy A) LaNi _{4.6} Al _{0.4} (Alloy B)	403 / 368 / 298	0.4	50.6	35
LaNi _{4.61} Mn _{0.26} Al _{0.13} (Alloy A) La _{0.6} Y _{0.4} Ni _{4.8} Mn _{0.2} (Alloy B)	393 / 353 / 298	0.436	53	40
Zr _{0.9} Ti _{0.1} Cr _{0.9} Fe _{1.1} (Alloy A) Zr _{0.9} Ti _{0.1} Cr _{0.6} Fe _{1.4} (Alloy B)	408 / 358 / 298	0.378	43.8	50

5.2 Numerical Results of Double-Stage Metal Hydride Based Heat Transformer

In this section, the effects of operating temperatures viz., heat output (T_H), heat input (T_M) and heat rejection (T_L) temperatures on the performance of DS-MHHT system working with LaNi_{4.7}Al_{0.3}, LaNi₅ and MmNi_{4.6}Al_{0.4} is presented. The changes in reaction bed temperature, hydrogen concentration and equilibrium pressure of all reactors over a complete cycle are also discussed.

5.2.1 Transient variation of reaction bed temperature and HTF inlet and outlet temperatures

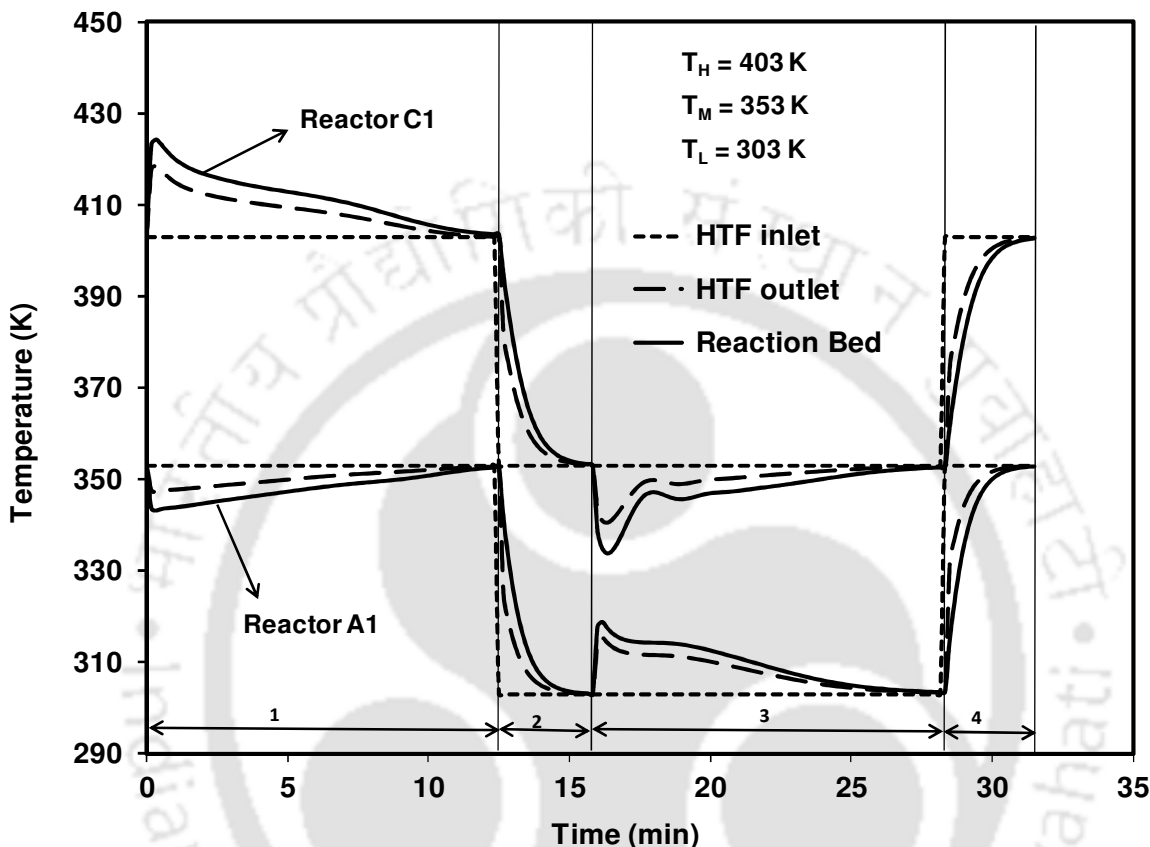


Fig. 5.12 Variation of temperatures (reaction bed, heat transfer fluid inlet and outlet)

Figure 5.12 shows the transient variation of reaction bed temperature and HTF inlet and outlet temperatures over a complete cycle. It is observed that due to the poor thermal conductivity of the reaction bed, the required amount of heat is not being transferred from/to the HTF during initial rapid desorption/absorption processes. Hence, the sudden fall/rise in temperature of the reaction beds occurred as soon as the process is started. Finally, all the reaction beds attain the respective HTF temperatures. From Fig. 5.12, it is observed that initially the difference between the HTF outlet temperature and reaction bed temperature is high and it decreases gradually as

time progresses. As a result, the heat transfer rate from/to the reactors is initially high and decreases gradually as the time elapses. It is also seen from Fig. 5.12 that the reaction bed temperature is higher than the HTF temperature during absorption process, while the reverse happens during the desorption process. The change in bed temperature of reactor C1 is high compared to reactor A1. This is due to the higher heat of formation of the alloy C1 than the alloy A1.

5.2.2 Variation of hydrogen concentration over a complete cycle

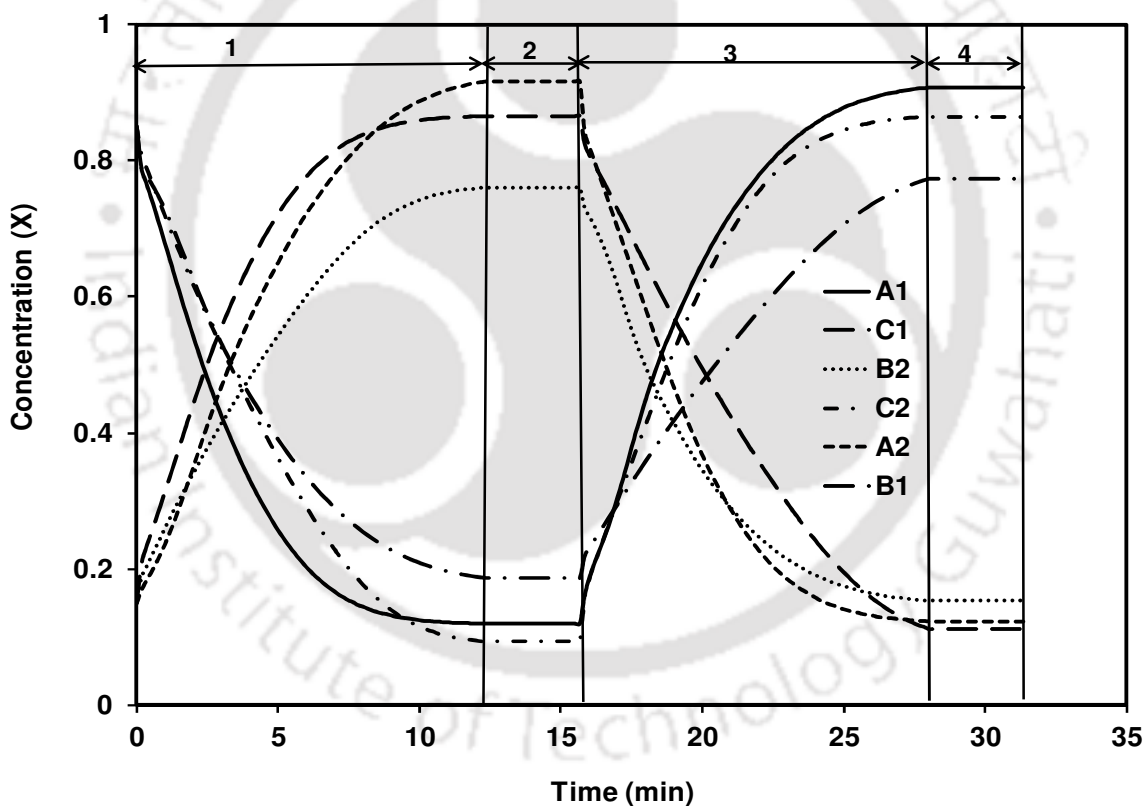


Fig. 5.13 Variation of hydrogen concentration over a complete cycle

The variation of hydrogen concentrations in all the six reaction beds over a complete cycle is shown in Fig. 5.13. The four processes of the DS-MHHT are respectively indexed as 1, 2, 3 and 4. During the first and second half cycles the hydrogen concentration in the reaction beds are

varied between the fixed limits based on the P-C-T characteristics. During processes 2 and 4, only heat transfer takes place but there is no mass (hydrogen) transfer, thus the concentration remains unchanged.

5.2.3 Variation of cumulative heat transfer over a complete cycle

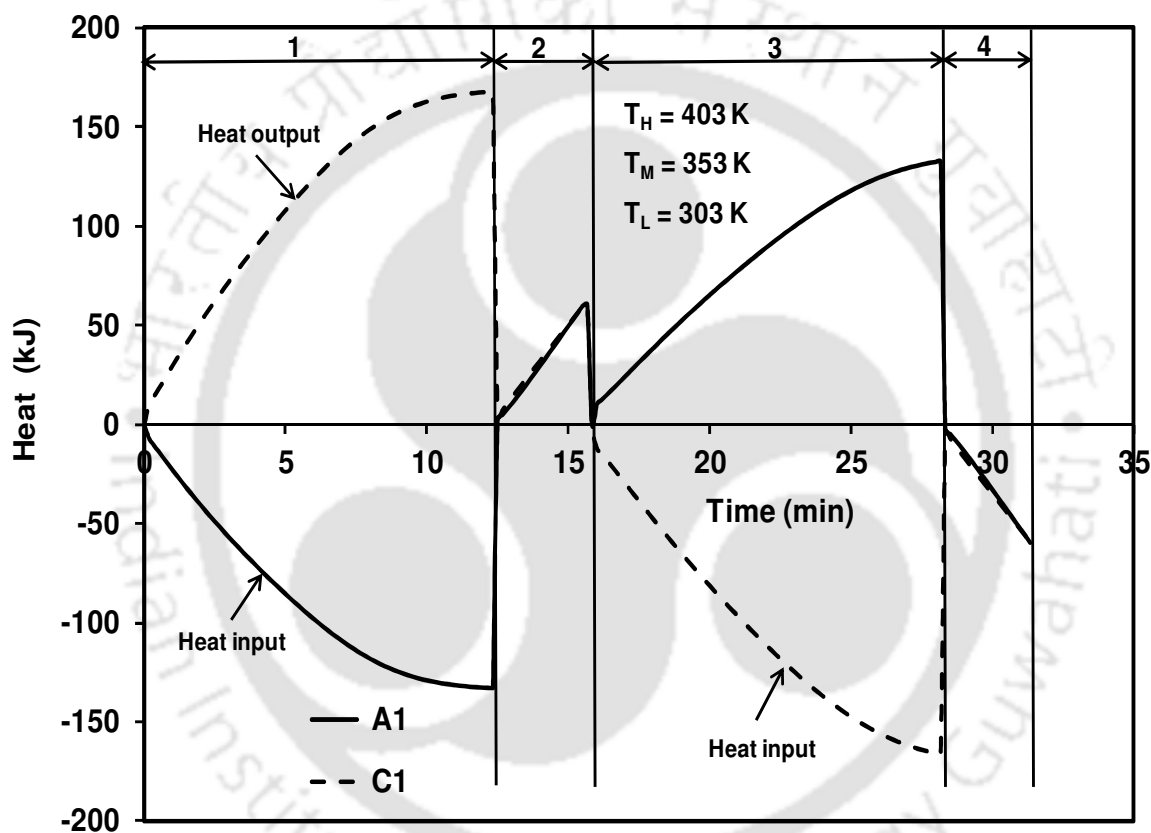


Fig. 5.14 Variation of cumulative heat transfer over a complete cycle

Figure 5.14 show the variation in cumulative amount of heat transfer over a complete cycle for the reactors A1 and C1. It is observed that the amount of heat transfer for reactor A1 is lesser than C1. This is due to lower enthalpy of formation for reactor A1 compared to reactor C1. The amount of heat exchange in sensible heat transfer processes 2 and 4 is much lower than that

compared to heat and mass transfer processes 1 and 3. The amount of heat transfer in first half cycle for reactor A1 and reactor C1 are about 132 kJ/kg of alloy and 167 kJ/kg of alloy, respectively.

5.2.4 Effect of half cycle time on hydrogen transfer

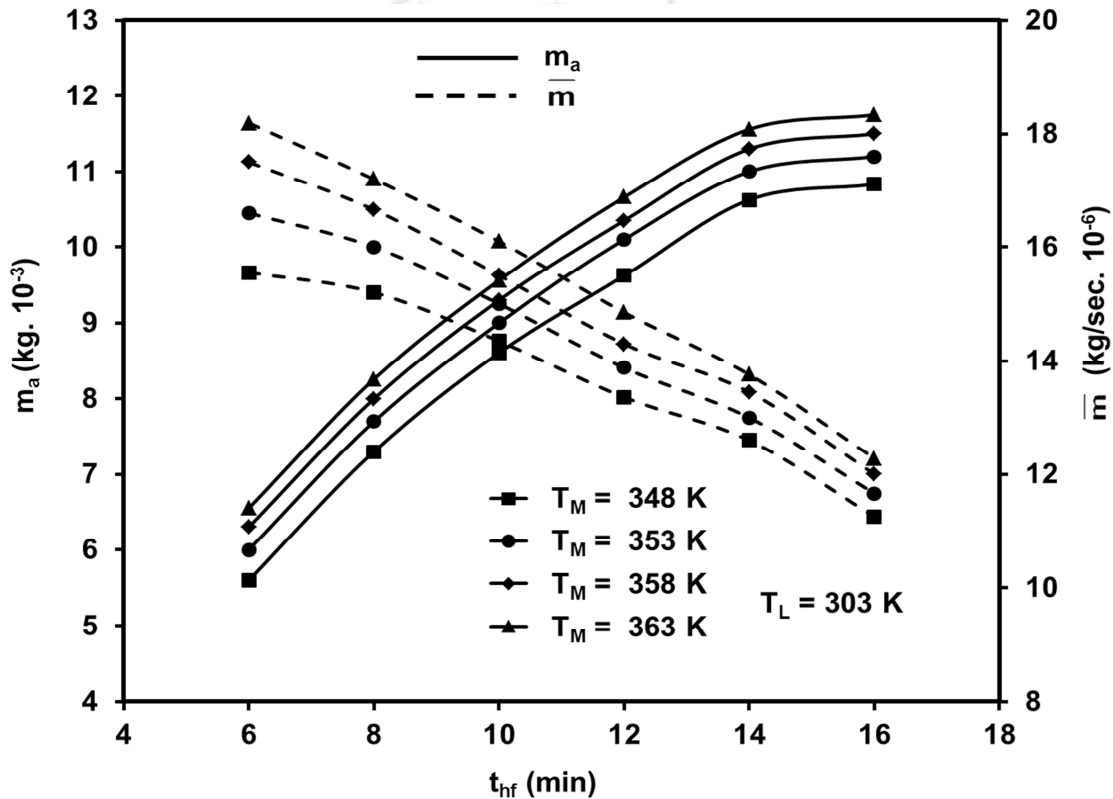


Fig. 5.15 Effect of half cycle time on hydrogen transfer

The half cycle time is defined based on the time taken for the first heat and mass transfer process between the coupled reactors. Figure 5.15 shows the influence of half cycle time (t_{hf}) on the amount of hydrogen transferred (m_{H2}) and average hydrogen flow rate ($\bar{m}$) at different heat source temperatures (T_M). It is observed that the amount of hydrogen transfer increases significantly with t_{hf} up to 14 min, beyond which the effect is negligible. Figure 5.15 also reveals that the average hydrogen flow rate decreases with an increase in t_{hf} . The average hydrogen flow

rate ($\bar{m}$) is decreased from 19.3×10^{-3} g/s to 12.7×10^{-3} g/s when the t_{hf} is increased from 6 min to 16 min at $T_M = 363$ K. Due to increase in driving potential at higher T_M 's, both the amount of hydrogen exchanged and hydrogen flow rate are found to increase with T_M .

5.2.5 Performance investigation of DS-MHHT

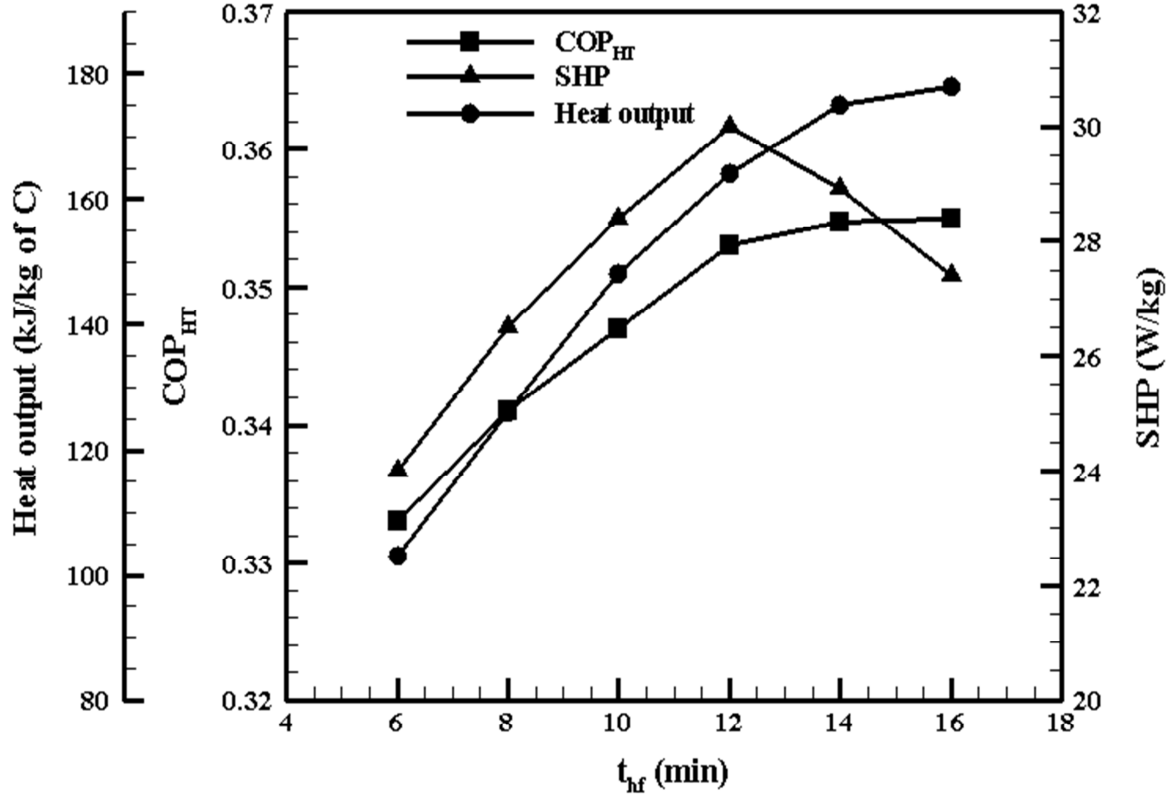


Fig. 5.16 Effect of half cycle time on COP_{HT} , SHP and heat output

Figure 5.16 shows the effect of t_{hf} on heat output, COP_{HT} and SHP . It is observed that the heat output (Q_{HT}) increases with t_{hf} as a consequence of the increase in the amount of hydrogen transfer. The COP_{HT} is also significantly increased with t_{hf} up to 14 min, beyond which the effect is negligible. The increase in SHP with t_{hf} is up to 12 min. This is due to increase in the heat output at the initial stage and later due to the dominance of t_{hf} compared to heat output, SHP is found to decrease.

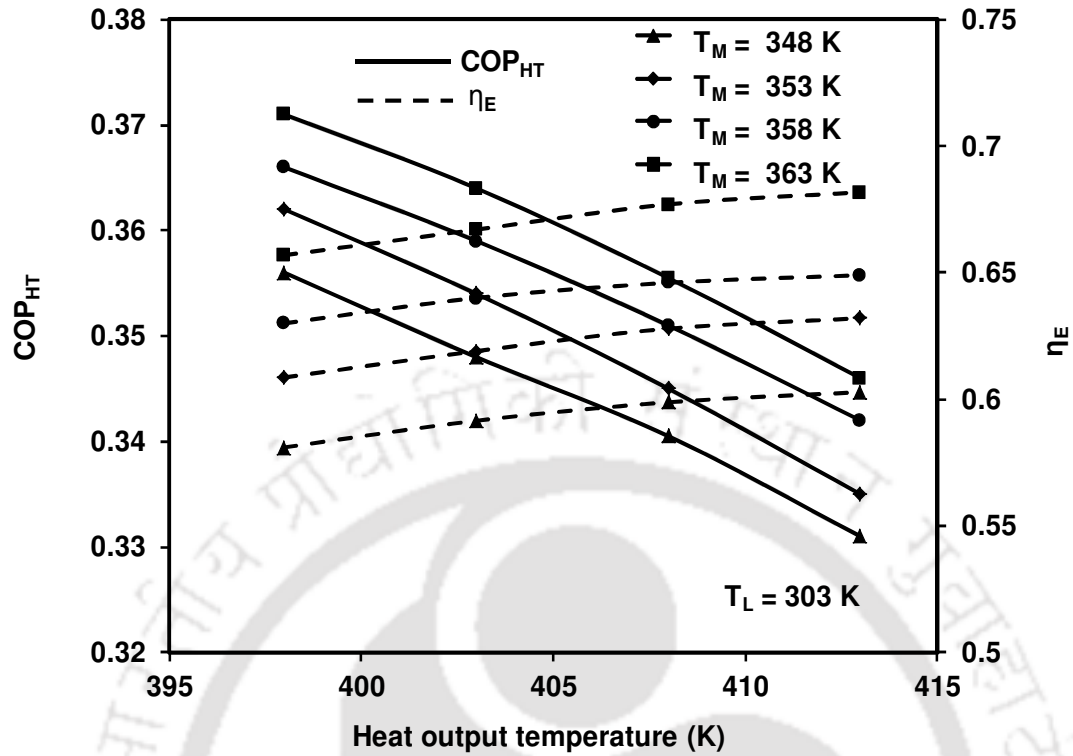


Fig. 5.17 Effect of heat source and heat output temperatures on COP_{HT} and η_E

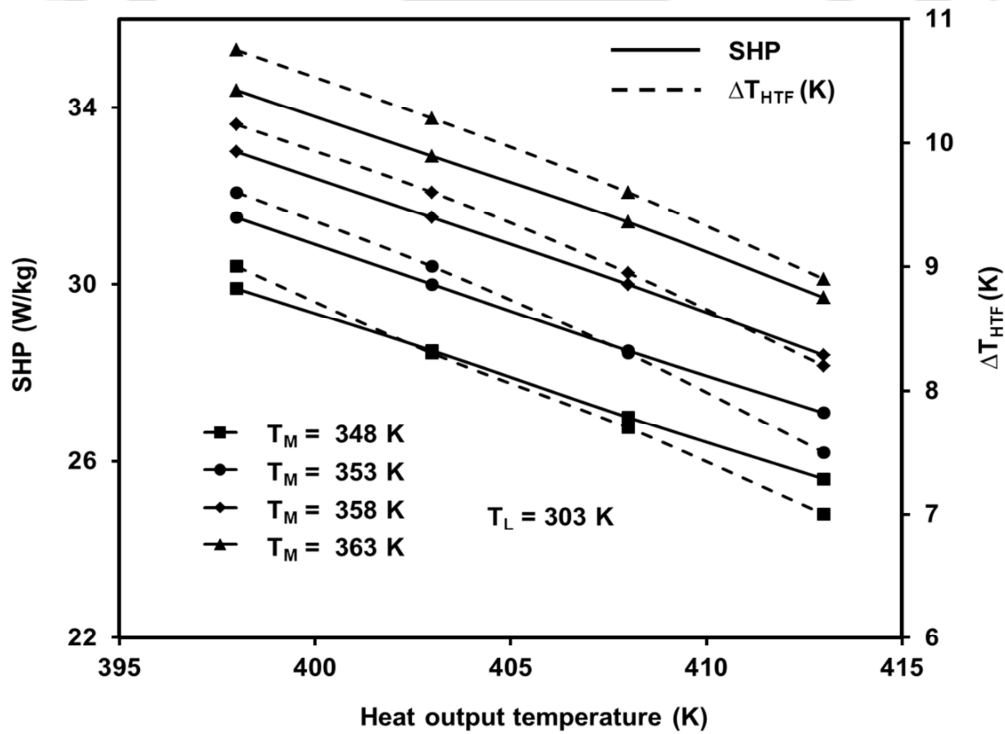


Fig. 5.18 Effect of heat source and heat output temperatures on SHP and ΔT_{HTF}

The effects of T_H and T_M on the performance of the DS-MHHT in terms of COP_{HT} , SHP , η_E and ΔT_{HTF} are presented in Figs. 5.17 and 5.18. For a given T_M and T_L , an increase in T_H decreases both the COP_{HT} and SHP . The reduction in COP_{HT} and SHP with T_H is mainly due to lesser amount of hydrogen exchange between the coupled reactors. As illustrated in Fig. 5.17, the COP_{HT} is found to decrease with T_H but at the same time the decrease in COP_{Carnot} is more dominant than the decrease in COP_{HT} with T_H . Since, the η_E is the ratio of COP_{HT} and COP_{Carnot} , it is found to increase marginally by about 3.0 % when the T_H is increased from 398 K to 413 K.

From Fig. 5.18, it is observed that the ΔT_{HTF} decreases as T_H increases, which is due to decrease in driving potential and less amount of hydrogen exchange with T_H . For a given T_H and T_L , higher T_M 's improve the COP_{HT} , SHP and ΔT_{HTF} but marginally decreases the η_E . Higher T_M 's increase the driving potential for hydrogen transfer and hence, more amount of hydrogen is exchanged between the paired reactors. Therefore, the COP_{HT} , SHP and ΔT_{HTF} increase with the T_M . As explained above, the COP_{HT} increases with T_M but at the same time the improvement in COP_{Carnot} is found to be more than the increase in COP_{HT} . As a result the η_E decreases with T_M .

The increase in COP_{HT} and η_E of the system with T_L is shown in Fig. 5.19. It is observed that at higher T_L , the COP_{HT} increases slightly due to the reduction in the sensible heating requirement of the reactor A1. But higher T_L reduces the COP_{Carnot} and as a net result, the η_E increases with T_L . Further higher T_L 's also decreases the driving potential for mass transfer during the second half cycle; as a result, the SHP is found to decrease with T_L . Since T_L is not related to heat output process as shown in Fig. 5.20, the ΔT_{HTF} is remaining constant when T_L varies.

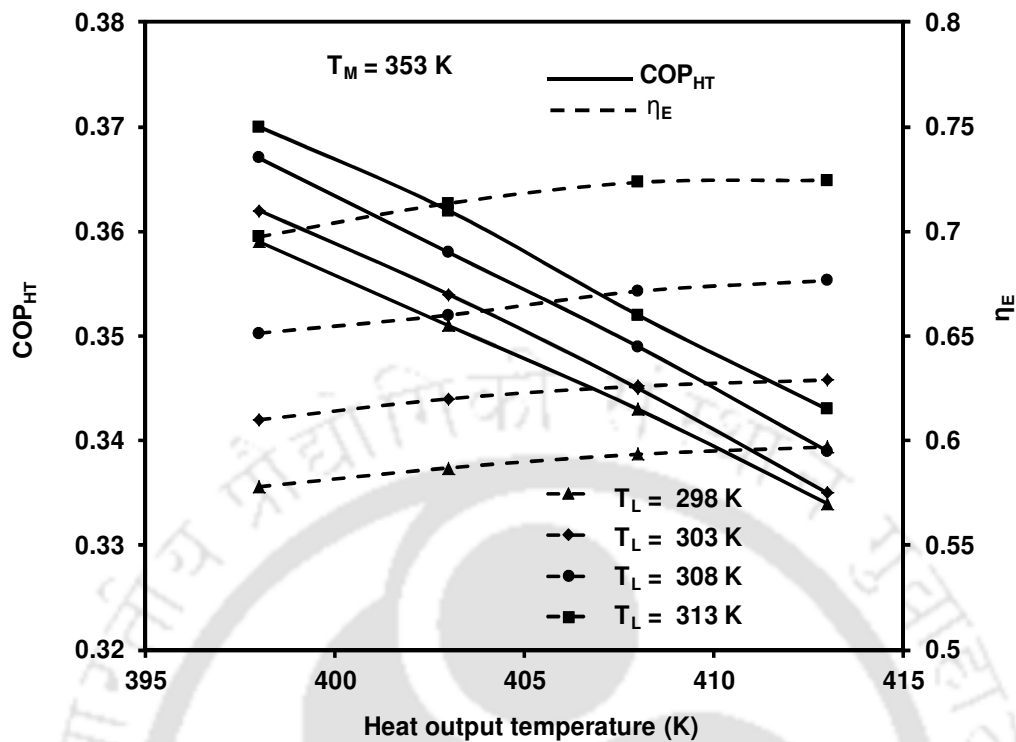


Fig. 5.19 Effect of heat rejection and heat output temperatures on COP_{HT} and η_E

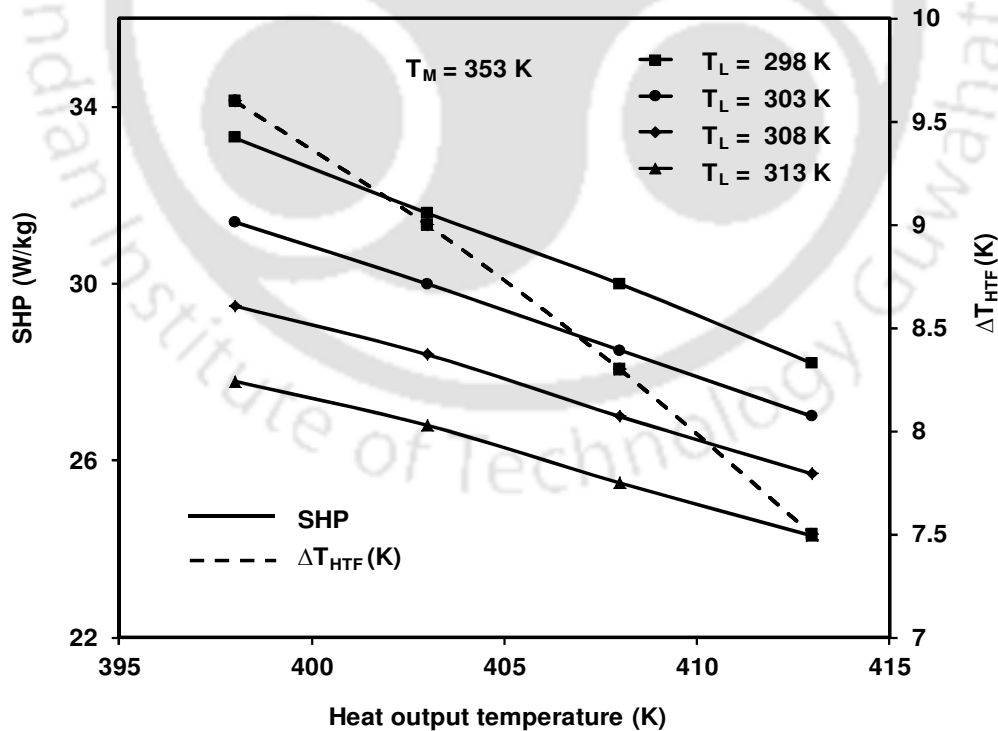


Fig. 5.20 Effect of heat rejection and heat output temperatures on SHP and ΔT_{HTF}

5.3 Experimental Results of Single-Stage Metal Hydride Based Heat Transformer

In this section, the results obtained from the experimental studies on SS-MHHT are presented. The performances of the SS-MHHT were tested at different heat source and heat sink temperatures. The uncertainty analysis is presented in Appendix B. The maximum uncertainty in the estimation of COP_{HT} and SHP are $\pm 12.3 \%$ and $\pm 8.78 \%$, respectively.

5.3.1 Variation of bed temperature of the reactors A and B

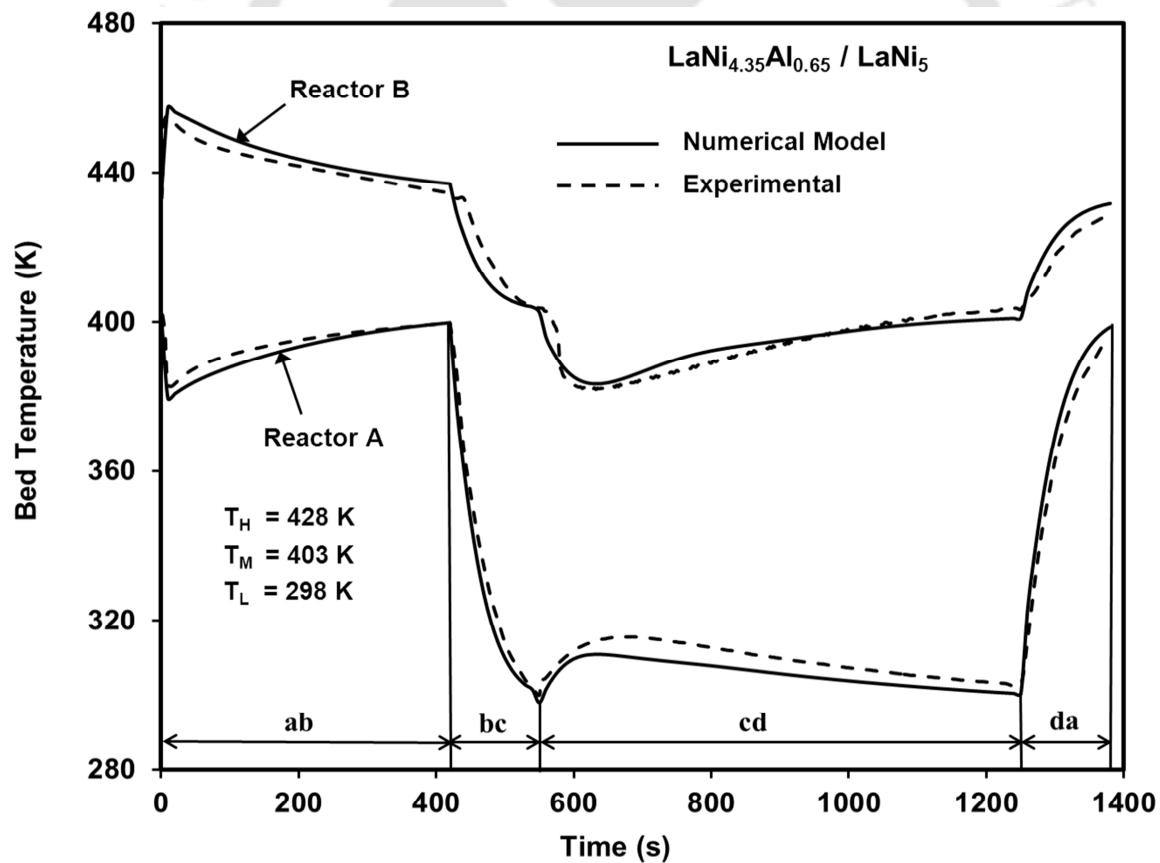


Fig. 5.21 Variation of hydride bed temperatures of the reactors A and B over a cycle

Figure 5.21 shows the variation of hydride bed temperature of both the reactors over a complete cycle. The four processes viz., first half cycle, sensible cooling, second half cycle and sensible heating processes of the SS-MHHT are respectively indexed as *ab*, *bc*, *cd* and *da*. It is observed that due to the poor thermal conductivity of the hydride bed, the required amount of heat is not being transferred from/to the HTF during initial rapid desorption/absorption process and hence, the sudden fall/rise in temperature of the reaction beds occurred as soon as the process is started. Finally, the hydride beds attained the respective HTF temperature. The magnitude of fall /rise in hydride bed temperature mainly depends on the difference between the hydride equilibrium pressures of the coupled reactors. From Fig. 5.21, it is observed that the numerically predicted temperature profiles of reactor A and B are in good agreement with experimentally measured temperature profiles over a complete cycle. A maximum deviation of about 3.2 % is obtained between the numerically predicted bed temperature and the experimental bed temperature during the process *cd*. A slight deviation is due to the experimental uncertainties, assumption of uniform void fraction and errors in the estimation of thermo-chemical properties of the metal hydride alloys.

5.3.2 Variation of hydrogen flow rate between coupled reactors

The variation of hydrogen flow rate and the cumulative amount of hydrogen exchanged between the coupled reactors are illustrated in Fig. 5.22. It is observed that initially the hydrogen flow rate is very high due to a large pressure difference between the coupled reactors and after that the hydrogen flow rate is decreased gradually. This process completes when there is no change in the totalized flow observed in the mass flow meter. From Fig. 5.22, it is noted that the total amount of hydrogen exchanged between the coupled reactors is about 4.5 - 4.6 g and the time

taken to complete *ab* and *cd* are about 420 s and 700 s, respectively. It has been observed that process *cd* takes more time as compared with process *ab*. This is due to small pressure difference available during process *cd* compared to process *ab*.

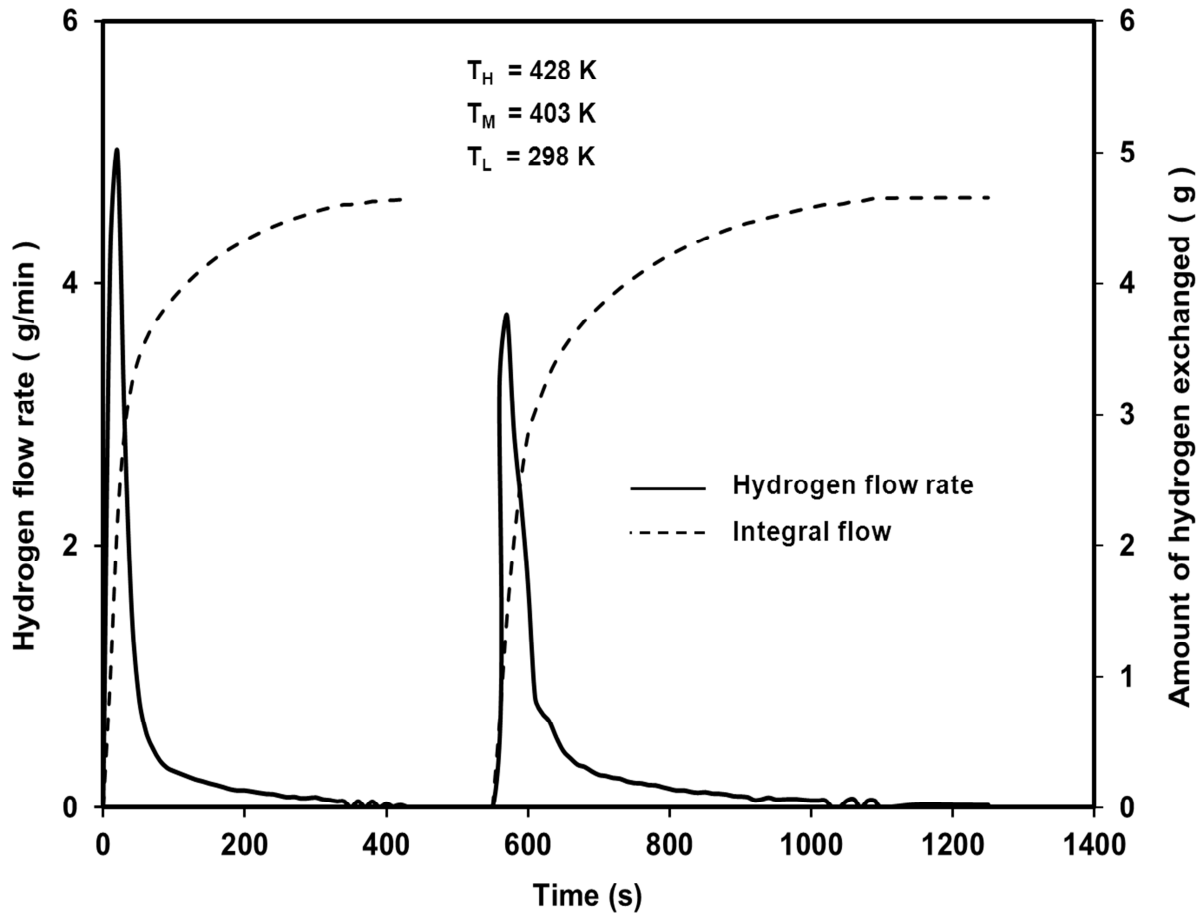


Fig. 5.22 Variation of hydrogen flow rate and amount of hydrogen exchanged over a cycle

5.3.3 Variation of heat interaction to/from the reactors A and B

Figure 5.23 shows the heat transfer from/to the reactors A and B during a complete cycle. Heat is removed from or supplied to metal hydrides during absorption or desorption of hydrogen owing to the endothermic/exothermic behavior of the reaction. It should be noted that the calculated Q

is the heat quantity actually exchanged between the HTF and the reactor bed. The heat transfer strongly depends on the rate of hydrogen flow between the coupled reactors. Initially hydrogen flow rate is high between the coupled reactors, due to this the heat transfer is also high. Then, the hydrogen flow rate is gradually decreased as a result the heat transfer is also decreased gradually. In Fig. 5.23, the peaks show the heat transfer during sensible heat transfer processes *bc* and *da*. Heat transfer rate in the reactor B is slightly higher than reactor A. This is due to temperature difference between hydride bed and HTF in the reactor B.

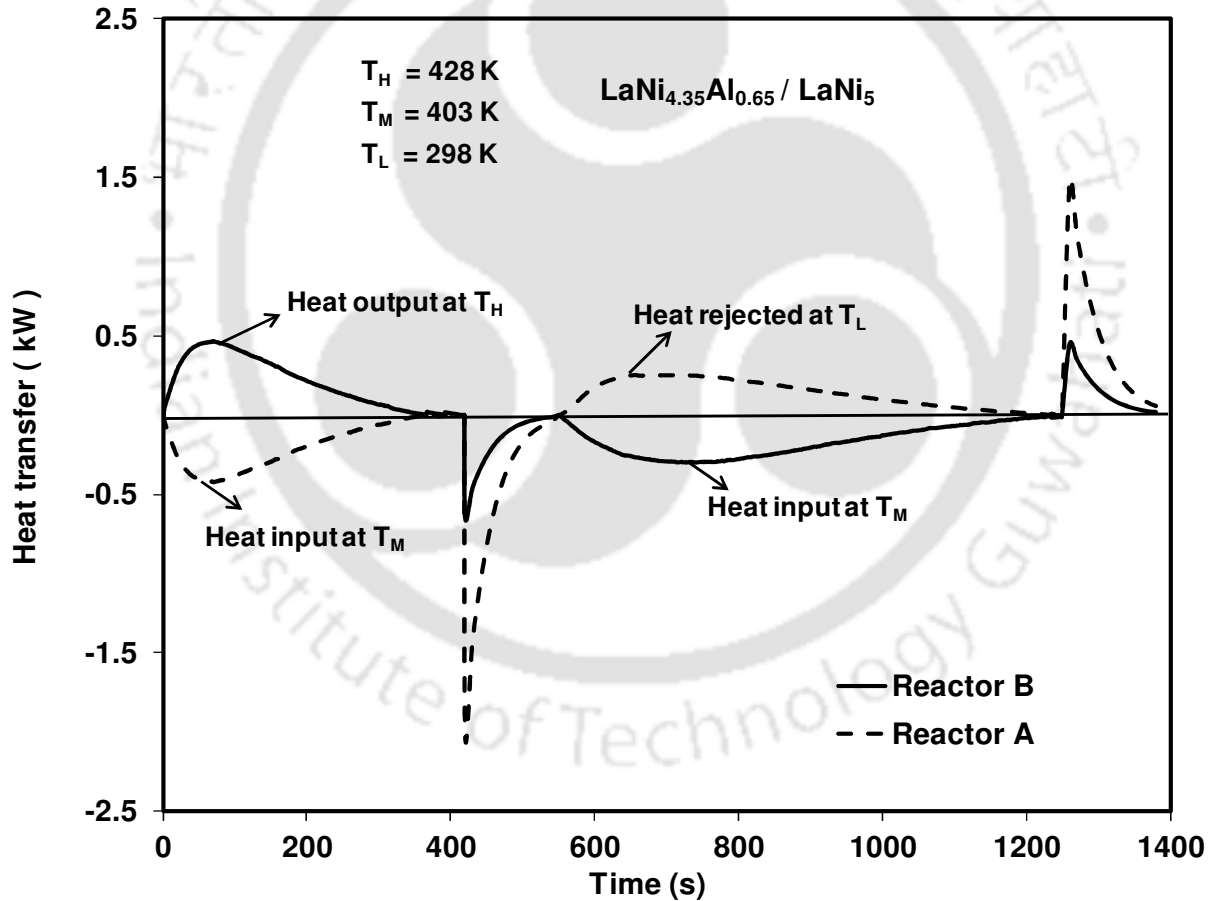


Fig. 5.23 Variation of heat transfer for a complete cycle

5.3.4 Effect of heat source temperature (T_M) on HTF temperature difference

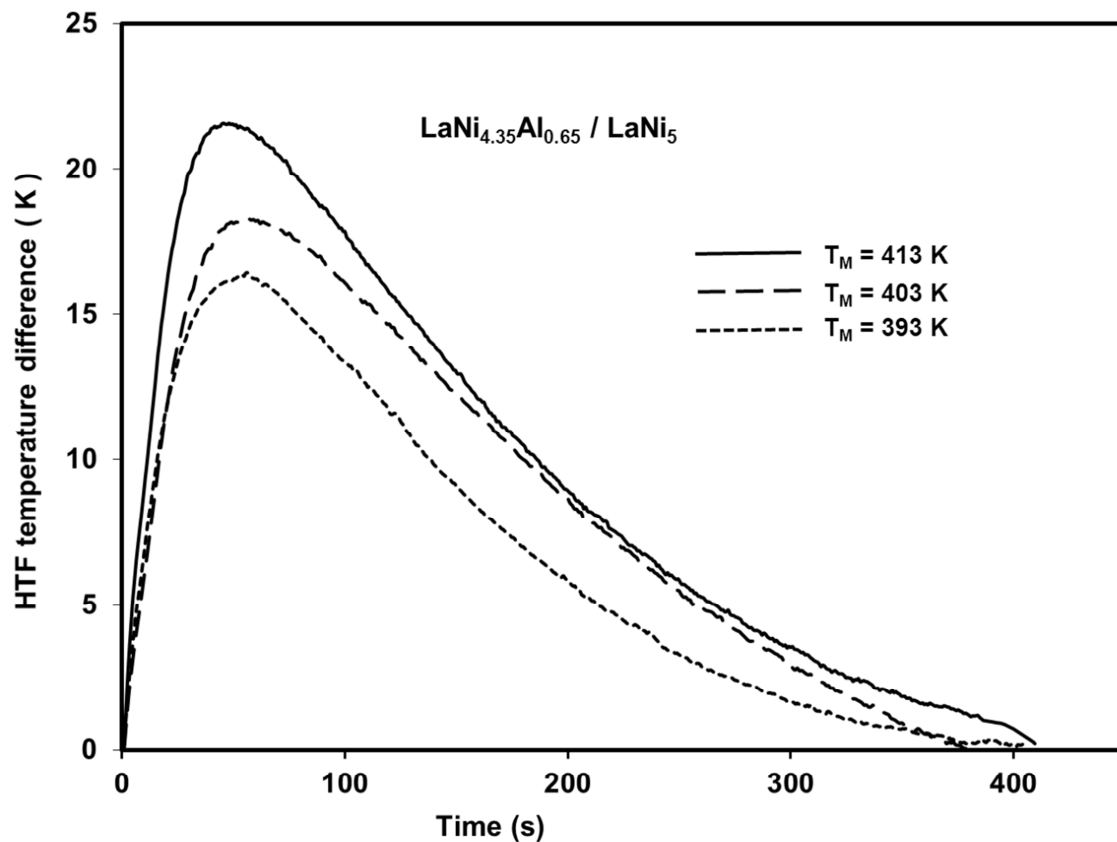


Fig. 5.24 Variation of HTF temperature difference during process *ab* (reactor B)

The HTF temperature difference (ΔT_{HTF}) at different T_M during high pressure hydrogen exchange process *ab* is shown in Fig. 5.24. Due to the rapid absorption/desorption processes at the initial stage, the ΔT_{HTF} is very high. As the time progresses, ΔT_{HTF} is found to decrease gradually. The ΔT_{HTF} variation is similar to hydride bed temperature variation with respect to cycle time. It is observed that average true temperature lift ΔT_{HTF} increases from 9 K to 12 K, when the T_M is increased from 393 K to 413 K. This is due to increase in the amount of hydrogen exchanged between the coupled reactors at higher T_M 's. The maximum achieved temperature up gradation is 35 K (difference between heat output and heat input temperatures).

5.3.5 Performance investigation of SS-MHHT

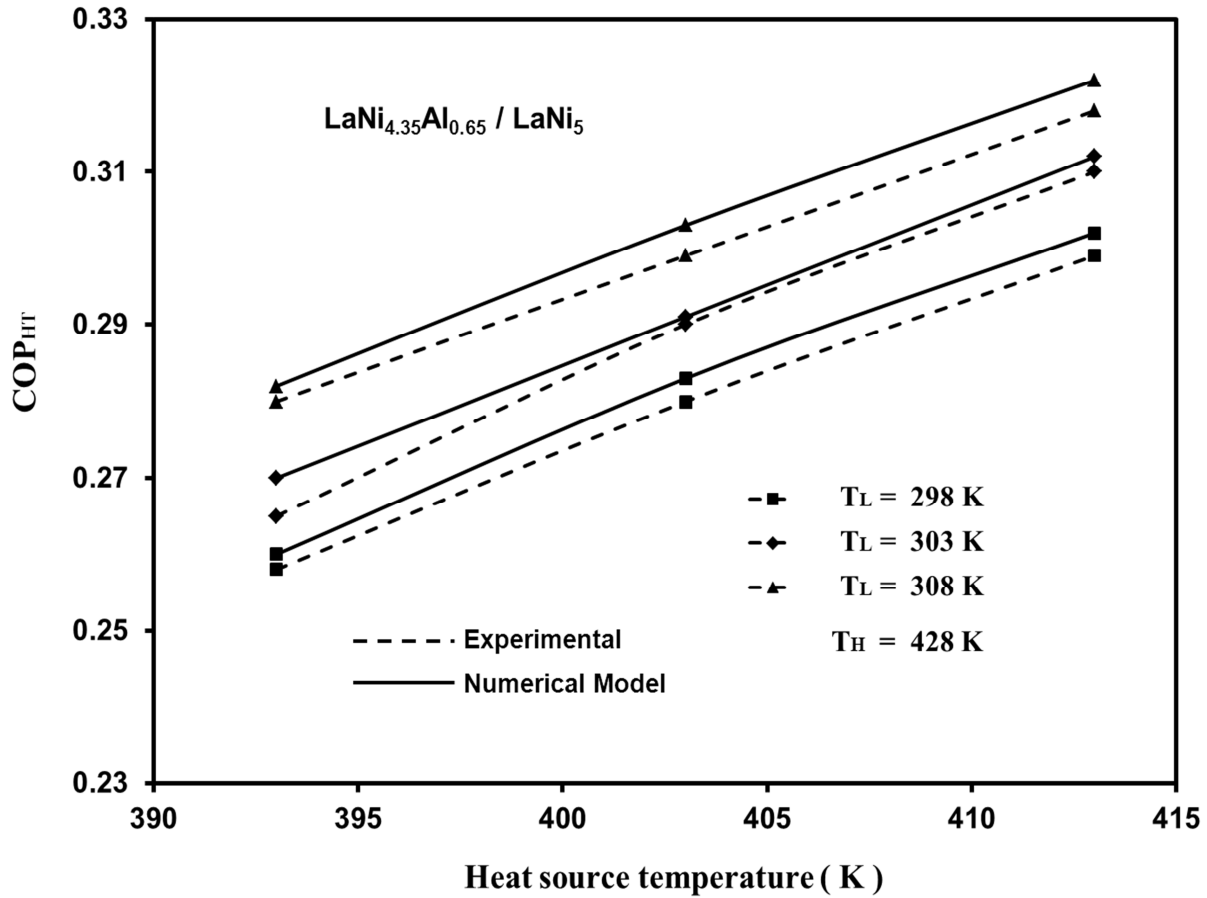


Fig. 5.25 Effect of heat source and heat rejection temperatures on COP_{HT}

The effects of the heat source temperature T_M and the heat rejection temperature T_L on the COP_{HT} and SHP are presented in Figs. 5.25 and 5.26. For a given T_H , higher T_M 's improve both COP_{HT} and SHP . The increase in COP_{HT} with T_M is mainly due to more amount of hydrogen exchanged between the coupled reactors and the increase in SHP with T_M is mainly due to the reduction in cycle time. At higher T_L , the driving potential for mass transfer during the process cd is small. This results in higher cycle time, leading to lower SHP . But the COP_{HT} increases slightly at higher T_L due to the reduction in the sensible heating requirement of the reactor A

during the process *da*. However, the increase in T_L beyond 313 K yields an adverse effect on both COP_{HT} and SHP as the amount of hydrogen transfer during the process *cd* decreases considerably due to the reduction in hydride equilibrium pressure difference between the paired reactors A and B.

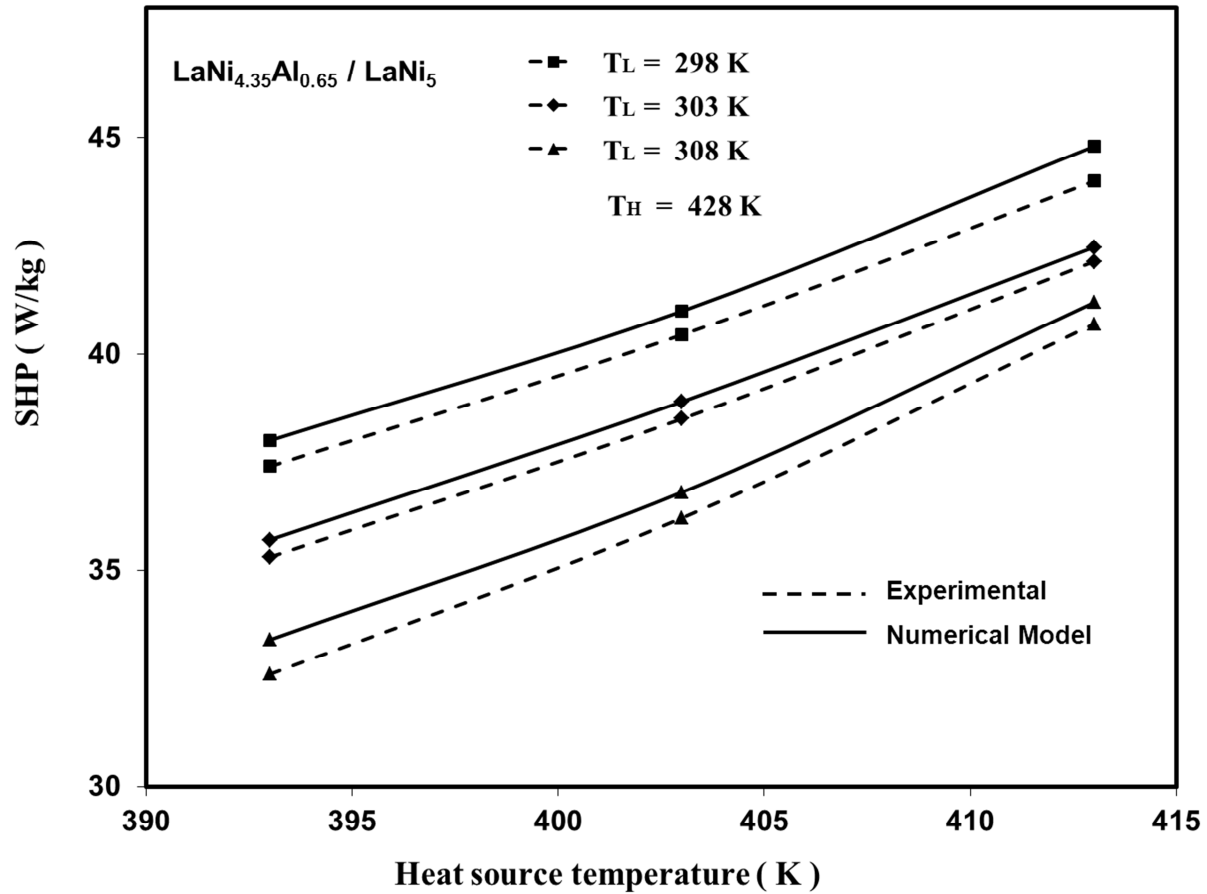


Fig. 5.26 Effect of heat source and heat rejection temperatures on SHP

At the operating conditions of $T_H = 428$ K and $T_L = 298$ K, the rise in T_M from 393 K to 413 K, increases the COP_{HT} and the SHP by about 14.5 % and 17.6 %, respectively. It is also seen from Figs. 5.25 and 5.26 that the increase in T_L from 298 K to 308 K, improves the COP_{HT} only by a marginal amount of about 5.8 % at $T_H = 428$ K and $T_L = 413$ K. But the reduction in SHP is about

9 %. The comparison between numerical and experimental results for the different heat source and heat rejection temperatures can be also seen in Figs. 5.25 and 5.26. It is observed that the agreement between the numerical prediction and the experimental value is satisfactory.

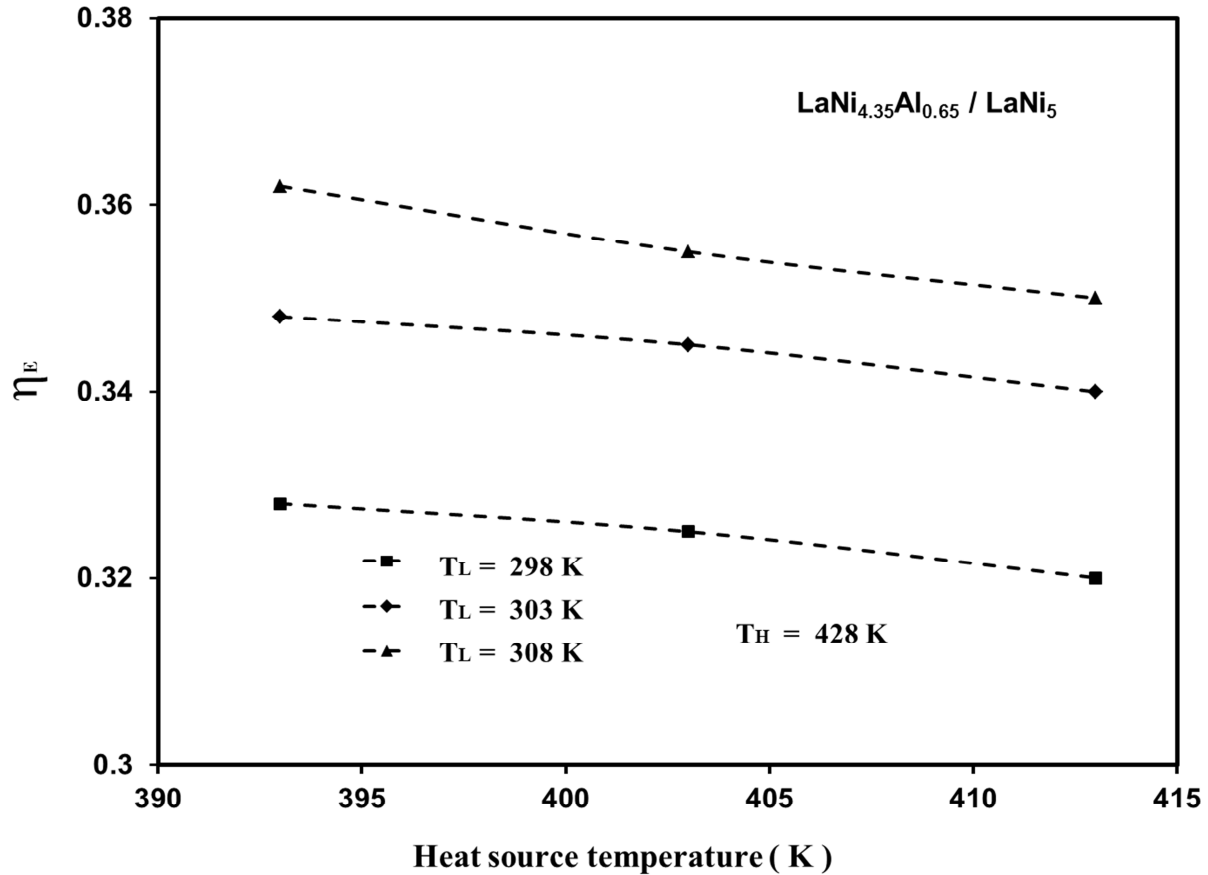


Fig. 5.27 Effect of heat source and heat rejection temperatures on η_E

Figure 5.27 shows the effects of heat source temperature T_M and heat rejection temperature T_L on the second law efficiency (η_E) of the SS-MHHT. For a given T_H and T_L , η_E is found to decrease marginally with T_M . As explained in Fig. 5.25 that the COP_{HT} increases with T_M but at the same time the improvement in COP_{Carnot} is more dominant than the increase in COP_{HT} with T_M . Since the η_E is ratio of COP_{HT} and COP_{Carnot} , its value is found to decrease by about 3.5 % when the T_M is increased from 393 K to 413 K. It is noted that for a given $T_M = 403$ K and $T_H = 428$ K, η_E

increases by about 9.3 % when the T_L is increased from 298 K to 308 K. This is due to the fact that higher T_L improves the COP_{HT} but reduces the COP_{Carnot} slightly. As a net result, for a given metal hydride combination, the η_E increases with T_L .

5.4 Experimental Results of Double-Stage Metal Hydride Based Hydrogen Compressor

Performance tests on a DS-MHHC were carried out by varying the supply pressure and heat source temperature. In the following sections the results obtained from the experiments are discussed.

5.4.1 Variation of hydride bed temperature with hot fluid temperature

The average hydride bed temperature profiles of $\text{La}_{0.35}\text{Ce}_{0.45}\text{Ca}_{0.2}\text{Ni}_{4.95}\text{Al}_{0.05}$ during desorption of hydrogen at different heat transfer fluid temperatures are illustrated in Fig. 5.28. Bed temperature at the beginning of the desorption process is equal to the heat transfer fluid temperature. When the endothermic dehydriding reaction begins, the hydrogen gas is released from the reactor. At the beginning of the desorption process, desorption rate is high and the required amount of heat of desorption is not able to transfer from the heat transfer fluid due to the low thermal conductivity of the hydride bed. As a result the bed temperature decreases initially. The decrease in bed temperatures is more at higher heat source temperature due to higher desorption rate. As the time progresses, desorption rate slows down and the bed temperature increases gradually towards the temperature of the heat transfer fluid.

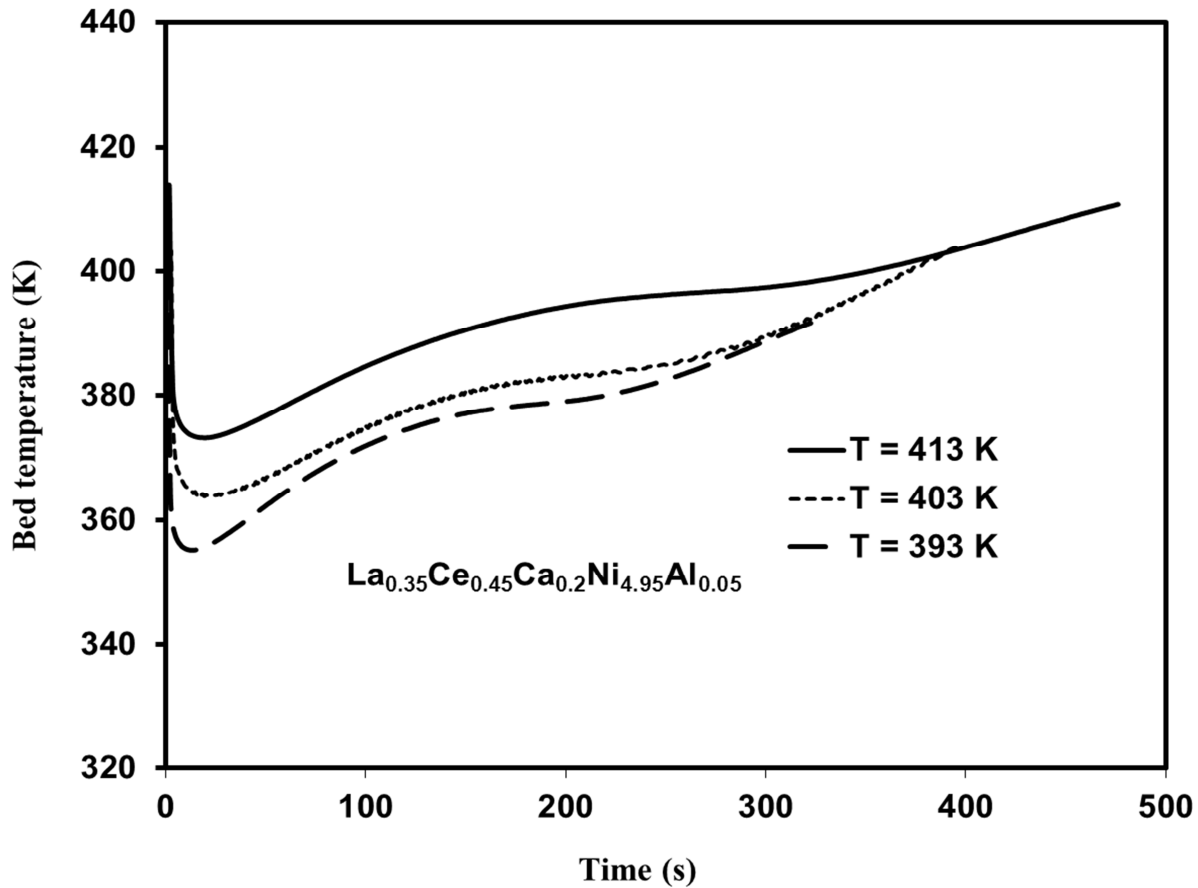


Fig. 5.28 Variation of bed temperature with hot fluid temperature

5.4.2 Effect of hydrogen supply pressure on delivery pressure

Figure 5.29 shows the effect of hydrogen supply pressure on the delivery pressure. The absorption temperature is kept constant at 298 K. The hydrogen delivery pressure of 56 bar is achieved at supply pressure 6 bar and 413 K heat source temperature. For a given heat source temperature, delivery pressure is found to increase with hydrogen supply pressure. This is due to increase in hydrogen absorption with increase in hydrogen supply pressure. As a result the final delivery pressure also increases. For a given heat source temperature of 413 K, the delivery pressure is found to increase from 56 to 74 bar when the hydrogen supply pressure is increased from 6 to 10 bar.

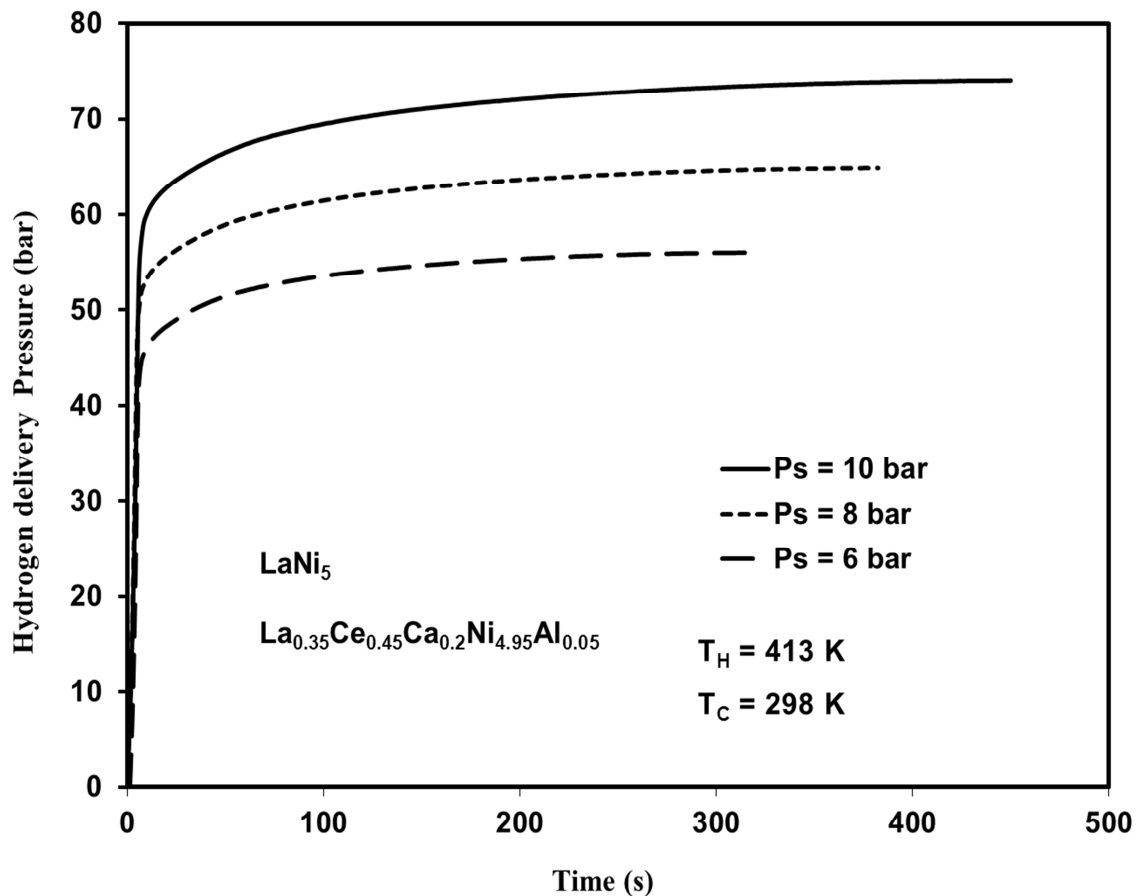


Fig. 5.29 Effect of hydrogen supply pressure on delivery pressure

5.4.3 Effect of hydrogen supply pressure and heat source temperature on delivery pressure and amount of hydrogen compressed

Table 5.2 shows the effects of hydrogen supply pressure and heat source temperature on the delivery pressure and the amount of hydrogen compressed. For a given hydrogen supply pressure, the delivery pressure increases with the heat source temperature. This is due to the increase in equilibrium pressure of the hydride bed with bed temperature as per the van't Hoff equation (Muthukumar *et al.*, 2005). For given hydrogen supply pressure of 10 bar, the delivery pressure increases from 61 to 74 bar when the heat source temperature is increased from 393 K

to 413 K. For a given heat source temperature of 393 K, the delivery pressure increases from 32 to 61 bar when the hydrogen supply pressure increased from 2 to 10 bar. Due to the plateau slope of hydrides, at a given heat sink temperature, the amount of hydrogen absorbed increases with supply pressure. In the experimental study, the volume of the storage tank is fixed. Therefore, for a given desorption temperature, the delivery pressure is found to increase with supply pressure. At operating temperatures of 413 K (desorption) and 298 K (absorption), the amount of hydrogen compressed increases from 3.8 to 5.9 grams when the hydrogen supply pressure increased from 2 to 10 bar.

Table 5.2 Effects of operating parameters on the delivery pressure and the amount of hydrogen compressed.

Supply pressure (bar)	Heat source temperature					
	393 K		403 K		413 K	
	$P_d(\text{bar})$	$m_{H_2}(\text{g})$	$P_d(\text{bar})$	$m_{H_2}(\text{g})$	$P_d(\text{bar})$	$m_{H_2}(\text{g})$
2	32	3.25	39	3.5	44	3.8
4	38	3.95	43	4.1	50	4.45
6	45	4.5	50	4.75	56	4.95
8	54	5.05	61	5.4	66	5.62
10	61	5.54	68	5.1	74	5.9

5.4.4 Effect of hydrogen supply pressure and heat source temperature on compressor work

Figure 5.30 shows the effect of hydrogen supply pressure and heat source temperature on the isentropic compression work. The maximum compression work that could be achieved is about

22.9 kJ/kg for 2 bar hydrogen supply pressure and 413 K heat source temperature. The compression work is found to decrease with increase in the hydrogen supply pressure from 2 to 6 bar due to domination of pressure ratio in the compressor work. It is also observed from Fig. 5.30 that for a given hydrogen supply pressure, the compression work increases with heat source temperature. This is due to increase of driving potential for hydrogen transfer between the coupled metal hydride beds.

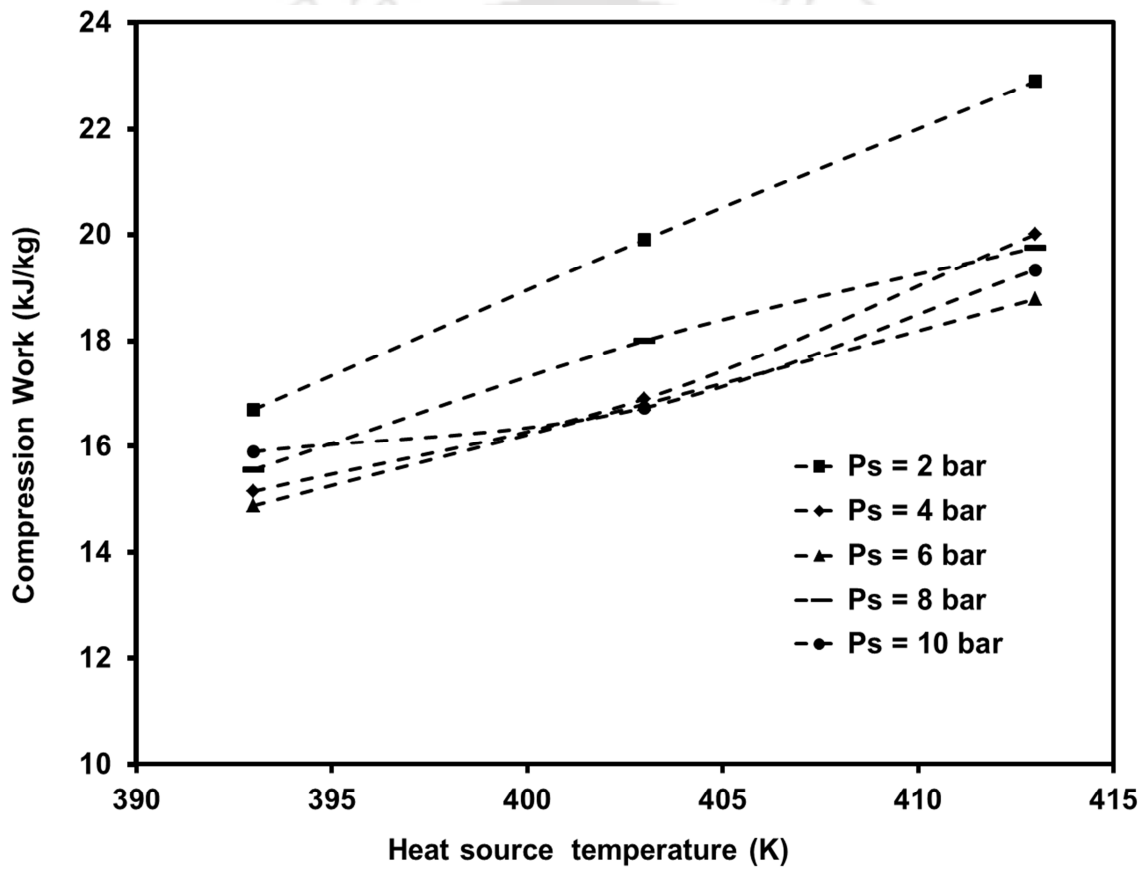


Fig. 5.30 Effect of hydrogen supply pressure and heat source temperature on compressor work

5.4.5 Effect of hydrogen supply pressure and heat source temperature on compression ratio (CR)

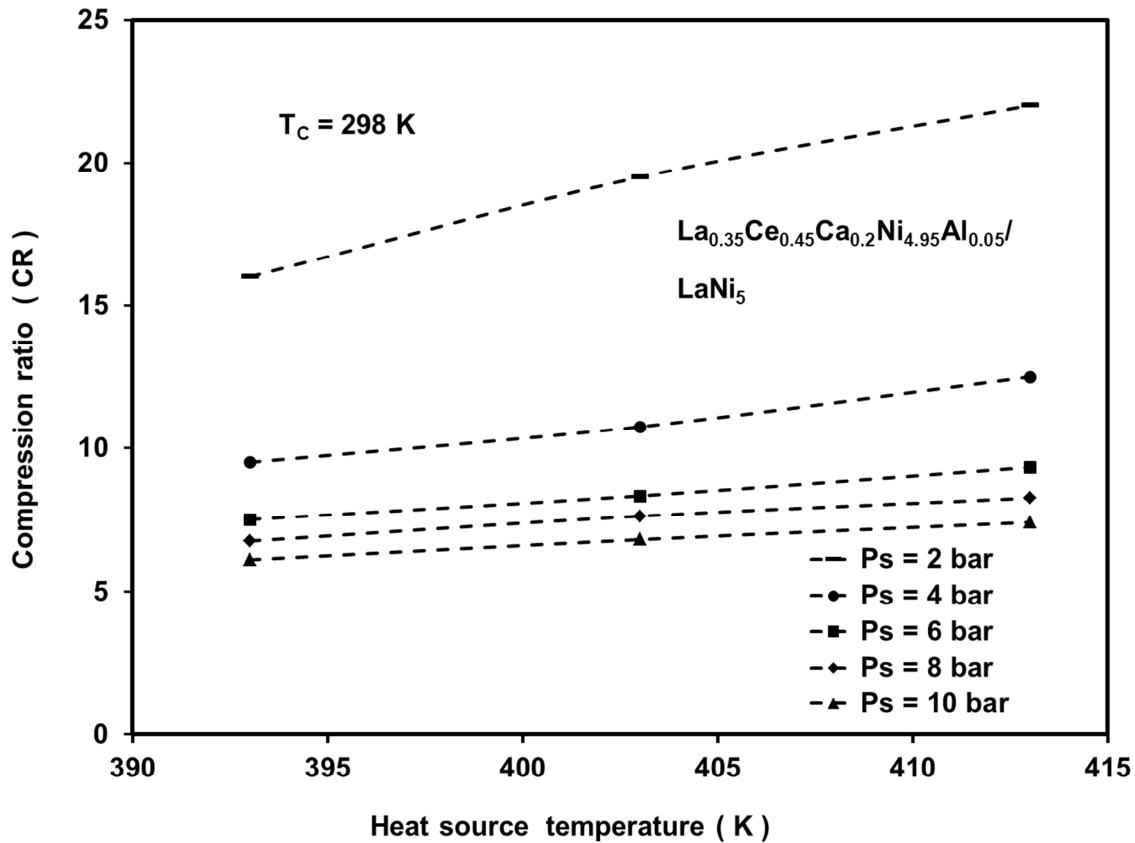


Fig. 5.31 Effects of hydrogen supply pressure and heat source temperature on compression ratio

The variations of compression ratio (CR; the ratio between the delivery pressure and the hydrogen supply pressure) with hydrogen supply pressure and heat source temperature is shown in Fig. 5.31. It is found that the CR increases with heat source temperature and decreases with the hydrogen supply pressure. The maximum CR of 22 is achieved when the DS-MHHC is operated at 2 bar hydrogen supply pressure and 413 K heat source temperature. For a given hydrogen supply pressure of 2 bar, the CR increases from 16 to 22 when the heat source temperature is increased from 393 K to 413 K. The increase in CR is more significant with the

hydrogen supply pressure compared to the heat source temperature. However, higher delivery pressures can be obtained only at higher heat source temperatures.

5.4.6 Effect of hydrogen supply pressure and heat source temperature on compressor efficiency (η_c)

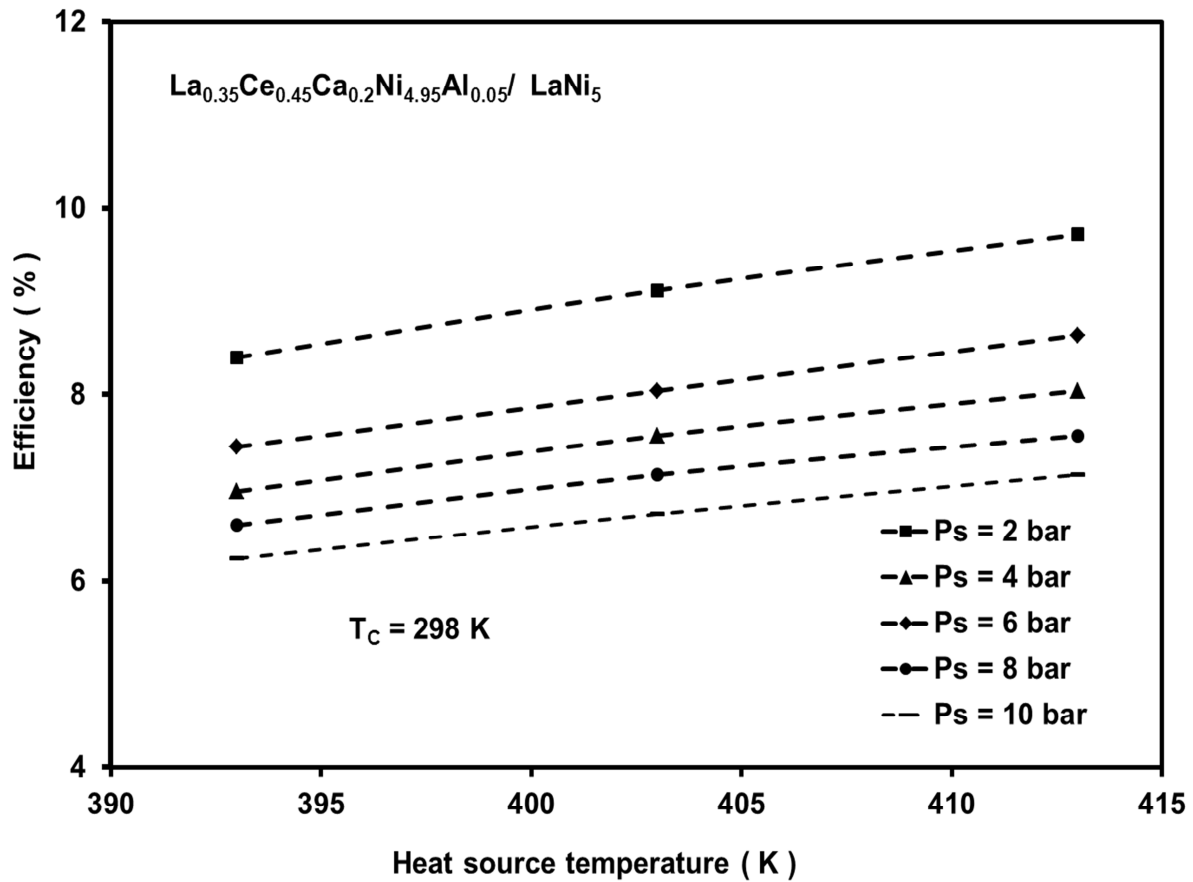


Fig. 5.32 Effects of hydrogen supply pressure and heat source temperature on η_c

Figure 5.32 shows the effect of hydrogen supply pressure and heat source temperature on the compressor efficiency (η_c). Compressor efficiency decreases with increase in the hydrogen supply pressure. As explained in Eq. (4.3), at higher hydrogen supply pressure, m_{H_2} is found to increase but CR decreases significantly. Due to domination of CR, compressor efficiency is

found to decrease at higher hydrogen supply pressures. For achieving higher compressor efficiency, hydrogen supply pressure should be low but it must be above the required absorption pressure corresponding to the absorption temperature. Fig. 5.32 also shows that the compressor efficiency increases with heat source temperature. The maximum compressor efficiency of 9.7 % is achieved at the operating conditions of 2 bar hydrogen supply pressure and 413 K heat source temperature.

In DS-MHHT, hydride B should absorb hydrogen at low pressure ($\sim 2 - 6$ bar) around ambient temperature and hydride A must desorb hydrogen at high pressure ($\sim 50 - 80$ bar) in the input temperature range ($120 - 140$ °C). Since, the combined performance of LaNi_5 and $\text{La}_{0.35}\text{Ce}_{0.45}\text{Ca}_{0.2}\text{Ni}_{4.95}\text{Al}_{0.05}$, fulfills the requirement of DS-MHHT between the heat input temperature range of 120 °C and 140 °C, they are selected for the development of DS-MHHT prototype by keeping the same heat transformer alloy, $\text{LaNi}_{4.35}\text{Al}_{0.65}$ which was employed in the SS-MHHT's prototype.

5.5 Experimental Results of Double-Stage Metal Hydride Based Heat Transformer

In the following sections, the results obtained from the experiments are discussed. The performance of the DS-MHHT was tested at different heat source and heat sink temperatures.

5.5.1 Variation of bed temperature of the reactors

Figure 5.33 shows the transient variation of reaction bed temperature of the reactors A, B and C over a complete cycle. The six processes viz., three coupled heat and mass transfer processes and

three sensible heating processes of the DS-MHHT are respectively indexed as *ab*, *bc*, *cd*, *de*, *ef* and *fa*.

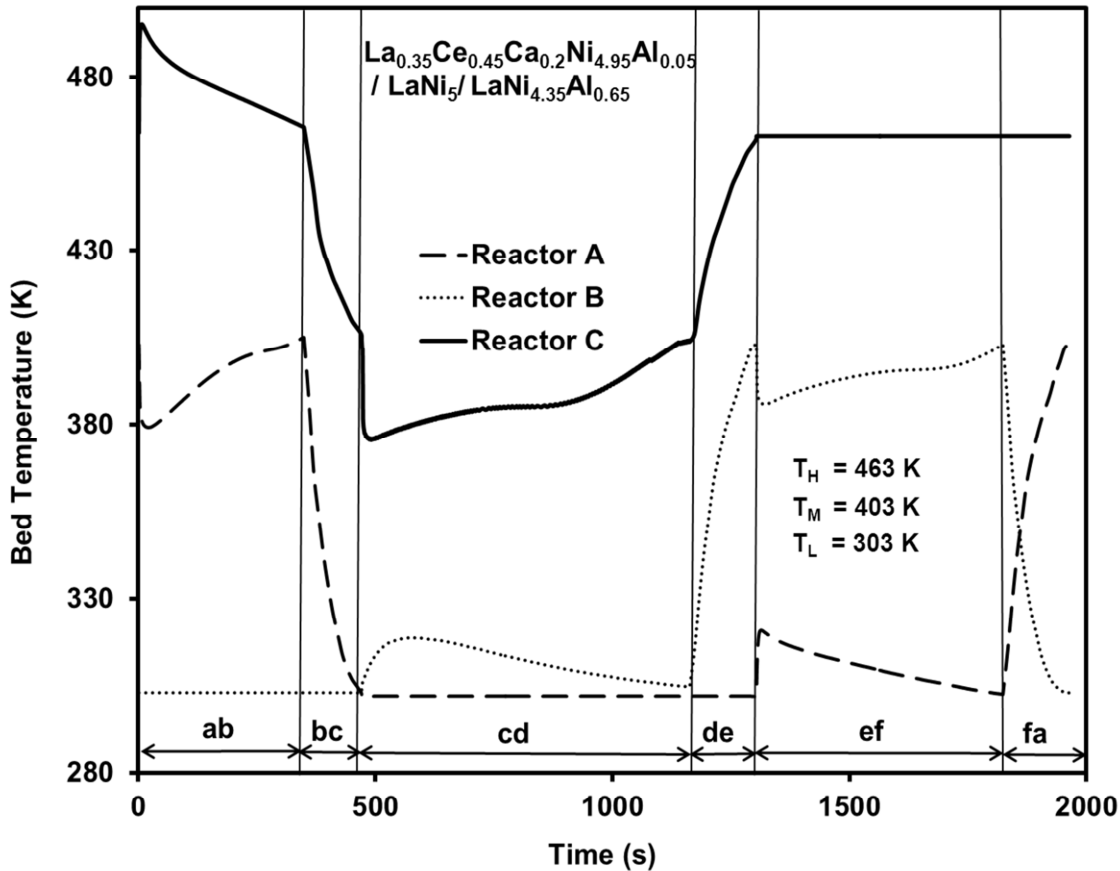


Fig. 5.33 Variation of bed temperatures over a complete cycle

It is observed that due to the poor thermal conductivity of the reaction bed, the required amount of heat is not able to admit/reject from/to the HTF during initial rapid desorption/absorption of hydrogen by the reaction bed. As a result, the bed temperature decreases/increases sharply during the initially period of desorption/absorption process. As the time progresses, desorption/absorption rate slows down. The heat transfer takes place from/to the HTF to/from the bed and as a result the bed temperature reaches gradually towards to the temperature of the HTF. Finally, all the reaction beds reach their respective HTF temperatures. The amount of fall /rise in

reaction bed temperature mainly depends on the difference between the equilibrium pressures of the coupled reactors.

5.5.2 Variation of heat interaction to/from the reactors A, B and C

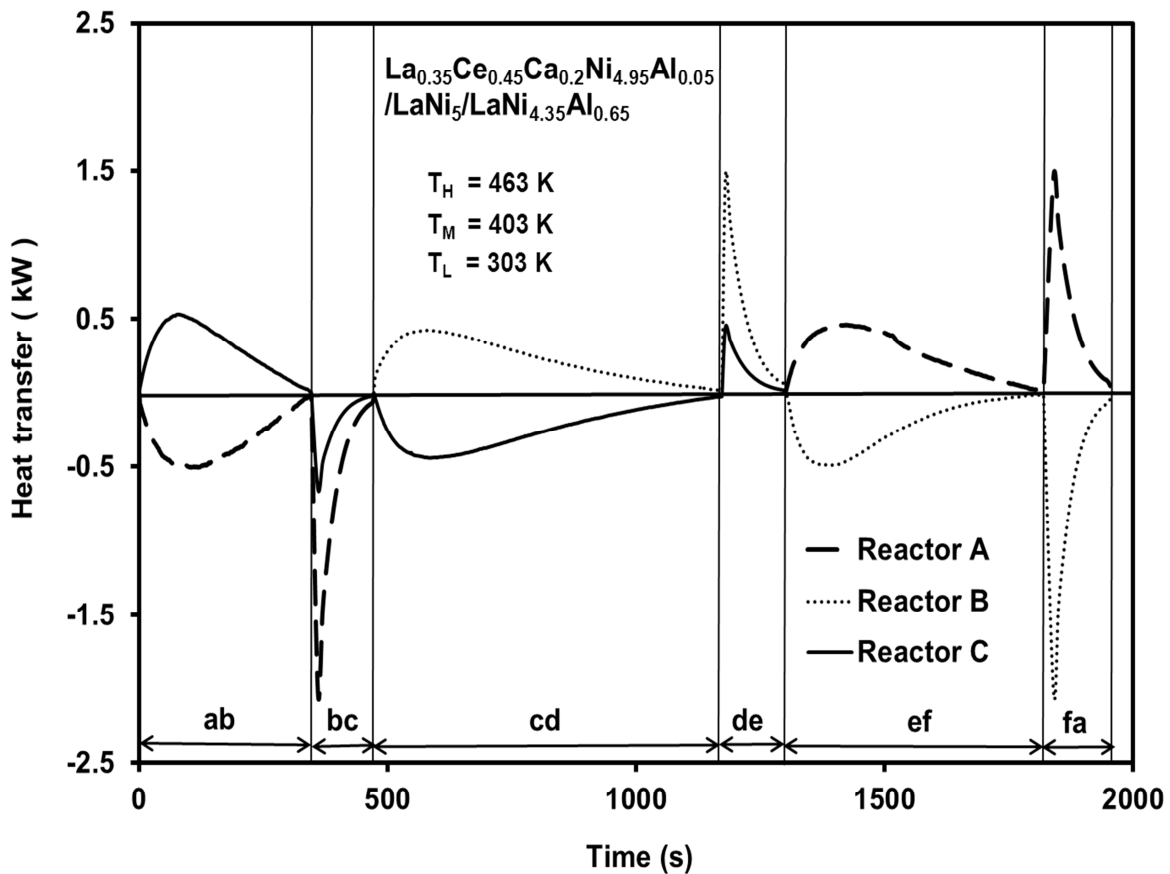


Fig. 5.34 Amount of heat exchanged over a complete cycle

The amount of heat removed / supplied from / to the reactors A, B and C over a complete cycle is presented in Fig. 5.34. The heat removal/supply rate is calculated using the Eq. (4.10). The heat transfer strongly depends on the rate of hydrogen flow between the coupled reactors. Due to the rapid absorption/desorption process at the initial stage of the hydrogen transfer process, the

amount of heat removed/supplied from/to the reactor is very high. As the time progresses, the heat removal/supply from/to the reactor is found to decrease gradually and becomes zero at the end of the process. Since, the rate of hydrogen absorbed/desorbed to/from the reactor decreases with time, the heat removed/supplied from/to the reactor is also found to decrease. In Fig. 5.34, the peaks show the heat transfer during sensible heat transfer processes *bc*, *de* and *fa*. The amount of energy interaction from/to the reactor C is higher in comparison with the reactors A and B. This is due to the higher heat of formation of the hydride C.

5.5.3 Effect of heat source temperature (T_M) on HTF temperature difference

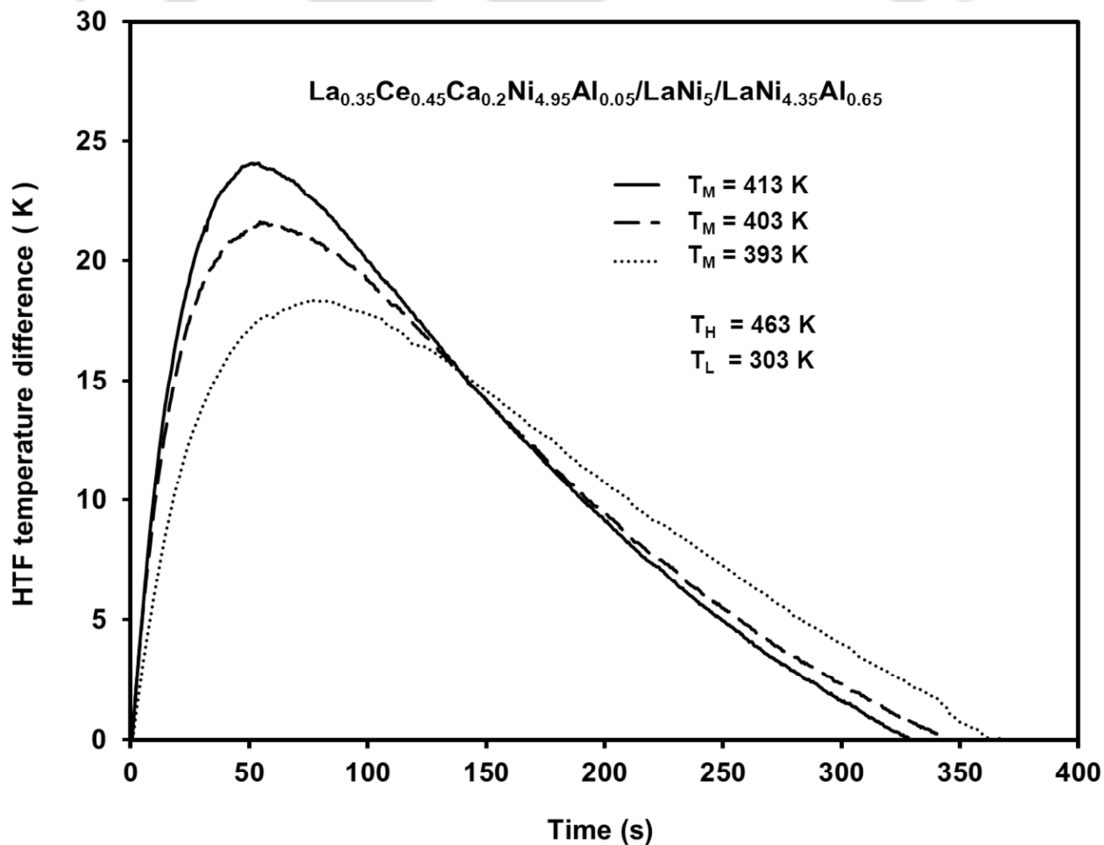


Fig. 5.35 Variation of HTF temperature difference during process *ab* (reactor C)

The HTF temperature difference (ΔT_{HTF}) at different T_M 's during high pressure hydrogen exchange process *ab* is shown in Fig. 5.35. Due to high hydrogen flow rate between the coupled reactors, ΔT_{HTF} is found to be higher at the initial period of the process. As the time progresses, ΔT_{HTF} is found to decrease gradually. It is observed that ΔT_{HTF} increases from 10.5 K to 12.9 K, when the T_M is increased from 393 K to 413 K. This is due to the fact that higher T_M increases the amount of hydrogen exchanged between the coupled reactors (for the same T_H and T_L). The maximum temperature lift of 70 K (difference between heat output and heat input temperatures) is achieved from the present experimental investigation.

5.5.4 Performance investigation of DS-MHHT

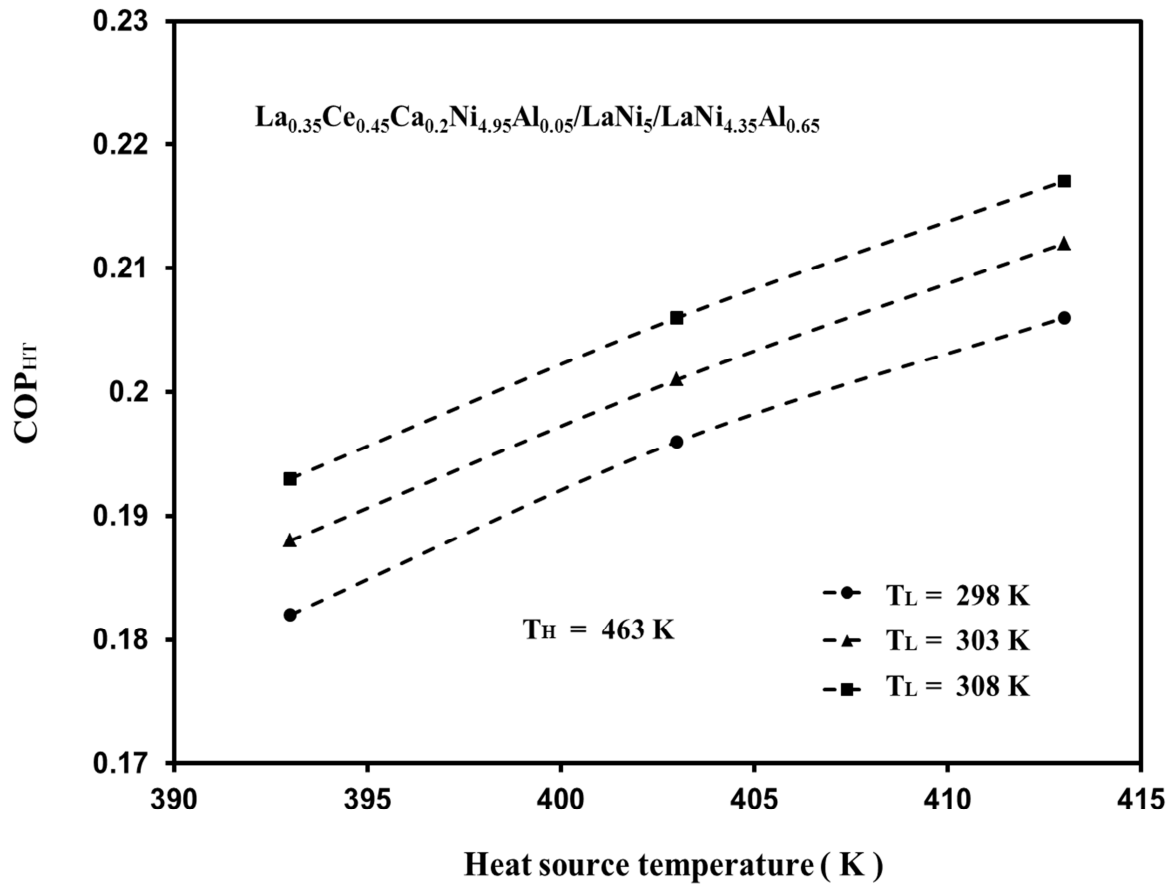


Fig. 5.36 Effects of heat source and heat rejection temperatures on COP_{HT}

The effects of the heat source temperature, T_M and the heat rejection temperature, T_L on COP_{HT} and SHP of the system are illustrated in Figs. 5.36 and 5.37. Heat source temperature influences both the sensible heating and the hydrogen transfer processes. For the given T_H and T_L , higher T_M increases the equilibrium pressure of reactors A, C and B during the processes ab , cd and ef respectively. Hence, the difference between the equilibrium pressures of two reactors increases, resulting in more amount of hydrogen exchange between the coupled reactors and decrease in cycle time. Consequently, both the COP_{HT} and SHP increase.

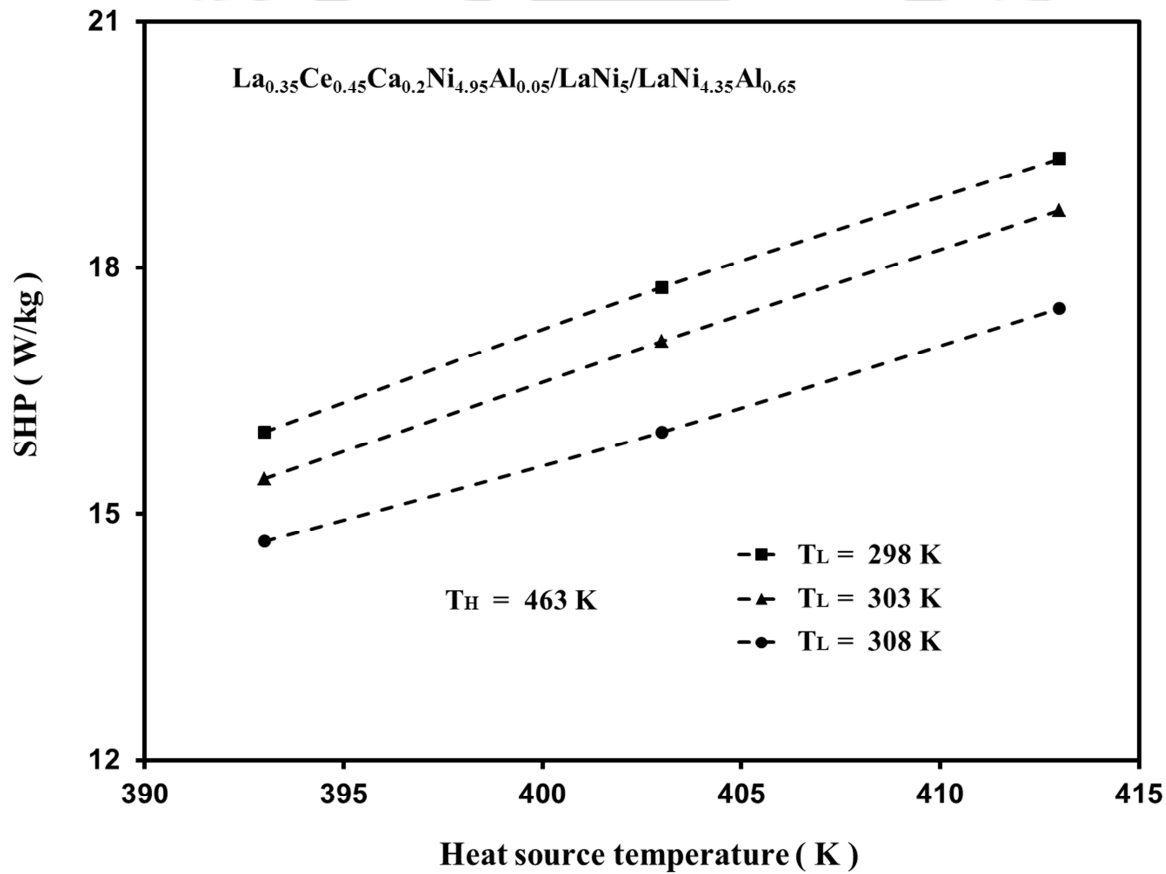


Fig. 5.37 Effects of heat source and heat rejection temperatures on SHP

At higher T_L , the driving potential for mass transfer during the processes cd and ef is small. This results in higher cycle time, leading to lower SHP . But the COP_{HT} increases slightly at higher T_L due to the reduction in the sensible heating requirement of the reactors B and A during the process de and fa . For the given operating conditions of $T_H = 463$ K and $T_L = 298$ K, the increase in T_M from 393 K to 413 K, increases the COP_{HT} and the SHP by about 11.9 % and 20.8 % respectively. It is also observed from Figs. 5.36 and 5.37 that the COP_{HT} increases marginally by about 3.8 % and reduces the SHP by about 8.3 % when the T_L is increased from 298 K to 308 K at the operating conditions of $T_H = 463$ K and $T_M = 393$ K.

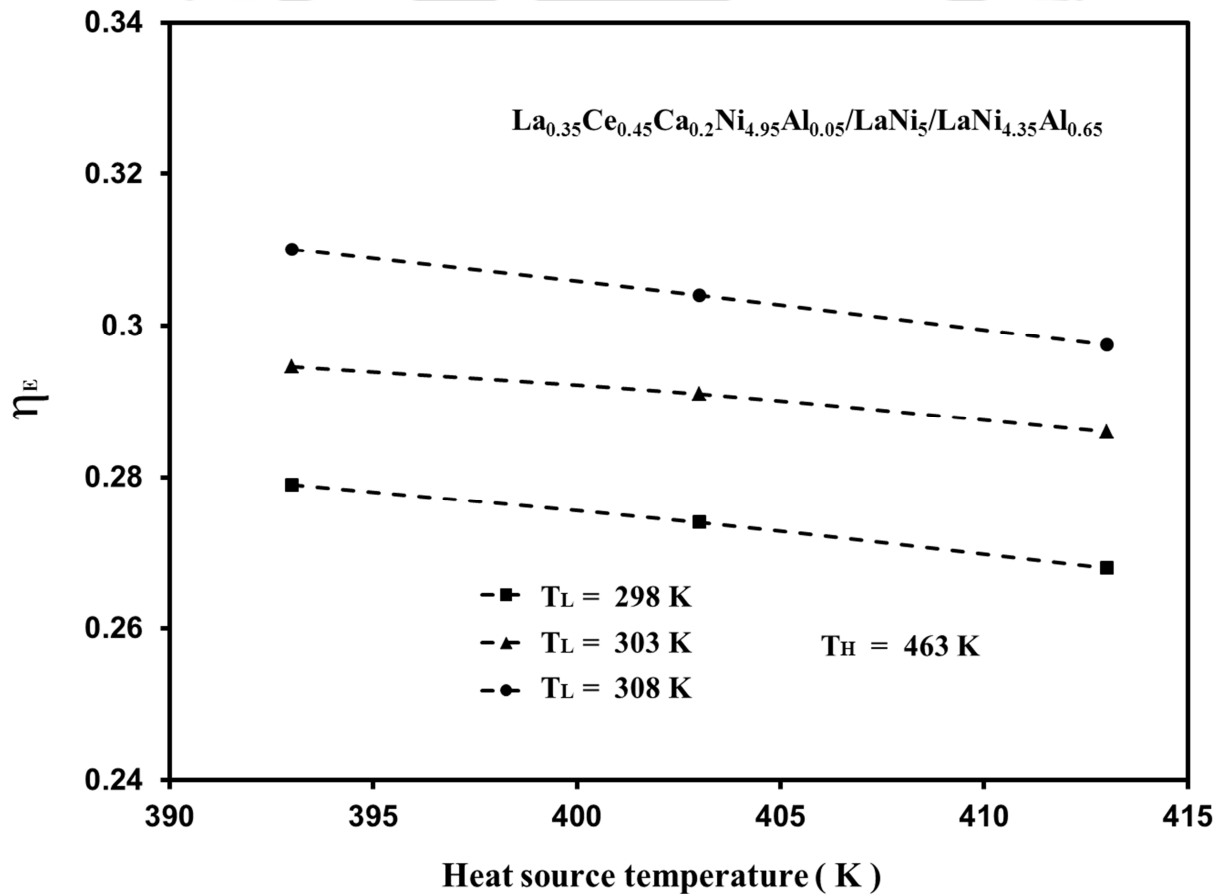


Fig. 5.38 Effects of heat source and heat rejection temperatures on η_E

The effects of the heat source temperature, T_M and the heat rejection temperature, T_L on the second law efficiency (η_E) is shown in Fig. 5.38. It is found that the η_E of the system decreases with increase in T_M . With increase in T_M , the COP_{HT} increases but at the same time COP_{Carnot} also increases. But increase in COP_{Carnot} is more as compared with COP_{HT} . Hence, the η_E of the system decreases. From Fig. 5.38, it is observed that the η_E decreases by about 4.2 % when the T_M is increased from 393 K to 413 K. It is also observed that at higher T_L , the COP_{HT} increases slightly due to the reduction in the sensible heating requirement of the reactors A and B. But higher T_L reduces the COP_{Carnot} and as a net result, the η_E increases with T_L . It is noted that for a given $T_M = 403$ K and $T_H = 463$ K, η_E increases by about 9.8 % when the T_L is increased from 298 K to 308 K.

5.6 Comparison of SS-MHHT and DS-MHHT Systems

Table 5.3 provides the comparison of actual performances of both SS-MHHT and DS-MHHT in terms of COP_{HT} , SHP and temperature lift.

Table 5.3 Comparison of the SS-MHHT and DS-MHHT systems

Heat Source Temperature (T_M)	COP_{HT}		SHP (W)		Temperature Lift (K)	
	SS	DS	SS	DS	SS	DS
393 K	0.28	0.193	37.4	16	35	70
403 K	0.299	0.206	40.45	17.76	25	60
413 K	0.318	0.217	44	19.33	15	50

5.7 Feasibility of Commercialization of the MHHT

Usually heat will be upgraded by using conventional liquid-gas absorption heat pumps or transformers (H_2O -LiBr and NH_3 - H_2O). But the temperature lift of these systems is limited to about 50°C because of properties of working solution (Werner and Groll, 1991). The MHHT is projected as a potential thermal device for upgrading the quality of heat/temperature of flue gas from the coal fired power plants and various process industries. Since the heat input is available at free of cost, even if the MHHT provides a COP in the range of 0.2 to 0.25, it will be more economical from energy conservation point of view. Employing a MHHT for the utilization of low grade heat would contribute not only the energy saving, but also reduces the environmental pollution and creates a better working environment.

In the frame of this thesis work, the performances of metal hydride based single-stage and double-stage heat transformer's prototypes were predicted by conducting the systematic experiments at a wider range of operating temperatures. Based on the results one can conclude that MHHT can be effectively used as a potential alternate device for upgrading the low grade heat of 120°C up to about 160 - 170°C using SS-MHHT and up to about 190 - 220°C employing DS-MHHT. By using the developed thermal models one can predict the optimum operating parameters range of SS-MHHT and DS-MHHT, such as heat source, heat output and heat sink temperatures and half cycle time without conducting the expensive experimental studies and also these models will be highly useful in identifying the optimum reactor geometry.

As pointed out in the thesis, for a given alloy pair, the performance of the system mainly depends on the heat and mass transfer characteristics of the coupled reactors. The heat and mass transfer characteristics can be enhanced further by adding Al foam, Cu band or cassette, etc. Compact reactor design with embedded heat transfer fluid tubes is a better option for achieving shorter

half cycle time. Recently, Dr. P. Muthukumar's research group at IIT Guwahati has developed metal hydride reactors with embedded heat transfer fluid tubes. These reactors could absorb 100-120 g of hydrogen (alloy charging capacity of about 10 kg) within 5 min. It was observed that the hydriding and dehydriding characteristics of these reactors are much better than the reactor with simple cylindrical configuration (Anbarasu et al., DOI:10.1016/j.ijhydene.2013.12.090). Therefore, the performance of the industrial scale system can be improved in the following ways;

- By sensible heat recovery: This is more effective for DS-MHHT
- By employing compact reactors with embedded heat transfer fluid tubes
- By optimizing heat transfer enhancement and thermal capacity of the reactor

One of the major hurdles for the possible commercialization of the MHHT is the cost of the host alloy. At present, no one is trading these metal hydride alloys in India. However, there are several manufactures (M/s. LABTECH Ltd, Sofia- 1784, Bulgaria, M/s. GFE Germany, Whole Win (Beijing) Materials Sci. & Tech Co., Ltd, China) around the world have started to offer various metal hydride alloys at competitive prices. Recently, Whole Win (Beijing) Materials Sci. & Tech Co., Ltd, China is ready to offer La and Mm series alloys at \$ 33 per kg and Ti based alloys at \$ 40 per kg. The price may be expected to reduce further, if one can go for a bulk order. In view of the above, MHHT deserve a major attention in elevating the temperature of the waste heat coming out from coal fired power plants, various process industries, etc. Later this upgraded heat can be used as a thermal input for several applications.

Overall, this thesis may provide some useful guidelines for developing the commercial / industrial scale system for upgrading the waste heat to a useful level.

The major conclusions arrived from the numerical and experimental studies on SS-MHHT and DS-MHHT and experimental studies on DS-MHHC are presented in Chapter 6.

Chapter 6

CONCLUSIONS AND FUTURE SCOPE

The major conclusions drawn from the numerical and experimental studies on SS-MHHT and DS-MHHT and the experimental studies on DS-MHHC are presented in this chapter.

6.1 Numerical Studies

6.1.1 Single-stage metal hydride based heat transformer (SS-MHHT)

A computational study of a SS-MHHT system working with $\text{LaNi}_5/\text{LaNi}_{4.7}\text{Al}_{0.3}$ hydride pair has been presented. The system of equations are solved by the fully implicit finite volume method (FVM) using the central difference scheme. The mathematical model developed for a SS-MHHT is extended to study the performance of the SS-MHHT system working with four different alloy pairs, namely $\text{LaNi}_5/\text{LaNi}_{4.7}\text{Al}_{0.3}$ (AP1), $\text{LaNi}_{4.6}\text{Al}_{0.4}/\text{MmNi}_{4.15}\text{Fe}_{0.85}$ (AP2), $\text{LaNi}_{4.61}\text{Mn}_{0.26}\text{Al}_{0.13}/\text{La}_{0.6}\text{Y}_{0.4}\text{Ni}_{4.8}\text{Mn}_{0.2}$ (AP3) and $\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.9}\text{Fe}_{1.1}/\text{Zr}_{0.9}\text{Ti}_{0.1}\text{Cr}_{0.6}\text{Fe}_{1.4}$ (AP4).

The important conclusions are as follows;

- The computational results are compared with the experimental data reported in the literature (Ni and Liu, 2007) for $\text{LaNi}_{4.61}\text{Mn}_{0.26}\text{Al}_{0.13}$ / $\text{La}_{0.6}\text{Y}_{0.4}\text{Ni}_{4.8}\text{Mn}_{0.2}$ hydride pair and a good agreement between these two is observed.
- The variation of reaction bed temperature, hydride concentration, cooling fluid temperature and hydride equilibrium pressures of the reactors are presented over a complete cycle. The heat interactions (cooling/heating) between the hydride beds and heat transfer fluids are also studied for a complete cycle.
- The cycle time of the variable wall convective temperature boundary condition is higher by about 3 min compared to the constant wall convective temperature boundary condition.
- The effects of thermal conductivity and bed thickness on cycle time and *SHP* of the SS-MHHT are presented. For a given bed thickness, the cycle time is found to decrease significantly with hydride bed thermal conductivity (λ) up to about 12 W/m K.
- The optimum operating temperatures of four selected metal hydride pairs are found out. From the selected hydride alloy pairs, the maximum COP_{HT} of 0.436 and *SHP* of 54 W/kg are obtained for $\text{LaNi}_{4.61}\text{Mn}_{0.26}\text{Al}_{0.13}/\text{La}_{0.6}\text{Y}_{0.4}\text{Ni}_{4.8}\text{Mn}_{0.2}$ pair at the operating conditions of $T_H = 393$ K, $T_M = 353$ K and $T_L = 298$ K.

6.1.2 Double-stage metal hydride based heat transformer

A thermal model for predicting the performance of a DS-MHHT working with $\text{LaNi}_{4.7}\text{Al}_{0.3}$, LaNi_5 and $\text{MmNi}_{4.6}\text{Al}_{0.4}$ (low/intermediate/high pressure hydride alloy) has been developed. The following are some important conclusions drawn from the numerical studies on DS-MHHT.

- The variation of reaction bed temperature and heat transfer fluid inlet and outlet temperatures, hydrogen concentrations of hydride beds and the cumulative amount of heat transfer over a complete cycle are discussed.
- The effect of half cycle time (t_{hf}) on COP_{HT} , SHP , total heat output and amount of hydrogen exchanged between the paired reactors are also presented. The SHP increases with t_{hf} up to 12 min, after that it decreases with the t_{hf} .
- The performance parameters of the DS-MHHT such as coefficient of performance (COP_{HT}), specific heating power (SHP), second law efficiency (η_E) and HTF temperature difference (ΔT_{HTF}) are predicted at different heat output (T_H), heat input (T_M) and heat rejection (T_L) temperatures.
- At the given operating conditions of heat output temperature 403 K, heat input temperature 353 K and heat sink temperature 303 K, the COP_{HT} , SHP and η_E of the DS-MHHT are found to be 0.35, 30 W/kg and 0.62, respectively.

6.2 Experimental Studies

6.2.1 Single-stage metal hydride based heat transformer

The following conclusions are drawn from the performance tests on SS-MHHT working with LaNi_5 / $\text{LaNi}_{4.35}\text{Al}_{0.65}$.

- A prototype of a SS-MHHT has been built and tested for upgrading the waste heat available from 393 - 413 K to about 428 K.

- The transient behavior of hydrogen exchange and associated heat transfer of both the reactors were presented. The effects of heat source and heat rejection temperatures on the COP_{HT} , SHP and η_E were investigated.
- It was observed that the numerically predicted average hydride bed temperature profiles of the reactors A and B were in good agreement with experimentally measured temperature profiles over a complete cycle.
- At the given operating conditions of heat output temperature 428 K, heat input temperature 413 K and heat sink temperature 308 K; the experimentally estimated values of COP_{HT} and SHP of the MHHT were 0.318 and 44 W/kg, respectively.
- At the operating conditions of $T_H = 428$ K and $T_L = 298$ K, the rise in T_M from 393 K to 413 K, increased the COP_{HT} and the SHP by about 14.5 % and 17.6 %, respectively.
- At the operating conditions of $T_H = 428$ K, $T_M = 393$ K and $T_L = 298$ K, the maximum achieved temperature lift was about 35 K.

6.2.2 Double-stage metal hydride based hydrogen compressor

Experimental investigation on a DS-MHHC was carried out using $LaNi_5$ and $La_{0.35}Ce_{0.45}Ca_{0.2}Ni_{4.95}Al_{0.05}$. The effects of supply pressure and heat source (desorption) temperature on the delivery pressure, amount of hydrogen compressed and isentropic efficiency of the DS-MHHC were investigated. The following conclusions are drawn from the performance tests on DS-MHHC.

- Hydrogen delivery pressure was found to increase with supply pressure and heat source temperature.

- The highest delivery pressure of 74 bar was achieved at 10 bar supply pressure and 413 K heat source temperature. For a given hydrogen supply pressure of 10 bar, the delivery pressure increases from 61 to 74 bar when the heat source temperature is increased from 393 K to 413 K.
- For the given operating conditions of 2 bar supply pressure and 413 K heat source temperature, the maximum compression ratio (CR) 22 and compressor efficiency (η_c) 9.7 % were achieved. The CR was found to increase with heat source temperature and however decrease with the supply pressure.
- It was observed that increase in supply pressure up to 10 bar significantly increase the storage pressure and however which reduced the compressor efficiency.

6.2.3 Double-stage metal hydride based heat transformer

Experimental investigations on DS-MHHT were carried out at different heat source and heat sink temperatures. The waste heat was upgraded from 393 - 413 K to about 463 K employing LaNi_5 , $\text{La}_{0.35}\text{Ce}_{0.45}\text{Ca}_{0.2}\text{Ni}_{4.95}\text{Al}_{0.05}$ and $\text{LaNi}_{4.35}\text{Al}_{0.65}$ combination. The following conclusions are drawn from the performance tests on a double-stage metal hydride based heat transformer system.

- The effects of operating temperatures such as heat source temperature and heat reject temperature on the performance of DS-MHHT in terms of coefficient of performance (COP_{HT}), specific heating power (SHP) and second law efficiency (η_E) were investigated.
- At the given operating conditions of heat output temperature 463 K, heat input temperature 413 K and heat sink temperature 308 K; the experimentally estimated values of COP_{HT} , SHP and η_E of the system were 0.217, 19.33 W/kg and 0.29 respectively.

- The COP_{HT} and the η_E were found to increase with heat sink temperature, while SHP of the system decreased with heat sink temperature.
- For a given $T_H = 463$ K and $T_M = 403$ K, SHP was found to decrease by about 9.5 % when the T_L was increased from 298 K to 313 K.
- The maximum temperature lift achieved was about 70 K at the operating conditions of heat output temperature 463 K, heat input temperature 393 K and heat sink temperature 298 K.

6.3 Scope of Future Work

The work presented in this thesis opens up several avenues for further development of the MHHT systems. The scope of future work is outlined as follows:

1. The re-absorption/re-desorption which takes place during the sensible heat transfer process can be considered in the mathematical modeling.
2. The development of MHHT system with embedded heat transfer fluid tubes inside the reactor.
3. The development of MHHT system with automatic monitoring.
4. The investigation of issues related to up scaling of MHHT system.

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APPENDIX A

DISCRETIZATION OF GOVERNING EQUATIONS

The mathematical model of the coupled heat and mass transfer processes in a paired reaction beds is solved numerically using the finite volume method presented in Section 3.1. Two-dimensional cylindrical coordinate system is considered. The reaction beds are assumed to axisymmetric. Hence, only the top half of the reaction bed is considered for the present investigation. As a first step in the finite volume method, the domain is to be divided into discrete control volumes. Each nodal point is surrounded by a control volume. The boundaries (or faces) of control volumes are positioned mid-way between adjacent nodes. Near the edge of the domain, the physical boundaries coincide with the control volume boundaries. A general nodal point is identified by P and its neighbour points in a two-dimensional geometry is identified as north, south, east and west and they are denoted respectively by N , S , E and W . The north side face of the control volume is referred to be ' n '. Similarly south, east and west are

denoted as s , e and w , respectively. The distance between the nodes W and P , and between nodes P and E is denoted by ΔZ . Similarly, the distance between and N and P , and P and S is denoted by ΔR . The distances between the control volumes faces n , s , e and w are denoted as Δr and Δz , respectively.

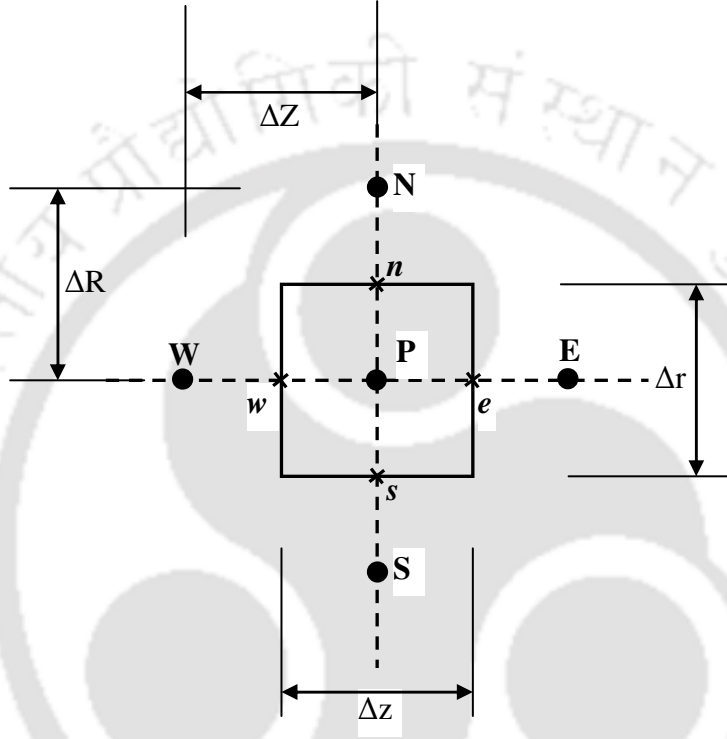


Fig. A.1 Two-dimensional grid generation technique

A.1 Energy Equation

$$\begin{aligned}
 (\rho C_p)_{eff} \frac{\partial T}{\partial t} = & \frac{1}{r} \frac{\partial}{\partial r} \left(r k_e \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left(k_e \frac{\partial T}{\partial z} \right) - (\rho C_p u)_{g,r} \frac{\partial T}{\partial r} - (\rho C_p u)_{g,z} \frac{\partial T}{\partial z} \\
 & - m_{H_2} \left[\frac{\Delta H}{M_g} - T (C_{p,g} - C_{p,s}) \right]
 \end{aligned} \tag{A.1}$$

Integrating over the control volume

$$\begin{aligned}
 (\rho C_p)_{eff} \frac{T_P^{n+1} - T_P^n}{\Delta t} r_p \Delta r \Delta z = & \left(r k_{eff} \frac{\partial T}{\partial r} \right)_n \Delta z - \left(r k_{eff} \frac{\partial T}{\partial r} \right)_s \Delta z + r \left(k_{eff} \frac{\partial T}{\partial z} \right)_e \Delta r \\
 & - r \left(k_{eff} \frac{\partial T}{\partial z} \right)_w \Delta r - \left(r (\rho C_p u)_{g,r} T \right)_n \Delta z + \left(r (\rho C_p u)_{g,r} T \right)_s \Delta z \\
 & - \left(r (\rho C_p u)_{g,z} T \right)_e \Delta r + \left(r (\rho C_p u)_{g,z} T \right)_w \Delta r - m_{H_2} \frac{\Delta H}{M_g} r_p \Delta r \Delta z \\
 & + m_{H_2} (C_{P,g} - C_{P,s}) r_p \Delta r \Delta z T_P^{n+1}
 \end{aligned} \quad (A.2)$$

The central difference scheme is applied for the convection term. Hence Eq. (A.2) can be written as

$$\begin{aligned}
 a_p^o (T_P^{n+1} - T_P^n) = & D_n (T_N^{n+1} - T_P^{n+1}) - D_s (T_P^{n+1} - T_S^{n+1}) + D_e (T_E^{n+1} - T_P^{n+1}) \\
 & - D_w (T_P^{n+1} - T_W^{n+1}) - F_n \left(\frac{T_N^{n+1} + T_P^{n+1}}{2} \right) + F_s \left(\frac{T_P^{n+1} + T_S^{n+1}}{2} \right) \\
 & - F_e \left(\frac{T_E^{n+1} + T_P^{n+1}}{2} \right) + F_w \left(\frac{T_P^{n+1} + T_W^{n+1}}{2} \right) + S_u + S_p T_P^{n+1}
 \end{aligned} \quad (A.3)$$

where,

$$D_n = \frac{r_n k_{eff} \Delta z}{\Delta R}; \quad D_s = \frac{r_s k_{eff} \Delta z}{\Delta R}; \quad D_e = \frac{r_e k_{eff} \Delta r}{\Delta Z}; \quad D_w = \frac{r_w k_{eff} \Delta r}{\Delta Z}; \quad (A.4)$$

$$\begin{aligned}
 F_n = r_n \Delta z (\rho C_p u)_{g,r}; \quad F_s = r_s \Delta z (\rho C_p u)_{g,r}; \quad F_e = r_e \Delta r (\rho C_p u)_{g,z}; \quad F_w = r_w \Delta r (\rho C_p u)_{g,z}; \\
 ; \quad (A.5)
 \end{aligned}$$

$$a_p^o = \frac{(\rho C_p)_{eff} r_p \Delta r \Delta z}{\Delta t}; \quad (A.6)$$

$$S_u = - \frac{m_{H_2} \Delta H r_p \Delta r \Delta z}{M_g}; \quad S_p = m_{H_2} (C_{P,g} - C_{P,s}) r_p \Delta r \Delta z; \quad (A.7)$$

$$a_p T_p^{n+1} = a_N T_N^{n+1} + a_S T_S^{n+1} + a_E T_E^{n+1} + a_W T_W^{n+1} + a_p^o T_p^n + S_u; \quad (\text{A.8})$$

where,

$$a_p = a_p^o + D_n + D_s + D_e + D_w + F_n - F_s + F_e - F_w - S_p; \quad (\text{A.9})$$

A.2 Continuity Equation

Absorption or desorption of hydrogen to or from the metal hydride is obtained from the conservation of mass expressed using the following equation

$$\varepsilon \frac{\partial(\rho_g)}{\partial t} + \nabla(\rho_g \vec{u}_g) = \pm m_{H_2} \quad (\text{A.10})$$

where, + sign denotes the absorption of hydrogen to the metal hydride and – sign denotes desorption of hydrogen. ρ_g denotes the density of the hydrogen gas at any time (t) and u_g the velocity of the hydrogen in the reaction bed.

Metal hydride particles are of porous form. Velocity inside the porous region is calculated using the Darcy's law

$$\vec{u}_g = -\frac{K}{\mu_g} \nabla P_g \quad (\text{A.11})$$

By substituting the density (ρ_g) and velocity (u_g) of the gas in Eq. (A.12) the gas pressure (P_g) inside the reactors are determined using the following equation

$$\left(\frac{\varepsilon M_g}{R_u T} \right) \frac{\partial P_g}{\partial t} + \left(\frac{\varepsilon M_g P_g}{R_u} \right) \frac{\partial}{\partial t} \left(\frac{1}{T} \right) - \frac{K}{\nu_g r} \frac{\partial}{\partial r} \left(r \frac{\partial P_g}{\partial r} \right) - \frac{K}{\nu_g} \frac{\partial}{\partial z} \left(\frac{\partial P_g}{\partial z} \right) = m_{H_2} \quad (\text{A.12})$$

$$\begin{aligned}
& \frac{\varepsilon M_g}{R_u T} \left(\frac{P_g^{n+1} - P_g^n}{\Delta t} \right) r_p \Delta r \Delta z + \left(\frac{\varepsilon M_g P_g^{n+1}}{R_u} \right) \left(\frac{1}{T_g^{n+1}} - \frac{1}{T_g^n} \right) r_p \Delta r \Delta z \\
& - \left(\frac{Kr}{\nu_g} \frac{\partial P_g}{\partial r} \right)_n \Delta z + - \left(\frac{Kr}{\nu_g} \frac{\partial P_g}{\partial r} \right)_s \Delta z - \frac{K}{\nu_g} \left(\frac{\partial P_g}{\partial z} \right)_e \Delta r + \frac{K}{\nu_g} \left(\frac{\partial P_g}{\partial z} \right)_w \Delta r \\
& = -m_{H_2} r_p \Delta r \Delta z
\end{aligned} \tag{A.13}$$

$$\begin{aligned}
& a_p^o (P_p^{n+1} - P_p^n) + S_p P_p^{n+1} - D_n (P_N^{n+1} - P_p^{n+1}) + D_s (P_p^{n+1} - P_s^{n+1}) \\
& - D_e (P_E^{n+1} - P_p^{n+1}) + D_w (P_p^{n+1} - P_W^{n+1}) = -m_{H_2} r_p \Delta r \Delta z
\end{aligned} \tag{A.14}$$

where,

$$D_n = \frac{Kr_n \Delta z}{\nu_g \Delta R}; \quad D_s = \frac{Kr_s \Delta z}{\nu_g \Delta R}; \quad D_e = \frac{Kr_e \Delta r}{\nu_g \Delta Z}; \quad D_w = \frac{Kr_w \Delta r}{\nu_g \Delta Z}; \tag{A.15}$$

$$a_p^o = \frac{\varepsilon M_g r_p \Delta r \Delta z}{R_u T_g \Delta t}; \tag{A.16}$$

$$\begin{aligned}
S_u &= -m_{H_2} r_p \Delta r \Delta z; \\
S_p &= \frac{\varepsilon M_g r_p \Delta r \Delta z}{R_u} \left(\frac{1}{T_p^{n+1}} - \frac{1}{T_p^n} \right);
\end{aligned} \tag{A.17}$$

$$a_p P_p^{n+1} = a_N P_N^{n+1} + a_S P_S^{n+1} + a_E P_E^{n+1} + a_W P_W^{n+1} + a_p^o P_p^n + S_u; \tag{A.18}$$

where,

$$a_p = a_p^o + D_n + D_s + D_e + D_w + S_p; \tag{A.19}$$

APPENDIX B

ERROR ANALYSIS

Klein and McClintock [1953] proposed a procedure for estimating the uncertainty of any measured quantity in experimental studies. If an estimated quantity, R depends on the independent variables like $x_1, x_2, x_3, \dots, x_n$ then,

$$R = R(x_1, x_2, x_3, \dots, x_n) \quad (B-1)$$

Then the maximum value of uncertainty is given by:

$$W_R = W_R = \left[\left(\frac{\partial x_1}{x_1} \right)^2 + \left(\frac{\partial x_2}{x_2} \right)^2 + \left(\frac{\partial x_3}{x_3} \right)^2 + \dots + \left(\frac{\partial x_n}{x_n} \right)^2 \right]^{1/2} \quad (B-2)$$

Where $W_R = \partial R/R$ and $\partial x_1/x_1, \partial x_2/x_2$, etc., are the errors in the independent variables.

The important quantities measured/estimated during the experiments are temperature, pressure, mass of hydrogen and alloys, heat transfer fluid rate, heat supplied/removed, compressor work and efficiency, COP_{HT} and SHP .

B.1 Estimated Quantities

Estimated quantities both in heat transformer and hydrogen compressor are amount of hydrogen transferred during absorption and desorption processes, mass flow rate of heat transfer fluid, heat supplied/removed, compressor work and efficiency, COP_{HT} and SHP .

The maximum uncertainty of these estimated quantities are calculated as follows:

Hydrogen transferred

As explained in Chapter 4, the amount of hydrogen absorbed/desorbed between a set duration is measured using a mass flow meter. The minimum value of hydrogen absorbed/desorbed is 0.6 g in 100 s and the accuracy of the mass flow meter is 0.001 g. the accuracy of stop watch is 0.1 s. Hence, using Eq. (B-2) the maximum uncertainty associated with this measurement is given by;

$$\begin{aligned} \frac{\partial m_{H_2}}{m_{H_2}} &= \pm \left[\left(\frac{0.001}{0.6} \right)^2 + \left(\frac{0.1}{100} \right)^2 \right]^{\frac{1}{2}} \\ &= \pm 0.194\% \end{aligned} \quad (B-3)$$

Heat transfer fluid flow rate

Initially it is measured by using a standard jar and a stopwatch. Uncertainty in the estimation of heat transferred fluid flow rate is calculated from the volume and time measurements.

$$\begin{aligned} \frac{\partial m_f}{m_f} &= \pm \left[\left(\frac{10}{500} \right)^2 + \left(\frac{0.1}{60} \right)^2 \right]^{\frac{1}{2}} \\ &= \pm 2\% \end{aligned} \quad (B-4)$$

Heat supplied

Uncertainty in heat supplied/removed is estimated from the heat transfer fluid flow rate and temperature and is given by;

$$\frac{\partial Q}{Q} = \pm \left[\left(\frac{\partial m_f}{m_f} \right)^2 + 2 \left(\frac{\partial T}{T} \right)^2 \right]^{1/2} \quad (\text{B-5})$$

$$= \pm \left[(0.02)^2 + (0.06)^2 + (0.06)^2 \right]^{1/2}$$

$$= \pm 8.7\%$$

Compressor work

The uncertainty involved in the estimation of compressor work is obtained from the uncertainties of temperature, pressure and amount of hydrogen transfer.

$$\frac{\partial W}{W} = \pm \left[\left(\frac{\partial m_{H_2}}{m_{H_2}} \right)^2 + \left(\frac{\partial T}{T} \right)^2 + 2 \left(\frac{\partial P}{P} \right)^2 \right]^{1/2} \quad (\text{B-6})$$

$$= \pm \left[(0.019)^2 + (0.06)^2 + 2(0.005)^2 \right]^{1/2}$$

$$= \pm 6.3\%$$

Compressor efficiency

The uncertainty involved in the estimation of compressor efficiency is obtained from the uncertainties of compressor work and heat supplied.

$$\frac{\partial \eta}{\eta} = \pm \left[\left(\frac{\partial W}{W} \right)^2 + \left(\frac{\partial Q}{Q} \right)^2 \right]^{1/2} \quad (\text{B-7})$$

$$= \pm \left[(0.063)^2 + (0.087)^2 \right]^{1/2}$$

$$= \pm 10.7\%$$

COP_{HT}

The uncertainty involved in the estimation of COP_{HT} is obtained from the uncertainties of heat removed and heat supplied.

$$\frac{\partial COP_{HT}}{COP_{HT}} = \pm \left[\left(\frac{\partial Q}{Q} \right)^2 + \left(\frac{\partial Q}{Q} \right)^2 \right]^{1/2} \quad (B-8)$$

$$= \pm \left[(0.087)^2 + (0.087)^2 \right]^{1/2}$$

$$= \pm 12.3 \%$$

 $Specific\ heat\ output\ (SHP)$

The uncertainty involved in the estimation of SHP is obtained from the uncertainties of heat removed, mass of alloy and time measurements.

$$\frac{\partial SHP}{SHP} = \pm \left[\left(\frac{\partial Q}{Q} \right)^2 + \left(\frac{\partial m}{m} \right)^2 + \left(\frac{\partial t}{t} \right)^2 \right]^{1/2} \quad (B-9)$$

$$= \pm \left[(0.087)^2 + (0.005)^2 + (0.00166)^2 \right]^{1/2}$$

$$= \pm 8.78 \%$$

APPENDIX C

DETAILS OF INSTRUMENTATION

The important details of the various instruments used in the experiments are given below:

C.1 Data logger

Make	: Agilent technologies
Model	: Agilent 34970 A
Reading rate	: 600 readings/second
Scanning rate	: 60 channels/second
Scan intervals	: 0 to 99 hours; 1ms step size.

C.2 Weighing balance

Make	: Sartorius
Model	: CP8201
Capacity	: 0-5 kg
Accuracy	: 0.5 g

C.3 Regulated DC power supply

Make	: Scientific Mes-Technik
Model	: PSD3304
Output	: 0-30 V DC
Input power	: 230 V AC, 50 Hz

C.4 Metal sheathed K type thermocouples

Make	: Industrial Heaters
Range	: 0 to 1360 °C
Sensitivity	: ± 0.1 °C
Accuracy	: ± 0.5 °C

C.5 Pressure transmitter

Type	: Piezo resistive type
Model	: PT series
Range	: 0 to 160 bar
Operating temperature	: 0 to 200 °C
Accuracy	: ± 0.5 %

C.6 Stopwatch

Make	: Pacer
Model	: SW-101
Accuracy	: ± 0.1 s

C.7 Mass flow meter

Make	: Emerson Process Management
Type	: Coriolis

Model	: CMF010P323NQB2E222
Pressure range	: 0 to 200 bar
Temperature range	: -200 to 200 °C
Accuracy	: ± 0.35 % of full scale
Sensitivity	: 0.001 g
Range	: 0-50 g/min

C.8 Thermostatic bath

Make	: Julabo, Germany
Model	: SE-12
Heating Capacity	: 3 kW
Temperature range	: 20 to 300 °C
Accuracy	: ± 0.1 °C

C.9 Thermostatic bath

Make	: NR Enterprise
Model	: Microprocessor based
Heating Capacity	: 3 kW
Cooling Capacity	: 3 kW
Temperature range	: -30 to 250 °C
Accuracy	: ± 0.5 °C

C.10 Vacuum pump

Make	: Vacuum technologies
Model	: VT-2035
Rotary pump specifications	
Model	: VT-2035
Pumping speed	: 0-200 l/min

Pump speed	: 1440 rpm
Vacuum pressure range	: 1 to 10^{-3} mbar

Diffusion pump specifications

Pumping speed	: 280 litre/s
Heating rating	: 500 W
Ultimate vacuum	: 10^{-3} to 5×10^{-7} mbar

C.11 Hydrogen valves

Make	: Swagelok, USA
Type	: Packless Metallic bellow type needle
Model	: SS-4UW
Pressure range	: 0 to 120 bar
Temperature range	: 0 to 482 °C
End connection	: ¼" NPT

C.12 Hydrogen filter

Make	: Finix Filters Pvt. Ltd.
Model	: M series
Pore size	: 2 microns
Material and size	: Sintered SS-316, 16 mm OD

List of Publications

List of publications based on the present thesis work

International Journal Papers

1. Sekhar BS, Muthukumar P. Performance Analysis of a Metal Hydride Based Heat Transformer. Int Energy Journal 2012; 13: 29-44.
2. Sekhar BS, Pailwan SP, Muthukumar P. Studies on Metal Hydride based Single-Stage Heat Transformer. Int J Hydrogen Energy 2013; 38: 7178-87.
3. Sekhar BS, Suresh P, Muthukumar P. Performance Tests on Metal Hydride based Hydrogen Storage Devices. Int J Hydrogen Energy 2013; 38: 9570-9577.
4. Sekhar BS, Muthukumar P. Performance Tests on a Double-Stage Metal Hydride based Heat Transformer. Int J Hydrogen Energy 2013; 38: 15428-15437.
5. Sekhar BS, Muthukumar P. Performance Investigations of a Metal Hydride Based Heat Transformer. Int J Green Energy 2013 (Under review).
6. Sekhar BS, Muthukumar P. Thermal Modelling and Performance Investigations of a Double-Stage Metal Hydride Heat Transformer. Numerical Heat Transfer, Part A 2013 (Under review).

International Conference Papers

1. Sekhar BS, Muthukumar P. Heat and mass transfer studies in metal hydride based heat transformer. Presented at 21st National & 10th ISHMT-ASME Heat and Mass Transfer Conference, 27-30 December 2011, IIT Madras, India.
2. Sekhar BS, Muthukumar P, Suresh P. Performance tests on metal hydride based hydrogen storage devices. Presented at the 3rd International Conference on Fuel cell & Hydrogen Technology, 22-23 November 2011, Kuala Lumpur, Malaysia.
3. Sekhar BS, Muthukumar P, Tiwari VK. Experimental studies on a double-stage metal hydride based hydrogen compressor. Presented at 21st National & 10th ISHMT-ASME Heat and Mass Transfer Conference, 27-30 December 2011, IIT Madras, India.

4. Sekhar BS, Muthukumar P. Performance studies on metal hydride based heat transformer. Presented at 3rd International Conference on Advances in Energy Research, 9-11 December 2011, IIT Bombay, India.
5. Sekhar BS, Muthukumar P. Thermal modeling of a double-stage metal hydride based heat transformer. Presented at 9th International Conference on Flow Dynamics, 19-21 September 2012, Sendai, Japan.
6. Sekhar BS, Muthukumar P. Performance studies on a double-stage metal hydride based hydrogen compressor. Presented at Processing and Fabrication of Advanced Materials XXI. 10-13 December 2012, IIT Guwahati, India.
7. Sekhar BS, Muthukumar P. Development of double-stage metal hydride based hydrogen compressor for heat transformer application. Accepted for Presentation at International Symposium on Innovative Materials for Processes in Energy Systems, 4-6 September 2013, Fukuoka, Japan.