

DESIGN AND PERFORMANCE ASSESSMENT OF MULTISTAGE METAL HYDRIDE HYDROGEN COMPRESSORS

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Doctor of Philosophy

by

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CERTIFICATE

This is to certify that the work contained in the thesis entitled “**Design and Performance Assessment of Multistage Metal Hydride Hydrogen Compressors**” submitted by **Abhishek Parida (Roll No. 206103101)**, to the Indian Institute of Technology Guwahati for the award of the degree of Doctor of Philosophy has been carried out under our supervision in the Department of Mechanical Engineering, Indian Institute of Technology Guwahati. This work has not been submitted elsewhere for the award of any other degree or diploma.

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Dedicated to my Parents

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and

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Abstract

The global energy landscape is undergoing a rapid transformation, marked by an unprecedented surge in demand following the post-COVID economic recovery, reported as the fastest growth in over 80 years. This sharp rise in consumption, driven by resumed industrial activity and lifted social restrictions, has led to energy shortages and escalating electricity prices worldwide. Meeting this rising demand is increasingly difficult due to the depletion of fossil fuel reserves and growing climate concerns, primarily linked to elevated CO₂ emissions. Achieving Net Zero Emissions by 2050 thus necessitates a decisive transition from fossil fuels to low-emission alternatives such as solid, liquid, and gaseous bioenergy and most crucially, hydrogen. Hydrogen, with its high gravimetric energy density and carbon-free combustion, is regarded as a key energy vector for a sustainable future. Currently, most hydrogen is produced via carbon-intensive methods like steam methane reforming (SMR), coal gasification, and biomass gasification. However, increasing attention is being directed toward green hydrogen, produced through water electrolysis powered by renewable energy sources like solar, wind, and hydro. While electrolytic hydrogen is typically generated at pressures below 30 bar, many end-use applications, particularly in mobility and large-scale storage, require pressures between 200 and 700 bar. This necessitates effective hydrogen compression systems as a vital link in the hydrogen value chain. Traditionally, hydrogen is compressed using mechanical systems: positive displacement or dynamic compressors, which suffer from limitations such as vibration, wear, contamination, and complex design. These drawbacks have accelerated interest in non-mechanical alternatives, including metal hydride-based hydrogen compressors (MHHCs). This thesis explores the development and performance evaluation of MHHC, which leverage waste heat or renewable thermal energy for compression, offering quiet, safe, and efficient operation ideal for future green hydrogen infrastructure.

A MHHC operates by reversibly absorbing hydrogen at low pressure and temperature and desorbing it at high pressure upon heating, leveraging the thermodynamic behavior of metal hydride alloys. A comprehensive literature review conducted during this study revealed a significant research gap: the absence of any MHHC system capable of compressing hydrogen from a low pressure of 15 bar to beyond 200 bar while operating within a maximum temperature of 100 °C. This temperature constraint is critical, as it enables the utilization of low-grade waste heat or solar thermal energy, aligning with the principles of energy recovery and sustainable utilization. Moreover, it contributes directly to reducing the cost of hydrogen

energy supply chain, supporting the realization of Sustainable Development Goal 7: Clean and Affordable Energy.

Based on the identified research gap, the following technical specifications were established: low hydrogen supply pressure of 10-20 bar, maximum available source temperature of 120-130 °C, and a target delivery pressure of 250-300 bar. The thermal energy was intended to be harnessed from the waste heat recovery system of NTPC NETRA, a thermal power plant in India. To address this, a three-stage MHHC was conceptualized and developed to span the entire desired pressure range while operating efficiently within the targeted temperature window.

LaNi₅-based La_{0.8}Ce_{0.2}Ni₅ was selected as the first-stage alloy due to its ability to absorb hydrogen from low-pressure sources (10-20 bar) with a storage capacity of 1.4 wt%. La_{0.3}Ce_{0.7}Ni₄Fe was chosen for the second stage, capable of absorbing hydrogen at 30 bar and 25 °C, and delivering a high equilibrium pressure of over 90 bar at 100 °C. For the final stage, Ti_{0.8}Zr_{0.2}CrMn_{0.3}Fe_{0.6}Ni_{0.1} was selected for its ability to absorb hydrogen at 70 bar and 10 °C and desorb at pressures exceeding 300 bar at 90 °C, with a useable storage capacity of 1.3 wt%, making it ideal for high-pressure delivery. Given that metal hydride (MH) systems are thermally driven, achieving efficient thermohydraulic performance is essential for MH reactor operation. A major design challenge in MH-based hydrogen compressors, compared to other MH applications, lies in the dual requirement of high heat transfer effectiveness and mechanical robustness to withstand elevated pressures. These competing demands make tubular reactor configurations the most suitable choice. This study outlines a novel design methodology to develop high-strength reactors, a critical aspect often overlooked in prior research.

Furthermore, an improved comprehensive mathematical model was developed, accounting for key MH system characteristics such as hysteresis, slope factors, and alloy volume expansion during sorption. This model was used to analyse coupled reactor operation, a crucial feature in multistage compression. Simulations revealed that an internal reactor diameter of 20-30 mm offers the optimal balance between hydrogen transfer rate and weight ratio. To meet the goal of compressing over 5000 L of hydrogen per cycle, a modular reactor design was adopted using 19 tubes of 24.3 mm inner diameter and 4.55 mm wall thickness. A total of six such reactors were fabricated and deployed in three stages (two per stage), each housing 25 kg of alloy, thereby allowing each stage to compress approximately 6200 L of hydrogen.

Apart from the reactor assembly, other critical components, namely the heat transfer fluid (HTF) circuit and the gas handling circuit, were meticulously designed and developed to

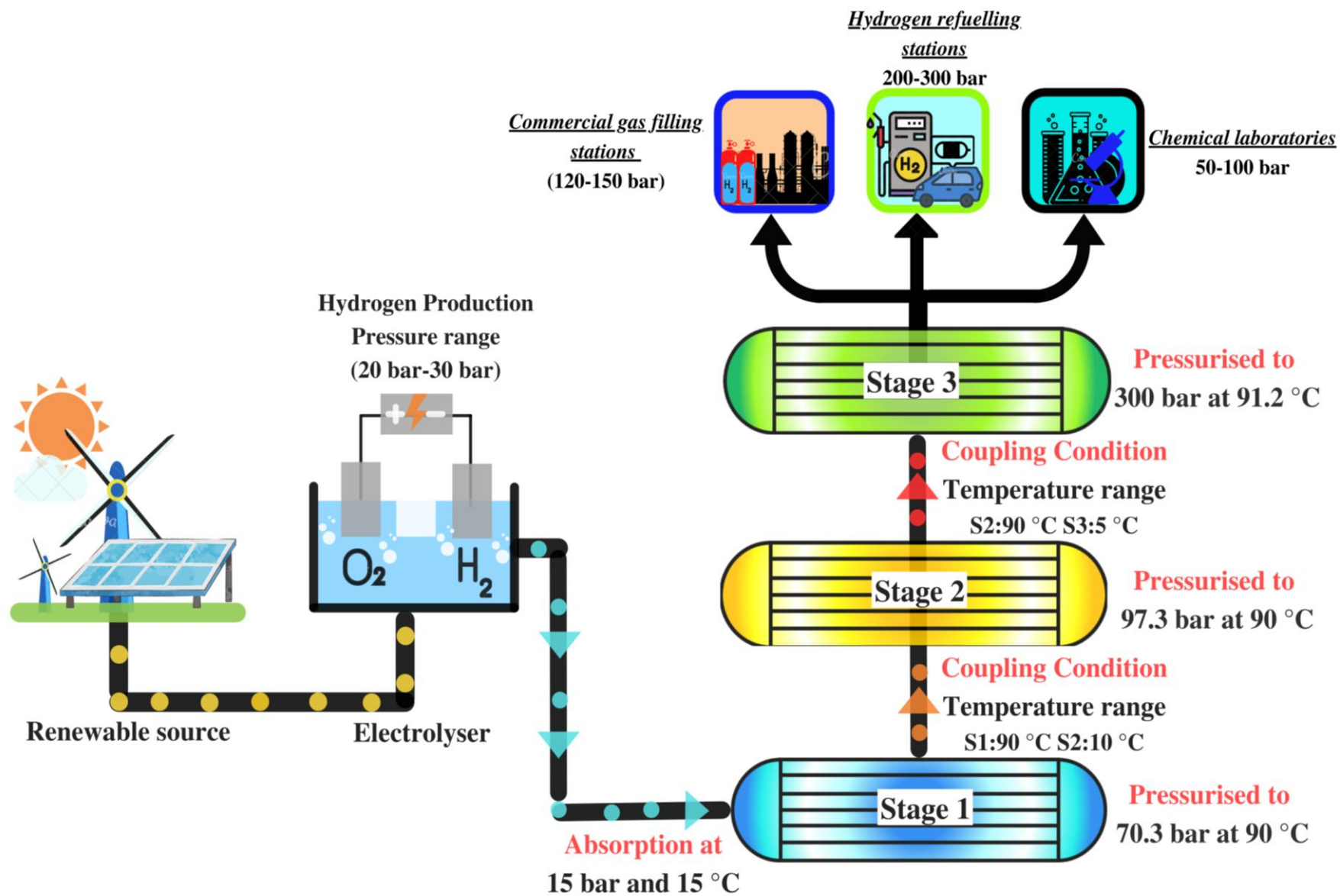
support the experimental studies conducted in this thesis. The setup was configured to facilitate experiments focused on identifying the activation strategies of each alloy and determining their optimum operating pressure and temperature ranges. Additionally, the multi-stage system was uniquely designed to function as a hydrogen compressor for refuelling applications at commercial gas filling stations, a capability not previously demonstrated in existing literature. The industrial-scale system developed through this research is currently deployed at NTPC NETRA, Greater Noida, marking a significant step toward real-world application.

Further, individual reactor experiments were conducted for all selected alloys at both prototype and industrial scales. The activation strategies implemented during these experiments were systematically analysed, and the procedures for the prototype and large-scale systems were compared to assess scalability and performance consistency. The modular compact tubular reactor, containing 1.4 kg of $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMn}_{0.3}\text{Fe}_{0.6}\text{Ni}_{0.1}$, was fully activated in five cycles, achieving a storage capacity of 1.6 wt%. Activation involved exposure to 130 bar hydrogen, with HTF circulated at 5 °C, followed by heating to 100 °C and evacuation. In contrast, when 19 such tubes were assembled into a single industrial-scale reactor, 8 activation cycles were required. This process involved heating to 220-240 °C for outgassing, followed by injection with 120 bar hydrogen, using air as the HTF supplied at 20 °C. The variation in the number of activation cycles and the maximum heating temperature required for the large-scale prototype was attributed to the limited availability of hydrogen (approximately 0.5 wt%) in Type I cylinders at pressures above 120-130 bar. An embedded cooling tube reactor configuration, featuring five spiral-finned cooling tubes with a fin pitch of 8 mm and housing 3.5 kg of $\text{La}_{0.3}\text{Ce}_{0.7}\text{Ni}_4\text{Fe}$, was activated using 60 bar pure hydrogen at 20 °C, followed by heating to 90 °C, requiring six cycles to reach full storage capacity. In contrast, the industrial-scale reactor comprising 19 tubes and containing 25 kg of the same alloy achieved the maximum storage capacity of 1.3 wt% in just four cycles, under identical activation conditions. Lastly, activation of the prototype and industrial-scale reactors containing 3.5 kg and 25 kg of $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ni}_5$ respectively was achieved at 40 bar and 10 °C, reaching a storage capacity of 1.4 wt% in four and five activation cycles respectively.

According to the outcomes of the parametric studies conducted on $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMn}_{0.3}\text{Fe}_{0.6}\text{Ni}_{0.1}$, it was concluded that injection pressure was the most critical factor, boosting system efficiency by ~13% as the hydrogen uptake improved by 2.5 times, with cumulative absorption increasing from 13.17 g to 20.82 g as injection pressure rose from 70 to 100 bar. Additionally, it was observed that HTF flow rate influenced half cycle time (21% during absorption) but had minimal impact on efficiency (<3.5%). The alloy exhibited excellent hydrogen compression,

reaching >160 bar at 40 °C and 210 bar at 50 °C with an inlet pressure of 90-100 bar, proving its suitability for high-pressure hydrogen storage achieving a gravimetric storage density of 0.55% and an exergy recovery rate of 14.8 W/kg_{MH}. Parametric studies on La_{0.3}Ce_{0.7}Ni₄Fe revealed that the optimal injection pressure lies in the range of 40-50 bar, with the HTF inlet temperature during absorption best maintained at 10 °C. A desorption temperature of ≥60 °C was identified as ideal, enabling complete hydrogen release (~100% reversibility) and ensuring faster discharge rates. Studies on La_{0.8}Ce_{0.2}Ni₅ demonstrated excellent absorption performance, with the alloy capable of absorbing hydrogen at injection pressures as low as 15 bar, even when the HTF inlet temperature was maintained at 25 °C. However, the optimum absorption conditions were identified to be in the range of 15-25 bar at an HTF inlet temperature of 15 °C. In contrast, the desorption performance was less favourable, requiring a minimum temperature of 70 °C for complete hydrogen release.

A prototype dual-stage compressor, utilizing La_{0.3}Ce_{0.7}Ni₄Fe and Ti_{0.8}Zr_{0.2}CrMn_{0.3}Fe_{0.6}Ni_{0.1} as the alloy pair, was developed to compress 500 NL of hydrogen from 40–50 bar to 313 bar within a temperature range of 5-80 °C. Detailed studies were conducted to assess the influence of coupled bed temperature, hydrogen inventory, and injection pressure on compressor performance. Based on these insights, a third alloy La_{0.8}Ce_{0.2}Ni₅ was introduced to form a three-stage system, and an industrial-scale compressor was built with a 6200 L capacity, compressing hydrogen from 15 bar to 300 bar within 5-91.2 °C, making it suitable for operation with low-grade thermal sources. Both systems demonstrated a first-law efficiency of 5-8% and a second-law efficiency of 22-24%. Refilling a Type I hydrogen cylinder to 155 bar required four refill cycles, during which the hydrogen throughput decreased from 600 L/min (STP) initially to 153.6 L/min (STP) in the fourth cycle, owing to the diminishing pressure gradient between the compressor and the receiving cylinder.



Nomenclature

B	:	Shape factor
b	:	Dimensionless constant
c	:	Specific heat (kJ/kg/K)
C	:	Reaction Constant (1/s)
d	:	Diameter (m)
D	:	Diameter (m)
E	:	Activation Energy (J/mol)
H	:	Enthalpy (J/mol)
k	:	Thermal conductivity (W/m/K)
K	:	Boltzmann Constant (m)
l	:	Length of reactor (m)
$\dot{m}$	:	Volumetric rate of mass transferred by MH (kg/m ³ /s)
m	:	Mass (kg)
M	:	Molecular weight (kg/mol)
n	:	Normal vector
N	:	Number of hydrogen atoms
p	:	Bed pressure (Pa)
P	:	External or equilibrium pressure (Pa)
Q	:	Heat (J)
r	:	Radius (m)
S	:	Entropy (J/K)
R	:	Universal gas constant (J/kg/K)
t	:	Time (s)/ Fin thickness (mm)
T	:	Temperature (°C)
v	:	Superficial velocity (m/s)
V	:	Volume of hydrogen transferred (L)
wt%	:	Weight percentage
X	:	Reacted fraction
Z	:	Compressibility factor

Greek letters

α	:	α -phase
β	:	β -phase
ε	:	Bed porosity
κ	:	Permeability (m ²)
λ	:	Mean free path (m)
μ	:	Dynamic viscosity (Pa.s)
ρ	:	Density (kg/m ³)
γ	:	Hysteresis
σ	:	Stress tensor (N/m ²)
δ	:	Strain tensor
Ψ	:	Concentration
φ_s, φ_o	:	Slope factor
ω	:	Specific internal energy (J/kg)
ξ	:	Volume expansion factor

Subscripts

a	:	Absorption
$alloy$	:	Metal hydride alloy
d	:	Desorption
ed	:	Empty
e	:	Effective
eq	:	Equilibrium
f	:	fluid
F	:	Fin
g	:	Gas
H_2	:	Hydrogen gas
i	:	Initial
$inlet$	:	Inlet boundary
MH	:	Metal hydride
o	:	Empty/outer
p	:	Particle
r	:	Radial distance

rad : Radiation

Acronyms

MH : Metal hydride

HTF : Heat transfer Fluid



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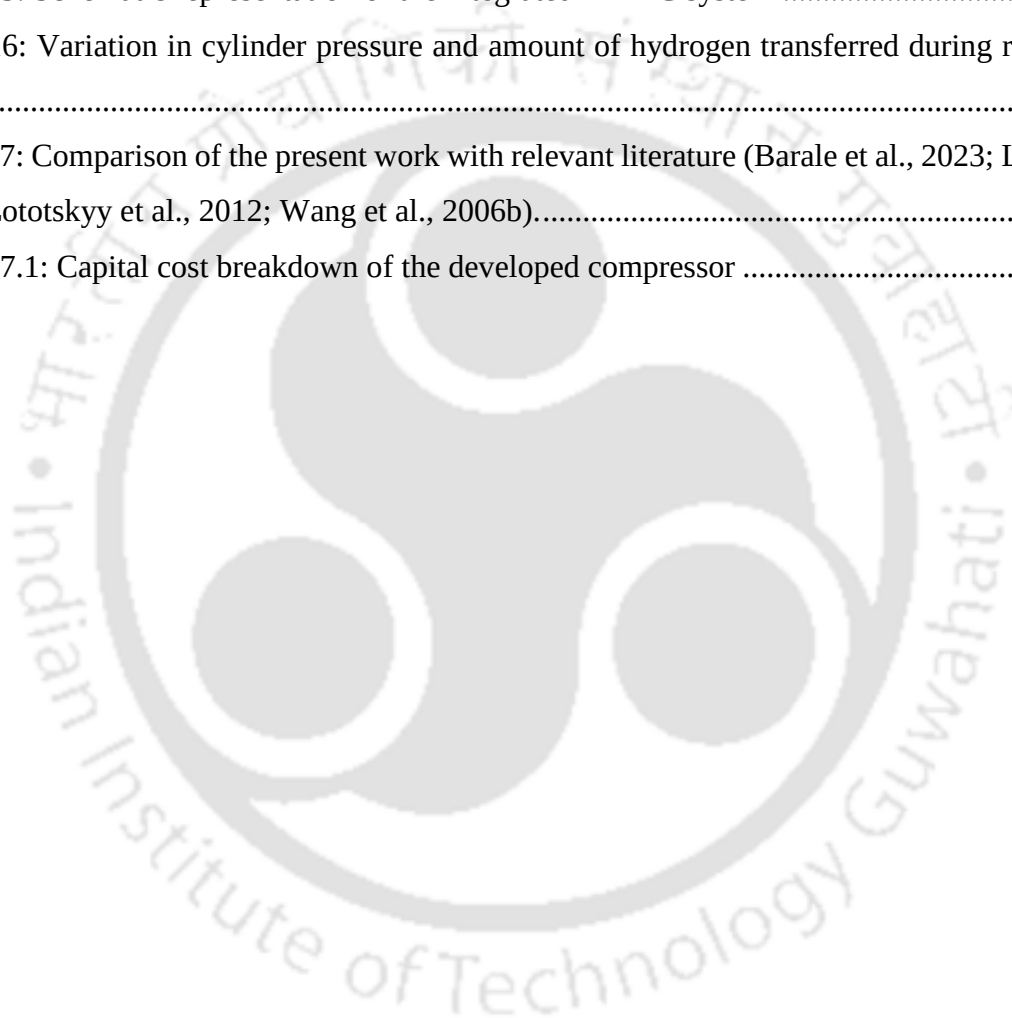
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Chapter 1

Introduction

1.1 Preface

To ensure global energy security and achieve net-zero emissions by 2050, reducing fossil fuel dependence and advancing scalable, low-carbon, and affordable clean energy technologies is essential. Fig. 1.1 (a) illustrates per capita energy consumption (in kWh) for the year 2023, highlighting the disparity between developed and developing nations. Countries such as the United States, China, Russia, United Kingdom, and United Arab Emirates consumed as much as 30 MWh of electricity per person from coal, whereas in developing nations like India, this figure stood at approximately 7.5 MWh per person (“Energy - Our World in Data,” n.d.). Furthermore, carbon dioxide emissions per kWh of electricity generated remained above 300 g for most nations, despite ongoing mitigation efforts. Given that the global population is projected to grow by at least 1% annually over the next decade, achieving further reductions in carbon emissions is imperative. The integration of renewable energy sources, particularly solar energy, has been expanding. In 2023, the United States and China generated approximately 238.12 TWh and 584.15 TWh of electricity from solar energy, respectively, while India contributed 113.41 TWh. However, despite these efforts, solar energy still accounts for only 5-10% (Fig. 1.1, (b)) of total electricity production, emphasizing the need for a more aggressive transition toward renewables (“Renewable Energy - Our World in Data,” n.d.).

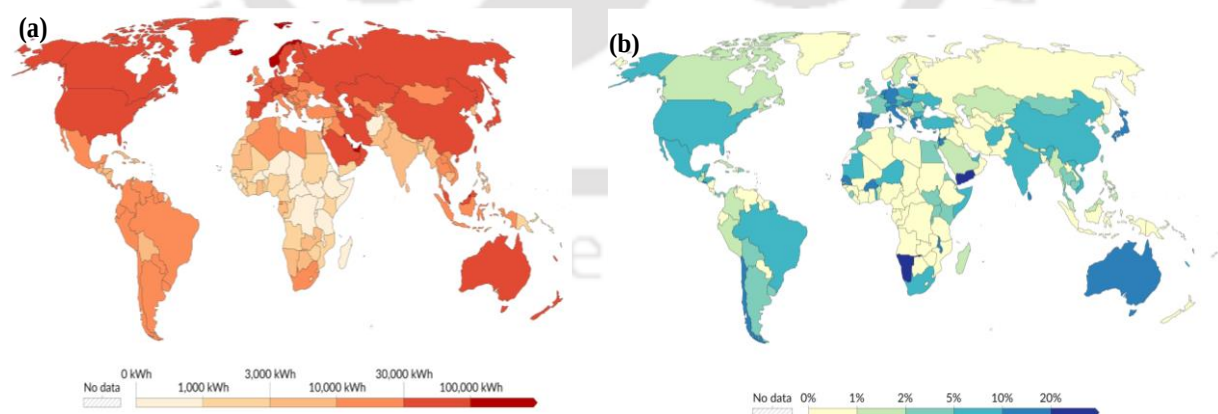


Fig. 1.1 : Global distribution of (a) per capita energy consumption (“Energy - Our World in Data”) and (b) share of electricity from solar energy (“Renewable Energy - Our World in Data”)

This chapter explores the role of hydrogen as an energy carrier in the transition to a cleaner energy future. Additionally, it discusses the need for hydrogen compression, providing a

detailed overview of existing hydrogen compression technologies and their relevance in scaling up hydrogen-based energy solutions.

1.2 Importance of hydrogen as energy carrier

Hydrogen is emerging as a key energy carrier in the transition toward sustainable and decarbonized energy systems. With a gravimetric energy density of 33.3 kWh/kg, it surpasses conventional fuels such as gasoline (12.7 kWh/kg) and natural gas (13.9 kWh/kg), making it ideal for high-energy applications. Additionally, hydrogen offers several advantages, including zero carbon emissions and long-term storage capability. Unlike lithium-based batteries, hydrogen fuel cells do not degrade over time, ensuring longer operational lifespans.

Global hydrogen demand increased from 97 Mt in 2023 to approximately 100 Mt in 2024 and is projected to reach 125 Mt by 2030. Currently, the majority of hydrogen production is derived from natural gas and coal, contributing significantly to carbon emissions. To meet global decarbonization targets, this hydrogen must be replaced with clean hydrogen produced from renewable energy sources by 2030. According to a 2024 IRENA report, achieving the 1.5°C climate goal by 2050 will require 14% of the world's final energy consumption to come from the indirect electrification of key sectors using low-carbon hydrogen. Green hydrogen is expected to play a dominant role, accounting for 40% of total hydrogen production by 2030 and increasing to 94% by 2050. This transition demands a significant expansion in electrolyser capacity, from less than 3 GW in 2023 to 5,722 GW by 2050. Governments worldwide are taking decisive steps to support this shift, with nearly 50 countries formulating national hydrogen strategies to meet the growing demand. India, through its National Green Hydrogen Mission, aims to become a global leader in green hydrogen production, targeting 5 million metric tons per year by 2030, backed by substantial investments in renewable-powered electrolysis infrastructure. These ambitious initiatives underscore the pivotal role of green hydrogen in the global energy transition.

Need for hydrogen compression

Hydrogen production through electrolysis typically occurs at pressures below 30 bar and is projected to increase to 70 bar by 2050 (IRENA 2020, 2020; Salehmin et al., 2022). Hydrogen densification is essential to enhance its storage, transportation, and usability, as its low volumetric density of 0.0899 kg/m³ at ambient conditions makes direct utilization inefficient. Increasing hydrogen density enables efficient onboard storage for fuel cell vehicles (FCVs), large-scale industrial applications, and grid energy storage systems. Densification is

particularly critical for reducing storage volume, minimizing infrastructure costs, and ensuring a stable supply for various end-use applications.

There are two primary methods to achieve hydrogen densification: compression and liquefaction. Liquid hydrogen (LH₂) at -253 °C achieves a higher density of 70.8 kg/m³ but requires 10-13 kWh/kg of energy for liquefaction, making it energy-intensive and costly, with expensive infrastructure requirements. In contrast, compressed hydrogen gas at 700 bar achieves a density of 42 kg/m³, offering a more cost-effective and widely adopted solution for hydrogen storage and transportation (Aziz, 2021).

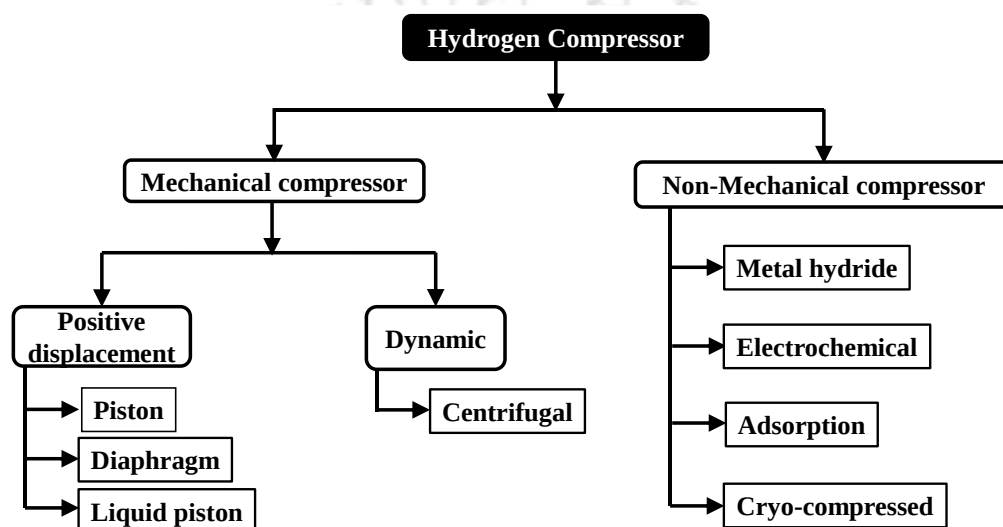


Fig. 1.2 : Classification of various hydrogen compressors

Hydrogen compression methods can be broadly classified into mechanical and non-mechanical techniques. Mechanical compression relies on moving parts to reduce hydrogen volume and increase pressure, while non-mechanical compression utilizes hydrogen phase transformation or electrochemical processes to achieve high pressures. The primary types of mechanical compressors include piston compressors, diaphragm compressors, ionic compressors, and centrifugal compressors (Genovese et al., 2025; Zou et al., 2020a). On the other hand, non-mechanical compressors can be categorized as metal hydride hydrogen compressors, electrochemical compressors, adsorption compressors, and cryo-compressed compressors (Sdanghi et al., 2019a). The classification is depicted in Fig. 1.2.

1.3 Overview of mechanical hydrogen compressors

Hydrogen compression is conventionally carried out by mechanical compressors which can be predominantly classified into positive displacement and dynamic compressors. The positive displacement type compressor reduces the gas volume to pressurise hydrogen. In contrast, the

dynamic type compressor transforms the kinetic energy of hydrogen imparted by the rotating blades to pressure energy thereby elevating the pressure. Each type of mechanical compressor presents certain constraints that need to be addressed. Early attention should be paid to issues such as continuous vibration and noise brought on by moving parts, hydrogen contamination in the presence of lubricating oils, wear and tear in the absence of lubricants, and complexities in design elements. Additionally, mechanical compressors consume a significant amount of high-grade energy.

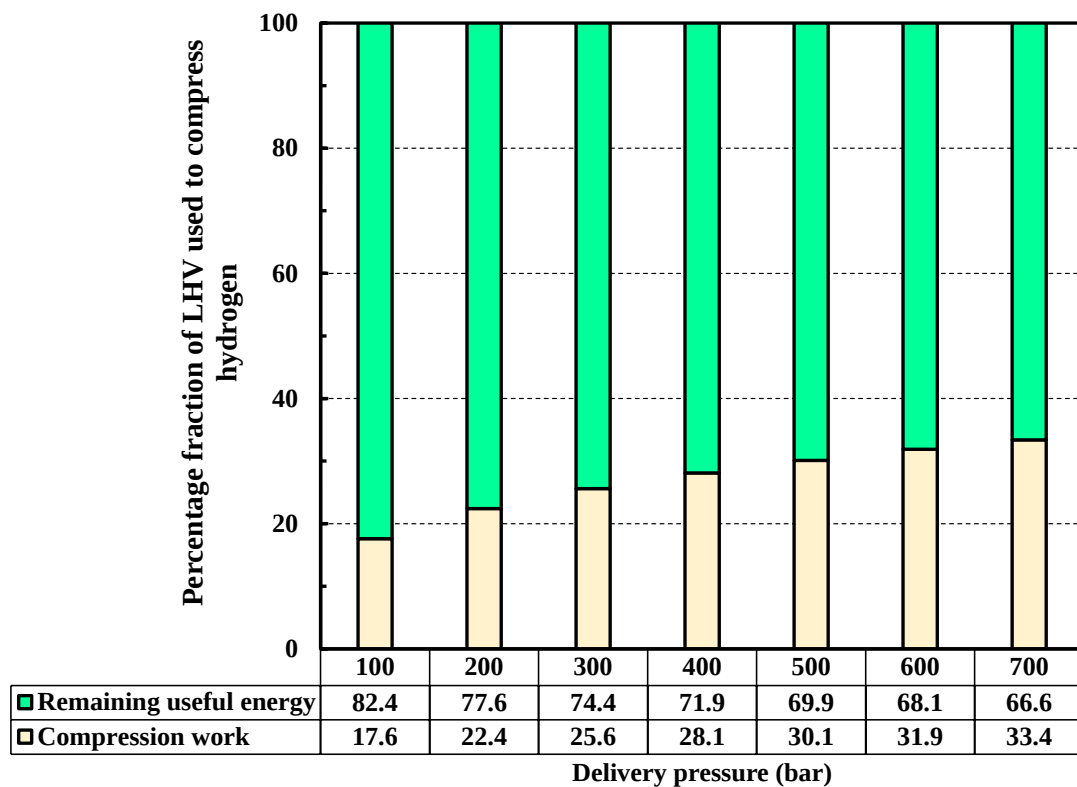


Fig. 1.3: Percentage fraction of LHV of hydrogen spent to compress hydrogen

Fig. 1.3 illustrates the percentage fraction of lower heating value (LHV) of hydrogen utilised to compress hydrogen to various delivery pressures. The polytropic index (ψ) for hydrogen compression is assumed to be 1.32 (Luo et al., 2014) and the compression factor at varied pressures ($Z(p, T)$) is also taken into account during the evaluation of compression work. The percentage fraction of LHV of hydrogen spent (Ω) to compress hydrogen at ambient temperature (T_{amb}) is evaluated using Eq. 1.1.

$$\Omega = \frac{\frac{\psi}{\psi-1} \left(Z(p,T) n_{H_2} R_u T_{amb} \left(\left(\frac{P_H}{P_{amb}} \right)^{\frac{\psi-1}{\psi}} - 1 \right) \right)}{LHV} \quad (1.1)$$

It is observed that about 33.4% of the total energy content in hydrogen is utilised in compressing up to 700 bar above atmospheric pressure (P_{amb}). Hence, there is a considerable need to investigate the possibilities of non-mechanical compressors. The operating principle and other relevant aspects of various mechanical compressors are mentioned in Table 1.1. Fig. 1.4 presents the schematic of mechanical compressors highlighting their operating principle.

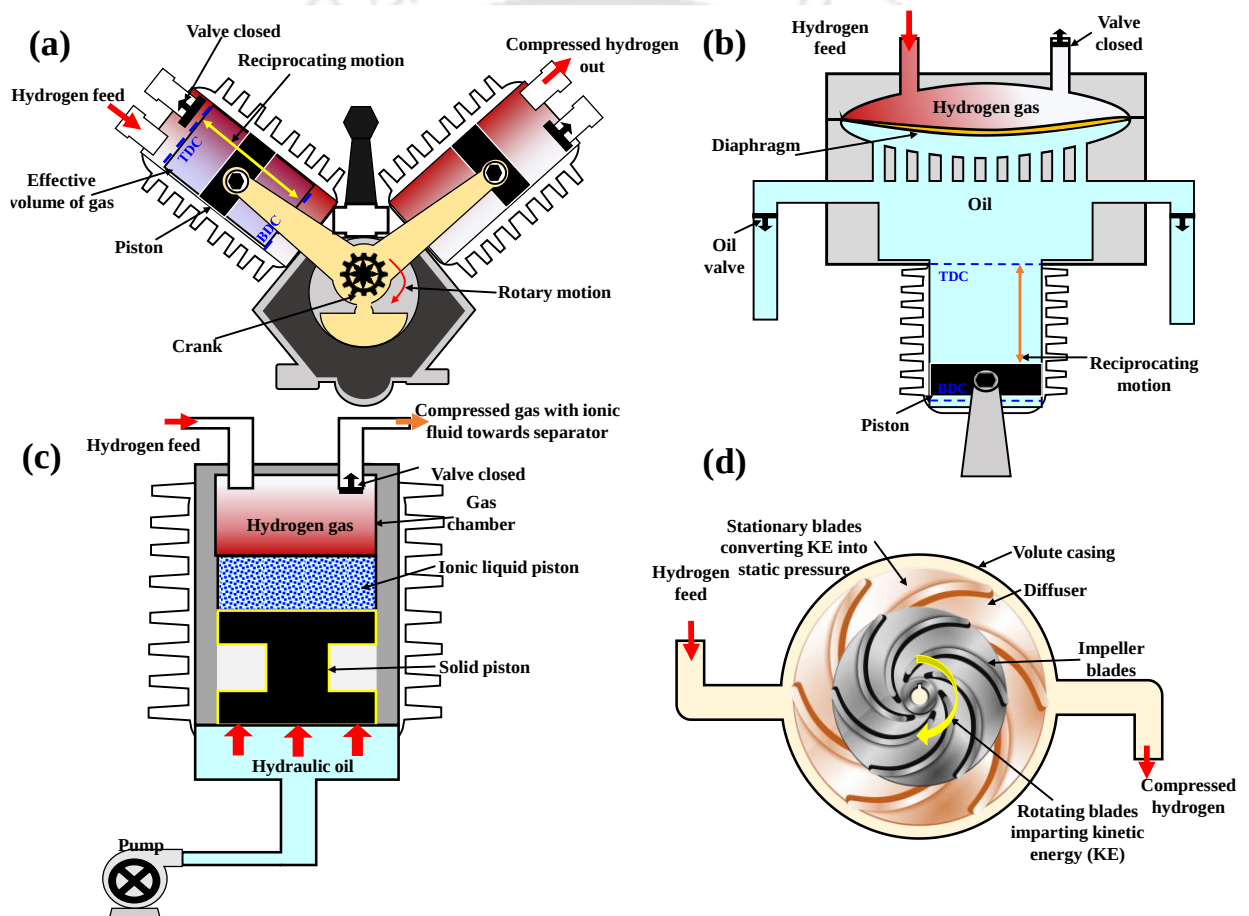


Fig. 1.4: Schematic representation of operating principle of (a) piston compressor, (b) diaphragm compressor, (c) ionic liquid compressor and (d) centrifugal compressor

Table 1.1 : Overview of mechanical compressors

Compressor types	Working principle	Technical Specification	Commercialisation	Drawbacks
Reciprocating hydrogen compressor	Piston compressor Movement of the piston from the bottom dead centre to the top dead centre through rotary motion of the crankshaft to reduce the gas volume and elevate the static pressure	• Moderate pressure ratio (4-5) (Amos, 1998) • High delivery pressure through multistage (250-1000 bar) (Han et al., 2020) • High flow rate (10723 N m³/h at 250 bar, 5180 N m³/h at 850 bar) (“Hydro-Pac: high pressure gas compressors, pumps and related products,” n.d.)	• Atlas Copco high-pressure compressor for mobility H2Y (“Reciprocating hydrogen compressor - Power to Gas - H2P,” n.d.). • Neuman & Esser Group hydraulic driven piston compressors (“Hydrogen Compressors,” n.d.)	• High maintenance requirements due to continuous wear and tear (Han et al., 2020) • Significant vibration and noise due to moving parts • Contamination due to lubricants • Lower efficiency at part load
	Diaphragm compressor The piston compresses a hydraulic fluid (oil), which transmits the force onto a thin metal membrane (diaphragm) to pressurise the gas confined in a gas cavity.	• Ultra-high delivery pressure (5000 bar) (“Hydrogen Compressors,” n.d.) • High-pressure ratio (6-7) (“HOFER Hochdrucktechnik GmbH / Neuman & Esser - Diaphragm Compressors,” n.d.)	• HOFER Hochdrucktechnik Diaphragm compressors (“HOFER Hochdrucktechnik GmbH / Neuman & Esser - Diaphragm Compressors,” n.d.) • PDC Machines Diaphragm compressors (PDC-3, PDC-4) (“Diaphragm	• Complex design • Low flow rate • Diaphragm failure due to mechanical stresses (Wang et al., 2019)

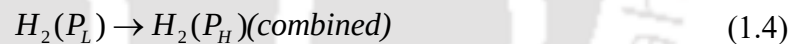
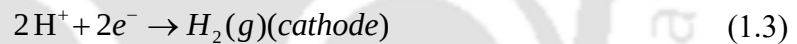
		• Highly pure hydrogen (Godula-jopek et al., 2012) • Low flow rate (100-600 N m³/h at 150-500 bar)	Compressors Industrial High Pressure Process Gas Compressors Manufacturer,” n.d.) • Toplong compressors (“Oil free high pressure two stage hydrogen diaphragm compressor,” n.d.)
	Ionic Liquid compressor	Gas is compressed by the back and forth movement of an immiscible ionic fluid (molten salt) column which in turn is moved by solid piston driven by hydraulic oil. Gas is separated from ionic fluid in the separator.	• Moderate to high pressure (450-900 bar) (“Hydrogen Linde Engineering,” n.d.) • Low flow rate (200 N m³/h) (The Linde Group, 2022) • Reduces the moving parts drastically • Linde Group Ionic Compressor (“Linde Hydrogen Fueling Overview Enhanced Reader,” n.d.; The Linde Group, 2022) • Cavitation phenomenon • Ionic liquid rupture
	Dynamic hydrogen compressor	High kinetic energy imparted to gas through the impeller is converted into static pressure as the gas is directed through the diffuser	• High flow rate (50000 N m³/h) (Tahan, 2022) • Extremely low-pressure ratio (1-1.2) • Howden centrifugal hydrogen compressor (“Compressors Products and Services Howden,” n.d.) • Hydrogen embrittlement • Delivery pressure is sensitive to the gas being compressed

1.4 Non-mechanical hydrogen compressor

1.4.1 Electrochemical hydrogen compression (EHC)

Electrochemical hydrogen compressors (EHC) are electricity powered devices designed to compress hydrogen. An assembly of electrodes, end plates, gas diffusion layer and specialised membrane are arranged to form a single compressor unit. Proton Electron Membrane Fuel Cell (PEMFC) and EHC operate on similar principles. The schematic presentation of a single-stage EHC is presented in Fig. 1.5.

Low-pressure hydrogen enters through the bipolar plate (BP) along the channel, reaching the Gas Diffusion Layer (GDL) which acts as a conduit for the gas moving through the bipolar plate's channels and onto the electrode. Subsequently, hydrogen gets split into protons and electrons at the Anode Catalyst layer (ACL), as shown in Eq. 1.2. Protons migrate towards the specialised membrane called the Proton Exchange Membrane, which permeates only protons through them. Electrons move to the cathode via an external electric circuit. Protons and electrons recombine at the Cathode Catalyst layer (CCL) to form hydrogen gas (Eq.1.3). Continuous supply of low-pressure hydrogen in a closed air-tight chamber generates high-pressure hydrogen at the CCL (Eq. 1.4) (Sdanghi et al., 2019b; Sdanghi et al., 2020).



According to Faraday's law, the number of protons (n) generated at the electrode is directly proportional to the magnitude of electric current (Eq. 1.5).

$$n = \frac{It}{Fv} \quad (1.5)$$

where I is the constant current applied for time t . F denotes Faraday's constant (9.648×10^4 C/mol), while v is denoted as the valency number of moles of electrons passed for 1 mol of hydrogen oxidised (2 for hydrogen).

The potential difference applied across the anode and cathode to pressurise hydrogen at the cathode is theoretically determined by Nernst voltage (Eq. 1.6), Marciuš et al., (2022)).

$$E_{Nernst} = E_o + \frac{R_u T}{vF} \ln \left(\frac{P_H}{P_L} \right) \quad (1.6)$$

where (E_o) is denoted as cell potential at standard conditions, which is zero in the case of electrochemical compression (Zou et al., 2020b). It is observed that Nernst voltage is directly proportional to the targeted elevated pressure.

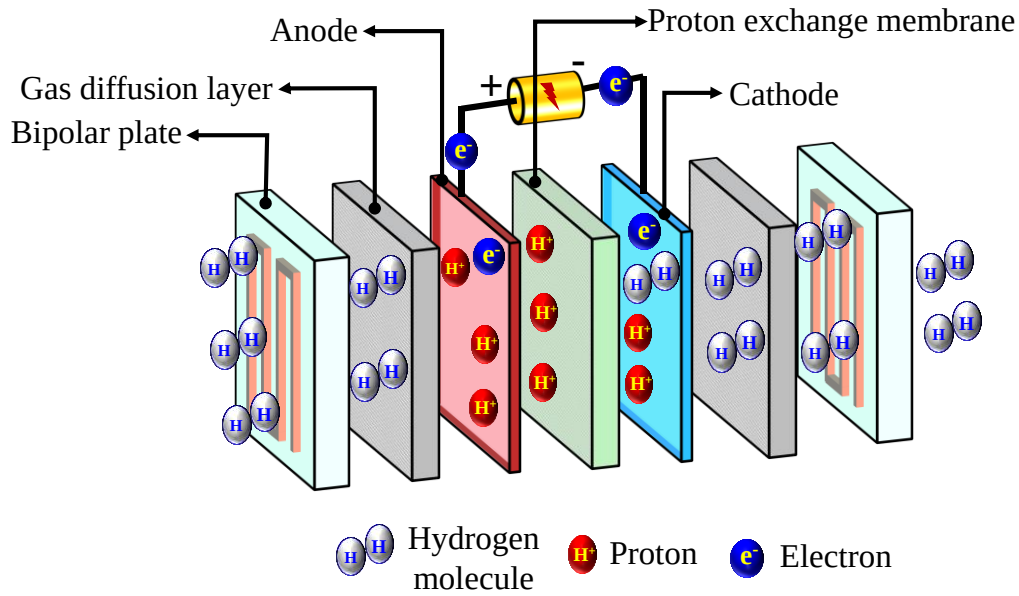


Fig. 1.5: Schematic representation of single-stage ECHC

Theoretically, only 0.085 V is required to compress hydrogen from 1 bar to 700 bar at 30 °C. In contrast, higher voltage is supplied to overcome the losses undergone by ECHC. The significant losses include ohmic losses, activation and concentration overpotential (Durmus et al., 2021). Hence, the required cell potential (E_{cell}), considering all the losses, is represented in Eq. 1.7:

$$E_{cell} = E_{Nernst} + \Delta E_{ohmic} + \Delta E_{activation} + \Delta E_{Conc} \quad (1.7)$$

The resistance to protons and electrons moving through the cell's components is the cause of ohmic losses (Durmus et al., 2021; Huth et al., 2009). The ohmic overpotential (E_{ohmic}) is determined using the Ohm's law as shown in Eq. 1.8.

$$\Delta E_{ohmic} = jR_{ohmic} = j \frac{\Delta t_m}{\sigma} \quad (1.8)$$

Where R_{ohmic} is denoted as cell ohmic resistance and j represents current density (A/cm²). The ohmic resistance is evaluated by taking the ratio of membrane thickness (Δt_m) and ionic conductivity σ . Studies suggest the thickness generally lies between 50 μ m and 175 μ m (Sdanghi et al., 2019; Zhang et al., 2006). Ohmic overpotential increases linearly with current density.

Activation overpotential ($\Delta E_{activation}$) is due to the potential drop due to the reaction kinetics resulting from oxidation and reduction at the anode and cathode, respectively. The activation over potential at anode and cathode is determined using Tafel equation (derived from Butler

Vomer equations) as expressed in Eq. 1.9. At the anode, hydrogen undergoes oxidation, primarily governed by the Volmer-Tafel mechanism, while at the cathode, hydrogen evolution occurs, dominated by the Volmer-Heyrovsky mechanism. Studies have also reported that the activation overpotential is higher at the cathode, attributed to the slower reaction kinetics of the Volmer-Heyrovsky mechanism (Frano, 2012; Marciuš et al., 2024).

$$E_{activation}^{anode/cathode} = \frac{R_u T}{2\alpha_{anode/cathode} F} \ln \left(\frac{j}{j_{o_{anode/cathode}}} \right) \quad (1.9)$$

where α is the charge transfer coefficient, and j is the exchange current density (A/cm²). At low current densities, activation overpotential is dominant.

Concentration overpotential (ΔE_{Conc}) occurs when the current density surpasses the limiting threshold, causing hydrogen or proton consumption at the electrode surface to outpace its replenishment. This leads to mass transport limitations, resulting in increased voltage loss and reduced electrochemical efficiency. It is determined by Eq. 1.10 derived from the Nernst potential. This overpotential is generally disregarded at lower current density (Frano, 2012).

$$E_{conc}^{anode/cathode} = \frac{R_u T}{2F} \ln \left(\frac{j_L}{j_L - j} \right) \quad (1.10)$$

where j_L denotes the limiting current density. It is the current density at which the reactant concentration at the electrode surface drops to zero, or the consumption rate matches the diffusion rate. Thus, as current density increases, the concentration overpotential also rises. The overall polarisation curve results into Eq. 1.11.

$$E_{cell} = \frac{R_u T}{2F} \ln \left(\frac{P_H}{P_L} \right) + j \left(\frac{\Delta t_m}{\sigma} \right) + \frac{R_u T}{2\alpha_{anode} F} \ln \left(\frac{j}{j_{o_{anode}}} \right) + \frac{R_u T}{2\alpha_{cathode} F} \ln \left(\frac{j}{j_{o_{cathode}}} \right) + \frac{R_u T}{2F} \ln \left(\frac{j_{L,anode}}{j_{L,anode} - j} \right) + \frac{R_u T}{2F} \ln \left(\frac{j_{L,cathode}}{j_{L,cathode} - j} \right) \quad (1.11)$$

Hydrogen may tend to flow backward, a phenomenon known as back diffusion, as the pressure increases at the cathode side (Chouhan et al., 2020; Marciuš et al., 2022; Trégaro et al., 2020). The back-diffusion flux reduces the efficiency of ECHC. Theoretically, ECHC are isothermal compressors, i.e. the temperature is maintained constant during the compression. In actual cases, the temperature rises due to the heat gained from Joule heating. Hence, efficient thermal management must be carried out to maintain temperature (Wu et al., 2014).

1.4.2 Adsorption hydrogen compressor (AHC)

In contrast to metal hydride hydrogen storage systems, which rely on chemisorption for hydrogen, adsorption-desorption systems primarily utilise physisorption to store hydrogen. Physisorption is a process where gas molecules bind with the adsorbent surface through weak

van der Waals force, unlike the strong chemical bonding in metal hydrides. As a result, hydrogen can be recovered reversibly with relatively lower energy input (order of 1-10 kJ/mol)(Vidal et al., 2022; Shet et al., 2021; Usman, 2022), making adsorption-desorption systems a promising alternative.

During adsorption, exothermic heat is released, similar to absorption. Adsorption is generally favoured at a lower temperature due to the lower enthalpy of formation as compared to the kinetic energy of hydrogen at ambient temperature. For instance, the adsorption of hydrogen by activated carbon is generally carried out at 77 K to overcome the higher kinetic energy of molecules at elevated temperature (Vidal et al., 2022; Sdanghi et al., 2019c). When energy is available, the adsorbed hydrogen is desorbed at a much lower temperature typically ranging from 77 K- 115 K (Jhi et al., 2004). Literature (Chen et al., 1999; Liu et al., 1999; Noh et al., 1987) reports dedicated efforts to uplift the desorption temperature to about 200 K. Fig. 1.6 illustrates the schematic of hydrogen adsorption.

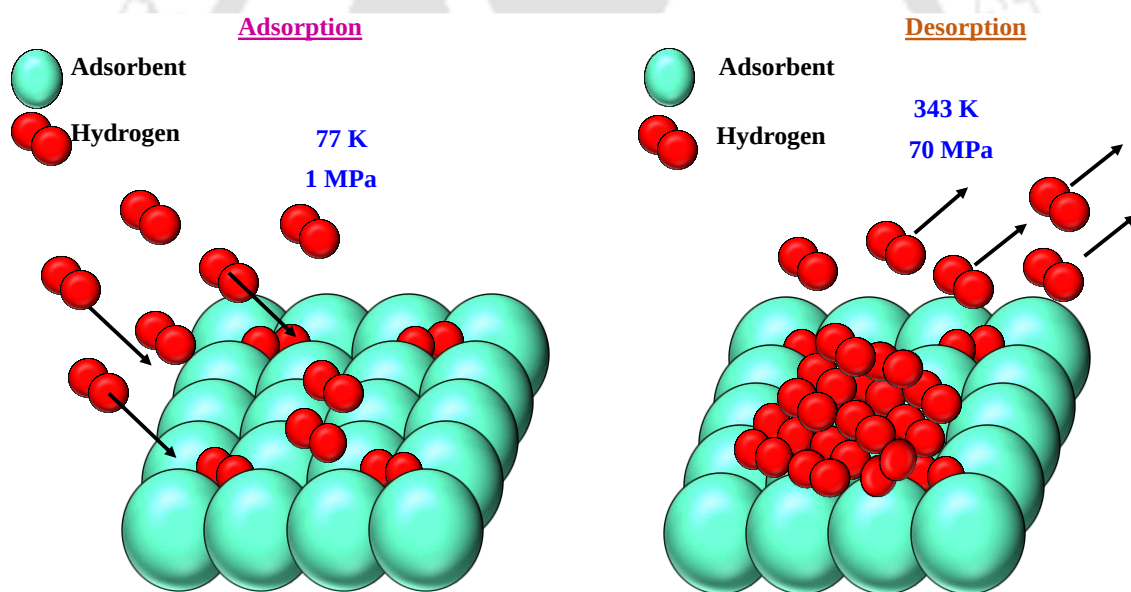


Fig. 1.6: Schematic representation of an adsorption hydrogen compressor

1.4.3 Cryo-compressed hydrogen (CCH₂)

Liquid hydrogen (LH₂) is well-known for its advantages, including an excellent volumetric density of 70.85 kg/m³ at 20 K and 101.325 kPa, compared to 39.05 kg/m³ for gaseous hydrogen at 300 K and 700 bar (Krasae-in et al., 2010; Muthukumar et al., 2023; Nandi and Sarangi, 1993; Peschka, 1992; Ratnakar et al., 2021). However, studies (Aceves et al., 2010; Ahluwalia et al., 2018; Petitpas et al., 2014) have reported major challenges during liquefaction, such as boil-off losses, high specific power consumption and excess heat generation due to ortho-para conversion. Aceves et al., (2010) were among the first to pioneer

a novel way of enhancing the volumetric density of hydrogen by combining cryogenic liquefaction with gaseous compression. This is accomplished by compressing hydrogen in several stages to obtain the desired pressure (350-500 bar). It is to be noted that intercooling is carried out after each compression stage to prevent excessive heating and optimise the power requirement. Subsequently, compressed hydrogen is cooled using refrigerants (liquid nitrogen) up to 77-100 K before storing it in a specially designed container to resist cryogenic temperature and elevated pressure. Fig. 1.7 shows the schematic of the operation of cryo-compressed hydrogen (CCH₂).

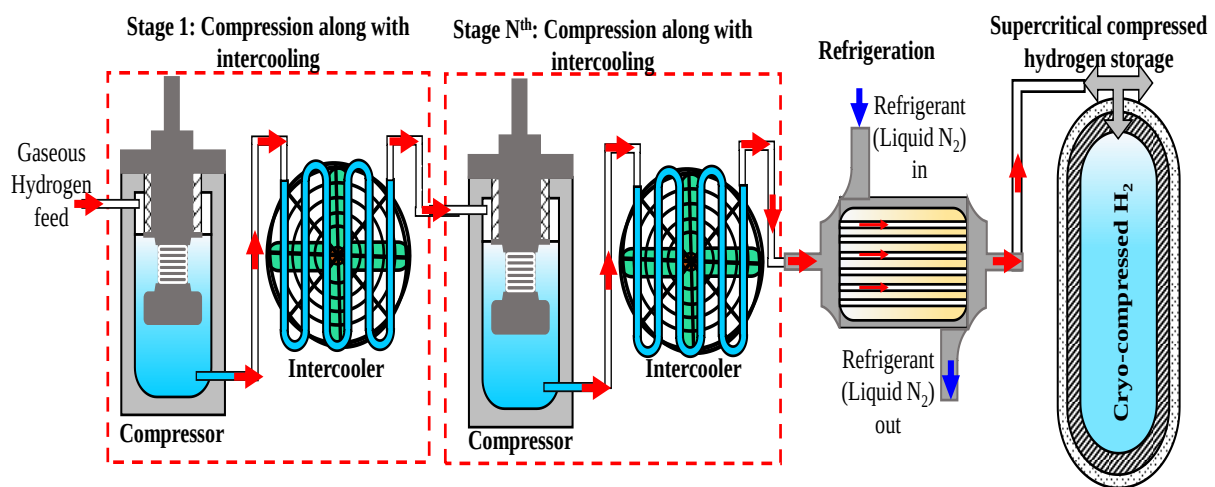


Fig. 1.7: Schematic representation of the operating principle of a Cryo-compressed hydrogen storage

According to Aceves et al., (2010), CCH₂ containers exhibit promising thermal endurance of 5-10 times greater than conventional LH₂. Conventional cryogenic containers were designed to withstand up to 4-7 bar pressure (Fesmire and Swanger, 2021; Ratnakar et al., 2021). In contrast, cryogenic pressure vessels can sustain pressure above 350 bar without significantly increasing container mass, enabling a longer storage period of boil-off gas. It was also revealed that this methodology can densify hydrogen to as high as 80 kg/m³ at 60 K and 500 bar. Fig. 1.8 illustrates the pressure-temperature-density plot of hydrogen in the temperature range of 20-300 K. Liquid hydrogen region is marked between 20 K and 33 K below the critical pressure of 12.84 bar. CCH₂ is marked between 33 K and 230 K above the critical pressure, whereas compressed gas storage (CGH₂) is marked above 230 K. It is observed that LH₂ offers a volumetric density of about 70 kg/m³ at 1 bar and 20 K (*Point A*) at a specific energy consumption (SEC) of 3.25 kWh/kg. On the other hand, it requires a little over 2.25 kWh/kg to cryogenically compress up to 1000 bar at 158 K (*Point B*), saving over 31% energy intake

for each kg of hydrogen. Compared to CGH_2 at 700 bar and ambient temperature (*Point D*), CCH_2 exhibits almost 61% higher volumetric density at 500 bar and 100 K (*Point E*) at just 25% higher energy consumption.

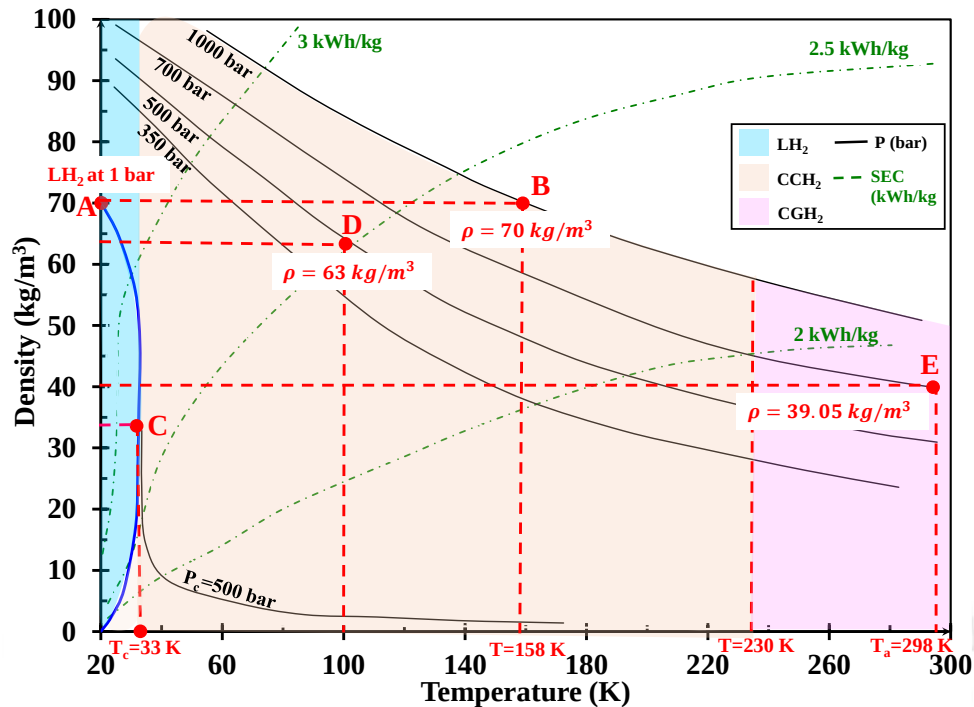


Fig. 1.8: Graphical representation of favourable regions of liquified, cryo-compressed and compressed hydrogen storage, including energy consumption (Aceves et al., 2010)

Regardless of the superior storage density and dormancy time, CCH_2 faces other challenges like heat intake, stress fracture, and hydrogen embrittlement at cryogenic temperature. Hence, the design of the cryogenic-compressed container is of paramount importance. Lawrence Livermore National Laboratory was among the first to develop the prototype of a cryo-compressed vessel incorporating aluminium liner and carbon fibre reinforced plastics (CFRP) shell surrounded by an outer vacuum vessel and multiple layers of insulations to minimise heat loss.

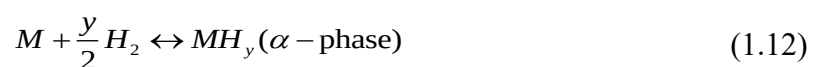
1.4.4 Metal hydride hydrogen compression (MHHC)

Fundamentals of metal hydride (MH)

Intermetallic compounds react with hydrogen to form metal hydrides under specific pressure and temperature conditions. The formation of metal hydrides (MH) occurs through the reversible absorption and desorption of hydrogen in metal alloys. This process is characterized by distinct phase transitions, primarily involving the α -phase (solid solution), β -phase

(hydride phase), and the $\alpha+\beta$ coexistence region. The formation of metal hydrides follows a multi-step mechanism, which includes the following stages:

- *Physisorption – Surface Hydrogen Adsorption*: Initially, hydrogen molecules approach the metal surface and undergo physisorption, where they are weakly bound to the surface through van der Waals forces. This stage is reversible and does not involve significant energy changes. The physisorbed hydrogen remains molecular and is not yet involved in the hydride formation process.
- *Chemisorption, Dissociation and Atomic Absorption (α -phase Formation)*: As the hydrogen concentration increases, hydrogen molecules dissociate into atomic hydrogen upon interacting with the metal surface. These hydrogen atoms chemically bond with the metal atoms through chemisorption. The dissociated hydrogen then diffuses into the interstitial sites of the metal lattice, forming the α -phase. The α -phase is a solid solution where hydrogen atoms occupy interstitial spaces without significantly altering the metal's crystal structure. This process involves minimal structural changes.
- *Hydride formation (β -phase- hydride formation phase)*: As the hydrogen concentration increases beyond a critical limit, the metal can no longer accommodate hydrogen in its interstitial sites without structural modification. The hydrogen atoms then cluster and induce a crystal lattice expansion, forming the β -phase, or metal hydride phase. The β -phase is a well-defined metal hydride with a stoichiometric hydrogen composition, leading to significant structural changes in the metal matrix.
- *Coexistence of α and β phase*: Between the α -phase and β -phase, a two-phase coexistence region is observed in the Pressure-Composition-Temperature (PCT) isotherm, where both phases exist simultaneously. The transition from α -phase to β -phase occurs through a first-order phase transition, which is accompanied by an enthalpy change (heat release or absorption). This transformation is observed as a plateau region in the pressure-composition-temperature (PCT) isotherm, where the system maintains a nearly constant pressure as hydrogen is absorbed or desorbed. This region is the most critical part of the PCT diagram as most of the hydrogen is absorbed in this region under constant pressure. The chemical reaction is:



where M is the metal or intermetallic complex. MH_x denotes metal hydride formed where the hydrogen content in the metal lattice increases from y to x as the system absorbs more hydrogen. ΔH denotes the change in enthalpy of formation.

Metal hydride systems' changing state functions are investigated using the van 't Hoff equation. The van 't Hoff equation can be written as:

$$\ln\left(\frac{P_{eq}}{P_o}\right) = \frac{\Delta H}{R_u T} - \frac{\Delta S}{R_u} \quad (1.14)$$

where P_{eq} denotes the bed equilibrium pressure of the alloy at temperature T , whereas P_o denotes atmospheric/reference pressure. ΔS represents the change in the entropy of the reaction while R_u denotes the universal gas constant. In actual cases, metal hydrides encounter hysteresis and plateau slopes. Hysteresis is experienced due to the plastic deformation during hydriding and dehydriding (Oian and Northwood, 1988), resulting in higher equilibrium pressure during absorption at a particular temperature. It is observed that hysteresis decreases with increase in temperature (Esayed and Northwood, 1997; Fan et al., 2025). Several studies have considered varying the alloy composition (Nomura et al., 1985), particle size (Oian and Northwood, 1988), and absorption and desorption cycle (Oian and Northwood, 1988) to study the effect on the amount of hysteresis. Larsen and Livesay, (1980) reported that the inhomogeneity during the intake and release of hydrogen is the cause of the slope of the pressure lines. Two prominent equations are frequently cited in the literature. One approach employs a polynomial function with multiple fitting constants to represent the correlation between equilibrium pressure and hydrogen concentration at a constant temperature (Nasrallah and Jemni, 1997; Jemni and Nasrallah, 1995a). The other approach, proposed by Nishizaki et al., (1983), incorporates both hysteresis and the slope factor to develop a modified van't Hoff equation expressed as an exponential function which is given by Eq. 1.15.

$$\ln\left(\frac{P_{eq}}{P_o}\right) = -\frac{\Delta H}{R_u T} + \frac{\Delta S}{R_u} + (\varphi_s \pm \varphi_o) \tan\left(\pi\left(\frac{\Psi}{\Psi_{max}} - 0.5\right)\right) \pm \frac{\gamma}{2} \quad (1.15)$$

where φ_s and φ_o are taken to consider the slope of the pressure isotherms while γ is utilised to evaluate the hysteresis. Ψ denotes the hydrogen concentration within the metal hydride (MH) bed at any time. Ψ_{max} represents the maximum storage capacity of the specific alloy. '+

' is used in the absorption cycle, while ' – ' is used in desorption cycle to evaluate the equilibrium pressure.

Types of metal hydrides

Metal hydrides are broadly classified into four types based on their hydride-forming constituent elements:

- ***AB-type Alloys (Titanium-Based):*** Titanium exhibits high hydrogen absorption capacity due to its low atomic weight, forming TiH and TiH_2 upon hydrogenation. However, pure titanium reacts with hydrogen at high temperatures (~ 793 K) with equilibrium pressures below 1 atm, making it impractical for reversible hydrogen storage. To enhance its usability, titanium is alloyed with transition metals such as Fe, Co, Ni, Cr, and V, reducing its stability while maintaining hydrogen storage capacity. Among these, TiFe is widely studied for hydrogen storage. TiFe alloys are highly sensitive to impurities like oxygen and water vapor, which lead to hydrogen capacity degradation due to the formation of an impermeable titanium oxide layer. This is mitigated by, heat treatment to remove oxide layers and repeated hydrogen absorption-desorption cycling to expose fresh metal surfaces.
- ***AB₅-type alloys (Rare Earth-based):*** Rare earth metals such as La, Ce, Pr, Nd, Sm, Gd, and Er form AB₅ intermetallic compounds with Ni and Co, resulting in AB₅H₆ hydrides upon hydrogenation. Among these, LaNi₅ is widely used due to its high hydrogen storage capacity (~ 1.44 wt%), low hysteresis and fast kinetics, flat pressure-composition (P-C-T) isotherm with a plateau pressure of 1.8 bar at 25 °C. Due to its ability to absorb/desorb hydrogen near atmospheric conditions, LaNi₅ is widely applied in heat pumps, refrigerators, and air conditioning systems. Partial substitution of La or Ni with elements like Al, Fe, Mn, Co, Ga, Zn, Ce, Pr, and Nd is commonly employed to optimize thermodynamic and kinetic properties for specific applications.
- ***A₂B-type alloys (Magnesium-based):*** Magnesium forms a reversible hydride (MgH_2) with a high hydrogen storage capacity of 7.65 wt%, far exceeding conventional metal hydrides like FeTiH_{1.95} (1.75 wt%) and LaNi₅H₆ (1.37 wt%). The heat of formation ($\Delta H = -75$ kJ/mol) requires high temperatures for hydrogen release, making MgH_2 more suitable where high-temperature heat sources are available and is thus used in thermal energy storage applications. However, hydrogen absorption/desorption kinetics are slow. To improve this, Mg is alloyed or mechanically mixed with metals like Ni, Cu,

Al, and In, forming intermetallic compounds such as Mg_2Ni and Mg_2Cu , which enhance reaction rates.

- ***AB₂-type alloys (Zirconium based):*** Zirconium forms ZrH_2 with a high heat of formation ($\Delta H = -163 \text{ kJ/mol}$), making direct hydride formation highly stable and less practical for storage. It also forms AB-type compounds like ZrNi and ZrCo , but their high stability and low plateau pressures make them unsuitable for hydrogen storage applications. However, Zr-based AB₂ intermetallic compounds (ZrMn_2 , ZrV_2 and ZrCr_2) exhibit high hydrogen storage capacity, ease of activation and fast reaction kinetics. The low plateau pressure at room temperature limits their practical use. To overcome this, transition metals such as Ti, Mn, Fe, and Co are substituted to increase plateau pressure without significantly reducing hydrogen storage capacity.

Hydrogen compression using MH

Metal Hydride Hydrogen Compressor (MHHC), also known as a thermal compressor, utilises the thermal energy input to uptake the pressure from the ambient to the desired pressure. Eq. 1.14, which depicts the exponential dependency of pressure and temperature, governs this behaviour. Fig. 1.9 represents the schematic of the MHHC operating principle. In MHHC, hydrogen is initially absorbed by the alloy bed at a low feed or injection pressure, with the bed temperature maintained such that the equilibrium pressure remains below the feed pressure. Once absorption is complete, the container valve is closed, and the bed is sensibly heated, causing an exponential rise in pressure due to the thermodynamic properties of the hydride. The compressed hydrogen is then discharged into an external cylinder for storage or further utilization.

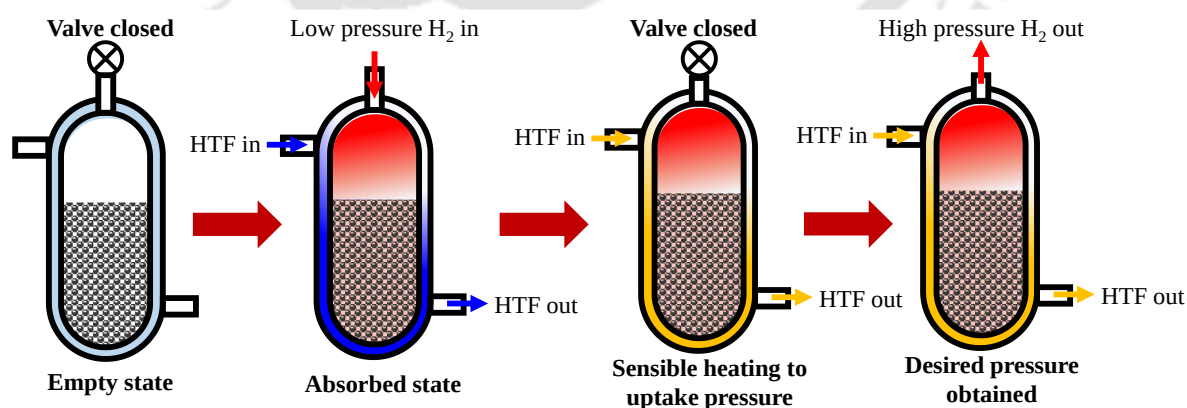


Fig. 1.9: Schematic representation of operating principle of a MHHC

MHHC systems have evolved from single-stage (Au and Wang, 1993; Muthukumar et al., 2005; Wiswall and Reilly, 1970) to multi-stage (Laurencelle et al., 2006a; Shmal'ko et al.,

1999b; Vanhanen et al., 1999). In an on-board hydrogen vehicle, typical pressure ranges from 350 to 700 bar (Rivard et al., 2019; Stetson, 2016). Thus, a single alloy may not compress hydrogen up to 200 bar (IRENA 2020, 2020). This challenge has led to the development of multi-stage metal hydride hydrogen compressors.

1.5 A critical comparison of the compressor techniques

Apart from understanding the distinct differences in operating principles, the compressor techniques should be critically compared based on key parameters such as thermodynamic efficiencies, compression rate, economic viability, and inherent advantages and disadvantages. Evaluating these factors will help identify the most suitable technologies for specific applications.

MHHC typically achieve efficiencies between 6-12% (Li et al., 2010; Muthukumar et al., 2005; Zhan et al., 2022), primarily due to the high thermal energy demands of the metal hydride (MH) alloy and reactor housing. MHHCs have been reported to consume approximately 36 MJ/kg of specific thermal energy. These systems require substantial sensible heat input; however, when integrated with waste heat recovery systems, the emphasis shifts from efficiency to economic viability, leveraging otherwise wasted energy (Karagiorgis et al., 2017b; Kelly and Girdwood, 2012; Sdanghi et al., 2020). The economic feasibility of constructing and operating an MHHC, from prototype to large-scale implementation, has been found comparable to that of mechanical compressors with similar specifications for nearly two decades, with studies (Da Silva, 1993; Tamhankar et al., 2009) suggesting cost parity even before 2010. For instance, Da Silva, (1993) reported that an MHHC built in Brazil (compressing hydrogen from 10 to 100 bar at a rate of 0.42 Nm³/h) cost \$23,000 USD, whereas a mechanical compressor from Pressure Products Industries, USA, was priced at \$27,000 USD (1989 prices). Two decades later, in 2009, the capital expenditure for an MHHC operating between 0.5 to 430 bar, as reported by Line North America Group, Member Reactor Technologies, and Ergenics Group, was \$66,000 USD, with potential for further cost reductions (Tamhankar et al., 2009). By 2017, an MHHC with a pressure range of 6.9–248.2 bar and a compression rate of 56.63 Nm³/h was estimated to cost approximately \$175,000 USD, compared to \$195,000 USD for a mechanical compressor of identical specifications. Moreover, MHHCs exhibit significantly lower annual maintenance costs, reported at just 1% of the capital expenditure, compared to 5.5% for mechanical compressors (Stamatakis, 2017). The most recent cost estimate, from 2022, reported that an MHHC capable of compressing 100 kg H₂/h from 150 bar to 875 bar had a capital expenditure of \$2,000,000 USD. However, this reactor was assumed to be fabricated from Nitronic 50, a

high-cost material. If instead constructed using a Type III pressure vessel, the cost could be reduced by approximately 50% (Johnson et al., 2022). The major cost component of MHHCs is attributed to compressor parts, MH alloys, and assembly, accounting for 50-60% of the total expenditure (Johnson et al., 2022; Lototskyy et al., 2020, 2014). This underscores the need for efficient system design to optimize costs, enhance performance, and improve overall economic viability.

ECHC are highly efficient, with efficiencies ranging from 85-95% (Kim et al., 2013; Ströbel et al., 2002), largely due to their isothermal operation and the use of higher-grade energy (electricity). ECHCs consume 14-15 MJ/kg (1 bar -137 bar) but is purely dependent on the operating pressure ratio (Grigoriev et al., 2011; Prokopou et al., 2024). Studies indicate that the capital cost of ECHC is primarily influenced by compression capacity and manufacturing rate. Research indicates that for an ECHC compressing 250 kg/day of hydrogen from 3.5 bar to 70 bar, with a manufacturing rate of 500 units per year, the MEA accounts for up to 45% of the total cost, with the gas diffusion layer (GDL) being the most expensive component (Moton et al., 2014). A 2016 scientific report by Lipp projected that increasing manufacturing capacity from 1,000 to 10,000 stacks per year could reduce stack costs to \$720,000 USD, falling below the DOE target of \$864,000 USD for a compression rate of 100 kg/h (Lipp, 2016). Additionally, a 2017 study focused on designing and developing an ECHC system for hydrogen compression up to ~875 bar, targeting a capital cost below \$170,000 USD, with annual operation and maintenance costs under \$3,400 USD. However, a 2018 report estimates the actual capital cost to be approximately \$450,000 USD (Hamdan, 2018). This figure may vary depending on the compressor capacity, operating pressure, and system configuration. Recent cost data is limited and not widely available in public sources. Despite high efficiency, these costs highlight the financial challenges associated with widespread ECHC adoption.

AHC rely on physisorption using materials like activated carbon, which are relatively inexpensive. While the reactor assembly is similar to MHHCs, AHCs aim to improve reaction kinetics through efficient reactor design. However, due to limited research, key data on efficiency, compression rate, and costs for large-scale AHC systems are scarce (Myekhlai et al., 2024; Sdanghi et al., 2020, 2019c). Given that AHCs operate at cryogenic temperatures and require substantial thermal energy for adsorbent regeneration, large-scale efficiencies are estimated to remain below 5%. Additionally, the high energy demands associated with cryogenic operation contribute to potentially elevated operating costs. Although AHCs could be economically viable in small-scale applications, current data suggest they may face significant scalability challenges for industrial use.

CCH₂ systems tend to have high energy consumption due to the essential step of hydrogen liquefaction, which requires approximately 36-54 MJ/kg, therefore an energy-intensive process (Muthukumar et al., 2023). Compressing this cryogenic hydrogen to around 500 bar further adds an estimated 9 MJ/kg (Aceves et al., 2010). Given these substantial energy demands, CCH₂ systems generally achieve efficiencies of only 10-30% (Ahluwalia et al., 2011), even with high-grade energy inputs. Beyond operational costs, significant capital expenditures are also associated with the balance-of-system components, such as cryogenic fittings, specialized valves, and in-house heat exchangers (Ahluwalia et al., 2018). While the exact installation costs for such facilities remain unspecified, the initial investment is substantial. However, CCH₂ systems offer remarkable compression rates of up to 1000 Nm³/h (Aceves et al., 2006; Sdanghi et al., 2019a) and volumetric storage capacities of 60-70 kg/m³ (Ahluwalia et al., 2011), making them highly viable for industrial-scale applications and hydrogen refuelling stations.

Table 1.2 provides a critical comparison of non-mechanical hydrogen compressors and assesses their commercialization potential.

Table 1.2: Comparisons of various Non-Mechanical hydrogen compression technologies

Non- Mechanical Compression Techniques	Advantages & Limitations	Efficiency (%)	Compress ion rate (Nm ³ /h)	Specific Energy consumption (MJ/kg H ₂)	Commercialization and Opportunities
Metal-hydride hydrogen compressor	Advantages - Storage, compression and purification simultaneously - Low-grade heat as energy intake (can be coupled to renewables (20-150 °C)) - Silent operation with almost negligible maintenance - Tunable pressure range based on the alloy selection (200-700 bar) Limitations - Bulky systems due to the heavier tank body - Expensive alloy powder - Alloy disproportionation - Lower efficiency	Low 6-12%	Low (<5)	Moderate ~36	- Whole Win (Beijing) Materials Sci & Tech. Co. Ltd (Hydrogen discharge capacity-5-30 m³/h, Pressure Range-30 bar-450 bar, Temperature- 20-80 °C) (“Company Product - Whole Win (Beijing) Materials Science and Technology Company Limited,” n.d.) - HySA Systems (“Solid State Hydrogen - HySA Systems,” n.d.)
Electrochemical hydrogen compressor	Advantages - Higher Compression Efficiency (55-80%) - Absence of moving parts - Purification is an added advantage	High (85-95%)	Low (<1)	Low 15	HyET Hydrogen (Capacity- 120 kg H₂/day, Delivery Pressure-400/900 bar (“Commercial Projects HyET Hydrogen,” n.d.)

	• Very high compression ratio is achievable • Compact and scalable Limitations • High-grade energy as input (electrical energy) • Hydrogen back diffusion • Complex cell design • Low compression rate (maximum flow rate: 7.23 m³/h)				• Giner ELX (Delivery pressure 875 bar) (Hamdan, 2018)
Adsorption-based hydrogen compressor	Advantages • High hydrogen storage capacity at 77 K (10 wt%) • Reduces the tank volume (22%) • Excellent reversibility • Cheaper adsorbent (Activated carbon) • Thermal-driven compressor Limitations • Operate at cryogenic temperature (77 K) • Storage capacity drops drastically when heated to ambient temperature (1 wt% at 298 K)	Low (<5%)	Unknown	Data unavailable	• Ongoing research

	Advantages	Moderate	Very high	High	
Cryo-compressed hydrogen storage	• Offers the highest volumetric density among all compression methods. • Consumes lesser energy as compared to liquid hydrogen • High dormancy/inactivity period • Reduces boil-off losses • Can be used in automobile applications	(10-30%)	(1000)	>50	• BMW Hydrogen • Air Products Cryogenic Compressor (Liquid flow rate-3400 m³/h, Delivery pressure-700 bar) (“Cryogenic Hydrogen/Helium Compressor,” n.d.)
	Limitations • Operate at cryogenic temperature (77 K-110 K) • Difficulty of restricting heat transfer. • Hydrogen embrittlement at extreme temperature and pressure				

1.6 Scope and motivation of the thesis

The transition toward a hydrogen-based energy economy necessitates the development of efficient hydrogen storage and compression technologies. Conventional mechanical compressors suffer from high energy consumption, noise, and maintenance requirements, making non-mechanical hydrogen compression systems, such as Metal Hydride Hydrogen Compressors (MHHCs), a promising alternative. MHHCs leverage the thermally driven absorption-desorption cycle of metal hydrides, enabling reliable, energy-efficient, and scalable hydrogen compression for hydrogen refuelling stations, industrial applications, and energy storage systems.

The primary motivation of this research is to address the critical challenges associated with metal hydride-based hydrogen compressors, including low thermal efficiency, slow kinetics, and design scalability. The study focuses on the design, development, and optimization of multi-stage MHHCs to achieve high-pressure hydrogen compression (10–300 bar) using low-grade heat sources ($<90\text{ }^{\circ}\text{C}$), making it suitable for integration with renewable energy-driven hydrogen infrastructure. This thesis systematically investigates metal hydride selection, emphasizing AB₅-type alloys for their fast kinetics and AB₂-type alloys for their higher plateau pressures. The study includes numerical modelling, experimental validation, and performance optimization of dual-stage and three-stage MHHC systems. The developed systems are designed to compress hydrogen efficiently while minimizing thermal losses and improving sorption kinetics through enhanced reactor designs with embedded cooling tubes and optimized finned structures. Furthermore, this work explores the real-world applicability of MHHC technology, including hydrogen cylinder refilling, and compares its performance with existing compression technologies. The outcomes of this research contribute to advancing hydrogen compression science, supporting the global transition toward a sustainable hydrogen economy.

1.7 Structure of the thesis

The present thesis is structured into seven chapters. The details of each chapter are mentioned below.

Chapter 1 introduces the global energy landscape and highlights hydrogen's role as a key energy carrier in addressing major challenges. The barriers to hydrogen adoption are discussed, emphasizing compression as the most challenging problem. Various hydrogen compression technologies, including mechanical and non-mechanical compressors, are reviewed and compared. The chapter also covers the formation and classification of metal hydrides, along with the working principle of MHHC. Finally, the motivation behind this research is outlined.

Chapter 2 presents a comprehensive review of the state-of-the-art advancements in Metal Hydride Hydrogen Compressors (MHHCs). It covers key aspects such as alloy selection, reactor design, and numerical modelling to analyse the physics of the compression process. Additionally, MHHC setups developed worldwide over the past five decades at various scales are thoroughly discussed. Based on the insights gained from the literature survey, the research objectives of this thesis are formulated.

Chapter 3 focuses on the design methodology of metal hydride reactors for high pressure and low-pressure compression applications. It provides a detailed description of the mathematical formulations and optimization methodology. The finalized reactor design, derived from numerical simulations, has been fabricated. Additionally, the alloy selection for this study is discussed, highlighting its relevance to the thesis objectives.

Chapter 4 focuses on the experimental setup developed for hydrogen compression studies. It presents two systems: a prototype dual-stage compression setup and an industrial-scale three-stage compression system. The chapter provides a detailed description of the setup, components, and operational framework. Additionally, the experimental protocols for conducting hydrogen compression studies are outlined.

Chapter 5 addresses the activation challenges encountered in both prototype and industrial-scale reactors. It also presents a comprehensive parametric study on the prototype reactors to determine the optimum operating parameters for the alloys selected at each stage of the multistage compressor system.

Chapter 6 focuses on the experimental studies conducted on multistage compressor systems, presenting the world's first demonstration of an MHHC system capable of compressing hydrogen up to 300 bar using waste heat below 100°C. The study examines the influence of key operating parameters, including injection pressure, hydrogen inventory, cycle time, and bed temperature, on compressor performance. Additionally, the energy dynamics of the system are thoroughly analysed. The chapter concludes with a novel investigation on the filling of a commercial Type I-cylinder post-compression in the industrial-scale system.

Chapter 7 presents the key conclusions derived from this study. It also outlines recommendations for future research, highlighting potential areas for further investigation and improvements in MHHC technology.

1.8 Summary

This chapter outlines the role of hydrogen in addressing the global energy challenge and highlights the need for efficient hydrogen compression technologies to enable the development

of a large-scale hydrogen infrastructure. Various mechanical and non-mechanical hydrogen compression techniques are reviewed and compared. Additionally, the scope and motivation of the thesis are discussed, followed by a clear explanation of the thesis structure.



Chapter 2

Literature Review

2.1 Preface

With growing concerns over climate change, energy security, and fossil fuel depletion, the need for clean energy sources is critical. Hydrogen, with its high energy density and zero emissions, is a promising alternative, but efficient storage and compression are essential for large-scale adoption. MHHC offers a non-mechanical, energy-efficient solution, leveraging the absorption-desorption cycle of metal hydrides for high-pressure hydrogen compression. As demand for hydrogen refuelling stations and industrial storage rises, MHHC continues to be a key area of research and development.

This chapter presents a comprehensive review of the state of the art in MHHC technology, discussing key aspects crucial for its performance and scalability. One of the fundamental aspects is the selection of appropriate metal hydrides, as the selection criteria for MHHC differ significantly from other metal hydride applications such as hydrogen storage, purification, and thermal energy storage. For MHHC, alloys must possess optimal equilibrium pressures, fast kinetics, low hysteresis, and good cyclic stability under repeated compression cycles. A detailed discussion on suitable alloy classes, including AB₅-type and AB₂-type alloys, is provided, along with the impact of elemental substitution on their performance.

Another critical aspect of MHHC is the design and configuration of the reactor. Unlike metal hydride reactors used for storage or thermal energy applications, compression-specific reactors must be designed to handle large pressure differentials, effective heat management, and hydrogen flow dynamics. This chapter explores various reactor configurations, including tubular, helical, and embedded cooling tube designs, specifically tailored for hydrogen compression applications. The role of enhanced heat transfer mechanisms in improving reaction kinetics and compressor efficiency is also discussed.

Furthermore, mathematical modelling plays a pivotal role in understanding the complex physics governing MHHC operation. Several research studies have developed numerical models to investigate the coupled heat and mass transfer mechanisms during hydrogen absorption and desorption. This chapter provides an overview of the existing models, highlighting their applicability in predicting reaction kinetics, thermal management, and overall compressor performance. In addition, specific models dedicated to studying coupled

MH reactor operation are discussed, as they are essential for multi-stage hydrogen compression, where heat and hydrogen transfer occur dynamically between multiple reactors. The chapter also reviews experimental studies conducted on MHHC systems developed thus far, ranging from lab-scale prototypes to large-scale industrial implementations. Key findings from these studies, including hydrogen flow rates, compression efficiencies, thermal management strategies, and cycle durability, are summarized to provide insights into the current state and future research directions. Additionally, relevant patents in MHHC technology are examined to understand recent innovations and commercial advancements in MHHC.

By addressing alloy selection, reactor design, mathematical modelling, coupled reactor studies, and experimental advancements, this chapter provides a comprehensive foundation for understanding the current state and future prospects of MHHC technology.

2.2 Selection of suitable alloy for hydrogen compression

Table 2.1: Required characterisation in an ideal MHHC alloy

Characteristics	Purpose
High hydrogen storage capacity (>1.2 wt%)	• To reduce the amount of MH alloy, energy input and reactor size
Lower plateau slope in the absorption and desorption pressure isotherm	• To enhance the absorption at low supply pressure and maintain high-pressure delivery
Lower hysteresis	• To minimise the energy loss
Fast reaction kinetics	• To enhance productivity during mass transfer
Higher cyclic stability (>10000 cycles)	• To improve the life span of the alloys to prevent disproportion
Tolerance to impurities	• To prevent bed poisoning during impure hydrogen absorption
Easy activation	• To activate the alloy in a lesser number of cycles
Low reaction enthalpies in absorption and desorption half-cycles ($\Delta H > 24$ kJ/mol)	• To obtain higher delivery pressure with lesser thermal energy input

Selecting suitable MH alloy is crucial for MHHC design. Ideal alloys should efficiently absorb hydrogen from low-pressure source, transport larger amount of hydrogen faster, deliver hydrogen at high pressure with minimal energy input, and resist degradation from thermal cycling. Key characteristics are listed in Table 2.1.

Active alloy components such as La, Ti, Zr, Ca, and Ce form oxide layers when exposed to atmospheric oxygen, which hinders hydrogen absorption (Peng et al., 2022a). The process of oxide layer removal, known as "activation," involves subjecting the alloy to hydrogen at elevated pressures in an evacuated chamber, followed by high temperature heating to desorb hydrogen. Alloys like TiFe, with poor activation characteristics, require high-pressure hydrogen (above 100 bar) and multiple absorption-desorption cycles for activation (Guo et al., 2021; Li et al., 2021; Reilly and Wiswall, 1974). Alloys with better activation characteristics are thus preferred for compression. Fig. 2.1 illustrates the schematic of the activation process. The unactivated alloy is initially heated to a high temperature to provide sufficient energy to break the metal-oxide bonds (Fig. 2.1 (a)). Simultaneously, the alloy bed is evacuated to enhance the oxide removal process. The duration of heating and evacuation depends on the alloy's affinity for impurities. Following this, the alloy bed is cooled to the desired low temperature before being exposed to pure hydrogen at elevated pressure (Fig. 2.1 (b)). The bed is then reheated, allowing the absorbed hydrogen to be released along with any remaining impurities (Fig. 2.1 (c)). This is followed by reintroducing hydrogen to the cooled bed, completing the second activation cycle (Fig. 2.1 (d)). The process is repeated until the bed reaches its maximum storage capacity.

Typically, electrolyzers produce hydrogen below 30 bar (IRENA 2020, 2020) while the DOE target for stationary gaseous hydrogen tanks falls in the range of 160-925 bar ("DOE Technical Targets for Hydrogen Delivery"). Therefore, adequate attention must be given while choosing the pressure ranges for hydrogen intake and distribution in the design of a multi-stage MHHC. An ideal MHHC should be able to absorb hydrogen from a low-pressure source (<10 bar) and also deliver at elevated pressure (>200 bar). Out of various types of intermetallic compounds, AB₅ and AB₂ alloys are largely used in MHHC. Another type of alloy that has been used in a few instances includes TiFe-based AB-type alloys and vanadium-based BCC solid solutions.

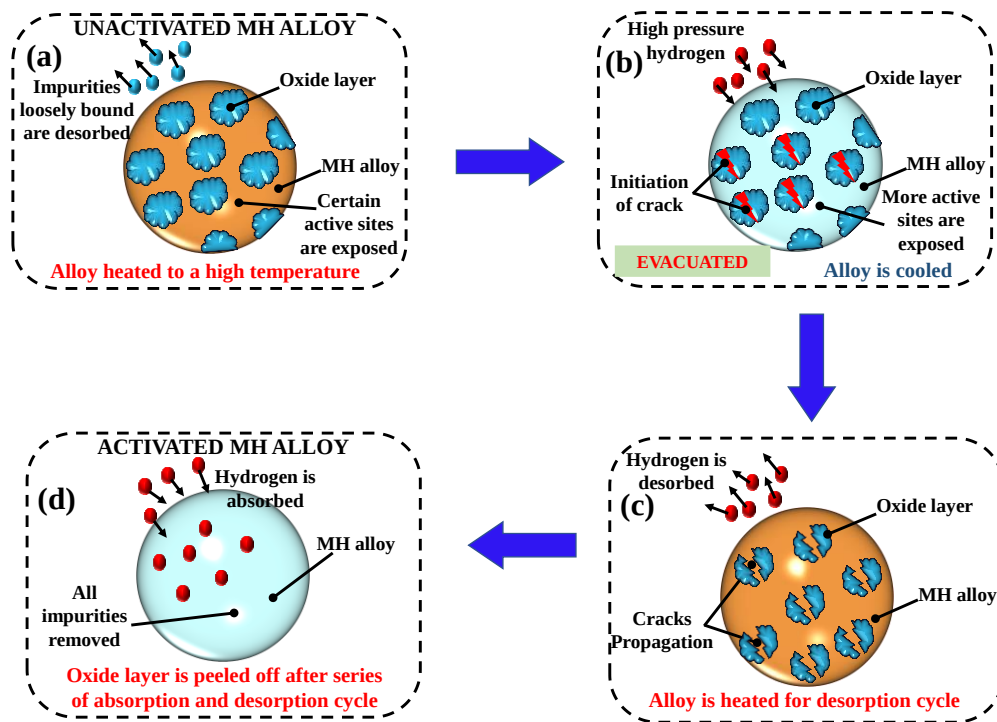


Fig. 2.1: Schematic of the metal hydride activation process

TiFe was the first alloy used in MHHCs by Wiswall and Reilly (Wiswall and Reilly, 1970), due to its significant hydrogen storage capacity (~1.9 wt%), moderate operating pressure (10 bar for absorption, 4 bar for desorption), and accessible raw materials, making it cost-effective. However, high activation pressures of TiFe (100 bar) (Endo et al., 2013; Inui et al., 2002; Patel et al., 2018) and sensitivity to contamination (Zeaiter et al., 2019) have limited its adoption. Researchers have attempted to improve activation properties through doping (Park et al., 2021; Patel et al., 2018; Zeaiter et al., 2019), annealing (Patel et al., 2018), and ball milling (Guo et al., 2021), but TiFe remains less favoured for high pressure MHHC applications. Vanadium hydride was first used by Reilly et al., (1971) in MHHC systems, elevating pressures from 7 bar to 24 bar within a temperature range of 18-50°C. Vanadium hydrides dehydrogenate in stages: $\text{VH}_2 (\gamma) \rightarrow \text{V}_2\text{H} (\beta) \rightarrow \text{VH} (\alpha)$, with dehydrogenation occurring at 300 K, 450 K, and 750 K, respectively (Kumar et al., 2015). Vanadium-based alloys offer excellent hydrogen storage capacity (~4 wt%), fast kinetics at ambient temperature, and high enthalpy/entropy changes. However, these alloys face challenges such as poor reversibility, high thermal stability at room temperature and thus cannot be utilised in compressing hydrogen up to pressure in excess of 200 bar at moderate temperature range (50-90 °C)

LaNi₅ is widely used in the initial stages of compressors (Gkanas and Khzouz, 2017; Muthukumar et al., 2012a) for its excellent sorption properties, including high cyclic stability,

fast reaction kinetics, and near-ambient absorption pressure at room temperature (Joubert et al., 2021; Kumar et al., 2022; Lototsky et al., 2014). To enhance its properties, La is often substituted with elements like Ce and Ca, while Ni is replaced with Al, Co, and Fe. Substituting La with Ce, as studied by Yuan et al., (2003) and Odysseos et al., (2013), leads to a reduction in lattice parameters 'a' and 'c', decreasing cell volume, hysteresis, and thermodynamic stability, while maintaining ease of activation. It was showed that increasing Ce content in $\text{La}_{1-x}\text{Ce}_x\text{Ni}_5$ (with x up to 0.5) significantly raises equilibrium absorption pressure from 2 to 42 bar at 20 °C, though storage capacity eventually declines as x increases further. This is attributed to Ce's higher hydrogen affinity than La, leading to stronger bonding (Fig. 2.2 (a)). Similar findings (Wang et al., 2007) were reported for Ca substitution, where desorption pressure initially rises but later drops due to geometric and electric effects (Fig. 2.2 (b)). Due to the high cost of Lanthanum, Mischmetal, a mixture of rare earth elements primarily composed of Ce (48.6%), along with La (23.8%), Pr (8.1%), Nd (16.8%), and others (2.7%) (X. H. Wang et al., 2007), is also found to be used in MHHC applications (Laurencelle et al., 2009; Muthukumar et al., 2005; X. H. Wang et al., 2007). Researchers have substituted Al, Co, Cu, and Fe for Ni to study hydriding and dehydriding in LaNi_5 . Diaz and Achard, (1979) found that increasing Al content in $\text{LaNi}_{5-y}\text{Al}_y$ ($y=0-1.5$) reduced hydrogen storage capacity and equilibrium pressure, while the reaction rate remained constant, attributed to the increase in unit cell volume (Fig. 2.2 (c)). Similarly, Co substitution lowered absorption/desorption plateaus (Asano et al., 2003) (Fig. 2.2 (d)), while Fe substitution improved hydrogen storage due to Fe's larger atomic size (Pandey et al., 2007).

Despite their impurity tolerance and thermal stability, AB_5 alloys have low dissociation pressures (~200 bar at 150°C for La-Ce-Ni alloys) (Tarasov et al., 2021, 2018), making AB_2 alloys like TiCr_2 and ZrFe_2 more suitable for high pressure hydrogen compression at moderate temperature. Substitutions at the A-site in TiCr_2 with elements like Zr, V, and Nb have significantly enhanced alloy performance. Zr addition notably increases the unit cell volume, lowering dissociation pressure and boosting hydrogen storage capacity, which improves activation and reduces hysteresis (Cao et al., 2021; Li et al., 2022; Pickering et al., 2018). A similar effect is observed with Mn replacing Cr (Hagström et al., 1999; Peng et al., 2022a). Nayeboossadri and Book, (2019) highlighted Mn substitution as the most effective for destabilizing the hydride phase, thereby increasing dissociation pressure. However, Li et al., (2022) noted contamination in the melting vessel due to Mn's high vapor pressure, requiring an over-stoichiometric Mn addition to compensate for losses (Charbonnier et al., 2021). Over-

stoichiometric tailoring also improves storage capacity and reduces the plateau slope, though Kojima et al., (2006) cautioned that excess Ti strengthens M-H bonds, increasing formation

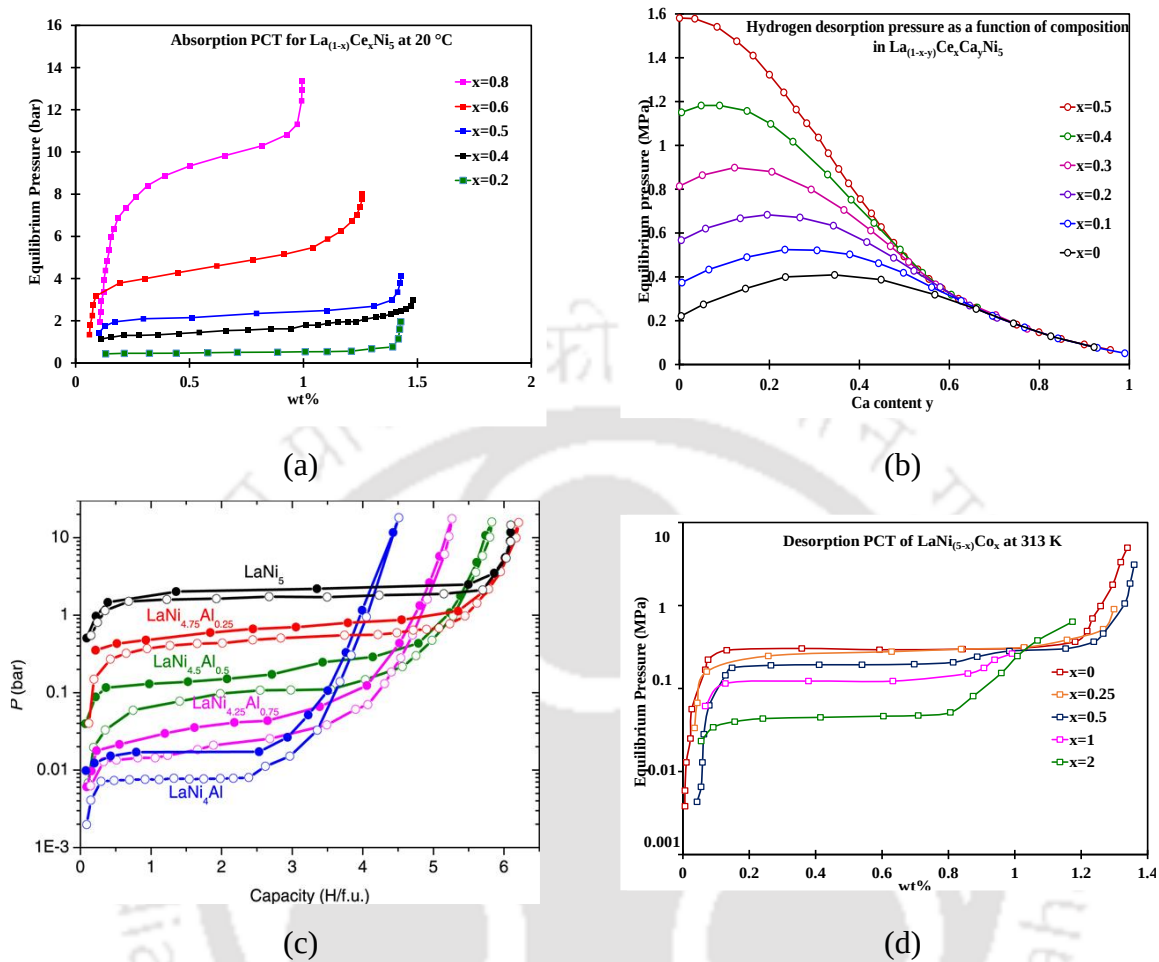


Fig. 2.2: Schematics of (a) Absorption PCT of $\text{La}_{(1-x)}\text{Ce}_x\text{Ni}_5$ (M. Odysseos et al., 2013), (b) hydrogen desorption pressure as a function of composition in $\text{La}_{(1-x-y)}\text{Ce}_x\text{Ca}_y\text{Ni}_5$ (X. Wang et al., 2007), (c) absorption PCT of $\text{LaNi}_{5-x}\text{Al}_x$ (Diaz and Achard, 1979) and (d) desorption PCT of $\text{LaNi}_{(5-x)}\text{Co}_x$ (Asano et al., 2003)

enthalpy and reducing storage capacity. Substitutions at the B-site with Mo, W, V, and Al have also been studied (Cao et al., 2015; Li et al., 2020; Ulmer et al., 2017). ZrFe₂ alloys have been extensively modified to optimize their sorption characteristics. Kouloukakis et al., (2014) found that Cr substitution in ZrFe₂ resulted in higher hysteresis loss and desorption plateau pressure than V substitution. Qin et al., (2020) explored ZrFe₂ substitution with Mn, Ti, and V. Table 2.2 summarises various AB₂ alloys developed recently, primarily for MHHC application. To harness the advantages of both AB₅ and AB₂-type alloys, LaNi₅-based alloys are typically used in the primary stages, while TiCr₂ and ZrFe₂-based alloys are employed in the intermediate and higher stages to achieve hydrogen compression at elevated pressures.

Table 2.2: Details of the AB₂ alloys developed for MHHC applications

Author (Year)	Studied alloy	Findings
Vanhanen et al., (1998)	• TiCrMn_(1-3x)Fe_{2x}V_x (x=0, 0.05, 0.1, 0.15 or 0.2) • Ti_(1-y)Zr_y(Cr_z Mn_(1-z))₂ (y=0.05 or 0.15 and z=0.5 or 0.6)	• Fe and V substitutions reduced hysteresis at the cost of hydrogen capacity. • Zr-containing hydrides maintained capacity at high temperatures.
Hagström et al., (1999)	• Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_(0.8-x)V_x (x=0,0.05, or 0.1) • Ti_{0.95}Zr_{0.05}Cr_{1.2}Mn_(0.8-y)Co (y=0,0.1 or 0.2) • Ce_{0.8}La_{0.2}Ni_(5-z)Co_z	• Mn substitution with V or Co lowered hysteresis. • Ce-La-Ni alloys displayed a double plateau beyond Co >1.5.
Pickering et al., (2015)	• Ti_{0.5}V_{0.4}TM_{0.1}Mn (TM=Nb, Cr, Mo, Ta) • Ti_{0.5}V_{0.5-x}Nb_xMn (x=0.05 and 0.2)	• Nb substitution reduced hysteresis and improved desorption pressure, making Ti_{0.5}V_{0.45}Nb_{0.05}Mn suitable for compression.
Pickering et al., (2013)	• Ti_{0.47}V_{0.46}Mn • Ti_{0.5}V_{0.51}Mn	• Alloys showed good storage capacity (1.53-1.56 wt%) and high plateau pressure.
Pickering et al., (2018)	• AB₂ (A=Ti+Zr, B=Cr+Mn+Ni+Fe+V)	• V variation enabled wide sorption property control with low Zr/(Ti+Zr) ratios.
Nayebossadri and Book, (2019)	• Ti-V-Mn-Zr-Cr-Fe	• Increased Mn destabilized hydride phase. After 655 cycles, storage capacity reduced by 9%.
Puszkiet et al., (2020)	• Ti_{0.9}Zr_{0.1}Cr_{0.85}Mn_{1.1}Mo_{0.05} + 10wt% ENG	• Arc-melted alloy with 10% ENG achieved 15-248 bar across 3-85°C.

Cao et al., (2021)	• $\text{Ti}_{0.85}\text{Zr}_{0.17}\text{Cr}_{(1.2-x)}\text{Fe}_{0.8}\text{V}_x$ ($x=0-0.2$) • $\text{Ti}_{0.85}\text{Zr}_{0.17}\text{Cr}_{(1.2-y)}\text{Fe}_{(0.7+y)}\text{V}_{0.1}$ ($y=0-0.25$) • $\text{Ti}_{(0.87-z)}\text{Zr}_{(0.15+z)}\text{Cr}_{0.95}\text{Fe}_{0.95}\text{V}_{0.1}$ ($z=0-0.4$)	• V improved activation kinetics, Fe raised plateau pressure, Zr enhanced storage capacity and reduced plateau pressure. • $\text{Ti}_{0.85}\text{Zr}_{0.17}\text{Cr}_{0.95}\text{Fe}_{0.95}\text{V}_{0.1}$ was optimal.
Peng et al., (2022b)	• $\text{Ti}_{(1.04+x)}\text{Cr}_{(2-y-z)}\text{Mn}_y\text{Fe}_z$ ($x = 0.02, 0.04, 0.06, y = 0.2, 0.3, 0.4, z = 0.5, 0.6, 0.7$)	• Ti increased storage capacity and reduced hysteresis. • $\text{Ti}_{1.08}\text{Cr}_{1.3}\text{Mn}_{0.2}\text{Fe}_{0.5}$ was promising, desorbing >800 bar.
Li et al., (2022)	• $(\text{Ti}_{(1-x)}\text{Zr}_x)_y\text{Cr}_{(2-z)}\text{Fe}_z$ ($x=0.1, 0.2, 0.3; y=1, 1.05, 1.1; z=0.9, 1, 1.1$)	• Zr and Fe variation adjusted cell volume, formation enthalpy, and desorption pressure. • $\text{Ti}_{0.85}\text{Zr}_{0.15}\text{Cr}_{1.1}\text{Fe}_{0.9}$ exhibited 455 bar at 90°C.
Kouloukakis et al., (2014)	• $\text{ZrFe}_{1.8}\text{V}_{0.2}$ • $\text{ZrFe}_{1.8}\text{Cr}_{0.2}$	• V substituted alloy possessed lower plateau pressure compared to Cr substituted. • Cr substituted alloy exhibited large hysteresis (0.74) compared to V substituted alloy.
Qin et al., (2020)	• ZrFe₂ substituted by Mn, Ti and V	• V reduced hysteresis, Ti lowered plateau slope, and Mn increased dissociation pressure (20.58 atm at 25°C). • $\text{Zr}_{1.05}\text{Fe}_{1.6}\text{Mn}_{0.4}$ exhibited higher dissociation pressure, i.e. 20.58 atm at 25 °C.

2.3 Designing of reactor configuration for hydrogen compression

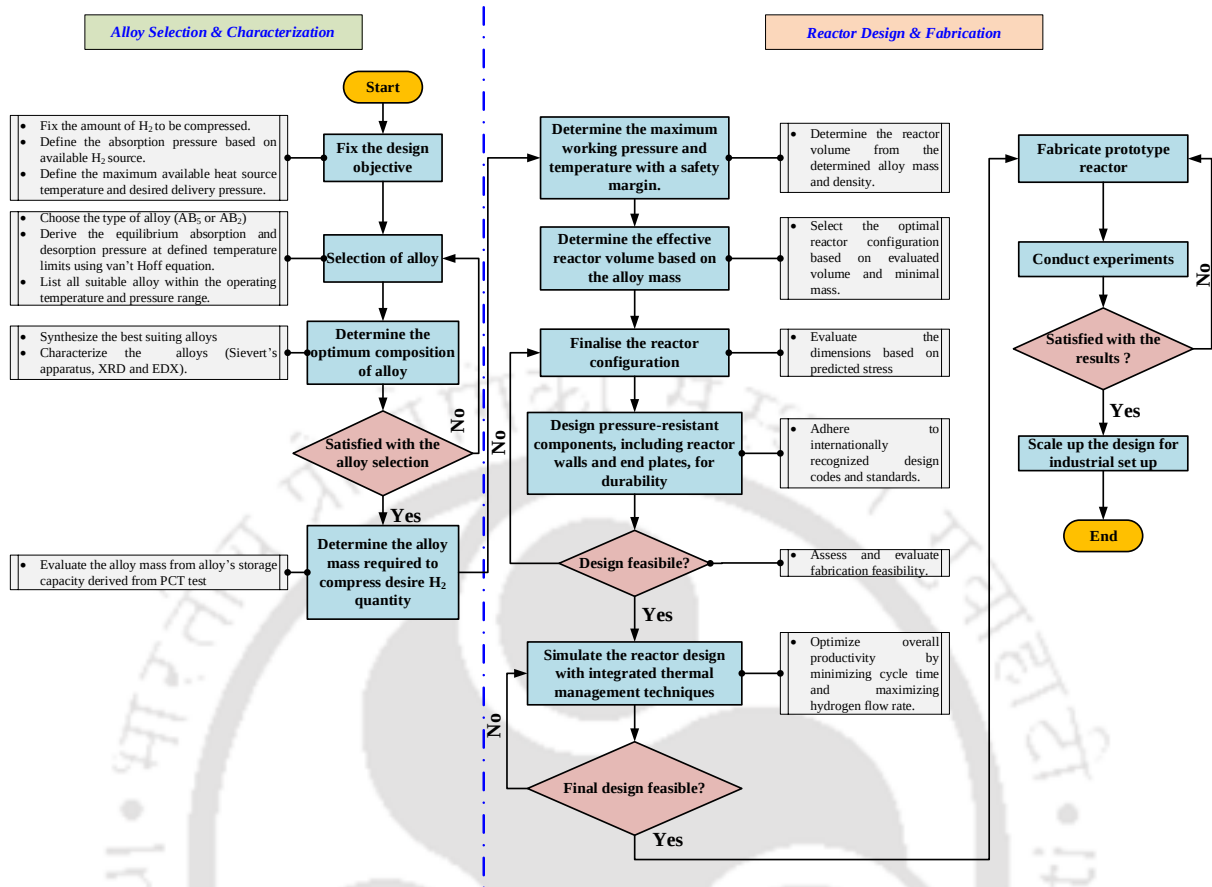


Fig. 2.3: Fundamental design process for a large-scale MHHC system

Fig. 2.3 details the fundamental design process for a large-scale MHHC system. The design process comprises two key segments: *Alloy Selection & Characterization*, which involves identifying suitable alloys based on operating conditions, synthesizing and characterizing them to determine properties like equilibrium pressure, storage capacity, hysteresis, and plateau slopes, and calculating the required alloy mass for hydrogen compression; and *Reactor Design & Fabrication*, which focuses on optimizing reactor configuration with effective thermal management through simulations and prototype testing before scaling up. Reactor design plays a critical role in developing efficient MHHC, particularly for achieving high delivery pressure and enhanced thermo-hydraulic performance simultaneously. Over the years, various reactor geometries have been developed for various niche MH thermal applications (Dong et al., 2022; Ranong et al., 2009; Shi et al., 2022; Sreeraj et al., 2022; Wang et al., 2023). Unlike other niche MH applications, MHHC must balance two critical yet opposing requirements: exceptional mechanical strength and structural integrity to withstand high pressures, and optimal thermohydraulic performance to facilitate rapid hydrogen absorption and desorption for

efficient discharge. Hence, the literature on MHHCs highlights a limited range of reactor configurations, which can be broadly categorized into tubular reactors, embedded cooling tube (ECT) reactors, and helical coiled tube reactors.

2.3.1 Tubular reactors

Tubular reactors represent one of the simplest designs among the various configurations reported. In these reactors, the MH alloy is housed within a cylindrical structure, where hydrogen is introduced axially via a central tubular filter or a disc filter positioned at the end. The reactor wall thickness, determined by the reactor diameter, is designed to withstand the targeted delivery pressure.

The use of tubular reactors in MHHC applications dates back to the first demonstration of such systems. Wiswall and Reilly, (1970) utilized a tubular reactor to store and compress hydrogen using TiFe alloy, achieving pressures of 257 bar and temperatures of 137 °C. Since then, numerous researchers (Barale et al., 2023; Da Silva, 1993; Wang et al., 2007) have adopted this configuration for hydrogen compression, with delivery pressures reaching up to 450 bar. This design is favoured for its minimal number of joints and ease of fabrication. Hu et al. (Hu et al., 2012) employed seven tubular reactors, arranged in a circular pattern, to compress hydrogen to 350 bar, thereby increasing storage capacity. Reactor diameters are typically kept lower to minimise the effective bed thickness. However, to increase the internal diameter of these reactors for accommodating more alloy and reducing the number of units in large-scale operations, advanced heat transfer augmentation techniques must be employed. These include including cooling jackets (Bogdanović et al., 1995; Malleswararao et al., 2022; Muthukumar et al., 2005), exterior fins (Lee et al., 1996), internal fins of various designs (Bai et al., 2021; Garrison et al., 2012; Prasad and Muthukumar, 2021), and additions like metal foams (Laurencelle and Goyette, 2007; Mellouli et al., 2009c), graphite flakes (Chaise et al., 2009; Sánchez et al., 2003), metal wires (Nagel et al., 1986), etc. based on simplicity in integration, ease of production, and thermo-hydraulic performance (Costamagna et al., 2022; Malleswararao et al., 2022; Urunkar and Patil, 2021). Incorporating a metal wire matrix (Nagel et al., 1986), adding metal flakes (Singh et al., 2017a) and expanded natural graphite (ENGs) (Chaise et al., 2009) are other techniques to augment the effective thermal conductivity of the tubular reactor bed.

2.3.2 Embedded cooling tube (ECT) reactors

Embedded cooling tube reactors incorporate multiple coolant channels within a cylindrical space that houses MH alloy and sintered filters. These embedded channels facilitate improved

heat transfer, accelerating reaction kinetics by efficiently removing the heat generated during hydrogen sorption reaction. These reactors have mostly been utilised for fuel cell applications (Jana et al., 2022a; Raju et al., 2022), hydrogen storage (Raju et al., 2019), heating and cooling (Anbarasu et al., 2014; Jana et al., 2022b, 2022a; Kumar et al., 2021), as well as hydrogen purification (Kumar and Muthukumar, 2022). This is primarily due to the lower operating pressures typically observed in such MH thermal machines. In order to further enhance heat dissipation, researchers (Singh et al., 2017b, 2017a) have incorporated multiple U-tubes instead of straight tubes to extend the cooling fluid route within the alloy bed. Researchers have further enhanced the performance of these reactors by incorporating fins of various configurations on the embedded cooling tubes (Gkanas et al., 2016). However, ECT reactors typically have larger diameters, necessitating thicker walls to withstand high pressures. This results in increased thermal parasitic mass, which lowers the overall efficiency of the system. Consequently, no MHHC system targeting high pressure to date has adopted ECT as a viable reactor configuration.

2.3.3 Helical coiled tube reactors

In helical coiled tube reactors, a helical coolant tube is embedded within the MH bed, replacing the straight tubes used in ECT reactors. This configuration demonstrates superior thermal performance due to the increased heat transfer area and the phenomenon of secondary circulation (Eisapour et al., 2021; Raju and Kumar, 2012). Visaria and Mudawar, (2012) explored the use of helical coiled tubes in high-pressure metal hydride reactors, showing that the helical coil configuration occupied only 7% of the pressure vessel volume, compared to 29% occupied by finned tube reactors, while also providing better storage efficiency. Few studies have employed helical tube reactors for MHHC applications (Chalkiadakis et al., 2022; Karagiorgis et al., 2017b), with maximum pressures reaching around 220 bar at 80 °C. The utilization of this reactor configuration for achieving delivery pressures exceeding 250 bar has not yet been reported.

For high-pressure MHHC applications, tubular reactors remain the most widely adopted due to their ability to withstand high pressures with relatively thin walls. While ECT and helical coiled reactors have demonstrated strong potential in hydrogen storage systems, their larger diameter requirements and increased thermal mass make them less ideal for applications demanding pressures above 200 bar.

2.4 Mathematical formulations on MH hydrogen systems

Preliminary research on metal hydride (MH) systems dates back to the 1970s (Diaz et al., 1979; Van Mal et al., 1974; Wiswall and Reilly, 1970), with the first notable advancement in mathematical modelling emerging in the 1980s, when El Obery, (1983) developed a foundational one-dimensional model. This model focused exclusively on cylindrical bed geometries and incorporated several simplifying assumptions, such as considering temperature variation to be solely radial and neglecting the influence of hydrogen flow. The model was a basic conductive framework, solved through a non-dimensional approach using a finite-difference method. Similarly, Lucas and Richards, (1984) developed a one-dimensional mathematical model to examine radial temperature variations in a magnesium-hydride bed enclosed in an aluminium shell, incorporating the effects of hydrogen flow. However, the predicted reaction rates exhibited significant deviations from experimental measurements, indicating the limitations of the model in accurately capturing the intricate dynamics of hydrogen-metal interactions and heat transfer processes within the porous MH bed. Sun and Deng, (1989) developed a more advanced model by considering the coupled heat and mass transfer in two dimensions. However, the model excluded the inertial term in the energy conservation equation, effectively neglecting the influence of hydrogen flow dynamics within the porous bed. Additionally, the model assumed boundary conditions such as constant temperature and heat flux, which are often unrealistic under actual operating conditions, thereby limiting its applicability to real-world scenarios.

Aside from model development, one of the most important fundamental contributions was the recognition that the kinetics of hydrogen uptake in a powdered bed is dominated by heat flow rather than the intrinsic rate kinetics of the metal-hydrogen reaction, because the effective thermal conductivity is much lower than that of the metal itself (Goodell and Rudman, 1983; Pons and Dantzer, 1991).

The works by Jemni and Nasrallah (1995-1997) (Ben Nasrallah and Jemni, 1997; Jemni et al., 1999; Jemni and Nasrallah, 1995a) explored various two-dimensional mathematical models for a cylindrical MH reactor containing LaNi_5 during absorption and desorption. These models made significant advances toward generalising solutions across different geometries and analytical challenges related to MH systems. Notably, the hydrogen momentum equation was addressed using Darcy's Law, and the models considered the non-thermodynamic equilibrium between the solid bed and the entrapped hydrogen gas. Sensitivity analyses were conducted on key parameters, including reactor geometry, inlet and outlet pressure, heat-transfer fluid

temperature, and thermal conductivity, to evaluate their impact on the thermal response of the bed. The studies revealed that the assumption of one-dimensional heat transfer is only applicable at extreme h/R ratio (either very low or very high) where h represents reactor height and R is reactor radius. For intermediate aspect ratios, two-dimensional effects become significant and should not be ignored. However, these models had several limitations: they neglected bed expansion and contraction, assumed constant thermal conductivity and permeability, and relied on a constant-heat flux boundary condition during the sorption process. Despite these drawbacks, these foundational studies paved the way for more advanced models, establishing a critical baseline for future research in MH reactor modelling.

During the 2000s, researchers increasingly focused on utilising mathematical models to design MH reactors with various geometries, aiming to develop thermally effective systems. Mellouli et al., (2010, 2009a, 2009b) demonstrated the mathematical modelling of MH storage tanks by comparing configurations with finned and un-finned spiral tube heat exchangers. Their model, solved using the finite-volume method, was based on the control domain concept previously introduced by Jemni and Nasrallah, (1995a). The primary focus was on optimising charging and discharging times by analysing the influence of geometric parameters. However, the model did not account for volume expansion within the alloy bed or the dynamic effects of heat transfer fluid flow, relying instead on an empirical formula for a constant heat transfer coefficient at the solid-fluid interface. Similarly, Muthukumar et al., (2012b, 2007) and Muthukumar and Ramana, (2009) developed both two-dimensional and three-dimensional models using COMSOL Multiphysics to study reactors ranging from prototype to industrial scale. These models also neglected the effects of volume change in the alloy bed. However, the study incorporated an unique expression for equilibrium pressure, developed by Nishizaki et al., (1983), which accounted for the inherent bed hysteresis and sloping plateau characteristics of the alloy, the factors that had been previously overlooked. The study primarily examined the impact of increasing the number of embedded coolant tubes within the porous bed, in addition to varying operating parameters such as supply pressure and heating and cooling fluid temperature. Despite these advances, the omission of volume change effects remains a critical gap in accurately modelling the thermal and mass transfer dynamics in MH systems. Meanwhile, the models developed by Hardy and Anton, (2009a, 2009b) bypassed the impact of hysteresis and concentration variation on the equilibrium pressure by relying on the ideal van't Hoff equation (Eq. 1.14). Such models, despite their simplifications, are valuable tools for analysing various reactor geometries and fin configurations. Subsequent studies (Bao et al.,

2013; Bhourri et al., 2011; Krishna et al., 2022; Nyamsi et al., 2012) have employed these models to evaluate and identify optimal geometrical configurations.

However, when assessing the effectiveness of MH reactors in real-world applications such as charging from an electrolyser or supplying a fuel cell (FC) at a constant rate, these models often fall short in providing accurate predictions. This discrepancy arises primarily from the boundary conditions assumed at the hydrogen inlet and outlet. Most models assume constant injection and discharge pressures, whereas real systems typically operate under flow control. This represents a significant research gap that has been addressed by only a limited number of studies. Raju and Kumar, (2011) developed a zeroth-order (only temporal) model to examine the refuelling dynamics of an MH tank during fuel cell operation. Mohammadshahi et al., (2016a, 2016b) went further by creating a two-dimensional computational model using COMSOL Multiphysics. This model accounted for flow rate-controlled filling, simulating electrolyser injection by a Heaviside function, and discharging at a set flow rate unlike prior models that assumed constant pressure desorption. The study also incorporated volume changes during reactions.

Practical thermal machines employing MH, such as compressors, thermal energy storage systems, heat pumps and refrigeration units operate using pairs of interconnected reactor beds for hydrogen exchange. The dynamics of hydrogen transport in these systems extends beyond the thermal and chemical behaviour of individual reactors, relying on the coupled interaction between pairs of reactors. Despite numerous advances, current mathematical models still fail to capture fully the complexities of the processes involved in hydrogen transport and thermal management in coupled MH systems. For instance, d'Entremont et al., (2017) developed a 2-D hydrogen transport model to simulate a high-temperature thermal energy storage module using Mg_2Fe and Na_3Al , operating at 400–450 °C. Although this model aimed to assess the technical feasibility of such coupling, it overlooked critical factors like hysteresis and plateau slope, which significantly influence the coupling process (Gray, 2021). Malleswararao et al., (2020) made efforts to improve upon these shortcomings, yet their 2-D model still neglected volume change and assumed constant permeability when simulating dynamically coupled thermal energy storage systems. Similarly, Minko et al., (2018) studied a dual-stage MH hydrogen compressor using simplified one-dimensional mass and energy balance equations that disregarded volume change. In another case, the dual-stage compressor model by Gkanas et al., (2021) adopted a constant heat flux boundary condition to simplify the conjugative heat transfer problem. Some of the other similar studies are (Askri et al., 2024; Bhogilla, 2021).

To summarise, there is an urgent need for a comprehensive spatio-temporal mathematical model that addresses shortcomings in existing models by incorporating factors such as volume-change effects, variations in bed permeability due to changes in alloy particle diameter during sorption, pressure hysteresis, sloping plateaux, and fluctuations in coolant flow rate. Moreover, this model should be adaptable to various reactor geometries without requiring significant modifications to the governing equations. Such a model would significantly enhance the predictive accuracy and design efficiency of MH systems in real-world applications

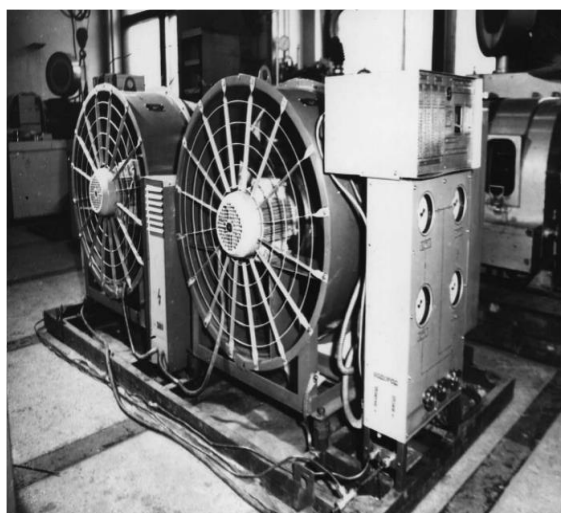
2.5 Experimental studies and granted patents

In the year 1970, Wiswall and Reilly, (1970) were the first to develop a single stage MHHC. To store and compress hydrogen, TiFe (made from 68% Ti and 32% Fe) was used. It was discovered that it could store hydrogen upto 2 wt% at 20°C and 27.57 bar. 57 g of powdered TiFe could pressurize hydrogen up to 257 bar at 137 °C. In addition, it was asserted that hydrogen could be compressed to 690 bar at 200 °C. Additionally, Reilly et al., (1971) demonstrated a lab scale gas pump which could pump any gas at a pressure up to 17 bar employing Vanadium hydride (VH₂).

Subsequently, Nomura et al., (1979) developed a lab scale prototype of piston engine using 700 g of LaNi₅ to obtain a pressure of 20 bar at 80 °C. Water was utilized as the thermal fluid in the temperature range of 20 °C and 80 °C. The setup also produced 28 W of mechanical work with a thermal efficiency of 7.7%, compared to a theoretical prediction of 15.5%. La-Ni based alloys have predominantly been utilised to obtain pressure under 200 bar at a maximum temperature limit of 150 °C (Pearson et al., 2007; Yartys et al., 2016). Other studies that focused on improving system efficiency and identifying the critical variables influencing system performances are (Da Silva, 1993; Muthukumar et al., 2005; Nomura et al., 1983; Northrup and Heckes, 1980). A single stage hydrogen compressor using MnNi_{4.6}Al_{0.4} as alloy was explored by Muthukumar et al., (2005) that successfully compressed hydrogen from 5.5 bar to 43.8 bar at 95 °C with an efficiency of 7.3%.

Multi-stage MHHC are employed to obtain a delivery pressure in excess of 200 bar. Hence, researchers like Shmal'ko et al., (1999b) demonstrated a 2-stage compressor to deliver hydrogen at a pressure of 150 bar. LaNi_{4.5}Mn_{0.5} and LaNi₅ was used as alloy in first and second stage respectively. Electric heaters were used to provide endothermic heat up to 250 °C. The compressor could fill up 6 parallelly joined gas cylinders with a capacity of 40 l each in less than 210 minutes. The authors (Shmal'ko et al., 1999a) further added an additional cryogenic compressor to obtain pressure over 4000 bar. Few other studies on dual stage MHHC system

are reported elsewhere (Hossain et al., 2011; Cieslik et al., 2009; Hossain et al., 2014; Hu et al., 2012; Lototskyy et al., 2012; Odysseos et al., 2013; Sekhar and Muthukumar, 2015; Tarasov et al., 2020). The key findings have been highlighted in Table 2.3. Fig. 2.4 illustrates large scale MHHC developed worldwide in last decades.



(a)



(b)



(c)



(d)

Fig. 2.4: Pictorial view of MHHC (a) KM-1510 developed at Lviv Chemical plant, Ukraine (Shmal'ko et al., 1999b) (b) TSC2-3.5/150 developed at SKTBE and IPCP, Moscow (Tarasov et al., 2020) (c) prototype developed at UWC, South Africa (Lototskyy et al., 2012) (d) developed at HYSTORE, South Africa (Karagiorgis et al., 2017b)

By employing over stoichiometric Ti in TiFe, Wang et al., (2006a) developed a single stage hydrogen compressor to elevate hydrogen from 20 bar to 450 bar with heat addition supplying

oil at 230 °C. It was discovered that doping of 5 wt% of La in $\text{Ti}_{1.1}\text{Fe}$ increased the storage capacity to 1.96 wt%. Further, a two-stage hydrogen compressor was developed using $\text{Ml}_{0.55}\text{Mm}_{0.2}\text{Ca}_{0.25}\text{Ni}_5$ and $(\text{Ti}_{0.97}\text{Zr}_{0.03})_{1.1}\text{Cr}_{1.6}\text{Mn}_{0.4}$ by Wang et al., (2006b). The study reported a delivery pressure of 450 bar at just 99 °C. The same research group also synthesised other high-pressure alloys (Wang et al., 2011; X. Wang et al., 2007; X. H. Wang et al., 2007) and built lab scale MHHC systems. Li et al., (2010) constructed a two-stage MHHC that coupled 18 kg of $\text{La}_{0.35}\text{Ce}_{0.45}\text{Ca}_{0.2}\text{Ni}_{4.95}\text{Al}_{0.05}$ (1.35 wt%) and 9 kg of $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{Cr}_{0.95}\text{Fe}_{0.95}\text{V}_{0.1}$ (1.72 wt%) in first stage and second stage respectively. The compressor was able to compress hydrogen to a pressure of 700 bar at 150 °C with a compression rate of 34.6 l/min lasted for more than 60 min. Similar work was carried out by Wang et al., (2011) that reported a thermal efficiency of 12.5 %.

When it comes to three-stage MHHC system, Vanhanen et al., (1999) demonstrated an integrated three-stage hydrogen compressor along with heat pump. The MH materials chosen for this operation were Hydralloy C₂, Hydralloy C₀ and $\text{TiCrMn}_{0.55}\text{Fe}_{0.3}\text{V}_{0.15}$. The first two stage could compress hydrogen from 18 bar to 110 bar within a temperature range of 20-65 °C. Adding the third alloy ($\text{TiCrMn}_{0.55}\text{Fe}_{0.3}\text{V}_{0.1}$), the hydrogen could be compressed to 200 bar at 80 °C. Other prominent studies pertaining to three stage MHHC at varied pressure ranges are reported in Ref. (Galvis et al., 2020, 2018; Laurencelle et al., 2006b; Popeneciu et al., 2009). The researchers at HYSTORE have examined several MHHC systems that were eventually commercialised. In a lab size prototype of a two stage MH compressor, Lototsky et al., (2009) employed the alloys La-Ce-Ni for the first stage and Ti-Zr-Mn-Fe-Cr-Ni for the second stage to compress hydrogen from 10 bar to 230 bar in stages below 150 °C. A 10-minute cycle time was observed, with a productivity of 60 L/h. Even patents were filed by the author for the built system. It can be found in Ref. (Lototsky et al., (2016, 2012)). Further, to utilise waste heat available below 100 °C, a six-stage metal hydride compressor was constructed that pressurised hydrogen from 7 bar to 200 bar in the operating temperatures of 10 °C and 80 °C obtaining a specific productivity of 67.2 kg/hr (Karagiorgis et al., 2017b). La-Ce-Ni based AB₅ type alloy was used in the first stage while Zr-Ti-Mn-Co-Cr-Fe-V based AB₂ type was used in subsequent stages. Spiral copper tubes were used to enhance the heat transfer inside the bed. Reactor with internal helical tube was even used by Chalkiadakis et al., (2022) in a six stage MHHC.

Studies using alloys based on vanadium hydride for hydrogen compression are quite rare. One of the them was reported recently by Goshome et al., (2021). A single stage metal hydride hydrogen compressor employing $\text{V}_{40}\text{Ti Cr}$ based MH alloy was demonstrated that achieved a

pressure of 100 bar at 160 °C. The compression rate was found to be 0.23 Nm³/h in the operating temperature range between 10 °C and 160 °C. According to the findings, even BCC alloy has the potential to be an MH compressor alloy.

Patents

Ovshinsky et al., (2003) filed a patent regarding developing an integrated hydrogen storage and compression solution. TiMn₂ based AB₂ alloy was used to store and compress hydrogen. In accordance to International Patent Number: WO 2014/126455 (Mahidzal and Loh, 2014) , the inventors revealed a three stage MHHC operated with water as HTF. Additionally, efficient water bath system design to improve the performance of the hydrogen compressor was also discussed. More recently, European Patent no: EP3722653A1 by Noris and Andreas, (2020) reported a combined hydrogen storage-compression unit that is capable of filling high pressure (350 bar) hydrogen vessels. Despite the fact that the alloy was kept a secret, it was stated that the delivery pressure was around 350 bar based on the desorption pressure at 260 °C. Several similar works have also been demonstrated (Chaise, 2018; Noris and Zuttel, 2019; Yartys et al., 2017).



Table 2.3: Details of the experimental investigations along with the key findings pertaining to MHHC

Author (Year)	Stage	MH alloys used	T _L - T _H (°C)	P _L - P _H (bar)	CR	Key findings
Wiswall and Reilly, (1970)	1	S1: TiFe	20-137	27.57-257	9.32	57 g of TiFe was used to compress hydrogen up to 257 bar at 137 °C
Reilly et al., (1971)	1	S1: VH ₂	18-50	7-24	3.42	- Lab scale gas pump was demonstrated that could pump any gas up to 17 bar. - Gas circulation rate of 50 ml/min was reported.
Nomura et al., (1979)	1	S1:LaNi ₅	20-80	2.5-20	8	- Hydrogen was pumped to 20 bar at 80 °C using 700 g of alloy to activate piston engine. 28 W of mechanical work was obtained.
Northrup and Heckes, (1980)	1	S1:LaNi _{4.63} Al _{0.37}	23-68	1.2-3.3	2.75	1.5 kg alloy was employed to pump water to 3.34 bar. 2.4% efficiency was achieved in comparison to theoretical thermal efficiency of 6.8%. - Influence of heat transfer coefficient on hydrogen flow rate was investigated.
Nomura et al., (1983)	1	S1:LaNi ₅	27-90	3-18	6	Reactor showed an excellent heat transfer coefficient of 300-1200 kcal/m²h⁻¹°C and maximum

						hydrogen flow rate of 360 l/min was encountered for 3 min.
Au and Wang, (1993)	1	S1:Mm _{1-x} Ca _x Ni ₅ Al _{5-y}	20-95	16-100	6.25	• Single stage MHHC was developed to compress hydrogen to be used in semiconductor factory.
Da Silva, (1993)	1	S1: TiFe+2 wt% Mn	20-250	10-100	10	• Electrical heater was used as heat source. • Efficiency of compression is directly proportional to compression rate.
Shmal'ko et al., (1999b)	2	S1:LaNi _{4.5} Mn _{0.5} S2:LaNi ₅	25-250	3-150	50	• Double stage compression was achieved to deliver hydrogen up to 150 bar. • Six 40 l gas cylinders were filled in 210 minutes. • MHHC and cryogenic compressor were combined to form hybrid hydrogen compressor.
Shmal'ko et al., (1999a)	1	S1:MmNi ₅	15-327	15-400	26.6	• 1.6 kg of MmNi₅ was employed to compress hydrogen up to 400 bar.
Vanhanen et al., (1999)	3	S1: Hydralloy C2 S2: Hydralloy C0	20-60	12-200	11.1	• Three stage MHHC was developed to uptake hydrogen to a pressure of 200 bar at 80 °C.

		TiCrMn _{0.55}				
		Fe _{0.3} V _{0.15}				
Golubkov et al., (2001)	1	S1: VHx	20-527	100-5000	50	• Effect of hydrogen isotopes at 5000 bar were generated from hydrogen desorbed from MHHC. • Pressure ratio of about 8.8 was attained achieving an isentropic efficiency of 7.3%.
Muthukumar et al., (2005)	1	S1:MmNi _{4.6} Al _{0.4}	20-95	5-43.8	8.76	• Decrease in supply pressure and increase in heat source temperature boosted the performance of the compressor.
Laurencelle et al., (2006b)	3	S1:LaNi _{4.8} Sn _{0.2} S2:LmNi _{4.9} Sn _{0.1} S3:MmNi _{4.7} Al _{0.3}	20-80	1-20	20	• Three AB₅ type alloys were used to set up a multi-stage hydrogen compressor. • Compression rate of 20 lph was reported along with an isentropic efficiency of 5%. • Integrated with an electrolyser.
Wang et al., (2006a)	1	S1:Ti _{1.1} Fe+5wt%La	20-230	20-450	22.5	• Ti was used above its stoichiometric quantity in TiFe along with minor doping of 5 wt% La obtaining a storage capacity of 1.96 wt%. • Activation behaviour of TiFe improved remarkably.

Wang et al., (2006b)	2	S1:Ml _{0.55} M m _{0.2} Ca _{0.25} Ni	20-99	20-450	22.5	- Hydrogen at 450 bar was obtained when La-rich Misch metal was coupled with TiCr₂ based alloy. - Temperature range was fixed below 100 °C to use water as HTF. - Isentropic efficiency of 18.6% was obtained. - Ca was added with La-Ce-Ni based alloy to develop a potential MHHC alloy.
		S2:(Ti _{0.97} Zr _{0.03}) _{1.1} Cr _{1.6} Mn _{0.4}				
Wang et al., (2007)	1	S1:La _{0.4} Ce _{0.4} Ca _{0.2} Ni ₅	25-98	19-120	6.31	- An equation was deduced to evaluate hydrogen dissociation pressure corresponding to the composition of La-Ce-Ca-Ni. 99.9999% purity hydrogen was claimed to have obtained at the outlet of the compressor.
Pearson et al., (2007)	1	S1:LaNi _{4.78} Sn _{0.22}	-3-177	3-48	16	- The sorption compressor pressurises hydrogen above 48 bar by supplying Joule heating at 177 °C - In order to harness the advantage of MmNi₅, substitutions were added at Mm site.
Wang et al., (2007)	2	S1:Mm _{0.2} Ca _{0.2} La _{0.6} Ni ₅ S2:Ti _{1.1} Cr _{1.5} Mn _{0.4} V _{0.1}	20-99	12.5-450	36	- Single stage and multi stage MHHC were developed to compress hydrogen to varied pressure. - Oil was used as HTF in double stage compressor to operate at temperature up to 170 °C.

Cieslik et al., (2009)	2	S1:LaNi _{4.25} Al _{0.25} S2:LaNi _{4.8} S n _{0.2}	39-174	16.5-33	2	• Compression rate of 20 l/min was obtained in double stage MHHC while 40 l/min in a single stage. • Lab-scale prototype (scale 1:13) of MHHC was used to investigate the performance. • Minimal changes in storage capacity was discovered even after 207 cycles. • Aluminium reactors were used to compress hydrogen within which aluminium foam was press fitted.
Laurencelle et al., (2009)	3	S1:LaNi _{4.8} S n _{0.2} S2:LaNi ₅ S3:MmNi _{4.7} Al _{0.3}	20-80	0.6- 35.19	58.6	• Maximum hydrogen flow rate reached to about 20 l/min (NTP) without back pressure regulator when compared to consistent discharge of 3.3 l/min with compressor.
Popeneciu et al., (2009)	3	S1:LaNi _{4.85} Al _{0.15} S2:LaNi _{4.9} C u _{0.1} S3:MmNi _{4.0} 5Fe _{0.95}	20-80	2-56	28	• Excellent hydrogen flow rate of 300 l/h was reported for a small hydride quantity of 360 g. • Based on the temperature range, water was used as the heat transfer fluid.
Lototsky et al., (2009)	2	S1: La-Ce-Ni	15-110	7-200	28.6	• Double stage MHHC was developed to obtain hydrogen up to 200 bar at 150 °C.

Li et al., (2010)	2	S2:(Ti,Zr)(Fe,Mn,Cr,Ni) ₂	25-150	19.1-700	36.7	• A cycle time of 10 minutes was reported for compression having 160 g of AB₅ type and 120 g of AB₂ alloy delivering a productivity of 60 L/h. • Large scale double stage MHHC was developed that achieved a compression rate of 34.6 l/min. • Simple tubular reactors were combined to carry alloy up to 18 kg in first stage while 9 kg in the second stage. • Oil was used as HTF as the operating temperature was more than 100 °C. • Double stage MHHC was developed employing two TiCr₂ based AB₂ type alloys in order to achieve pressure above 700 bar. • Assuming specific heat capacity of 0.5 kJ/kg.K, an efficiency of 12.5% was obtained. Additionally, oil was used as the medium for heat transfer. • Three AB₅ type alloys were examined based on their compression ratio. Ca_{0.2}Mm_{0.8}Ni₅ showed 56% and 14% higher compression ratio than LaNi₅ and Ca_{0.6}Mm_{0.4}Ni₅, respectively.
		S1:La _{0.35} Ce _{0.45} Ca _{0.2} Ni _{4.9} Al _{0.05}				
Wang et al., (2011)	2	S2:Ti _{0.8} Zr _{0.2} Cr _{0.95} Fe _{0.95} V _{0.1}	25-150	40-700	17.5	
		S1:(Ti _{0.97} Zr _{0.03}) _{1.1} Cr _{1.6} Mn _{0.4}				
Bhuiya Md Mainul Hossain et al., (2011)	2	S2:Ti _{0.8} Zr _{0.2} Cr _{0.95} Fe _{0.95} V _{0.1}	10-125	7-160	22.9	
		S1:LaNi ₅				

Lototskyy et al., (2012)	2	S1:La-Ce-Ni	20-150	10-200	20	- Owing to higher compression performance at higher pressure $\text{Ca}_{0.6}\text{Mm}_{0.4}\text{Ni}_5$ was chosen as second stage and LaNi_5 as first stage in the developed dual stage compressor. - Copper encapsulation was adapted to enhance thermal conductivity. - Average productivity up to $1 \text{ m}^3/\text{h}$ was obtained employing a dual stage compressor. - Efficient heat transfer is a prominent factor in improving the productivity.
		S2:Ti-Zr-Mn-Fe-Cr-Ni				
Hu et al., (2012)	2	S1: $\text{La}_{0.4}\text{Y}_{0.6}\text{Ni}_{4.8}\text{Al}_{0.2}$	20-155	25-375	15	- Over 594 g of each alloy was filled in two stages. - Two LaNi_5 based alloys were investigated for single stage compression system to select for the lower stage in dual stage compressor. Single stage compressor desorbed at the rate of 207.8 ml/g. - Vanadium was chosen for second stage. Ball milling in the presence of catalyst was suggested as a method to handle the activation challenge of Vanadium.
		S2:Vanadium				

M Odysseos et al., (2013)	4	S1:(La,Ce) Ni ₅	20-80	2-42	21	- Ce was doped at the La site of LaNi₅ in varying composition to develop a potential compressor alloy. - Based on desorption pressure and storage capacity, four different alloy starting from LaNi₅ can be coupled to develop a four stage MHHC. - In order to utilise the waste heat available in the range of 20-140 °C, double stage hydrogen compressor was developed.
Sekhar and Muthukumar, (2015)	2	S1:LaNi ₅ S2:La _{0.3} Ce _{0.45} Ca _{0.2} Ni _{4.95} Al _{0.05}	25-140	10-74	7.4	- It was concluded that the increase of supply pressure reduced the isentropic efficiency drastically. - Supply pressure up to 10 bar significantly increase the delivery pressure.
Yartys et al., (2016)	1	S1:La _{0.85} Ce _{0.15} Ni ₅	20-150	35-200	5.7	2.234 kg of alloy were employed to develop a single stage 350 L compressor unit. - Thermal energy from solar thermal collectors was utilised to power six-stages MHHC.
Karagiorgis et al., (2017a)	6	S1:AB ₅ S2-S6:AB ₂	10-80	7-220	31.4	Copper helical tube along with cooling jacket was employed as reactor to carry 6.2 kg of alloy in each stage.

Galvis et al., (2020)	3	S1:Ti _{0.85} Zr _{0.15} Mn _{1.33} V _{0.3}	23-132	2-183	91.5	- Approximately 2121 sl/h of hydrogen was pumped in to the storage cylinder which amounts to about 59.5 l of hydrogen per kg of alloy per hour. - Semi-empirical method was developed to design a three stage MHHC using thermo-physical data collected from literatures. - Three TiMn₂ based alloys were synthesised and characterised so as to integrate to design three stage MHHC. - A medium scale and a large scale MHHC systems were developed and investigated at different operating temperature.
		S2:Ti _{0.9} Zr _{0.1} Mn _{1.2} Cr _{0.6} V _{0.2}				
		S3:Ti _{0.9} Zr _{0.1} Mn _{1.4} Cr _{0.4} V _{0.2}				
Tarasov et al., (2020)	2	S1:LaNi ₅	20-160	3.5-150	42.8	- Productivity of 11-15 Nm³/h was reported for the systems. 23% reduction in storage capacity was observed in LaNi₅ after 18000 cycles due to disproportionation of the alloy. No such phenomenon was found in La-Ce-Ni based alloy.
		S2:La _{0.5} Ce _{0.5} Ni ₅				

Goshome et al., (2021)	1	S1:V ₄₀ TiCr	10-160	10-100	10	• A single stage MHHC was demonstrated employing V₄₀Ti₂₂Cr₃₈ that compressed hydrogen up to 100 bar at 140 °C. • A compression rate of 0.23 Nm³/h was observed for a cycle time of 1 hr. • Total heat requirement of 814 kJ was reported. • Electrolyser supplies hydrogen at 16 bar which is reduced by pressure regulating valve corresponding to the inlet pressure of six-stage MHHC. • Water was used as HTF as the operating temperature range is below 100 °C
Chalkiadakis et al., (2022)	6	NA	NA-100	16-220	13.8	

2.6 Literature closure

On the basis of extensive literature review, it is understood the metal hydride-based hydrogen compressor present promising solution towards hydrogen energy economy. The following conclusions can be made from the presented literature review:

2.6.1 Design of optimized reactors for MHHC applications

Beyond the judicious selection of alloys, reactor design plays a crucial role in the efficient performance of metal hydride-based hydrogen systems. Experimentally identifying key design parameters influencing reactor performance is often constrained by cost and resource limitations, underscoring the importance of mathematical modelling. These models serve as a powerful tool to bridge the gap by providing insights into the complex interplay of thermal, mass, and momentum transfer phenomena in MH systems. A bibliometric analysis reveals that, over the past two decades, studies on reactor design have been primarily focused on metal hydride-based hydrogen storage applications. The analysis was conducted using Scopus (“Scopus,” n.d.), with keywords including *metal hydride*, *reactor design*, *numerical study*, *performance*, *pins*, and *tubes*. The results indicate that 42 publications emerged in the last two decades (2004-2025), yet none have explored or developed a methodology for MH reactors dedicated to compressor applications. Unlike storage applications, MHHC design prioritizes maximizing mechanical strength and minimizing cycle time, making it fundamentally different. The bibliometric analysis is presented in Fig. 2.5.

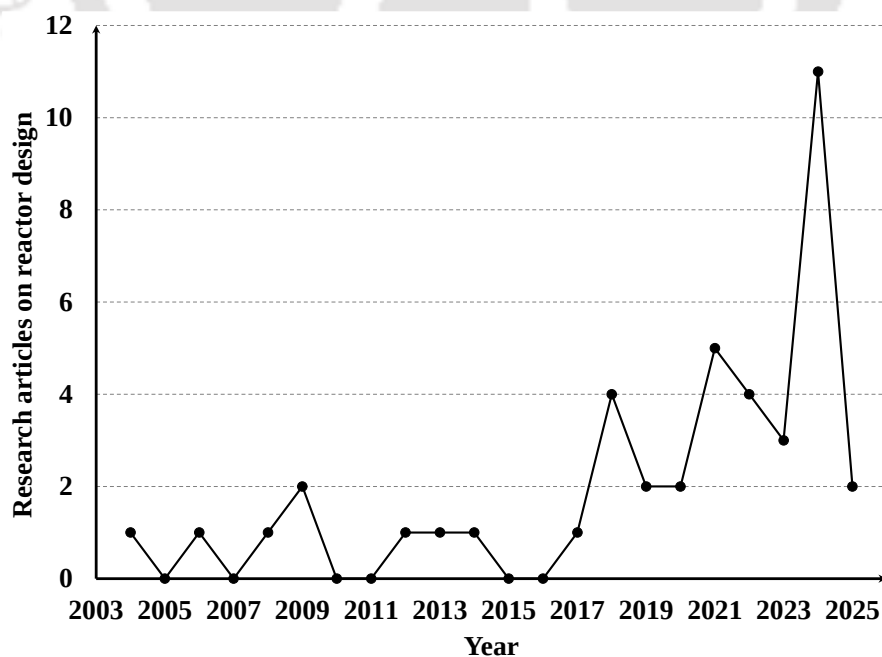


Fig. 2.5 : Research articles published on reactor design in last two decades (“Scopus ”)

2.6.2 Modelling hydrogen dynamics in a coupled reactor system

When modelling a single MH bed, hydrogen absorption or desorption at constant pressure simplifies the determination of pressure gradients. However, in a coupled MH bed system, the pressure gradient becomes complex due to multiple influencing parameters. Fig. 2.6 (a, b) illustrates the hydrogen transfer dynamics between two alloys during coupled MH bed operation. The driving mechanism is the pressure differential, where increasing the desorbing bed temperature and lowering the absorbing bed temperature amplifies the pressure difference ($\Delta P_1 < \Delta P_2 < \Delta P_3$).

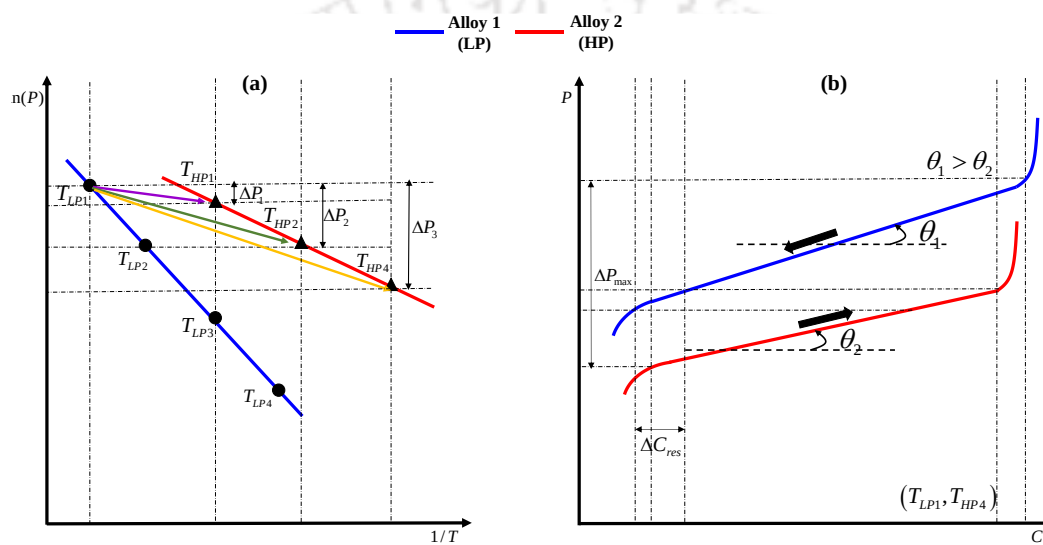


Fig. 2.6 : Schematic representation of operation of coupled reactors in which Alloy 1 (low pressure; LP) desorbs while Alloy 2 (high pressure; HP) absorbs. Panel (a) illustrates the coupling of these two alloy beds, driven by temperature, and the resulting initial pressure difference ($\Delta P_1, \Delta P_2, \Delta P_3$). Panel (b) highlights the complexities encountered when hydrogen mass transfer, linked to changes in H concentration, becomes a function of both bed temperature and concentration.

Additionally, the hydrogen concentration within each MH particle plays a critical role in determining transfer rates. As shown in Fig. 2.6 (b), two alloys with different pressure–concentration–temperature (PCT) characteristics exhibit varying rates of pressure reduction. Alloy 1, with a steeper slope ($\theta_1 > \theta_2$ ($\theta = \Delta P / \Delta C$)), shows a more significant pressure drop during desorption compared to Alloy 2. Although the initial pressure gradient may be favourable (ΔP_{max}) for hydrogen transfer, the rate of pressure change with respect to hydrogen concentration affects the overall transfer rate. Furthermore, scenarios may arise

where the equilibrium pressure of the desorbing bed drops below that of the absorbing bed, halting the transfer process and leaving residual hydrogen in the desorbing bed (ΔC_{res}). Additionally, temperature variations due to the endothermic and exothermic reactions further complicate the behaviour. These factors must be carefully considered when developing mathematical models for coupled MH reactors, which are essential for optimizing hydrogen transfer in various engineering applications.

Practical thermal machines employing metal hydrides (MH), such as compressors, thermal energy storage systems, heat pumps and refrigeration units operate using pairs of interconnected reactor beds for hydrogen exchange. The dynamics of hydrogen transport in these systems extends beyond the thermal and chemical behaviour of individual reactors, relying on the coupled interaction between pairs of reactors. Despite numerous advances, current mathematical models still fail to capture fully the complexities of the processes involved in hydrogen transport and thermal management in coupled MH systems.

2.6.3 Development of multistage MHHC set up

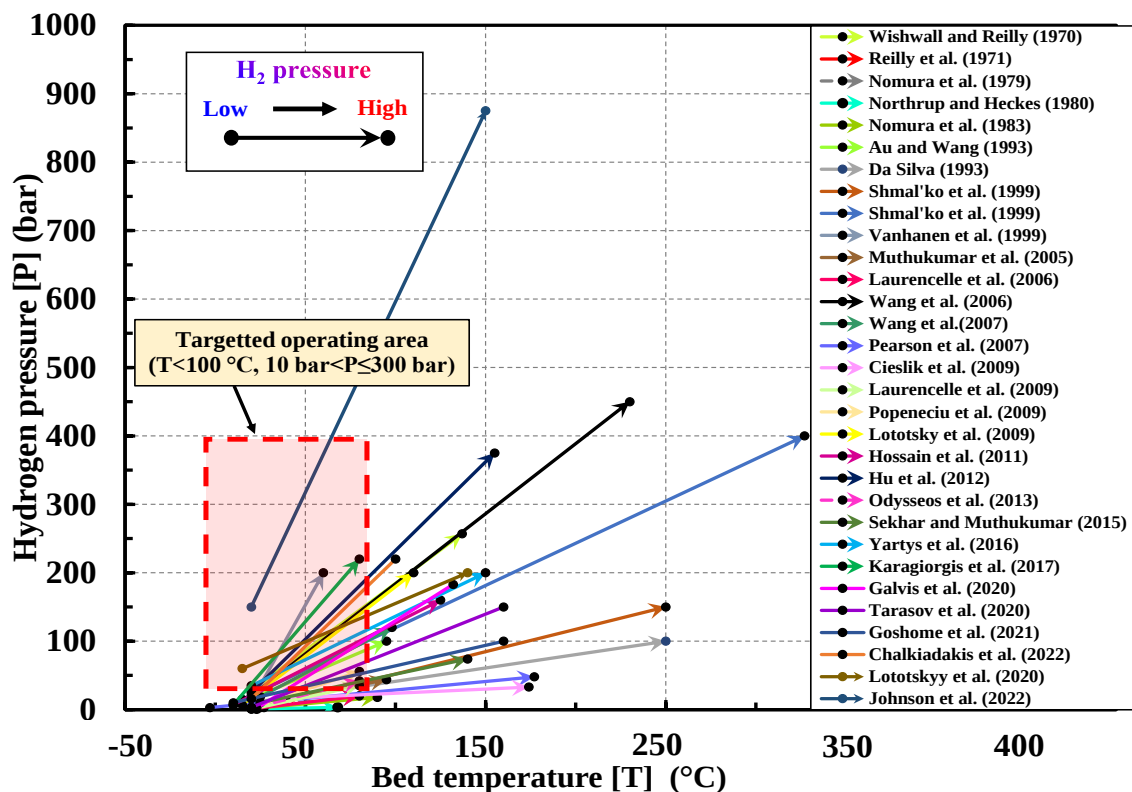


Fig. 2.7 : Identification of research gaps through literature review

Over the past two decades, more than 30 experimental studies have investigated hydrogen compression at various delivery pressures. However, no study has successfully achieved 300

bar compression using low-grade heat ($<100^{\circ}\text{C}$) in three or fewer compression stages. This gap is significant, as it limits the potential of solar thermal energy-driven MHHC systems, which typically operate below 100°C . The research void (highlighted in red in Fig. 2.7) underscores the need to identify key parameters that govern hydrogen transfer dynamics while minimizing energy consumption. Furthermore, an in-depth energy analysis of MHHC systems is largely absent, leaving uncertainties regarding their efficiency and industrial feasibility. Additionally, the real-world implementation of MHHC technology, particularly in hydrogen refuelling stations, remains unexplored, hindering its commercial adoption.

2.7 Objectives of the present work

Considering the insights drawn from the literature, this thesis aims to design and develop an industrial-scale metal hydride-based hydrogen compressor system. Based on the literature closure, the following broad objectives were formulated for this thesis work:

- To develop a comprehensive numerical model of a multi-stage metal hydride hydrogen compressor (MHHC) that accounts for coupled heat and mass transfer, particle volume expansion, and bed deformation to optimize reactor geometry and operating conditions for efficient hydrogen compression.
- To design and fabricate a high-capacity MHHC system capable of compressing over 5000 L of hydrogen per stage from a low-pressure source (10-20 bar) to 300 bar through multistage delivery, ensuring efficient operation in narrow temperature range of $5\text{--}130^{\circ}\text{C}$.
- To experimentally identify the activation behaviour and absorption–desorption kinetics of each stage in the MHHC system for determining the optimal operating pressure and temperature ranges.
- To experimentally assess the performance of the developed system and demonstrate its applicability in hydrogen refuelling stations for filling Type I storage cylinders.

2.8 Summary

This chapter presents a comprehensive literature review on key aspects of MHHC, including alloy selection and reactor design. It also explores the evolution of mathematical models used to study the thermodynamics and hydrogen transfer dynamics in MH systems. Additionally, the chapter provides an in-depth review of experimental MHHC setups developed over the past decades, along with significant findings reported in literature. Based on this review, prominent research gaps were identified, leading to the formulation of the thesis objectives.

Chapter 3

Design and fabrication of reactors

3.1 Preface

The selection of a suitable alloy and the design of a dedicated reactor are fundamental to the efficient development of an MHHC system. Alloy selection is primarily dictated by operating temperature constraints, which are determined by the available heat source, whereas reactor design is governed by maximum design pressure requirements and the need for effective heat transfer to optimize hydrogen absorption and desorption kinetics. For reactor selection, key considerations include maximum operating pressure, temperature range, and hydrogen transfer rate, ensuring optimal mechanical integrity and efficient heat transfer. The first half of this chapter focuses on the reactor design for both high-pressure and low-to-medium-pressure applications, incorporating Finite Element Analysis (FEA) simulations, followed by the fabrication of the proposed reactor. Based on the comprehensive literature review presented in the previous chapter, AB₅ and AB₂-type alloys were selected for hydrogen compression. The choice of these alloys was driven by hydrogen storage capacity, equilibrium pressure at a predefined temperature, and critical material properties, including hysteresis and plateau slope characteristics. The second half of this chapter focuses on the alloy selection process, followed by post-procurement processing and preliminary characterization of the selected alloy.

3.2 Mathematical formulation of MH hydrogen systems

In a metal hydride (MH) system, hydrogen is introduced into a porous alloy bed housed within a metal reactor, which is equipped with heat augmentation mechanisms to facilitate thermal management. The process involves three primary transport phenomena:

- Mass transfer: Governing the diffusion and transport of hydrogen into and out of the MH bed.
- Chemical reaction: Representing the reversible hydrogen absorption/desorption kinetics at the metal interface.
- Heat transfer: Accounting for the exothermic/endothermic reaction heat generated during hydrogen-alloy interactions, as well as heat dissipation via an external heat transfer fluid (HTF).

A numerical model of an MH-based hydrogen storage/compression system must therefore solve intercoupled mass transport, reaction kinetics, and thermal transport equations to accurately capture system behaviour.

In a single MH reactor simulation, only one hydride bed interacts with hydrogen, whereas a coupled MH reactor system (a common configuration in multistage MHHC systems) involves two reactors dynamically exchanging hydrogen. The complex hydrogen transfer and thermal interactions in such systems necessitate an advanced finite element analysis (FEA) model. The governing equations remain identical for both cases; however, the key distinction lies in the hydrogen transfer mechanism. In a coupled MH reactor system, hydrogen is dynamically transported from the desorbing reactor (high-pressure side) to the absorbing reactor (low-pressure side), with the pressure difference gradually decreasing in both directions over time. In contrast, in a single MH reactor operation, hydrogen interacts with the porous bed at a constant pressure, leading to a unidirectional reduction in pressure difference, thereby requiring only a single system configuration. Consequently, a comprehensive coupled-reactor model can be simplified to a single-reactor model with appropriate modifications to boundary conditions. The governing equations are implemented in their respective domains using built-in physics interfaces and user-defined functions within COMSOL Multiphysics. The mass and momentum conservation for hydrogen gas and the heat transfer fluid (HTF) are modelled using the *Brinkman Equation* and *Laminar Flow* physics modules, respectively. The mass conservation for the solid alloy bed is formulated as an independent *ordinary differential equation*. Energy conservation across all domains is governed by the *Heat Transfer in Fluids* physics module. Additionally, the *Non-Isothermal Flow Multiphysics* interface is utilized to couple laminar flow and heat transfer within the HTF domain. To simplify the model, a few assumptions are made, which is elaborated on below:

- The alloy bed is assumed to possess uniform initial porosity throughout, regardless of location within the bed.
- The alloy bed and hydrogen are assumed to be in a state of local thermal equilibrium.
- Radiative heat transfer is neglected due to the system operating at $<100\text{ }^{\circ}\text{C}$.

3.3 Governing equations

3.3.1 Conservation of mass

The mass conservation equation is solved for hydrogen gas within the porous MH bed (during absorption or desorption), within the hydrogen transfer tubes (in the case of a coupled reactor operation), for the alloy bed to account for hydride formation, and for the heat transfer fluid (HTF) circulating through the coolant channels.

In a coupled MH reactor system, the dynamic exchange of hydrogen between the desorbing and absorbing reactors necessitates the simultaneous solution of mass conservation equations

for both reactors, ensuring an accurate representation of hydrogen transport, pressure evolution, and reaction kinetics. In contrast, in a single reactor system, only one mass conservation equation is required, as hydrogen interacts with the porous MH bed without inter-reactor exchange. The specific governing equations applied to each domain are as follows:

Hydrogen in desorbing MH tank

$$\frac{\partial(\varepsilon\rho_g)}{\partial t} + \nabla \cdot (\rho_g \vec{v}_g) = -\dot{m}_d \quad (3.1)$$

where ρ_g denotes the density of hydrogen gas and ε denotes the bed porosity, indicating the volume fraction of the bed occupied by hydrogen gas. $\vec{v}_g$ denotes the velocity vector for hydrogen gas. $\dot{m}_d$ denotes the mass source term arising from the volumetric desorption of hydrogen from the bed. In summary, the equation characterises the temporal variation in hydrogen density (mass of hydrogen per unit volume within the specified control volume). This change is attributed to the net mass flux, represented by the divergence of the product of density and velocity vector, crossing the control surface, as well as the volumetric mass accumulation within the control volume.

Hydrogen in absorbing MH tank

$$\frac{\partial(\varepsilon\rho_g)}{\partial t} + \nabla \cdot (\rho_g \vec{v}_g) = -\dot{m}_a \quad (3.2)$$

where the absorbing mass source term is denoted as $\dot{m}_a$. Inherently, the mass source term should be negative in the absorbing bed due to the migration of hydrogen mass from the hydrogen control volume into the porous bed. Conversely, it must be positive in the desorbing bed. To maintain uniformity in the governing equation, an additional negative sign is incorporated into both source terms. The flow direction is governed by the pressure difference, which is considered in the definition of the mass source term.

Mass source term during desorption	$\dot{m}_d = (1-\varepsilon)C_d \left(\frac{p - P_{eqd}}{P_{eqd}} \right) e^{\frac{-E_d}{RT}} (\rho_{sd} - \rho_{ed})$	(3.3)
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Mass source term during absorption	$\dot{m}_d = (1-\varepsilon)C_a \log \left(\frac{p}{P_{eqa}} \right) e^{\frac{-E_d}{RT}} (\rho_{sata} - \rho_{sa})$	(3.4)
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Here, C_d , C_a , E_d and E_a represent the first order reaction rate constants and activation energy during desorption and absorption. p denotes the pressure of hydrogen flowing in the entire computational domain. The reaction is driven by the pressure difference between the driving pressure and the equilibrium bed pressure, which is governed by temperature and the instantaneous concentration of hydrogen in the bed. Thermodynamic drive depends on free-energy difference and is thus expected to be proportional to $\log(p/P_{eq})$. Assuming small pressure difference during desorption, this leads to the commonly employed expressions $\log(p/P_{eqa})$ for absorption and $((p - P_{eqd})/P_{eqd})$ for desorption (Chang et al., 2023; Jemni and Nasrallah, 1995b, 1995a; Mellouli et al., 2024). During desorption, the magnitude of p is less than P_{eqd} , making the entire source term negative. Conversely, during absorption, p happens to be more than P_{eqa} , resulting in a positive source term. The transport of hydrogen halts when these differences approach zero. The concentration difference is accounted for by the variation in the density of the porous bed, which results from the addition or removal of hydrogen within the metal alloy. During absorption, the density of the porous bed (ρ_{sa}) increases to approach the saturation density of the absorbing alloy (ρ_{sata}). Conversely, during desorption, the density (ρ_{sd}) decreases to approach the desorbing alloy's density at its empty state (ρ_{ed}). The relationship between the density of the porous bed and the concentration of the solid solution (Ψ) is

$$\Psi = \frac{2(\rho_s - \rho_{ed})M_{alloy}}{\rho_{ed}M_g N_{alloy}} \quad (3.5)$$

where M_{alloy} and M_g denotes the molecular mass of the alloy and hydrogen gas respectively. N_{alloy} indicates the number of hydrogen atoms that can be absorbed or stored by a single metal atom in a hydride compound, which is notionally 6 for an AB₅ alloy. The instantaneous reacted fraction (X) is evaluated by employing

$$X = \frac{(\rho_s - \rho_{ed})}{(\rho_{sata} - \rho_{ed})} = \frac{\Psi}{\Psi_{\max}} \quad (3.6)$$

Hydrogen in interconnecting tube

Hydrogen within the interconnecting domain does not undergo any volumetric mass addition or deduction. Hence, the mass source term is taken as zero:

$$\frac{\partial(\varepsilon\rho_g)}{\partial t} + \nabla \cdot (\rho_g \vec{v}_g) = 0 \quad (3.7)$$

Metal alloy in desorbing MH tank

$$(1-\varepsilon) \frac{\partial \rho_{sd}}{\partial t} = \dot{m}_d \quad (3.8)$$

The absence of the divergence term in the mass balance equation for the solid porous matrix simplifies the equation, reducing it to a single degree, first-order ordinary differential equation.

Metal alloy in absorbing MH tank

$$(1-\varepsilon) \frac{\partial \rho_{sa}}{\partial t} = \dot{m}_a \quad (3.9)$$

The mass source term has the opposite sign in the porous alloy bed domain with respect to hydrogen in the corresponding MH bed.

Heat-transfer fluid

$$\frac{\partial \rho_f}{\partial t} + \nabla \cdot (\rho_f \vec{v}_f) = 0 \quad (3.10)$$

Here, ρ_f and $\vec{v}_f$ denote the density and velocity vector respectively of the HTF. No additional mass accumulation takes place during the flow of HTF resulting in a zero-mass source term.

3.3.2 Conservation of momentum

The velocity vector and pressure fields for the hydrogen gas and HTF are determined by solving the equation for the conservation of momentum. Hydrogen gas migrates through the porous bed and the interconnecting tube (in the case of a coupled reactor operation). In contrast, the HTF flows exclusively through the unrestricted domain. Consequently, distinct governing equations are employed for the porous domain and the fluid domain to accurately capture the different transport phenomena.

Hydrogen in desorbing MH tank

Momentum conservation for hydrogen gas within the porous domain is modelled by using the Brinkmann equation. The first term $\left(\partial \vec{v}_g / \partial t \right)$ on the left-hand side of the resulting equation encompasses the temporal variations of the velocity vector. This term represents the local (or temporal) acceleration of the gas, which is the rate of change of the velocity at a point with time. The convective (or advective) term $\left(\vec{v}_g \cdot \nabla \vec{v}_g \right)$ represents the change in velocity due to the movement of the gas within the velocity field itself. Division by the porosity (ε) accounts for the effective flow area, which is reduced by the presence of the porous matrix. Similarly, the term (ρ_g / ε) normalises the gas density to effectively scale the density based on the available void space. The density of the gas is coupled with the temperature field through the modified ideal gas equation $\rho_g = (pM_g) / (Z(p)RT)$, where $Z(p)$ denotes the compressibility factor of hydrogen, taken to be a function of pressure only in the regime of interest since the effect of temperature is much smaller. Due to the low velocity regime, the convective term can be neglected, simplifying the equation by deleting the second term on the left-hand side.

On the right-hand side, the first term represents the change in pressure per unit distance within the fluid. This term accounts for the driving pressure gradient responsible for the flow of the gas. μ_h denotes the dynamic viscosity of the fluid i.e. hydrogen gas in this case. The Laplacian of the velocity vector

$\left[\nabla \cdot \left[\frac{1}{\varepsilon} \left\{ \mu_h \left(\nabla \vec{v}_g + \left(\nabla \vec{v}_g \right)^T \right) - \frac{2\mu_h}{3} \left(\nabla \cdot \vec{v}_g \right) \right\} \right] \right]$ represents the diffusion

of momentum within the fluid accounting for the viscous effects in the fluid flow. The effect of the porous medium is represented by (μ_h / κ) , where κ is the permeability of the porous bed, depicting how easily the fluid can flow through the pores. This term represents the drag force experienced by hydrogen within the porous medium. It is analogous to Darcy's law, which

describes the flow through a porous medium driven by a pressure gradient. The term $\left(\dot{m}_d / \varepsilon^2 \right)$

scales the mass flow rate by the square of the porosity to account for the viscous drag force due to the flow rate through the effective flow area available within the porous medium. The result is

$$\frac{\rho_g}{\varepsilon} \left(\frac{\partial \vec{v}_g}{\partial t} + \vec{v}_g \cdot \frac{\nabla \vec{v}_g}{\varepsilon} \right) = -\nabla p + \nabla \cdot \left[\frac{1}{\varepsilon} \left\{ \mu_h \left(\nabla \vec{v}_g + \left(\nabla \vec{v}_g \right)^T \right) - \frac{2\mu_h}{3} \left(\nabla \cdot \vec{v}_g \right) \right\} \right] - \left(\frac{\mu_h}{\kappa} + \frac{\dot{m}_d}{\varepsilon^2} \right) \vec{v}_g \quad (3.11)$$

Hydrogen in absorbing MH tank

$$\frac{\rho_g}{\varepsilon} \left(\frac{\partial \vec{v}_g}{\partial t} + \vec{v}_g \cdot \nabla \vec{v}_g \right) = -\nabla p + \nabla \cdot \left[\frac{1}{\varepsilon} \left\{ \mu_h \left(\nabla \vec{v}_g + \left(\nabla \vec{v}_g \right)^T \right) - \frac{2\mu_h}{3} \left(\nabla \cdot \vec{v}_g \right) \right\} \right] - \left(\frac{\mu_h}{\kappa} + \frac{\dot{m}_a}{\varepsilon^2} \right) \vec{v}_g \quad (3.12)$$

Hydrogen in interconnecting tube

In the unrestricted domain, the terms accounting for the viscous drag due to the porous bed are omitted. With the porosity considered as 1, this simplification results in the standard Navier-Stokes equation:

$$\rho_g \left(\frac{\partial \vec{v}_g}{\partial t} + \vec{v}_g \cdot \nabla \vec{v}_g \right) = -\nabla p + \nabla \cdot \left[\mu_h \left(\nabla \vec{v}_g + \left(\nabla \vec{v}_g \right)^T \right) - \frac{2\mu_h}{3} \left(\nabla \cdot \vec{v}_g \right) \right] \quad (3.13)$$

Heat-transfer fluid

Similarly, the velocity field of the heat transferring fluid is also simulated by the Navier-Stokes equation. Here, $\vec{v}_f$, p_f and μ_f denote respectively the velocity vector, pressure and dynamic viscosity of the HTF.

$$\rho_f \left(\frac{\partial \vec{v}_f}{\partial t} + \vec{v}_f \cdot \nabla \vec{v}_f \right) = -\nabla p + \nabla \cdot \left[\mu_f \left(\nabla \vec{v}_f + \left(\nabla \vec{v}_f \right)^T \right) - \frac{2\mu_f}{3} \left(\nabla \cdot \vec{v}_f \right) \right] \quad (3.14)$$

3.3.3 Conservation of energy

The energy balance equation is solved to investigate the thermodynamic variations within the bed due to hydrogen sorption. Additionally, to examine the energy exchange with the HTF and its potential impact on the rate of hydrogen transfer, the fluid dynamics of the HTF are coupled with the energy equation.

Hydrogen and solid porous alloy bed in MH tank

A single governing equation is developed under the assumption of local thermal equilibrium to address the thermodynamics of hydrogen transport within and between the reactors. This equation invokes the bed porosity to simultaneously solve the temperature fields for both hydrogen gas and the porous bed:

$$(\rho c_p)_e \frac{\partial T}{\partial t} + (\rho c_p)_g \left(\vec{v}_g \cdot \nabla T \right) = k_e \nabla^2 T - Q_s \quad (3.15)$$

where $(\rho c_p)_e$ represents the effective heat capacity of the porous bed and hydrogen gas which is determined using Eq. 3.16. The second term $(\rho c_p)_g (\vec{v}_g \cdot \nabla T)$ on left hand side of equation represents the transport of thermal energy due to advection.

k_e in Eq. 3.15 denotes the effective thermal conductivity (discussed further below). The term $k_e \nabla^2 T$ represents the heat diffusion or dissipation due to temperature gradients within the porous bed. Q_s is the volumetric heat generation term, which accounts for the heat energy released or absorbed to drive the chemical reaction forward or backward. It is evaluated using Eq. 3.17, which calculates the product of the volumetric mass flow rate of hydrogen and the enthalpy of formation. The enthalpy of formation is typically negative for this exothermic reaction:

$$(\rho c_p)_e = \varepsilon (\rho c_p)_g + (1 - \varepsilon) (\rho c_p)_s \quad (3.16)$$

$$Q_s = \dot{m}_{a/d} \left(\frac{\Delta H_{a/d}}{M_g} \right) \quad (3.17)$$

Solid components of the reactor (reactor body, coolant tube and fins)

$$\rho_s c_{ps} \frac{\partial T}{\partial t} = k_s \nabla^2 T \quad (3.18)$$

where ρ_s , $c_{p,s}$ and k_s denote respectively the density, heat capacity and thermal conductivity of the solid components of the MH tanks.

Heat-transfer fluid

$$\rho_f c_{pf} \frac{\partial T}{\partial t} + \rho_f c_{pf} (\vec{v}_f \cdot \nabla T) = k_f \nabla^2 T \quad (3.19)$$

where ρ_f , $c_{p,f}$ and k_f denote respectively the density, heat capacity and thermal conductivity of the HTF.

3.3.4 Effective thermal conductivity

The thermal conductivity of the bed varies due to changes in pressure, particle radii, and porosity. The present work employed the Zehner-Bauer-Schlunder (ZBS) model to determine the effective thermal conductivity k_e (Pons and Dantzer, 1991). The ZBS model incorporates a complex expression that includes multiple parameters, capturing the intricate interplay between different factors affecting thermal conductivity:

$$\frac{k_e}{k_g} = \left(1 - \sqrt{1 - \varepsilon}\right) + \frac{2\sqrt{1 - \varepsilon}}{1 - \frac{k_g}{k_s} B} \left[\frac{\left(1 - \frac{k_g}{k_s}\right) B}{\left(1 - \frac{k_g}{k_s} B\right)^2} \log\left(\frac{k_g}{k_s} B\right) - \frac{B+1}{2} - \frac{B-1}{1 - \frac{k_g}{k_s} B} \right] \quad (3.20)$$

where k_g is the instantaneous thermal conductivity of hydrogen gas. B denotes the deformation factor and is considered as 1 assuming the alloy particle to be spherical. The thermal conductivity of hydrogen gas is evaluated by using Eq. 3.21 (Lin et al., 2019):

$$k_g = \frac{k_{g_{ref}}}{1 + \frac{2b\lambda_m}{d_p}} \quad (3.21)$$

where $k_{g_{ref}}$, λ_m and b refer to the thermal conductivity of the gas at reference pressure (1 bar), mean free path of the gas and a dimensionless constant (9.87 for H_2), respectively. The mean free path of the gas is assumed to be given by the classical ideal-gas model:

$$\lambda_m = \frac{K_B T}{\sqrt{2} \pi d_{H_2}^2 p} \quad (3.22)$$

where K_B is the Boltzmann constant and d_{H_2} is the diameter of hydrogen molecule, which is taken as 2.9×10^{-10} m. The equation is coupled with the energy equation for the packed bed to derive the temperature to evaluate mean free path at each time step.

3.3.5 Bed porosity

The bed porosity (ε) is defined as the ratio of the void volume (the volume not occupied by solid alloy particles) to the total volume of the reactor, where 0 represents a fully solid bed and 1 represents a completely open space. It is well established that the porosity changes due to the relative expansion and contraction of the solid alloy particles during the absorption and desorption processes, respectively. A robust formula proposed by Wijayanta et al., (2011) to correlate the instantaneous porosity with the reacted fraction (X) was employed to determine dynamic variation of the bed porosity.

$$\varepsilon = 1 - (1 - \varepsilon_i) [1 + (\xi - 1) X] \quad (3.23)$$

where ε_i and ξ denote initial bed porosity (assumed to be 0.5 in the present case) and expansion coefficient (1.3 for AB_5 type alloy and 1.25 for AB_2), respectively (Lototskyy et al., 2014). The alloy bed consists of irregularly shaped particles in reality that are computationally challenging to model. Therefore, the particles are approximated as regular spheres with a

defined initial diameter, which changes during the sorption process based on the alloy's expansion coefficient. The model dynamically accounts for this variation, partitioning the computational domain into separate regions corresponding to the varying occupied volume within a constant bed volume, as illustrated in Fig. 3.1. This approach reduces the complexity of the heterogeneous domain, treating it as two homogeneous subdomains while capturing the inherent heterogeneities through empirical relations coupled with variables like temperature, alloy density, hydrogen velocity, and mass of absorbed hydrogen.

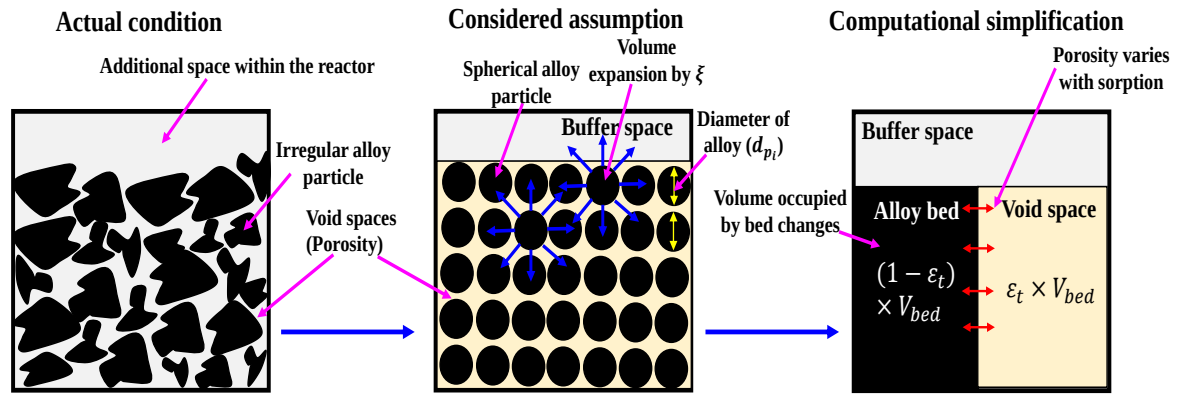


Fig. 3.1: Computational simplification to consider the volume change effects.

3.3.6 Bed permeability

The permeability (κ) of the packed bed is dependent on the particle size and bed porosity. It is determined by Kozeny-Carman's equation:

$$\kappa = \frac{d_p^2 \varepsilon^3}{180(1 - \varepsilon)^2} \quad (3.24)$$

The particles are assumed to be spherical with a diameter d_p , which is assumed to expand or contract according to

$$d_p = d_{p_i} [1 + (\xi - 1) X]^{1/3} \quad (3.25)$$

3.3.7 Equilibrium pressure

The equilibrium pressure within the MH bed during the sorption process is calculated using a modified van't Hoff equation that incorporates pressure hysteresis and plateau slope to provide a more accurate representation of the equilibrium conditions (Nishizaki et al., 1983):

$$\log \left(\frac{P_{eq}(X)}{P_o} \right) = -\frac{|\Delta H|}{RT} + \frac{\Delta S}{R} + (\varphi_s \pm \varphi_o) \tan [\pi \times (X - 0.5)] \pm \frac{\gamma}{2} \quad (3.26)$$

In this context, the positive sign is used during the absorption process, and the negative sign is used during desorption. The fitted parameters φ_s and φ_o account for plateau slope while γ incorporates the effect of hysteresis.

3.4 Initial value

3.4.1 Conservation of mass

The mass conservation equation is formulated with density ($\rho_g(r, z, t)$) as the dependent variable. The initial hydrogen density ($\rho_g(r, z, 0)$) within the porous MH bed is determined based on the initial equilibrium pressure (P_{eqdi} or P_{eqai}) and temperature of the bed.

$$\rho_g(r, z, 0) = \frac{p_i M_g}{Z(p)RT_i} \quad (3.27)$$

For a coupled reactor operation, the initial hydrogen density within the interconnecting tube is assigned a finite pressure (P_{gi}), representing an infinitesimally small amount ($m_d + m_a$) of hydrogen present at the onset of desorption, simulating the initial transfer (m_d) from the desorbing reactor. The mass-averaged temperature (T_{gi}) is considered for accurate representation.

$$\rho_g(r, z, 0) = \frac{P_{gi} M_g}{Z(p)RT_{gi}} \quad (3.28)$$

$$T_{gi} = \frac{m_d T_{di} + m_a T_{ai}}{m_d + m_a} \quad (3.29)$$

$$m_d = \frac{P_{eqdi} V_{MHT} M_g}{Z(p)RT_{di}} \quad (3.30)$$

$$m_a = \frac{P_{eqai} V_{MHT} M_g}{Z(p)RT_{ai}} \quad (3.31)$$

$$P_{gi} = \frac{(m_d + m_a)Z(p)RT_{gi}}{M_g V_{tube}} \quad (3.32)$$

The density of the HTF ($\rho_f(r, z, 0)$) is assumed constant due to its incompressible nature. The initial density of the alloy bed is determined using Eq. 3.5, based on the initial hydrogen concentration (Ψ), which varies from 0 to 1.

3.4.2 Conservation of momentum

The momentum conservation equation is formulated with velocity field and pressure field as the dependent variables. The initial velocity of both hydrogen gas and the HTF is set to zero. While the HTF pressure is maintained at atmospheric pressure, the hydrogen pressure within the MH bed and the interconnecting tube is defined using distinct expressions to accurately represent their respective initial conditions. The initial hydrogen pressure within the MH bed during coupled bed operation is set to (P_{gi}) for a brief period (0.05 s), after which it equilibrates to the driving pressure, defined as the equilibrium pressure (P_{eqdi} or P_{eqai}) corresponding to the initial bed temperature and hydrogen concentration.

$$\text{Desorbing MH bed} \quad p_i = P_{gi} - (S(t) \times (P_{gi} - P_{eqdi})) \quad (3.33)$$

$$\text{Absorbing MH bed} \quad p_i = P_{gi} - (S(t) \times (P_{gi} - P_{eqai})) \quad (3.34)$$

where ($S(t)$) is a step function that returns 0 if $t < 0.05$ s and 1 if $t \geq 0.05$ s. For a single-reactor system, the bed is initially set at its equilibrium pressure (P_{eqdi} or P_{eqai}), which subsequently transitions to the driving pressure; either the supply pressure during absorption (P_s) or the desorption pressure (P_d) during desorption. The expression pans out to:

$$p_i = P_{eqdi/eqai} - (S(t) \times (P_{eqdi/eqai} - P_{d/s})) \quad (3.35)$$

3.4.3 Conservation of energy

The initial temperature of the MH bed, hydrogen gas, and HTF is set to the specified initial bed temperature, as defined by the simulation requirements.

$$T(r, z, 0) = T_{ai/di} \quad (3.36)$$

3.5 Boundary conditions

3.5.1 Conservation of mass and momentum

The mass and momentum conservation equations for hydrogen gas within the MH bed and interconnecting tube are solved using a single physics interface, with the no-slip condition imposed as a key boundary condition.

$$\vec{v}_{g_{r_{\text{solidsurface}}}} = 0 \quad (3.37)$$

For a single-reactor system, a constant pressure is applied as the boundary condition.

$$T(r, z, 0) = T_{ai/di} \quad (3.38)$$

The HTF flow is governed by a velocity inlet boundary condition at the inlet and an atmospheric pressure boundary condition at the outlet ($p_{f\text{ outlet}} = 0$). No slip boundary condition is also imposed at HTF-HTF interface.

$$\vec{v}_{f\text{ inlet}} = \frac{\dot{m}_f}{A_{\text{inlet}}} \quad (3.39)$$

3.5.2 Conservation of energy

Heat flux continuity is imposed as the primary boundary condition at the MH bed-HTF interface and the MH bed-fin interface (if present). The outer reactor walls are treated as

$$\text{adiabatic} \left(\frac{\partial T}{\partial n} = 0 \right).$$

$$-k_e \nabla T|_{MH} = -k_{HEX} \nabla T|_{HEX} \quad (3.40)$$

Since hydrogen gas and the MH bed are assumed to be in local thermal equilibrium, separate boundary conditions for hydrogen are not required. A temperature boundary condition is applied at the HTF inlet to define the thermal state of the incoming fluid.

$$T_{\text{inlet}} = T_{\text{ai/di}} \quad (3.41)$$

3.6 Solution methodology

Both the single reactor operation and coupled reactor operation are modelled in COMSOL Multiphysics 6.1. Both the models employ a segregated approach under a time-dependent solver to manage the numerical integration of partial differential equations (PDEs) over time. Given the potential for asymmetrical matrices, the PARDISO linear solver was used, with a relative tolerance set to 0.0005.

3.7 Model validation

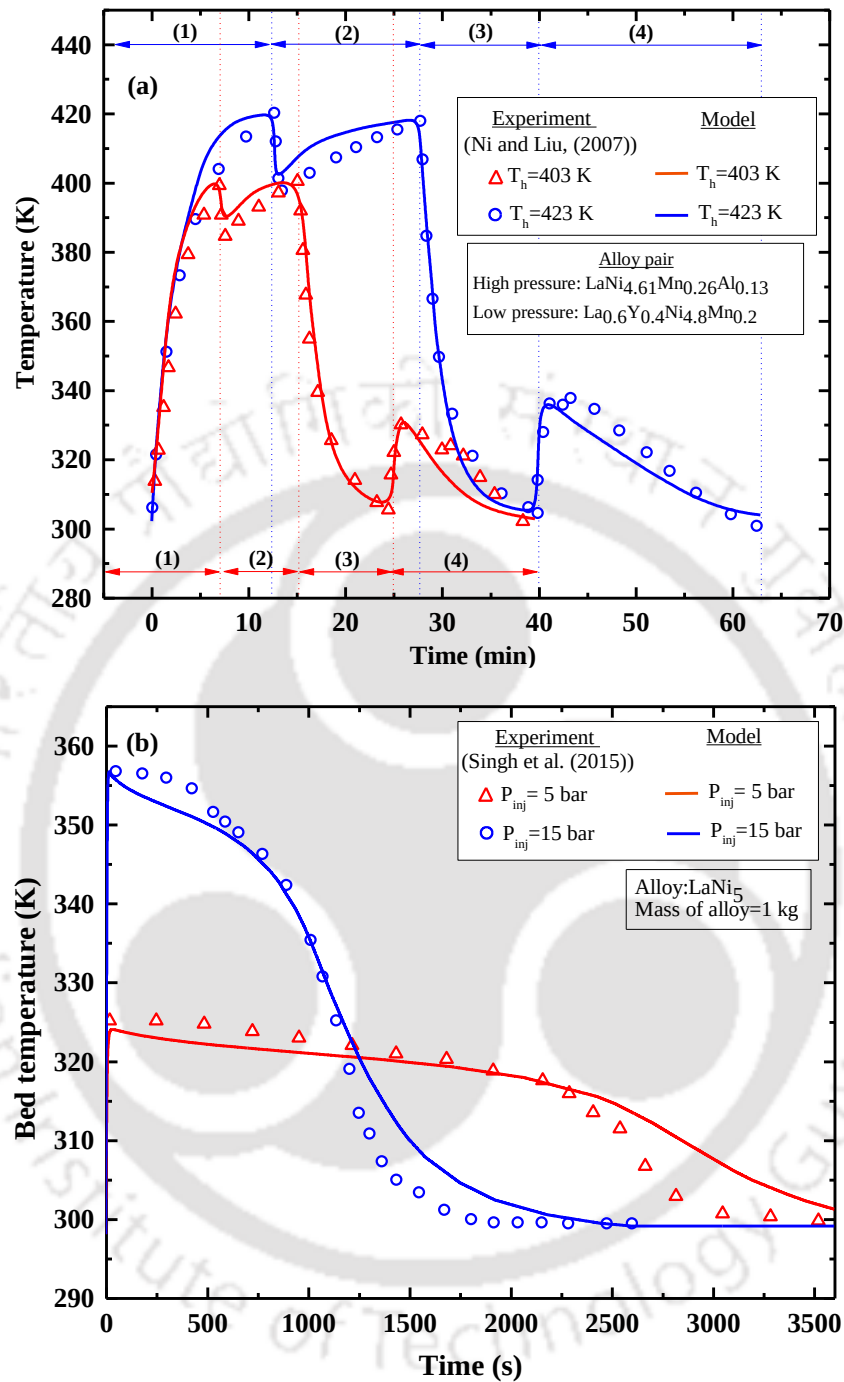


Fig. 3.2: Validation of the (a) coupled reactor operation model with the experimental datasets of Ni and Liu, (2007). The temperature in the high-pressure bed ($\text{LaNi}_{4.6}\text{Mn}_{0.26}\text{Al}_{0.13}$) was recorded during a sequence in which it was heated to T_h (403 K and 423 K) (1), followed by dehydriding (2) after which the bed was cooled down to T_l (3) before absorbing hydrogen (4) from the low-pressure bed ($\text{La}_{0.6}\text{Y}_{0.4}\text{Ni}_{4.8}\text{Mn}_{0.2}$) and (b) single reactor operation model with experimental datasets of Singh et al., (2015).

The model developed for coupled reactor operation is rigorously validated by comparing its predictions with experimental datasets reported by Ni and Liu, (2007), who explored a MH-based refrigeration system comprising two high-pressure beds containing $\text{LaNi}_{4.6}\text{Mn}_{0.26}\text{Al}_{0.13}$ and two-low pressure beds containing $\text{La}_{0.6}\text{Y}_{10.4}\text{Ni}_{4.8}\text{Mn}_{0.2}$. The present model was configured to replicate the identical geometry (50 mm outer diameter and 500 mm length) and alloys used in the experimental studies. Critical properties, such as hysteresis and plateau slope, are derived from the Pressure-Composition-Temperature (PCT) data of the alloys. Fig. 3.2 presents the predicted temperature evolution when the high-pressure bed was initially heated to 403 K and 423 K. The comparison reveals a maximum discrepancy of <3% between the predicted and the experimental temperatures. This minor discrepancy is likely due to inherent bed heterogeneities and their temperature-dependent variations, which are treated as constants in the current mathematical framework. Further, the model developed for single reactor is validated with experimental study conducted by Singh et al., (2015). A cylindrical reactor housing with transverse copper fins, containing 1 kg of LaNi_5 , was simulated under hydrogen operating pressures of 5 bar and 15 bar with an HTF flow velocity of 1 m/s to analyse the dynamic bed temperature evolution. The numerical datasets of bed temperature profile with respect to time showed a deviation of less than 5 K as shown. These validations underscore the model's robustness at two injection pressure (P_{inj}), 5 bar and 15 bar with inlet of HTF maintained at 298 K and velocity of 1 m/s.

3.8 Design of reactors for high pressure compression (>140 bar)

3.8.1 Physical systems

A tubular reactor configuration was selected for this study, considering the target compression pressure of 400 bar, along with an appropriate design safety margin. This configuration offers advantages such as structural integrity under high pressure, cost-effectiveness, and ease of scalability, as the system can be extended to larger capacities by simply increasing the number of reactor units. However, the effective reactor bed diameter plays a critical role in ensuring optimal thermal and mass transfer performance and must be carefully optimized, as discussed in the following section.

The reactor body is assumed to be constructed using commercially available ASTM A312-compliant SS316 stainless steel seamless tube. The required wall thickness (t) of this section is determined by its outer diameter (d_o), as specified in Eq. 3.42, derived from the ASME Section VIII, Division 1 of the Boiler and Pressure Vessel Code (ASME, 2011).

$$t = \frac{d_o}{2} \left(1 - \exp \left(\frac{-p_{max}}{SE} \right) \right) \quad (3.42)$$

where S denotes the allowable stress of the considered material at the designed temperature. In the present work, SS316 grade stainless steel was selected which possesses an allowable stress of 134 MPa at 200 °C. p_{max} denotes the maximum radial pressure subjected on the reactor wall. Joint efficiency (E) was considered 1 for the seamless tube. The closing metal caps also withstand longitudinal pressure and are therefore designed in accordance with Eq. 3.43 (ASME, 2011).

$$t_2 = (d_o - 2t) \sqrt{\frac{CP}{SE}} \quad (3.43)$$

where t_2 denotes thickness of head flange while C denotes design parameter which was considered as 0.17 in the present case. The schematic of the tubular reactor is shown in Fig. 3.3.

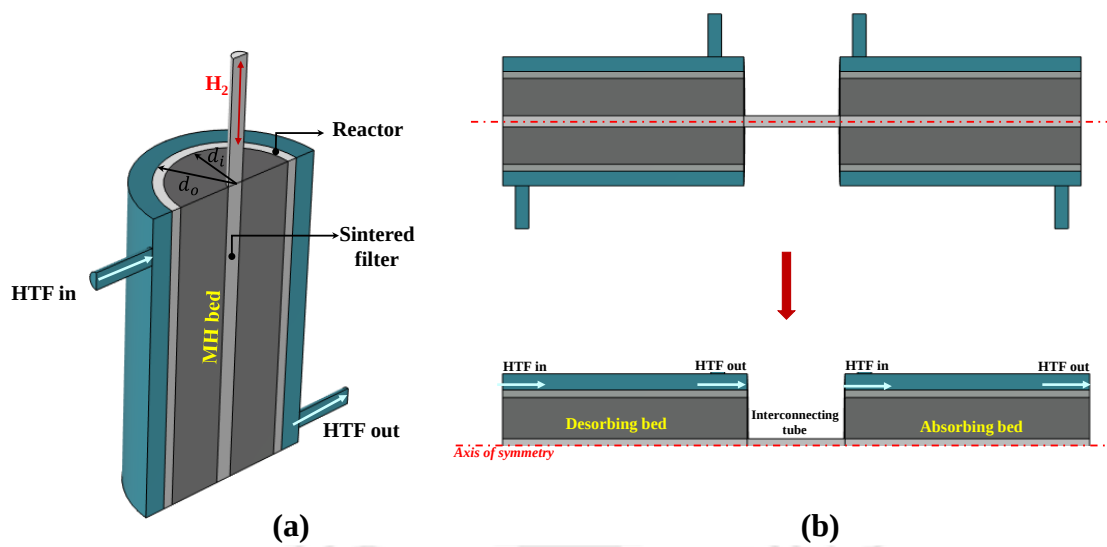


Fig. 3.3: (a) Schematic of tubular reactor and (b) description of 2-D axisymmetric coupled reactors computational domain

3.8.2 Geometry of the reactor and the computational domain

To determine the optimal reaction bed diameter for the tubular reactor, a series of numerical simulations were conducted for hydrogen transfer under coupled reactor operation. Multiple reactor dimensions were considered, each designed to withstand pressures up to 300 bar at an assumed operating temperature of 200 °C, ensuring structural integrity under extreme conditions. The reaction bed diameters were varied between 20 mm and 60 mm, as this range balances mechanical strength and thermal-mass transport performance. The specific

dimensions of each simulated configuration are summarized in Table 3.1. All reactor designs were configured to accommodate a maximum hydrogen storage volume of approximately 79 L, corresponding to 500 g of AB₅-type alloy. The computational domain of the coupled reactor assembly is illustrated in Fig. 3.3 (b).

Table 3.1 : Specifications of the tubular MH reactors

Reaction bed diameter (mm)	Filter diameter (mm)	Internal diameter (d_i) (mm)	External diameter (d_o) (mm)	Wall thickness (mm)	Length of reactor (L) (mm)	Mass of reactor (kg)
20	13	33	41.38	4.19	379.13	1.45
30	13	43	53.9	5.45	168.5	1.1
40	13	53	66.4	6.7	94.78	0.93
50	13	63	79	8	60.66	0.84
60	13	73	91.5	9.25	42.12	0.79

3.8.3 Grid independence test

Table 3.2 : Details of the mesh independence test result

Number of elements	Time for 50% hydrogen transfer (s)	Percentage difference (%)	Computation Time	Percentage Difference (%)	Minimum element quality
Grid 1: 26,173	1810	-	2215	-	0.779
Grid 2: 30,198	2300	27.07	3725	68.2	0.794
Grid 3: 40,979	2345	29.56	7320	230.5	0.806
Grid 4: 49,356	2346	29.6	9958	349.6	0.809

A grid independence test was conducted to ensure the numerical accuracy of simulations for a coupled metal hydride reactor system. Four progressively refined grids: Grid-1 to Grid-4 were evaluated based on the mean time required to reach 50% hydrogen transfer between the desorbing and absorbing beds. The corresponding times were 1810 s (Grid-1), 2300 s (Grid-2), 2345 s (Grid-3), and 2346 s (Grid-4). The marginal difference between Grid-3 and Grid-4 (<0.04%) confirmed solution convergence, validating Grid-3 for further simulations. However,

a significant increase in computation time was observed with finer grids, with Grid-4 requiring nearly 1.3 times more than Grid-3, highlighting the trade-off between accuracy and computational efficiency. Summary of the grid independence study is shown in Table 3.2.

3.8.4 Details of the alloys used

Table 3.3 : Thermophysical properties (Sharma and Anil Kumar, 2014)

Input parameters	La _{0.8} Ce _{0.2} Ni ₅	La _{0.4} Ca _{0.4} Ce _{0.2} Ni ₅	
Activation energy (J/mol) (E_a, E_d)	31040, 30000	23000, 21000	
Empty alloy density (kg/m ³) (ρ_o)	8400	8400	
Maximum hydrogen storage capacity (wt%)	1.4	1.4	
Initial bed porosity (ε_i)	0.5	0.5	
Reaction enthalpy (J/mol) ($\Delta H_a, \Delta H_d$)	27000, 27500	27500, 28200	
Reaction entropy (J/(mol.K)) ($\Delta S_a, \Delta S_d$)	105, 105	115.3, 115.3	
Alloy's specific heat capacity (J/(kg.K)) ($c_{p,MH}$)	500	500	
Hysteresis	0.74	0.56	
Thermal conductivity (W/(m.K)) (k_s)	1.6	1.6	
Reaction constants	75, 20	75, 100	
Initial particle diameter (m) (d_{p_i})	100×10 ⁻⁶	100×10 ⁻⁶	
Volume expansion factor (β)	1.25	1.25	
	HTF (water)	Reactor body	Hydrogen
Specific heat capacity (J/(kg.K)) (cp)	4200	500	14283
Thermal conductivity (W/(m.K)) (k_s)	0.6	16	0.18
Viscosity (Pa.s) (μ_l)	100×10 ⁻⁶	-	-

La_{0.8}Ce_{0.2}Ni₅ and La_{0.4}Ca_{0.4}Ce_{0.2}Ni₅ were selected for simulation due to its operating pressure and temperature range aligning with the study's requirements. Additionally, its thermophysical properties are well-documented in the literature, making it suitable for use in simulations. Water is employed as the HTF. The required properties of the alloy, HTF, hydrogen and reactor materials are summarized in Table 3.3.

3.8.5 Optimization of reaction bed diameter

The optimization study was conducted by balancing two critical performance metrics: the hydrogen transfer rate, representing the efficiency of coupled thermal and mass transport, and the weight ratio, indicative of the passive thermal mass associated with the reactor structure. The primary objective is to maximize the hydrogen transfer rate, which is essential for enhancing compression efficiency, while simultaneously maximizing the weight ratio, thereby reducing the overall reactor mass. However, achieving elevated delivery pressures inherently necessitates increased reactor wall thickness, which in turn contributes to higher reactor mass. This introduces a design trade-off, demanding a judicious balance between mechanical robustness and thermal efficiency. The parameters can be mathematically evaluated as:

H₂ transfer rate (ω): The transfer rate is evaluated as the ratio of the amount of hydrogen transferred from the desorbing reactor to the absorbing reactor, maintained at the desired bed temperature, to the duration of the transfer process. This metric directly represents the rate of hydrogen compression and serves as a key indicator of the dynamic performance of the MHHC system.

Weight ratio (WR): The weight ratio is defined as the ratio of the mass of the alloy contained within the reactor to the mass of the reactor itself. This parameter reflects the reactor's material efficiency, with higher values indicating reduced passive thermal mass and improved compactness and performance efficiency.

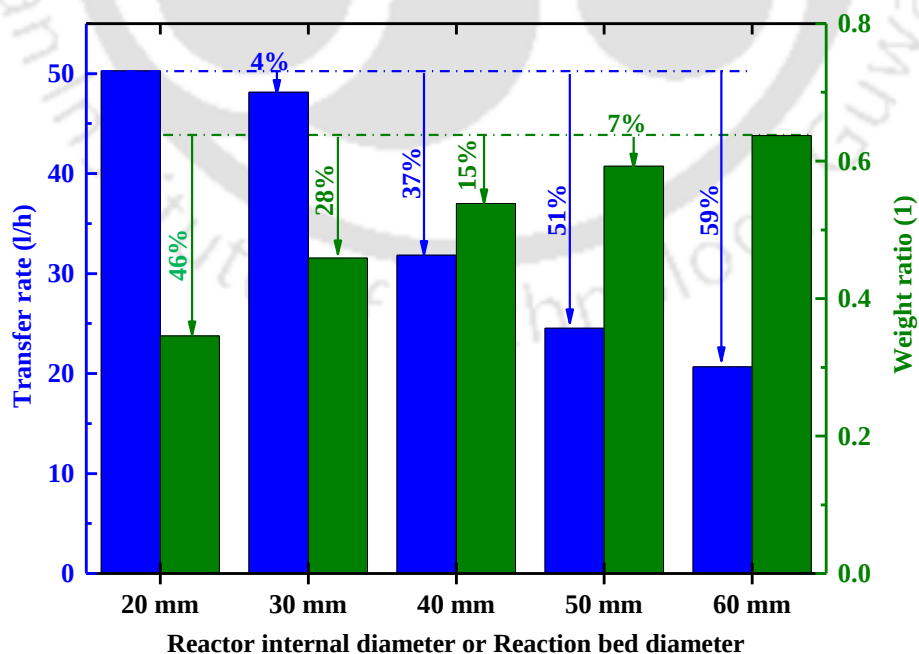


Fig. 3.4: H₂ transfer rate and weight ratio for various cases of tubular reactor

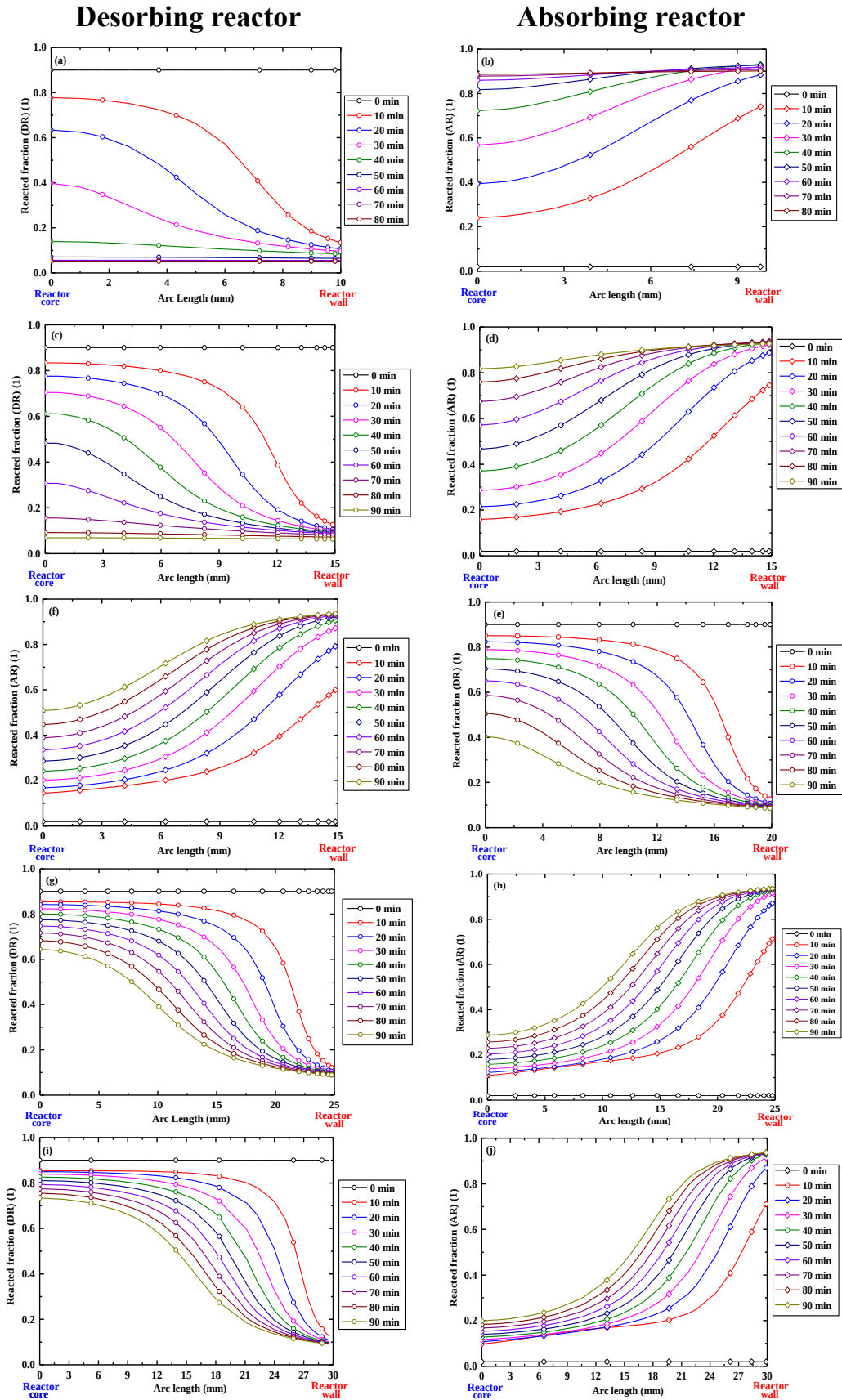


Fig. 3.5 : Spatio-temporal variation of reacted fraction within desorbing and absorbing reactor bed (a-b) 20 mm, (c-d) 30 mm, (e-f) 40 mm, (g-h) 50 mm, and (i-j) 60 mm

The H_2 transfer rate and weight ratio for all simulated cases are evaluated and presented in Fig. 3.4. As the reaction bed diameter increases from 20 mm to 60 mm, the transfer rate shows a significant decline of approximately 60%, dropping from 50.2 L/h to 20.7 L/h. This reduction is attributed to increased bed heterogeneities, as discussed below. Conversely, the weight ratio nearly doubles over the same diameter range. This trend is primarily due to the reduced reactor length required to accommodate the same amount of alloy. For instance, a reactor with a 20 mm bed diameter requires a length of approximately 379.13 mm to store 79 L of hydrogen, resulting in a high aspect ratio (L/d_i) (~ 11.5). In contrast, a 60 mm diameter reactor requires only a 0.6 aspect ratio, reducing the overall reactor mass from 1.45 kg to 0.79 kg, and yielding a more compact and lightweight configuration.

To evaluate the development of bed heterogeneities within the reactor, the spatio-temporal evolution of the reacted fraction is presented in Fig. 3.5. This analysis provides valuable insight into the non-uniform progression of hydrogen absorption and desorption reactions across the bed over time. Fig. 3.5 (a) and Fig. 3.5 (b) illustrate the temporal variation of the reacted fraction within the desorbing and absorbing beds, respectively, for a reaction bed diameter of 20 mm, at intervals of 10 minutes. In the desorbing bed, the reacted fraction decreases from 0.9 to nearly 0, indicating the progressive release of hydrogen. The rate of decrease is relatively high, as evident from the larger spacing between the successive reacted fraction contours, representing faster hydrogen removal. A similar trend is observed in the absorbing bed, where the reacted fraction increases from 0.02 to 0.9, indicating hydrogen uptake. However, as the reaction bed diameter increases from 20 mm to 60 mm, the rate of hydrogen transfer significantly decreases. This is evidenced by the reduced spacing between successive contours, signifying a sluggish progression of the reaction front. In particular, Fig. 3.5 (g) and Fig. 3.5 (h) show that, even after 90 minutes, the desorbing bed retains a reacted fraction above 0.6, and the absorbing bed remains below 0.3 at the core of the reactor for the 50 mm diameter case. Notably, the regions adjacent to the reactor walls exhibit nearly complete transfer, indicating a strong radial gradient in reacted fraction. For the 60 mm diameter, the bed non-uniformity is even more pronounced, with reacted fractions exceeding 0.7 in the desorbing bed and remaining around 0.2 in the absorbing bed at the center, even after 90 min. This highlights the increased concentration gradients and hydrogen transfer limitations associated with larger diameters, ultimately resulting in a significant decline in hydrogen transfer rates. These findings confirm that increasing the reaction bed diameter beyond 30 mm leads to pronounced bed heterogeneities, adversely impacting compression performance.

These results indicate that while smaller diameters enhance hydrogen transfer performance, they also lead to excessively elongated reactor geometries, which are impractical for fabrication and handling. Based on this trade-off, a reaction bed diameter in the range of 20-30 mm is identified as optimal, balancing both transfer efficiency and reactor compactness.

Table 3.4 : ASTM standard table for SS316L stainless steel seamless tubes (NPS 20-25)

Temperature (°C)					50	100	150	200	250	300
Design strength (MPa)					138	138	138	134	125	119
Size			Schedule No.	Wall thickness (mm)	Allowable working pressure (bar)					
Nominal Diameter	Nominal Pipe Size	mm								
20	¾	26.67	5S	1.65	158	158	158	152	143	136
			10S	2.11	205	205	205	198	186	177
			40S	2.87	287	287	287	277	260	247
			80S	3.91	406	406	406	391	368	350
25	1	33.40	5S	1.65	125	125	125	120	113	108
			10S	2.77	216	216	216	208	196	186
			40S	3.38	268	268	268	258	243	231
			80S	4.55	374	374	374	360	338	322

The ASTM standard specification sheet for SS316L grade stainless steel was referenced to finalize the geometric dimensions based on commercially available configurations. Table 4 presents an excerpt from the standard, focusing on the reaction bed diameters below 30 mm. It is observed that, for a maximum working pressure exceeding 300 bar, only two tube configurations meet the required criteria with an adequate safety factor i.e. with nominal diameters of 20 mm and 25 mm and schedule 80S. These configurations correspond to reaction bed diameters of 18.85 mm and 24.3 mm, respectively. Based on the optimization studies, the final reactor dimensions are selected with an external diameter of 33.4 mm and an internal diameter of 24.3 mm. The wall thickness of 4.55 mm is also well above the minimum required thickness calculated using Eq. 3.42, offering a design margin of 35.8%.

The closing metal caps were finalized with a thickness of 15 mm, considering both the structural strength and the welding challenges associated with integrating a sintered filter and

an alloy filling port (weldnut, make: Swagelok) at the end of each metal cap. The length of the reactor tube was determined based on the required alloy mass and the type of alloy to be filled. In the present study, two compressor setups of different scales were developed to facilitate both comprehensive experimental investigations and performance evaluations aligned with industrial requirements. The prototype setup was designed to compress approximately 500 NL of hydrogen, while the industrial-scale system was configured to compress over 6000 NL of hydrogen per stage.

To achieve compression of 500 L (STP) of hydrogen, an average of 3.2 kg of AB₅-type alloy and 2.6 kg of AB₂-type alloy was required. The requisite length (L) of the reactors was then determined by considering the alloy density (ρ_{MH}) of 8400 kg/m³ for AB₅ type (stage 1 and stage 2) and 6000 kg/m³ for AB₂ type (stage 3) alloys using Eq. 3.44.

$$L = \left(\frac{\xi \times m_{MH}}{\varepsilon \times \rho_{MH} \times A_c} \right) \quad (3.44)$$

where ε indicates the initial porosity within the packed MH bed which is considered to be 0.5. Further, ξ denotes volumetric expansion coefficient (1.3 (AB₅) and 1.25 (AB₂) for allowing 25-30% expansion of alloys). A_c denotes cross-sectional area corresponding to the inner diameter of the reactor ($d_o - 2t$). The dimensional specification of the designed prototype reactor for high pressure application is shown in Fig. 3.6. For the prototype setup, two such reactors were finalized, each designed to accommodate 1.4 kg of AB₂-type alloy.

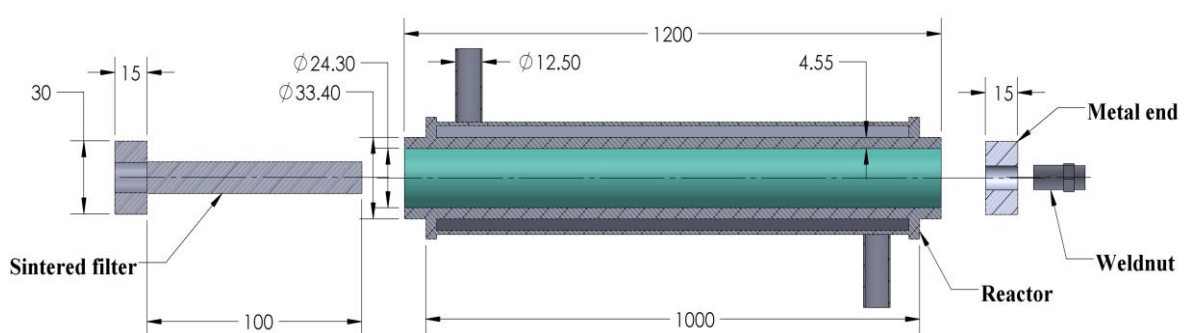


Fig. 3.6 : Detailed schematic of dimensional specification of the prototype tubular reactor

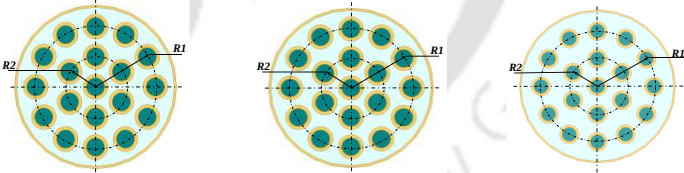
To achieve the target of compressing over 6000 L of hydrogen per stage, approximately 50 kg of metal hydride alloy need to be distributed across 38 such reactor tubes, with each tube designed to accommodate a maximum of 1.3 kg of alloy. While the number of reactor tubes could theoretically be reduced by increasing their length, the tube length was fixed at

approximately 1000 mm to ensure fabrication feasibility and structural manageability. To achieve a compact and robust reactor assembly, the tubes were grouped together. Consequently, 19 reactor tubes were arranged within a single reactor vessel, resulting in two such reactors per stage to meet the required alloy capacity.

Furthermore, the arrangement of the tubes within the reactor was strategically designed to maximize heat and mass transfer effectiveness while ensuring mechanical integrity and uniform heat distribution across the reactor during operation.

3.8.6 Effect of positioning of reactor tubes.

Table 3.5 : Specification of the considered configurations

	Configuration I	Configuration II	Configuration III
Outer shell diameter (mm)	220	233	272
Radial distance of inner stack (R2) (mm)	40.53	43.4	49.12
Radial distance of outer stack (R1) (mm)	81.06	86.8	98.24
Inter stack spacing (mm)	7.13	10	15.72
Radial pitch (mm)	9	12	18
Desorbing temperature (°C)	90	90	90
Desorption pressure (bar)	1	1	1
Figure			

The 19 reactor tubes were arranged in a two-stack configuration, with the inner stack uniformly accommodating 6 tubes and the outer stack comprising 12 tubes. An additional single tube was positioned at the center to complete the assembly.

To ensure optimal thermal performance and structural compactness, the angular pitch and inter-stack spacing were optimized using a computational simulation model of a single MH reactor operation during desorption. Three configurations were evaluated:

- Configuration I: Inter stack and inter-tube spacing less than 10 mm
- Configuration II: Spacing in the range of 10-15 mm
- Configuration III: Spacing greater than 15 mm

The detailed of each configuration are shown in Table 3.5.

All configurations were simulated under desorption conditions at 90 °C, starting from a fully absorbed state and discharging to ambient pressure. $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ni}_5$ was used as the alloy for simulation. The resulting temperature distributions and hydrogen discharge profiles were evaluated for three representative reactor positions: the central reactor, a reactor from the inner stack, and a reactor from the outer stack. The comparative results for the three configurations are illustrated in Fig. 3.7.

The local bed temperature distribution at the three monitored locations exhibited a similar trend across all configurations; an initial temperature drop followed by a gradual rise over time. However, a closer examination reveals notable differences in temperature uniformity. In Configuration I and Configuration III, significant temperature variations are observed at specific instances, whereas Configuration II demonstrates a more uniform temperature profile across all positions. Regarding hydrogen discharge, Configuration II showed a faster and more synchronized desorption process, with complete discharge occurring within 660 s. In contrast, Configuration I require about 750 s for complete desorption. Although the outer stack reactor in Configuration III completes desorption within 620 s, the inner stack reactors exhibit delayed desorption, taking up to 690 s, indicating uneven hydrogen transfer within the configuration. Thus, although Configuration I is more compact and structurally robust, with the maximum shell diameter confined within 220 mm, the more spacious Configuration II is preferred due to its superior thermal uniformity and balanced hydrogen discharge characteristics.

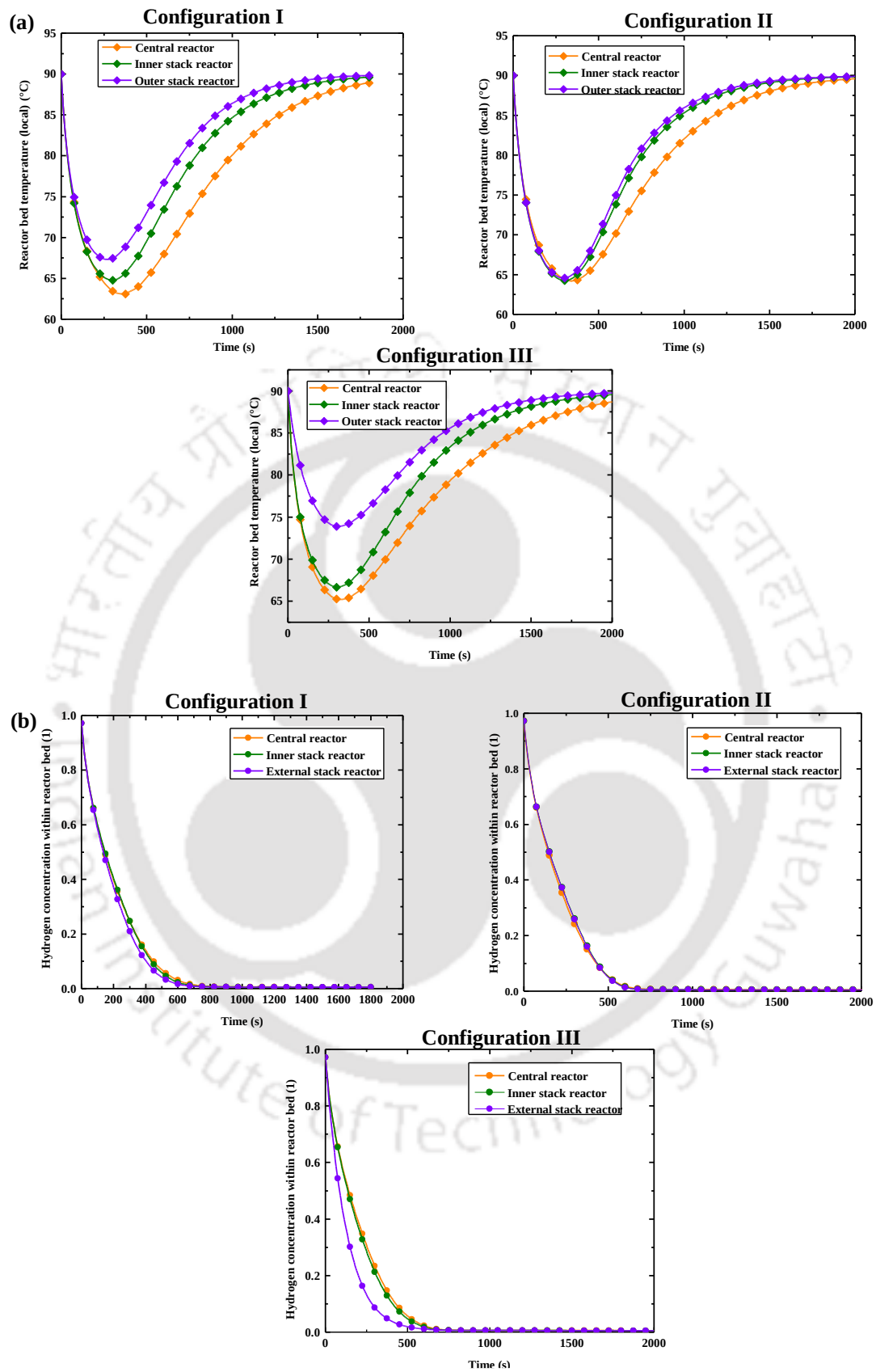


Fig. 3.7 : Comparison of temperature distributions and hydrogen discharge profiles for three configurations

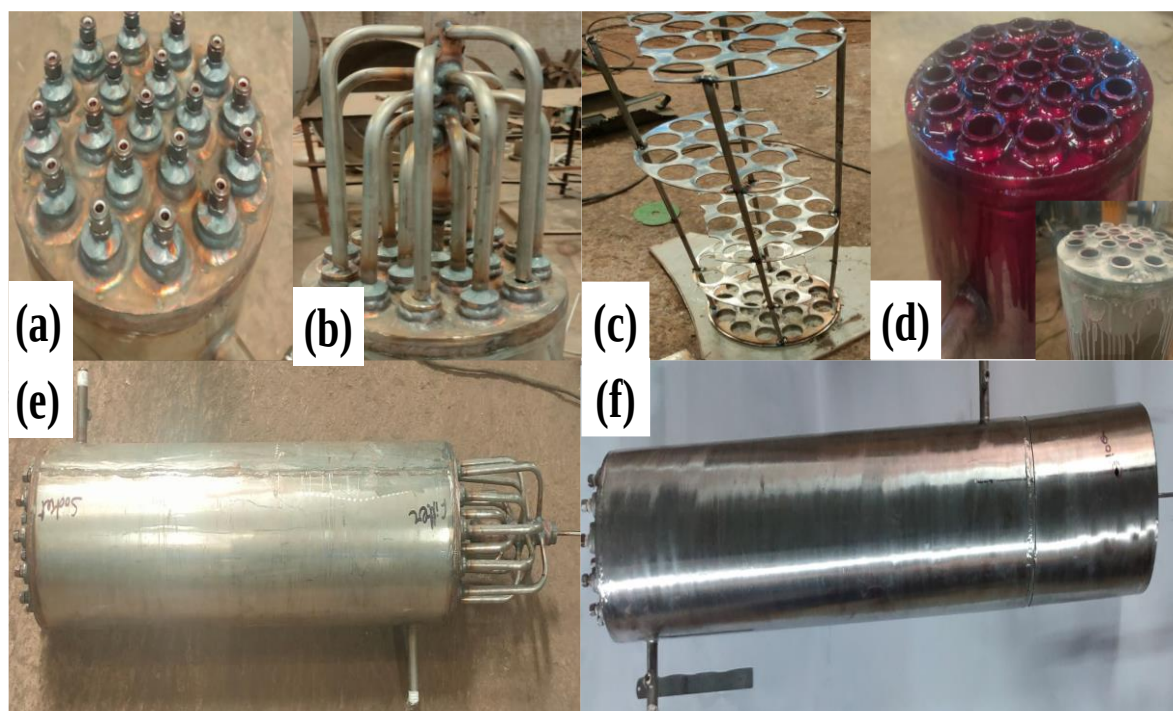


Fig. 3.8 : Pictorial view of the reactor components (a) tubes welded on tubesheet with alloy filling ports, (b) gas manifold inlet, c) baffles, (d) Welding inspection with penetrant testing solutions, (e) Fabricated reactor, and (f) Furnished reactor with safety cover for manifold inlet.

Based on the finalized geometric specifications, the corresponding SS316 seamless tubes and sheets were procured and fabricated. The fabrication process began with welding the seamless tubes to their respective metal end caps, followed by welding the assembled tubes to 15 mm thick tube sheets. An alloy filling port was integrated at the rear end of each reactor, while a manifold inlet arrangement was incorporated at the front end to enable modular reactor design. To ensure proper alignment and structural stability, the tubes were mounted on four equally spaced baffles, serving dual purposes, providing mechanical support, maintaining correct tube positioning during assembly and enhancing heat transfer effectiveness by directing and regulating the HTF flow around the tubes. Additionally, 1.5 mm thick SS316 sheets were bent into a C-shape and welded to the tube sheets, enclosing the assembly and completing the reactor fabrication.

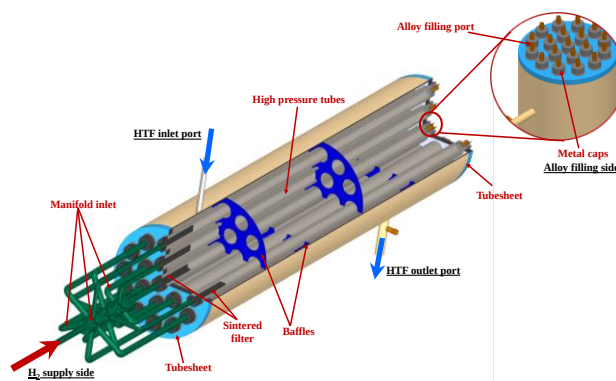
Post-fabrication, all weld joints were inspected using penetrant testing solutions to detect potential porosities or weld defects. The reactors were then hydrostatically tested up to 400 bar to ensure leak-proof performance under high-pressure conditions. Representative images of the fabrication process are shown in Fig. 3.8. Five K-type thermocouples (TC₁-TC₅) of varying lengths were used to record temperature variation along the longitudinal direction within

separate tubes in a single reactor. A pair of thermocouples (TC_{in} and TC_{out}) were also provided to monitor the inlet and outlet temperature of the HTF. Details on the thermocouple and reactor specifications can be found in Table 3.6.

Table 3.6 : Detailed specifications of the reactor and thermocouples

Part name	Detailed specifications
Tubes	Number of tubes: 19
	Outer diameter of tubes: 33.4 mm
	Wall Thickness: 4.55 mm
	Length: 1000 mm for stage 1 and 2 reactors and 1200 mm for stage 3 reactors
Tubesheet	Radial distance of stacks: Stack 1-43.4 mm Stack 2-86.8 mm
	Diameter: 233 mm
Metal caps	Thickness: 15 mm
	Diameter: 30 mm
Sintered filter	Thickness: 15 mm
	Pore Size: 0.5 μ m
Thermocouples	Diameter: 13 mm
	Length: 50 mm
	TC ₁ : 350 mm
	TC ₂ : 500 mm
	TC ₃ : 750 mm
	TC ₄ : 800 mm
	TC ₅ : 900 mm
	TC _{in} : 30 mm
	TC _{out} : 30 mm

Figure



3.9 Design of reactor for low to moderate pressure compression (<140 bar)

3.9.1 Physical systems

An Embedded Cooling Tube Reactor (ECTR) configuration is selected for reactors intended to operate at pressures up to 140 bar, even at temperatures as high as 200 °C, making it suitable for application in primary stages of compression. To the best of our knowledge, this configuration has not yet been explored in the context of hydrogen compression in existing literature. While ECTR designs have been recognized as promising for small- to large-scale hydrogen storage systems, their potential for compressor applications, particularly in low-pressure stages, warrants investigation. Accordingly, a prototype ECTR was designed to operate within a pressure range of 1-140 bar and a temperature range of 0-100 °C. However, with increasing design pressure, the minimum required wall thickness of the reactor also increases substantially, contributing to a higher thermal parasitic mass, which can adversely affect the reactor's thermal efficiency. According to the ASTM standard specifications for SS316L seamless pipes (as presented below), an outer reactor diameter exceeding 101.6 mm cannot be used with a wall thickness below 5 mm to safely withstand pressures in the range of 140 bar. As alternatives, reactor configurations with external diameters of 88.9 mm and 101.6 mm were explored to ensure compliance with the required pressure criteria while maintaining structural integrity.

To enhance heat transfer effectiveness, ECTs were wound with spiral aluminium fins and strategically arranged in a circular configuration to minimize hotspots during the sorption reaction. In the present design, 13.5 mm diameter tubes were utilized as ECTs. Additionally, an Outer Cooling Jacket (OCJ) was incorporated to further optimize thermal management.

Table 3.7 : ASTM standard table for SS316L stainless steel seamless tubes (NPS 80-100)

Temperature (°C)				50	100	150	200	250	300	
Design strength (MPa)				138	138	138	134	125	119	
Size			Schedule No.	Wall thickness (mm)	Allowable working pressure (bar)					
Nominal Diameter	Nominal Pipe Size	mm								
80	3	88.9	5S	2.11	59	59	59	56	53	50
			10S	3.05	85	85	85	82	77	74
			40S	5.49	158	158	158	152	143	136
			80S	7.62	224	224	224	216	203	193
90	3 ½	101.6	5S	2.11	51	51	51	49	46	44
			10S	3.05	74	74	74	72	67	64
			40S	5.74	144	144	144	138	130	124
			80S	8.08	206	206	206	199	187	178
100	4	114.30	5S	2.11	45	45	45	44	41	39
			10S	3.05	66	66	66	64	60	57
			40S	6.02	133	133	133	129	121	115
			80S	8.56	206	206	199	187	175	167

3.9.1 Details of the alloy used

La_{0.8}Ce_{0.2}Ni₅ was selected for the simulation of the prototype reactor, as it is the same alloy intended for use in the primary stage of the compressor system. The requisite thermophysical properties of the alloy are already provided in Table 3.3.

3.9.2 Geometry of the reactor

The required reactor wall thickness, based on the fixed outer diameter, was determined using Eq. 3.42. Considering commercial availability, the final wall thickness was selected from Table 3.7, choosing the closest standard size equal to or greater than the value calculated from Eq. 3.42. Subsequently, the number of ECT tubes and the radial positioning of the stack were established following the methodology proposed by Raju et al., (2019). The bed thickness was stringently maintained within the range of 5-10 mm. Based on this constraint, three distinct designs were developed. The details of the resulting configurations are presented in Table 3.8.

Table 3.8 : Specification of the considered configurations for prototype reactor

	Configuration I	Configuration II	Configuration III
Outer diameter of the reactor (mm)	88.9	101.6	101.6
Inner diameter of the reactor (mm)	77.9	90.12	90.12
Wall thickness (mm)	5.49	5.74	5.74
Number of stacks	1	1	1
Number of ECTs	4	5	6
Radial distance of stack (RI) (mm)	22.5	27.5	27.5
Diameter of OCJ (mm)	109	131	131
Radial pitch (mm)	7.8	7.1	1.3
Fin pitch (mm)	10	10	10
Fin width (mm)	10	10	10
Desorbing temperature (°C)	90	90	90
Desorption pressure (bar)	1	1	1

3.9.3 Grid independence test

Table 3.9 : Summary of the results of the grid independence test

Number of elements	Equilibrium pressure at $t=500$ s (bar)	Percentage difference (%)	Computation time (s)	Percentage Difference (%)	Average element quality
Grid 1: 2,97,470	26.437	-	18,353	-	0.62
Grid 2: 5,97,635	25.537	-3.4	33,106	80.38	0.78
Grid 3: 8,43,566	25.999	-1.66	40,365	120	0.79
Grid 4: 11,27,980	25.993	-1.67	54,864	199	0.8

Due to the complex geometry of the prototype reactor, user-defined meshing was employed for accurate simulation. Separate mesh sizes were applied across different domains to optimize element distribution. This approach ensured accurate capture of critical gradients while managing resource constraints. Grid 3 was chosen for further analysis as it provided an optimal

balance between the variation in equilibrium pressure at $t = 500$ s and computational time, while maintaining appreciable average element quality across the domains (~ 0.8). The results of the grid independence test, validating the chosen mesh configuration, are presented in Table 3.9.

3.9.4 Optimisation of reaction bed diameter and number of spiral finned tubes

Configuration I was designed with an outer diameter of 88.9 mm and a wall thickness of 5.49 mm, incorporating four spiral finned tubes, which yielded a minimum bed thickness of 7.8 mm. Configuration II featured a larger outer diameter of 101.6 mm and a wall thickness of 5.74 mm, with five spiral finned tubes, resulting in a slightly reduced bed thickness of 7.1 mm. These configurations represent optimized designs based on the methodology proposed by Raju et al., (2019), within the constraints of the selected external diameters and wall dimensions. Additionally, an oversized variant of Configuration II was examined by incorporating six spiral finned tubes, leading to a significantly lower minimum bed thickness of 1.3 mm. The width and pitch of the spiral fin are 10 mm and 10 mm respectively. The comparative performance results for these configurations are presented in Fig. 3.9 and Fig. 3.10.

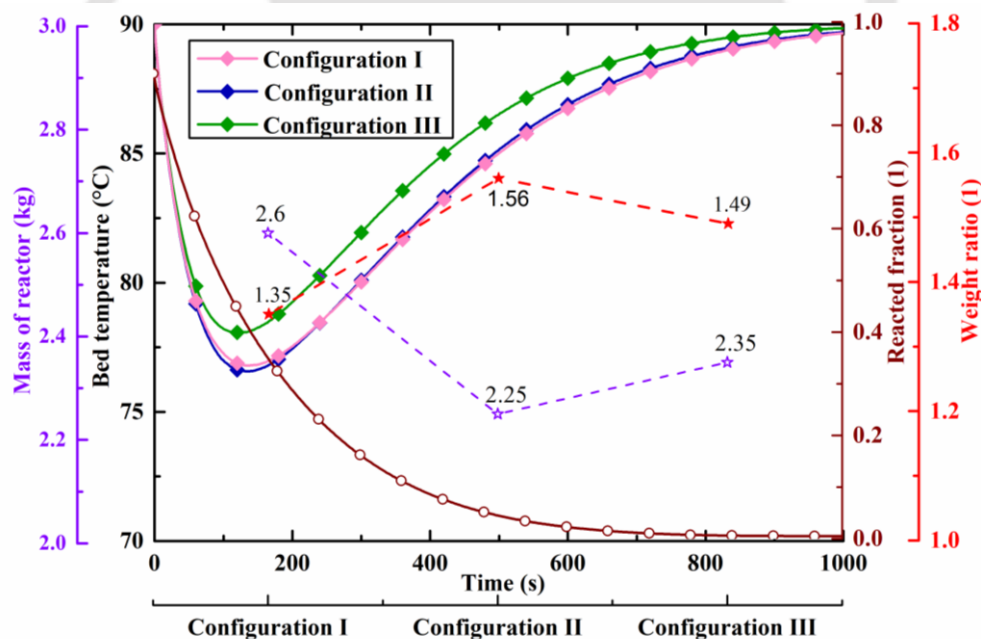


Fig. 3.9 : Comparison of bed temperature and reacted fraction for 3 considered configuration

Only desorption kinetics were analysed, as desorption typically represents the rate-limiting step in metal hydride systems. Configurations I and II exhibited comparable bed temperature profiles, despite Configuration I incorporating four spiral cooling tubes. This similarity in heat transfer performance is attributed to their nearly identical minimum bed thicknesses. The

additional cooling tube in Configuration II effectively compensated for the marginally slower reaction kinetics expected due to the increased radial diameter (from 88.9 mm in Configuration I to 101.6 mm). Configuration III, representing an overdesigned case with six spiral cooling tubes and a reduced bed thickness of 1.3 mm, demonstrated only marginal improvement in thermal performance over the desorption cycle. This limited enhancement suggested diminishing returns with further reduction in bed thickness. Interestingly, the reacted fraction profiles across all three configurations were nearly identical, with minor variations considered negligible under experimental conditions.

To further investigate the reaction dynamics within the reactor bed, the volumetric hydrogen discharge rate was analysed at the mid-plane of each configuration, as illustrated in Fig. 3.10 for different time instances starting from $t = 50$ s. As desorption progressed, spatial non-uniformity in the discharge rate increased up to $t = 400$ s and gradually became uniform by $t = 500$ s. This behaviour was attributed to the temperature gradients driven by non-uniform heat dissipation, which in turn influenced local reaction kinetics based on proximity to cooling surfaces or conductive structures such as fins. Configuration I exhibited wider and more pronounced low-discharge regions due to the presence of fewer cooling tubes, resulting in less effective thermal management. In contrast, Configuration III showed slightly improved discharge uniformity, owing to enhanced heat extraction via six cooling tubes. However, the marginal gains in discharge dynamics for Configuration III came at the cost of increased complexity and weight. Importantly, the overall reacted fraction within the bed remained nearly identical across all configurations, suggesting that the observed differences in local discharge dynamics may be less critical for overall system performance.

Therefore, the final selection of reactor configuration was guided by mass and volume efficiency (Fig. 3.9). Configuration II was found to offer the lowest reactor weight and highest weight ratio (mass of reactor 2.25 kg, weight ratio: 1.56) for delivering the target hydrogen capacity of 500 L, corresponding to 3.5 kg of AB₅-type alloy. This advantage resulted from a shorter reactor length compared to Configuration I (mass of reactor: 2.6 kg, weight ratio : 1.35) and a lower number of finned cooling tubes than Configuration III (mass of reactor 2.35 kg, weight ratio : 1.49). Accordingly, Configuration II was selected as the optimal design.

Based on the finalized design, requisite SS316-grade seamless tubes and pipes were procured. Helical aluminium fins with a width of 10 mm were procured separately and brazed onto the ECT. Flanges of the finalized thickness were acquired and machined with holes as per the specified requirements to complete the assembly of all reactor components. All parts were joined using TIG welding, with provisions made for alloy filling and thermocouple placement.

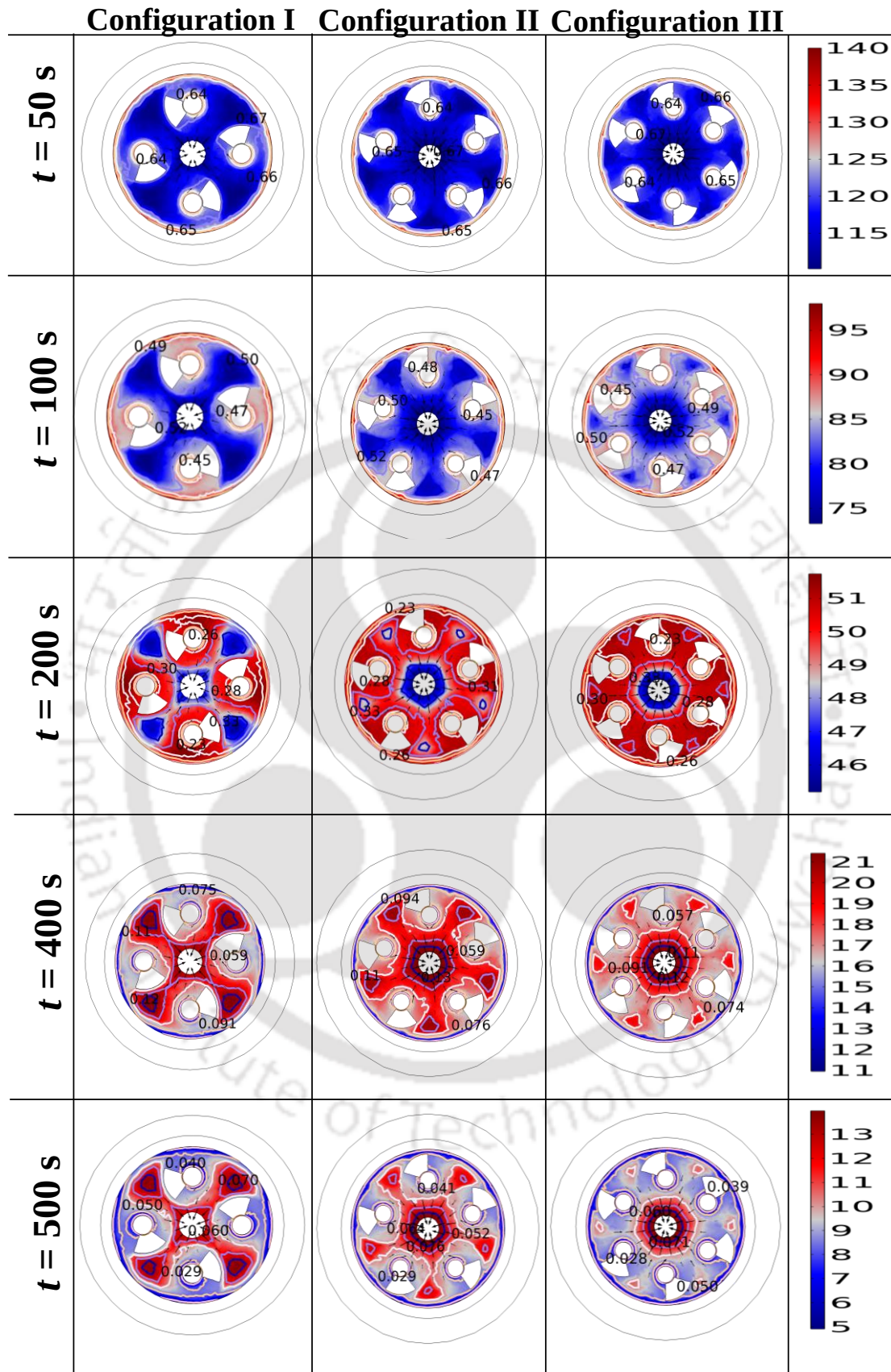


Fig. 3.10 : Spatio-temporal distribution of volumetric discharge rate (L/h) and reacted fraction at the midplane for 3 considered configuration

The detailed reactor specifications and photographs taken during and after fabrication are presented in Fig. 3.11. Post-fabrication, all joints were inspected using a dye penetrant test and subsequently leak-tested by maintaining the reactor under pressurized argon at 150 bar overnight.

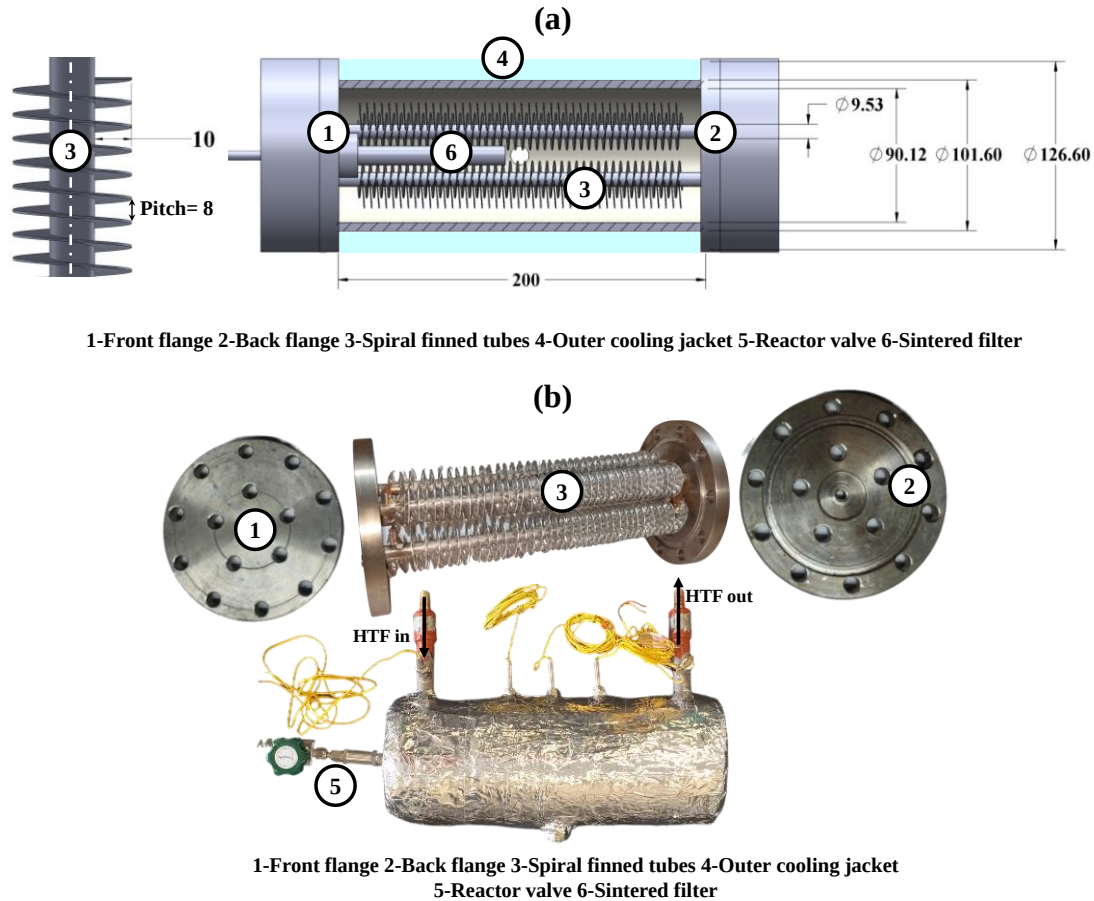


Fig. 3.11: (a) Detailed schematic of the multi-spiral finned reactor with an outer cooling jacket and (b) Pictorial representation of various components

3.10 Selection of alloys

The selection of the suitable metal hydride alloys is a fundamental component in the design and development of thermal hydrogen compressors. The alloys are selected based on parameters such as the maximum hydrogen supply pressure available at the source, maximum source temperature, targeted delivery pressure, choice of heat transferring fluid and thermo-kinetic interaction amongst the alloys. The following technical specifications were outlined based on which the screening of alloys was conducted:

- Low hydrogen supply pressure: 10-20 bar
- Maximum source temperature available: 120-130 °C
- Targeted delivery pressure: 250-300 bar
- Hydrogen storage capacity: 6000 l of hydrogen

To operate according to the given constraints, an absorption temperature of 5-20 °C while the desorption set point of 80-90 °C was chosen. The AB₅ and AB₂ type alloys were primarily considered as the candidate MH materials corresponding to the intended delivery pressure and the established temperature range. LaNi₅ based AB₅ type alloy was chosen as the primary stage alloy due to its ability to absorb hydrogen at a lower supply pressure, excellent reaction kinetics, easy activation characteristics and greater thermal stability. Further, Ti-Cr-Mn based AB₂ type alloy was chosen as the final stage alloy to obtain higher plateau pressure at moderate temperature (<100 °C) and lower hysteresis.

Extensive literature review indicates that partial substitution of Lanthanum with Cerium in LaNi₅ enhances the plateau pressure, albeit with a trade-off in hydrogen storage capacity. Thus, to balance these effects, La_{0.8}Ce_{0.2}Ni₅ was selected as the primary stage alloy. For the final stage, a Ti-Cr-Mn-based alloy, Ti_{0.8}Zr_{0.2}CrMn_{0.3}Fe_{0.6}Ni_{0.1}, capable of achieving pressures up to 350 bar at 120 °C, was chosen. To thermodynamically couple these two alloys, La_{0.5}Ce_{0.5}Ni₄Fe and MnNi_{4.7}Fe_{0.3} were identified as suitable intermediate-stage materials. Owing to its cost-effectiveness and availability, La_{0.5}Ce_{0.5}Ni₄Fe was employed as the intermediate alloy in the present study. Summarising, the MH alloys used in the present multi-stage thermal compressors are La_{0.8}Ce_{0.2}Ni₅, La_{0.5}Ce_{0.5}Ni₄Fe and Ti_{0.8}Zr_{0.2}CrMn_{0.3}Fe_{0.6}Ni_{0.1}.

3.10.1 Preparation of the alloys

The metal hydride alloys were procured from the Institute of Resources Utilization and Rare Earth Development (IRURD), China, in the form of chips ranging from 5 to 10 mm. Prior to reactor loading, the alloys were subjected to ball milling to obtain powder form. The ball milling was performed using a Multi-Chamber Attrition Planetary Ball Mill Machine (Make: Insmart Systems), available in the Materials Science Laboratory at IIT Guwahati. Hardened steel balls of 9 mm diameter, each weighing approximately 2 g, were used as the grinding media. Around 100 balls were loaded into each bowl. Each bowl was charged with 600 g of alloy, maintaining a ball-to-powder mass ratio of 1:3. Four such bowls were mounted on the planetary wheel, which was operated at 180 RPM to achieve a target particle size of $\geq 200 \mu\text{m}$. The milled alloy was subsequently sieved to remove finer particles. The step-by-step ball milling procedure is illustrated in Fig. 3.12.

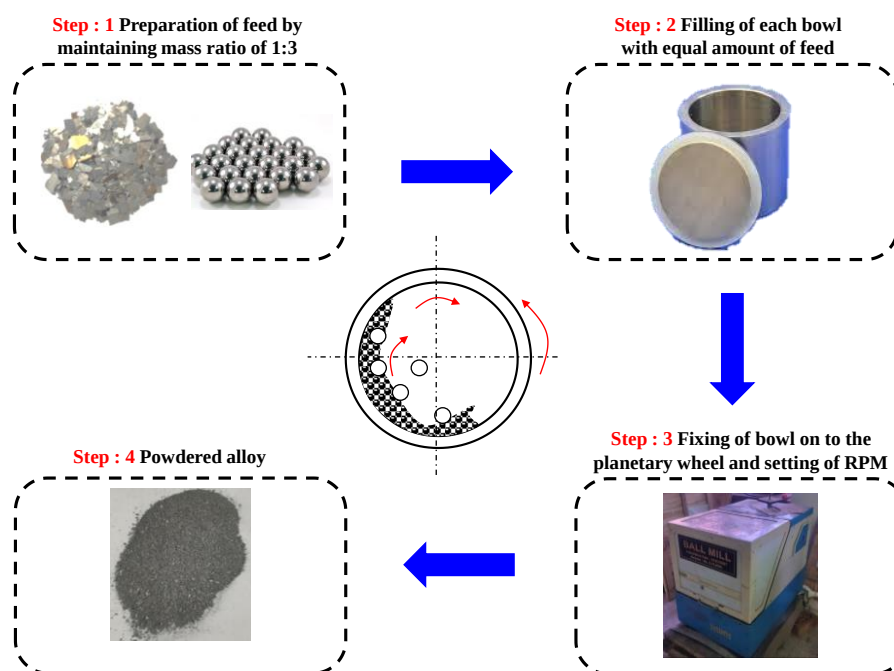


Fig. 3.12 : Systematic steps undertaken for preparation of alloy

3.10.2 Characterization of alloys

Scanning Electron Microscopy/ Energy Dispersive X-ray Spectroscopy

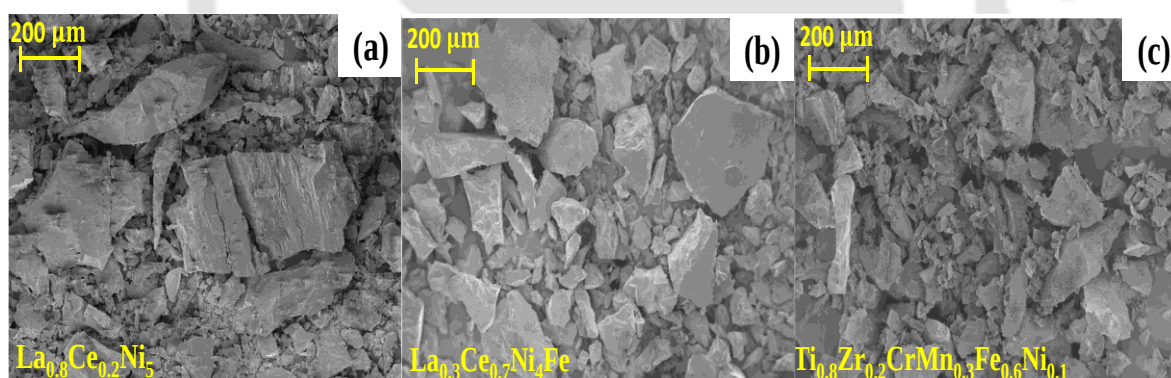


Fig. 3.13: SEM images of (a) $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ni}_5$, (b) $\text{La}_{0.3}\text{Ce}_{0.7}\text{Ni}_5\text{Fe}$ and (c) $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMn}_{0.3}\text{Fe}_{0.6}\text{Ni}_{0.1}$

The surface morphology and elemental composition of the all the alloys were analysed using Scanning Electron Microscopy (SEM) coupled with Energy Dispersive X-ray Spectroscopy (EDX). The alloy sample, prepared post-ball milling, was mounted on a carbon stub and sputter-coated with a thin gold layer to prevent charging during imaging. SEM images at varying magnifications revealed a heterogeneous microstructure with irregularly shaped particles. The average particle size was observed to be approximately 100-200 μm for all the alloys, consistent with the target size obtained through controlled ball milling as illustrated in Fig. 3.13. EDX analysis (Table 3.10) revealed that the experimentally derived atomic

percentages closely matched the empirical formula specified by the vendor, namely $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ni}_5$.

Table 3.10 : Elemental distribution from EDX analysis versus theoretical atomic ratios for $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ni}_5$

$\text{La}_{0.8}\text{Ce}_{0.2}\text{Ni}_5$	Zone 1		Zone 2		Zone 3		Theoretical	
	wt%	at%	wt%	at%	wt%	at%	wt%	at%
Ni	82.9	92	82.4	91.7	82.2	91.6	67.8	83.3
La	13.7	6.4	13.9	6.5	14.3	6.7	25.7	13.3
Ce	3.4	1.6	3.7	1.7	3.5	1.6	6.5	3.3

Based on averaged atomic percentage data obtained from three EDX measurement sites Table 3.11, the experimental composition of the alloy approximates $\text{La}_{0.27}\text{Ce}_{0.73}\text{Ni}_{4.12}\text{Fe}_{0.87}$. This closely resembles the empirical formula specified by vendor, namely $\text{La}_{0.3}\text{Ce}_{0.7}\text{Ni}_4\text{Fe}$.

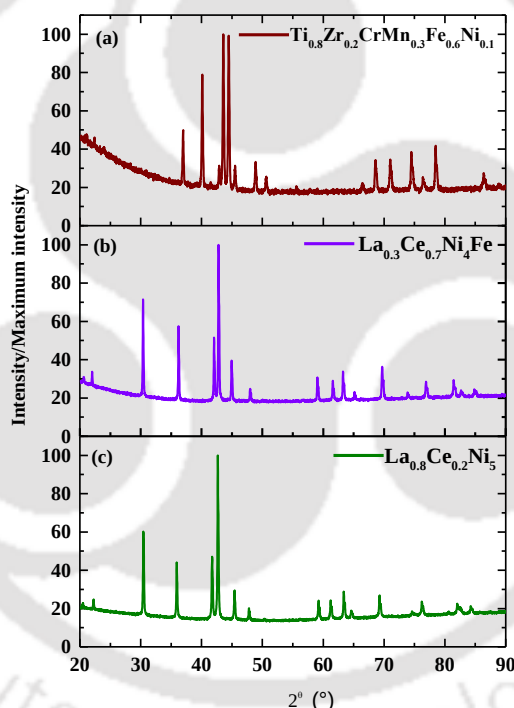
Table 3.11 : Elemental distribution from EDX analysis versus theoretical atomic ratios for $\text{La}_{0.3}\text{Ce}_{0.7}\text{Ni}_5\text{Fe}$

$\text{La}_{0.3}\text{Ce}_{0.7}\text{Ni}_5\text{Fe}$	Zone 1		Zone 2		Zone 3		Theoretical	
	wt%	at%	wt%	at%	wt%	at%	wt%	at%
Ni	53.5	67.2	52.7	66.4	57.3	70.6	54.6	66.7
Ce	26.4	13.9	24.2	13	25	12.8	13	16.7
La	10.5	13.9	11.7	15.3	10.9	13.9	22.8	11.7
Fe	9.6	5.1	11.4	5.3	6.8	2.7	9.7	5

The empirical formula determined from EDX analysis (Table 3.12) was found to be $\text{Ti}_{0.87}\text{Zr}_{0.13}\text{CrMn}_{0.31}\text{Fe}_{0.57}\text{Ni}_{0.15}$. The experimental formula closely resembles the intended $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMn}_{0.3}\text{Fe}_{0.6}\text{Ni}_{0.1}$ composition. Slight deviations include Ti enrichment and Zr, Fe underrepresentation, likely due to surface segregation or EDX detection sensitivity.

Table 3.12 : Elemental distribution from EDX analysis versus theoretical atomic ratios for $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMn}_{0.3}\text{Fe}_{0.6}\text{Ni}_{0.1}$

$\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMn}_{0.3}\text{Fe}_{0.6}\text{Ni}_{0.1}$	Zone 1		Zone 2		Zone 3		Theoretical	
	wt%	at%	wt%	at%	wt%	at%	wt%	at%
Cr	32.6	34.9	30	32	31.4	33.6	23.3	33.3
Ti	25.8	30.5	27	32.7	28.2	34.4	11.1	26.7
Fe	18.6	18.3	20.6	20.2	18.9	18.6	31.6	20
Mn	9.9	10.5	10.8	11.4	10.4	11.2	10	10
Zr	8.0	3.6	8.5	3.8	6.9	3	20.4	6.7
Ni	5.1	2.3	3	2	4.1	2.2	3.6	3.3

X-ray diffractionFig. 3.14: XRD pattern of alloys (a) $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMn}_{0.3}\text{Fe}_{0.6}\text{Ni}_{0.1}$ (Stage:3), (b) $\text{La}_{0.3}\text{Ce}_{0.7}\text{Ni}_4\text{Fe}$ (Stage:2), and (c) $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ni}_5$ (Stage:1)

The X-ray diffraction (XRD) analysis was performed using a $\text{Cu-K}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$) and the corresponding pattern is shown in Fig. 3.14. Data were collected over a 2θ range of 20° to 100° , with a step size of 0.02° and a scan speed of $20^\circ/\text{min}$. Both $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ni}_5$ and $\text{La}_{0.3}\text{Ce}_{0.7}\text{Ni}_4\text{Fe}$ retained the CaCu_5 -type hexagonal structure of LaNi_5 (space group: $P6/mmm$), with refined lattice parameters of $a = 4.98 \text{ \AA}$, $c = 3.96 \text{ \AA}$ and $a = 4.94 \text{ \AA}$, $c = 4.03 \text{ \AA}$, respectively. Partial substitution of La with Ce resulted in a decrease in unit cell volume

from 86.71 nm³ (LaNi₅) to 85.04 nm³ for La_{0.8}Ce_{0.2}Ni₅ and 84.96 nm³ for La_{0.3}Ce_{0.7}Ni₄Fe, indicating lattice contraction due to the smaller atomic radius of Ce. Ti_{0.8}Zr_{0.2}CrMn_{0.3}Fe_{0.6}Ni_{0.1} based AB₂ type alloy was identified as a single-phase C14 Laves intermetallic hydride with a hexagonal crystal structure. The refined lattice parameters were determined to be $a = 4.541 \text{ \AA}$ and $c = 8.095 \text{ \AA}$.

Pressure-Composition-Temperature (PCT) plots of alloys

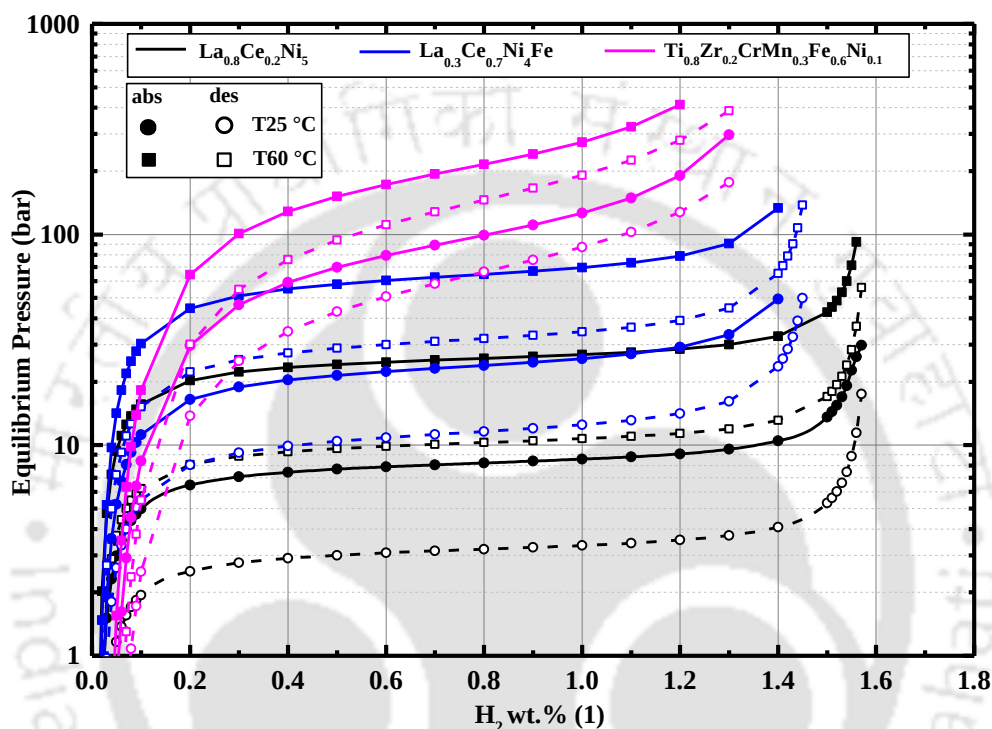


Fig. 3.15 : PCT plot for La_{0.8}Ce_{0.2}Ni₅ (black), La_{0.3}Ce_{0.7}Ni₄Fe (blue), and Ti_{0.8}Zr_{0.2}CrMn_{0.3}Fe_{0.6}Ni_{0.1} (pink)

The pressure-concentration-temperature (PCT) of the selected alloys are shown in Fig. 3.15. Based on the PCT plot of the employed alloys at two different temperatures, thermophysical properties such as formation enthalpy (ΔH), entropy (ΔS), and hysteresis (γ) were determined using the van't Hoff plot for both absorption and desorption reactions. These values were obtained by measuring the equilibrium pressure at the midpoint of the plateau at each temperature (i.e., 0.75 H₂ wt% for La_{0.8}Ce_{0.2}Ni₅, 0.65 H₂ wt% for La_{0.3}Ce_{0.7}Ni₄Fe, and 0.65 H₂ wt% for Ti_{0.8}Zr_{0.2}CrMn_{0.3}Fe_{0.6}Ni_{0.1}). Table 3.13 presents the thermophysical properties for all the alloys during absorption and desorption. The AB₅-type alloys (La_{0.8}Ce_{0.2}Ni₅ and La_{0.3}Ce_{0.7}Ni₄Fe) were observed to possess higher hysteresis and a lower sloping plateau compared to the AB₂-type alloy (Ti_{0.8}Zr_{0.2}CrMn_{0.3}Fe_{0.6}Ni_{0.1}) used in the final stage. Based on these values, the predicted mid-plateau equilibrium absorption pressure at 5 °C are 3.8 bar,

11.9 bar, and 55.3 bar, while during desorption at 60 °C, they are 10.3 bar, 31.5 bar, and 145.7 bar for stage 1, stage 2, and stage 3 alloys, respectively.

Table 3.13 : Thermophysical properties of the alloys used

	(ΔH_{abs}) (kJ/mol)	(ΔS_{abs}) (kJ/mol/K)	(ΔH_{des}) (kJ/mol)	(ΔS_{des}) (kJ/mol/K)	Hyste resis (γ)	Storage capacity (wt.%)
Stage 1: La _{0.8} Ce _{0.2} Ni ₅	27	0.105	27.5	0.105	0.74	1.4
Stage 2: La _{0.5} Ce _{0.5} Ni ₄ Fe	23.5	0.103	24	0.1028	0.497	1.3
Stage 3: Ti _{0.8} Zr _{0.2} CrMn _{0.3} Fe _{0.6} Ni _{0.1}	18.3	0.098	18.5	0.0976	0.157	1.3

3.11 Summary

This chapter presented the comprehensive design methodology adopted for both the industrial-scale and prototype reactor configurations intended for metal hydride-based hydrogen compressor applications. It also highlighted the fabrication challenges encountered during the construction of the finalized reactor configuration. Most importantly, the chapter detailed the development of a robust numerical model applicable to a wide range of MH-based hydrogen systems, encompassing scenarios from single-reactor operation to coupled multi-reactor configurations.

Chapter 4

Development of the experimental set up

4.1 Preface

This chapter details the development of the experimental setup for a multi-stage metal hydride-based hydrogen compressor (MSMHHC). The setup was designed to facilitate comprehensive testing and performance evaluation of metal hydride hydrogen compression under various configurations. The test setup consists of three primary sections: reactor assembly, heat transfer fluid (HTF) circulation system, and gas transfer circuit. The reactor assembly was modular, allowing for easy modification of reactor configurations by replacing individual reactors. Additionally, the number of compression stages could be adjusted with minor modifications, which are discussed in detail in this chapter. The system was developed to enable detailed parametric studies, covering single-reactor performance evaluation, coupled-reactor interaction analysis, and external hydrogen storage cylinder refilling. This versatile setup provides a robust platform for investigating hydrogen compression dynamics, optimizing system parameters, and assessing real-world applications of MSMHHC technology.

4.2 Components of experimental setup

An experimental setup was developed with MH reactors, tubes, hoses, tube fittings, and valves for the gas circuit, hot and cold constant temperature recirculating baths for facilitating effective heat transfer (supplying and removing heat from MH bed), gas cylinders for supplying and storing compressed hydrogen, vacuum pump for evacuation, Coriolis mass flow meter (CFM) for measuring the amount of hydrogen transferred and a data acquisition system (DAQ) for monitoring and recording temperature and pressure changes throughout the experiment. Needle valves were used as reactor valves while ball valves were used as gas circuit valves. Pressure regulators were used to deliver hydrogen from gas cylinders at a constant pressure while keeping an eye on the pressure reading recorded by the pressure transmitters. The number of pressure transmitters used was according to the number of stages employed in the compressor (one in each stage, accuracy: $\pm 0.5\%$ of full scale and make: Equinox). K-type thermocouple (accuracy: ± 0.5 °C make: Industrial Heaters) were used to measure the temperature at different location within the MH bed and the heat transfer fluid (HTF). The CFM (accuracy: 0.25% of flow rate, make: Emerson) was used to measure the rate of hydrogen transferred through the circuit. Hot and cold constant temperature baths (accuracy: ± 0.5 °C, make: Siskin) were used to supply/remove the heat required/generated by the MH bed using

suitable HTF. A helix type positive displacement flow rate meter (make: ATN Instruments) was used to measure the flow rate of HTF (water in this case) during the experiment. SS316 ball valves of ½ inch size were used to control the direction and the flowrate of water flowing through the HTF circuit. The temperature, pressure and the hydrogen flow rate were measured and recorded for every second by using DAQ (make: Keysight Technologies). The reactors were insulated to reduce the heat loss to ambient by wrapping multiple layers of nitrile rubber.

4.3 Experimental Protocol

The whole experiment can be divided into three major steps: absorption of hydrogen at low pressure, sensible heating and transfer of hydrogen from lower stage to higher stage and filling of hydrogen cylinder from the final stage. The detailed procedures followed during each of these steps are mentioned below:

4.3.1 Absorption of hydrogen at low pressure

Initially, stage 1 reactors were maintained at temperature ranging from 5-20 °C by recirculating HTF through the HTF line from cold water bath. Further, the reactors were supplied with hydrogen ($P_{inj} = 10\text{-}50$ bar) from the supply cylinder. The variations of temperature in the reactor assembly were monitored through DAQ. Once the temperature was attained, gas circuit valves were opened. The hydrogen gas cylinder was then opened, at fixed supply pressure with the aid of pressure regulator. The pressure within the gas circuit were also checked with the help of P1 transducer. Further, reactor valve was opened to charge reactor 1 (or reactor 2). The direction of the gas flow through CFM was always maintained unidirectional. As the absorption is an exothermic reaction, the cold-recirculating bath was constantly operated to remove the generated heat. At the end of absorption, the valves were closed firmly to prevent the leakage.

4.3.2 Sensible heating and transfer of hydrogen from desorbing reactor to absorbing reactor

Once the low-pressure (LP) stage reactors completely absorb hydrogen, it was sensibly heated (50-90 °C) to pressurize the hydrogen absorbed by the MH bed. The sensible heating was facilitated by recirculating hot HTF through the HTF circuit and the reactors. The gas circuit valves were kept closed, while the reactor valves were kept open to record the pressure rise in the reactor bed through the respective pressure transducer. Meanwhile, the high-pressure (HP) stage reactors were prepared for absorption by maintaining a lower temperature (5-20 °C) depending on the P-C-T of the alloy by recirculating cold HTF through cold-recirculating bath. Once the required pressure and temperature were attained, gas circuit valves were opened to guide the flow of hydrogen from the desorbing reactor (LP reactor) to the absorbing reactor

(HP reactor) via CFM. Once the hydrogen transfer was complete, all the reactor and gas circuit valves were firmly shut to prevent any leaks.

4.3.3 Refilling of empty gas cylinder

Once hydrogen was absorbed by the final-stage reactors, they were sensibly heated to achieve the required delivery pressure. The detailed sensible heating procedure is outlined in the previous section. During this process, pressure was continuously monitored using a transducer connected to a DAQ system interfaced with a PC by keeping the reactor valves open. Once the target pressure was reached, the hot recirculating bath temperature was stabilized by switching off the heater while maintaining continuous HTF recirculation through the HTF circuit. Before initiating hydrogen discharge, the reactor valves of the final stage were closed to isolate the system. To transfer hydrogen into the empty cylinder, the corresponding gas circuit valves were opened, followed by the gradual opening of the reactor valve to prevent mechanical failure due to rapid gas expansion. Throughout the desorption process, the maximum pressure limit was carefully monitored using the transducer readings from the gas circuit. Once hydrogen transfer was complete, all reactor and circuit valves were securely closed, and the hot recirculating bath was shut down.

4.4 Experimental Setup for multi-stage MHHC

4.4.1 Dual stage MHHC set up

The dual-stage experimental setup comprised a multi-spiral finned reactor with an outer cooling jacket in the primary stage, while the final stage featured a pair of tubular reactors equipped with an outer cooling jacket. The reactors were integrated with inline filters, reactor valves (V_{g3} , V_{g7} and V_{g8}), and pressure transducers (P1 and P2), all housed within the reactor assembly. The gas circuit included strategically placed gas circuit valves (V_{g1} , V_{g2} , V_{g4} - V_{g6} , V_{g9} - V_{g12}) to ensure unidirectional hydrogen flow through the CFM during all operations. Additionally, a pressure transducer (P3) was installed to monitor the pressure within the gas circuit. For thermal management, the HTF circuit was equipped with recirculating baths and HTF ball valves (V_{f1} - V_{f8}), ensuring precise temperature control during the compression process. The schematic circuit diagram of the dual-stage MHHC, along with the detailed flow diagram of its cyclic operation, are presented in Fig. 4.1 and Fig. 4.2 respectively.

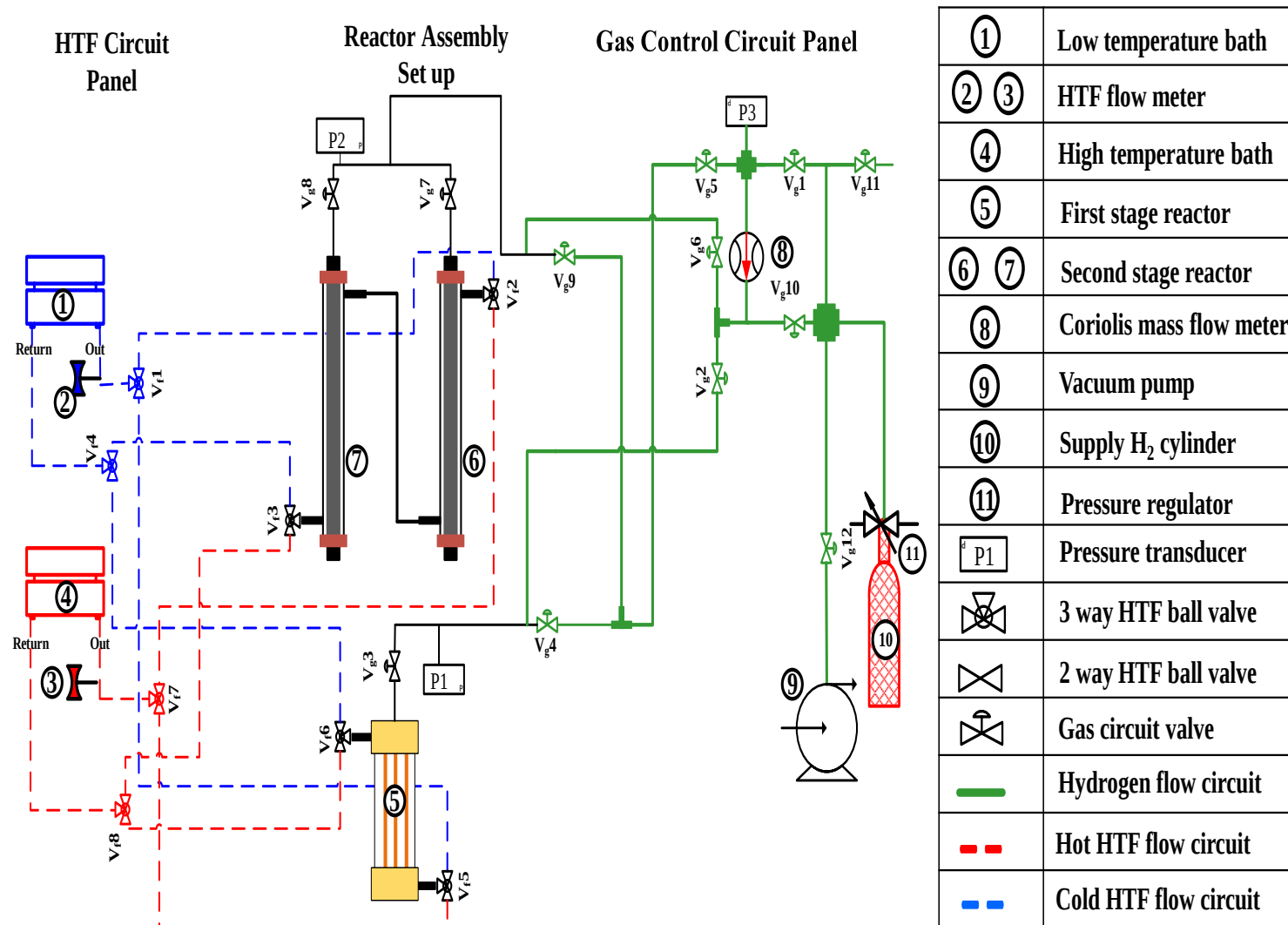


Fig. 4.1: Schematic of circuit diagram of the dual stage MHHC

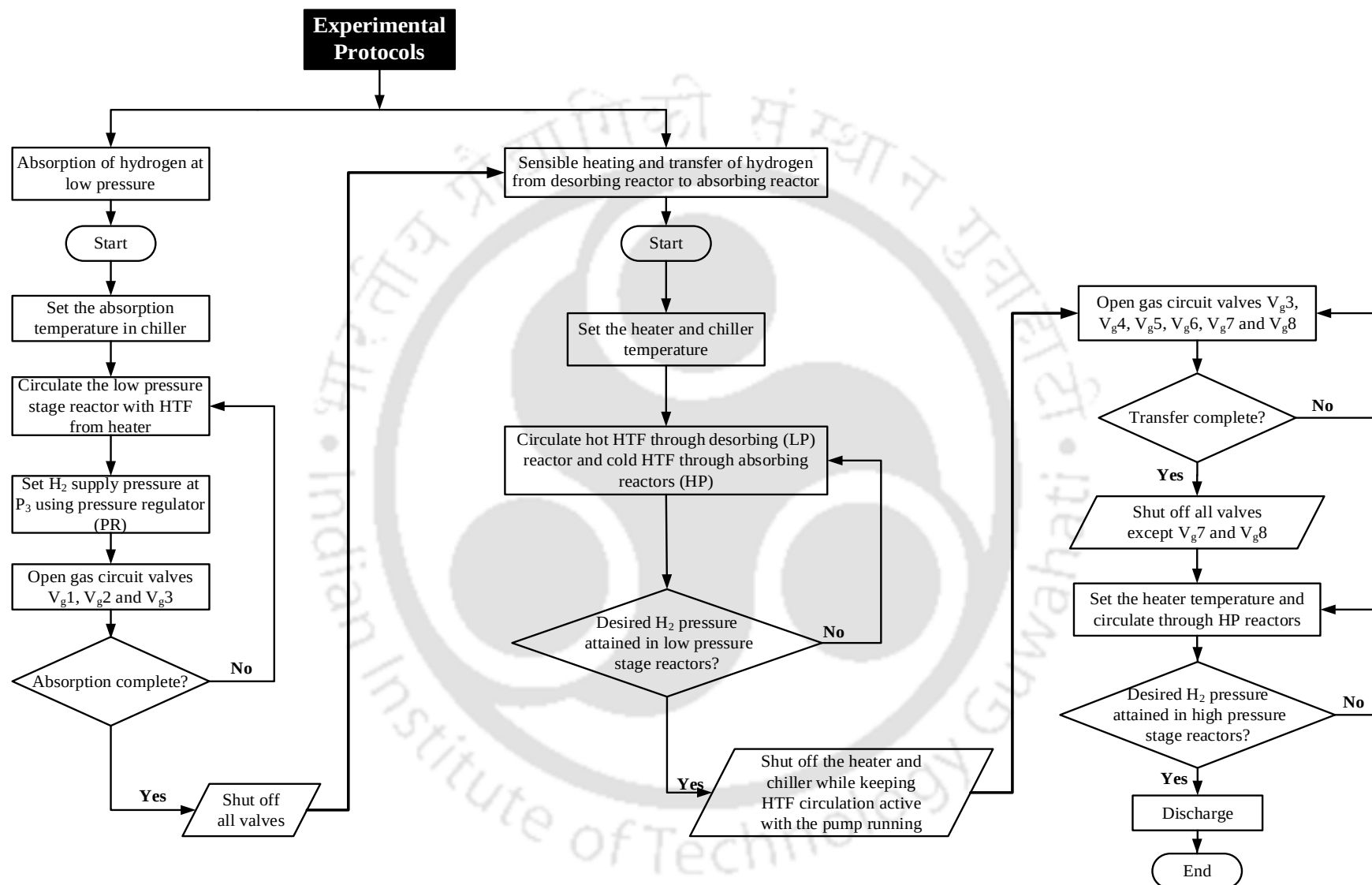


Fig. 4.2: Schematic of experimental protocol of cyclic operation of the dual stage MHHC

4.4.2 Three-stage MHHC set up

The three-stage experimental setup comprised six industrial-scale reactors (two per stage), each containing 25 kg of the corresponding alloy. To monitor temperature distribution, a total of 42 K-type thermocouples were strategically placed within the MH bed and HTF circuit. In each reactor, five thermocouples were positioned at different longitudinal locations inside the MH bed, while two thermocouples measured the HTF inlet and outlet temperatures. This thermocouple arrangement was consistently applied across all reactors. Similar to the dual-stage setup, the reactors were equipped with inline filters, reactor valves (V_{g6} - V_{g11}), and pressure transducers (P1, P2 and P3), all housed within the reactor assembly. The gas circuit consisted of gas circuit valves (V_{g1} - V_{g5} and V_{g12} - V_{g17}), a CFM, and an additional pressure transducer (P4). However, unlike the dual-stage system, the three-stage compressor incorporated an empty hydrogen cylinder in addition to the supply hydrogen cylinder, enabling post-compression hydrogen storage. For thermal management, the HTF circuit utilized recirculating baths with a greater number of HTF ball valves (V_{f1} - V_{f8}) to accommodate the increased system complexity. The schematic circuit diagram of the three-stage MHHC, along with the detailed flow diagram of its cyclic operation, are presented in Fig. 4.3 and Fig. 4.4.

In both setups, the cold-HTF line is marked in blue, the hot-HTF line in red, the gas circuit line in green, and the reactor assembly in black. Additionally, single-reactor performance analysis can be conducted in each system by modulating the valves as per the specific experimental requirements. The pictorial representation of the developed dual-stage (prototype) compressor and the three-stage (industrial-scale) compressor is shown in Fig. 4.5 and Fig. 4.6, respectively. The industrial-scale setup is currently deployed at NTPC NETRA, Greater Noida.

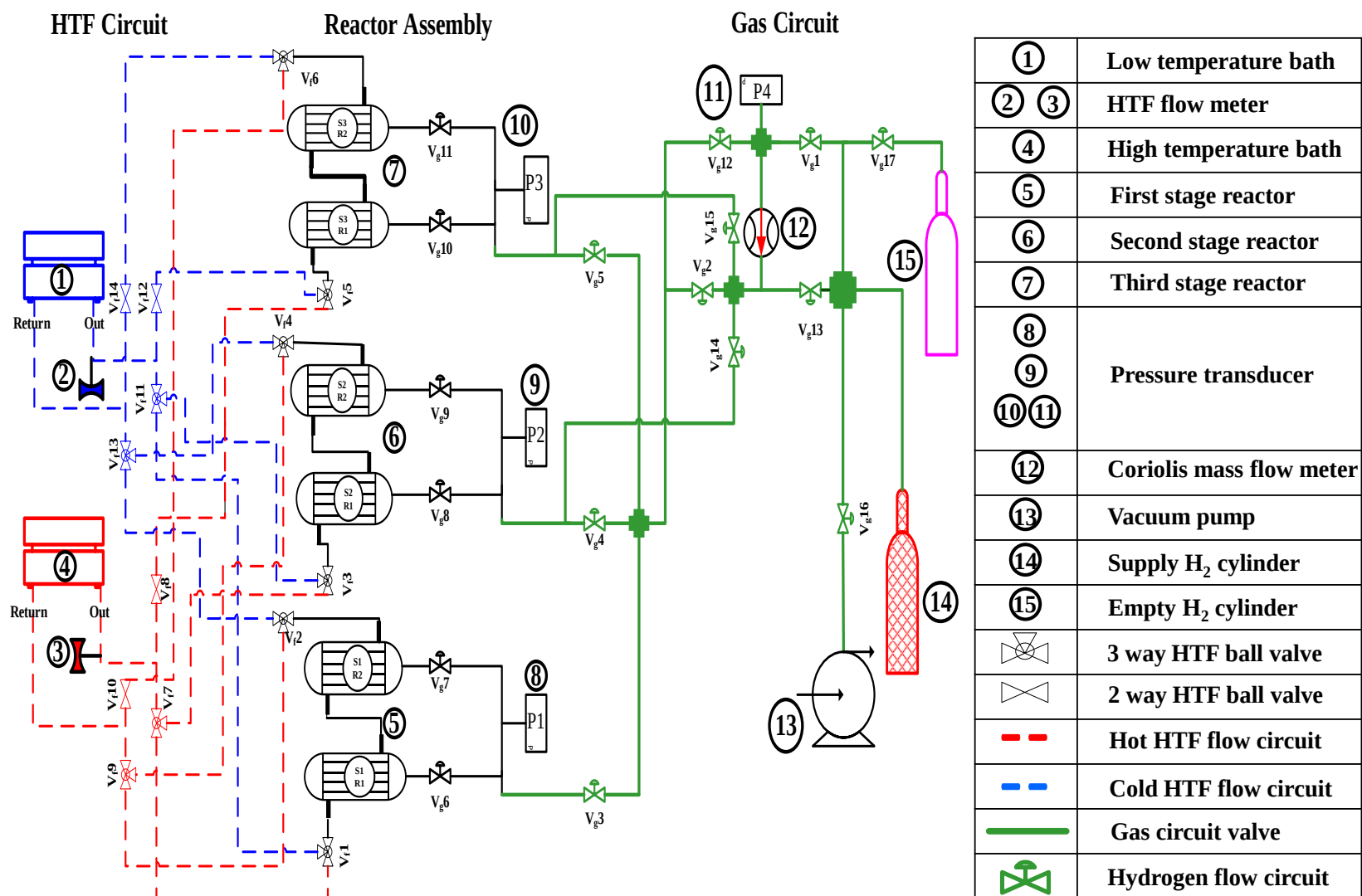


Fig. 4.3: Schematic of circuit diagram of the three stage MHHC

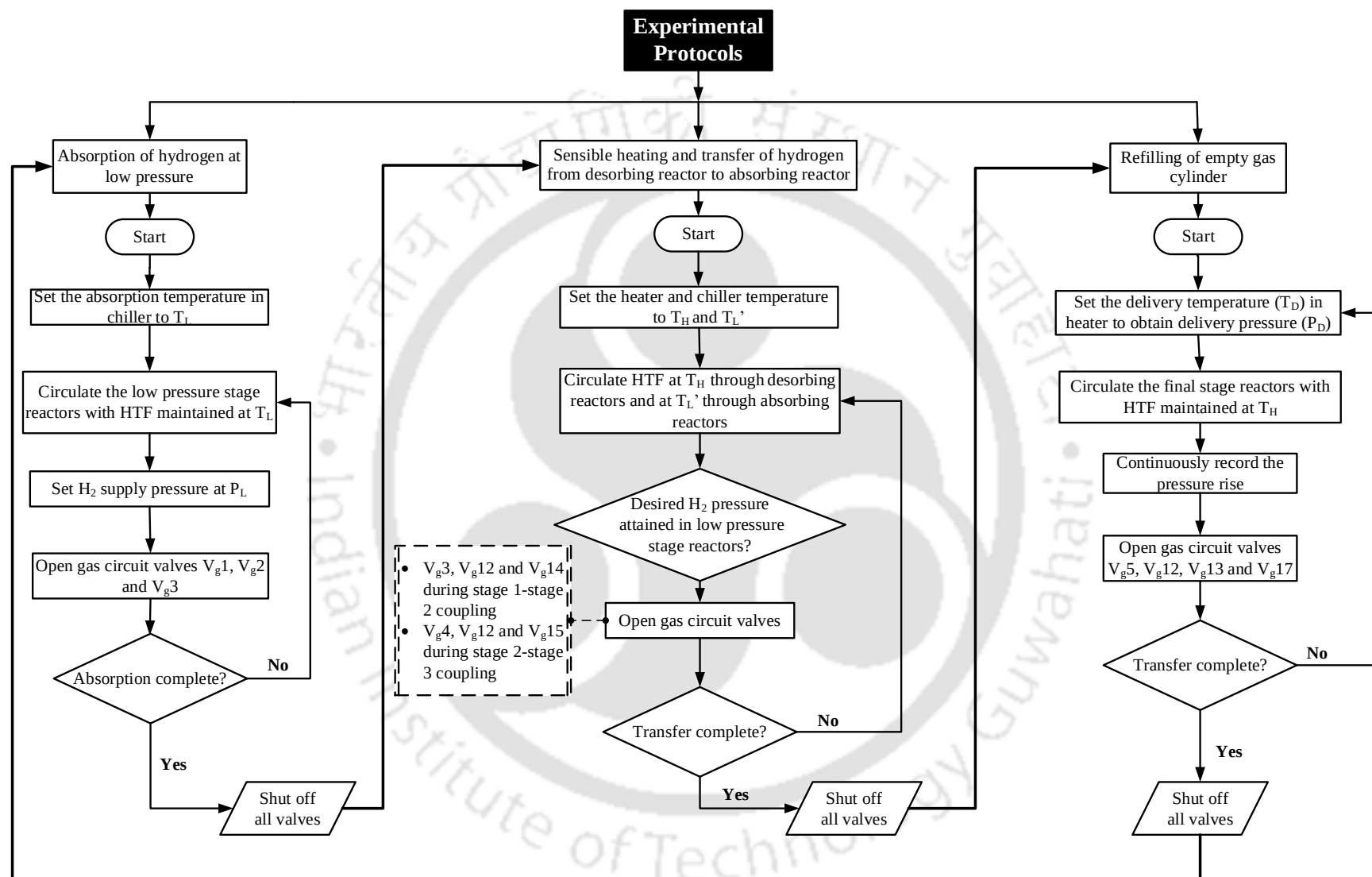
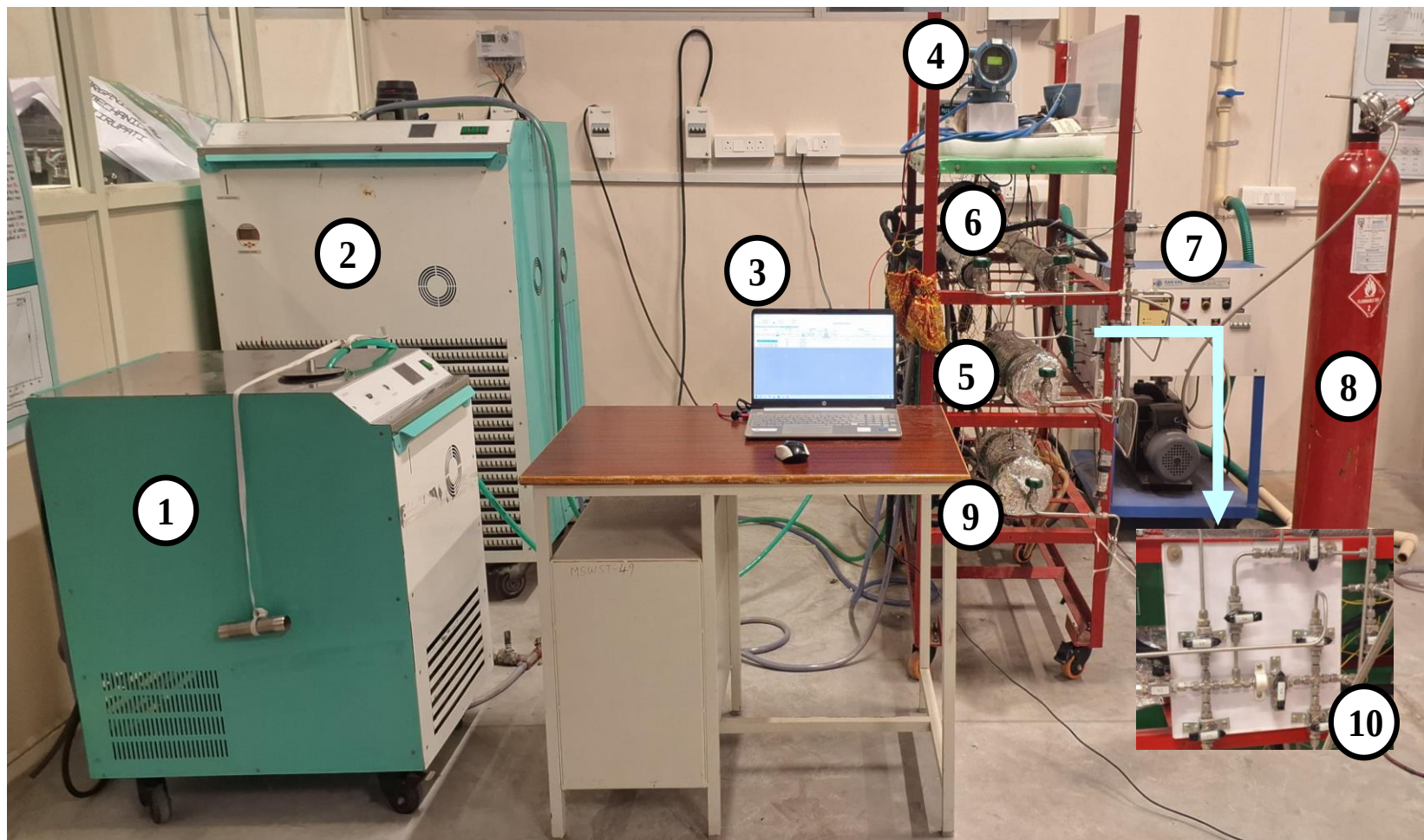


Fig. 4.4: Schematic of experimental protocol of cyclic operation of the three stage MHHC



1-Hot recirculating bath 2-Cold recirculating bath 3-Desktop 4-Coriolis mass flow meter 5-First stage reactor 6-Second stage reactors 7-Vacuum pump 8-H₂ supply cylinder 9-Additional low pressure reactor 10-Gas controlling circuit panel

Fig. 4.5 : Pictorial view of the dual stage MHHC set up



1-Cold recirculating bath 2-Hot recirculating bath 3-H₂ empty cylinder 4-H₂ supply cylinder 5- HTF circuit panel
6-First stage reactors 7-Second stage reactors 8-Third stage reactors 9-Coriolis mass flow meter
10-Gas circuit panel 11-Vacuum pump 12-PC

Fig. 4.6: Pictorial view of the three stage MHC set up

4.5 Summary

This chapter provides a comprehensive overview of the experimental setup for MSMHHC, detailing the equipment specifications and operational principles within the experimental framework. It explains the HTF flow dynamics and gas circuit operation during low-pressure hydrogen absorption, sensible heating, reactor coupling across two stages, and compressed hydrogen refilling into an empty gas cylinder. Additionally, the chapter highlights the key differences between the dual-stage and three-stage compressor systems, each designed for distinct operational requirements



Chapter 5

Activation and identification of optimum parameters of alloys

5.1 Preface

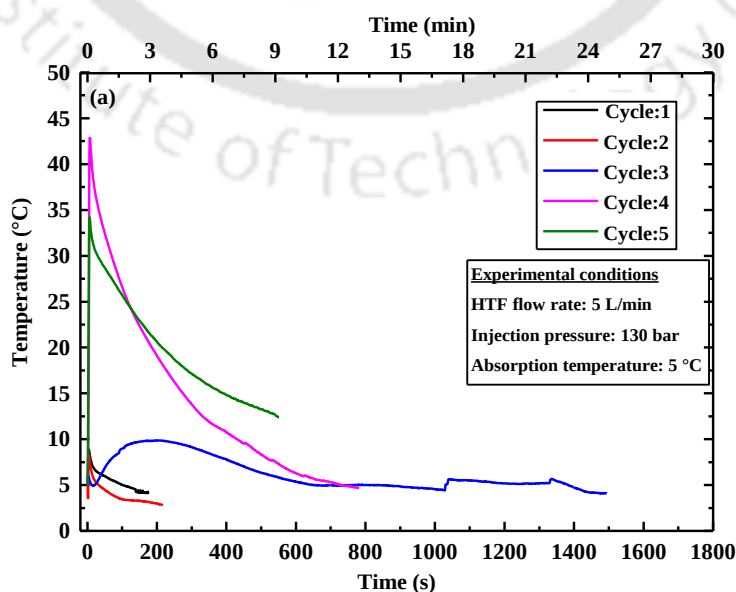
In the previous chapter, the development and fabrication of the experimental setup were discussed in detail. It is important to note that the setup was designed not only for hydrogen compression studies but also to enable comprehensive storage characterization of individual reactors. This allowed for the identification of optimal operating parameters and evaluation of hydrogen storage performance under varying conditions. Reactor configurations have been outlined in Chapter 3. The current chapter presents the detailed activation strategies employed for each stage reactor, configured with distinct alloys at both prototype and industrial scales. Additionally, it includes extensive parametric studies conducted to determine the optimal pressure and temperature ranges for each alloy.

5.2 Study on $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMn}_{0.3}\text{Fe}_{0.6}\text{Ni}_{0.1}$

5.2.1 Activation strategy

Prototype reactor

Before activation, the gas circuit, including the MH reactor, was checked for leaks by pressurizing the system with argon at 100 bar and monitoring the pressure overnight using a pressure transducer. After confirming no leaks, the circuit and reactor were evacuated to 10^{-5} bar while heating to 100 °C for 2 h by circulating HTF from a hot bath.



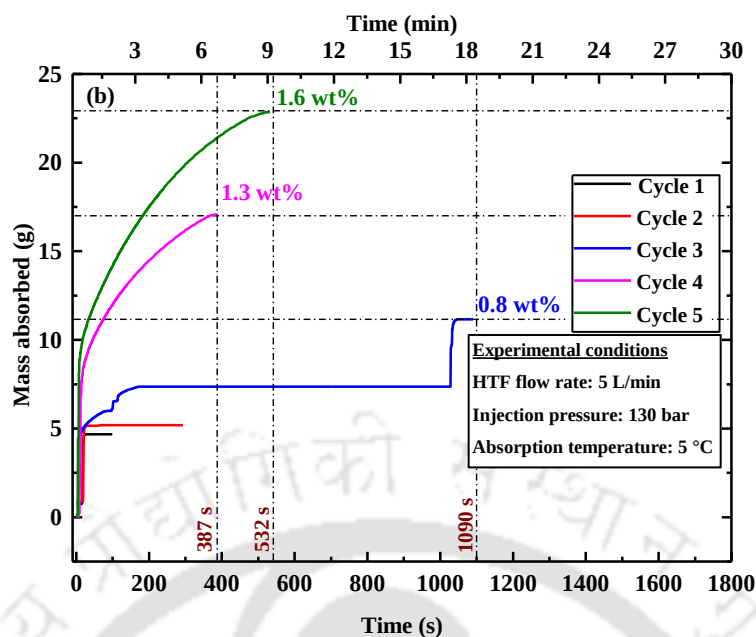


Fig. 5.1: Activation cycles on prototype reactor (a) temperature variation and (b) variation in mass of hydrogen absorbed

The reactor was then cooled to 5 °C using HTF from a cold bath. Once the system stabilized at 5 °C, the alloy was exposed to hydrogen (99.999% purity) at 130 bar. In the first cycle, the alloy absorbed only 4.68 g (0.3 wt%). The reactor was reheated to 100 °C to release the absorbed hydrogen, and heating continued for 2 h. The bed was then cooled again to 5 °C and supplied with hydrogen at 130 bar. In the third cycle, the gravimetric capacity improved to 0.8 wt%, but the absorption rate was slow, taking 1090 s to absorb 11.16 g of hydrogen. Hydrogenation and dehydrogenation cycles were repeated until consistent absorption rates and maximum storage capacity were achieved over three consecutive cycles. The activation process required five cycles under the specified conditions. By the fifth cycle, the alloy absorbed 22.85 g (1.6 wt%) of hydrogen within 532 s, confirming successful activation. The HTF flow rate was maintained at 5 L/min throughout. Fig. 5.1 shows the temperature profile and hydrogenation characteristics during the first five cycles.

Industrial scale reactor

The activation of high-pressure AB₂-type alloys on a large scale (>10 kg) has been rarely reported. Large-scale activation is challenging due to the limited hydrogen availability above 120 bar in Type I cylinders. To address this, a customized activation methodology was developed. This section presents the activation results of the large-scale reactor (Fig. 5.2 (a-c)), containing 25 kg of Ti_{0.8}Zr_{0.2}CrMn_{0.3}Fe_{0.6}Ni_{0.1}.

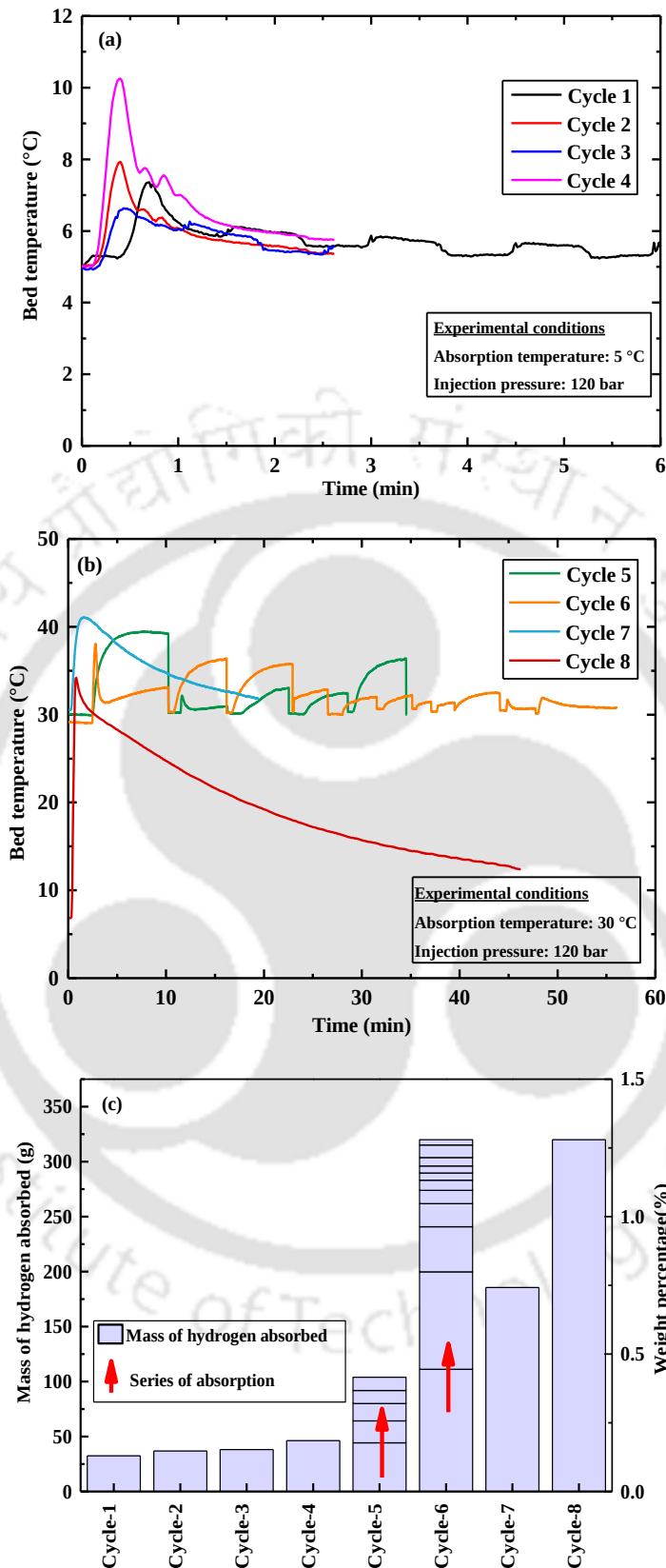


Fig. 5.2: Activation cycles on industrial-scale reactor with 25 kg alloy (a) bed temperature variations during cycles 1–4, (b) bed temperature variations during cycles 5–8, and (c) incremental increase in cumulative hydrogen absorption across cycles 1–8.

Before activation, the reactor was leak-tested at 120 bar using argon and monitored overnight. After confirming no leakage, the argon was purged, and the reactor was heated to 100 °C and evacuated for 2 h. It was then cooled to 5 °C and supplied with hydrogen at 120 bar. This approach was adopted as the available hydrogen mass above 130 bar was insufficient to remove the oxide layer from the alloy particles. During the first four hydrogenation-dehydrogenation cycles, the alloy absorbed minimal amount of hydrogen, with a maximum uptake of 46.17 g (~0.2 wt%) in the fourth cycle (Fig. 5.2 (a)). However, the alloy's performance improved in subsequent cycles, as indicated by rising peak bed temperature. Despite this improvement, the gravimetric storage density showed no significant increase. The system was subsequently heated to 220-240 °C using air as the HTF, evacuated to 10^{-3} mbar for 2 h. After this, the reactor was cooled to 30 °C before supplying hydrogen at 120 bar. The poor heat transfer properties of air as HTF resulted in high bed temperature and slower hydrogen transfer rate due to reduced heat dissipation. Hydrogen absorption was conducted after cooling the bed back to 30 °C (Fig. 5.2 (b)) without desorbing the previously absorbed hydrogen, gradually increasing the cumulative uptake to 104 g (~0.4 wt%) in Cycle 5. In the subsequent cycle, the alloy absorbed 320 g of hydrogen over 11 steps, partially confirming activation. In the following cycle, 185.6 g (~0.7 wt%) was absorbed in a single step. Finally, the reactor was switched to water circuit, and hydrogen was supplied at 120 bar from four connected Type I cylinders, with HTF circulated at 5 °C. In Cycle 8, the alloy absorbed 320 g within 50 min (Fig. 5.2 (c)).

5.2.2 Parametric studies

Influence of hydrogen injection pressure

Based on the PCT characteristics of the alloy, the influence of hydrogen injection pressure was examined by varying the pressure in 10-bar increments from 70 to 100 bar. Fig. 5.3 (a-c) illustrates the variations in temperature, pressure, and mass transfer within the bed at the investigated injection pressure throughout the operational cycle, including absorption, sensible heating, and desorption. During absorption, the HTF inlet temperature was maintained at 5 °C, while it was set to 40 °C during desorption for all cases. Post-absorption, the system was heated from 5 °C to 40 °C. HTF flow rate of 5 L/min was maintained throughout the cycle.

The bed temperature (Fig. 5.3 (a)) was observed to peak instantaneously at the onset of hydrogen interaction with the bed due to the exothermic heat generated during metal hydride formation. Interestingly, the peak bed temperature increased with higher injection pressures, reaching a maximum of 33.5 °C when the injection pressure was set at 100 bar (Fig. 5.3 (b)).

The rate of hydrogen absorbed for first 10 g (0.7 wt%) by the bed increased by approximately 2.5 times as the injection pressure rose from 70 to 100 bar.

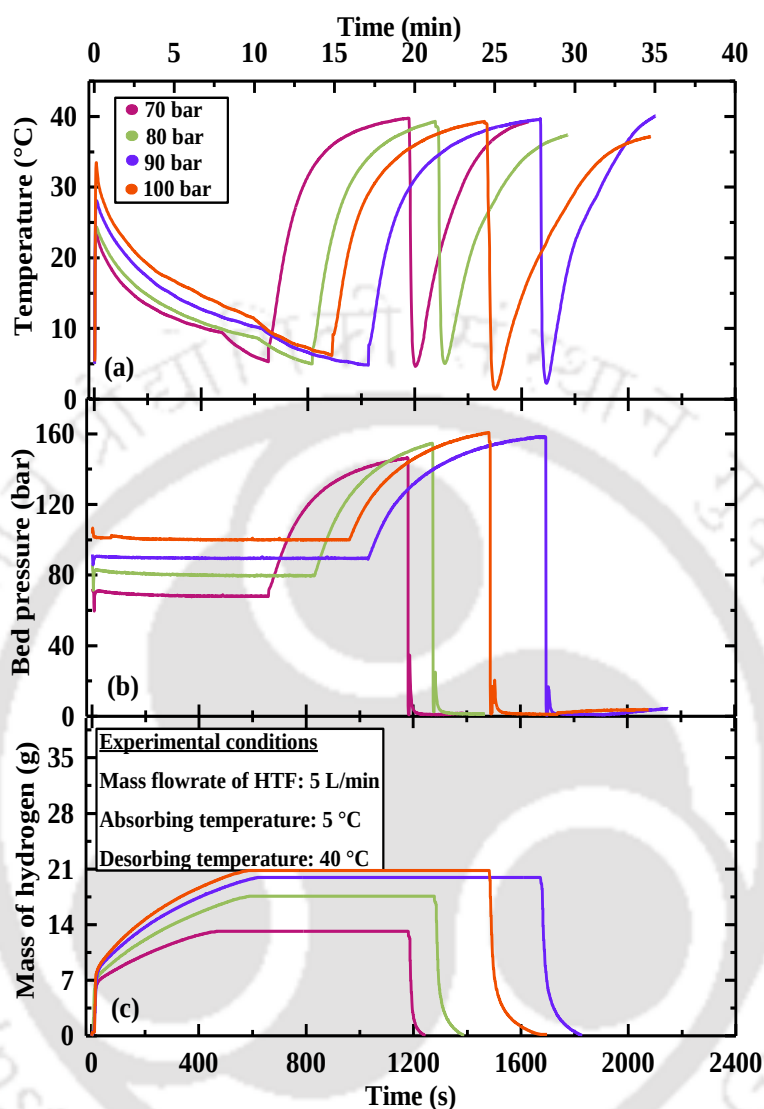


Fig. 5.3: Temporal change in (a) bed temperature variation, (b) the reactor pressure and (c) variation in mass of hydrogen transferred due to variation in injection pressure

In addition to the uptake rate, the cumulative hydrogen mass varied significantly, increasing from 13.17 g (0.9 wt%) to 20.82 g (1.5 wt%) with the same pressure range. The absorption half-cycle completed more quickly at pressures of 70 and 80 bar, but the alloy did not reach its maximum storage capacity. Maximum capacity was achieved at both 90 and 100 bar, with higher pressure reaching saturation faster. This was attributed to the larger pressure differential between the injection pressure and the instantaneous equilibrium pressure of hydrogen in the alloy bed at the corresponding temperature.

Table 5.1: Influence of injection pressure on mass transfer and duration of absorption and desorption half cycle

Injection pressure (bar)	Mass of H ₂ absorbed (g)	Absorption time (s)	Average absorption rate for first 100 s (g/s)	H ₂ pressure post sensible heating (bar)	Mass of H ₂ desorbed (g)	Desorption time (s)	Reversibility (%)
70	13.17	476	0.09	146	13.13	63	~100
80	17.58	592	0.1	154	17.56	122	~100
90	19.92	620	0.11	158	19.9	156	~100
100	20.82	590	0.12	161	20.82	183	~100

During sensible heating of the bed to 40 °C, the bed pressure gradually increased, achieving 161 bar when the injection pressure was set at 100 bar. For an injection pressure of 90 bar, a minor reduction in hydrogen pressure (156 bar) was observed, while for 70 bar, the pressure dropped to 146 bar. This behaviour was primarily influenced by the amount of hydrogen absorbed during the previous absorption half-cycle, highlighting that bed pressure depends not only on the supply pressure but also on the hydrogen content within the bed. The rate of desorption was nearly identical across all injection pressures, with marginally higher discharge rates observed for 100 bar and 90 bar. This was attributed to the higher initial discharge pressures at the HTF inlet temperature maintained during the desorption half-cycle. This observation was further supported by the minimum bed temperatures recorded during desorption. The bed reached the lowest temperature of 1.4 °C for the 100 bar injection pressure case, followed by 2.2 °C for the 90 bar case. The reversibility of the entire cycle was found to be 100% in all cases. Table 5.1 summarizes the key quantitative measurements for the tested conditions.

Influence of HTF inlet temperature during absorption

Fig. 5.4 (a-c) illustrates the impact of HTF inlet temperature on the bed's thermal response and its interaction with hydrogen during a complete storage cycle. The highest rise in bed temperature was observed when the HTF inlet temperature was maintained at 5 °C, resulting in a peak bed temperature of 33.5 °C, compared to 34.8 °C for HTF inlet temperature of 10 °C. This indicates greater heat accumulation within the bed at lower HTF inlet temperatures. An analysis of hydrogen mass transfer dynamics revealed a superior mass transfer rate at lower

HTF inlet temperatures, leading to shorter cycle times. The enhanced mass transfer facilitated greater hydrogen interaction with the alloy, resulting in increased exothermic heat generation. The bed reached its maximum storage capacity of 20.82 g (1.5 wt%), 18.85 g (1.4 wt%), and 16.81 g (1.2 wt%) as the HTF inlet temperature increased incrementally from 5 °C to 15 °C.

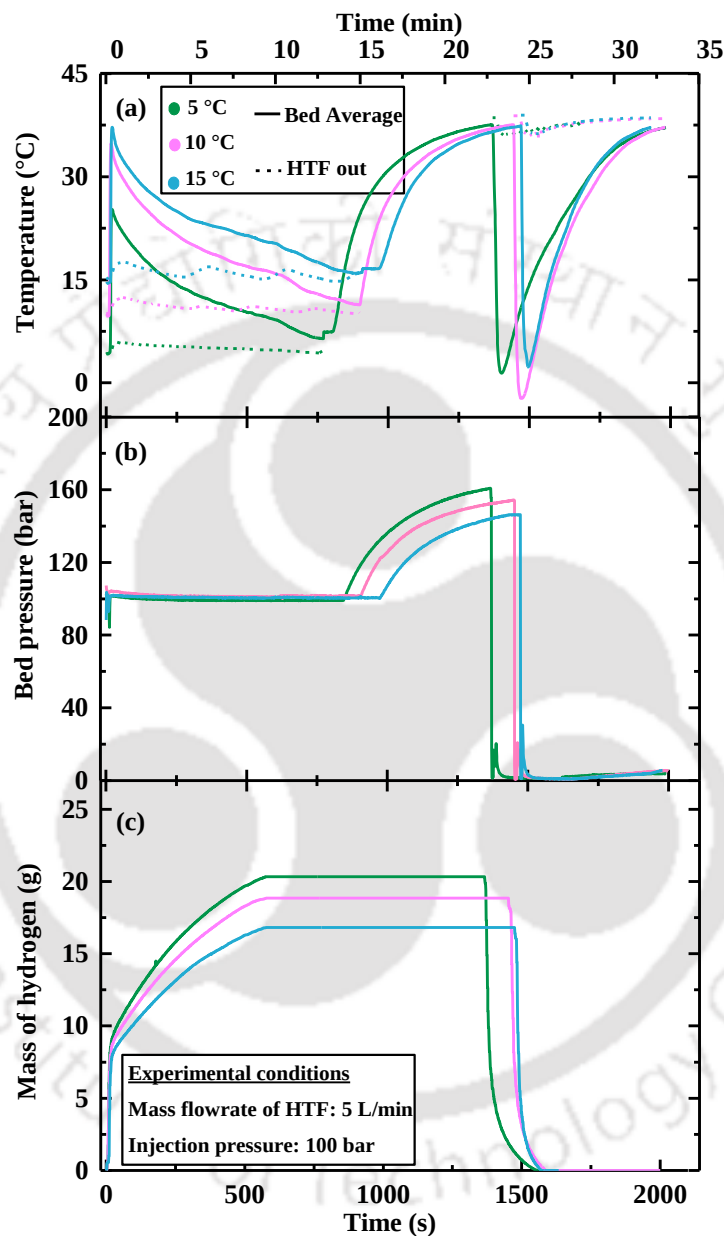


Fig. 5.4: Temporal change in (a) bed temperature variation, (b) the reactor pressure and (c) variation in mass of hydrogen transferred due to variation in HTF inlet temperature during absorption

After absorption, the reactor was sensibly heated to 40 °C to measure the hydrogen pressure attained within the reactor. As expected, the pressure correlated directly with the mass of hydrogen absorbed during the preceding absorption cycle. A pressure of 161 bar was recorded for an HTF inlet temperature of 5 °C, followed by 154 bar and 147 bar for HTF temperatures

of 10 °C and 15 °C, respectively. The HTF inlet temperature was observed to have a negligible impact on the average desorption rate during the desorption cycle. In all cases, desorption was carried out by continuously supplying HTF at 40 °C. Although the initial desorption rate was marginally higher for the case with an HTF inlet temperature of 5 °C which was attributed to the higher discharge pressure of 161 bar prior to desorption. However, it remained nearly identical across the other two tested conditions.

Influence of HTF inlet temperature during desorption

To investigate the influence of HTF inlet temperature on bed temperature and desorption kinetics, the preceding absorption half-cycle was carried out by supplying hydrogen at an injection pressure of 100 bar while circulating HTF at 5 °C and a flow rate of 5 L/min. Fig. 5.5 (a) and (b) shows the bed temperature and the mass of hydrogen desorbed after absorption and sensible heating of the alloy bed. At the onset of desorption, the endothermic reaction heat caused an abrupt drop in bed temperature initially due to the energy required to break the metal-hydrogen bonds. In the absence of sufficient external energy, the system consumed on the internal energy of the bed, resulting in a temperature drop. The magnitude of this drop was primarily influenced by the amount of hydrogen desorbed and the desorbing pressure achieved after sensible heating. For instance, when desorption was initiated with HTF at 50 °C, the initial desorbing pressure was recorded to be 212 bar. Upon opening the reactor valve, the sudden gas expansion caused the bed temperature to drop sharply from 50 °C to 10 °C, a decrease of approximately 40 °C. The temperature drops reduced with lower HTF inlet temperatures of 40 °C and 30 °C. The reversibility of the alloy bed was found to be 100%, as all the absorbed hydrogen was successfully desorbed. The initial desorption rate was identical across all cases, with up to 8 g (38.7%) of absorbed hydrogen desorbed. This was attributed to the rapid expansion from a pressure range of 140–212 bar to ambient pressure (1 bar absolute). Beyond this point, the desorption rate was governed by the HTF inlet temperature, with 50 °C achieving the maximum desorption rate. The corresponding half-cycle times to desorb 90% (18.6 g) of absorbed hydrogen were 62 s at 50 °C, followed by 111 s at 40 °C, and 122 s at 30 °C.

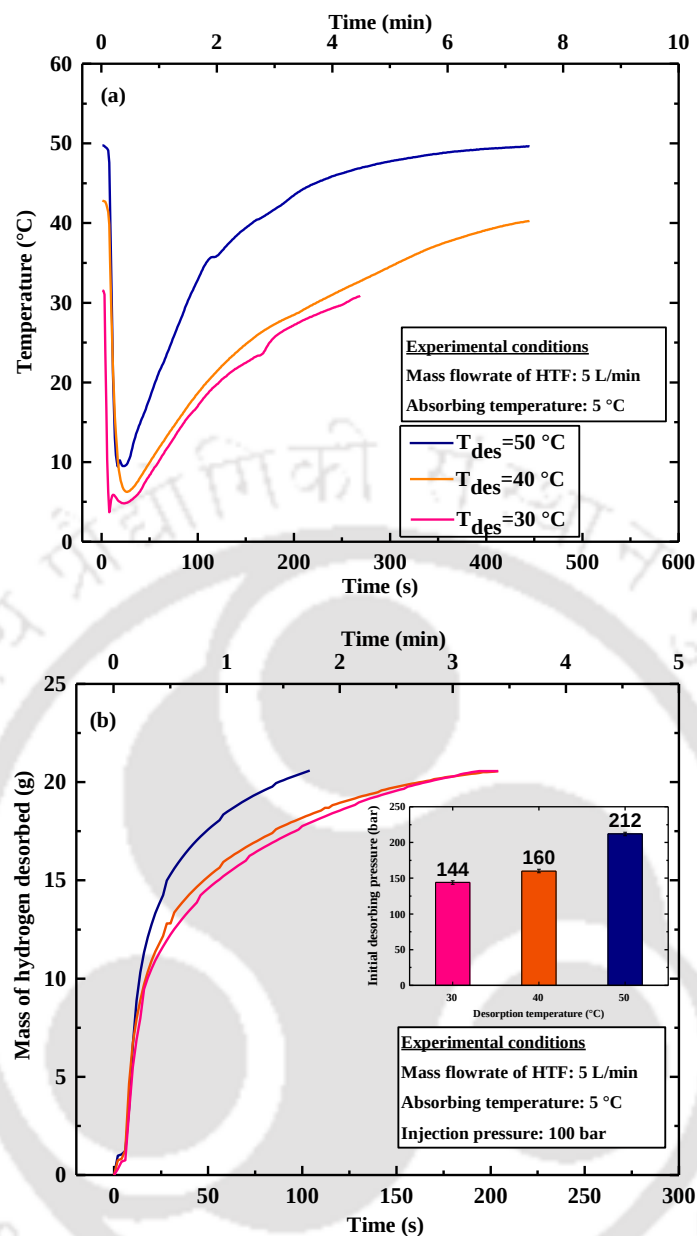


Fig. 5.5: Temporal variation in (a) bed temperature and (b) mass of hydrogen desorbed due to variation in HTF inlet temperature during desorption

Influence of HTF flow rate

The influence of HTF flow rate on the absorption and desorption behaviour of the reactor system was investigated by varying the flow rate to 2.5 L/min, 5 L/min, and 10 L/min. During the study, the hydrogen injection pressure was fixed at 100 bar, and the HTF inlet temperature was maintained at 5 $^{\circ}\text{C}$ during absorption. For desorption, the HTF temperature was fixed at 40 $^{\circ}\text{C}$ after the bed absorbed hydrogen at 100 bar and 5 $^{\circ}\text{C}$. Fig. 5.6 (a) and (b) depicts the bed temperature variations and reaction kinetics of the alloy bed during absorption.

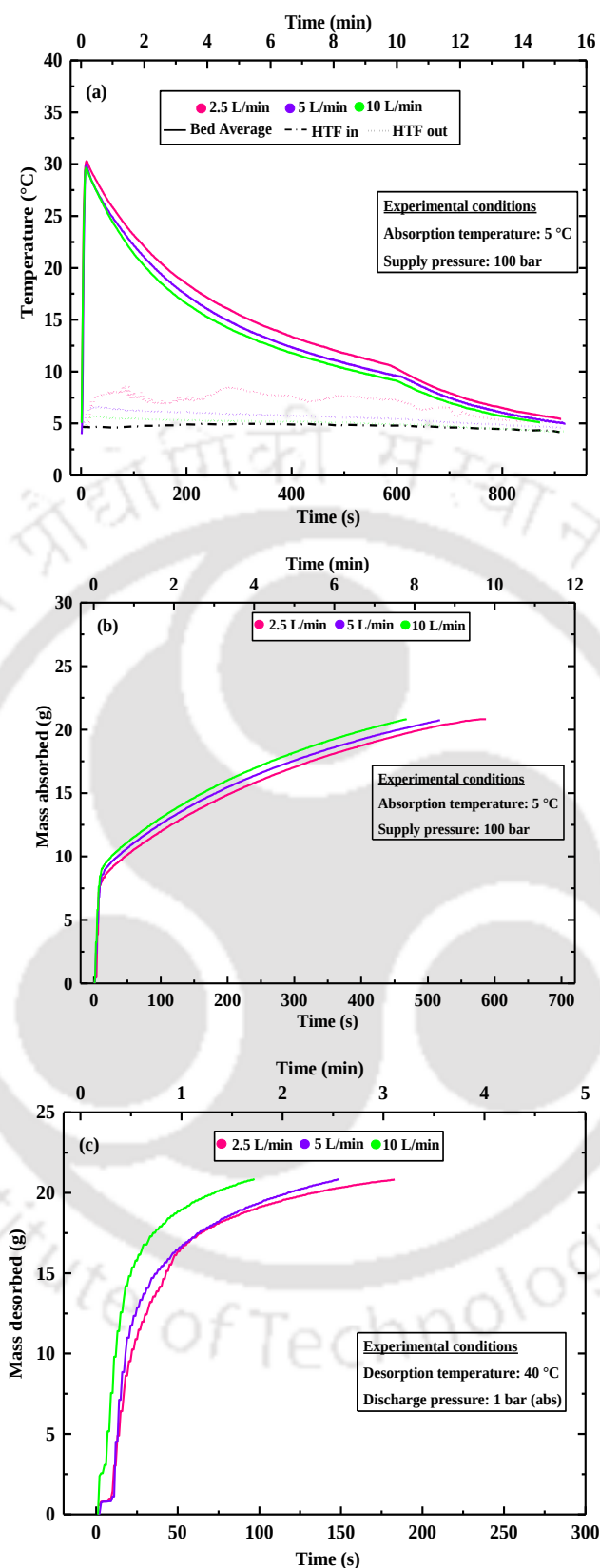


Fig. 5.6: Variation in (a) bed temperature and (b) mass of hydrogen absorbed due to variation in HTF flow rate during absorption half cycle, and (c) mass of hydrogen desorbed due to variation in HTF flow rate during desorption half cycle

The peak bed temperature during absorption was nearly identical across all tested HTF flow rates. However, the slope of the temperature curve following the peak varied slightly until the completion of the absorption half-cycle. This variation was attributed to differences in heat transfer rates, which became significant only after the maximum temperature was reached. The peak temperature was primarily governed by the initial pressure differential, which remained consistent across all tested conditions. The HTF outlet temperature was highest when the flow rate was set to 2.5 L/min due to reduced heat transfer. This higher outlet temperature slightly prolonged the absorption half-cycle duration due to reduced heat removal efficiency. The impact of HTF flow rate on hydrogen absorption was observed to have minimal influence on mass transfer, as the bed temperature varied marginally. This limited temperature variation directly affected the pressure differential between the injection pressure and the equilibrium pressure, which governs hydrogen transfer kinetics. As a result, the hydrogen uptake was nearly identical across all cases, with 20.82 g absorbed in 594 s at 2.5 L/min, in 529 s at 5 L/min, and in 472 s at 10 L/min. Based on these results, an HTF flow rate of 5 L/min was determined to be optimal for absorption, balancing heat transfer performance and cycle duration.

Fig. 5.6 (c) illustrate variation in mass of hydrogen desorbed at various HTF flow rates during desorption. Similar to absorption, the bed temperature profile remained largely unaffected by changes in HTF flow rates. However, the desorption duration was more significantly impacted than absorption, varying from 97 s at 10 L/min to 183 s at 2.5 L/min, representing almost 50% increase in time for a 70 % reduction in flow rate. Although the cumulative mass of hydrogen discharged did not vary significantly between 10 L/min and 5 L/min flow rates, the desorption rate was notably higher at 10 L/min.

5.2.3 Performance index

Gravimetric storage density (GSD): It is defined as the ratio of the mass of hydrogen stored (m_{H_2}) during a complete effective storage cycle to the total mass of the reactor (m_r). It is expressed as:

$$GSD = \frac{m_{H_2}}{m_r} \quad (5.1)$$

Gravimetric exergy recovery rate (GERR): It is defined as the ratio of the rate of exergy recovered during a complete effective storage cycle to the mass of the alloy (m_{MH}) contained within the reactor. It is expressed as:

$$GERR = \frac{\Psi_{rec}}{m_{MH} t_{abs}} \quad (5.2)$$

$$\Psi_{rec} = n_{H_2} \left(RT_o \ln \left(\frac{P_{H_2}}{P_{inj}} \right) \right) \quad (5.3)$$

where Ψ_{rec} represents the exergy recovered in the storage system, starting from hydrogen injection at P_{inj} to reaching the final pressure P_{H_2} . It is defined using Eq. 5.3. T_o is denoted as ambient temperature. t_{abs} denotes the time required for the alloy bed to achieve 90% of its saturation capacity.

5.2.4 Evaluation of storage performance

The high-pressure hydrogen storage system achieved a gravimetric storage density of 0.55% and a gravimetric exergy recovery rate of 14.8 W/kg_{MH} under optimum operating parameters. The system consistently demonstrated a maximum hydrogen storage capacity of 1.5 wt% even after 40 cycles.

5.2.5 Energy efficiency and sensitivity analysis

The energy efficiency of metal hydride (MH)-based hydrogen storage systems is typically evaluated using the first law of thermodynamics, which focuses on the overall thermal energy interactions within the system. The thermal energies supplied during hydrogen storage to a MH reactor can be enumerated as:

$$E_{in} = E_{SC} + E_a + E_{SH} + E_d \quad (5.4)$$

Where E_{SC} denotes the sensible cooling of the alloy bed below ambient temperature (T_o) to initiate the absorption half cycle. E_a represents thermal energy removed from the MH system by the HTF during the exothermic reaction due to hydrogen interaction with MH alloy whereas E_d signifies the thermal energy supplied through the HTF during discharge of absorbed hydrogen. E_{SH} denotes the sensible heat required to raise the temperature of the MH bed from the absorption temperature to the temperature to initiate desorption. These energy interactions are evaluated using the following equations:

$$E_{SC} = m_r c_{p_r} (T_o - T_a) + m_{MH} c_{p_{MH}} (T_o - T_a) \quad (5.5)$$

$$E_a = \int_{t_1}^{t_2} \dot{m}_f c_{p_{HTF}} (T_{outlet}(t) - T_{inlet}(t)) dt \quad (5.6)$$

$$E_{SH} = m_r c_{p_r} (T_d - T_a) + m_{MH} c_{p_{MH}} (T_d - T_a) + m_{H_2} c_{p_{H_2}} (T_d - T_a) \quad (5.7)$$

$$E_d = \int_{t_2}^{t_3} \dot{m}_f c_{p_{HTF}} (T_{outlet}(t) - T_{inlet}(t)) dt \quad (5.8)$$

The useful energy during MH based hydrogen storage corresponds to the exothermic heat released. This energy can be theoretically estimated as the product of the number of moles of hydrogen absorbed and the reaction enthalpy. However, a more practical approach involves experimentally determining the energy removed by the HTF during the absorption process. Some researchers have referred to the output energy as the residual combustion energy after deducting the thermal energy supplied to the storage system. While this perspective may hold for systems integrated with fuel cells, it appears less applicable to standalone storage systems.

$$E_{out} = E_a = \int_{t_1}^{t_2} \dot{m}_f c_{p_{HTF}} (T_{outlet}(t) - T_{inlet}(t)) dt \quad (5.9)$$

The thermal efficiency of the storage system was evaluated by:

$$\eta = \frac{E_{out}}{E_{in}} \quad (5.10)$$

The impact of hydrogen injection pressure on thermal efficiency is depicted in Fig. 5.7 (a). Increasing the injection pressure from 70 bar to 100 bar (a 42.8% rise) at 5 °C led to an efficiency increase from 23.2% to 51.4%, representing more than a two-fold enhancement. This significant improvement is attributed to the higher exothermic heat release resulting from the increased mass of hydrogen interacting with the alloy bed.

However, closer analysis revealed a modest efficiency increase from 49.3% to 51.4% when the injection pressure was raised from 90 bar to 100 bar. This minor improvement correlates with a slight rise in hydrogen absorption, as the bed approached near saturation under both conditions. The influence of HTF inlet temperature on thermal efficiency is depicted in Fig. 5.7 (b). The thermal efficiency of the storage system decreased from 51.4% to 42.1% as the HTF inlet temperature increased from 5 °C to 15 °C, with the injection pressure at 100 bar. This decline is attributed to the reduced driving force for hydrogen interaction with the alloy bed due to the increased bed equilibrium pressure at higher HTF temperatures. However, the reduction in sensible cooling requirements partially offsets this effect, mitigating the overall efficiency loss as the HTF inlet temperature rises during absorption. The impact of HTF inlet temperature during desorption and HTF flow rate on thermal efficiency is illustrated in Fig. 5.7 (c) and Fig. 5.7 (d). In both cases, the impact was relatively minor. Thermal efficiency decreased from 53% to 45.5% as the HTF inlet temperature increased from 30 °C to 50 °C, primarily due to the higher sensible heat requirements for handling the same mass of absorbed

hydrogen. Similarly, while the HTF flow rate significantly influenced cycle time, its effect on the amount of hydrogen transferred was minimal. Consequently, the change in thermal efficiency was also minimal and exhibited a linear relationship with flow rate, reflecting the increased exothermic heat removal at higher flow rates.

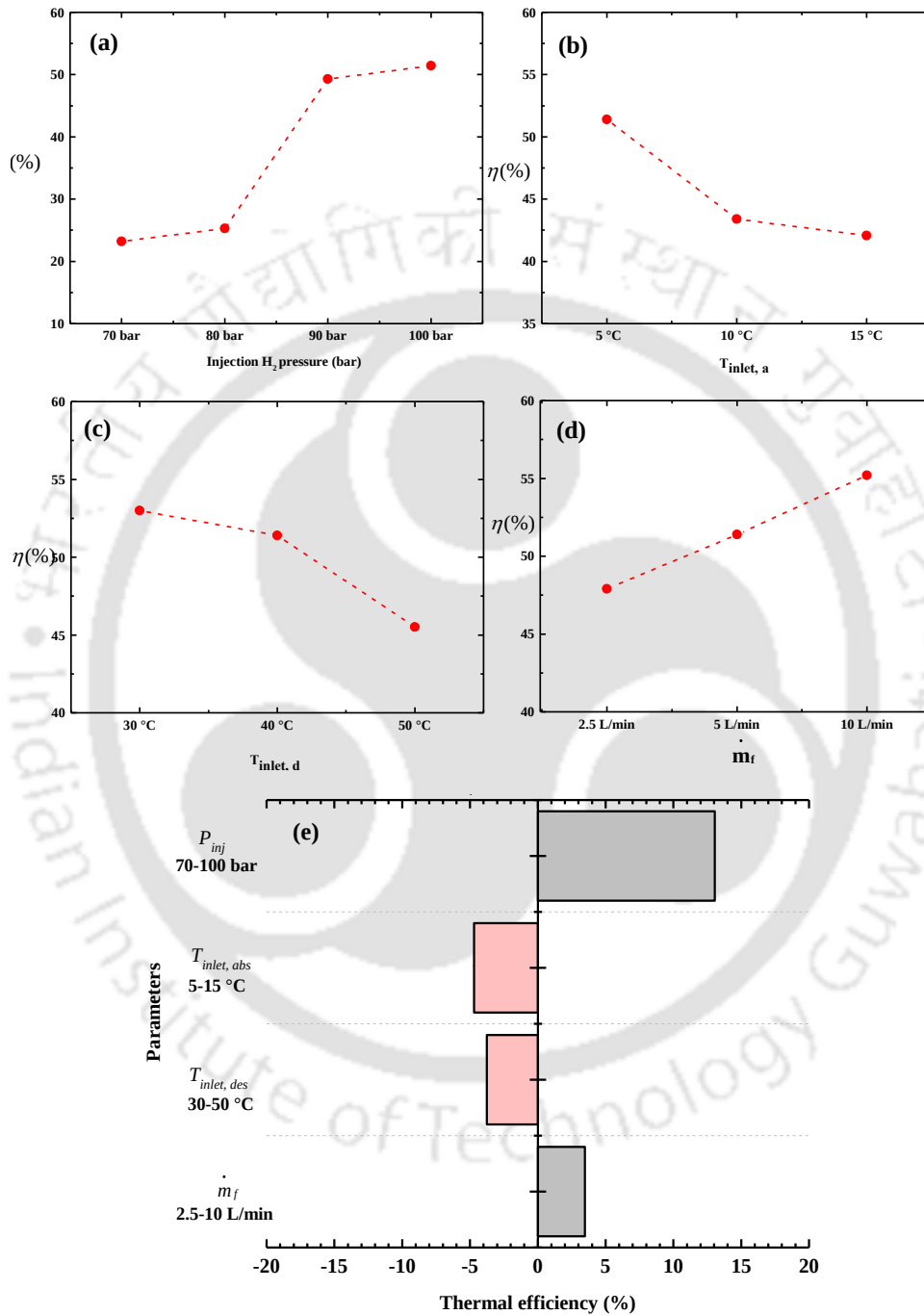


Fig. 5.7: Impact of (a) hydrogen injection pressure, (b) HTF inlet temperature during absorption, (c) HTF inlet temperature during desorption, (d) HTF flow rate on thermal efficiency and (e) Sensitivity analysis

The summarized effects of all tested parameters on thermal efficiency are illustrated in Fig. 5.7 (e). The analysis revealed that injection pressure had the most significant impact on the thermal efficiency of the developed storage system, resulting in a positive deviation of 13%. In contrast, the HTF flow rate exhibited the least influence, with only a 3.5% positive variation. Additionally, the HTF inlet temperature during both absorption and desorption was found to negatively affect the system's efficiency.

5.2.6 Additional cooling effect

The endothermic reaction during metal hydride desorption facilitates system cooling. While previous studies have demonstrated cooling using metal hydrides, few have explored the temperature range of 15–25 °C (Jana et al., 2022c). This section investigates the potential of the tested alloy to provide cooling at temperatures as low as 7 °C. Two modular MH reactors, as described earlier, were arranged in tandem to operate alternately in successive half-cycles (Fig. 5.8 (b)). The operation of the prototype metal hydride-based open-cycle cooling system is illustrated in Fig. 5.8 (a). Prior investigation revealed that the alloy bed absorbed approximately 20 g of hydrogen within a pressure range of 90–100 bar, enabling the reactor assembly to function as a secondary air-conditioning system for automobiles, as proposed by (Weckerle et al., 2020).

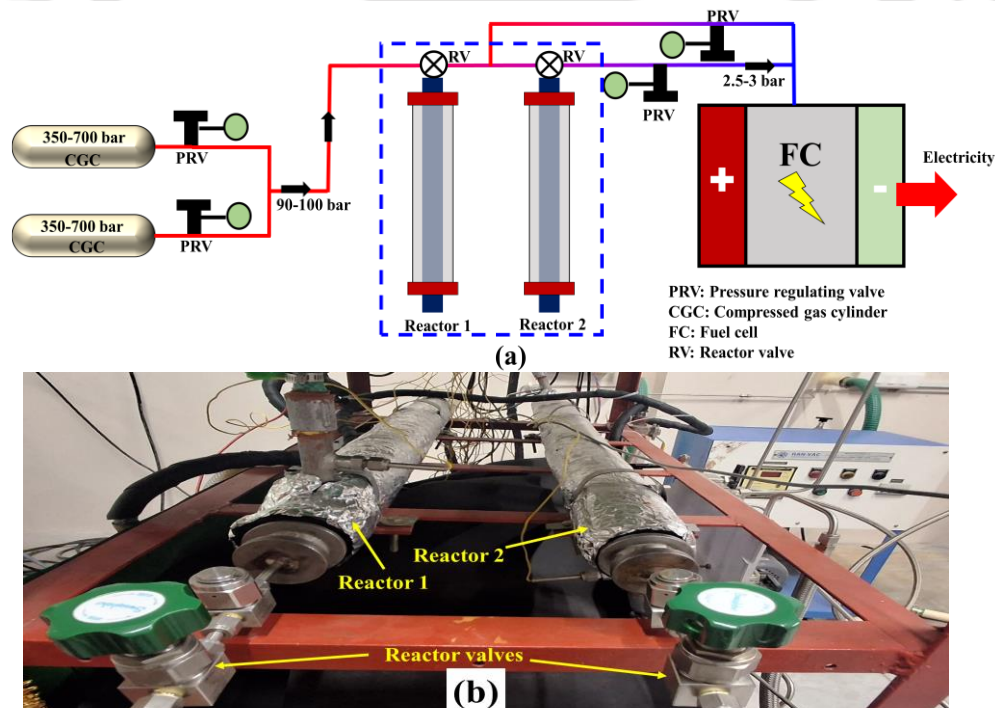


Fig. 5.8: Schematic representation of (a) operation and (b) experimental set up demonstrating additional cooling provided during MH desorption at $P_d=3$ bar

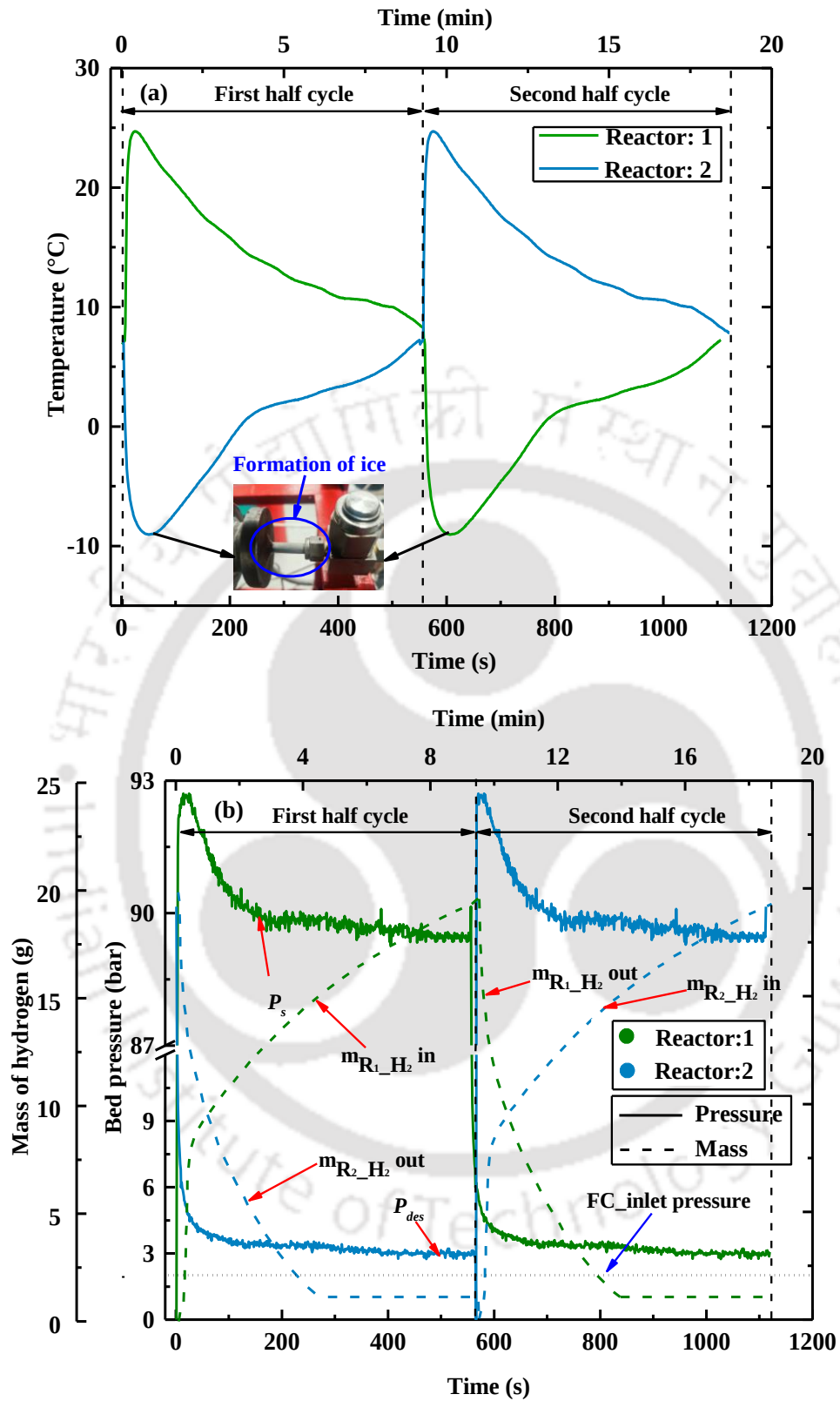


Fig. 5.9: (a) Bed temperature variation and (b) bed pressure and mass of hydrogen transferred during one complete cycle with MH desorbing at constant discharge pressure of 3 bar

In the first half-cycle, hydrogen from a compressed gas cylinder was transferred to the MH reactor for absorption at a set pressure of 90 bar and a fixed HTF inlet temperature of 7 °C. In the subsequent half-cycle, the absorbed hydrogen was desorbed at a regulated pressure, fixed by a line pressure regulator, to power a fuel cell (FC). The exit pressure was maintained at 3 bar. The two MH reactors were operated alternately to ensure a desorption half-cycle occurred during each operational half-cycle. The continuous discharge of hydrogen from the MH reactor at constant pressure provided the cooling effect, as demonstrated in Fig. 5.9 (a) and (b).

During the first half-cycle, hydrogen injected into *Reactor 1* at 90 bar caused the bed temperature to rise from an initial 7 °C due to the exothermic heat of absorption. Simultaneously, *Reactor 2*, which had absorbed hydrogen in the preceding half-cycle, began desorption at a set pressure of 3 bar while circulating HTF at 7 °C. This operational strategy ensured that one reactor was always in the desorption phase during each half-cycle. The alloy bed in *Reactor 1* absorbed 19.68 g of hydrogen at 90 bar and 7 °C. Reactor 2 discharged nearly 97% of its absorbed hydrogen at 3 bar, maintaining HTF at 7 °C. The desorption process caused the bed temperature to drop as low as -9 °C, visually confirmed by ice formation on the reactor surface. Initially, a rapid desorption rate was observed, with 10 g of hydrogen released within 64 s due to the high internal pressure. However, the rate slowed as the bed pressure approached 3 bar, with the remaining 9.1 g desorbed over the next 200 s. The total cycle time for one complete cycle, including two cooling half-cycles, was 1120 s. The cooling effect achieved during one cycle was evaluated to be 348 kJ

5.3 Study on $\text{La}_{0.3}\text{Ce}_{0.7}\text{Ni}_4\text{Fe}$

5.3.1 Activation strategy

Prototype reactor

Following circuit and reactor leak tests, the filled reactor was heated to 90 °C, followed by evacuation for 15 min. The reactor was then cooled to 20 °C, after which the MH bed was exposed to hydrogen at 60 bar. Throughout the experiment, the HTF flow rate was maintained at 5 L/min. The MH bed initially absorbed 3.72 g of hydrogen, which was subsequently desorbed upon heating to 90 °C. To enhance hydrogen absorption capacity, the cooling-absorption-heating-evacuation sequence was repeated until the maximum storage capacity was consistently achieved over three consecutive cycles. The sequence-wise cyclic absorption, desorption, and cycle time are illustrated in Fig. 5.10. It was observed that the alloy's hydrogen absorption capacity progressively improved from 0.11 wt% to 1.3 wt% over six complete

cycles. Additionally, the cycle time also decreased eventually, indicating successful alloy activation.

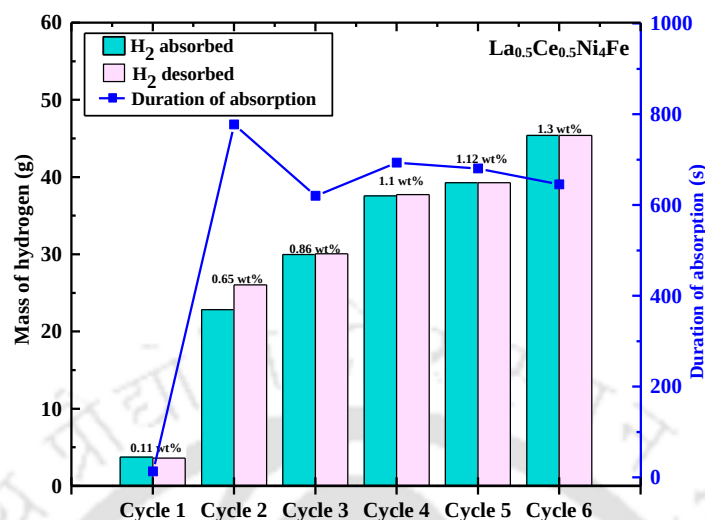


Fig. 5.10: Sequential variation in hydrogen absorption, desorption, and absorption duration during activation of $\text{La}_{0.3}\text{Ce}_{0.7}\text{Ni}_4\text{Fe}$

Industrial scale reactor

Following the completion of the leak test as outlined previously, the bed was subsequently heated to 90 °C and evacuated to 10^{-5} bar for 30 min. Thereafter, the alloy bed was cooled down to 20 °C by recirculating water from low temperature bath. Hydrogen was supplied at 60 bar while maintaining the bed at the same temperature. During the initial activation cycle, merely 28 g of hydrogen was absorbed, and the peak bed temperature of 26 °C was reached. Additional activation cycles were performed until the maximum storage capacity was achieved. In this study, the alloy was activated in the fourth activation cycle absorbing 326.06 g in 40 min. Subsequent activation cycles did not yield any improvements in storage capacity or reaction kinetics. The successive bed temperature variation and improvement in rate of hydrogen intake during activation cycles is depicted in Fig. 5.11.

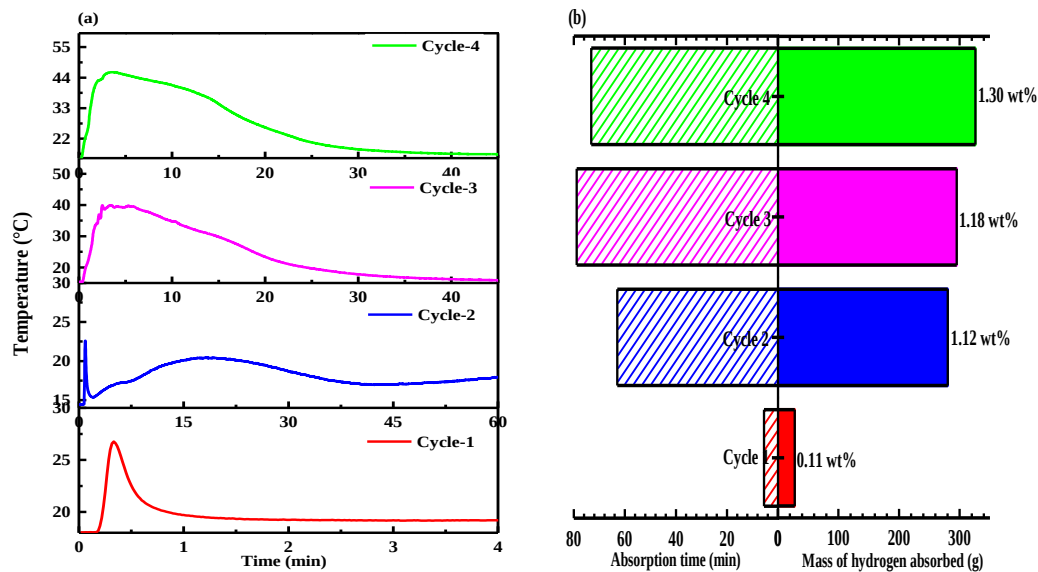


Fig. 5.11: Variation of (a) bed temperature and (b) absorbed hydrogen mass and absorption time during successive activation cycles

5.3.2 Parametric studies

Influence of injection pressure

To identify the optimum injection pressure for the alloy, hydrogen was injected at pressures ranging from 30 to 60 bar in 10 bar increments. The HTF was circulated at an inlet temperature of 15 °C and a flow rate of 5 L/min. The variations in bed temperature, HTF outlet temperature, and corresponding injection pressures are illustrated in Fig. 5.12 (a), while the mass of hydrogen absorbed at each pressure is presented in Fig. 5.12 (b).

Referring to the temperature variation within the bed, the highest injection pressure resulted in the maximum bed temperature. This is attributed to the larger mass of hydrogen interacting with the metal hydride bed, generating greater exothermic heat during absorption. The heat is dissipated by the HTF circulating through the embedded cooling tubes and outer jacket, as evidenced by the higher peaks in the HTF outlet temperature profile at elevated injection pressures. However, the rate of heat removal for 40, 50, and 60 bar was found to be nearly identical, indicating minimal change in the bed's thermohydraulic performance beyond 40 bar.

The total hydrogen absorbed at injection pressures of 30, 40, 50, and 60 bar was 29.16 g, 42.07 g, 45.56 g, and 45.6 g, respectively, over durations of 741 s, 888 s, 816 s, and 616 s. While the absorbed mass increased by only 8.4% beyond 40 bar, the absorption time decreased significantly, i.e. by 30.6%. This indicates that a 50% increase in injection pressure can reduce the absorption cycle time by ~31%, with only a marginal gain in hydrogen capacity. Therefore,

an injection pressure of 40-50 bar, along with a slightly lower HTF inlet temperature, offers an optimal trade-off, detailed in the following subsection.

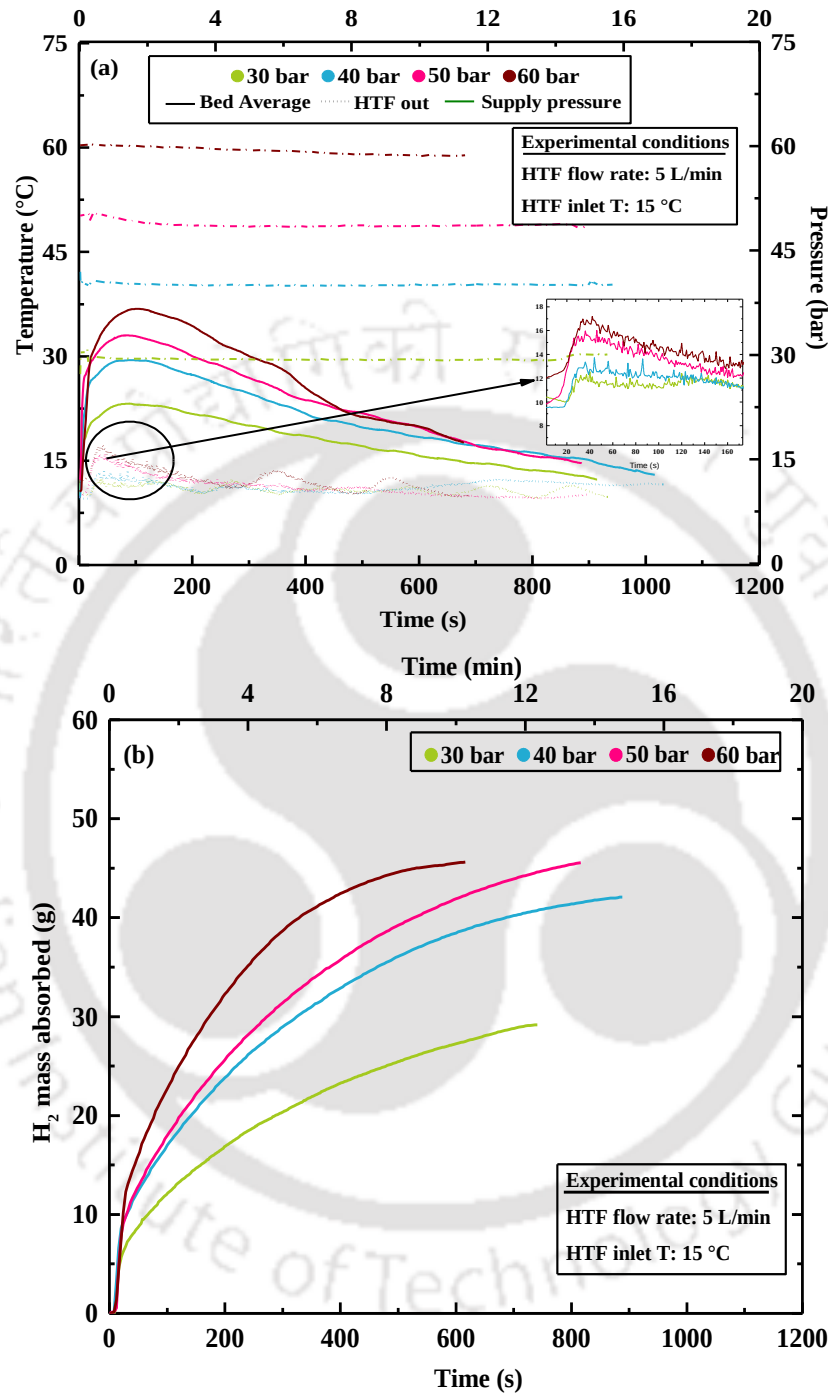


Fig. 5.12 : Temporal change in (a) temperature variation and (b) variation in mass of hydrogen transferred due to variation in injection pressure

Influence of HTF inlet temperature during absorption

At a sustained injection pressure of 40 bar, the HTF inlet temperature was varied from 5 °C to 20 °C in 5 °C increments, while maintaining a constant flow rate of 5 L/min. The results of this study are illustrated in Fig. 5.13, showing the temperature variation within the bed, HTF inlet

and outlet temperatures, and the corresponding mass of hydrogen absorbed under each condition. It was observed that the bed temperature profiles were nearly identical after the peak for both 5 °C and 10 °C cases, as well as for 15 °C and 20 °C cases.

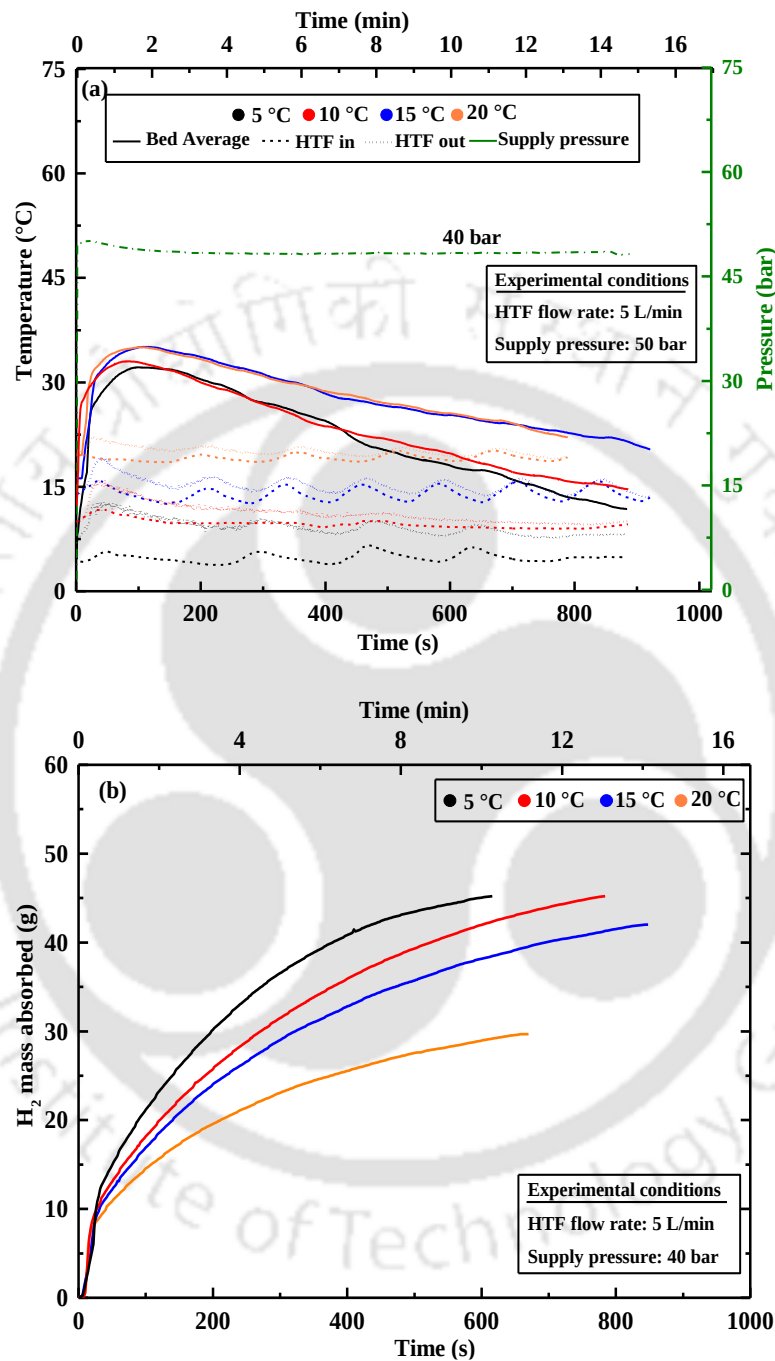


Fig. 5.13: Temporal change in (a) temperature variation and (b) variation in mass of hydrogen transferred due to variation in HTF inlet temperature during absorption

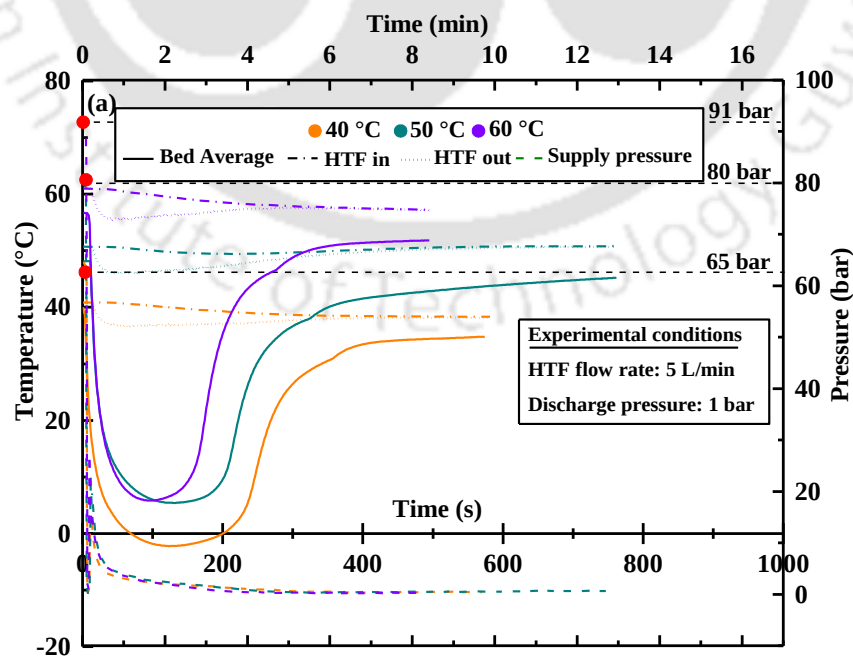
The initial temperature rise in the bed following hydrogen–alloy interaction was highest for the 5 °C HTF condition, attributed to more favourable absorption conditions at a lower bed temperature (~27 °C) compared to ~15 °C in the 20 °C case. This confirms that the thermohydraulic performance of the bed remains effectively identical at HTF inlet

temperatures of 5 °C and 10 °C. The cumulative hydrogen absorbed was identical for both 5 °C and 10 °C HTF inlet conditions, each recording 45.22 g. However, the absorption half-cycle time was shorter at 5 °C (616 s) compared to 784 s at 10 °C. At 15 °C, the absorbed mass decreased slightly to 42.07 g, while the half-cycle time further increased to 888 s. These results indicate that the optimal absorption conditions for the selected alloy lie within an injection pressure range of 40-50 bar and an HTF inlet temperature of around 10 °C, provided the HTF flow rate is maintained at 5 L/min.

Influence of HTF inlet temperature during desorption

Although determining the adequate desorption temperature in single-reactor operation may not fully reflect the optimum conditions during coupled-bed operation with another alloy bed, the bed pressure attained after sensible heating i.e., at the onset of desorption, serves as a critical indicator. It provides a reliable initial estimate for selecting the appropriate desorption temperature during coupled-stage hydrogen transfer.

This study was conducted by first absorbing hydrogen into the bed at an injection pressure of 40 bar, resulting in an absorbed mass of 45.22 g. Subsequently, the desorption temperature was varied across 40 °C, 50 °C, and 60 °C, while maintaining a constant HTF flow rate of 5 L/min. The results of the study are presented in Fig. 5.14. It was observed that the bed pressure rose to 91 bar from an initial 40 bar when desorption was initiated at 60 °C, whereas it only reached 65 bar at 40 °C. This higher-pressure gradient at 60 °C facilitated faster hydrogen discharge, resulting in a rapid drop in bed temperature to 5.8 °C.



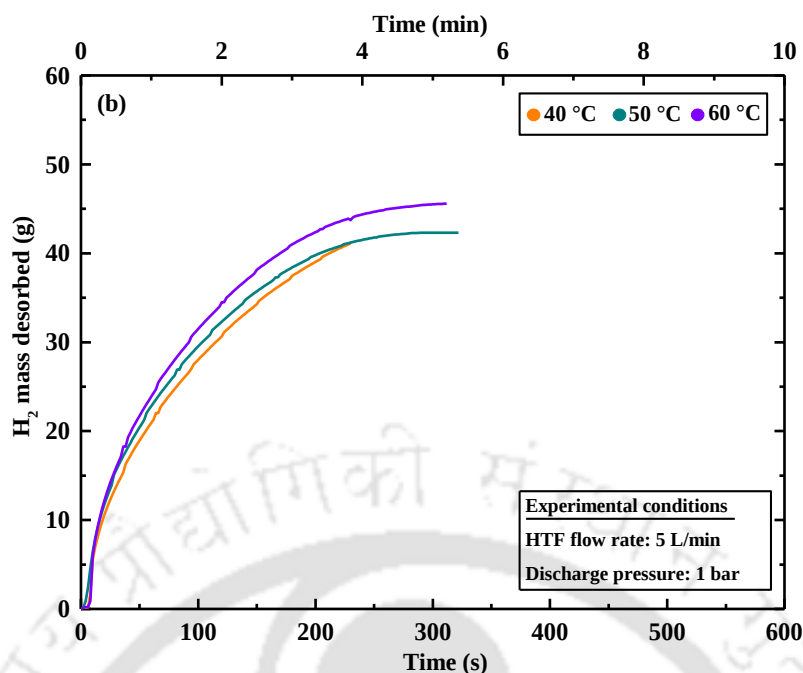


Fig. 5.14 : Temporal variation in (a) temperature and (b) mass of hydrogen desorbed due to variation in HTF inlet temperature during desorption

The hydrogen mass discharge rate further confirmed this behaviour, with approximately 30 g of the total 45.22 g desorbed within 100 s at 60 °C. In comparison, it took 104 s and 116 s at 50 °C and 40 °C, respectively. However, complete desorption (reversibility ~100%) was not achieved at 40 °C and 50 °C, indicating that the optimum desorption temperature for the alloy is greater than or equal to 60 °C.

5.4 Study on La_{0.8}Ce_{0.2}Ni₅

5.4.1 Activation strategy

Prototype reactor

The reactor was initially leak-tested by filling it with argon and monitoring overnight for any pressure drop. After confirming leak-tightness, argon was purged, and HTF was circulated at 10 °C to stabilize the bed. Once cooled, hydrogen (99.999% purity) was injected at 40 bar. In the first cycle, the bed absorbed 27.9 g (0.8 wt%). The bed was then heated to 80 °C and evacuated to 10⁻⁵ bar for 30 min, followed by cooling to 10 °C and reinjection of hydrogen at 40 bar. This time, the bed absorbed 36.63 g (1.05 wt%). The cycle, comprising of heating, evacuation, cooling, and hydrogen charging was repeated three more times. By the fifth cycle, the alloy reached full activation, achieving a storage capacity of 1.4 wt%. Fig. 5.15 illustrates the sequential improvement in hydrogen uptake during activation.

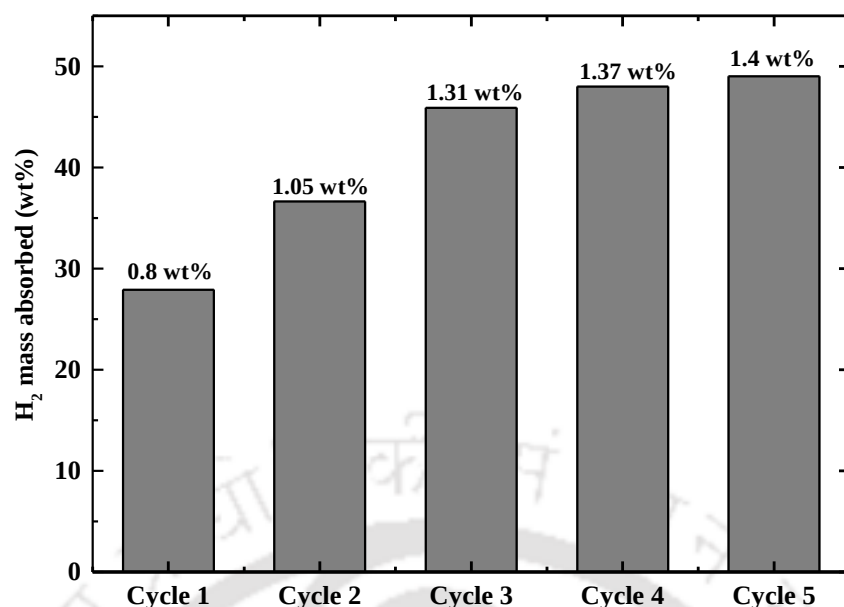


Fig. 5.15: Variation in storage capacity during successive activation cycles

Industrial scale reactor

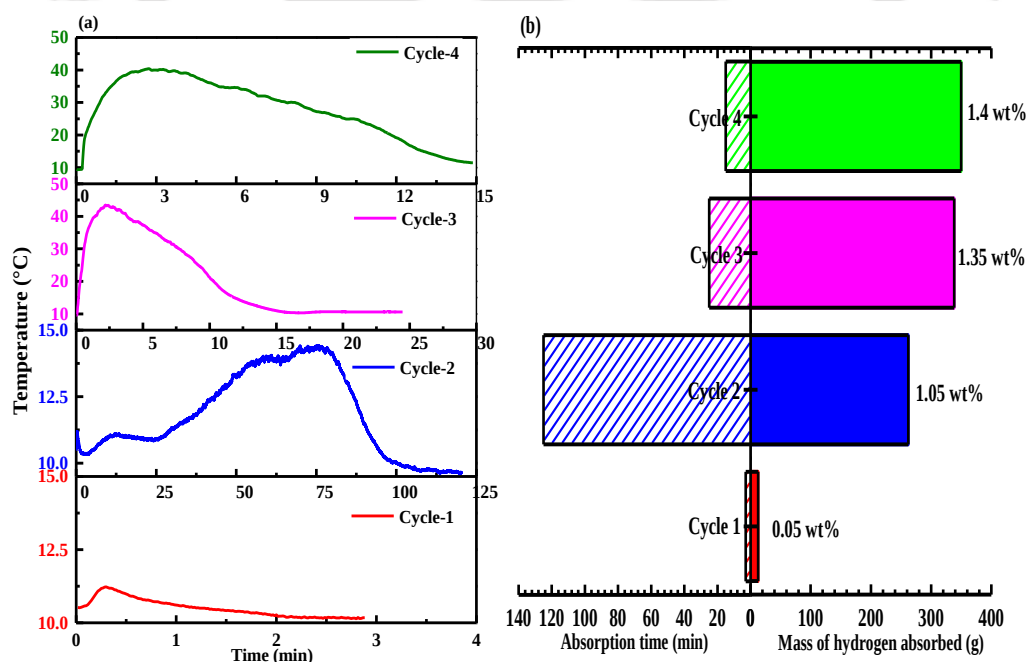


Fig. 5.16: Variation of (a) bed temperature and (b) absorbed hydrogen mass and absorption time during successive activation cycles

The reactors were initially leak tested with argon at 150 bar and left for 24 h. Subsequently, Argon was purged out before heating the bed up to 90 °C, and outgassing using the vacuum pump to 10^{-5} bar pressure. The reactors were then cooled down to 10 °C before charging hydrogen at 40 bar. In the first activation cycle, the alloy absorbed 12.9 g of hydrogen (0.05 wt%). Subsequently, during the second cycle, it absorbed 262 g (1.05 wt%), reaching a peak

bed temperature of 14 °C in about 125 min. To maximize storage capacity, the alloy underwent reheating, evacuation, and reabsorption. In the third cycle, it absorbed 338.2 g (1.35 wt.%) in 25 min. Alloy activation concluded after the fourth cycle, absorbing 350 g (1.4 wt.%) within 15 min, with no significant change in reaction kinetics, indicating completion of activation. %. Fig. 5.16 illustrates the sequential improvement in hydrogen uptake for the large scale reactor during activation

5.4.2 Parametric studies

Influence of injection pressure and HTF inlet temperature during absorption

The injection pressure was adjusted to 15 bar and 25 bar to determine the optimal operating pressure range, with the HTF inlet temperature varied between 5 °C and 25 °C. The experimental results are illustrated in Fig. 5.17. It was observed that the alloy bed absorbed 48.37 g of hydrogen when the injection pressure was set at 25 bar and the HTF inlet temperature at 15 °C. When the injection pressure was reduced to 15 bar and the HTF inlet temperature lowered to 5 °C, a slightly lower but comparable hydrogen uptake was achieved. This behaviour is attributed to the larger pressure driving force at higher injection pressures, which necessitates a ~10 °C reduction in HTF inlet temperature at lower pressures to achieve similar hydrogen uptake rates. A detailed analysis showed that at a fixed injection pressure of 15 bar, varying the HTF inlet temperature as 5 °C, 10 °C, 15 °C and 25 °C resulted in hydrogen absorption of 48.23 g, 47.80 g, 47.51 g, and 46.12 g, respectively: an overall variation of only 4.57%. In all cases, the reacted fraction exceeded 90%. Although operating at 25 bar reduced the absorption half-cycle time by approximately 25.5% compared to the 15 bar/15 °C condition, it would limit compatibility with AEM electrolyzers, which typically operate at a maximum hydrogen production pressure of 30 bar. Therefore, an injection pressure of 15 bar coupled with an HTF inlet temperature of 15 °C was identified as the optimum absorption condition.

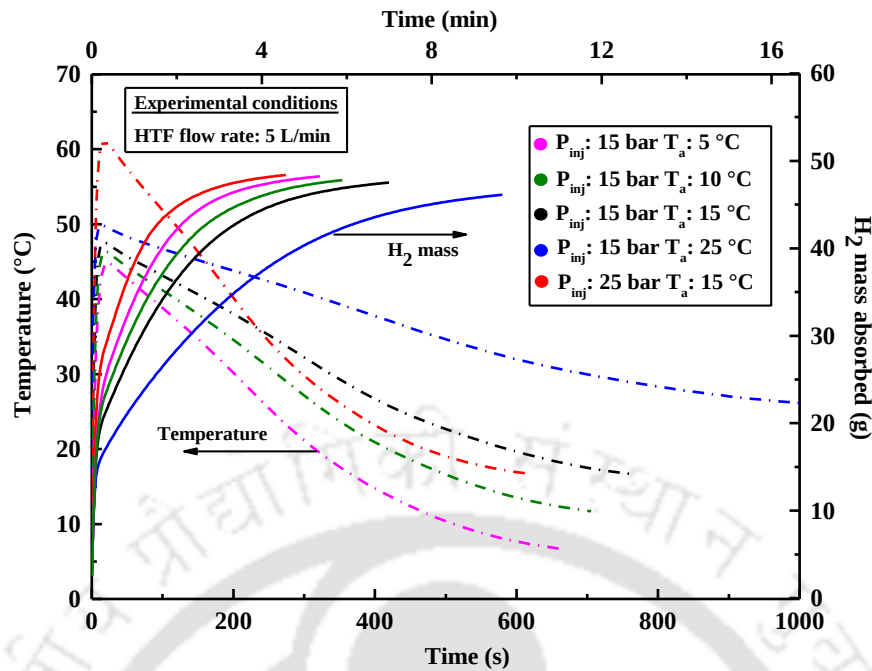


Fig. 5.17: Temporal variation in temperature and mass of hydrogen absorbed due to variation in injection pressure and HTF inlet temperature during absorption

Influence of HTF inlet temperature during desorption

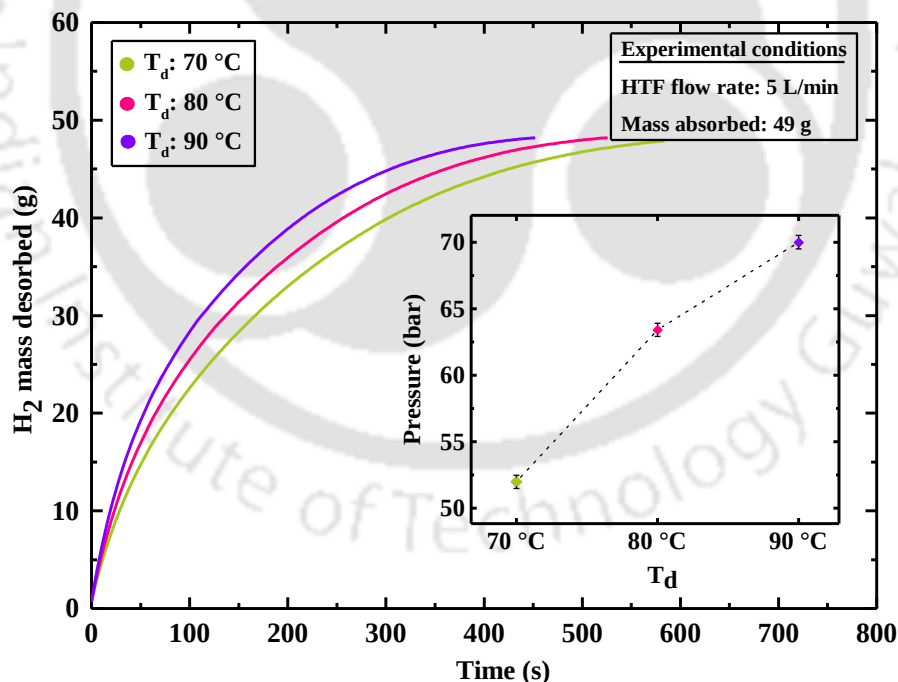


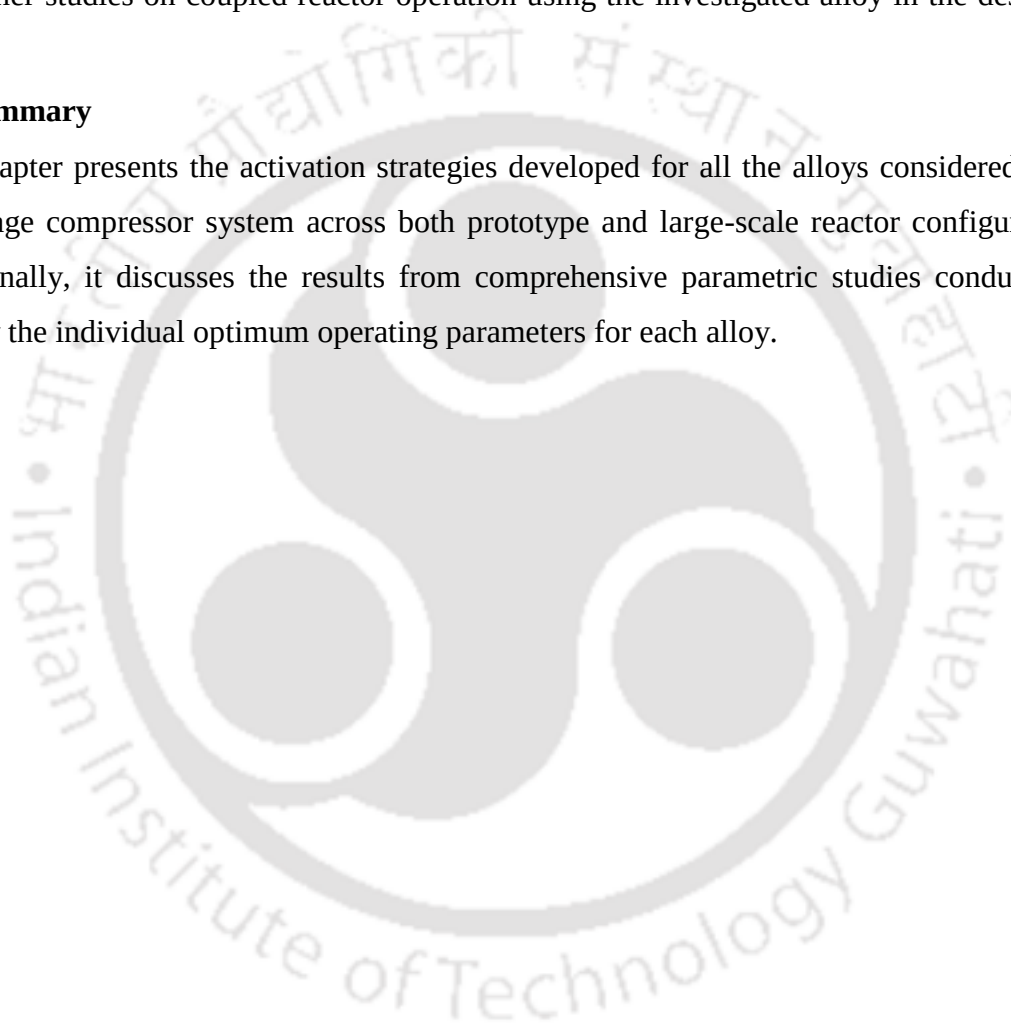
Fig. 5.18 : Temporal variation of temperature and the bed pressure at the onset of desorption

The influence of HTF inlet temperature during desorption was investigated by varying the temperature from 70 °C to 90 °C, while maintaining a constant flow rate of 5 L/min (Fig. 5.18). In each case, the preceding absorption half-cycle yielded 49 g of absorbed hydrogen. More than 95% of the stored hydrogen was successfully desorbed across all conditions (>47.88 g),

confirming that the selected desorption temperatures were sufficient for complete recovery in single-reactor operation. However, for coupled reactor operation, the bed pressure attained after sensible heating, i.e., at the onset of desorption, becomes a critical parameter. It was observed that bed pressures of 52 bar, 63.4 bar, and 70 bar were achieved at HTF inlet temperatures of 70 °C, 80 °C, and 90 °C, respectively. Efficient hydrogen transfer from the desorbing to the absorbing alloy bed generally requires a minimum pressure differential of at least 20 bar. Based on these results, a minimum HTF inlet temperature of 70 °C was selected for further studies on coupled reactor operation using the investigated alloy in the desorbing bed.

5.5 Summary

This chapter presents the activation strategies developed for all the alloys considered in the multistage compressor system across both prototype and large-scale reactor configurations. Additionally, it discusses the results from comprehensive parametric studies conducted to identify the individual optimum operating parameters for each alloy.



Chapter 6

Performance Evaluation of the Hydrogen Compressor

6.1 Preface

This chapter provides an exhaustive study of the hydrogen compressor, covering both small-scale prototype and large-scale industrial implementations. The prototype compressor is a dual-stage system, designed to compress 500 NL of hydrogen per cycle. The primary stage contains 3.5 kg of $\text{La}_{0.3}\text{Ce}_{0.7}\text{Ni}_4\text{Fe}$, while the secondary stage consists of 2.8 kg of $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMn}_{0.3}\text{Fe}_{0.6}\text{Ni}_{0.1}$, equally distributed in two separate tubular reactors. The compressor is designed to operate within a pressure range of 30-300 bar. The study systematically evaluates the influence of coupling bed temperature, hydrogen gas inventory, cycle time, and injection pressure on compressor performance. Additionally, a first-law thermodynamic analysis is performed to assess system efficiency. The large-scale compressor setup features a three-stage compression system, with an additional pre-stage incorporated to accommodate a supply pressure as low as 10 bar. The primary stage reactor is filled with $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ni}_5$, enabling the system to compress approximately 6200 L of hydrogen from 10 bar to 300 bar in three stages. This study focuses on the demonstration of the compression process and the optimization of key operating parameters for the three-stage system. A detailed first-law and second-law thermodynamic analysis is also conducted to assess system performance and energy efficiency. Furthermore, to showcase the practical application of the developed compressor, the study includes an investigation of Type-I commercial cylinder refilling using the MHHC system. Finally, the performance of the developed compressor is benchmarked against existing compressors reported in the literature, leading to a critical assessment and key conclusions.

6.2 Operation of multistage MHHC

The multistage MHHC operates through metal hydride reactors functioning in both single-reactor and thermally coupled reactor modes. Fig. 6.1 illustrates the schematic thermodynamic operations (outlined below) of a three-stage hydrogen compressor, encompassing all relevant processes involved.

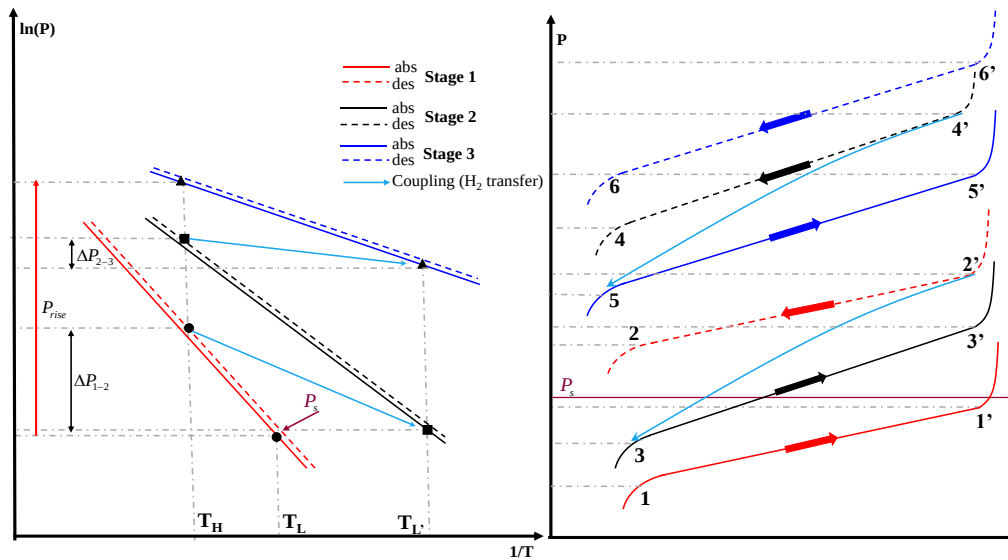


Fig. 6.1: Schematic representation of thermodynamic operations of a three-stage hydrogen compressor.

- *Hydrogen absorption (Stage 1)*: The MH reactor in the first stage absorbs hydrogen at low feed pressure (P_{inj}) and ambient temperature (T_L) from a hydrogen-producing source such as an electrolyser.
- *Preheating and precooling (Stage 2 preparation)*: The second-stage MH reactor is pre-cooled with cold fluid (T_L') to prepare for hydrogen absorption from the first-stage reactor, which is sensibly heated (T_H).
- *Hydrogen transfer (Stage 1 to Stage 2)*: Hydrogen moves from the high-pressure first-stage reactor to the low-pressure second-stage reactor (blue arrow).
- *Preheating and precooling (Stage 3 preparation)*: The third-stage MH reactor is pre-cooled (T_L') with cold fluid to prepare for hydrogen absorption from the second-stage reactor, which is sensibly heated (T_H).
- *Hydrogen transfer (Stage 2 to Stage 3)*: Hydrogen is transferred from the second-stage reactor to the third-stage reactor (blue arrow).
- *Pressurization and discharge (Stage 3)*: The third-stage alloy bed is heated (T_H) to achieve the desired pressure for hydrogen discharge.

6.3 Study on the dual stage MHHC compressing 500 NL of hydrogen

6.3.1 Details of compression process

Fig. 6.2 illustrates a complete hydrogen compression cycle, from hydrogen injection from a constant pressure source to achieving the final delivery pressure. In this study, hydrogen was compressed from a feed pressure of 40-50 bar to a delivery pressure of 200 bar.

Hydrogen was supplied at a constant pressure of 40 bar, simulating an electrolyser. The stage 1 reactor and MH bed were preconditioned for absorption by circulating HTF at 10 °C. Once thermal stability was achieved, the reactor valve was opened, allowing hydrogen to interact with the activated alloy bed. This triggered a sudden temperature rise from 10 °C to 36 °C due to the exothermic metal hydride formation reaction. The MH bed exhibited rapid hydrogen absorption, initially taking up 20.1 g within the first minute due to its unoccupied state. The flow rate peaked at 22.5 NL/min in the initial phase. The effect of HTF became prominent after this transient stage, as volumetric heat removal led to a temperature drop. The absorption rate then declined sharply as the bed approached saturation, and pressure gradient between the injection pressure and equilibrium bed pressure diminished. This was reflected in the decreasing slope of the hydrogen mass uptake curve. The system gradually equilibrated with the 40 bar supply pressure, reaching saturation. The bed absorbed 45.84 g in 7.4 min (444 s), while the final 25.84 g taking over 6.4 min (384 s). Due to the significant thermal inertia of the powdered alloy, an additional 2 min was required for the bed to return to the initial HTF inlet temperature.

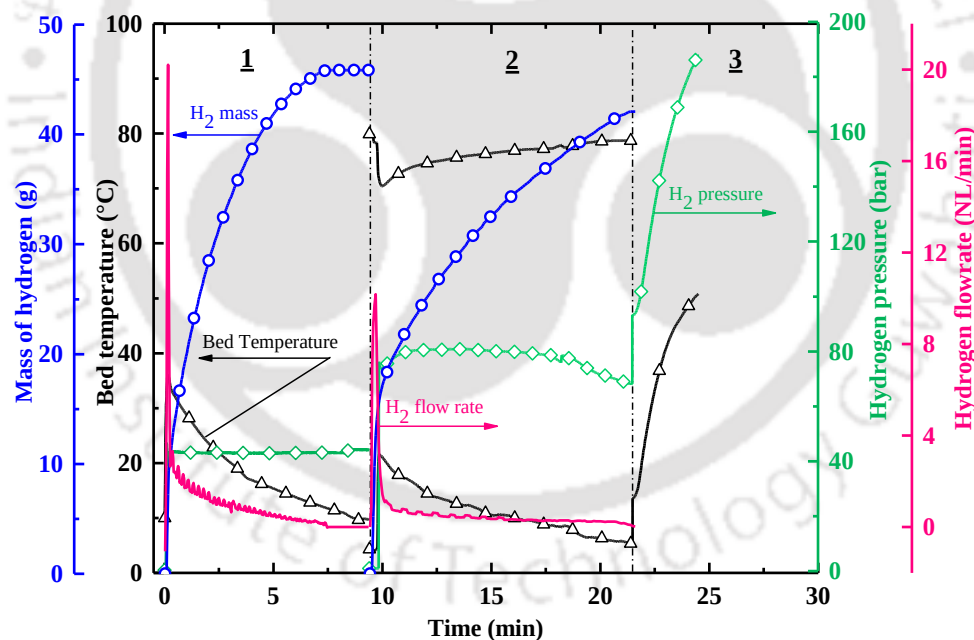


Fig. 6.2: Variation in bed temperature, hydrogen pressure, mass and flowrate in dual stage MHHC

The reactor in the absorbed state was sensibly heated to 80 °C before initiating hydrogen transfer to the stage 2 reactor. This heating step increased the hydrogen pressure, enhancing the pressure gradient between the desorbing and absorbing reactors to facilitate faster hydrogen transfer. Once the target temperature or pressure was reached, hydrogen was introduced into the absorbing MH bed, which had a lower hydrogen concentration and equilibrium bed

pressure. During transfer, the absorbing reactor pressure increased from vacuum, while the desorbing reactor pressure gradually decreased from its post-heating state, eventually stabilizing at 78 bar. The simultaneous pressure drops in both reactors resulted in a two-fold reduction in the hydrogen transfer rate. The maximum flow rate observed was 10 NL/min, significantly lower than the 22.5 NL/min recorded in the initial absorption stage. A total of 42.1 g of hydrogen was transferred from stage 1 to stage 2 in 12 min (720 s). Due to the reduced hydrogen-metal hydride interaction rate, the exothermic heat generation was lower, with the bed temperature rising from 5 °C to 22 °C. Finally, as the stage 2 bed was heated to 50 °C, the hydrogen pressure increased, reaching 188 bar. A critical observation in the overall compression cycle was that the coupling stage governs the total cycle duration. Therefore, further analysis was focussed on identifying key parameters influencing this stage and their impact on overall compression performance.

6.3.2 Comprehensive analysis of factors influencing compressor performance

The system's performance was judged by key parameters such as hydrogen transfer rate, reversibility and delivery pressure, which collectively define its practical viability and operational effectiveness. The impact of key operating parameters, including coupling bed temperature, injection pressure, hydrogen concentration, and cycle time, was analysed in relation to the overall performance metrics.

Effect of low-pressure (LP) bed and high-pressure (HP) bed temperature during coupling

After absorption in the stage 1 reactor at 40 bar and 10 °C, hydrogen was transferred to the stage 2 reactor for further processing. To evaluate the influence of coupling bed temperature, both individually and simultaneously, the low-pressure bed (stage 1) temperature was varied between 50 °C-70 °C, while the high-pressure bed (stage 2) temperature ranged from 5-15 °C. Fig. 6.3 illustrates the impact in terms of (a) reversibility, (b) transfer rate and (c) delivery pressure at the end of stage 2 compression.

The low-pressure bed absorbed 45.84 g of hydrogen during the initial absorption phase. Upon heating the low-pressure bed to 50 °C, while maintaining the high-pressure bed at 15 °C, only 13.13 g of hydrogen was desorbed, yielding a 30% reversibility. When the high-pressure bed temperature was lowered to 5 °C, reversibility improved to 40%, despite maintaining the same low-pressure bed temperature at 50 °C. Further increasing the low-pressure bed temperature to 70 °C, while holding the high-pressure bed constant at 5 °C, resulted in a significant improvement in reversibility to 85%. However, raising the high-pressure bed temperature to 15 °C led to a drop in reversibility to 44%. In summary, at a constant low-pressure bed

temperature of 70 °C, increasing the high-pressure bed temperature from 5 °C to 15 °C led to a 48.2% decrease in reversibility (from 85% to 44%). Conversely, maintaining the high-pressure bed at 5 °C, while reducing the low-pressure bed temperature from 70 °C to 60 °C, resulted in a smaller drop in reversibility from 85% to 60% (17.6%). This analysis demonstrated that in the coupling stage, high-pressure bed temperature has a more significant influence on hydrogen transfer mass than low-pressure bed temperature, making it the critical governing parameter in the process.

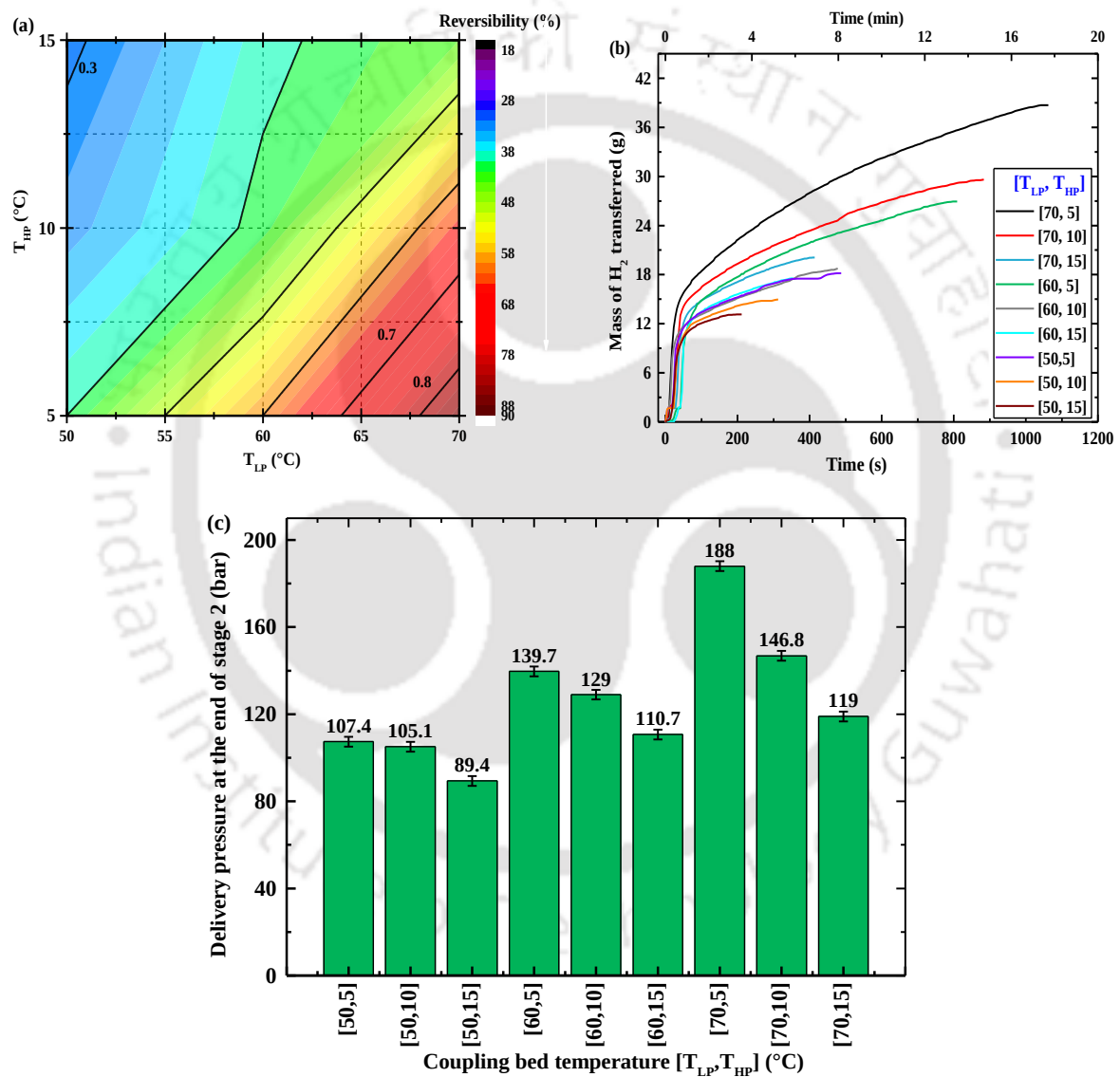


Fig. 6.3: Impact of coupling bed temperature on (a) reversibility, (b) hydrogen transfer rate and (c) delivery pressure

The mass transfer rate was analysed under the same temperature combinations. A key observation was that the initial hydrogen transfer rate remained nearly identical across all cases. All alloy beds achieved 25% reversibility at the same time, indicating that early-stage mass

transfer is independent of bed temperature. This behaviour can be attributed to the rapid gas expansion from high pressure to vacuum, which occurs irrespective of temperature effects. The influence of temperature-driven pressure differentials became evident after this initial phase, as the curves diverged. The fastest hydrogen transfer was recorded when the low-pressure bed was maintained at 70 °C and the high-pressure bed at 5 °C, achieving a mass exchange of 38 g in 1020 s (~17 min). At the same low-pressure bed temperature, but with a higher high-pressure bed temperature of 10 °C, both the transfer rate and cumulative mass transferred declined by 1.5 times and 25%, respectively. This highlights the strong dependence of hydrogen absorption kinetics on the high-pressure bed temperature, making it a critical parameter in governing overall mass transfer efficiency.

The delivery pressure achieved after sensible heating of the stage 2 reactor (high-pressure alloy bed) to 50 °C following the coupling stage was analysed. The maximum pressure recorded was 188 bar when the low-pressure bed was maintained at 70 °C and the high-pressure bed at 5 °C. This was primarily due to the higher hydrogen content in the high-pressure bed, amounting to 38 g (~90% concentration), which directly influenced the equilibrium pressure of the bed. A strong correlation was observed between hydrogen mass transferred and delivery pressure, where a 48.2% reduction in mass transfer resulted in a 51.7% drop in delivery pressure, highlighting the critical role of hydrogen inventory in determining final compression performance. Further analysis on the correlation between hydrogen inventory and cycle time on the overall compressor performance is presented in the next subsection.

Effect of hydrogen inventory and cycle time

Fig. 6.4 illustrates the mass transfer dynamics during the coupling stage of a compression cycle for varying hydrogen inventories within the low-pressure bed. At a bed temperature of 10 °C, and an injection pressure of 40 bar, the system required 9.4 min (564 s) to reach its maximum storage capacity of 45.84 g (~1.3 wt%). A detailed analysis revealed that 80% of the total storage capacity was attained within 3.5 min, while 90% was reached in 5.1 min. Notably, the final 10-20% of absorption, leading to saturation, accounted for over 63% of the total absorption time. This underscores the highly sluggish absorption kinetics as the system approaches saturation. The correlation between hydrogen inventory and cycle time was analysed to assess its impact on overall compression performance. At 80% inventory (36.6 g), approximately 20.7 g of hydrogen was transferred to the high-pressure bed (maintained at $T_{LP}=70$ °C and $T_{HP}=5$ °C) in 8.2 min, achieving a reversibility of 56.5%. At 90% inventory (41.2 g), 28.5 g of hydrogen was transferred in 14.6 min, yielding a reversibility of 67.8%.

These results, illustrated in Fig. 6.5 (a), highlight the direct relationship between reversibility and hydrogen inventory.

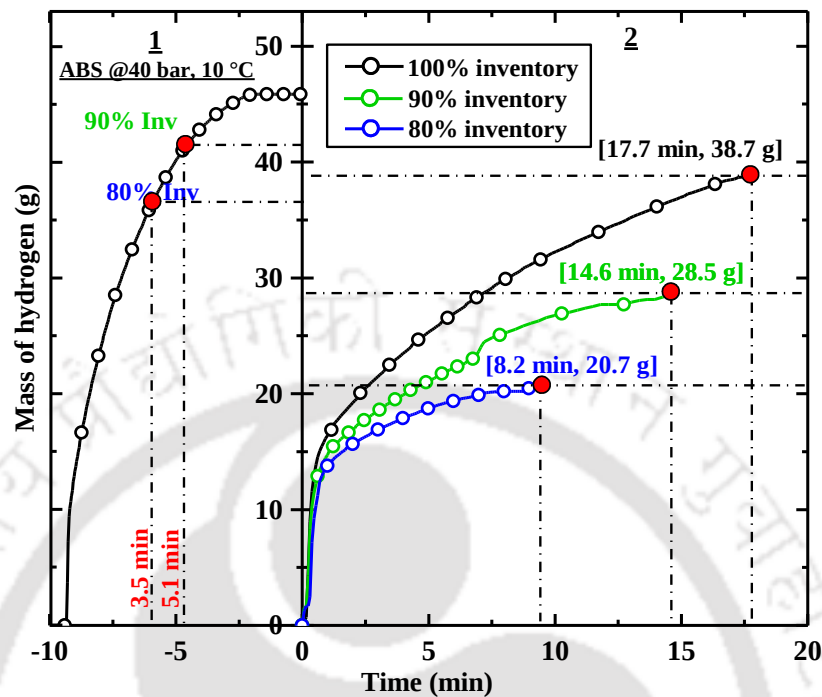


Fig. 6.4: Impact of hydrogen inventory on hydrogen transfer

Interestingly, the transfer rate exhibited a non-linear trend (Fig. 6.5 (b)), with the highest average rate observed for the 100% inventory case at 28.36 L/min, followed by 80% inventory (24.56 L/min) and 90% inventory (21.96 L/min). This behaviour can be attributed to the sluggish transfer kinetics caused by a drop in bed pressure as hydrogen exchange progresses. Post-coupling, the rate of pressure rise in the high-pressure stage (stage 2) during sensible heating from 20 °C to 50 °C was fastest for the 100% inventory case, reaching 188 bar in about 2.6 min as illustrated in Fig. 6.5 (c), followed by 90% and 80% inventory cases as illustrated in Fig. 6.5 (b). The final delivery pressure decreased by 14.3% and 23.9% for 90% and 80% inventory cases, respectively, due to lower hydrogen content. The reduction in the absorption phase cycle time by 62.7% for 80% inventory and 45.7% for 90% inventory lead to an overall cycle time reduction of 37.8% and 21.2%, respectively. However, lower hydrogen handling by the high-pressure bed significantly impacted both delivery pressure and compression rate. The 100% inventory case achieved a compression rate of 14.6 L/min, compared to 13.7 L/min for 90% and 12.6 L/min for 80% inventory cases.

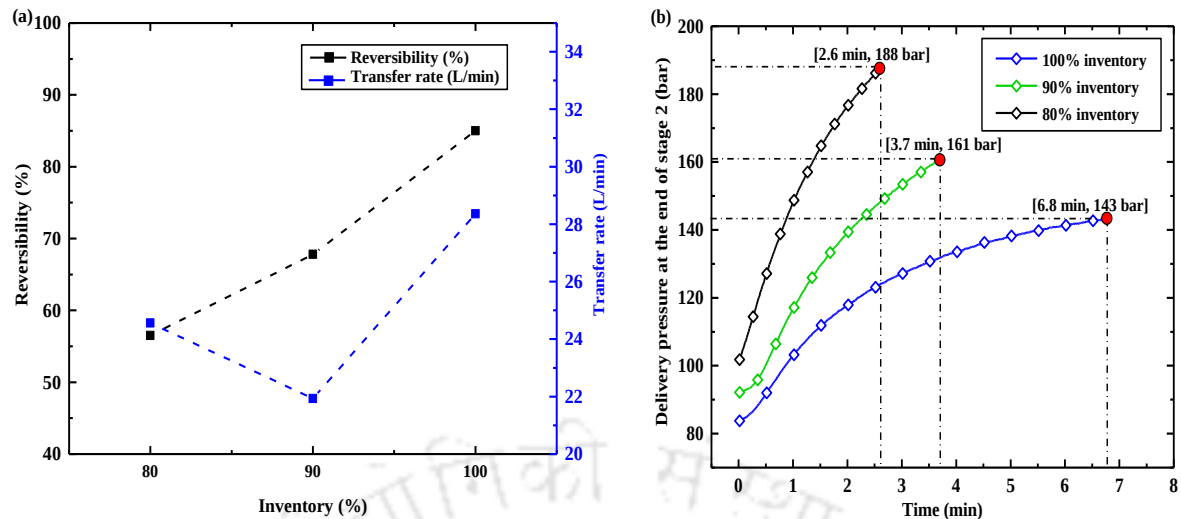


Fig. 6.5: Impact of hydrogen inventory on (a) reversibility and hydrogen transfer rate and (b) rate of pressure rise

Effect of injection pressure

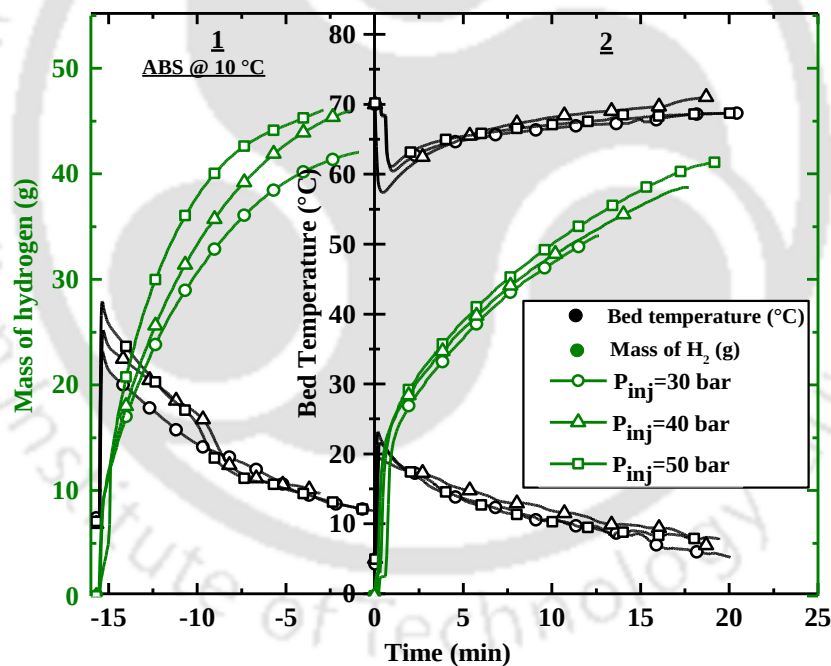


Fig. 6.6: Impact of injection pressure on thermal response and hydrogen transfer

Injection pressure is a key operating parameter influencing reaction kinetics, storage density, operating pressure range, and compression ratio, thereby impacting overall compressor performance. Fig. 6.6 presents the thermal response and mass transfer dynamics of the dual-stage compressor subjected to injection pressures ranging from 30 to 50 bar at 10 °C bed temperature. A reduction in injection pressure from 50 bar to 30 bar resulted in an 8.7%

decrease in hydrogen absorption, from 46.06 g to 42.07 g. However, within this pressure range, the hydrogen transfer rate remained largely unaffected. Notably, the initial absorption phase exhibited significant variations in thermal response, attributed to the rapid reaction kinetics. Following absorption, the low-pressure bed was heated to 70 °C, while the high-pressure bed was maintained at 5 °C. Once thermal equilibrium was reached, hydrogen transfer was initiated, marked by a corresponding temperature drop in the desorbing bed and a rise in the absorbing bed. Although the transfer rate remained unaffected, a substantial increase in mass transfer was observed, from 34.11 g at 30 bar to 41.07 g at 50 bar. Despite this variation in transferred mass, reversibility remained nearly unaffected, ranging from 80% to 89% with increasing pressure (Fig. 6.7 (a)). Interestingly, the highest transfer rate was recorded at 30 bar injection pressure, likely due to its lower cycle time while transferring a theoretically comparable mass of hydrogen. Furthermore, the delivery pressure at the end of stage 2 compression varied insignificantly, from 183 bar to 192 bar. However, the compression ratio exhibited a notable decrease, from 6 at 30 bar to 3.9 at 50 bar (Fig. 6.7 (b)). This emphasizes the need for optimal injection pressure selection, balancing hydrogen transfer and compression ratio, which governs the operating pressure range of the system.

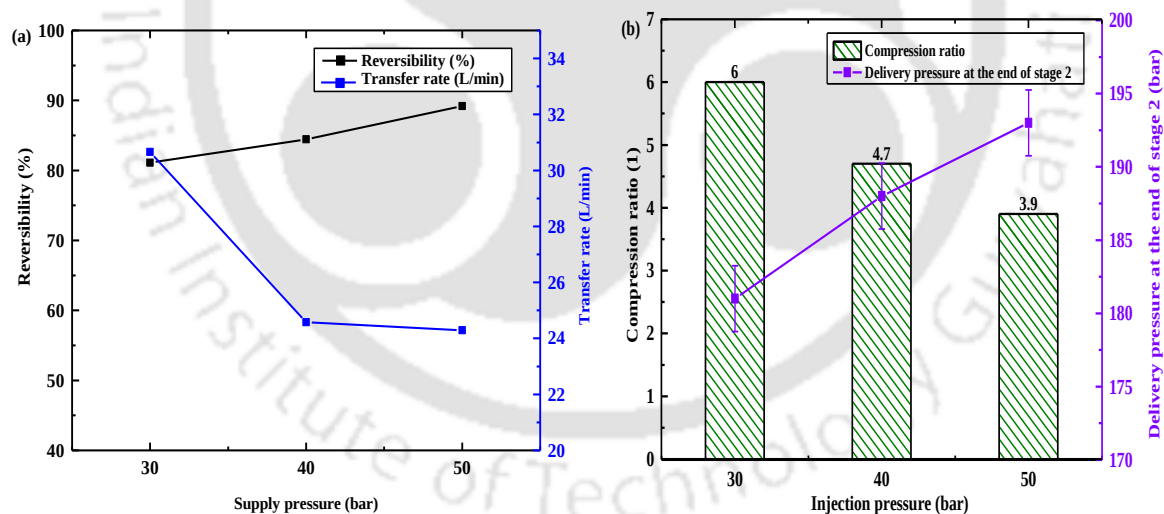


Fig. 6.7: Impact of injection pressure on (a) reversibility and hydrogen transfer rate and (b) compression ratio and delivery pressure

6.3.3 Energy dynamics of the compressor

This section analyses the stepwise energy requirements for operating a dual-stage, 500 L compressor designed to achieve a delivery pressure of 300 bar. The thermal power ($\dot{Q}$) spent to run the compressor was evaluated using Eq. 6.1.

$$\dot{Q} = \dot{m}_{HTF} c_{p,HTF} |T_{inlet} - T_{outlet}| \quad (6.1)$$

where $\dot{m}_{HTF}$ denotes the mass flow rate of the cooling fluid measured using HTF flow meter. $c_{p,HTF}$ represents the specific heat of HTF which is 50-50 water glycol mixture. $T_{inlet/outlet}$ is the temperature recorded by the thermocouple at the reactor's inlet and outlet. The area under the thermal power curve, determined graphically, represents the energy consumed (Q) by the system during that specific step. The isentropic compression work (W_{isen}) for the dual-stage compressor was calculated using Eq. 6.2. The isentropic efficiency (η_{isen}), which quantifies the compressor's effectiveness in converting thermal energy into useful hydrogen potential energy at elevated pressure, was evaluated using Eq. 6.3.

$$W_{isen} = \frac{\psi}{\psi - 1} \sum_{i=1}^2 \left(n_{H_{2i}} R_u T_{ai} \left(\left(\frac{P_{Hi}}{P_{Li}} \right)^{\frac{\psi-1}{\psi}} - 1 \right) \right) \quad (6.2)$$

$$\eta_{isen} = \frac{W_{isen}}{Q} \times 100 \quad (6.3)$$

where n_{H_2} denotes moles of hydrogen compressed to elevated pressure P_{Hi} from P_{Li} at absorption temperature T_a for stage i^{th} . R_u is universal gas constant. ψ denotes the ratio of specific heat which was considered to be 1.4 for isentropic process.

As previously discussed, the first step in the compression cycle involved the sorption reaction, where hydrogen absorption occurred in the stage 1 reactor at a constant pressure. This process requires efficient thermal management, as the exothermic heat of reaction must be dissipated to maintain optimal absorption kinetics. To achieve this, cold HTF (maintained at 10 °C) was continuously circulated through the reactor coolant channels, effectively removing the heat generated during absorption. The thermal power dynamics exhibited a sharp initial rise, attributed to the increase in HTF outlet temperature caused by the volumetric heat generation within the alloy bed. The total energy exchange during this phase was determined by integrating the thermal power curve, yielding a value of 609.8 kJ. Applying a steady-state energy balance, incorporating the mass of absorbed hydrogen and the reaction enthalpy of the alloy, the theoretical energy expenditure was calculated to be 540.5 kJ. The experimentally determined value was approximately 11.5% higher, primarily due to additional cooling demands from HTF circulation, which also dissipated heat from auxiliary components such as

reactors, filters, fins, and circuit elements. The next step involves the sensible heating of the alloy bed in the absorbed state, raising its temperature from the absorption temperature to the desired elevated temperature. This phase does not involve mass transfer, yet an abrupt rise in the thermal power curve was observed initially, attributed to the large temperature difference between the heat source and the alloy bed. As heating progressed, the alloy bed gradually approached the source temperature, stabilizing the thermal power profile. The experimentally determined energy expenditure was found to be 252.3 kJ almost comparable to the value predicted by the steady-state energy balance (262.5 kJ).

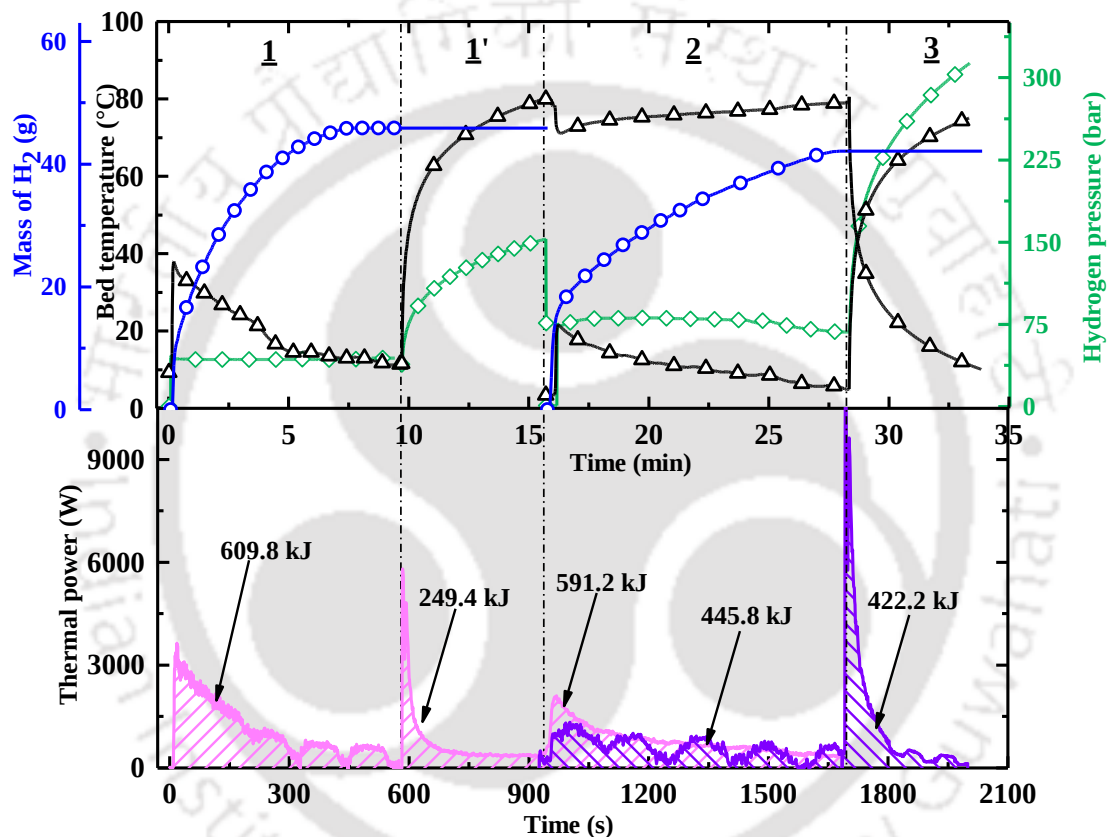


Fig. 6.8: Variation in thermal power in a single compression cycle (1: Hydrogen absorption from a source at 40 bar, 1': Sensible heating of Stage 1, 2: Coupling of Stage 1 and Stage 2, 3: Sensible heating of Stage 2)

The second major step involves hydrogen transfer from the low-pressure (stage 1) bed to the high-pressure bed, facilitated by maintaining the low-pressure bed at an elevated temperature through HTF circulation while keeping the high-pressure bed at a lower temperature to enhance the hydrogen transport rate. Fig. 6.8 presents the thermal power dynamics, depicting two curves: one representing the energy supplied to sustain the high temperature in the low-pressure bed and the other indicating the cooling demand for removing the volumetric heat from the high-pressure bed. While both thermal power curves are plotted on the positive axis for

absolute magnitude representation, in reality, heat is added to the low-pressure bed and removed from the high-pressure bed. The corresponding energy expenditures were determined to be 591.2 kJ for heating and 445.8 kJ for cooling, exceeding theoretical predictions by 14.8% and 12.5%, respectively. In the final step, the high-pressure bed in the absorbed state was heated to 75 °C to further pressurize hydrogen beyond 300 bar. This process required approximately 422.2 kJ of thermal energy.

The total thermal energy expenditure was determined to be 2318.4 kJ resulting in a specific energy consumption of 55.2 kJ/g of hydrogen to uptake hydrogen from 40 bar to 313 bar. The isentropic work required for two-stage hydrogen compression, calculated using Eq. 6.2, was determined to be 171.1 kJ. Consequently, the isentropic efficiency of the compressor was evaluated at 7.4% (Eq. 6.3). Considering the cooling demand during the sensible cooling phase, where reactors are cooled from their elevated temperature to the absorption temperature, an additional 675.5 kJ of thermal energy is required, further reducing the isentropic efficiency to 5.7%. However, this efficiency drop can be offset by utilizing solar thermal systems, which can supply almost 55% of the total energy required for compressor operation. A detailed analysis, summarized in

Table 6.1, reveals key insights into energy consumption during the compression cycle. The mass transfer steps exhibited higher energy consumption than theoretically predicted values, which primarily account for reaction heat. In reality, the thermal inertia of solid compressor components contributes an additional 10-15% to overall energy expenditure, depending on the temperature differential between the system and ambient. Theoretical energy estimates deviated by less than 5% from experimental values during sensible heating stage. Additionally, a significant energy demand was observed during the coupling stage, suggesting that energy efficiency can be significantly improved by minimizing the number of compression stages while achieving the required operating pressure range.

Table 6.1: Summary of the energy dynamics of the dual stage MHHC

Steps	Energy expenditure: experiment (kJ)	Energy expenditure: theoretical (kJ)	Variations (%)
Step 1	609.8	540.5	11.4
Step 1'	249.4	262.5	5.2
Step 2	1037	892.5	13.9
Step 3	422.2	410.2	2.8

6.4 Study on three stage MHHC compressing 6200 NL of hydrogen

6.4.1 Details of compression process

Variation in bed temperature

The variation of bed temperature during a single cycle operation of 3-stage hydrogen compression is illustrated in Fig. 6.9. Hydrogen was initially absorbed from a constant pressure source at 15 bar while maintaining the first stage reactors at 10 °C. The alloy bed readily absorbed hydrogen, generating exothermic heat, evidenced by the sudden increase in the bed temperature. The temperature surged from the initial level to 49 °C as hydrogen continuously interacted with the alloy bed. The heat dissipation within the bed was slower due to its lower inherent thermal diffusivity ($7.62 \times 10^{-7} \text{ m}^2/\text{s}$). However, the heat transfer rate gradually improved as the absorption rate decreased. This improvement was attributed to the diminishing pressure difference between the supply and bed pressure. Such behaviour can be explained by the first-order reaction equation governing the hydrogen-alloy interaction, which illustrates a direct correlation between the equilibrium pressure and the operating pressure (supply pressure in this scenario). The absorption process ceased upon reaching the initial bed temperature.

Thereafter, the stage 1 reactors were sensibly heated to 90 °C before initiating the coupling between stage 1 and stage 2 reactors. It is noteworthy that a single reactor, along with the alloy bed, required approximately 0.8 h (2880 s) to reach the target desorption temperature of 90 °C from the initial absorption temperature of 10 °C. The required heat for this process would eventually be supplied by a large source integrated with a waste heat recovery system. Thus, duration required for sensible heating would reduce further as per the heating rate. The desorbing reactor temperature was chosen to achieve a hydrogen pressure sufficient to promote complete absorption in the absorbing reactor. Meanwhile, the stage 2 reactors were maintained at 10 °C by recirculating HTF at a rate of 10 L/min. Hydrogen was allowed to transfer from

the stage 1 reactor, continuously maintained at 90 °C, to the stage 2 reactor held at 10 °C. As hydrogen was released from the stage 1 reactor, a decrease in bed temperature was observed, while an increase in bed temperature was noted in the absorbing reactor, indicating the direction of hydrogen flow. The rise in bed temperature during the absorption was relatively lower as compared to absorption from a constant supply pressure source. This difference can be attributed to the reduced pressure gap resulting from the simultaneous decrease and increase in equilibrium bed pressure in the desorbing and absorbing reactors, respectively. The stage 3 reactors were prepared to absorb hydrogen from the stage 2 reactors by recirculating HTF at 5 °C at a rate of 10 L/min. The stage 2 reactors were heated up to 90 °C before initiating the coupling between stage 2 and stage 3. It is noteworthy that the alloy configured in stage 3 exhibits a higher equilibrium pressure compared to the alloys considered in the prior stages. Therefore, a wider pressure gap was ensured by reducing the absorbing temperature. The interaction between the alloy and hydrogen was observed as a rise and drop in the absorbing (stage 3) and desorbing (stage 2) alloy beds, respectively. Once the alloys attained the initial temperature, the stage 3 reactors were sensibly heated to 91.2 °C to compress the absorbed hydrogen to the targeted pressure (300 bar in the present case). It was discovered that the overall cycle time to compress about 550 g (~6200 L) of hydrogen was 4.65 h (~280 min).

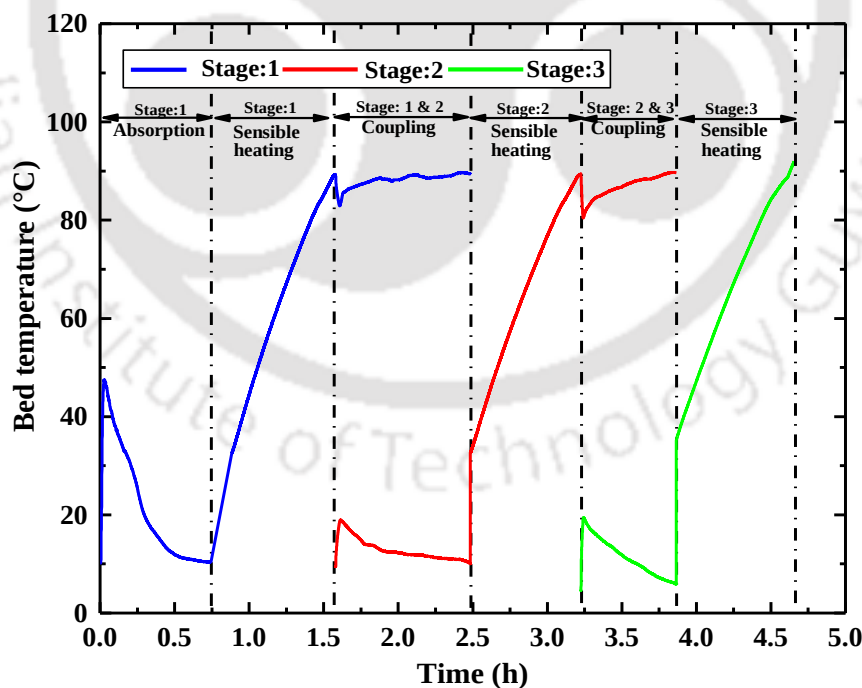


Fig. 6.9: Variation in the bed temperature during a compression cycle by the developed three stage MHHC

Variation in hydrogen pressure

The variation in hydrogen pressure during compression is visualised in Fig. 6.10. To streamline the data, only the pressure profile of a single reactor is displayed. The constant pressure source mirrors an electrolyser producing hydrogen at 15 bar. The bed efficiently stored hydrogen, attaining 15 bar by the end of absorption, which occurred in approximately 0.74 h (44.6 min). Post sensible heating, the coupling between stage 1 and stage 2 was established by navigating the flow of hydrogen from the high-pressure source (stage 1) to the low pressure (stage 2). The pressure of hydrogen in stage 1 was elevated by sensibly heating the alloy bed to the appropriate temperature (90 °C in present case). The pressure obtained post heating was observed to be 70.3 bar which was sufficient to promote rapid absorption in stage 2 reactor by examining the PCT plot of $\text{La}_{0.5}\text{Ce}_{0.5}\text{Ni}_4\text{Fe}$. Stage 2 reactors actively absorbed hydrogen and reached a pressure of 20.5 bar at the end of coupling (2.48 h) between stage 1 and stage 2. Expediting the transfer of hydrogen could have been achieved by either elevating the desorption temperature above 90 °C or lowering the absorption temperature further below. However, such adjustments would lead to increased energy consumption with only marginal enhancements in the mass of hydrogen transferred. The quantity of hydrogen transferred can be deduced from Fig. 6.11.

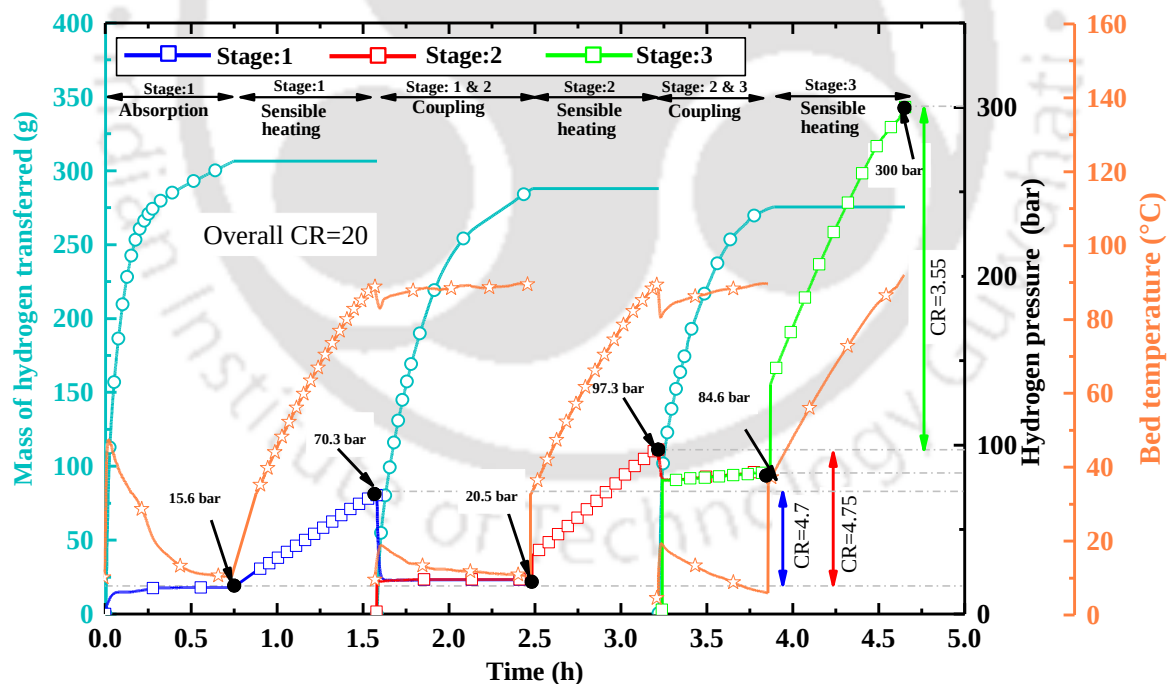


Fig. 6.10: Variation in the hydrogen pressure during compression by the developed three stage MHHC

The hydrogen stored in stage 2 reactors was pressurized to 97.3 bar by heating up to 90 °C. The stage 3 alloy demonstrated an equilibrium pressure of 50 bar at 5 °C, with significant plateau slope. To maintain a maximum pressure gradient, the absorbing reactor was kept at the

lowest possible temperature using water as the HTF. A final equilibrium pressure of 84.6 bar was achieved at the end of coupling between stage 2 and 3, which lasted approximately 40.2 min, transferring over 90% of the hydrogen absorbed in the preceding step. The transfer rate was faster compared to the coupling of stage 1 and 2, attributed to the faster absorption characteristics of the AB₂ type alloy considered for stage 3. Following hydrogenation, the reactors (S3R1 and S3R2) were heated to compress the hydrogen up to 300 bar. The pressure reached 300 bar at 91.2 °C, and the heating was promptly ceased upon reaching the target pressure. The overall compressor time was 4.65 h. Stage compression ratios were 4.7 (stage 1 and 2), 4.75 (stage 2 and 3), and 3.55 (stage 3) sequentially. The maximum pressures of 70.3 bar and 97.3 bar attained post-heating of stage 1 and 2, respectively, indicated potential uses for the intermediate compressed hydrogen in various applications such as prolonged FC operation, chemical labs and drug manufacturing. An overall compression ratio of 20 was achieved within the operating temperature range of 5-91.2 °C.

Variation in hydrogen flow rate

Hydrogen was compressed in three stages to 300 bar within the system after being absorbed from a constant pressure source at 15 bar. The transfer of hydrogen among the stages facilitates the increase in pressure in each stage, contributing to the overall compression process. Faster hydrogen transfer enhances the overall productivity of compression. Fig. 6.11 depicts the variation in reacted fraction and hydrogen transfer during the steps involved in mass transfer. The hydrogen transfer rate was notably highest during the hydrogenation of the stage 1 alloy bed. Initially, almost 307 g (1.23 wt%, 0.88 reacted fraction) of hydrogen was absorbed in just 44.6 min by the stage 1 reactor bed. The maximum transfer rate exceeded 23.1 g/min, with an average rate of 6.87 g/min during the stage 1 absorption. The rate of hydrogen transfer decreased as the hydrogen moved to the stage 2 reactor during the coupling of stage 1 and 2. Approximately 94% of the absorbed hydrogen, totalling 288 g (1.15 wt% of stage 2, 0.88 reacted fraction), was transferred to stage 2 in 54.3 min, with an average transfer rate of about 5.29 g/min. This drop-in transfer rate can be attributed to the diminishing pressure gap between the equilibrium pressure of the alloy beds involved. However, the transfer rate was higher during the coupling of stage 2 and 3. Around 275.5 g (1.10 wt% of stage 3, 0.85 reacted fraction) was transferred in 40.2 min, at an impressive average flow rate of 6.85 g/min, owing to the excellent reaction kinetics of the stage 3 alloy. Table 6.2 provides a comparison of the maximum hydrogen transfer rates.

Table 6.2: Details about the hydrogen flow through various stages

Process	Maximum mass flow rate	Average mass flow rate
	(g/min)	(g/min)
Stage 1 Absorption	23.1	6.87
Stage 1 and 2 Coupling	19.9	5.29
Stage 2 and 3 Coupling	97.71	6.85

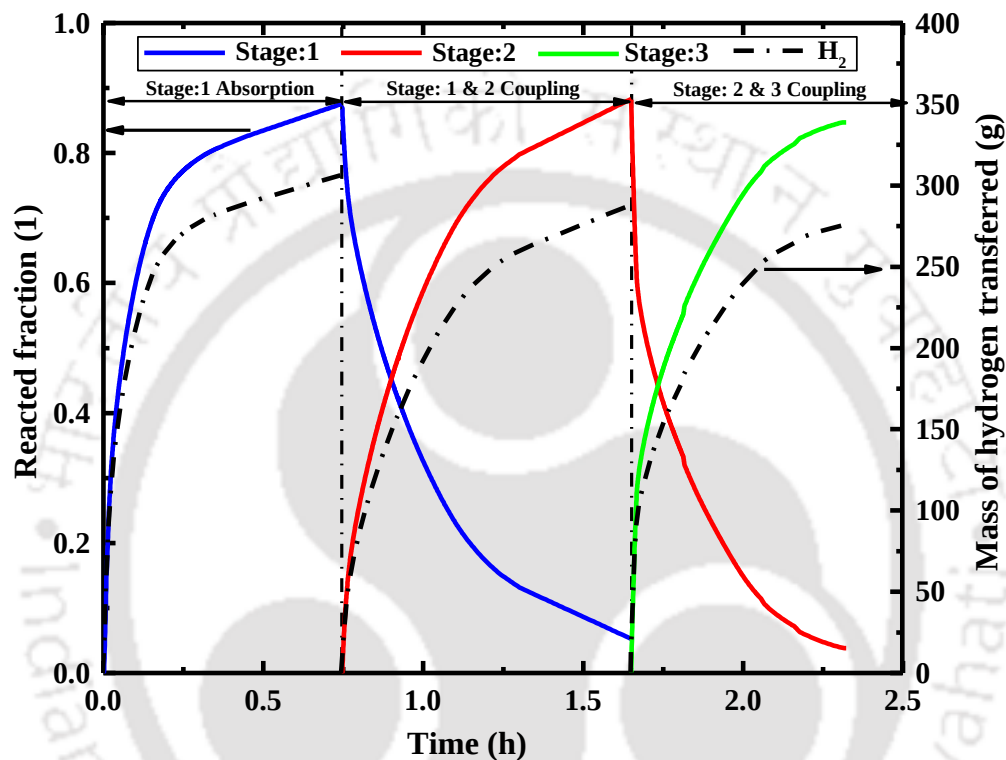


Fig. 6.11: Variation in the mass of hydrogen transferred and reacted fraction in the corresponding stages during a compression cycle

6.4.2 Optimisation of operating parameters

Optimising the operating parameters is necessary to obtain the best working conditions to compress maximum amount of hydrogen to the desired delivery pressure in shortest time. Several compression cycles were performed by varying the intermediate temperature, supply pressure and the source temperature. The overall impact was analysed based on three deciding parameters: mass of hydrogen transferred, transfer duration and amount of energy consumed.

Influence of supply pressure

The examination of influence of supply pressure on compressor performance is pivotal, as excessively high pressure accelerates hydrogen absorption, whereas lower pressure widens the operational range. This section thus scrutinizes the impact of supply pressure on the MHHC's

operational efficiency and depicts the inferences in Fig. 6.12. Within the investigation, supply pressure ranged from 5 to 30 bar, with absorption temperature fixed at 15 °C which was decided after examining the PCT of stage 1 alloy. The optimal supply pressure was determined through analysis of various factors, including absorbed hydrogen mass, reacted fraction, stage 1 absorption duration, and compression ratio. These considerations were made with the target delivery pressure set at 300 bar. At supply pressures of 5 bar and 10 bar, the observed hydrogen absorption masses were merely 100 g and 149.26 g, respectively, resulting in reaction fractions of only 0.31 and 0.46. Additionally, absorption time exceeded 1 h, indicating sluggish reaction kinetics. However, supply pressure exceeding 15 bar yielded reacted fractions surpassing 0.9, indicating saturation. Interestingly, absorption times decreased significantly with increasing supply pressure beyond 15 bar. Specifically, absorption duration halved when supply pressure increased from 5 to 15 bar, further reducing by 52.1% at 30 bar. Notably, compression ratios dropped drastically from 60 to 10 as supply pressure rose from 5 to 30 bar, signifying a diminished operational range. This implies that, to maintain a constant 300 bar supply pressure, hydrogen production must exceed 30 bar, an uncommon occurrence with current electrolyser technology. Considering these factors, a supply pressure of 15 bar was deemed optimal at an absorption temperature of 15 °C.

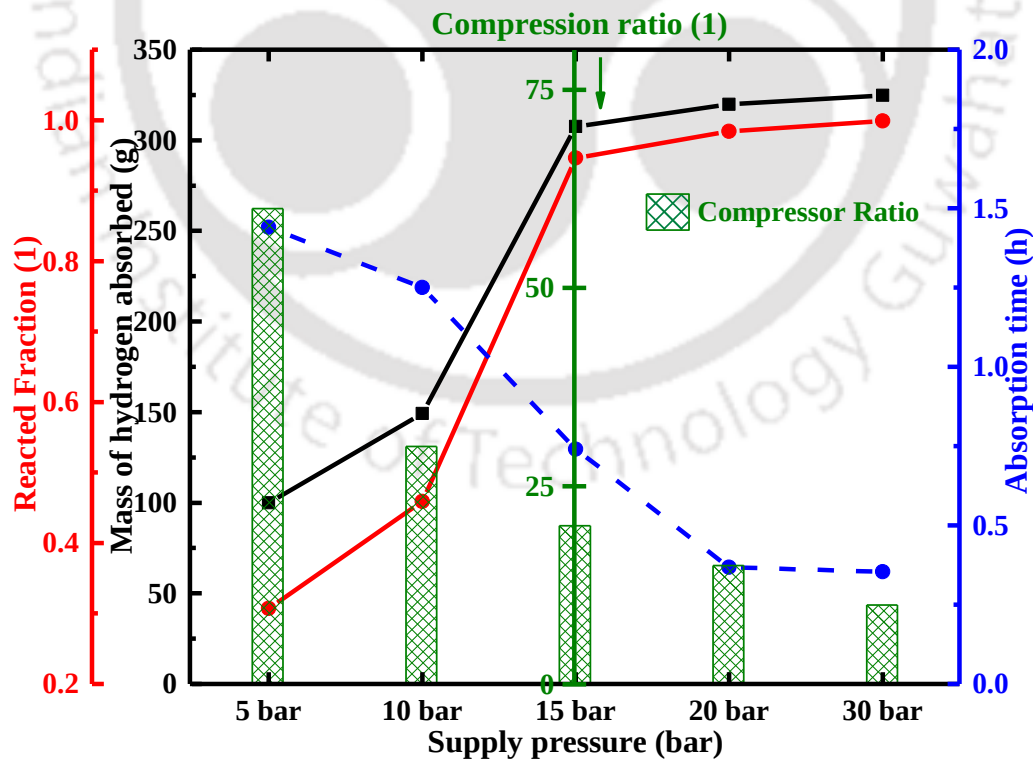


Fig. 6.12: Influence of supply pressure

Influence of intermediate temperature during coupling of stage 1 and 2

The transfer of hydrogen from the desorbing reactor (stage 1) to the absorbing reactor (stage 2) relies heavily on maintaining a temperature difference between the two reactors. Fixing the higher and lower temperature limits during coupling is crucial for optimizing hydrogen transfer rates. In this investigation, the desorbing temperature was systematically varied between 70 °C and 90 °C while maintaining the absorption temperature between 5 °C and 10 °C.

The selection of temperature combinations was methodically guided by several key factors, including the mass of transferred hydrogen, the reversibility obtained, and the duration of transfer. As depicted in Fig. 6.13, maintaining the desorbing reactor at 70 °C and the absorbing reactor at 10 °C resulted in a modest transfer of 160.35 g of hydrogen, with a reversibility of 52.1%. However, fixing the desorbing temperature to 70 °C while reducing the absorbing temperature to 5 °C yielded significantly improved results, with 245 g of hydrogen transferred and a reversibility rate of 79.6%, representing a noteworthy 52.7% increase in transferred hydrogen mass. Nonetheless, this enhancement was accompanied by an increase in transfer duration from 14.4 min to 51.25 min due to the additional hydrogen mass transfer.

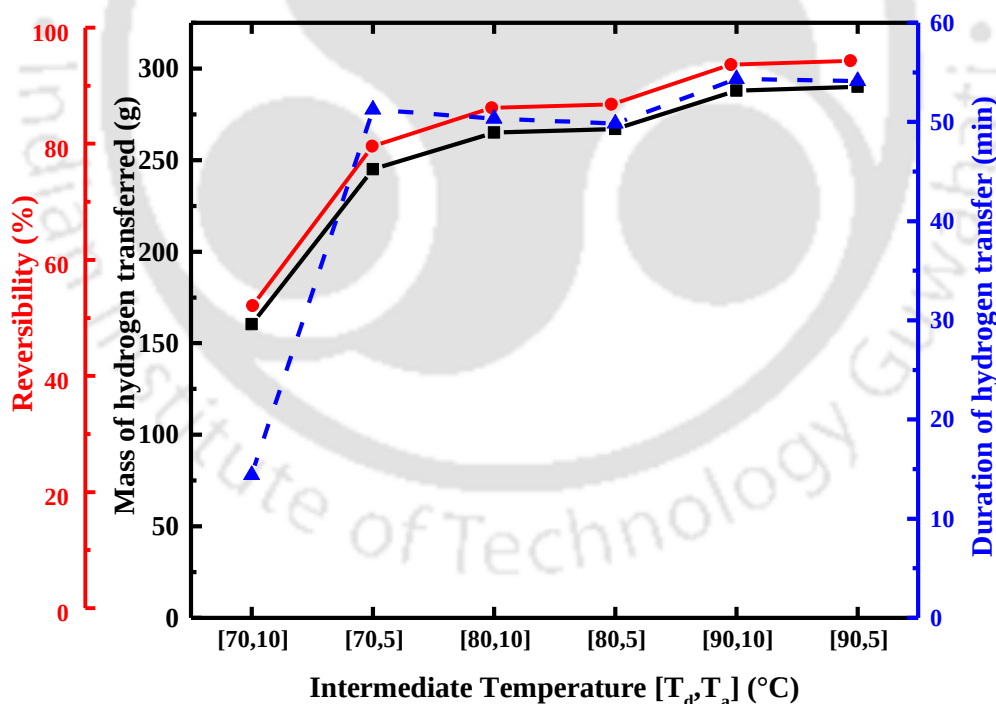


Fig. 6.13: Influence of temperature combinations during the coupling of stage 1 and 2

Further, raising the desorption temperature to 80 °C while maintaining the absorbing reactor at 10 °C, resulted in the transfer of 265 g of hydrogen with an 86.2% reversibility. This adjustment notably reduced the transfer duration from 51.25 min to 50.33 min owing to the heightened

pressure difference. Subsequent adjustments by maintaining the desorption temperature at 80 °C and lowering the absorption temperature to 5 °C, yielded a marginal increase in transferred hydrogen mass to 267 g, a reversibility rate of 86.8% and improving the transfer duration to 49.86 min. The improvement in the amount and rate of hydrogen transfer in case of lower absorption temperature was mainly due to increase in the pressure gradient of the coupled reactors.

In pursuit of reversibility exceeding 90%, the desorption temperature was elevated to 90 °C while maintaining absorption temperature at 5 and 10 °C. This notably increased the mass of transferred hydrogen, although the improvement was minimal when the absorption temperature was reduced from 10 to 5 °C. A maximal reversibility of 94.5% was achieved at a desorption temperature of 90 °C and an absorption temperature of 5 °C. Notably, the maximum hydrogen transfer rate was also observed at the same temperature combination (290.06 g in 54.15 min). It's noteworthy that there was only a slight change in the average hydrogen transfer rate when the desorption temperature was raised above 80 °C. This observation was attributed to decreased reaction kinetics during the concurrent hydrogenation/dehydrogenation phases after reaching 80% reversibility, due to a diminishing potential drive (pressure difference). However, comparing the significant variation in the mass of hydrogen transferred, a desorption temperature of 90 °C and absorption temperature of 10 °C was opted as the optimum temperature combination during the coupling of stage 1 and stage 2 reactors.

Influence of intermediate temperature during coupling of stages 2 and 3

Given the higher absorption equilibrium bed pressure of the stage 3 alloy, the desorption bed temperature (stage 2 alloy) was set above 80 °C to facilitate a significant amount of hydrogen transfer. However, the absorption temperature was varied in the range of 5-15 °C. The temperature combination of 80 °C for desorption and 15 °C for absorption was not considered due to the minimal pressure difference observed. The impact of consideration of various temperature combinations is depicted in Fig. 6.14.

At a desorption temperature of 80 °C and absorption temperature of 10 °C, the transfer of hydrogen from stage 2 to stage 3 resulted in an exchange of 205.2 g, achieving a reversibility of 70.7%. Lowering the absorption temperature to 5 °C marginally increased the reversibility by 2% and the mass transferred by 5.4 g, albeit with a longer transfer duration. To optimize energy consumption, the desorption temperature was set at 90 °C while maintaining the absorption temperature at 15 °C. However, this yielded unsatisfactory results in terms of both hydrogen exchanged and transfer duration.

Subsequently, maintaining the desorption temperature at 90 °C, experiments were conducted by varying the absorption temperature to 5 °C and 10 °C. Notably, the mass of hydrogen exchanged increased significantly, reaching up to 269.1 g, with a reversibility exceeding 90% (92.8%) when the absorption temperature was set at 10 °C. Further lowering the absorption temperature to 5 °C led to a substantial improvement in the mass of hydrogen transferred, achieving a maximum of 275.5 g and a reversibility of 95.6%, accompanied by a significant reduction in transfer duration to 40.3 min.

The enhanced transfer rate can be attributed to the superior reaction kinetics of the AB₂ type alloy used in the final stage. This observation is further supported by comparing the transfer duration during the coupling of stage 1 and 2 alloys.

Table 6.3 summarises the optimum operating parameters. It is noteworthy that the reversibility reported in the results reflects only the hydrogen transfer within the coupled reactor system. However, when the reactors were desorbed under ambient conditions, nearly 100% reversibility in hydrogen storage was achieved. This high reversibility was consistently observed during the reactor activation process.

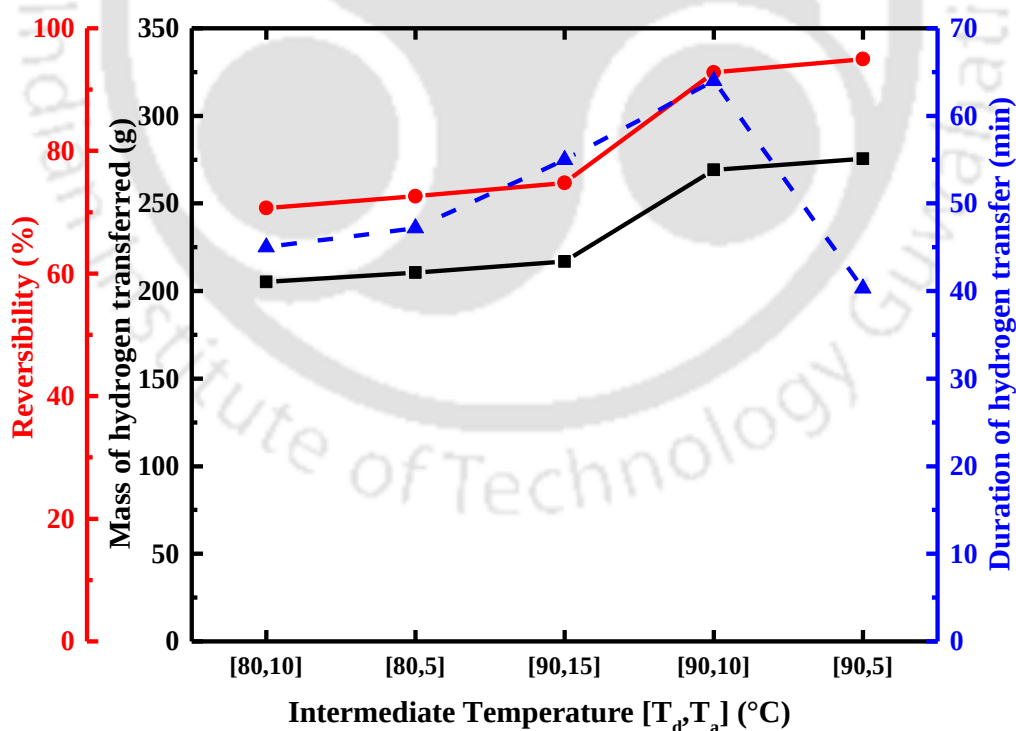


Fig. 6.14: Influence of temperature combinations during the coupling of stage 2 and 3

Table 6.3: Optimum operating parameters

Operation	Temperature set (°C)	HTF flow rate (l/min)	Other parameters	Mass of hydrogen transferred (g)	Reversibility (%)
Stage 1 absorption	15	10	Hydrogen supply pressure: 15 bar	307 g	-
Stage 1 and 2 coupling	Stage 1: 90 Stage 2: 10	10	-	288 g	93.8
Stage 2 and 3 coupling	Stage 2: 90 Stage 3: 5	10	-	275.5 g	95.6

Energy consumption and performance analysis

Thermal energy consumption

The prominent steps where the energy was removed/supplied to handle the exothermic or endothermic heat are:

- Sensible cooling of stage 1 reactor from its desorption temperature (90 °C) to optimum absorbing temperature (15 °C)- Q_1
- Removal of exothermic heat to absorb hydrogen at the desired supply pressure (15 bar)- Q_2
- Sensible heating of stage 1 reactor to the desired desorption temperature (90 °C) from absorption temperature (15 °C)- Q_3
- Sensible cooling of stage 2 reactor from its desorption temperature (90 °C) to optimum absorbing temperature (10 °C)- Q_4
- Removal of exothermic heat from absorbing reactor (Stage-2) and supply of required endothermic heat to the desorbing reactor (Stage-1) after attaining the optimum temperature combination ($T_d=90$ °C and $T_a=10$ °C)- Q_5
- Sensible heating of stage 2 reactor to the desired desorption temperature (90 °C) from its absorption temperature (10 °C)- Q_6
- Sensible cooling of stage 3 reactor from desorption temperature (90 °C) to optimum absorbing temperature (5 °C)- Q_7
- Removal of exothermic heat from absorbing reactor (Stage-3) and supply of required endothermic heat to the desorbing reactor (Stage-2) after attaining the optimum temperature combination ($T_d=90$ °C and $T_a=5$ °C)- Q_8
- Sensible heating of stage 3 reactor to the desired desorption temperature (90 °C) from absorbing temperature (5 °C)- Q_9

The total thermal energy accounted for operating a single compression cycle is the sum of absolute values of sensible heat and reaction heat (Eq. 6.4).

$$Q_{total} = |Q_{sensible}| + |Q_{reaction}| \quad (6.4)$$

$$Q_{sensible} = |Q_1| + |Q_3| + |Q_4| + |Q_6| + |Q_7| + |Q_9| \quad (6.5)$$

$$Q_{reaction} = |Q_2| + |Q_5| + |Q_8| \quad (6.6)$$

The sensible heat was calculated by considering the mass of the compressor units, which comprise the reactor body and the alloy configured within the reactor, their respective heat capacities and the temperature differential. It can be expressed as Eq. 6.7:

$$Q_{sensible} = \sum_{i=1}^n (m_i \times c_{p,i}) \times \Delta T \quad (6.7)$$

here m_i is the mass of a constituent compressor unit i and $c_{p,i}$ denotes its corresponding heat capacity. The summation is performed over the components undergoing heating or cooling, with ΔT representing the temperature change of the system. The total mass of the 19 stainless steel tube assembly is 61 kg, and each reactor contains 25 kg of hydride material. The specific heat of the stainless-steel reactor and hydride alloy are approximately 500 J/(kg·K). The calculated magnitude of all sensible heat energy are shown in Table 6.4.

Table 6.4: Energy expenditure during the sensible heating of compressor units

Sensible heat	Components of compressor	Thermal energy consumption (MJ)
Q_1	Stage 1 reactor and alloy	3
Q_3	Stage 1 reactor and alloy	3
Q_4	Stage 2 reactor and alloy	3.1
Q_6	Stage 2 reactor and alloy	3.1
Q_7	Stage 3 reactor and alloy	3.4
Q_9	Stage 3 reactor and alloy	3.4

Reaction heat encompasses the energy expended to either form or break metal-hydrogen bonds. It is evaluated by multiplying enthalpy of formation with the number of moles of hydrogen being absorbed or desorbed. It is expressed as (Eq. 6.8):

$$Q_{reaction} = n_{H_{2i}} \times \Delta H_{a/d} \quad (6.8)$$

The enthalpy of formation during absorption (ΔH_a) and desorption (ΔS_a) is determined from the pressure composition temperature (PCT) plot, as illustrated in Fig. 3.15. The masses of hydrogen absorbed and desorbed were obtained from *Variation in hydrogen flow rate*. The calculated magnitude of all the considered reaction heat is shown in Table 6.5.

The total thermal energy required to operate the compressor over one complete cycle to compress effective hydrogen amount of 275.5 g (3.1 Nm³) was found to be 36.2 MJ or 10.1 kWh.

Table 6.5: Energy expenditure during the sorption reactions

Reaction heat	Mass of hydrogen absorbed or desorbed (g)	Enthalpy of alloy (J/mol)	Thermal energy consumption (MJ)
Q_2	307	27000	3.9
Q_5	288	27500, 23500	7.5
Q_8	275.5	23800, 18300	5.8

Compression work

The compression work for MHHC was assessed using equations primarily employed for determining compression work in conventional mechanical compressors. Three main schemes were utilized for this purpose. The first scheme was applied to evaluate compression work under conditions where it was minimal, namely reversible isothermal compression. However, it is practically unfeasible to execute a process that is entirely isothermal. It is expressed as (Eq. 6.9):

$$W_{isothermal} = \sum_{i=1}^3 n_{H_{2i}} R_u T_{ai} \ln \left(\frac{P_{Hi}}{P_{Li}} \right) \quad (6.9)$$

Table 6.6: Evaluated compression work for various type of compression process

Type of compression work	Magnitude of work (MJ)
Isothermal	1.7
Adiabatic	1.9
Polytropic	1.8

Maximum compression work was supplied under reversible adiabatic conditions, known as an isentropic process. Gas compression typically generates heat, raising its temperature. Isentropic compression occurs when this heat was prevented from escaping the system, rendering it

adiabatic. The temperature rise increases the gas's specific volume, necessitating more compression work. The adiabatic compression work was evaluated using (Eq. 6.2):

Polytropic compression work, which falls between these two extremes, is commonly used to evaluate real-world compression processes. The equation required to evaluate the polytropic compression work resembles with that of isentropic work with polytropic coefficient in place of γ which was considered to be 1.3. The evaluated compression work for all the three cases discussed above are given in Table 6.6.

Compression efficiency

MHHC can be treated as a heat engine which converts low grade thermal energy to compress hydrogen (mechanical work) to desired delivery pressure. The maximum thermal efficiency that a heat engine can achieve cannot exceed the Carnot efficiency. Hence, the Carnot efficiency is treated as a limiting efficiency which is influenced only by the maximum (T_h) and minimum (T_l) temperature limits. It is expressed as Eq. 6.10:

$$\eta_c = \left(\frac{T_h - T_l}{T_l} \right) \times 100 \quad (6.10)$$

In the present study, Carnot efficiency was calculated for each individual stage as well as for the overall compressor system. Given the variation in the minimum temperature at each stage, the average of these minimum temperatures (absorption temperature) was utilized to determine the Carnot efficiency of the entire system. The presence of various irreversibilities leads to a decline in the efficiency of a thermal machine. Consequently, first law efficiency is used to determine the fraction of thermal energy converted into useful work. It is evaluated by using Eq. 6.11:

$$\eta_I = \left(\frac{W_c}{Q_{total}} \right) \times 100 \quad (6.11)$$

where W_c denotes compression work. Based on the type of work, the first law efficiency can be classified as isothermal efficiency, isentropic efficiency and polytropic efficiency. Second law efficiency (η_{II}) measures how effectively a thermal machine approaches to its maximum possible efficiency i.e. Carnot efficiency. It is determined by taking the ratio of first law efficiency and Carnot efficiency. The evaluated efficiencies of the developed MHHC is depicted in Table 6.7.

As previously mentioned, adiabatic and isothermal compression processes represent the upper and lower limits of a real-world compressor's performance. Actual compression processes

typically fall between these two extremes. Consequently, it was observed that polytropic efficiency lay between isentropic and isothermal efficiencies. Carnot efficiency primarily depended on the temperature of the heat source and sink. The optimal temperature combinations for the various stages of compression had already been identified. During the third stage of hydrogen compression, the maximum source temperature and minimum sink temperature were reached, resulting in the highest Carnot efficiency (23.7%) for this stage. Similarly, first law efficiency is significantly influenced by the compression ratio, the mass of hydrogen compressed, sink temperature, and the thermal energy utilized. It was observed that the efficiency of the compressor decreased in successive stages (6.9% to 3.7%) due to a reduction in the mass of hydrogen being compressed. Additionally, there was a decline in the pressure ratio during the third stage (4.7 in first stage, 3.5 in third stage), which accounted for its lower efficiency compared to the first and second stages. Conversely, the greatest increase in pressure was achieved in the third stage, from 84.6 bar to 300 bar within the reactor. The overall efficiency of the compressor was determined to be 4.9%, considering the polytropic process, with bounds of 5.1% and 4.8% for isentropic and isothermal processes, respectively. The second law efficiency of the overall compressor, ranging from 22% to 24%.

Table 6.7: Compression efficiency for various type of compression process

Type of compression efficiency		Carnot efficiency	First law efficiency	Second law efficiency
Isothermal	Stage:1	20.7	5.4	26.1
	Stage:2	22.0	3.8	17.2
	Stage:3	23.7	3.2	13.4
	Overall	22.0	4.8	18.2
Isentropic	Stage:1	20.7	7.2	34.8
	Stage:2	22.0	4.8	21.9
	Stage:3	23.7	3.8	16
	Overall	22.0	5.1	23.2
Polytropic	Stage:1	20.7	6.9	33.3
	Stage:2	22.0	4.6	21
	Stage:3	23.7	3.7	15.5
	Overall	22.0	4.9	22.2

The overall first-law efficiency of the developed compressor ranged from 4.8% to 5.1% across all considered classification of compression processes. This closely aligns with previously reported values in the literature. Some studies have reported efficiencies in the range of 10% to 20%, primarily due to differences in the assumptions made during the evaluation of system efficiency. For instance, Barale et al., (2023) reported an adiabatic efficiency of 11%, not accounting for the thermal energy required to remove the exothermic heat during absorption and the sensible cooling from the desorption temperature. Other relevant studies with target pressures over 200 bar include that of Wang et al. (Wang et al., 2006b), that compressed only 4.5 mole of hydrogen from 20 bar to 450 bar and reported an isothermal efficiency of 18.6%. The authors did not consider the sensible heat required to raise the compressor body temperature from 20 °C to 99 °C or the sensible cooling required to bring back the reactor body to the requisite absorption temperature. Furthermore, the desorption temperature was used instead of the absorption temperature to evaluate the isothermal efficiency, which resulted in an overestimation. Similar considerations was observed in another study (Wang et al., 2011). Despite these assumptions, works such as those by Northrup and Heckes, (1980) and Muthukumar et al., (2005) demonstrated theoretical efficiencies in the range of 2-8%, emphasizing the need for optimized reactor design, compression ratios, and alloy selection.

Thermodynamic evaluation of an integrated waste heat recovery and MHHC system

Fig. 6.15 illustrates the schematic of a multistage MHHC system integrated with both a waste heat recovery system and a solar thermal heating unit. The thermodynamic analysis presented herein is based on experimental data obtained from an industrial-scale prototype. The integrated system is functionally divided into three subsystems: the heat supply unit, the cooling supply unit, and the multistage MHHC module. The heat supply unit comprises a waste heat recovery system (WHRS) interfaced with a thermal power plant, and a solar water heater system (SWHS). The cooling unit consists of a chiller driven externally by electricity.

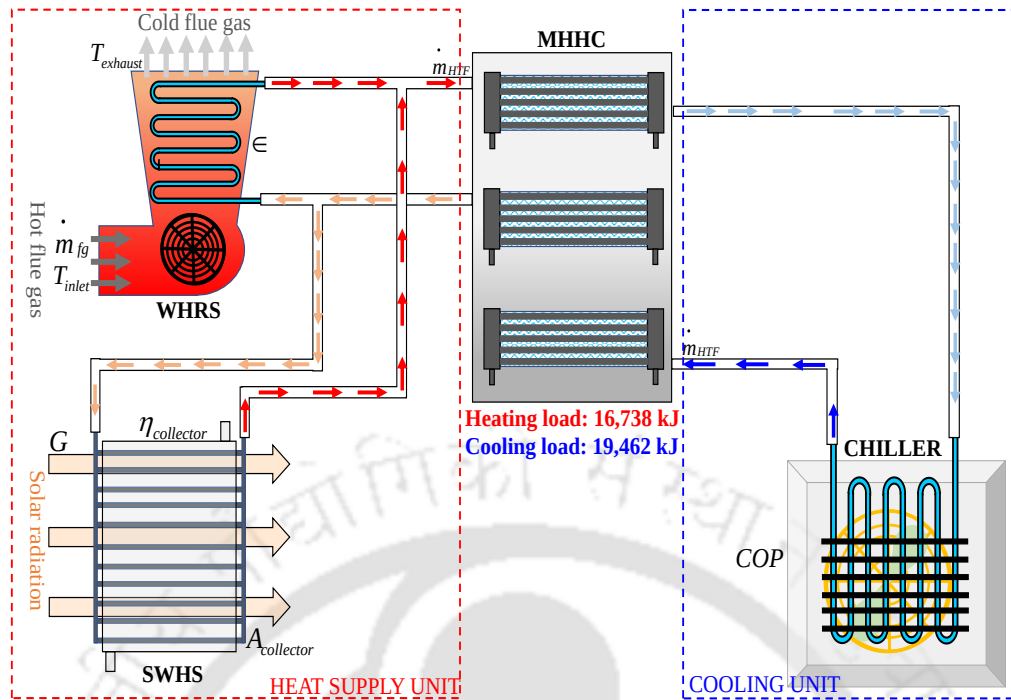


Fig. 6.15: Schematic representation of the integrated MHHC system

a. Waste heat recovery system

The waste heat recovery system is integrated as an auxiliary module with a coal-fired thermal power plant to utilize the residual thermal energy of flue gases that would otherwise be discharged unused. Assuming medium-grade waste heat availability in the temperature range of 150 °C to 200 °C, the flue gas flow rate ($\dot{m}_{fg}$) was maintained at approximately 0.5 kg/s in this analysis. The specific heat of flue gas ($c_{p,fg}$) was taken to be 1.1 kJ/kg. To prevent condensation and subsequent corrosion, the flue gas is not cooled below 50 °C. Accordingly, the total recoverable waste heat was estimated using Eq. 6.12, considering the effective temperature differential above the condensation threshold and a heat transfer effectiveness (ϵ) of 0.7. It was evaluated to be 57.75 kW.

$$HP_{WHRS} = \epsilon \times \dot{m}_{fg} \times c_{p,fg} \times (T_{inlet} - T_{exhaust}) \quad (6.12)$$

b. Solar water heater system (SWHS)

The solar water heating system harnesses thermal energy from incident solar radiation using flat-plate solar collectors. For the present analysis, a collector area ($A_{collector}$) of 2 m² was considered, with an average solar irradiance (G) of 650 W/m². The collector efficiency ($\eta_{collector}$) was considered to be 0.7. Based on these parameters, the maximum thermal energy available from the solar water heater was estimated to be approximately 0.91 kW using Eq. 6.13.

$$HP_{SWHS} = \eta_{collector} \times A_{collector} \times G \quad (6.13)$$

c. Chiller

The chiller unit was externally powered using electricity, and its performance was characterized by a coefficient of performance (COP) of 5.

The required heating and cooling loads were obtained from the preceding section. To compress 275.5 g of hydrogen, the heating and cooling load was determined to be 16,738 kJ and 19,462 kJ respectively. The required thermal input can be readily supplied by the combined output of the waste heat recovery system and the solar water heater system which accounts to be 58.66 kW. As previously discussed, the availability of excess heat is also expected to reduce the overall heating duration. The cooling demand was assumed to be fully met by the externally powered chiller. A comprehensive heating load balance and the corresponding operation durations are presented in Table 6.8.

Table 6.8 : Energy balance of the integrated MHHC system

Steps	Heating load (kJ)	Experimental duration (s)	Duration in an integrated system (s)
Stage 1 sensible heating	3000	2880	51.14
Stage 1 desorption during coupling	3960	3260	-
Stage 2 sensible heating	3100	2880	52.85
Stage 2 desorption during coupling	3278	2418	-
Stage 3 sensible heating	3400	2880	57.96

It was observed that the overall cycle duration significantly decreased due to the reduction in sensible heating time, from approximately 48 min (experimentally determined) to under 1 min, resulting in a 51.6% reduction in total cycle time when integrated with the waste heat recovery and solar thermal systems. Consequently, the only external energy input (Q_{input}) required was for the cooling load, which could be met using a chiller with a coefficient of performance (COP) of 5. The corresponding electricity consumption, calculated using Eq. 6.14, was found to be 3892.4 kJ.

$$Q_{input} = \frac{Q_{CL}}{COP} \quad (6.14)$$

The desired output of the integrated system was compressed hydrogen, quantified by the polytropic work ($W_{polytropic}$) of compression, previously determined to be 1800 kJ. Accordingly,

the overall system efficiency ($\eta_{overall}$), calculated using Eq. 6.15, was found to be 46.25%, which represents a highly promising performance level in comparison to other non-mechanical hydrogen compression technologies.

$$\eta_{overall} = \frac{W_{polytropic}}{Q_{input}} \quad (6.15)$$

Comparison with other H₂ compression technologies

The developed MHHC system demonstrated a thermal efficiency of approximately 5%, which aligns with values reported in the literature, where large-scale MHHCs typically do not exceed 8% efficiency. Given their relatively low standalone efficiency, it is advisable to operate MHHCs using waste heat or solar thermal energy. Integration with such renewable or recovered heat sources significantly enhances the overall system efficiency, which was found to reach as high as 46.25% in the present study. Compared to other compressors, Electrochemical Hydrogen Compressors (EHCs) achieve much higher compression efficiencies (up to 80-95%), but their sensitivity to impurities, low throughput, and high capital and operating costs limit their viability (Durmus et al., 2021; Grigoriev et al., 2011). Mechanical compressors, while offering higher throughput and efficiency (30-50%), suffer from issues such as high noise levels, substantial electrical energy consumption, and costly maintenance (Sdanghi et al., 2019a). In contrast, MHHCs, when integrated with waste heat recovery systems, excel in safety, simplicity, low operating costs, and inherent hydrogen purification, making them a promising alternative for large-scale hydrogen compression applications.

6.4.3 Hydrogen refilling

After compression, hydrogen was transferred into Type I cylinders (47 L water capacity, 7 m³ hydrogen capacity) to assess refilling time and average throughput. While commercial Type 1 cylinders are engineered to withstand pressure of 200 bar, they are commonly used to store hydrogen up to 150 bar. In this study, hydrogen was compressed up to 160 bar using the MHHC. Subsequently, the compressed hydrogen was transferred into storage cylinders at empty and half-filled conditions. The study determines the hydrogen throughput during the course of refilling.

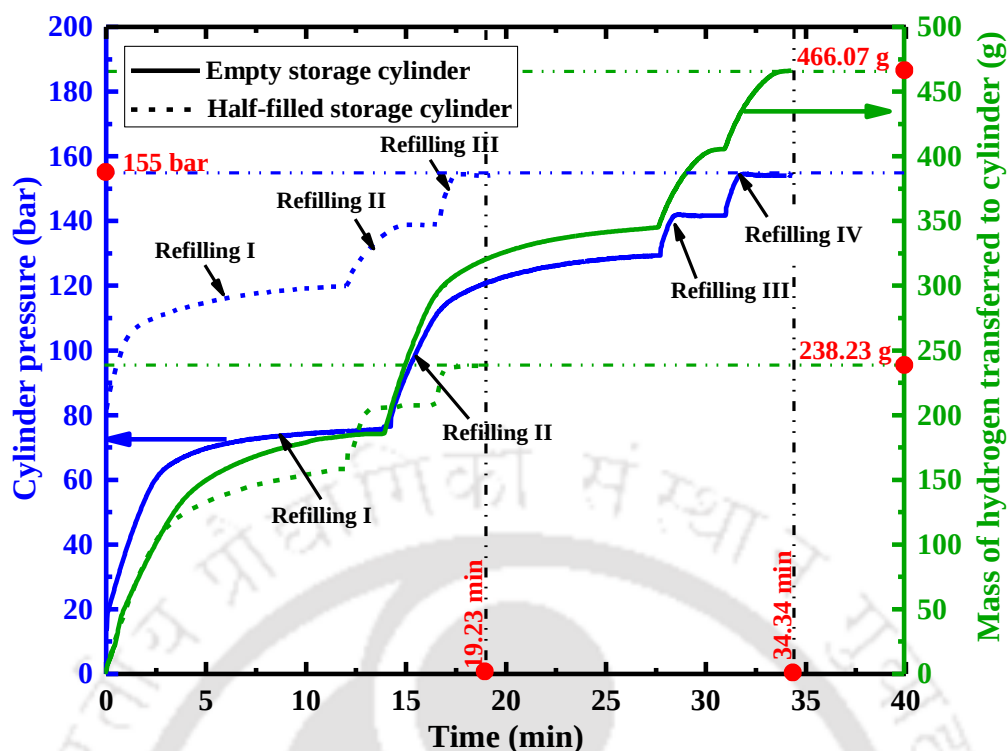


Fig. 6.16: Variation in cylinder pressure and amount of hydrogen transferred during refilling

Fig. 6.16 illustrates the variation of cylinder pressure and mass of hydrogen discharged during refilling after compression in the both the cases. It was reported that an empty cylinder required four refills to accommodate 466.07 g of hydrogen at 155 bar. Initially, the cylinder was filled with hydrogen from reactor 1 of stage 3 (S3R1), transferring 185.6 g of hydrogen to reach a pressure of 76 bar. The reactors were continuously supplied with HTF at 43 °C to sustain the discharge. However, as hydrogen continued to discharge, the alloy bed pressure gradually fell thereby slowing down the refilling process. As the discharge stopped, compressed hydrogen from reactor 2 of stage 3 (S3R2) was discharged to continue refilling. The second refill transferred about 160 g of hydrogen, elevating the pressure to 130 bar in the cylinder. As the discharge ceased, the reactors were reheated to 70 °C to recompress the remaining hydrogen up to 160 bar before discharging into the cylinder. An additional 120.47 g of hydrogen was discharged in two refills to completely fill the cylinder and obtain a pressure of 155 bar. The filling of an empty cylinder took approximately 34.34 min. Upon investigation it was found that a half-filled cylinder is refilled within 19.23 min in 3 refills. As mentioned, a total of 466.07 g out of 551 g of compressed hydrogen was successfully stored at a discharge pressure of 160 bar, equating to approximately 85%. This indicates that 85% of hydrogen compressed to 160 bar could be effectively stored externally at 155 bar. The compression capacity would likely

improve if hydrogen were compressed to 300 bar and then discharged to refill Type I cylinders; however, this approach was not pursued due to safety concerns, as the design pressure of the cylinder is below 200 bar.

Table 6.9: Maximum, average hydrogen flow and empty cylinder pressure during refilling

Cases	Refilling sequence	Maximum throughput (NL/min)	Average throughput (NL/min)	Empty cylinder pressure	
				Initial (bar)	Final (bar)
Case: 1 Empty Cylinder	I	600	329.9	13	77
	II	197	175.5	77	130
	III	150.3	148.2	130	144
	IV	150.3	153.6	144	155
Case: 2 Half-filled Cylinder	I	549	297.9	80	119
	II	173.6	159.1	119	141
	III	154.4	147.6	141	155

Table 6.9 shows the maximum and average hydrogen throughput during the refilling process, and the initial and final cylinder pressure during the series of refilling. The maximum throughput occurred at the outset of the refilling process, gradually diminishing as refilling progressed. This decline can be attributed to the diminishing pressure difference between the MHHC reactor and the storage cylinder, leading to a decrease in throughput from 600 NL/min during the first refilling to 150.3 NL/min by the fourth refilling. Moreover, the equilibrium pressure of hydrogen within the MH bed, being influenced by the concentration of hydrogen, further contributed to the reduction in throughput as the hydrogen content within the bed decreased. Consequently, the bed was reheated to achieve the same discharge pressure (160 bar) at a higher temperature (70 °C). During the filling of half-filled cylinder, the throughput of the first refilling was found to be lower as compared to the empty cylinder case. This can be attributed to the inadequate pressure difference between the MHHC and the cylinder. Hence, the drop in throughput results in the reduced improvement (80 bar to 119 bar) in cylinder pressure attained at the end of first refilling. This can be confirmed post comparison of the initial and final cylinder pressure during both the cases. A single cycle of MHHC operation was enough to refill one empty cylinder and two half-filled cylinders under 40 min.

6.4.4 Assessment of compressor performance with relevant literature targeting pressure over 200 bar

This section evaluates the performance of the developed compressor system by comparing it with previous research targeting pressures of 200 bar or more, as shown in Fig. 6.17. The comparisons considered weight ratio, compression rate, absorption and delivery pressures, compression ratio, number of stages, and maximum delivery temperature. An efficient compressor system is characterized by optimal design for maximum mechanical strength and efficient thermo-hydraulic performance, high compression rate, low absorption pressure, high delivery pressure, high compression ratio, fewer stages, and low maximum delivery temperature. The present work was compared with the work reported by Wang et al., (2006b), Li et al., (2010), Lototskyy et al., (2012) and Barale et al., (2023).

When comparing weight ratios, Lototskyy et al., (2012) reported an enhanced weight ratio of 0.78, attributed to their lower targeted delivery pressure of 200 bar. As the delivery pressure increased, the weight ratio of the designed compressor reactor was observed to decrease. This trend was confirmed by Wang et al., (2006b) and Li et al., (2010), who targeted delivery pressures of 450 bar and 745 bar, respectively, resulting in reduced weight ratios of 0.34 and 0.24. The present work demonstrated an improved weight ratio of 0.41 compared to Barale et al., (2023), who achieved a weight ratio of 0.4 with a targeted delivery pressure of 250 bar. The present study targeted a delivery pressure of 300 bar, highlighting enhanced performance in terms of weight ratio. This work demonstrated an impressive hydrogen compression rate of 22.2 L/min, indicating the effectiveness of the thermal compressor in achieving target pressure rapidly. It was evaluated by finding the ratio of amount of hydrogen compressed to the cycle time. The cycle time refers to the duration from the initial absorption of hydrogen at low pressure to the completion of sensible heating in the final stage, ensuring the system reaches the required delivery pressure. Notably, this performance surpasses that of previous studies by Li et al.,(2010), Lototskyy et al., (2012), and Barale et al., (2023), which reported compression of only 1005 L , 2023 L and 119 L of hydrogen, compared to 6191 L in the present study.

Examining the compression ratio, most of the considered research, including this study, apart from Barale et al., (2023), exhibited a good compression ratio in the range of 14-25. However, an absorption pressure exceeding 20 bar limits the usability of MHHCs coupled with electrolyzers. In the present work, the absorption pressure of 15 bar makes it viable for such applications. In contrast, Li et al., (2010) absorption pressure of 50 bar, makes it infeasible for low-pressure Anion Exchange Membrane (AEM) based electrolyzers. The study reported by

Lototskyy et al., (2012) proves to be most viable for low pressure absorption as the absorption pressure is as low at 10 bar.

The present work employs three stages to operate within a pressure range of 15-300 bar and a temperature range of 5-91.2 °C, promoting its use as a coupled system extracting thermal energy from solar thermal or waste heat recovery systems. In contrast, other studies require temperatures exceeding 100 °C, inhibiting the use of water as a heat transfer fluid and limiting their potential application with solar thermal and waste heat recovery systems. The developed system's capability to absorb hydrogen from a low-pressure source of 10-15 bar and compress it up to 300 bar requires the addition of an extra stage.

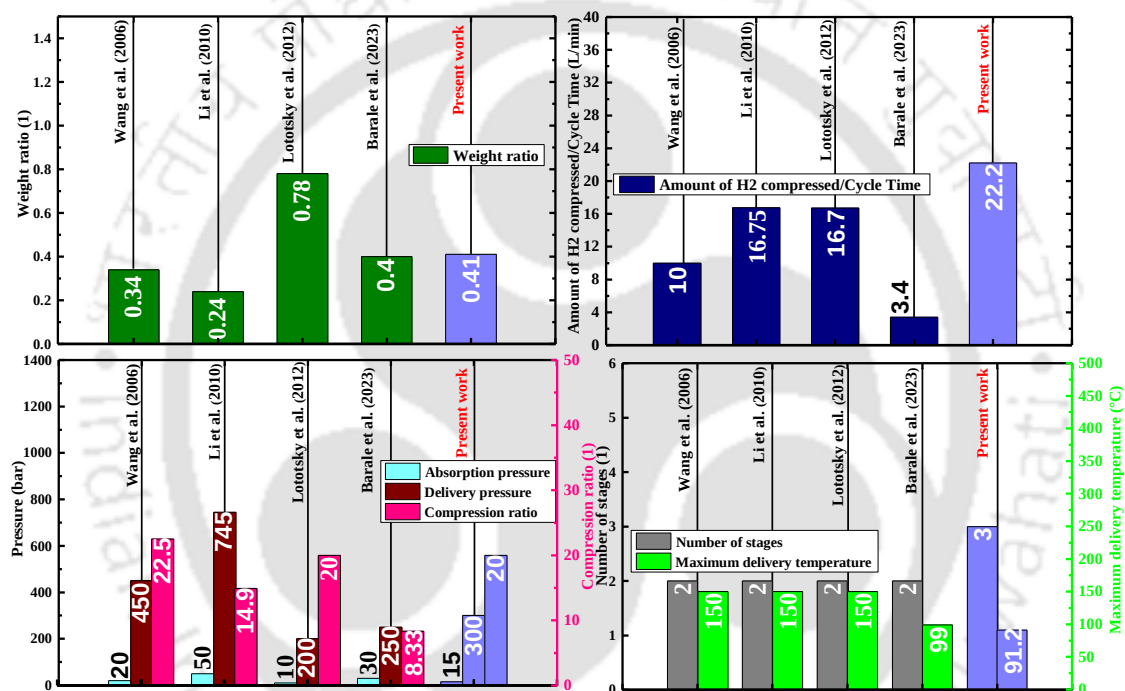


Fig. 6.17: Comparison of the present work with relevant literature (Barale et al., 2023; Li et al., 2010; Lototskyy et al., 2012; Wang et al., 2006b).

The present work did not follow the same methodology of experimentation as followed by Lototskyy et al., (2012). Hence, comparing the productivity or hydrogen discharge rate would not be logical. However, the developed compressor demonstrated the capability to refill a Type I-cylinder up to 155 bar within 5.2 h (including compression and discharge) within a temperature range of 5 °C-91.2 °C discharging 85% (466.07 g out of 551 g) of compressed hydrogen is promising. The cycle time can further be improved if the maximum temperature is further increased beyond 100 °C which studies like Lototskyy et al., (2012), Li et al., (2010) and Wang et al., (2006b) have attempted. In the present scenario the productivity of compressor while refilling a Type I-cylinder post compressing up to 160 bar was derived to be 16.8 L/min

6.5 Summary

This chapter presents a comprehensive study on multi-stage Metal Hydride Hydrogen Compressors (MHHC). An exhaustive investigation was conducted on a prototype reactor to examine the key factors influencing MHHC performance. Insights gained from these studies guided the design and construction of an industrial-scale hydrogen compressor, for which a detailed energy analysis was also performed. Furthermore, the developed compressor system was experimentally evaluated for its capability to refill a Type I hydrogen cylinder, demonstrating its practical applicability.



Chapter 7

Conclusions and Future Scope

This thesis presents a comprehensive study on the design, development, and evaluation of metal hydride-based hydrogen compression systems. It encompasses the development of specialized reactors for compressor applications, the selection and characterization of suitable metal hydride alloys, the fabrication of both prototype and large-scale experimental setups, and the experimental validation of the system for high-pressure hydrogen compression. The work addresses critical research gaps related to achieving target delivery pressures using low-grade thermal energy. Notably, it identifies the absence of any previously reported thermally driven hydrogen compressor capable of achieving pressures beyond 250 bar within a narrow operational temperature window of 5-100 °C. In addition, the thesis highlights the development of a comprehensive mathematical model for multistage MHHC systems, incorporating essential physical phenomena such as volume expansion, variable permeability, thermal hysteresis, and sloped PCT characteristics of metal hydride alloys. This model served as a foundation for designing stage-specific reactors optimized for performance and scalability. The thesis also details the establishment of dedicated experimental test setups at both prototype and industrial scales to facilitate in-depth studies on high-pressure hydrogen compression. Exhaustive experimental investigations were conducted on the developed systems to evaluate performance, efficiency, and practical viability. The key findings and conclusions drawn from this work, along with recommendations for future research, are summarized in this chapter.

7.1 Design of reactors for high pressure compression (>140 bar)

- A tubular reactor configuration was chosen for high-pressure hydrogen compression, targeting a delivery pressure of 300 bar while ensuring an appropriate design safety margin.
- Increasing bed diameter beyond 30 mm significantly impairs hydrogen transfer, resulting in pronounced spatial non-uniformities and slower reaction progression due to thermal and mass transfer limitations.
- Smaller diameters (<20 mm) promote uniform hydrogen transfer, but may lead to impractically long reactor geometries, posing fabrication and operational challenges.
- An optimal bed diameter of 20-30 mm is recommended, balancing efficient hydrogen absorption/desorption kinetics with manageable reactor size for practical implementation

7.2 Design of reactor for low to moderate pressure compression (<140 bar)

- The embedded cooling tube reactor (ECTR) configuration, enhanced with spiral fins and an outer cooling jacket, presents a structurally viable and thermally optimized solution for low- to mid-pressure hydrogen compression (1-140 bar).
- Configuration II (five spirally finned embedded cooling tubes with outer cooling jacket) emerged as the optimal design, offering the best trade-off between thermal performance, reactor weight, and volume efficiency, achieving a weight ratio of 1.56 with a reactor mass of 2.25 kg for 500 NL hydrogen delivery.
- Marginal thermal improvements in Configuration III (six spirally finned embedded cooling tubes with outer cooling jacket), achieved by reducing bed thickness to 1.3 mm and adding a sixth cooling tube, did not justify the added complexity and weight, indicating diminishing returns beyond five tubes.
- All the considered configurations showed nearly identical reacted fraction profiles, suggesting that local variations in hydrogen discharge dynamics had minimal impact on overall sorption performance under tested conditions.

7.3 Study on $\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMn}_{0.3}\text{Fe}_{0.6}\text{Ni}_{0.1}$ in single reactor operation mode

- The prototype reactor was activated in 5 cycles, reaching 1.6 wt% storage by exposing the alloy to 130 bar hydrogen at 5 °C HTF, followed by 100 °C heating and evacuation. In contrast, large-scale reactors required 220-240 °C heating and evacuation before introducing 120 bar hydrogen with room-temperature air as HTF, needing 8 cycles for full activation.
- Hydrogen uptake rate improved 2.5 times, with cumulative absorption increasing from 13.17 g to 20.82 g as injection pressure rose from 70 to 100 bar. Injection pressure was the most critical factor, boosting system thermal efficiency by ~13%.
- HTF inlet temperature during absorption significantly affected hydrogen uptake, with an increase from 5 °C to 15 °C reducing hydrogen absorption by 19.2% at 100 bar. This reduced system efficiency by 4.7%. During desorption, increasing temperature from 30 °C to 50 °C in 10 °C steps had a lower impact, causing only a 3.8% variation in efficiency.
- HTF flow rate influenced cycle time but had minimal impact on efficiency. Increasing flow rate from 2.5 L/min to 10 L/min reduced absorption cycle time by 21% without affecting hydrogen uptake, while reducing it from 10 L/min to 2.5 L/min during desorption increased cycle time by 50%, with an overall efficiency sensitivity of <3.5%.

- The alloy exhibited excellent hydrogen compression, reaching >160 bar at 40 °C and 210 bar at 50 °C with an inlet pressure of 90-100 bar, proving its suitability for high-pressure hydrogen storage. It achieved a gravimetric storage density and exergy recovery rate of 0.55% and 14.8 W/kg_{MH} respectively.
- Tandem operation of two reactors provided a cooling effect of 348 kJ during discharge at 3 bar, with HTF inlet temperature at 7 °C for both absorption and desorption cycles. The bed temperature dropped to -9 °C during desorption at 7 °C.

7.4 Study on La_{0.3}Ce_{0.7}Ni₄Fe in single reactor operation mode

- Successful alloy activation was achieved at 60 bar hydrogen pressure and 20 °C bed temperature, requiring six cycles for the prototype reactor, achieving ~1.3 wt% with 45.22 g hydrogen stored and four cycles for the industrial-scale reactor, achieving 1.3 wt% with 326.06 g hydrogen stored.
- Optimal absorption performance was achieved at 40–50 bar injection pressure with an HTF inlet temperature around 10 °C, balancing high hydrogen uptake (~45.22 g) and shorter absorption cycle times, while maintaining efficient thermohydraulic performance at a flow rate of 5 L/min.
- A desorption temperature of ≥60 °C was identified as optimal, enabling complete hydrogen release (~100% reversibility) and faster discharge rates, with 30 g desorbed in 100 s, while lower temperatures (40–50 °C) resulted in incomplete desorption and slower kinetics.
- A desorption temperature of ≥60 °C was identified as optimal, enabling complete hydrogen release (~100% reversibility) and faster discharge rates, with 30 g desorbed in 100 s, while lower temperatures (40–50 °C) resulted in incomplete desorption and slower kinetics.

7.5 Study on La_{0.8}Ce_{0.2}Ni₅ in single reactor operation mode

- Full activation of the prototype and industrial-scale reactors was achieved at 40 bar and 10 °C, reaching a storage capacity of 1.4 wt%, with the prototype absorbing 27.9 g to ~49 g over five cycles and the industrial reactor absorbing 12.9 g to 350 g over four cycles, demonstrating consistent hydrogen storage capacity of 1.4 wt% across scales.
- The alloy demonstrated excellent absorption performance even at low hydrogen pressures in the range of 10–20 bar, making it highly suitable for integration with low-pressure hydrogen sources such as electrolyzers.
- Based on desorption performance and the need for adequate pressure differential during coupled reactor operation, a minimum HTF inlet temperature of 70 °C was identified as optimal for the desorbing bed.

7.6 Study on dual stage MHHC compressing 500 NL of hydrogen

- The study on the impact of coupled bed temperature revealed that the high-pressure bed temperature had a dominant impact on hydrogen transfer mass, transfer rate, and final delivery pressure, compared to the low-pressure bed temperature. Reversibility in the low-pressure bed dropped by 48.2% as the high-pressure bed temperature increased from 5 °C to 15 °C, while keeping the low-pressure bed at 70 °C. Although the initial transfer rate was independent of bed temperature, it declined 1.5 times eventually as the high-pressure bed temperature increased by 10 °C from 5-15 °C. As a result, the final delivery pressure in the second compression stage dropped by 36.7% (from 188 bar to 119 bar) due to reduced hydrogen content in the high-pressure bed at higher temperature during the coupling stage.
- The final 10-20% of hydrogen absorption accounted for 63% of the total absorption time, highlighting the need to balance shorter absorption time with hydrogen inventory. Reducing inventory from 100% to 80% lowered reversibility from 86% to 56.5%, transferring only 20.7 g out of 36.6 g. The rate of pressure rise in stage 2 was highest for 100% inventory, achieving 188 bar in under 3 min at 50 °C, as both the rate of pressure rise and final delivery pressure were largely dictated by hydrogen inventory. However, reducing inventory shortened the overall cycle time by 37.8% for 80% inventory and 23.7% for 90% inventory, though 100% inventory achieved the highest compression rate (14.6 L/min) due to greater hydrogen handling mass at the expense of longer cycle time.
- Injection pressure had minimal impact on compressor performance, with an increase from 30 bar to 50 bar resulting in only an 8.7% improvement in absorption rate and negligible variation in reversibility (80% to 89%) and final delivery pressure (183 bar to 192 bar at 50 °C). However, compression ratio remains a critical factor in selecting the optimal injection pressure to accommodate a wider operating pressure range.
- The dual-stage compressor effectively compressed hydrogen from 40-50 bar to 313 bar within a 5-80 °C temperature range, making it adaptable to low-grade heat sources like solar thermal systems. The total thermal energy consumption was ~2320 kJ for compressing 500 NL of hydrogen, yielding a specific energy consumption of 4.64 kJ/L. The isentropic efficiency was 7.4%, with potential for improvement by utilizing low-grade heat. The coupling stage consumed the highest energy, emphasizing the need to minimize the number of stages to achieve the desired operating pressure range efficiently.

7.7 Study on three stage MHHC compressing 6200 NL of hydrogen

- Hydrogen compression to 300 bar from involved three stages, operating in the temperature range of 5-91.2 °C and absorbing hydrogen from a constant pressure source of 15 bar. Stage 1 reactor bed absorbed 307 g of hydrogen in 44.6 min (max. flow rate 23.1 g/min and avg. flow rate 6.87 g/min), while 288 g was transferred to stage 2 at a reduced rate (max. flow rate 19.9 g/min and avg. flow rate 5.3 g/min) due to the decreasing pressure gap. The transfer rate increased again between stages 2 and 3, with 275.5 g transferred in 40.2 min (max. flow rate 97.71 g/min and avg. flow rate 6.85 g/min), highlighting the excellent reaction kinetics of the stage 3 alloy.
- Based on experiments, it was concluded that, for stage 1 reactors, a supply pressure of 15 bar at 15 °C was optimal, balancing hydrogen absorption mass, reacted fraction, cycle time, compression ratio and attaining a maximum reacted fraction of 0.88 (1.23 wt%) in 0.74 h. Hydrogen transfer from stage 1 to stage 2 was optimized at a desorption temperature of 90 °C and an absorption temperature of 10 °C, achieving a ~94% reversibility and the hydrogen transfer rate of 5.3 g/min. The coupling of stage 2 and stage 3 was found to be optimum at a desorption temperature of 90 °C and an absorption temperature of 5 °C, transferring 275.5 g of hydrogen with a reversibility of ~95%. All the studies were considered at a fixed HTF flowrate of 10 L/min.
- The thermal energy required to run one cycle of the developed MHHC to compress 275.5 g hydrogen from 15 bar to 300 bar in the operating temperature range of 5-91.2 °C was evaluated to be 36.2 MJ or 10.1 kWh. A mechanical compressor driven to compress identical amount of hydrogen over the same target pressure will incur 1.8 MJ when operated polytropically. The energy expended was evaluated to be 1.9 and 1.7 MJ when operated through adiabatic and isothermal process which happens to be theoretical processes. The first law efficiency of the developed system when operated polytropically was found to be ~5%.
- Refilling a Type I hydrogen cylinder to 155 bar required four refills, with throughput dropping from 600 L/min STP initially to 153.6 L/min STP by the fourth refill due to decreasing pressure difference.
- The weight ratio of the compressor system decreases with increasing delivery pressure, potentially hindering reaction kinetics. Therefore, efficient reactor design is crucial. A system with a compression ratio of 14-25 and an absorption pressure of 10-15 bar can be compatible with low-pressure AEM-based electrolyzers and achieve high pressure suitable for hydrogen refuelling station. By operating efficiently within 5-100 °C, and using an

optimal number of stages, the system can leverage solar thermal and waste heat recovery applications, addressing the low thermal efficiency of MHHC.

7.8 Scope of future work

The work presented in this thesis highlights several opportunities for further improvement and identifies key research gaps that can be explored in future studies. Some of the scopes are:

- The developed model can be further refined by considering the stress generated by the expansion of the alloy on the reactor walls. Incorporating this factor will enable researchers to evaluate and quantify the stress induced by sorption processes, facilitating the determination of the optimal porosity level when loading the alloy into the tank.
- Future research could explore a five-stage alloy configuration for an extended pressure range of 10 bar to 700 bar within a 5-130 °C temperature window. The first stage could employ $\text{La}_{0.9}\text{Ce}_{0.1}\text{Ni}_5$ to absorb hydrogen below 15 bar and compress up to approximately 40 bar. The second stage may use alloys such as $\text{La}_{0.4}\text{Ce}_{0.4}\text{Ca}_{0.2}\text{Ni}_5$ or $\text{Mm}_{0.2}\text{La}_{0.6}\text{Ca}_{0.2}\text{Ni}_5$ to reach 80-100 bar, followed by Mischmetal-based AB_5 -type alloys such as $\text{MmNi}_{4.15}\text{Fe}_{0.55}$ or La-based AB_5 -type alloy $\text{La}_{0.35}\text{Ce}_{0.45}\text{Ca}_{0.2}\text{Ni}_{4.95}\text{Al}_{0.05}$ for pressure lift from 100 bar to 250 bar. $\text{Ti}_{1.1}\text{Cr}_{1.5}\text{Mn}_{0.4}\text{V}_{0.1}$ can then elevate pressure up to 500 bar, while $\text{TiCr}_{1.1}\text{Mn}_{0.3}\text{Fe}_{0.6}$ can boost it to 700 bar.
- Ti- and Zr-based AB_2 alloys pose significant manufacturing challenges due to their high melting points (1500–1650 °C), strong reactivity, and the high vapor pressure of certain B-site elements like Mn. These factors complicate melting, homogenization, and alloy integrity. Oxygen contamination during preparation further reduces hydrogen storage capacity by forming undesirable oxide phases. To address these issues, techniques such as pre-melting, using deoxidisers (e.g., Mischmetal), and controlled rare-earth additions are applied to improve activation and hydrogenation performance. Despite higher processing costs compared to AB_5 alloys, Ti- and Zr-based AB_2 alloys remain critical for high-pressure hydrogen compression because they offer superior pressure-temperature characteristics, higher cyclic stability, and better hydrogen storage capacity, enabling pressures above 200 bar within low-to-moderate temperature ranges suitable for low-grade thermal energy utilisation. Notably, previous studies using only AB_5 -type alloys have failed to achieve pressure beyond 150 bar at a maximum temperature below 100 °C, highlighting the necessity of AB_2 -type alloys for advanced compression systems.
- Bed thermal conductivity could be enhanced by exploring the possibility of using composite MH compacts. The composite can be formed by compacting powder of alloy,

ENGs and metal particles. This would significantly improve the hydrogen transfer dynamics

- Further advancements in reactor design are also recommended to reduce sensible heat consumption and improve overall thermal efficiency. These enhancements would significantly optimise the performance of MHHC technology for high-pressure hydrogen applications.
- The cycle time of the thermal compressor can be further reduced by minimising the mass of solid components, such as the reactor and alloy. Adopting advanced and efficient reactor configurations can significantly decrease the reactor assembly weight, while selecting alloys with higher hydrogen storage capacity can lower the required alloy mass, thereby reducing overall system mass. Additionally, employing heating and cooling units with higher power ratings would shorten sensible heating and cooling durations, further improving cycle time.
- The efficiency of the developed MHHC primarily depends on three factors: first, the compression ratio achieved in each stage; second, the mass of hydrogen compressed; and third, the sensible heat added to the system. To enhance the compression ratio, suitable alloys must be selected or developed to extend the operating pressure range within a minimal temperature span. Increasing the compression ratio per stage significantly improves overall efficiency. Another critical aspect is enhancing the storage capacity of alloys, which increases hydrogen handling capability and system productivity, thereby improving efficiency. Reducing the sensible heat requirement offers the most practical route to efficiency improvement. Utilising waste heat recovery, as demonstrated in this thesis, effectively meets part of this thermal demand. Additionally, optimising high-pressure reactor configurations to minimise thermal parasitic mass can further mitigate efficiency losses. Exploring alternative pressure vessel materials may also contribute to performance improvement, although this approach may increase capital costs.
- Integration of control systems combined with AI/ML techniques could be explored to enable real-time feedback, predictive optimization, and adaptive performance enhancement of the metal hydride compressor system.

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Appendix-A: Cost Estimation for developed MHHC

The capital cost of the Metal Hydride Hydrogen Compressor (MHHC) includes various elements such as the cost of alloys, reactor fabrication, installation of the heat transfer fluid (HTF) circuit, and the gas circuit, along with the procurement of necessary components. The alloys used in the MHHC system were sourced from Zhonghe Scientific & Technical Co., China, while the reactors were fabricated by Shefa Engineers Pvt. Ltd. The gas circuit components, including 1/4-inch gas tubing, high-pressure reactor valves, navigating valves, and high-pressure sintered filters, were procured from Swagelok. To ensure durability and reliability in prolonged operations, the HTF circuit components were made from SS316 stainless steel. A summary of the total expenditure for all these units is presented in Table A. 1, providing a comprehensive overview of the costs involved in setting up the MHHC system.

Table A. 1: Details of capital cost incurred

Components	Quantity	Unit cost (USD)*	Total cost (USD)*
Stage 1 alloy: $\text{La}_{0.8}\text{Ce}_{0.2}\text{Ni}_5$	50 kg	40	2000
Stage 2 alloy: $\text{La}_{0.5}\text{Ce}_{0.5}\text{Ni}_4\text{Fe}$	50 kg	40	2000
Stage 3 alloy:			
$\text{Ti}_{0.8}\text{Zr}_{0.2}\text{CrMn}_{0.3}\text{Fe}_{0.6}\text{Ni}_{0.1}$	50 kg	50	2500
Reactors	6 units	900	5400
HTF circuit components	-	900	900
Gas control system	-	8000	8000
Miscellaneous	-	500	500

*All costs are reported based on the May 2024 Indian Rupees to USD conversion rate.

The total capital cost of the Metal Hydride Hydrogen Compressor (MHHC) is estimated at 21,300 USD. To evaluate the operational cost, it was assumed that the HTF pump operates continuously for 24 h daily, reflecting the continuous storage and compression of hydrogen. During the experiments, a single 1 BHP (0.746 kW) pump was utilized. Over a 4.65 h compression cycle, the pump consumed approximately 3.47 kWh to compress 0.55 kg of hydrogen in one cycle. Based on these parameters, a single system can compress a maximum of 2.8 kg of hydrogen per day. Therefore, per day, the electricity consumption would be 17.9 kWh. At an electricity rate of 12 cents per kWh (Indian commercial electricity tariff), and 300 operational days per year, the annual energy cost is estimated to be around ~645 USD for the

current system. To achieve a daily compression capacity of 10 kg of hydrogen, either four such systems are required or the number of reactors per stage must be increased to eight. The projected annual operating cost is estimated at approximately 2,580 USD for compressing 3000 kg of hydrogen. The capital cost break out of the developed compressor is shown in Fig. A. 1.

Capital Costs Breakdown

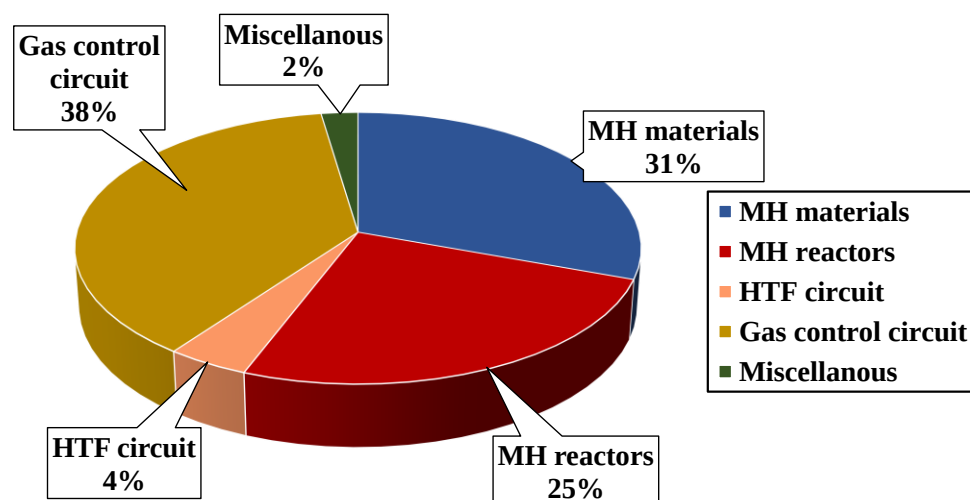


Fig. A. 7.1: Capital cost breakdown of the developed compressor

Appendix-B: Key terminologies used in the thesis

Absorption time: It is defined as the duration of hydrogen intake, starting from the initial observable rise in bed temperature until it approaches the initial HTF temperature. Alternatively, it can be defined as the time taken for hydrogen to transfer into the absorbing bed until the absorption rate drops below the measurable threshold (<0.001 g/s) of the Coriolis mass flow meter.

Reacted fraction (Ψ): It is defined as the ratio of the mass of hydrogen absorbed m_{H_2} by the MH bed to the maximum storage capacity ($\text{wt}\% \times m_{\text{alloy}}$) of the alloy contained within the reactor. It can be expressed as:

$$\Psi = \frac{100 \times m_{H_2}}{\text{wt}\% \times m_{\text{alloy}}} \quad (\text{B.1})$$

Reversibility: It is defined as the ratio of the mass of hydrogen desorbed by the MH bed during desorption to the mass of hydrogen absorbed by the same bed in the preceding absorption half-cycle. It is generally represented in percentage. It can be expressed as:

$$\text{Reversibility} = \frac{m_{d,H_2}}{m_{a,H_2}} \times 100 \quad (\text{B.2})$$

Weight ratio (WR): It is defined as the ratio of mass of the MH alloy filled in the reactor to mass of the reactor. It is determined by:

$$\text{WR} = \frac{m_{\text{alloy}}}{m_{\text{reactor}}} \quad (\text{B.3})$$

Appendix-C: Uncertainty Analysis

C.1 Directly measured data

The accuracy limits for directly measured variables such as temperature, pressure, mass flow rate of hydrogen and HTF are shown in Table B.1.

Table B. 1: Details of capital cost incurred

Measuring apparatus	Measurement range	Accuracy
Thermocouple: K Type	-200-1300 °C	± 0.5 °C
Gauge pressure transducer-1	0-100 bar	± 0.5% FS [± 0.5 bar]
Gauge pressure transducer-2	0-250 bar	± 0.5% FS [± 1.25 bar]
Gauge pressure transducer-3 and 4	0-400 bar	± 0.5% FS [± 2 bar]
HTF flow meter	0-60 LPM	±0.5%
Coriolis mass flow meter	0-10 g/s	± 0.35% RD
Weighing balance	0-2000 g	± 0.01 g

C.2 Estimated Data

Equipment and measuring sensors inherently carry uncertainties due to their accuracy limits and potential human error in readings. The uncertainty in the results is determined using the root sum square method (Moffat, 1988), given in Eq. B. 1:

$$\delta_R = \sqrt{\left(\frac{\partial R}{\partial X_1} \delta_{X_1}\right)^2 + \left(\frac{\partial R}{\partial X_2} \delta_{X_2}\right)^2 + \dots + \left(\frac{\partial R}{\partial X_n} \delta_{X_n}\right)^2} \quad (\text{B.1})$$

In the expression, δ_R represents the uncertainty of a quantity R , which arises from the individual uncertainties ($\delta_{X_1}, \delta_{X_2}, \dots, \delta_{X_n}$) of the independent variables $X_1, X_2, \dots, X_n$, governing R . A human reaction time uncertainty of ± 0.2 s was considered for all cases.

C.2.1 Measurement of hydrogen transferred

The uncertainty in the amount of hydrogen transferred was evaluated by accounting for the individual uncertainties associated with the measurement of mass flow rate and time. The resulting combined uncertainty was then calculated. The calculated uncertainty in the amount of hydrogen transferred was found to be ± 1.05 %.

C.2.2 Measurement of thermal energy

The uncertainty associated with the thermal energy was attributed to the mass flow rate of the heat transfer fluid (HTF) and temperature measurements, and was evaluated to be ± 10.05 %.

C.2.3 Measurement of compression work

The uncertainty in the compression work was primarily due to the measurements of temperature, hydrogen mass, and pressure. The maximum uncertainty was evaluated to be approximately $\pm 5.1\%$.

C.2.5 Measurement of compressor efficiency

The uncertainty in compressor efficiency is approximately $\pm 11.2\%$.



Appendix-D: Equipment Specifications

The detailed specifications of the equipment used during the experimental analysis are:

D.1 Coriolis mass flow meter

Make	:	Emerson
Model	:	1700R12ABFEZZZ
Type	:	Coriolis mass flow meter
Fluid	:	Hydrogen and any other gas
Flow band	:	0-50 g/s
Accuracy	:	$\pm 0.35\%$ RD
Precision	:	4 digits after decimal
Sensitivity	:	0.01 g/s
Operating pressure range	:	up to 413 bar at 37 °C
Operating temperature range	:	-10 °C - 80 °C
Output signal	:	4-20 mA

D.2 Data acquisition system (DAQ)

Make	:	Keysight
Model	:	DAQ970A
Scan intervals	:	0-99 hour; 1 ms record time step
Accuracy	:	$\pm 0.004\%$
Precision	:	6 digits after decimal
Record signals	:	DC (100 mA – 1A; 100 mV – 300 V) AC (100 mA – 2A; 100 mV – 100 V)
Scan temperature	:	-100 – 1820 °C

D.3 Pressure transducer

Make	:	Equinox
Model	:	EQ-PT-1000
Output signal	:	4 – 20 mA
Accuracy	:	$\pm 5\%$ FS
Range	:	0–100 bar (Stage 1), 0-250 bar (Stage 2) and 0–400 bar (Stage 3 and Circuit)

D.4 Thermocouple

Make	:	Industrial Heaters
Model	:	Specifically configured for application
Type	:	K-type

Sensitivity	:	$\pm 0.5\text{ }^{\circ}\text{C}$ (0-100 $^{\circ}\text{C}$)
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D.5 High temperature recirculation bath

Make	:	Siskin Instruments Co. Pvt. Ltd.
Model	:	HCB200S
Type	:	Recirculating
Fluid	:	Water/Silicon oil
Flow band	:	up to 50 lpm
Bath stability	:	$\pm 0.1\text{ }^{\circ}\text{C}$
Precision	:	2 digits after decimal
Operating temperature range	:	30-180 $^{\circ}\text{C}$
Bath volume	:	50 l
Heating capacity	:	9 kW
Power input	:	3 Phase AC; 240 V; 32 A (max)
Volts-frequency	:	400 V; 50 Hz

D.6 Low temperature recirculation bath

Make	:	Siskin Instruments Co. Pvt. Ltd.
Model	:	Profichil RCC 7000 ST400
Type	:	Recirculating
Fluid	:	Water/Silicon oil
Flow band	:	up to 50 lpm
Bath stability	:	$\pm 0.1\text{ }^{\circ}\text{C}$
Precision	:	2 digits after decimal
Operating temperature range	:	-40 – 40 $^{\circ}\text{C}$
Bath volume	:	50 l
Heating capacity	:	7 kW at 0 $^{\circ}\text{C}$
Power input	:	3 Phase AC; 240 V; 32 A (max)
Volts-frequency	:	400 V; 50 Hz

D.7 Vacuum pump

Make	:	Ran-Vac Technologies Pvt. Ltd.
Model	:	Vacpro -2063
Type	:	Rotary vane pump
System cooling	:	Air cooled
Operating fluid	:	Vacpro ultra 3 (6 l)
Pumping speed	:	63 m ³ /h (at 50 Hz)

Vacuum pressure range	:	1 – 10 ⁻³ mbar
Operating temperature range	:	30 – 180 °C
Bath volume	:	50 l
Heating capacity	:	9 kW
Power input	:	2.24 kW
Rotation speed	:	1440 rpm
Frequency	:	50 Hz

D.8 Weighing balance

Make	:	Saffron
Model	:	SES 20TH
Capacity	:	up to 20 kg
Accuracy	:	± 0.1 g

D.9 Valves

Make	:	Swagelok
Model	:	SS-4SKPS4, SS-3HNRS4-G-SS
Pressure range	:	615 bar at 137 °C
Type	:	Ball valve, Needle valve

D.10 Filter

Make	:	Swagelok
Model	:	SS-4TF-05-SS
Type	:	Inline
Pressure range	:	615 bar at 137 °C
Pore Size	:	0.5 µm
End fittings	:	¼ inch NTP

D.11 Other tube fittings

Make	:	Swagelok
Model (2-way connector)	:	SS-400-6
Model (3-way connector)	:	SS-400-3
Model (4-way connector)	:	SS-400-2
Model (Braided hose)	:	SS-FX4SL-79 FX
Model (Tube)	:	THT-3R60-6.35-1.24

List of Publication and Patent

Patents

1. **P. Muthukumar, Abhishek Parida, Alok Kumar**, Multistage Thermochemical System for Hydrogen Compression and method thereof, Filed, App. No: 202411040547.

Peer Reviewed Journals

1. **Abhishek Parida**, Alok Kumar, P. Muthukumar, Amaresh Dalal, Shanta Kumar, Experimental study and performance evaluation of a large-scale multistage metal hydride-based hydrogen compressor, Applied Energy, [10.1016/j.apenergy.2025.125798](https://doi.org/10.1016/j.apenergy.2025.125798)
2. **Abhishek Parida**, P. Muthukumar, Amaresh Dalal, Experimental Investigation of Ti-Cr-Mn-based AB₂ type Metal Hydride Alloy for High-Pressure Hydrogen Storage, Journal of Energy Storage, [10.1016/j.est.2025.118047](https://doi.org/10.1016/j.est.2025.118047)
3. **Abhishek Parida**, P. Muthukumar, Amaresh Dalal, A Review on Non-Mechanical Hydrogen Compressors for Hydrogen Refuelling Stations, Int. J. of Hydrogen Energy, [10.1016/j.ijhydene.2025.05.282](https://doi.org/10.1016/j.ijhydene.2025.05.282)
4. **Abhishek Parida**, Evan Gray, P. Muthukumar, Amaresh Dalal, An improved mathematical model and finite-element study of dynamically coupled metal-hydride reactors – Part 1: Model development, Int. J. of Hydrogen Energy, [10.1016/j.ijhydene.2025.150692](https://doi.org/10.1016/j.ijhydene.2025.150692).
5. **Abhishek Parida**, Evan Gray, P. Muthukumar, Amaresh Dalal, An improved mathematical model and finite-element study of dynamically coupled metal-hydride reactors – Part 2: Model application, Int. J. of Hydrogen Energy, [10.1016/j.ijhydene.2025.150693](https://doi.org/10.1016/j.ijhydene.2025.150693).
6. **Abhishek Parida**, P. Muthukumar, Amaresh Dalal, Numerical study of a three-stage metal hydride hydrogen compressor considering alloy bed deformation, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, [10.1080/15567036.2024.2396520](https://doi.org/10.1080/15567036.2024.2396520)
7. **Abhishek Parida**, Prasad J.S., P. Muthukumar, Amaresh Dalal, A dynamic model for predicting the absorption and desorption behaviors of metal hydride systems and its implementation for screening of alloys for metal hydride hydrogen compressor, Int. J of Hydrogen, [10.1016/j.ijhydene.2023.06.275](https://doi.org/10.1016/j.ijhydene.2023.06.275)

8. **Abhishek Parida**, P. Muthukumar, Reactor design and numerical study on metal hydride based finned reactor configurations for hydrogen compression application, Int. J of Hydrogen Energy, [10.1016/j.ijhydene.2022.10.183](https://doi.org/10.1016/j.ijhydene.2022.10.183)
9. **Abhishek Parida**, P. Muthukumar, Amaresh Dalal , Experimental Investigation on Hydrogen Transfer and Delivery Pressure in Metal Hydride-based Hydrogen Compressor, J. of alloys and compounds, [Under review, Manuscript no: JALCOM-D-25-14867.](#)

Publications from other works

1. **Abhishek Parida**, Alok Kumar, P. Muthukumar, Amaresh Dalal, Experimental and Numerical Investigations on Synergistic Coupling of Metal Hydride Hydrogen Storage Systems with Low-Temperature Proton Exchange Membrane Fuel-Cell, Thermal Science and Engineering Progress, [10.1016/j.tsep.2024.102620](https://doi.org/10.1016/j.tsep.2024.102620)
2. A. More A., **Abhishek Parida**, P. Muthukumar, P. Kalita, A. Dalal, Comparative performance analysis of finned and metal foam metal hydride reactors for efficient heating and cooling operations, Thermal Science and Engineering Progress, [10.1016/j.tsep.2024.102620](https://doi.org/10.1016/j.tsep.2024.102620)
3. P. Muthukumar P., A. Kumar, M. Afzal, B. S. Sekhar, P. Sharma, **Abhishek Parida**, S. Jana, E. A. Kumar, R.K. Pai, I. P. Jain, Review on Large-Scale Hydrogen Storage Systems for Better Sustainability, Int. J. of Hydrogen Energy, [10.1016/j.ijhydene.2023.04.304](https://doi.org/10.1016/j.ijhydene.2023.04.304)

Conference Publications

1. **Abhishek Parida**, P. Muthukumar, Design, Development and Testing on Multistage Metal Hydride Based Thermochemical H₂ Compression System, UK and World Energy Storage System, Sheffield, United Kingdom, 14th-17th April 2025.
2. **Abhishek Parida**, P. Muthukumar, Amaresh Dalal, Development and Testing on Multistage Metal Hydride Based Thermochemical H₂ Compression System, PMRF Symposium, IIT Hyderabad, 15th-16th March 2025.
3. **Abhishek Parida** and P. Muthukumar, Design and Development of Metal Hydride based Hydrogen Compressor, INVENTIV-2024, IIT Hyderabad, 19th January 2024.
4. **Abhishek Parida**, P. Muthukumar, Design, Development and experimental research on industrial scale MH based hydrogen compression and purification system, Third

- Youth School on Hydrogen Energy Technologies Utilizing Metal Hydrides, Moscow State University, Moscow, 1st-4th October 2024.
5. **Abhishek Parida**, Evan Gray, Muthukumar P., Amaresh Dalal, COMSOL model of coupled desorbing and absorbing metal-hydride beds, Saint-Malo, 26th-31st May, 2024.
 6. **Abhishek Parida**, P. Muthukumar, Amaresh Dalal, Investigation of the effect of bed heterogeneities in multi-stage metal hydride hydrogen compressor: An improved numerical model, GGV Bilaspur, 7th-8th December 2023.
 7. **Abhishek Parida**, Alok Kumar, Muthukumar, Amaresh Dalal, Experimental and Numerical Studies on Metal Hydride based Embedded Cooling Tube reactor for Controlled Hydrogen Discharge, ICP, Bali, Indonesia, 26th-28th July, 2023.
 8. **Abhishek Parida**, P. Muthukumar, Amaresh Dalal, Development and Testing on Multistage Metal Hydride Based Thermochemical H₂ Compression System, PMRF Symposium, IIT Madras, 17th-19th March 2023.
 9. **Abhishek Parida**, P. Muthukumar, Amaresh Dalal, A Simple Dynamic Model for Predicting the Absorption and Desorption Behaviour of Metal Hydride Systems, WHEC, Turkey, 26th-30th June 2022.
 10. **Abhishek Parida**, P. Muthukumar, Thermal Performance Comparisons of ECT and Helical-Coiled based Metal Hydride Reactor, 26th National and 4th International ISHMT-ASTFE Heat and Mass Transfer Conference, 17th-20th December 2021.

Awards and Achievements

1. Recipient of India's highest doctoral research fellowship "*The Prime Minister Research Fellowship*"
2. Received "Recommended with commendation" in the PMRF Annual Review 2024.
3. Received "Recommended with commendation" in the PMRF Annual Review 2022.
4. Invitation to deliver a keynote speech at the Third Youth School Hydrogen Energy Technologies Utilising Metal Hydrides, Moscow, Russia
5. Received Griffith University Postgraduate Fellowship to work as a visiting scholar under the supervision Prof. Evan Gray, November 2023-May 2024.
6. Selected to attend the Summer School, organized by CNRS, France on the eve of 18th International Symposium on Metal Hydrogen Systems
7. Received Science and Engineering Research Board, International Travel Support (ITS/2024/001083), DST, Govt. of India, for attending 18th International Symposium on Metal Hydrogen System, May 2024.